TẠP CHÍ KHOA HỌC
TRƯỜNG ĐẠI HỌC QUY NHƠN

Nghiên cứu lý thuyết sự hấp phụ sulfamethoxazole trên bề mặt rutile-TiO_2 (110) bằng phương pháp hóa học lượng tử

Nguyễn Ngọc Trí*, Nguyễn Tiến Trung

Phòng thí nghiệm Hóa học tính toán và Mô phỏng, Khoa Khoa học Tự nhiên, Trường Đại học Quy Nhơn, Việt Nam

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TÓM TẮT

Sự hấp phụ sulfamethoxazole (SMX) trên bề mặt rutile-TiO_2 (110) (r-TiO_2) được khảo sát bằng các tính toán hóa học lượng tử. Quá trình này được đánh giá là hấp phụ hóa học với năng lượng tương ứng khoảng 20 kcal. mol^{-1} cùng với sự hình thành các tương tác tĩnh điện O···Ti_{5f}. Các cấu trúc bền hình thành trong quá trình sắp xếp phân tử SMX lên trên bề mặt r-TiO_2 được phân tích chi tiết. Sự tồn tại và vai trò của các tương tác bề mặt trong quá trình tạo phức được làm rõ dựa trên các phân tích AIM và NBO. Đáng chú ý, sự tương tác khá mạnh giữa phân tử SMX với bề mặt r-TiO_2 tập trung tại nhóm >S=O và các vị trí Ti_{5f}. Các liên kết hydro kiểu N/C-H···O đóng vai trò bổ trợ trong việc làm bền các phức thu được.

Từ khóa: *Thuyết phiếm hàm mật độ, sulfamethoxazole, rutile-TiO_2 (110), bề mặt vật liệu.*

**Tác giả liên hệ chính.*
Email: nguyenngoctri@qnu.edu.vn

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Theoretical study on adsorption of sulfamethoxazole on rutile-TiO_2 (110) surface using quantum chemical method

Nguyen Ngoc Tri*, Nguyen Tien Trung

Laboratory of Computational Chemistry and Modelling (LCCM), Faculty of Natural Sciences, Quy Nhon University

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ABSTRACT

The adsorption of sulfamethoxazole (SMX) molecule on rutile-TiO_2 (110) surface (r-TiO_2) is examined by using quantum chemical computations. This process is evaluated as chemisorption with associated energies *ca.* 20 kcal.mol^{-1} and determined mainly by O···Ti_{5f} electrostatic interactions. The stable configurations are observed in detail following the arrangement of SMX on r-TiO_2. The existence and role of surface interactions are clarified by AIM and NBO analyses upon complexation. It is noticeable that the stable interactions between SMX and r-TiO_2 are mainly focused on >S=O groups and Ti_{5f} sites. The hydrogen bonds of the N/C-H···O_b type play an additional role in the stabilization of complexes.

Keywords: *DFT, sulfamethoxazole, rutile-TiO_2 (110), material surface.*

1. INTRODUCTION

Sulfamethoxazole (SMX) is one of the sulfonamide antibiotics and is widely used for bacterial infections. The overuse of SMX affected aquatic environments such as low quality and pollution because of their deposition, which can cause genetic mutations and the growth of organisms.[1-3] Many previous studies were performed with the aim to remove SMX and polluted compounds.[4-10] It is noted that nanomaterials based on chemical oxidation were remarkably applied in many cases, such as energy, health, and life sciences.[6] Recently, photocatalytic technologies have emerged as an efficient solution for water treatment. The semiconductor photocatalysts are primarily low-cost, non-toxic, and considered the most promising environmental protection materials.[6-8] Remarkably, TiO_2, regarded as one of the potential candidates, has been commonly used for many fields of photocatalysis and the environment. Among the phase surfaces of TiO_2, rutile-TiO_2 (110) (denoted by r-TiO_2) is the most stable surface and investigated widely on the removal of organic pollutants because of its exciting properties.[11-13] In previous reports, materials based on TiO_2 such as TiO_2-Fe, Bi_2O_3-TiO_2, TiO_2-zeolite were investigated for the removal of sulfonamides.[4-6] However, the formation and role of surface interactions between compounds containing > S=O functional groups such as SMX with material surfaces, especially TiO_2, have not yet been examined in detail. Moreover, investigations on the adsorption mechanism of

**Corresponding author.*
Email: nguyenngoctri@qnu.edu.vn

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substances on the r-TiO_2 have recently been of considerable interest because of their importance to understanding surface phenomena.[12-16] Hence, it is necessary to investigate the interaction between the SMX molecule and the r-TiO_2 to clarify intermolecular forces and their contributions to the adsorption process. This work provides a basic understanding of surface phenomena and the removal ability of SMX antibiotics by using semiconductor materials, especially TiO_2. Besides, quantum chemistry calculation is emerging as a highly efficient approach for evaluating the adsorption process as well as an understanding of characteristics of surface interactions.[12] In the present work, we use density functional theory (DFT) calculations to observe the adsorption of SMX on r-TiO_2.

2. COMPUTATIONAL METHOD

The structures of SMX and r-TiO_2 are considered from experimental data and then optimized by using the VASP program.[17] The stable configurations of adsorption of SMX on r-TiO_2 are obtained from density functional theory (DFT) calculations at PBE functional by VASP. The cut-off energy is considered at 500 eV with *2 x 2 x 1* k-points at the Gamma-centered grids. The force constant on the atoms and ions is set up at 0.01 meV for geometry optimization and energetic aspects computation. The unit cell is designed with dimensions size of *14.85 x 13.15 x 25.00* Å. The valence electron configurations used in the calculation are Ti $3d^24s^2$, O $2s^22p^4$, S $3s^23p^4$, N $2s^22p^5$, C $2s^22p^2$, H $1s^1$ implemented in the PAW pseudopotentials, respectively. The adsorption energy (E_{ads}), interaction energy (E_{int}), and deformation energies ($E_{def\text{-}mol}$, $E_{def\text{-}surf}$) are calculated as follows:

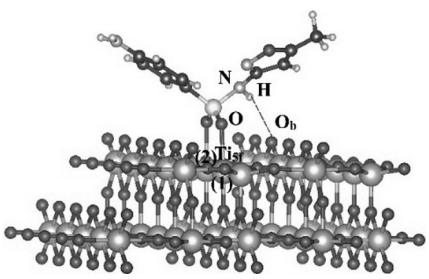
$$E_{ads} = E_{comp} - E_{mol} - E_{surf};\ E_{int} = E_{comp} - E_{mol}^{\#} - E_{surf}^{\#};\ E_{def\text{-}mol} = E_{mol}^{\#} - E_{mol};\ E_{def\text{-}surf} = E_{surf}^{\#} - E_{surf}.$$

Where E_{comp}, E_{mol}, E_{surf} are energy values of optimized structures for complexes, SMX molecule, and r-TiO_2, respectively. The $E_{mol}^{\#}$, $E_{surf}^{\#}$ are the single-point energy values of molecule and surface part from the optimized complex. In addition, the formation of surface interactions and their role in the stability of complexes are analyzed using the atoms-in-molecules (AIM) and the natural bond orbital (NBO) approach. Topological geometries of stable structures are observed by the AIM2000 program at the B3LYP/6-31G(d,p) level of theory.[19] The electron density transfers between SMX and r-TiO_2 in complexes are calculated by the NBO5.G package integrated into Gaussian 03 program at the B3LYP/6-31G(d,p) level.[18,20]

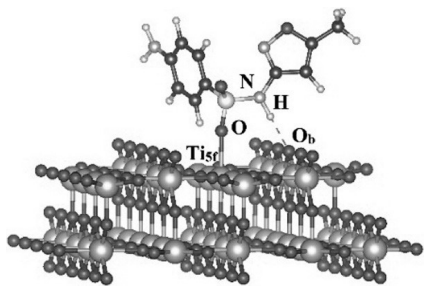
3. RESULTS AND DISCUSSION

3.1. Geometrical structures

Using DFT calculations, four stable structures of the adsorbent-surface complexes between SMX and r-TiO_2 are observed, as displayed in Figure 1. The stability of complexes is mainly due to the interactions between functional groups, including > S=O, C/N-H in SMX and Ti_{5f} and O_b sites on the surface of r-TiO_2. This result is consistent with the trend of forming intermolecular interactions for adsorption of organic molecules on TiO_2 surfaces in previous studies.[12-16] Besides, the selected parameters for the formation of interactions upon complexation are listed in Table 1.



P1



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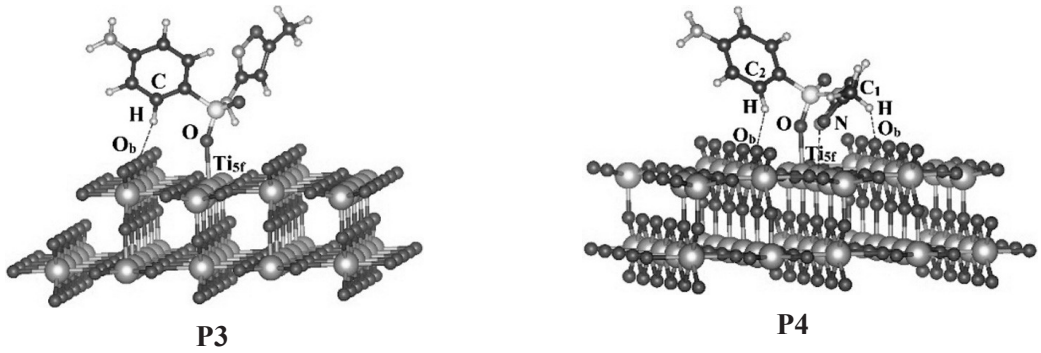

Figure 1. Optimized structures for adsorption of SMZ on r-TiO_2

Table 1. Some selected parameters of stable complexes in Figure 1 (distances (d) and change of bond length (Δr) in Å, angle (α) in °)

	d(Ti···O/N)	d(N/C-H···O)	α(S-O···Ti)	α(N/C-H···O)	Δr(S-O)	Δr(N/C-H)
P1	2.34(1)/2.31(2)	2.70	125.7-126.4	150.8	0.017-0.027	0.008
P2	2.25	1.87(3)/2.69(4)	171.4	177.1(3)/146.6(4)	0.023	0.017(3)/0.002(4)
P3	2.28	2.15(4)	160.2	155.4(4)	0.024	0.001(4)
P4	2.29(1)/3.38-3.10(2)	2.49-2.65(4)	164.8	112.1;103.3(4)	0.017	0.002-0.004(4)

((1), (2), (3), (4) for Ti···O, Ti···N, N-H (N-H···O), and C-H (C-H···O), respectively)

The calculated results show that the distances of Ti_{5f}···O, Ti_{5f}···N intermolecular interactions in the complexes are in the range of 2.25-2.34 Å and *ca.* 3.10 Å (Table 1), respectively. The Ti_{5f}···O contacts are close to the length of Ti-O bonds in the rutile phase (1.8-2.1 Å).[21] Besides, the H···O_b distances in complexes are *ca.* 1.87-2.70 Å, smaller than the total van der Waals radii of the H and O atoms (2.72 Å). Accordingly, the Ti_{5f}···O and H···O_b contacts are suggested in the adsorption configurations. Moreover, the change in length of S-O bonds of 0.017-0.027 Å is larger than that of C/N-H bonds (ca. 0.001-0.017 Å) upon complexation. The angles of S-O···Ti_{5f} and C/N-H···O_b following the interaction range from 125.7° to 164.8° and from 103.3° to 177.1°, respectively. The interaction distances and the changes in bond length as well as the contact angle in the configurations, are similar to previous studies on adsorption of organic molecules, antibiotics onto r-TiO_2.[12,13,22] Noticeably, the electrostatic interactions focus on > S=O and Ti_{5f} sites in the horizontal arrangement of SMX on r-TiO_2 as found in *ref. 22*. Furthermore, the elongation of > S=O bonds of 0.017-0.027 Å is slightly smaller than that of > C=O in the antibiotic molecules upon the adsorption process.[12,13,22] This result is due to the larger polarizability of > C=O compared to the > S=O group. Moreover, the calculated angles of S-O···Ti_{5f} range from 126 to 171°, slightly larger than that of C-O···Ti_{5f} (ca. 134-163°) upon complexation.[22]

3.2. Energetic aspects of the adsorption process

The energy components upon the adsorption of SMX on r-TiO_2 are calculated and gathered in Table 2. The adsorption energies (E_{ads}) of the complexes are quite negative, in the range of -12.8 to -20.4 kcal.mol^{-1} and increase in the ordering of **P1** < **P4** < **P2** < **P3**. In addition, the interaction energies of the complexes tend to change in the same order with E_{ads} values. Hence, **P1** is evaluated as the most stable configuration of adsorption of SMX on r-TiO_2, and the least stable one is **P3**. It can be found that two electrostatic interactions of Ti_{5f}···O (**P1**) or Ti_{5f}···O and Ti_{5f}···N (**P4**) are formed and contribute mainly to the stabilization of configurations. For the **P2**

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or **P3**, only one $Ti_{5f}\cdots O$ electrostatic interaction exists upon complexation. As a consequence, the electrostatic interactions such as $Ti_{5f}\cdots O$ and $Ti_{5f}\cdots N$ play an essential role in the significant strength of **P1**, **P4**. Besides, the adsorption of SMX on r-TiO_2 is slightly weaker than that for antibiotic molecules, which contain > C=O, -COOH groups.[12,22]

Table 2. Adsorption energy (E_{ads}), interaction energy (E_{int}), and deformation energies for molecule ($E_{d\text{-}mol}$), for surface ($E_{d\text{-}surf}$) following adsorption process (all in kcal.mol^{-1})

	P1	P2	P3	P4
E_{ads}	-20.4	-16.3	-12.8	-18.1
E_{int}	-29.8	-22.3	-18.0	-24.7
$E_{d\text{-}mol}$	3.3	1.1	1.1	1.9
$E_{d\text{-}surf}$	6.1	4.9	4.1	4.7

Deformation energy of molecule and material surface in adsorption process is an important factor in considering interaction ability and separation of the molecule on the material surface. As shown in Table 2, the deformation energy values for r-TiO_2 and SMX in the investigated configurations are in turn in the range of 4.1-6.1 kcal.mol^{-1}, and 1.1-3.3 kcal.mol^{-1}. This result indicates a stronger distortion of r-TiO_2 in comparison to SMX. The energy values in this work are slightly smaller than those in the configurations for the adsorption of molecules containing > C=O, -COOH, -NH_2, -OH functional groups on r-TiO_2.[12,13,22] As a result, the adsorption of SMX on the surface of r-TiO_2 causes smaller changes of the isolated geometries than in previous investigations.[12,13,22]

3.3. Topological geometry and electron density transfer

In order to have deep insight into the characteristics of surface interactions in the adsorption process, we performed calculations on topological geometry based on AIM theory and electron density transfers from the NBO approach. In these computations, the first layered structures of the configurations are considered due to the changes of geometrical, electronic structures, as well as their properties are mainly focused on the first layer of r-TiO_2.[12,13,22] The topological geometries for the investigated structures are displayed in Figure 2. The selected results of AIM analyses and the electron density transfers are given in Table 3.

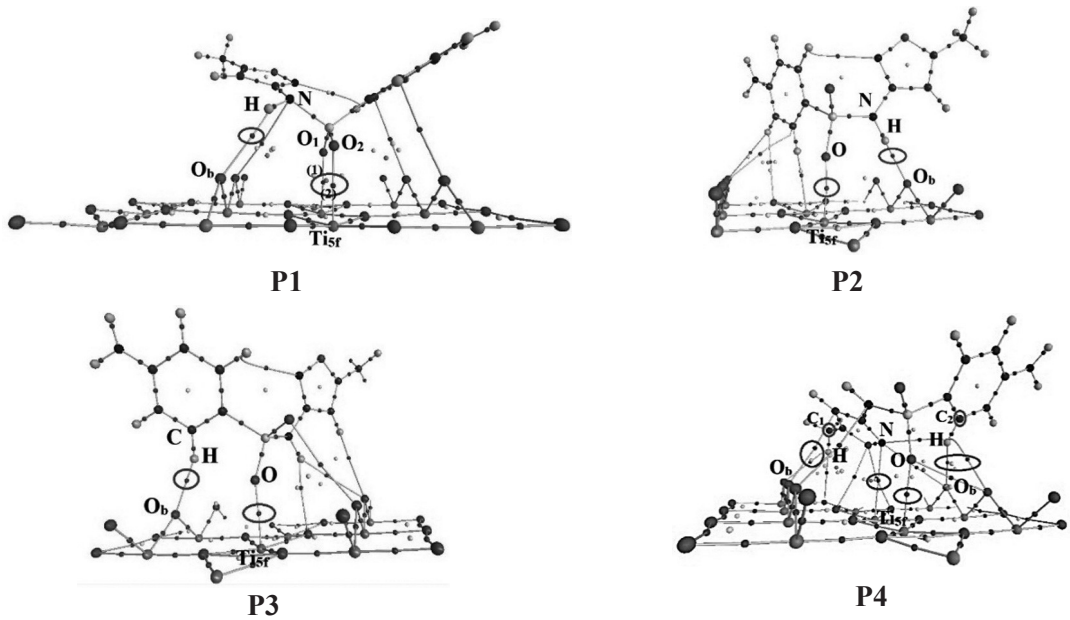

Figure 2. Topological geometries of the first-layered structures of the complexes

Table 3. Electron density (ρ(r), au), Laplacian (∇(ρ(r)), au), total electron density energy (H(r), au) at bond critical points (BCPs) and electron density transfers (EDT, e), intermolecular hyper-conjugative energy (E^2, kcal.mol^{-1}) in the first-layered structures of complexes

	BCPs	ρ(r)	∇(ρ(r))	H(r)	EDT	Transfers	E^2
P1	O···$Ti_{5f(1)}$	0.034	-0.041	0.004	0.21	n(O) → LP*(Ti), BD*(Ti-O)	11.68
	O···$Ti_{5f(2)}$	0.041	-0.056	0.001		n(O) → LP*(Ti), BD*(Ti-O)	19.55
	N-H···O_b	0.005	-0.005	0.001		n(O) → BD*(N-H)	0.87
P2	O···Ti_{5f}	0.043	-0.062	0.003	0.29	n(O) → LP*(Ti), BD*(Ti-O)	26.13
	N-H···O_b	0.029	-0.039	-0.001		n(O) → BD*(N-H)	10.55
P3	O···Ti_{5f}	0.040	-0.054	0.003	0.22	n(O) → LP*(Ti), BD*(Ti-O)	22.34
	C-H···O_b	0.018	-0.020	0.001		n(O) → BD*(C-H)	3.46
P4	O···Ti_{5f}	0.039	-0.053	0.003	0.26	n(O) → LP*(Ti), BD*(Ti-O)	21.85
	N···Ti_{5f}	0.012	-0.010	0.000		n(N) → LP*(Ti), BD*(Ti-O)	2.27
	C_1-H···O_b	0.010	-0.009	0.002		n(O) → BD*(C-H)	0.83
	C_2-H···O_b	0.011	-0.010	0.002		n(O) → BD*(C-H)	0.63

((1), (2) as shown in Figures 1 and 2)

Table 3 implies that the values of electron density (ρ(r)) at the bond critical points (BCPs) of Ti_{5f}···O, Ti_{5f}···N, H···O_b contacts range from 0.034 to 0.043 au, *ca.* 0.012 au and from 0.005 to 0.029 au, respectively. All values are within the range of non-covalent interactions.[19] Hence, these intermolecular interactions have non-covalent in nature. The slightly positive values of H(r) at the Ti_{5f}···O, Ti_{5f}···N, H···O_b BCPs imply further the non-covalent properties of these contacts, except for the H···O_b contact in **P2**. It is noteworthy that the Ti_{5f}···O/N interactions in the complexes have quite large ρ(r) values, implying their remarkable stability, and contribute considerably to the strength of complexes. Consequently, the **P1** and **P4** complexes are more stable than the **P2** and **P3** ones. The addition of the N-H···O_b hydrogen bond in the **P2** complex induces its higher stability relative to **P3**. These obtained results are in good agreement with the data taken from Table 2 and similar to the previous studies.[12,13,22] Moreover, the calculated results indicate that the ρ(r) values at O···Ti BCPs in **P1** are smaller than those in complexes of AP, AX, TC in *ref.22*. It is noted that in AP, AX, and TC systems, the important addition of O-H···O hydrogen bonds leads to the high stability the of complexes. As a result, the adsorption ability of SMZ on TiO_2 is weaker than that for AP, AX, TC.

The total electron density transfer (EDT) in the complexes is a characteristic for forming intermolecular interactions. As presented in Table 3, the EDT values are positive, implying the stronger electron density transfers from SMX to r-TiO_2 compared to the reverse transfers from r-TiO_2 to SMX. It is noted that the electron density transfers from the lone pairs of O in SMX (n(O) to the unoccupied lone pairs of Ti (n*(Ti)) and the anti-bonding orbitals (σ*(Ti-O)) are quite strong with the large hyper-conjugated energies (E^2) in the range of 12-26 kcal.mol^{-1}. These transfers are much stronger than the reverse ones from n(O) (in r-TiO_2) to σ*(N/C-H) (in SMX), which have E^2 values in the range of 1-11 kcal.mol^{-1}. Thus, it affirms that there exist the Ti_{5f}···O and H···O_b intermolecular interactions following complexation. The electron density transfer to form the Ti···N contact in **P4** is found with a small E^2 value of *ca.* 2 kcal.mol^{-1}. Besides, the formation of N-H···O_b hydrogen bond with a large E^2 value implying that it plays a considerably additional role in stabilizing **P2** in comparison

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to C-H···O in **P3**. The considerable transfers of electron density in **P1** with high values of E^2 lead to stable interactions as compared to that in the rest complexes. These are consistent with the trend of adsorption energy as analyzed above.

4. CONCLUSION

Four stable complexes for adsorption of the SMX molecule on the surface of r-TiO_2 were located at PBE functional. The calculated adsorption energy of the complexes is about 20 kcal.mol^{-1}. The stability of configurations is mainly contributed by the attractive electrostatic forces between the O atom of > S=O group (SMX) and the Ti_{5f} site (r-TiO_2) and an addition of the N/C-H···O hydrogen bonds. AIM analysis indicates that the interactions between > S=O···Ti_{5f} and N/C-H···O have non-covalent in nature. Furthermore, the NBO results show that the electron density transfers occur significantly from SMX to r-TiO_2. The obvious existence and significant importance of Ti_{5f}···O interaction contributing to the complexes' strength are determined by a high hyper-conjugated energy value of 26 kcal.mol^{-1}. The obtained results show that the adsorption process of SMX on the surface of r-TiO_2 is chemical adsorption.

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