### PHOTODISSOCIATION DYNAMICS OF MOLECULES ON SURFACES

by

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MCPS-PHYSICS

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#### Abstract

Methyl iodide and methyl bromide on Cu(110) surfaces have been studied by retarding potential spectroscopy, temperature programmed desorption, and time-of-flight mass spectrometry. The  $\lambda = 337$  nm photodissociation of methyl iodide on Cu(110) is found to occur by both charge transfer and direct photodissociation processes. Methyl bromide dissociated exclusively due to charge transfer processes on Cu(110). Charge transfer results from hot substrate photoelectrons dissociatively attaching to the adsorbate. The workfunctions of the dosed Cu(110) surface are at all times greater than the energy of a single photon, therefore desorption processes had a high probability of being neutral. Retarding potential spectroscopy measurements found that the workfunction of the Cu(110)-I surface increased by 1.2 eV as compared to the Cu(110) surface ( $\Phi_{Cu} = 4.48 \text{ eV}$  [26]). Methyl bromide on the Cu(110)-I surface did not show any evidence of photodynamics due to the  $\lambda = 337$  nm light, which is thought to be due to the increased workfunction of the semi-conductor CuI substrate preventing the formation of hot photoelectrons of the right energy for attachment. Methyl iodide dissociation on the Cu(110)-I surface is assigned to direct neutral photodissociation only, since there is no evidence for charge transfer processes. Methyl iodide on Cu(110)-I is found to be tilted at  $20^{\circ}$  off normal in the  $[1\overline{1}0]$  direction and is found to be significantly more ordered than on the Cu(110) surface. On both surfaces methyl iodide yields were found to maximize on completion of the second layer of adsorbate. Yields decreased rapidly for higher coverages on both surfaces. TOF spectra on both surfaces is assigned to desorption and/or dissociation from the exposed top layer. There is some evidence that overlayers do not completely cover underlayers. Methyl iodide on both Cu(110) and Cu(110)-I show evidence of altered  $\lambda = 337$  nm photodissociation dynamics as compared to similar wavelengths in the gas-phase. On both surfaces methyl iodide cross-sections are enhanced by approximately two orders of magnitude. Further evidence of altered neutral photodynamics is found in the  $I^*/I$  branching ratio for dissociation from the  ${}^{3}Q_{0}$  and  ${}^{3}Q_{1}$  excited states of adsorbed methyl iodide. Dissociation of adsorbed methyl iodide is found to favour the higher energy  $I^*$  channel rather than the I channel. The altered direct photodissociation dynamics in methyl iodide is thought to be due to changes in the excited state potential energy surfaces due to adsorption and proximity to the copper surface.

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# Chapter 1

# Photodynamics at Surfaces

## 1.1 Introduction

This thesis is an investigation of the photodynamics of adsorbate molecules attached to a metal surface. The photodynamics of such systems cannot be accurately predicted because the physics of adsorbates on metal surfaces are not well understood. As a result experimentally verified solutions to the Schrödinger equation for adsorbate-substrate systems are not available in the literature. In adsorbate-substrate physics the outer orbitals of the adsorbate interact closely with the orbitals of the substrate surface. The energy states of the outer adsorbate electrons are perturbed to a greater or lesser extent depending on the adsorbate and the substrate. Adsorbates often have been well studied and well-understood in their gas-phase form. Insight into surface physics is often achieved by comparing an adsorbate's experimental photodynamics to its gas-phase dynamics. Differences and similarities between surface and gas-phase physics will often indicate when the surface is affecting the adsorbate's energy states and when it has little or no effect.

Data is obtained in this thesis in time-of-flight (TOF) studies by adsorbing molecules on a substrate surface, forming an adsorbate-substrate system which is in equilibrium with its surroundings, and then directing coherent pulsed laser light is onto the system. See figure 1.1. Since photons can penetrate the surface, there are in general three distinct possibilities in the system for photon absorption. Photons may be absorbed in the adsorbate, in the substrate, or in the adsorbate-substrate bond. The last case, absorption of photons in the adsorbate-substrate bond, can only occur when the adsorbate and the substrate form a strong chemical bond such as a covalent or an ionic bond.

The absorbed photons cause a non-equilibrium situation in the system by initiating molecular excited states. Typically the excited states are unstable and energy is transferred inter-molecularly and/or intra-molecularly in the substrate and in the adsorbate as the excited system relaxes. Inter-molecular transfers are exchanges of energy between molecules whereas intra-molecular transfers are exchanges of energy within a molecules' energy states.

An adsorbate molecule may transfer its energy by (1) radiative decay such as fluorescence and phosphorescence, (2) non-radiative decay such as charge transfer to the substrate, and (3) chemical transformations [44]. Fluorescence is radiative decay where the transition is between electronic states of the same spin or multiplicity; phosphorescence is between electronic states of different multiplicities such as a singlet and a triplet state. Phosphorescence



Figure 1.1: Simple schematic of light directed onto an adsorbate-substrate system in equilibrium with its surroundings.

takes place only in excited states that are long lived, since such transitions are forbidden [1]. The studies in this thesis are concerned with process (3). Chemical transformations result in the adsorbate undergoing dissociative processes which sever the inter-molecular bond to the surface or the internal bonds of the molecule. In either case if the dissociation is to occur, it must proceed on a timescale that is competitive with processes (1) or (2). In the first adsorbate layer on metals, the excited state lifetime is on the order of femtoseconds (1 femtosecond =  $10^{-15}s$ ). Therefore if dissociation is to be a significant process in the first adsorbate layer, it must occur on the order of femtoseconds. Particle ejection occurs as a direct result of dissociative processes. Intra-adsorbate bonds or surface bonds are broken to cause molecular fragments or molecules to be ejected. Particle ejection processes are generally referred to as **desorption induced by electronic transitions (DIET)**.

Experimentation is often done on ordered surfaces because the resulting data tends to be characteristic and reproducible. Ordered surfaces are formed from the polished surfaces of bulk crystalline solids. Crystals do occur naturally, however, to guarantee that the crystals used in experiments are very pure and hence well-ordered, experimenters use artificially grown crystals. Crystalline solids are categorized by their electrical properties as metals, semi-conductors, and insulators. The electrical properties of the substrate crystals are known to have significant effects on the adsorbate photodynamics. Adsorbate molecules tend to arrange in characteristic patterns on the crystal surface. Many species of molecules on crystalline surfaces have preferred bonding sites and typically align in preferred directions. Features of surfaces relevant to this experimental work are discussed in the next sections.

### **1.2** Substrate and Surface

#### **1.2.1** Bulk Crystal Structure and Cleavage Planes

A bulk crystal is made up of fundamental volume units called primitive cells; the cells are made up of atoms in periodic volume arrangements. The primitive cells that make up an ordered periodic crystal occur at regularly spaced intervals. When a bulk crystal is cleaved or cut the periodicity of the crystal is broken at the newly formed surface. Reconstruction



Figure 1.2: Electrons leak out of the bulk into the space just above the surface causing a smoothing of the surface and contractive relaxation(arrows) of the layer of atoms nearest the surface.(Diagram from Zangwill [43, pg 29]; Finnis and Heine [14].)

of the atoms in the first layers nearest the surface usually follows. In metals the surface conduction electrons lower their kinetic energy by rearranging their distribution in space [43]. The electrons leak out of the bulk into the space just above the surface as in figure 1.2. The charge density of the electrons decreases in the solid and results in a smoothing of surface features [43]. The screening on the outermost layer of atoms decreases as a result and the layer is subject to a contractive relaxation in the dimension perpendicular to the surface. The contractive relaxation is opposed by electron-electron repulsive effects ; equilibrium is reached when the two effects are balanced. Reconstruction can also affect deeper layers [43].

The crystal structure of surfaces is described with surface nets, or two vectors in the plane of the surface. Every lattice point can be reached by the primitive translation vectors of the surface net  $\mathbf{T}$ , which has the form  $\mathbf{T} = \mathbf{m} \mathbf{a}_s + n\mathbf{b}_s$ .  $\mathbf{a}_s$  and  $\mathbf{b}_s$  are the primitive vectors and  $\mathbf{m}$  and  $\mathbf{n}$  are integers.

The periodicity in three dimensions of a real periodic crystal is also broken by dislocations, or misplacement of atoms. The presence of dislocations and the fact that a bulk crystal cannot be perfectly cleaved along any of the three Miller indices of figure 1.3 results in steps and holes on the surface. Some of these steps and holes are removed by polishing the crystal face to a high degree of smoothness at an angle close to the (110) cleavage face. The steps and holes that are left after the crystal surface has been polished are electronically smoothed by electrons which leak out of the solid. Because the electron density is higher in the area where electronic smoothing has taken place, surface chemistry can often occur at these sites. Step and holes have more surface area for molecules to interact with because of the local curvature. Adsorbate atoms which bond to steps and holes often have a lowered adsorption energy and a stronger bond.

Figure 1.3 shows the placement of atoms in an ideal face-center-cubic (FCC) unit cell. The structure of the FCC cell is a cube with atoms on each of the 8 corners and with an atom in the center of each of the 6 faces. Cleavage of the FCC unit cell in the (110) plane shown in the FCC unit cell produces the FCC (110) crystal surface. The surface is corrugated. The  $[1\bar{1}0]$  and [001] directions on the surface are shown in the diagram.



Figure 1.3: Face-Centered-Cubic(FCC) Unit Cell and the surface of an FCC crystal cut in a (110) orientation.

#### **1.2.2** Band Structure of Substrates

The band structures of bulk crystals are well-known. The periodicity of bulk crystal structures makes it possible for approximate solutions of the Schrödinger equation. The electron wavefunctions that participate in the bonds between atoms in the bulk are energetically split creating a large number of closely spaced discrete energy states. These allowed energy states form an allowed band of energies. There may be several allowed bands with disallowed energy bands between them. The disallowed bands are known as forbidden bulk energy bands. The bands of allowed energy states are full up to a maximum energy and empty above this energy. When the crystal is at a temperature T = 0 Kelvin, the maximum occupied energy state is known as the Fermi energy  $(E_F)$ . At higher temperatures T > 0 electrons can be thermally excited above  $E_F$ . Cleavage of a bulk crystal leaves the bulk band structure generally intact at the newly formed surface, however, allowed surface energy states often form in the forbidden bulk energy bands.

There are essentially three broad classes of crystals: Insulators, semi-conductors, and conductors. The location of the maximum occupied energy determines the electrical characteristics of the substrate. At T = 0 the Fermi energy lies at the top of an energy band in insulators. If the band is full, it is referred to as a valence band. The energy gap to the next allowed band of energies is large and is therefore, a large barrier to the thermal excitation of electrons. If electrons cannot be exited into the conduction band by increasing the temperature, thereby increasing the conductors the Fermi energy also lies at the top of a valence energy band at 0 K, but the energy gap to the higher energy conduction band is small enough that at higher temperatures electrons can be thermally excited across the en-



Figure 1.4: Image, surface, and bulk potentials as a function of a line z normal to the surface. The image potential smoothly joins onto the surface potential, which in turn is joined to the bulk potential. Diagram from Inglesfield [18, pg 120].

ergy gap. The excitement leaves some holes in the valence band and some excited electrons in the conduction band. Light of sufficient energy, depending on the energy gap between the valence band and conduction band, can induce photoconductivity when directed onto this material.

For metals, the conduction band of energies is only partially filled and the Fermi energy lies far below the top of the band. Due to the close spacing between energy levels within the conduction band, electrons can be excited from discrete energy levels below the Fermi energy to discrete energy levels above the Fermi level. As a result metals are good conductors and are very photoconductive. Light of sufficient energy can produce excited photoelectrons within the metal. Some of these photoelectrons can escape the bulk and be transmitted to the surface.

#### **1.2.3** Image and Surface Potentials

A charged particle at a crystalline surface disturbs the electronic equilibrium of the surface. Charge density of opposite sign to the particle increases on the surface and the particle sees an attractive potential. The potential far from the surface is the asymptotic image potential. Using simplified units:

$$V(z) = V_0 + \frac{e}{4z} (\frac{\epsilon - 1}{\epsilon + 1}) \quad , \quad -\infty < z < 0 \tag{1.1}$$

where  $V_0$  is the potential of the vacuum, where  $\epsilon = 0$  for a metal surface and  $\epsilon = 1$  for a perfect insulator, and where z defines the distance of the particle from the surface. If |z| is large the potential the electron experiences is that of the vacuum. Near the surface where |z| is small, the attractive image potential is large but the repulsive bulk and surface potentials compete and reduce the attractive affect. The result is that the image potential smoothly matches onto the surface potential. Near the surface the real potential is fairly linear and attractive; this potential joins onto the bulk periodic potentials. Figure 1.4 shows the image, surface, and bulk potentials as a function of a line z normal to the surface. The attractive image potentials means that work will have to be expended in removing an electron or a charged particle from the surface. The workfunction energy is the minimum energy an electron needs to escape the surface. It is defined as the energy required to remove an electron from the surface to the vacuum.

### 1.3 Adsorption

#### 1.3.1 Introduction

One of the first steps in studying adsorbate-surface systems is in determining how molecules adsorb to surfaces. The bonds that are formed result from an interaction between the surface and the adsorbate's valence electrons. If the interaction is strong, molecules can be broken apart as they approach the surface. Whether an adsorbate is characterized as physisorbed or as chemisorbed depends on the nature of the surface bond. Physisorption is a weaker form of bonding and chemisorption is a stronger form of bonding. Adsorption of a molecule also implies that the molecule is not able to penetrate the surface. When a molecule adsorbs its valence electrons interact with substrate valence electrons. The Fermi exclusion principle keeps the adsorbate electron, and hence the molecule, out of the lower energy states of the substrate. Therefore, adsorption results from attractive and repulsive potentials. Adsorbates have vibrational quantum states within these potentials.

#### 1.3.2 Physisorption

Physisorption results from Van der Waals' forces. When a neutral molecule is near a surface electron-electron interactions are initiated between the surface and the nearby molecule. Dipole interactions between the molecule and the surface arise essentially from image effects. For example figure 1.5 shows a hydrogen atom near a metal surface.

Although the hydrogen atom is in neutral state, dipole interactions with the surface result because the instantaneous distance between electron and the surface is not the same as the distance between the proton and the surface. The total electrostatic energy for this system, U, can be defined as the sum of four terms, each term results from the image potential [43]. For a metal surface [43, pg185],

$$U = \frac{1}{2} \left[ \frac{-e^2}{2z} - \frac{e^2}{2(z-r)} + \frac{e^2}{2z-r} + \frac{e^2}{2z-r} \right]$$
(1.2)

Simplifying this with a r/z power expansion [43, pg185],

$$U = \frac{-1}{8} \frac{e^2 r^2}{z^3} - \frac{3}{16} \frac{e^2 r^3}{z^4} - \dots$$
(1.3)

Since the r distance is less than the z distance the leading term of this expansion indicates that the interaction has a  $\frac{1}{z^3}$  dependency. The magnitude terms of the  $\frac{1}{z^3}$  variable are not considered to give the correct magnitude of the dispersion force due to the simplified treatment. Therefore the physisorption potential V(z) is given as,

$$V(z) = \frac{-C}{z^3} \tag{1.4}$$



Figure 1.5: Hydrogen atom and it image near a metal surface. Van der Waals' forces arise because of interactions between the charges of the hydrogen atom and their images. Diagram from Zangwill [43, pg186].

where the C is a constant. On approach to the surface the Pauli exclusion principle will repel the molecule due to overlapping wavefunctions of the molecule and the surface. The net potential on the molecule will be a result of the repulsive Pauli potential and the attractive van der Waals potential and be of the form [43, pg 188]:

$$V(z) = Kn(z) - \frac{C}{|z - z_v|^3}$$
(1.5)

and the second

Where n(z) is the ground state charge density of the surface resulting from the surface electrons spilling out of the bulk into the vacuum. K is a constant and  $z - z_v$  defines a reference plane from which the van der Waals potential should be measured from. V(z) invariably has a shallow minimum a few Angstroms from the surface [43].

Figure 1.6 shows the process of a molecule physisorbing to a surface. If the molecule has sufficient energy it will scatter off the surface and escape. It can also inelastically scatter and be trapped in the well created by the van der Waals potential and the exclusion principle. It will continue to inelastically scatter off the surface until its translational energy is absorbed by surface.

If a large number of molecules are physisorbed on a surface, collisions between adsorbed molecules will cause vibrational energy transfers. The transferred energy will allow some molecules to escape the potential well. The time a molecule stays in the well depends on the adsorption potential of the molecule and the temperature of the surface. Cooling removes thermal energy from the adsorbate which helps the molecules stick to the surface.

#### **1.3.3** Chemisorption

Chemisorption is a stronger form of bonding than physisorption. Chemisorption results in the outer orbitals of the adsorbate molecule and the Fermi or outer energy states of the surface fusing into combined quantum energy states. Bonding and anti-bonding orbitals are formed with electrons filling the lower energy bonding orbitals first. Fig 1.7 illustrates a schematic potential for a molecule to chemisorb to a surface. The molecule initially induces



Distance from surface z

Figure 1.6: Physisorption of Molecules on Surfaces. Inelastic scattering traps a molecule at a surface due van der Waals potential. (Diagram from Zangwill [43, pg361]; Tully [35])

van der Waals effects that produce a physisorbed potential well. The molecule may be initially trapped in this well and then moved into the deeper chemisorption well which is localized closer to the surface [43]. Chemisorption is a form of conventional chemical binding with a heat of adsorption on a scale of 1-10 eV [43].

#### **1.3.4** Adsorbate Overlayer Structures on Surfaces

When gas-atoms condense on a substrate they form overlayer structures. There are essentially two types of adsorbate overlayer structures. A commensurate overlayer structure is a two-dimensional space group that overlaps the substrate space group symmetrically. An incommensurate overlayer structure has no symmetry related to the substrate space group. The difference between overlayer groups is related to the binding site preferences of adsorbed molecules or lack of preference. An incommensurate overlayer generally does not have binding site preferences on the surface it is attached to. Molecules may absorb on top of substrate atoms, between substrate atoms, and in hollow sites. Molecules may stand up, lie down, or tilt at an angle with respect to the surface [43].

# 1.4 Energy Transfer Mechanisms between the Adsorbate and Substrate

#### 1.4.1 Introduction

There are several means whereby photoenergy can be transferred to the adsorbate. The simplest means is for a photon to be directly adsorbed by the adsorbate or by the adsorbate-substrate bond. This is referred to as direct photoabsorption. A second means of transferring energy results from absorption of photons in the substrate. An excited electron and hole



Figure 1.7: Chemisorption of Molecules on Surfaces. Adsorption potential with a precursor physisorbed well and a deeper chemisorbed well closer to the surface. One-dimensional model of chemisorption by Lennard-Jones(1932) Diagram from Zangwill [43, pg366].

are created, which relax independently. It is possible for either the electron or the hole to be transferred to the adsorbate or adsorbate-substrate bond.

A third means for transferring energy to the adsorbate results from thermal excitation of the substrate-adsorbate system. Thermal excitations occur when energy dissipates into vibrational or rotational modes. Excited electrons or holes which are produced in the substrate and do not attach to the adsorbate must be thermalized in the substrate [44]. This thermal energy can be transferred to the adsorbate and result in ejection of particles when molecular vibrational or rotational energy is converted to translational energy. Generally we will want to avoid conditions in our photoabsorption experiments which will initiate significant thermal energy transfer, since this would complicate the study. Avoiding significant thermal effects is relatively simple to do, since the photoabsorption experiments in this thesis are all done at light intensities below the threshold  $(1mJ/cm^2 \text{ per pulse})$  [44] considered necessary to initiate thermal effects from a laser. Therefore thermal effects are not considered significant in the photodynamic experiments done for this thesis.

After energy is transferred to the adsorbate, there are relaxation channels available to the excited adsorbate molecules. If chemistry is to occur in the adsorbate, the relaxation channel for the chemistry must be temporally competitive with the quenching process. Quenching transfers the electronic excitation from the adsorbate's states to the energy states in the substrate. On metals the electronic excitations are quenched on a timescale of femtoseconds. Quenching is slower or non-existent for semi-conductors or insulators.

In this thesis we collect particles from desorption processes as a result of the surface photodynamics, therefore these relaxation processes must be competitive on the particular adsorbate-surface systems we are studying. Desorption results in molecules or molecule



Figure 1.8: Charge Transfer at a surface. Hot electrons are produced at a surface which then dissociatively attach to the adsorbate. The LUMO is the lowest unoccupied molecular orbital and the HOMO is the high occupied molecular orbital. Diagram from Wolf [40].

fragments being ejected from the system. The ejected particles contain information on the final state distributions of the resulting degrees of freedom [45]. Since these degrees of freedom include internal, vibrational, rotational or translational excited states, they contain a great deal of useful information for studying the surface chemistry. Information can be extracted from the ejected particles by collecting them and analyzing them with regard to such variables as species, intensity, energy, and trajectory angle.

We know that two general processes result in desorption from the surface when energy is transferred to the adsorbate. In one process the energy transferred to the adsorbate causes dissociation of adsorbate molecules which produces fragments with translational energies. In another process energy transferred to the adsorbate causes intact molecules to desorb from the surface when internal energy is converted into translation energy. In both dissociation and molecular desorption translational energy is a necessary condition for a particle to escape the surface, however it is not a sufficient condition. Factors which affect escape will be discussed later in this chapter. Dissociation and desorption initiated by photoabsorption in the system are respectively referred to as photodissociation and photodesorption. Their kinetics will be described in detail in the succeeding sections of this chapter.

#### 1.4.2 Charge Transfer from the Substrate to Adsorbate

Charge transfer occurs when charge is transferred between the adsorbate and the substrate. The process for charge transfer, see figure 1.8, results from the photoelectric effect. Photons penetrate to various depths in the substrate depending on the energy of the photons and the dielectric properties of the substrate. For photons with energy  $h\nu < 10eV$  the optical penetration depth is  $\approx 100\dot{A}$  in metals [40]. Electrons in the metal substrate absorb and are energetically excited by incident photons creating what is known in band structure as electron-hole pairs. Relaxation of the electron and the hole are independent following



Figure 1.9: Mean Free Path of Electrons in various Solids. The meanfree path of electrons in solids is of the same order but less than the optical penetration depth of  $\approx 100 \dot{A}$ . Therefore most excited electrons will undergo scattering processes. The dashed curve is that expected from theory. (Zangwill [43, pg21]; Rhodin and Gadzuk [29]; Somorjai [31]. Theoretical curve from Penn [28].)

creation. The excited electron is often referred to as a photoelectron.

Relaxation of the photoelectron and the hole is the result of scattering. Fig 1.9 shows the measured and theoretical meanfree paths for electrons in various solids. The meanfree path of electrons in solids is of the same order but less than the optical penetration depth of  $\approx 100 \text{Å}$ . Therefore most excited electrons will undergo scattering processes. Scattering with cold electrons produces secondary photoelectrons and holes [40, 44]. Both photoelectrons and holes can be transported to the surface by scattering events [44]. Due to surface screening effects, photoelectrons and holes are not correlated, that is they do not form an electron-hole pair known as an exciton [44]. Photoelectrons on the surface with energy less than the vacuum energy are further designated as hot photoelectrons. If photoabsorption is characterized by a high probability of single-photon processes and a low probability of multi-photon processes, there will be a distribution of photoelectrons at the surface with a maximum kinetic energy equal to the energy of the incident photons. Multiphoton processes are insignificant when light intensities are low. Multiphoton processes can be initiated for laser power densities above  $10^3$  MW /  $cm^2$  [44] and therefore they can be avoided for intensities much lower than that.

Photoelectrons and holes scattered at an adsorbate covered surface are subject to the electronic interface potential between the substrate and the adsorbate. Due to the quantum mechanical nature of electrons, scattering at a surface may result in electrons and holes tunnelling through the interface potential causing valence ionization of the adsorbate. An electron attaching to the adsorbate can be represented by

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 $A - B + e^- \rightarrow A - B^-$ 

where A-B represents an absorbed molecule and  $e^-$  represents an excited electron which attaches to the adsorbed molecule. A hole attaching to the adsorbate can be represented by

 $A - B + e^+ \rightarrow A - B^+$ 

### 1.4.3 Direct Excitation of the Adsorbate or Adsorbate-Substrate bond

Direct photoabsorption by the adsorbate or the adsorbate-substrate bond can promote molecules to repulsive excited states. In the case of direct excitation of a physisorbed adsorbate, valence electrons are excited to higher energy states. The excitations can cause repulsion of the adsorbates' nuclei which can lead to dissociation or desorption if these processes occur on a timescale competitive with quenching. The surface bonds of chemisorbed molecules are typically formed by shared orbitals of the substrate and the adsorbate. Photoexcitation in chemisorbed molecules promotes electrons from bonding orbitals to antibonding orbitals which can lead directly to desorption or dissociation [3]. Direct excitation of a molecule A-B by light of energy  $h\nu$  can be symbolically represented by

 $A - B + h\nu \rightarrow A - B^*$ 

Dissociation and desorption are described with potential energy surfaces in the Surface Dynamics section in this chapter. See figure 1.10 for a potential energy surface resulting from a direct excitation from the ground state A-B to an excited  $A - B^*$  state.

#### **1.4.4** Thermal Processes

Most photoelectrons excited by photon absorption undergo scattering processes, since the optical penetration depth of the light is larger than the mean-free-path of the scattering photoelectrons [44]. Photoelectrons with sufficient energy may be photoemitted from the substrate through the adsorbate-substrate interface. However photoelectrons with insufficient energy to be photoemitted will be absorbed in the substrate through scattering processes [44]. Collisions between holes, electrons, and phonons will cause excitation energy to be transformed to lattice phonons [44]. Such thermal excitation can transfer vibrational energy to the adsorbate. If sufficient vibrational energy is transferred the adsorbate can dissociate or desorb.

For pulsed laser light the rate of dissociation due to thermal excitation depends exponentially on the intensity of the light [44]. Lasers with low light intensities and less pulses per second will result in fewer thermal excitations. In this research thermal effects are avoided by using light intensities below the threshold for significant thermal effects to be present.

#### 1.4.5 Quenching

Molecular quenching is a process that transfers electronic energy from the states of the adsorbate to the states of the substrate. The rate of quenching depends sensitively on the nature of the substrate and on whether resonant tunnelling between the adsorbate states and the substrate states is available. Resonant tunnelling occurs when the energy of the electron state in the molecule is the same as the empty states that are available on the surface. Electrons can tunnel between the molecule states and the empty surface states without gaining or losing energy. Resonant tunnelling is not available when the energy of the electron state in the molecule coincides with an energy in a forbidden bulk band of the substrate or filled surface states. When resonant tunnelling is not available quenching must proceed by the Auger process, which is considerably slower. In this Auger process, a higher energy electron from the substrate enters a lower energy orbital of an adsorbate ion, displacing an electron already in the state, with some energy is transfer to an electron in an adjacent orbital of the ion. This extra energy is sufficient for the electron to enter an allowed and empty state of the substrate, leaving the adsorbate molecule in a neutral state.

Whether the substrate surface is an insulator, semiconductor, or metal can have a large effect on the time factor for quenching. Efficient quenching mechanisms do not exist on ideal insulator surfaces because of the large energy gap between the fully occupied band of energies and the higher energy unoccupied band [45]. Metal and semiconductor surfaces, in contrast, are often strongly quenched and typically quenching rates are of the order of femtoseconds [40, 44, 45].

### **1.5** Surface Dynamics

#### **1.5.1** Introduction

Surface dynamics in this thesis are studied primarily by collecting desorbing particles, therefore understanding the desorption processes is important. There are only three processes which can transfer photoenergy to the adsorbate: thermal transfer from the substrate to the adsorbate, charge transfer from the substrate to the adsorbate, and direct photoabsorption by the adsorbate. The photodynamic experiments are done at laser light intensities below the threshold needed to initiate thermal effects so we need only consider charge transfer and direct effects in that particular experiment. However thermal energy transfers will be significant in the temperature desorption experiments. The particles ejected from the surface as a result of direct and charge transfers in the photodynamic experiments can either be neutral or charged. Neutral particles require less energy to escape a metal surface than charged particles due to the attractive image effects on ions.

For an ion to escape the surface the energy transfer creating the ion must be greater than the workfunction of the surface. The workfunction is the minimum energy an electron and any singly charged particle requires to escape the surface. At the laser light intensities that we work at, energy transfers occur as a result of single-photon processes and each photon has less energy than the workfunction. Therefore in the direct photoabsorption process less energy than the workfunction is transferred. In the charge transfer process the maximum energy of any electron transferred to the adsorbate is the energy of a single photon. If charged particles are to escape the surface additional energy must be provided. Chemical reactions and adsorbate electron affinities can provide the additional energy.

If a particle does not have sufficient energy to escape as an ion, it may neutralize and escape by neutral desorption mechanisms. Both direct photoabsorption and charge transfer to the adsorbate can give rise to neutral particle ejection. The processes are described with



Interatomic Distance (A-B)

Figure 1.10: Frank-Condon transitions on potential energy surfaces (PES) are vertical transitions. The internuclear separation is unchanged during the transition. The Franck-Condon transitions have an envelope determined by the localization of molecules in the well (gaussian figure).

potential energy surfaces(PES), although knowledge of adsorbate potential energy surfaces is very limited. Knowledge of excited PES is more limited than the ground state PES [44]. Potential energy surfaces derived from detailed quantum mechanical calculations are not available, therefore as a substitute, simplified models are proposed to account for the observed behaviors [44]. Gaining information about a surface PES is an objective of surface studies. It should be clarified, that we do not have the means to create accurate simplified surface PES for the systems in this study. We can only gather qualitative information that will give us better insight. Gas-phase PES are often used in the analysis for insight into an adsorbates' chemical behavior, with the understanding that adsorption changes the PES more or less.

#### 1.5.2 The Franck-Condon Principle

When a gas-phase diatomic molecule absorbs a photon the excitation causes the molecules nuclei to reposition. Franck and Condon realized that the energy transfer to the diatomic molecule occurs on a much faster timescale than the repositioning of the nuclei [1]. Therefore the energy transfer can be approximated as a vertical transfer of energy, with the nuclei of the diatomic atoms in the ground-state position.

In figure 1.10 the potential energy of a molecule attached to a surface is represented by a ground state potential energy surface. A transfer of energy to the molecule results in a sudden Franck-Condon transition, represented as a vertical line, to an excited potential energy surface. The intranuclear separation does not change during the transition. An envelope for the Franck-Condon transitions is determined by the wavefunction that describes the vibrational energy state in the ground state wavefunction. When a molecule undergoes a Franck-Condon transition the shape of the excited dissociative curve and the Franck-Condon envelope result in a broadening of the energy distributions of dissociated particles. Steep potential energy curves in the Franck-Condon region and wider envelopes result in broader energy distributions.

#### **1.5.3** Potential Energy Surfaces for Desorption and Dissociation

A widely accepted model of desorption induced by electronic transition (DIET) is the model of figure 1.11 proposed by Menzel, Gomer and Redhead (MGR) in 1964 [44]. In figure 1.11 a Franck-Condon transition takes an adsorbate from the v=0 vibrational state of ground state wavefunction to a repulsive excited state. On the excited state the adsorbate experiences nuclear motion and is repulsed from the surface. Escape from the surface on the excited state curve is possible, however due to efficient decay channels the adsorbate may undergo a deexcitation back to the ground state potential energy curve. The de-excitation is a quenching process and the energy is converted into substrate excitation. As a result of excitation to the dissociative state and the subsequent quenching, the adsorbate A gains potential and translation energy. The adsorbate A returns to the ground state with potential energy  $E'_n$ plus vibrational energy equal to  $E'_k$ . If in figure 1.11  $E'_k > D'$  at the de-excitation point, then the adsorbate A may desorb in the ground state and can be detected by time-of-flight mass spectrometry(TOF-MS)<sup>1</sup>The total energy gained after return to the ground state must be greater than  $D_0$  to overcome the attractive potential of the ground state.  $D_0$  is the energy the adsorbate requires to desorb from the v = 0 vibrational state in the ground state. If the energy is insufficient,  $E'_k < D'$ , the adsorbate vibrates in the ground state well and can lose the energy it gained from the excitation by coupling with phonons of the surface. The coupling can return the adsorbate to the v = 0 vibrational state in the ground state.

On metal surfaces efficient fast quenching mechanisms result in the probability of direct desorption on the excited state PES being low [44]. Nuclear motion occurs on a much slower timescale than electronic quenching. The probability of desorption is determined from the initial excitation probability times the probability of survival on the excited state to obtain an energy  $E'_k > D'$  [44].

The Menzel, Gomer and Redhead model is particularly useful when describing the direct excitation process of photoabsorption. In the case of direct photoabsorption, an electron in an adsorbate molecule absorbs a photon and is excited to a dissociative state where quenching processes can occur. Desorption by the Menzel, Gomer and Redhead model can occur as a result. For some chemisorbed adsorbates, valence ionization can lead directly to repulsive states [3]. Valence ionization occurs when the adsorbate gains or loses an electron creating a negative or positive ion.

The MGR model can be extended to describe intra-adsorbate bond dissociation [44]. In figure 1.12 an adsorbed molecule is excited to a repulsive excited state. The molecule may dissociate in the excited state or quenching can bring the molecule back to the ground state potential energy surface. If the energy gained on the excited state is sufficient, the molecule A-B may dissociate in the ground state or one or both elements A, B can enter

<sup>&</sup>lt;sup>1</sup>TOF-MS is described in the experimental section and is one of principle means of obtaining data in this thesis. Data obtained by TOF-MS is described in Chapter 4 of this thesis.



Figure 1.11: Potential Energy Surface showing the MGR desorption mechanism. Diagram from Zhou [44].

the chemisorption well. If the energy gained is insufficient for dissociation, the molecule A-B may also remain in the physisorption well. The chemisorption well in this case results from one or both of the fragments forming a chemical bond (chemisorbing) to the surface. One or both of the fragments A, B may escape the surface after entering the chemisorption well if the molecule acquires sufficient energy after transferring to the ground state potential energy surface from the excited state,

The Antoniewicz desorption mechanism in figure 1.13 describes desorption from bound excited states. This mechanism occurs as a result of a Franck-Condon transition from a bound ground state wavefunction to an excited bound state. The excited state is attractive with the result that the molecule is moved towards the surface. When the distance between the surface and the molecule is small enough, the molecule is repulsed by the Fermi exclusion principle. Franck-Condon de-excitation transitions back to the molecular ground state result from quenching. If sufficient energy has been gained as a result of the excitation and quenching processes, the molecule may desorb in the ground state.

This mechanism is particularly useful for describing desorption processes due to charge transfer between a metal substrate and an adsorbate. In that case the excitation to the excited state is the result of an electron attaching to the adsorbate or an electron from the adsorbate escaping to the substrate in a process referred to as valence ionization. In one case a negative ion is formed and in the other a positive ion is formed. A bound state is formed as a result of ionization because the ion is attracted to its image charge in the substrate. Ionization of an adsorbate can result in dissociative states of the molecule or in stable ionic states; desorption can generally occur for both dissociative and stable ionic states. Whether an unstable ion will dissociate or desorb can depend on the competition between the two processes and on the Franck-Condon transition energies. Excitation to the bound excited



**Reaction Coordinate** 

Figure 1.12: Potential energy surface showing a surface dissociation mechanism similar to the MGR model for desorption. One or both of the dissociative products can chemisorb to the surface. Diagram from Zhou [44].

state followed by quenching to the ground state can also lead to containment of molecule in the ground state well if there is insufficient energy gained. Coupling to substrate phonons can return the molecule to the v=0 vibrational energy state.

#### 1.5.4 Concluding Remarks

This concludes the section on potential energy surfaces for desorption and dissociation and also the chapter on surface photodynamics of adsorbates on surfaces. The potential energy surfaces described above can generally describe the surface dissociation and desorption processes. Detailed potential energy surfaces, however, are not available. Detailed PES would provide a predictive means for understanding the photodynamics on surfaces. Quantum mechanical calculations of detailed PES require better understanding of the surface processes on individual surface systems. That is what this thesis represents. It is an attempt at a better understanding of several specific surface systems. These systems are introduced in Chapter 3.

Some of the factors which are significant to surface photodynamics have been reviewed in this chapter although the review is by no means exhaustive. There are many detailed factors which result in the photodynamics of adsorbate-surface systems. I have just described some of the important structural and electronic factors. The next chapter will describe the experimental apparatus and experimental techniques whereby data is obtained for the study of surface systems for this thesis.





# Chapter 2

# **Experimental Methods**

### 2.1 Introduction

The experimental methods chapter discusses the experimental apparatus and the experimental techniques for acquiring data. But before I begin a description of the experimental details I must answer an important question, "what is the aim of the experiments?" As a surface experimentalist I must be able to form carefully controlled adsorbate-substrate systems and must have precise tools for manipulating those systems. In a very general sense, the aim of the experiments is to modify the adsorbate-substrate system in some significant and measurable way. With the experimental data, I can say something significant about the surface physics.

Saying something significant about the surface physics means I must know what molecules are on the surface. The sample used in the experiments must be of a high purity and it must also be clean when I dose molecules onto it. The molecules I dose must also be of high purity and I must be able to maintain a clean adsorbate-substrate system at least while the experiment is in progress. Cleanliness is of course a relative term and is limited by the experimental apparatus. There will always be low concentrations of undetectable species in the experimental environment. Understanding the surface processes in an experiment is to a large degree predicated on assumptions about which molecules are significantly present in the experiment. Good assumptions make good understanding more probable.

In this thesis surface experiments are done in an ultra-high-vacuum(UHV) environment with a base pressure of  $5 \times 10^{-10}$  torr. High temperature heating and  $Ar^+$  ion bombardment is available in the UHV to clean the sample. Auger spectroscopy and Low Energy Electron Diffraction (LEED) are available to check the samples' cleanliness and good orderliness of the surface structure. The molecules dosed onto the sample are bought from a manufacturer in a high purity concentration. Once an adsorbate-substrate system is formed in the UHV environment the system is modified by the addition of thermal energy or light photons. Thermal energy transfers to the sample are monitored by measuring the sample temperature and light photons are monitored by measuring the number of photons per  $cm^2$  on the sample. As energy is added to the system, detectors measure species desorbing from the surface of the system.



Figure 2.1: Schematic of experimental system

### 2.2 Apparatus

Various data acquisition electronics and computer software are used in this thesis work. All computer functions were controlled using a Macintosh PowerPC clone(PC120) running commercially available software, although many of the programs are custom written. A commercial visual constructs program (LABVIEW) was used to write computer programs to control various lab equipment such as Auger, Quadrupole Mass Spectrometer, the workfunction experiment, and the laser pulses. These control programs were written by Dr Jensen. A commercial graphing program (Igor) was used to plot the data after it had been acquired in an experiment.

The experimental system (see fig 2.1) is composed of a custom-built Ultra HighVacuum (UHV) chamber, a crystalline sample, and is equipped with a rear-view LEED/RFA Auger analyzer (OCI Vacuum engineering), a quadrupole mass-spectrometer (UTI 100C), a low energy electron gun, and an  $Ar^+$  ion gun. The system has the ability for doing standard surface science techniques including Low Energy Electron Diffraction (LEED), Auger Electron Spectroscopy (AES), Quadrupole Mass Spectroscopy (QMS), Temperature Programmed Desorption (TPD), and Work Function ( $\Delta\Phi$ ) measurements. The  $Ar^+$  ion gun is used for sputtering the sample. A heating system and a cooling system is available for



Figure 2.2: Cutaway drawing of the UHV Chamber. Apparatus is arranged on the UHV chamber in two tiers facing the central vertical axis. A sample manipulator can raise, lower, rotate the sample in convenient orientations for each experiment.

maintaining the temperature of the sample from  $\sim 95K$  to temperatures in excess of 1200 K. The upper limit is not known since the samples used in the chamber melt before this temperature is reached. There is a laser, not part of the UHV system, which produces light of wavelength  $\lambda = 337$  nm. The various parts of the experimental system are described below.

#### 2.2.1 Ultra-High Vacuum Chamber

The ultra high vacuum (UHV) chamber (See figure 2.2 for a cutaway drawing) has a base pressure in the low  $10^{-10}$  torr range and a working pressure in the mid  $10^{-10}$  torr range. It is pumped using a mechanical pump (Edwards RV5) and a turbomolecular pump (Varian V250). The turbomolecular pump has a number of turbine blades which rotate at a high rpm. This pump can only be operated when the chamber pressure is low (approx.  $10^{-3}$  torr). When molecules in the chamber come in contact with the turbine blades they are knocked into the mechanical pump, which removes them from the UHV system. Because the mechanical pump is used to initially reduce the pressure to  $\approx 10^{-3} torr$  it is frequently referred to as the roughing pump. An interlock valve is used between the chamber. There are two ion pumps (Perkin Elmer) attached to the quadrupole mass spectrometer(QMS). The pumps ionize residual gas and cause it to collide with reactive metal plates. This 'removes' the gas from the UHV environment.

There is an external heating system for baking the chamber. The chamber is baked at 120 degrees C for at least 48 hours in order to remove water  $(H_2O)$  molecules that condense on its inner walls. Water molecules are always present in air and enter the chamber when it is opened. The water vapour pressure prevents the chamber from pumping down to UHV pressures. Water molecules adsorbed on the inner chamber walls outgas very slowly. Heating the chamber hastens their removal. When the water is gone low chamber pressures are attainable.

Gas handling was done using a glass gas rack and leak valves on the chamber. The glass gas rack allows storage of chemical liquids in small glass flasks (100ml capacity). The gas rack is pumped by a mechanical vacuum pump(Edwards RV5). A variable leak valve (Duniway) is used to control the admission of gases into the chamber from the glass rack. A high volume all-metal (MDC) valve was used for flooding the chamber with gaseous nitrogen when bringing it up to air for various maintenance and modification work. To bring gaseous nitrogen into the chamber a line was connected to coiled copper tubing immersed in water. One end of the copper tubing was connected to a line immersed in liquid nitrogen was sucked into the copper tubing, acting as a heat exchanger, where it was converted to gaseous nitrogen before entering the chamber.

An ion gauge (Varian) and an ion gauge controller (Granville-Phillips 350) was used to measure the UHV pressure. Several UV compatible windows were mounted on the chamber. One was used to allow UV laser light into the chamber. The other was used to visually align the laser light onto the sample using a HeNe laser( Scientific SLC). The visible red He-Ne laser beam (0.95mW output) was aligned with the invisible UV laser beam, and then the combined beams were visually aligned onto the sample using the visible He-Ne beam.

#### 2.2.2 Sample and Manipulator

The Cu(110) sample is mounted on a tantalum plate by tungsten wires that pass through the edges of the sample and also through the tantalum plate. The tantalum plate is attached to a manipulating rod with sapphire spacers between the mounts of the tantalum plate and the manipulating rod. The sapphire spacers allow thermal contact but electrically insulate the sample from the manipulating rod. The manipulating rod is hollow and liquid nitrogen at its boiling temperature is passed through the rod. The base temperature of the sample is  $\sim 96$  K. Two K-type thermocouples are spot welded to the tungsten mounting wires next to the sample. An additional wire used for grounding the sample as necessary is spot welded to another tungsten mounting wire.

Apparatus is arranged on the UHV chamber in two tiers facing the central vertical axis. Appropriate placement of apparatus on the chamber ports is necessary if two or more apparatus are required in an experiment. The manipulating rod that the sample is attached to is part of a translation stage and rotary feedthrough allowing it to be moved in X-Y-Z directions and rotated about an axis. Translation is limited to 15 cm in a vertical Z direction and 3 cm in a horizontal X and Y plane; rotation about the Z-axis is 360 degrees.

Thermocouple wires and an additional wire for grounding are attached to the sample and then externally exited from the vacuum chamber using commercially available connectors.


Figure 2.3: Circuit for controlling the temperature of the sample, including heating and cooling. There are two thermocouple wires attached to the sample which are used for measuring the sample temperature.

The additional wire allows the sample to be grounded to the chamber potential, or to have a potential placed on it.A tungsten filament is mounted in a filament holder behind the sample to allow heating of the sample.

#### 2.2.3 Heating the Sample

The temperature control circuit is shown in figure 2.3. Heating of the sample is controlled by a programmable temperature controller(Omega CN3000) using a PID (proportional integral derivative) algorithm. Sample temperature is measured by the controller using a Chromal-Alumal (type K) thermocouple, which is attached to the sample. The controller heats the sample by controlling a variable DC current to the coiled tungsten wire mounted behind sample. The filament is made by coiling a tungsten wire and is connected to external connectors on the vacuum chamber. The DC current (0-8 amperes) is put through the filament using a DC Power Supply(HP Harrison 6286A). Electrons and photons produced from the tungsten wire radiate in all directions. Some are thermally absorbed by the grounded sample. When electrons from the filament strike the sample, their kinetic energy is transferred resulting in heating of the sample.

The filament can be biased from ground to -800 volts by a DC offset (Sorensen DCR-B Power Supply). The negative bias is used when flashing or annealing the sample to high temperatures. The bias repels electrons produced at the filament, increasing their kinetic energy. The temperature controller can linearly ramp the sample temperature as a function of time to a specified value. However, it has not been possible to linearly ramp the temperature using the DC bias offset in the current set-up. Without the bias, heating of the sample is limited to about 400 C. With the bias sample temperatures can be reached in excess of 1200 C.

### 2.2.4 Quadrupole Mass Spectrometer

The quadrupole mass spectrometer (QMS) (UTI 100C) is mounted in a stainless steel tube on the UHV chamber. The tube is part of the UHV system and is also pumped by two magnetic ion pumps (Perkin-Elmer) with a combined capacity of 50 L/s. The QMS is separated from the main chamber by a grounded metal shield with a 4-mm-diam aperture surrounding the QMS ionizer. There is metal grid over the aperture that is electrically insulated from the metal shield. When the ionizer is turned on, the grid is charged up by electrons produced in the QMS ionizer. The potential on the grid repels electrons back into the ionizer and prevents them from entering the chamber where they could cause reactions in an experiment. As a result the current incident on the sample from the ionizer is not measurable (less than 0.01  $\mu$ A) [6]. Ions in the chamber are also prevented from entering the ionizer region of the QMS. As a result, only neutral particles produced in the time-of-flight experiments can enter the ionizer. In most experiments the distance from the center of the chamber, where the sample is situated in an experiment, to the QMS ionizer is 8.3 cm.

The UTI 100C QMS can measure masses in the range from 0 to 300 atomic mass units (amu). Neutral molecules and neutral fragments produced from the sample enter the ionizer by passing the electrically floating metal grid and going through the 4mm aperture in the metal shield. The small aperture in the metal shield selectively increases the probability that the molecules entering the ionizer subtend a small solid angle. Particles which come from large solid angles are scattered away from the ionizer by the shield. In the ionizer molecules and fragments can be positively ionized and then mass-selected by the quadrupole massfilter to enter the channeltron. There is a delay between time when the molecule or atom is ionized and the time when it enters the channeltron. For the UTI 100C the delay time for m/e = 115 amu ions has been determined to be  $\sim 20\mu$  s [32]. In the channeltron electron multiplier, the positive particles cause electron cascades. The electron cascades in turn initiate a measurable electric signal that indicates that a positive particle entered the channeltron. The channeltron can be operated in pulse counting mode or in an analogue mode. In pulse counting mode each selected fragment that enters the ionizer is registered as a pulse, whereas in analogue mode the intensity of fragments entering the channeltron are registered as an analogue current signal.

### 2.2.5 Laser

The laser used in the experiments is a pulsed nitrogen laser (Molectron UV-12, $\lambda = 337.1$  nm) for surface photochemical experiments. It delivers an energy of  $0.87mJ/cm^2$  per pulse and is operated at 10Hz with a pulse time width of 10ns. The laser is not part of the UHV system. A commercially available light meter(Molectron PowerMax 500D) with a light meter probe (Molectron PowerMax PM3Q) was used to measure the light power of the laser.

## 2.3 Standardized Surface Techniques

### 2.3.1 Sample Preparation

The Cu(110) sample surfaces were initially prepared by cycles of Argon ion  $(Ar^+)$  bombardment and annealing to high temperatures in the UHV chamber. The argon ion bombardment process began by lowering the sample in the chamber to the level of the Argon ion gun, which consists of a tungsten filament and focussing lenses. The power supplies to the filament and the lenses were turned on. The chamber was backfilled with Argon gas to a pressure of  $6 \times 10^{-5}$  torr. To make sure that the Argon ion beam was actually striking the sample the current on the sample was measured. This was done by putting a current meter between the sample and ground. Typically a current of  $1\mu$  A was detected when the beam was on the sample surface. The sample was then biased to -250 eV in order to increase the kinetic energy of the bombarding  $Ar^+$  ions to 750 eV. After 20 minutes the bias and the Argon gas supply was turned off. The sample was annealed to a high temperature(920° C) and allowed to cool.

Auger Electron Spectroscopy was done to check if the sample was clean. If the Auger scan showed only the presence of substrate atoms, the surface was then checked by Low Energy Electron Diffraction(LEED). The appearance of a sharp LEED pattern, in conjunction with a clean Auger spectrum, verifies that the sample is crystalline and that there are few, if any, foreign atoms on the surface. It is "clean" in other words. Large and fuzzy LEED spots are a good indication that foreign atoms are disrupting the periodicity of the surface. This can occur even when the Auger scan shows no sign of foreign peaks due to the limited sensitivity of the Auger to some elements. The cycles of  $Ar^+$  bombardment for 20 minute periods and annealing of the sample were continued until the sample was determined to be clean. The cleaning process could take several days or a week depending on how dirty the sample was when cleaning began. This is because the cycles of cleaning and heating increase the UHV background pressure which can take a day to recover to normal levels.

During an experiment, the sample is cooled using liquid nitrogen to ~ 95 K. At that time the  $CH_3Br(Sigma Aldrich 99.5\%)$  or  $CH_3I(Sigma Aldrich 99.5\%)$  gas introduced into the chamber. Methyl bromide is a gas in a pressurized lecture bottle attached by a teflon line to the gas rack. Methyl iodide is a liquid which is held in glass container attached to the gas rack. The vapour pressure of the liquid at room temperature is used to introduce the  $CH_3I$  into the glass handling rack. Degassing of the glass rack system is done by pumping the methyl iodide or methyl bromide gas away several times just before an experiment.

The unit used to measure the amount of gas let into the chamber is the Langmuir  $(1 \text{ L} = 10^{-6} \text{ torr} \cdot \text{seconds})$  and is referred to as the "dose". Molecules from the gas phase condense onto the sample in the UHV and in the ideal case form solid layers. Each layer of condensed molecule on the sample is referred to as a Monolayer(ML). Because the number of molecules that actually stick to the sample is small compared to the number that is let into the chamber, the number of monolayers formed is independent of the surface area of the sample. The number of layers formed as a function of dose is governed by the sticking coefficient of the particular molecule injected into UHV and its ionization efficiency in the ion gauge. Ion gauges measuring pressure are typically standardized for nitrogen measurement. The gas doses in this thesis are all based on the uncorrected ion gauge readings.



Figure 2.4: Ewald sphere for electrons at normal incidence to a crystal surface. (Diagram from Zangwill, [43, pg34];Kahn [20].)

### 2.3.2 Low Energy Electron Diffraction(LEED)

Low Energy Electron Diffraction(LEED) is a diffraction technique which can be used to study crystal surfaces. Electron diffraction of surfaces is similar to X-ray diffraction of three-dimensional crystals. Surfaces however are periodic in only the two-dimensions of the planar surface and the 3-D diffraction conditions relax to allow diffraction in two dimensions. A principle reason for the relaxation of the diffraction condition is the short mean free path of low energy electrons in solids. A diffraction experiment requires that the probe must have a wavelength  $\lambda$  that is smaller than interatomic spacing. The interatomic spacing between molecules on a surface are typically  $\sim 1A^{\circ}$  and so electrons used as the probe must have a minimum energy  $E = (h/\lambda)^2/2m \approx 150$  eV in order to be sensitive to the crystal structure [43]. As it turns out the minimum on the universal curve for the mean free path of electrons in solids is near this energy (see figure 1.9). Electrons at the minimum on this curve have a mean-free-path on the order of several lattice spacings. Electrons of this energy that penetrate deeper than several lattice spacing will likely be inelastically scattered and therefore diffraction in 2-dimensions becomes possible. Elastically backscattered electrons from crystal surfaces in the range 20-500 eV form Fraunhofer diffraction patterns [43]. The LEED pattern is a reciprocal image of the surface. The distance between bright spots in a LEED image is inversely proportional the lattice spacing in the real crystalline surface.

In reciprocal space, electrons are typically described by the wave vector  $\mathbf{k}$ . The de Broglie relation

$$\lambda = \frac{2\pi}{k} \tag{2.1}$$

can be used to convert k, where k is the magnitude of the wavevector k, to the wavelength  $\lambda$ .



Figure 2.5: Diagram of Rear-view LEED Optics. Electron gun is at the center of the phosphorous screen. Electrons are backscattered off the sample towards the LEED optics.

The surface net which defines the crystal surface lattice was previously defined as  $T=ma_s + nb_s$ , m and n are integers.  $a_s$  and  $b_s$  are the primitive vectors of the surface net. The two-dimensional Lau equations are satisfied when

$$(\mathbf{k_i} - \mathbf{k_f}) \cdot \mathbf{a_s} = 2\pi m \text{ and } (\mathbf{k_i} - \mathbf{k_f}) \cdot \mathbf{b_s} = 2\pi n$$
 (2.2)

where  $k_i$  and  $k_f$  are the incident and outgoing wavevectors for the electron, and m and n are integers.

The surface net in reciprocal space is described by  $\mathbf{g}_s = h\mathbf{A}_s + k\mathbf{B}_s$ , where h and k are integers.  $\mathbf{A}_s$  and  $\mathbf{B}_s$  are the primitive vectors of the reciprocal space net. The Lau equations are graphically illustrated by the Ewald sphere of figure 2.4. The radius of the sphere is given by the magnitude of the incident wavevector  $\mathbf{k}_i$  and a reciprocal rod passes through every point defined by the reciprocal net  $\mathbf{g}_s$ . The two-dimensional diffraction condition is met where the sphere intersects the reciprocal rod.

The LEED optics are shown in figure 2.5. The electron gun is at the center of the phosphorous screen, where the (00) spot would appear. Low energy electrons of the order of 100 eV are directed towards a single crystal sample surface in a narrow beam. The surface atoms scatter electrons inelastically and elastically. Some are backscattered towards the phosphorous screen. The retarding grids in front of the screen have a potential which is sufficient to repel the lower energy inelastically scattered electrons. The higher energy elastically scattered electrons are unaffected by the grids and they pass through to the phosphorous screen. Bright spots appear where the diffraction condition is met. The rest of screen is dark. Multiple scattering processes affect the intensity of the various spots but it does not affect the number or the placement of spots.



Figure 2.6: (a)The three-electron Auger process. An inner shell electron is knocked out of its orbital by a high energy bombarding electron (3k eV). An electron from an upper orbital fills the gap and at the same time passes energy to an adjacent electron, which is kicked out of its orbital as a result. (b) Backscattered N(E) distribution. Inset is the N'(E) distribution. (Diagrams from Zangwill [43, pg22,23]; (b) Park and den Boer [27]. )

### 2.3.3 Auger Electron Spectroscopy(AES)

Auger Electron Spectroscopy(AES) is a surface sensitive technique where core-level electrons in atoms are ionized and the subsequent electron emission is studied. In this technique a surface is bombarded with relatively high energy electrons of 3 keV. The bombarding electrons cause elastic and inelastic scattering of electrons at the surface and in the bulk. Electrons that are backscattered from the surface are collected in a detector.

The Auger process is only one of a number of processes which is occurring due to electron scattering. Fig 2.6(a) shows the steps in an Auger process. This particular one is referred to as a KLL Auger process because a K orbital and two L orbitals are involved. The Auger process is a three electron process. The first electron is scattered out of an inner atomic orbital, creating a "core hole". A second electron decays from a higher energy orbital to fill the core hole in the low energy orbital by transferring energy to a third electron in the same or an adjacent orbital. The transferred energy is equal to the energy difference between the two orbitals and it scatters the third electron out of its orbital. Auger electrons produced in the first few layers of a surface will have a much smaller probability for scattering than those produced deeper in the bulk. Auger electrons that inelastically scatter contribute to the background. Therefore the Auger process is highly surface sensitive. The measured Auger signal is derived from those atoms in the first few layers of the surface.

Typically the energies of the Auger electrons are on the order of hundreds of eVs whereas the workfunction of a surface is on the order of a few eV. Therefore Auger electrons have sufficient energy to escape the surface. Figure 2.6(b) shows a schematic spectrum of the electron energy distribution  $N(E)^1$  of backscattered electrons collected from a Titanium

 $<sup>{}^{1}</sup>N(E) = \frac{\#_{E} \cdot e}{E \cdot t}$ , where  $\#_{E}$  is the # of electrons with energy E, e is the electron charge and t is time.



Figure 2.7: The Auger circuit for measuring N'(E).  $E_B = 3$  keV is the energy of the bombarding electrons.  $\Delta V \approx 10$ V is the peak-to-peak voltage of a small sinusoidal voltage.  $V_0$  ramps from  $\approx 90$  volts to 1000 volts for copper. The phase  $\omega = 2\pi f$  where f = 1.4 kHz is the frequency of the sinusoidal voltage.

surface as a function of the energy. The energy  $E_p$  is the energy of the bombarding electrons. The Auger electrons show up as small peaks on a large background of inelastically scattered electrons. The energies E where the peaks appear are characteristic of the element, in this case Titanium, that is being bombarded and so each atomic species has a characteristic Auger spectrum. The inset in figure 2.6(b) shows a spectrum of the derivative dN(E)/dEof the electron energy distribution N(E). The Auger peaks are enhanced in this spectrum and are easy to to recognize. For this reason Auger spectrums are typically done with the derivative dN(E)/dE.

Auger spectra are done with a circuit that uses the LEED optics as a retarding field analyzer (RFA) (see figure 2.7). The electron gun in the center of the LEED optics bombards the surface with  $E_B = 3$  keV electrons. The backscattered electrons are collected as a current I on the phosphorous screen. The current at the collector is affected by the retarding potential on the retarding grids. If the potential on the grids is  $V_0$ , than all electrons with less energy than  $E_0 = eV_0$  will be repelled away from collector. In that case the current on the detector can be expressed as an integral [41].

$$I = \int_{E_o}^{E_p} N(E) dE \tag{2.3}$$

Electrons arriving at any time t on the detector have energy from  $E_0$  to the bombarding energy  $E_p$ . If the retarding potential  $V_0$  on the grids is modulated with a sinusoidal potential  $\Delta V sin(\omega t)$ , then at any time t the minimum energy of electrons arriving at the detector is  $E = e(V_0 + \Delta V sin(\omega t))$ . The current I arriving at the detector can be expressed as a sum



Figure 2.8: When dipolar molecule attach to a metal surface they may orientate in a particular direction. In this case dipoles are shown orientated in an 'up' direction. The negative end of the dipole is closer to the surface.

of harmonics using a Taylor series expansion, that is

$$I = \int_{E}^{E_{p}} N(E)dE = A_{0} + A_{1}sin(\omega t) + A_{2}sin(2\omega t) + \dots$$
(2.4)

where  $A_0$  is the d.c. current  $(A_0 = \int_{E_0}^{E_p} N(E) dE)$  and  $A_1, A_2, \dots$  are the amplitudes of the harmonics [41]. The amplitude of the first harmonic  $A_1$  can be shown to be

$$A_1 = \Delta E N(E_0) + \frac{\Delta E^3}{8} N''(E_0) + \dots$$
(2.5)

and the amplitude of the second harmonic  $A_2$  can be shown

$$A_2 = \frac{\Delta E^2}{4} N'(E_0) + \frac{\Delta E^4}{48} N''' + \dots \dots$$
(2.6)

In practice we do not measure N(E) but rather its derivative N'(E). The lock-in amplifier is a phase sensitive detector and is able to lock-in on the  $2\omega$  phase. In figure 2.7 the Lock-In amplifier is used to measure the amplitude  $A_2$  of the second harmonic  $sin(2\omega t)$  when the retarding voltage on the detector is modulated by a sinusoidal potential of frequency f. That is the retarding voltage is  $V = V_0 + \Delta V sin(\omega t)$ , where  $\Delta V \approx 10V$  and  $\omega = 2\pi \times f$ (f = 1.4kHz). The Auger controller is used to ramp  $V_0$  from 90 volts to 1000 volts, which is sufficient to get all the Auger peaks in an Auger spectrum of crystalline copper. Since  $\Delta E = e\Delta V$  is a small constant number significantly smaller than unity, the lower order terms of  $A_2$  dominate and

$$N'(E_0) \propto A_2 \tag{2.7}$$

#### 2.3.4 Retarding Potential Spectroscopy

Retarding potential spectroscopy is a surface technique for measuring the changes in the workfunction of a surface as molecules are dosed onto it. The workfunction changes are significant because they are an indication of surface processes. Dipolar molecules on a metal surface, for example, may have a predominant orientation which can increase or decrease the workfunction. The change in the workfunction will likely indicate the predominant dipole



Figure 2.9: The ideal representation for measuring workfunctions. Since the chemical potential does not differ a great deal from the Fermi potential in metals even at the temperatures  $T \sim 2800 \text{ K}$  that the tungsten filament is heated to, I will follow the usual practice of referring to the maximum potential energy as the Fermi energy.  $V_0$  is variable in order to maintain a constant  $\delta \Phi$  space potential difference between the two metals.  $\Phi_A$  changes with the addition of molecules to the metal surface. The metal sample receives electrons and is called the anode as a result. The tungsten filament of the electron gun produces electrons and is called the cathode.

orientation on the surface. Figure 2.8 shows a layer of dipolar molecules orientated on the surface in an 'up' direction. The negative end of the molecule is close to the surface and the dipole is pointed away from the surface. This orientation will decrease the workfunction because the electric dipoles are assisting the electrons away from the surface. Dipoles predominantly oriented in the 'down' direction, not shown, would increase the workfunction.

The basic principle for measuring changes in the workfunction of the sample as it is dosed with molecules is as follows. Figure 2.9 shows the ideal representation for measuring the changes in the workfunctions at T = 0 Kelvin. Ideal in this case just means that the maximum potential in the metal is called the Fermi potential. In actual fact this is only strictly true at T = 0 Kelvin. For T > 0 Kelvin the maximum potential is somewhat greater than the Fermi energy but not significantly so. In figure 2.9 the space potentials of the metal sample and the tungsten filament of the electron gun are maintained at a constant difference  $\delta \Phi$ . Since space is insulating, the space potential of a metal in a vacuum is at  $\Phi$  above the maximum potential energy of an electron on the surface.  $\Phi$  is the workfunction potential. The relative position of the space potential of a metal in a vacuum can be manipulated by applying a DC potential to the metal. Increasing the potential on the metal raises the space potential. The  $V_0$  potential in figure 2.9 is variable and it is used to maintain the constant potential difference  $\delta \Phi$  between the space potential of the tungsten cathode and the space potential of the metal surface anode.  $V_0$  is variable because the metal samples' workfunction  $\Phi_a$  changes as molecules are dosed on to it. In order to maintain the constant difference  $\delta \Phi$ ,  $V_0$  is varied by the exact amount that the workfunction changes by. The changes in  $V_0$  are the retarding potential difference that we measure in the workfunction experiments.



Figure 2.10: The electrons produced from the electron gun have an approximately gaussian distribution. The peak in the distribution is labelled  $E_B$ . Only electrons with energy greater than  $E_0 = e\delta\Phi$  will contribute to the current on the sample. Electrons with less energy than  $E_0$  will be deflected away from the sample.

In the real system, a low energy beam  $(E_B \sim 5eV)$  of electrons is directed towards the metal sample. The electron gun that produces the electrons is comprised of a hot tungsten filament and focussing elements. Electrons in the tungsten are thermally excited above the vacuum potential. Electrons of energy E are produced in an approximately gaussian distribution about the energy  $E_B$ , the nominal energy of the beam as in figure 2.10. N(E) is the electron energy distribution. In order for any electron to reach the metal surface it must have more kinetic energy than  $E_0 = e\delta\Phi$ . All electrons with less energy than  $E_0$  will be repulsed away from the metal. The current on the sample can be described by an integral

$$I = \int_{E_0}^{E_{max}} N(E) dE \tag{2.8}$$

where  $E_{max}$  is the largest electron energy in the beam. Figure 2.11 shows the current on the sample as a function of the retarding potential  $V_0$ . When the retarding potential is sufficiently strong, the lower energy electrons in the beam are deflected away from the sample and the current begins to decrease.

The definition of the current I on the sample in equation 2.8 is reminiscent of Auger theory where the current on the LEEED/RFA collector due to backscattered electrons from the sample has a similar integral. The retarding potential measurements can also be done with the use of harmonics by modulating  $V_0$  with a small sinusoidal potential  $\Delta V sin(\omega t)$ . This modulates the space potential and results in a alternating current on the sample. In this case the current I can be expressed as a sum of harmonics

$$I = \int_{E_0 + e\Delta V \sin(\omega t)}^{E_{max}} N(E) dE = A_0 + A_1 \sin(\omega t) + A_2 \sin(2\omega t) \dots$$
(2.9)

where  $A_0$  is the DC current and  $A_1, A_2, \dots$  are the amplitudes of the harmonics. Using the



Figure 2.11: The current on the sample varies with the retarding potential  $V_0$ . When  $V_0$  is increased such that it begins to deflect the electron beam away from the sample, the current begins to drop off.



Figure 2.12: This data is proportional to the derivative of N(E), the distribution of electron energies. As the current on the sample decreases due to an increasing  $V_0$  there is a zero-crossing point on the N'(E) graph. It is marked with  $E_B$ 

Lock-in amplifier with an appropriate circuit (Figure 2.13)we can measure the amplitudes  $A_1, A_2$ .....

Figure 2.13 shows the circuit used to measure the retarding potential of the sample. The  $\Delta V \sin(\omega t)$  sinusoidal voltage couples to the  $V_0$  variable voltage through a transformer. The 10 K $\Omega$  resister in the circuit does not affect the DC voltage on the sample, it is there to separate the inputs of the lock-in amplifier. The DC voltage on the sample is the retarding voltage  $V_0$ . We used the circuit to lock-in on the  $sin(2\omega t)$  signal, which is proportional to N'(E), the derivative of the N(E) electron distribution of figure 2.10. As it turns out it is easier to follow the peak in the N(E) distribution by using the derivative N'(E). In figure 2.12 N'(E) is shown as a function of  $V_0$ . The significance of this graph is that there is a zero crossing at  $E_B$ . We know that

$$N'(E_0) \propto A_2 \tag{2.10}$$

Therefore we vary  $V_0$  such that we measure a zero amplitude on the  $sin(2\omega t)$  harmonic, which is the zero crossing point. All we require at that point is to maintain the DC retarding potential  $V_0$  on the sample at this zero crossing point as the surface is dosed and the workfunction changes. By tracking the zero-crossing feature we can measure the changes in the workfunction. If  $V_0^i$  is the initial potential on the sample to maintain the zero crossing, then the retarding potential differences  $\Delta V = V_0^f - V_0^i$ .  $V_0^f$  are the measurements for the zero-crossing on the dosed surface.

### 2.3.5 Temperature Programmed Desorption(TPD)

Temperature programmed desorption(TPD) is used to examine the temperature dependent desorption of atoms and molecules from a surface. The TPD experiment uses the sample heating circuit and the mass spectrometer. A computer program written to do TPD spectra controls the heating circuit (figure 2.3) for warming the sample and the QMS for sampling particles of mass m. The analogue mode of the mass spectrometer produces a voltage signal where the size of the signal depends on intensity of mass-selected particles.

TPD measurements start with a cooled (100 K) and dosed sample. The sample is warmed at a controlled rate with respect to time using the temperature control circuit. Molecules and atoms desorbing from the sample enter the ionizer of the mass spectrometer. A spectrum of mass-selected intensity as a function of temperature is produced.

Peaks arise in the TPD spectra due to the strength of the binding in various layers. For example, the bond of the first layer of molecules to the surface is usually stronger than the bond of succeeding layers to underlayers. Since the bond strengths are different, different energies will be required to break the bonds. If the first layer is more strongly bound than overlayers, as is usually the case, then the first layer will require a higher temperature for removal than the overlayers. If the temperatures are sufficiently different than the massselected intensity spectra will show distributions as a function of temperature.

One of the uses of TPD spectra is for determining the dosage that corresponds to a monolayer, a single layer, on the surface. As gas is let into the UHV chamber the vacuum pumps are pumping it out and only a small fraction of gas let into the chamber actually strike and stick to the sample. The sticking coefficient relates the fraction of molecules that stick to the sample after striking it. The sticking coefficient depends sensitively on such



Figure 2.13: Circuit design used to measure the workfunction changes of the sample as it is being dosed with molecules. The Lock-In amplifier measures the amplitude of the  $sin(2\omega t)$  harmonic. The amplitude is directly proportional to the derivative of the electron energy distribution N(e).

factors as temperature, surface, and coverage which will vary depending on the experiment. Most of the gas let into the chamber is pumped away. Because only a small fraction of the molecules let into the chamber actually strike and stick to the sample, the number of Langmuirs that corresponds to a monolayer is independent of the size of the sample.

## 2.4 Surface Photolysis Experiments: Time-Of-Flights

### 2.4.1 Introduction

The Time-of-Flight (TOF) experimental apparatus is composed of the UHV chamber, a crystalline sample, a quadrupole mass spectrometer, a multichannel scaler, a pulsed nitrogen laser, and a PowerMac computer. (See Fig 2.1.) In addition there is a provision for interfacing the computer to various lab equipment. During the TOF experiment, the dosed sample surface inside the UHV chamber is illuminated with pulses of photons from the laser. The laser light enters the chamber through a UV grade fused silica window along a pathway that is at an angle of 45 degrees to the mass spectrometer detector. The sample can be rotated as described in the experimental section. Therefore, TOF data can be obtained with the sample surface normal at various angles to the QMS. Light that is incident on the dosed sample surface can cause photodissociation and desorption processes on the dosed surface.

The laser is a pulsed nitrogen laser (Molectron UV-12) that delivers energy of  $0.87 \text{mJ}/cm^2$  per pulse. Each pulse has a 10ns (nanosecond) duration and the pulses occur at a 10Hz frequency. In a typical TOF experiment hundreds or thousands of laser pulses are used. The laser beam enters the chamber through a UV grade fused silica window at an angle of  $45^{\circ}$  to the QMS. The QMS is operated in pulse counting mode in the TOF experiments. Molecules and dissociation products entering the QMS are ionized. Ions are mass selected to go through the channeltron where they cause electron cascades that produce a single pulse signal for each ion. The pulse signals from ions in the QMS are amplified by a fast preamplifier(EG&G VT120) and are processed by a multichannel scaler(MCS, EG&G Turbo MCS). The MCS is a high speed counting device which records the arrival times of the pulse signals from the channeltron in sequential time bins. The bins are typically a time interval of  $2\mu s$ ; the first bin coincides with the laser pulse time. For higher resolution TOF spectra,  $1 \mu s$  bins were used.

The QMS detector is a 'density' detector since the TOF signal is a distribution in space [45]. Therefore the signal in a TOF spectra does not directly represent an energy distribution of particles. The measured counts in the TOF spectra differ from the actual TOF distribution because the probability of a detecting any particle decreases as its speed increases. Slower particles stay in the ionizer longer than faster particles and therefore have a greater probability of being detected. The relationship between TOF spectra and TOF distributions can be mathematically defined in the following way. The TOF signal S results from a TOF distribution of particles entering the mass spectrometer per time t at a particular radial distance r. At any point r, the TOF distribution of particles from a sample surface is given by the flux I(t). The flux I(t) is the number of particles per area per time;  $I(t) = v\rho$  where v is the velocity distribution and  $\rho$  is the number of particles per volume. Since the probability of detecting particles is inversely proportional to their speed, or the time it takes to arrive at the detector.  $S(t) \propto \rho(t)$ , and therefore  $I(t) \propto t^{-1}S(t)$ . This last equation tells us that multiplying the TOF spectra by 1/t converts it to a distribution in time. The counts of the fast particles are been enhanced in comparison to the counts of the slower particles. The 1/t factor must be taken into account when comparing the intensities of fast and slow particles in a TOF spectrum

TOF experiments in this thesis are done as a function of sample angle to the mass

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Figure 2.14: Rotation of the sample through  $\Theta$  about z-axis is the [001] azimuth. Rotation of the sample through  $\Phi$  about the x-axis is the [110] azimuth.

spectrometer detector (angular-dependency), as a function of dose on the sample (dosedependency), and as a function of total laser shots on the sample (depletions). The angulardependency experiments were done with respect to the two azimuths of the sample as in figure 2.14. The coordinate system is fixed and the detector is also fixed on the y-axis. In the diagram the sample can be rotated through  $\Theta$  or  $\Phi$ . The [110] direction of the sample is on the x-axis and the [001] direction of the sample is the z-axis. Rotation of the sample through  $\Phi$  about the x-axis is the [110] azimuth. Rotation of the sample through  $\Theta$  about z-axis is the [001] azimuth.

### 2.4.2 Yields as a function of total photons

The yield as a function of total photons on the surface system were done with the idea of finding a cross-section for depletion in the surface system. A cross-section for depletion measurement is a measure of the probability of molecular dissociation as photons are directed onto the system. The number of molecules N on the sample available for dissociation and the number of molecules that dissociate dN are related by

$$dN = -Nd(\sigma\theta) \tag{2.11}$$

where  $\theta$  is the number of photons per unit area on the system and  $\sigma$  represents the probability for dissociation. We assume that  $\sigma$  the cross-section is positive and independent of  $\theta$ .  $\sigma$  has units of area in order that the fraction  $d(\sigma\theta)$  is unitless.

There are surface effects that make it it difficult to measure  $\sigma$ . Surface reordering effects resulting from dissociation may make more molecules available for dissociation. In that case yield N may effectively increase with respect to the initial yield  $N_0$  and the relationship in equation 2.11 may not be applicable. In addition in the real surface system  $\sigma$  is not generally independent of large  $\theta$ . The accumulation of dissociative by-products may affect local potentials with the end result that the overall cross-section changes [44]. Dissociative by-products are generally more important for large  $\theta$ .

By separating the variables in equation 2.11 and integrating we get the exponential decay relationship:

$$N = N_0 e^{-\sigma\theta} \tag{2.12}$$

where  $N_0$  is the initial number of molecules on the surface and N is the number after photodepletion. By combining equations 2.11 and 2.12 we get

$$dN = -N_0 e^{-\sigma\theta} \sigma d\theta \tag{2.13}$$

and then the natural logarithm of this equation is taken

$$ln(dN) = ln(-N_0\sigma d\theta) - \sigma\theta \tag{2.14}$$

If reordering effects do not affect the yield significantly and if  $\sigma$  is constant and positive, ln(dN) should be linear with respect to  $\theta$  and represent a depletion of  $N_0$ . That is, a plot of ln(dN) vs  $\theta$  should produce a line with slope  $\sigma$ .  $ln(-N_0\sigma d\theta)$  in that case, is also a constant. Experimentally we do not directly measure dN. The signal S we measure in the TOF spectra is a small fraction of dN, that is S= q dN. As long as q does not have a  $\theta$  dependency the linear relationship remains valid, ie

$$ln(S) = constant - \sigma\theta \tag{2.15}$$

In the yield as a function of total photons experiment, the angle of the sample is fixed and a number of TOF spectra are done. The angle where the sample is fixed at is usually the angle where the yields were greatest. Each of the TOF spectra is done with the same number of laser pulses and each is numbered in a consecutive fashion. After the data has been taken the counts S in the TOF spectra are summed and plotted on a semi-logarithmic scale as a function of total photons on the sample. That is  $log_{e}(S)$  vs  $\theta$  is plotted.

Below is an example calculation of how a laser pulse is converted to numbers of photon. Before beginning an experiment, the laser power was measured to be 5.4 mJ/s with the pulse frequency at 10Hz. The surface area of the detector is  $0.6cm^2$ . The total energy per pulse is  $E_{pulse}$ :

$$E_{pulse} = \frac{0.54mJ}{pulse \cdot 0.6cm^2} = \frac{0.9mJ}{pulse \cdot cm^2}$$
(2.16)

The wavelength  $\lambda = 337.1$  nm and the energy  $E_{photon}$  of each photon is

$$E_{photon} = \frac{hc}{\lambda} = 5.9X10^{-19} J/photon = 3.67 \ eV/photon$$
(2.17)

where h is Planck's constant and c is the speed of light. Therefore the total photons number of photons in each pulse is given by

$$\frac{E_{pulse}}{E_{photon}} = \frac{0.9mJ/(pulse \cdot cm^2)}{5.9 \times 10^{-19}J/photon} = \frac{1.5 \times 10^{15}photon}{pulse \cdot cm^2}$$
(2.18)

Therefore if each spectrum is done with 500 laser pulses, for the first spectrum  $\theta = 500 \times 1.5 \times 10^{15}$  photons, for the second spectrum  $\theta = 1000 \times 1.5 \times 10^{15}$  photons, and so on. If the slope of the line in the  $log_e(S)$  vs  $\theta$  is reasonably linear and negative, then we may with confidence interpret the slope of the line to be the cross-section  $\sigma$  for depletion.

The power intensity of the laser pulse is found by dividing the energy in a single pulse by the time for a single pulse to occur. The power intensity is

$$\frac{0.9 \times 10^{-3} J}{10^{-9} s} \frac{1}{pulse \cdot cm^2} \sim \frac{0.1 \ MW}{pulse \cdot cm^2}$$
(2.19)

This value is significantly less than the  $10^3$  MW  $/cm^2$  [44] required to initial multi-photon effects. The energy transfer processes are single-photon processes.

### 2.4.3 Yields as a function of dose

The yield as a function of dose experiment measures the yields in TOF spectra as the dose is varied on a prepared surface. If reordering effects as the experiment proceeds do not make more molecules available for dissociation and if the cross-section is  $\sigma$  is constant and positive then the yields are governed by equation 2.15 ie

$$ln(S) = constant - \sigma\theta \tag{2.20}$$

TOF spectra done as a function of dose are each done with the same number of pulses, therefore  $\theta$  is the same and constant for all the coverages. Therefore the signal S = qdNin the TOF spectra has three dependencies: the fraction q that is collected to create the signal S, the number of molecules  $N_0$  that are in dissociative sites, and the cross-section for dissociation. Interpreting the counts as a function of dose should be done with respect to those three variables.

In the yields vs dose experiment the angle of the sample is fixed, usually at an angle where the density of desorbing particles is greatest. There are two methods of doing yields vs dose spectra. The first method is to do each TOF spectrum with a new dose on the sample and with a large number of laser pulses (~ 2000). The first TOF spectrum is done on the smallest dose because sequential dosing and flashing to high temperatures increases the residual pressure in the UHV chamber. The increase in pressure results in an increase in the background counts in the TOF spectra. Flashing cleans the dosed molecules off the sample and recooling to < 100K readies it for the next dose. By keeping the sequential dose larger than the previous dose, the increased background counts have less significance as the signal in the TOF spectra gets larger. Flashing to high temperatures has an additional negative effect however. The Cu(110) sample is of high purity but is contaminated by low concentrations of foreign atoms. Sulfur is one of the more common contaminants. Heating the sample causes contaminants in the bulk to transfer to the surface.

The second method avoids heating of the sample during the experiment by dosing on top of previous doses. In this method TOF spectra are taken with a relatively small number of laser pulses ( $\approx 500$ ) in order that the dose be minimally depleted. The smallest dose to be studied is put on the sample and a TOF spectrum is done. Then the sample is dosed with additional molecules. In this case the total dose is considered to be the first dose plus the second dose. Another TOF spectrum is taken with the same number of laser pulses. The process is repeated with the total dose being the sum of all doses on the sample. Other advantages of this method over the first method is that it can be done faster and the background counts in the TOF spectra are kept relatively low. A disadvantage is that the statistical error in the counts as a function of dose is larger than in the first method due to the lower number of counts in each TOF spectrum.

### 2.4.4 Angular Distributions

Angular distributions were done by taking TOF spectra of the dosed sample at various angles. The angles were done with respect to the two azimuths  $[1\overline{10}]$  and [001] of a 3-D coordinate system. All angles were measured as with respect to the surface normal.

There are two methods for investigating an angle dependence. The first method is easiest to describe. In this method the sample is dosed, an angle is chosen and the TOF spectrum is taken. The number of counts is measured in the resulting peaks. Then the sample is cleaned by flashing to a high temperature, redosed and a new measurement is taken at a different angle. This process is repeated until enough data is accumulated. As stated in the Yields vs Dose section, heating can bring contaminants to the surface from the bulk which can affect the photodynamics.

The second method avoids flashing between angular measurements. The second method uses a single dose for all the angles measured. In this method each TOF spectrum was collected with 1000 laser pulses but every third TOF was done at a normalizing angle, for example  $0^{0}$ . The TOF spectra done at the normalizing angle were used to normalize the depletions of the signal. Although depletion normally follows an exponential curve, for a small number of pulses this curve is fairly linear as compared to the curve for a large number of pulses. Therefore counts in the TOF spectra done at angles between the normalizing measurements could be increased by some multiplication factor based on extrapolation of a linear depletion between measurements. We found that this was a more accurate method for doing angular experiments.

## Chapter 3

# Methyl Halides on Copper: Standardized Surface Experiments

## 3.1 Introduction

The object of this research is to work on model systems to advance the understanding of the surface photochemistry of adsorbed molecules. There is a general theme in recent (less then 15 years) surface research papers that small molecules have been extensively studied in the gas-phase both with theoretical means and with experimental means [25, 13, 30] but the research on the photochemistry of small molecules on surfaces is not as well developed [19, 30]. This is a motivation for this thesis work.

My research is on the methyl halide group of molecules on crystalline metal surfaces. As the name implies methyl halide molecules are a combination of a methyl and a halide. The formula is  $CH_3X$  where the X can be a F,CL,Br, I. My research data is drawn from research done by my supervisor, Dr Erik Jensen, and myself in the summer of 1999. This research data has also been used to publish two papers by Dr Jensen, with myself as a coauthor [6, 5]. The research data used in this thesis is primarily of methyl iodide on crystalline copper cut in the (110) orientation, although I have included some data for methyl bromide on the same surface.

Why are metal surfaces used for this research? Metal surfaces are interesting because of the strong quenching and strong photoelectric effects that occur on metal surfaces. When light of sufficient energy is directed onto a metal surface, excited electrons are produced by the photoelectric effect. By using light with energy less than the workfunction of the surface at an intensity below that needed to initiate multi-photon adsorption, excited electrons can be produced at the surface with maximum energies less than the vacuum energy of the surface. In single-photon adsorption, the maximum energy of the hot photoelectrons produced on the surface will always be the energy of a single photon. This is a difficult task if the surface is bombarded with an external source of electrons. External electrons on approaching a surface are influenced by the attractive image potential of the surface and gain energy as they approach, by the time these electrons reach the surface they will have gained energy on the order of a few eV. There is a great deal of interest in electrons with energy with very low energies because in the gas-phase many molecules have large dissociative resonances for these electrons. Of all molecules that are available for study, why study methyl halides on surfaces? One answer is that if the excited electrons are to cause dissociation in absorbed molecules, the absorbed molecules must dissociate faster than the quenching rate of the metal. Close to the metal surface, quenching is on the order of femtoseconds. Methyl halides also have a dissociation rate, at least in the gas-phase, that is on the order of femtoseconds. Therefore dissociation of methyl halides on metal surfaces is often able to compete with quenching.

Research focusses on the first several layers of adsorbate molecules on clean surfaces. This is because the photochemistry of the adsorbate is usually only perturbed close to the surface. Methyl halides are described as rod-like shaped with a dipole moment [8]. Because of this rod-like characteristic and the dipole, they typically have a predominant orientation in the first layer on a metal surface. The molecules dipole typically orientates with the halogen close to the metal surface and at an angle with respect to the surface. This orientation can be affected by the coverage.  $CH_3I$ ,  $CH_3Br$ , and  $CH_3Cl$  on Pt(111) all lie down on the surface for low coverages but change their orientation towards the surface normal as the first layer is filled [7].

## **3.2** Auger Spectroscopy of Cu(110)

Auger spectroscopy was primarily used to determine sample cleanliness. This was done by taking an Auger spectrum of the sample and comparing the scan to an accepted Auger scan of clean copper. Figure 3.1 is an Auger scan of clean Cu(110). The position of the peaks in an Auger scan are characteristic of the atoms in the first several layers on the surface. An Auger scan is sensitive only to the first several layers of atoms. If the only peaks showing in the Auger scan are those which are characteristic of copper, then the sample was determined to be clean within the sensitivity of the Auger. If the sample was not clean, the Auger would show peaks at energies not consistent with copper and these could be used to determine the necessary sample cleaning process. The element contaminating the sample could be identified by comparing the energy of the additional peaks to standardized Auger scans of elements. Knowing which element was on the sample determined the cleaning process. Certain elements like iodine or oxygen could be removed from the sample by flashing to high temperatures but other elements, like sulfur, required  $Ar^+$  ion bombardment for removal.

Auger scans were also used to confirm that iodine was left on the copper surface after  $CH_3I$  was thermally dissociated on the surface. An iodided copper surface was formed by dosing 20 L of  $CH_3I$  onto a clean Cu(110) surface. The surface was then warmed to 525 K, below the temperature needed to remove iodine from copper but above the temperature to remove methyls and their byproducts [24]. The iodided surface is referred to as iodided Cu(110) or as Cu(110)-I. Figure 3.2 is an Auger scan of a Cu(110)-I surface, done after the surface has cooled somewhat. Within the sensitivity of the Auger spectrometer, the surface shows only iodine and copper peaks.



Figure 3.1: AES spectrum for Cu(110). The scan is done by measuring the amplitude of the second harmonic  $(sin2\omega t)$ . The signal is proportion to N'(E), the Auger electron signal. Sample cleanliness is confirmed by the appearance of Auger peaks consistent with copper only.



Figure 3.2: AES spectrum for Cu(110)-I. The scan is also done by measuring the amplitude of the second harmonic  $(sin2\omega t)$ . The iodine peaks show up near 510 eV.



Figure 3.3: Picture of the LEED screen with a clean Cu(110) surface. The electron beam energy is 105 eV. The reciprocal net is rectangular and is characteristic of well-ordered crystalline copper in a (110) cut.

## **3.3** LEED patterns of Cu(110),Cu(110)-I

LEED was primarily used in conjunction with Auger spectroscopy to confirm that the sample was clean and ordered. If the Auger showed only copper peaks, the possibility still existed that the sample surface was disordered due to various contaminants or poor annealing. Fuzzy spots or an irregular pattern in the LEED indicate some surface disorder. A sharp and characteristic LEED pattern for a surface determined to be clean by an Auger spectrum is additional confirmation that the surface is really clean. Figure 3.3 shows a picture taken of the phosphor screen in a LEED experiment with clean Cu(110). The LEED of clean Cu(110) shows the surface net characteristic of well-ordered crystalline copper in a (110) cut.

The LEED was also used with Auger to confirm that iodine was left on the surface after a 20 L dose of  $CH_3I$  on a cold Cu(110) surface was warmed to 525 K. This temperature is high enough to desorb methyl fragments which adsorb to the surface but not high enough to remove the iodine [24]. Figure 3.4 is a picture taken of the LEED with a Cu(110)-I sample. The graphics in figure 3.5 illustrate the spots as dots, squares and X's. The dots are in the position of the copper spots as on the clean surface, although in this case the intensity of these spots have contributions from iodine and copper atoms. The squares and X's are spots that are not apparent on the clean surface. The square spots are bright and the X's are dimmer. The dots and squares form a reciprocal surface net that could come from a real space c(2x2) pattern. Figure 3.6 illustrates a  $c(2\times2)$  overlayer surface net. A  $c(2\times2)$  structure is a rectangle with an atom at the center. The sides are 2 times the length of the real space rectangular surface net of, in this case, the copper atoms on the (110) surface. However in figure 3.4 additional dimmer spots (the X's in figure 3.5) are observed in the  $[1\overline{10}]$  direction. These spots indicate that there is likely some additional longer range order in this direction. A possible reason for the longer range ordering is that there is a lattice mismatch of the larger iodine atoms on the smaller copper atoms [6]. The sizes of iodine and of copper atoms were estimated from chemical bond lengths. An  $I_2$  molecule has bond length of 2.66 $A^{\circ}$ [26]. The diameter of each iodine atom is therefore ~ 2.66 $A^{\circ}$ . The copper atom diameter was determined from the FCC unit cell size. The crystalline copper FCC unit cell has each side of  $3.61A^{\circ}$  [2]. Therefore the diameter of a Cu atom is give by  $\frac{1}{2}(3.61)sin(45^{\circ})A^{\circ} = 1.27A^{\circ}$ . Therefore the diameter of the I atom is ~ 2× as large as the diameter of the Cu atom. Using these atom diameters an attempt was made to produce a  $c(2\times2)$  overlayer structure on a Cu(110) surface. It was found that iodine was too large to fit into such a structure. A  $c(2\times2)$  LEED pattern from an overlayer on Cu(110) can only be produced if each overlayer atom is centered between two copper atoms on the substrate in a  $c(2\times2)$  surface net. One possibility has the overlayer in two-fold sites on the ridges of the (110) rows, and another possibility has the overlayer in four-fold sites in the troughs of the rows.

Figure 3.7 (a) shows a  $c(2\times 2)$  overlayer structure, not iodine, in four-fold sites on a Cu(110) surface. In this case the hypothetical atoms used in the overlayer structure are smaller in size than the iodine atoms, but are the largest that could be fit into the  $c(2\times 2)$  overlayer. Figure 3.7 (b) shows the relative sizes of the iodine, copper, and the hypothetical overlayer atoms. If the real space surface net of the iodine overlayer on Cu(110) is generally  $c(2\times 2)$ , and if the size of iodine is twice as large as copper, then it is likely that significant changes must take place in the positioning of the copper atoms. That is, the surface must reorder to accommodate the iodine atoms. The exact overlayer structure and the reordering of the surface is at this point is unknown. There is no information in the literature at this time on the exact overlayer structure of iodine on Cu(110).



Figure 3.4: Picture of the Screen in a LEED experiment with Cu(110)-I at an electron beam energy of 101 eV. The reciprocal surface net is similar to a  $c(2\times 2)$  pattern but additional satellite spots are visible in the  $[1\overline{10}]$  direction. The additional spots likely indicate longer range ordering.



Figure 3.5: This schematic illustrates the LEED patterns is dots, squares and X's. The dots are the position of the  $(1 \times 1)$  copper spots. The iodine also contributes to the dots. The squares are iodine spots. The X's are the additional satellite spots. Diagram from Johnson et al. [6].



Figure 3.6: A  $c(2\times 2)$  real space overlayer structure is a rectangle with an atom in the center. The length of the sides are 2 times the length of the real space rectangular surface net of the copper atoms on the (110) surface.



Figure 3.7: (a) shows a  $c(2\times 2)$  overlayer structure, not iodine, in four-fold sites on a Cu(110) surface. In this case the hypothetical atoms used in the overlayer structure are smaller in size than the iodine atoms, but are the largest that could be fit into the  $c(2\times 2)$  overlayer. (b) shows the relative sizes of the iodine, copper, and the hypothetical overlayer atoms.



Figure 3.8: TPD spectrum for  $CH_3I/Cu(110)$ . The first layer is complete at a dose of 9.0 L and desorbs from the surface at 140 K.

## **3.4** Temperature Programmed Desorption(TPD)

During a TPD experiment the prepared surface is warmed at a controlled rate. The mass spectrometer samples for a species of ion produced in the QMS ionizer from particles or molecules desorbing from the surface. A graph is produced of the ion intensity as a function of temperature. We measured the principle fragment  $CH_3^+$  produced in the ionizer by fragmentation of the  $CH_3$ I and  $CH_3$ Br molecules. One problem is that various hydrocarbon species as well as methyl halides produce  $CH_3^+$  upon contact with the ionizer. Therefore when a  $CH_3^+$  signal is found it must be determined if molecules are desorbing from the sample or if fragments from dissociation on the surface are entering the ionizer.

### 3.4.1 $CH_3I/Cu(110)$

Temperature programmed desorption spectra for doses of 5.0 L to 20.0 L of  $CH_3I$  on Cu(110) are shown in figure 3.8. In these spectra the principle fragment  $CH_3^+$  is sampled in the mass spectrometer. At low coverage, less than 3 L, a single peak was evident at 160 K. When the dose is increased past 3 L there are two desorption peaks, one of which is centered at 160 K and the additional second peak is centered at 140 K. The 160 K peak shows up as a small step in the spectrums of figure 3.8. The intensity or size of the second peak at 140 K increases as the dose is increased to 9.0 L, where the peak size saturates. For doses larger than 9.0 L there are three peaks, two of which are centered at 140 K and 160 K. The additional third peak is centered at 137 K. The intensity of this peak increases with the dose on the sample and we saw no evidence of saturation of this peak.

All the data is assigned to molecular desorption of  $CH_3I$  from the surface rather than pro-

duction of CH<sub>3</sub> from dissociation of CH<sub>3</sub>I on the surface based on the following. We looked for hydrocarbon production, such as methane( $CH_4$ ), ethane( $C_2H_6$ ), and ethylene( $C_2H_4$ ) , from the CH<sub>3</sub>I/Cu(110) system in separate TPD experiments but none was found for temperatures below 300 K. This is consistent with findings from other works [9, 24]. Products from thermal dissociation of methyl iodide have only been shown to be dissociated from copper at temperatures in excess of 300 K [9, 24]. Chiang et al. adsorbed methyl iodide on Cu(110) at 110 K and then studied the methane, ethylene, and propylene( $C_3H_6$ ) production from the surface in TPDs. They found these products are desorbed from the surface at temperatures of 350-500 K, although methyl iodide dissociation occurs at much lower temperatures. They also reported that they saw molecular desorption at 135 K for exposures above 3.0 L of CH<sub>3</sub>I [9]. Lin et al. did a similar study of methyl iodide adsorbed on Cu(111). They noted that they saw two molecular desorption peaks at 135 K and at 165 K for exposures above 3 L of CH<sub>3</sub>I [24]. They estimate methyl groups are formed on the surface by 200 K but hydrocarbon products(methane, ethylene, and propylene) desorb at 300 K.

Based on our experiments and the previous work, the CH<sub>3</sub><sup>+</sup> measured in the mass spectrometer for figure 3.8 must come from molecular desorption. As already outlined above, these TPD spectra show dose dependent molecular desorption peaks at 160 K,140 K, and 137 K. Saturation of the peak at 160 K has two possibilities. Saturation of this peak may indicate completion of the first layer. Alternatively this peak may indicate saturation of stronger bonding sites in the first layer. One such possibility is step and defect sites [6]. Molecules attached to step or defect sites have more contact with the surface, therefore, the bonds at defect sites are expected to be stronger and require more energy to break. Previous work [44] on Ag(111) has shown evidence of adsorption of methyl halides at defect sites in the first layer. Zhou et al. found that increasing the defects on Ag(111), by sputtering the surface without subsequent annealing before adsorption, enhanced the TPD desorption of  $CH_3Br$  and  $CH_3Cl$  in the first monolayer at higher temperatures. Zhou et al. did not report a similar finding for  $CH_3I$  on Ag(111) but they reported that  $CH_3I$  adsorbed more strongly to Ag(111) in the first layer than the monolayers of  $CH_3Br$  and  $CH_3Cl$  to Ag(111). The strong chemisorption of  $CH_3I$  in the first layer through the I atom to Ag(111) may mask adsorption at defect sites. Chemisorption is indicated by the much higher temperature required for desorption of the first layer;  $CH_3I$  on Ag(111) desorbs and dissociates from the complete first layer near 210 K [44].

Time of flight data and retarding potential spectroscopy of  $CH_3I/Cu(110)$  will show that the peak at 160 K is consistent with attachment at stronger bonding sites in the first layer and saturation of the 140 K peak at 9.0 L indicates completion of the first monolayer. Therefore the peak at 137 K on  $CH_3I/Cu(110)$  is assigned to desorption of the second and any additional layers. It is referred to as the multilayer peak.

### 3.4.2 $CH_3I/Cu(110)$ -I

Temperature programmed desorption spectra from  $CH_3I/Cu(110)$ -I are shown in Fig 3.9. For low coverage of 5.0 L on the sample, the desorption peaks at 144 K. As the coverage increases, the center of this peak shifts to slightly higher temperatures. At 10.0 L the center of the peak is at 149 K. Saturation of this peak is taken as completed at about 9.5 L since



Figure 3.9: TPD spectra of  $CH_3I/Cu(110)$ -I. The first layer is complete at a dose of 9.5 L and desorbs at 149 K

the second peak can be seen emerging at 10.0 L but is not evident at 9.0 L. The second peak is centered at 137 K for 12.0 L but as coverage is increased the peak center shifts to higher temperatures. This peak size increases with coverage and is not observed to be saturated within the measured coverages.

The signal in figure 3.9 is assigned to molecular desorption for the same reasons that the TPD spectra of  $CH_3I$  on clean Cu(110) in figure 3.8 were determined to arise from molecular desorption. The peaks in both figures 3.9 and 3.8 show up at temperatures below the observed temperatures for the production of methyl fragments from copper in other research [24, 9]. We interpret the data for  $CH_3I/Cu(110)$ -I in figure 3.9 as follows: the high temperature peak corresponds to the desorption from the monolayer and the low temperature peak corresponds to the multilayer. Saturation of the first peak for  $CH_3I/Cu(110)$ -I at 9.5 L is taken as completion of the first layer on the surface. The second peak results from the second and multilayers on top of the first monolayer. Retarding potential spectroscopy and time-of-flight measurements, which will be discussed later, will support this interpretation. The shift in the center of the peak to higher temperatures as coverage is increased is indicative that the binding energy of molecules to the surface is increasing as the layer is filled.



Figure 3.10: TPD spectrum for  $CH_3Br/Cu(110)$ 

### 3.4.3 $CH_3Br/Cu(110)$

It will be useful to discuss the TPD spectra of  $CH_3Br$  on Cu(110).  $CH_3Br$  was not as extensively studied as  $CH_3I$  was, however, the surface dynamics of  $CH_3Br$  on the Cu(110)surface are later used for analysis of the  $CH_3I/Cu(110)$  and  $CH_3I/Cu(110)$ -I systems. Temperature programmed desorption spectra from  $CH_3Br/Cu(110)$  are shown in Fig 3.10. For low coverage there is a single peak at 140 K. When the coverage increases to 5.0 L a second peak appears at 128 K. This second peak saturates at 9.2 L, where the symmetry of the peak begins to break with the third peak growing in, and the temperature for desorption increases to 130 K. The third peak grows in relation to the coverage, and temperature for desorption increases from 124 K at 10.2 L to 129 K at 18.3 L. This peak is assigned to the second and multilayers.

The increasing temperature for desorption in the first and second layers indicate that intermolecular attraction is increasing as the layers are filled. The second peak that occurs at 128 K to 130 K is assigned to the first layer. The completion of the first layer is approximated to occur at 9.0 L. Attachment at step and defect sites are the most likely origin of the peak at 140 K.



Figure 3.11: Workfunction of Cu(110) surface as a function of  $CH_3I$  dose

## **3.5** Retarding Potential Spectroscopy (RPS)

Retarding Potential spectroscopy (RPS) was used to measure the changes in the workfunction of a prepared surface as it was dosed. The workfunction is the energy required to remove an electron from the surface. As molecules are added to the surface changes can occur in the workfunction. Methyl halides are dipolar molecules and their addition to a metal surface in the first layer has often been shown to decrease the workfunction. This is consistent with halide end of the  $CH_3X$  molecule being closer to the surface on average. The halide end, **X**, of  $CH_3X$  is negatively charged. Adsorption of methyl halide with the negative end down creates a dipole layer near the surface. This arrangement tends to assist electrons away from the surface.

### 3.5.1 $CH_{3}I / Cu(110)$

Fig 3.11 is a graph of the changes in workfunction of the clean Cu(110) surface as function of  $CH_3I$  dose. The workfunction decreases rapidly to a dose of 5 L. After 5 L the workfunction decreases somewhat to 7 L, then begins a slow increase to 16 L. The workfunction remains roughly constant thereafter.

The initial decrease in the workfunction up to a dose of 5 L is good evidence that the dipolar  $CH_3I$  is being attached to the surface with the I end down. This is consistent with the finding of other authors of  $CH_3I$  on other surfaces [24, 44]. Lin and Bent found that  $CH_3I$  adsorbed molecularly on Cu(111) at 120 K in the first layer with the I end of the molecule closer to the surface. Zhou et al. found that various methyl halides adsorbed to Ag(111) in submonolayer coverages caused a significant decrease in the workfunction, indicating that the molecules are orientated with the halide closer to the surface.

Figure 3.11 provides evidence to help determine the dosage that corresponds to one monolayer for this system. The TPDs of figure 3.8 showed that for doses larger than 3 L there were peaks at 160 K and at 140 K. For doses less than 3 L there was only a single

peak at 160 K. The argument made in the TPD section was that saturation of the 160 K peak at 3 L was either indicative of methyl iodide attachment at stronger bonding sites such as at step and defect sites or it indicated completion of the first monolayer. If we examine the figure 3.11 we see that the workfunction decrease does not change noticeably until after 5 L; there is no significant change in the workfunction decrease at 3 L. This is significant because in many studies of methyl halides on clean metals a significant difference has been observed in the workfunction once the first layer is complete. Therefore, completion of the first monolayer at 3 L is unlikely. Saturation of the 140 K TPD peak occurs at 9 L, which we assigned to the completion of the first monolayer. Figure 3.11 shows that at 9 L there is again no significant changes in the workfunction; it is slowly increasing till coverage reaches 15 L, where it remains constant thereafter. The only significant change occurs at 6 L; there are no such significant changes after 9 L.

The variations in this workfunction is in fact typical of dipole systems on clean metal surfaces. Figure 3.12 is the workfunction of Cesium on various surfaces of single-crystal Tungsten, referred to as the Cs/W system [43]. When Cs is deposited on W an electron from the Cs atom is donated to the metal. The electron stays on the W surface in the vicinity of the Cs ion; a dipole moment is created that causes a decrease in the workfunction. As a monolayer of Cs approaches the close-packing of the Cs atoms causes a depolarization of nearby neighbours and causes the workfunction to increase somewhat. The monolayer is complete in figure 3.12 near  $6 \times 10^{14} cm^2$  The workfunction graph for the first layer of Cs/W is very similar in shape to the CH<sub>3</sub>I/Cu(110) system.

Figure 3.11 is interpreted in a similar fashion. At 6 L the  $CH_3I$  molecules begin to close-pack and depolarize on Cu(110). The depolarization reduces the effective charges on the I atoms and on the C atoms, and thereby allows the  $CH_3I$  molecules to close-pack with the I end down. Atoms with similar charges tend to repel each other. The depolarization of the layer increases the workfunction slightly as the dose is increased past 7 L.



Figure 3.12: Workfunction measurements of cesium on single crystal Tungsten surfaces. (Diagram from Zangwill [43, pg293]; Kiejna and Wojciechowski [22].)



Figure 3.13: Workfunction of Cu(110)-I surface as a function of  $CH_3I$  dose

## 3.5.2 CH<sub>3</sub>I /Cu(110)-I

The Cu(110)-I surface is formed by warming the CH<sub>3</sub>I dosed Cu(110) surface to 525 K. After recooling the surface the workfunction was measured to have increased by 1.2 eV as compared to the clean Cu(110) surface. The increase in the workfunction is consistent with the formation of dipolar Cu-I orientated with the positive end of the dipole closest to the surface. This is a typical result for electronegative atomic adsorbates on metal surfaces.[6]

Figure 3.13 is a graph of the workfunction changes of Cu(110)-I surface as a function of  $CH_3I$  dose. The graph shows that the workfunction decreases non-linearly in the first, second and third layer. The most rapid decrease is in the first layer, followed by a smaller and slower decrease in the second. The third layer has a smaller and slower decrease in the workfunction than the second layer.

The rapid workfunction decrease in the first layer is suggestive that most of the  $CH_{3}I$ adsorb with the I end down. The non-linear decrease in the first layers suggests that some  $CH_3I$  are adsorbing with the I end up. This is supported by the absence of depolarization in the first layer on Cu(110)-I; evidence for depolarization was seen in the first layer on the clean Cu(110) with the local minimum at 7 L in the workfunction scan. The continued decrease in workfunction for the second and third layers on Cu(110)-I suggests that more than half of the  $CH_3I$  must adsorb with the I end down in those layers. Further more, the decrease in the workfunction changes in going from the first layer to the third layer suggests that the CH<sub>3</sub>I absorbs with the I end down progressively less from the first layer to the third. This is a natural progression considering the bulk structure of  $CH_3I$ . Figure 3.14 shows the ideal crystal structure of solid  $CH_3I$ . In the solid  $CH_3I$  is 50 % down and 50% up. As layers of  $CH_3I$  on Cu(110) or on Cu(110)-I get thicker they must at some point have this ideal structure. It is likely that on the Cu(110)-I semi-conductor surface,  $CH_3I$  is able to adopt the alternating position of the molecule's dipoles earlier than on the clean surface. That is, the up and down arrangement begins in the first layers, and as the layers progress the 50:50 ratio is achieved. This would help to explain the observed tilt of the molecules on



Figure 3.14: The crystal structure of solid  $CH_3I$ . In the solid  $CH_3I,50$  % of the dipoles are orientated down and 50 % are orientated up. The dipoles are tilted at 20<sup>0</sup> from normal. As layers of  $CH_3I$  on Cu(110) or on Cu(110)-I get thick, they will at some point have this ideal structure. This occurs when the surface effects are no longer significant. Diagram modified from Kawaguchi et al. [21].

the Cu(110)-I surface. It is possible that alternation of some of the dipoles on the surface lead to a surface structure where all of the dipoles are tilted whether or not they alternate.

## Chapter 4

# Surface Photolysis:Time-Of-Flight Experiments

## 4.1 Introduction

Time-of-flight (TOF) experiments are done with  $CH_3I$  on clean Cu(110) surfaces and also on Cu(110)-I surfaces. Some TOF surface experiments were also done with  $CH_3Br$  for comparison to the  $CH_3I$  photodynamics. The adsorbate photodynamics observed in these TOF experiments are the result of photoenergy transferred to the adsorbate by the direct and by the charge transfer processes. Only neutral particles can be observed in the TOF spectra due to the apparatus set-up. We cannot exclude the possibility, though small, that some ions are escaping the surface but we are not able to detect them with the QMS TOF apparatus. As a result all TOF spectra in this chapter result from neutral pathways.

A principle reason that prototypical systems are formed from  $CH_3I$  and  $CH_3Br$  adsorbed on metal surfaces is the fast intra-adsorbate bond dissociation times of the molecules. These dissociation times are on the order of femtoseconds and are comparable and, consequently competitive, with electronic quenching times on metal surfaces.  $CH_3I$  dissociation occurs in 65fs [16] and  $CH_3Br$  is somewhat faster at ~ 15 fs [44]. Intra-adsorbate bond dissociation times are determined from the speed of the fragment v and the bond extension l; the time for dissociation is then l/v [44]. Typically l is ~  $2\dot{A}$  and v is on the order of  $10^5 cm/s$ , therefore bond dissociation times are ~ 200 fs [44].

 $CH_3I$  and  $CH_3Br$  have similar gas-phase photodynamics and kinetics. In the gas-phase both  $CH_3I$  and  $CH_3Br$  undergo photodissociation due to direct adsorption of light and also due to dissociative electron attachment(DEA). Direct dissociation is represented by

$$h\nu + CH_3 X \to CH_3 X^* \to CH_3 + X \tag{4.1}$$

where  $h\nu$  is the energy of the light that is adsorbed by the  $CH_3X$  molecule. Absorption of a photon by a  $CH_3X$  molecule results in a non-bonding  $\pi$  electron centered on the X atom excited to a dissociative  $\sigma^*$  state, ie  $CH_3X^*$  [25]. During dissociation the excitation energy  $h\nu$  dissipates into vibrational, translational, and internal energy modes. Dissociative electron attachment(DEA) in methyl halide molecules is symbolically represented by
$$e + CH_3 X \to CH_3 X^- \to CH_3 + X^- \tag{4.2}$$

where the electron e has some kinetic energy and is captured into an anti-bonding unoccupied molecular orbital of the  $CH_3X$  molecule [17]. An anionic state  $CH_3X^-$  is created by the attachment which can dissociate into a methyl radical and a halogen ion.

DEA as a result of incident light on adsorbed  $CH_3I$  and  $CH_3Br$  occurs because of charge transfer processes and is referred to as charge transfer photodissociation(CT-PDIS). As discussed in Chapter 1, photons incident on substrates can produce photoelectrons in single-photon processes with a distribution of energies with a maximum equal to the photon energy. Photoelectrons produced at the substrate can attach to the adsorbate and cause it to dissociate. In the gas-phase  $CH_3I$  and  $CH_3Br$  have a high probability, that is a large crosssection, for attachment of low energy electrons. The gas-phase DEA of  $CH_3I$  is  $10 \times$  larger than the DEA of gas-phase  $CH_3Br$  [10]. In order to assist in distinguishing in the surface studies between photolysis resulting from direct photoabsorption and from CT-PDIS, the kinematics of gas-phase dissociation is reviewed.

In the gas-phase, absorption of ultra-violet light is continuous for  $CH_3I$  and  $CH_3Br$ in their respective A-band energies. The gas-phase A-band adsorption cross-sections as a function of wavelength  $\lambda$  for methyl iodide and methyl bromide are shown in figures 4.1 and 4.2. Adsorption cross-sections are a measure of the probability that photons will be absorbed. A large cross-section indicates a high probability of adsorption whereas a small cross-section indicates a low probability.

The CH<sub>3</sub>I A-band (3.5  $eV < h\nu < 5.5 eV$ ) is centered at 4.8 eV ( $\lambda = 260 \text{ nm}$ ) [13], where the cross-section is ~ 140 × 10<sup>-20</sup> cm<sup>2</sup>. [39] At 3.5 eV the cross-section is less than  $2 \times 10^{-21} cm^2$ . [39] The CH<sub>3</sub>Br A-band (4.4  $eV < h\nu < 6.9 eV$ ) is centered at  $\lambda = 200 \text{ nm}$ (6.2 eV) where the cross-section is ~  $60 \times 10^{-20} cm^2$  [23, 38]. At 4.4 eV the cross-section is less than  $10^{-21} cm^2$  [23]. In other words the CH<sub>3</sub>Br A-band is at much higher energies than the CH<sub>3</sub>I A-band. The wavelength, $\lambda = 337 \text{ nm}$ , at which the TOF experiments are done in this thesis is just on the edge of the CH<sub>3</sub>I A-band but it is far outside the CH<sub>3</sub>Br A-band. We do not see evidence in the  $\lambda = 337 \text{ nm}$  TOF experiments of direct photoabsorption in CH<sub>3</sub>Br adsorbed on the Cu(110) surfaces.

## 4.2 Kinematics and Potential energy surfaces

The kinematics for methyl halide gas-phase direct photodissociation are well understood. In the gas phase, dissociation of the  $CH_3X$  molecule occurs with the  $CH_3$  fragment and the X fragment separating at  $180^{\circ}$  to each other in a process referred to as axial recoil. Dissociation occurs on a faster timescale than the rotational period  $\sim 3 \times 10^{-12}$  s of the molecule [16]. If the momentum of the electron or photon that causes the dissociation is small, the conservation of momentum equation is given by

$$m_X v_X - m_{CH_3} v_{CH_3} = 0 (4.3)$$

where  $v_{CH_3}$  and  $v_X$  are the respective velocities of the CH<sub>3</sub> and X fragments,  $m_X^{-1}$  the

 $^1m_I = 127amu, m_{Br} = 80amu$ 



Figure 4.1: Gas-phase adsorption cross-section of the A-band for  $CH_3I$  as a function of wavelength. Diagram modified from Waschewsky et al. [39].



Figure 4.2: The total gas-phase cross-section for photodissociation of  $CH_3Br$  as a function of wavelength in the A-band. Diagram modified from Van Veen et al. [38].

mass of the halide atom, and  $m_{CH_3}^2$  the mass of the  $CH_3$  fragment. Since the total energy for translation  $T_{avail}$ , is split between the  $CH_3$  fragment and the X fragment, the  $CH_3$ translational energy,  $T_{CH_3}$ , is related to the X fragment translational energy  $T_X$  by

$$T_{\text{avail}} = T_{\text{CH}_3} + T_X = \frac{1}{2} m_{\text{CH}_3} V_{\text{CH}_3}^2 + \frac{1}{2} m_X v_X^2$$
(4.4)

Using this relationship and equation 4.3 we can solve for the fraction of total energy available for translation of the  $CH_3$  fragment,  $T_{CH_3}$ .

$$T_{CH_3} = \frac{m_X}{m_{CH_3} + m_X} T_{avail}$$
(4.5)

#### 4.2.1 Kinematics for Direct Gas-phase Dissociation

Neutral direct photodissociation of  $CH_3X$  is described by the kinematics equation,

$$T_{\text{avail}} = E_{\text{photon}} - D_0 - E_X^{\text{Internal}} - E_{\text{CH}_3}^{\text{Internal}}$$
(4.6)

where  $T_{avail}$  is the total energy available for translation,  $D_0^{3}$  is the energy required to cause dissociation of the CH<sub>3</sub>X molecule from its ground state vibrational energy, and  $E_{photon}$  is the energy of the photon causing the dissociation.  $E_X^{Internal}$  and  $E_{CH_3}^{Internal}$  are the internal energies of the fragments. In this equation the CH<sub>3</sub>X molecule is assumed to be at rest and in its vibrational ground state before dissociation. The photon is assumed to have zero momentum, since it is small compared to the molecular momentum.

Using equations 4.5 and 4.6 we can estimate the range of  $CH_3$  velocities. Dissociation can proceed with the iodine atom in a ground state  $(E_I^{Internal} = 0)$  or in an excited state  $(E_I^{Internal} = 0.943 \text{ eV})$ . Each of these possibilities is referred to as a dissociation channel. They are respectively referred to as the ground state  $({}^2P_{3/2})$  I channel and the excited state  $({}^2P_{1/2})$  I\* channel.

As the methyl halide molecule begins to dissociate, vibrational motions can be induced in the CH<sub>3</sub> fragment. The internal energies of the CH<sub>3</sub> fragment, ie  $E_{CH_3}^{Internal}$  include possible vibrational states such as the umbrella mode and the C-H stretch mode. No evidence has been found for a C-H stretch mode being significant [16]. However, a symmetric vibrational umbrella mode has been found to be significant [16]. The  $CH_3$  fragments vibrate with quanta  $v \sim 75meV$  in gas phase dissociation [34]. For the  $\lambda = 248$  nm and  $\lambda = 266$  nm dissociation of gas phase CH<sub>3</sub>I, CH<sub>3</sub> fragments predominantly vibrate in the umbrella mode at v=2 in the ground state I channel and at v = 0 in the excited state I\* channel [34, 12].

There is no vibrational data available in the literature for  $CH_3I$  dissociation at the wavelength of 337.1 nm. Therefore we must estimate the vibrational energies of the fragments. The umbrella mode energies at 337.1 nm will likely be similar to those in the gas phase at 248 nm and 266 nm. Therefore we assume  $CH_3$  umbrella mode vibrational energies in the I and I\* channels of  $CH_3I$  dissociation to be less than v = 4 quanta. We use v = 0 to v = 4 quanta for the internal energy of the  $CH_3$  fragment,  $E_{CH_3}^{Internal}$ . Using equation 4.5, we find that  $CH_3$  fragment energies,  $T_{CH_3}$ , for the I channel have a distribution ranging from

 $<sup>^2</sup>$ m<sub>CH<sub>3</sub></sub> = 15 amu

 $<sup>^{3}</sup>D_{0}(CH_{3}-I) = 2.39 \text{ eV}$ 



Figure 4.3: Gas-phase potential energy surfaces of CH<sub>3</sub>I in the A-band. The ground state and the three excited states are shown. The  ${}^{1}Q_{1}$  and the  ${}^{3}Q_{0}$  states curve-cross. (Diagram from Eppink et al. [12]; Gedanken and Rowe [15].

1.15 eV for v = 0 to 0.89 eV for v = 4, and similarly for the  $I^*$  channel the distribution ranges from 0.31 eV for v = 0 to 0.046 eV for v = 4.

#### 4.2.2 Potential Energy Surfaces for Direct Photoabsorption

The potential energy surfaces for dissociation due to direct photoabsorption in  $CH_3I$  and  $CH_3Br$  are described in this section.  $CH_3I$  and  $CH_3Br$  exhibit very similar direct photodynamics except that  $CH_3Br$  dissociation requires higher photon energy. Figures 4.3 and 4.4 are potential energy surfaces for methyl iodide and methyl bromide direct dissociation in the gas-phase. In each figure there is a ground state configuration labelled  ${}^{1}A_{1}$ . This state describes the potential energy of the  $CH_3X$  molecule (X = I or X = Br), as a function of C-X bond length. The molecule has a non-zero vibrational energy in this state. The higher energy dissociative states in the graphs are reached by promotion of a non-bonding  $\pi$  electron centered on the halogen atom to a C-X anti-bonding state [39]. In the A-band there are five excited states but only three optically allowed transitions from the  ${}^{1}A_{1}$  state to higher energy dissociative states for both  $CH_3I$  and  $CH_3Br$ . Figure 4.5 shows an energy level diagram of the five excited states. There are two weak perpendicular transitions to the 2E  ${}^1Q_1$  and the 3E  ${}^3Q_1$  states that correlate to production of  $I({}^2P_{\frac{3}{2}})$  and there is a strong parallel transition to the  $2A_1 {}^3Q_0$  state that correlates to production of  $I^*({}^2P_{\frac{1}{2}})$  [12]. The  $({}^{1}Q_{1}, {}^{3}Q_{1}, {}^{3}Q_{0})$  terms are the Mulliken notation and the  $(2A_{1}, 2E, 3E)$  terms are the corresponding  $C_{3\nu}$  notation [12].

Dissociation of the  ${}^{3}Q_{1}$  and  ${}^{1}Q_{1}$  states produce  $CH_{3} + I$  whereas dissociation of the  ${}^{3}Q_{0}$  state produces  $CH_{3} + I^{*}$ . Due to a curve-crossing of the potential energy curves of the  ${}^{1}Q_{1}$  and the  ${}^{3}Q_{0}$  states, dissociation which initially proceeded in the  ${}^{3}Q_{0}$  state may transform to the  ${}^{1}Q_{1}$  state [12, 13]. Curve-crossing involves a non-adiabatic transition in the conical curve-crossing region [12]. Curve-crossing has been found to be significant in methyl-iodide



Figure 4.4: Gas-phase potential energy surfaces of  $CH_3Br$  in the A-band. The ground state and the first three excited states are shown. (Diagram from Van Veen et al. [38].)



Figure 4.5: Gas-phase potential energy states of  $CH_3X$  in the A-band. Energy states shown with and without spin-orbit interactions. There are three optically allowed transitions from the  ${}^1A_1$ ground state to the states with spin-orbit interactions. Diagram from Yabushita et al. [42].



Figure 4.6: (a) The gas-phase branching ratio for excitation to the  ${}^{3}Q_{0}$  state.  $\phi_{0}^{*} = N_{0}^{*} / (N_{0} + N_{0}^{*})$  where absorption of photons leads to a production of initial populations  $N_{0}^{*}$  in the  $I^{*}({}^{3}Q_{0})$  channel and  $N_{0}$  in the I channel. (b) The probability of curve crossing as a function of wavelength. For both (a) and (b) the dashed and solid lines are alternate interpolations of the data points. In (b) the dashed line is similar to that expected from the Landau-Zener probability curve. Diagrams from Eppink et al. [12].

dissociation [12, 13, 42].

The yield of fragments from the I vs  $I^*$  channels is strongly dependent on the curve crossing. Absorption of photons leads to a production of initial populations  $N_0^*$  in the  $I^*$  channel and  $N_0$  in the I channel. The population change is described by

$$N^* = (1 - P_{cc})N_0^* \text{ and } N = N_0 + P_{cc}N_0^*$$
 (4.7)

where N and N<sup>\*</sup> are the final populations in the I and I<sup>\*</sup> channels and  $P_{cc}$  is the probability for curve crossing [12]. The total populations are normalized to unity (N + N<sup>\*</sup> = N<sub>0</sub> +N<sub>0</sub><sup>\*</sup> = 1) [12]. There are two branching ratios of interest. There is the branching ratio after dissociation is complete, ie  $\phi^* = N^* / (N + N^*)$  and the branching ratio of the initial population, ie  $\phi_0^* = N_0^* / (N_0 + N_0^*)$ . Figure 4.6 shows the methyl iodide gas phase  $\phi_0^*$  branching ratio and curve crossing probability  $P_{cc}$  as a function of wavelength. For wavelengths less than  $\lambda \sim 280$  nm, the branching ratio  $\phi_0^*$  of the initial absorption is close to unity and the curve crossing probability  $P_{cc} \sim 0.25$  [12]. Excitation is predominantly to the  ${}^3Q_0$  state at these wavelengths. Above 280 nm the  $\phi_0^*$  branching ratio decreases rapidly and the probability  $P_{cc}$  for curve crossing increases to 0.85 [12]. The reason for the decrease in the  $\phi_0^*$  value in the long red tail of the A Band is that more excitation is taking place to the  ${}^3Q_1$  state [13, 12]. Excitation to the  ${}^1Q_1$  state is insignificant above 280 nm [12]. More curve crossing is taking place as excitation to the dissociative  ${}^3Q_0$  state nears the conical curve crossing region [12].

Measurement of the dissociative products after dissociation is complete allows determination of the  $\phi^* = N^* / (N + N^*)$  branching ratio. From 222 nm to 304 nm the branching ratio  $\phi^*$  for dissociation of the states is significant, being greater than 0.43 [12]. Although there is no data in the literature for the exact wavelength we are working at ( $\lambda = 337$  nm) there is data near the wavelength we are working at. At 333 nm the  $\phi^*$  branching ratio in the  $I^*$  channel is  $\phi^* = 0.1$  [13].

The dissociation of methyl bromide has characteristics similar to methyl iodide dissociation although higher energy photons are required to promote the ground state to the excited states. (See figure 4.4.) The  ${}^{3}Q_{0}$  and the  ${}^{3}Q_{1}$  states dissociate to produce  $CH_{3} + Br({}^{2}P_{\frac{3}{2}})$ and the  ${}^{3}Q_{0}$  state produces  $CH_{3} + Br^{*}({}^{2}P_{\frac{1}{2}})$ . Although the  ${}^{1}Q_{1}$  and the  ${}^{3}Q_{0}$  states curvecross, for methyl bromide dissociation curve crossing has not been found to be significant [38]. Since we saw no evidence of direct photodissociation of  $CH_{3}Br$  on the Cu(110) and Cu(110)-I surfaces in the TOF spectra at  $\lambda = 337$  nm, no further mention is made of the direct dissociation of this molecule.

### 4.2.3 Kinematics Equations for Dissociative Electron Attachment Dissociation in the Gas-phase

A kinematics equation for the dissociative electron attachment mechanism to gas-phase  $CH_3X$  can also be found. In this case the energy for translation,  $T_{avail}$ , is given by

$$T_{\text{avail}} = E_{\text{electron}} - D_0 + EA_{X^-} - E_{X^-}^{\text{Internal}} - E_{\text{CH}_2}^{\text{Internal}}$$
(4.8)

where  $E_{electron}$  is the energy of the attaching electron and  $EA_{X-}$  is the electron affinity of the halide atom.  $D_0^4$  is the energy required to cause dissociation from the lowest vibrational state of the  ${}^1A_1$  ground state. The internal energy of the halide atom  $E_{X-}^{Internal} = 0$  for both iodine and bromine.

In the gas phase the most important resonance for DEA for  $CH_3I$  is at low energy  $(E_{electron} = 0.15 \text{ eV})$  [33], although there are other resonances below this energy. The electron affinity  $EA_{I-}$  for iodine is 3.06 eV [26]. We assume a range of 0 to 4 quanta for the internal energies of the  $CH_3$  fragment and using equation 4.8, we arrive at translational energies,  $T_{avail}$ , of 0.82 eV to 0.52 eV. If the electron momentum is ignored then we can use equation 4.5 to solve for the  $CH_3$  translational energies. A range of 0 to 4 quanta for the internal energy of the  $CH_3$  fragment gives a translational energy distribution,  $T_{CH_3}$ , of 0.73 eV to 0.47 eV.

For  $CH_3Br$  the gas-phase peak in the DEA cross-section occurs at an incident electron energy of 0.4 eV. [37, 17], and the electron affinity of bromine  $EA_{Br-}$  is 3.36 eV [37, 26]. Using a range of 0 to 4 quanta for the vibrational energy of the  $CH_3$  fragment and using equation 4.8 we find for gas phase  $CH_3Br$ , that  $T_{avail}$  ranges from 0.89 eV for v=0 to 0.59 eV for v=4. We use equation 4.5 to solve for the  $CH_3$  translational energies and find that  $T_{CH_3}$ is 0.75 eV for v=0 and is 0.5 eV for v = 4.

#### 4.2.4 Potential Energy Surfaces

Figure 4.7 shows potential energy surfaces for excitation of the ground state of  $CH_3X$  by adsorption of a photon and for dissociative electron attachment(DEA) to dissociative states. One of the main points in this diagram is to show that the potential energy of the  $CH_3X$ 

$${}^{4}D_{0}(CH_{3}-I) = 2.39 \ eV, D_{0}(CH_{3}-Br) = 2.87 \ eV$$



Figure 4.7:  $CH_3X$  potential energy surfaces for the electron attachment mechanism. Diagram modified from Ukraintsev et al. [37].

molecule is lowered in the DEA dissociative states compared to the direct dissociative states for large C-X bond distances. There are two potential energy surfaces for the DEA energy transfer mechanism. One potential energy surface shows  $CH_3$  and X dissociation with both fragments in the gas-phase, and the other shows  $CH_3$  and X dissociating with the X adsorbed. The adsorption of the X fragment lowers the potential energy of the state.

As a result of the lowered energy of the DEA potential energy surfaces, charge transfer is expected to be more competitive with quenching than the direct photoabsorption process. After electron attachment promotes the ground state of the  $CH_3X$  molecule to the dissociative state, separation of the C-X fragments quickly results in the potential energy of the molecule being lower than in the ground state [6]. In order to return to the ground state, energy would have to be put into the system [6]. This is opposite to the situation in direct dissociation, where after promotion to the excited state, the potential energy of the excited state is higher than the ground state. With direct dissociation there is more time for quenching of the excited state back to the ground state, therefore it is more likely that quenching will occur than for CT-PDIS.

# 4.3 Surface Photolysis of $CH_3Br$ on Cu(110) and Cu(110)-I

The method for doing TOF experiments was described in the experimental section. In brief each TOF experiment is done with a prepared and dosed surface, laser pulses are directed onto the surface system, and  $CH_3^+$  ions are counted in the TOF analyzer. A  $CH_3^+$  ion signal results from fracture and ionization of particles that desorb from the sample and enter the mass spectrometer ionizer. There is a delay between time when the molecule or atom is ionized and the time when it enters the channeltron. For the UTI 100C this delay time for m/e = 15 amu ions has been determined to be  $\sim 20\mu$  s [32]. True arrival times are found by subtracting this  $20\mu s$  delay.

The surface photolysis of  $CH_3Br$  on Cu(110) is presented first, although this system is not as well-studied as  $CH_3I$  on Cu(110) and Cu(110)-I. One of the reasons for presenting this system first is that the energy transfer dynamics of the system is easy to understand. Gas-phase  $CH_3Br$  does not have a significant cross-section for direct dissociation anywhere near  $\lambda = 337$  nm, therefore unless adsorption changes the potential energy surfaces significantly,  $CH_3Br$  adsorbed on a metal surface will dissociate primarily via the charge transfer mechanism.  $CH_3Br$  adsorbed on Pt(111) with hydrogen was found to photodissociate by CT-PDIS with TOF studies at  $\lambda = 308$  nm [36]. Therefore it is not surprising that the evidence also points to the charge transfer mechanism in the  $\lambda = 337$  nm TOF spectra for dissociation of  $CH_3Br$  adsorbed on Cu(110).

In figure 4.8 the  $\lambda = 337$  nm TOF spectra for various doses of CH<sub>3</sub>Br on clean Cu(110) are shown. TOF spectra for all doses of  $CH_3Br/Cu(110)$  show  $CH_3^+$  signal from a fast distribution for times less than  $110\mu s$  and a slow distribution for times greater than  $110\mu s$ . TPD experiments indicated that the first layer was complete on this system at a 9.0 L dose. The TOF signal from the fast distribution is generally featureless and broad for all doses. The lack of sharp features in the fast TOF signal is consistent with an energy transfer mechanism with a range of energies, ie the charge transfer mechanism. In figure 4.9 the counts in the spectra of figure 4.8 have been summed as a function of the fast distribution and the slow distribution and plotted as a function of dose. In figure 4.9 both the fast and the slow  $CH_3^+$  signals peak at completion of the first monolayer. From TPD measurements, a single monolayer was found to be 9.0 L of  $CH_3Br$  on clean Cu(110). The peak in the spectra at 1 ML can be understood as resulting from competition between quenching and charge transfer. Both charge transfer and quenching are expected to be most proficient in the first adsorbate monolayer on a metal surface. Additional layers on the monolayer are expected to provide a barrier to the movement of electrons and reduce the efficiency of both quenching and charge transfer. The peak at 1 ML in figure 4.9 results because dissociation is reduced for coverages greater than 1 ML. Dissociation of molecules is reduced for coverages greater than 1 ML because the proficiency of quenching is reduced less than the proficiency of charge transfer processes.

In figure 4.10 the significant times in the TOF spectrum of 10 L of  $CH_3Br$  on clean Cu(110) have been labelled with letters A,B,C, D and E. These times are listed in Table 4.1. Each time has been converted into a  $CH_3$  fragment and a  $CH_3Br$  molecule arriving at the QMS detector from the sample with that time. Kinetic energies,  $E_m$ , have been

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Figure 4.9: Slow and Fast Peak Counts as a function of  $CH_3Br$  dose on Cu(110)

Significant Point	Time( $\mu$ s)	$E_{CH_3}$ (eV)	$E_{CH_3I}$ (eV)
A	12	3.7	23.6
В	34	0.46	2.94
C	110	0.04	0.28
D	300	0.006	0.038
E	830	0.0008	0.005

Table 4.1: Significant times on the TOF spectrum for figure 4.10. The energies of  $CH_3$  (15 amu) fragments and  $CH_3Br$  (95 amu) molecules corresponding to those times are also calculated from  $E = \frac{1}{2}mv^2$ .

calculated for  $CH_3$  fragments and  $CH_3Br$  molecules arriving at the significant times, where

$$E_{m} = \frac{1}{2}mv^{2} = \frac{1}{2}m(\frac{d}{t})^{2} = \frac{1}{2}m(\frac{8.3x10^{-2}}{t})^{2}$$
(4.9)

This relationship is used in later sections for calculating energies for CH<sub>3</sub>I on Cu(110) and Cu(110)-I as well. The distance d between the sample and the ionizer is 8.3 cm. Where m is the mass of the  $CH_3$  fragment(15 amu) or  $CH_3X$  molecule ( $m_{Br} = 80amu, m_I = 127amu$ ) and t is its arrival time(A,B,C...) in the mass spectrometer.

From the energetics in the table 4.1 many of the  $CH_3^+$  fragments from the fast distribution between times corresponding to the significant points A and C could only come from  $CH_3$  fragments from dissociation of the C-Br bond. The significant point B in figure 4.10 has an energy of 0.46 eV for  $CH_3$  fragments and 2.94 eV for  $CH_3Br$  molecules. We determined earlier that DEA resulting in C-Br bond dissociation of the gas-phase  $CH_3Br$ molecule produced  $CH_3$  fragments with energies of 0.75 eV(v = 0) and 0.5 eV(v = 4). Since the fast distribution is peaked near an energy we expected  $CH_3$  fragments to have, the fast distribution is assigned to production of  $CH_3$  fragments from dissociation of the C-Br bond. The slower distribution is assigned to molecular desorption of  $CH_3Br$  due to DEA.

This is the extent of our interest in this system. We turn now the photodynamics of  $CH_3Br$  on Cu(110)-I. In figure 4.11 TOF spectra are shown for  $CH_3Br$  on Cu(110)-I at doses of 10 L and 20 L. The spectra show no evidence of dissociation or desorption of  $CH_3Br$  molecules. The signal is all background counts. We know that on the clean Cu(110)surface that  $CH_3Br$  was dissociating and desorbing at these coverages. The coverage of  $CH_3Br$  on Cu(110)-I is probably very similar to the coverage on clean Cu(110). The lack of dissociation and desorption on this surface indicates that charge transfer from the surface to the adsorbate  $CH_3Br$  is not taking place. The iodine on the Cu(110) is likely forming a layer of CuI. CuI is a semi-conductor and on the Cu(110) surface it likely presents a barrier to the production of hot electrons. In the retarding potential experiments in Chapter 3 we found that the retarding potential of the Cu(110)-I surface decreases by 1.2 eV relative to the clean Cu(110) surface. This means that the workfunction of the surface has increased due to adsorption of iodine [6]. Photoelectrons formed in the bulk of the Cu(110) with  $\lambda = 337$  nm photons likely do not have sufficient energy to tunnel through the semi-conductor CuI layer, which would explain the lack of photodynamics of  $CH_3Br$  on Cu(110)-I. At  $\lambda = 337$  nm direct and charge transfer mechanisms are not available for this system.



Figure 4.10: Time-of-flight spectrum of  $CH_3Br/Cu(110)$  at a dose of 10 L



Figure 4.11: Time-of-flight spectra of  $CH_3Br/Cu(110)$ -I at doses of 10 L and 20 L. In this case the  $CH_3$  collected in the TOF apparatus is background. Apparently  $CH_3Br$  is not dissociating. The CuI on the surface is likely acting as a barrier to the production of hot electrons. There is insufficient energy in the light photons to produce photoelectrons with enough energy overcome the CuI barrier.

## 4.4 Surface Photolysis of $CH_3I/Cu(110)$ -I

#### 4.4.1 Examination of the Detector Resolution

The signal from  $CH_3I$  on Cu(110)-I is particularly strong and therefore it can be used to study the resolution of the TOF apparatus. The resolution is studied by doing two TOF spectra, one with a short flight path and one with a long flight path. In one case the flight path d is measured to be 8.3cm and in the other it is 16 cm.

Resolution error in the TOF spectra is not due to the time width of the laser pulse. The time width of the laser pulse is 10ns; after subtraction of the  $20\mu s$  delay, all flight times are more than  $10\mu s$ . The ratio of the laser pulse width to the flight times is less than  $\frac{10ns}{10\mu s} = 0.001$  or 0.1%. Therefore the laser pulse width is insignificant to the flight times.

There is resolution error due to the length of the ionizer. The mean or average time  $CH_3$  fragments are measured is  $20\mu$ s after entering the ionizer. However there is some variation from this mean time, which is the primary cause of the resolution error. The significance of the resolution error is primarily affected by the ratio of the length of the ionizer region  $(\Delta x \approx 1 cm)$  in the mass spectrometer to the length of the flight path, d. Smaller ratios  $\frac{\Delta x}{d}$  result in better resolution of the signal, although they also result in decreased signals. The time t a particle is measured is

$$t \pm \Delta t = \frac{d \pm \Delta d}{v} \tag{4.10}$$

where v is its velocity. Since  $\Delta d$  will be less than the length of the ionizer, increasing d decreases the significance of  $\Delta d$  and , consequently, also the significance of  $\Delta t$ .

The resolution is analyzed by looking at the fastest and slowest particles in a distribution of particle energies. The real time t a particle of velocity v arrives in the ionization region is  $t = \frac{d}{v}$ . For the short flight path, a distribution of fragments with velocities  $v_1$  to  $v_2$  should arrive at the ionizer with a time interval  $\Delta t_{short} = t_1 - t_2 = \frac{8.3 cm}{v_1} - \frac{8.3 cm}{v_2}$ . Increasing the length of the flight path results in the distribution of velocities  $v_1$  to  $v_2$  arriving at the ionizer in a wider time interval. The time width of the velocity distribution for the long flight path of  $d = 16 \ cm$  should be  $\Delta t_{long} \approx 2\Delta t_{short}$ .

Figure 4.12 shows two TOF spectra of  $CH_3I/Cu(110) - I$  done respectively for flight paths of 8.3cm and 16 cm. Measurement of the full-widths at half the maximum (FWHM) for the fastest of the two fast peaks give  $\Delta t_{long} = (16 \pm 2)\mu s$  and  $\Delta t_{short} = (12 \pm 2)\mu s$ , and for the slower of the two fast peaks  $\Delta t_{long} = (26 \pm 2)\mu s$  and  $\Delta t_{short} = (17 \pm 2)\mu s$ . If the width of the FWHM were entirely due to the width of the TOF distribution, then the FWHM in each peak should double when the length of the flight path is doubled. Since the FWHM do not quite double within error, the TOF spectrum for the short flight path is somewhat less resolved than the long flight path.

From equation 4.10, the TOF spectrum with the long flight path is expected to be more resolved than the TOF spectrum with short flight path. The increased width of the FWHM for the longer flight path clearly indicates that the TOF distributions have a temporal width. This confirms that the width in the TOF signal is due to an energy distribution with some resolution error. This is significant because it asserts that we should see a broadening of the TOF signal if the TOF distribution were to vary significantly due to surface conditions.

Although the resolution was poorer for the short flight path of d = 8.3 cm, the signal



Figure 4.12: Time-of-flight spectra of 20 L  $CH_3I/Cu(110)$ -I. In one TOF spectrum the flight path d is 16 cm and in the other d is 8.3 cm. The width of the signal is largely due to the energy distribution of particles desorbing from the sample, however, the resolution of the detector also affects this width.

was larger. This is the reason that the short flight path of 8.3 cm was used in all other TOF spectra.

## 4.4.2 Characterizing the energy transfer mechanisms and dissociation

TOF ( $\lambda = 337 \text{ nm}$ ) spectra for various coverages of CH<sub>3</sub>I adsorbed on Cu(110)-I are shown in figure 4.13. The yield of  $CH_3$  fragments from the surface depends on the  $CH_3$  coverage on the Cu(110)-I sample. (Only neutral particles can enter the QMS; they are ionized after they enter the ionizer region.)  $CH_3^+$  fragments are not observed above the background counts for doses less than 9 L, which from TPD experiments is 1 ML. For coverages greater than 1 ML, there is a  $CH_3^+$  signal and it is bimodal. The signal maximizes when the second layer is complete at a 20 L dose but decreases rapidly for higher coverages. The distinct shape of the two peaks in the TOF spectra remains consistent from low coverage to high coverage. The TOF signal does not broaden due to high coverage, which indicates that  $CH_3^+$  originate from the top layer only.  $CH_3^+$  originating as a result of desorption from deeper layers would undergo scattering with overlayer molecules, which would broaden the energy distribution and spectra at higher coverages. Methyl iodide molecules are effectively prevented from dissociating in buried layers. This effect is referred to as caging in the literature. Caging of  $CH_3I$  has been observed in  $CH_3I$  dissociation in rare gas matrices [4]. In a TOF study of  $CH_3I$  on Ag(111) at  $\lambda = 248$  nm all  $CH_3$  fragments from surface dissociation were attributed to the uppermost layer with the underlayers caged and prevented from dissociating [19].

We looked for particles such as  $CH_2^+$ ,  $CH_4^+$ ,  $C_2H_4^+$ ,  $C_2H_6^+$  in the TOF analyzer as a result of neutral desorption from the  $CH_3I/Cu(110)$ -I system. We saw no evidence for them at any coverage. Since none of these particles appeared to be present, the  $CH_3^+$  signal in the TOF spectra could only come from  $CH_3$  fragments from surface dissociation or from molecularly desorbed  $CH_3I$ .

In figure 4.14 the  $CH_3^+$  yields in the TOF spectra of figure 4.13 have been summed and plotted as a function of dose. The total counts in I and I<sup>\*</sup> peaks were summed and plotted as a function of dose. The  $CH_3^+$  signal clearly begins when the coverage is increased past 1 ML, reaches a maximum on completion of the 2 ML, and then rapidly decreases for higher coverages. The distribution of the yield as a function of coverage is asymmetrical. The counts increase much faster as the coverage is increased to 20 L then they fall off after the 20 L dose is reached.

In order to assist in the determination of whether the TOF signal results from dissociated  $CH_3$  fragments or from desorbed  $CH_3$  I the significant times for figure 4.15 were tabulated. Table 4.1 lists the significant times (with electronic delay time removed) and kinetic energies that correspond to the A,B,C,... times in the TOF spectrum of figure 4.15. The significant times are the onset , the peak(s), and the end of a signal.

In figure 4.15 the peaks at times B and D correspond to arrival times  $21\mu s$  and  $42 \mu s$ . From table 4.2, the energies of methyl fragments arriving at these times are 1.2 eV for the fast peak and 0.3 eV for the slow peak. These values are the same, with somewhat more error, as calculated for the gas-phase methyl iodide. Recall that methyl fragments were calculated to have energies of 1.15 eV and 0.31 eV for dissociation of methyl iodide in the I and I\* dissociation pathways at 337 nm for v = 0 quanta of umbrella vibrations.

From the energetics in table 4.2, particles which arrive from the first fast peak distribution between times A and C must be  $CH_3$  fragments from intra-adsorbate surface dissociation. Molecules distributed about the peak time of  $21\mu s$  would have a peak energy



Time of Flight



Significant Point	$Time(\mu s)$	$E_{CH_3}$ (eV)	$E_{CH_{3}I}$ (eV)
A	12	3.7	35.2
В	21	1.2	11.5
С	28	0.7	6.5
D	42	0.3	2.9
E	106	0.05	0.5

Table 4.2: Significant times on the TOF spectrum for  $CH_3I/Cu(110)$ -I in figure 4.15. The energies of  $CH_3$  fragments and  $CH_3I$  molecules corresponding to those times are also calculated from  $E = \frac{1}{2}mv^2$ .



Figure 4.14: The total counts in I and I<sup>\*</sup> peaks were summed and plotted as a function of dose. The  $CH_3^+$  signal begins when the coverage is increased past 1 ML, reaches a maximum on completion of the 2 ML, and then rapidly decreases for higher coverages.



Figure 4.15: Time-of-flight spectrum of  $CH_3I/Cu(110)$ -I at a dose of 20 L

of 11.5 eV and a minimum of 6.5 eV. This is much larger than the 3.7 eV expected to be available in the single-photon processes believed to be occurring at the light intensities we are using. The intra-adsorbate dissociation that give rise to the  $CH_3$  fragments must also occur as a result of direct energy transfers. Fragments from the CT mechanism can arrive as early as fragments from the direct mechanism, however, the charge transfer mechanism cannot explain the origin of a distribution about 1.2 eV in figure 4.15. A comparison can be made to the TOF spectra of  $CH_3Br$  on clean copper. In figure 4.10 TOF spectra of a monolayer of  $CH_3Br/Cu(110)$  system resulted from a fast and a slow distribution; the fast distribution is assigned to hot electron DEA causing intra-adsorbate dissociation. The peak in the spectra from the fast distribution is not sharp and distinct like the peaks in figure 4.15. Sharp TOF peaks arise because of a very narrow energy distribution, which are not characteristic of charge transfer processes. Therefore the first peak is assigned to direct energy transfers from intra-adsorbate dissociation.

From the table 4.2, the second peak in figure 4.15 centered at a time of 42  $\mu s$  seconds can have energy of 0.3 eV for  $CH_3$  fragments or 2.9 eV for  $CH_3$ I molecules, both within the 3.7 eV available. However the evidence is against molecules contributing to the peak. CT is the most likely mechanism to cause molecular desorption. Electron attachment resonances to  $CH_3$ I in the gas-phase are most significant at energies below 0.5 eV. It is doubtful that the CT mechanism would cause molecular desorption at 2.9 eV. Molecular desorption also results in molecules preferentially leaving perpendicular to the surface whereas dissociation of the C-I bond results in the  $CH_3$  fragment having a trajectory in the direction of the dipole moment before dissociation.

Spectra of  $CH_3$  yields as a function of angle, figure 4.16, indicate that the preferred dissociation angle is not perpendicular to the surface. (See the angular yields section.) Since methyl iodide dissociation occurs by axial recoil, where the C-I bond dissociation occurs on a much faster timescale than the rotational motion of the  $CH_3$ I molecule, the preferred desorption angle at 20<sup>0</sup> in the [110] azimuth is highly indicative of the molecules tilted orientation on the surface and C-I bond dissociation. Therefore the second peak is assigned to  $CH_3$  fragments from dissociation of the C-I bond.

The energetics of the  $CH_3$  fragments in the second peak indicate the possibility of a direct photodissociation mechanism and/or a charge transfer mechanism. The translation energy of 0.3 eV is consistent with direct processes in the gas-phase for 337.1 nm photons. In addition, charge transfer processes for methyl iodide in the gas-phase were calculated to give rise to  $0.7 \text{ eV} CH_3$  fragments, also near the 0.3 eV peak energy. Strong evidence against a charge transfer mechanism contributing is in figure 4.11, the TOF spectrum of  $CH_3Br$  on Cu(110)-I. There is no  $CH_3$  signal above the background in this system; this is different than  $CH_3Br$  on clean Cu(110) in figure 4.10. Photolysis of  $CH_3Br$  on Cu(110) indicates a charge transfer mechanism where hot electrons from the substrate attach to the CH<sub>3</sub>Br overlayers. CH<sub>3</sub>Br is very sensitive to electrons in the gas-phase and dissociates readily for attaching electrons near 0 eV as does  $CH_3I$ . The lack of signal in the  $CH_3Br/Cu(110)$ -I system indicated that Cu-I on the surface acts as a surface barrier, as evidenced by the increased workfunction ( $\Delta \Phi = 1.2 \ eV$ ), to the photoelectric process that produces hot electrons. CuI is typically referred to as a semi-conductor surface which does not transmit electrons as readily as a clean copper surface. Therefore hot substrate electrons are likely unavailable in the  $CH_3I/Cu(110)$ -I system also.

Other evidence against a charge transfer mechanism operating in the  $CH_3I/Cu(110)$ -I system is in figure 4.13. The TOF spectra of  $CH_3I/Cu(110)$ -I as a function of coverage show that the shape and relative sizes of the two  $CH_3^+$  signal peaks in each spectrum remains consistent as the dose is varied. This is contrary to what is expected to occur when a charge transfer mechanism is operating. As adsorbate layers increase, it is more difficult for electrons to be transmitted through the layers and the numbers transmitted should decrease. If charge transfer were contributing to the intra-adsorbate dissociation, the decrease in available electrons would affect the yield from dissociation. If two distinct mechanisms were operating in the peaks, it is likely that their relative sizes would differ as the dose is increased. Cross-sections for molecules dissociating due to the charge transfer mechanism would have a dependence on the thickness of the adsorbate [6]. Additionally the shape of the second peak is not consistent with other observations of methyl fragments arising because of charge transfer mechanisms. Typically the  $CH_3$  fragments from charge transfer processes arrives in much broader distributions as for  $CH_3Br$  on clean Cu(110). Therefore the second peak of the  $CH_3I/Cu(110)$ -I system is also assigned to intra-adsorbate dissociation resulting from direct photodissociation.

#### 4.4.3 Angular Yields

The angular yields TOF experiment that we do here is similar to a technique known as electron stimulated desorption ion angular distributions. ESDIAD is a technique which has been used to determine molecular orientations on surfaces. A high energy electron beam  $(\sim 100 \ eV)$  directed onto a surface induces dissociation of adsorbates. Ions resulting from dissociation are detected in angle resolved experiments. As long as the dissociation is along the bond that is breaking [8]. If the ions produced by dissociation have a high probability of desorption, then the angular yield of ions will be roughly proportional to the adsorbate bond orientations. If the dissociation do not have high probability of desorption, then a significant number of ions are undergoing collisions in the adsorbate layers with the likely result of changing surface chemistry. In that case the angular yield cannot be a reliable indication of the bond orientations prior to the experiment.

We can interpret our neutral angular yields experiments in a similar fashion. We know that dissociation is primarily taking place in the exposed top layer, since the CH<sub>3</sub> fragment signal shows little evidence of inelastic collisions. The workfunctions for this system also indicated a preference for the iodine end of the molecule to be closer to the surface. The signal in the angular yields experiment in figure 4.16 is significant for angles less than 40<sup>o</sup>. Therefore desorption of CH<sub>3</sub> fragments are very likely to follow dissociation. Dissociation of the CH<sub>3</sub>I molecule occurs on a faster timescale than molecular rotation, therefore the yield indicates the direction of the C-I bond orientation prior to dissociation. CH<sub>3</sub>I dissociation occurs in 65fs whereas the molecular rotational period is  $\sim 3 \times 10^{-12}$ s [16].

Figure 4.16 shows the TOF yield of  $CH_3I$  on Cu(110)-I as a function of angle in two azimuths. Orientational ordering is indicated by the peaks in the angular yields. In the  $[1\bar{1}0]$ azimuth the yield of  $CH_3$  has a significant peak when the sample angle is  $20^{\circ}$ . In the [001]azimuth the yields are greatest at with the sample angle is at  $0^{\circ}$ . The [001] azimuth dependencies indicates that the molecules are preferentially normal in this orientation although the orientational ordering in this azimuth is less pronounced than in the  $[1\bar{1}0]$  azimuth. The  $[1\bar{1}0]$  azimuthal dependencies indicate that there is a pronounced preference for the  $CH_3I$ molecular dipole to be tilted at  $20^{\circ}$  off surface normal in the direction of the [110] rows on the surface.

Interestingly enough, the bond tilt of  $20^{\circ}$  on the surface is close to the bond tilt found in solid CH<sub>3</sub>*I*.(See figure 3.14) In the solid, the molecules C-I bonds orient in an alternating up and down structure. RPS experiments indicated that in the second layer, the CH<sub>3</sub>*I* molecules orientate preferentially with the I end down. Since there are no yields for less than 1 ML we do not have direct evidence that the molecules are tilted in the first layer. However it is possible that preferential tilting in the first layer is responsible for preferential tilting in overlayers.

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Figure 4.16: Angular experiments in the [110] and [001] azimuth

Parameter	Description
n	number of peaks
B	Background counts
$A_i$	Amplitude
v	velocity of a fragment as a function of time t
$T_i$	effective temperature parameter
$v_{0I}$	streaming velocity parameter for improving the fit

Table 4.3: Description of the parameters for equation 4.11

#### 4.4.4 Altered photodissociation dynamics

Evidence for altered photodissociation dynamics are found in the  $\phi^*$  branching ratio. The two fast peaks are an representation of the distribution of CH<sub>3</sub> fragments from dissociation in the I and  $I^*$  pathways. It is approximate because there is resolution error from the TOF apparatus. By separating the distributions and counting the amount of CH<sub>3</sub> fragments in each peak we can infer the relative yield from the I and  $I^*$  pathways. The peaks in the TOF spectra as a function of dose were deconvolved using the following fitting function[6]:

$$F(t) = B + \sum_{i=1}^{n} A_i \exp\left[\frac{-m(v - v_{0i})^2}{2kT_i}\right] t^{-4}$$
(4.11)

Each of the variables in the function is defined in table 4.3. The maximum summation index n is the number of peaks in the TOF spectra. This fitting function is based on a variation of the Boltzmann function [6, 46]. There is no physical basis for why the peaks would be fit by a modified Boltzmann distribution, it just happens that the function fits well to the spectra. This allows a good estimate of the yield in each peak. An example of the fit to a TOF spectrum at 20 L is shown in figure 4.17.

After the peaks were deconvolved and the counts in the I and  $I^*$  channels were summed, the counts were multiplied by  $\frac{1}{t}$ , where t is the peak time. By using the fitting function to approximate the counts in each peak, the relative yield of the  $\phi^* = \frac{N^*}{N^*+N}$  (N is the measured counts in each channel) branching ratio is plotted as a function of coverage in figure 4.18 [6]. It is found that  $\phi^*$  is close to 0.66 for all coverages [6]. The  $\phi^*$  value is not as reliable at high coverage since TOF yields decrease rapidly as the coverage is increased. However, the  $\phi^*$  branching ratio is clearly larger at all coverages than the gas-phase value at 333 nm where  $\phi^* = 0.1$ . The  $I^*$  excited state is more active in the surface experiments and therefore, the dynamics of CH<sub>3</sub>I on Cu(110)-I are perturbed in all layers as compared to the gas-phase CH<sub>3</sub>I in the long  $\lambda$  tail of the A band [6].

Further evidence for altered photodissociation dynamics is found in the depletion yields as a function of total photons. Depletion yields as a function of total photons are done by taking successive TOF spectra on the same dose. The logarithm of the signal S is plotted as a function of total photons  $\theta$ . The relationship between the signal S in the TOF spectra and the total photons  $\theta$  on the surface system is investigated to see if it fits to equation 2.15 ie



Figure 4.17: Example fit to a TOF distribution  $CH_3I/Cu(110)$ -I. Graph is from Johnson and Jensen [6].



Figure 4.18:  $\phi^*$  branching ratios from the fits to the distributions in the TOFs on CH<sub>3</sub>I/Cu(110)-I as a function of dose. The dashed line is the  $\phi^* = 0.1$  branching ratio for gas-phase CH<sub>3</sub>I at 333nm. Graph is from Johnson and Jensen [6].

$$ln(S) = constant - \sigma\theta \tag{4.12}$$

The 2 ML coverage seemed to be most significant since at this coverage the yields were largest. Figure 4.19 shows a graph of the photodepletion of 2 ML CH<sub>3</sub>I on Cu(110)-I on semi-logarithmic scale. Over the range of photons put onto the surface, the graph is generally linear and therefore it is likely that equation 2.15 can be considered valid. From the slope of this graph and others like it, the cross-section was estimated to be  $(1.5\pm0.5)\times10^{-19}cm^2$ . The gas phase cross-section of  $CH_3I$  at the same wavelength is  $2\times10^{-21}cm^2$ , therefore the surface cross-section is larger by a factor of ~ 100.

The enhanced cross-section cannot be attributed to adsorption of methyl iodide. Donaldson et al. reported that the A-band adsorption spectrum blue shifts in the gas-phase when  $CH_3I$  forms clusters [6, 11]. Increasing the concentration of  $CH_3I$  decreased the probability of adsorption. We know from the yields as a function of coverage experiment that the first layer in the surface system does not dissociate, therefore only the second layer is contributing. It might seem surprising therefore that a single layer of solid  $CH_3I$  has at least 100 times the probability of adsorbing a photon than a gas of  $CH_3I$  molecules in a three-dimensional volume. Gas-phase cross-sections are given in terms of adsorption crosssections rather than dissociation cross-sections that we measure here. Although we measure dissociation cross-sections of  $CH_3I$ , because we work at laser light intensities where only single-photon process are available, we know each dissociation is a result of adsorption of a single photon.

The cross-section determined by measuring the depletion of the signal is the total crosssection for depletion of the molecules on the surface. The total cross-section may be a combination of dissociation processes where some  $CH_3$  desorbs after dissociation and some attaches to the surface after dissociation. Lamont et al. observed that  $CH_3$  attaches to a Cu(111) surface after the  $CH_3Br/Cu(111)$  surface is illuminated with UV light [23]. It is most likely that iodine remains attached to the surface after the  $CH_3I$  molecules dissociate. Iodine was not observed in TOF spectra.

A depletion spectrum at 20 L with larger numbers of photons than in figure 4.19 is shown in figure 4.20. As the number of photons gets large, at  $\approx 12 \times 10^{18}/cm^2$ , the slope of the semilogarithmic graph changes. The slope is measured to be  $5.6 \times 10^{-20} cm^2$ . The change in the slope of graph indicate changes in the surface chemistry due to dissociation and adsorption of byproducts. The change in the slow peak could simply indicate a reduced  $CH_3$ I crosssection for photon capture and dissociation due to changes in the surface chemistry. We must be cautious about accepting this interpretation. The data is showing some non-linear tendencies as the number of photons gets large. Recall that the number of fragments that dissociate  $dN = -N_0 e^{-\sigma\theta} \sigma d\theta$  and that the yield of fragments collected in the detector is S=qdN, where q is a fraction. Reordering effects can change the number of molecules  $N_0$ available for dissociation and also change the fraction q that we collect, by changing the angular distributions, between subsequent TOF spectra. It is quite likely that the yields S at large photon numbers are affected by reordering effects. The slope of the semi-logarithmic graph at large photon numbers is likely not strictly representative of the cross-section.

A semi-logarithmic graph of the yields vs total photons for a 40 L dose of  $CH_3I/Cu(110)$ -I is shown in figure 4.21. Over the range of total photons the graph shows some non-linear tendencies at very low photon numbers. It is quite likely that this is not due to counting error



Figure 4.19: Depletion spectrum for a 20 L dose on  $CH_3I/Cu(110)$ -I



Figure 4.20: Depletion spectrum with a larger number of photons for a 20 L dose on  $\rm CH_3I/Cu(110)\text{-}I$ 



Figure 4.21: Depletion spectrum for a 40 L dose on  $CH_3I/Cu(110)$ -I. The cross-section or slope of the graph changes as the total number of photons increase on the sample.

in the yield but rather to a surface phenomena. The yield as a function of total photons for  $CH_3I$  on the clean Cu(110) surface showed similar non-linearity for low numbers of photons. In figure 4.21, the slope changes from  $20 \times 10^{-20} cm^2$  to  $4.1 \times 10^{-20} cm^2$ , which is a reduction in slope by a factor of 5. Due to the low photons numbers where the yields S rapidly decreased it is quite likely that the number of molecules available to dissociate has rapidly decreased. Since the accumulation of byproduct is small at low photon numbers, a possible explanation is that at a dose of 40 L the coverage of the fourth layer is incomplete leaving the third and possibly second layers exposed. If the exposed layers rapidly deplete and reordering of the surface covers them up the slope  $0.41 \times 10^{-19} cm^2$  may represent the cross-section for the fourth layer. This value is about  $4 \times$  smaller than the cross-section estimate at 20 L. The initial slope of  $20 \times 10^{-20} cm^2$  is possibly the cross-section value for depletion of these sites, since it is within error of the cross-section for 2 ML coverage. It is also quite possible that other surface reordering effects could be responsible for the rapid initial decrease in the yields at the low photon numbers.

## 4.5 Further Discussion

The fact that all layers have a similar branching ratio of  $\phi^* = 0.66$ , is interesting in comparison to the observation that the yields are peaked at 2 ML in the coverage experiments. It is clear from the dose dependency spectra that proximity to the copper surface is somehow responsible for the enhanced yields and large cross-sections. Yields increase when the coverage increases to a complete second layer and then decrease as the coverage increases. The peak in the yields at 2 ML is attributed to the effect of the surface on the potential energy surfaces for intra-adsorbate dissociation. The potential energy surfaces are modified by the presence of the surface. It is apparent that this effect weakens as additional layers are added to the second layer. However the surface effect that causes the  $\phi^* = 0.66$  branching ratio on the surface apparently is not weakened by additional layers. This is further evidence that additional layers do not fully cover the underlayers so that the yield comes from several different layers. In that case the most significant proportion of the yield would come from exposed portions of the second layer, since this layer likely has the largest cross-section.

The large cross-section for dissociation, especially in the second layer, indicates that the excited states have been made more accessible. The difference in energy between the vibrational state of the molecule in the  ${}^{1}A_{1}$  ground state and the excited state must equal the energy of the photon in order for excitation to occur. In order for the excited states to become more accessible the relative positions of the excited state and the ground state well must have changed. One possibility is that the excited state(s) have moved downwards in potential energy towards the  ${}^{1}A_{1}$  ground state. Another possibility is that bond lengthening has resulted in the  ${}^{1}A_{1}$  ground state well widening or moving to the right, which would result in lengthening of the C-I bond. Lengthening of the C-I bond would require substantial changes to the ground state wavefunction, which is not likely to occur in the physisorbed second layer. Therefore the large cross-section is attributed to the repositioning of the excited states.

The repositioning of the excited state(s) is presumably also responsible for the  $\phi^*$  branching ratio being significantly larger than the 0.1 value of the gas-phase CH<sub>3</sub>I at 333 nm. In the gas-phase at 333 nm, only a fraction of the photoexcitation is to the  ${}^{3}Q_{0}$  state, a large proportion of the excitation takes place to  ${}^{3}Q_{1}$  state [13]. In figure 4.6 from Eppink (et al) gas-phase  $CH_{3}I$  excitation to the  ${}^{3}Q_{0}$  state decreases to less than 50 % and the probability of curve crossing increases to 90 % as the wavelength is increased to 340 nm. To account for the  $\phi^{*} \sim 0.66$  value, excitation to the  ${}^{3}Q_{0}$  state likely has increased and likely curvecrossing is less significant. The repositioning of the excited states could have resulted in excitation from the ground state to the dissociative state taking place very near the curve crossing region of the  ${}^{1}Q_{1}$  and the  ${}^{3}Q_{0}$  states. The excitation to the  ${}^{3}Q_{0}$  state in that case either takes place above or below the curve crossing region. If excitation is below the curve crossing region, then the  $\phi^{*}$  branching ratio represents the ratio of molecules excited to the two different states  ${}^{1}Q_{1}$  and the  ${}^{3}Q_{0}$ , which then directly dissociate respectively via the I and  $I^{*}$  channels. However, if excitation is above the curve crossing region to the  ${}^{3}Q_{0}$  state, then we may expect that the relevant factors which affect curve crossing to be significant.

After excitation to the  ${}^{3}Q_{0}$  state, the probability for curve crossing to the  ${}^{1}Q_{1}$  state to form  $CH_{3} + I^{*}$  is approximated by the Landau-Zener(LZ) transition probability P [5, 38]:

$$P = 1 - \Phi^* = 1 - \exp^{\left(-\frac{2\pi(V_{12})^2}{h\nu|\Delta F|}\right)}$$
(4.13)

where  $V_{12}$  is the singlet-triplet coupling between the  ${}^{1}Q_{1}$  and the  ${}^{3}Q_{0}$  states,  $\nu$  is the velocity of the fragment at the curve crossing point, and  $\Delta F$  is the difference in slopes of the two potential energy surfaces at the curve crossing point.

A first approximation has  $V_{12}$  proportional to the spin-orbit coupling in iodine [38]. <sup>5</sup> The velocity v of the  $CH_3$  fragments in our surface study on Cu(110)-I at  $\lambda = 337$  nm is very similar to the velocity of the  $CH_3$  fragments in the gas-phase at 333 nm, where the curve crossing probability  ${}^1Q_1$  and the  ${}^3Q_0$  states to produce  $CH_3 + I^*$  is P = 1-  $\phi^* = 90\%$ . This leaves two possibilities to account for a lower transition probability, a reduction of the  $V_{12}^2$  term on the surface or an increase in the  $\Delta F$  value. A likely choice is an increase in the  $\Delta F$  value due to a repositioning of the excited states, since in order for the cross-section to have dramatically increased  $100 \times$  as it has, the excited states have likely repositioned in order that excitation from the ground state is more probable.

<sup>&</sup>lt;sup>5</sup>One of the reasons curve crossing is much less significant in CH<sub>3</sub>Br is the spin orbit coupling in Br is about half that in I; the ratio of the spin orbit couplings of Br and Iodine is 0.456/0.942 [38]. As a result the  $V_{12}^2$  term is smaller in CH<sub>3</sub>Br curve crossing by a factor of 4.3.

# 4.6 Surface Photolysis of $CH_3I/Cu(110)$

#### 4.6.1 Coverage experiments

TOF spectra at  $\lambda = 337.1$  nm as a function of coverage for  $CH_3I$  on clean Cu(110) are shown in figure 4.22. The TOF spectra show a  $CH_3^+$  signal from a fast distribution for times less than  $120\mu s$  and from a slow broad distribution for times greater than  $120\mu s$ . There is  $CH_3^+$  signal from a fast and a slow distribution at all coverages. The  $CH_3^+$  signal from the fast distribution shows a single peak for coverages less than 9.0 L and is bimodal for coverages greater than 9.0 L (1 ML by TPD measurements for this system). The  $CH_3^+$ signal maximizes from both distributions as the coverage is increased to 20 L. At 20 L the second layer is complete. <sup>6</sup> As the coverage is increased past 20 L, the  $CH_3^+$  signal from both the fast and the slow distributions decreases.

Particles such as  $CH_2^+$ ,  $CH_4^+$ ,  $C_2H_4^+$ ,  $C_2H_6^+$  were looked for in the  $\lambda = 337.1$  nm TOF experiments with  $CH_3I$  on clean Cu(110) but no significant signals were found. Therefore the  $CH_3^+$  signal in figure 4.22 could only come from  $CH_3$  fragments produced from C-I bond dissociation on the surface or from molecularly desorbed  $CH_3I$ .

The shape of the  $CH_3^+$  signal from the fast distribution varies with coverage. For coverages less than 1 ML, the  $CH_3^+$  signal is broad and featureless. As the coverage is increased, the  $CH_3^+$  signal becomes sharply peaked. There are significant differences between these and the  $CH_3^+$  signal from the  $CH_3I/Cu(110)$ -I in figure 4.13. The fast  $CH_3^+$  signal in figure 4.22 is broader and shorter. The peak times do not have as many counts as those in figure 4.13. This observation is indicative that there are significant differences between the two systems. From the outset orientational ordering, which results in larger yields, is likely less significant in this system. There is no evidence in the fast TOF signal of inelastic collisions since the width of the signal remains consistent from low coverage to high coverage. Therefore the  $CH_3$  fragment signal in the fast peak is the result of photodissociation in the topmost layer of  $CH_3I$ . This was also the result of  $CH_3I/Cu(110)$ -I. Therefore caging is significant for buried layers in both systems.

We hypothesized that in the  $CH_3I/Cu(110)$ -I system the presence of iodine atoms on the copper surface was preventing the formation of hot photoelectrons having the correct energy for DEA. We know that when photoelectrons are available,  $CH_3I$  has a large cross-section for their capture, and since we see production of  $CH_3^+$  from the fast distribution for less than 1 ML we know that CT-PDIS is probably operating in this system. The position of the  $CH_3I$  PES for CT-PDIS (see figure 4.7) make this mechanism more competitive with quenching than the direct photodissociation mechanism.

The  $CH_3^+$  counts from figure 4.22 are summed and plotted as function of coverage. The  $CH_3^+$  counts are summed as a function of times less than  $120\mu s$  and also as a function of times greater than  $120\mu s$ . The results are shown in figure 4.23. The  $CH_3^+$  counts from the fast distribution are produced with varying efficiency at low coverage. The probability of dissociation is  $\sim 3 \times$  smaller at 0-2 L coverage than for coverages in the completed 1 ML at 9.0 L [6]. In the TPD data of this system in figure 3.8 we observed there was a desorption peak at 160 K for less than 3 L, which is indicative of molecules attached at higher binding energy sites. Increasing the dose resulted in observing two peaks, one at 160 K and one

<sup>&</sup>lt;sup>6</sup>Due to the cold surface (~ 95K) the sticking probability for each layer is likely similar and close to 1.



Figure 4.22: Various TOF spectra of  $CH_3I/Cu(110)$ . From TPD measurements, a dose of 9.0 L is a monolayer of coverage on the Cu(110) surface.

at 140 K; the 140 K peak is indicative of the reduced binding energy sites for higher doses in the first layer. It is quite likely that the reduced photodissociation efficiency observed in the 0-2 L dosages is the result of higher binding energy sites observed at these doses and a more rapid quenching mechanism for these molecules [6]. These sites are quite likely more efficiently quenched. The orientation of the molecules on the surface at low coverage may be different than at higher coverages. This could either inhibit dissociation by making quenching more efficient, or reduce the probability for detection of the dissociation. If the  $CH_3$ I molecule is in a lying down orientation on the surface, dissociation could result in the  $CH_3$  fragment attaching to the surface, or escaping at a large enough angle from normal that it is not detected.

At completion of the second layer, production of  $CH_3^+$  fragments maximized in both the fast and the slow distributions. (See figure 4.23) The counts from the slow distribution were slower to fall off than the faster distribution. It is interesting that  $CH_3^+$  fragments maximized at completion of the second layer for  $CH_3$ I on both the clean Cu(110) and the Cu(110)-I surfaces. The  $\lambda = 248nm$  photolysis of  $CH_3$ I on Ag(111) showed that  $CH_3$ fragment production saturated when the coverage was 3 layers[19]. In that study  $CH_3$ fragment production began when the coverage was greater than 1 ML and increased when the coverage was increased to 3 layers, after which the  $CH_3$  yield was constant [19]. For lack of better understanding, the enhanced yields in the second layer on Cu(110) and Cu(110)-I are simply attributed to changes in the excited state potential energy surfaces.

High resolution scans of the  $\lambda = 337.1 nm$  TOF of  $CH_3I$  on clean Cu(110) are shown in figure 4.24. The scans demonstrate that for a coverage of 7 L, which is an incomplete first layer, the CH<sub>3</sub><sup>+</sup> signal from the fast distribution (time-of-flight less than  $120\mu s$ ) is not sharply peaked. The signal peak is centered about 64  $\mu$ s, which corresponds to a  $CH_3$  fragment energy of 0.13 eV. The lack of sharp features and the energetics are consistent with  $CH_3$ fragments produced from CT-PDIS from dissociative resonances of gas-phase  $CH_3I$ . In the gas-phase,  $CH_3I$  has dissociative attachment resonances for electrons of energy less than 0.15 eV and produces  $CH_3$  fragments from CT-PDIS of energy less than 0.7 eV.

In figure 4.24, the  $CH_3^+$  signal from the fast distribution at 20 L, where the second layer is complete, is bimodal, asymmetric and sharply peaked. Significant points in the  $CH_3ICu(110)$  system are marked with the letters A,B,C... in figure 4.25. The times that correspond to these points are tabulated in table 4.4 and energies are calculated for  $CH_3$ fragments and  $CH_3I$  molecules arriving at these times in the table. The sharp peaks in the TOF signal that correspond to points B and D have times 22  $\mu s$  and at 42  $\mu s$  and result from particles arriving in a narrow energy distribution.  $CH_3$  fragments arriving at these times would have energies of 1.1 eV and 0.25 eV, which are very similar to the  $CH_3$  fragment energies of 1.15 eV and 0.31 eV in the I and  $I^*$  channels for direct neutral dissociation of gas-phase  $CH_3I$ . The asymmetry of the bimodal signal at 20 L coverage indicates that there are also particles arriving in a broad energy distribution. It is likely that this broad distribution is  $CH_3$  fragments from CT-PDIS. In contrast to this study  $CH_3I$  adsorbed on Ag(111) did not show  $CH_3$  yield at 248 nm for less than 1 ML [19]. For low coverages above 1 ML the  $CH_3$  yields were attributed to a mixture of CT-PDIS and direct photodissociation. This is evidence that  $CH_3I$  on Cu(110) is less strongly quenched than  $CH_3I$  on Ag(111), at least in the first layer. This is consistent with the observation of the higher TPD desorption temperatures for  $CH_3I$  on Ag(111) and the characterization of  $CH_3I$  as chemisorbed on


Figure 4.23: The slow and fast peak counts in the TOF spectra of figure 4.22 are summed and plotted as a function of dose.

that surface [44, 19]. The first layer of  $CH_3I$  on Ag(111) desorbs at ~ 190K as compared to 140 K for  $CH_3I$  on Cu(110)[44]. Multilayers on both surfaces desorb at similar temperatures ~ 136K [44].

Further understanding of the  $\lambda = 337.1$  nm TOF dynamics of the  $CH_3I/Cu(110)$ system can be achieved by comparison to the TOF spectra of  $CH_3Br/Cu(110)$  and of  $CH_3I/Cu(110)$ -I. The  $\lambda = 337.1nm$  TOF of  $CH_3Br$  on clean Cu(110) as a function of coverage was shown in figure 4.8. The sharp bimodal  $CH_3^+$  signal, indicative of direct photodissociation processes and evident in the  $CH_3I/Cu(110)$  and the  $CH_3I/Cu(110)$ -I systems for coverages greater than 1 ML, do not appear at any coverage for  $CH_3Br/Cu(110)$ . The dissociation of the adsorbed  $CH_3Br$  was attributed to charge transfer processes. The  $CH_3^+$ signal was the result of intra-adsorbate dissociation of adsorbed  $CH_3Br$  producing a fast distribution for times less than  $110\mu s$ . The  $CH_3^+$  signal at times greater than  $110\mu s$  were assigned to molecular desorption of  $CH_3Br$  resulting from charge transfer processes. Charge transfer processes can result in desorption via the Antoniewicz mechanism. (See the first



Figure 4.24: High Resolution Scans on  $CH_3I/Cu(110)$  at 7 L and 20 L. The counts in these scans were summed in  $1\mu s$  MCS-TOF bins. The scans demonstrate that for less than 1 ML the  $CH_3$ + signal from the fast distribution is not sharply peaked. At 2 ML however the  $CH_3$ + signal from the fast distribution is bimodal, asymmetrical and sharply peaked.

Significant Point	$Time(\mu s)$	$E_{CH_3}$ (eV)	$E_{CH_3I}$ (eV)
Α	12	3.7	35.2
В	22	1.1	10.5
C	30	0.59	5.6
D	42	0.30	2.9
E	113	0.04	0.4
F	300	0.006	0.056
G	800	0.0008	0.008

Table 4.4: Significant times on the TOF spectrum for  $CH_3I/Cu(110)$  in figure 4.25. The energies of  $CH_3$  (15 amu) fragments and  $CH_3I$  (127amu) molecules corresponding to those times are calculated with  $E = \frac{1}{2}mv^2$ .



Figure 4.25: Time-of-flight spectrum for 20 L of  $CH_3I$  on Cu(110).

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The similarities of the  $CH_3I/Cu(110)$  spectra to the  $CH_3Br/Cu(110)$  spectra indicate that the slow distribution for times greater than  $120\mu s$  in the  $\lambda = 337.1$  nm TOF spectra of the  $CH_3I/Cu(110)$  system is likely the result of molecular desorption from charge transfer processes. The clean Cu(110) workfunction is 4.48 eV [26] and on the CH<sub>3</sub>I dosed surface the maximum workfunction decrease is  $\Delta \Phi = -0.53 \ eV$ , therefore the  $CH_3I/Cu(110)$ workfunction exceeds the photon energy by 0.27 eV [6]. The most likely desorption and dissociation channels for the CT-PDIS mechanism will be neutral, since photoelectron attachment resonances to gas-phase  $CH_{3}I$  is far below the photon energy at 0.15 eV [33]. It is unlikely that direct neutral photoabsorption is causing molecular desorption in the  $CH_3I/Cu(110)$  system. The absence of molecular desorption in the  $\lambda = 337.1 nm$  TOFs of  $CH_3I/Cu(110)$ -I indicates that molecular desorption due to direct photoabsorption is an ineffective process on this system and likely for  $CH_3I/Cu(110)$  also. The molecular desorption counts are for all coverages much larger than the intra-adsorbate dissociation counts in the TOF spectra, however, due to detection efficiencies this is not a reliable indication of the numbers of fragments in each distribution. Normalizing the spectra by  $\frac{1}{t}$ , where t is time, would significantly enhance the faster intra-adsorbate dissociation yields. There is also an additional factor to consider. The ionization efficiencies of  $CH_3I$  molecules and  $CH_3$ fragments are different and have not been quantified.

The yields from CT-PDIS are most significant in the first and second layers. The decrease in the yield of the fast peak after the second layer is complete indicates that CT-PDIS and direct photodissociation are decreasing. The percentage of the yield attributed to CT-PDIS is about the same in all layers. (See the section on  $I^*$  Branching Ratio and CT-PDIS.) The yield of molecular desorption however are nearly as large in the third layer as they are in the second. The yields for the  $\lambda = 337.1 nm$  CH<sub>3</sub>Br/Cu(110) in figure 4.9 as a function of coverage showed that molecular desorption also remains large at coverages for where the intra-adsorbate dissociation, due to CT-PDIS, are decreasing. The photodynamics on this system is entirely attribution to charge transfer processes.

The most likely desorption process to explain these effects in both  $CH_3I$  and  $CH_3Br$ on Cu(110) is photoejection. Photoejection is a mechanism where an overlayer molecule is ejected from the surface by caged ionic molecules in underlayers. When a photoelectron attaches to a  $CH_3X(X=I \text{ or } X=Br)$  molecule, the C-X bond distance increases and at the same time the negatively charged molecule attracts an overlayer molecule. Dissociation is halted in the caged molecule when the electronic excitation is quenched, however if the translation energy of the overlayer  $CH_3X$  molecule is sufficient it can overcome the van der Waals forces that bind it to the surface. In the  $CH_3I/Cu(110)$ -I system hot photoelectrons are unavailable so ionic photoejection is not possible. However there are also neutral photoejection processes where overlayer molecules are ejected as a result of excited underlayer molecules. The fact that molecular desorption are not evident in the  $CH_3I/Cu(110)$ -I system indicates that a neutral photoejection process is not as significant.

### 4.6.2 Angular Dependency Experiments

Figures 4.26 and 4.27 show the results of the angular experiments at a coverage of 20L in the  $[1\bar{1}0]$  azimuth and the [001] azimuth. The angular dependency was similar for all coverages. Angular experiments show that the TOF  $CH_3^+$  signal is maximized by having the surface normal at  $0^0$  to the detector in both the  $[1\bar{1}0]$  azimuth and the [001] azimuth.

Both CT-PDIS and direct photodissociation are fast processes, faster than molecular rotation, so the direction of the dissociating  $CH_3$  fragment is indicative of the instantaneous bond direction before dissociation. The fact that the yields are largest with the surface normal at  $0^0$  to the detector in both azimuths indicates that the molecular C-I bond axis are predominantly normal to the surface and therefore intra-adsorbate dissociation and molecular desorption are both preferentially normal to the surface. The distribution of bond directions is quite broad in this system however. In the  $CH_3I/Cu(110)$ -I system the largest angle where significant yield was obtained in both azimuths was  $40^0$  off-normal. (See figure 4.16.) In contrast the  $CH_3I/Cu(110)$  system showed significant yields at larger angles than  $40^0$  in both the azimuths for both the fast and the slow peaks. This larger distribution of bond angles can be explained by greater disorder in this system than for the  $CH_3I/Cu(110)$ -I system, where bonds showed a preference for tilting at  $20^0$  in the  $[1\overline{10}]$ azimuth. More disorder in this system also explains the smaller number of counts in the TOF spectra.

#### 4.6.3 I<sup>\*</sup> Branching Ratio and CT-PDIS

The fitting function, equation 4.11, that was used to deconvolve the peaks in the  $CH_3I/Cu(110)$ -I system, was also used to deconvolve the three dissociation channels in the fast distribution



Figure 4.26: Fast Peak Counts as a function of Angle for 20L on  $CH_3I/Cu(110)$ 



Figure 4.27: Slow Peaks Counts as a function of Angle for 20L on  $CH_3I/Cu(110)$ 

in the  $CH_3I/Cu(110)$  system. The counts in the I, the  $I^*$ , and the CT-PDIS channels were separated using the fitting function for times less than  $110\mu$ s. The fitting function did not produce good fits to the slow photodesorption peak. An example of a fit is shown in figure 4.28. Using the counts in the I and  $I^*$  channels, the  $\phi^*$  ratio of was estimated. The values for  $\phi^*$  were found to be in the range 0.4-0.6, but with more uncertainty than for  $CH_3I/Cu(110)$ -I [6]. As a result it is not clear that the  $\phi^*$  ratio for neutral dissociation of  $CH_3I$  on clean Cu(110) is different than on Cu(110)-I, although it is clear that the  $\phi^*$  value is larger than the 0.1 value at 333 nm in the gas-phase [6]. Large values for  $\phi^*$  have also been found for  $CH_3I$  on the metal surface Ag(111) [19]. The  $\phi^*$  branching ratio for the  $\lambda = 248nm$  of  $CH_3I$  on Ag(111) was found to vary continuously with coverage [19]. At high coverage above 10 layers  $\phi^* = 0.40$  and  $\phi^*$  was larger for lower coverages [19]. The large  $\phi^*$ values in layers near the surface for  $CH_3I$  on Cu(110), Cu(110)-I and Ag(111) suggest an addition possibility that the  $I^*$  channel is less efficiently quenched than the I channel.

Figure 4.29 shows the estimated CT-PDIS yield in the fast peak as a function of coverage. The fits indicate that the proportional yield of CT-PDIS is significant and varied with coverage from 20 to 60 % [6]. This graph is interesting because the CT-PDIS percentage of the yield apparently does not decrease as the dose is increased. This is contrary to what we would expect the top adsorbate layer completely covers the underlayers. The decrease of hot electrons through increasing layers of adsorbed molecules has been noted in previous studies [37]. We would expect that as additional layers are added, that charge transfer would become a less effective process and more of the signal would result from direct photodissociation. In figure 4.29, the efficiency of CT-PDIS, in comparison to direct photodissociation, appears to be as high in 1 ML as it is in  $\sim 4$  layers (40 L). Due to the large error in the data, this appearance may not be correct. If it is correct this is additional evidence that the top layer does not completely cover the underlayers. In that case the exposed underlayers could continue to dissociate by the charge transfer mechanism.

#### 4.6.4 Cross-section Measurement

The total depletion cross-section of  $CH_3I/Cu(110)$  includes CT-PDIS, neutral photodissociation, and photodesorption of  $CH_3I$ . It also possible that the total cross-section includes processes that cannot be measured, such as methyl fragments bonding to the surface after dissociation. Figures 4.30 to 4.35 show the logarithm of the depletion measurements as a function of total photons for various coverages. The depletion measurements have been done with respect to the fast distribution of  $CH_3$  fragments and the slow distribution of  $CH_3I$ molecular desorption. The depletion measurements for 9 L and 20 L on a semi-logarithmic scale are generally linear as a function of  $\theta$ , the total photons on the sample. At 9 L the cross-sections as determined from the slope give  $8.2 \times 10^{-20} cm^2$  and  $9.1 \times 10^{-20} cm^2$  for the fast and the slow peaks of the TOF spectra. At 20 L the cross-sections are determined to be  $2.2 \times 10^{-19} cm^2$  and  $2.4 \times 10^{-19} cm^2$  for the fast and the slow peaks. Since the measurements of the molecular desorption and the intra-adsorbate dissociation are done on the same systems, the total cross-sections are similar as they are expected to be. The cross-section determined at 20 L is significantly larger than the gas-phase cross-section at the same wavelength and is also larger than the cross-section for  $CH_3I/Cu(110) - I$ . It is clear that photodissociation is significantly enhanced although it is not clear the enhancement can be attributed to either



Figure 4.28: A example fit to the spectrum of  $CH_3I/Cu(110)$  system using the fitting function, equation 4.11. Graph from Johnson and Jensen [6].



Figure 4.29: CT-PDIS proportion as a function of coverage of the fast peak on the TOFs  $CH_3I/Cu(110)$  system. The estimates were done using the fitting function, equation 4.11. Graph from Johnson and Jensen [6].

charge transfer or to direct neutral photodissociation. We do not have enough information to separate the total cross-section into individual cross-sections.

At 40 L the yields as a function  $\theta$  on a semi-logarithmic scale show rapid decrease in the yields and non-linearity at low photon numbers. This was a typical result for doses over 20 L. A possible explanation of the rapid decrease is that the coverage of the top layer is insufficient to completely cover the underlayers. At 40 L it is possible that the third and possibly second layers have been left somewhat exposed. However the slope is measured to be  $4.80 \times 10^{-19} cm^2$  and  $4.85 \times 10^{-19} cm^2$  respectively from the fast and the slow distributions. This is  $2 \times$  as large as the cross-section determined at 20 L on the same system. It also possible that reordering on the surface is responsible for the rapid depletion. In any event the non-linearity of the graph make estimating the cross-sections from the slope a doubtful process. The average of the slope may have little to do with the cross-section and more to do with site depletion and/or reordering effects.

#### 4.6.5 Further Discussion

The photodesorption of  $CH_3I$  molecules from the  $CH_3I/Cu(110)$  system is attributed to the charge transfer mechanism, since photodesorption of  $CH_3I$  did not occur in the  $CH_3I/Cu(110)$ -I system. Photodesorption due to charge transfer was observed on the  $CH_3Br/Cu(110)$  system also.

The lack of direct PDIS in the first layer of  $CH_3I/Cu(110)$  is likely due to fast quenching of the electronic excitation. CT-PDIS is a faster process than direct neutral photodissociation and is therefore better able to compete with the fast surface quenching. The reason CT-PDIS of  $CH_{3}I$  is a faster process than direct neutral photodissociation was demonstrated by the potential energy surfaces in figure 4.3. Direct neutral photodissociation of ground state  $CH_3I$  results from a Franck-Condon transition to a higher energy dissociative potential energy surface where the C-I bond lengthens. Quenching can result in a transition from the excited state back to the ground state potential well. CT-PDIS also results in a Franck-Condon transition to a negative ion potential energy dissociative state but C-I bond lengthening quickly results in the dissociative state being at a lower potential energy than the neutral ground state [6]. Quenching processes are ineffective at this point. In order for the molecule to return to the ground state, the molecule's kinetic energy would have to be turned into potential energy say as the result of a collision. The overall time for direct dissociation of the  $CH_3I$  molecule is 50 fs, and therefore the neutral/ionic curve crossing is reached in a fraction of the dissociation time. For adsorbed  $CH_3I$  the dielectric properties of the surface result in image charge stabilization that lower the potential energy of the CT-PDIS dissociative curve and therefore make the dissociation process more rapid [6]. Therefore CT-PDIS is more likely than direct photodissociation to be able to compete with quenching and cause dissociation of  $CH_3I$  in direct contact with the metal substrate when the total coverage is less than a single layer. The lack of direct PDIS signal from the first ML support this interpretation. When coverage is greater than a single layer the efficiency of quenching is reduced largely because the propagation of electrons through the adsorbed layers to the surface is less efficient. As a result direct dissociative processes are better able to compete with quenching. Therefore in the second layer of  $CH_3I/Cu(110)$  we see the two characteristic sharp peaks of the direct I and  $I^*$  channel dissociation processes.



Figure 4.30: Yields from the fast distribution as a function of total number of photons for a dose of 9.0 L



Figure 4.31: Yields from the slow distribution as a function of total number of photons for a dose of 9.0 L  $\,$ 



Figure 4.32: Yields from the fast distribution as a function of total number of photons for a dose of 20.0 L



Figure 4.33: Yields from the slow distribution as a function of total number of photons for a dose of 20.0 L



Figure 4.34: Yields from the fast distribution as a function of total number of photons for a dose of 40 L. The non-linearity of this graph is making it difficult to interpret the slope as the cross-section.



Figure 4.35: Yields from the slow distribution as a function of total number of photons for a dose of 40 L. The graph is again non-linear.

## 4.7 Conclusions

The study of the  $CH_3I$  on Cu(110) and Cu(110)-I surfaces has shown some unusual properties. Measurements of the cross-sections show that photodissociation is greatly enhanced in the second layer at  $\lambda = 337$  nm compared to gas-phase studies. On the Cu(110)-I surface the enhancement is solely due to direct neutral photodissociation. On clean Cu(110), the enhancement was a combination of direct photodissociation and of CT-PDIS, where hot electrons tunnel into dissociative states of the adsorbed  $CH_3I$  molecules. The enhancement on this system cannot be attributed to charge transfer or to direct neutral photodissociation since we do not have enough information to separate the total cross-section into individual cross-sections. The presence of CT-PDIS for submonolayer coverage of  $CH_3I$  on clean Cu(110) and the lack of direct photodissociation for submonolayer coverage of  $CH_3I$ on Cu(110)-I indicates that CT-PDIS is a faster dissociation process and better able to compete with quenching.  $CH_3$  yields on both surfaces were found to peak on completion of the second layer and to decrease significantly as the coverages were increased past two layers. The  $\phi^* = N^*/(N + N^*)$  branching ratio was found to be altered at all coverages in both systems from the  $\lambda = 333$  nm gas phase value of  $\phi^* = 0.1$ . This branching ratio indicates more fast  $CH_3$  fragments from dissociation of adsorbed  $CH_3I$  were produced from the  $I^*$  dissociation channel. Adsorption of  $CH_3I$  is structurally different depending on the substrate: Cu(110) or Cu(110)-I.  $CH_3I$  adsorbed on Cu(110)-I is found to have a preference for tilting ~  $20^{\circ}$  off-normal in the [110] azimuth. CH<sub>3</sub>I adsorbed on Cu(110) showed a preference for orientating the C-I bond normal to the surface, although the counts fell off significantly more slowly from this system as the angle of the surface was increased than for the  $CH_3I/Cu(110)$ -I system. The difference is attributed to the greater orientational ordering that occurs on the iodided Cu(110) surface. There was some evidence that overlayer adsorbate layers do not completely cover underlayers. The depletion yield measurements as a function of total photons often showed significant rapid non-linearity at very low photon numbers when the coverage was greater than two layers. It is possible that exposed sites were rapidly depleting. On the iodided surface, the charge transfer portion of the  $CH_{3}I$ dissociation signal was constant as a function of coverage although the error is large. This was additional evidence that the underlayers were left somewhat exposed.

The  $\lambda = 337$  nm photolysis of  $CH_3Br$  on Cu(110) and Cu(110)-I surfaces was used to further understand the  $CH_3I/Cu(110)$  and  $CH_3I/Cu(110)$ -I systems.  $CH_3Br$  on Cu(110) was found to dissociate and desorb by the charge transfer mechanism but  $CH_3Br$  on Cu(110)-I did not dissociate or desorb. The most likely explanation of this effect is that hot electrons are unable to tunnel through a CuI barrier when the photon wavelength is  $\lambda = 337$  nm. The workfunction of Cu(110)-I surface was found to have increased by 1.2 eV as compared to the clean Cu(110) surface. The direct neutral dissociative states of  $CH_3Br$  on the surface are not accessible at this wavelength.

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