Effect of doping on the radial breathing mode in carbon nanotubes

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ABSTRACT

Using density functional theory and a spring constant model we have calculated the change of the radial breathing frequency as a function of nitrogen substitution configuration and concentration. The calculations show that the stable substitution configurations do not favor the formation of nitrogen-nitrogen bonds at low concentration in zig-zag tubes and that the radial breathing frequency depends strongly on the substitution site in the tube. Considering the local symmetry of the radial breathing mode and zone center optical phonons in graphene, we find that the ratio of the two frequencies is determined by the ratio of the carbon-carbon bond length and tube diameter.

Keywords: carbon nanotubes, density functional theory, doping, nitrogen substitution, spring constant model

1 INTRODUCTION

Doping CNTs is an attractive alternative to control the electronic conductivity of CNTs independent of their diameter. Highly conducting nanotubes are of interest for applications in transparent thin film electrodes. Doping of CNTs through substitution leads to quasi bound states which can induce significant modifications of the density of states (DOS) in the vicinity of the Fermi level. Raman spectroscopy is one of the most frequently used non-invasive diagnostic tools for CNTs. Resonant excitations make Raman spectroscopy sensitive to individual tubes. The low frequency mode observed by Raman spectroscopy corresponds to the radial breathing mode (RBM), an in-phase motion of the atoms in radial direction. The RBM frequency is inversely proportional to the tube diameter apart of a constant shift which depends on its interaction with the environment.

The energy of the RBM on undoped tubes has been studied in detail experimentally and theoretically by means of zone folding schemes [1] spring constant models [2] and first-principles calculations. [3,4,5] Several important advances in carbon nanotube research such as sorting tubes or the determination of transition energies of individual CNTs [6] are directly related to the observation of RBMs. The influence of doping on RBMs have been examined using silver (n-doping) [7] or applying electrical potentials in electrochemical cells. [8] We consider the influence of substitution site and doping concentration on the RBM frequency.

2 COMPUTATIONAL DETAILS

To determine the RBM shift with nitrogen doping, we have carried out DFT calculations using the Vienna *ab initio* simulation package VASP. [9, 10] The code uses the full potential Projector Augmented Waves (PAW) framework. [11,12] Exchange-correlation effects have been approximated using the PBE functional and applied in spin-polarized calculations. A kinetic energy cutoff of 400 eV was found to be sufficient to achieve a total energy convergence within several meV considering k-point sampling. All atoms were fully relaxed to forces on individual atoms smaller than 0.02 eV/ Angstrom. We selected (8,0) zigzag CNTs for the calculations and considered 2 primitive unit cells containing 64 atoms. The unit cell is sufficiently large in the two perpendicular directions (1.6 x 1.6 nm^2) to reduce interactions to a threshold of less than 1 meV/atom for the cohesive energy. The doping concentration was controlled by the substitution of one to two carbon atoms with nitrogen atoms resulting in a maximum doping concentration of 5%. We have applied the frozen-phonon approximation to calculate the RBM mode with and without doping in the (8,0) CNTs by means of fitting the total energy for several atomic positions. To compare with the results of first-principles calculations, we use a one dimensional spring constant model which takes into account nitrogen substitution by scaling of the pristine RBM frequency.

3 SPRING CONSTANT MODEL

Considering armchair tubes we can apply a linear chain model. The radial breathing mode has the consequence that all the bonds are stretched. The optical phonon mode in graphene corresponds to an out of phase stretching mode of the two atoms in the primitive unit cell of graphene. As a result of the similarity of the two modes we find a simple relation between the frequency of the RBM and the G band for armchair tubes. When considering Newton's equation for a linear chain of atoms (spring constant k) and considering the vibrational mode of the G band which corresponds to an out of phase stretching motion of neighboring atoms with mass m_C, we can write for the frequency :

$$\omega_G^2 = \frac{4k}{m_C}$$

Considering a closed linear chain in circumferential direction we have :

$$\frac{1}{K_{tube}} = \sum_i \frac{1}{k} \quad \Rightarrow \quad K_{tube} = \frac{ka}{\pi d}$$

where a is the bond length and d the diameter. The mass for a closed chain or tube section is :

$$M_{tube} = m_C \frac{\pi d}{a}$$

The Lagrangian L for a tube section is :

$$L = \frac{1}{2} M_{tube} \dot{r}^2 - \frac{1}{2} K_{tube} \Delta l^2$$

where $\dot{r}$ is the speed in radial direction and Δl is the change of the length of circumference. We can rewrite this expression as :

$$L = \frac{1}{2} M_{tube} \dot{r}^2 - \frac{1}{2} K_{tube}^{radial} (\Delta r)^2$$

when introducing a spring constant along the radial direction. Using the Euler-Lagrange equation, we obtain:

$$\omega_{RBM}^2 = \frac{K_{tube}^{radial}}{M_{tube}} = 4\pi^2 \frac{ka}{\pi d} \frac{a}{m_C \pi d} = \omega_G \frac{a^2}{d^2}$$

With $\omega_G = 1581 cm^{-1}$ and $a = 0.142$ nm, the RBM is given by :

$$\omega_{RBM}^2 [cm^{-1}] = \omega_G \frac{a}{d} = \frac{225}{d} [nm^{-1}] \qquad (1)$$

The G band frequency multiplied by the bond length is strikingly close to experimentally determined constants ranging from 207 to 226cm^{-1}.

We can modify the previous expressions for the frequency of the RBMs of pristine tubes to include changes induced by nitrogen doping. Substitution has the effect of changing the mass and the spring constant. We assume no modification of bond length in first approximation. By defining the atomic fraction of nitrogen as $x = n_N/(n_N + n_C)$ and by taking the double of a primitive unit cell of a (8,0) tube (64 atoms) with 96 bonds, a single substitution modifies three bonds which yields an atomic fraction of nitrogen of 3/96 = 2/64 = 2x. We can then replace the energy of the optical phonon in Eq. (9) ω_G by an effective phonon energy ω_{eff}. It has been reported that nitrogen substitution in carbon leads to a localized C-N vibrational mode (ω_{C-N}) in tetrahedral configuration at 1100 cm^{-1}. We can scale the energy of the localized vibrational mode by the fraction of the number of C-C bonds which have been replaced by C-N bonds. We find after substitution in Eq. (1) with the corresponding definition of the effective phonon energy :

$$\omega^{eff} = (1 - 2x) \cdot \omega_G + 2x \omega_{C-N}$$

$$\omega_{RBM}^{doped} (x) = \omega_{RBM} \left(1 - 2x \frac{\omega_G - \omega_{C-N}}{\omega_G} \right)$$

By including the effect of mass and spring constant, we can estimate doping effects as a function of concentration for SWNTs. We can treat the case for two adjacent dopants

by taking into account five modified bounds. With $x = 2/64 = 1/32$ and considering that four C-N and one N-N bond are formed, the effective phonon energy is : $\omega_{eff} = (1-5/96) \omega_G + 4/96 \omega_{C-N} + 1/96 \omega_{N-N}$ which yields a downshift of -4.8 cm^{-1} for the RBM frequency which is slightly larger than in the single substitution case (-3.4 cm^{-1}).

4   RESULTS DFT CALCULATIONS

We have considered two primitive unit-cells containing 64 carbon atoms of a (8,0) tube with a single and several double substitution configurations. The different double substitution configurations are summarized in Fig. 2. First studies of nitrogen doped CNTs have appeared recently [13-16]. It has been stated that deformations induced by substitution are small and not much attention has been given so far to structural modifications of the tube wall induced by doping. We show here that structural modifications induced by doping can have a sizeable effect on the RBM frequency. We start with a pristine nanotube with a fixed carbon bond length of 0.142nm. Energy optimization leads to an increase of the bond length of less than 1 % for circumferential bonds ($d_{zz, C-C}$) and a reduction of the bond length of up to 0.2 % for bonds along the tube axis ($d_{axis C-C}$). This difference along the two main directions of the tube is confirmed by changing the size of unit cell. We assume that the bond length changes are induced by curvature.

When substituting one carbon atom, the nearest neighbors are the most affected, leading to C-N bond lengths smaller the C-C bond length. Modifications in the second nearest neighbor positions are small while bonds along tube axis ($d_{axis C-C}$) are reduced by 2 % whereas bonds in circumferential direction stay identical. We observe no change in the pyramidal angle.

The pyramidal angle is a measure of the angle between the σ and π orbitals $\theta_p = 10.2$ deg. This means that the nitrogen atom does not project out of the tube wall. This absence of any radial displacement is also reflected in the deformation parameter, defined as $\delta = d_{min}/d_{max}$; for pristine tubes $\delta = 1.0$. With a second substituted carbon atom within the unit cell we need to consider several substitution configurations. The substitution configurations can be grouped in two subgroups: two directly bound nitrogen atoms (in Fig. 1, configuration A and B) and two well-separated nitrogen atoms (in Fig. 1, from C to H configurations). In all the considered cases, the modifications of the second nearest neighbor positions are small, with reductions of C-C bond lengths along the tube axis and an increase of $d_{zz C-C}$. The C-N bonds along the tube axis are smaller than the C-C bonds while $d_{zz C-N}$ are systematically longer than 0.142 nm. In the cases A and B with two associated nitrogen atoms, there is a relative large distortion of the diameter $\delta = 0.94$ and $\delta = 0.91$ respectively.

The pyramidal angle θ_p is also larger compared to the case with a single substitution. This shows that the nitrogen

atoms tend to repel each other by increasing their displacement in the radial direction. All others configurations with two nitrogen atoms show only minor changes compared to the configuration with one nitrogen atom.
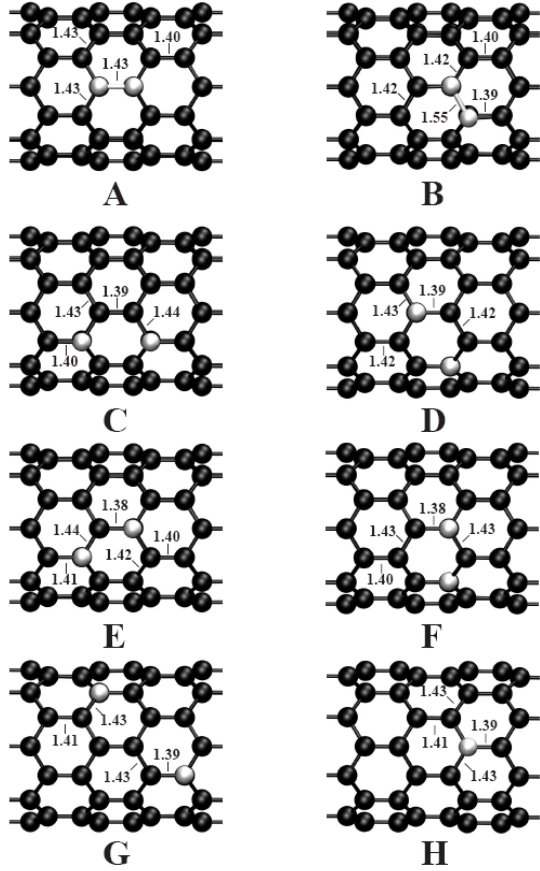

Figure 1: Different double substitution configurations (C atoms in black, N atoms in white). The H configuration corresponds to two N atoms in diametric opposite position. Bond lengths are given in Angstrom.

The formation energy of SWNT's doped with nitrogen (E_f^{dop}) can be written in terms of the cohesive energy per atom of the pristine tube E_c^{prist} containing l carbon atoms. The cohesive energy per atom of doped tubes with k nitrogen atoms (E_c^{kn}) is :

$$E_c^{prist} = \frac{E_t^{prist} - lE_C}{l}$$

$$E_c^{kN} = \frac{E_t^{dop} - kE_N - (l-k) \cdot E_C}{l}$$

$$E_f^{dop} = l \cdot (E_C^{kN} - E_c^{prist})$$

where E_t^{prist}, E_t^{dop}, E_C and E_N denotes the total energy of the pristine tube, the total energy of a doped tube and the energy of a single carbon and nitrogen atom respectively. We use $E_C = E_t^{prist} / l$ as the reference energy of a carbon

atom, and $E_N = 1/2 E_t(N_2)$ for a nitrogen atom. To compare the formation energy from different nanotubes as a function of concentration, we can define a formation energy per substituted atom :

$$E_f^{kN} = \frac{(E_t^{dop} + kE_C) - (E_t^{prist} + kE_N)}{k}$$

Figure 2 shows the formation energy for all configurations containing two nitrogen atoms. We find that configurations with two associated nitrogen atoms are less stable which is coherent with what has been previously reported.[13-16] The largest energy difference between the most stable (C) and the less stable (A) configuration is 0.58 eV per nitrogen atom which compares relatively well with the differences of 0.46 eV [13] and 0.77 eV [15] per nitrogen atom for a (10,0) tube, but is only half of the value published recently for the (8,0) tube using cluster model calculation. [16] This difference can be attributed to the cluster model calculation in which tubes are modeled with open ends terminated with hydrogen atoms. From the difference in the formation energies we see that there is a driving force that ensures that the nitrogen atoms are not neighbors. We find that the most stable configuration is not the H configuration where the nitrogen atoms are diametrically opposed, but the C configuration.

The formation energy of configuration C is even smaller than a single substitution by 40 meV per nitrogen atom. This indicates that the correlation between two additional electrons tend to improve the stability. The high formation energy of the A and B configurations can be explained by the energy cost to bind two nitrogen atoms. We observe in configuration A $d_{N-N} = 0.144$nm and B $d_{N-N} = 0.155$nm that the influence of the sp^2 bonding in its neighborhood is important. The structure of the tube wall keeps the nitrogen atoms bound to three neighbors. This effect is more pronounced in the A configuration where the N-N bond direction is axial, while in B case, nitrogen atoms can move slightly in radial direction decreasing the cohesive energy. The same effect has been observed in the case of (10,0) tubes with an energy difference between the two configurations of 0.11 eV per atom [13] and 0.31 eV per atom. [16] This is clearly different from armchair tubes where it has been shown that nitrogen atoms can be first-nearest neighbors associated with structural adjustments without increasing the formation energy considerably. [14] Using the following definition of the formation energy of the vacancy:

$$E_f^{vac} = E_t^{def} - (l-1) \cdot E_t^{prist} / l$$

is the total energy of the defective tube, we find 5.32 eV for the (8,0) tube. This compares well with previous published estimations of 4.8 eV [17] and 5.5 eV [18], but is relatively high compared to the energy of a single substitution.

We use in the following the frozen-phonon approach to evaluate the RBM frequency as a function of doping. RBM frequencies in pristine CNTs have been previously calculated using zone folding [1], classical mechanics and using first-principles calculations. [2] RBM Raman bands

are resonantly enhanced when the incident or the scattered photon coincide with one of the singularities in the joined density of states. The resonance profile for RBMs is typically 50−80 meV wide for individual SWNTs. The formation of excitons in CNTs has the effect to lower the transition energies and modifies the tube structure at the location of the exciton. Excitonic effects are not taken into count in our frozen phonon approach. Considering the (8,0) pristine nanotube, and only taking into account radial components, we obtain from our PBE-based calculations, a RBM frequency of 357.3 cm^{-1}.
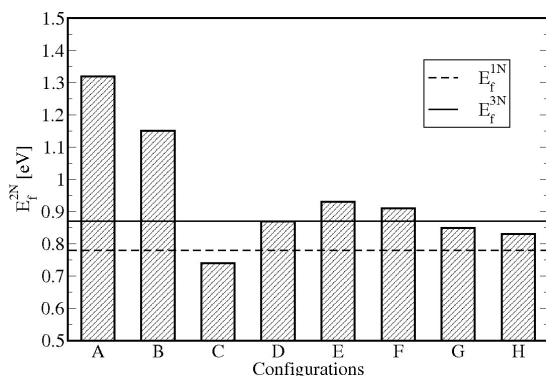

Figure 2: Formation energies of the considered substitution configurations of two nitrogen atoms in two primitive unit cells.

This value agrees within thirteen wavenumbers with results of Ref. 4 and 5, 363.6 cm^{-1} and 370 cm^{-1} respectively. The difference with the value of Kürti et al [4] is believed to be due to the level of approximation used in the calculation. We use here a more accurate approximation of the exchange-correlation functional compared to earlier reports. It is known that LDA tends to over bind carbon atoms which results in a contraction of the tube diameter and a large value of the force constants. As a result, LDA calculations overestimate RBM frequencies. Using the PBE functional we obtain smaller force constants and smaller tube diameters resulting in smaller RBM frequencies. The agreement between the DFT calculations and the one dimensional spring constant model is within 1.2 cm^{-1} corresponding to an error of less than 1%. DFT calculations predict a downshift of −5.8 cm^{-1} while the one dimensional spring constant model predicts a downshift of −3.4 cm^{-1} for 3.1 % nitrogen doping. The effect of the additional electron is to downshift or soften the phonon. As the doping concentration increases one has to take into account the possible formation of N-N bonds. For the A and B configuration (Fig. 2) the one dimensional spring constant model gives −4.8 cm^{-1}, which is smaller than DFT calculation, −9.1 cm^{-1}. A second additional electron leads to larger structural modifications and a larger downshift of the RBM band. For the other configurations, i.e from C to H, the downshift are smaller, ranging from −2.9 to −7.2 cm^{-1} using the DFT calculations.

The one dimensional spring constant model cannot discriminate between the different dopant sites and gives the same downshift of −6.7 cm^{-1} for all substitution configurations. The one dimensional spring constant model neglects completely the local distortion induced by the nitrogen atom as well as the correlation effects of the two extra electrons in the unit cell considered in the calculation. The largest difference between the two methods occurs for the H configuration. The small downshift in the highly symmetric configuration is unexpected. This points to the fact that the symmetry of the dopant sites is important for the RBM frequency. In summary, nitrogen substitution leads to a downshift of −2.9 to −9.1 cm^{-1} depending on susbtitution configuration and softening of the chemical bonds.

5 CONCLUSION

We have studied the influence of nitrogen doping on the RBM frequency in (8,0) CNTs using DFT and frozen phonon approximation. Considering several doping configurations, we find that the downshift of the RBM band depends on the exact position of the dopant within the tube wall. The formation of N-N bonds are not favored for zigzag tubes. Symmetric position of the dopant leads to only small downshifts of RBM frequencies. The one dimensional spring constant model predicts similar frequency downshifts but, due to its simplicity, different doping configurations cannot be discriminated.

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