Carbon Nanotube Raman Spectra Calculations using Density Functional Theory

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Abstract

Utilizing density functional theory (DFT) the Vienna Ab initio Simulation Package (VASP) was used to calculate the Raman spectra for five single-walled carbon nanotubes (SWCNTs) with chiralities (4,4), (6,6), (8,0), (12,0) and (7,1). The radial breathing mode (RBM), when compared with experimental frequencies, shows good correlation. When compared to RBM:s calculated with tight binding the frequencies calculated with DFT displayed higher accuracy. The precision of G-band frequencies were inconclusive due to lack of experimental data. The frequencies did not agree well with the results from tight-binding theory. The correctness of the Raman activity estimations using results from DFT calculations was found to be questionable. An unknown mode, which was found to be highly Raman active in the calculated spectra of (4,4), (6,6), and possibly (8,0), and (12,0), is also discussed. It was concluded that further calculations on larger tubes, especially armchair tubes are relevant for future studies. Further verification of the determination of Raman activity is also needed.
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Objective

The aim was to calculate Raman spectra for a number of single-walled carbon nanotubes (SWCNT) using density functional theory (DFT) through Vienna Ab initio Simulation Package (VASP). These were to be compared to previous experimental and theoretical findings to determine the accuracy of Raman spectrum calculation using DFT. This may indicate if DFT could give more precise predictions of the Raman scattering behavior of SWCNTs, reducing the risk of assuming incorrect tube chiralities.

1 Introduction

Consisting of a cylindrical structure of carbon atoms the single-walled carbon nanotube (SWCNT) resembles a rectangular piece of graphene curved into a cylinder with the sides joined together. This resemblance is used in tube classification [1] giving, from chiral indices $n$ and $m$, the circumfering vector of a nanotube unit cell as

$$C_h = n\mathbf{a}_1 + m\mathbf{a}_2,$$

(1)

where $\mathbf{a}_1$ and $\mathbf{a}_2$ are lattice vectors between neighboring atoms in the graphene sheet, as can be seen in figure 2. The length of the unit cell could be expressed as

$$\mathbf{T} = t_1\mathbf{a}_1 + t_2\mathbf{a}_2$$

where

$$t_1 = \frac{2m+n}{d_r}, \quad t_2 = -\frac{2n+m}{d_r}$$

and

$$d_r = \begin{cases} d & \text{if } n-m \neq 3k \\ 3d & \text{if } n-m = 3k \end{cases} \quad k \in \mathbb{N}$$

with $d$ being the greatest common divider of $m$ and $n$. SWCNTs are further grouped into series depending on the sum of $m$ and $n$, giving a rough estimate of the tube size. Thus a series consist of an armchair tube where $m = n$, a zigzag tube where $m = 0$ and a number of chiral tubes where $n > m > 0$. Examples of these are illustrated in figure 1.

Figure 1: 3D illustration of three SWCNTs of different chiralities. From left to right: 3 cells of (4,4), 1 cell of (7,1) and 2 cells of (8,0).

The diameter of a SWCNT can be calculated assuming that the length of the chiral vector (1) is the same as the circumference. This length can be calculated from the chiral indices, $(n,m)$, yielding the diameter

$$d = C_h/\pi = \sqrt{3}a_{CC}\sqrt{m^2 + mn + n^2}/\pi,$$

(2)

where $a_{CC}$ is the assumed C-C bond length in graphene, 1.421 Å.
Since current production methods often give a variety of chiralities, although pure chirality methods are on the horizon [2], it is relevant to accurately recognize which chiralities that are present in a given sample. This is important, because the structure of the SWCNT determines its electric properties, i.e. whether it is metallic, semi-metallic, or semiconducting.

Due to its sensitivity to electron structure, Raman spectroscopy is a powerful tool in tube categorization since each chirality has a unique spectroscopic signature.

In experiments the electrons in the tube molecular structure are excited using a laser and in the excited state they may lose some energy to phonon excitations. Just as photons are quanta of light, phonons are quanta of structural vibrations on a quantum mechanical level. A given lattice has a certain set of oscillatory motions called phonon modes. A discrete number of phonons may occupy such a mode, giving rise to lattice vibrations. Each mode has a specific energy per phonon, in addition to a zero-point energy. [5] When the electron afterwards relaxes the lost energy expresses itself through a shift in the frequency of the outgoing photon, thus giving the phonon mode energies. Figure 3 contains a simple illustration of the process. Different modes give different energy shifts in the outgoing photon, the process of which is called Stokes scattering. If no phonons are excited, the outgoing photon has the same energy as the incident photon, which is called Rayleigh scattering.
Obtaining a reliable map of these spectral shifts is therefore vital for accurate characterization. This map can be calculated using different theoretical approaches. Tight binding is one possibility but gives inaccurate results for small diameter tubes [1]. Another popular possibility is density functional theory (DFT) [8]. In this work we focus on calculating the Raman spectra for a number of tubes using DFT and comparing the results with tight binding calculations and experimental data.

Calculations on SWCNTs using DFT can be performed using the Vienna Ab initio Simulation Package (VASP), further discussed in section 2.1, and an external Python script [9]. We have had access to the High Performance Computing Center North (HPC2N) resources for our calculations. Because of time and resource constraints this work is focused on the five tubes (4,4), (6,6), (8,0), (12,0) and (7,1). This gives the armchair and zigzag tubes of the 8-series and 12-series and a chiral tube from the 8-series, thus giving a wider impression of the calculation method rather than focusing on a certain type of tube. The choice of tubes was based on two criteria: The unit cell of each tube needed to contain few atoms to allow for high-precision calculations with limited resources. In order to make the calculations relevant and comparable, there also had to be prior results from experiments and results from computational methods based on the tight-binding approximation for the selected tubes. The Raman spectra of the benzene molecule has also been calculated for further comparison and validation of the method. The benzene molecule resembles SWCNTs in the sense that it is a piece of hydrogen-terminated graphene and that it demonstrates a radial symmetry similar to an SWCNT. Thus it may possess some similar vibrational properties. A phonon mode of benzene similar to the RBM of SWCNTs is illustrated in figure 4.

1.1 Radial breathing mode

The vibrational mode in which all atoms coherently oscillate in radial direction is called, from the tube motion assembling breathing, radial breathing mode (RBM). An illustration of this can be seen in figure 6. In the spectrum in figure 5 RBM can be seen as the peak around 300 cm$^{-1}$. Due to the mode emerging from the tubular shape, RBM is a unique characteristic of single-walled carbon nanotubes. Depending on the radius of the tube and thus the nature of the radial oscillation the Raman frequency varies with different tube sizes. The RBM frequency, $\omega_{RBM}$, is shown to have a linear relation to the inverse of the tube diameter $1/d$ [1], i.e.

$$\omega_{RBM} = A/d + B,$$

where $A$ and $B$ are real constants. This being derived from Tight binding and experimental results it would, given the results from the DFT simulations, be relevant to in addition to comparing RBM
Figure 5: Experimental spectrum for a mixture of SWCNTs. The spectrum was produced at Luleå University of Technology.
1.2 G-band

The G band is a Raman active mode in graphene centered at about 1582 cm\(^{-1}\), as can be seen in figure 5. In contrast to graphene, SWCNTs have two distinct peaks due to the symmetry breaking curvature. One is the \(G^+\) feature centered at about 1590 cm\(^{-1}\) and is associated with vibrations along the tube axis. Another is the \(G^-\) feature centered at about 1570 cm\(^{-1}\) and is associated with circumferential vibrations. The frequency of the latter is dependent on the tube diameter. These are illustrated in figure 7. For metallic tubes it has a Breit-Wigner-Fano lineshape and for semiconducting tubes it has a Lorentzian lineshape. \[1\]

1.3 Density functional theory

The Hamiltonian for a system of several electrons and nuclei makes it impossible to solve the Schrödinger equation for the wave functions. By considering the total energy as a functional of an electron probability density, i.e.

\[ E = E[\rho(r)], \]

density functional theory (DFT) makes it possible to efficiently approximate the properties of the system. The total energy is minimized with respect to the electron probability density in order to
find the ground state of the system. [8]

2 Method

We have chosen to perform calculations on SWCNTs that i) contains few atoms in the unit cell to reduce computation time ii) are documented in previous works in a way that makes the results comparable iii) have different chiralities, e.g. armchair, chiral, or zigzag, to assess the versatility of the method. Initially some tests had to be conducted in order to validate the VASP settings used to achieve accurate Raman spectra, for which we have used the (4,4) SWCNT containing only 16 atoms. For details about VASP, which is the mainly used software, see section 2.1. The calculation of a Raman spectrum for a tube was performed as follows.

1. An initial geometry of the tube unit cell was generated using Virtual NanoLab. See section 2.2 for details.
2. The geometry was optimized to approach its lowest energy state with respect to cell shape and ion positions. This was done using VASP. See section 2.3 for details.
3. For the optimized geometry the phonon modes were calculated, also using VASP. See section 2.4 for details.
4. The Raman spectrum was calculated using the result from step 3. This was done with a Python script [9] which utilized VASP. See section 2.5 for details.

2.1 VASP

The Vienna Ab initio Simulation Package (VASP) is a software package for solving electronic structure theory computations of atoms, molecules, clusters and crystals. In our calculations VASP 5.4.1 has been used. VASP was run in a given directory using several files as input. The most important ones are named INCAR, KPOINTS, POTCAR and POSCAR. Most settings are controlled by the INCAR file. A k-point sampling grid, which indicates which sites in reciprocal space that are used when evaluating the band-structure energy, was specified in the file KPOINTS. A description of the ion species, e.g. the carbon atom, was contained in the POTCAR file. The unit cell of the structure was provided in POSCAR. [4] In the following subsections some important INCAR parameters and files are described further.

2.1.1 Plane-wave cutoff

VASP performs calculations using plane-waves up to a given cut-off energy, controlled by the INCAR-parameter ENCUT. If this is too small, it introduces errors.[3],[4] The total energy of the system was investigated for increasing cut-off energies until the total energy had converged with respect to the ENCUT value.

2.1.2 k-points

VASP performs sampling in reciprocal space at a number of k-points, specified in the KPOINTS file. [4] We have used automatically generated Γ-centered k-point grids. All points were chosen along the tube axis, regarding the tube-tube distance as relatively large and thus assuming the tube-tube interaction to be negligible. As with ENCUT, the number of k-points was increased until no significant change in total energy was observed.

2.1.3 Energy convergence criteria

EDIFF controls how small a change in free energy should be observed before the system is considered converged during the electronic relaxation loop. EDIFFFG does the same during the ionic relaxation loop for positive values. For negative values, the loop will stop if all forces are smaller than $|\text{EDIFFFG}|$ [4]. Smaller values should improve accuracy, but increase the number of ionic iterations required.
2.1.4 Type of ionic calculation

The INCAR parameter IBRION controls the type of ionic calculations performed by VASP. Specific values are described in the sections 2.3 and 2.4.

2.1.5 Description of ion species

In our calculations we have used plane-wave augmented wave method (PAW) potentials. These are provided to VASP in the POTCAR file. Both normal and hard potentials were tested on (4,4). Testing of the parameters ENCUT, EDIFF and EDIFFG and the number of k-points was performed using normal potentials. It was decided that hard potentials were to be used for the other SWCNT calculations and the benzene calculations.

2.1.6 Fundamental temperature

VASP performs finite temperature calculations controlled by the INCAR parameter SIGMA, \( \sigma = k_B T \), which is the fundamental temperature. Performing calculations at a lower temperature gives better accuracy at the cost of a larger computational effort [4]. For both the SWCNTs and benzene, SIGMA = 0.2 has been used. Lower values were tested on benzene.

2.1.7 Cell optimization

The INCAR parameter ISIF mainly controls whether the stress tensor is calculated, which is time consuming. It also controls whether ion relaxation is performed and whether cell shape and volume is changed. Cell changes are only supported during relaxations [4]. We have used ISIF = 4 for the SWCNTs, which means that the stress tensor was calculated, the ions were relaxed, the cell shape was changed and the cell volume was held constant. For benzene we have used ISIF = 2, which differs in that the cell shape is also held constant.

2.2 Geometry generation

The geometries used in VASP were generated using Virtual NanoLab (VNL). VNL builds a tube structure based on a given carbon-carbon bond distance, in this case the bond distance for graphene, and the atom positions were then exported to a POSCAR-file. Since the bond distance varies depending on tube this gives a slightly inaccurate representation of a relaxed tube and thus it is necessary to perform a geometry optimization.

2.3 Geometry optimization

It is important for accuracy to properly represent the SWCNT geometry since we want to know how a carbon nanotube vibrates and not how a distorted carbon-nanotube vibrates. Though a perfect representation is impossible we intend to get as close as possible.

When optimizing the ion positions we have used a conjugate gradient scheme by setting the INCAR parameter IBRION = 2. In this procedure the ions are moved and, if indicated by ISIF, the cell shape is changed based on the forces and the stress tensor. Then the energy and forces are recalculated. An approximate system energy minimum is determined and based on the forces some corrections are made to the ion positions. The energy and forces are recalculated and, if the forces are parallel to the initial search directions, the minimization is improved with more correction steps. The procedure is repeated until a convergence criterion is fulfilled. [4]

2.4 Calculation of phonon modes

The Hessian matrix contains the second derivatives of the energy with respect to the position of an ion. From this, the phonon modes of a system can be determined. VASP provides two methods of calculating the Hessian. With IBRION = 5 or 6 in the INCAR file, VASP uses a finite displacement method. With IBRION = 7 or 8, density functional perturbation theory is used.

In the finite displacement method, ions are displaced in the directions of the Cartesian axes. We have used NFREE = 2, corresponding to two displacements along each axis. The Hessian matrix
is given by the resulting Hellmann-Feynman forces. The latter method is an analytic approach based on perturbation theory.

With IBRION = 6 or 8, symmetry considerations are used to fill out part of the hessian matrix. This is supposed to improve performance, if the symmetries of the system are found. [4]

All four settings were tested on the (4,4)-tube with different settings of EDIFF and EDIFFG. It was decided that IBRION = 7 was to be used for most calculations. IBRION = 5 was occasionally used to circumvent a bug in VNL and thus allow for visualization of the phonon modes.

2.5 Calculation of Raman spectra

The Raman intensity for each mode can be calculated using

\[ I_{\text{Ram}} = 45\alpha'^2 + 7\beta'^2, \] (5)

[6] where

\[ \alpha' = \frac{1}{3}(\bar{\alpha}'_{xx} + \bar{\alpha}'_{yy} + \bar{\alpha}'_{zz}) \] (6)

is the mean polarizability derivative and

\[ \beta'^2 = \frac{1}{2}((\bar{\alpha}'_{xx} - \bar{\alpha}'_{yy})^2 + (\bar{\alpha}'_{xx} - \bar{\alpha}'_{zz})^2 + (\bar{\alpha}'_{yy} - \bar{\alpha}'_{zz})^2 + 6(\bar{\alpha}'_{xy} + \bar{\alpha}'_{xz} + \bar{\alpha}'_{yz})) \] (7)

is the anisotropy of the polarizability tensor derivative. \( \bar{\alpha} \) is the polarizability tensor and derivatives are taken with respect to the normal mode coordinate, \( Q \). \( Q \) signifies the amount of displacement along one eigenvector of the system. The eigenvectors are found through direct diagonalization of the hessian matrix. By displacing the atoms along the eigenvectors of each mode twice, letting VASP calculate \( \bar{\alpha} \) (per volume) using density functional perturbation theory, [4] \( \bar{\alpha}' \) is approximated as a finite difference quotient. Thus we find the Raman intensity of the mode. These calculations were performed using a python script [9], indirectly using VASP.

2.6 Calculation of SWCNT diameters

The formula for calculating SWCNT diameters described in the introduction, (2), does not take into account that the relaxed SWCNT may have a structure with somewhat different bond lengths. Another estimate of the diameter can be obtained from direct calculations on the optimized structure. The positions of the ion centers, \( p_i \), are projected onto a plane with the longitudinal lattice vector, \( a_3 \), as normal vector. If the shape of the cell is optimized, being initially a cuboid, this vector may differ somewhat from the z-axis. Thus the projected points are

\[ p^*_i = p_i - \frac{p_i \cdot a_3}{a_3^2} a_3 \] (8)

The position of the tube axis, \( q \), is taken to be the average value of all \( N \) projected ion positions. I.e.

\[ q = \frac{1}{N} \sum_{i=1}^{N} p^*_i \] (9)

The average distance of the projected positions to this point is the estimated radius,

\[ \frac{d}{2} = \frac{1}{N} \sum_{i=1}^{N} ||p^*_i - q||. \] (10)

3 Results and discussion

3.1 Parameters

3.1.1 ENCUT

The convergence study of ENCUT on the (4,4)-tube suggested that 700 eV was an adequate value, which was used for all other calculations. The total energy of the system as a function of ENCUT is shown in figure 8. There is an especially deviant point at ENCUT = 950, which has been dismissed as a potential calculation error.
3.1.2 KPOINTS

In the case of the (4,4)-tube with a direct lattice tube axis unit cell length of 2.47 Å, the number of k-points was chosen to 36. For the remaining tubes, the required number of k-points was assumed to be inversely proportional to the unit cell length along the tube axis. For benzene, however, only the Γ-point was used. The total energy of the (4,4)-system as a function of the number of k-points is shown in figure 9.

3.1.3 EDIFF and EDIFFG

We have tested EDIFF = 1.0E-6 eV, 1.0E-8 eV and 1.0E-9 eV with EDIFFG = -1.0E-3 eV/Å, -1.0E-4 eV/Å and -1.0E-5 eV/Å, respectively, on (4,4). At increasing accuracy we found higher frequencies of the phonon modes, but at a significant increase in computation time. Therefore we chose to perform the remaining calculations with EDIFF = 1.0E-8 eV and EDIFFG = -1.0E-4 eV/Å. We were occasionally forced to lower EDIFF to 1.0E-9 eV in order to allow the system to converge.

3.1.4 The POTCAR file

In testing normal and hard potentials on the (4,4)-tube it was decided that hard potentials were to be used, since these appeared to give more accurate phonon mode frequencies when comparing RBM and G-band to prior results. Coincidentally, the VASP-manual [4] recommends the cut-off energy decided on for hard potentials.

3.1.5 SIGMA

In testing lower values of SIGMA than 0.2 on benzene, it was discovered that the calculations failed to converge at lower values than 0.1. In addition, it was much more resource-demanding. Therefore SIGMA = 0.2 was used for all other calculations.

3.1.6 Finite displacements vs. Density functional perturbation theory

There was no substantial difference in the results from the finite displacement method (IBRION = 5, 6) and density functional perturbation theory (IBRION = 7, 8). In addition, the computation time was not improved in the symmetry-observant methods (IBRION = 6, 8). It is possible that
the relaxed (4,4)-tube is insufficiently symmetrical. Therefore, IBRION = 7 was used for most calculations, since it was by a narrow margin the fastest of the methods.

3.2 Tube Spectra

Since the modes with higher intensities often differ from other relevant intensities with several orders of magnitude the difference will not be discussed further than whether or not a mode is active. Because of the large difference, the logarithms of the intensities are presented for the sake of visibility. Spectra of the tubes (4,4), (6,6), (8,0), (12,0), and (7,1) are presented in figures 10, 11, 12, 13, and 14, respectively. These only contain the largest intensities of their respective spectrum. In figure 13 and 14 the intensities are scaled in relation to the mean value. Complete spectra are to be found in the appendix.

RBM and G-band assignment to frequencies was clear for (4,4), (6,6) and (8,0). The unit cell of (7,1) contains the most atoms of the tubes included in the study, thus having the most phonon modes and requiring the most calculation time per mode. Due to shortage of time and resources only outer modes were calculated to locate the RBM and G-band. The (12,0) spectrum has high intensities at virtually all modes and the G$^-$ feature could not be identified with a peak in the spectrum. The high intensity makes the determination of Raman activity questionable. A similar amplification was observed when ions slightly displaced from equilibrium were accidentally used, suggesting that the geometry may not have been properly optimized. The identification for both (12,0) and (4,4) was verified by investigating the motions of the modes graphically using the eigenvectors calculated by VASP.

3.3 RBM

As can be seen in table 1 the calculated frequencies undershoots both experimental, in the two cases where experimental data were available, and the two linear models. All calculated frequencies are also presented in figure 15 in relation to calculated diameters together with a linear least-square relation, the experimental results and the two linear relations. The parameters for the least-square fit on the calculated RBM are $A = 221.3517$, $B = 7.9427$. As can be seen in the figure the relations resemble each other though the calculated linear relation has a lower offset. It should however also be taken into account that the calculated frequencies are for relatively small tubes and that the observed linear relation for larger tubes might differ in this range due to the high curvature of
Figure 10: Raman spectrum for the (4,4) tube

Figure 11: Logarithm of Raman spectrum for the 6-6 tube
Figure 12: Logarithm of Raman spectrum for the 8-0 tube

Figure 13: Logarithm of Raman spectrum for the 12-0 tube
Figure 14: Logarithm of Raman spectrum for the 7-1 tube

Table 1: Calculated, experimental and expected RBM-frequencies for selected tubes. Least square for calculated: $A = 221.3517$, $B = 7.9427$, Kataura [1]: $A = 248$, $B = 0$ and Bachilo [7]: $A = 223.5$, $B = 12.5$ (C-C bond distance assumed to be 0.144) using (3). Calculations from tight-binding molecular dynamics (TBMD) and other tight binding (TB) calculations.

<table>
<thead>
<tr>
<th>n,m</th>
<th>Calculated $\omega_{RBM}$ (cm$^{-1}$)</th>
<th>Experimental $\omega_{RBM}$ (cm$^{-1}$)</th>
<th>Linear adaption $\omega_{RBM}$ (cm$^{-1}$)</th>
<th>TBMD [10], TB [13] $\omega_{RBM}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4</td>
<td>413.5</td>
<td>-</td>
<td>418.8, 450.9</td>
<td>- , 430</td>
</tr>
<tr>
<td>8,0</td>
<td>354.5</td>
<td>-</td>
<td>364.4, 390.5</td>
<td>- , 375</td>
</tr>
<tr>
<td>7,1</td>
<td>368.0</td>
<td>-</td>
<td>385.4, 413.8</td>
<td>- , 370</td>
</tr>
<tr>
<td>6,6</td>
<td>281.3</td>
<td>288 [11]</td>
<td>283.4, 300.6</td>
<td>276.6, 300</td>
</tr>
<tr>
<td>12,0</td>
<td>240.0</td>
<td>247.9 [7]</td>
<td>247.1, 260.3</td>
<td>238, 265</td>
</tr>
</tbody>
</table>

the small tubes. For both the tight-binding (TB) calculations and the tight-binding molecular dynamics (TBMD) we find that DFT has a closer agreement with the experimental results.

3.4 G-band

As mentioned in section 1.2 $G^+$ should have a frequency centered about 1590 cm$^{-1}$ and $G^−$ should be centered at about 1570 cm$^{-1}$. The frequencies presented in table 2 are generally lower than what is expected for both the DFT and the tight-binding (TB) calculations. The $G^-$ feature is however known to be diameter-dependent [1], which explains the low values of the smaller tubes. The $G^+$ feature appears to exhibit similar behavior. There is however a difference in that the $G^+$ frequency consistently is smaller than the $G^-$ frequency in the DFT calculations, whereas they are not in the TB calculations. In those the $G^-$ frequencies were found to be larger for semiconducting tubes [13], especially for moderately big tubes.

3.5 Diameter

In table 3 the tube diameters based on the optimized geometries are compared to the analytic diameters given from (2). All calculated diameters are slightly larger than the theoretical probably due to the large curvature of small tubes affecting carbon-carbon bond distance. In figure 15 the diameters based on the optimized geometries are used for the calculated frequencies while the theoretical diameters are used for the experimental diameters.
Figure 15: RBM-radius relation. $A = 221.4$ and $B = 7.9$ for the least-square fit of the calculated frequencies.

Table 2: Calculated values for the G-band. Our calculations are presented to the left and tight-binding (TB) calculations are presented to the right.

<table>
<thead>
<tr>
<th>$n, m$</th>
<th>$G^{+}$ (cm$^{-1}$)</th>
<th>$G^{-}$ (cm$^{-1}$)</th>
<th>$G^{+}$ TB [13] (cm$^{-1}$)</th>
<th>$G^{-}$ TB [13] (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4</td>
<td>1479.7</td>
<td>1454.6</td>
<td>1595</td>
<td>1395</td>
</tr>
<tr>
<td>8,0</td>
<td>1561.9</td>
<td>1532.6</td>
<td>1515</td>
<td>1572</td>
</tr>
<tr>
<td>7,1</td>
<td>1523.7</td>
<td>1513.1</td>
<td>1512</td>
<td>-</td>
</tr>
<tr>
<td>6,6</td>
<td>1543.3</td>
<td>1539.0</td>
<td>1538</td>
<td>1455</td>
</tr>
<tr>
<td>12,0</td>
<td>1506.1</td>
<td>-</td>
<td>1547</td>
<td>1595</td>
</tr>
</tbody>
</table>

Table 3: Calculated and experimental tube diameters. Theoretical values are calculated using (2) with an assumed bond distance of 0.144 nm.

<table>
<thead>
<tr>
<th>$n, m$</th>
<th>calculated diameter (nm)</th>
<th>theoretical diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4</td>
<td>0.5536</td>
<td>0.54</td>
</tr>
<tr>
<td>8,0</td>
<td>0.6372</td>
<td>0.63</td>
</tr>
<tr>
<td>7,1</td>
<td>0.6022</td>
<td>0.59</td>
</tr>
<tr>
<td>6,6</td>
<td>0.8223</td>
<td>0.81</td>
</tr>
<tr>
<td>12,0</td>
<td>0.9478</td>
<td>0.94</td>
</tr>
</tbody>
</table>
3.6 Unknown mode

There is an especially protuberant peak between 800 and 850 cm\(^{-1}\) in the spectra of the armchair tubes (4,4) and (6,6). There is a similar, but reduced, peak in the same frequency range in the spectra of the zigzag tubes (8,0) and (12,0). The mode in the (4,4) tube is similar to the RBM, with the exception of every other atom around the circumference being in antiphase with the rest, forming alternating in-phase rows along the tube axis. An illustration of this can be seen in figure 16. This frequency range has not been investigated for the (7,1)-tube. If this mode is nonexistent for that tube, one possible explanation could be that it mainly occurs in highly regular tubes with small unit cells, allowing for a group-wise antiphase RBM. Otherwise, and considering that the mode does not appear to be well known from experiments, it may be suppressed by finite-size effects or the nature of the tube ends.

3.7 Benzene

Phonon calculations were performed for benzene with both ISIF=2 and ISIF=4, where the parameter change did not affect the frequencies to any higher degree. Since the change in ISIF allows for reshaping of the unit cell this suggests that the molecule experienced negligible pressure. Performing phonon calculations with a lower sigma resulted in a slight shift in frequency of about 3% for some modes. While having a relevant impact on the result a lowered sigma also required a significantly longer computation time. The calculated frequencies using ISIF=2 and the same sigma as for the carbon nanotubes are shown in table 4 together with assumed corresponding experimental frequencies. As can be seen, the consistency is quite good for most modes, but occasionally quite bad. In addition, several Raman active modes in the calculations could not be identified with experimental results, though the similarity in neighboring frequencies would make them difficult to distinguish experimentally.
4 Conclusions

Raman spectra calculations for the carbon nanotubes of chirality (4,4), (6,6), (8,0), (12,0) and (7,1) were performed using VASP and an external Python script. The RBM was clearly visible in all spectra and while being slightly low when compared there was good correspondence to experimental and expected frequencies. It appears these DFT calculations make somewhat better predictions about RBM frequency than those within the framework of tight-binding theory, but more experimental result are needed for comparison. When investigating the G-band frequencies, few conclusions regarding correctness can be made. It seems that the tight-binding calculations do not agree very well with the DFT calculations in these aspects.

Regarding determination of Raman intensities, the DFT calculations appeared to give some hints about important features of the spectra, but also had some significant abnormalities. Some unknown modes were present in both the carbon nanotube calculations and the benzene calculations. It is conceivable that finite-size effects have some role in this on the carbon nanotubes. The presence of a substrate and a closed end could suppress some motions.

The tubes focused on in this work are relatively small and thus the high curvature has a larger impact on the Raman scattering behavior than for larger tubes. The DFT calculations performed in this way requires large computational behavior and may thus be inappropriate for large tube structures.

The high activity of the (12,0) spectrum suggests that the Raman calculations or possibly the geometry optimization occasionally gives erroneous results. If the nanotube is not properly relaxed, this could also affect the phonon mode frequencies. The Raman calculations involve numeric derivatives, making them highly sensitive to convergence deficiencies [6]. Density functional theory is based on several approximations, which may also affect the accuracy of the results.

Future studies could involve further examination of differences in the results and performance of phonon mode calculations using the methods based on finite differences and density functional perturbation theory or investigating possibilities to use symmetry for improved performance. Density functional perturbation appeared to increase memory requirements for large tubes. This in turn forced us to allocate more processors than may have been optimal. The finite difference method may be preferable for efficient calculations. It would also be relevant to investigate more tubes to further determine the method’s reliability, primarily larger tubes since there are more experimental and theoretical data concerning larger diameters. (6,5) was considered since there is much experimental and calculated data concerning that tube. The tube unit cell was however too large for it to be reasonable to perform calculations on with our limited resources and thus makes a good candidate for future studies. The mode of unknown origin should be investigated, especially for large armchair tubes, and compared to experimental data in order to find whether it is Raman active in reality. If it is, as suspected, not Raman active, the cause would need further investigation. It could indicate errors in our chosen method for detecting Raman activity.
5 Appendix

Figure 17: Logarithm of calculated Raman spectrum for the 4-4 tube

Figure 18: Logarithm of calculated Raman spectrum for the 6-6 tube
Figure 19: Logarithm of calculated Raman spectrum for the 8-0 tube

Figure 20: Logarithm of calculated Raman spectrum for the 12-0 tube
Figure 21: Logarithm of calculated Raman spectrum for the 7-1 tube
References


