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Molecular dynamics simulation of the interface between sulfur mustard and graphene

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ABSTRACT

Using molecular dynamics simulations, the interface between sulfur mustard (SM) which is one of the most toxic chemical warfare agents, and single layer graphene (G) was investigated for the first time to find a new class of adsorbents. Various analyses have been done in order to atomistically understand the adsorption mechanism. Results show that: (1) A solid-like SM layer of 6 Å thick is formed near G, and its density approximates to 2.5 times as large as that of the bulk SM; (2) Adsorption is occurred in three layers, and due to two distinct orientations of SM relative to G surface, i.e. parallel and tilted, there are fine structures within first layer; (3) Study of surface self-diffusion shows that the diffusion coefficient of SM molecules on G surface is half of the diffusion coefficient of SM molecules in the bulk. Furthermore, the diffusion coefficient of SM molecules with parallel orientation is half of the diffusion coefficient of tilted SM molecules and the lifetime of parallel orientation in the first adsorption layer is about three times more than that of tilted; (4) Pair interaction energy calculation between SM and G revealed that the adsorption energy of parallel SM molecules (−11.875 kCal/mol) is greater than that of the tilted SM molecules (−6.125 kCal/mol) and parallel orientation is the favorable orientation for adsorption. SM-SM pair interaction energy analysis also revealed that SM-SM pairs near G are more associated than SM-SM pairs in the bulk of SM. In summary, our results clearly show that G can be a good candidate for adsorption of SM and similar toxic chemical warfare agents.

1. Introduction

Sulfur mustard [bis-(2-chloroethyl) sulfide, SM], Fig. 1, also known as the mustard gas is a vesicant or blistering chemical warfare agent (CWA). It is one of the oldest CWAs which was employed as a chemical weapon for the first time during the World War I. It was used by some military forces around the world. Unfortunately it was utilized on a large scale in Iran–Iraq war [1–3]. Sulfur mustard can be absorbed by all parts of the body, resulting in skin and eye injuries, airway lesions, gastrointestinal effects, hematological disorders, cancer and sometimes even death. It is also a biological alkylating agent which reacts with cellular components such as DNA, RNA, proteins, lipid membranes and glutathione [4–9]. Regarding the high degree of toxicity and reactive nature of sulfur mustard, it is crucial to develop an appropriate adsorbent in order to achieve protection against this extremely hazardous compound.

Results of a number of experimental and computational studies have been previously reported regarding the adsorption and interaction of SM or its stimulants with different adsorbents including activated carbon [10–14], metal oxides [15–18], zeolites [19,20], metal organic frameworks (MOFs) [21,22], and some others [23–26]. It should be noted that activated carbon is the most preferred material which is still used by many countries for protective purposes. Although this material provides suitable protection against almost all kinds of chemical warfare agents, it has some drawbacks like heavy weight and moisture retention, resulting in adsorbing oxygen from the environment and breathing difficulties [27,28]. So, there is a need to find new classes of adsorbents.

Graphene is a new carbon nanostructure with unique physicochemical properties such as high surface area, extraordinary thermal and electric conductivities and great mechanical strength which make it a good candidate in diverse fields ranging from electronics to bioscience [29–32]. It has also been extensively used as an adsorbent for different kinds of organic and inorganic compounds [33–40].

The aim of this work is to study the adsorption behavior of SM molecules on graphene through molecular dynamics (MD) simulations for the first time to find a new class of adsorbents. First, adsorption of SM molecules on G surface was investigated in vacuum without

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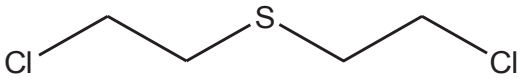

Fig. 1. The structure of sulfur mustard.

presence of other SM molecules. Next, to understand the structures and adsorption behavior of SM molecules, distribution of SM molecules was studied in liquid state near G surface. Then, dynamic behavior of adsorbed molecules was examined through the calculation of self-diffusion coefficients and it compared with the behavior of SM molecules in the bulk (i.e. regions far from G surface). In order to identify the underlying driving forces behind the adsorption of SM by G, careful analyses of the interaction energies between SM and G, and between SM molecules in the adsorption layer and into the bulk were conducted. To the authors' best knowledge, no theoretical and experimental investigation results on all structural, energetic and dynamic aspects of the interface between SM and G has been reported.

2. Methods

2.1. General procedure

All MD simulations were carried out using NAMD package [41]. The atomic force field used here is the OPLS [42] potential for both liquid SM [43,44] and graphene [45]. In order to be sure about the accuracy of the results, the bulk properties of SM were examined by calculation of the simulated densities. These results were 1.2606 g/ml^3 at 298 K and 1.2649 g/ml^3 at 293 K which were consistent with the experimental values of 1.2685 [46] and 1.2741 [47] g/ml^3, respectively. A single-layer graphene sheet with dimensions of 50 × 40 Å^2 was considered in the middle of an orthorhombic box with its basal plane parallel to *xy*-plane. The graphene surface was taken as a reference *z* position (z = 0 Å). Then 646 SM molecules were equally distributed on both sides of the simulation box with periodic boundary conditions applied in all directions. For SM-G system, the dimensions of system was adjusted to insure that the density of SM in the region far from G surface matches the density of pure SM, so a side length of 52.1 × 43.0 × 62.7 Å^3 was designated for it. The central atom of the graphene sheet was fixed during the simulations.

The simulation was performed under canonical (*NVT*) ensemble at 298 K using a Langevin dynamics method. Energy minimization was performed to eliminate undesirable interactions in the initial configuration of the system. The particle-mesh Ewald method [48,49] was applied to calculate the electrostatic interactions, whereas non-bonded van der Waals interactions were modeled by a Lennard–Jones potential with a cut-off distance of 15 Å. The system was initially equilibrated for 5 ns followed by a 5 ns production run. A time step of 1 fs was used to integrate the equation of motion and data was saved every 1 ps.

2.2. Diffusion coefficient

The diffusion coefficient was evaluated from the MD trajectories using the Einstein's equation [Eq. (1)] where r is the location of each atom at time t.

$$D = \frac{1}{6}\lim_{t\to\infty}\frac{\langle |r(t+\Delta t)-r(t)|^2\rangle}{\Delta t} \quad (1)$$

According to this equation, the diffusion coefficient can be derived from the slope of the mean square displacement (MSD) curves versus interval time (Δt) [50].

2.3. Adaptive biasing force

The adaptive biasing force (ABF) [51,52] method was used to calculate the free energy profile of approaching of a single SM molecule to the graphene surface in gas phase. The various free energy calculation methods have different advantages and disadvantages. In this work, ABF method was chosen which relies on estimating forces on the transition coordinate, providing a suitable physical framework and long-time convergence [53,54]. "ABF is based on the computation of the mean force along the reaction path which is then canceled out by an equal and opposite biasing force, allowing the system overcome barriers and escape from minima of the free energy landscape. Ultimately, the dynamics of the reaction path corresponds to a random walk with zero mean force, and only the fluctuating part of the instantaneous force exerted along the reaction path remains. Virtual erasure of the roughness of the free energy landscape yields a uniform sampling along the reaction path" [53b].

To implement the ABF method, the reaction coordinate was defined as the distance between the sulfur atom of SM molecule and graphene surface. We covered a 20 Å span, by approaching a single SM molecule from a distance 20 Å far from graphene surface to the graphene surface proximity. We divided the reaction path to 20 non-overlapping windows of length 1 Å. At the beginning we placed SM molecule within first window, somewhere between 19 and 20 Å. We considered a threshold of 500 force samples to obtain a reasonable estimate of the force distribution. The upper and lower wall force constants for boundary potentials was set to 50 kCal/mol Å^2. In each window 2 ns trajectories were sampled.

2.4. Definition of orientational angle

The definition of orientational angle (α) is illustrated in Fig. 2. The orientation angle (α) is defined as the angle between the normal vector (the *z* axis) perpendicular to G surface and the vector that is formed between two terminal carbons of SM molecule.

3. Results and discussion

3.1. Adsorption of SM molecule on graphene surface in vacuum

Although the primary target of this work is investigation of the properties of the interface between SM molecules in liquid state and G

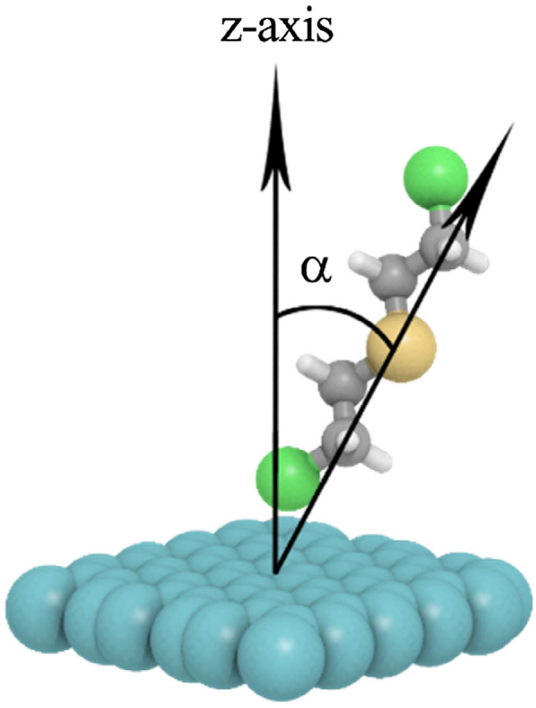

Fig. 2. Illustrations of the orientation angle (α) in this study.