Reaction Dynamics of Alkyl Bromides at Silicon; Experiment and Theory

by

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Abstract

Physisorption and reaction at silicon surfaces of a series of brominated organic molecules: bromoethane, 1,2-dibromoethane, 1-bromopropane, 1-bromobutane and 1-bromopentane were examined by Scanning Tunneling Microscopy (STM).

On Si(111)-7×7, a widely-spaced “one-per-corner-hole” pattern was observed, formed by the physisorption and reaction of several alkyl bromides. This “one-per-corner-hole” pattern suggested long-range repulsion between the adsorbates. Density Functional Theory (DFT) calculations, performed by others in parallel with these experiments, showed that this long-range repulsion was due to lateral charge transfer in the Si(111)-7×7 surface consequent on the physisorption of an alkyl bromide or chemisorption of a Br-atom.

The reaction rate of bromine ‘abstraction’ (transfer of a Br-atom from the adsorbate to the silicon) was examined for two physisorbed states of 1-bromopentane on Si(111)-7×7, one vertical and one horizontal, each distinguishable by STM. The energy barrier was found to be significantly lower for abstraction of Br-atom from the vertical than for the horizontal 1-bromopentane, both for thermal and electron-induced reaction. This finding accords with
previous DFT calculations for methyl bromide, for which theory exhibited a clear preference for a vertical transition state in the bromination of Si(111)-7×7.

The effect of alkyl chain-length on the rate of thermally-induced dissociative attachment reactions was investigated for a series of primary bromo-alkanes (bromoethane, 1-bromopropane and 1-bromobutane) on a different face of silicon; Si(100)-c(4×2). These three bromo-alkanes all physisorbed exclusively ‘inter-row’, bridging the gap between Si dimer-rows of Si(100)-c(4×2). Thermal reaction was highly ‘localized’, i.e. the chemisorbed Br-atom was formed directly below the parent bromo-alkane. The thermal barrier heights were found experimentally to increase systematically with chain length. This trend was interpreted, on the basis of DFT calculations performed by the author, as being due to the extra energy required to lift the alkyl group in going from the initial physisorbed state to the more-nearly vertical transition state.
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### List of Abbreviations

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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-Coupled Device</td>
</tr>
<tr>
<td>CI</td>
<td>Configuration Interaction</td>
</tr>
<tr>
<td>CI-NEB</td>
<td>Climbing Image Nudged Elastic Band</td>
</tr>
<tr>
<td>DAS</td>
<td>Dimer-Adatom-Stacking-Fault</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of States</td>
</tr>
<tr>
<td>FIRE</td>
<td>Fast Inertia Relaxation Engine</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier Transformation</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized Gradient Approximation</td>
</tr>
<tr>
<td>HREELS</td>
<td>High-Resolution Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>LAR</td>
<td>Localized Atomic Reaction</td>
</tr>
<tr>
<td>LDA</td>
<td>Local Density Approximation</td>
</tr>
<tr>
<td>LEED</td>
<td>Low Energy Electron Diffraction</td>
</tr>
<tr>
<td>MEP(s)</td>
<td>Minimum Energy Pathway(s)</td>
</tr>
<tr>
<td>NEB</td>
<td>Nudged Elastic Band</td>
</tr>
<tr>
<td>PAW</td>
<td>Projector Augmented Wave</td>
</tr>
<tr>
<td>PBE</td>
<td>Perdew-Burke-Ernzerhof</td>
</tr>
<tr>
<td>PID</td>
<td>Proportional–Integral–Derivative</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>SAP</td>
<td>Surface-Aligned Photochemistry</td>
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<tr>
<td>SCF</td>
<td>Self Consistent Field</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
</tr>
<tr>
<td>TPR</td>
<td>Temperature Programmed Reaction</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra-high Vacuum</td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>USPP</td>
<td>Ultrasoft Pseudopotential</td>
</tr>
<tr>
<td>VASP</td>
<td>Vienna <em>ab-initio</em> simulation package</td>
</tr>
<tr>
<td>VT</td>
<td>Variable Temperature</td>
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Chapter 1

1 Introduction

1.1 Motivation

Molecular reaction dynamics, as the study of the motions of individual molecules during chemical reactions, originated in gas phase studies of elastic, inelastic and, finally, reactive collisions. Molecular reaction dynamics aims to probe and control reactive collisions. For example, the crossed-beam method permits only single collisions, based on which dynamics has often been successfully extracted from the measured scattered products. The weakness of this method lies at the varied nature of the reactive encounters. Current progress of this method stresses the control over the geometry of reagent approach.

On a solid surface, adsorbed molecules are aligned and oriented as a natural consequence of localized adsorption phenomena. The alignment and orientation of adsorbed molecules offers an important advantage for surface reactions, as opposed to gas-phase reactions, that the initial geometry is well defined. Early studies that took advantage of the alignment of reagents at a surface in our laboratory centered on surface chemistry induced by lasers, and hence were termed “Surface-Aligned Photochemistry” (SAP). More recently, the study of surface reactions “a molecule at a time” has been made possible using Scanning Tunneling Microscopy (STM) as the measurement tool.

Since its invention in the 1980s by Binnig and Rohrer, STM has been used as a powerful technique to study molecular dynamics at a surface. STM has succeeded, with atomic precision, in detailing a wide range of molecular dynamics. Molecular translation, rotation, desorption, isomerization, and dissociation, including dissociative chemisorption, have all been studied using STM. In the ideal case, the system of interest is imaged before and after a dynamical event, and then the motions during the event are inferred. This is the burgeoning new field of molecular dynamics, studied one molecule at one time, at a solid surface.

Beyond the imaging capability of STM, this instrument may also be used to trigger and, as noted, subsequently monitor a dynamical event. Compared with conventional ensemble-averaged techniques, STM is unique in its ability to apply an extremely high electron density, $10^6 \, \text{A cm}^{-2}$,
equivalent to a dose of $10^{25}$ electrons per cm$^2$) in activating surface processes of very low efficiency. The high electron density arises because the tunneling current of the STM, typically of order 100 pA, is applied over a very small area.

In other laboratories, recent experiments have started to exploit the pump-probe idea rooted in the photochemistry community; nanosecond temporal resolution was attained in studying the spin-relaxation of Fe atom on a metal supported Cu$_2$N overlayer$^7$. This is an important development of STM in the time domain that will enable the study of transient motions.

1.2 Thesis organization

This thesis is organized as follows. In the rest of Chapter 1, I describe the operation of a scanning tunneling microscope, and briefly introduce the silicon surface structures that are later referred to. Chapter 2 describes the particular apparatus employed in these studies, together with relevant experimental techniques. Chapter 3 reviews the theoretical background to the computations made for this thesis.

Further chapters detail my experiments and calculations on particular systems. In Chapter 4, an unexpected long-range repulsion at a silicon surface is reported exceeding by over an order-of-magnitude than on metals, as induced by both physisorption and chemisorption of alkyl bromide molecules. In Chapter 5, I examine the substantial and characteristic effect of molecular alignment upon reactivity for 1-bromopentane on Si(111)-7×7. Chapter 6 reports for the first time and also analyzes theoretically the role that alkyl chain length plays in affecting reactivity of primary bromo-alkanes on Si(100)-c(4×2).

Finally in Chapter 7, I give a summary and a perspective of this thesis. In the appendix, a brief report is given for two systems that were subject to preliminary experiments; 1,2-dichloroethane and 1,2-dibromoethane on Si(100).

1.3 Scanning tunneling microscopy

Scanning Tunneling Microscopy is a powerful tool for determining structural and electronic properties of conducting (metal and semiconductor) surfaces. This section briefly introduces the basic principle of STM together with common models for tunneling current and bias-dependent imaging in routine STM measurements.
1.3.1 Simple model of tunneling

Figure 1. Schematic of one-dimensional tunneling model. Taken from Ref. 8.

The operating principle of STM is based on the tunneling effect in quantum mechanics\(^8\). The wave functions of the sample and the tip can overlap with each other with a separation of several Angstroms, allowing the transfer of electrons through an energy barrier. A one-dimensional model of the tunneling process is shown in Fig. 1. The gap between the sample and tip gives rise to an energy barrier. When a bias voltage is applied across the sample and the tip, electrons can tunnel through the gap, thereby giving a measurable electric current. The current can be quantitatively expressed as:

\[
I \propto V \exp\left(-\frac{2m\Phi}{\hbar^2}s\right). \tag{1}
\]

V represents the bias voltage between the tip and sample (indicated in Fig. 1 as ‘eV’); \(\Phi\) denotes the average work function between the tip and sample (shown for the sample in Fig. 1); and \(s\) is the “tunneling gap”, the distance between the tip and the sample.

The exponential dependence of the tunneling current with respect to the tunneling gap, illustrated in Eqn. (1), provides STM with a sufficiently high sensitivity in the vertical (gap) direction (horizontal in Fig. 1). The small change of only one Angstrom in the tunneling gap causes almost an order of magnitude change in the value of the corresponding tunneling current. That is why the vertical resolution of STM can be as sensitive as 0.01 nm. In principle, and often in practice, one single leading atom at the end of the tip can act as the probe to detect the surface, giving a lateral resolution of around 0.1 nm.
1.3.2 Interpretation of tunneling current

Although it captures the physical picture for tunneling, the above one-dimensional model is oversimplified. To describe the tunneling current more exactly, Tersoff and Hamann\textsuperscript{10} formulated a widely referenced model on the basis of Bardeen’s tunneling theory.

According to the first-order perturbation theory, Bardeen derived the tunneling current between a sample and a tip as:

$$I = \frac{2\pi}{\hbar} \sum_{s,t} |f(E_s) - f(E_t)| M^2 \delta(E_t - V - E_s)$$

(2)

where $f(E)$ is the Fermi distribution function, $V$ is the bias voltage across the barrier, $E_s$ is electron energy level in sample, $E_t$ is the electron energy level in tip and $M$ is the matrix element\textsuperscript{9}. The matrix element, $M$, represents the amplitude of electron transfer across the barrier and can be formally written as:

$$M = \frac{\hbar^2}{2m} \int dS \cdot (\Psi_t \nabla \Psi_s - \Psi_s \nabla \Psi_t) .$$

(3)

In this expression, an integral over the sample surface emerges, involving the wave functions of both tip and sample, $\Psi_t$ and $\Psi_s$.

To gain an explicit insight into tunneling current, Tersoff and Hamann further assumed a locally spherical symmetry for the STM tip, a small bias voltage across the barrier and zero temperature\textsuperscript{10}. Consequently, the expression for tunneling current under these conditions was derived as:

$$I = \frac{2\pi e^2 V}{\hbar} \sum_{s,t} |M|^2 \delta(E_t - E_v) \delta(E_s - E_v) .$$

(4)

In other words, this model ensures that STM effectively maps out a contour of constant density of states (DOS) at the Fermi level by scanning the tip over the sample and keeping the tunneling current constant. For metal surfaces, STM images taken in this manner correspond nicely to the surface topography since the DOS at the Fermi level is fairly constant. However, this is not the
case for semiconductors, e.g. silicon, where the Fermi level usually lies inside the band gap and produces a large variation of the DOS as a function of position at the surface.

On semiconductors, in order to work outside the band-gap of the material, the bias voltage employed in an STM measurement is typically of the order of several volts, invalidating the low bias assumption in the Tersoff-Hamann model. In the high bias region, Hamers\textsuperscript{11} suggested the use of semi-classical Wentzel-Kramers-Brillouin expression for planar tunneling:

$$I = \int_{0}^{eV} \rho_{s}(r,E)\rho_{t}(r,-eV+E)T(E,eV,r)dE$$ \hspace{1cm} (5).$$

In this expression, $T(E,eV,r)$ is the transmission probability given by

$$T = \exp\left(-\frac{z\sqrt{2m}}{\hbar}\sqrt{\frac{(\Phi_{s} + \Phi_{t})}{2} + \frac{eV}{2} - E}\right)$$ \hspace{1cm} (6),$$

where two important new quantities enter, the sample and tip work functions, $\Phi_{s}$ and $\Phi_{t}$. As a result, the contour mapped by STM at a constant tunneling current is a convolution of DOS for both sample and tip, as well as the transmission probability between the two.

1.3.3 Unoccupied state image and occupied state image

Fig. 2 sketches the tunneling process when STM is used to image a semiconductor surface.\textsuperscript{12} As shown in Fig. 2(a), the Fermi level of the semiconductor is assumed to be at the middle of the band gap (a condition which only holds for undoped semiconductors), and is aligned to the Fermi level of the metal tip when no bias is applied across the junction. At positive sample bias, as in Fig. 2(b), electrons tunnel from the occupied states of the tip into the unoccupied states of surface; the tunneling current is dominated by the electrons close to the Fermi level of the tip. Since the DOS of the tip in this region can be taken as constant, the tunneling current largely corresponds to the unoccupied states of the sample surface. Hence, the STM images taken at a positive sample bias are termed as unoccupied state images or empty-state images. As in Fig. 2(c), the situation is reversed if a negative sample bias is employed. Consequently, the STM images taken at a negative sample bias is termed as occupied state images, or filled-state images.
Figure 2. Energy diagram for metal-vacuum-semiconductor junction at (a) no sample bias, (b) positive sample bias and (c) negative sample bias. Here, the sample Fermi level is assumed midway at its band gap. Taken from Ref. 12 with modification.

1.4 Silicon surfaces

Silicon is an important material that has been heavily studied for several decades. The research is mainly motivated by its technological value in fabricating electronic devices, such as transistors and integrated circuits\(^1\). The functionalization of silicon surfaces using organic molecules is expected to enable the creation of useful hybrid molecular electronics\(^2\).

Clean silicon surfaces feature dangling bonds, as extensively examined, governing the surface structure\(^3\). If silicon surfaces are taken as cleaved from the bulk, the bonds for the atoms at the topmost layer are broken, forming highly energetic dangling bonds. These dangling bonds have their orbitals filled incompletely by non-paired electrons. To reduce the number of these dangling bonds, atoms of silicon surfaces undergo, quite often, certain dramatic rearrangement, known as surface reconstructions. In the section below, the structures of two silicon surfaces studied in this thesis, Si(111)-7×7 and Si(100)-c(4×2), are briefly described.

1.4.1 Si(111)-7×7 surface

Si(111), upon heating above 800 K, reconstructs into the complex 7×7 structure that consists of 49 surface atoms in the new unit cell. As shown in Fig. 3a, based on the dimer-adatom-stacking-fault (DAS) model, this reconstruction has only 19 dangling bonds per 7×7 unit cell: 12 at adatoms, 6 at rest atoms and 1 at a corner-hole atom. This greatly reduces the number of dangling bonds from 49 on the unreconstructed Si(111) surface.
The DAS model\textsuperscript{15} of the 7×7 reconstruction was arrived at before STM was developed. However, the confirmation, by STM of the detailed structure of the Si(111)-7×7 reconstruction is a textbook example that shows the power of STM in determining surface structure\textsuperscript{16,17}. In an empty-state image by STM, as shown in Fig. 3b, the 12 adatoms in one unit cell are clearly visible. Most amazingly, the filled-state image in Fig. 3c unambiguously shows the difference between neighboring halves within one unit-cell, combined with first principles calculation, crucially supporting the existence of a stacking-fault which occurs 4 silicon layers deep within the bulk crystal. In addition, the ‘rest’ Si layer was directly imaged on Si(111)-7×7 after the adatom layer was stripped off by annealing a chlorine-saturated surface; within the 7×7 periodicity, a total of 42 rest atoms were observed\textsuperscript{18}. All these observations are in accord with the DAS model, decisively ending the long-standing debate over this surface reconstruction.

Figure 3. Si(111)-7×7 reconstruction: a is a schematic of the 7×7 unitcell, taken from Ref.4; All different dangling bond Si atoms are labeled. (refer to the text for details). b and c are constant current (\(I=0.2\) nA) STM images on clean Si(111)-7×7 at 300 K, taken at a sample bias of +1.5 V and -1.5V respectively. In d (taken from Ref.18), the
top-layer Si atoms of Si(111)-7×7 are stripped off to expose the rest atom layer that resembles closely with the DAS model. STM image of d was taken at a sample bias of +3 V and a tunneling current of 0.35 nA. Rhombohedral shape 7×7 unit cell is outlined through b, c to d.

On Si(111)-7×7, dangling bonds show variation in both topographic and electronic structure\textsuperscript{12}. On the basis of surface symmetry, the 19 dangling bond atoms per unitcell are of 7 different types that are shown in Fig. 3c as corner-hole (CH) atom, faulted corner (FC) adatom, faulted rest (FR) atom, faulted middle (FM) adatom, unfaulted middle (UM) adatom, unfaulted rest (UR) atom and unfaulted corner (UC) atom. Electron transfer occurs from adatoms to rest atoms, yielding positively charged adatoms and negatively charged rest atoms.\textsuperscript{12} Of adatoms, middle adatoms are usually more positively charged than corner adatoms. This is explained in terms of the number of rest atoms adjacent to the adatoms; each middle adatom is close to two rest atoms, while each corner adatom has only one rest atom in its proximity.\textsuperscript{12} In addition, the stacking fault gives rise to a more negative charged electronic structure for all dangling bond atoms in the faulted half-cell than in the unfaulted half-cell.\textsuperscript{12} The nature of these various dangling bonds often leads to rich chemistry on Si(111)-7×7 surface.\textsuperscript{12} See Ref. 12 for details.

1.4.2 Si(100)-c(4×2) surface

At room temperature, Si(100) reconstructs into an apparently symmetric p(2×1) structure (discussed below). However, at low temperature the system settles into the ground state configuration, Si(100)-c(4×2). We can understand this reconstruction as a tendency to minimize the surface energy\textsuperscript{19}. First, adatoms dimerize and form rows on this surface, so that the number of dangling bonds is halved. Second, these silicon dimers buckle out of the surface plane by \(\sim 19^\circ\), as caused by the Jahn-Teller effect. This small distortion in surface structure breaks the surface symmetry and lifts the corresponding orbital degeneracy, thereby effectively lowering the total energy. Third, the buckling directions for adjacent dimers alternate, either along or across the dimer row, due to dipole interactions and stress relaxation. The enhanced attraction, between the dimers of anti-correlated bucklings, plays a role in stabilizing the surface. All these three features regarding Si(100)-c(4×2) are schematically shown in Fig. 4.
The buckling of silicon dimers is accompanied by an electron transfer process from the down atom to the up atom, as clearly evident in STM imaging. Only down atoms are visible in the empty state image, whereas the filled state image sees only the up atoms. Electron transfer causes the DOS of down atoms to partially empty hence becoming accessible to tunneling; on the other hand, the tunneling of electrons to an STM tip is enabled because the DOS of up atoms become partially filled. Fig. 5a and 5b are typical empty and fill state STM images of Si(100)-c(4×2).

The bucked silicon dimers are bi-stable; that is, on this surface, silicon atoms oscillate between the up and down states, with an experimentally measured barrier of 136±110 meV. The wide barrier range was proposed to be induced by the long-ranged strain field from defects and steps on the surface. This oscillation produces a flip-flop motion for each dimer in terms of buckling direction. At room temperature, this flip-flop motion occurs at a rate that is several orders of magnitudes higher than the imaging frequency by STM, averaging out the difference between two silicon atoms within the same dimer, as seen in Fig 5d, 5e and 5f. Historically, this surface structure was interpreted as formed by symmetric dimers and termed as p(2×1) reconstruction. This notation, though artificial, is still widely used to describe Si(100) close to room temperature. The imaging behavior of Si(100) by STM close to room temperature has been understood as a resembled symmetry of the bonding and anti-bonding orbital of the silicon dimer.
with a recently refined interpretation\textsuperscript{21}. A set of typical STM images of Si(100)-p(2×1) is given in Fig. 6.

**Figure 5.** Typical STM images of Si(100) at 110 K (panel a, b and c) and at 300 K (panel d, e and f). At 110 K, both filled- (a) and empty-state (b) images (20×20 nm\(^2\) in size, different surface area) exhibit a hexagonal pattern that is characteristic of the c(4×2) reconstruction. In the close-up empty-state image (c), only the down Si adatom per dimer is visible; the locations of both dimer atoms are labeled, red circle for up Si and black circle for down Si. (d) and (e) are filled- and empty-state images (20×20 nm\(^2\) in size, different surface area) taken at 300 K. As zoomed in (f) for the empty-state image, both Si adatoms per dimer are visible and labeled by white circles. Note dimer row direction rotates by 90° beyond a step. STM images were taken at constant current mode (0.3 nA for a, and 0.1 nA for the rest) with the applied sample bias given in each panel.
The consensus view that c(4×2) is the ground state of the reconstructed Si(100) surface was recently challenged by a series of experiments performed at extremely low temperatures\textsuperscript{22}. In these experiments, a further phase transition from c(4×2) to p(2×1) or p(2x2) was observed in the temperature range of 40-80 K; and this puzzling transition appears to correlate defect-concentration, doping species and level. Regardless, c(4×2) is generally accepted as the most stable structure for the temperature above 80 K. Given the work on Si(100), as examined in Chapter 5 of this thesis, was performed between 100 K and 200 K, the Si(100)-c(4×2) reconstruction is employed for experimental interpretation and theoretical computation.
Chapter 2

2 Instrumentation and experimental procedure

The STM data presented in this thesis were collected using two STM systems, an RHK-300 Variable Temperature STM and an Omicron Variable Temperature-STM, respectively. Both STM systems operate in ultrahigh vacuum (UHV) with a temperature range from 50 K to 400 K. They are usually referred as UHV-VT-STM systems.

In this chapter, these two STM systems are briefly described, followed by a description of general procedures for the experiments presented in Chapter 4 to 6.

2.1 Microscope instrumentation

2.1.1 Vacuum system

To characterize phenomena at a solid surface with atomic precision, the surface composition must remain essentially unchanged during an STM measurement that typically takes several hours. Therefore the system of interest should be studied in an extremely high vacuum. Both STMs are housed inside a stainless steel vacuum chamber pumped by both ion pumps and titanium sublimation pumps. The system pressures are measured by an ion gauge that is calibrated for nitrogen gas, and usually reach \( \sim 3 \times 10^{-11} \) Torr following bake-out. Under the vacuum of this level, it takes \( \sim 9 \) hours to form a monolayer adsorption from residual gas in the background, even with a worst assumed unity sticking probability. This fits into the timescale that STM measurements take in this thesis.

In both systems a second UHV preparation chamber equipped with independent vacuum pumping is connected to the STM chamber and by a gate-valve that can be closed to avoid sample and/or microscope contamination. In the Omicron system, the preparation chamber serves as the location for surface sample preparation and characterization by Low Energy Electron Diffraction (LEED) and Auger Electron Spectroscopy (AES). However, in the RHK system, the preparation chamber is not currently equipped with any instrumentation and it is largely redundant. There is a load-lock for both systems that can be pumped within \( \sim 1 \) hour from 760 Torr down to \( 10^{-7} \) Torr using a molecular-turbo pump "backed" by a rotary pump. The load-lock may be used for both sample and tip transfer into and out of the UHV systems. However,
the system vacuum tends to degrade slightly after each use of a load-lock. We find that it is more
efficient to let the systems up to atmospheric pressure (using dry nitrogen or argon), and replace
all samples and tips simultaneously, followed by a system bake-out.

2.1.2 Vibration isolation

Effective vibration isolation is crucial in performing STM measurements. During an STM
imaging, the typical atomic corrugation is as small as 10 pm. This distance must be maintained
to a small fraction of this separation in order to provide good measurements. Therefore, great
harm arises from even a small disturbance from any external vibration.

To address the importance of vibration isolation deeper, one needs to consider the frequency
bandwidth that STM operates. The scan speed of an STM is determined by the response of the
feedback loop. This loop response must be slower than the intrinsic resonance frequency of each
STM scan head, usually on the order of a few kHz; otherwise, an unwanted tip oscillation occurs
as the resonance of the STM scan head is triggered by the feedback loop. As a result, the
vibration noise in the range of a few kHz and below, is the most harmful to the feedback loop
and hence the imaging of STM.

Unfortunately, the typical frequency of vibration in buildings ranges from 10 to 200 Hz. For
example, the building-frequency in our laboratory peaks at 60 Hz*, with secondary peaks at 120,
180, 240, 300, 360, 420, 480 and 600 Hz were also observed. Vibration isolation from the
environment is as therefore the prerequisite for any working STM unit. As detailed separately
below, different strategies for vibration isolation are adopted for our RHK and Omicron
microscopes.

* We arrived at this conclusion based on our measurement (using an oscilloscope) of the frequency of tunneling
current when the tip was brought into tunneling region with the feedback disabled. Repeated measurements on both
RHK and Omicron systems at the same location (2nd floor) of the Lash Miller gave the same primary 60 Hz noise; a
systematic noise reduction was consistently observed as vibration isolation function was operative. It was puzzling
that this 60 Hz noise coincided with the building electric line frequency, though all electronics operative on these
two systems were grounded via a cold copper pipe rather than provided by the electrical sockets. A more direct
(absolute) measurement of the building vibration noise requires a seismometer.
2.1.2.1 RHK 300

The lack of internal vibration isolation in the RHK system renders this microscope extremely vulnerable to acoustic noise. In order to compensate for the lack of internal vibration isolation, the vibration isolation on our RHK system is achieved externally. The whole system (of two vacuum chambers and their associated ion pumps) is supported by a two-tier vibration isolation system. The bottom layer of the structure is a Stacis 2000 active control system. This Stacis system consists of three piezo-electric damping legs under active electronic control, to provide a high degree (~90%) of noise reduction in the range 0.3-200 Hz. The upper layer of the structure consists of three pneumatic isolation stabilizers (Newport "air-legs"), allowing a transfer of less than 10% for the noise above 10 Hz. The "air-legs' are mounted directly above the piezo-electric legs, but the two systems are physically separated by a rigid platform. The rigid platform consists of three 5 mm thick metal plates between the stacis legs and the air-legs, connected into a rigid assembly using 4"×2" rectangular cross section steel girders. This combination effectively reduces the overall vibration between 2 and 600 Hz by a factor of ~6. It is possible for the combined vibration-isolation system to be forced into a resonant feedback condition, which gives high vibration; fortunately, the conditions that cause this unwanted resonance are not often encountered during normal operation.

2.1.2.2 Omicron VT-STM

The primary vibration isolation on the Omicron VT-STM is an internal system. During measurements, the microscope stage is isolated from the environmental vibration by being suspended on an internal system of four soft springs. Any transmitted vibrations are rapidly damped by an eddy-current damping system that consists of strong permanent magnets that move (without contact) between copper fins; a damping force is generated by eddy currents so as to oppose the motion, thereby resisting the vibration motion\(^8\). The spring suspension system has a resonance frequency of 2 Hz, and hence it is effective in isolating the microscope from vibration noise lower than 20 Hz. The secondary vibration isolation on the Omicron VT-STM is provided by three pneumatic "air-legs" on which the whole system (including vacuum chambers and ion pumps) is suspended. The air-legs provide excellent vibration isolation above 10 Hz.
2.1.3 Sample cooling and temperature control

Conventional STM, as determined by the apparatus resonance frequency of a few kHz\(^8\), usually has a response time of several minutes for consecutive imaging traces. As a result, only slow processes can be measured dynamically. For direct observation of reactions, this time-scale of the STM imaging is a limiting factor.

Nevertheless rates of chemical change can be measured. For first-order processes, the Arrhenius rate law\(^1\) tells us that:

\[
k = A \exp\left(-\frac{E_a}{k_B T}\right),
\]

where \(k\) is the rate of the process at unit concentrations, \(A\) is a constant called as pre-exponential factor, \(E_a\) is the activation energy of the process, \(k_B\) is the Boltzmann constant, and \(T\) is the absolute temperature. Therefore, we can use the inverse exponential relationship between rate and temperature to slow down reactions by working at low temperatures. For example, the dimer flipping frequency on Si(100) can be effectively slowed down from \(10^8\) Hz at 300 K to 1 Hz at 90 K\(^2\); that is, a temperature drop by a factor of 3 lowers the rate by of 8 orders-of-magnitude! A great number of motions on a solid surface, e.g. molecular translation, rotation, desorption and dissociation, have been examined in this manner\(^6\).

Both the RHK and Omicron microscopes may be cooled using a continuous-flow cryostat coupled to the microscope stage. This coupling is permanent in the RHK design but detachable in the Omicron design. Both designs have pros and cons. Sample cooling is more effective in the RHK-300 than in the Omicron VT-STM; for a given cryogen (liquid nitrogen, or liquid helium) the RHK achieves an ultimate sample temperature about \(\sim 20\) K lower than the Omicron. However, the permanent coupling also couples vibration directly into the STM head, even when cooling is not being used. This is a nuisance for measurements at or above 300 K.

Sample temperature is regulated, on both microscopes, in a two-stage scheme. First, great care is taken to adjust the coolant flow rate. The coolant flow rate is controlled by regulating the gas pressure inside the coolant container, as well as by the opening of a needle valve for the coolant line. Second, an offset heater is used under control of active feedback to give fine adjustment and temperature stability. Typically, temperatures can be maintained stable to within 1 K over a few hours of measurement. For the RHK-300, fine temperature control is provided by a heater close
to the sample. This heater is a tungsten filament powered by a digitized controller (PreVac) that simultaneously reads the temperature from a C-type thermocouple positioned at the back of the sample. A scheme, known as PID algorithm, is used to dynamically adjust the heating power, thereby stabilizing the sample temperature. The equation for the PID algorithm\textsuperscript{24} is given as:

\[
Heater \ Output = P(e) + I \int (e) dt + D \frac{de}{dt}.
\]

In this equation, I is the heater current, t is the time, e is defined as the difference between set and real temperature. Additionally, proportional term (P), the integral term (I), and the derivative term (D) are three variables that tune the heating so that real temperature is forced to approach the set value. In this way, a stable temperature for the sample can be quickly reached.

For the Omicron VT-STM the heater is attached directly to the cooling block, while either of two nearby silicon diodes (one at the microscope stage into which the sample holder is inserted, one at the cryostat) may be used to infer the sample temperature. Fine temperature control is established by a controller (Lakeshore, Model 331), again with PID-based programming to stabilize the temperature.

In general the Omicron design shows better performance in controlling the sample temperature that is perhaps due to a better thermal coupling between the heater and the sample.

2.1.4 Scan heads

The scan head of the RHK microscope is based on the Beetle design by Besocke\textsuperscript{25}, as shown in Fig. 7 (a). The scan head in this design employs four identical piezo tubes, one central tube and three outer tubes. The central tube is attached to a tungsten tip that images the surface physically, while the three outer tubes, arranged evenly apart in a circle, support the whole body of scan head on the sample holder, as in Fig. 7(b). By contrast, the design for scan head of the Omicron microscope is much simpler with only one single-tube piezo adhered rigidly at the center of a heavy metal cup.
The introduction of three additional piezo tube, compared with the single tube design as in the Omicron version, offers a second slow feedback in the imaging mode to compensate the thermal drift along surface normal direction. The RHK microscope gives less drift than the Omicron design: the intrinsic drift at 300 K is ~0.3 Å/sec for RHK, and 0.85 Å/sec for Omicron.

2.1.5 Control electronics

Our microscopes are both driven by the electronics controller (Model: SPM 1000) manufactured by RHK. This is a hybrid system, with digital communication between a controlling computer, and analog electronic control of the microscope head. The analog control system is equipped with 10 high-voltage output channels and can be used to drive a wide range of STM scan heads. This control of multiple outputs is uniquely important for the Beetle versioned scan head (RHK) that employs more than a single piezo tube (Omicron).

2.1.6 STM tip approach

As introduced in Chapter 1, the STM tip must be brought rather close to the sample before a measurement starts. In reality, such tip approaching motion can easily lead to crashing the tip into the sample. In order to approach an STM tip into tunneling region safely, we rely on our feedback loop for both our RHK and Omicron microscopes, as described below. For clarity, we define the sample surface as in the x-y plane, while the z-axis is the direction perpendicular to the surface.
In the RHK microscope, the tip approach relies on the rotation of the whole scan head that is technically achieved by applying waveforms of different amplitudes to the x and y axis sectors of each outer piezo tube. Since the RHK sample holder that supports the three outer tubes is constructed as a triple helix as in Fig. 7 (b), the rotation motion causes the STM tip to move closer into the sample. Meanwhile, the feedback loop is enabled to monitor the tunneling current and stops the approaching motion once the current reaches set value.

As opposed to the rotation in the RHK design, the Omicron microscope approaches the STM tip strictly by the translation motion along z direction in a two-step scheme. First, a ‘slip-stick’ piezo motor is used to quickly bring in the tip towards to the sample and this coarse approach is monitored using a Charge-Coupled Device (CCD) camera. Second, the z segment of the STM piezo is activated to approach the tip, while the tunneling current behavior during the fine approach step is monitored by a feedback loop. As identical to RHK microscope, the fine approach is terminated once a tunneling current of the set value is detected.

2.1.7 STM imaging and processing

For all the work reported in this thesis, "constant current mode" was employed in imaging the sample surface. In this mode as the tip is rastered over the surface, a feedback mechanism operates to vary the tip height so as to maintain a pre-defined tunneling current (typically of the order of 0.1 nA). Therefore the image of the surface contour is built up from a record of tip height (for a particular tunneling current and bias voltage) against x-y position across the surface. Typically, STM images were taken with a sample bias from -3 V to + 3 V, and a set tunneling current from 0.02 to 0.3 nA. These images were processed using either XProM or WSxM software to correct the background and adjust contrast. Occasionally, Fast Fourier transformation (FFT) was employed to smooth the images by filtering out the unwanted noise from the environment.

2.2 Silicon preparation

Two silicon samples employed in this thesis are both n-type, phosphorus-doped with a resistivity of 0.02-0.05 Ω×cm for the (111) face and 0.01-0.02 Ω×cm for the (100) face. In vacuum, a fresh silicon sample was degassed at 900 K for ~ 8 hours by passing a direct current. The sample was then flashed several times to 1500 K to remove the native oxide layer and activate the
reconstruction. In our laboratory, the sample preparation is automatically done with a Lab-view based program, SMAFLASH, written by Drs. Iain R. McNab and Peter A. Sloan. This program ensures a gentle cooling (~3-4 K/s) from 1260 K at the end of the final flash, giving nice large terraces free of defects.

2.3 STM tip preparation

STM tips were made from polycrystalline tungsten by a direct-current etch in a 3 M NaOH solution under control of a “Schrodinger Sharpener Tip Etching station” (SS01C, Obbligato Objectives). The tip shape was then examined in an optical microscope to ensure the sharpness before mounted to the tip holder.

2.4 Adsorbate purification and exposure

All the adsorbate chemicals used were liquids at 300 K and were purified by the standard freeze-pump-thaw cycles as described below. The vials that contain the chemicals are frozen into solids using liquid nitrogen and then pumped by a scroll pump down to $10^{-3}$ Torr. As the last step in one cycle, the vials are sealed and thawed by replacing the liquid nitrogen bath with a bath of warm water. During this phase transition from solid to liquid, the dissolved contaminant gases escape into the vapor phase and are pumped away during in the next cycle. This purification procedure is repeated for 7-8 times until no visible bubbles arise during the thaw step. Between different runs the gas line is usually flushed 6-7 times by the chemical that has been purified by the freeze-pump-thaw cycles.

The adsorbate chemicals are introduced into the vacuum chamber through a leak valve for background dosing. By adjusting the pressure measured inside the chamber as well as the dosing time, the exposure amount is controlled and reported in Langmuir (L, 1 L=$10^{-6}$ Torr ×s), at pressure measured using an uncorrected ion-gauge.
Chapter 3

3 Density Functional Theory calculations and surface modeling

In the last decades it has become possible routinely to apply quantum mechanics to solve problems of geometry and electronic structure for systems of more than 100 atoms. This has been possible because of greatly increased computer speeds, large computer memory storage, and computational algorithms that can efficiently solve Schrodinger's equation for arbitrary symmetries with large numbers of electrons (principally Density Functional Theory). Quantum mechanics is now commonly applied in surface physics to study the geometric and electronic structures of surfaces both with and without adsorbates. In this work, we use the Vienna ab-initio simulation package (VASP)\textsuperscript{27} to optimize surface structures and calculate total energies. The algorithms used in VASP are an implementation of Density Functional Theory (DFT) using plane wave basis sets\textsuperscript{28} that efficiently represent the electronic structure of crystals. This chapter describes several salient features of the theory and details of techniques that can be used with VASP.

3.1 Density Functional Theory

The systems in solid state and surface physics are many-body problems as they usually consist of multiple electrons and nuclei. Under the Born-Oppenheimer approximation, one can treat nuclei classically after separating them from motions of electrons; the electrons adapt to the positions of the nuclei almost instantaneously\textsuperscript{29}. In other words, the system is pictured as mobile electrons that move around static nuclei. The Born-Oppenheimer approximation simplifies the many-body electrons/nuclei problem into a many-electron problem.

However, the interaction between electrons is complex because of their mutually correlated motions. In general, such interaction are described by the many-electron wave functions that rapidly become unwieldy (and expensive to calculate) as the number of electrons increases. Most commonly used algorithms for computing electronic wavefunctions rely upon solving the motion for each electron in a "Self Consistent Field" (SCF) that allows for the average positions of all other electrons, but does not include the effects of electron correlation. The traditional approach
to account for electron correlation requires the use of "configuration interaction" (CI) wavefunctions that include combinations of excited (SCF) electronic states\textsuperscript{30}. Such SCF-CI wavefunctions are expensive to calculate.

An alternative method of accounting for electron correlation, Density Functional Theory (DFT), has been developed on the foundation of the Hohenberg-Kohn theorem.\textsuperscript{31} For a many-electron system in the ground state, this theorem ensures an invertible one-to-one correspondence between the electron density and the energy. As a result, the energy is calculable from the electron density rather than wave-functions. However, the exact functional that connects electron density and energy is unknown, calling for further approximations.

In DFT, electron correlation is partially accounted for by the exchange-correlation potential. This exchange-correlation potential, as suggested by Kohn and Sham, emerges as a correction to treating electrons as non-interacting particles in the kinetic energy term. There are two popular approximations\textsuperscript{31}: Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA). The LDA neglects the contribution to exchange-correlation energy that arises from the non-homogeneities of electron-density, and treats the electrons as in the case of a uniform electron gas. This approximation works extremely well, but with a clear tendency to overbind atoms. For systems of greatly different electron localizations, the non-homogeneous nature can be captured, as is done in GGA, by introducing a correction term that depends on the gradients of electron-density.

In DFT, calculations are done self-consistently; that is, the calculations are performed iteratively and terminate when defined criteria are satisfied for convergence. Specifically, the electron density calculated in one iteration step is mixed with the old electron-density from the previous step to generate a new electron-density and electronic-potential. The obtained electron-density and electronic-potential are then used as a new input in the next iteration to construct the Kohn-Sham equation, the solution of which generates a new electron density. This procedure repeats until the electron densities from two consecutive iterations are sufficiently close.
3.2 Cluster and slab models

Two models are commonly employed to study the problems that involve a solid state surface. The surface can either be represented by a cluster of finite size, or else by a slab with infinite, self-repeating units (see Chapter 3.3); both approximations have strengths and weaknesses\textsuperscript{32}.

The cluster model usually uses atom-centered basis sets, such as gaussians; and these basis sets are highly efficient in dealing with valence orbitals. Because of its finite size, it is possible to treat the electron-correlation effect in a rather sophisticated fashion. However, the cluster model suffers from two well-known problems\textsuperscript{33}.

First, finite model size limits the degree to which cluster atoms may relax in response to the surface process of interest, e.g. molecular adsorption. In the cluster model, a geometry optimization is often performed with the positions of the atoms at the cluster edge frozen. Such a constrained optimization scheme may not permit sufficient geometry relaxation to represent the given surface process. This problem is most obvious in employing small clusters. Second, it is difficult to control the convergence with respect to the localized basis set. In order to improve the basis set in the cluster model, pains are taken to achieve a balanced increase in the number of split-valence, split-core, polarization, and diffuse functions.

In the slab model, the problem associated with the edge-atom effect, as often encountered in the cluster model, is removed by the infinite size. The periodicity embedded in the slab model leads naturally to a selection of the plane wave as the basis set. Compared with an atom-centered basis, the plane wave basis set treats the full system directly and globally, with an easy but tight convergence control by a single parameter, the kinetic energy cut-off.

But calculations made with the slab model suffer from different problems; it is not possible to approach an infinite dilution of adsorbates on a surface, nor is it possible to place adsorbates other than in a regular self-repeating pattern. Nonetheless, in practice as we have sufficient computing power, we prefer the slab model with periodic boundary condition, as coded in VASP, to perform DFT calculations, mainly because of its high paralleling performance.
3.3 Periodic boundary conditions

As noted, in the periodic-boundary condition calculation, crystal surfaces are represented as an extended structure that consists of infinite repeating units. The origin of this representation is the periodicity of a single crystal, as described mathematically in the Bloch theorem. The periodic boundary condition is not, therefore, a natural representation for the surface of a crystal; but in practice surface states are well represented by plane wave basis sets calculated in the periodic boundary condition approximation.

The repeating unit in a periodic system is known as a supercell. The supercell used in practical calculations employs a slab of limited thickness to represent a crystal surface; the periodicity permits expanding wave functions of this slab into plane waves. In this method, slabs must be sufficiently thick and well separated along the surface normal to avoid artificial couplings between slabs in neighboring images. Six or more layers of a crystal lattice are usually sufficient to ensure that surface properties are adequately calculated.

Strictly speaking, this supercell method can only apply to periodic systems. However, interesting surface phenomena, such as defects or molecular adsorption, are usually non-periodic. In such systems, a large supercell is usually used so that non-periodic features are well separated from neighboring images and hence do not interact with each other to produce unphysical results.

3.4 Pseudopotential

In order to reduce the cost of calculations, the pseudopotential approximation is often employed. In this approximation, the tightly bound core electrons are frozen in the same states as in isolated atoms; the impact of bare nuclei and frozen core electrons on valence electrons is described by a pseudopotential. The concept behind this pseudopotential approximation is that the role that core electrons play in almost all processes of interest, is far less important than that of valence electrons. From a chemist’s point of view, it is the valence electrons that participate in chemical bonding, and that largely determines both the physical and chemical properties of a given system.

The pseudopotential approximation greatly reduces the effective number of electrons for heavy elements. For example, the number of electrons considered in the pseudopotential approach for a bromine atom, $^{35}$Br, is only 7 for the valence level rather than the real total electron number of 35.
In addition, this approximation permits a lower energy cut-off to be used for the plane wave basis set since the highly oscillating wave functions in the core region are smeared out in the pseudopotential. As a consequence, the total energy is significantly reduced and the absolute value no longer has a clear physical meaning. However, it is almost always relative energies that are of interest, and these are meaningful provided the energies to be compared are calculated to the same approximation.

Two pseudopotentials are employed in the work of this thesis: the Ultrasoft Pseudopotential (USPP)\textsuperscript{35,36} in Chapter 4, and the Projector Augmented Wave (PAW)\textsuperscript{37,38} in Chapter 6. The USPPs are less accurate, and less consistently defined than the newer PAW potentials, but allow cheaper (faster) calculations for a system of a given size. For expensive calculations such as Nudged Elastic Band calculations of the minimum energy path in a chemical reaction, the creators of VASP recommend the use of USPPs.

### 3.5 Brillouin zone sampling

Brillouin zone sampling is an issue specific to this supercell method in studying periodic systems. Although this method succeeds greatly in simplifying the system size, it creates a challenge, namely that the total energy can only be fully recovered by integrating over the corresponding reciprocal space, also known as k-space.

Evaluation of total energy at all k points is obviously not practical. Fortunately, the energy variation with k is so slow that one can make reasonable calculation by sampling a limited number of k points. Several Brillouin zone sampling schemes are developed, combining high efficiency and accuracy. Specific points in k-space are chosen that give a minimum error of integration for a selected number of points\textsuperscript{39,40}. In general, the points chosen are high-order symmetry points of the Brillouin zone. The lowest order approximation is to make an integration at the single k-point with highest symmetry, the so-called gamma point.

The scheme of sampling limited k points in the Brillouin zone introduces an energy error. This error is obvious in calculations of absolute energies, demanding a rather dense sampling mesh; the energy differences, on the contrary, are far less sensitive so that calculations based on a single k-point are usually sufficient. A systematic test on Brillouin zone sampling is usually performed to ensure the convergence of quantities of concern, for example, the relative energies.
3.6 Nudged elastic band method

The Nudged Elastic Band (NEB) method\textsuperscript{41} is widely employed to find minimum energy pathways between initial and final states. In principle, the NEB can locate the saddle point for any given transition. The initial and final states of interest need only be related by a physical (or chemical) transformation. In addition to knowledge of both initial and final states, an NEB calculation is initiated with a set of intermediate states. Such intermediate states are preferred to be generated from an estimate of the minimum energy path. These states are connected by a spring force to ensure the continuity of the band, while a constrained optimization in the presence of this spring force is performed on each intermediate state to converge the band onto the minimum energy pathway.

A recent advance in the NEB method is the climbing image nudged elastic band (CI-NEB) calculation\textsuperscript{42}. The climbing image method automatically drives the intermediate state of the highest energy to the saddle point. This is achieved by inverting the force of the highest energy state so that its energy is maximized along the band but minimized in all the other directions. Hence, in principle, the state of the highest energy is located at the exact saddle point once such a CI-NEB calculation converges.

3.7 Modeling for silicon surfaces

In this thesis, DFT calculations are performed on both Si(111)-7×7 and Si(100)-c(4×2) reconstructed surfaces of silicon. Here, the parameterization for each slab used is described as follows.

3.7.1 Si(111)-7×7 surface

The Si(111)-7×7 slab employed in Chapter 4 was built up mainly as an effort of Dr. Iain McNab. Detailed procedure of building this slab is given in the Supplementary Information of Ref. 43. Two Si(111)-7×7 supercells were used in Chapter 4, a thin unit-cell and a thick unit-cell, both developed from the experimental LEED data of Tong \textit{et al.} and their coordinates\textsuperscript{44}.

3.7.2 Si(100)-c(4×2) surface

The Si(100)-c(4×2) slab employed in Chapter 6 was built as a collaboration between Dr. Iain R. McNab and the author of this thesis.
As shown in Fig. 8, this Si(100)-c(4×2) slab consists of a total of 112 Si-atoms in 7 layers. The 16 Si-atoms at the bottom layer were passivated by 32 valance-H atoms. The geometry relaxation was performed in two steps. First, the valence-H atoms were allowed to relax with all Si-atom position fixed, until the forces at each atom was less than 0.02 eV/Å. Second, the Si-atoms in the top five layers were allowed to relax, while the positions for valance-H atoms and Si-atoms at the bottom two layers were held, again until the forces at each atom was less than 0.02 eV/Å. The silicon slab structure obtained has a Si-Si dimer bond length of 2.36 Å, and a buckling angle of 19.7°, in agreement with the literature\textsuperscript{19}.

Figure 8. Optimized Si(100)-c(4×2) reconstruction viewed along [100] direction as in (a), along [01-1] direction as in (b), and along [011] as in (c). A closer-up of a single dimer along [011] is displayed in (d) shows that the most characteristic features of this surface geometry are reproduced from our optimization: a dimer bond length of 2.36 Å, and a buckling angle of 19.7°. The top layer Si-atoms are re-colored as red for up Si-atom, and balck for down Si-atom, so that they are distinguishable from the bulk Si-atoms (yellow). Valance-H atoms are colored in white.
Chapter 4

4 Long-range repulsion induced by physisorption or chemisorption on the Si(111)-7×7 surface

4.1 Introduction

Adsorbates on metals\textsuperscript{45,46,47,48,49,50,51,52,53,54,55,56,57}, but not previously on semiconductors, have been observed to display long-range repulsive interactions. On metals the repulsions are weak, typically of order 5 meV at 10 Å, and are often transmitted by standing waves of electron gas at the surface\textsuperscript{55}. Another type of long-range repulsion was reported for dipolar molecules at distances of 20-30 Å, which depends upon dipole-dipole interactions\textsuperscript{54}. The interaction strengths were 20 meV at 15 Å, ~2 times greater than gas-phase dipole-dipole interaction at the same distance. The enhanced interactions were due to image dipoles within the metal surface.

Here we show long-range repulsion between adsorbates at the Si(111)-(7×7) surface. The maximum range of repulsion observed was between two corner silicon adatoms opposite one another at a corner-hole, a distance of 13.4 Å. For a representative system, we calculated \textit{ab initio} that the magnitude of the repulsion was 200 meV, which is ~10 times greater than on metals, over a similar distance. To the best of our knowledge, this is the first report of a long-range repulsion at a semiconductor surface.

The repulsion reported here was shown experimentally to be occurring between either physisorbed or chemisorbed species, in four different adsorbates. \textit{Ab initio} computation revealed that the source of the repulsion was a long-range lateral flow of charge in the surface. On the 7×7 reconstruction of the Si(111) surface, charge transport through the surface has been demonstrated by others using charge injection by STM tips. Electron injection, it was shown, can result in “hopping” of chlorine atoms on Si(111)-(7×7)\textsuperscript{58}, or non-local removal of molecularly adsorbed chloorebenzene on Si(111)-(7×7)\textsuperscript{59}. Hole injection can result in non-local activation of a bistable H atom on Si(100)-(2x1):H\textsuperscript{60}.
4.2 One-Per-Corner-Hole (OPCH) physisorption and chemisorption pattern on Si(111)-7×7

In the present work, the repulsion was induced by adsorbates, rather than by the transfer of electrons from an external source. This resulted in self-assembly of both physisorbed and chemisorbed species in a previously unobserved but highly characteristic pattern that we shall term ‘one per corner-hole’ (OPCH). This is shown for three different brominated adsorbates in Fig. 9, and will subsequently be shown for a fourth case. We use the designation OPCH to describe such well-separated patterns of, physisorbed species, chemisorbed species, and mixtures of both. All the molecules studied evidenced OPCH bromination, evidencing, therefore, repulsion between the physisorbed pre-cursor to bromination as well as repulsion between chemisorbed Br-atoms and physisorbed pre-cursor. In some cases the physisorbed OPCH precursor was directly observable by STM.

In Fig. 9 we show molecular adsorption of physisorbed molecules, RBr, in OPCH patterns (left column), and also the chemisorbed Br-atoms resulting from thermally induced chemical reaction in OPCH patterns (right column). The physisorbed molecules (RBr=1,2-dibromoethane, 1-bromopropane and 1-bromopentane) in each case attached preferentially at one of the Si adatoms that surround a corner-hole of the Si(111)-(7×7) surface. In general no more than one molecule attached to the adatoms of a corner-hole, but in some exceptional cases double-occupancy was observed at a corner-hole. The percentage occurrence of the rare double-occupancy provides information as to the magnitude of the repulsion (see later; Chapter 4.9).

For bromobenzene, physisorbed pre-cursors were not observable by STM in our range of surface temperatures; instead, randomly-distributed molecular chemisorption was observed (Fig 10a, left column) due to the well-known reactivity of the phenyl group at Si(111)-7×7. The binding energy of the phenyl to the silicon surface, through two strained sigma bonds, is ~ 1 eV. On heating to ~400 K, these adsorbates are presumed in part to have desorbed and in part have reacted to brominate the surface by way of a mobile physisorbed precursor state. The evidence for the mobile pre-cursor is indirect in this case, but is clear from the highly-ordered nature of the subsequent chemisorptions. The observed bromination (Fig 10b, right-hand column) shows a clear OPCH pattern attributable to adsorbate-adsorbate repulsion in a mobile physisorbed pre-cursor as inferred in the three examples of Fig 9.
Figure 9. STM topographs (140×140 Å², I = 0.2 nA, constant current, bias given in each panel) showing initial molecularly adsorbed arrangements (left hand column) and their corresponding chemisorbed Br-atoms arrangement (right hand column), both forming characteristic “one-per-corner-hole” (OPCH) patterns on Si(111)-7×7. The molecular adsorbates image dark compared to silicon-adatoms. To guide the eye physisorbed molecules are highlighted with white circles enclosed by larger black circles surrounding the adjacent corner silicon ad-atoms. Chemisorbed Br-atoms image bright compared to the silicon adatoms. White dashed circles are drawn around the corner silicon adatoms. Exceptional cases of more than one adsorbate at a single corner-hole have been circled with dashed blue lines. Individual panels show (a) physisorbed 1,2-dibromoethane dosed at 110 K, distributed OPCH in wide area (top) and close-up (below) (a’) corresponding chemisorbed Br-atoms, OPCH, arising from 1,2-dibromoethane dosed at 300 K in wide area (top) and close-up (below) (b) Physisorbed 1-bromopropane dosed at 50 K, distributed OPCH and (b’) corresponding chemisorbed Br-atoms, OPCH, arising from 1-bromopropane dosed at 300 K. (c) Physisorbed 1-bromopentane dosed at 100 K, distributed OPCH and (c’) corresponding...
chemisorbed Br-atoms, OPCH, arising from 1-bromopentane dosed at 300 K. A set of unmarked topographs are enclosed on the right side.

Figure 10. STM topographs (140×140 Å², I = 0.2 nA, constant current, Vₛ=+1.5 V) showing (a) Bromobenzene dosed at 300 K chemisorbs molecularly in a random pattern by forming two sigma-bonds with the surface, (b) chemisorbed Br-atoms, in an ordered OPCH pattern, arising from chemisorbed bromobenzene after an anneal to 400 K.

In no case of bromine chemisorption thermally-induced at Si(111)-7×7 did we find evidence of attachment of the hydrocarbon radicals to the surface. This implies that the transition state geometries in all our four examples favored ejection of the hydrocarbon residue away from the surface. This same reaction mechanism has been found previously for CH₃ radicals from methyl bromide on Si(111)-(7×7)⁸⁵.

4.3 Site-selective adsorption

The observed OPCH patterns were highly site-selective. Adsorption or reaction occurred almost exclusively at corner silicon-adatoms adjacent to a corner-hole, rather than on middle silicon-adatoms. Typically the ratio of occupied corner silicon-adatoms to middle silicon-adatoms was greater than ~13.

On Si (111)-7×7, the two adjacent triangular half unit-cells are not equivalent; one is located above a stacking fault (termed as a faulted half unit-cell), whereas the stacking underneath the other half unit-cell is normal (termed as an unfaulted half unit-cell). It is well known that the selectivity of adsorption and reaction of various adsorbates differs between these two half unit-cells⁴. However, in the present study, we found no statistical difference in site-selectivity between faulted and unfaulted half unit-cells. This is detailed below.

For example, in the case of 1,2-dibromoethane, we analyzed the relative probabilities of bromination at corner and middle adatom sites, for both faulted and unfaulted half unit-cells at
300 K. As bromination proceeds fast at 300 K, statistics permits us to quantify the relative probabilities of different adsorption configurations by counting the numbers of reacted sites at different coverages\textsuperscript{62}. As seen in Fig. 11, the number of Br-atom at each surface site, normalized to the surface area, is linear to the total Br coverage, and fitted into a straight line. Hence, the slopes of these straight lines are relative bromination probabilities, as 0.47±0.02, 0.46±0.02, 0.04±0.01 and 0.03±0.01, for unfaulted corner Si site, faulted corner Si site, faulted middle Si site and unfaulted middle Si site, respectively. The corner Si site is strongly favored over middle Si site by a factor of 13±2, as determined by the ratio of relative probabilities. No statistically significant difference is found in site selectivity between faulted and unfaulted half-cells.

Figure 11. Site-selective bromination for 1,2-dibromoethane at 300 K. Brominated Si adatoms are divided into four categories as unfaulted corner Si (black), faulted corner Si (red), faulted middle Si (green) and unfaulted middle Si (blue). The number bromination at each adsorption site, normalized by surface area, is plotted against the total surface Br coverage up to ~0.80 per unit-cell, and fitted into a straight line. Similar site-selectivity was found for other OPCH patterns. Experimental uncertainties are statistical, taken as the square-root of the count for each image.
4.4 Statistical significance analysis of measured distribution.

For both physisorption and chemisorption once one of the six available silicon-adatoms around one corner-hole site was occupied, further adsorption rarely occurred at any of the remaining five corner adatoms of that corner-hole.

The furthest distance between two silicon corner-adatoms at a single corner-hole is 13.4 Å, the distance between opposing silicon corner adatoms. The observed OPCH distributions indicated that a long-range repulsion must operate over at least 13.4 Å for the four physisorbed and chemisorbed adsorbate species examined. In all cases single occupancy at a corner-hole was favored by a factor >25, as compared with two or more adsorbates appearing at the same corner-hole. This distribution is highly statistically significant, $p \approx 7 \times 10^{-5}$, compared with the same results arising from independent identically distributed random events.

A detailed sample analysis by Dr. I. R. McNab is given below. This is not part of my work, but this shows quantitatively the statistical significance of the OPCH pattern, and hence is reported here.

I.R. McNab calculated the statistical significance of the observed pattern in a single image, as given in Fig. 12. This image shows 196 unit-cells free of defected corner Si adatoms, that is 196 corner holes, with 1176 corner adatoms, with a total of 72 chemisorbed Br-atoms. He then calculated the probability of obtaining the observed OPCH pattern by random occupancy of corner-adatoms. As the increase in OPCH coverage is linear with dose (up to a limiting coverage of 0.8 Br-atoms per unit-cell), no allowance is made for changing surface site occupation. Also, for the purpose of this analysis, we ignore middle adatom sites.
The null hypothesis was that silicon corner-adatom sites are populated by independent identically distributed (i.i.d.) random events. He estimated the probability of occupation of a corner hole adatom, $p$, from the observed count as the number of (chemically imprinted Br-atoms / number of available corner adatom sites) = $p = 72 / 1176$. He further assumed that for one corner-hole, with a set of six active-sites, that the number of occupied active-sites is binomially distributed, with distribution function:

$$B(6, p)$$

The probability that at a particular corner-adatom site is unoccupied is $(1-p)$. Therefore the probability that at a corner hole all six corner-adatom sites remain unoccupied, $p(0)$, is given by:

$$p(0) = (1 - p)^6 \approx 0.6845$$

The probability of only a single corner adatom site being occupied is given by the probability of a single corner adatom site being occupied, multiplied by six to allow for the six possible corner sites ($6p$), multiplied by the chance that the remaining 5 sites are unoccupied:

$$p(1) = 6p(1 - p)^5 \approx 0.2678$$
The probability of either zero occupancy or single occupancy is therefore the sum
\[ s = p(0) + p(1) \approx 0.9523 \]

From \( K \) corner-holes (\( K=196 \)) we expect the number with either 0 or 1 corner adatom sites occupied to be binomially distributed,
\[ B(K, s) \]

The probability of getting \( a \) successes from \( K \) trials is given by the probability mass function and we can therefore write that the probability of obtaining occupancy of zero or one, \( a \) times is
\[ P(a) = \binom{K}{a} s^a (1-s)^{K-a} \]

The probability of obtaining 0 or 1 as the occupancy 196 times (as observed) is therefore \( 1.7 \times 10^{-5} \). Similarly, the probability of obtaining an occupancy of 2 or more is given by
\[ P(a) = \binom{K}{a} (1-s)^a s^{K-a} \]

The probability of obtaining no event with occupancy 2 or more (as observed) is \( p = 7 \times 10^{-5} \).

Therefore, the observed distribution is concluded to be highly ordered compared to the null hypothesis, with a statistical significance of order \( 10^{-4} \).

The calculation reported above was benefited from consultation with Prof. Jeffrey Rosenthal, Department of Mathematics, University of Toronto.

### 4.5 Comparison with adsorption of trichloroethylene

The OPCH pattern which forms the subject of this chapter is discernible, in light of the present observations, in the chlorination of the Si(111) 7×7 surface by trichloroethylene in the STM study by the Patitsas group at the University of Lethbridge, Alberta. The exposure of trichloroethylene used by these workers was insufficient to reveal the one-per-corner-hole (OPCH) pattern of halogenation which is the topic of the present work, but a preference for reaction at corner-datoms leading to a product separation of 30 Å, was observed. The indication from all five chemically different adsorbates –Patitsas’ and the four examples cited here-- is that the molecular physisorption of organic halides on Si(111) 7×7 gives a strong preference for ‘one-per-corner-hole’ physisorption and hence, subsequently, OPCH surface-halogenation.
4.6 Relationship between OPCH Coverage and exposure.

For the three cases of 1,2-dibromoethane, 1-bromopropane and 1-bromopentane, both the physisorbed and the subsequently chemisorbed OPCH patterns were imaged. We made extensive measurements for the case of 1,2-dibromoethane and 1-bromopentane and found that physisorption and subsequent chemisorption coverage was linear with dose until saturation was reached at a coverage of ~80% OPCH adsorption, after which no further molecules physisorbed. It appears likely that beyond this coverage, repulsive interactions between OPCH physisorbed 1,2-dibromoethane at adjacent occupied corner-holes (not adjacent corner adatoms, as described above) combined to prevent further attachment at the adatoms of remaining unoccupied corner-holes. A graph of OPCH Br coverage against 1,2-dibromoethane exposure at 300 K is given in Fig. 13. This effect may be relevant to saturation of ~0.8 per unit-cell previously observed by others at the Si(100)-2×1 surface for the adsorption of ethylene$^{65,66}$ and cyclopentene$^{67}$.

![Figure 13. Relationship between OPCH Br coverage and 1,2-dibromoethane exposure at 300 K. Br coverage in OPCH fashion scales with the 1,2-dibromoethane exposure (reported in Langmuir, 1 L = 1×10^{-6} Torr × s) until a saturation of ~80% was reached at ~1.5 L. Note the exposures were measured by an ion gauge calibrated for nitrogen and reported with no correction for the ionization sensitivity. Experimental uncertainties are statistical, taken as the square-root of the count for each image.](image)
4.7 Evidence that chemisorbed OPCH arises from repulsion between physisorbed pre-cursors.

For the chemisorption patterns of Br-atoms from four adsorbates in Fig. 9a’, b’, and c’ and 10b, the overwhelming preference for forming chemisorbed OPCH implies a mobile physisorbed precursor. Mobile precursors were first directly imaged by Brown, Moffatt and Wolkow, for the system of benzene on Si(111)-(7×7) at 78 K\(^{68}\). The mobile pre-cursor is inferred by STM as the physisorbed pattern shown in Fig. 9a, b and c. Adsorption directly upon impact with the surface, in the absence of a mobile state, would have resulted in random patterns of attachment, such as that shown for chemisorbed bromobenzene in Fig. 10a, rather than the OPCH patterns of Fig. 9a, b and c.

4.8 Observation of repulsion by co-adsorption of chemisorbed and physisorbed species.

Our physisorption images in Fig. 9a, b and c are consistent with the physisorbed molecule being located directly above the site of subsequent chemical attachment, since the patterns of physisorption and chemisorption are the same. ‘Localized atomic reaction’ has several times been reported for halides reacting with silicon, and has been the subject of theoretical analysis\(^4,69\). The lowest-energy pathway to chemical reaction, it was argued, involved concurrent breaking of an old bond and formation of a new bond. Such ‘concerted’ reaction can only occur locally.

After finding favorable locations at different corner-holes, the mobile physisorbed molecules react locally to yield chemisorbed Br-atoms. Further physisorbed molecules arriving at the same corner hole are repelled while still in their mobile precursor state. This repulsion originates either from a previously physisorbed molecule as evidenced in Fig 9a, b and c, or, as will now be shown, repulsion from a reacted Br-atom.

The scenario of chemisorbed Br-atoms repelling physisorbed molecules was established for the case of 1,2-dibromoethane by direct observation (Fig. 14). A silicon surface was partially brominated with Br-atoms distributed OPCH, using a moderate dose of 1,2-dibromoethane at 300 K (Fig. 14a). The surface was then cooled to 110 K, and further dosed with 1,2-dibromoethane which physisorbed. The OPCH pattern was thereupon simultaneously observed for both chemisorbed Br-atoms and physisorbed 1,2-dibromoethane molecules, co-existant at the
surface (Fig. 14b). Thermal bromination could confuse this picture but the thermal rate of reaction was shown by successive traces to be negligible at 110 K; in four hours of observation, the total number of Br-atom did not change.

It was found, in this dual adsorbate experiment that some corner-hole sites were occupied by chemically attached Br-atoms and others by physisorbed 1,2-dibromoethane molecules, but rarely by both Br and 1,2-dibromoethane. A surface area of 165 corner holes was examined to show adsorbates at 130 corner-holes, by either one (single occupancy) or two species (double occupancy); multiple occupancy greater than two adsorbates at the a corner hole was absent. We found 121 (93±8%) for single occupancy (93 by Br-atom, and 28 by 1,2-dibromoethane), and 9 (7±2%) for double occupancy (6 by one Br-atom and one 1,2-dibromoethane, and 3 by two 1,2-dibromoethane). This observation clearly evidenced a substantial repulsion between chemisorbed Br-Si and mobile 1,2-dibromoethane(ad) at the same corner-hole. The repulsion must be sufficient to induce migration of the mobile 1,2-dibromoethane precursors away from corner-holes occupied by Br, on a timescale faster than reaction.

Figure 14. Chemisorbed Br-Si (one-per-corner-hole) repels physisorbed 1,2-dibromoethane(ad). (a) 300 K STM image (~ 210×210 Å², V_s=+2.7 V, I_t=0.2 nA) showing chemisorbed Br one-per-corner-hole, OPCH, coloring as Fig. 9. After cooling to 110K and further exposure to ~0.4 L 1,2-dibromoethane(g), the surface was re-imaged: (b) different area 110 K STM image (~ 210×210 Å² in size, V_s=+2.8 V, I_t=0.2 nA). In addition to brominated corner-hole adatoms we now also see physisorbed 1,2-dibromoethane(ad) (dim spots, circled by small solid white lines) in OPCH adsorption (outlined with dotted black lines) and also on middle adatoms. Only in one exceptional case, circled by a dotted blue line, did 1,2-dibromoethane(ad) and Br adsorb around the same corner-hole on corner Si-adatoms. 1,2-dibromoethane(ad) prefers to adsorb at corner-holes that did not previously contain Br-atoms.

4.9 Activation-energy differences from OPCH patterns.

For each pattern of adsorption by physisorbed species, chemisorbed Br-atoms, or a mixture of both, we also found a minor occurrence of multiple adsorptions in addition to observing the dominant OPCH distribution. That is, we very occasionally observed two or more species adsorb
at a corner hole. (Examples are highlighted with blue circles in Fig. 9). From the observed ratio of occurrences of single and multiply adsorption, we can use Arrhenius expressions to estimate the differences in activation energies required to reproduce the observed ratios. This analysis attributes the differences in occupancy to a difference in activation energies, \( \Delta E \) (Table 1), at a corner-hole with and without a previous occupant on one of the six corner adatoms. The activation energy for the second physisorption at a corner-hole with a previous physisorbed molecule is calculated to be \( \Delta E = 15-30 \text{ meV} \) greater than for the first physisorption, depending on the nature of the physisorbed halide (see Table 1). The activation energy for the physisorption at a brominated corner-hole is calculated to be \( \Delta E = 15 \text{ meV} \) greater than for first physisorption at a clean corner-hole. The counts for each system upon examination are given in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>System</th>
<th>( \Delta E ) (meV)</th>
<th>Temperature (K)</th>
<th>Number of corner-holes with single occupancy</th>
<th>Number of corner-holes with multiply occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1,2-dibromoethane repels 1,2-dibromoethane</td>
<td>30±7</td>
<td>110</td>
<td>460</td>
<td>19</td>
</tr>
<tr>
<td>b</td>
<td>1-bromopropane repels 1-bromopropane</td>
<td>15±1</td>
<td>50</td>
<td>92</td>
<td>2</td>
</tr>
<tr>
<td>c</td>
<td>1-bromopentane repels 1-bromopentane</td>
<td>22±2</td>
<td>100</td>
<td>229</td>
<td>18</td>
</tr>
<tr>
<td>d</td>
<td>Br repels 1,2-dibromoethane</td>
<td>15±6</td>
<td>110</td>
<td>28</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 1. Differences between energy barriers necessary to account for the observed ratios of single to multiple adsorption at single corner holes on the Si(111)-7×7 surface. (a) physisorbed 1,2-dibromoethane repels further physisorption from 1,2-dibromoethane. (b) physisorbed 1-bromopropane repels physisorbed 1-bromopropane (c) physisorbed 1-bromopentane repels physisorbed 1-bromopentane. (d) chemisorbed Br-atoms repel physisorbed 1,2-dibromoethane.

4.10 Physisorption geometry of 1,2-dibromoethane at Si(111)-7×7

The physisorption geometry of 1,2-dibromoethane was obtained from an analysis of height profiles averaged from multiple STM images obtained at 110 K, as shown in Fig. 15. The measured height profiles are consistent with one Br-atom above a corner silicon-adatom and the other above the adjacent silicon rest-atom. This configuration agrees with that calculated \textit{ab initio} (see Fig. 16).
Figure 15. Height profiles of 1,2-dibromoethane(ad) at 110 K. The averaged height profiles of 20 1,2-dibromoethane(ad) sites along three directions (black curves), as illustrated in (a), (b) and (c), are compared with clean silicon sites (green curves). The apparent height decrease at both corner and rest silicon sites in (a) suggests that 1,2-dibromoethane(ad) is aligned above these two silicon atoms. STM images were taken at $V_s=+1.5$ V, $I_t=0.26$ nA. Corner-, middle- and rest- Si positions are marked in each panel.

4.11 DFT calculations

In support of the experimental findings, DFT calculations were performed jointly by Prof. Werner A. Hofer and Drs. M. Ebrahimi, I. R. McNab and H. Lin. These calculations were not part of my work, but are reported here as they clarify the nature of the interactions underlying OPCH patterning.

These four co-workers simulated, \textit{ab initio}, a system that displayed OPCH behavior, namely coexisting chemically attached Br-atoms and physisorbed 1,2-dibromoethane molecules at a single corner-hole of the Si(111)-(7×7) surface. The physisorption energies in the presence and absence of a chemisorbed Br-atom were calculated at the smallest and greatest separations between adatoms at a corner-hole. Density Functional Theory (DFT) calculations\cite{note1}, and also semi-empirical DFT-D calculations that included van der Waals interactions\cite{note2}, were made with the Vienna ab-initio simulation package (VASP 5.2.8). See ref.43 for details.

In the gas phase 1,2-dibromoethane (DBE) exists as both \textit{gauche} and \textit{trans} rotational isomers; \textit{gauche}-DBE is 10% of the total population, and is excited by 73±5 meV relative to \textit{trans}-DBE\cite{note3}. This energy difference, together with the calculated (DFT-D) physisorption energies for \textit{gauche}-DBE (-392 meV) and \textit{trans}-DBE (-256 meV) allowed a calculation of the population ratio at equilibrium at the Si(111)-(7×7) surface. It was found that at room temperature, \textit{gauche}-DBE was 96% of the total physisorbed population, which increased to 99.9% at 110 K; all further analysis assumed that the only rotational isomer present at the silicon surface was \textit{gauche}-DBE.
Unusually, in order to reproduce the experimentally observed long-range repulsion ($\Delta E$, Table 1) it required the use of a Si(111)-7×7 unit-cell of eight silicon layers thickness, some 298 Si-atoms in total. Initial DFT calculations with a six-layer supercell (200 Si-atoms) found no effect greater than expected error of integration (~10 meV). For gauche-1,2-dibromoethane adjacent to a chemically attached Br-atom, the calculated physisorption energy decreased (DFT with van der Waals) by some 200 meV, a measure of the inter-adsorbate repulsion, in the presence of the chemisorbed Br. At the same time the 1,2-dibromoethane, lifted by almost 1.0 Å from its unperturbed physisorbed height over the surface., This is shown in Fig. 16, in which a hexagonal unit-cell of the Si(111)-7×7 is highlighted, and the 1,2-dibromoethane shown in top and side-views. (The relationship between the coordinates of the hexagonal unit-cell used here and the more usually pictured rhombohedral unit-cell were given by Tong et al.44)

To analyze the nature of the interaction, they calculated the energy distribution, and partial-densities of states (p-DOS) for physisorbed 1,2-dibromoethane at the surface, then added a Br-atom to the surface to observe the resultant changes in all these quantities. The chemisorbed Br-atom decreased the binding of the 1,2-dibromoethane to the silicon surface. A Bader charge analysis74,75 showed that the major effect of the chemisorbed Br was to withdraw electron-charge from the surface, by removing it from all the corner-hole adatoms (see Fig. 17). A projected

![Figure 16](image-url)
partial densities of states analysis, further showed that the charge redistribution caused by chemisorbed Br prevented the hybridization of the surface with the 1,2-dibromoethane. This finding was interpreted as evidence that the redistribution of charge caused by the attached Br-atom made the surface less polarizable. The resulting equilibrium distance was ~1 Å further from the surface than in its equilibrium distance without chemisorbed Br. (compare Fig. 16a and b, top pannels)

Such lateral charge transfer is visible occasionally in our STM images with a special tip-state. As shown in Fig. 18, recorded under these special tip-conditions, the two corner Si-adatom adjacent to a physisorbed 1-bromopentane, or adjacent to a chemisorbed Br-atom at a corner-hole, are imaged extremely brightly. The brightening effect shown for chemisorbed Br-atoms in Fig. 18(b) clearly resembles the computed charge loss contour in Fig. 17.

![Isodensity charge difference contours](image)

**Figure 17.** Isodensity charge difference contours around the corner-hole (black circle) of Si(111)-7×7 occupied by a single Br located on a corner adatom. The difference in charge distributions is for a clean silicon surface, and a silicon surface with a chemisorbed Br-atom. Isosurfaces contours of electron density differences are drawn at ±5×10^{-4} e/Å⁴, using cyan for electron density gain, and magenta for electron density loss. The Br-atom (brown) is positioned at the top-left corner-adatom and draws charge from all the corner-hole adatoms and neighboring rest-atoms. Surface silicon atoms are shown with vdW radii. Silicon-adatoms are shown in yellow, all other Si-atoms are shown in gray. One hexagonal unit-cell of the surface is outlined as a hexagonal white dashed line passing through the centers of all Middle adatoms, the white dashed circles corresponds to the dashed circles shown on the STM images of Figs 9, 10 and 14. Representative Corner adatoms (C), Middle adatoms (M) and Rest atoms (R) are labeled.
The decrease in physisorption energy of 1,2-dibromoethane due to a chemisorbed bromine atom at the same corner-hole as the 1,2-dibromoethane, was calculated at ~200 meV irrespective of relative position (at adjacent corner adatoms or opposed corner adatoms) provided only that the interaction occurred at a single corner-hole. The 200 meV decrease in physisorption energy is to be compared with the change in activation energy for physisorption, estimated from the Arrhenius expression (Table 1), as ΔE=15 meV. The physisorption energy and the activation energy for physisorption are related but different quantities; both of which are decreased by repulsion between the chemisorbed Br atoms and physisorbed 1,2-dibromoethane molecules at the same corner-hole.

4.12 Conclusions

Our experiments show that for four different bromine-containing molecules repulsion was observed between physisorbed species and also between chemisorbed and physisorbed species. This repulsion acted over at least the 13.4 Å that separates the corner adatoms at opposite sides.
of the same corner-hole. The repulsion was calculated ab-initio, by others, for the case of Br-atom/physisorbed 1,2-dibromoethane at the same corner-hole, to be \( \sim 200 \text{ meV} \) in magnitude.

The result of long-range repulsive interaction was a preference for physisorption and subsequent chemisorption of bromine-containing organic molecules in a novel ‘one-per-corner-hole’ pattern on Si(111)-(7×7). The statistical significance of the observed OPCH patterns was extremely high. The probability of obtaining the same pattern randomly, as calculated by others, was \( p \sim 7 \times 10^{-5} \).

Theoretical analysis showed that the OPCH patterns resulted from charge flow between the adatoms at a corner-hole of Si(111) (7×7). This previously unremarked repulsive interaction, due to charge-flow across the surface, is likely to be a general property of halogenation at Si(111)-(7×7).

The ability to achieve regular separation between adsorbates should be of value in molecular beam epitaxy, en route to controlling doping in solids. If dopant levels are one per billion and the device has features that are only 1 billion atoms in extent, there is a 50\% chance that a component is dopant-free. There is, therefore, applied interest in the regular spacing of potential dopant molecules in layer-by-layer construction of nano-devices.
Chapter 5

5 Effect of molecular alignment on reaction rate; bromination of Si(111)-7×7

5.1 Introduction

Reactions of simple unsaturated molecules adsorbed on a solid surface often proceed via the dissociative attachment mechanism\(^\text{76}\), also known as dissociative adsorption, or dissociative chemisorption. The molecule dissociates and adsorbed fragments are produced at the surface following the cleavage of internal molecular bonds. If two bonds are formed with the surface, following single bond breaking in the parent molecule, the mechanism is usually exoergic. Such dissociative attachment reactions have been reported for many molecule-surface systems\(^\text{4}\).

Dissociative attachment can result in only a single fragment being adsorbed at the surface; the other fragment being ejected away from the surface. This mechanism is often described as an ‘abstraction’ reaction in an analogy with the gas phase\(^\text{1}\). The surface abstraction mechanism was first confirmed experimentally in the Ceyer laboratory in studying F\(_2\) on Si(100)-2×1\(^\text{77}\). In that work, they estimated the probability for abstraction as \(~10\%\), as opposed to the probability of 90\% for dissociative attachment. Later, the Kummel laboratory showed that the branching ratio for these two processes can be controlled by varying the collision energy of the impinging molecules\(^\text{78,79,80,81}\).

Here, we report two surface abstraction reactions studied by STM in ultrahigh vacuum, for different configurations of the single molecule 1-bromopentane physisorbed on Si(111)-7×7 as represented in the following equation:

\[
1\text{-C}_5\text{H}_{11}\text{Br(ad)/Si(111)} \xrightarrow{\text{heat or electrons}} 1\text{-C}_5\text{H}_{11}\text{•(gas) + Br-Si(111)}}
\]

Two different configurations of the physisorbed reagents, at the left hand side of this equation, were distinguishable by STM as horizontally \((h)\) and vertically \((v)\) aligned at the surface. Both physisorbed reagents \((v\) and \(h)\), energized by heat or electrons, show only bromine abstraction reactions. The silicon surface abstracts the bromine atoms from 1-bromopentane, whereas the resulting 1-pentyl radicals, 1-C\(_5\)H\(_{11}\text{•}\), do not attach to the surface but escape into the gas phase.
For both thermal and electron-induced reactions, we shall show that bromine abstraction proceeds more rapidly from the vertical precursor than from the horizontal precursor. This is a rare example of molecular alignment at a surface determining reactivity.

5.2 Two physisorbed reagent configurations at 100 K

Fig. 19a shows an STM image of Si(111)-7×7 after being exposed to 0.60 L of 1-bromopentane at 100 K. The 7×7 reconstruction is still observed, but some Si adatoms, mostly at corner Si-adatom sites, became dark as a result of the physisorption of 1-bromopentane. These dark 1-bromopentanes image as 1.0 Å lower than bare Si-adatoms, as shown in Fig. 19a”.

The appearance of these dark features in our STM images are similar to missing Si-adatoms, which are the most common defects on Si(111)-7×7. However, we can rule out the missing Si-adatom defects, on the basis of the two following observations. First, we found a linear correlation between the number of dark features and the exposure, up to ~0.80 L, while the defect concentration would show no correlation with the exposure. Second, we were able to induce reactions from these features to yield reacted Br-atoms (see Chapter 5.5 and 5.6), clearly showing these features are bromine-containing adsorbates.
Figure 19. STM images (350×350 Å²) of physisorbed 1-bromopentane on Si(111)-7×7 in different configurations at 100 K: (a) horizontal physisorbed configuration, h; (b) vertical physisorbed configuration, v; and (c) an adlayer of vertical physisorbed configuration, v-adlayer. (a’), (b’) and (c’) are closer-ups; (a”), (b”), (c”) are corresponding apparent height profiles along axes shown in (a’), (b’) and (c’), respectively. Compared with the Si adatoms, the apparent height of h is 1.0 Å lower (see a”), while that of v is 0.8-0.9 Å higher for single v molecules (see b”) and v-adlayer (see c”). STM imaging conditions were as follows: (a) $V_s=+1.5$ V, $I_t=0.2$ nA; (b) $V_s=+1.5$ V, $I_t=0.2$ nA; and (c) $V_s=+1.0$ V, $I_t=0.2$ nA. We expose 1-bromopentane via a leak valve to a clean Si(111)-7×7 at 100 K at a constant background pressure of $4\times10^{-9}$ Torr with varied exposure time: 150 s for (a), 600 s for (b) and (c). Note the exposure reported was not corrected for the sensitivity of used ion gauge.

Further exposure to 1-bromopentane, above 1.0 L, gave rise to a second physisorbed state in co-existence with the dark features. Fig. 19b is an STM image taken at 100 K after a 1-bromopentane exposure of 2.40 L onto Si(111)-7×7. The new physisorbed state imaged as bright features that adsorbed preferentially over Si middle adatoms. (See Fig. 19b). These bright
features have an apparent height of 0.9 Å with respect to the clean Si adatoms. At the same exposure of 2.40 L, we observed an adlayer structure with an apparent height of 0.8 Å (see Fig. 19c), leading us to assign the adlayer as being formed by the bright 1-bromopentane. Refer to the caption of Fig. 19 for exposure details.

5.3 Assignment of the two physisorbed states

We assigned the dark 1-bromopentane to a horizontally aligned geometry and the bright 1-bromopentane to a vertical aligned geometry, on the basis of their heights in our STM images and their observed mobility. The analysis is given below.

The bright 1-bromopentane is 0.8-0.9 Å higher than the bare Si adatoms (see Fig.19b” and c”). We therefore assign them as vertically aligned with respect to the surface. This assignment is supported by earlier work\textsuperscript{82,83} from this laboratory, of bromoethane, 1-bromopropane and 1-chlorododecane on Si(111)-7×7. In that work, vertical physisorbed state for all these three molecules were observed as similar bright features by STM at 50 K. Vertical 1-bromopropane had a height of 0.6 Å higher than bare Si-adatoms\textsuperscript{84}. It follows that the bright 1-bromopentane reported here adopts the same vertical alignment, with a measured height 0.2-0.3 Å greater than the shorter chain of vertical 1-bromopropane.

By contrast, as shown in Fig. 19a”, the apparent height for dark 1-bromopentane adsorbed on a Si adatom is 1.0 Å lower than the clean Si-adatoms. An STM image is a convolution of surface topography and surface density of states (see Chapter 1). It appears that in the present case the height is not an effect of surface topography, but of the adsorbed molecule on the density of states of the silicon. The following accords with it. With a special tip-state, we obtained STM images (as in Fig. 18a in Chapter 4, the special tip-state STM image) in which the two corner Si adatoms adjacent to the dark 1-bromopentane become extremely bright. This shows that a dramatic change in electronic structure occurs upon the physisorption of the dark 1-bromopentane, which affects the two closest Si-adatoms by lateral charge flow.

We measured the averaged height profiles along corner-rest Si-atom direction for both dark 1-bromopentane and clean Si, see Fig. 20. This suggests the involvement of both corner and rest Si-atoms in governing the physisorption geometry of dark 1-bromopentane. Accordingly, we assign this dark 1-bromopentane as physisorbed horizontally aligned between a corner and a rest
Si-adatom. This assignment is in accord with that previously made (Chapter 4) for 1,2-dibromoethane, also horizontally aligned between a corner and a rest atom, on the same surface. Similar height profile signature show no dependence of applied sample bias between +1.0 and +2.5 V, with a constant tunneling current of 0.2 nA. It is of great interest, in the future, to examine this effect more systematically with respect to the tunneling current and sample temperature.

Additional evidence regarding the molecular alignment, vertical as compared with horizontal, is obtained from the large difference in mobility between the two physisorbed configurations. The bright 1-bromopentane is highly mobile at 100 K, on the basis of our consecutive STM imaging over the same area. This mobility also accounts for the fuzziness that consistently appears in our STM images of bright 1-bromopentane. The observation of mobility is in accord with the early work from this laboratory that the vertical physisorbed states for bromoethane, 1-bromopropane

Figure 20. Averaged height profiles along the corner-middle Si atom axis for a clean Si (a-a', red) from 10 cases, and for a horizontal 1-bromopentane (b-b', black) from 8 cases. The locations for corner-, rest-, and middle- Si atoms are labeled. It is clear that horizontal 1-bromopentane adopts a physisorption geometry between a corner- and a middle-Si atoms. Insert is a sample STM image (V_s=+1.5 V, I=0.2 nA) to show how the height profiles were taken.
and 1-chlorododecane were mobile even at 50 K\textsuperscript{82,83}. By contrast, dark 1-bromopentane is immobile for the whole temperature range we examined, from 100 K to 160 K. The observed mobility difference indicates that a greater surface attraction is operative for dark 1-bromopentanes than bright 1-bromopentanes. Given that both precursors have Br-atoms engaged with the surface (inferred from reactions, see Chapter 5.5, 5.6, and 5.7), this enhanced attraction must arise from a better engagement of the alkyl chain with the surface, in the case of the dark 1-bromopentane which we considered to be horizontally aligned.

5.4 Intermolecular interactions

As examined in Chapter 4, a long-range repulsion is evident between horizontal 1-bromopentane in forming the one-per-corner-hole pattern, as in Fig. 19a. This repulsion is caused by a lateral charge flow as horizontal 1-bromopentane physisorbs, being operative at least over a distance of 13.4 Å.

In contrast, vertical 1-bromopentanes exhibit attractions to one other, accounting for the formation of closely packed adlayers of vertical precursors, \textit{v-adlayer}, in co-existence with the bare Si terrace, as seen in Fig. 19c. Otherwise, we should be only able to observe a randomly distributed vertical 1-bromopentane phase. Attractive interaction was reported from this laboratory for bromoethane and 1-bromopropane, both in the vertical state at Si(111)-7×7 at 50 K. As in the earlier work\textsuperscript{82,83}, we ascribe this attraction as acting between parallel carbon-hydrogen chains in the vertical alignment. This attraction can be also inferred from the fact that reaction products arising from the vertical precursors are clusters of Br-atoms, rather than separate single Br-atoms. This Br cluster formation is consistent with the proposal that an attractive force guides mobile vertical precursors to form molecular clusters before reaction.

5.5 Electron-induced reactions

We made a preliminary examination\textsuperscript{†} of the electron-induced reactions of both physisorbed configurations, \textit{vertical} and \textit{horizontal}, and found that \textit{vertical} 1-bromopentane is more reactive than \textit{horizontal} 1-bromopentane. Fig. 21 shows one such reaction event at 100 K for a

\textsuperscript{†} A systematic study in electron-induced reaction requires an examination of the reaction rate as a function of tunneling current and tip height above the voltage threshold. These measurements are lacking at this moment.
horizontally physisorbed 1-bromopentane. This was induced by scanning this surface region with a sample bias of +3.0 V for 15 times. The dark horizontal physisorbed 1-bromopentane, marked in Fig. 21a, converted into a surface bromine atom, which is known to image very brightly relative to Si-atoms at the image bias of +2.5 V in Fig. 21b. Thermal reaction was negligible at 100 K as detailed in Chapter 5.6, so reaction was electron-induced by the +3.0 V scan. This is a further proof that the dark feature in Fig. 21b is indeed a physisorbed 1-bromopentane molecule. The lowest bias at which we obtained an electron-induced reaction for horizontal 1-bromopentane was +3.0 V. Higher voltage biases (> +3.2 V) tended to destroy the silicon surface.

We also measured the electron-induced reaction from the vertical 1-bromopentane at 100 K. Compared with the measurements of reaction threshold for the horizontal physisorbed 1-bromopentane, two challenges were present. First, the thermal reaction of vertical 1-bromopentane occurs readily at 100 K as described in Chapter 5.6, making it difficult to extract statistics on the electron-induced process; second, the vertical 1-bromopentane are highly mobile, especially at an elevated surface bias, making it difficult to correlate observed physisorbed precursors with the products of reaction.

We overcame these difficulties in the following manner. We first obtained a “before” image at a non perturbative bias. In the following image of the same area, we switched to a reactive bias “during” a scan. We then re-scanned the surface to obtain an “after” image. In this manner we obtained on a single image, areas in which only thermal reaction, and the sum of thermal and
electron induced reaction were present. By varying the perturbative bias voltage, we were able to extract the threshold energy for electron-induced reaction.

One such set of images is shown in Fig. 22, where Fig. 22a is a *before* image taken at a non-perturbative bias of +1.4V. In Fig. 22b, the bias voltage was switched *during* the scan, the top portion image was scanned at the non-perturbative imaging bias of +1.4 V, while the bottom portion was scanned at an elevated perturbative bias of +2.5 V. Finally, the whole surface region was re-imaged at a non-perturbative bias of 1.4 V as shown in Fig. 22c. A comparison between Fig. 22a and 22c reveals strikingly that the vertical 1-bromopentane shows an enhanced reaction rate (judged by the increased number of Br-atoms as reaction products) by a factor of ×30 for electron plus thermal reaction (V_s = +2.5 V), compared with thermal reaction alone (V_s = +1.4 V).

![Figure 22.](image)

Accordingly, we conclude that an electron-induced reaction channel is present. By varying the perturbative bias voltage, we were able to extract a threshold voltage for electron-induced reaction of ~ +2.0 V. This value is close to the reported threshold voltages of +1.8 V for the vertical bromomethane\(^85\) and of +2.1 V for the vertical 1-bromopropane\(^83\) at 50 K, in the course of electron-induced reactions, on Si(111)-7×7.
5.6 Thermal reaction

We were able to cause thermal abstraction reactions for both configurations of physisorbed 1-bromopentane molecules and measure their reaction rates, and hence calculate the energy barriers to reaction for each configuration, vertical and horizontal. Measurements were made of thermal reaction rates for vertical 1-bromopentane at 100 K and for horizontal 1-bromopentane at 160 K. In each measurement, a surface area was imaged for a sufficient length of time for a statistically useful sample of molecules to react. The number of Br-atoms reacted from 1-bromopentane molecules was recorded as a function of time. Examples of such a measurement are given in Fig. 23. In Fig. 23a a surface area with unreacted horizontal 1-bromopentanes at 160 K is shown; after 21 min, three horizontal 1-bromopentane molecules (imaged dark, indicated by the white arrows in Fig. 23a), reacted to form Br-atoms (imaged bright, indicated by the white arrows in Fig. 23b). Similarly, Fig. 23c and 23d show the thermal reaction for vertical 1-bromopentanes at 100 K; after 2 min, three vertical 1-bromopentane molecules (imaged bright, circled in Fig. 23c), reacted to form Br atoms (imaged dark, circled in Fig. 23d).

To determine reaction rates, the logarithms of the number of Br-atoms, ln N(Br), were plotted against measurement time, for both horizontal and vertical 1-bromopentanes, and were fitted by straight lines, yielding slopes, $k=(2.5\pm0.9)\times10^{-4}$ s$^{-1}$ for horizontal 1-bromopentanes and $k=(6.3\pm1.0)\times10^{-4}$ s$^{-1}$ for vertical 1-bromopentane, as shown in Fig. 23e. By assuming a prefactor of $10^{13}$ Hz in the Arrhenius formula, we report the activation energies for thermal bromination reactions as 0.54±0.01 eV for the horizontal 1-bromopentane, and 0.32±0.01 eV for vertical 1-bromopentane. The assumed prefactor is usually the greatest source of uncertainty in such a calculation, but for the present case, where it is relative energies that are of interest, and the systems being compared are both 1-bromopentane on Si(111)-7×7, assuming the same prefactor in both cases should be a good approximation.
Figure 23. Measurements of thermal reaction barriers for horizontal and vertical 1-bromopentane. (a) shows a surface area with horizontal 1-bromopentane (imaged dark) at 160 K. In (b), three horizontal 1-bromopentane molecules, as indicated by the white arrows, reacted to form Br-atoms (imaged bright) after 21 min. (c) shows a surface area with vertical 1-bromopentane (imaged bright, circled) at 100 K. After 2 min, these three vertical 1-bromopentane, reacted to form Br atoms (circled in d). (e) is a graph showing the logarithm of the numbers of surface Br-atom against time for each measurements, and fitted into straight lines, respectively. By assuming a prefactor of $10^{13}$ Hz in the Arrhenius formula, we are able to calculate the activation energies for thermal bromination reactions as $E_a(h)=0.54$ eV for the horizontal precursor, and $E_a(v)=0.32$ eV for the vertical precursor. All images are $\sim 127 \times 127$ Å$^2$ in size.

Imaging conditions: $V_s=+1.4$ V and $I_t=0.2$ nA for (a) and (b), $V_s=+1.5$ V, $I_t=0.2$ nA for (c) and (d). The Experimental uncertainties are statistical, taken as the square-root of the count.

Care was taken in the above measurement to ensure that any effects induced by the scanning process were negligible. In particular, the scanning biases used, +1.4 V for horizontal
1-bromopentane and +1.5 V for vertical 1-bromopentane, were well below those required for electron-induced reaction as measured in section 5.5. In addition, images in these measurements were taken at uneven time intervals. In this manner, any influences associated with scans would cause a shift in the fitted straight lines in Fig. 23e; but the slopes, as quantities of our measurements, are not affected.

5.7 Reaction mechanism

For both horizontal and vertical physisorbed 1-bromopentane, it was found that in all reactive events the Br-atom products were formed at the location of the prior physisorption site. This is another case of ‘Localized Atomic Reaction’ (LAR). The observation of LAR has been explained \(^4,6^9\) by the lowest-energy pathway to chemical reaction involving concurrent cleavage of an old bond and formation of a new bond. On this basis, we postulate that physisorption geometries for both horizontal and vertical physisorbed 1-bromopentane have the Br-atoms located above Si-adatoms. It follows that vertical physisorbed 1-bromopentane is oriented with the C-Br bond pointing towards the surface. This molecular orientation is consistent with our previous work on methyl bromide\(^8^5\) and long chain halo-alkanes\(^8^2\) on Si(111)-7×7. In support of this, in the case of methyl bromide\(^8^6\) the binding energies were computed as 0.39 eV with Br atom pointing down, against 0.15 eV with methyl group pointing down.

In no case of the reaction (for horizontal or vertical physisorbed 1-bromopentanes) did we find evidence of attachment of the hydrocarbon radicals to the surface. This implies that the transition state geometries all favored ejection of the hydrocarbon residue away from the surface, as found previously for \(\bullet\)CH\(_3\) radicals from methyl bromide on Si(111)-(7×7)\(^8^5\). The outcome of electron-induced reactions resembles that of thermal reactions in terms of bromine abstraction and reactivity difference between horizontal and vertical 1-bromopentanes, suggesting similarity in reaction dynamics.

The finding that for both thermal and electron induced reaction, that the energy barrier to abstractive bromination is greater for horizontal 1-bromopentane than for vertical 1-bromopentane is consistent with the following mechanism. Our findings indicate that vertical 1-bromopentane is in a more favorable geometry for reaction. We therefore assume that the greater energy barrier required for the horizontal physisorbed 1-bromopentane molecules is due to the additional work required to lift the 1-pentyl group away the surface from its original
alignment into a vertical alignment before reaction occurs. This motion aligns the horizontal 1-bromopentane to a transition state in which the geometry favors the recoil of the 1-pentyl radical away from the surface into the vacuum. For the vertical 1-bromopentane, in contrast, the molecular geometry already favors such abstraction. This lifting motion during reaction was implied previously for methyl bromide on Si(111)-(7×7). The novelty here is that we are able to extract the energy difference of 0.22 eV experimentally between the horizontal and the vertical physisorbed 1-bromopentane, assuming reaction proceeds via the same transition state for both physisorbed states.

5.8 Chain-length effect

The mechanism suggested above is that the alkyl chain must be raised from the surface in order for 1-bromopentane to be at a favorable geometry for bromine abstraction. This mechanism is likely to be general, and the observations are in accord with the effect of increased alkyl chain length for reactions of other simple bromides on Si(111)-7×7, as found in this laboratory. The thermal reaction barriers, Ea, are summarized in Table 2, compared with the dissociation energies, De for the molecules in the gas phase.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Ea (horizontal) in eV</th>
<th>Ea (vertical) in eV</th>
<th>De (gas phase) in eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>bromomethane</td>
<td></td>
<td>0.2(^{85})</td>
<td>3.05±0.02(^{87})</td>
</tr>
<tr>
<td>1-bromopropane</td>
<td>0.46(^{84})</td>
<td>0.34(^{84})</td>
<td>3.09±0.04(^{87})</td>
</tr>
<tr>
<td>1-bromopentane</td>
<td>0.54±0.01</td>
<td>0.32±0.01</td>
<td>3.06±0.04(^{87})</td>
</tr>
<tr>
<td>1-bromododecane</td>
<td>1.2(^{82})</td>
<td>0.2(^{82})</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Thermal Dissociation Barriers. Activation energies (in eV) for the dissociation of simple bromo-alkane molecules, in horizontal physisorbed state, Ea(horizontal), and in vertical physisorbed state, Ea(vertical). The dissociation energies for examined molecules are also included, as De(gas phase), for the purpose of comparison.

Horizontal physisorbed molecules have been found to exhibit increased activation energies with increased alkyl chain length for thermal bromine abstraction reactions of 1-bromopropane (Ea=0.46 eV), 1-bromopentane (Ea=0.54 eV) and 1-bromododecane (Ea=1.2 eV). This supports
the assigned horizontal geometry for the physisorbed species, because in a horizontal geometry each extra methylene (CH$_2$) segment results in additional physisorption attraction to the silicon surface, and hence a greater expenditure of energy in lifting the alkyl group.

Vertical physisorbed molecules were found for bromine-abstraction reactions of bromoethane (Ea=\~0.2 eV), 1-bromopropane (Ea=0.35 eV), 1-bromopentane (Ea=0.32 eV), and 1-bromododecane (Ea=\~0.2 eV). These low activation energies indicate that abstraction occurs readily from vertical physisorbed molecules. The almost invariant barrier mainly reflects the constant thermal dissociation energy of 3.0 eV for many bromides in the gas phase$^{87}$. The effect of increasing chain length on the reaction barrier for bromine abstraction is minor, as expected for the vertical physisorbed molecules.

5.9 Comparison with dissociative attachment of bromoalkanes on Si(100)

Bromine abstraction reactions that release the organic radicals into the vacuum are completely absent in comparable studies of numerous simple alkyl bromides examined on Si(100), as discussed further in Chapter 6. On Si(100), both fragments, the organic radical and the atomic bromine are always captured by the surface via dissociative attachment. As revealed in our DFT calculations, a concerted bond cleavage is operative on Si(100), in a sharp contrast to that on Si(111)-7×7 involving only interaction with a single Si adatom in the transition state. This is perhaps due to adatoms on Si(100) being more reactive than on Si(111)-7×7.

5.10 Control of surface patterning

The existence of two physisorbed 1-bromopentane molecules, vertical and horizontal, with different intermolecular interaction and reactivity enables us to control pattern formation on Si(111)-7×7. As shown in Fig. 24, both well spaced one-per-corner-hole (Fig. 24a) and closed-packed circular Br patterns (Fig. 24b) are attained at 300 K. The one-per-corner-hole pattern was achieved by exposure of 1-bromopentane at 300 K, thereby facilitating the formation of horizontal physisorbed molecules from which highly localized surface bromination reaction occurred. At 100 K, by contrast, the lifetime for vertical 1-bromopentane was sufficiently long to form self-assembled circles over middle Si-adatoms prior to surface reactions energized by very gentle heat, e.g. \~2 K/min, to form Br-atom circles.
Figure 24. Chemisorbed Br-atom on Si(111)-7×7 by 1-bromopentane. In both images, bright features are chemisorbed Br atoms as the dissociation products, from horizontal 1-bromopentane to given a well spaced “one-per-corner-hole” pattern (a), or from vertical 1-bromopentane to give closed packed circular pattern (b). Both images (both ~118×96 Å²) were taken at 300 K with the following scanning parameters: (a) Vs=+2.7 V, I=0.2 nA; (b) Vs=+3.0 V, I=0.2 nA. Refer to the text for details.

5.11 Conclusions

To summarize, we studied the bromination of 1-bromopentane on Si(111)-7×7 from two different physisorbed 1-bromopentane configurations, vertical, v and horizontal, h, with differing molecular alignment with respect to the underlying surface plane. For both thermal and electron-induced reaction, it was more difficult to induce horizontal adsorbate to react than the vertical configuration, as seen in a difference of 0.22 eV in barrier for thermal reaction and of +1.0 eV in onset for electron-induced reaction. To account for the distinctive reactivity difference, we correlate reactivity with molecular alignment. We propose an energy requirement for lifting the alkyl chain for horizontal adsorbates, as opposed to vertical adsorbates which are already aligned for abstraction reaction. Vertical and horizontal adsorbate configurations have previously been proposed for long chain halo-alkanes (1-chlorododecane and 1-bromododecane) at this surface\textsuperscript{82}. The novelty of the current study is the direct observation of the two physisorbed configurations, together with the measurement of their absolute reaction rates, both thermal and electron-induced.
6 Dissociative attachment of bromo-alkanes on Si(100)-c(4×2): effect of alkyl chain-length.

6.1 Introduction

In this chapter, we report a study by Scanning Tunneling Microcopy (STM) of the adsorption and subsequent dissociative attachment of a series of primary bromo-alkanes, bromoethane (EtBr), 1-bromopropane (PrBr) and 1-bromobutane (BuBr) on the Si(100)-c(4×2) surface between 100-180 K. The objective is to obtain the trend in activation energy for surface bromination along this series of three reagents, and to relate changing activation energy to the increasing alkyl chain-length. At these temperatures these three bromo-alkane molecules all physisorbed and subsequently reacted exclusively at inter-row sites between two depressed Si-atoms (termed “down” Si-atoms). Further, we found that the energy barriers for dissociative attachment increased with increasing alkyl chain-length. Density Functional Theory (DFT) calculations of Minimum Energy Pathways (MEPs) for the dissociative attachment reactions suggest that the increase in barrier height with chain-length has a simple physical interpretation, being due to the need to overcome the attraction between the alkyl chains and the silicon surface in going from the initial state to the transition state.

6.2 Initial states: physisorption geometries of the bromo-alkanes

6.2.1 Experiment

The temperature range of the present work was between 100 K and 180 K, at which temperatures the flipping motion of Si-dimer was frozen out, giving a c(4×2) reconstruction. Fig. 25a is an STM image of clean Si(100)-c(4×2) at 100 K. In this image, the Si dimer rows run vertically from top to bottom. At the scanning conditions used for this image only the “down” Si-atoms are imaged as bright; the “up” Si-atoms are dark (see Chapter 1).

Upon exposure of the surface to 0.04 L of bromoethane at 100 K, bright features were observed (see Fig. 25b). These features consistently appeared with bright streaks in the scanning direction, indicative of a species moving under the tip suggesting a physisorbed species only weakly held to the surface. We assigned this feature as physisorbed C\(_2\)H\(_3\)Br(ad). The physisorption of
bromoethane was found exclusively at inter-row sites between two “down” silicon atoms. Adsorption between two “up” Si atoms was not observed. This site-selectivity is consistent with our DFT calculations (see below).

To confirm the assignment of the bright feature as physisorbed C$_2$H$_5$Br(ad), we caused thermal reactions from these features and found atomic bromine as reaction products (see Chapter 6.3, below). Similar reaction was also induced by electrons from the STM tip in a voltage pulse (V=+2.5 V, t=100 ms). This is a conclusive proof of our assignment of physisorbed C$_2$H$_5$Br(ad). The observation of physisorbed C$_2$H$_5$Br(ad) at 100 K is, moreover, in agreement with a previous study of the same system by Ultraviolet Photoelectron Spectroscopy (UPS$^{88}$). In that study, Keeling et al. concluded that bromoethane physisorbed at 110 K, as they were able to resolve the $\sigma$(C-Br) state at 4.8 eV in their UPS spectra of a dosed surface.

We also found that 1-bromopropane (BrPr) physisorbed at the Si(100)-c(4×2) surface at 123 K (Fig. 25c) and as did 1-bromobutane (BrBu) at 129 K (Fig. 25d). Once again, the molecules physisorbed exclusively at the inter-row sites between two down Si-atoms. The nature of the physisorbed species was confirmed by reactions (induced by heat or electrons) to form atomic Br-atoms as products.
Figure 25. Physisorption of bromoalkane on Si(100)-c(4×2). Panel a is an empty-state image of a clean Si(100)-c(4×2) surface taken at 100 K. At these imaging conditions, only the down Si atoms are visible. Panel b, c, d are typical empty-state STM images, showing the physisorption of bromoethane at 100 K, 1-bromopropane at 123 K, and 1-bromobutane at 129 K, respectively. All physisorbed bromoalkanes adopt the inter-row sites exclusively. All STM images are of ~77×77 Å², taken at a constant current of 0.2 nA. Sample biases are given in each panel. The adsorption site of physisorbed bromides was deduced using the clean Si surface lattice, as shown in b; each black circle represents the position of a down Si atom. All bromides were found to physisorb over two down Si-atoms of adjacent rows.

We note that in all three cases the physisorbed molecules were only observable in our empty-state (positive surface bias) images. In filled-state images (negative surface bias) the molecules are invisible. This is understandable for the case of bromoethane on Si(100)-c(4×2), in
light of the early UPS study \cite{88}. According to this early study, all electronic bonding states that originate from \( \text{C}_2\text{H}_5\text{Br}(ad) \) are more than 4 eV below the Fermi level, and are therefore inaccessible over the typical bias range used in STM imaging of silicon (\( V_s = -0.6 \text{ V to } -3.0 \text{ V} \)). It is reasonable to suppose that the invisibility of PrBr and BuBr in our filled-state images indicates that they also have no accessible states within -3 V of the Fermi level. Similar imaging behavior as seen by STM was also reported for 1,4-cyclohexadiene on \( \text{Si(100)}-\text{c(4×2)} \) at 80 K \cite{89}.

### 6.2.2 Calculated initial-state physisorption geometries

Plane-wave based density functional theory (DFT) total energy calculations were employed to search for stable physisorbed structures, using the Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation (GGA) for exchange-correlation potentials, the projector augmented waves (PAW) method, and a plane-wave basis set of with an energy cutoff of 450 eV, as implemented in the Vienna \textit{Ab-initio} Simulation Package (VASP). We employed throughout a slab of \( \text{Si}_{112}\text{H}_{32} \) with a \( \text{c(4×2)} \) periodicity in a supercell of \( 15.36125 \text{ Å} \times 15.36125 \text{ Å} \times 30.00000 \text{ Å} \) in size. This slab consists of seven layers of Si-atoms with the bottom terminated by 32 H-atoms. The adsorbate molecule was placed on the top face of the slab. The bottom two silicon layers were frozen and then all other atoms were fully relaxed until the net force on each atom was less than 0.02 eV/Å. The surface Brillouin zone was sampled using a \( 2\times2\times1 \) k-mesh, and calculations were performed without spin-polarization. We tested the convergence of our results with a \( 3\times3\times1 \) k-mesh with spin-polarization applied, and found a difference of only 9 meV in the relative energies for the worst case. Because of the high cost of these calculations, we chose to calculate only two extreme cases from our experiments, EtBr and BuBr.

The calculated geometries for both physisorbed EtBr and BuBr, and also for meta-stable states of EtBr and BuBr are shown in Figure 26. The metastable states will be discussed later in this chapter; they have a well-depth with respect to the adjacent points along the minimum energy path of 0.2-0.3 eV.
Figure 26. Physisorbed geometries for bromoethane (a and b) and 1-bromobutane (c and d) by DFT calculations. Panel (a) and (c) are most stable geometries, with the heats of adsorption computed as 0.41 eV for C₂H₅Br(ad), and 0.44 eV for 1-C₄H₉Br. Panel (b) and (d) are the meta-stable physisorbed geometries, en route along the thermal reaction pathway, with the heats of adsorption computed as 0.26 eV for C₂H₅Br(ad), and 0.23 eV for 1-C₄H₉Br. A large slab of Si₁₁₂H₃₂ were used for the DFT calculations; but only the molecule and 12 Si atoms underneath are shown for simplicity.

For the case of bromoethane on Si(100)-c(4×2), initial calculations of the physisorbed geometry were begun by relaxing five different trial initial configurations at an inter-row site, and comparing the total energies for each optimized structure‡. The most stable geometry

‡ The trial initial configurations differed in the location of Br-atom and the molecular alignment with respect to the underlying surface: in three trial initial configurations, we placed the Br-end atop one Si atom of the inter-row site, with three molecular alignments; vertical, tilted (by ~45°) and horizontal alignments. In another two trial initial
physisorption geometry found is shown in Fig. 26a, the calculated physisorption energy of this state is 0.41 eV. The EtBr is adsorbed at an inter-row site between two down Si atoms. In this configuration, the bromoethane molecule is horizontally aligned, with the Br-atom almost vertically above one down atom of a Si-dimer§.

Although the experimental images clearly show that EtBr adsors between two down Si-atoms, we also calculated an energy for the case of physisorption between two up Si-atoms. This geometry was far less stable; the heat of adsorption being only 0.13 eV. The energy difference of ~0.3 eV is consistent with our experimental observation of inter-row sites between down Si atoms as the exclusive physisorption sites for C$_2$H$_5$Br(ad). The Si dimer tilt causes electron charge to transfer from the down Si-atom to the up Si-atom. It is to be expected that the lone pair electrons at the bromine atom interact more strongly with the positively charged down Si-atoms forming a dative bond.

Similar calculations for BuBr gave the physisorbed state shown in Fig. 26c. The heat of adsorption was slightly greater than that for EtBr (0.44 eV rather than 0.41 eV), but the geometry was almost identical.

For both EtBr and BuBr, during calculations of reaction pathways (see below), as already noted, we found a meta-stable configuration, separated by barriers from both the initial physisorbed configuration and the reaction products. These metastable configurations are shown in Fig. 26b for EtBr and Fig. 26d for BuBr. The principal difference between the metastable configurations configurations, we placed the Br-end midway between the two Si atoms of the inter-row site, with vertical and horizontal alignments. In all our five trial initial configurations, we placed the Br atom ~2 Å above the surface before structure relaxation. In general the more stable structures were obtained from molecules when the C-C bond was aligned parallel to the surface. For structures obtained starting with the C-C axis vertical or tilted to the surface, the total energies were higher by 0.2-0.3 eV. The initial configurations with Br placed midway inter-row led to a relaxed structure with the Br-atom located atop one of the two Si adatoms.

§ In this configuration, this Si-atom is raised by 0.2 Å relative to the clean Si surface; this movement also resulted in a reduced Si dimer bond length, r$_1$ = 2.41 Å (from 2.35 Å for clean Si), and a decreased dimer-tilt angle, $\theta_1$ = 14.5° (from 19.9° for clean Si). The calculated Si-Br separation is r$_2$ = 2.56 Å, which is only ~0.3 Å longer than the covalent Si-Br bond length of 2.29 Å. Despite the close approach of the Br-atom to a Si-atom, we consider that this state to correspond to physisorbed EtBr, C$_2$H$_5$Br(ad), because the C-Br distance (2.01 Å) is essentially unchanged from that in the free molecule (1.99 Å).
and the physisorbed configurations are that the direction of the buckling of the Si-dimers underneath the alkyl chains has reversed. The Si-atoms underneath the alkyl chains have become “up” (negatively charged) Si-atoms. This metastable state is as a result of the bi-stable nature of buckled Si dimers (see Chapter 1).

For EtBr in the metastable state, the tilt angle of the Si-dimer underneath the alkyl chain is \( \theta_1 = -17.9^\circ \) (as compared with 19.9° for clean Si; the negative sign here refers to the opposite tilting direction.). The heat of adsorption for this configuration was computed as 0.25 eV, so that it is less stable than the physisorbed initial state of C\(_2\)H\(_5\)Br(ad). Tentatively, we ascribe the streaks often observed in our STM images for C\(_2\)H\(_5\)Br(ad) to the thermal switching between these states at 100 K, as justified below. In our experiment, the switching rate must be around the same order-of-magnitude as our imaging-line frequency (100 Hz), so that the motion could be captured in our STM images as streaks\(^90\). Assuming a prefactor of \(10^{13}\) Hz in the Arrhenius formula, we could estimate the barrier to switching to be 0.22 eV, in a remarkable agreement with the computed barrier of 0.25 eV for the switching from the physisorbed state to the metastable state. A more careful examination would require a systematic investigation of the dependence of switching rate on temperature, sample voltage, tunneling current and tip height, which is beyond the scope of current study.

For BuBr in the metastable state, the tilt angle of the Si-dimer underneath the alkyl chain is -16.0° and the heat of adsorption was computed as 0.23 eV, so that it is less stable than the physisorbed initial state of 1-C\(_4\)H\(_9\)Br(ad). The thermal barrier was computed as 0.27 eV for the switching from the physisorbed state to the metastable state. It appears that the rate of this switching process should be also comparable to our imaging-line frequency. However, we did not observe any streaks in imaging 1-C\(_4\)H\(_9\)Br(ad), in contrast to C\(_2\)H\(_5\)Br(ad). We speculate that this difference arises from the increased chain-length in the 1-bromobutane. In both cases, the main switching motion is the flipping of Si dimers, as shown in Fig. 26. In the geometry of 1-bromobutane, this Si dimer is underneath the butyl group, whereas the dimer is more exposed to the vacuum in the case of bromoethane. Thus, it may follows that the motion of flipping the Si dimers is more likely to be captured in our STM images as streaks for the case of bromoethane than for 1-bromobutane.
6.3 Dissociative attachment reactions

Thermal dissociative attachment reactions were observed for EtBr, PrBr and BuBr. Fig. 27 shows one example of each reaction, the left hand column shows an initial physisorbed state, while the right hand column shows the same molecule following thermal dissociative attachment reactions.

6.3.1 Experiment

Figure 27. Thermal dissociation events imaged for (a) bromoethane at 100 K, (b) 1-bromopropane at 123 K, (c) 1-bromobutane at 150 K, with schematics given in panel (d). All STM images (~46×68 Å$^2$ in size) were taken in the constant current mode with a tunneling current of 0.2 nA for (a) and (b), 0.05 nA for (c). Sample biases are given in each panel. Dotted lines in panel (a) through (c) represent the locations of dimer rows.
In Fig. 27a, thermally induced dissociative attachment of EtBr is shown. The particular molecule reacted after two minutes at 100 K. The reaction products are shown imaged on the right of Fig. 27a. The final state consists of two different fragments that we shall assign as C$_2$H$_5$(ad) and Br(ad) at an inter-row site. As shown in Fig. 27a, the reaction products are located at the same surface site where bromoethane physisorbs. Thermally induced dissociative attachment reactions are also shown for 1-bromopropane at 123 K (Fig. 27b), and for 1-bromobutane at 150 K (Fig. 27c). The correspondence between the position of reactants and products is known from the wide area images (not shown) of which these are part. The dissociative attachment of EtBr, PrBr and BuBr provide further examples of “Localized Atomic Reaction” (LAR)$^{4,69}$ that involves a concerted bond cleavage/formation process, as confirmed in our DFT calculations below.

All three reactions studied proceeded exclusively by the dissociative attachment mechanism. That is, reaction products always consisted of two different fragments, R(ad) and Br(ad), at an inter-row site. The schematic for the observed reaction is given in Fig. 27d. In no case did we find an isolated R(ad) and Br(ad) fragment indicative of surface abstraction mechanism on Si(100)-c(4×2), though abstraction has frequently been reported for bromoalkane on Si(111)-(7×7)$^{85}$ (see Chapter. 5 for more examples). Abstraction is completely absent in our present study of bromoalkanes on Si(100)-c(4×2) in the temperature range of 100-180 K.

Our assignment of the reaction products is deduced from the appearance of the silicon dimers to which the fragments attach in our STM images, as interpreted by our DFT calculations. As an example, a set of high-resolution empty-state and filled-state images of the reaction products from bromoethane is given in Fig. 28a and b. In both images, the two product fragments differ in relative brightness. Closer examination reveals a more striking difference in terms of imaging behavior at the position of the two unbonded Si atoms at the far end of the two Si dimer involved in binding the product fragments (see Fig. 28a’ and b’).
Figure 28. High resolution images of reaction products from bromoethane on Si(100)-c(4×2). Images are ~50×50 Å² in size. Imaging parameters are as following: (a) $V_s=+1.5$ V, $I_t=0.1$ nA; (b) $V_s=-1.5$ V, $I_t=0.6$ nA. (a’) and (b’) are duplicates of (a) and (b), with labels to locate the involved two Si-dimers and individual surface fragments. In (a’), the left Si-atom (adjacent to C$_2$H$_5$) is bright, while the right Si-atom (adjacent to Br) is dark; in (b’) the right Si is brighter than the left Si-atom.

At a sample bias of +1.5 V as in Fig. 28a, the unbonded Si atom *adjacent* to the bright fragment is visible suggesting that the tilt direction of this Si dimer is reversed to make this a down Si-atom. The Si-dimer tilt direction for the other Si dimer appears unchanged. In our DFT calculations below, such a reversed Si-dimer tilt is reproducible only for the Si-dimer that has a chemisorbed ethyl group, C$_2$H$_5$(ad), whereas the Si-dimer tilt direction is preserved for the Si dimer that has a chemisorbed bromine atom, Br(ad). Therefore, we assign the bright fragment in
our empty-state image (with unbonded Si visible) as C$_2$H$_5$(ad), and the dark fragment (with unbonded Si visible) as Br(ad).

This assignment is consistent with our filled-state images. At a sample bias of -1.5 V, as shown in Fig. 28b, the unbonded Si atom images brighter adjacent to Br(ad) than adjacent to C$_2$H$_5$(ad). As the Si adjacent to Br(ad) stays as an up Si-atom, it is expected to be higher than the Si adjacent to C$_2$H$_5$(ad). This assignment is in line with measurements of typical filled-state STM images from our laboratory on bromomethane$^{91}$ and chloromethane$^{92}$ in which it was found that the Si-atom adjoining Cl(ad) or Br(ad) appeared brighter than the Si-atom beside CH$_3$(ad).

6.3.2 Thermal reaction

The thermal reactions of EtBr, PrBr and BuBr were measured experimentally by observing populations of physisorbed molecules react. The results are plotted in Fig. 29. From the measured rates of reaction, we obtained thermal activation energies in each case. Each set of measurements were performed at a single temperature, and therefore no experimental determination of the Arrhenius “A-factor” was possible. In the absence of a measured “A-factor”, it is normal to assume that $A=10^{13}$ Hz. The uncertainty in the A-factor is the greatest experimental unknown. It will be a very good approximation to assume that the A-factor for all three cases is identical. Hence comparisons of the activation energies are dependable.
Figure 29. Graphs of number of unreacted physisorbed molecule against time after molecular exposure, for bromoethane at 100 K (in panel a), 1-bromopropane at 123 K (in panel b), and 1-bromobutane at 150 K (in panel c), on Si(100)-c(4×2). By fitting the experimental measurements into an exponential decay formula (red curve in each panel), we were able to calculate the thermal activation energies, as 0.34, 0.41 and 0.53 eV, for bromoethane, 1-bromopropane and 1-bromobutane, assuming an Arrhenius formula with a prefactor of $10^{13}$ Hz. The experimental uncertainties are statistical, taken as the square-root of the counts. Note differing time-scales in panel a, b and c.

Measurements of thermal reaction rate were made at 100 K for bromoethane, at 123 K for 1-bromopropane and 150 K for 1-bromobutane. In each measurement, a surface area was imaged for a sufficient length of time for a statistically useful sample of molecules to dissociate; no other processes, such as molecular migration or desorption, was observed during these measurements.
The thermal reaction rates were determined by plotting out the number of physisorbed molecules against time and fitting each plot to an exponential decay function. In the past, it would have been more usual to plot the logarithm of the population and fit straight lines; we prefer the direct fit to the correct functional form because it enables uncertainties in the fit parameters to be determined. The decay constants obtained from the fits are the thermal rate constants, calculated as $\lambda=(5.0\pm0.3)\times10^{-5}\text{ s}^{-1}$ for bromoethane, $\lambda=(1.6\pm0.7)\times10^{-4}\text{ s}^{-1}$ for 1-bromopropane, and $\lambda=(1.0\pm0.1)\times10^{-5}\text{ s}^{-1}$ for 1-bromobutane.

The absolute uncertainty arising from the assumed prefactor in the derived activation energies is around 0.04-0.05 eV** for the temperature range of our measurements, the relative energies being more accurate. We found activation energies for thermal dissociations as 0.343±0.005 eV for bromoethane, and 0.410±0.006 eV for 1-bromopropane and 0.536±0.002 eV for 1-bromopentane. The assumed prefactor is usually the greatest source of uncertainty in such a calculation, but for the present case, where it is relative energies that are of interest, and the systems being compared are all primary bromoalkane on Si(100)-c(4×2), assuming the same prefactor in all cases should be an excellent approximation.

A known problem in determining reaction rates by STM is that reactions may be caused by the process of observation: that is by the STM tip itself, either by electron-induced or field-induced processes. For the present measurements we were able to conclude that the influence of the measurements was negligible, on the basis of two arguments.

First, we used a self-consistency check; using the measured rate of reaction and the final number of reacted molecules, we back-calculated to determine the original physisorbed population at the start of the measurement. If a measurement effect existed then the measured rates would be increased hence back-extrapolation from the final measurement, using the measured rate of reaction would give a markedly different calculated total number of initial physisorbed molecules. Note that this check is only valid if the measurements by STM which could contribute induced-reaction were made at uneven time intervals (Not the case for 1-bromopropane; see Fig. 29(b)). No such discrepancy was found for bromoethane or 1-bromobutane, within the statistical uncertainties.

** This was calculated using a prefactor of $10^{13\pm2}\text{ Hz}$.
Second, we checked for a possible the tip-induced effect directly at lower temperatures where thermal reaction was negligible. Tip-induced reactions, as determined by the nature of electronic excitation or electric field, are expected to be insensitive to temperature. If there was a tip effect in our thermal rate measurements, we would observe the dissociations at any temperatures by using the same scanning parameters. However, no detectable reactions were observed in our preliminary tests of bromoethane at 50 K \(^84\) (rather than 100 K in thermal rate measurement), and 1-bromopropane at 100 K (rather than 123 K in thermal rate measurement). It follows again that the tip effect is negligible in our thermal rate measurements.

6.3.3 Calculated Minimum Energy Pathways (MEPs) for dissociative attachment.

6.3.3.1 Calculated final states.

In order to calculate Minimum Energy Pathways (MEPs) for the dissociative attachment reactions we first calculated the geometries for the chemisorbed reaction products, from bromoethane and 1-bromobutane at an inter-row site of Si(100)-c(4×2). All calculations were made with the same parameters used for calculating the physisorbed states.

In all of our initial geometries, the two bonded Si atoms began as down Si atoms before relaxation. After structure optimizations, the Si dimer attached to the alkyl group, Si-C\(_2\)H\(_5\), or Si-C\(_4\)H\(_9\), changed the Si-dimer tilt direction, becoming an “up” Si, while the Si-dimer tilt direction for the Si atom attached to Br was preserved. The most stable geometries are shown in Fig. 30a and b for the products of bromoethane and 1-bromobutane, where the alkyl groups both adopt an upright geometry. It might be thought that further energy would be gained by bringing the alkyl chain close to the silicon surface, but this results in too much strain of the alkyl chain. That the products of dissociative reaction are chemisorbed is evident in the heats of adsorption, computed as 2.31 eV for products of bromoethane and, 2.34 eV for the products of 1-bromobutane. It is also consistent with the obtained bond lengths; the Br-Si separation of 2.29 Å, and the C-Si separation of 1.90 (1.91) Å, in accord with the documented covalent bond lengths\(^87\).
6.3.3.2 Calculated minimum energy pathways (MEPs)

The reaction pathways for dissociative chemisorption of bromoethane and 1-bromobutane were determined using the Climbing Image Nudged Elastic Band (CI-NEB) method as implemented in VASP. We found that in our minimum energy pathway calculations structure relaxations were best performed using the algorithm of Fast Inertial Relaxation Engine (FIRE). The FIRE algorithm was considerably faster (by a factor of 3 in the number of structure relaxation steps) than the default quasi-Newton or quick-min algorithms provided by VASP.

The computed minimum energy profiles are shown in Fig. 31a for bromoethane (11 images), and in Fig. 31b for 1-bromobutane (13 images). The transition state geometry for each case is displayed below the corresponding energy profile, labeled as ≠. The initial and final state geometries are also included for comparison.

As briefly discussed above, during the MEP calculations a metastable state was found for both molecules.†† The reaction paths can be described simply as follows for the case of bromoethane;

†† We also found another reaction pathway for both molecules in which the Si-dimer is reversed after the global transition state geometry. But the computed barriers are 0.1-0.2 eV higher than that presented in the main text. It
first the molecule reaches a metastable state (image #4 in Fig. 31a) in which the silicon-dimer under the alkyl chain changes its tilt direction, bringing one silicon atom closer to the alkyl tail. The metastable state is also shown in Fig. 32b, above. In the next stage (image #4-7), the C-Br extends with the expenditure of ~0.2 eV, partially transferring C from Br to Si. In the transition state (image #7 in Fig. 31a) the Br-atom has essentially already moved into its bonding position, while the ethyl tail is approximately centrally placed between the Br-atom (to which it was bound) and Si-atom (to which it will be bound). The C-Br bond length, $r_3$, has extended from 2.01 Å to 2.36 Å, and concurrently the C-Si distance, $r_4$, has decreased from 4.12 Å to 2.83 Å, which is approaching the length of 1.9 Å for C-Si covalent bond. This transition state is suggestive of the coexistence of the old and new bonds, in a concerted reaction. Similar pathway was found for 1-bromobutane, as in Fig. 31b.

The activation energies for dissociative attachment were computed by CI-NEB as 0.34 eV for bromoethane, and 0.41 eV for 1-bromobutane, in satisfactory agreement with the experimental values of 0.34 eV for bromoethane and 0.54 eV for 1-bromobutane (see Table 3). Further, the computed activation energies for both are less than the corresponding computed physisorption energies (by 0.07 for bromoethane and 0.03 eV for 1-bromobutane), consistent with our experimental observation of dissociation in the absence of desorption in our extensive thermal-rate measurements. This suggests that the DFT method we employed constitutes as a reasonable approach for the systems under study.

We are aware of the limitation of the present calculations. First, quantum zero-point energies were not considered. The neglect of zero-point energies usually overestimates the calculated reaction barrier, since the transition state lacks one vibrational mode (along the reaction coordinate) compared with the initial physisorbed state, and additionally force-constants tend to be less in the saddle-point region of the potential-energy surface. Second, van der Waals interactions, which play a predominant role in the physisorbed systems, are usually not dealt with

appears that reduced global barrier as stated in the main text originates from the consequence of the Si dimer flipping in which the raised Si atom is brought into closer proximity of the carbon atom with which it will form a sigma bond.
adequately in the classical DFT method. However, for the present study, it is *relative* barrier energies for bromoethane and 1-bromobutane that are of interest. As both systems computed are both primary bromo-alkanes on Si(100)-c(4×2), we expect that these two effects would alter the absolute barrier heights, but with less effect on the relative barrier energies.

Figure 31. Reaction pathways calculated by DFT for (a) bromoethane and (b) 1-bromobutane on Si(100)-c(4×2)
6.4 Reaction mechanisms

Strikingly, we found experimentally that barrier to thermal dissociation increases with chain length, by ~0.1 eV per CH$_2$ unit, for bromoethane, 1-bromopropane and 1-bromobutane$^{\ddagger\ddagger}$. The trend found here is in a sharp contrast to the dissociation energies in the gas-phase where no variation with chain length was reported for C-Br dissociation energies, within experimental uncertainties$^8$. The experimental and calculated thermal barriers for the dissociation on Si(100)-c(4×2) are summarized in Table 3, in comparison with the gas phase dissociation energies documented in Ref. 87.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Ea in eV (Experiment)</th>
<th>Ea in eV (DFT)</th>
<th>De(C-Br in gas phase) in eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromomethane (MeBr)</td>
<td>&lt;0.2$^{\ddagger\ddagger}$</td>
<td></td>
<td>3.05±0.02$^8$</td>
</tr>
<tr>
<td>Bromoethane (EtBr)</td>
<td>0.343±0.005</td>
<td>0.34</td>
<td>3.04±0.04$^8$</td>
</tr>
<tr>
<td>1-bromopropane (PrBr)</td>
<td>0.410±0.006</td>
<td></td>
<td>3.09±0.04$^8$</td>
</tr>
<tr>
<td>1-bromobutane (BuBr)</td>
<td>0.536±0.002</td>
<td>0.41</td>
<td>3.07±0.04$^8$</td>
</tr>
</tbody>
</table>

Table 3. **Thermal Dissociation Barriers.** Activation energies, Ea in eV, for the dissociation of simple bromo-alkane molecules on Si(100)-c(4×2) by experiments and by DFT calculations compared with the dissociation energies of C-Br bonds for examined in the gas phase. Note the reported errors are only from the uncertainties in the decay constants. The absolute error in the experimental measurements is likely to be around 0.05 eV, arising from the uncertainty of the A-factor in the Arrhenius formula.

The observed increase in activation energy for dissociative attachment along the series of bromoalkanes (EtBr, PrBr, and BuBr) is reproduced in our DFT calculations for bromoethane and 1-bromobutane, by an increase of 70 meV in computed barriers. This increase is due to the resistance to motion of the extra (CH$_2$)$_2$ segments, as the four-atom geometry of Si-Br-C-Si are essentially identical for both bromoethane and 1-bromobutane in terms of bond lengths and

$^{\ddagger\ddagger} \text{This trend is also consistent with the upper limit for the dissociation barrier of bromomethane of } ~0.2 \text{ eV, estimated from earlier experiments of this laboratory. This estimation was based on the observation that the dissociation of bromoethane completed within 15 min after exposure to Si(100)-c(4×2) at 50 K.}$
angles. Closer examination reveals that the $\gamma$- and $\delta$- carbon atoms in the physisorbed 1-bromobutane are lifted away from the surface by 0.22 Å and 0.31 Å respectively, in going from the physisorbed state to the transition state. There is no corresponding displacement in the case of bromoethane. Accordingly, we attribute this increased activation energy with increase in chain-length to the energy required to lift the alkyl chain away the surface; as the length of the alkyl chain increases, so too does the energy required to separate it from the surface in going to the nearly vertical alignment of the alkyl group that characterizes the transition state.

An earlier study\textsuperscript{95} by Lin and Bent examined the dependence of thermal dissociation rates with alkyl chain length for a series of primary halo-alkanes on copper surfaces, measured by temperature programmed reaction (TPR) and high-resolution electron energy loss spectroscopy (HREELS). For the systems considered, they found no chain length dependence for the rate of thermal dissociation of carbon-halogen bonds on copper surfaces. They proposed that the physisorbed haloalkanes adopted a “flat” geometry at the copper surface that was \textit{retained} in the transition state for carbon-halogen bond dissociation, and that the alkyl chain reoriented to an “upright” alignment \textit{subsequent} to this “flat” transition state. This is in contrast to our current study on Si(100)-c(4×2), where the dissociation barrier scales with the alkyl chain length in our experiments and the alkyl chain is lifted in the transition state geometry from initial physisorbed state as evidenced by our DFT calculations. It appears possible that this subtle variation in the reorientation of alkyl chain as the system proceeds along the reaction coordinate causes the observed different dependence of the activation barrier on the length of the alkyl chain for the dissociative attachment of primary halo-alkanes on copper as compared with silicon surface.

It would appear that Lin and Bent observed sequential halogen bonding to the copper surface, followed by alkyl bonding. By contrast our findings are consistent with concurrent halogen and alkyl bond-formation at Si(100)-c(4×2). Our observation that two new bonds (halogen-silicon and carbon-silicon) are required to form at the surface if one old bond (the carbon-halogen bond) is to be severed, accords with the prevalent view of dissociative attachment. It is supported by our failure to observe any ‘abstraction’ reaction in which one bond breaks (here C-Br) and one forms (Br-Si). Lin and Bent’s contrary finding would lead one to expect that the abstraction pathway would be observable for haloalkanes on copper. Evidence appears to be lacking at the present time on this interesting point.
A noteworthy feature of the present study is the observation of inter-row attachment to the exclusion of inter-dimer and on-dimer. This observation is in qualitative accord with an earlier study of this laboratory of the dissociation of bromomethane on a Si(100)-2×1 surface, performed at 270 K. In that work, it was found that the inter-row dissociative attachment was the predominant pathway (88%), but significant dissociative attachment was also observed to occur to inter-dimer sites (11%), and on-dimer sites (1%).

The earlier study of bromomethane was carried out at 270 K, and at this temperature the Si-dimer flipping motion is fast. The Si-dimer flipping enables the possibility of a transient state of the silicon surface in which two adjacent Si-atoms are “down” at both the inter-dimer or on-dimer sites. Such dimer flipping motions were frozen at the temperature range of 100-180 K in the present study, giving the c(4×2) reconstruction that only permits two adjacent “down” Si atoms at the inter-row site. The alteration in surface mobility between the two different measurement temperatures may account for the multiple dissociation pathways observed for bromomethane at the higher temperature as compared with the exclusively inter-row dissociative attachment found here at a reduced surface temperature.

6.5 Conclusions

We have used STM to study the dissociative attachment (sometimes termed ‘dissociative chemisorption’) of bromoethane, 1-bromopropane and 1-bromobutane on Si(100)-c(4×2). In all three cases, molecular bromoalkanes, physisorbed exclusively over the inter-row site of Si(100)-c(4×2), selectively between the two adjacent topographically depressed down Si adatoms. Localized dissociative attachment reaction was induced by heat, with thermal barriers measured experimentally as 0.343±0.005 eV for bromoethane, 0.410±0.006 eV for 1-bromopropane, and 0.536±0.002 eV for 1-bromobutane; the absolute error in these measurements is likely to be around 0.05 eV, arising from the uncertainty of the prefactor of 10^{13} Hz in the Arrhenius formula. This series of experiments reveals for the first time that the barrier to thermal dissociative attachment increases with chain length, by ~0.1 eV per CH₂ unit. This systematic increase in barrier height is interpreted, on the basis of our DFT calculations, as being due to the additional energy required to lift the longer alkyl group away the surface in going from the initial physisorbed state to the reactive transition state.
Chapter 7

7 Conclusions

7.1 Thesis summary

In this work, Scanning Tunneling Microscopy (STM) and Density Functional Theory (DFT) *ab-initio* calculations were employed to investigate the physisorption and subsequent reactions at silicon surfaces for a series of halogenated organic molecules: bromoethane, 1,2-dibromooethane, 1-bromopropane, 1-bromobutane and 1-bromopentane. The silicon surfaces used were Si(111)-7×7, and Si(100)-c(4×2).

A widely-spaced “one-per-corner-hole” physisorbed pattern was observed on Si(111)-7×7 by STM formed for 1,2-dibromoethane, 1-bromopropane and 1-bromopentane. “One-per-corner-hole” bromination stemming from thermal reaction of the physisorbed adsorbates was observed at the Si(111)-7×7 surface for 1,2-dibromoethane, 1-bromopropane, 1-bromopentane and bromobenzene. These “one-per-corner-hole” patterns were attributed to a long-range repulsion between individual physisorbates or reacted Br-atom and the physisorbate, computed as 200 meV at 13.4 Å, on the basis of DFT calculations. This long-range repulsion was linked to a lateral charge transfer in the Si(111)-7×7 surface induced by the adsorption of either a physisorbed brominated organic molecule (as listed above), or a chemisorbed Br-atom.

The effect of molecular alignment on the reaction rate of *bromine abstraction* (i.e. transfer of a Br-atom from the physisorbed adsorbate to the silicon surface) was investigated for 1-bromopentane on Si(111)-7×7. Two distinctive physisorbed alignments of 1-bromopentane with respect to the surface plane were directly observed by STM; vertical and horizontal. Bromine abstraction reactions took place more readily from the vertical state than from the horizontal state: the energy barrier for the thermal reaction was 0.22 eV lower for the vertical states than for the horizontal state, and the energy threshold for electron-induced reaction was ~1.0 eV lower for the vertical state than the horizontal state. These energy differences are consistent with reaction mechanisms that require the alkyl chain to be lifted from the surface during reaction.
The effect of alkyl chain-length on the rate of dissociative attachment reaction was investigated for a series of primary bromo-alkanes (bromoethane, 1-bromopropane and 1-bromobutane) on a different surface; Si(100)-c(4×2). All three bromo-alkanes physisorbed exclusively over the inter-row site of Si(100)-c(4×2), followed by highly-localized thermal dissociative attachment reactions. The thermal barrier heights were found experimentally to increase with chain length, by ~0.1 eV per CH$_2$ unit. This increase in energy barrier was interpreted, on the basis of DFT calculations, as due to the work done in lifting the alkyl group away the surface to form an approximately vertical transition state.

7.2 Discussion

7.2.1 Localized Surface reaction

The work of this thesis stresses the generality of ‘Localized Atomic Reaction’ (LAR) at silicon surfaces$^{69,4}$, in which surface reactions occur in the close vicinity to the reagent molecules. By its very nature, LAR enables the process of chemical reaction of physisorbed reagents, to reproduce, with high fidelity, the original pattern in which physisorbed reagent were adsorbed. This was stressed in Chapters 4-6. It has been argued that the reason for LAR is that the transition state geometry must have concurrently partial chemical bonds being broken and being formed. For these partial chemical bonds, “co-existence in time, requires proximity in space”$^{96}$. This proposal is further supported, by *ab-initio* DFT calculations such as those presented in Chapter 6.

7.2.2 Charge-transfer in physisorption and chemisorption

Surface charging plays an important role in governing the physisorption patterns at silicon surfaces. On Si(111)-7×7, it was shown (Chapter 4) that the lateral charge transfer, as a result of the adsorption of brominated adsorbates, induced a long-range repulsion, guiding these adsorbates to form a self-assembled “one-per-corner-hole” pattern.

This charge effect is also evident in the site-selective physisorption of simple primary bromo-alkanes on Si(100)-c(4×2) which is discussed in Chapter 6. The three molecules that were examined (bromoethane, 1-bromopropane and 1-bromobutane) were found to physisorb exclusively at the inter-row sites over two positively-charged “down” Si atoms. In contrast, at the other inter-row sites with two negative “up” Si atoms the physisorption was completely absent. Given the identical Si atom separation for these two inter-row sites of Si(100)-c(4×2), this subtle
site selectivity cannot be ascribed to a simple match between the size of the molecular adsorbates and the separation between Si atoms. It follows that the partial positive-charge at the down Si atom interacts more strongly with the lone pair electrons at the bromine atom of physisorbed bromo-alkanes, forming a partial dative bond.

Because of the localized nature of surface reaction following physisorption, this surface charge effect also determines the patterns that are observed following chemisorption. It is also interesting to note that \textit{ab-initio} calculations of the dissociation of the primary bromo-alkanes on Si(100)-c(4×2), showed that en route to the transition state, a buckled Si dimer flipped its orientation. As a consequence of the flipping, a raised Si-atom is brought into closer proximity of the carbon atom with which it will form a sigma bond.

### 7.2.3 Molecular re-alignment during the course of surface reaction

Remarkably, on both Si(111)-7×7 and Si(100)-c(4×2) surfaces, it was found that for surface bromination reactions, increasing the chain length of the primary bromo-alkanes led to an increase in the energy barrier to thermal reaction (Chapter 5 and 6). This increase in activation energy, corresponding to increase in alkyl chain length, was interpreted on the basis of \textit{ab-initio} calculations, as being due to the energy required to lift the alkyl chain away from the surface in order to form an approximately vertical transition state, starting from an initial horizontal physisorbed configuration. The generality of this effect is remarkable given the different dynamics on the two silicon surfaces: abstraction on Si(111)-7×7 and dissociative attachment on Si(100)-c(4×2). It appears that the lifting of alkyl chain is a general requirement for surface reactions of bromo-alkanes at a silicon surfaces.

### 7.2.4 Effect of surface temperature on adsorbate alignment and reactive patterning

Cooling decreases the rate of surface bromination. The lifetime of the vertical physisorbed 1-bromopentane is sufficiently increased at 100 K that the vertical molecules can migrate to form self-assembled circles before thermal dissociation. In this way, temperature can be used to control dynamics, and therefore surface patterning. At low temperature, circular patterns of the chemisorbed Br atoms were formed, in contrast to the predominant dynamics at room temperature, which favored the bromination by way of a horizontal physisorbed state to give a well-spaced “one-per-corner-hole” Br-pattern (see Chapter 5). The results presented in the
Appendix suggest that the dissociation dynamics of 1,2-dichloroethane and 1,2-dibromoethane on Si(100) differ also significantly at 110 K and 300 K: only single-halogenation was observed at 110 K, while di-halogenation prevailed at 300 K. It appears that the different reconstructions of Si(100), c(4×2) at 100 K and (2×1) at 300 K, accounts for this variation in dissociation dynamics.
Appendix

A. A preliminary STM study of physisorption, diffusion and dissociation of 1,2-dichloroethane and 1,2-dibromoethane on Si(100)-c(4×2) at 110 K

A.1 Introduction

Earlier work\textsuperscript{97} of this laboratory examined 1,2-dichloroethane and 1,2-dibromoethane on Si(100)-2×1 at 300 K. In that work, it was found that dissociative attachment reaction occurred, but large separations were found up to 80 Å, between pairs of chemisorbed halogen atoms and chemisorbed ethylene as the reaction products from the thermal dissociation of 1,2-dichloroethane and 1,2-dibromoethane. This large product separation was ascribed to a ‘cartwheeling’ rotation motion of the nascent physisorbed ethylene molecules generated by the instantaneous dihalogenation reactions. In these measurements at 300 K, it was also reported that a significant loss (as much as half) of surface halogen atoms occurred, indicating that a second reaction must occur, in addition to the dihalogenation reactions investigated.

In this work, we studied the physisorbed 1,2-dihaloethane (C\textsubscript{2}H\textsubscript{4}X\textsubscript{2}, X=Cl, Br) on a Si(100) surface at low temperatures and subsequently induced dissociation reactions. At 110 K, both 1,2-dichloroethane and 1,2-dibromoethane were found to physisorb exclusively at the inter-row site of Si(100)-c(4×2), between the two topographically “down” Si atoms. The products of subsequent dissociations (electron-induced reaction for 1,2-dichloroethane, and thermal reaction for 1,2-dibromoethane) suggest that only a single carbon-halogen bond was cleaved (single-halogenation), giving a halogen atom and a haloethyl group, both chemisorbed at the inter-row site of Si(100)-c(4×2), in accord with the other measurements of low temperature dissociative attachment reported in Chapter 6 of this thesis.

The preliminary results presented here show that the dynamics of the dissociative attachment reactions for these molecules are highly temperature dependent, and it would be interesting in future work to investigate these reactions in the temperature range of 110-300 K. Tentatively, we speculate that the variation of surface reconstructions, c(4×2) at 110 K and (2×1) at 300 K, causes different dissociation dynamics of 1,2-dihaloethanes on a Si(100) surface (single-halogenation at 110 K and di-halogenation at 300 K).
A.2 Results and discussions

Fig. 32 is an empty-state STM image of Si(100)-c(4×2) after an exposure of 0.10 L 1,2-dichloroethane at 110 K. In this image, the Si dimer rows run vertically from top to bottom. As previously established (see Chapter 1 and 6), with these scanning conditions the “down” Si-atoms are imaged as bright, and the “up” Si-atoms are imaged as dark. As shown in Fig. 32, the exposure of 1,2-dichloroethane gave a new bright symmetric feature that we assign as physisorbed 1,2-dichloroethane. The physisorbed 1,2-dichloroethane was found to exclusively adopt inter-row sites between two “down” silicon atoms; adsorption between two up Si atoms was not observed. Similar to the study of bromoethane, 1-bromopropane and 1-bromobutane on Si(100)-c(4×2) (see Chapter 6), we again assign this site selectivity to the partial dative bonds formed between lone pair electrons at the chlorine atom and the partially positively charged down Si-atoms; the attraction must be considerably weaker between partially negatively charged up Si-atoms and the lone pair electrons at the chlorine atoms.

Our assignment of these bright feature being physisorbed 1,2-dichloroethane is based on the following three observations. First, we observed a linear correlation between the number of the bright features and the exposure of 1,2-dichloroethane, up to 0.40 L. Second, these bright features are highly mobile at 110 K. For example, Fig. 33(a) and (b) are a set of STM images of the same surface were taken 5 min apart, in which a hopping event was captured. The bright feature, as circled in both panels, was found to have hopped 21 Å. This observed mobility
suggests a weak attraction to the surface, as expected for the molecular physisorption. Third, we caused electron-induced dissociation reactions and found dissociation reactions (see below).

Figure 33. A hopping event of physisorbed 1,2-dichloroethane on Si(100)-c(4×2) at 110 K. The circled C₂H₄Cl₂(ad) was found to hop a distance of 21 Å in 5 min. STM images are both ~93×114 Å² in size, taken at Vₛ=+1.5 V, Iₜ=0.1 nA.

We performed a preliminary study of the electron-induced reaction of 1,2-dichloroethane on Si(100)-c(4×2) at 110 K. Fig. 34 shows one such reaction at 110 K induced by scanning the surface with a sample bias of +3.0 V (not shown, because the +3.0 V scan was at a fast scanning speed of 3000 nm/s with no useful topographic information). The physisorbed 1,2-dichloroethane, marked in Fig. 34(a), converted into asymmetric features at the inter-row site in Fig. 34(b). These asymmetric features were immobile and inert to repetitive +4.0 V scans, indicating that they are chemisorbed reaction products from the electron-induced dissociative reactions. We do not have sufficient measurements to determine if it is a single electron or multiple electron process.

The product fragments in Fig. 34(b) are displaced from the location of physisorbed 1,2-dichloroethane in Fig. 34(a), in contrast to measurements reported in Chapter 6. We ascribe this displacement as being due to the diffusion of the physisorbed 1,2-dichloroethane, before undergoing electron-induced dissociation. This diffusion motion also explains the decreased number of reaction product features from the number of physisorbed 1,2-dichloroethane in this
sampled area before the +3.0 V scan. It appears that three of the seven physisorbed 1,2-
dichloroethane in Fig. 34(a) had diffused out of the sampled frame before the +3.0 V scan
occurred; the other four molecules, although they had also diffused, stayed in the sample area
and were subsequently dissociated upon the +3.0 V scan. This interpretation is based on the
observation of non-dissociative molecular diffusion of 1,2-dichloroethane, as shown in Fig.
33. We do not have sufficient measurements to attribute the observed diffusion of physisorbed
1,2-dichloroethane as induced by heat, or by an STM-tip effect via electric field or electronic
excitation.

![Figure 34. Electron-induced reaction of 1,2-dichloroethane on Si(100)-c(4×2) at 110 K by +3.0 V scan. (a) is the STM
image of the sampled area where seven physisorbed 1,2-dichloroethane were circled. The same surface area was
imaged once again following a +3.0 V scan, as shown in (b), generating four asymmetric features that were assigned
as reaction products. Both images are ~88×66 Å² in size, taken at $V_s=+1.2$ V, $I_t=0.05$ nA.](image)

At 110 K, the thermal dissociation reaction of 1,2-dichloroethane was slow, one area of the
surface of ~200 physisorbed molecules was imaged consecutively for four hours, without any
reactions being observed. Assuming a prefactor of $10^{13}$ Hz in the Arrhenius formula, we are able
to extract a lower limit for the energy barrier to thermal dissociation of physisorbed
1,2-dichloroethane: $E_a > 0.4$ eV.

We also performed a preliminary study of 1,2-dibromoethane on Si(100)-c(4×2) at 110 K. Fig.
35 is an STM image after the exposure of 0.03 L of 1,2-dibromoethane onto Si(100)-c(4×2),
where both symmetric bright feature and asymmetric features were found at inter-row sites. In
analogy with 1,2-dichloroethane, we assign the symmetric bright feature as physisorbed
1,2-dibromoethane and the asymmetric feature as the reaction products (chemisorbed bromine
atom and chemisorbed bromoethyl group). Because Fig. 35 is the first image of the sample surface area, obtained with a low imaging voltage of +1.5 V, it is likely that the formation of the chemisorbed bromine atom and chemisorbed bromoethyl group were due to thermal reaction, rather than electron-induced reaction, although this remains to be checked. Assuming thermal reaction, and a prefactor of $10^{13}$ Hz in the Arrhenius formula, we are able to estimate the range for the thermal barrier for the dissociation of physisorbed 1,2-dibromoroethane as $E_a = 0.3 - 0.4$ eV.

Figure 35. An STM image (~99×160 Å$^2$ in size, $V_s=+1.5$ V, $I_t=0.2$ nA) of physisorbed 1,2-dibromoethane and products caused by thermal reaction at 110 K.

The emergence of asymmetric features at inter-row site after the dissociation of 1,2-dihaloethane suggests that only a single carbon-halogen bond was cleaved. This differs interestingly from the
early study of this laboratory at 300 K\textsuperscript{97}, where dihalogentation prevailed. We speculate that the variation in surface reconstruction, c(4×2) at 110 K and (2×1) at 300 K, causes different dissociation dynamics of 1,2-dihaloethanes on a Si(100) surface. In this aspect, a careful examination of this system is needed in the temperature range of 100-300 K.

We do not yet have sufficient evidence upon which to assign the imaged reaction products; we could assign the bright fragment as chemisorbed haloethyl group and the dark fragment as atomic halogen, or vice versa.

### A.3 Conclusions

We performed a preliminary study of 1,2-dichloroethane and 1,2-dibromoethane on Si(100)-c(4×2) at 110 K. Both molecules were found to physisorb exclusively at the inter-row site of Si(100)-c(4×2), between the two topographically “down” Si atoms. The products of subsequent dissociations (electron-induced reaction for 1,2-dichloroethane, and thermal reaction for 1,2-dibromoethane) suggest that only a single carbon-halogen bond was cleaved (single-halogenation), giving a halogen atom and a haloethyl group, both chemisorbed at the inter-row site of Si(100)-c(4×2). The presented results differ interestingly from the earlier 300 K study of this molecule in which dihalogentation prevailed. This variation might be caused by the different surface reconstruction presented at 100 K and 300 K. To reconcile these studies, a careful examination of this system is needed in the temperature range of 110-300 K.
References

1 Levine, R. D. Molecular Reaction Dynamics; Cambridge University Press, 2005.


84 Polanyi, J. C.; Yang, J. (S. Y.) unpublished work


96 McNab, I. R.; Polanyi, J. C. Frontiers of Nanoscience 2011, 2, 79.