https://adv-j-sci-eng.com eISSN: 2717-0705

Advanced Journal of Science and Engineering

Original Research

DFT Calculations of a Cubic B_4N_4 Cubane-Like Particle for CO Gas Adsorption

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Received: 10 June 2021 / ***Revised***: 24 June 2021 / ***Accepted***: 27 June 2021 / ***Published Online***: 30 June 2021

ABSTRACT

A cubic boron-nitride (B_4N_4) cubane-like model was investigated in this work for carbon monoxide (CO) gas adsorption through performing density functional theory (DFT) calculations. The parent model was optimized first to be prepared for participating in CO adsorption process. Next, bi-molecular models of B4N4 and CO were optimized, in which two models were obtained regarding the orientation of CO in C and O direction towards the B_4N_4 model. In addition to the optimized structures, molecular orbitals features were also obtained for the models regarding the highest occupied and the lowest unoccupied ones (HOMO and LUMO). Related features including other parameters in both quantitative values and qualitative representation were all obtained for the models. The results indicated that the proposed cubic B_4N_4 cubane-like model could work for sensing and removal purposes of CO gas, which could be detectable by means of infrared (IR) and ultra-violet (UV) spectroscopic measurements.

KEYWORDS Boron nitride, Cubane, Carbon monoxide, Gas adsorption, DFT.

CITE Ariaei S. DFT Calculations of a Cubic B_4N_4 Cubane-Like Particle for CO Gas Adsorption. Advanced Journal of Science and Engineering. 2021;2(2):93-98.

DOI https://doi.org/10.22034/advjscieng21022093

URL https://sciengpub.com/adv-j-sci-eng/article/view/advjscieng21022093

INTRODUCTION

Gas sensing has been always an important topic of research especially for those gases with harmful impacts on human life.[1] Several materials have been proposed up to now for doing functions of sensing and also removal of harmful gases.[2-5] Since the innovation of nanotechnology, investigations have been mostly oriented to explore nanostructures for achieving the purpose.[6-10] However, the story has not beet yet finalized and performing further investigations are still required to reach a point of technology with optimum function against the harmful gases.[11] Carbon monoxide (CO) has been always among those gases with high importance of detection and removal because of its deathful impacts on human health and life.[12] This gas has neither smell nor color making its existence very dangerous in the environment for those people under CO exposure.[13] In this case, it is very much important to explore very much powerful sensors for its detection or removal from the environment.[14] Indeed, CO could be generated during the hydrocarbons burning in the lack of enough oxygen leading to high-level of poisoning by human inhalation.[15]

In addition to conventional nanostructures, other small particle such as cubane could be explored to show their function in adsorption processes.[16] Cubane (Fig. 1) itself is a cubic carbon structure, in which such carbon atoms could be substituted by boron and nitrogen atoms as indicated earlier by formation of BN nanostructures.[17] Earlier works indicated that BN nanostructures could adsorb CO gas in more or less efficient ways.[18] Addition of gases to nanostructures have been investigated for more than two decades, in which various types and models have been

introduced for such purpose.[19] In addition to pure nanostructures, doped models have been also seen to work for gas adsorption.[20] The small size cubic particle might help to adsorb small CO gas, which was investigated in this work through computer-based density functional theory (DFT) calculations. The models were examined regarding the orientation of CO gas underlying at the surface of BN cubane model. Indeed, this work was done by advantage of employing computational methods for exploring solutions for problems of science and engineering.[21-23] All the required information for achieving the purpose of this work were summarized in Table 1 and Figs. 1-3 for careful examination and discussion.

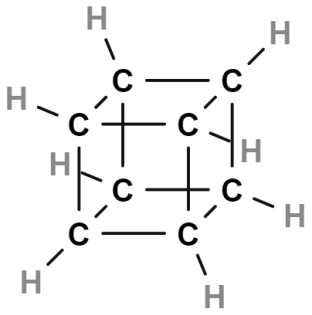

Fig. 1: Cubane model.

MATERIALS & METHODS

Within this work, a cubic model of B_4N_4 cubane particle was investigated for CO gas adsorption through performing B3LYP/6-31G* DFT calculations using the Gaussian program.[24] First, the parent B_4N_4 model was optimized to reach the minimized energy structure. Next, combination of B_4N_4 and CO were examined through performing additional optimization processes to reach the minimized relaxation of CO at the cubic surface (Fig. 2). Dispersion correction of bimolecular optimization calculation were considered by including IOp(3/124=3) in the route section of program.[25] The model structures were confirmed by vibrational frequency calculations, in which infrared (IR) spectra were evaluated by the results. Further calculations were performed for evaluating molecular orbital features as presented by distribution patterns and electrostatic potential (ESP) surfaces for molecular orbital systems. The highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO) were those of important orbitals for characterizing the electron occupied and vacant levels of molecular orbital systems. Ultra-violet (UV) spectra were also evaluated for the optimized model systems to show variations of absorption conditions for the models (Fig. 3). Parameters such as energy (E), adsorption energy (Eads), energy values of HOMO and LUMO, energy gap (Eg), Fermi energy (Ef), dipole moment (Dm) and volume (V) were all summarized in Table 1 for examining and discussing about the topic. Indeed, it is an advantage of computer-based works to provide insightful information for investigating the materials at the lowest molecular and atomic scales.[26-30]

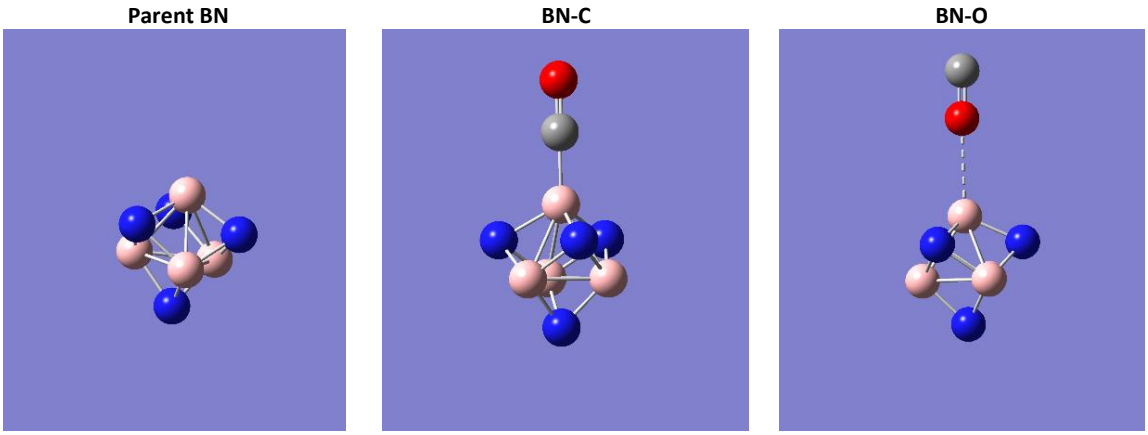

Fig. 2: The cubic B_4N_4 cubane-like optimized models.

RESULTS & DISCUSSION

Within this work, a model of cubic B_4N_4 cubane-like model was investigated for participating in CO adsorption through performing DFT calculations. In addition to the parent BN model, two models including BN-C and BN-O models were obtained through optimization processes of bi-molecular systems (Fig. 2). The models were assigned by relaxation of

C or O side of CO towards the cubic BN model yielding each of BN-C or BN-O models. All models were stabilized and they were confirmed by vibrational frequency calculations avoiding existence of any imaginary frequency.

Table 1: Evaluated properties for the optimized models.

Model	E eV	Eads eV	D Å	HOMO eV	LUMO eV	Eg eV	Ef eV	Dm Debye	V cm3/mol
Parent BN	-8663.386	n/a	n/a	-8.661	-3.897	4.764	-6.279	0.001	67.886
(CO)	(-3083.377)								
BN-C	-11747.964	-1.201	1.567	-7.556	-3.155	4.401	-5.356	2.892	94.676
BN-O	-11746.965	-0.202	2.336	-8.353	-3.506	4.847	-5.929	1.241	65.835

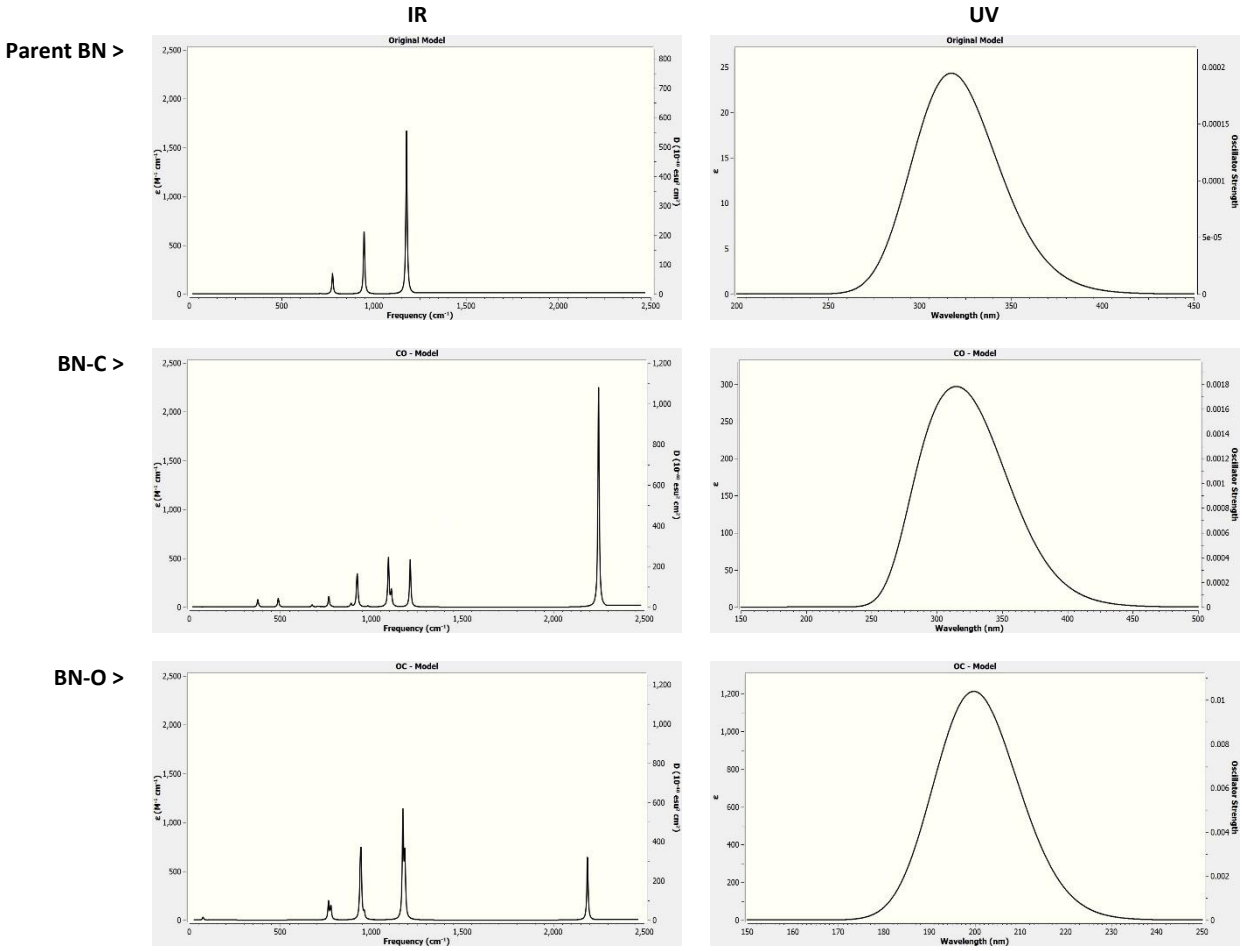

Fig. 3: Evaluated IR and UV spectra for the optimized models.

According to the results of Table 1, BN-C model was more stable than BN-O model in both of total energy and adsorption energy values. Interaction distance was also meaningful for BN-C model than BN-O model. In both models, CO was relaxed towards the B atom with formation for almost a covalent bond for BN-C model versus physically interacting BN-O model. Comparing the evaluated IR and UV spectra of Fig. 3 could show variations of frequencies and absorption energies for the models during the adsorption process of CO gas. Indeed, both models were seen to be suitable for this purpose and each of IR and UV techniques could detect such CO-sensing process. Additionally, values of energies for HOMO and LUMO levels could show variations of such molecular orbital systems from the parent BN model up to each of the BN-C and BN-O models. Molecular orbitals systems are very much important features for the molecules due to their importance in electron localization. As shown in Fig. 4, distribution patterns of HOMO and LUMO showed significant variations from the parent model to each of BN-C and BN-O models, which could reveal impact of the attached CO molecule to the properties of BN model. This was not only for HOMO and LUMO distribution patterns and their own energy levels, but the impact was almost significant for energy differences of two levels and also Fermi level variations. Energy gap could show the electron transfer possibility for a model system, in which it could be dominantly working for assigning such electron transferring possibility for the specified molecular system. In this

case, UV spectra could be recorded to show changes of such electron transferring or transitions for the related molecular orbitals of the models. Diagrams of ESP also could reveal changes of the electrostatic surface distributions different from those models with different interacting environment. Values of Dm and V also revealed changes of electric charge distribution at the molecular systems and the required occupancy for formation of such molecular models. As a consequence, the proposed cubic B_4N_4 cubane-like model was important for adsorption processes of CO gas regarding its role of sensing and removal of hazardous gases from the polluted environment.

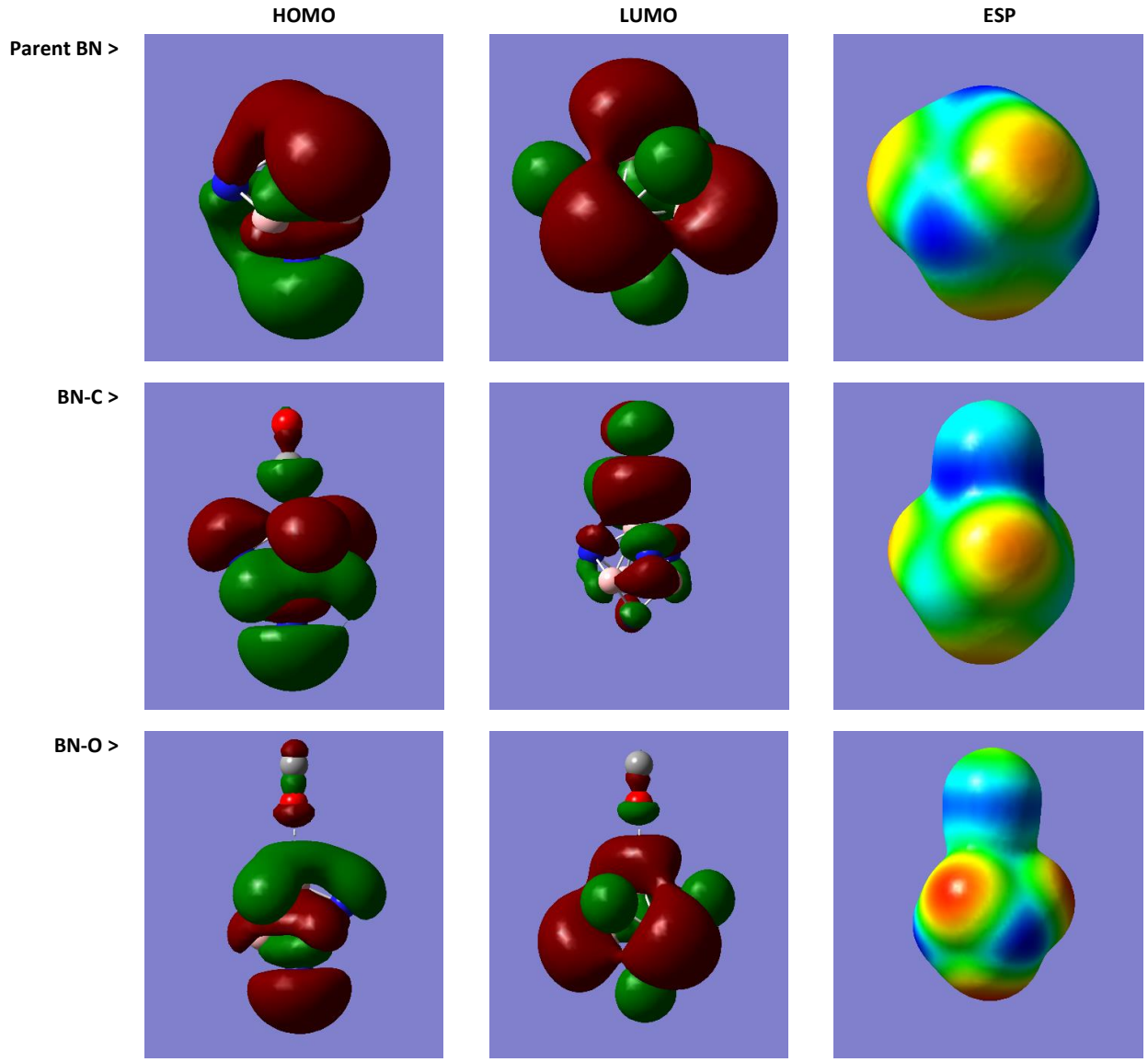

Fig. 4: Representations of molecular orbital patterns and ESP surface distributions for the optimized models.

CONCLUSION

Within this work, DFT calculations were performed to explore function of a cubic B_4N_4 cubane-like model for CO gas adsorption. The models were optimized to reach the minimized energy structures. Two models were obtained for CO adsorption processes with C or O orientation of CO towards the BN model making BN-C and BN-O models. These models were examined regarding values of their energies, in which the BN-C model was seen to be more stable than the BN-O model. The models were also examined by evaluating IR and UV spectra, in which variations of properties in the CO-adsorbed models were clearly seen through the obtained spectral features. In this case, the results were revealing that first, the B_4N_4 cubane-like model was suitable for CO-adsorbing and second, and the adsorption process could be detected by evaluating molecular orbital features. As a consequence, the model could be proposed for further investigating in the case of CO gas sensing and removal.

DISCLOSURE STATEMENT

The author(s) did not report any potential conflict of interest.

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