Nghiên cứu lý thuyết cấu trúc và độ bền của sulfamethoxazole hấp phụ trên bề mặt rutile TiO$_2$ (001)

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TÓM TẮT

Trong những năm gần đây, sự hiểu biết về các quá trình trên bề mặt vật liệu là chủ đề quan tâm đối với các nhà khoa học. Giai đoạn hấp phụ quan trọng đối với những nhìn nhận xa hơn về các tương tác bề mặt và các phản ứng quang xúc tác. Trong nghiên cứu này chúng tôi sử dụng các tính toán lý thuyết phiếm hàm mật độ để khảo sát sự hấp phụ sulfamethoxazole (SMX) trên bề mặt rutile TiO$_2$ (001) (r-TiO$_2$). Các kết quả chỉ ra rằng quá trình SMX hấp phụ trên r-TiO$_2$ là khá mạnh với năng lượng hấp phụ khoảng -51 kcal.mol^{-1} thu được tại phiếm hàm vdW-DF2. Các cấu hình hấp phụ được làm bền chủ yếu bởi các tương tác tĩnh điện giữa nhóm >S=O với các vị trí Ti$_{5f}$. Bên cạnh đó, các liên kết hydro kiểu C/N-H···O$_b$ được đánh giá như sự bổ sung quan trọng trong việc làm bền các phức. Các phân tích AIM và sự chuyển mật độ điện tích khẳng định sự tồn tại và vai trò của các tương tác bề mặt trong quá trình hấp phụ.

Từ khóa: *Sulfamethoxazole, rutile-TiO$_2$ (001), DFT, phiếm hàm vdW.*

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Theoretical investigation on structure and stability of sulfamethoxazole adsorbed on the rutile TiO$_2$ (001) surface

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ABSTRACT

In recent years, the understanding of processes on material surfaces has drawn considerable interest from scientists. The adsorption stage is important for further insights into surface interactions and photocatalytic reactions. In this study, we use density functional theory computations to investigate the adsorption of sulfamethoxazole (SMX) molecules on the rutile-TiO$_2$ (001) surface (r-TiO$_2$). Results show that the process of SMX adsorbed on r-TiO$_2$ is quite strong with an adsorption energy of -51 kcal.mol^{-1} obtained at vdW-DF2 functional. The adsorption configurations are stabilized mainly by electrostatic interactions between >S=O group and Ti$_{5f}$ sites. Besides, the C/N-H···O$_b$ hydrogen bonds are evaluated as an important addition in stabilizing complexes. The AIM and charge density transfer analyses confirm the existence and role of surface interactions in the adsorption process.

Keywords: *Sulfamethoxazole, rutile-TiO$_2$ (001), DFT, vdW functional.*

1. INTRODUCTION

Photocatalysts have recently emerged as attractive interests and are widely applied in energy, environmental, and health fields because of their significant properties. Semiconductor materials were evaluated as an efficient approach in advanced photocatalytic processes.[1] It is noticeable that TiO$_2$ is one of the potential candidates and is commonly used for photocatalysis.[2] Besides, the rutile-TiO$_2$ (001) found considerably upon the rutile phase formation is regarded as a highly reactive, photocatalytic facet.[3-5] However, this facet has not been wholly investigated about reactions or interactions on its surface before.

In addition, sulfamethoxazole (SMX) is a wide-board antibiotic and widely used for bacterial infections. The existence of their residues in aquatic environments significantly affects to life and growth of organisms.[6,7] The removal of polluted compounds is thus paid more attention by scientists. In previous reports, materials based on TiO$_2$ were investigated to remove various organic pollutants, especially for antibiotics.[8-11] Further, adsorption is critical in complex processes on material surfaces,

including photocatalysis, sensing, and storage. Understanding of surface interactions plays an essential role in evaluating the adsorption ability and reaction mechanism.[12]

Recently, computational chemistry methods have been applied for evaluating and understanding surface phenomena.[13] Using quantum chemical calculations clarified the intermolecular interactions between molecules and material surfaces such as TiO_2.[14,15] Significantly, including van der Waals forces in computations provided a better evaluation of the adsorption ability of molecules on material surfaces.[16] However, the origin and role of surface interactions between compounds containing $>S=O$ functional groups such as sulfamethoxazole (SMX) with material surfaces, such as rutile-TiO_2 (001) facet (r-TiO_2), have not been examined entirely yet. Hence, in this work, we use quantum chemical computations to investigate the adsorption of SMX on r-TiO_2 to gain insights into the surface interactions.

2. COMPUTATIONAL DETAILS

The SMX molecule, r-TiO_2 structures, and adsorption configurations are optimized using density functional theory (DFT). The vdW-DF2 functional is used to include van der Waals forces in calculations.[17] The kinetic cut-off energy is set up at 500 eV with a 10^{-5} eV convergence index. The Brillouin zone is sampled at the Gamma center with the k-point mesh of *2 x 2 x 1*. The model slab (a = b = 18.38 Å, c = 30.00 Å) is designed with a vacuum space of 15 Å to ignore boundary interactions. The adsorption energy (E_A) is calculated by expression:

$$E_A = E_C - E_M - E_S.$$

Where E_C, E_M, E_S are energy values of optimized structures for complexes, SMX molecule, and r-TiO_2, respectively. Besides, the interaction and deformation energies are computed as follows:

$$E_I = E_C - E_M^* - E_S^*; \ E_{DM} = E_M^* - E_M; \ E_{DS} = E_S^* - E_S.$$

Here, E_I is the interaction energy. E_{DM} and E_{DS} are deformation energy values for molecule and surface. E_M^* and E_S^* are the single-point energy values of isolated SMX and r-TiO_2 in the optimized complexes. These calculations are performed by the VASP program.[18] Besides, the characteristics such as molecular electrostatic potential (MEP) map, deprotonation enthalpy (DPE), and proton affinity (PA) at sites of SMX molecule are considered at the B3LYP/6-31G(d,p) level of theory and carried out by the Gaussian 09 program.[19] The existence and strength of surface interactions are determined by the atoms-in-molecules (AIM) theory and charge density transfers at the B3LYP/6-31G(d,p) level.[20] Moreover, the hydrogen bond energy (E_{HB}) is computed from electron density potential (V(r)) through AIM analysis and followed by the expression: $E_{HB} = 0.5 \ V(r)$.[21]

3. RESULTS AND DISCUSSION

3.1. Optimized structures

Performing the optimization of the geometrical structures, we obtain four stable adsorption configurations denoted by **S1**, **S2**, **S3**, and **S4**, as shown in Figure 1.
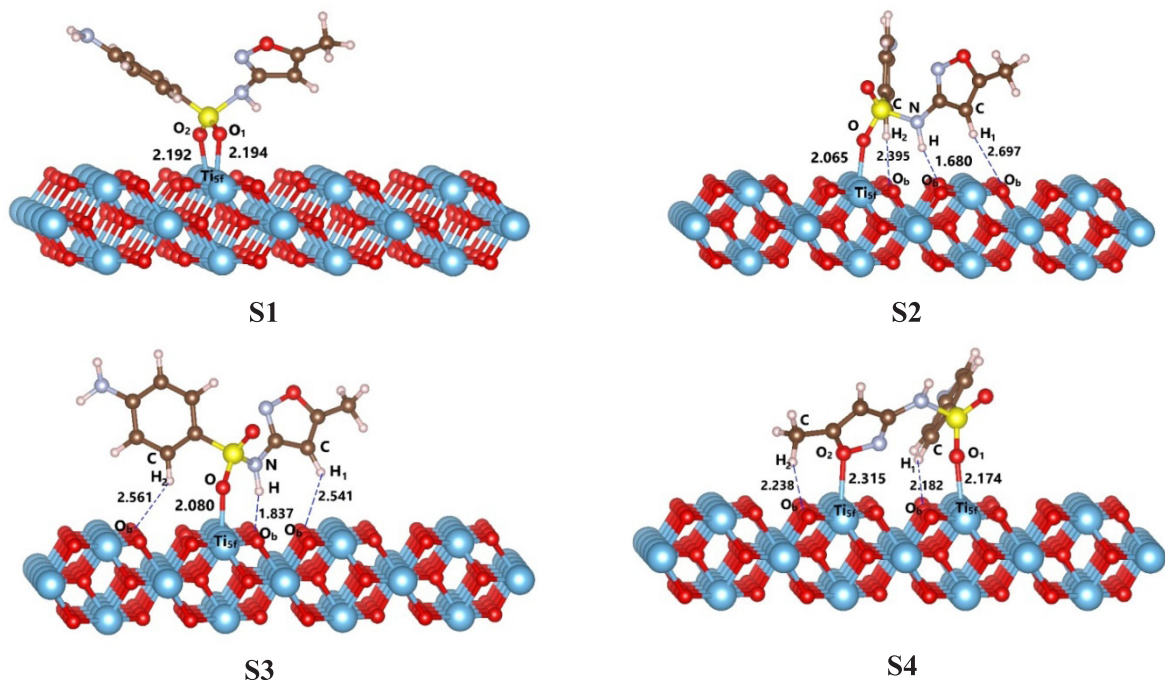
Figure 1. The stable configurations of adsorption of SMZ on r-TiO$_2$ (distances in Å)

The intermolecular distances of Ti$_{5f}$···O, H···O$_b$ contacts are in the ranges of 2.065 - 2.315 Å, 1.680 - 2.697 Å, respectively. These values are smaller than the total of van der Waals radii of atoms involved in interactions. The bonding angles between C/N-H···O$_b$ and S-O···Ti$_{5f}$ contacts range of 129.75 - 168.23° and 131.11 - 168.26°, respectively. The bond length changes in forming intermolecular interactions for C/N-H, S-O are also examined. Accordingly, the bond elongations of 0.011 - 0.037 Å, 0.033 - 0.049 Å, and 0.001 - 0.004 Å are found for S-O, N-H, and C-H bonds. Besides, the adhesion of SMX onto r-TiO$_2$ is arranged horizontally. The electrostatic interactions appear at the high negative/positive charge density sites of >S=O and Ti$_{5f}$ in configurations similar to recent reports.[22] These results are consistent with the formation of geometrical structures of other molecules adsorbed on TiO$_2$ surfaces.[14-16,22] Consequently, the stability of adsorption configurations depends on the Ti$_{5f}$···O, H···O$_b$ interactions in a horizontal arrangement of SMX on r-TiO$_2$.

3.2. Energy aspects

The adsorption, interaction, and deformation energies for the stable configurations and monomers are observed at vdW-DF2 functional as gathered in Table 1.

Table 1. The energy aspects of the adsorption configurations (in kJ.mol^{-1})

	E_A	E_I	E_{DS}	E_{DM}
S1	-167.3	-215.0	29.9	17.9
S2	-190.4	-237.6	25.7	21.5
S3	-187.7	-220.8	13.9	19.2
S4	-214.4	-247.5	22.7	10.4

The calculated results imply that the E_{ads}, E_{int} values are in the range of -167.3 to -214.4, -215.0 to -247.5 kJ.mol^{-1}, respectively, and decrease similarly in the order of **S1 > S3 > S2 > S4**. Therefore, **S4** is the most stable complex, and **S1** is the less stable one. It is noted that **S4** is stabilized by two Ti$_{5f}$···O interactions and C-H···O$_b$ hydrogen bonds while the stability of **S1** is contributed significantly by two Ti$_{5f}$···O interactions. The strength of **S2** and **S3** is based on one Ti$_{5f}$···O interaction and N/C-H···O$_b$ hydrogen bonds. Hence, the stability of complexes mainly depends on Ti$_{5f}$···O electrostatic interactions and the essential addition of C/N-H···O$_b$ hydrogen bonds. Besides, the adsorption of SMX on the

(001) facet of rutile-TiO$_2$ is slightly weaker than that for other antibiotics.[14] It is due to the horizontal arrangement of these molecules on TiO$_2$ being more convenient than SMX. At >C=O, -COOH groups, the negative charge density is higher than at >S=O. Consequently, stable intermolecular contacts are favorably formed in these systems as compared to SMX-TiO$_2$.

In addition, the deformation energy is an essential factor in evaluating the interaction ability and separation of the molecule on the material surface upon the adsorption process. Table 1 shows that the deformation energy values for r-TiO$_2$ (E$_{DS}$) and SMX (E$_{DM}$) are ca. 13.9 - 29.9 kJ.mol^{-1}, and 10.4 - 21.5 kJ.mol^{-1}, respectively. It can be seen that a more considerable change in geometry of r-TiO$_2$ following the complexation in comparison to SMX. Calculated results are

similar to rutile-TiO$_2$ (110) surface changes following the adsorption of molecules containing functional groups on its surface.[14,15,22] Particularly, the E$_{DS}$ and E$_{DM}$ values of rutile-TiO$_2$ surface and molecules in these reports are of 10.5 - 56.5 kcal. mol^{-1} and 3.3 - 54.0 kJ.mol^{-1}, respectively. Indeed, the interaction between SMX and r-TiO$_2$ causes slight changes of the isolated geometries for the surface and molecule upon complexation.

3.3. Existence and role of surface interactions

3.3.1. MEP analysis and DPE, PA at sites of molecules

To evaluate the formation ability of intermolecular interactions, we carried out computations on characteristics of molecules including MEP and DPE, PA at sites. The calculated results are illustrated in Figure 2 and given in Table 2.
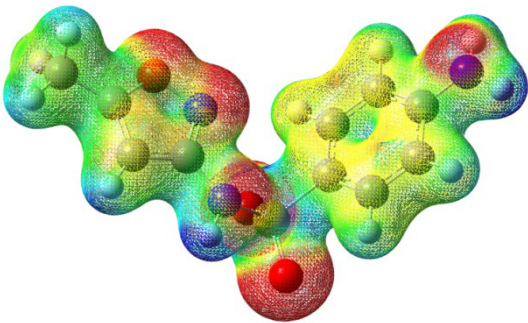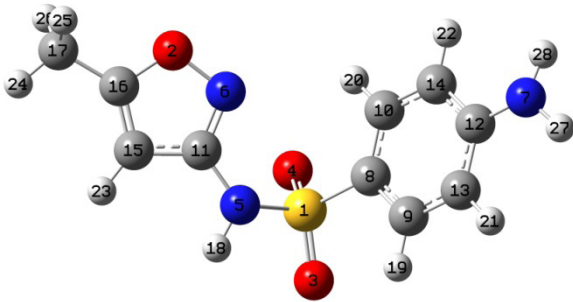

Figure 2. The optimized geometry and MEP map of sulfamethoxazole at B3LYP/6-31G(d,p) level (electron density = 0.02 au; region of -5.10^{-5} to 0.20 au)

Table 2. The deprotonation energy (DPE) and proton affinity (PA) at bonds and atoms in sulfamethoxazole at B3LYP/6-31G(d,p) level (all given in kJ.mol^{-1})

	N$_5$-H$_{18}$	N$_7$-H$_{27}$	C$_{13}$-H$_{21}$	C$_9$-H$_{19}$	C$_{17}$-H$_{24}$	C$_{15}$-H$_{23}$
DPE	1482.0	1552.7	1691.2	1689.5	1700.8	1666.5
	O$_3$	O$_4$	O$_2$	N$_6$	N$_5$	N$_7$
PA	888.7	956.0	766.1	977.0	925.9	869.4

The MEP map for sulfamethoxazole indicates that the O$_{(2,3,4)}$ and N$_{(5,6,7)}$ sites have high negative electron densities (red color regions). These sites strongly interact with positive charge regions at Ti$_{5f}$ on r-TiO$_2$ to form Ti$_{5f}$···O attractive electrostatic interactions, especially at >S=O group. Meanwhile, the significant positive regions at H atoms (in C-H, N-H bonds) conveniently interact with the negative charge

sites at O$_b$ lying on the surface to form C/N-H···O$_b$ stable hydrogen bonds.

As presented in Table 2, the proton affinity of atoms decreases in the order of N$_6$ > O$_4$(O$_3$) > N$_5$ > N$_7$ > O$_2$. The electrostatic interactions between O/N sites with the Ti$_{5f}$ on r-TiO$_2$ are thus stable, especially at N$_6$ and O$_4$ sites. Besides, the hydrogen bonds formed between H atoms and O$_b$ on r-TiO$_2$ are more favorable

at N_5-H_{18} than at N_7-$H_{28/27}$ as compared to C-H bonds. This is understood that the DPE values of N-H are smaller than those of C-H bonds (cf. Table 2). Indeed, the interactions between SMX and r-TiO$_2$ are favorable at the opposite regions of high charge density as well as at the sites that have strong proton affinity or slight deprotonation energy.

3.3.2. AIM analysis and electron density transfers

The characteristics of topological geometries for the first-layered structures are displayed in Figure 3 and listed in Table 3. The electron density transfers upon complexation are also displayed in Figure 4 for whole adsorption configurations.
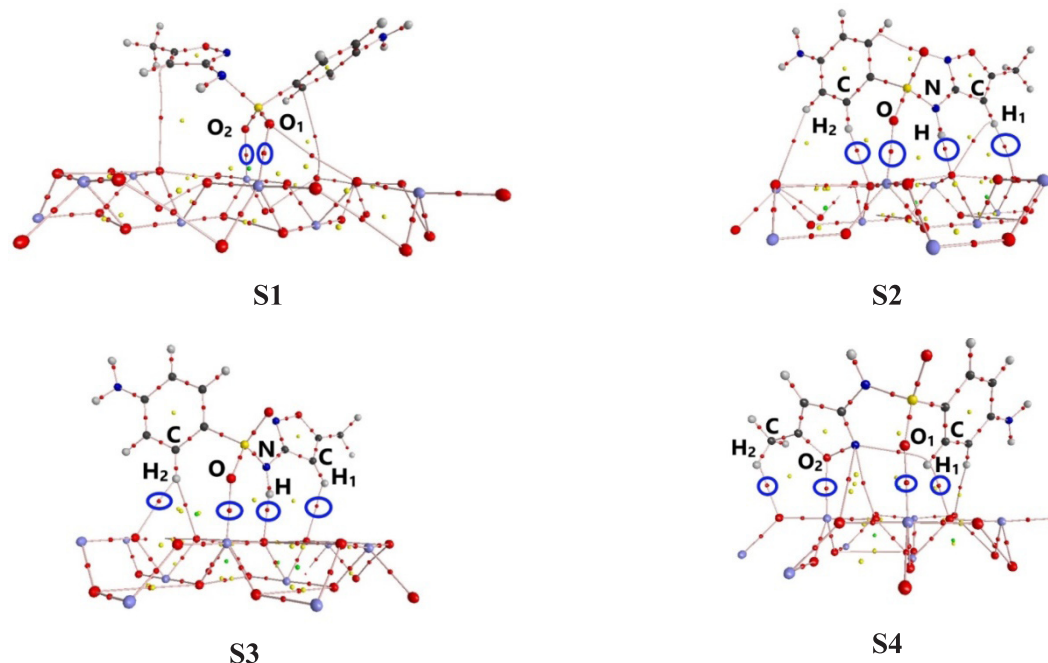

Figure 3. The topological geometries for first-layered structures of complexes
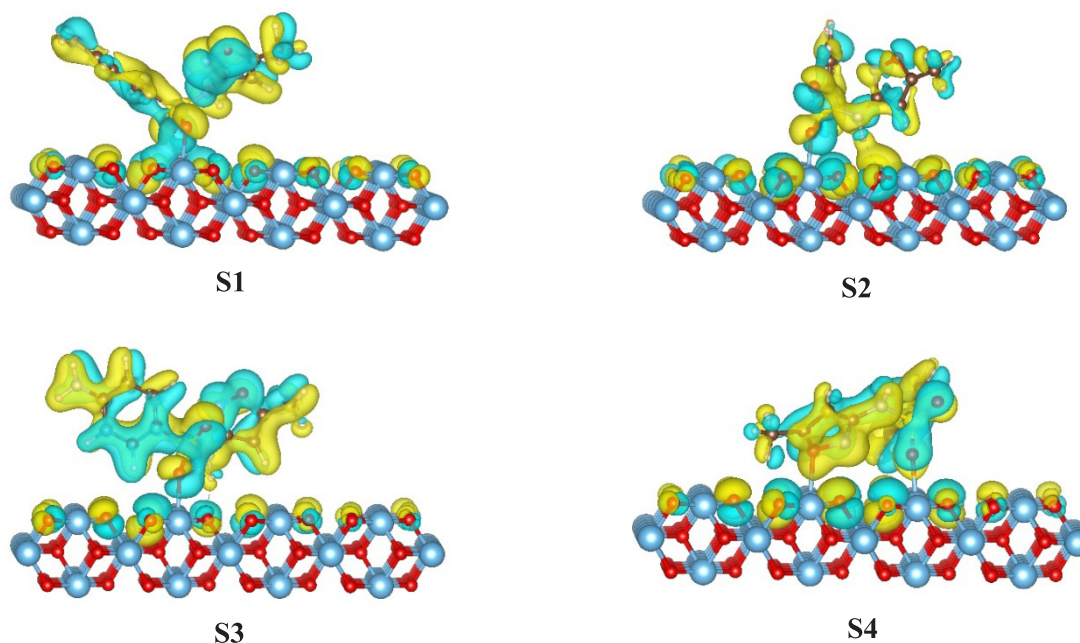

Figure 4. The charge distribution upon complexation

Table 3. The AIM analysis for structures in Fig.3 at the B3LYP/6-31G(d,p) level ($\rho(r)$, $\nabla(\rho(r))$, $H(r)$ (in au); E_{HB} (in kJ.mol^{-1}))

	BCPs	$\rho(r)$	$\nabla(\rho(r))$	$H(r)$	E_{HB}
S1	$O_1 \cdots Ti_{5f}$	0.046	0.265	0.005	
	$O_2 \cdots Ti_{5f}$	0.046	0.264	0.005	
S2	$O \cdots Ti_{5f}$	0.064	0.373	0.002	
	$N-H \cdots O_b$	0.048	0.127	-0.008	-62.2
	$C-H_1 \cdots O_b$	0.007	0.021	0.001	-4.1
	$C-H_2 \cdots O_b$	0.011	0.034	0.001	-7.8
S3	$O \cdots Ti_{5f}$	0.063	0.358	0.001	
	$N-H \cdots O_b$	0.033	0.089	-0.002	-35.7
	$C-H_1 \cdots O_b$	0.008	0.027	0.001	-5.1
	$C-H_2 \cdots O_b$	0.009	0.029	0.001	-6.2
S4	$O_1 \cdots Ti_{5f}$	0.045	0.281	0.007	
	$O_2 \cdots Ti_{5f}$	0.035	0.182	0.004	
	$C-H_1 \cdots O_b$	0.017	0.052	0.001	-13.9
	$C-H_2 \cdots O_b$	0.019	0.065	0.002	-17.2

Figure 3 shows that the BCPs are found between $Ti_{5f} \cdots O$, $H \cdots O_b$ intermolecular contacts. As presented in Table 3, the electron density ($\rho(r)$) values of $Ti_{5f} \cdots O$, $H \cdots O_b$ BCPs are of 0.035 to 0.064 au, 0.007 to 0.048 au, respectively. These intermolecular contacts are thus regarded as non-covalent interactions.[20] It can be confirmed further by the slightly positive values of $H(r)$ at most of $Ti_{5f} \cdots O$, $H \cdots O_b$ BCPs. Noticeably, the $N-H \cdots O_b$ contacts in **S2**, **S3** have negative $H(r)$ values of -0.01 au, indicating their partly covalent nature. The large $\rho(r)$ values at $Ti_{5f} \cdots O$ BCPs imply their high strength and significant contribution to the stability of complexes. Moreover, the hydrogen bond energy (E_{HB}) values are calculated and listed in Table 3. Accordingly, the more negative values of E_{HB} in **S2** imply the more significant contribution of hydrogen bonds to its stability as compared to **S3**, **S4**, and **S1**. The cooperation of two $Ti_{5f} \cdots O$ stable interactions and hydrogen bonds brings the considerable strength of **S4** as related to other ones. Indeed, the adsorption ability of SMZ on the (001) facet of rutile-TiO_2 is quite strong.

The electron density transfer (EDT) is one of the crucial characteristics to determine the existence and strength of intermolecular interactions. The considerable transfers of electron density in complexes lead to form stable interactions. The calculated EDT values for **S1**, **S4** are 0.057 e and 0.011 e, implying the more substantial electron density transfers from SMX to r-TiO_2 to form $Ti \cdots O$ contacts than the reverse transfers from r-TiO_2 to SMX to form $O \cdots H$ hydrogen bonds. In contrast, the EDT values for **S2** and **S3** are -0.033 and -0.012 e, indicating the more substantial electron density transfers from r-TiO_2 to SMX than the reverse transfers from SMX to r-TiO_2. Therefore, it can be suggested that the $Ti_{5f} \cdots O$ and $H \cdots O_b$ intermolecular interactions exist following the complex formation.

4. CONCLUSIONS

The stable complexes for adsorption of the SMX molecule on the rutile TiO_2 (001) surface are examined at vdW-DF2 functional. The adsorption energy of the complexes is in the range of -167.3 to -214.4 kJ.mol^{-1}. The main contribution is determined by the attractive electrostatic forces between >S=O group and Ti_{5f} site, while the vital addition of the N/C-H $\cdots$ O hydrogen bonds is found in stabilizing of adsorption configurations. AIM analysis indicates that the interactions between >S=O $\cdots Ti_{5f}$ and N/C-H $\cdots O_b$ mostly have non-covalent in nature. It is noticeable that the C/N-H $\cdots O_b$ partly covalent hydrogen bonds play a crucial addition in stabilization. Furthermore, the electron density transfers occur significantly from SMX to r-TiO_2 following the formation of the interaction. Indeed, the process of SMX adsorbed on the surface of r-TiO_2 is evaluated as chemical adsorption.

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