We present a theoretical study of the vibrational spectrum, in the G band region, of laterally hydrogenated single wall carbon nanotubes through molecular dynamics simulations. We find that bilateral hydrogenation – which can be induced by hydrogenation under lateral strain – causes permanent oval deformations on the nanotubes and induces the splitting of vibrational states in the G-band region. We propose that such splitting can be used as a Raman fingerprint for detecting nanotubes that have been permanently modified due to bilateral hydrogenation. In particular, our results may help to clarify the recent findings of Araujo and collaborators [Nano Lett. 12, 4110 (2012)] which have found permanent modifications in the Raman G peaks of locally compressed carbon nanotubes. We have also developed an analytical model for the proposed phenomenon that reproduces the splitting observed in the simulations.

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the G\textsuperscript{−} peak was not fully reversible, that is, in some experiments the SWCNT did not recover the non-split state (observed before the contact with the AFM tip), after the AFM tip was retracted. Such a result shows that something prevents the SWCNT to recover its cylindrical symmetry after being compressed by the AFM tip. A possible explanation for the observed permanent G\textsuperscript{−} splitting is the covalent bonding between the most curved parts of the tube and chemical species of the environment during the compression process [35,36]. The tip induced radial deformation which severely increased the local curvature in some parts of the tube. It was shown that locally, highly curved regions of carbon nanotubes strongly affects local reactivity by increasing the sp\textsuperscript{3} character of the sp\textsuperscript{2} C–C bonds [37–39]. Such a lateral functionalization may prevent the tube to recover its original curvature and/or provide an asymmetrical distribution of mass, which could result in the observed splitting in vibrational modes.

In order to test the hypothesis described above, we employed molecular dynamics simulations to investigate the effects of lateral functionalization in vibrational modes of SWCNTs. Our calculations show that even if a small fraction of the tube atoms bind to hydrogen atoms, the G\textsuperscript{−} peak splits into distinct vertical and horizontal contributions (which we will call G\textsubscript{v} and G\textsubscript{h}, respectively). We also found that the magnitude of the G\textsuperscript{−} splitting (>20 cm\textsuperscript{−}1 for more than 10 adsorbed hydrogens as can be seen Fig. 4) is much larger than the experimental frequency resolution (2 cm\textsuperscript{−}1) of modern Raman setups. Supporting our simulation results we developed a simple model which explains the origin of such splitting in the G\textsuperscript{−} peak in terms of changes in the tube curvature. The present work can contribute to understand how molecules in the environment may change SWCNT properties.

This paper is organized as follows. In Section 2 we present the molecular dynamics simulation details. Section 3 contains the simulation results while the analytical model is shown in Section 4. Section 5 is reserved for final remarks.

2. Simulation details

We performed molecular dynamics simulations using the LAMMPS package [40]. The system considered consists of a (10,0) single wall carbon nanotube composed by 520 carbon atoms with length of approximately 55 Å along to the z-axis (the longitudinal axis). Thus x- and y-axis are the transversal ones.

We consider a bi-lateral functionalization of the carbon nanotubes, where hydrogen atoms are chemically bound to opposite sides of the nanotubes (see Figs. 1 and 2). Only four rows of the tube (two on each side) are allowed to adsorb hydrogens. Each row have 26 carbon atoms, thus the maximum number of adsorbed hydrogens is 104. In this work, we considered cases in which up to 20 hydrogens are randomly adsorbed in the carbon nanotubes. Our simulations show that at temperature $T = 300$ K hydrogenated SWCNTs become unstable if more than 20 hydrogens are adsorbed, and the so called unzipping effect is observed. We notice that at $T = 100$ K the tubes become stable even when 104 H atoms are adsorbed. This result is consistent with the experimental findings which show that hydrogenated carbon nanotubes unzip at temperatures above certain critical value [41].

Periodic boundary conditions were considered in all directions with the simulation box, which has dimensions of 100 Å in the x- and y-directions and 55.26 Å along the z-axis. Those dimensions have shown to be suitable for simulating an infinite tube along its longitudinal axis whereas isolated laterally.

The timestep used was $\Delta t = 0.01$ fs. Pressure and temperature
were kept constant at 1 bar and 300 K, respectively, by using the Nosé-Hoover thermostat [42] and barostat [43]. Finally, interactions between atoms (C–C, C–H, and H–H) were modeled classically with the ReaxFF potential [44].

Before the production stage, i.e., the stage in which the data are collected, there was an equilibration stage. In the equilibration stage the temperature was kept at 300 K during 10 ps. After that, the followed production stage in which the velocities of the carbon atoms were collected for each 500 steps (or 5 fs) along 525000 steps (or 5.25 ps). To calculate the phonon DOS, 1024 data points were used among those 1050 collected. The phonon DOS is calculated through the Fourier transform of the velocity autocorrelation function, between the velocity \( \bar{v} \) in a time \( t_0 \) and a later time \( t \),

\[
\hat{f}(t) = \frac{1}{N} \sum_{i=1}^{N} \bar{v}_i(t_0) \cdot \bar{v}_i(t),
\]

where the summation runs over the N carbon atoms. In order to improve the sample data, this procedure was performed five times, in which every one has a different, random hydrogen distribution for a certain degree of hydrogenation. The average of vertical and horizontal contributions to the G-band were calculated and the standard deviation was computed based on the referred five measurements.

3. Simulation results

Our results from simulations are summarized in Figs. 3 and 4. Fig. 3 shows the transversal (in the xy plane) contributions to the phonon density of states (DOS) to the G-band against the frequency. \( G_h \) and \( G_v \) distinguish between the horizontal (x-axis) and vertical (y-axis) modes in the transverse plane, respectively. The projection of the G-modes into the transverse plane of the tube. We see that for 10 H adsorbed in the G-band approximately 200 cm\(^{-1}\) potential, for example, present results for the G-band upshifted by 100 cm\(^{-1}\) to higher frequencies. The G\(^+\) mode is an in plane stretching mode along the tube axis [47–50]. Therefore, it is natural that the G\(^+\) mode is very sensitive to changes in the SWCNT curvature while the G\(^-\) is not. This curvature effect naturally appears in SWCNT with different diameters and the G\(^-\) mode frequency is softened with decreasing tube diameter, while the G\(^+\) mode remains unaltered [47,48,51–53].

Inspired by this curvature effect, we propose a simple model, consisting of eight identical masses (m) and connected by eight identical springs (k), to explain how transversal deformations change the G\(^+\) mode behavior [see Fig. 5(a)]. The (10,0) nanotube studied in this work has more than 8 atoms along the circumference. However, to obtain analytical solutions under the symmetry constraints of the problem, eight masses are largest possible system. Due to transversal deformations [see Fig. 5(b)], the tube circumference flattens leading to different vertical and horizontal normal modes. We will show that such a normal modes splitting effect can be explained by purely geometrical arguments.

For developing our mass–spring model we start by building the behavior of vectors \( \mathbf{r}_1, \mathbf{r}_2, \) and \( \mathbf{r}_3 \) under system deformation. It is possible to derive the normal modes of the 8 masses/spring system by investigating the motion of the three masses localized by the three cited vectors due symmetry arguments. We assume that \( r_1 \) decreases and \( r_3 \) increases by the same amount \( \delta r \) due to radial deformation. For \( r_2 \), we assume that its horizontal component increases by \( c_x \delta r \) while its vertical one decreases by \( c_y \delta r \) when the system is deformed. Considering that the length of \( \mathbf{r}_1, \mathbf{r}_2, \) and \( \mathbf{r}_3 \) is \( r_0 \) in the symmetrical case and by simple inspection of Fig. 6, we conclude that

\[
\begin{align*}
  r_1 &= r_0 - \delta r \\
  r_3 &= r_0 + \delta r \\
  X &= \frac{r_0 + c_x \delta r}{\sqrt{2}} \\
  Y &= \frac{r_0 - c_y \delta r}{\sqrt{2}}.
\end{align*}
\]

where \( X \) and \( Y \) are the components of \( \mathbf{r}_2 \). Here, \( c_x = c_0 / \sqrt{2} \) and \( c_y = c_0 / \sqrt{2} \). \( c_0 \) and \( c_y \) are parameters related to the tube’s response to external agents acting on its morphology. For example, \( c_x = c_y = 0 \) means that \( X \) and \( Y \) remain unchanged (\( X = Y = r_0 / \sqrt{2} \) and \( \theta_0 = \pi / 4 \)) while \( \alpha_y \) decreases and \( \alpha_x \) increases under external
intervention (see Fig. 6). If \( c_x = c_y = \sqrt{2} \), the deformation is entirely absorbed by \( X \) and \( Y \) with \( a_x \) and \( a_y \) keeping their initial values. Our choice for \( r_1 \) and \( r_3 \) given by Eq. (2) is based on the assumption that the C–C bond is the hardest one in nature thus few susceptible to length variations. In this sense, we expect that the distance between masses are not sensible to system deformations and the perimeter of the ring must approximately coincide with the perimeter of the circle, \( 2\pi r_0 \), before deformation. We consider our 8 masses/spring system tend to assume an ellipsoidal shape when deformed, with \( r_3 \) and \( r_1 \) being the major and minor axis, respectively. With help of Eq. (2), its perimeter \( p \) can be written as

\[
p = 2\pi r_0 \left( 1 + \frac{1}{4}r_0^2 + \frac{1}{64}r_0^4 + \ldots \right),
\]

where we have defined the dimensionless quantity \( \gamma = \delta r / r_0 \), which measures the deformation of the vector positions in relation to its original length. Note that \( 0 \leq \gamma < 1 \), where \( \gamma = 0 \) refer to the symmetric case, whereas \( \gamma \to 1 \) means a tendency to the system to assume a bilayer conformation (highly deformed). For maintaining the same perimeter as the ring before deformation, we must neglect terms of degree 2 and higher in \( \gamma \). We consider the maximum value for \( \gamma = 1/2 \) at 20 \( \text{H} \) (this is discussed later in the text) thus we estimate the maximum error due to this approximation of the order of 1/16 in comparison to the unity, which is not an absurd.

Within SWCNT symmetry, anti-symmetric modes belong to the \( E_1 \) and \( E_2 \) irreducible representations and are not expected to show significant intensity in those spectra in Fig. 3, which are dominated by the totally symmetric \( A_1 \) modes [51]. The \( G^- \) modes observed in this work are symmetric so that it must be understood how symmetric modes are affected by transversal deformations. In this sense, we focused on the symmetric modes due to small displacements from the equilibrium as shown in Fig. 7. The variations from the equilibrium of the vector positions \( r_1, r_2, \) and \( r_3 \) are given by

\[
\theta = \frac{r_0}{\sqrt{2}}.
\]
The equation of motion of the mass localized by \( r_2 \) is given by

\[ m \ddot{r} = -k \Delta R \]

which leads to the equations

\[ \theta' + \omega_0^2 \theta = 0 \]

and

\[ \phi' + \omega_0^2 \phi = 0 \]

respectively. With help of Eq. (2), the displacement of the vector \( r_2 \) relative \( r_1 \) and \( r_3 \) is given by

\[ \Delta \mathbf{R} = 2 \Delta \mathbf{r}_2 - \Delta \mathbf{r}_1 - \Delta \mathbf{r}_3 = (2 r_2 \sin \theta_0 + r_1 \sin \theta_1 - (2 r_2 \cos \theta_0 + r_3 \sin \theta_j). \]

where we have considered \( \sin \theta = \theta \) and \( \cos \theta = 1 \). \( i \) and \( j \) are the unit vectors pointing towards the positive direction of \( x \) and \( y \) axis, respectively. With help of Eq. (3), the displacement of the vector \( r_2 \) relative \( r_1 \) and \( r_3 \) is given by

\[ \Delta \mathbf{R} = 2 \Delta \mathbf{r}_2 - \Delta \mathbf{r}_1 - \Delta \mathbf{r}_3 = (2 r_2 \sin \theta_0 + r_1 \theta_1 - (2 r_2 \cos \theta_0 + r_3 \theta_j). \]

The frequencies become different and increasingly split as seen in the G mode splitting was observed. In this case, this work can help to understand how environmental factors, such as different atmospheres for instance, can change SWCNT properties.

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