INTERACTION BETWEEN ADATOMS ON A POLYCRYSTALLINE TUNGSTEN SURFACE AND A SUPERTHERMAL ATOMIC BEAM OF ALKALI NEUTRALS.

YOU-FONG. HSIEH

University of Windsor

Follow this and additional works at: https://scholar.uwindsor.ca/etd

Recommended Citation
HSIEH, YOU-FONG., "INTERACTION BETWEEN ADATOMS ON A POLYCRYSTALLINE TUNGSTEN SURFACE AND A SUPERTHERMAL ATOMIC BEAM OF ALKALI NEUTRALS." (1979). Electronic Theses and Dissertations. 2468.
https://scholar.uwindsor.ca/etd/2468

This online database contains the full-text of PhD dissertations and Masters’ theses of University of Windsor students from 1954 forward. These documents are made available for personal study and research purposes only, in accordance with the Canadian Copyright Act and the Creative Commons license—CC BY-NC-ND (Attribution, Non-Commercial, No Derivative Works). Under this license, works must always be attributed to the copyright holder (original author), cannot be used for any commercial purposes, and may not be altered. Any other use would require the permission of the copyright holder. Students may inquire about withdrawing their dissertation and/or thesis from this database. For additional inquiries, please contact the repository administrator via email (scholarship@uwindsor.ca) or by telephone at 519-253-3000ext. 3208.
The quality of this microfiche is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us a poor photocopy.

Previously copyrighted materials (journal articles, published tests, etc.) are not filmed.

Reproduction in full or in part of this film is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30. Please read the authorization forms which accompany this thesis.

THIS DISSERTATION HAS BEEN MICROFILMED EXACTLY AS RECEIVED

La qualité de cette microfiche dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de mauvaise qualité.

Les documents qui font déjà l'objet d'un droit d'auteur (articles de revue, examens publiés, etc.) ne sont pas microfilmés.

La reproduction, même partielle, de ce microfilm est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30. Veuillez prendre connaissance des formules d'autorisation qui accompagnent cette thèse.

LA THÈSE A ÉTÉ MICROFILMÉE TELLE QUE NOUS L'AVONS RÉCU
INTERACTION BETWEEN ADATOMS ON A POLYCRYSTALLINE TUNGSTEN SURFACE AND A SUPERTHERMAL ATOMIC BEAM OF ALKALI NEUTRALS

by

You-Fong Hsieh

A Dissertation submitted to the Faculty of Graduate Studies through the Department of Physics in Partial Fulfillment of the requirements for the Degree of Doctor of Philosophy at The University of Windsor

Windsor, Ontario, Canada

1979
TO MY PARENTS
ABSTRACT

A new effect, stimulated surface ionization, was found and studied. A superthermal neutral alkali atomic beam with an energy typically between 20 and 200 eV impinged upon a tungsten surface coated with a thin layer of alkali atoms. This caused previously adsorbed alkali atoms to be surface ionized.

Various negative ion species were released from a surface by the impinging superthermal neutral beam. The quantitative increase of negative ion production by an auxiliary alkali coating beam was investigated.

Evidence was found that the superthermal neutral beam could also give rise to chemical reactions. This effect, believed to be new, is of interest to the physics of catalytic reactions.

A statistical theory has been developed to explain the experimental data. Although still in its beginning it allows to determine the various adsorption levels of the species used as coating material on tungsten, as well as the number of adsorption sites associated with each energy. Estimates can be derived for other surface-adatom parameters.
ACKNOWLEDGEMENT

It is a great pleasure to acknowledge the constant guidance and supervision of Dr. R.K.B. Helbing throughout the entire period of this work.

I would also like to thank Dr. V. Pol, Dr. M. Kick, Dr. C. K. Kwan and Mr. D. Marchand for their help and many useful discussions. The work done by the personnel of the Machine Shop and Electronic Shop at the Department of Physics, University of Windsor is gratefully acknowledged.

Financial support from the National Research Council of Canada, the Petroleum Research Fund, administered by the American Chemical Society, and the University of Windsor are gratefully acknowledged.
TABLE OF CONTENTS

ABSTRACT ........................................................................................................ iii
ACKNOWLEDGEMENTS ...................................................................................... iv
LIST OF FIGURES AND TABLE ........................................................................ viii

CHAPTERS

I. INTRODUCTION TO SURFACE EFFECTS RELATED TO THIS WORK .......................................................... 1
   Surface Crystallography .............................................................. 1
   Clean Surface .................................................................... 4
   Adsorption .......................................................................... 6
   Work Function ................................................................... 10
   Sputtering ........................................................................ 12
   Superthermal Molecular Beam ............................................. 15

II. THE SCOPE OF THIS WORK ........................................................................ 21
   Stimulated Surface Ionization .................................................... 21
   Surface Ionization Detector .................................................... 21
   Universal and Bolometer Detectors ........................................ 22
   SSI Detector ....................................................................... 23
   Negative Ions ..................................................................... 25
   Chemical Reactions on a Surface ............................................ 30

III. STIMULATED SURFACE IONIZATION ......................................................... 35
   Apparatus ........................................................................... 35
      Vacuum System ................................................................. 35
      Primary Beam Source ...................................................... 36
      Thermal Particle Rejector ................................................. 37
      Double Frequency Chopper .................................................... 37
      Detector Arrangement .......................................................... 39
      Detection Electronics ............................................................. 41
      Secondary Beam Source ....................................................... 43
Experimental Procedure .......................... 44

Detector Filament Cleaning Process ................ 44
Alkali Metal Beams ................................. 45
Data Taking Cycle .................................. 46

Results ............................................. 49
Energy Shift ........................................ 58
Discussion .......................................... 60
Evidence of SSI for Beam Species
      Other than Alkali ............................. 61

IV. FORMATION OF NEGATIVE IONS ON A SURFACE ........ 63

Apparatus .......................................... 63
Vacuum System ...................................... 63
Quadrupole Mass Spectroscopy .................... 65
Magnetic Mass Spectroscopy ....................... 67

Experimental Procedure ............................ 69
Results ............................................. 72
H⁻ Formation ....................................... 72
O⁻ Formation ....................................... 77
D⁻ Formation ....................................... 79
Isotope Effect ..................................... 80

V. CHEMICAL REACTIONS - ALKALI DIMER FORMATION
ON THE SURFACE ........................................ 86

Apparatus .......................................... 86
Local Mode
Remote Mode

Experimental Procedure ............................ 90
# LIST OF FIGURES AND TABLES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>Potential energy and surface crystallography of single crystal tungsten surfaces</td>
<td>8</td>
</tr>
<tr>
<td>1-2</td>
<td>Work function change versus surface coverage</td>
<td>13</td>
</tr>
<tr>
<td>2-1</td>
<td>Comparison of the efficiencies between an electron bombardment and a stimulated surface ionization detector</td>
<td>24</td>
</tr>
<tr>
<td>2-2</td>
<td>Comparison of systems for the production of high energy neutral beams</td>
<td>27</td>
</tr>
<tr>
<td>3-1</td>
<td>Schematic of the apparatus for the study of the stimulated surface ionization</td>
<td>38</td>
</tr>
<tr>
<td>3-2</td>
<td>Detector arrangement</td>
<td>40</td>
</tr>
<tr>
<td>3-3</td>
<td>Detector electronics</td>
<td>42</td>
</tr>
<tr>
<td>3-4</td>
<td>Typical data taking cycle for SSI Studies</td>
<td>47</td>
</tr>
<tr>
<td>3-5</td>
<td>Efficiency versus energy curves for Rb → K and Na → K</td>
<td>51, 52</td>
</tr>
<tr>
<td>3-6</td>
<td>Efficiency versus energy curves for Na → Rb, Na → Cs, K → Na, K → Rb and K → Cs</td>
<td>53, 54, 55</td>
</tr>
<tr>
<td>3-7</td>
<td>Efficiency versus energy curves for Rb → K, Rb → Cs, Rb → Na, Cs → Rb, Cs → K and Cs → Na</td>
<td>53, 54, 55</td>
</tr>
<tr>
<td>3-8</td>
<td>Energy shift versus primary beam energy</td>
<td>59</td>
</tr>
<tr>
<td>4-1</td>
<td>Schematic of vacuum system</td>
<td>64</td>
</tr>
<tr>
<td>4-2</td>
<td>Schematic of apparatus</td>
<td>66</td>
</tr>
<tr>
<td>4-3</td>
<td>Channeltron electronics</td>
<td>68</td>
</tr>
<tr>
<td>4-4</td>
<td>Magnetic multiplier electronics</td>
<td>70</td>
</tr>
<tr>
<td>4-5</td>
<td>H⁻ intensity versus time</td>
<td>74</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>4-6</td>
<td>$H^-$ intensity versus time</td>
<td>75</td>
</tr>
<tr>
<td>4-7</td>
<td>$H^-$ intensity versus surfacc temperature</td>
<td>76</td>
</tr>
<tr>
<td>4-8</td>
<td>$O^-$ intensity versus time</td>
<td>78</td>
</tr>
<tr>
<td>4-9</td>
<td>$H^-$, $D^-$ and $O^-$ mass spectrum</td>
<td>81</td>
</tr>
<tr>
<td>5-1</td>
<td>PDP8 Mini-Computer block diagram</td>
<td>89</td>
</tr>
<tr>
<td>5-2</td>
<td>KNa$^+$ intensity versus time</td>
<td>92</td>
</tr>
<tr>
<td>5-3</td>
<td>KNa$^+$ intensity versus time with delayed coating beam</td>
<td>94</td>
</tr>
<tr>
<td>5-4</td>
<td>KNa$^+$ intensity versus time with delayed primary beam</td>
<td>95</td>
</tr>
<tr>
<td>5-5</td>
<td>K$_2^+$ intensity versus time with various speeds of thermoparticle rejector</td>
<td>98</td>
</tr>
<tr>
<td>5-6</td>
<td>KNa$_2^+$, Na$_2^+$ and K$_2^+$ intensities versus time</td>
<td>100</td>
</tr>
<tr>
<td>5-7</td>
<td>KNa$_2^+$, Na$_2^+$ and K$_2^+$ intensities versus time</td>
<td>102</td>
</tr>
<tr>
<td>5-8</td>
<td>Na$_2^+$ intensities versus time with different bake-out time spans</td>
<td>104</td>
</tr>
<tr>
<td>5-9</td>
<td>Na$_2^+$ intensity versus time with various coating beam intensities</td>
<td>108, 109</td>
</tr>
<tr>
<td>6-1</td>
<td>$\theta_1$ and $\theta_2$ versus $\theta_{\text{total}}$ curves</td>
<td>114</td>
</tr>
<tr>
<td>6-2</td>
<td>Na$_2^+$ intensity versus time curves with theoretical fitting curves</td>
<td>118</td>
</tr>
<tr>
<td>6-3</td>
<td>Na$_2^+$ intensity versus time curves with theoretical fitting curves (two levels in the first layer and one in the second)</td>
<td>124</td>
</tr>
</tbody>
</table>
Figure 6-4 \[ \theta_i\nu_i \theta_i\nu_i j_i\nu_i \exp(-D\varepsilon_{j_{i+1}l_i}) \text{ and } j_i \]
(j(two levels in the first layer and one each in the second to sixth layer) compares with experimental result 125, 126

6-5 Energy level diagram 127

APPENDIX

A1-1 Surface temperature versus heating current for a 6 cm long tungsten filament 128

A2-1 Primary beam particle trajectory relative to the thermoparticle rejector teeth 129

A2-2 Relative beam intensity versus rejector speed 134

A3-1,2, 3,4 Residual gases mass spectrum 135, 136, 137, 138

A4-1 Schematic diagram of secondary beam source and detector 139

A5-1 Dimer \(\beta\) maxima intensities versus surface temperature 141

List of Tables

Table 1 SSI Efficiency for Various Alkali Pairs 56
CHAPTER I
INTRODUCTION

1. **Surface Crystallography**

Due to the wide interest in the role of beam-solid interactions in such diverse fields as plasma physics, sputtering, thin films and catalysis, the study of processes between various kinds of beams with the solid surface is at present a rapidly growing field of both physics and chemistry. Most surface research today is characterized by the clean single crystal surface approach. A growing body of research deals with the presence of one single species on the surface. A more limited effort goes into the study of interactions between different adsorbed species, and then mostly at thermal energies. Impinging particles at KeV energies lead to sputtering and implantation which are not surface specific. As far as the in-between superthermal energy is concerned the field is almost bare. However, recent interest has emerged due to its application in plasma physics (wall effects).

The discovery of interference phenomena in electrons scattered by metal surfaces is closely related to the development of quantum mechanics. The wavelength for 100 eV electrons is about 1 Å, so that interference of these waves from periodic surface structure is to be expected. Before 1960, few research groups employed low energy electron diffraction (LEED) as a tool for surface investigations, because of the stringent vacuum requirements and surface preparation for single crystals.
as well as the tedious detection procedure by means of a moveable Faraday cup. In 1962, Lander et al. [1] constructed a system with spherical grids to accelerate the diffracted electrons onto a spherical fluorescent screen which allowed the total diffraction pattern to be made visible at once. This device is the basis of many of the modern systems of the display type. The beauty of LEED is not only its ability to display the periodic structure for a crystal surface, it can also be used to analyze ordered adsorbed layers.

Although the work of many theoretical physicists has resulted in considerable progress in recent years, as yet there is no complete LEED theory available. Several reviews on LEED have been published recently: Ertl and Kuppers [2], and Somorjai [3]. In most cases the basic ordered or disordered surface structure can be understood without too much difficulty.

The field-ion microscope (FIM) is the most powerful microscopic device known today in investigating surface structures. One major difference between LEED and FIM is that with the former one can only detect the surface atoms periodic arrangement through the diffraction of electrons from a macroscopic surface area while with the latter a direct magnified picture of each individual surface atom or dislocation can be obtained.
Handling of large electric fields became a possibility after the introduction of the field emission microscope by Müller in 1936, and when the field range beyond 100 million volts per centimeter became accessible, the discovery of field desorption followed.

The realization that the resolution of the field electron microscope is inextricably limited by the lateral velocity component of emitted electrons, which cannot be controlled under prevailing conditions, led Müller [4] in 1951 to his successful attempt to image the emitter surface with positive ions of hydrogen rather than electrons. With the discovery of FIM, atomic resolution was achieved for the first time. In FIM, a metal tip about 100Å in diameter is kept at positive potential to produce a field of about 500 MV/cm.

The image information of the tip surface is carried to a screen by radially projecting surface field ionized hydrogen ions. The magnification is up to several million diameters of the tip and the resolution is about 1Å in a modern FIM experiment. The ions are produced in the immediate proximity of the specimen surface by field ionization of the image gas which is introduced into the microscope tube at a pressure of a few millitorrs, low enough to provide sufficient free path to let the ions travel to the screen without disturbing collisions.
The greatest advantage offered by the field ion microscope tip is the ease with which geometrically well defined, as well as perfectly clean surfaces can be provided by the unique process of field evaporation. Also, all crystallographic orientations are accessible in one experiment. However, the effect of high electric fields upon the surface to be investigated is not clear. It is also, so far, only applicable to a surface tip and, unlike LEED, it is not useable with a flat surface. Most adsorbates will desorb in the presence of such high fields and the difficulties involved in image interpretation also make experimental results uncertain.

2. **Clean Surface**

   The definition of a clean surface at present is still much less strict than for its three dimensional counterpart, the solid. In a metal or liquid solution the impurity can be controlled to parts per million, but for a metal surface the detection limit of its impurity contents with current analytical methods is about 0.1% of a monolayer. It is still somewhat uncertain whether or not still smaller amounts of surface contaminations can give rise to noticeable effects in various surface experiments. Actually, the cleanliness of the surface has been the subject of direct measurements since the development
of Auger electron spectroscopy (1968), at which time it became clear that even more care was necessary in preparation and maintenance of clean surfaces than was previously thought.

In 1953, Lander [5] studied the energy distribution of secondary electrons emitted from solid samples irradiated with slow electrons. He observed small characteristic peaks which he attributed to Auger electrons. He pointed out that these might be used as a tool for surface analysis. Tharp and Scheiner [6] demonstrated that the ordinary electron optics for LEED experiments could be used as a retarding field energy analyzer for the detection of Auger electrons by differentiation of the integral energy distribution. A disadvantage, however, was the fact that only very small peaks appeared on the large slowly varying background of secondary electrons which were emitted from a surface bombarded by low energy primary electrons. A marked increase in sensitivity could be obtained by using a glancing angle primary electron gun instead of the usual excitation by electrons striking the surface under normal incidence as in LEED. Another important step in experimental development of this method was made by Palmberg et al. [7] by using a cylindrical mirror analyzer to detect Auger electrons. With this technique the sensitivity, resolution and signal to noise ratio could be improved to the extent that even a fast oscillo-
graph scan of the Auger spectra and the detection of surface impurities with concentrations as low as one thousandth of a monolayer became possible.

3. Adsorption

In the adsorbate-substrate system, one atomic layer ($\theta = 1$) is defined as one adatom per atom in the outer layer of the substrate. In contrast, one physical layer ($\theta_P = 1$) is the maximum number of adatoms on a surface forming a single adlayer. One physical monolayer forms with $\theta$ smaller than one if the adatoms are larger than the substrate atoms. The exact number of adsorbed particles per unit area is somewhat uncertain. It depends on the coating beam intensity and the vapour pressure of the adsorbed particle and, therefore, upon the temperature of the substrate.

It has become clear over the years of LEED studies that the formation of an ordered adsorbed phase is more the rule than the exception. The structures of Na atoms on a W(112) surface have been reported by Chen and Papageorgopoulos [8]. Accordingly, Na forms a p(2x1) structure in the $0<\theta<0.5$ range, and a one-dimensionally periodic array for $0.5<\theta<0.8$, where $\theta$ is the coverage in monolayer units. For $\theta>0.8$, a second layer of Na begins to form.
In order to understand the adsorption phenomenon, it is necessary to consider the energetics for adsorbed particles on a single crystal surface in more detail. If a particle approaches a surface from the gas phase, it will experience a potential as shown in Fig. 1.1a. The depth of the potential trough depends on the location with respect to the surface atoms and consequently varies periodically across the surface. The adsorption sites are characterized by a local minimum in energy. According to the surface temperature the adsorbed particles oscillate about their equilibrium positions and will desorb from the lattice if they have enough thermal energy to overcome the energy barrier in the direction normal to the surface. The residence time of the particle on the surface is given by the so-called Frenkel equation [9]

\[ t = t_0 \cdot e^{\frac{E_{ad}}{kT}} \]

where \( E_{ad} \) is the adsorption energy and \( t_0 \) is of the order of a single vibration period. For Na on a W(110) surface, Hurkmans [10] reported \( t(1250^\circ K) = 2 \) msec, \( t_0 \approx 10^{-13} \) sec and \( E_{ad} = 2.55 \) eV. Let \( E' \) be the surface diffusion activation energy for the adsorbed particle in a certain direction on the surface as shown in Fig. 1.1b. There will always be at least one specific direction on
(a) Variation of the potential energy with respect to the distance \( z \) normal to the surface for a particle adsorbed on a surface.

(b) Variation of the potential in the \( x \) direction parallel to the surface at \( z = z_0 \).

(c) W(110) single crystal surface.
Surface density: \( 1.4 \times 10^{15} \text{ (atoms/cm}^2 \) \)

(d) W(100) single crystal surface.
Surface density: \( 1 \times 10^{15} \text{ (atoms/cm}^2 \) \)

(e) W(112) single crystal surface.

(f) W(111) single crystal surface.

Fig. 1-1
the surface with minimum diffusion activation energy \(E'_0\), depending on the particular nature of the adsorption bond.

So far \(E'_0\) has always been found smaller than \(1/2 E_{ad}\). For an adsorbed atom, the time spent on a specific adsorption site is then

\[
\frac{E'_0}{kT} \\
\text{t' = c}
\]

and is therefore always very much smaller than the total residence time \(t\) on the surface. When the surface is very cold or \(1 < T < E'_0\), the adsorbed particle will be nearly immobile on the particular site. If \(0.1 E'_0 < kT < E'_0\), the particle may jump from one adsorption site to a neighbouring one. However, it will be resident on an adsorption site for most of the time. When \(kT\) is larger than \(E'_0\), but smaller than \(E_{ad}\), the particle will move freely over the surface like a two-dimensional gas particle.

The situation is a little different when the coverage is high. Then the interaction between the adsorbed particles comes into play. This interaction can be either repulsive or attractive [11], as alkali atoms on nickel surface under different surface coverage, and can also operate indirectly, that is via the valence electrons of the substrate atoms. As the surface coverage increases the pressure of the two dimensional lattice increases too and even at \(kT=E'_0\) the motions of the adsorbed...
particles become restricted by lateral interactions until finally a closed dense structure is formed [12]. At this stage the adsorbed particles abandon the original low coverage adsorption sites. The substrate either determines only the orientation of the surface layer to give an incoherent surface structure, or partial registry between overlayer and the substrate lattice occurs as the result of a compromise between the adatom-adatom and the adatom-substrate interaction [13].

4. Work Function

The presence of different crystal planes on a polycrystalline metal surface results in a heterogeneous distribution of adsorption forces on the face. This heterogeneity of the metal surface is apparent from many experiments employing field emission or thermionic emission. Investigations of the electron work function of metal surfaces have also shown a marked dependence on the crystal planes that constitute the surface. The results seem to indicate that the value of the work function depends also on the density of packing in a particular crystal plane. The greater the number or nearest neighbours and the shorter the distance between them, the greater the work function.

For a polycrystalline metal surface, the experimentally determined value of the work function \( \Phi \) is a weighted average of the work functions \( \Phi_i \) of the individual crystal planes present on
the surface, i.e., \( \bar{\phi} = \sum_{i} C_i w_i \phi_i \), where \( C_i \) is the fraction of the metal surface that is occupied by the \( i \)th crystal plane and \( w_i \) is the corresponding weight. Different experimental methods are associated to different \( w_i \), thus leading to the possibility for seemingly inconsistent results. Riviere [13] gave a detailed review on work functions measured by all methods developed to date.

In recent years considerable progress has been made in work function measurements. Krahl–Urban et al. [14] investigated the work function of regularly stepped tungsten single crystal planes as a function of terrace width and step orientation. They found that the terraces were always formed by (110) planes and that the work function decreases linearly with step density for a given step orientation. Different step orientations give rise to slightly different work function reductions. They attributed this to the dipole moments of edge atoms since different edge structures have different dipole moments.

Recently Kohn and Lang [15] published a quantitative description. The calculations were based on an explicit evaluation of the charge density below and above the surface. This model results in a dipole contribution to the value of \( \bar{\phi} \).

In nearly all cases of adsorption the work function of the substrate either increases or decreases with coverage. This is due to a modification of the dipole layer at the surface. The formation of a chemisorption bond is associated with a partial electron transfer between substrate and adsorbed particles, as
in the case of Na adsorbed on a tungsten surface. In the case of physisorption the polarization of the adsorbed particles by the electric field at the surface gives rise to the build-up of a dipole layer as in the case of H on a tungsten surface. The variation of the work function is related to the number density \( n \) of adsorbed particles and to the dipole moment \( \mu \) of the individual adsorbate complex. The simplest picture assumes a continuous and infinite double layer of charges separated by a distance \( d \). Then the total dipole moment per \( \text{cm}^2 \) is given by \( n \cdot \mu \), from which follows \( \Delta \varphi \sim n \mu d \). Hence \( \varphi \) should vary linearly with the coverage, \( \theta \), at least when \( \theta \) is small, provided that the dipole moment \( \mu \) is independent of \( \theta \). Two typical examples are plotted in Fig.1-2. When \( \theta \) is large, the effect of the mutual influence of the adsorbed dipoles is generally complex and depends on the nature of the adsorption bond. The simplest model applicable to physisorbed layers assumes only direct interactions between the dipoles leading to mutual depolarization and thus to a reduction of the individual dipole moments. As the alkali metals are adsorbed, the work function of the substrate metal decreases and often exhibits a minimum in a plot of \( \Delta \varphi \) against coverage, as in Fig.1-2b [17].

5. Sputtering

The emission of target particles under the impact of
(a) Increase in work function of W(110) surface with hydrogen exposure at 300°K.

1 Langmuir (L) = $10^{-6}$ Torr sec.

(b) Work function of W(110) surface as a function of potassium surface coverage at 78°K.

\[ \theta_p = \text{corresponding to } 5 \times 10^{14} \text{ (atoms/cm}^2\text{)} \]

(c) Increase in work function of W(100) surface as a function of oxygen coverage at 300°K.

The work function increases nearly linearly with coverage. The change of slope is explained by the structure rearrangement within the adsorbed layer.

\[ \theta_M = 1, \text{ corresponding to } 10^{15} \text{ (atoms/cm}^2\text{)} \]

Fig. 1-2
neutral or charged particles on metal targets has been under investigation for more than a century. Numerous parameters determine the sputtering process for a target such as the type and charge of the incident ion, energy of the incoming particles and the angle of incidence. There are a number of differences between the conventional sputtering process and those investigated in this work. Here a neutral alkali superthermal beam is used instead of an ion beam of usually much higher energy. The main interest of this work focuses on the processes on the adsorbed surface layer instead of the substrate itself as in a sputtering process.

For a polycrystalline tungsten target the sputtering thresholds for various incident ion beams are found at about 30 eV [19]. While the threshold value for the sputtering process is not very different for different types of materials, there are nevertheless quite marked deviations in the rate at which the sputtering yields of different materials rise with increasing primary ion energy. Basically, two models have been suggested to describe sputtering processes. (1) The energy of the impinging particles raises the temperature of a small localized region around the point of impact to such a high temperature that sputtering takes place by an evaporation process. The derivation of the relationship between the number of sputtered
particles and the energy transferred to the target surface is based on macroscopic concepts of temperature and heat flow. However, the angular distribution of the sputtered particles is not represented by a cosine law as the thermal evaporation theory would predict. Also, the strong dependence of the sputtering process on the angle of incidence cannot be explained by an evaporation process. (2) A momentum transfer takes place from the incident particle to an atom of the target lattice which in turn may transfer momentum in successive collisions. Depending on the energy of the incident particle, three types of interactions are considered. Particles with high energies interact through the Coulombic repulsions of their nuclear charges. At medium energies the electron clouds cause a partial screening of the positively charged nuclei and the collisions are treated as weakly screened Coulomb collisions. At low energies the collisions are approximately of the hard-sphere type.

6. Superthermal Molecular Beam

During the last two decades the molecular beam method has proven extremely successful in many applications [20]: gas kinetics, gas and solid surface interaction, mutual interactions of atoms and molecules, direct sampling of chemical processes and catalysis. In the beginning, atomic and molecular beams of
thermal energy were used to investigate elastic scattering and to derive the intermolecular potentials for a particular collision. Recently with the availability of direct inversion methods, spherical potentials can be derived directly from experimental data. Datz and Taylor [21] showed that the molecular beam method could be used for chemical reaction studies. A wealth of chemical reaction studies have followed since. This concept was immediately generalized to include all types of inelastic and reactive collision processes, such as collisional excitation, ionization, charge transfer and dissociation. However, in most cases, the available energy was too small to facilitate investigations of other than special cases, even when use was made of the high velocity tail of the Maxwellian distribution by employing velocity selectors. Therefore, the interest in a superthermal atomic or molecular beam source with beam energy from one eV to one hundred eV has been growing steadily through the years.

When Amdur did his famous studies of atomic collisions at energies of several hundreds of electron volts and higher, there were difficulties in producing a neutral beam at lower than the above-mentioned energies. This was particularly true at the lower end of the superthermal energy scale, i.e. below 20 eV. Intensive studies during the last ten years have
overcome some of these difficulties. Three methods have gained general acceptance: (1) supersonic nozzles, (2) sputtering and (3) charge exchange beam sources.

Recently renewed interest has developed in the energy range from 1 eV to about 30 eV for a number of reasons. First of all, the binding energies in molecules are of the same order of magnitude and therefore one expects the most interesting information in a range where beam energy and the energy of relevant internal states are about equal. Then characteristic resonance and interference phenomena can be seen even in the elastic scattering channel which inevitably accompanies inelastic processes. When details are wanted about a particular channel which occurs concurrently with others, one must look into the inelastic scattering of that particular channel. In some cases, however, the channel in question may be identified beforehand and an investigation of the elastic channel, which provides a mirror image of the inelastic process may yield already all the information needed. This principle has been successfully used at thermal energies when investigating some chemical reactions with low or no energy thresholds.

In recent years much work has been done to study the interaction of an atomic or molecular beam with surfaces. C. R. Helms et al. [22] reported on the measurement of the desorption rate for Co on Ni (110) by a chopped Co beam with 45° incidence
angle on the Ni surface. J. M. Horne et al. [23] observed the diffraction of He and H$_2$ from Ag(111). This was an important result because it was commonly believed the potential periodicity of the Ag(111) surface was too weak, i.e. the surface too smooth to exhibit diffraction of light gases. In fact the only clean metal surface to previously show diffraction has been the strongly corrugated W(112) surface [24]. S. P. Singh-Boparai et al. [25] used a molecular beam technique for the determination of sticking probabilities and surface coverage of nitrogen on various single crystal tungsten surfaces for a wide range crystal temperature. A. Hurkmans et al. [26] measured the fraction of K and Na atoms initially trapped by the W(110) surface as a function of incident K and Na beam energy and angle. C. T. Foxon et al. [27] used a modulated molecular beam technique to study the interaction of Ga and As$_2$ on a GaAs(100) surface. The catalytic decomposition of formic acid by a polycrystalline platinum surface was studied by F. Steinbach [28] by the use of modulated molecular beam techniques with mass spectrometric phase sensitive detection, which led to the identification of several types of reaction processes occurring on the surface.

Somorjai et al. [29] using molecular beam surface scattering techniques studied the mechanism of catalytic surface
reactions. Usually a well-collimated beam of the reactant gas or gas mixture is scattered from a crystal surface and the products that are desorbed after a single scattering event at a given solid angle are detected by mass spectrometry. By rotation of the mass spectrometer around the sample, the angular distribution of the scattered products can be determined. If the incident molecular beam is chopped at well defined frequencies, the time of flight of the incident molecules between the chopper and the detector is determined by a phase shift measurement. This information yields the residence time of molecules on the surface. Chopping the product molecules that desorb from the surface permits determination of their velocity. The experimental variables of this system are the temperature, atomic structure and composition of the surface and the energy and angle of incidence of the molecular beam. In reactive scattering experiments, the mass spectrometer detects the product distribution and rates of formation of product molecules as a function of the system variables. From the dependence of the reaction rate on the beam energy, the activation energy for adsorption can be determined. From the surface temperature dependence on the reaction rate the activation energy of the surface reaction is obtained. The residence time of molecules, the angular and energy distribution of the products reveal the nature of energy transfer during the beam-surface interaction.
In the present work a variety of phenomena are observed when a superthermal atomic beam impinges upon a tungsten surface with one or more atomic species adsorbed. Depending on the surface coverage, temperature and energy and also the incident angle, some of the incoming neutral atoms experience kinetic surface ionization and are reflected. Alternatively, some of them cause other atoms that are adsorbed in an ionic state to leave the surface.

Some of the incoming fast particles enter the two-dimensional world of the surface and are scattered by other adsorbates. Most of those will become thermalized, reach equilibrium with the surface, and become an addition to the already present adsorption layer. Some of them then enter into chemical reaction directly or indirectly to form molecules on the surface.
CHAPTER II

THE SCOPE OF THIS WORK

1. **Stimulated Surface Ionization**

   In the molecular beam experiments, an intense, collimated and energywise well-defined beam is of primary importance. But of equal importance is the availability of a detector with high efficiency, more significantly, with a high signal to noise ratio and fast response. Unfortunately, at the low energies appropriate to molecular beam scattering, the detection methods are severely handicapped. A detector based on the newly found stimulated surface ionization effect has been proven useful for application to detect beams with superthermal energies.

**Surface Ionization Detector**

In the case of the Langmuir-Taylor detector, beam molecules are dissociated upon a hot surface and then one part of the molecule with the ionization potential lower than the surface work function of the detector filament is ionized. This detector is very successful in detecting beams of alkali atoms and alkali halides. Also, this surface ionization detector has been used in the reverse sense [30]. Thus, the collision of an atom or molecule having a large electron affinity with a hot surface of low work function can lead to electron transfer from the metal surface and the formation of a negative
ion. But such negative surface ionization is a much less efficient process than the formation of positive ions. For ionization of alkali metal the efficiency can be as high as almost 100 percent, but amounts to only a few percent for negative ionization. It has been found that ionization of some species other than alkali, such as Mg, Ca and Sr, can be accomplished on an oxygenated tungsten wire with a higher work function [31]. For hydrogen and rare gas beams, ionization potentials are well above the work functions of all known surfaces, so a surface ionization detector is not usable.

**Universal and Bolometer Detectors**

A universal detector ionizes the molecule or atom by electron bombardment and then measures the resultant ion current. In the case of superthermal energies (1 - 100 eV), electron bombardment detectors have the disadvantage of favouring slow particles because it is the number density which is measured and this is inversely proportional to the velocity.

A bolometer detector [32] has been very successful for measurements with low thermal energy atomic beams such as a hydrogen beam and rare gas beams with the detector at several degree Kelvin. The bolometer, although it favours high energy particles, is still sensitive to the thermal particles and the associated noise. Therefore, it would not represent the ideal
solution in the case of a low intensity superthermal beam against a high thermal background.

**Stimulated Surface Ionization Detector**

Stimulated surface ionization detector is one of the solutions for the detection of superthermal beams. Low ionization potential alkali atoms are coated on a lukewarm and high work function surface such as tungsten. Lukewarm temperature is defined as the temperature set just below the threshold where thermal surface ionization could occur. The adsorbed alkali atom is partially positively ionized on the low coverage surface. As a superthermal beam of alkali atoms or other gas molecules impinges on the surface, stimulated surface ionization process occurs, i.e. the adsorbed alkali adions will be desorbed as ion. The desorbed ion signal could be calibrated against the intensity of the superthermal beam. Since the efficiency increases with the incoming superthermal beam particle energy, at least in the range of interest, the drawback of the electron bombardment detector is reversed here.

Fig. 2-1 gives a typical comparison between a stimulated surface ionization detector and an electron bombardment detector. In the low energy range of a few eV, they both have a detection efficiency of about the same order of magnitude, but when the energy is around 100 eV, the efficiencies generally
Detection efficiency for stimulated surface ionization as function of energy of incident superthermal atomic potassium beam. Dotted line indicates typical behaviour of electron bombardment detector (universal detector).
differ by 2 to 3 orders of magnitude.

2. **Negative Ions**

In the last few years, interest in the production of negative hydrogen ion sources has greatly intensified [33]. Before the demands of the controlled thermonuclear reaction (CTR) negative ions were virtually a curiosity. Chemists were interested in the binding energies in negative ions, or in the fact that some chemical reactions appeared to proceed through anionic intermediates. In nuclear physics, negative ions are used for injection into accelerators, and in particular into tandem Van de Graaff accelerators. Typical $^1H^-$ ion beams attained maximum intensities of a few milliamperes. The intensities for other species are much lower. Applications other than CTR that could profit from higher $^1H^-$ beam intensities are high energy accelerators and storage rings. Developments to date have resulted in beam intensities that are just about sufficient for all these applications, but an increase in intensity is more than welcome or even a necessity.

Three approaches are being pursued presently with the goal to produce intense high energy beam of neutral particles for injection into a fusion device. These three methods are:

(a) direct extraction of negative ions from a plasma source,
(b) a system based on a proton beam source, (c) same as (b) but with a double charge exchange method. Fig. 2-2 shows that the system based on a direct extraction $D^-$ source has the highest efficiency [34]. And it also has the advantage of being quite compact, and is expected to have smaller emittances and smaller energy spread.

The formation of negative ions by surface ionization has been investigated by various authors [35]. In the early works it can be seen that a preponderance of the investigations have been with halogen atoms on polycrystalline tungsten hot surface, since the halogen atoms have the highest electron affinities among all the elements. In 1962, Krohn [35] studied the emission of negative ions from targets of polycrystalline Cu, Ag, Au, Ta, W, etc.; bombarded by a Cs$^+$ ion beam at energies of several keV. Krohn also made the interesting observation that the yield of negative ions from a copper target increased whenever an auxiliary beam of neutral cesium beam was directed against the target. This indicates that the presence of cesium on the target effectively lowers the work function of the target surface and enhances the negative ion emission.

Within the last few years, a magnetron-type negative hydrogen ion source has been developed by Belchenko, Dimov and Dudnikov [36] that has the remarkable capability of producing negative-ion current densities of up to 3.7 A/cm$^2$. The novel
Comparison of Systems for the Production of High Energy Neutral Beams

Fig. 2-2
feature of this source is a plasma discharge, maintained in an atmosphere of hydrogen and cesium, and employing a cold cathode of either tungsten or molybdenum. A similar source has been developed by Prelec and Sluyters [37]. Their source employs a cold molybdenum cathode and achieves a current of 1.7 A/cm². The negative ions are believed to be formed primarily on the cathode in a gas-discharge device. Thus, hydrogen gas is originally adsorbed on the cathode surface, in the presence of cesium vapor. The hydrogen in the gas phase is presumed to be atomic H. Dimov has suggested, based in part on the work of Kishinevski [38], that the hydrogen is adsorbed as a negative ion on the cathode surface. At first glance, this seems unlikely. The electron affinity of H is about 0.75 eV, while the work function on the cesiated surface cannot be reduced below 1.4 eV. This implies that the surface would take away the electron. However, Kishinevskii invokes electric image potentials to explain this apparent discrepancy. Then these H⁻ ions are desorbed from the cathode by the action of fast atoms and positive ions bombarding the cathode surface. Although it might be thought that the negative ions would give up their electrons to the surface as they depart, they apparently may leave with such speed that this adiabatic transition to neutral H does not occur.
Alternatively, Hiskes [39] has interpreted the desorption in terms of a surface catalysis involving a Cs–H interaction at the cathode. The formation of the negative ion has involved two catalytic processes: the Cs–H molecular configuration has catalysed the transfer of an electron from the cesium atom to the hydrogen atom, and the tungsten cesium interaction has catalysed the transfer of the second electron, thereby leaving the cesium in its initial state.

In Krohn's experiment the negative ions are of the sputtering target bulk material itself. The validity of the production of negative ions of the adsorbed particles based on coating the metal surface with alkali metal has never been tested. On the other hand, lacking any direct experimental evidence, it is only a hypothesis to assume that the H<sup>−</sup> ions from a magnetron plasma source come from the cathode surface rather than from inside the plasma.

In our experiment a clean tungsten filament, baked out in high vacuum, is used as the surface under study. Upon the adsorption of hydrogen, oxygen or deuterium gas, a neutral potassium superthermal beam with the energy of 100 eV was directed onto the gas covered surface. No negative ions could be detected unless the surface was coated by a secondary thermal alkali beam. The collected negative ion signal increased as the alkali metal
coverage increased and finally reached a saturation maximum. Our results clarify a few points: (a) The negative ion production threshold energy is lower than 10 eV in primary beam energy. (b) The alkali metal coating is a necessity. (c) Since sodium is used as the coating alkali metal, the work function on the sodium coated surface cannot be reduced to below 2 eV. That is 0.6 eV higher than the value possible with a cesium coated surface. It only weakly supports Kishinevskii's electric image potential explanation about the discrepancy between work function and electron affinity, and it favours the catalytic explanation by Hiskes. (d) The negative deuterium ion signal was found to be significantly lower than the negative hydrogen ion signal. This new isotope effect is dealt with in more detail in chapter IV.

3. Chemical Reactions on a Surface

The catalytic function of surfaces is exhibited in two ways. The catalyst reduces the potential energy barrier in the path of the reaction, which is otherwise thermodynamically unfeasible, by temporarily forming chemical bonds with the adsorbing particles. The ability of the surface to break some of the strong chemical bonds of the reactant molecules, for example H–H, and to bind them by strong enough surface bonds so that the residence time of the adsorbate is sufficiently long.
for the necessary chemical rearrangement to occur, and to then permit the release of the product molecules to make the various active surface sites available for new reactions, is one of the essential features of heterogeneous catalysis [40]. It is well known that too strong chemical bonds between the surface atom and the reaction intermediate lead to permanent blocking of the catalyst surface, i.e. catalyst poisoning. If the chemical bonds between the reactant molecules and the surface are too weak, either the crucial bond breaking processes will not occur or the adsorbate residence time becomes too short for the necessary and sometimes complex chemical rearrangement.

There is another, equally important, function of a good catalyst surface that leads to selectivity. A proper catalyst will facilitate the formation of only one out of many possible reaction products. This enzymelike characteristic of heterogeneous catalysis has not been receiving as wide an attention as the ability of the catalyst to lower the activation energy of the chemical reaction by forming temporary chemical bonds with reactants. Most technological important catalysts, especially those that exhibit the ability to catalyze the production of structurally complex molecules, exhibit both of these features.

Identification and study of the active site where
chemical bond scission or rearrangement occurs, so crucial to the working of a catalyst, requires the investigation of the structure and the chemical composition of the catalyst surface on the atomic scale. Now a multitude of new techniques exists as discussed in chapter I.

In this work, evidence is presented that superthermal neutral alkali beams can also give rise to chemical reactions on a polycrystalline tungsten surface. Among diatomic molecules, the alkali dimer species are a curious family. These molecules have extremely long bond lengths (ranging from 2.7 Å for Li$_2$ to 4.5 Å for Cs$_2$), low vibrational frequencies (351 to 42 cm$^{-1}$), and very low bond strengths (1.04 to 0.434 eV)[41]. The bond strength of M$_2^+$ is substantially greater (~50%) than that of the M$_2$ molecules. Under ordinary thermal equilibrium conditions the dimer species constitute only a small fraction of alkali vapour (e.g. at 500$^\circ$K the mole fraction of Na$_2$ is 0.5%). Nozzle expansion studies have demonstrated the enhanced dimerization which accompanies the drop in local temperature. Intense alkali beams of up to 30% mole fraction of K$_2$, Rb$_2$, Na$_2$ and Cs$_2$ have been generated, with oven temperatures up to 900$^\circ$K, corresponding to alkali vapour pressure of up to 350 torr [42]. Since then a systematic investigation of reactive scattering of alkali dimer molecules with alkali atoms and
with other atoms or molecules has been carried out. For example, Mascord et al. [43] have investigated the reactive scattering of alkali dimers. From the velocity analysis measurements of reactive scattering from the alkali-dimer exchange reaction \( \text{Na} + \text{Rb}_2 \rightarrow \text{NaRb} + \text{Rb} \), the total reaction across section is found to be large \( (\sim 120 \text{ Å}^2) \).

The formation of an alkali diatomic molecular ion from the reaction of a superthermal neutral alkali atom with surface adsorbed alkali particles could proceed through three basic channels.

Subscripts
KE : particle with superthermal kinetic energy.
Ads : adsorbed particle.

(a) \( A_{\text{KE}} + B_{\text{Ads}} \rightarrow AB \) \hspace{1cm} (3-1)

The fast atom loses most of its kinetic energy and picks up an adsorbed atom to form a molecule.

(b) \( A_{\text{KE}} + B_{\text{Ads}} \rightarrow B_{\text{KE}} + A \) \hspace{1cm} (3-2)

\( B_{\text{KE}} + C_{\text{Ads}} \rightarrow BC \) \hspace{1cm} (3-3)

Energy transfers to an adsorbed atom from the incoming fast atom and the former then picks up another adsorbed atom to form a molecule.

(c) \( A_{\text{KE}} B_{\text{Ads}} \rightarrow AC + B \) \hspace{1cm} (3-4)

The molecule from process (a) goes through a two-
dimensional exchange reaction with an adsorbed atom to form another molecule similar to the exchange process in the three-dimensional case.

For each of these paths there are three possibilities concerning the electron transfer. For example the $A_{KE}^+ + B_{Ads} \rightarrow AB^+$ reaction could go through three different paths.

(i) $A_{KE}^+ + B_{Ads} \rightarrow AB^+$ \hspace{1cm} (3-5)

The fast particle has lost its electron before picking up the adsorbed atom.

(ii) $A_{KE}^+ + B_{Ads}^+ \rightarrow AB^+$ \hspace{1cm} (3-6)

The adsorbed particle is in a highly polarized state or in an ionic state. The incoming atoms combine with the partially ionized atom to form the molecular ion.

(iii) $A_{KE}^+ + B_{Ads} \rightarrow AB \rightarrow AB^+$ \hspace{1cm} (3-7)

The incoming atom forms the molecule first with the adsorbed atom. Since the ionization potential for the molecule is almost always lower than the constituent atoms, ionization may occur.
CHAPTER III

STIMULATED SURFACE IONIZATION

1. Apparatus

A schematic of the apparatus is shown in figure 3-1. The vacuum system is very similar to the one used by R. L. Gay (U.C.L.A.) [44]. Only a very brief review will be given here.

Vacuum System

A cubic stainless steel vacuum chamber (91.5 cm each side) was internally divided in a 2:1 ratio to form the oven and detector chambers. The oven side is equipped with a 10" NRC VHS diffusion pump with a liquid nitrogen cooled baffle to prevent backstreaming. The detector side is pumped with a 6" NRC VHS diffusion pump again with a liquid nitrogen cooled baffle. A 15 cfm Welch Duo Seal mechanical pump was used for initial evacuation of the system and as a forepump for the diffusion pumps. Operating pressure are monitored through thermocouples and ionization gauges. Typical readings are 100 millitorr for the forline, $2 \times 10^{-6}$ torr for the oven chamber and $1 \times 10^{-6}$ torr for the detector chamber. Later a freon-12 refrigeration unit was used for cooling both baffles. There was no noticeable pressure change. The advantage of such a system are savings in the liquid nitrogen expense and avoiding the tedious work of filling the baffles every few hours.
Primary-Beam Source

The superthermal neutral alkali beam source was based on the design by Helbing and Rothe [45]. Alkali ions are formed by surface ionization on a hot tungsten ribbon. They are accelerated by an electric field between the ribbon and a grid which is mounted very close by. After the ions have reached the desired energy, they travel through alkali vapour of the same species and undergo resonant charge transfer, thereby resulting in a beam of fast neutrals. Two modifications have been made. Due to the sputtering effect of fast ions impinging on the nickel grid causing serious damage to it, a 200 wires per inch tungsten grid was used to ensure a longer service life span. The lava insulation pieces which were used inside the oven to mount the ionization filament and acceleration grid are replaced by high temperature castable ceramic material (AREMCO Product Inc. N. Y.) to prevent voltage break down under the influence of high temperature and high alkali metal vapour pressure. Two iron-constantan thermocouples (one mounted beside the beam exit slit and the other mounted under the bottom of the reservoir) were used to measure the oven temperatures. The slit was heated roughly 10°K higher than the reservoir to prevent condensation. The back plate
where electric feedthroughs pass was maintained at a higher temperature to prevent an electric short between the feedthrough and its current carrying wire due to the condensation of alkali between the feedthrough and wire. The ionization ribbon was spring loaded to ensure straightness under all heating conditions.

**Thermal Particle Rejector**

The rejector consisted of a single thick aluminum disk with machine cut teeth on its circumference and was driven by an A.C. hysteresis synchronous motor (TRW Globe) using a Heathkit sine wave generator, a phase shifter and a 30 W power stereo amplifier as driver. Typically the rejector was running from as low as 5 Hz up to 160 Hz. The signal from a photocell was used to monitor the speed of the rejector on an Aries Inc. electronic pulse counter. A detailed efficiency calculation for the rejector is given in Appendix I.

**Double Frequency Chopper**

The chopper was made out of a thin aluminum disk. It is cut to the shape as shown in Figure 3-1 (D). The inner rim intercepted the primary beam with a frequency the same as the rotation speed of the disk while the outer rim intercepted the beam at twice this frequency. The photocell signal from the rotating chopper is fed into two Ithaco Dynatrac 391
Schematic of the Apparatus for the Study of Stimulated Surface Ionizations:

A = superthermal primary beam source, B = thermal beam rejector, C = ion rejector, D = twin frequency chopper, E = protruding nose to shield lower part of filament from coating, F = detector filament, G = coating beam source, H = superthermal primary beam, later split into $H_1$ (18 Hz) and $H_2$ (9 Hz), J = coating beam, K = ions to be mass analyzed. Insert = Na signal stimulated by 60 eV superthermal K beam. Intentional misalignment enhances 9 Hz component for clarity.

Fig. 3-1
Lock-In Amplifiers as the reference frequency. A sine wave generator, audio power amplifier, phase shifter and audio transformers are used to drive the synchronous motor of the chopper.

Detector Arrangement

As shown in Figure 3-2, a nose made of a piece of thin stainless-steel metal (0.010") is carefully mounted close to the detector filament such that the higher frequency, 18 Hz, primary beam passes over the top of the nose and strikes the upper half of the detector filament while the lower frequency 9 Hz primary beam passes underneath the nose and strikes the lower half of the filament. In order to reduce the possibility of the secondary coating beam striking the lower half of the detector filament, one edge of the nose was bent at 40 degree angle. A 10 mil diameter tungsten wire from A. D. MacKay Inc. was mounted on two spring loaded clips which kept the detector filament straight under all working temperatures (300 to 2200°C). The detector was heated by a D.C. power supply. When heat treating the filament we never went into a high temperature region, e.g. 2800°C, as mentioned in some of the literature [46]. Since the heat treated filament is very brittle and the nose piece was mounted as close as possible to it, we often accidentally broke the filament. Pieces of the broken filament under
Detector and Nose arrangement for SSI Studies

Fig. 3-2
microscopic (100 x) study appeared slightly smoother than a new filament but the basic structure was not changed, and the phenomenon of so called D.C. etching [41] was not noticeable.

Detection Electronics

The block diagram, Figure 3-3, gives a schematic of the signal detection electronics. The ions leaving the filament pass through a 90° sector magnetic mass spectrometer. A Bendix M-306 magnetic multiplier was used to amplify the ion signal. Typical signal amplification with this multiplier is in the order of $10^6$. The output signal from the multiplier passed through a one-megaohm resistor to ground, the resulting voltage drop being amplified by a Princeton Applied Research Model 113 pre-amplifier. This signal could be monitored through an oscilloscope or through a Federal Scientific Inc. Ubiquitous Signal Averager Correlator, used in the signal averaging mode.

Two Ithaco dynatrac 391 Lock-In amplifiers, one tuned to 18 Hz and the other to 9 Hz, were used to separate and amplify the signal from the upper and lower halves of the detector filament. The upper half of the detector filament receives the 18 Hz primary beam and is coated by the secondary beam while the lower half receives the 9 Hz primary beam and is uncoated by the secondary beam. The 9 and 18 Hz, $Y_1$ and $Y_2$ signals, were plotted on an X-Y recorder either versus time or mass. A laboratory-made voltage programmer can be set on one of two.
Detector Electronics.

Fig. 3-3
preamjustable focussing voltages. These two voltages can be adjusted to the accelerating voltages of the alkali metals being used as primary and secondary beams. The programmer can also sweep slowly through the related mass range to plot out an ion spectrum. To prevent both the A.C. 60 Hz background noise and scattered ions from entering through various openings, the Bendix Multiplier was surrounded by aluminum foil except at the ion beam entrance.

**Secondary Beam Source, Beam Shutters, Ion Rejector**

The secondary beam source was made of stainless-steel. Tantalum wire (0.38 mm dia.) was used for heating elements in both the primary and secondary ovens. Two iron-constantan thermocouples were mounted to measure the slit and body temperature of the secondary oven. The operating temperature for this oven is between 300°K and 600°K. Three laboratory-made transformer isolated low voltage A.C. power supplies were used for heating, one for the secondary oven, one for the primary oven body heating and the third for the back plate of the primary oven.

Two low voltage A.C. magnetic shutters were made in the laboratory to switch the beams on and off. An ion rejector consisting of two stainless steel plates, one grounded and the other biased with negative 400 volts was installed in the path
of the primary beam to deflect the remaining ions from the source.
No noticeable beam signal difference was observed when the ion
rejector was on or off and so it is reasonable to assume at
least 99% of the fast particles from the primary oven are neutrals.

2. Experimental Procedure

Detector Filament Cleaning Process

The commercially produced tungsten filament used
contained less than 1% of Na₂O, K₂O, CaCl₂ and other impurities
before the sintering process. To reduce the alkali and other
impurities inside the wire and to reduce strain and possible
dislocations of the raw drawn tungsten, an extensive heat treat-
ment is necessary. The fibrous crystals in a polycrystalline
wire have the 110 axis preferentially along the wire direction.
The wire recrystallizes when heated and the resulting equiaxed
crystals have the same degree of alignment locally as the
original fiber structure. In this work the filament had been
heated to 1800°K for more than 8 hours. This does get rid of
most of the background alkali noise. For every data taking
cycle, the filament is baked out at 1600°K for 3 minutes to
clean the surface of contaminants. Then the temperature is
lowered to 1200°K in order to use the filament as a Langmuir-
Saha hot wire detector [48], or it is lowered to the "lukewarm"
region which corresponds to the highest temperature at which
thermal alkalis are not yet surface ionized. This clean surface is by no means a pure tungsten surface. It is possible that small amounts of oxygen atoms are still on the (110) and (112) crystalline surfaces, but the two loosely packed crystalline surfaces (100) and (111) [49] are indeed oxygen free. Besides oxygen there is a small amount of carbon that stays on the surface. Some carbon atoms will diffuse to the surface from inside the crystal while others may be the residue from the diffusion pump oil used.

Alkali Metal Beams

A systematic study of alkali pairs using sodium, potassium, rubidium, and cesium beams was carried out using each alkali alternately as the primary or secondary beam in combination with one of the other three alkalis. A total of twelve different combinations are reported here. The accelerating voltages applied to the detector filament for Na(mass number 23), K (39.1), Rb(85.47) and Cs(132.9) are 646, 380, 190 and 112 volts, respectively, with the magnet used. The resolution of the magnetic mass spectrometer \( R = \frac{V}{\Delta V} = \frac{M}{\Delta M} \) depends on the size of the entrance and exit slits. For a 0.010" entrance and 0.015" exit slit the resolution is about 80 [50].

The body temperatures of the primary and secondary ovens were adjusted differently for each element to obtain the
maximum stimulated ionization rate. From the vapor pressure
data of alkali metals, the best oven temperature range
corresponds to a vapor pressure between $10^{-4}$ to $10^{-3}$ torr.
These ovens were also equipped with water cooling coils for
a quick cool down to save cesium or rubidium.

Thermal speed atoms in the primary beam were filtered
out by the rejector which is shown in Figure 3-1(B). Under normal
operating conditions the ionization filament inside the primary
oven was heated to about 1400°K. Ninety-five percent or more
of the primary thermal beam was cut-off when the rejector was
running at a speed of 120 Hz or higher, depending on the oven
temperature and the alkali chosen. The fast beam signal relative
to the left-over thermal beam usually had a ratio between 2:1
to 1:1.

**Data Taking Cycle**

A typical data taking cycle is shown in Figure 3-4
in the form of a strip-chart recording. Initially, the surface
under study (tungsten filament of 10 mil dia.) is baked-out at
1600°K for 3 min. At first, as soon as possible after the bake-
out, the superthermal primary beam mass peak is located by a
quick mass scan in the expected mass range. This is necessary
because the superthermal atoms have enough kinetic energy
left after being ionized by kinetic surface ionization to cause
a significant apparent shift in the mass scan (approximately $1/3$
Typical Data Taking Cycle for S. S. I. Studies.

Stimulated surface ionization of K on tungsten by superthermal Na. The 18 Hz signal is from the upper half of the filament, being coated continuously with K, the 9 Hz signal is from the lower half (not coated). Mass spectrometric sweeps identify the species before and after a measurement (as shown). In the beginning, and occasionally later on, the mass spectrometer is switched from K⁺ to Na⁺ in order to obtain the time dependence of the Na⁺_fast signal. Sources temperatures: T_Na = 513⁰K, T_K = 333⁰K. Filament: Tungsten, 10 mil diameter, 6 cm long, heating current at 1.3A.

Fig. 3-4
of the primary accelerating voltage) when utilizing a magnetic mass spectrometer. Another bake-out follows. The "lukewarm" temperature not only depends on which alkali is used, but also on the beam intensity. Hirai et al. [51] demonstrated experimentally for a thermal potassium beam that the threshold temperature on a polycrystalline tungsten surface varies from $770^\circ K$ to $880^\circ K$ corresponding to a beam intensity range of $5.9 \times 10^9$ to $5.4 \times 10^{12}$ atoms/cm$^2$ sec.

After opening the primary beam shutter, the initial primary beam intensity $I_{10}$ (from the output signal of the Lock-In Amplifier tuned to 18 Hz) is recorded. Then the accelerating voltage corresponding to the two alkali masses is switched back and forth as time progresses. The stimulated surface ionized coating alkali ion signal $I_2$ and the fast beam ion signal $I_1$ are progressively recorded. Both the 9 Hz and 18 Hz signals are recorded simultaneously as they are measured by two parallel Lock-In Amplifiers. After the secondary beam shutter is opened for coating, one observes the build-up of the 18 Hz signal of the species used for coating. At the same time, the 9 Hz signal is monitored to check that the lower portion of the filament remains uncoated. The maximum surface coverages is largely determined by the temperature of the surface, but also by the coating beam intensity.
Typically, it takes several minutes to an hour to establish this equilibrium coat, at which time the final reading of \( I_2 \) of the signal due to stimulated surface ionization is taken. After subtracting background noise, we arbitrarily define the ratio \( R = \frac{I_2}{I_{10}} \) as efficiency (expressed in percentage).

Naturally, an absolute efficiency would require a knowledge of \( I_{10} \) and \( I_2 \) in absolute terms.

3. Results

The efficiency ratio \( R(\%) \) vs. kinetic energy (eV) is plotted on a double log scale as shown in Figure 3-5 to 3-7. Basically, the data points cover the range of primary beam kinetic energies in the region of 30 to 150 eV. In all cases, a least squares fit straight line is drawn through the experimental data points. A systematic and accurate measurement of every pair of alkali metals with variable primary oven, secondary oven and surface temperatures is very time consuming and is not the original intention of this work. A modest amount of time was initially spent for each pair of alkali metals in order to locate various temperature settings that would give the maximum signal output. Then one or more sets of data were taken. A list of the efficiency ratio for all possible pairs is presented in Table 1. The efficiency ratio \( R \) at 40 eV and at 120 eV is listed. The number in parentheses is the exponent in the energy dependence.
Efficiency Ratio

Energy Va

Fig. 3-5
SSI yield as function of incident energy.
( primary beam → coating beam )

Fig. 3-6
Fig. 3-7
(c) \( Rb \rightarrow Na \)

\[
\begin{array}{c}
\% \\
\hline \\
30 & 50 & 100 \\
30 & 50 & 100 \\
\end{array}
\]

(d) \( Cs \rightarrow Rb \)

\[
\begin{array}{c}
\% \\
\hline \\
30 & 50 & 100 \\
30 & 50 & 100 \\
\end{array}
\]

Fig. 3-7
<table>
<thead>
<tr>
<th>Coating Beam</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>-</td>
<td>13/110(1.3)</td>
<td>1.5/55(2.2)</td>
<td>0.9/100 (2.9)</td>
</tr>
<tr>
<td>K</td>
<td>4.7/29(1.1)</td>
<td>-</td>
<td>18/146(1.3)</td>
<td>19.5/336 (1.7)</td>
</tr>
<tr>
<td>Rb</td>
<td>1.4 /9.5(1.2)</td>
<td>0.9/7.7(1.3)</td>
<td>-</td>
<td>5.9/47(1.3)</td>
</tr>
<tr>
<td>Cs</td>
<td>0.5/6.0(1.5)</td>
<td>0.4/4.4(1.5)</td>
<td>2.6/13(1.0)</td>
<td>-</td>
</tr>
</tbody>
</table>

TABLE 1

Incident Beam

R(40 eV)%/R(120 eV)% (Slope)
A plot of the shift in the efficiency ratio as the surface temperature increases is shown in Figure 3-5(a). These curves are taken at five different detector-filament currents: 0.8, 1.2, 1.5, 1.62 and 1.8A, which corresponds to different temperatures. The temperature vs. current relationship can be found in Appendix I of this dissertation.

A higher temperature will increase the vibrational energy of the adsorbed alkali in the metal alkali potential well. This in turn reduces the energy needed to overcome the potential barrier and increases the efficiency ratio. On the other hand, a higher surface temperature reduces the residence time of the adsorbed alkali atoms which limits the coating coverage and reduces the efficiency ratio. In the case mentioned above, the yield increase from the reduced potential barrier is larger than the yield reduction due to loss of residence time, i.e. there is a net increase in the efficiency ratio.

An increase in the secondary oven temperature will cause an increase in the coating rate which then shifts the efficiency ratio curves upward as shown in Figure 3-5(b). The corresponding secondary oven temperatures are listed in brackets beside each curve. Efficiency curves for a sodium primary beam with rubidium and cesium coating beams are shown in Figure 3-6(a), (b) respectively.
similar results for a potassium primary beam source and sodium, rubidium and cesium as the secondary coating beams are presented in Figure 3-6(c), (d) and (e) respectively. Results for a rubidium primary beam and sodium, potassium and cesium secondary beams are in Figure 3-7(a), (b) and (c). With cesium as primary and sodium, potassium and rubidium as secondary beams we obtain the curves shown in Figure 3-7(d), (e) and (f).

A high ratio is achieved in the cesium and potassium pairs. For various temperature combinations the efficiency ratio as well as the slope of the curve changes quite drastically.

Energy Shift

There are mass peak shifts for both the primary fast beam and the stimulated surface ionization peaks relative to the corresponding thermal mass peaks. For stimulated surface ionization the shift for all different pairs of alkali beams is always around 2V. It is apparently independent of the primary beam kinetic energy. The shift for fast alkali beams on a lukewarm surface depends on the incoming energy. This shift can be explained as the result of the incoming fast atom reflecting as an ion from the surface such that not all the kinetic energy is transferred to the surface. A typical example is shown in Figure 3-8. If we plot the mass (focusing voltage) shift as the kinetic energy of the ion vs. incoming kinetic energy of the atom, a linear relationship in the range from
Kinetic energy of potassium ions formed by impact ionization as a function of incident energy of fast potassium. Insert: mass spectrum. Note slight shift of $K^+$ from fast beam with respect to $K^+$ from thermal beam. Ionization by direct impact with surface is differentiated from SSI by much larger kinetic energy of ion formed.

Fig. 3-8
10 to 120 eV of the primary beam energy results. From the slope of the least squares fit straight line we see that the ion retains approximately 30% of its incident kinetic energy as it leaves the surface.

4. Discussion

The mass shift of reflected primary particles has a few distinctive features, it is dependent on the incoming kinetic energy while it is independent of surface temperature and surface coating coverage. The primary beam signal is reduced as the coating coverage increases, and so we can assume that only those atoms that collide directly with the surface are formed by kinetic surface ionization. The SSI ions were found to have a mean kinetic energy of about 2 eV. Similar results are found in some sputtering experiments: Honig [52] studied the energy distribution of Ge$^+$ and Na$^+$ ions sputtered from a (111) plane of a Ge single crystal by Kr$^+$ ions in the energy range from 100 to 400 eV. The maximum of the distribution curve occurs at an energy of 2 eV for both species. There is one main difference between this experiment and sputtering experiments. In sputtering, the main interest is in the production of particles from the bulk of the target. In contrast, in this work, only the adsorbed surface layer species is detected with no noticeable W$^+$ signal. The number of bonds and bond strength for an individual atom inside the substrate
is stronger than that between an adsorbed particle and substrate. Consequently, in sputtering experiments the impinging particles usually have kinetic energies in the keV range and higher. A more detailed study should be carried out on a single crystalline plane such as the (100), (112), (111), or (110) surfaces. Varying the incident angle and observing the angular intensity distribution of the SSI ions from a single crystal plane could also reveal more information about the basic process behind it.

Evidence of SSI for Beam Species other than Alkali:

The original aim of the SSI study is the possibility of using this principle for a competitive detector for superthermal beam experiments. Litvak et al. [53] reported that when a neutral CH$_3$I molecular beam, with kinetic energy 2.5 to 3 eV, impinging upon a Re surface which is never exposed to an alkali beam before, a significant signal was found at the m/e ratio corresponding to K and Na ions. Those ions occurred only after strong heating of the Re surface. Those alkali atoms are believed to originate from the impurities inside the Re filament. The strong heating causes them to diffuse to the surface layer of the filament.

Gordon et al. [54] reported that the SSI principle was used to detect a hot H atomic beam (2900 °K, corresponding to a kinetic energy 43 eV at peak of the flux distribution). Pt, W, Mo and Ta filaments paired with K, Rb and Cs beam coating were tested. All combinations worked well. The stimulated
surface ionization and the bolometer detectors have comparable sensitivities for the hot H beam. However, the SSI detector is considerably less sensitive to the radiation from the furnace. Another advantage is that the thermal background noise can be eliminated by using an unheated filament. The SSI detector has a much more pronounced dependence on the kinetic energy of the beam particles than the bolometer. The ion signal disappeared completely when the beam temperature was reduced to 400 °K. This energy dependence is similar to the results we reported previously. The peak H atom flux at the detector was $10^{14}$ atoms/cm$^2$ sec, beams with three orders of magnitude weaker still yielding detectable signals. All these results certainly enhance our confidence in this new detector in principle.
CHAPTER IV

FORMATION OF NEGATIVE IONS ON A SURFACE

1. Apparatus

Vacuum System

A new vacuum system was built for this and all following experiments. It consists of two identical cubic stainless-steel vacuum chambers separated by a four inch diameter gate valve. The oven chamber is pumped by a 10" diffusion pump and the detector chamber by a 6" diffusion pump. Both diffusion pumps are equipped with Freon-12 cooled baffles to prevent backstreaming of pump oil into the vacuum chambers. A mechanical pump with 15 ft$^3$/min speed is used for foreline pumping. There is an automatic emergency system to cut off power to the diffusion pumps if the water cooling system breaks down. Two magnetic valves are mounted on the foreline to isolate the vacuum system from the foreline pump in the case of a power failure.

A block diagram of the vacuum system is shown in Figure 4-1. The main advantages of two smaller vacuum chambers instead of the big one are: (1) whenever there is a necessity to open one side of the vacuum system for a short period of time, the other side can still be kept under vacuum, (2) in the initial stage of pumping down the system and heating the ovens, the 4" gate valve is closed which keeps the outgassing contaminants of one chamber from the other.
SCHEMATIC OF VACUUM SYSTEM

Fig. 4-1
Under normal operating conditions, the foreline pressure is approximately 100 microns and the pressure readings for oven and detector chambers are $10^{-6}$ and $10^{-7}$ torr, respectively. Inside the liquid nitrogen shielding (refer to Figure 4-1) where the detector wire is located, the pressure is estimated to be in the order of $10^{-8}$ torr, or even lower. Under these vacuum conditions the main contaminants that have been absorbed on the surface are oxygen and hydrogen atoms.

**Quadrupole Mass Spectrometer**

A Balzer radio frequency quadrupole mass spectrometer (QMG 101) was mounted on a side plate of the detector chamber. It has two mass ranges, one from 0 to 100 and the other 10 to 400 atomic mass units. This commercial unit is specially designed for partial pressure measurements in high vacuum systems. The ionizer of the unit was replaced by a stainless steel plate with a hole which was covered by a tungsten mesh. This was used as the entrance for the ions and was at ground potential. A modification was made in the control unit to enable us to use the spectrometer to detect both positive and negative ions. Under operating vacuum conditions the position of the entrance of the Q.M.S. could be adjusted with respect to the filament under study.
Schematic of Apparatus

Fig. 4-2
A Bendix model 4029 channel electron multiplier was mounted at the exit of the quadrupole. The multiplier has an entrance cone of 8 mm diameter. The end of the spiral channel of the multiplier is open so that it can be used in both the analog and pulse counting mode. Since the Q.M.S. control unit only supplied the negative high voltage to the multiplier, a Keithley 246 power supply, which can provide high voltage of either polarity, was used. An outline of the circuit for the multiplier and its associated electronic block diagram is given in Figure 4-3. Typical high voltage values which were applied to the multiplier leads are given in the figure.

In this part of the experiment the Q.M.S. is used to identify the primary beam, the coating beam positive ions and the negative oxygen ions. An inherent disadvantage of the R.F. quadrupole mass spectrometers are their degraded performance at every low mass range around mass one. For the studies on negative hydrogen and deuterium ions an additional magnetic mass spectrometer for the lower mass range was therefore installed.

**Magnetic Mass Spectrometer**

The magnetic mass spectrometer is the same one used in the previous stimulated surface ionization experiment. The magnets were turned around to reverse the direction of the
Channel Electron Multiplier circuit for positive or negative ions.
the magnetic field. Steel bolts and rods were placed parallel to the magnets in order to reduce the field strength in the path of the ions. The resulting accelerating voltages are -400, -200, and -25 volts for hydrogen, deuterium and oxygen atomic ions respectively. A laboratory made pulse amplifier and integrator were linked to the Bendix magnetic multiplier. A detailed drawing is presented in Figure 4-4.

Gas Feeding

Deuterium gas was fed into the detection chamber through a needle valve. A tube was used to connect the other end of the needle valve with a hypodermic needle which would spray the gas onto the filament from about 1 cm away. Initially oxygen and hydrogen gases were fed in through the same needle valve. During the operation of the apparatus it was found that the vacuum system, even under optimum conditions, still contained more than enough background oxygen and hydrogen gases for our experiments.

2. Experimental Procedures

For a typical data taking cycle, the filament (10 mil. tungsten wire) is first baked-out at a bright yellow glow (5A, 1850°K) for three minutes. Since the surface is surrounded by a liquid nitrogen cooled copper housing, the pump oil vapour, water vapour and other organic vapours are reduced to a negligible
Magnetic Mass Spectrometer
and its electronic circuit.

Fig. 4-4
amount around the filament. The remaining residual gases are mainly hydrogen, oxygen, nitrogen and carbon monoxide. After the bake-out procedure the surface is clean. Then the heating current is turned down and there is a 30 sec. time interval for the surface to settle down to the desired temperature. During this 30 sec. time span the surface is partially covered by the remaining background gases.

The shutters for the primary fast neutral beam and secondary coating beam are now opened, usually simultaneously. The negative ions pass through the quadrupole mass spectrometer or through the magnetic mass spectrometer when a negative accelerating voltage is applied to the filament. The amplified negative ion signal from the magnetic mass spectrometer is plotted on a time based chart recorder. On the other hand the negative ion signal from the quadrupole mass spectrometer can be fed into a PDP-8 controlled signal averager. A more detailed description of the operation and the interface of the mini computer controlled system will be given in the next chapter, since this arrangement was originally designed for that experiment.

The variables which can be manipulated are the temperature of the primary and coating beam ovens, the speed of the primary beam thermal particle rejector, the surface temperature of the filament and the kinetic energy of the primary fast
particles. The temperature of the primary oven is adjusted to obtain a maximum fast beam intensity. Adjusting the coating oven temperature results in a higher or lower coating beam intensity which affects the alkali coverage on the filament surface in a fixed time span. Changing the speed of the primary thermal particle rejector affects the surface coverage by primary alkali atoms. The relationship between the rejector speed and the left over thermal beam intensity is described in Appendix 2. The filament surface temperature affects not only the surface coverage of all the gas and alkali atoms but also increases the mobility of the adsorbed particles on the surface.

3. Results

H⁻ Formation

The negative ion signals were collected through the 90° sector magnetic mass spectrometer which covers the mass range from 1 to 20 atomic mass units. The background pressure inside the detector chamber is normally around $2 \times 10^{-7}$ torr and inside the liquid nitrogen housing is estimated at $10^{-8}$ torr or better. It is found that under optimum alkali surface coverage (about a half physical layer) the largest negative ion signal was in fact $H^-$. The $O^-$ signal under this coverage is about one tenth of the $H^-$ signal.
At a pressure of $2 \times 10^{-6}$ torr it was found that feeding hydrogen or oxygen gas onto the filament only slightly reduced the time span to attain the maximum signal output. This indicates that there is hydrogen and oxygen adsorbed on the surface from background gases. Figure 4-5 is a typical result of the $H^-$ signal evolution with increasing sodium coverage. The insert is a mass spectrum of $H^-$ and $O^-$ signals which is taken at the maximum intensity.

The effects of alkali coverage is best demonstrated in Figure 4-6. In this case the primary potassium beam oven temperature is at $416^0K$ which corresponds to a $3 \times 10^{-4}$ torr vapour pressure inside the oven. The ionization filament of the oven is at $590^0K$ and the fast K atoms are impinging onto the surface with a kinetic energy of 100 eV. When the selector speed is at 162 Hz, there are practically no thermal K atoms passing through the rejector to be adsorbed on the surface. No $H^-$ signal was observed even 60 minutes after opening the beam shutter. When the selector speed is at 10 Hz the primary K thermal beam intensity is about $2 \times 10^{10}$ (no. of atoms/cm$^2$ sec). If we assume that all the thermal K atoms arriving at the surface were adsorbed, then the surface K coverage after 1 hour was less than one tenth of a layer. Curve number 2 indicates only a weak $H^-$ signal after 60 minutes coating by the thermal component of the primary beam. Curves number 3, 4, 5, 6 were taken when
Time dependence of $\text{H}^-$ signal, obtained with 100 eV neutral K beam impinging upon Na covered W surface (at 560 °K). Coating source: 519 °K, 2.25 mm diameter aperture. Primary beam source at 401 °K; aperture .25 mm x 9.5 mm. Distance to source: 22 cm. Rejeter speed at 10 Hz. Insert, Mass spectrum for masses 0 to 20. Peak heights are in comparable units.

Fig. 4-5
100 V<sub>a</sub> Φ on W

\[ T_K = 416^\circ K \]
Selector Speed
No. 1, 3, 4, 5, 6 → 162 Hz
No. 2 → 10 Hz

\[ T_{Na} = 551^\circ K \]
6
5
\[ T_{Na} = 532^\circ K \]
\[ T_{Na} = 512^\circ K \]
4
3
\[ T_{Na} = 500^\circ K \]

Time dependence \( H^- \) signal.

Fig. 4-6
$H^-$ yield as function of surface temperature

Fig. 4-7
the secondary Na coating beam was allowed to reach the surface. Higher intensity of the coating beam corresponds to a higher \( H^- \) signal after the same time span.

The surface temperature dependence of \( H^- \) production is plotted in Figure 4-7. Here, a series of measurements of maximum production of \( H^- \) were carried out with the filament heated at different D.C. currents. The results indicate that when the surface is at 520\(^\circ\)K the maximum intensity could be achieved. The lower production rate at lower temperatures is probably due to surface contamination by pump oil vapour. At a temperature higher than 760\(^\circ\)K no \( H^- \) ions could be detected. From flash desorption data [55] we know that most adsorbed hydrogen on a clean tungsten surface desorbs as \( H_2 \) at 400 - 600\(^\circ\)K, which is why the \( H^- \) intensity is reduced at higher surface temperatures.

**0^- Formation**

The 0^- signals generally behave similarly to the \( H^- \) signals. The necessity for the alkali coating is demonstrated in Figure 4-8. In order to stretch the time scale, the minimum oxygen pressure (background) was used. The 0^- ions were detected through the PDP8E controlled quadrupole mass spectrometer. The primary thermal particle rejector allowed suppression of the thermal component of the otherwise superthermal potassium beam. The rejector speeds of 10, 40, 80 and 163 Hz lead to a rejection of the thermal beam down to 27.4%,
Time dependence of $O^-$ signal, same conditions as Fig. 4-5, except surface temperature at 300 K. Open symbols: No Na coating. Full circles: same as open circles, except with Na coating applied.
18.4%, 13.4% and 1.1% of the intensity when measured with the rejector removed. The increased yield in $\text{O}^-$ at low rejector speed settings indicates the importance of the thermal potassium component as a coating. When a coating is provided by means of a separate beam (here, Na), this is proven even more strikingly. The solid circle data and the open circle data in Figure 4-8 are comparable, since the only difference between the two runs is the coating action by a separate sodium beam. All other parameters were kept the same.

**D⁻ Formation**

First the detector chamber was pumped down to a $2 \times 10^{-7}$ torr ion gauge pressure reading outside the LN₂ shield. Then the filament was baked out to $1600^\circ$K. Then, still during bakeout, the needle valve was opened and both gate valves connected to the detector chamber were closed. The pressure reading of the deuterium gas is more than $10^{-5}$ torr. After a three minute bake out in the presence of deuterium gas the excess deuterium gas was pumped out. The $D_2$ pressure was maintained at $2 \times 10^{-6}$ torr during the data taking process. By following the above procedure we are sure that the $D_2$ gas density is at least one order of magnitude higher than all the other vapours around the filament.

The $D^-$ yield follows the same pattern as $H^-$ and $O^-$, i.e. without alkali coating no $D^-$ could be detected. The striking
difference is that the D⁻ intensity is always smaller than O⁻ or H⁻ intensity. When the D₂ gas was sprayed onto the filament the D⁻ signal appeared while the H⁻ signal was reduced relative to the O⁻ signal. In a series of runs it was found that the D⁻ intensity is always only 15% of the H⁻ intensity or less. A typical mass spectrum using the magnetic mass spectrometer is shown in Figure 4-9. Here a 100 eV fast potassium beam was used with a sodium coating beam. When the D⁻ intensity reached maximum the mass spectrum was taken.

**Isotope Effect**

In our study, the negative H⁻ and D⁻ are produced on a polycrystalline W surface coated by an alkali beam under the bombardment of a superthermal potassium neutral beam (30 - 200 eV). No negative ion signal is detectable without thermal alkali beam coating.

The generally accepted explanation is that the work function of the metal surface is reduced when alkali atoms are co-adsorbed with H or D atoms. Therefore, a general increase in negative ion yield from surfaces under bombardment with energetic particles is expected which is of equal or at least comparable size for both isotopes. However, in our experiment we found the D⁻ signal much smaller than the H⁻ signal. The residual hydrogen background pressure in our experiment is $i_H = 5 \times 10^{-8}$ torr measured with a partial pressure gauge. The
$H^-$, $D^-$ and $O^-$ mass spectrum at their maximum intensities, same settings as Fig. 4-5.

Fig. 4-9
gas spectrum around the tungsten surface inside the LN₂ cooled copper housing is shown in the Appendix III of this dissertation. The filament is first baked-out at 1600°K, then exposed (still at bakeout) to a D₂ atmosphere of 2.6×10⁻⁵ torr for three minutes to remove oxygen from the surface. After bakeout the chamber deuterium pressure was maintained at i_D = 5×10⁻⁶ torr measured with a Bayard Alpert ion gauge which really measures number density rather than pressure.

The ratio of fluxes arriving on the surface is

\[
\frac{j_D}{j_H} = \sqrt{\frac{m_H}{m_D}} \cdot \frac{i_D}{i_H}
\]

(4-1)

where \(i_D\) and \(i_H\) are the pressure readings for deuterium and hydrogen respectively and \(m_H/m_D\) is the mass ratio of hydrogen to deuterium molecules.

Other surface studies [56] indicate that the sticking coefficient is about the same for these isotopes, so that the ratio of coverages of adsorbed D to H atoms is maintained in accordance with the fluxes of incoming particles leading to

\[
\frac{\theta_D}{\theta_H} = \sqrt{\frac{m_H}{m_D}} \cdot \frac{i_D}{i_H}
\]

(4-2)

Our results from several runs indicate that the H⁻ signal is about seven times higher than the D⁻ signal.
The proposed explanation of the different efficiencies of these two isotopes is outlined below. It incorporates certain features of a so-called "post collision interaction". The probability for an electron initially to attach itself to the hydrogen or deuterium atom is likely to be the same for both species, being determined by essentially identical electronic configurations. Whenever an impinging superthermal particle initiates a desorption process which may result in a negative ion, the same probability \( P_0 \) applies to the initial formation of \( D^- \) as well as \( H^- \), so that initially \( D^- \) ions/\( H^- \) ions is the same as the ratio in coverage of the two isotopes. However, as the desorbing negative ion is receding from the surface, at each distance \( z \) from the surface, it may decay into the neutral atom and an electron returning to the surface or a free electron. The lifetime \( \tau = h/\Gamma \) is assumed to be only a function of \( z \) for reasons similar to the above, where \( z \) is the distance to the surface. The overall probability for the negative ion to survive is then

\[
P = P_0 \exp \left( -\int_0^\infty \frac{dt}{\tau} \right)
\]

where \( t \) is the time. The receding negative ion interacts with the surface according to a potential \( V(z) \). Its instantaneous speed \( v \) at each distance \( z \) is
\[ v(z) = \frac{2[E' - V(z)]^{1/2}}{m} \]  

(4-4)

where \( E' \) is the final kinetic energy and \( m \) the mass of the desorbing negative ion. This results in

\[ P = P_0 \exp \left( -\sqrt{m \cdot G(E')} \right) \]  

(4-5)

where

\[ G(E') = \frac{1}{\pi} \int_{z_0}^{\infty} \frac{T(z) dz}{[2(E' - V(z))]^{3/2}} \]  

(4-6)

Thus, at a given final kinetic energy \( E' \), the production ratio of \( D^- \) versus \( H^- \) is

\[ \frac{P_{D^-}}{P_{H^-}} = \exp \left[ - (\bar{m}_D - \bar{m}_H) \cdot G(E') \right] \]  

(4-7)

If the surface coverage is not the same for both isotopes, this ratio must be multiplied by the ratio in coverage of the two isotopes. When ions of all final energies \( E' \) are collected, \( G(E') \) is replaced by an appropriate average, \( \overline{G} \). The negative ion signal ratio is
\[
\frac{I_D^-}{I_H^-} = \frac{\bar{P}_D^-}{\bar{P}_H^-} \times \left( \frac{\theta_D}{\theta_H} \right) \quad (4-8)
\]

where \( \theta_D/\theta_H \) is the coverage ratio of the respective isotopes.

In our experiments we find \( I_D^-/I_H^- \approx 1/7 \) in the average over several runs. Combining this with Eq. (4-2) and using the quoted value, this leads to

\[
\exp[0.4142\tilde{G}] \sim 500 \quad (4-9)
\]

and

\[
\tilde{G} \sim 15.
\]

Similar isotope effects were reported in other experiments. For the formation of \( H^- \) and \( D^- \) in molecular hydrogen and deuterium by low energy electrons, Rapp et al. [57] found a ratio of 200 leading to \( \tilde{G} \approx 13 \). Madey [58] first observed that the ratio for electron stimulated desorption of \( H^+ \) and \( D^+ \) was \( \geq 100 \) on \( W(100) \) surface leading to \( \tilde{G} \approx 11 \).

Menzel [59] reported a similar effect: A ratio of 154 on \( W(100) \), leading to \( \tilde{G} \approx 12 \). For similar potentials \( V(z) \) and reciprocal lifetimes \( \Gamma(z)/h \) one expects similar values of \( \tilde{G} \), according to Eq. (4-6). This is verified above.
CHAPTER V
CHEMICAL REACTIONS
ALKALI DIMER FORMATION ON THE SURFACE

1. Apparatus

The basic apparatus arrangement is the same as before, but the magnetic mass analyser is removed. A new thermal particle rejector came into service in the latter part of this work. It consisted of seven thin stainless steel disks instead of a single thick disk. It proved far more effective. It is completely capable of cutting off the thermal component of the primary beam passing through it. Still, about 1% of the thermal particles bypass the rejector by bouncing off walls.

Sodium and potassium metals are chosen in this work for a number of reasons. The various mass numbers of interest for this combination are 23(Na$^+$), 39(K$^+$), 46(Na$_2$$^+$), 62(KNa$^+$) and 78(K$_2$$^+$) which are in the first mass range (1 - 100) of the quadrupole mass spectrometer, which has higher resolution.

The next best choice would be the potassium and rubidium combination with mass number 39(K$^+$), 78(K$_2$$^+$), 85(Rb$^+$), 124(KRb$^+$) and 170(Rb$_2$$^+$) of interest. In a typical run the maximum signal of molecular ions represents only three percent of the corresponding atomic ion signal. When the channeltron high
voltage is set for detection of molecular ions, a large signal is produced at mass 85, corresponding to the primary rubidium beam. This distorts the molecular ion signal at mass 78. In the latter part of this work the mass sweep ramp voltage is replaced by a step voltage controlled by the PDP8 mini computer. There is still a large pulse from the channeltron when the mass sweep quickly passes through mass 78. Thus, the sodium and potassium combination is certainly more economical and easier to handle than the combination of cesium and rubidium.

**Local Mode**

The quadrupole mass control can be set in either the local mode or remote mode. In the local mode the mass sweep is set at a speed of 2.5 millisec per mass number. After receiving the start signal, the signal averager gives a pulse to the quadrupole control unit to trigger a mass sweep every 100 millisec. This is the time needed to sweep from mass number 42 to 82. The mass spectrum is then in the 256 channels of the signal averager's memory.

After every $2^N$ sweeps, ($N$ can be entered through the teletype) the averaged mass spectrum is transferred to a buffer in the PDP8 memory. Part of the spectrum between mass number 62 and 78 is chosen as the background signal. This is the dark current of the channeltron. The integrated mass peaks for $\text{Na}_2^+$,
$\text{KNa}^+$ and $\text{K}_2^+$ are then background adjusted and the resulting three values are stored into three separate buffers, one each for $\text{Na}_2^+$, $\text{KNa}^+$, and for $\text{K}_2^+$. This data taking and data handling sequence is repeated 128 times. Finally the three buffers are stored on a cassette tape for later reference and plotted out on an X-Y recorder.

Remote Mode

When the quadrupole mass control is set to the remote mode, the PDP8 controls the mass sweep in a stepwise fashion. Firstly, the exact mass peak locations are identified. The basic data taking cycle is then as follows. Rather than performing a piece-wise mass sweep through each of the three mass peaks, the computer jumps from mass peak to mass peak, dwelling there for a period of time, adjustable by the appropriate teletype input. An exponential averaging is performed for $N$ such cycles ($N$ controlled by teletype), and after adjusting for the background, the results are again stored into the three separate buffers mentioned above. The remaining steps are the same as before. There are two advantages in having the computer directly controlling the mass sweeps. First, the signal averager can be eliminated and used in other experiments. Second, most of the dwell time is then spent on the mass peaks, thus reducing the statistical errors. A block diagram for the remote data taking procedure is shown in Figure 5-1.

88
PDP8 mini-computer block diagram

Fig. 5-1
2. **Experimental Procedure**

When we use a new filament, the 10 mil diameter tungsten wire is first baked out by D.C. heating at $1600^\circ K$ for more than 12 hours and then at $2400^\circ K$ for four hours to reduce ion background. Then, before each run, the polycrystalline tungsten surface is heated up to $1600$, $1850$, $2150$ or $2400^\circ K$, for three minutes. A 30 sec time span is then allowed for the surface to settle at the desired temperature. Immediately afterward the computer controlled data taking program is started and at the same time one or both of the beam flags are opened. The molecular ions of $Na_2^+$, $NaK^+$ and $K_2^+$ formed by way of chemical reaction between superthermal primary atoms and the coating alkali atoms are drawn into the quadrupole mass spectrometer.

3. **Results and Discussion**

$\theta < 1$ and $T(bake\ out) \sim 1600^\circ K$

The first step, of course, is to establish that a molecule is indeed formed by the reaction of a fast superthermal alkali atom with an adsorbed alkali atom on the surface. To avoid the possibility that alkali molecular ions form in the primary or secondary beam before arriving at the surface, or that two adsorbed alkali particles, through their thermal energy motion, combine to a molecule on the surface, two different species of alkali metals are chosen. In this case, the primary beam is
potassium and the coating beam is sodium. It was found that the KNa\(^+\) production is largely due to the superthermal potassium beam with little effect on whether or not other potassium has been deposited previously, or is simultaneously impinging at thermal energy. This is shown in Figure 5-2 where several runs were taken at a constant Na coating rate. The rejector speeds of 10 Hz, 40 Hz, 84 Hz and 159 Hz correspond to a rejection of the thermal beam component down to 27.4\%, 18.4\%, 12.3\% and 1.2\% of the intensity measured with the rejector removed. Note that the start up portion of the curve is the same for all runs, whereas the curves split later on. This is probably due to a larger coverage from thermal potassium, thus reducing the chance for a fast K atom to meet an Na atom adsorbed on the tungsten surface. This leads us to believe that the most important process is indeed that a superthermal K atom somehow picks up a previously adsorbed Na atom on the surface.

In order to elucidate the validity of this model, we ran a separate series of measurements at 150 Hz rejector speed where in one case, the superthermal K beam and thermal Na beam were switched on simultaneously after bake out; while in the other cases one of the beams was delayed. It was found that a delay of the coating Na beam made no difference except for the corresponding overall shift on the time scale as shown in Figure 5-3.
Formation of NaK⁺ ions on W surface as a function of time. Various rejector speeds which correspond to different thermal K coating rates allow a study of the influence of the thermal potassium component.

Fig. 5-2
On the other hand, the effect of a delay of the superthermal primary beam (indicated by arrows) is shown in Figure 5-4. The delayed curve reaches full height immediately after switching on the superthermal beam and then merges with the underlayed curve. Contamination of a clean tungsten surface by adsorption of oxygen or hydrogen atoms increases the electron work function. This is in turn increases the ion formation both by surface ionization of thermal alkali atoms on a hot surface and by collisional ionization of fast alkali atoms on a cold or lukewarm surface. However, contrary to the above-mentioned cases, the contamination of a clean tungsten surface actually reduces the molecular ion signal as shown in Figure 5-3. The maximum KNa\(^+\) signals are progressively lower as the delay time increases.

Two possible explanation can be given, (A) the adsorbed oxygen and hydrogen atoms block the superthermal atom from meeting an adsorbed alkali atom, or (B) oxygen and hydrogen atoms change the electronic structure of the adsorbed alkali which in turn reduces the chemical reaction cross section so that the atoms are less likely to form a molecule even though the superthermal atoms do have a chance to meet the adsorbed alkali atoms.

With a superthermal/thermal potassium beam reacting with adsorbed sodium atoms on the tungsten surface, not only KNa\(^+\) ions were collected but also Na\(^+_2\) and K\(^+_2\) ions. If we assume all these reactions to be through one process only
Time dependence of NaK⁺ signal. Same conditions as Fig. 5-2. The fast K beam shutter opens at time 0 min and the Na beam shutter opens at 0, 4 and 7th min respectively.
Effect of delaying the superthermal potassium beam. Arrows indicate the delay.

Fig. 5-4
(a direct pick up of an adsorbed alkali by a fast atom), then certainly it is impossible to reason how the Na\textsuperscript{+} ions are formed. The other explanation is that it is not a direct pick up process. The fast atom may travel on the surface before forming a molecule, so it is possible for such a K atom moving on the surface to transfer part of its kinetic energy to an adsorbed Na atom. Then this fast, though adsorbed, Na atom can form a molecule with another adsorbed Na atom.

\textbf{\(\beta\)-Maximum}

From the previous section we conclude that the dimers detected are indeed originally formed on the tungsten surface, not somewhere else. In this section we take a close look at the variation of the signal intensity versus surface coverage. From literature \cite{60}, the sticking coefficient \(s\) is one for an alkali atom with thermal energy impinging onto a cold or warm surface (surface temperature below lukewarm condition), when the surface adatom coverage is less than one monolayer. As far as we know, there is no information to indicate how the sticking coefficient behaves for a coverage greater than one monolayer for a warm surface. If we assume in our case that the superthermal beam has no significant effect on the sticking coefficient for the coating beam, the coverage as a function of time is given by \(\theta(t) = \frac{\dot{n}t}{\rho}\), where \(\theta\) is the atomic layer, \(\dot{n}\) is the coating beam intensity (not of
atoms/sec cm²), ρ is the tungsten surface atom density (no. of W atoms/cm²) and t is the time in seconds.

Fig. 5-5 shows that the time duration for the K₂⁺ signal to attain a maximum value (β-maximum) is dependent on the primary coating beam intensity which is adjusted by varying the angular speed of the rejector. The β-maximum is reached in 10 minutes after the opening of the beam shutter when the rejector speed is 10 Hz. With a rejector speed of 80 Hz, the time needed is 45 minutes. The ratio 45/10 is reciprocally equal to the coating beam intensities, i.e. the coating beam intensity at 10 Hz is 4.5 times larger than at 80 Hz. If the sticking coefficient is indeed 1, then this indicates that a β-maximum is reached when the surface coverage of potassium is at a certain fraction of a monolayer.

γ-Maximum

Initially the dimer signal intensity increases, then after reaching a maximum value, it gradually declines. This behaviour applies to all three dimer ions: Na₂⁺, NaK⁺ and K₂⁺. Exposing the surface under the coating beam for a longer time period, the signal intensity could turn upward to a maximum value, which is designated as γ, for one or both the Na₂⁺ and K₂⁺ signals. The existence of γ-maximum depends on a strong coating beam intensity. Fig. 5-6 gives a typical
$K^+_2$ intensity versus time with various rejector speeds (i.e., various thermal K beam coating rate, see Appendix II).

Fig. 5-5
example, here we can consider that there are three beams impinging on the surface: a primary potassium beam with 100 eV energy, a thermal coating K of the rejector and a thermal Na coating beam. The dimer signals reach a maximum (β) about 4.5 minutes after opening the beam shutters. In the experiment shown in Fig. 5-6, the second Na coating beam has a stronger intensity compared to the thermal K coating beam intensity. The $Na_2^+$ signal, after reaching a minimum at 20 minutes, turns upward again to a γ maximum, while both the $K_2^+$ and $KNa^+$ curves keep going downward. If one reduced the secondary Na beam intensity to a degree such that the thermal beam K intensity was much larger than the Na beam, the $K_2^+$ and not the $Na_2^+$ signal would have a γ-maximum. From the geometry of the apparatus and oven temperature, a calculation was performed to determine the time needed for the build up of a monolayer coverage on the tungsten surface. The method of calculation is contained in Appendix IV. It is found that the minimum $Na_2^+$ signal in Fig. 5-6 at 20 minutes should be the starting time for building up of the second layer. Since the second monolayer could begin to build up before the first one is completed [61], a gradual transition will occur between layers. The fact that under no circumstances can one produce a so-called γ-maximum for the NaK$^+$ signal leads us to surmise that either the mechanism for dimer formation on the second layer is quite
Time dependence $\text{NaK}^+$, $\text{K}_2^+$ and $\text{Na}_2^+$ intensities. Rejector speed 5 Hz.

Fig. 5-6
different than that on the first layer, or that some conditions to form a mixed dimer, like KNa+, are not met on the second layer.

**α-Maximum**

When the filament is baked out at higher temperature (7 A) for 1 minute and then allowed to stabilize at a desired surface temperature for 30 seconds, the dimer signals versus time curves change. An extra maximum (α) appears at a much lower coverage (~ 0.1 layer) as shown in Fig. 5-7. Since all other parameters remain unchanged through repeated runs, this maximum (α) could only correspond to the higher baked-out temperature. The α peak which puzzled us for quite a while was first thought to be due to a surface contamination from the vacuum system which we had not encountered before. After rechecking the vacuum system, changing to sodium as the primary beam element, replacing the detector tungsten filament and so on, it still appeared that only by baking out the filament to 2400°K could an α-maximum appear. Actually, because of the minor improvement in the vacuum pressure, the α maximum appeared more dominant.

In the experiment shown in Fig. 5-8, a relationship between longer bake-out time at 7 A and the dimer signals was obtained, where only a superthermal Na beam (100 eV) and thermal Na beam were used. The longer the bake-out time of 3 minutes
Time dependence $\text{KNa}^+$, $\text{Na}^+$ and $\text{K}^+$ intensities, with 7 A and 1 min. bake-out procedure.

Fig. 5-7
to 10 minutes the more pronounced the θ-maximum. Through literature we conclude that the θ maximum is promoted by carbon which diffuses onto the surface through high temperature bake-out in a good high vacuum. This leads us to propose a new model as described in the next sections.

Carburized Tungsten Surface

The carburized tungsten surface has always been an interesting subject for surface physicists. Carburization of W(110) surface by methane was reported by Bauer [62]. Boudart et al. [63] reported carburization of (110), (100) and (111) surfaces of W by methane and cyclopropane. Tharp et al. [64] have reported similar carbide layers on W(110) after heating freshly-prepared W crystals in a vacuum. Chen et al. [65] reported various stable carbon structures on (112)W. Unlike most of the other adsorbed particles these carbon layers cannot be removed by heating the surface at elevated temperatures in a high vacuum. They can be removed by repeated oxidation followed by flashing to high temperatures [66].

Basically the carbon layers come from two sources. First, carbon is diffused from the bulk tungsten to the surface by heating at 2500K. Second, it comes from dissociative adsorption of various hydrocarbon compounds which are present in the vacuum system. Upon heating the surface, the hydrogen will desorb from the surface leaving carbon atoms tightly bonded with
$\beta$ and $\alpha$ intensities versus time with different bake-out time spans.

Fig. 5-8
the tungsten atoms.

Interesting effects have been reported concerning carbon covered surfaces. Radon [67] found that the work function for a polycrystalline tungsten surface is linearly increasing from 4.5 eV with an increase in carbon coverage and then goes asymptotically to 4.7 eV, which agrees with the value proposed for graphite. Hurkmans et al. [10] reported that the residence time for hyperthermal sodium atoms on W(110) surface is reduced by a factor of 3 just by heating the surface at 2500 K for about 30 sec. The reduction is believed to be due to the carbon that diffuses from the bulk.

The removal of the carbon from the surface by oxygen treatment is as follows. The oxygen molecules are first, through dissociative adsorption process, adsorbed as atomic oxygen on the surface. When the temperature is raised to 1200 K the atomic oxygen becomes very mobile and is hopping on the surface. This results in a high probability of formation of CO which desorbs at this temperature. If this is correct, isotopic mixing should be observed for CO on the surface. Coymour and King have reported a series of exchange experiments in which the W surface was presaturated with \(^{12}C^{16}O\) and then exposed to \(^{18}O^{18}C\). CO desorption spectra were observed at masses 28 and 30 and confirmed this idea. Since excess oxygen on the surface will desorb at temperatures higher than those required for desorption of CO, flashing the
Surface to 2500°K will desorb excess oxygen. Repeating these processes is essential in order to obtain a truly clean surface.

The Formation of Dimers on Carburized Tungsten

The formations of dimers on a carburized tungsten surface are progressively higher as the bake-out time increases which corresponds to higher carbon concentration. The relationship between bake-out time and concentration can be expressed as follows:

\[
dN = k \rho dt - \sigma j_o N dt
\]

\[
N(t) = \frac{k \rho}{\sigma j_o} \left( 1 - e^{-\sigma j_o t} \right)
\]

where \( N \) is the number of carbon atoms per unit area, \( \rho \) is the carbon concentration inside the bulk, \( j_o \) is the oxygen flux, \( t \) is the time, \( k \) is the diffusion constant which is a function of surface temperature and \( \sigma \) is the probability of CO formation.

One of the features of the carbon promoted \( \sigma \), maximum is that it always occurs at low alkali coverage. This is one indication that the carbon concentration must be very low, possibly 0.02 fractional layers. In the low alkali coverage region the carbon atoms produce preferable adsorption sites for alkali atoms. Furthermore, the dimer formation probability for a carburized tungsten surface is at least one order of magnitude higher than a clean surface.
The initial upswing of the carbon promoted maxima is very steep in Fig. 5-8. A series of experiments were carried out to monitor the rate of dimer formation with respect to different alkali coating rates. The results are plotted in Fig. 5-9a. The sodium beam intensity in terms of the number of Na atoms per cm$^2$ per sec is written on each curve. The linear relationship between an increase in the Na$_2^+$ rate and Na coating rate is found by taking the initial slope of each curve and plotting this versus the coating rate (see Fig. 5-9b). The deviation from a straight line can be attributed to the time resolution of the curves. All the data were taken under a background pressure of approximately $10^{-8}$ torr. Reducing the coating beam intensity prolongs the whole data taking process accordingly (i.e. time resolution is improved) with side effects from background gas contamination hardly noticeable. Thus, we find the LN$_2$ shield around the surface under study to be very effective, leading to good control of the surface for 15 ~ 20 minutes, more than enough for the studies described. If, however, U.H.V. methods could be applied background contamination could be excluded with absolute certainty.
Fig. 5-9a: Time dependence of the $\text{Na}^+_2$ signal as a function of Na-coating rate. Surface temperature $T = 725^\circ\text{K}$, 100 eV Na fast beam.
CHAPTER VI

A Proposed Theoretical Model

1.1 Underlying Concepts

With the above-mentioned improvements concerning the vacuum system and data handling and with the high temperature bake-out procedure at 2400°K implemented the persistent appearance of the α-peak as well as one or more γ-maxima could no longer be explained in terms of a single adsorption energy. Consequently, we now introduce a basic theory of adsorption of a single species, assuming several energy levels $E_v$ at which this species may be adsorbed. The index $v$ identifies the particular energy level. We denote by $g_v$ the number of adsorption quantum states per unit area which are associated with the energy level $E_v$. Thus $g_v$ describes the capacity of adsorption level $E_v$. Let $N_v$ be the number of atoms or molecules actually adsorbed in the level $E_v$, i.e. occupying one of the $g_v$ available quantum states. Then, $N_v/g_v$ represents the occupancy of level $E_v$, denoted by $\Theta_v$. Each such quantum state is characterized by a set of quantum numbers, including the spatial coordinates of the equilibrium position at each adsorption site. Then each available quantum state would be occupied by either one adparticle or none. Furthermore, as long as we have essentially single species coating, an interchange of two adparticles of the same species is indistinguishable from the original situation, as far.
as adsorption is concerned.

These two facts lead to the probability \( W_{\nu} \) to have the level \( E_{\nu} \) occupied as

\[
W_{\nu} = \frac{g_{\nu}!}{N_{\nu}!(g_{\nu}-N_{\nu})!}
\]  

(6-1)

By maximizing the total probability

\[
W_{\text{total}} = \prod_{\nu} \frac{g_{\nu}!}{N_{\nu}!(g_{\nu}-N_{\nu})!}
\]  

(6-2)

and incorporating the boundary conditions.

\[
N_{\text{total}} = \sum_{\nu} N_{\nu}
\]  

(6-3)

for the total number of adparticles per unit area as well as

\[
E_{\text{total}} = \sum_{\nu} E_{\nu} N_{\nu}
\]  

(6-4)

for the total energy of the adparticles, we arrive at

\[
N_{\nu} = \frac{g_{\nu}}{e_{\nu} - e_{F} + 1}
\]  

(6-5)

in complete analogy to the case of Fermi statistics. Here,
\( \epsilon_v = E_v/kT \) and \( \epsilon_F = E_F/kT \), \( E_F \) being the "Fermi level"; \( k \) the Boltzmann constant. It should be noted that no claim is made that the adsorbed particles are indeed fermions, but only that as far as adsorption is concerned they behave according to Fermi statistics. Also note that the Fermi level \( E_F \) is, at present, nothing but a parameter which came in as an integration constant on the energy scale to describe the total number \( N_{\text{total}} \) or any of the other quantities to be derived. It does not imply other connotations like overall electrostatic balance, or other, as it does for electrons in a metal.

In analogy to normal usage, \( \theta_v \) will also be called the coverage of the sublayer \( v \),

\[
\theta_v = \frac{N_v}{g_v} = \frac{1}{e^{\frac{\epsilon_v - \epsilon_F}{kT}} + 1} \tag{6-6}
\]

which spans the range 0 to 1 as \( \epsilon_F \) goes from \(-\infty\) to \(+\infty\). If there were only one level \( E_v \) in a single layer, \( \theta_v \) would represent the physical coverage in monolayer units. It is obvious that

\[
g_{\text{total}} = \sum_v g_v \tag{6-7}
\]

is the overall capacity, and

* The same is true of the audience in a theatre from the standpoint of the manager who does not know nor care about the individual names or other identification marks.
\[ \theta_{\text{total}} = \frac{N_{\text{total}}}{e_{\text{total}}} = \sum_{\nu} \frac{\gamma_{\nu}}{g_{\nu}} \sum_{\nu} \frac{\theta_{\nu}}{g_{\nu}}, \text{ with } \gamma_{\nu} = \frac{g_{\nu}}{e_{\text{total}}}, \]

is a possible definition of overall coverage (see section 4, however).

2. Two Adsorption Energy Levels in a Single Layer. Sub-Monolayer Region.

The simplest case would represent the one where a physical monolayer is made up by two sublayers \( (\nu = 1, 2) \), each with its own different adsorption energy \( E_{\nu} \). This case is the closest at hand as it appears to be the situation when the \( \alpha \)-peak shows up. At the same time it may serve as an illustration and example.

The overall physical coverage \( \theta_{\text{total}} \) (in monolayer units) is 
\[ \theta_{\text{total}} = \gamma_1 \theta_1 + \gamma_2 \theta_2 \] (with \( \gamma_1 + \gamma_2 = 1 \)) and is again a function of the parameter \( E_F \). It is convenient for numerical calculations to introduce some reference \( E_0 \) and then work with the quantities \( E_{\nu} - E_0 \) and \( E_F - E_0 \). We choose \( E_0 = (E_1 + E_2)/2 \) and denote \( E_2 - E_1 \) by \( \Delta E \), the energy gap. Then with \( x = (E_F - E_0)/kT \) and \( \delta = \Delta E/2kT \),

\[ \theta_\nu = \frac{1}{1 + e^{+\delta-x}} \] \[ (6-8) \]

where the -sign holds for \( \nu = 1 \), the lower energy level, and the +sign for \( \nu = 2 \), the upper energy level.

A quick survey shows the general behavior of \( \theta_1 \) and \( \theta_2 \)
\( \theta_1 \) and \( \theta_2 \) versus \( \theta \) total curves, \( T = 520^\circ K \), \( \gamma_1 = 0.1 \).

Fig. 6-1
versus $\theta_{\text{total}}$. The four points with the coordinates $(0,0), (\gamma_1,0), (\gamma_1,1),$ and $(1,1)$ stake out the region within which the curves must fall. Thus, they never go into the shaded region in Fig. 6-1. For a small value of $\theta_{\text{total}}$, a small value of $\Delta E$ is first noticed in the enhancement of $\theta_1$ whereas $\theta_2$ is almost unaffected. As $\Delta E$ increases, the limiting lines are quickly reached. Thus, the sensitive range of $\Delta E/kT$ would roughly be from 0.5 to about 8.

3. Ion Formation

From a large number of experimental data taken, the following basic ideas about dimer ion formation on the surface have been gleaned. (a) The ion signal is proportional to the influx of superthermal particles. This may seem to be false for very intensive beams. However, first of all we have chosen a very weak superthermal beam and, secondly, even if the surface coverage is modified by a strong beam through sputtering or coating action and possible beginning of neutral atom implantation at the high end of energies used, it is reasonable to assume that at each instant in time this proportionality is still valid. (b) The Langmuir-Saha equation represents the probability for an adatom to be found in the ionic state. It reads

$$P_{\text{ion}} = e^{(kT - I)/kT} \quad (6-9a)$$
for a positive ion species, with \( \phi \) being the electronic work function of the surface and \( I \) the ionization energy of the adsorbed atom. In analogy, for a negative ion, it reads

\[
P_{\text{ion}} = e^{(\phi - A)/kT}
\]

(6-9b)

with \( A \) the electron affinity of the adsorbed atom. Generally, the work function \( \phi \) is to be considered a function of coverage \( \theta \). It will be approximated by

\[
\phi = \phi_0 - a\theta
\]

(6-10)

thus neglecting quadratic and higher terms in \( \theta \). This can be done without much harm since in the case of tungsten (high value of \( \phi \)) covered by alkali (low value of \( \phi \)) the electron work function decreases rather sharply as \( \theta \) goes from 0 to about 1/2 of a monolayer. Once \( \phi \) is drastically reduced, the higher order terms in \( \theta \) do not matter anymore for ion formation.

(c) The probability to meet an adsorbed particle is proportional to the number of \( N_v \) in relation to the layer capacity (here \( g_{1} + g_{2} = g_{\text{layer total}} \)), or in other words, proportional to \( \gamma_v \theta_v \). (d) Finally, there would have to be a constant, \( P_v \), which describes the probability to go through with the ion
producing process after all other probabilities have been met favourably. Thus, it represents the closest equivalent to a cross section for ion formation on the surface.

As a result of our considerations we then have the following expression for the ion flux \( j \) originating from a particular adsorption energy level \( E_v \):

\[
j_v = j_{\text{incident}} \cdot P_v \cdot \gamma_v \cdot \theta_v \cdot \exp[(\phi_v - \alpha_v \theta_v)/kT] \cdot \exp[-I/kT] \quad (6-11)
\]

The measured ion flux would then be \( j_{\text{total}} = j_1 + j_2 \), or, if common factors are omitted,

\[
j_{\text{total}} \sim \tilde{P} \gamma_1 \theta_1 e^{-a_1 \theta_1 /kT} + (1-\gamma_1) \cdot \theta_2 \cdot e^{-a_2 \theta_2 /kT} \quad (6-12)
\]

with

\[
\tilde{P} = \frac{P_1}{P_2} \cdot (\phi_{10} - \phi_{20})/kT
\]

with the surface temperature \( T \) known, the parameters to be fitted are then (in decreasing priority) \( \Delta E \), \( \gamma_1 \), \( \tilde{P} \), \( a_1 \) and \( a_2 \). Fig. 6-2 shows such a 'two level fit' to some experimental data. Note that for a coverage of more than about half a monolayer (corresponding to about 100 sec. on the time scale) the experimental data are always higher than the theoretical fit. No fit was found which would reproduce the whole range of measured data equally well. Hence we
Two level fit to experimental data, $\Delta E = 0.23\text{eV}$, $\gamma_1 = 0.1$, $P = 5$ (a) and 15 (b), $a_1 = 0.5$ and $a_2 = 0.4$.

Fig. 6-2
placed higher weight on the low coverage data and assume that the surplus in ions measured at higher coverage is due to the onset of ions from yet another adsorption energy level (see below).

4. Many Layers with Several Adsorption Levels Each

The extension of the previous results to this situation is fairly straightforward. Some modifications, however, seem necessary.

The process of collision stimulated desorption (as observed here in the forms of ions) is proportional to $\gamma_v \theta_v$ as outlined above only for small values of $\theta_v$. A fast particle which is scooting across the surface is more liable to stimulate others into desorption than one that hits the surface perpendicularly. That also means that islands and monolayer patches which may form at higher values of $\theta$ are much less important than their rims. In order to account for this we have split $P_v$ into two parts, one which is associated with the lateral motion of the superthermals and one which describes the effectiveness of the motion normal to the surface. It is realized that the factor $(1-\theta)$ is proportional to the unoccupied adsorption sites.

$$P = P_{\text{lateral}}(1-\theta) + P_{\text{normal}}$$  \hspace{1cm} (6-13)

In practice, $P_{\text{normal}}$ seems to be insignificant when compared to $P_{\text{lateral}}$, and thus has been chosen as zero in later work.

Since the physical layer can be composed of several
sub-layers' (one for each $E_v$) we now have to group the levels $\nu$ by layers $i$. Consequently, we introduce now the index $i$ for the layer and $\nu$ for the sub-layer rather than the single index $\nu$. Each level $i$, $\nu$ is now identified as being part of the $i$-th layer but representing the $\nu$-th energy level in that layer. Accordingly, we define for each layer $i$

$$\gamma_{i\nu} = \frac{g_{i\nu}}{g_{i\text{total}}} \quad (6-14)$$

with

$$g_{i\text{total}} = \sum_{\nu} g_{i\nu} \quad (6-15)$$

as the layer capacity. The physical layer $i$ is then

$$\theta_i = \sum_{\nu} \gamma_{i\nu} \theta_{i\nu} = \frac{N_{i\text{total}}}{g_{i\text{total}}} \quad (6-16)$$

and $\theta_i$ is defined as being between 0 and 1 for all $i$. The number of adatoms in layer $i$ is $N_i = \sum_{\nu} N_{i\nu}$; of course.

Similarly, we can define capital gamma values which relate to the global capacity $G_{\text{global}}$ of all layers together. Thus

$$G_{\text{global}} = \sum_i g_{i\text{total}} = \sum_{i} \sum_{\nu} g_{i\nu} \quad (6-17)$$

and
\[
\Gamma_{i \nu} = \frac{g_{i \nu}}{g_{\text{global}}} \tag{6-18}
\]

The global number of adsorbed particles per unit area is then

\[
N_{\text{global}} = \sum_{i \nu} N_{i \nu} \tag{6-19}
\]

It seems to be natural to define the global coverage as

\[
\theta_{\text{global}} = \frac{N_{\text{global}}}{G_{\text{global}}} \tag{6-20}
\]

however, its range is only from 0 to 1. Even if multiplied by the number of possible layers it can give rise to trouble when \(G_{\text{global}}\) goes to infinity. And after all, it just represents \(N_{\text{global}}\) in disguise. An alternative way to define \(\theta_{\text{global}}\) is

\[
\theta_{\text{global}} = \sum_{i \nu} \theta_{i \nu} \tag{6-21}
\]

but its relation to \(N_{\text{global}}\) is not simple. In order to avoid the above difficulties we have chosen \(N_{\text{global}}\) as the 'independent variable'. Also keep in mind that with a constant sticking coefficient [60] \(N_{\text{global}}\) is proportional to time which is the natural independent variable in the laboratory.

Another modification seems indicated due to the shielding of lower lying layers by upper ones. The incident fast beam is
attenuated before it reaches the i-th layer and so is the outgoing ion flux. This effect is taken into account by the factors 
\[ \exp(-\sum_{j=i+1}^{\infty} D_{ij}^{in}) \text{ and } \exp(-\sum_{j=i+1}^{\infty} D_{ij}^{out}) \], respectively. They can be combined into one of the form \( \exp(-\sum_{j=i+1} D_{ij} \theta_j) \). Both \( D_{ij}^{in} \) and \( D_{ij}^{out} \) should be about 1, so that 
\[ D_j = D_{ij}^{in} + D_{ij}^{out} \sim 2 \]
seems reasonable, as well as assuming that all \( D_j \)'s are roughly the same.

Finally the isotope effect found in Chapter IV can be taken into account by a factor \( \exp(-\sqrt{m \cdot \bar{K}}) \) where \( \bar{K} \) is a suitable constant as described in Chapter IV. Thus, we finally arrive at the following expression for the ion production by each individual level \( i \), \( \nu \):

\[
j_{i\nu}^{\text{incident}} \cdot \exp\left(-D_{ij}^{\Sigma} \sum_{j=i+1}^{\infty} \theta_j \right) \cdot e^{-\sqrt{m \cdot \bar{K}}} \cdot e^{(\eta_{i\nu} - I)/kT} \]

(6-19)

\[ e^{-\frac{\varphi_{i\nu}}{\gamma_{i\nu} \cdot \theta_{i\nu} \cdot (1 - \theta_{i\nu})}} \]

and the measured total current is the sum over all \( i \) and \( \nu \).

Keep in mind that all quantities are dependent upon \( E_F \) as the independent variable. Since there is a one-to-one relation between \( E_F \) and \( N_{\text{global}} \), everything can also be expressed in terms of \( N_{\text{global}} \). This has been done in a computer program for several situations: (a) two levels in the first layer and one in the second, (b) two levels in the first layer and

122
one each in the second to sixth layer (as shown in Fig. 6-3 and 4).

Considering the basic simplicity of the model the agreement with the experiment is remarkable. Accordingly, we can draw an energy level diagram as shown in Fig. 6-5 with the capacities indicated.

Further work, experimental and theoretical, is planned to systematically test the validity of this theory over a wider range.
Three level fit to the experimental data: Two levels in the first layer and one level in the second layer.

Fig. 6-3
Fig. 6-4: \((i, \nu)\)

<table>
<thead>
<tr>
<th>((i, \nu))</th>
<th>(E_{i\nu} (eV))</th>
<th>(E_{i\nu})</th>
<th>(P_E)</th>
<th>(\phi_{i\nu} (eV))</th>
<th>(a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>1,2</td>
<td>0.23</td>
<td>3</td>
<td>8</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>2,1</td>
<td>0.38</td>
<td>20</td>
<td>0.74</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3,1</td>
<td>0.53</td>
<td>40</td>
<td>1.27</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4,1</td>
<td>0.65</td>
<td>40</td>
<td>0.90</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5,1</td>
<td>0.65</td>
<td>40</td>
<td>0.90</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6,1</td>
<td>0.65</td>
<td>40</td>
<td>0.90</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Multi-level fit to experimental data.
(e) Total dimer ion current from all six layers. This curve is a first attempt to reproduce the measured data of Fig. (f) below.

(f) $\gamma_2$, $\gamma_3$ maxima of Na$_2^+$ versus time. Heating current 1 A, 100 eV Na primary beam, surface temperature $T = 535 \degree K$.

Fig. 6-4
Energy level diagram for two levels in the first layer and one each in the second to sixth layer. These values are used in the calculation which is shown in Figs. 6-4.

Fig. 6-5
APPENDICES
Surface temperature versus heating current.


Fig. Al-1
APPENDIX II

THE EFFICIENCY OF THE PRIMARY THERMAL PARTICLE REJECTOR

The speed distribution of the atoms leaving the oven follows the Maxwellian distribution:

\[ f(v) = \frac{4}{\sqrt{\pi}} \left( \frac{m}{2kT} \right)^{3/2} v^2 e^{-mv^2/2kT} \]

where \( v \) is the velocity and \( m \) is the mass of the beam atoms, \( k \) is the Boltzmann constant and \( T \) is the temperature of the oven in °K.

The thermal beam intensity before passing the rejector is, therefore, given by:

\[ I(\text{no. of atoms/cm}^2\text{sec}) = \int n \cdot v \cdot f(v) \, dv \quad (A2-1) \]

where \( n \) is the density of the beam (no. of atoms/cm\(^3\)).

The above figure shows the geometry and beam path. In this drawing \( L \) is the thickness of the rejector disk, \( s \) is the slit width, \( p \) is the thickness of the tooth and \( \alpha \) is the angle between the normal of the rejector and the direction of the primary beam.
For simplicity, we define the following

\[ v_m = \sqrt{\frac{2kT}{m}}, \]

\[ a = \frac{s}{t}, \quad R : \text{radius of the disk} \]

\[ b = \frac{L \tan \alpha}{t}, \quad \omega : \text{angular speed} \]

\[ c = \frac{\frac{1}{v} \omega RL}{t \cos \alpha} = v_m h = v_m \omega \gamma \]

For the rejector running in the forward or reverse direction, the transmission coefficient \( T(v) \) for the atoms with speed \( v \) are:

**Forward:**

\[ T_f = 0, \quad \frac{c}{a-b} > v > 0 \]

\[ T_f = \frac{s}{t} - \frac{1}{t} (L \tan \alpha - \frac{\omega RL}{v \cos \alpha}), \quad \omega > v > \frac{c}{a-b} \]

**Reverse:**

\[ T_r = 0 \]

\[ T_r = \frac{s}{t} + \frac{1}{t} (L \tan \alpha - \frac{\frac{1}{v} \omega RL}{v \cos \alpha}), \quad \frac{c}{b} > v > \frac{c}{a+b} \]

\[ T_r = \frac{s}{t} + \frac{1}{t} (\frac{\omega RL}{v \cos \alpha} - L \tan \alpha), \quad \omega > v > \frac{c}{b} \]
In general
\[ T = a + b \pm \left( \frac{m}{v} \right) h \]  \hspace{1cm} (A2-2)

\[ v_{\text{cutoff}} = \frac{c}{a-b} \quad ; \quad v_{\text{cutoff}} = \frac{c}{a+b} \]

\text{forward} \quad \text{reverse}

Further, we define the following:
\[ x = \frac{v}{v_m} \]
\[ v_1 = \frac{c}{a-b} \quad , \quad x_1 = \frac{v_1}{v_m} = \frac{\omega y}{a-b} \]
\[ v_2 = \frac{c}{a+b} \quad , \quad x_2 = \frac{v_2}{v_m} = \frac{\mid \omega \mid y}{a+b} \]
\[ v_3 = \frac{c}{b} \quad , \quad x_3 = \frac{v_3}{v_m} = \frac{\mid \omega \mid y}{b} \]

The thermal beam intensity after the rejector from equation (A2-1)
and (A2-2) is:
\[ I = \int_{v=0}^{\infty} n \cdot T \cdot v \cdot f(v) dv \]
\[ I = n \left( \frac{4}{\sqrt{\pi}} \right) \frac{v_m}{4} \int_{x=0}^{\infty} (a+b)x^3e^{-x^2} dx \pm \int_{x=0}^{\infty} hx^2e^{-x^2} dx \]  \hspace{1cm} (A2-3)

Let \( n \frac{4}{\sqrt{\pi}} v_m = A \), and since
\[ \int_{x=0}^{\infty} x^{a-1}e^{-x} = \Gamma(a, x) \],
\[
\int_{x_1}^{x_2} x^n e^{-x^2} = \frac{1}{2} \Gamma\left(\frac{n+1}{2}, x^2\right), \quad \text{the transmission } T_f \text{ and } T_r
\]

can be put into the forms:

\[
I_{f/A} = (a-b)\frac{1}{2} \Gamma(2, x_1^2) - \omega \frac{1}{2} \Gamma(\frac{3}{2}, x_1^2)
\]

(A2-4)

\[
I_{r/A} = (a+b)\frac{1}{2} \Gamma(2, x_2^2) - \frac{1}{2} \gamma \Gamma(\frac{3}{2}, x_2^2)
\]

\[- b \Gamma(2, x_3^2) + |\omega| \gamma \Gamma(\frac{3}{2}, x_3^2) \]

(A2-5)

Since

\[
\Gamma(\frac{1}{2}, z^2) = \sqrt{\pi} \text{erfc} z
\]

\[
\Gamma(2, z^2) = (1+z^2)e^{-z^2}
\]

\[
\Gamma(\frac{3}{2}, z^2) = \frac{1}{2} \Gamma(\frac{1}{2}, z^2) + ze^{-z^2} \frac{\sqrt{\pi}}{2} \text{erfc} z + ze^{-z^2}
\]

From eq. (A2-4) and (A2-5)

\[
\frac{2I_f}{A} = (a-b)\left(e^{-x_1} - \frac{\sqrt{\pi}}{2} x_1 \text{erfc} x_1\right), \quad (A2-6)
\]

\[
\frac{2I_r}{A} = (a+b)\left(e^{-x_2^2} - x_2^2 \frac{\sqrt{\pi}}{2} \text{erfc} x_2\right)
\]

\[- 2b\left(e^{-x_3^2} - x_3^2 \frac{\sqrt{\pi}}{2} \text{erfc} x_3\right) \]

(A2-7)
Let \( g(z) = e^{-z^2} - z \frac{\sqrt{\pi}}{2} \text{erfc} z \); we have

\[
I_r = 2n \sqrt{\frac{2kT}{nm}} (a-b) \cdot g(x_1) \tag{A2-8}
\]

\[
I_r = 2n \sqrt{\frac{2kT}{nm}} [(a+b) \cdot g(x_2) - 2b \cdot g(x_3)] . \tag{A2-9}
\]

From Eqs. (8) and (9), \( I_r \) and \( I_f \) are both functions of \( m \), \( T \), \( a \) and \( \omega \). Since the mass \( m \) and angular speed \( \omega \) are well defined, \( T \) and \( a \) can be deducted from the experimental data.

A typical example is shown in Fig. A2-2 where dots are experimental values and the smooth curve is the fit using \( a = 2.7^\circ \) and \( T = 900^\circ K \). Generally, for \( a = 0 \), the relative maximum intensity occurs at \( \omega = 0 \). The shift from \( \omega = 0 \) to \( \omega = \omega_0 \) is proportional to angle \( a \). The half width at half maximum, on the other hand, increases as the temperature \( T \) rises.

A PDP Fortran program, which is listed in a separate laboratory report, was written to search for \( a \) and \( T \) through an iterative process.
Relative primary thermal beam intensity versus thermal particle rejector speed.

Fig. A2-2
Appendix III

Residual Gases Analysis

(a) This is the residual gas spectrum of the detector vacuum chamber, with no LN$_2$ cooling. Multiplier high voltage = 2500V and electron emission current = 2.4 mA. Ion gauge reading $1.2 \times 10^{-6}$ torr.

These are the typical background gas constituents for the S.S.I. studies reported. Besides hydrogen, nitrogen and oxygen, there are hydro carbons and large amounts of water contamination.

Fig. A3-1
(b) Residual gas spectrum inside the detector vacuum chamber when both diffusion pump trap and detector housing are cooled with LN$_2$. Ion gauge reading is $2.8 \times 10^{-7}$ torr. The signal intensity for water is reduced by a factor of 50 and for N$^+$ by a factor of 2.
(c) Same as (b), except ion gauge outgassing filament is on. The $H^+$ increases by a factor of 5 and $C^+$ by more than 10. No change is found for the other mass peaks. The origin of carbon atoms is believed to be from the outgassing filament which is approximately 40 cm down stream relative to the quadrupole entrance.

Similarly the carbon diffused from the detector filament is the cause of a maximum in the dimer formation work.
(d) Same as (b), except the quadrupole entrance is inside the detector filament N_2 cooled housing which is inside the detector vacuum chamber. The background pressure is estimated by a factor 10 lower than outside the cooling housing.

The filament is under similar conditions as in the work of negative ions and alkali dimer formation. The small amount of C^+ is probably from the cathode filament of the quadrupole ionizer and the water and hydrocarbon content is almost nil.
APPENDIX IV

Calculation of Coating Rate Due to Secondary Oven Based on Effusive Flow

Given the following conditions:

\[ n_0, P_0, T_0 \]

where:

- \( n_0 \) = number density inside effusive oven
- \( P_0 \) = vapor pressure inside effusive oven
- \( T_0 \) = temperature of effusive oven
- \( A \) = area of slit of effusive oven
- \( D \) = diameter of detector filament
- \( l \) = length of detector filament

Let \( J \) = the incoming flux at the detector. Then, for effusive flow at the source, the flux at the detector is given by

\[
J = \frac{P_0 A \sqrt{\pi D}}{kT_0 4\pi (L)^2} \quad \text{atoms/sec} \quad (L \gg l)
\]

where \( P_0 = n_0 kT_0 \).
\[ \langle v \rangle = 2 \sqrt{\frac{2kT_o}{nm}} \]

\[ k = \text{Boltzmann's constant} \]

\[ m = \text{mass of an effusive atom} \]

Eliminating \( \langle v \rangle \), one obtains

\[ j_d = \frac{P_o A_o 2kT_o L_D}{kT_o nm 4\pi(L)^2} \left( \frac{\text{atom}}{\text{sec.}} \right) \]

Assuming for a (100) surface the adatoms and substrate atoms have the arrangement as shown in Fig. A4-2.

![Fig. A4-2](image)

One obtains for the coating rate, \( \dot{\lambda} \), in monolayer/sec., approximately

\[ \dot{\lambda} = \frac{J(\text{atoms})}{\text{sec.}} \times d^2 \left( \frac{\text{cm}^2}{\text{atom}} \right) \times \frac{2}{\pi D_L} \left( \frac{1}{\text{cm}^2} \right) \]
Appendix V

Yield of dimer ions as function of surface temperature, as obtained with a 100 eV primary beam.

- o x K primary beam
- □ Rb primary beam

Fig. A5-1
REFERENCES


54. Gordon, R. T., Hsu, D. S. Y., Lee, Y. T. and Herschbach, D. R.,
VITA AUCTORIS

I was born in Kiang-Su (江蘇) Province, China on December 8, 1945. In March 1969 I graduated with a B. Sc. degree from the Automotive Engineering Department at Chung-Cheng Institute of Technology in Taiwan (R.O.C.). I completed my M. Sc. degree in Physics at the University of Tennessee (Knoxville, U.S.A.) in March 1972. In January 1973 I began to work for my Ph.D. degree at the University of Windsor.
PUBLICATIONS


PAPERS PRESENTED AT CONFERENCES
