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Characterization of Carbon Nanotube (CNT) in Adsorption Gas: Monte Carlo and Langevin Dynamic Simulation

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ABSTRACT

Nanostructures have considerably higher surface areas than their bulk counterparts; therefore surfaces often play important, sometimes even dominant, roles in the nanostructure properties. The nanocrystalline and nanotubes have low band gaps and high carrier mobility, thus offering appealing potential as absorption gas. Interaction between methanol molecules and carbon nanotube is investigated using Monte Carlo (MC) and Langevin dynamic (LD) simulation methods. We study the structural, total energy, thermodynamic properties and the acceptance ratio methanol gas passing through an armchair carbon nanotube (7,7) have obtained in different temperatures. Passing gases in it changed the proportion CNT. In this study presented a comprehensive on effects of gases on CNT that it is on its electronic structure and transfer of charge from the atoms to the CNT. The total energy is increasing with addition temperatures.

We study the structural, total energy and energy band gaps of absorption CH3OH and passes through CNT. They are computed with MC and LD Simulation methods at different temperatures. All the calculations were carried out using HyperChem 7.0 program package.

Keywords: Carbon Nanotubes (CNT); Adsorption CH3OH; Mont Carlo Simulation; Interaction of CNT with methanol.

INTRODUCTION

Carbon Nanutube (CNT) structure. Carbon nanotubes (CNTs) are quasi one-dimensional objects and may be derived from graphite sheets[1]. The tubes are uniquely characterized by a pair of integers (n,m) that are components of the vector defining the direction in which the graphite sheet was rolled up.

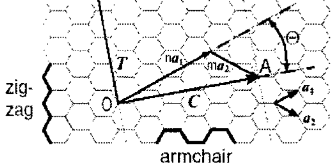

Fig 1. Schematics of the generation of a carbon nanotube by folding a section of a graphene sheet.

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In this study, only open ended, single-walled carbon nanotubes (SWCNTs) will be considered. These single-walled carbon nanotubes (hereafter referred to only as SWCNTs) are composed of (benzene-like) hexagons and therefore are expected to be highly aromatic structures.

Semi-empirical quantum chemical methods performed by Erkoc, indicated that the total energy of SWCNTs depends almost linearly on the length of the tubes and that the total energy divided by the number of hexagons in SWCNTs converges [2].

SWCNTs can be chiral or nonchiral, again depending on the way of the rolling up vector (Fig. 1), , where a1 and a2 are the primitive lattice vectors of the graphene and n, m are integers [3,4]. SWCNTs are classified into three types namely, armchair (n,n) nanotubes, zigzag (n,0) nanotubes, and chiral (n,m) nanotubes with n m [5]. SWCNTs are metals when (n- m)/3 is an integer, otherwise they are semiconductors [6]. The tubes are uniquely characterized by a pair of integers (n,m) that are components of the vector defining the direction in which the graphite sheet was rolled up (Fig. 2).

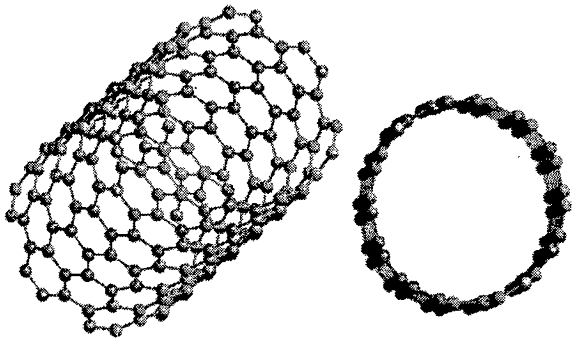

Fig. 2. Optimized configuration Top-view and Side-view SWCNT (7,7).

Nowadays, first-principles methodologies based on Monte Carlo and Langevin dynamics simulation can provide precise calculations of the total energetic and potential energy of the adsorption. Moreover, faster codes and new computational facilities allow dealing with numbers of surface adsorb configurations in moderate computing times. In this context, the aim of the present work is to provide theoretical hints for the development of improved CH3OH gas sensors using CNT (7,7) as the base sensing material. The energy of interaction between CNT and a molecule methanol calculated in presentation 34 molecules of H2O vapor in 398K and calculations are done in absence H2O molecules at different temperatures.

There are three steps in carrying out any quantum mechanical calculation in HyperChem7.0 program package [7]. First, prepare a molecule with an appropriate starting geometry. Second, choose a calculation method and its associated (Setup menu) options. Third, choose the type of calculation (single point, geometry optimization, molecular dynamics, Langevin dynamics, Monte Carlo, or vibrational analysis) with the relevant (Compute menu) options. These geometry optimization calculations can use either molecular mechanics or quantum mechanics to further refine the molecular geometry beyond that given by the Model Builder.

HyperChem uses the Metropolis method [8], which chooses random configurations with this probability, to concentrate sampling of configurations in regions of space that make important contributions to the calculation of thermodynamic averages.

COMPUTATIONAL DETAILS

Langevin dynamics (LD) Simulation :

The Langevin equation is a stochastic differential equation in which two force terms have been added to Newton's second law to approximate the effects of neglected degrees of freedom [9]. These simulations can be much faster than molecular dynamics. The molecular dynamics method is useful for calculating the time dependent properties of an isolated molecule. With HyperChem, we can add solvent molecules to the simulation explicitly, but the addition of many solvent molecules will make the simulation much slower. Langevin dynamics simulates the effect of molecular collisions and the resulting dissipation of energy that occur in real solvents, without explicitly including solvent molecules. This is accomplished by adding a random force (to model the effect of collisions) and a frictional force (to model dissipative losses) to each atom at each time step. Mathematically, this is expressed by the Langevin equation of motion:

$$\frac{\vec{F_i}}{m_i} - \gamma_i \vec{v_i} + \frac{\vec{R_i}(t)}{m_i} = \vec{a_i} \qquad (1)$$

Here, $\vec{F_i}$ is force on each atom as a function of time, γ_i is the friction coefficient of the solvent, in units of ps^{-1}, and $\vec{R_i}$ is the random force imparted to the solute atoms by the solvent and the change in velocities, $\vec{v}_i$, is equal to the integral of acceleration over time. The friction coefficient is related to the diffusion constant D of the solvent by Einstein's relation: $\gamma_i = \frac{K_B T}{mD}$. The random force is calculated as a random number, taken from a Gaussian distribution, with an average value of zero and no correlation with the atom's velocity [10].

Molecular mechanics (Monte Carlo simulation):

Studying the equilibrium thermodynamics of many-body systems has developed the Metropolis implementation of the Monte Carlo algorithm. Choosing small trial moves, the trajectories obtained applying this algorithm agree with those obtained by Langevin's dynamics [11]. With effectively search in the resultant energy landscape, we exploited the recently developed parallel hyperbolic sampling algorithm in our Monte Carlo (MC) simulations. Previously, this protocol was shown to be more effective than general replica sampling in searching for low-energy structures. Especially the energy landscape is significantly more rugged for proteins of large size than the energy landscape of small proteins [12]. This is understandable because the Monte Carlo simulations always detect the so-called "important phase space" regions which are of low energy [13]. Because of imperfections of the force field, this lowest energy basin usually does not correspond to the native state in most cases, so the rank of native structure in those decoys produced by the force field itself is poor. Therefore, the rank of native structure could be relatively better when ranked by the second force field [14]. In order to compute the average properties from a microscopic description of a real system, one shall evaluate integrals over phase space. It may be calculated For an N-particle system in an ensemble with distribution function $P(r^N)$, the experimental value of a property $A(r^N)$ from:

$$\langle A(r^N)\rangle = \int A(r^N)P(r^N)dr^N \quad (2)$$

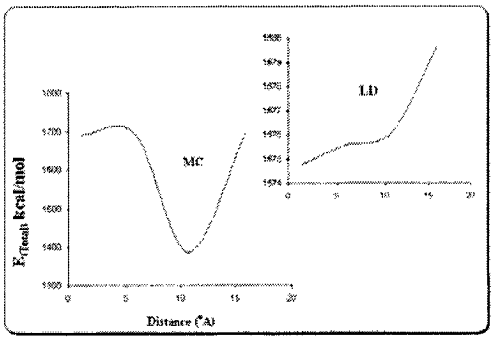

Fig. 3. The total energy calculated for methanol thorough SWCNT with 34 molecules H2O vapor in 398K.

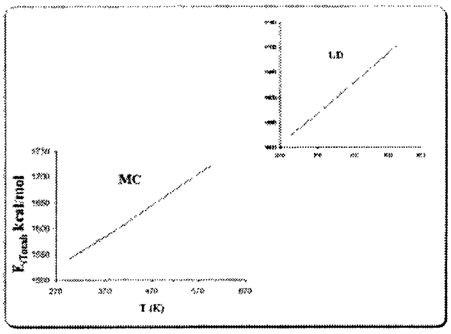

Fig. 4. The total energy calculated for methanol thorough SWCNT in different temperatures at 5.75oA main distance.

The problem with direct evaluation of this multi-dimensional integral (apart of the huge number of phase space points as a sample) is that most of the configurations sampled contribute nothing to the integral.

Having energy is so high that the probability of their occurrence is vanishingly small. For LD and MC calculation the energies are essentially the only quantities available from a single point calculation. An analysis of the components of this molecular mechanics energy is placed in the log file for further detail. In the case of MM+, a much more complete description of the individual contributions to the energy, including individual stretch energies, bending energies, etc., is placed in the log file along with the system dipole moment, if bond dipoles are available.

RESULTS AND DISCUSSION

The geometry optimization for methanol and SWCNT have obtained with Density Function Theory (DFT) method with 6-31G basis set and they were not used at the energy calculation of methanol thorough SWCNT because structures are too big and link died in with the program Gaussian A7 package suite of programs. Langevin Dynamic and Mont Carlo simulation with HyperChem7.0 program package fulfilled the calculations.

The methanol passed thorough length of SWCNT (7,7) in four stages. Initial, The effects these interactions calculated in H2O vapor that were shown by Table 1. The prominent peak is corresponding to increasing mean distances (oA) passing of methanol thorough SWCNT at 398K that is depended to dielectric constant in MC simulation. No peak corresponding in LD simulation is observed. Fig.3 is shown that the lower energy is for 10.71 oA length SWCNT at 398K.

Table 1. The different energies (kcal/mol), acceptance ratio (ACCR), dipole and RMS gradient (kcal/mol•Å) calculated in different distances for methanol and SWCNT with 34 H2O molecules by Monte Carlo and Langevin Dynamic simulations at 398K

Distance (°A)	***Monte Carlo Simulation***					
	398K					
	E_{total}	**ACCR**	**E_{kin}**	**$E_{(kin+pot)}$**	**Dipole Moment (D)**	**RMS**
1.13	1675.30	0.997	361.861	1690.92	6.064	17.38
5.75	1677.28	0.996	361.861	1693.22	7.299	17.37
10.71	1132.64	0.487	361.861	1387.02	7.434	17.36
16.00	1681.27	0.997	361.861	1696.55	4.812	17.49
Distance (°A)	***Langevin Dynamic Simulation***					
	E_{total}	**E_{kin}**	**E_{pot}**	**$E_{(kin+pot)}$**	**Dipole Moment (D)**	**RMS**
1.13	1674.54	345.81	1328.92	1674.73	6.825	20.97
5.75	1675.51	342.72	1332.82	1675.54	7.400	21.30
10.71	1675.65	349.56	1326.49	1676.05	7.107	20.90
16.00	1680.21	337.03	1342.66	1679.69	3.971	22.11

MC and LD simulations that they are tabulated in tables 2-3 calculate the results of interaction between a molecule methanol thorough SWCNT. They are shown different energies (kcal/mol), acceptance ratio (ACCR), dipole moment (D) and RMS gradient (kcal/mol•Å) related to passing of methanol in length SWCNT in different temperatures. In Fig.2 shown, the total energy has linear ratio with temperature in 5.27 oA by both methods these interactions were endothermic.

Mont Carlo calculation for these interactions was shown in Fig. 5. The trajectories obtained applying this algorithm agrees with those obtained by Langevin dynamic simulations in Fig.6. The efficiency of a Monte Carlo-based search engine depends on the interplay of the energy update protocol and the type of conformational movements used to modify a given conformation.

The variation method for geometric optimized methanol– SWCNT, potential drop and its increase have different energy through SWCNT because angel and bond position atoms in relation to other atoms are different for each method and basis set. The total energy with two methods was decreased in the begging of SWCNT to the middle of the length so it was increased in middle to the end of the length that have indicated interaction between amino acids and SWCNT axis in length.

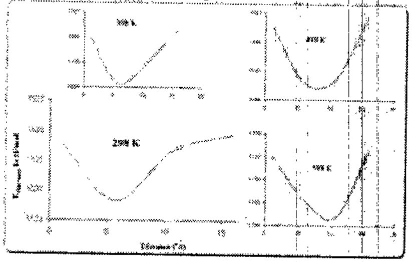

Fig. 5: Effect of methanol intake on the total energy across in SWCNT (7,7) by Mont Carlo simulations.

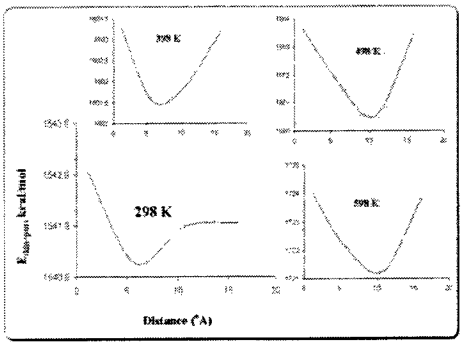

Fig. 6. Effect of methanol intake on the total energy thorough SWCNT (7,7) by Langvin Dynamic simulations.

In tables (2-3) are shown RMS and ACCR that the RMS gradient gives an indication of the deviation from an optimized structure. The computations of two electron integrals and their derivatives are time-consuming, because of the huge number of the two electron integrals even for a medium size of molecule. This option applies to single point calculations only. Hyper Gauss always computes the gradients in doing geometry optimization, molecular dynamics, and vibration calculations. We choose the precision of the optimization in the Semi-empirical optimization or ab initio optimization dialog box in Hyperchem 7.0 program package. Suitable default values for ending an optimization calculation are either an RMS gradient of 0.1 kcal/mol.Å or a maximum number of cycles that is 15 times the number of atoms involved in the calculation. In general, we must use a gradient limit. For improved precision, use a lower gradient limit. For most organic molecules, this will result in an acceptance ratio of about 0.9, which means that about 50% of all moves are accepted.Increasing the size of the trial displacements may lead to more complete searching of configuration space, but the acceptance ratio will, in general, increase.Smaller displacements generally lead to higher acceptance ratios but result in more limited sampling. There has been little research to date on what the optimum value of the acceptance ratio should be.

CONCLUSION

It is well able to predict the potential, kinetic and total energy of passing of methanol thorough SWCNT studied in this work and calculated with Mont Carlo and Langevin dynamic simulations. The geometry of all stages intervening in passing of methanol related to mention compounds has been investigated on DFT level by using 6-31G basis set. Therefore to overcome the shortcoming as discussed in this work, methanol can pass in the length of SWCNT. If molecular structure is spherical, diffusion behavior can be clearly distinguished as either normal-mode or single file mode in time scales of about 1000 ps. If molecular shape is asymmetrical, transition mode diffusion occurred when molecules could pass each other if they were perfectly aligned parallel to the nanotube axis but could not pass each other if they had undergone small-angle rotational motion during diffusion. In this case molecules can pass each other some of the time but not at other times. Applying this procedure to a simplified molecule, it is possible to show that setting a threshold of 1 on the movement of the dihedrals of the methanol backbone in a single Monte Carlo step, the mean quantities associated with the off-equilibrium dynamics are well reproduced, while the good description of higher moments requires smaller moves. An important result is that the time duration of a MC and LD step depends linearly on the temperature. A methanol molecular passed thorough in SWCNT (7,7) that these processes are not stable for methanol in length tube by both methods. Then in the middle of length the nanotube, the total energy begins to decrease and at the end of it begins to increase again. The minimum value of the interaction is 1525.87 kcal/mol in 5.75oA at 298K by MC simulation. In Langevin dynamic simulation method, the total energy begins to decrease in the initial length of the nanotube for methanol that the minimum value of the interaction is 1521.11 kcal/mol in 5.75oA at 298K.

Table 2. The different energies (kcal/mol), acceptance ratio (ACCR), dipole moment (D) and RMS gradient (*kcal/mol·?*) calculated in different distances for methanol and SWCNT by Monte Carlo at different temperatures.

Distance (°A)	**Methanol in CNT**											
	298K						**398K**					
	E_{total}	**ACCR**	**E_{kin}**	**$E_{(kin+pot)}$**	**Dipole Moment (D)**	**RMS**	**E_{total}**	**ACCR**	**E_{kin}**	**$E_{(kin+pot)}$**	**Dipole Moment (D)**	**RMS**
1.13	1527.55	0.994	179.43	1542.86	1.052	20.91	1587.87	0.996	239.64	1603.33	1.051	21.04
5.75	1525.87	0.995	179.43	1541.07	1.050	20.91	1586.13	0.996	239.64	1601.54	1.052	20.96
10.71	1528.72	0.995	179.43	1541.79	1.051	21.02	1587.68	0.996	239.64	1601.90	1.054	21.02
16.00	1525.84	0.994	179.43	1541.85	1.050	20.73	1587.86	0.996	239.64	1603.24	1.051	20.88
Distance (°A)	**498K**						**598K**					
1.13	1647.22	0.997	299.86	1663.65	1.049	21.00	1707.02	0.997	360.07	1723.98	1.050	21.02
5.75	1645.75	0.997	299.86	1661.83	1.052	20.95	1704.76	0.997	360.07	1722.10	1.051	20.92
10.71	1644.20	0.997	299.86	1660.51	1.054	20.79	1704.50	0.997	360.07	1721.25	1.055	20.85
16.00	1647.61	0.997	299.86	1663.56	1.052	20.91	1707.02	0.997	360.07	1723.83	1.051	20.88

Table 3. The different energies (kcal/mol), acceptance ratio (ACCR), dipole moment (D) and RMS gradient (*kcal/mol·?*) calculated in different distances for methanol and SWCNT by Langvin Dynamic at different temperatures.

Distance (°A)	**Methanol in CNT**											
	298K						**398K**					
	E_{total}	**ACCR**	**E_{kin}**	**$E_{(kin+pot)}$**	**Dipole Moment (D)**	**RMS**	**E_{total}**	**ACCR**	**E_{kin}**	**$E_{(kin+pot)}$**	**Dipole Moment (D)**	**RMS**
1.13	1522.98	204.76	1320.77	1525.53	1.132	23.15	1585.06	239.72	1346.29	1586.02	1.142	24.95
5.75	1521.11	204.77	1318.89	1523.66	1.132	23.15	1583.19	239.72	1344.43	1584.15	1.141	24.96
10.71	1523.81	177.75	1347.58	1525.33	1.060	21.16	1583.43	236.79	1348.22	1585.01	1.061	21.41
16.00	1523.33	204.81	1321.08	1525.89	1.139	23.14	1585.41	239.78	1346.6	1586.37	1.150	24.95
Distance (°A)	**498K**						**598K**					
1.13	1647.13	274.72	1371.77	1646.5	1.150	26.59	1709.20	309.79	1397.18	1706.98	1.157	28.13
5.75	1645.27	274.72	1369.91	1644.63	1.149	26.60	1707.34	309.78	1395.33	1705.11	1.156	28.13
10.71	1643.05	295.82	1348.86	1644.69	1.062	21.95	1702.68	354.84	1349.52	1704.36	1.063	21.89
16.00	1647.49	274.79	1372.07	1646.86	1.159	26.59	1709.56	309.86	1397.47	1707.33	1.166	28.12

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