

Adsorption of quaternary ammonium salt hydrophobic modifiers on the α -quartz (001) surface: a density functional theory study

Chunfu Liu, Weitao Wang, Han Wang, Chenyu Zhu, Bao Ren

Department of Materials Science and Engineering, Anhui University of Science and Technology, Huainan 232001, China

Corresponding author: chfuliu@aust.edu.cn (Chunfu Liu)

Abstract: To investigate the adsorption mechanism of quaternary ammonium salt on the α -quartz (001) surface, the adsorption models of hydrophobic modifiers 1231, 1431, 1631 and 1831 were constructed and simulated using the density functional theory (DFT). Results indicate that the adsorption energy of quaternary ammonium salt increases with the increase of carbon chain length, and the adsorption energy reaches the maximum at 18 carbon atoms; however, the adsorption capacity of 1631 is weak owing to the carbon chain deflection. Based on the Mulliken bond population analysis, reagent 1831 has the strongest interaction with α -quartz (001) surface compared with 1231, 1431 and 1631; and during the adsorption process, charge transfer and electrostatic attraction occur between the reagent and α -quartz (001) surface with similar degrees of charge transfer observed. This study emphasizes that electrostatic attraction plays a key role in the adsorption process, while the weak hydrogen bonding plays a secondary role.

Keywords: α -quartz (001) surface, quaternary ammonium salt, density functional theory, adsorption mechanism

1. Introduction

Quartz is a common mineral in the natural world, and it is an important industrial raw material, widely used in the manufacturing of glass, microchips, optical devices, and so on. In the process of coal mining and washing, friction and impact occur between minerals represented by quartz minerals and coal, resulting in crushing, or expansion and dissociation occurring after contact with water. This process subsequently generates highly muddy slime water. In this scenario, muddy slime will adhere to the coal particle surface, change its physical and chemical properties, and seriously affect the flotation recovery effect of fine coal (Song et al., 2020). This highly muddy coal slurry water is characterized by having a fine particle size, strong electronegativity on particle surface, large amount of clay minerals, and strong hydrophilic clay minerals particle surface in coal slurry easily forms a strong hydration film. Due to the existence of hydration repulsion force and spatial steric effect when micro particles are close, the coal slurry water dispersion system maintains strong stability (Israelachvili and Mcguiggan, 1988). This leads to the unsatisfactory settlement effect using conventional sedimentation technology which is to add electrolyte coagulant and polymer flocculant. Subsequently, it is necessary to research and devise new coal slurry water settlement technologies based on the characteristics of difficult-to-settle coal slurry water.

In industrial applications, cationic surfactants are used to change the hydrophobicity of the quartz surface so that it can be separated from the quartz as it mixes with other minerals. Quaternary ammonium salt is a new type of agglomeration settling reagent currently being applied in this field of coal slurry water treatment (Chen et al., 2015), and is also a commonly used reagent for regulating the surface hydrophobicity of quartz. Due to the negative charge on the minerals surface such as quartz, it is easy to adsorb amine salts on the mineral particles surface through electrostatic physical adsorption, and characteristic adsorption, becoming hydrophobic surfaces. It is widely used in the field of quartz cluster sorting and sedimentation (Peng et al., 2012). Subsequently, it is used for exploring the application of

quaternary ammonium salt-based hydrophobic modifying reagents, adsorption behavior and significance of the α -quartz (001) surface. Traditionally, the adsorption mechanism on α -quartz (001) surface is often investigated using common analytical methods, such as micro flotation testing (Yupin et al., 2007), contact angle measurement (Iranildes et al., 2007), zeta potential measurement, adsorption capacity measurement, Fourier transform infrared spectroscopy (FTIR) analysis, X-ray photoelectron spectroscopy (XPS) analysis (Zhang et al., 2014), and atomic mechanical microscopy (AFM) analysis (Xiao and Liu, 2012). The foresaid traditional methods do not only analyse quantitatively calculate and summarize the adsorption behaviour, but also the adsorption mechanism of the α -quartz (001) surface. However, sometimes it is limited to the macro scale, and the mechanism of reagent adsorption regulation is not intuitive and clear enough.

Compared with the traditional methods, molecular simulation can understand the adsorption mechanism and adsorption kinetics from the microscopic scale. According to the quantitative calculation of the interaction between the adsorbent and the substrate, including adsorption force, chemical bond and electrostatic interaction, new reagent formulations can be developed to improve the selectivity or recovery of flotation. Due to the presence of a liquid phase, the molecular mechanisms are difficult to investigate with experimental methods (Foucaud et al., 2019). DFT has become one of the main methods for studying the adsorption of water or reagents on mineral surfaces owing to its high calculation accuracy and speed. This is very important for developing an in-depth understanding of the surface phenomena of modified reagent compound and its development in practical applications. Studying its adsorption configuration, adsorption energy, and adsorption mechanism provides theoretical guidance for further optimizing the design and application of this type of compound. For example, Wang et al. (2018) simulated the structure and electronic properties of Si-terminal, O-intermediate terminal, and O-rich terminal on α -quartz (001) surface, as well as the adsorption of water molecules on the surface. These findings demonstrate that the surface properties of different terminals mainly depend on the surface exposed silicon and oxygen atoms. In the water molecular adsorption model, the molecules are mainly adsorbed on the surface Si and O atoms through van der Waals forces and weak hydrogen bonding. Liu et al. (2019) employed density functional theory to assess the adsorption of a single water molecule on the surface of α -quartz (001) with or without Na^+ , Mg^{2+} and Ca^{2+} ions. The results suggest that the best adsorption configuration of a single water molecule on the surface of α -quartz (001) is a bridge formed by two hydrogen bonds. Chen et al. (2016) used the DFT to calculate and simulate the adsorption of four cations on kaolinite (001) surface. The results demonstrate that all four cations can be stably adsorbed on kaolinite (001), but the adsorption mechanism of amine cations and quaternary ammonium cations is different. Amine cations act on the kaolinite (001) surface through electrostatic attraction and hydrogen bonding, while quaternary ammonium cations only interact with the kaolinite (001) surface through electrostatic attraction. Foucaud et al. (Foucaud et al., 2018) studied the adsorption of fatty acids with different chain structures on the fluorite (111) surface based on density functional theory. The results indicated that the molecular adsorption is superior to the dissociation under acidic conditions, and the molecules can be adsorbed on the surface calcium atoms with the energy of -78.2 kJ/mol. In addition, the carboxylate anion can be adsorbed on the surface in a bidentate binuclear one or a monodentate one, the bidentate binuclear being favored. Liu et al. (Liu et al., 2015) used the DFT method to investigate the properties of dodecyl amine (DDA), dodecyl-propyl ether amine, and aliphatic amine ethoxide (AC1201) as flotation collectors for quartz. The outcomes indicate that these aggregates found it difficult to form covalent bonds with silica atoms on the quartz surface. Foucaud et al. (Foucaud et al., 2021, Foucaud et al., 2019) employed diffuse infrared Fourier transform spectroscopy in combination with ab initio calculation to investigate the adsorption mechanism of fluorite and fatty acid, as well as the synergistic adsorption effect of sodium silicate (Na_2SiO_3) and sodium carbonate (Na_2CO_3) on mineral surfaces. At low concentrations, carboxylate molecules are adsorbed onto sodium ions in a bridging form, while at high concentrations, carboxylate anions are only adsorbed in monodentate or a bidentate binuclear configuration. The Na_2CO_3 exhibits a strong affinity for forming an adsorption layer on the surface of carbonate fluorite. The Na_2SiO_3 is initially absorbed as monomer protonation at low concentrations but undergoes mass polymerization and deprotonation at high concentrations. Eskinlou et al. (2022) infers that dissolved lattice metal ions (such as Al^{3+} and Mg^{2+}) had a significant effect on the adsorption of the collector on the fluorapatite surface in the flotation process.

These results offer Al^{3+} and Mg^{2+} ions to be beneficial in the interaction between fatty acids and fluoapatite, thus improving flotation selectivity. Nikita et al. (2013) studied the adsorption behaviors of Ag atoms and cations on the α -quartz (001) surface with or without Al defects utilizing the DFT method. The results confirm that they have different energies at different adsorption sites. Zhu et al. (2016) studied the adsorption mechanism of α -bromolauric acid ($\text{CH}(\text{CH}_2)_7\text{CHBrCOOH}$, α -BLA) on α -quartz (101) surface based on the first-principles calculations. Their results infer that α -BLA cannot be adsorbed on the surface of α -quartz (101) because of the hydration shell on the surface, but $\text{Ca}(\text{OH})^+$ can remove this effect and adsorb on the surface of quartz, so that the anion of α -BLA molecules can be adsorbed on the $\text{Ca}(\text{OH})^+$ activated quartz surface. The DFT method is widely used to study the reagent adsorption, while few studies have thought about the adsorption of quaternary ammonium cation on the α -quartz (001) surface. In this work, the adsorption characteristics of four quaternary ammonium cation reagents on the hydroxylated α -quartz (001) surface were simulated. The research result may provide a theoretical basis for the development of settlement and clarification technology of mine wastewater rich in fine quartz particles.

2. Calculation method and model

2.1 Calculation method

The CASTEP (Cambridge Sequential Total Energy Package) module of Materials Studio (MS) software is utilized for the calculations. The GGA-PBE (Generalized Gradient Approximation) function is employed as the exchange correlation function for geometric optimization of α -quartz phase lattice, with a plane wave truncation energy set to 400 eV. The interaction between valence electron and ion particles was described using super soft pseudopotential (Liu, 2019). The BFGS algorithm is used to optimize the model and execute property calculations, with a self-consistent field convergence accuracy of 1.0×10^{-6} eV/atom. Geometric optimization convergence criteria include a maximum atomic displacement of 1.0×10^{-4} nm, interatomic force of 0.03 eV/Å, interatomic internal stress of 0.05 GPa, total energy change of the system at 1.0×10^{-5} eV/atom, and density of states analysis smoothing value set to 0.2 eV. Differential electron density analysis uses edit sets to define density difference for quaternary ammonium salts in each adsorption configuration to calculate their differential electron density difference and derive a differential electron density diagram through analysis. All calculations are carried out in the reciprocal space (Lingqui, 2015).

The $2 \times 2 \times 2$ supercell model of α -quartz (001) surface was constructed, with a 40 Å vacuum layer added on top (Andre et al., 2013). The volume phase is set to $(1 \times 1 \times 1)$ (Thiel et al., 1982), and the Monkhorst-Pack k-point is Gamma. For the pseudopotential calculation, the valence electrons considered for the involved atoms are Si $3s^2 3p^2$, N $2s^2 2p^3$, C $2s^2 2p^2$, O $2s^2 2p^4$ and H $1s^1$. Since the bottom plate model of α -quartz contains five layers of along the C-axis lattice structure, in order to enhance accuracy and minimize any influence from lower-layer atoms on upper-layer adsorbed atoms, appropriate constraints are applied to fix the corresponding bottom atomic layer. After performing geometric optimization, the atomic layer thickness of α -quartz (001) surface in $2 \times 2 \times 2$ supercells were determined to be 9.1998 Å (Chen et al., 2011). Four quaternary ammonium salt hydrophobic modified reagents ($\text{C}_{15}\text{H}_{34}\text{N}^+$) (1231), ($\text{C}_{17}\text{H}_{38}\text{N}^+$) (1431), ($\text{C}_{19}\text{H}_{42}\text{N}^+$) (1631) and ($\text{C}_{21}\text{H}_{46}\text{N}^+$) (1831) were optimized in the $10.1033 \text{ Å} \times 10.1033 \text{ Å} \times 40 \text{ Å}$ periodic cells.

The CASTEP module was functioned optimize the surface model and four quaternary ammonium hydrophobic modified reagents for energy optimization. This approach enabled us to calculate the frontier orbital properties with the Gamma point selected as the k-point (Rout et al., 2014). Calculation parameters for frontier orbit included exchange correlation function GGA-PBE, effective core and DNP base set usage, fine precision setting, and a self-consistent field convergence standard of 1.0×10^{-6} eV/atom.

2.2. Simulation model

2.2.1. Surface model

The α -quartz is composed of a continuous framework of SiO_2 and consists of four silicon oxygen tetrahedra, with each oxygen shared between the two tetrahedra (Liu et al., 2015). It passes through the

covalent bond with available cation (Si^{4+}) or oxygen atom of adjacent tetrahedron, and exhibits an equal bonding force in each direction. low-temperature quartz in nature (α -quartz), given that it is the main component of rocks/mineral deposits, often appears as a gangue mineral in various mineral mining and beneficiation processes. Unlike many brittle crystals, α -quartz does not have a perfect cleavage crystal plane and easy to be hydroxylation encountering solution. And the α -quartz (001) surface is predicted to be relatively stable according to atomic potential and the DFT methods (Chunfu et al., 2019). The figure below and appears the main view (a) and side view (b) of the hydroxylated α -quartz (001) surface.

2.2.2. Reagents models

The stable configurations of quaternary ammonium salt-based hydrophobic modifying reagents were constructed using the materials studio (Kumar et al., 2010). The geometric optimization of these four agents used the same exchange correlation function, truncation energy, and convergence criteria as the volume (Verdejo et al., 2011). Figure 2 illustrates the stable configurations of different quaternary ammonium salt-based hydrophobic modifying agents after geometric optimization.

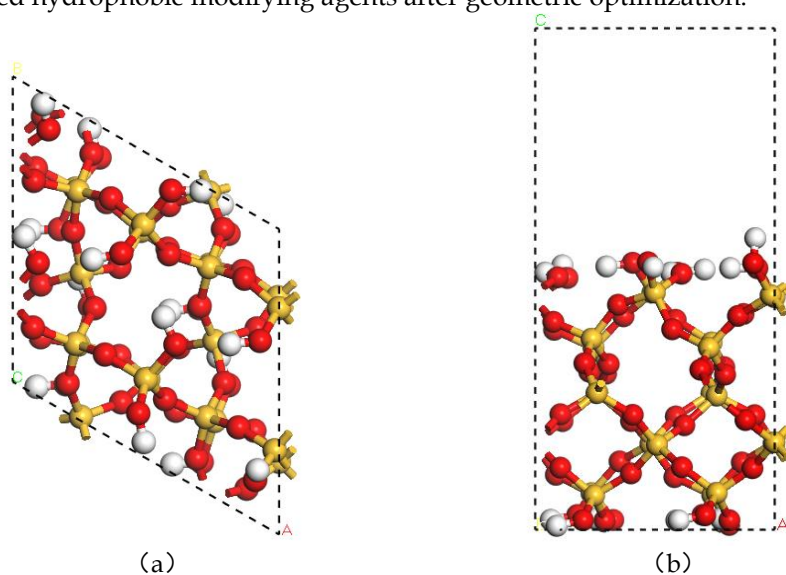


Fig. 1. Structures of top (a) and side (b) views for the hydroxylated α -quartz (001) surface

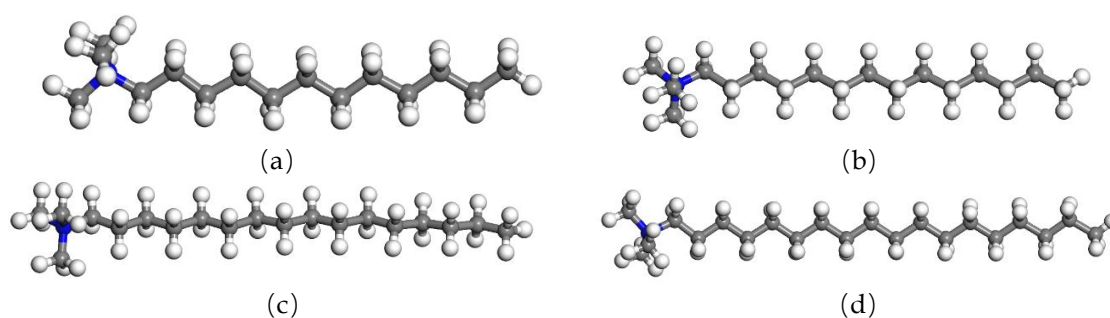


Fig. 2. Stable configurations of hydrophobic modified agents of different quaternary ammonium salts

3. Results and analysis

3.2. Optimal adsorption configuration and adsorption energy

3.2.1. Optimal adsorption configuration

The stable configurations of four reagents, namely 1231, 1431, 1631 and 1831 on α -quartz (001) surface are displayed in the figure below.

3.2.2. Adsorption energy

The adsorption of 1231, 1431, 1631, and 1831 on the α -quartz surface is accompanied by changes in energy. According to calculations, the adsorption of the four reagents on the α -quartz surface is an exothermic process, and the heat released by the interaction between reagents with different carbon chain lengths on the α -quartz surface varies. The energy released by the four reagents during adsorption on the α -quartz surface is summarized in the table below. The adsorption configurations of four hydrophobic modified agents on the α -quartz (001) surface were investigated, and the adsorption energy (E_{ads}) of reactants on quartz surface were calculated:

$$E_{ads} = E_{reagent/\alpha\text{-quartz}} - (E_{\alpha\text{-quartz}} + E_{reagent}) \quad (1)$$

where: $E_{reagent/\alpha\text{-quartz}}$ was the total energy of the reagent/ α -quartz adsorption system, $E_{\alpha\text{-quartz}}$ and $E_{reagent}$ were the energy of a α -quartz and a free reagent cation, respectively.

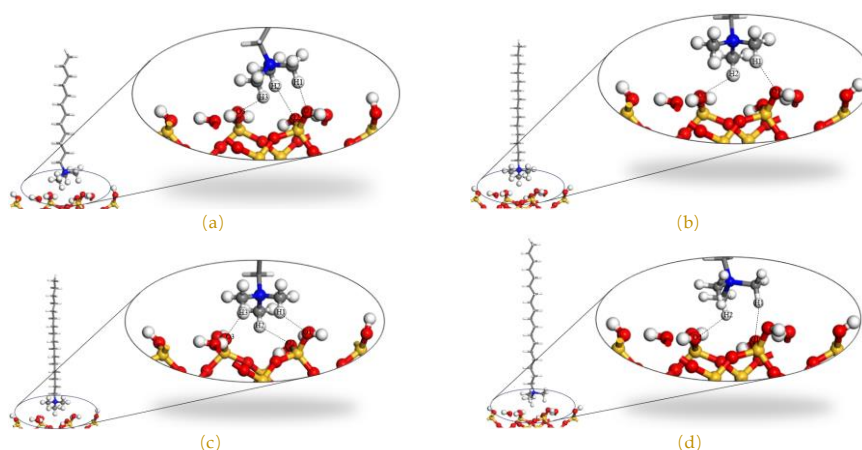


Fig. 3. Stable configurations of 1231, 1431, 1631 and 1831 adsorbed on α -quartz (001) surface

Table 1. Adsorption energies of 1231, 1431, 1631 and 1831 on the α -quartz (001) surface

Adsorption system	Adsorption energy (eV)
1231/ α -quartz (001) surface	-1.68
1431/ α -quartz (001) surface	-1.71
1631/ α -quartz (001) surface	-1.56
1831/ α -quartz (001) surface	-1.72

It can be seen from Table 1 that when 1231 is adsorbed on the α -quartz (001) surface, the adsorption energy is -1.67 eV, and the overall trend of the adsorption energy of the agent on the α -quartz (001) surface is that the adsorption energy increases when the carbon chain in the agent molecule also increases (Victor, 2014). When the carbon chain length is 18 carbon atoms, the adsorption energy is the largest, specifically -1.72 eV. However, the adsorption energy of 1631 reagent and the α -quartz (001) surface is relatively small, because the carbon chain of the agent molecule deflected during the adsorption process, which weakens the interaction between the reagent molecules and quartz, forming weaker intermolecular forces (Hai-huan et al., 2019).

3.3. Bonding analysis

Table 2. depicts the Mulliken population of different seasonal ammonium salt hydrophobic modified agents adsorbed on α -quartz (001) surface.

Analysis indicates that the average bond lengths formed by 1231, 1431, 1631, and 1831 when adsorbed on the α -quartz (001) surface are 2.624, 2.509, 2.378, and 2.328 Å, respectively. The Mulliken bond populations between the four reagents and the surface are 0.01, 0.02, 0.025, and 0.05, respectively. This means that the interaction between 1831 and the α -quartz (001) surface is stronger than the interaction between 1231, 1431, and 1631 with the α -quartz (001) surface.

Table 2. Mulliken bond populations of 1231, 1431, 1631 and 1831 adsorbed on α -quartz (001) surface

Adsorption system	Bond	Bond length / \AA	Mulliken bond population
1231/ α -quartz (001) surface	H1-O1	2.458	0.01
	H2-O2	2.692	0.00
	H3-O3	2.721	0.02
1431/ α -quartz (001) surface	H1-O1	2.667	0.01
	H2-O2	2.351	0.03
1631/ α -quartz (001) surface	H1-O1	2.335	0.02
	H2-O2	2.368	0.02
	H3-O3	2.431	0.01
1831/ α -quartz (001) surface	H1-O1	2.287	0.04
	H2-O2	2.369	0.06

3.4. Density of states analysis

The changes in the density of states of hydrogen atoms and surface oxygen atoms in the adsorbed reagent ions of different quaternary ammonium salt reagents on the α -quartz (001) surface are shown in Fig. 4 (The energy zero point is set at the Fermi level (E_F)).

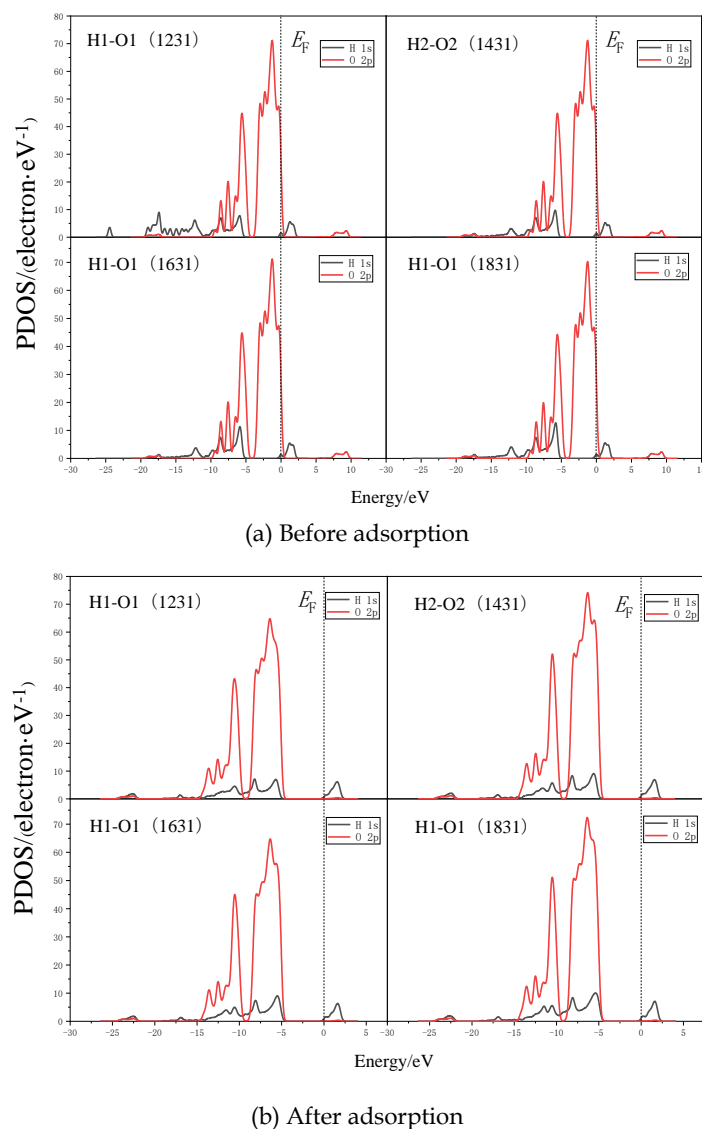


Fig. 4. Adsorption of different quaternary ammonium hydrophobic modified reagents on α -quartz (001) surface

According to Fig. 4, the O 2p energy on the α -quartz (001) surface after adsorption of the four different quaternary ammonium salt-based hydrophobic modified reagents have undergone a significant negative shift compared to before adsorption. However, the range of movement is relatively small. From Fig. 4(b) after adsorption, no bond has formed between H 1s and O 2p in the adsorption configuration of the four quaternary ammonium salt-based hydrophobic modified reagents (Dekany et al., 1989). The bonding range in each adsorption configuration is relatively small, which indicates that the bonding between the hydrogen atoms of the four different quaternary ammonium salt-based hydrophobic reagents and the oxygen atoms on the α -quartz (001) surface is weak.

Based on the above analysis, it can be concluded that when adsorbed on the α -quartz (001) surface, the four different quaternary ammonium salt-based reagents all meet the conditions for hydrogen bonding with the surface (Princy et al., 2019). However, the peak values in the density of states (DOS) graph also indicate that the adsorption energy differences between 1231, 1431, and 1831, and the α -quartz (001) surface are not significant. Nonetheless they are all larger than the adsorption energy of 1631 with the α -quartz (001) surface. The adsorption energy of 1631 with the α -quartz (001) surface is the lowest. Overall, the bonding between the four different quaternary ammonium salt-based hydrophobic modified reagents, and the α -quartz (001) is not strong. This strongly suggests that the bonding between the molecules of the four reagents and the α -quartz (001) surface is not the main reason for the reagents' adsorption (Hughes et al., 2016).

3.5. Charge analysis

Different quaternary ammonium salt hydrophobic modified agents were adsorbed on the α -quartz (001) surface, and the changes in charge between bonding atoms or adjacent atoms can be intuitively represented by the electron density difference. Fig. 5 illustrates the electron density difference of four different quaternary ammonium salt hydrophobic modified reagents adsorbed on the α -quartz (001) surface [35]. The blue area represents electron accumulation, and the red area represents electron depletion. The figure depicts a significant charge transfer between the quaternary ammonium salt modified hydrophobic reagent and the adjacent atoms on the α -quartz (001) surface in the four adsorption systems. The electrons are transferred from the hydrogen atoms of the drug molecules to the surface oxygen atoms, and the degree of charge transfer is similar in the four quaternary ammonium salt hydrophobic modified agent adsorption systems. At the same time, in the adsorption systems of different quaternary ammonium salt hydrophobic modified reagents, in addition to the hydrogen atoms that directly form hydrogen bonds and the surface oxygen atoms that exist in charge transfer, there is also a certain amount of electron accumulation in other surface oxygen atoms close to the hydrogen atoms in the reagent molecules. Indicated here is that the charge transfer is not related to hydrogen bonds (Eskanlou et al., 2022).

Due to the transfer of electrons from different hydrophobic modified reagents to the α -quartz (001)

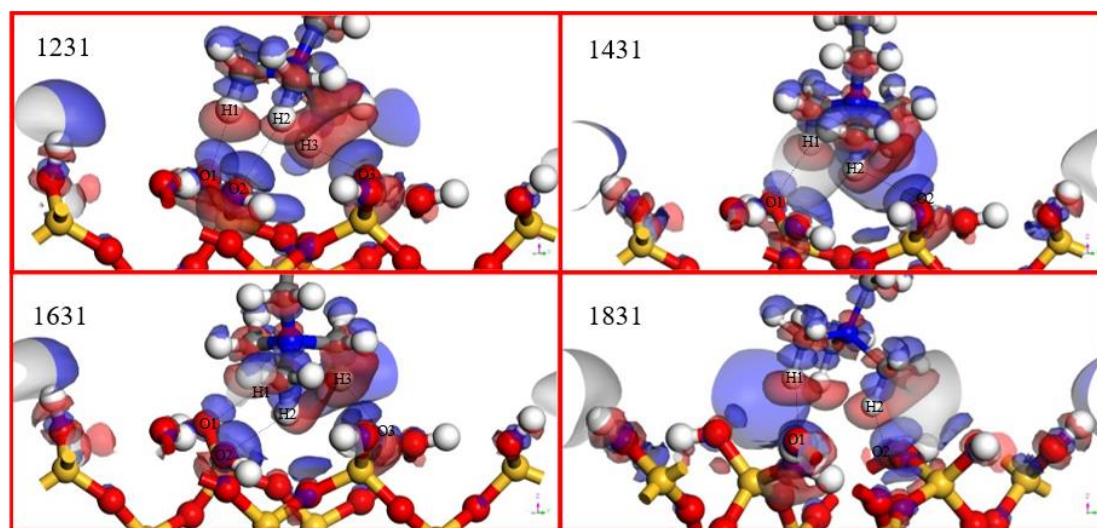


Fig. 5. Electron density difference of adsorption systems of quaternary ammonium salts hydrophobic modified reagent (Equivalent par value: 0.0038, 0.004, 0.0048, 0.005 electrons/ \AA^3)

surface, the α -quartz (001) surface becomes negatively charged, causing the positively charged quaternary ammonium salt cations to adsorb on the negatively charged α -quartz (001) surface due to electrostatic force. This confirms that there are indeed other non-hydrogen bond interactions between quaternary ammonium salt reagents and the α -quartz (001) surface, leading to a certain degree of adsorption, and this interaction is known as the electrostatic attraction [36-37].

Mulliken charge populations of interact atoms before and after different quaternary ammonium salts reagents adsorption on the α -quartz (001) surface are shown in Table 3. The net charges of each agent molecule and the α -quartz (001) surface before and after adsorption were also calculated. The H1s state of the hydrogen atoms that interact with surface oxygen atoms in the four ammonium salt agents lost (0.01~0.04) e. The Mulliken charge distribution of oxygen atoms on the α -quartz (001) surface is almost unchanged by four hydrophobically modified ammonium salts. The electrons lost by the ions of the four ammonium salt agents mainly originated from the adjacent methyl hydrogen atoms on the surface. Although electron accumulation did occur around the surface oxygen atoms after the adsorption of the ammonium salt reagent molecules, the oxygen atoms themselves did not gain electrons. The four ammonium salt cations transferred 8.30e, 8.29e, 8.15e, and 8.19e charges to the α -quartz (001) surface, respectively. There was no significant difference in the amount of charge transfer between the four ammonium cations. This result is similar to the electron density difference outcome mentioned above.

Combined with the adsorption energy results, the more charges the ammonium salt reagent molecules transfer to the α -quartz (001) surface, the smaller the adsorption energy; the more stable the adsorption system will be. Due to the large number of electrons transferred by the ammonium salt ions to the α -quartz (001) surface, the surface carries a large amount of negative charge (-8.15e~-8.30e), and the electrostatic attraction between the ammonium salt ions and the adsorbed α -quartz (001) surface occurs. The electron density difference and Mulliken charge population analysis indicates that there is a significant amount of charge transfer between the cations, and the α -quartz (001) surface when different quaternary ammonium salt hydrophobic modified reagents are adsorbed onto the surface. Electrons transfer from the cations to the α -quartz (001) surface, making the α -quartz (001) surface negatively charged, while the cations themselves become more positively charged due to the loss of electrons. This leads to strong adsorption between the quaternary ammonium salt hydrophobic modified reagents and the α -quartz (001) surface due to electrostatic attraction (Zhang et al., 2010). Mulliken bond population and density of states analysis reveal that hydrogen bonding is not the main reason for the adsorption of different quaternary ammonium salt hydrophobic modified agents onto the α -quartz (001) surface, the dominant force in this process is electrostatic attraction (Han et al., 2007).

Table 3. Mulliken charge population of atoms before and after different quaternary ammonium salts adsorption on the α -quartz (001) surface

Atomic number	Adsorption state	Mulliken charge /e			
		1231	1431	1631	1831
H1	before	0.27	0.27	0.27	0.27
	after	0.31	0.31	0.28	0.30
H2	before	0.27	0.28	0.28	0.28
	after	0.30	0.28	0.27	0.27
H3	before	0.28	-	0.27	-
	after	0.28	-	0.29	-
O1	before	-1.08	-1.08	-1.08	-1.07
	after	-1.09	-1.09	-1.08	-1.04
O2	before	-1.07	-1.09	-1.07	-1.09
	after	-1.05	-1.10	-1.03	-1.11
O3	before	-1.09	-	-1.09	-
	after	-1.10	-	-1.10	-
Quaternary ammonium salt	before	0.00	0.00	0.00	0.00
	after	8.30	8.29	8.15	8.19
α -quartz(001) surface	before	0.00	0.00	0.00	0.00
	after	-8.30	8.29	8.15	8.19

4. Conclusions

This study investigated the quaternary ammonium salt hydrophobic modified reagents adsorption on the α -quartz (001) surface using the DFT method. The main findings are summarized below:

- (1) According to adsorption energies, 1231, 1431, 1631 and 1831 can spontaneously adsorb on the α -quartz (001) surface. The adsorption energy of the reagent increases with the increase of the carbon chain and reaches the maximum value (-1.72 eV) at 18 carbon atoms. However, the adsorption energy of 1631 is small owing to its carbon chain deflection.
- (2) The comprehensive analysis results of electron density difference and Mulliken bond population show that there is a large amount of charge transfer when the four quaternary ammonium cations are adsorbed on the α -quartz (001) surface, and the electrons move from reagent cation to the α -quartz (001) surface. Which makes the α -quartz (001) surface negatively charged. At the same time, the charge of cation itself increases due to electron loss, which leads to the quaternary ammonium cation strong adsorption on the α -quartz (001) surfaces due to electrostatic attraction.
- (3) The hydrophobic modified reagents of various quaternary ammonium salts were found to adsorb onto the α -quartz (001) surface mainly through the electrostatic attraction, with similar degrees of charge transfer observed. In addition, the weak hydrogen bonding playing a minor role in the process compared to the dominant effect of electrostatic attraction.

Acknowledgements

This research was supported by the University-level key projects of Anhui University of Science and Technology (xjzd2020-21), National Natural Science Foundation of China (No. 52104243), Anhui Provincial Natural Science Foundation (2108085QE212), Talent Introduction Fund of Anhui University of Science and Technology (13200007). The authors gratefully acknowledge financial support of the above-mentioned agencies.

References

- ANDRÉ, DANKERT, LENNART LANGOUCHE, MUTTA VENKATA KAMALAKAR, SAROJ PRASAD DASH., 2013. *High-Performance Molybdenum Disulfide Field-Effect Transistors with Spin Tunnel Contacts*. *Acs Nano*. 8(1), 476-482.
- ATO Y, HAYASHI A, KOGA H, KAWAKAMI T, YAMANAKA S, OKUMURA M., 2019. *Theoretical study of aerobic oxidation of alcohols over Au₃₈ nanocluster by a two-step-modeling approach*. *Chem. Phys. Lett.* 724, 115-121
- CHEN JUN, MIN FANFEI, LIU LINGYUN, PENG CHENLIANG., 2016. *DFT calculations of different amine/ammonium cations adsorption on kaolinite (001) surface*. *J. China Coal Soc.* 41(12), 3115-3121.
- CHEN Y W , CHU I H , WANG Y , ET AL., 2011. *Water thin film-silica interaction on α -quartz (0001) surfaces*. *Phys. Rev.* 84(15), 155444.
- CHEN JUN, MIN FANFEI, PENG CHENLIANG ET AL., 2015. *Hydrophobic agglomeration of fine particles in coal slime water under the action of quaternary ammonium salt*. *J. China Univ. Min. Technol.*, 44(02), 332-340.
- CHUNFU LIU., 2019. *Research on Adsorption Mechanism of Water Molecules and Hydrated Cations on the Fine Quartz Particle Surface*. Anhui University of Science & Technology, Anhui, China.
- CHIKH ZA, CHEBABE D, DERMAJ A, ET AL., 2005. *Electrochemical and analytical study of corrosion inhibition on carbon steel in HCl medium by 1,12-bis(1,2,4-triazolyl) dodecane*. *Corros. Sci.* 47(2), 447-459.
- CHUNFU LIU, FANFEI MIN, LINGYUN LIU, JUN CHEN., 2019. *Density Functional Theory Study of Water Molecule Adsorption on the α -Quartz (001) Surface with and without the Presence of Na⁺, Mg²⁺, and Ca²⁺*. *ACS Omega*, 4(7), 12711-12718.
- DÉKÁNY, I, F. SZÁNTÓ, WEISS A ., 1989. *The liquid-crystal structure of adsorbed layers and the stability of dispersed systems in organic liquids*. *Colloids & Surfaces*. 41, 107-121.
- ESKANLOU, AMIR, QINGQING HUANG, YANN FOUCAUD, MICHAEL BADAWI, ALDO H. ROMERO., 2022. *Effect of Al³⁺ and Mg²⁺ on the flotation of fluorapatite using fatty- and hydroxamic-acid collectors – A multiscale investigation*. *Appl. Surf. Sci.*, 572, 151499.
- FOUCAUD Y, BADAWI M, FILIPPOV L, ET AL . , 2019. *A review of atomistic simulation methods for surface physical-chemistry phenomena applied to froth flotation*. *J. Min. Eng.* 143, 106020.

- FOUCAUD, YANN, JULIETTE LAINÉ, LEV O. FILIPPOV, ODILE BARRÈS, WON JUNE KIM, INNA V. FILIPPOVA, MARIACHIARA PASTORE, SÉBASTIEN LEBÈGUE, MICHAEL BADAWI. 2021. *Adsorption mechanisms of fatty acids on fluorite unraveled by infrared spectroscopy and first-principles calculations*, J. Colloid Interface Sci., 583, 692-703.
- FOUCAUD, YANN, MICHAËL BADAWI, LEV O. FILIPPOV, ODILE BARRES, INNA V. FILIPPOVA, SÉBASTIEN LEBÈGUE., 2019. *Synergistic adsorptions of Na₂CO₃ and Na₂SiO₃ on calcium minerals revealed by spectroscopic and ab initio molecular dynamics studies*. Chem. Sci, 10, 9928-9940.
- GNANASARAVANAN S , RAJKUMAR P ., 2013 *Characterization of minerals in natural and manufactured sand in Cauvery River belt, Tamilnadu, India*. Infrared Phys. Technol. 58, 1-31.
- HAI-CHUAN QIN, QIAO-QIAO QIN, HUI LUO, WEI WEI, LIU-XIE LIU, LAI-CAI LI.,2019. *Theoretical study on adsorption characteristics and environmental effects of dimetridazole on TiO₂ surface*. Comput. Theor. Chem.1150, 10-17.
- HAN Y, DAI Y, DA S, WANG J, SUN B., 2007. *Electronic and bonding properties of TiB₂*. J. Alloy. Compd. 438(1-2), 327-331
- HUGHES A E, MOL J M C, ZHELUDKEVICH M L, BUCHHEIT R G., 2016. *Active Protective Coatings. Active Protective Coatings: New-Generation Coatings for Metals, Springer Series in Materials Science, Springer Science+Business Media Dordrecht*, 2016.
- IRANILDES DANIEL DOS SANTOS, JOSÉ FARIAS OLIVEIRA., 2007. *Utilization of humic acid as a depressant for hematite in the reverse flotation of iron ore*. Miner. Eng., 20(10), 1003-1007.
- ISRAELACHVILI J N, MCGUIGGAN P M.,1988. *Forces Between Surfaces in Liquids*. Science, 241 (4867).
- KUMAR, P., K.P. SANDEEP, S. ALAVI, V.D. TRUONG, R.E. GORGA., 2010. *Effect of Type and Content of Modified Montmorillonite on the Structure and Properties of Bio-Nanocomposite Films Based on Soy Protein Isolate and Montmorillonite*. J. Food Sci. 75(5), N46-N56.
- LINGQIU MA., 2015. *Elements in Quartz Research on Migration and Diffusion Mechanism of Metallic*. Wuhan University of Technology, Hubei, China.
- LIU, A., FAN, J.-C., FAN, M.-Q., 2015. *Quantum chemical calculations and molecular dynamics simulations of amine collector adsorption on quartz (0 0 1) surface in the aqueous solution*. Int. J. Miner. Process. 134, 1-10.
- NIKITA I. VAKULA, GULNARA M. KURAMSHINA, LEONID G. GORB, FRANCES HILL, JERZY LESZCZYNSKI., 2013. *Adsorption and diffusion of a silver atom and its cation on a-SiO₂ (001): Comparison of a pure surface with a surface containing an Al defect*. Chem. Phys. Lett.567,27-33.
- PENG CHENLIANG, MIN FANFEI, ZHAO QING, LI HONGLIANG.,2012. *Research status and progress of surface hydration membranes of fine mineral particles*. Acta Mineral. Sin., 32(04), 515-522.
- PRINCY M.J., R. BHUVANESWARI, V. NAGARAJAN, R. CHANDIRAMOULI., 2019. *Diethanolamine and quaternium-15 interaction studies on antimonide nanosheet based on first-principles studies*. Comput. Theor. Chem.1157,19-27.
- ROUT, ALOK, SIL WELLENS, KOEN BINNEMANS., 2014. *Separation of rare earths and nickel by solvent extraction with two mutually immiscible ionic liquids*. RSC Adv. 4, 5753-5758.
- SONG SHUAI, FAN YUPING, MA XIAOMIN, DONG XIANSHU., 2020. *Simulation Study on Interaction between Coal and Different Minerals in Coal Slurry*. Multipurp. Util. Miner. Resour., 221(01), 168-172+102.
- SONG, S., C. PENG, M.A. GONZALEZ-OLIVARES, A. LOPEZ-VALDIVIESO, T. FORT., 2005. *Study on hydration layers near nanoscale silica dispersed in aqueous solutions through viscosity measurement*. J. Colloid Interface Sci., 287(1), 114-120.
- THIEL P A , HOFFMANN F M , WEINBERG W H ., 1982. *Coadsorption of Oxygen and Water on Ru (001): Vibrational and Structural Properties*. Phys.rev.lett.49(7), 501-504.
- VERDEJO, RAQUEL, MARIANELLA HERNANDEZ, NATACHA BITINIS, JOSE MARÍA KENNY, AND MIGUEL ANGEL LOPEZ-MANCHADO. 2011. *Vulcanization Characteristics and Curing Kinetic of Rubber–Organoclay Nanocomposites, Rubber-Clay Nanocomposites*. John Wiley & Sons, Ltd.
- VICTOR, A, RANEA., 2014. *Dimethylamine formation from N-nitroso dimethylamine adsorbed on the Ni{1 1 1} surface from first principles*. J. Mol. Catal. A: Chem. 392,157-163.
- XIAO NI, QI LIU.,2012. *The adsorption and configuration of octyl hydroxamic acid on pyrochlore and calcite*. Colloids Surf. A.411,80-86.

- XIANCHEN WANG, QIN ZHANG, XIANBO LI, JUNJIAN YE, LONGJIANG LI., 2018. *Structural and Electronic Properties of Different Terminations for Quartz (001) Surfaces as Well as Water Molecule Adsorption on It: A First-Principles Study*. Minerals, 8(2), 58.
- YANN FOUCAUD, SÉBASTIEN LEBÈGUE, LEV O FILIPPOV, INNA V FILIPPOVA, MICHAËL BADAWI.,2018. *Molecular insight into fatty acid adsorption on bare and hydrated (111) fluorite surface*. J Phys Chem B., 122(51), 12403-12410.
- YIMIN ZHU, BINBIN LUO, CHUANYAO SUN, JIE LIU,HAITAO SUN ,YANJUN LI, YUEXIN HAN.,2016. *Density functional theory study of α -Bromolauric acid adsorption on the α -quartz (1 0 1) surface*. Miner. Eng. 92, 72-77.
- YOGAMALAR N R, BOSE A C., 2011. *Tuning the aspect ratio of hydrothermally grown ZnO by choice of precursor*. J Solid State Chem. 184(1), 12-20.
- YUPIN ZHANG, KELONG HUANG, SUQIN LIU, 2007. *Separation of clinocllore from powder quartz by reverse flotation and its mechanism*. J. JCSU (Sci. & Tech.). (02), 285-290.
- ZHANG W, SHERRELL P, MINETT A I, RAZALA J M, JUN CHEN., 2010. *Carbon nanotube architectures as catalyst supports for proton exchange membrane fuel cells*. Energy Environ. Sci. 3(9), 1286-1293.
- ZHANG JIE, WANG WEIQING, LIU JING, HUANG YANG, FENG QIMING, ZHAO HONG., 2014. *Fe(III) as an activator for the flotation of spodumene, albite, and quartz minerals*. Miner. Eng. 61, 16-22.