# Sulfur mustard gas adsorption on ZnO fullerene-like nanocage: Quantum chemical calculations

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## A R T I C L E   I N F O

## A B S T R A C T

In the present study, we used density functional theory calculations (at B3LYP and ωB97XD Levels) to search on the adsorption of Sulfur mustard gas (defined as mustard gas) on the surface of fullerene-like ZnO nanocage as a semiconductor. We found three different configurations of adsorbed gas on the surface of this nanostructure semiconductor. The values of adsorption energy of mustard gas are calculated in the range of $-144 \sim -200$ kJ/mol with enthalpies in the range of $-132 \sim -195$ kJ/mol and Gibbs free energies in the range of $-88 \sim -144$ kJ/mol (T = 298 K, based on ωB97XD level), which indicate exothermic and spontaneous chemisorption. For all geometries, we calculated geometry parameters by taking into account the charge analysis and frontier molecular orbital study. The result of this study can be a support for next studies to develop new nanomaterials as adsorbent/ sensor for mustard gas.

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## 1. Introduction

Sulfur mustard or mustard gas (bis-2-(chloroethyl) sulfide, see Fig. 1) is known as a substance war agent that categorized in armament of mass annihilation [1]. Mustard gas was one of the primary chemical armaments organized in contradiction of troops on a battleground throughout World War I. Later, the military usage of mustard gas has been considered many times. In 1988, mustard gas was utilized with overwhelming consequences by Saddam Hussein's militaries against citizen goals in Halabja and later in the Iran-Iraq war [1]. It is very possible that mustard gas can be utilized by terrorists because it is a simple compound voluntarily produced without sumptuous equipment. Furthermore, as a "persistent agent" (US Military organization) aerosolized mustard gas results a hazard for up to 1 week under dry and warm weather circumstances since it remains in the environment until completely hydrolyzed. Decontamination of such stubborn agent provides a leading challenge for investigators. For decontamination purpose, there are different methods in literature [2–4]. Nanomaterial adsorbents have been recognized as potential materials for the decontamination purpose [2]. Nano-sized in-organic oxide particles such as MgO [2] and Al2O3 [3,4] were found as hopeful materials for the decontamination of mustard gas.

For example, Prasad et al. [2] used restacked manganese oxide nanosheets and nanotubes as reactive sorbents for the detoxification of mustard gas. Saxena et al. [4] used $Al_2O_3$ nanoparticles towards adsorption study of mustard gas. In another work, Saxena et al. [5] synthesized silica nanoparticles as reactive adsorbent and investigated its potential towards removal of sulfur mustard from solutions.

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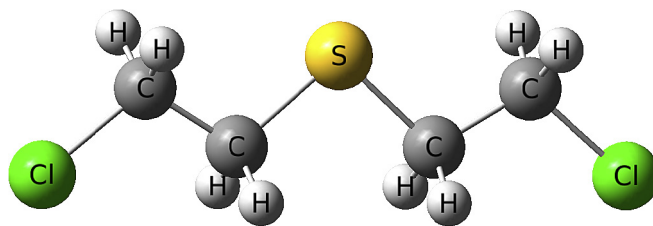
**Fig. 1.** The scheme of mustard gas.

From the first discovering of fullerene C60 in 1985 by Kroto et al. [6], much attentions have been pointed on discovering new classes of stable chemical with spherical (or near spherical) forms, named here as nanocage. One of the fascinating nanocages is semiconductors with (XY)n formula where X and Y correspond to metallic and nonmetallic elements and n is the number of each atom and the most steadiness structure was achieved when n = 12 [7].

Each $(XY)_{12}$ nanocage is a condensed octahedron involving of 8 hexagons (six-membered ring) and 6 squares (four−membered ring). There are different applications of such nanocages in recent literature [8−18]. One of the fascinating and well-investigated nanostructure is zinc oxide (ZnO). It is well established as piezo-electric, semiconductor, catalyst and gas sensor [18].

Despite several forms of synthesized ZnO reported in literature such as nano-wires [19], nano-tubes [20], and nano-particles [21], however a new class of ZnO structure ($Zn_{12}O_{12}$ nano-cage) has been extremely investigated recently, which its spherical shape is known as the most stable one in comparison with other structures [18,22−24]. On the other hand, potential of the $Zn_{12}O_{12}$ as an adsorbent for absorption of diverse gases has been searched recently [25,26].

In this study we used quantum calculation to search on the potential of the $Zn_{12}O_{12}$ nanocage towards decontamination of mustard gas. To the best of our knowledge, this is the first time investigation of mustard gas adsorption on fullerene-like semiconductor. We are looking for the following properties by means of DFT calculations: relaxed structure, adsorption energy, bond distance, thermochemistry parameters including enthalpy and Gibbs free energy, charge analysis including molecular electrostatic potential, reactivity parameters, and frontier molecular orbital analysis.

## 2. Computation details

Initial optimized structures were achieved using DFT method with B3LYP functional at 6-311G (d,p) basis set, however the resulted structures were subjected to the next optimization (re-relaxation) using ωb97XD functional at the same basis set. Both above-mentioned levels of theory are implemented in the Gaussian 09 suite of program [27]. Despite B3LYP is well known as reliable functional in the study of different nanostructures [18,25,28,29], however B3LYP is not the best choice for considering dispersion forces. Actually, in non-polar system, fast charge oscillations happen because of dispersion forces arises. Even if dispersion forces are weak, nevertheless they have protuberant part at molecular level. Therefore, we persuaded to repeat all optimization with dispersion corrected functional (wB97XD) [30].

We have defined the adsorption energy ($E_{ad}$) of mustard gas (M) on ZnO nanocage as:

$$E_{ad} = E_{ZnO-M} - (E_{ZnO} + E_M) \tag{1}$$

Where $E_{ZnO-M}$ is the total energy of the adsorbed mustard gas molecule on the surface of ZnO nanocage, whereas $E_{ZnO}$ and $E_M$ are the total energies of the free $Zn_{12}O_{12}$ and a free mustard gas molecule, respectively. We have used the definition of mustard gas adsorption enthalpy change (ΔH) for a cation (at T = 298 K and P = 1 atm) as follows:

$$\Delta H = H_{ZnO-M} - (H_{ZnO} + H_M) \tag{2}$$

where $H_{ZnO-M}$, $H_{ZnO}$, and $H_M$ are sum of electronic and thermal enthalpies of $Zn_{12}O_{12}$-M complex, $Zn_{12}O_{12}$, and mustard gas molecule, correspondingly, as acquired from the frequency calculations. We should consider that a negative value of ΔH links to an exothermic process. We calculated Gibbs free energy alteration (ΔG) similar to the ΔH, by means of related data of frequency calculations. The gap of energy between HOMO and LUMO (Eg) is well-defined as

$$E_g = E_{LUMO} - E_{HOMO} \tag{3}$$

Whereas $E_{LUMO}$ and $E_{HOMO}$ are energy of HOMO and LUMO.

The electrophilicity concept was stated by Parr et al. [31]. Chemical potential (μ) is well-defined based the following equation [32]:

$$\mu = -(E_{HOMO} + E_{LUMO})/2 \tag{4}$$

In addition, hardness (ŋ) can be calculated using the Koopmans' theorem [32] as: