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# Determination of Ru and Ni-Doped Carbon Nanotube as Sensor Identifying $CHCl_3$ Molecular using DFT Method

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**Key words:** Chloroform, electronic results, adsorption process, energy, dipole moments

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**Abstract:** First-principles computations have been applied to scrutinize the adsorption behavior of Chloroform $CHCl_3$ molecule on the external surface of Ruthenium (Ru) and Nickel (Ni) -doped (8,0) zigzag single-walled carbon nanotubes (SWCNTs) with 10 and 12A° length. Binding energy corresponding to the most stable configuration of $CHCl_3$ on the Ru-doped CNT at the length 10 A°is found to be −9.080 eV which is high typical sensitivity to $CHCl_3$ molecule. In this study, two sensitive nanotube is configured of the $CHCl_3$ molecule by replacing one carbon atome of the SWCNT with Ru and Ni atom. Our results indicate that the adsorption of $CHCl_3$ molecular on pristine carbon nanotube is weak because there is no marked change in the energy gap but Ru- and Ni-doping CNT can lowering the energy gap of $CHCl_3$/CNTs complexes. Our electronic results reveal that there is a notable orbital hybridization among two species in adsorption process being an evidence of strong interaction. For the $CHCl_3$/CNTs complexes, the energy gaps, dipole moments, natural atomic orbital occupancies and global indices are computed. Finally, we reported a novel type of Chloroform sensor that can be used for detecting the presence of $CHCl_3$ molecule.

## INTRODUCTION

Since, the discovery of Carbon Nanotubes (CNTs) through 1991 via. Iijima, Carbon Nanotubes (CNTs) the promise is pretty much substance it can revolutionize the electronics and nanoelectronics technologies. Along with that unusual electronic characteristics (Rahmanifar *et al*., 2016; Boroznina and Zaporotskova, 2018; Amorim *et al*., 2013). CNT are so, interesting systems from both, the physical and the technological, viewpoint further to their prominent mechanical properties such as high stiffness and an formidable young's modulus of almost 1 TPa (Wagner *et al*., 2012). Crbon nanotubes based gas sensors due to their exquisitely sensing capability, like high sensitivity, speedy reaction, small size and occasional running temperature (Cui *et al*., 2018). (CNT) can be either Single-Walled [SW] with discrete fragment of curved carbon sheet or Multi-Walled [MW] (Rahmanifar *et al*., 2016). Single-wall CNTs are perfect applicants to study general transport properties of quasi-one-dimensional systems (Latessa *et al*., 2007).

Every SWCNT can be indicated with a pair of integers [n, m] and categorized to 3 types, particularly, armchair nanotubes [n, n], zigzag nanotubes [n, 0] and

chiral nanotubes [n, m] with n m. These residences have made probable the application of CNTs in lots of areas including electronic devices, fuel cell, hydrogen storage, electrode catalysis, gas sensing, etc., (Kanchanatip *et al*., 2018; Correa *et al*., 2016).

Chloroform (trichloro-methane) $CHCl_3$ is an organic compound, colorless, sweet smelling, dense liquid and is considered somewhat carcinogenic, toxic and hazardous, several million tons are produced annually as a precursor to industry as poly-tetrafluoroethylene and refrigerants, but its use for refrigerants is being phased out, it was once a widely used anesthetic and used as a solvent in the pharmaceutical industry and for producing dyes and pesticides (Flanagan and Pounder, 2010; Leikin and Paloucek, 2008). Chloroform vapors depress the central nervous system of human beings and animal. It is immediately treacherous and perfidious to life and health. Breathing about 1000 ppm for a short time can cause dizziness, fatigue, eyesight disturbance, headache, lung congestion, kidney damage, cancer and even death. Chronic chloroform exposure can damage the liver and the kidneys (where chloroform is metabolized to phosgene) and some people develop sores when the skin is immersed in chloroform (Perillo and Rodriguez, 2013). The national institute for occupational safety and health set two limits for chloroform, recommended exposure limit of 2 ppm [for 60 min] based on risk evaluations using human or animal health effects data and permissible exposure limit of 50 ppm as carcinogen substance with targeted organs such liver, kidneys and central nervous system (Zhang *et al*., 2013; Liu *et al*., 2013).

They reported that the interaction of CHCl3 on Ru and Ni-doped carbon nanotubes surface are weak, while the Ru- and Ni-doped on the (8,0) CNT at the length 10 A can slightly enhance adsorption capability of the $CHCl_3$ molecule in comparison with pristine CNT and other nanotubes (Kanchanatip *et al*., 2018). In this study, the adsorption of $CHCl_3$ molecule on the Ru- and Ni-doped CNT at the length 10 and 12 A has been investigated. The analyses considered the $CHCl_3$ adsorption capability and examined the effect of Ru- and Ni-doped on the electronic and structural properties, potential applications as nanosensor and adsorption capability of CNT through DFT calculations. The optimized geometries, electronegativity, electronic chemical potential, global softness, global hardness, electrophilicity index, were calculated and compared with the Ru- and Ni-doped (8, 0) zigzag SWCNTs at the length 10 and 12 A . We hope our results can provide experiments with useful information on designing sensors employing the carbon nano-materials.

## MATERIALS AND METHODS

**Computational methods:** In this research, we examined the adsorption behavior of the $CHCl_3$ molecule on zigzag single wall Ru and Ni-doped (8, 0) CNT. All atoms, the optimizations and energy calculations are performed using Gaussian 09 program package at the level of Density Functional Theory (DFT) with B3LYP/6-31G. The Ru-doped and Ni-doped (8,0) zigzag CNTs al the length 10 and 12 . The binding energy (Ead) of a $CHCl_3$ on the CNT is determined through the following equation (Ghalib, 2014):

$$E_{ad} = E_{Ru-CNT-CHCl_3} - \left(E_{Ru-CNT} + E_{CHCl_3}\right) \quad (1)$$

$$E_{ad} = E_{Ni-CNT-CHCl_3} - \left(E_{Ru-CNT} + E_{CHCl_3}\right) \quad (2)$$

where, $E_{Ru\text{-}CNT\text{-}CHCl3}$ and $E_{Ni\text{-}CNT+ECHCl3}$ are the total energy of the Ru doped and Ni-doped interacting with the $CHCl_3$. $E_{Ru\text{-}CNT}$ and $E_{Ru\text{-}CNT}$ are the total energy of Ru and Ni-doped on the CNT and is the total energy of an isolated $CHCl_3$ molecule. The electrophilicity index which calculates the stabilization in energy when the system obtains an additional electronic charge. Thus, μ is defined according to the following equation:

$$\mu = \frac{I.P + E.A}{2} \quad (3)$$

$$I.P = -E_{HOMO} \quad (4)$$

$$E.A = -E_{LOMO} \quad (5)$$

where, $E_{HOMO}$ is the energy of highest occupied molecular orbital and $E_{LOMO}$ is the energy of lowest unoccupied molecular orbital. X is defined as the negative of μ, as follows: X = -μ. Furthermore, η can be determined as: η = (ELUMO−EHOMO)/2. S and ω are specified as the following equations, respectively:

$$S = \frac{1}{2\eta} \quad (6)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (7)$$

## RESULTS AND DISCUSSION

**The CHCl3 adsorbed on the Ru and Ni-doped CNT:** Considering the detailed properties and behavior of transitional metal doping on the adsorption of $CHCl_3$ molecule on the (8, 0) CNTs at the different length systems for most stable configurations, we substitute a carbon atom in the middle of CNT at length 10 A° by one Ru and Ni atoms Fig. 1 indicates the schematic of the possible adsorption sites of a $CHCl_3$ molecule adsorbed on the Ru and Ni-doped (8,0) CNT surface.

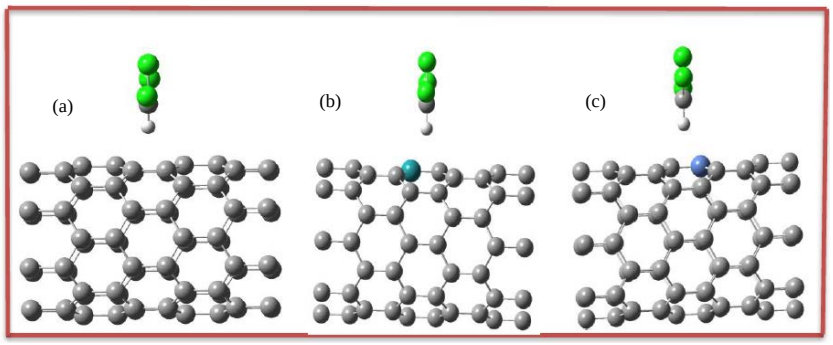


Fig. 1(a-c): The optimized structure for the most stable configuration of $CHCl_3$ molecule on Ru- and Ni-doped CNTs/ at length 10 A° systems: (a) CNT-$CHCl_3$, (b) CNT-Ru-$CHCl_3$ and (c) CNT-Ni-$CHCl_3$

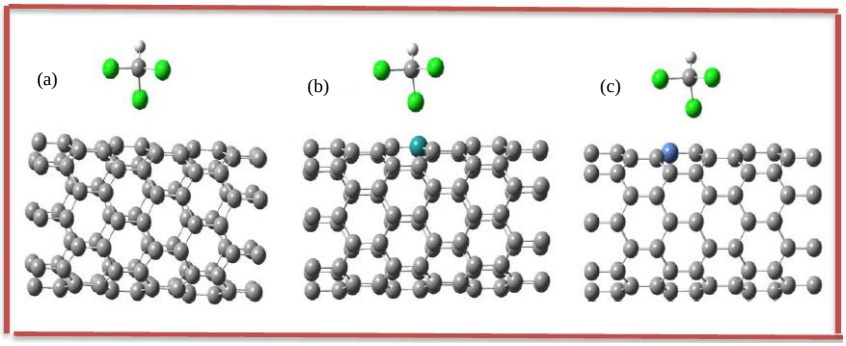


Fig. 2(a-c): The optimized structure for the most stable configuration of $CHCl_3$ molecule on Ru- and Ni-doped CNTs at length 12 A°/systems: (a) CNT-$CHCl_3$, (b) CNT-Ru-$CHCl_3$ and (c) CNT-Ni-$CHCl_3$

The binding energy for $CHCl_3$ adsorption on the Ruthenium and Nickel-doped CNT are with a well maximum about -9.080 eV and -12.425 eV, respectively. In contrast, the adsorption of $CHCl_3$ molecule on the Ru-doped CNT can be attributed to the strong hybridization between the Ruthenium orbitals and carbon orbitals. In this case, the binding energy for $CHCl_3$ on the Ru site is more than the Ni site with a similar configuration. The average Ru C and Ni C bond lengths are about 1.414 and 1.421 A°, respectively. While with the $CHCl_3$ adsorption on Ru and Ni-doped CNT at length 10 A° due to increase of the average Ru C and Ni C bond lengths are about 1.422 and 1.422 A°, respectively. We believe that the doping of Ru atom on the CNT is slightly eligible than the Ni-doped CNT. The current calculations show that the adsorption energy of $CHCl^3$ on the Ru-doped and Ni-doped CNT with an equilibrium distances Fig. 1. The computations indicate that the adsorption of $CHCl_3$ molecule on surfaces of Ru and Ni-doped (8, 0) CNT at length 12 A° are about −8.364 and -45.693 eV with distances of 2.194 and 2.428 A°, respectively (Fig. 2). Our calculations result show that the interaction between $CHCl_3$ and zigzag CNT at length 12 A° are slightly stronger than zigzag CNT at length 10 A°. Recently, these computations indicate that the Ru and Ni atoms play a significant role in enhancing the $CHCl_3$ adsorption on the CNT in comparison with pristine CNT.

**Electric dipole moment:** When a chloroform is adsorbed on such systems, the charge distribution would be scrutinized by the dipole moment vector of species which prominently the size and direction of the dipole moment vector are changed when a CHCl3 approaches to the surface of Ru and Ni-doped carbon nanotubes have dependence on the adsorption configurations. The results of the electric dipole moment for CHCl3 and sites show that the adsorption energy is the highest in the equilibrium distances which are listed (Table 1 and 2). The result demonstrates that during $CHCl_3$ adsorption for all systems the total dipole moment increases. We consider that dipole moment for Ru and Ni-doped CNTs at length 10 and 12 A° are about 0.727, 0.623, 0.412 and 1.332 Debye, respectively. In the case of the $CHCl_3$ adsorption on the Ru and Ni-doped CNTs at length 10 and 12 A° are about 10.100, 8.039, 9.140 and 3.934 Debye,

Table 1: HOMO (eV), LUMO (eV), bond Gap (eV) and dipole moment (Debye) for $CHCl_3$ adsorptions on the Ru and Ni-doped CNT/at length 10 A° surfaces at the B3LYP/6-31G level

| Property | $E_{HOMO}$(eV) | $E_{LUMO}$(eV) | Energy gap (eV) | Binding energy (eV) | Dipole moment (Debye) |
|---|---|---|---|---|---|
| CNT | -6.347 | -5.505 | 0.842 | - | 0.000 |
| CNT-Ru | -6.230 | -5.642 | 0.588 | - | 0.727 |
| CNT-Ni | -6.231 | -5.687 | 0.544 | - | 0.623 |
| CNT-$CHCl_3$ | -5.893 | -5.264 | 0.629 | -9.327 | 8.080 |
| CNT-Ru-$CHCl_3$ | -5.884 | -5.346 | 0.538 | -9.080 | 10.100 |
| CNT-Ni-$CHCl_3$ | -5.911 | -5.395 | 0.516 | -12.425 | 8.039 |

Table 2: HOMO (eV), LUMO (eV), bond Gap (eV) and dipole moment (Debye) for CHCl3 adsorptions on the Ru and Ni-doped CNT/ at length 12 A° surfaces at the B3LYP/6-31G level

| Property | $E_{HOMO}$(eV) | $E_{LUMO}$(eV) | Energy gap (eV) | Binding energy (eV) | Dipole moment (Debye) |
|---|---|---|---|---|---|
| CNT | -6.089 | -5.570 | 0.519 | - | 0.000 |
| CNT-Ru | -6.056 | -5.487 | 0.569 | - | 0.412 |
| CNT-Ni | -5.942 | -5.404 | 0.538 | - | 0.324 |
| CNT-$CHCl_3$ | -5.994 | -5.496 | 0.498 | -7.851 | 2.980 |
| CNT-Ru-$CHCl_3$ | -5.726 | -5.283 | 0.443 | -8.364 | 9.140 |
| CNT-Ni-$CHCl_3$ | -5.878 | -5.415 | 0.463 | -45.693 | 3.934 |

Table 3: Chemical potential (μ), hardness (η), Softness (S) and electrophilicity (ω), of $CHCl_3$ molecule adsorptions on the Ru and Ni-doped CNTs at the length 10 A° surfaces at the B3LYP/6-31G level. All parameters are in units of eV

| Property | I.P (eV) | E.A (eV) | Chemical potential (eV) | Hardness (eV) | Softness (eV) | Electrophilicit (eV) |
|---|---|---|---|---|---|---|
| CNT | 6.347 | 5.505 | -5.926 | 0.421 | 1.187 | 41.706 |
| CNT-Ru | 6.230 | 5.642 | -5.936 | 0.294 | 1.700 | 59.925 |
| CNT-Ni | 6.231 | 5.687 | -5.959 | 0.272 | 1.838 | 65.273 |
| CNT-$CHCl_3$ | 5.893 | 5.264 | -5.578 | 0.314 | 1.592 | 49.544 |
| CNT-Ru-$CHCl_3$ | 5.884 | 5.346 | -5.615 | 0.269 | 1.858 | 58.662 |
| CNT-Ni-$CHCl_3$ | 5.911 | 5.395 | -5.653 | 0.258 | 1.937 | 61.930 |

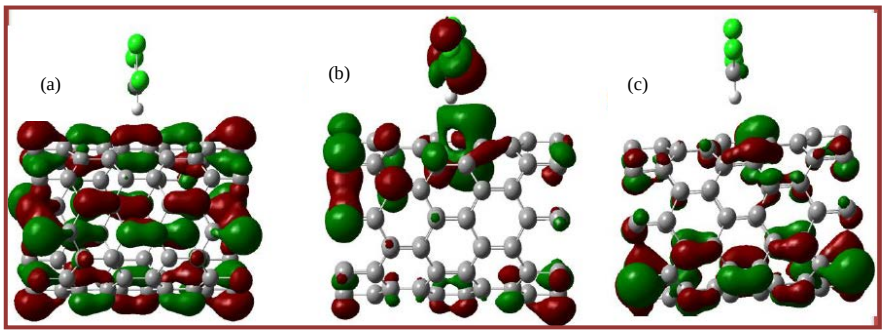


Fig. 3(a-c): Charge distribution of HOMO and LUMO orbitals on the Ru- and Ni-doped CNTs at length 10 A° loaded with one $CHCl_3$ molecule at the B3LYP/6-31G method

respectively. Substantially, both electron transfers and dipole moment imply this concept that Ru and Ni-doped CNT with absorption of the $CHCl_3$ are caused to increase the polarization and change dipole moments (Fig. 3-6).

**Global indices:** The global hardness of types is specified as its endurance toward deformation in the presence of an electric field. Increasing in global hardness leads to increase in stability and diminish in reactivity of the species (Soltani *et al*., 2012). The global indices of reactivity in the basis of the DFT for $CHCl_3$ adsorption on the Ru and Ni-doped zigzag CNTs at the length 10 A are presented in Table 3. When $CHCl_3$ adsorbs on the Ru and Ni- doped, hardness, electrophilicity and electronic chemical potentials of CNTs will be reduced, also softness will be increased. The results also indicate that when $CHCl_3$ is chemisorbed on the exterior surface of the Ru and Ni-doped/CNTs, a fairly large charge transfer to the $CHCl_3$ could occur which suggests that their electronic transport properties could be notably changed upon chemisorptions of $CHCl_3$. The direction of electron flow will be characterized via. electronegativity or chemical potential. When $CHCl_3$ is added to Ru- and Ni-doped/CNTs electrons are transferred from the higher chemical potential to the lower chemical potential, in order to the electronic chemical potentials become identical. As a result, electrons will flow from a definite occupied orbital in a Ru and Ni-doped/CNTs and will go into a definite empty orbital in a $CHCl_3$.

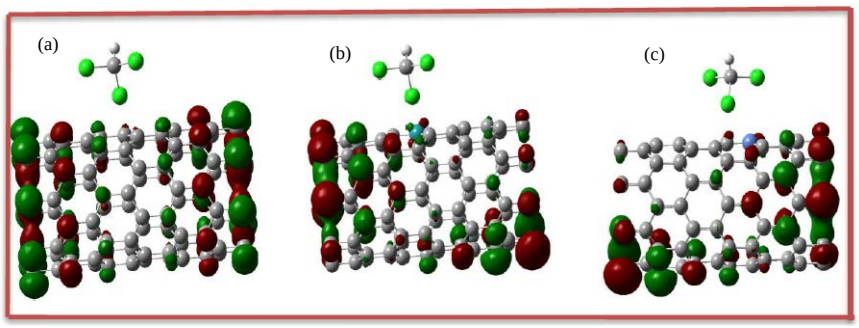


Fig. 4(a-c): Charge distribution of HOMO and LUMO orbitals on the Ru- and Ni-doped CNTs at length 12 A° loaded with one $CHCl_3$ molecule at the B3LYP/6-31G method

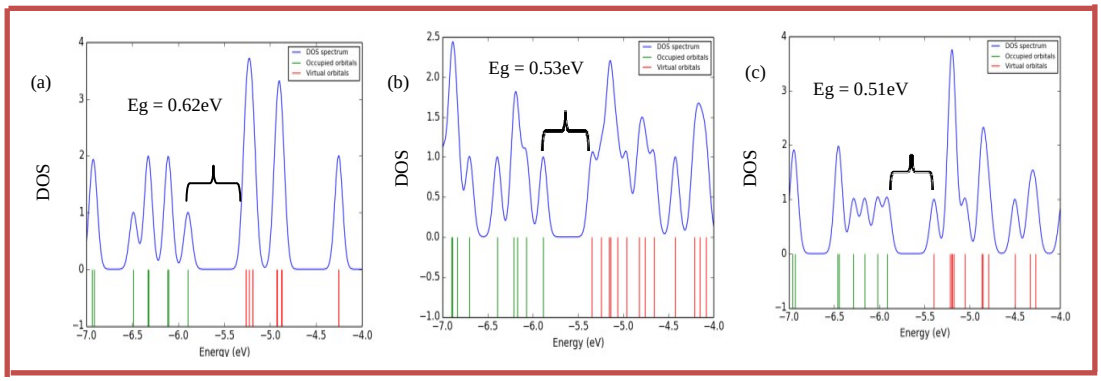


Fig. 5: Total Density of States (DOS) for $CHCl_3$ molecule on Ru- and Ni-doped CNT at length 10 A° (a) CNT-$CHCl_3$, (b) CNT-Ru-$CHCl_3$ and (c) CNT-Ni-$CHCl_3$

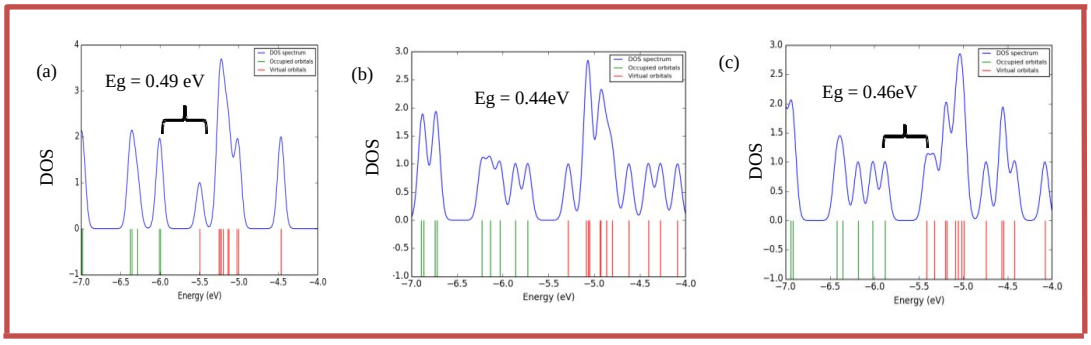


Fig. 6: Total Density of States (DOS) for $CHCl_3$ molecule on Ru- and Ni-doped CNT at length 12 A° (a) CNT-$CHCl_3$, (b) CNT-Ru-$CHCl_3$ and (c) CNT-Ni-$CHCl_3$

Table 3 consists of variable information regarding the quantum molecular descriptor which could be explained as follows: Considering the amount of chemical potential the table shows that, there is downward trend for Ru and Ni-doped CNT at the length 10 A from -5.936, -5.959 eV to −5.615, 5.53 eV CNT/$CHCl_3$. Hardness is also scrutinize and it is decreased in Ru-doped (10, 0) CNT from 0.294 to 0.269 eV, while the mode is reverse for Ni-doped CNT at the length 10 A° of reduction. It is extracted from the data that there is a reverse result for doping of Ru and Ni atoms. And, no noticeable changes have been found to happen as result of the increasing of length CNT (Table 4).

Table 4: Chemical potential (μ), hardness (η), Softness (S) and electrophilicity (ω), of CHCl3 molecule adsorptions on the Ru and Ni-doped CNTs at the length 12 A° surfaces at the B3LYP/6-31G level. All parameters are in units of eV

| Property | I.P (eV) | E.A (eV) | Chemical potential (eV) | Hardness (eV) | Softness (eV) | Electrophilicit (eV) |
|---|---|---|---|---|---|---|
| CNT | 6.089 | 5.570 | -5.829 | 0.259 | 1.930 | 65.593 |
| CNT-Ru | 6.056 | 5.487 | -5.771 | 0.284 | 1.760 | 58.633 |
| CNT-Ni | 5.942 | 5.404 | -5.673 | 0.269 | 1.858 | 59.817 |
| CNT-CHCl3 | 5.994 | 5.496 | -5.745 | 0.249 | 2.008 | 68.538 |
| CNT-Ru-CHCl3 | 5.726 | 5.283 | -5.504 | 0.221 | 2.262 | 68.997 |
| CNT-Ni-CHCl3 | 5.878 | 5.415 | -5.646 | 0.231 | 2.164 | 8.218 |

## CONCLUSION

The adsorption behavior and electronic properties of $CHCl_3$ adsorption on transitional metal doping of Ru and Ni atoms on outer surface of (8, 0) single walled carbon nanotube at the length 10 and 12 A were studied through DFT calculations. For CHCl3 adsorption on the Ru- and Ni-doped- CNTs, electronic properties of the tubes will be changed. Our results indicated that the transfer of charge from $CHCl_3$ to doping atoms (Ru and Ni atoms) is a remarkable factor in the change of the electrical conductance of the carbon nanotubes. On the basis of our calculations, it seems that doping effection on CNTs can detect $CHCl_3$ molecule. Diminish in HOMO–LUMO energy gaps, ionization potential, and global hardness with the adsorption of $CHCl_3$ on the transitional metal doped in CNT surface due to increase of the chemical reactivity and also lead to the lowering of stability in the complexes.

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