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DFT Study of CO_2 Adsorption on the $Zn_{12}O_{12}$ Nano-cage

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Covalent functionalization of a $Zn_{12}O_{12}$ nano-cage with CO_2 molecule in terms of energetic, geometry, and electronic properties was investigated by density functional theory method. For chemisorption configurations, the adsorption energy of CO_2 on the $Zn_{12}O_{12}$ nano-cage for the first CO_2 was calculated −1.25 eV with a charge transfer of 1.00|e| from the nano-cage to the CO_2 molecule. The results show that CO_2 molecule was significantly detected by pristine $Zn_{12}O_{12}$ nano-cage, therefore the nano-cage can be used as CO_2 storage. Also, more efficient binding could not be achieved by increasing the CO_2 concentration. For Physisorption configurations, HOMO–LUMO gap of the configurations has not changed, while slight changes have been observed in the chemisorption configurations.

Key Words : Zinc oxide nano-cage, Adsorption, Functional group, CO_2

Introduction

Carbon dioxide (CO_2) is known as a greenhouse gas (GHG) and has an important contribution in global climate changes.[1,2] The main source of CO_2 emission worldwide comes from fossil fuel electric power plants.[3] Capture and sequestration of the CO_2 emitted from different sources is thus one of the most pressing issues in the environmental protection. Therefore, it is very important to develop a simple, rapid and reliable method for the capture and sequestration of CO_2 in many cases. Adsorption of CO_2 on zinc oxide (ZnO) surfaces has attracted considerable attention in the last decade. Adsorption of carbon dioxide on the ZnO surface has been studied by different groups.[4,5]

Fink[4] has studied adsorption of CO_2 on the ZnO (000$\bar{1}$) surface. Its results showed CO_2 dissociation at oxygen vacancy of (000$\bar{1}$) surface. Also, Sergio *et al.*[5] have reported CO_2 adsorption on polar surfaces of ZnO. They showed a clear interaction between the CO_2 molecule and the surface.

Nanostructures due to their novel properties are intriguing in cluster protection, nano-ball bearings, nano-optical magnetic devices, catalysis, gas sensors, and biotechnology.[6,7] In recent years, there have been numerous studies of the adsorption of CO_2 on solid surfaces[4,5]; while there are few studies about the adsorption of CO_2 on nanostructures surfaces. Therefore, further study of CO_2 adsorption on the nanoclusters is important task. ZnO nanoclusters have been widely investigated both theoretically and experimentally.[6,7] Recently, stability of fullerene-like cages of $(XY)_n$ nanostructures have been investigated and it has been suggested that the fullerene-like cage $(XY)_{12}$ is energetically the most stable cluster among different types of $(XY)_n$ structures.[8,9] Therefore, it can be concluded that the fullerene-like cage $(ZnO)_{12}$ is energetically the most stable cluster in this family and would thus be an ideal inorganic fullerene-like cage. The aim of this work is to investigate theoretically adsorption of CO_2 on $Zn_{12}O_{12}$ nano-cage based on analyses of structure, energies, stability, electronic properties, *etc.* Our results are likely to be useful in functionalization of ZnO nanoclusters, construction of a CO_2 storage material, nano electronic devices, and other applications.

Computational Methods

Spin-unrestricted B3LYP/6-31G* level of theory has been largely used to describe the adsorption CO_2 molecule on surfaces of $Zn_{12}O_{12}$ nano-cage, specifically the structural and electronic properties. For the Zn atoms, the standard LANL2DZ basis set[10] was used. Earlier studies indicated that the computations based on the B3LYP/6-31G* level of theory could yield reliable results in study of different nanostructures.[6,11] This method was used to calculate the adsorption energy (E_{ad}) of CO_2 molecule on the surface of $Zn_{12}O_{12}$ nano-cage as follows:

$$E_{ad} = E_{CO_2/ZnO} - [E_{ZnO} + E_{CO_2}] \quad (1)$$

Where $E_{CO_2/ZnO}$ is the total energy of an adsorbed CO_2 molecule on the pure $Zn_{12}O_{12}$ nano-cage, E_{CO_2} is referred to the energy of a single CO_2 molecule, and E_{ZnO} is the energy of the pristine $Zn_{12}O_{12}$ nano-cage. Negative or positive value for E_{ad} is referred to exothermic or endothermic processes, respectively. All the calculations were carried out by using the GAMESS suite of programs.[12]

Results and Discussion

Optimized Structure of $Zn_{12}O_{12}$. The pristine $Zn_{12}O_{12}$ nano-cage was allowed to relax in the optimization at B3LYP/ LANL2DZ level of theory. Optimized structure of the $Zn_{12}O_{12}$ nano-cage is formed from eight 6-membered (hexagon) rings and six 4-membered (tetragon) rings with T_h symmetry. Optimized structure and geometrical parameters of the $Zn_{12}O_{12}$ nano-cage is shown in Figure 1. As is shown in Figure 1, two types of Zn–O bonds are computed in

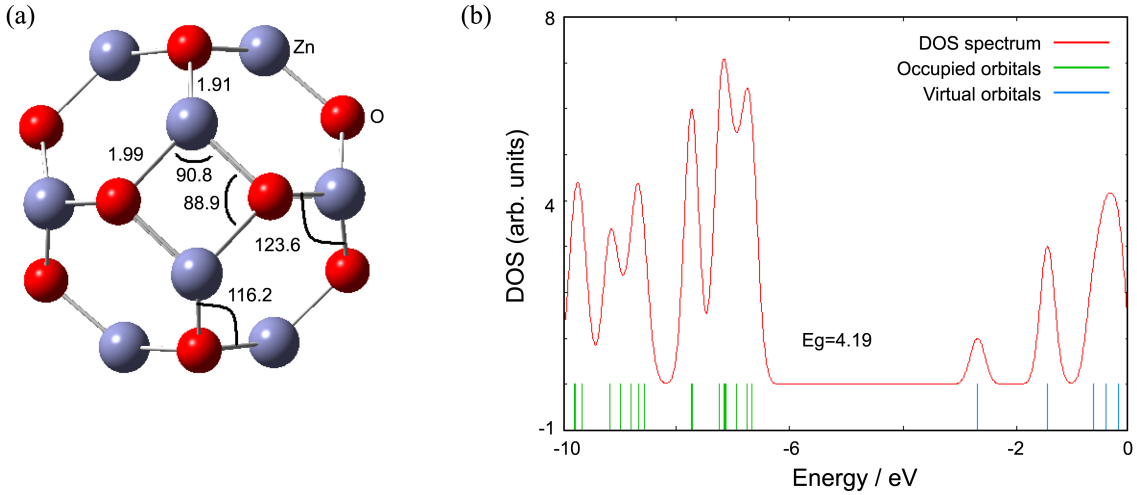

Figure 1. Structure of optimized $Zn_{12}O_{12}$ nano-cage and its electronic density of states (DOS). Distances are in angstrom.

$Zn_{12}O_{12}$ nano-cage, one with the bond length of 1.91 Å which is shared between two hexagon rings, and the other which is shared between a tetragon and hexagon ring with length of 1.98 Å. The angles in 4-membered and 6-membered rings in $Zn_{12}O_{12}$ nano-cage vary from 88.9 to 90.8 and from 116.2 to 123.6, respectively. The calculated energy gap ($E_g = E_{LUMO} - E_{HOMO}$) of the $Zn_{12}O_{12}$ nano-cage was calculated from the total densities of states (DOS) results. As is shown in Figure 1(b), the E_g of nano-cage is 4.19 eV, indicating that the nano-cage is a semiconductor.

Adsorption of CO_2 on the $Zn_{12}O_{12}$. In order to determine the minimum adsorption energy structure of adsorbed CO_2 on the $Zn_{12}O_{12}$ nano-cage, various possible initial adsorption geometries including both the carbon and oxygen atoms of CO_2 close to hexagon and tetragon rings, oxygen atom close to Zn atom, two oxygen atoms locating top of the two Zn atoms of a hexagon or tetragon rings and one of the oxygen atoms above the center of 4-hexagon or tetragon rings. After careful structural optimizations without any constraints, re-orientation of the molecule has been observed in some states, and finally it was found that only three kinds of the considered configurations are stable and are shown in Figure 2.

As shown in Figure 2(a), the C atom of CO_2 molecule is bonded to O atom of the nano-cage, so that the plane of CO_2 has bent due to the intramolecular steric repulsion. In configuration (a), length of the newly formed C-O bond is 1.36 Å. The adsorption of CO_2 shows an apparent local structural deformation on both the CO_2 and the $Zn_{12}O_{12}$ nano-cage. In the configuration, O–C–O angle of CO_2 molecule is reduced from 180° to 128.6° and the bond length of C-O is increased from 1.17 Å in isolated CO_2 to 1.27 Å in the adsorbed state. In addition, the length of Zn–O bonds in adsorbed ring increased from 1.91 and 1.98 Å to 2.14 and 2.39 Å in the configuration. Further indication of the deformation degree in the geometry of CO_2 due to the adsorption process is given by the bond reorganization energy (E_{br}). E_{br} is as the calculated energy difference between the full relaxed CO_2 molecule and its adsorbed state, in which for each state is summarized in Table 1. E_{br} of CO_2 molecule for this configuration is 2.5 eV and the E_{ad} is −1.25 eV, indicating a strong interaction and chemisorption process. Natural bond orbital (NBO) analysis shows a charge transfer of −1.00|e| from the nano-cage to the CO_2 molecule. In the configuration, the vacant π^* orbital of C=O in the CO_2 molecule accepts the electrons from the $Zn_{12}O_{12}$ nano-cage and CO_2 π-bond breaking due to electron backdonation from the $Zn_{12}O_{12}$ to CO_2 and the CO_2 molecule undergoes the structural distortion to a bent structure. Therefore, the O-C-O angle is reduced to 128.6°, and the broken C-O bond is significantly elongated to 1.27 Å.

In configuration (b) (Fig. 2(b)), one of the oxygen atoms of CO_2 molecule is close to a Zn atom of the $Zn_{12}O_{12}$ nano-cage by an interaction distance of 2.37 Å. The E_{ad} and E_{br} of CO_2 molecule for this configuration are −0.40 and 0.01 eV, respectively and a charge of 0.03|e| is transferred from the CO_2 molecule to the nano-cage. The results indicate that this interaction is weak and should be considered as a physisorption. Another CO_2 physisorption approach is shown in Figure 2(c), in which the interaction distance between both of the oxygen atoms of CO_2 molecule and the Zn atoms of a tetragon ring of the nano-cage is about 2.80 Å. This configuration has an E_{ad} −0.37eV and do not shows charge transfer to take place between the CO_2 and $Zn_{12}O_{12}$ nano-cage. Also, E_{br} of CO_2 molecule for this configuration is zero.

There are several hexagon and tetragon rings in structure of the $Zn_{12}O_{12}$ nano-cage as potential adsorption site; therefore the possibility of the second adsorption is interesting for consideration. In this configuration (Fig. 3(d)), two CO_2 molecule is adsorbed on the $Zn_{12}O_{12}$ nano-cage. The E_{ad} and E_{br} of CO_2 molecule for this process is about −1.03 and 2.44 eV per CO_2 molecule with a charge transfer of −0.98|e|, which are slightly lower than that of one CO_2 adsorption due to the steric repulsion between two CO_2 molecules. In the next step, three and four CO_2 molecules are adsorbed on the $Zn_{12}O_{12}$ nano-cage (Fig. 3(e) and (f)). The E_{ad} for these configurations are about −1.05 and −1.12 eV per CO_2 molecule for three and four molecules adsorption. E_{br} of CO_2 molecule for these processes are 2.43 and 2.45 eV per CO_2,

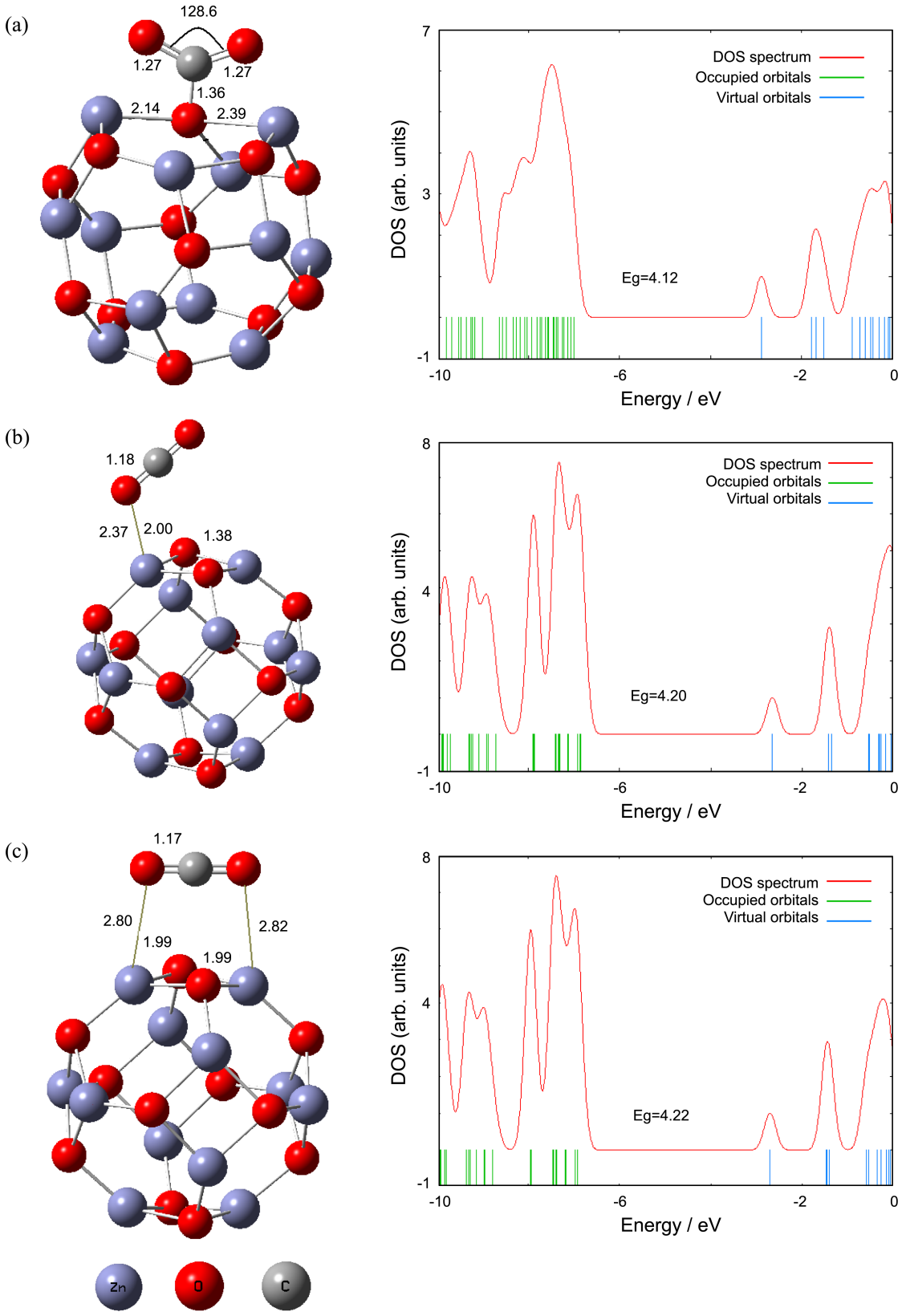

Figure 2. Models for three optimized structure of $CO_2/Zn_{12}O_{12}$ configurations and their density of state (DOS) plots. Distances are in angstrom.

respectively. In comparison with the one CO_2 adsorption model (Fig. 2(a)), the E_{ad} and E_{br} of CO_2 molecule due to the steric repulsion between the CO_2 molecules is reduced.

Adsorption of CO_2 on the Electronic Properties of $Zn_{12}O_{12}$ Nano-cage. Finally, to better understand the interaction between CO_2 with the $Zn_{12}O_{12}$ nano-cage, the influence of

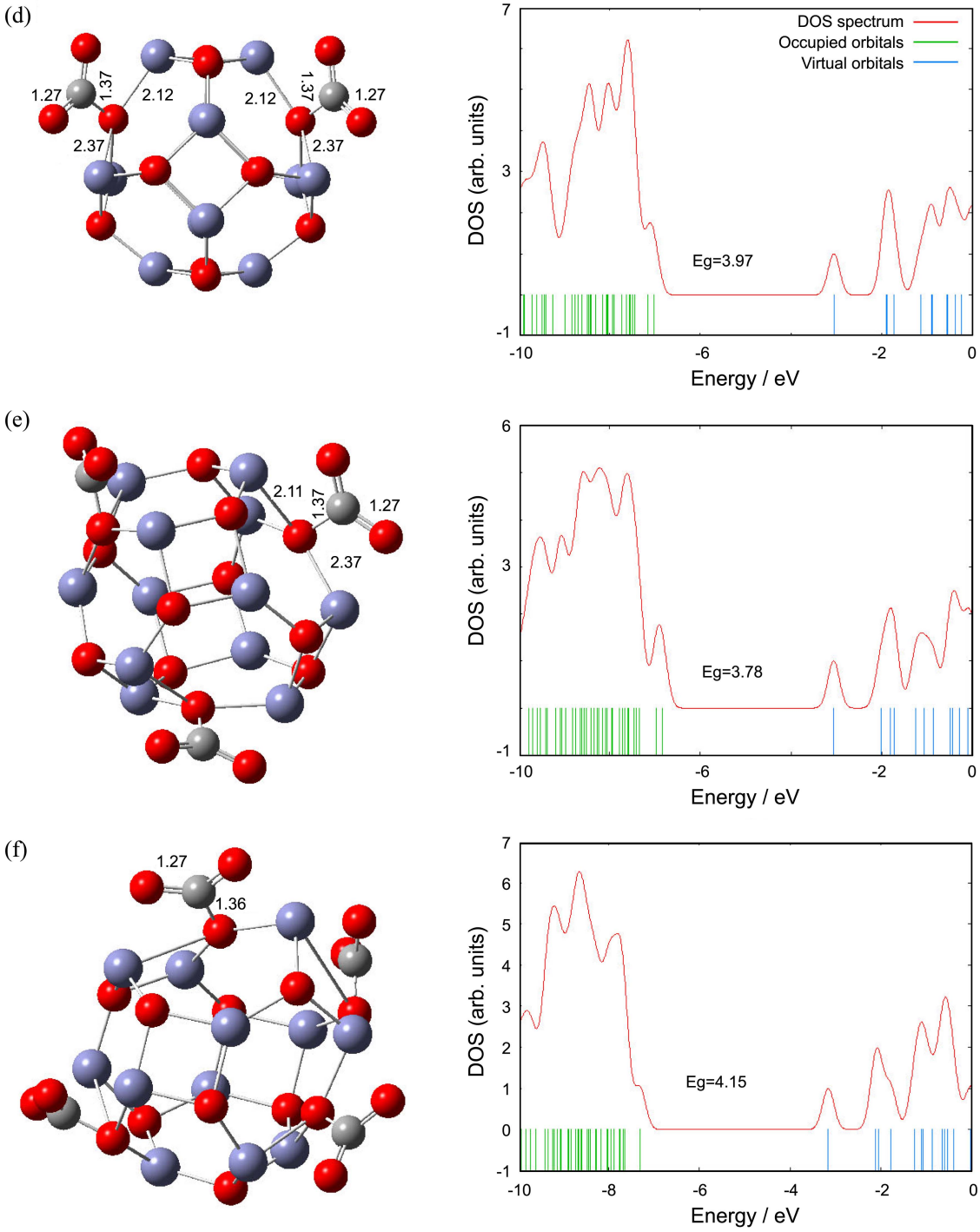

Figure 3. Model for $2CO_2$, $3CO_2$, and $4CO_2$ chemisorbed- $Zn_{12}O_{12}$ configurations and their density of states (DOS) plots. Distances are in angstrom.

CO_2 adsorption on the electronic properties of the nano-cage was studied. The difference in energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), E_g, was calculated from DOS plots. As shown in Table 1, with comparison of DOS of the free ZnO nano-cage and the physisorption configurations (Fig. 2(b) and (c)), it is found that their E_g value have changed about 0.24-0.72% after the CO_2 adsorption. In the physisorption configurations the valence and conduction level energies are relatively the same as for the pristine $Zn_{12}O_{12}$ valence and conduction level energies. Therefore, the results show that the CO_2 adsorption through these configurations has not sensible effects on the electronic properties of the nano-cage. For functionalization or chemisorption cases (Fig. 2(a) and Fig. 3(d)-(f)), it is revealed from DOS plots that their valence level energies in the cases are approximately similar to that of the $Zn_{12}O_{12}$, while the conduction level energies some shift downwards. As

Table 1. Calculated adsorption energy per molecule (E_{ad}), HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), HOMO–LUMO energy gap (E_g), Sum of NBO charge on the adsorbed CO_2 per molecule (Q_T), Fermi level energy (E_{FL}), and bond reorganization energy (E_{br}) per molecule. Energies are in eV

Structure	E_{ad}	E_{HOMO}	E_{LUMO}	E_g	$^a\Delta E_g$ (%)	$^bQ_T\|e\|$	E_{FL}	$^cE_{br}$
$Zn_{12}O_{12}$	-	-6.94	-2.75	4.19	-	-	-4.84	-
A	-1.25	-7.00	-2.88	4.12	1.67	-1.00	-4.94	2.50
B	-0.40	-6.85	-2.65	4.20	0.24	0.03	-4.75	0.01
C	-0.37	-6.92	-2.70	4.22	0.72	0.00	-4.81	0.00
D	-1.12	-7.02	-3.05	3.97	5.25	-0.98	-5.04	2.44
E	-1.05	-6.84	-3.06	3.78	9.78	-1.00	-4.95	2.43
F	-1.03	-7.31	-3.16	4.15	0.95	-0.99	-5.24	2.45

[a]The change of HOMO–LUMO gap of $Zn_{12}O_{12}$ nano-cage after CO_2 adsorption. [b]Q is defined as the average of total natural bond orbital charges (NBO on the CO_2 molecule). [c]E_{br} is calculated as the average of energy difference between the geometry of CO_2 after adsorption on $Zn_{12}O_{12}$ nano-cage and the full relaxed molecule

shown in Table 1, upon the CO_2 adsorption on the $Zn_{12}O_{12}$ nano-cage, the E_g value of the nano-cage are more changed compared to the physisorption cases, in other words, when number of CO_2 molecules increased from 0 to 3, band gap of the ZnO nano-cage has changed about (1.67-9.78%). However, when $4CO_2$ molecules are adsorbed, the band gap has changed about 0.95% due to the steric repulsion between the CO_2 molecules. In fact, with increasing of CO_2 numbers, the E_{ad} of CO_2 molecules is decreased (see Table 1) and increasing of CO_2 molecules has no sensible effects on the electronic properties of the nano-cage. Therefore, Change of E_g value in the configuration **F** (with $4CO_2$ molecules) is reduced.

In a molecule at 0 Kelvin, Fermi level lie approximately middle of the E_g. Table 1 indicates that the Fermi level energy (E_{FL}) of the physisorption configurations is increased from −4.84 eV in the pristine $Zn_{12}O_{12}$ nano-cage to −4.75 and −4.81 eV in the (b) and (c) configurations. This increasing of E_{FL} with CO_2 adsorption leads to a decrement in the work function which is important in field emission applications. The work function is the minimum energy required for one electron to be removed from the Fermi level to the vacuum. The decrement in the work function shows that the field emission properties of the configurations are improved upon the CO_2 adsorption. While, the E_{FL} of the chemisorption configurations is shifted down (see Table 1) which leads to an increment in the work function. The increment in the work function shows that the field emission properties of the configurations are impeded upon the CO_2 adsorption and have a disadvantageous effect on the field emission properties of $Zn_{12}O_{12}$ nano-cage.

Conclusions

Physisorption and chemical functionalization of CO_2 molecule on the $Zn_{12}O_{12}$ nano-cage were studied using density functional calculations. Binding energy corresponding to adsorption of CO_2 on the $Zn_{12}O_{12}$ in the most stable configuration was calculated to be −1.25eV with a charge transfer of 1.00|e| from the nano-cage to the CO_2 molecule. On the basis of our calculations, it seems that attachment of the CO_2 molecule on the walls of the $Zn_{12}O_{12}$ nano-cage induces some changes in electronic properties of the cluster and its E_g is slightly reduced after covalent functionalization process. The results show that pristine $Zn_{12}O_{12}$ nano-cage can significantly detect CO_2 molecule. Also, more efficient binding could not be achieved by increasing the CO_2 concentration. The strong adsorption of the CO_2 on the $Zn_{12}O_{12}$ nano-cage shows the potential application of the ZnO-based materials for CO_2 capture and storage.

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