Thermal Transformations and Low Energy Electron Irradiation of 1,3,5-Trimethylbenzene on Au(111) Surfaces and on Alkanethiol SAMs

by

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ABSTRACT

THERMAL TRANSFORMATIONS AND LOW ENERGY ELECTRON IRRADIATION OF 1,3,5-TRIMETHYLBENZENE ON Au(111) SURFACES AND ON ALKANETHIOL SAMS

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This thesis investigates the application of low energy electron irradiation to 1,3,5-trimethylbenzene films to test whether site-selective C–H bond cleavage can be achieved in a molecule presenting both aliphatic and aromatic target sites. IRRAS was used to characterize the orientation of vapour-deposited 1,3,5-trimethylbenzene on Au(111) and alkanethiolated gold under UHV and cryogenic conditions. On both substrates, the disordered as-deposited films were transformed by thermal treatment, producing two film structures – within the first 4-monolayers, aromatic rings lie nearly parallel to the metal surface, while molecules in additional layers are more upright. Low energy electron irradiation (0-10 eV) produced no dissociations in 1,3,5-trimethylbenzene; however, low energy electron transmission spectra indicate charge accumulates at interstitial sites in the mesitylene film, decelerating subsequent incident electrons. These decelerated electrons traverse the charged film and are reaccelerated, inducing dissociations in the underlying SAM. Contrary to literature claims, 1,3,5-trimethylbezene is a poor molecule for adsorption studies such as BET as the initial adsorption is disordered and thermodynamically unstable.
DEDICATION

Dedicated to
my Grandma
Ruth Lorraine Vandergust

In loving memory of Reverend Larry Marshall

“He was a man, take him for all in all,
    I shall not look upon his like again.”
– Shakespeare, Hamlet
I have taken a very scenic route through my university studies, and while I have never regretted taking the road less travelled, I owe a sincere debt of gratitude to those who cheered-on this Odyssey from the sidelines or even travelled this road by my side.

Five years ago, my advisor Dr. Paul Rowntree offered me a summer research position because he was “intrigued by my dynamic personality”. That I remember his words to this day should give some indication of the impression he has made on me. Over the years, we have shared stimulating and often entertaining conversations about the nature of elections, education, economy, and of course, electrons. He perpetually challenges me to stretch my understanding and look beyond the obvious to probe the robustness of my conclusions, all while remaining infinitely supportive when I struggle or doubt my own abilities; I could not have asked for a better advisor.

As part of the Rowntree research group, I have had the pleasure of working with a number of individuals who assisted with everything from experimental techniques to staging interventions for malfunctioning equipment to commiserating over a pint of coffee. Thank you to group members past and present, including Stuart, Marco, Alina, Jake, Mike, Gabrielle and Joe, for making our lab a pretty great place to work. I also owe a heartfelt thank you to Dr. Golam Moula who mentored me on UHV systems and taught me all I know about Phoenix.

I would like to thank my advisory committee members, Dr. Aziz Houmam and Dr. Dan Thomas. Dr. Thomas joined us in many group meetings along with Jong Park, to offer suggestions and ask probing questions to guide my research. Thank you to
Dr. Jacek Lipkowski for being part of my examination committee, and to Dr. Marcel Schlaf for chairing my defence.

Financial support from the Natural Sciences and Engineering Research Council is gratefully acknowledged, including a Research Tools and Instruments (RTI) grant for the purchase of a new (badly needed) IR spectrometer.

I would like to thank my friends at Guelph for so many memorable moments, some civilized, some scandalous; you shall therefore remain anonymous, but you know who you are, and you should know you have enriched my life both on- and off-campus.

My family also deserves recognition; my mom always insisted her 3 daughters pursue post-secondary educations, and my dad has thrice supported this. He often offered (at least until he learned better) to help edit whatever chemistry lab report or comparative German literature essay I was working on, and I would like to thank him for all the things he has done, big and small, to help me get where I am going in life. I owe no small thanks to Jill for being the teacher who first introduced me to chemistry, and for making her classes so fun and easy that she tricked me into believing chemistry would always be so. My grandma, at the age of 93, is assuredly the oldest member of my cheerleading squad, but I am so grateful for how close we have become. Karen, my elder sister, has always inspired me to reach higher, try harder and go further, and her encouragement has meant the world to me. Her enthusiasm is so infectious that I followed her all the way to the lost city of the Incas – something we both regretted for approximately 3.5 days and 47 grueling kilometers, though it was ultimately an extremely rewarding experience. Despite living on the other side of the country, three time zones away, she has been one of my most important supporters, and “thank you” seems woefully inadequate.
And finally, my gratitude to Sean. Words could never truly capture all that you’ve been and continue to be to me; for nearly a decade, you have been my sounding board and confidante, my personal chef and chauffeur, a recurring vexation, and a dependable source of laughter, love and joy – you are my friend and my partner, and this Odyssey would have been much too lonely a journey without you beside me. This has been one hell of a year, but together, we made it through.

And so, in the words of the immortal Jonathan Swift,

“Where I am not understood, it shall be concluded that

something very useful and profound is couched underneath.”
# Table of Contents

Abstract ........................................................................................................................................... ii  
Dedication ........................................................................................................................................ iii  
Acknowledgements ........................................................................................................................... iv  
Table of Contents ............................................................................................................................. vii  
List of Tables ...................................................................................................................................... ix  
List of Figures ...................................................................................................................................... x  
List of Abbreviations ......................................................................................................................... xiv  

## Chapter One: Introduction ........................................................................................................... 1  
1.1 Focus of Thesis ......................................................................................................................... 1  
  1.1.1 Scope of Thesis ................................................................................................................... 2  
1.2 Low Energy Electron Induced Reactions ................................................................................ 3  
  1.2.1 Electron Induced Damage in Condensed Organic Films ................................................. 8  
  1.2.2 Chemisorbed Organic Thin Films: Self-Assembled Monolayers ................................. 12  
  1.2.3 Low Energy Electron Irradiation of Self-Assembled Monolayers ............................... 16  
  1.2.4 Coupling Rare-Gas Energetics to DEA to Influence Film Damage ............................... 19  
1.3 Research Plan ........................................................................................................................... 28  

## Chapter Two: Theory of IR and Characterization of Organic Films ........................................ 32  
2.1 Infrared Radiation ..................................................................................................................... 32  
  2.1.1 Surface Selection Rules ..................................................................................................... 33  
2.2 Infrared Characterization of Organic Molecules ..................................................................... 37  
  2.2.1 C–H Stretching Vibrations of Alkyl Chains ...................................................................... 37  
  2.2.2 Vibrational Bands of Adsorbed Mesitylene ...................................................................... 40  
  2.2.3 Surface Selection Rules for Adsorbed Mesitylene ......................................................... 43  
2.3 Orientation of Adsorbed Aromatic Molecules ....................................................................... 44  
  2.3.1 Effect of Temperature on Organic Film Orientation and Order ................................... 47
Chapter Three: Experimental Methods and Procedures ........................................... 49
3.1 Substrate Preparation ....................................................................................... 49
  3.1.1 Gold Film Preparation .............................................................................. 49
  3.1.2 Substrate Cleaning Procedure .................................................................. 49
  3.1.3 SAM Formation ......................................................................................... 50
3.2 UHV Chamber ................................................................................................. 50
  3.2.1 Sample Transfer Via the Load Lock ......................................................... 52
  3.2.2 Temperature Control ............................................................................... 52
  3.2.3 Vapour Preparation and Dosing ............................................................... 53
3.3 Infrared Reflection Absorption Spectroscopy .................................................. 54
3.4 Low Energy Electron Irradiation ................................................................. 55
  3.4.1 Monitoring Surface Charging .................................................................. 56
3.5 Experimental Sequence ................................................................................... 58

Chapter Four: Adsorption of Mesitylene on Au and on a SAM ......................... 60
4.1 Vibrational Band Assignments for Adsorbed Mesitylene ............................... 60
4.2 Vapour Deposition of Mesitylene Thin Films ............................................... 62
4.3 Thermal Treatment of Condensed Mesitylene .............................................. 66
4.4 Discussion ....................................................................................................... 74

Chapter Five: Low Energy Electron Irradiation of Mesitylene Films .................. 77
5.1 Low Energy Electron Irradiation of Mesitylene on Au(111) ......................... 77
5.2 Irradiation of Films on C\textsubscript{16}SAM ....................................................... 83
5.3 Discussion ....................................................................................................... 89

Chapter Six: Conclusions and Future Work ....................................................... 91
6.1 Conclusions .................................................................................................... 91
6.2 Future Work .................................................................................................. 92

Chapter Seven: References .................................................................................. 94
LIST OF TABLES

Table 2.1: Frequency Assignments for the C–H and C–D Stretching Modes of C\textsubscript{n} Films ..............................................................39

Table 2.2: The Vibrational Frequencies in the Infrared Spectrum of Mesitylene ..........41

Table 4.1: The Frequencies Observed in the IRRAS Spectrum for the Vibrational Bands ........................................................................60
LIST OF FIGURES

Figure 1.1: Relative electronic energies of temporary negative ions showing shape and Feshbach type core-excited and single-particle resonances .................................................................4

Figure 1.2: Schematic diagram showing two possible decay channels, dissociative electron attachment and autodetachment, for a temporary negative ion ........................................................................7

Figure 1.3: Yield distribution for H⁻ formation in 6-8 ML thick films of the normal saturated hydrocarbons deposited on the platinum substrate, for the parent species identified .................................................................10

Figure 1.4: Illustration of a model SAM on a Au(111) substrate showing the three main parts of each molecule ................................................................................................................13

Figure 1.5: Illustration of time lapse of self-assembly from solution of dodecanethiol monolayer on gold substrate .................................................................15

Figure 1.6: Relative depletion of absorbance of C₁₆SAM on Au(111) as a function of the injected electron energy at 25 K .................................................................18

Figure 1.7: The gas phase UV absorption spectrum of benzene in the 6-9 eV region, where a benzene valence band and several Rydberg series converging to the first ionization potential are located ................................................21

Figure 1.8: Infrared spectra of a C₁₆ SAM at 25 K before (solid curve) and after (dotted curve) adsorption of 60 L Xe. The reference for both spectra was the reflectivity of a clean Au surface ................................................23

Figure 1.9: Relative depletion of absorbance of C₁₆SAM on Au(111) with a 60 L coverage of Xe as a function of the injected electron energy at 25 K .................................................................24
Figure 1.10: The difference spectra of a C16SAM with a 60 L Xe overlay showing the effect of rare-gas mediated coupling to DEA during electron irradiation. Top panel: 7.7 eV electron beam. Bottom panel: 8.5 eV electron beam. Difference spectra obtained by referencing the post-irradiation reflectivity to that measured prior to exposure to the electron beam .................................................................25

Figure 1.11: The gas phase absorption spectrum of mesitylene in the 6-9 eV region, where the 1\textsuperscript{1}E\textsubscript{1u} benzene valence band and several Rydberg series converging to the first ionization potential are located .........................29

Figure 2.1: Schematic representation of a beam of radiation of s polarized light (top) and of p polarized light (bottom) where \textbf{E} is the electric field ............36

Figure 2.2: Illustration of the symmetric and asymmetric C–H stretching vibrations of alkanethiols. The arrows are to indicate the direction of the transition dipole of the vibration .................................................................38

Figure 2.3: Adapted illustration of mesitylene vibrations in the IR spectrum. The blue arrows in the top images indicate the in-plane and out-of-plane components of the transition dipoles with respect to the plane of the ring .............................................................................................................42

Figure 2.4: Perspective view of the molecular packing in phase I (left) and phase II (right) of mesitylene .................................................................................................48

Figure 3.1: Schematic view of Phoenix - the \textit{in situ} IRRAS apparatus ..................51

Figure 3.2: Injection curves obtained from an uncharged and an increasingly charged alkanethiolated gold surface with a 60 L overlayer of xenon showing the shift in the accelerating energy required to maintain a set current .................................................................57

Figure 4.1: IRRAS absorption spectra from 680-890 cm\textsuperscript{-1} during adsorption of mesitylene on a Au(111) surface at 22 K, referenced to the pristine Au(111) sample immediately preceding the gas dosing .........................63
Figure 4.2: IRRAS absorption intensities of four key vibrations of mesitylene with increasing exposure during vapour dosing. Mesitylene is adsorbed on a Au(111) surface ..........................................................65

Figure 4.3: 672-710 cm\(^{-1}\) (left) and 825-860 cm\(^{-1}\) (right) regions of the IRRAS spectra of mesitylene on Au(111) during annealing at two exposure levels: 206 L (white background) and 800 L (grey background) ............68

Figure 4.4: C–H stretching region of the IRRAS spectra of mesitylene during annealing. Top: adsorbed on Au(111) referenced to pre-exposed Au(111) surface. Bottom: adsorbed on D\(_3\)C\(_{16}\)SAM/Au referenced to pre-exposed D\(_3\)C\(_{16}\)SAM/Au .................................................................70

Figure 4.5: IR absorption intensity of the 4 diagnostic vibrations of mesitylene on Au(111). Top: 206 L, Bottom: 800 L .................................................................72

Figure 5.1: C–H stretching region of mesitylene during low energy electron irradiation at 7.7 eV of an annealed 482 L film on Au(111). Top: Spectra referenced to Au(111); Bottom: Spectra referenced to the pre-irradiated mesitylene spectrum .................................................................78

Figure 5.2: Current Injection curves of annealed 800 L mesitylene film on Au(111) with increasing charge deposition from 10 eV electrons ..........80

Figure 5.3: Charging profiles of mesitylene films of 206 L, 400 L and 800 L exposures plotted as the accelerating potential required to maintain 1 µA as a function of injected charge based on the measured injection curves ..................................................................................82

Figure 5.4: IRRAS spectra of the C–H stretching region of 227 L mesitylene on D\(_3\)C\(_{16}\)SAM/Au(111) irradiated at 10 eV. Top: traditional absorption spectra referenced to Au(111); Bottom: difference spectra referenced to 227 L mesitylene film immediately prior to irradiation........84

Figure 5.5: IRRAS difference spectra of the C–H stretching region of 800 L mesitylene on D\(_3\)C\(_{16}\)SAM/Au(111) irradiated at 10 eV referenced to 800 L mesitylene film immediately prior to irradiation ........................................................................87
Figure 5.6: IRRAS difference spectra for the C–H stretching region of 170 L mesitylene on C_{16}SAM/Au(111) with a 116 L xenon overlayer irradiated at 7.7 eV referenced to the mesitylene + xenon film immediately prior to irradiation .................................................................88
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>eV</td>
<td>Electron Volt</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>SAM</td>
<td>Self-Assembled Monolayer</td>
</tr>
<tr>
<td>IRRAS</td>
<td>Infrared Reflection Absorption Spectroscopy</td>
</tr>
<tr>
<td>TNI</td>
<td>Transient/temporary Negative Ion</td>
</tr>
<tr>
<td>DEA</td>
<td>Dissociative Electron Attachment</td>
</tr>
<tr>
<td>TVD</td>
<td>Thermal Vapour Deposition</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>kJ</td>
<td>Kilojoules</td>
</tr>
<tr>
<td>C&lt;sub&gt;16&lt;/sub&gt;SAM</td>
<td>Hexadecanethiol Self-Assembled Monolayer</td>
</tr>
<tr>
<td>D&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;16&lt;/sub&gt;SAM</td>
<td>Terminally Deuterated Hexadecanethiol Self-Assembled Monolayer (SHC&lt;sub&gt;15&lt;/sub&gt;H&lt;sub&gt;30&lt;/sub&gt;CD&lt;sub&gt;3&lt;/sub&gt;)</td>
</tr>
<tr>
<td>RG</td>
<td>Rare Gas</td>
</tr>
<tr>
<td>L</td>
<td>Langmuir</td>
</tr>
<tr>
<td>ML</td>
<td>Monolayer</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra-violet</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra High Vacuum</td>
</tr>
<tr>
<td>OFHC</td>
<td>Oxygen Free High Conductivity</td>
</tr>
<tr>
<td>LN</td>
<td>Liquid Nitrogen</td>
</tr>
<tr>
<td>MCT</td>
<td>Mercury Cadmium Telluride</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>vCH&lt;sub&gt;3s&lt;/sub&gt;</td>
<td>Methyl C–H Symmetric Stretch</td>
</tr>
<tr>
<td>vCH&lt;sub&gt;3as&lt;/sub&gt;</td>
<td>Methyl C–H Asymmetric Stretch</td>
</tr>
<tr>
<td>vCH&lt;sub&gt;3FR&lt;/sub&gt;</td>
<td>Methyl C–H Symmetric Stretch Fermi Resonance</td>
</tr>
<tr>
<td>vCH&lt;sub&gt;2s&lt;/sub&gt;</td>
<td>Methylene C–H Symmetric Stretch</td>
</tr>
<tr>
<td>vCH&lt;sub&gt;2as&lt;/sub&gt;</td>
<td>Methylene C–H Antisymmetric Stretch</td>
</tr>
<tr>
<td>vCH&lt;sub&gt;ar&lt;/sub&gt;</td>
<td>Aromatic C–H Stretch</td>
</tr>
<tr>
<td>αCH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt; Group Next to Terminal Methyl Group</td>
</tr>
</tbody>
</table>
\[ \beta \text{CH}_2 \quad \text{CH}_2 \text{ Group 2}\text{nd From the Terminal Methyl Group} \]

\[ \text{ip} \quad \text{In Plane} \]

\[ \text{oop} \quad \text{Out of Plane} \]

\[ \chi_{\text{ring}} \quad \text{Ring Torsion} \]

\[ \rho \text{CH} \quad \text{Out of Plane C–H Deformation} \]

\[ \delta \text{CH} \quad \text{C–H Bend} \]

\[ \rho \text{CH}_3 \quad \text{Methyl Rocking Vibration} \]

\[ \delta \text{CH}_3 \quad \text{Methyl Group Deformation} \]

\[ \nu_{\text{ring}} \quad \text{CC Ring Stretch} \]

\[ \nu_{\text{C–Me}} \quad \text{Ring Carbon–Methyl Carbon Bend} \]

\[ \text{FWHM} \quad \text{Full Width Half Max} \]

\[ E \quad \text{Electric Field Strength} \]

\[ E_0 \quad \text{Amplitude of the Electric Field} \]

\[ E_s \quad \text{Electric field perpendicular to the plane of incidence} \]

\[ (s = \text{senkrecht, German}) \]

\[ E_p \quad \text{Electric field parallel to the place of incidence} \]

\[ t \quad \text{Time} \]

\[ T \quad \text{Period} \]

\[ \nu \quad \text{Frequency} \]

\[ \bar{\nu} \quad \text{Wavenumber} \]

\[ r \quad \text{Position in Space of Electric Field for IR Radiation} \]

\[ \delta \quad \text{Phase Angle in the Electric Field for IR Radiation} \]

\[ k_0 \quad \text{Wave Vector} \]

\[ \lambda_0 \quad \text{Wavelength} \]

\[ u \quad \text{Unit Vector} \]

\[ I \quad \text{Intensity of Transmitted Radiation} \]

\[ I_o \quad \text{Intensity of Incident Radiation at x=0} \]

\[ k \quad \text{Extinction Coefficient} \]

\[ A \quad \text{Absorption} \]
$E$  Energy

$h$  Planck’s Constant

$N_i$  Population of Molecules

$\rho(\nu)$  Radiation Energy Density

$B_{12}$  Einstein Coefficient for Absorption
1 CHAPTER ONE: INTRODUCTION

1.1 FOCUS OF THESIS

The interaction of matter with high-energy irradiation, such as high energy electrons, X-rays and ion beams, produces an abundance of low energy electrons, which typically have energies below 10 eV (~4 x 10^4 e-/MeV of deposited energy). Inelastic collisions between molecules and this cascade of low energy secondary electrons produce energetic species that drive many radiation-induced chemical reactions\(^1\), and inelastic interactions with charged and energetic particles are a consequence of numerous surface characterization techniques. The scattering of these secondary electrons, and not the incident X-rays themselves, are the principal cause of damage by XPS to organic films\(^2,3\). Lithographic considerations, in particular, necessitate the study of low energy electrons (< 20 eV), as it is the scattering of secondary electrons that ultimately limits the spatial resolution of electron beam patterning of resist materials\(^4-7\). While a thorough understanding of the sensitivity of organic films to low energy electrons can only improve our control over nanoscale applications, it is the ability to effect predetermined changes in the film that will be most valuable for thin film modifications. The ability to target specific bonds in a molecule for cleavage is largely absent in gas phase chemistry and remains one of the continuing challenges of thin film chemistry. Unfortunately, the chemical and physical homogeneity of many thin film systems, particularly extended alkanethiol self-assembled monolayers (SAMs), makes site-selectivity extremely challenging.
Site-selective cleavage of C–H bonds in extended alkanethiol SAMs on gold has been achieved by Garand et al.⁸, however this site-selectivity is currently limited to the terminal methyl groups. Application of this method to more complex heterogeneous molecules offers the potential for site-selective bond rupture to move beyond the current restriction of methyl terminations of alkanethiol SAMs, toward controlling chemical reactions by selecting pathways for molecular dissociation. The long-range goal of this project will be to probe whether dissociations at different sites, particularly aliphatic and aromatic C–H sites, are energetically distinguishable. Consequently, this work is concerned with investigating the effects of low energy electron irradiation of condensed thin films of molecules with both aliphatic and aromatic C–H target sites. Before addressing the question of site-selectivity, however, the films will need to be characterized to ensure stability and reproducibility.

1.1.1 Scope of Thesis

This thesis is divided into seven chapters. Chapter 1 gives a brief overview of the motivation for this research, followed by a review of the literature results pertinent to this work, including the theory of dissociative electron attachment. Chapter 2 includes a more detailed explanation of the theory of infrared radiation and its spectroscopic application to organic thin films, and Chapter 3 describes the experimental methods and instrumental techniques used for this work. Chapter 4 explores the results of vapour depositions of 1,3,5-trimethylbenzene (mesitylene) thin films on a Au(111) surface and on an alkanethiol SAM substrate and also includes the characterization of the films when subjected to thermal treatment. Chapter 5 presents the results of low energy electron irradiation of the mesitylene films on gold and on the alkanethiol SAM substrate.
Chapter 6 summarizes the results of the characterization and irradiation experiments and presents the final conclusions as well as gives an indication of the potential direction of future work. The final chapter contains a listing of all the references cited in this work. Note that all uncited figures are products of my own work.

1.2 Low Energy Electron Induced Reactions

Electron-induced molecular dissociations can proceed through one of three initial steps: electron impact ionization, electron impact excitation and electron attachment forming a transient anion.\(^9\) While the first two paths are non-resonant processes with short interaction times (~10\(^{-16}\) s), our process of interest in this work, electron attachment, is a resonant process characterized by interaction times longer than the time it takes for the electron to traverse molecular dimensions. A transient or temporary negative ion (TNI) or negative ion resonance (lifetime 10\(^{-15} - 10^{-2}\) s), forms when the incoming electron temporarily occupies a previously unfilled low lying molecular orbital, typically the LUMO, which exists at a specific energy. Thus, to be captured, the incident electron must have energy consistent with the narrow Franck-Condon transition to a discrete final state of specific energy.\(^{10}\) This vertical transition satisfies the preservation of nuclear positions during essentially instantaneous electronic transitions. Resonant processes give rise to narrow spectral features, while non-resonant processes result in broad spectra.

The TNI formed can originate from either a low energy (0-5 eV) single-particle resonance or from a higher energy (5-15 eV) core-excited resonance. Each type can be further defined as either open channel (shape) resonances or closed channel (Feshbach)
resonances based on the resonance being above or below the neutral molecule’s corresponding ground or electronically excited states\textsuperscript{10} as illustrated in Figure 1.1.

**Figure 1.1:** Relative electronic energies of temporary negative ions showing shape and Feshbach type core-excited and single-particle resonances.\textsuperscript{9} Reprinted from Surface Science Reports, 65, Arumainayagam et al., Low-energy Electron-induced Reactions in Condensed Matter, p.7, Copyright (2010), with permission from Elsevier.

When the incoming electron occupies a previously empty or half-filled ground state molecular orbital, without changing the configuration of the other electrons, it is called a single-particle resonance. The single-particle Feshbach resonance, also called a vibrationally-excited Feshbach resonance, is formed when the incident electron is trapped in a bound state of the vibrationally excited electronic ground state of the neutral molecule.\textsuperscript{10} The extra electron cannot be directly emitted because the Feshbach resonance lies below the ground electronic state of the molecule, resulting in relatively long anionic
lifetimes. In contrast, core-excited resonances occur at higher energies and involve the simultaneous excitation of the molecule and capture of the incident electron, such that the TNI formed has a hole in the inner filled MOs and two electrons occupying previously empty molecular orbitals. Core-excited resonances are known as “two particle, one hole” resonances. If the resonance energy lies below that of the “parent” molecular excited state, it is termed a core-excited Feshbach resonance (Figure 1.1), and the autodetachment lifetimes are relatively long, since it requires a two-electron process to decay (i.e. electron relaxation and electron emission). Feshbach resonances have a small electron affinity, whereas core-excited shape resonances, which lie above the parent state, have negative electron affinity, and generally have much shorter lifetimes since they can decay into the parent state.

TNIs have lifetimes ranging from $10^{-15}$ to $10^{-2}$ seconds, during which the extra electron can destabilize the system and cause the nuclei to move apart, beyond the equilibrium bond distance of the ground state molecule. Four competing channels exist for the TNI decay: radiative cooling; associative attachment; autodetachment; and dissociative electron attachment (DEA).$^9$

Radiative cooling depends on the emission of a photon for the TNI to relax to a stable negative ion:

$$AB^{*-} \rightarrow AB^- + h\nu$$

However, radiative cooling is a very slow process with lifetimes on the order of $10^{-8}$-$10^{-9}$ s, and thus it is not appreciably competitive with the three other processes listed.$^9$
Associative attachment of a low energy electron, a special case only possible in a cluster or condensed matter, involves energy loss to neighbouring molecules (ie. vibrational de-excitation collisions) to form the anion ground state:

$$AB^+ \rightarrow AB^- + \text{energy} \quad 1.2$$

The TNI formation involves capture of the electron into a state lying above the vacuum level, followed by vibrational de-excitation via interactions with the local environment (ie. collisions) to stabilize the resonance to a state below the vacuum level.$^9$ This process is therefore not possible in the gas phase, which involves only single collision conditions.

In two particle DEA, the resonance lifetimes are sufficiently long and the inter-atomic potential of the anion is repulsive in the Franck-Condon region such that the increasing separation of the nuclei leads to dissociation. The bond cleavage in the TNI ($AB^-*$) results in a neutral atom or molecular radical and a thermodynamically stable anion:

$$AB^-* \rightarrow A^* + B^- \quad 1.3$$

Alternatively, the TNI ($AB^-*$) can autoionize or autodetach before it reaches the critical separation distance (Figure 1.2), which is where the potential energy curves for the ground anion and the ground neutral molecule cross. Autodetachment forms a neutral parent molecule in the ground state ($AB$) or in a rotationally, vibrationally or electronically excited state ($AB^*$).

$$AB^-* \rightarrow e^- + AB \text{ (elastic scattering)} \quad 1.4$$

or

$$AB^-* \rightarrow e^- + (AB)^* \quad 1.5$$
The phase of the matter has a strong impact on the proportion of TNIs that follow each of the four decay channel as interactions with neighbouring molecules provide increased opportunities for decay, such as in the case of associative attachment. As well, molecules in the condensed phase on a metal substrate have additional quenching processes available to them.

The following section will discuss the damage induced by low energy electrons in physisorbed and chemisorbed organic films, including exploiting dissociative electron attachment for film modification and ultimately, site-selective bond cleavage.
1.2.1 Electron Induced Damage in Condensed Organic Films

Less than thirty years ago, the concept of controlling surface structure at the molecular scale through a rational approach was largely a fantasy. Molecular monolayers that could be designed by the experimenter remained largely unexplored, though inspiration had begun to take root from naturally occurring structures, such as micelles and lipid bi-layers; it was becoming clear that there was immense technological potential for molecular thin films and many promising areas of research.\textsuperscript{12} Three primary approaches to attaching structurally well-defined molecular monolayers to a solid substrate have since emerged: (1) Langmuir-Blodgett films, (2) self-assembly of organic molecules from the liquid phase, with or without electrochemical potential assistance, and (3) self-assembly of organic molecules from the vapour phase. It is also possible to vapour deposit monolayers of molecules at cryogenic temperatures, effectively physisorbing them to the surface. However, the well-defined structure associated with self-assembly is not assured with cryogenic deposition procedures. A more detailed description of the self-assembly process is provided in section 1.2.3.

Characterization of organic thin films often involves experimental techniques that expose the organic film to energetic particles, such as electrons, photons, and X-rays, leaving the film vulnerable to damage, particularly from the cascade of secondary low energy electrons. For example, Auger electron spectroscopy (AES)\textsuperscript{13}, X-ray photoelectron spectroscopy (XPS)\textsuperscript{14} and ultraviolet photoelectron spectroscopy (UPS)\textsuperscript{15} are frequently used to probe film composition, while scanning tunneling microscopy (STM)\textsuperscript{16-19} and low energy electron diffraction (LEED)\textsuperscript{19} are two methods commonly used to characterize film structure.
Electron bombardment studies with low energy electrons (0-20 eV) of thin films of condensed saturated hydrocarbon chains on Pt primarily resulted in C–H bond cleavage, producing H⁻ via both DEA and dipolar dissociation. Dipolar dissociation is a non-resonant process with a dissociation onset at ~16 eV for a diatomic molecule, primarily producing R⁺/H⁻ pairs in the reaction below.

\[
AB + e^- \rightarrow (AB) \cdot \rightarrow A^+ + B^- + e^- \quad 1.6
\]

Non-resonant processes have a large number of electronically excited states available in the 10-20 eV range, giving rise to broad, unstructured dissociation profiles. At lower energies, however, the DEA process dominates with a single resonance that exhibits little variation in energy as the chain length is changed (Figure 1.3), further evidence of the DEA process. In gas phase electron impact studies from 0-18 eV, the H⁻ formation varies slightly with chain length, while electron capture in the condensed films for 0-20 eV studies shows very little change with respect to chain length and corresponds to a broad maxima from 7.5–12.5 eV, centred 10 eV. The H⁻ formation is followed by reactive scattering at another site in the film, which abstracts a proton in a bimolecular reaction, and the excess energy is kinetic. The sequence is described by:

\[
\begin{align*}
R\text{–C–H}_x + e^- &\rightarrow [R\text{–C–H}_x]\cdot \quad (\text{electron capture, 7.5–12.5 eV}) \\
[R\text{–C–H}_x]\cdot &\rightarrow R\text{–C}^\bullet \text{–H}_{x-1} + H^- \\
R\text{–C}^\bullet \text{–H}_x + H^- &\rightarrow R\text{–C}^\bullet \text{–H}_{x-1} + H_2 \\
\end{align*}
\]
Figure 1.3: Yield distribution for $\text{H}^-$ formation in 6-8 ML thick films of the normal saturated hydrocarbons deposited on the platinum substrate, for the parent species identified. The curves are vertically displaced by 4000 counts/s for clarity; each division of the vertical scale represents 2000 counts/s.\textsuperscript{20} (Reprinted with permission from Rowntree \textit{et al.}, J. Phys. Chem. 95. p.4904. Copyright 1991. American Chemical Society.)
Since the process is common to both methyl sites and methylene sites due to similar energetics for both transitions, DEA results in C–H bond ruptures along the hydrocarbon chain, which does not permit energetic control of site-selectivity in such a physically and electronically homogeneous system.

Concurrent study of the unsaturated C$_2$H$_4$, C$_3$H$_6$ and C$_4$H$_8$ condensed systems shows H$^-$ yield distributions to be very similar to the unsaturated chains.$^{20}$ For both saturated and unsaturated systems, the dipolar dissociation process dominates at higher energies, though the onset for saturated systems is approximately 17 eV, while unsaturated systems exhibit an earlier onset around 14 eV.$^{20}$ For the saturated systems, the DEA resonance is centered at 8.5 eV for sub-monolayer coverages and ~9.5 eV for 11 monolayer films, both slightly below the 10 eV resonance observed for unsaturated films.

Further decreasing the saturation and introducing aromaticity to simple hydrocarbons results in one of the most stable classes of known organic compounds, able to absorb a considerable quantity of radiation excitation energy without suffering bond rupture by forming triplet states.$^{23}$ Benzene in particular has an observed “protection effect”, and many of its derivatives demonstrate this high stability.$^{23}$ Irradiation of benzene films produces only small amounts of hydrogen and methane, but levels grow with increasing number or size of the alkyl substitutions.$^{23}$ For example, a low energy irradiation study (~1 eV) of benzene and its derivatives demonstrates that decreased capture rates result upon addition of a methyl group in place of an aromatic hydrogen.$^{24}$ DEA processes for benzene do exist as low energy electron bombardment was shown to successfully cleave C–H bonds with a resonance centered at 8.5 eV in thin films of condensed benzene.$^{25}$ Electron stimulated desorption studies conducted on adsorbed films
of deuterated ethane (C$_2$D$_6$) and of deuterated benzene (C$_6$D$_6$) on platinum yield broad desorption peaks centered around 10 and 8.5 eV, respectively. The low energy electron irradiation induces bond cleavage that releases D$^-$, which is the most abundant species detected during irradiation of each film. The anion desorption has an onset of ~7.5 eV, peaking around 10 eV for the physisorbed ethane multilayers, while the benzene system demonstrates a slightly lower onset at 6.6 eV, peaking at 8.9 eV, ascribed to DEA processes.

1.2.2 Chemisorbed Organic Thin Films: Self-Assembled Monolayers

Self-assembled monolayers provide an opportunity to maintain the hydrocarbon environment, while imposing a more rigid and defined two-dimensional structure on the adsorbed film. Interest in SAMs ranges from applications in biological and chemical sensing to molecular electronics and corrosion prevention. While significant progress has been made in the study of SAMs, some phenomena remain poorly understood, particularly those concerning the Au reconstruction and etch pit formation, as well as adsorbed species mobility, adsorption sites and the formation of various phases.

The standard model for visualizing SAMs is of a head group that interacts with the substrate, an interior spacer group, and a terminal group (Figure 1.4); each region presents an opportunity to design the properties of the thin film by manipulating their composition and introducing functional groups.
Figure 1.4: Illustration of a model SAM on a Au(111) substrate showing the three main parts of each molecule.

One defining feature of SAMs is the specific affinity of the headgroup for the substrate, which results in the chemisorptions. The investigation by Nuzzo and Allara of dialkyl disulfides adsorbed on gold, which exhibited strong headgroup-substrate interactions, was one of the first studies to introduce the potential for modification of the tail to form organic films of various surface properties. These properties can be tuned by choosing a terminal group to facilitate interactions with bio- or nano-molecules or to modify the hydrophobicity of the surface. Terminal methyl groups, for example, tend to make a film more hydrophobic, while hydroxide and carboxyl groups increase hydrophilicity. Since the interior spacer group is often an alkane chain, van der Waals interactions play an important role in the film packing and help to minimize defects. The most common head group is a sulfur atom, such as in alkanethiols, thiocyanates, sulfides and disulfides, because of the strong chemical interaction between the sulfur and gold (~2 eV). SAM formation has been studied on a number of metal substrates,
including nickel\textsuperscript{40}, palladium\textsuperscript{41, 42}, platinum\textsuperscript{41, 43}, mercury\textsuperscript{44}, silver\textsuperscript{13, 45} and copper\textsuperscript{15}, however, gold\textsuperscript{11, 13, 34, 45-49} remains one of the most widely studied substrates; not only is gold relatively inert, limiting both oxide formation and reaction with most atmospheric contaminants, but the strong sulfur-gold bond allows for preferential bonding to the exclusion of coexisting contaminants. Au(111) surfaces can be created in a variety of ways such as thermal vapour deposition (TVD) of gold deposited on mica\textsuperscript{18, 50, 51} or gold deposited on a thin layer of chromium on glass.\textsuperscript{52} Au(111) surfaces can even be formed at the surfaces of annealed gold beads.\textsuperscript{53}

Alkanethiol molecules on Au(111) serve as a model system\textsuperscript{33} as they are particularly well suited to self-assembly; the sulfur head group preferentially chemisorbs to the gold (120-170 kJ/mol)\textsuperscript{54, 55}, occupying all possible surface sites, while the neighbouring alkyl chains experience favourable van der Waals interactions with increasing chain length (4-8 kJ/mol per CH\textsubscript{2}).\textsuperscript{56} Alkanethiols spontaneously adsorbed on gold from dilute solutions have been shown to assume a (√3×√3)R30° overlayer structure on Au(111), occupying 3-fold hollow sites.\textsuperscript{57} An organized monolayer of octadecanethiol on Au(111) with an average area of 18.4 Å\textsuperscript{2}/molecule, can be formed from solution or vapour deposition such that the resulting film is indistinguishable by electrochemical methods.\textsuperscript{58} An average separation of chemisorbed terminal sulfur atoms is ~5 Å resulting in \(\frac{1}{3}\) coverage of sulfur on gold with monolayer coverage of 4.6×10\textsuperscript{14} molecules/cm\textsuperscript{2}.\textsuperscript{59}

The van der Waals interactions of the alkyl chain tend to limit monolayer defects. Since longer-chain alkanethiols have stronger van der Waals interactions, they exhibit fewer defects and are typically more well-ordered than shorter-chain alkanethiol SAMs.\textsuperscript{45, 46, 60} Pinhole and gauche defects occasionally arise during the assembly process,
however, prolonging the exposure of the substrate to the thiol solution reduces film defects as the alkyl chains straighten from highly kinked conformations to predominantly trans-extended conformations. A final ordering of the monolayer occurs with the incorporation of the final 10-20% of the adsorbates and a highly ordered film can be achieved in a matter of hours. The formation of densely packed, stable monolayers can often be achieved simply by exposing a clean gold surface to a diluted alkanethiol solution without special equipment or conditions.

Figure 1.5: Illustration of time lapse of self-assembly from solution of dodecanethiol monolayer on gold substrate.

Deposition and formation of SAMs from the gas phase is generally conducted inside an ultra-high vacuum (UHV) chamber, which offers the opportunity to clean the metal substrate immediately before exposure with either thermal or sputtering treatments and helps limit atmospheric contaminants during exposure. Introduction of the vapour to the UHV chamber is typically through a leak valve, which allows the flux to be controlled such that submonolayer coverages and SAM formation kinetics can be
studied.\textsuperscript{61} Though UHV chambers can be cost prohibitive compared to the relatively simple solution deposition, the availability of analytical equipment, such as IRRAS, to probe the surface in situ offers a distinct advantage.

The favourable van der Waals interactions orient the alkyl chains into a trans-extended configuration, and the chains achieve optimal spacing when the main axes are tilted $30^\circ$–$40^\circ$ from the surface normal. This tilt orients the molecule and its transition dipole moments such that the stretching bands of both the methyl and methylene groups are detected by infrared spectroscopy. This spectroscopic consequence will be discussed in more detail in Chapter 2.

\subsection*{1.2.3 Low Energy Electron Irradiation of Self-Assembled Monolayers}

Irradiation of alkanethiol SAMs on Au(111) with low energy (0–15 eV) electrons by Olsen \textit{et al.} resulted in a decrease in the optical absorption in the C–H stretching region, which was attributed to dehydrogenation.\textsuperscript{11} IRRAS studies of irradiated alkanethiol films show significant decreases in the methyl stretching frequencies and decreases in the methylene bands that were non-uniformly distributed within the film. The dehydrogenation has been shown to be more probable near the methyl termination rather than distributed throughout the film, and longer alkane spacer groups increase the dissociation yields at C–H sites further from the metal. This has been explained using a dipole-image dipole quenching model in which the excited state lifetimes are reduced by proximity to the underlying metal substrate.\textsuperscript{11} At close proximity, the electronically excited state can be dampened by coupling between the substrate and its image, which quenches the excited state, precluding dissociation. The quenching lifetime is distance dependent and determines the dissociation probability; consequently, short-chain systems
have lower dissociation cross sections. Comparison of gas phase C₈, C₁₂ and C₁₆ alkanes to their condensed alkanethiol film analogues demonstrates a decrease in the exited state lifetimes from ~26 fs to only 2-10 fs due to proximity to the metal.¹¹ The cross-section for the methyl depletion approximately doubles from the C₈SAM to C₁₂SAM and again to the C₁₆SAM¹¹, by which point the dissociations are so effective that further increases in length have minimal impact on yield.

Despite the slight enhancement of the dehydrogenation yields near the film vacuum interface, both the bulk methylene and the terminal methyl sites are subjected to C–H bond cleavage, limiting the site-selectability.⁸,¹¹ The cross sections for the depletion of the methyl and methylene symmetric stretching modes in the 0–20 eV range (Figure 1.6) demonstrate that the CH₂ depletions is slightly lower than that of the CH₃. However, both vibration bands show a broad maximum in the 7.5–12.5 eV range¹¹, and this shared response indicates a common physical process that makes any sort of site-selectivity challenging. It also confirms the resonant nature to the initial energy deposition event, which is consistent with DEA. The energy spread of the electron-energy spectrum is due to the width of the Franck-Condon overlap and is therefore due to the dissociative nature of DEA.
Figure 1.6: Relative depletion of absorbance of C$_{16}$SAM on Au(111) as a function of the injected electron energy at 25 K (Q = 0.5 mC/cm$^2$).$^8$ (Reprinted with permission from Garand et al. Langmuir. 24. p.13853. Copyright 2008. American Chemical Society.)
1.2.4 Coupling Rare-Gas Energetics to DEA to Influence Film Damage

The dissociative attachment yields of physisorbed ethane were observed to be enhanced by application of a rare-gas overlayer, Ar, Kr, or Xe, followed by irradiation with low energy electrons at 11.6±0.2, 9.7±0.2 and 7.7±0.2 eV, respectively.\textsuperscript{25}

The narrow dissociation enhancements are attributed to formation of a relatively long-lived, Rydberg-type core-excited rare gas (RG) negative ion state, which transfers its energy to the underlying molecules.\textsuperscript{62} The RG negative ion is formed by an incident electron with energy slightly less than the threshold for a neutral RG exciton. Each rare gas solid has a bulk exciton spectrum that converges at the band gap of the solid. The surface exciton states are 0.1-0.4 eV lower in energy than the bulk state\textsuperscript{63}, and the narrowness (±0.2 eV) of the energetic width is due to the atomic nature of the RG anionic exciton. The RG negative ion formed diffuses or “hops” through the bulk RG layer (\(\text{RG}_a^\bullet^-\text{RG}_b\rightarrow\text{RG}_a\text{RG}_b^\bullet^-\)) and may reach the vacuum-solid interface where it can interact with a co-adsorbed molecule. Providing the co-adsorbed molecule has a dissociative Rydberg-resonance that overlaps with the RG negative ion, the extra excitation energy and charge can be transmitted to the molecule, leading to sharp enhancements in the dissociation signal superimposed on signal from direct DEA.\textsuperscript{25}

As previously mentioned, the C–H bond cleavage in \(n\)-alkanes and alkanethiol SAMs has a broad maxima with an onset of ~7.5 eV and a peak around 10 eV. Low energy electron scattering in Ar, Kr and Xe rare-gas solids was achieved at 11.6±0.2, 9.7±0.2 and 7.7±0.2 eV, respectively – all three of which fall within the range of the excitation energy of DEA process of \(n\)-alkanes and alkanethiol SAMs. Subsequently, a thin film of ethane experiences enhancement with all three rare-gas solids, though the
The greatest enhancement is seen for Xe and then Kr.\textsuperscript{25} The enhancement is only observed in DEA yields due to the decay of core-excited Rydberg resonance states, while yields tied to the decay of core-excited valence resonance states do not demonstrate such an enhancement. In the case of benzene films, the enhancement in anion yields was only observed for the Kr and the Ar overlayers, not for the Xe adsorbate.\textsuperscript{25} Since benzene has only valence states below 8 eV (Figure 1.7), it is unable to experience coupling between its higher energy Rydberg states and the 7.7 eV anionic exciton of xenon.\textsuperscript{25} The DEA yields of benzene are centered on 8.9 eV\textsuperscript{25, 26} and enhanced yields can be achieved with Ar and Kr anionic excitons as their higher energy give them access to the Rydberg states of benzene. Irradiation of xenon overlayers at 7.7 eV does not produce such an enhancement.

Exploitation of the inherent energy limits of coupling rare-gas anionic excitons to organic transition states may provide a method for selective modification of other organic molecules. Site-selectivity may be achievable by coupling RG anionic excitons to dissociative Rydberg states corresponding to specific sites on the molecule.
Figure. 1.7: The gas phase UV absorption spectrum of benzene in the 6-9 eV region, where a benzene valence band and several Rydberg series converging to the first ionization potential are located.\textsuperscript{64} (Reprinted with permission from Bolovinos et al. J. Phys. Chem. 75. p.4344. Copyright 1981, American Institute of Physics.)

The formation of xenon multilayers on alkanethiol SAMs at 25 K results in a dramatic transformation in the CH\textsubscript{3} associated bands in the IRRAS spectra even before the introduction of electrons. Similar to the changes observed in other adsorbate/alkanethiol SAM systems\textsuperscript{22, 65}, the addition of a xenon overlayer causes the methyl bands to decrease in intensity and new bands to appear 6-10 cm\textsuperscript{-1} lower with \textasciitilde30\% lower intensities than the bands of the pristine C\textsubscript{16}SAM (Figure 1.8).\textsuperscript{8} The
molecular basis for this perturbation, however, remains unclear; a study of H$_2$O/SAM suggested that the perturbations were a result of dipolar interactions$^{66}$, but the observation of the strong effect with xenon indicates this is an incomplete description and that dispersion interactions are also important.$^{65}$ In particular, complete transformation of the methyl-derived band (~2875 cm$^{-1}$) in the IRRAS spectra suggests that most of the methyl groups are in contact with physisorbed xenon, which completely wets the surface$^{8}$, but it is not clear whether the changes to the methyl bands are evidence of conformational changes at this site.$^{8}$ For intentionally disordered or mixed alkanethiol SAMs of two different chain lengths, changes to the methylene absorbance bands are also observed, particularly to the methylenes closest to the terminal methyl groups.$^{67}$ These changes to the CH$_2$ bands are absent for well-ordered SAMs, which have minimal defects that would expose methylenes to the xenon, and therefore indicate limited penetration of the xenon into the bulk of the film.$^{8}$ The transformation of this band provides a unique tool to characterize the coverage of an adsorbate on the SAM as total transformation of the CH$_3$s band to lower wavenumbers indicates completion of a monolayer. This insight is useful for determining the relationship between vapour exposure in UHV and surface coverage of the adsorbed molecules (ie. the conversion of Langmuirs to monolayers) as will be used in Chapter 4 to estimate film thickness.
Figure 1.8: Infrared spectra of a C\textsubscript{16}SAM at 25 K before (solid curve) and after (dotted curve) adsorption of 60 L Xe. The reference for both spectra was the reflectivity of a clean Au surface.\textsuperscript{8} (Reprinted with permission from Garand \textit{et al.} Langmuir. 24. p.13852. Copyright 2008. American Chemical Society.)

Irradiation of the C\textsubscript{16}SAM + Xe overlayer system at energies of 0–15 eV results in a slight decrease for the CH\textsubscript{2} dissociation cross-sections over irradiation of the SAM in the absence of the RG. While the resonant dehydrogenation process at 10 eV is still evident (Figure 1.9), the dissociation cross section reveals a new sharp peak for damage in only the methyl loss curve at 7.7 eV, with a very narrow width of ±0.2 eV. This energy and its narrow width correspond precisely to the energy of the anionic exciton of Xe.\textsuperscript{8} This suggests an alternative resonant process that affects only the terminal methyl groups.
Figure 1.9: Relative depletion of absorbance of C$_{16}$SAM on Au(111) with a 60 L coverage of Xe as a function of the injected electron energy at 25 K ($Q = 0.5$ mC/cm$^2$).$^8$


The difference spectra in Figure 1.10 are the IRRAS spectra referenced to the pre-irradiation C$_{16}$SAM+Xe system. The bottom panel demonstrates that at 8.5 eV, depletion of both CH$_3$ and CH$_2$ associated bands is observed, with slightly greater decrease to the CH$_3$s band, which is consistent with the depletion profiles of Figure 1.9. The top panel of Figure 1.10 demonstrates that at 7.7 eV, there is significant depletion of the CH$_3$ associated bands with minimal damage to the subsurface methylenes. This is consistent with the sharp, narrow feature in the Figure 1.9 loss curve, illustrating the enhancement provided by the xenon mediated process at 7.7 eV, but absent at 8.5 eV.
Figure 1.10: The difference spectra of a C_{16}SAM with a 60 L Xe overlayer showing the effect of rare-gas mediated coupling to DEA during electron irradiation. Top panel: 7.7 eV electron beam. Bottom panel: 8.5 eV electron beam. Difference spectra obtained by referencing the post-irradiation reflectivity to that measured prior to exposure to the electron beam.
The anionic excitation of Xe and the subsequent coupling to the C_{16}SAM can be described as follows:

\[ \text{Xe} + e^- \rightarrow \text{Xe}^•^- \quad \text{(electron capture, 7.7±0.2 eV)} \quad 1.10 \]
\[ \text{Xe}^•^- + \text{Xe} \rightarrow \text{Xe} + \text{Xe}^•^- \quad \text{(diffusion of the anionic exciton)} \quad 1.11 \]
\[ \text{Xe}^•^- + \text{CH}_3 \rightarrow \text{Xe} + \text{•CH}_3^•^- \quad \text{(transfer to terminal CH}_3\text{ group)} \quad 1.12 \]
\[ \text{•CH}_3^•^- \rightarrow \text{•CH}_2 + \text{H}^- \quad \text{(dissociation of the CH}_3\text{ group)} \quad 1.13 \]

The preferential dehydrogenation at the terminal methyl groups revealed by irradiation of the C_{16}SAM+Xe system is maximized when the xenon film thickness is between 60-70 Langmuirs, which is due to the finite lifetime and diffusion of the anionic excitons in the overlayer.\(^8\) A film that is too thick will prevent the xenon anionic exciton from diffusing to the organic film interface prior to auto-detachment, while a too thin film reduces the probability of electron capture by the xenon such that the electron would pass through the overlayer and interact with the SAM as described for the bare SAM system in Section 1.2.3. Coherent scattering in the xenon layer can result in the lateral movement of an electron in the conduction band of the xenon layer, ultimately increasing the probability of an interaction with a CH\(_3\), while decreasing the number of electrons that penetrate into the bulk SAM, explaining the slight decrease in the CH\(_2\) dissociation crosssection.\(^8\)

For dissociations in the C\(_{16}\)SAM in the absence of Xe, the dominant product is neutral molecular hydrogen, which reactively scatters to abstract a proton. In contrast, for the xenon coated system, H\(^-\) becomes trapped in the overlayer, resulting in an accumulation of charge on the system surface and a reduction in the transmitted current. This phenomenon is virtually absent in the case of C\(_{16}\)SAMs without the Xe overlayer as
well as in systems in which the C$_{16}$SAM film is coated with Xe, but irradiated at energies not at the resonance peak at 7.7 eV. Details of the technique for measuring this charge accumulation are available in Chapter 3.

The electron-induced damage is strongly localized to the organic-overlayer interface and reduces damage to the bulk system because the transfer of the anionic excitation is via overlapping Rydberg orbitals of the donor and acceptor species.$^{25}$ Only the terminal methyl groups are in physical contact with the xenon layer, and the extremely short-range nature of the charge- and energy- transfer process results in no significant transfer directly from the Xe film to the methylene groups. Further, there is no significant transfer of the anionic excitations from the terminal methyl group to the methylene group, efficiently trapping the excitation and the excess electron on the methyl group during their 5–10 fs lifetime before C–H bond rupture.$^8$ This strongly localizes the anionic excitation transfer to the chain termini and makes it possible to site-selectively rupture the C–H bonds at the film-vacuum interface, despite it being a relatively homogeneous system with respect to bond energies throughout the SAM. However, this geometric site selection remains limited to the terminal methyl groups of alkanethiol SAMs. Application of the inherent energy limits of coupling of RG anionic excitons to DEA resonances may provide a method for selective modification of organic molecules. One of the goals of this project is to determine if the technique can be exploited to achieve chemical selectivity as well as geometric selectivity by coupling the RG anionic excitons to DEA dissociations at specific target sites.
1.3 Research Plan

The rare-gas mediated approach described above provides a technique for coupling RG anionic excitons, created at very specific energies, to the C–H dissociative states of organic thin films. In alkanethiol SAMs, using xenon as the RG mediator and 7.7 eV electrons achieves site-selective C–H bond rupture at the methyl terminations. In benzene, which has only valence states below 8 eV, the narrow 7.7 eV energy used for alkanethiol bond rupture is too low to effect bond rupture, providing a potential tool for selectively dissociating aliphatic C–H bonds in the presence of the aromatic C–H bonds of benzene. This would provide a valuable tool for site-selectively dissociating C–H bonds in a more complex, heterogeneous environment. The motivation for this project is to determine whether dissociation sites are energetically distinguishable. The ideal molecule, therefore, would not only have aromatic hydrogen sites like benzene, but also aliphatic hydrogen sites – either simple methyl groups or longer alkyl chains. The simplest candidates would be the mono-, di- and tri-methyl substituted benzene rings, such as toluene, p-xylene, o-xylene, m-xylene, and 1,3,5-trimethylbenzene (mesitylene).

Figure 1.11 shows the gas adsorption UV spectrum of mesitylene, which exhibits the expected valence transitions between 6-7 eV. Between 7-8 eV, the band system is attributed to overlapping broad Rydberg bands, rather than to a pronounced valence transition with superimposed Rydberg bands, since such a valence transition is not displayed by solid mesitylene. The Rydberg states of mesitylene are primarily located between 7.5-7.9 eV, with only a few bands outside this range, potentially allowing for the coupling of the dissociative Rydberg states of mesitylene to the anionic exciton of xenon at 7.7 eV. In contrast, most of the Rydberg states of toluene and o-xylene, and
$m$-xylene are above 8 eV$^{64}$, increasing the likelihood that enhanced dissociation will not be achieved with Xe$^{-}$ as the 7.7 eV energy will be too low for a Rydberg excitation. Previous work has suggested that Xe presents the optimal enhanced yields among the Ar, Kr, and Xe rare gas series$^{25}$, making xenon the preferred rare gas for these investigations.

**Figure 1.11:** The gas phase absorption spectrum of mesitylene in the 6-9 eV region, where the $^1E_{1u}$ benzene valence band and several Rydberg series converging to the first ionization potential are located. The superimposed bar system corresponds to calculated positions of the transition of each series.$^{64}$ (Reprinted with permission from Bolovinos et al. J. Phys. Chem. 75. p.4344. Copyright 1981, American Institute of Physics.)
To investigate whether mesitylene has dissociation sites that are energetically distinguishable, condensed films will be created by vapour depositing mesitylene on a clean Au(111) on mica in a UHV chamber at cryogenic temperatures. IRRAS will be used to characterize the as-deposited films during and after deposition. These as-deposited films will be subject to thermal annealing conditions to determine the effect of temperature on the molecular orientation and film structure of condensed mesitylene and to ensure a stable, equilibrated initial state. Once the film has been characterized, it will be subject to low energy electron irradiation to look for evidence of C–H bond cleavage, which would be indicated by a decrease in the absorption of the C–H stretching region in the IRRAS spectra. Clear distinction between methyl aromatic C–H stretches in IRRAS spectra allows for discrimination between dissociation sites, making IRRAS ideally suited to monitor electron-induced chemical events in the organic layer. Evidence of bond cleavage would be a signal to proceed with application of a RG overlayer and low energy irradiation to investigate whether the RG anionic excitons show evidence of coupling to dissociation states of mesitylene, enhancing or otherwise affecting the dissociation rates at different sites.

To assess the effect of substrate on the mesitylene film structure and its sensitivity to low energy electrons, the above experiments will also be repeated with the mesitylene vapour deposited instead onto an alkanethiol SAM on Au(111) substrate. This will provide for a comparison of the results on the metal Au(111) surface and on the organic SAM substrate for evidence of relaxation channels offered by the gold substrate with respect to the insulating dielectric organic monolayer. However, both the underlying SAM and the adsorbed mesitylene will have vibrations in the C–H stretching region,
which will complicate interpretation of the spectra. Though the spectrum of the SAM on gold system can be subtracted from the spectra acquired during mesitylene exposure, as outlined in Section 1.2.5, adsorption of an overlayer to the SAM results in the transformation of the methyl symmetric stretching band. The CH$_{3s}$ stretch will therefore appear at a different frequency in the presence of the adsorbate, making it difficult to subtract the SAM spectra without interfering with the intensity of the mesitylene C–H stretches. For this reason, a terminally deuterated alkanethiol (SHC$_{15}$H$_{30}$CD$_3$) will be used for the SAM formation to eliminate this complication by relegating the methyl stretches to the C–D stretching region of 2000–2200 cm$^{-1}$. SAMs formed from this terminally deuterated alkanethiol will be designated by the notation C$_{16}$D$_3$SAM.
2.1 INFRARED RADIATION

Like other forms of electromagnetic radiation, infrared radiation is represented as electric and magnetic fields undergoing in-phase, sinusoidal oscillations perpendicular to each other and to the direction of propagation. Since it is not the magnetic field, but the electric field that is responsible for the phenomena observed with infrared spectroscopy, this is the component we are concerned with describing. The electric field strength, \( E \), is represented as a vector with a length proportional to its magnitude, and it can be calculated at any instantaneous moment at any position by equation 2.1.

\[
E = E^0 \exp [i(\omega t - k_0 r + \delta)]
\]

where \( E^0 \) is the electric field amplitude, a complex function of Cartesian coordinates and time \( t \), \( i = \sqrt{-1} \), \( \omega = 2\pi / T = 2\pi \nu \), where \( T \) is the period and \( \nu \) is the frequency, \( r \) is the position in space, \( \delta \) is the phase angle. \( k_0 \) is the wave vector and is calculated using equation 2.2 where \( \lambda_0 \) is the wavelength, \( u \) is the unit vector in the direction of propagation, and \( \bar{\nu} = I/\lambda_0 \), which is the frequency of the radiation in wavenumbers.

\[
k_0 = \frac{2\pi}{\lambda_0} u = 2\pi \bar{\nu} u
\]

The mean square of the electric field strength \(<E^2>\) is proportional to the intensity \( I \) of the linearly polarized light, which relates to absorption through the Beer-Lambert Law, allowing us to described the propagation of an infrared wave though an absorbing medium in direction \( x \) using equation 2.3, where \( k \) is the extinction coefficient.
Absorption of light by molecules excites them from the initial energy level, \( E_1 \), to an excited state, \( E_2 \), a discrete absorption of a photon \( h\nu_0 \) as shown in the Planck relationship in equation 2.4.

\[
\Delta E = E_2 - E_1 = h\nu_0 \tag{2.4}
\]

The intensity of the spectral absorption is equal to the rate of absorption described by equation 2.5.

\[
I = \frac{dE}{dt} = h\nu(N_2 - N_1)\rho(\nu)B_{12} \tag{2.5}
\]

where \( N_i \) is the population of molecules in energy level \( E_i \), \( \rho(\nu) \) is the radiation energy density, and \( B_{12} \) is the Einstein coefficient for absorption from the initial energy level to the excited state. \( B_{12} \) is proportional to the probability of energy transition per unit time and is defined by the interaction of the electromagnetic field with the molecule’s transition dipole moment.\(^{68}\) This equation gives rise to the surface selection rules as the intensity of the spectral absorption will only be nonzero if \( B_{12} \) is nonzero, which ultimately means a vibration will only be observed in the infrared spectrum if i) a transition dipole moment exists, and ii) it interacts with the electromagnetic field.\(^{68}\) It is this second point that gives rise to the surface selection rules.

2.1.1 Surface Selection Rules

Selection rules determine the transitions that can occur between electric dipoles of vibrational modes, and for molecules adsorbed on metal surfaces, additional selection rules apply. The dipole moment of a molecule can be described using Cartesian
coordinates with symmetry considerations. For a vibration of a molecule at a surface to be observed in the infrared spectrum, it must interact with the electric field at the surface, which is the vector sum of the electric fields from the incident, refracted and reflected light. In the case of a reflective metal, the refracted contribution is negligible, and we need only consider the incident and reflected beams.

The incident plane wave electric field vector $\mathbf{E}^i$ can be decomposed into two independent perpendicular components, each linearly polarized. $\mathbf{E}_s$ is the electric field perpendicular to the plane of incidence and is called s-polarized light, while p-polarized light has an electric field $\mathbf{E}_p$ that is in the plane of incidence. The amplitude of the electric field at the surface ($z=0$) for a plane wave incident at angle $\theta$ can be calculated for each polarization.\textsuperscript{69} For the electric field parallel to the surface (s-polarized light), the amplitude is:

$$E^\text{vacuum}_y(z = 0) = \left[1 - \frac{(\varepsilon - \sin^2 \theta)^{1/2} - \cos \theta}{(\varepsilon - \sin^2 \theta)^{1/2} + \cos \theta}\right] \mathbf{E}^0$$

For the electric field in the plane of incidence (p-polarized light), the $xz$ plane, the amplitude is:

$$E^\text{vacuum}_x(z = 0) = \left[1 - \frac{\varepsilon \cos \theta - (\varepsilon - \sin^2 \theta)^{1/2}}{\varepsilon \cos \theta + (\varepsilon - \sin^2 \theta)^{1/2}}\right] (\cos \theta \mathbf{E}^0)$$

$$E^\text{vacuum}_z(z = 0) = \left[1 + \frac{\varepsilon \cos \theta - (\varepsilon - \sin^2 \theta)^{1/2}}{\varepsilon \cos \theta + (\varepsilon - \sin^2 \theta)^{1/2}}\right] (\sin \theta \mathbf{E}^0)$$

Inspection of these three equations reveals that for a large $\varepsilon$, found for metals, the reflected light will have in-plane components ($E_x$ and $E_y$) of similar amplitude to the incident field. However, the s component undergoes a phase shift of approximately $180^\circ$.
at all angles of incidence, which results in largely destructive interference and a very small resultant electric field at the surface. The consequence is that molecular dipoles at metal interfaces will have extremely low interaction with $E_s$, effectively making them invisible in the IRRAS spectrum. p-polarized light has components parallel ($E_x$) and normal ($E_z$) to the surface, but the phase shift remains small for low angles of incidence. It reaches an optimum of $90^\circ$ phase shift at approximately $88^\circ$ incident angle for gold surfaces. As such, the incident and reflected field vectors add constructively in the $z$-direction for nearly all angles, but the $E_z$ field is largest at grazing angle incident light. Therefore, only vibrations with a normal component will couple to $E_z$ and be observed in the infrared spectrum. Consideration of these surface selection rules allows use of IRRAS to deduce orientation information about molecules on the surface, particularly when they are arranged in a uniform and organized manner, as will be discussed in the following section. Figure 2.1 is a schematic of s- and p-polarized light interacting with a reflective interface.
Figure 2.1: Schematic representation of a beam of radiation of s polarized light (top) and of p polarized light (bottom) where E is the electric field.
2.2 Infrared Characterization of Organic Molecules

Infrared spectroscopy can be used to characterize a variety of organic thin films, including alkanethiol SAMs and aromatic condensates. The C–H stretching region (2800 – 3100 cm$^{-1}$) is of particular interest as it allows for clear discernment in alkyl systems between terminal methyl and methylene C–H bonds. In aromatic systems, C–H bonds on the aromatic ring have stretching frequencies exclusively above 3000 cm$^{-1}$, allowing for clear differentiation between hydrogens bonded directly to carbons in the aromatic ring and those bonded to other carbons, such as an alkyl functional group. As described in the previous section, only vibrations with a normal component will couple to the surface normal component of the electric field and will therefore be observed in the IRRAS spectrum.$^{68}$ These surface selection rules therefore give rise to orientation information based on local geometry of the vibrational modes and their presence and intensity in the infrared spectrum.

2.2.1 C–H Stretching Vibrations of Alkyl Chains

Figure 2.2 is an illustration of the symmetric and asymmetric/antisymmetric C–H stretches of alkyl chains. The transition dipoles of both symmetric stretches are in the plane of the carbon-backbone. The antisymmetric stretch of the methylene is out of this plane, while the asymmetric stretch of the methyl has components both in and out of the plane of the carbon-backbone.
For an alkanethiol adsorbate in the all-trans configuration with the backbone aligned normal to the surface, the transition dipoles of both the both symmetric and antisymmetric stretches of the methylene groups would align in the plane of the metal surface and would therefore not absorb p-polarized light. Accordingly they would not be observed in the IRRAS spectrum. However, in this orientation, the methyl groups would be projected upwards from the surface, giving both the symmetric and asymmetric stretches vibrational components perpendicular to the surface, so both stretches would appear in the IRRAS spectrum. As previously discussed, however, alkanethiol monolayers on gold arrange such that the chains are tilted ~30° from the surface normal\textsuperscript{57}, similar to Figure 1.4. Thus, the transition dipoles of the methylene groups are no longer parallel to the surface, and the methyl groups retain components perpendicular to the surface, and as such, both the methyl and methylene stretches would be observed in the IRRAS spectrum.

In an alkyl chain system, such as alkanethiol SAMs, there are five absorption bands: the methyl symmetric stretch ($\nu$CH\textsubscript{3s}, 2876 cm\textsuperscript{-1}), the in- and out-of-plane methyl asymmetric stretches ($\nu$CH\textsubscript{3as}, ~2955-2965 cm\textsuperscript{-1}), the Fermi-resonance coupled methyl symmetric stretch ($\nu$CH\textsubscript{3s}, 2936 cm\textsuperscript{-1}), the symmetric methylene stretch
(νCH$_{2s}$, 2851 cm$^{-1}$) and the antisymmetric stretch of the methylene groups (νCH$_{2as}$, 2922 cm$^{-1}$). The stretching vibrations are summarized in Table 2.1 below.

**Table 2.1: Frequency assignments for the C–H and C–D stretching modes of C$_n$ films**

<table>
<thead>
<tr>
<th>Mode</th>
<th>Approximate Frequency (cm$^{-1}$)</th>
<th>C–H$^{67}$</th>
<th>C–D$^{37}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>νCH$_{2s}$</td>
<td>2850, 2854(β), 2862(α)</td>
<td>2097</td>
<td></td>
</tr>
<tr>
<td>νCH$_{3s}$</td>
<td>2876</td>
<td></td>
<td>~2078</td>
</tr>
<tr>
<td>νCH$_{2as}$</td>
<td>2917, 2924(α)</td>
<td>2198</td>
<td></td>
</tr>
<tr>
<td>νCH$_{3FR}$</td>
<td>2932</td>
<td></td>
<td></td>
</tr>
<tr>
<td>νCH$_{3as}$ oop</td>
<td>2954</td>
<td>2217</td>
<td></td>
</tr>
<tr>
<td>νCH$_{3as}$ ip</td>
<td>2961</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Notations: α and β refer to the CH$_2$ groups in the 2$^{nd}$ and 3$^{rd}$ positions of the chain with respect to the terminal methyl group; FR, Fermi Resonance; oop, out of plane; ip, in plane.

IRRAS can be used to probe chain order as it is commonly held that, in addition to improved peak resolution, highly ordered films demonstrate dominant methylene stretching bands at slightly lower frequencies.$^{37, 71}$ This is believed to be due to fewer gauche defects, which have vibrational frequencies at slightly higher wavenumbers than all-trans conformations. The clear distinction between methyl and methylene C–H stretches additionally allows for discrimination between dissociation sites within the film bulk (CH$_2$ bands) and those at the film-vacuum interface (CH$_3$ bands), which makes IRRAS ideally suited to monitor electron-induced chemical events in the organic layer.
2.2.2 Vibrational Bands of Adsorbed Mesitylene

Assigning the vibrations of aromatic compounds can be relatively complex as even simple benzene has thirty vibrational degrees of freedom; fortunately, considerable work has been done to identify and assign the frequencies of benzene, helping to inform the assignments for substituted benzenes, which have lower symmetry that complicate the vibrational assignments. 1,3,5-trimethylbenzene (“mesitylene”) has fifty-seven normal vibrations, but the relative arrangement of the hydrogen atoms of the methyl groups is unknown, which makes it difficult to name the proper symmetry of the molecule. The vibrations are most closely described by $D_{3h}$ symmetry of the $C_6H_3C_3$ skeleton and $C_3$ symmetry of the methyl groups. The majority of IR studies of mesitylene are conducted using gas or liquid mesitylene. Those IR results that address surface adsorbed mesitylene typically limit their scope to a particular spectral region, such as the C–H stretching region, or focus on a few particular vibrations, making it difficult to find definitive assignments for all of the IRRAS observed vibrations in the 600-3300 cm$^{-1}$ spectral range of this work. The vibrational assignments in the present work are therefore heavily reliant on the detailed work by Lokshin et al., which used the Varsányi predictions and expected frequency ranges to assign the frequencies of mesitylene for Raman spectra of liquid mesitylene and IR spectra of liquid and gaseous mesitylene. A summary of the mesitylene vibrational bands that appear in the Lokshin work for liquid and gas mesitylene are presented in Table 2.2 and described below. Figure 2.3 is an illustration of the C–H stretching and bending vibrations as well as the skeletal vibrations based on the normal vibrations of benzene illustrated by Varsányi.
### Table 2.2 The Vibrational Frequencies in the Infrared Spectrum of Mesitylene<sup>73</sup>

<table>
<thead>
<tr>
<th>Frequency (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Assignment</th>
<th>Symmetry</th>
<th>Linear Plane</th>
<th>Vibration&lt;sup&gt;77&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>Liquid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3023s</td>
<td>3017s</td>
<td>νCH&lt;sub&gt;ar&lt;/sub&gt;</td>
<td>E'</td>
<td>(x,y) 20a, 20b</td>
</tr>
<tr>
<td>2932s</td>
<td>2970sh</td>
<td>νCH&lt;sub&gt;3as&lt;/sub&gt;</td>
<td>A', A''</td>
<td>x,y</td>
</tr>
<tr>
<td></td>
<td>2946sh</td>
<td>νCH&lt;sub&gt;3s&lt;/sub&gt;</td>
<td>A'</td>
<td>x,y</td>
</tr>
<tr>
<td>2877m</td>
<td>2860s</td>
<td>1448x2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2745w</td>
<td>2730m</td>
<td>1379x2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1615, 1609</td>
<td>1608vs</td>
<td>ν&lt;sub&gt;ring cc&lt;/sub&gt;</td>
<td>E'</td>
<td>(x,y) 8a, 8b</td>
</tr>
<tr>
<td>1519, 1505</td>
<td>1579vw</td>
<td>Combination tones</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1563vw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1511vw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1490</td>
<td>1473vs</td>
<td>δCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>A', A''</td>
<td>x,y</td>
</tr>
<tr>
<td>1460</td>
<td>1443w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1418w</td>
<td>ν&lt;sub&gt;ring&lt;/sub&gt;</td>
<td>E'</td>
<td>(x,y) 19a, 19b</td>
</tr>
<tr>
<td>1376, 1387</td>
<td>1376m</td>
<td>δCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>A'</td>
<td>x,y</td>
</tr>
<tr>
<td>1056</td>
<td>1038s</td>
<td>ρCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>A'</td>
<td>x,y</td>
</tr>
<tr>
<td>1042</td>
<td>1017w</td>
<td>ρCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>A''</td>
<td>z</td>
</tr>
<tr>
<td>929, 937</td>
<td>929w</td>
<td>νC–Me</td>
<td>E'</td>
<td>(x,y) 7</td>
</tr>
<tr>
<td>828-836-845‡</td>
<td>836s</td>
<td>ρCH</td>
<td>A''</td>
<td>z</td>
</tr>
<tr>
<td></td>
<td>754vw</td>
<td>Combination tones</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>737vw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>729vw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>678-683-694‡</td>
<td>687s</td>
<td>ν&lt;sub&gt;ring&lt;/sub&gt;</td>
<td>A''</td>
<td>z</td>
</tr>
</tbody>
</table>

Notations: vw, very weak; w, weak; m, medium; s, strong; vs, very strong; z-linear plane, perpendicular to the plane of the ring; x- and y-linear plane, in the plane of the ring

‡PQR structure with a strong Q branch
Figure 2.3: Adapted illustration of the mesitylene vibrations in the IR spectrum. The blue arrows in the top images indicate the in-plane and out-of-plane components of the transition dipoles with respect to the plane of the ring. The frequencies listed are from literature.
2.2.3 Surface Selection Rules for Adsorbed Mesitylene

Many of the vibrational bands of mesitylene presented in Table 2.2 have extremely weak IR absorptions and the low intensities are difficult to discern in the IRRAS spectra even at high exposures. For the purpose of determining molecular orientation, it is only necessary to consider a few representative vibrations – those with transition dipoles that clearly indicate relative molecular orientation based on consideration of the surface selection rules. For example, in the C–H stretching region of 2800-3100 cm\(^{-1}\), the methyl asymmetric stretches (\(\nu_{\mathrm{CH}}^{\text{as}}\)) have both in-plane and out-of-plane components with respect to the plane of the ring, and should therefore be visible in the IRRAS spectra regardless of the orientation of the molecule. The methyl symmetric stretches (\(\nu_{\mathrm{CH}}^{\text{s}}\)) have only an in-plane component with respect to the ring, which is also true of the aromatic C–H stretches (\(\nu_{\mathrm{C-H}}^{\text{ar}}\)). They will therefore only be observed if the ring of the molecule is not parallel to the surface, such that the vibrations have a transition dipole component normal to the surface. In contrast, the two skeletal vibrations, \(\chi_{\text{ring}}\) and \(\rho_{\text{CH}_{\text{oop}}}\), which have only an out-of-plane component with respect to the plane of the ring, will be strongly observed if the ring is parallel or even at some angle on the surface, but they will not be observed if the plane of the ring is completely perpendicular to the surface as their transition dipole moment will then be exclusively parallel to the surface and will not couple to the normal electric field. Since the \(\nu_{\mathrm{CH}}^{\text{3s}}, \nu_{\mathrm{C-H}}^{\text{ar}}, \chi_{\text{ring}}\) and \(\rho_{\text{CH}_{\text{oop}}}\) vibrations have relatively strong intensities in the IR spectra, they are ideal candidates for monitoring molecular orientation, and we can consider them as representative for the case of interpreting molecular orientation with respect to surface selection rules. Discussions in Chapters 4 and 5 will focus on these four aforementioned vibrational bands to interpret behavior and molecular orientation from the IRRAS results.
2.3 Orientation of Adsorbed Aromatic Molecules

In the absence of strong chemisorption (such as the sulfur-gold bond that anchors alkanethiol SAMs to gold substrates), predicting the orientation of a molecule such as mesitylene on a surface and its behavior with increasing coverage is difficult. In the case of hydrocarbon aromatic rings, such as benzene, it is believed that the interaction with the π-orbitals will be the defining influence.\textsuperscript{78, 79} An example is provided by a comparison between the ring orientation in films of benzene and of benzenethiol, the closest SAM analogue. The chemisorption anchoring of the sulfur–gold bond in benzenethiol suggests that the phenyl ring would have an approximately upright orientation, and in fact, it was found to be tilted about 30° from the surface normal.\textsuperscript{80} Monolayers of benzene, in contrast, have been shown to adsorb on nearly all metals with benzene flat-to-the-surface, which is consistent with anticipated back donation of electron density from the metal surface to the benzene π*-antibonding orbitals.\textsuperscript{78} Syomin et al. observed only the C–H out-of-plane bending mode (ρCH) in the IR, indicative of a flat orientation, for monolayer and submonolayer coverages of benzene adsorbed on Au(111) at 90 K in vacuum.\textsuperscript{81} Aqueous electrochemical experiments confirmed the flat orientation of benzene on gold and on silver,\textsuperscript{78} and vapour studies of benzene adsorbed on silver at 11 K also indicate a flat orientation.\textsuperscript{82} In contrast, a similar study in which the benzene film was subjected to a post-adsorption heating and cooling process (adsorbed at 70 K, heated to 95 K, then cooled to 20 K) suggested benzene adopts a slightly tilted orientation, or rather, has a more fluxional structure yielding distributed orientations.\textsuperscript{78} However, the study pointed to the greater likelihood of a contamination layer being present at the metal-vacuum interface than in an electrochemical environment, which consistently yielded the flat-orientation model; such a contamination layer could weaken
or prevent benzene chemisorption from occurring as it had in the electrochemical experiments. 78

The near flat-to-the-surface orientation of toluene in both aqueous studies and vacuum deposition at 20 K was also deduced from surface selection rules. 78, 83 Toluene, o-xylene and mesitylene, have been shown to adopt similar orientations on Rh(111) under aqueous conditions, and p-xylene lies with the ring parallel to the surface on Pt(111) and on Rh(111) when adsorbed from both and aqueous and vacuum environments, though the vacuum deposited film is more disordered. 89

Each of these experiments investigated molecular orientation at coverages at or below one monolayer and found the molecules each adopt an orientation with their ring parallel to the surface at submonolayer coverages. Increasing the coverage of benzene beyond a monolayer to a bi-layer and ultimately to a 10-monolayer thick film results in appearance of several in-plane bands, 81 which can only be observed in the IRRAS spectrum if the molecules adopt a tilted orientation, projecting the planar bands such that they display a z-component to their transition dipole moments and interact with the normal component of the electric field. This is consistent with either a uniform change in orientation or some fraction of the molecules changing from a parallel orientation, with multilayers having more randomly oriented molecules. 81 The presence of the additional layers disrupts the π-interactions between the first monolayer and the metal substrate, and the separation of multi-layers from the underlying substrate competing with the π-interactions with gold, weakening the effect that would otherwise dictate ring orientation. A perpendicular orientation was also observed when a liquid drop of benzene, toluene, m-xylene and mesitylene were each sandwiched between two NaCl
plates. FT-IR indicates that they all adopt a tilted orientation and stack with their rings against one another and perpendicular to the surface plane.\textsuperscript{75}

Cyclohexane lacks the π-bonds for strong interaction with the metal surface and therefore provides for an interesting comparison to the aromatic cyclic hydrocarbons above. At submonolayer coverages on Cu(111), the molecular plane of cyclohexane is relatively parallel to the surface, but with completion of the first monolayer, the ring adopts a more tilted orientation.\textsuperscript{90} On Au(111), however, the lying down and tilted phases are believed to co-exist at monolayer coverages.\textsuperscript{91} The film structures of cyclohexane and of benzene multilayers highlights the potential for evolving and complex film structures with increasing coverages, particularly when the π-interactions with the substrate are limited.

In the case of mesitylene, our molecule of interest, temperature programmed desorption studies indicate mesitylene exhibits no chemical reaction when adsorbed on a film of MgCl$_2$-supported titanium chloride.\textsuperscript{92} This is attributed to the high level of stability of the conjugated π-electron ring. Due to its disk-like geometry, with a radius of 4.5 Å and little conformational freedom, mesitylene has been identified as an ideal molecule for surface area measurements; BET experiments have found that mesitylene occupies an area of 71±5 Å/molecule when adsorbed on silicate surfaces.\textsuperscript{93} It was noted, however, that that the area occupied by mesitylene may be affected by the surface on which it is absorbed\textsuperscript{93}, which is typical of organic molecules.\textsuperscript{94}

Because orientation and film morphology information for surface adsorbed mesitylene is extremely limited, one of the first challenges to this work was to characterize the adsorbed films using IRRAS with the goal of determining film
morphology, the effect of increasing coverage on the orientation of the adsorbed molecules, and the thermodynamic stability of the films. The characterization of these as-deposited films can be found in Chapter 4.

2.3.1 Effect of Temperature on Organic Film Orientation and Order

To ensure a stable and reproducible film, the as-deposited films will be subjected to a heating and cooling cycle to investigate the effect of temperature on molecular orientation.

Thermotropic studies of long chain alkanethiol SAMs on gold from 150 to 450 K demonstrate that the chains gradually untilt with heating, though they remain predominantly all-trans up to about 350 K, above which, an irreversible transition to a liquid-like phase is observed.\textsuperscript{71} This transition is reported to be quite gradual rather than occurring sharply over only a few degrees. From 150 to \(~350\) K the gauche defects that occur are primarily near the chain termini\textsuperscript{47} and are reversible, while the conformational gauche defects within the chains that occur above 350 K are not reversible, and significant desorption occurs above 400 K. The linewidth (FWHM) remains roughly constant to \(~300\) K, but then begins to increase linearly and the peaks broaden.\textsuperscript{71} As temperatures are decreased down to 25 K, the C–H stretching modes tend to shift by several wavenumbers to lower frequencies with the minimization of conformational defects, which typically have vibrational frequencies higher than all-trans conformations.\textsuperscript{37}

Benzene adsorbed on Au(111) is found to have four desorption temperatures: 239 K, corresponding to submonolayer coverages, and 210 K, 155 K and 151 K, corresponding to one monolayer, the second layer, and thicker films, respectively.\textsuperscript{81}
Mesitylene adsorbed on a MgCl$_2$-supported titanium chloride film was found to desorb in the range of 170–350 K. Exposures above 4 L resulted in a multilayer desorption peak around 170 K, though the desorption profiles of mesitylene differed between the MgCl$_2$ supported titanium chloride film and another inorganic catalyst.

Ibberson et al. identified three low temperature crystallographic structures that can exist in bulk mesitylene samples depending on the cooling rate and thermal procedure. Freezing mesitylene at liquid nitrogen temperatures and grinding with a mortar results in phase I packing (Figure 2.4). Slow cooling (< 2 K/min) results in over-cooled liquid passing through phase I and freezing in phase II, which is a metastable structure that transforms to phase III around 90 K. This second transformation is reversible if the sample is kept below 180 K.; above 190 K phase II transforms to phase I.

![Figure 2.4](image)

**Figure 2.4:** Perspective view of the molecular packing in phase I (left) and phase II (right) of mesitylene. For clarity the disordered hydrogen atoms have been omitted from phase II. Full structure of phase III is not available. (Reprinted with permission from Structure Determination and Phase Transition Behaviour of Mesitylene, Ibberson et al., Z. Kritallog. Suppl. 26. © 2007. Oldenbourg Wissenschaftsverlag GmbH.)
3.1 Substrate Preparation

3.1.1 Gold Film Preparation

Gold films were evaporated onto mica sheets (Axim Mica, V1/V2 MicaWindow), following a procedure adapted from that of DeRose et al.\textsuperscript{50} and similar to that recommended by Dishner et al.\textsuperscript{51}, which has been shown to prepare high quality Au(111) films\textsuperscript{18} with strong adhesion to the mica substrate.\textsuperscript{51} Thermal vapour deposition is accomplished in Midas, an in-house built all-metal evaporation chamber evacuated to $10^{-7}$ Torr by a turbomolecular pump coupled to a mechanical pump. Freshly cleaved mica is secured, fresh side out, to a copper plate, which is suspended in an inverted position, approximately 30 cm above the evaporation source. Under vacuum, the copper plate with the mica is heated to 300 °C for 12 hours before evaporation to allow the mica to degas; water, in particular, can prevent the gold film from adhering to the mica. 1.2 g of gold (Kurt J. Lesker, 99.999\%) is evaporated from a resistively heated molybdenum boat at a rate of \(~1\ \text{Å/s}, monitored with a quartz crystal microbalance to a thickness of 200-250 nm. Heating of the Au/mica is continued for 3 hours under vacuum to anneal the films, which are then allowed to cool in the vacuum chamber and are stored in a desiccator until use.

3.1.2 Substrate Cleaning Procedure

Gold substrates were cleaned in a two-step process involving acid treatment followed by UV-ozone cleaning. Gold films were cleaned with sulfochromic acid (chromium trioxide in concentrated sulfuric acid) to remove macro-contaminants and
adventitiously adsorbed hydrocarbon material (NOTE: chromium trioxide is extremely corrosive, toxic and carcinogenic, and it should be handled with extreme caution). The slides were then rinsed profusely with ultrapure water (Milli-Q, 18.2 MΩ.cm), then with methanol following the cleaning procedure of Kang and Rowntree. Substrates to be used for SAM formation were then treated following the procedure described in the next section. Substrates to be used for vapour deposition experiments were cut to size, mounted in holders, and placed in a UV-ozone cleaner for 25 minutes, immediately before transfer to the vacuum chamber.

3.1.3 SAM Formation

Substrates to be used for SAM formation were cleaned using the sulfochromic acid cleaning procedure above, then submerged in 1 mmol thiol in methanol solutions (Caledon, Reagent 99.8%), and left gently heating at 30 °C for at least 24 hours. d3-hexadecanethiol, a C16 alkanethiol with the terminal group deuterated, was available in our laboratory from a previous synthesis, and the gentle heating was to improve the solubility of the long chain C16 thiol in methanol. After 24 hours, the substrates were removed from solution, rinsed generously with fresh methanol, cut to size, mounted in holders, and transferred to the vacuum chamber for immediate use.

3.2 UHV Chamber

Experiments were performed using Phoenix, our in situ IRRAS ultra-high vacuum (UHV) system consisting of two subchambers separated by a UHV-compatible gate valve. The smaller “load lock” section allowed accelerated sample exchange without exposing the main chamber to atmospheric contaminants. The main chamber is equipped
with a 220 L/s TNB-X ion pump-Titanium Sublimator pump combo and achieves a base pressure of $1 \times 10^{-10}$ Torr. Phoenix is illustrated in Figure 3.1 below and described in detail in the following sections.

**Figure 3.1:** Schematic view of Phoenix – the *in situ* IRRAS apparatus. The principal vacuum chamber contains the sample manipulator (S) connected to the heater and cryostat tip, the electron gun, and a leak valve for gas dosing. The external optical compartment consists of deflecting and focusing mirrors and an MCT-A detector. The electron gun controller, heater and the FT-IR system are interfaced with the computer.
3.2.1 Sample Transfer Via the Load Lock

Samples were cut to size (1 cm x 2 cm) and secured to a copper holder by screwing two copper bars across the top and bottom edge, providing both electrical and thermal contact to the gold face of the mica sheet. Sample holders are placed onto a support mounted on a magnetically coupled long-stroke feedthrough in the load lock, which was pumped by a 250 L/s turbomolecular pump (Pfeiffer). Following evacuation of the load lock to a pressure of $1 \times 10^{-6}$ Torr, the isolation valve is opened, and the transfer rod can be advanced into the UHV main chamber where the sample is transported with a wobble-stick to the sample stage, a XYZ-tilt-rotation manipulator assembly (home built). The copper sample holder is supported on the support stage by two rear-facing extensions that hook over the top of the stage’s vertical support as well as by a 5 x 10 mm tab on the bottom of the copper sample holder that slots loosely into a gallium-filled well on the sample stage. Gallium is UHV compatible as it has a very low vapour pressure ($9.8 \times 10^{-10}$ Torr at 840 K). Gallium ensures good electrical contact and thermal link and provides a rigid link below 29 °C, the freezing point of gallium. 2 mm glass spheres press-fit into the sides of the sample stage act as tilt pivot points and provide thermal and electrical isolation of the sample support from the manipulator. A sapphire plate clamped between oxygen free high conductivity (OFHC) copper plates provides electrical insulation from the grounded cryostat.

3.2.2 Temperature Control

The sample support block has an embedded 25 W heater as well as OFHC copper braids connecting it to the tip of the closed cycle-helium cryostat head (ADP Cryogenics HC-2D). These braids allow for translation, rotation and tilt of the sample stage for
alignment purposes. Temperatures at the sample support are measured using a 0.07% Fe/Au thermocouple attached to a commercial controller system (Omega Engineering CYC-3000), and the heating rate is controlled with a LabView computer program. There was no evidence to suggest that a significant temperature gradient existed between the thermocouple and the film surface when using a maximum cooling rate of 2 K/min and a heating rate of less than 10 K/min. During the multi-hour experiments, there was no evidence of contamination by adsorbed species as determined by infrared spectroscopy. The cryostat is able to cool sample to cryogenic temperatures, achieving a base temperature of 22 K.

### 3.2.3 Vapour Preparation and Dosing

A custom built gas board allows gas or vapour dosing into the main chamber through a precision leak valve (Varian). A few drops of mesitylene (Aldrich, 98%) are added to a pyrex vial, which has a pyrex to metal junction (Kurt J. Lesker) so it can be swaged onto the gas board. Dissolved gases were removed by performing freeze-pump-thaw cycles; the vial of mesitylene was submerged in liquid nitrogen (LN) to freeze the mesitylene, the vial was opened to vacuum and pumped on for 5 minutes, then the LN was removed and the vial closed to vacuum while the mesitylene melts. This process was repeated 4-6 times to degas the mesitylene. Immediately prior to and during dosing, the mesitylene vial and dosing lines were heated to ~35 °C by wrapped rope heaters (Omega, HTC) to facilitate evaporation of the mesitylene and dosing onto the surface at $1 \times 10^{-7}$ Torr. No freeze-pump-thaw cycle or heating was applied during rare gas dosing as ultra high purity xenon was provided in a compressed gas cylinder (BOC, 99.999% research grade), and dosing was carried out at $1 \times 10^{-8}$ Torr. Pressures were
measured with a cold cathode gauge interfaced with the computer to output a cumulative exposure reading in Langmuirs (Note: 1 L = 1x10^6 Torr.s), and all pressures were uncorrected for detector sensitivity. Cold cathode gauges are sensitive to gas composition and are generally calibrated to pure nitrogen. Smaller molecules and lighter gases (He, H₂) are generally harder to ionize and will give lower pressure readings, while heavier gases (Ar, Xe) will read higher pressures. For example, Xe will give a reading 2.87 times higher than the actual pressure, while benzene, toluene and p-xylene will give readings 6, 6.8 and 7.9 times higher, respectively, than the true pressure. The sensitivity factor of mesitylene is not known, but the detector is expected to be approximately 9 times more sensitive to mesitylene based on the trend of the methyl-substituted benzenes. All pressures in this work have been given as uncorrected values, which is common practice in the literature.

3.3 **Infrared Reflection Absorption Spectroscopy**

The vacuum system is coupled to an FT-IR system with the post-interferometer beam redirected through a rigid PVC tube into a purged optics compartment mounted directly to a single flange securing two differentially pumped NaCl windows to the chamber. The beam from the FT-IR bench (Nicolet Magna 560, ThermoInstruments) is directed with Au-surfaced mirrors, including two adjustable mirrors inside the UHV chamber, such that the incident angle on the target surface is ~85°. A parabolic mirror focuses the beam onto the surface, and an ellipsoidal mirror refocuses the light to the detector. The reflected beam is directed onto an external, LN-cooled MCT-A detector, and Omnic Instrument software is used to process the signal, though custom LabVIEW-based software is used to control the spectrometer, acquire data, and display
the spectra. A 2 cm\(^{-1}\) resolution and 2 cm/s moving mirror velocity were used, and 512 mirror scans were typically co-added to produce each absorption-versus-wavenumber spectrum. Unless otherwise specified, the standard reference was the reflectivity of a pristine Au/mica surface. For some experiments, a SAM/Au/mica surface was used as a reference surface.

Infrared reflection absorption spectroscopy is both non-destructive and extremely sensitive to compositional and structural variations of organic thin films, making it an attractive candidate for surface analysis. IRRAS can be used to assess the cleanliness of a metal substrate with respect to organic contaminants, to evaluate the quality of a pristine organic film\(^{37, 71}\), and to monitor damage induced by incident electrons\(^6, 25, 99\). A more detailed explanation of the theory of infrared radiation and IRRAS and its spectroscopic application to organic thin films was provided in Chapter 2.

3.4 LOW ENERGY ELECTRON IRRADIATION

Electron irradiation is accomplished using a home-built electron gun/controller system that is interfaced with the computer. An in-house built low energy electron source is mounted between the two NaCl windows on the UHV chamber, with the main source axis aligned perpendicular to the IRRAS flange. Three cylindrical lenses deliver the 1-10 \(\mu\)A electron beam from a resistively heated tungsten filament with a tantalum disk (Kimball Physics CB-102) at normal incidence to the surface. For uniform irradiation, the beam can be rastered (10-100 Hz) across the surface by two orthogonal fields located beyond the final lens. Surface current is measured with an electrometer that allows for the sample potential to be adjusted with respect to the chamber potential. The sample voltage
is typically held at –2.0 eV to reduce backscattered current from returning to the surface and to stop low energy electrons scattered off the deflectors or lenses from reaching the surface. The incident electron beam energy is operationally defined as the potential between the filament centre and the surface, and it is conservatively estimated to have an accuracy of 0.5 eV with a distribution of 0.3-0.4 eV (FWHM). The computer monitors the beam current at one second intervals during irradiation, integrating current versus time to yield the quantity of total charge delivered.\textsuperscript{11}

3.4.1 Monitoring Surface Charging

Anion fragments produced by DEA of alkanethiol SAMs and of condensed H\textsubscript{2}O and O\textsubscript{2} are known to become trapped in RG layers.\textsuperscript{25, 26} One method of monitoring the accumulation of these anions on the surface is by obtaining a low energy electron transmission scan (LEET), which involves recording the current arriving at the surface as a function of the potential applied between the filament and the surface.\textsuperscript{101} This produces a spectrum, called an injection curve, which has a sharp rise when the potential creates electrons with sufficient energy to enter into the film from vacuum. Figure 3.2 is the injection curves for an alkanethiol SAM/Au with a xenon overlayer irradiated at 7.7 eV to produce H\textsuperscript{−} ions via DEA that become trapped in the RG overlayer as described in Section 1.2.5. The injection curves reflect the increasingly repulsive surface by shifting the onset of current detected at the sample to higher accelerating potentials as the incident electrons must now have higher kinetic energy to overcome the negative potential barrier.\textsuperscript{102} Though the LEET scan itself does deliver electrons to the surface, the current reaches a maximum of only a few \(\mu\)A for less than a tenth of a second, minimizing the damaging effect of this initial energy probe.
Figure 3.2: Injection curves obtained from an uncharged and an increasingly charged alkanethiolated gold surface with a 60 L overlayer of xenon showing the shift in the accelerating energy required to maintain a set current.

A series of injection curves for a sample are obtained by rapidly recording the initial injection curve of the freshly deposited film, followed by electron bombardment at a given filament-to-surface potential for a longer period to deliver a set quantity of charge. Another injection curve is then measured for comparison to the initial curve to determine the shift in accelerating voltage. Electron bombardment at a particular voltage followed by measuring the current injection curve is repeated on the same film multiple times and represents the accumulation of charge on the surface.
3.5 Experimental Sequence

Au(111) on mica substrates were freshly prepared and cleaned following the procedures outlined in section 3.1. For the deposition experiments on bare gold and on the SAM/Au, the samples were loaded into the UHV chamber and an initial room temperature IRRAS spectrum was obtained to evaluate the cleanliness of the gold surface or the quality of the SAM film.

For both substrates, samples were cooled by the cryostat and reference spectra were collected at a base temperature of approximately 22 K and a base pressure of 1x10^{-10} Torr. With the samples held at 22 K, mesitylene was introduced to the chamber, dosing was monitored with the mass spectrometer, and IRRAS spectra were collected during the exposure. Once the desired exposure had been reached, mesitylene dosing was stopped, and IRRAS spectra continued to be collected while the chamber pressure decreased.

For the thermal treatment experiments, the samples were heated up to 145 K where they could be held overnight to verify stability. Typically, however, the samples were only held at 145 K for an hour before the heat was turned off and the cryostat was allowed to resume cooling the samples to 22 K. IRRAS spectra were collected during both the heating and cooling phases to monitor changes in the absorption bands, and the mass spectrometer was used to monitor desorption of mesitylene at temperatures above 160 K. Samples were prepared with exposures ranging from 60 L to 800 L, and reproduced at 200, 400 and 800 L.

Once the mesitylene has been deposited on the Au(111) or SAM/Au(111) substrates and subjected to the thermal treatment, a final pre-irradiation IRRAS spectrum was
acquired for reference. Electron irradiation is accomplished with a home-built electron gun/controller system interfaced with the computer, as described in section 3.4. An initial current injection curve is obtained and irradiation is commenced with periodic IRRAS spectra collection (every 0.1-0.25 mC) to monitor surface damage.

The thermally treated samples were irradiated at one of three energies, 7.7 eV, 8.5 eV or 10 eV. These energies were selected based on the following considerations: i) 7.7 eV was selected both because the Rydberg states of mesitylene are concentrated in this energy region and because 7.7 eV is the energy required to create the xenon anionic exciton needed for rare-gas mediated experiments; ii) 8.5 eV would act as a control for rare-gas experiments as it would not produce xenon anionic excitons; iii) 10 eV produces the maximum amount of DEA-induced damage to alkanethiol SAMs as well as a high level of damage to adsorbed benzene molecules, and it therefore was used to probe the robustness of the adsorbed mesitylene.

IRRAS is used to characterize the irradiated films and look for evidence of bond cleavage, which would be indicated by a reduction in the absorbance of the C–H stretching bands. Two types of IRRAS spectra are presented in this work: traditional absorption spectra referenced to pristine Au(111) or SAM/Au(111) as well as difference spectra in which the post-irradiation spectra are referenced to the mesitylene film immediately prior to irradiation. These later spectra are useful for highlighting small electron-induced changes in the spectra. Cleavage of C–H bonds would be presented as negative-going peaks in these difference spectra.
4.1 Vibrational Band Assignments for Adsorbed Mesitylene

Table 4.1 summarizes the vibrational bands observed in the IRRAS spectrum for mesitylene adsorption on Au(111) and on C₁₆SAM/Au(111) presented alongside the literature frequencies of liquid mesitylene from Lokshin et al.⁷³

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Assignment</th>
<th>Symmetry</th>
<th>Linear Plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbed on Au(111)</td>
<td>Adsorbed on SAM/Au(111)</td>
<td>Liquid⁷³</td>
<td></td>
</tr>
<tr>
<td>3015, 3035</td>
<td>3017</td>
<td>νCH₂⁺</td>
<td>E'</td>
</tr>
<tr>
<td>2970</td>
<td>2970</td>
<td>νCH₃as</td>
<td>A', A''</td>
</tr>
<tr>
<td>2947</td>
<td>2946</td>
<td>νCH₃s</td>
<td>A'</td>
</tr>
<tr>
<td>2912</td>
<td>2918</td>
<td>νCH₃s</td>
<td>A'</td>
</tr>
<tr>
<td>2853</td>
<td>2860</td>
<td>1448x2</td>
<td></td>
</tr>
<tr>
<td>2728</td>
<td>2730</td>
<td>1379x2</td>
<td></td>
</tr>
<tr>
<td>1609</td>
<td>1608</td>
<td>νring cc</td>
<td>E'</td>
</tr>
<tr>
<td>1478</td>
<td>1473</td>
<td>δCH₃</td>
<td>A', A''</td>
</tr>
<tr>
<td>1444</td>
<td>1443</td>
<td>δCH₃</td>
<td>A'</td>
</tr>
<tr>
<td>1418</td>
<td>1418</td>
<td>νring</td>
<td>E'</td>
</tr>
<tr>
<td>1373</td>
<td>1376</td>
<td>δCH₃</td>
<td>A'</td>
</tr>
<tr>
<td>1165</td>
<td>1166</td>
<td>δCH</td>
<td>E'</td>
</tr>
<tr>
<td>1037</td>
<td>1038</td>
<td>δCH</td>
<td>E'</td>
</tr>
<tr>
<td>1017</td>
<td>1017</td>
<td>δCH₂⁺</td>
<td>A''</td>
</tr>
<tr>
<td>928</td>
<td>929</td>
<td>νC–Me</td>
<td>E'</td>
</tr>
<tr>
<td>840</td>
<td>836</td>
<td>ρCH₂⁺</td>
<td>A₂''</td>
</tr>
<tr>
<td>689</td>
<td>687</td>
<td>χring</td>
<td>A₂''</td>
</tr>
</tbody>
</table>

Notations: z-linear plane, perpendicular to the plane of the ring; x- and y-linear plane, in the plane of the ring
The bands above 3000 cm\(^{-1}\) are unambiguously assigned to the aromatic C–H stretches (\(\nu_{\text{CH}}\)) and agree well with literature. In the liquid phase\(^{73}\), the skeleton of mesitylene exhibits vibrations at 687 cm\(^{-1}\) and 836 cm\(^{-1}\), corresponding to the ring torsion (\(\chi_{\text{ring}}\)) and out-of-plane aromatic C–H bends (\(\rho_{\text{CH}}\)), respectively; these appear in the as-deposited film at 685 cm\(^{-1}\) and 840 cm\(^{-1}\), respectively. The two vibrations each have \(A_2\)" symmetry and are therefore infrared active in the direction perpendicular to the plane of the aromatic ring (\(z\)-direction).\(^{73, 103}\) The as-deposited film demonstrates a slightly higher frequency for the \(\rho_{\text{CH}}\) band, but a slightly lower frequency for the \(\chi_{\text{ring}}\) band when compared to the liquid phase results. In contrast, an adsorption study on aerosils by Galkin et al. found the \(\chi_{\text{ring}}\) frequency of adsorbed mesitylene, 688 cm\(^{-1}\), to be slightly higher than the liquid frequency from literature, 686 cm\(^{-1}\).\(^{76}\) However, this vibration is sensitive to the redistribution of \(\pi\)-density, so the nature of the substrate may affect the disturbance of the \(\pi\)-electron system of the ring upon adsorption.\(^{76}\)

The strongly IR active CC stretches of the ring (\(\nu_{\text{ring}}\)) are observed at 1608 cm\(^{-1}\) in spectra from both liquid and adsorbed samples. The liquid spectra\(^{73}\) contain weak ring stretches at 1418 cm\(^{-1}\) (\(\nu_{\text{ring}}\)), CC stretches of the ring to methyl carbons (\(\nu_{\text{C–Me}}\)) at 929 cm\(^{-1}\), and the C–H bend (\(\delta_{\text{CH}}\)) at 1166 cm\(^{-1}\), which are classified as E’ vibrations and are infrared active in the (x,y) directions. In the IRRAS spectra, however, they have very low relative intensity.

Based on good agreement with the liquid frequencies, the vibration of the methyl groups are assigned as follows: 2912 cm\(^{-1}\) (\(\nu_{\text{CH}_3s}\)) of class A’ and two asymmetric vibrations (\(\nu_{\text{CH}_3as}\)) at 2948 and 2970 cm\(^{-1}\) of classes A’ and A". On the basis of local \(C_s\) symmetry, the vibrations in liquid mesitylene at 1017 cm\(^{-1}\) and 1038 cm\(^{-1}\) were
assigned by Lokshin et al. to the methyl rocking vibrations (ρCH₃) of classes A” and A’, respectively. However, the former is difficult to discern in the IRRAS spectra even at high coverages. IRRAS frequencies 1373, 1444, and 1478 cm⁻¹ correspond well to the liquid phase study, which assigned them to the symmetric and two asymmetric deformations of the methyl groups (δCH₃), the first of which is A’, while the second two are A’ and A”.

4.2 VAPOURS DEPOSITION OF MESITYLENE THIN FILMS

IRRAS spectra of the low frequency bands ρCHₒₒ and χᵣᵣ of mesitylene on Au(111) during increasing exposure at cryogenic temperatures, showing the increasing intensity of each band as the film grows are shown in Figure 4.1. The spectra have been labeled according to their exposure in Langmuirs. However, the phenomenon described in Section 1.2.5 in which the adsorption of a monolayer of adsorbate on a SAM causes the transformation of the methyl band can be used to estimate the relation between exposure and coverage for the vapour dosed mesitylene. Based on the transformation of the deuterated-methyl band, the first monolayer of mesitylene is estimated to be complete after approximately 50-60 Langmuirs of exposure. The 787 L exposure therefore corresponds to approximately 14 monolayers, while the 200 L films correspond to about 3-4 monolayers.
Figure 4.1: IRRAS absorption spectra from 680-890 cm\(^{-1}\) during adsorption of mesitylene on a Au(111) surface at 22 K, referenced to the pristine Au(111) sample immediately preceding the gas dosing. The band at 687 cm\(^{-1}\) corresponds to the ring torsion vibration (\(\chi_{\text{ring}}\)), and the band at 839 cm\(^{-1}\) is due to an oop bending of the ring C-H groups (\(\rho\text{CH}_{\text{oop}}\)). The exposure is measured in Langmuirs (L). **NOTE:** All but the final spectra were acquired during dosing, so the designated exposure represents an average of the range over which each spectrum was acquired. For example, the 26 L spectrum was acquired during the dosing period of 1-52 L of exposure. The 787 L spectrum was acquired after the chamber pressure had returned to base-levels.
While the bands can be clearly discerned in films of 60 L exposure, those around 30 L are difficult to distinguish from the background noise. The band shapes, frequencies and intensities are similar for equivalent exposures of mesitylene adsorbed on Au(111) and on an alkanethiol SAM on Au(111). An examination of the above spectra with consideration for surface selection rules gives an indication of the orientation of the molecules on the surface; if the molecules were adsorbing with the rings aligned perpendicular to the surface plane, neither of these two out-of-plane vibrations would be observed in an IRRAS spectrum as they would fail to interact with the electric field in the z-direction. If instead the molecules were adsorbing with the ring plane parallel to the surface, these out of plane vibrations would have increased intensity, while the in-plane vibrations would not be observed in the IRRAS spectra as the vibrations would not have a transition dipole component in the z-direction to interact with the p-polarized light. A plot of the infrared absorption intensity of the four diagnostically important vibrations, $\nu\text{CH}_3$, $\nu\text{CH}_{ar}$, $\chi_{\text{ring}}$ and $\rho\text{CH}$, as a function of exposure (Figure 4.2). The two in-plane vibrations have lower intensity than the two out-of-plane vibrations, but the fact that they are observed in the IRRAS spectra precludes the rings lying completely flat to the surface.

Because it is difficult to distinguish low exposures (<50 L) from the background noise, the slight deviation from linearity observed in the 20-100 L region of the graph, particularly for the out-of-plane vibrations, may only be an artifact of measuring the peak values. Generally speaking, however, all four bands display evidence of linear growth with increasing exposure, which is possible if the molecules are adsorbing with some uniformly tilted orientation, or more likely, in a random fashion with various orientations.
on the surface. The linear trend indicates the film grows homogeneously with molecules in the \( n^{th} \) layer adsorbing the same as those in the \( 2^{nd} \) monolayer.

**Figure 4.2:** IRRAS absorption intensities of four key vibrations of mesitylene with increasing exposure during vapour dosing. Mesitylene is adsorbed on a Au(111) surface. Two coloured strips have been drawn to help identify the two out-of-plane and two in-plane vibrations.

In gas phase absorption spectra\(^{104}\), the C–H stretching bands have the largest relative intensity and are 2.5 times larger than the \( \chi_{ring} \) absorption and 1.5 times larger than the out-of-plane \( \rho_{CH} \). However, the relative absorptions observed for the adsorbed mesitylene more closely resemble the liquid phase absorption spectra\(^{105}\) in which the \( \chi_{ring} \) and \( \rho_{CH} \) absorption intensities are larger than those of the C–H stretches, demonstrating
the effect of the near-neighbour environment on the relative intensities. In the liquid phase, the $\rho_{\text{CH}}$ absorption is approximately twice the intensity of the $\nu_{\text{CH}_3}s$, which is consistent with the results from the adsorbed mesitylene characterization and suggests a highly disordered film. Though the relative absorbance of the in-plane $\nu_{\text{CH}_ar}$ is approximately 40% less in the adsorbed spectrum than in the liquid spectrum, while the out-of-plane $\chi_{\text{ring}}$ absorbance is approximately 30% greater, and the strong intensity of the two out-of-plane vibrations would point to an average molecular tilt that is more parallel than perpendicular to the surface, consistent with results previously mentioned for the adsorption of substituted benzenes on metals$^{81}$, these results suggest that proximity to the metal substrate has a strong impact on the ring torsion vibration, increasing the intensity of its absorption.

4.3 **Thermal Treatment of Condensed Mesitylene**

There is very little information on the thermodynamic stability condensed mesitylene films on metal or organic substrates, and so the remainder of this chapter will be dedicated to characterization of the mesitylene thin films following thermal treatment.

Following vapour dosing of the mesitylene films on Au(111) and on the C$_{16}$SAM/Au(111) at cryogenic temperatures, they were characterized with IRRAS and then subjected to a thermal treatment. Desorption of mesitylene was observed above 160 K both with the mass spectrometer and as a significant decrease in the IRRAS band intensities until the spectra were comparable to the pre-deposition Au(111) film. This desorption temperature agrees with desorption observed for multi-layers of mesitylene on the MgCl$_2$ supported titanium surface at 170 K.$^{92}$ Though the previous study suggests that
a remaining monolayer will desorb at a much higher temperature, there is little evidence (< 1%) of mesitylene on the surface in the IRRAS spectra above 160 K.

Between 22 and 155 K, just prior to desorption, the bands of the IR spectra undergo profound changes in line shape, and the film demonstrates irreversible changes in molecular orientation. Figure 4.3 illustrates the effect on the low-frequency bands of heating the mesitylene films to 145 K and then cooling back to 23 K. The low coverage (206 L) film demonstrates a four-fold increases in the intensity of the two low-frequency out-of-plane skeletal vibrations, \( \chi_{\text{ring}} \) and \( \rho_{\text{CH}} \), and the peak widths narrow, resulting in very sharp, well resolved peaks. Recooling the films to cryogenic temperatures preserves the improved spectral resolution; both low frequency bands maintained their amplitude and narrowness, reversibly shifting up slightly in frequency from the bands during the 145 K annealing. The higher exposure (800 L) mesitylene film demonstrates a similar frequency shift. Such shifts to lower frequency in the C–H stretching region are typically an indication of improved film order.\(^{37}\) These skeletal vibrations are sensitive to redistribution of \( \pi \)-density, so the frequency shifts may also be an indication of a disturbance of the of the \( \pi \)-electron system of the ring.\(^{76}\)
Figure 4.3: 672-710 cm\(^{-1}\) (left) and 825-860 cm\(^{-1}\) (right) regions of the IRRAS spectra of mesitylene on Au(111) during annealing at two exposure levels: 206 L (white background) and 800 L (grey background). The films were deposited at 22 K (black), heated to 145 K (red), then recooled to 23 K (blue). Referenced to pre-exposure Au(111).
If we were to only consider these two out-of-plane vibrations, the large increase in absorption intensity would suggest, based on surface selection rules, a significant change in molecular orientation to increase absorption by the out-of-plane vibrations. This could be evidence of the molecules adopting an orientation with the ring more parallel to the surface. However, such a change in orientation would decrease the optical absorption of the in-plane vibrational modes as it would reduce their projection onto the z-axis and therefore limit their interaction with the p-polarized light. A cursory examination of the C–H stretching region (Figure 4.4) demonstrates that both $\nu CH_3s$ and $\nu CH_{ar}$, the in-plane vibrations, experience an increase rather than a decrease in absorbance intensity on both Au(111) (Figure 4.4 top) and on the SAM/Au (Figure 4.4 bottom) and a sharpening of the individual linewidths upon recooling to 23 K after annealing.
**Figure 4.4:** C–H stretching region of the IRRAS spectra of mesitylene during annealing. Top: adsorbed on Au(111) referenced to pre-exposed Au(111) surface. Bottom: adsorbed on D$_3$C$_{16}$SAM/Au referenced to pre-exposed D$_3$C$_{16}$SAM/Au. The films were deposited at 22 K (black), heated to 145 K (red) and then recooled to cryogenic temperatures (blue).
The slight spectral differences between mesitylene on Au(111) and on an alkanethiols substrate are most likely due to subtle changes in the rotations of the methyl groups, affecting their degree of coupling to other vibrational bands, including their interactions with the methyl groups of the underlying SAM. Since there was no observed change in the relative absorbance of the ip to oop bands, it suggests the molecules have the same orientation on both substrates.

Examining the relative intensity enhancement during the heat-cool cycle with respect to surface coverage (Figure 4.5) reveals that the effect if the annealing is far more pronounced on the lower exposure (206 L) than on the 800 L film.
Figure 4.5: IR absorption intensity of the 4 diagnostic vibrations of mesitylene on Au(111). Top: 206 L, Bottom: 800 L. The three bars in each series correspond to the as-deposited mesitylene film at 22 K (black), the film upon heating to 145 K (red) and the same film recooled to cryogenic temperatures (blue).
For both low and high coverage films, heating narrowed the low-frequency bands, but it did not provide the same intensity enhancement for both exposures. The absorbance of the as-deposited films was previously shown to scale linearly with exposure and can be approximated as 0.8 and 1.2 mAbs/ML of mesitylene for the $\chi_{\text{ring}}$ and $\rho$CH bands, respectively (using a conversion of 50 L = 1 ML). The post-annealed absorption intensity of the $\rho$CH is 70% larger than that of the $\chi_{\text{ring}}$ for both low and high coverage films. Heating the 206 L film results in the intensity of the $\chi_{\text{ring}}$ and $\rho$CH absorptions increasing to more than four-times their initial as-deposited intensity, and recooling has minimal effect on the peak intensity, for a net absorbance of 3.2 and 5.5 mAbs/ML of mesitylene, respectively. In contrast, heating the 800 L film results in only a small increase in the intensity of the $\chi_{\text{ring}}$ from 13.5 to 17 mAbs, and recooling decreases this band back down to 15 mAbs units, for a net enhancement of only 10%. If we assume the first 4 ML of the 800 L film behave similarly to the 4 ML (200 L) film, despite the presence of the additional monolayers, we can subtract the absorbance of the 4 ML film from the 14 ML film to reveal the contribution of the additional layers to the overall absorbance intensity. Though the first 4 ML of the annealed film account for 3.2 and 5.5 mAbs/ML for the $\chi_{\text{ring}}$ and $\rho$CH bands, respectively, the additional 10 ML contribute approximately 15-fold less, only 0.2 and 0.4 mAbs/ML, respectively. This would be consistent with the upper layers having an average molecular orientation with the ring more perpendicular or tilted on the surface.

The C–H stretching vibrations also exhibit different enhancements from the heat-cool cycle with respect to coverage. The $\nu$CH$_3$s band intensity is doubled upon heating the 206 L film from 0.6 to 1.2 mAbs/ML, which is maintained upon returning to
cryogenic temperatures, but the additional 10 ML in the annealed 800 L film account for only 0.25 mAbs/ML, nearly five times less than the first 4 ML. The νCH₉ intensity is also doubled by the heat-cool cycle from 0.2 to 0.4 mAbs/ML, and increasing the coverage an additional 10 ML contributes a further 0.35 mAbs/ML. The aromatic C–H stretching band is therefore the only vibration to demonstrate a relatively consistent absorbance per annealed ML. The out-of-plane vibrations, χ₉ and ρCH, demonstrate the greatest decrease in optical absorbance of the multilayers with respect to the first 4 ML. The relative absorbance of the two oop bands in the upper 10 ML is similar to their ratio of absorbance for liquid mesitylene, and the ratio of the two ip bands is also consistent with the liquid spectrum, however the relative absorbance of the ip bands to the oop bands for the upper 10 ML deviates from similarity to the liquid spectra and instead indicates an average molecular tilt that is more perpendicular to the surface, increasing the projection of the ip bands on the z-axis.

**4.4 DISCUSSION**

The high relative intensities of the out-of-plane ρCH and χ₉ vibrations compared to the in-plane νCH₃ and νCH₉ vibrations, and in particular, the 2-to-1 ratio of the ρCH to νCH₃ intensities was consistent with the relative absorption of the liquid spectrum. This suggests the as-deposited film is disordered.

Annealing the mesitylene film at 145 K results in band broadening of the C–H stretching bands, which can be attributed to anharmonicity. Cooling to cryogenic temperatures causes a narrowing of the absorption peaks and a shift of the C–H stretching bands to lower frequencies. This narrowing indicates the molecules are in a more
homogeneous environment, suggesting the heating process allows the molecules to adopt a more uniform orientation, and the shift to lower frequencies in the stretching region typically indicates improved film order.\(^{37}\)

Annealing the mesitylene films produces a four-fold enhancement to the low-frequency oop vibrations for the 208 L coverage, which is consistent with the monolayer adopting a more uniform orientation, nearly parallel to the surface – generally improving the opportunity for back donation of electron density from the metal surface to the benzene \(\pi^*\)-antibonding orbitals. The in-plane stretching vibrations also increase in intensity after annealing the 208 L film, however this enhancement is only 2-fold, and the intensities remain relatively low – further support for the nearly parallel-to-the-surface model.

Interpretation of the increased intensities of the absorptions upon annealing is complicated by the fact that they can couple to other vibrations, making them sensitive to their near-neighbour interactions. The low frequency oop vibrations experience the largest absorption enhancement, which is consistent with their sensitivity to perturbations of the \(\pi\)-interactions. Additionally, according to the relationships of a harmonic oscillator, the amplitude of the vibration is inversely proportional to the frequency and the mass of the atoms, and as such, the \(\rho\)CH vibrations will be larger in amplitude than the \(\nu\)CH\(_{ar}\) vibrations, making it more sensitive to near-neighbour interactions and helping explain the strong enhancement to these low frequency vibrations.

It is reasonable to assume that if annealing caused all of the molecules on the surface to adopt a particular orientation, absorption intensities would increase linearly with coverage. While this is true for the as-deposited film, this has been explained by the
highly disordered nature of the as-deposited film. For the post-annealed films, the relative intensities for the 208 L and 800 L exposures no longer correspond to those of the as-deposited film, suggesting reorientation of the molecules has occurred, and the molecules in the multilayers of the post-annealed film do not all have the same orientation as the molecules at low coverage.

The model proposed is of a post-annealed 208 L film with 3-4 monolayers lying with the rings nearly parallel to the surface. With increasing coverage, the first few monolayers remain lying flat-to-the-surface, while additional layers adopt tilted orientations, increasing the projection of the in-plane vibrations on the z-axis and increasing their absorption intensity disproportionately to the out-of-plane vibrations. Though the orientations are not uniform between the multilayers, the higher order within each monolayer would create more uniform near-neighbour interactions, particularly as the methyl groups could also adopt more ordered rotational configurations. This is consistent with studies of benzene that showed that in monolayers and bi-layers, the molecules orient with their ring parallel to the surface, but as coverage increases to 10-monolayers thick, some fraction of the molecules adopt a tilted orientation.⁸¹
5.1 Low Energy Electron Irradiation of Mesitylene on Au(111)

In the case of mesitylene, very little information on low energy electron irradiation or DEA processes exists, though a series of Rydberg orbitals between 7-8 eV has been identified.\(^6\) One of the goals of this thesis was to establish whether low energy electron irradiation in this regime will induce electronic excitation and capture of the incident electron to one of these dissociative Rydberg-states in the Franck Condon region. Additionally, we wanted to investigate whether these dissociations are energetically distinguishable at different sites. Hydrogen anions would be expected to be liberated from the film by bond cleavage, which would be observed in the IRRAS spectra as a decrease in the associated C–H stretching vibrational bands.

Figure 5.1 is a series of IRRAS spectra of the C–H stretching region during irradiation of mesitylene with 7.7 eV electrons. The top graph is a traditional absorption spectrum of 482 L mesitylene annealed on Au(111), referenced to pristine Au(111), and contains five individual spectra superimposed on each other. To better emphasize variations between the spectra, the bottom graph in Figure 5.1 presents the difference spectra in which the irradiated mesitylene film is referenced to itself immediately prior to electron irradiation. These difference spectra present the change in optical absorption, and thus a loss of C–H bonds results in negative going peaks in the difference spectra. The bottom figure shows that 7.7 eV irradiation of the 482 L mesitylene film up to 0.5 mC/cm\(^2\) of delivered charge has no IRRAS-observable effect on the C–H bonds; the difference spectra show only noise when referenced to the pre-irradiated film.
Figure 5.1: C–H stretching region of mesitylene during low energy electron irradiation at 7.7 eV of an annealed 482 L film on Au(111). Top: Five superimposed spectra referenced to Au(111); Bottom: Spectra referenced to the pre-irradiated mesitylene spectrum.
By way of comparison, for alkanethiol films, this level of irradiation would have resulted in a 10% change (-0.1 mAbs) in IRRAS intensity for methylene peaks at 2850 cm\(^{-1}\) and 2920 cm\(^{-1}\). This shows that the sensitivity of mesitylene to electron-induced damage is at least 50x less than previously studied alkanethiol SAMs. It was expected that irradiation of mesitylene in the energy regime of its Rydberg states (7.5±0.5 eV) would lead to DEA as for the case of alkanethiol SAMs (7.5–12.5 eV) and benzene films (6.5-10.5 eV). However, all three electron energies investigated failed to produce any decrease in IR absorption of the annealed mesitylene films at any of the coverages tested.

Figure 5.2 is a series of current injection curves for an annealed 800 L film of mesitylene on Au(111) irradiated at 10 eV. Despite the absence of bond cleavage, which suggests a lack of sensitivity to the electrons, charge injection curves reveal that the irradiation leads to increasingly negative charge accumulating on the surface and impeding the subsequent incident electrons. These current injection curves show rapid charging of the surface, and despite the 10 eV accelerating voltage, the electrons are decelerating as they approach the sample.
Figure 5.2: Current Injection curves of annealed 800 L mesitylene film on Au(111) with increasing charge deposition from 10 eV electrons.

In the case of alkanethiol SAMs with a rare-gas overlayer, the accumulation of charge is due to DEA produced H\(^-\) fragments becoming trapped in the RG layers.\(^{25, 26}\) In the case of mesitylene, however, the IRRAS results do not support the occurrence of bond cleavage leading to H\(^-\) production or any other molecular fragmentation. The charge accumulation must instead be due to the incident electrons themselves becoming trapped at the surface. Work on H\(_2\)O films has demonstrated that 0-1 eV electrons can be permanently trapped in the film; the additional electrons are believed to be in trap sites of the solid rather than bound to individual molecules.\(^{106}\)
The accelerating potential required to maintain 1 μA of current can be plotted from the current injection curves as a function of injected charge and compared between the thicknesses of the mesitylene film (Figure 5.3). The thickest films of mesitylene, 14 monolayers (800 L), demonstrate the most rapid charging profile, while the 4 monolayer (200 L) films exhibited the smallest level of charging. For example, the 800 L film in Figure 5.2 initially required an accelerating potential of only 1.5 eV to achieve 1 μA of current, however after 0.5 mC of injected 10 eV charge, the incident electrons required on average 6 eV of accelerating voltage to overcome the surface repulsion and maintain a 1 μA current. After the same amount of injected 10 eV charge, the 200 L films require only 4.5-5 eV accelerating voltage (Figure 5.3).
Figure 5.3: Charging profiles of mesitylene films of 206 L, 400 L and 800 L exposures plotted as the accelerating potential required to maintain 1 µA as a function of injected charge based on the measured injection curves.

The above results demonstrate that the charging potential of the organic surface is proportionally related to the quantity of mesitylene on the surface. This increased charging is consistent with the thicker films having more interstitial sites for electron trapping. However, it is also possible that the trapped electrons in thinner films have greater opportunity for relaxation pathways due to proximity to the metal substrate. Some evidence of this is provided by the slight discharge observed when two sequential
injection curves are collected for an irradiated sample – the charge injection curve shifts slightly back to the left over time. Irradiation at 10 eV of a mesitylene film that was not subjected to the thermal treatment demonstrates that the as-deposited 400 L film accumulates charge at the same rate as an annealed 800 L film despite having only half the quantity of mesitylene. This is further indication that the as-deposited film is disordered and has more interstitial sites for charge trapping.

5.2 Irradiation of Films on C₁₆SAM

Irradiation of mesitylene films on Au(111) failed to provide evidence of bond cleavage; however, the above experiments were repeated with mesitylene adsorbed on a SAM substrate to look for evidence of relaxation channels offered by the gold substrate with respect to the insulating dielectric organic monolayer.

Irradiation of mesitylene films on the hexadecanethiol SAM resulted in similar charging trends to the mesitylene on Au(111); the highest coverages exhibited more rapid charging and ultimately the greatest retardation to incoming electrons (Figure 5.3). The charging profile of 800 L mesitylene films on the C₁₆SAM fell precisely within the range of charging for the 800 L film on Au(111).

With respect to evidence of DEA and C–H bond cleavage in mesitylene on SAM/Au system, the IRRAS absorption spectra of the C–H stretching region did in fact show decreases in intensities when referenced to the SAM/Au substrate (Figure 5.4 top).
Figure 5.4: IRRAS spectra of the C–H stretching region of 227 L mesitylene on D₃C₁₀SAM/Au(111) irradiated at 10 eV. Top: absorption spectra referenced to Au(111); Bottom: difference spectra referenced to 227 L mesitylene film immediately prior to irradiation
While this might initially suggest bond cleavage in the mesitylene film, the difference spectra in which the post-irradiated mesitylene spectra are referenced to the pre-irradiated mesitylene spectrum (Figure 5.4 bottom) reveals that the C–H bond cleavage is occurring not in the mesitylene film, but in the underlying SAM substrate. The negative peaks in the referenced spectra clearly align with the symmetric and asymmetric stretches of the SAM methylene groups at 2850 and 2920 cm\(^{-1}\).

Injection curve results indicate that the incident electrons are being strongly retarded by increasing surface charge such that they are arriving at the mesitylene surface with significantly decreased energy; at 10 eV accelerating current, the electrons have decelerated by >2 eV after 0.5 mC of deposited charge, yet the difference spectra of mesitylene on the SAM clearly demonstrates that electrons are exiting the opposite side of the mesitylene film with sufficient energy to induce DEA processes in the underlying SAM. Recall that DEA in the SAM occurs at 10±2.5 eV. This suggests that, though the incident electrons are being strongly decelerated as they approach the surface, slowing significantly, those electrons that are transmitted through the mesitylene film are being reaccelerated by their repulsion from the surface charge so that they once again have an energy that falls within this DEA yield region. Figure 5.5 is the IRRAS difference spectra of mesitylene on the SAM/Au substrate at 800 L exposure. As with the 200 L film in Figure 5.4, there was no evidence of damage to the mesitylene film, only damage to the underlying SAM. In the 200 L film, the 2850 cm\(^{-1}\) CH\(_2\)s peak decreases by 0.5 mAbs units after 1 mC/cm\(^2\) of irradiation. With the 800 L mesitylene overlayer, the 2850 cm\(^{-1}\) band of the SAM decreases only 0.1 mAbs after the same irradiation. The SAM under the
200 L film therefore sustained more damage than the SAM under the 800 L mesitylene film. The 207 L film exhibits the least amount of charging and allows the greatest damage to the underlying substrate, while the 800 L film, which exhibited the most amount of charging, ultimately best protects the underlying SAM substrate from damage. If both charged films are reaccelerating the electrons to their initial energy of approximately 10 eV, then the reduced damage in the 800 L film could only be explained by fewer electrons successfully traversing the mesitylene film. This would be consistent with the greater charge accumulation in the thicker film as more electrons are being trapped at interstitial sites in the 14-monolayer film than in the 4-monolayer. Alternatively, it is possible the electrons in each system are being reaccelerated to different energies as they penetrate the SAMs, and as such, the electrons in the 800 L system may only be achieving a high enough energy to induce DEA as they penetrate deeper into the film, cleaving fewer bonds in the SAM and only at sites closer to the SAM-metal interface.
When a RG overlayer was applied to the mesitylene on Au(111) system, there was no evidence of C–H bond cleavage, let alone enhanced or selective bond cleavage as had been predicted for this work. When the experiment was repeated with 116 L xenon adsorbed on 170 L (3 ML) mesitylene film annealed on the SAM/Au, there was no observed enhancement to dissociations in the underlying SAM substrate. The lack of enhancements to dissociation events at the terminal methyl groups is further verification
that mesitylene is completely wetting the surface; if the 3 ML film was not wetting the surface, xenon atoms would be in contact with the terminal methyl groups, allowing transfer from the rare gas anionic exciton to the dissociative Rydberg states of the SAM.

**Figure 5.6:** IRRAS difference spectra of the C–H stretching region of 170 L mesitylene on C\textsubscript{16}SAM/Au(111) with a 116 L xenon overlayer irradiated at 7.7 eV referenced to the mesitylene + xenon film immediately prior to irradiation.
5.3 Discussion

Irradiation of mesitylene layers on Au(111) resulted in no observable decrease in optical absorbance in the IRRAS spectra at 7.7 eV, 8.5 eV or 10 eV. This suggests adsorbed mesitylene has low sensitivity to low energy electrons and does not undergo DEA at these energies.

Charge injection curves of the annealed films demonstrated that charge accumulation was proportional to quantity of mesitylene; 800 L films charge more rapidly and to a greater extent than 200 L films. It is difficult to predict whether the accumulation would scale linearly with coverage if the electrons were being captured in bound states, however, if this was the case, some evidence would be observed in the IRRAS spectra as bound electrons would perturb the vibrations of the molecule, causing a shift in the absorption peaks, and this was not the case. It was, however, observed that the unannealed 400 L films had similar charging profiles as annealed 800 L films, accumulating a similar amount of charge despite a lesser quantity of mesitylene. Unannealed films were characterized in Chapter 4 as being disordered and would therefore have more film defects and interstitial sites, which supports the proposal that electrons are accumulating in trap sites in the films rather than bound to the molecules.

Irradiation of mesitylene layers on a SAM resulted in a decrease in optical absorption in the C–H stretching region, however, the observed decrease was in bands identified as belonging to the underlying SAM. Irradiating a bare SAM at 10 eV is expected to result in a 26% loss in intensity of the CH$_2$s band after 0.5 mC/cm$^2$ of irradiation. Irradiation with the 200 L mesitylene overlayer resulted in a decrease of 36% for the same band for the same irradiation level. This suggests the electrons are still
arriving at the SAM surface with approximately the same initial energy, despite being
decelerated as they approach the mesitylene surface by the accumulation of negative
charge. Recall that DEA of SAMs occurs at 10±2.5 eV; therefore, the electrons must be
reaccelerated on the other side of the mesitylene film so that they are energetic enough to
induce bond cleavage in the SAM. Irradiation of 800 L coverages of mesitylene exhibited
a stronger protecting effect of the underlying SAM as there was reduced damage to the
CH₂ groups. This is consistent with the model that greater quantities of mesitylene
(ie. monolayers), trap more electrons in interstitial sites, preventing them from reaching
the SAM. Though the electrons are decelerated by 3-4 eV as they approach the 800 L
film, the observation of damage to the underlying SAM is evidence that they are
reaccelerated to within 7.5-10 eV, close to their initial energy in order to induce DEA
processes.
6.1 CONCLUSIONS

The primary objective of this work was to probe whether dissociations at different sites, particularly in molecules of mixed aliphatic and aromatic targets, are energetically distinguishable. Mesitylene was chosen for its Rydberg states in the energy region of interest, however little information was available about its adsorption on surfaces, particularly orientation and thermal stability, or its sensitivity to electrons. Therefore, before addressing the main purpose of this research, the mesitylene films had to be characterized to ensure stability and reproducibility.

Mesitylene was adsorbed on Au(111) substrates and IRRAS characterization of the as-deposited films were compared to liquid phase relative intensities, demonstrating the as-deposited films were quite disordered.

Thermal treatment of mesitylene resulted in transformations of the film to a more well ordered system in a more thermodynamically stable ground state system with the first 4-monolayers lying with the ring nearly parallel to the surface and additional multilayers assuming a more upright orientation. This was consistent with the behaviour of benzene on a metal surface.

The results of the orientation studies suggest that, contrary to literature claims, it is not a good molecule for adsorption studies such as BET. The disordered nature of the initial adsorption makes the adsorption unpredictable and unstable, and the changes in orientation and film order with temperature will cause errors in experiments involving thermal treatment.
Low energy irradiation of mesitylene on Au(111) resulted in no IRRAS observable decrease in the C–H stretching region, indicating no DEA processes or bond cleavages occur. Addition of a xenon overlayer did not improve the sensitivity of the film to incident electrons; however, application of the xenon on a mesitylene/SAM/Au substrate verified the mesitylene was wetting the surface as no coupling of the xenon to the SAM was observed. Irradiation of mesitylene on alkanethiol SAMs resulted in bond dissociations in the underlying SAM, yet the mesitylene remained insensitive to the low energy electrons. Despite no bonds being broken in the mesitylene, negative charge accumulated at the surface, indicating trapping of incident electrons in interstitial sites. Thicker mesitylene films accumulated charge faster and to a greater degree than thinner films, which provided less of a protective effect, allowing more electrons to traverse the film to dissociate bonds in the underlying SAM.

6.2 Future Work

As a result of the insensitivity of mesitylene to low energy electrons, the primary research objective of determining whether dissociations at different sites are energetically distinguishable remains unanswered. Therefore, further investigation into the promising technique of coupling RG anionic excitons to the dissociative states of organic molecules is still required. The Rydberg states of other substituted benzenes are available, making toluene and o-xylene potential candidates for these experiments, particularly because their adsorptions have been more thoroughly characterized. To simplify the determination of molecular orientation, chemisorbed systems may be preferable. Benzenethiol has been shown to form ordered monolayers, and it would make a good candidate for comparison to the rare gas mediated process in benzene to determine the effect of the chemisorption
on the dissociation yields. *p*-toluenethiol is another molecule which is predicted to form ordered chemisorbed monolayers, providing an alternative opportunity to investigate whether the C–H sites are energetically distinguishable in mixed systems of both aliphatic and aromatic C–H target sites.

One question that arose from the experiments of irradiation of mesitylene on a SAM is after deceleration and reacceleration of electrons by the charged film, how close is the final energy of the electrons to the initial energy. Based on the DEA events in the underlying SAM, the electrons must be reaccelerated to >7.5 eV, close to their initial energy, but it remains unclear how narrow this window actually is. To further investigate this phenomenon, an experiment could be designed involving adsorption of mesitylene on a 60 L layer of xenon on a SAM/Au(111) substrate to form a mesitylene/Xe/SAM/Au system that would be irradiated at 7.7 eV. Charge accumulation in the mesitylene would decelerate the incoming electrons. However, if they were reaccelerated to 7.7±0.2 eV, they could couple to the RG anionic exciton and transfer their charge and energy to the terminal groups of the SAM, selectively dissociating these bonds as happens for the same system without the mesitylene overlayer. If bond rupture was not limited to the terminal groups in contact with the xenon, this would suggest that the electrons are being reaccelerated to some energy outside of this 0.2 eV range, and are thus not being captured by the RG, but are instead penetrating into the SAM film with some unknown energy. Deuterating the chain in different regions (ie. near the termini or near the sulfur) would allow for determination of how deep the electrons penetrate before they re-attain energy high enough to induce bond cleavage.


– 95 –


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