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Vibrational G peak splitting in laterally functionalized single wall carbon nanotubes: Theory and molecular dynamics simulations

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ABSTRACT

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.

1. Introduction

Carbon nanotubes are considered to be the ideal form of fibers with superior mechanical properties compared to the best carbon fibers and are excellent load-bearing reinforcements in composites [1,2]. The mechanical, thermal stability and heat-transport properties of carbon nanotubes have been studied by researchers, given the strength of the carbon–carbon bond [3]. Due to their high Young's modulus, carbon nanotubes are exceptionally stiff [4–6]. These properties indicate that single wall carbon nanotubes (SWCNT) may be used in many different kinds of applications, as for example reinforcement of composite materials [7] and fabrication of electronic devices [8].

SWCNT properties are highly affected by its surrounding environment. In order to achieve the stage of full technological applications, it is necessary to correlate such properties with environmental factors [9–12], including external forces [9,13–23]. For example, the electronic and structural properties of carbon nanotubes deposited on substrate are not yet clarified. In fact, recent experiments have shown a strong interaction between carbon nanotubes and substrate inducing important deformation of the nanotube on top of substrate [10,24,25].

The identification of the chirality (n,m) of an individual single-walled nanotube from Raman scattering can be significantly affected by the surrounding environment. There are different results when the SWCNT is freely suspended or when interacting with the substrate [26–29]. Differences also appear when SWCNTs are deformed by applied strain [30,31], if it is uniform throughout the length of the SWCNT or not, etc [17].

The G-band is known to greatly facilitate the study of environmental effects upon carbon nanotubes in general. Such a frequency can be used for diameter characterization, to distinguish between metallic and semiconducting SWCNTs, through strong differences in their Raman lineshapes [32,33], to probe the charge transfer arising from doping a SWCNT; and to study the selection rules in the various Raman scattering processes and scattering geometries to cite a few examples.

It has been recently shown by Araujo and collaborators [34] that the breaking of SWCNTs cylindrical symmetry leads to the splitting of vibrational modes associated with C–C vibrations in the plane transversal to the tube axis (G^- peak). In such an experiment radial deformations on SWCNTs were induced by the tip of an atomic force microscope (AFM) simultaneously with the measurement of the Raman G band. The observed deformation-induced splitting of

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the G^- 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^- 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^3 character of the sp^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^- peak splits into distinct vertical and horizontal contributions (which we will call G_v^- and G_h^-, respectively). We also found that the magnitude of the G^- splitting (>20 cm^{-1} for more than 10 adsorbed hydrogens as can be seen Fig. 4) is much larger than the experimental frequency resolution (2 cm^{-1}) of modern Raman setups. Supporting our simulation results we developed a simple model which explains the origin of such splitting in the G^- 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

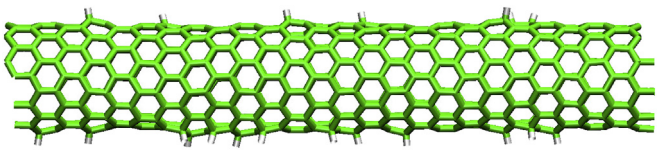

Fig. 1. Lateral view (*xz*- plane) of the hydrogenated SWCNT (twenty hydrogen atoms per unit cell) at $T = 300$ K and $P = 1$ bar. (A color version of this figure can be viewed online.).

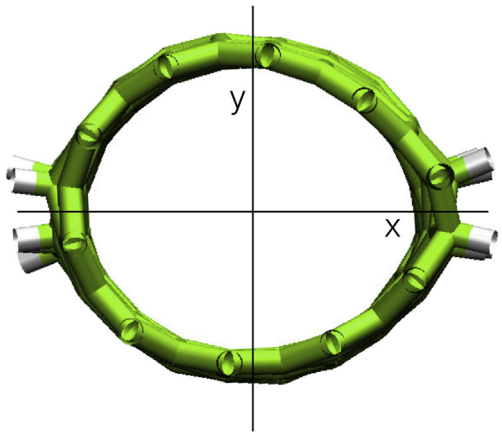

Fig. 2. Frontal view (*xy*- plane) of the hydrogenated SWCNT (twenty hydrogen atoms per unit cell) at $T = 300$ K and $P = 1$ bar. (A color version of this figure can be viewed online.).

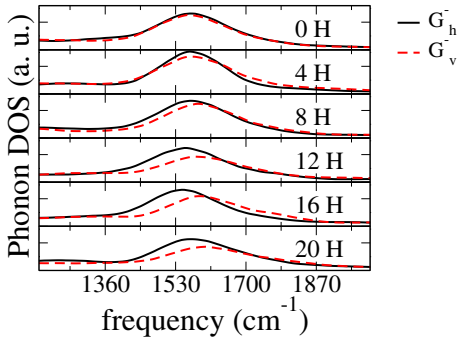

Fig. 3. Phonon DOS versus frequency for the hydrogenated SWCNT with 0 (perfect tube), 4, 8, 12, 16, and 20 hydrogens obtained through simulations for one of the five measurements. (A color version of this figure can be viewed online.).

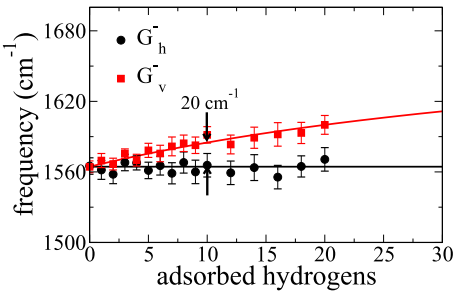

Fig. 4. Average positions of the maxima in the transverse modes of the G-band, G_h^- (horizontal) and G_v^- (vertical), over five measurements for hydrogen adsorptions from 0 up to 20. Error bars were obtained by calculating the standard deviations over five measurements. Symbols are data from simulations and lines are the results from our theoretical model, developed in Section 4. We see that at 10 H the separation between G_h^- and G_v^- is about 20 cm^{-1} which is 10 times the resolution of modern Raman apparatuses. (A color version of this figure can be viewed online.).