



Matrix and substrate interactions and their influence on secondary ion emission
by Michael J Connolly

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry

Montana State University

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Abstract:

The full analytical potential of particle induced desorption mass spectrometry, fast atom bombardment mass spectroscopy (FABMS) and the secondary ion mass spectroscopy (SIMS), has not been achieved.

The reason for this is that the relationship between the emitted secondary ions and the chemistry occurring in solution and the chemistry and structure of the surface complexes is not fully understood. The purpose of the present investigation is to study the relationship between emitted secondary ions and well defined surface structures and well defined solution equilibria.

Interactions of acetic acid (CH_3COOH) and acetate (CH_3COO) with a well defined Ag(110) single crystal surface have been studied using electron energy loss spectroscopy (EELS), ultra-violet photoelectron spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS). The secondary ions detected in SIMS of $\text{CH}_3\text{COOH}/\text{Ag}(110)$ and $\text{CH}_3\text{COO}/\text{Ag}(110)$ are then related to the observed interactions determined using EELS, UPS and XPS. It is shown that the $(\text{CH}_3\text{COOH}+\text{Ag})^+$ secondary ion is formed by a recombination mechanism and hydrogen bonding is responsible for formation of the $(\text{CH}_3\text{COOH}+\text{H})^+$ secondary ion. It is further postulated that the $((\text{CH}_3\text{COO})_2\text{Ag})^-$ secondary ion emitted from $\text{CH}_3\text{COO}/\text{Ag}(110)$ is formed by a combination of intact emission of CH_3COOAg followed by recombination with CH_3COO^- to produce $((\text{CH}_3\text{COO})_2\text{Ag})^-$.

The solution equilibria for the reaction between glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) and copper(II) ions in glycerol is shown to be essentially analogous to the equilibria established in water. FABMS of glycerol solutions of $\text{NH}_2\text{CH}_2\text{COOH}/\text{Cu(II)}$ show that the FAB process induces chemical reactions that include reduction, dehydration and protonation. It is further shown that FABMS does not quantitatively reflect the ionic solution equilibria established in $\text{NH}_2\text{CH}_2\text{COOH}/\text{Cu(II)}$ glycerol solutions.

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Date

May 14, 1985

I would like to dedicate this to my wife Joan, whose support of me never faltered and to my mother who will be proud of my accomplishments.

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ABSTRACT

The full analytical potential of particle induced desorption mass spectrometry, fast atom bombardment mass spectroscopy (FABMS) and the secondary ion mass spectroscopy (SIMS), has not been achieved. The reason for this is that the relationship between the emitted secondary ions and the chemistry occurring in solution and the chemistry and structure of the surface complexes is not fully understood. The purpose of the present investigation is to study the relationship between emitted secondary ions and well defined surface structures and well defined solution equilibria.

Interactions of acetic acid (CH_3COOH) and acetate (CH_3COO) with a well defined Ag(110) single crystal surface have been studied using electron energy loss spectroscopy (EELS), ultra-violet photoelectron spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS). The secondary ions detected in SIMS of $\text{CH}_3\text{COOH}/\text{Ag}(110)$ and $\text{CH}_3\text{COO}/\text{Ag}(110)$ are then related to the observed interactions determined using EELS, UPS and XPS. It is shown that the $(\text{CH}_3\text{COOH}+\text{Ag})^+$ secondary ion is formed by a recombination mechanism and hydrogen bonding is responsible for formation of the $(\text{CH}_3\text{COOH}+\text{H})^+$ secondary ion. It is further postulated that the $((\text{CH}_3\text{COO})_2\text{Ag})^-$ secondary ion emitted from $\text{CH}_3\text{COO}/\text{Ag}(110)$ is formed by a combination of intact emission of CH_3COOAg followed by recombination with CH_3COO^- to produce $((\text{CH}_3\text{COO})_2\text{Ag})^-$.

The solution equilibria for the reaction between glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) and copper(II) ions in glycerol is shown to be essentially analogous to the equilibria established in water. FABMS of glycerol solutions of $\text{NH}_2\text{CH}_2\text{COOH}/\text{Cu(II)}$ show that the FAB process induces chemical reactions that include reduction, dehydration and protonation. It is further shown that FABMS does not quantitatively reflect the ionic solution equilibria established in $\text{NH}_2\text{CH}_2\text{COOH}/\text{Cu(II)}$ glycerol solutions.

CHAPTER 1

INTRODUCTION

Background Material

If a solid or nonvolatile organic liquid is bombarded by ions or neutral atoms in the kiloelectron-volt (KeV) range, complex processes of energy transfer and electronic interaction occur in the surface zone, the top 80-100 Å. As a result of these interactions, atomic and molecular particles are emitted. This phenomena is called sputtering (1). Sputtering of positively and negatively charged atoms and molecules with subsequent analysis of their mass-to-charge (m/z) ratio forms the basis of two powerful techniques called secondary ion mass spectrometry (SIMS) and fast atom bombardment mass spectrometry (FABMS). In SIMS the sample is bombarded with a KeV ion beam and in FABMS the sample is bombarded with a KeV neutral atom beam. Applications of these techniques are extremely broad, ranging from the sequencing of polypeptides to the determination of reaction intermediates in heterogeneous catalysis (2-9). Extension of these techniques to more complex problems will become possible as the instrumentation becomes more sophisticated and the relationship between the emitted ions and the chemistry occurring in solution or between the adsorbate and substrate become better defined (5,8,20).

The mechanism of particle emission from a sample surface under KeV particle bombardment involves momentum transfer from the primary

bombarding particle to sample atoms. To date, the best model for describing this momentum transfer process has been developed by Sigmund (1).

Upon impact with the sample surface, the primary particle transfers its momentum to the sample atoms through screened coulombic interactions between the respective nuclei. In Sigmund's model these are strictly binary elastic collisions. Because it is this sequence of binary elastic collisions that is responsible for the ejection of material from the surface, it is not important to distinguish the bombarding particles as being either primary atoms or primary ions (21,22). This process will produce a "collision cascade" within the sample, displacing or recoiling many sample atoms along the penetration track of the primary particle. The large number of atomic displacements induced by the primary particle are apparent at the surface within a radius of $20 \text{ \AA}$ at the point of impact. This atomic displacement with resulting bond breaking extends to a depth roughly equivalent to the range of the primary particle in the sample, $80\text{-}100 \text{ \AA}$ (1,13). The resulting damage is referred to as radiation damage. Sputtering occurs only when the collision cascade extends to the sample surface.

Ejection of material from the surface will then occur by two principal mechanisms (1); "direct-knock-on" and "linear cascade" sputtering. Both of these regimes are depicted in Figure 1. In the direct-knock-on regime, the bombarding particle transfers energy to target atoms which, after undergoing a small number of further collisions, are ejected from the surface. This will occur only if

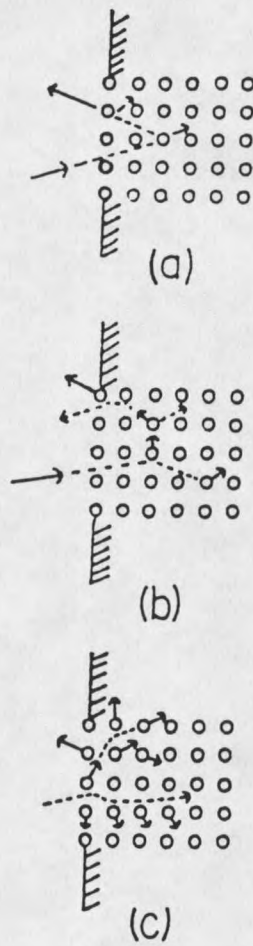


Figure 1. Regimes of sputtering by elastic collisions. (a) Direct-knock-on, (b) linear cascade, (c) spike (from ref. 1).

these displaced atoms are energetic enough to overcome surface binding forces. In the other two cases, recoil atoms are energetic enough to generate secondary and higher generation recoils, some of which intersect the surface with enough kinetic energy to overcome the surface binding forces. The spike regime is a special case of linear cascade sputtering differing in that the spatial density of moving atoms in the active volume is greater. For organic molecules, these ejection mechanisms will produce secondary particles which vary considerably in kinetic energy, angle of emission and number of constituent atoms (12).

When a linear cascade extends to a distance of 40 Å from the track of the primary particle, the energy of the recoiled atoms is small and sputtered particles are emitted with low kinetic energy (< 2 eV). A large organic molecule absorbed on the surface might be ejected, intact, by a concerted push from these low energy recoils (14). At this point, in a linear cascade, the motion of the recoil atoms is random and particles are emitted with a cosine distribution (1). Direct-knock-on sputtering produces emitted particles with high kinetic energies, 5-100 eV (1), and also induces a lot of fragmentation of surface species.

The relationship between intact emission, fragmentation and the energy transfer to a surface molecule is shown schematically in Figure 2. This diagram describes the average of a large number of primary impacts. Surface species are ejected by the fast transfer of relatively small amounts of kinetic energy to the surface. Surface species are ejected intact if the average energy transferred to the

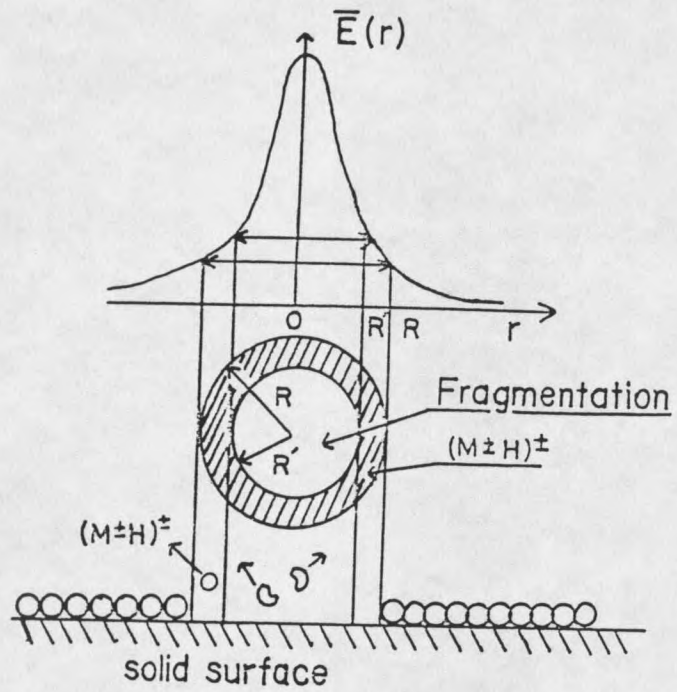


Figure 2. Energy transfer to surface species during sputtering (from ref. 15).

surface lies between $R' < r < R$. Here r represents the distance from the surface species ejected to the point of impact of the primary particle. This diagram is also supported by Monte Carlo calculations of trajectories of recoiled atoms (12). The extremely short time period, $< 10^{-12}$ s (1), in which the energy transfer occurs seems to be responsible for the fact that there is very little vibrational excitation of the emitted molecules. The final charge state of the emitted species may be neutral, positive or negative. This depends strongly on its bonding state at the surface (15,20) and on electronic interactions with the surface as the species is ejected (16).

Experimentally, the generation and detection of the emitted ionic species in a particle induced desorption ionization (DI) experiment is split into two related techniques. The first uses a charged primary ion beam, typically an inert gas, and a sample that is in the form of a solid. The subsequent mass analysis is performed using a quadrupole mass analyzer with an energy filter (17). This technique is shown schematically in Figure 3, and is called secondary ion mass spectrometry or SIMS. The name is derived from the experimental procedure of using a primary ion beam to generate the sputtered secondary ions. The second technique uses a neutral primary atom beam with a nonvolatile liquid sample with subsequent mass analysis performed with a double focussing mass spectrometer. This technique has been given the name fast atom bombardment mass spectrometry or FABMS, derived from using an atom beam as the primary particle. This technique is shown schematically in Figure 4. It is

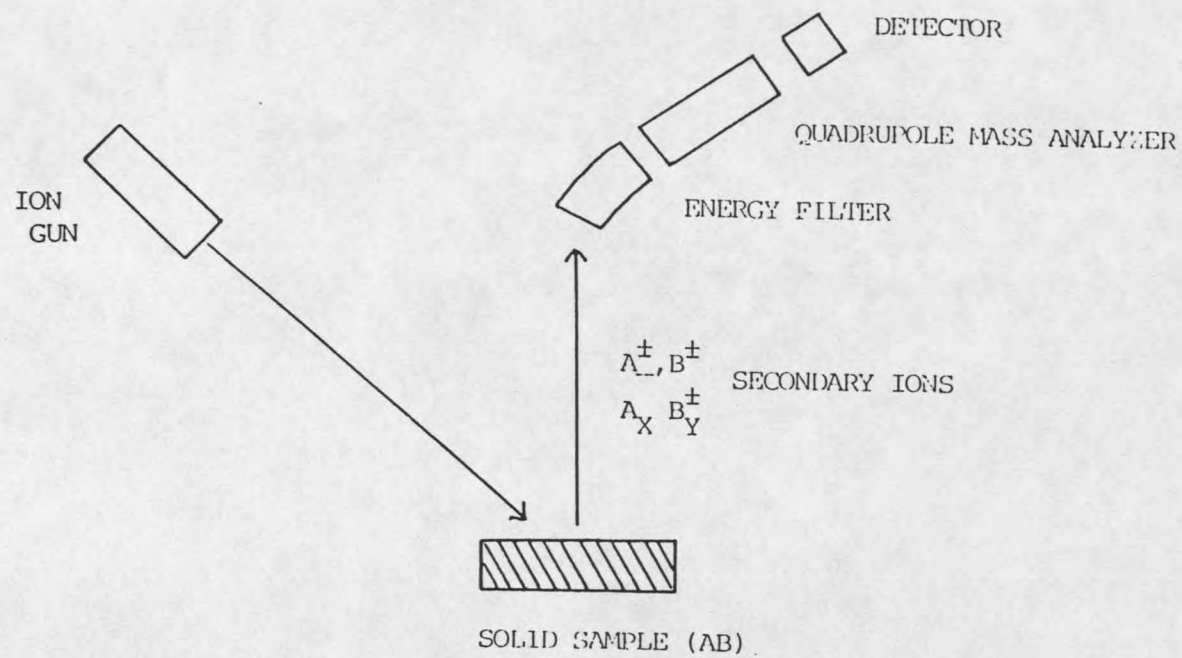


Figure 3. Schematic diagram of the SIMS experiment.

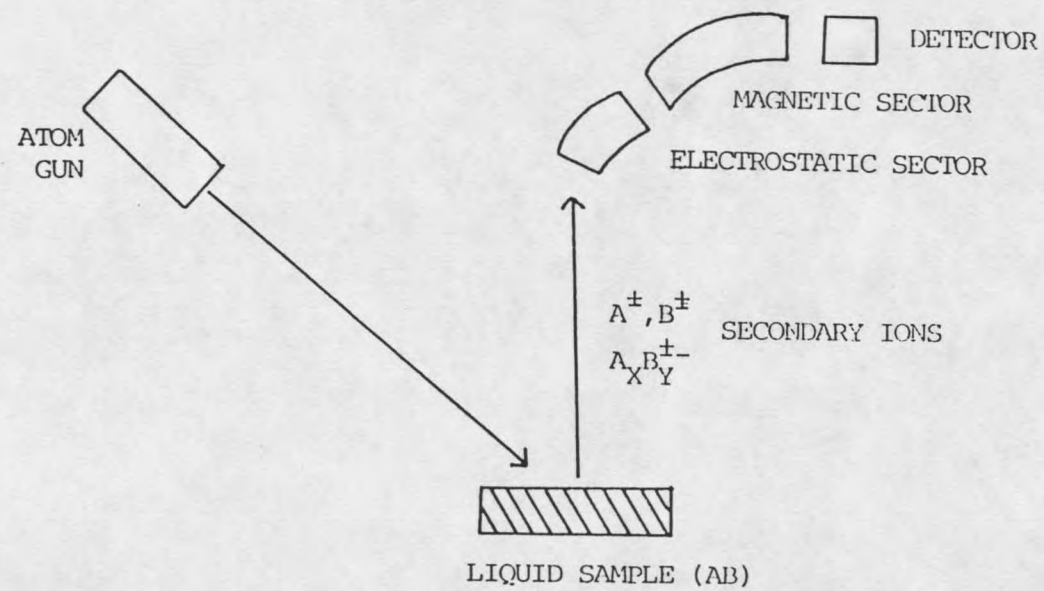


Figure 4. Schematic diagram of the FABMS experiment.

also possible to use a charged primary ion beam (SIMS), with a liquid sample and perform the subsequent mass analysis with either a quadrupole or magnetic mass spectrometer. However, with a magnetic sector instrument the sample needs to float at the operating potential of the spectrometer, typically 3-8 KeV. This limits the choice of ion gun sources, most ion guns are limited to 5 KeV, and presents the problem of primary ion beam transfer into the source which is at high potential.

Bennighoven (15) has found that the transformation probabilities, i.e. the probability that a surface molecule disappearing from a surface during particle bombardment will result in the emission of a secondary ion, are of the same order of magnitude, for sputtering the same molecule, for both a glycerol matrix and a metal surface. It has also been demonstrated that the same results are obtained when a glycerol matrix is bombarded with either a charged or neutral primary beam (21,23,24). Cook (25) has done a comparison study of SIMS and FABMS and in it concluded that SIM spectra will display more fragmentation than the FABM-spectra, obviating that there is more energy deposition in the SIMS experiment.

Since Barber (18) introduced the concept of using a nonvolatile liquid sample matrix in FABMS experiments, the analytical applications of the two matrix techniques have become divided. The concept of dissolving or suspending the sample in a liquid matrix prolongs the generation of sputtered ions from a few seconds duration with no liquid matrix to longer than thirty minutes with liquid

matrix (18). The liquid matrix technique is capable of producing a more intense molecular secondary ion beam than the corresponding solid sample and thereby expands the application of the technique to include high resolution, high mass and tandem sector mass spectrometers. These advantages coupled with the fact that fast atom beam sources are inexpensive and easily retrofit onto existing spectrometers of this type have increased the popularity and hence analytical application of FABMS.

Analytical applications of FABMS range from the analysis of complex mixtures by tandem mass spectrometry techniques to the determination of high molecular weight biomolecules (19). Applications of SIMS involve studies aimed at understanding the fundamentals of ion desorption, analysis of submonolayer quantities of molecular species on solid surfaces and depth profile analysis of layered devices used in the semiconductor industry (6).

The high sensitivity of these techniques allows routine investigation of analytes in a liquid matrix or adsorbed on a solid substrate. The detected ions contain a wealth of information concerning the chemistry occurring in solution (19) and the structure and composition of the surface of a solid sample (5). Because ion formation mechanisms can be influenced by a large number of factors, often in a complicated way, interpretation of the FABMS or SIMS spectrum is often difficult (26). A better understanding of the relationship of the emitted secondary ions to the chemistry occurring in solution and to the chemistry and structure of the solid surface

is needed before the full potential of these techniques can be realized (11,15).

Purpose of Present Investigation

The purpose of the present investigation is two-fold. The first is to examine the relationship between the secondary ions observed in SIMS and the chemistry and structure of adsorbed organic species on a well defined Ag(110) single crystal surface. The second is to examine the relationship between the desorbed ions in FABMS and the chemistry occurring between metal ions and organic ligands in a glycerol matrix. This thesis is organized into four chapters, each of which is self-contained with its own introduction.

Chapter 2 examines the ejection mechanisms of molecular adsorbates using CH_3COOH and CH_3COO on Ag(110) as a model system. The interactions of these species with Ag(110) are probed using high resolution electron energy loss spectroscopy (HREELS), x-ray photoelectron spectroscopy (XPS) and ultra-violet photoelectron spectroscopy (UPS). These interactions are then used to relate the observed secondary ions in SIMS to current existing ion ejection mechanisms. It is shown that the $\text{CH}_3\text{COOH}/\text{Ag}(110)$ interaction at 90 K is very minimal and both the intact emission and recombination models of secondary ion emission can be invoked to explain the observed secondary ions. It is also shown that $\text{CH}_3\text{COO}/\text{Ag}(110)$ undergoes a coordination change from 210 K to 290 K. The observed secondary ions in SIMS cannot definitively distinguish between these modes of coordination.

Chapter 3 examines the desorbed ions in FABMS to determine if these ions quantitatively reflect the chemistry occurring in solution. The system chosen to investigate this relationship is the reaction between $\text{NH}_2\text{CH}_2\text{COOH}$ and Cu^{2+} . First, the solution chemistry in glycerol is verified to be qualitatively equivalent to that occurring in the aqueous system. It is then shown that the observed ions in FABMS do not reflect all the chemistry occurring in solution and these results are analyzed in relation to existing ideas on particle induced desorption of ions from liquid samples. The results of this study are summarized in Chapter 4.

CHAPTER 2

ADSORBATE - SUBSTRATE INTERACTIONS AND THEIR INFLUENCE
ON THE FORMATION OF SECONDARY IONSIntroduction

Secondary ion emission of molecular ions has been well known since the early investigations of Honig (27), Benninghoven (28) and McHugh (29). For example, secondary ions of the general composition $C_M H_N^+$, were observed in many spectra. These ions disappeared, however, after removal of several monolayers during the sputtering process and were generally attributed to contaminants on the surface. Benninghoven (28) was the first investigator to actually study molecular ion emission. These early investigations dealt with molecular ion emission of ions from acetate salts on a copper substrate.

The original SIMS experiments employed ion beams with ion current densities in the range of 10^{-6} amps/cm². This corresponds to a particle flux of 6.2×10^{12} ions cm⁻² sec⁻¹. If we assume a sputtering yield of unity then several monolayers could be removed in five minutes. This assumes a monolayer has 5×10^{14} molecules/cm², which is a reasonable value for small organic adsorbates (30). The mean escape depth of sputtering particles has been analytically determined by Sigmund (31) and is given by the expression $n\Delta x = 4.1 \times 10^{15}$ cm⁻², where Δx is the mean escape depth and n is the number

density of the target material. Δx for metal targets lies between 5 and 10 Å. More recently (32) Monte Carlo calculations have shown the escape depths to be on the order of 10-15 Å. Escape depths of this magnitude give SIMS the potential of being an extremely surface sensitive technique. However, the investigation of monolayer and sub-monolayer coverages by SIMS was inhibited by the amount of radiation damage caused during ion impact. If we assume that each individual ion impact damages surface zone molecules over an area of 100 Å^2 (1,8,12), then in less than 30 seconds of ion bombardment at $10^{-6} \text{ amps/cm}^2$, 1 cm^2 of surface zone will be damaged due to ion impact. The resulting changes in the surface zone due to the energy transfer process can be grouped into four categories:

- 1) Loss of surface atoms out of the emission zone as a consequence of the emission of atomic and molecular species.
- 2) Implantation of primary ions and recoil surface atoms.
- 3) Changes in the lattice structure, both super lattice and main lattice.
- 4) Chemical effects such as bond breaking.

In order to use SIMS as an analytical tool to investigate the structure and composition of surfaces or to investigate molecular ion emission, the surface zone damage needs to be reduced.

This was recognized by Benninghoven (33) and in 1970 he developed the technique of "static SIMS." The requirement to be satisfied in a static SIMS experiment is the lifetime of a monolayer must be long in comparison to the time of ion bombardment during the investigation. This can be accomplished by lowering the primary ion

current density into the 10^{-9} amps/cm² range. Assuming again that a molecular monolayer contains 5×10^{14} molecules/cm² and molecular secondary ions can only be sputtered intact from a previously unbombarded area on the sample surface (34). For molecular adsorbates this will be the case until $\sim 10\%$ of the surface has suffered damage (12). Surface damage of 10% for a molecular monolayer corresponds to damaging 5×10^{13} molecules/cm². At an ion current density of 10^{-9} amp/cm² one could sputter for ~ 2 hours, giving a particle flux of 5×10^{13} ions/cm² which corresponds to 10% surface damage if each impact fragments only one molecular surface species. However, if we assume each bombarding particle destroys 100 $\text{\AA}^2$ (12), then each impacting ion would damage 5 molecules. At a primary ion current density of 10^{-9} amps/cm², $\sim 50\%$ of a molecular monolayer would be destroyed in ~ 2 hours.

Experimentally, the use of low particle flux presents several problems. At such low primary ion current densities the number of secondary ions detected becomes extremely small. This can be offset by rastering the primary ion beam so that a larger sample area is bombarded. Low particle flux experiments require more time for data collection, typical collection times are in the vicinity of 1 hour. If one is interested in investigating surface reactions of monolayer to sub monolayer coverages, then vacuum requirements become very stringent. Assuming a sticking coefficient of unity, a monolayer will form in one second at 10^{-6} torr and 1000 seconds at 10^{-9} torr. Therefore, in order to perform a static SIMS experiment on monolayer coverages without interference from residual gases in the vacuum

chamber, the pressure must be in the low 10^{-10} torr range or lower. To summarize, a static SIMS experiment is conducted at low ion current densities to minimize surface damage and ultra high vacuum to prevent residual gas contamination. Because of the low surface damage and low detection limits of a given component in a monolayer, typically between 10 and 0.01 ppm (8), static SIMS is being applied to a broad range of problems (6). Of particular importance is the static SIMS analysis of organic molecules.

Presently, there is a great deal of work which has examined the SI emission of many groups of compounds under many different conditions. All of this gives some qualitative direction when a compound needs to be analyzed. However, there is no clear evidence as to the specific nature of the process of forming the secondary ions, nor is there a clear set of rules to guide one when a compound is to be analyzed. There are several models (35) which do fit the observations but none has sufficient experimental evidence to be accepted over the others. In fact, there is no reason why all the methods of forming secondary ions or clusters could not be operating simultaneously. Therefore, there is a definite need to examine the process of SI emission under carefully controlled conditions and by different surface techniques.

Particle induced formation of secondary ions from solids is characterized by the formation of secondary ions composed of molecular ions, ions attributable to reactions and cluster ions. The static SIMS spectra of frozen benzene (36) displays ions attributable to molecular ions, fragment ions, clusters and ions due to reactions.

Another class of secondary ions are cationized or anionized secondary ions. Cationized secondary ions are formed by simply placing the molecule of interest on a metal substrate or mixing it with an alkali salt (37,38) and then bombarding it with high energy particles. The cationized secondary ion is simply a secondary ion composed of the molecular species and a metal ion. Cationized secondary ions have been used effectively to extend the capabilities of secondary ion emission by enhancing the ability to identify molecules. At this time, there is very little known about the matrix effect, nor is there a systematic way to choose the correct metal to yield the desired secondary ion.

The study of the mechanism for formation of secondary ions has generally revolved around two theoretical pictures, the direct emission model (39-42) and the recombination model (36,43,44). Both models require a binary collision cascade in order to eject a secondary particle. The difference in the methods arises in how a cluster ion or cationized ion is formed during the emission process. Neither model addresses how an ion is formed. It is worth noting that in the studies of the secondary ion emission of metal oxides that both mechanisms could be observed depending on the properties of the sample.

If MX is the ejected cationized pair where M is the cation and X is the adsorbed molecule, then in the direct emission model co-emission of strong-bonded nearest neighbors occurs when enough momentum is imparted to M or X such that:

$$P(MX) < B_{in}(MX)$$

where $P(MX)$ is the momentum of MX and $E_{in}(MX)$ is the bond energy of the MX bond. In order to observe the cationized pair, the kinetic energy must be greater than the surface bonding energy of the pair.

In the recombination model two or more ejected particles recombine in the selvedge region to form the observed cluster species. The ejected particles need not be nearest neighbors in order to recombine. If the ejected particles have the appropriate correlation in time and space they will form a bonding pair if:

$$\sum_{ij} (E_{ij} + V_{ij}) < 0$$

where E_{ij} is the relative kinetic energy of the pair and V_{ij} is the potential energy between the pair.

The parameters that generally characterize these models are the angular distribution, energy distribution and the sputtering yields of the secondary ions. The angular distribution is very important and can be used to find the orientation of adsorbed species on the surface (45). The energy distribution does not necessarily differentiate between the models. Both predict narrow distributions and lower average energies for ejected clusters vs. ejected atoms or molecular species. The sputtering yields, however, can be used to differentiate between the models, as illustrated for the case of metal oxides (43).

It is apparent that if the cationized secondary ions are formed by recombination, the interaction between the metal substrate and the molecule on the surface should not have a great influence on whether or not the cationized pair is observed. What does matter is the

potential energy interaction between the ejected particles. In the case of the direct emission model, the surface interaction is important and, in fact, could state that this interaction on the surface can be described as a precursor interaction (15). If the recombination model is a proper description of the formation of the cationized secondary ion, then all that is required is to choose the metal substrate that will yield an ejected metal ion that will interact strongly with an ejected organic molecule. It is interesting to note that the nature of the metal substrate, i.e. pure, oxidized or alloyed, influences the degree of organic fragmentation (46). Also, the charge state of the emitted organic secondary ions is dependent on the metal and the adsorbate coverage (47).

One of the requirements for understanding the formation mechanism for cationized secondary ions and clusters is the need for a combination of surface methods utilized in situ. This permits characterization of the surface before bombarding with primary ions and allows the identification of interactions between surfaces and adsorbed species. With this information it will then be possible to correlate the importance of the interaction with the observed emission of secondary ions. Many combinations of surface methods require a transfer of the sample between UHV systems. This is not the case for the experiments to be carried out in this study. For example, it is possible to use the combined methods of photoelectron spectroscopy, electron energy loss spectroscopy, low energy electron diffraction spectroscopy and SIMS when studying a sample.

Presently, most organic samples to be analyzed by SIMS are prepared by depositing the organic molecule of interest on the surface of a metal substrate or solution. This of course does not lend itself to easily controlled surface conditions. Consequently, it is necessary to deposit the samples under UHV conditions onto well characterized metal substrates. Studies have been carried out in which UHV deposited amino acids were examined (47). The surface, however, was characterized only by correlating surface coverage with the observed yield in the secondary ion emission spectra. The surface coverage was determined in a separate chamber with a static Auger spectrometer.

The major objective of the present study is to investigate the interactions of an organic adsorbate on a single crystal metal substrate and to determine whether or not a correlation exists between the observed secondary ions and the surface interactions. Specifically, the interest lies in whether the substrate-adsorbate interaction prior to particle bombardment is significant or the bombardment itself causes the observed secondary ions.

The chemical system chosen to investigate the question of whether or not substrate-adsorbate interactions are important in the formation of secondary ions is the interaction of acetic acid (CH_3COOH) with a clean and oxygen dosed $\text{Ag}(110)$ single crystal surface. This system was investigated by Madix (48) because it is thought that acetate species participate in the oxidation of ethylene to CO_2 and H_2O which compete with the partial oxidation of ethylene to ethylene oxide on silver catalysts. Madix found that CH_3COOH has

very little interaction with the Ag(110) surface, determined by thermal desorption, but that acetate has a much greater interaction with this same surface (48). For the present investigation, these species present adsorbate-substrate interactions that vary from very weak to extremely strong and should provide a good test for the importance of substrate-adsorbate interactions on the formation of secondary ions during ion bombardment.

The objective is to identify surface structure using combined surface analysis methods and determine if a correlation exists between the SIMS results and the observed surface species. This objective has been achieved for secondary ion emission from small molecules on Ru (49) and for ethylene on Pt (50) where the comparison was made with previous surface studies. The adsorbate interaction with the substrate will be examined by electron spectroscopic techniques to determine if the adsorbate-substrate bonding is strong or weak and to determine the orientation of the adsorbate, which should also help in determining which adsorbate orbitals are participating in bonding to the substrate.

The two electron spectroscopies that will be employed are photoelectron spectroscopy and low energy electron energy loss spectroscopy. In the photoelectron experiment, photons incident on the surface excite electrons within the adsorbate and the substrate. The result of this excitation is the ejection of an electron from the substrate or adsorbate. The kinetic energy, E_k , of the photoemitted

electron is measured and subsequently related to its binding energy by:

$$E_k = h\nu - E_b - \phi$$

where $h\nu$ is the incident photon energy, E_b is the electron binding energy and ϕ the work function of the spectrometer. Photoelectron experiments will be conducted using two different photon sources. The first method will employ x-rays and is called x-ray photoelectron spectroscopy (XPS). The incident energy of these photons is 1250 eV and the photoemitted electrons come from core atomic levels. The second method will employ ultra-violet photons from a helium discharge lamp and is called ultra-violet photoelectron spectroscopy (UPS). The incident energy of these photons is less than 50 eV and hence the photoemitted electrons come from high lying valence states or high lying molecular orbitals. UPS yields information regarding the extent of bonding between the adsorbate and substrate while XPS gives information on bonding within the adsorbate.

In low energy electron energy loss (EELS), the surface is irradiated with a highly monochromatic beam of low energy (< 5 eV) electrons. These low energy electrons interact with the oscillating dipoles of adsorbed species and inelastically scatter off the surface. The kinetic energy of the inelastically scattered electrons is measured and related to the excited vibrational mode of the adsorbate or substrate by:

$$E_{se} = E_e - \hbar\omega$$

where E_{se} is the kinetic energy of the scattered electron, E_e is the kinetic energy of the incident electron and $\hbar\omega$ is the energy of the

excited vibrational mode. The nature of the interaction between the incident electron and the surface vibration is complex (51,52) and will not be covered here. However, it will suffice to mention that theory distinguishes between three limiting cases: dipole scattering, negative ion resonance and impact scattering. The analysis of surface vibrations comes under dipole scattering and experimentally the kinetic energy of the scattered electron beam is measured in the specular direction. This technique yields information regarding the orientation on the surface of the adsorbed species.

The orientation of adsorbed species is determined by comparison with gas phase vibrational spectra and the application of group theory (51). However, in conjunction with this, it must be remembered that:

- 1) When a molecule adsorbs on a surface, the symmetry of the molecule is lowered, relative to the gas phase molecule.
- 2) There generally are detectable shifts in the frequencies of certain vibrational modes with the adsorption of the molecules.

Because the inelastic scattering is caused by electron-dipole interaction, the selection rule that applies is that only vibrations with a perpendicular component to the surface contribute to the observed spectrum (51,52). On the other hand, due to the lower symmetry at the surface, any vibration that is not required by symmetry to be exactly parallel to the surface is dipole active. Therefore, modes that are Raman active only in free molecules may become dipole active when adsorbed on the surface. Specific

consideration of the question of activity has to be given to each surface species and each orientation with respect to the surface.

Experimental

Instrumentation

The spectrometers (EELS, LEED, UPS, XPS, SIMS) used in these studies are all housed in one custom work chamber. This instrument is located in the CRISS (Center for Research In Surface Science) laboratory which is located in the Physics Department at Montana State University. Figure 5 shows an overall schematic of the instrument.

The work chamber is an ultra-high vacuum ($< 10^{-9}$ torr) chamber. It is pumped by two 360 l/s turbomolecular pumps, an ion pump and a liquid N_2 cooled titanium sublimation pump. Typical base pressure for this instrument, after a 24 hour bake-out at 150°C , is 1×10^{-10} torr or less.

As shown in Figure 5 there are two sample introduction systems. There is a rapid insertion hot/cold rod, h in Figure 5. Experiments that involved using XPS, UPS and SIMS can be performed using this sample introduction system. However, if pressures $< 10^{-9}$ torr are needed, then this rod cannot be used. The X, Y, Z, θ hot/cold sample manipulator, i in Figure 5, is capable of traversing the whole work chamber and thus allows all spectroscopies to be performed on the same sample. This is an all metal introduction system and is capable of maintaining pressures of $< 10^{-9}$ torr during sample alignment. The

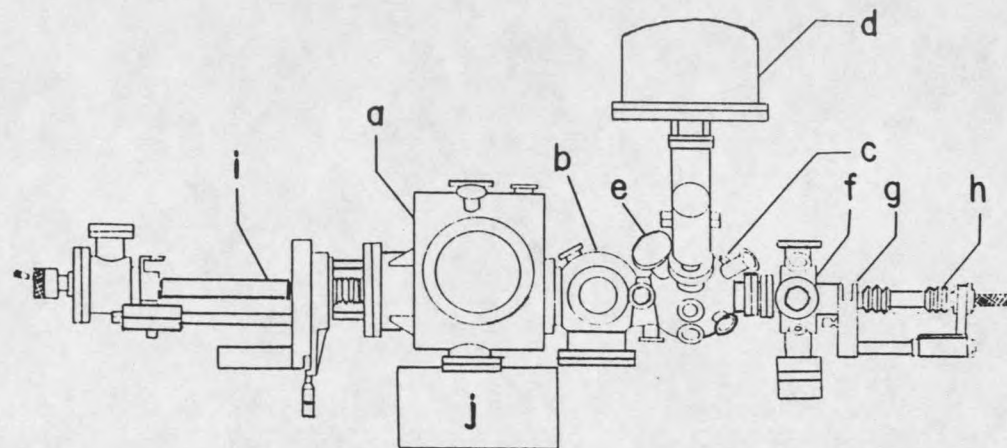


Figure 5. Schematic diagram of the UHV work chamber. (a) EELS analysis chamber, (b) LEED analysis chamber, (c) XPS, UPS, SIMS analysis chamber, (d) XPS, UPS hemispherical analyzer, (e) SIMS detector, (f) sample preparation chamber, (g) direct insertion interlock, (h) hot/cold sample rod, (i) X,Y,Z, θ hot/cold sample manipulator, (j) main chamber pump station.

Ag(110) crystal used in the following experiments was mounted on this manipulator so that all spectroscopies could be performed on the same sample. This manipulator also allows the desired temperature range of 90 K to 900 K, along with electrical isolation, to be attained.

The HREEL spectrometer, Leybold-Heraeus model 22, consists of a low energy electron gun and double pass 127° capacitor monochromator and analyzer, coupled to a pulse counting detection system. A maximum in the reflectivity, for a highly specular Ag(110) sample, was found at a primary electron energy of 2.85 eV. All electron energy loss experiments were run at 2.85 eV primary energy and 4 nA primary electron current. All spectra were recorded in the specular direction, dipole scattering regime. Experiments that involved collecting data at 90 K were time consuming because before data could be collected, the whole sample manipulator had to reach thermal equilibrium. If thermal equilibrium was not achieved then the sample would continuously move and hence the scattering angle was continuously changing. Therefore, to achieve high resolution, $< 80 \text{ cm}^{-1}$, the sample had to thermally equilibrate for at least 5 hours before data collection could begin.

Resolution in experiments that involved collecting data as the sample warmed up from 90 K was limited by thermal motion of the sample and the rate of warming. Spectra obtained as a function of temperature were collected as fast as possible, usually in less than 15 minutes. Sometimes the sample would move far enough that the analyzer would not detect any scattered electrons. If this happened

the sample manipulator generally had to be moved several millimeters in the up (X) direction.

The SIMS spectrometer, a modified Leybold-Heraeus SS B/10, consists of the secondary ion optics lens stack and a quadrupole mass filter with a mass range of 2-500 AMU. Energy prefiltering of the secondary ions is achieved with the secondary ion optics. This type of prefiltering system does not allow you to generate ion intensity vs. ion energy curves, for a given m/z value, which are necessary if one is interested in the dynamics of secondary ion emission. This type of energy filtering also makes it difficult to analyze for negative ion clusters because their energy distribution curves are extremely narrow and peak at very low energies (26).

Two approaches were used to detect negative ion clusters with this spectrometer. The first involved relaxing the resolution so that more ions could traverse the quadrupole field and reach the detector. The second method involved floating the sample to -15 volts so as to give the secondary ions more energy. The best results were obtained by relaxing the resolution.

Measurement of the primary ion current density was possible because the sample was electrically isolated. These measurements were necessary to insure that the experiments were carried out under static SIMS conditions, primary ion current $< 50 \text{ nA/cm}^2$ (8). The ion gun was operated at 4 KeV to assure the sputtering yield was at a maximum (53,54). Argon was used as the sputter gas in all experiments. In attempts to increase the cluster ion yield, xenon was used for some experiments, but at 90 K the Xe gas began to

condense on the Ag(110) sample. The 4 KeV ion beam was incident on the sample surface at a 50° polar angle with respect to the surface normal. The collection angle for the emitted secondary ions was 60° with respect to the surface normal. The primary ion current density was 3×10^{-9} amps/cm² with the ion beam rastered over an area of 8 x 8 mm on the sample surface.

The XPS spectrometer, Leybold-Heraeus EA11, has a spherical capacitor type energy dispersive analyzer with an input lens column for variable retardation. All data was collected in the constant E mode. This mode of scanning is achieved by applying a fixed voltage onto the spherical analyzer and varying the retardation voltage. All data was collected using Mg K α x-rays (1253.6 eV) and plotted with an X-Y recorder.

The UPS spectrometer uses the Leybold-Heraeus EA11 analyzer. The photon source is a home built (55) differentially pumped helium discharge lamp. This lamp is capable of emitting both the He(I) and He(II) lines at 21.22 and 40.8 eV respectively. Enhancement of the He(II) line is accomplished by adjusting the He flow into the discharge tube. To allow difference spectra to be calculated, all UPS data was collected using a Tektronix 4052. Typical operating parameters for data collection were 0.5 second dwell time with an energy interval of 0.05 eV and a total energy scan from 0-50 eV.

The LEED spectrometer is a display type system. The primary electron energy was usually in the range of 10-130 eV.

Sample Preparation

The Ag(110) sample was purchased from Monocrystals Company, Cleveland, Ohio. The disc, 1/2 OD and 1.8 mm thick as received, was oriented to within $\pm 1^\circ$ of the (110) plane as determined by back-reflection Laue photographs and a Grentinger net (56).

Temperature requirements of the experiments dictated that the sample needed to be made thinner. This was accomplished by mounting the crystal in the goniometer such that the (110) plane could be flat ground without a severe loss of orientation. The Ag(110) disc was coarse ground down to a thickness of 1.2 mm using 800 and 600 grit paper. The disc was then polished using 400, 200 and 100 grit abrasives and Texmet polishing cloths purchased from Buehler, Lake Bluff, Illinois. At this point back-reflected Laue photographs were taken and the surface orientation was still within $\pm 1^\circ$ of the (110) plane. Examination of the surface under a microscope revealed a very coarse surface finish. Final polishing steps were done using Rayvel polishing cloths, a synthetic silk material, and polishing suspensions available from Buehler. Alpha alumina suspensions starting with 5 micron then 1 and finally 0.3 micron particle size were used to remove surface roughness. The final polish was done with 1 micron Cerium Oxide suspension. Cerium Oxide was used last because it is less abrasive than the alumina particles and hence gave a more specular finish. Back-reflected Laue photographs taken after the final polish showed the sample to be oriented to well within $\pm 1^\circ$ of the (110) plane.

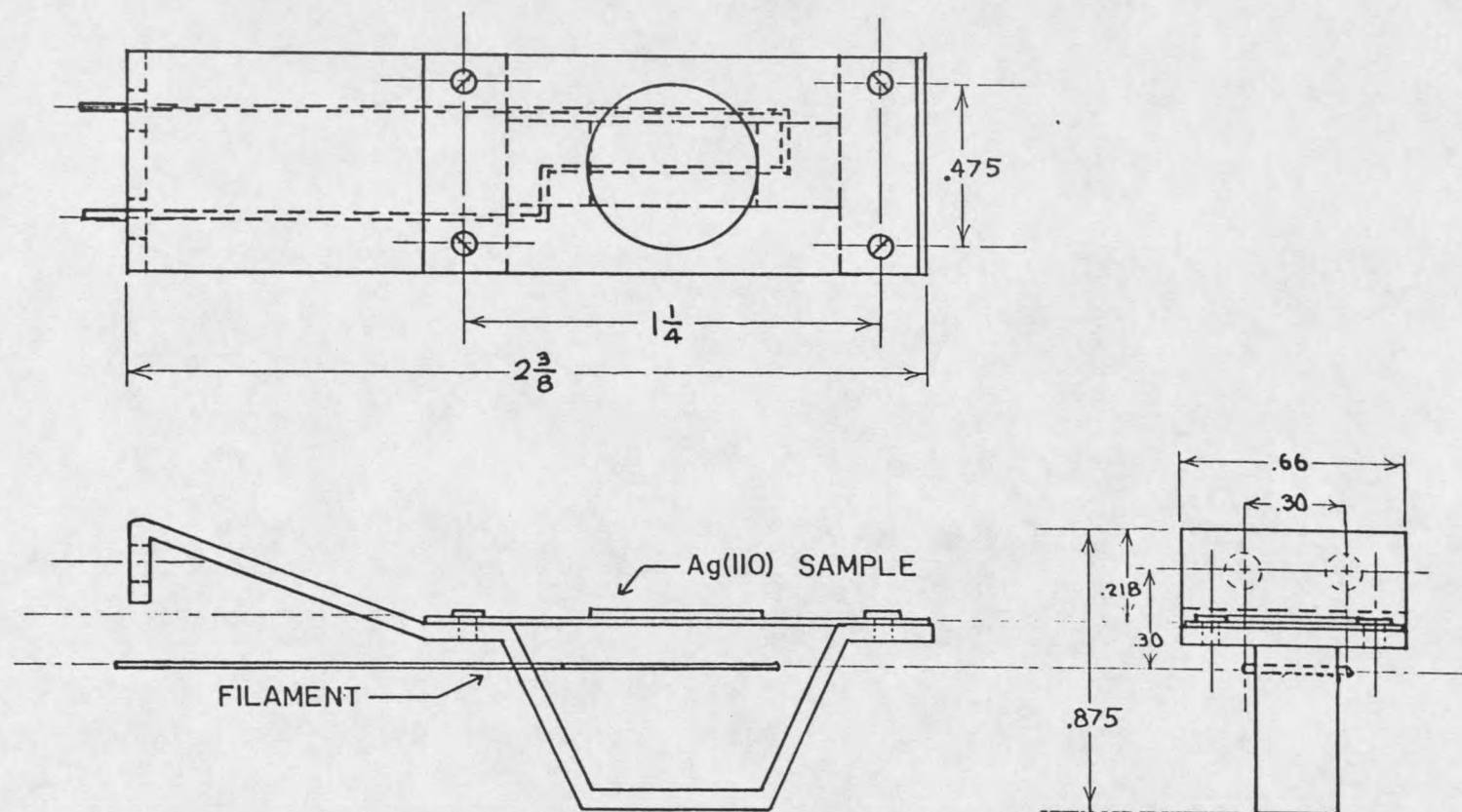


Figure 6. Ag(110) single crystal sample holder.

The surface strain introduced by mechanical polishing needed to be removed before the top atomic layers could be ordered. This was accomplished by chemically etching the Ag(110) disc in a solution of 3% $\text{H}_2\text{O}_2:\text{HNO}_3$. The sample needed to be immersed in this solution for only a few seconds. Prolonged exposure to this chemical etch resulted in a pitted sample.

The sample was now ready to be mounted on the manipulator and put into the work chamber. A schematic of the sample holder is shown in Figure 6. The sample is mounted, by means of spot welded tabs, onto a 0.020" thick tantalum foil which has a 7/16" hole punch in it. The sample was mounted directly over this 7/16" hole. The tantalum foil was then screwed onto the oxygen free high conductivity (OFHC) support which is, in turn, secured to the manipulator via an electrically isolating OFHC copper block. Next, a 0.007" tungsten wire was secured, via two tantalum to platinum leads, about 4 mm below the sample. The tantalum leads were connected to the manipulator via the electrically isolating OFHC copper block. This type of sample mounting procedure allows the sample to be heated by electron bombardment from the backside. Heating to 850 K was achieved by floating the tungsten filament to 500 volts and using an emission current of 45 mA with the sample at ground potential. Cooling was achieved by pumping liquid N_2 into the reservoir to which the OFHC copper connecting block was attached. The lowest temperature achieved with this method was 90 K measured with a platinum-platinum 10% rhodium thermocouple attached to the side of the Ag(110) disc. The Pt/Pt - 10% Rh thermocouple was calibrated

against a chromel-alumel thermocouple. The Ag(110) disc was sputter ion cleaned and annealed using a different work chamber from that described previously.

The work chamber used for this cleaning and ordering procedure had LEED and Auger spectrometers and a sputter ion gun. By using this work chamber it was possible to determine which chemical etch formulation worked best. Using 3% $\text{H}_2\text{O}_2:\text{HNO}_3$ for a few seconds followed by many cycles of Ar ion sputter cleaning and annealing at 850 K, both at 6×10^{-9} torr, produced a clean and surface ordered sample. Sputter ion cleaning was done at a primary ion current density of $1 \times 10^{-6} \text{ A/cm}^2$ with the beam rastered over 1 cm^2 . The sample was considered clean when the Auger spectrum showed impurity peaks were less than 0.5%. When the LEED pattern displayed non-diffuse spots and had good contrast, the Ag(110) surface was considered to be atomically ordered. Once the sample was ordered it was left in this work chamber, at 1×10^{-9} torr, until the Leybold-Heraeus instrument was available.

The sample was transferred to the Leybold-Heraeus instrument by simply unscrewing the tantalum foil from the copper support and reattaching it to the copper support on the Leybold-Heraeus manipulator. It was only necessary to go through a few sputter ion cleaning and annealing to 850 K cycles to attain a clean and ordered surface. Surface cleanliness was determined using XPS and was considered clean when impurity peaks were less than 0.2% of the $\text{Ag}3d_{5/2}$ signal.

Glacial CH_3COOH was purchased from J.T. Baker, Phillipsburg, NJ, as "Baker Instra-Analyzed." Approximately 2 mls of CH_3COOH was put into a glass tube and mounted onto a UHV leak valve. The CH_3COOH was then put through several freeze-pump-thaw cycles to degas it. Deposition of the CH_3COOH onto the Ag(110) disc, at 90 K, was initially done using a gas doser. The doser nozzle was located approximately 3/8" away from the working surface of the Ag(110) disc. However, the CH_3COOH would condense on the leak valve seat and would continue to deposit onto the crystal face after closing the valve. This made it very difficult to make controlled despositions of the acid and was abandoned after several attempts. The method finally used for depositing CH_3COOH involved leaking in the acid, via the same leak valve, to a pressure two orders of magnitude above base pressure, approximately 10^{-8} torr. This was done while monitoring the XPS signal due to $\text{Ag}3d_{5/2}$. Deposition of O_2 was done in a similar manner except the growth of the adsorbed layer was monitored using EELS and observing the O_2 vibrational intensity at 650 cm^{-1} .

In addition, an ultra-high vacuum ($\sim 1 \times 10^{-9}$ torr) custom work chamber was designed and constructed. This chamber was constructed to allow us to perform SIMS experiments in our own laboratory. The chamber was designed to accept different types of mass analyzers. The details of this apparatus are given in the Appendix.

Results and Discussion

Calibration of Adsorbate Thickness

Before attempting to characterize the structure of the adlayer, the Ag(110) surface needed to be clean and ordered. XPS showed the Ag(110) surface to be contaminated with C, O, S and Cl. The S and Cl were easily removed during the first Ar^+ ion sputter cleaning cycle. The carbon and oxygen were more difficult to remove, taking several cycles of sputter ion cleaning followed by annealing at 850 K. XPS showed the Ag(110) surface to be clean after a few cycles. SIMS, however, showed the surface was still contaminated with O, Na, Cl, K and small chain hydrocarbons. The Ag(110) was then subjected to more cycles of Ar^+ ion sputter cleaning followed by annealing to 850 K. These extra cycles of cleaning showed no great effect on the SIMS spectra. At this point, it was decided to obtain EEL-spectra of the Ag(110) surface. EELS showed a very small peak corresponding to CH, intensity $< 0.05\%$ of the elastic peak. The LEED pattern displayed good contrast and the spots were relatively non-diffuse. It was decided at this point to proceed with the experiment despite the fact that SIMS still showed C, O, Na, K and Cl were still present. This decision was based on the fact that SIMS is a more sensitive technique than XPS (57) with detection sensitivities approaching 10^{-7} of a monolayer or 1 ppb atomic (58).

Because the following experiments required controlled deposition of known amounts, in monolayers, of CH_3COOH at 90 K, it was necessary to devise a method to monitor the thickness of the adsorbed CH_3COOH .

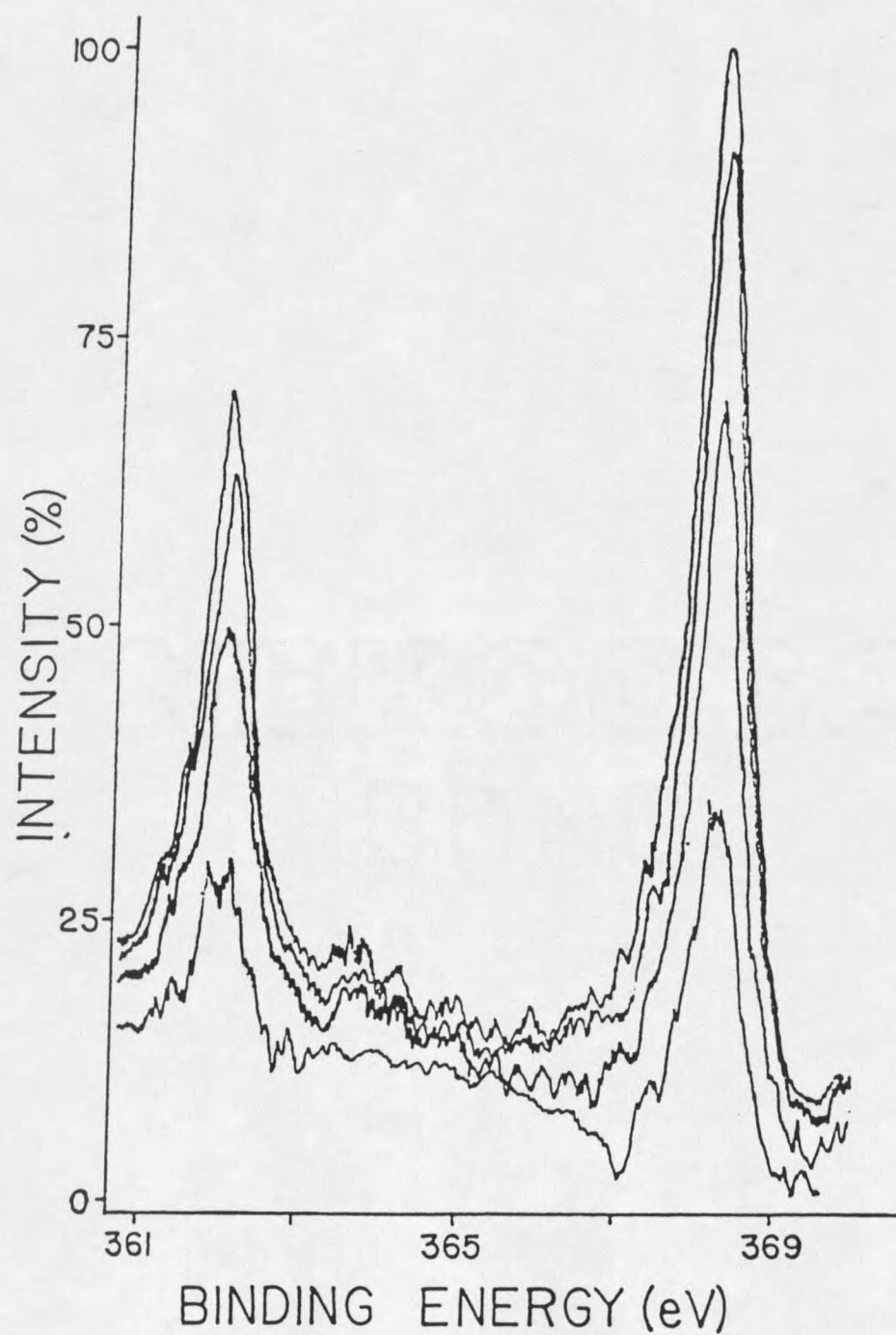


Figure 7. Attenuation of $\text{Ag}3d_{3/2,5/2}$ XPS intensity during deposition of CH_3COOH at 90K.

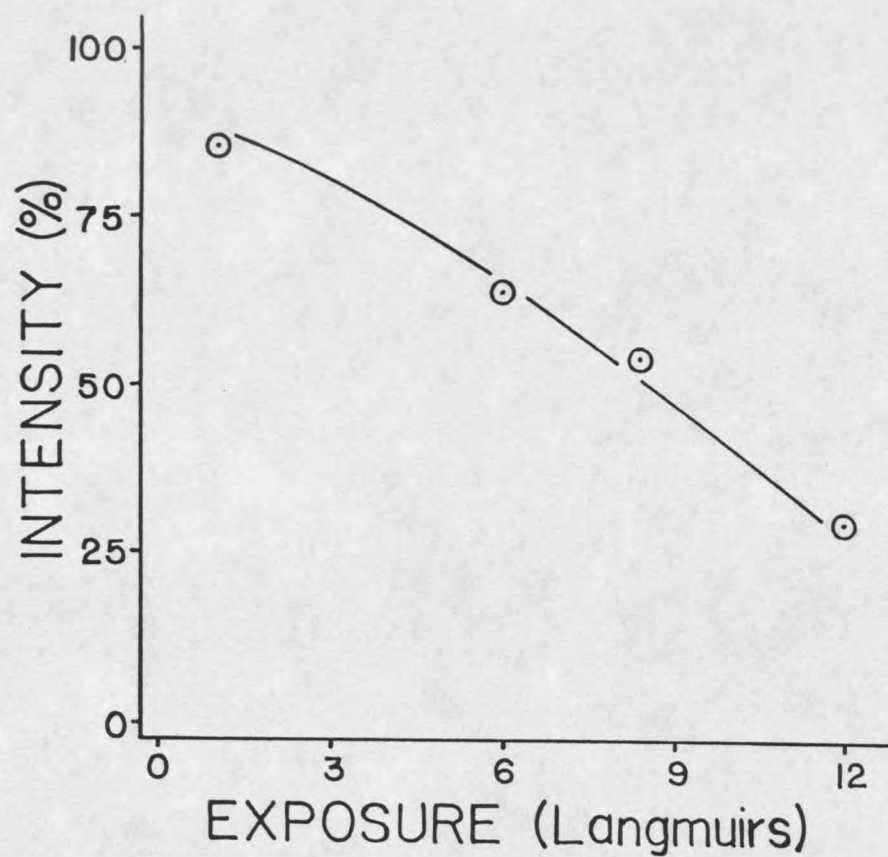


Figure 8. Attenuation of $\text{Ag}3d_{5/2}$ XPS intensity during CH_3COOH deposition at 90 K. Exposure expressed in Langmuirs (10^{-6} torr/s). $\text{Ag}3d_{5/2}$ intensity expressed as percentage of $\text{Ag}3d_{5/2}$ intensity for a clean $\text{Ag}(110)$ surface.

layer. It has been shown (59) that the attenuation of the intensity of photoemitted electrons can be related to the thickness of the adsorbed layer by using:

$$I = I_0 \exp(-d/\lambda \cos \theta) \quad (1)$$

where I is the observed photoelectron intensity with adsorbate, I_0 is the observed photoelectron intensity for a clean substrate, d is the average adsorbate layer thickness, λ is the inelastic electron mean free path and θ is the collection angle of the spectrometer analyzer. Using XPS one can measure both I and I_0 for $\text{Ag}3d_{5/2}$ electron for CH_3COOH on $\text{Ag}(110)$.

Figure 7 shows that attenuation of the photoemitted $\text{Ag}3d_{5/2}$ and $\text{Ag}3d_{3/2}$ electrons with increasing coverage of CH_3COOH at 90 K. By using the attenuation of the $\text{Ag}3d_{5/2}$ signal in conjunction with Equation 1, we can determine the adsorbate layer thickness. Figure 8 shows the intensity, relative to a clean $\text{Ag}(110)$ surface, of the $\text{Ag}3d_{5/2}$ signal as a function of exposure, expressed in Langmuirs (L). One Langmuir is 10^{-6} torr-second and is a useful quantity for expressing exposure because it allows us to deposit CH_3COOH reproducibly by going to the same number of Langmuirs to achieve a given coverage. However, before we can use Equation 1 to calculate the adlayer thickness we need a value for λ . Recent measurements of for organics with densities which are similar to CH_3COOH vary by a factor of 2 or more (60, 61) and for 1 KeV electron the values are in the range $\sim 20\text{-}40 \text{ \AA}$. Using a value of $30 \text{ \AA}$ for λ and with $\theta=0$, i.e. collection angle normal to the sample surface, we can calculate the adlayer thickness using Equation 1 and the data in Figure 8.

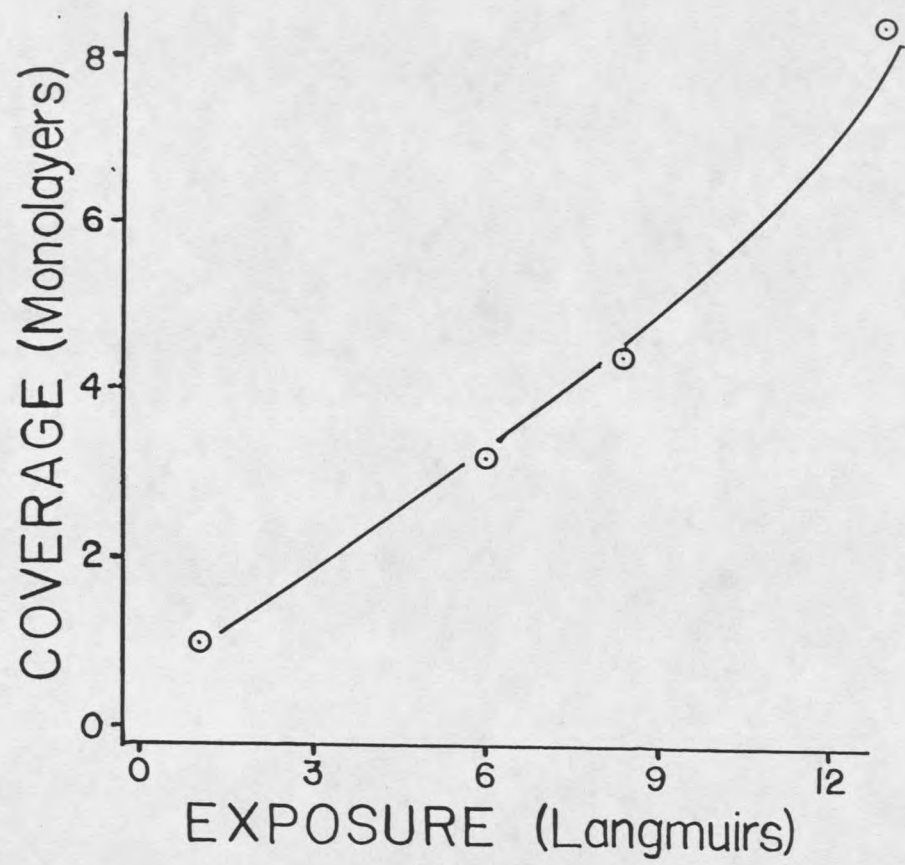


Figure 9. Calculated CH₃COOH coverage (monolayers) at 90 K as a function of exposure (Langmuirs).

The results of these calculations are shown in Figure 9. Here the adlayer thickness is expressed in monolayers. The conversion from adlayer thickness expressed in Angstroms to an equivalent coverage expressed in monolayers was achieved using the density of acetic acid. The density of acetic acid is 1.4092 g/cm^3 and the molecular weight is 60.05 g/mole (62). Using these two quantities we get $1.4 \times 10^{22} \text{ molecules/cm}^3$ which is equivalent to $4.1 \times 10^{-8} \text{ cm/molecule}$. This gives the thickness of one monolayer to be $4.1 \text{ \AA}$ and the number of molecules in a monolayer as $5.8 \times 10^{14} \text{ molecules/cm}^2$ which is in good agreement with that reported for formic acid (30). One Langmuir exposure is equivalent to the formation of a monolayer if you assume a sticking coefficient of unity for the adsorbate of interest. This gives another method of determining the thickness of a monolayer of acetic acid. If it is assumed that acetic acid has a sticking coefficient of unity at 90 K for the first monolayer, then by recording the attenuation of the $\text{Ag}3d_{5/2}$ signal for a one Langmuir exposure and it should be possible to determine the adsorbate thickness corresponding to one monolayer. This experiment gave a value of $4.8 \text{ \AA}$ for the thickness of one monolayer, one Langmuir exposure, and is in good agreement with our previous determination of $4.1 \text{ \AA}$.

Determination of the Interaction Between Acetic Acid and $\text{Ag}(110)$

Figure 10 shows the EEL-spectrum obtained for 5 monolayers of CH_3COOH on $\text{Ag}(110)$ at 90 K . This spectrum was run at a resolution of $\sim 100 \text{ cm}^{-1}$, resolution in EELS being defined as the full width half

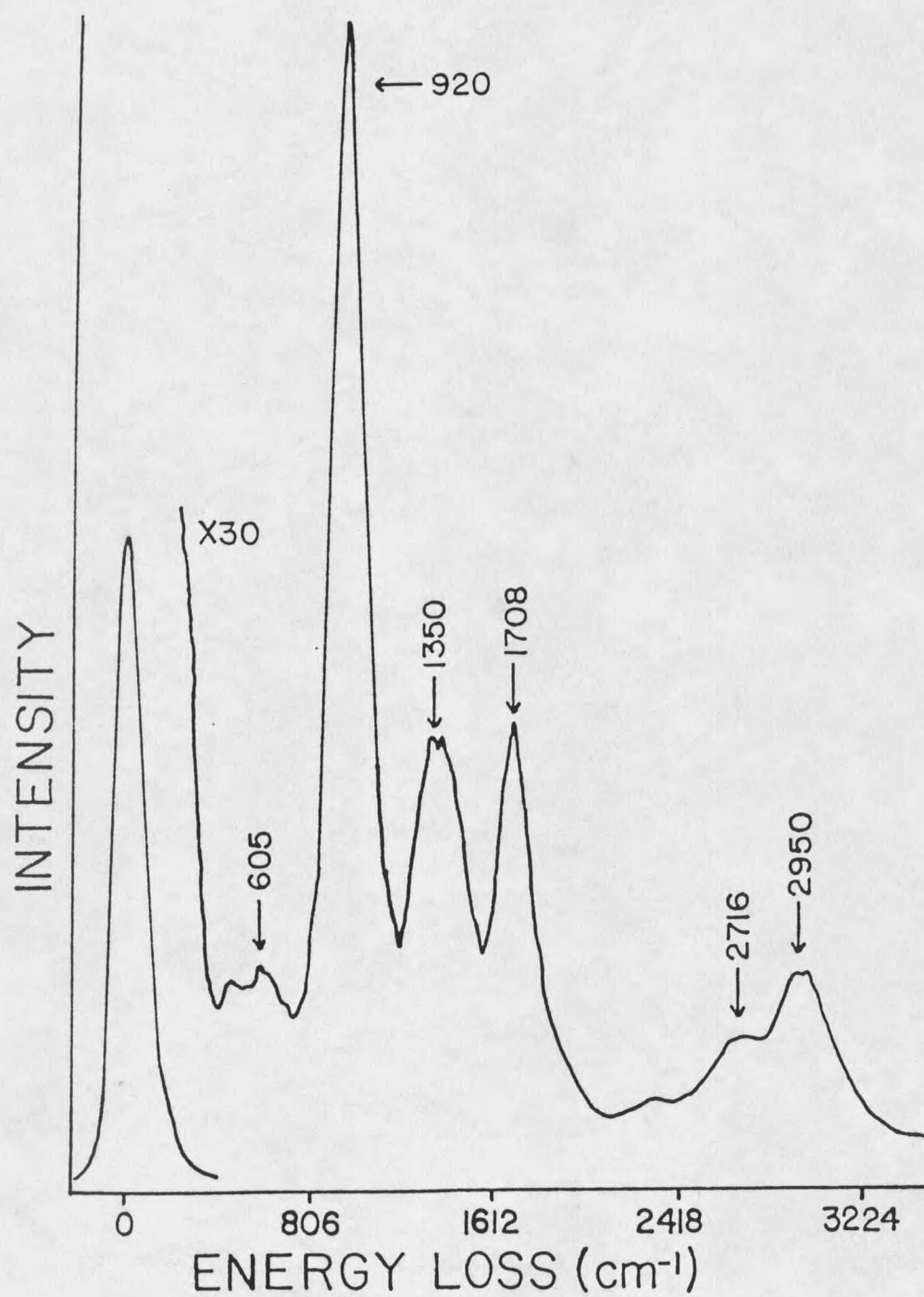


Figure 10. Electron energy loss spectra of CH_3COOH (5 monolayers) on $\text{Ag}(110)$ at 90 K. Beam energy 2.8 eV. Resolution 100 cm^{-1} .

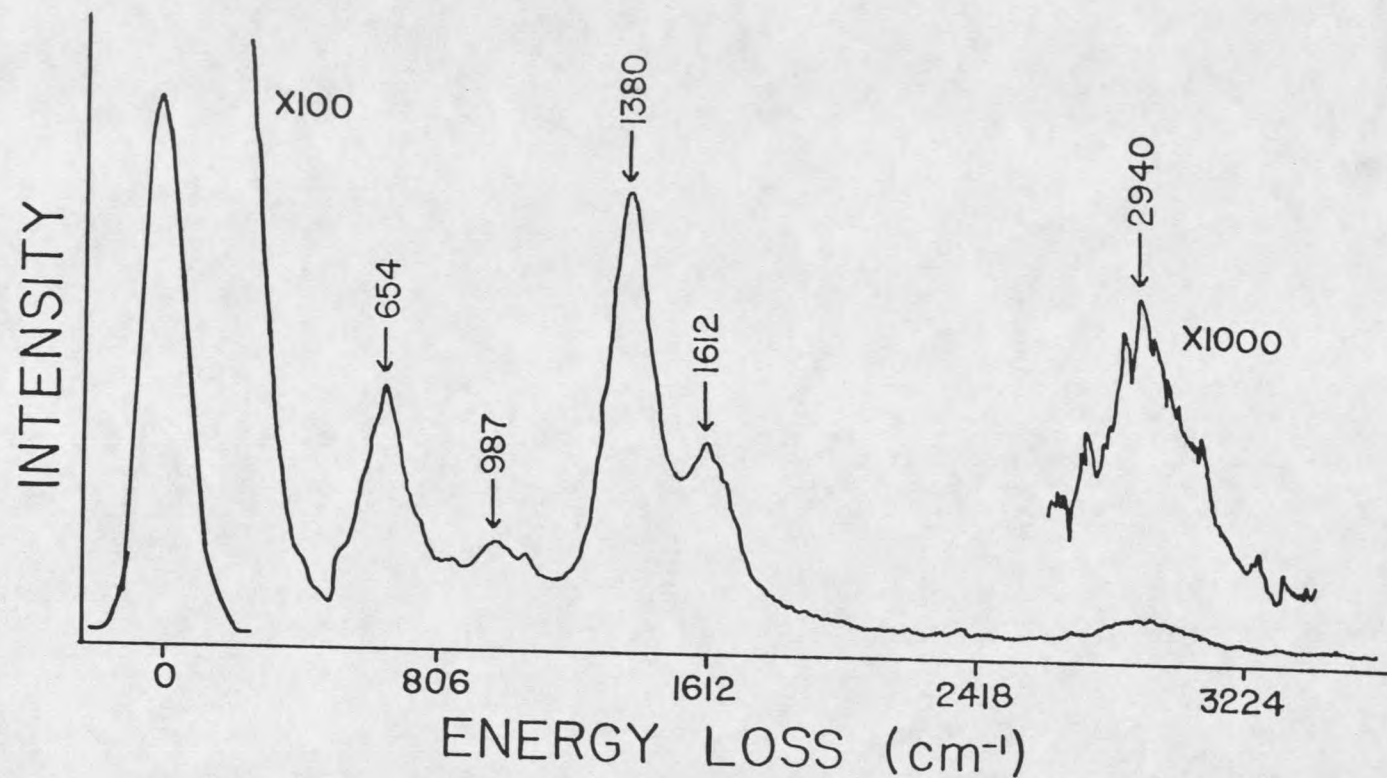


Figure 11. Electron energy loss spectra of CH_3COOH (5 monolayer) on $\text{Ag}(110)$ at 90 K. Beam energy 2.8 eV. Resolution 70 cm^{-1} .

maximum (FWHM) of the elastic peak. The count rate for the elastic peak was 1×10^5 Hz at a primary electron energy of 2.8 eV. Considerable intensity was observed in the inelastic scattering and magnifications of X30 were sufficient to amplify the inelastic peaks. To determine if the bands centered at 605 and 1350 cm^{-1} were doublets, the instrument was tuned to give a resolution of $\sim 70 \text{ cm}^{-1}$. Figure 11 shows the EEL-spectra of 5 monolayers of CH_3COOH condensed on Ag(110) at 90 K and run at $\sim 70 \text{ cm}^{-1}$ resolution. The spectra shows that the band centered at 605 cm^{-1} has split into a doublet centered at 484 cm^{-1} and 605 cm^{-1} . Also, the band centered at 1350 cm^{-1} in Figure 10 has been resolved into a doublet centered at 1290 cm^{-1} and 1410 cm^{-1} . The frequencies and assignments are displayed in Table 1. The high frequency vibrations include a broad band with maxima at 2716 cm^{-1} ($\nu(\text{OH})$) and 2950 cm^{-1} ($\nu(\text{CH})$). The (CH) stretching frequency agrees very well with that reported for gas phase acetic acid (63), but the (OH) stretching frequency is considerably lower than in gas phase acetic acid. However, the lowering of the OH stretching frequency is consistent with weakening of the OH bond and the lowering of the observed frequency reported for the infrared study of solid formic acid (64, 65). The band at 1708 cm^{-1} is assigned to the (C=O) stretching mode of molecular CH_3COOH but is somewhat lower than the 1799 cm^{-1} value reported for gas phase acetic acid determined using IR spectroscopy (63). The band at 1410 cm^{-1} is assigned to the (CH_3) asymmetrical bend and the band at 1290 cm^{-1} assigned to the (C-O) symmetrical stretch, both of which are in excellent agreement with gas phase frequencies (63).

The band at 920 cm^{-1} has been assigned to the (COH) bending mode. The gas phase (COH) bending mode was reported at 1192 cm^{-1} (63) but Mikawa (64) assigned the (COH) bending mode at 950 cm^{-1} due to hydrogen bonding. The bands at 605 cm^{-1} and 484 cm^{-1} have been assigned to the (COO) bending mode and (CO_2) rocking mode, respectively, both of which are somewhat lower, $\sim 50\text{ cm}^{-1}$, than the gas phase values (63).

Table 1. Frequencies and assignments for multilayer $\text{CH}_3\text{COOH}/\text{Ag}(110)$ at 90 K.

Vibrational Mode	Description	EELS Frequency (cm^{-1})
$\nu(\text{CH}_3)$	CH_3 asymmetrical stretch	2950
$\nu(\text{OH})$	O-H stretch	2716
$\nu(\text{C=O})$	C=O stretch	1708
$\delta(\text{CH}_3)$	CH_3 symmetrical bend	1410
$\nu(\text{C-O})$	C-O stretch	1290
$\delta(\text{OH})$	COH bend	920
$\delta(\text{O-C=O})$	OCO bend	605
$\pi(\text{O-C=O})$	CO_2 rock	484

The preceding analysis has shown that for multilayer coverages acetic acid is randomly oriented on the $\text{Ag}(110)$ surface at 90 K. EEL-spectra recorded at a coverage of 3 monolayers displayed the same bands but they were broader and less intense. This would be expected to be the case if the first monolayer were oriented with the C_2 axis parallel to the $\text{Ag}(110)$ surface. This may be the reason for Sexton

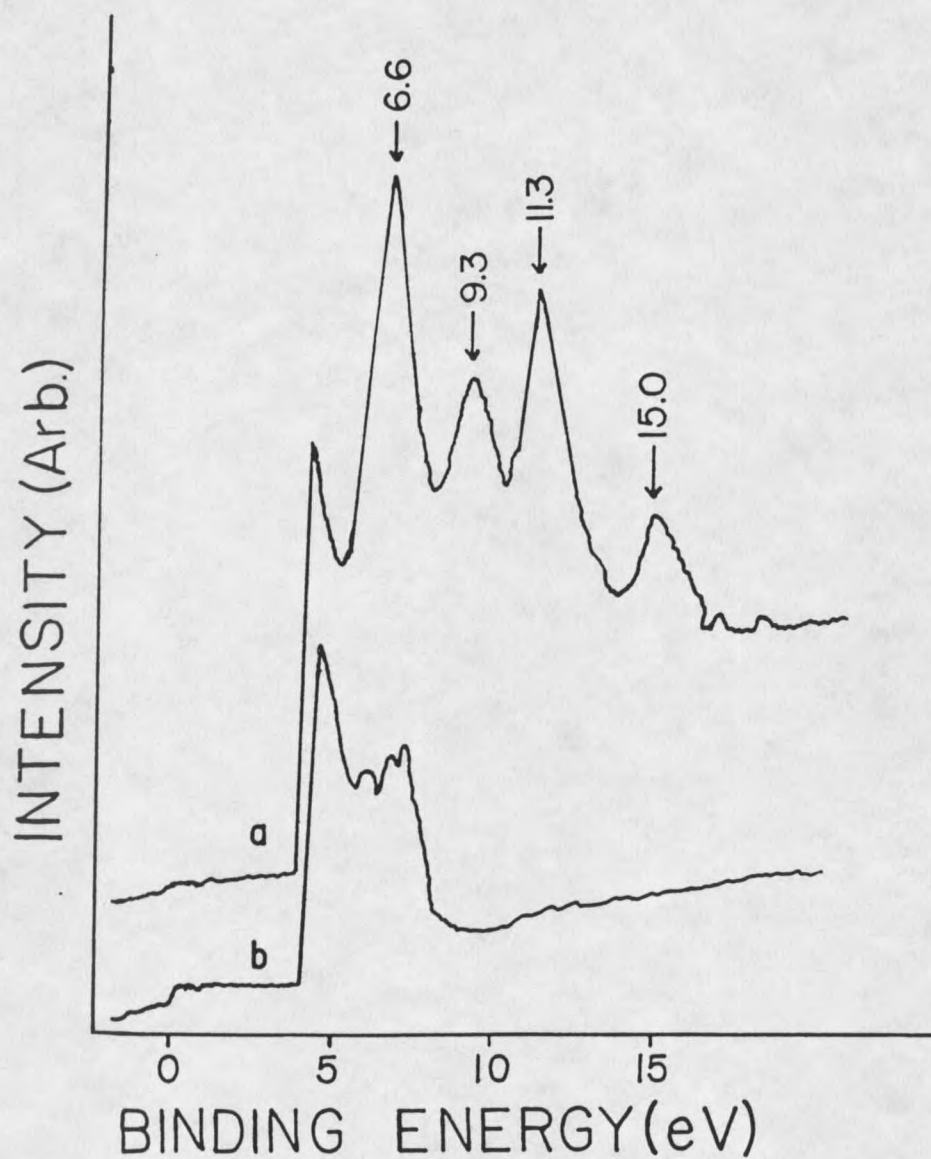


Figure 12. Ag(110) helium(II) UP-spectra. Curve (a) CH₃COOH (1 monolayer) on Ag(110) at 90 K. Curve (b) clean Ag(110) single crystal at 90 K. Binding energy relative to the Fermi level.

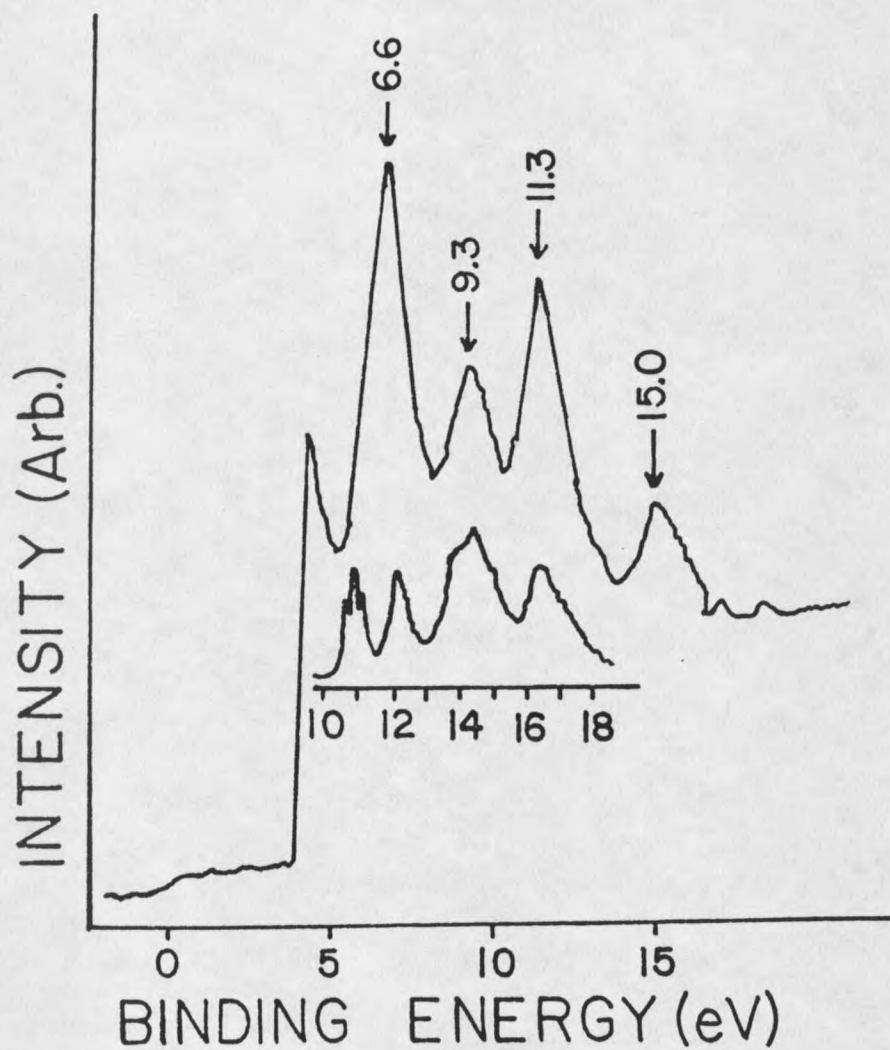


Figure 13. UP-spectra. Outer curve He(II) spectra of CH_3COOH on Ag(110) at 90 K. Inner curve He(I) spectra of gas phase CH_3COOH (from ref. 67). Binding energy; inner scale relative to the vacuum level, outer scale relative to the Fermi level.

(66) not being able to obtain an EEL-spectra of formic acid on Ag(110) at one monolayer coverage.

Figure 12a and b show the He(II) UP-spectra for one monolayer at CH_3COOH on Ag(110) at 90 K and clean Ag(110) at 90 K. The binding energy is with respect to the Fermi level. Attempts were made to obtain He(I) UP-spectra but no peaks were observed using the He(I) line. Figure 13 shows the He(II) UP-spectra of one monolayer of CH_3COOH on Ag(110) at 90 K with the gas phase He(I) UP-spectra (67).

Observed molecular orbital shifts, for adsorbates, can be divided into two types: initial state shifts and final state hole-relaxation shifts (68-72). Initial state shifts are due to orbital interaction between the adsorbate and substrate, i.e. bond formation, and the changed chemical environment of the adsorbed species (71). Final state relaxation shifts are due to electrons readjusting to the positive hole potential remaining after photoemission and thus lowering their energy. Relaxation energies are always positive (70,71) and the net effect is to reduce the binding energy of the observed photoelectron. It has been experimentally determined that this change in binding energy, due to relaxation, is constant for all orbitals for a given adsorbate-substrate system (68,73). The comparison of gas phase and condensed phase binding energies is complicated further by the choice of a reference level for the condensed phase spectra (72).

The condensed phase He(II) UP-spectra, Figure 13, has been overlaid with the gas phase He(I) UP-spectra by aligning the band at 11.3 eV, with respect to the Fermi level ($11.3 \text{ eV}/E_F$), in the

condensed phase spectra, with the band at 16.4 eV, with respect to the vacuum level ($16.4 \text{ eV}/E_V$), in the gas phase UP-spectra. This technique has been used for formic acid on copper (74) and other physisorbed systems (68). Calculations predict that hydrogen bonding perturbs only the n_0 and π_2 orbitals, the two highest filled orbitals in carboxylic acids (67,75). Comparison of the two spectra show that the n_0 and π_2 orbitals have coalesced into one band at $6.6 \text{ eV}/E_F$ when condensed onto Ag(110) at 90 K. This is in excellent agreement with the He(I) UP-spectra reported for formic acid on copper at 80 K (74). It has been determined by Sweigart (67) that the n_0 orbital is the highest occupied orbital and is associated with the carbonyl oxygen lone pair (p orbital) and the π_2 orbital is the next highest occupied orbital. The π_2 orbital is nonbonding and is associated with p orbitals on the C, O and OH group. These associations were made for gas phase UP-spectra by observing vibrational fine structure associated with each band as substituents attached to carbonyl carbon were varied (67). It should be noted that if conjugation were not present, then the π_2 orbital would correspond to the lone pair p orbital on the hydroxyl oxygen (67).

Comparison of the relative energy differences between bands, see Table 2, shows that the bands at $9.3 \text{ eV}/E_F$ and $11.3 \text{ eV}/E_F$ do not interact with the Ag(110) surface. To distinguish relaxation shifts from bonding shifts, the work function can be added onto the binding energies for the condensed phase UP-spectra and compare the resulting binding energies ($E_F + \phi$) to the binding energies (E_V) obtained from the gas phase UP-spectra. This method has been used by Eastman (73).

to separate relaxation shifts from bonding shifts for hydrocarbons on nickel. Using a value of 4.7 eV (76) for the work function of Ag(110), the binding energy values ($E_F + \phi$) for the second and third bands in the condensed phase UP-spectra are ~ 0.3 eV lower than the corresponding gas phase bands. This positive 0.3 eV difference in binding energies is attributed to relaxation and is in accord with relaxation shifts reported for physisorbed organics (68,73).

Comparison of n_0 and π_2 band in the condensed phase UP-spectra with the n_0 and π_2 bands in the gas phase UP-spectra shows that the coalesced (n_0 , π_2) band has shifted 0.65 volts to higher binding energies. This binding energy shift is arrived at by adding the relaxation energy (E_R) onto the binding energy ($E_F + \phi$) for the first band in the condensed phase UP-spectra. This binding energy value is then compared with the average binding energy for the n_0 and π_2 bands in the gas phase UP-spectra, see Table 2. Barteau (48) has determined the activation energy for thermal desorption of acetic acid on an Ag(110) surface to be 11 kcal/mole or 0.47 eV/molecule. Our experimentally determined interaction energy value of ~ 0.65 eV is in qualitative agreement with Barteau's (48) thermal desorption data.

Analysis of the condensed phase UP-spectra has shown that there is < 1.0 eV of bonding energy between acetic acid molecules and the Ag(110) surface at 90 K. This is in good agreement with thermal desorption data (48) on this system. The acetic acid orbitals participating in bonding with the Ag(110) surface are those associated with the n_0 and π_2 molecular orbitals. This is in qualitative agreement with the lack of being able to generate an

EEL-spectra of a monolayer of formic acid in Ag(110) (66). This suggests that, for monolayer coverages, small carboxylic acids are physisorbed on Ag(110) with their C_2 axis parallel to the Ag(110) surface at 90 K.

Table 2. UPS assignments for $CH_3COOH/Ag(110)$ at 90 K.

He(II)		He(I) (ref. 12)
E_F (eV)	$(E_F + \phi)$ (eV)	E_V (eV)
6.6	11.3	10.8
---	---	11.1
9.3	14.0	14.3
11.3	16.0	16.3
15.0	19.7	---

XPS shows that the oxygen (1s) binding energy is 533.6 eV with a FWHM of 2.9 eV. This is in excellent agreement with Siegbahn's (77) values. A FWHM of 2.9 eV indicates the occurrence of hydrogen bonding in the condensed phase. The oxygen (1s) FWHM of 2.9 eV also indicates that there is a charge difference between the two oxygen atoms, i.e. the acid is not dissociated and hence the oxygen atoms are in chemically different environments.

In summary, we have determined that there is very little interaction energy, < 1.0 eV, between CH_3COOH and Ag(110) at 90 K. We have also determined that for more than 2 monolayers, CH_3COOH is randomly oriented on the surface but at one monolayer coverage, CH_3COOH molecules may be oriented with their C_2 axis parallel to the surface.

SIMS of CH₃COOH/Ag(110) at 90 K

Positive and negative ion static SIMS spectra were obtained for CH₃COOH on clean Ag(110) at 90 K as a function of coverage. Figure 14 shows the positive ion static SIMS spectrum for 4.5 monolayer coverage of CH₃COOH on Ag(110) at 90 K. Figure 15 shows the static negative ion SIMS spectra of the same sample. The protonated and deprotonated cluster ions, $(M_n + H)^+$ and $(M_n - H)^-$ where $M = CH_3COOH$, are indicative of frozen solids that contain molecules which exhibit strong hydrogen bonding (11,78). Hydrogen bonding has been shown in this study to be very prominent, as demonstrated by its effect on the UP-spectra and EEL-spectra. However, in a previous study of frozen H₂O (78), it was shown that for clusters of the type $H_n(H_2O)^+$ with $n > 2$ formation is via the recombination model. Unfortunately, it is not possible to generate intensity vs. kinetic energy distribution curves with the SIMS instrument used in these studies. Therefore, it is not possible to ascertain what the energy of the larger clusters is, however, one would speculate that they are formed via recombination. It has been shown (78) that the average kinetic energy of large $H_n(H_2O)^+$ clusters is around 2.2 eV. The average energy of a typical hydrogen bond is only ~ 0.25 eV (79). Using these values it can be seen that hydrogen bonding would not be strong enough to hold the cluster together during the sputtering process (43).

The most striking feature of the positive ion static SIMS spectra is the observation of the Ag cationized CH₃COOH molecule.

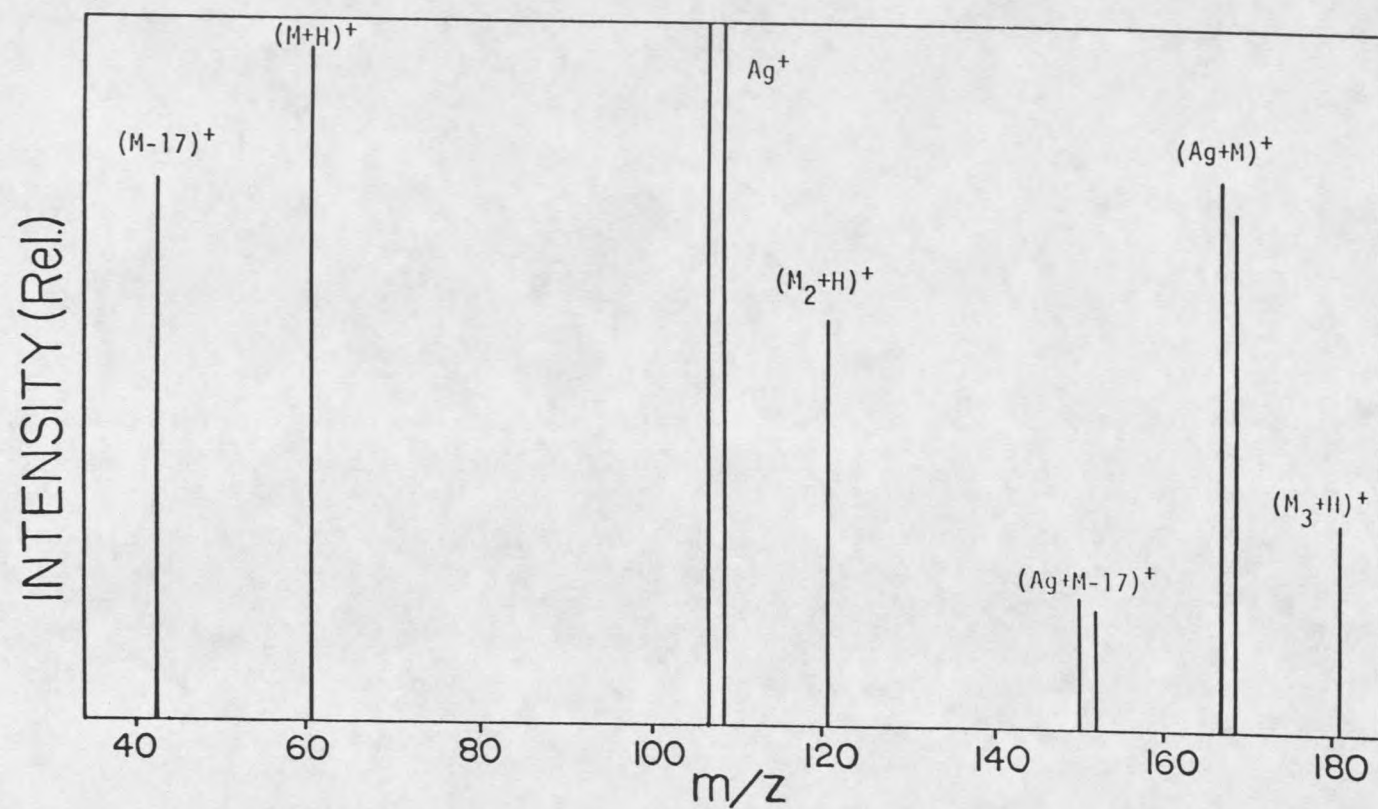


Figure 14. Positive ion SIM-spectra of CH_3COOH (5 monolayers) on $Ag(110)$ at 90 K. Ion intensities relative to $(M+H)^+$.

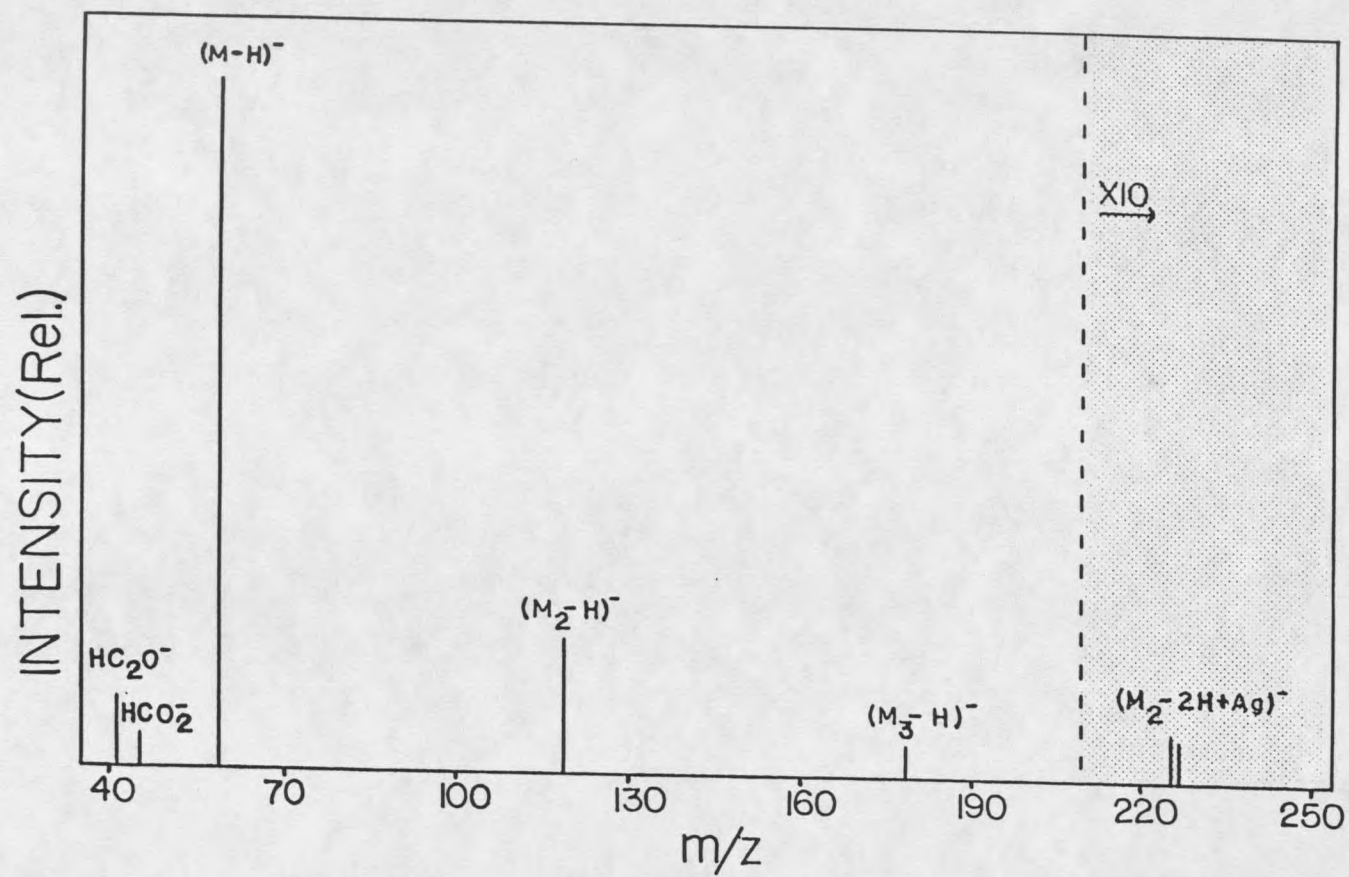


Figure 15. Negative ion SIM-spectra of CH_3COOH (5 monolayers) on $Ag(110)$ at 90 K. Ion intensities relative to $(M-H)^-$.

This adduct ion appears at m/z of 167 and has the ^{109}Ag isotope peak at m/z 169. This ion was totally unexpected based on the fact that there is very little interaction between CH_3COOH and the $\text{Ag}(110)$ surface. Also, in previous SIMS studies of amino acids (10,47) or molecules possessing both amine and carboxylic groups (46), it was found that decarboxylation is the major fragmentation pathway for Ag cationized molecular ions. This indicates that the Ag^+ ion is associated with the amine group and not the carboxylic group.

Table 3 shows the results of positive and negative ion static SIMS experiments on $\text{CH}_3\text{COOH}/\text{Ag}(110)$ as a function of CH_3COOH coverage. Here, the coverage is expressed in monolayers as determined by the previously described XPS technique. Observing the intensity of the AgM^+ ion, the Ag cationized molecular ion, it can be seen that its intensity continues to increase as the CH_3COOH coverage increases. If this ion were directly emitted from the surface as an intact species, then its intensity should have leveled off between 1 and 2 monolayers (80). However, as can be seen, this is not the case, indicating that this ion is not ejected intact but rather forms via recombination between ejected Ag^+ ions and neutral CH_3COOH molecules. Molecular dynamics calculations (44) have shown that it is possible to form cationized species via recombination of coejected atomic and molecular species. Also, UPS data from this study and thermal desorption data (48) have shown that the interaction energy between CH_3COOH molecules and the $\text{Ag}(110)$ surface is less than 1.0

eV/molecule. Therefore, it is not possible to eject a (Ag + CH₃COOH)⁺ species, which probably has a kinetic energy of ~ 2 eV (78).

Table 3. Relative mass peak intensities^(a) for CH₃COOH/Ag(110) at 90 K as a function of CH₃COOH coverage.

Ion	m/z	Coverage (monolayers)		
		1	3	4.5
MH ⁺ (b)	61	1.0	1.0	1.0
M ₂ H ⁺	121	0.08	0.12	0.60
M ₃ H ⁺	181	0.002	0.077	0.31
AgM ⁺	167	0.10	0.23	0.83
(M-H) ⁻	59	1.0	1.0	1.0
(M ₂ -H) ⁻	119	0.06	0.10	0.22
(M ₃ -H) ⁻	179	0.003	0.015	0.045
(M ₂ -2H + Ag) ⁻	225	0.002	0.004	0.007

^aPositive ions relative to MH⁺, negative ions relative to (M-H)⁻.

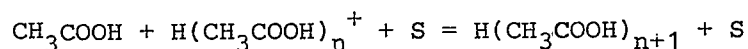
^bM = CH₃COOH

Table 3 also shows that the protonated cluster ions increase in intensity as the coverage increases from ~ 1 to ~ 5 monolayers of CH₃COOH. These ions were previously shown to have been formed via recombination based on energy arguments. Intensity as a function of coverage also points to the conclusion that these ions are formed via recombination.

Negative ion SIMS data, shown in Table 3, shows that the formation of deprotonated cluster ions is via recombination of

ejected acetate ions and acetic acid molecules. The ion observed at m/z 225, which corresponds to a combination of two acetate ions and one silver ion, is definitely formed via recombination of coejected species. It should also be noted that the intensity (counts/sec of the deprotonated cluster ions was low, hence their relative intensity appears low relative to the protonated cluster ions. The low count rate for deprotonated cluster ions is attributed to energy discrimination caused by the secondary ion extraction optics of the secondary ion mass spectrometer. This is the case because it has been shown that negative ion clusters have extremely narrow and low energy distribution curves (26).

The type of clustering reactions responsible for the formation of either protonated or deprotonated clusters are three body reactions. Based on the scheme proposed for protonated H_2O clusters (78), the following is proposed for protonated CH_3COOH clusters:



where S is the third body. The third body can be the surface itself, and is required for the deactivation of the initially excited association products. A single primary ion collision is sufficient to generate a collection of these particles moving through the surface zone (selvedge) (44). These particles can be found together, in the activated region, if they are synchronized in space and time and they satisfy the relationship:

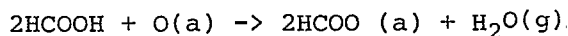
$$(E^k + V) < 0$$

where E^k is the relative kinetic energy of the particles and V is the potential energy between each pair of particles (81).

The ratio of absolute intensities of the protonated to deprotonated acetic acid molecules as a function of coverage did not vary considerably going from single monolayer coverage to multilayer coverages. This can be explained by assuming proton exchange is taking place between physisorbed acetic acid molecules during the sputtering process. Apparently, the Ag(110) surface has no influence on the formation of protonated and deprotonated acetic acid ions. Benninghoven (47,82) has observed the same relationship for multilayers of amino acids where the layers are physisorbed to one another.

Formation and Characterization of Acetate on Ag(110)

The reaction between carboxylic acids and atomic oxygen adsorbed on Ag(110) have been studied by Barteau and co-workers (48,83,84). They have found that atomic oxygen chemisorbed on the Ag(110) surface exhibits the properties of a strong base. The reaction observed between carboxylic acids and adsorbed oxygen is a simple acid-base reaction, with adsorbed oxygen acting as the surface base. For surface reactions involving deprotonation, the role of adsorbed oxygen is analogous to that of OH^- for similar reactions in aqueous solution. The reaction scheme proposed for the deprotonation of formic acid (83) by adsorbed atomic oxygen was:



It is assumed acetic acid would follow a similar mechanism.

It appears that the crucial step in this sequence is converting molecular oxygen to atomic oxygen. Engelhardt (85) has studied the

formation of atomic oxygen on Ag(110) and has found that for a 1500 Langmuir O_2 exposure at room temperature, a 3×1 superstructure of atomic oxygen is formed. A sticking coefficient of 3×10^{-4} for molecular oxygen was determined. Sexton (86) has done a vibrational study of the conversion of molecular oxygen to atomic oxygen and found that this conversion occurs around 200 K.

For this present investigation EELS has been used to monitor the amount of molecular oxygen adsorbed on Ag(110) at 90 K. The subsequent conversion to atomic oxygen was also monitored using EELS. Figure 16 shows a plot of the intensity of the O_2 vibration at 650 cm^{-1} , determined by EELS, vs. exposure, in Langmuirs, of O_2 at 90 K. It can be seen that the intensity has leveled off at ~ 3000 Langmuirs. The conversion to atomic oxygen is shown in Figure 17. The EEL-spectra of molecular oxygen (3000 Langmuirs) at 85 K is shown along with the corresponding EEL-spectra after warming to 240 K. The EEL-spectra at 240 K shows a new vibration appearing at 260 cm^{-1} , which has been assigned to a (Ag-O) stretching vibration (86). According to Engelhardt (85) a 3×1 superstructure of atomic oxygen should have formed, based on the O_2 exposure. However, no ordered LEED pattern was observed after conversion to atomic oxygen. This deposition monitoring scheme was used in conjunction with the scheme previously described for the monitoring of CH_3COOH , in order to produce the desired coverages of surface reactant species needed to form the acetate.

The EEL-spectra of $(CH_3COOH + O)/Ag(110)$ at 90 K is shown in Figure 18. The sample was made by exposing the Ag(110) crystal at 90

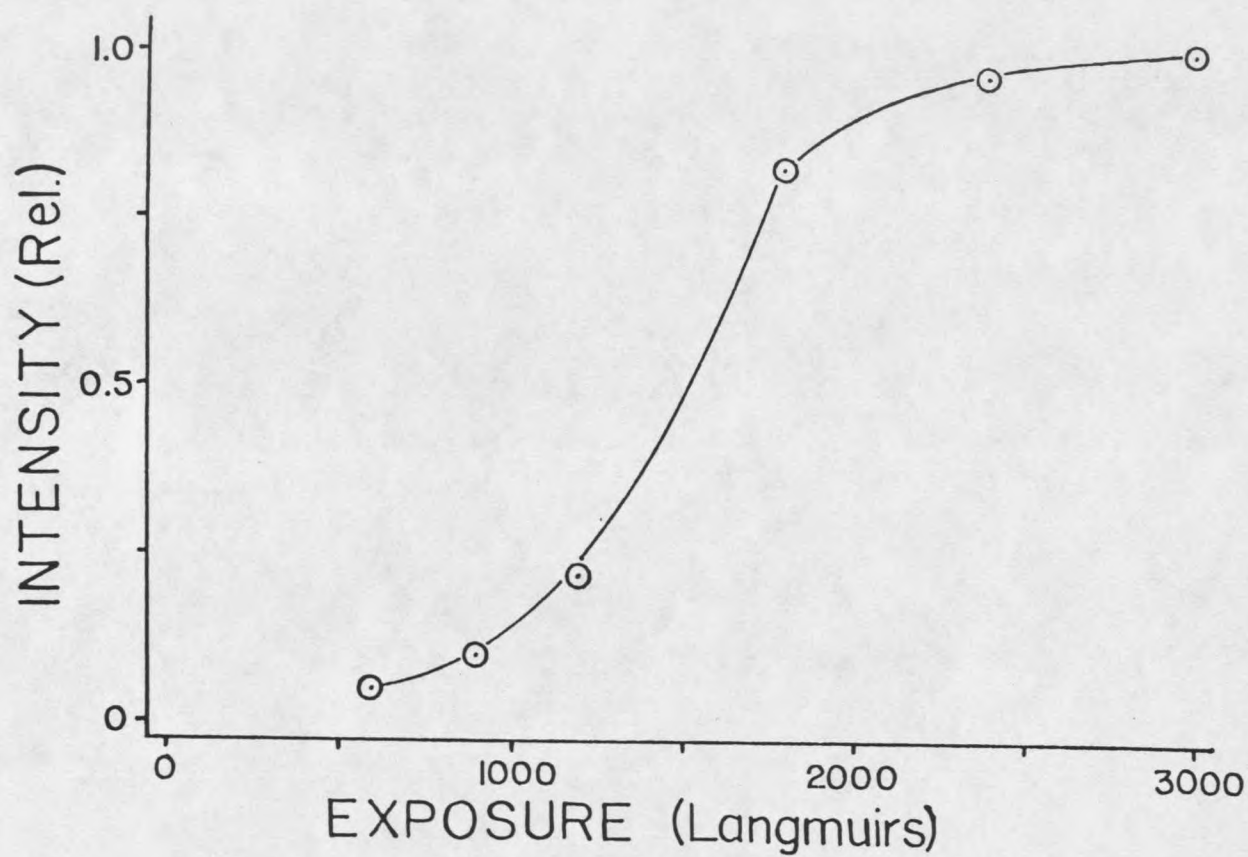


Figure 16. Intensity of the O_2 vibration at 650 cm^{-1} as a function of O_2 exposure (Langmuirs) on $\text{Ag}(110)$ at 90 K. Intensity values relative to O_2 vibrational intensity at 3,000 L exposure.

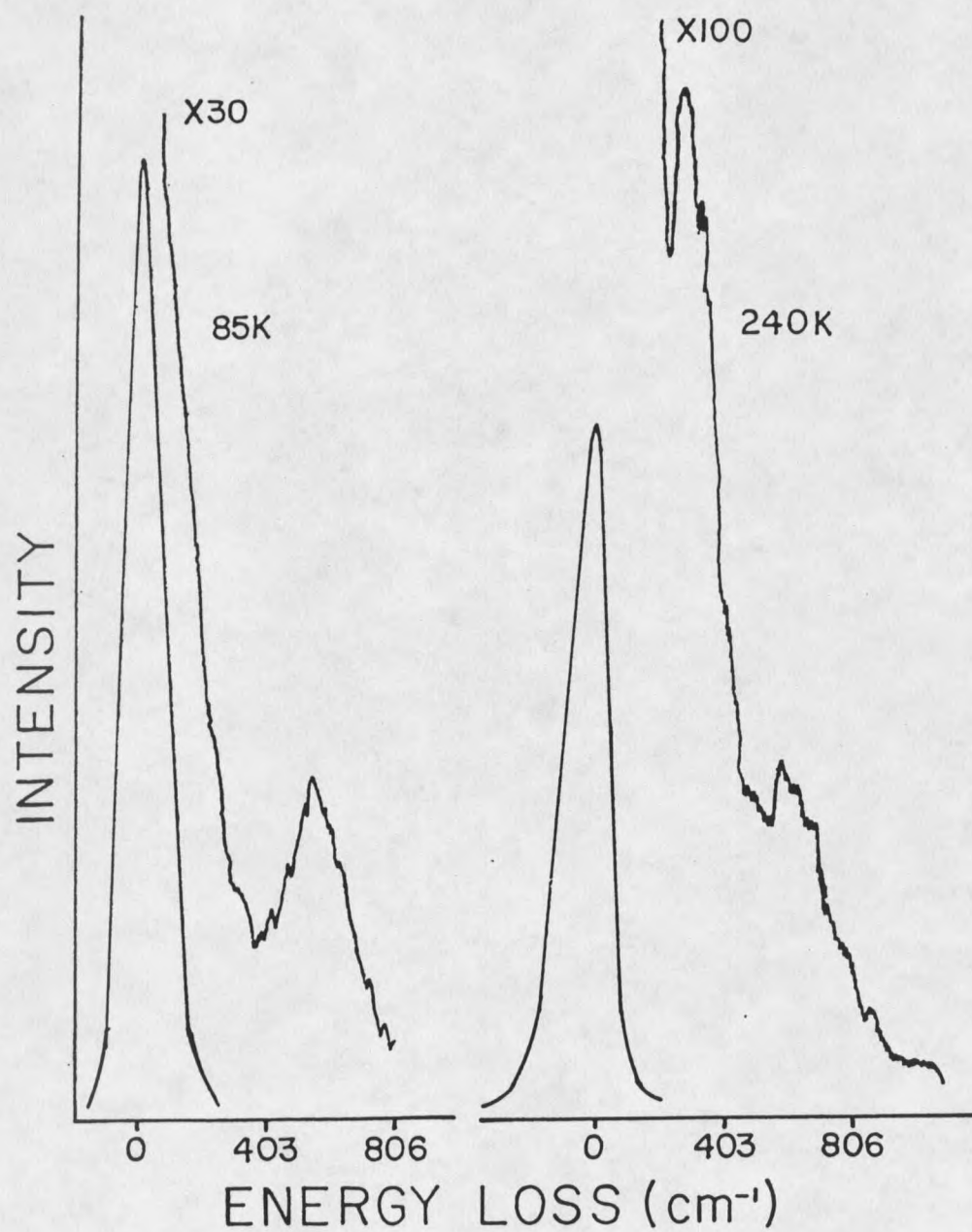


Figure 17. Electron energy loss spectra of Ag(110) after exposure to 3000 L of O₂ at 90 K and subsequent warming to 240 K. Spectra reveals the conversion of molecular oxygen at 90 K to atomic oxygen at 210 K.

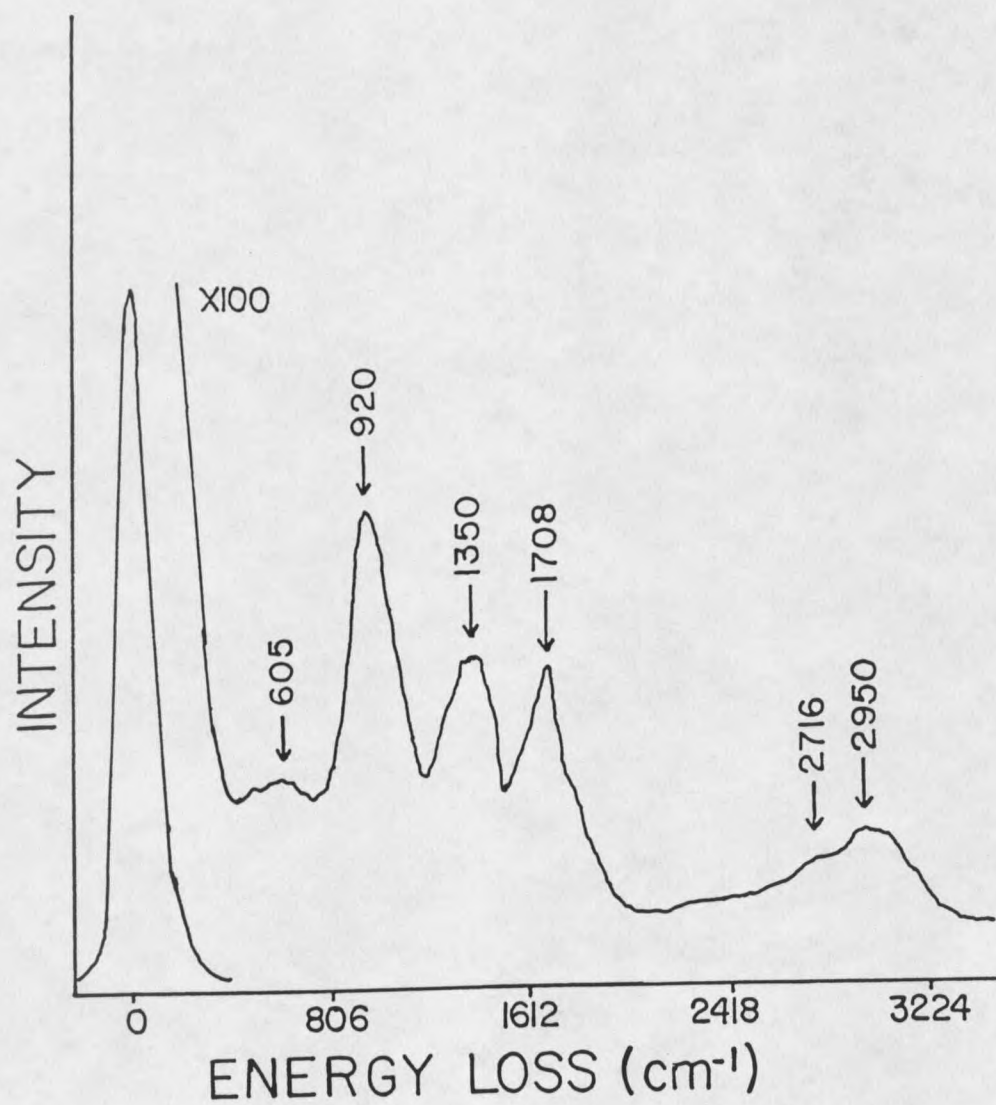


Figure 18. Electron energy loss spectra of CH₃COOH (5 monolayers) exposed to atomic oxygen on Ag(110) at 90 K. Spectra recorded at 90 K.

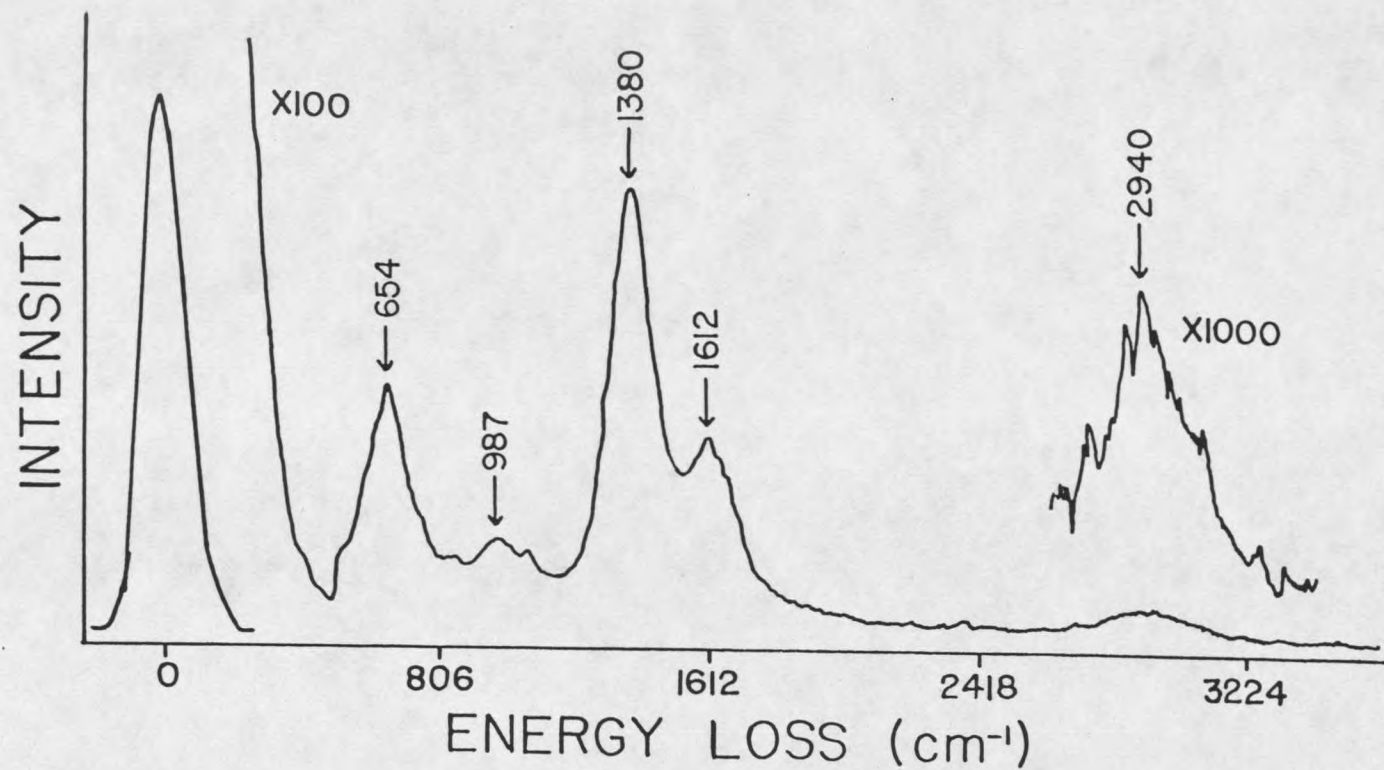


Figure 19. Electron energy loss spectra of CH₃COOH (5 monolayers) exposed to atomic oxygen on Ag(110) at 90 K. Spectra recorded at 210 K.

K to 3000 Langmuirs of O_2 followed by warming to 260 K. The sample was then cooled to 90 K and ~ 5 monolayers of CH_3COOH was deposited. The EEL-spectra was then recorded. Examination of this spectra shows that the acetic acid has not deprotonated and in fact the spectra is nearly identical to that obtained for CH_3COOH on a clean Ag(110) surface (Figure 10).

Figure 19 shows the EEL-spectra for the $(CH_3COOH + O)/Ag(110)$ system at 210 K. This spectra does not resemble the spectra obtained at 90 K (Figure 10), and hence some reaction must have taken place. The most obvious feature of the spectra at 210 K (Figure 19) is the absence of any hydroxyl group vibrational frequencies. This indicates that a deprotonation reaction has occurred.

Comparison of the EEL-spectra obtained at 210 K with the IR spectra reported for solid CH_3COONa (87) shows that at 210 K we have formed the acetate species. The frequency assignments are given in Table 4. The band at 2940 cm^{-1} is due to (C-H) stretching vibration. The bands at 1612 cm^{-1} and 1380 cm^{-1} are attributed to (COO) asymmetric and symmetric stretches respectively. The band at 987 cm^{-1} is assigned to the (C-C) stretch and the band at 654 cm^{-1} to the (COO) deformation. The frequencies observed in this study for acetate on Ag(110) are very similar to those reported for acetate on Cu(100) (89).

XPS results show that the FWHM O(1s) photoelectron peak was 1.6 eV and the binding energy was 531.1 eV. Comparing these values to those previously measured for acetic acid on Ag(110) at 90 K shows that the binding energy is lower, by 2.5 eV, and the FWHM has been

reduced by 1.4 eV. The narrow O(1s) FWHM is indicative that the two oxygen atoms are now in chemically equivalent environments and both are involved in bonding to the Ag(110) surface. The shift to lower binding energies is also consistent with the formation of an acetate species (74).

Table 4. Vibrational frequencies for acetate species on Ag(110) at 210 K and acetate ion (87).

Vibrational Mode	Description	EELS Frequency (cm^{-1})	IR Frequency (cm^{-1}) (87)
ν_a (CH_3)	CH_3 asymmetric stretch	2940	2936
ν_a (COO)	(COO) asymmetric stretch	1612	1578
ν_s (COO)	(COO) symmetric stretch	1380	1414
ν (C-C)	(C-C) stretch	987	924
δ (OCO)	(COO) deformation	654	646

Figure 20 shows the EEL-spectra obtained when the sample has been warmed to room temperature (290 K). Comparing the EEL-spectra obtained at 290 K with that obtained at 210 K shows that the asymmetric ν (COO) stretch is not observed at 290 K. This is consistent with the observed EEL-spectra of formic acid on Ag(110) at room temperature (88). Sexton (88) interpreted not observing the asymmetric ν (COO) stretch as indicating a change in orientation of the formate species at 290 K. The reasoning behind this interpretation deals with the orientation of the surface dipole. If the surface dipole is oriented parallel to the surface then it induces an image dipole of opposite polarity within the substrate.

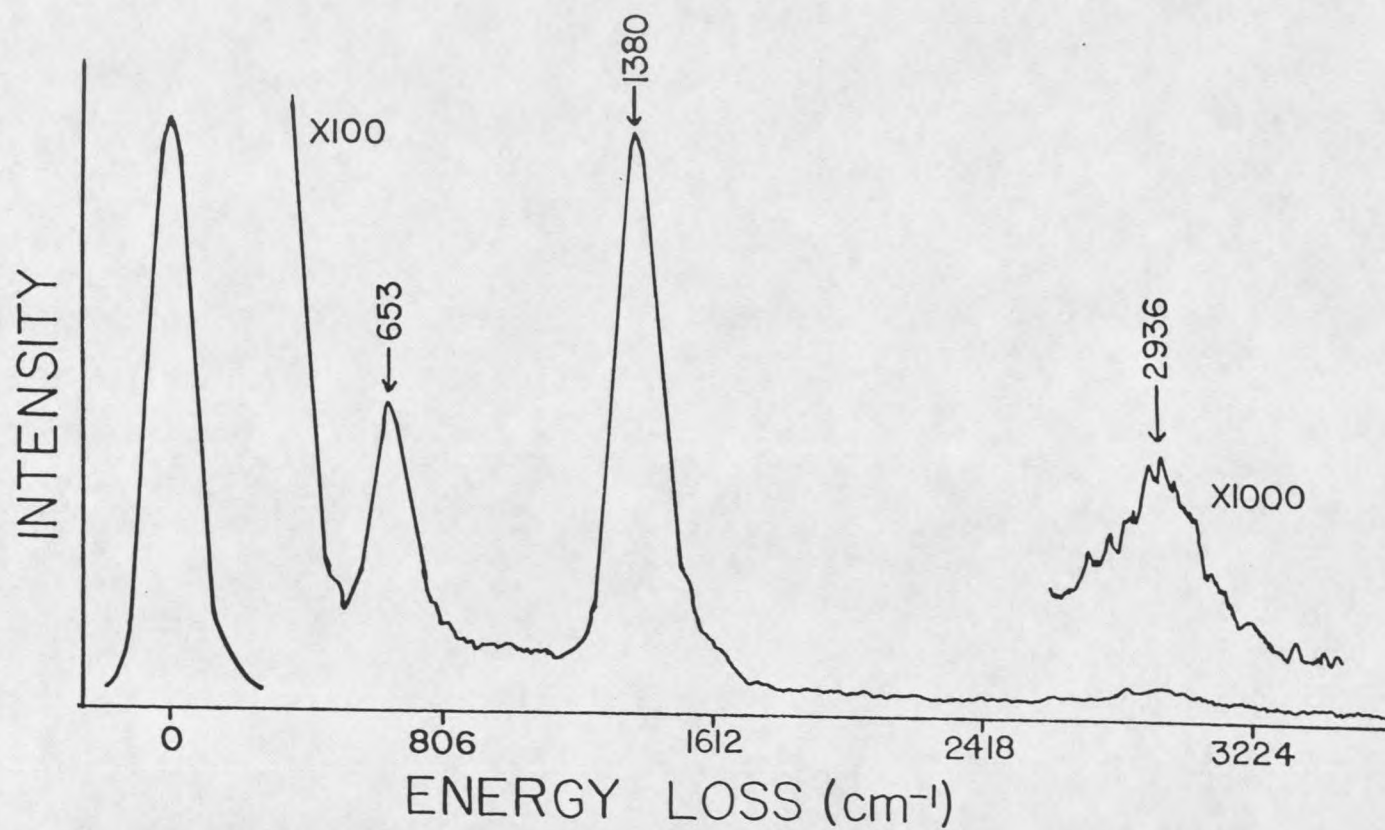


Figure 20. Electron energy loss spectra of CH₃COOH (5 monolayers) exposed to atomic oxygen on Ag(110) at 90 K. Spectra recorded at 290 K.

This image dipole then screens the surface dipole so that it does not interact with the oscillating field of the probing electron beam.

The net effect is that there is no inelastic scattering of the probing beam due to this adsorbate vibration.

Figure 21 a and b show top and side views of a Ag(110) crystal along with the possible orientations of acetate molecules at 290 K (21c,d) and at 210 K (21e). At 210 K the asymmetric $\nu(\text{COO})$ vibration is observed in the EEL-spectra and hence the C_2 axis, assuming C_{2v} symmetry, must be at some angle to the surface normal. A possible bonding orientation at 210 K would be if one acetate oxygen atom were in the two-fold hollow and the other were on the "hill." This situation is depicted in Figure 21e. This type of orientation would tilt the acetate molecule towards the surface and would make the $\nu(\text{COO})$ vibration EELS active, assuming dipole scattering. At 290 K the $\nu(\text{COO})$ vibration is not observed in the EEL-spectra and hence the C_2 axis, assuming C_{2v} symmetry, must be parallel to the surface normal. Having the C_2 axis parallel to the surface normal makes the dipole associated with the $\nu(\text{COO})$ vibration parallel to the surface and hence EEL inactive, assuming dipole scattering. Figures 21c and 21d show two possible bonding configurations for adsorbed acetate molecules on Ag(110) which would put the C_2 axis parallel to the surface normal. Figure 21c is the bridging structure and 21d is the symmetrical bidentate structure. Because of the limited resolution, EELS is not able to differentiate between these two structures.

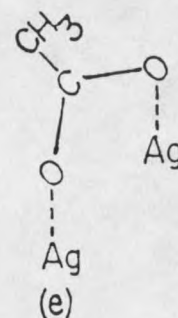
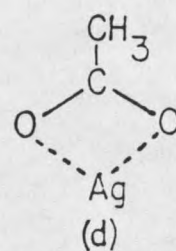
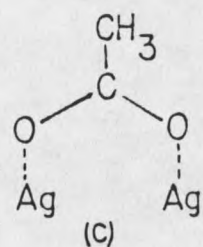
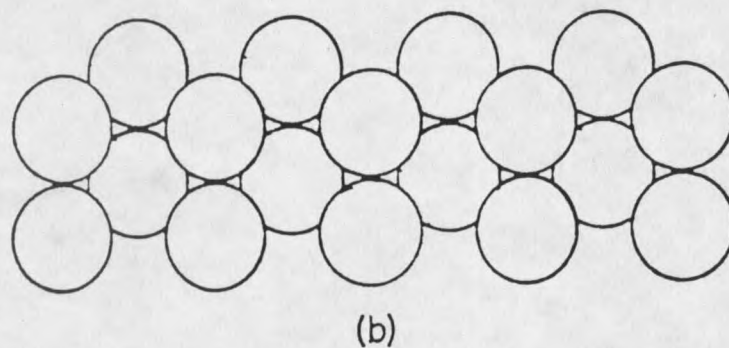
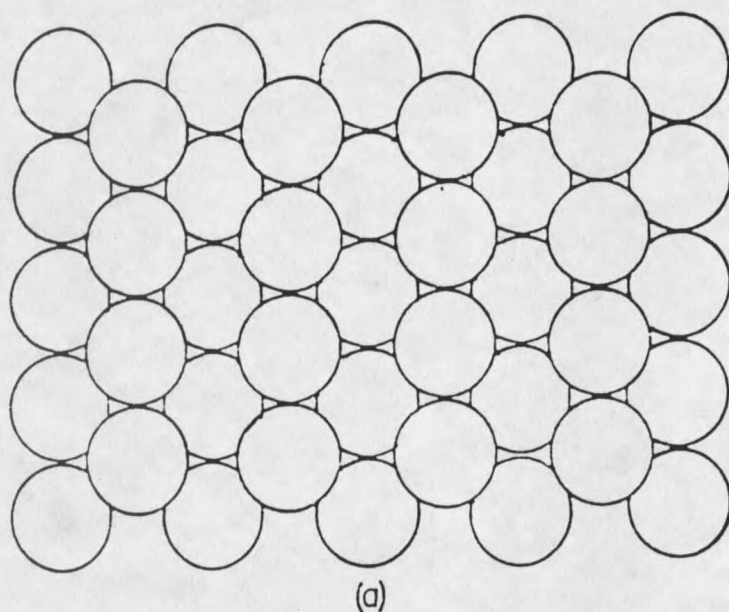


Figure 21. Bonding configurations of CH_3COO on Ag (110). (a) Top view of Ag(110) single crystal, (b) side view of Ag(110) single crystal, (c) $\text{CH}_3\text{COO}/\text{Ag}(110)$ bridging structure at 290 K, (d) $\text{CH}_3\text{COO}/\text{Ag}(110)$ symmetrical bidentate structure at 290 K, (e) $\text{CH}_3\text{COO}/\text{Ag}(110)$ bridging structure at 210 K.

XPS results show that the O(1s) FWHM is still 1.6 eV and the binding energy is 531.1 eV. These are the same values obtained for this system at 210 K. Therefore, the acetate molecule is oriented such that the two oxygen atoms are in chemically equivalent environments, i.e. both are involved with bonding to the Ag(110) surface. This is in agreement with the two postulated orientations for the acetate molecules.

A He(I) UP-spectra for adsorbed formate on copper has been reported (74). Previous EELS results of formic acid on Ag(110) (88) are analogous to those obtained in this study and the EEL-spectra reported for acetate on Cu(100) (89) is also analogous to that obtained in this study. Also, the gas phase UP-spectra of acetic acid and formic acid are very similar through the four highest energy molecular orbitals (67). Based on these similarities it is highly probable that the UP-spectra of acetate on Ag(110) should be analogous to the UP-spectra obtained for formate on copper.

Comparing the UP-spectra of formate on copper with calculated binding energies (74), Joyner found that chemisorption had stabilized the formate ion. After correcting for the reference levels, Joyner (74) found that most of the formate orbital energies shifted by about 4 eV to higher binding energies. This shift by 4 eV to higher binding energies is considerably higher than the 32.8 kcal/mole or 1.4 eV/molecule activation energy reported for the thermal desorption of formate from the Ag(110) surface (83). The reference level correction method used by Joyner (74) is questionable and may actually be responsible for such large binding energy shifts.

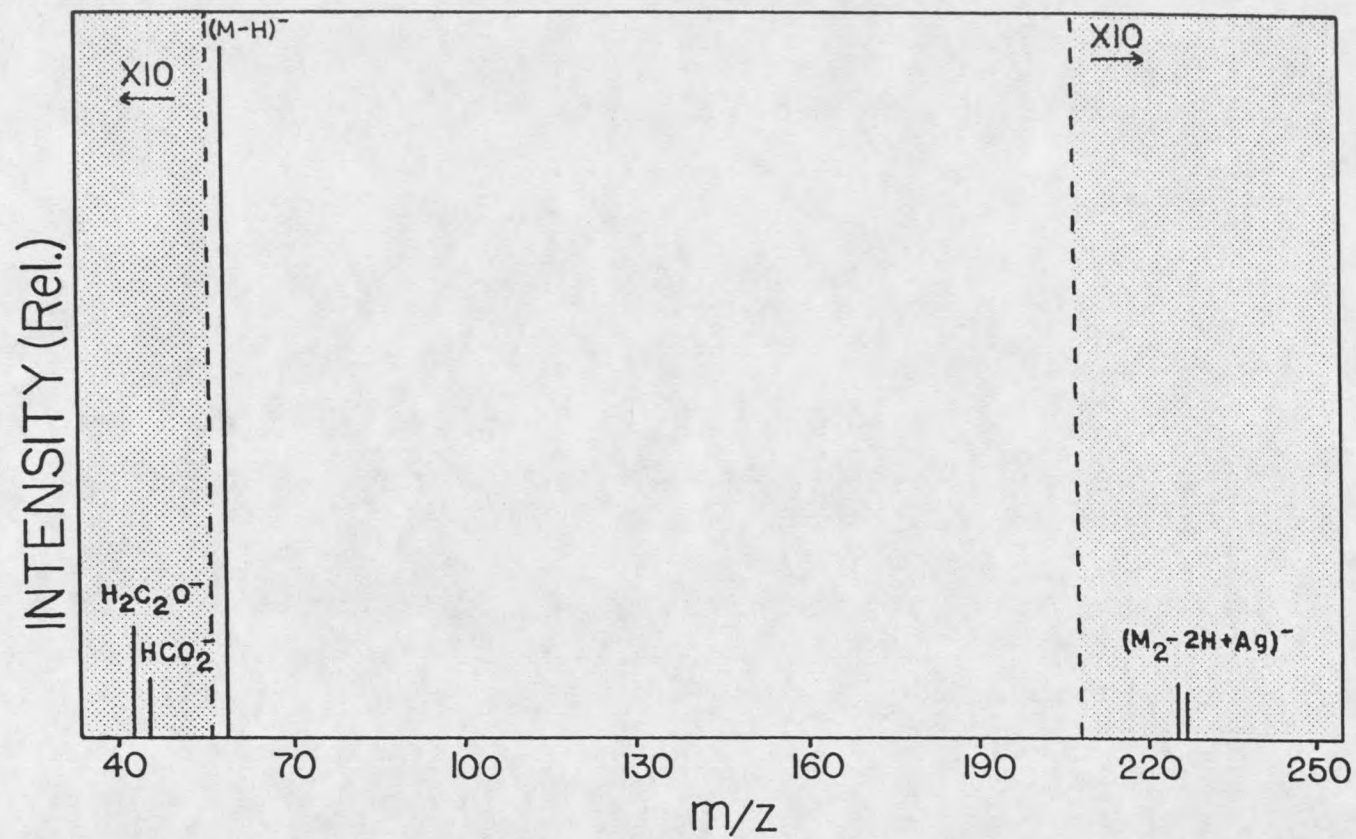


Figure 22. Negative ion SIM-spectra $CH_3COO/Ag(110)$ at 290 K. Ion intensities are relative to $(M-H)^-$.

Regardless, it can be seen that the acetate molecule is chemisorbed to the Ag(110) surface with a binding energy in the range of ~2 eV.

SIMS of CH₃COO/Ag(110) at 290 K

Figure 22 shows the negative ion static SIMS-spectra of acetate on Ag(110) at 290 K. It has been determined, using XPS, that there is ~ 0.5 of a monolayer of acetate adsorbed on the Ag(110) surface at 290 K. Intensity values are relative to the CH₃COO⁻ ion intensity. It can be seen that the major ion in the SIMS-spectra is CH₃COO⁻ and is essentially the only ion observed with good intensity. The lack of any deprotonated cluster ions is evidence that acetic acid has deprotonated totally to the acetate ion via acid-base reaction with adsorbed atomic oxygen. Positive ion static SIMS showed no ions attributable to acetic acid or acetate.

Static SIMS analysis of submonolayer coverages of amino acids on reactive metal surfaces displays only the deprotonated molecular ion and no protonated molecular ions (82). These authors have inferred from these results that amino acids have deprotonated on the metal surface and that is why they do not observe any protonated molecular ions. These same authors (82) have made multilayer amino acid samples on reactive metal substrates, where the amino acid layers are physisorbed to one another. They found that with heating, the protonated molecular ion disappears before the deprotonated molecular ion. Based on this data they concluded that amino acids deprotonate to form stable deprotonated amino acid-metal complexes which desorb at higher temperatures than the physisorbed amino acid molecules.

Results of this present study prove that deprotonated species emit only deprotonated molecular ions. Also, we have shown that physisorbed multilayers, hydrogen bonded layers, emit protonated and deprotonated molecular ions with equal intensity. Lange (82) also found that multilayer amino acid samples emit protonated and deprotonated molecular ions with equal intensity. If the surface acetate is formed and then the sample is cooled to 90 K and about 5 monolayers of acetic acid is deposited on top, the same SIMS results, as a function of temperature, that Lange (82) obtain with multilayer amino acids would be obtained. Therefore, this present study has proved that you can draw conclusions regarding surface species produced via acid-base reactions based on static SIMS results.

Positive ion SIMS of multilayer phenylalanine on Ag as a function of temperature showed that Ag containing adduct ions disappeared at the same temperature as the protonated molecular ion (47). The results from our present study and the phenylalanine results (47) indicate that this is due to the parent species deprotonating on the metal surface. However, these results do not help in differentiating between the direct emission model and the recombination model for the formation of cationized adduct ions. The cationized species may still be present but are not detected because their overall charge is neutral. However, by comparing the intensity of the $((\text{CH}_3\text{COO})_2 + \text{Ag})^-$ ion observed for $\text{CH}_3\text{COOH}/\text{Ag}(110)$ vs. $\text{CH}_3\text{COO}/\text{Ag}(110)$ it might be possible to differentiate between direct emission and recombination.

Comparing the relative intensities of the $((\text{CH}_3\text{COO})_2 + \text{Ag})^-$, at m/z 225, in Figure 22 with those listed in Table 3 shows that for equivalent coverage the $\text{CH}_3\text{COO}/\text{Ag}(110)$ system displays greater intensity. At one monolayer coverage of CH_3COOH the relative intensity of $((\text{CH}_3\text{COO})_2 + \text{Ag})^-$ ion is 0.002. However, for ~ 0.5 monolayer coverage of acetate the relative intensity of $((\text{CH}_3\text{COO})_2 + \text{Ag})^-$ ion is 0.008. For $\text{CH}_3\text{COOH}/\text{Ag}(110)$ at 90 K this ion is formed via recombination of coejected CH_3COO^- and Ag^+ ions. If the $((\text{CH}_3\text{COO})_2 + \text{Ag})^-$ ion were also formed via recombination only for the $\text{CH}_3\text{COO}/\text{Ag}(110)$ system, then the relative ion intensity should be smaller than the $\text{CH}_3\text{COOH}/\text{Ag}(110)$ system because the coverage is less. However, if it is assumed that some acetate-silver complexes are ejected intact and these recombine with coejected acetate ions, in the selvedge, then this would give a larger intensity for the $\text{CH}_3\text{COO}/\text{Ag}(110)$ system. If the binding energy of acetate on $\text{Ag}(110)$ is as high as 4 eV, then it might be possible to impart enough energy to the Ag atom to eject this complex intact. If this sequence of events occurs then this study has shown that for chemisorbed acetate on $\text{Ag}(110)$ the direct emission of secondary ions does occur. Also, if direct emission is occurring then this indicates that the symmetrical bidentate structure would be the correct binding configuration for the acetate-silver complex formed on the $\text{Ag}(110)$ surface at 290 K. An obvious experiment to test the above hypotheses concerning direct emission and bonding configuration would be to obtain positive and negative ion static SIMS data on $\text{CH}_3\text{COO}/\text{Ag}(110)$ at 210 K. EELS data shows that the acetate species is in the

bridging configuration at this temperature. Therefore, comparison of the relative intensity of $((\text{CH}_3\text{COO})_2 + \text{Ag})^-$ at 210 K and 290 K should indicate whether direct emission is occurring and if we can use static SIMS data to determine the bonding configuration of acetate on Ag(110) as has been done for CO on Ru(001), Ni(111) and Pd(111) (90,91).

CHAPTER 3

RELATIONSHIP BETWEEN SOLUTION EQUILIBRIA AND SECONDARY ION
INTENSITIES IN FAST ATOM BOMBARDMENT MASS SPECTROMETRYIntroduction

In the last four years FABMS has become a very successful technique. It has been used to obtain the molecular weight of and structural information on many non-volatile and high molecular weight materials (2,3,18,92). However, little emphasis has been placed on the evaluation of this technique as a tool for studying the bulk composition of liquids (93). The relationship between the observed ions in the FABM-spectra and the near bulk and surface layer composition is dependent upon how ions are desorbed from the liquid surface (96).

On the time scale of a collision cascade (10^{-12} s), particle bombardment of a liquid is identical to that of a solid (12). During this period, the molecules of a typical liquid (with a diffusion coefficient of 10^{-5} cm²s⁻¹) are essentially stationary and thermal vibrations may be ignored (12). One interesting model proposed to account for ionization and desorption from liquids requires the formation of ions in solution followed by desolvation and ion ejection (92). The energy for ejection is the vibrational energy transferred through the medium due to the collision cascade. Once

the ions are formed at the surface, only desolvation remains to be accomplished. This desolvation process has been described by Vestal (94) as the evaporation of preformed ions from splash droplets. Macfarlane (20) describes desorption of ions in a FAB experiment by invoking the concept of molecular aggregates. Here the aggregate is the involatile analyte solvated by molecules of the liquid polar matrix (glycerol). The desorption of the involatile molecule is described as a multiphonon excitation of the bonds holding the analyte ion to the aggregate (20). The phonons having been generated during the primary energy desposition event.

Higher secondary ion yields using liquid matrices have been attributed to the lower surface binding energies of liquids (12,92). In Macfarlane's model (20), higher secondary ion yields are rationalized in a similar fashion. Macfarlane proposes that the solvated molecular aggregate modifies the strong interactions of other analyte molecules thereby reducing the analyte to aggregate binding energy (20). Therefore, the analyte molecule is more easily dissociated from the aggregate upon excitation.

The concept that molecules had to be surface active in order to be observed in FABMS was first proposed by Barber and co-workers (18). These authors claimed that for maximum sensitivity, sample molecules should form a perfect surface monolayer. However, this does not imply that only molecules in the top surface layer are desorbed during FAB. Standing and co-workers (95) have shown that ions are ejected from as deep as $80\text{\AA}$ using liquid matrices. In a study designed to separate effects attributable to sputtering

efficiency from those attributable to real changes in surface composition, Ligon and Dorn (96) obtained results similar to Standing (95). Ligon (96) found that FABM-spectra of surfactants represented both the composition of the surface monolayer and the bulk. This implied that the FABMS technique was sampling more than just the surface monolayer. From this work Ligon and Dorn concluded that the observed secondary ion intensity ratio of two analyte molecules would depend on their bulk concentration and their relative surface activity (96).

Johnstone and co-workers (97) studying the mechanisms of energy transfer during FAB arrived at a very interesting conclusion regarding the relationship between solution concentration and mass spectral peak heights. These authors found that regardless of the energy transfer mechanism, equilibrium or non-equilibrium in nature, the observed FABM-spectral peak heights for desorbed crown ether/cation complexes were proportional to the concentrations of these species in solution. However, in this study the crown ether/cation solutions were deposited onto a glycerol substrate. These authors did not observe any ions attributable to glycerol. Therefore, it appears they had a multilayer film of the crown ether/cation solution on the glycerol surface. From this work, Johnstone and co-workers (97) were able to calculate crown ether/cation stability constants.

Caprioli (93) has shown that by using FABMS it is possible to determine the pKa's of weak acids. This author has shown that FAB is sensitive to subtle ionic changes in the liquid sample and that the

secondary ions emitted accurately reflect the ionic distributions in the liquid sample. However, Caprioli's samples were made in mixed glycerol/water solvents and his data needed to be corrected for the effect of change in the dielectric constant. This correction was achieved by plotting the calculated pKa (calculated using the Henderson-Hasselbach equation) versus the percent glycerol in the mixed glycerol/water solvent system. Caprioli then extrapolated from 50% to 0% glycerol and used this extrapolated pKa value as that obtained from his FABMS data. In addition to the dielectric constant correction, the data was also corrected for ionic strength. Caprioli's data for glycylglycine shows that the measured pKa would vary from ~ 3.0 to ~ 4.2 as the ionic strength changed from 0.4 to 0.2. The pKa value at zero ionic strength was then obtained by extrapolation of this data to zero ionic strength. However, this linear extrapolation was performed on a curve that was nonlinear in shape. The combination of these two pKa correction factors together with obtaining FABMS data from samples with 50% water make the results almost impossible to believe. However, the final pKa values determined by this method were within 5% of published pKa values (93).

Johnstone and co-workers (97) have shown that it is possible to calculate stability constants based on FABMS data. However, their data is for crown ether/cation solutions with glycerol acting as a solid support material rather than the actual solvent. Caprioli (90) has shown that it is possible to calculate pKa's for weak acids using mixed glycerol/water solvents. However, there has been no study

reported aimed at determining the bulk glycerol solution chemistry via FABMS. In the following study we propose to perform such a study.

This investigation centers around the relationship between secondary ion intensities observed in FABMS and glycerol ionic solution chemistry. The system chosen for this study is the reaction between glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) and copper(II) ions. This system is suitable to study because it has many different ionic species existing in solution. The first step in this study was to determine if the glycerol solution chemistry was analogous to the aqueous solution chemistry. Since the aqueous chemistry and the glycerol chemistry were essentially analogous, aqueous equilibrium constants were used to calculate equilibrium concentrations for species existing in glycerol solutions. Finally, FABMS data was obtained on these glycerol $\text{NH}_2\text{CH}_2\text{COOH}/\text{Cu(II)}$ solutions and the secondary ion intensities observed were compared with the calculated equilibrium concentrations.

Experimental

Fast Atom Bombardment Mass Spectrometry

FAB mass spectra were obtained with a VG7070EHF mass spectrometer. This is a double focussing mass spectrometer of normal geometry, i.e. electrostatic sector precedes the magnetic sector. A gas collision cell is located in the first field free region, between the source exit slit and the entrance slit on the electrostatic sector. This configuration allows the electrostatic sector voltage

to be uncoupled from the accelerating voltage and enables the electrostatic sector to be scanned simultaneously with the magnetic sector. This type of energy and momentum scanning has been called linked scans and allows one to observe metastable decompositions and, when used with the collision cell, to obtain collision-induced dissociation mass spectra (98-100). The source housing is also fitted with an Ion Tech BFN11 modified saddlefield ion gun.

The primary fast neutral argon beam is generated by resonance charge exchange between neutral argon atoms and 8 KV argon ions formed in the discharge regions of the Ion Tech saddlefield gun. The ion gun was operated at a discharge current of 1.2 mA and 8 KeV acceleration voltage. The primary atom flux at the sample target is not known for this instrument but has been estimated to be between 10^{12} particles $\text{cm}^{-2}\text{s}^{-1}$ and 10^{14} particles $\text{cm}^{-2}\text{s}^{-1}$ (96) for the same gun on a different mass spectrometer. These operating parameters correspond to a source housing pressure of 2.5×10^{-6} mbar, ion gauge reading not corrected for Ar. Sputtered ions were accelerated to 6 KeV and subsequently analyzed for their mass-to-charge ratio.

Data collection and subsequent mass analysis were performed using a VG 2000 data system. This is a Digital PDP/8a based system and is equipped with a digital scanner. The digital scanner contains 16 bit A/D and D/A converters along with real time clocks, a microprocessor with PROM's and is used to control the mass spectrometer and digitization of analogue signal. The data system was mass-to-charge calibrated using a (1:1:1) molar mixture of NaI, RbI and CsI. A saturated solution of these halide salts was heated

and applied to the FAB probe tip for subsequent FABMS analysis. All data was collected using an exponential down scan relation at 25 sec/dec from m/z 700 AMU to 200 AMU under current control. It has been this investigator's experience that current control yields more reproducible negative ion mass assignments than does field control.

A possible explanation for this increased precision is that under field control the Hall probe output is adjusted, by means of diode function generators, to give a linear relationship with $m^{1/2}$ in positive ion mode. The data system is mass calibrated in the positive ion mode and then the polarity is switched and negative ions are detected and subsequently mass analyzed using the positive ion mass calibration file. The characteristics of the magnet change when the polarity is switched and the Hall probe output is no longer linear with $m^{1/2}$. As a consequence of this nonlinearity, the centroid times of the masses shift and hence the mass assignments are incorrect. This problem can be remedied if the instrument is run under current control or if field control is desired one should have two diode function generator boards to linearize the Hall probe output for both polarities.

Standard VG FAB probe tips were used in all experiments. These tips are fabricated from non-magnetic stainless steel and are approximately 1x4 mm in size. The amount of sample applied to the probe tip was not quantitatively controlled, but amounts sufficient to apply a thin layer on the probe tip were used in all experiments. Experiments that involved using mixed glycerol water as the solvent

required special treatment. In these cases care was taken so that droplet formation on the bottom of the probe tip was minimized.

A recent article by Field (101) has demonstrated that chemical changes occur in neat glycerol after prolonged exposure to 5 KeV argon atoms. To minimize these fast atom induced chemical changes, all data collection was limited to six minutes or less per sample. Exceptions to this time requirement were allowed when collecting linked scan data or accurate mass data. Because each sample was introduced via a direct insertion probe inlet system, a method was devised to allow for more reproducible results between samples. This method involved adjusting the intensity of m/z 93, the $(M+H)^+$ ion from glycerol, to 5 volts at a detector sensitivity of 10^{-5} amps. The $(M+H)^+$ ion of glycerol was chosen because it gave the most intense signal in the mass range studied in these experiments. Also, adjusting the $(M+H)^+$ ion of glycerol to 5 volts allowed less intense signals to be recorded at higher detector sensitivities and subsequently normalized to signals recorded at lower detector sensitivities. The same procedure was used for negative ions except m/z 91, $(M-H)^-$ ion from glycerol was adjusted to give 1 volt at a detector sensitivity of 10^{-5} amps. All normalized mass intensity values represent the average of three scans per sample.

Accurate mass-to-charge values were determined by peak matching at a resolution ($M/\Delta M$) of 5000, 10% valley definition. Glycerol background peaks were used as reference masses for accurate mass determinations. Elemental compositions were calculated using the VG 2000 data system elemental composition program and the accurate

mass-to-charge values obtained from peak matching. All B/E linked scan data was obtained in the analogue mode for both metastable decompositions and collision-induced dissociations. Helium was used as the collision gas for collision-induced dissociations. The pressure of helium used was sufficient to reduce the intensity of the parent ion intensity by 50%.

In order to obtain the x-ray photoelectron (XPS) spectra of the black residue left on the FAB probe tip, the sample had to be made vacuum compatible with the XPS spectrometer. The reason for this is that glycerol has a vapor pressure of 2×10^{-4} torr at 20° (102) and the photoelectron spectrometer is housed in an ultra-high vacuum chamber ($< 10^{-9}$ torr). Also, the amount of residue obtained was small and, coupled with the small size of the FAB probe tip, dictated that several applications of sample had to be applied to the probe tip, without cleaning between applications. Repeated application of sample resulted in coating most of the probe tip with the black residue. Vacuum compatibility was achieved by allowing the probe, with sample residue, to remain in the mass spectrometer for 48 hours. The base pressure in the source housing after 48 hours was 5×10^{-8} torr. The sample was then considered vacuum compatible with the XPS spectrometer.

X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectra were obtained on a Leybold-Heraeus EA-11 photoelectron spectrometer. This spectrometer has a spherical capacitor-type energy dispersive analyzer with an input lens column

for variable retardation. Mg K_{α} radiation was used to generate the photoemitted electrons. The FAB probe tip with black residue was dissected and mounted on the rapid insertion probe and placed into the analyzer chamber. The standard CuO was deposited on Mo Foil and inserted into the analyzer chamber using the same direct insertion sample system. Spectra were recorded on an X-Y recorder.

Sample Preparation

The $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, glycine and glycerol were purchased from Baker and were reagent grade. All chemicals were used as received with no further processing.

To insure that all samples had the same concentration of glycine, a stock solution containing 10 mg/ml (0.133 M) glycine in pure glycerol was prepared. Stock solutions of 10 mg/ml glycine in varying volume % glycerol:water were also prepared.

Because the viscosity of glycerol is high, 1490 cp at 20°C (103), samples made in pure glycerol were heated to 75°C, using a water bath, to facilitate dissolving the added analytes. To ensure that all samples containing varying mole ratios of $\text{NH}_2\text{CH}_2\text{COOH}:\text{Cu(II)}$ contained the same concentration of glycine, the mole ratios were varied by adjusting the concentration of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ to give the desired mole ratios. All samples were initially prepared in 10 ml volumetric flasks but were transferred to small amber bottles after cooling to room temperature. Samples were kept a maximum of two weeks after which time new samples were prepared. The hydrogen ion activity was varied by adding, with a micropipette, either HNO_3 or

NaOH while determining the pH with a glass electrode and pH meter. For mixed solvent systems, the pH was determined for samples containing up to 50% glycerol. Cis-bis(glycino)Cu(II)-monohydrate was prepared according to Condrate (104).

Ancillary Equipment

Visible absorption spectra were obtained using a Cary Model 14 dual beam spectrophotometer. Spectra were recorded from 400 nm to 850 nm using 10 mm and 2 mm path length cells. Samples that were highly adsorbing were diluted with the respective solvent if 10 mm cells were used. Reference cell solvent always had the sample composition as the sample solvent.

Hydrogen ion activities were measured using a Sargent-Welch Model RB pH meter at 25°C. Index of refraction values were determined using a Bausch & Lomb Model 33-45-58 refractometer. Equilibrium concentrations for $\text{NH}_2\text{CH}_2\text{COOH}/\text{Cu(II)}$ system were calculated using the COMICS (105) program which was run on the University's Honeywell CP6 computer.

Results and Discussion

Determination of Glycerol Solution Chemistry

In a previous study (93) apparent pKa's of weak acids, in glycerol/water mixtures, were determined by FABMS. However, because mixed glycerol/water solutions were employed in this study (93), the measured pKa's had to be corrected for the change in dielectric constant. Also, with mixed glycerol/water solutions the water

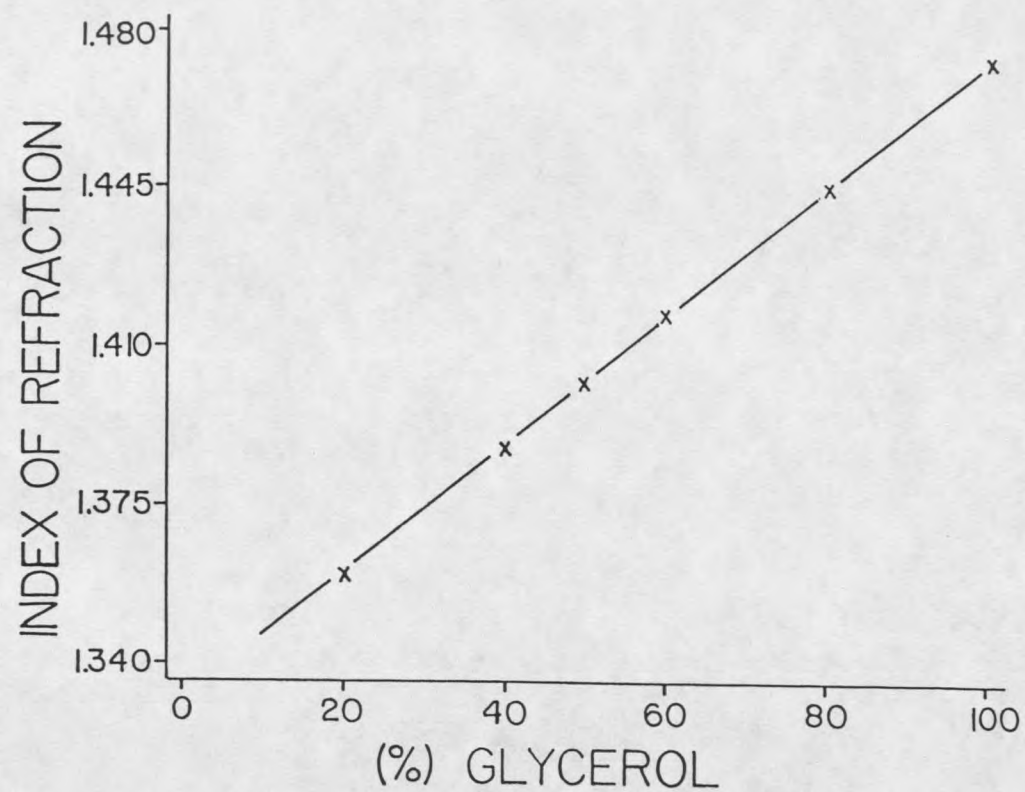


Figure 23. Mixed glycerol/water solvent composition working curve.

component is preferentially pumped away because of its higher vapor pressure.

To investigate the change in composition of mixed glycerol/water solutions the following experiment was performed. Glycerol/water solutions with compositions ranging from pure glycerol to 40% glycerol/60% water were prepared. The index of refraction was determined for each composition and a working curve of index of refraction versus composition was generated. This is shown in Figure 23. Next, each glycerol/water sample was applied to the FAB probe tip and inserted into the mass spectrometer. Each sample was exposed to the fast atom beam for 3 minutes and then promptly removed from the spectrometer. After removing the sample from the mass spectrometer, the index of refraction was measured. The composition of each sample, after FAB, was determined using Figure 23 and the results are shown in Table 5.

Table 5. Composition of glycerol/water samples after FAB exposure.

Composition Before Exposure (% glycerol)	Composition After Exposure (% Glycerol)
100	100
80	91
60	92
50	92
40	92

The results of this experiment show that water is preferentially pumped away on a time scale that is fast compared with FABMS data collection time. Because water is pumped away so fast we cannot apply Caprioli's (93) correction method for the change in dielectric

constant for FABMS data collected using the VG 7070 mass spectrometer. Therefore, all of our solutions will be made in pure glycerol.

However, it is desired to compare the ratio of the intensities of ions generated in the FAB experiment to the ratio of the concentration of species existing in the glycerol solution. The concentrations of species existing in aqueous solution, for the $\text{NH}_2\text{CH}_2\text{COOH}/\text{Cu(II)}$ system, can easily be calculated using the COMICS program (105) and the equilibria listed in Table 6.

Table 6. Pertinent equilibria for $\text{NH}_2\text{CH}_2\text{COOH}$ and Cu(II) in H_2O

$^+\text{HN}_3\text{CH}_2\text{COO}^- + \text{H}_2\text{O}$	$\longleftrightarrow$	$\text{NH}_2\text{CH}_2\text{COO}^-$	$\text{pK}_a = 9.60$ (107)
$^+\text{NH}_3\text{CH}_2\text{COO}^- + \text{H}_2\text{O}$	$\longleftrightarrow$	$\text{NH}_2\text{CH}_2\text{COO}^-$	$\text{pK}_a = 11.95$ (107)
$\text{H}_2\text{O} + \text{Cu}^{2+}$	$\longleftrightarrow$	$\text{Cu(OH)}^+ + \text{H}^+$	$\text{pK} = -8.00$ (106)
$\text{H}_2\text{O} + \text{Cu}^{2+}$	$\longleftrightarrow$	$\text{Cu(OH)}_2 + 2\text{H}^+$	$\text{pK} = -17.30$ (106)
$\text{H}_2\text{O} + \text{Cu}^{2+}$	$\longleftrightarrow$	$\text{Cu(OH)}_3^- + 3\text{H}^+$	$\text{pK} = -27.80$ (106)
$\text{H}_2\text{O} + \text{Cu}^{2+}$	$\longleftrightarrow$	$\text{Cu(OH)}_4^{2-} + 4\text{H}^+$	$\text{pK} = -39.60$ (106)
$\text{H}_2\text{O} + \text{Cu}^{2+}$	$\longleftrightarrow$	$\text{Cu}_2(\text{OH})_2 + 2\text{H}^+$	$\text{pK} = -10.36$ (106)
$\text{NH}_2\text{CH}_2\text{COO}^- + \text{Cu}^{2+}$	$\longleftrightarrow$	$(\text{Cu}(\text{NH}_2\text{CH}_2\text{COO}))^+$	$\beta_1 = 8.23$ (107)
$2\text{NH}_2\text{CH}_2\text{COO}^- + \text{Cu}^{2+}$	$\longleftrightarrow$	$\text{Cu}(\text{HN}_2\text{CH}_2\text{COO})_2$	$\beta_2 = 15.19$ (107)

The equilibrium constants listed in Table 6 are for species in a 100% H_2O medium. Stability constants for mixed methanol/water and dioxane/water solvent systems are ~ 0.5 pK units larger than those listed in Table 6 (107). However, the equilibrium constants for the ligand-proton complexes differ by < 0.2 pK units going from pure

water to mixed water/organic systems (107). From this it appears that the solution chemistry occurring in glycerol may not be significantly different from that of mixed glycerol/water systems.

Equilibrium concentrations of the species listed in Table 6 were calculated as a function of the molar ratio of $\text{NH}_2\text{CH}_2\text{COOH}$ to Cu(II) and pH using the COMICS program (105). Equilibrium concentrations for selected species at a $\text{NH}_2\text{CH}_2\text{COOH}:\text{Cu(II)}$ ratio of 4:1 are shown in Table 7.

Table 7. Calculated equilibrium concentrations (moles/liter) of selected species for $\text{NH}_2\text{CH}_2\text{COOH}:\text{Cu(II)}$ ratio of 4:1.

pH	H_2^+A	$\text{HA}(10^2)$	$\text{A}^-(10^8)^*$	$\text{CuA}^+(10^2)$	$\text{CuA}_2(10^3)$	free $\text{HA}(10)^{**}$
2.6	0.0407	7.23	7.23	1.77	1.17	1.13
3.2	0.0120	8.47	3.37	2.25	6.91	0.967
4.3	8.20×10^{-4}	7.34	36.80	0.76	25.60	6.742
9.5	2.60×10^{-9}	3.70	2.94×10^6	1.2×10^{-5}	33.30	0.642

* $\text{A}^- = \text{NH}_2\text{CH}_2\text{COO}^-$

** free HA = $[\text{H}_2^+\text{A}] + [\text{HA}] + [\text{A}^-]$

To determine if the solution chemistry occurring in pure glycerol paralleled that occurring in pure aqueous solutions, samples containing different mole ratios of $\text{HN}_2\text{CH}_2\text{COOH}:\text{Cu(II)}$ in pure and mixed glycerol/water solvents at various hydrogen ion concentrations were prepared. Mole ratios of 8:1, 6:1, 4:1, 2:1, and 1:1 of $\text{NH}_2\text{CH}_2\text{COOH}:\text{Cu(II)}$ in 100, 50, 25 and 0% (V:V) glycerol solvent mixtures were prepared. Hydrogen ion activities were selected based on the equilibrium concentrations of species desired for the FABMS experiments to follow. Equilibrium concentrations were obtained from

the COMICS program output. Hydrogen ion activities were adjusted by adding the required amount of HNO_3 or NaOH to achieve the desired pH for a given $\text{NH}_2\text{CH}_2\text{COOH}:\text{Cu(II)}$ ratio.

Initially, the pH was measured on 0% glycerol samples while adding HNO_3 or NaOH until the desired pH was attained. Then, the amount of HNO_3 or NaOH added to the 0% glycerol samples was added to the samples made in varying percent glycerol samples. pH was measured on samples containing up to 50% glycerol and there were no significant differences in pH as a function of % glycerol for a given $\text{NH}_2\text{CH}_2\text{COOH}:\text{Cu(II)}$ ratio. The pH readings obtained on mixed glycerol/water solvent samples do not necessarily reflect the true hydrogen ion activities in these samples. However, the term "pH" will be used throughout this chapter as a means of comparing samples that have the same amount of acid or base added. In addition, visible absorption spectra were obtained for all samples prepared. There were no significant differences in absorption curves obtained going from 0-100% glycerol for the same $\text{NH}_2\text{CH}_2\text{COOH}:\text{Cu(II)}$ ratio. This data is shown in Table 8. Also, the visible absorption curves for mixed glycerol/water samples at a $\text{NH}_2\text{CH}_2\text{COOH}:\text{Cu(II)}$ ratio of 2:1 as a function of pH were very similar to those reported for the aqueous 2:1 $\text{NH}_2\text{CH}_2\text{COOH}:\text{Cu(II)}$ system (108).

The data in Table 8 shows that there has been no appreciable shift in equilibrium concentrations of the major species present for the $\text{NH}_2\text{CH}_2\text{COOH}:\text{Cu(II)}$ system going from pure water to pure glycerol. To further verify this finding the COMICS program output was examined. It was found that at a pH of 10 and a $\text{NH}_2\text{CH}_2\text{COOH}:\text{Cu(II)}$

ratio of 8:1 the $\text{Cu}(\text{NH}_2\text{CH}_2\text{COOH})_2$ concentration was 0.0167 M, which was equal to the initial concentration of Cu(II) added. Therefore, it should be possible to calculate the molar absorption coefficient (ϵ) for $\text{Cu}(\text{NH}_2\text{CH}_2\text{COOH})_2$ for varying % glycerol samples and compare these to that obtained for pure cis-bis(glycine)Cu(II) monohydrate. The results of this experiment are shown in Table 9.

Table 8. Measured pH values and visible absorption data for $\text{NH}_2\text{CH}_2\text{COOH}/\text{Cu}(\text{II})$.

$\text{NH}_2\text{CH}_2\text{COOH}:\text{Cu}(\text{II})$	pH	% Glycerol	λ_{max} (nm)	Intensity at λ_{max} (OD units)
1:1	4.5	0	740	0.69
1:1	4.4	50	740	0.69
1:1	---	100	740	0.67
2:1	2.6	0	740	0.32
2:1	2.5	50	740	0.35
2:1	---	100	740	0.35
4:1	4.3	0	645	0.26
4:1	4.3	50	640	0.23
4:1	---	100	645	0.22
8:1	10.0	0	630	0.17
8:1	10.0	50	635	0.16
8:1	---	100	630	0.15

The data in Table 9 shows that the complexation reaction between $\text{NH}_2\text{CH}_2\text{COOH}$ and Cu(II) has gone to completion in all solvent mixtures. Also, the experimentally measured molar extinction coefficients are in excellent agreement with the values given in the literature for the cis-bis(glycino)Cu(II) complex (108,109). The data shown in Table 9 together with the data shown in Table 8 indicate that the solution chemistry occurring in pure glycerol is not significantly different from that occurring in pure water for the $\text{NH}_2\text{CH}_2\text{COOH}/\text{Cu}(\text{II})$

chemical system. Therefore, this allows equilibrium concentrations in glycerol to be calculated using aqueous equilibrium constants in conjunction with the COMICS program. These calculated equilibrium concentrations can then be compared with the respective ion intensities obtained from FABMS data.

Table 9. Comparison of $\lambda_{\max}$ and ϵ for 8:1 ($\text{NH}_2\text{CH}_2\text{COOH}:\text{Cu(II)}$) solutions and pure cis-bis(glycino) Cu(II) monohydrate.

cis-bis(glycino) Cu(II)		% glycerol		
		0	50	100
$\lambda_{\max}$ (nm)	630	630	635	630
Intensity at $\lambda_{\max}$	0.15	0.17	0.16	0.15
ϵ	45	51	48	48

FABMS of $\text{NH}_2\text{CH}_2\text{COOH}/\text{Cu(II)}$ Solutions

Figure 24 shows the positive ion FABM-spectra of a 4:1 mixture of $\text{NH}_2\text{CH}_2\text{COOH}:\text{Cu(II)}$ at pH 2.6. The glycerol solvent background peaks have been subtracted out and the ion intensities are relative to the $((\text{C}_3\text{H}_8\text{O}_3)_2+\text{H})^+$ ion at m/z 185. The $((\text{C}_3\text{H}_8\text{O}_3)_2+\text{H})^+$ ion is the protonated glycerol dimer which was not completely removed during the spectrum enhancement procedure. The major ions observed in this spectra are $\text{NH}_3\text{CH}_2\text{COOH}^+$, protonated glycine at m/z 76, the $((\text{H}_2\text{A})(\text{C}_3\text{H}_8\text{O}_3))^+$ cluster ion at m/z 168 and the $((\text{H}_2\text{A})(\text{C}_3\text{H}_8\text{O}_3)_2)^+$ ion at m/z 260. The protonated glycine-glycerol cluster ion at m/z 168 was identified by peak matching. Peak matching gave a mass of 168.0854 AMU for the $(\text{H}_2\text{A}(\text{C}_3\text{H}_8\text{O}_3)_2)^+$ ion which is 0.0018 AMU higher than the exact mass of $\text{H}_2\text{A}(\text{C}_3\text{H}_8\text{O}_3)_2$. The composition and structure

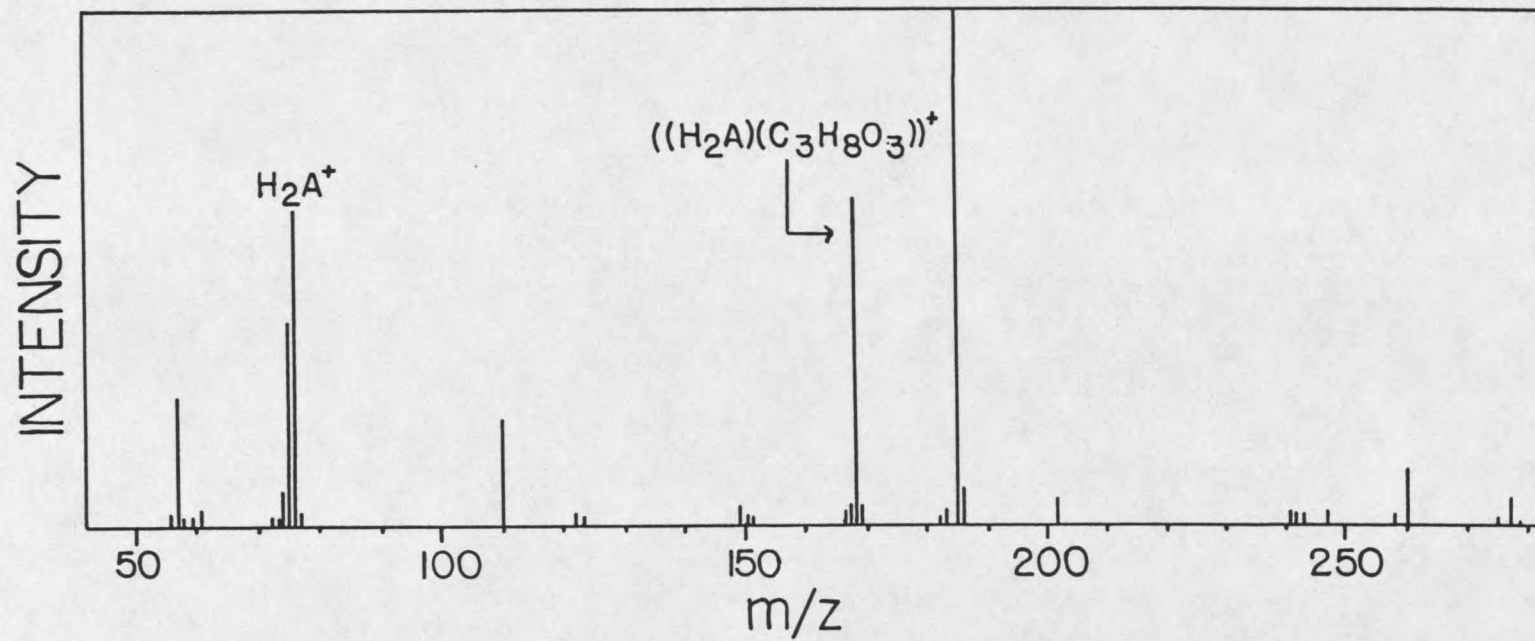


Figure 24. Positive ion FABM-spectra of 4:1 molar ratio of $\text{NH}_2\text{CH}_2\text{COOH}:\text{Cu}(\text{II})$ in pure glycerol at pH 2.6.

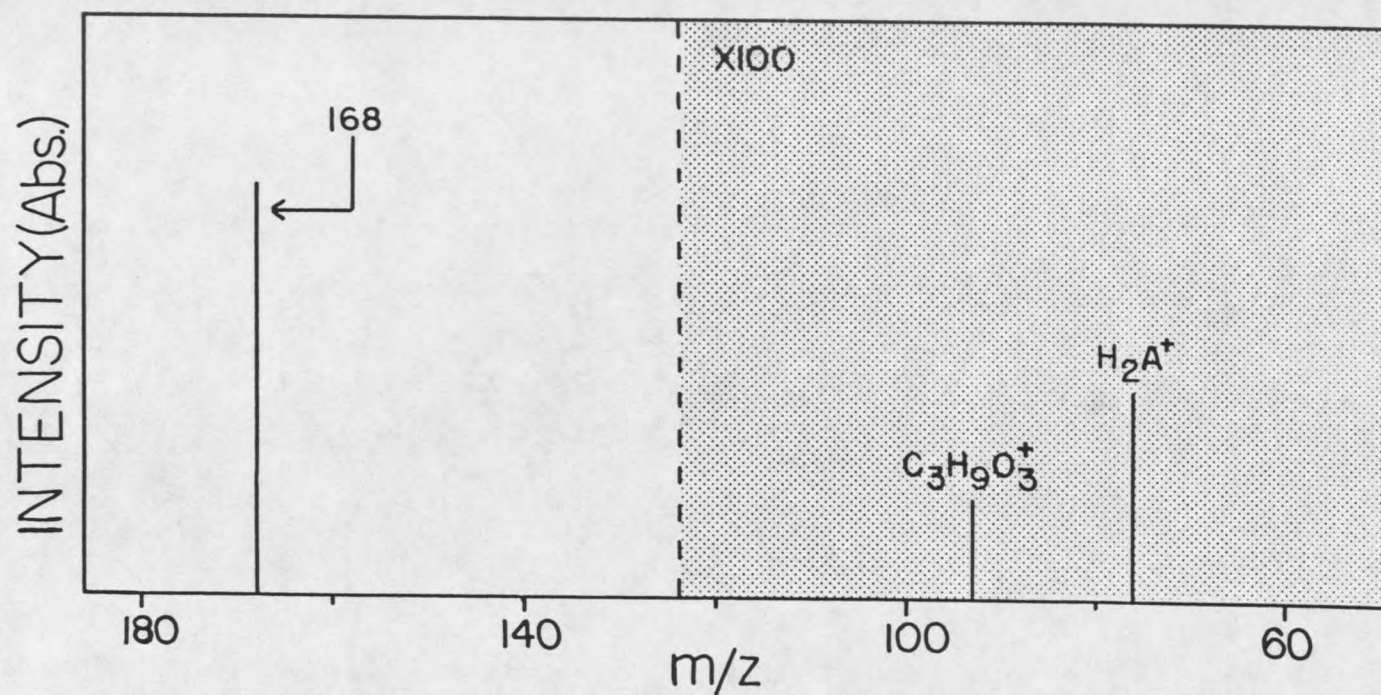


Figure 25. Collision-induced dissociation B/E scan of m/z 168. Daughter ions at m/z 93 and 76 show m/z 168 corresponds to $(H_2A(C_3H_8O_3))^+$.

of the ion at m/z 168 was further verified by B/E collision-induced dissociation mass spectra which is shown in Figure 25.

The B/E linked scan shows daughter ions corresponding to protonated glycerol at m/z 93 and protonated glycine at m/z 76. This spectra proves that the structure of the ion at m/z is $(\text{HA}(\text{C}_3\text{H}_8\text{O}_3)+\text{H})$. The intensity of the daughter ions indicates that the gas phase basicity of glycerol is not that much different from that of glycine. Therefore, it is difficult to associate the proton exclusively with either glycine or glycerol.

The most striking feature of the FABM-spectra shown in Figure 24 is the lack of any ions containing copper. The data shown in Table 7 indicates that the $(\text{CuNH}_2\text{CH}_2\text{COO})^+$ species is present in solution at 50% of the molar concentration of H_2^+A . Previous studies (93,97) have indicated that ions in solution are quantitatively sampled by the FAB process. If the FAB process does sample solution ions quantitatively, then the intensity of the $(\text{CuNH}_2\text{CH}_2\text{COO})^+$ ion should be approximately one-half the intensity of H_2^+A .

Figure 26 shows the positive ion FABM-spectra of a 4:1 mixture of $\text{NH}_2\text{CH}_2\text{COOH}:\text{Cu}(\text{II})$ at pH 2.6. The glycerol solvent background ions have been subtracted out and the ion intensities are relative to the $(\text{Na}(\text{C}_3\text{H}_8\text{O}_3))^+$ ion at m/z 115. The two Na-glycerol clusters ions at m/z 115 and m/z 207 are the result of using NaOH to adjust the hydrogen ion activities. This spectra also shows a complete lack of ions containing copper. Table 7 indicates that the equilibrium concentration of $\text{Cu}(\text{NH}_2\text{CH}_2\text{COO})_2$ species is ~ 30% of the H_2^+A species. The lack of observing either $(\text{CuNH}_2\text{CH}_2\text{COO})^+$ or $\text{Cu}(\text{HN}_2\text{CH}_2\text{COO})_2$

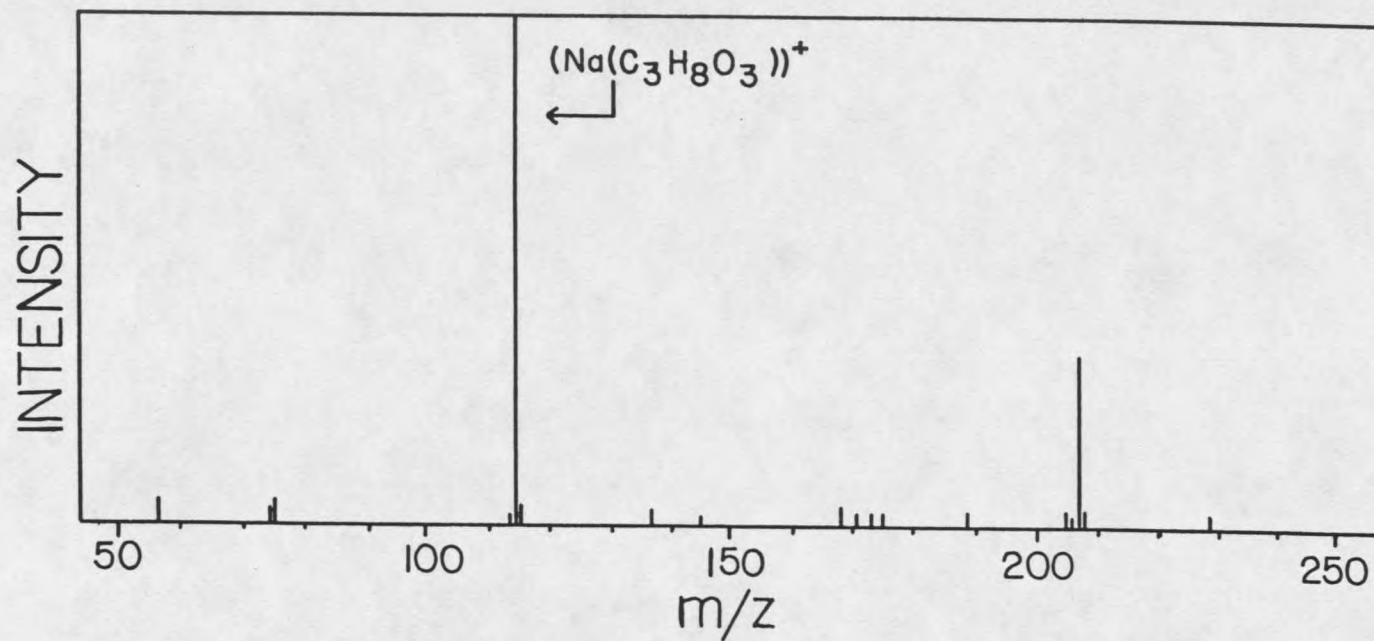


Figure 26. Positive ion FABM-spectra of 4:1 molar ratio of $\text{NH}_2\text{CH}_2\text{COOH}:\text{Cu}(\text{II})$ in pure glycerol at pH 9.5.

indicates that the FAB process is not quantitatively or qualitatively sampling the solution chemistry for the $\text{NH}_2\text{CH}_2\text{COOH}/\text{Cu(II)}$ system. The only copper species observed in any FABM-spectra were the $(\text{CuC}_3\text{H}_8\text{O}_3)^+$ and $(\text{Cu}(\text{C}_3\text{H}_8\text{O}_3)_2)^+$ ions. The $(\text{CuC}_3\text{H}_8\text{O}_3)^+$ ion was identified by the ^{65}Cu isotope peak and by peak matching, which gave a mass of 154.930 AMU. The $(\text{Cu}(\text{C}_3\text{H}_8\text{O}_3)_2)^+$ ion was identified by the ^{65}Cu isotope peak and by B/E linked scan data. The Cu(II) ion has been reduced to Cu(I) in both of these cluster ions. Also, these ions were only observed when there was an excess of Cu(II) ions in solution and the intensity of the $(\text{Cu}(\text{C}_3\text{H}_8\text{O}_3)_2)^+$ was always greater than $(\text{CuC}_3\text{H}_8\text{O}_3)^+$.

Recently, it has been shown that species in solution need to be surface active in order to be observed in FABMS (96,110,111) using a glycerol matrix. Ligon (96) has shown that species are sampled from both the surface layer and the near surface bulk layers. However, the secondary ion yields of subsurface species are considerably lower than surface species. The complete absence of any copper-glycinate species in the FABM-spectra shows that surface activity is not solely responsible. Surface activity does not explain the complete absence of these species in the FABM-spectra. If the FAB process is sampling both bulk and surface species as proposed by Ligon (96) then we should have observed these copper-glycinate ions. Also, this does not account for the fact that free Cu(II) ions have been reduced to Cu(I) ions and are observed in FABM-spectra as Cu(I) -glycerol ions.

Cerny and co-workers (112) have shown that FAB of Cu(II) chelates, in glycerol, produce no Cu(II) chelate ions in the

FABM-spectra. Their results show that Cu(II) chelates produce +1 cations by formal reduction of Cu(II) to Cu(I). These authors have also shown that for chelates with two Cu(II) ions, both are reduced to Cu(I). Pelzer and co-workers (113) have shown that oxidation-reduction processes do occur in glycerol solutions as a result of the FAB process. These authors speculate that the reduction process occurs in the liquid phase and conclude that the degree of reduction depends upon the value of the redox potential. However, these authors did not propose a mechanism to account for this reduction process. It has been shown by Field (101) that radiation damage caused by fast atoms produces aldehydes and ketones in neat glycerol. Field proposed that hydrogen atoms and free radicals are produced via a hot atom chemistry and these species were precursors to the aldehydes and ketones. It is well known that hydrogen atoms can reduce Cu(II) to Cu(I) ions and the rate constants are typically near diffusion rate limited values (114). If hydrogen atom reduction is occurring in glycerol solutions then this would explain why the $\text{Cu}(\text{NH}_2\text{CH}_2\text{COO})_n$ species are not observed.

If $(\text{Cu(II)} \text{ NH}_2\text{CH}_2\text{COO})^+$ is the predominate species, then hydrogen atom reduction would yield a neutral species and would not be observed in the FABM-spectra. Hydrogen atom reduction of the $(\text{Cu(II)})(\text{NH}_2\text{CH}_2\text{COO})_2$ species would dissociate the complex into the neutral $(\text{Cu(I)}\text{NH}_2\text{CH}_2\text{COO})$ species and $\text{NH}_2\text{CH}_2\text{COO}^-$. Therefore, no Cu(II) species would be observed in the FABM-spectra if $(\text{Cu(II)})(\text{NH}_2\text{CH}_2\text{COO})_2$ were the predominant species in solution. If hydrogen atom reduction is occurring in solution then it does not

matter if these $(\text{Cu(II)NH}_2\text{CH}_2\text{COO})$ species are surface active, because they would be reduced to neutral species during the FAB process.

It has been observed that some glycerol solutions developed a black precipitate during exposure to the fast atom beam. Samples that turned black had an excess of Cu(II) ions in solution at higher pH values. XPS was used to identify the chemical composition of the black precipitate. Figure 27 shows the XP-spectra of the black precipitate and the XP-spectra of CuO . The XP-spectra of the black precipitate shows that the Cu(II) band is a doublet. The observed peaks have been assigned to CuO and CuCl_2 . CuCl_2 was the original source of Cu(II) ions in solution. Therefore, this XP-spectra shows that the black precipitate formed during FAB of $\text{NH}_2\text{CH}_2\text{COOH/Cu(II)}$ solutions is CuO . How CuO is formed is not known but we can postulate the following scheme.

It has been estimated that the instantaneous temperature in the collision cascade region during FAB can be as high as 10^4 K (115). Also, the black precipitate forms only with samples that have an excess of Cu(II) ions at high pH's. Under these solution conditions we probably have Cu(OH)_n^{n-2} species in solution. Also, it is known that Cu(OH)_n^{n-2} species can be converted to CuO by heating (116). Therefore, it may be possible to form CuO from Cu(OH)_n^{n-2} species during the FAB process.

At this point, this study has shown that $\text{NH}_2\text{CH}_2\text{COOH/Cu(II)}$ glycerol solutions are not quantitatively sampled in FABMS. This study and others (101,112) have shown that there is a tremendous amount of solution chemistry induced by the FAB process. However,

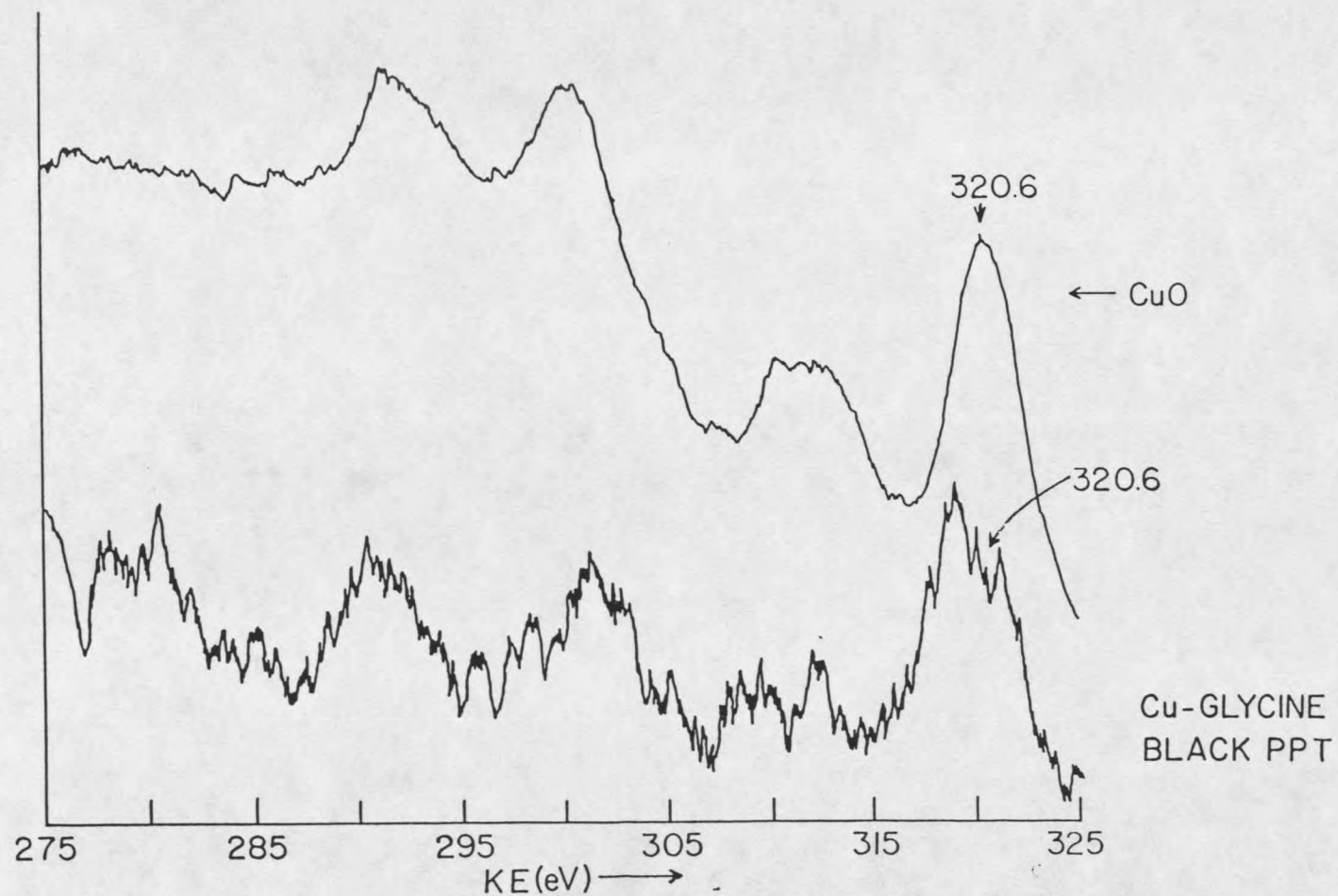


Figure 27. XP-spectra of the black precipitate formed during FAB of $\text{NH}_2\text{CH}_2\text{COOH}/\text{Cu(II)}$ glycerol solutions.

the only concern thus far was the analysis of Cu(II) species, without much attention given to the $\text{NH}_2\text{CH}_2\text{COOH}$ -proton species.

Before analyzing the $\text{NH}_2\text{CH}_2\text{COOH}$ -proton data, a method is needed to normalize ion peak intensities of the H_2^+A species. A normalization procedure is necessary to remove variations in ion intensities caused by changes in the total ion current and sample probe placement and to allow peak intensities from different samples to be compared. Equation 2 shows the method used to eliminate variations in peak intensities caused by variations in total ion current (TIC).

$$\frac{(\text{TIC } 10 \text{ mg/ml } \text{NH}_2\text{CH}_2\text{COOH})}{(\text{TIC sample})} \frac{(\text{area } \text{H}_2^+\text{A peak})}{(\text{H}_2^+\text{A } 10 \text{ mg/ml } \text{NH}_2\text{CH}_2\text{COOH})} = X \quad (2)$$

These normalized values were made relative to the sample that gave the highest normalized value according to Equation 3.

$$X_{\text{relative}} = \frac{X}{X_{\text{max}}} \quad (3)$$

All the following H_2^+A ion intensity data was normalized using Equations 2 and 3.

If H_2^+A ion intensities are proportional to $[\text{H}_2^+\text{A}]$ in solution, then it is necessary to compare ratios of ion intensities to ratios of equilibrium concentrations. To determine if H_2^+A ions in solution are sampled quantitatively, the comparison between intensities and equilibrium concentrations needs to be made as a function of the hydrogen ion activity. Table 10 shows the FABMS data for H_2^+A ions

for a 4:1 ratio of $\text{NH}_2\text{CH}_2\text{COOH}:\text{Cu(II)}$ along with the calculated equilibrium $[\text{H}_2^+\text{A}]$. The data is presented as ratios of ion intensities and ratios of equilibrium concentrations for the indicated species at different pH values. The data for free $[\text{HA}]$ and $[\text{H}_2^+\text{A}]$ concentrations was taken from Table 7.

Table 10. Comparison of calculated equilibrium concentration ratios with FABMS ion intensity ratios. Ratio of $\text{NH}_2\text{CH}_2\text{COOH}:\text{Cu(II)}$ is 4:1

pH(1)/pH(2)	Ratios		
	(H_2^+A) ion intensity	$[\text{H}_2^+\text{A}]$	free $[\text{HA}]$
2.6/3.6	1.28	3.4	1.17
2.6/4.4	1.77	49.0	1.53
2.6/9.5	3.83	1.5×10^7	1.70
3.6/4.4	1.38	14.6	1.30
3.6/9.5	3.00	3.6×10^6	1.45
4.4/9.5	2.17	3.2×10^5	1.12

Comparing the H_2^+A ion intensity ratios with the $[\text{H}_2^+\text{A}]$ ratios, it is obvious that the FAB process is not sampling the glycerol solution quantitatively for this species. However, comparing the H_2^+A ion intensity ratios with the free $[\text{HA}]$ ratios shows that the values are in good agreement for ratios obtained on samples where the pH values are close. This indicates that the FAB process is inducing a tremendous amount of proton transfer to $\text{HN}_2\text{CH}_2\text{COOH}$ species in solution. Ligon (117) has recently proposed that protonation of species in glycerol solutions results from proton transfer from $(\text{C}_3\text{H}_8\text{O}_3\text{H})^+$ to the analyte species. However, for higher hydrogen activity samples the predominant $\text{NH}_2\text{CH}_2\text{COOH}$ species in solution is the $\text{NH}_2\text{CH}_2\text{COO}^-$ anion. This species needs to pick up two protons to

be observed as H_2^+A in the FABM-spectra. Apparently, there is not enough FAB induced protonation occurring to fully protonate all the $\text{NH}_2\text{CH}_2\text{COO}^-$ anions to H_2^+A at the higher pH's. This would explain why the H_2^+A ion intensity ratios for pH(1)/pH(2) ratios of 2.6/9.5, 3.6/9.5 and 4.4/9.5 are higher than the corresponding free [HA] ratios. The data presented in Table 10 has shown that, for the $\text{NH}_2\text{CH}_2\text{COOH}/\text{Cu(II)}$ chemical system, FABM-spectra represents proton solution chemistry that has been induced by the FAB process. The FABMS data in Table 10 is representative of samples that contain Cu(II) ions. This study has shown that there is a tremendous amount of Cu(II) FAB induced chemistry occurring in the glycerol samples. Therefore, it is desirable to compare the $\text{NH}_2\text{CH}_2\text{COOH}$ -proton chemistry in glycerol with and without Cu(II) to determine if Cu(II) is affecting the $\text{NH}_2\text{CH}_2\text{COOH}$ FAB induced proton chemistry.

The data in Table 11 represents the H_2^+A FABMS ion intensity obtained as a function of hydrogen ion activity for $\text{NH}_2\text{CH}_2\text{COOH}$ samples with and without Cu(II) present. The $[\text{NH}_2\text{CH}_2\text{COOH}]$ in samples without Cu(II) corresponds to the free [HA] for samples with both $\text{NH}_2\text{CH}_2\text{COOH}$ and Cu(II) present at some given hydrogen ion activity. The pH of the $\text{NH}_2\text{CH}_2\text{COOH}$ samples was adjusted, using the same procedure developed earlier, to be the same as samples containing Cu(II).

Table 11. H_2^+A FABMS ion intensity as a function of the free [HA] with and without Cu(II).

pH	H_2^+A FABMS ion intensity	
	with Cu(II) ($\text{NH}_2\text{CH}_2\text{COOH}:\text{Cu(II)}$)	without Cu(II)
3.0	0.67 (1:1)	0.62
3.6	0.72 (4:1)	0.67
4.4	0.52 (4:1)	0.49
9.0	0.59 (8:1)	0.65

The data presented in Table 11 shows that the Cu(II) ion is not disturbing the FAB induced protonation of $\text{NH}_2\text{CH}_2\text{COOH}$ species present in solution. This presents more evidence that the FAB process is inducing a tremendous amount of solution chemistry. The FAB process is inducing protonation, reduction and dehydration reactions in glycerol solutions containing $\text{NH}_2\text{CH}_2\text{COOH}$ and Cu(II) ions. It seems amazing that the reduction process occurs simultaneously with protonation and neither appear to have an effect on the other.

CHAPTER 4

SUMMARY

This study has shown that CH_3COOH is weakly bound to the $\text{Ag}(110)$ single crystal surface. Results of EELS and UPS have shown that the first monolayer of CH_3COOH is physisorbed with its C_2 axis parallel to $\text{Ag}(110)$ single crystal surface. EELS has shown that for multilayer CH_3COOH , the molecules are randomly oriented with strong hydrogen bonding existing between CH_3COOH molecules.

SIMS of $\text{CH}_3\text{COOH}/\text{Ag}(110)$, for one monolayer of CH_3COOH , has shown that the $\text{Ag}(110)$ single crystal surface has minimal influence on the formation of protonated and deprotonated CH_3COOH ions. For multilayer CH_3COOH coverages the formation of protonated and deprotonated monomers, dimers and trimers of CH_3COOH were formed with equal probability. These results indicate that for physisorbed hydrogen bonded multilayers, proton exchange between adjacent molecules is an important ionization mechanism. SIMS, in combination with EELS and UPS, has shown that the Ag -cationized CH_3COOH adduct ion was definitely formed via a recombination mechanism.

SIMS, in conjunction with EELS and XPS, has shown that for $\text{CH}_3\text{COO}/\text{Ag}(110)$ only negative ions attributable to CH_3COOH are emitted from the surface. This indicates that any organic acid that forms a polarized bond, chemisorbed with a metal surface, should only emit parent negative secondary ions. This implies that SIMS can be used

to determine the structure of organic-metal complexes existing on surfaces. These results also show that Benninghoven's interpretation of amino acid SIMS results is correct (15,82). EELS has shown that chemisorbed CH_3COO undergoes a change in orientation on the $\text{Ag}(110)$ single crystal surface. Using this EELS data in combination with SIMS data, this study has shown that intact emission of CH_3COOAg from $\text{CH}_3\text{COO}/\text{Ag}(110)$ is possible.

This study has also shown that desorption of ions from mixed water/glycerol samples should not be used for quantitative purposes because of the preferential loss of water. A normalization procedure was developed to allow quantitative comparison of FABM-spectral data from different samples. However, this study showed that FAB of glycerol solutions containing metal ions and organic ligands induces protonation, reduction and dehydration reactions. Because of these reactions it was not possible to extract any quantitative solution chemistry data by FABMS on these samples. These results are in sharp contrast to Caprioli's FABMS results (93). In light of Pelzer and co-workers (113) results on FAB induced oxidation/reduction processes in glycerol solutions, future studies of the type initiated in this study using different metal ions and ligands should be pursued.

In addition, a novel rapid insertion probe inlet system for SIMS was designed and built. This type of system is relatively inexpensive and easily fabricated. The sample rod designed to be used in conjunction with this inlet system incorporated many features including LN_2 cooling, rapid sample mounting and electrical

isolation. The materials needed to fabricate this sample rod are readily available and very inexpensive. The equipment needed to machine these components is readily available and the procedures used were not very complex, the only exceptions being the the fabrication of ceramic and OFHC components.

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APPENDIX

DESIGN AND CONSTRUCTION OF A UHV SIM-SPECTROMETER

The homebuilt ultra-high vacuum (UHV) SIMS work chamber is shown in Figure 28. This work chamber was designed and constructed using existing facilities on campus and commercially available components. All design ideas and machining were conceived and performed by this author.

The work chamber was designed to meet the following requirements:

1. UHV SIMS analysis chamber, Figure 28h.
2. Differentially pumped ion gun, Figure 28i.
3. High vacuum preparation chamber with capabilities to prepare samples in situ, Figure 28c.
4. High vacuum manifold, using 150 l/s turbomolecular pump, to be used for system venting, ion gun differential pumping and preparation chamber pumping, Figure 28e and f.
5. Rapid sample insertion inlet system.

The vacuum system designed for this chamber consists of two 150 l/s turbomolecular pumps with associated forepumps and isolation valves, Figure 28f and k. After baking at 150°C for 15 hours the preparation chamber pressure was 9×10^{-9} torr and the SIMS analysis chamber pressure was 8×10^{-10} torr. These pressures were recorded with the isolation gate valve, Figure 28g, closed. With the isolation gate valve open and the sample rod inserted into the SIMS chamber, the pressure in the SIMS analysis chamber would increase to 1×10^{-9} torr. The specially designed rod guide, Figure 28d, was designed to

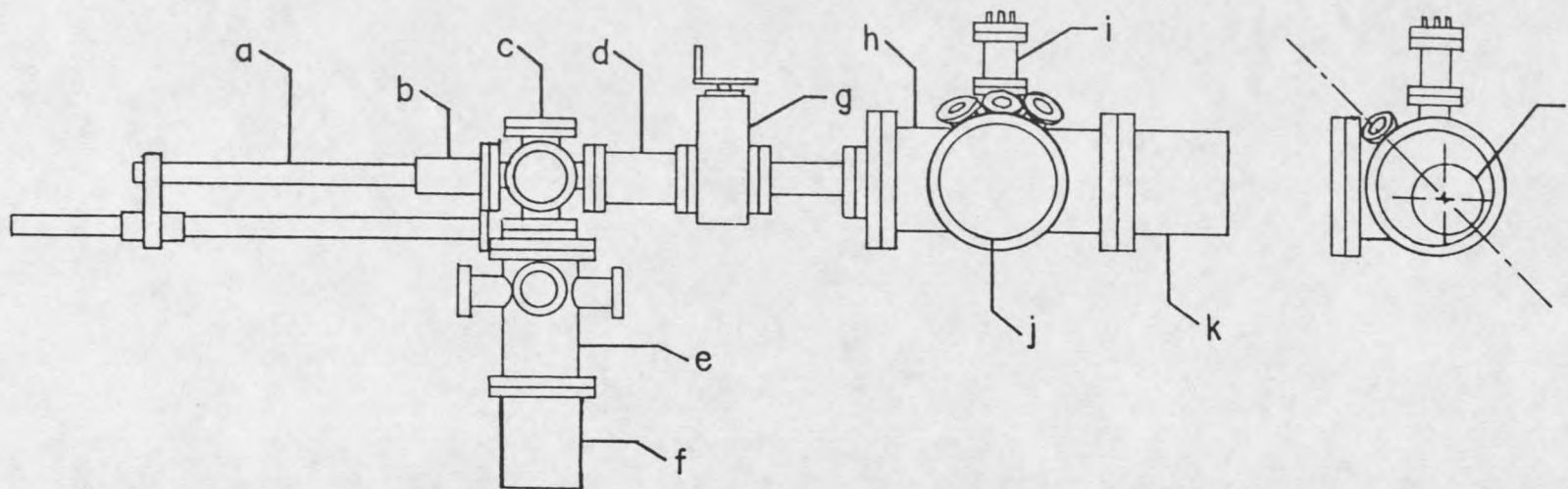


Figure 28. Schematic diagram of the homebuilt SIMS work chamber. (a) Rapid insertion, LN_2 cooled, electrically isolated sample rod with guide, (b) differentially pumped o-ring stack, (c) 6-way cross prepchamber, (d) teflon lined rod guide with o-ring, (e) 6-way cross vacuum manifold, (f) 150 l/s turbomolecular pump, (g) gate valve, (h) SIMS analysis chamber, (i) differentially pumped ion gun, (j) quadrupole mass analyzer with secondary ion optics, (k) 150 l/s turbomolecular pump, (l) 45° offset adapter flange.

guide the sample rod and reduce the leak rate between the SIMS analysis chamber and preparation chamber.

This was accomplished by machining a solid 2.0 inch O.D. rod of stainless steel to accept a machined teflon guide that was 1.25" x 1.50" O.D. x 1.250" I.D. An o-ring groove was machined into the teflon guide and the whole assembly, teflon and o-ring, was secured inside the stainless steel using a threaded retaining ring. The o-ring is made of viton and is the proper size for a 1.248" O.D. rod. This design works very well and a pressure differential of 1000:1 can be maintained between the preparation and analysis chambers.

The differentially pumped inlet o-ring stack, Figure 28b, is shown drawn to scale in Figure 29. This assembly was designed to meet several requirements. The first of these was rapid sample insertion capabilities and the second was the ability to mount samples while maintaining vacuum in the preparation chamber. The first requirement dictates several stages of differential pumping with each stage separated by o-rings. Figure 29d shows the first stage which is pumped by a small rotary vane pump and Figure 29e shows the second stage which is pumped by a small diffusion pump. The o-rings shown in Figure 29b provide both rod seal and face seal. The o-ring groove dimensions were calculated to allow one o-ring to perform both functions. To allow rapid insertion the conductance of the volume between o-rings has to be the same or greater than that of the differential pumping foreline. The conductance of this volume was determined by assuming a rectangular duct shape. The dimensions of this rectangular duct were determined by conductance and physical

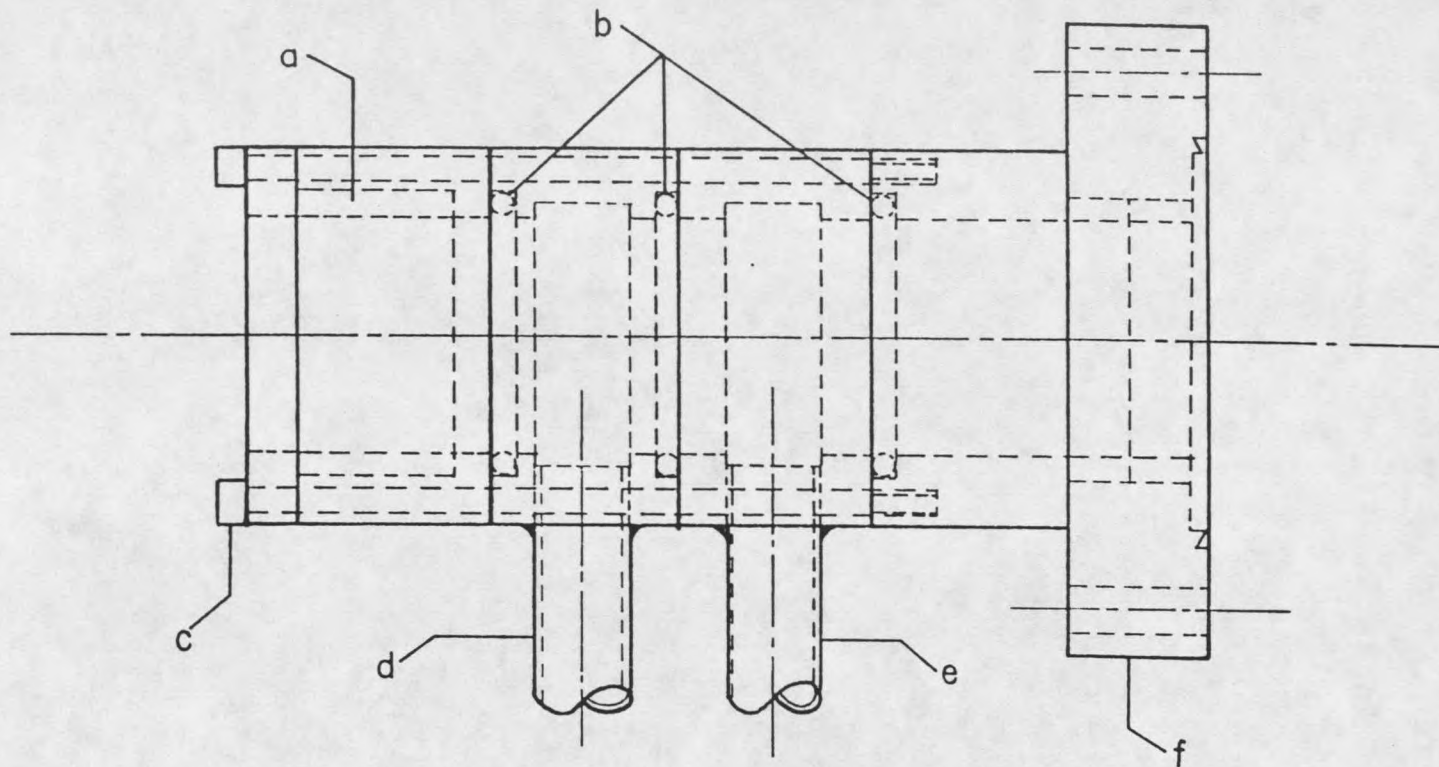


Figure 29. Sample rod differentially pumped o-ring inlet system. (a) Teflon rod guide, (b) viton o-rings, (c) securing screw, (d) first stage of differential pumping, (e) second stage of differential pumping, (f) UHV flange.

space requirements. This design allowed rapid sample insertion, < 2 minutes, of the sample rod without degrading the preparation chamber vacuum. This whole o-ring assembly is modular and is secured onto a flange by using four securing screws, Figure 29c. The ability to mount samples without loss of vacuum was achieved by designing the sample rod to be long enough to remain in contact with the three o-rings while mounting a sample.

The sample rod is shown in Figure 30. This rod was designed for electrical isolation, rapid insertion and cooling. The overall length of the sample rod is 46 inches, 29.5 inches are needed to traverse the work chamber. The rod is composed of 40.5 inches of ground and polished stainless steel tube with 1.248" O.D., Figure 30b, and 5.5 inches of oxygen free high conductivity copper (OFHC), Figure 30h. Liquid nitrogen (LN_2) cooling is accomplished by pumping LN_2 through 1/4 inch stainless steel tube, Figure 30a, into the LN_2 reservoir, Figure 30c. Electrical isolation is achieved by using ceramic insulators, Figure 30d, f and i. The OFHC rod section is isolated from the stainless steel section using a 1/8 inch thick ceramic disc, Figure 30d. The securing screws used to attach the OFHC section are electrically isolated using ceramic spacers, Figure 30f, and ceramic sleeves, Figure 30i. The sample is mounted on the milled flat using two 2-56 screws, Figure 30e. To maintain vacuum during sample mounting, the length of OFHC after the sample flat is long enough to remain in contact with all three o-rings, Figure 29b.

The SIMS analyzer chamber was designed to perform UHV experiments, allow electrical measurements to be made on the sample

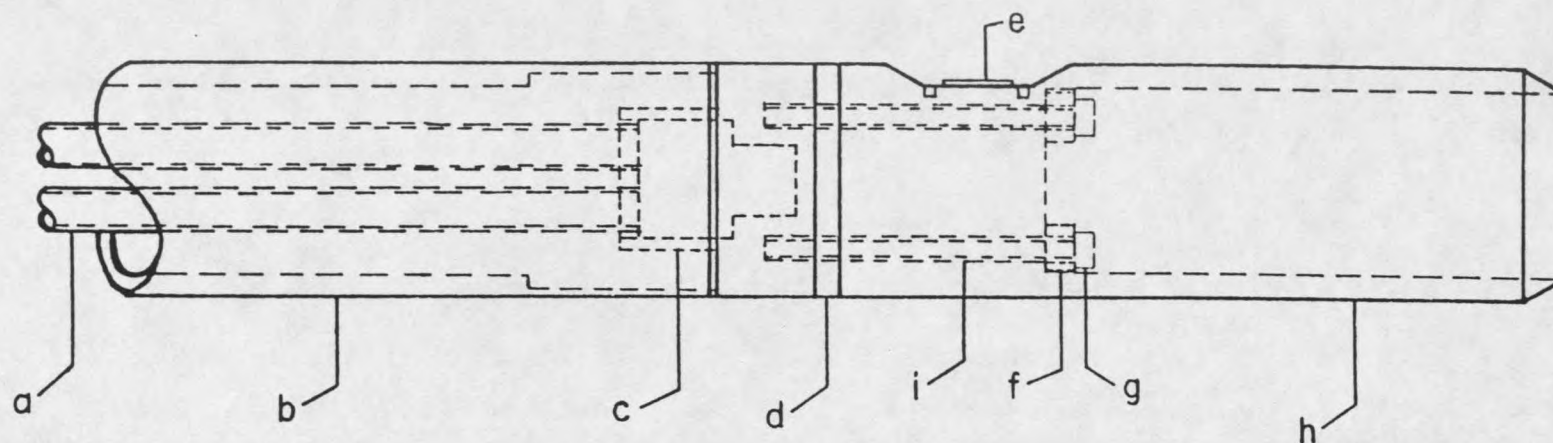


Figure 30. Sample rod. (a) LN_2 inlet, (b) ground and polished stainless steel tube, (c) LN_2 reservoir, (d) ceramic insulator, (e) sample stage, (f) ceramic insulator, (g) securing screw, (h) polished OFHC, (i) ceramic insulator.

and to have several direct line of sight ports incident on the sample, Figure 291. Fabrication of this chamber was made simpler by offsetting the sample rod. The sample rod was offset by machining a 4 1/2 inch flange 1/2 inch off on a 45° angle, with respect to center axis of the chamber, on the face of an 8 inch flange. This is shown in Figure 291. A flat was milled on the sample rod to give an effective rod O.D. of 1.00 inch. This effectively gives an angle of incidence, for the ion gun, of 45° and a secondary ion collection angle of 45°, both with respect to the surface normal. Offsetting the sample rod allowed the ion gun to be mounted perpendicular to the mass analyzer. The mass analyzer used for SIMS experiments conducted with this chamber was a Leybold-Heraeus SS B/10 system, which was described in Chapter 2. The ion gun used for these experiments was a Vacuum Generators AG61 differentially pumped ion gun. Differential pumping was achieved using a port on the 6-way cross vacuum manifold, Figure 28e, with bellows tubing. A small, 2 3/4 inch, butterfly valve was used to isolate the AG61 ion gun from the 6-way cross vacuum manifold. The AG61 ion gun was purchased without the associated power supply. The ion source on the AG61 ion gun was operated using the ion source controls on a Varian MAT CH5 mass spectrometer. Ion beam focus and deflection voltages were supplied by Ortec high voltage power supplies. Using these supplies, primary ion current densities ranging from 15 nA/cm² to 600 nA/cm² were achieved.

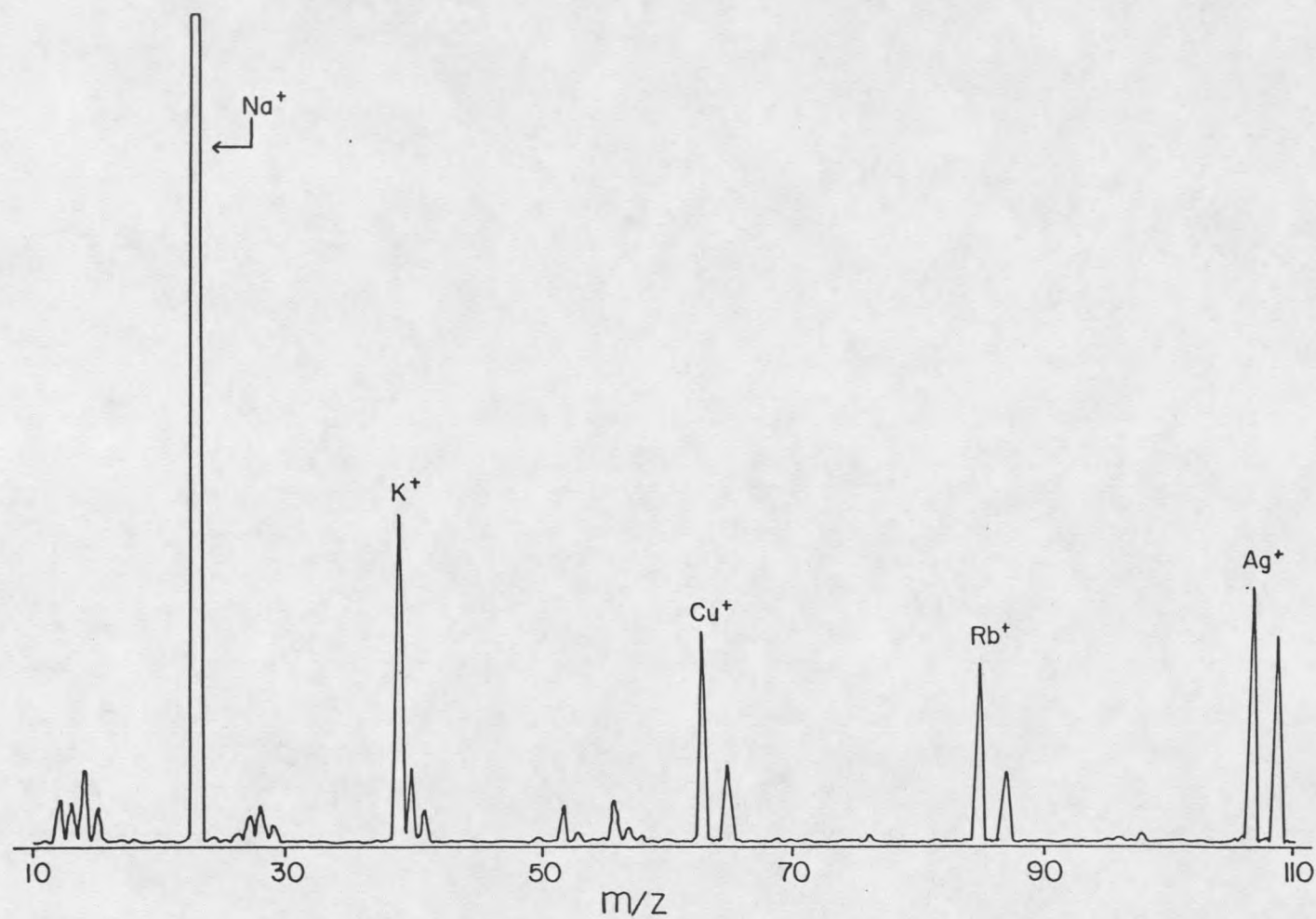


Figure 31. Positive ion SIM-spectra of a phosphor screen. 3KeV Ar⁺ ion, 100nA/cm².

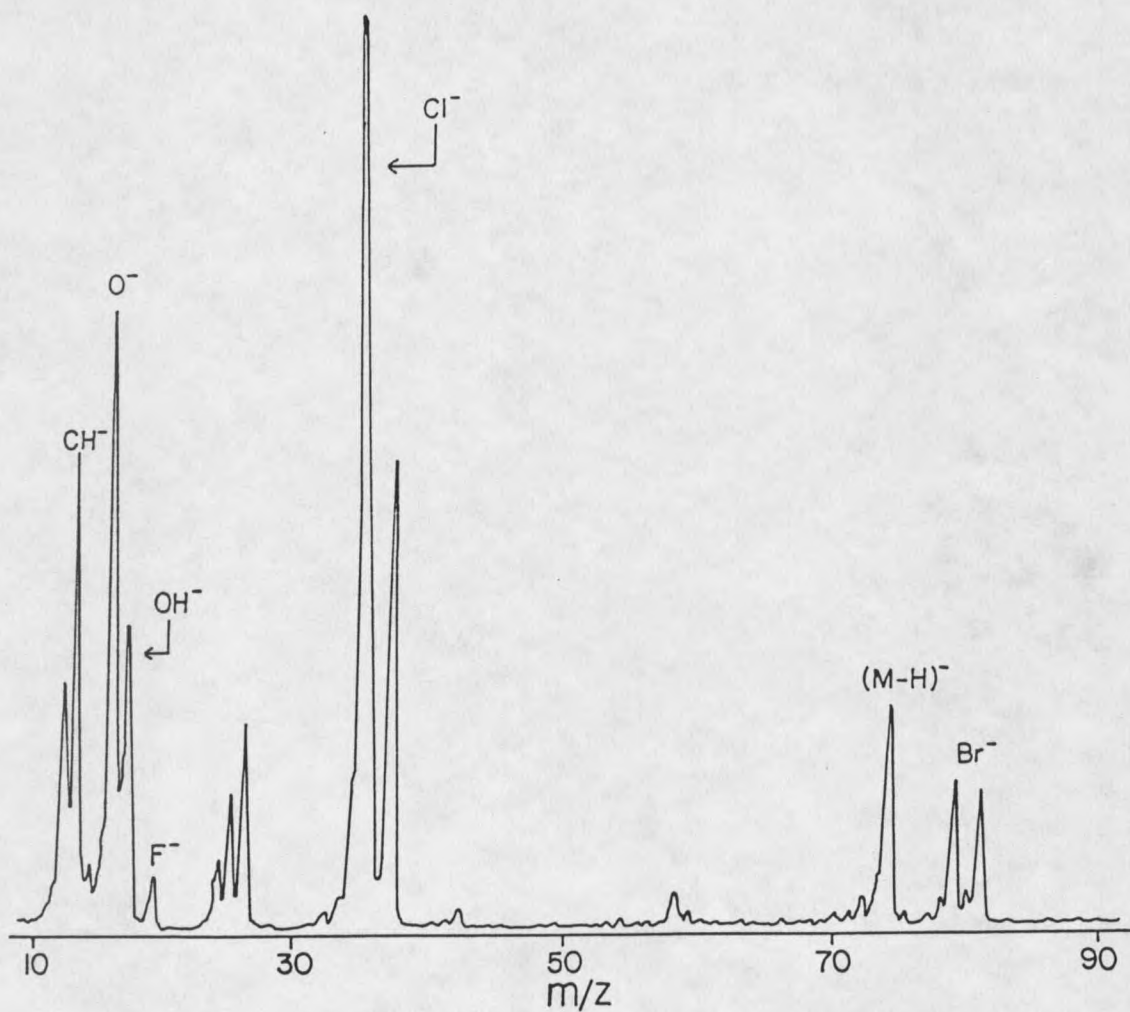


Figure 32. Negative ion SIM-spectra of glycine on Ag. 3Kev Ar^+ ion, $60\text{nA}/\text{cm}^2$.

Figure 31 shows the positive ion SIM-spectra of a phosphor screen (Kimball Physics, Wilton, NH) obtained with this instrument. The spectra was obtained using a 3 KeV Ar^+ ion beam with a primary ion current density of 100 nA/cm^2 . The phosphor screen was used for ion beam alignment and focussing. This spectra displays good resolution and the count rate for the Na^+ peak was $\sim 9.8 \times 10^4 \text{ Hz}$. This spectra indicates the phosphor material is probably composed of inorganic salts. Figure 32 shows the negative ion SIM-spectra of glycine on Ag. The spectra was obtained using a 3 KeV Ar^+ ion beam at a primary ion density of 60 nA/cm^2 . The sample was prepared by depositing 50 μl of a 5 mg/ml aqueous glycine solution onto a HNO_3 etched Ag foil. The glycinate anion, $(\text{M}-1)^-$, at m/z 74 gave a count rate of 8 KHz. Figures 31 and 32 demonstrate this homebuilt SIM-spectrometer is capable of detecting molecular and atomic secondary ions of both polarities with good sensitivity and resolution.

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