Methylchloride adsorbed on Si(0 0 1): an ab initio study

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Abstract

We present ab initio calculations of the adsorption of methylchloride (CH₃Cl) on Si(0 0 1). Among multiple plausible adsorption geometries, we find five thermodynamically favorable configurations. These lead to strong geometrical changes in the Si surface structure as well as to significant charge transfer processes. The stability of the adsorption structures is discussed in terms of electrostatics. The results are compared to recent experimental and theoretical findings.

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1. Introduction

The (0 0 1) surface of silicon is the starting point for the fabrication of most microelectronic devices. Therefore, Si surface reactions with metals, hydrogen, oxygen and halogens have been intensively studied in the past [1]. The microscopic understanding of molecule-covered Si surfaces, however, is very limited. That concerns both the details of the bonding as well as the electronic properties. In order to gain insight in the adsorption mechanisms of small organic molecules on Si surfaces, we study the prototypical case of methylchloride adsorption. The chemistry of chlorine species on Si(0 0 1) is relevant in the context of silicon growth from precursor molecules such as dichlorosilane. Chlorine is also frequently used as an etching species in the processing of Si. The interaction of alkyl species with Si is of interest for applications like silicon carbide film growth. The CH₃Cl/Si interface has been investigated by electron energy loss spectroscopy, Auger electron spectroscopy, and temperature programmed desorption as well as scanning tunneling microscopy (STM) [2–4]. From the experiments it was concluded that methylchloride adsorbs dissociatively on Si. Recently, the adsorption process has also been investigated computationally. However, cluster calculations by Lee and Kim [4] and pseudopotential calculations by Romero et al. [5] arrived at very different results concerning the adsorption energetics.

In the present work we study a large variety of adsorption geometries. We find five of them to be energetically favored. These models are compared with findings previously published and analyzed with respect to their bonding and charge transfer characteristics.
2. Method

The total-energy and electronic-structure calculations are performed using the Vienna Ab Initio Simulation Package (VASP) implementation [6] of the gradient-corrected (PW91) [7] density functional theory (DFT). The electron–ion interaction is described by non-norm-conserving ultrasoft pseudopotentials [8], allowing for the accurate quantum-mechanical treatment of first-row elements with a relatively small basis set of plane waves. We expand the electronic wave functions into plane waves up to an energy cutoff of 25 Ry, which has been demonstrated to be sufficient in our previous studies on pyrrole and uracil adsorption on Si(0 0 1) [9,10] and on DNA base molecules [11].

The Si(0 0 1) surface is modeled with a periodically repeated slab. The supercell consists of eight atomic layers plus adsorbed molecules and a vacuum region equivalent in thickness to 12 atomic layers. The Si bottom layer is hydrogen saturated and kept frozen during the structure optimization. All calculations are performed using the c(4 × 2) surface periodicity with the calculated Si equilibrium lattice constant of 5.456 Å. Properties of gas-phase methylchloride are calculated using a 12 × 12 × 12 Å³ supercell. No symmetry constraints were applied during the structure optimization.

Our calculations employ the residual minimization method–direct inversion in the iterative subspace (RMM–DIIS) algorithm [12,13] to minimize the total energy of the system. The molecular und surface atomic structure is considered to be in equilibrium when the Hellmann–Feynman forces are smaller than 10 meV/Å. The Brillouin zone integrations for the surface calculations are carried out with four \( k \) points in its irreducible part. The \( \Gamma \) point is used for treating the gas-phase molecule.

3. Results and discussion

3.1. Gas-phase methylchloride

In order to accurately describe the adsorption of methylchloride (Fig. 1) on the silicon surface the proper reproduction of the gas-phase molecule’s properties from first principles must be guaranteed. Table 1 shows that for a cutoff of 25 Ry the calculated bond lengths and angles of methylchloride agree within an error bar of fractions of a percent with experimental data. Our data are comparable in accuracy to a very recent DFT pseudopotential calculation [5]. Also, the calculated dipole moment of \( \mu = 1.833 \) D is very close to the experimental value of \( \mu_{\text{exp}} = 1.892 \) D [14]. In order to probe the reliability of our method to describe bonding and dissociation processes we examine the dissociation of gas-phase methylchloride. The main fragmentation channel leads to the formation of the anion \( \text{Cl}^- \) and the cation \( \text{CH}_3^+ \), if the C–Cl distance is increased. Although density functional theory with a plane-wave basis set has shortcomings when treating isolated ions because of the enforced periodic boundary conditions [15] it is possible to obtain a fair estimate for the dissociation energy by calculating the total energies of the system \( \text{CH}_3\text{Cl} \) with increasing anion-cation separation. The system

<table>
<thead>
<tr>
<th>Bond length (Å)</th>
<th>This work</th>
<th>DFT-BLYP [5]</th>
<th>Experimental [14]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–Cl</td>
<td>1.78</td>
<td>1.82</td>
<td>1.79</td>
</tr>
<tr>
<td>C–H</td>
<td>1.09</td>
<td>1.09</td>
<td>1.09</td>
</tr>
</tbody>
</table>

Table 1
Structural properties of isolated \( \text{CH}_3\text{Cl} \)
remains stable as long as there is a small overlap of the ionic wavefunctions; for methylchloride this is the case for a CH3–Cl distance of up to about 4.0 Å. The resulting energies are then fitted to a generalized Morse potential [16] of the form

\[
E(r) = E_D \left\{ Q e^{-\sqrt{(Q+1)k_e/Q}E_D(r-r_e)}} \right. \\
\left. - (Q + 1) e^{-\sqrt{Qk_e/(Q+1)}E_D(r-r_e)}} \right\}
\]

with the dissociation energy \( E_D \), the quality factor \( Q \), the elastic constant \( k_e \) and the equilibrium separation \( r_e \). It can be seen in Fig. 2 and from the fitting parameters in Table 2 that the interaction potential (1) allows for a good (correlation coefficient \( R = 0.9999 \)) description of the dissociation of methylchloride. The calculated dissociation energy \( E_D = 4.81 \text{ eV} \) agrees qualitatively with the experimental value of \( E_D^{\exp} = 3.62 \text{ eV} \) [14].

### 3.2. Adsorption geometries

Clean Si(0 0 1) surfaces reconstruct due to the dimerization of the topmost atoms. The dimers are asymmetric, consisting of an \( sp^2 \)-like bonded “down” atom, which moves closer to the plane of its three nearest neighbors, and an “up” atom, which moves away from the plane of its neighbors and possesses an \( s \)-like dangling bond. The process of rehybridization is accompanied by a charge transfer from the “down” to the “up” atom. The direction of buckling alternates within each dimer row. To reduce the energy due to relaxation of local stress and electrostatics, the buckling in the neighboring dimer rows is such that the Si(0 0 1) surface ground state is \( c(4 \times 2) \) reconstructed [1,17]. This \( c(4 \times 2) \) reconstructed Si(0 0 1) surface serves as starting point for our calculations on the adsorption of methylchloride. In the following we consider a coverage where one molecule is adsorbed per \( (4 \times 2) \) surface unit cell.

The energetically most favorable adsorption geometries are sketched in Fig. 3. We find two physically adsorbed states, labeled P and P’ , two dissociated states, labeled D and D’ , as well as the fragmented state F. Their adsorption energies and structural details are given in Table 3. In order to calculate the adsorption energy for the fragmented structure F, we assume that the surface is in equilibrium with a Cl2 reservoir. Due to the temperature and pressure dependence of the Cl chemical potential, the relative stability of F will strongly depend on the preparation conditions. The most stable geometry D, yielding an adsorption energy of 3.21 eV, is the dissociation of methylchloride into a Cl atom and a methyl group which are bonded to the same surface dimer, in accordance with previous theoretical results [5]. Common to the five configurations is their strong influence on the Si surface structure. Most of these adsorbate-induced changes can be explained by electrostatic considerations.

As far as a comparison can be made (see Table 3), our adsorption energies and equilibrium geometries are in excellent agreement with the calculations of [5]. Remaining discrepancies, in particular with respect to the adsorption energies, are most likely related to the usage of different parametrizations of the exchange and correlation energy. On the other hand, our results deviate significantly from the ones obtained by recent cluster calculations [4]. Lee and Kim calculate for the structure D, e.g., an adsorption energy of 1.3 eV, much smaller than the 3.2 eV calculated here. These discrepancies are probably related to two substantial differences in the calculation: The usage of a fully

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**Fig. 2.** Dissociation of the isolated CH3Cl molecule into fragments CH2 and Cl–, \( r \) denotes the C–Cl distance. For details, see text and Table 2.

### Table 2

Curve-fitting parameters for the dissociation of an isolated CH3Cl molecule

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_D )</td>
<td>4.81 eV</td>
</tr>
<tr>
<td>( Q )</td>
<td>0.23</td>
</tr>
<tr>
<td>( k_e )</td>
<td>17.46 Nm(^{-1})</td>
</tr>
<tr>
<td>( r_e )</td>
<td>1.78 Å</td>
</tr>
<tr>
<td>( \chi^2 )</td>
<td>0.0262</td>
</tr>
<tr>
<td>( R )</td>
<td>0.9999</td>
</tr>
<tr>
<td>( \text{rms} )</td>
<td>0.0267%</td>
</tr>
</tbody>
</table>

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The adsorption of methylchloride goes along with a more or less strong charge redistribution, depending on the adsorption geometry. To quantify this effect we calculate the spatially resolved charge density difference
\[
\Delta q(r) = q_{\text{ads/subs}}(r) - q_{\text{subs}}(r) - q_{\text{ads}}(r),
\]
where \(q_{\text{ads/subs}}, q_{\text{subs}}\) and \(q_{\text{ads}}\) are the (negative) charge densities of the relaxed adsorbate–substrate system, of the clean relaxed surface and of the adsorbate without substrate, respectively.

The number of electrons transferred during the adsorption process is consequently given by
\[
Q^\pm = \int_{\Delta q(r) \geq 0} dr \Delta q(r).
\]

The length of the \(Q^+–Q^-\) dipole projected onto the surface normal is defined as
\[
d_z = \frac{1}{Q^+} \int_{\Delta q(r) > 0} dr z \Delta q(r)
- \frac{1}{Q^-} \int_{\Delta q(r) < 0} dr z \Delta q(r).
\]

### Table 3

<table>
<thead>
<tr>
<th>Model</th>
<th>(E_{\text{ad}}) [eV]</th>
<th>(d_{\text{Si–C}}) [Å]</th>
<th>(d_{\text{Si–Cl}}) [Å]</th>
<th>(d_{\text{C–Cl}}) [Å]</th>
<th>(a^*) [Å]</th>
<th>(\phi^\pm) [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>3.21 (3.07)</td>
<td>1.88 (1.91)</td>
<td>2.09 (2.12)</td>
<td>3.68 (3.84)</td>
<td>2.41 (2.44)</td>
<td>2.0 (2.4)</td>
</tr>
<tr>
<td>D'</td>
<td>2.64 (2.83)</td>
<td>1.88</td>
<td>2.09</td>
<td>–</td>
<td>2.34\textsuperscript{a}</td>
<td>1.7\textsuperscript{a}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.43\textsuperscript{d}</td>
<td>2.7\textsuperscript{d}</td>
</tr>
<tr>
<td>P</td>
<td>0.34 (0.10)</td>
<td>–</td>
<td>2.56 (2.56)</td>
<td>1.81 (1.82)</td>
<td>2.39 (2.42)</td>
<td>8.6</td>
</tr>
<tr>
<td>P'</td>
<td>0.32 (0.04)</td>
<td>3.38</td>
<td>2.91 (2.53)</td>
<td>1.80 (1.83)</td>
<td>2.30 (2.41)</td>
<td>4.2</td>
</tr>
<tr>
<td>F</td>
<td>3.12</td>
<td>1.88</td>
<td>–</td>
<td>–</td>
<td>2.34</td>
<td>7.8</td>
</tr>
</tbody>
</table>

For comparison DFT results from \([5]\) are included in parentheses.

\textsuperscript{a} Dimer length, \(d_{\text{clean}} = 2.35\) Å.

\textsuperscript{b} Dimer angle, \(\phi_{\text{clean}} = 10.9\)°.

\textsuperscript{c} Value for chlorated Si dimer.

\textsuperscript{d} Value for methylated Si dimer.

Fig. 3. Sketches of the five adsorption geometries considered. For clarity only relevant Si surface atoms are indicated.
The \( z \) component of the dipole moment is given by \( p_z = |Q| \frac{dz}{C} \). By convention the dipole points from the negative to the positive center of charge, i.e., a positive (negative) \( p_z \) equals a dipole parallel (antiparallel) to the surface normal, respectively. This corresponds to a charge transfer from the molecule to the substrate, or vice versa, respectively. In order to quantify the vertical charge redistribution along the surface normal we define

\[
Q^+_z = \int_{\Delta q(z) \geq 0} \Delta q(z), \quad (5)
\]

with \( \Delta q \) representing the charge density difference averaged over the surface area,

\[
\Delta q(z) = \frac{1}{A} \int dxdy \Delta q(r). \quad (6)
\]

The corresponding vertical charge separation length \( d_k \) is then given by Eq. (4) with \( \Delta q(r) \) replaced by \( \Delta q(z) \). Numerical values are compiled in Table 4, and Fig. 5 illustrates the charge transfer for the five adsorption geometries.

A possible precursor state for the dissociative attachment of methylchloride to the surface is structure P. The Cl atom binds to the “down” Si atom while the methylchloride molecule remains intact. It should be noted that our calculations do not favor an adsorption process seemingly observed in [3], in which, after binding of CH\(_3\)Cl to the surface dimer, the methyl group drifts away into vacuum. Structure P gives rise to an adsorption energy of 0.34 eV. A lone electron pair of the highly electronegative Cl atom donates charge into the empty dangling bond of the “down” Si atom and forms a dative bond from Si to Cl. The bond length \( d(Si-Cl) = 2.56 \text{ Å} \) is about 0.5 Å larger than the sum of the covalent radii of Si and Cl. As the charge accumulation in this bond is rather weak (see also Figs. 4 and 5), the amount of rehybridization of

| Geometry | \( |Q^+| \) | \( |Q^-| \) | \( d_k \) [Å] | \( d_{||} \) [Å] | \( p_z \) [Å] |
|----------|----------|----------|-----------|----------|---------|
| P        | 2.39 e   | 0.57 e   | 0.10      | 0.43     | 1.2     |
| D        | 3.46 e   | 0.81 e   | -0.42     | -1.78    | -7.0    |
| P'       | 4.49 e   | 1.85 e   | 0.83      | 2.00     | 17.9    |
| D'       | 7.02 e   | 1.15 e   | 0.18      | 1.06     | 5.9     |
| F        | 3.33 e   | 1.49 e   | 0.86      | 1.92     | 13.8    |

Fig. 4. Total valence charge density in the dimer plane for the five adsorption structures. Large (small) white circles represent Si (H) atoms, hashed circles Cl atoms, black circles C atoms. The contour lines are equidistantly spaced from 0.25 e/Å\(^3\) (light gray) to 2.00 e/Å\(^3\) (dark gray) with an increment of 0.25 e/Å\(^3\).

![Image of diagrams](image-url)
the surface dimer decreases only slightly, resulting in a reduction of the dimer angle by 2° compared to the clean surface and a very small increase of the dimer length by 0.04 Å. Consistently, the adsorption in geometry P is accompanied with the smallest charge transfer of the configurations studied of only $Q^\dagger = +2.39e$, the smallest absolute dimer length $|d_c| = 0.10$ Å and therefore also the smallest absolute dipole moment $|p_z| = 1.2$ Debye (D).

In configuration $P'$ the intact molecule hovers above the Si dimer in such a way that Cl is close to the “‘up’” Si atom and the methyl group close to the “‘down’” Si atom. This is the only geometry of the type “Cl-near-‘up’-Si-atom” we find to be stable; all other configurations are of the type “Cl-near-‘down’-Si-atom”. Because of the relatively large distances $d_{Si-C} = 3.38$ Å and $d_{Si-Cl} = 2.91$ Å one might think of the interaction between molecule and surface being even weaker as in the case P, and a glance at Fig. 4 seems to confirm this notion. But Fig. 5 shows that the physisorption goes along with a strong charge redistribution among molecule and substrate. The mutual Coulomb repulsion between the “electron-rich” Cl atom and the filled Si dangling bond on the one hand reduces the buckling angle to 4.2°. On the other hand, it leads to a charge transfer from the filled to the empty Si dangling bond, so that the whole structure is stabilized. Remarkable for the geometry $P'$ is the large absolute dipole moment $|p_z| = 17.9$ D inspite of only modest electron transfer of $Q^\dagger = +4.49e$. This may be related to the quite clear separation of electron-rich and electron-poor regions after the charge transfer process, see Fig. 5.

The structures D (adsorption energy 3.21 eV) and D' (adsorption energy 2.64 eV) are both characterized by strong ionic Si–Cl and Si–C bonds which lead to the near complete reduction of the dimer buckling. The total valence charge density plots in Fig. 4 show charge accumulations around the Cl and C atoms as is to be expected because of the electronegativity values of the species (C: 2.5, Cl: 2.8, Si: 1.7). For the structure D, we calculate a negative dipole moment, $p_z = -7.0$ D. This corresponds to an average charge transfer from substrate to molecule, as can be expected from the large, by comparison to the substrate, electronegativities of the molecule constituents. Intriguingly, however, all other adsorption geometries are seemingly accompanied by electron transfers from the molecule into the substrate. This can hardly be explained by simple electronegativity arguments.

Fig. 5. Charge density difference (see text and Eq. (2) ) in the dimer plane for the five adsorption structures. Large (small) white circles represent Si (H) atoms, hashed circles Cl atoms, black circles C atoms. The contour lines are equidistantly spaced from $-0.25$ e/Å$^3$ to 0.45 e/Å$^3$ with an increment of 0.05 e/Å$^3$. Contour lines in gray (white) regions correspond to electron accumulation (depletion).
On the other hand, clean Si(0 0 1) surfaces experience a reduction of the ionization energy by about 0.35 eV upon exposure to atomic hydrogen. This is explained by the hydrogen-induced conversion of tilted into untitled dimers, neutralizing the electric double layer formed by filled and empty Si dimer atom dangling bonds [18]. A similar mechanism is responsible in the present case. The tilting of the dimers is reduced upon adsorption of (fragmented) methylchloride. In the case of the adsorption model D the corresponding electron transfer is overcompensated. The actual sign of \( p_z \) thus crucially depends on the details of the charge distributions of the adsorbate–substrate system, the substrate and the adsorbate all of which are comprised in the quantity \( \Delta q \).

The starting geometry for configuration F is CH\(_3\)Cl with the Cl–C bond parallel to the surface normal and the methyl group pointing towards the “up” Si atom. The structure optimization leads to fragmentation: while the methyl group ionically bonds to the Si atom, the C–Cl bond length increases so that at last the Cl atom is abstracted from the molecule and ejected into the vacuum region.

4. Summary

In summary, the adsorption of methylchloride on Si(0 0 1) was investigated by means of first principles calculations. We find a strong tendency for molecular fragmentation. The most favorable structure found here corresponds to CH\(_3\) and Cl fragments bonded to the same dimer. We investigated in detail the charge transfer accompanying the adsorption process and found a remarkable influence of the adsorption geometry on the sign of the average electron transfer parallel to the surface normal.

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