CHAPTER 1

INTRODUCTION

1.1. Motivation

“The surfaces of bodies are the field of very powerful forces of whose action we know but little.”¹ This quotation by Lord Rayleigh exemplifies the complexities of the unpredictable behaviors of surfaces, despite the ongoing progress in the field of surface science. Many scientific investigations into physical and electronic surface properties have utilized the interactions of gas-phase particles with a solid surface. Historically, the surface science field evolved as a result of scientific efforts in the early 19th century to understand the mysterious phenomenon, now known as catalysis. For example, the presence of platinum increases the reaction rate of hydrogen with oxygen.¹ Although macroscopic qualitative details for catalysis were uncovered throughout the 19th and 20th centuries, the ability to quantitatively predict the final products when gas-phase particles interact with metal surfaces remains limited.

Despite the lack of quantitative predictive power of gas-surface interactions, many technological applications developed from empirical results, but continue to require fundamental understanding for these interactions to improve the efficiency of each application. More than 90% of chemical manufacturing utilizes heterogeneous catalysis for the production of such important items such as food, clothing, automobiles, ammonia production for fertilizers, and medicine.² As the
microelectronics industry continues to strive to manufacture electronic chips on the atomic scale, quantitative and detailed microscopic descriptions for reactive ion etching rates of the surfaces are pertinent. Analytical chemists exploit ion/surface collisions to identify the chemical composition of unknown samples in tandem mass spectrometry techniques. Satellites in the low-earth orbit encounter energetic ions that react with and remove materials from the surfaces. Consequently, scientists must quantify the removal rates and obtain a fundamental understanding of the reaction mechanisms involved in the degradation of spacecraft materials. The interaction between some ions and surfaces promotes thin-film growth that can be utilized in the manufacturing of optical materials. The ability to predict the behavior of gas-surface interactions will allow for the optimization of all the technologies mentioned, and for the development of future applications.

Numerous experiments have shown that the amount of kinetic energy of the incident gas-phase projectiles promotes particular types of reaction mechanisms. Figure 1.1 illustrates the most common fundamental reactions that occur for gas-surface interactions for three energy regimes of the incident projectiles—thermal, hyperthermal, and low energy. The longest-range interactions between the gas and surface are most important in the thermal energy regime, where the collision energy is typically less than an electronvolt (eV). Due to the very low translational energies, the gas particles may weakly absorb on the surface, a process called physisorption, or the entire molecule may strongly absorb to the surface, named molecular chemisorption, or the gas may not react with the surface at all resulting in a direct scattering mechanism. In the low energy regime, the gas projectiles have enough kinetic energy to inflict permanent modifications or damage to the surface. Commercially available equipment to monitor the structures and chemical composition of surfaces have led to numerous investigations into the fundamental processes activated in the thermal and low energy regimes. However, relatively few
Figure 1.1. Fundamental gas/surface collision processes from thermal to low collision energies. The indicated regions are those energy ranges where these processes are typically studied. (Reproduced with permission from Ref. 11).
experiments have investigated the reactions that occur within the hyperthermal energy regime.

Despite the challenges of preparing incident projectiles with kinetic energies between a few and ~300 eV, characterizing the hyperthermal energy regime spans an important gap in our understanding of the fundamental gas-surface interactions. Particles within this regime have just enough energy to overcome activation barriers to promote such chemical reactions as reactive ion etching, abstraction reactions, and dissociative scattering. Reactive ion etching reactions occur when an incident ion reacts with particular atoms on the surface causing specific features and patterns to be created on the surface. When incident molecules collide with the surface in this energy regime, the interaction may induce the fragmentation of the projectile, a process called dissociative scattering. Some incident projectiles react with preadsorbed species on the surface resulting in the emergence of a product composed of atoms from both the adsorbed species and the incident projectiles, a process called abstraction reactions. Although each of these processes have been observed in scattering experiments, current models and theories still cannot predict the necessary experimental conditions for the occurrence of each process.

A common fundamental process that occurs across all the energy regimes is electron transfer. Many theoretical models have been developed and modified to understand the charge exchange that occurs between the surface and an impinging gas-phase projectile. Several scattering experiments have measured the fraction of incident ions that either neutralize or capture two electrons from the surface. The ability to quantitatively predict charge transfer behavior is critical to optimizing the formation of negative ions or neutral species. Despite the significant progress in conventional charge transfer models over the past few decades, the experiments described in Chapters 3 and 4 underscore their limitations.
Studying reaction dynamics usually involves the redistribution of energy from the incident projectile to the surface and emerging products. Incident projectiles are prepared with a specified amount of translational, vibrational, or rotational energy, and the scattered species are analyzed to determine the amount of energy retained in the emerging products. The quantity of energy retained by the products, and the dependence of the product formation on the collision energy provide signatures for particular reaction mechanisms.

The investigations of the reaction processes that occur in the hyperthermal energy regime require complex instrumentation. The development of space exploration promoted the concept of utilizing ultrahigh vacuum chambers to provide an environment that allows scientists to prepare clean metal surfaces that can be studied for long periods of time. Moreover, extremely low chamber pressures ensure that only the desired incident projectiles impact the surface under study. The chambers are usually equipped with instrumentation for surface preparation, techniques to monitor the cleanliness and structure of the surface, and methods for delivering the incident projectiles to the surface. For scattering experiments, instrumentation is also required to monitor the identity and energies of the emerging products.

The remainder of this chapter introduces the concepts necessary to understand the fundamental reaction processes that may occur when hyperthermal reactive ions scatter from well-characterized surfaces. Section 1.2 describes the fundamental concepts applicable to conventional charge transfer theories. The subsequent section focuses on the energy transfer processes that provide signatures for specific reaction mechanisms. Section 1.4 introduces the modifications to the surface when the temperature is increased. Finally, the chapter closes with a detailed description of abstraction reactions, which is applicable to Chapter 5 in the dissertation.
1.2. Charge Transfer Dynamics

Within the hyperthermal energy regime, the exchange of electrons between the surface and the projectile is a crucial step in the formation of many final scattered products. When atomic or molecular projectiles scatter from surfaces, some probability exists for the products to emerge as positive ions, negative ions, or neutral species. Furthermore, molecular projectiles may dissociate as a result of capturing an electron from the surface. Several review articles have provided the complex details of charge transfer theory\textsuperscript{2,7-11}, so only a brief overview is provided here. Many theoretical and experimental studies have concluded that the final charge state (positive, negative, or neutral) of the scattered product is independent of the initial charge state, but dependent on the collision velocity.\textsuperscript{12} An explanation for this behavior relies on dividing the trajectory of the projectile into three different interaction regimes—the incident trajectory prior to impact with the surface, the point of the collision, and the exit trajectory after the collision.

It is well established that hyperthermal energy atomic and molecular ions efficiently neutralize along the incident trajectory a few angstroms above a metal surface.\textsuperscript{11,13,14} The predominant charge transfer mechanisms responsible for neutralization of incident ions are Auger Neutralization (AN) or Resonant Neutralization (RN). Figure 1.2 (a) illustrates the AN process, where a valence electron from the metal surface tunnels nonresonantly to a low-lying affinity level hole (1); the excess energy liberated by this process is gained by a second electron located in the valence band of the metal; if the second electron has sufficient energy, it can escape into the vacuum (2). AN becomes an efficient mechanism when the atomic affinity level lies well below the Fermi level. Comparatively, the RN process involves only a single electron transferred from an occupied electronic state from the metal to an unoccupied state of the ion, where both electronic states are degenerate.
Figure 1.2. Schematic diagram for two neutralization processes for an ion scattered on a metal surface: (a) auger neutralization (AN) occurs when an electron tunnels from the metal to a core hole in the atom (1) causing a second electron (Auger Electron) to become excited (2) and (b) resonant neutralization (RN) occurs when an electron tunnels from the metal to an isoenergetic level on the atom.
The RN process is expected to dominate neutralization, because single-electron transfer rates are faster than rates for multi-electron processes.\textsuperscript{9,11} Moreover, the higher density of states available to molecular ions compared to atoms provides more opportunities for the RN mechanism in molecule-surface scattering.

Theoretical models, such as the Anderson-Newns formalism, are often employed to quantitatively treat resonant charge-exchange during scattering.\textsuperscript{8} A one-electron energy level diagram (Figure 1.3) illustrates a simplistic representation of the energetics involved in the transfer of an electron from a metal surface to an atomic cation. The vacuum level indicates the zero energy level for removing an electron from either the neutral atom or the metal surface. The far right side of the diagram represents the energy level (ionization potential) of the valence electronic state for a neutral atom located at an infinite distance from the surface. The left side of the diagram represents the occupied electronic states of a static clean metal surface, where \[ \square \] indicates the work function of the surface. The Fermi level of the metal indicates the energy that separates the occupied states from the unoccupied states.

When the valence electron energy level for the atom is located below the Fermi level, some probability exists for neutralization of the cation. However, this probability depends on the amount of overlap between the atomic and metallic wave functions. When the ion is located at very large \( z \) values, very little, if any, overlap exists, resulting in a very low probability for neutralization. However, as the ion approaches the surface (\( z \) decreases), the amount of wave function overlap increases, and two additional effects—the level shift and the level width—modify the probability for RN.\textsuperscript{15}

The level shift alters the alignment of the atom’s affinity level relative to the Fermi level as the orbitals of the impinging ion are perturbed by electrostatic forces at the surface.\textsuperscript{10} As illustrated in Figure 1.4, the attractive interaction of a positive ion
Figure 1.3. One-electron energy level diagram illustrating the perturbation of the affinity level as the cation approaches the surface. Stabilization of the positive ion by its image charge lowers the ionization potential by an amount $\Delta E$, and the short lifetime of this state near the surface broadens it by an amount $\Delta$. (Reproduced with permission from Ref. 11).

Figure 1.4. An image charge is induced when a charged particle is located a close distance $z$ above the metal surface. (Reproduced from Ref. 16).
with its image charge stabilizes the ion, effectively lowering the ionization potential by an amount $\Delta E$:

$$\Delta E = \frac{1}{4z} \tag{1.1}$$

where $z$ is the distance between the cation and the surface.\(^{16}\)

When the ion is located very far from the metal surface, the energy level for the atom’s valence electron is discrete. However, when the atom approaches the metal, this electronic energy level broadens, an effect called the level width. This broadening is a direct consequence of the ion’s shortened lifetime. When the ion is located at an infinite distance from the surface, the lifetime is extremely large, due to the very slow tunneling rate for the electron transferring from the metal to the ion. In other words, the ion is unlikely to neutralize when it is located very far from the surface. According to Heisenberg’s uncertainty principle, the ion’s lifetime is inversely proportional to the width of the affinity level. Therefore, when the ion is infinitely far from the metal, the energy level for the valence electron is extremely sharp or discrete. As the ion approaches the surface, the electron-tunneling rate increases exponentially and the atom’s affinity level broadens. The relationship between the lifetime broadening, or level width, $\square$ is described by the following equation

$$\square(z) = \square_0 \exp(-\square z). \tag{1.2}$$

where $z$ is the ion-surface distance, $\square_0$ is the level width at the surface, and $\square$ is a tunneling parameter. The value for $\square(z)$ has been calculated to be on the order of 1 eV to 3 eV at the classical turning point for typical hyperthermal energy scattering.\(^{8,17}\)

The final charge state of the product depends on the evolution of the equilibrium charge state of the atom along the trajectory. Figure 1.3 illustrates the relationship of
the atomic charge state on the level shift and the level width for each value of z. Atomic energy levels below the Fermi level are resonant with the occupied states of the metal. The equilibrium charge state is depicted by the fraction of the atomic affinity-level Lorentzian that lies below the Fermi level. For example, an atom located at 4 Å above the metal surface has 100% of its level width profile in resonance with the occupied states of the surface as illustrated by the complete shading shown in Figure 1.3. This results in a filled affinity level or an equilibrium charge state equal to 0.0. When the stationary atom is located 2 Å above the metal, the projectile has approximately 70% of its level width profile located in resonance with the occupied states of the metal causing the atom to adopt an equilibrium charge equal to +0.3. The charge state for a moving particle will try to track the equilibrium charge state at every point along the trajectory. When the particle is in the near-surface region it maintains its equilibrium charge state, because the tunneling rate is fast compared to the timescale for translation close to the surface. Because the equilibrium charge state is typically at or below zero when most atoms are close to the surface, neutralization is an efficient process when cations scatter on metal surfaces.

After the incident ion neutralizes, the atom collides with the surface. Electronic couplings are strong when the atom is located within a few angstroms of the surface. The charge transfer dynamics associated with this portion of the trajectory is extremely important in determining the final charge state of the scattered product. During this interaction time, the neutral atom has a finite probability of capturing a second electron from the surface to form a negative ion in a process called electron attachment. The nascent anion can also lose the electron back to the surface in a process called electron loss.

The energetics for electron attachment are similar to that previously discussed for the neutralization of cations. Figure 1.5 represents the one-electron transfer diagram
Figure 1.5. A one-electron energy level diagram illustrates the energetics for negative ion formation near a metal surface. The dashed and solid curves represent the potential energy for an electron when the atom is at infinite and close distances to the surface, respectively. The affinity level for the neutral atom shifts downward and broadens as the atom approaches the surface. (Reproduced with permission from Ref. 11).
for the formation of an atomic negative ion. Similar to neutralization, the probability for electron transfer depends on the electronic coupling between the atom and the metal. The electron affinity level represents the energy released when a neutral atom captures an electron to form a negative ion. The level shift for the electron affinity is given by

\[ \square E = -\frac{1}{4z} \]  

(1.3)

where only the sign changes when compared to equation 1.1 for neutralization. As the neutral atom approaches the surface, no image charge exists, but the attractive forces between the surface and the negative ion causes the electron affinity to increase. Consequently, the binding energy of an electron to a negative ion increases when the projectile is brought close to the surface. Similar to neutralization, the electron tunneling rate broadens the level width as the projectile approaches the surface as given by equation 1.2.

Electron attachment can only occur if the neutral atom penetrates close enough to the surface for the affinity level to become resonant with the occupied states. Since the projectile continues to track its equilibrium charge state, the resonance allows the neutral atom to obtain a partially negative-charge state near the surface. For example, Fig. 1.5 demonstrates that a cation that neutralizes near 4 Å above the metal remains neutral when \( z = 3.5 \) Å as determined by the complete resonance of the level width profile and the unoccupied states of the surface. Therefore, the instantaneous charge state of the particle at 3.5 Å is 0, corresponding to a neutral atom. As the projectile translates even closer to the surface to \( z = 2 \) Å, 1/3 of the level width profile is in resonance with the occupied states of the metal resulting in an equilibrium charge state close to \( 0 - 0.3 = -0.3 \), which corresponds to an atom with some negative character. When the atom is closest to the surface -- the point of collision, commonly
called the classical turning point—the equilibrium charge state becomes the most negative and the electron–tunneling rate is at a maximum, resulting in the highest probability to form a negative ion. After impact, the nascent negative ion scatters from the metal surface.

Along the exit trajectory, the negative ion must overcome the processes that result in the loss of the electron, including back electron transfer or autodetachment. As the ion leaves the surface, sufficient wave function overlap still exists between the orbital on the ion and the unoccupied states of the metal for an electron to transfer back to the surface. However, the particle reaches a point along the exit trajectory, commonly called the freezing distance, where the tunneling rate becomes too slow for any additional charge exchange to occur.\(^{18}\) At this point, the particle’s charge state becomes frozen to the value of the equilibrium charge state. If the equilibrium charge state is negative at the freezing distance, then there exists a finite probability that a negative ion will emerge from the surface. The negative ion can be detected only if it survives autodetachment. Autodetachment occurs if the electron occupies an affinity level above the vacuum level.

An ion formed at the surface will often lose its electron along the outgoing trajectory, unless it is moving fast enough to escape nonadiabatically.\(^ {13}\) Accordingly, negatively charged scattered products are only observed if the component of their translational energy directed along the surface normal exceeds a few electronvolts.\(^ {8}\) Therefore, the velocity of the projectile, especially along the exit trajectory, is expected to significantly influence the emergence of negative ions. Although lower velocity projectiles have a higher probability to capture an electron from the surface, they also have a higher probability for electron loss as a consequence of the longer interaction time with the surface after the classical turning point. Therefore, the velocity of the projectiles after the collision determines if a negative ion emerges from the surface. This dependence has been observed in several experiments,\(^ {12,19,20}\)
including the increase of the $C_{60}^-$ negative ion yield with an increase in the incident velocity of hyperthermal $C_{60}$ molecules scattered on a graphite-covered nickel surface. The results of experiments and conventional charge transfer theory predict that, for the same incident projectile and surface, the exit velocity of the scattered products is the most crucial parameter for controlling the emergence of negative ions. As the exit velocity increases, the negative ion yield also increases.

Consistent with predictions from theory and observations from scattering experiments, the neutralization, negative ion formation, and electron loss processes depend on the work function of the surface, the ionization potential of the incident ion, and the electron affinity of the neutral atom. When the ionization potential is lowered or the surface work function is raised, the probability for neutralization decreases due to the reduced wave function overlap as the ion approaches the surface. Several experiments investigating the dependence of negative ion formation on the surface work function concluded that increasing the work function decreases the formation of negative ions. Relatively few experiments have observed the formation of negative ions in the hyperthermal energy regime, because of the low yields expected when incident projectiles with modest electron affinity values scatter from high work-function surfaces. In fact, the absolute yield of scattered anionic products detected in the hyperthermal energy regime is typically $\leq 10^{-3}$.

The incident scattering angle at which the projectile strikes the surface also influences the probability for negative ion formation. An incident projectile that is directed along the surface normal only interacts locally with one or a few surface atoms, depending on the impact site and the surface structure (i.e. Al(111) versus Al(100)). Hence, scattering at normal incidence probes local charge transfer effects, where the atomic states interact primarily with the electronic states of the surface atoms at the point of impact. In contrast, the majority of ion-surface scattering experiments performed to date have investigated the ‘non-local’ charge-transfer
effects, where the incident projectile approaches the surface at a glancing angle, resulting in interactions with numerous surface atoms along the entire trajectory. In the latter case, the surface work function is the most important parameter in regulating the charge-transfer process. The experiments discussed in Chapter 3 provide a unique opportunity to investigate local charge transfer effects in the emergence of Br\(^-\) when Br\(^+\) is backscattered (180° relative to the incident angle) from the surface.

Conventional charge transfer models assume that the surface is static during the scattering event. This assumption is justified when the mass of the incident projectile is very small compared to the mass of the target. However, nature provides numerous opportunities for heavy incident projectiles to undergo violent collisions that cause the surface atoms to move significantly during the critical interaction time within the trajectory.\textsuperscript{23,27} In such violent collisions the transient motion of the surface atom(s) is expected to modify the electronic coupling between the projectile and the moving surface in a manner that modifies the resonant charge transfer process. To date, neither experiments nor theories have addressed how the surface electronic structure changes as a result of the motion of a few surface atoms.

Despite this lack of dynamic information, more recent theories have investigated the static effects that adsorbates and vacancies exert on charge transfer at surfaces. During a violent collision, the surface atom(s) are pushed into the bulk creating a temporary vacancy site on the surface. Eventually, the displaced atoms may recoil to the surface, possibly even protruding from the surface like an adsorbate, if sufficient kinetic energy is transferred to the surface atoms. When modeling the electron transfer process, an atomic vacancy in an Al(111) surface causes the atomic energy level to shift upward and the level width to decrease.\textsuperscript{28} Oppositely, an adatom on Al(111) causes a downward shift in the atomic level and an increase in the level
Clearly, these modifications to the level shift and level width will modify the probability for anions to emerge from a static metal surface.

The significance of electronic couplings to resonant charge transfer between the projectile and the surface also applies to molecular incident projectiles. The simple charge-transfer picture described for atoms becomes significantly more complex, due to the numerous excited states of the incident molecular ions, neutral molecules, and negative molecular ions. In even the simplest case, the model for diatomic molecules must also incorporate the vibrational and rotational motions that occur along with translation. The application of the Franck-Condon principle to electron transfer for molecules is reasonable, because the nuclear motion is slow compared to the electronic motion. In the classical limit, the energy of an electronic transition within the diatomic molecule equals the vertical difference in energy between the two relevant potential energy surfaces evaluated at the instantaneous nuclear coordinates. Consequently, as the molecule translates, rotates, and vibrates, the molecular affinity level and tunneling rate are continuously shifting along the trajectory.

Similar to the scattering of an atomic projectile, charge-transfer may occur before, during, or after an incident molecule’s collision with the surface. Dissociative neutralization (DN) occurs when a surface electron resonantly occupies a neutral repulsive state of the molecule. When DN occurs on the inbound trajectory, the nascent fragments will impact the surface. Subsequently, the emergence of negative ions may occur if a second electron transfers to any of the fragments within the close surface interaction region. If the first electron transfers to a bound electronic state, then the intact neutral molecule may capture a second electron in the interaction region near the surface to form a negative molecular ion. Dissociative attachment (DA) occurs if the second surface electron populates a repulsive electronic state for the negative ion, resulting in the emergence of anionic fragments. If the second electron transfer from the surface populates a bound electronic state, then the
molecular anion can emerge from the surface without dissociating. The reaction
dynamics for molecule-surface scattering depend on the interaction of the molecule’s
electronic states with the occupied states of the surface and on the incident and
outgoing velocities of the scattered projectile. Similar to the behavior for atomic
projectiles, the emergence of molecular negative ions is expected to increase as the
velocity of the scattered projectiles increases.

The scattering experiments described in Chapters 3 and 4 demonstrate the unique
charge-transfer behavior associated with hyperthermal Br\(^+\) and Br\(_2\)^+ projectiles
scattering on a clean Pt(111) surface. An anomalous resonance in the formation of
negative ions is explored through careful analysis of the energy-transfer that occurs
between the incident projectile and the surface. The conclusions from these systems
support a charge-transfer process that is not only highly sensitive to the collision
energy, but also to the particular impact site on the surface and to the transient motion
of the surface atoms at the point of impact.
1.3. Energy Transfer Dynamics

1.3.1. Translational Energy

Investigating the relationship between the incident translational, vibrational, and rotational energy of an incident projectile and the final energy of the scattered product provides many interesting details about a system’s reaction dynamics. Many experimental and theoretical investigations have revealed that the majority of hyperthermal projectiles transfer more than 75% of their initial translational energy into the surface. The remainder of the energy is distributed among the vibrational, rotational, and translational degrees of freedom of the emerging products. When light atoms scatter on a metal surface, the final kinetic energy of the products, irregardless of the final charge state, is expected to increase with the collision energy as supported by numerous experiments. The reaction dynamics become much more complex for molecules scattered on surfaces, because many competing charge transfer and mechanical processes may result in the emergence of the parent molecule or of atomic products that result from the dissociation of the incident projectile before, during, or after the collision with the surface. Correlating how the product energy depends on the incident energy allows one to assign a particular scattering mechanism to the emergence of each scattered product.

The majority of hyperthermal scattering experiments focus on the role of the incident translational energy on the reaction dynamics. The most common model used to predict the amount of kinetic energy transferred in a high-energy atom-surface collision is the binary collision model (BCM). This two-dimensional model treats a single collision between a projectile and a target atom while conserving energy and linear momentum. When the mass of the incident projectile is less than the mass of
the target atom \((q < 1)\), the ratio of translational energies for the outgoing and incoming particle is given by

\[
\mathcal{Q}(\mathcal{Q}_s) = \frac{\mathcal{Q}^2}{(1 + \mathcal{Q})^2} \cos \mathcal{Q}_s + \left( \frac{1}{\mathcal{Q}^2} \sin^2 \mathcal{Q}_s \right)^{\frac{1}{2}}
\]

(1.4)

where the relative final energy \(\mathcal{Q} = E_f/E_i\), the mass ratio \(\mathcal{Q} = m_{\text{projectile}}/m_{\text{target}}\), the total scattering angle \(\mathcal{Q}_s = \mathcal{Q}_i + \mathcal{Q}_f\), and \(i\) and \(f\) correspond to the initial and final portions of the trajectory (See Fig. 1.6). \(^{23,30}\) Equation 1.4 does not depend on the interaction potential.

Figure 1.6. An incident projectile collides with the surface at a specified angle \(\mathcal{Q}_i\) relative to the surface normal with a specific amount of translational energy \(E_i\). The scattered product emerges from the surface at a measured angle \(\mathcal{Q}_f\) with exit kinetic energy \(E_f\).
The BCM predicts that for a fixed scattering geometry, the fraction of kinetic energy transferred by the incident projectiles to the surface is constant for varying collision energies. However, when Cooper and coworkers scattered 10-250 eV Rb\(^+\) on Cu(001), the fraction of translational energy lost by the incident projectiles decreased as the collision energy decreased below 50 eV, a phenomena attributed to sequential collisions with multiple surface atoms.\(^{23}\) Kang and coworker also observed deviations from the constant energy ratio value when 3-300 eV Cs\(^+\), Xe\(^+\), and Ar\(^+\) scattered on Si surfaces.\(^{27}\) In these experiments, the ions scattered from the surface with higher kinetic energies than predicted by the BCM, a consequence of the heavy projectile mass that increases the projectile-surface interaction time. The BCM provides a good quantitative description of ion/surface collision kinematics for incident energies in the keV range, but requires modifications when the velocity of the incident projectiles are slow enough to encounter attractive and repulsive interactions with the surface.\(^{30-32}\)

The relationship between the energies of the incident projectile and the final products helps to determine whether molecular dissociation occurs as a result of an electron attachment process (See Section 1.2) or collision-induced dissociation (CID). In the latter mechanism, a collision of the ion with the surface causes an impulsive transfer of translational energy to internal energy, which can exceed the dissociation limit for the molecule. Thus rovibrational energy rather than electronic excitation causes the incident molecule to dissociate.\(^{13,33}\) The threshold energy for the emergence of CID products is typically 4-5 times the bond energy for the molecule.\(^{19}\) Despite the expected inefficiency for CID, several authors have implicated the CID mechanism in the dissociative scattering of hyperthermal energy molecules on surfaces.\(^{13,19,34}\) Experiments and classical trajectory simulations have also revealed that fragments formed through CID can emerge with a greater velocity than that of a surviving parent molecule; yet they emerge at a lower velocity than that expected if the
fragment had scattered directly on the surface.\textsuperscript{19} For example, scattering OCS$^+$ from Ag(111) resulted in the emergence of O$^-$ at an exit velocity greater than the calculated exit velocity for OCS and with an O$^-$ final velocity less than the calculated exit velocity for scattering O atoms. The combination of the high threshold value for dissociated products, the monotonic increase of the ion yield with collision energy, and comparisons of the exit velocities between various product channels led to the unambiguous assignment of a CID scattering mechanism.

Comparatively, when dissociative neutralization (DN) is the operative mechanism for fragmenting the incident projectile, the threshold energy for emergence of fragments is very low—only a few electronvolts. As discussed in Section 1.1, DN results when an electron transfers from the surface to form a repulsive electronic state of the incident molecule. Conventional charge transfer theory predicts an increase in fragmentation with an increase in the projectile collision energy, since electron loss processes becomes less efficient. However, as collision energy increases, the incident projectile has less time to separate prior to surface impact. This incomplete fragmentation along the incident trajectory alters the overall dissociation dynamics and electron transfer processes. Experiments that implicated the DN mechanism, including the emergence of S$^-$ when OCS$^+$ scattered on Ag(111),\textsuperscript{19} measured a maximum yield value on the order of $10^{-4}$ for the emerging fragments. At higher collision energies the fragment yield gradually decreased with increasing energy. When DN causes fragmentation prior to surface impact, the nascent fragments transfer momentum to the surface with similar efficiency as if they had approached the surface from the gas phase.

Unfortunately, the incident-exit velocity relationship of the projectile is often insufficient to unambiguously assign a detailed scattering mechanism, especially when a molecular projectile dissociates. Therefore, the dependence of the scattered product velocity distribution on the collision energy provides additional information
regarding the kinematics of the collision. If the molecule dissociates after the collision with the surface, both the intact parent molecule and the dissociated fragments emerge from the surface with similar median velocity distributions.\textsuperscript{35} Likewise, if the velocity distribution for a scattered fragment is similar to that for the atom scattering directly on the surface, then DN, prior to impact with the surface, is implicated.

In addition to providing details about the point along the trajectory where dissociation occurs, the velocity distributions reveal information about the surface-projectile interaction. The presence of multiple peaks in the product velocity distributions have been assigned to particular types of trajectories, including single scattering—the interaction with a single surface atom, and multiple scattering—sequential collisions with multiple surface atoms.\textsuperscript{32,36} Single scattering trajectories produce velocity distributions with lower velocities and narrower distributions compared to multiple scattering pathways. However, these trajectory-sensitive distributions have only been observed for particles scattered away from the surface normal.

The first two scattering systems described in this dissertation investigate the detailed reaction dynamics for scattering halogen projectiles on metal surfaces. Chapter 3 investigates the energy-transfer mechanisms for scattering state-selected Br\textsuperscript{+} on a Pt(111) surface. The subsequent chapter probes the charge-exchange and dissociation reaction dynamics for scattering state-selected Br\textsubscript{2}	extsuperscript{+} on Pt(111). The unique geometry–normal incidence and normal detection–of the experimental apparatus allows the investigation of the local charge transfer dynamics for both scattering systems. The ionic product yields and velocities are measured as a function of the collision energy and exit angles. A curve-fitting procedure applied to the data set supports a site-specific scattering mechanism and charge-transfer rate for the atomic projectiles. When the molecular bromine cations scatter from the surface, the incident
molecules dissociate to form Br⁻. The details of this dissociation mechanism are discussed by examining the threshold energy value, comparing the velocity distributions of the fragments to the parent molecule, and comparing the velocity distributions of the fragments to the Br⁻ products observed when Br⁺ is scattered on the surface.

1.3.2 Vibrational Energy

Investigating the roles that each internal degree-of-freedom within an incident projectile plays on the reaction dynamics allows one to identify new features in the potential energy surfaces that govern the interactions between molecules and surfaces. Of the gas-surface experiments that have probed the effects of the incident projectile’s internal energy (ro-vibration), the majority have involved state-selected neutral molecules scattering on single-crystal surfaces. Although the results from these molecular-beam experiments have revealed the role of internal energy in thermal-energy reactions, including dissociative chemisorption and surface trapping, few studies have investigated the effects of internal energy on processes such as dissociative neutralization and collision induced dissociation where additional kinetic energy is required to overcome the reaction barriers.

In the pioneering experiments where state-selected molecular ions were scattered from surfaces, Jacobs and coworkers observed that an increase in incident NO⁺ vibrational energy is an order of magnitude more effective in promoting O⁻ formation compared to a similar increase in the translational energy. Intuitively, an increase in fragmentation is expected for a collision induced dissociation mechanism, because the additional energy is deposited directly into the reaction (molecular stretching) coordinate. However, predicting the role that incident vibrational energy plays on
charge-transfer rates is significantly more complex. Vibrational excitation can change the Franck-Condon overlap between the initial and final electronic states involved in the charge transfer process.\textsuperscript{39} Moreover, vibrational excitation shifts the resonance between the molecular energy levels and the density of states at the surface modifying the probability for the DN mechanism.\textsuperscript{39}

Previous experiments performed by Martin \textit{et al.}\textsuperscript{38} showed that for a \textit{particular} collision energy, an increase in incident vibrational energy enhanced the dissociation of the NO\textsuperscript{+} projectile. Section 4.3.4 discusses the role that incident Br\textsubscript{2}\textsuperscript{+}(\textsuperscript{2}P\textsubscript{3/2}, v = 0 and v = 2) vibrational energy plays on the formation of Br\textsuperscript{-} and Br\textsubscript{2}\textsuperscript{-} across a \textit{range} of collision energies between 5 and 100 eV. These experiments show that for the Br\textsubscript{2}\textsuperscript{+} projectiles, an increase in vibrational energy most significantly inhibits the dissociation mechanism at the lowest collision energies and has no significant effect at higher collision energies. The reasons for these unexpected observations are explored through a discussion about how the electron transfer process couples to each electronic state of the bromine molecule.

1.4. Surface Temperature Effects

Surprisingly, very few experiments have investigated the role of the surface temperature on scattering hyperthermal projectiles on surfaces. Somorjai and coworkers reported the first comprehensive study of how energy is redistributed within translational, rotational, and vibrational degrees of freedom in the molecule and surface phonons during a thermal energy collision.\textsuperscript{40} Energy redistribution can significantly affect the absorption, trapping, and scattering of projectiles, because the amount of energy transferred is comparable to that required to activate the reaction processes. In the pioneering work of Overbosch \textit{et al.}, the investigators observed a charge-transfer
temperature-dependence for ionizing 30 - 400 eV Na scattered on W(110) at surface temperatures ranging from 300–2000 K range. When Tully, Amirav, and coworkers investigated the effect of the surface temperature for scattering 1–8 eV Xe on GaAs, neither experiments nor theoretical models suggested a surface temperature dependence to the scattering dynamics. However, Bu et al. later observed a surface temperature dependence in the charge transfer of Na, K, and Ca on Si(111) at collision energies below 10 eV. As the incident kinetic energy of the alkali atoms increased above 10 eV, the fraction of incident atoms ionized was independent of the surface temperature. Sosolik et al. reported a large enhancement in the Na⁺ neutralization probability on Cu(001) as the temperature was increased. Some theoretical treatments examining the role of surface temperature on the reaction dynamics resulted in discrepancies with the experimental results of Overbosch et al. either for low collision energies or for low surface temperatures. Despite the numerous theoretical papers devoted to investigating the relationship between surface temperature and charge exchange, very few hyperthermal scattering experiments attempt to measure a surface temperature sensitivity to the reaction dynamics.

The bromine-platinum scattering experiments described in Chapters 3 and 4 include a study of the surface temperature effects on the formation of negative ions across the entire collision-energy range 5-110 eV. These unprecedented experiments reveal two additional scattering systems that show a charge-transfer sensitivity to the surface temperature. Since a temperature increase in the surface atoms only corresponds to a fraction of an eV increase in vibrational energy of the surface phonons, the discussion focuses on the coherence between the motion of the surface atoms and the scattering projectiles. The detailed dynamics for both systems are further supported by comparing the scattering data (i.e. mean kinetic energies, exit angles, velocity distributions, and ion yields) when Pt(111) is at room temperature and at 400 °C.
1.5. Abstraction Reactions

Thus far, the discussion has only considered reaction mechanisms for projectiles scattered on clean surfaces. When atoms or molecules are adsorbed on a surface, many additional reaction pathways become available, including abstraction reactions, where an atom is transferred to or from an incident molecule as the molecule impacts the surface. In the case of hyperthermal molecular ion/surface scattering, the incident molecule is more likely to abstract an atom from the surface. These reactions are often assigned to one of two limiting mechanisms: Langmuir-Hinshelwood (LH) or Eley-Rideal (ER). In the LH mechanism both reagents thermally equilibrate with the surface prior to reaction, whereas in the ER mechanism, an incident gas particle reacts directly with a surface adsorbate. Distinguishing between LH and ER mechanisms is difficult unless one carefully probes the reaction dynamics. Three clear signatures are often associated with an ER mechanism: products emerge with a nonthermal energy distribution, the mean kinetic energy of the products correlates with the incident energy of the reactant gas, and the product angular distribution is peaked near the specular angle rather than the surface normal. Perhaps the first definitive evidence of an ER process was obtained by Kuipers et al. who demonstrated that \( \text{N(C}_2\text{H}_4\text{)}_3\text{N} \) abstracts a proton from hydrogen-covered Pt(111) at collision energies above 1.5 eV. The translational energy of the scattered product ion was found to increase with incident energy.

Recent studies of the ER mechanism have involved exothermic reactions initiated under near-thermal conditions. Exploring the dynamics of these systems has revealed how energy is partitioned into different degrees of freedom within the products. Hyperthermal molecular ions are relatively efficient at abstracting atomic/molecular fragments from surface adlayers. For example, Qinyuan and Hanley established that 32 eV pyridine projectiles can abstract a proton from pyridine-covered Ag(111).
Cooks and co-workers demonstrated that polyatomic projectile ions, such as pyrazine and pyrene, can abstract H, F, CH₃, or C₂H₃ fragments from self-assembled monolayers.⁵⁴ Despite these pioneering studies, many mechanistic questions about atom abstraction remain unaddressed: What is the nature of the transition state? Is the abstracted fragment transferred as a neutral or charged moiety? How is energy consumed or partitioned in the reaction? Chapter 5 investigates these questions for an improbable reaction: the abstraction of an oxygen atom by scattering hyperthermal NO⁺ on an oxygen-covered Al(111) surface. In these experiments, the NO₂⁻ product yield and kinetic energy are measured as functions of the oxygen-coverage on the surface and the translational energy of NO⁺.
1.6 References


