The Dynamics of Gas-Surface Energy Transfer in Collisions of Diatomic Gases with Organic Surfaces

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Thesis submitted to the faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE
IN
CHEMISTRY

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November 21, 2014
Blacksburg, VA

Keywords: Self-assembled monolayers, Molecular beam, Ultra-high vacuum, Energy transfer, Solubility
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(ABSTRACT)

Understanding interfacial interactions at the molecular level is important for interpreting and predicting the dynamics and mechanisms of all chemistry processes. A thorough understanding of the interaction dynamics and energy transfer between gas molecules and surfaces is essential for the study of various chemical reactions. The collisions of diatomic molecules on organic surfaces are crucial to the study of atmospheric chemistry. Molecular beam scattering experiments performed in ultra-high vacuum chambers provide insight into the dynamics of gas-surface interactions.

Many questions remain to be answered in the study of gas-surface interfacial chemistry. For example, what affects the energy transfer between gas molecules and surfaces? How do intermolecular forces affect the interfacial interaction dynamics? We have approached these questions by scattering diatomic gas molecules from functionalized self-assembled monolayers (SAMs). Our results indicate that the intermolecular forces between gas molecules and surfaces play an important role in the energy transfer processes. Moreover, the stronger the intermolecular forces, the more often the incident molecules come into thermal equilibrium with the surface. Furthermore, most of the previous approaches toward understanding gas-surface interaction dynamics considered the interactions as independent incidents. By scattering O$_2$, N$_2$, CO and NO on both CH$_3$- and OH- terminated SAM, we found a correlation between the gas-surface interactions and a bulk property, solubility. Both being strongly affected by intermolecular forces, the gas-surface energy transfer and solubility of gases in surface-similar solvents (water for OH-SAM, n-hexane for CH$_3$-SAM) have a positive correlation. This correlation facilitates the understanding of interfacial dynamics at the molecular level, and helps predict the outcome of the similar-size gas collisions on surfaces.
ACKNOWLEDGEMENTS

This thesis would not have been possible without the hard work and commitment of many individuals during my academic development.

First, I sincerely thank my advisor, Prof. John Morris for his strong and intelligent leadership, patience, academic expertise, and dedication to science. I thank him for being both a superb teacher and a good friend, and for encouraging me to keep going on my academic track. I am truthfully grateful for the precious opportunities I have had in the Morris Group, at Virginia Tech, that helped me improve myself as a student, a communicator, a scientist, and most importantly, an individual. I can never adequately express my gratitude.

I would like to thank my committee members, Prof. Brian Tissue and Prof. Alan Esker, for their encouragement, inspiration, expertise, and helpful discussions. Their enthusiasm for science and dedication to work make me want to improve myself.

I also acknowledge Prof. Diego Troya, for his advanced knowledge in interfacial interaction dynamics, and for his help in performing theoretical calculations that deepen my understanding of my project.

The Morris group has been like a family to me. I am grateful to all Morris group members, past and present, particularly Alec Wagner, Amanda Wilsmeyer, Steve Burrows, Yafen Zhang, Joshua Abelard, Chikki Chan, Robert Chapleski, Angela Edwards, Cecilia Smith, Darren Driscoll, Christopher Tydings, and Dallas Mann. Thank you all for all your extensive help and making work in lab a treat. Thank you for being my second family.

I am extremely grateful for the help from the all the other faculty members and students in Chemistry Department. Thank you for providing such a great academic environment.

My great thanks go to my dear family, my father, Yixun Wang, my mother Lida Liu, and my brother Jinpeng Wang. I thank them for their unconditional love and support in my life. They taught me about the art of life, about how to love, about how to sacrifice, and about how to fight for a better future.
# Table of Contents

Chapter 1 Introduction .............................................................................................................. 1  
  1.1 Overview ......................................................................................................................... 1  
  1.2 Background Introduction ............................................................................................... 3  
    1.2.1 Overview of the Previous Research about Gas-Surface Interactions .................... 3  
    1.2.2 Motivations of this Project ..................................................................................... 5  
  1.3 Introduction of Basic Concepts ..................................................................................... 6  
    1.3.1 Impulsive Scattering and Thermal-Desorption ....................................................... 6  
    1.3.2 Thermal Desorption Fraction and Energy Transfer Fraction ............................... 8  
  1.4 Gas-Surface Scattering Models ....................................................................................... 9  
    1.4.1 Hard-Cube Model .................................................................................................... 9  
    1.4.2 Soft-Cube Model .................................................................................................... 11  
    1.4.3 Hard Sphere Model ............................................................................................... 12  
    1.4.4 Washboard Model ............................................................................................... 14  
  1.5 Solubilities of Diatomic Gas Molecules (O\textsubscript{2}, N\textsubscript{2}, CO, and NO) in Different Liquid Phases ................................................................................................................. 16  
    1.5.1 Solubilities of O\textsubscript{2}, N\textsubscript{2}, CO, and NO in Polar and Nonpolar Solvents ................................. 17  
    1.5.2 Factors that Affect Solubility .................................................................................. 18  
  1.6 Research Objectives ..................................................................................................... 20  

Chapter 2 Experimental Setup ................................................................................................. 21  
  2.1 Overview ....................................................................................................................... 21  
  2.2 Self-Assembled Monolayer ........................................................................................... 23  
    2.2.1 Introduction ............................................................................................................ 23  
    2.2.2 Structure and Characterization of Self-Assembled Monolayers on Gold ............. 24  
  2.3 The Ultrahigh Vacuum Chamber .................................................................................. 28
2.3.1 Introduction................................................................. 28
2.3.2 The Main Chamber, Detector Chamber and Load Lock System.................. 28
2.4 Molecular Beam .................................................................. 30
  2.4.1 Supersonic Molecular Beam ........................................... 31
  2.4.2 Molecular Beam Chamber Structure .................................. 33
  2.4.3 Molecular Beam Characterization ..................................... 34
2.5 Experimental Method .......................................................... 36
  2.5.1 Preparation of Gas Sources and Sample Surfaces ....................... 36
  2.5.2 Sample Transfer ............................................................ 38
  2.5.3 Instrumental Alignment ................................................... 41
  2.5.4 Incident Beam Energy Measurement ................................... 43
  2.5.5 Molecular Beam Scattering .............................................. 44
  2.5.6 Quadrupole Mass Spectrometry ........................................ 45
2.6 Data Analysis .................................................................... 46
  2.6.1 Timing ........................................................................ 46
  2.6.2 Incident Beam Energy .................................................... 54
  2.6.3 Analysis of TOF Data Detected by the Extrel QMS ................... 55

Chapter 3 Results and Discussion ................................................. 60

3.1 Dynamics of Oxygen and Nitrogen Collisions with an OH-SAM ................. 60
  3.1.1 Introduction ............................................................... 60
  3.1.2 Energy Transfer and Thermalization .................................... 62
  3.1.3 Possible Factors that Affect Energy Transfer ......................... 64
3.2 Solubilities of O₂, N₂, CO and NO in Water ....................................... 70
  3.2.1 Introduction to Solubility ................................................ 70
  3.2.2 Correlation between Gas – OH-SAM Interactions and Solubilities in Water .......... 70
3.3 Interactions of Diatomic Gas Molecules with Methyl (CH₃)-terminated SAMs .... 73
3.3.1 Correlation between Gas-CH$_3$-SAM Interactions and Solubilities in Hexane........ 73

3.3.2 Comparison between Hydroxyl-terminated SAMs and Methyl-terminated SAMs ... 74

3.4 Summary and Future Work.......................................................................................... 76

Reference:.......................................................................................................................... 77
Table of Figures

Figure 1.1 Available dynamic pathways in gas-surface interactions .................................................. 2
Figure 1.2 Potential energy surface (PES) of O2-methanol interaction (for the approach
geometry shown in figure) ............................................................................................................. 7
Figure 1.3 Schematic of the hard-cube model.51 ............................................................................ 10
Figure 1.4 Schematic of the soft-cube model.45 ........................................................................... 12
Figure 1.5 Schematic of hard sphere model.56 .............................................................................. 13
Figure 1.6 The schematic of the washboard model.59,58 ................................................................. 15
Figure 2.1 Top view schematic of the UHV chamber for surface-diatom gas molecules
interactions ................................................................................................................................. 22
Figure 2.2 Schematic of sulfur-gold spacing in SAM.45 ................................................................ 24
Figure 2.3 Schematic of SAM on gold.46 ...................................................................................... 25
Figure 2.4 IR spectra of CH$_3$-SAM and OH-SAM. ..................................................................... 26
Figure 2.5 Schematic of the ultrahigh vacuum main chamber.45 ................................................... 29
Figure 2.6 Side view of the molecular beam chamber.45 ................................................................ 34
Figure 2.7 Top view of the in-line beam energy characterization system.45 .................................. 35
Figure 2.8 Schematic of apparatus for gas source preparation. ..................................................... 37
Figure 2.9 Schematic of the load lock system. ............................................................................... 39
Figure 2.10 Picture of the sample mount. ..................................................................................... 40
Figure 2.11 Z-axis view of the sample alignment schematic. 45 .................................................... 42
Figure 2.12 TOF distribution of Ar in a 2%Ar/98%H$_2$ molecular beam detected by RGA. .......... 43
Figure 2.13 TOF distribution of an Ar (2%Ar/98%H$_2$) beam scattered from an OH-SAM. ....... 45
Figure 2.14 Side view and front view of the chopper wheel and trigger ....................................... 46
Figure 2.15 Front view of chopper wheel for demonstration of the time lag between the beam
pulse and the trigger pulse. ......................................................................................................... 48
Figure 2.16 Schematic of the chopper wheel time offset calculation. ................................................................. 49
Figure 2.17 Signal pulses in an oscilloscope. ........................................................................................................ 49
Figure 2.18 TOF distributions of a molecular beam under CCW and CW rotation of the chopper wheel. ................................................................. 50
Figure 2.19 The TOF distribution (A) and the final energy distribution (B) of pure Ar scattering on an OH-SAM. The open circles represent the experimental data and the solid lines are the Boltzmann distributions at the surface temperature. ................................................................. 52
Figure 2.20 Time-corrected TOF distribution of Ar in the 2%Ar/98%H₂ beam after colliding with an OH-SAM. ......................................................................................................................... 53
Figure 2.21 Time corrected TOF distribution of Ar in an incident 2%Ar/98%H₂ molecular beam detected by RGA. .......................................................................................................................................................... 55
Figure 2.22 (A) TOF distribution of Ar atoms in a 2%Ar/98%H₂ beam after scattering from an OH-SAM; (B) The corresponding translational energy distribution P(E_f) from (A).................................................. 58
Figure 3.1 Final energy distributions of ¹⁶O₂ and ¹⁴N₂ scattering from an OH-SAM. Solid lines represent for the TD fraction. ................................................................. 63
Figure 3.2 Final energy distributions of ¹⁵N₂ and ¹⁴N₂ scattering from OH-SAM. Solid lines represent for the TD components. ......................................................................................................................... 65
Figure 3.3 Theoretical calculations of Potential Energy Surface (PES) diagrams for the interactions between O₂, N₂ and methanol with four different approaches. .................................................. 66
Figure 3.4 The final energy distributions comparison: ¹⁴N₂ and CO (A), ¹⁵N₂ and NO (B). Solid lines represent for the TD components. .......................................................................................................................... 68
Figure 3.5 Final energy distributions of NO, O₂, N₂, and CO scattering from an OH-SAM. ........ 71
Figure 3.6 Thermal desorption fractions of gas scattering on an OH-SAM versus the solubilities of gas molecules in water. ⁶³ ................................................................................................................................................................................ 72
Figure 3.7 Final energy distributions of NO, O₂, N₂, and CO scattering from a CH₃-SAM. ........ 73
Figure 3.8 Thermal desorption fractions of gas scattering on CH$_3$-SAM versus the solubilities of gas molecules in hexane.$^{61, 62, 64, 65}$
List of Tables

Table 1.1 Solubilities of N\textsubscript{2}, CO, O\textsubscript{2} and NO in water and n-hexane\textsuperscript{61, 62, 63, 64, 65} .......................... 17

Table 2.1 Comparison of IR peak positions of the observed and well-ordered SAMs. ............ 27

Table 3.1 Selected similarities of \textsuperscript{16}O\textsubscript{2} and \textsuperscript{14}N\textsubscript{2}. \textsuperscript{84} ........................................................................................................ 60

Table 3.2 Other properties of \textsuperscript{16}O\textsubscript{2} and \textsuperscript{14}N\textsubscript{2}. \textsuperscript{84} ........................................................................................................ 61

Table 3.3 Results of \textsuperscript{16}O\textsubscript{2} and \textsuperscript{14}N\textsubscript{2} scattering on an OH-SAM. ................................................................. 64

Table 3.4 Results of \textsuperscript{15}N\textsubscript{2} and \textsuperscript{14}N\textsubscript{2} scattering on an OH-SAM......................................................... 65

Table 3.5 Comparison between \textsuperscript{15}N\textsubscript{2} and NO, \textsuperscript{14}N\textsubscript{2} and CO scattering on an OH-SAM for

E\textsubscript{i}=43kJ/mol. .................................................................................................................. 69
Chapter 1 Introduction

1.1 Overview

Gas-surface interactions have been an attractive field of study for centuries. Being involved in all gas-surface interfacial reactions, the interactions between gases and surfaces not only play an important role in the maintenance of the atmospheric balance and the control of air pollutant concentrations, but also have significant practical applications in catalysis, material science, and astrochemistry.\textsuperscript{1-14} Therefore, being able to understand gas-surface interactions is beneficial for predicting the concentrations of environmentally critical compounds.

In the real world, gas molecules are constantly bombarding on all types of surfaces with a variety of impact angles and translational energies. Hence, a model system is needed to help study atmospherically relevant reactions. In our experiments, molecular beams (MB) and self-assembled monolayers (SAM) serve as the models of the gas source and the surface, respectively.

Molecular beam methods are widely employed in the research of gas-surface interactions. A molecular beam is created by expanding a gas of interest into a vacuum chamber through a small aperture. After the expansion, a steady stream of gas molecules is formed. This gas stream has well defined cross sectional area, unified direction, and well characterized average translational energy. Molecular beams help ensure the gas source used in the experiments is well defined.

Self-assembled monolayers are highly ordered, well-characterized and highly reproducible thin layers. They are usually used as models of organic surfaces in many types of interfacial studies.\textsuperscript{15-17} In our work, SAMs serve as model organic surfaces.
The combination of MBs and SAMs is the foundation of the research presented in this thesis. By applying MBs and SAMs, the complex situation (uncharacterized gas molecules and complicated surfaces) is simplified, which affords one the ability to systematically study how surface properties affect the interactions.

![Diagram showing dynamic pathways in gas-surface interactions](image)

Figure 1.1 Available dynamic pathways in gas-surface interactions.

As illustrated in Figure 1.1, gas molecules in the MB are introduced to a functionalized SAM in the experiments. Previous work showed that there are two possible pathways for the incident gas molecules in the gas-surface interactions. One is called thermal-desorption (TD), and the other one is impulsive scattering (IS). The gas molecules may hit on the surface then directly recoil back to the gas phase without further interactions. These gas molecules are described as impulsively scattered molecules. On the other hand, before leaving the surface, the gas molecules that go through the thermal-desorption pathway become completely thermalized with the surface. In the gas-surface interactions, a gas molecule may go through either of these two pathways.
By using different gas sources and modifying the functionality of the SAMs, we are able to explore a variety of gas-surface interactions. Then, based upon the interpretation of the experimental results, the role of surface and incident gas molecule structure on gas-surface collisions can be deduced.

Facilitated by both experiments and theoretical calculations, the research project presented in this thesis is aimed at developing a fundamental understanding of the dynamics of interactions between gases and surfaces. Diatomic gas molecules (O\textsubscript{2}, N\textsubscript{2}, CO and NO) and organic surfaces (OH-terminated and CH\textsubscript{3}-terminated SAM) are employed as the gas sources and model surfaces to help study the essential factors that affect gas-surface interactions, and furthermore, search for possible correlations between gas-surface interactions and bulk phase properties (solubility).

1.2 Background Introduction

1.2.1 Overview of the Previous Research about Gas-Surface Interactions

Interfacial collisions, as the very first step of all gas-surface reactions, are one of the most critical factors that affect the equilibrium between gases and surface-adsorbates. Therefore, interfacial collisions and the following interactions play important roles in material degradation and the regulation of pollutant concentrations\textsuperscript{18,19}. It is important to acquire knowledge about the dynamics of gas-surface interactions. Intensive work has been done to study these interactions and help understand the mechanisms and dynamics. Thanks to several outstanding scientists’ dedication to the study of gas-surface interfacial science, extensive experimental investigations and theoretical work show that quite a few chemical and physical properties affect the gas-surface collision dynamics and energy transfer processes\textsuperscript{20-44}.
Day et al. studied how surface functional groups affect the gas-surface energy transfer process.\textsuperscript{45} Comparison of scattering dynamics of argon atoms from CH$_3$-SAMs (self-assembled monolayers with CH$_3$- terminal groups), CH$_2$=SAMs, OH-SAMs and COOH-SAMs were made under identical experimental conditions. The results showed that the energy transfer between argon atoms and CH$_3$-SAMs, and (CH$_2$=SAMs) are more efficient than the energy transfer with the other two SAMs.\textsuperscript{45} They concluded that this phenomenon is caused by the formation of intra-monolayer hydrogen bonds in the OH-SAMs and COOH-SAMs. Hydrogen bonds make the surface more rigid, which limits the energy transfer from gas molecules to the surface. Further study of the terminal group effect is demonstrated in the work of Lu et al.\textsuperscript{46} They studied the scattering of triatomic molecules on CH$_3$-SAMs, OH-SAMs and CF$_3$-SAMs. Compared with the CH$_3$-SAM and OH-SAM, a significant decrease in the TD fraction was found in the scattering on the CF$_3$-SAM. The CF$_3$-SAM has a much bigger moment of inertia than the other SAMs, as a result, the decreased flexibility leads to less efficient energy transfer.\textsuperscript{46} Also, in the same study, they did not observe an obvious TD difference for scattering from the CH$_3$-SAM versus the OH-SAM. Even though the OH-SAM is more rigid due to the formation of intra-monolayer hydrogen bonds, the attractive forces between the polar triatomic gas molecules (CO$_2$, O$_3$ and NO$_2$), and the OH-SAM were responsible for bring more molecules into thermal equilibrium. Therefore, energy transfer depends on the properties of both the incident gas molecules and the surfaces.

Extensive research has been done to help unveil how the properties of gas molecules affect the gas-surface interactions. As shown in the work of Alexander et al., changing the mass of incident gas molecules (Ne, Ar and Kr) significantly varied the final scattering results.\textsuperscript{47} The increase of molecular mass facilitated the transfer of energy and resulted in a higher TD fraction. This result can be explained by using the concept of momentum. The energy transfer in gas-surface interactions for a simple model can be quantified by using equation (1). In equation (1), $\Delta E$ stands for the energy transferred from the gas molecules to the surface, it is defined as the
difference between the incident energy and final energy of the gas molecules; \( \mu \) is the mass ratio of gas molecule and surface, \( m_g/m_s \); \( E \) is the incident energy.

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

(1)

In gas-surface collisions, the effective mass of the surface (the mass of the surface segment that interacts with gas molecules) is much higher than the mass of gas molecules. Heavier gas molecules correspond to a smaller mass difference between the gas and the surface. Based upon the energy transfer equation, (1), smaller mass differences are beneficial for energy transfer. Therefore, under the same experimental conditions, the gas molecules with higher mass can transfer more energy to the surface.

Saecker et al. have done further research about how the properties of gas molecules affect gas-surface interactions. They focused on the study of interactions between polar or non-polar gas molecules and liquid surfaces. Their research demonstrated that the stronger the intermolecular forces (dipole-dipole interactions) between the gas molecules and the liquid surfaces are, the more efficient the energy transfer will be during the interactions.\(^{48}\)

1.2.2 Motivations of this Project

Even though various studies have been performed to help understand the dynamics of gas-surface interactions, we cannot observe the gas-surface interactions directly. Consequently, how gas molecules and surfaces behave during and after the collisions and what factors affect their behavior during the interactions, are still not fully understood.

Diatom molecules compose approximately 99% of the ambient gas molecules in the environment. Oxygen and nitrogen are the two most abundant gases in the atmosphere (21% and 78% respectively\(^{49}\)). However, few studies have been done on the scattering of diatomic gas molecules on organic surfaces. Oxygen and nitrogen are simple, closed shell diatomic molecules. They have very similar properties, such as bond lengths, degrees of freedom,
polarizability and molecular masses. Because oxygen and nitrogen possess several similar properties, it is interesting that their solubilities in both water and hydrocarbon solvents are quite different. In water, the solubilities of oxygen and nitrogen are 0.230 and 0.117 (×10⁻⁴ mole fraction), respectively; and in hexane, the corresponding values are 20.5 and 13.9 (×10⁻⁴ mole fraction).

The significant difference between the solubilities of oxygen and nitrogen indicates the two types of gas molecules interact with the liquid phase differently. This thesis probes whether these differences are reflected in the dynamics of gas-surface collisions. Saecker et al. have reported a positive correlation between solubilities of gas molecules (in the solvents that have similar structure with the liquid surfaces) and the TD fractions in gas-liquid surface interactions.⁴⁸ However, the studies described below are the first to explore such trends at the gas-solid organic surface interface.

1.3 Introduction of Basic Concepts

1.3.1 Impulsive Scattering and Thermal-Desorption

A gas molecule may go through two possible pathways after its first impact with a surface. One of them is called impulsive scattering (IS), the other pathway is thermal desorption (TD).⁴⁶ These two limiting pathways often determine the fate of the collisions.

After the interfacial collision, the gas molecules that hit on the surface once or multiple times, then bounce back into the gas phase directly without further interactions are considered as following the mechanism of impulsive scattering. These types of gas molecules only transfer part of their incident translational energy to the surface and retain the remainder. Alternatively, the molecules following the other mechanism (thermal-desorption) will not leave the surface so easily. The TD gas molecules will dissipate all their incident translational energy to the surface by going through multiple interfacial collisions. At this point, they may become thermally
accommodated on the surface. Then, after gaining energy from thermal fluctuations of the surface, the TD gas molecules can desorb back into the gas phase. Therefore, after recoil back into the gas phase, the TD gas molecules maintain the same statistical energy distribution as the surface, which is the Boltzmann distribution at the surface temperature.

Figure 1.2 Potential energy surface (PES) of O2-methanol interaction (for the approach geometry shown in figure).

The description above shows the general idea about IS and TD. These two pathways are governed by the potential energy surface (PES) and the collision energy. Take the interaction of O2 and methanol as an example; the PES is shown in Figure 1.2. In the gas-surface interaction, a gas molecule typically is attracted at first, and so accelerated as the gas molecule approaches a surface. After this acceleration, the gas molecule will hit the repulsive
wall. At this point, because of the impinging momentum, the gas molecule continues its trajectory toward the surface. But the repulsive wall will slow the gas molecules down and finally stop the gas molecules from getting closer to the surface. This is where the majority of energy transfer occurs. After the energy transfer process, the scattering gas molecules exit along the attractive tail of the potential energy surface. If the gas molecule only loses part of its initial translational energy to the surface, and the retained energy is higher than the potential well, it will be able to escape and return to the gas phase. This type of molecules is considered as going through the IS pathway. However, if a gas molecule loses all of its initial energy to the surface, then during this reflection, it will need to gain energy from the thermal fluctuations of the surface. When this type of gas molecules obtains enough energy, they will desorb into the gas phase with a Boltzmann distribution of energies at the surface temperature. Gas molecules may also go through the TD pathway when they encounter very corrugated surfaces or their translational energies in the grazing direction are not conserved after the collisions. For these cases, the gas molecules are more likely to go through multiple collisions with the surface and redistribute their energy, then they will either gain enough energy and escape from the surface or they will encounter the surface and collide with it again.

1.3.2 Thermal Desorption Fraction and Energy Transfer Fraction

The percentages of gas molecules that go through IS and TD pathways ultimately determine the fate of a gas-surface interaction. In this thesis, unreactive gas-surface interactions will be discussed. Therefore, the gas molecules will either go through the IS pathway or the TD pathway. Compared with gas molecules that go through IS pathway, the TD gas molecules lose more of their initial energy to the surface. Hence, the gas-surface interaction with a higher percentage of TD gas molecules will be more intensive and have more efficient energy transfer between the gas molecules and the surfaces.
Energy transfer fraction is another important criterion for evaluating the interactions between gas molecules and surfaces. It usually is represented by the Greek symbol alpha (\( \alpha \)) and defined by equation (2).\(^{45} \) In equation (2), \( E_i \) and \( E_f \) are the initial and final energy of the gas molecules, respectively.

\[
\alpha = \frac{E_i - E_f}{E_i}
\]  

(2)

The energy transfer fraction is the difference of initial and final translational energy per unit of initial energy. As shown by equation (2), with specific initial energy, a higher final energy corresponds to a lower energy transfer fraction. During gas-surface interactions, TD gas molecules transfer more energy to the surface than the IS molecules do;\(^{46} \) as a result, their final energies are lower. Hence, with well-defined gas sources and surfaces, a higher TD fraction always indicates a higher energy transfer fraction.

1.4 Gas-Surface Scattering Models

The dynamics of gas-surface interactions are quite complex. To help understand these interactions, gas-solid surface models have been developed based upon classical mechanics.\(^{50,51} \) By using these classical models, the interaction processes can be broken into parameters that can be verified experimentally. Therefore, predictions of the outcomes of gas-surface interactions and energy transfer become possible. Here, several classical models built by previous scientists will be introduced.

1.4.1 Hard-Cube Model

After gas-surface scattering experiments emerged during the late 1960s,\(^{52,53} \) a model was needed to help interpret the scattering data. Therefore, Logan and Stickney\(^{54} \) developed a model based upon classical mechanics to fulfill the requirement at that time. This model is now known as the hard-cube model.
In this model, the gas molecules are treated as rigid spheres and they fly toward the flat upper surface of a cube, which is also rigid. As shown in Figure 1.3, the momentum of the gas molecules in the direction that is parallel to the cube’s surface is conserved throughout the interaction, $V_{pi} = V_{pf}$. The energy transfer is considered to occur in the normal direction with respect to the surface. Furthermore, the incident angle and final angle ($\theta_i$ and $\theta_f$, respectively) are both defined for a given surface temperature, $T_{surf}$, and the initial momenta of both the surface and the gas molecule. At this point, the only adjustable parameter will be the mass ratio of the gas molecule and the surface. Hence, this enables the simplification of the original problem to a one-variable problem. As shown in equation (1), $\mu$ is this mass ratio with $m_g$ as the mass of one gas molecule and $m_{surf}$ as the effective surface mass.

The main accomplishment of this model is that it provides a direct conclusion: the energy transfer between gas molecules and solid surfaces will maximize when the mass of the gas

Figure 1.3 Schematic of the hard-cube model.\textsuperscript{51}
molecules is equal to the mass of the surface groups ($\mu=1$). In scattering experiments, if one can probe the amount of energy transferred during the collision, one may be able to apply this result to help predict how many surface groups are involved in the interactions. Despite the rudimentary nature of this model, it provides a rough prediction of how the mass ratio of the gas and the surface affects energy transfer.

### 1.4.2 Soft-Cube Model

As an upgrade of the previously mentioned hard-cube model, the soft-cube model is a little bit more advanced than its predecessor since it includes additional aspects of the system. The soft-cube model was devised by Logan and Keck in 1968.\textsuperscript{54} In this model, instead of assuming that the surface is a rigid face of a cube, it considers an attractive well and an exponential repulsive component during the gas-surface interaction.\textsuperscript{55}

As shown in Figure 1.4, in the soft-cube model, the cube is considered as attached to a rigid wall through a linear spring. Therefore, rather than an isolated cube, this model simulates the solid-solid interactions during the gas-surface collision.

Hence, this model simulates the interaction between an incident gas molecule and a one-dimensional cube oscillator with a frequency $\omega$. When a gas molecule approaches the oscillator, it will reach the line of the potential well illustrated by the box in the lower right side of the Figure 1.4. The interaction between the gas molecule and the cube oscillator will initially be attractive, and then become exponentially repulsive. Thus, there are two adjustable parameters in this model in addition to $\mu$, the oscillation frequency $\omega$ and the potential well depth $D$. This large number of variables makes this model much more complex than the hard-cube model. However, this model appears to be a more accurate approximation of reality. More importantly, the model provides insight into several key aspects of gas-surface collision dynamics.
Figure 1.4 Schematic of the soft-cube model.\(^{45}\)

There are two main benefits achieved in the upgrade from the hard-cube model to the soft-cube model. One is that the interactions between gas molecules and surfaces are not treated as completely impulsive collisions, but they have a finite interaction time. This understanding basically built up the foundation for the later understanding of the thermal-desorption pathway of gas-surface interactions. The other benefit is despite a collision being defined as a single gas molecule colliding with a single atom on the surface, the later motion of the surface atom may couple with its surrounding atoms and, as a result, approximates the collision between the gas molecule and a segment of the surface.

### 1.4.3 Hard Sphere Model

Both the hard-cube and soft-cube models are built on the assumption that the surface behaves as a flat solid cube. However, that is not always an appropriate approximation. There are conditions under which a surface can be highly corrugated. For example, a gas molecule
may just interact with an individual terminal functional group of the surface that protrudes into the gas phase. In this case, the gas molecule and the surface are more likely to behave as two rigid spheres rather than a sphere and a flat surface. To model this type of gas-surface interaction, the hard sphere model was developed.

![Figure 1.5 Schematic of hard sphere model.](image)

A schematic of the hard sphere model is provided in Figure 1.5. In this model, the calculation of the amount of energy transferred between gas molecules and surfaces is similar to the procedure demonstrated in the cube-models, as shown in equation (3). In this case, the energy transfer is directly related to the mass ratio and another parameter called deflection angle, $\chi$. There is no potential well involved in the energy transfer equation for this model, so the collision between these two spheres is treated as being completely impulsive.
The definition of the deflection angle is \( \chi = 180^\circ - \theta_{i,lo} - \theta_{f,lo} \). From equation (3), we can see that with a defined mass ratio, the energy transfer will be maximized when \( \chi \) is 180° and minimized when \( \chi \) is 0°. That is, based upon Figure 1.5, the energy transfer will be greatest when the two spheres undergo a head-on collision. When the collision is glancing, the energy transfer will be the least efficient. This model has been successfully applied to the study of thermal roughening effects on the angular distribution of scattering in gas-liquid collisions by the Nathanson group.\(^{57}\)

\[
\frac{E_{inc} - E_{fin}}{E_{inc}} = \frac{2\mu}{(1 + \mu)^2} \left[ 1 - \cos \chi (1 - \mu^2 \sin^2 \chi)^{1/2} + \mu \sin^2 \chi \right]
\] (3)

### 1.4.4 Washboard Model

Developed by Tully,\(^{58}\) the washboard model is another extension of the classical hard-cube model. However, this model accounts for the corrugation of the surface.

To simulate the corrugation of the surface, the impact interface is modeled as a cosine wave. As illustrated by Figure 1.6, the flat surface of the cube is defined by the local incident and final angle; the tangential momentum is conserved with respect to the local normal, but will change with respect to the global normal. The cosine-wave shape of the surface is defined by equation (4).

\[
Z(x) = A \cos \left( \frac{2\pi x}{a} \right)
\] (4)
Once the incident gas molecule crosses a defined point, its direction may change due to the existence of a potential well. Within the washboard model, there are three parameters that affect energy transfer. They are the mass ratio ($\mu$), the potential well depth ($D$), and the newly introduced parameter called corrugation strength parameter ($\alpha_m$). As shown in equation (5), the definition of this parameter is the maximum obtainable angle between the local surface normal and the global surface normal.

$$\alpha_m = \tan^{-1}\left(\frac{2\pi A}{a}\right)$$

To apply the washboard model to analysis of experimental scattering results, other parameters must be defined. These parameters are the momentum distribution of the surface, surface temperature, and the incident and final angle of the gas molecules. Even though it is an obvious oversimplification to simulate a corrugated surface as a cosine wave, this model has demonstrated that surface roughness and corrugation are essential for the modeling of gas-
surface interactions. For example, by applying the washboard model, Kondo et al. studied the effect of molecular structure on gas-surface scattering, and Yan et al. further developed a washboard model that takes moment of inertia into account. By employing this model, they successfully modeled Ar and Ne scattering from an alkythiolate self-assembled monolayer surface and reproduced the major results obtained by classical trajectory simulation of the same system.

All the models described above provide insight into the initial gas-surface collision dynamics. However, after the first impact, influences such as intermolecular forces may dominate the interaction. To gain the knowledge of interaction dynamics after initial collision, it is reasonable to look into gas molecule solubility in liquids. As a bulk property, solubility may provide insight into gas-liquid collisions, which can be used as references for gas-surface interactions after the initial impact.

1.5 Solubilities of Diatomic Gas Molecules (O\textsubscript{2}, N\textsubscript{2}, CO, and NO) in Different Liquid Phases

Solubility is the property that shows the extent to which a solid, liquid or gaseous chemical dissolves into a solid, liquid or gaseous solvent to form a homogeneous solution. The value of solubility is usually used to identify how much a solute can be dissolved into a unit amount (volume or mass) of solvent. The solubility of a substance depends upon the physical and chemical properties of both the solute and the solvent. The interactions between solute molecules and solvent molecules significantly affect the dissolving process.
1.5.1 Solubilities of O₂, N₂, CO, and NO in Polar and Nonpolar Solvents

In this thesis, water and n-hexane are used as examples for polar and nonpolar solvents, respectively. The solubilities of O₂, N₂, CO, and NO in both water and n-hexane at room temperature and atmospheric pressure are shown in Table 1.1.

The solubility data clearly shows that for the four types of gas molecules, their solubilities in water are consistently two orders of magnitude smaller than the solubilities in n-hexane. Compared with all the diatomic gas molecules studied in this project, water molecules have much bigger dipole moments (1.85 D). Therefore, the interactions between water molecules are more favorable than the interactions between water molecules and gas molecules. As a result, during the solvation process, water molecules will pack around gas molecules and form ordered shells. Furthermore, each water molecule can form two hydrogen bonds with other water molecules; the formation of the hydrogen-bonding networked structure of water also makes the interaction between gas molecules and water molecules less favorable. However, this problem does not exist in gas-hexane interactions. Therefore, the entropy of solvation of the more ordered water-gas system will be relatively smaller than the hexane-gas system.

Another point suggested by Table 1.1 is that for both solvents, either polar or nonpolar, the solubilities of the gas molecules all follow the trend: \( S_{\text{NO}} > S_{\text{O}_2} > S_{\text{CO}} > S_{\text{N}_2} \). Thus, in both solvents, the significance of gas-liquid interactions decreases in the same trend.

Table 1.1 Solubilities of N₂, CO, O₂ and NO in water and n-hexane

<table>
<thead>
<tr>
<th>Gas</th>
<th>N₂</th>
<th>CO</th>
<th>O₂</th>
<th>NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility in water (( \times 10^{-4} ) mole fraction)</td>
<td>0.117</td>
<td>0.172</td>
<td>0.230</td>
<td>0.348</td>
</tr>
<tr>
<td>Solubility in hexane (( \times 10^{-4} ) mole fraction)</td>
<td>13.9</td>
<td>17.55</td>
<td>20.5</td>
<td>23.5</td>
</tr>
</tbody>
</table>

The solubility data provides particularly clear trends for both the comparison between polar and nonpolar solvents, and the comparison between different types of gas molecules. The
first step for a gas molecule to enter a liquid is energy transfer, thermal accommodation and then solvation. So you might expect them to be related; are they? $S_{N_2}$ is about a factor of 3 smaller than $S_{N_O}$; does this predict a different gas-surface energy transfer dynamics? It is interesting to learn about atomic scale scattering dynamics from bulk-phase properties and even more exciting to explore if there is a correction between these two. The research project presented in this thesis will help answer these questions.

1.5.2 Factors that Affect Solubility

The solubility of a specific solute in a specific solvent is determined by both the physical and chemical properties of the system. Factors like pressure, temperature, pH, and entropy of solvation all play significant roles in governing solubility.

Other than those factors that are mentioned above, the intermolecular force is also one of the most important factors that affect the solubility. The intermolecular forces are attractive and repulsive forces between neighboring particles. Even though these forces are not as strong as intramolecular forces, such as covalent bonds, they are still quite critical for atomic level and molecular level interactions. There are several types of intermolecular forces, such as dipole-dipole forces, ion-dipole forces and van der Waals forces.

Dipole–dipole forces only exist between molecules that possess permanent dipole moments. This type of force is an electrostatic force that tends to align the molecules to maximize the attraction. One typical example of dipole-dipole interactions is the formation of hydrogen bonds. Hydrogen bonds are often cited as the strongest type of dipole-dipole interaction; generally, the bond energy of hydrogen bonds is about 20 kJ/mol. Consider two polar atoms interacting with each other, the potential energy possessed by the system depends upon the dipole moment, $\mu$, of each molecule and the separation, $r$. This energy of the dipole-dipole interaction is given by equation (6), where $\epsilon$ is the permeability of space.
Ion-dipole forces, or sometimes ion-induced dipole forces lead to interactions between ions and molecules with dipole moments. Since ions have higher charge than just a dipole moment, ion-dipole interactions are usually stronger than dipole-dipole interactions. And also, because of the high charge of an ion, it can sometimes distort a non-polar molecule to form an induced dipole moment in this molecule. Then the interactions will be considered as ion-induced dipole moment interactions. The energies of both an ion-permanent dipole interaction and an ion-induced dipole interaction are inversely proportional to the fourth power of the distance \((1/r^4)\). \(^{67}\)

The van der Waals forces, are considered the most common intermolecular force. It is the sum of all the attractive and repulsive intermolecular forces other than the types described above (dipole-dipole, ion-dipole forces). Generally, van der Waals forces include three types of forces, Keesom force, London dispersion force, and Debye force. The London dispersion force is the force between two instantaneously induced multipoles in molecules without permanent multipole moments. The Keesom force is the attractive interaction of dipoles that are ensemble averaged over different rotational orientations of the dipoles. It is assumed that the molecules are constantly rotating and never get locked into place. The Debye force is considered as the force between a permanent dipole and a corresponding induced dipole. Both the Keesom force and Debye force depend upon the inverse sixth power of the separation and are far weaker than dipole-dipole forces, which are proportional to the inverse third power of the distance, but stronger than the London dispersion force, \(^{68}\) which also depends on \(r\) as \((1/r^4)\).

The balance of intermolecular forces is not only play an important role in the determination of solute solubility in a specific solvent, but also the key factor in the study of the interactions between gas molecules and organic surfaces. Theoretically, a deeper potential well

\[
V = -\frac{2\mu_1\mu_2}{4\pi\varepsilon_0 r^3}
\]  \((6)\)
and a repulsive wall that is closer to the surface are beneficial for more efficient gas-surface energy transfer.

1.6 Research Objectives

The research presented in this thesis is focused on developing a fundamental understanding of the dynamics of interactions between diatomic gas molecules (O₂, N₂, CO, and NO) and organic surfaces (OH-terminated and CH₃-terminated self-assembled monolayers), analyzing the factors that affect these interactions, and exploring the possible correlations between gas-solid surface interactions and bulk thermodynamic properties of analogous system.
Chapter 2 Experimental Setup

2.1 Overview

The experimental setup has been described in detail in several previous papers. As indicated in Figure 2.1, all experiments are performed under vacuum. In order to gain a well-controlled gas source, the characterization of the incident molecular beam is set to be the first step of the experiments. A molecular beam is generated in the high vacuum (10\(^{-7}\) Torr) molecular beam chamber and introduced into the ultrahigh vacuum (UHV) main chamber. Using the sample manipulator, we can change the position of the surface inside the main chamber. With the sample mount away from the gas pathway, the molecular beam passed directly into a Residual Gas Analyzer (RGA) (Stanford Research System), which is a quadrupole mass spectrometer (QMS). During experiments, the RGA is set to record the time of flight (TOF) distribution of particles with a specific mass-charge ratio, which will be 32, 28, 28 and 30 for O\(_2\), N\(_2\), CO and NO, respectively. Based upon the dimensions of the chamber, the distance from the mechanical chopper wheel to the RGA is 45.3cm. Therefore, after acquiring TOF distribution, the incident energy of the molecular beam can be determined according to the relationship shown in equation (7).

\[
E_{in} = \frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{L}{t}\right)^2 \quad (7)
\]

After the characterization of the incident beam, the sample mount can be moved back to the gas-pathway. At this point, the sample mount may house one or two surface samples. With pre-aligned surface coordinates, the molecular beam can be introduced to impinge upon one surface with an incident angle of 30° with respect to the surface normal. After interacting with the surface, the gas molecules recoil back into the gas phase. Another QMS (Extrel) is employed to detect the reflected gas molecules with a final angle of 30° with respect to the
surface normal. By setting the detected mass-to-charge ratio, the TOF distribution of the gas molecules scattered from the surface is simultaneously generated while the molecules are detected by the QMS. With a known distance from the surface to the Extrel QMS, 29 cm, and the TOF distribution, the final energy distribution of the reflected gas molecules can be calculated. Analysis of the energy distributions for both the incident beam and the scattered gas molecules provides insight into how the diatomic molecules exchange energy with both CH$_3$-SAMs and OH-SAMs.

![Diagram of the UHV chamber](image)

**Figure 2.1** Top view schematic of the UHV chamber for surface-diatomic gas molecules interactions.

The load lock (LL) sample transfer system is another important component of the instrument. The employment of the LL chamber eliminates the possibility of directly exposing the main chamber to the atmosphere during sample transfer, and as a result, helps maintain the low pressure inside the UHV main chamber and avoid contamination.
2.2 Self-Assembled Monolayer

2.2.1 Introduction

SAMs that were employed in this experiment were prepared by using alkanethiols and “gold slides” (Au evaporation onto Cr-coated glass slides). To clean the gold slides, they were immersed into piranha solution, which is the mixture of 70% sulfuric acid and 30% hydrogen peroxide (volume/volume ratio) for at least 1 hour, and then rinsed by copious amounts of deionized water followed by ethanol to get rid of the piranha solution residue. Then, the cleaned gold slides were placed into a 1 mM ethanolic solution of alkanethiols (1-octadecanethiol (Sigma-Aldrich) for CH₃-SAMs and 16-mercapto-1-hexadecanol (Sigma-Aldrich) for OH-SAMs). The gold slides remained in the alkanethiol solution for at least 24h prior to use. During this 24h period, the alkanethiols in the solution chemisorbed to the surface of the gold slides by forming a covalent bond through sulfur atoms at the end of the chains. Furthermore, 24-hour immersion ensures the SAMs possess good chain order and packing density. After removal from the solution, the slides were rinsed thoroughly by ethanol, blown dry by ultra-high purity (UHP) nitrogen (Airgas), placed on a sample mount, and immediately transferred into the UHV chamber through the load lock sample transfer system. In the UHV chamber, a high precision manipulator was employed to precisely modify the coordinates of the sample mount to satisfy experimental needs.

The preparation method of SAMs described above has been confirmed to be reliable by several previous research projects. The prepared SAMs were highly ordered in both long range and short range. To optimize the chain-chain interactions, the distance between each chain turns out to be about 5Å, and in both the CH₃-SAMs and OH-SAMs that are employed in this experiment, all the chains tilt approximately 30° with respect to the surface normal.
2.2.2 Structure and Characterization of Self-Assembled Monolayers on Gold

As previously described, the SAMs that are employed in our research project are n-alkanethiols on gold. In this type of SAM, the sulfur atoms at the end of each long carbon chain bond to the pre-cleaned gold surface. The sulfur-gold spatial relationship is depicted in Figure 2.2.

Figure 2.2 Schematic of sulfur-gold spacing in SAM.\textsuperscript{45}

The formation of Au-S covalent bonds produces a final average intermolecular alkane chain distance of 5 Å. As shown in Figure 2.2, each of the sulfur atoms interacts with three gold atoms on the substrate. The nearest spacing of the top sulfur atoms is $\sqrt{3} \times 2.88$ Å (the nearest spacing of the bottom Au atoms), and the sulfur lattice is rotated 30° relative to the gold lattice. Therefore, the overlay of sulfur and gold atoms forms an overall ($\sqrt{3} \times \sqrt{3}$) R30° lattice.\textsuperscript{45} After the
formation of bonds between the alkanethiols and the gold substrate, the conformation of the alkane chains is optimized and stabilized at the lowest energy state. For OH-SAMs and CH$_3$-SAMs, the optimized structure are reached when the tilt angle of chains is approximately 30° to 34° with respect to the surface normal, as shown in Figure 2.3.

Figure 2.3 Schematic of SAM on gold.$^{45}$

Previous literature shows that, when the alkane chain of an alkanethiol contains 6 or more carbons, the formed SAMs exhibit very high stability and crystal-like long-range order. Since the alkanethiols that are employed in this research project are 1-octadecanethiol ((Sigma-Aldrich), CH$_3$-SAMs) and 16-mercapto-1-hexadecanol ((Sigma-Aldrich), OH-SAMs), which contain 18 and 16 carbons in the alkane chains, respectively, the SAMs that are prepared based on the method described above most likely produce highly ordered structures.
Characterization of the SAMs is critical for verifying their structures before performing a gas-surface collision experiment. Therefore, reflection absorption infrared spectroscopy (RAIRS) was employed. The structure of a surface can be characterized by using RAIRS.

![IR spectra of CH$_3$-SAM and OH-SAM.](image)

Figure 2.4 IR spectra of CH$_3$-SAM and OH-SAM.
As shown in Figure 2.4, the IR spectrum of a highly ordered CH₃-SAM shows clear and sharp peaks for the symmetric and asymmetric C-H stretch for both CH₃ groups and CH₂ groups. In the spectrum of an OH-SAM, the two peaks for the C-H stretch of CH₂ groups can be identified. The wavenumbers of these modes in highly ordered SAMs have been reported previously. The peak positions in the IR spectra, Figure 2.4, agree well with the literature values (as shown in Table 2.1). Therefore, we are confident that the SAM samples we employed in our experiments were well ordered.

Table 2.1 Comparison of IR peak positions of the observed and well-ordered SAMs.

<table>
<thead>
<tr>
<th>CH₃-SAM</th>
<th>OH-SAM</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Observed Wavenumber (cm⁻¹)</strong></td>
<td><strong>Well-ordered SAM⁷⁸ Wavenumber (cm⁻¹)</strong></td>
</tr>
<tr>
<td>2850</td>
<td>2851</td>
</tr>
<tr>
<td>2878</td>
<td>2878</td>
</tr>
<tr>
<td>2918</td>
<td>2919</td>
</tr>
<tr>
<td>2964</td>
<td>2958</td>
</tr>
</tbody>
</table>
2.3 The Ultrahigh Vacuum Chamber

2.3.1 Introduction

The UHV chamber is the main part of the apparatus that is employed in our study. The upper-limit pressure for ultrahigh vacuum is $10^{-9}$ Torr. The application of the UHV chamber provides several advantages in the experiments. Firstly, this chamber helps eliminate most of the interferences from the surrounding gas molecules during the experiments. Secondly, it keeps the surface clean for a period of time that is enough for performing experiments. Furthermore, based upon the mean free path equation for air at 20°C (shown in equation (8)), a lower pressure corresponds to a longer mean free path of gas molecules.

$$\lambda = \frac{5}{P(\text{torr})} \text{ cm}$$ (8)

Mean free path is the characteristic distance a molecule can travel before it hits another molecule. During our experiments, the pressure is $10^{-10}$ Torr (ultrahigh vacuum) in the main chamber; so, the mean free path of gas molecules is approximately 500 km. A mean free path of 500 km ensures the gas molecules in the incident molecular beam travel toward the surface without colliding with background gases during the experiments. Hence, both the incident energy distribution and the travel direction of the molecular beam can be maintained before the gas molecules collide with the surfaces.

2.3.2 The Main Chamber, Detector Chamber and Load Lock System

The schematic of the UHV chamber that is employed in our gas-surface interaction study project is provided in Figure 2.5. There are four important parts in this UHV chamber. (1) main chamber, (2) detector chamber, (3) load lock sample transfer system, and (4) sample manipulator.
The main chamber is equipped with a 1500 L/s turbomolecular pump (Pfeiffer TMU1601P). This pump helps maintain the pressure in the main chamber below $1 \times 10^{-9}$ Torr. A sample manipulator (McCallister MA2012) is located on top of the main chamber; it can be used to change the coordinates of the sample mount. Therefore, the main chamber is employed for two purposes; one is to provide a clean environment for gas-surface interactions and minimize background interferences, the other is to modify the position of the surface to achieve good gas-surface alignment.

Figure 2.5 Schematic of the ultrahigh vacuum main chamber.\textsuperscript{45}

The detector chamber is connected to the main chamber through a 4.3 mm diameter aperture. Gas molecules scattered from the surface may travel into the detector chamber through this aperture, and go through the first differential pumping stage. Then, these molecules may pass through another aperture with a diameter of 4.7 mm to enter the second stage of the
detector chamber. The first stage is equipped with a small turbomolecular pump (Pfeiffer TMU261P) with a 250L/s pumping speed, and the second stage is equipped with a 500L/s turbomolecular pump (Pfeiffer TMU521P). The combination of the turbomolecular pumps in the main chamber and the detector chamber helps maintain the pressure in the detector chamber at 1×10^{-10} Torr throughout the experiments. The Extrel QMS is located in the second stage of the detector chamber. This QMS is set to detect the scattered gas molecules with a certain mass-charge ratio. The MS signal from the scattered molecules as a function of time is recorded via a multichannel scaler (MCS) to provide the final TOF distribution.

Both the detector chamber and the main chamber are monitored and controlled by a LabVIEW program. This program helps make sure the pressures in both chambers are always below certain pressures. The pressure limits can be set in the software as set points. Once the pressure in any chamber increases and exceeds the set point value, the software will automatically shut down the system to protect the instruments.

Before starting experiments, surface samples need to be transferred into the main chamber. However, directly exposing the main chamber to the atmosphere will cause immediate pressure jump and possible chamber contamination. Hence, a technique that helps prevent the main chamber from being exposed to the atmosphere is needed during sample transfer. The load lock system in our apparatus is employed to fulfill the experimental requirement of transferring the sample without breaking the vacuum in the main chamber. The procedure of sample transfer is explained in detail in Section 2.5.2 of this thesis.

### 2.4 Molecular Beam

A molecular beam is a stream of gas molecules with unified direction, near single energy, and well-controlled cross sectional area. In our experiments, we seed the gas of interest in UHP H₂ (Airgas). The prepared mixture is then introduced into the molecular beam chamber, which is a high vacuum chamber with a pressure of 10^{-7} Torr. In the molecular beam chamber,
gas molecules are supersonically expanded through a 0.05 mm diameter nozzle. A 0.4 mm diameter conical skimmer is located 6 mm downstream from the nozzle. This skimmer selects the core of the gas stream. Then, a rotating 2-slit mechanical chopper wheel converts the continuous gas beam into gas pulses. The period of one gas pulse is about 50 µs, for a rotation frequency of 250 Hz. After passing another differential pumping stage, the molecular beam is introduced into the UHV main chamber.

2.4.1 Supersonic Molecular Beam

In our experiments, the supersonic molecular beam technique is employed to acquire a well-characterized incident gas source. This technique requires the application of a nozzle and a pressure difference in between the gas source and the differentially pumped molecular beam chamber. The backing pressure for the nozzle is set to approximately one atmosphere. In this condition, the mean free path of the gas molecules is smaller than the diameter of the nozzle. As a result, the flow of the gas molecules is hydrodynamic, which means this flow follows the same dynamics with liquid fluid. The gas molecules will be pushed through the hole and enter the first differential pumping stage. The vacuum condition of this differential pumping stage makes the flow of the gas molecules change from a continuum flow to a molecular flow. Then, the skimmer located down stream from the nozzle selects the core of the gas flow and produces the supersonic molecular beam. The continuum flow and molecular flow here are defined by using the Knudsen number, $K_n$. As shown in equation (9), $K_n$ is equal to the mean free path of the gas molecules ($\lambda$) over the size of the chamber ($L$).

$$K_n = \frac{\lambda}{L} \quad (9)$$

When $K_n < 0.001$, the gas is considered to be in the continuum regime, and the molecular flow regime occurs when $K_n > 10$. At one atmosphere; therefore, $\lambda$ is approximately $10^{-8}$ m. The dimension of the nozzle is about $10^{-2}$ m. Hence, the corresponding $K_n$ equals $10^{-6}$, which places
the gas source in the continuum regime. After the gas source enters the differential pumping stage of the molecular beam chamber, which has a pressure of $10^{-6}$ Torr, the $\lambda$ of the gas molecules increases significantly to about 50 m. Since the size of the molecular chamber is no bigger than 1 m, the $K_n$ of the gas molecules is much larger than 10. Therefore, after the supersonic expansion, the gas molecules are in the molecular flow regime.

Because of the pressure drop from the gas source to the molecular chamber, the gas molecules are accelerated when they pass through the nozzle and enter the high vacuum chamber. This occurs due to continuum flow mechanics. If gas molecules flow through an aperture and there is a significant pressure difference (around a ratio of 2) between the two stages, the speed of the gas molecules will be accelerated to around the local speed of sound.$^{82}$

During expansion, the highest pressure is reached at the throat of the nozzle aperture. When the gas molecules enter the high vacuum chamber, the dramatic pressure difference makes them go through an expansion to get adjusted to the low pressure of the vacuum chamber. This expansion lowers the pressure and increases the velocity of the gas. When the velocity is approximately constant, the mean free path of gas molecules at this low pressure is large enough to avoid intermolecular collisions in the molecular beam. Therefore, the unified direction and well ordered cross sectional area are maintained in the molecular beam.

The velocity of the gas molecules increases upon expansion, and the average translational energy of the expanded gas is predicted by employing Equation (10). In this equation, the $T$ is the temperature of the nozzle, $\gamma$ is the heat capacity ratio ($C_p/C_v$) of the gas species, and $R$ is the gas constant. This equation is developed under the assumption that the gas molecules behave ideally.$^{45}$

$$E = \frac{RT\gamma}{(\gamma - 1)}$$  \hspace{1cm} (10)

From equation (10), one can tell that the energy is proportional to the temperature of the nozzle. Therefore, we can tune the average translational energy of the expanded gas beam to
desired values by controlling nozzle temperature. Other than this method, the energy of a beam can also be manipulated by using the seeding technique. The detailed procedure of this technique is described in Section 2.5.1.

2.4.2 Molecular Beam Chamber Structure

A side view schematic of the molecular beam chamber is shown in Figure 2.6. There are three pumping stages in total in the molecular beam system. The first stage is equipped with a 5000 L/s VHS10 diffusion pump (Varian Vacuum Technologies). Gas molecules are introduced into the chamber with an initial pressure of approximately one atmospheric pressure through a Teflon tube. They enter the first pumping stage right after being expanded through a 0.05 mm diameter nozzle, where a molecular beam is created through a supersonic expansion. This beam then travels toward the 0.4 mm diameter conical skimmer that is located 6 mm downstream from the nozzle. This skimmer only allows the molecules that travel toward the main chamber to pass. As a result, after being selected by the skimmer, the modified molecular beam has a unified direction and a well defined cross sectional area.

The second pumping stage is equipped with a 1500 L/s Diffstak MK2 Diffusion Pump (BOC Edwards). After flowing through the skimmer, the continuous molecular beam is modulated by a two-slit chopper wheel located about 1.5 cm from the skimmer. There is a resulting gas pulse created every 2.02 ms (corresponding to a frequency of 495 Hz).

After further collimation by a 1.5 mm aperture, the gas pulses enter the final differential pumping stage of the molecular beam chamber. This pumping stage is equipped with a 250 L/s turbomolecular pump (TMU 261P, Pfeiffer) and separated from the UHV main chamber by a 2.2 mm aperture. A gate valve is applied to cover this aperture, so when experiments are not being performed, the gate valve is kept closed to isolate the main chamber from the molecular beam chamber. This can help maintain the low pressure in the main chamber and avoid contamination. During an experiment, the gate valve is open to connect the molecular beam chamber and main
chamber through the 2.2 mm aperture. Gas molecules that travel through this small aperture produce a 1 cm$^2$ spot on the surface sample, which is pre-aligned with the incident molecular beam.

Figure 2.6 Side view of the molecular beam chamber.$^{45}$

### 2.4.3 Molecular Beam Characterization

As mentioned in the previous section, the incident energy of a molecular beam can be tuned by modifying the ratio of the gas of interest and the carrier gas. Facilitated by the sample manipulator, the coordinates of the sample mount in the UHV chamber can be modified, as shown in Figure 2.5. With the surface mount away from the pathway of the molecular beam, the RGA can be employed to measure the TOF distribution of incident beam. A schematic of the experimental setup is provided in Figure 2.7.
To characterize the incident beam, the sample mount is moved away from the path of the beam. Therefore, as depicted in Figure 2.7, after entering the UHV main chamber, instead of colliding with the sample surface, the incident beam travels directly through the main chamber and enters the RGA. By analyzing the recorded TOF distribution of the incident beam, the travel time, $t$, of gas molecules from chopper wheel to RGA can be acquired. The distance from the chopper wheel to the RGA, $L$, is known from the chamber dimensions. Therefore, by using equation (7), the energy of the incident beam can be characterized.

Figure 2.7 Top view of the in-line beam energy characterization system.\textsuperscript{45}
2.5 Experimental Method

The procedure of the experiments presented in the thesis is described in this section. Generally, a well-characterized incident molecular beam and a model organic surface are prepared first. Then, the surface is aligned with the molecular beam, and the energy distribution of the recoiled gas molecules after they interact with the surface is determined. Information about the dynamics of the gas-surface collision can be obtained by detailed comparisons between the incident and final energy distributions.

2.5.1 Preparation of Gas Sources and Sample Surfaces

Preparation of the gas source is the first step of an experiment. The seeding gas technique is employed. The key point of this technique is: one can increase the incident energy of a gas beam by mixing the gas molecules with a higher velocity carrier gas. At a specific temperature, different types of gas molecules all possess the same amount of average energy. Accordingly, based upon equation (11), equation (12) can be derived to show that the gas molecules with difference molecular mass have different velocity.

\[ E = \frac{1}{2} m v^2 \]  
\[ v = \frac{\sqrt{2E}}{\sqrt{m}} \]

More specifically, the higher the molecular weight, the lower the corresponding velocity. For example, at room temperature, the velocity of argon atoms is far lower than the velocity of helium atoms.

In this work, molecular beams of different gases with unified incident energy are required. The mixing ratio of the gas of interest and a carrier gas is modified to tune the incident energy of a molecular beam to a desired value. The carrier gas employed in our experiments is UHP H\(_2\) (Airgas). H\(_2\) molecules have the lowest molecular weight, so they travel faster than all the other
types of gas molecules. In the mixture, H\textsubscript{2} carries the gas of interest at higher velocities than that of the pure gas under static condition. As a result, the incident energy of the gas beam increases. The incident energy of all the molecular beams employed in this research project was tuned to 48\(\pm\)5 kJ/mol with the full width at half maximum (FWHM) of 10 kJ/mol. (The details of the determination of the beam energy is presented in Section 2.5.4).

![Diagram of apparatus for gas source preparation](image)

**Figure 2.8** Schematic of apparatus for gas source preparation.

A schematic of the apparatus for the preparation of gas source is provided in Figure 2.8. Taking the preparation of the O\textsubscript{2} (UHP, Airgas) -carrier gas (UHP H\textsubscript{2}) mixture as an example, the preparation procedure of the gas source is described below.

a) Liquid nitrogen is used to cool a sorption pump for 30 mins. Open valve B, with valve A and C closed. The pre-cooled sorption pump is then employed to pump down a stainless steel mixing tank (Swagelok, DOT-3A1800) for another 30 min. Then valve B is closed. At this point, the pressure in the tank is far lower than atmospheric pressure. Thus, when the mixing tank is connected to a gas cylinder, this pressure difference will cause the gas molecules to flow into the mixing tank. Furthermore, pumping down the tank before making the gas mixture significantly lowers the interferences from other gas molecules and keeps the gas mixture clean.
b) Then, O$_2$ is introduced through regulator II at about 10 psi. The pressure in the mixing tank is allowed to stabilize for about 30 s, then valve C is closed.

c) The carrier gas (UHP H$_2$) is then connected to the mixing tank. Valve C is kept closed and regulator II is employed to gradually increase the deliver pressure to about 50 psi.

d) Then, valve C is opened to connect the H$_2$ gas cylinder and the mixing tank. Since the deliver pressure of H$_2$ (50 psi) is much higher than the pressure in the mixing tank (10 psi), H$_2$ molecules will flow into the mixing tank. During this time, the deliver pressure of H$_2$ is gradually increased to about 250 psi. The pressure in the mixing tank is allowed to stabilize for approximately 30 s.

e) Valve C and the H$_2$ cylinder are both closed after 30 s. At this point, the mixing tank contains 250 psi of O$_2$ - H$_2$ gas mixture. This mixture is the gas source for the study of interactions between O$_2$ and model organic surfaces.

2.5.2 Sample Transfer

The load-lock system is employed to achieve the goal of transferring samples without breaking the vacuum in the UHV chamber. A schematic of this system is shown in Figure 2.9. As shown in Figure 2.9, a gate valve, A, is located between the load-lock chamber and the main chamber. When there is no need for sample transfer, valve A is kept closed to maintain low pressure in the UHV chamber. The detailed procedure for transferring samples into and out from the chamber is provided here in steps.

a) To transfer surface samples out from the UHV chamber, the first step is to pump down the load lock chamber. A sorption pump is cooled by liquid nitrogen for 30 mins, then valve B is opened to connect the sorption pump and the load lock chamber for another 30 min or until the pressure in the load lock chamber is approximately $10^{-4}$ Torr.

b) After valve B is closed, valve C is opened to let a turbomolecular pump further pump down the load-lock chamber to about $10^{-7}$ Torr.
c) Then, the sample mount coordinates are modified in the UHV chamber to achieve a good alignment with the load-lock arm. At this point, due to the significant pressure difference between main chamber ($10^{-10}$ Torr) and load-lock chamber ($10^{-7}$ Torr), once the gate valve A is opened, there will be an immediate pressure rise in the main chamber. To prevent the system from being instantly shutdown, the set point for the main chamber pressure is temporarily set to a higher value ($1 \times 10^{-6}$ Torr).

![Diagram of the load lock system](image)

**Figure 2.9** Schematic of the load lock system.

...continued...

d) Then, gate vale A is opened, and the load-lock arm is pushed into the main chamber until it holds the sample mount. A lock-in-key mechanism then engages the sample mount for removal from the sample manipulator. After steadily pulling out the load-lock arm (containing the sample mount) from the main chamber, valve A is closed to isolate the main chamber from the load lock chamber.

e) Valve C is then closed. The load-lock chamber is vented to atmospheric pressure by UHP nitrogen (UHP300, Airgas). Then the gate of the load-lock chamber is opened. After taking out the sample mount, this gate is kept closed during sample preparation to avoid contamination.
After the clean sample surfaces are positioned on the sample mount, they can be transferred to the UHV chamber and prepared for the gas-surface scattering experiments. In our experimental apparatus, as shown in Figure 2.10, two sample surfaces can be placed on the same sample holder. During experiments, the alignment of a molecular beam and each surface can be achieved by modifying the sample mount coordinates. Therefore, the interaction dynamics between the gas molecules and different surfaces can be studied under the same experimental conditions.

The procedure of putting the sample mount back is quite similar to the procedure for removal. After mounting the sample holder back on to the load-lock transfer arm, the sample mount can be transferred back to the UHV chamber by following steps a), b), c) and d) provided above. After the sample installation, the set point of the main chamber should be set back to the original value in the LabVIEW program.
2.5.3 Instrumental Alignment

To ensure that the molecular beam collides with the surface sample, and the reflected gas molecules be detected by the QMS located in detector chamber, the whole system must be aligned before performing any experiments. A laser source is employed to accomplish this alignment. The whole experimental setup is built to have the centers of all the apertures aligned in the same level. Therefore, if we shine a laser through the apertures in the detector chamber and let it hit a reflective surface with a specific angle, the reflected laser should go directly through the apertures in the molecular beam chamber, as shown in d) of Figure 2.11. Therefore, at this point, if a molecular beam enters the main chamber and collides on the surface, the reflected gas molecules will follow the same pathway to enter the detector chamber, pass through the two apertures and undergo analysis by the QMS.

The detailed procedure of performing alignment is shown in Figure 2.11. This is the view along the Z-axis. The first step of the alignment is to find the zero degree position. When the shined laser hits the surface with an incident angle of 0° with respect to the surface normal, as shown in (a) of Figure 2.11, the surface is considered as being located at the zero degree position. To identify the zero degree angle, the reflection of the laser is employed. The reflection follows the same path of the incident laser and travels back to the laser source. Therefore, the angle of the sample mount is altered until the reflected beam is co-linear with the primary beam.

The second step of the alignment is the modification of the Y coordinate of the sample surface. Therefore, the Y coordinate of the surface is modified through the sample manipulator to make sure that the laser hits right at the center of the surface, as shown in graph (b) of Figure 2.11.
The surface is then rotated 30° counter clockwise as shown in (c) of Figure 2.11. At this point, the laser goes through the detector chamber, hits on the surface center and is reflected. As shown in (c) of Figure 2.11, the reflected laser may hit on the inner wall of the UHV chamber at this stage. To fulfill the experimental requirements, the laser needs to go directly into the molecular beam chamber. Thus, the fourth step of the alignment is to adjust the X coordinate of the sample until the reflected laser passes into the aperture in between the main chamber and the molecular beam chamber, as shown in (d) of Figure 2.11. Finally, the Z coordinate of the sample is adjusted to ensure that the laser hits the vertical center of the sample. Hence, in a well-aligned system, a generated molecular beam will enter the UHV main chamber through an aperture and hit on the center of the sample surface. Further, the mass spectrometer views a spot at the center of the surface sample.
2.5.4 Incident Beam Energy Measurement

The determination of the incident energy of a molecular beam is critical for studying the dynamics of gas-surface interactions. The detailed procedure for obtaining an incident beam with a specified incident energy is explained here by taking the preparation of an argon beam as an example.

The RGA is set to detect particles with a mass-to-charge ratio of 40, which is the molecular weight of the argon molecules. The data collected by this RGA is simultaneously output by the pre-installed MCS software to generate a graph of total RGA counts versus time for the particles with the set mass-charge ratio. When the incident molecular beam is 2%Ar/98%H₂ (Airgas, specialty gas), Figure 2.12 is the generated plot by the MCS.

![Figure 2.12 TOF distribution of Ar in a 2%Ar/98%H₂ molecular beam detected by RGA.](image)

For the data shown here, the parameters in the MCS software are: preset=200,000, path length=198, and dwell=10 µs. The preset indicates the total number of runs in each data file. By
setting the dwell time as 10 µs, the software is arranged to collect the data in 10 µs bins, summed them and then output one data point. The path length of 198 means the software will collect 198 data points in one period, which makes the period of one run 198×10 µs=1980 µs=1.98 ms. After the collection of 198 data points, the software starts a new period. Each data file is the sum of 200,000 periods.

There is one gas pulse generated every 2.02 ms. Consequently, the real period is 40 µs longer than the detected period set in the software. Right after the detection of one period, the computer and the other electronic parts need some response time to start a new period. This difference is set to ensure the computer has enough time to start a new period, so that each pulse can be detected after being generated.

To determine the incident energy of a specific molecular beam, the position of the peak in the distribution recorded by the MCS is employed. However, instead of picking the direct reading of the peak position, there are several timing corrections required to get the true arrival time. The details of timing corrections are presented in Section 2.6.1. After all the timing corrections, the arrival time of the incident beam can be obtained. The velocity of the incident molecular beam is calculated by using the corrected arrival time and the distance from chopper wheel to RGA. Then the incident beam energy can be easily calculated by applying equation (7).

2.5.5 Molecular Beam Scattering

After characterization of the incident molecular beam, the sample mount is repositioned to the pre-aligned coordinates. At this point, the scattering experiments of molecular beams on sample surfaces can be performed following the procedure presented here.

a) After connecting the prepared gas source (as presented in Section 2.5.1) to the molecular beam chamber, the mechanical chopper wheel and electronic trigger can be turned on. The rotational frequency of the chopper wheel is typically tuned to 495 Hz (2.02 ms).
b) The gate valve between the molecular beam chamber and the main chamber can then be opened to introduce the molecular beam into the UHV chamber. Since the sample position has been aligned, the incident molecular beam should collide with the center of the model surface. After the collisions with the surface, the gas molecules are recoiled back into the gas phase. Among these recoiled gas molecules, the ones with a final angle of 30°, with respect to the surface normal, can go through two collimating apertures, enter the detector chamber, and get analyzed by the Extrel QMS.

c) The TOF distribution of the scattered gas molecules can be recorded by employing the Extrel QMS and MCS software.

2.5.6 Quadrupole Mass Spectrometry

The recorded, raw time of flight distribution of Ar molecules (in 2%Ar/98%H2 beam) scattered from an OH-SAM is shown in Figure 2.13.

![Figure 2.13 TOF distribution of an Ar (2%Ar/98%H2) beam scattered from an OH-SAM.](image)

The ionizer of the Extrel QMS is located 29 cm away from the surface and it views an approximately 1 cm$^2$ spot of the surface through the two apertures in the detector chamber. To obtain the TOF distribution shown in Figure 2.13, the mass-to-charge ratio (m/z) of argon is set as 40. Analysis of this raw data is accomplished by the following the general guidelines in Section 2.6.1, which describe corrections for timing and intensity aspects of the experiments.

### 2.6 Data Analysis

#### 2.6.1 Timing

The molecular beam passes through the aperture of the skimmer, and then is chopped into gas pulses by a 2-slit chopper wheel. During the rotation of the chopper, as shown in Figure 2.14, the gas molecules pass through the slits to form a pulse every time the slit of the chopper wheel is aligned with the skimmer aperture.

![Diagram of chopper wheel and trigger](image)

Figure 2.14 Side view and front view of the chopper wheel and trigger.
There is a LED-photodiode trigger located at the edge of the chopper wheel. This trigger is connected to a computer and an oscilloscope. It triggers the computer to start a new period of data collection by sending an electronic signal every time a chopper slit is aligned with the trigger (the position that is shown in the front view of Figure 2.14). The voltage of the trigger is 4.5 V and the trigger frequency of the chopper is set to be 495 Hz.

There are two slits on the chopper. In one rotation, each slit passes the trigger once, so there will be two gas pulses generated. After the gas pulses enter the main chamber and collide with the surface, the desorbed gas molecules are detected by the QMS. Since the MCS software starts to collect data every time a slit of the chopper wheel is aligned with the trigger, the time of this alignment is the “time zero” for the raw data of Figure 2.13.

There are four main timing corrections in our experiments: electronic time offset, chopper wheel time offset, chopper-surface time offset, and mass spectrometer time offset. The electronic time offset is caused by the employment of the LED-photodiode trigger. When a slit of the chopper wheel is aligned with the trigger, the trigger will send an electronic signal to the computer to start a new run. However, due to the response time of the electronics, there will be a delay for this procedure. Based on previous literature, this time offset is estimated to be approximately 2 µs. Although the electronic time offset is included in the overall analysis, the data is summed into 10 µs bins, therefore, this offset has a negligible influence on the final TOF distribution.

The chopper wheel time offset is the time difference between trigger-chopper slit alignment and skimmer-chopper slit alignment. As demonstrated in Figure 2.15, in our experiments, the chopper is set to rotate counter clockwise (CCW). The LED-photodiode trigger will generate a trigger pulse to make the computer start a new run every time a chopper slit is aligned with it. The “time zero” in Figure 2.13 is the moment of this alignment. However, the gas pulse is generated when the chopper slit is aligned with the skimmer aperture. Therefore, the
beam pulse is generated after the computer starts a new run, which is a significant timing offset for which the data must be corrected.

Figure 2.15 Front view of chopper wheel for demonstration of the time lag between the beam pulse and the trigger pulse.

To calculate the chopper wheel time lag, the pulse frequency is set to 495 Hz. As shown in Figure 2.16, if the chopper wheel rotates CCW, the travel time of one slit from the trigger to the source aperture is considered as $y$, and $x$ is the time from this source-slit alignment to the moment when the other slit is aligned with the trigger. So, $y$ should be the time lag that we have in the experiments. Since the beam pulse is after the signal pulse, $y$ should be deducted from the total time. On the other hand, if the chopper wheel rotates CW, $y$ will be the travel time of the slit from the source aperture to the trigger, and $x$ is the time from this slit-trigger collimation to the moment when the other slit is aligned with the source aperture. Then in this case, $x$ will be
the time lag. Since the beam pulse is still after the signal pulse, x should also be subtracted from the total time.

Figure 2.16 Schematic of the chopper wheel time offset calculation.

By employing an oscilloscope, we observe a pulse signal every time a slit passes the trigger. Therefore, as shown in Figure 2.17, the rotation period of the chopper with two slits should be equal to the time difference between the first pulse signal and the third following signal.

Figure 2.17 Signal pulses in an oscilloscope.
The rotation period can also be defined by using $x$ and $y$ in Figure 2.16 as $2(x+y)$. To solve $y$, another equation relating $x$ and $y$ is needed. Therefore, experiments that measure the TOF distribution of an incident beam under both CCW and CW conditions are performed. The TOF distribution of the incident molecular beam is measured by employing the RGA. By comparing the peak positions of the TOF distributions measured under these two conditions, the time difference, $x-y$, can be obtained. By combining these two equations, $x$ and $y$ can be solved. Since in our research, the chopper wheel is set to rotate CCW, $y$ is the time lag that needs to be subtracted from the total time.

The chopper-surface time is the next offset that needs to be considered. This time offset is the time it takes for the molecular beam to travel from the chopper wheel to the surface. Before performing gas-surface scattering experiments, the velocity of the molecules is calculated by using the arrival time and the distance from the chopper to the RGA. With the known velocity and the distance from the chopper wheel to the surface, which is 31 cm, the flight time of gas molecules from the chopper wheel to the surface can be obtained.

![Figure 2.18 TOF distributions of a molecular beam under CCW and CW rotation of the chopper wheel.](image)
After the reflected gas molecules enter the QMS, they require time for the ions to reach the detector. Therefore, the flight time of the gas ions in the QMS (mass spectrometer time offset) also needs to be subtracted from the total time. Based on previous literature, an ion’s flight time in a QMS before arriving at the detector can be calculated by applying equation (13).

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

(13)

\( L_q \) is the effective length of the flight path in the quadrupoles, \( E \) is the translational energy of the ion and \( m \) is the mass-charge ratio. However, it is not necessary to obtain the exact values of \( L_q \) and \( E \). As shown in equation (13), the flight time in quadrupoles is in proportional to the square root of the mass-charge ratio. So, if the pre-factor, \( L_q \sqrt{\frac{1}{2E}} \) is known, the flight time of a specific ion can then be obtained by employing equation (13).

The value for this pre-factor has been determined in previous literature as 6.5. We re-tested this value by performing argon (Airgas) scattering on a CH\textsubscript{3}-SAM. In this experiment, a pure Ar beam is employed as the incident beam. Due to the low velocity and translational energy, the Ar atoms will collide and get fully accommodated with the surface. Therefore, after all the time corrections, the final TOF distribution should be a Boltzmann distribution at the surface temperature. As shown in Figure 2.19, by setting the pre-factor as 6.5, the corrected TOF distribution and the corresponding final energy distribution are both well fitted by the Boltzmann distribution at 298 K (surface temperature). Thus, it is reasonable to set the pre-factor as 6.5 in the data analysis.
Figure 2.19 The TOF distribution (A) and the final energy distribution (B) of pure Ar scattering on an OH-SAM. The open circles represent the experimental data and the solid lines are the Boltzmann distributions at the surface temperature.

Based upon all timing correction-related descriptions above, the time-axis of TOF distributions that are measured by the QMS in the detector chamber should be corrected by...
using equation (14). In this equation, $t_{\text{arrival}}$ is the flight time for reflected gas molecules to travel from the surface to the entrance of the QMS; $t_{\text{total}}$ is the measured flight time, which is the x-axis of Figure 2.13.

To sum up, $t_{\text{electronic}}$ is the response time of the LED-photodiode trigger, $t_{\text{chopper-wheel}}$ is the time difference between the beam pulse and the trigger pulse; $t_{\text{chopper-surface}}$ is the flight time from the chopper to the surface and $t_{\text{mass-spec}}$ is the flight time in the quadrupoles before reaching the detector. The directly measured $t_{\text{total}}$ originally contains all these time factors. By doing the time corrections shown in equation (14), the travel time from the surface to the detector entrance can be obtained. This corrected time can provide straightforward information about the behavior of gas molecules after their collisions with the surface. The corrected TOF distribution of Ar atoms (in 2%Ar/98%H$_2$ beam) after they collide with an OH-SAM is provided in Figure 2.20.

![Figure 2.20 Time-corrected TOF distribution of Ar in the 2%Ar/98%H$_2$ beam after colliding with an OH-SAM.](image-url)

Figure 2.20 Time-corrected TOF distribution of Ar in the 2%Ar/98%H$_2$ beam after colliding with an OH-SAM.
The distance from the surface to the entrance of QMS is known as 29 cm. Therefore, based upon the corrected TOF distribution and this distance, the final energy distribution of the reflected gas molecules can be calculated. The energy transfer fraction during the gas-surface interactions can then be calculated by using equation (2).

\[ t_{\text{arrival}} = t_{\text{total}} - (t_{\text{electronic}} + t_{\text{chopper-wheel}} + t_{\text{chopper-surface}} + t_{\text{mass-spec}}) \]  

(14)

2.6.2 Incident Beam Energy

The procedure of measuring the incident beam energy has been presented in Section 2.5.4. A 2%Ar/98%H\textsubscript{2} beam is employed as an example here to show exactly how to calculate this value.

The original TOF distribution of this beam is measured by the in-line RGA as shown in Figure 2.12. Since the calculation of the incident beam energy requires the flight time from the chopper to the RGA and the distance between these two parts, the time-axis of this TOF distribution must be corrected. In the raw data plot, the time shown in Figure 2.12 includes the electronic response time of the trigger, the chopper wheel time lag, and the flight time in the quadrupoles of the RGA before the ions reach the detector. To acquire the flight time from the chopper wheel to the entrance of the RGA, all these timing corrections must be subtracted according to equation (15).

\[ t'_{\text{arrival}} = t'_{\text{total}} - (t'_{\text{electronic}} + t'_{\text{chopper-wheel}} + t'_{\text{RGA}}) \]  

(15)

Both the electronic time offset and the chopper wheel time offset have been described above. However, the RGA and the Extrel mass spectrometer have different dimensions. Therefore, before reaching the detectors, the same ions’ flight time in the two quadrupole mass spectrometers will be different. Equation (13) can be applied to calculate the time correction term, \( t_{\text{RGA}} \). The slope of this equation was previously determined to be 3.6. After all the time
corrections, the TOF distribution of Ar in the 2%Ar/98%H₂ incident molecular beam is shown in Figure 2.21.

![Time corrected TOF distribution of Ar](image)

Figure 2.21 Time corrected TOF distribution of Ar in an incident 2%Ar/98%H₂ molecular beam detected by RGA.

As shown in Figure 2.21, after making all the time corrections, the flight time from the chopper wheel to the entrance of RGA can be determined, which in this case is 200 µs. The distance from the chopper wheel to the entrance of RGA is 45.3 cm. So, the energy of this incident Ar beam is determined to be 103±5 kJ/mol.

### 2.6.3 Analysis of TOF Data Detected by the Extrel QMS

With the pre-characterized incident molecular beams and SAMs, the final TOF distribution of the reflected gas molecules can be analyzed to acquire information to help interpret the dynamics of gas-surface interactions. Here, the scattering data of the 2%Ar/98%H₂ beam is employed to demonstrate how the final TOF distributions are analyzed.
As explained in Section 1.3.1 of this thesis, there are two possible pathways for the gas molecules to go through, impulsive scattering and thermal desorption. The gas molecules that are thermalized with the surface have a final TOF distribution that is the same as a Boltzmann distribution at the surface temperature. Therefore, the final TOF distribution can be fit by two components, the Boltzmann distribution at the surface temperature and the TOF distribution of the gas molecules that goes through the impulsive scattering pathway.

The detected signal in the final TOF distribution is proportional to the number density of the gas molecules, \( N(t) \). With the known arrival time and distance from the surface to the QMS, the final energy of the gas molecules can be obtained. The intensity of the final energy distribution, \( P(E_f) \), is proportional to \( t^2 \cdot N(t) \). This correlation is related to the ionization probability of gas molecules when they enter the QMS that has an electron impact ionizer.\(^8\) The probability of ionization is determined by the time the neutral species spend in the ionizer of the mass spectrometer. Compared with the high-speed gas molecules, the gas molecules that travel slower have a higher probability of ionization.

Figure 2.22 (A) shows the TOF distribution of Ar atoms after a 2%Ar/98%H\(_2\) molecular beam is scattered from an OH-SAM. As previously mentioned, the data of Figure 2.22 (A) can be transformed to provide the final energy distribution, shown in Figure 2.22 (B). The data in Figure 2.22 (B) is then modeled with two limiting scattering pathways: impulsive scattering and thermal desorption. The two corresponding fitting components, impulsive scattering component (IS) and thermal-desorption component (TD) in Figure 2.22 (B) can then be transformed back to the TOF distribution.

In Figure 2.22 (B), the final energy distribution of the gas molecules is separated into an IS component and a TD component. After complete thermalization with the surface, the gas molecules have an identical energy distribution to that of the surface, which is the Boltzmann distribution at the surface temperature. Therefore, the first step of this fitting is to assign the Boltzmann distribution to the final energy distribution. At the surface temperature (298K), the
translational energy Boltzmann distribution can be calculated by using equation (16). Then the IS component is determined by taking the difference between the total experimental energy distribution and the TD distribution.

\[
P_{\text{TD}}(E_f) = \frac{E_f}{(RT_{\text{surf}})^2} \exp\left(-\frac{E_f}{RT_{\text{surf}}}\right)
\]

(16)

Based upon the final energy distribution, the energy that is below 2.5 kJ/mol (RT_{surf}) is all assigned to the Boltzmann distribution, which means, \( P_{\text{IS}}(E) = 0 \) for \( E \leq 2.5 \) kJ/mol. In Figure 2.22 (A), the IS (the sharp, high velocity component with a peak position of approximately 256 µs (solid line)) and TD (the broad peak with later arrival time) in the final TOF distribution is transformed from the IS and TD in Figure 2.22 (B). In both (A) and (B) of Figure 2.22, the dashed lines are the Boltzmann distributions at the surface temperature and the solid lines represent the impulsive scattering components.
Figure 2.22 (A) TOF distribution of Ar atoms in a 2%Ar/98%H₂ beam after scattering from an OH-SAM; (B) The corresponding translational energy distribution \( P(E_f) \) from (A).

The most important parameter employed in the next chapter to facilitate understanding the dynamics, is the thermal-desorption (TD) fraction in the final energy distribution. The TD fraction is defined as the area fraction of the Boltzmann component in the final energy distribution.

The TD (Boltzmann) component in a specific gas-surface interaction provides information about how well the incident gas molecules thermalize with the surface, the rigidity of the surface, the ability of the surface to dissipate the energy transferred from the gas molecules, and the percentage of incident gas molecules that go through the thermal desorption pathway.

The other parameter defined here is the IS fraction. The IS fraction is equal to the difference between the probability of the whole distribution (which is 1) and the calculated TD fraction.

\[
TD = \frac{\int_0^{\infty} P_{TD}(E_f)dE_f}{\int_0^{\infty} P(E_f)dE_f}
\]  

(17)
By performing different molecular beam scattering experiments from clean, well-characterized organic surfaces, the work described in this thesis has provided insight into the energy transfer efficiency between different gas molecules and surfaces. Overall, this information is providing a more complete understanding for how gas properties and surface structure and functionality affect the outcome of gas-surface interactions.
Chapter 3 Results and Discussion

3.1 Dynamics of Oxygen and Nitrogen Collisions with an OH-SAM

3.1.1 Introduction

The two most abundant gas molecules in ambient air, $^{16}{\text{O}}_2$ and $^{14}{\text{N}}_2$, are similar with respect to a number of physical properties, as shown in Table 3.1. At room temperature, both oxygen and nitrogen are closed shell diatomic gas molecules with no dipole moment. They are colorless, odorless, tasteless, and nonpolar gases. Furthermore, oxygen and nitrogen molecules also share similar polarizabilities, diameters, molecular weights, and molar heat capacities.

Table 3.1 Selected similarities of $^{16}{\text{O}}_2$ and $^{14}{\text{N}}_2$.  

<table>
<thead>
<tr>
<th>Gas</th>
<th>$^{16}{\text{O}}_2$</th>
<th>$^{14}{\text{N}}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipole moment (D)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mass (g/mol)</td>
<td>32</td>
<td>28</td>
</tr>
<tr>
<td>Polarizability (cm$^3$)</td>
<td>$1.570 \times 10^{-24}$</td>
<td>$1.74 \times 10^{-24}$</td>
</tr>
<tr>
<td>Degrees of Freedom</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Diameter (pm)</td>
<td>109.76</td>
<td>120.74</td>
</tr>
<tr>
<td>Molar heat capacity (J•mol$^{-1}$•K$^{-1}$)</td>
<td>29.378</td>
<td>29.124</td>
</tr>
</tbody>
</table>

Despite their similarities, oxygen and nitrogen have several different distinguishing characteristic properties as shown in Table 3.2. Both oxygen and nitrogen are formed through covalent bonds between two atoms. However, with a different number of valence electrons in
atomic nitrogen and oxygen, their electronegativities and ionization energies are not the same. And also, in water at atmospheric pressure, the oxygen content is approximately twice that of nitrogen. In hexane, the solubility of oxygen is also significantly higher than nitrogen.

Table 3.2 Other properties of $^{16}\text{O}_2$ and $^{14}\text{N}_2$.\textsuperscript{84}

<table>
<thead>
<tr>
<th>Gas</th>
<th>$^{16}\text{O}_2$</th>
<th>$^{14}\text{N}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond order</td>
<td>Double</td>
<td>Triple</td>
</tr>
<tr>
<td>Bond energy (kJ/mol)</td>
<td>498</td>
<td>945</td>
</tr>
<tr>
<td>Color of liquid</td>
<td>Light blue</td>
<td>Colorless</td>
</tr>
<tr>
<td>Solubility in water ($\times 10^{-4}$ mole fraction)</td>
<td>0.230</td>
<td>0.117</td>
</tr>
<tr>
<td>Solubility in hexane ($\times 10^{-4}$ mole fraction)</td>
<td>20.5</td>
<td>13.9</td>
</tr>
<tr>
<td>Boiling point (K)</td>
<td>90.188</td>
<td>77.355</td>
</tr>
<tr>
<td>Melting point (K)</td>
<td>54.36</td>
<td>63.15</td>
</tr>
</tbody>
</table>

On the basis of the melting point and boiling point of $\text{O}_2$ and $\text{N}_2$, we know that compared with nitrogen, oxygen is easier to liquefy, but harder to solidify. Therefore, despite the physical similarities, the intermolecular interactions in the liquid phase and solid phase for oxygen and nitrogen are different. Beyond these differences, there are also quite a few differences between oxygen- and nitrogen-contacting functional groups within molecules. Atomic nitrogen has an electronegativity of 3.04 (Pauling scale). The five electrons in its outer shell lead to trivalent associations in most compounds. However, the triple bond in nitrogen gas is one of the strongest bonds. The large bond energy (945 kJ/mol) leads to the difficulty of converting $\text{N}_2$ into other compounds. Therefore, molecular nitrogen is the dominant form of nitrogen. On the other hand, with an electronegativity of 3.44 (Pauling scale) and six valence electrons, molecular
oxygen contains a double bond. The bond energy of this double bond is about 498 kJ/mol, which is only about half of the energy in the nitrogen triple bond. O₂, the most abundant form of oxygen, is used in the respiration of nearly all the creatures on earth.

Despite the many well-documented properties of these vital molecules, surprising little is known how they behave on a surface, where the fate is controlled both by physical and chemical dynamics. The study presented in this thesis is focused on addressing this intriguing science issue. To learn how oxygen and nitrogen gas molecules interact with organic surfaces, uncover what factors influence these interfacial interactions, and reveal differences (or similarities) in oxygen and nitrogen surface dynamics, several comparison experiments of O₂ and N₂ scattering on OH-SAM were performed.

3.1.2 Energy Transfer and Thermalization

As previously mentioned, there are two possible pathways for the gas molecules after they strike a surface. One is called thermal-desorption (TD) and the other one is impulsive scattering (IS). On one hand, after the first impact with the surface, if a gas molecule stays on the surface and transfers all its initial energy to the surface prior to desorbing, then this molecule is considered as following the TD pathway. In this case, the gas molecule, once thermalized with the surface, may desorb back to the gas phase propelled by thermal fluctuations. The energy distribution of this type of gas molecule is represented by a Boltzmann distribution at the surface temperature. On the other hand, if a gas molecule goes directly back to the gas phase after impinging the surface and retains part of its initial energy, then it is referred to as impulsive scattered. This type of gas molecules is not thermalized with the surface. They preserve part of their initial momentum and rebound from the surface without full thermal accommodation. Therefore, the TD gas molecules interact with the surface more significantly (longer residence times, more collisions, and possible trapping) than the IS gas molecules and (under most conditions) transfer more energy to the surface.
In our study, a well-characterized molecular beam is directed at a sample surface (see Figure 3.1). After the gas-surface collisions, the recoiled gas molecules are detected and analyzed by a quadrupole mass spectrometer to generate a time of flight distribution. With the flight time from surface to the mass spectrometer and the known distance, the time-of-flight distribution is converted to a final energy distribution. This energy distribution can be separated into two components that represent the two possible pathways. As shown in Figure 3.1, the TD component is described well by a Boltzmann distribution at the surface temperature. The IS component is represented by the difference between the experimental data and the calculated TD component. The fractions of TD and IS are determined by calculating the relative area of each component. For example, TD fraction is equal to the area of the TD component over the total area.

![Figure 3.1](image)

**Figure 3.1** Final energy distributions of $^{16}O_2$ and $^{14}N_2$ scattering from an OH-SAM. Solid lines represent for the TD fraction.
Significant differences in the TD fraction are observed in the experiments of $^{16}\text{O}_2$ and $^{14}\text{N}_2$ scattering from an OH-SAM. Table 3.3 shows that the TD fraction of $^{16}\text{O}_2$ scattering is higher than the TD fraction of $^{14}\text{N}_2$ scattering. So, during the interactions with an OH-SAM, compared with $^{14}\text{N}_2$, $^{16}\text{O}_2$ molecules accommodate better with the surface and transfer more energy ($\pm 0.02$ is experimental error bar). The following discussion focuses on developing an understanding for the physical and chemical properties responsible for these intriguing differences.

Table 3.3 Results of $^{16}\text{O}_2$ and $^{14}\text{N}_2$ scattering on an OH-SAM.

<table>
<thead>
<tr>
<th>Gas source</th>
<th>Incident beam energy (±2 kJ/mol)</th>
<th>TD (±0.02)</th>
<th>IS (±0.02)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{16}\text{O}_2$/H$_2$</td>
<td>50</td>
<td>0.62</td>
<td>0.38</td>
</tr>
<tr>
<td>$^{14}\text{N}_2$/H$_2$</td>
<td>50</td>
<td>0.51</td>
<td>0.49</td>
</tr>
</tbody>
</table>

3.1.3 Possible Factors that Affect Energy Transfer

In this thesis, the study of two factors is mainly presented to show how they affect gas-surface interaction dynamics. One is the mass difference (4 g/mol) between $^{16}\text{O}_2$ and $^{14}\text{N}_2$ molecules (mass effect); the other one is the effect of electronic structure.

3.1.3.1 Mass Effect: Isotopic Studies of $^{15}\text{N}_2$ and $^{14}\text{N}_2$ Scattering on an OH-SAM

To learn how the mass difference of the gas molecules affects their collision dynamics with surfaces, experiments of $^{14}\text{N}_2$ and $^{15}\text{N}_2$ scattering on identical OH-SAMs were performed. The results from this work are presented in Table 3.4. These scattering experiments show very similar TD fractions (0.62 and 0.61 for $^{15}\text{N}_2$ and $^{14}\text{N}_2$, respectively) as demonstrated in both Table 3.4 and Figure 3.2. Especially in Figure 3.2, the TD distributions of the two scattering experiments almost perfectly overlap with each other. Thus, the small mass difference of the gas molecules does not play a significant role in energy transfer during the gas-surface interactions. Therefore,
what factors are responsible for the significant difference shown in Figure 3.2? Clearly, the electronic structure differences between O₂ and N₂ must be largely responsible for the differences in gas-surface energy transfer. So in section 3.1.3.2, the electronic structures of gas molecules are studied to reveal its effect on energy transfer efficiency in gas-surface interactions.

Table 3.4 Results of ¹⁵N₂ and ¹⁴N₂ scattering on an OH-SAM.

<table>
<thead>
<tr>
<th>Gas source</th>
<th>Incident beam energy (±2 kJ/mol)</th>
<th>TD (±0.02)</th>
<th>IS (±0.02)</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹⁵N₂/H₂</td>
<td>43</td>
<td>0.62</td>
<td>0.38</td>
</tr>
<tr>
<td>¹⁴N₂/H₂</td>
<td>43</td>
<td>0.61</td>
<td>0.39</td>
</tr>
</tbody>
</table>

Figure 3.2 Final energy distributions of ¹⁵N₂ and ¹⁴N₂ scattering from OH-SAM. Solid lines represent for the TD components.
3.1.3.2 Electronic Structure Effect: Theoretical Calculations of the Interactions of O₂ and N₂ with Methanol

To gain knowledge about how electronic structure affects gas-surface interaction dynamics, theoretical calculations were performed to approximate the potential energy surface (PES) for O₂/N₂ approaching the hydroxyl groups of an OH-SAM.

Figure 3.3 Theoretical calculations of Potential Energy Surface (PES) diagrams for the interactions between O₂, N₂ and methanol with four different approaches.

The calculated PES for O₂ and N₂ interactions with methanol shows that in approaches a), b) and c), demonstrated in Figure 3.3, O₂ approaches the hydroxyl group more closely than N₂ before being affected by the repulsive wall. However, when the gas molecules approach the surface along the path shown in d), N₂ may approach more closely to the OH group of methanol. Thus, to learn how gas molecules behave during gas-surface interactions, it is necessary to describe which approach geometry likely predominates the interaction.
Due to the formation of intra-monolayer hydrogen bonds between terminal –OH groups,\textsuperscript{42} the–OH groups tilt toward the plane of the surface. Therefore, the approach geometry shown in a) and d) of Figure 3.3 are not likely to happen during collisions between gas molecules and an OH-SAM. Therefore, approaches similar to those shown in b) and c) are the most likely dominating pathways. So, O\textsubscript{2} molecules most likely approach the OH-SAM more closely than N\textsubscript{2}. This observation helps to explain the experimental result that O\textsubscript{2} molecules have more interactions with, hence transfer more energy to, the OH-SAMs.

In addition to O\textsubscript{2} and N\textsubscript{2}, there are some other abundant diatomic molecules in the atmosphere, CO and NO. While these molecules are similar in mass to O\textsubscript{2} and N\textsubscript{2}, they differ in some critical ways that may have an effect on gas–surface collision dynamics. Therefore, the O\textsubscript{2}/N\textsubscript{2} experiments have been complemented by CO/NO studies.

### 3.1.3.3 Dipole Effect: Collision of $^{14}$N\textsubscript{2}, $^{15}$N\textsubscript{2}, CO and NO on OH-terminated SAMs

Section 3.1.3.2 hinted at how electronic structure may affect gas-surface interaction dynamics. Based on the results, one might hypothesize that dipole-dipole forces play a major role in gas-surface energy transfer and accommodation. This problem was studied by the energy exchange of CO and NO in collisions on an OH-SAM and the results are presented in Table 3.5 and Figure 3.4.
Figure 3.4 The final energy distributions comparison: $^{14}\text{N}_2$ and CO (A), $^{15}\text{N}_2$ and NO (B). Solid lines represent for the TD components.

$^{14}\text{N}_2$ has the same molecular weight with CO, and $^{15}\text{N}_2$ has the same molecular weight with NO. However, CO and NO have permanent dipole moments that may lead to dipole-dipole
interactions with the terminal groups of OH-SAMs. $^{14}$N$_2$, $^{15}$N$_2$, CO, and NO gas-surface scattering experiments were performed under the same conditions (same incident beam energy, incident angle, temperature, etc.). If intermolecular force plays an important role in determining gas-surface interaction dynamics, then CO, and NO may exhibit higher TD fractions than $^{14}$N$_2$, $^{15}$N$_2$, respectively. The experimental results of $^{15}$N$_2$, $^{14}$N$_2$, NO and CO scattering on an OH-SAM are summarized in Table 3.5 and the corresponding final energy distribution comparisons are provided in Figure 3.4.

Table 3.5 Comparison between $^{15}$N$_2$ and NO, $^{14}$N$_2$ and CO scattering on an OH-SAM for $E_i=$43kJ/mol.

<table>
<thead>
<tr>
<th>Gas source</th>
<th>Dipole moment (D)</th>
<th>TD (±0.02)</th>
<th>Gas source</th>
<th>Dipole moment (D)</th>
<th>TD (±0.02)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{15}$N$_2$/H$_2$</td>
<td>0</td>
<td>0.62</td>
<td>$^{14}$N$_2$/H$_2$</td>
<td>0</td>
<td>0.61</td>
</tr>
<tr>
<td>NO/H$_2$</td>
<td>0.169</td>
<td>0.67</td>
<td>CO/H$_2$</td>
<td>0.101</td>
<td>0.64</td>
</tr>
</tbody>
</table>

The experimental results shown in Table 3.5 demonstrate that the TD fraction is higher for the molecules with a dipole moment (NO and CO). Thus, dipole-dipole interactions may play a role in controlling energy exchange. This idea is reinforced by the comparison between NO and CO. Compared with CO, NO possesses a higher dipole moment, a higher TD fraction. Even though the experimental results of only four gases may not be a very solid foundation for the conclusion that dipole moment significantly affects the gas-surface energy transfer, it justifies the need for further experiments and theoretical calculations. Beyond fundamental ideas about how mass and electronic structure may affect energy transfer, the results described above suggest that gas-surface accommodation might be predicted by bulk properties such as solubility.
3.2 Solubilities of O₂, N₂, CO and NO in Water

3.2.1 Introduction to Solubility

Solubility is the property that predicts the extent to which a solid, liquid or gaseous chemical dissolves into a solvent to form a homogeneous solution. The value of solubility defines how much a specific solute can be dissolved into a unit amount (volume or mass) of solvent. The solubility of a substance depends on the physical and chemical properties of both the solute and the solvent. More significant intermolecular interactions between solute molecules and solvent molecules favor dissolution, and, as a result, contribute to an increase in solubility. Therefore, one might hypothesize that gas-surface energy exchange might be predicted by relative solubilities. However, such correlations have not previously been explored for collisions on solid organic surfaces.

3.2.2 Correlation between Gas – OH-SAM Interactions and Solubilities in Water

The solubilities of O₂, N₂, CO and NO in both water and hexane were shown in Table 1.1. This data clearly shows that the solubilities of these four gases follow the trend $S_{NO} > S_{O2} > S_{CO} > S_{N2}$. We find the exact same trend describes the relative TD fractions for these molecules scattering from the OH-SAM. The final energy distribution of these four gases scattering from an OH-SAM is shown in Figure 3.5. Figure 3.6 provides a plot of TD fraction versus solubility of gas molecules in water. The trend that is shown in this figure demonstrates that a higher solubility corresponds to a higher TD fraction, and, as a result, more efficient energy transfer.
Figure 3.5 Final energy distributions of NO, O$_2$, N$_2$, and CO scattering from an OH-SAM.

To explain the solubility trend, O$_2$ and N$_2$ are taken as an example. Theoretically, solubility depends both on enthalpy and entropy. However, for molecules with similar degrees of freedom, size, and geometry, the differences in $\Delta S$ likely play a minor role. Therefore, the intermolecular force between solvent and solute is the most critical factor that needs to be considered. Stronger attractive intermolecular forces favor higher solubility. Both O$_2$ and N$_2$ are nonpolar gas molecules, so when they interact with water (or the OH-SAM), the dominating intermolecular force will be the Debye force, which is the attractive force between a permanent dipole (water or the hydroxyl groups in an OH-SAM) and an induced dipole. This attractive force can be calculated by using equation (18).

$$V = -\frac{m^2 \alpha^2}{16 \pi^2 \varepsilon_0^2 \varepsilon_r^2 r^6}$$  \hspace{1cm} (18)
As shown in equation (18), the Debye force is directly related to, \( m \) (the charge per length), \( \varepsilon_0 \) (the permittivity of free space), \( \varepsilon_r \) (the dielectric constant of surrounding material), \( \alpha \) (the polarizability), and \( r \) (the molecule-dipole separation). Under the same experimental conditions, \( \varepsilon_0 \), and \( \varepsilon_r \) are constants. The gas molecules studied here have similar mass. Therefore, for the interactions of different solutes with the same solvent, the polarizability and the molecule-dipole separation have the greatest effect. Smaller separation and bigger polarizability leads to stronger Debye forces. Hence, the equation of the Debye force provides the information that can be employed to determine the relative significance of intermolecular interactions between the nonpolar molecules and the molecules with a permanent dipole moment. From Table 3.1 and the theoretical calculations presented in section 3.1.3.2 of this thesis, we know that O\(_2\) and N\(_2\) have similar polarizabilities and \( r \) is smaller for O\(_2\). These properties contribute to a higher solubility for O\(_2\) in water.

![Figure 3.6 Thermal desorption fractions of gas scattering on an OH-SAM versus the solubilities of gas molecules in water.](image)

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72
3.3 Interactions of Diatomic Gas Molecules with Methyl (CH$_3$)-terminated SAMs

The results and correlations acquired from the gas-OH-SAM scattering experiments raises the question of whether the same idea holds for scattering from pure hydrocarbon surfaces. Thus, the same experiments were performed on CH$_3$-SAMs. The final energy distributions of NO, O$_2$, N$_2$, and CO scattering from a CH$_3$-SAM are shown in Figure 3.7.

![Figure 3.7 Final energy distributions of NO, O$_2$, N$_2$, and CO scattering from a CH$_3$-SAM.](image)

3.3.1 Correlation between Gas-CH$_3$-SAM Interactions and Solubilities in Hexane

A plot of TD vs. solubility in hexane is shown in Figure 3.8. As with the OH-SAM, there is a correlation between solubilities in hydrocarbon and TD fractions in scattering from a CH$_3$-SAM.
Figure 3.8 Thermal desorption fractions of gas scattering on CH$_3$-SAM versus the solubilities of gas molecules in hexane.  

3.3.2 Comparison between Hydroxyl-terminated SAMs and Methyl-terminated SAMs

When compare the two solvents, water and hexane, both Gibbs free energies of solvation and solubilities of gas molecules in water and hexane show that it is easier for the four gases to dissolve into hexane than water. This phenomenon was explained by Frank and Evans in 1945, “the nature of deviation found for non-polar solutes in water leads to the idea that the water forms frozen patches or microscopic icebergs around such solute molecules. The word ‘iceberg’ represents a microscopic region, surrounding the solute molecule, in which water molecules are tied together in some sort of quasi-solid structure”.  

The water molecules
interact more strongly with each other due to the existence of hydrogen bonds than with the diatomic gases, N2, O2, CO, and NO. As a result, the water molecules form somewhat structured shells around a solute. This makes the whole system more ordered upon dissolution and therefore leads to a decrease in entropy. At a constant temperature, based on 18,

$$\Delta G = \Delta H - T\Delta S$$  \hspace{1cm} (19)

the decrease of entropy corresponds to increase of Gibbs free energy of solvation. Thus, compared with dissolving in a hydrocarbon solvent, the gas molecules in water have more positive Gibbs free energy of solvation. In hydrocarbon solvents, there are no favorable solvent-solvent interactions. Hence, compared with water, hydrocarbon solvents are more flexible, solute-friendly, and as a result, correspond to higher solubilities of non-polar and small-dipole gas molecules.

The hydrogen bonds in liquid bulk (water) affect solubility; likewise, the hydrogen bonds on solid surfaces (OH-SAM) affect energy transfer. Interestingly, the reasons behind these two effects are related. The gas-surface interaction dynamics not only depend on the properties of gas molecules, but also the characteristics of the surface. The experimental results of gas scattering from CH3-SAMs and OH-SAMs show that, with the same incident gas species and energy, the TD fraction in CH3-SAM scattering is always higher than the TD fraction in OH-SAM scattering. This is because, compared with the OH-SAM, the CH3-SAM is more flexible. In OH-SAMs, the terminal OH groups form intra-monolayer hydrogen bonds, this makes the surface relatively rigid. When the incident gas molecules hit the solid surface, part of the incident energy is transferred to the surface from the gas molecules and distributed into the subtle motions of the surface chains, such as vibrational and rotational degrees of freedom. With the existence of intra-monolayer hydrogen bonds on the OH-SAMs, some of those possible motions are restricted. Therefore, the rigid surface structure will significantly limit the energy transfer between the gas molecules and the OH-SAMs. Also, because the chains on the CH3-SAMs
are freer to wag, twist, and become disordered, the $\Delta S$ may increase faster when the gas molecules impinge on the CH$_3$-SAMs.

### 3.4 Summary and Future Work

The research project presented in this thesis demonstrated that intermolecular forces between gas molecules and surfaces play an important role in affecting the gas molecules’ behavior and energy transfer. Most importantly, this work showed that O$_2$ and N$_2$, though similar in many ways, experience different energy transfer dynamics in collisions on organic surfaces. Further, a positive correlation between TD fractions in gas-surface scatterings and solubilities for analogous solute-solvent combinations was observed.

For now, by applying the molecular beam of these four species of gas molecules and the SAMs into the study of gas-surface interactions, we were able to compare their energy transfer to the surface by probing the behaviors of the reflected gas molecules after they collide with the surface. In addition, the facilitation of theoretical calculation enables us to further understand and elucidate the interaction dynamics.

Further work will may explore how the enthalpic and entropic contributions to gas-surface interactions affect energy exchange, thermal accommodation, and scattering.
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