Journal of Hazardous Materials 306 (2016) 269–277

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Structural flexibility of the sulfur mustard molecule at finite temperature from Car–Parrinello molecular dynamics simulations

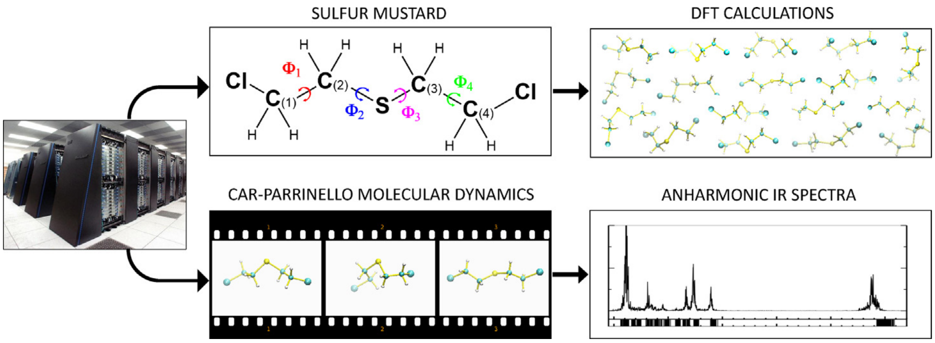
Joanna Lach[a], Jakub Goclon[b], Pawel Rodziewicz[c,*]

[a] Department of General Physics and Spectroscopy, Vilnius University, Sauletekio av. 3-9, Vilnius 10222, Lithuania
[b] Interdisciplinary Center for Molecular Materials (ICMM) and Computer-Chemistry-Center (CCC), Friedrich-Alexander-University Erlangen-Nürnberg, Nägelsbachstr. 25, 91052 Erlangen, Germany
[c] Institute of Chemistry, University of Bialystok, Hurtowa 1, 15-399 Bialystok, Poland

HIGHLIGHTS

- Full conformational analysis of sulfur mustard (SM) molecule in the gas phase.
- Structural rearrangements between SM conformers from by CP-MD simulations.
- Stability of the SM conformers and their lifetime at the finite temperature.
- Anharmonic IR spectrum of SM is derived on-the-fly from the CP-MD simulation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 October 2015
Received in revised form
12 December 2015
Accepted 16 December 2015
Available online 23 December 2015

Keywords:
Sulfur mustard
Mustard gas
Bis(2-chloroethyl) sulfide
Yperite
S-LOST
Car–Parrinello molecular dynamics
Density functional theory
IR spectrum

ABSTRACT

Sulfur mustard (SM) is one of the most dangerous chemical compounds used against humans, mostly at war conditions but also in terrorist attacks. Even though the sulfur mustard has been synthesized over a hundred years ago, some of its molecular properties are not yet resolved. We investigate the structural flexibility of the SM molecule in the gas phase by Car–Parrinello molecular dynamics simulations. Thorough conformation analysis of 81 different SM configurations using density functional theory is performed to analyze the behavior of the system at finite temperature. The conformational diversity is analyzed with respect to the formation of intramolecular *blue-shifting* C—H···S and C—H···Cl hydrogen bonds. Molecular dynamics simulations indicate that all structural rearrangements between SM local minima are realized either in direct or non-direct way, including the intermediate structure in the last case. We study the lifetime of the SM conformers and perform the population analysis. Additionally, we provide the anharmonic dynamical finite temperature IR spectrum from the Fourier Transform of the dipole moment autocorrelation function to mimic the missing experimental IR spectrum.

1. Introduction

Sulfur mustard (bis(2-chloroethyl) sulfide), also known as the mustard gas, yperite, Schwefel-Lost or simply LOST, is one of the major chemical warfare agents (CWAs) [1]. The large-scale production and the massive usage of this extremely toxic chemical

---

* Corresponding author.
E-mail address: pawel.rodziewicz@fau.de (P. Rodziewicz).

http://dx.doi.org/10.1016/j.jhazmat.2015.12.027
0304-3894/© 2015 Elsevier B.V. All rights reserved.

compound started during World War I. Sulfur mustard (SM) was produced massively during the World War II (WWII) but was never used [2]. After the WWII the arsenals of the chemical weapons and disposed stockpiles of SM and other CWAs were neutralized by direct submerging it into the sea, as the cheapest and the simplest method in those times. Due to the barrels corrosion, the dumped CWAs now have become a potential danger not only to the water environment but also to the citizens of the seaside areas [3]. SM is, in principle, insoluble in water, however, it undergoes slow hydrolysis reaction via S_N1 mechanism [4,1]. The majority of the submerged SM is still in the unchanged form and the direct contact with skin or when inhaled is a real danger. It happens, for example, during a stormy weather, when the corroded barrels with SM may drift and be beached. Bearing in mind the conditions of the barrels, we can anticipate the increase of such dangerous accidents. Moreover, SM was used after the WWII as a chemical weapon, for example against the Kurds in Iraq [2]. Therefore, the highest priority should be given to the precise detection of even the lowest concentration of SM in the environment [5]. For this purpose all structural, electronic and spectroscopic properties of SM should be investigated in detail. The toxicity of this compound makes the experimental work quite difficult and only a limited number of certified laboratories is allowed to work with the different types of CWAs. From the other side, the small size of the SM molecule and small number of electrons make this system an ideal target for the state-of-the-art theoretical methods, including *ab initio* molecular dynamics (AIMD). The advantage of *in silico* research is the precise description of the physicochemical properties of CWA without the risk of the direct exposure.

In the first theoretical study of the SM molecule, the conformation considered as the global minimum was all-*trans* (*t t t t*) structure with the C_{2v} symmetry [6]. The obtained theoretical spectroscopic parameters were later used in the assignments of the vibrational modes in the IR and Raman spectra of neat liquid samples of the SM [7]. Similar to the previous computational studies, the only all-*trans* conformation, was considered in the calculations utilizing HF and MP2 levels of theory [8]. However, the experimental IR and Raman spectra suggested the existence of other conformations: “the presence of *gauche* conformers is evident in the number of strong Raman lines in this region” [7]. An elegant demonstration of the detailed conformational study of the SM molecule utilizing molecular mechanics, semiempirical and *ab initio* methods was provided by Donovan and Famini [9]. The conformational search was based on the MM2 Monte Carlo simulations where 12 the most stable conformations were generated using *ab initio* methods. The authors have proven that the all-*trans* conformation turned out not to be the lowest energy structure. The true global minimum (*t g+ g+ t*) was estimated to have two dihedral angles in the *gauche* position. These calculations have been recently corrected with the help of a more advanced method, namely MP2/aug-cc-pVDZ, and were used to improve the MM3 and MMFF94 force fields [10]. The authors have reported the exhaustive conformational analysis combined with the potential energy surfaces obtained by rotation about the C—C bond. Furthermore, the results of the Boltzmann distribution of the relative free energies, were presented for ten the most popular conformers of the SM molecule. However, the work of Nadas et al. [10] is a comprehensive and valuable source of information, it suffers from some errors, namely the wrong number of SM conformers considered and incorrect degeneracy. Since these errors influence the given results, in particular the population analysis, they are discussed in details in our work.

The CH_2 groups present in the SM molecule may act as a proton donor, whereas S or Cl atoms as a proton acceptor. Therefore in some of the SM conformers the intramolecular C—H···Cl or/and C—H···S hydrogen bonds may be present. Recent studies of such interactions (present in the inhibitors of TIBO family) suggest the strong influence of weak intramolecular C—H···Cl and C—H···S hydrogen bonds on their conformation [11]. In the case of the SM molecule the C—H···Cl hydrogen bonds are particularly important since the cleavage of the C—Cl is responsible for the neutralization of the sulfur mustard. The C—Cl bond undergoes the heterolytic cleavage in the gas phase and the bond-breaking energy for such process was estimated to be 154.8 kcal/mol [12]. Such high cost of the bond cleavage is a problem in the thermal decomposition of the SM molecules, since this is one of the methods of its neutralization. Other ways of the destruction of SM is application of advanced oxidation technologies (AOTs) [14] or biotechnology [15]. Recent studies reveal very efficient way of the robust decomposition of the toxic vapors of diisopropyl fluorophosphate (DFP) in the air using TiO_2 aerosol [13]. This powerful method of air purification suggests a possibility of the neutralization of other dangerous molecules, like chemical warfare agents, in particular SM molecules. The knowledge about structural rearrangements between SM local minima and their population at finite temperature may help in finding appropriate substrate to efficiently immobilize the adsorbate and later deactivate it in the heterogeneous catalytic process. Such neutralization technique could be used in the air purification in confined spaces. Furthermore, the properties of the SM molecules should be calculated taking into account the temperature impact. So far the theoretical studies of the SM molecules were restricted to the static *ab initio* calculations where the temperature refers to 0 K.

The aim of this study is to describe the *dynamics* of the SM molecule in the gas phase at room temperature, in particular to define the intramolecular structural rearrangements and to determine the lifetime of the global and local minima. The detailed description of such properties is crucial in a proper understanding of the adsorption process of SM molecules on nanoparticles [16]. Furthermore, we also study the spectroscopic properties of the SM molecule, namely harmonic and anharmonic IR spectra. The latter were obtained using the Fourier Transform of the dipole moment autocorrelation function and refer to the finite temperature. It is worth mentioning that the experimental IR spectra of the sulfur mustard in the gas phase are not available in the literature. Thus, the theoretically generated anharmonic IR spectrum might be used as a substitute of the experiment.

2. Computational methods

All static DFT calculations and Car–Parrinello molecular dynamics simulations were performed using the CPMD program package [17] and the gradient-corrected Becke–Lee–Yang–Parr (BLYP) exchange-correlation functional [18,19]. Previous DFT calculations showed that the gradient-corrected BLYP exchange-correlation functional properly describes weak hydrogen bonds [20]. The electronic wave functions were expanded in a plane-waves basis with a kinetic energy cutoff of 80 Ry. The atomic cores were described by standard norm-conserving Troullier–Martins pseudopotentials [21]. Brillouin zone sampling was restricted to the Γ-point. The empirical D2 dispersion correction proposed by Grimme was used [22]. The SM molecule was placed in a cubic box of length of the 18.0 Å. The runs were carried out screening the periodic boundary conditions using Martyna and Tuckerman’s method [23].

The Car–Parrinello molecular dynamics [24] simulations were performed in the canonical ensemble (NVT) utilizing Nosé–Hoover chain thermostats [25,26] for the nuclear degrees of freedom. The temperature in the CP-MD simulations was set to 300 K to mimic the standard ambient temperature. The fictitious electronic mass was set at 400 a.u. and the equations of motion were integrated with the time step of 4 a.u. For the CP-MD runs the optimized global