The Dynamics of Gas-Surface Energy Transfer in Collisions of Rare Gases with Organic Thin Films

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(ABSTRACT)

Understanding mechanisms at the molecular level is essential for interpreting and predicting the outcome of processes in all fields of chemistry. Insight into gas-surface reaction dynamics can be gained through molecular beam scattering experiments combined with classical trajectory simulations. In particular, energy exchange and thermal accommodation in the initial collision, the first step in most chemical reactions, can be probed with these experimental and computational tools.

There are many questions regarding the dynamic details that occur during the interaction time between gas molecules and organic surfaces. For example, how does interfacial structure and density affect energy transfer? What roles do intramonomolayer forces and chemical identity play in the dynamics? We have approached these questions by scattering high-energy, rare gas atoms from functionalized self-assembled monolayers. We used classical trajectory simulations to investigate the atomic-level details of the scattering dynamics. We find that approximately six to ten carbon atoms are involved in impulsive collision events, which is dependent on the packing density of the alkyl chains. Moreover, the higher the packing density of the alkyl chains, the less energy is transferred to the surface on average and the less often the incident atoms come into thermal equilibrium with the surface. In addition to the purely hydrocarbon monolayers, organic surfaces with lateral hydrogen-bonding networks create more rigid collision partners than surfaces with smaller inter-chain forces, such as van der Waals forces. Finally, we find some interesting properties for organic surfaces that possess fluorinated groups. For argon scattering, energy transfer decreases with an increasing amount of surface fluorination, whereas krypton and xenon scattering transfer most energy to monolayers terminated in CF₃ groups, followed by purely hydrocarbon surfaces, and then perfluorinated surfaces.
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Chapter 1

Introduction to Scattering from Organic Surfaces

Thesis Statement

The objective of the research presented here is to develop a fundamental understanding of how physical and chemical characteristics of organic surfaces influence the extent of energy transfer, thermal accommodation, and trapping in gas-surface collisions.

1.1 Introduction and Motivation

The interfaces between states of matter are interesting because of the role they play in much of the world’s technology. Catalysis, corrosion, and materials growth all depend on the chemistry that takes place within interfacial environments. Over the past 40 years a considerable amount of progress has been achieved in understanding the chemical processes that occur at surfaces. In particular, probing the dynamics of gas atom/molecule-surface interactions has provided atomic-scale descriptions of elementary physical and chemical processes.

In an ambient environment, gas-phase molecules approach a surface with a range of energies and angles. Specifically, the gas-phase molecules have a Maxwell-Boltzmann distribution of velocities, and a cosine distribution of incident flux. As illustrated in Fig. 1.1, several processes are available to gas molecules as they encounter a surface, including: (1) recoil directly back into the gas phase (impulsive scattering), (2) reaction in a single collision, (3) direct penetration into the surface with sufficient incident energy, and (4) loss of sufficient energy to the surface during the initial collision to become temporarily trapped or adsorbed.1-6 The gas molecules that are trapped may reach thermal equilibrium with the surface. Once in
thermal equilibrium, the gas molecules have a wide variety of processes available to them. They may immediately desorb (thermal desorption) without reaction, or diffuse into the bulk material for long-time solvation, or return to the surface and desorb. Reactive gas species can react with the surface groups (or buried groups after diffusing into the bulk) forming new surface moieties. Following reaction, the products may return to the surface and desorb into the gas phase.

Figure 1.1 Dynamic pathways available during the gas-surface interaction.

A complete understanding of the reaction mechanisms at the gas-surface interface would include knowledge of each of the processes outlined in Fig. 1.1 on the atomic level. However, understanding these dynamic processes is best achieved by investigating the individual steps during the interaction dynamics, rather than the system as a whole. The first step in many gas-surface chemical reactions is determined by the initial collision, where the energy exchange dynamics determine whether the gas-phase reactant
scatters directly away from the surface or thermally accommodates (equilibrates) with the material. The sticking probability, or uptake coefficient, is a measurement of the partitioning between gases sticking to the surface or simply scattering back into the gas phase. Sticking probability measurements are often examined by the King and Wells technique, but only provides time-averaged information. However, understanding the atomic-level details of energy exchange between gas-phase species colliding with surfaces is crucial to developing a complete picture of gas-surface reaction dynamics. Energy transfer at this level of detail should include translational and internal energy transfer of the gas molecules along with energy changes of the surface groups. To take one step back, atomic gases scattering from surfaces removes some complexity from the system where energy transfer is restricted to translation-to-surface vibrational modes and vice versa. The mechanism(s) of translational-to-vibrational energy transfer for various surface properties is best studied with noble gases due to their non-reactive nature and absence of internal degrees of freedom.

Molecular beam techniques in ultrahigh vacuum (UHV) environments coupled with velocity and angular resolved detection provide the experimental tools needed to obtain this energy transfer information (see chapter 2 for an explanation of these techniques). Molecular beams offer control over the energy, angle and flux of the incident gas while the UHV environment maintains a clean sample and eliminates interfering gas-gas collisions.

The earliest studies using molecular beam scattering techniques from surfaces employed solid surfaces, but more recently, scattering experiments have been extended to liquid organic surfaces and some model, solid organic surfaces. However, there are
still many questions regarding the dynamic details that occur during the interactions of
gas molecules and organic surfaces. For example, how does interfacial structure and
density affect energy transfer? What role do intramonomolayer forces and chemical identity
play in the dynamics? The random conformational nature of liquids and typical, organic
surfaces is an experimental challenge that must be addressed before these questions can
be fully answered. Scattering gas molecules using molecular beams from functionalized,
self-assembled monolayers (SAMs) provides control over the surface order, structure,
and the exact chemical nature of an interface. The structure of the SAMs makes them
ideal for identifying properties of organic surfaces that either absorb energy efficiently
from the incident gas or scatter the gas away with little energy transfer. The principle
ideas of gas-surface energy transfer can be gained from classical mechanical models used
as guidelines and physical pictures to understand the dynamics of gas-surface scattering.

1.2 Classical Models

The interactions of gas atoms/molecules with surfaces are complex, but the
development of models based on classical mechanics has provided physical pictures that
are used to understand the underlying processes in a qualitative way. Below, we outline
four of these classical models that have been developed and used in gas-surface scattering
dynamics studies. The classical models provide first order ways of thinking about both
impulsive scattering events and trapping-desorption dynamics, the two limiting pathways
available to inert gas atoms scattering from organic surfaces.

1.2.1 Hard-Cube Model

During the first part of the 1960s, a considerable amount of experimental data on the
scattering of low-energy atomic beams from solid surfaces became available. To understand
the origin of the scattering distributions obtained from these experiments, a simplistic approach was devised by Logan and Stickney using classical mechanics, commonly known as the hard-cube model.\textsuperscript{11,12} The hard-cube model has been used to qualitatively predict and to compare trends in experimental scattering results of gas atoms with solid surfaces.\textsuperscript{12} A schematic of this model is illustrated in Fig. 1.2.

![Figure 1.2 Schematic illustration of the hard-cube model of gas-surface scattering. The subscripts on the velocity components, n and p, denote normal and parallel while i and f represent initial and final, respectively.](image)

The gas atom is treated as a rigid sphere that undergoes impulsive collisions with the upper, flat surface of a cube. The tangential component of the gas momentum is conserved, $v_{p,i} = v_{p,f}$, so that energy transfer only occurs in the normal direction of the cube surface. For comparison with experimental data, the incident angle relative to the surface normal and the incident energy of the gas species are adjustable. To compare scattering with surfaces at any given temperature, $T_{\text{surf}}$, the initial velocity of the cube in each collision, $u_{n,i}$, is sampled from a Maxwell-Boltzmann velocity distribution characterized by that temperature. The advantage of this model is that there is only one adjustable parameter for data fitting, the mass ratio, $m_g/m_{\text{surf}}$. 

\begin{align*}
\text{Figure 1.2} & \quad \text{Schematic illustration of the hard-cube model of gas-surface scattering. The subscripts on the velocity components, n and p, denote normal and parallel while i and f represent initial and final, respectively.}
\end{align*}
\[ \mu = \frac{m_g}{m_{\text{surf}}} \], where \( m_g \) is the mass of the gas atom and \( m_{\text{surf}} \) is the effective surface mass.

Though rudimentary, the hard-cube model provides an intuitive perspective of how the final scattering angle and energy transfer depend on the mass ratio, incident energy and angle, and surface temperature of the system.\(^4\)

One important outcome of this model shows that energy transfer is maximal when the mass ratio is unity and falls off with larger or smaller values, though asymmetrically. The fractional energy transfer to the surface can be derived from conservation of energy and momentum to give the following relationship for a normal approach angle

\[
\frac{\Delta E}{E_i} = \frac{4\mu}{(\mu + 1)^2}
\]

where \( \Delta E \) is the change in energy of the gas atom, \( E_i \) is the incident gas energy and \( \mu \) is the mass ratio. The fitted value of the mass ratio, \( \mu \), provides an ‘effective’ surface mass, which lends insight into the collective response of the surface during impulsive collisions.\(^12\) Although, it is difficult if not impossible to predict \textit{a priori} the response of the surface involved in the collisions, the values calculated can nevertheless often be rationalized by atoms or surface segments, which may include several groups acting jointly.\(^8\)

1.2.2 Soft-Cube Model

The soft-cube model, proposed by Logan and Keck in 1968,\(^{13}\) is an extension of the hard-cube model that takes into account some of the more extreme assumptions in that model. The gas atom interacts with the surface cube through a potential function that includes an attractive component and an exponential repulsive component. Another
difference is that the surface cube involved in the collision is attached to a rigid wall by a linear spring to model solid-solid interactions, rather than an isolated cube. The spring is given an oscillator frequency, $\omega$, characteristic of surface vibrations of the system under investigation. Finally, the ensemble of cube oscillators is given an equilibrium distribution of energies at the surface temperature. The model thus contains three adjustable parameters, the mass ratio ($\mu$), the potential well depth ($D$), and the oscillator frequency ($\omega$). Figure 1.3 shows a schematic illustration of the soft-cube model and the gas-surface potential curve with an exponential repulsion component and a constant attraction component.

![Diagram of soft-cube model](image)

**Figure 1.3** A schematic illustration of the soft-cube model. The space between the incident and final velocity vectors of the gas represent a finite time spent of the surface (i.e. soft collision). The box in the lower right corner illustrates the form of the potential function between the gas and surface.

The soft-cube model is not as elegant as the hard cube model as there are additional adjustable parameters needed to fit the model to experimental data. However, due to the
success of the model in predicting experimental results where the hard cube model fails, parameters that need to be considered in gas-surface scattering dynamics become obvious. Two important considerations arise from the model. First, the gas-surface interactions are not impulsive, but have a finite interaction time governed by the potential of interaction between the gas and surface. Second, the gas atoms may interact with individual surface atoms, but the movement of those surface atoms after the collision is coupled to the motion of surrounding surface atoms. Both of these observations show that large segments of the surface can be involved during the scattering events.

1.2.3 Washboard Model

The washboard model is another broadening of the hard-cube model that incorporates surface corrugation effects in gas-surface scattering. The washboard model takes advantage of the assumption used in the hard cube model of conservation of tangential momentum, but on the local scale rather than the global surface scale. Rather than modeling the surface as a flat cube, the washboard model represents the gas-surface interaction by a hard wall with the impact location given by a wave function:

\[ z(x) = A \cos\left(\frac{2\pi x}{a}\right) \]

A square well can be added to the interaction potential, which changes the direction of impact once the gas atom has crossed the leading edge. Figure 1.4 shows a schematic illustration of the washboard model to illustrate the definition of the parameters used in the model. Energy transfer occurs between a gas atom of mass \( m_g \) with some incident energy and angle and a hard cube of effective mass, \( m_{\text{surf}} \). The location of the flat region of the cube is defined by the contour at the location of the gas impact. Therefore, the local tangential momentum is conserved, but the global momentum defined by the
surface plane in not conserved. Like the hard-cube model, the initial velocity of the cube is sampled from a Maxwell-Boltzmann distribution defined by the surface temperature. Three adjustable parameters are used to define the model; the mass ratio ($\mu$), the well depth ($D$), and the corrugation strength parameter ($\alpha_m = \tan^{-1}(2\pi A/a)$). The corrugation strength parameter provides the maximum obtainable angle between the global surface normal and the local cube normal. In addition to these three adjustable parameters, the incident energy of the gas, the global incident approach angle, and the surface temperature have to be defined for comparison with experiment.

![Figure 1.4 Schematic representation of the washboard model for gas-surface scattering][14,15] The change in direction of the gas atom at a distance away from the cube before and after the impulsive collision is due to the additional translational energy from the square well potential (only acts in local normal direction).

To calculate final energy and angular distributions, integration over a Maxwellian distribution of cube velocities and a distribution of impact sites are needed.
The details of the washboard model are less important for the discussion here, but the idea of needing to incorporate surface corrugation into a model is important. For solid metals, surface corrugation is well defined and the model makes a reasonable physical attempt to incorporate that effect on scattering. Although most liquid surfaces do not have well-defined interfacial regions, the model organic surfaces used in our scattering experiments are well-ordered and surface corrugation contributes to the scattering dynamics we measure.

1.2.4 Hard Spheres Model

In gas-surface scattering where the interfacial region of the surface is not well-ordered, e.g. organic liquid interfaces, the surface is very rough and may have individual functional groups protruding out into the gas phase. Impulsive collisions between the gas and surface species appear to be more like two spheres colliding rather than a gas sphere colliding with a cube. The hard spheres model is a classical model that can be used to gain a physical picture of the dynamics in these systems. Both the gas atom/molecule and the surface groups are modeled as hard spheres, but the calculations of energy transfer are familiar from the cubes models. Figure 1.5 provides a schematic illustration of the hard spheres model to define some of the variables used in the calculations.
Figure 1.5 Hard-spheres scattering model of gas-surface collisions.\textsuperscript{16}

Two important quantities that come out of this model, which helps us gain a physical picture of gas-surface scattering dynamics, are the dependence of the mass ratio, and the deflection angle, $\chi = 180^\circ - \theta_{i,loc} - \theta_{f,loc}$, on energy transfer. The following relationship can be constructed for energy transfer from the conservation of linear momentum and kinetic energy when two hard spheres undergo impulsive collisions without attractive potentials included:\textsuperscript{18}

$$
\frac{E_{inc} - E_{fin}}{E_{inc}} = \frac{2\mu}{(1 + \mu)^2}[1 - \cos \chi(1 - \mu^2 \sin^2 \chi)^{1/2} + \mu \sin^2 \chi]
$$

The above equation accounts for energy transfer along the line of centers of the two spheres. Ignoring angular dependencies, energy transfer increases with mass ratio, $\mu = m_g/m_{surf}$, and, for a given mass ratio, head-on collisions, $\chi = 180^\circ$, are the most efficient for energy transfer while energy transfer decreases with glancing collisions up to $\chi = 0^\circ$. 
1.2.5 Trapping and Desorption

The discussion of the classical models up to this point has focused on energy transfer and angular distributions of gas atoms impulsively scattering from surfaces. Another pathway that is available during gas-surface interactions is trapping. We define trapping as a collision in which a gas species strikes a surface and does not immediately scatter back into the gas phase because it has insufficient energy to escape a potential energy well. The classical models outlined above can help illustrate how trapping occurs in gas-surface scattering dynamics when a potential well is included in the model.

We begin the discussion with the simplest case for trapping, the hard cube model including a square well potential of depth, $D$. For a gas atom impacting a cube at rest to trap on the surface, it must lose sufficient energy in the normal direction so that its total energy is less than the well depth energy. The trapping probability in this case will have a step function dependence on the normal energy, $E_{\cos^2(\theta)}$, where the trapping probability is one below some critical value and zero above the critical value of the normal energy. However, if the gas-surface collisions are integrated over a distribution of cube velocities, corresponding to a surface with a given temperature, the step function broadens as a result of the relative momentum between the gas and surface. The gas strikes some cubes with velocities moving toward it and some cubes with velocities moving away from the incident gas. The trapping probability, thus increases for relative energies less than the critical value and decreases for relative energies greater than the critical value.

The actual gas-surface potential energy function is not composed of a hard repulsive component and a square well attractive component, but is more like a smooth
curve with a minimum in the well and a smoothly varying repulsive wall and attractive tail. If we imagine this type of potential energy surface, we can extend the model to include the dynamics of trapping events. As a gas atom approaches the surface, it is accelerated due to the attractive potential, strikes the repulsive wall where energy transfer occurs, then climbs back up the attractive tail and tries to escape back into the gas phase. If it has lost enough of its initial translational energy to the surface that its total energy is less than the well depth, then it will turn around (‘outer turning point’) and accelerate back into the surface, oscillating back and forth in the potential well. The only way for this trapped gas-phase species to leave the surface is by a thermal fluctuation from the surface where the atom is ejected back into the gas phase.

Trapping also occurs when the surface is corrugated and the component of the gas atom in the plane of the surface is not conserved. This type of trapping can be illustrated by the washboard model with an attractive potential well. In this case, the gas atom strikes the surface, exchanges energy in both the normal and tangential directions (globally) such that it cannot escape the potential well in the global normal direction. If the gas atom does not have enough energy to escape the potential well, it will turn around and approach the surface for a second time. The gas atom will make another collision with the surface, and redistribute energy again, either providing the atom with enough energy to leave the surface or causing another outer turn and return into the surface. The gas atoms may undergo a number of these escape attempts with each inner to inner turning point referred to as a ‘hop’. It should be noted that the atom can be trapped on a corrugated (or rough) surface for two reasons: (1) the gas atom has insufficient energy in the normal direction only to escape the potential well, collisions that can couple the gas
atom’s normal and parallel momentum are needed to send it back to the gas phase, or (2) the gas atom has reached thermal equilibrium with the surface and can only escape after a thermal fluctuation provides it with enough energy to leave the surface. The term “trapping desorption” generally refers to the gas processes of trapping in a potential energy well, reaching full thermal equilibrium with the surface, and then being propelled back into the gas phase by collisions with thermally fluctuating surface molecules (thermal desorption). In this description, thermal desorption is equivalent to the concept of evaporation or vaporization in thermodynamics.

1.3 Scattering from Liquid Organic Surfaces

The interfacial regions of molecular liquid surfaces are unlike single crystal solids, in that they are not well-ordered with precisely defined lattice constants. The surface structures of molecular liquids are highly disordered, which means that there are more molecular configurations for incident gas species to impact. Despite the additional complexity of molecular liquid surfaces, experiments conducted in the Nathanson group,\textsuperscript{8,9,19-23} which is where nearly all molecular beam scattering studies from liquid, organic surfaces have been conducted, have found that guidelines derived from several of the classical models can be used to predict the outcome of gas collisions with liquid surfaces.\textsuperscript{16} They have scattered various small-molecule and atomic gases from a series of low-vapor pressure organic liquids, including the hydrocarbon squalane, highly hydrogen-bonding glycerol, and a perfluoropolyether, PFPE. These experiments provide the means to study how gases stick to, rebound from, and exchange energy with liquid surfaces.

The experiments are conducted in a vacuum chamber by directing a molecular beam of nearly monoenergetic gas particles at a continuously renewed liquid surface.
The velocity and direction of the scattered gas-phase species are monitored using the time-of-flight technique with a rotatable mass spectrometer for detection.

1.3.1 Atomic Gas Scattering

1.3.1.1 General Trends in Scattering and Thermal Accommodation

The collision dynamics of inert atomic gases scattering from organic liquid surfaces studied by the Nathanson group revealed that organic surfaces, although disordered, have enough surface structure to have dependencies on the incident gas parameters. In particular, atomic gases including neon, argon, and xenon scatter from the surfaces of squalane (C₃₀H₆₂), and a perfluoropolyether (F-[CF(CF₃)CF₂O]₁₄(avg)-CF₂CF₃) have revealed that impulsive energy transfer depends on the deflection angle, $\chi$, corresponding with collisions similar to those predicted from the hard spheres model.³,⁸,⁹,²³

The importance of the scattering angles on the energy transfer dynamics was studied using 32 kJ/mol Ne, 80 kJ/mol Ar, and 185 kJ/mol Xe atoms incident on the surfaces of squalane and PFPE.⁹ Insight into the average energy transfer in the impulsive scattering channel can be gained by comparing the scattering results to those predicted with the hard spheres model. In the hard spheres model, head-on collisions ($\chi = 180^\circ$) transfer the most energy and glancing blows ($\chi \approx 0^\circ$), the least. A similar type of behavior occurs in the liquid surface systems. The average energy transferred in the inelastic scattering channel increased when atoms approach and exit more perpendicular to the surface. Notice that the deflection angle must be at least $90^\circ$ for the gas phase species to exit the surface when $\theta_i = 0^\circ$. Moreover, a given gas probe scattered from each surface with a series of incident and detection angles was found to fall onto a single curve when energy transfer was plotted against deflection angle. Since inelastic energy transfer depends only on the angle of
deflection, $\chi = 180^\circ - (\theta_i + \theta_f)$, the inert gases must undergo one or more hard sphere-like collisions with the protruding C-H or C-F groups of the squalane and PFPE molecules.

Besides the angular dependence on energy transfer in the IS channel, the flux of atoms in the impulsive and trapping-desorption channels also showed angular dependencies. The flux of impulsive scattering tended to be greater for larger values of the deflection angle. The extent of trapping-desorption increased at the expense of impulsive scattering, but peaked in the surface normal direction in a cosine-like pattern as expected for desorption of thermally accommodated gas atoms. The partitioning of the IS and TD channels is related to the energy transfer dependence on deflection angle. Since head on collisions transfer more energy, it is easier to bring gas atoms into thermal equilibrium with the surface than in more glancing blows.

**1.3.1.2 The Role of Surface and Gas Identity of Scattering and Thermalization**

Up to this point, the discussion has been general for gases impacting the surfaces of liquid squalane and PFPE, but the identity of both the impinging gas and the liquid surface are important in terms of impulsive energy transfer and the extent of trapping-desorption. The surfaces of squalane, PFPE, and glycerol were probed with inert gases to determine how various surface properties determine the outcome of the initial gas-surface collision.

The hard-sphere model can be used to describe the inelastic scattering channel of the neon and argon atoms from the glycerol surface, similar to squalane and PFPE, for incident energies of 6, 25, 32, 60, 75 kJ/mol for neon and 42 kJ/mol for argon. However, the surfaces do not behave the same in terms of the extent of energy transfer and trapping-desorption. The fractional energy transferred follows the order squalane > glycerol > PFPE for each incident gas studied. The fractional energy transfer in the impulsive scattering channel is
related to the ‘effective’ surface mass of the liquids. The fluorinated groups afford a smaller mass ratio and absorb the least amount of energy. The difference in squalane and glycerol is likely related to the hydrogen-bonding network in glycerol, which allows more surface groups to participate in the collision.

The thermal accommodation coefficient for neon follows the order squalane > PFPE > glycerol. Neon accommodates to glycerol less than PFPE possibly because of enhanced multiple collisions with the PFPE. Glycerol is a small molecule and may be able to pack more tightly than PFPE at the surface exposing a flatter interface, which inhibits sequential collisions. In addition, they observed that high-energy neon atoms reach thermal equilibrium more readily on squalane than on glycerol. Although the atomic scale structures of these two surfaces are likely different, this result suggests that hydrogen-bonding organic materials may present a more rigid surface than analogous non-hydrogen-bonding systems, limiting the flow to thermal equilibrium.

In contrast to the neon scattering results, the thermal accommodation coefficient decreases in the order squalane > glycerol > PFPE for argon scattering. This trend, along with the results from neon scattering, suggests that squalane is either softer or rougher than glycerol since increased energy transfer during the initial impact and multiple collisions enhance large amounts of energy transfer. The small thermal accommodation fraction to the PFPE surface is partly attributed to the more massive CFₙ groups that absorb energy less efficiently in comparison to the CHₙ and OH groups of squalane and glycerol. Overall, the fraction of atoms that thermally equilibrate with the surface decreases as the incident energy is increased on all three surfaces.
The experimental results are also consistent with predictions of energy transfer based on kinematics for a series of gases with different masses as well as scattering from surfaces with different masses. For example, gas-surface energy transfer from the perfluorinated surface in the inelastic channel increases with increasing gas mass in the series neon, argon and xenon. The increased energy transfer is attributed to the difficulty in reversing the heavier gas atoms’ direction and sending it back into the gas phase. The heavier atoms strike the surface and continue pushing forward, hitting more and more surface atoms, which brings them into thermal equilibrium more readily. Within this picture of scattering, the incident momentum, not the energy, is the most important parameter in predicting the outcome of the collision.

1.3.1.3 The Role of Surface Roughness on Energy Transfer and Thermalization

Another interesting set of experiments conducted by the Nathanson group reveals that gas scattering from liquid organic surfaces have a strong dependence on the microscopic structure of the interface. Scattering experiments using Ne, Ar, and Xe with PFPE over an 85 K temperature range reveal how gas-liquid energy transfer depends on the atomic-scale roughness of the liquid. Three trends emerge from the TOF data for $\theta_i = \theta_f = 45^\circ$ scattering. First, for low incident energies (~ 6.5 kJ/mol for each gas), neon, argon, and xenon all readily thermalize, departing at velocities approaching Maxwell-Boltzmann distributions at the liquid temperature, $T_{liq}$. Second, at high incident energies, inelastic energy transfer remains almost unaltered by changes in $T_{liq}$. Third, the apparent trapping-desorption flux increases and the inelastic scattering flux decreases as the liquid becomes hotter, almost independent of the gas identity and collision energy. This trapping-desorption component is labeled “apparent”
because the temperature at which the Boltzmann function was fitted to the data is higher than the actual surface temperature.

The first trend observed from the TOF data is understood from the ideas for trapping provided by the classical models. Less energy has to be transferred to the surface for low-energy gases to become trapped at the interface, thus high thermal accommodation fractions are likely. The second trend observed from the data, the similar impulsive scattering distributions over the range of surface temperatures, is probably due to encounters within the scattering plane dominated by single collision events. This idea can be understood from the hard spheres collision model. If the gas atoms are making impulsive collisions with protruding functional groups, the fraction of energy transfer should be independent of the surface roughness. The third trend observed suggests that hotter liquids have rougher surfaces. The decreased flux of the impulsively scattered atoms may be due to either additional collisions bringing them into thermal equilibrium rather than direct scattering or that the increased roughness allows some impulsive events to scatter in directions other than the mass spectrometer.

Atomic beam scattering experiments were also used to investigate the effects of thermal roughening on the angular distributions of trapping and scattering using 71 kJ/mol argon atoms and PFPE. The fraction of trapping events in argon atom collisions with the PFPE surface increased with closer-to-normal impact angles and with increased liquid temperature, while the fraction of impulsive events decreased with closer-to-normal impact angles and higher liquid temperatures. In addition, the IS flux decreased for forward scattering events, but actually increased slightly for backward scattering at small angles. Since higher temperatures caused an increase in surface roughness, the increased signal for
impulsive events at backward scattering angles implies that rough surfaces increase the size of the angular distribution for impulsive events.

1.3.2 Polyatomic Scattering from Organic Liquid Surfaces

Nathanson and coworkers scattered the polar and nonpolar gases CH₄, NH₃, and D₂O from squalane, glycerol, and a perfluoropolyether over a range of incident energies from about 6 to 85 kJ/mol. These gases have similar masses and sizes but different chemical properties, which allows combinations of gases and liquids with different gas-liquid bond strengths to be studied and compared. Energy transfer measurements were restricted to translational energy and the TOF spectra were deconvoluted into the impulsive scattering channel and a channel that was fitted by a Boltzmann distribution of velocities at the liquid temperature.

Impulsive scattering events for these polyatomic molecules, from glycerol and squalane have remarkably similar energy transfer dynamics, reflecting similar masses and sizes of the gases scattering from protruding OH and CH₂ functional groups of the two liquids. The similarity of glycerol and squalane is in contrast to scattering from the PFPE surface where energy transfer is less efficient. The difference is correlated to energy lost in single and multiple hard sphere-like collisions of the incoming particle and the protruding functional groups of the liquid phase molecules similar to the results for atomic gases scattering from these three liquids.

The trapping-desorption fractions, however, vary significantly between glycerol and squalane: D₂O is trapped more efficiently by glycerol, NH₃ accommodates equally well on both liquid surfaces, and CH₄ equilibrates more readily on squalane. Moreover, glycerol shows more sensitivity than squalane to the composition of the gas. Water and ammonia are
trapped more efficiently than methane on glycerol while each gas equilibrates nearly equally on squalane. This trend is most likely due to dipole-dipole or hydrogen bonding interactions during collisions between the protic gases and the OH groups of glycerol that is absent when NH₃ and D₂O collide with the hydrocarbon surface. These trapping-desorption trends roughly follow differences in the free energies and enthalpies of solvation, suggesting that trends in trapping-desorption fractions can be used to predict trends in gas-liquid binding energies at liquid surfaces.³ The “like dissolves like” rule appears to provide valuable guidance in predicting relative energy transfers and rates of approach to thermal equilibrium.³ The weakly attractive CFₓ groups of PFPE on the other hand, seem to impede thermal accommodation without respect to the gas identity.⁸

1.4 Atomic Gases Scattering from Self-Assembled Monolayers

The experimental challenge of making well-defined organic surfaces in a highly reproducible manner has limited the number of studies aimed at exploring gas-surface energy transfer dynamics involving organic collision partners. Despite this added complexity, significant advances in the interaction details have been revealed from scattering experiments from liquid organic surfaces as described above. The results of those interactions are a fundamental incentive to study the scattering dynamics from self-assembled monolayers where the ambiguity of the liquid surfaces can be systematically studied. Self-assembled monolayers are easy to create and offer control over the order, structure, and chemical nature of the interface in a highly reproducible manner.²⁵,²⁶

1.4.1 Earliest Studies Involving Self-Assembled Monolayers

Self-assembled monolayers (SAMs) form well-ordered films, which provide ideal surfaces for studying energy transfer pathways in organic surfaces. The long-range order
of SAMs makes them particularly good candidates for identifying properties of organic thin films that are either efficient for energy absorption or hinder energy transfer to the surface. One of the first studies using SAMs as well-ordered models was carried out by Cohen et al. for investigating the gas-surface energy transfer dynamics of Ar, He, O₂, and NO scattering from amphiphilic monolayers. Changing the chain constituents of the amphiphilic monolayers revealed different interactions between the probe molecule and the surface. The three surfaces used were n-octadecyltrichlorosilane (OTS) on glass and polished quartz slides, Cd(II) arachidate transferred by the Langmuir-Blodgett method on freshly cleaved LiF(100), and perfluorinated acid ester (PFAE) on glass.

In these pioneering experiments, the beam-surface-detector angle was fixed at 60° with normal detection and the incident energies of the impinging gas atoms/molecules were ~6.0 kJ/mol. The extent of energy transfer from the gas to the surface was correlated with the rigidity of the monolayer chains and the gas-to-surface mass ratio. For example, ~6 kJ/mol argon atoms scattering from the perfluorinated SAM transfer less energy than in scattering from the OTS SAM. The increased rigidity of the perfluorinated surfaces relative to the hydrogenated surfaces may be a result of differences in the masses of fluorine and hydrogen, as well as differences in the repulsive intermolecular forces of fluorine and hydrogen atoms.

Due to the experimental scattering geometry, the observation of an impulsive scattering channel at normal detection implies that tangential momentum is not conserved in these systems. Instead, there must be energy modes of the chains in the plane of the surface that are involved in the energy transfer dynamics. Low-frequency concerted waving motion of chains parallel to the surface plane, hindered rotation of the end
groups, and vibrations along the chain axis are probably responsible for the large extent of gas-surface energy transfer in these films.

### 1.4.2 Classical Trajectory Simulation Studies Involving Self-Assembled Monolayers

A key to understanding both scattering and trapping dynamics in gas-surface interactions is to perform classical trajectory simulations using realistic gas-surface potential energy surfaces (PES). Molecular dynamics simulations allow the researcher to overcome three experimental limitations for scattering studies: (1) typical experimental apparatus either have a fixed geometry between the source and detector or can only measure in-plane angular distributions, (2) the dynamics that occur at the surface can only be inferred from the experiment by evaluating the incident and final gas energies and directions, and (3) study system properties not accessible with experiments, like high incident energies of the gas or scattering along particular azimuthal angles of the surface. Classical trajectory simulations can provide full angular distributions and allow the researcher to ‘see’ the play-by-play dynamics occurring at the interface.

Hase *et al.* performed classical trajectory simulations using neon as the impinging gas atoms and *n*-hexyl thiolate self-assembled monolayers adsorbed on Au(111) as their model surfaces. In their first study, neon collisions with incident energies of 1.2, 5, 20, and 40 kcal/mol at a polar angle of 45° and incident polar angles of 10°, 30°, 45°, 60°, and 80° with $E_i = 20$ kcal/mol were used to determine incident energy and angular dependencies on the energy transfer dynamics. The final distributions from their results could be separated into the two limiting pathways for inert scattering events: direct inelastic scattering and trapping desorption. The overall energy transfer depended on the magnitude of the incident energy. For the 1.2 kcal/mol incident energy beam, no net energy transfer was measured ($2RT \approx 1.2$ kcal/mol).
kcal/mol in these simulations). However, the fraction of energy transferred increased as the incident energy of the neon atoms was increased. In addition, the fraction of atoms that undergo trapping desorption decreased as both the incident energy and the incident angle increased. This is the same trend that was found by Nathanson in scattering neon from the surface of squalane. A comparison of these simulation results to results predicted by the cubes models with an attractive well potential and energy transfer restricted to the normal direction, shows that the high-density monolayers behave similar to inorganic solid surfaces.

The Boltzmann component in the final neon translational energy distribution in the previous trajectories is surprising because a careful examination of the trajectories composing this channel indicated that the trapping time is very short (0.5-1.0 ps). In two following studies, Hase et al. used molecular dynamics simulations to determine the origin of the Boltzmann component in the translational energy distribution. Although a component of the final energy distributions could be fit with a Boltzmann distribution of velocities, the dynamics of the collisions showed that the gas atoms do not form an intermediate, long-lived physisorbed state with the SAM. Both the angular distribution of the gas atoms normal to and backward from the incident approach angle, normally associated with the statistical Boltzmann distribution, arise from efficient energy transfer in direct collisions. The classical trajectory simulations also suggest that penetration of energetic atoms into the monolayer plays a role, albeit a minor one, in the overall energy exchange dynamics. These studies show that there may be problems in associating a trapping-desorption intermediate with fitted low energy scattering distributions, particularly for relatively, light gases interacting with a very weakly-attractive surface.
The results from the two studies aimed at discovering the origin of the Boltzmann component led to another study to investigate the gas-surface model used in the trajectory calculations. A range of attributes in the molecular dynamics model for neon scattering investigated the sensitivity of the model to the trajectory results including: (1) an investigation of the gas-SAM intermolecular potential, (2) a comparison of the representation of the alkyl groups, united atom (UA) constituents versus explicit atom constituents (EA), (3) an examination of the number of alkyl chains in the model, and (4) a comparison of a static versus dynamic description of the gold substrate.

Changes in the gas-surface intermolecular potential function showed that the interaction of the neon atoms with the hydrogen and carbon atoms of the SAM is well represented by a neon + CH$_4$ intermolecular potential derived from ab initio theory. For the united atom models, the intermolecular potentials were derived by isotropically averaging the neon-explicit atoms models. Energy transfer appears to be insensitive to the details of the analytical function used to fit the ab initio potential.

Scattering results from the united atom and explicit atom models show ~10% more energy transfer to the UA model than the EA model. The explicit representation of the hydrogen atoms provide increased repulsive interactions, thus the EA model is denser and stiffer that the UA model. With its more flexible structure, the UA model has lower energy barriers to conformational changes and absorbs the collisional energy more readily than the EA model. In particular, the authors showed that low-energy extended motions of monolayer alkane chains play the largest role in dissipating the energy of a gas-surface collision, whereas the high-energy C-H motions are less active in the scattering dynamics.
Energy transfer also appears to be independent of the size of the model used for the SAM. A SAM represented by 35 alkyl chains gave the same scattering results as one represented by 100 alkyl chains. Moreover, energy transfer is insensitive to whether the gold substrate layer is treated as rigid or as a thermal heat bath.

The results from this comparison of models suggest that the model used in the former investigations is adequate for studying the collisional energy transfer dynamics in these systems. Therefore, studying the atomic-scale details of the trajectories can provide insight into the origin of the Boltzmann and non-Boltzmann components of final energies. In addition, the comparison of models provides a basis that can be used by other investigators to choose a model surface for scattering simulations.

Following the investigation of the surface model employed in the dynamics simulations, a combined experimental and computational effort from the Hase and Sibener groups provided important insights into how energy is partitioned between the gas and the organic surface upon collision.\textsuperscript{33,34} They showed that the impact site of neon on the surface governs the types of surface modes excited. Collisions with the most efficient energy transfers resulted from trajectories in which the neon atom strikes the alkyl chain from the side.\textsuperscript{33}

Side-on collisions are more efficient in transferring energy to the surface for two reasons. Low-frequency modes are more easily excited and intramolecular vibrational energy redistribution takes place on the time scale the neon atom is in contact with the surface, which in turn couples more surface modes to the energy transfer coordinate. Furthermore, their calculations demonstrated that penetration of incident neon atoms into the monolayer is limited to the first few atomic layers and that the extent of penetration
decreases with decreasing incident energy. The bimodal distributions observed from all the previous studies were, therefore, attributed to the different impact parameters for the neon atoms with the alkyl chains.

Following the neon scattering discoveries, a modified classical washboard model was developed to represent the surface response to impact parameter. The model added a rotational degree of freedom to the surface to account for the high efficiency of side-on impacts in energy transfer. Indeed, a bimodal distribution of final energy scattering without a trapping-desorption channel followed from this added rotational degree of freedom.

In addition to neon, the interactions of argon with well-ordered decanethiolate SAMs on Au(111) have been studied experimentally and computationally by the Sibener group. Unlike the neon scattering results, the low-energy component of the final energy distributions for argon could be directly attributed to trapping desorption. Experimentally, the low-energy component was well fit by a Boltzmann distribution for a range of surface temperatures and exhibited a cosine angular intensity profile. More direct evidence for a true trapping-desorption channel came from simulations that showed a fraction of the trajectories reside on the surface for long times (> 2ps) and that both normal and parallel components of the incident momentum thermally accommodate with the surface. The presence of the trapping-desorption channel for argon scattering and the absence of this channel in neon scattering are related to the difference in the polarizability of the two gases. The potential well depth between an individual methyl group and argon is approximately 1.34 kJ/mol compared to 0.50 kJ/mol for the neon-methyl well depth. In addition to the differences in the gas-surface potential, the argon atoms are
approximately double the mass of neon which may also contribute to greater energy transfer and multiple collisions.

Finally, Sibener and co-workers have also reported simulations of high-energy xenon scattering from alkanethiolate SAMs similar to the neon and argon simulations. They found that a significant number of the xenon atoms penetrate the surface groups of the SAMs. Rather than coming into thermal equilibrium with the surface, these xenon atoms, upon ejection from the chains, leave the surface with higher than average-thermal energies.

1.5 Ion Scattering from Self-Assembled Monolayers

In addition to the body of work using neutral molecular beams, several researchers have also studied the fragmentation patterns and reactivity of ions when they impact the surface of organic monolayers. Hanley and co-workers have combined experimental and computational approaches to study the energy transfer of SiMe$_3^+$ on a 6-carbon alkanethiol SAM. Their work shows that energy transfer to a surface is markedly greater for a monolayer-covered surface than it is for a bare gold surface and that penetration into the monolayer, even for $> 10$ eV ions, is limited to the topmost two-to-three layers of carbon atoms. Cooks et al., have explored the characteristics of high-energy ionic collisions using a variety of $\omega$-functionalized SAMs including hydroxyl-terminated and methyl-terminated monolayers. They observed that translational to internal energy conversion of the polyatomic ions is greater for the hydroxyl SAM than the methyl SAM.

In additional scattering experiments, several investigations of ion-surface scattering from model fluorinated organic surfaces have been performed. It has been
shown that translational to vibrational energy transfer of internal modes in polyatomic ions is higher when scattering from fluorinated surfaces in comparison to hydrocarbon surfaces.\textsuperscript{49,50} The differences in energy transfer have been attributed to the effective masses of the target surface species.\textsuperscript{48-50} In addition, an investigation by Wysocki \textit{et al.} scattering low-energy ions (10-100eV) from Langmuir-Blodgett films terminated with CF\textsubscript{3}(CH\textsubscript{2})\textsubscript{n}, \textit{n}-perfluoroalkyl, and \textit{n}-alkyl groups suggested that the outermost surface group (CF\textsubscript{3} vs. CH\textsubscript{3}) plays the largest role in energy transfer.\textsuperscript{44} For example, W(CO)\textsubscript{6}\textsuperscript{+} ions with incident energies in the range of 10 to 70 eV scattering from monolayers terminated with a CF\textsubscript{3} group or fully fluorinated chains have similar energy transfer dynamics. Translation to internal energy transfer of the incident ion scattering from these two surfaces is approximately equal, but scattering from the pure hydrocarbon monolayer provides only half as much translational to internal energy transfer. A similar result was obtained for low-energy ion-surface scattering from alkanethiolate self-assembled monolayers with varying degrees of fluorination at the terminus.\textsuperscript{42} These results lend some insight into the importance of the effective mass of the terminal groups versus the increased rigidity of the perfluorinated chain.

\textbf{1.6 Summary and Research Outlook}

A complete understanding of the reaction mechanisms at the gas-solid interface includes a detailed knowledge of all the processes available to the system. The first step in many gas-surface chemical reactions is determined by the initial collision, where the energy exchange dynamics determine whether the gas-phase reactant scatters directly away from the surface or thermally equilibrates with the material. For organic surfaces, previous scattering experiments have shown that many of the physical pictures derived
from the classical models give insight into the intimate details of these scattering
dynamics. However, there are still many questions regarding dynamics that occur during
the interactions of gas molecules with organic surfaces. For example, how does
interfacial structure and density affect energy transfer? What role do intramonomolayer
forces and chemical identity play in the dynamics?

My research goals are to extend the understanding of gas-organic surface
interactions by scattering inert gas atoms from functionalized self-assembled monolayers.
We have studied the influence of alkane packing structure and density, alkane chain
length, and terminal group orientation on energy transfer dynamics for argon atoms
impacting $n$-alkanethiol self-assembled monolayers. We have also studied scattering
dynamics from monolayers with intramonomolayer hydrogen-bonding groups and
monolayers with fluorinated groups incorporated into the chain. Finally, we have used
classical trajectory simulations to further understand the atomic-level details of alkane
chain packing density on energy transfer dynamics.
Chapter 2

Experimental Approach

2.1 Background and Motivation

Understanding the mechanistic details at the molecular level is essential for interpreting and predicting the outcome of elementary processes in all fields of chemistry. Insight into these details for gas-surface reaction dynamics can be gained through molecular beam scattering experiments. However, the experimental challenge of making well-defined organic surfaces in a highly reproducible manner has limited the number of studies aimed at exploring the gas-surface energy transfer dynamics involving organic substrates. Coupling molecular beams and functionalized self-assembled monolayers allows the complicated nature of the interface to be partitioned into elementary processes. The primary objective of our experimental studies is to explore how the order, molecular structure, and the hydrogen-bonding nature of an organic surface influence the extent of energy transfer and thermalization in gas-surface collisions.

Figure 2.1 provides a schematic representation of our approach in using molecular beam techniques and self-assembled monolayers (SAMs). The atomic beam is directed at the SAM with a given incident energy and either scatters directly away from the surface in an impulsive collision or gets trapped in the gas-surface potential well and approaches thermal equilibrium before it desorbs back into the gas phase. The scattered atoms and the thermally accommodated atoms are then detected with a quadrupole mass spectrometer. Energy transfer is determined by a time-of-flight (TOF) spectrum for the atoms as they travel to the surface, interact with the surface, and then travel to the detector. For rare gas collisions, $\tau = 0$, and since we know the chopper to surface time,
we can calculate the surface to mass spectrometer time. We know the surface to mass spectrometer distance precisely which allows us to easily determine the final velocities and convert to final energies. The difference in the initial and final energies tells us how much energy was transferred to the surface.

Figure 2.1 Schematic illustration of our experimental approach for scattering high-energy gases from functionalized self-assembled monolayers. The dark circles bonded to the gold substrate are the sulfur atoms and the gray circles are the methyl and methylene units.

2.2 Self-Assembled Monolayers

2.2.1 Introduction

Self-assembled monolayers (SAMs) offer well-ordered and highly-reproducible thin films that serve as model surfaces for studying organic surface properties in gas-surface collisions. There are a wide variety of SAMs with the typical defining feature
related to the headgroup/substrate pair. The most common SAM is made by adsorbing sulfur containing compounds (thiols, sulfides, and disulfides) on gold substrates. The simplest and most thoroughly studied of these compounds are $n$-alkanethiols with relatively long chains, $n > 10$. It is now well-established that $n$-alkanethiols chemisorb onto Au(111) through a strong Au-S bond to form dense monolayers with an average intermolecular alkane chain separation of 5 Å, which produces an overall $(\sqrt{3} \times \sqrt{3})R30^\circ$ lattice.\textsuperscript{25,51-55} Figure 2.2 shows a schematic representation of the basic $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer of sulfur atoms adsorbed to threefold hollow sites of the (111) plane of a gold substrate.

![Figure 2.2 The basic overlayer structure of $n$-alkanethiolate monolayers on Au(111).](image)

The figure illustrates that the nearest neighbor spacing of the sulfur atoms is $\sqrt{3}a$, where $a$ is the lattice spacing of gold, 2.88 Å. The figure also shows that the nearest
neighbor direction of the sulfur atoms is rotated by 30° relative to the nearest neighbor
direction of the underlying gold surface.

Optimal packing of the alkane chains occurs with the carbon chain axis tilted by
approximately 30° with respect to the surface normal. Figure 2.1 shows a side view of
the \( n \)-alkanethiols adsorbed to gold as an illustration of the chain packing structure of the
SAMs. The densely packed monolayers have high binding energies\(^{25} \) which make them
robust and easy to work with. In addition, alkanethiol self-assembled monolayers on
gold have been demonstrated to be stable in ultrahigh vacuum (UHV) environments over
time scales of several hours to several days.\(^{52,53,56-58} \)

A simple modification to the \( n \)-alkanethiol molecules used to produce SAMs is to
change the terminal group structure. However, modification to the individual assembling
units can change the overall structure of the SAM since the equilibrium structure is a
delicate balance of many factors, which includes the adsorbate-adsorbate interactions.\(^{26} \)
A more detailed review of the structural characteristics of the SAMs employed in the
scattering experiments are provided in the relevant chapters.

2.2.2 Acquiring the Alkanethiols

Most of the alkanethiols used in the experiments are commercially available. The
\( n \)-alkanethiols \( \text{(HS(CH}_2\text{)}_{n-1}\text{CH}_3 \text{ where } n = 2 - 12, 14 - 16, 18) \), hydroxyl terminated
\( \text{(HS(CH}_2\text{)}_{11}\text{OH and HS(CH}_2\text{)}_{16}\text{OH) alkanethiols, carboxylic acid terminated}
\( \text{(HS(CH}_2\text{)}_{10}\text{COOH) alkanethiols, and perfluorinated (HS(CH}_2\text{)}_{2}\text{(CF}_2\text{)}_{7}\text{CF}_3 \) alkanethiols
were purchased from Aldrich and used as received. In addition, we performed scattering
experiments using SAMs constructed of 11–aminoundecanethiol \( \text{(HS(CH}_2\text{)}_{11}\text{NH}_2\text{) which}
was purchased from Dojindo as the stable hydrochloride, \( \text{HS(CH}_2\text{)}_{11}\text{NH}_3^+\text{Cl}^-\).
Other alkanethiols used in the scattering studies were either synthesized in our lab or received from collaborators. The olefin terminated alkanethiols (HS(CH₂)₉CHCH₂) were synthesized and purified in our lab by Gwen M. Davis according to the procedure reported by Peanasky.⁵⁹,⁶⁰ Methyl ester terminated alkanethiols, methyl 11-mercaptoundecanoate (HS(CH₂)₁₀COOCH₃), were synthesized in our lab by James R. Lohr according to two previously published routes.⁶¹,⁶² The terminally fluorinated alkanethiols (HS(CH₂)$_n$-1CF₃ where $n = 15$ or 16) were synthesized by collaborators in the lab of T. Randall Lee by their own published methods.⁶³ Finally, monolayers formed with carbamate functional groups were synthesized by a procedure developed by Ferguson et al.⁶⁴,⁶⁵

2.2.3 Substrate Preparation and Monolayer Formation

The SAMs used in this research were prepared primarily by spontaneous chemisorption of the alkanethiol of interest from 1 mM ethanolic solutions onto clean gold surfaces. The gold substrates were created by: (1) evaporation onto heated mica (Molecular Imaging) and (2) evaporation onto Cr-coated glass slides (EMF Corp.). The chromium serves as an adhesive layer for the gold on glass substrates. To prepare the gold-coated glass substrates for monolayer coverage, they were cleaned in a piranha solution (70/30 (v/v) mixture of concentrated H₂SO₄/ 30% H₂O₂) for at least one hour prior to use. Slides removed from piranha solution were thoroughly rinsed with deionized water followed by absolute ethanol before placing them into the corresponding ethanolic thiol solution. No cleaning procedure was used for monolayers formed on the gold coated mica surfaces. Each monolayer that was solution deposited onto gold substrates was submerged in the desired thiol solution for at least 12 hours. The time the
gold samples remained in solution did not have a measurable effect on the experimental results (over the range 1 h to 24 h). The freshly prepared SAMs were then rinsed with absolute ethanol and dried with ultra-high purity nitrogen before being transferred into the main ultra-high vacuum (UHV) chamber through a load-lock system (described below).

The aminoundecanethiol SAMs were prepared in a different way since they come from Dojindo as the HCl salt. We created monolayers by dissolving the aminoundecanethiol in ethanol at a concentration of ~1 mM. The sample was rinsed and dried as the other monolayers, and then rinsed a final time in copious amounts of triethylamine (TEA) to deprotonate the SAM and remove the chlorine. After the TEA rinse, the sample was again rinsed in ethanol and dried in a stream of nitrogen. XPS measurements for TEA-rinsed and non-TEA-rinsed SAMs demonstrated that the TEA rinse effectively removed all chloride ions from the surface.

We also performed some experiments where the alkanethiols were vapor deposited onto the gold substrates. After cleaning the gold substrates, they were placed into a sealed jar purged with nitrogen and charged with a drop of the liquid alkanethiol. The container was mildly heated (~50-60 °C) to increase the vapor pressure of the adsorbate and left overnight. Monolayers that were prepared by vapor deposition were taken directly from the jar, rinsed with ethanol to remove any alkanethiol multilayers and dried with nitrogen before being transferred into the UHV chamber.

Silver substrates were prepared by thermal evaporation of 100-150 nm of silver (99.9999% purity, Aldrich) onto freshly cleaved 0.5 x 0.5 in² mica surfaces (SPI Supplies, V-1 Muscovite Mica). The silver substrates were prepared in a bell jar
evaporator with a liquid-nitrogen trapped diffusion pump. The mica surfaces were baked out at 300 °C for at least 2 hours before deposition to eliminate residual water and prepare the surfaces for epitaxial growth. The base pressure typically reached 1x10^{-7} Torr with an increase in pressure to 1x10^{-5} Torr during deposition. Silver deposition was conducted at a surface temperature of 250 °C, and was then allowed to cool to ~100 °C. This procedure produces large domains of flat Ag(111) terraces on the mica substrates.\textsuperscript{66} Surfaces prepared with extended post evaporation annealing gave indistinguishable results in our scattering experiments. Once the surfaces cooled to 100 °C, the system was vented with nitrogen, which further cooled them to < 70 °C. The fresh silver surfaces were immediately taken from the deposition chamber and placed in an ethanolic thiol solution to avoid surface oxidation. All surfaces exposed to ambient conditions for less than 15 minutes provided monolayers with reproducible scattering results.

2.2.4 Structural Confirmation and Characterization

The pure self-assembled monolayers used in the scattering experiments in these studies have been previously well-characterized and documented.\textsuperscript{25,26,51-56,59,61,62,67-71} To confirm that we are able to make SAMs by published procedures and that we obtain the same monolayer structures, we used X-ray photoelectron spectroscopy (XPS) and reflection absorption infrared spectroscopy (RAIRs) as characterization tools. The XPS measurements were carried out on a Physical Electronics spectrometer using unmonochromatized Mg(K\textsubscript{α}) radiation (1235.6 eV). The RAIR measurements were performed on a Bruker IFS 66v/S spectrometer. The atomic scale structure of the monolayers on gold for dodecanethiol and 11-mercaptoundecanol were also measured by scanning tunneling microscopy (STM) for the preparation conditions employed in this
study by a previous group member.\textsuperscript{72} We found that pure monolayers prepared under the conditions described above give monolayers consistent in structure to those reported in the literature. Finally, the carbamate monolayers were prepared by a novel method designed in our group.\textsuperscript{64,65}

Characterization of the monolayers is important for both the initial preparation of the SAMs as well as affirmation that the SAM structures are stable in UHV conditions. We also found that the alkanethiolate SAMs were stable in ultra-high vacuum for >24 hrs.

Verification of the structure of two types of SAMs needs special attention here. (1) The $n$-alkanethiols adsorbed to silver surfaces because we prepared the substrate surfaces in our lab. (2) The mixed monolayers, HS(CH\textsubscript{2})\textsubscript{11}CH\textsubscript{3} and HS(CH\textsubscript{2})\textsubscript{11}OH, since they were prepared from a binary solution mixture and needed to be characterized for monolayer concentration from our preparation conditions.

2.2.4.1 $n$-Alkanethiols on Ag

The structure of the monolayers prepared on silver substrates was confirmed through STM by Tochko Tzetkov at the University of Notre Dame and RAIR measurements in our lab. For the STM images, we prepared octadecanethiolate SAMs on Ag/mica substrates and mailed them under a nitrogen atmosphere to Tochko. Figure 2.3 shows a high-resolution STM topography image of the well-ordered SAM on the silver substrate. The scale shows that the nearest neighbor spacing is near 4.6\textAA, in good agreement with previous STM images from the literature.\textsuperscript{73,74} The good agreement of the lattice spacing of the $n$-alkanethiol verifies both that the silver surfaces are epitaxially
grown on mica to provide the (111) plane and that the solution deposition of the monolayers is adequate to prevent an oxide layer from forming on the silver surface.

Figure 2.3 High-resolution STM topographic image of an octadecanethiolate monolayer on silver.

2.2.4.2 Mixed SAMs

In addition to the one-component SAMs, we created a series of mixed monolayers of varying concentrations of HS(CH₂)₁₁CH₃ and HS(CH₂)₁₁OH. These SAMs were created by the immersion technique using solutions containing differing ratios of OH-terminated and CH₃-terminated alkanethiols so that the total concentration for any given ratio of CH₃:OH alkanethiols was 1 mM. The solutions were created by weight and mixed extensively prior to immersion. For each ratio, we placed two clean gold surfaces in the solutions. One surface was used for the scattering experiments and the other for surface composition measurements by XPS. We determined the mole fraction at the surface by taking the ratio of the O(1s) intensity for the mixed monolayer and the O(1s) intensity obtained for the pure OH-terminated monolayer. The integrated intensity of the
O(1s) peak was normalized to the Au(4f$_{7/2}$) peak for each sample to account for any instrumental instability. A plot of the surface mole fraction versus the solution composition is shown in Fig. 2.4.

**Figure 2.4** A plot showing the mole fractions of OH groups in mixed HS(CH$_2$)$_{11}$CH$_3$ : HS(CH$_2$)$_{11}$OH monolayers as a function of mole fraction in solution. The OH mole fraction in solution is determined by weight during the preparation procedure and the surface mole fractions are measured using the integrated XPS intensity for the O(1s) peak.

The XPS data shows that the correlation between solution and surface oxygen concentrations deviate from 1:1 below solution mole fractions of about $\chi = 0.75$. This preferential adsorption that we observe for the CH$_3$-terminated alkanethiols in mixed SAMs is well-documented by many groups and is likely due to hydrogen-bonding interactions of the OH-terminated alkanethiols with the polar solvent, ethanol."
2.3 Ultra-High Vacuum Chamber

An ultra-high vacuum (UHV), pressures \(< 10^{-9} \) Torr, chamber is necessary in gas-surface scattering dynamics studies to provide an environment that prevents the surface from interacting with background gas and keeps it clean. In addition, the UHV atmosphere allows gas-phase species to traverse the chamber, both before and after the interaction with the surface, without colliding with residual gas molecules. Gas-gas collisions change the energy and direction of the gas atoms/molecules and distract from a pure assessment of the gas-surface encounters.

Figure 2.5 Schematic illustration of the main ultra-high vacuum chamber used in the experiments for probing gas-surface dynamics.

Figure 2.5 shows a schematic representation of the UHV chamber employed in our studies of gas-surface energy transfer dynamics. The main chamber is equipped with
a turbomolecular pump (Pfieffer TMU1601P, 1500 ls⁻¹) and a cryogenic pump (CryoPlex 8 UHV Cryopump from Austin Scientific Inc., 1000 ls⁻¹) which provides a base pressure of ~5 x 10⁻¹⁰ Torr. The main chamber is designed to function on two tiers, where the top portion is used for sample transfer and the bottom tier is used for the scattering experiments. Included in the UHV chamber is also a manipulator system (McCallister, MA2012) for sample alignment and translation between the two tiers.

Introduction of the surface samples into the main chamber occurs via a load lock system (MDC Vacuum Products Corp.). The purpose of the load lock system is for quick sample transfer without compromising the pressure within the main chamber. Typical transfer includes venting the load lock system with nitrogen, introducing the sample into the load lock chamber, and pumping the load lock chamber back down (~10⁻⁶ Torr). The total duration for venting and pump down is usually 20 minutes. Once the load lock chamber is back to ~10⁻⁶ Torr, the sample is introduced into the main UHV chamber on a load lock arm and transferred onto the manipulator. The pressure in the main chamber typically reaches ~ 1 x 10⁻⁸ Torr while the gate valve separating the load lock chamber and the main chamber is opened. After the sample is transferred, the load lock arm withdrawn, and the gate valve is closed, the base pressure in the main chamber is regained within about 15 minutes.

After the sample is transferred into the UHV chamber, the manipulator is used to lower the surface down to the bottom tier and align it for scattering experiments. The detector chamber, which contains an ABB Extrel (MEXM1000) quadrupole mass spectrometer, is also illustrated in Fig. 2.5. The detector chamber is differentially pumped with a turbomolecular pump (Pfieffer TMU261P, 250 ls⁻¹) on the first
differential stage and another turbomolecular pump (Pfeiffer TMU521P, 500 ls⁻¹) on the second differential stage. The quadrupole mass spectrometer (QMS) is completely within the second differential stage. The detector chamber is separated from the main chamber by a 4.3 mm aperture, while the first and second differential stages are separated by a 4.7 mm aperture.

The source chamber for creating the molecular beam is on the lower stage and is described in detail in section 2.4.2 below. In addition to the source chamber and the Extrel QMS, there is also another mass spectrometer (UTI, model 100C Precision Mass Analyzer) on the lower tier used for beam characterization.

2.4 Molecular Beam Sources

Molecular beams used in conjunction with ultra-high vacuum chambers are well adapted to study the dynamic interactions of gas molecules colliding with surfaces. One would like to study the actual dynamics that take place at the interface, but there is an experimental limitation to ‘seeing’ these dynamics. We therefore probe the dynamics by investigating the motions of the gas molecules before and after their interactions on the surface. We infer the dynamics that occur while the gas is in contact with the surface by measuring the change in the molecules’ motion since those changes are a direct response to the potential of interaction between the gas species and the surface species. To gain this type of information we use a molecular beam source that allows control over the incident properties of gas atoms/molecules and UHV chambers which provide experimental conditions that allow the surfaces to remain clean and eliminate gas collisions with species other than the surface.
A molecular beam is a beam of molecules with a well-defined cross sectional area, mean velocity, and direction. These molecular beams are created by expanding a gas through an aperture into a vacuum. In principle, the beam can be tuned to obtain a range of average incident energies and directed to strike the surface with any angle of incidence. There are two kinds of molecular beams that are employed in gas-surface scattering techniques and are typically referred to as effusive and nozzle source beams. We have exclusively used the nozzle, or supersonic, beam technique in our scattering experiments, but a discussion of the effusive beam properties is instructive for understanding the flux-weighted Boltzmann distributions we measure after gas-phase species come into thermal equilibrium with the surface.

2.4.1 Effusive Beams and Flux-Weighted Properties of Gases

In an effusive beam, the gas pressure behind the aperture separating the gas from the vacuum chamber (which is assumed to have negligible thickness) is relatively low such that the mean free path of the molecules is larger than the diameter of the hole. The numbers of molecules that actually pass through the aperture are related to the probability of striking the wall in the vicinity of the aperture. This probability allows the properties of an effusive beam to be calculated from the kinetic theory of gases. Typically, when the kinetic theory of gases is considered, one is discussing the instantaneous properties of the gas as a whole within some volume. In contrast, with a flux of gas species, we want to calculate the properties of the gas in that volume that would cross a plane of arbitrary size (the aperture on the wall for example) somewhere in the volume during some time interval. Figure 2.6 (a) and (b) provides schematic diagrams of gas atoms in isolated
containers to illustrate the difference between the properties of the gas species crossing a plane and the properties of the gas as a whole.

\[ V_1 \rightarrow V_2 \rightarrow V_3 \]

\[ V_1 \rightarrow V_2 \rightarrow V_3 \]

Figure 2.6 (a) A one-dimensional illustration of gas molecules in some volume. (b) A two-dimensional illustration of gas molecules striking a plane in some volume.

From Fig. 2.6 (a), imagine that gas species V₁, V₂, and V₃ have velocities 1v, 2v, and 3v and only make elastic collisions with the left and right walls (ignore gas-gas collisions). If we calculate the instantaneous average velocity of the gas species in this one-dimensional volume, the value would be 2v. However, if we calculate the average velocity of a gas species striking, say, the left wall of the chamber in a certain time interval then we would obtain a different result. Let’s say that in a time period, t, gas species V₃ makes 3 collisions with the left wall, V₂ makes two, and V₁ makes only one collision. The average velocity of a gas species striking the wall is then: 

\[
\frac{1}{6}V_1 + \frac{1}{3}V_2 + \frac{1}{2}V_3 = 2.33v
\]

Thus, the average velocity of a gas species striking a plane in a time interval is larger than the average velocity of the instantaneous gas as a whole. This is simply a consequence of the fast species crossing the plane more frequently.
The ideas from Fig. 2.6 (a) can be extended to three dimensions and many molecules to calculate ensemble probability distributions, i.e. a Boltzmann distribution of velocities. The velocity distribution of an effusive beam is then characterized by a flux-weighted Boltzmann distribution at the temperature of the stagnant gas. The instantaneous average energy of the gas at thermal equilibrium in some volume is well known from kinetic theory as $3/2kT$, but the average energy of the same system of gas species crossing a plane in some time interval is $2kT$. This gives an upper limit to the energy accessible with an effusive beam based on properties of the source materials at high temperatures.

The angular distribution of gas species crossing a plane inside the volume is also different than the angular distribution of the gas as a whole. The instantaneous distribution of the gas as a whole is isotropic, but the distribution of the gas crossing a plane is weighted by a cosine distribution. Fig. 2.6 (b) illustrates this angular dependence for gases striking a surface in two dimensions. The probability of a gas crossing the plane is directly related to the normal component of the velocity of the gas species relative to the velocity component lying in the plane. From the diagram, gas species $V_1$, $V_2$, and $V_3$ all have components normal to the plane and have some probability of crossing the plane, but $V_4$ will never cross it.

Like the velocity distribution described above, the ideas derived from the simple model in Fig. 2.6 (b) can be extended to three dimensions. In three dimensions, we need two angles to define the direction an incident gas species approaches the plane. One angle, the polar angle, is defined as the angle relative to the surface normal and will have a cosine probability dependence on striking the plane. The second angle, the azimuthal
angle, is defined as the projection of the incident velocity vector onto the plane and will have a uniform dependence on this angle on striking the plane. The cosine probability of the gas crossing the plane/hole is the basis for the directed motion from an effusive beam source along with apertures placed downstream of the source for collimation.

The ideas derived from the discussion above for an equilibrium volume of gas atoms/molecules striking a plane inside that volume is similar to a surface in thermal equilibrium with a gas. Since the gas is in thermal equilibrium with the surface, we can apply detailed balance and say that the velocity and angular distributions of atoms striking the surface and the distributions of atoms leaving the surface must be the same. When we scatter a high-energy beam (energy greater than 2kT) from a surface, a fraction of those atoms will come into thermal equilibrium with the surface and upon desorption, they will have the same properties as those described above in an effusive beam. The average energy will be 2kT_{surf}, where T_{surf} is the temperature of the surface, the polar angle probability distribution will have a cosine dependence, and the azimuthal angle probability distribution will be uniform.

### 2.4.2 Nozzle Source Beams

In the effusive beam sources, the probability of the gas passing through the hole separating the gas reservoir from the vacuum chamber was shown to depend on the probability of the gas striking the wall in the vicinity of the aperture. If the backing pressure of the gas is increased such that the mean free path of the gas is smaller than the cross section of the hole, then the flow is hydrodynamic and the gas molecules are actually pushed through the hole (the gas passing through the aperture in an effusive beam is described as free-molecular flow). The gas molecules undergo a transition from
a continuum flow regime through the nozzle into a molecular flow regime in the vacuum chamber and the core of the beam is extracted with a conical skimmer. The gas species in the stagnation state, the gas reservoir with negligible flow, accelerates through the nozzle due to the imposed pressure differential toward the exit. The flow through the converging nozzle, based on continuum flow mechanics, allows the gas to accelerate to the local speed of sound at the exit of the nozzle when the ratio of pressure across the two chambers is large, around 2 for all gases. The maximum pressure reached at the throat of the nozzle is approximately one half of the stagnation pressure. Since the pressure in the vacuum chamber is still lower than the pressure at the mouth of the nozzle, the gas is said to be underexpanded and a subsequent expansion occurs as the flow tries to reduce the pressure to meet the pressure of the vacuum chamber (expanding supersonic flow increases velocity and decreases pressure). A region develops in the expanding stream, some distance downstream of the nozzle, where the flow velocity becomes nearly constant and the frequency of intermolecular collisions becomes nearly zero.

The properties of the gas once expanded into the vacuum chamber are different for a nozzle beam compared with an effusive beam. The average translational energy of these gas particles is slightly larger than those in an effusive beam and can be approximated for an ideal gas as:

$$E = \frac{RT\gamma}{(\gamma - 1)}$$

where $\gamma$ is the heat capacity ratio $C_p/C_v$ and $T$ is the nozzle temperature.

In addition to pure beams, supersonic molecular beams with even higher energies can be obtained by a seeding technique. During the expansion, there are around $10^2$ to $10^3$ binary collisions experienced by each molecule. If a heavy gas atom/molecule is
seeded in a lighter gas balance, the heavier gas will be accelerated to nearly the velocity of the lighter gas. By changing the ratio of the heavy and light gas species and the temperature of the nozzle, the translational energy of the beam can be tuned over a wide range of values. The average final speed of the gas mixture is related to the average speed of a gas with a mass calculated by the mean molecular mass (calculated from the concentration of the seeded gas mixture). Thus, high energy beams of inert gases, such as argon, can be attained by seeding them in large quantities of light gases, such as hydrogen. However, unlike the situation with effusive beams, relations between the properties of the nozzle beam and those of the gas in the source are not simple, especially for seeded beams. The most reliable way of determining the properties of a molecular beam are by direct measurements.

Figure 2.7 shows a schematic description of the beam source used in our lab to create and collimate the atomic beams.
Figure 2.7 Side view of the molecular beam chamber used in our experiments.

High-energy atomic beams are created by expanding gases at 700 Torr through a 0.05 mm diameter nozzle (General Valve). After passing through a 0.40 mm diameter, conical skimmer located 6 mm from the nozzle, the beam enters a differential pumping stage where it collides with a mechanical chopper wheel. The slotted wheel, rotating at 300 Hz for most experiments, produces approximately 60 µs pulses of gas that then pass through a 1.5 mm collimating aperture and into a final differential pumping stage. The final pumping stage (pressure = 1x10⁻⁸ Torr) is separated from the main UHV chamber by a 2.2 mm aperture through which the beam passes to produce a 1 cm² spot size on the surface sample located in the main chamber, 36 cm from the nozzle. The triply differentially pumped source chamber is constructed with a VHS 10 Diffusion pump (Varian Vacuum Technologies, 5000 ls⁻¹) on the first pumping stage, a Diffstak® MK2
Diffusion Pump (BOC Edwards, 1500 ls$^{-1}$) on the second differential stage, and a Pfeiffer TMU 261P turbomolecular pump (250 ls$^{-1}$) on the final pumping stage.

The molecular beam energy is characterized with a mass spectrometer (UTI) located in the beam path directly behind the surface sample location. By translating the surface out of the path of the beam and performing TOF measurements on the incident gas pulse, we determine the peak energies, $E_i$, and the energy spread, $\Delta E_i$, for each beam. The distance between the chopper wheel and the ionizer of the mass spectrometer is calculated from a pure atomic beam of argon. From the relation given above where the energy of the molecular beam is related to the heat capacities of the gas and the nozzle temperature, we calculated the energy of a pure argon beam as 6.2 kJ/mol. Using the relation of kinetic energy to gas velocity, we then calculated the flight distance from the peak arrival time in the TOF measurement. In our apparatus, the flight path was calculated as 58 cm.

A top view of the scattering orientation for characterizing the molecular beams is provided in Fig. 2.8.
The following high-energy beam values were calculated from the beam measurements. Argon beams of two different energies: 5% Ar in He (35 kJ/mol, FWHM = 6 kJ/mol) and 2% Ar in H₂ (80 kJ/mol, FWHM = 13 kJ/mol), two different beam energies of krypton; 3.5 % Kr in He (61 kJ/mol, FWHM = 12 kJ/mol) and 2.5 % Kr in H₂ (102 kJ/mol, FWHM = 19 kJ/mol) and two different beam energies of xenon: 5.0 % Xe in He (61 kJ/mol, FWHM = 12 kJ/mol) and 4.0 % Xe in H₂ (95 kJ/mol, FWHM = 21 kJ/mol).
2.5 Sample Transfer, Alignment and Scattering

Upon monolayer formation, the samples were removed from solution, rinsed with copious amounts of ethanol, dried in a stream of nitrogen, and transferred via the load-lock system into the scattering chamber. The total time between removal from the preparation solution and introduction into the load-lock chamber was about 10 minutes. The pressure in the load-lock chamber reached $\sim 10^{-6}$ Torr in about 20 minutes, after which the samples were transferred into the main UHV chamber, which operates at $5 \times 10^{-10}$ Torr with the source beam off and at $1 \times 10^{-9}$ Torr with the beam entering the chamber. The total time between removal of the samples from the preparation solution and complete TOF data collection was $\sim 60$ minutes. We found the TOF spectra to be highly reproducible over this time period. The experimental data shown in subsequent chapters was also found to be highly reproducible from day to day and from sample batch to sample batch. In addition, our surface mount holds two surfaces so that scattering can be performed under the same UHV and beam conditions enabling us to compare surfaces on relative scales. The time period between scattering from surfaces installed simultaneously was less than 5 minutes for a given beam. Switching between the two surfaces only requires a 1 cm translation of the manipulator.

The surface samples are laser-aligned so that the normal is in-plane and at $\theta_i = 30^\circ$ to the molecular beam. One must be careful to get the samples in the middle of our chamber for every scattering experiment. Caution is important because we only know the precise distances (used when calculated velocity distributions) from the chopper to surface and from the surface to the ionizer of the mass spectrometer when it is in the middle of the chamber. The manipulator has 4 degrees of freedom for sample alignment.
A z-axis, which we designate as the up and down direction, two axes, x and y defined arbitrarily, that control the movement in the plane of the scattering orientation and one rotation degree of freedom about the z-axis. The x and y axes are oriented such that one axis is normal to the plane of the mass spectrometer aperture and the other is parallel to it.

We align the surface by shining a laser beam through a window on the rear part of the mass spectrometer, through the aperture of the mass spectrometer and onto the surface as shown in Fig. 2.9(a). We move the surface position with the manipulator until the laser beam is hitting the center of the sample surface (by eye) and reflecting directly back through the mass spectrometer aperture such that the reflected beam is co-linear with the incident beam. The sample center is in-line with the axis of the mass spectrometer, which is aimed at the center of the main chamber. We then rotate the sample by 30° to position the sample into the specular scattering position, Fig. 2.9 (b). If the center of the sample is in the middle of the chamber, then the laser beam will shine through the aperture of the detector chamber, reflect off the surface and pass through the aperture of the source chamber. Otherwise, we adjust the x-axis micrometer to meet this condition, Fig. 2.9 (c). Once the laser beam is shining through the source aperture, we know that the sample is correctly aligned and in the center of the chamber, Fig. 2.9(d).
Figure 2.9 Schematic representation of sample alignment viewed along the z-axis. (a) Sample is aligned normal to mass spec aperture so laser reflects back on itself. (b) Sample has been adjusted in the y-axis so laser hits center. (c) Sample has been rotated by 30° for scattering but the x-axis is not aligned properly. (d) Sample has been adjusted along the x-axis until the laser reflects into the aperture of the source.

Once the sample is in scattering position, the atomic beam is introduced into the main chamber by opening a gate valve between the source chamber and the main chamber. A fraction of the atoms that scatter from the surface are intercepted by a doubly differentially pumped Extrel mass spectrometer oriented at 60° to the incident beam such that $\theta_f = 30°$. The ionizer of the mass spectrometer is positioned 29 cm from the surface and views a 1 cm² spot size on the surface through two collimating apertures.

The TOF distributions of the scattered atoms are determined by monitoring the mass spectrometer signal at the singly ionized parent mass as a function of time. Each
TOF scan is initiated when a slit of the chopper wheel passes a LED-photodiode arrangement that sends a voltage pulse to trigger a multi-channel scaler (Ortec). The multi-channel scalar integrates signal from the spectrometer in 10 µs intervals.

The intensities and shapes of the TOF spectra were found to be highly stable over the course of these studies. The stability in the experiments enabled studies to be performed on many different surface samples under identical conditions, facilitating direct comparisons of TOF spectra on relative scales. For each set of experiments presented in the following chapters, where the data are plotted on relative scales, we performed the measurements during the course of a one-day period to minimize the effects of any slight changes in the beam intensity or mass spectrometer efficiency that may occur from day to day. An example of a typical one-day experiment involved recording TOF spectra for up to ten samples while the beam, the chopper, and the mass spectrometer remained in operation during sample removal and introduction. The surfaces of a given study were introduced and TOF data recorded in pseudo-random order. Unless otherwise specified, the surface samples were held at 298 K during the data collection.

2.6 Data Analysis

2.6.1 Raw Data and Timing Corrections

The raw data that we record in our TOF measurements have several timing offsets and mass spectrometer sensitivity issues that need to be taken into account in order to compute final energy probability distributions. In our raw data collection, we measure the signal from a mass spectrometer after a trigger pulse from an LED-photodiode. The recorded TOF distribution includes a response time of the photodiode used in the
triggering apparatus, a lag time between the LED pulse and the time the chopper slit passes in front of the aperture of the source beam, the flight time of the incident gas from the chopper wheel to the sample, the time the gas spends on the surface, the flight time from the sample to the ionizer of the mass spectrometer, and the ion flight time in the quadrupoles. Each of these electronic and timing offsets are accounted for according to established protocols.\textsuperscript{82,83} The following discussion explains how each of these timing issues is corrected.

\[
t_{\text{arrival}} = t_{\text{total}} - (t_{\text{elec}} + t_{\text{chopper-off}} + t_{\text{chopper-surf}} + t_{\text{mass spec}})
\]

The arrival time is calculated from the above equation, where \( t_{\text{total}} \) is the total flight time measured, \( t_{\text{elec}} \) is the electronic timing offset, \( t_{\text{chopper-off}} \) is the chopper/beam timing offset, \( t_{\text{chopper-surf}} \) is the flight time from the chopper to surface, and \( t_{\text{mass spec}} \) is the time spent in the mass spectrometer.

We estimated the electronic timing offsets of the photodiode response time by measuring the time delay between exciting the photodiode with a laser pulse and the signal output on an oscilloscope. This timing delay was about two microseconds for our arrangement.

The timing offset for the lag time between the LED-photodiode trigger and the actual beam pulse is illustrated in Fig. 2.10. The LED-photodiode, the chopper slit, and the source aperture are all labeled in the schematic. The LED-photodiode sends a TTL pulse to the computer when the slit passes between the LED and the photodiode. The beam pulse occurs sometime later when the chopper slit passes in front of the source aperture.
If the chopper wheel is spinning in the clockwise direction (CW), the beam pulse will occur before the trigger pulse. If the chopper wheel is spinning in the counter clockwise direction, the opposite is true. We measure the time period of one rotation of the chopper on an oscilloscope by recording the time between pulses of the LED-photodiode. To calculate the actual time lag between the trigger and the beam pulse, we record a TOF spectrum with the wheel spinning in one direction then reverse the direction of the chopper and record another. Then, we measure the difference in the peak arrival times from the TOF spectra recorded for the chopper spinning in the two opposite directions. These two timing measurements provide us with two equations with two unknowns. The total time of the chopper is equal to the sum of the time lag between the pulse to slit (use $x$) and slit to pulse (use $y$). The difference in the peak arrival times gives the difference in the time between $x$ and $y$. From the two equations, we calculate the time lag between the trigger pulse and the beam pulse for both directions of spinning. We then subtract this time from the raw TOF spectra. In our TOF distributions where the chopper wheel is spinning in the CCW direction at 250 Hz, the timing offset is 933 $\mu$s ($84^\circ$ between LED-photodiode and source aperture).
We have also used a chopper wheel with two slits, ~180° apart, for faster data collection. Including two slits in the chopper wheel makes calculating the timing offset a little more challenging, but can be approached in the same way. When we have a two-slit chopper wheel, we measure every other pulse from the LED-photodiode/oscilloscope setup to obtain the chopper rotation period. We then measure TOF distributions, but only trigger off every other LED-photodiode pulse spinning the chopper wheel in each direction. This provides signal from two consecutive gas pulses in the TOF distributions. We then measure the time of the second peak spinning the chopper wheel in the CW and CCW directions. The differences in the two peak times for spinning the chopper wheel in each direction allows the trigger pulse and the gas pulse to be calculated in a similar way as described for the single slit chopper wheel.

The next timing offset to consider is the flight time of the gas from the chopper wheel to the surface. We calculate this timing offset directly since we have characterized
the beam energies and we know the dimensions of our chamber. We then subtract this value from the raw TOF data. For example, an 80 kJ/mol beam of argon atoms takes 155 μs to travel from the chopper to the surface (31 cm).

The flight time of the ions in the mass spectrometer can be obtained from recording the TOF distribution for a gas that fragments into several ionic species or a series of multiply ionized atoms. We have used a molecular beam of CO\textsubscript{2} and multiple mass to charge (m/z) species of xenon for this calculation. When using CO\textsubscript{2}, we recorded TOF distributions at m/z = 16, 28, and 44. For xenon, we used the m/z values of 44, 66, and 132. The parent molecules will have the same flight time until they reach the ionizer of the mass spectrometer at which time they will fragment and have different trajectories through the quadrupoles. We then use the TOF distributions recorded for the three mass to charge fragments to obtain a calibration curve for the flight time of a given ion fragment in the quadrupoles. We can derive the formula

\[ t_q = \left( L_q \sqrt{\frac{1}{2E}} \right) \sqrt{m} \]

from the kinetic energy expression, where \( t_q \) is the time spent in the quadrupoles, \( L_q \) is the flight path in the quadrupoles, \( E \) is the translational energy, and \( m \) is the mass to charge ratio. We do not need to specifically know the values of each term, but plot the peak arrival time from the TOF spectra, \( t_q \), as a function of the \( \sqrt{m} \). The slope of the line is then used to calculate an ion flight time for other mass to charge species. Multiplying the slope derived from the calibration curve by the square root of the mass to charge ratio of the ionized gas species under investigation provides the appropriate timing offset. We then subtract this time from the raw TOF distribution. We find that a slope of 6.5
provides a good fit when using the Extrel mass spectrometer. The characterization slope provides timing offsets in the range of 40 to 75 $\mu$s for the gases used in our studies.

After we make all of the timing corrections to our TOF distributions, we are left with the residence time of the gas species on the surface and the flight time from the surface to the ionizer of the mass spectrometer. For the inert gases used in the experiments outlined in this thesis, the residence time is negligible since the gas-surface interactions are on the picoseconds time scale $^{29,75}$ and the timing resolution of our experiments are on the tens of microseconds time scale. The final form of the TOF distributions for beam scattering data are plots of the mass spectrometer signal versus the flight time for atoms to traverse the distance, $L$, between the surface and the ionizer of the mass spectrometer.

**2.6.2 Transformation of TOF to Probability Distributions and Deconvolution**

The raw spectrometer signal is proportional to number density, $N(t)$, and is used to compute the probability, $P(E_f)$, that a gas atom leaves the surface with final translational energy, $E_f$. The translational energy distributions are computed from the relations $E_f = (1/2)m_g (L/t)^2$ and $P(E_f) \sim t^2N(t)$, where $t$ is the gas atom flight time from the surface to the ionizer and $m_g$ is the gas atom mass. The second relation for computing the probability distributions from the number density comes from the ionization probabilities of electron impact mass spectrometers. $^{80}$ The faster moving atoms have a lower probability of ionization than the slower moving atoms which is related to the time the neutral species spends in the ionizer of the mass spectrometer.

Figure 2.11 (a) shows TOF data for a high-energy argon beam scattering from a pure gold surface to illustrate the transformation of TOF data into probability
distributions and the deconvolution of the data into the two limiting scattering pathways. The high velocity peak at early arrival times (~250 μs) is indicative of direct inelastic scattering and the broad component at later arrival times represents the atoms that have lost all or the majority of their excess energy to thermalize on the surface before recoiling back into the gas phase with a Boltzmann velocity distribution at the temperature of the surface.\textsuperscript{84-90} Deconvolution of the data into the two limiting channels is performed after transformation into energy space.

Figure 2.11 (a) A time-of-flight spectrum for 80 kJ/mol argon scattering from a pure gold surface. (b) The corresponding translational energy distribution, $P(E_t)$, from (a). The dashed curve is a Boltzmann distribution at the temperature of the surface, and the solid lines are the inelastic scattering components.
The translational energy distribution in Fig. 2.11 (b) is separated into a direct-inelastic scattering component (IS) and a trapping-desorption component (TD) by assigning the TD component to the part of the final energy distribution, \( P(E_f) \), that falls within a Boltzmann distribution: 
\[
P_{TD}(E_f) = E_f (RT_{surf})^{-2} \exp(-E_f/RT_{surf}).
\]
The inelastic component is assigned to the difference between \( P(E_f) \) and \( P_{TD}(E_f) \), constrained such that \( P_{IS}(E_f) = 0 \) for \( E_f \leq RT_{surf} \). The TD components are provided in Figs. 2.11 (a) and (b) by the dashed curves and the IS components are represented by the solid lines. Notice that the time-of-flight IS and TD components were transformed from the energy distributions back into time space.

As discussed in subsequent chapters, the dynamics of gas-surface collisions are revealed through analysis of the fractional energy transferred to the surface in the inelastic channel, \((E_i - \langle E_{IS}\rangle)/E_i\), and the fraction of atoms that recoil (at \( \theta_f = 30^\circ \)) with a thermal distribution of velocities (TD fraction). The TD fraction is defined as the weighting coefficient, \( \alpha \), in the relation: 
\[
P(E_f) = \alpha P_{TD}(E_f) + (1-\alpha)P_{IS}(E_f).
\]
Impulsive scattering at the specular angle results from those atoms that ricochet off the outermost layer of the surface atoms. Analysis of the energy distribution in this channel provides insight into the collective mass of the surface atoms involved in the collision and the relative rigidity of the surfaces studied. Measurement of the fraction of atoms that thermalize, or nearly thermalize, on the surface before desorption provides complementary information about the gas-surface interaction. Specifically, TD fractions reveal the propensity for atoms to undergo multiple collisions or the ability of a surface to efficiently dissipate large amounts of collisional energy through extended, non-localized motions. As an example of data analysis, Fig. 2.11 (a) and (b) shows that 80 kJ/mol
argon atoms have a TD fraction of 0.20 and an average energy transferred in the impulsive scattering channel of 0.67 for collisions with a clean gold surface.

2.6.3 Sensitivity of Scattering on SAM Preparation

The scattering distributions for argon scattering from gold is instructive for data analysis and definitions, but we are mainly interested in studying the gas-surface dynamics in collisions with organic surfaces. One concern we have is with the preparation conditions of the monolayers employed in those studies. We have therefore tested the sensitivity of scattering on the preparation conditions of SAMs. The scattering experiments included SAMs created from solution deposition onto gold coated Cr/glass slides (polycrystalline surface), solution deposition onto gold-coated Mica (large single crystal domains), and vapor deposition onto gold-coated mica slides.

Figure 2.12 demonstrates that, despite differences in the polycrystalline structure of the two gold surfaces, the scattering results are nearly independent of the underlying substrate. Furthermore, we have also prepared SAMs using the vapor deposition technique described by Gorman et al.\textsuperscript{54} Their scanning-tunneling microscopy studies demonstrate that this procedure produces SAMs that are of much higher quality and free from many of the defects typically observed in solution-prepared SAMs. The remarkable agreement among the three different deposition techniques highlights the fact that the argon scattering appears to be insensitive to changes in the long-range order of the self-assembled monolayers. We therefore used the solution deposited SAMs on the glass/Cr/Au substrates for convenience since nearly identical scattering results are obtained for both substrates and both SAM preparation procedures.
Figure 2.12 Final probability distributions for 80 kJ/mol argon scattering from C$_{12}$ SAMs constructed on a gold/Cr/glass substrate (open circles) and gold coated mica substrates from solution deposition (filled circles) and vapor deposition (crosses).
Chapter 3

The Role of Packing Density, Chain Length, and Terminal Group Orientation on Energy Transfer Dynamics


3.1 Background

The fate of the gas-phase particle in gas-surface reactions is determined to a great extent by the energy exchange between the gas-phase projectile and the surface during the initial collision. The energy exchange dynamics of gas-surface collisions involving atomic gases and organic surfaces have been the subject of recent studies. In these studies, rare gas atoms are often used to eliminate reactions and focus on the initial impact. For inert atomic gases, the type of gas-surface interactions can be, in most cases, separated into two limiting processes, direct impulsive scattering (IS) and trapping-desorption (TD). Atoms that make up the trapping-desorption channel have lost memory of their incident parameters and leave the surface with thermal energy and cosine-like angular distributions. In contrast, those atoms that scatter from the surface impulsively only lose a fraction of their energy in one or a very few number of collisions with the surface. Analysis of these two scattering channels is often used to infer the dynamics that take place during the gas-surface interactions.

Self-assembled monolayers (SAMs) form well-ordered films, which provide ideal surfaces for studying energy transfer pathways in organic surfaces. The long-range order of SAMs makes them particularly good candidates for identifying properties of organic thin films that are either efficient for energy absorption or hinder energy transfer to the
surface. The first gas-surface scattering studies using SAMs were performed by Cohen et al. when they scattered atomic and diatomic gases from long-chain amphiphilic monolayers.\textsuperscript{10,27} They proposed that the low-frequency concerted waving motion of chains parallel to the surface plane, hindered rotation of the end group, and vibration along the chain axis are responsible for the large extent of gas-surface energy transfer in these films.\textsuperscript{10}

In the Hase research group, molecular dynamics simulations of neon scattering from a model of a $n$-hexyl thiolate SAM on Au(111) revealed some unexpected results.\textsuperscript{28} Although the final energy distributions were bimodal, the low-energy component, which is commonly assigned to trapping-desorption, could not be fit with a Boltzmann distribution at the surface temperature. This important discovery led to a series of detailed investigations aimed at understanding the origin of the bimodal distribution for impulsive energy transfer from these surfaces.\textsuperscript{29,30,32} Combined experimental and computational efforts revealed that efficient energy transfer results from trajectories in which the neon atom strikes the alkyl chain from the side.\textsuperscript{33} Side-on collisions are more efficient in transferring energy to the surface for two reasons. Low-frequency modes are more easily excited and intramolecular vibrational energy redistribution takes place on the time scale the neon atom is in contact with the surface, which in turn couples more surface modes to the energy transfer coordinate. The bimodal distributions were, therefore, attributed to the different impact parameters for the neon atoms with the alkyl chains.

The neon scattering discoveries led to the development of a modified classical washboard model\textsuperscript{15} to represent the surface response to impact parameter. The model
added a rotational degree of freedom to the surface to account for the high efficiency of side-on impacts in energy transfer. Indeed, a bimodal distribution of final energy scattering without a trapping-desorption channel followed from this added rotational degree of freedom.

In addition to neon, the interactions of argon with well-ordered decanethiolate SAMs on Au(111) have been studied experimentally and computationally. Unlike the neon scattering results, the low-energy component of the final energy distributions for argon could be directly attributed to trapping-desorption. Experimentally, the low-energy component was well fit by a Boltzmann distribution for a range of surface temperatures and exhibited a cosine angular intensity profile. More direct evidence for a true trapping-desorption channel came from simulations that showed a fraction of the trajectories reside on the surface for long times (> 1ps) and that both normal and parallel components of the incident momentum thermally accommodate with the surface. The presence of the trapping-desorption channel for argon scattering and the absence of this channel in neon scattering are related to the difference in the polarizability of the two gases. The potential well depth between an individual methyl group and argon is approximately 1.34 kJ/mol compared to 0.50 kJ/mol for the neon-methyl well depth. In addition to the differences in the gas-surface potential, the argon atoms are approximately double the mass of neon which may also contribute to the dynamics of desorption after the gas-surface collisions.

Several investigators including Cooks et al., have explored the characteristics of high-energy ionic collisions on model organic surfaces using a variety of ω-functionalized SAMs. Hanley and co-workers have combined experimental and computational approaches to study the energy transfer of SiMe$_3^+$ on a hexanethiol
Their work shows that energy transfer to a surface is markedly greater for a monolayer-covered surface than it is for a bare gold surface and that penetration into the monolayer, even for greater than 10 eV ions, is limited to the topmost two-to-three layers of carbon atoms. Wysocki and co-workers,92 and Bernasek et al.,39 have also investigated the reaction dynamics of ion-surface scattering using SAMs. This set of work has provided important insight into how end-group orientation and the overall chain-length of a monolayer influence the ion-surface reaction dynamics.

The focus of this chapter is to further the understanding of energy dissipation pathways in gas collisions on organic surfaces. Particularly, the influence of alkane packing structure and density, alkane chain length, and terminal group orientation on energy transfer dynamics is explored when argon atoms impact \( n \)-alkanethiol self-assembled monolayers of the form \( \text{HS(CH}_2\text{)}_n\text{CH}_3 \) (\( 2 \leq n \leq 18 \)) adsorbed to gold and silver substrates.

### 3.2 Structural Considerations of \( n \)-Alkanethiol SAMs on Gold and Silver Substrates

The (111) planes of gold and silver have lattice spacings that are nearly identical, but the structures formed from adsorption of \( n \)-alkanethiols to these two substrates are quite different.73,95-97 It is now well-established that \( n \)-alkanethiols chemisorb onto Au(111) through a strong Au-S bond to form dense monolayers with an average intermolecular alkane chain separation of 5.0 Å, which produces an overall \((\sqrt{3}\times\sqrt{3})R30^\circ\) lattice.25,51-57 Alkanethiols adsorbed to Ag(111), on the other hand, form an incommensurate hexagonal structure that is similar to a \((\sqrt{7}\times\sqrt{7})R10.9^\circ\) overlayer and an alkane chain separation of 4.7 Å.98 In both cases, the chains are well-ordered and pack in the all trans configuration. The chain tilt angle relative to the surface normal changes
from ~30° on gold to ~12° on silver. Figure 3.1 shows representative top and side views of C_{10} SAMs adsorbed to gold and silver substrates, respectively. The top view illustrates the hexagonal structure of the methyl-terminal groups for each SAM scaled to the proper lattice spacing, demonstrating the difference in packing density. The side view is also scaled to the proper lattice spacings for two adjacent chains illustrating the tilt angle relative to the surface normal for these two types of monolayers. Another interesting feature of these SAMs, which is exemplified in the side view representations, is the relative orientation of the carbon-carbon bonds. For the SAM on silver, each carbon-carbon bond has approximately the same angle relative to the surface normal, whereas the carbon-carbon bonds for the SAM on gold oscillate between relatively normal to relatively parallel to the surface plane.
Figure 3.1 Schematic representation of SAMs on gold (left) and SAMs on silver (right) to demonstrate the difference in packing density and chain tilt angle. The top view shows the hexagonal structure of the terminal methyl-groups scaled to nearest neighbor spacing of 4.98 Å and 4.67 Å for the SAMs on gold and silver, respectively. The side view shows two chains for each SAM.

The long-chain monolayers on gold, with $n \geq 6$, have been shown to exhibit very high stability and crystalline-like long-range order characterized by a c(4x2) superlattice. Although the short-chain monolayers have not been explored to the extent of the long-chain systems, several studies have shown that they readily form a complete monolayer of density and structure similar to that of the long-chain systems. In comparison, the monolayers of the short chain alkanethiols on silver exhibit a higher degree of order than the corresponding monolayers on gold. In general, alkanethiol self-assembled monolayers have been demonstrated to be stable in ultrahigh
vacuum (UHV) environments over time scales of several hours to several days.\textsuperscript{52,53,56,57,103}

3.3 Data Analysis

The probability distributions of argon atoms leaving the surface with a particular final translational energy are separated into two channels: direct impulsive scattering and trapping-desorption. To separate these two channels, we assume that those atoms that become momentarily trapped in the gas-surface potential well reach thermal equilibrium and can be fit with a Maxwell-Boltzmann distribution of energies. The remaining area is assigned to the direct impulsive scattering channel with the added restriction that scattering in this channel has zero probability for $E_f$ less than $kT_{\text{surf}}$.

Separation of the energy distribution into the two limiting channels can be performed when the incident argon energy is sufficiently large so that separation of the impulsive scattering distribution and the Boltzmann distribution is maximal. Figure 3.2 shows a translational energy probability distribution for an 80 kJ/mol argon beam scattering from a room temperature decanethiol SAM on gold. This figure demonstrates how energy distributions are deconvoluted into the two scattering channels.
As discussed below, the dynamics of gas-surface collisions are revealed through:

(a) analysis of the fractional energy transferred to the surface in the IS channel \((E_i - <E_{IS}>) / E_i\),
(b) the relative number of atoms that recoil (at \(\theta_i = 30^\circ\)) with a thermal distribution of velocities (TD fraction), and
(c) the relative number of atoms that recoil (at \(\theta_i = 30^\circ\)) as part of a higher energy impulsive scattering channel.\(^3\)

### 3.4 Alkane Chain Packing Density

Argon beams of three different energies (see section 2.4.2 for beam energy measurements): neat Ar (7.0 kJ/mol, full width at half maximum (FWHM) = 0.6 kJ/mol), 5% Ar in He (35 kJ/mol, FWHM = 6 kJ/mol), and 2% Ar in H\(_2\) (80 kJ/mol, FWHM = 13 kJ/mol) were used in this study to explore the energy transfer dynamics from long chain SAMs on silver and gold. Figures 3.3 (a) - 3.3 (c) show energy distribution plots, \(P(E_f)\), for argon scattering from C\(_{12}\) SAMs on gold and silver. The distributions are shown with

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**Figure 3.2** Translational energy distribution showing the deconvolution of the two limiting pathways: direct impulsive scattering (IS) and trapping-desorption (TD).
increasing incident beam energy from Figure 3.3 (a) to 3.3 (c) and are plotted on relative scales.

Figure 3.3 Final translational energy distributions for three different incident argon beam energies, (a) 7 kJ/mol, (b) 35 kJ/mol, and (c) 80 kJ/mol scattering from C\textsubscript{12} monolayers adsorbed to gold substrates (filled circles) and silver substrates (open circles). The incident beam profile is included in (a), normalized to the peak height of the scattering distributions. The Maxwell-Boltzmann distributions used to fit the TD channel for scattering from the SAMs on gold and silver are represented by the solid and dashed lines for T\textsubscript{surf} = 300 K, respectively.
3.4.1 Low-Energy Scattering ($E_{\text{inc}} = 7 \text{ kJ/mol}$)

Figure 3.3 (a) is a comparison of final energy distributions for a 7 kJ/mol argon beam scattering from C$_{12}$ monolayers on silver and gold. The incident beam is also included in the figure to show the extent of energy transfer from the gas to the surface and vice versa. The impulsive and trapping-desorption components are indistinguishable for both SAMs on silver and gold, and the global distribution is well fit by a Maxwell-Boltzmann (MB) distribution at the surface temperature of 300 K.

Although the structures of the two surfaces are different, it is not surprising that we observe full thermal equilibration for the 7 kJ/mol incident argon beam. Gibson et al. showed that argon atoms scattered from a decanethiol SAM on Au(111) with a ~6.3 kJ/mol beam and small incident polar angles come off the surface with average final energies near 2k$T_{\text{surf}}$ at $T_{\text{surf}} = 135 \text{ K}$.\textsuperscript{35} They also measured final angular distributions for $\theta_i = 10^\circ$ and $45^\circ$ with best fits of the intensity profiles with $\cos^{1.0}(\theta_{\text{fin}})$ and $\cos^{0.82}(\theta_i)$, implying that nearly all scattered atoms have reached thermal equilibrium with the surface. In addition, Cohen et al. measured average final energies near 2k$T_{\text{surf}}$ for a low-energy argon beam scattering from an $n$-octadecyltrichlorosilane monolayer on glass with $\theta_i = 60^\circ$ and $\theta_{\text{fin}} = 0^\circ$.\textsuperscript{10} For incident argon beams with near thermal energies and near normal approach angles, the only gas-surface process observed is trapping-desorption for alkane-based monolayers. This implies that every incident argon atom becomes temporarily trapped in the gas-surface potential well through weak, non-bonding interactions (physisorption). It also implies that the surfaces are corrugated enough that the atoms trapped in the wells lose sufficient energy in both the normal and parallel directions to reach thermal equilibrium and desorb with a statistical energy distribution.
3.4.2 High-Energy Scattering (E_i = 35 and 80 kJ/mol)

In contrast with low-energy scattering, where the incident argon atoms fully thermalize on both surfaces, the final energy distributions for beam energies much greater than kT_{surf} can be deconvoluted into the two limiting scattering channels. Figures 3.3 (b) and 3.3 (c) show comparative plots for 35 and 80 kJ/mol argon beams scattering from C_{12} SAMs on gold and silver. The final probability distributions demonstrate that the argon atoms retain a larger amount of their incident energy after scattering from the SAM on silver than retained after scattering from the SAM on gold. It is important to note that the final probability distributions are on the same relative scale since the surfaces are placed in the UHV chamber at the same time on the same sample holder. (see section 2.5)

The Boltzmann distributions used to fit the trapping-desorption channel are also included in each figure. In addition to greater overall average energy transferred to the surface, the TD fraction is larger (larger Boltzmann component) for scattering from the SAM on gold than the SAM on silver. The TD fraction decreases from 0.73 to 0.62 when scattering from SAMs on gold relative to SAMs on silver at E_i = 35 kJ/mol. The difference increases for scattering with the 80 kJ/mol beam where the TD fraction for the SAMs on silver is 25% smaller than for the SAMs on gold (TD fractions: 0.46 and 0.61, respectively).

The principle of detailed balance requires that the angular distribution for thermally-desorbing gas particles from a surface to be well-defined as a cosine function around the surface normal. Therefore, although we detect at only one final angle, the measured intensity of the TD component is representative of the total number of atoms in the TD channel. Figures 3.3 (b) and 3.3 (c) demonstrate that the total number of argon
atoms that reach thermal equilibrium with the SAM on gold is greater than the extent of thermalization with the SAM on silver. We also find that thermal Boltzmann distributions provide excellent fits to the TD channel over a temperature range from 135K to 350K for both the SAMs on gold and the SAMs on silver. This suggests, in conjunction with the results from low-energy scattering, that the low-energy Boltzmann component of the data truly represents a trapping-desorption process in these systems.

The high-energy argon scattering experiments presented by the Sibener group showed that argon atoms assigned to the low-energy portion of the final energy distribution arise from a trapping-desorption channel. Simulation results described in chapter 4 show that the same is true for SAMs on silver. This is not surprising since the chemical nature of the interfacial regions of the two surfaces is identical.

In addition to the differences in the fraction of atoms that reach thermal equilibrium with the two surfaces, the average energy transferred in the impulsive scattering channel is ~7% higher for the SAM on gold than the SAM on silver. This trend may stem from differences in the interfacial region of the SAM on gold and the SAM on silver. The SAM on gold may look rougher to the incident argon atoms since the lattice spacing of the terminal methyl groups is larger than the SAM on silver, see Figure 3.1.

We attempted to explore how minor differences in surface roughness affect the IS and TD intensities by creating a SAM composed of approximately a 1:1 mixture of C\textsubscript{11} and C\textsubscript{12} alkanethiols. The monolayers for this analysis were made on gold substrates. Figure 3.4 is a comparison of the translational energy probability distributions for 80
kJ/mol argon atoms scattering from a pure dodecanethiol SAM and the intentionally roughened SAM.

The comparison shown in Fig. 3.4 demonstrates, as expected from previous work,\textsuperscript{9,19,22} that the TD intensity is greater on the mixed (rough) SAM. We find that many of the atoms that scatter impulsively on the smooth surface instead undergo additional collisions to dissipate their excess energy and approach thermal equilibrium on the mixed surface. Although we have not quantitatively determined the surface structures or degree of roughness of the mixed SAM, the data shows that a decrease in the IS channel due to roughness is balanced, to some extent, by an increase in the TD intensity. Our simulation data, discussed in the following chapter, verify this hypothesis.
Figure 3.4 Relative translational probability distributions for 80 kJ/mol argon scattering from a SAM created in a solution composed of a 1:1 mixture of C\textsubscript{11} and C\textsubscript{12} alkanethiols (open symbols) and from a pure C\textsubscript{12} SAM.

Surface corrugation may enhance the fraction of atoms that reach thermal equilibrium with alkanethiols adsorbed to either silver or gold, but does not likely explain the higher average energy transferred to the SAM on gold in the impulsive scattering channel. The similar profile of the IS channel in Fig. 3.4 implies that atoms scattered inelastically at the specular angle experience similar types of events on both atomically smooth and rough surfaces. The higher average energy transferred in the impulsive channel for the SAM on gold, as illustrated in Fig. 3.3, reflects the surfaces’ intrinsic ability to more readily absorb the excess energy of the colliding argon atoms compared to the SAM on silver.
The variation in the scattering dynamics of these two surfaces must stem from the differences in the packing structures and densities of the alkane chains. For argon beams with $\theta_i = 30^\circ$, the projection of the incident velocity vectors onto the chain axes is different for the SAMs on silver and gold substrates due to the difference in the chain tilt angles. Detailed molecular dynamics studies of neon scattering from decanethiolates on gold show that argon trajectories with side-on approaches transfer more energy to the surface than on-top collisions. In addition, simulations of argon scattering from SAMs on gold were performed to test the dependence of the chain tilt direction on energy transfer. The results showed that energy transfer is enhanced for trajectories aimed along the tilt direction. This type of structural scattering likely contributes to the differences in energy transfer between the alkanethiols adsorbed on the gold and silver substrates.

In addition to chain tilt effects, the two types of surfaces have different packing densities of the alkyl chains that might affect energy transfer pathways. For the SAMs on silver, the chains are closer together and experience more repulsive interactions for a given change in equilibrium position. The intermolecular van der Waals frequencies are therefore higher for the more densely packed SAM on Ag surface. Consequently, higher packing densities prevent chains from moving in the plane of the surface, thereby rendering it more difficult to excite some of the low-frequency wagging modes.

Interestingly, frictional force measurements, performed by Brewer et al., that probed the influence of packing density on the coefficient of friction reached a parallel conclusion for energy dissipation. In an experimental investigation comparing frictional properties of $C_{11}$ monolayers, a higher coefficient of friction was reported for
monolayers on gold than silver. The authors argue that the creation of gauche defects and other chain deformations would be more facile for low packing density monolayers. This conclusion is supported by molecular dynamics simulations where the role of packing density effects was shown to influence frictional forces under high loads. The authors observe a resistance to deformation for the more densely packed hydrocarbons.

3.5 Chain Length Effect

The \( n \)-alkanethiol SAMs, in conjunction with atomic-beam time-of-flight (TOF) scattering techniques, enable investigations into key aspects of the gas-surface collisional dynamics. By scattering from the series of \( n \)-alkanethiol SAMs, we are able to explore the number of surface carbon atoms along an alkane chain that participate in the collision. Such studies lend insight into the importance of long-range molecular motions versus localized torsions and vibrations in controlling the outcome of a gas-surface collision.

3.5.1 \( n \)-Alkanethiols on Gold

Figure 3.5 shows translational probability distributions for the 80 kJ/mol Ar beam scattering from \( C_2, C_4, C_6, \) and \( C_{12} \) \( n \)-alkanethiol SAMs on gold. The probability energy distributions demonstrate that, as the chain-length increases from 2 carbons atoms to 4 carbon atoms, the IS channel shifts to lower energy and the TD intensity increases. Increasing the carbon chain from 4 to 6 has a similar affect on the dynamics where the IS channel shifts to even lower energy accompanied by an increase in the intensity of the TD channel. However, increasing the number of carbon atoms from \( n = 6 \) to \( n = 12 \) has an insignificant influence on the final energy of the IS channel and the relative intensity of the TD channel compared to the shorter chain SAMs.
Figure 3.5 Final translational energy distributions for 80 kJ/mol Ar scattering from the $n = 2, 4, 6, \text{ and } 12$ SAMs. The dashed lines are the Boltzmann distributions.

We have scattered from a total of 15 surfaces ranging from $n = 2$ to $n = 18$ and calculated the relative TD intensities, IS intensities, and fractional energy transfer in the IS channel for each surface. Figure 3.6 reveals that as the total number of alkanethiol carbon atoms in the monolayer chains, $n$, increases from 2 to 6, the surface becomes a more effective energy sink for impinging atoms. Under the specular scattering conditions employed in this work ($\theta_i = \theta_f = 30^\circ$), the TD intensity increases by a factor of 2, the IS intensity decreases by a factor of 3.4, and the fractional energy transfer increases from 0.71 to 0.84. However, the TD intensities and the energy transfer fractions are not sensitive to overall monolayer chain length for SAMs with greater than about 6 total carbon atoms.
Figure 3.6 Summary of the scattering data for the entire range of SAMs from \( n = 2 \) through \( n = 18 \). Experiments were not performed on \( \text{C}_{13} \) and \( \text{C}_{17} \) SAMs. The solid symbols in (a) are the relative IS intensities and the open symbols are the TD intensities. The error bars are smaller than the size of the points. (b) is a plot of the fractional energy transfer, \((E_i - \langle E_{IS}\rangle)/E_i\), in the IS channel for each surface.

In contrast to trapping-desorption, the IS intensity is found to oscillate by approximately \( \pm 7\% \) of the mean value depending on whether the alkane chains contain an even or an
odd number of carbon atoms. Below, we discuss the effect that the chain length and the even-odd character of the SAMs have on the gas-surface scattering dynamics.

As discussed above, the angular distribution of argon atoms that leave the surface after reaching thermal equilibrium (TD channel) likely consists of a cosine distribution according to the kinetic theory of gases and as revealed by several scattering experiments.\textsuperscript{18,35,80,106-108} The cosine angular distribution for the TD channel is not expected to depend on surface alkane chain-length. Although the data shown here represents only one final angle ($\theta_f = 30^\circ$), the TD intensities reported in Fig. 3.6 (a) reveal the relative change in overall thermalization probability as a function of chain-length. In contrast, the angular distribution of the impulsively scattered atoms has not yet been measured and is currently unknown for these systems. The IS intensities of Fig. 3.6 (a) are sensitive to changes in both the IS angular distribution and the overall number of argon atoms that scatter impulsively from the surface. Interpretation of the trends in the IS intensity must take into account both effects. For cases where a decrease in IS intensity is balanced to some extent by an increase in TD intensity, such as the data for the short-chain SAMs, some of the atoms that would have scattered impulsively instead thermalize on the surface.

The nearly monotonic increase in the TD intensity, decrease in the IS intensity, and increase in the energy transfer fractions for SAMs with $2 \leq n \leq 6$ are likely the result of one or a combination of two factors: (a) a steady change in the surface structure with overall chain length, or (b) a systematic increase in the available degrees-of-freedom within the surface as the chain length increases. The following discussion attempts to elucidate the relative importance of these two influences on the scattering dynamics.
Significant changes in the monolayer structure as the chain-length increases could alter the IS angular distributions as well as the total amount of impulsive scattering and thermalization. The structural characteristics of SAMs of the type used in this study are generally grouped into two categories: (1) a "striped" phase that occurs at low coverage, and (2) a full-coverage high-density standing phase. Poirier et al. have used scanning-tunneling microscopy to investigate the molecular-level structure of butanethiol monolayers on gold.\textsuperscript{109-111} Their results, along with the XPS work of Leggett and co-workers\textsuperscript{112} and the IR measurements of Rowntree et al.,\textsuperscript{102} indicate that 4-carbon alkanethiols initially form a full-coverage, high-density monolayer on the surface under the preparation conditions employed in the work presented here. Desorption of alkanethiols from this high-density monolayer in UHV has been shown to be slow, occurring on the time-scale of days and the longer chain SAMs have even greater stability. Our TOF data collection is complete in less than 1 h after insertion into the chamber and the distributions are found to be highly consistent over a five-hour period. Therefore, it is reasonable to assume that the experiments presented here are all performed on the full-coverage standing phase of the SAMs for both short-chain and long-chain systems.

Despite similar coverage, the short-chain SAMs can differ structurally from the long-chain monolayers. Most significantly, the short-chain systems may form a 2-dimensional liquid-like phase, as opposed to the solid crystalline-like phase formed by long-chain monolayers.\textsuperscript{109-111} Interestingly, the phase transition from the liquid phase to the crystalline phase occurs for chains with 6-7 carbon atoms,\textsuperscript{113} which coincides with the point at which the TD and IS intensities of Fig. 3.6 (a) cease to depend on chain length.
However, previous structural studies have established that annealing even short-chain \( n \)-alkanethiol SAMs orders the monolayers into the crystalline superlattice.\textsuperscript{100} Since we have found that annealing, which re-orders the monolayers, has no measurable influence on the energy transfer dynamics,\textsuperscript{76} we suggest that the trends presented here are not due solely to changes in surface order as a function of chain length.

An alternative explanation for our results is that the available energetic degrees-of-freedom within the surface increase with chain-length and that as many as 6-carbon atoms along an individual chain participate in dissipating the energy of the gas-surface collisions. This explanation is consistent with the expected time scales for the impulsive gas-surface collision and the rate at which energy propagates along a hydrocarbon chain. Molecular dynamics simulations indicate that for rare-gas collisions with an organic monolayer, the interaction time is about 0.5 to 1 ps.\textsuperscript{28} During this short time, a limited group of atoms in the monolayer can respond collectively, regulated by the speeds of accessible inter- and intra-molecular motions.\textsuperscript{3} An estimate of the rate of energy propagation away from the point of collision is the speed of sound along an alkane chain. This speed has been estimated to be \( \sim 15 \ \text{Å/ps} \) for a 30-carbon alkane chain,\textsuperscript{114} yielding propagation distances within the monolayer of 7.5 Å to 15 Å for the 0.5 ps to 1 ps interaction time. Given a C-C bond length of 1.53 Å,\textsuperscript{115} these distances indicate that 5 to 10 carbon atoms along the alkane chains can participate in the gas-surface collision. Indeed, our results show that 6 or more atoms are needed to dissipate the collisional energy. The picture that emerges from this discussion is that long-range molecular motions such as C-C stretches, bends, wags, and possibly conformational changes\textsuperscript{32} play
the most important role in determining the extent of energy transfer and thermalization in collisions of gases with these organic thin films.

3.5.2 \( n \)-Alkanethiols on Silver

The comparative effect of chain length for \( n \)-alkanethiols adsorbed to silver surfaces is a way to study energy exchange pathways for different monolayer densities. Figure 3.7 is a summary of the TD fraction versus the number of carbon atoms in the alkyl chain for both the SAMs on silver and gold. We report TD fraction rather than TD intensity to make a direct comparison between the SAMs made on the different substrates. Three main differences in the TD fraction are revealed in this comparison: (1) The TD fraction is greater for every chain length SAM on the gold substrate than the silver substrate except for propanethiol, (2) The point at which the TD fraction becomes independent of chain length is about six for the SAMs on gold compared to ten for the SAMs on silver (represented by the horizontal dashed lines), (3) The TD fraction does not oscillate (within our experimental sensitivity) between even and odd chain length monolayers for the longest chains on silver.

The fraction of atoms that reach thermal equilibrium with the surface is consistently higher for the SAMs on gold than SAMs on silver, except in the case of propanethiol SAMs. The reversal in the TD fraction for the shortest chain-length SAM used in this study may reflect the nature of the argon atom interactions with the substrate rather than the degrees of freedom available in the organic overlayer. The propanethiol SAMs may not form monolayers thick enough to shield the underlying substrate from the impinging argon atoms. Based on kinematic arguments, the argon atoms are expected to transfer less energy to the gold substrate than silver since gold atoms are nearly twice as
massive as silver.\textsuperscript{18} We do not have the data included in the figure for the C\textsubscript{2} SAMs because of a reproducibility problem on the silver substrate.\textsuperscript{116}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.75.png}
\caption{Summary of TD fractions for the range of alkyl chain lengths, \( n = 3 \) to \( n = 18 \), on both gold (top) and silver (bottom) substrates. The horizontal dashed line represents the average TD fraction value for the longest chain SAMs.}
\end{figure}

The most striking difference in scattering from the \( n \)-alkanethiol series adsorbed to gold and silver substrates is the turning point at which the TD fractions become independent of chain length. Since the monolayers on the two substrates have identical
chemical nature, the differences must arise from the packing structure and density of the alkyl chains. The packing structure may contribute to the types of modes most easily excited as discussed in section 3.4.2 above. In particular, the side-to-side chain motions are expected to absorb less energy for the higher density SAMs. The difference in the inflection point in the TD fraction plots from six to ten carbon atoms may be the result of different types of low-energy modes that are most easily excited. For example, chain wagging motions contributing to energy transfer in SAMs on gold are arrested in the more densely-packed SAMs on silver.

3.6 Terminal Group Orientation

The equilibrium structure of SAMs is a delicate balance of many factors, including the adsorbate-substrate bond energy and adsorbate-adsorbate interactions. Alkanethiols adsorbed to Ag(111) and Au(111) are examples of how subtle differences in these interactions result in different final structures. For gold surfaces, the strong bonding of the sulfur atoms to the substrate pins the alkane chains into a commensurate overlayer. As illustrated in Figure 3.1 the alkane chain axis of monolayers formed on gold substrates have a ~30° tilt angle with respect to the surface normal which results in an orientation change of the C-C bond for chains with an even number of carbon atoms compared to chains with an odd number of carbon atoms. In contrast, the sulfur-silver bond is relatively weak and the chain interactions control the packing to form monolayers similar in density to solid, bulk alkanes. The alkane chains only tilt by ~12° with respect to the surface normal causing the terminal C-C bond to have nearly the same orientation for monolayers with an even or an odd number of carbon atoms. We used this variation in the terminal group orientation to probe the dynamics of gas-surface collisions
to help further elucidate the importance of localized C-C stretches, torsions, or bends in energy transfer and accommodation on organic surfaces.

\[ \text{Final Energy (kJ/mol)} \]

\[ \text{Relative Probability } P(E_f) \]

\[ \text{SAMs on Au} \]

\[ \text{SAMs on Ag} \]

**Figure 3.8** Probability distributions for 80kJ/mol argon scattering from SAMs of C\textsubscript{11} and C\textsubscript{12} alkanethiols adsorbed to (a) gold and (b) silver substrates.

For SAMs on gold with \( n > 6 \) we find that the impulsive energy transfer and the extent of thermalization on the surface are independent of overall chain length (see Figure 3.6). However, the amount of impulsive scattering at the specular angle \( (\theta_i = \theta_f = 30^\circ) \) depends on whether the alkane chains contain an even or an odd number of
carbon atoms. Figure 3.8 (a) shows a direct comparison on a relative scale of the translational probability distributions for 80 kJ/mol argon scattering from an $n = 11$ and an $n = 12$ monolayer. The probability distributions reveal that the Boltzmann components for scattering from the two surfaces are indistinguishable. As discussed above, since the angular distribution of thermally-desorbing atoms is expected to be the same for both surfaces, it follows that the total number of argon atoms that reach thermal equilibrium is nearly the same for both chain-length monolayers. The main difference in the scattered distributions comes from the impulsive scattering component. The IS intensity for argon scattering from the C$_{11}$ monolayer is found to be measurably larger than the IS intensity for scattering from the C$_{12}$ monolayer. Figure 3.6 shows that this trend holds for the entire range of $n > 6$ monolayers studied, indicating that there is greater propensity for argon to scatter impulsively to the specular angle of 30° for an $n = \text{odd}$ than for an $n = \text{even}$ monolayer. Since the increase/decrease in the IS intensities are not balanced by a decrease/increase in the TD channel, the even/odd oscillations are most likely due to a dependence of the IS angular distributions on the even/odd character of the monolayer.

As in the previous discussion of the chain-length effect on scattering, the phenomena responsible for the even-odd effect is likely one or a combination of two possibilities: available degrees-of-freedom and structural influences. The well-documented structural difference between the long-chain monolayers on gold is that the orientation of the terminal C-C bond alternates from predominately parallel to perpendicular relative to the surface normal depending on whether the total number of carbon atoms is odd or even, respectively.$^{51,96,97}$ Differences in orientation may influence
the ability of argon to excite terminal C-H stretches, C-C stretches, methyl torsions and C-C-C bends. Minor differences in the amount of impulsive energy transfer between the even and odd surfaces would affect the final parallel momentum of the atoms in the IS channel thereby altering the angular distribution. Alternatively, slight differences in the surface roughness could lead to the observed trends. The second carbon from the methyl-terminal group is actually closer to the outer-most layer of the surface for the odd chain-length SAMs than it is for the even-chain monolayers. In this picture, the \( n = \text{odd} \) monolayers may appear slightly less rough on the atomic scale; thereby, reducing the amount of out-of-plane impulsive scattering relative to the even-chain monolayers.\(^9,19,22\)

Since what may be a minor change in surface roughness is found to have a measurable influence on the TD channel (see Fig. 3.4), the even-odd effect is probably not due to changes in the atomic scale roughness of the two monolayers. A more likely explanation for the observed even-odd effect is that slight differences in the impulsive energy transfer for even and odd surfaces lead to differences in the final parallel momentum, hence different IS angular distributions for impulsively scattered atoms. These differences should also be evident in the fractional energy transfer plots of Fig. 3.6 (b), but the relatively large error bars in the data may preclude its observation.

Figure 3.8 (b) shows a comparison of 80 kJ/mol argon scattering from \( C_{11} \) and \( C_{12} \) monolayers on silver. The final energy probability distributions significantly overlap for argon scattering from these two surfaces. The impulsive scattering channel is slightly more intense for the SAM with an odd number of carbon atoms in the chain, but within our experimental sensitivity, the distributions are the same. The similarity in scattering from even and odd chain length SAMs on silver is consistent with the proposed
explanation for the even-odd effect for scattering from SAMs on gold. The terminal
group orientations for the monolayers on silver are similar for even and odd chain length
SAMs. This orientation similarity provides the possibility for argon atoms to excite the
terminal group modes with equal efficiencies and therefore have similar angular
distributions.

Although the above explanation for the even-odd effect is consistent with the
experimental results presented here, there is currently not sufficient evidence to rule out
other possibilities and further experiments are required. In particular, angle-resolved
studies and classical trajectory simulations are expected to more fully elucidate the
scattering dynamics.

3.7 Summary

Atomic beam scattering of argon from self-assembled monolayers composed of \( n \)-
alkanethiols adsorbed on gold and silver substrates ranging from 2 to 18 total carbon
atoms have provided insights into the impulsive energy transfer and thermalization
dynamics of gas collisions on organic surfaces. These two types of SAMs were chosen
due to their structure and density differences. For low-energy argon scattering from long
chain monolayers, energy distributions from both types of surfaces are well fit by a
Boltzmann distribution at the surface temperature, implying full thermalization. In
contrast, the two types of SAMs are not equally efficient at absorbing the excess
translational energy from high-energy argon collisions. For 80 kJ/mol argon scattering
from the SAM on silver surface, a smaller fraction of atoms reach thermal equilibrium,
0.46 versus 0.61 for long chains, and the average energy transferred for impulsive
scattering is lower by about 7%. We attribute the differences in scattering to excitation efficiencies of different types of low-frequency surface modes.

A chain-length effect is observed for both types of surfaces for high-energy argon scattering. As the total number of alkanethiol carbon atoms increase from the shortest chains measured to the inflection point, the surfaces become progressively less rigid leading to greater energy transfer in the impulsive scattering channel accompanied by a larger extent of thermalization on the surface. Surprisingly, the number of carbon atoms in which the scattering dynamics become independent of chain length is different for the two surface types, approximately 6 and 10 for the SAMs on gold and silver, respectively. Since this chain-length effect cannot be directly related to changes in surface structure as the number of carbon atoms increase, it is attributed to the importance of long-range motions along the alkane chains. It appears that between 6 and 10 carbon atoms participate in the dynamics of the gas-surface collisions depending on the alkane chain packing density.

For long chain \( n \)-alkanethiols adsorbed to gold substrates, the scattered intensity of atoms in the impulsive channel is found to oscillate about a mean value depending on whether the alkane chains contain an even or an odd number of carbon atoms. It is speculated that small changes in the angular distribution of atoms scattered in this channel are responsible for the experimental observations. These changes are likely the result of the ability to couple energy into the various surface modes of the terminal groups. This explanation is consistent with the scattering results from SAMs on silver that show an invariance to whether the chains are composed of an even or odd number of carbon atoms. Since the terminal group orientation is nearly the same for these SAMs,
we expect the argon atoms to excite the terminal group modes with equal efficiency and thus have similar angular distributions.

We have also used classical trajectory calculations, described in the following chapter, to provide additional insight into some of the questions left to speculation from this chapter. In particular, we have focused on the role of alkane chain packing density on energy transfer dynamics by studying argon scattering from a series of monolayers with different packing densities as a function of incident energy and approach angle.
4.1 Background

The first step in many gas-surface chemical reactions involves a collision where the energy exchange dynamics determine whether the gas-phase reactant scatters directly away from the surface or accommodates with the material. Energy exchange between gas-phase species colliding with surfaces is a portion of the total dynamics that needs to be understood in order to develop a complete picture of gas-surface reaction dynamics. The mechanism(s) of translational to vibrational energy transfer for various surface properties is best studied with noble gases due to their non-reactive nature and absence of internal degrees of freedom.

Scattering experiments\(^9,10,16,19,75,76,91,117\) have begun to probe the dynamics of energy transfer when gas-phase species collide with organic surfaces. Morris \textit{et al.} scattered high-energy argon atoms from \textit{n}-alkanethiolate SAMs adsorbed to gold and silver surfaces to study alkane chain packing density and structure on energy transfer dynamics.\(^75\) In that study, it was shown that argon atoms scattering from \textit{n}-alkanethiolate monolayers adsorbed to silver substrates (high packing density) transfer less energy than analogous monolayers formed on gold. For 80 kJ/mol argon scattering at incident and final polar angles of 30° from the SAM on silver surface, a smaller fraction of atoms reach thermal equilibrium, 0.46 vs. 0.61 for long chains, and the average energy transferred for impulsive scattering is lower by about 7%. These results showed that
lower energy transfer to the higher packing density monolayers is related to the excitation efficiencies of low-frequency motions. High chain packing densities may restrict certain modes from absorbing the excess energy of the argon atoms as readily as lower packing density surfaces.

Molecular dynamics simulations\textsuperscript{34,35,118} have also played a large role in understanding the dynamics of gases colliding with organic surfaces. Of importance to the molecular dynamics simulation results provided in this study is that efficient energy transfer depends on the impact site of the collision.\textsuperscript{15,33,34} The simulations have shown that chains struck on top appear more stiff than chains struck from the side. Gas atoms that strike the alkane chains from the side excite low-frequency modes more easily and energy transfer through vibrational energy redistribution, which occurs on the time scale the gas atom is in contact with the surface, is more efficient than on top collisions.

We invoke classical trajectory simulations to more fully understand the role of alkane chain packing density on energy transfer dynamics. Molecular dynamics simulations allow us to overcome three experimental limitations: (1) our experimental apparatus has a fixed geometry between the source and detector which prohibits measuring angular distributions, (2) we can only infer the dynamics that occur during the gas-surface interactions from experiment based on the incident and final gas energies, and (3) we are restricted in the number of monolayer densities we can study.

The focus of the work presented in this chapter is to further the understanding of energy dissipation pathways in gas collisions with organic surfaces. Particularly, the influence of alkane chain packing density on energy transfer dynamics is explored. We begin by simulating the dynamics of energy transfer for 80 kJ/mol argon scattering from
C₁₀ monolayers on gold and silver substrates to compare and more fully understand our experimental results. The simulations were modeled from previous argon/SAM systems using variables for the argon incident parameters and surface conditions from our experiments. We also use classical trajectory simulations to develop a more general understanding of how alkane chain packing density influences energy transfer and thermal accommodation pathways. These simulations are carried out for argon atoms impacting a series of monolayers with incident energies of 60, 80, and 120 kJ/mol and incident polar angles of 15, 30, 45, 60, and 75°.

4.2 Introduction to Classical Trajectory Calculations

Classical trajectory calculations are an approach used to simulate the dynamics of molecular systems. One of the goals of molecular dynamics simulation is to provide insight into experimentally challenging problems. For many problems, the classical description is adequate to provide both qualitative and quantitative comparisons to experimental results. A quantum mechanical treatment is more costly in time and efficiency, so is only used when affordable. For example, the classical description is not valid for systems that have processes like tunneling and diffraction.

The central idea of molecular dynamics simulations is to numerically solve the N-body problem of classical mechanics. There are three basic steps to performing a molecular dynamics simulation. (1) construct a model of the system of interest, (2) simulate the movement of that system for a period of time, and (3) analyze the simulation data for the desired phenomena. These three steps are described in general below and in detail of our simulation procedure in section 4.3.
4.2.1 Constructing the Model

The Hamiltonian of a molecular system is composed of kinetic energy terms for nuclei and electrons as well as potential terms for nuclear-nuclear, nuclear-electron, and electron-electron interactions. The Born-Oppenheimer approximation takes advantage of the long time scale of nuclear motion compared to electronic motion due to the differences in mass. A Hamiltonian for nuclear motion can be constructed from this approximation by assuming that the nuclei move in a force field governed by the average positions of the electrons. By averaging out the electronic motion, the nuclear positions alone can be used as the dynamic variables of the system. If a classical description of the system is valid, then the nuclear Hamiltonian is just a sum of kinetic and potential energy functions of coordinates $\vec{q}_i$ and momenta $\vec{p}_i$ of each interaction center, $i$.

$$H(\vec{q}, \vec{p}) = K(\vec{p}) + V(\vec{q})$$

The kinetic energy function takes the form:

$$K(\vec{p}) = \sum_i^N \frac{p_i^2}{2m_i}$$

where the index, $i$, runs over all interaction sites, $N$, of mass, $m_i$.

The potential energy function relates the way interatomic sites interact with one another. The specific potential energy function of the system depends on the interaction sites involved in the simulation and the properties of the system that are under investigation.

Once the Hamiltonian of the system is generated in functional form, the classical equations of motion, which govern the time-evolution of the system, can be constructed. The equations of motion can take on the Hamiltonian, Lagrangian, or Newtonian
If the equations of motion of the system are chosen to take on the Newtonian form, then the force acting on site, \( i \), is related to its acceleration by:

\[
\ddot{F}_i(t) = m_i \ddot{q}_i(t)
\]

The force on interaction center, \( i \), is also related to the global potential energy function by

\[
\dot{F}_i(t) = -\frac{\partial V(\vec{q})}{\partial \vec{q}}
\]

The equations of motion are then determined by setting the forces equal to each other in the above two equations. Therefore, the central input of the model is defined in the choice of the global potential energy surface, \( V(\vec{q}) \), the initial conditions, and the choice of classical method to define the equations of motion.

### 4.2.2 Integrating the Equations of Motion

Once the equations of motion are constructed and initial values given to the set of \( \vec{q}_i \)'s and \( \vec{p}_i \)'s, the time evolution of the system can be obtained by integrating the equations over some period of time, \( t' \). An approach to solving these equations of motion for a Hamiltonian with a smoothly varying potential term in time is with finite difference methods. The idea for using a finite difference method is that positions and momenta for all the interaction centers in the system at some time, \( t + \Delta t \), can be calculated from a set of positions and momenta at a time, \( t_0 \). In this approach, the equations of motion are solved in incremental time steps of \( \Delta t \) until the system has evolved to the final state at the later time, \( t' \).

As an example of integrating the equations of motion using finite difference algorithms, consider a system where the potential function is smoothly varying over time.
The positions and momenta for each nucleus can be estimated at time $t + \Delta t$ using a Taylor series expansion about time, $t$.

\[
\ddot{q}_i(t + \Delta t) = \ddot{q}_i(t) + \Delta t \dddot{v}_i(t) + \frac{1}{2} \Delta t^2 \dddot{a}_i(t) + \ldots \n\]
\[
\dddot{v}_i(t + \Delta t) = \dddot{v}_i(t) + \Delta t \ddot{a}_i(t) + \ldots \n\]

where $\dddot{a}_i$ is the acceleration of interaction site, $i$.

Given a set of initial positions and momenta, a new set of positions and momenta can be calculated after one time step, $\Delta t$. To repeat this process, the new forces, or the accelerations as defined explicitly in this example, are calculated from the equations of motion based on the new positions at time, $t + \Delta t$.

There are many choices of algorithms that can be used to integrate the equations of motion including Verlet’s algorithm, Runge-Kutta algorithms, and Gear’s Predictor-Corrector algorithms. Each of these methods has strengths and weaknesses as far as speed and accuracy, so the decision of which method to use depends on the properties of the system investigated.

4.2.3 Analyzing the Results

Analysis of the results will entirely depend on the properties of the system under investigation. The analysis may provide calculations of thermodynamic variables, nonequilibrium properties of macroscopic systems, or a ‘view’ of atomic scale dynamics.

4.3 Implementation of Molecular Dynamics Simulations for Argon Scattering

Classical trajectory calculations were performed with the software package VENUS developed by Hase et al. We used simulations in our research as a complementary method to the experimental results. In particular, we studied the role of alkane chain packing density on energy transfer dynamics. In section 4.4, a description
of the simulation results that correspond to argon scattering from decanethiolates adsorbed to gold and silver surfaces is given. Section 4.5 describes the results of argon scattering from a series of models covering a range of densities as a function of incident energy and incident angle.

4.3.1 Surface Model

The surface models used for the simulations were adapted from a model by Hautman and Klein to simulate the structure and dynamics of SAMs.\textsuperscript{122} Adaptation of this model to study gas-surface energy transfer was first employed by Bosio and Hase\textsuperscript{28} for studying neon collisions with hexanethiol SAMs on gold. The method was successful for modeling experimental results for neon scattering from liquid squalane and has led to a series of papers further investigating gas-surface energy transfer.\textsuperscript{29,30,32-35}

The models used in our simulations consists of united atom methyl and methylene groups of the decanethiolate chains chemisorbed to planes of rigid (111) substrates through the sulfur atom. United atoms assume that groups like, CH\textsubscript{3} or CH\textsubscript{2}, are spherically symmetric, and are represented as a single unit. By using united atoms in the model, the motions of the hydrogen atoms are neglected in the dynamics calculations. The intramolecular (SAM) potential energy surface is a sum of bonding and nonbonding potential terms. The bonding terms include two atom bond stretching potentials, three atom bending potentials, and four atom dihedral angle potentials. The nonbonding potential terms are Lennard-Jones (6-12) potentials for atoms on neighboring chains and along a single chain separated by more than three atoms. The functional form of the intramolecular potential is
\[ V(r, \theta, \phi, R) = \sum_{\text{stretches}}^{\frac{1}{2}} k_r (r - r_0)^2 + \sum_{\text{bends}}^{\frac{1}{2}} k_\theta (\theta - \theta_0)^2 + \sum_{\text{dihedrals}} \sum_{n=1}^{n} \frac{1}{2} k_n [1 + \cos(n\phi - \phi_n)] + \sum_{\text{Lennard–Jones}} \left( \frac{R^6}{R^12} \right) \]

The variables \( r_0 \) and \( \theta_0 \) represent the equilibrium bond lengths and bond angles. The harmonic force constants for stretches and bends are given by \( k_r \) and \( k_\theta \). The dihedral potential term consists of a summation of terms with force constants \( k_n \) multiplied by functions expanded around the angles of \( \phi_n \). Finally, the Lennard-Jones potential has terms \( a \) and \( b \) which relate to the strength of repulsions and attractions, respectively. Figure 4.1 illustrates the definition of the variables in the above equation and the potential parameters are given in table 4.1.

**Figure 4.1** Schematic illustration to define the variables used in the intramolecular potential energy function.
Table 4.1 Intramolecular Potential Energy Parameters

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C stretch</td>
<td>$k_r = 4.86$ (mdyn/Å), $r_0 = 1.52$ (Å)</td>
</tr>
<tr>
<td>S-C stretch</td>
<td>$k_r = 5.70$ (mdyn/Å), $r_0 = 1.82$ (Å)</td>
</tr>
<tr>
<td>S-substrate stretch</td>
<td>$k_r = 2.80$ (mdyn/Å), $r_0 = 2.55$ (Å)</td>
</tr>
<tr>
<td>C-C-C bend</td>
<td>$k_0 = 0.862$ (mdyn Å/°), $θ_0 = 109.5°$</td>
</tr>
<tr>
<td>S-C-C bend</td>
<td>$k_0 = 0.862$ (mdyn Å/°), $θ_0 = 114.0°$</td>
</tr>
<tr>
<td>(S/C)-C-C dihedral</td>
<td>$k_1 = 3.705$ (kcal/mol), $φ_1 = 0$</td>
</tr>
<tr>
<td></td>
<td>$k_2 = -0.135$ (kcal/mol), $φ_2 = 180°$</td>
</tr>
<tr>
<td></td>
<td>$k_3 = 1.571$ (kcal/mol), $φ_3 = 0$</td>
</tr>
<tr>
<td>CH$_2$-CH$_3$ Lennard-Jones</td>
<td>$a = 5915000$ (kcal/mol Å$^{12}$), $b = 1668$ (kcal/mol Å$^6$)</td>
</tr>
<tr>
<td>CH$_2$-CH$_2$ Lennard-Jones</td>
<td>$a = 7204000$ (kcal/mol Å$^{12}$), $b = 2030$ (kcal/mol Å$^6$)</td>
</tr>
<tr>
<td>CH$_3$-CH$_3$ Lennard-Jones</td>
<td>$a = 8751000$ (kcal/mol Å$^{12}$), $b = 2468$ (kcal/mol Å$^6$)</td>
</tr>
<tr>
<td>CH$_2$-S Lennard-Jones</td>
<td>$a = 48590200$ (kcal/mol Å$^{12}$), $b = 1825$ (kcal/mol Å$^6$)</td>
</tr>
</tbody>
</table>

In section 4.5, the results of the molecular dynamics simulations will be described for argon scattering from models of decanethiolates adsorbed to gold and silver substrates. A ten carbon chain SAM was chosen for the models since structures of C$_{10}$ SAMs have been experimentally characterized on both gold and silver substrates.$^{73,123}$ In addition, the energy transfer dynamics become independent of chain length near ten carbon atoms on silver and an even shorter chain length for SAMs on gold, see Figure 3.7. These models are representative of long chain SAMs and minimize the computational demands of larger systems. The model for decanethiolates self-assembled on gold consists of 36 chains with the sulfur groups bound to threefold hollow sites of a Au(111) plane, corresponding to the ($\sqrt{3} \times \sqrt{3}$)R30° overlayer. We approximated the structure of the decanethiolates self-assembled on silver using this same model, but changed the lattice spacing of the substrate from 2.88 Å to 2.67 Å. The change in lattice spacing is necessary to obtain the structure and density of the alkyl chains measured.
experimentally on a Ag(111) substrate. Since both models have the \((\sqrt{3}\times\sqrt{3})R30^\circ\) overlayer structure, the lattice spacing of the nearest neighboring sulfur atoms on the gold model is 4.98 Å and the lattice spacing of the nearest neighboring sulfur atoms on the silver model is 4.67 Å. Although the true binding of thiols to Au(111) and Ag(111) is different, the correct hexagonal structure and tilt angle of the alkyl chains are attained in each case for these models.

In section 4.6, molecular dynamics simulation results for argon scattering from a series of five C\(_{10}\) monolayers are described. Two correspond to SAMs on gold and silver surfaces, the others are theoretical models created to test chain packing density on energy transfer dynamics. The five models consist of nearest neighbor sulfur lattice spacings of 4.30, 4.67, 4.98, 5.20, and 5.40 Å. The structures of the three new models were produced in the same way as the SAM on silver model. From the structures and lattice spacings of the models, we calculate two dimensional surface densities of 16.0, 18.9, 21.5, 23.6, and 25.3 Å\(^2\)/molecule.

To represent an infinite two dimensional surface in our models, we used periodic boundary conditions. We invoke periodic boundary conditions by allowing chains on opposite sides of the model to interact with each other. Fig. 4.2 is an example of how the methyl groups interact. Each circle in the figure represents a methyl group. The filled circles are the methyl groups at the end of the 36 chains, the real groups, and the open circles are the images of real methyl groups translated across the model cell. As an illustration of periodic boundary conditions, consider methyl group number six in the bottom left corner of Fig. 4.2. We only consider nearest neighbor interactions in our
model, so we need Lennard-Jones potentials for the interactions of methyl group 6 with real groups 5 and 12 and image groups 1, 7, 35, and 36.

![Diagram of periodic boundary conditions](image)

**Figure 4.2** An example of periodic boundary conditions used in our simulations for the terminal methyl groups. The filled circles represent real groups and the open circles represent images.

We used a surface temperature of 300 K in the simulations to make a direct comparison with the experimental results for argon scattering from SAMs on gold and silver. The temperature of the system is calculated by setting the sum over the kinetic energy terms of each interaction site to the total translational energy of the system

\[
\frac{1}{2} \sum_{i} m_i \dot{v}_i^2 = \frac{3}{2} NkT
\]

Rearranging this equation for temperature provides a way to calculate the instantaneous temperature of the system.

\[
T(t) = \frac{1}{3Nk} \sum_{i} m_i \dot{v}_i(t)^2
\]
Taking the ratio of the instantaneous temperature to the desired temperature and solving for new values of velocity provides a way to put thermal energy into the system.

\[
\vec{v}_i\,(\text{new}) = \vec{v}_i\,(\text{old}) \sqrt{\frac{T(\text{desired})}{T(\text{inst})}}
\]

In order to achieve the desired temperature, this process of velocity rescaling was repeated for ten thousand time steps. The large number of time steps is important because kinetic energy is not a constant in time for the system. The system will exchange kinetic and potential energy as the energy is placed into or taken out of the system through velocity rescaling. After velocity rescaling is completed, the system is allowed to equilibrate (integrate the equations of motions without velocity rescaling) for ten thousand more time steps. The system is then in an equilibrium state with an average temperature of 300 K. The standard deviation of the instantaneous fluctuations in temperature is proportional to the inverse square root of the number of particles in the system. Therefore, our surface models have an average temperature of 300 ± 15°. In our calculations, we use a time step of 2.5 x 10^{-16} seconds and a fourth-order Runge-Kutta algorithm to integrate the equations of motion.

To compare the structure of our SAM models to experiment, we performed energy minimization calculations. The method of energy minimization used in our study begins by providing the N interaction sites in the model with positions and momenta. The equations of motion are then integrated for 20 time steps at which point the momenta for each atom is set to zero. The equations of motion are integrated for an additional 20 time steps which allows the total energy to be partitioned into both potential and kinetic energy. The momenta are again set to zero and these steps are repeated until all the
energy is drained from the system. At this point, the system is in a potential energy minimum. The structure of the SAM model is then determined from this geometry.

The lattice spacings and chain tilt angles, determined from the energy minimum calculations, were used to compare our models of decanethiolates on gold and silver substrates to their experimentally determined structures. The minimum energy structures have lattice spacings of 4.98 Å for the SAM on gold and 4.67 Å for the SAM on silver, providing surface densities of 21.5 and 18.9 Å²/molecule, respectively. The average chain tilt angle for the SAM on gold model is ~33° while the tilt angle for the SAM on silver model is ~14°. The tilt angles are calculated from the vector connecting carbon atoms 1 (carbon atom adjacent to the sulfur) and 9 (carbon atom adjacent to methyl group) and the surface normal. Overall, the models are in good agreement with experimental data. Dhirani et al. report a lattice spacing of 4.61 ± 0.15 Å for SAMs on silver. In comparison, Porter and coworkers measured a lattice constant of 5.0 ± 0.2 Å for SAMs on gold. Experimentally, average tilt angles of 30° and 13° have been measured for SAMs on gold and silver with $n \geq 10$, respectively. The parameters for the other three models were also determined by the geometry of the potential energy minimum technique described above. The structural variables for the five models are provided in Table 4.2.
An additional column is included for the average volume of an individual alkyl chain for each surface model. The total volume of the 36 chain model was calculated based on the chain tilt angles and methyl to sulfur height difference, then divided by 36 to get an average volume per chain. This free volume provides a way to compare the available space each molecule can move when energy is placed into the vibrational modes from the incident argon atoms.

### 4.3.2 Trajectory Calculations

The argon-CH₃ and argon–CH₂ interaction parameters were obtained from previous work describing argon scattering from a decanethiolate SAM on Au(111).³⁵ The potential function was derived from crossed molecular beam experiments of argon scattering with methane molecules. The potential energy for this system was fit with the analytical function of the form:

\[
V(r) = \sum \frac{a}{r^{2}} + \frac{b}{r^{6}} + c \exp(-d r) + \frac{e}{r^{3}}
\]

In this equation, \(r\) represents the distance between the argon atom and each united atom in model. The following table provides the parameters used in this function.

#### Table 4.2 Minimum Energy Structure Parameters of the SAM models

<table>
<thead>
<tr>
<th>Model</th>
<th>NN S-S distance (Å)</th>
<th>Average Chain Tilt Angle, °</th>
<th>Avg. Methyl Height above Substrate (Å)</th>
<th>Surface Density (Å²/molecule)</th>
<th>Volume (Å³/molecule)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.30</td>
<td>5</td>
<td>14.73</td>
<td>16.0</td>
<td>181</td>
</tr>
<tr>
<td>2(Ag)</td>
<td>4.67</td>
<td>14</td>
<td>14.16</td>
<td>18.8</td>
<td>207</td>
</tr>
<tr>
<td>3(Au)</td>
<td>4.98</td>
<td>33</td>
<td>12.62</td>
<td>21.5</td>
<td>214</td>
</tr>
<tr>
<td>4</td>
<td>5.20</td>
<td>36</td>
<td>12.37</td>
<td>23.6</td>
<td>223</td>
</tr>
<tr>
<td>5</td>
<td>5.40</td>
<td>38</td>
<td>11.98</td>
<td>25.2</td>
<td>229</td>
</tr>
</tbody>
</table>
Table 4.3 Intermolecular Potential Energy Parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>3720000 (kcal/moleÅ^{12})</td>
</tr>
<tr>
<td>b</td>
<td>-787.1 (kcal/moleÅ^{6})</td>
</tr>
<tr>
<td>c</td>
<td>338100 (kcal/mole)</td>
</tr>
<tr>
<td>d</td>
<td>3.657 (Å^{-1})</td>
</tr>
<tr>
<td>e</td>
<td>-128200 (kcal/moleÅ^{9})</td>
</tr>
</tbody>
</table>

Figure 4.3 shows a plot of the intermolecular potential energy function for argon interacting with a single methyl group.

Although this intermolecular potential energy function reproduces experiments adequately enough to gain some insight into the molecular level details of the gas-surface interactions, we have found that analytical functions derived from *ab initio* calculations provide superior results.\textsuperscript{118}

In our initial study of argon scattering from decanethiolate SAMs on gold and silver surfaces, we calculated 15,000 trajectories for argon with incident energy of 80 kJ/mol and incident polar angle of 30°. The large number of trajectories were performed...
so the final energy distributions could be analyzed with restricted angles of $\theta_f = 30 \pm 12^\circ$ and $\varphi_f = 180 \pm 30^\circ$ to compare with our experimental conditions. The polar scattering angle ($\theta_\text{f}$) is measured between the velocity vector of the argon atoms and the surface normal. The azimuthal angle ($\varphi_\text{f}$) corresponds to the angle between the projections of the incident and final argon velocity vectors onto the plane of the surface. In-plane scattering is defined as $\varphi_f = 180^\circ$. Since our experiments probe scattering from surfaces with a distribution of SAM domains, the incident azimuth angle was randomly sampled over a uniform distribution for each trajectory.

In the simulation study of argon scattering from the series of 5 varying density monolayers, we calculated 1000 trajectories for each set of incident argon variables. The incident argon variables used in this study were incident energies of 60, 80, and 120 kJ/mol and incident polar angles of 15, 30, 45, 60, and 75°. The azimuthal angle was again sampled over a uniform distribution.

The aiming point of the argon atom onto the SAM surface was randomly sampled over the central unit cell of the 36-chain surface. The box in Figure 4.1 connecting the four methyl groups in the central unit cell illustrates the sampling region. The trajectories were terminated when their height above the average plane of the terminal methyl groups reached 8 Å or the integration time exceeded 25 ps. In the latter case, these trajectories were assumed to reach thermal equilibrium and the final energies were sampled from a Boltzmann distribution, polar angles from a cosine distribution, and azimuthal angles from a uniform distribution.
4.4 Comparison of Classical Trajectory Simulations with Experimental Results

The simulations of argon scattering from the C_{10} alkyl thiolates on gold and silver described in section 4.2 reasonably represent experimental data for argon scattering. Figure 4.4 shows a comparison of experimental data to simulation results for each type of SAM. The final polar angle for the simulated data is $\theta_f = 30 \pm 12^\circ$ with the azimuth in the range $\phi_f = 180 \pm 30^\circ$. The distributions include ~850 trajectories for the SAM on gold and silver models. As reported in previous work using similar models, Fig. 4.4 shows good qualitative agreement between experiment and simulation.$^{34,35}$ Below, we apply these models to gain insight into the atomic-scale processes inferred from experiments.
Figure 4.4 A comparison of experimental and simulation final translational energy probability distributions for 80 kJ/mol argon scattering from SAMs on silver (top) and gold (bottom) substrates. The simulation results are restricted to $\theta_f = 30 \pm 12^\circ$ and $\phi_f = 180 \pm 30^\circ$. The distributions are normalized to total area.

4.4.1 Molecular Dynamics Definitions Compared to Experimental Fitting

Figure 4.5 shows three probability distributions, calculated from molecular dynamics simulations, for argon scattering off the C$_{10}$ SAM on silver model. The circles represent the total probability distribution integrated over all final scattering angles. The total energy distribution is deconvoluted into two components: argon trajectories with a single inner turning point (square symbols) and argon trajectories that have at least one
outer turning point (triangles) relative to the surface plane. Also included in the plot is a Maxwell-Boltzmann distribution at the surface temperature. The Boltzmann distribution is included to compare the traditional method of assigning trapping-desorption events to the low-energy portion of the probability distribution. These calculations reveal that multiple collisions appear Boltzmann with a low final energy distribution, whereas single collision events make up nearly the entire high-energy portion of the total distribution. The difference in intensity of the Maxwell-Boltzmann fit and the multiple collision distribution shows that some impulsive scattering contributes to the Boltzmann component. This result helps verify previous studies that suggest that the two scattering channels are closely related to the number of collisions the gas atoms make with the surface.\textsuperscript{126,127} Impulsive scattering is composed primarily of single collision events with the surface whereas trapping-desorption mainly result from multiple collisions. By defining trapping-desorption as trajectories that undergo multiple collision events, we can deconvolute the two limiting scattering channels without using a fitting procedure.
Figure 4.5: Molecular dynamics final translational energy distributions for 80 kJ/mol argon scattering from the SAM on silver model. Included is the total distribution (circles), the distribution for single collision events (squares), the distribution for multiple collision events (triangles) and a fitted Maxwell-Boltzmann distribution at $T_{surf} = 300$ K (solid).

The fitting procedure for trapping-desorption assumes that those atoms which scatter in this channel have reached thermal equilibrium with the surface. There is no guarantee that a single collision event has not attained thermal equilibrium. Likewise, multiple collision events may not completely thermally accommodate to the surface temperature. However, the use of a definition rather than a fitting procedure is helpful when making direct comparisons between scattering from different density surfaces.

4.5 Simulations of Argon Scattering from $C_{10}$ Monolayers on Silver and Gold

Molecular dynamics simulations are used as a complimentary tool to experiment to gain insight into the dynamics of gas-surface collision dynamics. In this section, molecular dynamics simulations are used to gain insight into the experimental data of argon scattering from the SAMs on gold and silver. The limitations in our scattering experiments are detection of one final scattering angle and the dynamics that occur during the gas-surface interactions are only inferred from the final energy distributions.
Using molecular dynamics simulations, we want to answer the following questions: Are the angular distributions similar for argon scattering from \(n\)-alkanethiols adsorbed to silver and gold? Does penetration into the monolayer affect TD fractions measured experimentally for the two different packing density surfaces?

Comparison of the angular distributions allows us to investigate the role of interfacial, methyl group, corrugation on the energy transfer dynamics of these systems (see chapter 3, section 3.4.1). Monitoring the fraction of atoms that penetrate the monolayers may provide an explanation for the difference in the trapping-desorption fractions measured experimentally (see Figure 3.7).

4.5.1 Argon Scattering as a Function of Final Scattering Angles

There are two angles that need to be defined in order to calculate the final angular distributions of argon scattering from a surface, the polar and azimuthal angles. The polar scattering angle (\(\theta\)) is measured between the velocity vector of the argon atoms and the surface normal. The azimuth angle (\(\phi\)) corresponds to the angle between the projections of the incident and final argon velocity vectors onto the plane of the surface. In-plane scattering is defined as \(\phi = 180^\circ\). Figure 4.6 (a) shows the scattered intensity of argon as a function of the final polar angle. The distributions for each surface are very broad with the largest intensity around 45°. Restricting to more in-plane scattering with \(\phi_f = 180 \pm 30^\circ\) gives similar results (data not shown). The distributions from each surface are nearly identical within statistical uncertainty.

Figures 4.7 (a) and 4.7 (b) show the final azimuthal angle distributions for both surfaces. The scattering is broad, but peaked for in-plane scattering (\(\phi_f = 180^\circ\)) with a slightly narrower distribution for the SAM on silver surface. This effect is not due to
differences in the corrugation of the methyl groups but represents differences in the TD fractions. The final azimuth angular dependence is expected to be uniform for those atoms that come off the surface after reaching thermal equilibrium, thus the peak near 180° is a result of directional scattering from impulsive collisions. The angular distributions for impulsive scattering events can be illustrated by utilizing the results discussed in section 4.4.1 that shows impulsive events are dominated by single collisions. Figure 4.7 (b) shows the azimuth angular distributions for trajectories that have a single inner turning point relative to the surface and for trajectories with one or more hops. The single collision and multiple collision distributions from the two models were normalized for comparison. The distributions are nearly identical for SAMs on gold and silver within both channels of scattering. Those trajectories with one or more hops have nearly uniform dependencies on the azimuthal angle as expected for thermally desorbing atoms, whereas single collision events are peaked in the forward scattering direction as expected for impulsive scattering.\(^4\) Based on these similarities, differences in the interfacial corrugation between these two types of SAMs seem to make little or no contribution to the final angular distributions of the scattering dynamics. This implies that the TD fractions measured experimentally for the long-chain SAMs (see section 3.5.2) closely resemble the overall scattering dynamics.
Figure 4.675 Calculated final polar angle distributions for 80 kJ/mol argon scattering from SAMs on gold (solid lines) and silver (dashed lines). (a) Final polar angle probability distribution. (b) Average final energy as a function of final polar angle. (c) Average final energy as a function of final polar angle restricted to in-plane scattering, $\phi_f = 180 \pm 30^\circ$. 
Figure 4.7 Calculated final azimuthal angle distributions for 80 kJ/mol argon scattering from SAMs on gold (solid lines) and silver (dashed lines). (a) Final azimuth angle probability distributions. (b) Final azimuth angle probability distributions for single collision events (top) and for multiple collision events (bottom). (c) Average final energy as a function of final azimuthal angles.
4.5.2 Energy Transfer Dependence on Final Angle

Average final energy values as a function of final polar and azimuthal angles are given in Figures 4.6 (b), 4.6 (c), and 4.7 (c). The average energy for argon atoms scattering from the SAM on silver is consistently higher for all scattering angles. The fractions of atoms in the trapping-desorption channel and energy transfer for impulsive collisions each play a part in this difference. Trajectories that leave the surface after reaching thermal equilibrium have an average final energy of $2kT_{\text{surf}}$. The total average final energy will be weighted by the fraction of TD at each scattering angle. Since the TD fraction from the SAM on gold is higher and provides more weight, the average energies calculated at each angle are lower. In addition, the average final energy for single collision events is greater for the SAM on silver than the SAM on gold.

The structure of the two surfaces changes the partitioning of trapping-desorption and impulsive scattering of the incident argon atoms. However, two common trends are observed for these surfaces, which may be general for alkane-based monolayers. Energy transfer increases with increasing deflection angle, $\chi = 180 - (\theta_i + \theta_f)$, a behavior characteristic of scattering in the structure regime where the surface can be approximated as a collection of hard spheres. This behavior is most notable in Figure 4.6 (c) where the average energy values for each polar angle have been restricted to in-plane scattering, $\phi_f = 180 \pm 30^\circ$. The second interesting feature, consistent for the two SAMs, is that the impulsive scattering channel contributes to all final angles. This feature can be seen at $\theta_f = 0^\circ$ and $\phi_f$ between $0^\circ$ and $20^\circ$ and $340^\circ$ to $360^\circ$ where the average energy values are higher than $2kT_{\text{surf}}$ (5 kJ/mol).
4.5.3 Penetration/Minimum Height Dependence

For these systems penetration into the monolayer occurs with 80 kJ/mol incident argon atoms. Previous studies have shown that a small fraction of argon trajectories with incident energy of $\sim 57$ kJ/mol and near normal incident angles penetrate the monolayer surface for a C$_{10}$ monolayer on Au(111).$^{35}$ Since the structures of the two monolayers investigated in this study have different packing densities, we expect different fractions of penetration into the monolayers. During each trajectory, the minimum distance, $z$, the argon atoms reach relative to the rigid substrate plane is recorded. To compare the minimum height distributions for the two surfaces, the $z$-distance is shifted from the substrate to the average $z$ value of the methyl groups. This linear shifting is necessary since the tilt angles of the chains place the terminus at different distances above the substrates (see Table 4.2). We consider that a trajectory has penetrated into the monolayer if its minimum height is below the value of the average methyl height.

Figure 4.8 shows a comparison of the minimum height distributions for the two surfaces. The vertical dashed line at zero designates the average terminal group height with negative values representing penetration into the monolayer. The larger fraction of atoms that penetrate the monolayer is evident by the larger area in the probability distribution for the SAM on gold below the terminal methyl group.
The fractions of trajectories that penetrate the monolayer contribute to the lower portion of the energy distribution. Nearly all the trajectories truncated (see section 4.3.2) were those that penetrated the SAM and those trajectories that escaped the surface but still penetrated the monolayer had lower average final energies than those that scattered directly from the terminal groups. The fraction of trajectories that penetrate the monolayer for each surface is 0.07 and 0.16 for the high and low density models. Interestingly, the difference in the fraction of penetration roughly scales with the difference in TD fractions observed experimentally, where the high and low density models relate to the SAMs on silver and gold, respectively. The packing of the chains in the higher-density SAM prevents the argon atoms from penetrating the methyl groups as frequently as penetration into the lower density SAM. We suggest that the difference in
the fraction of atoms that reach thermal equilibrium with the SAM on gold and silver surfaces is controlled in large part by the ability of the atoms to penetrate the monolayer.

4.6 General Alkane Chain Packing Density Effects on Energy Transfer Dynamics

Molecular dynamics simulations are complementary to experiment to gain insight into gas-surface collision dynamics. The scattering experiments and simulations performed for argon scattering from alkanethiols adsorbed on silver and gold surfaces showed that overall, less energy is transferred to the higher packing density monolayers.\textsuperscript{75} This is a result of two distinct effects: (1) lower energy transfer in impulsive collisions and (2) a lower fraction of atoms that reach thermal equilibrium with the higher packing density films. To explain the difference in energy transfer for impulsive collisions we suggested that the alkyl chain motions parallel to the surface plane are restricted from absorbing the energy from the incident argon atoms as efficiently in the higher packing density surface compared with the lower packing density surface.\textsuperscript{75} For the trapping-desorption channel, we proposed that the extent of argon atoms that reach thermal equilibrium with the surface is controlled in part by the ability of the atoms to penetrate the monolayer.

This section aims to develop a fundamental understanding of the role of alkane chain packing density on gas-surface scattering. In particular, our goal is to answer the following questions: How does energy transfer in the impulsive scattering channel change with packing density? How does the fraction of trapping-desorption events change with packing density? Are there different processes that control the extent of thermalization, such as penetration, and what influence does packing density have on the partitioning of this process?
Below, we analyze the role of chain packing density on the total energy transfer, impulsive energy transfer, and trapping-desorption, in terms of the average chain volume for the different models. As described in section 4.3.1, the chain volume is calculated by averaging the space available for each individual chain in the 36 chain model. This free volume provides a way to compare the available space each chain can move when energy is transferred into the vibrational modes from the incident argon atoms.

Conformational changes induced by external stimuli for different alkyl packing densities have been previously examined. Wang et al. reported the packing and thermal stability of octadecylsilane (OTS) monolayers relative to their three dimensional analogues, polyoctadecylsiloxane (POS), using FTIR and Raman spectroscopy. The authors found that conformational changes induced by thermal energy treatments were more pronounced in the OTS SAMs than POS. A careful analysis of the three dimensional packing of POS suggested that the alkyl chains are more closely packed than the alkyl chains in the OTS SAMs. The decreased thermal stability in the OTS monolayers was attributed to the increased free volume of the chains.

In addition to the thermal stability study described above, there have been a number of SAMs designed to undergo conformational changes from external stimuli such as light and electric fields. One characteristic that any SAM must possess for dynamic control of surface properties is sufficient free volume. For example, Lahann and co-workers have created SAMs on gold with a large tail group, (2-chlorophyl)diphenylmethyl ester), as a precursor for a reversibly switching monolayer. The bulky groups are removed by a hydrolysis reaction to form a carboxylic acid SAM with a lower packing density than a SAM created initially from carboxylic acid
alkanethiols. The decreased packing density allows the chain to undergo conformational transitions when an electric field is applied, which is not permitted in the higher density SAMs.

In our volume calculations from the equilibrium structures of the SAM models, we find that increasing the lattice spacing of the surface-bound sulfur atoms also increases the average volume of the chains. Therefore, we use the free volume of the individual chains as a way to compare the range of motion that a chain can exert when exposed to an external stimulus, namely an argon collision.

4.6.1 Total Energy Transfer as a Function of Alkyl Chain Packing Density

The influence of alkane chain packing density on energy transfer dynamics is illustrated in Figure 4.9 for argon scattering from the 5 SAM models with an incident polar angle of 45° and incident energy of (a) 60 kJ/mol, (b) 80 kJ/mol, and (c) 120 kJ/mol.
**Figure 4.9** Final probability energy distributions for argon scattering with an incident polar angle of 45° and incident energy of (a) 60 kJ/mol, (b) 80 kJ/mol, and (c) 120 kJ/mol from a series of monolayers with different packing densities.
Focusing on Figure 4.9 (a), a trend in energy transfer for 60 kJ/mol energy argon scattering from the series of monolayers is observed. The higher the packing density, the more probable an argon atom will scatter from the surface impulsively and retain more of its incident energy. The most dramatic difference in energy transfer occurs between the two highest packing density monolayers. The probability energy distributions demonstrate that, as the packing density decreases from 181 Å³/molecule (closed circles) to 207 Å³/molecule (open squares), the high-energy tail of the distribution, characteristic of impulsive scattering, shifts to lower energies and the low energy portion of the distribution, typical of trapping-desorption, increases in intensity. Decreasing the packing density further to 214 Å²/molecule (filled triangles) and then to 223 Å²/molecule (open circles) exhibits the same trend, the high-energy tail shifts to lower energies and the intensity of atoms leaving the surface with the lowest energies increases. However, the shift in the distribution between the intermediate densities is much less dramatic than the shift between the highest density surfaces. Finally, the two lowest packing density surfaces, open circles and filled squares, have nearly the same distributions.

For argon scattering with an incident polar angle of 45°, as shown in Figure 4.9, increasing the incident energy from 60 kJ/mol to 80 kJ/mol and 120 kJ/mol does not alter the general trend that energy transfer is larger for monolayers that have a lower alkyl chain packing density. Figure 4.10 is a summary of the average total energy transferred to monolayers as a function of the average alkyl chain volume. For each incident polar angle studied, energy transfer increases with decreasing packing density. However, the magnitude of energy transfer for a given surface depends on the approach angle of argon relative to the surface normal, θ.
Figure 4.10 Summary of the average total energy transferred as a function of the volume per molecule for high energy argon atoms with incident polar angles of (a) 15°, (b) 30°, (c) 45°, (d) 60°, and (e) 75°.

For each surface, the total average energy transfer fraction from argon with a fixed incident energy decreases with increasing incident polar angle. This trend is likely the result of one or perhaps two factors. More atoms come into thermal equilibrium with the surface for more normal incident approach angles and/or the energy transfer in impulsive collisions decreases with incident angle.

Energy transfer fractions for argon atoms impacting the surfaces with incident angles more normal to the surface plane appear to converge to a single value as the packing density decreases. The leveling off is related to the limiting values of energy
transfer in these systems. If all the incident argon atoms were to reach thermal equilibrium with a surface before desorbing back into the gas-phase, their average final energy would be ~5 kJ/mol, based on a 300 K flux-weighted Maxwell-Boltzmann distribution. This translates into energy transfer fractions of 0.92, 0.94, and 0.96 for 60, 80 and 120 kJ/mol argon beams, respectively. This upper limit to the energy transfer fractions is the approximate value of the plateau for incident angles of 15 and 30°, implying that the lowest density surfaces are capable of bringing nearly every incident argon atom into thermal equilibrium, even for atoms with 120 kJ/mol incident energy. The energy transfer fractions appear more linear for the 60 and 75° incident angles, and somewhat in-between for an incident angle of 45°. For more glancing incident angles, energy transfer convergence extends beyond the monolayers we have investigated.

In the following section, we attempt to provide, in part, an atomic-level description for the mechanisms of energy transfer when argon atoms scatter from well-ordered \( n \)-alkyl monolayers. The underlying fundamentals, including some new definitions, will then be used to analyze the energy transfer dependence on packing density.

**4.6.2 Atomic Scale Mechanisms**

The mechanisms that control energy transfer and thermalization in gas-surface scattering have been shown to depend on a large number of global and local variables. Some models that have been used to understand the energy transfer mechanisms include the cubes models,\(^{11-13}\) washboard models,\(^{14,15}\) or a hard sphere collision model.\(^{16,18}\) The elegance of these models arise from using a small number of adjustable parameters to fit experimental data. The fitted parameters are then used to gain insight into the importance
of particular system variables in the gas-surface collision event. However, as noted by Bolton et al.\textsuperscript{133} “the underlying assumptions [of the gas-surface collision models] may hide important details of the energy transfer mechanism.” Detailed mechanisms for energy transfer have been obtained by using more realistic molecular dynamics simulations.\textsuperscript{29,30,33,118,133} For example, Hase et al. showed that energy transfer in high-energy neon scattering from self-assembled monolayers exhibit a Boltzmann-like component in the probability distribution in the absence of a trapping-desorption channel.\textsuperscript{29,30,33} In a more detailed study, Hase and coworkers showed that the impact site of neon on the surface governs the types of surface modes excited. The most efficient energy transfer comes from excitation of low-energy modes and modes that can redistribute energy away from the impact site on the time scale the gas atom is in contact with the surface.\textsuperscript{15,33}

We monitored the argon atoms’ position in the direction normal to the surface to gain insight into the atomic scale dynamics of these systems. Examples of single trajectory calculations are given in Figure 4.11 to illustrate the types of trajectories we observe in these systems. The plots are given as the argon atoms’ position relative to the rigid substrate as a function of time. Each of these trajectory examples are taken from the lowest density surface for argon scattering with an incident energy of 80 kJ/mol and an incident polar angle of 30°. Included in each of the four plots is a horizontal dashed line that represents the average height of the terminal methyl groups above the rigid substrate plane.
Figure 4.11  Single trajectories from our molecular dynamics simulations that were selected for illustration from 80 kJ/mol argon atoms scattering from the 229 Å³/molecule monolayer model. The dynamic processes include: (a) direct impulsive scattering, (b) surface trapping-desorption, (c) ballistic penetration-desorption, and (d) surface trapping-penetration-desorption.

Figure 4.11 (a) is a plot of an argon atoms height versus time as an illustration of direct impulsive scattering. In general, the total time that the argon atom is in ‘contact’ with the surface for direct impulsive scattering events is about 1-2 ps.\textsuperscript{28,35} We define direct impulsive scattering as those trajectories with a single inner turning point relative to the surface plane and do not penetrate below the average plane of the terminal methyl groups. This is a slightly different definition for approximating impulsive scattering than the one given in section 4.4.1. We make this added restriction because some argon atoms penetrate the monolayer and only have a single inner turning point. If we use this definition for impulsive scattering or the definition given in section 4.4.1, the results for
80 kJ/mol argon with an incident polar angle of 30° scattering from the SAMs on gold and silver models produce the same results.

Surface trapping-desorption, illustrated in Fig. 4.11 (b), is defined as trajectories that have at least one outer turning point (or hop) before desorption back into the gas-phase. It is important to note from this definition that a trajectory that undergoes trapping may not reach full thermal equilibrium with the surface. An incident argon atom is considered trapped if it cannot escape the gas-surface potential well on its first attempt to desorb back into the gas phase.\(^1\) The time scale for the argon atoms in contact with the surface is longer than direct impulsive scattering and can last anywhere from 2 ps to more than 25 ps (cutoff time used to terminate the trajectory).

A trajectory where the argon atom penetrates below the plane of the average terminal group height on impact is considered as a ballistic penetrating trajectory, Fig. 4.11 (c). We find that the average energy of atoms desorbing into the gas phase after a ballistic penetration is always near, but slightly higher than \(2kT_{\text{surf}}\). This final average energy implies that ballistic penetration leads to thermal accommodation for argon atoms. However, we find that the average final energy of atoms that undergo ballistic penetration is closer to \(2kT_{\text{surf}}\) the lower the packing density. Atoms that reach thermal equilibrium after ballistic penetration is not the case for neon atoms that have a small gas-surface potential well.\(^2\)\(^9\) Interestingly, simulations by Sibener et al. involving high-energy xenon atoms scattering from decanethiolate SAMs leave the surface with average final energies much higher than average energies expected for thermal accommodation after penetrating collisions.\(^3\)\(^6\)
The final dynamic process outlined in Figure 4.11 (d) is given the name surface trapping-penetration-desorption. Penetration in this process occurs after the argon atom has already had its initial impact with the surface, which is different than the ballistic penetration channel. In Figure 4.11 (d), the argon atom in that trajectory makes 8 hops on the surface before crossing the plane defined for the average methyl height. This channel is actually a special case of surface trapping events where the argon atoms penetrate or diffuse into the monolayer before desorption rather than remaining in the interfacial region. However, atoms that undergo this process are in thermal equilibrium with the surface prior to penetration. Since the gas atoms are already accommodated to the surface, these diffusion events do not provide a means for increasing the fraction of gas atoms that thermally equilibrate. However, calculating the fraction of atoms that undergo thermalization followed by penetration (monolayer diffusion) as a function of packing density lends insight into the importance of monolayer density for other types of gas-surface dynamics mechanisms, such as solvation into bulk materials.

The definitions for trajectories that undergo direct impulsive scattering, surface trapping-desorption, and ballistic penetration-desorption are used as an aid to interpret the data for argon scattering from the series of alkyl SAMs with varying chain packing density. Tables at the end of the chapter provide a complete summary of the argon atom dynamics we calculated for all the trajectories.

4.6.3 Direct Impulsive Scattering as a Function of Packing Density

In section 4.6.2, we noted that the total energy transfer increased with decreasing alkyl packing density for all sets of incident energies and angles. The increase in energy transfer with decreasing packing density is the result of more atoms coming into thermal
equilibrium with lower density surfaces and/or energy transfer in impulsive collisions increasing with decreasing packing density. We also noted in section 4.6.2, for a given incident energy and surface model, energy transfer decreases with increasing polar angle. Increasing energy transfer with decreasing incident polar angle seems to be general for high-energy argon atoms impacting well-ordered \( n \)-alkyl monolayers since we find this trend for all SAM models.

In the previous section, we introduced definitions for the fundamental types of dynamical processes available to argon atoms as they interact with well-ordered monolayers of the type in this study. We invoke the definition for impulsive scattering to compare the dependence of energy transfer in this channel as a function of alkane packing density.

Figure 4.12 is a five plot series showing the dependence of energy transfer on the chain packing density for impulsive scattering events. Each plot summarizes the dependence of energy transfer on packing density for a constant incident polar angle, including the results for all three incident energies of 60, 80, and 120 kJ/mol.

The dependence of impulsive energy transfer on packing density for impact angles of 60 and 75°, Figures 4.12 (d) and 4.12 (e), appear relatively the same. As the packing density of the monolayers decreases, the fractional energy transfer increases. This trend is nearly linear for both incident angles. For incident angles of 15, 30, and 45°, the curve shapes are not as well-defined. In some cases, energy transfer fractions increase with decreasing packing density, (i.e. \( \theta_i = 15^\circ \) and \( E_i = 60 \text{ kJ/mol} \)), in some cases they increase, then level off with decreasing packing density (i.e. \( \theta_i = 45^\circ \) and \( E_i = 60 \text{ kJ/mol} \)), and in other cases, they have maximum values with decreasing packing density.
(i.e. $\theta_i = 45^\circ$ and $E_i = 80$ kJ/mol). However, the highest packing density monolayer absorbs the lowest amount of energy for impulsive collisions compared to the other four monolayers in for every set of conditions.

Our simulation results for the dependence of impulsive energy transfer on alkane chain packing density can be explained from conclusions drawn from molecular dynamics simulations of neon scattering from alkanethiols adsorbed to gold.\textsuperscript{33} The simulation results showed that the most efficient energy transfer for impulsive collision events occurs when the incident neon atom strikes the alkyl chains with side-on impacts. Two major observations were provided as an explanation for the high-energy transfer efficiencies from side-on impacts.\textsuperscript{15} Side-on impacts excite low-frequency vibrational modes more easily. Intramolecular vibrational energy redistribution (IVR), which dissipates the energy into the monolayer away from the collision site, is more efficient when inter-chain modes are excited during the collision.
Figure 4.12 Average energy transfer fractions for direct impulsive scattering (IS) events as a function of volume per molecule for incident polar angles of (a) 15°, (b) 30°, (c) 45°, (d) 60°, and (e) 75°.

For each plot in Figure 4.12, we observe a general trend that energy transfer in impulsive collisions increases with decreasing packing density. This generalizes and confirms what was suggested from experimental data for argon scattering from SAMs on gold and silver substrates. Higher packing densities prevent chains from moving in the plane of the surface, thereby rendering it more difficult to excite some of the low-frequency wagging modes. However, there are exceptions where energy transfer has a maximum value at an intermediate density. For example, the average fractional energy
transfer for 120 kJ/mol argon scattering with incident polar angles of 15, 30, or 45° have maxima for the 214 Å³/molecule surface.

The increase in energy transfer with decreasing packing density up to the maximum can be explained with excitation efficiencies related to the free volume of the chains, but fail to explain the negative slope with continued increasing chain volume. A maximum in the data suggests that a competition exists between the efficiency of exciting low-frequency modes and some other process. We suggest a slow rate of energy dissipation away from the collision site is the competing process. In the simulation studies by Hase et al. aimed at understanding the role of surface dynamics on energy transfer, the authors found that energy transfer is enhanced when the rate of vibrational energy transfer occurs on the time scale the neon atoms are in contact with the surface. Overall, efficient energy transfer occurs for low density monolayers, relative to the 181 Å³/molecule model, because sufficient ‘room’ exists for the chains to move and thus conformational changes in the chain backbone or larger amplitude motions can occur. However, the rate of energy dissipation away from the collision site may slow down as the alkane chains begin to separate. For some initial conditions, energy transfer is maximized when the alkyl chains have a sufficiently large space for molecular motions and a high enough packing density to couple many vibrational modes that can redistribute the energy away from the collision site.

A competition between the rate of energy dissipation away from the collision site and the ability to excite low-frequency motions is consistent with the observed trends in the data, but further investigation is needed to make such a strong conclusion. To study dissipation away from the collision site, it may be beneficial to start the surface in the
classical potential energy minimum, at 0 K, so that all the carbon atoms are motionless until the initial gas collision. The incident argon atom would be aimed at a central alky chain and the initial motion of carbon atoms in adjacent chains would be monitored in time. The impact parameter should be sampled over a uniform distribution to calculate the average rate motion propagates away from the collision site for each surface model. The initial motion of carbon atoms on the adjacent chains would serve as a comparison for the rate of inter-chain vibrational energy redistribution.

Another method that could be used to study the importance of energy dissipation away from the collision site as a function of packing density would be to include rigid chains in the model. For example, the six nearest neighbor (NN) chains in the hexagonal structure could be restricted from motion. This restriction could be applied by either not updating the positions of the atoms in the simulation or by giving those atoms extremely high masses such that their motions would be dampened. The central chain that is impacted by the argon atom would still ‘feel’ the potential from the neighboring chains. In this case, energy transfer to the individual chain motions would still be available to the argon atoms. This initial step would allow some insight into the importance of chains with a larger free volume to absorb more energy. The next step would be to remove the restriction for the NN chains and put the same restriction on the 12 next nearest neighbor (NNN) chains. If the energy transfer probabilities changed, then the NNNN chains could be restricted in the same way. Comparison of the translational energy probability distributions from the different packing density monolayers with these two/three restrictions would provide information on the energy dissipation away from the collision site. Additionally, the importance of inter-chain vibrational energy redistribution for
argon atoms striking the chains along or against the direction of the chain tilt angle could be obtained from this analysis.

4.6.4 Trapping Desorption as a Function of Alkane Chain Packing Density

The dependence of the total energy transfer distributions on chain packing density summarized in section 4.6.2 was suggested to depend on the fraction of energy transferred through impulsive scattering and/or the fraction of atoms that come into thermal equilibrium with the surface. In the previous section, we found that the average energy transferred to the surface in impulsive scattering events does depend on the available space for the alkane chains to move, especially when the incident argon atoms approach at glancing angles. In this section, we focus on the number of atoms that are trapped, either with or without reaching thermal equilibrium, and the different mechanisms that bring about trapping for the different packing density monolayers.
Figure 4.13 Fraction of argon atoms that undergo trapping-desorption as a function of the volume per molecule for incident impact angles of (a) 15°, (b) 30°, (c) 45°, (d) 60°, and (e) 75°.

Figure 4.13 shows the fraction of incident argon atoms that undergo trapping-desorption events as a function of alkane chain volume. The data points include both types of trapping-desorption events: ballistic-penetration desorption and surface-trapping desorption. The remaining trajectories are considered to scatter impulsively back into the gas phase. Each plot in the figure summarizes the results for a constant incident polar angle. Incident trajectories approaching the surface with polar angles of 15° and 30°, Fig. 4.13 (a) and (b), have trapping-desorption fractions that are roughly independent of
incident energy. Incident energy begins to have an influence on the fraction of trapping-desorption events for incident angles greater than 45°. In general, the higher the incident energy, the less often trapping-desorption occurs. For $\theta_i = 75^\circ$, argon atoms with an incident energy of 60 kJ/mol become trapped approximately 1.5 times more often than atoms with incident energies of 120 kJ/mol, independent of the monolayer density. We also observe from these summary plots that the difference in the trapping-desorption fraction between the highest and lowest packing density monolayers is maximal (~0.1 and ~0.9), for argon atoms with $\theta_i = 15^\circ$, but approaches zero for argon atoms with $\theta_i = 75^\circ$.

Figure 4.14 is a summary of the ratio of trajectories that undergo ballistic penetration into the monolayers relative to the total number of trajectories in the trapping-desorption channel. For all incident polar angles, the fraction of trajectories that ballistically penetrate the monolayers is greatest for the lowest density surface and nearly zero for the highest density surface. With the exception of argon atoms impacting with 120 kJ/mol at an approach angle of 15°, no ballistic penetration occurs for the 181 Å³/molecule model. However, roughly 60% of trajectories in the trapping-desorption channel result from ballistic penetration for the other four monolayers under the same incident argon conditions. As the incident polar angle is increased, the fraction of atoms that ballistically penetrate the monolayers decreases substantially. Even for the lowest density surface, less than 10% of the trapping-desorption trajectories fall into this channel for argon atoms with an incident angle of 75°. In general, the ability of argon atoms to penetrate the monolayers on impact appears to be related to the magnitude of the argon atoms momentum normal to the surface.
Figure 4.14  The fraction of the total number of trapping-desorption events where the argon atoms undergo ballistic penetration into the monolayers for incident impact angles of (a) 15°, (b) 30°, (c) 45°, (d) 60°, and (e) 75°.

A comparison between the data from Figs. 4.13 and 4.14 sheds light on what is controlling the difference in the fraction of trapping-desorption events in these monolayers. There is a direct correlation between the fraction of trapping-desorption and the ability of the argon atoms to ballistically penetrate the monolayers. Beginning with $\theta_i = 15^\circ$, the dramatic difference in the total fraction of trapping-desorption is likely related to the ability of the incident argon atoms to penetrate the monolayers. As the incident polar angle is increased, the relative difference in trapping-desorption decreases along with the relative difference in ballistic penetration. This can be explained by the free
volume of the different packing densities. The larger the spacing between alkane chains, 
the easier it is for high-energy argon atoms to squeeze between the chains on impact. 
Once the argon atoms penetrate into the monolayers, they jostle around among the chains 
exchanging energy and approaching thermal equilibrium. Figure 4.15 shows the size of 
an argon atom relative to the lattice separation and methyl diameter for the highest and 
lowest density monolayers in this study. The open circles in the figure represent the 
diameter of the methyl groups based on the minimum energy distance of two interacting 
methyl groups from the Lennard-Jones parameters used in the simulations. The circles 
are scaled to the lattice spacings for the models given in Table 4.2. The gray circles 
represent argon atoms scaled to their van der Waals diameter. From the figure, it is easy 
to image than an argon atom could squeeze between the chains more easily in lower than 
higher density SAMs.

*Figure 4.15* Schematic representation of the lattice spacing of the methyl groups in the highest 
and lowest density monolayers studied. The open circles represent the approximate diameter of a 
methyl group (see text) and the gray circle represents an argon atom scaled to its van der Waals 
diameter.
There are a substantial number of argon atoms that are trapped on the monolayers in the absence of ballistic penetration. For example, the trapping-desorption fraction for incident argon atoms with 80 kJ/mol and an incident polar angle of 60° is near 0.4 for the 207 Å³/molecule model, in the absence of ballistic penetration. In addition, the fraction of trapping-desorption increases with increasing polar angle for the highest packing density monolayer, but decreases with increasing polar angle for the other monolayers. It is important to note that ballistic penetration leads to near thermal accommodation, whereas, the definition given for trapping-desorption in section 4.4.1 implies accommodation in the surface normal direction only; the argon atoms are not necessarily in full thermal equilibrium with the surface.

Figure 4.16 shows five summary plots of the fraction of trapping-desorption as a function of incident polar angle for each monolayer. This figure contains the same data as Fig. 4.13, but illustrates the dependence of trapping-desorption fraction on incident polar angle for each monolayer. The dependence of trapping-desorption on the incident angle of argon is different for the highest and lowest density monolayers. For the highest packing density monolayer, 181 Å³/molecule, the fraction of trapping-desorption increases with increasing incident angle, independent of incident energy. This means that for the highest density SAM, more glancing angles lead to more trapping. For the next highest packing density model, 207 Å³/molecule, trapping-desorption is roughly constant for each angle at collision energies of 60 and 80 kJ/mol, but decreases with increasing polar angle for the highest energy beams. The other three monolayers show a decrease in trapping-desorption fraction for increasing incident polar angle for all energies studied.
The decrease in the fraction of trapping-desorption with increasing polar angle in the lower density monolayers can be understood from the penetration channel discussed above. However, the more glancing the incident angle, the more dependent the trapping-desorption fraction is on incident energy. For a given incident angle, the higher the incident energy is, the lower the TD fraction. For normal incident angles, ballistic penetration is most important, but surface trapping becomes progressively more important as the incident angle increases. In glancing collisions, surface trapping is the predominant trapping pathway. An incident argon atom is less likely to become trapped by the monolayer, the more energy it has to lose on impact.

![Graph showing fraction of trapping-desorption events for each monolayer, as a function of incident polar angle of argon.]

**Figure 4.16** Fraction of trapping-desorption events for each monolayer, as a function of incident polar angle of argon.
The fraction of trapping desorption has a different dependence on incident polar angle for the different packing density monolayers. For surfaces that show a decrease in trapping desorption with an increase in polar angle, ballistic penetration controls the trapping channel. For the 181 Å³/molecule model, ballistic penetration does not occur and the trapping-desorption fraction actually increases with increasing polar angle. Conservation of parallel momentum during the gas-surface collision is a characteristic of an atomically smooth surface.\textsuperscript{11,13} The probability of trapping is related to the amount of energy the argon atom has to lose in the direction normal to the surface. Figure 4.17 shows the dependence of trapping-desorption on the \textit{normal} energy, $E_{\text{i}}\cos^2(\theta_i)$, of the incident argon beam for the 181 Å³/molecule model. The trapping-desorption fractions for the three different incident energies and 5 incident angles nicely fit a monotonic dependence on the normal energy. This implies conservation of momentum in the direction parallel to the surface plane.
Figure 4.17 The fraction of argon trajectories that make multiple collisions with the 181 Å³/molecule model as a function of the normal incident energy.

Figure 4.18 gives a hypothetical potential energy diagram with two trajectories superimposed to represent an argon atom interacting with the surface when it approaches with a 15 or 45° incident angles. As illustrated in the diagram, the potential is fairly smooth in analogy with the 181 Å³/molecule. For small incident angles, the atom does not transfer enough energy in the surface normal direction to influence its trajectory away as it scatters impulsively back into the gas phase. In comparison, the argon atom that approaches the surface at 45° transfers sufficient energy in the normal direction to become temporarily trapped in the gas-surface potential well before desorption.
Figure 4.18 Hypothetical potential energy diagram for argon interacting with a surface. The two plots have a trajectory mapped out for an argon incident at 15° (top) and 45° (bottom).

Energy transfer is lowest for argon scattering from the 181 Å³/molecule model compared to the other models. Since there is conservation of momentum parallel to the surface plane for the highest density monolayer, excitation of the side-to-side chain motions must be limited. This conservation of parallel momentum in the highest density surface provides further evidence for our conclusion that chain motions parallel to the surface plane are more difficult to excite in high packing density monolayers because their freedom of motion is arrested. Moreover, the average energy of atoms desorbing
after multiple collisions with the 181 Å³/molecule model is not thermal. For example, the average energy of argon atoms that undergo multiple collisions with the surface before desorbing into the gas-phase is 59.1 kJ/mol after striking the surface with incident energy of 120 kJ/mol and an incident angle of 75°.

4.6.5 Diffusion

The atomic scale processes that we observe in argon scattering from well-ordered n-alkyl monolayers were defined and used to help understand the role of packing density on gas-surface energy transfer. The final process discussed in section 4.6.2 was defined as surface trapping-penetration-desorption. Some argon atoms come into thermal equilibrium with the surface and then penetrate below the terminal methyl groups. We noted that calculating the fraction of atoms that penetrate the monolayers after coming into thermal equilibrium lends insight into the importance of surface density for gas-surface dynamic mechanisms such as solvation into bulk materials.

We probed the influence of packing density on this ‘argon diffusion’ channel by calculating the number of argon atoms that penetrate below the terminal methyl groups for gas atoms that are initially in thermal equilibrium with the surface. This is different than the trajectories discussed above where the incident energies were monoenergetic and well above kT_{surf}. In these trajectories, the incident argon atoms approach normal to the surface plane with a distribution of impact energies sampled from a Maxwell-Boltzmann distribution characterized a 300 K temperature. These scattering conditions mimic a situation where thermal equilibrium exists between the two phases. During the gas-surface interaction time, we monitored the height of the argon atoms relative to the surface plane to calculate the number of atoms that penetrate the monolayers. Figure
4.19 shows the argon atoms’ minimum height probability distributions calculated from 500 trajectories when a thermal beam of atoms scatter from the five surfaces. A minimum height of zero is defined as the height of the rigid substrate. The vertical line between 11 and 15, see Table 4.2 for the methyl height of each monolayer, represents the average plane of the terminal methyl groups.

As one might expect, the profiles of the distributions have a dramatic dependence on the density of the monolayer. The narrowest distribution corresponds to the 181 Å³/molecule model while the broadest corresponds to the 229 Å³/molecule model. The three models with intermediate packing density provide distributions between the two extreme cases. The portion of the probability distribution that is on the left hand side of the vertical line corresponds to those argon atoms that have penetrated the monolayer. For the two highest packing density models, no trajectories cross this line within 25 ps. For the 214 Å³/molecule model, there is a small number of penetrating atoms, although the depth of penetration is very shallow. The two lowest density models allow a significant number of atoms to penetrate and some of them even make it down five or six methyl units of the chains. The percent of trajectories that penetrate the monolayers is a lower limit since some trajectories are still trapped on the surface after 25 ps, the integration time we cut off the trajectory.

The thermal beam scattering distributions from the surfaces provides two pieces of information concerning gas-surface dynamics. First, the maximum in the distributions gets closer to the average methyl group plane as the density decreases, which implies that the surfaces are increasingly more corrugated. Second, the transition between no penetration and significant penetration provides approximate sizes of holes or channels
needed for diffusion. Figure 4.15 illustrates this difference for the highest and lowest density surfaces for the methyl groups in their equilibrium positions relative to the size of an argon atom. The sizes of the holes/channels may be applied to system designs when the number of particles penetrating the film needs to be controlled.

**Figure 4.19** Probability distributions for the distance an argon atom penetrates the monolayer relative to the rigid substrate of the five monolayers for a thermal energy distribution at $T = 300$ K of argon atoms striking normal to the surface.
4.7 Summary

Molecular dynamics simulations were used as an aid in interpretation of experimental results for argon scattering from \( n \)-alkanethiolates adsorbed to gold and silver surfaces. The models used in our study sufficiently reproduce experimental data providing us with confidence to study the atomic scale mechanisms of energy transfer. Total final angular distributions for the two types of monolayers show that the difference in energy transfer dynamics observed experimentally is not a consequence of our restriction in monitoring only one final scattering angle. Similar angular scattering distributions were calculated for each surface with differences related to the partitioning of the trapping-desorbing and impulsive scattering events. The classical trajectory calculations also show that single collision events dominate the impulsive scattering channel and provide a dynamic level definition that can be used as criteria for comparing similar gas-surface systems.

The comparative role of alkane chain packing density on energy transfer for impulsive scattering events revealed that energy transfer is more efficient when the chains have more space to move. This trend in the data has exceptions and sometimes a maximum is observed in the energy transfer fractions for an intermediate packing density model. We suggest that these maxima are related to a competition between the ability to excite low-frequency vibrational modes and the rate at which energy is dissipated away from the collision site to neighboring chains.

Lower packing density surfaces trap more argon atoms than higher packing density surfaces. The ability of argon to undergo ballistic penetration plays a large role in determining the total fraction of atoms that are trapped by the surface. We find that the
fraction of atoms that undergo ballistic penetration is directly related to the average
distance between alkane chains. The larger the spacing in the chains, the easier it is for
argon to squeeze between them and penetrate below the interface. We also find that the
distribution of argon atoms that experience ballistic penetration desorb from the surface
with average energies near 2kT_{surf}.

The highest packing density model used in this study shows a trapping
dependence directly related to the normal energy of the argon atom. We observe a
normal energy scaling dependence on trapping when all the incident argon parameters are
plotted on one curve. However, the argon atoms that are trapped do not come into full
thermal equilibrium, but desorb with average energies higher than 2kT_{surf}. The
conservation of parallel momentum for argon scattering from the highest density
monolayer provides further evidence for the importance of exciting surface modes
parallel to the surface plane when large amounts of energy transfer are observed.

Finally, we observe a diffusion channel for argon atoms that have come into
thermal equilibrium with the monolayers that has a strong dependence on the packing
density of the monolayers. We find that changing the lattice spacing of the nearest
neighbors by about one Å dramatically changes the ability of argon to penetrate the
monolayers. This finding lends insight into the important role of pockets for gas-surface
dynamic processes. Fundamental processes such as gas atom/molecule solvation into
bulk materials or the design of protective coatings are applications of this diffusion
channel.
### 4.S.1 Summary of Impulsive Scattering and Trapping Desorption

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<tr>
<th>Density (Å³/molecule)</th>
<th>Incident Energy, kJ/mol</th>
<th>Fraction of Total Energy Transfer</th>
<th>$&lt;E_r&gt;$ Impulsive SC$^a$</th>
<th>Fraction of Trapping-Desorption$^b$</th>
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**Incident Polar Angle = 75°**

a. Average energy of trajectories with single inner turning points without penetrating below the terminal methyl groups.

b. All trajectories that have one or more outer turning points and trajectories that penetrates with only one inner turning point.
4.5.2 Dynamic Processes Partitioned

| Density (Å³/molecule) | Incident Energy, kJ/mol | Fraction of Impulsive SC<sup>a</sup> | Fraction of Ballistic Penetration<sup>b</sup> | Fraction of STPD<sup>c</sup> | Fraction of STD<sup>d</sup> |
|-----------------------|-------------------------|------------------------------------|--------------------------------VALIDATE|----------------------------|----------------------------|
| 181                   | 60                      | 0.875                              | 0.000                                          | 0.000                      | 0.125                      |
| 207                   | 60                      | 0.515                              | 0.089                                           | 0.000                      | 0.396                      |
| 214                   | 60                      | 0.313                              | 0.206                                           | 0.002                      | 0.479                      |
| 223                   | 60                      | 0.135                              | 0.381                                           | 0.042                      | 0.442                      |
| 229                   | 60                      | 0.069                              | 0.465                                           | 0.196                      | 0.279                      |
| 181                   | 80                      | 0.933                              | 0.000                                           | 0.000                      | 0.067                      |
| 207                   | 80                      | 0.524                              | 0.164                                           | 0.000                      | 0.312                      |
| 214                   | 80                      | 0.321                              | 0.249                                           | 0.003                      | 0.427                      |
| 223                   | 80                      | 0.140                              | 0.393                                           | 0.044                      | 0.423                      |
| 229                   | 80                      | 0.073                              | 0.467                                           | 0.200                      | 0.260                      |
| 181                   | 120                     | 0.968                              | 0.002                                           | 0.000                      | 0.030                      |
| 207                   | 120                     | 0.457                              | 0.319                                           | 0.000                      | 0.224                      |
| 214                   | 120                     | 0.305                              | 0.374                                           | 0.004                      | 0.317                      |
| 223                   | 120                     | 0.112                              | 0.565                                           | 0.063                      | 0.260                      |
| 229                   | 120                     | 0.068                              | 0.519                                           | 0.222                      | 0.191                      |

Incident Polar Angle = 15°

| Density (Å³/molecule) | Incident Energy, kJ/mol | Fraction of Impulsive SC<sup>a</sup> | Fraction of Ballistic Penetration<sup>b</sup> | Fraction of STPD<sup>c</sup> | Fraction of STD<sup>d</sup> |
|-----------------------|-------------------------|------------------------------------|--------------------------------VALIDATE|----------------------------|----------------------------|
| 181                   | 60                      | 0.857                              | 0.000                                          | 0.000                      | 0.143                      |
| 207                   | 60                      | 0.494                              | 0.035                                           | 0.000                      | 0.471                      |
| 214                   | 60                      | 0.376                              | 0.098                                           | 0.001                      | 0.525                      |
| 223                   | 60                      | 0.193                              | 0.272                                           | 0.030                      | 0.505                      |
| 229                   | 60                      | 0.108                              | 0.363                                           | 0.155                      | 0.374                      |
| 181                   | 80                      | 0.894                              | 0.000                                           | 0.000                      | 0.106                      |
| 207                   | 80                      | 0.538                              | 0.071                                           | 0.000                      | 0.391                      |
| 214                   | 80                      | 0.350                              | 0.159                                           | 0.002                      | 0.489                      |
| 223                   | 80                      | 0.164                              | 0.318                                           | 0.035                      | 0.483                      |
| 229                   | 80                      | 0.114                              | 0.405                                           | 0.173                      | 0.308                      |
| 181                   | 120                     | 0.917                              | 0.000                                           | 0.000                      | 0.083                      |
| 207                   | 120                     | 0.575                              | 0.132                                           | 0.000                      | 0.293                      |
| 214                   | 120                     | 0.343                              | 0.231                                           | 0.002                      | 0.424                      |
| 223                   | 120                     | 0.202                              | 0.376                                           | 0.042                      | 0.380                      |
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Incident Polar Angle = 75°

a. Fraction of trajectories with single inner turning points without penetrating below the terminal methyl groups. SC ≡ Single Collisions
b. Fraction of trajectories that penetrated below the terminal methyl group on impact
c. Fraction of trajectories that are trapped above terminal methyl groups then penetrate the SAM and later desorb. STPD ≡ Surface Trapping-Penetration-Desorption
d. Fraction of trajectories that are trapped above terminal methyl groups then desorb into the gas-phase without penetrating the monolayer. STD ≡ Surface Trapping-Desorption
Chapter 5

The Effect of Intra-Monolayer Hydrogen Bonding and Terminal Group Structure on the Dynamics of Argon Collisions with Self-Assembled Monolayers


5.1 Introduction

The first step in a gas-surface chemical reaction involves a collision where the energy exchange dynamics determine whether the gas-phase reactant scatters directly away from the surface or accommodates with the material. These two processes have been explored in depth for atoms and molecules colliding with a wide variety of highly-characterized single-crystal or polycrystalline inorganic materials. Molecular-beam scattering experiments and classical trajectory simulations of such systems have led to the development of a detailed understanding of the factors that affect energy transfer in gas-surface collisions. However, the experimental challenge of making well-defined organic surfaces in a highly reproducible manner has limited the number of studies aimed at exploring the gas-surface energy transfer dynamics involving organic substrates. The primary objective of the experimental studies presented below is to employ self-assembled monolayers (SAMs) of various alkanethiols on gold and atomic-beam scattering techniques to begin to explore how the order, molecular structure, and the hydrogen-bonding nature of an organic surface influence the extent of energy transfer and thermalization in gas-surface collisions.
Some of the most detailed insight into the dynamics of energy exchange between gases and organic surfaces has come from the molecular beam studies of Nathanson et al.\textsuperscript{3,9,19} They have scattered various small-molecule and atomic gases from a series of low-vapor pressure organic liquids, including pure hydrocarbon squalane, highly hydrogen-bonding glycerol, and fluorocarbons. Of particular relevance to the work presented below, are their studies exploring the energy transfer of atomic neon when it collides with the surface of squalane and glycerol. In this work, they observed that high-energy neon atoms reach thermal equilibrium more readily on squalane than on glycerol.\textsuperscript{3} Although the atomic scale structures of these two surfaces are likely different, this result suggests that hydrogen-bonding organic materials may present a more rigid surface than analogous non-hydrogen-bonding systems. In addition to exploring the influence of hydrogen bonding, they also used thermal motions to study the affect of atomic-scale roughness on the energy exchange dynamics.\textsuperscript{19} This work demonstrated that microscopic roughness leads to a greater propensity for gas-surface accommodation due to multiple collisions. However, they found that, for direct inelastic scattering at the specular angle, the fractional energy transferred to the surface was independent of the atomic-scale surface roughness.

One of the first studies that utilized SAMs as well-ordered models for investigating the gas-surface energy transfer dynamics focused on Ar, He, O\textsubscript{2}, and NO scattering from amphiphilic monolayers.\textsuperscript{10,27} This work, by Cohen \textit{et al.} demonstrated that the extent of energy transfer from the gas to the surface can be correlated with the rigidity of the monolayer chains and the gas-to-surface mass ratio. They further suggested that the
concerted waving motions of the chains and the hindered rotation of the end groups play the dominant role in controlling the energy exchange dynamics.

In addition to these experimental efforts, Hase and co-workers have performed classical-trajectory simulations of various gases scattering from alkanethiol SAMs on gold. They have shown that low-energy extended motions of monolayer alkane chains play the largest role in dissipating the energy of a gas-surface collision, whereas the high-energy C-H motions are not very active in the scattering dynamics. Furthermore, their calculations demonstrate that penetration of incident neon atoms into the monolayer is limited to the first few atomic layers and that the extent of penetration decreases with decreasing incident energy. Their simulations have also been used to investigate the nature of the low-energy scattering channel often described as trapping desorption. They find that for neon scattering from a methyl-terminated SAM, the apparent low-energy component to the energy distribution does not arise from an actual trapping-desorption intermediate. Rather, the low-energy scattered atoms leave the surface with a non-statistical distribution of energies and recoil directions. However, more polarizable gases like argon are found to scatter in two distinct pathways corresponding to direct inelastic and actual trapping-desorption channels.

Further experimental studies using atomic-beam scattering techniques have provided new insights into monolayer structure and thermal motions. The pioneering studies of Scoles et al. employed He atom diffraction methods to perform highly detailed monolayer structure determinations. In addition, they have performed Debye-
Waller type measurements on single-crystal organic surfaces to demonstrate the rigidity of a hydrogen-bonding surface relative to a methyl-terminated surface.\textsuperscript{141} The highly-detailed molecular beam studies of Sibener and co-workers have also helped to develop a microscopic understanding of monolayer structure and have been used to follow the dynamics of monolayer formation.\textsuperscript{58,103} Their studies provide an unprecedented look into the nature of molecular self-assembly on surfaces. Furthermore, this group has employed high-momentum and high-energy resolution He scattering to study the surface vibrations of self-assembled monolayers.\textsuperscript{58}

In addition to the body of work using neutral molecular beams, several researchers have also studied the fragmentation patterns and reactivity of ions when they impact the surface of organic monolayers.\textsuperscript{37-41} Cooks et al., have explored the characteristics of high-energy ionic collisions using a variety of ω-functionalized SAMs.\textsuperscript{37} Hanley and co-workers have combined experimental and computational approaches to study the energy transfer of SiMe\textsubscript{3}\textsuperscript{+} on a 6-carbon alkanethiol SAM.\textsuperscript{38,40} Their work shows that energy transfer to a surface is markedly greater for a monolayer-covered surface than it is for a bare gold surface and that penetration into the monolayer, even for > 10 eV ions, is limited to the topmost two-to-three layers of carbon atoms. Wysocki and co-workers,\textsuperscript{92} and Bernasek et al.,\textsuperscript{39} have also investigated the reaction dynamics of ion-surface scattering using SAMs. This set of work has provided important insight into how end-group orientation and the overall chain-length of a monolayer influence the ion-surface reaction dynamics.

The aim of the work presented in this chapter is to help further elucidate the dynamics of energy transfer in collisions of non-reactive gases with organic surfaces. It
has been shown that the scattering dynamics of neutral argon colliding with a long-chain methyl-terminated (CH$_3$-terminated) alkanethiol SAM is markedly different than scattering from a hydroxyl-terminated (OH-terminated) monolayer.$^{72,142}$ This study suggested that the OH-terminated SAM is more rigid than the CH$_3$-terminated monolayer. There may be a combination of factors responsible for the relative rigidity of the OH-terminated SAM including differences in the available energy modes of the two terminal groups, differences in the monolayer structures, differences in the argon-SAM potential energy surfaces (PES), and the hydrogen-bonding network and location of the hydroxyl-terminated monolayer. We have therefore performed a series of experiments designed to provide some initial insight into the influence of these aspects on the overall gas-surface energy transfer dynamics. Specifically, we present scattering results from five types of SAMs. (1) A monolayer constructed from olefin-terminated alkanethiols provides some insight into the importance of terminal group vibration and torsional motions in the energy exchange dynamics. (2) Hydroxyl-, amine-, and carboxylic acid-terminated SAMs are compared to investigate energy transfer and thermalization for argon scattering from a series of hydrogen-bonding monolayers. (3) A series of mixed monolayers containing varying concentrations of CH$_3$-terminated and OH-terminated alkanethiols are used to regulate the concentration of hydrogen-bonding groups and study their role in controlling the outcome of the gas-surface collision. (4) A SAM terminated with a methyl ester is used to study the role of the gas-surface PES for terminal groups containing elements other than carbon. (5) Finally, a series of monolayers with highly-hydrogen-bonding carbamate groups buried under $n$-alkyl chains, where $0 < n \leq 11$, are
used to study the role of intra-monolayer hydrogen-bonding interactions in energy transfer as a function of distance from the gas-surface interface.

5.2 Structural Considerations of Functionalized Alkanethiol SAMs on Gold

Self-assembled monolayers, grown from both solution-phase or gas-phase procedures, produce well-ordered and highly-reproducible thin organic films. There are a wide variety of systems that are classified as SAMs with the typical defining feature related to the headgroup/substrate pair. Of particular interest, is the chemisorption pair of sulfur containing compounds (thiols, sulfides, and disulfides) and gold substrates. The simplest and most thoroughly studied of these compounds are \( n \)-alkanethiols with relatively long chains, \( n > 10 \). A summary of the structural characteristics for this class of SAMs is given in chapter 3, section 3.2.

A simple modification to the alkanethiol molecules used to produce this class of SAMs is to change the terminal group structure. However, modification to the individual assembling units can change the overall structure of the SAM since the equilibrium structure is a delicate balance of many factors, which includes the adsorbate-adsorbate interactions. We discuss the impact of modifying the terminal group on the overall SAM structures below to help understand how structural differences may contribute to our scattering experiments.

The structure of monolayers formed from alkanethiols with terminal group structures \(-\text{CH}_3\), \(-\text{CH}=\text{CH}_2\), \(-\text{OH}\), \(-\text{COOH}\), and \(-\text{COOCH}_3\) have been extensively studied and have revealed that their packing density, order, and stability are all similar. A schematic representation of the average structure of \( \omega \)-functionalized SAMs on gold is given in Figure 5.1. Since the \( \text{CH}_3 \)-terminated SAMs
have been discussed in chapter 3, we will compare the structures of these other monolayers relative to them.

![Figure 5.1](image-url)

**Figure 5.1** Schematic representation of SAMs derived from ω-functionalized alkanethiols illustrating the similarities in their overall structures.

Modifying the terminal group of the \(n\)-alkanethiols to form monolayers with an unsaturated unit, -\(\text{CH}=\text{CH}_2\), at the SAM/gas interface contributes little difference to the overall SAM structure. A \(C(4 \times 2)\) superlattice structure of the \((\sqrt{3} \times \sqrt{3})R30^\circ\) overlayer has been reported for these alkene terminated monolayer with similar chain tilt angles as analogous alkanethiols.\(^{26,55,59}\)

Placing an unsaturated unit at the terminus of the alkyl chain has relatively little effect on the overall structure of the SAM formed. However, strong intra-monolayer terminal group interactions have more dramatic influences on the equilibrium structures. Monolayers assembled from ω-functionalized alkanethiols with the ability to form intra-monolayer hydrogen-bonding interactions are an example of this behavior. The structural changes that accompany replacement of the \(\text{CH}_3\)-terminal group with \(\text{OH}^-, \text{NH}_2^-,\) or \(\text{COOH}\)-terminal groups are most significant near those functional groups. The structural
characteristics of the alkyl spacer are relatively insensitive to changes in the terminal groups used in this study, especially when the alkyl chain backbone has more than ten carbon atoms. Chain tilt angles ranging from 28° to 44° have been reported from infrared data and NEXAFS data for OH-terminated SAMs with the methylene groups mainly in the all trans configuration, similar to the analogous CH₃-terminated SAMs. However, the COOH-terminated SAMs show a larger number of gauche defects than the corresponding OH-terminated monolayers. A comparison of C₆ OH- and CH₃-terminated SAMs by White and co-workers indicates that the two monolayers have identical packing densities, although the OH-terminated SAM chains arrange in an oblique lattice, as opposed to a hexagonal lattice in the case of CH₃-terminated SAMs. The STM work of Carroll and co-workers and Li et al. show that the COOH SAM may form a unique double-row structure. Infrared data also suggest that the alkyl spacer of the COOH monolayers is not as well ordered as the CH₃ monolayers. Monolayers formed from NH₂-terminated alkanethiols have been examined less often than the other hydrogen-bonding groups. However, the alkyl chains appears to form in similar all trans configurations with comparable packing densities to the CH₃-terminated SAMs.

Self-assembled monolayers formed from binary mixtures of alkanethiols have been investigated as a potential method to control surface properties. As long as the alkanethiol components are similar in size and chemical structure, well-ordered monolayers are formed. Monolayers assembled from long-chain alkanethiols with different terminal groups form monolayers similar in structure to those outlined above. In particular, binary mixtures of CH₃- and OH-terminated alkanethiols with similar chain lengths have been shown to produce monolayers with near uniform
molecular mixing. The reflection absorption infrared (RAIR) data by Leidberg, et al., suggest that the hydrogen-bonding nature of pure OH-terminated SAMs is completely disrupted for surface concentrations less than 1:1 (OH:CH$_3$). For monolayers with OH compositions greater than 50%, the extent of hydrogen bonding increases with increasing OH concentration. Details of the surface preparation procedure for these mixed SAMs are given in Chapter 2, section 2.2.4.2, and in a former group member’s thesis.

Monolayers formed with terminal groups that do not have intra-monolayer hydrogen-bonding abilities, but are more bulky than the CH$_3$-groups may also display slightly different overall structures. SAMs composed of methyl-ester terminal groups have been characterized using contact angle measurements, ellipsometry, and RAIRS. The alkyl chains appear to form well-ordered, high-density structures analogous to the CH$_3$-terminated SAMs, but no literature providing atomic-scale resolution characterization of methyl-ester terminated SAMs could be found.

Characterization of monolayers formed with lateral hydrogen-bonding carbamate-linkages, Au/S(CH$_2$)$_{16}$OCONH(CH)$_{n-1}$CH$_3$, has been achieved using XPS, contact angle goniometry, and RAIRS. In these systems, the organic portion of the monolayer is divided into three segments to describe monolayer structure; an underlayer [(CH$_2$)$_{16}$], a carbamate linkage [OCONH], and an overlayer [(CH$_2$)$_{n-1}$)CH$_3$]. The sixteen unit methylene segment above the sulfur headgroup is well-ordered, similar to CH$_3$-terminated SAMs, as demonstrated by RAIRS. RAIRS data also suggests that, overall, well-ordered monolayers are formed when the number of carbon atoms in the overlayer exceeds five. For overlayers with fewer than five carbon atoms, the order of the $n$-alkyl
overlayer and the extent of hydrogen-bonding interactions between adjacent chains of the carbamate segment have a monotonic dependence on chain length.

5.3 Comparison of Argon Scattering from ω-Functionalized SAMs

Figure 5.2 shows final energy probability distributions recorded for 80 kJ/mol argon atoms scattering from CH\textsubscript{3}-, CH\textsubscript{2}=CH-, OH-, COOH, and NH\textsubscript{2}-terminated SAMs on gold. As in previous chapters, the dynamics of gas-surface collisions are revealed through analysis of the average fractional energy transferred to the surface in the impulsive scattering (IS) channel, \((E_i-\langle E_{IS}\rangle)/E_i\), and the fraction of atoms that recoil (at \(\theta_f = 30^\circ\)) with a thermal distribution of energies (TD fraction). Three trends emerge from Fig. 5.2. (1) The fraction of incident energy transferred to each surface is large, greater than 75%, for every monolayer studied. (2) The CH\textsubscript{3}- and CH\textsubscript{2}=CH-terminated SAMs yield nearly identical final translational energy distributions with trapping-desorption fractions greater than 0.60. (3) The OH-, COOH-, and NH\textsubscript{2}-terminated SAMs produce final translational energy distributions that are similar to each other, but with much smaller trapping-desorption fractions (~0.45) than the CH\textsubscript{3}- and CH\textsubscript{2}=CH- SAMs. These results are summarized in Table 5.1.
Figure 5.2 Final translational energy probability distributions for 80 kJ/mol argon scattering from (a) CH$_3$-, (b) CH$_2$=CH-, (c) OH-, (d) COOH- and (e) NH$_2$-terminated SAMs. The dashed curves are Boltzmann distributions at the temperature of the surfaces, and the solid lines are the inelastic scattering components. The inset in (c) is a schematic representation of the experimental arrangement.
Table 5.1 Summary of results for 80 kJ/mol argon scattering from ω-functionalized SAMs.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Argon Beam Energy, $E_i$ (kJ/mol)</th>
<th>TD Fraction</th>
<th>IS Fractional Energy Transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-S(CH$<em>2$)$</em>{11}$CH$_3$</td>
<td>80</td>
<td>0.61 ± 0.01</td>
<td>0.83 ± 0.01</td>
</tr>
<tr>
<td>Au-S(CH$_2$)$_9$CH=CH$_2$</td>
<td>80</td>
<td>0.61 ± 0.01</td>
<td>0.80 ± 0.01</td>
</tr>
<tr>
<td>Au-S(CH$<em>2$)$</em>{11}$OH</td>
<td>80</td>
<td>0.42 ± 0.01</td>
<td>0.77 ± 0.01</td>
</tr>
<tr>
<td>Au-S(CH$<em>2$)$</em>{10}$COOH</td>
<td>80</td>
<td>0.41 ± 0.01</td>
<td>0.76 ± 0.01</td>
</tr>
<tr>
<td>Au-S(CH$<em>2$)$</em>{11}$NH$_2$</td>
<td>80</td>
<td>0.49 ± 0.01</td>
<td>0.76 ± 0.01</td>
</tr>
</tbody>
</table>

The extensive energy transfer for collisions of high-energy gases with self-assembled monolayers is likely a general phenomenon that can be attributed to numerous factors. The monolayer-covered surfaces provide several degrees of freedom into which the translational energy of the impinging atoms can be partitioned. Sagiv and Naaman speculated that end-group rotation, vibration along the chain axis, and concerted waving motions of the chains parallel to the surface control the energy transfer in collisions of gases with amphiphilic organic monolayers. The concerted waving motions of the chains, vibrational modes along the chains, and hindered rotations of the end groups can all be excited by the 80 kJ/mol incident argon atoms. The following sections focus on elucidating why the scattering dynamics from the OH-, COOH-, and NH$_2$-terminated SAMs differ from the pure hydrocarbon monolayers, and why, despite significant differences in the bonding structure, the OH-, COOH-, and NH$_2$-terminated SAMs produce similar final translational energy distributions, as do the CH$_3$- and CH$_2$=CH-terminated SAMs.

5.3.1 Terminal Group Structure: CH$_3$- vs. CH$_2$=CH-Terminated SAMs

We have investigated the importance of the terminal C-C stretching motion and methyl torsion in gas-surface energy transfer dynamics by comparing scattering from CH$_3$- and CH$_2$=CH-terminated SAMs. Previous STM measurements show that the
surface structures of these monolayers are indistinguishable so any differences in the scattering dynamics can be correlated directly to the terminal group structure.

![Graph showing relative probability vs. final energy for CH₃-SAM and CH₂=CH-SAM.](image)

**Figure 5.3** A direct comparison of 80 kJ/mol argon scattering from the HS(CH₂)₁₁CH₃ SAM and the HS(CH₂)₉CH=CH₂ SAM.

Our results from this study are shown in Fig. 5.3 and reveal that, despite restricting the end-group torsional motion and increasing the rigidity of the terminal C-C bond, the CH₂=CH-terminated surface is as effective as the CH₃-terminated surface in dissipating the argon incident energy and subsequently bringing the atoms into thermal equilibrium with the surface. The strong similarities in scattering from these two surfaces suggests that the energy modes associated with the terminal C-C bond play only a minor role in controlling the extent of energy transfer during the impulsive gas-surface collision. Therefore, it appears that lower energy waving-motions, or even conformational changes, are the major contributors to the gas-surface energy exchange. This description of the dynamics is further supported by the scattering experiments and
simulation results discussed in chapters 3 and 4. In particular, Figures 3.4 and 3.5 show that the CH$_3$-terminated surface is very rigid for short carbon chains and becomes progressively less rigid until the chain length is greater than about 6 total carbon atoms. Those results indicate that extended motions involving perhaps as many as seven carbon atoms participate in the gas-surface collisions. The picture that emerges from this work is that the energy mode structure of the terminal group is not as important in determining the extent of energy transfer and subsequent thermalization as the flexibility of the entire polymethylene chain.

### 5.3.2 Surface Rigidity and Intra-Monolayer Hydrogen Bonding

The time-of-flight (TOF) and P(E$_f$) distributions for 80 kJ/mol argon scattering from monolayers constructed from HS-(CH$_2$)$_{11}$-CH$_3$ and HS-(CH$_2$)$_{11}$-OH alkanethiols on gold were previously reported.$^{72,142}$ These experiments were reproduced for the current study and the probability distributions are shown in Fig. 5.2 (b) and (c). The shift to lower final energies for the direct inelastic component and the increase in the trapping-desorption component for scattering from the methyl-terminated surface relative to the hydroxyl-terminated surface may be attributed to a combination of factors including differences in the available vibrational degrees-of-freedom and the hydrogen-bonding nature of the OH-terminated SAM. The different available degrees-of-freedom for the CH$_3$-terminated SAM include the terminal group torsional mode (~2 kJ/mol), stretching (~37 kJ/mol) and deformation modes (~15 kJ/mol), which can all be excited by the impinging argon atoms (~80 kJ/mol). Based on the data presented in the previous section, however, it is unlikely that the energy partitioned into the local modes of the terminal groups is responsible for the observed trends in the scattering data. The
extensive hydrogen bonding of the OH-terminated monolayers may form a network across the surface and anchor the end groups of the alkane chains rendering the individual surface molecules less labile than the monolayer composed of CH$_3$-terminated alkanethiols. This idea is consistent with the explanation of the data presented in chapters 3 and 4 which rationalized that monolayers with high-packing densities prevent the chains from moving in the plane of the surface, thereby making it more difficult to excite some of the low-frequency chain wagging modes. Differences in the intermolecular potential energy surface (PES) between argon atoms and the CH$_3$ or OH groups could also contribute to differences in the scattering results, since energy transfer dynamics for argon scattering from alkanethiolate self-assembled monolayers has been shown to depend on the intermolecular potential energy surface topology.\textsuperscript{118} Elucidating the origin of the differences in scattering from these two structurally-similar monolayers is the focus of the experiments presented below.

5.3.2.1 40 kJ/mol Argon Scattering from CH$_3$- and OH-Terminated SAMs

In chapter 4, the influence of ballistic penetration into a monolayer was shown to contribute to the fraction of atoms that reach thermal equilibrium with the surface. Furthermore, the extent of ballistic penetration increases with increasing beam energy. The classical trajectory simulations of Hase \textit{et al.} for neon atom scattering from a hexylthiolate SAM also suggests that penetration of energetic atoms into the monolayer plays a role, albeit a minor one, in the overall energy exchange dynamics.\textsuperscript{28-30} The CH$_3$- and OH-terminated monolayers have slightly different overall structures, so we speculate that variation in the degree of penetration into the monolayers may contribute to the trends we observe for the TD fractions from these two surfaces. Since the calculations
show that the contribution of penetration to the scattering dynamics diminishes with decreasing incident energy, we have explored the affect that incident energy has on the TD fractions for scattering from the hydrogen-bonding and hydrocarbon surfaces.

Figure 5.4 A comparison of lower-energy, 40 kJ/mol, argon scattering from (a) HS(CH₂)₁₁OH and (b) HS(CH₂)₁₁CH₃ SAMs. The dashed Boltzmann curves show that a greater fraction of atoms thermalize on the non-hydrogen-bonding CH₃-terminated surface than the OH-terminated monolayer.

Figures 5.4 (a) and (b) show probability distributions for 40 kJ/mol argon scattering from the CH₃- and OH-terminated surfaces. The distributions in this figure
demonstrate that, although lower incident energy leads to greater overall thermalization, the fraction of atoms that approach thermal equilibrium on the CH$_3$-terminated surface remains much greater than on the OH-terminated surface, despite the limited penetration that likely occurs for the low-energy beam. It appears that if penetration of argon into the monolayer occurs, it does not help explain the differences in the energy transfer dynamics we observe from of these two surfaces.

The results presented here are in accord with previous experimental studies in which high- and low-energy neon atoms were scattered from hydrogen-bonded liquid glycerol and purely hydrocarbon squalane. In that work, neon was found to thermalize much more readily on the hydrocarbon surface than on the hydrogen-bonding surface and ballistic penetration into the liquid appeared to play an insignificant role in the overall scattering dynamics. Therefore, our observation, that interfacial hydrogen bonding limits gas-surface energy transfer and thermalization in self-assembled monolayers, may be a general characteristic on functionalized organic materials.

**5.3.2.2 Mixed OH- and CH$_3$-Terminated SAMs**

Several groups have demonstrated that extensive hydrogen bonding occurs in pure OH-terminated SAMs and this hydrogen-bonding ability is thought to contribute to the differences in argon scattering we have measured from CH$_3$- and OH terminated SAMs. Liedberg *et al.* have explored the structure and hydrogen-bonding nature of mixed OH- and CH$_3$-terminated self-assembled monolayers in detail. Their RAIR measurements demonstrate that the hydrogen bonding in pure OH-terminated monolayers decreases as the surface is mixed with CH$_3$-terminated alkanethiols. We have therefore performed atomic-beam studies of 80 kJ/mol argon scattering from surfaces composed of mixed
SAMs containing OH- and CH₃-terminated alkanethiols to reduce the extent of hydrogen bonding within OH-terminated surfaces. By scattering from mixed surfaces, we are able to explore the influence of hydrogen bonding on energy transfer and thermalization.

The experiments have been performed on thirteen surfaces ranging in OH concentration from 100% to 0% (pure CH₃-terminated surface). Figure 5.5 (a) – (e) shows probability distributions for scattering from the mixed monolayers at five representative surface compositions. These distributions show a change in the intensity of the inelastic channel relative to the broad thermal component as the surface OH concentration decreases from 100 % to 25 %. A comparison of the distributions in the figure also shows a change in the extent of energy transfer for the inelastically scattered atoms. The peak of the inelastic contribution is almost 13 kJ/mol for the pure OH-terminated surface, while it falls below 10 kJ/mol for the pure CH₃-terminated surface. The average fractional energy transfer in the inelastic channel ((Eᵢ - <Eᵢₜₕ>)/Eᵢ) and the TD fractions for each of the mixed SAMs are plotted in Fig. 5.6, where the trend in the data is much more clear.
Figure 5.5 Final translational energy probability distributions for 80 kJ/mol argon atoms scattering from a series of mixed HS\((\text{CH}_2)_11\text{CH}_3\) and HS\((\text{CH}_2)_11\text{OH}\) SAMs. The surface concentrations listed in each figure were determined from the XPS measurements described in chapter 2.
Figure 5.6 A summary of the entire range of data collected for a series of OH- and CH$_3$-terminated mixed SAMs. The mole fractions were determined from XPS data. The TD fractions (a) and fractional energy transferred for the inelastic channel (b) were determined according to the procedure described in section 2.2.4.2. The dashed line is shown to highlight the surface concentration where the mixed SAMs appear to behave like the pure CH$_3$-terminated surface. The error bars in (b) represent a 95 % CI. The error bars in (a) are approximately the same size as the symbols that represent the data points.
There is virtually no change in the probability distributions as the OH concentration decreases from 30% to the pure CH₃-terminated surface. This trend is even more apparent when we plot five probability distributions on a relative scale as shown in Fig. 5.7. These five distributions were recorded over the course of six hours in an effort to preserve the experimental conditions for each run. Two important observations emerge from this comparison. (1) The decrease in the direct inelastic component with decreasing OH concentration is accompanied by an increase in the intensity of the Boltzmann component. (2) The probability distributions for all OH concentrations below 30% are identical within the signal-to-noise level.

**Figure 5.7** Final translational energy probability distributions for five representative surface OH concentrations for argon scattering from the mixed OH- and CH₃-terminated SAMs. The distributions shown here were all recorded on the same day to minimize small fluctuations in the signal. The two dashed curves represent the Boltzmann distribution fits to the 0% and 100% OH surfaces.
Although we only present data collected at the specular angle, the first observation from Fig. 5.7 provides some information about how the angular distribution must change as the surface OH concentration decreases. Specifically, this comparison demonstrates that a large fraction of the atoms that scatter inelastically at the specular angle after a collision with the 100% OH-terminated surface, lose enough energy on the mixed monolayers to reach thermal or near-thermal accommodation. The reduction in the relative intensity of the direct inelastic channel is not due solely to increasingly off-specular scattering; rather, thermal accommodation increases as OH concentration decreases.

Further analysis of the plots of Figs. 5.6 and 5.7 show that the monolayer becomes less rigid only to the point where the surface consists of a 3:1 mixture of CH₃:OH terminal groups. We find that every mixed SAM composed of less than about 30% OH groups behaves, to within our signal to noise, like the pure methyl-terminated monolayer. This data suggests that intra-monolayer hydrogen bonding is disrupted sufficiently below the 3(CH₃):1(OH) ratio that it does not have a measurable influence on the scattering dynamics. Although previous measurements have indicated that aggregation of hydrogen-bonding chains may occur in mixed SAMs, our data suggests that the hydrogen-bonding domains may be small enough for monolayers containing less than 30% OH-terminated alkanethiols to have an immeasurable influence on the gas-surface energy exchange dynamics.

The data presented above reveal that as the OH concentration decreases, the direct inelastic component has lower average energies coming off the surface and the trapping-desorption component increases in intensity. These results are in agreement with the
description that intra-monolayer hydrogen bonding creates a more rigid surface and
decreasing the extent of hydrogen-bonding enables the otherwise inactive low-energy
motions of the chains to participate in the gas-surface energy transfer.

5.3.2.3 Intra-Monolayer Hydrogen Bonding in ω-Functionalized SAMs

We have further explored interfacial hydrogen bonding in gas-surface collisions
by scattering 80 kJ/mol argon from other hydrogen-bonding ω-functionalized SAMs.
Figure 5.8 is an overlay of the final translational energy probability distributions for
argon scattering from OH-, COOH-, NH2-, and CH3-terminated SAMs.

![Figure 5.8](image.png)

**Figure 5.8** Final translational energy probability distributions for 80 kJ/mol argon scattering
from three monolayers terminated with hydrogen-bonding functional groups. For comparison,
the distribution for the argon scattering from the CH3-terminated SAM is included.
As summarized in Table 5.1, the clear trend in this data is that the direct inelastic channel dominates the distributions for monolayers terminated with hydrogen-bonding groups. The close agreement in the distributions is even more notable given the likely differences in the atomic-scale structure of these four SAMs.\textsuperscript{147}

The atomic-scale roughness of the surfaces may play a role in gas-surface energy exchange by promoting sequential collisions and energy dissipation. However, the atomic beam work of Nathanson and co-workers\textsuperscript{19} suggest that the surface corrugation has a much larger influence on the TD fractions than on the IS energy distribution. They used thermal energy to alter the atomic-scale roughness of a liquid fluorocarbon surface. Despite a large temperature-induced corrugation, they observed virtually no change in the IS energy distributions for 93 kJ/mol argon atom scattering from the surface.

![Normalized energy distributions for the atoms scattering in the inelastic channel from Fig. 5.8.](image)

**Figure 5.9** Normalized energy distributions for the atoms scattering in the inelastic channel from Fig. 5.8.
We have plotted normalized $P(E_{IS})$ distributions in Fig. 5.9 to illustrate that monolayers consisting of hydrogen-bonding terminal groups are less efficient at dissipating the impact energy than the non-hydrogen-bonding methyl-terminated SAM. We therefore do not attribute the large differences in the IS energy distributions to dissimilarities in the roughness of the four monolayer systems.

These results provide support to the assertion that intra-monolayer hydrogen-bonding plays a dominant role in determining the extent of energy transfer and thermalization in rare gas collisions with functionalized organic monolayers. Although the data presented here is consistent with the description that hydrogen-bonding plays a role in energy exchange and thermalization, these monolayers are complicated systems with many variables that can affect scattering and further studies are needed. In particular, classical trajectory calculations, angular resolved scattering, and He atom diffraction measurements will help to more completely elucidate the influence of monolayer order, packing density, roughness, chain tilt, and hydrogen bonding in the gas-surface scattering dynamics.

5.4 Influence of Buried Intra-Monolayer Hydrogen Bonding

The data presented above suggests that when gas atoms collide with a surface containing a highly-hydrogen-bonding network, energy transfer to the surface is hindered relative to non-hydrogen-bonding surfaces. Hydrogen bonds may anchor the terminal groups thereby rendering a monolayer less flexible than a methyl-terminated surface. The results that were used to obtain this explanation focused on monolayers with hydrogen-bonding capabilities at the terminus of the SAM. In this section, we have
explored the ability of hydrogen-bonding groups buried farther below the methyl terminus to influence the outcome of the gas-surface collision.

We have scattered from a series of monolayers with a hydrogen-bonding network whose location relative to the gas-surface interface is controlled by a hydrocarbon chain of various chain length at the terminus. The monolayers consist of hydrogen-bonding carbamate-linkages, Au/S(CH$_2$)$_{16}$OCONH(CH)$_{n-1}$CH$_3$, sandwiched between segments of purely saturated hydrocarbon chains. Characterization of these monolayer structures has been achieved using XPS, contact angle goniometry, and RAIRS.$^{64,65}$ The 16 unit methylene segment above the sulfur headgroup is well-ordered, similar to CH$_3$-terminated SAMs, as demonstrated by RAIRS. RAIRS data also suggests that, overall, well-ordered monolayers are formed when the number of carbon atoms in the overlayer exceeds five. For overlayers with less than five carbon atoms, the order of the $n$-alkyl overlayer and the extent of hydrogen-bonding interactions with adjacent chains of the carbamate segment have a monotonic dependence on chain length.
Figure 5.10 Final translational energy distributions for 80 kJ/mol argon scattering from the carbamate-terminated SAMs with n number of total carbon atoms above the hydrogen-bonding group. The solid and dashed curves represent Boltzmann fits at the surface temperature. The dashed curve is fit to the n = 1 data and the solid curve is fit to the n = 8 data.

Figure 5.10 shows final energy probability distributions for 80 kJ/mol argon scattering from the CONH(CH$_2$)$_n$-CH$_3$-terminated SAMs with n = 1, 4, 8. The data indicate that the trapping-desorption component increases in intensity with increasing n while, concomitantly, the impulsive component decreases in intensity and shifts to lower final energies. The trapping-desorption fractions for the entire range of monolayers studied are plotted as a function of chain length above the carbamate group in Fig. 5.11. The data point for n = 0 corresponds to scattering from a carbamate monolayer terminated with the NH$_2$ group and no carbon chain. The plot indicates that the fraction of atoms that leave the surface in a Boltzmann distribution increases from n = 1 to n = 5 and becomes constant for n > 5. Since all of the carbamate SAMs are expected to have
similar packing densities, order, and orientation, we hypothesize that the observed trend in the energy exchange dynamics is due to the increasing degrees of freedom above the hydrogen-bonding group as $n$ increases.

![Graph showing TD fraction as a function of the number of carbon atoms above the carbamate functional group.](image)

**Figure 5.11** TD fraction as a function of the number of carbon atoms above the carbamate functional group.

The effect of alkane chain length in rare-gas scattering from SAMs has been explored in detail in previous studies (See chapter 3). The investigations revealed that, for collisions of 80 kJ/mol argon on $n$-alkanethiol SAMs, long-range molecular motions involving at least six methylene groups along the individual chains participate in the energy transfer dynamics. This observation agrees well with the expected time scale for the impulsive gas-surface collision and rate at which energy propagates along the
Therefore, we suggest that the trend observed in Fig. 5.11 can be attributed to the same effect. Within this picture, the C=O--NH hydrogen-bonding network serves as a rigid platform and the non-hydrogen-bonding alkane chains above the network provide an effective energy sink for dissipating the translational energy of the impinging argon atoms. As in scattering from \( n \)-alkanethiol SAMs on gold, we find that 5-6 methylene groups are needed to fully shield the underlying rigid platform.

5.5 Comparison of Acid-, Ester-, and Methyl-Terminated Alkanethiols

In the previous sections, we discussed the role of hydrogen-bonding groups on energy transfer dynamics and proposed that hydrogen-bonding groups restrict some types of surface modes from being excited by the incident argon atoms. Although all of our data is consistent with this picture, we cannot rule out the possibility of major contributions to energy transfer from differences in the PES between the argon atoms and the terminal functional groups. Troya et al. have shown that energy transfer from argon to alkanethiolate SAMs is very sensitive to the intermolecular potential energy surface.\textsuperscript{118} Potential functions with relatively steep repulsive walls and deep well depths were shown to be the most efficient in absorbing energy during the gas-surface collisions. We speculate that the PES between argon and surfaces terminated with carbon, oxygen, or nitrogen is different and likely contributes to the differences in energy transfer dynamics. We have therefore scattered 80 kJ/mol argon atoms from monolayers that contain carbonyl groups without hydrogen-bonding ability to gain insight into the relative importance of the PES and the hydrogen-bonding network.

We have scattered from three monolayers to compare the relative roles of the PES topology and hydrogen-bonding on energy transfer dynamics.\textsuperscript{117} The monolayers include
a purely hydrocarbon surface (HS(CH$_2$)$_{15}$CH$_3$), a monolayer containing a terminal acid group which forms intramolecular hydrogen bonds (HS(CH$_2$)$_{15}$COOH), and a monolayer containing an ester terminal group which does not form intra-monolayer hydrogen bonds (HS(CH$_2$)$_{15}$COOCH$_3$). Infrared data shows that the polymethylene chains of the acid and ester surfaces form crystalline-like packing configurations analogous to the purely hydrocarbon surface. Moreover, the IR data provides strong evidence that the acid monolayers have extensive hydrogen bonds since the carbonyl stretching peak is broad and significantly red-shifted relative to the carbonyl of the ester (1700 vs. 1746 cm$^{-1}$).

![Figure 5.12](image)

**Figure 5.12** Final probability energy distributions 80 kJ/mol argon scattering from an acid-, a methyl ester-, and a methyl-terminated SAM. The dashed curve is fitted to the COOH-terminated scattering data and the solid curve is fitted to the CH$_3$-terminated scattering data at the temperature of the surface.

Figure 5.12 shows final energy probability distributions for 80 kJ/mol argon scattering from the COOH-, COOCH$_3$-, and CH$_3$-terminated SAMs. Within this set of three SAMs, the scattering dynamics are found to depend on the particular functional
groups at the termini of the monolayer chains. In particular, direct impulsive scattering is the primary channel for atoms recoiling from the COOH-terminated surface, while the trapping-desorption component dominates scattering from the COOCH$_3$- and CH$_3$-terminated surfaces. The distributions for the COOCH$_3$- and CH$_3$-terminated surfaces are not identical, but are more similar to each other than the COOCH$_3$- and COOH-terminated monolayers. This suggests that the hydrogen-bonding nature of the COOH surface is more important than the PES of the argon and terminal groups of the SAMs. However, we need additional information, such as classical trajectory calculations, to more fully understanding of the role of the gas-surface PES for these $\omega$–functionalized SAMs.

5.6 Investigation of Monolayer Order and Roughness

Despite the many structural similarities of the monolayers investigated in the above experiments, the studies do not rule out the possibility that subtle differences in the atomic-scale roughness or local structure of the monolayers play a significant role in the scattering dynamics.

5.6.1 Annealing Studies

Since altering the terminal groups of these self-assembled monolayers are expected to have an influence on the overall order of the systems, we have explored the influence of monolayer order through annealing studies. Several investigations have demonstrated that $n$-alkanethiol SAMs reorder upon heating to 380 K.\textsuperscript{52,53,100,140,155,156} The helium-diffraction and STM work of Scoles \textit{et al.}\textsuperscript{52,53,100,140} and others\textsuperscript{109-111,157} have well-established that annealing CH$_3$-terminated SAMs on gold alters the order of the monolayers. For example, they found that the diffraction pattern from “poor quality” C$_{10}$
SAMs is completely destroyed upon annealing to 343 K, while the order of “high quality” samples improved significantly upon annealing to 373 K. Their work is consistent with other studies that show that well-annealed solution-prepared SAMs of long-chain monolayers crystallize into the highly-ordered c(4X2) superlattice of the basic (√3X√3) R30° unit mesh. In another case, Eisenberger and co-workers used X-ray diffraction to demonstrate that while the polymethylene chains of C₁₂ CH₃-terminated SAMs are crystalline at room temperature, the monolayer undergoes a melting transition to a liquid-like phase at 373 K. In addition, IR and molecular dynamics studies have found that the concentration of gauche defects at a monolayer surface is greater than in the interior, but that below 250 K the concentration becomes negligible. These annealing studies suggest a means for testing how sensitive the argon distributions are to overall monolayer order without changing the chemical composition of the SAM. We have hence performed argon scattering studies with a monolayer held at temperatures above the melting transition, an annealed monolayer, and a monolayer cooled well below the temperature where gauche defects exist.

The annealing studies involved installing a new SAM into the UHV chamber and immediately cooling the monolayer to 240 K where we recorded a TOF spectrum for the 80 kJ/mol argon beam. The surface was annealed by ramping at approximately 1 K/s to the specified temperature. The surface was then cooled back to the original temperature where we recorded a post-anneal TOF spectrum. Figure 5.13 (a) shows final translational energy probability distributions for argon scattering from a CH₃-terminated SAM at different temperatures during a typical annealing cycle to a maximum temperature of 375 K. As the surface is heated above the melting transition, the scattering component
described by a Boltzmann distribution shifts to higher energies, but the fractional energy transfer in the inelastic channel and the relative inelastic and Boltzmann contributions change little. In addition, the probability distributions for the pre- and post-annealed SAMs are nearly identical, suggesting these distributions are not sensitive to any restructuring that may occur upon annealing. Similar conclusions can be drawn from the annealing studies of the OH-terminated monolayer reported in Fig. 5.13 (b). This SAM actually appears to further increase in rigidity after annealing, which may be due to the reordering of the hydrogen-bonding network into a more stable arrangement. Finally, Fig. 5.13 (c) shows that the scattering dynamics are not altered at surface temperatures well below the point where the concentration of gauche defects becomes negligible. In every case, it is not until the surface is annealed above the temperature at which desorption becomes significant that the distributions markedly change.
Figure 5.13 Three final energy probability distributions recorded during a single annealing cycle where a pre-annealed scan was recorded at 240 K, the surface was heated to 375 K, and then the surface was returned to the original temperature where the post-annealed scan was recorded for a CH₃-terminated surface (a) and an OH-terminated surface (b). In (a) and (b), the solid and dashed curves show a Boltzmann distribution at 240 K and 375 K, respectively. (c) A direct comparison of 80 kJ/mol argon scattering from the CH₃- and the OH-terminated SAMs at a surface temperature of 210 K.
The annealing experiments reveal two important details about the 80 kJ/mol argon measurements. (1) The structural changes that likely accompany annealing do not have a large influence on the extent of energy transfer in the inelastic channel or on the scattered intensities in the inelastic and Boltzmann components. (2) The small changes in surface roughness caused by thermal energy do not have significant influence on the scattering dynamics. The general insensitivity of the argon scattering to monolayer order or roughness suggest that the variance observed between the monolayers with and without intra-monolayer hydrogen bonding is the result of differences in the available energetic degrees-of-freedom of the monolayer systems rather than structural influences.

5.6.2 Mixed Long- and Short-Chain SAMs

Since the structural changes that accompany thermal annealing do not influence the argon scattering data, we have created mixed CH₃-terminated alkanethiols of different chain lengths to more dramatically affect surface roughness and study its influence on the final energy probability distributions. Figure 5.14 shows final energy probability distributions for the pure $n = 12$ CH₃-terminated SAM and a monolayer assembled from an alkanethiol solution containing a mixture of $n = 12$ and $n = 8$ alkanethiols in a mole ratio of 1:6. This ratio is based on the work of Jiang et al., who have demonstrated that this solution concentration produces well-mixed monolayers with limited aggregation of similar chain-length alkanethiols.¹⁶⁰ Their AFM images reveal that this surface is significantly rougher, on the atomic scale, than a pure C₁₂ SAM.
Figure 5.14 (a) Final energy probability distributions for 80 kJ/mol argon scattering from a C\textsubscript{12} methyl-terminated SAM and an intentionally roughened/disordered SAM created by mixing long (C\textsubscript{12}) and short (C\textsubscript{8}) alkanethiols. The solid lines represent the inelastic and Boltzmann components for the mixed SAM and the dashed lines represent the inelastic and Boltzmann components for the pure C\textsubscript{12} SAM. (b) Final energy distributions for the inelastic components only from panel (a). Also shown for comparison is the final energy distribution for the inelastic component scattering from the pure OH-terminated SAM.

The comparison of Fig. 5.14 (a) clearly shows that the Boltzmann component is greater on the rougher surface relative to the smooth surface. The differences in these distributions indicate that some of the atoms that would scatter inelastically on the
smooth surface instead undergo additional collisions to dissipate their excess energy and approach thermal equilibrium. However, Fig. 5.14 (b) demonstrates that the fractional energy transfer in the inelastic component is nearly independent of the roughness of the mixed monolayer. The similar P(E_{IS}) profiles imply that atoms scattered inelastically at the specular angle experience similar types of single-collision events on both atomically smooth and rough surfaces. This result is in agreement with the experiments of Nathanson et al. that show minimal changes in the inelastic scattering energy distributions for high-energy argon scattering from flat and thermally-roughened liquid surfaces. Furthermore, the molecular dynamics simulations reported in chapter 4, section 4.4, demonstrate that single collision events dominate the scattering dynamics for in-plane trajectories. Together, these findings indicate that the inelastic component, for in-plane scattering at the specular angle, may be an effective probe of the amount of energy exchanged in single-collisions events. Within this framework, multiple collisions either lead to thermalization, removing atoms from the inelastic component, or deflect the incoming atoms out of the flight path to the mass spectrometer.

To investigate whether roughness alone accounts for the differences in scattering from purely hydrocarbon SAMs versus SAMs with hydrogen-bonding terminal groups, a direct comparison of the normalized P(E_{IS}) energy distribution for the pure CH$_3$-, mixed CH$_3$-, and OH-terminated SAMs is given in Fig. 5.14 (b). Unlike the results for scattering from a smooth and rough surface, the energy distributions differ considerably for the CH$_3$- and OH-terminated SAMs. It appears that for single-collision events, more energy is transferred to the CH$_3$-terminated surface than the OH-terminated surface. This result suggests that the methyl surface is actually less rigid, rather than rougher, than the
hydroxyl surface. In this case, the relatively large trapping desorption component for the methyl surface may be the result of very large energy transfers in the initial collision and not the type of corrugation-induced thermalization we observe for an atomically-rough surface.

5.7 Summary

Atomic beam scattering studies of argon collisions with functionalized alkanethiol self-assembled monolayers on gold have begun to explore the relative importance of terminal group molecular structure and intra-monolayer hydrogen bonding on energy exchange dynamics. Among all of the $\omega$-functionalized monolayers studied, the long-chain methyl-, olefin-, and methyl ester-terminated SAMs are the most effective at dissipating the translational energy of impinging argon atoms. The similarity in the scattering results for these SAMs suggests that the vibrational degrees-of-freedom of the terminal groups play a relatively minor role in collisions of high-energy argon with the surfaces.

In contrast to three monolayers mentioned above, the OH-terminated surface appears to provide a more rigid collision partner. For 80 kJ/mol argon scattering, an average of 78% of the energy is transferred to the C$_{11}$ OH-terminated surface and the fraction of atoms that approach thermal equilibrium is only 0.43. Other monolayers functionalized with hydrogen-bonding groups produce scattered energy distributions that are indicative of rigid surfaces similar to the OH-terminated SAM. COOH- and NH$_2$-functionalized SAMs both result in more inelastic scattering and lower fractional energy transfers than CH$_3$-terminated SAMs of similar chain length.
Monolayers constructed from alkanethiols containing carbamate groups, \( \text{Au/S(} \text{CH}_2\text{)}_{16}\text{OCONH(CH)}_{n-1}\text{CH}_3 \), were used to study the influence of buried hydrogen-bonding groups within monolayer films on gas-surface energy exchange and thermalization. A chain length effect is observed for this series of monolayers where the rigidity of the monolayers steadily decrease with increasing chain length up to about 5-6 carbon atoms above the carbamate groups. We suggest that the C=O--NH hydrogen-bonding network serves as a rigid platform and the non-hydrogen-bonding alkane chains above the network provide an effective energy sink for dissipating the translational energy of the impinging argon atoms. As in scattering from \( n \)-alkanethiol SAMs on gold, we find that 5-6 methylene groups are needed to fully shield the underlying rigid platform.

Further studies are needed to explore the possible combined effects of hydrogen bonding and monolayer structure. However, the results presented above suggest that intra-monolayer hydrogen bonding dampens low-energy extended motions within the monolayer to render the individual alkane chains less labile than free, non-hydrogen-bonding monolayers.
Chapter 6

Mass Effects in Gas-Surface Scattering from Organic Thin Films

6.1 Introduction

The properties of both gas and surface molecules govern the dynamics which occur when a gas-phase atom or molecule impacts the surface of a solid. Due to the extensive research performed in the field of gas-surface scattering over the last 40 years, a number of guidelines have emerged that can be used to predict the outcome of the collision event. Of particular interest to the experiments outlined in this chapter is the role of gas and surface masses in the initial collision.

The role of gas and surface masses has been recognized as an extremely important factor in the collision dynamics since the early developments of gas-surface scattering theory. In 1966, Logan and Stickney published the now very familiar hard-cube model of gas-surface scattering.\(^{11}\) The model consists of gas atoms undergoing impulsive collisions with hard cube surfaces with the restriction that momentum is conserved in the tangential direction of the surface during the collision. One important outcome of this model shows that energy transfer is maximal when the mass ratio, \(\mu = \frac{m_{\text{gas}}}{m_{\text{surface}}}\), is unity and falls off with larger or smaller values, though asymmetrically. A fitting of the mass ratio from this model to experimental data provides an ‘effective’ surface mass which lends insight into the collective response of the surface during impulsive collisions.\(^{12}\)

In addition to the hard cubes model, other surface models have been reported that include properties of the gas-surface system in efforts to predict the outcome of the collision events. Models such as the soft cubes model,\(^{13}\) washboard model,\(^{14}\) and hard spheres model\(^{18}\) have all contributed to fundamental pictures of gas-surface scattering.
The models have been successful for predicting the outcome of gas-surface scattering events from single crystal metals and other inorganic crystals, but is more difficult to apply to organic surfaces. Organic surfaces present a challenge since they have low densities, directional bonding features, and generally lack molecular order compared to single crystal materials. Despite these challenges, the key ideas of mass effects in gas-surface scattering have been extended to studies of gas atoms scattering from liquid and liquid-like surfaces.

As noted in previous chapters, some of the most detailed insight into the dynamics of energy exchange between gases and liquid surfaces has come from the molecular beam studies of Nathanson et al. In their scattering experiments, they have found that guidelines derived from several of the classical models can be used to predict the outcome of gas collisions with liquid surfaces. They have scattered various small-molecule and atomic gases from a series of low-vapor pressure organic liquids and a series of low-vapor pressure liquid metals. In particular, energy transfer of gases colliding with the surfaces of squalane and perfluorinated polyethers have been studied in their lab. A comparison of the bulk properties of these liquids, such as compressibility and surface tension, would suggest more favorable energy transfer to the fluorinated surface; however, scattering results from these surfaces suggest that the perfluorinated surface is ‘stiffer’ than the hydrogenated surface. The rate of momentum change of the massive CF\textsubscript{x} groups on the short time scale of the collision events appears to dominate the scattering dynamics. The experimental results are consistent with predictions of energy transfer based on kinematics for a series of gases with different masses as well as scattering from surfaces with different masses. For example, gas-
surface energy transfer from the perfluorinated surface in the inelastic channel increases with increasing gas mass in the series neon, argon and xenon. The increased energy transfer is attributed to the difficulty in reversing the heavier gas atoms’ direction and sending it back into the gas phase. The heavier atoms strike the surface and continue pushing forward, hitting more and more surface atoms, which brings them into thermal equilibrium more readily.17

Self-assembled monolayers have also been used to study energy transfer for organic surfaces containing hydrogenated and perfluorinated groups.10 In particular, the atomic gases helium and argon were scattered from monolayers of \( n \)-octadecyltrichlorosilane and a perfluorinated acid ester. Like the energy transfer studies by Nathanson et al., differences in energy transfer to these surfaces are consistent with the kinematic models described above in which energy transfer is related to the gas to surface mass ratio. More energy is transferred to the hydrocarbon monolayer than the fluorinated monolayer, due to the more massive CF\(_x\) groups.

In addition to these neutral atom scattering experiments, several investigations of ion-surface scattering from model fluorinated organic surfaces have been performed.42-48 It has been shown that translational to vibrational energy transfer of internal modes in polyatomic ions is higher when scattering from fluorinated surfaces in comparison to hydrocarbon surfaces.49,50 The differences in energy transfer have been attributed to the effective masses of the target surface species.48-50 In addition, an investigation by Wysocki et al. scattering low-energy ions (10-100 eV) from Langmuir-Blodgett films terminated with CF\(_3\)(CH\(_2\))\(_n\)-, \( n \)-perfluoroalkyl, and \( n \)-alkyl groups suggested that the outermost surface group (CF\(_3\) vs. CH\(_3\)) plays the largest role in energy transfer.44 For
example, W(CO)$_6^+$ ions with incident energies in the range of 10 to 70 eV scattering from monolayers terminated with a CF$_3$ group or fully fluorinated chains have similar energy transfer dynamics. Translation to internal energy transfer of the incident ion scattering from these two surfaces is approximately the same, but scattering from the pure hydrocarbon monolayer provides only half as much translational to internal energy transfer. A similar result was obtained for low-energy ion-surface scattering from alkanethiolate self-assembled monolayers with varying degrees of fluorination at the terminus.$^{42}$ These results lend some insight into the importance of the effective mass of the terminal groups versus the increased rigidity of the perfluorinated chain.

The focus of the work presented in this chapter is to further the understanding of mass effects in gas collisions with organic surfaces. We have scattered high-energy argon, krypton and xenon from five alkanethiolate self-assembled monolayers. The alkanethiols used to form the monolayers in this study were CH$_3$(CH$_2$)$_{15}$SH [C16F0], CH$_3$(CH$_2$)$_{14}$SH [C15F0], CF$_3$(CH$_2$)$_{15}$SH [C16F1], CF$_3$(CH$_2$)$_{14}$SH [C15F1], and CF$_3$(CF$_2$)$_7$(CH$_2$)$_2$SH [C10F8], where the two numbers refer to the total number of carbon atoms and the number of fluorinated carbon atoms. In addition, we have performed molecular dynamic simulations on some primitive model systems to gain insight into the role of mass effects on the molecular-level dynamics of the system.

### 6.2 Structural Considerations of SAMs Containing Fluorinated Groups

Self-assembled monolayers composed of alkanethiol molecules on gold substrates provide the opportunity to explore the dynamics of gas-surface interactions on highly-ordered and well-characterized organic thin films. We have employed alkanethiols adsorbed to gold substrates as a way to systematically study the effect of surface mass on
energy transfer at organic interfaces. Five types of alkanethiols were used in this study to create SAMs. We have included two purely hydrocarbon monolayers, C16F0 and C15F0, two terminally fluorinated monolayers, C16F1 and C15F1, and a monolayer with nearly every carbon saturated with fluorine atoms, C10F8.

The structure of self-assembled monolayers created from \textit{n}-alkanethiols adsorbed on gold was outlined in chapter 3, section 3.2, and is summarized here. It is well-established that \textit{n}-alkanethiols chemisorb onto Au(111) through a strong Au-S bond to form dense monolayers with an average intermolecular alkane chain separation of 5.0 Å, which produces an overall \((\sqrt{3}\times\sqrt{3})R30^\circ\) lattice.\textsuperscript{25,51-57} The chains are well-ordered and pack in the all \textit{trans} configuration with an average chain tilt angle relative to the surface normal of \(-30^\circ\).\textsuperscript{99} The long-chain monolayers on gold, with \(n \geq 6\), have been shown to exhibit very high stability and crystalline-like long-range order characterized by a \(c(4\times2)\) superlattice.\textsuperscript{52,53,56,57} The terminal carbon-carbon bond has an orientation dependence on the total number of carbon atoms in the chain. The terminal carbon-carbon bond is relatively normal to the surface plane when the total number of carbon atoms is even and relatively parallel to the surface plane when the carbon chain is odd.

A simple modification to the \textit{n}-alkanethiol molecules used to create SAMs is to change the terminal group structure. In this study, we have substituted the terminal methyl groups in long-chain alkanethiol molecules with trifluoromethyl groups. The equilibrium structure of the SAMs formed from these alkanethiol molecules are very similar to the analogous SAMs created from purely hydrocarbon chains.\textsuperscript{41,161-165} Polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) measurements indicate that monolayers formed with alkanethiols containing either a
CH$_3$-terminal group or a CF$_3$-terminal group produced films with a high degree of conformational order.$^{165,166}$ For monolayers containing a total of 16 carbon atoms, the absorption frequencies and intensities of the methylene stretching bands are indistinguishable for the two types of SAMs, indicating similar packing and crystallinity. Atomic force microscopy (AFM) imaging have provided further evidence to support similar structures for the CH$_3$- and CF$_3$-terminated SAMs.$^{167}$ The measured lattice constants from Fourier transformation of lateral force images are $4.9 \pm 0.2$ Å for the C13F0 SAM, and $4.8 \pm 0.2$ Å for the C13F1 SAM. The lattice spacings are indistinguishable which implies that the orientations of the terminal groups are similar. Further evidence for similar chain structures and interfacial orientations have come from a combined time-of-flight scattering and recoiling spectroscopy study with classical trajectory simulations.$^{41}$ The results imply similar structures and that the terminal CF$_3$ groups are freely rotating. This is an interesting point, considering the van der Waals cross sections of the methyl and trifluoromethyl groups are 13 Å$^2$ and 23 Å$^2$, respectively.$^{166}$

As mentioned above, there is a difference in the terminal group orientation of $n$-alkanethiolate SAMs with an even or odd number of carbon atoms in the chains. This difference is a result of the carbon chain backbone being in the all trans configuration and tilted from the surface normal. The orientation of the methyl and trifluoromethyl groups is similarly oriented for odd and even chain length SAMs. However, the effect of this orientation on external probes is quite different. The introduction of a CF$_3$ group at the terminal position of an aliphatic chain creates a dipole between the terminal carbon-carbon bond.$^{168}$ Therefore, a monolayer constructed of chains terminated in fluorinated
groups present an array of oriented dipoles. The interesting feature of even and odd chain
length SAMs is that the orientation of the terminal carbon-carbon bond changes the
orientation of the surface dipoles. Contact angle measurements using a series of
contacting (polar and nonpolar) liquids show that the CF₃-terminated SAMs are wetted
by the polar solvents more readily than corresponding CH₃-terminated SAMs.¹⁶¹,¹⁶⁹ In
addition, the extent of polar solvent wetting on the CF₃-terminated SAMs has a strong
dependence on whether the total number of carbon atoms in the chain is even or odd.
Monolayers with an even number of carbon atoms are wetted more by polar solvents than
monolayers constructed of an odd number of carbon atoms. The terminal carbon-carbon
bond for even chain-length monolayers is nearly normal to the surface plane such that all
the dipoles are oriented parallel to each other causing a net electric field on the surface.
For monolayers with an odd number of carbon atoms, the terminal carbon-carbon bonds
are more parallel with the surface. This orientation places the CF₃ group close to the CH₂
group of an adjacent chain and partially cancels out the net field on the surface. The net
electric field for the even and odd chain length monolayers is used to explain the
difference in the wetting behavior of polar solvents.¹⁶¹,¹⁶⁹

In contrast to pure hydrocarbon and terminally fluorinated SAMs, monolayers
constructed from alkanethiols on gold that are nearly perfluorinated have different
structures than alkanethiols with all hydrogen atoms.²¹,¹⁶⁵,¹⁷⁰-¹⁷⁴ An early attempt to
characterize the structure of the C₁₀F₈ SAM using ellipsometry and infrared
spectroscopy indicated that the chains pack nearly normal to the surface plane and with a
lattice spacing near 5.6 Å.⁷¹ A more direct measurement of the lattice spacing resulted
from AFM work by Alves and Porter which showed a lattice spacing of 5.8 ± 0.2 Å, very
similar to the expected 5.76 Å for a p(2x2) monolayer. The interpretation of the structure was attributed to the tendency of a perfluorinated carbon chain to adopt a helical structure with a twist angle of about 13-15° per carbon-carbon bond, resulting in a total chain twist of ~115°. The twist angle of the chain, a result of the fluorine-fluorine repulsive forces, and the slightly larger fluorine atoms causes larger lattice spacing in the monolayer. Further experimental evidence for the packing of fluorinated n-alkane SAMs (C14F12, C10F8, and C8F6) came from Salmeron and coworkers using a combined AFM and grazing incidence X-ray diffraction (GIXD) study. The lattice spacing of the chains were determined to be approximately double the nearest neighbor spacing of gold but they do not pack in a simple p(2x2) commensurate overlayer. The authors also determined the tilt angle of the chains from the GIXD study to be 12 ± 2°.

Using the general formula F(CF₂)ₓ(CH₂)ᵧSH, it appears that monolayers with large x and y < 4 have structures similar to the n-alkanethiols. For monolayers with y ≥ 4, the terminal fluorinated groups begin to adopt a helical structure and bend toward the surface normal. A comprehensive study of the structural properties of SAMs with varying values of x and y based on ellipsometry, XPS, and PM-IRRAS data has been documented.

6.3 Experimental Results

6.3.1 Data Analysis

The final translational energy probability distributions of gas atoms leaving a surface after a high-energy collision are separated into two limiting channels: direct impulsive scattering and trapping desorption. To separate these two channels, we assume that those atoms that become momentarily trapped in the gas-surface potential well reach
thermal equilibrium and can be fit with a Maxwell-Boltzmann distribution of energies. The remaining area is assigned to the direct impulsive scattering channel with the added restriction that scattering in this channel has zero probability for $E_f$ less than $kT_{\text{surf}}$. As discussed below, the dynamics of gas-surface collisions are revealed through: (a) analysis of the fractional energy transferred to the surface in the direct impulsive scattering (IS) channel $(E_i - \langle E_{\text{IS}} \rangle)/E_i$ and (b) the relative number of atoms that recoil (at $\theta_f = 30^\circ$) with a thermal distribution of energies (TD fraction).³

The energy transfer dynamics of argon, krypton, and xenon collisions from the five surfaces highlighted above are investigated in terms of two surface properties: (1) the number of fluorinated surface groups within the SAM (0, 1, or 8) and (2) the orientation of terminal groups with different elemental compositions, CH₃ or CF₃. By systematically changing the extent of fluorination of the chains and observing the ability of the monolayers to absorb energy from inert gas collisions, we have begun to develop a fundamental understanding of mass effects in organic surfaces on energy transfer dynamics. Table 6.1, provided in section 6.5.1.1, is a complete summary of the data calculated for argon, krypton and xenon scattering from the C₁₆F₀, C₁₆F₁, and C₁₀F₈ SAMs.

### 6.3.2 Argon Scattering

Argon beams of two different energies (see section 2.4.2 for beam energy measurements): 5% Ar in He (35 kJ/mol, FWHM = 6 kJ/mol) and 2% Ar in H₂ (80 kJ/mol, FWHM = 13 kJ/mol) were used in this study to explore the energy transfer dynamics from five different SAMs adsorbed on gold.
6.3.2.1 Extent of SAM Fluorination

Figure 6.1 (a) and (b) show final energy distribution plots, $P(E_f)$, for argon scattering from C16F0, C16F1, and C10F8 SAMs on gold with $E_i = 35$ and 80 kJ/mol beams, respectively. The probability distributions were recorded under the same conditions for each incident beam and are plotted on relative scales. The final translational energy probability distributions for high-energy argon scattering demonstrate that the extent of energy transfer is large ($> 60\%$ for all surfaces) but not equivalent for the three surfaces. The total energy transfer for high-energy argon is most efficient in collisions with the purely hydrocarbon SAM, followed by the terminally fluorinated SAM and then the fully fluorinated SAM. The scattered probability distributions from the purely hydrocarbon SAM have the highest intensity near 2.5 kJ/mol final energies (TD component) for the three surfaces with both incident energy beams. The probability distributions from the CF$_3$-terminated SAM decrease in intensity for the lowest final energies while the high energy portion of the distribution increases in intensity and shifts to higher final energies (IS component) relative to the CH$_3$-terminated SAM. Scattering from the perfluorinated SAM presents the lowest intensity for the TD component and the highest final energies in the IS component.
Figure 6.1  Final translational energy distributions for two different incident argon beam energies, (a) 35 kJ/mol and (b) 80 kJ/mol scattering from C16F0 (filled circles), C16F1 (open circles), and C10F8 (filled triangles) monolayers adsorbed on gold substrates. The Maxwell-Boltzmann distributions used to fit the TD channel for scattering from the SAMs are represented by the solid lines for $T_{\text{surf}} = 300$ K.
The Boltzmann distributions used to fit the trapping-desorption channel are included in each figure. The TD fractions calculated for scattering at $\theta_i = \theta_f = 30^\circ$ decrease from 0.73 to 0.64 to 0.43 when scattering from the C16F0, C16F1, and C10F8 SAMs on gold at $E_i = 35$ kJ/mol. For argon atoms with 80 kJ/mol of incident energy, the TD fractions are slightly lower than the 35 kJ/mol beam, 0.61, 0.53, and 0.36 for the C16F0, C16F1, and C10F8 SAMs, respectively.

Atoms that scatter from the C10F8 after impulsive collisions transfer the lowest amount of energy, 0.52 and 0.60 for the 35 and 80 kJ/mol beams, respectively. Impulsive collisions from the terminally fluorinated SAM also absorb less of the argon translational energy when compared to the purely hydrocarbon SAM. Impulsive energy transfers of 0.63 and 0.72 were calculated for the C16F1 SAM while values of 0.71 and 0.82 were calculated for the C16F0 SAMs for the 35 and 80 kJ/mol beams.

### 6.3.2.2 Even-Odd Effect

In addition to scattering from the three SAMs described above, we have also studied the even-odd effect for SAMs terminated in CH$_3$ and CF$_3$ groups. This study was motivated by earlier work that showed an even-odd effect in the impulsive scattering channel for 80 kJ/mol argon scattering from a series of $n$-alkanethiols adsorbed on gold surfaces.$^{91}$ We have scattered 80 kJ/mol argon atoms from C15F0, C16F0, C15F1, and C16F1 SAMs to study the even-odd effect for different terminal groups. Figure 6.2 shows direct comparisons on relative scales of the translational probability distributions for 80 kJ/mol argon scattering from an $n = 15$ and an $n = 16$ monolayer terminated with CH$_3$ groups (a) and CF$_3$ groups (b).
Figure 6.2 Probability distributions for 80 kJ/mol argon scattering from SAMs of C\textsubscript{15} and C\textsubscript{16} \(n\)-alkanethiols terminated with (a) CH\textsubscript{3} and (b) CF\textsubscript{3} groups.

Figure 6.2 (a) is very similar to Fig. 3.8 (a), which shows argon scattering from SAMs with \(n = 11\) and \(n = 12\) total carbon atoms in the chains. The number of argon atoms that are detected at \(\theta_f = 30^\circ\) in the TD channel are indistinguishable for the even and odd chain length SAMs. The only differences in the distributions occur in the higher energy component where the odd chain length SAMs scatters more atoms into the specular angle than the even chain length SAMs. Figure 6.2 (b) shows scattering from CF\textsubscript{3}-terminated SAMs with \(n = 15\) and \(n = 16\) total carbon atoms in the chains. For the
CF$_3$-terminated SAMs, we measure a significant difference in both the trapping-desorption component and the impulsive-scattering component.

6.3.3 Krypton and Xenon Scattering

The influence of mass on energy transfer dynamics can be explored by changing the mass of the impinging gas as well as the surface groups. We have scattered two different beam energies of krypton (see section 2.4.2 for beam energy measurements): 3.5 % Kr in He (61 kJ/mol, FWHM = 12 kJ/mol) and 2.5 % Kr in H$_2$ (102 kJ/mol, FWHM = 19 kJ/mol) and two different beam energies of xenon: 5.0 % Xe in He (61 kJ/mol, FWHM = 12 kJ/mol) and 4.0 % Xe in H$_2$ (95 kJ/mol, FWHM = 21 kJ/mol) from the five different SAMs on gold mentioned above.

6.3.3.1 Extent of SAM Fluorination

Figures 6.3 and 6.4 show energy distribution plots, $P(E_f)$, for krypton and xenon scattering from C16F0, C16F1, and C10F8 SAMs on gold, respectively. Energy transfer for high-energy krypton and xenon scattering from these three types of SAMs is extensive. The energy distribution with the lowest average energy transfer fraction, 61 kJ/mol krypton from perfluorinated SAM, is greater than 0.75. However, the total energy transfer is dependent on the surface structure and composition. The most efficient surface for absorbing the translational energy of the impacting gases is the CF$_3$-terminated SAM, followed by the CH$_3$-terminated SAM and then the perfluorinated SAM for both gases.

The fitted Boltzmann curves are provided in the plots and show that the intensity of the TD component is highest for the C16F1 SAM followed by the C16F0 SAM, then the C10F8 SAM. In the case of xenon scattering from the C16F1 SAM, the Boltzmann
curve nearly fits the total distribution, even for scattering with 95 kJ/mol of incident energy. A loss in intensity in the TD component is balanced by an increase in intensity of the IS component when comparing the CF₃- to the CH₃-terminated SAM and changes further for the fully fluorinated SAM.

Figure 6.3 Final translational energy distributions for two different incident krypton beam energies, (a) 61 kJ/mol and (b) 102 kJ/mol scattering from C16F0 (filled circles), C16F1 (open circles), and C10F8 (filled triangles) monolayers adsorbed on gold substrates. The Maxwell-Boltzmann distributions used to fit the TD channel for scattering from the SAMs are represented by the solid lines for T_{surf} = 300 K.
Figure 6.4 Final translational energy distributions for two different incident xenon beam energies, (a) 61 kJ/mol and (b) 95 kJ/mol scattering from C16F0 (filled circles), C16F1 (open circles), and C10F8 (filled triangles) monolayers adsorbed on gold substrates. The Maxwell-Boltzmann distributions used to fit the TD channel for scattering from the SAMs are represented by the solid lines for $T_{\text{surf}} = 300$ K.

6.3.3.2 Even-Odd Effect

In addition to the series of progressively fluorinated SAMs, we have also studied the even-odd effect for SAMs terminated in CH$_3$ and CF$_3$ groups for krypton and xenon
scattering. Figures 6.5 and 6.6 are plots of krypton and xenon scattering from alkanethiolate SAMs with \( n = 15 \) and \( n = 16 \) total carbon atoms in the chain. Scattering from the purely hydrocarbon SAMs are given in (a) for each gas and scattering from SAMs terminated in fluorine atoms are given in (b) for each figure.

**Figure 6.5** Probability distributions for 102 kJ/mol krypton scattering from SAMs of C\textsubscript{15} and C\textsubscript{16} \( n \)-alkanethiols terminated with (a) CH\textsubscript{3} and (b) CF\textsubscript{3} groups.
Figure 6.6 Probability distributions for 95 kJ/mol xenon scattering from SAMs of C\textsubscript{15} and C\textsubscript{16} \textit{n}-alkanethiols terminated with (a) CH\textsubscript{3} and (b) CF\textsubscript{3} groups.

The distributions for scattering from the purely hydrocarbon SAMs show that the intensity of the TD channel is independent of chain length while the intensity of inelastic scattering is higher for SAMs composed of odd chain length alkanethiols than even. The same effect is measured for high-energy xenon scattering from the \( n = 15 \) and \( n = 16 \) CF\textsubscript{3}-terminated SAMs in Fig. 6.6 (b). However, high-energy krypton scattering from the
terminally fluorinated SAMs appear to be nearly independent of chain length for both the TD and IS components.

6.4 Simulation Results

6.4.1 Models, Simulations and Data Analysis

Classical trajectory calculations were used to gain insight into the role of terminal group mass effects in gas-surface energy transfer dynamics. The simulations were used as a next step from the kinematic models to gain a fundamental understanding of the energy transfer dynamics occurring in these systems. The surface model that corresponds to the C_{10} SAM on gold described previously\textsuperscript{28,32,35,75} and in chapter 4 was used for this study. Modifications to the model included changing the methyl group masses from 15 to 69 amu in relation to CH\textsubscript{3} and CF\textsubscript{3} groups. We also used masses of 40, 84, and 132 amu to mimic argon, krypton and xenon gas atoms, respectively. However, the potentials describing the interactions involving the fluorinated groups were left unchanged. The intra- and intermolecular potential energy functions described in Tables 4.1 and 4.3 were used for all model systems. Consequently, our models for these systems are a rudimentary approximation to the corresponding monolayers and future work should test the legitimacy of them. All atom models with more realistic potential energy functions, both intra- and intermolecular, should be used. Nonetheless, these simulations provide a great deal of insight into how the gas-to-surface mass ratio affects scattering since we are able to separate the mass effects from the potential energy effects in scattering.

Classical trajectory calculations were performed with the software package VENUS developed by Hase \textit{et al.}\textsuperscript{121} The atomic scale dynamics were monitored in this study in a similar way as the simulations of argon scattering from the five different
density SAMs reported in chapter 4. The height of the gas atom above the rigid substrate and the number of inner turning points were recorded during each trajectory. Impulsive scattering was defined as a trajectory with a single inner turning point that does not penetrate the average plane of the terminal methyl groups. Ballistic penetration is defined as a trajectory where the gas atom goes below the average terminal group plane on impact.

Data analysis included calculating the fraction of atoms that undergo ballistic penetration, the average final energy of those atoms that undergo ballistic penetration, and the average energy transferred in impulsive collisions for each gas-SAM model.

6.4.2 Scattering Results

Figure 6.7 shows translational energy probability distributions for model systems of argon, krypton, and xenon scattering from surfaces with terminal groups of mass 15 and 69. The final translational energy distributions for each gas include all final angles after collisions with 80 kJ/mol incident energy integrated over 1000 trajectories. The probability distributions for all systems have low final energies indicating extensive energy transfer, which corresponds well with the experimental results. For argon scattering, the distribution from the more massive terminal groups is shifted to higher final energies than the less massive terminal groups. In the cases of krypton and xenon, the scattering distributions from the terminal groups with masses of 15 amu have higher final energies than the more massive terminal groups. The high fractions of energy transfer and the relative difference in energy transfer between \( \text{CH}_3 \) and \( \text{CF}_3 \) groups for argon, krypton, and xenon present the same qualitative trends as the experimental data.
This is a remarkable observation, especially because the potential energy surfaces are the same in each of the models.

\[ E_i = 80 \text{ kJ/mol} \]

![Figure 6.7](image)

**Figure 6.7** Final energy probability distributions calculated from molecular dynamics simulations for 80 kJ/mol (a) argon, (b) krypton, and (c) xenon scattering from model surfaces with terminal group masses of 15 amu (open symbols) and 69 amu (filled symbols).
6.5 Discussion

The focus of the work presented in this chapter is to further the understanding of energy transfer dynamics for gas collisions with organic surfaces. New insight into gas-surface dynamics is provided by high-energy argon, krypton and xenon scattering from five alkanethiolate self-assembled monolayers and molecular dynamic simulations on some rudimentary model systems similar to simulations previously reported. As described below, we have learned that the mass of the surface groups plays a dominant role in the extent of energy transfer. In addition, the dynamics of gas atoms colliding with monolayers terminated in CH₃ and CF₃ groups are quite different and can be understood on the basis of the terminal group masses, independent of potential energy effects.

6.5.1 Scattering from SAMs with Increasing Fluorination

The extensive energy transfer for high-energy argon, krypton, and xenon collisions with the self-assembled monolayers employed in this study can be attributed to a number of factors. Organic monolayers have several degrees of freedom into which the gas translational energy can be transferred including concerted waving motions of the chains, vibrational modes along the chains, and hindered rotations of the end groups. Although we measure extensive energy transfer for each system, the scattering dynamics depend on the impinging gas atoms and the structure and composition of the SAMs. The following discussion focuses on why the scattering dynamics depend on the extent of fluorination in the SAMs and, for a given surface, why the scattering dynamics depend on the mass of the impinging gas atoms.
6.5.1.1 Trends

Figure 6.8 (a), (b), and (c) shows summary plots for the dependence of the fraction of trapping-desorption, impulsive energy transfer, and total energy transfer on the mass of the gas atom scattering from the three surfaces with incident energies of 80 kJ/mol. The values for the TD fractions, impulsive energy transfers, and total energy transfers for krypton and xenon scattering with incident energy of 80 kJ/mol were interpolated from values calculated from the higher and lower energy beams. Nathanson et al. have interpolated values in a similar way to compare energy transfer dynamics when comparing small molecule scattering from the surfaces of squalane and glycerol.3

Table 6.1 is a complete summary of the data calculated for argon, krypton and xenon scattering from the C16F0, C16F1, and C10F8 SAMs. The fraction of atoms that scatter into the impulsive channel is so small for xenon scattering from the CF3-terminated SAM that we cannot make a confident calculation on the average energy transfer.

Table 6.1 Summary of TD fractions and energy transfer in the impulsive scattering channel

<table>
<thead>
<tr>
<th>Gas</th>
<th>E_i (kJ/mol)</th>
<th>C16F0</th>
<th>C16F1</th>
<th>C10F8</th>
<th>C16F0</th>
<th>C16F1</th>
<th>C10F8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar/He</td>
<td>35</td>
<td>0.73</td>
<td>0.64</td>
<td>0.43</td>
<td>0.71</td>
<td>0.63</td>
<td>0.52</td>
</tr>
<tr>
<td>Ar/H2</td>
<td>80</td>
<td>0.61</td>
<td>0.53</td>
<td>0.36</td>
<td>0.82</td>
<td>0.72</td>
<td>0.60</td>
</tr>
<tr>
<td>Kr/He</td>
<td>61</td>
<td>0.71</td>
<td>0.85</td>
<td>0.51</td>
<td>0.81</td>
<td>0.78</td>
<td>0.70</td>
</tr>
<tr>
<td>Kr/H2</td>
<td>102</td>
<td>0.59</td>
<td>0.69</td>
<td>0.37</td>
<td>0.89</td>
<td>0.87</td>
<td>0.77</td>
</tr>
<tr>
<td>Xe/He</td>
<td>61</td>
<td>0.76</td>
<td>0.93</td>
<td>0.67</td>
<td>0.83</td>
<td>---</td>
<td>0.78</td>
</tr>
<tr>
<td>Xe/H2</td>
<td>95</td>
<td>0.74</td>
<td>0.93</td>
<td>0.60</td>
<td>0.89</td>
<td>---</td>
<td>0.84</td>
</tr>
</tbody>
</table>

* estimated error: ± 0.01
# estimated error: ± 0.02
Figure 6.8 A summary of the dependence of (a) the fraction of atoms in the trapping-desorption channel, (b) the fractional energy transferred in the impulsive scattering channel, and (c) the total fractional energy transferred as a function of incident gas mass for 80 kJ/mol incident energies. Lines are drawn to guide the eye.
The argon scattering data (40 amu) shows that the total energy transfer to the surface decreases with an increasing extent of fluorination within the SAM (Fig. 6.8 (c)). Separating the data into the two limiting scattering pathways shows similar trends where the fraction of atoms that comes into thermal equilibrium and the amount of energy transferred in impulsive collisions both decrease with increasing fluorination. The fluorinated groups thus add structural rigidity to the surface preventing energy transfer and inhibiting atoms from coming into thermal equilibrium. High-energy krypton and xenon scattering from the same three surfaces show very different trends than argon. Fig. 6.8 (a) shows that the relative fractions of trapping desorption from argon collisions with the CH3- and CF3-terminated SAMs is reversed for scattering with krypton and xenon. The extent of trapping desorption decreases with increasing fluorination of the SAMs for argon scattering, while the observed trend follows the order C16F1 > C16F0 > C10F8 for krypton and xenon scattering. The fraction of total energy transfer and the fraction of energy transfer in impulsive collisions for both krypton and xenon scattering from the C10F8 SAM is lower than the other two surfaces. However, scattering from CH3- and CF3-terminated SAMs are the same within our estimated error.

6.5.1.2 Comparison with Literature

High-energy inert gas scattering from the surfaces of organic liquids have been performed by Nathanson and co-workers.\textsuperscript{3,8,9,19,23} Of particular relevance to the systems studied here, they have scattered neon, argon, and xenon from the surfaces of squalane, 2,6,10,15,19,23-hexamethyltetrasane (C\textsubscript{30}H\textsubscript{62}), and a perfluorinated polyether, F-[CF(CF\textsubscript{3})CF\textsubscript{2}O\textsubscript{14(avg)}-CF\textsubscript{2}CF\textsubscript{3}. To a first approximation, we can compare scattering from squalane to purely hydrocarbon SAMs and scattering from the perfluorinated polyether to
the C10F8 SAMs. The trends observed in their data qualitatively agree with the trends observed in our data. For a given surface, energy transfer increases with increasing mass of the incident gas atom,\(^{9,19,23}\) and for neon\(^{8,9,23}\), argon\(^{9}\), and xenon,\(^{9,23}\) less energy is transferred to the perfluorinated polyether surface than to the squalane surface.

In addition to the scattering experiments at the liquid interface, Cohen et al. performed time-of-flight scattering experiments of low-energy argon scattering from well-ordered amphiphilic monolayers.\(^{10}\) SAMs created from \(n\)-octadecyltrichlorosilane (OTS) attached to substrates through covalent silane bonds and a perfluorinated acid ester assembled on glass are similar to our C16F0 and C10F8 alkanethiolate SAMs on gold. The authors found that \(\sim 6\) kJ/mol argon atoms scattering from the perfluorinated SAM transfer less energy than in scattering from the OTS SAM. This trend is in agreement with our results for high-energy argon scattering. The increased rigidity of the perfluorinated surfaces relative to the hydrogenated surfaces may be a result of differences in mass of fluorine and hydrogen, as well as differences in the repulsive intermolecular forces of fluorine and hydrogen atoms.

It appears that the observations from our experiments for gases scattering from purely hydrocarbon and perfluorinated surfaces is general for inert gases colliding with organic films. However, less is known about the influence individual fluorinated groups have on energy transfer for inert gas scattering. Wysocki and coworkers have shown that translational to internal vibrational energy transfer in molecular-ion surface scattering with incident energies in the range 10 – 70 eV (\(\sim 980\) to \(6860\) kJ/mol) is nearly the same for a CF\(_3\)-terminated SAM as a perfluorinated SAM.\(^{42,44}\) The results suggest that the effective mass of the terminal group is more important in those systems than the
increased rigidity of the perfluorinated chains. We find quite different results for energy transfer when inert gases in the energy range of 35 – 100 kJ/mol scatter from CF₃-terminated and perfluorinated SAMs. Energy transfer from argon, krypton, and xenon to the CF₃-terminated SAM is higher than the perfluorinated SAM for all incident conditions. In the case of krypton and xenon scattering, the total energy transferred to the CF₃-terminated SAM is even as high as the purely hydrocarbon SAM. These unexpected results are considered in the following sections. In particular, we focus on the influence of surface mass and the global potential energy surfaces (PES) on energy transfer dynamics for these systems.

6.5.1.3 Mass Effects

Gas and surface masses have been recognized as extremely important factors in collision dynamics since the early developments of gas-surface scattering theory. In 1966, Logan and Stickney published the now very familiar hard-cubes model of gas-surface scattering.¹¹ The model consists of gas atoms undergoing impulsive collisions with hard cube surfaces and restricting momentum transfer to only the normal direction of the surface during the collision. One important outcome of this model shows that energy transfer is maximal when the mass ratio is unity and falls off with larger or smaller values, though asymmetrically. The fractional energy transfer to the surface can be derived from conservation of energy and momentum to give the following relationship for normal incidence.

\[
\frac{\Delta E}{E_i} = \frac{4\mu}{(\mu + 1)^2}
\]

where \( \Delta E \) is the change in energy of the gas atom, \( E_i \) is the incident gas energy and \( \mu \) is the mass ratio, \( m_{\text{g}}/m_{\text{s}} \).
The hard cubes model, along with the hard spheres model, can be used directly to calculate the mass ratio from the average energy transferred in the impulsive channel. The optimized fit to the mass ratio, \( \mu \), provides an ‘effective’ surface mass, which lends insight into the collective response of the surface during impulsive collisions.\(^{12}\) It is difficult if not impossible to predict \textit{a priori} the response of the surface involved in the collisions. However, the calculated effective surface mass can usually be attributed to segments of the surface e.g. surface masses close to the mass of CF\(_3\)CF\(_2\) groups have been calculated for neon scattering from a perfluorinated polyether surface in single collision events.\(^8\) For well-ordered organic monolayers, the collective response of the surface from inert gas scattering has been shown to depend on alkyl packing density,\(^{75}\) hydrogen-bonding networks within the monolayer,\(^{76,117}\) and the number of carbon atoms in the alkyl chains.\(^{91}\) All of these surface properties contribute to the effective mass of the surface. Additionally, the response of these properties can be dependent on the incident parameters and identity of the gas atom.

Despite these limitations, the models are beneficial tools to gain a qualitative view of the dynamics that occur during impulsive collisions. Consider the results for 80 kJ/mol incident argon, krypton, and xenon scattering from the perfluorinated SAM. The average fractional energy transferred during impulsive collisions increases from 0.60 for argon to 0.74 and 0.81 for krypton and xenon, respectively. The hard cubes model predicts that energy transfer increases for increasing values of \( \mu \) up to one. Assuming that the surface mass is larger than the gas mass and responds to the impact from the three different gases in the same way, we would predict that energy transfer will increase from argon to krypton to xenon since the mass ratio is increasing. We can also apply the
ideas of mass ratio in a comparison of scattering from the purely hydrocarbon and perfluorocarbon surfaces as well. Considering mass effects only and ignoring structural dissimilarities, we would predict that the C10F8 SAM would have a higher mass than the C16F0 SAM and from the cubes model, presume that energy transfer will be larger for the purely hydrocarbon SAM. Indeed, the average fractional energy transferred for all three gases to the purely hydrocarbon SAM is consistently higher than the perfluorinated SAM.

Qualitatively, the experimental results for the energy transfer dependence on mass ratio is consistent with the hard cubes model for SAMs composed of light hydrocarbon chains relative to SAMs composed of heavy fluorocarbon chains. Again if we assume that the CF3-terminated surface responds to impulsive scattering from argon, krypton, and xenon in the same way, we would predict that energy transfer should increase with the mass of the gas atoms. This is exactly what we see in Fig. 6.8 (b). Energy transfer is lowest for argon followed by krypton and it appears that energy transfer is so efficient for xenon, that nearly every atom approaches thermal equilibrium. However, the ideas derived from the cubes model are not as clear-cut in predicting the outcome of scattering from the CF3-terminated SAM compared to the CH3-terminated SAM. Specifically, we find that energy transfer and thermalization trends for argon and krypton/xenon scattering from the CH3 and CF3-terminated SAMs have reverse trends.

Classical trajectory calculations were performed to gain insight into the fundamental dynamics that occur for argon, krypton, and xenon scattering from SAMs terminated with CH3 and CF3 groups. The models are crude, but they allow mass effects to be studied separately from forces arising from differences in potential parameters
within the SAM and differences in the intermolecular interactions of the three gases with the SAMs. Data analysis included calculating the fraction of atoms that undergo ballistic penetration, the average final energy of ballistic penetrating trajectories, and the average energy transferred in impulsive collisions for each gas-SAM model. A summary of each of these calculated values is given in Table 6.2.

Table 6.2 Summary of molecular dynamics results for 80 kJ/mol atomic gas scattering from SAMs

<table>
<thead>
<tr>
<th>System</th>
<th>Fraction of Penetration</th>
<th>$&lt;E_f&gt;$ penetration</th>
<th>Fraction of IS</th>
<th>$&lt;\Delta E_{IS}&gt;/E_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar + CH$_3$</td>
<td>0.16</td>
<td>6.37</td>
<td>0.37</td>
<td>0.89</td>
</tr>
<tr>
<td>Ar + CF$_3$</td>
<td>0.03</td>
<td>---*</td>
<td>0.56</td>
<td>0.76</td>
</tr>
<tr>
<td>Kr + CH$_3$</td>
<td>0.40</td>
<td>9.22</td>
<td>0.35</td>
<td>0.88</td>
</tr>
<tr>
<td>Kr + CF$_3$</td>
<td>0.13</td>
<td>7.04</td>
<td>0.29</td>
<td>0.86</td>
</tr>
<tr>
<td>Xe + CH$_3$</td>
<td>0.54</td>
<td>11.69</td>
<td>0.32</td>
<td>0.87</td>
</tr>
<tr>
<td>Xe + CF$_3$</td>
<td>0.22</td>
<td>8.32</td>
<td>0.37</td>
<td>0.89</td>
</tr>
</tbody>
</table>

*Not enough trajectories to obtain a meaningful distribution

As illustrated in Fig. 6.7, the final energy distributions for argon scattering from the CH$_3$ and CF$_3$-terminated SAM models have a different trend than krypton and xenon scattering from the same two surfaces. We have begun to unravel the origin of the final probability distributions by analyzing the data from the average energy transfer in impulsive collisions and the dynamics of atoms that undergo ballistic penetration.

For impulsive collisions (trajectories with single inner turning points that do not penetrate the SAMs), the average energy transferred to the surface and the fraction of atoms that undergo impulsive collisions is quite different for argon scattering from the heavy and light terminal group models. These differences are in direct contrast to krypton and xenon impulsive scattering, where the average energy transferred is nearly independent of the terminal group mass. The differences in the impulsive scattering
channel for argon and krypton/xenon may be related to the number of groups that participate in the collision.

In impulsive gas-surface collisions, the ‘effective’ mass of the surface is always larger than the gas atoms; otherwise the gas cannot reverse its normal direction. Consider the simple case of an atom impulsively striking a cube (effective surface) at rest in a one-dimensional problem. From conservation of linear momentum and kinetic energy we can derive the relation:

\[ v_{f,i} = \frac{m_1 - m_2}{m_1 + m_2} v_{i,i} \]

where \( v_{i,i} \) and \( v_{f,i} \) are the final and initial velocities of the gas atom. In order for the gas atom to change direction and scatter away, \( (v_{f,i} < 0) \), the mass of the block must be larger than the mass of the gas particle \( (m_2 > m_1) \). Since argon has a mass of 40 and the CF₃ group has a mass of 69, the mass ratio meets the requirement and the gas can scatter from individual surface groups. The situation is different for krypton and xenon since they have larger masses than individual CF₃ groups, therefore, more surface groups have to participate in the collision. The similarities in the impulsive scattering channel for krypton and xenon suggest that excitation of extended chain motions dominates energy transfer in these systems and the terminal group mass plays a relatively smaller role. This situation is similar to argon scattering from CH₃-terminated SAMs, where as many as 6 carbon units participate in the collision.⁹¹

The atomic scale dynamics of energy transfer ‘seen’ through the classical trajectory calculations provide several surprising results for processes other than impulsive collisions. A comparison of scattering from a given surface model shows that
the fraction of xenon atoms that penetrate into the monolayers is highest followed by krypton and then argon (see Table 6.2). We rationalize this trend by taking into account the initial momenta of the gas atoms. Since the gas atoms in all the trajectories were given 80 kJ/mol of incident energy, the ratio of the incident gas momenta increases from 1: 1.5: 1.8 for gases with masses of 40, 84, and 132, respectively. Simulations show that the fractions of atoms that penetrate the monolayers scale with the incident momenta of the gas atoms. However, changing the terminal group mass from 15 (CH₃) to 69 (CF₃) reduces the fraction of atoms that undergo ballistic penetration by more than half for all three gases. Again, this result is consistent with simple kinematics arguments. Consider high-energy gas atoms with a mass of 132 amu colliding with a terminal group of only 15 amu or even two to three terminal methyl groups with a collective mass up to 45 amu. The relatively light surface groups have a difficult time slowing down the heavy gas atoms and cannot prevent them from driving their way into the monolayer. When those same gas atoms collide with terminal groups of 69 amu, momentum transfer is more efficient in the initial gas-surface impact and fewer atoms penetrate into the monolayer. This result agrees with previous notions that the mass of individual CFₓ groups play a large role in energy transfer from perfluorinated surfaces.⁸⁻⁹

The fraction of atoms that penetrate the monolayers for heavy and light terminal groups is surprising, but a more unexpected result from the simulations is the final energy of the heavy gas atoms after a penetrating collision. The average final energy is found to be well above 2kTₐₘ, revealing that a penetrating trajectory does not come into thermal equilibrium with the surface despite long-time contact involving many collisions. It
appears that when the atoms penetrate the monolayer, restoring forces of the monolayer expel the gas atom back into the gas phase.

Figure 6.9 shows a schematic representation of a trajectory that undergoes ballistic penetration into the SAM. The terminal group plane is defined by the average height of the methyl groups (light gray circles in Fig. 6.9) above the rigid substrate plane.

![Image](image_url)

**Figure 6.9** Schematic representation of a gas atom with 80 kJ/mol incident energy penetrating the terminal group plane (methyl groups depicted by gray circles) causing a perturbation in the chain conformation followed by an ejection into the gas phase.

Sibener and co-workers have reported xenon simulations with alkanethiolate SAMs similar to the work presented here where they observed atoms ejected from the SAMs with higher than average-thermal energies following penetration. The main differences between their simulations and ours are the energy of the incident xenon atoms and the potential energy surface employed. We observe this penetration-ejection channel with 80 kJ/mol energy compared to nearly 350 kJ/mol in their simulations.

For penetrating trajectories into the CH$_3$-terminated SAM, the final average energy increases with the mass of the gas atom. The final energy of argon atoms that penetrate the monolayers is close to thermal average energies, but are most likely not in
thermal equilibrium with the surface. It appears that the direct penetration channel does not lead to thermal equilibrium for these relatively high density SAMs. Although the final energy distribution of argon atoms that penetrate the CH$_3$-terminated SAMs closely resembles a Boltzmann distribution, we measure differences in the final energies for gas atoms with different masses without changing the potential parameters.

When scattering from the SAM models terminated with groups of either 15 or 69 amu, the atoms that penetrate the monolayers leave the surface with higher average energies than thermal. However, the final energies after penetration into these two surfaces are not the same for a given gas. For example, the average energy for a xenon atom that penetrates the CH$_3$-terminated monolayer is $\sim$11.7 kJ/mol, which is nearly 1.5 times more energy than an average penetrating collision with a CF$_3$-terminated monolayer. During the initial impact, the gas atoms must move the heavy terminal groups to penetrate the SAM and likewise, upon ejection from the SAM into the gas phase, the gas atoms must push aside the CF$_3$ groups again. Changing the momenta of the CF$_3$ groups, both upon impact and ejection, should decrease the atom’s energy relative to moving CH$_3$ groups.

6.5.1.4 Potential Effects

The trends observed in our experiments for high-energy argon, krypton, and xenon scattering from the C16F0 and C10F8 monolayers were shown to be general for inert gas scattering from organic surfaces composed of hydrocarbon and fluorocarbon chains. The trends can be rationalized from the masses of the gas atoms and the relative masses of hydrogen and fluorine. However, intra-monolayer forces can contribute to the ‘effective mass’ of a surface as well as the masses of the elements composing them.
High-energy argon scattering from monolayers terminated with hydroxyl groups appear more rigid than purely hydrocarbon monolayers even though the masses of OH and CH groups are nearly the same. The hydroxyl groups form a hydrogen-bonding network that restricts certain chain motions from absorbing energy as efficiently from high-energy argon collisions and hence, they appear more massive based on analysis using one of the kinematics models. In addition, molecular dynamics simulations by Hase et al. scattering neon from united atom and all atom models of a hexylthiolate monolayer showed differences in energy transfer. The all atom model was ~10% less efficient in absorbing the incident energy of the neon atoms than the united atom model. The decreased energy transfer was attributed in part to increased repulsive interactions between the hydrogen atoms, which make the surface stiffer. Again, monolayers with differences in the inter-chain repulsive forces would appear to have a higher effective mass based on a kinematics analysis of energy transfer from the cubes model.

We expect that real (as opposed to the simulation models) monolayers composed of hydrocarbon and fluorocarbon chains experience different intramonolayer forces after displacement by high-energy gas collisions. It is apparent that the intramonolayer potential energy surfaces of the two types of SAMs are dissimilar, since the chain orientations and the lattice spacing of the monolayers are different. The most likely explanation for the differences in the structures is the high electronegativity of the fluorine atoms. Fluorine-fluorine repulsive forces are likely responsible for both the helical structure of the chains and the increased lattice spacing between the chains relative to the hydrocarbon SAMs. Since chain vibrations parallel to the surface plane are thought to be the most efficient modes in energy transfer, chain-chain repulsive
forces, in addition to the mass effects, could play a large role in the difference between energy transfer to hydrocarbon and fluorocarbon SAMs.

The packing structures of the CH₃- and CF₃-terminated SAMs are very similar to each other.⁴¹,¹⁶¹,¹⁶⁵,¹⁶⁷ We therefore expect the excitation of collective motions of the chains to be similar for these SAMs after a collision with a gas atom. However, the intermolecular potential between the surface and the gas atom may contribute to the trends we observe for argon and krypton/xenon scattering from the CH₃ and CF₃-terminated SAMs. Molecular dynamics simulations have shown that energy transfer to well-ordered monolayers is sensitive to the intermolecular PES in the gas-SAM model.¹¹⁸ The slope of the repulsive wall in addition to the well depth contributes to the energy exchange dynamics. The electronegativity of the fluorine atoms at the terminal position of the alkyl chains creates a dipole moment between the terminal carbon-carbon bond.¹⁶¹,¹⁶⁸,¹⁶⁹ The dipole moment in the terminal group position may have a dramatic influence on the potential energy surface of the noble gas atoms since the polarizability of the gases increase from argon (1.64 Å³) to krypton (2.48 Å³) to xenon (4.04 Å³).¹⁷⁵ From values of the polarizabilities, we expect the dipole induced-dipole interactions to create a deep potential well for xenon followed by krypton and then argon interacting with the CF₃-terminated SAMs. An increased potential well should lead to higher thermal accommodation fractions. When a gas atom impacts a surface and reverses direction, a deep potential well will prevent the atom from escaping back into the gas phase if the normal energy is less than the well depth. This barrier to desorption will redirect the gas atom back into the surface. The longer the gas atoms are in contact with the surface, the more energy is transferred, which brings them into thermal equilibrium with surface.
Since the polarizabilities of the three inert gases increase from argon to krypton to xenon, we expect more trapping on the surface in the same order, argon < krypton < xenon. This analysis is consistent with what we observe for argon, krypton and xenon scattering from the CH$_3$ versus the CF$_3$-terminated SAMs (see Table 6.1).

### 6.5.2 Even-Odd Effect

Figures 6.2, 6.5, and 6.6 show high-energy argon, krypton, and xenon scattering from monolayers composed of $n = 15$ and $n = 16$ total carbon atoms in the chains. Panel (a) in each of the figures provide the scattered distributions from the CH$_3$-terminated SAMs and panel (b) provides the distributions from the CF$_3$-terminated SAMs. A similar trend exists for scattering from the CH$_3$-terminated SAMs for all three of the incident gases. For the CH$_3$-terminated SAM, the TD component is essentially independent of chain length, whereas we detect more atoms scattering impulsively from the surfaces with $n = 15$ chain length SAMs for the scattering geometry employed in these experiments ($\theta_i = \theta_f = 30^\circ$). The even-odd effect has been extensively discussed in section 3.6 for 80 kJ/mol argon scattering from methyl-terminated SAMs. The well-documented structural difference between the long-chain monolayers on gold is that the orientation of the terminal C-C bond alternates from predominately parallel to perpendicular relative to the surface normal depending on whether the total number of carbon atoms in the chains is odd or even.\footnote{51,96,97} Figure 6.10 shows an idealized schematic of the terminal group orientation of a SAM with an even and an odd number of carbon atoms.
Differences in orientation may influence the ability of argon to excite terminal C-H stretches, C-C stretches, methyl torsions and C-C-C bends. Minor differences in the amount of impulsive energy transfer between the even and odd surfaces would affect the final parallel momentum of the atoms in the IS channel thereby altering the angular distribution. Since we measure a fixed final angle, a change in the angular distribution for impulsive scattering events could explain our results.

We have also scattered argon, krypton, and xenon from monolayers with $n = 15$ and $n = 16$ SAMs terminated in CF$_3$ groups. These scattering experiments were performed for two reasons. First, we wanted to know if the differences for scattering from even and odd chain length SAMs with CH$_3$-groups is general for SAMs terminated in other elements. Second, we wanted to determine if the orientation of the dipole moment affects the scattering dynamics of the more polarizable gases. The net electric field of the SAMs changes when the terminal CF$_3$ groups are at the end of chains with even or odd numbers of carbon atoms.$^{161,169}$ The terminal carbon-carbon bond for even
chain length monolayers is nearly normal to the surface plane such that all the dipoles are
oriented parallel to each other causing a net electric field on the surface. Monolayers
with an odd number of carbon atoms place the terminal carbon-carbon bonds more
parallel to the surface plane. This orientation situates the CF₃ groups close to the CH₂
groups of a neighboring chain and partially cancels out the net field on the surface. The
difference in the net electric field could have a strong influence on the scattering from
high energy argon, krypton, and xenon. The dipole orientation is expected to have the
most dramatic influence on the more polarizable gases.

The distributions of argon, krypton, and xenon scattering from the $n = 15$ and $n =
16$ CF₃-terminated SAMs are difficult to interpret and further work is needed. We find
that both the TD and IS components change for argon scattering from the even and odd
chain length SAMs (Fig. 6.2 (b)), the high-energy krypton scattering seems to be
independent of the terminal group orientation (Fig. 6.5 (b)), and the xenon scattering
follows the same trend as scattering from the even/odd CH₃-terminated SAMs (Fig. 6.6
(b)). To relate these results to the goals outlined above for scattering from the CF₃-
terminal groups we can say: (1) that the trends observed for scattering from the CH₃-
terminated SAMs are not general for monolayers with other elements at the terminal
groups and (2) it seems that the difference in the net electric field makes little
contribution to the scattering dynamics. We expect that krypton and xenon scattering
would be most influenced by the differences in the net electric field since they have
higher polarizabilities than argon. However, differences in the scattering distributions of
these gases from the even and odd chain length SAMs are relatively small.
6.6 Summary

The dynamics of high-energy argon, krypton, and xenon scattering from hydrocarbon and fluorocarbon SAMs is interesting and an important step forward in understanding energy transfer at the gas-surface interface. The scattering results can be rationalized through mass effects of the gas atoms and surface compositions using simple models such as the hard cubes model. However, the PES between the gas-SAM and the monolayers likely contribute to the dynamics of energy transfer in these systems.

For argon scattering, both the TD fraction and the fractional energy transfer in the impulsive scattering channel increase with increasing fluorination. In contrast, krypton and xenon scattering exhibit the highest TD fraction for the CF$_3$-terminated SAM followed by the CH$_3$-terminated SAM and then the perfluorinated SAM.

From our molecular dynamics simulations we deduce that the heavy fluorinated groups act as a barrier to penetration for gases impinging on well-ordered monolayers. The effect of atoms penetrating the monolayers on the measured final energy distributions becomes more important for the heavier gases. The higher the mass of the incident gas atom, the more often it penetrates the SAM and has a final energy distribution shifted to higher energies after ejection into the gas phase. Argon atoms that penetrate SAMs only come into an apparent thermal equilibrium with the surface since heavier gases are expelled out of the chains with energies well above thermal using the exact same potential parameters. Classical trajectory simulations, more accurate than those used in this study, will be an essential factor to understanding the relative roles of mass and potential effects in these systems.
We observe that SAMs composed of even and odd chain length alkanethiols terminated with CH$_3$-groups bring high-energy gases into thermal equilibrium with the same efficiency, independent of the gas identity. We also observe that the odd chain length SAMs scatter more atoms impulsively into our detection angle than the even chain length SAMs for all three gases. These changes are likely the result of the ability to couple energy into the various surface modes of the terminal groups, which change the angular distribution of the impulsive channel. The even-odd effect is different when the SAMs are terminated with CF$_3$ groups rather than CH$_3$ groups for both argon and krypton scattering. It appears that argon scattering from the C15F1 and C16F1 SAMs have different thermal accommodation coefficients and may change the angular distribution of the impulsive channel as well. High-energy krypton scattering seems to be independent of the terminal group orientation for SAMs with CF$_3$ groups.
Chapter 7
Summary and Concluding Remarks

7.1 General Comments

A full appreciation of any chemical reaction hinges on understanding the fundamental details that govern the transformation of reactants into products. Technology has increased over the last half century to the point that many elementary pathways of chemical reactions are being explored on the atomic level. We have joined the effort by researching chemical dynamics that occur at the gas-surface interface. The first step in gas-surface chemical reactions is the initial collision, where the energy exchange dynamics control whether the gas-phase reactant scatters directly away from the surface or thermally accommodates (equilibrates) with the material. The objective of the research performed for this dissertation was to help build a fundamental understanding of the energy transfer dynamics that occur when gas-phase molecules collide with organic surfaces. We investigated the roles physical and chemical properties of organic surfaces play in energy transfer by scattering inert atomic gases from self-assembled monolayers.

Self-assembled monolayers are surfaces composed of single layers of organic molecules that coat a substrate due to strong interactions between a functional group and the surface of an inorganic solid. In all the experiments described in this dissertation, molecules having a thiol group are adsorbed onto either a gold or silver substrate. Due to the high affinity of sulfur for these precious metals, the monolayers form, or assemble, by simply placing the substrates into a solution containing the thiol functionalized
molecules. The sulfur groups bind to the substrates with a high packing density with the organic (aliphatic) chains standing upright, in the surface normal direction. The monolayer structures and driving force for assembly can be compared to a room full of helium balloons with bricks tied to the end of each string. The bricks ‘assemble’ on the ground with the balloons projecting away from the ground. Thiol functionalized molecules assemble with the thiol group attached to the substrate (the brick and ground) and the terminal functional group away from the substrate (the balloon). By tailoring the functional group structure (like having different colored balloons), monolayers with various properties can be constructed.

Energy transfer is found to be very efficient for all types of organic surfaces we studied relative to scattering from the clean, metal surfaces they are adsorbed on. The energy transfer dynamics for gases scattering from organic and inorganic surfaces can be compared to bouncing a tennis ball off a brick wall compared to bouncing the same ball from a bed mattress. The organic monolayers appear soft, and dissipate the excess energy from the impinging gas atoms more readily than the inorganic surfaces. However, within a series of these monolayers, we observe differences in energy transfer for different physical properties investigated. We have focused our studies on alkane chain length, interfacial structure, alkane chain packing density, intramonomolayer hydrogen bonding, and interfacial chemical identity.

7.2 Alkane Chain-Length Effects on Energy Transfer

We scattered argon atoms from organic monolayers with a total number of carbon atoms ranging from 2 to 18. A chain-length effect is observed when high-energy argon atoms collide with these monolayers. As the total number of carbon atoms in the chain
increases from the shortest chains measured up to about 6 or 7, the surfaces become progressively less rigid, leading to greater overall energy transfer. This chain-length effect is attributed to the importance of long-range motions along the alkane chains. It appears that between 6 and 7 carbon atoms participate in the dynamics of the gas-surface collisions.

### 7.3 Chain Packing Density Effects on Energy Transfer

To gain insight into the effect of chain packing density on the ability to transfer energy to the surface from gas collisions, we scattered argon atoms from \( n \)-alkanethiols adsorbed on gold and silver surfaces. These monolayers have been well-characterized previously, with the chains having a higher packing density on the silver substrates. When the argon atoms strike either of the two surfaces with energies slightly above thermal energies, the two monolayers behave similarly. The final energy distributions are well fitted to a Boltzmann distribution at the surface temperature, implying that full thermal equilibrium is achieved. In contrast, the two types of SAMs are not equally efficient at absorbing the excess translational energy from high-energy argon collisions. Argon atoms transfer less energy to the higher density surface than the lower density surface.

Molecular dynamics simulations were used as an aid in interpretation of the experimental results for argon scattering from \( n \)-alkanethiols adsorbed on gold and silver surfaces. The models used in our study sufficiently reproduce experimental data providing us with confidence to study the atomic scale mechanisms of energy transfer. We also studied other models with packing densities to go beyond the experimental results and generalize the effect of packing density on energy transfer dynamics. For the
five models studied, we observed the same trend as found in the experimental data. Namely, energy transfer increases with decreasing packing density. We attribute the differences in scattering to the freedom of motion of the chains when struck by the gas atom.

7.4 The Effect of Terminal Group Structure on Energy Transfer

Argon collisions with ω-functionalized monolayers on gold have begun to explore the relative importance of terminal group molecular structure and intra-monolayer hydrogen bonding on energy exchange dynamics. Among all of the ω-functionalized monolayers studied the long-chain methyl-, olefin-, and methyl ester-terminated SAMs are the most effective at dissipating the translational energy of impinging argon atoms. The similarity in the scattering results for these SAMs suggests that the vibrational degrees of freedom of the terminal groups play a relatively minor role in collisions of high-energy argon with the surfaces. In contrast to these three surfaces, monolayers functionalized with hydrogen-bonding groups (OH, NH₂, and COOH) are more rigid collision partners when scattering high energy argon atoms from them. These results suggest that intra-monolayer hydrogen bonding dampens low-energy extended motions within the monolayer to render the individual alkane chains less labile than free, non-hydrogen-bonding monolayers.

7.5 Mass Effects on Energy Transfer

Finally, we have studied the dynamics of high-energy argon, krypton, and xenon scattering from hydrocarbon and fluorocarbon surfaces. The scattering results can be rationalized by mass effects of the gas atoms and surface compositions using simple
classical models. For instance, argon transfers more energy to the hydrocarbon monolayers (lower mass groups) than the fluorocarbon monolayers (higher mass groups).

7.6 Concluding Remarks

The energy exchange dynamics during the initial collision between gas-phase molecules and surfaces determine whether the gas-phase reactant scatters directly away from the surface or comes in contact with the surface for prolonged periods of time. Most gas-surface reactions, whether at the interface or after diffusion into the bulk material, take place only after the gas-phase molecules come into thermal equilibrium on the surface. Interfacial reactions mediated by thermal equilibrium require sufficient energy transfer in the initial steps of the chemical reaction. We have found that organic surfaces in general facilitate large amounts of energy transfer from high energy gases. However, surfaces with intrinsic two-dimensional networks or surfaces with massive functional groups tend to restrict energy transfer compared to pure aliphatic monolayers or monolayers void of strong lateral interactions between the chains. These trends can serve as a guide to predict reaction rates for systems involving interfacial organic systems. In addition, these trends can be used as a means of surface design in cases of organic surfaces where aerodynamic drag is a concern.
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(116) Sometimes, the surfaces of the monolayers would turn a cloudy-white color after the silver slides were place in solution. The rate of color change, which we attribute to the silver surface oxidizing, was much faster for the short chain-length SAM.


Vita

Brian Scott Day was born to Lloyd and Patty Day on February 20, 1979 in Huntington, West Virginia and was raised with a brother Steve and sister Stacie. Scott graduated from Cabell Midland High School and went on to attend Marshall University in 1997. Upon graduation in May of 2001 with a Bachelor of Science degree in Chemistry, Scott moved to Blacksburg, Virginia to begin graduate study in August of the same year. In 2002, he began working under the direction of Dr. John Morris in gas-surface scattering dynamics in pursuit of a Ph.D. Upon completion of his graduate studies at Virginia Tech, Scott plans to return to Marshall University and join the research group of Dr. Michael Norton as a postdoctoral fellow.