Raman spectroscopy of small-diameter nanotubes

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Abstract. Results based on Raman measurements of small-diameter nanotubes (NTs) are presented and discussed in this paper. The NTs with diameters from 1 nm down to 0.4 nm were produced either as the inner tubes in the double-wall carbon NTs (DWCNTs) or as tubes embedded in the channels of the zeolite crystals. While analysing the Raman spectra attention was paid to the radial breathing mode (RBM), the D line and the G band. For both NT systems the RBM frequency was found to follow the same functional diameter dependence as the tubes with larger diameters. However, in contrast to the latter, the diameters of the thin tubes obtained from density functional theory calculations must be taken into account to explain satisfactorily the observed line positions. The resonance behaviour of the RBM intensities was recorded for the tubes in zeolites. It allows us to ascribe a position of the RBM to a particular NT. This result also demonstrates the breakdown of a simple tight-binding approach to the electronic structure but agrees with predictions from ab initio calculations. The D line of the outer tubes in DWCNTs is dispersive, similar to the single-wall carbon NTs. However, the rate of dispersion is reduced for the inner tubes in DWCNTs. This is attributed to the fact that the inner and outer tubes are probed with the same laser excitation. The linear shift due to the increasing laser energy is compensated by the negative shift due to the NT diameter. The latter is smaller for the inner NTs which leads to a stronger compensation of their dispersive behaviour. This effect is even stronger for the NTs in zeolites. In the extreme case, the strong Raman lines are not dispersive at all. This unexpected behaviour was explained by the detailed ab initio calculation of the phonon structure. The G bands of the inner semiconducting tubes were observed as new features in the Raman spectra of DWCNTs. On the other hand, no lines of metallic inner tubes were found. G bands of semiconducting as well as metallic NTs were detected for the zeolite samples. In either case, Raman lines due to the recently proposed Peierls-like mechanism for the thin metallic tubes were not indentified. This mechanism must therefore cause a significant reduction in Raman intensity.
1. Introduction

Material science is called upon to provide new materials that could be used to overcome future problems. Carbon nanotubes (NTs) are, without doubt, very promising from this point of view. Possessing a conductivity as good as that of metals, a thermal conductivity better than that of diamond and a strength higher than that of steel, carbon NTs appear as the idealized prototype of a technological material. While individual single NTs can be extracted and studied, yielding the exceptional properties mentioned above, most of the unique properties disappear if bulk systems made of NTs are studied. There is a gap between the single NT-based and the bulk-based measurements. A reliable method to produce bulk samples consisting of only one or a few different types of NTs is still missing. Geometrically, one can obtain a NT by rolling up a 2D graphene layer. An individual single-wall NT is fully characterized by its diameter and the chirality, the way the carbon atoms are arranged on the NT surface. Two chiral indices \( n \) and \( m \) determining the chirality define the components of the NT folding vector on the graphene layer [1]. Bulk samples can be characterized by the diameter distribution of the NTs involved. It can be obtained from optical absorption, x-ray measurements [2, 3] and Raman spectroscopy [4, 5].

There are several production methods for single-wall carbon NTs (SWCNTs). The most widely used ones are based on laser ablation, arc discharge or chemical vapour deposition. The tubes produced have a Gaussian-like diameter distribution, which peaks between 1.2 and 1.4 nm with the width of about 0.1 nm. The tubes prepared by the high-pressure CO decomposition (HiPCO) do not follow such a simple distribution and the NT diameters span a large range from 0.7 to 1.3 nm [6]. The diameter of 0.7 nm seems to be the lower limit for tubes grown in free space. The appearance of tubes with even smaller diameter becomes less favourable because of the high curvature energy [7]. On the other hand, small diameters have interesting consequences on the physical properties of the tubes. Many of these properties are found to be diameter-dependent. Examples are, among others, frequencies of the Raman-active modes and the transition energies between van Hove singularities in the 1D electronic density of states [10]. Whereas for standard tubes these properties can be derived in a good approximation from zone folding of the graphene sheet, this is not so for small-diameter tubes \( (d_t \lesssim 1 \text{ nm}) \). For the latter, the strong curvature of...
the tubes needs more expensive theoretical treatment. It has turned out that the small-diameter N Ts may be stabilized when embedded in templates. To date, there are two approaches to this problem. The first one utilizes the ability of single-wall N Ts to incorporate fullerene molecules inside the NT cage, making the so-called NT peapods [8]. The fullerenes can then be fused together to form an inner NT by heating the material to temperatures above 1200 °C. The diameter of the inner tube when compared with the outer one is expected to be about 0.68 nm smaller, twice the interplanar distance in graphite. Consequently, the diameter distribution of the inner tubes will roughly follow the diameter distribution of the outer ones, but it will be downshifted and narrower. The narrowing of the diameter distribution is a consequence of the fact that tubes with diameters less than about 1.2 nm cannot be filled with C_{60}.

In the second approach, NTs are grown in channels of zeolite crystals [9]. Such channels have a typical diameter of 0.73 nm. Since the channel diameters are rather uniform with small deviations, the tubes in the channels have very similar diameters. To obtain the tube diameter, only 0.34 nm must be subtracted from the channel diameter, in this case resulting in a tube diameter of the order of 0.4 nm.

This paper is devoted to the electronic and dynamical properties of narrow tubes and will elucidate the shortcomings of the tight-binding (TB) approximation. We present results of Raman measurements performed on small-diameter NTs acquired by the two methods mentioned above. Particular attention will be paid to the tubes grown inside the zeolite and inside a primary SWCNT. From the experimental point of view, we concentrate on the three most important parts of the Raman spectrum: the radial breathing mode, the defect-induced (D) line and the graphitic (G) line.

2. Experimental procedure

2.1. Inner-shell SWCNTs

SWCNTs with a mean diameter of 1.4 nm were filled by C_{60} molecules to form the so-called NT peapods [13]. The concentration of the filling was almost 100%. The tubes were then heated to above 1200 °C under dynamic vacuum for 12 h. The fullerene molecules transform into an inner tube and create, in this way, double-wall carbon NTs (DWCNTs). Subtracting twice the graphite interplanar distance (0.34 nm) the mean diameter of the inner tubes is about 0.7 nm. The double-wall nature of the final material was proven by high-resolution transmission electron microscopy.

2.2. Tubes grown from zeolites

Crystals of AlPO_{4} zeolite contain parallel channels of diameter of about 0.73 nm. They were grown with tripropylamine (TPA) molecules inside the channels as a precursor for the NTs. During subsequent pyrolysis of TPA, the NTs grow [9]. Subtracting twice the van der Waals radius of a carbon atom (0.17 nm), the resulting diameter of NTs is around 0.4 nm. NTs with diameter 0.42 ± 0.02 nm were indeed found by high-resolution TEM [14]. There are only a few specific NTs fitting into this narrow channel: (5,0), d_{G} = 0.392 nm; (3,3), d_{G} = 0.407 nm; (4,2), d_{G} = 0.414 nm; and (5,1), d_{G} = 0.436 nm, where d_{G} is the diameter derived from the graphene lattice. The diameter distribution is thus extremely narrow when compared with the distribution of the inner tubes in DWCNTs.
More than 20 different laser lines in the visible range were used for Raman measurements. These lines were generated from an Ar+ Kr+ ion laser, a dye laser and a Ti:sapphire laser. For zeolite-grown samples, a 325 nm line from a UV laser was used in addition. The spectra were recorded by a Dilor triple monochromator in normal and high resolution. Raman lines were fit with Voigtian spectral lines with a constant value of 2 cm$^{-1}$ (normal resolution) and 0.5 cm$^{-1}$ (high resolution) for the Gaussian component.

3. Results and discussion

3.1. Radial breathing mode

Representative spectra for different laser energies are shown in figures 1 and 2 for DWCNTs and NTs in the zeolite crystals, respectively. Extremely small widths and high intensities of the lines are observed for the spectra of the DWCNTs. The Lorentzian line widths are of the order of 0.5 cm$^{-1}$ and can decrease to 0.35 cm$^{-1}$ in some cases and for temperatures below 90 K. The RBM peak intensities from the inner tubes are more than 10 times stronger than the response from the outer tubes when the spectra are excited with red lasers. The unusual narrow widths of the inner shell RBM lines were explained by an almost defect-free growth of the inner shell tubes [12]. The inner space of the SWCNTs thus provides an excellent nano-clean room where the secondary NTs grow under ideal conditions.

It was found that the RBM frequencies of the inner tubes in DWCNTs scale as

$$\frac{C_1}{d} + C_2,$$

where $C_1 = 233$ cm$^{-1}$ nm and $C_2 = 14$ cm$^{-1}$ [25]. Note that the value for $C_1$ is similar to that found for SWCNTs with $d > 1$ nm. From the observed lines one can estimate that the tube diameters span the range from 1 nm down to 0.52 nm. Furthermore, the NT chiral indices
Figure 2. Low-energy part of the Raman spectrum for NTs in zeolite crystals. The spectra were excited with several lasers as indicated on the right side of the figure. The spectra excited with the visible light lasers are normalized to the laser power.

\((n,m)\) could be assigned to all peaks observed in the spectra [12]. The important difference for the small tubes when compared with the standard tubes is that the diameter \(d\) in the above equation has to be calculated from density functional theory (\(d_{\text{DFT}}\)), instead of the graphene-based values (\(d_G\)). The \(d_{\text{DFT}}\) diameters minimize the rms error when as-calculated RBM frequencies are comparable with experimental values [25]. This implies that the curvature can no longer be omitted and its physical consequences must be taken into account. As the diameter increases, the \(d_{\text{DFT}}\) value approaches \(d_G\). The difference between the two values is about 0.1% for the \((7,4)\) NT \((d_{\text{DFT}} = 0.7557 \text{ nm}, \ d_G = 0.7551 \text{ nm})\) and 3% for the \((5,0)\) tube with \(d_{\text{DFT}} = 0.4028 \text{ nm} \) and \(d_G = 0.3915 \text{ nm}\).

The position of the spectra also changes as the laser energy changes because of the selective resonance enhancement. This resonance enhancement is a consequence of the dependence of transition energies on the tube diameter. Figure 3 displays these transition energies as a function of the (inverse) diameter. The calculation was based on a TB method followed by a simple zone-folding process to obtain the electronic structure of NTs. The horizontal box determines the laser energies used for measurements, whereas the vertical box defines the diameters of the inner tubes of DWCNTs. Circles and squares denote transition energies for semiconducting and metallic tubes, respectively. The solid lines represent a simple \(1/d\) dependence of the transition energies with a slope characteristic for each transition. The trigonal warping effect is responsible for the scattering of the individual transitions around the \(1/d\) lines. The effect is more pronounced for the higher-order transitions.

As can be seen in figure 3, mostly the \(E_{22}\) electronic transition of the semiconducting tubes is probed with the lasers used in figure 1. For excitation with green and blue lasers, also the response from metallic tubes also becomes relevant. As the laser energy is decreased from yellow to deep red, NTs with larger diameters reach resonance. Since the diameter distribution is quasi-continuous, there are always NTs present in the sample whose RBM intensity is enhanced.
Figure 3. Transition energies between van Hove singularities in the valence and conduction bands. Circles are for semiconducting NTs and squares are for metallic tubes. The correspondence between the inverse diameter and the RBM frequency was established by making use of the values for $\gamma_0$, $C_1$ and $C_2$ shown at the bottom of the figure [25]. The horizontal area enclosed between the light grey lines determines the laser energies used for measurements and the vertical area enclosed between the light grey lines defines the diameters of the inner tubes of DWCNTs.

On the other hand, spectra from zeolites are rather noisy and more complicated with a small number of well-resolved peaks. Examples are depicted in figure 2. The differences between the tubes grown in zeolites and the inner NTs of DWCNTs can be explained by a quite different diameter distribution of the tubes involved. Owing to the very limited number of tubes fitting into the zeolite channels, no continuous shift in the positions of the Raman lines is expected. Rather, spectra become stronger and weaker depending on whether there are NTs in resonance or not. This is indeed the case as demonstrated in figure 4 and can be used for a mode assignment. The spectra are particularly strong for the excitation energies of 616 nm (2.0 eV), 514 nm (2.4 eV) and 325 nm (3.8 eV; not shown in figure 4) and weak otherwise. In ab initio theoretical calculations [16, 17], transition energies at 2 and 2.4 eV were found for the (4,2) and (5,0) NTs, respectively. Combining these calculations with the results shown in figure 4, one can safely ascribe the resonances in the visible region to the (4,2) and (5,0) NTs.

According to the simple TB/zone-folding approach, both NTs are semiconducting. As shown in figure 3, the $E_{11}$ transition of the semiconducting tubes can be in resonance with the laser energies used in the experiments. For the (4,2) NTs ($1/d_{DFT} = 2.360 \text{ nm}^{-1}$), the relation between the transition energy and the diameter (see equation (4) below) gives a value of 1.95 eV for the former. Thus the TB/zone-folding method gives a transition energy in agreement
Figure 4. Normalized integrated intensity of NTs/zeolite Raman spectra in the spectral window 450–650 cm$^{-1}$ as a function of the laser energy. As-measured spectra were corrected for the sensitivity of the Raman system and normalized to the laser power. Squares represent values from the experiments and the solid line is a guide for the eye [11].

with the experiment for the (4,2) NT. As shown in [17], this is just an incidental coincidence since the ab initio approach changes the electronic structure considerably when compared with the TB/zone-folding method. Moreover, the (5,0) should have resonance energies similar to the (4,2) tubes because of their very similar diameters ($1/d_{\text{DFT}} = 2.483$ nm$^{-1}$). As is evident from the experiment, this is not the case.

Using the above results one can also assign RBM frequencies for the two NTs. The position of the strongest peak at 543 cm$^{-1}$ as recorded with the 514 nm laser line agrees very well with the value of 536 cm$^{-1}$ obtained from density functional calculations (DFT) for free tubes with chirality (5,0) [11]. The (4,2) NTs are in resonance for the 616 nm (2.01 eV) excitation. As seen in figure 2, for this excitation energy there is a doublet of peaks located at 514 and 545 cm$^{-1}$. The lower frequency value is assigned to the RBM of the (4,2) tubes. The result from DFT is 538 cm$^{-1}$, which is about 5% higher than the observed value. The peak at 545 cm$^{-1}$ has an almost identical position to the (5,0) peak of the spectrum recorded with 514 nm. Even though the (5,0) NTs are not in resonance for a 2 eV excitation, their smaller cross-section may be compensated by their higher relative abundance when compared with the (4,2) tubes. This is a reasonable assumption since the (5,0) tubes have a smaller diameter and thus fit better to the zeolite channels than the (4,2) tubes. For the same reason, the zeolite environment may have a stronger influence on the RBM frequency for the (4,2) tubes than for the (5,0) tubes, shifting the RBM to lower frequencies. RBM frequencies and resonance energies are summarized in table 1 for the NTs in zeolite crystals.

In addition to the above-described lines from the fundamental RBM modes there are other features, which are at best seen in the spectrum excited with 514 nm. The particularly strong line at 390 cm$^{-1}$ corresponds to a band in the phonon density of states (PDOS) as shown in [11].
Table 1. As-calculated and as-observed frequencies of the radial breathing mode for the NTs embedded in the zeolite crystals. Resonance energies of the tubes are for the energy range covered by the experiments. n.o., not observed.

| Nanotube $\langle n, m \rangle$ | $\nu_{\text{RBM}}$ (cm$^{-1}$) (calc. DFT) | $\nu_{\text{RBM}}$ (cm$^{-1}$) (exp.) | Resonance energy (eV) (calc. [16, 17]) |
|-------------------------------|---------------------------------|---------------------------------|---------------------------------|
| (5,0)                         | 536                             | 543                             | 2.4                             |
| (3,3)                         | 551                             | n.o.                            | 3.1                             |
| (4,2)                         | 538                             | 515                             | 2.0                             |
| (5,1)                         | 495                             | 500                             | –                               |

The line widths of some Raman features reach several tens of cm$^{-1}$, much more than the typical line widths for larger diameter NTs. The reasons for that may be three-fold: (i) the Raman mode of a tube couples strongly to the vibration of the zeolite, (ii) NT vibrational modes from the vicinity of the central peak position become Raman-active making the Raman line broader and (iii) the peaks are broad because of imperfection of the tubes grown in the zeolite channels.

RBM of other possible candidates were also checked. Calculations from DFT predict a resonance of the (3,3) tubes at around 3.1 eV [16, 17] with the RBM frequency of 551 cm$^{-1}$. Although several spectra were excited with the 406 nm laser line (3.06 eV), no clear evidence for a resonance enhancement of an RBM was found. There is a broad feature between 500 and 570 cm$^{-1}$ and a peak at 641 cm$^{-1}$ for this excitation. The peak at 641 cm$^{-1}$ is much too high and therefore certainly not the response from an RBM. Moreover, the spectrum does not exhibit an expected resonance behaviour. Possible explanations for the weak response at 406 nm are two-fold: either for some reason there is only a very small amount of the (3,3) tubes grown in the zeolite crystals or the resonance is very sharp and the laser line used is already off resonance.

On the other hand, the spectrum excited with the UV laser at 325 nm showed unexpectedly a strong line at 500 cm$^{-1}$. Probably, it may be due to the RBM response from (5,1) whose calculated DFT frequency is 495 cm$^{-1}$. This assignment is highly reliable since its ‘neighbours’ on the NT diameter scale, the (4,2) and (6,0) tubes, have their calculated RBM frequencies considerably shifted from 500 cm$^{-1}$. The diameter of the (5,1) tube is about 10% larger than the diameter of the (5,0) tube. The stronger interaction of the (5,1) NT with the zeolite environment is compensated by the curvature energy saved when the tube diameter is larger. This indicates that the graphite interplanar distance of 0.34 nm, defining the tube diameter with respect to the diameter of the zeolite channels, is not a rigid value.

It is instructive to test the validity of the $1/d$ law also for the tubes in the zeolites. Taking the values for constants the $C_1$ and $C_2$ from DWCNTs and a tube diameter $d_{\text{DFT}}$ as calculated from DFT, we obtain values for the RBM frequencies, which are 30–50 cm$^{-1}$ larger than those seen in the experiment. The constant $C_2$ is assumed to describe the intertube interaction in the bundles. It is therefore omitted in what follows. The DFT diameters obtained for the (5,0), (4,2) and (5,1) NTs are 0.4028, 0.4238 and 0.4447 nm, respectively. The values for the constant $C_1$ obtained from a correlation between the RBM frequencies and $1/d_{\text{DFT}}$ lie in the narrow interval between 217.8 and 220.1 cm$^{-1}$ nm for the three above-mentioned tubes. The similarity of the constant for the observed tubes ensures reliability of the assigned RBM frequencies.
3.2. D line

The D line located between 1280 and 1400 cm\(^{-1}\) is in some sense exceptional among other Raman-active lines of carbon NTs. It is closely related to the defect-induced D line of graphite. As has been known for many years, its position in graphite depends on the laser excitation wavelength [18], but an explanation for this effect was missing for a long time. The puzzle was solved recently and a mechanism called a double resonance was found to be responsible for dispersion [19]. The mechanism for graphite was immediately transferred to the D line of the SWCNTs [26].

In contrast to RBM, the D line exhibits a weaker resonance enhancement. In the case of SWCNTs, it is expected that various tubes contribute almost equally to the final shape of the D line. Selected spectra taken for SWCNTs and DWCNTs are shown in figure 5 in the range 1250–1450 cm\(^{-1}\) for excitation with two different laser wavelengths. A more detailed analysis will be published elsewhere [27]. The shift of the D-line position is evident as the laser energy changes. Moreover, for the 488 nm excitation, there is a new shoulder appearing on the left side of the band for DWCNTs. Its intensity is about half of the intensity for the outer tubes. Since the filling factor for the inner tubes is almost 100% [12], it is consistent with the smaller concentration of defects for the inner tubes.

In order to have a better insight, we performed a line shape analysis by making use of a set of Lorentzian lines (not shown here). The D line was found to have a two-component structure even for the SWCNTs. It is a direct manifestation of the double resonance mechanism. As was explained recently, four different processes are allowed by the double resonance mechanisms and give rise to the two components of the D band in graphite [20].

As shown from the experiments at the single NT level the D-line position is related to the tube diameter according to

\[ \nu = \nu_0 - \frac{C_D}{d}. \]
Figure 6. The dispersion of the D line for DWCNTs. Line positions are the averaged value of the components analysed for each D line. The results for the outer tubes are displayed by circles, those for the inner tubes by squares. Solid lines represent linear fits with the values of 52 and 42 cm$^{-1}$ eV$^{-1}$ for the outer and the inner NTs, respectively.

The constant of proportionality, $C_D$, was found to be 16.5 cm$^{-1}$ nm [10]. This value is an average and is valid for various semiconducting as well as metallic transitions. It provides an estimate of the position of the D line from the inner tubes. The mean diameter of the latter is approximately 0.7 nm. This yields a downshift of 12 cm$^{-1}$ for the D lines of the inner tubes with respect to the outer NTs. Our experimental value is 20 cm$^{-1}$ and then considerably larger. Accordingly, with the experimental value for the downshift, we estimate the value of $C_D$ to be 28 cm$^{-1}$ nm for the thin tubes.

The measured dispersion of the D line was $51 \pm 2$ cm$^{-1}$ eV$^{-1}$ for SWCNTs and this value was also preserved for the outer tubes in DWCNTs. For the inner tubes, the value was about $42 \pm 4$ cm$^{-1}$ and thus smaller. This is demonstrated in figure 6 where results for DWCNTs are shown. Values for the outer tubes were obtained as an average of the line positions of the two components of the band. The different values of the dispersion for the outer and inner NTs can be explained by the fact that the same laser wavelength generates a response from the tubes with different diameters and thus different electronic transitions are probed. For the inner tubes, the $E_{22}$ transition is mostly in resonance whereas for the outer tubes higher transitions are involved. The linear shift due to the increasing laser energy is compensated by the negative shift due to the tube diameters. Thus a term expressing laser energy dependence must be added to equation (2):

$$\nu = \nu_0 - \frac{C_D}{d} + C_E E_{\text{laser}},$$

(3)

In the TB/zone-folding method, the transition energies between van Hove singularities in the electronic density of states is related to the diameter of the tube by

$$E_{ii} = \frac{2n \gamma_0 a_{\text{CC}}}{d},$$

(4)
where $\gamma_0 = 2.9 \text{ eV}$ is the overlapping integral and $\alpha_{CC} = 0.142 \text{ nm}$ is the carbon–carbon distance. The integer $n$ has the values $1, 2, 4, 5, \ldots$ for the transitions $E_{11}, E_{22}, E_{33}, E_{44}$ of the semiconducting tubes, respectively, and $3, 6, \ldots$ for the transitions $E_{11}, E_{22}$, of the metallic tubes, respectively. Now equation (3) reads

$$
\nu = \nu_0 - \frac{C_D E_{ii}}{2n\gamma_0 \alpha_{CC}} + C_E E_{\text{laser}}.
$$

If for most NTs the same transition is in the resonance with a particular laser line then the transition energy $E_{ii}$ can be identified with the laser energy $E_{\text{laser}}$. Then the final form of equation (5) is

$$
\nu = \nu_0 + \left( -\frac{C_D}{2n\gamma_0 \alpha_{CC}} + C_E \right) E_{\text{laser}}.
$$

The first term in the parentheses reduces the value of the net coefficient of the linear dependence. The compensation is stronger the lower the order of the electronic transition. The diameters of the outer tubes of DWCNTs lie in the range $1.2–1.6 \text{ nm}$. By inspection of figure 3 we see that the $E_{33}$ transitions of the semiconducting outer tubes are in resonance with the laser energies used. From the experimental value of $51 \text{ cm}^{-1} \text{ eV}^{-1}$ for the coefficient of the linear dependence, a value of $59.5 \text{ cm}^{-1} \text{ eV}^{-1}$ was obtained for $C_E$. On the other hand, for the inner tubes the $E_{22}$ transition dominates. Using the same value for $C_E$ as for the outer tubes, the net value for the coefficient is now $42.5 \text{ cm}^{-1} \text{ eV}^{-1}$ for the inner tubes. This agrees very well with the value obtained from the experiment. Note that the result does not change too much when higher transitions for the outer tubes are taken into account.

The spectra taken for the zeolite samples in the spectral region $1200–1450 \text{ cm}^{-1}$ are shown in figure 7. They are more complicated than the spectra recorded for DWCNTs in spite of the fact that only a few different NTs are allowed in zeolites. On the high-frequency side, there

**Figure 7.** The medium-energy part of the spectra for the zeolite samples. The laser excitation wavelengths are as indicated. The intensities of the spectra were not corrected for the laser power.
are two broad bands centred at 1375 and 1400 cm\(^{-1}\). They exhibit almost no dispersion as the laser wavelength changes. Furthermore, they almost disappear for excitations with red lasers (not shown here). Owing to the lack of dispersion, it is tempting not to assign the D line to the broad response around 1380 cm\(^{-1}\).

In addition to the response at 1380 cm\(^{-1}\), there are lines at 1240 and 1270 cm\(^{-1}\), which are particularly strong for blue and green laser excitations. The line at 1270 cm\(^{-1}\) gets weaker as the laser wavelength increases. The pattern changes considerably when the spectrum is excited with the UV laser. Then the line at 1240 cm\(^{-1}\) is very weak whereas the line at \(\sim1400\) cm\(^{-1}\) becomes exceptionally strong. There are also two narrow lines at 1281 and 1385 cm\(^{-1}\) whose intensity depends on the position of measurement.

The dispersive behaviour of the lines at 1240/1270 cm\(^{-1}\) was also checked. The line at 1270 cm\(^{-1}\) does not exhibit a definite dispersion when the laser energy changes but it disappears when the laser energy drops. A possible dispersion may be obscured by this effect. On the other hand, for \(E_{\text{laser}} < 2.2\) eV (\(\sim560\) nm), the line at 1240 cm\(^{-1}\) is dispersive and changes its position with the laser energy. Above this wavelength, the line does not shift. Dispersion of the lines as a function of the excitation energy is shown in figure 8.

The position of the 1240/1270 cm\(^{-1}\) lines is about 70–100 cm\(^{-1}\) lower than the positions of the D line in DWCNTs. Using relation (2) one would expect a D-line position at \(\sim1290\) cm\(^{-1}\) (for the 514 nm excitation) which is much higher than the observed position. Therefore the smaller diameter alone cannot fully account for the downshift. The softening of the phonon frequencies by the sp\(^2\)–sp\(^3\) mixing or by the zeolite crystal might cause an additional downshift. In analogy to the RBM, the dispersive part of the 1240 cm\(^{-1}\) line can be ascribed to the (4,2) tubes for \(E_{\text{laser}} < 2.2\) eV. A value of 26 cm\(^{-1}\) eV\(^{-1}\) for the line shift with respect to the laser excitation energy was obtained. DFT calculations revealed phonon branches, which have proper frequencies in the interior of the Brillouin zone. The double-resonance process may thus play
Figure 9. The high-energy part of the DWCNTs spectra. From top to bottom: the spectra were excited with the 514, 568, 633 and 755 nm laser lines. The arrows point to features at 1506, 1526 and 1581 cm\(^{-1}\), which are not present in SWCNTs spectra.

a crucial role. The dispersion of the phonon branch responsible for the line shift must be weak enough to give rise the value observed. The compensation mechanism described for the inner tubes in DWCNTs may also be important. For such small-diameter NTs even the lowest electronic transition can be in resonance, leading to a stronger compensation than for the inner tubes in DWCNTs.

Lines at 1240 and 1270 cm\(^{-1}\) due to the (5,0) NTs are dominating in the spectra for \(E_{\text{laser}} > 2.2\) eV. The non-dispersive behaviour can be explained by inspection of the phonon branches. DFT calculations yield Raman-active modes grouped around 1250 and 1280 cm\(^{-1}\) in the centre of the Brillouin zone [11]. This means that double resonance is not operative in this case and we are dealing with the ‘standard’, first-order Raman process.

3.3. G band

Raman spectra for DWCNTs are shown in figure 9 in the range 1450–1700 cm\(^{-1}\) for several different laser excitations. For the green laser (514 nm), the highest intensity line is centred at around 1591 cm\(^{-1}\). There is a broad and structured line at \(\sim 1570\) cm\(^{-1}\) seen in DWCNTs as well as in SWCNTs. On the other hand, a line at 1581 cm\(^{-1}\) was observed in the DWCNT spectra which is not present in SWCNTs, in addition to a couple of weak lines at \(\sim 1506\) and 1526 cm\(^{-1}\). The line at 1506 cm\(^{-1}\) disappears for the 531 (not shown) and 568 nm excitations. For the 568 nm excitation, the strongest line contains evidently two components; one at 1591 cm\(^{-1}\) and a new component at 1587 cm\(^{-1}\) which dominate the band. It appears that the latter is identical with the 1581 cm\(^{-1}\) line but now slightly upshifted for the red laser excitations. The spectra change significantly for red laser at 633 and 676 nm. There is essentially a single G line at 1587 cm\(^{-1}\) and a broad M line at 1542 cm\(^{-1}\) for the 633 nm excitation. The M line is well known to originate from standard-size metallic tubes. All weak lines have disappeared for this red line. In the far-red, 746 and 755 nm, the lines at 1506, 1526 and 1581 cm\(^{-1}\) appear again in addition to
the 1591 cm\(^{-1}\) line, whereas the M line at 1542 cm\(^{-1}\) is strongly reduced. The line positions do not exhibit an observable linear shift with respect to the laser energy. Our observations are in agreement with the experiments of Bandow et al.\[28\].

The results for DWCNTs can be summarized as follows. Taking into account the mean diameter of the outer tubes (1.4 nm), it is well known that the blue, green and far-red laser excitation wavelengths probe semiconducting NTs. The line at 1591 cm\(^{-1}\) can therefore be safely assigned to the semiconducting outer tubes. For the yellow laser (568 nm, 2.18 eV) the semiconducting inner tubes with diameters around 0.7 nm also resonate as seen in figure 3. Thus the line at 1587 cm\(^{-1}\) is ascribed to them. For red excitation (633 nm), a response from semiconducting inner shell tubes at 1587 cm\(^{-1}\) fully dominates the spectrum according to a strong E\(_{22}\) resonance. The broad Breit–Wigner–Fano (BWF) line at 1542 cm\(^{-1}\) is a manifestation of metallicity of the outer NTs \[21\]. The 755 nm spectrum is a mixture of a response from the metallic outer NTs (weak BWF line) and from the semiconducting tubes (1591 cm\(^{-1}\) line).

For inner tubes, it was assumed that the E\(_{22}\) transition is operative for all laser excitations. Therefore the lines at 1506, 1526 and 1581 cm\(^{-1}\) can be as well ascribed to the semiconducting inner tubes.

Jorio et al.\[22\] investigated the diameter dependence of the components constituting the G band. They found a line whose position is diameter-dependent (\(\omega_{G^-}\) in their notation) and a line, \(\omega_{G^+}\), which does not have this property. The line position scales as \(1/d^2\) with a constant of proportionality of 47.7 cm\(^{-1}\) for the semiconducting tubes. If we identify the \(\omega_{G^+}\) line with the peak at 1581 cm\(^{-1}\), the \(\omega_{G^-}\) line should be at 1486 cm\(^{-1}\). This is much lower than the line at 1526 cm\(^{-1}\), which seems to be a natural candidate for the \(\omega_{G^-}\) line. On the other hand, one has to keep in mind that the result is an extrapolation of a rule, which was obtained for NTs having fairly larger diameters than the inner tubes in DWCNTs. Even though the line at 1506 cm\(^{-1}\) is evidently related to the inner tubes, its origin is not clear.

In principle, we should also observe a shift for the \(\omega_{G^-}\) line of metallic inner NTs. For the 568 nm laser line, the RBM response was observed for some metallic tubes \[12\]. However, for this excitation, no additional lines were detected in the G band part of the spectrum, which could be assigned to the metallic inner tubes.

Recently, another physical mechanism leading to a line shift was found as a result of DFT calculations \[23\]. It resembles Peierls instability in 1D metals. A particular phonon mode of metallic NTs having A\(_{1g}\) symmetry couples to the electrons opening a gap at the Fermi level. The phonon frequency is down-shifted since the gap opening utilizes some energy. From our results, it follows that the frequency softening is accompanied by a reduction of Raman intensity.

The G bands of the NTs in zeolites are displayed in figure 10. The excitation wavelengths are selected to show the spectra for which the (4,2) and the (5,0) NT response dominates. The (5,0) NTs respond predominantly for the 514 nm excitation whereas the (4,2) NTs are in resonance with the 676 nm red laser line. The 568 nm spectrum represents a transition between these two resonance regimes. Also shown is the UV spectrum with a strong signal from the (5,1) tubes. The spectra excited with the visible light are composed of several lines. As shown in figure 10, the spectral weight of the G band is distributed differently for the (5,0) and (4,2) tubes. No definite dispersive behaviour was found while inspecting the spectra taken with other laser lines. The G-band position and shape for the (5,1) NTs is distinct from that for the (5,0) and (4,2) tubes.

Similar to the case of the inner tubes of DWCNTs, we can look for a line shift due to the small diameters of the SWCNTs in zeolites. However, no such lines could be clearly detected because of the complicated shape of the spectra. The downshift of the \(\omega_{G^-}\) line should be as
large as 300 and 500 cm\(^{-1}\) for semiconducting and metallic tubes, respectively. Even though the (5,0) NTs are metallic, the Peierls mechanism is not operative because the electronic bands at the Fermi level have a different character compared with the metallic tubes considered in [23, 24]. Thus the A\(_{1g}\) mode of the G band does not shift. According to DFT calculations, its frequency is about 50 cm\(^{-1}\) lower than that observed in the experiment. The discrepancy was accounted for when the zeolite environment was taken into account. It stiffens the phonon mode when the (5,0) NT is forced to take on a lattice constant commensurate with the lattice constant of the zeolite crystal [15].

4. Conclusion

In this paper, we presented the results of Raman measurements performed on two systems containing SWCNTs with small diameters. To stabilize the tubes, they are either embedded in larger tubes as in the case of DWCNTs or in zeolite crystals. The diameter distributions of the two systems are quite different, broad for DWCNTs and very narrow for the NTs in zeolites. Raman spectra of the inner tubes in DWCNTs follow the pattern known for the larger-diameter NTs. The frequencies of the RBMs scale in accordance with the 1/d rule and the line intensities are resonantly enhanced. A better agreement of as-calculated RBM frequencies with experiment was obtained when the diameters from DFT calculations were taken into account instead of simple graphene-based values. The resonance behaviour of the RBM intensities was recorded for the tubes in zeolites. This result agrees with a prediction from \textit{ab initio} calculations and demonstrates a breakdown of the simple TB approach to the electronic structure.

The D line of the inner tubes was also recorded. It downshifts due to the smaller diameter in a qualitative agreement with the results of [10] for NTs with \(d > 1\) nm. A dispersion of the line position with the laser excitation energy was found. Its rate is about 10\% smaller when compared with that for the outer tubes. It was explained as a direct consequence of the two rather different
NT diameters in DWCNTs and the fact that different electronic transitions are in resonance with the laser excitation energies.

The lines due to the inner NTs were also identified in the G-band part of the spectra. For semiconducting inner NTs, the line positions shift down with respect to the outer tubes because of the smaller diameter of the inner tubes. On the other hand, no additional lines, which could be assigned to the G lines of the metallic inner tubes, were found in the spectra. This suggests that the proposed Peierls-like mechanism for frequency softening of the metallic G band is accompanied also by the intensity reduction.

In general, Raman spectra of NTs in the zeolite crystals are much more complicated. This is unexpected as only four different NTs contribute to them. Their diameters are about 40% smaller than the mean diameter of the inner tubes in DWCNTs.

Three of the four possible tubes were identified according to their RBM frequencies and resonance behaviour. In order to achieve this, the analysis must go beyond the TB approach and results of ab initio calculations have to be used.

The frequencies still obey the $1/d$ scaling but the absolute values are reduced. They cannot be explained by the differences in the tube diameters of DWCNTs and the NTs in the zeolites. Rather an interaction with the zeolite environment plays a decisive role for this reduction.

Individuality of the NTs manifests itself completely for the D lines. The dispersive behaviour was found for the (4,2) NTs only. The zeolite crystals soften the D-line frequencies when compared with those observed for DWCNTs. The G-band profiles and positions were found to depend on which of the NTs are in resonance with the energy of the incoming laser light. Even though the (5,0) NTs are metallic, no evidence for the Peierls instability or for a Breit–Wigner–Fano line shape was found. This confirms the theoretical results for a different character of the electronic bands in the vicinity of the Fermi level when compared with standard metallic NTs with larger diameters.

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