International Journal of New Chemistry, 2014, 1 (3), 134-144
/ Published online 2014 in http://www.ijnc.ir
Original Article

ISSN: 2383-188X

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Pyrrole detection by BeO nanotube: DFT studies

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Received: 20October 2014; Accepted: 10 November 2014

Abstract:

Electrical sensitivity of a beryllium oxide nanotube (BeONT) was examined toward (C_4H_5N) molecule by using density functional theory (DFT) calculations at the $B_3LYP/6-31(d)$ level, and it was found that the adsorption energy (E_{ad}) of pyrrole on the pristine nanotubes is a bout -48.58kcal/mol. But when nanotubes has been doped with S and P atomes , the adsorption energy changed. Calculation showed that when the nanotube is doping by P, the adsorption energy is about -29.04kcal/mol and also the amount of HOMO/LUMO energy gap (E_g) will reduce significantly. Beryllium oxide nanotube is not suitable adsorbent for pyrrole, but when the BeONT doped by P atom the amount of E_g was less than pristine BeONT and that is a suitable semiconductor.

Keywords, Nanotube, DFT, pyrrole,Sensor

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1. Introduction:

It is well known that substituted pyrroles are an important class of heterocyclic compounds due to their remarkable biological and physical properties [1]. Pyrrole cross-links have been identified in long-lived proteins such as lens crystallins and skin collagen and implicated in the stiffening of arteries and joints associated with aging [2-3]. Since the discovery of carbon nanotube (CNT) by Iijima [4] the properties and applications of this novel material have been investigated extensively[5-7] .CNTs have recently emerged as a promising substitute for materials of different properties and various applications in hydrogen storage, gas sensors ,textiles and many more[8-9].More recently, models of pristine beryllium oxide nanotubes (BeONT) were proposed and their structural, cohesive and electronic properties were predicted [10-11].BeO compound often demonstrates different properties from the counterpart of C , BN and SiC because of the large iconicity of Be-O bond. For example, wurtziteBeO is an insulator with a wide band gap, high melting point, high thermal conductivity and large elastic constants [12] .Previously adsorption different molecules toward nanostructures has been studied [13-16]. In this study, the adsorption of pyrrol on the pristine case BeONT while S and P atoms are in its structure has been investigated.

2. Computational methods:

Computation procedures are including the following:

We have optimized the pyrrole molecule and BeONT at the B_3LYP/6-31G (d) level of theory. BeONT is made up of 56O , 56Be atoms was saturated by 16 hydrogen atoms which are in initial and end part of nanotube. The reason for this act had been done to decrease the boundary effects and totally nanotube is involving 128 atoms (Fig.1)

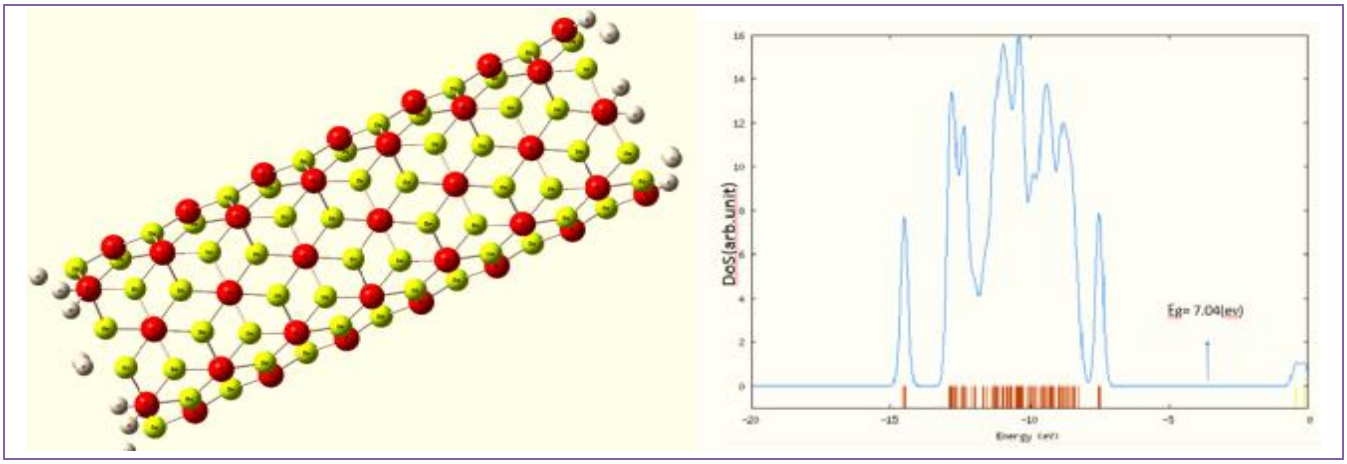

Figure1: BeONT and DOS diagram for E_g of nanotube.

The BeONT that has been selected is armchair (4, 4) type and GAMESS software [17] is used to perform these calculations. The B_3LYP is demonstrated to be a reliable and commonly used functional in the study of different nanostructures [18-20].We made pyrrole molecule from different positions of the site to be close to the nanotube and its adsorption has been calculated by using the equation 1.

$$E_{ad}=E_{Nanotube\ +Pyrrole} - [E_{Pyrrole} + E_{Nanotube}] + \delta_{BSSE}[1]$$

According to the mentioned equation EPyrrole is pyrrole molecule's energy, ENanotube is the nanotube energy and E Nanotube +Pyrrole is the nanotube's energy whit pyrrole. In addition, δBSSE is representing the basis set super position error. In the following steps S and P atoms in the nanotube structure have been doped to examine the pyrrole adsorption on the nanotube and conductivity that which is doping with S and P atoms.

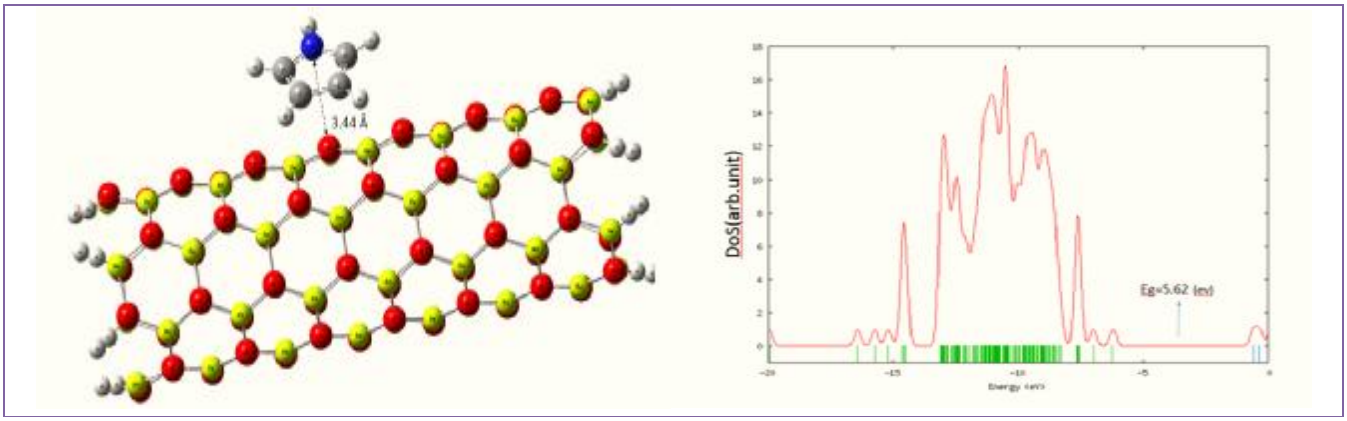

Figure 2: Pyrrole adsorption on the BeONT and DOS diagram for observing E_g of nanotube.

3. Results and discussion:

In Figure 1, is showing the structure of beryllium oxide nanotube (BeONT), in order to obtain the most stable adsorption mode of C_4H_5N molecule on different position of BeONT, the most stable configuration has shown in Figure 2, that oxygen atom of pyrrole is 3.44A0 far from beryllium atom of the nanotube .Detailed information of the structure and electronic properties of the BeONT including the HOMO/LUMO energy gap (E_g) is shown in table 1. In which adsorption energy (E_{ad}) for mentioned configuration of pyrrole and nanotube is about -48.58kcal/mol and then we calculated the HOMO/LUMO energy gap (E_g) for pristine nanotube since the pyrrole molecule is adsorbed on the nanotubes(Table1). Diagram which shows HOMO/LUMO energy gap (E_g) has been calculated, and the diagram which shows E_g has been obtained by using density of state (DOS) software.

Table 1. E_{ad} (kcal/mol), eV for the others

System	E_{ad}	E_{HOMO}	E_{LUMO}	E_g
BeONT	-	-7.74	-0.7	**7.04**
BeONT-Pyr	-48.58	-6.21	-0.59	**5.62**
S_{Be}	-	-6.29	-1.58	**4.71**
S_{Be}-pyr	-36.69	-5.69	-1.52	**4.17**
P_{Be}	-	-5.08	-0.73	**4.32**
P_{Be}-pyr	-29.04	-5.86	-0.58	**5.28**

3.1 Adsorption of C_4H_5N on P doped BeONT:

To examine the sensitivity of the adsorption of BeONT of C_4H_5N as an adsorbent for C_4H_5N examining has been done two times, once Be atom doped by P atom and other time O atom by P atom has been doped. Doped calculation of P on BeONT shows that the value of E_g is less than the pristine nanotube (Fig.3). DOS diagram clearly shows that when P doped on the BeONT it will become a semiconductor. The BeONT is a suitable absorbent for pyrrole molecule. But when BeONT doped by P the adsorption energy is less than when we just use the pristine BeONT .If E_{ad} is significantly increased then it expect that recovery will be so long, meanwhile according to transition state theory and recovery time can be explain as equation[2].

$$\tau = \upsilon 0\text{-}1 \exp(-E_{ad}/kT) \qquad [2]$$

Where T is the temperature, k is the Boltzmann's constant, and $\upsilon 0$ is the attempt frequency.

According to this equation as often as adsorption energy (E_{ad}) is increasing the recovery time becomes longer and calculation in table1 show that the recovery time and adsorption energy is suitable level. (Fig.4)

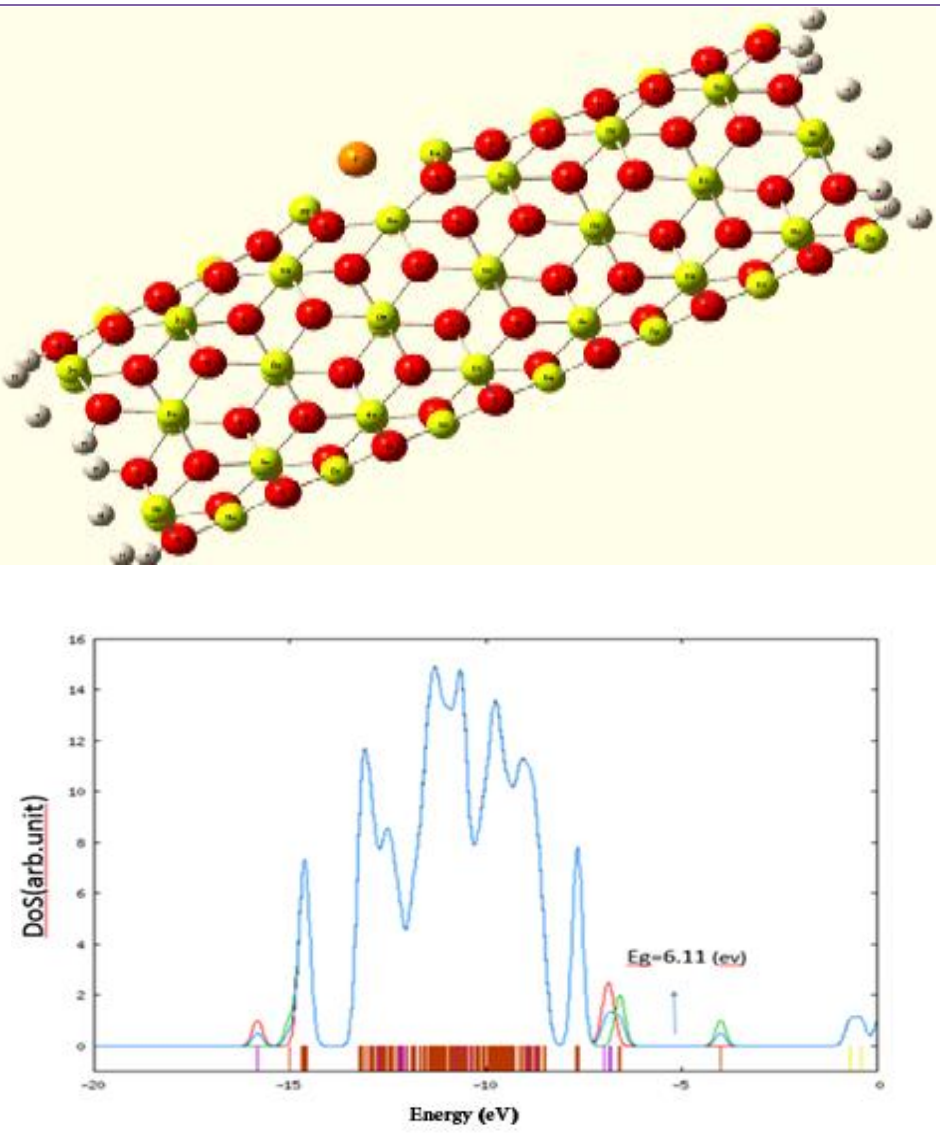

Figure 3: Doped nanotube by p and DOS diagram for E_g of nanotube.

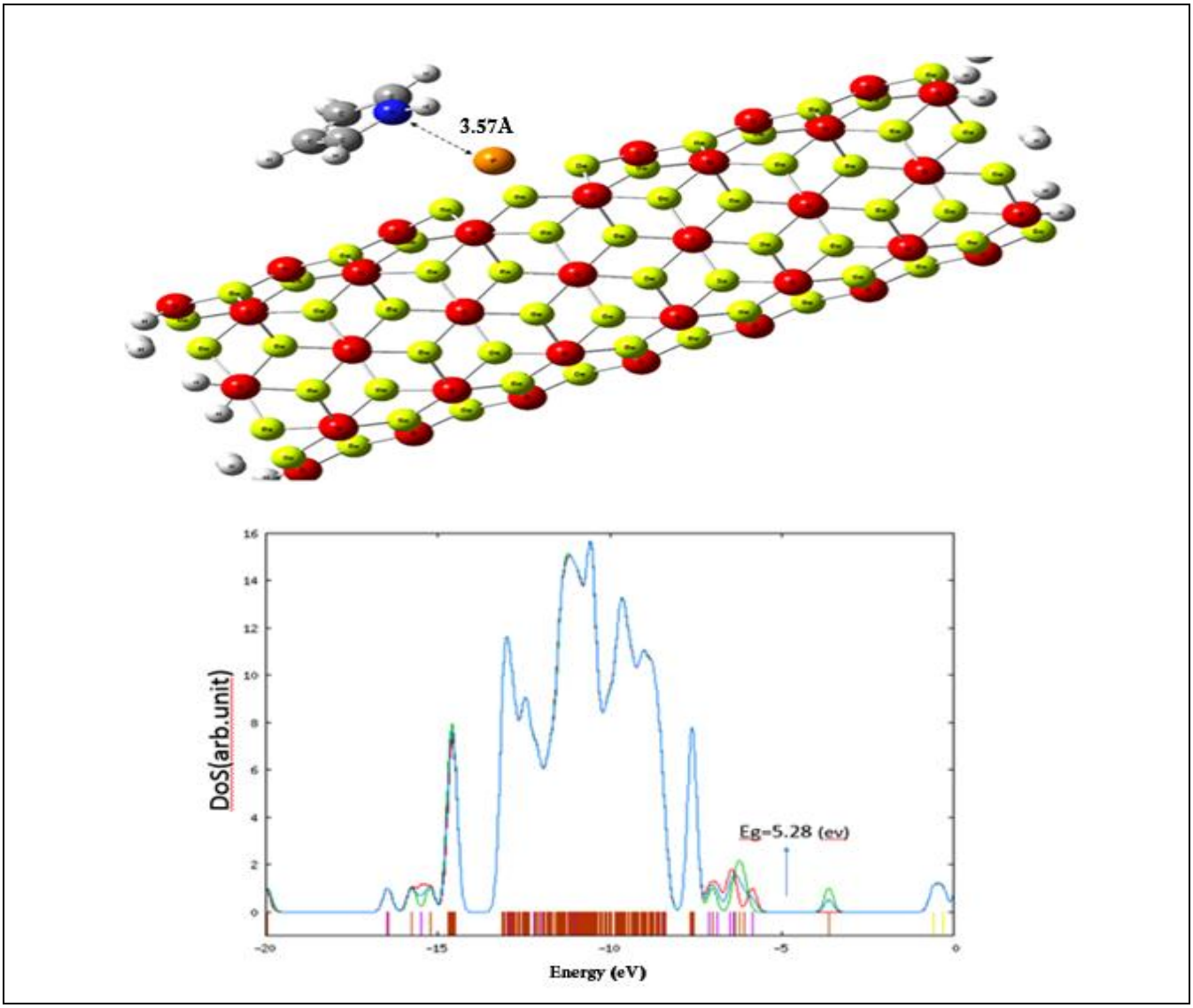

Figure 4: Pyrrole adsorption on doped nanotube by P and DOS diagram for observing E_g of nanotube.

3.2 Adsorption of C_4H_5N onS doped BeONT:

At this stage doping have been studied with another element. First, instead of Be atom in the beryllium oxide nanotube a S atom and then instead of O atom in the S atom replaced in a nanotube(Fig.5), and then geometrical structures and electronic properties of BeONT has been doped and its adsorption behavior have been studied. Computations showed that when S replaced by Be in BeONT the E_g will become less (Fig.6).When S is sitting of O and Be, and the adsorption energy of pyrrole on nanotube is less than when we just use the pristine

nanotube (not doped). After adsorption of C_4H_5N on the mentioned nanotube that has doped by S the HOMO/LUMO energy gap (E_g) will decrease and therefore a substantial increasing will happen in conductivity that this phenomenon can be explain as equation 3,[21]

$$\sigma \propto \exp(-E_g /2kT) \qquad [3]$$

Where σ is conductance, T is temperature, k is Boltzmann constant. According to this equation as often as E_g is smaller it leads the conductivity to be more.

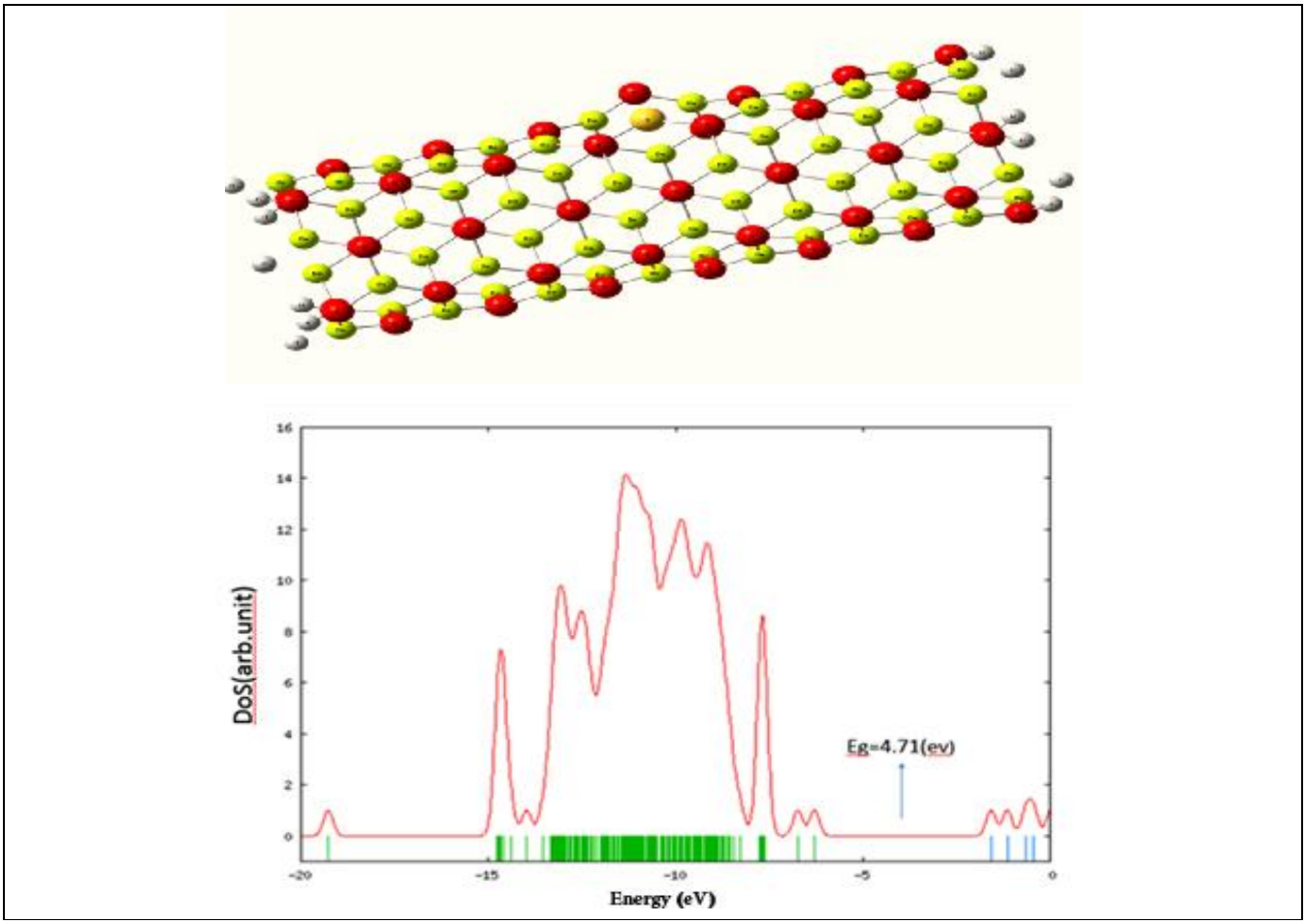

Figure 5: Doped nanotube by S and DOS diagram for E_g nanotube.

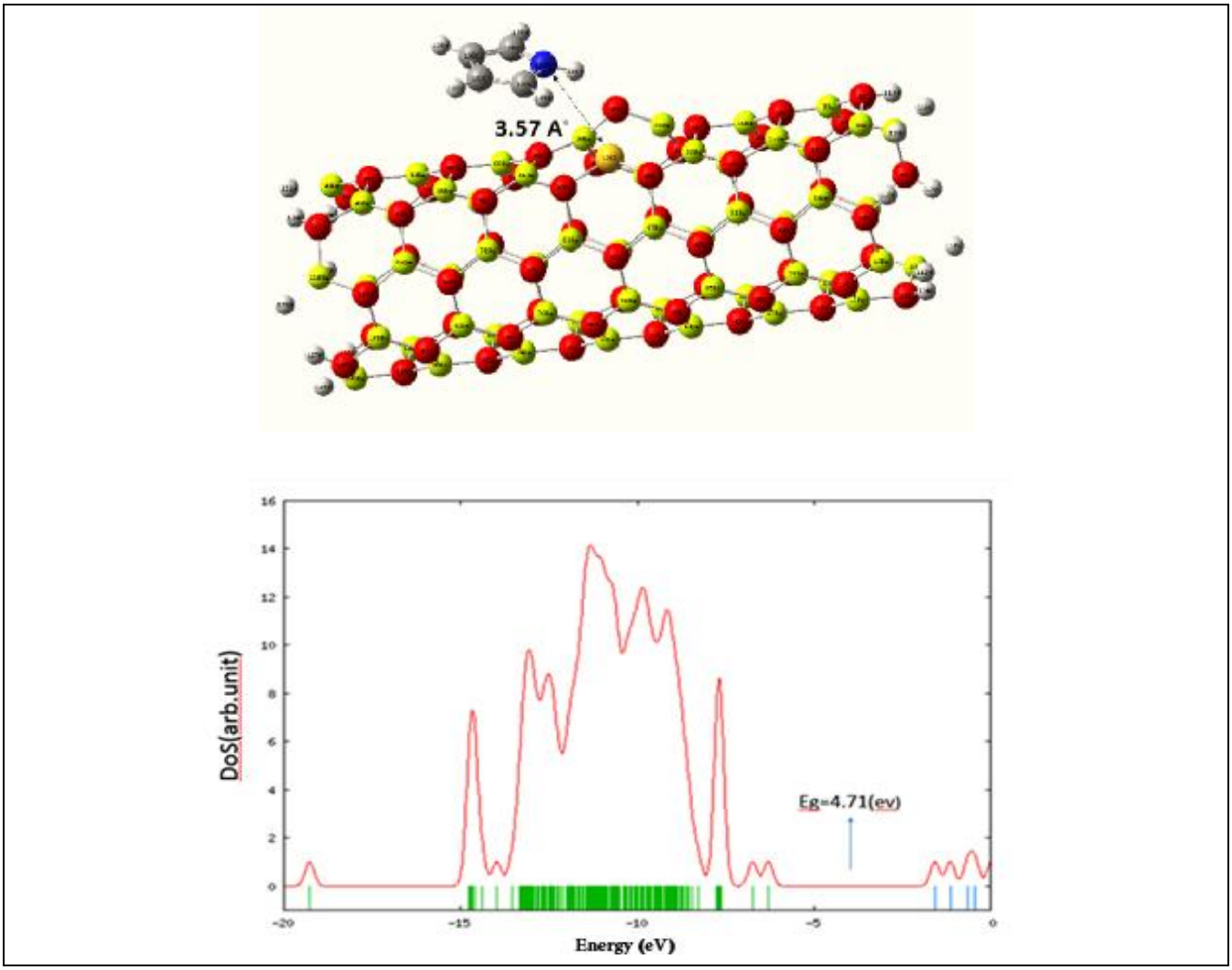

Figure 6: Pyrrole adsorption on doped S nanotube and DOS diagram for observing E_g nanotube.

4. Conclusion:

The adsorption of an pyrrole (C_4H_5N) molecules on the surface of BeONT (beryllium oxide nanotube) has studied by using density functional theory (DFT) and then we doped the S and P atoms in the structure of the nanotube, the results show the nanotube is not suitable adsorbent of pyrrole molecule in gas sensors. When P is doped on BeONT the E_g is less than piristineBeONT and it lead to more conductivity. The BeONT doped with P is a suitable semiconductor than the piristineBeONT.These results may be open a new gate to chemically

modifiing the nanotubes in away to expand the fields of its applications in industry and technology.

5. Acknowledgment:

We are appreciating and thanking Islamic Azad University of Mahshahr in advance due to their financial supports.

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