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# Theoretical assessment of phosgene adsorption behavior onto pristine, Al- and Ga-doped $B_{12}N_{12}$ and $B_{16}N_{16}$ nanoclusters

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ABSTRACT

The adsorption of phosgene molecule onto pristine as well as Al- and Ga-doped $B_{12}N_{12}$ and $B_{16}N_{16}$ nanoclusters is investigated using density functional theory calculations. It is found that in contrary to the pristine clusters, Al- and Ga-doped clusters effectively interact with the phosgene molecule with considerable electronic response. The HOMO–LUMO gaps of the Al-doped clusters decrease about 50% by the adsorption of phosgene molecule. Since the adsorption of phosgene onto pristine clusters is physiorption in nature, dispersion forces play important role in these interactions and they should be considered in calculations. The obtained results for both clusters are nearly the same, which imply to this fact that the adsorption process is independent of cluster size. The obtained results introduce Al- and Ga-doped cluster as promising chemical sensors for phosgene monitoring.



## 1. Introduction

Phosgene is the colorless gas gained infamy as a chemical weapon during World War I and II. It is a highly toxic substance that exists as a gas at room temperature [1]. However, because it is poorly water-soluble, in lower concentrations it does not cause immediate upper airway or skin irritation. Thus, an exposed individual may inhale phosgene for prolonged periods deeply into the lungs, where it is slowly hydrolyzed to hydrochloric acid. The odor threshold for phosgene is significantly higher than current inhalation exposure limits. Thus, odor provides insufficient warning of hazardous concentrations [2]. Owing to its poor water solubility, one of the hallmarks of phosgene toxicity is an unpredictable asymptomatic latent phase before the development of non cardiogenic pulmonary edema. Exposure to moderate-to-high concentrations of phosgene (>3–4 ppm) can produce an immediate irritant reaction that typically lasts 3–30 min and includes lacrimation, conjunctival irritation, burning sensation in mouth and throat, throat swelling and changes in phonation [3]. Furthermore phosgene is also a valuable industrial reagent and building block in synthesis of pharmaceuticals and other organic compounds. Phosgene is the main reagent in polyurethane industry to produce the polymeric isocyanates, and also in manufacturing the carbamates and related pesticides, dyes, pharmaceuticals, and isocyanates [4]. Thus, controlling the phosgene concentration in the air requires a sensitive, reliable, and specific method for monitoring its content in work environments [5]. These facts have stimulated research activities in the field of phosgene sensor technology.

Boron nitride nanomaterials exhibit different desirable physical and chemical properties in comparison to their carbon counterparts. Recently fullerene-like cage of boron nitride nanostructures have attracted considerable attention due to their remarkable chemical and physical properties [6–10]. These materials are insulator with wide band gap. The geometries and stability of fullerene-like $(BN)_n$ nanoclusters have been theoretically investigated by many researchers [11–15]. Fowler et al. [11] theoretically showed that the $B_{12}N_{12}$ and $B_{16}N_{16}$ are magic stable BN fullerenes. Theoretical studies demonstrated that these clusters consist entirely of tetragonal and hexagonal BN rings. Oku et al. [16] have synthesized these magic clusters, detected by laser desorption time-of flight mass spectrometry. They confirmed that $B_{12}N_{12}$ cluster is a semiconductor, which consist of square and hexagonal rings. Recently the interaction of pristine $B_{12}N_{12}$ nanocluster with different molecules such as methylamine [17], CO [18], $CO_2$ [19], $NO_2$ [20], NO, $H_2$, $N_2$ and $CH_4$ [21] are investigated through density functional theory. Soltani et al. studied $SCN^-$ adsorption on $B_{12}N_{12}$ and $B_{16}N_{16}$ nanoclusters [22].

In this study DFT calculations have been performed to scrutinize the adsorption of phosgene molecule onto pristine as well as

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Al- and Ga-doped $B_{12}N_{12}$ and $B_{16}N_{16}$ nanoclusters. The purpose of this work is to exploit the potential application of boron nitride-based gas sensor. The obtained results may provide a new insight to the gas sensor nanotechnology.

## 2. Computational details

The geometries of all considered structures are fully optimized using B3LYP [23,24] method and 6-31+G(d) basis set and the nature of the stationary points are checked by frequency analysis at the same computational level of theory. It is noteworthy that the interaction of phosgene molecule with pristine clusters are also investigated at M06-2X/6-31+G(d) level of theory for considering dispersion forces which is the main constituent part of a van der Waals interaction [25,26]. Indeed, the B3LYP/6-31+G(2df) method is used for the natural bond orbital (NBO) analysis of the systems. All calculations are performed using Gaussian 09 package [27].

The adsorption energy ($E_{ads}$) of the phosgene on the considered cluster is defined as:

$$E_{ads} = E_{cluster-phosgene} - \left(E^{iso}_{cluster} + E^{iso}_{phosgene}\right) + E_{BSSE} \quad (1)$$

where $E_{cluster-phosgene}$ denotes the total energy of the adduct BN cluster with the phosgene molecule. $E^{iso}_{cluster}$ and $E^{iso}_{phosgene}$ terms are the

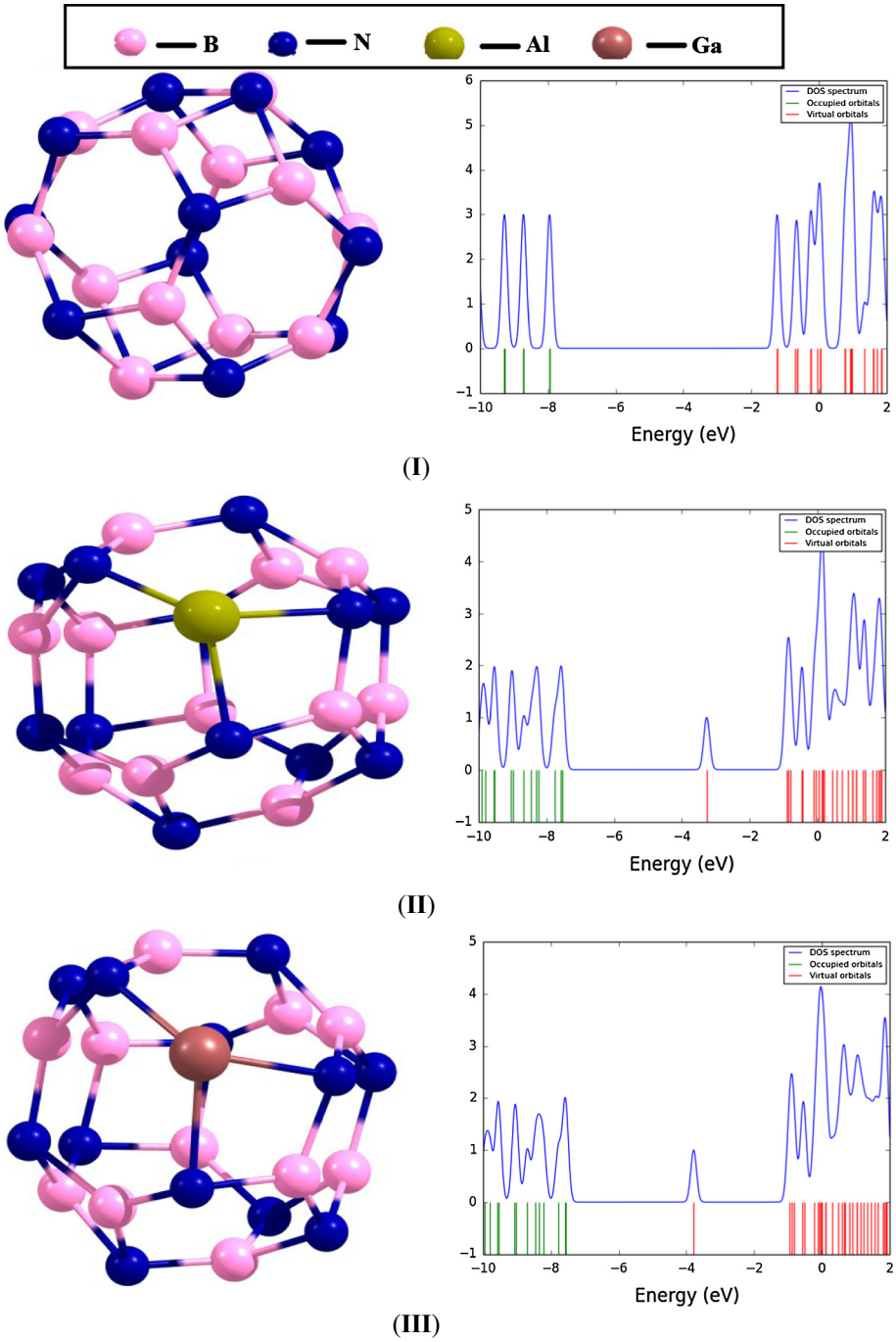


**Fig. 1.** The optimized geometries as well as DOS spectra of (**I**) $B_{12}N_{12}$, (**II**) $AlB_{11}N_{12}$, (**III**) $GaB_{11}N_{12}$, (**IV**) $B_{16}N_{16}$, (**V**) $AlB_{15}N_{16}$ and (**VI**) $GaB_{15}N_{16}$ using B3LYP/6-31+G(d) level of theory.