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Spin polarized metastable deexcitation spectroscopy as a probe of gases absorbed on metal surface

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Rice University, 1992
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SPIN POLARIZED METASTABLE DEEXCITATION SPECTROSCOPY AS A PROBE OF GASES ABSORBED ON METAL SURFACE

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

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ABSTRACT

Spin polarized metastable deexcitation spectroscopy provides an important surface probe, in which a beam of thermal energy metastable noble gas atoms is deexcited at the target surface under study, releasing its energy through ejection of electrons. The electrons are collected and their energy distributions measured to reveal the surface electronic structure. By spin polarizing the incoming metastable atoms and measuring the polarization of the ejected electrons, additional insight into the reaction mechanisms can be obtained. In the investigation reported in this thesis, polarized He(2^3S) atoms are used to probe a thin film of gases frozen on a cooled Cu(100) surface. The experimental results show that the reaction mechanisms occurring are similar to gas phase Penning ionization, although some differences are apparent that can be attributed to interaction with neighboring particles and to the presence of the substrate metal surface.
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Chapter 1 Introduction

Among a multitude of surface spectroscopic techniques, spin polarized metastable deexcitation spectroscopy (SPMDS) is unique. It is extremely surface sensitive because the thermal energy noble gas atoms used as probing particles do not penetrate the target surface. In SPMDS, a beam of noble gas atoms in a long lived excited state is directed at the surface under study. Upon reaching the vacuum extension of the surface electronic wavefunctions, the atoms deexcite and the energy released ejects electrons, which are collected and energy-analyzed to reveal surface electronic properties. Spin labeling techniques, namely polarizing the metastable atom beam and measuring the polarization of the ejected electrons, provide us with additional insight into the deexcitation mechanisms, which are still not completely understood.

In the investigations reported in the following sections, SPMDS is used to probe properties of several different gases when frozen on a Cu(100) surface. The lowest triplet state of the helium atom, He(2\(^3\)S), is used for most studies. The ionization that occurs when metastable helium atoms react with various atomic or molecular targets in the gas phase -- so called Penning Ionization (PI) -- has been thoroughly investigated by other researchers. SPMDS investigation of frozen films provides the opportunity to study solid phase PI reactions involving "solid" gases, so-called surface PI, the mechanisms of which are supposedly similar to gas phase PI. However, complications arise due to the interaction between the substrate and the adsorbate and between the neighboring adparticles. First, the presence of the metal substrate induces screening effects that influence both the incoming metastable atoms and the ejected electrons. Second, the adsorbate modifies the substrate surface work function which may in turn change the
adsorbate electronic structure. Finally, the presence of neighboring particles may also shift and/or broaden the adsorbate electronic energy levels. Unraveling the roles played by these effects will enhance the understanding of both surface Penning Ionization and of the way gases are absorbed on metal surfaces.
Chapter 2 Theory

A. Spin - Polarized Metastable Deexcitation Spectroscopy

Spin-polarized metastable deexcitation spectroscopy (SPMDS) is an attractive probe of the surface because it is very surface specific. In SPMDS, a thermal energy beam of long lived metastable noble gas atoms is directed at the sample surface under study. The atoms deexcite near the surface, and the energy released can lead to ejection of electrons. Information about the surface can be obtained by analyzing the energy and polarization distributions of the ejected electrons.

Fig. 2.1 Resonance Ionization and Auger Neutralization
He ($^2\text{S}$) is used in this experiment because of its high excitation energy (19.8 eV) compared to other noble gas atoms. It is also the only noble gas metastable state without orbital angular momentum. When the helium metastable atom is within reach of the vacuum extension of the surface electronic wavefunctions, deexcitation may occur via one or both of the two processes first proposed by Hagstrum [Hagstrum].

In the two step process, Resonance Ionization (RI) followed by Auger Neutralization (AN) (shown in Fig. 2.1), the helium 2s electron tunnels into an empty surface state (RI) and the resulting helium ion is then neutralized by an electron from the surface (AN). The energy released is communicated to an Auger electron, which may be ejected from the surface if given enough energy. Since two surface electrons are involved, the energy distribution of the ejected electrons represents approximately the self-convolution of the surface density of states, and is typically broad and featureless.

![Diagram](image)

Fig. 2.2 Auger Deexcitation
In the simpler Auger Deexcitation (AD) process (Fig. 2.2), an electron from the surface tunnels into the 1s hole in the helium atom, simultaneously ejecting the He 2s electron. The energy spectrum of the ejected electrons is a direct reflection of the surface density of states, and therefore may have sharp features.

The conventional model is that RI + AN is dominant at high work function surfaces. This results because RI occurs at distances where the He* 2s orbital appreciably overlaps the vacant surface states above the target Fermi level, typically at ~5 Å from the surface. The AD process, which requires appreciable overlap of the inner 1s vacancy of the helium atom with the surface electronic wavefunction, would occur at a smaller atom-surface distance, hence is much less likely. There are two cases when RI is effectively blocked, allowing AD to occur. One is when the surface is covered with adsorbate, which physically prevents the overlapping of wavefunctions necessary for RI. In this case surface Penning Ionization occurs, which we shall discuss in more detail in the following section. The other case is when the surface has a low work function, so that the electronic states in resonance with He* 2s electron are already filled.

A direct way to determine which mechanism is operative is by spin polarizing the metastable helium beam and measuring the ejected electron spin polarization (ESP). In AD, the He* 2s electron is ejected and the electron spin is preserved (Fig. 2.2). This would result in 100% electron polarization normalized with respect to the incident beam polarization. However in RI+AN (Fig. 2.1), the ejected electron is from the surface. Therefore its spin direction is independent of the incoming metastable atom polarization, resulting in zero polarization, unless there is a spin-correlation between the two surface electrons involved. The experimental results from several high work function surfaces indicate that the ESP has a lower bound of ~20%. According to the conventional model that RI + AN is the exclusive channel, this would require that the pair of reacting surface
electrons have opposite spins. An alternative explanation from recent theoretical studies [Dunnning, et al] suggests that AD might be a competing channel even at high work function surfaces, also accounting for the non zero polarization. The theory shows that upon approaching the surface, the hybridization of the 2s and 2p states causes the $2^3S$ electron probability density to peak toward the vacuum, leading to saturation of the 2s electron tunneling rate. As a result, metastable atoms might survive passage to within 4 Å from the surface, where it is argued that the reaction rate for AD might become comparable to that for RI + AN. The same study also shows that the $2^3P$ state will be oriented toward the surface as a consequence of the hybridization enhancing 2s tunneling rate. Therefore the $2^3P$ state will deexcite exclusively through the RI + AN channel.

However, recent experiments in this laboratory show that deexcitation of the He($2^3P$), He($2^1S$) and He($2^3S$) at Cu(100) surface give identical electron energy distributions (EED's), which rules out any significant AD. Because the He($2^3P$) and He($2^1S$) states have higher excitation energy than the He($2^3S$) state, AD would produce electrons of higher energy than would AD of He($2^3S$), but no such effects are observed.

B. MDS as a Probe of Gases Frozen on Surfaces

When the metastable atom beam is directed at the sample surface with a frozen adsorbed gas film, reactions similar to gas phase Penning Ionization are expected to occur. Thus surface studies may prove to be a powerful probe of the mechanisms of Penning Ionization especially considering the advantage of a much larger (unity) reaction probability for condensed phases as compared to gas phase targets.
Penning Ionization in the gas phase has been studied extensively in this and other laboratories. For a detailed review see Yencha [Yencha]. In 1927, F. M. Penning proposed the process:

\[ X^* + A \rightarrow X + A^+ + e^- (E) \]

in which a metastable noble gas atom \( X^* \) ionizes an atomic or molecular target and returns to its ground state, releasing its energy through the ejected electron.

Several reaction mechanisms for Penning Ionization have been proposed:

a) Direct Channel

An electron from the target tunnels into the core vacancy of the noble gas atom, while the excited electron in \( X^* \) is ejected. The electrons produced are expected to have the same spin polarization as the metastable atoms. This happens in the case of a closed shell target with negative electron affinity (A target has negative electron affinity when the ground state energy level of its negative ion is higher than that of the neutral.).

b) Ionic Channel

A target with positive electron affinity can form an intermediate ionic complex \((X^+A^-)^*\) with the metastable atom via the channel

\[ X^* + A \rightarrow (X^+A^-)^* \rightarrow X + A^+ + e^- (E) \]

which subsequently autoionizes.

In this type of reaction, the spin polarization of the ejected electrons can be degraded as a result of exchange and/or spin-orbit interactions in the \((X^+A^-)^*\) collision
complex. Hence the polarization of the product electrons is expected to be less than that of the metastable atoms.

c) Autoionization Channel

In some cases an excitation transfer mechanism of the type

\[ X^* + A \rightarrow X + A^{**} \rightarrow X + A^+ + e^- (E) \]

can occur, leading to formation of autoionizing states \( A^{**} \) which decay to produce the ejected electron. As in the case of ionic channels, the polarization of the product electrons is in general degraded as a result of exchange and/or spin-orbit interactions in \( A^{**} \).

From the analysis above, we can see that the polarization of the ejected electrons can be used to help identify the reaction channel.

The ejected electron energy distributions (EED's) can be understood in terms of a intermolecular potential curve model, first proposed by Herman and Cermak [Cermak et al.]. In the following diagrams (See Fig. 2.3, for example), the potential curves of the approaching reaction partners are denoted by \( V^*(R) \), which varies greatly for different types of targets. \( V^*(R) \) at asymptotically large \( R \) is taken to be the excitation energy of \( X^* \). \( V^+(R) \) denotes the manifold of states consisting of a ground state rare gas atom \( X \) and the positive ion \( A^+ \) in its ground or excited state. The asymptotic energies at large \( R \) are taken to be the excitation energies of \( A^+ \). Except near the target surface, \( V^+(R) \) is usually nearly flat due to the inert nature of the rare gas atoms. The arrows in the following figures represent the transitions from reactants to products.
Fig. 2.3 Weakly Interacting Channel
To proceed with this model we invoke the Born-Oppenheimer approximation, assuming that the relative velocity of the colliding particles is so small that the electronic configuration of the system will only depend upon the internuclear separation $R$. Transitions between states occur on a time scale sufficiently short that $R$ does not change significantly. Hence the transition arrows are vertical in the diagrams. The ejected electron energy will reflect the difference between the entrance and exit channel energies. The EED will depend on the transition rate $W(R)$ at separation $R$. We now consider separately the weakly and strongly interacting systems.

1. Weakly Interacting (Covalent) Systems

Fig. 2.3 shows schematically the potential curves of a weakly interacting system. $V^*(R)$ is expected to be relatively flat with a repulsive barrier at small $R$. $V^+(R)$ is also drawn flat with the repulsive barrier at slightly smaller $R$ because of the smaller size of the ion. The transition rate is typically highest near the classical turning point. Thus the EED typically has sharp features at energies slightly higher than the nominal energy $E_0$ (the energy difference between the asymptotic levels of the entrance and exit potential), because the $V^*(R)$ repulsive barrier at the turning point is greater than that of $V^+(R)$. 
Fig. 2.4 Strongly Interacting System
2. Strongly Interacting Systems

Fig. 2.4 shows an example of a strongly interacting system. It is similar to the covalent system except for the presence of the attractive ionic channel. According to the non-crossing rule, the system will proceed adiabatically from the covalent to the ionic channel if the two crossing curves, $V^*(R)$ and $X^+A^-$ possess the same symmetry. As a result, the EED is broadened toward lower energy. Generally the transition rate is highest near the bottom of the potential well.

3. Autoionization Channel

There are two situations in which autoionization channels can become important. First, if there are autoionizing states that are close in energy to the He(2$^3$S) level, the system may undergo a near resonant transition to the autoionizing state. Alternatively, the system might first follow an ionic curve through an avoided crossing transition followed by another avoided crossing transition to the autoionizing potential at closer distances, as illustrated in Fig. 2.5.
In the present investigations, the measured EED's show that metastable deexcitation at condensed atomic and molecular films is analogous to gas-phase PI, except for the observation that there is a coverage-dependent energy shift. Three factors may contribute to these peak shifts.

First and most important, is screening of the final state A+ ion by conduction electrons of the metal substrate (image charge). In the point-charge image potential model, the interaction of an electron with a metal surface at a distance d from the surface is given by a potential of the form \(-q^2/[4(d - x_0)]\) [Lang, et al.], where \(x_0\) is the distance between the image plane (center of mass of the induced surface charge distribution) and the metal surface. \(x_0\) is calculated using the jellium model. The dielectric effects of the adsorbate underlayers on the relaxation shifts can be described by a homogeneous dielectric slab with dielectric constant \(\varepsilon\) extending from the image plane to a distance \(d - x_d\) from the metal surface.

Second, the orbital energies of the adsorbate in the initial state might change as a result of the interactions between the adsorbate and the substrate and/or by interactions between the neighboring ad-particles. In SPMDS, the EED's quantitatively reflect the work function change of the sample surface. A clean metal surface of work function \(\phi_0\) covered with an adsorbate is equivalent to a new surface with work function \(\phi = \phi_0 + \Delta\phi\). This adsorbate induced work function change \(\Delta\phi\) varies with increasing coverage. Hence a coverage-dependent shift of the ejected electron energy results. The effect of this mechanism is expected to be greatest for the first few monolayers of adsorbate.

Finally, the helium electronic state changes as it approaches the target due to the presence of the substrate metal surface. Consider an excited atom at a particular distance outside a metal surface. The total effective potential for the atom consists of four parts: the excited-electron-surface interaction in the absence of the helium ion which for a
A perfect conductor is just the image attraction, the change in the electron-surface potential induced by the positive ion, which for a perfect conductor is the repulsion between the electron and the negative charge induced in the surface by the helium ion, the attractive interaction of the positive ion core with its image, and the excited-electron-core-ion interaction. The energy levels at small atom-surface distance excluding the interaction between the ion core and its image from a recent calculation [Dunning, et al.] are shown in Fig. 2.6.

![Graph showing energy levels versus distance](image)

**Fig 2.6** Spatial dependence of the He* energy levels. (…) is the core-ion-surface-interaction potential and (----) is the total atom-surface potential. Distances are measured from the jellium edge. (Taken from [Dunning, et al.])

It can be seen that the He(2^3S) energy level moves up relative to the vacuum level as the atom approaches the surface. Therefore for low coverage, this effect would shift
the ejected electron energy down as the coverage grows. At large atom-surface distances, the atom-surface interaction consists of the attraction of the electron by its image and the repulsion by the image of the core ion, and the attraction of the ion core by its image. These terms cancel out, making the excitation energy level of the helium atom quite flat as a function of the atom-surface distance.
Chapter 3 Apparatus

The SPMDS apparatus is illustrated in Fig 3.1. The source vacuum system is designed to produce a thermal beam of spin-polarized $2^3S$ metastable helium atoms. It consists of two chambers: the source chamber, where the metastable atom beam is formed; and the optical pumping chamber, where the beam is polarized. The experimental chamber, equipped with various diagnostic devices, is used for surface investigations. The beam may pass through the experimental chamber into a Stern-Gerlach analyzer where the polarization is measured. Detailed discussions of the design considerations and operating parameters can be found in the theses of previous students [Hart, Onellion, Oró]. A brief discussion pertinent to the current experiments follows.

![Diagram of SPMDS Apparatus](image)

Fig. 3.1 Top View of SPMDS Apparatus
A. Metastable He(2^3S) Beam

Helium gas is introduced through a liquid nitrogen trap, where impurities such as water are eliminated, and then into the source chamber through a multichannel array (MCA) to form a collimated thermal beam. The excitation of a fraction of the ground state helium atoms to the 2^3S metastable state is achieved by coaxial electron beam bombardment. The electron gun is shown in Fig. 3.2. The electrons are provided by a 7 mil tungsten filament wound helically around the beam axis. A Pierce type electrode extracts the electrons and an axial 400 Gauss magnetic field helps to confine the electrons around the beam axis.

![Fig. 3.2 Schematic View of the Helium Source](image)

In addition to the He(2^3S) atoms, the excitation process also produces other species of particles that can cause ejection of electrons from a target:
1) Singlet state metastable helium atoms [He(2^1S)],

2) Fast helium neutrals and photons,

3) Helium ions, electrons and long lived helium Rydberg atoms.

Charged particles are removed from the beam by an electrostatic deflector. Rydberg atoms can be easily field-ionized and then deflected in the electrical field.

Fast neutrals and photons can not be removed from the beam once they are present. This problem is solved by a time-of-flight (TOF) chopping/gating technique. A speed-controllable chopper with a slotted disk is installed in the source chamber. The data collecting electronics is programmed to discriminate against signals originating from fast neutrals and photons.

The singlet helium atoms are removed by illuminating the beam with 2.06 µm light from a DC excited flowing helium discharge lamp, which excites the He(2^1S) to the 2^1P state. Atoms in the 2^1P state decay to 1^1S_0 ground state of helium with a branching ratio of about 1000:1.

Once these impurities have been removed, the He(2^3S) atoms are spin polarized in the optical pumping chamber. The process is illustrated in Fig. 3.3.
In the unpolarized He(2^3S) atom beam, the three magnetic sublevels characterized by \( m_j = -1, 0, 1 \) are equally populated. When illuminated by circularly polarized 1.08 \( \mu \)m radiation, the 2^3S state is excited to 2^3P state subject to the selection rule \( \Delta m = +1 \) for right handed circularly polarized (RHCP) light and \( \Delta m = -1 \) for left handed circularly polarized (LHCP) light. The 2^3P state decays back to 2^3S state by spontaneous electric dipole emission subject to the selection rules \( \Delta m = -1, 0, 1 \). In Fig. 3.3, the allowed excitations for RHCP radiation are shown by solid arrows and the allowed decays by dashed arrows. It is easy to see that the 2^3S atoms are partially transferred from \( m_j = -1, 0 \) levels to the \( m_j = 1 \) level after one 2^3S -> 2^3P -> 2^3S cycle. Repeating the cycle results in a spin polarized beam, with the polarization defined by

\[
P = \frac{N_{+1} - N_{-1}}{N_{+1} + N_0 + N_{-1}}
\]

(3.1)

where \( N_i \) is the number of atoms in the \( m_j = i \) sublevel.

The radiation provided by a radio frequency (RF) excited helium discharge lamp illuminates the beam through a quartz window over approximately 20 cm of the beam path, to pump the beam to around 36\% polarization. The direction of the polarization can be reversed easily by rotating a quarter wave plate by 90\°, thus converting the pumping radiation from RHCP to LHCP.

The polarization and the purity of the beam are monitored by a Stern-Gerlach analyzer, a schematic view of which is shown in Fig. 3.4. The beam passes through two collimating apertures and enters an inhomogeneous magnetic field with a uniform field gradient of 4500 G/cm, where the different \( m_j \) levels are spatially separated. The field region is followed by a 50 cm flight tube which enlarges the separations to be resolvable by the detector. A movable channeltron driven by a computer-controlled stepper motor detects the signal.
A profile for an unpolarized $^3S$ helium beam is shown in Fig. 3.5 (a). The three peaks result from $m_j = -1, 0, +1$ components of the triplet atoms. For a pure beam, the areas under the three peaks should be the same since the beam contains equal number of each $m_j$ component. Impurities which are not deflected will result in a larger central peak and therefore can be detected by comparing the three peak areas. Fig. 3.5 (b) shows the profiles of the polarized beams obtained by optically pumping with RHCP and LHCP radiation. Fig. 3.5 (c) shows the profiles obtained by Ti-Sapphire laser pumping. 98% polarization is achieved due to the high intensity of the laser. Hopefully, the reliability of the laser will be improved sufficiently to allow its routine use in the near future.
Fig. 3.5 Stern-Gerlach Profiles: a) no optical pumping, b) optically pumped by RF lamp, LHCP and RHCP, c) optically pumped by Ti-Sapphire laser, LHCP and RHCP.

B. Experimental Chamber

Surface investigations are performed in a stainless steel ultra-high vacuum (UHV) chamber. It is separated from the optical pumping chamber by small apertures and a gate valve. The chamber is pumped by a 500 L/sec turbomolecular pump, a 400 L/sec differential ion pump and a titanium sublimation pump with a liquid nitrogen cryoshroud. Pressures of about $10^{-10}$ Torr are routinely achieved after baking the chamber at $=170$ °C for several days. The total pressure is measured by a UHV ionization gauge. An RF quadruple mass spectrometer is used to determine background gas composition.
The chamber is divided into two levels. The bottom level is used for preparation and characterization of the sample. Usually the sample surface is cleaned by ion bombardment using an ionization gun followed by electron bombardment annealing using a heated filament attached to the sample holder. The whole cycle is repeated several times. The cleanliness of the sample is monitored by Auger Electron Spectroscopy (AES). A LEED/Auger retarding field electron energy analyzer is used for both AES and Low Energy Electron Diffraction (LEED) studies. Also in the bottom level is a leak valve through which controllable amounts of gases can be admitted to the chamber.

A rotary manipulator with tilt motion is mounted on a long vertical drive to allow the sample to be moved between the upper and lower levels of the chamber. The sample is mounted on a copper holder welded to the end of a stainless steel cryostat. Flowing liquid nitrogen or liquid helium can cool the sample to temperatures as low as 30 °K.

The top level of the chamber is for the surface experiment itself. A retarding field energy analyzer is used to measure the energy distributions of electrons ejected from the target surface when metastable helium atoms are deexcited there. The retarding grid can be ramped at 0.2 V intervals. The resolution of the analyzer is approximately 0.5 V. A mini-Mott analyzer developed in this laboratory (Fig. 3.6) provides the capability of energy resolved polarization measurements. A detailed description of the mini-Mott is given by Oró [Oró]. Following is a brief discussion.

In the 1920's, Mott pointed out that electrons scattered elastically from nuclear targets experience a spin dependent force due to spin-orbit interaction. This results in a scattering asymmetry about the beam axis for electrons incident on a target foil, because the direction of the magnetic force on an electron of given spin incident to the left of the scattering nucleus is opposite from that on an electron of the same spin incident to the right. The asymmetry is greatest for high Z targets (Thorium is used in our case). The incident
electrons are accelerated to 20 KeV, collimated and collected at $\pm 120^\circ$ scattering angles by channeltrons. The retarding potential grids shown in Fig. 3.6 are used for energy resolved polarization measurements.

![Diagram of electron scattering apparatus](image)

**Fig. 3.6 Schematic view of the $\mu$Mott**

We define the electron polarization $P$ by

$$P = \frac{N_u - N_d}{N_u + N_d}$$

where $N_u$ ($N_d$) is the number of electrons in spin-up (spin-down) state. Mott showed that the relation between the scattering cross section and the electron polarization is
\[ \sigma (\theta) = I (\theta) \left( 1 + S (\theta) P \cdot n \right) \]

where \( n \) is the unit vector normal to the scattering plane, and \( I (\theta) \) and \( S (\theta) \) are symmetric with respect to the incident beam axis. \( S (\theta) \) is the Sherman function reflecting the scattering asymmetry. Its effective value, \( S_{\text{eff}} \), must be determined experimentally for each Mott polarimeter.

If we denote the count rates of channeltrons placed at \( \pm 120^\circ \) scattering angle by \( R_l \) and \( R_r \), we have

\[ \frac{R_l}{R_r} = \frac{\sigma_l}{\sigma_r} = \frac{1 + S_{\text{eff}} P}{1 - S_{\text{eff}} P} \delta \]

where the possible existence of instrumental asymmetries that might also contribute to differences in \( R_l \) vs. \( R_r \) is accounted for by introducing an instrumental asymmetry factor \( \delta \). The effect of \( \delta \) can be eliminated by reversing the electron polarization direction, which can be achieved easily by rotating the quarter wave plate in the pumping light beam by 90°. The new ratio of count rates is then

\[ \frac{R'_l}{R'_r} = \frac{1 - S_{\text{eff}} P}{1 + S_{\text{eff}} P} \delta \]

Eliminating \( \delta \) from the above two equations we get

\[ P = \frac{1}{S_{\text{eff}}} \left[ \frac{X - 1}{X + 1} \right] \]

where

\[ X = \sqrt{\frac{R_l R'_r}{R_r R'_l}} \]
Chapter 4  Experimental Results and Analysis

This chapter describes the experimental procedures and results of SPMDS experiments, in which metastable helium atoms react with gases frozen on a Cu(100) surface. Ejected electron energy distributions (EED's) and electron spin polarizations (ESP) from a clean copper surface and from a copper surface covered by varying thickness of the frozen gases are presented and compared with the corresponding data from gas phase Penning Ionization.

Before insertion into the UHV chamber, the copper surface was cleaned with organic solvents. This may leave contaminants such as water and CO chemically bonded to the surface. The EED and polarization of such a surface are shown in Fig. 4.1. The ejected electron polarization is expressed as a percentage of the polarization of the incident metastable helium beam, and a positive polarization means that the direction of the electron spin is the same as that of the incident helium beam. As illustrated in Fig. 4.1, the energy distribution has a low-energy peak, which may be due to surface contaminants, secondary electrons and rediffused inelastically scattered primary electrons. The polarization is around 50% at the low energy peak and increases to around 100% at the high energy end. The rather high polarization is expected for an absorbate covered surface where RI is effectively blocked. The reduced low-energy polarization may be attributed to an admixture of secondary electrons that have zero polarization.
The sample is then cleaned by several cycles of 500 eV argon ion bombardment for 30 minutes followed by annealing at 500 °C (30 minutes for the first cycle and 15 minutes thereafter). The energy distribution and polarization obtained after cleaning are shown in Fig. 4.2. The energy distribution is broad and featureless, as expected of the RI + AN process. The polarization is around 25% for the most part but increases abruptly at the high energy end. This non-zero polarization implies that the spins of the two electrons involved in the AN process are correlated, tending to be antiparallel.
Fig. 4.2 Electron Energy Distribution and polarization for Atomically Clean Cu(100) Surface

To study gases absorbed on the Cu(100) surface, we first cool the sample by flowing liquid helium through the cold finger upon which it is mounted. Sample temperatures as low as 30 K can be maintained, which is more than adequate to obtain a stable adsorbed film of most gases. (The temperatures corresponding to vapor pressure of $10^{-11}$ Torr are shown in Table 4.1. for several gases.)

The research grade gases are admitted through a leak valve allowing exposures from less than 1 Langmuir (= $1 \times 10^{-6}$ Torr · sec) up to several hundred Langmuirs.
Temperature at which the vapor pressure is $10^{-11}$ Torr

<table>
<thead>
<tr>
<th>Gas</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>65</td>
</tr>
<tr>
<td>Xe</td>
<td>43</td>
</tr>
<tr>
<td>NO</td>
<td>41</td>
</tr>
<tr>
<td>O$_2$</td>
<td>25</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>110</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>72</td>
</tr>
</tbody>
</table>

$10^{-7}$ Torr at 30K

Table 4.1 Gases Investigated

1. Xenon

The solid line in Fig. 4.3 represents the EED obtained in gas phase Penning ionization of Xe by Brian [Brian et al.], and the dashed line is the typical EED from SPMDS on a Cu(100) surface covered with sufficient Xe that the EED shape does not change with the thickness of the adsorbate. The two high energy peaks that appear in both spectra correspond to ionization into the Xe$^+$ $^2$P$_{1/2}$ and $^2$P$_{3/2}$ states (called $p_{1/2}$ and $p_{3/2}$ hole states), both reached through the ejection of a $5p$ electron. Notice that the $p_{3/2}$ peak is broader than the $p_{1/2}$ peak. This is due to the lifting of the $l=|m_l|$ degeneracy of the $P_{3/2}$ hole state and a splitting into its $l=1/2$ and $l=3/2$ sublevels. The splitting has been detected in high resolution photoemission spectra [Vogt, et al., 1991], and is attributed to lateral interactions between the neighboring xenon atoms [Horn, et al., 1982]. In the SPMDS spectrum, there is a low energy peak around 0 V that is absent in the gas phase spectrum. It grows faster with increasing coverage than the other two peaks.
as shown in Fig. 4.4. This peak probably arises from RI of the incident He(2\textsuperscript{3}S) atoms, followed by AN of the resulting He\textsuperscript{+} ion, with both neutralizing and ejected electrons coming from Xe(5p) levels. Such a process is not possible in gas phase PI of Xe, but apparently can occur in the solid phase where collective many-body interactions become important. Studies of this system are being continued in order to better understand details of the processes leading to the low energy SPMDS feature.

![Graph showing Electron Energy Distribution and Polarization Measured Following Penning Ionization of Xe](image)

**Fig. 4.3** Electron Energy Distribution and Polarization Measured Following Penning Ionization of Xe
The electron polarization of the high energy features is nearly 100% as expected for AD processes. The lower ~50% polarization of the low energy feature might arise as a result of spin-correlation effects in the He\textsuperscript{+} AN events.

Fig 4.4 shows the EED for various coverage of Xe on Cu(100). The spectra change gradually from that characteristic of clean copper to the three peak structure. The EED peaks shift to lower energy as more Xe is deposited on the surface. This phenomenon has also been detected in photoemission [Küppers, et al., 1979] and inverse photoemission [Wandelt. et al., 1986] spectra of Xe covered metal surfaces. As mentioned before, the reasons for this energy shift have not been clearly resolved. A discussion of the possible causes is given here.

The studies of Küppers [Küppers, et al., 1979], Wandelt [Wandelt, et al., 1981], Ertl, and co-workers have shown that the Xe 5p-valence electron energy with respect to the vacuum level is independent of the substrate work function. If we denote by $E^V$ and $E^F$ the binding energy with respect to the vacuum and Fermi level, respectively, and $\varphi$ the substrate work function, they obey the relationship $E^V = E^F + \varphi$. Since $E^V$ is substrate independent, changes in $E^F$, hence the energies of ejected electrons, reflect the work function difference, namely $\Delta E^F = -\Delta \varphi$. Therefore a decrease of the surface work function with increasing coverage might contribute to the shift of the EED feature. This mechanism may contribute significantly at low coverages of adsorbate. At high coverage, depositing more adsorbate should have a negligible effect on the substrate work function.

As for the helium metastable atom energy level shift, Fig 2.6 shows that it would be downward at low coverage, if we neglect the absorbate induced change. At high coverage, the helium energy level is relatively flat.
The remaining possibility is the final state image charge screening effect. Considering the dielectric effect of the Xe sublayers, it would induce a negative energy shift in the order of 1 eV between monolayers [Appelbaum, et al., Kaindl, et al.].

To summarize, all three mechanisms: the initial state work function change, the helium metastable energy level shift, and the final state image charge effect, may contribute to the negative layer dependent shift of the EED features at low surface coverages of adsorbate. Only the image charge effect could contribute significantly at high coverage.
Fig. 4.4 Exposure Dependence of He(2S) Deexcitation at Xe-covered Cu(100) Surface
2. Carbon Dioxide

Fig. 4.5 Electron Energy Distribution and Polarization Measured Following Penning Ionization of CO₂

As shown in Fig. 4.5, the EED obtained through SPMDS agrees very well with the gas phase Penning Ionization spectrum [Hotop et al., 1978]. CO₂ is a closed shell, negative electron affinity molecule. We observe four sharp features (clearly resolved in Hotop's data) indicating that the reactions proceed through covalent channels. The peaks correspond to the X^2Π_g, A^2Π_u, B^2Σ_u^+, and C^2Σ_g^+ final states of the CO₂⁺ ion, obtained
respectively by the removal of CO$_2$ 1π$_g$, 1π$_u$, 3σ$_u$ and 4σ$_g$ electrons. The ESP is 100\% within experimental error, as expected of reactions that proceed via the direct channel.

The MDS energy spectra as a function of CO$_2$ exposure is shown in Fig. 4.6. We observe a gradual change from the clean Cu(100) spectrum to that typical of CO$_2$. 
Fig. 4.6 Exposure Dependence of He(2\(^3\)S) Deexcitation at CO\(_2\)-covered Cu(100) Surface
3. Water

Fig. 4.7 Electron Energy Distribution and Polarization Measured Following Penning Ionization of H₂O

Fig. 4.7 shows the SPMDS EED and polarization for water frozen on Cu(100) together with the gas phase data. The three peaks in the EED correspond to formation of H₂O⁺ X²B₁, A²A₁ and B²B₂ final states and match those in the gas phase spectrum. The nearly 100% polarization is as expected for a closed shell, negative electron affinity target.
Fig. 4.8 Exposure Dependence of He(2^3S) Deexcitation at H_2O-covered Cu(100) Surface
Fig. 4.8 shows the EED from water-covered Cu(100) after different exposures. A gradual change from the clean Cu(100) profile to that typical of water is evident.

4. Oxygen

Fig. 4.9 shows the EED from oxygen covered Cu(100) following different exposures. Again the gradual change from the Cu(100) spectrum to that typical of O₂ is seen.

The EED and polarization for O₂ frozen on Cu(100) are shown in Fig. 4.10, compared with the gas phase measurements. The EED for O₂ has a broad, relatively featureless background indicating reactions via ionic channels. This is as expected because oxygen is an open shell molecule with +0.45 eV electron affinity. A number of sharp features are superimposed on the background corresponding to ionization through covalent channels into O₂⁺ X²Πg, a²Πu and b⁴Σg⁻ final states. The low energy peak in the solid phase EED near 0 eV is attributed to secondary electrons.
Fig. 4.9 Exposure Dependence of He(2^3S) Deexcitation at O_2-covered Cu(100) Surface
Fig. 4.10  Electron Energy Distribution and Polarization Measured Following Penning Ionization with \( O_2 \)

The measured electron polarization is considerably smaller than that of the incoming helium metastable atoms even at the peaks corresponding to reactions through covalent channels, due to electron exchange and the contributions from the ionic channel ionization. This can be explained by considering possible spin states of the reactants which may be written [Rutherford, et al.]:
The two triplet reactants can form quintet, triplet and singlet spin states. Expressing the three uncoupled $| M_s(\text{He}), M_s(O_2) \rangle$ entrance channels in terms of the possible $| S, M_s \rangle$ states for the total system, we have

\[
|1, 1 \rangle = |2, 2 \rangle
\]

\[
|1, 0 \rangle = \frac{1}{\sqrt{2}} (|2, 1 \rangle + |1, 1 \rangle)
\]

\[
|1, -1 \rangle = \frac{1}{\sqrt{6}} (|2, 0 \rangle + \frac{1}{\sqrt{2}} |1, 0 \rangle + \frac{1}{\sqrt{3}} |0, 0 \rangle)
\]

But the ionic complex, consisting of $O_2^-$ and $\text{He}^+$ spin doublets, can only have triplet and singlet spin states. Therefore the ionic channel in case (a) is spin forbidden, case (b) can happen for 1/2 of the collisions and case (c) can happen for 5/6 of the collisions. By energy conservation, the portion of the EED above 4 eV corresponds to ionization into the $O_2^+ \ X^2\Pi_g$ ground state. Assuming one of the $O_2 \ 1\pi_g$ electrons tunnels into the helium 1s hole, ejecting either the He 2s electron or the remaining $1\pi_g$ electron with equal probability, case (b) reactions yield 100% polarization of the ejected electrons and case (c) 0%. So the total polarization of the ejected electrons is 3/8. This result agrees very well with experimental observations within the error range.

For the low energy part of the EED, we need to consider ionization into the $O_2^+ \ a^4\Pi_u$ and $b^4\Sigma_g^-$ states. In a similar manner to that discussed above, the electron polarization in such reactions can be calculated to be close to zero. The polarization below 4 eV could be qualitatively explained if we consider contributions from ionization
into $O_2^+$ $a^4\Pi_u$ and $b^4\Sigma_g^-$ final states via the covalent channels and ionic channel ionization into both ground and excited states.

5. Nitric Oxide

Fig. 4.11 shows the EED from NO-covered Cu(100) with different exposures. We can see the gradual change from the Cu(100) profile to that of NO.

The EED and polarization for NO frozen on the Cu(100) surface are shown in Fig 4.12, together with measurements from the gas phase PI. The EED and polarization of the solid phase match that of the gas phase PI. Nitric Oxide has an electron affinity of 0.026 eV, so we would expect the ionic channel to contribute to a lesser extent than for oxygen. But the EED still exhibits a broad underlying continuum indicating ionic channel reaction. In Hotop's data, there is a sharp feature at 3.2 eV attributed to ionization via the covalent channel to the NO$^+$ $b^3\Pi$ final state.
Fig. 4.11 Exposure Dependence of He(2^3S) Deexcitation at NO-covered Cu(100) Surface
Fig. 4.12 Electron Energy Distribution and Polarization Measured Following Penning Ionization of NO

The polarization is significantly lower than the incoming He* atoms due to depolarization in the ionic channel.
6. Chlorine

Fig. 4.13 shows the EED from chlorine-covered Cu(100) surface with different exposures. Again the gradual change from the characteristic Cu(100) profile to that of Cl\textsubscript{2} is seen.

The EED and polarization for Cl\textsubscript{2} frozen on Cu(100) surface are shown in Fig 4.14, together with measurements of gas phase PI.

Chlorine's electron affinity is 2.38 eV. The large, broad and relatively featureless background in its EED can be attributed to reactions through the ionic channel. Model calculations of ionization via the autoionization channel reproduce very well the peak just below 1.45 eV, indicating that the collision complex forms a Cl\textsubscript{2}** molecular Rydberg state that may dissociate into ground-state and highly excited Cl** atoms, which subsequently undergo autoionization.

The sharp peak at 5.5 eV is attributed to ionization via the covalent channel into the Cl\textsubscript{2}+ A2\Pi\textsubscript{u} state. Two other peaks corresponding to the Cl\textsubscript{2}+ X2\Pi\textsubscript{g} and b2\Sigma\textsubscript{g}⁻ final states have been observed in gas phase PI. The peaks are not clearly resolved in the solid phase EED due to the large background of electrons ejected in ionic channel reactions. This is possibly because, in the solid phase, the interactions between the adsorbate atoms and between the adsorbate and substrate change the symmetry of the reactants and enhance the probability of ionic channel reactions.
Fig. 4.13 Exposure Dependence of He(2S) Deexcitation at Cl₂-covered Cu(100) Surface
Fig. 4.14 Electron Energy Distribution and Polarization Measured Following Penning Ionization of Cl₂

In the gas phase PI data, the polarization at the $A^2Π_u$ peak is nearly equal to that of the metastable helium atoms within experimental error. However in the solid phase, the polarization is significantly reduced indicating ionic channel reaction is more important than in gas phase. At lower energy characteristic of ionization via the autoionization channels, the polarization is much higher than that of gas phase presumably because the autoionization channel reaction is limited in the solid phase.
Chapter 5 Conclusion and Future Directions

This thesis reports the first SPMDS experiments with solid phase gases as targets. The present results demonstrate that SPMDS is a valuable technique for studying surface electronic structure and the dynamics of SPMDS. The mechanisms through which metastable helium atoms are deexcited at a gas-covered metal surface are shown to change gradually from that typical of a clean metal surface to a process analogous to gas phase Penning Ionization as the amount of gases absorbed increases.

SPMDS experiments verified earlier PI results obtained in the Rice Flowing Afterglow machine, also using spin labeling techniques. The direct exchange model is shown to be applicable for collisions with closed shell, negative electron affinity targets, in which the excited electron from the metastable atom is ejected and the spin polarization is preserved. For open shell, positive electron affinity targets and targets for which excitation transfer to autoionizing states is possible, an intermediate ionic complex and/or autoionizing states may be formed during the interaction, resulting in reduced ejected electron polarization.

Interactions between the absorbed particles and between the substrate and the absorbed particles are shown to be important, especially in the case of Xenon. The presence of the substrate causes the binding energy of the orbitals of the adsorbate to shift, and may also induce image charge screening effects. In addition, the adsorbed particles may interact among themselves, broadening and shifting the energy levels. Hopefully the experiments reported here will encourage further theoretical and experimental work.
In the course of this work, it was demonstrated that use of a stabilized Ti:Sapphire laser for optical pumping produces nearly 100% polarization of the He(2^3S) beam. Its routine use can be expected to greatly improve the accuracy and resolution of the polarization measurements. The Ti:Sapphire laser can also be used to excite the He(2^3S) state to the He(2^3P) state at the sample surface, which would make possible studies of He(2^3P) deexcitation.

The exact calibration of the adsorbed layer thickness was not possible in these experiments, though they can be estimated from the known exposures if unit sticking probability is assumed. In addition, the energy resolution of the retarding grid analyzer is not good as desired for some studies. Improvements to the configuration of the final chamber could make the quantitative studies possible.

Questions regarding the electronic structure of the various frozen molecular targets, especially Xe, remain unanswered. In future experiments we will try to gain additional insight by varying the surface work function and measuring the corresponding changes in the EED's and electron spin polarizations.
References


