

Physisorption and Chemisorption of SF₆ by Transition Metal-Porphyrin Structure Embedded on Graphene Surface with Different Hapticities

Hyeonhu BAE, Yongbum LEE, Hoonkyung LEE and Jin Sik CHOI*
Department of Physics, Konkuk University, Seoul 05029, Korea

Ki Chul KIM
Department of Chemical Engineering, Konkuk University, Seoul 05029, Korea

Tanveer HUSSAIN
School of Molecular Sciences, The University of Western Australia, Perth 6009, Australia

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The adsorption of sulfur hexafluoride (SF₆) by a transition metal-porphyrin structure embedded on the surface of graphene (MN₄-graphene) was evaluated using first-principles density functional theory calculations by constructing the adsorption energy profile. The mutual balance between physisorption and chemisorption was assessed by analyzing the characteristics of the interaction between each central metal atom as an adsorption center and the SF₆ molecule. CaN₄- and CrN₄-graphene had moderate adsorption energies of about -1.5 eV. The results indicate the feasibility of these species as reusable SF₆ adsorbents, even under ambient conditions. This study provides deeper insight into the adsorption of SF₆ and the potential of transition metal-porphyrin structures as SF₆ capture materials for mitigating global warming.

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I. INTRODUCTION

Sulfur hexafluoride (SF₆) is an anthropogenic chemical with an atmospheric lifetime of approximately 3200 years and high global warming potential. Despite human endeavors to reduce greenhouse gases (GHG), SF₆ emissions continue to increase linearly from year to year [1]. SF₆ is used as an insulating material in circuit breakers and gas insulated substations due to its highly dielectric nature. Non-toxic SF₆ decomposes under electric discharge into various toxic oxyfluorides, and humans could be potentially exposed to this chemical in workplaces [2,3]. It is important to detect and remove these harmful gases from the environment. Moreover, converting the unwanted byproducts into safe chemicals is crucial. Recently, based on first-principles calculations, many candidates have been designed and suggested as efficient capture materials or gas sensors [4–9]. A systematic, theoretical investigation and deeper understanding of the physical and chemical properties of SF₆ and related compounds would be instructive for the design of

efficient alternatives, reusable adsorbents, and sensitive detectors.

In this study, a transition metal-porphyrin structure embedded in graphene (MN₄-graphene) is explored as an adsorbent for SF₆, in which the gas molecules are captured via physisorption-chemisorption processes. Metal-porphyrin embedded carbon nanomaterials have previously been synthesized [10], and it has been reported that these materials exhibit high efficiency as well-known catalysts [11,12]. We previously reported the notable CO₂ and NH₃ adsorption capacity of these materials, with high selectivity, under ambient or humid conditions [13–15]. Herein, we focus on the absorption capacity of MN₄-graphene and the mechanisms of SF₆ adsorption by exploring the mutual balance between physisorption and chemisorption.

II. COMPUTATIONAL DETAILS

The energy profiles for the physisorption-chemisorption of SF₆ on MN₄-graphene were constructed by applying density functional theory (DFT) [16] as im-

*E-mail: jinschoi@konkuk.ac.kr

plemented in the Vienna ab initio simulation package (VASP), with the projector-augmented wave (PAW) method [17]. The generalized gradient approximation parameterized by Perdew-Burke-Ernzerhof (PBE) was adopted as the DFT exchange-correlation functional [18]. The zero-damping DFT-D3 method of Grimme was used to compensate the underestimated binding parameters for the physisorption process [19]. A kinetic energy cut-off of 500 eV was used for the plane-wave basis set. Interatomic spin integration was ignored. In order to avoid the unwanted interactions of adsorbed molecules between contiguous cells in the periodic cell scheme, the metal-porphyrin structure (Metal-N₄) as an adsorption center was implanted in a 6 × 6 graphene supercell, with the formula C₆₆N₄M₁ (M is a metal atom, ₂₀Ca~₃₀Zn) and a vacuum slab of 20 Å was specified. The lattice parameter of the MN₄-graphene hexagonal cell is 14.82 Å, which is based on the graphene unit cell, 2.47 Å. Brillouin zone sampling was performed within the Monkhorst-Pack scheme with a 2 × 2 in-plane mesh [20]. The convergence criteria for electronic optimization and Hellman-Feynman force in ionic relaxation were set to 10⁻⁶ eV and 0.01 eV/Å, respectively.

First, the respective structures of the free SF₆ molecule and MN₄-graphene without the adsorbate were optimized. Thereafter, to investigate the physisorption characteristics, the complexes comprising the gas molecule and adsorbent with given distances were frozen to prevent changes in the bond lengths of the adsorbate or adsorbent in the self-consistent field (SCF) cycles, in order to exclude bond breaking by chemisorption. For investigation of the chemisorption of SF₆ on MN₄-graphene, the fluorine atoms were freed while the sulfur atom remained fixed to provide constant distances from the metal atom.

The adsorption energy (E_{ads}) of each system was calculated by applying Eq. (1).

$$E_{\text{ads}} = E_{\text{total}} - E_{\text{adsorbent}} - E_{\text{SF}_6} \quad (1)$$

Here, E_{total} , $E_{\text{adsorbent}}$, and E_{SF_6} indicate the total energies of the SF₆-adsorbent complex, isolated MN₄-graphene unit cell, and free SF₆ molecule, respectively. A negative sign for the adsorption energy in this study indicates that the reaction is exothermic.

III. RESULTS AND DISCUSSION

1. Model analysis of MN₄-graphene and SF₆ molecule

The periodic cell model of MN₄-graphene and the SF₆ molecule are presented in Fig. 1. The S-F bond length in the SF₆ molecule converged to 1.60 Å, which is consistent with the results of NMR analysis (1.58 Å), with an error of ~1% [21]. The MN₄-graphene structures

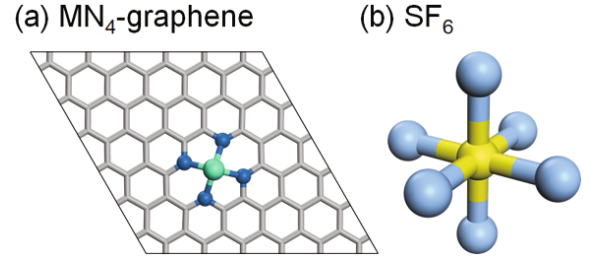


Fig. 1. (a) Top-view of metal-porphyrin structure embedded in 6 × 6 graphene supercell (MN₄-graphene). Gray, deep blue, turquoise, yellow, and pale blue denote the graphene backbone, nitrogen, transition metal, sulfur, and fluorine atoms. (b) molecular structure of SF₆.

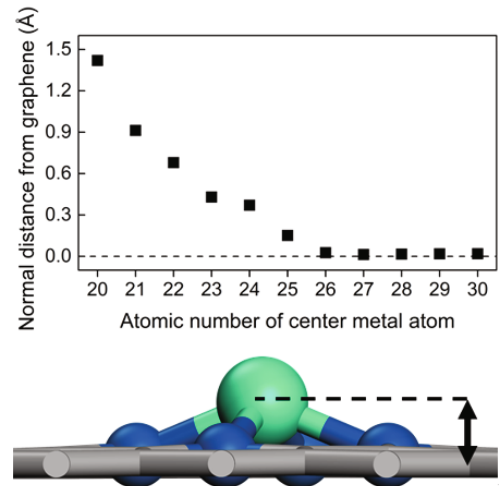


Fig. 2. Normal distance between the central metal atom and graphene sheet, for each MN₄-graphene system. Side-view of MN₄-graphene structure is shown under the graph.

were based on a 6 × 6 graphene supercell, which guarantees sufficient intermolecular separation (10 Å as a minimum) between the adsorbed molecule and molecules in adjacent cells. Ionic relaxation was carried out for various MN₄-graphene structures having 3d transition metal (₂₀Ca~₃₀Zn) atoms as the adsorption center. Calcium ([Ar] 3d⁰ 4s²) was treated as a member of the 3d transition metal family because the energy difference between the 3d and 4s level is about 0.3 eV based on our calculation.

After ionic relaxation, it was found that the distance between the central metal atoms and the graphene sheet was determined by the atomic size of the metal. For atoms with a smaller atomic number, the distance from the graphene sheet in the normal direction was larger (Fig. 2). Physisorption of the SF₆ molecules is affected by these structural characteristics and the exposed area of the adsorption center, as discussed in the following section.

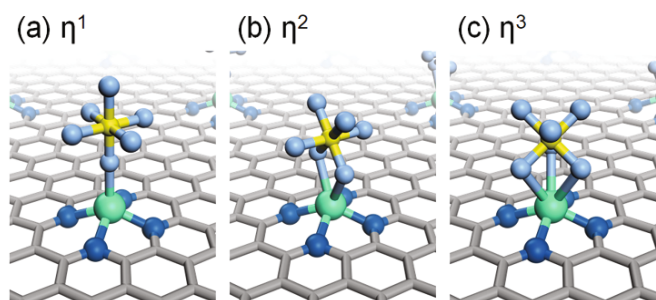


Fig. 3. Hapticity of SF₆ molecules in contact with transition metal atom as an adsorption center; the molecular coordination is shown.

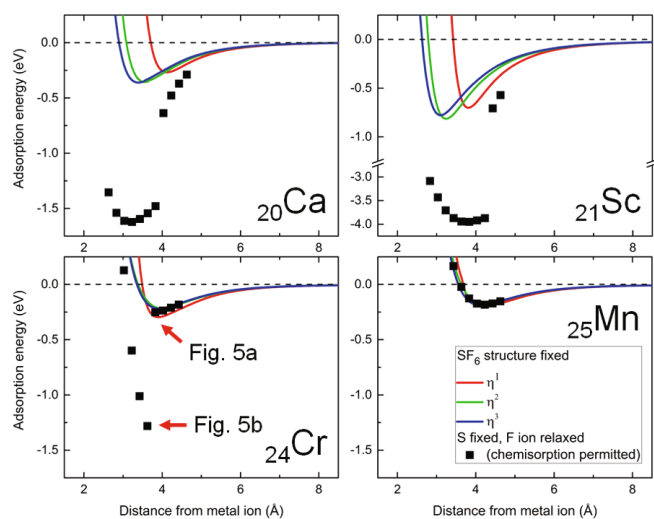


Fig. 4. Adsorption energy profiles for SF₆-(MN₄-graphene) complexes. M is (a) ²⁰Ca, (b) ²¹Sc, (c) ²⁴Cr, and (d) ²⁵Mn. Discrete data for physisorption models with η^1 , η^2 , and η^3 hapticity are smoothly connected as a red, green, and blue lines, respectively. Black, filled squares denote results from chemisorption-permitted calculation.

2. Energy profile for physisorption and chemisorption

We adopted the concept of hapticity to describe the interaction between the polyatomic molecules and the metal center in the physisorption of SF₆, although this phenomenon leads to weak interactions. The hapticity of a molecule is described by the Greek letter ‘ η (eta)’ with a superscript, which indicates the number of contiguous atoms of the ligand in contact with the ligated atom. The three types of hapticity for the SF₆ molecule are illustrated in Fig. 3. There is a tendency for an adsorbed molecule to adopt the least sterically hindered configuration [14] and to preferentially maximize the contact area. In the present case, physisorption via the molecular configurations with η^2 and η^3 hapticity seems to be preferred over that with η^1 . Chemisorption was also considered by optimizing the position of the fluorine atoms

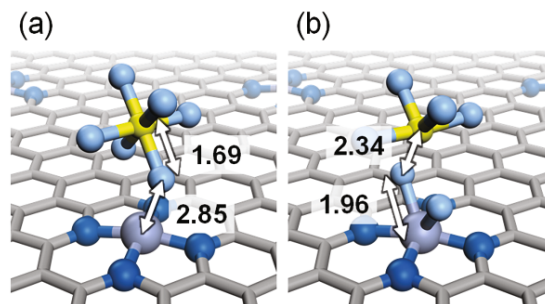


Fig. 5. Molecular structures of SF₆-(CrN₄-graphene) complex near the critical point, as indicated in Fig. 4. Bond lengths of Cr-F and S-F are shown in units of Å.

that were bound to the sulfur atom. In this case, classifying the hapticity of the adsorbate is meaningless due to fragmentation of SF₆ into F+SF₅, 2F+SF₄, *etc.*, by the catalytic effect of the metal atom.

The adsorption energy profiles for the physisorption and chemisorption of SF₆ by MN₄-graphene (M = ²⁰Ca, ²¹Sc, ²⁴Cr, and ²⁵Mn) are shown in Fig. 4. The results for ²²Ti and ²³V are omitted due to the strong binding energies of approximately -3 to -4 eV, similar to that of the ScN₄-graphene system, and the results for ²⁶Fe to ³⁰Zn as metal centers are omitted because the trends are very similar to those of the MnN₄-graphene system.

A sharp increase in the adsorption energies of the CaN₄-, ScN₄-, and CrN₄-graphene systems is apparent in Fig. 4. These discontinuities originate from the initial atomic coordinates at the beginning of the DFT calculations. The black, filled squares in the physisorption region indicate competition between the sulfur atom and metal center for the fluorine atoms, but the attractive forces between fluorine and the metal atom are not strong enough to break the S-F bond. Figure 5 presents the molecular structures of CrN₄-graphene near the critical point. One image corresponds to the SF₆ molecule retaining its structure, and the other represents fragmentation induced by the adsorption center. Figure 5(a) shows lengthening of the S-F bond by weak interaction with the metal atom, but the bond is not broken. However, if the SF₆ molecule approaches closer, the S-F bond will immediately break, as shown in Fig. 5(b). Fluorine atoms that are drawn away from the SF₆ molecule still interact with the SF₄ fragment by weak chemical interaction rather than by van der Waals interaction as the distance between the fluorine atom bound by the metal atom and the sulfur atom of SF₄ is about 2.3 Å, which is significantly less than the van der Waals bond length (~ 3.7 Å, based on the universal force field [22]). The black, filled squares under the lines in Fig. 4 suggest that SF₆ molecules approaching the CaN₄- to CrN₄-graphene structures experience stronger forces than the van der Waals forces. This is attributed to chemical attraction of the fluorine atoms facing the metal atom. However, the MnN₄- to ZnN₄-graphene systems are inert to the

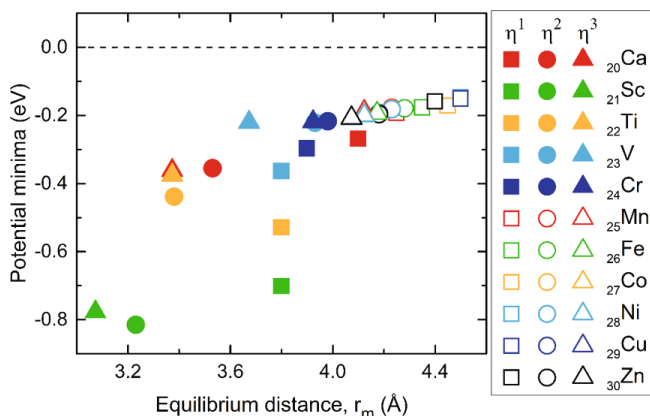


Fig. 6. Potential minima in the adsorption energy profile for physisorption of SF_6 by MN_4 -graphene systems. Chemisorption-dominated adsorbents are indicated by filled symbols and physisorption-dominated adsorbents are indicated by empty symbols.

SF_6 molecules, where the energy profiles do not differ based on the hapticity of the SF_6 molecules, compared to the former cases, and the results are similar regardless of ionic relaxation of the SF_6 molecules.

Figure 6 shows the energy minima as the SF_6 molecule approaches the MN_4 -graphene system with the structure fixed to that of free SF_6 based on the relation between the equilibrium distance in the potential well and the depth. As stated above, chemisorption dominates in the CaN_4 - to CrN_4 -graphene structures, where this process cannot be ascribed to van der Waals interaction at the metal-sulfur distance of 4.0 Å. However, the MnN_4 - to ZnN_4 -graphene structures are physisorption-dominated, where only van der Waals-like energy dispersions are observed, suggesting that these systems are not effective for SF_6 capture or decomposition.

Among these MN_4 -graphene systems, the CaN_4 - and CrN_4 -graphene structures can be used as SF_6 capture materials, in view of the energetics. Singh and co-workers [7] reported that reversible gas sensing may be possible when the adsorption energy is moderate, in-between that of physisorption and chemisorption. In cases of SF_6 -decomposition materials, adsorption energies of about -1.0 to -1.3 eV are needed to capture the harmful gas, even at dilute concentrations, and to release the gas under controlled conditions by heating the adsorbent. The adsorption energy of CaN_4 -graphene is still slightly higher than the recommended range, which led to low efficiency, whereas the adsorption energy of CrN_4 -graphene is adequate for its use as a suitable capture material with good recyclability.

IV. CONCLUSION

In this work, the physisorption-chemisorption of SF_6 on transition metal-porphyrin structures embedded in

graphene sheets (MN_4 -graphene) was discussed based on first-principles calculations. CaN_4 - and CrN_4 -graphene have moderate adsorption energies of about -1.5 and -1.3 eV, respectively and may be utilized as reusable SF_6 adsorbents, considering the thermodynamic equilibrium. ScN_4 -, TiN_4 -, and VN_4 -graphene have strong adsorption energies of about -4 eV. These compounds may prospectively exhibit good charge transfer and bandgap changing for SF_6 , as novel chemical sensors. This point will be explored more deeply in further studies. The MnN_4 - to ZnN_4 -graphene structures are inert to SF_6 .

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