A Scanning Tunneling Microscopy Study on Atomic Carbon and Nitrogen on Pt(111)

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THESIS
Submitted as partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate College of the University of Illinois at Chicago, 2014

Chicago, Illinois

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Acknowledgements

I am grateful to Michael Trenary, who advised me over the past five years towards my Ph.D. thesis. The support and advice given by him encouraged me to start each project with optimistic prospects, and to hold on when things are getting tough.

Special thanks go to Yousoo Kim for collaborating on the project of “formation and hydrogenation of nitrogen on Pt(111)”. His supports and help during my stay in the Surface and Interface Science Laboratory (SISL) in RIKEN was essential for me to carry out the proposed research plan smoothly.

I would like to thank Alexander Uhl for passing on the knowledge and skills of STM and UHV system to me during my first year in the laboratory. Thank Yuan Ren for his help in numerous ways when I needed a hand. Thank Hyowon Kim, Hyun Jin Yang, and Junepo Oh in SISL for their help and discussion on both experimental and scientific aspects.

Also thanks to all other member at the Trenary group in UIC, and members at Surface and Interface Science Laboratory in RIEKN, who shared the good and rough time with me as a group.

I am also very grateful to Daniel Killelea, Robert Gordon, and Preston Snee, who carefully read the manuscript.

Financial support through the National Science Foundation and RIKEN is acknowledged.
To my parents,

who put up with many years of being apart from their only child in supporting her to pursue the childhood dream, the so called “scientist”.

To Gu Wang,

who shared every moment with me through the good and the tough time. He is the first reader of every manuscript I wrote.
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<th>Description</th>
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<tbody>
<tr>
<td>AS</td>
<td>Action Spectroscopy</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of States</td>
</tr>
<tr>
<td>EBL</td>
<td>Electron Beam Lithography</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>HREELS</td>
<td>High Resolution Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>IETS</td>
<td>Inelastic Tunneling Spectroscopy</td>
</tr>
<tr>
<td>LEED</td>
<td>Low Energy Electron Diffraction</td>
</tr>
<tr>
<td>LDOS</td>
<td>Local Density of States</td>
</tr>
<tr>
<td>LT</td>
<td>Low Temperature</td>
</tr>
<tr>
<td>PPM</td>
<td>Push-Pull Motion drive</td>
</tr>
<tr>
<td>RAIRS</td>
<td>Reflection Adsorption Infra-Red Spectroscopy</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TM</td>
<td>Transition Metal</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature Programed Desorption</td>
</tr>
<tr>
<td>TPG</td>
<td>Temperature Programed Growth</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra High Vacuum</td>
</tr>
<tr>
<td>VT</td>
<td>Variable Temperature</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
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Chapter 1 reviews the background and the literature in the field of my research and gives the outline of this dissertation. Portions of this chapter were previously published in (Surface Science, 606/21-22, pp 1643-1648. Copyright (2012) Elsevier; J. Phys. Chem. Lett., 2013, 4 (17), pp 2900–2905. Copyright (2013) American Chemical Society; J. Chem. Phys. 140, 114707. Copyright (2014) AIP Publishing LLC.) for which the contribution of authors is detailed below. Chapter 2 describes the instruments and experimental methods used. Chapter 3 includes some of my unpublished results in Section 3.2 and a published manuscript (Surface Science, 606/21-22, pp 1643-1648. Copyright (2012) Elsevier) for which I was the first author. Dr. Homa Khosravian and Dr. Alexander Uhl assisted me in the experiments. Dr. Randall J. Meyer and my advisor Dr. Michael Trenary contributed to the writing of the manuscript. Chapter 4 represents a published manuscript (J. Phys. Chem. Lett., 2013, 4 (17), pp 2900–2905. Copyright (2013) American Chemical Society) for which I was the first author. Dr. Hyowon Kim assisted me in the experiments. Dr. Yousoo Kim and Dr. Michael Trenary contributed to the writing of the manuscript. Chapter 5 includes a published manuscript in Section 5.2 (J. Chem. Phys. 140, 114707. Copyright (2014) AIP Publishing LLC.) for which I was the first author. Dr. Hyun Jin Yang assisted me in the experiments. Dr. Yousoo Kim and Dr. Michael Trenary contributed to the writing of the manuscript. Section 5.3 represents some of my unpublished results of the hydrogen and NH on N covered Pt(111). Chapter 6 is an unpublished work on the tip manipulation of single atoms and molecules. I expect that this work will be submitted for publication soon.
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Chapter 1: Introduction

Section 1.1 outlines the background of the research, and the main technique used is described in Section 1.2. Section 1.3 reviews the method for nanocluster fabrication, and the advantage of using graphene as a template is discussed. Section 1.4 reviews aspects of manipulating single molecules and atoms. Finally, Section 1.5 includes an outline of the remaining chapters in this thesis.


1.1 Background

Understanding the structure of materials at the atomic scale has been the goal of fundamental research for decades. The development of ultra-high vacuum (UHV) techniques makes it possible to study the elementary steps of a reaction on surfaces with desired adsorbates, which facilitates understanding at a fundamental level. In heterogeneous catalysis, the structure and reactivity of elemental carbon and nitrogen on transition metal surfaces are important to a variety of catalytic processes. Compared to the techniques that obtain the information of surface species by averaging over the surface monolayer, such as reflection adsorption infrared spectroscopy (RAIRS), temperature programmed desorption (TPD), low-energy electron diffraction (LEED), and X-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM) provides us with a direct probe of the atomic structure of the surface layer. Knowledge of adsorbates structure – including adsorption site,
two-dimensional periodicity, and the nature of the defects in the overlayer structure –
is essential for a detailed understanding of surface reaction mechanism. Such
information on surface morphology also supports and facilitates theoretical
calculations. Previous examples of studies of atomic adsorbate structure are those of
oxygen (O) and hydrogen (H) on Pt(111) surfaces (1-5). Because an STM image is a
view of the electronic structure rather than the actual topography of a surface,
interpreting the images can be problematic. However, for small molecules and atoms
on a flat surface, developing an interpretation is feasible by combining experimental
results and theoretical calculations. For example, the surface structures and
appearances of O/Ru(0001) (6-7), O/Pt(111) (1, 8), and O/Pd(111) (9-10) have been
studied by STM and interpreted via theoretical calculations. O atoms appear as
depressions and form (2 × 2) islands on all three surfaces. The fact that O appears as
a depression instead of a protrusion was attributed to contributions from a perturbed
surface electronic state (11). Theoretical calculations of STM images have been
carried out by Sautet (11) who discussed the differences and trends in STM images
of several atomic adsorbates ranging from electronegative atoms, like O and N, to
electropositive metal atoms, such as K and Na. In this thesis, I provide a microscopic
picture on the structure of atomic carbon and nitrogen on Pt(111).

1.1.1 Graphene on Pt(111)

In early studies of the catalytic properties of transitional metals (TM), the
interaction of carbon with TM surfaces was of interest because carbon is one of the
major poisons of the catalysts (12). Carbonaceous species are usually formed from
dehydrogenation of hydrocarbons (13-14), which are common reactants in TM-
catalyzed reactions. Formation of carbonaceous species usually reduces the catalyst
activity by blocking the active sites and related effects. However, experimental results
also indicate the formation of a graphitic overlayer, known as monolayer graphite or graphene (15-21). In STM studies, the superlattices formed by graphene on TM surface are manifested as moiré patterns in the images (22-23). Such superlattices then have been proved to be perfect templates for nanocluster formation (24-26), due to the uniform periodically arranged nucleation sites. Moreover, the thermal and chemical stability of graphene in principle can largely reduce the substrate effect in model catalysts. Thus graphene/transition metal (Gr/TM) systems are of great interest in the preparation of metal nanoclusters, as well as in catalytic reaction studies. We focus on platinum, which is widely used in industrial catalysis, such as in water-gas shift and methane reforming. Previous studies have shown that a graphene layer weakly interacts with the Pt substrate (27), resulting in a small corrugation in the graphene superlattice, in contrast to other transition metals, such as Ru (28-29). Whether this weak corrugation is sufficient to serve as a template for nanocluster formation is of interest to us. Chapter 3 presents the results regarding this topic.

1.1.2 Atomic nitrogen on Pt(111)

The synthesis of nitric acid (30) and the reduction of NOx by automotive catalytic converters (31) are examples of important industrial catalytic processes that involve surface nitrogen as a reaction intermediate. In contrast to the extensive studies of O and H, studies of atomic nitrogen (N) on Pt(111) are scarce, presumably because of the difficulties in producing a clean and well-ordered N layer. Dissociative chemisorption of N2 does not occur on Pt(111). Dissociation of ammonia on Pt(111) also has a high reaction barrier with less than 3% of the ammonia proceeding to dissociation (32). Electron-induced dissociation of ammonia is another approach but produces a mixture of NH, N, and H on the surface rather than a pure N layer (33). A well-ordered (2 × 2)-N overlayer on Pt(111) has been reported by Amorelli et al.
where they utilized ammonia oxydehydrogenation by atomic oxygen (3O(ad) + 2NH₃(ad) → 2N(ad) + 3H₂O(g)) as a low energy pathway to form N (34). Later studies by Herceg et al. (35) and Mudiyanselage et al. (36) followed a similar method that involved annealing a Pt(111) surface to 400 K on which ammonia was coadsorbed with molecular oxygen at 85 K.

Regarding the ammonia oxydehydrogenation, a previous RAIRS study of ammonia adsorbed on an O₂ overlayer on Pt(111) indicated the possibility of forming an NH₃–O₂ complex (35), which had also been suggested to form on Ag(111) (37), Cu(111) (38), and Zn(0001) (39). The complex is characterized by a strongly blue-shifted O–O stretch vibration indicating significant perturbation of the O–O bond. However, determination of the local geometry of such an NH₃–O₂ complex was not achieved in the previous studies.

Previous information on the surface morphology of the N layer was limited to LEED results where two superstructures, (2 × 2) and (√3 × √3)R30°, were observed (35). Although there is a lack of experimental data for atomic N on Pt(111), in the calculated topographic profiles, N atoms appear as depressions which are not as deep as those for O atoms. Atomic N on Ru(0001) has been studied by LEED (40), high resolution electron energy loss spectroscopy (HREELS) (41), and STM (42-43), where the N atoms were found to adsorb at hcp-hollow sites with a Ru–N stretch frequency of 581 cm⁻¹, in agreement with a later DFT calculation (44). Atomic N on Ru(0001) appears as a depression in STM images reported by Zambelli et al. (43) with a tunneling condition of −0.6 V and 1 nA.

With LT-STM, we were able to probe the local structure of surface layers. Chapter 4 presents the surface morphology and local configuration of a molecular O₂ network and a mixed NH₃–O₂ layer. Chapter 5 discusses the surface morphology
of the atomic N layer on Pt(111).

1.2 Scanning Tunneling Microscopy (STM)

Since the first scanning tunneling microscope was developed by Binnig and Rohrer in the early 1980s (45-46), it has been demonstrated to be a powerful tool in understanding the structure and properties of materials at the atomic scale. The atomic structure of materials, the electronic properties of surface species, the interaction between adsorbates and substrates, and the mechanism of reactions of atoms and molecules on surfaces have been investigated with STM and related techniques. When experiments are conducted at cryogenic temperatures, individual atoms and molecules can be manipulated using the STM as the tip can be precisely positioned over a specific atom or molecule on the surface. Also at cryogenic temperatures, the reduced thermal broadening provides sufficient resolution for vibrational spectroscopy, which makes it possible to conduct tunneling spectroscopy of a single molecule. Tunneling spectroscopy not only complements other vibrational spectroscopies, but also solves the problem of identifying adsorbed species, which is absent in the topographic images alone.

In this thesis we are not attempting to develop a theoretical approach to the tunneling microscopy or testifying as to the accuracy of proposed models, rather, we use STM as a technique to investigate the systems that we are interested in. Therefore, we will limit our description of the general operation and give a brief introduction of tunneling theory without going into details from a theoretical point of view.

1.2.1 Basic principle

In STM, an atomically sharp metal tip (typically chemically etched tungsten) is brought into close proximity to the sample (conductive substrate). By applying a
small voltage \((V)\) between them, electrons tunnel between the sample and the tip or vice versa, depending on the polarity of the bias. The exponential decay of the tip and sample wavefunctions into the vacuum gap achieves a sufficient overlap when their distance is about 10 Å apart; at this point a tunneling current \((I)\) can be measured.

The tip is raster-scanned across the surface by using a piezo-electric tube (see Section 2.1.3). The variation in the tunneling current with distance \((z)\) between the sample and the tip reflects the corrugation of the surface. The current decreases by approx. an order of magnitude with an increase of the gap distance by 1 Å (see Section 1.2.2). The whole STM operation is usually computer-controlled and the scanning parameters like \(V_t\), \(I_t\), and the scan speed are set via an programmed interface, as shown in Figure 1.1.

There are basically two modes of operating the STM, specifically, at constant-current or at constant-height. In the constant-current mode, the current \(I\) is compared to a preset current by a feedback circuit. It provides a correction voltage to the scanner tube, which adjusts the z position of the tip to keep \(I\) constant. The correction feedback signal is recorded together with the x-y position of the tip while raster scanning the surface; as a result, an STM image is obtained. In the constant-height mode, the z-position of the tip is kept constant and the tunneling current is recorded as it varies while raster scanning the sample surface. Generally, the constant-current mode yields better resolution while the constant-height mode allows faster scanning.
Figure 1.1: Schematic representation of the main components of a scanning tunneling microscope. The tip is mounted on a piezotube, which deformed by applied voltages and translates into lateral and vertical movements of the tip. The positions of the tip is adjusted according to the tunneling current via an electronic feedback loop, and a two-dimensional current contour is recorded (constant-current mode).

1.2.2 Theory of tunneling

As the tip is brought to the sample surface within a 1 to 10 Å range, the tip and the sample can be treated as two metal electrodes separated by a vacuum gap. An elementary model of this junction is shown in Figure 1.2.
In quantum mechanics, an electron with energy $E$ moving in a one-dimensional rectangular potential barrier $U(z)$ satisfies the Schrödinger’s equation,

$$-\frac{\hbar^2}{2m} \frac{d^2}{dz^2} \phi(z) + U(z)\phi(z) = E\phi(z), \tag{1.1}$$

where $\phi(z)$ is the electron wave function. Solutions of the Schrödinger’s equation in the classically allowed region ($E > U$) is,

$$\phi(z) = \phi(0)e^{\pm ikz}. \tag{1.2}$$

where $k = \frac{\sqrt{2m(E-U)}}{\hbar}$ is the wave vector.

In the classically forbidden region ($E < U$), which is the vacuum gap region in our case, the solution is,

$$\phi(z) = \phi(0)e^{-kz}, \tag{1.3}$$
where \( \kappa = \frac{\sqrt{2m(U - E)}}{h} \) is the decay constant. It shows that the electron has a nonzero probability to penetrate a barrier. The probability density of observing an electron in the +z direction is proportional to \( |\phi(0)|^2 e^{-2\kappa z} \) and has a nonzero value in the barrier region.

Now we consider the tunneling junction presented in Figure 1.2. By applying a negative bias voltage \( V \) to the sample, the energy levels of the sample are shifted upwards. A net tunneling current occurs when electrons are tunneling from the sample into the unoccupied states of the tip. The sign of the tunneling current is reversed if a positive bias voltage is applied, wherein the electrons tunnel from the tip into the unoccupied states of the sample. Given that the bias is much smaller than the work function (\( eV \ll \Phi \)), the shifted energy levels \( E_n \) lying between \( E_F - eV \) and \( E_F \) are very close to \( E_F \), and thus we can take \( E_n \approx -\Phi \). The probability \( w \) of an electron in the sample state \( \phi_n \) to be present at the tip surface with a distance of \( a \), is

\[
    w \propto |\phi_n(0)|^2 e^{-2\kappa a},
\]

(1.4)

where \( \phi_n(0) \) is the nth sample state at the surface \( (z = 0) \), and \( \kappa = \frac{\sqrt{2m\Phi}}{h} \), which is the decay constant of a sample state near the Fermi level in the vacuum (barrier) region. The tunneling current is thus proportional to the number of states on the sample surface within the energy interval \( eV \). The sum of all the sample states in the interval \( eV \) is written as

\[
    I \propto \sum_{\epsilon_n = E_F - eV}^{E_F} |\phi_n(0)|^2 e^{-2\kappa a},
\]

(1.5)
If the density of states does not vary significantly within the interval (i.e. $V$ is small enough), the tunneling current in Eq. 1.5 can be expressed using the local density of states (LDOS) at the Fermi level, $\rho_S(z, \varepsilon_F)$, which is defined as

$$\rho_S(z, \varepsilon_F) = \frac{1}{eV} \sum_{\varepsilon_n=\varepsilon_F-eV}^{\varepsilon_F} \left| \phi_n(z) \right|^2, \quad (1.6)$$

The LDOS is the number of electrons per unit volume per unit energy, at a given point in space and at a given energy. Then we can write the tunneling current in terms of the LDOS of the sample at the tip surface $z = a$,

$$I \propto V \rho_S(a, \varepsilon_F) = V \rho_S(0, \varepsilon_F) e^{-2\kappa a}, \quad (1.7)$$

Because of the exponential decay, the tunneling current is very sensitive to the variations in the tip-sample distance. Therefore, by rastering the tip over the sample surface with constant current, a contour map of the surface topography can be obtained.

The above simplified model only takes into account the LDOS of the sample at the tip surface. A more appropriate model that describes the complete tip-sample system was developed by Tersoff and Hamann (47-48). They applied Bardeen’s approach (49), which was originally used for describing a planar metal-oxide-metal junction, to the metal-vacuum-tip system encountered in STM. Considering the wavefunctions of both the tip $\phi_t$ and the sample $\phi_s$, a matrix element $M$ describing the overlap of the two wavefunctions was introduced,

$$M = \frac{\hbar^2}{2m} \int \left( \phi_t^* \nabla \phi_t - \phi_t^* \nabla \phi_t \right) dS, \quad (1.8)$$

From Fermi’s golden rule, the probability $w$ of an electron to tunnel between states $\phi_t$ and $\phi_s$ is given by,
The tunneling current is then given by,

\[
I = \frac{2\pi}{\hbar} \int_{\varepsilon_f}^{\varepsilon_f+eV} \rho_s(\varepsilon) \rho_d(\varepsilon)eV |M|^2 d\varepsilon ,
\]

where \( f(\varepsilon) = [1+\exp(\varepsilon-\varepsilon_F)/kT]^{-1} \) is the Fermi-Dirac distribution. For low temperatures and small applied bias voltage, where the Fermi-Dirac distribution can be approximated as a step function, Eq. 1.9 reduces to the simpler form,

\[
I = \frac{2\pi}{\hbar} \int_{\varepsilon_f}^{\varepsilon_f+eV} \rho_s(\varepsilon) \rho_d(\varepsilon)eV |M|^2 d\varepsilon ,
\]

The difficulty still lies in evaluating the matrix \( M \) in Eq. 1.11. Tersoff and Hamann’s approach to solve this issue is to assume an s-type wavefunction at the tip, assuming the tip has a spherical symmetry with a radius of curvature \( R \). With the so-called s-wave approximation, the tunneling matrix element can be evaluated and yields,

\[
M \propto \kappa Re^{sR}\varphi_s(r_0) ,
\]

where \( \kappa = \sqrt{2m\Phi}/\hbar \) is the decay length for the wavefunctions in the vacuum gap with an effective local barrier height \( \Phi \), and \( \varphi_s(r_0) \) is the sample wave function at the center of tip curvature \( r_0 \). The tunneling current is then given by,

\[
I \propto V \frac{R^2}{\kappa^4} e^{2sR} \rho_s(\varepsilon_F) \rho_d(\varepsilon_F, r_0) ,
\]

The tunneling current is proportional to the LDOS of the sample at the Fermi level at the center of curvature of the tip. Since \( \rho_s(\varepsilon_F, r_0) = \sum |\varphi_s(r_0)|^2 \delta(\varepsilon - \varepsilon_F) \) and \( |\varphi_s(r_0)|^2 \propto \exp(-2\kappa(R+a)) \), the tunneling current also decays exponentially with the
tip-sample distance. The exponential dependence of tunneling current on the tip-sample distance can be simplified as

\[ I \propto e^{-2\kappa x_{\text{in}}}, \quad \kappa = \frac{\sqrt{2m\Phi}}{h} \]  \hfill (1.14)

Using eV as the unit of the work function \( \Phi \) and Å\(^{-1} \) as the unit of the decay constant, we obtain \( \kappa = 0.51\sqrt{\Phi(eV)\text{Å}^{-1}} \). On metal surfaces, typical values of work function are 4 to 5 eV \((50)\). Thus, for every Angström increase in the tip-sample distance (tip is moved out from the sample), the tunneling current will decrease by about one order of magnitude.

1.2.3 General operation

The general operation of an STM involves raster scanning across a flat surface, using an atomically sharp tip. When a bias voltage is applied between the tip and the sample, the net flow of the tunneling current is nonzero and can be detected and measured. The tunneling current is measured as the tip moves across the desired area of the surface. As a stable tunneling junction is required, a feedback system is used to control the tip-sample spacing as the variation in the sample topography and electronic structure will affect the tunneling current. The feedback system is used to adjust the gap between the tip and sample until the desired tunneling current is achieved. Once the tunneling current is changed due to the variation of the topography or electronic structure, the feedback system will react and bring the current back to the desired value, which is also called the “set point”. There are two modes of operation: constant current and constant height. In the constant current mode, the tunneling current is maintained constant at the set point by the feedback loop and the tip is moved in or out from the surface. The movement of tip is realized by applying an adjustment voltage to the Z-scan piezo; the value is determined by the difference
between the set point and the measured current. An image produced under the constant current mode reflects the variations of the LDOS of the surface. In constant height mode, the gap between the tip and the sample is kept constant and the variation of tunneling current is recorded as the tip rasters over the surface. Constant current mode is generally used in practice as it reduces the risk of tip crashing into the surface when the surface is not atomically flat. The tip might run into large protrusions (adsorbates, atomic steps, etc.) if it is fixed above the surface.

Figure 1.3: Schematic drawing of two operation modes. (a) Constant current. (b) Constant height.

1.3 Manipulation of atoms and molecules on the surface

Invention of STM makes it possible for imaging atomic structure of material surfaces. As a local probe to individual atoms and molecules on surfaces, the STM tip is capable of doing more than just imaging. Beyond topography, manipulation of atoms and molecules with STM has been demonstrated with a variety of systems. There are plentiful examples of tip manipulated lateral transitions (atom/molecule
moves across the surface) and vertical transitions (atom/molecule is picked up by the tip), which have been discussed in a review article on STM manipulation (51). The first example of writing letters on the surface with atoms was reported by Eigler and Schweizer, where they used an STM tip to move Xe atoms on a Ni(110) surface forming an “IBM” logo (52). Besides “writing” with the STM tip, motions of atoms/molecules induced by tunneling electrons provides a new approach to detect the vibrational energies at single-molecule level, which will be discussed in the following topic.

**Action spectroscopy (AS)**

Tunneling electrons from the STM tip can excite a specific vibrational mode of single atoms and molecules adsorbed on surfaces as observed in $d^2I/dV^2$ spectra at energies corresponding to the vibrational modes. This method, known as inelastic electron tunneling spectroscopy (IETS), has been applied to probe the vibrational state of adsorbates on surfaces in a wide range of systems. Because of the ability to probe the vibrational properties of individual adsorbates, STM-IETS can be used to identify molecules and atoms on the surfaces, and to investigate the effects of local environments on the vibrational states. In STM-IETS studies, the measured $d^2I/dV^2$ signal reflects the change of conductance $dI/dV$, which has both elastic and inelastic contributions. Ideally, one would expect that the opening of the inelastic tunneling channel increases the tunneling conductance. Because of this increase, a peak can be observed in the $d^2I/dV^2$ signal at the corresponding vibrational energy. The real picture is more complicated. Experimentally observed $d^2I/dV^2$ spectra show not only peaks, but also dips. Theoretical calculations visited this issue and found that the elastic conductance decreases when an adsorbate is vibrationally excited. The decrease is due to the change of the LDOS by electron-vibration coupling. Ueba et al.
attribute this decrease to the broadening of the LDOS near the Fermi level associated with energy dissipation to the vibrational excitation. The overall change of the tunneling current is thus a competition between the elastic (negative) and inelastic (positive) contributions (54-55). The competition sometimes makes the IETS measurement problematic when the elastic and inelastic contributions to the tunneling current cancel out. It also explains the unclear selection rule of IETS in experimental observations. In many cases, excitation of the vibrational modes will induce a motion of the atom or molecule, which is called vibrationally mediated motion. Measuring the response of the motion against an applied bias voltage generates the “action spectra”, which reflects the active vibrational modes that are responsible for inducing a given motion. The so called “Action Spectroscopy” was introduced by Sainoo et al. in studying the configuration change of cis-2-butene on Pd(110) (56). It opens a new window for revealing the microscopic elementary processes of single molecule reactions. The motion probed by AS is induced solely by the excitation of particular vibrational modes through inelastic tunneling, which means AS measures only the contribution from inelastic tunneling. Using a theoretical approach, Ueba and Persson have shown that \( \frac{d^2I_{el}}{dV^2} \) is directly proportional to the vibrational density of states \( \rho(\Omega) \) (57). Because a measured action spectrum directly probes the \( \rho(\Omega) \), AS has the advantage and possibility to detect vibrational modes that may not be observed in IETS. In action spectroscopy, the response of a motion to an applied bias voltage is expressed as the motion yield \( Y \), which characterizes the probability per electron to trigger the motion. Thus the thresholds obtained from a \( Y(V) \) curve reveals the energy required to activate the motion, which is also the energy of the corresponding vibrational mode.
1.4 Fabrication of nanoclusters

Metallic nanoclusters have attracted intense interest because of their unique properties as manifested in semiconductor quantum dots (58), plasmon resonances in spherical metal particles (59), and size-dependent reactivity and selectivity in heterogeneous catalysis (60-61). Studies of mono-dispersed metal nanoclusters on supports promise to bridge the “materials gap” between model catalyst systems and industrial heterogeneous catalysts (62). Numerous methods have been developed to prepare dispersed metal nanoclusters, including traditional approaches such as co-precipitation (63), sol-gel (64), and incipient wetness impregnation (65-66) from salts or organometallic compounds as precursors. Newer approaches include electron beam lithography (EBL) (67), colloidal synthesis with metal nanoclusters encapsulated in polymers (62) or dendrimers (68), and evaporation of metal clusters on supported oxide thin films (69-70). The EBL method can prepare uniform and reproducible nanoclusters of arbitrary size and shape. However, the main disadvantage of EBL is the low throughput and high cost. In colloidal synthesis, core-shell nanoparticles are formed with cores consisting of metal atoms and shells with capping agents that are used to stabilize the particles against aggregation. Although colloidal synthesis has the advantages of size and shape control, the organic shells that surround the metal nanoclusters hinder their catalytic applications by blocking the active sites. For the bare metal atoms to be exposed at the surface, the organic shells must be removed. In UHV studies of model catalyst systems, evaporation of metal films onto oxide supports is generally used for nanocluster fabrication. Oxide single crystals (71) as well as thin oxide films (69) grown on metal single crystal surfaces have been widely studied. The improved electrical and thermal conductivity of the thin films make it easier to employ surface science tools such as LEED and STM in these studies. For
example, various metals deposited onto thin alumina films grown on NiAl(110) (69) or on Ni$_3$Al(111) (72) have been studied, where in the former, a correlation of cluster size with interaction at the metal-oxide interface was found. With an increase in interaction, the clusters will be smaller and flatter. Periodic matching of the lattice of the film with the lattice of the substrate produces large scale periodicities that can serve as nucleation sites for the metal nanoclusters. The oxide thin film can thus serve as a “template” for nanocluster growth in a way that the surface of a bulk oxide cannot. However, oxide-supported nanoclusters are observed to diffuse through oxide films into the metal substrate at elevated temperatures (73), and their catalytic properties can be affected by charge transfer from the oxide substrate (69, 74). At elevated temperatures, coalescence of the clusters and diffusion to step edges or domain boundaries can also occur. In the study of metal deposition onto alumina on Ni$_3$Al(111), covering the oxide surface with Pd seeds prior to deposition of the target metal is required to obtain a well-ordered array of metal clusters (70, 75).

An alternative way to produce two-dimensional arrays of monodispersed metal nanoparticles is to use a graphene monolayer grown on a metal surface as a template. This is suitable for the study of model catalysts under UHV conditions. Although metal nanoclusters on crystalline oxide surfaces provide good models for real catalysts consisting of metals on high-area oxide supports, metals on graphene monolayers serve as a model for the carbon-supported Pt catalysts used in fuel cells (76). N’Diaye et al. first demonstrated that the superlattice observed as a moiré pattern in STM images of graphene on Ir(111) can provide a novel template for formation of a two-dimensional Ir-cluster array (26). Compared to the low diffusion barrier of metal atoms on graphite (77), higher barriers are associated with the increased corrugation in the periodic potential of the graphene/metal superlattice. The
metal clusters that nucleate on the superlattice sites are thus less prone to agglomeration. Unlike oxide surfaces, the use of graphene as a template avoids the problem of nanocluster oxidation, making it easier to directly characterize the catalytic properties of the metal nanocluster. In more recent investigations, it was found that there is considerable variation in the periodicity of the moiré patterns of graphene on different transition metals. Graphene interacts strongly with Ru(0001), Rh(111) (78), and Ni(111) (79); but weakly with Cu(111), Pt(111), Au(111) (27), and Ir(111) (26). Thus, graphene on transition metals provides various templates of periodically arranged nucleation sites for nanocluster formation.

Many of the possible combinations of metal-graphene-metal have been investigated in recent years, including Ir (26), Rh (80), Pt, W, Re, Fe, and Au (24) on graphene on Ir(111), Ni (81) on Rh(111), and Pt (25, 82-84), Ru (85), Rh, Pd, Co, and Au (83) on Ru(0001). In each case the metal nanoclusters are preferentially adsorbed at specific sites within the moiré domains.

1.5 Thesis Outline

Chapter 2 describes the instruments and some general methods used. Specific experimental procedures are described in the “Experimental” sections at the beginning of each chapter. In Chapter 3, the results concerning graphene formation on Pt(111) are presented, where the best method to grow graphene under UHV condition is detailed. The properties of graphene as a template for nanocluster fabrication are discussed in detail. Chapter 4 shows the mixed ammonia-oxygen overlayer formed on Pt(111) at low temperatures, which serves as the precursor for obtaining the N layer. The structure of a molecular oxygen network and an ammonia-oxygen complex are discussed in detail. Chapter 5 contains the results of atomic nitrogen on Pt(111). The surface morphology of the N layer, as well as the NH layer formed after
hydrogenation, are discussed. In Chapter 6, we show two examples of vibration-mediated reactions: NH dissociation and H hopping are investigated by action spectroscopy. The mechanism and elementary process associated with each reaction are discussed. Finally, Chapter 7 gives a summary of the results presented, and closes this thesis with a conclusion and outlook.
Chapter 2: Instruments and Methods

This chapter describes the instruments and methods used in this thesis. Section 2.1 describes the instruments used. Section 2.2 outlines the general method employed in each chapter. Section 2.3 lists the procedure for sample preparation. Section 2.4 discusses how the data was acquired and analyzed.

2.1 Instruments

2.1.1 The Omicron UHV VT-STM system

The Omicron UHV VT-STM system was used on graphene formation and nanocluster fabrication as discussed in Chapter 1. A picture and schematic view of the VT-STM system are shown in Figure 2.1.

Figure 2.1: Picture (a) and schematic view (b) of the VT-STM system.

This UHV system consists of a preparation chamber and an STM chamber. The preparation chamber is equipped with manipulator and heater, sputter gun, LEED, etc.
The STM chamber houses an Omicron VT-STM. As shown in Figure 2.2, the STM stage is suspended by four springs and is damped by an eddy current stage, as shown in Figure 2.2(b). The copper plates centered between the magnets provide the eddy current. For ease of sample transfer and tip exchange, the stage can be locked using a push-pull motion drive (PPM). For scanning the PPM is unlocked and the STM stage is suspended, which provides vibration isolation from other parts of the chamber. The chamber is pumped down by a turbomolecular pump, an ion getter pump, and a Ti-sublimation pump to achieve a base pressure of $4 \times 10^{-10}$ Torr.

**Figure 2.2:** The Omicron VT-STM. (a) Front view. (b) Back view showing the eddy current damping stage.

A cooling facility is available for reduced temperature scanning on the VT-STM. Although cooling the sample with the VT-STM will not be discussed in this thesis, the general concept of how it is achieved on this setup is easy to understand. A clamping block on top of the STM stage is connected to the cryostat by flexible copper braid. This block can be slid over the sample plate to make the thermal contact with the sample. The cryostat is fixed to the base flange of the STM stage and can be
either filled with cryogen, or a constant flow of cryogen with additional pumping. Because only the sample is thermally connected to the cryostat, and other parts on the STM stage stay at room temperature, the sample can only be cooled to around 90 K by liquid nitrogen, or 30 K by liquid helium. An LT-STM is used for the low temperature experiment, which will be described in section 2.1.2.

2.1.2 The Omicron UHV LT-STM system

The Omicron UHV LT-STM system used in this thesis is located in the Surface and Interface Science Laboratory (SISL) at RIKEN, Japan, and is designed specifically for low temperature experiments. When in the locked position the STM head is cooled by the cryostat, which is filled with liquid nitrogen in the outer dewar and liquid helium in the inner dewar. The entire apparatus is held by pneumatic isolators with constant nitrogen gas feed, which allows the system to be decoupled from the ground and thus reduces the vibrational noises. The decoupling is essential for measuring atomically resolved images. The picture and the schematic view of the LT-STM are shown in Figure 2.3.

![Figure 2.3: Picture (a) and schematic view (b) of the LT-STM system.](image-url)
As with other UHV systems, the vacuum is maintained by a turbomolecular pump, an ion getter pump, and a Ti-sublimation pump. The STM chamber and the preparation chamber are separated by a gate valve and each chamber has its own pumping system, with which the base pressure is kept at $1 \times 10^{-10}$ Torr (Prep. chamber) and $3 \times 10^{-11}$ Torr (STM chamber).

**Figure 2.4:** The Omicron LT-STM. (a) The STM with the cryostat. (b) The stage with the shield. (c) LT-STM stage showing the eddy current damping.
Figure 2.4 shows images of the microscope. Because the temperature needs to be held at 4.7 K, a shield is mounted around the scanner head to reduce thermal exchange with other parts of the apparatus. The cryostat consists of an outer and an inner dewar for holding the cryogen. Different temperatures can be achieved depending on which cryogen is used. For most of the LT experiments, the sample and the scanner are cooled to 4.7 K with liquid helium (inner dewar) and liquid nitrogen (outer dewar). Figure 2.4(c) shows the LT-STM stage when the shield is removed, note that there is no scanner installed in this particular image. Copper plates used for eddy current damping follows the same design as in the VT-STM.

2.1.3 The scanner

The Omicron design of the STM scanner uses a single piezo tube, which was first reported by Binig and Smith in 1986 (86). While other geometries of the scanner, such as bar tripod, tube tripod, and stacked disks are also used (87), the single tube design has become popular due to its compact and simple structure. Figure 2.5 shows photographs of the scanner tube used in Omicron VT-STM. In addition to controlling the accurate movement of the tip during scanning, coarse motion of the scanner is generally required to bring the tip to the sample at a much larger length scale (typically in the cm range). The purpose of the coarse motion is for sample transfer when the scanner has to be retracted far enough away from the sample and tip approaching when the scanner has to be brought close enough to the sample within the range of the z-motion of the piezo tube. In the Omicron STM the coarse motion is controlled by an X/Y table and a Z-slider, which uses piezoelectric bars to control the movements.
Figure 2.5: Pictures of the scanner of the Omicron VT-STM. (a) Scanner at the stage with a loaded tip, which is the golden tripod on top of the white ceramic. (b) A back view of the scanner showing the piezo block for coarse motion along the z slider (the black bars).

When scanning, either the tip moves against the fixed sample, or the sample moves against the fixed tip (88). The former is more common and used in the Omicron VT-STM. The tip is loaded on a piezo-ceramic scanner, which changes its dimensions under an applied voltage. The schematic drawing of a hollow-tube scanner (89) is shown in Figure 2.6. The outside surface of the tube is separated into four longitudinal segments, namely (+/−) x and (+/−) y, on which electrodes are attached. An additional electrode is placed on the inner surface of the tube, which controls the vertical z motion. When a voltage is applied across the piezoelectrodes, stresses are developed which cause the electrodes to deform, resulting in motion in the desired directions. Different voltages to each pair of oppositely located outer electrodes induce tube bending, which provides the lateral motion for the tip. Different voltages applied to the outer and inner electrodes shrinks or extends the tube, which moves the tip vertically (88). A more detailed analysis of the piezo single tube scanner can be found in ref. (90).
In Instruments and Methods, Chapter 2, the vertical movement of the tip is adjusted according to the chosen feedback gain, while the lateral movement proceeds independently. The scanning from left to right is referred to as the “forward” scan, and the reverse as the “backward” scan. Conventionally, the fast and slow scanning directions are taken to be the x- and y-directions, respectively. By rotating the scanning direction, the fast-scanning direction can also be changed. Along the slow-scanning direction, the tip moves from one border to the other while performing the forward and backward scans alternately. Therefore, a square area of the sample is scanned by the tip and an image is produced.

2.2 Tip Preparation

The tips used in this thesis are electro-chemically etched tungsten (W) tips. A homebuilt etching device is used for making the tips as shown in Figure 2.7. The electro-chemical cell consists of a Pt thin foil with a hole in the middle (cathode), a tungsten wire with diameter of 0.15 mm (anode), and 10% KOH solution suspended in the hole (electrolyte). Etching occurs at the surface of the W wire interface with applied voltage of 4 V. W is oxidized to $\text{WO}_4^{2-}$ and dissolves at the interface. As a result, a sharp tip is formed as the W wire is etched away and falls apart. A beaker is
placed under the wire to hold the bottom half of the W wire when it drops. The fresh-
made tip is first dipped into HF for removal of contamination and then rinsed by de-
ionized water and acetone. Then the tip is loaded into the chamber to prevent any
contamination from the air. The tip is kept from touching any surface during the
whole process. Post-treatment of the tip is generally required to get images with high
resolution, which is achieved during scanning by numerous high voltage pulses and
soft crashes. A well-treated tip is stable and reliable for several months.

![Schematic drawing of the etching process.](image)

**Figure 2.7:** Schematic drawing of the etching process.

### 2.3 Sample preparation

#### 2.3.1 Cleaning the crystal

The Pt(111) crystal is cleaned by repeated cycles of sputtering and annealing,
followed by oxygen treatment to remove residual carbonaceous species on the
surface. Sputtering uses an argon-ion beam with energies of 1 to 3 keV. The crystal
surface is bombarded by the accelerated ion beam, which removes the
contaminations. Sputtering leaves the surface with damage and implanted argon atoms. To get an atomically clean and well-defined surface, annealing is necessary to heal the rough surface by rearranging surface atoms to achieve an equilibrium well-defined structure, as well as to desorb the implanted argon.

2.3.2 Gas exposure

The gas exposure is generally carried out in one of two ways: backfilling the chamber via the leak valve, or direct dosing to the surface, typically via a nozzle placed in front of the sample surface. In general backfilling the chamber is used for nonreactive gases (i.e. gases with low sticking coefficient), like noble gases and nitrogen. Reactive gases, like water or ammonia, stick to the walls of the chamber. Gradual desorption of the reactive gases from the walls after backfilling will increase the base pressure and cause problems for subsequent experiments. Exposure via a nozzle has much higher partial pressure at the surface than through backfilling, and thus the dosing time can be reduced and the chamber can be kept clean. We use backfilling for graphene growth in Chapter 3. When the surface is exposed to ammonia and oxygen gas, a gas doser is used as described in Chapter 4 and 5. Details of the gas exposure are provided in the “Experimental” section of each chapter.

2.3.3 Metal deposition

A triple electron beam evaporator (EFM 3T) with an integral flux monitor is used for metal deposition. A Pt rod with 1.5 mm diameter is used as the evaporant. For a deposition, a shutter at the end of the evaporator is kept closed until a stable flux is achieved, which allows for exact control of the evaporation time. Because electrons from the filament usually cause variations in the flux, the actual coverage is determined from STM images. A calibration is made for the same evaporant rod with
the same flux. The amount of deposition is then controlled by the evaporation time, which is easier and more reliable than controlling the flux.

2.4 Data acquisition and analysis

2.4.1 Topographic images

The topographic images were acquired with Omicron SCALA PRO 4.0 software and were processed via the WxSM program provided by Nanotec (91). Images presented in this thesis were acquired in the constant current mode. The STM tip was treated during scanning the clean surface by high voltage pulses and soft crashes.

2.4.2 Action spectra

Raw data of action spectra are acquired by recording the current ($I$) versus time ($t$) signal. To obtain an $I$–$t$ curve, the STM tip is placed over the targeted atom/molecule, and the feedback loop is turned off. Then the desired bias voltage is applied for a certain length of time. The current signal is monitored and recorded in real time. A jump of the current signal is taken as the time when the reaction occurs. When a reaction is observed, it is counted as one event. The number of electrons carried by the current is calculated by $(I \times t)/e$, where $t$ is the time between the beginning of the pulse and the time when the reaction occurs. The reaction yield per electron is then obtained as $1/($# of electrons$)$. By keeping the current at a constant value and varying the applied bias voltage, a series of trials are carried out. For trials under different bias voltages, the time when an event occurs varies as does the reaction yield. An action spectrum can thus be constructed by plotting the reaction yield versus the bias voltage. Figure 2.8 shows what an $I$–$t$ curve looks like in each trial. In practice, the SCALA software is used to program the macros, which control the actions taken by the microscope. A macro used for AS is shown in Appendix B.
Figure 2.8: An example of the $I-t$ curve measured.
Chapter 3: Graphene as a template for nanocluster fabrication

Chapter 3 details the results of graphene formation on Pt(111) and fabrication of Pt nanoclusters using the prepared graphene as a template. Section 3.1 outlines the experimental details for graphene growth and Pt deposition. Section 3.2 discusses the preparation method of growing graphene on Pt(111) under UHV. The best procedure was evaluated according to the comparison of different trails. Section 3.3 discusses the unique properties of graphene on Pt(111) as revealed by STM. Section 3.4 discusses the fabrication of Pt nanoclusters on graphene/Pt(111).

Portions (Section 3.3 and 3.4) of this chapter were previously published. (Reprinted from Surface Science, 606/21-22, Zhu Liang, Homa Khosravian, Alexander Uhl, Randall J. Meyer, Michael Trenary, Graphene domain boundaries on Pt(111) as nucleation sites for Pt nanocluster formation, 1643-1648, Copyright (2012), with permission from Elsevier.)

3.1Experimental

The Pt(111) surface was cleaned by repeated cycles of sputtering with argon gas (7.5 × 10⁻⁸ Torr) and annealing to 1250 K. An oxygen treatment (7.5 × 10⁻⁸ Torr O₂ at 700 K for 30 minutes) was carried out in the final cycle to remove residual carbon on the surface. The surface was verified to be clean and well ordered by LEED and STM. Graphene was prepared by first exposing to 3.4 L (7.5 × 10⁻⁸ Torr for 45 seconds) of ethylene at room temperature, followed by flash annealing to 1200 K for 45 seconds. Then the sample was kept at 1170 K and exposed to another 90 L (7.5 × 10⁻⁸ Torr for 20 minutes) of ethylene to ensure saturation coverage. After cooling back to room temperature, the sample was transferred to the STM stage for data acquisition. Platinum was deposited on the graphene layer via evaporation from a
pure platinum rod using an EFM 3T evaporator. The sample was held at room temperature during deposition.

### 3.2 Growth of graphene under UHV conditions

There are mainly two methods to grow graphene on metals: segregation of bulk-dissolved carbon to the surface and thermal decomposition of carbon-containing molecules. The later can be accomplished by two approaches, temperature programmed growth (TPG) and chemical vapor deposition (CVD), as has been used for graphene growth on Ru(0001) (29, 92), Ir(111) (93-94), and Pt(111) (16, 22). In the segregation method, a high annealing temperature is applied to cause the segregation of carbon to the surface. In the decomposition method, hydrocarbon species are mostly used. By means of the TPG method, the sample is first exposed to the carbon precursor at 300 K and is then subsequently annealed to the target temperature, usually above 900 K. In the CVD method, carbon precursor is directly dosed to a hot substrate. Small hydrocarbon molecules, like ethylene, acetylene, and methane, as well as large molecules, such as benzene, cyclohexane, and toluene, are used as precursor molecules.

![Ethylene decomposition on Pt(111)](image)

**Figure 3.1:** Schematic drawing of the formation of graphene from ethylene decomposition on Pt(111).
In our work presented here we used ethylene (H₂C=CH₂) and acetylene (HC≡CH) as carbon precursors, for which the dehydrogenation on the Pt(111) surface has been characterized from previous studies (95-97). As illustrated in Figure 3.1, ethylene first decomposes on the surface to form carbon clusters. Annealing the surface to elevated temperatures converts the carbon clusters into a graphene layer. Ethylene adsorbed on the Pt(111) surface is di-σ bonded and parallel to the surface below 240 K. It converts to ethylidyne (≡C-CH₃) at room temperature, which is stable up to 450 K. Ethylidyne (≡C-CH₃) on Pt(111) occupies the fcc 3-fold hollow site with the C-C bond perpendicular to the surface. It undergoes partial and complete dehydrogenation at temperatures above 450 and 800 K, respectively. Acetylene adsorbed on Pt(111) forms η³μ₃-vinylidene below 190 K. When heated to higher temperature, it converts to ethylidene and then ethylidyne. It is completely dehydrogenated above 750 K. The reaction scheme of dehydrogenation of ethylene and acetylene are shown in Figure 3.2.

![Reaction schemes of dehydrogenation of ethylene and acetylene.](image)

**Figure 3.2:** Reaction schemes of dehydrogenation of ethylene and acetylene.
A comparison of ethylene and acetylene as the precursor for graphene formation is made in section 3.2.1, where the best growth method of graphene on Pt(111) is discussed.

### 3.2.1 Temperature programmed growth

#### TPG method using ethylene as the precursor

An ethylene exposure of 4.6 L (1 L = 1.0 × 10^{-6} Torr) at 300 K and subsequent annealing at 820 K forms carbon islands on the Pt(111) surface. Figure 3.3(a) shows the STM image of the carbon islands, which were observed both along step edges and on terraces. After further annealing to 1070 K, small carbon islands disappear, forming larger islands attached to the lower step edges as shown in Figure 3.3(b). Note that the graphene-island-decorated step edges are very irregular, in contrast to the smooth, straight step edges on clean Pt surfaces.
With the TPG method, the graphene coverage on the Pt(111) surface is limited by the saturation coverage of ethylene at room temperature (0.21 ML (98)). To overcome this limitation, we carried out a modified TPG growth method. Specifically, instead of exposing the Pt(111) substrate to ethylene at room temperature, the initial exposure was at an elevated temperature (570-700 K) that is below the temperature of complete dehydrogenation (750-800 K). Figure 3.3(c) shows STM images taken after elevated TPG growth at 570 K and subsequent annealing to 700 K. It is obvious that the coverage of carbon species on the surface is greatly increased even though the dosing amount is lower compared to the room temperature adsorption TPG method. A new feature of large protrusions was also observed, which did not appear for room
temperature adsorption. Further annealing to 1070 K forms graphene flakes that extend across the step edge. The large protrusions, however, did not convert into a graphene layer and stayed as clusters as observed in Figure 3.2(d).

*Comparison between ethylene and acetylene with TPG method*

Ethylene and acetylene were both used as the precursor for graphene formation. As shown in Figure 3.4, both precursors form partially dehydrogenated clusters on the surface. Ethylene forms clusters that are evenly spread out on the whole surface. Compared to ethylene, acetylene shows a preference for adsorbing along step edges. Also the sizes of the formed clusters are bigger than those formed from ethylene. Experiments with higher dosing amounts show that ethylene is better suited than acetylene for graphene formation as smaller and more dispersed clusters are observed.

![Figure 3.4](image)

*Figure 3.4:* Comparison between ethylene and acetylene as the precursor. Images were acquired after exposing Pt(111) at 670 K to (a) 0.5 L ethylene. (b) 0.2 L acetylene. Both images, 200 nm × 200 nm, $V_s = 700$ mV and $I_t = 0.40$ nA, were acquired at 300 K.

### 3.2.2 Chemical vapor deposition growth using ethylene as the precursor

Based on the results presented above, it was found that TPG method has two limitations when using ethylene as the precursor. With the room temperature
adsorption TPD method, graphene coverage is limited by the saturation coverage of ethylene at room temperature. A modified TPG method with dehydrogenative adsorption at elevated temperature could increase graphene coverage, but carbon clusters that cannot be converted to graphene in the final course of growth are always present.

To fully cover a surface with graphene, the CVD growth method was carried out also using ethylene as the precursor, as it has been demonstrated to be a better precursor for graphene formation in TPG studies. In this CVD method, the Pt(111) substrate was held at 1135 K (above the complete dehydrogenation temperature) during ethylene exposure. The STM image shown in Figure 3.5(a) was acquired after cooling back to room temperature. A fully covered surface is observed. Figure 3.5(b) shows a moiré pattern, which is formed by the lattice mismatch between graphene and the Pt(111) substrate. The periodicity of the moiré is about 2.2 nm, consistent with previous studies of graphene on Pt(111) (22). Notice that the change in the middle of the image is caused by alterations of the tip condition during scanning, which causes the moire pattern to be resolved only in the bottom half of the image.
Chapter 3: Graphene as a template for nanocluster fabrication

3.2.3 Combination method of room temperature pre-adsorption and CVD growth

With the goal of forming a surface fully covered by graphene with an uniform orientation, we used a combination method that has been demonstrated to be successful in graphene formation on Ir(111) (99). Pre-adsorption at room temperature can help to maintain an aligned orientation of the moiré pattern during the subsequent growth, since it provides nucleation seeds with aligned orientation. The Pt(111) substrate was first exposed to 2.3 L ethylene at room temperature, followed by annealing to 1200 K, with the substrate kept at 1170 K during CVD growth with a 61.5 L ethylene exposure. The images shown in the figures in Section 3.3 were obtained by this combination method, where the details of the graphene structure are discussed.

3.3 Characterization of graphene on Pt(111)

3.3.1 Moiré pattern

Figure 3.6 shows the STM topographic images of a surface fully covered with graphene. A moiré pattern, which is formed by the lattice mismatch between graphene and the Pt(111) substrate, was clearly resolved in some areas but not in others. The

Figure 3.5: CVD growth of graphene on Pt(111) after exposing to 7 L of ethylene at 1135 K. (a) Large scale image showing the surface fully covered with graphene, 200 nm × 200 nm, $V_{s} = 700$ mV, $I_t = 0.4$ nA. (b) With moiré pattern resolved, 75 nm × 75 nm, $V_{s} = 700$ mV, $I_t = 1.0$ nA. Both images were acquired at 300 K.
presence of different rotational domains for the graphene is consistent with the observation of a ring structure in the LEED pattern. Such ring structure is due to the weak interaction between graphene and the platinum substrate. Unlike graphene on Ru and Ir surfaces, where single-domain graphene is favored across the surface (93, 100), graphene on Pt(111) always forms multi-moiré domains (16-17, 19, 22, 101-103). Two of the graphene domains with distinct moiré structure seen in Figures 3.6(a) and 3.6(b) with periodicities of 2.2 and 1.4 nm are enlarged in Figures 3.6(c) and 3.6(d), respectively. Due to limited resolution, structure within the graphene domains with moiré periodicities less than 1.4 nm is not observed here but has been seen in other studies. For example, Gao et al. (101) reported six different rotational domains for graphene on Pt(111) with moiré periodicities ranging from 0.5 to 2.1 nm. As they were also able to resolve the graphene lattice, whereas we do not, they could determine the angle between the moiré and graphene lattices. From the graphene images in Figures 3.6(c) and 3.6(d), we follow the relationships presented by N’Diaye et al. (104) to calculate that the angles between the Pt and graphene lattices for the 2.2 and 1.4 nm moiré lattices are $0^\circ$ and $8^\circ$, respectively. Given the likely error in the measurement, these are presumably the same rotational domains that Gao et al. (101) identify as having moiré periodicities and rotations of 2.1 nm and $2^\circ$ and 1.5 nm and $6^\circ$. The graphene rotational domains for which we don’t resolve moiré structure presumably correspond to one or more of the three domains that Gao et al (101) report with moiré periodicities less than 1.5 nm. Theory has been used to explain the formation of multidomain graphene on transition metals. Merino et al. (105) established a relation between the moiré periodicity and the minimization of the lattice strain through a geometrical model, in which they took into account the lattice strain between the atomic lattices of the graphene and the substrate at different
orientations. Their model predicts the stable moiré structures at some fixed number of orientations, which is in good agreement with experimental data in the literature. Moreover, Lim et al. (106) show that even at an identical rotational angle the lattice contraction affects the moiré periodicity. In their study, various moiré patterns are observed and are correlated to the degree of lattice contraction of graphene on Cu(111). In short, the moiré periodicity is correlated with the rotational angle, as well as with the lattice contraction.

**Figure 3.6:** STM topographic images of various moiré domains. (a) 100 nm × 100 nm STM image of the surface fully covered with graphene. (b) Zoomed image (40 nm × 40 nm) of the area in the rectangle in (a), which is differentiated in the x (horizontal) direction to highlight the two main periodicities observed. (c) and (d) 11 nm × 11 nm images of moiré structures with periodicities of 2.2 and 1.4 nm, respectively. The white rhombus indicates the unit cell. The insets shows models with the graphene layers rotated by 0° and 8° with respect to the Pt(111) lattice. Red solid arrows indicate the Pt(111) lattice while the yellow dashed arrows indicate the graphene lattice. All images: $V_s = 700$ mV and $I_t = 1.0$ nA.
3.3.2 Domain boundaries

We also observe graphene nanobubbles that have been reported recently by others (107). These nanobubbles appear as bright protrusions in STM images that form due to both electronic and geometric contributions. They are formed during cooling from the growth temperature to room temperature due to the difference in the thermal expansion coefficients between the graphene overlayer and the platinum substrate. In Figure 3.6(a), distinct moiré domains residing entirely within a large Pt terrace (the left side in Figure 3.6(a)) are observed while other graphene domains that extend across a Pt monatomic step edge (right side in Figure 3.6(a)) are seen. The straight and smooth step edges of clean Pt(111) become rough and irregular after being decorated by graphene, as is typically observed when graphene is formed on Pt(111) by decomposition of hydrocarbons at elevated temperature (22-23). Such roughing of the step edges is likely due to the hindered diffusion of Pt atoms along step edges by pinned carbon atoms (23). The moiré boundaries also appear higher by 50-60 pm than the interiors of the domains, which can be attributed to electronic and geometric effects. Early theoretical studies of the defects in two-dimensional graphene sheets have suggested that the grain boundaries in graphene contain pentagons “5” and heptagons “7” as the elementary defects (108). Although the elementary pentagons and heptagons can appear individually, their combination into 5|7 pairs is energetically favored (109). Experimental evidence of 5|7 pairs along grain boundaries have been observed in recent transmission electron microscopy (TEM) (110) and aberration-corrected annular dark-field scanning transmission electron microscopy (111) studies of suspended graphene membranes. The 5|7 pairs are generally formed in a series of lines along the grain boundaries to fit the intergrain
misorientation. When the pairs are organized in linear motifs, they form linear ridges (109), which could result in the bright contrast at boundaries seen in STM images.

Two types of graphene boundaries are illustrated in Figure 3.7. In Figure 3.7(a), the carbon atoms at the edge of a graphene island surrounded by bare Pt surface forms strong bonds to the adjacent Pt atoms thereby anchoring the island to the substrate. In contrast, the bonding between carbon atoms at a graphene domain boundary would lead to buckling, as indicated in Figure 3.7(b). The slight bulging away of the graphene layer from the substrate at the boundaries allows matching of rotational domains to form a continuous overlayer of graphene. Obviously the defects and lattice distortions would change the electronic structure at the boundaries and, therefore, should be visible in the STM images. The high contrast at the boundaries could also be induced by defect scattering. A profile analysis across the boundary shows the bright contrast (50-60 pm in height) decaying away from the boundary center with a decay length of 0.6 nm. A similar decay length of 0.8 nm was observed on graphene/Ni(111) (112), where a one-dimensional defect at the boundary between graphene domains was calculated to have metallic character (113). Although there are both geometric and electronic structure contributions, in our case where the metal surface is fully covered with a continuous graphene overlayer, geometric buckling likely contributes the most to the high contrast at the domain boundaries. In contrast, when the metal surface is partially covered with graphene flakes (or when sub-monolayer graphene is formed on the metal surface) the high contrast at the flake or island edges observed in STM images (22) is mainly due to electronic effects. Both theoretical (114) and experimental (115-116) studies indicate that the graphene islands formed on metal surfaces exhibit a dome-like structure with the edge carbon atoms bonded to the substrate through hybridization of the C 2p orbitals with the first-
layer metal $d$ band. In this case, edge atoms are at lower geometric positions compared to the atoms in the interior of the island. Thus it is reasonable to attribute the brightness along the island edges in sub-monolayer graphene to electronic inhomogeneity. The differences in properties of these two types of boundaries are further verified by the metal deposition experiments described below. Regardless of the origins of the graphene-layer defects, in general, higher chemical reactivity is expected at defects sites.

**Figure 3.7:** Schematic model of graphene island edge and moiré domain boundary. (a) Island edge. When the surface is covered with sub-monolayer graphene, the edge carbon atoms of a graphene island bond to the substrate metal atom. (b) Domain boundary. When the surface is fully covered with monolayer graphene, a ridge is formed at the moiré boundary.

### 3.4 Pt nanocluster formation on Gr/Pt(111)

#### 3.4.1 Surface morphology of the nanoclusters

Before depositing Pt onto the graphene overlayer, we did a control experiment by depositing platinum onto the clean Pt(111) surface. The deposited platinum formed flat islands on the terraces and attached to the step edges. As shown in Figure 3.8(a), triangular islands sit on the terraces. Most of them were monolayer islands and several show a few second-layer atoms as well. The down-pointing triangular shape is due to the difference in diffusion rate along two edges of the islands, which is related to the temperature of deposition and has been well studied (117-118). Roughening of step
edges due to Pt-atom attachment was also observed. Annealing the surface to 600 K converts the shape of the islands from distinctly triangular to a smoother roughly hexagonal shape and smooths the step edge (Figure 3.8(b)).

In contrast, deposition of Pt onto the graphene overlayer results in the formation of mono-dispersed nanoclusters, as shown in Figure 3.8(c) and 3.8(d). From Figure 3.8(c), it is evident that Pt deposited onto the graphene overlayer preferentially adsorbs along moiré boundaries. We also observe that the nanoclusters along the boundaries are higher than those inside the moiré domains, which indicates preferential initial nucleation at the boundaries. Based on the surface free energies of the metal, $\gamma_{\text{metal}}$, graphene, $\gamma_{\text{graphene}}$, and the metal-graphene interface, $\gamma_{\text{interface}}$, we can predict the growth mode from thermodynamics. If the sum of $\gamma_{\text{interface}}$ and $\gamma_{\text{metal}}$ is larger than $\gamma_{\text{graphene}}$, the metal is expected to form 3D clusters, since wetting of the graphene by metals is thermodynamically forbidden (free energy is lost by formation of the graphene-metal and metal-vacuum interface). The surface free energy of graphene is reported to be 46.7 mJ/m$^2$ (119). It is much smaller than that of the deposited metal clusters, e.g. 4.94 J/m$^2$ for the (111) face of platinum (120). Thus the observation of 3D metal cluster growth on supported graphene is expected. Moreover, enlarged scans of the nanoclusters show that they are vaguely hexagonal in shape, which is more apparent in some clusters than in others. This means that the diffusion rate along the edges of the initially nucleated Pt islands is the same along different facets of the cluster. This is in contrast to Pt deposition onto a clean Pt(111) surface, where different diffusion rates of the ad-atoms along the island edges results in the formation of triangle-shaped islands.
Figure 3.8: STM images of platinum deposited onto clean Pt(111) and a graphene overlayer. (a) Image of 0.12 ML of Pt on clean Pt(111) forms down-pointing triangular islands. (b) After annealing to 600 K, showing that the distinctly triangular islands changed to a smoother shape. (c) Image of 0.2 ML Pt on a graphene overlayer showing the formation of Pt nanoclusters. 100 nm × 100 nm. (d) Zoomed-in STM image of Pt nanoclusters. 20 nm × 20 nm. Histograms of the diameters (e) and heights (f) of the Pt nanoclusters. For all images: $V_s = 700$ mV and $I_t = 0.40$ nA.

The attraction of platinum atoms to the graphene domain boundaries is a clear manifestation of the higher activity of the moiré boundary sites. Since the carbon-carbon $sp^2$ planar bonding at moiré boundaries is broken or at least altered by the pentagon and heptagon pairs, dangling bonds of carbon provide active sites where Pt atoms or clusters tend to nucleate. During the growth, the ridge area has a higher diffusion barrier. Thus the Pt atoms that diffuse to the ridge area will be trapped and the clusters at boundaries will grow faster than those inside the domains. For Ir
clusters on graphene/Ir(111) (121), it was found that preferential nucleation within the moiré domains was due to the local rehybridization of the carbon-carbon bonds from $sp^2$ to $sp^3$. A similar effect may occur in the case of Pt on graphene/Pt(111) inside the moiré domains. In the moiré unit cell, the carbon atom sitting on top of a Pt atom will form a covalent bond by overlapping with a Pt $d_{z^2}$ orbital. The other carbon atom sitting at the hollow site will generate a dangling $sp^3$ bond, which can overlap with a deposited Pt atom $d$ orbital. Thus the enhancement of the carbon-Pt bonding by the carbon $sp^3$ dangling bonds results in the nucleation of Pt clusters inside moiré domains. In contrast to the preferential adsorption along moiré boundaries on a surface fully covered with graphene, if Pt atoms are deposited on a partially covered Pt(111) surface, no clusters along the island edges are observed (data not shown). Instead, platinum forms flat islands on clean Pt(111) or nanoclusters on top of the graphene islands. Metal deposition on Ir(111)-supported graphene also shows that metal clusters are formed inside graphene flakes or islands, rather than along the island edges (24). The distinct difference between moiré boundaries and graphene island edges towards metal nanocluster formation further illustrates the unique properties of the moiré boundaries. Because carbon atoms at graphene island edges interact with substrate metal atoms, it is not possible for them to provide dangling bonds that can overlap with metal $d$ orbitals and thus, along the edges, there are no active sites for metal atoms to nucleate. Inside the graphene islands, local rehybridization of the carbon-carbon bonds within the moiré structure still apply, where the nucleation of metal clusters inside the graphene island is expected.

Although our focus is on the Pt nanoclusters located along the domain boundaries, some nucleation is also seen within the domain interiors. According to the analysis of Gao et al. (101), the different graphene domains can be classified into two
types: those with large angles between the graphene and platinum lattices are relatively flat with low corrugation, whereas those with small angles are rippled with higher corrugation. It is reasonable to assume that these different domains would have different properties as templates for metal nanocluster growth. There is some evidence of this in Figure 3.8(c), where more Pt clusters are seen within the domains on the left side of the image, whereas the domain in the middle of the image is almost devoid of any nanoclusters. A full analysis of this relationship would require resolution of the moiré lattice for each domain in the presence of the nanoclusters, something that was not achieved in this study.

The formation of nanoclusters at the domain boundaries observed here for deposited Pt is likely to be observed for some other deposited metals, but not for others. N’Diaye et al. (24) studied several metals deposited onto graphene on Ir(111) and developed heuristic principles to predict which metals would form superlattices. They found that Ir, Pt, and W formed superlattices, but that Fe, Au, and Ni did not, at least for room temperature deposition. Re was an intermediate case. The low cohesive energy of Au leads to formation of large 3D clusters rather than a superlattice. In contrast, Zhou et al. (83) also found that Au deposited onto graphene/Ru(0001) did not form a superlattice but instead formed flat 2D islands. In the study of Starr et al. (103), for their high temperature graphene growth method, different graphene rotational domains were observed on Pt(111), but when Au was deposited onto the surface, neither a superlattice nor nucleation at graphene domain boundaries was observed. Instead, only very large Au clusters were seen with STM, consistent with the results for graphene on Ir(111). They obtained similar results with deposition of Au onto graphene prepared by a low temperature method, for which they reported only one moiré domain with a periodicity of about 2.2 nm, but as in our case, domains
with shorter periodicities were probably present. Experiments with more metals would have to be performed to establish if the trends identified by N'Diaye et al. (24) for superlattice formation on the graphene/Ir(111) system extends to nucleation at the domain boundaries of graphene on Pt(111).

### 3.4.2 Temperature stability

A key issue in the use of metal nanoclusters as heterogeneous catalysts is their thermal stability. Figure 3.9 shows the room temperature STM images of the Pt nanoclusters before (a) and after briefly annealing to 600 K (b), 700 K (c), and 800 K (d). Figures 3.9(e) to 3.9(h) are histograms of the nanocluster diameters corresponding to images in Fig. 4a-d, respectively. The Pt nanoclusters retain their size and shape up to 600 K. Their diameters did not change after annealing to 600 K, but became more uniform. At higher temperatures (700 and 800 K) the clusters start to agglomerate, becoming larger and less dense. Compared to metals deposited onto supported thin oxide films, where annealing will induce the metal clusters to diffuse though the oxide film into the metal substrate (73) causing a significant loss of cluster density, here metal deposited onto Pt(111)-supported graphene shows that cluster density decreases only due to the agglomeration at high temperatures. Thus, a significant advantage of nanoclusters formed on metal-supported graphene is a higher thermal stability compared with other nanocluster formation methods.
Figure 3.9: Thermal stability of Pt nanoclusters, before and after annealing. Before (a) and after annealing to (b) 600 K, (c) 700 K, and (d) 800 K. All images, 75 nm × 75 nm, $V_s = 400$ mV and $I_t = 0.70$ nA. Histograms of the nanocluster diameters (e)-(f) corresponding to the temperatures in (a)-(d). The surface densities of the Pt nanoclusters in (a)-(d) are 108, 114, 46, and 53 clusters per $10^4$ nm$^2$, respectively.

3.5 Conclusion

In this chapter, we discussed the preparation method for graphene on Pt(111) under UHV, where a combination of room temperature adsorption and elevated temperature annealing produce high quality graphene. In contrast to graphene on Ru(0001), Ir(111) and Rh(111), graphene on Pt(111) consists of various in-plane moiré domains with different periodicities. Although a variety of methods have been used to prepare graphene on Pt(111), they all show the co-existence of different moiré structures. A recent study used Monte Carlo simulations to understand the initial stages of graphene growth on Pt(111) (122) but it did not provide any insights into the formation of different graphene rotational domains. The multitude of moiré patterns on Pt(111) results in unique behaviour in the formation of Pt nanoclusters on graphene/Pt(111). After depositing Pt atoms onto Pt(111)-supported graphene, we found that instead of adsorbing inside the moiré domains and forming two-
dimensional arrays, Pt nanoclusters adsorb along moiré boundaries forming one-dimensional chains.
Chapter 4: Molecular Oxygen Network as a Template for Adsorption of Ammonia on Pt(111)

In this chapter, structures of a molecular oxygen network and the NH$_3$–O$_2$ overlayer are discussed. Section 4.1 details the experimental procedure. Section 4.2 presents the results on the O$_2$-network. Section 4.3 discusses the adsorption of ammonia on the O$_2$-network and the configuration of an NH$_3$–O$_2$ overlayer. Section 4.4 summarizes the results presented with key points highlighted.

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4.1 Experimental

The experiments in this chapter were carried out with the Omicron LT-STM system described in Section 2.1.2. The Pt(111) crystal was cleaned in the preparation chamber. The sample was heated by electron bombardment to 1220 K and held at that temperature for 10 min, followed by argon ion sputtering at room temperature for 10 min (Ar pressure, $3 \times 10^{-5}$ torr; 1000 eV energy). After 5 to 8 cycles of annealing and sputtering, the sample was treated by O$_2$ ($1 \times 10^{-7}$ Torr) at 750 K for 10 min, followed by flash annealing to 1220 K and then was transferred to the STM chamber where the surface may stay clean for several days. Surface cleanness was verified by STM and occasionally by LEED. As shown in Figure 4.1, a chemisorbed molecular O$_2$ overlayer on Pt(111) was prepared by repeated exposure to O$_2$(g) at 50 K via a nozzle in the STM chamber. The pressure measured with an ion gauge was $2.5 \times 10^{-10}$ Torr and the time was 20 seconds for each exposure. However, the actual partial pressure
at the nozzle exit should be considerably higher than that measured at the ion gauge.
After each O\textsubscript{2} exposure (2.5 \times 10^{-10} \text{Torr, 20 s) at 50 K, the crystal was cooled to 4.7 K for STM measurement to verify the coverage. After saturating the surface with molecular O\textsubscript{2} (2.5 \times 10^{-10}\text{Torr for 20 s, repeated 3 times), NH\textsubscript{3} gas was then exposed to the surface at 50 K via the nozzle in the STM chamber (6.0 \times 10^{-11}\text{Torr NH\textsubscript{3} for 20 s, repeated 2 times). The NH\textsubscript{3}–O\textsubscript{2} covered sample was then cooled down to 4.7 K for STM measurements. The temperature of 50 K for the O\textsubscript{2} and NH\textsubscript{3} exposures was based on the time it took to remove the sample from the STM sample holder, move it to the dosing position, and to complete the gas exposures. The relationship between time and temperature was established through a calibration procedure in which a thermocouple was directly attached to the sample. The accuracy of the dosing temperature is estimated to be ± 5 K.

![Figure 4.1](attachment:image.png)

**Figure 4.1:** Schematic drawing of formation of the NH\textsubscript{3}–O\textsubscript{2} overlayer on Pt(111).

### 4.2 Molecular oxygen network on Pt(111)

Previous studies have revealed several forms of O\textsubscript{2} on the Pt(111) surface depending on the adsorption temperature. At temperatures below 40 K, only physisorbed O\textsubscript{2} was observed (123). Chemisorbed molecular O\textsubscript{2} on Pt(111) exists in
the temperature range from 40 to 150 K. Two chemisorbed O$_2$ species were identified in studies by electron energy loss spectroscopy (EELS) (124) and RAIRS (125). In these studies O-O stretch vibrations were observed at 700 and 875 cm$^{-1}$, and were assigned to peroxo (O$_2^2-$) and superoxo (O$_2^-$), respectively. An STM study assigned the adsorption sites of peroxo and superoxo to top-bridge and bridge sites, respectively (8). Top-bridge means one oxygen atom sits at an atop site, while the other one sits at a bridge site. The same study also found compact islands formed exclusively by bridge site molecules, which was attributed to the long lifetime of the precursor state (126). A later RAIRS study indicated that peroxo dominates at low coverage and converts to superoxo as coverage increases (127). Although an explanation was not offered, it may be that repulsion between the doubly charged peroxo species makes it less stable at higher coverages than the singly charged superoxo species. At temperatures above 150 K, chemisorbed molecular O$_2$ dissociates to O atoms, which adsorb at fcc sites (8).

After low O$_2$ exposures at 50 K, we observe both peroxo and superoxo in the image of a single Pt(111) terrace shown in Figure 4.2(a), which is consistent with the STM observations by Stipe et al. (126) and calculations by Eichler and Hafner (128) and Bocquet et al. (129). Based on the previous studies (8, 124, 126-129), we assign isolated molecules, which are often seen as pairs and chains to peroxo, and compact islands to superoxo, indicated by solid and dashed arrows in Figure 4.2(a), respectively. The peroxo molecules in chains and pairs are separated by two Pt lattice constants. When superoxo islands start to grow on the surface, peroxo molecules are also found to sit along the island perimeters (see Figure 4.3(a-b)). As we gradually increase the coverage of molecular O$_2$, most of the surface was covered with superoxo islands (Figure 4.2(b)). Moreover, with a specific tip state, the detailed structure
within the superoxo islands (Figure 4.2(c)) can be resolved, which has not been reported previously. A frequent change in tip state occurred randomly, and more detailed structure was observed reproducibly as shown in Figure 4.2(c). Also under certain tip conditions, superoxo molecules appear in the shape of a four-leaf clover (Figure 4.2(d)). This shape was also observed by Stipe et al. (8) who suggested that its similarity to the shape of the $\pi^*$ orbital implies that this orbital makes the dominant contribution to the local density of states at the Fermi level. A drawing of overlapping four-leaf clovers centered on three O$_2$ molecules is shown in red in Figure 4.2(h) and is superimposed on the image. The fact that the peroxo and superoxo molecules appear so differently in the STM images is a clear manifestation of their different electronic structures, which is also reflected in their different adsorption sites (bridge for superoxo, fcc sites for peroxo), different formal charges (–2 for peroxo, –1 for superoxo), and their distinctly different O–O stretch frequencies. These differences are also readily apparent in simulated STM images based on electronic structure calculations (129).
Figure 4.2: STM images and models of chemisorbed molecular $O_2$ on Pt(111). (a) Low coverage (15 nm × 15 nm, $V_s = 80$ mV, $I_t = 2$ nA). (b) High coverage (20 nm × 20 nm, $V_s = 50$ mV, $I_t = 1.0$ nA). (c) Superoxo islands with individual $O_2$ molecule resolved (8 nm × 8 nm, $V_s = 200$ mV, $I_t = 0.7$ nA). (d) Four-leaf clover shape of superoxo (5.0 nm × 5.0 nm, $V_s = 2$ mV, $I_t = 4$ nA) (e-f) (√7 × √7)R19.1°-3$O_2$ structure. (g) Arrangement of superoxo in the square area of (c). (h) Zoomed-in image of the black square in (d), with superimposed drawing of three overlapping four-leaf clovers (2.0 nm × 2.0 nm, $V_s = 2$ mV, $I_t = 4$ nA).

Figure 4.2(c) shows that the superoxo molecules within islands form an ordered network. The “holes” that appear in the $O_2$ network are located at platinum atoms that are surrounded by, but not occupied by, $O_2$ molecules. Another characteristic feature in the $O_2$ network is the triple-hole structure, highlighted by the red circle in Figure 4.2(c). A model of the arrangement of the $O_2$ molecules inside the black square in Figure 4.2(c), including both single- and triple-holes, is shown in Figure 4.2(g). The single-hole seen in the STM image is surrounded by three bridge $O_2$ molecules (red) with the molecular axis aligned with the Pt lattice, while the triple-hole is surrounded by five $O_2$ molecules with four of them sitting at bridge sites (superoxo) and one molecule possibly sitting at a top-bridge site (peroxo). An image showing a close-up view of a triple-hole is given in Figure 4.3(c).
Figure 4.3. STM images of peroxo molecule, superoxo island, and mixed NH$_3$–O$_2$ overlayer. (a-b) Peroxo molecules (indicated by solid arrows) sit at the perimeters of superoxo islands (indicated by dashed arrows). (a) 10 nm × 10 nm, $V_s = 20$ mV, $I_t = 1.0$ nA. (b) 3 nm × 3 nm, $V_s = 2$ mV, $I_t = 0.5$ nA. (c) STM image of single-hole and triple-hole in a superoxo island (3 nm × 3 nm, $V_s = 50$ mV, $I_t = 1$ nA). Inset: Zoomed-in image of the black square, showing the “heart-shape” of the triple-holes. (d) STM image of a mixed NH$_3$–O$_2$ overlayer (20 nm × 20 nm, $V_s = 200$ mV, $I_t = 0.8$ nA). On the left side of the image the underlying O$_2$ layer is resolved.

The brighter appearance at the edge of the triple-hole in the STM image could be the effect of a conjugate π bond among the three O$_2$ molecules (two superoxo and one peroxo molecules). As superoxo islands grow in size, peroxo molecules are incorporated into their perimeters but not converted to superoxo. If we assume the surface was covered by a perfect network of superoxo islands, possible arrangements would be those shown in Figures 4.2(e) and 4.2(f). There would be three equivalent directions for the molecular axes of O$_2$ occupying bridge sites, which are the [$\bar{T}01$], [0$\bar{T}$1], and [1$\bar{T}$0] directions of the Pt(111) surface. When three O$_2$ molecules along these three directions come close to each other, the smallest unit cell they could form
is shown by the dashed rhombus in Figures 4.2(e) and 4.2(f). This is a \((\sqrt{7} \times \sqrt{7})R19.1^\circ\)–3O\(_2\) structure, which has a maximum O\(_2\) coverage of 0.43 ML, i.e., three times 1/7 (the coverage of the \((\sqrt{7} \times \sqrt{7})R19.1^\circ\) structure itself). Although the same unit cell describes the structures corresponding to the single-hole in Figures 4.2(e) and 4.2(f), the STM images clearly favor the structure in 4.2(e) in which three superoxo O\(_2\) molecules located at bridge sites surround each hole in a symmetric way. The saturation coverage of O\(_2\) on Pt(111) was reported to be 0.44 ML by Steininger et al. in their study of O\(_2\) adsorption on Pt(111) (124). They observed an ordered \((3/2 \times 3/2)R15^\circ\) overlayer with LEED after the surface was exposed to \(\geq 6 \times 10^{15}\) molecules/cm\(^2\) of oxygen at 100 K, while such an ordered overlayer could not be formed at a lower exposure \((2.4 \times 10^{14}\) molecules/cm\(^2\)). The matrix notation for the \((3/2 \times 3/2)R15^\circ\) superlattice, \[
\begin{pmatrix}
1.67 & 0.45 \\
-0.45 & 1.22
\end{pmatrix}
\], has irrational values, which indicates that it is incommensurate with respect to the Pt lattice (130). Consequently, in contrast to the \((\sqrt{7} \times \sqrt{7})R19.1^\circ\)–3O\(_2\) structure in Figure 4.2, a structure with \((3/2 \times 3/2)R15^\circ\) periodicity in which all O\(_2\) molecules occupy identical sites of the Pt lattice cannot be drawn. The fact that this latter superlattice was not observed here is presumably because the coverage was not quite high enough. Based on a Pt-Pt distance of 2.77 Å, the calculated hole-hole distance in the O\(_2\) network represented by Figures 4.2(e) and 4.2(f) is 0.73 nm, which exactly matches the values measured from the line profile of the STM images. However, from Figures 4.2(b) and 4.2(c), it is easily seen that there are many defects in the network with various arrangements of O\(_2\) molecules. The hole-hole distance varies corresponding to different arrangements of O\(_2\) molecules. For example, hole-hole distances of 0.48 nm (blue arrow) and 0.73 nm (green arrow) and the corresponding models are shown in Figures 4.4(b) and 4.4(h).
distance of 0.73 nm is expected to be most common as it achieves the highest density of holes that are surrounded by three equivalent O$_2$ molecules.

To understand the various structures and defects associated with the experimentally observed O$_2$ network, we tabulated all hole-hole distances in the network from the smallest value of 0.48 nm up to 1.54 nm. Larger distances are also possible but to simplify our analysis we consider only the holes adjacent to a given hole. As shown in Figure 4.4(a), colored arrows represent ten discrete values from 0.48 to 1.54 nm. The color for each value is chosen to go from blue, for the smallest distance, to red, for the largest. Figures 4.4(b-k) are the models corresponding to the ten hole-hole distances. One possible arrangement of O$_2$ molecules corresponding to each value is shown as an example. In Figures 4.4(h-k), there are two possible sets of hole-hole distances at each value, labeled as dark and light brown. They are mirror images of each other and are the rotational alternatives for the same distance on a hexagonal surface. Figure 4.5(c) is a histogram of the number of occurrences of each of the ten hole-hole distances corresponding to the ten structures in Figure 4.4. The color of each column in the histogram is the same as that of the models in Figure 4.4 for each value of the hole-hole distance. As anticipated, the distance of 0.73 nm predominates. The ten distances given in the histograms are the averages of the measured values clustered about the ideal values. A table with the average measured values and their standard deviations for both the hole-hole and the NH$_3$-NH$_3$ distances compared to their ideal values based on the structures of Figure 4.4 is given in Table 4.1.
Figure 4.4: Schemes showing the possible hole-hole distances on Pt(111). (a) Arrows corresponding to each possible value of the distance, from shortest (0.48 nm) to longest (1.54 nm), are colored from blue to red. (b)-(k) Models of each hole-hole distance.

Table 4.1 Theoretical and experimental values for hole-hole and NH₃-NH₃ distances

<table>
<thead>
<tr>
<th>theoretical values (nm)</th>
<th>measured values from STM images</th>
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<td>1.54</td>
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4.3 Adsorption of ammonia on oxygen network

Images obtained following ammonia adsorption on the saturated O\textsubscript{2} overlayer on Pt(111) are shown in Figure 4.5(d). Although the ammonia molecules are easily seen as bright protrusions, the underlying O\textsubscript{2} network is not observable in this image, although it can be observed at slightly lower ammonia coverages as shown in Figure 4.3(d). Nevertheless, analysis of the images indicates that the NH\textsubscript{3} molecules are adsorbed on top of the Pt atoms in the holes in the O\textsubscript{2} network structure. It is reasonable since the most stable adsorption site for ammonia on Pt(111) is the atop site\(^{(131)}\). There is some variability in the apparent height of the ammonia molecules, which presumably reflects the number and configuration of surrounding O\textsubscript{2} molecules. Although there is no long range ordered structure of NH\textsubscript{3} molecules, only certain NH\textsubscript{3}–NH\textsubscript{3} distances are observed. For example, an NH\textsubscript{3}–NH\textsubscript{3} distance of 0.74 nm (green arrow) and 0.47 nm (blue arrow) are shown in Figure 4.5(d). Models of the corresponding arrangements of O\textsubscript{2} and NH\textsubscript{3} are shown in Figures 4.5(b) and 4.5(e). A histogram of the measured NH\textsubscript{3}–NH\textsubscript{3} distances is shown in Figure 4.5(f). The number of these distances measured was 219, whereas 256 measured hole-hole distances were used for the histogram of Figure 4.5(c). For ease of comparison, we use the same color for the column if the value of the molecule-molecule distance is the same as that of the hole-hole distance (error range ±0.02 nm). The dominant NH\textsubscript{3}–NH\textsubscript{3} distance is 0.74 nm, which matches the value of 0.73 nm of the hole-hole distance in the O\textsubscript{2} network. Comparing the two histograms in Figures 4.5(c) and 4.5(f), we conclude that the distance among the adjacent NH\textsubscript{3} neighbors matches the hole-hole distance of the O\textsubscript{2} overlayer. This suggests that the preferred adsorption sites for NH\textsubscript{3} are the holes in the O\textsubscript{2} overlayer, which is also the atop site of the Pt substrate.
Figure 4.5: Images and models of the $\text{O}_2$ network and $\text{NH}_3$–$\text{O}_2$ overlayer on Pt(111). (a) STM image of the $\text{O}_2$ network (area = 3.5 nm × 3.5 nm, $V_s =$ 200 mV, $I_t =$ 0.7 nA). Hole-hole distance of 0.73 nm (green arrows) and 0.48 nm (blue arrows) are shown. (b) Model showing the $\text{O}_2$ molecular arrangements corresponding to the hole-hole distance of 0.73 nm and 0.48 nm. (c) Histogram of hole-hole distances of superoxo network. (d) STM image of mixed $\text{NH}_3$–$\text{O}_2$ overlayer on Pt(111) (area = 3.5 nm × 3.5 nm, $V_s =$ 20 mV, $I_t =$ 1 nA). (e) Model showing $\text{NH}_3$ molecules sitting inside the holes (also on top of Pt atoms). Oxygen molecules are colored red, nitrogen atoms blue, and hydrogen atoms white. (f) Histogram of $\text{NH}_3$–$\text{NH}_3$ molecular distances.

Based on the above results, we conclude that in the mixed $\text{NH}_3$–$\text{O}_2$ overlayer the $\text{NH}_3$ molecules are adsorbed on top of Pt atoms, each of which is surrounded by two or three $\text{O}_2$ molecules that adsorb at bridge sites, as shown in Figure 4.5(e), where $\text{NH}_3$ molecules are presumed to sit inside the hole, and are oriented such that their three H atoms point towards the $\text{O}_2$ molecules. The distance between the $\text{O}_2$ and $\text{NH}_3$ molecules in this proposed structure is 0.240 nm, which is less than the sum of the van der Waals radii of 0.305 nm (132), suggesting that molecules are in contact and that a favorable orientation must be adopted, such as the one shown. The interaction between the $\text{NH}_3$ and $\text{O}_2$ molecules associated with this bonding arrangement presumably corresponds to the $\text{NH}_3$–$\text{O}_2$ complex identified previously with RAIRS (35). The complex is characterized by an O–O stretch of 1451 cm$^{-1}$, compared to 1556 cm$^{-1}$ for gas phase (133) $\text{O}_2$ and 878 cm$^{-1}$ for the superoxo $\text{O}_2$ on Pt(111) (125, 127).
As the low O–O stretch frequency of the superoxo species is due to electron transfer into the $\pi^*$ orbital, which is antibonding with respect to the O–O bond, there is evidently little excess negative charge on the O$_2$ molecules that are part of the complex. Whether this occurs due to direct transfer to the H atoms of the NH$_3$ molecules or a reduction in charge transferred from the metal is unclear. As this complex precedes the dehydrogenation reaction, the results here show that the O$_2$ molecular network provides a template for adsorption of ammonia molecules in a configuration that facilitates subsequent reactivity. Such pre-reaction structures may exist transiently under the actual reaction conditions employed in catalysis, conditions that would preclude direct imaging by the methods employed here.

### 4.4 Conclusion

In this chapter, we show that prior to the oxydehydrogenation of ammonia, the adsorption of ammonia molecules in O$_2$-network sites is associated with the formation of an NH$_3$–O$_2$ complex. The structures of the O$_2$-network and the NH$_3$–O$_2$ complex were studied by STM and described with a molecular model for the first time. The O$_2$-network features a distributed set of holes corresponding to atop sites of the Pt lattice that are surrounded by two or three O$_2$ molecules. The holes in the network act as preferential adsorption sites for the ammonia molecules leading to the formation of the NH$_3$–O$_2$ complex.
In this chapter, the surface morphology of atomic nitrogen is discussed. Section 5.1 describes experimental details. Section 5.2 details the surface morphology of atomic N layer. Hydrogenation of the atomic nitrogen layer is discussed in Section 5.3. Section 5.4 summaries this chapter.

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5.1 Experimental

Sample cleaning and preparation of the NH$_3$–O$_2$ layer follows the same procedures as described in Section 4.1. Then the NH$_3$–O$_2$ covered surface was transferred to a heating stage and heated to the target temperature and held there for 60 seconds. Although the oxydehydrogenation reaction begins at $\sim$150 K, heating to temperatures between 300 and 400 K is needed to desorb the H$_2$O product and any excess NH$_3$, as shown in Figure 5.1. The annealing temperature was accurately controlled on the heating stage by a thermocouple mounted on the sample. An NH layer was formed by exposing the N covered surface to H$_2$ gas while the sample was held at 300 K. H$_2$ gas was introduced via the nozzle ($5.0 \times 10^{-9}$ Torr for 120 s, repeated 7 times). 20-minute intervals between each exposure were used for recovering the background pressure, with a total of 140 minutes to finish the exposure. The sample was then cooled to 4.7 K for STM measurements.
5.2 Morphology of surface nitrogen

5.2.1 Mixed N and O

When the exposures were high but the amount of ammonia was not enough to react and remove all the oxygen from the surface, a surface covered with a mixed N and O overlayer was obtained after annealing to 370 K. As shown in Figure 5.2(a) and 5.2(b), a (2 × 2) structure was clearly resolved. Figure 5.2(b) is a close-up image of the black square in Figure 5.2(a), in which two types of atoms can be seen. Nitrogen atoms (indicated by blue circles) appear brighter than oxygen atoms (indicated by red circles). The assignment of N and O was based on comparison to the N-covered surfaces which will be discussed in section 5.2.3. Moreover, the recombinative desorption of O$_2$ and N$_2$ occur at very different temperatures, [800 K for O(ad) + O(ad) → O$_2$(g) (2) and 450 K for N(ad) + N(ad) → N$_2$(g) (35)]. Images obtained after annealing the mixed N+O surface to above 400 K contain only surface O atoms, which have an appearance that is similar to the less bright atoms shown in
Figure 5.2(b). The N:O ratio was found to be 0.56:0.44, based on a 30 nm × 30 nm image containing a total of 3388 atoms. Although this analysis was based on a single image, many other images had the same general appearance and presumably contained a similar ratio, which was verified with a second image where the measured ratio was 0.55:0.45. Similar observations of coadsorbed N and O on Ru(0001) have been reported by Nagl et al. (134), where they found that N appears brighter than O in a mixed hexagonal (2 × 2)-N+O lattice. In our case, a honeycomb structure was observed, which consists of N, O, and Pt atoms. There are several patches of bare platinum surface visible in Figure 5.2(a) and 5.2(b). Individual Pt atoms are resolved in Figure 5.2(b), where a grid is superimposed onto the upper right area of the image. The unit cell of the Pt(1 × 1) lattice is indicated by a solid purple rhombus, as shown in the middle of Figure 5.2(b) on the bare Pt. The unit cells of the mixed (2 × 2)-N+O and Pt are shown as solid blue and dashed purple rhombuses, respectively. The appearance of the images changed depending on the condition of the tungsten tip. In most cases the mixed (2 × 2) pattern appears as shown in Figure 5.2(a) and (b), which are assumed to have been taken when the tip was terminated with an adsorbed atom or molecule. We made a tip clean by treating it with numerous large positive pulses (from 5 V to 10 V) until an atomically resolved image could be obtained with that tip. This is called a bare tip. Images of mixed (2 × 2)-N+O under modified and bare tips are shown in Figure 5.2(c). The images of Figure 5.2(c) were taken of the same area before (upper) and after (bottom) a sudden tip change. As shown in the upper image, with a modified tip both N and O were resolved as indicated by blue and red arrows, respectively. In the lower image of Figure 5.2(c), N atoms are still visible although they appear darker than in the upper image. An O atom seems to be missing in the bottom image as
there is nothing visible at the red arrow, as well as at other places where O atoms are seen in the upper image. No pulses were applied to the tip in between these two images. Rather, the tip changed spontaneously during scanning presumably by losing an attached atom or a molecule. Figure 5.2(d) and (e) show the surface of mixed (2 × 2)-N+O imaged by a bare tip where only N atoms are resolved. The change of the tip is reversible, which means that by applying pulses to the modified tip, we can restore a bare tip that images only N atoms. In addition, a soft-crash of the tip into a surface covered with adsorbates modifies the tip so that both N and O atoms can be imaged, generally with better resolution. Other STM studies have revealed similar changes in the appearance of atoms or molecules between bare and modified tips (6, 129, 135). Figure 5.2(f) shows an image taken at a step edge. The image was differentiated along the horizontal direction to show both terraces with the same contrast. A lattice grid placed on the two terraces reveals that both N and O atoms occupy face-centered-cubic (fcc-hollow) sites. The direct identification from STM images supports theoretical calculations by Ford et al. (131), who have shown that the most favorable site for atomic nitrogen and oxygen on Pt(111) is fcc, with the hcp site being 0.2 eV (N) and 0.4 eV (O) less stable.
Figure 5.2: Surface morphology of mixed N and O under different tip conditions. (a) Mixed (2 × 2)-N+O with a modified tip (15 nm × 15 nm, $V_s = 50$ mV, $I_t = 1$ nA). (b) Zoomed-in image of the black square in (a) (5 nm × 5 nm, $V_s = 10$ mV, $I_t = 1$ nA). Blue, red and black circles (arrows) indicate N, O, and Pt atoms, respectively. A Pt lattice grid was superimposed on the upper right of the image. Three rhombuses indicate the unit cells of (2 × 2)-N+O (blue), Pt(2 × 2) (dashed and purple), and Pt(1×1) (solid and purple). (c) Mixed (2 × 2)-N+O in the identical position before (upper) and after (bottom) a tip change. For both images, 5 nm × 2.5 nm, $V_s = 50$ mV, $I_t = 1$ nA. (d) Mixed (2 × 2)-N+O with a bare tip (10 nm × 10 nm, $V_s = 50$ mV, $I_t = 1$ nA). (e) Zoomed-in image of the yellow square in (d) (5 nm × 5 nm, $V_s = 50$ mV, $I_t = 1$ nA). (f) Differential image showing two terraces at a step edge (5 nm × 5 nm, $V_s = 50$ mV, $I_t = 1$ nA). Solid and dashed grids indicate upper and lower terraces, respectively. Inset: schematic model at the step edge with a fitted grid.

5.2.2 Atomic N at low coverages

When small but comparable amounts of ammonia and oxygen are exposed to the surface followed by annealing, areas partially covered with N atoms coexist with areas of local high N coverage. Imaged by a bare tip, isolated nitrogen atoms appear as depressions on the flat Pt(111) surface, as shown in Figure 5.3(a). As the tip moves closer to the surface, individual N and Pt atoms can be resolved, as seen in Figure 5.3(b) where N atoms that are part of a dense layer, or even just present as a pair of N atoms, have a bright spot in the middle surrounded by a darker halo. The
line profile in Figure 5.3(e) of the indicated isolated N atom in Figure 5.3(b) is consistent with a simple depression without a bright center surrounded by a halo. This is consistent with the theoretical calculations of Sautet (11). The contrast between isolated N atoms and a dense layer is clear in Figure 5.3(c). The left half of the image shows a bare surface with several isolated N atoms, which is similar to that in Figure 5.3(a). The right half of the image in Figure 5.3(c) shows a dense N layer in the p(2 × 2) phase. The dense p(2 × 2)-N island shows a honeycomb lattice, which is 0.2 Å lower than the bare Pt surface (see the line profile shown in Figure 5.3(d)). The details of the honeycomb structure are discussed in Section 5.2.3. A surface that was partially covered with nitrogen appears differently from one covered by a dense layer. Such different appearances of an isolated atom versus those in a dense layer can be explained by an interference effect between tunneling channels through overlapping orbitals at neighboring atoms. The effect of overlapping orbitals is significant in the dense layer but absent in the case of an isolated atom. Sautet and coauthors have discussed the interference effect of a dense layer in their studies of p(2 × 2)-S on Re(0001), with both experimental STM images and theoretical calculations (136). In their calculations, sulfur atoms in a fictitious p(4 × 4) layer, which are considered to be isolated, showed a round maximum, while in a p(2 × 2) layer a honeycomb structure was formed. A similar perturbation resulting from adsorbate-adsorbate interference was also found in the case of CO on Cu(110). Isolated CO appears as a depression, while dimers and any other chains appear as protrusions (137).
Figure 5.3: STM images of a surface partially covered with N. (a) 10 nm × 10 nm, $V_s = 20$ mV, $I_t = 1$ nA. (b) 4 nm × 4 nm, $V_s = 5$ mV, $I_t = 1.5$ nA. Nitrogen and platinum atoms are indicated by blue and black circles, respectively. (c) 6 nm × 3 nm, $V_s = 50$ mV, $I_t = 0.5$ nA. (d) Line profile along the dashed line in (c). The small bar indicates the starting point. (e) Line profile along the solid line in (b).

5.2.3 $(\sqrt{3} \times \sqrt{3})R30^\circ$-N and p(2 × 2)-N on Pt(111)

By increasing the ammonia exposure, a surface fully covered only with nitrogen atoms was obtained after annealing to temperatures above 360 K. Both $(\sqrt{3} \times \sqrt{3})R30^\circ$-N and p(2 × 2)-N phases were observed. These notations describe the surface structure of adsorbates with respect to the substrate unit cell. A detailed explanation of the notation is provided later in this section where the atomically resolved images of the two phases are discussed. The relative amount of the two phases varies with annealing temperature. Briefly, the $(\sqrt{3} \times \sqrt{3})R30^\circ$-N phase dominates for annealing temperatures below 360 K, whereas the p(2 × 2)-N phase dominates for a 400 K anneal. Between 370 and 390 K, as temperature increases the
area of the p(2 × 2)-N phase increases and that of the (√3 × √3)R30°-N phase decreases. This correlates with the thermal desorption of N₂, which has an onset just below 400 K. As temperature increases, the more dense (√3 × √3)R30°-N phase with a coverage of 0.33 ML converts into the less dense p(2 × 2)-N phase with a coverage of 0.25 ML. Although theoretical calculations of the Pt–N binding energy in different phases are lacking, Schwegmann et al. (40) have calculated the binding energy of Ru–N in the (2 × 2)-N and the (√3 × √3)R30°-N to be 5.82 and 5.59 eV, respectively. Nitrogen binds to Ru more strongly in the (2 × 2) phase, and thus has a higher activation energy for desorption than the (√3 × √3)R30° phase. This correlates with their observations that the (√3 × √3)R30°-N phase is formed at lower temperatures than the (2 × 2)-N phase. We would expect the same for N on Pt(111): the (√3 × √3)R30°-N phase forms at lower temperatures, and converts to a more stable (2 × 2)-N phase at higher temperatures. The p(2 × 2)-N islands appear about 0.1 Å higher than the (√3 × √3)R30°-N islands, as clearly seen in Figure 5.4(a-c) where the two phases coexist. The image in Figure 5.4(b) was obtained on a different Pt single crystal, which had a different azimuthal orientation with respect to the STM such that the lattice is rotated with respect to the other images in Figure 5.4. Otherwise, the images obtained with the two crystals are identical, thus demonstrating the reproducibility of the results.
Chapter 5: Atomic Nitrogen on Pt(111)

Figure 5.4: STM images of (√3 × √3)R30°-N and p(2 × 2)-N. (a) 20 nm × 20 nm, $V_s = 200$ mV, $I_t = 1$ nA; (b) 4.5 nm × 4.5 nm, $V_s = 20$ mV, $I_t = 0.5$ nA. (c) 4.5 nm × 4.5 nm, $V_s = 10$ mV, $I_t = 1$ nA. A Pt lattice grid was superimposed on the right. Light and dark blue circles indicate N atoms in (√3 × √3)R30°-N and p(2 × 2)-N phases, respectively. (d) p(2 × 2)-N under a tip state that only shows the N atoms (area = 9 nm × 9 nm, $V_s = 100$ mV, $I_t = 0.6$ nA).

Expanding a lattice grid fitted to the p(2 × 2)-N areas to the (√3 × √3)R30°-N areas implies that the N atoms occupy the same hollow sites in both phases. This is shown in Figure 5.4(c) where four N atoms in the p(2 × 2)-N phase are highlighted by dark blue circles, whereas another four N atoms in the (√3 × √3)R30°-N phase are colored light blue. Figure 5.4(d) shows an area covered with the p(2 × 2)-N phase only, obtained by annealing the NH$_3$–O$_2$ covered surface to 400 K. There are several bright and dark features in Figure 5.4(d), which were identified as NH molecules and N-vacancies, respectively. The dark depressions can be easily assigned to N vacancies. The bright features are assigned to NH molecules based on the following considerations. The reaction (ammonia oxydehydrogenation) used to form the N layer can produce other possible surface species such as NH$_2$, NH, OH, and H$_2$O. NH$_2$ is not a stable surface species and dissociates well below 300 K and H$_2$O desorbs around
240 K according to a previous TPD measurement (35). Moreover, the bright objects appear spherically symmetric and centered at hollow sites, but NH$_2$ and H$_2$O should appear asymmetric. Both calculations (138) and experimental STM results (139) have shown that OH sits on top of a Pt atom with the OH bond almost parallel to the surface. Finally NH$_3$ can be ruled out by its apparent height and lateral radius. When the surface is annealed to only 300 K, a high coverage of NH$_3$ molecules are observed, which appear circular with heights of ~ 1 Å and with bigger radii than the bright features seen in Figure 5.4(d). The only possibility remaining is NH, which is consistent with a symmetric appearance, a hollow site, and a relatively low apparent height. In addition, after injecting tunneling electrons (2.4 nA, 0.7 V, 4 sec), the bright feature is converted to an N atom within an undisturbed p(2 × 2)-N structure (see Figure 5.5). Thus we conclude that the bright features in Figure 5.4(d) are NH molecules.

**Figure 5.5:** Dissociation of NH on p(2 × 2)-N/Pt(111). (a) before and (b) after dissociation of an NH molecule (indicated by solid arrow). 4 nm × 4 nm, $V_s = 50$ mV, $I_t = 0.5$ nA.

After injecting tunneling electrons (2.4 nA, 0.7 V, 4 sec) into the NH molecule at the top-left corner of Figure 5.5(a), indicated by an arrow, an undisturbed p(2 × 2)-N structure was observed as shown in Figure 5.5(b). The NH molecule was converted
to an H atom (not observed under these conditions) and an N atom, which sits at the same fcc-hollow site.

Structural details of the (√3 × √3)R30°-N and p(2 × 2)-N phases are shown in Figure 5.6. The surface structure shown in Figure 5.6 (a) and (b) is called p(2 × 2), where “p” stands for primitive. In this structure, the lattice of nitrogen layer is orientated along the lattice of Pt(111), where its unit cell is twice as large as that of the underlying Pt(111). Figure 5.6 (c) and (d) show the surface structure designated as (√3 × √3)R30°, where the lattice of nitrogen is rotated by 30° with respect to the Pt(111) lattice and the length of the unit cell is √3 times as large as that of Pt(111). In the honeycomb structure of p(2 × 2)-N, as shown in Figure 5.6(a), there are two distinct types of atoms present with different apparent heights. The brighter dots were identified as N atoms while the less bright ones are Pt atoms. Figure 5.6(b) shows a model corresponding to 5.6(a). The Pt atoms that are visible in the STM images are colored purple in Figure 5.6(b) to distinguish them from the Pt atoms that are not visible. Although theoretically simulated STM images for p(2 × 2)-N on Pt(111) are not available, an STM image of p(2 × 2)-S on Re(0001) reported by Sautet and coauthors (136) is very similar to what we observe here. The (√3 × √3)R30°-N phase shows a more ordinary hexagonal lattice in the STM image as shown in Figure 5.6(c). A corresponding model in Figure 5.6(d) shows that there is only one type of Pt atom present in this phase, all of which are in direct contact with an adsorbed nitrogen atom. As we have shown in Figure 5.2(f), N and O both occupy fcc-hollow sites in the mixed (2 × 2)-N+O phase. The six-membered ring consisting of N, O and Pt shown in Figure 5.2(e) is identical to that in the p(2 × 2)-N phase, indicating that N atoms occupy the same sites as in the mixed (2 × 2)-N+O phase, which are the fcc sites.
Figure 5.6: STM images and models of p(2 × 2)-N and (√3 × √3)R30°-N phases. (a) Honeycomb structure of p(2 × 2)-N (2.5 nm × 2.5 nm, $V_s = 5$ mV, $I_t = 1$ nA). Blue and purple rhombuses indicate the unit cells of p(2 × 2)-N and p(2 × 2)-Pt, respectively. A Pt lattice grid was superimposed on the upper part of the image. (b) Model corresponding to the image shown in (a). Nitrogen and platinum (visible) atoms are colored dark blue and purple, respectively. (c) (√3 × √3)R30°-N phase (2.5 nm × 2.5 nm, $V_s = 20$ mV, $I_t = 1$ nA). Blue rhombus indicates the unit cell. A Pt lattice grid was superimposed on the upper part of the image. (d) Model corresponding to the image shown in (c). N atoms are colored light blue.

If the N atoms in the p(2 × 2)-N phase sit at different sites (for example, hcp-hollow) we expect to see rotated six-membered rings centered at the hollows (see Figure 5.7). A triangle in the six-membered ring connects three Pt atoms that are visible in STM images, and is centered at the hollow of that ring. Such a triangle in Figure 5.7(a) is rotated by 60° compared to that in Figure 5.7(b), if the N atoms sit at different hollow sites. Rotated triangles are not observed in the images. Thus we conclude that N atoms occupy fcc-hollow sites in both p(2 × 2) and (√3 × √3)R30° phases.
Figure 5.7: Model of p(2 × 2)-N with N atom occupying fcc/hcp hollow site. (a) N atom at fcc-hollow site. (b) N atom at hcp-hollow site. Blue and purple rhombuses indicate the unit cells of p(2 × 2)-N and p(2 × 2)-Pt, respectively. Nitrogen atoms are colored blue, Pt (visible) purple, and Pt (2nd layer) brown.

Structural details at the boundaries of the two N phases are shown in Figures 5.8(a) and 5.8(c). Figure 5.8(a) shows the area inside the black square of Figure 5.2(a) where there appear to be chains connecting the (√3 × √3)R30°-N domains. This image shows that the origin of the chain-like feature is the line defect at the boundaries between shifted (√3 × √3)R30°-N domains. Bare Pt atoms that were not adjacent to N atoms at the boundaries appear bright in the images and thus form the chains, as shown in Figure 5.8(b).
Figure 5.8: STM images and models of the defects in the nitrogen phases. (a) Zoomed-in image of the black square in Figure 5.2(a) (2 nm × 2 nm, $V_s = 10$ mV, $I_t = 1$ nA). Solid blue and dashed purple triangles indicate the half unit cell of p(2 × 2)-N and p(2 × 2)-Pt, respectively. Red arrows indicate the Pt atoms at the line defects between two domains of the $(\sqrt{3} \times \sqrt{3})$R30°-N phase. (b) Model corresponding to the area shown in (a). Nitrogen and platinum (visible) atoms are colored blue and purple, respectively. (c) Boundary between $(\sqrt{3} \times \sqrt{3})$R30°-N and p(2 × 2)-N (5 nm × 2.5 nm, $V_s = 20$ mV, $I_t = 1$ nA). Light and dark blue rhombuses indicate the unit cell of $(\sqrt{3} \times \sqrt{3})$R30°-N and p(2 × 2)-N. Distorted pentagons indicate the defects at the boundaries of the two phases. (d) Model corresponding to the area in (c).

The appearance of the p(2 × 2)-N phase also depends on the tunneling condition (bias voltage and gap resistance), as shown in Figure 5.9. The tunneling current was set at 0.6 nA, while the sample bias was varied from Figure 5.9(a-d). All images in Figure 5.9 were obtained at negative sample bias. In Figures 5.9(a) and 5.9(b) only Pt atoms are seen and appear as bright protrusions, and in Figures 5.9(c) and 5.9(d) both Pt and N atoms are observed. Moreover, Pt atoms appear brighter than N atoms in Figure 5.9(c), but darker in Figure 5.9(d). At a given gap resistance, the tunneling current is a measure of the electronic states near the Fermi levels of the surface and the tip. Because the actual atomic structure of the tip is not known, more information on the tip-surface junction is required to explain the observed effects. For example, theoretical calculations of the STM images under different types of tip apexes would be very useful to clarify the appearance change with gap resistance.
**Figure 5.9:** STM images of the p(2x2)-N phase with increasing gap resistance. All images: 3 nm × 3 nm, $I_t = 0.6$ nA. (a) $V_s = -10$ mV (17 MΩ). (b) $V_s = -30$ mV (50 MΩ). (c) $V_s = -50$ mV (83 MΩ). (d) $V_s = -70$ mV (117 MΩ). Blue and black circles indicate the position of N and Pt atoms, respectively. A Pt lattice grid was superimposed on each image.

Changing the polarity of the bias does not invert the contrast of the image, but only alters the relative brightness. As shown in Figure 5.10(a) and 5.10(b), images in the upper panels were obtained at negative sample bias (−), while those in the bottom panels were obtained at positive sample bias (+). In Figure 5.10(a), images are almost identical under (+) and (−) biases. In Figure 5.10(b), the brightness (apparent height) of a Pt atom relative to an N atom is slightly higher under (+) bias than that under (−) bias. However, inversion of contrast was not observed, which means Pt atoms are always brighter than N atoms under either (+) or (−) biases for a 50 MΩ gap resistance.
5.3 Hydrogenation of atomic nitrogen

5.3.1 Appearance of H and NH

Before $\text{H}_2(\text{g})$ exposure, a small amount of hydrogen atoms and NH molecules can also be observed on p(2 × 2)-N/Pt(111) as residual species from ammonia oxydehydrogenation when ammonia is present in excess. A slight excess amount of ammonia was exposed to the surface in order to achieve a pure nitrogen layer free of oxygen. To demonstrate the reproducibility, as well as to clarify the appearance of triangular NH molecules, two sets of images are presented in Figure 5.11. The left and right panels correspond to the results obtained on two different crystals with different azimuthal orientations with respect to the STM. Other than that, the images are identical. The NH molecule has a triangular shape under the scanning conditions, and occupies the fcc-hollow site, which is also where the nitrogen atom sits. H atoms can be easily detected on this p(2 × 2)-N layer, as they appear as protrusions in the STM images. The adsorption site of H on p(2 × 2)-N is the atop site, contrary to that on clean Pt(111) where the three-fold hollow site is preferred. The presence of N shifts the most stable binding site for H from a hollow to an atop site. It is similar to the case when H adsorbs on p(2 × 2)-O on Pt(111), where density function theory

Figure 5.10: Polarity effects on the appearance of p(2 × 2)-N. Both images, 3 nm × 3 nm, $I_t = 0.6$ nA. (a) $V_s = \pm 10$ mV (17 MΩ); (b) $V_s = \pm 50$ mV (50 MΩ). Blue and black circles indicate the position of N and Pt atoms, respectively.
(DFT) calculations have shown that the atop site becomes more preferred (140-141). Figures 5.11(e) and 5.11(f) show the appearance of NH (blue arrow) and H (white arrow). Figures 5.11(a) and 5.11(b) are the atomically resolved images on clean Pt(111), which help to assign the lattice orientation. Figures 5.11(c) and 5.11(d) are models of the p(2 × 2)-N structure drawn according to the orientation of each single crystal, which facilitate the interpretation of the adsorption site in other images. The half unit cell of the (2 × 2)-N (blue) and (2 × 2)-Pt (purple) structures are shown, which are the up- and down-pointing triangles centered at a hollow site (blue triangle) or a nitrogen atom (purple triangle), respectively. Such up- and down-pointing triangles reflect the azimuthal orientations of the crystal. The triangular shape of the molecule can be understood by the perturbation of the electronic properties of the nearest Pt atoms by the NH. As illustrated in Figures 5.11 (e) and 5.11(f), the triangle is centered at the NH molecule and spreads to the three nearest “visible” Pt atoms. Here “visible” refers to the Pt atom that is visible in the p(2 × 2)-N honeycomb structure, which has been discussed earlier in section 5.2.3. H atoms, although present in pairs in the two images shown in Figure 5.11, are not necessarily always present in pairs and single H atoms and groups of more than two are also observed.
Figure 5.11: STM images of NH and H on p(2 × 2)-N/Pt(111). (a-b) STM images of clean Pt(111) surfaces at two orientations. (a: 2.5 nm × 2.5 nm, $V_s = 2$ mV, $I_t = 6.45$ nA. b: 2.5 nm × 2.5 nm, $V_s = 2$ mV, $I_t = 6$ nA). (c-d) Models showing the p(2 × 2)-N on Pt(111) corresponding to the orientations in (a) and (b). Blue and purple triangles indicate the half unit cell of N(2 × 2) and Pt(2 × 2), respectively. (e-f) STM images of NH and H on p(2 × 2)-N covered Pt(111). The blue and white arrows indicate an NH molecule and a H atom, respectively. A honeycomb lattice is superimposed on the p(2 × 2)-N with blue and white circles indicating N and Pt atom, respectively. (e: 5 nm × 5 nm, $V_s = 100$ mV, $I_t = 0.5$ nA. f: 5 nm × 5 nm, $V_s = 50$ mV, $I_t = 1$ nA)

5.3.2 Inhomogeneous NH layer

After exposing the nitrogen covered surface to hydrogen gas at 300 K, we observed an increase in the number of NH molecules as shown in Figure 5.12. Before exposing to H$_2$ gas, there are several residual NH molecules on the surface, as indicated by blue arrows in Figure 5.12(a). H atoms are also present on the surface, one of which is indicated by the white arrow, which is consistent with images shown in Figures 5.11(e) and 5.11(f). Notice the brightest protrusions are excess ammonia,
similar to those observed in Figure 5.4(a). Images of Figures 5.12(b-d) show the topography of the surface after exposing to hydrogen gas. Two types of NH molecules are clearly distinguished by their appearances: scattered molecules and molecules forming an island. Scattered NH molecules are easily identified by their characteristic triangular shape. NH islands, however, cannot be identified at a first glance. The atomically resolved image inside the island shows a well ordered (2 × 2) structure (Figures 5.12(c-d)). The bright dots inside the island are not NH molecules but resemble the Pt(2 × 2) lattice, which means the bright dots seen in Figure 5.12(d) are Pt atoms. To clarify this point, we expand the Pt lattice from the p(2 × 2)-N (where the Pt and N atoms can be distinguished and labelled accordingly) to the (2 × 2) island. As shown in Figure 5.12(d), the black grid indicates the Pt(2 × 2) lattice and matches the positions where the bright dots sit. NH vacancies inside the island are imaged as holes, which are not in line with the bright dots but the hollow sites of the (2 × 2) lattice grid. We label the Pt atoms as white circles, NH molecules as blue dots, and N atoms (which appears as NH vacancies inside the island) as blue circles in Figure 5.12(d), which reveals the detailed structure within the island. There are very few NH islands present on the surface and they are found to grow to large sizes, up to 40 nm².
Figure 5.12: STM images of the p(2x2)-N before and after hydrogenation. (a) p(2 × 2)-N before exposing to H2(g). 15 nm × 15 nm, V_s = 100 mV, I_t = 1 nA. (b-d) NH islands after exposing to H2(g). (b: 50 nm × 50 nm, V_s = 50 mV, I_t = 1 nA. c: Zoomed-in image of the black square in b. 10 nm × 10 nm, V_s = 50 mV, I_t = 1 nA. d: 5 nm × 5 nm, V_s = 50 mV, I_t = 1 nA.) Black grid indicates the Pt(2 × 2) lattice. Open black circles indicate the Pt atoms, while open and filled blue circles indicate N and NH, respectively.

The formation of NH islands and scattered NH molecules indicate an inhomogeneous hydrogenation process. Moreover, as we increase the H2 exposure, the density of NH islands does not grow accordingly, but the number of scattered NH molecules does. A previous RAIRS study found that at the saturation coverage of NH, only about 60 to 68 % of the surface N atoms were converted to NH. From the STM observations, the existence of NH islands (though at very low density) excludes the possibility that the repulsive interaction between NH molecules makes the (2 × 2)-NH island less favorable than a mixed N and NH. Since the p(2 × 2)-N layer is homogeneous across the surface, the origin of this inhomogeneity is puzzling. Furthermore, the reason why all the N atoms cannot be converted to NH is unclear.
To understand this result, we shall look at the process in more detail. The hydrogenation of chemisorbed N atoms on the surface is expressed as the following:

$$H_2(g) + 2N_{\text{ad}} \rightarrow 2NH_{\text{ad}}$$ (5.1)

It can be divided into three steps, dissociative adsorption of $H_2(g)$, H diffusion across the surface, and surface reaction of H and N. Considering that H diffusion at 300 K is assumed to be very fast and would not affect the reaction rate, the process can be simplified to two steps:

$$H_2(g) \rightarrow 2H_{\text{ad}}$$ (5.2)

$$H_{\text{ad}} + N_{\text{ad}} \rightarrow NH_{\text{ad}}$$ (5.3)

Previous studies on the same system reveal that the formation of NH follows first order kinetics at 200 K. The effective rate of NH formation is independent of the hydrogen coverage and solely depends on the nitrogen coverage. This is reasonable considering the high mobility of hydrogen on the surface. (36) The reaction is not limited by hydrogen coverage as long as there is some hydrogen present on the surface. From the TPD results, the $N_2$ recombinative desorption peak from the $(2 \times 2)$-N phase starts at 400 K, which indicates that at 300 K the N atoms sit at the stationary fcc-hollow sites without diffusion across the surface. The reaction path of NH formation is the movement of H toward the stationary N. If the hydrogen coverage does not affect the rate of NH formation and the N atoms are homogeneous across the surface in the p$(2 \times 2)$ phase, then why do we observe such an inhomogeneous growth of the NH layer? I think the dissociative adsorption of $H_2(g)$ plays an important role here. Although dissociative adsorption of $H_2$ molecules on transition metal surfaces is generally considered a non-activated process, it does not necessarily mean that the rate of adsorption is fast. The rate of adsorption depends on the sticking probability.
Chapter 5: Atomic Nitrogen on Pt(111)

(S). Hydrogen gas adsorbs on the Pt(111) surface with a low initial sticking probability \(S_0 = 0.1\) at 150 K (Ref. (142)), and the presence of atomic nitrogen presumably further suppresses it. Studies on the interaction of \(\text{H}_2\) with nitrogen covered Pt(111) are scarce, and to our knowledge only a few published works have investigated this system (33, 35-36). This is probably because of the difficulty in obtaining a clean and pure atomic nitrogen layer on Pt(111), as has been discussed in section 1.1.2. Nevertheless, nitrogen atoms were reported to reduce the \(\text{H}_2\) adsorption rate on Ru(0001) (143), Ni(100) (144), and Pt(110) (145). Similar suppression of hydrogen uptake has been observed on oxygen covered Pt(111) as well (146). A molecular dynamics study of the hydrogen dissociation on p(2 \times 2)-O/Pt(111) indicates that the preferred dissociation site are the atop sites of the Pt atoms that are not bonded to the adsorbed oxygen atoms (equivalent to the “visible” Pt atom in the p(2 \times 2)-N honeycomb structure). In addition, the most stable binding site for an H atom shifts from the hollow site (on the clean surface) to the atop in the presence of p(2 \times 2)-O layer (141). Considering the similarity of nitrogen and oxygen bonding to metals, we expect that on a p(2 \times 2)-N covered surface, a hydrogen molecule would behave similarly. The picture for \(\text{H}_2\) dissociation on p(2 \times 2)-N/Pt(111) is thus as follow: \(\text{H}_2\) molecule landing on top of a Pt atom can either proceed to dissociation (oriented in a favorable geometry for dissociation, such as parallel), or be scattered back (unfavorably oriented, such as end-on) depending on the incident orientation. Because not all the incident molecules have the favored orientation, direct dissociation is slow. The situation is different at the steps, where higher reactivity is generally observed because of stronger adsorbate-substrate interaction at low-coordinated sites. Studies on the hydrogen dissociation on stepped Pt surfaces indicate that an additional indirect channel appears at low kinetic energy (147). In our case,
hydrogen exposure via a nozzle at 300 K ideally would yield motion along the molecular beam axis with a low kinetic energy of 64 meV ($E_{\text{kin}}=5/2*RT$). Thus the indirect channel for $H_2$ dissociation at steps has to be taken into account. Islands are formed where the indirect pathway prevails over the direct one, while scattered NH molecules are formed where the direct pathway predominates. The influence of “direct” and “indirect” pathways of dissociative chemisorption on the dynamics in the development of surface structures has been discussed by Salanov and co-authors (148-149). In their Monte Carlo simulations, at $S_{\text{indir}} / S_{\text{dir}} \geq 1.0$ the island type of adsorption dominates. The concentration of the adsorption islands is low and they grow to large size. This is consistent with our observation of large NH islands with a small density. As the indirect channel is facilitated at the steps, the formation of NH islands, as shown in Figure 5.12(b) can be explained in a straightforward way. In contrast, when the direct pathway dominates, a random distribution of NH molecules is observed.

The dynamics of $H_2$ dissociation on p(2 × 2)-N on Pt(111) also explains why only about 60% of the surface N can be converted to NH. Because the adsorbed nitrogen atoms reduce the activity of the nearest neighbor “invisible” Pt atoms, it is reasonable to assume that most of the dissociative adsorption on the terraces occurs at the “visible” Pt atom on the p(2 × 2)-N surface. Forming an NH molecule alters the electronic properties of those “visible” Pt atoms as can be seen by the triangular shape in STM images. The active Pt atoms are thus deactivated by forming an NH molecule, similar to a site blocking effect. Considering the small size of NH compared to that of the Pt atom, it is not a spatial blocking, but more of an electronic effect, and possibly may increase the dissociation barrier. Once the active Pt atoms are deactivated, the direct channel of $H_2$ adsorption is locally blocked around an NH molecule. As a result,
an H$_2$ molecule has to find an active Pt atom somewhere else to dissociate, and then an H atom can diffuse across the surface until being consumed by an N atom. Moreover, on Pt(111), hydrogenation of atomic N does not proceed beyond NH. Adding a second or third H atom to form NH$_2$ or NH$_3$ is not achievable due to a high activation barrier. Michaelides and Hu reported a 1.31 eV reaction barrier for NH + H → NH$_2$ on Pt(111) in their DFT calculation (150). Consequently there is no outlet channel for a product like NH$_3$ to desorb from the surface, and the active site for H$_2$ dissociation cannot be recovered. As the hydrogenation proceeds and the coverage of NH increases, fewer and fewer sites are available for H$_2$ to dissociate via the direct channel. Because one NH molecule blocks three Pt atop sites, an ideal surface (no defect or step) is completely blocked for H$_2$ dissociation with 50% of the N converted to NH. Thus the ~60% conversion from N to NH observed in RAIRS and XPS is a combination of 50% conversion on terraces (N converts to scattered NH) and 100% conversion near step edges (N converts to NH within the island).

5.4 Conclusion

In this chapter, experimental measurements of the surface morphology of atomic nitrogen on the Pt(111) surface, as well as the NH layer are presented. Coadsorbed N and O form a mixed (2 × 2)-N+O phase at high coverages. While both atoms appear as depressions, the O atoms appear deeper than the N atoms, which agrees with theoretical simulations (11). Isolated N atoms on Pt(111) appear as depressions in the STM images at low coverages. Dense N islands are present in two phases, (2 × 2) and (√3 × √3)R30°, at high coverages. The (√3 × √3)R30° phase converts to the (2 × 2) phase as the temperature increases from 360 to 400 K due to an N coverage decrease associated with the onset of N$_2$(g) desorption. The STM images reveal that under the optimized preparation conditions, the N layer
formed by ammonia oxydehydrogenation is almost entirely free of other adsorbed species. The impurities observed include excess NH$_3$, NH and H. Most of the defects in the N overlayer are at the boundaries between the two phases or at the boundaries between domains of the same phase. Within a domain the defect density is as low as 0.8%, while domain sizes as big as 20 nm × 20 nm were observed. By direct measurements at Pt step edges, the nitrogen atoms were found to occupy fcc-hollow sites; this information was not available from the previously observed LEED patterns. Hydrogenation of the N layer forms scattered NH molecules and islands of NH, which can be understood as a result of a direct and indirect channel for H$_2$ dissociative adsorption. Formation of NH hinders the dissociation of H$_2$, presumably by increasing the dissociation barrier as it alters the electronic states of the Pt atoms that are active for dissociating H$_2$. 
Chapter 6: Manipulation of Individual Atoms and Molecules

In this chapter, manipulation of individual atoms and molecules is discussed. A general description of how the action spectra were obtained is provided in Section 6.1. The dissociation of NH molecules induced by tunneling electrons is discussed in Section 6.2. Hydrogen atom hopping is discussed in Section 6.3. Section 6.4 describes the mathematical model used to fit the spectra. Section 6.5 discusses the fitted spectra and the mechanisms revealed for each reaction. Section 6.6 closes the chapter with conclusions.

6.1 Experimental

The action spectra were taken with the method described in Section 2.4.2. For each action spectrum, the initial tunneling junction was set with certain values of $I_0$ and $V_0$ in order to keep the total tunneling current fixed while varying the applied bias voltage. Specific values of the setting parameters used for NH(ND) dissociation and H(D) hopping are summarized in Table 6.1.

<table>
<thead>
<tr>
<th></th>
<th>$V_0$(V)</th>
<th>$I_0$(nA)</th>
<th>$I_e$(nA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH dissociation</td>
<td>0.1</td>
<td>1.2 – 3.3</td>
<td>14</td>
</tr>
<tr>
<td>ND dissociation</td>
<td>0.1</td>
<td>1.3 – 5.3</td>
<td>19</td>
</tr>
<tr>
<td>H hopping</td>
<td>0.1</td>
<td>0.8 – 1.1</td>
<td>2.8</td>
</tr>
<tr>
<td>D hopping</td>
<td>0.1</td>
<td>0.6 – 0.9</td>
<td>2.0</td>
</tr>
</tbody>
</table>
NH(ND) dissociations were conducted on islands after hydrogenation, which ensures the collection of data over a wide bias range as there are a sufficient number of NH(ND) molecules in the scanning area. Hydrogen atom hopping was measured prior to H₂ exposure, and action spectra were obtained with the residual H atoms on the p(2 × 2)-N surface. This was done to minimize the possible effect of NH on the H hopping. Deuterium atom hopping was measured after dissociating an ND island, where D atoms are occasionally dropped on the surface as the product of dissociation. A schematic drawing illustrating the action spectra processes is shown in Figure 6.1.

![Figure 6.1: Schematic drawing of the surface during action spectroscopy](image)

### 6.2 NH(ND) dissociation

As has been discussed in Section 5.2.1, O atoms can be imaged differently with a clean or a modified tip. The appearance of an NH molecule also shows a tip-state dependence. It appears as a bright protrusion under a modified tip, and changes to a triangular shape with a clean tip as shown in Figures 6.2(a) and 6.2(b). Although a
modified tip generally provides better image resolution, in this chapter only action spectra that were obtained with a clean tip are presented as a clean tip is more stable and more reliable for this purpose. Figures 6.2(b) to 6.2(d) show a series of images taken in the process of dissociating individual NH molecules. Two NH molecules are indicated by blue arrows in Figure 6.2(a) and are imaged with a modified tip. Scanning the same area with a clean tip generates the image shown in Figure 6.2(b), with triangular-shaped NH molecules. Placing the tip above the NH molecule identified by the yellow arrow in Figure 6.2(b) and applying a pulse of 0.7 V, 1 nA, 4 seconds, the H atom is removed from the NH, as shown in Figure 6.2(c). Repeating the same pulse on the NH molecule on the right in Figure 6.2(c) removes the H atom as well. Figures 6.2(c) to 6.2(d) recorded this reaction. An unperturbed p(2 × 2)-N structure is resolved after dissociating the two NH molecule, which is shown in Figure 6.2(d).

![Figure 6.2: NH dissociation induced by tunneling electrons. (a-b) STM images of two NH molecules on p(2 × 2)-N under different tip states (c-d) STM images after dissociating the NH molecules. All images: 5 nm × 5 nm, $V_s = 80$ mV, $I_t = 0.6$ nA. See text for detail.](image)

“Writing with an STM tip” is inspired by the pioneering work of Eigler and Schweizer, where they wrote “IBM” with Xe atoms on Ni(110) (52). Subsequently,
various logos have been written for various institutions by STM researchers, thus bringing art to the atomic world. Here we show another example of writing letters with an STM tip: by selective dissociation of NH molecules, “UIC” is formed on an NH island. Because we are scientists, rather than artists, we are interested in probing the mechanism of such a reaction of a single molecule. Action spectroscopy is then conducted and the results are discussed in Section 6.4 and 6.5.

![Image of STM writing](image_url)

**Figure 6.3:** “UIC” formed by selective dissociation of NH molecules. 20 nm × 10 nm, $V_s = 50$ mV, $I_t = 1$ nA.

### 6.3 H(D) hopping

On the p(2 × 2)-N surface, H sits on top of a Pt atom and appears as a protrusion, which makes it easier to detect and monitor with STM even at very low coverages. In Contrary, H atom on a clean surface usually appears as depression and occupies an fcc-hollow site as revealed by STM observations (151-153), which makes it difficult to distinguish H from impurities such as carbon and oxygen at low coverages. We also studied the motion induced by tunneling electrons of H atoms on the N covered surface and found that they respond to the pulses by hops. In Figure 6.4, the left panels show a series of images of the H hopping, while the right panels
show models corresponding to each image on its left. In the top image, several H atoms are present on the p(2 × 2)-N layer, where blue and white circles superimposed in the middle of the image indicate the (2 × 2) lattice of N and Pt, respectively. Only the Pt lattice (white circles) is used in Figure 6.4(b-d) in order to provide a better view. The tip was placed over the H atom at the right side of the image, shown in Figure 6.4(a), where a pulse (−0.24 V, 1.0 nA, 4 second) was applied. As a result, the H atom hops along the Pt(2 × 2) and moves to the nearest atop site (shown in Figure 6.4(b)). Applying pulses to the same H atom results in a series of hops, and each hop moves the H atom one Pt(2 × 2) lattice constant away. Hops are found to proceed with equal probability in all three directions. However, if the Pt atom is occupied by another H atom, it hops to another empty atop site.

**Figure 6.4:** STM images and models of the H hopping. (a-d) Left panel: STM image of the H hopping. Blue and white circles indicate the p(2 × 2)-N and Pt(2 × 2) lattice, respectively. (5 nm × 5 nm, $V_s = 50$ mV, $I_t = 0.5$ nA). Right panel: Models corresponding to each image.
6.4 Theoretical fitting of the action spectra

In practice, an action spectrum requires sampling a wide range of applied bias voltage (above and below thresholds) to get a relatively accurate value of the threshold. When the bias voltage is pushed to the lower limit for a given reaction, the reaction sometimes becomes undetectable within a reasonable period of time. Fitting the action spectra with a theoretical model can help better identify the threshold when only a limited amount of data is available. Moreover, the theoretical approach has the advantage of determining other parameters that affects the reaction yield, for example, the reaction rate.

The theory behind action spectroscopy has been developed by Paulsson and Ueba in a series of publications (54, 57, 154-155). In our studies, we utilized the model developed by Motobayashi et al. (154) for the spectral fitting. The mathematical model and physical descriptions are as follows:

The reaction yield is defined as

\[ Y(V) = \frac{R(V)}{I_{\text{tot}}(V) / e}, \]  

(6.1)

where \( R(V) \) is the reaction rate at a given bias voltage, \( I_{\text{tot}}(V) \) the total tunneling current (including elastic and inelastic tunneling), and \( e \) the elementary charge carried by a single electron. \( R(V) \) is defined as,

\[ R(V) = k(I_{\text{in}}(V) / e)^n, \]  

(6.2)

where \( k \) is the rate constant at a certain temperature, \( I_{\text{in}}(V) \) the inelastic tunneling current, and \( n \) the reaction order (here it is defined as the number of tunneling electrons required for inducing the motion). For single-electron inelastic tunneling events (\( n = 1 \)), \( k \) is expressed in terms of a dimensionless branching ratio of elementary processes involved. The energy of incident tunneling electrons is
expressed in the unit of electron volt (eV), which depends on the applied bias voltage. For a vibrational mode \( \nu \) associated with energy \( \Omega \), electrons with energy \( \geq \Omega \) can excite the mode which result in an observable inelastic tunneling current \( I_{\text{in}}(V) \). Given that \( d^2I_{\text{in}}/dV^2 \) directly reflects the vibrational DOS \( \rho(\Omega) \) near the threshold \( eV = \Omega \) (57), if we assume a Gaussian function (GF) for the effective vibrational DOS \( \rho(\Omega) \) of the vibrational mode \( \nu \), \( I_{\text{in}}(V) \) is given by double integration of the Gaussian function (GF) with respect to bias voltage \( (V) \) multiplied by the inelastic conductance \( (\sigma_{\text{in}}) \),

\[
I_{\text{in}}(V) = \sigma_{\text{in}} f(V, \Omega, \gamma),
\]

(6.3)

\[
f(V, \Omega, \gamma) = \frac{\gamma}{\sqrt{2\pi}} \exp\left(-\frac{(V-\Omega/e)^2}{2\gamma^2}\right) + \frac{(V-\Omega/e)}{2} \left(1 + \text{erf}\left(\frac{(V-\Omega/e)}{\sqrt{2}\gamma}\right)\right),
\]

(6.4)

\[
\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-t^2) / dt,
\]

(6.5)

The Gaussian distribution for the vibrational DOS in most cases provides the best agreement with experiments as it takes into account all the possible contributions to the broadening factor \( (\gamma) \) (thermal, instrumental, and intrinsic lifetime broadening). We then get the following expression for the reaction yield,

\[
Y(V) = K \frac{f(V, \Omega, \gamma)^n}{V},
\]

(6.6)

where \( K \) is an effective prefactor(dimensionless) determined by the elementary process involved in a given event (see Section 6.5), and is proportional to \( k \). Equation (6.6) can be extended to,

\[
Y(V)_{\text{tot}} = \sum_i K_i \frac{f(V, \Omega_i, \gamma_i)^n}{V},
\]

(6.7)
when multiple vibrational modes are taken into account for their contribution to the total reaction yield.

Using the described model, fitted curves are shown in Figure 6.5(c) for NH(ND) dissociation and 6.6(c) for H(D) hopping.

**NH(ND) dissociation**

In Figure 6.5(c), a threshold was found at 0.43 eV for NH dissociation, where both the experimental data (blue squares) and the fitted spectrum (blue curve) are shown. Compared to the values of the normal modes of NH on Pt(111), as shown in Figure 6.5(b), the dissociation is mediated by the internal stretching mode of NH ($\nu_s(N\text{-}H)$), which is 0.427 eV from theoretical calculations (138) and 0.411 eV from experimental measurement (35). The action spectrum for ND dissociation shows two thresholds, at 0.320 eV and 0.745 eV. The vibrational mode associated with 0.320 eV is the ND internal stretching ($\nu_s(N\text{-}D)$), with an isotope shift of −0.11 eV compared to $\nu_s(N\text{-}H)$. The value of 0.745 eV corresponds to a combination of internal stretching and frustrated rotation ($2\nu_s(N\text{-}D) + L(N\text{-}D)$). Values of the measured reaction yield are summarized in Table 6.1, with standard errors included. For a reaction that is difficult to observe with AS, the error value is not available due to the limited number of observed events. For instance, the error value is not listed in the ND dissociation at bias voltages of 0.36 and 0.40 V.
Figure 6.5: Schematic models and action spectra of NH(ND) dissociation. (a) Schematic model showing the excitation of NH stretching and NH bond breaking. (b) Normal modes of NH on Pt(111). *Values corresponding to each normal mode of NH were obtained from ref.(138) (c) Action spectra of NH (blue) and ND (orange) dissociation. (Fitted parameters for NH: $\Omega = 430$ meV, $K = 10^{-7.23}$, $\gamma = 15$ mV. Fitted parameters for ND: $\Omega_1 = 320$ meV, $K_1 = 10^{-9.35}$, $\gamma_1 = 6$ mV; $\Omega_2 = 745$ meV, $K_2 = 10^{-7.6}$, $\gamma_2 = 4$ mV.)
Table 6.2 Measured reaction yield (per electron) at various bias voltages for NH(ND) dissociation.

<table>
<thead>
<tr>
<th>Bias Voltage (V)</th>
<th>Yield per electron (Log(Y))</th>
<th>Bias Voltage (V)</th>
<th>Yield per electron (Log(Y))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.42</td>
<td>-9.44 ± 0.16</td>
<td>0.36</td>
<td>-10.64 ± N/A</td>
</tr>
<tr>
<td>0.44</td>
<td>-9.38 ± 0.11</td>
<td>0.40</td>
<td>-10.60 ± N/A</td>
</tr>
<tr>
<td>0.46</td>
<td>-8.37 ± 0.20</td>
<td>0.42</td>
<td>-9.74 ± 0.09</td>
</tr>
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<td>0.48</td>
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<td>0.46</td>
<td>-9.90 ± 0.32</td>
</tr>
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<td>0.50</td>
<td>-9.54 ± 0.03</td>
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</tr>
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</tr>
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<td>-7.75 ± N/A</td>
<td>0.78</td>
<td>-9.59 ± 0.27</td>
</tr>
<tr>
<td>0.64</td>
<td>-7.48 ± N/A</td>
<td>0.78</td>
<td>-9.09 ± 0.19</td>
</tr>
<tr>
<td>0.66</td>
<td>-7.41 ± N/A</td>
<td>0.80</td>
<td>-7.84 ± 0.50</td>
</tr>
<tr>
<td>0.68</td>
<td>-7.62 ± N/A</td>
<td>0.90</td>
<td>-8.11 ± 0.68</td>
</tr>
<tr>
<td>0.70</td>
<td>-7.67 ± 0.33</td>
<td>1.00</td>
<td>-8.16 ± 0.15</td>
</tr>
<tr>
<td>0.80</td>
<td>-7.70 ± 0.28</td>
<td>1.10</td>
<td>-8.34 ± 0.27</td>
</tr>
<tr>
<td>0.90</td>
<td>-7.57 ± 0.08</td>
<td>1.20</td>
<td>-8.33 ± 0.30</td>
</tr>
<tr>
<td>1.00</td>
<td>-7.71 ± 0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.20</td>
<td>-7.43 ± 0.15</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**H(D) hopping**

Experimental data (blue square) and the fitted spectrum (blue curve) are shown in Figure 6.6(c) for H atom hopping, wherein a threshold was found at 0.272 eV. Compared to the values of the normal modes of H on Pt(111), as shown in Figure 6.6(b), the hopping is mediated by the stretching mode of Pt–H (ν(Pt–H)). Substituting H by D, the action spectrum for D hopping is shown as the orange triangles and curve in Figure 6.6(c). The fitted curve again has two thresholds, at 0.188 and 0.245 eV. The vibrational mode associated with 0.188 eV is the Pt–D stretch (ν(Pt-D)), with an isotopic shift of −0.084 eV compared to ν(Pt–H). The value
of 0.245 eV corresponds to a combination mode of stretch and frustrated translation \((\nu(\text{Pt-D}) + T_\parallel(\text{Pt-D}))\). Table 6.2 summarizes the values of the measured reaction yields at each bias voltage applied, which are used to construct the shown action spectra in Figure 6.6(c).

**Figure 6.6:** Schematic models and action spectra of H(D) hopping. (a) Schematic model showing the excitation of the Pt–H stretching mode and the motion of H hopping. (b) Normal modes of H on Pt(111). *Values corresponding to each normal mode of NH were obtained from ref.(138) (c) Action spectra of H (blue) and D (orange) hopping. Fitted parameters are, H: \(\Omega = 272\) meV, \(K = 10^{-5.55}\), \(\gamma = 13\) mV; D: \(\Omega_1 = 188\) meV, \(K_1 = 10^{-7.6}\), \(\gamma_1 = 4\) mV, \(\Omega_2 = 245\) meV, \(K_2 = 10^{-5.8}\), \(\gamma_2 = 4\) mV.
Table 6.3 Measured reaction yield (per electron) at various bias voltages for H(D) hopping.

<table>
<thead>
<tr>
<th>H hopping</th>
<th>D hopping</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bias Voltage (V)</td>
<td>Yield per electron (Log(Y))</td>
</tr>
<tr>
<td>-0.25</td>
<td>-8.59 ± 0.26</td>
</tr>
<tr>
<td>-0.26</td>
<td>-7.96 ± 0.13</td>
</tr>
<tr>
<td>-0.27</td>
<td>-7.50 ± 0.07</td>
</tr>
<tr>
<td>-0.275</td>
<td>-7.51 ± 0.31</td>
</tr>
<tr>
<td>-0.28</td>
<td>-6.72 ± 0.16</td>
</tr>
<tr>
<td>-0.29</td>
<td>-6.45 ± N/A</td>
</tr>
<tr>
<td>-0.3</td>
<td>-6.08 ± 0.21</td>
</tr>
<tr>
<td>-0.31</td>
<td>-6.56 ± 0.22</td>
</tr>
<tr>
<td>-0.32</td>
<td>-6.47 ± 0.42</td>
</tr>
<tr>
<td>-0.33</td>
<td>-6.45 ± 0.29</td>
</tr>
<tr>
<td>-0.35</td>
<td>-6.20 ± 0.37</td>
</tr>
</tbody>
</table>

6.5 Mechanism of the vibrational mediated reaction

In addition to assigning the vibrational modes that are responsible for the motion observed, with the fitted action spectra we can determine the effective prefactor $K_{\text{eff}}$, which is the branching ratio determined by the rate of elementary process involved. In this section the mechanism revealed by AS for each of the observed motions is discussed.
Figure 6.7: Schematic drawing of the mechanism of NH(ND) dissociation. Dissociation proceeds by direct excitation of the reaction coordinate (RC) mode followed by tunneling through the barrier.

As shown in Figure 6.5(c), a clear suppression in the reaction yield is observed for ND dissociation. The $K_{\text{eff}}$ determined by the fitted spectra are $10^{-7.23}$ (NH diss.) and $10^{-9.35}$ (ND diss.). Therefore, the calculated value of the kinetic isotope effect (KIE) is, $K_{\text{eff}}(\text{NH})/K_{\text{eff}}(\text{ND}) \approx 10^{-7.23}/10^{-9.35} = 132$. Such a large value indicates that tunneling is involved, which accounts for the suppression of the reaction probability when D is substituted for H. Because the excited NH stretching mode is along the reaction coordinate, the mechanism involves direct excitation of the NH(ND) stretching mode, followed by tunneling through the barrier as shown in Figure 6.7. In this case, the effective prefactor $K_{\text{eff}}$ is proportional to the ratio of the rate of tunneling to the rate of damping (155). As shown earlier, the effective prefactor $K_{\text{eff}}(\text{NH})$ for NH dissociation is $10^{-7.23}$. If we assume that the damping rate $\Gamma_{\text{damping}}$ is about $10^{11}$ s$^{-1}$ by electron-hole excitation (156), the estimated tunneling rate for NH dissociation is $\approx 6 \times 10^{3}$ s$^{-1}$, while for ND dissociation, the rate of tunneling is $\approx 45$ s$^{-1}$.

H(D) hopping differs from NH(ND) dissociation as the activated mode is not along the reaction coordinate (parallel to the surface in the case of hopping). Thus a different mechanism is proposed as shown in Figure 6.8. Two cases are discussed here. Figure 6.8(a) shows the mechanism when the excitation energy is greater than the hopping barrier, which accounts for the H(D) hopping with energy larger than 245 meV. The calculated value of KIE is, $K_{\text{eff}}(\text{H})/K_{\text{eff}}(\text{D}) \approx 10^{-5.55}/10^{-5.8} = 1.78$. Comparable rates for H and D hopping indicate that the activation energy is sufficient to overcome the hopping barrier, where the Pt–H(D) stretch is first excited by tunneling electrons and its energy is transferred to the frustrated translation mode via
anharmonic coupling. In such a case, the observed effective prefactor $K_{\text{eff}}$ is proportional to the ratio of the rate of intermode transition to the rate of damping. Similarly by assuming a damping rate of $10^{11}$ s$^{-1}$, the intermode transition rate is estimated to be $3 \times 10^5$ s$^{-1}$ and $1.6 \times 10^5$ s$^{-1}$ for H and D, respectively. The second case is shown in Figure 6.8(b), where the excitation energy is lower than the reaction barrier. When reducing the bias voltage to a value lower than 245 mV, the tunneling electrons that cannot excite the $\nu$(Pt–H) mode excite the $\nu$(Pt-D) mode. Coupling of $\nu$(Pt-D) to the frustrated translation mode excites $T_{\parallel}$(Pt-D) from the vibrational ground state to a higher level but with energy below the hopping barrier, and tunneling is required for the excited D to hop to the next site. The reaction rate thus must include an additional term for tunneling. As shown in Figure 6.8(b), the effective prefactor $K_{\text{eff}}$ is proportional to $(\Gamma_{\nu \rightarrow \text{RC}} \times \Gamma_t)/ \Gamma_{\text{damping}}$. A numerical value of $0.016$ s$^{-1}$ is obtained for $\Gamma_t$ (the rate of D tunneling through the hopping barrier), by assuming $10^{11}$ s$^{-1}$ for $\Gamma_{\text{damping}}$ (e-h excitation), $1.6 \times 10^5$ s$^{-1}$ for $\Gamma_{\nu \rightarrow \text{RC}}$ (obtained as described earlier), and $10^{-7.6}$ for $K_{\text{eff}}$ (determined from the action spectrum fitting). With our observation of the hopping of D atoms with energies above and below the barrier, the hopping barrier for D on the p(2 × 2)-N on Pt(111) is estimated to be between 0.180 and 0.245 eV. Table 6.4 summarizes the fitted parameters of the action spectra. The corresponding vibrational modes, the elementary processes that account for the motions, and the estimated rates are summarized as well.
Figure 6.8: Schematic drawings of the mechanisms of H(D) hopping. Excitation of the mode $\nu$ and coupling with the RC mode: (a) when the excitation energy is greater than the barrier, the atom goes over the barrier. (b) when excitation energy is lower than the barrier, the atom tunnels through the barrier.

Table 6.4 Summary of the fitted parameters from the action spectra with the corresponding vibrational modes, elementary processes, and estimated rates.

<table>
<thead>
<tr>
<th>Fitted parameter for AS</th>
<th>$\Omega$ (meV)</th>
<th>$K_{eff}$</th>
<th>$\gamma$ (mV)</th>
<th>Corresponding vib. mode</th>
<th>Rate (s$^{-1}$)</th>
<th>(process)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH dissociation</td>
<td>430</td>
<td>10$^{-7.23}$</td>
<td>15</td>
<td>$\nu_1$(N–H)</td>
<td>$6 \times 10^3$</td>
<td>($\Gamma_{tunneling}$)</td>
</tr>
<tr>
<td></td>
<td>745 ($\Omega_1$)</td>
<td>10$^{-7.6}$</td>
<td>6</td>
<td>$2\nu_4$(N–D)+L(N–D)</td>
<td>$2.5 \times 10^3$</td>
<td>($\Gamma_{tunneling}$)</td>
</tr>
<tr>
<td></td>
<td>320 ($\Omega_2$)</td>
<td>10$^{-9.35}$</td>
<td>4</td>
<td>$\nu_1$(N–D)</td>
<td>45</td>
<td>($\Gamma_{tunneling}$)</td>
</tr>
<tr>
<td>ND dissociation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H hopping</td>
<td>272</td>
<td>10$^{-5.55}$</td>
<td>13</td>
<td>$\nu$(Pt–H)</td>
<td>$3 \times 10^5$</td>
<td>($\Gamma_{\nu \rightarrow RC}$)</td>
</tr>
<tr>
<td></td>
<td>245 ($\Omega_1$)</td>
<td>10$^{-5.8}$</td>
<td>4</td>
<td>$\nu$(Pt–D)+T$_1$(Pt–D)</td>
<td>$1.6 \times 10^5$</td>
<td>($\Gamma_{\nu \rightarrow RC}$)</td>
</tr>
<tr>
<td></td>
<td>188 ($\Omega_2$)</td>
<td>10$^{-7.6}$</td>
<td>4</td>
<td>$\nu$(Pt–D)</td>
<td>0.016</td>
<td>($\Gamma_{tunneling}$)</td>
</tr>
</tbody>
</table>
6.6 Conclusion

In this chapter we have presented results for two types of single molecule reactions. With action spectroscopy, the active vibrational modes associated with each reaction were determined. With a theoretical model, fitted curves provide us with an estimate of reaction effective prefactor $K_{\text{eff}}$, with which the reaction mechanisms were discussed according to each scenario. Selective dissociation of NH molecules was achieved by placing the STM tip on top of each specific molecule and injecting electrons. NH bond breaking occurs when the N‒H stretching mode was activated. Hopping of H atoms was observed when the Pt‒H stretching mode was activated through coupling with the hindered translational mode. The reaction rate for ND dissociation is reduced due to a smaller tunneling rate. The rate of D hopping with excitation energy larger than 245 meV is comparable to that of H hopping, consistent with the over-the-barrier mechanism that involves coupling of the Pt‒D vibration with the D atom frustrated translational mode. For energies smaller than the hopping barrier, which is the case for excitation of $\nu$(Pt‒D), the hopping rate is greatly reduced as it involves tunneling of the D atom.
Chapter 7: Conclusions

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In this thesis, the surface morphology of atomic carbon and nitrogen on Pt(111), including the atomic structure, defects, and boundaries, were studied by STM.

In contrast to graphene on Ru(0001), Ir(111) and Rh(111), graphene on Pt(111) consists of various in-plane moiré domains with different periodicities, which can be attributed to the weak interaction between graphene and the Pt substrate. The multitude of moiré patterns on Pt(111) results in unique behavior in the formation of Pt nanoclusters on graphene/Pt(111). After depositing Pt atoms onto Pt(111)-supported graphene, instead of adsorbing inside the moiré domains and forming two-dimensional arrays, Pt nanoclusters adsorb along moiré boundaries forming one-dimensional chains.

Atomic nitrogen is presented in two well-ordered phases, $(2 \times 2)$ and $(\sqrt{3} \times \sqrt{3})R30^\circ$, at high coverages, where it occupies the fcc-hollow sites in both phases. The $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase converts to the $(2 \times 2)$ phase as the temperature increases from 360 to 400 K due to recombinative $N_2(g)$ desorption. Hydrogenation of the $N$ layer forms scattered molecules and islands of NH, which is related to the direct and indirect channel for $H_2$ dissociative adsorption on the nitrogen covered surface.

Furthermore, two single molecule reactions were studied by action spectroscopy, namely the dissociation of NH and H hopping. A theoretical model used for spectral fitting allows the active vibrational mode associated with a given reaction, as well as an estimate of the reaction rates to be obtained. The mechanisms
thus revealed are the following: NH bond breaking occurs when the stretching mode of N–H is activated. Hopping of H atoms is observed when the Pt–H stretch mode is activated and is coupled to the hindered translational mode. Substituting hydrogen by deuterium reveals that the reaction rate of ND dissociation is reduced due to a smaller tunneling rate. The rate of D hopping with excitation energy larger than 245 meV is comparable to that of H hopping, indicating an over-the-barrier mechanism, where the rate is contributed from intermode transition. With energy smaller than the hopping barrier, which is the case of exciting the ν(Pt-D) mode, hopping rate is greatly reduced as tunneling of D is involved.

These results establish the conditions for preparing well-ordered layers of graphene and nitrogen on Pt(111), and enabled the determination of the structure of these layers at the atomic level. It paves the way for future studies by both experimental and theoretical methods of the interaction with other adsorbates, and also provides new insights into aspects of the mechanisms of surface chemical reactions that are of relevance to important problems in heterogeneous catalysis.

There are three possible directions for future work. First, as graphene also interacts weakly with a Cu(111) surface, this would be a suitable system to exploit the method established here and by others to use this system as a template for nanocluster fabrication. Second, results on hydrogenation of N indicate that the inhomogeneous NH layer possibly results from the existence of both direct and indirect channels for H₂ dissociative adsorption, where the presence of already formed NH molecules lowers the probability of H₂ dissociation by the direct channel. Thus, dynamic studies of H₂ dissociation on nitrogen-covered Pt surfaces would allow us to state the problem from a theoretical point of view. Third, the action spectroscopy on H(D) hopping conducted in this thesis focuses on the bias window of 200 mV and above,
which correlates with the energy of the Pt–H stretching mode. Exploring lower bias voltages within the energy range of the frustrated translation mode (tens of mV) would be a promising focus for future investigations.


Appendices

Appendix A

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Publication: Journal of Physical Chemistry Letters

Publisher: American Chemical Society

Date: Sep 1, 2013

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Author Zhu Liang, Hyun Jin Yang, Yousoo Kim et al.
Online Publication Date Mar 20, 2014
Volume number 140
Issue number 11
Type of Use Thesis/Dissertation
Requestor type Author (original article)
Format Print and electronic
Portion Excerpt (> 800 words)
Will you be translating? No
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Macro for action spectroscopy

set_i0, 1.0
set_v, 0.1

delay, 500000 ; Set the initial value for the tunneling junction

feedback, 0 ; feedback loop off

delay, 500000
set_v, 0.0

set_signal, 15

delay, 50000
reset_signal, 15

set_v, xx ; Set the desire value “xx” for the bias voltage

loop_times, 100

delay, 100000 ; 0.1 sec per delay, in total 10 sec (× the loop times)

feedback, 1 ; feedback loop on

reset_i0
reset_v
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