When the carbon monoxide molecule approaches the apex of ZnO-NC with its oxygen atom, the adsorption energy is -9.54 kcal/mol, whereas it increases to -39.53 kcal/mol when the carbon atom approaches the apex of ZnO-NC. Similarly, when the monoxide molecule approaches the neck of ZnO with its oxygen and carbon atom, the adsorption energy is -6.84 kcal/mol and -29.50 kcal/mol, respectively. As shown in Table 1, when carbon monoxide approaches with its carbon atom, the absorption energy is higher than approaching with the oxygen atom. According to the achieved adsorption energies, it is clearly evident that the CO is more likely adsorbed on the apex of ZnO-NC, Table 1.

Electronic properties of ZnO-NC

In order to evaluate the effect of CO adsorption on the electronic properties of ZnO-NC, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are considered. Herein, as can be seen (Table 1), HOMO and LUMO levels for ZnO-NC are at -6.48 and -3.31 eV, respectively, with a Fermi energy level of about -4.90 eV. On the other hand, when CO approaches the apex of ZnO-NC with its carbon atom, the energy gap is 2.93. The interesting thing is that the carbon monoxide approaching the apex of ZnO-NC with its oxygen atom and that approaching the neck of ZnO-NC with its carbon atom lead to the same variation of average energy gap equal to 11.36%. The energy gap and average energy gap are listed in Table 1.

When CO approaches the apex of ZnO-NC, the Mulliken charge on the adsorbed CO is negative, which means that the CO molecule may acts as an electron acceptor-like agent, whereas approaching the neck of ZnO-NC leads to a positive charge on the CO. The charge transfer from the Zn-NC to the carbon monoxide confirms this prediction (Fig. 1b).

Table 1. Adsorption energies of CO on the ZnO-NC (Ead, kcal/mol), Mulliken charge on the adsorbed CO (Q, e), and HOMO (EHOMO), LUMO energies (ELUMO), Fermi level energies (EFL), HOMO–LUMO energy gap (Eg) and average energy gap variation in (%) of ZnO-NC in eV.

CO adsorbed on ZnO-NC	*Ead* (kcal/mol)	Q (e)	*E*HOMO	*E*FL (eV)	*E*LUMO	*Eg* (eV)	%
a	-	-	-6.48	-4.90	-3.31	3.17	-
b	-39.53	-0.14	-6.13	-4.66	-3.20	2.93	7.57
c	-9.54	0.10	-6.15	-4.74	-3.34	2.81	11.36
d	-29.50	-0.39	-6.61	-4.84	-3.08	3.53	11.36
f	-6.84	0.09	-6.38	-4.76	-3.14	3.24	2.21

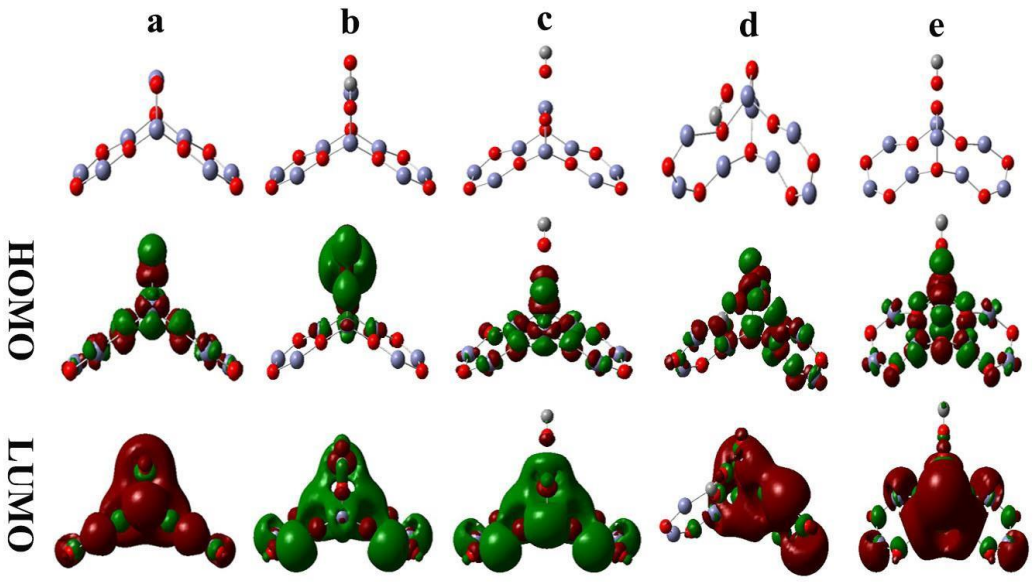

Fig. 1. HOMO–LUMO visualization of adsorbed CO on ZnO-NC: a) pure ZnO-NC b) adsorbed CO with its carbon atom on the apex of ZnO-NC c) adsorbed CO with its oxygen atom on the apex of ZnO-NC d) adsorbed CO with its carbon atom on the neck of ZnO-NC e) adsorbed CO with its oxygen atom on the neck of ZnO-NC.

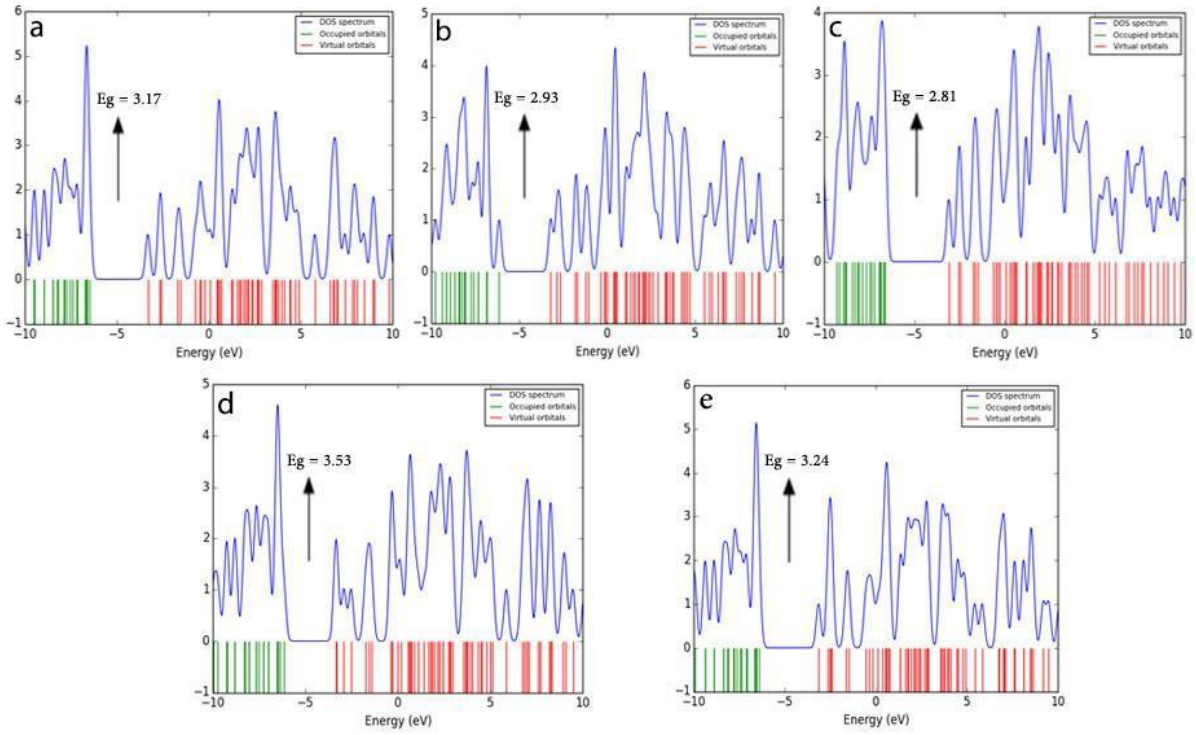

Fig. 2. HOMO–LUMO gap and DOS spectrum: a) pure ZnO-NC b) adsorbed CO with its carbon atom on the apex of ZnO-NC c) adsorbed CO with its oxygen atom on the apex of ZnO-NC d) adsorbed CO with its carbon atom on the neck of ZnO-NC e) adsorbed CO with its oxygen atom on the neck of ZnO-NC.

The density of state (DOS) of the molecule-nanocone was calculated, Fig. 2. Since the electronic configuration of zinc is $3d^{10}$ and oxygen is $2p^4$, for CO-ZnO-NC more peaks are observed in the virtual orbital than for pure ZnO-NC. Further approaching of carbon monoxide with its carbon atom to the apex of ZnO-NC increases peak amplitude more than other adsorption modes. Fig. 1b clearly reveals the fact that there is electron transfer from ZnO-NC to carbon monoxide.

CONCLUSIONS

We have explored the adsorption of a CO molecule on a ZnO nanocone (ZnO-NC) based on the DFT approach. The possible adsorption positions of CO on ZnO-NC were described in terms of HOMO-LUMO, adsorbed energy and energy gap. Mulliken charge on the CO adsorption and density of state spectrum confirmed the probability of CO absorption on the apex of ZnO-NC, it also revealed that the favored adsorption takes place between the carbon atom of CO and the oxygen atom of ZnO. So, in addition to existing structures of ZnO (nanowire, nanodisk, graphene-like, nanorod and nanotube), ZnO-NC can be a favorable structure for CO adsorption because of its excellent gas sensing properties.

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