The Effect of Temperature on Hydrogen Adsorption on a Single-Walled Carbon Nanotube: An Ab Initio Investigation

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Abstract: Hydrogen (H2) has been reported as the cleanest and most sustainable energy source. The large-scale utilization of hydrogen is continually being studied to replace fossil fuels as a renewable energy source, as the latter is fast-depleting and causes environmental problems. The bottleneck of the development of this technology lies with making H2 storage more efficient. In this aspect, Carbon nanotubes (CNTs) are seen as viable nanomaterials. In this study, computational techniques based on density functional theory (DFT) is used to predict the behavior and properties of materials, thereby aiding researchers in experimental designs. The effect of temperature on adsorption of a single H2 molecule on a single-walled (N = 6 and M = 6) carbon nanotube (CNT) (8.14 Å) was investigated through *ab initio* molecular dynamics (AIMD) simulation using Dmol3. The generalized gradient approximation (GGA) Perdew-Wang-91 (PW91) was used with the Ortmann, Bechstedt, and Schmidt (OBS) method of DFT-D correction. The massive Generalized Gaussian Moment (GGM) constant amount, volume, and temperature (NVT) thermostat was used for temperature control at T = 100 K, 150 K, 200 K, 250 K, 300 K, and 350 K. Dynamics calculations were carried out at a time step of 0.15 x 10-15 s with 75 increments for a total simulation time of 1.125 x 10-13 s. Results show that a linear relationship exists between the jerk of the H2 molecule during adsorption into the CNT cavity and the reciprocal of the absolute temperature of adsorption from 150 K to 350 K (R2 = 0.9915). For these simulations, adsorption was evidenced by the migration of the H2 molecule towards the CNT cavity. Future work may focus on the effect of varying operating pressures, H2 to CNT ratio and the capability of various porous carbon materials on H2 adsorption.

Key Words: *ab initio*; adsorption; carbon nanotubes; hydrogen storage; molecular dynamics simulation; temperature effects

I. INTRODUCTION

1.1 Hydrogen Storage in CNTs

Hydrogen is being considered as one of the cleanest and most sustainable energy systems due to its higher heat of combustion than liquid fuels and because its only byproduct is water. The challenge is the logistics management of hydrogen. It is necessary to devise an efficient way of storing hydrogen up to its actual use.

One of the recently studied promising materials for hydrogen storage is carbon nanotubes (CNTs). Hydrogen storage in carbon nanotubes occurs mainly because of the pores present in its structure which allows for molecular sorption. It was seen that CNTs have high hydrogen uptake capacities.

Initial investigation in the possibility of using nanotubes for hydrogen storage showed that the system temperature is one of the factors that can significantly affect the interaction of hydrogen and the nanotubes and may be an important parameter in enhancing the amount that could be stored.

Several experimental studies on the hydrogen storage of carbon nanotubes have been conducted at varying parameters. Dillon et al (2000) and Chen et al (1999) observed high hydrogen storage capacity at moderate temperatures (200-400^{o}C) and ambient pressures. It was concluded that high hydrogen storage capacity can be attained by doping nanotubes with lithium and potassium. Yang (2000) proposed that high uptake of hydrogen was mainly due to the moisture and weight gained by reactions with the alkali species. Liu et al. (2010) revisited old experiments using a pressure of 12 MPa at room temperature.

Froudakis (2011) argued that ambient conditions may not be right for the storage of hydrogen. This is because of the very low interaction energy between H_2 and the CNT. Thus, cryogenic conditions are more appropriate.
The reason for the contradictory experiments can be attributed to the demand for very sophisticated experimental conditions and measurement procedures (Froudakis, 2011). Hence, theoretical calculations were also made to provide some insights on this phenomenon. Lee et al. (2000) performed density-functional calculations to search for hydrogen adsorption sites and to predict the maximum storage capacity in single-walled carbon nanotubes. They found two chemisorption sites at the top sites of the exterior and interior of the tube wall and revealed that the storage capacity of H_2 in an empty space increases linearly with tube diameter. Storage capacity with good stability was predicted. Li et al. (2003) also performed a theoretical evaluation of hydrogen storage capacity in pure carbon nanostructures. Through theoretical analyses and total-energy density functional theory calculations, they show that hydrogen adsorption in nanotubes is negligible at room temperature and is only significant at liquid nitrogen temperatures.

With the studies mentioned in this paper, it is difficult to accurately say which temperatures would allow a high hydrogen storage capacity. For these reasons, more research must be conducted to determine the optimal conditions for hydrogen storage in carbon nanotubes. Using the results of previous researches, this study will conduct simulations to check the effect of temperature by molecular dynamic *Ab initio* calculations. Density functional theory (DFT) computational techniques will be done at cryogenic, ambient and high temperatures, and at ambient pressure.

1.2 Ab Initio Quantum Chemistry

Ab initio ("from the beginning") quantum chemistry is a vital tool in modelling atoms, molecules and complex systems such as those encountered in materials science. It falls under computation chemistry which is the branch of chemistry that deals with the use of computers to assist in the simulation and computation of different systems such as chemical reactions and materials (Leach, 20018). It relies on Schrodinger's equation in order to characterize and model the system or chemistry problem in question (Friesner, 2005). The Schrodinger equation can be used to compute the electronic structure or the wave function of all the electrons in the system in order to simulate its behavior.

Different approaches are available in solving Schrodinger's Equation for *ab initio* quantum chemistry. One approach is waveform-based in which the electronic wavefunction is expanded as the sum of Slater determinants, the orbitals, and coefficients which are then optimized using numerical methods (Friesner, 2005). Hartree-Fock theory is the simplest of this approach. The other approach is density functional theory (DFT) which takes that the expression of the total energy of the system is a functional of the electron density (Friesner, 2005).

Ab initio computational methods are often used because of its high accuracy since it relies solely on established laws, however at the cost of longer and more strenuous calculations.

Due to the accurate nature of *ab initio* methods, they are applied in the study of hydrogen adsorption inside carbon nanotubes particularly single-walled carbon nanotubes (SWCNT). Hydrogen adsorption in carbon nanotubes is emerging research in which the potential of storing hydrogen for fuel in carbon nanotubes is explored.

Solving the electronic form of Schrodinger's equation is the main concept of *ab initio* computational methods. Matter can be described at the fundamental level by the quantum theory, the central theme of which is the multi-body wavefunction:

$$\varphi(r_1, r_2, \dots, t) \qquad (1)$$

where r_1, r_2,..., are the vector positions (x,y,z) of all the fundamental particles in the system such as electrons, protons, and neutrons. The wavefunction describes probability distribution at which these fundamental particles are most likely to be located, distinct from Newtonian mechanics wherein each particle has an exact position. The wavefunction is determined by the Schrodinger Equation as shown in **Equation 2**.

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(r,t) + V(r)\psi\Psi(r,t) = i\hbar\frac{\partial\Psi(r,t)}{\partial t} \qquad (2)$$

where $\hbar = h/2\pi$ and h is the Planck's constant, m is the mass of the particle, ∇^2 is the Laplacian operator given by $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, and V(r) is the potential energy of the function.

II. METHODOLOGY

A single-walled carbon nanotube (SWCNT) with a diameter of 8.14 Å (N=6, M=6) was built in Material Studio software. The generalized gradient approximation (GGA) Perdew-Wang-91 (PW91) was used with the Ortmann, Bechstedt, and Schmidt (OBS) method of DFT-D correction for the geometric optimization of the structure. Hydrogen molecule was placed 4.8 nm away from the center of the carbon nanotube. **Figure 1** shows the hydrogen molecule at its initial distance from the carbon nanotube.

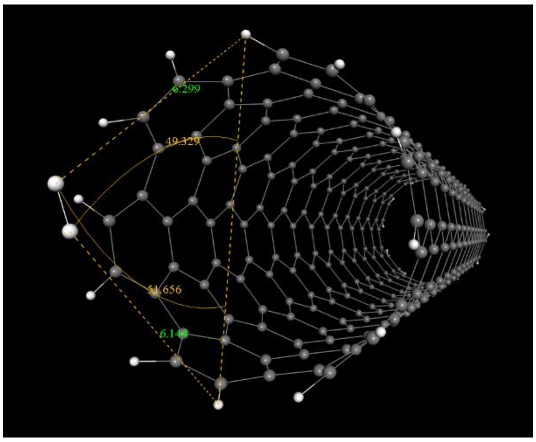


Figure 1. SWCNT with H_2 at initial position.

After optimizing the structure, dynamics calculations were executed at a time step of 0.15 x 10^{-15} s with 75 increments for a total simulation time of 1.125 x 10^{-13} s. Similar functional (GGA-PW91) and method (OBS) of DFT-D correction were used. The massive Generalized Gaussian Moment (GGM) constant amount, volume, and temperature (NVT) thermostat were used for temperature control at T = 100 K, 150 K, 200 K, 250 K, 300 K, and 350 K.

The logarithmic distance of the hydrogen (H_2) molecule from the center of the carbon nanotube was calculated at different temperatures.

$$a = \frac{2\Delta d}{(\Delta t)^2} \qquad (2.1)$$

where a = acceleration
Δd = logarithmic distance between the initial and final location of the H_2 molecule
Δt = total simulation time

Then jerk $\vec{J}$, as the changing rate of acceleration with respect to time, at different temperatures can be calculated using the following equation below:

$$\vec{J} = \frac{6}{(\Delta t)^3}\left(\Delta d + \frac{d_f d_i}{\Delta d}\right) \qquad (2.2)$$

where $\vec{J}$= Jerk [m/s^3]

According to Newton's second law of motion, jerk is viewed as the change of force magnitude for a unit mass in unit time. In this simulation study, the Jerk-value of a hydrogen molecule in a single-walled carbon nanotube subjected to different temperatures was investigated.

The logarithm of jerk (log $\vec{j}$) was calculated and plotted against temperature to the sixth power(T^6). The linear equation and R^2 values were determined.

III. RESULTS AND DISCUSSION

Table 1 shows the calculated values for logarithmic distance between the initial and final location of the H_2 molecule, while **Table 2** shows Jerk-values for each temperature, the calculated log of Jerk and reciprocal of temperature. The simulation shows that the final distance of the hydrogen molecule becomes nearer to the SWCNT as the temperature is increased from 150 K to 350 K. The jerk also decreased in correspondence with an increase in temperature. However, simulation at a temperature of 100 K had a different response as the distance of the hydrogen molecule moved away from the carbon nanotube. This may indicate that there may be an effective adsorption temperature range, and as observed at a temperature of 100 K, adsorption activity may be too slow.

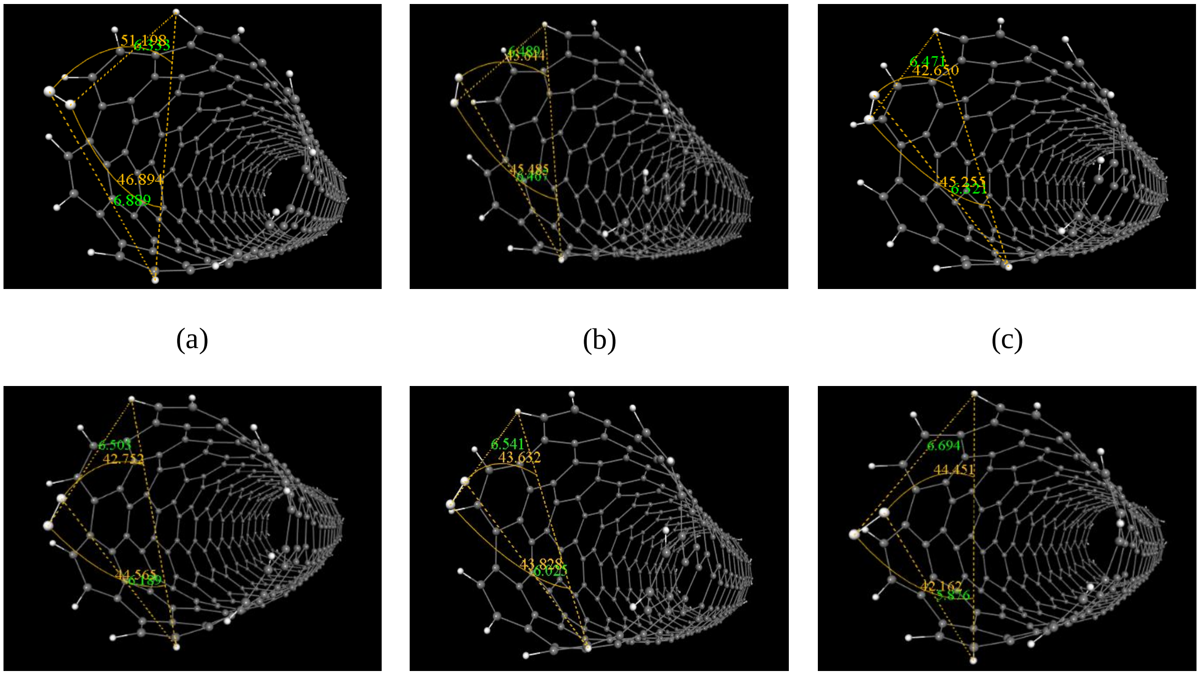
Table 1. Calculation of the logarithmic distance between the initial and final location of the H_2 molecule.

Temp. K	**H_2 $d_{initial}$,** (m^{-10})	**H_2 d_{final},** (m^{-10})	**Simulation time Δt** (sec^{-13})	**Δd** (m^{-11})
100	4.7998	4.9869	1.1250	-1.8812
150	4.7998	4.5447	1.1250	2.5405
200	4.7998	4.4375	1.1250	3.6134
250	4.7998	4.3798	1.1250	4.1902
300	4.7998	4.3408	1.1250	4.5795
350	4.7998	4.3013	1.1250	4.9748

Table 2. Calculation of Jerk, its log value and the reciprocal of temperature.

Jerk $\bar{J}$, $[(m/s^3)^{-31}]$	**log($\bar{J}$)**	**1/T,** (K^{-1})
-5.3686	-	$10.0000E^{-3}$
3.6282	3.1560	$6.6667E^{-3}$
2.4986	3.1398	$5.0000E^{-3}$
2.1313	3.1329	$4.0000E^{-3}$
1.9361	3.1287	$3.3333E^{-3}$
1.7694	3.1248	$2.8571E^{-3}$

Figure 2 shows simulation results of temperatures from 100K to 350K with increments of 50K.



(a) (b) (c)

(d) (e) (f)

Figure 2. SWCNT with H_2 at (a) 100K, (b) 150K, (c) 200K, (d) 250K, (e) 300K, and (f) 350K after 75 steps.

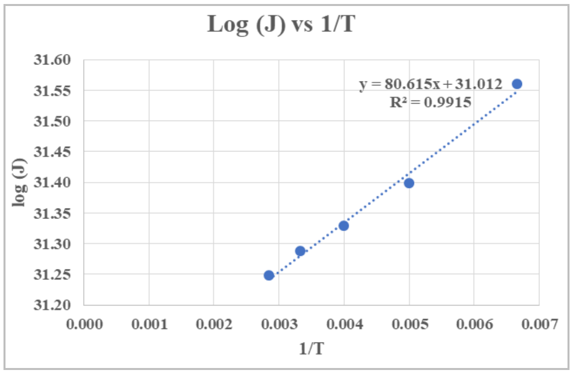


Figure 8. Plot of log J vs 1/T.

Figure 8 shows the plot of log J versus 1/T which shows a linear relationship with an r-squared value of 0.9915.

These results show that hydrogen adsorption is possible at ambient pressures. It was found that under normal pressure and non-cryogenic to high temperatures, the hydrogenation of carbon nanotubes is observed to increase at a steady state. It follows that the logarithm of Jerk and the inverse of the temperature follows the mathematical equation:

$$\log(J) = \frac{80.615}{T} + 31.012 \qquad (2.3)$$

where J = Jerk [m/s^3]
T = Temperature [K]

This also highlights another reproducible evidence that CNTs have potential as a hydrogen storage medium.

IV. CONCLUSION

Results show that a linear relationship exists between the jerk of the H_2 molecule during adsorption into the CNT cavity and the reciprocal of the absolute temperature of adsorption from 150 K to 350 K ($R^2 = 0.9915$). Adsorption was evidenced by the migration of the H_2 molecule towards the CNT cavity. Desorption observed at a temperature of 100 K may indicate that a range of absorption capacities may exist at different temperatures and pressures.

These results show that hydrogen storage exists at normal pressures and non-cryogenic to high temperatures. In a much wider perspective, these results further validate effective hydrogen storage of hydrogen at much controllable pressures and temperatures. And hence, the possibility for the advancement of H_2-driven fuel cells can be much more attainable.

Future work may focus on validating the temperature range for effective adsorption at ambient pressure, to study the effect of varying operating pressures, packing capacity, and the amount of H_2 (hydrogen to CNT ratio), as well as the capability of various porous carbon materials.

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