Adsorption of Toxic Heavy Metal Methylmercury (MeHg) on Germanene in Aqueous Environment: A First-Principles Study

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Abstract: *We perform first-principles calculations to investigate the adsorption process of methyl mercury (MeHg) on germanene with the presence of water molecules. We calculate the formation energy and density of states to determine the effect of the adsorption of MeHg on the structural and electronic properties of germanene. Our results show that MeHg is chemisorbed on germanene through a spontaneous reaction. The calculated formation energy of the system is -1.61 eV. We also carry out charge distribution and charge transfer calculations based on the Mulliken model to understand the adsorption mechanism of MeHg.*

Keywords: *methylmercury; germanene; adsorption; formation energy; the density of states*

■ INTRODUCTION

Mercury (Hg) poses a severe danger to humans and the environment, e.g., Hg exposure causes a wide range of health problems. This element can affect the lungs, brain, and skin and cause permanent damage to the nervous system [1-2]. Anthropogenic and natural sources contribute to the accumulation of Hg in soil. With intervention from microbial methylation reaction, inorganic Hg in the soil can be transformed into methylmercury (MeHg), one of the most toxic forms of organic Hg [3]. The MeHg molecule penetrates from soil to aquatic systems through runoff. It can bioaccumulate and biomagnify up the aquatic food chain. Therefore, MeHg is a major hazard to humans [4].

Remediation techniques are needed to control MeHg contamination in aquatic systems. Wang et al. reported several techniques that are needed to counter the MeHg pollution [5]. They explained the commonly used and emerging remediation techniques such as stabilization (solidification), nanotechnology, phytoextraction, etc. This study uses the adsorption mechanism by using germanene, as a host material. Germanene is a two-dimensional germanium-based material analog of graphene [6] and has been successfully grown on various substrates such as Au(111) [7], Pt(111) [8], and Al(111) [9]. Germanene exhibits strong sensitivity to chemical and environmental changes. Previous studies showed that germanene successfully adsorbs 3d transitional metal atoms (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) [10], alkali metal atoms (Li, Na, and K) [11-12] and various gas molecules [13]. From the calculated adsorption energy, germanene more easily adsorbs small gas molecules than silicene [14-15]. Therefore, the study of molecule adsorption on germanene, particularly that of a toxic molecule such as MeHg is necessary.

In the present work, we perform first-principles density-functional-theory (DFT) calculations to investigate the capability of germanene to adsorb the heavy metal MeHg in aqueous conditions. Supercell with 32 atomic sites is involved, and all atoms are relaxed to find the optimized geometry. We calculate the formation energy (E_{form}), the density of states (DOS), and charge transfer to study the adsorption mechanism of MeHg in germanene.

■ COMPUTATIONAL METHODS

The DFT calculations are performed using OpenMX (Open-source package for Material eXplorer) code [16-18] based on pseudo-atomic localized basis functions. In this code, the norm-conserving pseudopotential is used [19], and the wave functions are expanded by a linear combination of multiple pseudo-atomic orbitals [17-18]. The exchange-correlation functional is evaluated using the generalized gradient approximation with the Perdew-Burke-Ernzerhof method [20]. A 25-point grid is applied in the Brillouin zone integration. The energy convergence of the self-consistent calculations is adjusted at 10^{-4} Ha.

In this study, we use a supercell model in which the germanene surface lies on the x–y plane (Fig. 1). The supercell is generated by using a two-atoms unit cell with the optimized lattice constant. Lattice parameter optimization is carried out using the Murnaghan equation of states as follows [21-26]:

$$E(V)=E_0+B_0V_0\left[\frac{1}{B_0'\left(B_0'-1\right)}\left(\frac{V}{V_0}\right)^{1-B_0'}+\frac{1}{B_0'}\left(\frac{V}{V_0}\right)-\frac{1}{B_0'-1}\right] \quad (1)$$

where E_0, V_0, B_0, and B_0' are the fitting parameters calculated at the constant volume. E_0 is total energy, and V_0 is lattice volume while B_0 and B_0' are bulk modulus and its first derivative, respectively.

A 20 Å vacuum parameter, which is large enough to prevent interactions between adjacent layers, is applied perpendicularly to the germanene surface (Fig. 1(b)). A 4×4×1 supercell containing 32 atoms is used as the host material. To model the aqueous environment, we introduce water molecules on the surface of germanene. We then calculate the formation energy E_{form} and charge transfer. The E_{form} is defined by using the following equation [27-31]:

$$E_{form}=E_{subs/host}-\left(E_{subs}+E_{host}\right) \quad (2)$$

where E_{subs}, E_{host}, and $E_{subs/host}$ are the total energies of the isolated substrate, clean host material, and adsorption system, respectively. The same size of the unit cell is used for the system of interest. Using this definition, a negative value of E_{form} indicates spontaneous adsorption, and a positive value refers to non-spontaneous adsorption where the adsorbed state has more positive energy than the isolated one. Thus, external energy is needed to carry out the adsorption process. Meanwhile, the charge density difference was obtained by subtracting the total charge of the adsorption system from the individual charges of the isolated substrate and the host material [14,31], as follows:

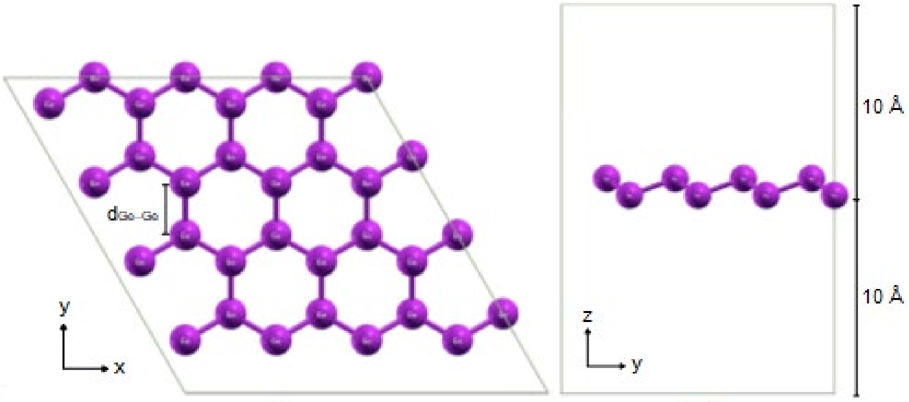
$$\Delta\rho=\rho_{MeHg/Ge}-\left(\rho_{MeHg}+\rho_{Ge}\right) \quad (3)$$

where ρ_{MeHg}, ρ_{Ge}, and $\rho_{MeHg/Ge}$ are the charge density of MeHg with water molecules, germanene, and the adsorption system, respectively.

■ RESULTS AND DISCUSSION

Germanene in an Aqueous Environment

We perform first-principles calculations of the germanene supercell with the presence of water molecules and MeHg molecule. We first optimize the



(a) (b)

Fig 1. Pristine germanene supercell: (a) front-view overlaying the x–y plane and (b) side-view showing the vacuum parameter in the z-direction. The purple balls denote germanium atoms germanene unit cell. The lattice constant of 4.06 Å is calculated using Eq. (1). This result agrees with the previous calculations [6,25]. The lattice constant of germanene is higher than that of silicene (3.86 Å) [32]. As for the bond lengths, the calculated Ge–Ge bond (d) is 2.46 Å, which is slightly higher than that of the Si–Si bond in silicene (2.24 Å) [33]. This result is in agreement with the results of previous theoretical [25,34] and experimental studies [7].

We next calculate the formation energy E_{form} using Eq. (2) and found that the system of germanene with water molecules (H_2Os/G) has E_{form} of +0.05 eV. The positive value of E_{form} implies the endothermicity of the adsorption process. Therefore, the adsorption only occurs in the presence of external energy.

We calculate the DOS to determine the electronic properties of the systems. Our results show that the presence of water molecules on the surface of germanene causes no change in the electronic state near the Fermi level, i.e., the shape of the DOS is the same, and there is no gap created. As shown in Fig. 2(a), the electronic state of pristine germanene is a semimetal with a zero bandgap at Dirac point. With the presence of water, the electronic state remains the same as in the pristine germanene (Fig. 2(b)). The difference in magnitude of the DOS at some energy ranges, e.g., at about -5 eV and +8 eV, is due to water molecules in the system.

Adsorption of MeHg on germanene

We introduce the MeHg molecule on germanene with water molecules, that is, MeHg/G. Fig. 3 shows the stable structure of this system. The calculated E_{form} of

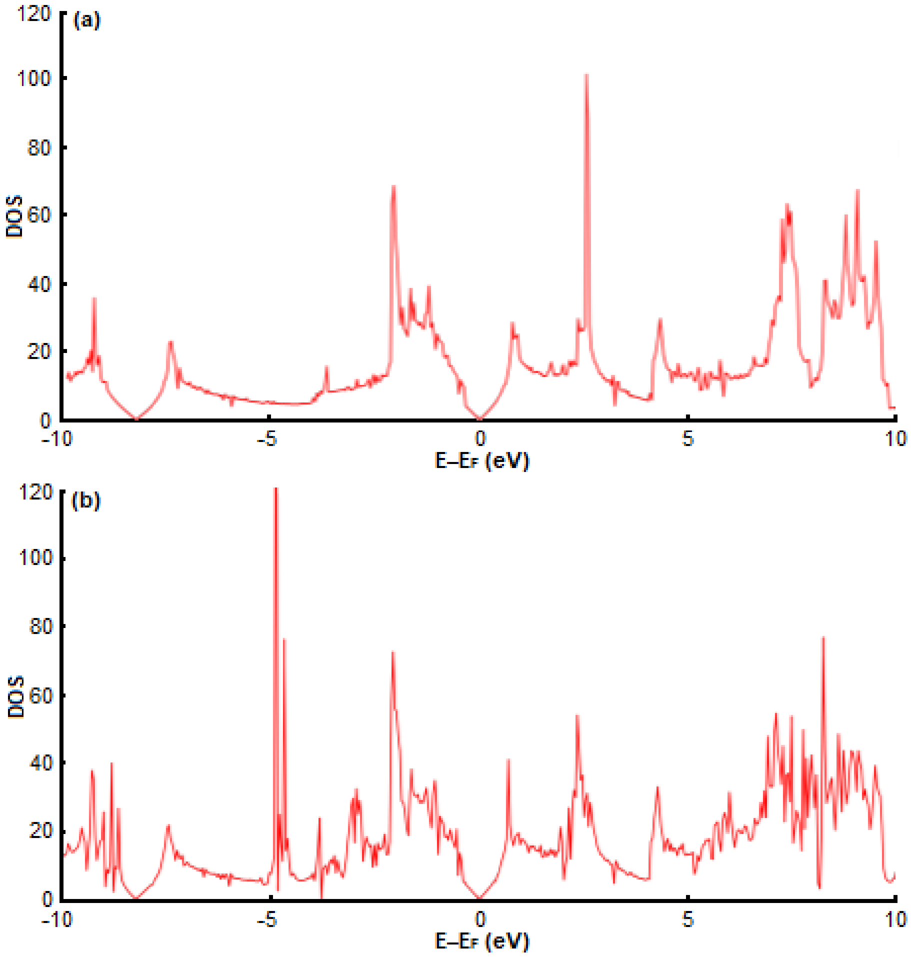


Fig 2. The density of states (DOS) of (a) pristine germanene and (b) germanene with water molecules. The Fermi level is set to zero

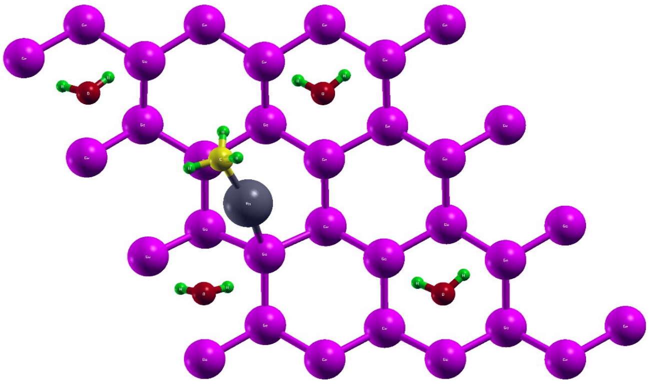


Fig 3. Stable structure of MeHg adsorption on germanene in aqueous condition. The black, yellow, green, red, and purple balls denote mercury, carbon, hydrogen, oxygen, and germanium atoms, respectively

MeHg/G is -1.61 eV. In contrast to the H_2Os/G system, the interaction between MeHg and germanene indicates a spontaneous reaction (negative E_{form}). Therefore, the adsorption of MeHg on germanene easily occurs without external energy.

Calculations for electronic properties showed that the DOS of germanene changes after adsorbing MeHg (Fig. 4). The MeHg adsorption opens a narrow bandgap, making germanene a semiconductor with a 0.20 eV bandgap. Ye et al. reported a similar result: germanene has a narrow bandgap ranging from 0.02 eV to 0.31 eV after adsorbing several alkali metal atoms [12].

The adsorption mechanism can be investigated by considering charge transfer between atoms in MeHg and germanium. We calculate the charge difference distribution Δρ as expressed in Eq. (3) to investigate the presence of charge transfer between two materials. Fig. 5 shows the isosurface of the charge and indicates the charge transfer between germanene and MeHg in an aqueous environment.

We then employ the Mulliken charge analysis to evaluate the net charge transfer between the materials. We observe that germanene loses its electron charge by about 0.25 e. On the other hand, heavy metal MeHg in an aqueous environment receives electron charge from germanene. This result agrees with the charge difference distribution as plotted in Fig. 5, where the depletion and accumulation of charges are observed between MeHg and Ge atoms of germanene.

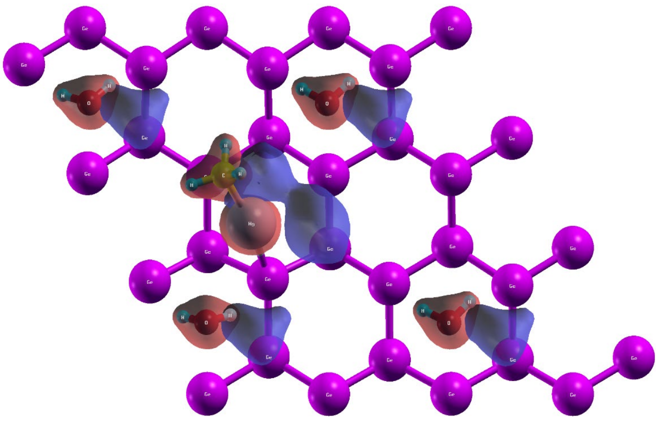


Fig 5. Charge difference distribution of the MeHg/G system. Red and blue areas illustrate the accumulation and loss of charge, respectively. Electron charges move from blue to red areas

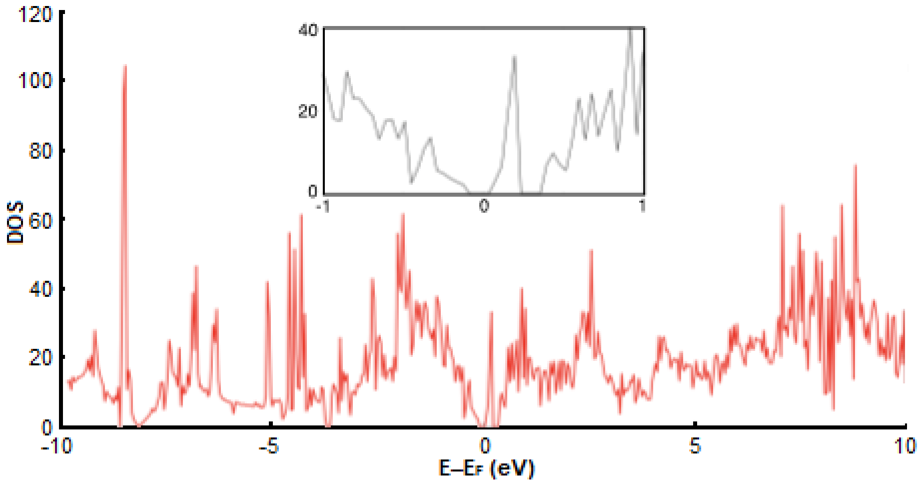


Fig 4. DOS of MeHg/G system with magnification around the Fermi level

Atomic Path

At the initial geometry, the Hg atom is placed on the center of the honeycomb structure of germanene with a vertical distance of 2.5 Å to the surface of germanene (Fig. 6). During relaxation, the Hg atom diffuses to the Ge1 atom and creates a covalent bond. The calculated bond length of Hg–Ge1 is 2.84 Å in the transition geometry, whereas the bond length shortens to 2.70 Å in the final geometry. The presence of MeHg affects the position of its adjacent atoms particularly Ge1–Ge13. As a result, the atoms undergo vertical distortions in various magnitudes, as listed in Table 1.

In the final geometry, the formation of MeHg remains as that of its molecular form with the Hg–C and C–H bond lengths of 2.19 and 1.11 Å, respectively. Given that MeHg is symmetric under C_3 (rotation by 2π) and symmetric under the vertical mirror σ_v, it shows a C_{3v} symmetry. Meanwhile, the water has a C_{2v} molecule with the O–H bond length of 0.99 Å.

■ CONCLUSION

We perform DFT calculations to investigate the adsorption mechanism of MeHg on germanene with the presence of water molecules. MeHg is chemisorbed on germanene with a E_{form} of -1.61 eV. To determine the mechanism of interaction, we carry out charge difference distribution and charge transfer calculations. Our results show that germanene distributes an electron charge of 0.25 e to MeHg under aqueous conditions.

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Table 1. Magnitudes of vertical distortion of MeHg neighboring atoms. The values are obtained by subtracting the initial state coordinates from the final state coordinates. Positive and negative values indicate that the Ge atom is moving away and moving closer to MeHg in the z-direction, respectively

Atom	Magnitude (Å)	Atom	Magnitude (Å)
Ge1	0.23	Ge8	0.22
Ge2	0.40	Ge9	0.17
Ge3	0.52	Ge10	-0.03
Ge4	0.60	Ge11	0.11
Ge5	0.98	Ge12	0.15
Ge6	0.72	Ge13	0.59
Ge7	0.45		

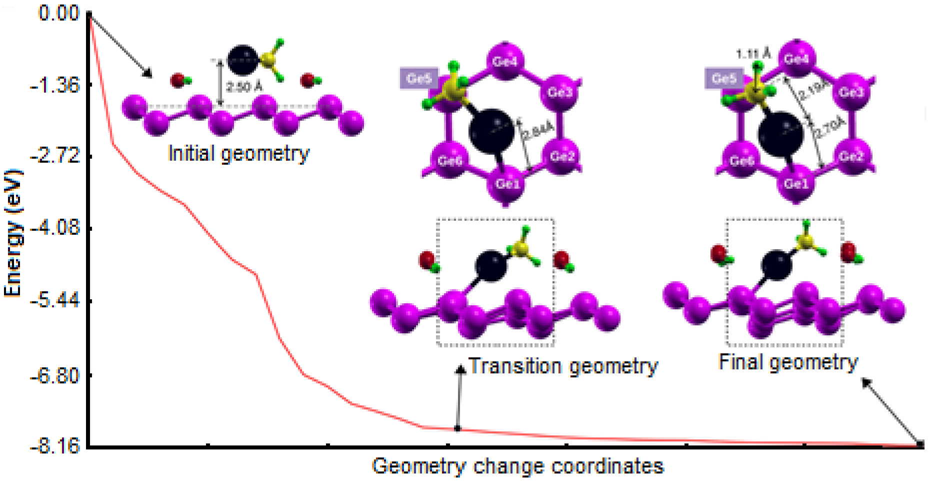

Fig 6. Atomic path of MeHg/G system, the initial, transition, and final geometries are shown. The areas inside the dashed rectangular are also illustrated in the top view for clarity. The zero level is referenced to that the energy of initial geometry

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