To the Graduate Council:

I am submitting herewith a dissertation written by Terence Michael Thomas entitled "Photoelectron Spectroscopy of Catalytically Important Small Ring Mono-Sulfur Heterocycles Adsorbed on a Copper Single Crystal." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

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PHOTOELECTRON SPECTROSCOPY OF CATALYTICALLY IMPORTANT SMALL RING MONO-SULFUR HETEROCYCLES ADSORBED ON A COPPER SINGLE CRYSTAL

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Terence Michael Thomas

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DEDICATED TO MY WIFE, ANITA

for her patience and understanding

during the years of my graduate studies

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ABSTRACT

Photoelectron spectra using He(I) radiation are presented for Cu(110) after exposure to thiacyclobutane, thiacyclopentane and thiacyclohexane as well as for the clean (110) surface of copper at ambient temperatures. Analysis of the spectra of the adsorbates suggested a strong sulfur-to-copper-dative bond, though the strength of the bond varies from adsorbate to adsorbate. Sulfur lone pair orbital stabilization energies were obtained for thiacyclobutane (1.4 eV), thiacyclopentane (1.1 eV) and thiacyclohexane (0.6 eV) and these stabilization energies were correlated to the dative-sulfur-to-surface bond strength. Ring strain and/or geometry are suggested as reasons for additional small shifts of adsorbate bonds in the thiacyclobutane spectrum. Relaxation energies were found to decrease in the order 4 > 5 > 6 member ring. An empirical linear relation was found between relaxation energy shifts and lone pair orbital stabilization energies for mono-heteroatom heterocycles bonded to Cu(110) by a lone pair dative bond. All adsorbates studied showed marked angular dependence, suggesting nonrandom orientation of the adsorbates on the surface. Al Kα X-ray data were used to calculate percent surface coverage. Other sulfur containing adsorbates were also studied and discussed, including thiophene, allyl mercaptan and thiacyclopropane. Thiacyclopropane was found to decompose upon exposure to copper.

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INTRODUCTION

A. General Overview of Catalysis[1-2]

It is difficult to overestimate the importance of catalysis in chemical technology. Catalytic processes utilized in chemical and petroleum refining industries account for well over 20% of the gross national product. Of the chemical compounds which are produced at a rate of greater than 10^9 pounds per year, more than 80% are produced by catalytic processes.

A distinction is generally made between homogeneous catalysis and heterogeneous catalysis. Homogeneous catalysis involves a molecular dispersion of all the reactants with the catalyst, whereas in heterogeneous catalysis the catalyst is a separate phase, most frequently a solid surface. Normally in heterogeneous catalysis a particle, grain, or pellet of porous catalyst is in contact with a liquid and/or gas phase in which reactants are present. The reactants diffuse to the surface of the catalyst, the reaction takes place, and the products diffuse away from the surface. Porous catalysts are used because these materials can be made with hundreds of square meters of catalytic surface per gram of catalyst. Although the diffusion processes are relatively well understood, the actual surface reaction itself is not well understood. The basic steps of heterogeneous catalysis which may be involved for a reaction are believed to be: (1) adsorption

of reactants on the surface; (2) surface diffusion to active sites on the surface; (3) the activation and reaction of the adsorbed reactants to form products; (4) surface diffusion of products away from the active site; (5) desorption of the products.

The efficacy of a catalyst is based upon two primary criteria:

1. Catalysts should have good activity and selectivity, i.e., they should convert reactants at a high enough rate to desired products without producing unwanted products;
2. Catalysts should have good lifetimes, which implies resistance to poisons normally present with reactants and physical durability under frequently severe conditions.

To comply with the above criteria and also for economic reasons, catalytically active material is usually dispersed onto a second or support material, frequently aluminum oxide or silica, which has the high surface area and strength necessary for the severe conditions in a chemical reactor. Virtually all catalyst systems used in industry also employ additional components which, by themselves, play no catalytic role but confer on the catalytic system considerable advantages of activity, selectivity, or stability. These "promoter" substances are of crucial importance and their almost universal use in industrial catalysis is a feature virtually ignored and little studied in surface chemistry and physics.

In all catalytic processes, the catalyst is subject to changes of its activity which may take the form of a change in the specificity of the reaction. As a rule, the activity of a catalyst

decreases during its use. Sometimes the rate of decrease is very large, even on the order of seconds. In other cases it may be so slow as to require regeneration, reactivation, or replacement of the catalyst only after years of use.

If the deactivation is rapid and is caused by deposition and a physical blocking of the surface, the process is usually called fouling. Removal of the solid is termed regeneration. There is little detailed knowledge on the mechanisms of deposition from the materials science point of view. In coal liquefaction, catalyst deactivation proceeds rapidly by carbon and mineral fouling.

In a second type of deactivation the catalyst surface is altered by chemisorption of materials on active sites which are not readily removed. This is called poisoning of the catalyst. Here the metal or compound on the surface reacts with some material in the fluid phase to form a new surface compound which is not catalytically active for the desired reaction. Since the thermodynamics of surface phases remain unknown for almost all materials, the occurrence of poisoning is currently extremely difficult to predict.

A third type of deactivation is sintering, either the loss of surface area of the catalytically active material or a decrease of porosity of the solid. For many reactions, especially those which are conducted at high temperatures, sintering results both in a decrease of active area and in a change of surface structure.

B. Energy and Catalysis[1]

Various sources of fuel are being considered for the future energy flow in the United States; petrochemical, uranium, natural gas, coal, shale, waste, solar, geothermal, and hydrogen. Applications of catalysis are being contemplated for virtually all of these. The general advantage of catalysis is the possibility of achieving a higher efficiency of energy utilization, obtaining interconversions under milder conditions than would otherwise be possible and to decrease the waste products by conversion of the waste heat and by-products into usable energy and/or usable by-products.

Since the world's chief energy source is oil and oil distillates, the other forms of energy must be converted to petroleum products to be usable in the present economy. The conversion of one chemical energy source to another chemical energy source involves irreversible energy loss in the conversion process. Catalysis is being utilized to minimize this loss. In fact, as long as chemical energy is part of this nation's energy demand, catalysis will be employed to provide for the nation's energy needs.

C. Early Contributions to the Study of Heterogeneous Catalysis[3]

Early studies of heterogeneous catalysis were mostly cataloging and mechanistic studies. A standard set of reactants were introduced to a catalyst and the distribution of products was cataloged and then mechanisms were proposed to account for the product distribution.

The process was then repeated with a new catalyst or by changing a promoter or by changing the catalyst support material.[4] Once interest changed from the macro scale of catalysis to the atomic scale of catalysis, a good deal of information emerged from simple thermodynamic measurements. From adsorption isotherms it was possible to extract information relating to: (1) the energetic uniformity of the surface; (2) distinguishing between localized adsorption and surface mobile adsorbates; and (3) coverage induced effects. Heats of adsorption ΔH_a, measured either by direct calorimetric methods or from the temperature dependence of adsorption isotherms, revealed that ΔH_a changed, sometimes dramatically, upon increasing surface coverage. The time of adsorption, which signifies the length of time for which an adsorbed species was retained on the surface, could therefore vary from several millenia for a very small coverage to a value of less than a microsecond at monolayer coverage. The actual magnitude of ΔH_a, once experimentally determined, can reveal much about the nature of the bond associated with the chemisorbed entity.

From some heats of adsorption work in 1935 came the beginning of the technique of desorption spectroscopy. This technique measures the intensity of desorption as a function of temperature from a gradually heated adsorbent-adsorbate system. Desorption spectra were of particular value in demonstrating that adsorbates may exist on a surface as two or more distinct adsorbed species and that preferential bonding of adsorbates to surface sites takes place.

Kinetic studies offered some insights into the dynamic nature of the surface. Measurements of kinetic order and activation energies offered more tools for the formulation of reaction mechanisms. Orders of reaction revealed whether the surface in question was sparsely or fully covered with reactant.

Work function measurements generally utilized the Helmholz equation:

$$\Delta\phi = 4\pi n_s \mu\theta \qquad (1)$$

where n_s is the number of sites per unit area, μ is the dipole moment, and θ is the fraction of the surface covered. An increase in ϕ indicated a donation of electrons from the solid to the adsorbed species. Such measurements, taken alone, are insufficient to indicate where exactly the bonding takes place at the surface; it must be emphasized the $\Delta\phi$ reflects the net flow of charge to or from the surface.

Infrared absorption, like most photon based spectroscopic measurements of the adsorbed phase, relies on the fact that the chemically significant linkage is spectroscopically active. Moreover, it is important to bear in mind that as extinction coefficients do not vary much from one surface bond to the next, the species which is most tenaciously bound to the surface is that which tends to dominate in the resulting spectrum.

In general, infrared studies of the adsorbed state detect the characteristics of bonds other than those which anchor the adsorbate

to the surface. Some examples of information extracted from infrared studies are:

1. Carbon monoxide may be bound in linear or bridged forms on metal surfaces;
2. When benzene is adsorbed it frequently loses its aromatic character; and
3. H_2 may be dissociatively adsorbed on metal surfaces.

Other spectroscopic techniques, especially the visible and ultraviolet varieties, have yielded helpful information about: (1) changes within $\eta \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions within adsorbed molecules; (2) charge-transfer spectra and the occurrence of carbocations, carboanions, and neutral diradicals; and (3) d-d transitions which serve to elucidate the nature of the site symmetry of transition metal dopants. Electron spin resonance (ESR) measurements are feasible when both the adsorbate and surface contained unpaired electrons after dynamic electron transfer had come to equilibrium. Nuclear magnetic resonance has found very limited application to date in the study of solid surfaces.

Isotope exchange experiments (analyzed by mass spectrometry) and radioisotopic methods contributed much to the understanding of: (1) the lability of adsorbates at metal surfaces; (2) the role of catalyst support material; (3) complex intermediates on surfaces; and (4) pathways of selectivity in a catalyst system which included promoters and support materials.

D. Recent Contributions to the Study of Heterogeneous Catalysis[5]

With the advent of ultra-high vacuum systems, a vast number of new methods have been applied to the study of heterogeneous catalysis. In many of these new methods high vacuums (10^{-7} to 10^{-2} Pa) must be maintained around the samples during some phase of the surface chemical experiment. A high vacuum of better than 10^{-7} Pa is needed to achieve a surface that is free from adsorbed gases. Also, many of the surface characterization techniques use electrons or ions as probing particles to reveal the surface structure, composition, and oxidation state. These particles need a long mean free path to be able to strike or exit the sample and then reach the detector without colliding with gas phase molecules. For this reason, pressures must be lower than 10^{-1} Pa.

One of the main advantages of the new methods is the overcoming of the difficulty of detecting a small number of surface atoms in the presence of a large number of bulk atoms (a typical solid surface has 10^{15} atoms/cm^2 as compared with 10^{23} atoms/cm^3 in the bulk). In order to be able to probe the properties of solid surfaces using conventional methods, powders with very high surface-to-volume ratios had to be used so that surface effects become dominant and therefore measurable. It turns out that electrons with energies in the range of 10 to 1000 eV are ideally suited for studying surfaces and are practically independent of the surface to volume ratio. This comes about since the mean free path of electrons in the region of 10 to 1000 eV is only 4 to 20 Å. Thus electron emission from solids with energies in this

range must originate from the top few atomic layers. By extension, all experimental techniques involving the incidence onto and/or emergence from surfaces by electrons having energies between 10 and 1000 eV are thus surface sensitive.

These new electron methods can be broken into sets corresponding to the manner in which the electron interacts with the adsorbates and surface atoms. Low Energy Electron Diffraction (LEED) elastically scatters electrons off of a surface to give a crystallographic picture of the surface. Inelastically scattered electrons also provide surface-structural information in a method called High-Resolutions Electron Energy Loss Spectroscopy (HREELS). Auger electrons can be produced either by electron impact or photon absorption. Auger Electron Spectroscopy (AES) can be used to study the chemical composition of the adsorbate covered surface. Impinging photons, ions, or atoms can cause electrons to leave the surface in ways characteristic of the surface structure, thus photoemission, Ion Neutralization Spectroscopy (INS), Surface Penning Ionization (SPI), and many other techniques have been applied in surface analysis. Low-energy atomic and ionic scattering of surfaces are uniquely surface-sensitive processes in which the scattered particles only come into contact with the outermost surface atoms. Light reflection can also be turned into a surface-sensitive tool as in Infrared Spectroscopy (IR). It must be emphasized that all the surface analysis techniques have particular limitations. Thus some are more sensitive to chemical composition, others to relative atomic positions, others still to vibrational modes, and some

to electronic structure. Thus one study may entail many complementary techniques.

A number of methods have been developed to study the atomic geometry of a surface. Three of these methods involve electron diffraction from ordered surface atoms [Low Energy (LEED), Medium Energy (MEED), and High Energy (RHEED) Electron Diffraction]. Electron microscopy also involves the scattering of electrons by atom cores of the surface (Scanning Electron Microscopy SEM) or by the surface and bulk in thin samples (Transmission Electron Microscopy TEM). The detection of secondary electron emissions from surfaces due to electron bombardment also gives rise to another method called Scanning Auger Microscopy (SAM). The next four methods are analogous to the above methods except that ions are used as the scattering particles instead of electrons [Low Energy (LEIS), Medium Energy (MEIS), High Energy (HEIS) Ion Scattering, and Field Ion Microscopy (FIM)]. A method called Atomic Diffraction, also analogous to the electron diffraction method, uses neutral atoms with thermal energies to diffract from surfaces. The final method to study atomic geometry is Surface Extended X-ray Absorption Fine Structure (SEXAFS). In this technique, X-ray induced Auger transitions occur and the electron patterns are analyzed as in all of the above techniques.

Three new methods have been used to study the chemical composition at surfaces. Auger Electron Spectroscopy (AES) studies surfaces by inducement of the emission of Auger electrons from all species at the surface. Ion-Scattering Spectroscopy (ISS) studies the masses of the

particles at the surface through collisional energy losses. Secondary Ion Mass Spectrometry (SIMS) analyzes the mass and angular distribution of clusters of atoms ejected during ion bombardment of the surface. Once the upper surface layer has been removed, exposing a new surface layer, this layer can then be studied, thus giving a depth profile of the catalyst surface.

Methods that have been used to study the electronic structure and geometry of surfaces include Ultraviolet Photoelectron Spectroscopy (UPS), X-ray Photoelectron Spectroscopy (XPS), and Angle Resolved Ultraviolet Photoelectron Spectroscopy (ARUPS). All of these methods use photon induced emission of electrons for structural analysis. Photon induced emission of electrons is sensitive to the initial density of states of the emitted electrons and therefore is sensitive to the surface geometry. Angular resolution of the emitted electrons gives additional information about the orbital shape and bonding symmetry. All of these techniques study the energies of the electrons contained in occupied orbitals. In this is the main distinction of the techniques. UPS and ARUPS study only the valence orbitals while XPS studies both core and valence orbitals. At the present, UPS has a factor of ten better resolution than XPS. Since each atom can be identified by its unique core spectrum, XPS can be used as a technique for chemical identification. A useful technique also available from core electron studies, is the shift of core level energies with change in atomic environment. These shifts are referred to as chemical shifts. UPS and XPS can give qualitative results

about the orientation of adsorbate, stabilities of adsorbate on a surface, surface penetration of adsorbates, etc., without the need of extensive theoretical calculations.[5] The interpretation of ARUPS relies heavily on model calculations. Thus these techniques are limited in their scope at this time until better model and cluster calculations can be made.

The remaining methods to be discussed do not use photon induced emission. Ion Neutralization Spectroscopy (INS) causes electron emission by imparting energy to the surface as the ions are neutralized by the outermost layer of the surface. Surface Penning Ionization (SPI) causes electron emission of the excited electrons in thermalized metastable helium atoms due to electron-electron interactions rather than the dipolar photon-electron interaction of UPS and XPS; though the techniques yield similar electronic structure information.

E. Objectives of the Present Investigation

The main objective of this study was to investigate the effect of a copper single crystal on the molecular orbitals of mono-heteroatom sulfur heterocyclic adsorbates by comparison of the ultraviolet photoelectron spectra of the adsorbates to the corresponding gas phase photoelectron spectra. X-ray photoelectron spectra were also measured for the extraction of chemical composition information as well as surface coverage information. Angle Resolved Photoelectron spectra were measured to ascertain the orientability of the adsorbates. Particular objectives of the investigation were: (1) to determine if

adsorption of the adsorbates on copper single crystals takes place, (2) to determine if associative or dissociative adsorption takes place; (3) to determine the type of copper to adsorbate bond formed, (4) to determine the orientability of the adsorbates on copper, (5) to determine if changes in ring strain occur upon adsorption, (6) to determine the effects of ring size on the adsorbate to copper bond, (7) to determine the effects of ring size on surface coverage.

F. Choice of Copper As the Surface To Be Studied

With the advent of synchrotron radiation and angle resolved photoelectron spectroscopy, solid state theory has taken a quantum jump in its ability to predict photoelectron solid state band structure. Copper has been the subject of numerous angle resolved photoelectron spectroscopy studies because of its accurately known band structure and therefore it has served as a model system for the theoretical interpretation of the details of the photoemission process. As of late, a tremendous volume of papers on angle resolved photoelectron spectroscopic studies of different faces of copper single crystals can be found in the literature. Some of these papers starting in 1978 are listed in the List of References.[6-17] This large volume of literature on copper insures a well characterized system on which to build a model of molecular adsorption.

There are many other benefits for using copper as the surface to be studied. One of the most important is surface cleanliness. The main contaminants found in an ultra-high vacuum chamber are H_2, CO, and

H_2O. Somorjai and Van Hove[5] list a series of adsorbates which have been studied on various transition metal single crystals. One of the results listed is the fact that H_2 does not adsorb on copper. Likewise, Küppers et al.[18] point out that at room temperature, carbon monoxide will not contaminate copper either. Unfortunately, Somorjai and Van Hove[5] as well as Sharma[19] agree that water does adsorb on copper. Sharma also points out that clean copper adsorbs water at a much slower rate than a dirty surface. The water contamination problem can be minimized by having a system which can be heated to 200° C and pumped for 72 hours to decrease the water in the vacuum system to below measurable limits. Thus, with the water minimized, the crystal spectra will show no trace of contamination for up to three hours at 1×10^{-7} Pa.

Another benefit of using copper single crystals is the fact that copper doesn't form bonds to π systems[20] such as benzene and ethylene. Thus the bonding mechanisms are simplified and the possibility of side reactions are reduced because the dehydrogenation products and decomposition products are unstable on the surface.

G. Advantages of a Single Crystal

The main advantage of using a single crystal is that the exact number of surface atoms can be calculated from crystallographic data and density data.

As Edmonds and McCarroll[2] have pointed out, real industrial catalysts are not a single component system. The metal is usually dispersed finely over a high surface area refractory support to which

is added one or more substances called promoters. This highly complex system must be reduced to its essential elements and studied, according to John T. Yates,[21] for simplification of experimental systems is a common theme in the history of science and the insights obtained from surface studies on model systems are conceptually transferable to catalytic science. Somorjai[22] goes beyond this to show that reactions on single crystals are equivalent to reactions on highly dispersed catalysts. He points out that reactions which took place on single crystals gave the same products and the same product distribution as those on highly dispersed catalysts. He also points out that the rate of reaction per surface site is the same for single crystals as for high surface area catalysts. Thus single crystal studies can be directly applied to catalytic problems. Since this is true, Somorjai states that fundamental studies of catalyst promoters and catalyst poisons on single crystals have the highest priority at the present time.

Another advantage of using single crystals is the fact that single crystals undergo much less roughening than polycrystalline surfaces upon ion bombardment.[23] Novinšek[24] summarized the processes which can take place upon ion bombardment depending on the acceleration voltage used. The processes (1) ion erosion, (2) growth of surface structure, (3) development of grain boundaries, (4) development of etch pits, (5) development of steps and furrows, (6) appearance of cellular structure, (7) faceting, (8) ion polishing, (9) pillar structure, (10) blistering, (11) induced amorphization or recrystallization, (12) formation of cones, (13) redeposition of sputtered material, and

(14) induced chemical changes, have been found by Naundorf and Macht[23] not to be evident in ion bombardment studies of copper single crystals. The authors only found shallow pits with argon, oxygen and nitrogen ion bombardment studies at 4 Kev accelerating potentials. Thus single crystals can be sputtered clean with almost no surface damage and then annealed to achieve a smooth, well ordered surface again.

The techniques and methods of extracting catalytic information from single crystal-adsorbate systems have been worked out in past studies. Somorjai and Van Hove[5] review the area of adsorbed species on single crystals, while Madix and Benziger[25] review kinetic reactions on single crystals. These authors list over 100 papers on single crystal studies, some of which contain studies on copper single crystals. This gives a basis for comparison of future studies to not only fundamental, but also applied catalysis studies.

H. Choice of Adsorbates

Somorjai[22] stated that the two most important areas in catalysis at the present time were promoters and catalyst poisons. Since promoters are usually a small percent metal alloy, the study of surface adsorbed molecules does not fit into the study of catalyst promoters. But many catalyst poisons are surface adsorbed atoms and/or molecules and thus can be studied not only to extract catalyst poison information, but also to extract adsorbate-surface chemical bonding information. Therefore, catalyst poisons were selected for this study.

Catalyst poisons can be broken down into three major sets of poisons: (1) nitrogen compounds, (2) sulfur compounds, and (3) heavy metals. Heavy metals would have been the hardest poisons to study because they are usually introduced to the catalyst as porphorins or with other complex ligand structures. At the operating conditions of temperatures higher than 500° C and high H_2 pressure, as are encountered in chemical reactors, the metals are usually reduced to the zero valence state and plate out onto the catalyst, thus contaminating the surface and/or covering reaction sites. The problem then becomes similar to promoters where in this case the new alloy may be thought of as an anti-promoter which promotes unwanted side reactions. But at room temperature and ultra-high vacuum pressures, the metals would not lose their complex ligand structure and may not be reduced upon coming in contact with the catalyst surface. These types of adsorbates could be studied but would be hard to obtain and/or purchase and may not have high enough vapor pressures to be usable in our gas delivery system—so were eliminated from consideration.

To simplify the study of the bonding of poisons to surfaces, adsorbates which would form only lone-pair bonds to the surface[26] were considered. This eliminated all aromatic and unsaturated adsorbates. The rest of the adsorbates were eliminated except the sulfur heterocycles by specifying that the adsorbates which are the most stable on copper will be studied. Thermodynamic and adsorption studies[27-29] have shown that heterocyclic compounds are the least reactive poisons and therefore would not decompose as readily upon interaction with copper.

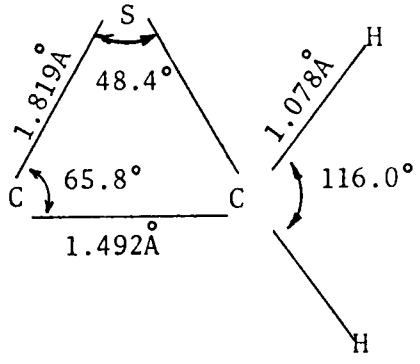
Two studies in 1967[30-31] have shown that sulfur heterocycles are less prone to ring cleavage than either oxygen or nitrogen heterocycles. Thus sulfur heterocycles should not decompose upon adsorption onto copper and thus information concerning the bonding of adsorbate to surface bonds should be obtainable as well as information as to the bonding of these known catalyst poisons. Drago et al.[32] in an attempt to correlate the Lewis basicity of lone pair donors to their heats of dative bond formation also have shown that complex coordinated heavy metal poisons form lone pair to surface bonds, thus revealing the need for further understanding of this bonding process.

One added advantage of studying heterocycles would be the stability of strained ring[30] adsorbates upon adsorption onto copper. Thus a study of ring systems with 3, 4, 5, and 6 members might give information as to which orbitals are affected the most upon bonding and thus provide a means to suggest a mechanism for decomposition, if the strained rings do decompose upon adsorption.

I. Introduction to the Adsorbates

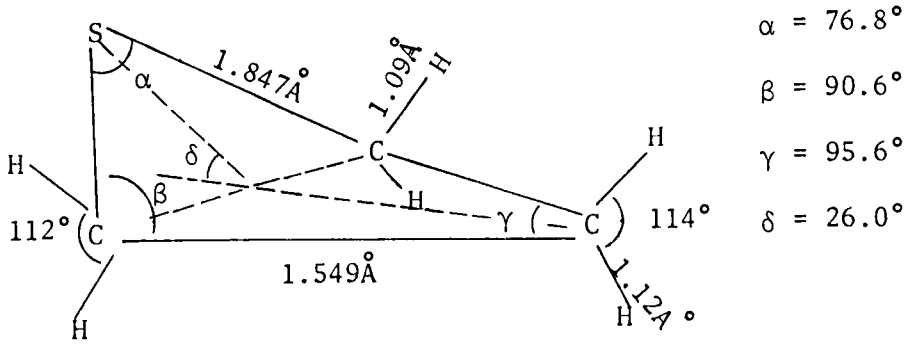
To introduce the reader to the actual molecular geometry of the adsorbates and their ring strain energies, the following section will be presented.

Thiacyclopropane is a three member ring sulfur heterocycle. The triangular shape necessitates a C_{2v} symmetry. The structure of thiacyclopropane[33-34] reveals a carbon-sulfur-carbon bond angle of



48.4°, as compared to the hydrogen-sulfur-hydrogen bond angle for hydrogen sulfide of 92.1°, and a sulfur-carbon-carbon bond angle of 65.8° as compared to a tetrahedral angle of 109.5°. Strain energy is not just composed of angle strain but is a balance of angle strain, lone-pair repulsion, hydrogen-hydrogen crowding, bond stretching, and atom size, among others. Stille and Empen[30] list the strain energy for the three member ring at 19.78 Kcal/mole, much less than the corresponding oxide or nitride rings (27.21 and 26.87 Kcal/mole respectively). The authors suggest the long sulfur to carbon bonds as the major factor for the lower ring strain. (C - O = 1.43Å, C - N = 1.47Å, C - S = 1.81Å).

Thiacyclobutane is a four member ring sulfur heterocycle. The structure of thiacyclobutane[35-37] resembles two triangles joined at the base and having a dihedral angle of ∿26°. The puckered structure causes it to have C_s symmetry. Even though the C-S-C angle of the four member ring is not as strained as the three member ring (76.8° as compared to 48.4°) and even though the S-C-C and C-C-C angles are not as strained as the S-C-C angle in the three member ring

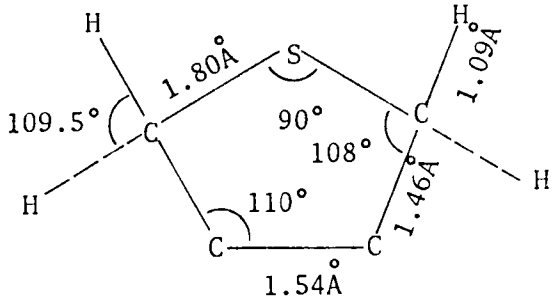


(90.6° and 95.6° as compared to 65.8°), the ring strain energies are almost identical according to Stille and Empen[30] (19.64 Kcal/mole—four member ring, 19.78 Kcal/mole—three member ring). Pasternak and Meyer[38] suggest that the amount of ring puckering reflects the balance between ring angle strain, which tends to keep the ring planar, and hydrogen-hydrogen interactions which drive the methylene groups into a staggered configuration. The authors also point out that the dihedral angle can be as large as 40° depending on the excited vibrational energy possessed.

Since the molecule is not planar, a double minimum vibrational bending potential function exists between the two possible configurations (i.e., sulfur-up or sulfur-down configurations).[39-40] Gilson et al.[39] point out that since the barrier height for interconversion is only 0.8 Kcal/mole, the puckering motion should be taking place at room temperature. In fact the authors presented evidence that the puckering motion takes place above 170 K at which time the heterocycle is still in the solid state. However, there is evidence that some substituted thiacyclobutanes do not undergo interconversion at room temperature.[41]

It is interesting to note that some vibrational states[39] and some electronic states,[42] if populated, cause the molecule to become planar.

Thiacyclopentane is a five member ring sulfur heterocycle. The actual structure was long thought to be planar, but was later found to have a very slight distortion to the molecule which is best described as C_2 symmetry.[43] This can be described best by pointing out that if one of the carbons adjacent to the sulfur is slightly depressed, the other adjacent carbon will be slightly elevated and so forth. The C_2 axis then goes through the sulfur and bisects the bond between the carbons farthest from the sulfur.



The bond lengths and angles for the five member ring as presented by Maggiora[44] are also presented here. The strain energy for the five member ring is almost nonexistent at 1.97 Kcal/mole.[30] Thus there is almost no gain in energy upon ring cleavage, which would suggest a relatively stable adsorbate.

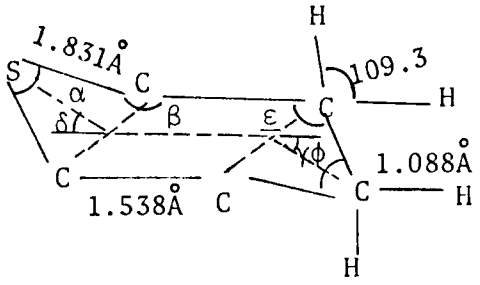
Thiacyclohexane is a six member ring sulfur heterocycle. The structure is very similar to the chair structure of cyclohexane.[45]

Since the dihedral angles are not both 60°, the symmetry of thiacyclohexane is reduced to C_s. The displayed bond lengths and angles come from Kitchin et al.[46] who studied the microwave spectrum of thiacyclohexane.

$\alpha = 96.6°$ $\delta = 52.6°$

$\beta = 110.7°$ $\phi = 110.7°$

$\gamma = 58.2°$ $\varepsilon = 110.7°$



A study by Harris and Spragg[47] suggests that vibrational bending motions also affect the six member ring. The suggested transition state for the bending modes is the half chair configuration. Stille and Empen[30] list the strain energy for the six member ring as -0.27 Kcal/mole. This would suggest that ring cleavage can take place only if energy is supplied in the reaction.

J. Gas Phase Photoelectron Spectra

There are three distinct advantages of having literature gas phase spectra available. First, one can check the purity of the adsorbate gas by comparison of the measured gas phase spectra to the literature gas phase spectra. If they match without extra peaks, the purity of the vapor is assured. Likewise, a decomposition check can be made by comparing the measured spectrum to the spectra of possible decomposition products. The second advantage of having the

literature gas phase spectra is comparison of spectral features and orbital assignments among a set of similar adsorbates. The particular similarity of the adsorbates in this study are the sharp, low binding energy peaks assigned to nonbonding orbitals. Also the valence spectra become more complex going from three to six member ring heterocycles. Orbital assignments in the literature also can give information on types of bonding possible and actual symmetry of the gas phase molecules. The third advantage of having literature gas phase photoelectron spectra deals with changes in the spectra upon adsorption of the gas molecule onto a surface. The molecular orbitals which enter into the adsorbate to surface bond should show a marked stabilization upon bonding, the amount of relaxation of the adsorbate levels can be related to the strength of surface bond, and symmetry changes of the adsorbate upon adsorption can be followed by calculating possible molecular changes and comparing the results to the spectra obtained to try to reassign the molecular orbitals of the surface adsorbed gas molecules.

Schweig and Thiel,[48] who have presented gas phase results for thiacyclopropane, used He I, He II photoelectron spectra as well as molecular orbital calculations to assign the orbitals to the three member ring assuming C_{2v} symmetry. Mollere and Houk[49] present gas phase results for thiacyclobutane. He I and molecular orbital calculations were used to assign the molecular orbitals of the four member ring assuming C_s symmetry. Pignataro and Distefano[50] present He I gas phase results to which they assigned some of the outermost valence orbitals for

thiacyclopentane. The authors assumed a symmetry of C_{2v}. Schmidt and Schweig[51] also present He I gas phase results for thiacyclopentane. Planckaert et al.[52] as well as Sweigart and Turner[53] present He I gas phase photoelectron spectra for thiacyclohexane. Neither group attempted to assign the molecular orbitals but Planckaert et al.[52] also presented ultraviolet absorption results for the six member ring.

K. Photoelectron Spectroscopy of Surface Adsorbed Molecules

The use of photoelectron spectroscopy for the study of surface adsorption and surface reactions has become widespread. A significant amount of work has been done on simple molecules as adsorbates and recently complex adsorbates have been studied.[5,25,54-65] Also a large volume of data has been collected for sulfur containing molecules,[66,67] but almost none on surface adsorbed complex sulfur containing molecules.

To fully apply photoelectron spectroscopy to surface chemistry problems, knowledge is needed not only of the surface and adsorbates but also of the theory and chemistry of solid state interactions. Also a convergence of the theoretical models and the empirical models is needed to find the nature of surface-adsorbate interactions and thus relate them to the study of catalyst poisons. With this in mind, a brief description of the solid state chemistry involved in surface-adsorbate interactions, which when followed by descriptions of the means of extracting chemical bonding information as well as surface

coverage information from photoelectron spectra, would introduce the reader to many complexities of surface photoelectron spectroscopy.

1. Solid State Chemistry of Surface-Adsorbate Interactions

The text, "Chemistry of Catalytic Processes,"[68] presents an excellent short review of solid state chemistry. Sections of the text will be incorporated into the discussion of surface chemistry which follows.

An understanding of the catalytic properties of metal surfaces requires first an understanding of the bulk properties of metals and second the properties of metal surfaces. Surface atoms differ from bulk atoms because their environment is intermediate between those of free and bulk atoms. A surface atom has fewer nearest neighbors than a bulk atom but more than a free atom, and so it should have different electronic properties and different interactions with adsorbates.

Though bonding in organic compounds can be accounted for quantitatively using only four atomic orbitals, one s and three p orbitals, the transition metals use nine atomic orbitals in bonding and in the metallic form can have a mole of electron levels which are closely spaced which form bands of possible filled and unfilled states. This band theory has been successfully used to explain many of the important bulk properties of metals. In band theory all of the s, p, and d orbitals have energies which fall within definite respective ranges and these energy ranges only span a few electron volts. Each orbital has its own energy level within this range and if there are a

mole of orbitals within the range, the energy levels are so close together that they form an almost continuous band. In band theory the Fermi level is defined as the highest occupied molecular orbital. Also according to the theory, all electrons are completely delocalized over the crystal. Looking at the bands individually, the s band is usually quite broad, ∿20 eV. The p band and d band are typically narrower, ∿4 eV. The appreciable width of the s band means that it frequently overlaps the d band. But there are five moles of d electrons to one mole of s electrons in a filled shell picture so that the d signal usually swamps the s orbital signal. Also, the one mole of s electron levels are spread over 20 eV as compared to the 4 eV for d levels, which broadens the s signal. There also is a periodic change in orbitals across the transition metals. At the extreme left of the transition metals, the s band is the lowest of the s, p or d bands and the d band is the highest; at the extreme right, the d band is lowest and is overlapped by the s band, and the p band is highest. In the case of copper, the d band is completely filled, and the highest occupied energy levels are of the s type. Also it is usually assumed that when a band such as the d band is completely filled, it can no longer contribute to bonding.

According to band theory, the surface of a metal has a slight positive charge because surface localized orbitals have less stability as compared to bulk orbitals and thus may be only partially filled, leaving unfilled, electron seeking orbitals on the surface. Thus metals with a large amount of unfilled surface levels will be more

reactive than a surface in which all surface levels have been filled. The strength of interactions of an unoccupied surface orbital with a filled nonbonding molecular orbital of an approaching adsorbate depends on the relative energetical positions of the surface orbital as compared to the filled adsorbate orbital as well as the degree of molecular orbital overlap of the orbitals. Also a number of more complex effects can enter into the bonding picture at high coverages. Normal chemisorption results in a significant decrease in the binding strength of surface metal atoms to the bulk metal atoms, thus the surface metal atoms are perturbed from their normal lattice position. If strong adsorbate-adsorbate interactions are present, a complete rearrangement of the surface lattice (corrosive chemisorption) can take place to accomodate a surface-compound formation. Chemisorption can also bring about a reduction in the contribution of the surface-metal-atom electrons to the band structure of the bulk metal, that is, a partial localization of the delocalized metal electrons into surface metal bonding orbitals. The strength of the bond between the adsorbate and surface atoms probably determines the extent of localization of delocalized electrons onto the surface metal atoms. Cluster calculations for Cu_8 clusters seem to suggest that surface bonding in copper is through the unfilled s band orbitals. These calculations also suggest that the 3d electrons as well as bulk conduction electrons take part in the chemisorptive bonds to some extent. The calculations also showed that the stability of adsorption decreases in the order of crystal planes (110) > (100) > (111) and that chemisorption site stabilities decrease from top > bridge > centered.

This discussion of possible effects of the adsorbate on surface orbitals and surface geometry points out the necessity of knowing where the adsorbed molecules are located at a metal surface as well as knowing the coverage and geometry of the adsorbate while on the surface. This knowledge can be used to shed light on such topics as surface-compound formation and localization of electrons onto surface metal atoms. Also the discussion points out the need of using single crystals to insure a well characterized initial system. Finally the discussion points out the need for theoretical calculations to help suggest a description of bond formation, bond strength, and to give a knowledge of the molecular orbitals involved in the bonding at the surface.

2. Photoelectron Spectroscopy Applied to Adsorbate Surface System

Eland[69] elegantly stated the importance of U.V. photoelectron spectroscopy to the study of adsorbates. He wrote, "It has become evident that molecular photoelectron bands can be recognized in adsorbates and that changes in adsorbate bands due to bonding are also detectable." He goes on to point out that angular distribution studies of photoelectrons can be used to determine the surface orientation of adsorbates. This suggests that surface induced changes in the adsorbate spectra can be measured as well as the effects of surface bonding on the adsorbate spectra. Brucker and Rhodin[54] suggest that the changes in the adsorbate bands upon adsorption can be related to the type of bonding to the surface. Thus a small change in orbitals indicates physical adsorption where a dramatic change in orbital

energies suggests either decomposition or strong chemisorption. The authors also pointed out that relaxation changes are more sensitive to the type of bond and can also be related to the type of surface bond formed. Bradshaw and Menzel[70] relate the means of studying these changes in relaxation and adsorbate energy levels; construction of a gas phase-adsorbed phase correlation diagram which shows the relative orbital shifts as well as the energy scale shifts.

The work function (ϕ) of a surface is defined by Broughton and Perry[71] as the energy required to remove an electron from the Fermi level to a distance outside the surface where chemical interaction with the solid has been reduced to approximately zero ($\sim\mu m$). The work function is not only a function of the bulk metal but also of the structure and composition of the exposed surface. The work function is also dependent upon the amount and nature of the adsorbate present at the surface, since adsorption generally results in some charge transfer between metal and adsorbate and therefore modifies the surface charge.

Spicer et al.[72] point out in the three step model that the change in the work function can be measured by UPS as a gain or loss of secondary electrons at the zero kinetic energy side of the spectrum. Thus adsorbate induced changes in the surface work function can be measured. The change in work function is measured relative to the Fermi level of the metal.

Angle Resolved Ultraviolet Photoelectron Spectroscopy can be applied in two different ways.[73] By fixing the photon source and surface and by varying the detector angle, the angular data obtained

can give information on the specific ordering of the molecular orbitals of the adsorbate. But the angular variations of these orbitals must first be found from theoretical calculations or empirical data, in order to correlate the observed spectra to the proposed angular variations of typical orbitals. By fixing the photon source and the detector and varying the crystal surface normal, an azimuthal angular variation can be found which can be related to the randomness of the orientation of the adsorbates on the surface. Thus orbital and orientation information can be obtained from angular resolved ultraviolet photoelectron data.

Surface coverage can be quantitatively studied, according to Ertl,[74] by XPS. The intensity of a core-electron XPS peak is proportional to the surface concentration of the corresponding element. Quantitative analysis of the elements which make up the adsorbate can be made on a surface from the relation

$$N_a = \frac{I_a}{I_s} \frac{A\sigma_s D\lambda\cos\theta}{\sigma_a M_a}$$

where N_a = number of atoms of an element per cm^2, σ_s, σ_a = surface and elemental photoelectron cross sections, I_s, I_a = measured photoelectron intensities of the clean surface and of the element, D = density of surface, θ = angle of incident X-rays, A = Avogadro's number, M_a = atomic weight of adsorbent component, λ = mean free path of an electron in the solid. Thus from ratios of elements found, an empirical formula can be calculated for the adsorbate from the XPS

elemental analysis results and compared to the empirical formula for the actual adsorbate. Also by comparing the number of adsorbed molecules to the number of surface atoms of the solid a percent coverage can be found. The number of surface atoms can be calculated for a single crystal, but must be measured experimentally for polycrystalline solids. XPS can measure surface coverages as low as 2% coverage.[75] In the case of S atoms adsorbed on copper, large sulfur coverages seem to distort the surface atoms (corrosive chemisorption) and also cause a loss of delocalization of electrons on surface metal atoms.[75] In this case, XPS could also be used to study core electron energy shifts for the surface metal atoms as compared to the bulk metal atoms.

This section then shows that UPS can be used to study the effect of surface bonding on the adsorbates and at large coverages, adsorbate effects on surfaces. ARUPS can be used to study the orientation of the adsorbates on the surface. And XPS can be used to study the empirical formula and amount of coverage of the adsorbate as well as any adsorbate induced changes in the surface metal atoms by core level shift studies.

CHAPTER II

EXPERIMENTAL

A. Adsorbates

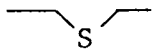
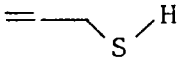
All chemicals used as adsorbates in this study were purchased from the Aldrich Chemical Company. The chemicals were used without further purification; although further purification may have come about by means of the vacuum vaporization process used to obtain the adsorbate molecules in the gaseous state. This process will be explained in the next section.

Table 1 contains the Aldrich names of the adsorbate molecules, their structural formulae, their percent purity, their experimental boiling point ranges, the literature values given for the boiling points of the pure adsorbates, as well as the types of analyses done to verify the composition of the adsorbate gases after expansion into the gas manifold.

B. Vaporization, Purification and Purity Analysis of Adsorbates

Before the adsorbates can be introduced into the analyzing chamber, they must be converted to the gaseous state by vacuum vaporization after the air and impurities are removed. To extract any air which had dissolved in the adsorbate and had been introduced into the gas system, a cycle of freezing the adsorbate, evacuating the manifold, and expanding the sample into the manifold during the warming phase

Table 1. Adsorbate Molecules

Compound Name[a]	Structural Formula	Purity[a] (%)	Boiling Point Range		Analysis[c] Type
			Experimental[a] (°C)	Literature[b] (°C)	
Ethylene sulfide		N.A.	55-56	55-56	1
Trimethylene sulfide		97	94-94.5	94.67	1,2
Tetrahydrothiophene		93+	119	121.12	1,2
Thiophene		99+	84	84.16	1
Pentamethylene sulfide		N.A.	140-142	141.75	1,2
Ethyl sulfide		98	90-92	92.10	1
Allyl mercaptan		70+	67-68	67-68	1

[a]Taken from the 1978-1979 Aldrich Chemical Company Catalog.

[b]Handbook of Chemistry and Physics, R. C. Weast, Editor, 52nd Edition, 1971-1972, Chemical Rubber Company, Cleveland, Ohio 44128.

[c]Analysis type (1) quadrupole mass spectrometry; (2) nuclear magnetic resonance.

N.A. Purity must be inferred from the boiling point range.

+ Indicates a percent purity greater than or equal to the stated percent.

was repeated until the adsorbate ceased to bubble during the warming phase. This process called freeze pumping insured that most of the air had been purged from the adsorbate and vacuum system. The second step to insure purity was to condense the first vapor fractions from the adsorbate onto a liquid nitrogen cooled cold finger. This insured that all of the remaining O_2 was removed from the system and also that any low boiling impurities were also removed at this time.

To analytically check the purity of the adsorbate vapor at this stage after purification, some of the adsorbate vapor was collected in a liquid nitrogen cooled cold finger and then removed from the vacuum system. The aliquot was then brought to ambient temperature and transferred to a 5mm NMR tube for proton NMR analysis. The proton NMR showed that within the experimental error of the equipment, no impurities could be found following these purification steps for the adsorbates tested.

During the initial studies of the adsorbate vapors, the adsorbate molecules were allowed to leak into the source volume at a constant rate. The rate chosen optimized the analysis of the vapor by Quadrupole Mass Spectrometry and also approximated the normal rate of exposure used in a typical experimental run ($\sim$20 L). A close comparison of the mass spectra with the literature spectra[76] showed no abnormal signals or intensities due to significant amounts of impurities.

When purifying thiacyclopropane an extra purification step was added since the technical grade liquid had a significant amount of the

disulfide present, enough to cause the liquid to have a cloudy color. The extra step was added after purging the system of air. One-third of the sample was allowed to vaporize and condense into a liquid nitrogen cooled glass finger. This one-third was then used as the source of the adsorbate vapor. This is a form of vacuum distillation.

C. Adsorbate Preparation

The gas manifold was initially heated with resistance heating tape while the manifold was evacuated. During this heating period, the adsorbate liquid was transferred into an acetone rinsed and oven dried glass finger by means of a Pasture pipette while working in a hood. The glass finger was then valved off and was connected to the gas manifold via metal seals. The manifold heating units were then shut off and the manifold was allowed to cool while the adsorbate was freeze-pumped. After the manifold had cooled to ambient temperature, the initial fractions of the adsorbate were allowed to expand into the gas manifold and subsequently were then condensed onto a liquid nitrogen cold finger. After all purification procedures were completed the adsorbate was allowed to expand into the gas manifold until a constant equilibrium vapor pressure was reached.

A large gas manifold was used to obtain a constant flow rate into the source volume by way of a NUPRO variable leak valve.

D. Copper Single Crystal

A copper single crystal was obtained from the Metallurgical Division of the Oak Ridge National Laboratory. From this crystal was cut a rectangular single crystal using a diamond wire saw. X-ray diffraction pictures showed that three faces were now exposed to the surface, since the opposite sides of a rectangular crystal have the same surface atom orientation. Figure 1 shows the dimensions and crystal planes of the copper single crystal. The copper single crystal was initially polished with aluminum oxide powder and then chemically polished by an etchant composed of concentrated nitric acid mixed with hydrogen peroxide. The crystal was rinsed with water, then alcohol.
To the (111) faces of the copper single crystal were spot welded tantalum foil. The tantalum foil was used to mount the sample to the manual manipulator and the crystal was then laser alined. The Ta foil allows good electrical contact between the crystal and the spinal arm of the manipulator and also resists temperature deformations which may arise during annealing of the crystal. The angle calibrations on the manual manipulater were then calibrated to the normals of the (110) and (111) crystal surfaces. The crystal was then ready for installation into the source volume.

E. In Situ Surface Cleaning

The main means used to clean adsorbates and impurities from the copper single crystal surface was by argon ion bombardment.

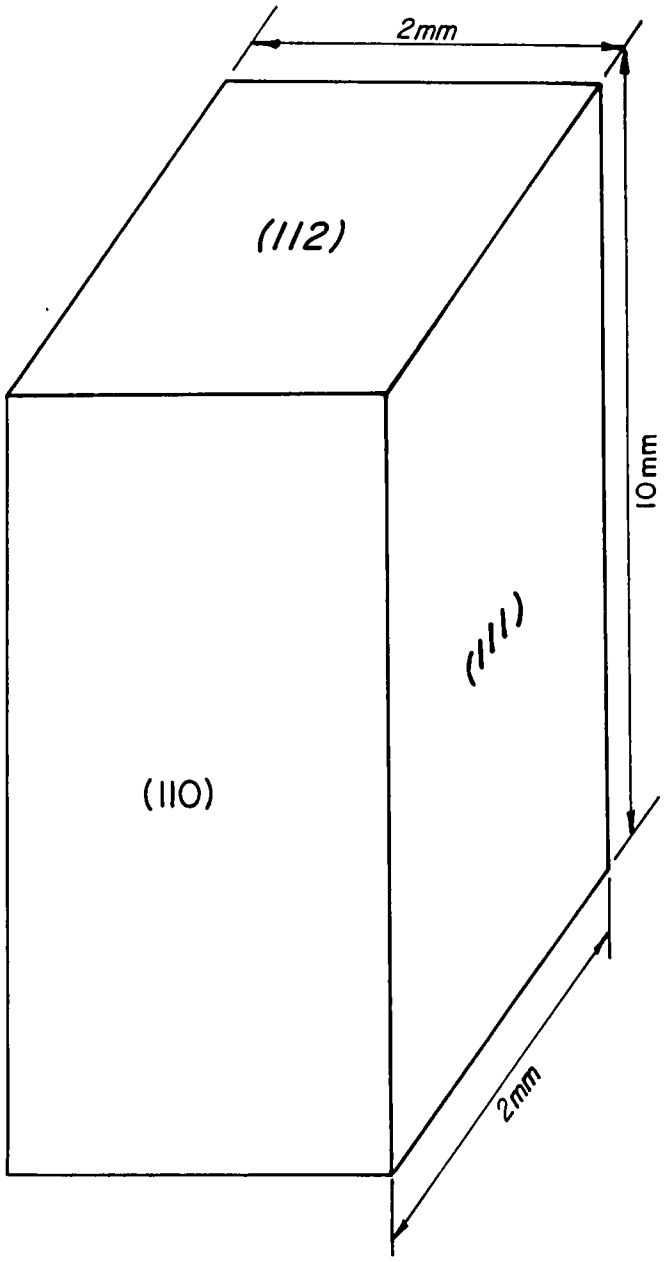


Figure 1. Copper single crystal.

Argon was allowed to leak into the source volume at a rate which kept the source volume pressure at 6.5×10^{-3} Pa. The argon ion gun was set at a potential of one kilovolt and the current was then adjusted to 10 ma. The Varian model 981-2046 ion gun automatically scanned the argon ion beam across the sample. To scan the beam across a larger area, the sample was raised and lowered manually and also rotated manually to ion bombard all of the crystal faces. This insured that any impurities which had mobile phases would not contaminate the argon cleaned surface. The typical length of argon ion bombardment was five minutes. The surface cleanliness was then checked via UPS If the first argon ion bombardment was not sufficient to clean the copper single crystal, the same procedure was repeated.

Once the surface had been cleaned of impurities, all of the surface defects caused by argon ion bombardment must be removed. This annealing was accomplished by heating the surface by electron impact. The procedure for heating the surface was initialized by moving the copper sample within a few millimeters of a tungsten heating element. Current was applied to the tungsten heating element until it glowed yellow. A positive voltage of 800 volts was applied to the crystal, at which time electrons crossed the vacuum between the heating element and impacted on the copper single crystal. These impacts imparted energy to the crystal and also induced a measurable current from the copper crystal. This induced current was measured and related to the crystal temperature by a thermocouple spot welded to the (112) face of the crystal. The current measured coming from the copper single

crystal was adjusted to 3 ± .2 ma which kept the crystal temperature between 600°C and 700°C. After the three minute annealing, the crystal was allowed to cool at least an hour to insure that it was at ambient temperature before adsorbates were introduced to the surface.

F. Experimental Apparatus and Operating Conditions

1. General Components

The source volume (see Figure 2) is made up of a stainless steel bell jar obtained from the Ultek Corporation. The bell jar has two ports on top and eight ports around the perimeter. Considering the detector port as zero degrees, the X-ray source port is ∿55° (magic angle) clockwise from it. The ion bombardment gun port is ∿135° from the detector. The ion gage is ∿157° from the detector. The view port is 180° from the detector port. The Residual Gas Analyzer and the gas inlet share the same port which is 225° clockwise from the detector. The ultraviolet photon source is set 270° clockwise or 90° counterclockwise from the detector. An unused port is found at 315° clockwise from the detector. The sample is introduced into the source volume through the topmost port after it has been connected and calibrated to the Varian manual manipulator. The manual manipulator is calibrated from 0° to 360° and two sources of error limit the accuracy of the angle setting to ±0.5°. One source of error is in laser alinement and calibration of the angle scale and the other source of error lies in the human error in manual setting of the desired angles. The remaining upper port contains electrical connections which lead to the transfer

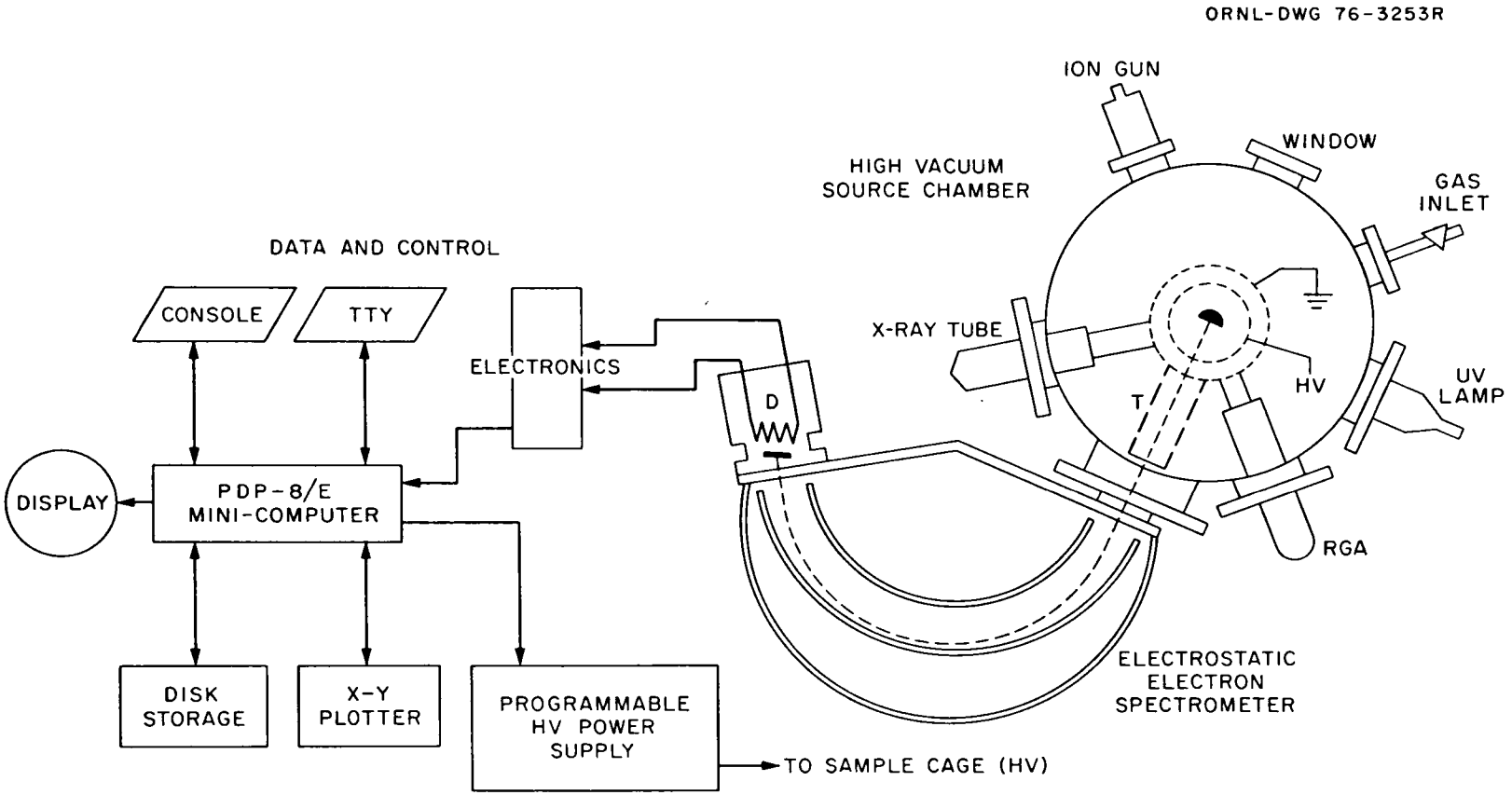


Figure 2. Experimental apparatus.

lens and the grid surrounding the solid sample. The manual manipulator contains the electrical contacts to the sample as well as to the tungsten filament.

The vacuum within the source volume is normally kept below 1×10^{-7} Pa by a liquid nitrogen trapped oil diffusion pump.[77] This oil diffusion pump model VHS-6, type 0184, was obtained from the National Research Company (NRC). Connected to the output of the diffusion pump is a direct drive roughing pump model D8A manufactured by Leybold-Heraeus. By the use of Sanovac 5 diffusion pump oil together with a constant cold surface liquid nitrogen trap developed by Granville-Phillips, the source volume was kept at this ultra high vacuum.

Some of the equipment was designed by Thomas A. Carlson and built by Frank Ward at Oak Ridge National Laboratory, such as the U.V. Photon source,[78] the electron spectrometer,[79] and the position sensitive detector,[80] which have been described previously in the literature. They also designed and built the X-ray photon source.

The equipment occupying the perimeter ports of the source volume will be described in clockwise fashion from the detector port. Following these descriptions, a chronological description of the equipment which affect an ejected electron from initial ejection to impact on the detector will be given.

The X-ray source is in the first port clockwise from the detector. Its anode was constructed from a rod of pure aluminum and its housing was shaped to conform to the small area next to the transfer lens and

was formed to fit as close to the sample as possible. The vacuum in the X-ray source was normally kept below 1×10^{-5} Pa by an NRC oil diffusion pump, model VHS-4, type 0180. The X-ray source was normally run at 11 kilovolts and 40 ma with a Sorensen High Voltage supply model 2012-250. The pressure in the X-ray source was measured by an ion gage connected to a Veeco Model RG-31A gage controller which has a pressure range of 10^{-2} to 10^{-7} Pa.

The argon ion gun was in the next port but has been previously described in Section E.

The pressure in the source volume was monitored by an ionization gage. The Varian model 971-1008 dual range Ion Gage Controller was able to measure pressures as high as 1×10^{-1} Pa and as low as 1×10^{-9} Pa. All exposure rate data and system pressure data recorded during an experimental run were read from this controller.

A Varian quartz window sealed by a viton O-ring was placed 180° from the detector to give a view of the inside of the bell jar. The window was used to inspect alinement of the crystal for annealing, argon cleaning, and vertical height adjustment calibration. (Once it revealed that the crystal had completely fallen from its mounting.)

The next port contained both the gas inlet and the mass spectrometer. The Varian model 978-1000 quadrupole gas analyzer was used to check the purity of the adsorbates and used to find air leaks in the vacuum system. The mass range of the gas analyzer was from 0 to 100 mass units. The resolution of the instrument was better than ±0.5 mass unit. This made the distinguishing of individual mass units easy.

The final port contained the ultraviolet photon source. The ultraviolet photon source was basically a gas discharge lamp with a rotatable polarizer. Operating the lamp at 1 Kv and 40 ma by means of the Sorensen High Voltage supply caused the necessary gas discharge from the platinum anode and by using various rare gases, photons of various energies could be obtained. The relatively high pressure of gas needed for discharge was differentially pumped until the gas entering the source volume only raised the pressure there to the 10^{-5} Pa range. The ultraviolet photons would have been better than 80% polarized upon a triple reflection on the rotatable gold mirrors but for this work the mirrors were removed, for polarization causes a large loss in photon intensity reaching the sample. One of the U.V. photon source differential pumps consisted of a Dresser Vacuum liquid nitrogen trapped oil diffusion pump, which in turn was connected to a Welch dual belt 500 L/m roughing pump. The other differential pump was a liquid nitrogen trapped 300 L/m Welch single belt roughing pump.

2. Electron Analysis Components

The first electrostatic interaction an ejected electron would "feel" was the retarding or accelerating potential used to select the range of kinetic energies to be studied. To insure that the initial states and final states of the crystal are not affected by the applied fields, a region of field free space was devised around the sample by charging a cylindrical grid to the same potential as the sample. Thus the ejected electron would not "feel" the effect of the applied field until it

passed through the grid. A Fluke Programmable Power supply model 3330B was installed to generate the retarding or accelerating potential.

Only the ejected electrons which passed into the spectrometer's slit system could be focused into the spectrometer by means of an electrostatic Einsel lens system. The electrostatic lens system was powered by a Hewlett Packard model 6110A D.C. voltage supply. The voltage required for focusing the ejected electrons into the spectrometer depended linearly upon the electrostatic plate voltage applied.

The electron spectrometer which electrostatically separated the electrons with varying kinetic energies was composed of two oppositely charged spherical sector plates. Each plate had its own Fluke model 412B high voltage power supply of opposite polarity connected to it. The range of voltages varied depending upon the photon source used to excite the ejected electrons. X-ray ejected electrons were measured at plate voltages of ±250V and ultraviolet ejected electrons were measured at plate voltages of ±100V. A Welch model 3102 turbomolecular pump (260 L/sec) was used to keep the pressure in the electron spectrometer below 10^{-4} Pa. The pressure in the spectrometer was measured with an ionization gage controlled by a Veeco model RG-840 ion gage controller which has a pressure range of 10^{-1} to 10^{-8} Pa.

To insure that no magnetic field interactions interfered with the kinetic energy analysis, the entire spectrometer was enclosed in Helmholz coils having eight foot sides. The Helmholz coils were energized by two Fluke Voltage Calibrators model 313A.

Each electron which reaches the detector must be counted and its kinetic energy must be measured. To do this simultaneously, a position sensitive detector was used. Electrons impinge on a channel plate which causes a pulse of electrons to impinge on a carbon resistor strip. The number of measured pulses is equal to the number of photoelectrons reaching the detector. The currents measured from the opposite ends of the carbon strip can be related to position of the impact of the photoelectron and the position of impact can be related to the kinetic energy of the photoelectrons. Therefore by either analog or digital methods, these signals can be interpreted and displayed as a spectrum by storing the count of electrons having the same kinetic energy in a space of analog or computer memory.

In this study the data were collected by a PDP 8/E minicomputer and stored in memory. The memory locations were then displayed to a Tectronix CRT model 602. The spectrum could be written onto a RK05 Megabyte disk and/or plotted on a Houston Instruments Plotter, Model DP-1-SH.

At a plate voltage of ±100V, the detector can simultaneously analyze an energy range of 20 eV. Thus if a 21.2 eV photon source is used, the entire spectrum could almost be obtained. At a plate voltage of ±250V, the detector simultaneously analyzes an energy range of 50 eV. Thus in an X-ray study, the spectrum of kinetic energies must be scanned by varying the retarding or accelerating potential.

Computer software for data acquisition and data analysis was written in Fortran IV by William B. Dress exclusively for the system at Oak Ridge National Laboratory.

G. General Experimental Procedure

In this section the general procedures and operating conditions for a typical run are presented.

Initially the manual manipulator was positioned so that the crystal face to be studied was facing the argon ion bombardment gun. The gas manifold was then filled, purged, and filled again with argon. The argon was allowed to leak into the source volume until a pressure of 6.5×10^{-3} Pa was constantly maintained. The argon gun was then set to 1 Kev and 10 ma and the crystal was bombarded for five minutes with changes in crystal height and also crystal face by manual adjustment. After the system was brought back to pressure following ion bombardment, helium was allowed to leak into the ultraviolet photon source until the source volume pressure was $\sim 1 \times 10^{-5}$ Pa. The lamp was then lit by applying a voltage surge to the lamp after the cooling water had cooled the photon source. The voltage was then set at $\sim$1 Kev and registered $\sim$40 ma. The crystal was then rotated so that the normal of the crystal face to be studied was 60° from the detector and also 30° from the ultraviolet photon source. After the electronics had been set to obtain a spectrum on the computer display (for copper: plate voltage ±100V, retarding voltage -396 V, transfer lens 0V) the spectrum was accumulated for 100 sec to ascertain whether or not

surface impurities were present in the spectrum. If impurities were still present, the procedure was repeated until there was no change in the spectrum or until the surface was clean. The retarding voltage was then removed from the sample and the grid. The crystal was then raised above the grid until it was opposite the tungsten heating wire. The crystal was rotated until the side of the crystal opposite the face being analyzed was facing the wire. Current was applied to the tungsten wire until it glowed yellow. Then +800 V was applied to the crystal to induce a current to the surface. This current was measured and the current to the tungsten wire was increased until the current to the crystal was 3 ma. After three minutes, the current to the tungsten wire was cut off as well as the voltage to the crystal. The crystal was allowed to cool for thirty minutes. The crystal was then repositioned for an ultraviolet photoelectron spectrum. The angle resolved ultraviolet photoelectron spectra were then obtained at angles 20°, 40°, 60°, and 70° measured between the surface normal and the entrance slit of the detector. The surface was then allowed to cool for the remainder of an hour. During these cooling times the adsorbates were vaporized and prepared for introduction into the source volume. Following the hour of cooling, the adsorbate was allowed to leak into the source volume at a fixed rate. Angle resolved ultraviolet photoelectron spectra were then taken at the same angles as for the clean surface. Following the data acquisition, the ultraviolet photon source was shut off and the X-ray photon source was prepared for energization. While the X-ray filament was

being warmed, the electronics were set to measure the core electron levels for Cu, S or C and the crystal was realined for interaction with the X-ray photon source. The normal of the surface was set to point to the detector. After sufficient time to warm the X-ray filament and make all the necessary changes, 11 Kv was applied to the anode in steps after the cooling water had cooled the anode. The X-ray filament current was increased until the anode current reached 40 ma. At this point the X-ray photoelectron spectra were obtained. The copper 2p, carbon 1s, and sulfur 2p XPS spectra were acquired. This entire procedure would take one day to perform. Variations on this procedure were numerous depending on the information required (e.g., coverage studies, desorption studies, adsorption studies, decomposition studies, etc.).

CHAPTER III

RESULTS

A. Gas Phase Spectra

Gas phase spectra were run for thiacyclopropane, thiacyclobutane, thiacyclopentane, thiacyclohexane, allyl mercaptan, thiophene, and diethyl sulfide. The spectra were compared to the corresponding gas phase spectra found in the literature[48-53, 81-84] to check on purity and whether decomposition had taken place. The gas phase spectra were also measured to acquire original gas phase results which could be stored in computer memory for the purpose of data analysis as well as for the accurate measurement of any energy shifts of the adsorbate molecular orbitals upon bonding of the adsorbate to the copper single crystal.

Figure 3 shows the unanalyzed gas phase spectrum of thiacyclopropane. For comparison of the simplest and the most complex gas phase spectra of the sulfur heterocycle adsorbates, Figure 4 shows the unanalyzed gas phase results for thiacyclohexane. Each of the two gas phase spectra was acquired for 200 seconds. The source volume pressure during thiacyclopropane introduction was 2.9×10^{-4} Pa and the source volume pressure during thiacyclohexane introduction was 3.0×10^{-4} Pa. Note the sharp peak to the right of both spectra, these are the lone pair orbitals.

In all of the spectra to be presented, the ordinate axis will be expressed in counts, which are units of intensity. The abscissa axis

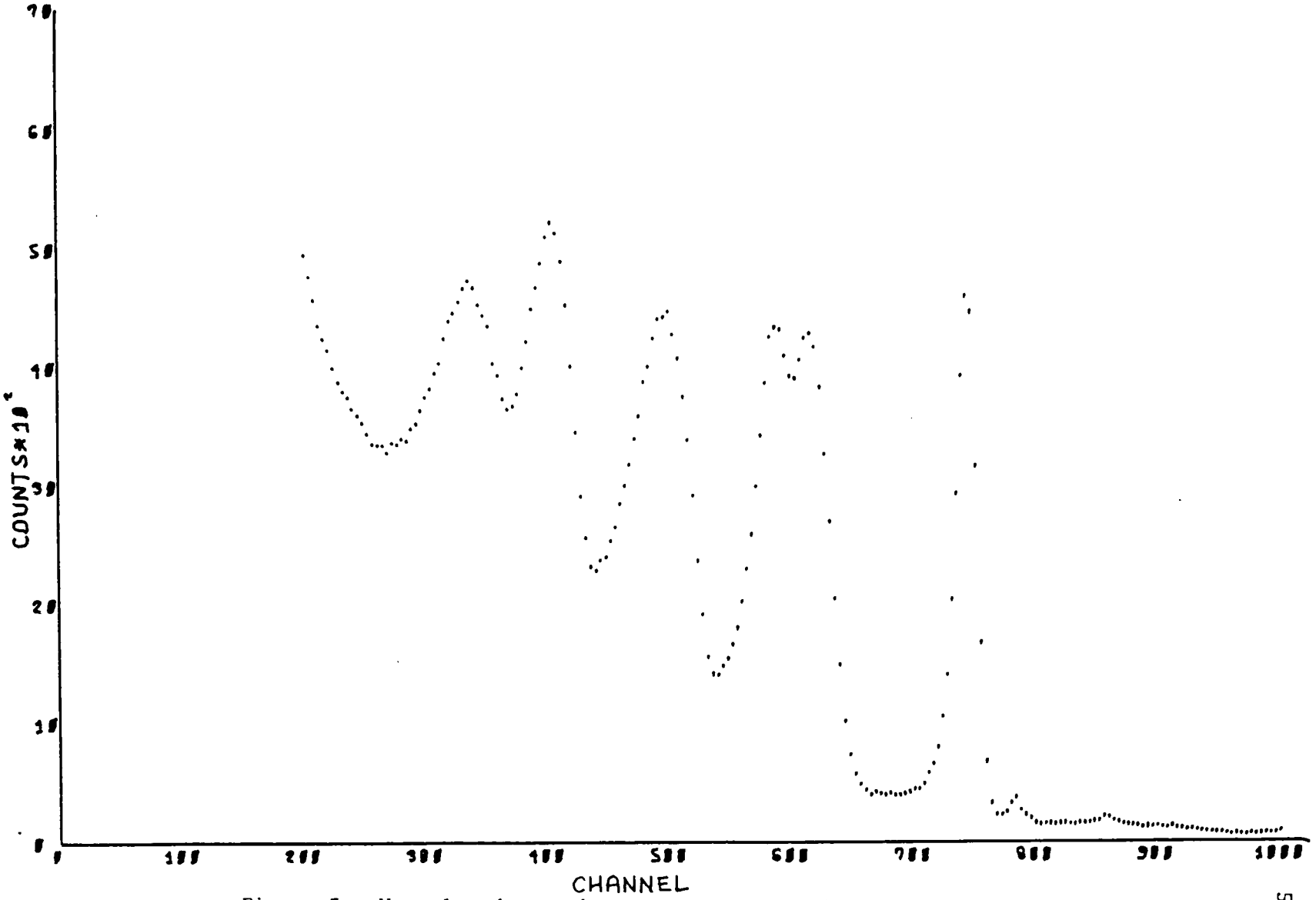


Figure 3. Unanalyzed gas phase spectrum of thiacyclopropane.

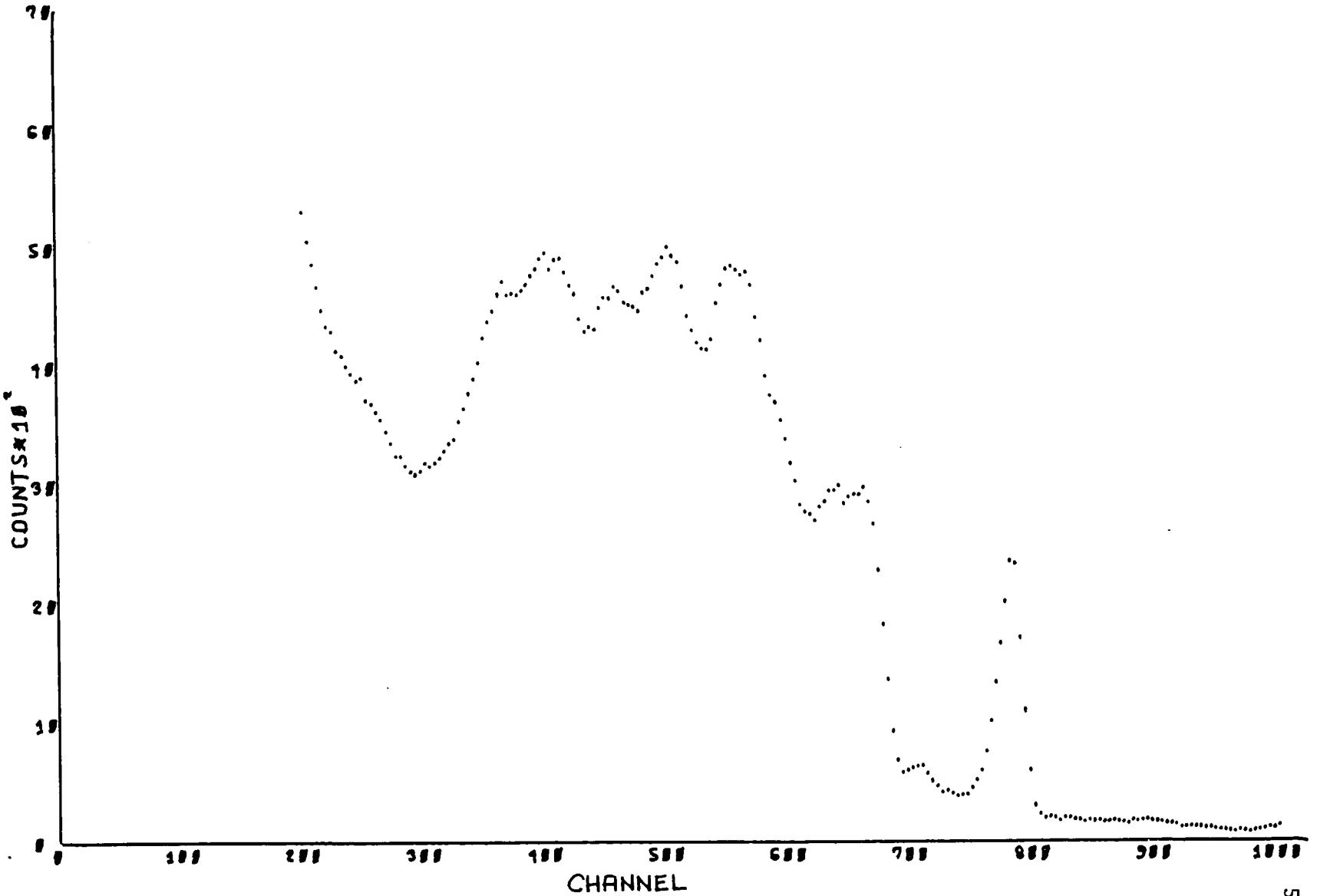


Figure 4. Unanalyzed gas phase spectrum of thiacyclohexane.

was initially expressed in channels from 1 to 1024, then converted to a binding energy scale after the detector had been calibrated. By scanning the major UPS peak of argon across the detector with small retarding voltage steps, the change in voltage with change in channel can be measured. The XPS signal of copper can also be scanned across the detector to give an XPS calibration of the detector. Also the energy scale of the spectra can be scaled to fit the spectra found in the literature, but this is only accurate for the main peaks and thus the energy scale between peaks is unreliable. A combination of all of these techniques gives the most reliable energy scale.

B. UPS Spectra of the (110) Surface of Copper

1. Angular Resolved UPS Spectra of Clean Copper

Adsorbate free angular resolved spectra have been recorded for both the (110) and the (111) surfaces of copper, though the present study has been limited to the Cu(110) surface. Azimuthal angular resolution was obtained by fixing the angle between the U.V. photon source and the detector to 90° and rotating the crystal, thereby varying the angle between the normal to the surface being studied and the path of the ejected electrons which pass through the detector slit. Figures 5-8 show the angular variation of the intensity of the copper (110) d band (approximately 650 to 900 channels which convert to 1.0 eV to 5.6 eV binding energy) as well as the changes in secondary electrons with increasing azimuthal angle. The angular variation could be due to such

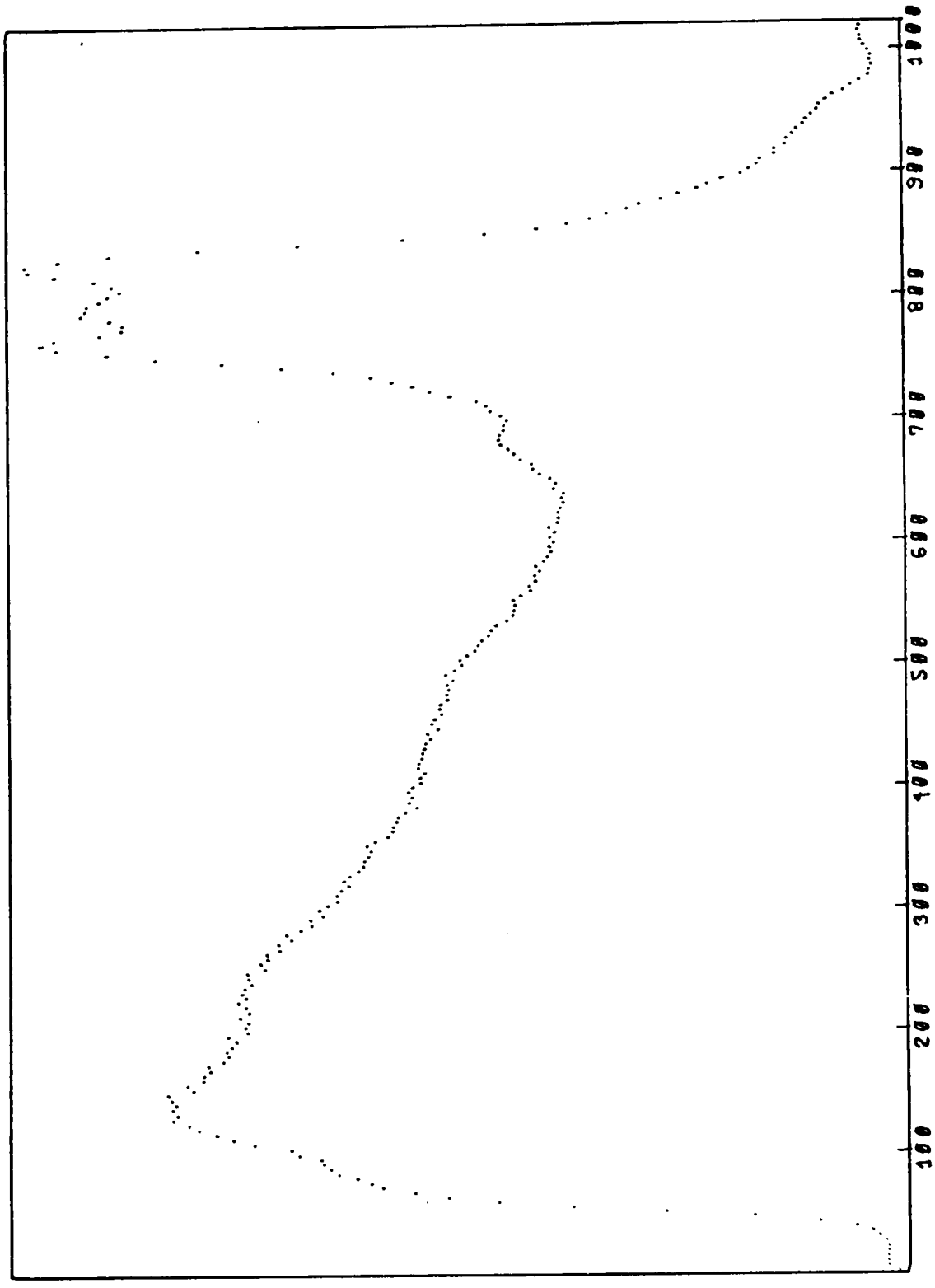


Figure 5. UPS spectrum of Cu(110) at 20°.

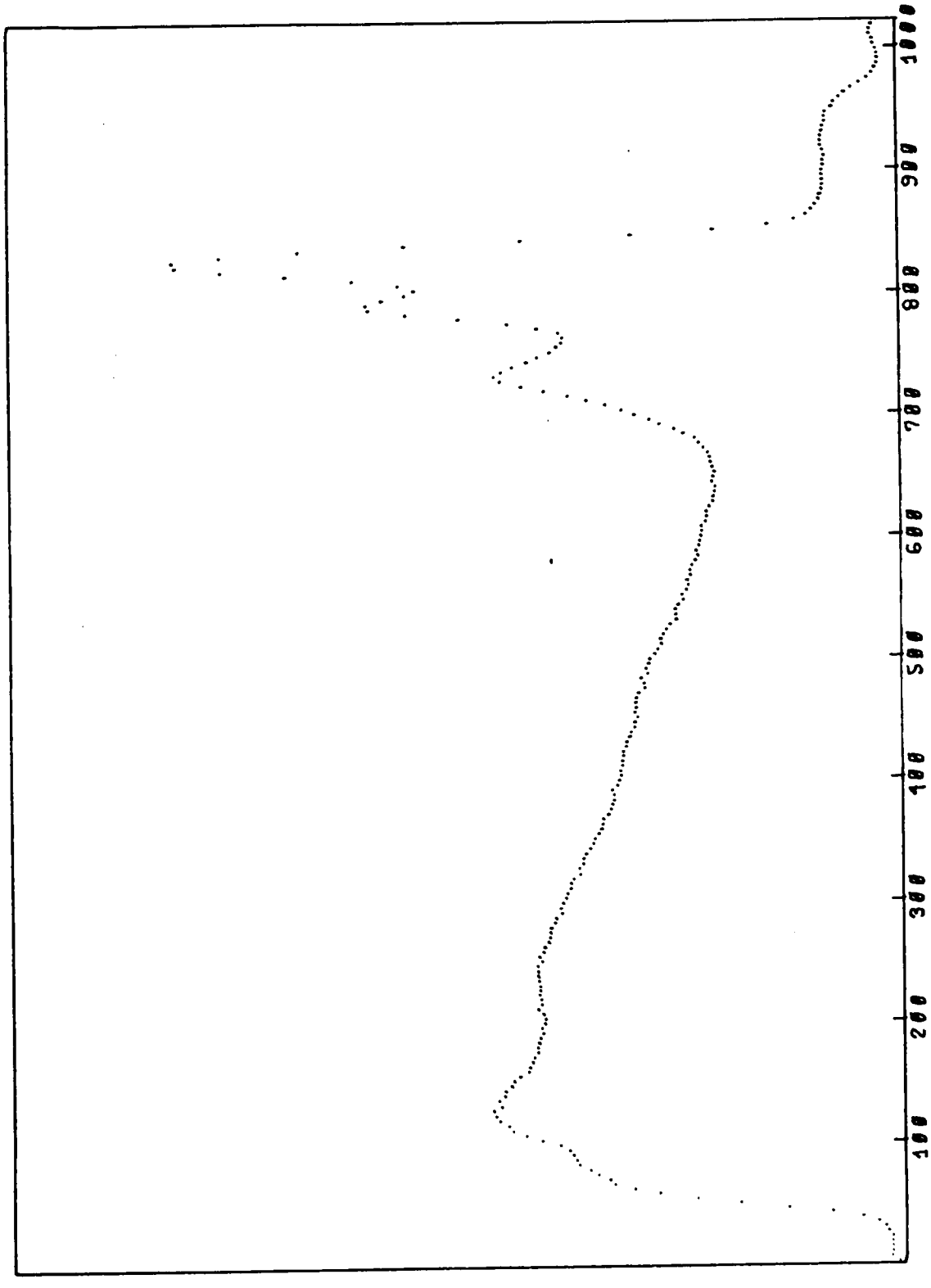


Figure 6. UPS spectrum of Cu(110) at 40°.

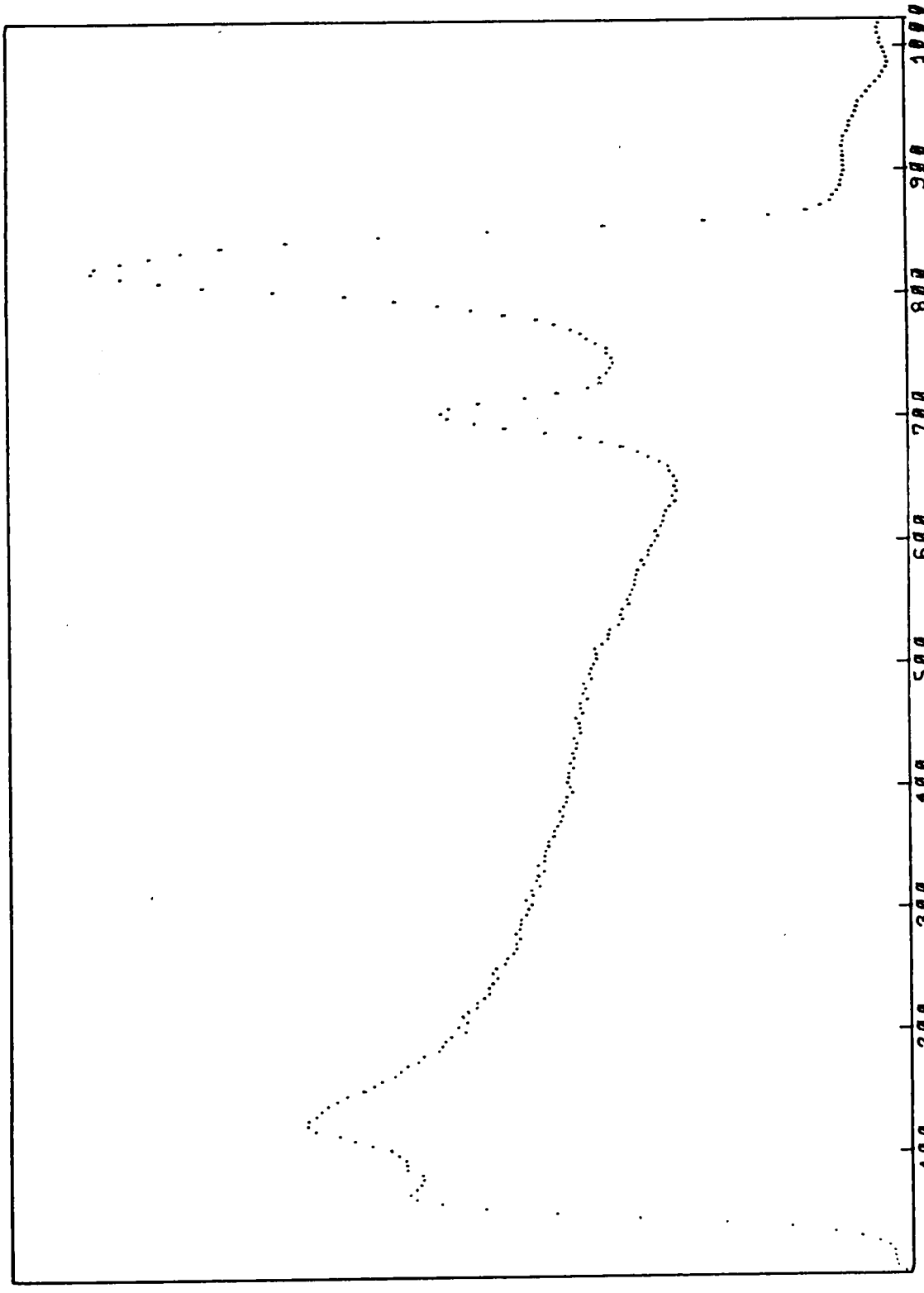


Figure 7. UPS spectrum of Cu(110) at 60°.

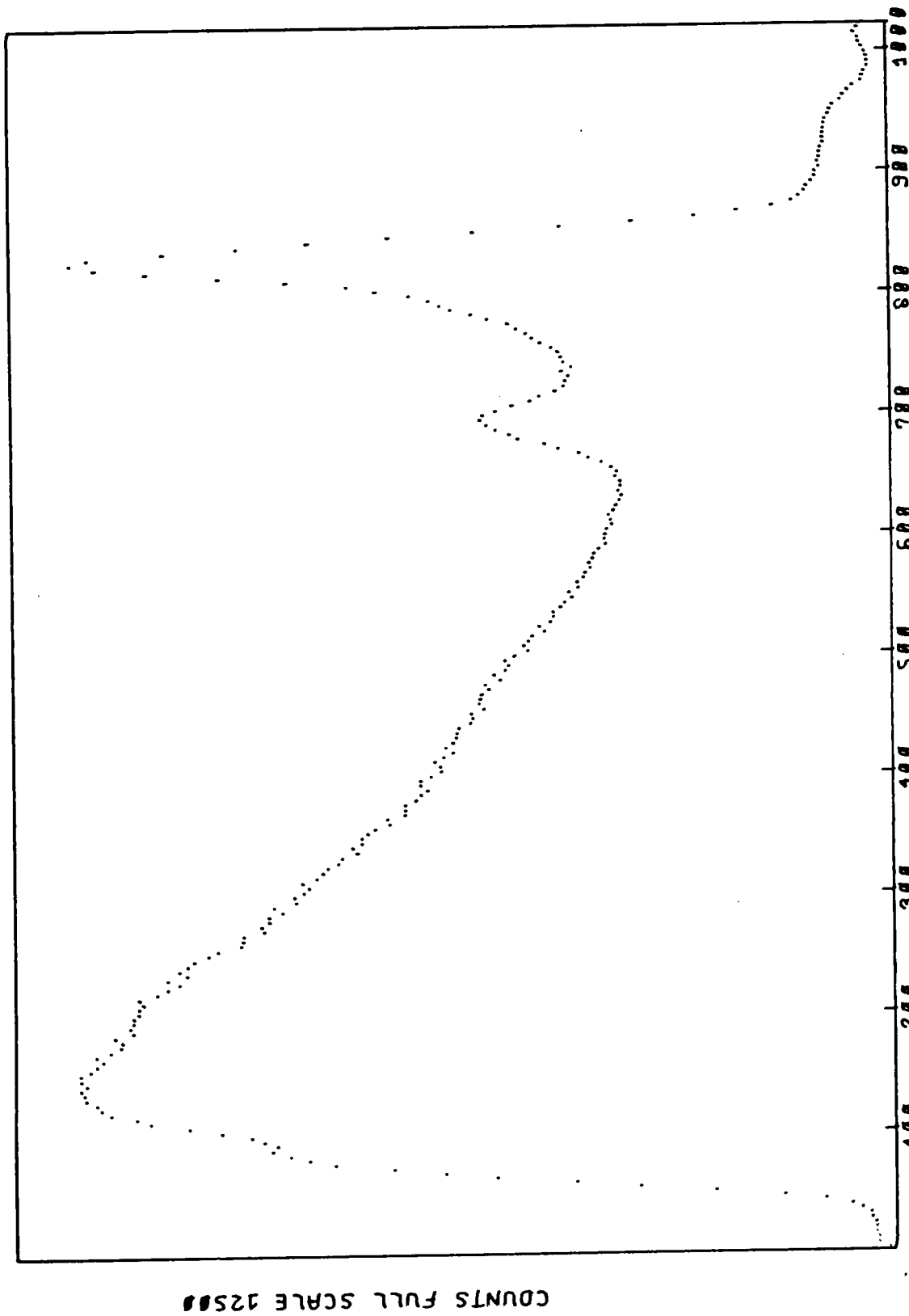


Figure 8. UPS spectrum of Cu(110) at 70°.

things as changes in electron emission cross sections, adsorption cross sections, scattering, diffraction, refraction at the surface, etc., with changes in azimuthal angle. Angular variation could also change the bulk to surface ratio of measured ejected electrons. Due to mean free path limitations on bulk electrons, at high azimuthal angles the surface to bulk ratio could increase if the bulk intensity decreases. The angular dependent UPS spectra of Cu(110) presented were measured immediately before the coverage study for thiacyclopropane was performed. Similar data were taken before every coverage study was performed. Typical counting times and counting rates varied with angular setting and experiment. The counting times used in the above copper study were 500 seconds per spectrum and the counting rates varied with angle. ($\theta = 20°$, 10.6×10^3 counts/sec; $\theta = 40°$, 15.5×10^3 counts/sec; $\theta = 60°$, 9.1×10^3 counts/sec; $\theta = 70°$, 5.8×10^3 counts/sec.)

2. UPS Spectra of Clean Cu(110) after Exposure to Thiacyclobutane

A good example of what happens to the copper UPS spectrum after copper had been exposed to a catalyst poison such as thiacyclobutane can be seen in Figure 9. This figure corresponds to the 40° clean copper spectrum, presented earlier, after an exposure of 10 L. Four important spectral features should be pointed out: (1) the decrease of the d band in intensity, (2) the increase in secondary electrons, (3) the addition of adsorbate bands to the spectrum, (4) lack of a significant change in the work function.

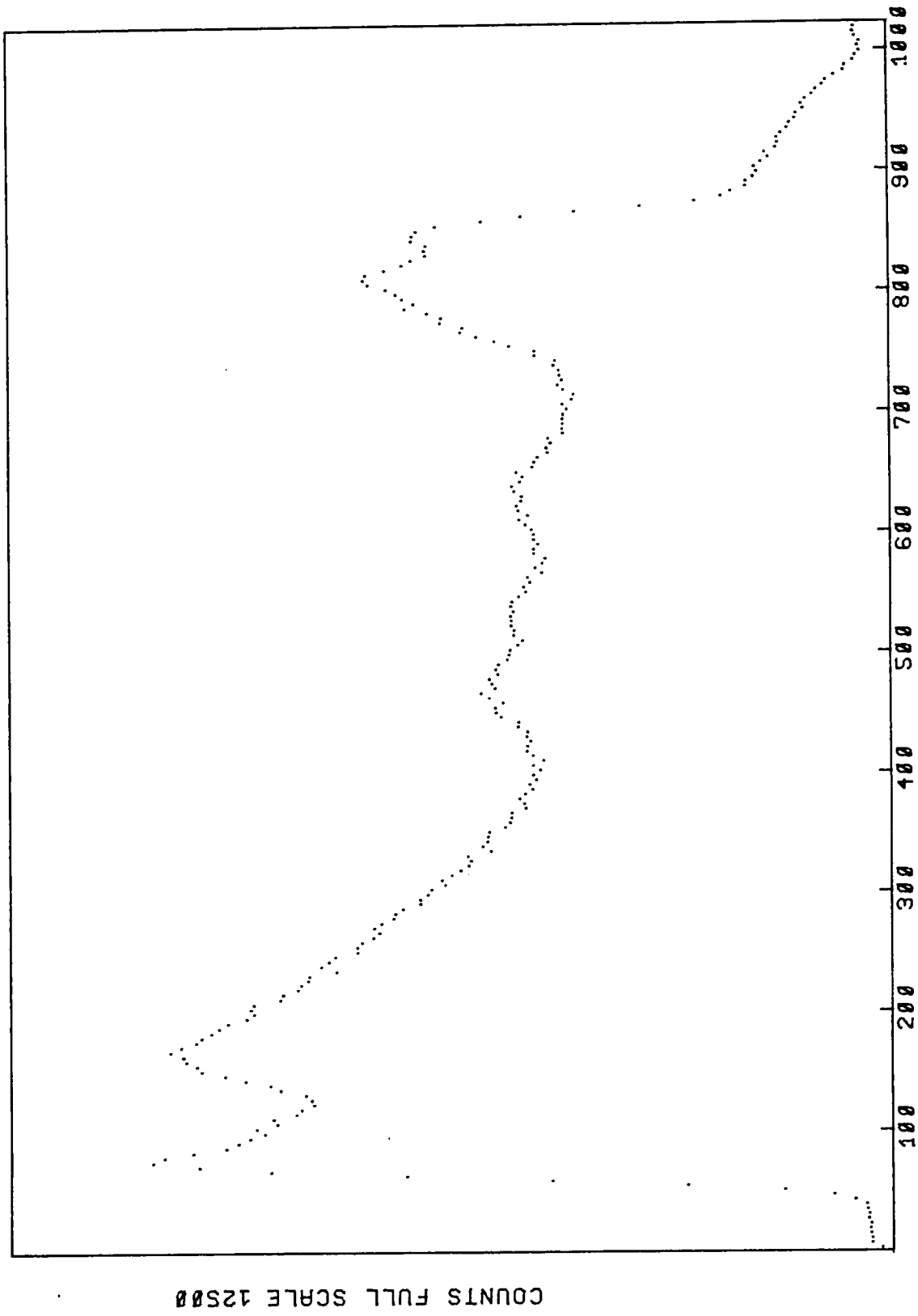


Figure 9. UPS spectrum of Cu(110) after exposure to 10L of thiacyclobutane at 40°.

A change in d band shape and intensity accompanies the adsorption of thiacyclobutane onto copper. The d band width doesn't change though. The adsorbate seems to suppress the bulk contribution to the d band upon coverage of the surface. The change in d band shape may be due to changes in surface metal atoms or due to the mixing of the d band with adsorbate molecular orbital bands. It could also be due to localization of conduction electrons into surface metal atom orbitals, thus changing the electron density of states near the surface.

When ejected electrons lose kinetic energy by interaction with matter before reaching the detector, these electrons are referred to as secondary electrons or background signal. Most of the secondary electrons lose a large portion of their kinetic energy and therefore increase the intensity of the lower channels in a spectrum. Adsorption of thiacyclobutane onto copper causes an increase in secondary electrons. Some of the increase in secondary electrons may be from the suppressed bulk copper d band. If true, this would mean that surface adsorption increases the cross section for bulk electron deenergization before the bulk electrons reach field free space. This cross section can be thought of as a catch-all reason for loss of kinetic energy and would be composed of structure changes, surface changes, diffraction changes, refraction changes, and all other changes that would be induced during adsorption which cause ejected electrons to lose kinetic energy. Since the adsorbates are confined to the surface, only electrons which are ejected into either the surface from the adsorbate or from adsorbate to adsorbate as well as any electrons scattered from the source volume

would add to the secondary electrons. In fact, the ratio of copper atoms to adsorbate molecules alone would suggest that the major contribution to the secondary electrons would normally come from the bulk copper atoms.

The apparent energy shift of the molecular orbitals of the adsorbate from their gas phase values is actually made up of two types of shifts. The work function of the surface reduces the kinetic energy of the electrons ejected from the bulk and surface copper atoms thus shifting the apparent binding energy scale of the surface atoms towards the scale of the adsorbates. A comparison of the energy range of the lowest filled orbitals from all of the adsorbates to the Fermi level of the surface will illustrate this effect. The range of binding energies for the lowest filled levels of the adsorbates taken from their gas phase spectra is 9.0 eV to 8.44 eV. The Fermi level is assigned a binding energy of 0 eV. If the work function for Cu(110) is taken as 4.85 eV, all electrons ejected from the copper atoms will lose 4.85 eV of kinetic energy. Because a loss in kinetic energy is interpreted by the detector as an increase in binding energy, the Fermi level moves 4.85 eV closer to the molecular levels of the adsorbates. The apparent shift seems to indicate that the levels of the adsorbate have shifted towards the Fermi level since the Fermi level has been arbitrarily fixed to zero binding energy, that is, the apparent binding energy scale has been referenced to the Fermi level. Thus the binding energy range for the lowest adsorbate levels seems to have shifted to (4.15 eV - 3.59 eV). [Note: the lowest filled molecular orbital has, at this point, shifted into the d band range of (5.6 eV - 1.0 eV).]

The second type of shift, relaxation, actually does shift all of the adsorbate orbitals. Balsenc[75] defines relaxation as the rapid shifting of valence orbitals towards a hole created by photoionization to screen the extra positive charge on the molecule; as a consequence the ejected electron acquires additional kinetic energy. An increase in the molecular relaxation energy accompanies the adsorption of the heterocycles onto copper. Thus an increase in kinetic energy shifts the molecular orbital levels towards the Fermi level. Each individual adsorbate has a unique change in relaxation energy. Thus the comparison of gas phase spectra of the adsorbates to the corresponding difference spectra necessitates a shift of the gas phase energy scale to account for the work function shifts and relaxation shifts. In all of the comparison spectra presented, the gas phase energy level scale has been shifted by a constant value of ϕ'. If the adsorbates shift electron density to the surface or remove electron density from the surface, the surface work function will then become a variable quantity dependent upon the adsorbates and the interpretation of ϕ' becomes more complex. None of the adsorbates studied in this work appreciably change the work function, except for the sulfur atoms deposited onto copper following the decomposition of thiacyclopropane. There are other adsorbate orbital shifts possible; shifts due to bonding of the adsorbate to the surface, shifts due to adsorbate-adsorbate interactions, shifts due to changes in molecular symmetry and/or shape.

Some of the problems which limit the usefulness of UPS to interpret orbital shifts due to surface bonding at room temperature are adsorbate

orbital intensities (signal to noise ratios), adsorbate orbital broadening, adsorbate orbital mixing, and the mixing of adsorbate bands with impurity bands aquired during long counting times or impurity bands acquired due to partial decomposition of adsorbates on the surface.

C. Comparison of Subtracted Spectra to Gas Phase Spectra

In Figure 10 are plotted four spectra adjusted to the same binding energy scale. The upper spectrum represents the photoelectron spectrum of the Cu(110) surface following a 10 L exposure to thiacyclobutane at ambient temperature. The spectrum was counted for 500 seconds and set at an azimuthal angle of 60°. The next spectrum corresponds to a clean Cu(110) surface counted for 500 seconds and also at 60°. The clean copper spectrum has been multiplied by a scale reduction factor to adjust the height of the copper d band to correspond to the height of the exposed copper spectrum. The difference between these two spectra is then displayed immediately below them. For ease of comparison, gas phase results for thiacyclobutane are plotted directly below the difference spectrum. The binding energy scale of the gas phase results has been adjusted by a constant value, $\phi' = 6.6$ eV, so that the high binding energy peaks of the gas phase spectrum correspond to peaks found in the difference spectrum immediately above it. The dashed area of the difference spectrum corresponds to an area of uncertainty where the largest errors due to subtraction should be found. The dot-dash line denotes the increase in secondary electrons due to adsorption

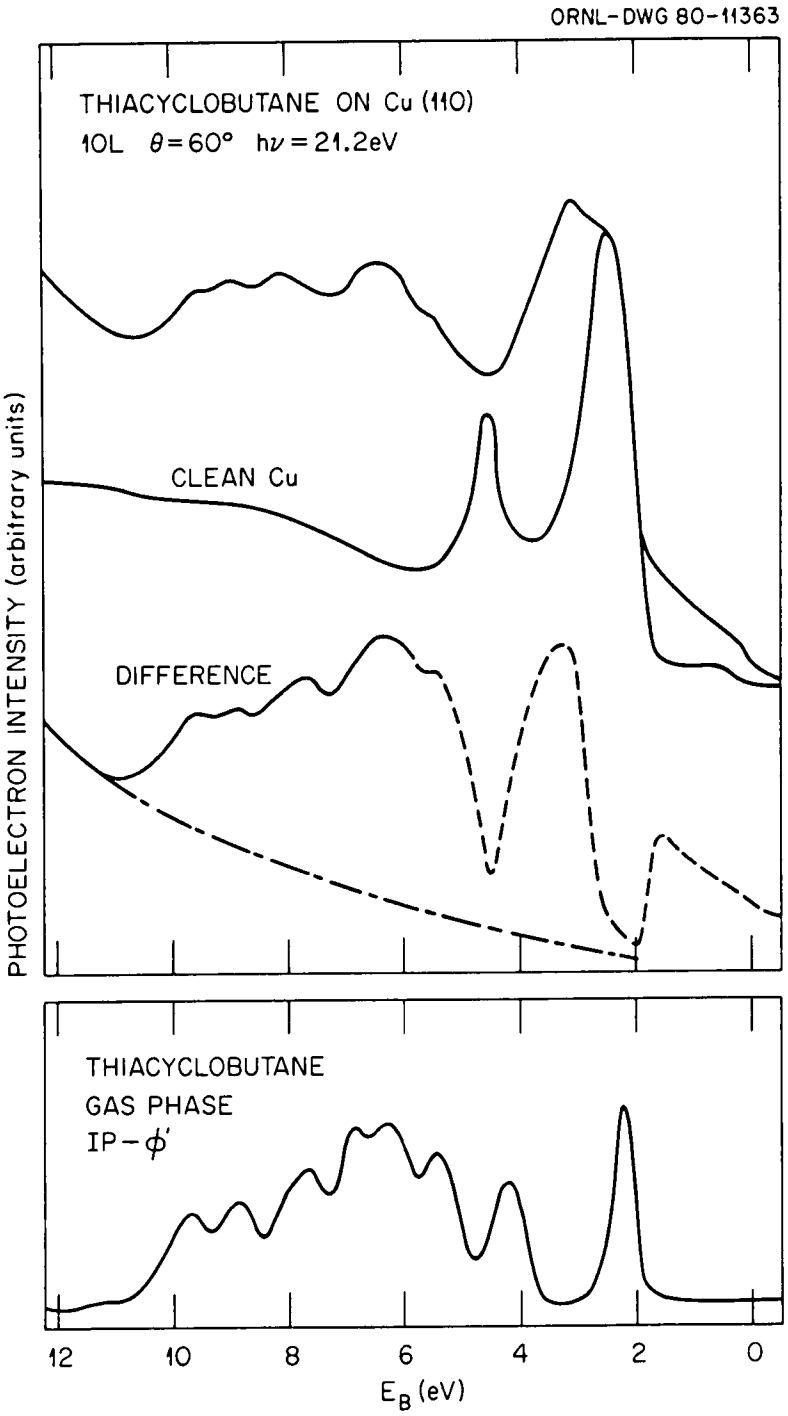


Figure 10. Comparison of UPS results for thiacyclobutane.

of thiacyclobutane onto copper. The binding energy scale E_B (eV) has been referenced to the Fermi level and calibrated from UPS-argon gas phase results.

Similar results for thiacyclopentane can be found in Figure 11 as well as for thiacyclohexane in Figure 12. The immediate difference between the five member ring and the four and the six member rings is that thiacyclopentane does not suppress the d band as much as the other two and thus its secondary electron increase denoted by the dot-dash line is much less than those of either the four or the six member rings. The difference spectrum for each of the displayed spectra has three distinct bands; a band between 1 to 2 eV, a band from 3 to 4 eV, and a set of well resolved molecular bands having energies larger than 5 eV.

D. Analysis of Lone Pair Stabilization Shifts and Relaxation Shifts

The 3p lone pair of each of the adsorbates was used to bond to the copper surface. Upon formation of the lone pair to surface bond, the lone pair orbital was shifted to higher binding energies. Since each of the adsorbate lone pair orbitals were shifted into the d band region and thus inseparable from the band, an average lone pair stabilization was calculated. For each of the adsorbates, the d band region of the corresponding difference spectra had a width of $\sim$0.8 eV. Thus, the lone pair orbital was assumed to shift to the midpoint of the band and the error bars were selected to include the entire d band region of the

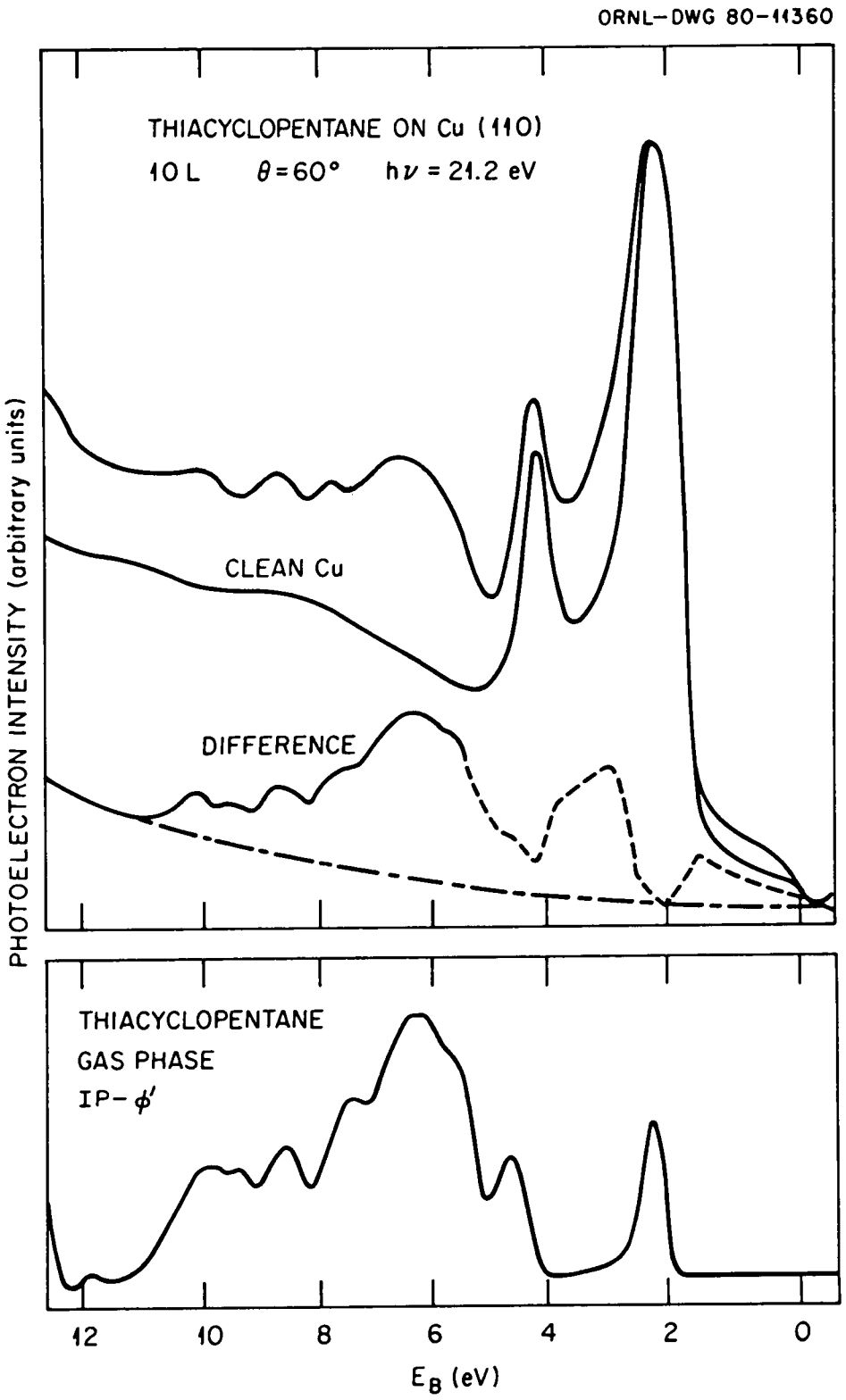


Figure 11. Comparison of UPS results for thiacyclopentane.

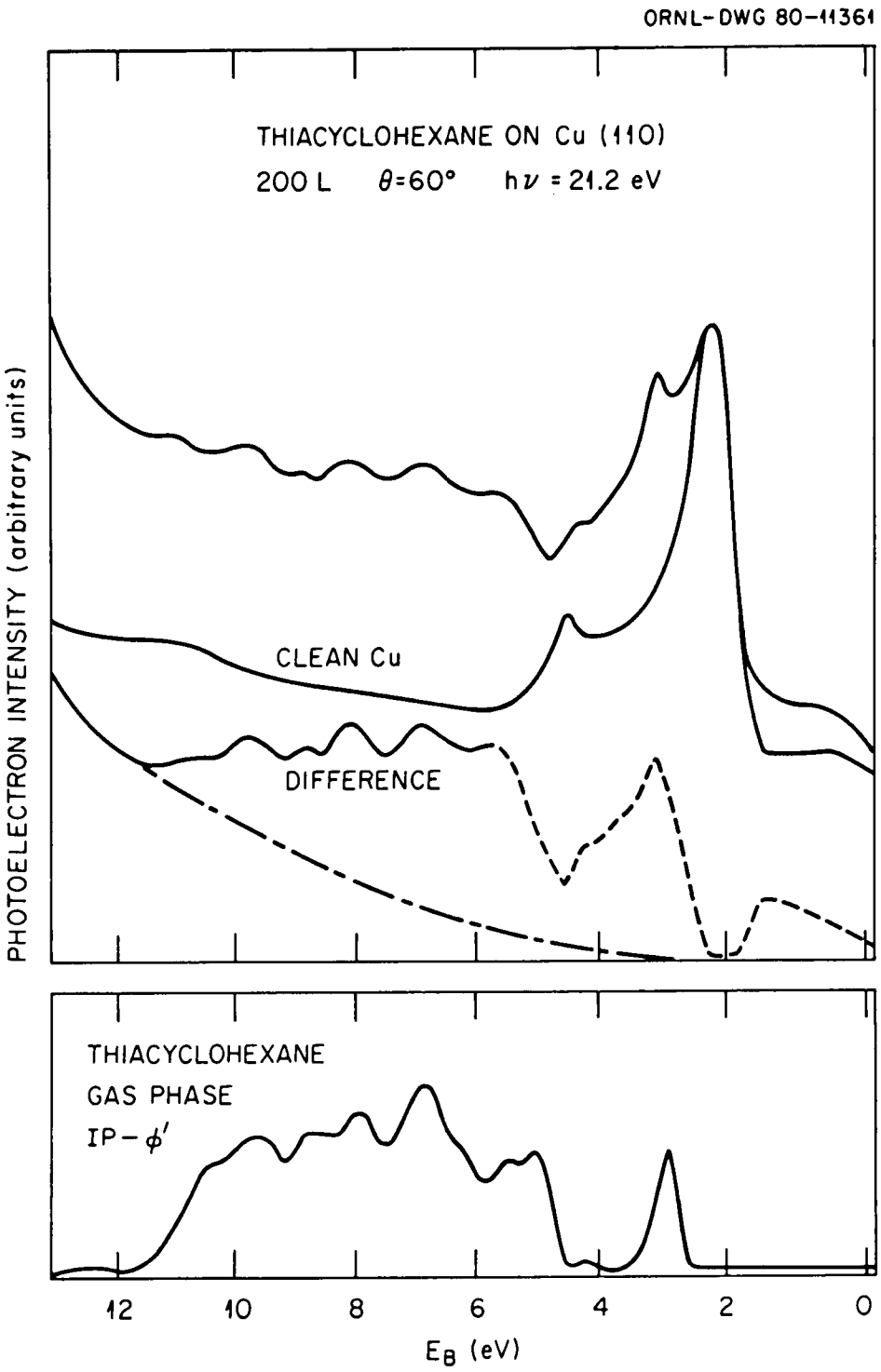


Figure 12. Comparison of UPS results for thiacyclohexane.

difference spectra. In this way the following lone pair stabilization energies (ΔE) were calculated; thiacyclobutane (1.4 eV ± 0.4 eV), thiacyclopentane (1.1 eV ± 0.4 eV), thiacyclohexane (0.6 eV ± 0.4 eV).

Since none of these adsorbates induced a measurable change in the work function of the Cu(110) surface, calculation of the relaxation energy changes became possible. A value of 4.85 eV was used as the work function for Cu(110). The origin of this work function will be discussed later in this chapter. From the gas phase energy scale shift values, ϕ', the relaxation energy shifts (ΔR) were calculated; thiacyclobutane (ϕ' = 6.6, ΔR = 1.75 eV), thiacyclopentane (ϕ' = 6.2, ΔR = 1.35 eV), thiacyclohexane (ϕ' = 5.6, ΔR = 0.75).

A plot of ϕ' vs lone pair stabilization energy (ΔE) showed a linear relationship which implies

$$\phi' = m\Delta E + b \qquad \text{but} \qquad \phi' = \Delta R + \phi$$

where $\phi \equiv$ Cu(110) work function (assumed to be a constant since no measurable change was observed). Thus upon rearrangement to plot ΔR vs ΔE

$$\Delta R = m\Delta E + b - \phi$$

According to the Brucker-Rhodin model,[54] one can assume $\Delta E = 0$ when $\Delta R = 0$, and thus one obtains $b = \phi$. In this way by plotting ϕ' vs ΔE, the intercept would equal the work function for Cu(110).

A linear regression analysis of the ϕ' vs ΔE data revealed an intercept of 4.85 ± .05 eV. The work function for Cu(110) obtained from the

literature was found to be 4.92[85] by the contact potential method which are usually higher than corresponding photoemission literature values. This was the reason for the previous use of 4.85 eV as the work function for Cu(110).

Figure 13 represents a plot of ΔR vs ΔE. The intercept does equal zero, which supports the Brucker-Rhodin model, and the slope was 1.25. To check the generality of this relation, the results of Bandy et al.[61] for pyridine were plotted along with the data presented in this work. There was excellent correlation of all of the heterocyclic data. But this relationship may not hold for heterocycles and/or only for d^{10} transition metals.

E. Decomposition Studies by Means of UPS

To insure that the spectra obtained in our studies were actually from the adsorbates initially introduced into the system, a set of possible decomposition products were studied. The assumed sole decomposition product from thiacyclobutane having the same empirical formula would have been allyl mercaptan, therefore it was included in our surface studies. Since thiacyclopentane had a much lower ring strain energy, and due to the fact that it was possible to form an aromatic product upon dehydrogenation, thiophene was added to the study. Diethyl sulfide was also added to the study as a possible hydrogenation product of the five member ring and also to see if a thioether would adsorb onto copper as readily as the cyclic groups. Figure 14 shows the comparison of allyl mercaptan to thiacyclobutane and

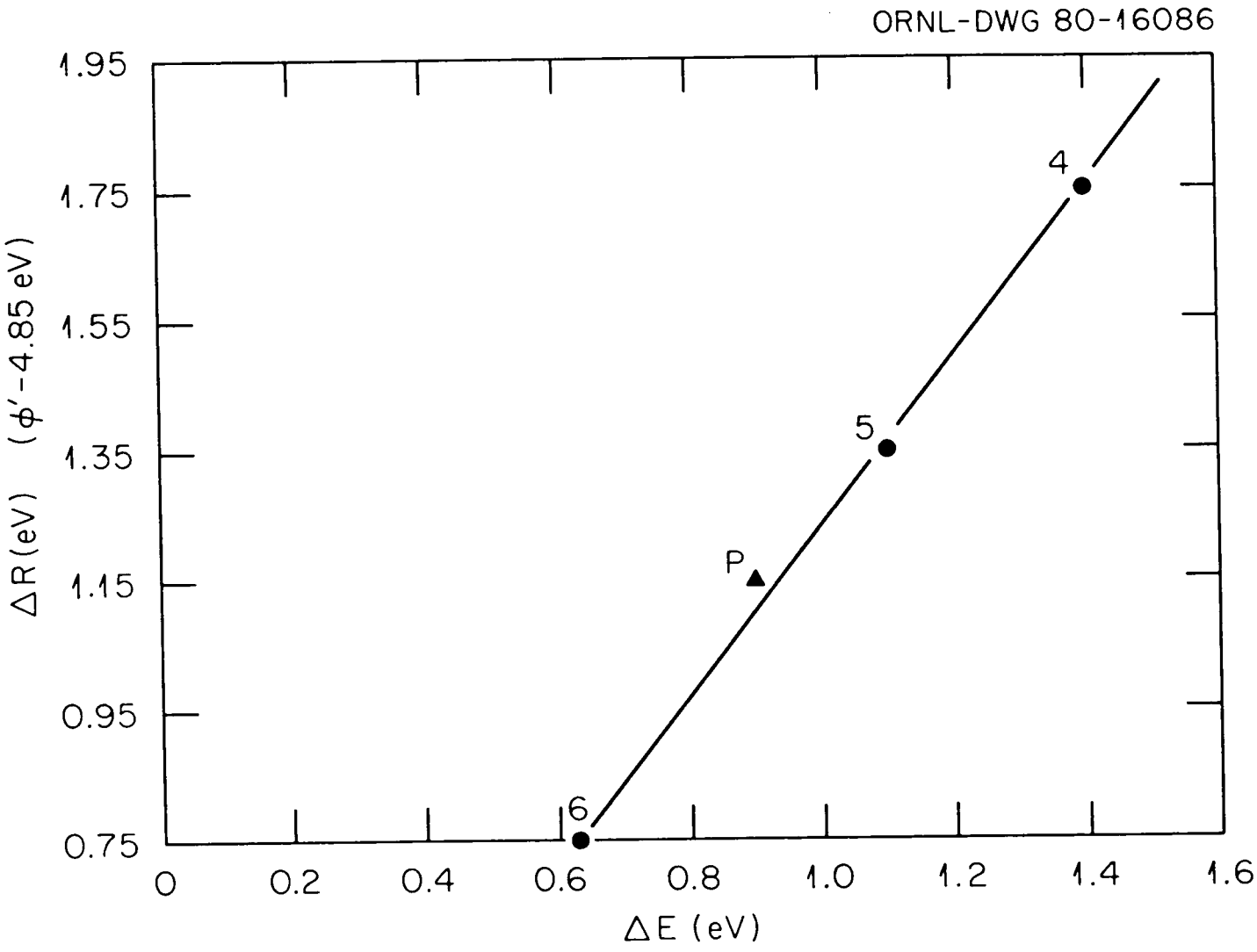


Figure 13. Relaxation energy shift (ΔR) versus lone pair stabilization energy shift (ΔE).

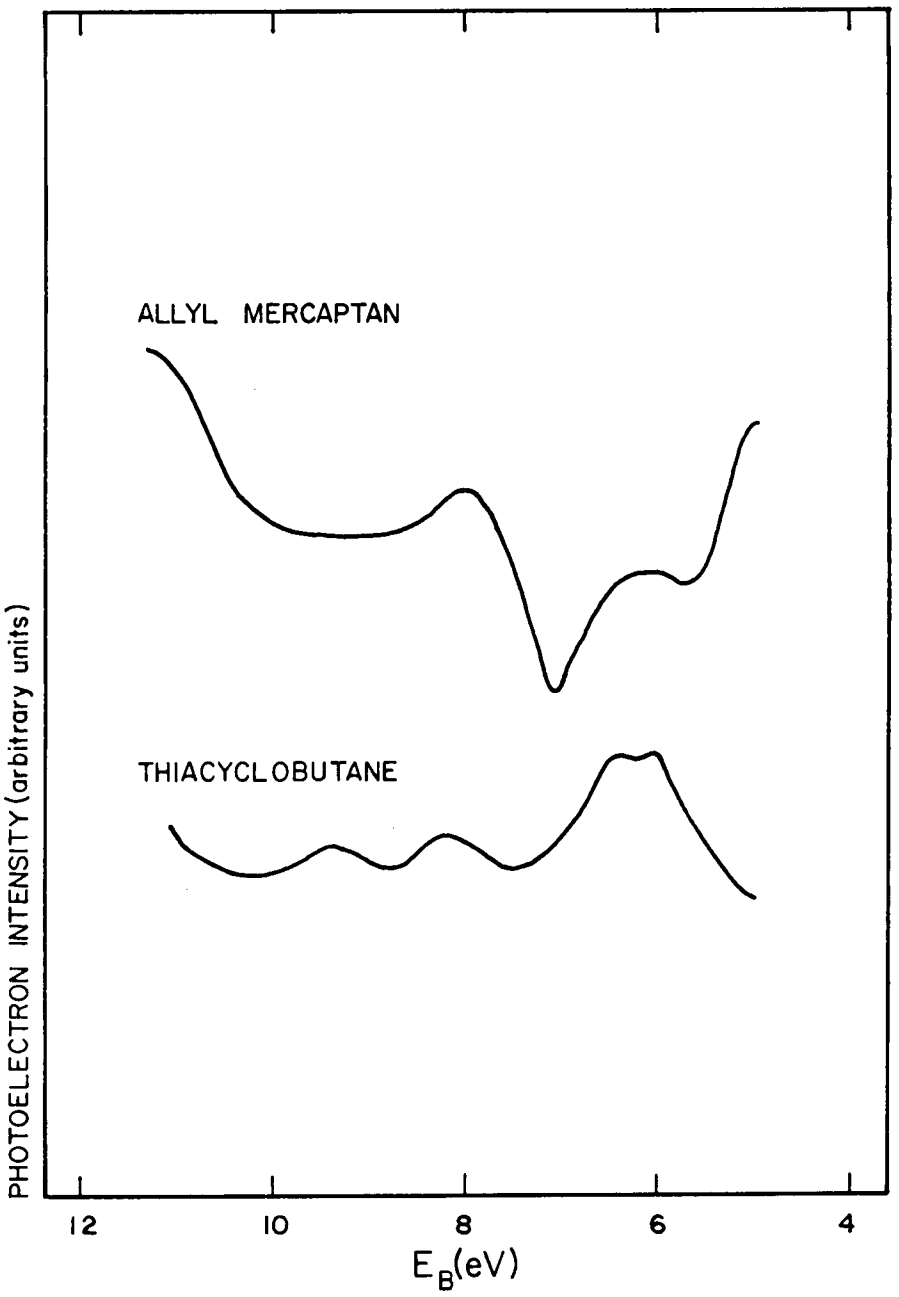


Figure 14. UPS comparison of allyl mercaptan to thiacyclobutane.

Figure 15 shows the comparison of thiophene and diethyl sulfide to thiacyclopentane. The spectra were analyzed for the number of valence bands which had energies above 5 eV, for the band maxima locations, for the intensities of the individual bands as well as for angular variations of the molecular bands. All studies seemed to show that these possible decomposition products were not present on the surface.

Thiacyclopropane was also adsorbed onto Cu(110). All evidence seemed to show that it decomposed to ethylene and sulfur, whereupon the ethylene then desorbed from the surface. The UPS spectra of thiacyclopropane can be found in Figure 16. They are very similar to the spectra of sulfur atoms adsorbed onto copper as shown in the literature.[86] The gas phase UPS spectrum of thiacyclopropane, which was presented previously (Figure 3, page 50) has no resemblance to the difference spectrum present for the three member ring. XPS results which will be shown later in this chapter for a 50 L exposure of thiacyclopropane revealed a surface 66% covered with sulfur and no trace of carbon was found within experimental limits of the equipment.

F. Angular Dependent UPS Spectra

The angular dependent spectra of the sulfur heterocyclic molecules will be presented in this section. Only the portion of the individual difference spectra at each angle for each molecule which does not mix

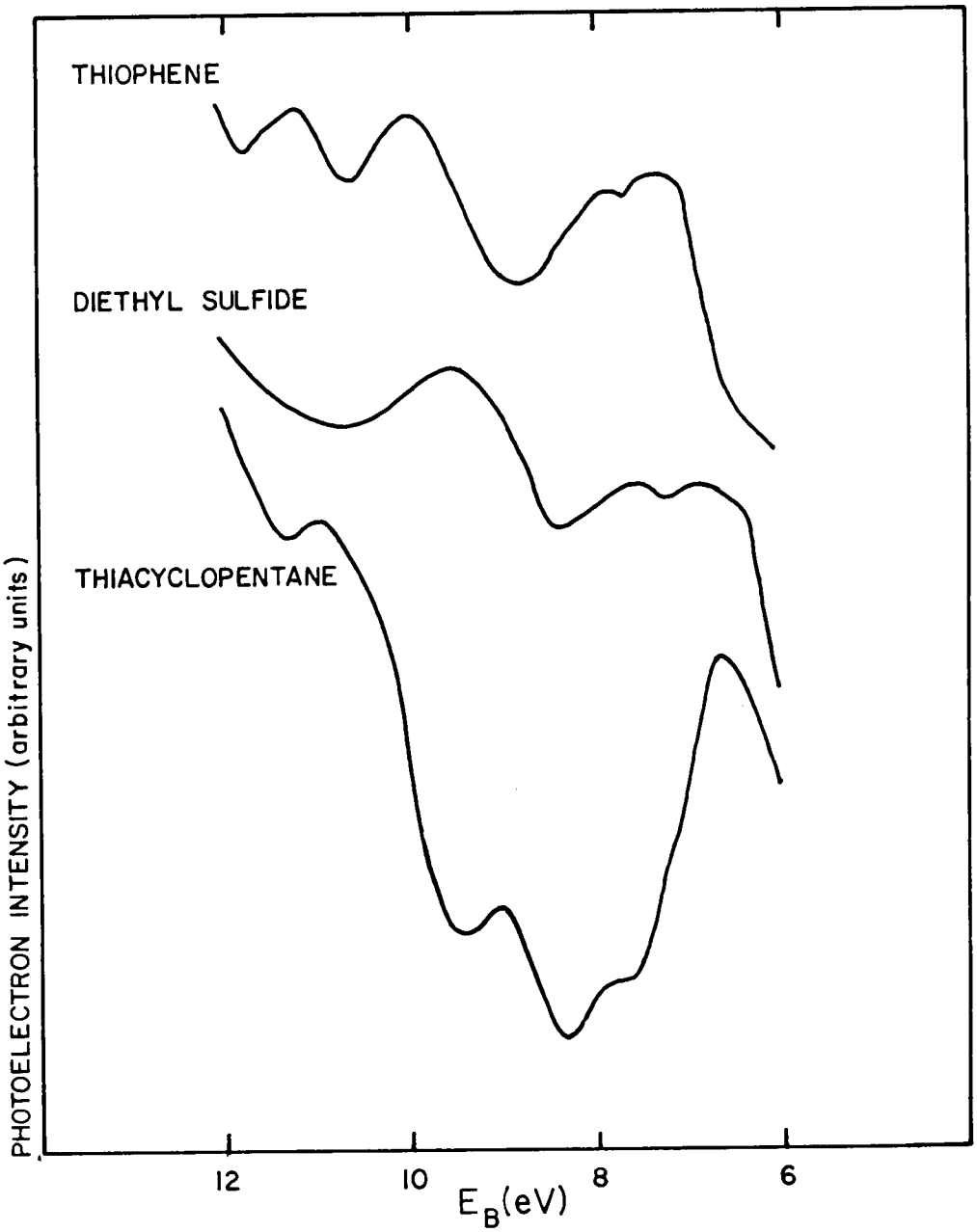


Figure 15. UPS comparison of thiophene and diethyl sulfide to thiacyclopentane.

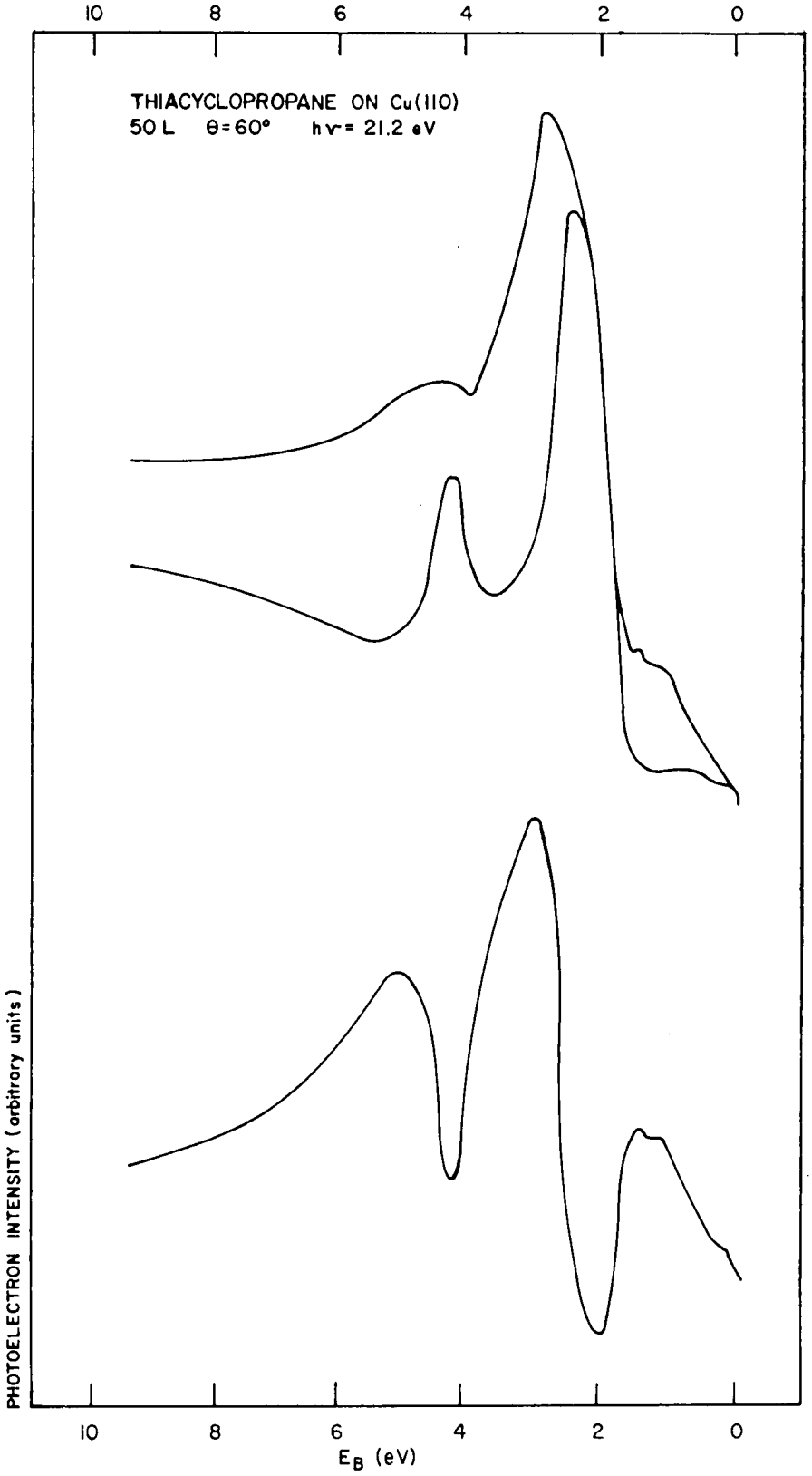


Figure 16. Difference spectrum for thiacyclopropane on Cu(110).

with the d band will be presented. Because of the fact that thiacyclopropane decomposed on copper, its angular dependent spectra will not be presented since the actual adsorbed species on the surface is not known. Figures 17-19 correspond to the angular dependent spectra of thiacyclobutane, thiacyclopentane, and thiacyclohexane respectively. All of the molecular bands in each figure display an intensity variation with angle. In general, the low angle spectra seem to have a propensity for increased band intensity as compared to the other respective angles for certain orbitals. The binding energy scale of these spectra have been referenced to the Fermi level and the change in energy per change in detector channel calibration in the presented molecular region was found to be fairly constant when the Ar calibration curve was consulted, thus an almost uniform binding energy scale results. Angular dependent spectra for a particular adsorbate may vary depending on the amount of surface coverage. That is, effects such as adsorbate-adsorbate interactions or surface bonding site variations could cause a change in the angular dependence spectra.

G. XPS Spectra and Analysis

X-ray photoelectron spectroscopic results were measured after adsorption of thiacyclopropane, thiacyclobutane, and thiacyclopentane had been adsorbed individually onto Cu(110). Figures 20 and 21 depict the unsmoothed C1S, S2P/XPS results for thiacyclopropane

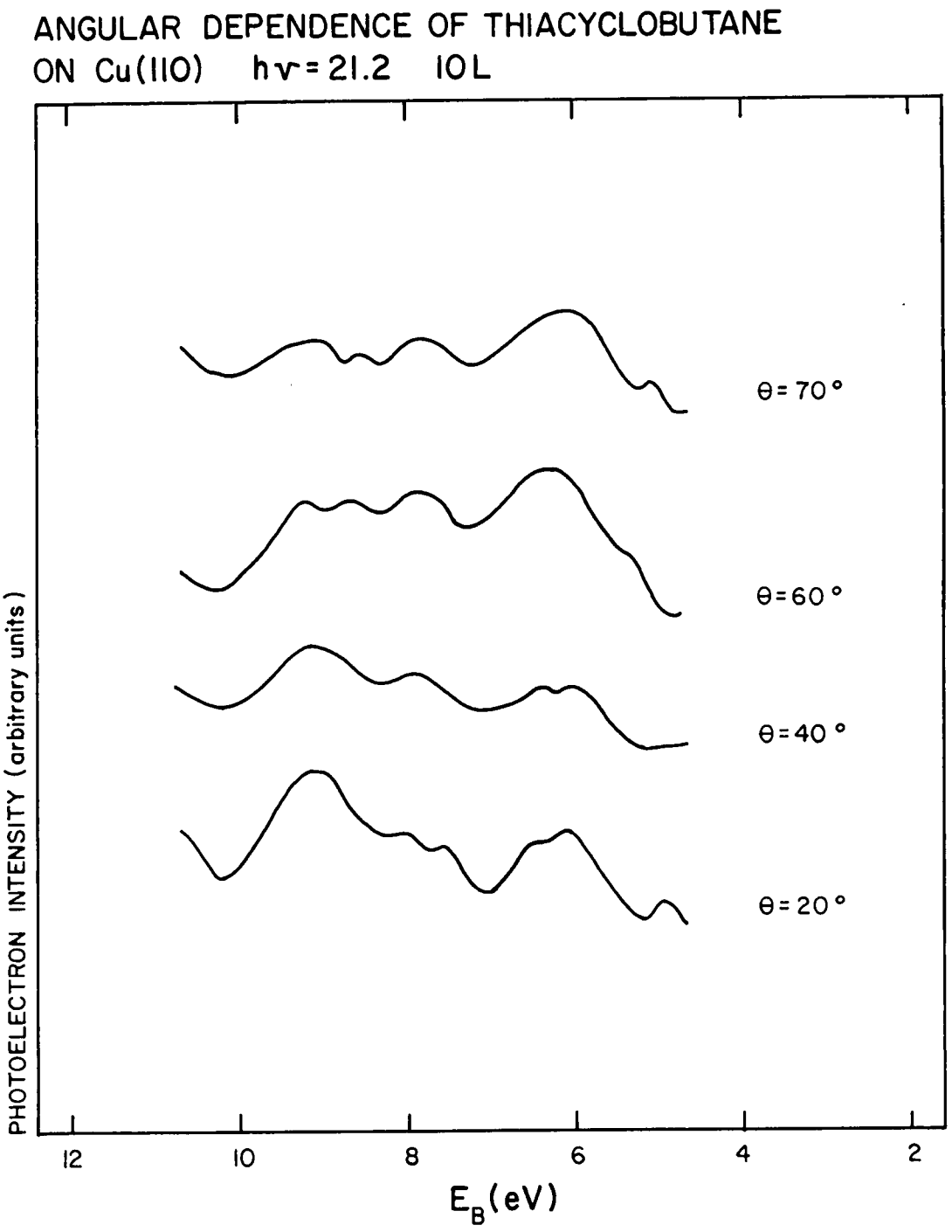


Figure 17. Angle dependent UPS results for thiacyclobutane on Cu(110).

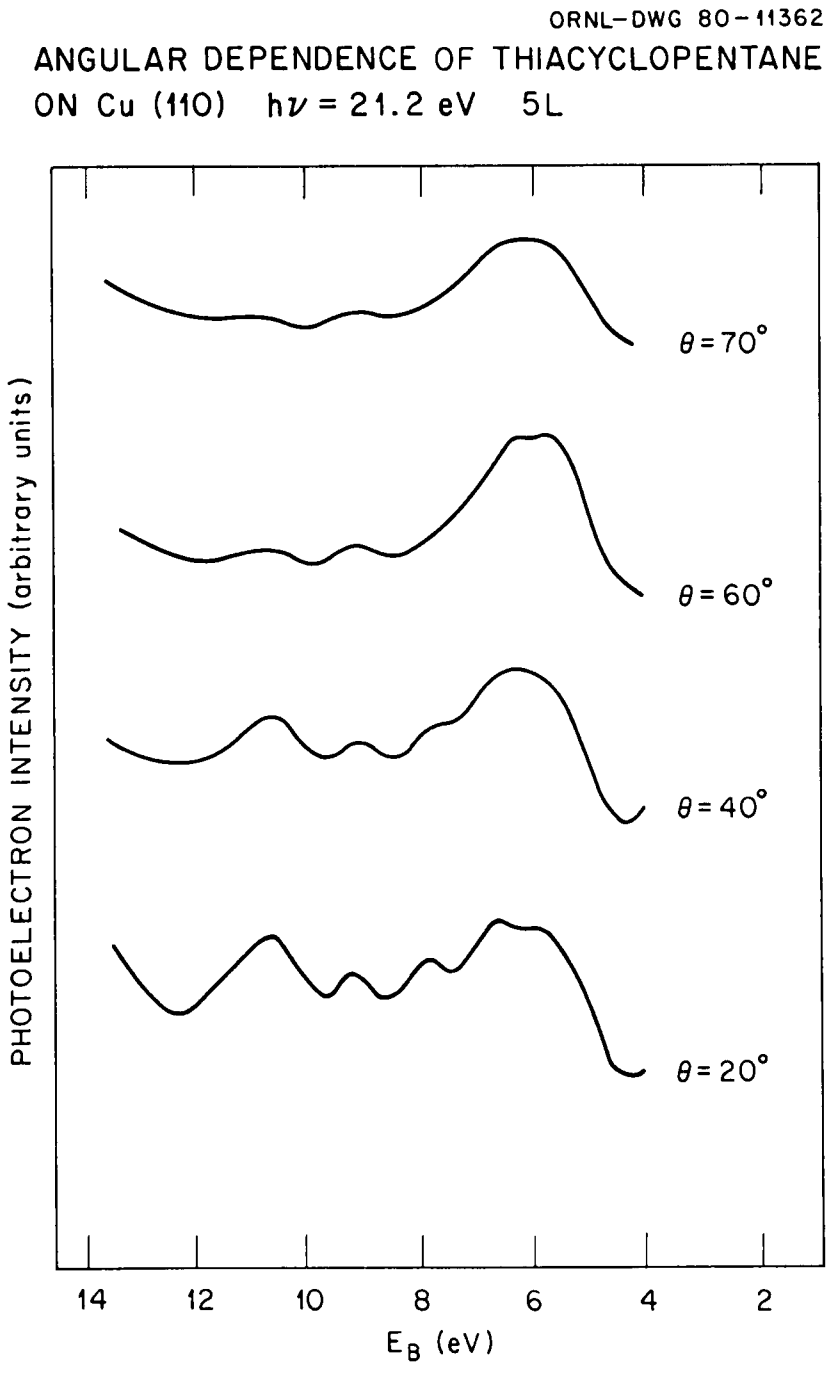


Figure 18. Angle dependent UPS results for thiacyclopentane on Cu(110).

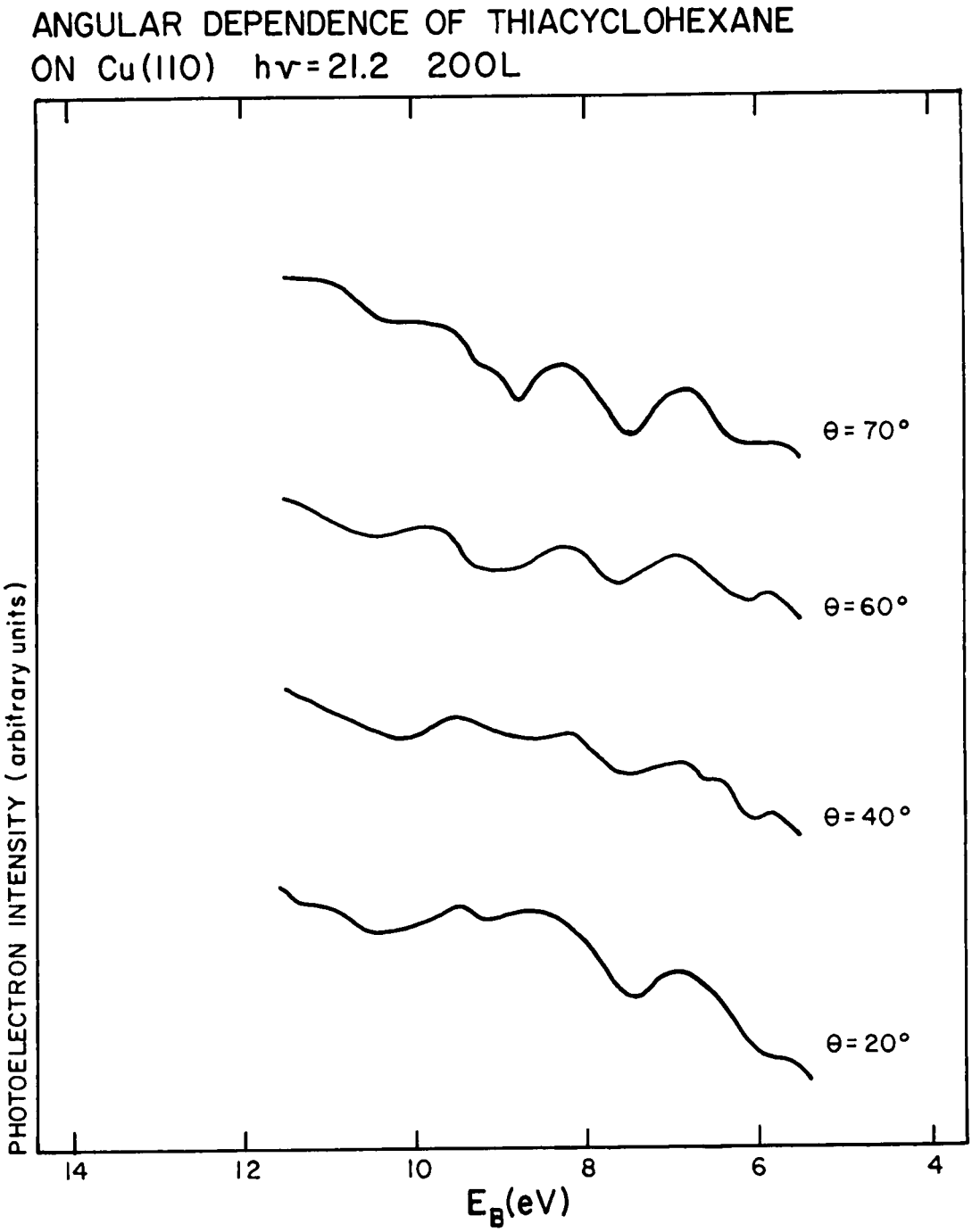


Figure 19. Angle dependent UPS results for thiacyclohexane on Cu(110).

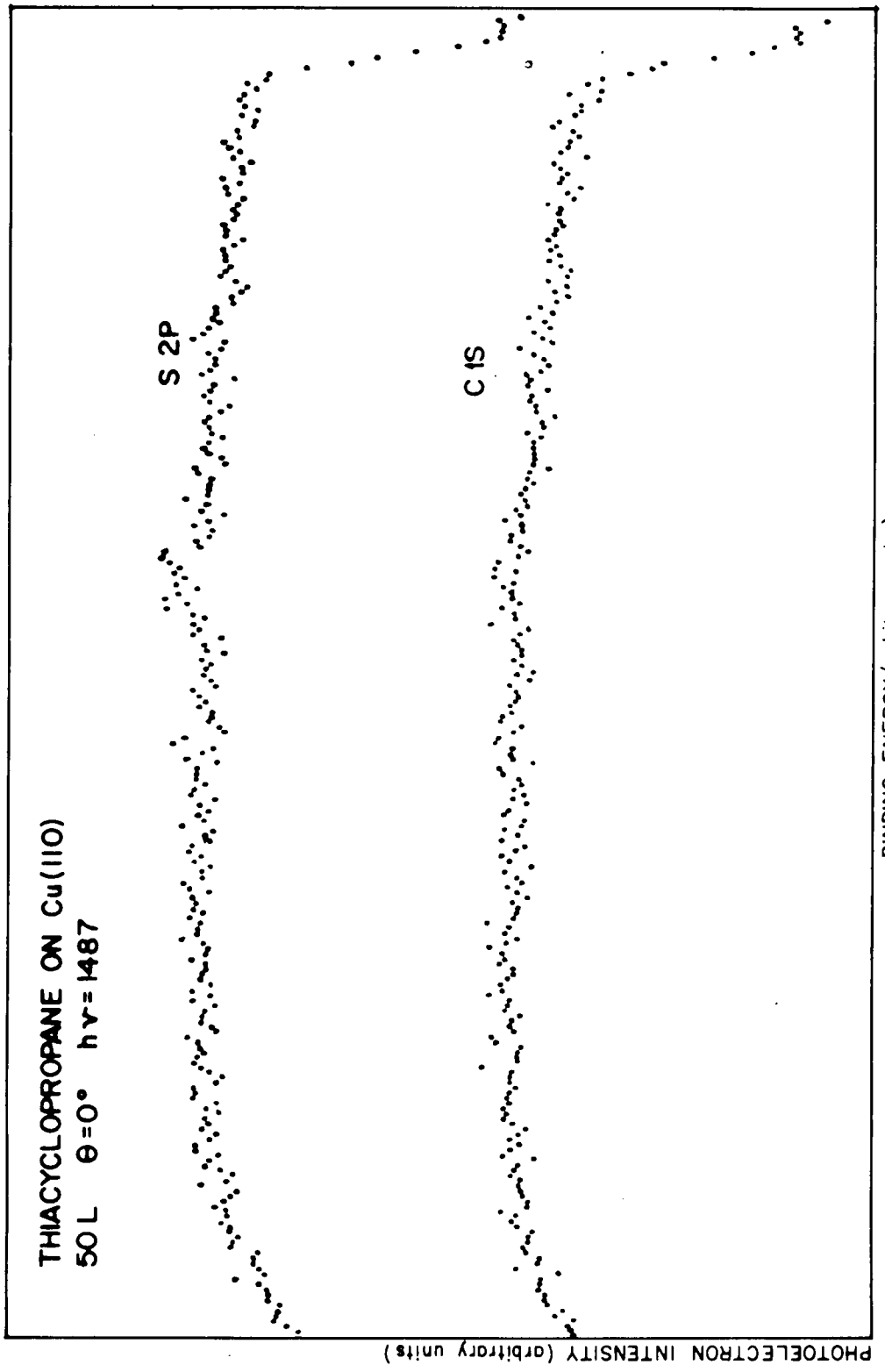


Figure 20. C1S and S2P spectra of thiacyclopropane after adsorption onto Cu(110).

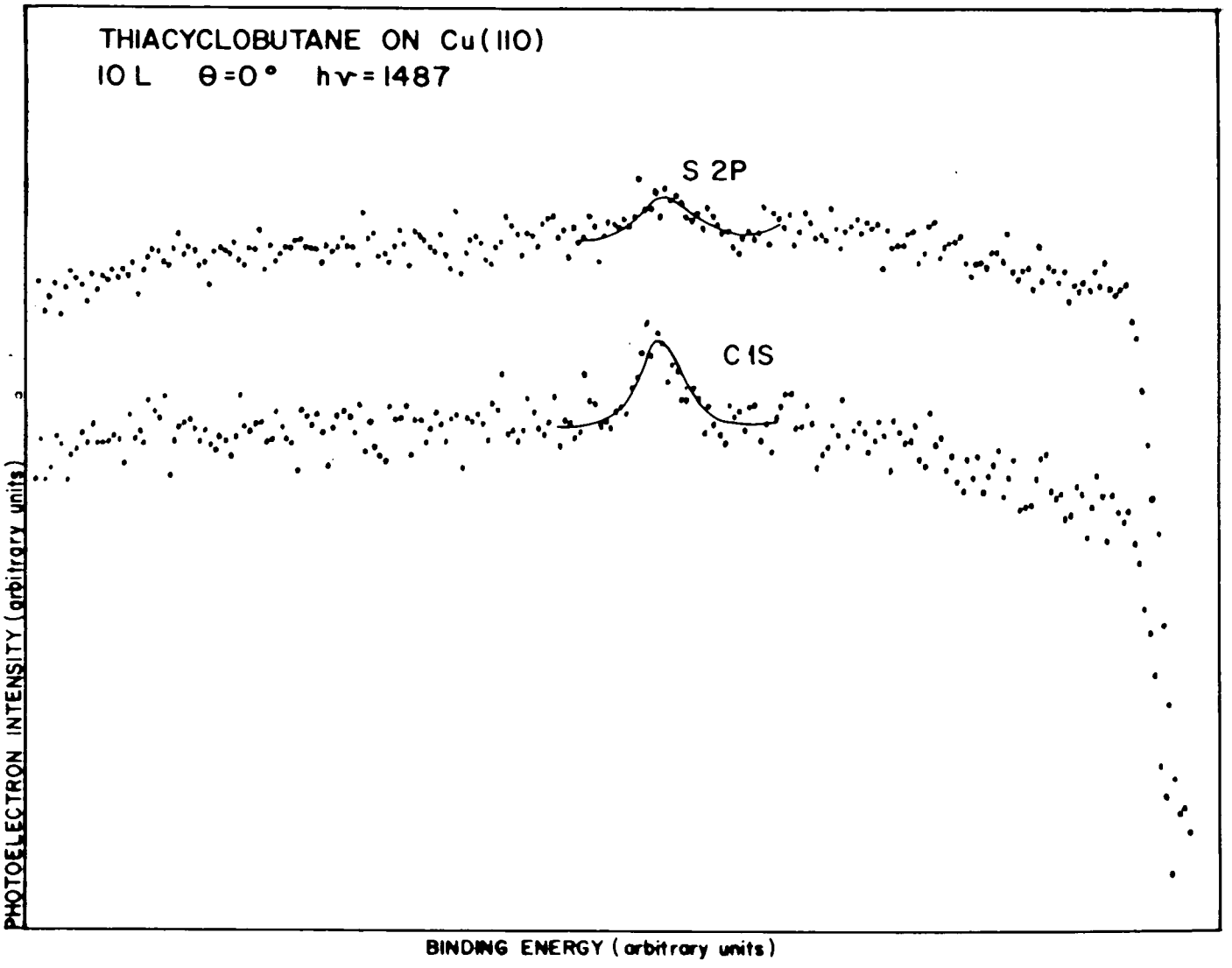


Figure 21. C1S and S2P spectra of thiacyclobutane after adsorption onto Cu(110).

and thiacyclobutane respectively. These two adsorbates were selected as example spectra for two reasons: (1) to show that no carbon can be found in the spectra of the three member ring, thus providing evidence of decomposition as well as showing the possible errors inherent in measuring small XPS peak areas, (2) to contrast the best XPS results obtained in this work, when adsorption does take place, with the three member ring results. Figures 22 and 23 depict the unsmoothed XPS results for copper after adsorption with thiacyclopropane and after adsorption with thiacyclobutane respectively. Integration of the XPS results provided a measure of the area under the bands in each spectrum. The ratios of these areas could then be substituted for the ratios of the respective photoelectron intensity values after proper scale factors were incorporated. With these ratios and the proper X-ray photoelectron cross sections for carbon, sulfur and copper, the ratios of carbon to sulfur, carbon to copper, and sulfur to copper could be calculated using the following relation:

$$\# = \frac{A(X) \cdot t(Cu) \cdot K.E.(X) \cdot \sigma(Cu) \cdot D(Cu) \cdot N \cdot \lambda(Cu)}{A(Cu) \cdot t(X) \cdot K.E.(Cu) \cdot \sigma(X) \cdot M.W.(Cu)}$$

where # $\equiv$ relative number of atoms of a given element (X) per cm^2; A(X), A(Cu) $\equiv$ areas of the element band, or copper band; t $\equiv$ counting time; K.E. $\equiv$ Kinetic Energy; $\sigma \equiv$ photoelectron cross section; D $\equiv$ density; N $\equiv$ Avogadro's Number; $\lambda \equiv$ mean free path; M.W. $\equiv$ Atomic Weight.

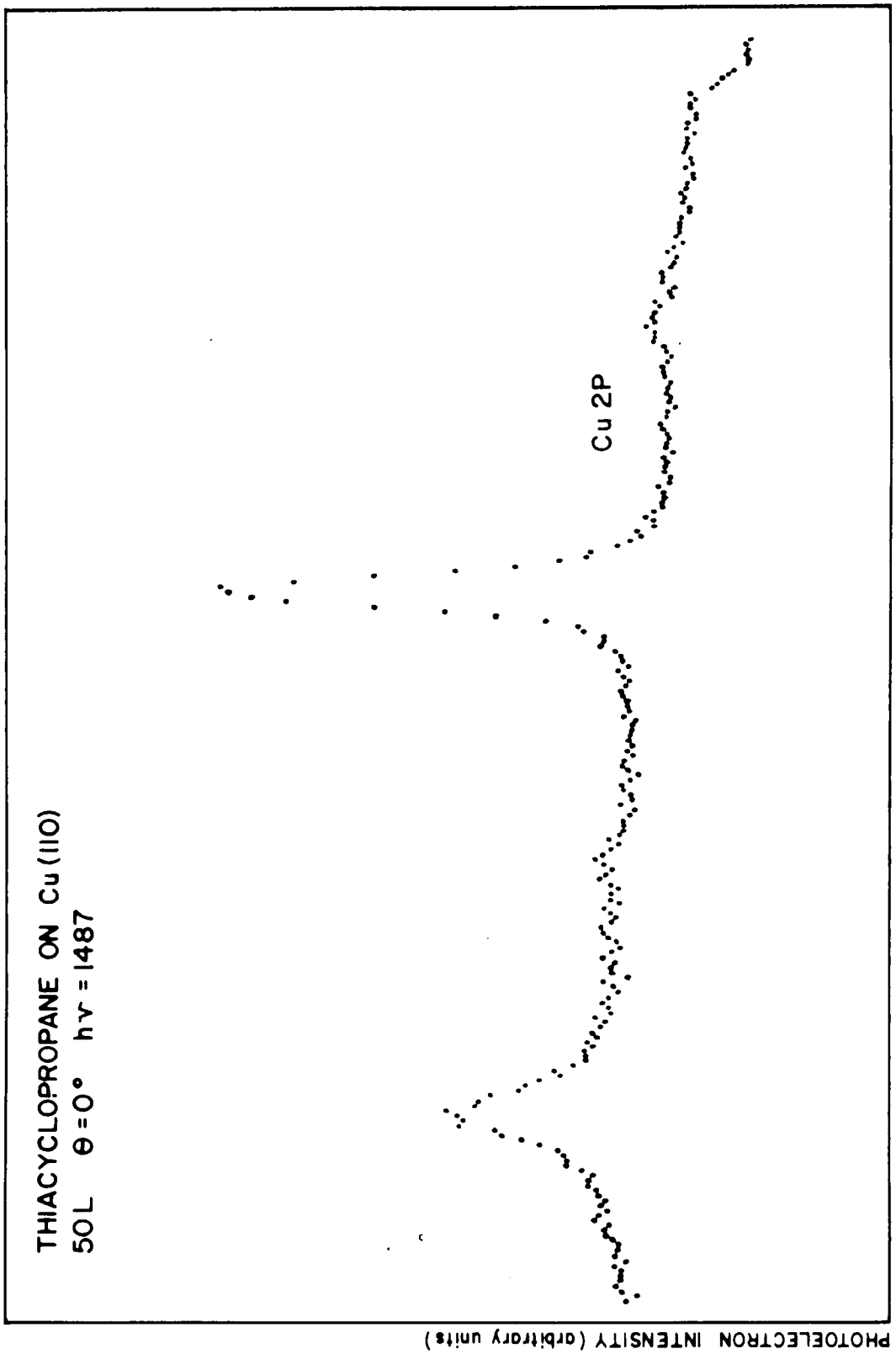


Figure 22. Cu 2P spectrum of copper after adsorption of thiacyclopropane.

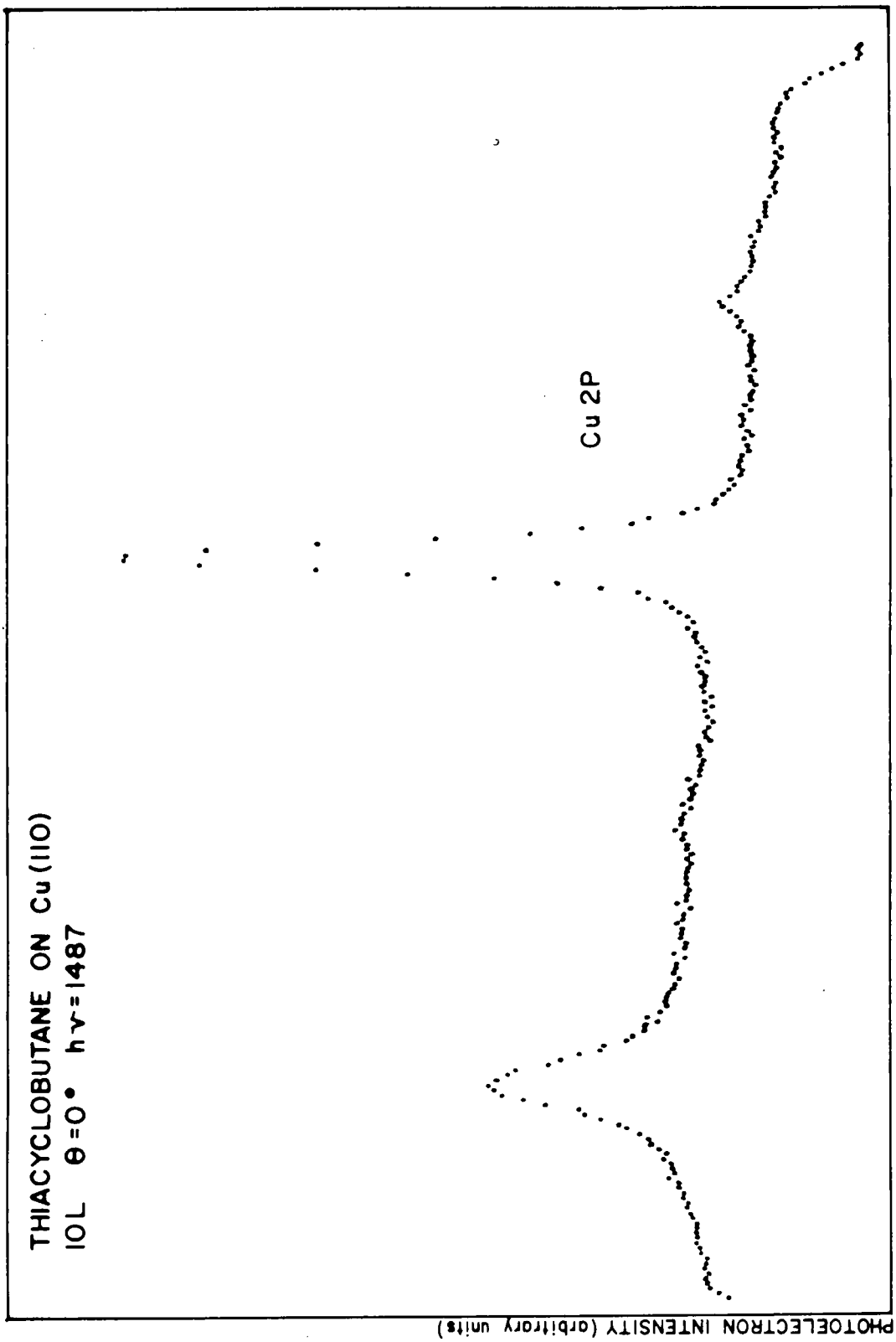


Figure 23. Cu 2P spectrum of copper after adsorption of thiacyclobutane.

The XPS spectra for thiacyclobutane presented earlier will now be analyzed:

A(Cu) = 72,980
A(C1S) = 1,400
A(S2P) = 1,794
} area under the XPS bands from computer integration

t(Cu) = 500 sec
t(C1S) = 3000 sec
t(S2P) = 6000 sec

λ = 11 Å
D = 8.92 g/cm^3
M.W. = 63.5 g/mole
N = 6.024×10^{23} atoms/mole

The values of σ were taken from reference 87; the values of K.E. were obtained from reference 88.

$$\#S \text{ atoms/cm}^2 = 3.87 \times 10^{14} \text{ atoms/cm}^2,$$

$$\#C \text{ atoms/cm}^2 = 1.08 \times 10^{15} \text{ atoms/cm}^2$$

implies that $C_{2.8}H_xS$ is the empirical formula as compared to C_3H_xS as the theoretical formula. Due to the fact that the number of sulfur atoms is equivalent to the number of molecules present, the number of adsorbate molecules/cm^2 = 3.87×10^{14}. The coverage of the surface can be calculated if the number of surface sites per unit area is known. For a single crystal the calculation of the number of surface sites is trivial. If the crystal lattice spacings are known (for Cu(110) 3.61 Å by 2.55 Å) then by multiplying the spacings together and converting from Å to cm the area of one surface site is calculated, but the inverse of this quantity is the number of sites per cm^2. Thus for Cu(110) the number of surface sites per cm^2 = 1.0863×10^{15} sites/cm^2. Thus for the four member ring approximately one in three surface sites were covered assuming one molecule per site or 36%

of the surface was covered. For the five member ring, one in five surface sites were covered or 20% of the surface was covered. Upon decomposition of the three member ring, the sulfur to copper ratio was measured and the surface coverage by sulfur atoms was found to be in one-and-one-half sites covered or 66% of the surfaces was covered.

CHAPTER IV

DISCUSSION

A. Discussion of Adsorbate-Surface Bonding Models

The overall model for the heterogeneous solid surface to gas phase adsorbate bonding process as studied by UPS is composed of three separate models. One model studies the theoretical path of the surface-adsorbate system from first interaction to the equilibrium configuration of the system.[89] The second model studies the qualitative results obtainable from the surface-adsorbate system while at equilibrium by means of ultraviolet photoelectron spectroscopy.[70] The third model attempts to obtain quantitative results by means of ultraviolet photoelectron spectroscopy from a vast number of empirical studies and correlations.[54] Each of these models will be briefly described and all three will be used in the interpretation of the spectra presented in this work.

Lundqvist et al.[89] present a theoretical discussion of the processes which take place during adsorbate to surface bonding. The authors arrange metals into groups depending upon their ability to break chemical bonds and catalyze chemical reactions. The authors explain that the reactivity of metals is composed of two parts, the metal's ability to destabilize the reactants and the metal's ability to stabilize the products. Each metal has a balance of these effects. The authors' model suggests that as a gas phase adsorbate approaches

a surface, interaction of the adsorbate with the surface conduction electrons causes large shifts in filled orbitals to levels above the Fermi level and unfilled orbitals to levels below the Fermi level from both the surface and the adsorbate. Thus the Fermi level electronic system then relaxes and in doing so emits photons or auger electrons. In this way adsorbates lose kinetic energy and become adsorbed on the surface. The shifts in adsorbate energy levels once the system has come to equilibrium are determined by the type of bond formed, and the types of orbitals participating in the bonding. In the case of adsorbates bonding to copper, since copper has no unfilled d orbitals, the adsorbate to surface bond should be rather weak. The stability of the adsorbate on the surface depends on the filling of molecular antibonding orbitals which fall below the Fermi level upon bonding. The authors picture adsorbate decomposition as molecules drowning in a sea of conduction electrons where the surface of the sea is the Fermi level. This model treats orbital energy changes in both metal orbitals and adsorbate orbitals as due to equilibrium changes which lower the overall energy of the system. This model does not predict types of orbital shifts and does not suggest which shifts are surface induced, bulk induced, adsorbate induced, etc. This model also does not suggest that the equilibrium configuration of the adsorbates may be one of constant translation,[90] rotation, or vibration,[38,39,47,91] thus an interpretation of the equilibrium configuration of the adsorbates while on the surface is needed.

Many qualitative studies of the adsorbate-surface system can be found in the literature which deal specifically with the application of photoelectron spectroscopy to this system. The studies range from general overviews of photoelectron spectroscopy and the information obtainable concerning the adsorption system,[70] to the study of particular adsorbates on particular surfaces,[92] to theoretical generation of the subtracted spectra obtained from UPS studies.[93] Broughton and Perry[71] discuss the types of energy shifts which take place due to surface bonding and the problems of choosing a reference level. The authors state that adsorption generally results in some charge transfer between adsorbate and metal and thus the surface work function may be shifted. The authors also point out that changes in adsorbate orbitals will occur due to chemical interaction with the surface (lone pair stabilization) as well as orbital energy changes due to interaction of the adsorbates with the surface conduction band (relaxation energy changes). Examples of these types of changes can be found in the literature. Bandy et al.[61] found the lone pair stabilization for pyridine on Cu(110) to be $\sim$0.9 eV. The authors found no shift in any other molecular orbitals from their relative gas phase band-separation energy differences. Whereas for pyridine on ZnO($1\bar{1}00$), Lüth et al.[57] found that not only the lone pair orbital was shifted due to bonding to the surface, but also the aromatic π orbital was shifted. This suggests that ZnO may not be a d^{10} system but may have some unfilled d orbital character which then can interact with the π systems of pyridine. Rubloff et al.[55] suggest

that the relaxation energy shift is uniform for all the adsorbate orbitals. But in a different article, Rubloff et al.[63] list over 50 studies where relaxation energy shifts are uniform for all the adsorbate orbitals and then go on to report some deviations from this uniform shift trend. The authors used molecular orbital calculations to show that adsorbates with bands having large atomic character show nonuniform relaxation energy shifts, but these are usually bands having high binding energies. Thus the authors suggest that molecular orbital calculations are needed to predict which adsorbates might exhibit this nonuniform effect.

Brucker and Rhodin[54] present a model for a quantitative method to interpret UPS results. The two authors suggest another means to change the orbital energy of adsorbate bands, the molecular environment the surface. Symmetry, shape, and vibrational changes due to interaction with the surface can all affect the orbital energies of the adsorbates (not to mention adsorbate decomposition[60]). Symmetry studies can be used to model interaction with the surface and possible bonding sites, but cannot give bond energy or bond type information.[94] Wendelken and Úlenla[95] pointed out that coverage can also affect the position of the adsorbates on the surface and thus changes in binding energy can accompany changes from one type of surface site to another.

Due to the large number and complexity of processes which can affect orbital energy levels of adsorbates, Brucker and Rhodin chose to study the changes in relaxation energy and lone pair stabilization energy with increased adsorbate to surface bond strength. The authors

suggested that if, upon adsorption, the adsorbate levels show a uniform relaxation shift but no stabilization of the nonbonding valence bands, the bonding taking place is physical adsorption. If upon adsorption a uniform relaxation shift is found which is accompanied by a stabilization of the orbital forming the adsorbate to surface bond, weak chemisorption is taking place. The authors then go on to suggest that if the adsorbate to surface bond is strong enough to destabilize some of the adsorbate molecular orbitals, as well as stabilize the adsorbate to surface bond and cause a uniform relaxation, the adsorbate is strongly chemisorbed to the surface.

This type of quantitative analysis falls short of actually calculating heats of adsorption, but can be used to categorize adsorbate to surface bond strengths. Somorjai and Van Hove[5] do quantize the regions of chemical and physical adsorption. The authors state that gas-surface systems that are characterized by weak interactions (i.e., $\Delta H_{ads} < 15$ Kcal/mole accompanied by short residence times), that require low temperature and high pressure conditions are called physical adsorption systems. Adsorbates that are characterized by stronger chemical interactions ($\Delta H_{ads} \geq 15$ Kcal/mole) where adsorption takes place at ambient temperatures and low pressures, $\leq 10^{-4}$ Pa, are called chemisorbed systems. The authors then point out that actual gas-surface systems exhibit a continuous spectrum of properties between these two extremes.

Other UPS studies relating lone pair stabilization to heats of adsorption of more quantitative nature have been carried out

by Lüth et al.[64] The authors presented a semi-empirical relation which they used to predict the heat of adsorption of oxygen on polycrystalline palladium.

The models of Lundqvist et al. and Brucker and Rhodin will be used to analyze the experimental UPS results presented in this work.

B. Interpretation of Ultraviolet Photoelectron Spectra in Light of the Presented Models

The discussion of the results presented in this work will follow the pattern set in the results section. First a discussion of the clean copper spectra, followed by a discussion of the covered copper spectra and then a detailed discussion of the difference spectra as compared to the respective gas phase results, will be presented. A general discussion of the overall adsorbate-surface system will also be presented along with a discussion of the decomposition of thiacyclopropane on copper.

A comparison of high temperature gas phase copper UPS results[96] to the UPS results on Cu(110) solid surface would show the range of the copper d bands in the gas phase results as less than 1 eV. The gas phase d bands are also sharp and resolved, as compared to the solid copper d band which has a width of ∿4.5 eV and is one continuous band of mixed levels. Also the gas phase copper atoms are no longer affected by a surface work function and therefore the d orbitals start at ∿10.5 eV on the gas phase binding energy scale. This analysis was presented to show the reader the complexity of the interpretation of

solid state metal UPS results which is due mainly to delocalization of metallic orbitals as well as closeness of orbital energies due to the ordered crystal structure environment.

A high-resolution UPS study of Cu(110) by Courths et al.[97] suggested that the photoemission from the (110) crystal face of copper using a photon excitation energy of 21.2 eV is a special case due to a Brillouin band gap which causes a forbidden emission from the (110) bulk atoms. Thus the intensity from the (110) copper spectra is an order of magnitude lower than that from the (111) or (100) surfaces of copper. The authors then state that the normal mean free path of electrons in Cu(110) would be 10 Å. But if the measured UPS spectrum arises from orbitals localized on the surface of copper, the mean free path may only be 4 Å. The authors point out that if the spectrum is from the upper surface layers, the UPS spectrum would represent the surface density of states. The authors then showed that the high resolution spectrum of Cu(110) does show that all of the d band peaks are in regions of high density of states calculated for copper, but that the intensities do not correspond to those predicted in the calculations. Eastman et al.[10] show that the mean free path of copper decreases from 15 Å to 11 Å with an excitation photon energy change from 10.5 eV to 13.5 eV. But the Brillouin gap only affects bulk photoelectron intensities when photon energies are between 14 eV to 22 eV.

Pendry and Hopkinson[98] have suggested that the valence band structure of copper as observed by photoelectron spectroscopy is a complicated mixture of interband transitions conserving momentum

normal to the surface, density of state effects, and occasionally some surface state structure. The authors also point out that surface state structure in copper tends to be swamped by a rich mass of structure coming from the bulk states.

Heimann et al.[14] reported that d band surface states do exist at the top of the d band of Cu(100) and Cu(111). They also stated that surface states in other noble metals usually are observed in the upper s bands. The authors stated that for Cu(110) they could not find any d band surface states using He(I) and Ne(I) photons. Thiry et al.[11] conducted studies on Cu(110) using synchrotron radiation from 15 eV to 100 eV and also found that the Cu(110) photoelectron spectra showed no evidence for surface states in this energy range. Sagurton and Shevchik[8] stated that no surface states at any photon energies should be observed on copper since the peaks near the Fermi level reported by other researchers are actually due to bulk transitions. The authors then went on to explain how they came to these conclusions using theoretical calculations to generate ARUPS spectra and studying the origins of the bands near the Fermi energy. These analyses were presented to suggest that surface states do not exist in the clean copper(110) spectra.

Although most authors[14] leave out the possibility of optical effects such as diffraction or refraction at the surface, Williams et al.[7] suggest that these effects may well add to measured UPS spectra. The authors then went on to show evidence that refraction of photoelectrons does take place on copper single crystals. The authors suggest that

refractive changes can be measured with change in the photon source to detector angle but did not address the problem of azimuthal changes in refraction. They also suggest that the UPS spectra obtained from Cu(110) using photon energies from 16 eV to 160 eV are mostly bulk bands.

From these discussions, it would seem that most of the clean copper signal comes from the bulk and that no surface states exist on Cu(110). In light of this and coverage studies performed during this work, in which it was found that the d band does not shift in energy or change shape with increased exposure to the adsorbates, the spectrum of clean copper was assumed to contain ∿100% bulk signal for the purpose of generating a difference spectrum. This subtracting out of the bulk contribution to the copper spectrum after exposure to an adsorbate was an attempt to resolve the bands which were added to the d band region of the covered spectrum due to adsorption. This added structure to the d band could contain both adsorbate induced changes in the d band as well as any lone pair orbitals which had shifted into the d band region. Thus it would seem that the d band region of an adsorbate covered surface contains electrons from three different sources. Some of the d band is still composed of unperturbed bulk electrons which had not changed shape but have changed in numbers, giving a smaller amount of contribution to the d band and it is this part that one attempts to subtract out. Another component of the d band would be the lone pair band of the adsorbate which was shifted into the band by the work function and/or the relaxation energy shift. If another d band component

exists, it would be composed of shifted d orbitals which had increased in intensity due to the adsorption process.

Upon adsorption of gases onto surfaces, the addition of molecular bands to the spectra and the complication of the d band are not the only effects taking place. The surface work functions could be modified, and since the chemical environment at the surface and at the adsorbate have changed, core spectral shifts may also take place in both the surface[99] and the adsorbate.[100] Work function changes vary from adsorbate to adsorbate but also vary with coverage. Delchar[85] reported that for oxygen on copper(110) the work function increased until it reached a maximum after 2000L had been added to the system. Benndorf et al.[101] and Habraken et al.[102] both suggest that the work function changes for the same system first increased until 100L was added and then decreased. Delchar reports a maximum work function shift of 0.7 eV where the other two authors report maximum shifts of only 0.4 eV. Benndorf et al. also list the change in work function with a 10L exposure to O_2 (0.2 eV). In this work, the work function changes could be measured to ±0.1 eV. None of the sulfur heterocycle adsorbates produced a measurable shift in work function. The work function changes were referenced from the Fermi level to the zero kinetic energy value of the binding energy. Any shift in this energy would represent a shift in work function.

When sulfur heterocyclic ring systems bond to the copper surface, they bond by donation of the sulfur 3p lone pair to empty copper 4s

or 4p orbitals. Lundqvist et al.[89] considered that since copper has a d^{10} structure, its d band would only have a small effect on primary bonding but could have considerable effect on back-bonding to empty adsorbate orbitals. This idea seems to be supported by many studies.[68] This electron pair donation can be envisioned from the UPS difference spectra presented in this work in the fact that the lone pair peak in each gas phase spectra has been shifted to the left in the respective difference spectra, i.e., to higher binding energies (suggesting a shift from a nonbonding orbital to a bonding orbital). This lone pair stabilization is not limited to adsorbate to surface bonding systems. Utsunomiya et al.[103] have studied hydrogen bonded complexes using gas phase photoelectron spectroscopy. They reported nonbonding orbital stabilizations of up to 3 eV using nitrogen containing bases. Weiner and Lattman[104] reported studies of gas phase transition metal complexes containing organosulfide ligands using UPS. They reported lone pair stabilization energies for two orbitals on the thioether ligands. The amount of stabilization for both orbitals was $\sim$1 eV.

A close inspection of the difference spectrum as compared to the gas phase spectrum for the four, five, and six member rings show no clear signs of destabilization of any of the molecular bands, which would suggest according to the Brucker-Rhodin model that all of these adsorbates are weakly chemisorbed to the (110) face of copper. Also according to the Brucker-Rhodin theory, the magnitudes of ΔE and ΔR would suggest that the four member ring is more strongly bound than the five member ring which is more strongly bound than the six member ring

[e.g., (ring, ΔE, ΔR): (four, 1.5, 1.75) > (five, 1.1, 1.35) > (six, 0.6, 0.75)]. The linear relationship between the relaxation energy shift and the lone pair stabilization energy shift may be only useful with heterocyclic compounds, or only with d^{10} metals, or only with a combination of the two. The relation does seem to give relatively good values of the work function.

The interpretation of the dashed areas of the difference spectra will be broken into two parts. The interpretation of the band at 3 eV in each spectrum is that it contains contributions from both the d band and adsorbate bands. The band near the Fermi edge will be interpreted as coming from an adsorbate virtual state which has been stabilized by the interaction of the adsorbate with the surface and has fallen below the Fermi level and thus has become populated. This last interpretation comes from the Lundqvist model.

The interpretation of the induced changes in the surface and in the adsorbate upon bonding starts with the suggested adsorbate to surface bond. Since p-p overlap is stronger than s-p overlap for a p orbital parallel to the surface, the 3p lone pair orbital on all of the adsorbates is suggested as interacting with the unfilled 4p orbitals of the copper surface to form a localized bond to the surface, even though the lowest unfilled orbitals of copper are s orbitals which usually form the adsorbate to copper bonds.[68] This donation of electron density to the surface causes the surface to build up charge.[105] This build-up of charge will limit coverage unless it is relieved; also, added charge to the surface will cause the work function of the surface

to change. From the presented experimental results one finds no measurable change in work function and therefore this donated charge must have been relieved by some mechanism in all of the exposure studies. The proposed explanation of this fact is that as the adsorbates approach the surface, the unfilled virtual orbitals of the adsorbates are shifted closer to the Fermi level. The lowest unoccupied band begins to fall below the Fermi level and thus becomes populated and electron density then flows from the surface back to the adsorbate thus the work function returns to the clean surface value. (Note: None of the adsorbate virtual states contain 3d contributions from the sulfur.[106,107]) This relief of charging may be envisioned as back-bonding of delocalized electrons to the adsorbate from the copper atoms. Tibbetts et al.[86] made the same suggestion for sulfur atoms adsorbed on Cu(100). The authors found a band at 1.3 eV and attributed it to shifted antibonding states. Adachi[108] reported a (DV-Xα) cluster calculation for sulfur adsorbed on copper. The calculated difference spectrum revealed that two sets of adsorbate bands were found. One set of bonding orbitals at 5 eV and one set of antibonding orbitals at 1.3 eV below the Fermi level. The calculation also showed a band at 3 eV which involved modifications to the copper d band. Gutmann[109] pointed out a process which may explain the peak at 3 eV in all of the difference spectra of this work. The author suggested that the surface of a crystal may be considered as an area of lattice distortion because the coordination number of a surface atom is smaller than that of a bulk atom. This imposes a lattice contraction within the surface area. The author

pointed out that this lattice contraction could be relieved by surface adsorption. This relief of lattice contraction should be independent of adsorbate and indeed other adsorbates on Cu(110) show a peak at 3 eV. Tibbets et al.[86] saw it for S on Cu(100), each of the adsorbates in this work showed a peak at 3 eV, Carlson et al.[60] saw a peak at 3 eV with simple alcohol adsorbates on Cu(110). The relief of surface contraction[68] could cause changes in surface atom positions, surface atom to bulk atom bond strengths, and also could cause localization of electron density around the surface atoms. Any of these effects could change the surface density of states and thus the d band, which would account for the band at 3 eV in the difference spectra. At this point, it is still not clear whether the peak at 3 eV is directly due to chemisorptive surface bonding or simply due to coverage relief of surface distortion. A simple temperature variation of the adsorbate to surface bond from physical to chemical adsorption might solve the question of chemisorptive versus coverage effects.

A close inspection of the spectra presented for the four, five, and six member rings show some small details which should be brought out. A close look at the difference spectrum for thiacyclobutane as compared to the gas phase spectrum will reveal that some of the higher binding energy peaks seem to have shifted slightly. This may be due to the insufficient counting time to resolve the bands or due to the fact than an apparent shift has taken place. Three reasons could account for the shift of the four member ring bands. For one, the four member ring may be strongly chemisorbed to the surface, as propounded by the

Brucker-Rhodin model. Secondly, the shifts may be due to changes in ring strain balancing forces. Or the band shifts may be due to changes in molecular symmetry on the surface.[38]

The next detail that should be pointed out is the difference between the six member ring clean copper spectra and that of the four and five member ring clean copper spectra. The six member ring spectrum is substantially different from the other clean spectra at the same angle and this is due to the centering of the copper crystal in the He(I) photon beam. In the six member ring spectrum, the x and y coordinates of the manual manipulator were set to maximize the spectrum at $\theta = 30°$. The x and y settings were then untouched. Thus as the angle diverged from 30° the measured spectra diverged from the spectra which would have been recorded had each angle been optimized. All of the copper spectra presented for the four and five member rings were optimized at all angle settings. This unoptimization of the six member ring spectra did not seem to affect the difference spectrum and the actual divergence was not noticeable until angles became larger than 50°.

The last detail of the spectra which should be discussed is the difference in the suppressions of the d band with exposure to the adsorbates. The spectra seem to imply that the four and six member rings as compared to the five member ring, have more coverage and therefore more suppression, but if one looks at the intensity of the molecular bands for all three spectra, there are no large intensity differences which would be visible if coverage was the major source of suppression. In fact, there may be a number of reasons why variable

suppression takes place like changes in de-excitation cross sections for bulk electrons, changes in emission or adsorption cross sections, or optical effects like surface refraction or diffraction. But another possibility to be considered is size of the molecules and/or vibrational effects of adsorbates. The four[38,39] and the six[47] member rings probably undergo ring puckering on the surface as well as rotation; these motions could influence the apparent size of the adsorbates as well as affect the surface layers under the adsorbates. (The five member ring does not seem to have a double minimum vibrational potential surface.) The actual verification of the effects may have to wait for calculational simulation of the processes or calculations of the unsubtracted UPS results.

It is interesting to note that the order of lone pair stabilization and the order of greatest relaxation shifts are the same as the order of basicities for the cyclic sulfide adsorbates. Stille and Empen[30] list the basicities of the ring system as 4 > 3 > 5 > 6 as measured from UV/ charge transfer measurements and by NMR shifts, but the order 5 > 6 > 4 > 3 is found for basicities in certain solutions. Many other studies of the basicities of these adsorbates have been performed, the following references are a few of the many.[110-112] Of further note is the report by Cheetham[113] which lists the base strength of pyridine and the base strength of thiacyclopentane as being approximately the same. If we refer to the ΔR versus ΔE plot, page 71, one finds the relaxation energies and lone pair stabilization energies for these two adsorbates are almost the same also. The basicity of nitrogen is the major reason

it acts more like thiacyclopentane than thiophene even though the first ionization potentials of pyridine and thiophene are equivalent (9 eV)[114] and that their orbital lone pair bond structures are very similar.[115] The hybridization of the nitrogen s and p atomic orbitals to form the lone pair in pyridine as compared to the unhybridized 3s sulfur lone pair orbital in thiophene probably accounts for the variation in basicities.

According to Smith[116] the application of angle-resolved photoemission spectroscopy to the study of surface systems can give two basic kinds of information: (1) the positions of atoms in the surface and in adsorbed species, (2) the nature of the electronic states characteristic of free surfaces and those involved in the chemical binding of adsorbates. He also points out that a theory or model of the photoemission process is required to bridge the gap between experimental photoemission data and the desired surface bonding information. Many theories exist for extraction of information from angle resolved spectra, though calculational procedures vary. Grimm et al.[117] use X-α scattered wave calculations to study the asymmetry parameters of gas phase molecules. Kambe and Scheffler[118] use a Green's function approach to analyze ARUPS results. Li et al.[119] combine the two approaches by using a Green's function formulation but cluster wave functions obtained from the self-consistent X-α scattered wave method.

Interpretation of the ARUPS data presented in this work will be limited to the fact that since all of the adsorbate bands have shown angular variation with a change in azimuthal angle, the adsorbates must

be partially oriented on the Cu(110) surface, because randomly oriented molecules would cause an equal distribution of ejected electrons at every angle.

C. Discussion of XPS and UPS Results for Thiacyclopropane

In support of the XPS evidence that thiacyclopropane decomposes on the surface, Huynh et al.[120] reported that copper catalyzes the ring opening of thiacyclopropane in THF solutions. Also in support of the XPS results that no carbon could be found on copper after exposure to thiacyclopropane, Itoh and Kunz[121] reported that ethylene, the most probable decomposition product besides sulfur, was not stable on copper in their ab initio calculations having negative binding energies to the copper surface.

Adachi[108] suggested that according to his calculations the bonding of sulfur to copper surfaces entails donation of 3s electron density to the surface followed by surface back-bonding to the 3p orbitals of sulfur. The calculations suggested that a net donation of electron density to the surface should take place. The work function change of the Cu surface measured after decomposition of thiacyclopropane would seem to be inconsistent with the calculation. The UPS results showed an increase in the work function of 0.3 eV ± 0.1 eV. Tibbetts et al.[86] also measured a work function change for sulfur adsorbed onto Cu(100), they measured a work function shift of 0.28 eV.

Domange[122] suggested that for sulfur on Cu(110) at coverages larger than 50%, a two dimensional surface structure begins to appear. In this work, XPS data suggested that 66% of the surface of copper was

covered by sulfur and thus a two dimensional surface overlayer may have formed. Both Domange and Balsenc[75] stated that the surface atoms of copper should have shifted to accommodate this surface compound. Balsenc also points out that sulfur will preferentially bond to Cu(111) and Cu(100) over Cu(110) so the Cu(111) surface may contain a larger surface coverage of sulfur than the Cu(110) in our study.

D. Summary and Conclusions

Photoelectron spectra using He(I) radiation were presented for Cu(110) after exposure to thiacyclopropane, thiacyclobutane, thiacyclopentane, thiacyclohexane, diethyl sulfide, thiophene, and allyl mercaptan. The last three spectra were used as comparison spectra for decomposition studies. Difference spectra were generated for the three, four, five, and six member ring adsorbates. The difference spectra all seemed to have the same general band sets. From 1 to 2 eV a band suggested as coming from stabilized antibonding orbitals. A band at 3 eV suggested as being composed of perturbed d states as well as the stabilized lone pair orbitals of the adsorbates. The remainder of the bands were ascribed to the adsorbate. From the comparison of the difference spectra to the corresponding gas phase spectra for the four, five and six member rings, average lone pair stabilization energies were calculated as well as individual relaxation energy shifts for the three adsorbates. The values of ΔR and ΔE were for thiacyclobutane 1.75 eV and 1.5 eV, for thiacyclopentane 1.35 eV and 1.1 eV, for thiacyclohexane 0.75 eV and 0.6 eV. Similar values

for pyridine were taken to be 1.15 eV and 0.9 eV from reference 61. A linear plot of ΔR versus ΔE was found for these values. It was suggested that this linear relation may only hold for heterocyclic adsorbates or only for d^{10} transition metal surfaces. A plot of ϕ' versus ΔE was performed to obtain the intercept of the line which would seem to be the Cu(110) work function. The intercept was found to be 4.85 eV. Ring strain, adsorbate geometry, adsorbate site, adsorbate coverage were discussed as possible reasons for shifts in nonsurface bonding adsorbate orbitals. Strong chemisorption was discussed as a possible source for surface as well as adsorbate orbital shifts. Angular dependent spectra of the adsorbate bonds were presented to show that all of the adsorbates which were stable on the surface showed azimuthal angular dependence of orbital intensities which was interpreted as arising from the nonrandom orientation of the adsorbates on the surface. Al Kα X-ray photoelectron spectra were presented for the three and four member rings. XPS data was used to calculate percent surface coverages for the three (66% sulfur covered), four (36%) and five (20%) member rings. XPS results were used to confirm that thiacyclopropane had decomposed upon exposure to Cu(110).

The proposed models and empirical methods presented in this work were merely tools to try to understand the phenomenon of surface adsorption. Without further correlations with other surface measurements and detailed molecular orbital calculations, the actual chemical interactions taking place between these complex adsorbates and the Cu(110)

surface are still supposition. But some general conclusions can be drawn from the results presented in this work. The saturated sulfur heterocycles all bond to the copper surface by means of the nonbonding p orbital on the sulfur heteroatom. Thiacyclobutane seems to have a stronger bond to copper than thiacyclopentane which in turn seems to have a stronger bond to copper than thiacyclohexane. Relaxation energies as well as average lone pair stabilization energies seem to decrease in the order thiacyclobutane > thiacyclopentane > thiacyclohexane. All three adsorbates show angular dependency of spectral intensities, suggesting nonrandom orientation of the adsorbates on the Cu(110) surface. Lastly, thiacyclopropane decomposes when exposed to a copper single crystal.

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VITA

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