Research Article

Boron Nitride Nanotubes-Based Gas Sensors of SF$_6$ Decomposed Components for Analyzing the Running Status of High-Voltage Insulated Equipment

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Abstract. Gas-insulated equipment using *sulphur hexafluoride* (SF6) as insulation and arc extinguishing media such as *Gas Insulated Station* (GIS) has been widely used in the field of high voltage power systems. However, the internal insulation defect existed in GIS would inevitably lead to *Partial Discharge* (PD), and cause the composition of SF$_6$ to HF, SF$_4$, SOF$_2$, SO$_2$F$_2$ and SO$_2$ and other characteristic component gases. The decomposition phenomenon would greatly reduce the insulation performance of SF$_6$ insulated equipment, and lead to insulation faults and power failure. Many sensing nonmaterial's such as carbon nanotube and graphene, metal oxides such as SnO$_2$ TiO$_2$, and ZnO were explored as chemical gas sensors to detect SF$_6$ decomposed species with rapid response, high sensitivity and selectivity, in order to guarantee the operation status of SF$_6$ insulation equipments. In this paper, we attempt to comprehensively understand the adsorption and sensing property of BNNT to SO$_2$, SOF$_2$ and SO$_2$F$_2$ were investigated based on the DFT method to explore its potential as a chemical gas sensor. Our theoretical simulation results show that BNNT could be a promising sensor for sensitive detection which would be beneficial for evaluating the running status of SF6 high voltage insulated equipments.

Keywords. Dielectric material; Gas SF$_6$; Decomposition products; BN nanotube; Molecular dynamics; Adsorption; Gap Energy; Density Functional Theory (DFT)

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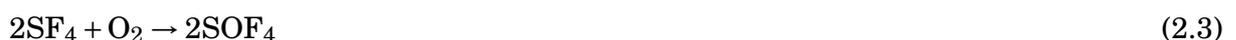*Corresponding author: chenaf.tahar@laghouat.sadeg.dz

1. Introduction

The use of gaz SF$_6$ in the industrial sector has been of particular importance in the field of sound and electrical insulation, which is based on the remarkable dielectric properties acquired thanks to the high electro negativity of this gas, which provides it with the ability to absorb and suppress electrical arcing in switchgear (circuit breaker, switch, disconnect switch, etc.) this gas has allowed the industrial sector to reduce the dimensions of electrical equipment (GIS) [6] by five times those of open air equipment (AIS) and a reduction in the costs of this equipment and its maintenance.

Although SF$_6$ gas is initially filled with high purity but after several operations under load and under tension and in the presence of impurities such as H$_2$O or carbon atoms contained in solid epoxy resin insulators, in this system new products are created from the decomposition of the gas SF$_6$ (HF, SF$_4$, F$_2$, SOF$_2$, SO$_2$, SO$_2$F$_2$, SOF$_4$, SO$_2$...), these products influence the proper functioning of high voltage equipment, which disrupts the quality and continuity of the distributed electrical energy. The analysis of the adsorption of its products and molecules by different processes can allow us to minimize or eliminate them from contaminated gases. And in order to find a better system to adsorb more molecules than those found in our studies conducted in our article [3] with the Single Wall Carbon Nanotube (SWCNT) we have chosen this time to use BN (Bore Nitride) (SWBNNT) nanotubes this choice is initially made by the similarity of these electronic properties.

Boron nitride is a compound that does not exist in nature and was first synthesized in 1842 by Balmain, it exists in two hexagonal and cubic forms, and since Bore B has $Z = 5$ and nitrogen N has $Z = 7$ which are located near carbon $Z = 6$ therefore isoelectronic BN with carbon, similar to SWCNT BN nanotubes can be designed by winding a BN sheet in hexagonal form. SWBNNT have the remarkable property of having a better chemical reactivity than SWCNT [5].

2. Decomposition Mecanisms

The nature of the decomposition products depends on the nature and region where this decomposition occurs and according to American researchers at the National Standard Institute [8, 9] who have conducted studies on the decomposition of SF$_6$ gas under partial discharge, they have found that its products differ according to the region within the equipment, near the electrodes, between its electrodes or further away that have named region of light or luminescence, region of ions drift and the region of the volume of the main gas Figure 1.

$$\text{SF}_6 \rightarrow \text{SF}_4 + 2\text{F} \tag{2.1}$$

$$\text{SF}_4 + \text{H}_2\text{O} \rightarrow \text{SOF}_2 + 2\text{HF} \tag{2.2}$$

$$2\text{SF}_4 + \text{O}_2 \rightarrow 2\text{SOF}_4 \tag{2.3}$$

$$\text{SOF}_4 + \text{H}_2\text{O} \rightarrow \text{SO}_2\text{F}_2 + 2\text{HF} \tag{2.4}$$

$$\text{SOF}_2 + 2\text{F} \rightarrow \text{SOF}_4 \tag{2.5}$$

$$\text{SOF}_2 + \text{O}_2 \rightarrow 2\text{SO}_2\text{F}_2 \tag{2.6}$$

$$\text{SOF}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_2 + 2\text{HF} \tag{2.7}$$

The mechanism of decomposition of SF$_6$ gas depends on the nature of the electrical stress and, therefore, on the place where it occurs. It was found, that under partial discharges, products of discharge differ depending on the region inside the GIS equipment, where the discharge occurs. These regions are near the electrodes, between the electrodes or further region, named as glow luminescent region, ion drift region and the region of the main gas volume:

Zone 1: Light zone.

Zone 2: Ion diffusion zone.
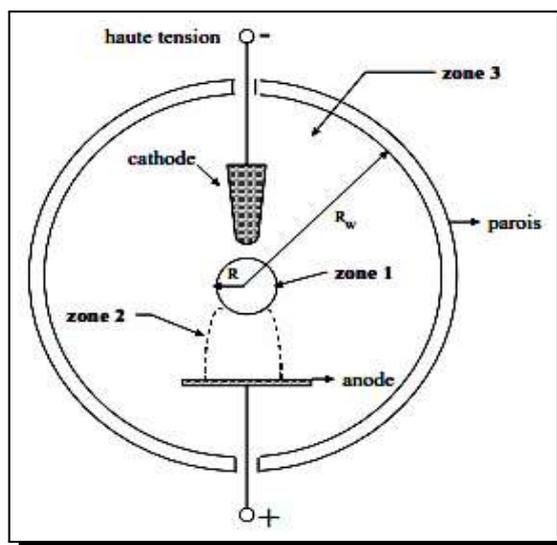
Zone 3: Gas volume and wall.

Figure 1. The decomposition of SF$_6$ gas under partial discharge

The detection of discharge products is possible using single wall carbon nanotubes SWNTs, which have a high surface adsorption capacity and good conductivity. The placement of a nanotube sensor in the discharge chamber with SF$_6$ gas and measurement of its resistance have allowed us to determine the sensitivity of the detector.

3. Simulation Method

In this study we have used Material Studio (MS) simulator developed by the American company Accelerys. The MS software package, based on density functional theory has been used extensively in the field of material science. Density functional theory is based on ab initio quantum mechanics to study the electronic structure of multi-electron systems. DMol3 module was used to prove the ability of nanotubes to detect the studied gases. The simulation method is based on the functional theory of density (DFT) adapted in the DMol3 module of Materials Studio, we have chosen a portion of BN nanotube in armchair form composed of 72 B atoms (Bore) and 72 N atoms (Nitrogen), the structure is identical to that of the Carbon nanotube with the only difference that the carbon atoms are replaced by B and N atoms successively.
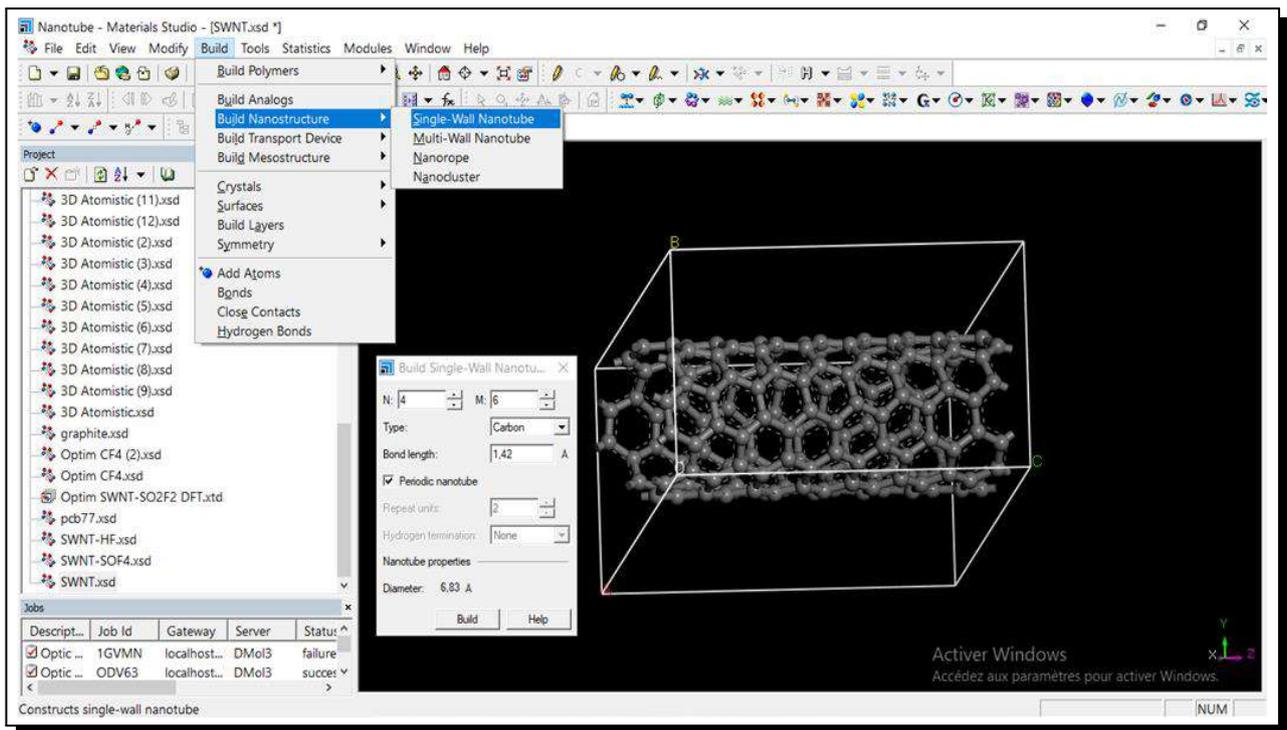
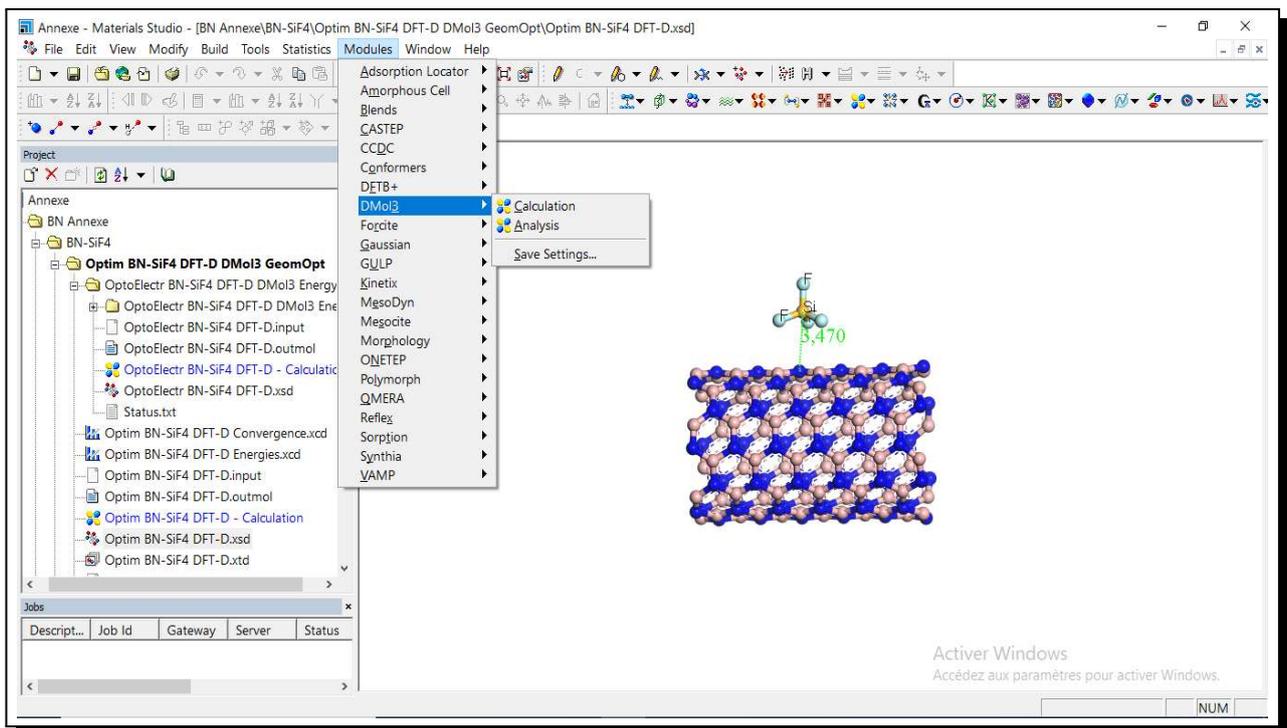**Figure 2.** Systems with the creation of molecules

Figure 3. Dmol3 Module Select window

The theory of the functional density theory, "*Density Functional Theory*" (DFT), makes it possible to reduce the complex problem of an interacting electron system to a problem of electron density. All properties (Ncorps-specific states) of an interacting particle system are determined

by the electron density (r) of the fundamental state. Any observable describing the system is thus a functional of this density (r). The DFT is based on Hohenberg's theorem and Kohn allows to express the fundamental state of a Nelectron system, undergoing the effects of an external V_{ext} potential, as a functional of the density of electronic charges $\rho(r)$ alone [4]:

$$E[\rho] = \int V_{\text{ext}}(\vec{r})\rho(\vec{r})d(\vec{r}) + \Gamma[\rho]. \tag{3.1}$$

$E[\rho]$ is the minimum that corresponds to the density of the fundamental state in this N-electron system.

In our simulation we optimized each system with the functional GGA (*Generalized Gradient Approximation*) and the PBE approximation (*Perdew-Burke-Ernzerhof*), each system is composed of a SWBNNT nanotube and a molecule resulting from the decomposition of the SF$_6$ gas (SF$_4$, F$_2$, SO$_2$F$_2$, SOF$_4$, SO$_2$, HF) and then we recover the energies of each system and the nanotube to calculate the adsorption energies which is given by the relation.

$$E_{ads} = E_{\text{SWBNNT-Molecule}} - (E_{\text{SWBNNT}} + E_{\text{MoleculeSWBNNT}}). \tag{3.2}$$

This relationship originates from the relationship called *Basic Superposition Error* (BSSE) or interaction energy between two fragments A and B obtained from the solution of Schrödinger's equation [1, 2].

$$\Delta E_{AB} = E_{AB} - E_A - E_B. \tag{3.3}$$

4. Results and Discussion

After having launched several calculations in order to find the energies of the optimization systems, we have to collect results to place them in Table 1 and Table 2. This table also contains the adsorption energies of systems with carbon nanotubes found in the study in our paper [3], and also of BN and ZnO.
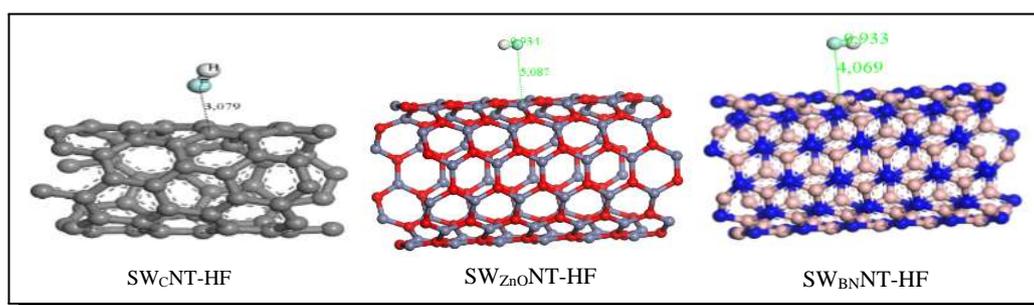

SW$_C$NT-HF   SW$_{ZnO}$NT-HF   SW$_{BN}$NT-HF

Figure 4. Molecular systems

Adsorption energy is calculated by the equation (3.2) and which has given us the values in Table 1. It should be noted that these values range from 1230 kJ to 1246 kJ for BN nanotubes with all molecules, -1475.45 kJ for SF$_4$ and -1472.84 kJ for SO$_2$F$_2$ with carbon nanotubes but for ZnO nanotubes the values vary between 0.28 kJ a-81.46 kJ which allowed us to deduce that ZnO nanotubes are not able to adsorb these decomposition products in our study since the values found are all below 100 kJ/mol so there is physisorption but very low, while other

values that are greater than 100 kJ/mol show that there has been chemisorption between BN nanotubes and all the molecule and between carbon nanotubes and SF4 and SO$_2$F$_2$ [7]. In what follows we will ignore the ZnO nanotubes since the calculations have shown us that they are useless in our study so they are discarded.

Table 1. Adsorption energy (Molecular systems Nanotube)

Molecules	E$_{ads}$ (kJ/mol)			Charge (eV)	
	SW$_C$NT[2]	SW$_{BN}$NT	SW$_{ZnO}$NT	SW$_{BN}$NT	SW$_C$NT [2]
SF$_6$	-102,37	-1230,66	-2,75	0.003	0.000
SF$_4$	-1475,45	-1235,95	-32,74	-0.001	-0.001
F$_2$	94,45	-1246,05	-81,4	-0.007	-0.300
SOF$_2$	-101,37	-1235,86	-2,37	0.000	0.003
SO$_2$F$_2$	-1472,84	-1233,29	0,28	-0.001	0.067
HF	-30,87	-1241,03	-8,50	-0.01	0.002
SO$_2$	-104,97	-1235,88	-16,85	-0.007	0.001

It is clear that the electron density curves of the molecules F$_2$, SOF$_2$, SO$_2$F$_2$, SOF$_4$, SO$_2$ and HF almost all coincide in the range between (-20 eV and 0 eV in the *Occupied Molecular Orbital* (OMO) valence band) and those of SWBNNT and that the electronic and conductive structures are unchanged, Figure 3(a) which is contrary to the results found in the study done in [3] on carbon nanotubes or electron density curves are different in this range, while in the range (0 eV and 6 eV *Unoccupied Molecular Orbital* (UMO) conduction band) Figure 3(b) the difference of density of stat DOS each SWBNNT molecular system has its own footprint in the range between (0 eV and 3,5 eV) with the same amplitude of 4 e/eV but the amplitude of SWBNNT has a value of almost 28 e/eV in this interval the (DOS) means that there is modification of the electron density hence the change of the electronic and conductive structures due to a charge transfer which means that there is adsorption of all molecules by the adsorbent SWBNNT.
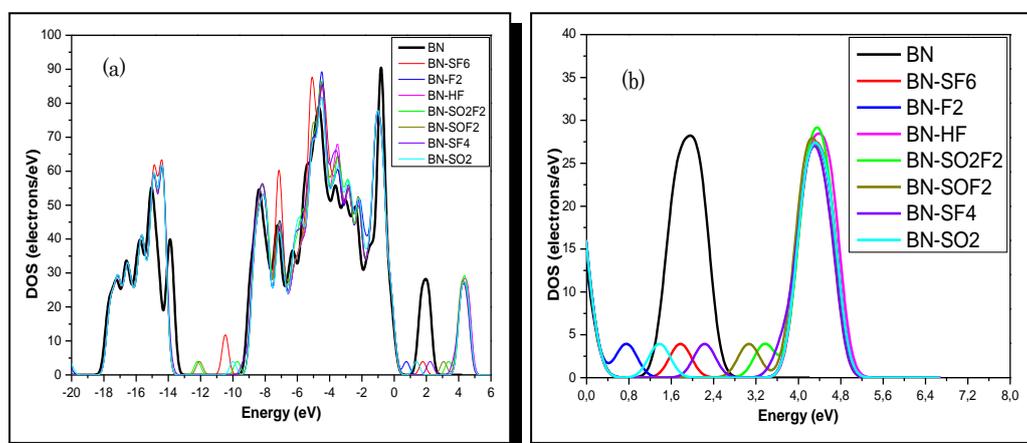

Figure 5. DOS of the SWXNT-Molecules systems in the (a) OMO and (b) UMO intervals

In Table 2, which groups the gap energies of *Highest Occupied Molecular Orbital* (HUMO) and *Lowest Unoccupied Molecular Orbital* (LUMO) of the SWCNT SWBNNT alone and in the presence of molecules, we notice that the HOMO energies of the SWXNT molecular systems have the same values below the level of firmness in the interval (-20 eV, 0 eV) but above the level of firmness in the interval (0 eV , 6 eV) LUMO energies vary for each molecule, hence the appearance of a gap energy specific to each molecule, this difference shows that there is a modification in the electronic and conductive properties of the systems in the presence of the molecules, which justifies the DOS modifications in Figure 5(b) in the interval (0 eV, 6 eV) equal to the square of the voltage of rod over this power.

Table 2. Gap energy

	HOMO (eV)	LUMO (eV)	$E_{gap}(\Delta E_{gap})$ SW$_{BN}$NT	E_{gap}(eV)[x] SW$_C$NT
SWNT	-5.74	-4.15	1,58	0,061
SWNT-SF$_6$	-6.36	-4.58	1,77 (0.19)	0,002
SWNT-SF$_4$	-6.39	-4.18	2,21 (0.63)	0,065
SWNT-F$_2$	-6.43	-5.68	0,74 (-0.84)	0,007
SWNT-SOF$_2$	-6.39	-3.32	3,07 (1.49)	0,003
SWNT-SO$_2$F$_2$	-6.36	-2.99	3,37 (1.79)	0,067
SWNT-HF	-6.30	-2.25	4,05 (2.47)	0,002
SWNT-SO$_2$	-6.32	-4.94	1,38 (-0.2)	0,001

Table 3. The fundamental absorption peaks of systems molecule

	SW$_{BN}$NT Optical peak (cm^{-1})	SW$_C$NT Optical peak (cm^{-1})
Materials only	35750-36350-37200-37620	1161-4353-4807-5265
SF$_6$	30674-31948-35335-35460	1159-4370-4798-5274
HF	36363-36900-37453-37735	1154-4342-4798-5257-6369
F$_2$	23584-26954	1192-4338-4840-5282
SF$_4$	33783-35211-35714-36496-36900	1156-4366-4800-5274
SO$_2$F$_2$	35714-36496-37593-37735	8650-2279-2086-1899
SOF$_2$	35714-36496-37037-37174-37593	8580-2276-2082-1898
SO$_2$	25706-26385-27777-28328-31055-31250	8538-2289-2082-1900

The absorption spectra for the case of SW$_C$NT and SW$_C$NT-molecule systems can be classified into four groups the first group in the range (4400 cm^{-1}-5200 cm^{-1}) and according to Table 2 this interval corresponds to the region NIR, IR-B concern the SWCNT and the molecules SF$_6$, F$_2$, HF, SF$_4$, the second group includes the molecules SO$_2$, SOF$_2$, SO$_2$F$_2$ in the interval (1600 cm^{-1}-2400 cm^{-1}) which corresponds to MIR-IR-C.
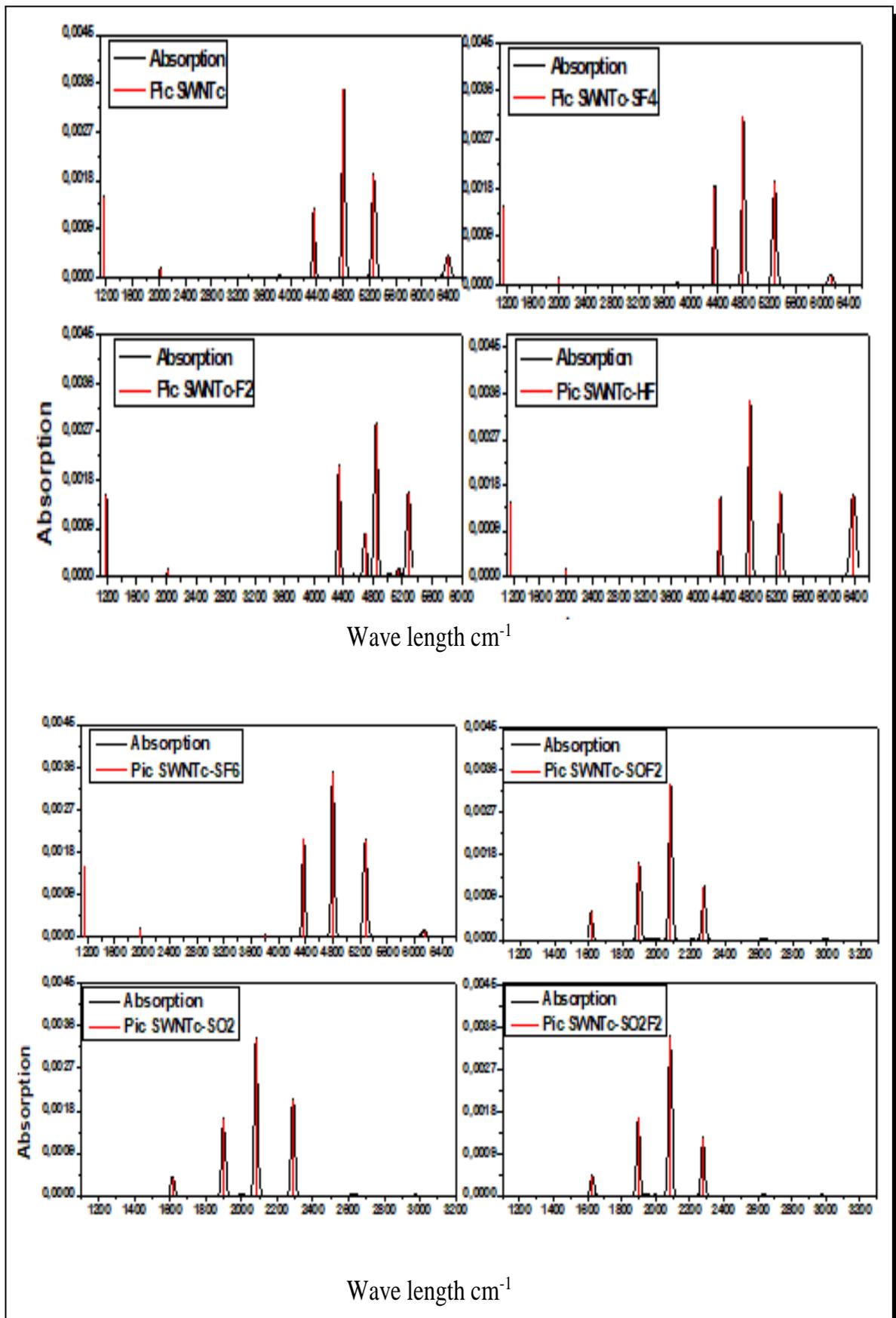
Figure 6. The absorption spectra for the case of SW$_C$NT and SW$_C$NT-molecule systems
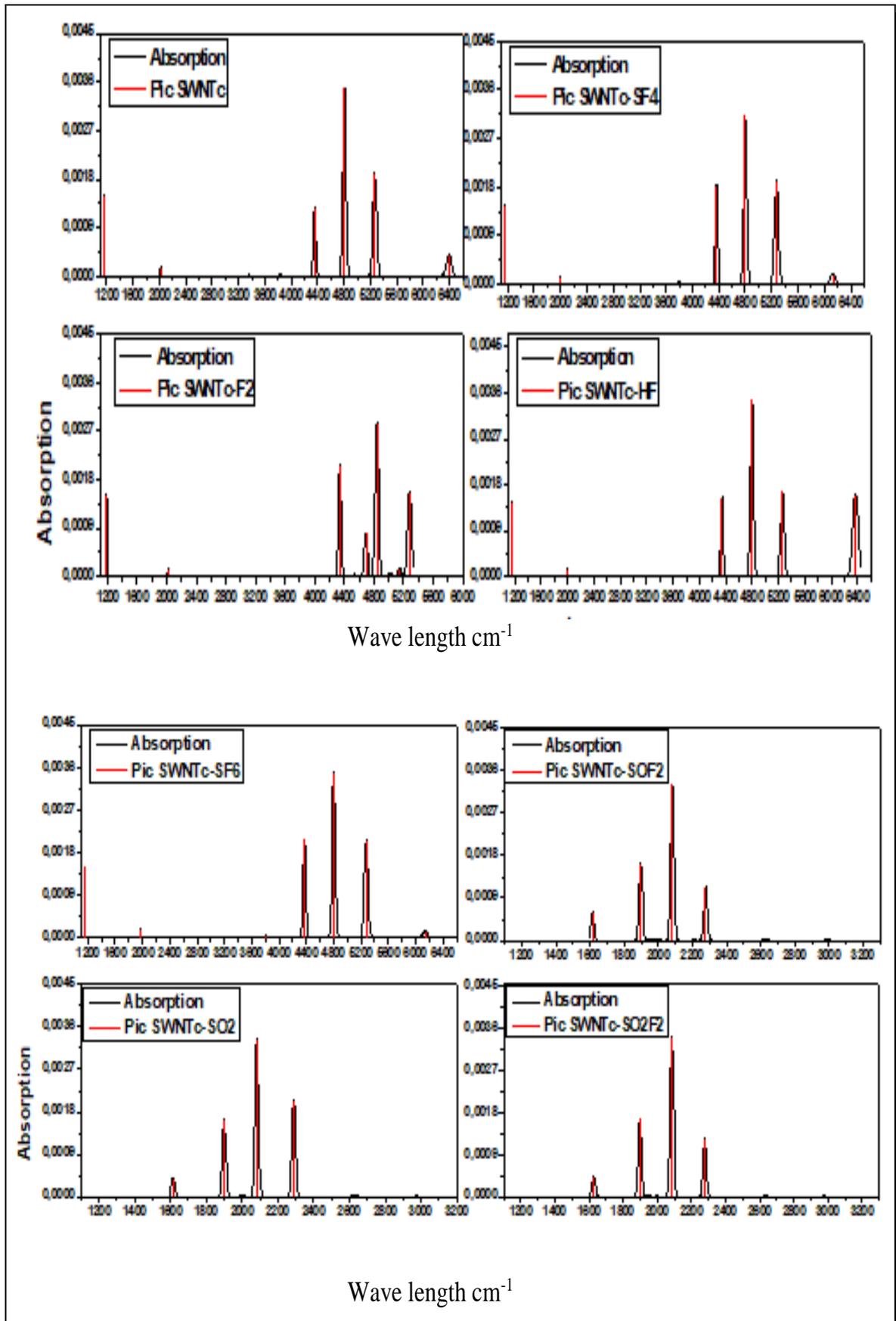
Figure 7. The absorption spectra for the case of SW_CNT and $SW_{BN}NT$-molecule systems

The values of the wavelengths in Table 2 and collected from Figure 7 which gives us the appearance of the optical absorption spectra of the SW$_{BN}$NT-molecule systems, the absorption domains for these systems are diversify compared to the others systems with SW$_C$NT, SW$_{BN}$NT exhibits absorption alone and with molecules in the VUV, UV-C range, the SF6 molecule in the UV-B and UV-A range, F$_2$ in visible violet, SF4 in UV-B , SO$_2$ in UV-A.

5. Conclusion

In this article, the MS software, based on functional density theory, which was used to simulate the adsorption of the five main decomposition products of SF$_6$, which are created during partial discharges. The optimization of the molecular systems SW$_X$NT and by the energy values of Table 1 allowed us to deduce that the BN nanotubes and more capable of adsorbing the molecules of decomposition of the SF6 gas than the carbon nanotubes and that the ZnO nanotubes do not react well with these molecules, the two molecules SF4 and SO$_2$F$_2$ reacted with SW$_C$NT while all the other molecules reacted with SW$_{BN}$NT and the last two, and according to Table 2 and Figure 3. The adsorption detection of the resulting molecules of this decomposition can be carried out by a sensor SW$_{BN}$NT since these electronic and conductive properties change in the presence of these molecules, an optical absorption study has been made to show that each molecule can be redetected in a well-determined wavelength interval, so we can say that each molecule has a wave print and an electronic density print.

Today, graphine and phagrafen (two graphene allotropes), carbon nitrides, hexatomic boron nitride (h-BN), and some metal oxides have not yet been studied for the detection of decomposed SF6 gases. We hope that this work can provide guidance for further research into gas detectors for these nanomaterials to achieve this goal in the near future. In addition, there would be full potential to expand and enrich detection research in many areas.

Acknowledgment

Competing Interests
The authors declare that they have no competing interests.

Authors' Contributions
All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

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