Research Article

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Nanosystem’s density functional theory study of the chlorine adsorption on the Fe(100) surface

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Abstract: This contribution investigates chlorine (Cl) interaction with the Fe(100) surface, with a focus on governing adsorption energies and geometrical features at the nanoscale using the density functional theory (DFT) approach. The Cl/Fe(100) system can be considered as a building block to create nanosystems with specific and desired electronic, material, mechanical, or environmental properties. We report adsorption energies, surface relaxations, and buckling distances for Cl adsorbed as a function of Cl coverage. The computational DFT framework employs a vdW-DF functional with coverages varying from 0.25 to 1 ML. Adsorption at a bridge site with coverage of 0.5 ML appears to be the most preferred site, with an adsorption energy of −4.44 eV. For all coverages, Cl adsorption at the bridge and hollow sites incurs slightly higher adsorption energies than adsorption at the top (T) site. The potential energy surface (PES) for the dissociation of a Cl molecule over the Fe(100) surface was calculated. Dissociative adsorption of the Cl molecule on Fe(100) ensues via a modest activation barrier of only 0.58 eV in a noticeably exothermic reaction of 2.94 eV. In agreement with experimental observations, the work function decreases upon Cl addition in reference to the clean iron surface. The electronic interaction between Cl and the Fe(100) surface was examined by calculating the differential charge density distribution of the most stable structure (B-0.5 ML). The vdW-DF interactions increase the adsorption energies and reduce the equilibrium distances when compared with the corresponding results from plain DFT.

Keywords: iron surfaces, chlorine, DFT calculations, vdW-DF functional, nanosystem

1 Introduction

The profound chemical reactivity of iron surfaces with chlorine species is of prime importance for several environmental and industrial concerns, including chlorination of aromatic pollutants (most notably notorious dioxins) and corrosion of equipment [1–3]. For instance, the system of halogens–iron plays a central role in deriving the halogenation cycle of aromatic compounds in scenarios pertinent to municipal waste incineration and recycling of electronic wastes [4]. From a safety perspective, the interaction of iron and chlorine has been extensively studied to comprehend chemical phenomena that prevail under corrosive HCl environments [5] and chlorine-containing salts (i.e., seawater) [6]. Chlorine chemisorption on the low-index (100) and (110) iron surfaces have been investigated on the basis of many aspects [7–9]. Dowbin and Jones [1] investigated the adsorption of Cl₂ on the Fe(100) surface using Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) approaches at room temperature. They illustrated that the change in the work function is proportional to the chlorine coverage, with a maximum value of 1.43 eV at complete saturation. Chlorine adsorption over a four-fold site (hollow site) is more stable than that at other sites. Upon heating, chlorine either desorbs into the vacuum or undergoes bulk diffusion. Along the same line of enquiry, Hino and Lambert [2] studied the interaction of chlorine with the Fe(100) surface at low pressure using Auger spectroscopy, thermal desorption, X-ray and ultraviolet photoemission spectroscopy (XPS and UPS) techniques. They demonstrated that the first adsorbate layer comprises FeCl₃ rather than FeCl₂ or non-dissociated chlorine molecules. After the complete formation of a chemisorbed overlayer and at 300 K, the growth of the iron chloride layer is sustained.

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Computationally, several density functional theory (DFT) studies have provided atomic-based insights into the Cl/Fe configurations with a focus on governing electronic/structural properties and thermodynamic stability at different chlorine coverages [3,7–9]. The binding, structures, and reactions of Cl, Cl₂, HCl, and HCl + O with the Fe(100) structure were investigated based on atom superposition and electron delocalization (ASED) molecular orbital theory [3]. Cl₂ was found to readily dissociate over one-fold and two-fold sites [3]. Previous theoretical calculations provided mechanistic insight into the growth of the FeCl₂ phase via the continuous adsorption of Cl atoms over the Fe(100) surface using generalized gradient approximation-projector augmented wave (GGA-PAW) [9] but without providing an intrinsic reaction barrier. At a 0.75 ML coverage, the four-fold (hollow) and two-fold (bridge) sites were found to be slightly more preferred than the top sites, with adsorption energies of −3.50, −3.39 and −3.29 eV, respectively. Nonetheless, the marginal difference in energies among the former values most likely resides within the accuracy benchmark of the adapted DFT calculations. Our comprehensive DFT study [9] on the interaction of atomic chloride over the Fe(100) surface presented binding chemisorption energies for on-surface and substitutional adsorption of chlorine using a plain DFT functional. A thermodynamic stability diagram was constructed over a wide range of chlorine chemical potentials to simulate real operational conditions encountered in iron corrosion by chlorine. Nonetheless, our previous study deployed a standard DFT functional without accounting for the long-term interactions that may result from van der Waals (vdW) forces.

To this end, this contribution reports values for adsorption energies, equilibrium geometries, and differential charge density distributions pertinent to the Cl/Fe(100) system. Furthermore, activation energies and work functions are calculated. Computed binding energies take into account the contribution from long-term interactions [10] using the van der Waals correction functional (vdE–DF) [11,12], which has been accounted for via the inclusion of a dispersion correction function (DFT-D). An important goal of the current study is to provide underlying kinetic parameters for the uptake of chlorine molecules by the Fe(100) surface. Such information is vital to attain a detailed understanding of processes that dictates the chlorination of iron into its chloride forms. Likewise, the acquired thermodynamic values are expected to enable the construction of stability phase diagrams of Fe–Cl phases at practical conditions germane to varying values of chlorine chemical potential.

2 Methodology

We carry out all computations using spin-polarized density functional theory (DFT) calculations. The PAW-GGA method of PW91 is used in all spin-polarized calculations [13–15] as implemented in the Vienna ab initio simulation (VASP) package [16,17]. The van der Waals correction functional (vdE–DF) by Dion et al. [11] refines adsorption energies taking into account the effect of long-range interactions. The calculations consider the ferromagnetism character of Fe atoms in which the magnetic moment of partially filled Fe sites rests at ±5.0 μB [18].

The Fe(100) surface was modeled using a supercell with six layers. To identify the most favorable sites, the bottom two layers were kept fixed at their bulk positions with the first four layers, and the adsorbate atoms were allowed to relax during the optimization. A sampling of the irreducible part of the Brillouin zone was carried out based on automatic generation of k-points based on a Monkhost-Pack mesh of (3 × 3 × 1) [19]. In the z direction, a vacuum spacing of 15 Å separates images along the z-direction in which a dipole correction is imposed. The kinetic energy cutoff was set at 400 eV. Optimizing one structure with eight atomic layers (H-0.25) at 500 eV cutoff energy and 4 × 4 × 1 k-points sampling has changed its associated adsorption energy marginally within 2.6%.

Relaxations (∇ab%) between layers a and b are calculated based on the d spacing in the bulk, 𝑑𝑖, with respect to the spacing on the surface 𝑑ab:

\[ \text{∇}_{ab} = \frac{d_{ab} - d_i}{d_i} \times 100\%. \]  

The adsorption energy (\(E_{ads}\)) and the chemisorption energy (\(E_{C}\)) are computed based on

\[ E_{ads} = \frac{1}{n} [E_{Cl+\text{surface}} - (nE_C + E_{\text{surface}})], \]  

\[ E_C = \frac{1}{n} \left[ E_{Cl+\text{surface}} - \left( \frac{n}{2} E_{ClCl} + E_{\text{surface}} \right) \right], \]  

where \(E_{Cl+\text{surface}}\) represents the total energy of the optimized surface with atomic Cl adsorbed, \(n\) stands for the number of adsorbed Cl atoms, \(E_C\) is the single Cl atom’s ground state energy, \(E_{\text{surface}}\) is the total energy of the clean surface without adsorption of the Cl atoms, and \(E_{ClCl}\) denotes the gas-phase Cl₂ molecule’s ground state energy.

Charge transfer was examined by calculating the differential charge density:

\[ \Delta \rho = \rho_{Cl+\text{surface}} - \rho_{\text{clean surface}} - \rho_{\infty(Cl)}, \]  

where \(\rho_{\infty(Cl)}\) is the density of chlorine gas at infinite distance.
where $\rho_{\text{Cl+surface}}, \rho_{\text{clean surface}}$, and $\rho_{\text{Fe(Cl)}}$ denote the charge distributions for the optimized structure of the relaxed surface with the adsorbate, the free Cl surface, and the Cl adsorbate fixed in their adsorption geometries, respectively. Bader’s formalism [20] provides partial charges for selected structures. Activation energies were estimated based on the climbing image nudged elastic band (CI-NEB) method [21]. This approach locates the minimum energy structure of the transition state by surveying the potential energy surface that consists of five images between the reactants and products.

3 Results and discussion

3.1 Fe(100) clean surface

The calculated lattice constant for the bulk Fe is 2.828 Å. This value was obtained by minimizing energy with respect to the volume of the unit cell. This value appears in very good agreement with previous experimental measurements of 2.845 Å [22] and other theoretically calculated values of 2.828 Å [9], 2.830 Å [23], and 2.834 Å [24]. The derived value of the bulk interlayer spacing ($d_o$) is 1.1 Å. The calculated relaxations between the first and second layers as well as second and third layers for the Fe(100) surface with analogous literature values are listed in Table 1. For the Fe(100) surface, the spacing between the first and second layers is lower than the bulk interlayer spacing ($d_{12} = -4.15\%$). This effect is compensated by an expansion between the second and third layers ($d_{23} = +2.65\%$). Bearing in mind the accuracy margin of the experimental measurements (i.e., ±3), computed values of $d_{12}$ and $d_{23}$ are in relative accord with literature values [9,25–27].

As shown in Figure 1(a), the Fe(100) surface displays three distinct adsorption sites on top of one of the Fe atoms (one-fold, T), a bridge between two surface Fe atoms (two-fold, B), and at a hollow between four surface Fe atoms (four-fold, H).

3.2 Cl adsorbed on the Fe(100) surface

Different Cl/Fe(100) configurations at coverages varying from 0.25 to 1 ML are studied. Adsorption and chemisorption energies and some important geometrical features for all configurations are presented in Table 2. For all coverages, adsorption at two-fold (B) and four-fold (H) adsorption sites is more favored than adsorption at the one-fold (T) sites. At 0.5 ML coverage, B and H sites are found to be more preferred than T sites with adsorption energies (chemisorption energy) of $-4.44$ (−3.00), $-4.39$ (−2.97), and $-4.06$ (−2.62) eV, respectively. For all sites, 0.5 ML coverage is shown to be the most stable configuration among the same site based on the values of adsorption and chemisorption energies. Overall, B site with coverage of 0.5 ML appears to be the most preferred site with chemisorption energy of −3.0 eV. At this site, the average Cl–Fe bond length is 2.31 Å, and the metal–adsorbate distance is 1.84 Å.

At the 0.75 ML coverage, the four-fold site (H) is found to be more preferred than the bridge (B) and top (T) sites, with adsorption energies of $-3.86$, $-3.65$ and $-3.64$ eV and chemisorption energies of $-2.42$, $-2.21$ and $-2.20$ eV, respectively. The latter results are in very good agreement with the result of Dowbin and Jones [1] and

| Relaxation | Refs. [9,25–27] | Current calculations |
|------------|-----------------|----------------------|
| Experimental values | Other theoretical values |
| $V_{12}$ (%) | $-1.40 \pm 3$ | $-3$, $-3.50$ | $-4.15$ |
| $V_{23}$ (%) | $5.0 \pm 2$ | $1.7$, $2.30$ | $2.65$ |

$V_{ab}$ (%) refers to the relative difference in spacing between the bulk and the two adjacent layers a and b (as calculated from equation (1)).

Figure 1: Potential adsorption sites for atomic Cl on the Fe(100) surface. For clarity, atoms in the second layer are denoted by lines.
are expected to play a noticeable role in reducing the coverages for all sites. The lateral repulsive interactions order of \( T \), average Cl iron relaxes up after interaction with chlorine, while the layer distance. This behavior shows that the causes an expansion of the coverages for H and B sites, the presence of chlorine binding of the clean surface are presented in Table 2. In all adding the adsorbate with respect to the interlayer space previous theoretical calculations [9]. The relaxations of the first three Fe layers of the considered surface after adding the adsorbate with respect to the interlayer spacing of the clean surface are presented in Table 2. In all coverages for H and B sites, the presence of chlorine causes an expansion of the first and second interlayer distance and a compression of the second and third interlayer distance. This behavior shows that the first layer of iron relaxes up after interaction with chlorine, while the second layer relaxes down with the attraction of the lower iron atoms. This is in contrast with the case at site T, where each coverage obtained a different behavior. The average Cl–Fe nearest distance (Cl–Fe) increases in the order of \( T < B < H \). The vertical buckling based on the \( H \) values in Table 2 in all configurations is very minimal (0.01–0.36 Å), with nearly no buckling observed at full coverages for all sites. The lateral repulsive interactions are expected to play a noticeable role in reducing the binding energy at high coverages [28].

In a corrosive chlorine-containing environment, interactions of chlorine with iron surfaces produce iron chlorides and oxychlorides. Thus, it is of interest to compare distances in Cl–Fe configurations with their corresponding values in bulk iron chlorides. The important geometrical parameters of the most stable configuration B (0.5 ML) are contrasted with analogous distances of bulk FeCl2 and FeCl3 [29], as presented in Table 3. The Cl–Cl distances in the latter structure overshoot their corresponding distances in bulk FeCl2 and FeCl3 by 0.45 and 0.79 Å, respectively. The shortest Fe–Cl spacing in B (0.5 ML) site deviates marginally by 6.5 and 4.9% relative to the analogous values in bulk FeCl2 and FeCl3, respectively.

**Table 2: Adsorption energies and structural parameters for Cl/Fe(100)**

| Site | Coverage \( \Theta \) (ML) | \( E_{\text{ads}} \) (eV) | \( E_{\text{C}} \) (eV) | (Cl–Fe) (Å) | \( R \) (Å) | \( H \) (Å) | \( (d_{25})\% \) | \( (d_{23})\% \) |
|------|----------------|----------------|----------------|-------------|--------|--------|-------------|-------------|
| T    | 0.25           | −2.75          | −1.31          | 2.15        | 2.08   | 0.11   | −1.01       | −0.77       |
|      | 0.5            | −4.06          | −2.62          | 2.14        | 2.16   | 0.03   | 5.87        | −2.94       |
|      | 0.75           | −3.64          | −2.20          | 2.15        | 2.30   | 0.36   | −4.93       | 0.09        |
|      | 1              | −3.08          | −1.64          | 2.10        | 2.11   | 0.00   | −5.81       | −0.78       |
| H    | 0.25           | −3.93          | −2.49          | 2.58        | 1.45   | 0.02   | 7.62        | −2.60       |
|      | 0.5            | −4.39          | −2.97          | 2.60        | 1.65   | 0.01   | 9.76        | −4.21       |
|      | 0.75           | −3.86          | −2.42          | 2.59        | 1.48   | 0.06   | 5.75        | −3.33       |
| B    | 0.25           | −4.38          | −2.94          | 2.34        | 1.99   | 0.17   | 5.65        | −2.01       |
|      | 0.5            | −4.44          | −3.00          | 2.31        | 1.84   | 0.04   | 1.27        | −4.18       |
|      | 0.75           | −3.65          | −2.21          | 2.30        | 1.81   | 0.08   | 7.27        | −2.06       |
|      | 1              | −3.44          | −2.00          | 2.27        | 1.78   | 0.01   | 9.60        | −4.57       |

\( E_{\text{ads}} \): adsorption energies, \( E_{\text{C}} \): chemisorption energies, (Cl–Fe): average distance between nearest Fe atoms and Cl atom(s), \( R \): average heights of Cl atoms above the first layers, \( H \): the height between the lowest and highest Fe layers, \( (d_{25})\% \): relaxation of first and second Fe layers with respect to the clean surface (calculated based on equation (1)), and \( (d_{23})\% \): relaxation of second and third Fe layers with respect to the clean surface (calculated based on equation (1)).

**Table 3: Nearest atomic distances (in Å) for the optimized bulk of FeCl2 and FeCl3 and B (0.5 ML) site**

| Bond length (Å) | FeCl2 [29] | FeCl3 [29] | B (0.5 ML) |
|----------------|------------|------------|------------|
| Cl–Cl          | 3.54       | 3.20       | 3.99       |
| Cl–Fe          | 2.47       | 2.26       | 2.31       |

Despite certain notable differences in some interatomic distances, comparing geometries of B (0.5 ML) with bulk FeCl3 reveals that B (0.5 ML) site retains analogous geometries of bulk FeCl3 to some extent.

Next, we turn our attention to computing activation energies for the dissociation of a chlorine molecule above the surface. Iron readily corrodes in a chlorine-containing environment [30]. This indicates that iron chlorination ensues modest reaction barriers in real scenarios. Figure 2 shows a potential energy surface (PES) for the dissociation of a gas-phase chlorine molecule over the Fe (100) surface. We found the chlorine molecule to be very weakly adsorbed (−0.15 eV, DFT–vdW) while adapting a horizontal-like configuration. This value slightly decreases to −0.10 eV when a plain DFT method is deployed. Rupture of the Cl–Cl bond at two hollow sites demands a modest barrier of only 0.58 eV in a noticeably exothermic reaction of 2.94 eV. The profound surface-mediated effect of the iron surface becomes evident when contrasting the sizable Cl–Cl bond dissociation energy in the gas-phase chlorine molecule at 2.52 eV. The nature of the located transition state as a saddle point was confirmed by evaluating the vibrational frequencies of the structure using the linear response method [31]. The configuration retains one major
frequency of \((258\text{ i})/\text{cm}\) along with a few other minimal values in the range \((34\text{ i}–87\text{ i})/\text{cm}\). The latter values most likely correspond to the movements of surface iron atoms.

By considering the surface area of iron surfaces \((0.3 \text{ m}^2/\text{g})\) and the density of active sites \((\sigma = 2.1 \times 10^{-9} \text{ mol/cm}^2)\), plots the reaction rate constant \((a)\) and the reaction rate for the dissociative adsorption \((b)\) of a chlorine molecule/over the Fe\((100)\) surface are plotted in Figure 3 according to:

\[
k(T) = \frac{s}{\sigma n} \sqrt{\frac{RT}{2\pi M}} e^{-E_a/RT},
\]

where \(s\), \(M\), \(E_a\), and \(T\) signify the sticking coefficient (assumed to be 1.0), the molecular weight of Cl\(_2\), activation energy, and temperature, respectively. The calculations of the reaction rate considered a gas-phase concentration at 500 ppm Cl\(_2\) that mimicked mild corrosion conditions. To the best of our knowledge, the literature presents no analogous experimental measurements to compare with computed values herein.

### 3.3 Comparison between GGA and van der Waals corrections

The most stable adsorption sites identified above were examined using the GGA-PAW functional. The computed adsorption energies and selected distances are shown in Table 4. The stability ordering of the configurations using GGA-PAW for Cl/Fe\((100)\) configurations is the same as that presented in our previous study [9]. The recalculated GGA-PAW adsorption energies herein depart minimally from our previously computed values [9] in the narrow range of 0.01–0.11 eV. This is due to the number of surface layers of the Fe\((100)\) surface for each study; the current study used six layers, while the previous study used five layers.

For Fe\((100)\) at 0.5 ML, the adsorption energy of the B and H configurations was found to increase by \(\sim 0.45\) and 0.43 eV, respectively, after the inclusion of van der Waals corrections. For T and B at full coverage, the corresponding adsorption energies increased by \(\sim 0.35\) and 0.46 eV, respectively. The inclusion of vdW interactions into standard DFT within the GGA brings a large increase in binding for closed-shell species, i.e., singlet-state molecules with surfaces. The enhancement factor, the calculated ratio of the adsorption energy with the inclusion of vdW to the adsorption energy without the inclusion of vdW \((\alpha = \frac{E_{\text{ads. vdW}}}{E_{\text{ads. GGA}}})\), herein, marginally departs from units (1.11–1.15) entailing a minor contribution of the
vdW function. This is expected in view of the strong interaction between the distinctly charged Cl and Fe ions. The average height \((R)\) of the Cl atoms above the Fe atoms on the Fe\((100)\) surface calculated using the vdW-DF functional minimally reduces by 0–0.04 Å with respect to that calculated using the GGA-PAW functional [9]. Nonetheless, it is necessary to report values at the vdW-DF level for molecular adsorption systems. In these systems, the two sets of binding energies may significantly differ [32].

Considering the B (0.5 ML) configuration at the Cl/Fe\((100)\) system as an example, the adsorption energy calculated by the vdW-DF functional overshoot calculated by the plain DFT method was a factor of 1.11. This rather small increase in the adsorption energy translates into a negligible difference in the measured height among the two methods at only 0.02%. This finding can now be attributed to the ionic nature of the formed Cl–Fe bonds. Nonlocal interaction increases the adsorption energy on both Fe surfaces and shrinks the equilibrium distance (Table 4). The overlap between the wavefunctions of the iron slab and the Cl atoms accounts for the movement of the electron to higher energy states, and the Cl atoms reach a shorter distance where the magnitude of the attractive force is larger, and the binding energy increases. An inconsistent influence of the inclusion of the vdW function (on geometries and binding energies) with the degree of chlorination most likely originates from the repulsion between electronegatively charged chlorine atoms at high coverages.

### Table 4: Values of \(E_{ads.}\) and distance \((R)\) using vdW-DF and GGA-PAW functional for chlorine atom adsorbates on the Fe(100) surface

| Site     | Surface      | vdW-DF          | GGA-PAW         | \(\alpha\) |
|----------|--------------|------------------|-----------------|------------|
|          |              | \(E_{ads.} (eV)\) | \((R) (\text{Å})\) | \(E_{ads.} (eV)\) | \((R) (\text{Å})\) |
| B (0.5 ML)| Cl/Fe\((100)\)| -4.44            | 1.84            | -3.99      | 1.88      | 1.11 |
| H (0.5 ML)|              | -4.39            | 1.65            | -3.96      | 1.66      | 1.11 |
| T (1 ML) |              | -3.08            | 2.11            | -2.73      | 2.11      | 1.13 |
| B (1 ML) |              | -3.44            | 1.78            | -2.98      | 1.79      | 1.15 |

3.4 Electronic analysis

The electronic interaction between chlorine and the Fe\((100)\) surface was examined by calculating the differential charge density distribution of the most thermodynamically stable structure (B-0.5 ML). As chlorine adsorbed on the Fe\((100)\) surface, in B (0.5 ML) site, a large degree of charge transfer takes place between Cl atoms and the iron slab. The charge transfer from Cl atoms into the Fe slab can be seen in the electrostatic potential maps. The yellow and blue areas represent a gain and a loss in charge, respectively. The brown and light green spheres represent Fe and Cl atoms, respectively.

**Figure 4:** Charge density difference of Cl adsorbed on the Fe\((100)\) surface in the B (0.5 ML) site. The isosurface was set as 0.005 e/Å\(^3\). The yellow and blue areas represent a gain and a loss in charge, respectively. The brown and light green spheres represent Fe and Cl atoms, respectively. (a) GGA and (b) vdW-DF.
surface Fe atoms using both GGA-PAW and van der Waals correction functions (Figure 4). Charge transfer from the surface to the adsorbate has significantly decreased using the van der Waals correction function in comparison to that obtained using the GGA function. The weak electrostatic interaction and dispersion forces contribute to the adsorption of Cl on the Fe(100) surface. According to the comparison between the above two functions, the charge that accumulates because of the electrostatic effect is larger and extends over a wider domain. Atomic partial charges for selected atoms in the B (0.5 ML) structure are presented in Figure 5. Across most of the investigated configurations, surface iron atoms are reduced by ~0.2 e, while adsorbed chlorine atoms entail a net negative charge of 0.3 e.

The work function (Φ) represents an important electronic fingerprint halogen/iron system. Through combined AES-LEED experiments, Yang et al. [33] observed a noticeable change in the work function of Fe(100) and Fe(110) surfaces upon bromine adsorption. The addition of a bromine atom was shown to decrease the work function of the Fe(110) surface while increasing it for Fe(100). The variation in Φ was primarily attributed to a surface charge redistribution that creates an inward pointing dipole. The latter prevails more in the open Fe(100) surface and is sustained by a larger probability of subsurface bromine penetration in reference to the more compact Fe(110) surface. Along the same note of enquiry, the inconsistent change in the work function among halogen (Br/I) –iron configurations prompted Wu and Klepeis [34] to propose a multidipole model in which the change in the work function is governed by the competition between dipoles in different directions. Chen et al. [35] illustrated a positive correlation between the changes in vertical dipole moments (with respect to the degree of sulfur coverage above the Fe(100) surface) and that of the work function. Our calculated Φ values for unsubstituted Fe(100) and Fe(110) surfaces amount to 3.92 and 4.09 eV, respectively. These values are in accord with analogous experimental and theoretical values [36–38]. To the best of our knowledge, the literature presents no account of the values of work functions for Cl–iron systems. Figure 6 contrasts Φ values between pure iron surfaces and selected Cl–Fe structures. Dissociation of a chlorine molecule over the Fe(100) surface increases its Φ value by 0.67 eV, while chlorine addition decreases the work function in reference to the pure Fe(110) surface. This trend prevails in bromine addition to the iron surfaces, as in previous studies [34].

4 Conclusions

In this study, DFT–vdW calculations were performed to determine the geometrical features and thermodynamic and kinetic parameters for the adsorption of chlorine on the Fe(100) surface. The obtained activation energy for the dissociative adsorption of the chlorine molecule, along with the density of active sites on the Fe(100) surface, was used to develop a reaction constant and reaction rate for the initial uptake of gaseous chlorine molecules by the Fe(100) surface. As a result of the ionic character of the interaction between chlorine and iron atoms, the enhancement factor characterizing the influence of the vdW functional resides around unity. Chlorine adsorption reduces the work function of the Fe(100) surface. Future research directions may include mapping out the mechanism for the growth of iron chlorides.
from the subsurface adsorption of chlorine atoms into the iron bulk.

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