Au Catalyst-Modified MoS$_2$ Monolayer as a Highly Effective Adsorbent for SO$_2$F$_2$ Gas: A DFT Study

Yingang Gui,†‡ Wenlong Chen,† Yuncai Lu,† Chao Tang,† and Lingna Xu†

†College of Engineering and Technology, Southwest University, Chongqing 400715, China
‡Electric Power Research Institute, State Grid Jiangsu Electric Power Grid Co. Ltd., Nanjing 211102, China

ABSTRACT: To ensure the stable operation of gas-insulated equipment, removal of SF$_6$ decomposition products of sulfur hexafluoride (SF$_6$) is one of the best methods. SO$_2$F$_2$ is one of the typical decomposition products of SF$_6$, while the Au-modified MoS$_2$ (Au–MoS$_2$) monolayer is a novel gas adsorbent. Therefore, based on the first-principles calculations, the adsorption properties of the SO$_2$F$_2$ molecule on the Au–MoS$_2$ monolayer are calculated. Furthermore, the adsorption energy, charge transfer, and structure parameters were analyzed to obtain the most stable adsorption structure. These results indicate that all of the adsorption processes are exothermic. To better study the adsorption mechanism between the SO$_2$F$_2$ molecule and the Au–MoS$_2$ monolayer, the density of states, the highest occupied molecular orbital, the lowest unoccupied molecular orbital, and electron density difference were obtained. At last, we conclude that the interaction between the SO$_2$F$_2$ molecule and the Au–MoS$_2$ monolayer was chemisorption. This study provides a theoretical basis to prepare the Au–MoS$_2$ monolayer for the removal of SF$_6$ decomposition products.

1. INTRODUCTION

Over the past decades, sulfur hexafluoride (SF$_6$) has been widely used in gas-insulated switchgear (GIS) and other gas-insulated equipment owing to its excellent insulating and arc extinguishing properties. Even so, during the long-term running equipment, partial discharge (PD) frequently occurs due to the inevitable internal insulation defects. Previous studies found that SF$_6$ gas insulation will decompose to low-fluorine sulfides (SF$_6$ x = 1−5) under partial discharge. These decomposed products would subsequently react with traces of gaseous O$_2$ and H$_2$O existing in SF$_6$-insulated equipment and form various characteristic decomposition products, including SOF$_2$, SO$_2$F$_2$, SO$_2$, etc. The running stability of gas-insulated equipment can be greatly affected by the decomposition products of SF$_6$ which may ultimately lead to the breakdown of the power system. To ensure the strong stability, good thermal stability, high specific surface area, and high surface activity, has become one of the research hotspots of gas adsorbent. Metal-modified MoS$_2$ materials have been investigated for application in gas molecules adsorption, which shows a broad application prospect. Furthermore, based on the first-principles calculations, researchers verified that a noble metal-modified MoS$_2$ monolayer shows great adsorption ability toward specific gas molecules. For MoS$_2$ modification, Wang et al. studied the adsorption and diffusion of noble metal atoms on MoS$_2$ based on the density functional theory (DFT). Studies proved that metal modification can effectively enhance the chemical activity and sensing sensitivity of modified MoS$_2$ compared to that of the intrinsic monolayer. Chen et al. studied the physical adsorption between Au-modified MoS$_2$ and gas molecules (SOF$_2$ and SO$_2$F$_2$) that did not break the structure of gas molecules. However, SOF$_2$ and SO$_2$F$_2$ may also chemically adsorb on metal-modified MoS$_2$. For this reason, a Au catalyst-modified MoS$_2$ monolayer was proposed as a highly effective adsorbent for SO$_2$F$_2$ removal in SF$_6$-insulated equipment.

In this study, based on the density functional theory (DFT), the adsorption of SO$_2$F$_2$ on the Au-modified MoS$_2$ (Au–MoS$_2$) monolayer with different initial conditions was studied to systematically analyze the adsorption mechanism. The adsorption energy, charge transfer, electron density difference, and density of states (DOS) were calculated to explore the interaction mechanism between SO$_2$F$_2$ and Au–MoS$_2$. This study results provide a theoretical basis for preparing a Au–
MoS$_2$ monolayer adsorbent for SO$_2$F$_2$ removal in the experiment.

2. RESULT AND DISCUSSION

2.1. Structural Property of Gas Molecule Models and Au−MoS$_2$ Monolayer. Before gas adsorption, to gain the most stable structure, the structures of a SF$_6$ gas molecule and its decomposed product SO$_2$F$_2$ and the Au−MoS$_2$ monolayer model were built and optimized. Figure 1 shows the optimized structure of SO$_2$F$_2$ and SF$_6$ molecules. The bond lengths and the bond angles are marked in the molecular structures. The central S atom in the SO$_2$F$_2$ molecule has an sp$^3$ hybridization and the bond angles are perpendicular to each other, and the bond length is similar to the S−F bond length in the SF$_6$ molecule, which is 1.616 Å. Analysis of Mulliken atomic charges shows that the S atom in the SO$_2$F$_2$ molecule has a positive charge of 0.868e, while the O and F atoms have negative charges of 0.214e and 0.220e, respectively. However, the S atom in the SF$_6$ molecule obtains a positive charge of 1.194e, which is transferred from the F atoms. A large number of electron transfers indicate that there is a strong interaction between F atoms and S atom in the SF$_6$ molecule, which ensures that the SF$_6$ molecule has a very stable structure.

As shown in Figure 2, the Au atom approaches the Mo atom from the top site and forms bonds with three surrounding S atoms. The bond lengths of the Au−S bond are 2.805 Å, and the Au atom shows a weak interaction with the Mo atom because of the long distance between them (3.767 Å). The bond angles of the Mo−S−Mo and S−Mo−S in the MoS$_2$ monolayer without Au atom modification are both 81.55°. However, the bond angles slightly decreased to 81.34° and 80.99°, respectively, after Au modification. The obvious changes of angle and the binding energy (−0.448 eV) indicate that the modified Au atom has a strong interaction with the MoS$_2$ monolayer. The carried charge of the Au atom after modification was also calculated, which is −0.038e. This indicates that the electron transfer from the Au atom to MoS$_2$ and further verifies the above conclusion.

To further investigate the influence of Au atom modification on the electronic properties of MoS$_2$, the total density of states (TDOS) and projected density of states (PDOS) of intrinsic MoS$_2$ and the Au−MoS$_2$ monolayer were calculated, as shown in Figure 3. It can be found that the waveform of TDOS nearly does not change except a distinct left shift after Au atom modification. This means that the MoS$_2$ monolayer is doped with Au atoms, the number of electrons in the system increases and the metallicity is enhanced. Near the Fermi level, the value of TDOS decreases significantly after Au atom doping, which means that doping of Au atom evidently enhances the metallic properties of MoS$_2$. According to the PDOS, the peaks of Au 5d orbitals and S 3p orbitals overlap at −5, −3, and −2 eV, indicating that the d orbital strongly hybridizes with the p orbital. Strong orbital hybridization means that the Au atom and MoS$_2$ monolayer can be well combined.

Furthermore, the band gap of MoS$_2$ and Au−MoS$_2$ was also calculated. It is found that the band gap changes from 2.057 to 0.266 eV after modification. The reduction of the band gap is conducive to electron transfer from the valence band and conduction band. As a result, the modified Au atom acts as an active site to form strong interaction between the Au−MoS$_2$ monolayer and the target gas molecules.

2.2. Adsorption Structures of the SF$_6$ Molecule. To ensure that the Au−MoS$_2$ monolayer can act as an adsorbent for decomposition products of the SF$_6$ molecule, we first studied the interaction mechanism between the Au−MoS$_2$ monolayer and the SF$_6$ molecule so as to ensure that the adsorbent would not affect SF$_6$ molecules. Figure 4a–c shows one F atom, two F atoms, and three F atoms close to the Au−MoS$_2$ monolayer, respectively. According to our analysis, the adsorption energies of the SF$_6$ molecule are −0.004, −0.001, and −0.003 eV and the transfer charges are −0.116e, −0.021e, and −0.018e, respectively, in three cases close to those of the
Au−MoS2 monolayer, indicating that there is only a weak force between the SF6 molecule and the Au−MoS2 monolayer. In the three cases shown in Figure 4, the distance between the SF6 molecule and the Au−MoS2 monolayer is so far that it is difficult to form a bond and the closest distance is 2.749 Å, which further verifies the above conclusion. Therefore, we believe that the Au−MoS2 monolayer can be used to study as an adsorbent for the decomposition products of the SF6 molecule.

2.3. Adsorption Structures of Single and Double SO2F2 Molecules. To obtain the most stable adsorption structure, several adsorption structures with different initial approaching sites were built for calculation. In this study, adsorption of single and double SO2F2 molecules was taken into account at the same time to systematically analyze the adsorption ability of the Au−MoS2 monolayer to the SO2F2 molecule. Figure 5 shows a typical adsorption of single SO2F2 molecule on the Au−MoS2 monolayer, which shows the largest adsorption energy in all monomolecular adsorption structures. The corresponding structural parameter, adsorption energy, and total charge transfer of the SO2F2 molecule adsorbed on the Au−MoS2 monolayer are given in Table 1. For double

![Figure 3](https://example.com/figure3.png)

Figure 3. (a) TDOS and (b) PDOS of Au−MoS2.

![Figure 4](https://example.com/figure4.png)

Figure 4. Adsorption structures of SF6 on the Au−MoS2 monolayer: (a) P1 structure; (b) P2 structure; and (c) P3 structure.

![Figure 5](https://example.com/figure5.png)

Figure 5. Adsorption structures of single SO2F2 on the Au−MoS2 monolayer: (a) top view and (b) side view.
Table 1. Parameters of Single SO$_2$F$_2$ Molecule Adsorption System: Adsorption Energy ($E_{\text{ads}}$ in eV), Total Charge Transfer ($Q_t$ in e), and Bond Length between the Major Atoms ($d$ in Å)

| system               | $E_{\text{ads}}$ (eV) | $Q_t$-Mulliken (e) | $Q_t$-Hirshefeld (e) | bond length (Å)                      |
|----------------------|------------------------|--------------------|----------------------|--------------------------------------|
| SO$_2$F$_2$/Au−MoS$_2$ | −0.559                 | −0.614             | −0.461               | 1.483(S−O1), 1.485(S−O2), 1.689(S−F1), 2.012(Au−F2) |

Figure 6. Adsorption structures of double SO$_2$F$_2$ on the Au−MoS$_2$ monolayer: (a) top view and (b) side view.

Table 2. Parameters of Double SO$_2$F$_2$ Molecule Adsorbed on the Au−MoS$_2$ Monolayer: Adsorption Energy ($E_{\text{ads}}$ in eV), Total Charge Transfer ($Q_t$ in e), and Bond Length ($d$ in Å)

| system               | $E_{\text{ads}}$ (eV) | $Q_t$-Mulliken (e) | $Q_t$-Hirshefeld (e) | bond length (Å)                      |
|----------------------|------------------------|--------------------|----------------------|--------------------------------------|
| 2SO$_2$F$_2$/Au−MoS$_2$ | −0.681                 | −0.664             | −0.572               | 1.471(S−O1), 1.473(S−O2), 1.701(S−F1), 2.001(Au−F2) |

Figure 7. TDOS and PDOS: (a1)−(a2) single SO$_2$F$_2$ adsorption and (b1)−(b2) double SO$_2$F$_2$ adsorption.
SO₂F₂ molecule adsorption, two typical structures were obtained, as shown in Figure 6, with its parameters exhibited in Table 2. As the negative adsorption energy shown in Tables 1 and 2, the adsorption process of the SO₂F₂ molecule on the Au−MoS₂ monolayer is exothermic, indicating that the adsorption process is spontaneous.

As shown in Figure 5 and Table 1, the Au−MoS₂ monolayer shows strong adsorption to the SO₂F₂ molecule with an adsorption energy of −0.559 eV. When the SO₂F₂ molecule approaches the surface of the Au−MoS₂ monolayer, the F₁ atom separates from the SO₂F₂ molecule and approaches the modified Au atom with an Au−F₁ bond length of 2.012 Å, indicating a chemical interaction between the SO₂F₂ molecule and the Au−MoS₂ monolayer. The corresponding charge transfer values, Qₜ, calculated by Mulliken and Hirshfeld methods are −0.614 and −0.461, respectively. Therefore, the SO₂F₂ molecule acts as an electron donor and the Au−MoS₂ monolayer acts as an electron acceptor. The bond lengths of S−O₁ and S−O₂ increase to 1.483 and 1.485 Å, respectively. The distance between the Au atom and the adjacent Mo atom changes from 3.740 to 4.223 Å, and the bond length of S−F₂ also increases. Therefore, a preliminary conclusion can be drawn from the above analysis that the Au−MoS₂ monolayer can effectively adsorb the SO₂F₂ molecule.

To fully analyze the adsorption capacity of the Au−MoS₂ monolayer to the SO₂F₂ molecules, it is necessary to explore the adsorption of double SO₂F₂ molecules. Therefore, we constructed all kinds of configurations with double SO₂F₂ molecules adsorbing on the Au−MoS₂ monolayer. Figure 6 shows the most stable adsorption structure of double SO₂F₂ molecules adsorbed on the Au−MoS₂ monolayer; the S−F₁ bond of the SO₂F₂ molecule is broken in the adsorption process, and the S atom and F₁ atom rebound to the Au atom. However, the other SO₂F₂ molecule keeps away from the Au modification site with a really long distance (3.778 Å) due to the repulsive force between gas molecules. The Qₜ by Mulliken for double molecules is −0.664 and −0.007, manifesting the weak interaction of the Au−MoS₂ monolayer toward the second molecule. In addition, comparing with the adsorption structures for the corresponding parameters of single and double SO₂F₂ molecule adsorption, we conclude that double gas molecule adsorption is basically similar to that of single gas molecule adsorption.

2.4. Electronic Property. To explore the interaction mechanism between the SO₂F₂ molecule and the Au−MoS₂ monolayer surface, the density of state (DOS), the molecular orbital theory (highest occupied molecule orbital, HOMO and lowest unoccupied molecule orbital, LUMO), and the electron density difference are discussed. Figure 7a₁,b₁ shows the TDOS before and after SO₂F₂ molecule adsorption, and Figure 7a₂,b₂ presents the PDOS of the characteristic atoms after SO₂F₂ molecule adsorption. For bimolecular SO₂F₂ adsorption, only one molecule is closer to the surface of the Au−MoS₂ monolayer. Therefore, only the SO₂F₂ molecule that is close to the Au−MoS₂ monolayer is analyzed in PDOS analysis.

It is obvious that SO₂F₂ molecule adsorption significantly changes the distribution of TDOS, which is mainly because of the interaction among Au 5d orbital, F 2p orbital, O 2p orbital, and S 3p orbital. For single SO₂F₂ molecule adsorption, the 6s and 5d orbitals of the Au atom, the 2p orbital of the F atom, and the 2p orbital of the O atom overlap in the range of −0.3−0 eV, as the PDOS shows in Figure 7a₂. The large overlapped area among Au 5d, F 2p, and O 2p indicates that these orbitals are highly hybridized during the adsorption process. The overlap between the F 2p orbital and the Au 5d orbital is larger than the overlap between the O 2p orbital and the Au 5d orbital, resulting in the formation of a new Au−F bond during the adsorption process. For the TDOS of double SO₂F₂ adsorption, as shown in Figure 7b₁,c₁, a large overlapping area exists among Au 5d, F₁ 2p, and S₁ 3p from −0.3 to 0 eV, indicating a strong hybridization between the SO₂F₂ molecule and the Au−MoS₂ monolayer. Comparing the changes in TDOS and PDOS, the hybridization degree of double SO₂F₂ molecule adsorption is similar to that of single SO₂F₂ molecule adsorption.

To further analyze the electronic property of the SO₂F₂ molecule adsorbed on the Au−MoS₂ monolayer, molecular orbital theory is taken into consideration. The distributions for highest occupied molecule orbital (HOMO) and lowest unoccupied molecule orbital (LUMO) are exhibited in Figure 8, and the HOMO energy (E_HOMO), LUMO energy (E_LUMO), and the energy gap (E_g) between HOMO and LUMO are also given in the figure.

![Figure 8. HOMO and LUMO distributions and related energies for Au−MoS₂ systems: (a) Au−MoS₂; (b) Au−MoS₂/SO₂F₂; and (c) Au−MoS₂/2SO₂F₂.](image_url)
Au–MoS₂ system. Therefore, we can draw a conclusion that there is chemical adsorption between the single SO₂F₂ molecule and the Au–MoS₂ monolayer. The electron density difference of the SO₂F₂ molecule adsorbed on the Au–MoS₂ monolayer with different systems is shown in Figure 9, where the increase and decrease of the electron density are represented by red and blue regions, respectively.

For single SO₂F₂ molecule adsorption, as shown in Figure 9a, both of the F atoms receive tiny electrons, while the electron density near the S atom decreases, which is in agreement with the conclusion that the SO₂F₂ molecule transfers quite a part of electrons to the adsorbent. For the double SO₂F₂ molecule adsorption, as shown in Figure 9b, the electron density near the Au atom decreases, which is similar to that of single SO₂F₂ molecule adsorption. For the SO₂F₂ molecule close to the Au atom, the electron density of the S atom suffers a decrease. For the other SO₂F₂ molecule away from the Au–MoS₂ monolayer surface, the electron density changes slightly. Therefore, we conclude that the SO₂F₂ molecule acts as the electron acceptor and the Au–MoS₂ monolayer acts as the electron donor in the SO₂F₂ molecule adsorption process. All of these indicate that there is a certain amount of electron transfer between the SO₂F₂ molecule and the Au–MoS₂ monolayer for the stable adsorption of the SO₂F₂ molecule on the Au–MoS₂ monolayer.

3. CONCLUSIONS

In this study, the interaction mechanism between the SO₂F₂ molecule and the Au–MoS₂ monolayer surface was analyzed based on DFT calculations. First, the most stable structures of SO₂F₂ and the Au–MoS₂ monolayer were discussed. Then, the most stable structures of single SO₂F₂ molecule adsorption and double SO₂F₂ molecule adsorption structures were obtained based on lots of initial adsorption structures. The density of states, HOMO and LUMO distributions, and electron density difference were analyzed to further explore its adsorption mechanism. It is found that the SO₂F₂ molecule tends to chemically adsorb on the surface of the Au–MoS₂ monolayer and the adsorption energies of the single SO₂F₂ molecule and the double SO₂F₂ molecules are up to −0.559 and −0.681 eV, respectively, indicating a strong interaction between the SO₂F₂ molecule and the Au–MoS₂ monolayer. In addition, the adsorption of the SO₂F₂ molecule can significantly change the conductivity and charge distribution of the Au–MoS₂ monolayer. Due the remarkable interaction between the SO₂F₂ molecule and the Au–MoS₂ monolayer, the Au-modified MoS₂ monolayer can be used as a promising adsorbent on removing the typical decomposition products of SF₆.

4. COMPUTATIONAL DETAILS

All of the calculations in this paper were carried out based on DFT.28−30 The generalized gradient approximation with the Perdew–Burke–Ernzerhof functional was chosen to calculate the electron exchange and correlation energy.31,32 The double numerical plus polarization was used as the basis set, and the density functional semicore pseudopotential was applied for core treatment.33,34 All of the geometry optimizations were performed with the energy tolerance accuracy, maximum force, and maximum displacement of 1.0 × 10⁻³ Ha, 2.0 × 10⁻³ Ha/Å, and 5.0 × 10⁻³ Å, respectively.35,36 The self-consistent field was set to 1.0 × 10⁻⁶ Ha.37,38 The Brillouin zone was determined by the 5 × 5 × 1 Monkhorst-Pack k-point sampling method.39,40

To avoid the interaction between adjacent structures, a 4 × 4 × 1 MoS₂ monolayer supercell with a 15 Å vacuum layer was constructed. The optimized lattice constant of MoS₂ is 3.180 Å in this study, which is consistent with other experimental and theoretical results.41 In the center of the 4 × 4 × 1 MoS₂ monolayer supercell, one Au atom was added at the top of the Mo atom, which bonds with three S atoms.

The adsorption energy (E_ads) of the gas molecule on the Au–MoS₂ monolayer is defined by eq 1 and the unit is eV, where E_{Au–MoS₂/gas mole} is the total energy of the system after adsorption and E_{Au–MoS₂} and E_{gas} represent the total energies of the Au–MoS₂ monolayer and the free gas molecule, respectively. The negative value of E_ads indicates that the adsorption process is exothermic and happens spontaneously.

\[ E_{ads} = E_{Au–MoS₂/gas} - E_{Au–MoS₂} - E_{gas} \]  

(1)

The charge transfer (Qₐds) between the gas molecule and the Au–MoS₂ monolayer can be obtained by eq 2 and the unit is e, where Qₐds represents the carried charge of the gas molecule after adsorption and Qₐds represents the carried charge of the gas molecule before adsorption. A negative Qₐds means charges transfer from the Au–MoS₂ monolayer to the gas molecule.

Figure 9. Electron density difference: (a) single SO₂F₂ adsorption and (b) double SO₂F₂ adsorption.
\[ Q_t = Q_{\text{ads}} - Q_{\text{neq}} \]  

The binding energy of the Au–MoS\(_2\) monolayer is defined in eq 3 and the unit is eV, where \( E_{\text{Au–MoS}} \) is the total energy of the Au atom-modified MoS\(_2\) monolayer and \( E_\text{Au} \) and \( E_{\text{MoS}_2} \) represent the total energy of the isolated Au atom and the intrinsic MoS\(_2\) monolayer, respectively. The negative \( E_{\text{bind}} \) indicates that the binding process is exothermic.

\[ E_{\text{bind}} = E_{\text{Au–MoS}} - E_\text{Au} - E_{\text{MoS}_2} \]  

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The authors declare no competing financial interest.

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**AUTHOR INFORMATION**

**Corresponding Author**
E-mail: yinganggui@swu.edu.cn. Tel.: +86-152-2357-2899.

**ORCID**
Yingang Gui: 0000-0003-1424-7082

**Notes**

The authors declare no competing financial interest.
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