First-principles molecular dynamics study of the stretching frequencies of hydrogen molecules in carbon nanotubes

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Abstract. We present a study of the vibrational frequencies of hydrogen molecules adsorbed in bundles of single wall carbon nanotubes. The frequencies are extracted from the analysis of first-principles molecular dynamics trajectories. We study the case of molecules inside the nanotubes (endohedral) and in the interstitial pores between the nanotubes (exohedral). We find that, in both configurations, the stretching frequencies are redshifted with respect to the free H$_2$ molecule. However, whereas all the exohedral molecules exhibit a redshift of around 45 cm$^{-1}$, the endohedral molecules show two frequencies, one close to that of the exohedral molecules and the other similar to that of free H$_2$.

Among the many exciting properties that carbon nanotubes have shown since their discovery, the ability to store large amounts of hydrogen is perhaps one of the most important due to the technological implications for energy storage and transportation. Since the first report of a large storage capacity was made [1], a great amount of work has been done, both experimentally [2, 3] (trying to reproduce the results of the initial reports and to optimize the absorption properties) and theoretically [4] (to explain the physical or chemical origin and mechanism of the storage). Still, there is no consensus about the amount of hydrogen that nanotubes can store,

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with wide variations in the numbers reported by different authors, and about the microscopic mechanism of incorporation of the hydrogen in the material. In this situation, experimental characterization techniques are essential to provide insight and to understand the process. Vibrational spectroscopy is one of the main materials characterization tools, since it can yield information about the form in which hydrogen is present in the material (atomic or molecular) and about the differences in local environment. However, the interpretation of vibrational spectra involves the assignment of the observed frequencies to microscopic atomic configurations, which is usually facilitated if there are theoretical predictions available for comparison.

Although many empirical or semi-empirical approaches can be used to predict the vibrational frequencies for particular atomic configurations, it is preferable to use first-principles methods. These, however, require an intensive computational effort, which limits their applicability to complex systems. In the case of the adsorption of H$_2$ in carbon nanotubes, the situation is complicated by the fact that the molecules are not strongly bound to the tubes, but rather bounce back and forth on the nanotube walls, and show a strongly diffusive behaviour. In this situation, the vibrational modes can (and indeed do, as we will see) depend strongly on the specific situation of the molecules with respect to the tube at a given time. Therefore, approaches such as linear response theory [5], that assume harmonic vibrations around a single, well-defined configuration, are not suited for this problem, since the calculation would have to be repeated for many configurations that would sample adequately the diffusion path of the molecules along the nanotubes.

In this work, we have used a dynamical approach to obtain the vibrational frequencies of H$_2$ adsorbed in nanotubes by analysing the molecular dynamics (MD) trajectories obtained from first-principles simulations. This approach allows us to separate the frequencies of the stretching modes in which we are interested from the translational and rotational molecular motions. Besides, we can trace the evolution of the stretching frequencies with variation of the local environment during the dynamics, and thus identify the vibrational shifts in terms of atomic arrangements. Another advantage of the method is that anharmonic effects, which can have an important contribution at high temperatures, are automatically included in the computed frequencies.

The MD simulations that we analyse here to extract the vibrational frequencies were performed by Cheng et al and are described in [6]. They were obtained by means of density functional theory (DFT) calculations using a pseudopotential plane wave approach (using the Vienna Ab initio Simulation Package (VASP)) [7], in the local density approximation (LDA) using the functional of Perdew and Zunger [8]. A similar computational approach was recently used by Arellano et al [9] to study the interaction of molecular and atomic hydrogen with single wall nanotubes of narrower diameter. The simulations were done for bundles of (9, 9) carbon nanotubes, with a concentration of one H$_2$ molecule per unit cell of the nanotubes (which contains 36 C atoms). The simulation supercell contains one nanotube that is repeated periodically in a triangular lattice in the plane perpendicular to the nanotube axis, to simulate a nanotube bundle. In the direction parallel to the nanotube axis, the supercell contains three unit cells of the (9, 9) nanotube (that is, 108 carbon atoms), and therefore there are three inequivalent H$_2$ molecules in the (periodically repeated) simulation cell. A snapshot of one of the MD simulations can be found in figure 1 of [6]. The Brillouin zone integration was done using 1 × 1 × 2 Monkhorst–Pack [10] sampling (\(z\) is the direction of the nanotube axis). The MD runs were done at three different temperatures: 77, 300 and 600 K. Different runs were made with the H$_2$ molecules placed at the interstitial pores between
nanotubes (which we will call exohedral sites) and inside the nanotubes (endohedral sites). The simulations ran for 5000 time steps, with a time step of 1 and 0.3 fs for the endohedral and exohedral cases, respectively.

In order to extract the vibrational frequencies from the MD trajectories, we have used the velocity autocorrelation method [11], in which the vibrational power spectrum is derived from the Fourier transform of the velocity autocorrelation function, defined as

\[ g(t) = \sum_{n=1}^{N_n} \frac{\langle v_n(t) \cdot v_n(0) \rangle}{\langle v_n(0) \cdot v_n(0) \rangle} \tag{1} \]

where the angle brackets denote an ensemble average. Here, we are only interested in extracting the H₂ stretching frequencies, and must be especially careful in separating the effect of the non-harmonic translations and rotations of the molecules. If this is not done, the frequencies obtained in the vibrational spectrum will be contaminated due to mixing with these non-harmonic modes. Therefore, we first define the stretching coordinate of each molecule as the distance between the two hydrogen atoms. We then compute the velocity autocorrelation using only this coordinate in equation (1). We do this for each of the molecules in the simulation cell. In order to allow for equilibration, the first 2000 steps of the simulations were not used in the vibrational analysis.

Figure 1 shows the vibrational spectra for the exohedral and endohedral molecules at the three simulation temperatures. Table 1 summarizes the values of the frequencies, as determined from the maxima of the peaks in figure 1. For the case in which the molecules are in the interstitial pores between the nanotubes, we observe a single peak for the stretching spectrum, centred at a frequency which is essentially independent of temperature. These frequencies are redshifted with respect to that of the free H₂ molecule (which in our calculation is obtained at 4190 cm⁻¹ and experimentally [12] is 4395 cm⁻¹) by about 40–50 cm⁻¹. The situation is different for the endohedral molecules, where we observe two different peaks in the vibrational spectrum, for the three temperatures considered. The low-frequency peak has approximately the same frequency as that of the exohedral case, whereas the higher peak is roughly at the free H₂ stretching frequency for the 77 K simulation, and slightly higher at 300 and 600 K. We note that the width of the peaks in the exohedral case is larger than in the endohedral case. This is a consequence of the difference in the total simulation time in both cases, since the velocity autocorrelation method yields widths which are inversely proportional to the length of the simulation.

The redshift of the vibrational frequencies can be understood in terms of the unusually strong interaction between the H₂ molecules and the nanotubes. Although the interaction of H₂ with a perfect graphene plane is relatively weak and of physical origin rather than a real chemical bond [9], Cheng et al [6] have proposed that the distortion of the nanotubes at finite temperature enhances the attraction of the H₂ molecules, yielding a stronger interaction between H₂ and C. There is a small degree of charge transfer from the C atoms with instantaneously distorted environment to the H₂ molecules, which weakens the H–H bond and therefore increases the H–H bond length [6]. This weakening of the bond is fully consistent with the redshift obtained in our calculations.

\[ \text{We found it necessary to use a smaller time step in the exohedral case in order to obtain satisfactory stability and conservation of the total energy during the dynamics. While 1 fs was adequate for the endohedral absorption, a similar quality in the dynamics was only achieved for the exohedral case if the time step was reduced to 0.3 fs, due to the different initial conditions in the simulation runs. It should be noted that the choice of the time step should not change the physical properties computed in the MD runs, as long as it is small enough to produce good conservation of the total energy.} \]

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Figure 1. Vibrational spectra for the hydrogen stretching vibrations for exohedral (left) and endohedral (right) $\text{H}_2$ molecules in a bundle of (9, 9) nanotubes, for three different temperatures.

Table 1. Calculated stretching frequencies (in $\text{cm}^{-1}$) for exohedral and endohedral $\text{H}_2$ molecules in a bundle of (9, 9) nanotubes, at different temperatures. For the endohedral case, the two frequencies observed in the vibrational spectrum are indicated. The calculated frequency for the free $\text{H}_2$ molecule is $4190 \text{ cm}^{-1}$.

| (K) | Exohedral | Endohedral |
|-----|-----------|------------|
| 77  | 4140      | 4162, 4195 |
| 300 | 4149      | 4150, 4207 |
| 600 | 4150      | 4150, 4202 |

We should note that it is now well established that LDA and generalized gradient approximations (GGA) do not contain dispersion contributions (see, for instance, [13]), which are the largest part of the binding of $\text{H}_2$ to static, perfect graphene and nanotubes. LDA tends to reproduce rather well the interaction curves and energies (see, for instance, [14] and [15] for the case of the interplanar interactions in graphite), due to its tendency to overbind, whereas GGA tend to yield repulsive interactions. The choice of LDA by Cheng et al (see [6]) was done on the basis of this fact. In the dynamic case, they observed strong deviations from planarity in the nanotube walls upon vibrational motion and collision with $\text{H}_2$ molecules, which enhances the contribution of interactions of binding character (see also [16]), which LDA describes correctly. We have checked that better levels of theory also yield to the charge transfer that is the cause of the redshift of the frequencies, and therefore we believe that our results for the trends in the vibrational spectra are not an artefact of the LDA (although the binding energies may be overestimated by the LDA). In particular, we did second-order Möller–Plesset (MP2) calculations for an $\text{H}_2$ molecule.
Figure 2. Stretching spectra of two endohedral H₂ molecules, adsorbed inside the (9, 9) carbon nanotube, at 77 K.

interacting with a distorted benzene ring, whose geometry was extracted from a snapshot of the MD runs. Both LDA and MP2 gave virtually the same charge transfer.

In order to understand the appearance of two different frequencies in the endohedral case, in contrast with the single, redshifted frequency of the exohedral molecules, we have carried out a detailed analysis of the origin of the peaks in the vibrational spectra. We first decomposed the spectra of figure 1 into contributions from each one of the molecules in the simulation cell. In the exohedral case, we find that all the molecules display the same frequency (with a maximum difference of less than 15 cm⁻¹), as would be expected from the appearance of a single peak in the total stretching vibrational spectrum of figure 1. For the case of endohedral molecules, we find that each molecule shows essentially a single peak, at one of the frequencies given in table 1 for the endohedral configuration (either the redshifted value around 4150 cm⁻¹ or the free molecule around 4200 cm⁻¹). A representative example is shown in figure 2, where we show the stretching spectra of two endohedral molecules for the 77 K simulation. Therefore, we conclude that the different peaks in the spectra of endohedral molecules originates from different atomic environments inside the nanotube.

The existence of different atomic environments in the endohedral case is not obvious from the MD trajectories. All the molecules in the simulation show a rapid diffusive behaviour, without a definite adsorption site at the wall of the nanotube. However, careful examination shows some subtle differences between the molecules with high and low frequencies. In figures 3(a) and (b) we show the distance from the hydrogen atoms to the nearest carbon atom in the nanotube, as a function of simulation time, for the two molecules for which we plotted the vibrational spectrum in figure 2. We see that the molecule in (a) displays a large variation in the distance to the nanotube wall. This molecule bumps frequently and strongly against the walls of the tube, being pushed away in every collision. The stretching frequency of this molecule is 4197 cm⁻¹, close to that of the free H₂ molecule. In the case of the second endohedral molecule (figure 3(b)), we see that it tends to stay close to the wall of the nanotube (<3 Å), with small variations in the distance, for most of the time, except in two short periods (at around 1.2 and 2.2 ps, respectively). The frequency of this molecule, from the spectrum of figure 2, is 4162 cm⁻¹.
Figure 3. Distance from the two atoms of the H$_2$ molecule to the closest carbon atom in the nanotube for three different cases: (a) and (b) show the two endohedral molecules of the 77 K simulation for which the vibrational spectra were shown in figure 2; (c) shows the case of an exohedral molecule at 77 K.

All the exohedral molecules show a behaviour more similar to the second endohedral molecule in figure 3, with small oscillations in the distance to the nanotube walls, which is always below 3 Å. A typical case for one of the exohedral molecules of the 77 K simulation is shown in figure 3(c).

The picture that emerges from this analysis is the following. Those H$_2$ molecules which spend long periods of time (of the order of picoseconds) close to the nanotube walls display a frequency which is redshifted by about 40–50 cm$^{-1}$ with respect to free H$_2$, whereas the molecules which collide with the walls and are expelled from them until the next bump show a frequency close to that of the free molecule. All the exohedral molecules belong to the first kind, and therefore they exhibit only one frequency. The endohedral molecules, however, show both kinds of behaviour, giving rise to the two peaks in the spectrum.

We note that endohedral molecules can change their behaviour during the dynamics, becoming more tightly bound to the nanotube wall, or getting more energy and bumping against the walls. The case shown in figure 3(b) is an example of this, where the molecule is ejected from the wall for two short periods of time. We have also observed this behaviour in other endohedral molecules. In these cases, it is interesting to see that the vibrational frequencies change when the molecule suffers this transition from tighter adsorption to loose dynamics. For instance, in the case of figure 3(b) the molecule gets loose from the wall during two short periods of time, marked II and IV in the figure. This time is too short to provide an accurate determination of the vibrational frequency, but is enough to give us an estimate of the change in frequency between the two regimes, for the same molecule. The results for this estimate are given in table 2. We observe that the value of the stretching frequency is always close to the redshifted value (around 4150 cm$^{-1}$) when the molecule is close to the nanotube walls, whereas it is larger and closer to the free molecule frequency when the H$_2$ is more loose and stays further from the nanotube walls. There is, therefore, a clear correlation between the degree of binding to the
Table 2. Estimate of the stretching frequencies for the endohedral molecule 2 (see figure 3(b)) computed at each of the different periods I–IV corresponding to different binding regimes.

| Time period | I   | II  | III | IV  |
|-------------|-----|-----|-----|-----|
| $\omega$ (cm$^{-1}$) | 4150 | 4170 | 4150 | 4190 |

nanotube wall and the vibrational frequency. We have seen a consistent behaviour in all the molecules and temperatures analysed.

It is interesting to note that our first-principles results give support to those obtained by Frankland and Brenner [17], who performed calculations of the vibrational frequencies of hydrogen in bundles of nanotubes by means of a qualitative model with empirical potentials. Their calculations were done for molecules inside the tubes and in the interstitial pores, as ours, but for much longer simulation times and as a function of the nanotube radius. One of the main conclusions of their work is that both types of adsorbed molecules give frequencies that are redshifted with respect to the free H$_2$ molecule, as we confirm in our first-principles calculations. They find that the exohedral molecules show a shift of about 30 cm$^{-1}$, which does not vary with the radius of the nanotubes. However, the endohedral molecules show, on average, a shift which decreases with the nanotube radius. This observation is consistent with our findings that there is only one type of absorption state for the exohedral molecules, giving rise to a single vibrational frequency, whereas the two frequencies in the endohedral case yield an average with a smaller frequency shift. We might expect that the component with frequency close to the free molecule would increase with increasing nanotube radius, because the space inside the nanotube increases with its radius. This would explain the observation of a decreasing frequency shift with increasing radius in the calculation of Frankland and Brenner.

Finally, we note that recent experiments by Shiraishi and co-workers [18, 19] seem to indicate that, at least in well-purified samples of bundles of single wall carbon nanotubes treated with NaOH aqueous solution after purification, most of the hydrogen is stored in the interstitial channels between nanotubes (exohedral sites). Therefore, these samples would be ideal candidates to test the predictions of the calculations presented in this work.

In summary, we have found by means of first-principles MD simulations that the adsorption of molecular hydrogen in bundles of carbon nanotubes produces a redshift in the molecular stretching frequency. This shift depends on the local environment of the molecule with respect to the nanotube walls. The molecules in the interstitial pores between the nanotubes, and some of the molecules inside the nanotubes, are more tightly bound to the walls, in the sense that the distance is always around or smaller than 3 Å. In these cases, the frequencies show a redshift of around 45 cm$^{-1}$ with respect to the free molecule. Other molecules inside the nanotubes are less bound, suffer collisions with the walls and spend longer periods of time away from them. These molecules show a frequency which is close to that of free H$_2$.

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