A photoemission study of the adsorption of benzotriazole on copper

Bo-Shung Fang

Iowa State University

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A PHOTOLUMINESCENT STUDY OF THE ADSORPTION OF BENZOTRIAZOLE ON COPPER

Iowa State University

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A photoemission study of the adsorption of benzotriazole on copper

by

Bo-Shung Fang

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1985
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I. INTRODUCTION

Benzotriazole (C₆H₅N₃) is a well-known corrosion inhibitor for copper and copper alloys.¹,²,³ It affords protection in aqueous and gaseous environments polluted with sulphur dioxide, hydrogen sulphide and salt mist.³,⁴ It can reduce the rate of oxidation of copper in air at temperatures up to about 350°C.⁵,⁶ Benzotriazole (BTA) is effective as a vapor phase inhibitor in enclosed environments such as display cabinets or in packing for storage. One particularly valuable way of achieving vapor treatment is wrapping the metal component with benzotriazole-impregnated paper.⁴ It finds great use in the protection of sheet copper during storage, reels of copper wire during adverse transport conditions, etc.... For domestic use, benzotriazole has been incorporated into neutral wax and mildly abrasive polishes, and a special lacquer has been developed for architectural application.⁷

Another application is to protect copper and its alloys under immersed conditions involving cleaning solutions, heating and cooling systems, and other fluids.⁸,⁹,¹⁰ The simplest benzotriazole treatment is to immerse the metal component in a 0.25% aqueous solution of the regent at a temperature of about 60°C for 2 minutes.³

Numerous attempts have been carried out to determine the essential characteristics of inhibition. However, the mechanism of this inhibition is still not completely
elucidated. For organic inhibitors, it is clear that adsorption on the metal substrate is the initial step in the inhibition process. A knowledge of the nature of the surface film formed after BTA adsorption would aid the understanding of the mechanism of corrosion inhibition. The recognition of the nature of the CuBTA surface film has been the main task of many experiments. We discuss them below.

A. Oxidation State of CuBTA Surface Film

The surface film was identified as two distinct alternatives: a cuprous surface complex, Cu(I)BTA, consisting of polymeric chains, and a cupric surface complex, Cu(II)BTA, with a more complicated structure.

Poling tried three different BTA treatments on an electropolished mirror milled from OFHC Cu. The Cu mirror was assumed to be rapidly covered by a film of Cu₂O about 10-20Å thick after removal from the electropolishing solution. The three BTA treatments were:

(1) Dipped in a H₂-purged, 3% NaCl(0.5N) solution at pH 3.0 containing 0.02M BTA at 26°C for 1.25 hours or longer. The surface film was identified as Cu(I)BTA

(2) Exposed to an air-saturated insulating oil containing 0.01 wt% BTA at 90°C for 1 hour and up to 133 hours, CuBTA films were reported without specifying Cu(I) or Cu(II).

(3) Enclosed in an air-filled 300ml vessel containing 50 mg of
BTA at room temperature for 8-33 days. A thin film of unreacted BTA was detected on top of the Cu(I)BTA film. Morito and Suetaka made the copper substrate by evaporating pure copper onto a copper plate under high vacuum, then dipping it in a 3% NaCl aqueous solution at a pH of 3.0, containing 0.02M BTA, at 25°C for 150 seconds or 20 hours, respectively. Infrared and ultraviolet-visible reflection spectra of the surface films indicated the Cu(I)BTA structure, but not Cu(II)BTA.

X-ray photoelectron spectroscopy (XPS) is a nice tool to distinguish the cuprous complex (d^{10} configuration) from the cupric complex (d^{9} configuration) because the copper 2p spectra are accompanied by satellite lines for the latter, but not the former. Roberts immersed both Cu_{2}O and CuO substrates in aqueous BTA (0.017M, pH 5.25, 60°C), and used XPS to monitor the copper 2p,3d and nitrogen 1s spectra. A three-minute immersion of a Cu_{2}O substrate resulted in the formation of both Cu(I)BTA and Cu(II)BTA surface compounds. However, it took four hours or more immersion time for the CuO substrate to observe the existence of Cu(II)BTA. Roberts then concluded that BTA adsorption favored cuprous oxide and that the relative amount of Cu(II)BTA increased with increasing exposure to aqueous BTA solutions.

However, Ogle and Poling considered the surface films formed in BTA solutions containing NaCl to be predominantly Cu(I) with approximately 10% Cu(II). They further suggested
that the Cu(II) arose from partial oxidation of the initially formed Cu(I)BTA, though it is not clear whether they envisaged this oxidation as taking place in situ.

Chadwick and Hashemi\textsuperscript{20} investigated a variety of conditions for the BTA treatment. In each case, a series of sample immersion times were examined and both polished copper samples and samples with electrochemically grown Cu$_2$O surfaces were used: Those conditions were: (i) 0.02M BTA, 0.5M NaCl at pH1 and 25°C. (ii) 0.02M BTA, 0.5M NaCl at pH3 and 60°C (iii) variation of BTA concentration at pH3 and 25°C; (iv) variation of NaCl concentration at pH3 and 25°C; (v) variation of the degree of agitation; (vi) adsorption from CHCl$_3$ at 25°C (one of the few organic solvents in which BTA is appreciably soluble). Under all the conditions, the X-ray photoelectron spectra showed a strong Cu(I) character with a small but similar amount of Cu(II) regardless of the immersion time. However, the spectra from the exposure of the BTA treated sample to air for a variety of times indicated progressive oxidation of Cu(I) in the surface film to Cu(II). This result suggested that the observation of a small but similar amount of Cu(II) in the immersion time experiment was obtained shortly after removal from the BTA solutions by oxidation, during the finite time (5-15 minutes) needed to dry the samples in air before insertion into the spectrometer. Thus, it was concluded that surface films formed on copper and Cu$_2$O surfaces by BTA under a wide variety of conditions consist of
a Cu(I)BTA surface complex.

Cotton\textsuperscript{23} and Poling\textsuperscript{12} reported previously that the adsorbed BTA inhibitor cannot be removed completely by wiping the copper surface. Chadwick and Hashemi\textsuperscript{21} wiped the sample gently with a tissue, the X-ray spectrum showed the presence of Cu(I)BTA but the Cu(II) was almost removed. The newly created surface also oxidized on exposure to air, forming more Cu(II). It was shown that if surface oxidized samples were immersed in water for a certain time, the amount of Cu(II) was substantially reduced relative to Cu(I). These results strongly support the conclusion that the surface film in situ is a Cu(I)BTA surface complex, if the substrate is Cu\textsubscript{2}O.

B. BTA Adsorption on Electrochemically Clean Copper Surfaces

An attempt to assess the importance of the surface oxide by multiple reflectance infrared spectroscopy and XPS has been made by Chadwick and Hashemi\textsuperscript{21}. They reduced the oxide by cathodic polarization in a pure NaCl electrolyte under a N\textsubscript{2} atmosphere and injected the BTA solution subsequently. The XPS spectrum of this sample revealed the characteristic peaks of BTA (C and N\textsubscript{ls}), but substantially reduced in relative intensity compared to the same exposure time without cathodic reduction of the oxide. A polished Cu mirror with a similar treatment results in no detectable spectrum of the Cu-BTA surface complex by infrared spectroscopy. Therefore, they
concluded that although BTA did adsorb on oxide-free copper, as is evident from the XPS spectrum, the film thickness must stay very low. However, no atomically clean copper substrates have been yet reported.

C. Thickness and Inhibition Action of CuBTA Surface Films

The thickness of the copper-benzotriazole film has been measured by several different methods, such as infrared spectroscopy, ellipsometry, XPS and an electrochemical capacitance method. The evaporated surface film was reported 50 Å thick after 8 days and 60 Å thick after 33 days. The surface film after the BTA solution treatment has been given as 40-140 Å and even up to 5000 Å. It is interesting that a single monomolecular layer of chemisorbed benzotriazole would have a thickness of only 4-5 Å. Poling have shown that typical protective films formed on copper by BTA are better described as multilayers, i.e., Cu/Cu₂O/chemisorbed monomolecular Cu(I)BTA(4-5 Å thick)/anodic corrosion product Cu(I)BTA (up to 5000 Å thick). It seems that the pH of the BTA solution is the controlling factor of the thickness of the CuBTA films. In near neutral and mildly acidic solutions, the total film thickness is usually less than 100 Å. The CuBTA film appears to exhibit the same surface topography as the underlying air-formed Cu₂O film on the copper according to scanning electron
microscopy (SEM) studies. In inhibited acidic chloride solutions of pH<4, more copper ions are produced and the outer layer of cuprous benzotriazole grows to a thickness of about 5000Å. These thick films have a more porous structure and contain networks of acicular crystallites with an appearance similar to that of a shag carpet.

Poling's electrochemical study indicated that the inhibition action was due to the films' acting as efficient physical barriers. Mansfeld et al. assessed from his immersion tests that inhibition action is caused by chemisorption of BTA on the copper surface. Walker suggested that a compact film of copper benzotriazole of thickness about 50Å gave greater protection than would be expected from a single chemisorbed film. Providing the surface layer is free from defects, the protection increased with thickness because the layer acts as a physical barrier. If defects such as holes are present in the surface film, these enable aggressive ions to penetrate to the copper surface and give localized attack and pitting. This effect may be reduced and a greater degree of protection afforded when there is free benzotriazole available in the environment to help plug these gaps.
D. The Chemisorption Nature of the BTA Interaction with Copper Oxide Surfaces

The physical properties of Cu(I)BTA complexes are compared with those of BTA in Table 1. To understand which group of atoms in benzotriazole was responsible to the adsorption on copper oxide surfaces, Cotton and Scholes studied the solubility and the tarnish resistance of cuprous complexes of the following compounds (see Figure 1): (a) benzotriazole (b) indazole (c) benzimidazole (d) indole and (e) methyl benzotriazole.

The experimental results are listed in Table 2. No insoluble complexes were obtained with indole or methyl benzotriazole. Benzimidazole could form insoluble complexes but failed a tarnish resistance test. Benzotriazole and indazole formed insoluble complexes and prevented staining, however, only the former retained tarnish-resistant properties after the treated copper surface was washed with chloroform or other organic solvents (acetone, isopropyl, alcohol,...). These results implied that both the N-H group and an unsaturated nitrogen in benzotriazole were involved in the formation of insoluble copper complexes and protective films on copper. The triazole ring provides maximum inhibition.

Chemical analysis showed that the composition of Cu(I)BTA complexes corresponds stoichiometrically with a metal/organic ratio of one atom of copper to one molecule of benzotriazole.
The pH titrations suggested hydrogen release during copper complex formation. Cotton and Scholes then gave this cuprous derivative a basic formula of $\text{C}_6\text{H}_4\text{N}_3\text{Cu}$. Moreover, they interpreted their data as indicating evidence for the formation of chemical bonds involving chelation of Cu via the nitrogen atom containing the labile hydrogen atom and one (or more) of the nitrogen atoms in the triazole ring. On this basis they suggested a linear structure in which copper was bonded by coordination involving a lone pair of electrons from one nitrogen atom and a covalent link formed by replacement of the hydrogen atom from the N-H group. This polymeric chain is shown in Figure 2(a), and lies flat on the copper surfaces. They also found that the cupric complexes are more difficult to define, and the 2:1 benzotriazole/copper ratio could not be deduced. After this study, many experiments have been done to determine hydrogen dissociation, stoichiometry and the structure of Cu(I)BTA. We discuss them below.

1. Hydrogen desorption

Even though Prall and Shreir$^{25}$ did not get the same results as Cotton and Scholes by a similar method, infrared$^{12,13}$ and Raman spectroscopic$^{26}$ studies supported the hydrogen desorption from the N-H group. Poling$^{12}$ showed the transmission spectra of solid BTA complexes. Strongly hydrogen-bonded N-H groups resulted in the broad, multipeaked band in the spectrum of solid BTA. No N-H bands were retained
<table>
<thead>
<tr>
<th>Property</th>
<th>BTA</th>
<th>Cu(I)BTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>$C_6H_4N_3H$</td>
<td>$C_6H_4N_3Cu$</td>
</tr>
<tr>
<td>Melting Point</td>
<td>98.5°C</td>
<td></td>
</tr>
<tr>
<td>Boiling Point</td>
<td>at 201°C, desorbed at about 280°C</td>
<td></td>
</tr>
<tr>
<td>Vapor Pressure</td>
<td>$8 \times 10^{-6}$ torr at room temperature</td>
<td></td>
</tr>
<tr>
<td>Solubility</td>
<td>$H_2O$: 2% at 20°C, insoluble</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Organic sol: benzene, sol: pyridine, ethane, alcohol</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>1.2</td>
<td>1.65</td>
</tr>
<tr>
<td>Magnetic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Suscept. ($X_m$)</td>
<td>$-70 \times 10^{-6}$</td>
<td>$0$ to $+330 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
Figure 1. Molecules (a) benzotriazole (b) indazole
(c) benzimidazole (d) indole (e) methyl benzotriazole
### Table 2. Solubility and tarnish resistance test

<table>
<thead>
<tr>
<th>Solubility</th>
<th>Tarnish Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Water pH 6</strong></td>
<td><strong>Organic reagents</strong></td>
</tr>
<tr>
<td>Benzotriazole..insoluble</td>
<td>insoluble</td>
</tr>
<tr>
<td>Indazole......insoluble</td>
<td>soluble</td>
</tr>
<tr>
<td>Benzimidazole. insoluble</td>
<td>insoluble</td>
</tr>
<tr>
<td>Indole........soluble</td>
<td>soluble</td>
</tr>
<tr>
<td>1-Methyl</td>
<td>benzotriazole..soluble</td>
</tr>
</tbody>
</table>
in the CuBTA complexes. Deuteration of the BTA (with N-D...N) shifted the original N-H...N band to a previously unoccupied region of the spectrum for solid BTA. The absence of an N-H group was also shown by the inability to produce detectable N-D...N and in attempts to deuterate the CuBTA complexes. Rubim et al.\textsuperscript{26} reported also the disappearance of the N-H in-plane bending mode by following a similar process.

The neutral BTA molecule is considered\textsuperscript{28} to exist in neutral and mildly acidic solutions but the cation is found in acidic solutions and the anion in alkaline solutions. Another opinion\textsuperscript{29} is that benzotriazole is present as an anion in most solutions, $C_6\text{H}_4\text{N}_2\text{NH}=C_6\text{H}_4\text{N}_2\text{N}^-$. Fox et al.\textsuperscript{30} suggested the dissociation of the oxides of copper in aqueous solutions, i.e.,

$$\text{Cu}_2\text{O} + 2\text{H}^+ \rightarrow 2\text{Cu}^+ + \text{H}_2\text{O}$$

$$\text{CuO} + 2\text{H}^+ \rightarrow \text{Cu}^{2+} + \text{H}_2\text{O}$$

and then the formation of CuBTA complexes. However, no discussion was made on the process of BTA vapor adsorption where Cotton and Scholes\textsuperscript{4}, Poling\textsuperscript{12} and Siedle et al.\textsuperscript{31} reported the formation of a Cu(I)BTA polymer also.

2. **Stoichiometry**

Stoichiometry studies often afford information about the coordination environment. For the CuBTA complexes prepared in
solution, the composition was not as simple as in the basic formula such as \((C_6H_4N_3)Cu\), which most people presented. After removing the sample from the solutions containing BTA, HCl or KCl, \(H_2O\) and Cl may incorporate into the complexes.

Cotton and Scholes \(^4\) showed that the cuprous complex is \((C_6H_4N_3Cu)g\cdot2H_2O\) and the cupric complex is \(\left[(C_6H_4N_4)Cu_3Cl_2CuCl_2\cdotH_2O\right]\). Poling \(^12\) reported that Cl existed in cuprous complexes. Siedle et al. \(^31,32\) obtained \(\left[(C_6H_5N_3)Cu(I)Cl\right]_4\) and \((C_6H_4N_3)Cu\) from different preparation processes. No hydrogen dissociation was discussed when Siedle reported the existence of the \(\left[(C_6H_5N_3)Cu(I)Cl\right]_4\) complex. Basically, most of the authors found the \(Cu/C_6H_4N_3\) ratio to be 1:1 for the cuprous complex prepared from BTA solutions.

Fox et al. \(^30\) showed the relative number of atoms of \(Cu\), \(N\) and \(O\) in the surface complexes on both oxides. Based on their analysis, one BTA molecule was associated with every \(O\) atom on both \(Cu_2O\) and \(CuO\) surfaces after short immersion times (i.e., the ratio of \(Cu(I)/BTA\) is 2:1 and \(Cu(II)/BTA\) is 1:1). But these changed to two BTA on \(Cu_2O\) and a half BTA on \(CuO\) after longer immersion times (i.e., the ratio of \(Cu(I)/BTA\) is 1:1 and \(Cu(II)/BTA\) is 2:1).

According to an electrochemical study on a BTA vapor treated copper disc, Angely et al. \(^33\) was led to the assumption that the adsorption of BTA molecules on a cuprous oxide (\(Cu_2O\)) surface was carried out with the blocking of two surface atoms of \(Cu\). The study suggested that the composition of \(Cu(I)BTA\)
from a vapor treatment was the same as that from solution treatment at short immersion times as reported by Fox et al.

3. The structure of Cu(I)BTA

Since Cu(II)BTA has a more complicated composition, we only discuss the structure of Cu(I)BTA in this section. In addition to hydrogen dissociation, an infrared study reached the conclusion that Cu was also coordinated to an unsaturated ring nitrogen by showing the shift of the main -N=N- band from 1215 cm\(^{-1}\) in BTA to 1150 cm\(^{-1}\) in the Cu(I)BTA surface film.

Morito and Suetaka came to the same conclusion as above by a high-sensitivity infrared reflection experiment. Moreover, according to the relative intensity of the absorption bands from C-H stretching and C-H out-of-plane deformation, he suggested that the plane of the BTA-Cu(I) molecule is parallel to the copper surface. Both of them supported Cotton and Scholes’ polymeric chain model (Figure 2(a)).

In an XPS study, the N 1s spectrum of solid BTA consisted of a broad (3.2 eV FWHM—Full Width Half Maximum) symmetric peak at a binding energy of 400.2 eV. The broadness of this peak indicated the presence of unresolved N 1s peaks. Roberts explained that a hydrogen-bonded structure involving N-H...N bonding could possibly give rise to two distinct N 1s peaks. After BTA treatment (solution), N 1s spectra of both Cu(I)BTA and Cu(II)BTA surface films consisted of a single
symmetrical peak at 399.9 eV binding energy which was narrower (2.3 eV FWHM). Roberts suggested the equivalent charge distribution on the two copper-bonded nitrogen atoms compared to the single nitrogen-bonded nitrogen atom in Cotton and Scholes' model. Therefore, he replaced the double bonds between the two nitrogen atoms by putting a circle inside the triazole ring to express the equivalent charge of three nitrogen atoms, see Figure 2(b).

Rubim et al.\textsuperscript{26} suggested that the BTA\textsuperscript{-} ion (Figure 3(a)) could be visualized as a transition state when the BTA lost the NH proton in the formation of the Cu complex. This ion has $C_{2v}$ symmetry and the bond orders of the two NN bonds are equal. Therefore, they proposed the same model as Roberts did (Figure 2(b)). The formation of the CuN bonds was envisaged as arising from the feeding in of two electrons with opposite spin to bonding molecular orbitals formed by the overlap of Cu sp-hybrid atomic orbitals with the N hybridized lone-pair atomic orbitals.

E. The Purpose of This Study

Even though Roberts proposed a Cu(I)BTA structure in which the molecular plane was oriented parallel to the copper (oxide) surface, he still found difficulty in describing how such a structure might be anchored to the substate. The interaction between BTA and Cu was only attributed to the Cu-N
Figure 2. Structures of Cu(I)BTA (a) The structure of Cu(I)BTA from Cotton and Scholes\(^4\) (b) The structure of Cu(I)BTA from Roberts\(^16\) and Rubim et al.\(^26\)
Figure 3. Benzotriazole molecule and ion (a) BTA⁻ ion after hydrogen dissociation (b) Atom order assignment on BTA.
bonds. It is hard to imagine how those Cu-N bonds bend themselves by approximately 90°. Both model 1 (Figure 2(a)) and model 2 (Figure 2(b)) were able to show the Cu-N bonding and hydrogen dissociation. However, the molecule orientation and the polymerization structure had some difficulties explaining the experimental results from several studies of BTA adsorption (on copper oxide):

(1) The van der Waals' diameter of the benzene plane is 6.8Å. The effective area covered by one benzotriazole molecule plane is probably 7.3Å\times 6.8Å. Compared to the area of the largest unit cell (in Cu(110)) which is 3.61Å\times 2.55Å, the stoichiometric results should give a Cu/BTA a ratio of 4:1 instead of 2:1 or 1:1 as reported.

(2) These two models can not explain the results from Cotton's solubility and tarnish resistance tests (in Table 2). Structure 1 has no difference between N2 and N3 (see Figure 3(b) for atom order assignment) and Structure 2 has three equivalent nitrogen atoms. If the polymeric chain is really connected through N-Cu-N bonds, why should the N2-Cu-N1 (indazole) be soluble but the N3-Cu-N1 (benzimidazole and benzotriazole) be insoluble? Generally speaking, tarnish resistance is inversely proportional to the number of active sites of copper atoms on the surface. With two Cu-N bonds and the molecule lying flat on the copper surface, it is really hard to tell the difference in covered areas made by benzotriazole and benzimidazole.
If the $N_2$ of benzotriazole makes these tarnish test results different, then, why does indazole pass the test? Therefore, a better model of chemisorbed Cu(I)BTA structure is demanded in order to understand its inhibition mechanism.

Photoemission spectroscopy contains much information on the energy distribution of the excited electrons that escape into the vacuum from both the valence level and core level. It is sensitive to the influence of adsorbates at the surface whose presence is reflected not only in a redistribution of the metallic electrons in the bands but also in the presence of perturbed features of the adsorbate molecular orbitals. Some of the most significant photoemission results for chemisorbed layers relate directly to the surface orientation and bonding of molecules. We elucidate this point below.

Hypothetical adsorbates are classified here as follows: donors, those that interact with the surface solely through an adsorbate filled orbital (lone pair); radicals, those that interact through a singly occupied orbital; and acceptor, those that interact through a vacant orbital. Since evidence has been found that benzotriazole bonds to copper through the nitrogen lone pairs, benzotriazole should be classified as a donor, and copper as an acceptor. From a fundamental quantum chemical point of view, orbital energy levels split due to the interaction of two discrete orbitals, $\phi_1$ and $\phi_2$, of energies $\varepsilon_1 < \varepsilon_2$, as shown in Figure 4. Applied to the Cu-BTA
interaction, \( \phi_1 \) represents the BTA nitrogen lone pair with energy \( \epsilon_1 \) and \( \phi_2 \) represents a Cu vacant orbital with energy \( \epsilon_2 \). The interaction between these orbitals induces an energy splitting to one lower-lying filled orbital with higher binding energy \( \epsilon \) and the other higher lying empty orbital with lower binding energy. Photoemission spectroscopy is capable of measuring the binding energies of filled orbitals. By comparing the photo-electron energy distribution curves (EDCs) measured from free BTA molecules to the one from chemisorbed BTA on copper, we will see a peak with energy \( \epsilon_1 \) in the free BTA spectrum and a peak with energy \( \epsilon \) instead of \( \epsilon_1 \) in spectrum of chemisorbed BTA. The common description is: the nitrogen lone pair orbital (with energy \( \epsilon_1 \)) has a chemical shift to a higher binding energy (\( \epsilon \)) upon chemisorption on copper surfaces. Therefore, photoemission spectroscopy is a very good tool to answer the question: which orbitals are responsible for the adsorbate (BTA)-substrate (Cu) interaction. Moreover, the theoretical analysis on charge distribution of each interacting adsorbate orbital would lead to a knowledge of the surface orientation of molecules.

The importance of combined data on both core and valence level exitation has been emphasized by Brundle\(^3\) and others. XPS (X-ray Photoelectron Spectroscopy) has been used to study core level electrons of the Cu-BTA chemisorption system and had two main contributions: (1) identify the oxidation state of CuBTA surface film. (2) give information on equivalent
Figure 4. Energy level diagram
charge distribution among the three nitrogen atoms in the chemisorbed state.

In this experiment, we will use UPS (Ultraviolet Photoelectron Spectroscopy) to study valence level electrons of the Cu-BTA chemisorption system. What we are interested in is how benzotriazole molecules are bonded to the copper (oxide) surface. If it is due to the nitrogen lone pair orbitals, we should be able to observe their chemical shift to the higher binding energy side in the photoelectron energy distribution curve (EDC) of a Cu-BTA film. If the molecule really lies parallel to the substrate surface at room temperature, then the π-orbitals of benzotriazole would interact with the Cu surface atoms, and one, or several, highest-lying π-orbitals should have chemical shifts to higher binding energy also. Combining information on such shifts, we will be able to make a judgement on whether benzotriazole molecules lie flat or stand up on the copper (oxide) surface after chemisorption. The hydrogen dissociation and polymerization effect definitely will perturb the valence photoelectron EDC. However, the lack of theoretical knowledge on the energy levels after these perturbations makes it difficult to relate the perturbed spectrum to hydrogen dissociation and polymerization. We, therefore, will combine both UPS and XPS data to set up a model for the Cu-BTA structure. The model should help us understand the perturbed spectrum due to hydrogen dissociation and polymerization, and
give a better understanding of the corrosion inhibition mechanism.

In this experiment, we will study BTA adsorption on polycrystalline copper films (clean and oxidized surfaces) in order to compare to numerous existing results on a similar system (BTA on polycrystalline copper oxide). Since the solution treatment often incorporates other materials into the CuBTA film and produces difficulties upon analysis, we choose BTA vapor treatment to grow the chemisorbed film. This method has several advantages:

(1) Vapor treatment can be carried out under UHV (Ultra High Vacuum) conditions. We will be able to study a highly isolated CuBTA system which never occurred in solution treatments.

(2) We can control the thickness of the CuBTA film and easily separate the chemisorption phase and pure condensed phase from more complicated phases due to the mixed coexistence of physisorbed and chemisorbed species, which are usually the products of solution treatment.

(3) Fox et al.\textsuperscript{30} showed a Cu/BTA a ratio of 2:1 for short immersion times (solution treatment). This result indicated that the thin film grown in solution treatment had the same stoichiometry as the one grown in vapor treatment according to the study of Angely et al.\textsuperscript{33} Therefore, we believe that the results from the vapor treatment study can be applied to chemisorbed films made
by solution treatment.

We will discuss the concerns in building our photoelectron energy analyzer in Chapter II, and will describe the sample preparation methods in Chapter III. We will also discuss our experimental results and set up a structure for CuBTA film in Chapter IV and make conclusions in Chapter V.
II. PHOTOELECTRON ENERGY ANALYZER

All experiments were performed at Tantalus, the 240MeV electron storage ring at the Synchrotron Radiation Center located at Stoughton, Wisconsin. A Photoelectron Energy Analyzer (PEA) has been built for this purpose and is shown in Figure 5 (5(a)-5(e)) together with other important parts (sample position in (g) and (h), evaporation system in (k)). The detailed cross-sectional view of the PEA are shown in Figure 6. Its geometric parameters are listed in Table 3.

After the photoelectrons are generated from the sample surface, they pass through a field-free region (Figure 6(a)) between two apertures A1 and A2. The input electron lenses (Figure 6(b)) then image them onto the entrance (EN) of the spherical analyzer (Figure 6(c)) to produce a collimated beam with a specific size. The analyzer determines a certain energy at which the electrons can pass through. The output lens (Figure 6(d)) then focuses these selected electrons on the spherical analyzer exit (EX) to an output aperture A3. The selected electrons will hit the entrance cone of the channeltron (Figure 6(e)). Each incoming electron results in a detectable pulse. The pulse frequency shown on the rate meter or counter is then proportional to the rate of arrival of electrons having this selected energy. The plot of electron current (counts per second) versus selected energy (eV) is the photoelectron energy distribution curve (EDC).
Figure 5. Cross-sectional view of the chamber

(a)-(e) Photoelectron energy analyzer (f) Mo shield disk (g) Sample position (UPS) (h) Sample position (sample preparation) (i) Photon beam (j) Chamber wall (k) Evaporation system
Table 3. Geometric parameters of the photoelectron energy analyzer

<table>
<thead>
<tr>
<th>Position</th>
<th>Distance (cm)</th>
</tr>
</thead>
<tbody>
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<td>EN(Entrance)</td>
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<tr>
<td>$L_3$</td>
<td>1.35</td>
</tr>
<tr>
<td>$L_2$</td>
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<td>4.95</td>
</tr>
<tr>
<td>$A_1$</td>
<td>10.03</td>
</tr>
<tr>
<td>EX(Exit)</td>
<td>0</td>
</tr>
<tr>
<td>$L_4$</td>
<td>1.630</td>
</tr>
<tr>
<td>$A_3$</td>
<td>1.75</td>
</tr>
</tbody>
</table>

Diameter of $A_1$ = 0.14cm
Diameter of $A_2$ = 0.40cm
Diameter of $A_3$ = 0.11cm
Diameter of cylinder tube = 1cm

$R_1$ = 3.25cm
$R_2$ = 4.05cm
$R_0$ = 3.65cm
$G$ = 0.1D
Figure 6. Cross-sectional view of photoelectron energy analyzer (a) Copper cone (b) Input lenses \((L_1, L_2, L_3)\) (c) Spherical analyzer (d) Output lens \((L_4)\) (e) Channeltron
A. Spherical Analyzer

Design data for a general spherical energy analyzer have been given by Purcell and Browne et al. Figure 7 shows that the source at point P and image at point Q lie on a straight line passing through the center of the spheres. A charged particle leaving a point at $-X_1$ in the source with energy $E_1$, such that its trajectory makes an angle $\alpha_1$ with the normal trajectory (dashed line) will arrive at the image at $X_2$ with an angle $\alpha_2$. The equations for $X_2$ and $\alpha_2$ are,

\[
X_2 = \frac{\delta E}{E_0} R_0 \left( 1 + \frac{q}{p} \right) + X_1 \left( \frac{q}{P} \right) - \alpha_1^2 R_0 \left( \frac{p^2}{q^2} + \frac{q}{p} \right)
\]

\[
\alpha_2 = \tan^{-1} (\alpha_1 \cos \gamma \cos \theta + \alpha_2 \sin \theta)
\]

where $\delta E = E_1 - E_0$. $E_0$ is the pass energy of the analyzer.

$R_0 = \frac{R_1 + R_2}{2}$. $p$ and $q$ are object and image distances measured from spherical center $O$.

In the equation for $X_2$, the first term on the right hand side is the energy dispersion due to the difference between $E_1$ and $E_0$. The third term is "trace width", i.e., the broadening of the image of a point source due to aberration. If we use the analyzer in a symmetric way, i.e., $p=q$, these equations are simplified to,
Figure 7. Schematic cross section of spherical analyzer
In practice, two real apertures of the same diameter \( W \) may be centered at \( P \) and \( Q \), and perpendicular to the normal trajectory. Based on eq. [1], the equation for the energy resolution \( \Delta E \) has been calculated. Its general expression is,

\[
\Delta E = \frac{W}{2R_0} + \frac{1}{2} \alpha_m^2
\]  

where \( \alpha_m \) is the maximum incident angle of electrons on the entrance aperture at \( P \). \( E_0 \) was called the pass energy with which all the electrons having zero incident angle can pass through the exit aperture at \( Q \).

The value of \( E_0 \) is determined by the potential difference \( \Delta V \) between two spherical surfaces. The equation is,

\[
E_0 = C \Delta V
\]  

\[
C = \frac{1}{(R_2/R_1 - R_1/R_2)}
\]  

When the magnitude of \( \alpha_m \) is small enough, we can neglect the contribution from the \( 1/2 \alpha_m^2 \) term and eq. [2] becomes,
The end plates of the analyzer have two functions:

1. To narrow the fringing field region (found by Herzog in 1935 and 1940, therefore, the end plates are called Herzog plates and their voltage is the Herzog voltage in some of the literature).

2. To select a specific energy of electrons the intensity of which will be analyzed by the analyzer, i.e., to accelerate or retard the incoming photoelectrons. For example, in order to measure the intensity of 6eV photoelectrons, the voltage of the end plate (Herzog voltage) should be set to -2V if $E_0=4eV$.

B. Cylinder Lenses

We first discuss several basic concepts of electron optics (or charged-particle optics) and then describe the focal properties of a two-cylinder and a three-cylinder lens.

1. Basic concepts of electron optics

   a. Brightness (B) In electron optics, a luminous object is usually defined by an aperture, called a window (see Figure 8(a), for object window) which is uniformly illuminated from one side by a stream of electrons (I). The angular spread of particles emanating from the window is limited by a second
aperture called a pupil (see Figure 8(a) for object pupil). If the distance between the window and pupil is sufficiently great that the angular spread of rays emanating from each point on the object is the same, then the integrated brightness of the object outlined by the window is

\[ B = \frac{I}{\pi r^2 \alpha^2} \]

where \( r \) is the window radius and \( \alpha \) is the half angle defined by the pupil relative to a point at the window.

In our case, the electrons are from a sample about 1cm away from the window (aperture \( A_1 \)). As long as the radial sizes of \( A_1 \) and \( A_2 \) (pupil) and the distances among the sample, \( A_1 \) and \( A_2 \) keep constant, the PEA looks at a constant sample area and accepts a constant solid angle. The brightness of the object (or say the incoming electron current from the sample) is affected only by the electronic properties of the sample and the photon beam intensity.

b. The Helmholtz-Lagrange Law Figure 8(a) shows the relation of object pencil angle \( \alpha_1 \) and beam angle \( \theta_1 \) to image pencil angle \( \alpha_2 \) and beam angle \( \theta_2 \). For most practical situations, the approximation \( \sin \theta \approx \theta \) is valid. (The treatment of optics based on this approximation is called Gaussian or paraxial optics.) This relation is given to first order by the Helmholtz-Lagrange law.
Figure 8. Electron lens (a) Window and pupil (b) Electron lens parameters and graphic construction of an image
\[(E_1)^{1/2} r_1 \alpha_1 = (E_2)^{1/2} r_2 \alpha_2 \]  

[6]

where \(E_1\) and \(E_2\) are the kinetic energies of the electron in the object plane and the image plane, respectively.

c. Zero total energy of an electron  
   The potential coordinate in an electron optics (E) calculation is different from that in the laboratory (L). In electron optics, the total energy of an electron is always chosen to be zero, i.e., \(-eV_E=E\) (For convenience, we set \(V_E=E\)). The bias voltages are, however, referenced to ground in the laboratory. We now find a relation between \(V_E\) and the corresponding \(V_L\) by one example: An electron leaves a source (grounded in the laboratory, \(V_{LS}=0\)) with a kinetic energy \(E_s=15\text{eV}\). After it enters an area with bias voltage \(V_{L1}=-11\text{V}\), its kinetic energy becomes \(E_1=4\text{eV}\). In an electron optical calculation, the potentials of this electron are \(V_{ES}=15\text{V}\) at the source and \(V_{EL}=11\text{V}\) in the next area. Therefore, \(V_{EL}=E_1=E_s+(V_{L1}-V_{LS})=E_s+V_{L1}\) or \(V_{L1}=V_{EL}-E_s\), if \(V_{LS}=0\). For convenience, we will assume \(V=V_E=E\) without further specification.

2. The focal properties of a two-cylinder lens

   Electron lenses having axially symmetric electrodes, when electrically biased, will produce equipotential surfaces with shapes similar to those of optical lenses. A charged particle passing across these surfaces will be accelerated or
decelerated, and its path will be curved so as to produce a focusing effect. Electron lenses are "thick" lenses, meaning that their axial dimensions are comparable to their focal lengths. The focal points of a thick lens are located by focal lengths, $f_1$ and $f_2$, measured from principal planes $PP_1$ and $PP_2$, respectively. As shown in Figure 8(b) the locations of the focal points with respect to the central plane (R) are given by $F_1$ and $F_2$, and hence the distances from the central plane to the principal planes are $F_1-f_1$ and $F_2-f_2$, respectively. The object and image distances with respect to the central plane are $P$ and $Q$, respectively.

As in light optics, it is possible to construct graphically the image produced by a lens if the cardinal points of the lens are known. This procedure is illustrated in Figure 8(b) $r_1$ and $r_2$ are the radial sizes of object and image, respectively. The linear magnification can be derived geometrically from Figure 8(b), it is given by

$$M = \frac{r_2}{r_1} = \frac{-f_1}{P-F_1} = \frac{Q-F_2}{-f_2}$$  \[7\]

Figure 9 illustrates the equipotential surfaces associated with the field produced by a pair of cylinders biased at $V_1$ and $V_2$. The focal properties of a two-cylinder lens depends upon the diameters (D) of the cylinders, the spacing (G) between them, and the ratio $E_2/E_1$ of the final to initial kinetic energies of the transmitted particles. The particle
Figure 9. Potential distribution in a two-cylinder lens
energies depend upon the bias potentials on the elements. In most cases, it is assumed that the bias voltage supplies are referenced to the particle source, so that $V_2/V_1 = E_2/E_1$.

Focal properties are usually presented as graphs or tables of $f_1$, $f_2$, $F_1$ and $F_2$ as a function of $V_2/V_1$. The chief sources of information on the focal properties of electrostatic lenses are the books by Harting and Read$^{40}$ and by E. Kareh and E. Kareh$^{41}$. To obtain desired focal properties with a given acceleration or deceleration ratios, two or more cylinder lenses can be used in series (see Figure 6(b)). The lens field is within about ±D (D is the lens diameter) about the lens central plane. When two gaps are sufficiently close that their lens field overlap strongly, it is convenient to treat the combination as a single lens, then called a three-cylinder lens (see Figure 6(d)).

3. The focal properties of a three-cylinder lens

Each focal length is a function of two independent variables, $V_2/V_1$ and $V_3/V_1$, where $V_1$, $V_2$ and $V_3$ are the potentials on the first, second and third lens elements. Comparing to Figure 6(d), $V_1$, $V_2$ and $V_3$ correspond to $V_h$, $V_c$ and $V_d$ respectively. Harting and Read$^{40}$ present data on three-element lenses for $V_3/V_1$ values between 1.0 and 30.0 in the form of tables of lens parameters ($f_1$, $f_2$, $F_1$, $F_2$) as a function of $V_2/V_1$. It was very useful for our output lens (a three-element lens) design.
C. Design Consideration

1. Spherical analyzer

The spherical energy analyzer we used is the Comstock Model AC-901. It consists basically of two concentric 160° spherical sector surfaces made of oxygen-free, high-conductivity copper; an inner convex one of radius $R_1=3.25\text{cm}$, and an outer concave surface of radius $R_2=4.05\text{cm}$. Therefore, for our analyzer,

$$R_0 = 3.65\text{cm}, C = 2.254.$$  

The present system is mainly for use in studies of surface adsorbates where our primary requirement is for better than 0.5eV resolution, constant over an incident electron energy range. We choose $\Delta E=0.15\text{eV}$ for $E_0=4\text{eV}$ to avoid overfilling the gap between the spherical sectors. If we could keep $\alpha_0(m)$ small enough, the radial size of the apertures totally determines the energy resolution and $r_0=W/2=0.14\text{cm}$ according to eq. [5]. This constant resolution requirement gives one restriction on the value of $\alpha_0(m)$

$$\alpha_0(m) \leq 0.0866 \quad [8]$$

After the diameter $W$ of the apertures has been selected, a constant energy resolution comes from a fixed pass energy $E_0$
for all the electron energy measurements, according to eq. [5].

2. **Field free region and lenses**

Two disadvantages in using the spherical analyzer alone were discussed by Noller et al.\(^{43}\) and Polaschegg\(^{44}\):

1. Over a range of electron energy measurements, the Herzog voltage keeps varying. Usually, the sample is grounded or at a specific potential. Therefore, the electric field distribution between the Herzog plate and the sample keeps changing. This changes the sample area analyzed and the effective solid angle of the incoming electrons.

2. The electrons scattered on the inner wall of the analyzer have a chance to reach the exit slit and so contribute to the background. This effect is particularly pronounced when secondary electrons produced by the scattered primary electrons arrive at the exit slit.

To avoid these problems, we added a copper cone (Figure 6(a)) and the input lenses (Figure 6(b)) to the entrance (EN in Figure 6) of the analyzer, and the output lens (Figure 6(d)) to the exit (EX in Figure 6). The copper cone is a field-free region with the same potential as the sample, the two apertures \(A_1\) and \(A_2\) at both ends of the cone defined the analyzer acceptance criteria, both solid angle and sample area independent of input kinetic energy or incident beam
profile. The function of the input lenses was then to accelerate or retard the incident electrons so that they have the correct pass energy on entering the analyzer. The output lens was designed for beam shaping before the final aperture $A_3$ which is located between the output lens and the channeltron (Figure 6(e)). We also took off the physical apertures at the entrance and exit planes of the analyzer. Instead, these planes were imaged by electron lenses onto other physical apertures in the analyzer, i.e., apertures $A_2$ and $A_3$. The purposes of this arrangement are:

1. Any secondary electrons produced at the apertures are prevented from reaching the electrostatic analyzer.
2. Electrons at very low energy do not go through the real apertures to avoid space charge effects, even though this is not a problem in our experiment.

We now discuss the copper cone and lenses in detail within next three sections.

3. Copper cone

The role of the copper cone is to afford two defining apertures, and to shield the field-free region in between. These two apertures $A_1$ and $A_2$ can be named window and pupil, respectively, and have been discussed in B-1-a Brightness. In our system, $A_1$ and $A_2$ are 0.14cm and 0.4cm in diameter, respectively. The distance between the two apertures, $D$, is
5.08 cm. The aperture $A_1$ is 1 cm away from the sample. These give the object radius 0.07 cm and the pencil angle 0.040 radian.

A solid conical piece of aluminum was put in a bath of 200 mg copper sulfate (CuSO$_4$·5H$_2$O), 25 ml sulfuric acid (H$_2$SO$_4$), 975 ml distilled water, 5 g phenol and 10 mg thiourea. A 200-300 μm thick copper film was electroplated onto the solid cone. After drilling a 0.14 cm diameter hole ($A_1$) on the tip, the aluminum was pickled in sodium hydroxide (NaOH) solution until it dissolved completely, leaving the hollow copper cone with the aperture $A_1$. The aperture $A_2$ was made of 3 mil molybdenum foil.

The copper cone and the two apertures are electrically grounded, as is the sample.

4. Input lenses

Input lenses play two important roles:

(1) To image the object ($A_1$) onto the analyzer entrance and to keep the linear magnification constant over a range of incident electron energies.

(2) To make the total angular spread in the beam as small as possible, especially at the entrance.

A 3-element lens was used as a zoom lens, but it failed to keep the linear magnification constant at the same time. Therefore, we adopted ideas from several authors and used a three 2-cylinder lens combination (i.e., four lens elements,
see Figure 6(b) for $L_1$, $L_2$ and $L_3$) to fulfill both requirements.

According to the Helmholtz-Lagrange Law (eq. [6]), it is clear that the pencil angle can not be made arbitrarily small, but by contrast the beam angle can be made zero. To let the total angular spread be as small as possible at the entrance of the analyzer, we could image the object pupil $A_2$ (Figure 8(a)) at infinity to make the beam angle zero. The total angular spread at the entrance is then $\alpha_o$ where $\alpha_o$ is the pupil angle, see Figure 8(a). The other way to make the total angular spread small is the reverse: We set $A_2$ to be the object and $A_1$ to be the pupil, see Figure 10. We image $A_2$ onto the entrance and $A_1$ at infinity. We prefer the latter way because it was easier to achieve in our ray tracing work which will be discussed later. The difference between these two choices is that the electrons organized in a different way. But in the energy analysis system, we only care about the energy distribution of the number of electrons passing through these two apertures. As long as the total number of electrons and their energy are not affected by the object choice, where a particular electron passes through an aperture is not important at all.

A ray tracing program EOPTICS\textsuperscript{47} can plot out several electron paths through $n$ independent 2-cylinder lenses at the same time. A general focal function $F$ for a 2-cylinder lens with unique diameter and $G=0.1D$ is given by
The program has used this expression to give numerical approximations to the lengths $f_1$, $f_2$, $F_1$ and $F_2$ for all the 2-cylinder lenses.

To image $A_2$ onto the entrance plane (EN), the rays 2, 3, and 4 originating from a point $c$ at $A_2$ (see Figure 10) should pass the same point $c'$ at EN, with a radial distance 0.14cm from the lens axis. To image $A_1$ at infinity, the rays 1 and 2 originating from a point $D$ at $A_1$ must be parallel to the lens axis with a radial distance 0.14cm, while passing through EN. Finally, the absolute values of ray angles of rays 3 and 4 at EN have to be smaller than 0.0866 (eq. [8]) to maintain the constant energy resolution requirement.

Before running the program, a set of geometry parameters and the radii and slopes of those four electron rays (1, 2, 3 and 4) are entered into an input data file. See Table 4. The unique diameter of all cylinder elements is 1cm. The lengths of four elements are 1.0cm, 1.0cm, 1.35cm, 1.31cm, along the electron path. If we want to image all the incoming electron with kinetic energy $E_k$ at $A_2$ onto the plane EN of the
Figure 10. Ray tracing input and output
Table 4. Input data of EOPTIC

| NUMLEN = 4 | number of Lens elements |
| Tasrade = 0.5 | radius of each cylinder tube (cm) |
| V(2) = $E_K$ | electron kinetic energy (eV) |
| length(2) = 1.0 | length of first element (cm) |
| V(3) = $V_a$ | voltage of second element (V) |
| length(3) = 1.0 | length of second element (cm) |
| V(4) = $V_b$ | voltage of third element (V) |
| length(4) = 1.35 | length of third element (cm) |
| V(5) = 4 | pass energy (eV) |
| length(5) = 1.31 | length of fourth element (cm) |
| RADS(1) = 0.20 | radius of ray 1 (cm) at A_2 |
| SLOS(1) = 0.039 | angle of ray 1 (rad) at A_2 |
| RADS(2) = -0.20 | radius of ray 2 (cm) at A_2 |
| SLOS(2) = -0.039 | angle of ray 2 (rad) at A_2 |
| RADS(3) = -0.20 | radius of ray 3 (cm) at A_2 |
| SLOS(3) = 0.053 | angle of ray 3 (rad) at A_2 |
| RADS(4) = -0.20 | radius of ray 4 (cm) at A_2 |
| SLOS(4) = -0.026 | angle of ray 4 (rad) at A_2 |
spherical analyer with a pass energy $E_o$, the values of $V(2)$ and $V(5)$ are the same as that of $E_k$ and $E_o$ respectively (Table 4). We then vary the values of $V(3)$ and $V(4)$ and run the ray tracing program. We describe the ray tracing method shown in Figure 11. Based on the input values of element voltages, the focal function $F$ calculates all the focal lengths and then locates the principal planes. An input electron ray with radius $r_1$ and slope $\alpha_1$ is linearly extended to cross the object principal plane ($PP_1$) and the radius becomes $R_1 = r_1 + \alpha_1 p$, where $p$ is the distance between the object and the object principal plane. If the object principal plane ($PP_1$) is conjugate to the image principle plane ($PP_2$), i.e., one is the object and the other is the image, the linear magnification is unity. Therefore, the image of this electron ray has a radius $R_2 = R_1$ and a slope $\alpha_2 = -R_1 / f_2 + \alpha_1 f_1 / f_2$. The same method will be repeated in the subsequent 2-cylinder lenses until reaching the last lens element. The graphic output is shown on the screen of a Textronix terminal. It gives a quick but coarse judgement on the final beam profile. The numerical output file gives the final radius and slope of each electron ray at EN of the spherical analyzer. We can vary the values of $V(3)$ and $V(4)$ until the expected beam profile discussed above is achieved. The element voltages $V(2)$, $V(3)$, $V(4)$ and $V(5)$ in EOPTICS correspond to $E_k$, $V_a$, $V_b$ and $E_o$ in the input lenses. Table 5 lists the values of $V_a$ and $V_b$ over a range of electron energy from 1eV to 25eV, both the calculated values and the
Figure 11. Ray tracing method
operating values in the laboratory. The conversion formula is \( V_L = V_E - E_K \) because the sample is grounded.

The numerical output file of EOPTICS also lists the maximum filling factor \( \eta \). In the case of accelerating lenses, the filling factor can be defined as the fraction of the lens diameter which would be filled with electrons if the incident trajectories in the field-free part of object space were to be extrapolated linearly to the center of the lens. For retarding lenses, for which the bundle of electron rays expands on going from object to image space, \( \eta \) has been defined\(^{48}\) by linearly extrapolating the trajectories in the image space backwards to the center of the lens. With these definitions, the filling factor is approximately equal to the ratio of the maximum diameter of the bundle of rays passing through the lens to the diameter of the lens elements, both for accelerating and retarding lenses. The filling factor is very useful in discussing lens aberrations. If \( \Delta r \) is the radius of the image disk caused by spherical aberration for a point object on the axis of the lens, it has been shown that for double cylinder lenses of diameter \( D \)\(^{48}\), the calculated values of \( \Delta r \) can be fitted approximately by \( (\Delta r/D) = 0.1\eta^3 \) and this expression can be used to obtain a quick estimate of \( \Delta r \). When the filling factor is 50%, the diameter of the spherical aberration disk is of the order of 2 or 3% of the lens diameter. In all the ray tracing calculations, we have kept the maximum filling factor \( \sim 50\% \).
Table 5. Input lens voltages ($E_o=4\text{eV, } r_o=0.14\text{cm}$)

<table>
<thead>
<tr>
<th>Electron Energy $E_K$(eV)</th>
<th>Calculated voltage $V_a$ (V) $V_b$ (V)</th>
<th>Operating voltage $V_a$ (V) $V_b$ (V) $V_h$ (V)</th>
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<tr>
<td>12</td>
<td>106 80.6</td>
<td>94 68.6 -8</td>
</tr>
<tr>
<td>11</td>
<td>98.2 78.2</td>
<td>87.2 67.2 -7</td>
</tr>
<tr>
<td>10</td>
<td>89.6 74.2</td>
<td>79.6 64.2 -6</td>
</tr>
</tbody>
</table>
Table 5. (continued)

<table>
<thead>
<tr>
<th>Electron Energy $E_K$ (eV)</th>
<th>Calculated voltage $V_a$ (V)</th>
<th>$V_b$ (V)</th>
<th>Operating voltage $V_a$ (V)</th>
<th>$V_b$ (V)</th>
<th>$V_h$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>80</td>
<td>69.8</td>
<td>71</td>
<td>60.8</td>
<td>-5</td>
</tr>
<tr>
<td>8</td>
<td>69.5</td>
<td>63.0</td>
<td>61.5</td>
<td>55</td>
<td>-4</td>
</tr>
<tr>
<td>7</td>
<td>57.8</td>
<td>62.2</td>
<td>50.8</td>
<td>55.2</td>
<td>-3</td>
</tr>
<tr>
<td>6</td>
<td>53</td>
<td>59.5</td>
<td>47</td>
<td>53.5</td>
<td>-2</td>
</tr>
<tr>
<td>5</td>
<td>46.2</td>
<td>60</td>
<td>41.2</td>
<td>55</td>
<td>-1</td>
</tr>
<tr>
<td>4</td>
<td>38</td>
<td>57</td>
<td>34</td>
<td>53</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>56.5</td>
<td>27</td>
<td>53.5</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>19.8</td>
<td>51</td>
<td>17.8</td>
<td>49</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>9.2</td>
<td>47</td>
<td>8.2</td>
<td>46</td>
<td>3</td>
</tr>
</tbody>
</table>
We can have quicker data acquisition by using a higher pass energy or have better resolution by using a lower pass energy. There is an interesting and quick way to calculate the values of $V_a$ and $V_b$ for different pass energies by analogy to those for $E_o=4eV$. This analogy is based on the fact that the focal lengths are a function of the voltage ratio of two subsequent elements. If the voltage ratios are kept the same, the output beam profile does not change even though the voltage on each element has been changed. The voltage ratios in Table 6 were calculated from part of the voltage values in Table 8. The corresponding values of $E_K$ for $E_o=4eV$ and of $E_K$, $V_a$ and $V_b$ for $E_o=5eV$ are also listed. The ray tracing work showed that those voltage sets of $(E_K, V_V, V_b, E_o=5eV)$ really gave the output electron beam a constant radius $r_o=0.14cm$.

In our ray tracing studies, all the potentials $(V_a, V_b)$ are generated to maintain constant resolution $(V_o=0.14cm$ and the maximum angular spread $\alpha_o(m)<0.0866$) over the range $1<E_K<30eV$. Since the beam angle is approximately zero ($<0.09^o$) at EN, the total angular spread is the same as the value of the image pupil angle $\alpha_o$ at EN. The Helmholtz-Lagrange Law (eq. [6]), therefore, affords a way to estimate an electron energy range adequate working at constant resolution. In the ray tracing work, $A_2$ (with $\alpha=0.0138$, $r=0.2cm$ and $E=E_K$) is imaged onto EN (with $\alpha_o$, $r_o=0.14cm$ and $E=E_o$). According to eq. [6], the relation between $E_K$, $\alpha_o$ and $E_o$ is given by
Table 6. Voltage analogy

<table>
<thead>
<tr>
<th>Voltage ratio</th>
<th>$E_o = 4\text{eV}$</th>
<th>$E_o = 5\text{eV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_K$ $V_a$ $V_a$</td>
<td>$E_o (\text{eV})$</td>
<td>$E_K (\text{eV})$</td>
</tr>
<tr>
<td>6</td>
<td>8.067</td>
<td>1.6835</td>
</tr>
<tr>
<td>5.5</td>
<td>8.127</td>
<td>1.6404</td>
</tr>
<tr>
<td>5</td>
<td>8.200</td>
<td>1.5922</td>
</tr>
<tr>
<td>4.5</td>
<td>8.289</td>
<td>1.5256</td>
</tr>
<tr>
<td>4</td>
<td>8.438</td>
<td>1.4642</td>
</tr>
<tr>
<td>3.5</td>
<td>8.614</td>
<td>1.3991</td>
</tr>
<tr>
<td>3</td>
<td>8.833</td>
<td>1.3151</td>
</tr>
</tbody>
</table>
When $E_o$ is fixed, the value of $\alpha_o$ increases when we measure the electrons with higher energy. The maximum value of $\alpha_o$ under the constant resolution requirement is 0.0866. Therefore, the highest electron energy for a constant resolution measurement is

$$E_K = 77\text{eV for } E_o = 4\text{eV}$$
$$= 96\text{eV for } E_o = 5\text{eV}$$

5. Output lens

Not only can the electrons with an energy range $(E_o \pm \Delta E)$ pass through the exit of the analyzer, but also some electrons with energies outside this range have the possibility of passing through because there is no physical aperture stopping them, or because of scattering from the inner wall of the analyzer (largely reduced by the input lenses). The output lens then plays two roles:

1. It allows only the selected electrons to hit the channeltron, in order to maintain the energy resolution defined by the input lenses and the analyzer.

2. It accelerates the electrons passing through aperture $A_3$, giving a maximum electron current.

At the exit plane (EX) of the spherical analyzer, all selected electrons have a unique energy equal to $E_o$ (pass energy)
regardless of their initial energies while escaping from the sample surface. The situation is not as complicated as for the input lenses. A three-cylinder lens is capable of fulfilling those requirements because it can be a zoom lens over a range of linear magnification. We can have a fixed distance between EX and $A_3$ and a fixed diameter of $A_3$, but still can obtain different linear magnifications for measurements at different energy resolutions. The focal properties of a three cylinder lens was mentioned before. To achieve the first role, the element voltages are chosen to image an object with $r_o=0.14\text{cm}$ on the EX plane, onto $A_3$ with radius $0.1\text{cm}$, i.e., $M=-0.37$. Therefore, the element lengths are $1.08\text{cm}$, $0.9\text{cm}$ and $1.2\text{cm}$ along the electron path. The gap $G$ is $0.1D$, and $D$ (diameter of each element) is $1.0\text{cm}$. At the same time, we set $V_h=E_o$ for the selected electrons, $V_c=1.2E_o$ and $V_d=30E_o$. This acceleration mode satisfies the second requirement.

The operating voltages for the lens elements are:

\begin{align*}
V_h &= E_o - E_K = 4 - E_K \\
V_c &= 1.2E_o - E_K = 4.8 - E_K \\
V_d &= 30E_o - E_K = 120 - E_K, \quad \text{for } E_o = 4eV
\end{align*}
6. Lenses and analyzer operation

All the lens voltages and Herzog voltages have to vary synchronously over a range of electron energy measurement. They are biased by operational amplifiers whose unique input is from another operational amplifier affording a voltage ramp (from 0 to -10V). The operating voltages for the input lenses are listed in Tables 5 and 6.

To have a continuous ramp from operational amplifiers, we linearly fitted the calculated values. The equations of the lens voltages versus electron energy are given by

\[ V_a = 6.4E + 16 \]

\[ V_b = 1.97E + 44, \quad \text{for } E = 4 \text{eV} \]

\[ V_a = 6.25E + 23.7 \]

\[ V_b = 1.91E + 57, \quad \text{for } E = 5 \text{eV} \]

The equations for the output lens voltages were shown in the
last section. When Camac, a microcomputer system used for data acquisition and process control operates the photoelectron energy analyzer, that negative voltage ramp is replaced by its internal ramp (0–10eV).

7. Electron detector and data acquisition

The electron detector used for direct counting is a Channeltron Electron Multiplier, Galileo Electro-Optics Corp. Model 4039, in Figure 6(e). A single electron pulse gain is typically $10^8$. The pulse width is approximately 20 nanoseconds. A metal plate after the channeltron collects these pulses for transfer to the pulse counting electronics. A preamplifier, Amptek A-101 PD, converts each negative input pulse to a positive 5V square pulse. The rate meter indicates the pulse rate (counts per second) and drives the vertical input of an X-Y recorder. When the Camac system is connected, the rate meter sends the data to a microcomputer in the Camac system. The digitized data are stored on floppy disks for further data analysis and graphing, and are sent in analog form to the vertical input of the X-Y recorder.

The voltage drop along the channeltron is about 3000V. The voltage of its input cone is the same as $V_d$ (Figure 6(d)) in order to avoid possible field disturbance on the image plane ($A_3$). The collector's voltage is about 200–300V higher than that of the end of channeltron.
8. **Magnetic shielding**

A cylindrical μ-metal shell (5.75 inches in diameter, 62 mil in thickness) was put inside the vacuum chamber (6 inches in diameter) in order to cancel the earth magnetic field which would affect the electron paths at lower energy. Three μ-metal disks (about 5.6 inches in diameter, 4 mil in thickness) were put near the top opening of the chamber to reduce the field penetration. The internal field was reduced to less than 50mG over the full working volume of the analyzer system according to gauss meter measurements. This magnetic field has been found to be adequate for 4eV pass energy operation.

**D. Determination of the Parameter C**

According to eq. [4], C is a geometric parameter. If \( R_2 \) or \( R_1 \) change a little bit, we might incorrectly interpret the value of \( E_0 \) with a preset \( \Delta V \) (eq. [3]). To show how sensitive the value of \( E_0 \) will be to variation of the value of C, we calculate \( E_0 \) with two values of \( R_2 \) different by 0.05cm.

1. **Set** \( R_2 = 4.05 \text{cm}, R_1 = 3.25 \text{cm}, \Delta V = 1.775 \text{V} \)
   
   then \( C = 2.254 \), and \( E_0 = 4.00 \text{eV} \)

2. **Set** \( R_2 = 4.00 \text{cm}, R_1 = 3.25 \text{cm}, \Delta V = 1.775 \text{V} \)
   
   then \( C = 2.391 \), and \( E_0 = 4.244 \text{eV} \)

The 0.05cm deviation in \( R_2 \) results in 0.24eV difference in \( E_0 \)!
If we presume $C=2.254$, we will set $\Delta V=1.775\text{V}$ in order to operate the analyzer at $E_0=4\text{eV}$. However, if the real value of $C$ is 2.391, the analyzer actually operates at $E_0=4.244\text{eV}$. In this case, all electron energies in the measured spectrum are then incorrectly scaled and the values are $0.244\text{eV}$ less than what they should be. The spectrum is shifted to the lower electron energy side by $0.244\text{eV}$. Moreover, if we set $\Delta V=3.55\text{eV}$ to operate at $E_0=8.488\text{eV}$, the scaled electron energies are then $0.488\text{eV}$ less than what they are. The spectrum will appear shifted further to the low electron energy side.

We now derive an equation to calculate the real value of the parameter $C$ in terms of its presumed value. First, we define notation as below.

\begin{itemize}
  \item $C_p$ - presumed parameter $C$
  \item $C_r$ - real parameter $C$
  \item $E_{oc}$ - pass energy corresponding to $C_p$
  \item $E_{or}$ - real pass energy corresponding to $C_r$
\end{itemize}

After we set a potential difference $\Delta V(1)$ across the two spherical sectors, we interpret

\[ E_{oc}(1) = C_p \Delta V(1). \]
But the real pass energy is

\[ E_{or}(1) = \Delta V(1)C_r = E_{oc}(1)(C_r/C_c). \]

The wrong scaling factor \( \Delta E(1) \) is

\[ \Delta E(1) = E_{oc}(1) - E_{or}(1) \]

If we take another spectrum by using a different potential difference \( \Delta V(2) \), we have another set of equations

\[ E_{oc}(2) = C_c\Delta V(2) \]

\[ E_{or}(2) = \Delta V(2)C_r = E_{oc}(2)(C_r/C_c) \]

\[ \Delta E(2) = E_{oc}(2) - E_{or}(2) \]

It is very easy to compare the energy shift difference between the two spectra, and its magnitude \( \Delta E \) should be

\[
\Delta E = \Delta E(2) - \Delta E(1)
\]

\[
= (E_{oc}(2) - E_{or}(2)) - (E_{oc}(1) - E_{or}(1))
\]

\[
= (E_{oc}(1) - E_{oc}(2))(\frac{C_r}{C_c} - 1)
\]

\[
C_r = C_c\left[1 - \frac{\Delta E}{E_{oc}(2) - E_{oc}(1)}\right]
\]
Based on this equation, an experiment was performed in order to determine the value of $C_r$ of the analyzer. To measure the energy shift difference $\Delta E$, we monitored the energy positions of the Cu(3d) peak through four independent measurements. The experimental conditions for the first two experiments are listed as below:

Measurement (1): presumed $C = 2.254$, set $\Delta V = 1.775V$ and the calculated pass energy is $4eV$.
Measurement (2): presumed $C = 2.254$, set $\Delta V = 3.55V$ and the calculated pass energy is $8eV$.

These energy positions of Cu(3d) peak are shown in line 4, Table 7. $\Delta E = 17.37eV - 17.60eV = -0.23eV$. From eq. [9], the value of $C_r$ equals 2.384. In order to check whether this value is the true value of the parameter $C$ or not, two measurements were taken and their experimental conditions were:

Measurement (3): presumed $C = 2.384$, set $\Delta V = 1.678V$ and the calculated pass energy is $4eV$.

The energy positions of Cu(3d) peak are shown in line 4, Table 7. The value of $\Delta E$ equals zero because of no relative shift between the two spectra. If the true value of $C$ is 2.384, the energy difference in the Cu(3d) peak of measurement
(1) and (3) should be the same as the value listed in line 7, measurement (1) and it does. The agreement can also be approached by comparing the data of measurement (2) and (4) in the same way. Therefore, we conclude that the true value of parameter C of our spherical analyzer is 2.384.

E. Resolution Test

The measurement of the Fermi edge is a good way to determine the energy resolution of our analyzer system. The measured Fermi edge width $\Delta E_m$ mainly comes from three contributions. The first is the energy resolution $\Delta E$ of the analyzer system. The second is the band width $\Delta E_p$ of the incident photons from the monochromator. The third is from the thermal spread $\Delta E_f$ of the fermi edge. Assuming Gaussian distributions, their relation can be expressed as,

$$\Delta E_m^2 = \Delta E^2 + \Delta E_p^2 + \Delta E_f^2 \quad [10]$$

where $\Delta E_f \sim 0.075 \text{eV at } 293 K$

All the resolution tests were done on the "Aluminum Seya" monochromator. The wavelength resolution $\Delta \lambda (\AA)$ corresponding to a specific slit width $d(\mu)$ (entrance and exit slits set equal) is,
Table 7. Measurement of parameter C

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Measurement</th>
<th>Measurement</th>
<th>Measurement</th>
<th>Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)</td>
<td></td>
</tr>
<tr>
<td>1. $C_c$</td>
<td>2.254</td>
<td>2.254</td>
<td>2.384</td>
<td>2.384</td>
</tr>
<tr>
<td>2. $\Delta V(V)$</td>
<td>1.775</td>
<td>3.55</td>
<td>1.678</td>
<td>3.36</td>
</tr>
<tr>
<td>3. $E_{oc}$(eV)</td>
<td>4</td>
<td>8</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>4. Cu(3d)(eV)</td>
<td>17.60</td>
<td>17.37</td>
<td>17.83</td>
<td>17.83</td>
</tr>
<tr>
<td>5. $C_r$</td>
<td>2.384</td>
<td>2.384</td>
<td>2.384</td>
<td>2.384</td>
</tr>
<tr>
<td>6. $E_{or}$(eV)</td>
<td>4.23</td>
<td>8.46</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>7. $E_{oc}-E_{or}$(eV)</td>
<td>-0.23</td>
<td>-0.46</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
\[ \Delta \lambda = d \left( \frac{8}{1000} \right) \left( \frac{\lambda^0}{\mu} \right) \]

The energy band width \( \Delta E_p \) for a photon with energy \( E(\text{eV}) \) and wavelength \( \lambda(\text{\AA}^0) \) is,

\[
\frac{\Delta E_p}{E} = \frac{\Delta \lambda}{\lambda}
\]

It is significant that \( \Delta \lambda \) only depends on slit width, but \( \Delta E_p \) depends on the magnitude of photon energy also. To simplify the problem, we used the same photon energy 26eV and chose four different slit widths during the Fermi edge measurements on the evaporated copper film. Therefore,

\[
\Delta E_p = 4.36 \times 10^{-4} d \tag{11}
\]

Table 8 shows all the measured and calculated data for the energy resolution test at \( E_o = 4 \text{eV} \) mode. The values of \( \Delta E_p \) were calculated from eq. [11] (Figure 12 shows a typical Fermi edge EDC measured at \( E_o = 4 \text{eV} \), but \( C = 2.254 \)). The values of \( \Delta E_m \) were chosen from the measured Fermi function by the following steps:

1. A program listed the values of \( f(E_K) \), Fermi function and its first and second derivatives, \( f'(E_K) \) and \( f''(E_K) \).
2. Choose a value of \( f(E_{K1}) \) at which the first derivative equals zero \( (f'(E_{K1}) = 0) \) on the low electron energy side.
Figure 12. EDC of Fermi function of copper
Table 8. Energy resolution test ($E_0 = 4\text{eV}$)

<table>
<thead>
<tr>
<th>$d(\mu)$</th>
<th>$\Delta E_p (\text{eV})$</th>
<th>$\Delta E_m (\text{eV})$</th>
<th>$\Delta E (\text{eV})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>360</td>
<td>0.157</td>
<td>0.25</td>
<td>0.180</td>
</tr>
<tr>
<td>310</td>
<td>0.135</td>
<td>0.24</td>
<td>0.184</td>
</tr>
<tr>
<td>260</td>
<td>0.113</td>
<td>0.23</td>
<td>0.186</td>
</tr>
<tr>
<td>210</td>
<td>0.092</td>
<td>0.22</td>
<td>0.185</td>
</tr>
</tbody>
</table>

average = 0.184

~ 0.18
of the Fermi edge, and choose the other value of \( f(E_{K_2}) \) at
which the first derivative is zero \( (f'(E_{K_2})=0) \) on the
higher energy side.

(3) Choose \( E_{K_3} \) and \( E_{K_4} \) at which Fermi function values are 90%
and 10% of \( f(E_{K_1})-f(E_{K_2}) \), respectively.

(4) \( \Delta E_m = E_{K_4} - E_{K_3} \)

From eq. (10), we calculated the value of \( \Delta E \) for each slit
width. The energy resolution of our analyzer system is then
0.184 eV. If the pass energy is 4 eV, the calculated value is
0.153 eV. However, when we did the measurement, the spherical
analyzer parameter \( C \) was presumed 2.254. This means the pass
energy is 4.23 eV and the calculated value of energy resolution
is 0.162, and there is 13.6% deviation. It could be from these
sources:

(1) During ray tracing, we kept the filling factor \( n \approx 50\% \). The
spherical aberration factor was estimated to be about 2 or
3\%. By considering this effect, the deviation is only 10%.

(2) The ray tracing program (EOPTICS) assumes that the
electric field exists only within two principal planes.
The electron rays outside this region are drawn as
straight lines. However, a distortion is possible due to a
small field interaction from two neighbor lenses.

(3) The machining errors of apertures, lens elements and
especially the lens spacing might have some contribution.
For example, the spacing is maintained by three 1/16 inch
diameter sapphire spheres. Three #57 holes are drilled in each end of a lens element to hold these sapphire spheres between two elements. The gap sizes are a little larger than 1mm. The difference in machining error of holes could affect the linearity of the lens axis, even though it is not detected by inspection. It also could cause the tube gaps to deviate from 0.1D.

No attempt was made to recalculate the lens voltages with any better program in order to match the theoretical and experimental energy resolution. Efforts were then put on the benzotriazole adsorption experiment instead of trying better lens voltages empirically, for the total energy resolution \( \Delta E_m \) is far better than the requirement of 0.5eV in surface adsorbate experiments.
III. SAMPLE PREPARATION

A substrate surface was made by cutting an OFHC (Oxygen Free High Conductivity) copper rod, 1/4 inches in diameter, at about 25° with respect to the rod axis (Figure 5(g) or (h)). After mechanical polishing, the substrate was rinsed in acetone, then methanol, with ultrasonic agitation. If cutting oil had been used instead of Tap Magic during machining, a 5-minute vapor degrease in trichloroethane was used before the acetone. After removal from the methanol, the substrate was dried under nitrogen gas and then put in the chamber. The chamber was pumped by a Thermionics Laboratory Inc. Model IP 200 ion pump (pumping speed=200 l/s). A turbomolecular pump, Leybold-Heraeus NT150 (pumping speed=150 l/s), was connected to a side arm. The base pressure was about 7x10^{-10} Torr with the chamber opened to the stainless steel Seya monochromator. We will discuss the sample preparation of clean copper, cuprous oxide and benzotriazole subsequently.

A. Copper Film Evaporation

To make a clean copper film, we first used Argon ions to clean the substrate surface. The typical working conditions were: \( P_{Ar} = 5\times10^{-5} \) Torr, \( Hv=700V \), beam current=7.8\mu A, and sputtering time from 5 to 10 minutes. After sputtering, less than a hundred angstroms of polycrystalline Cu film was
evaporated from a 99.99% pure Cu wire onto the cleaned substrate surface. The 1 mm diameter Cu wire was made by Johnson Matthey Chemicals Limited. The position and orientation of the substrate surface are shown in Figure 5(h). The chamber pressure was less than 2x10^{-9} Torr during evaporation.

UPS is very sensitive to atomic contamination on metal surfaces. Many studies have been done for gas adsorption (atomic or molecular) on clean metal substrates. The UPS EDCs from contaminated metal surfaces were compared to those of clean substrates. They are very useful for recognizing a clean metal surface. An RGA (Residual Gas Analyzer, a quadrupole mass spectrometer) showed that the main gases in our chamber were N_2, H_2O and H_2. It is well-known that H_2O^{49}, H_2, CO^{50} and N_2^{51} can not adsorb on clean copper surfaces at room temperature. O_2 adsorption on copper surfaces has been widely studied^{49,52-54} and it is very easily recognized. The UPS He(I) spectrum of carbon contamination on a copper surface was shown also by Evans^{52}. Figure 13 shows two EDCs measured on the same polycrystalline copper film right after evaporation (dots) at 1x10^{-9} Torr and 1 hour after the first measurement (solid curve) at 7.5x10^{-10} Torr. The only normalization factor is the averaged photon beam intensity during measurements. We can see that the two curves match very well almost over the whole range of the electron energy. In the lower kinetic energy region (below 4-5 eV), the intensity is easily affected
by even stray potentials. The spectrum has zero intensity at $E_K = 0$ eV because no electrons with zero kinetic energy on the sample surface can travel to the analyzer. The intensity rises to a maximum, then slowly drops towards the higher electron energy side. The electrons within this region are mainly inelastically scattered (secondary) electrons. The creation of inelastic electrons is described as follows: An electron excited into an unfilled state in the solid above the vacuum level may lose energy by scattering from a second electron in a valence state. Two secondary electrons are now produced which can escape and give rise to an energy distribution of low energy inelastic electrons. These secondary electrons have lost their initial state energy and can not be used to identify initial states.

The preparation conditions for the clean copper film (Sample 4) are listed in Table 9. The EDC will be shown in Figure 20 and will be discussed in the chapter on results and discussion.

B. Preparation of Cuprous Oxide Films ($Cu_2O$)

A leak valve was used to control the amount of oxygen gas in several steps from $10^{-10}$ Torr to $10^{-1}$ Torr. The ion pump gate valve was closed before opening the leak valve to oxygen. After the clean copper sample was in a $10^{-6}$ Torr atmosphere of oxygen for a while, we increased the oxygen pressure right
Figure 13. Clean copper EDCs at 21eV photon energy
after turning off the turbo pump to about 0.05 Torr and waited for about 3 minutes. Then, we closed the turbo gate valve and controlled the leak valve to make the pressure remain at 0.03 Torr for another 3 minutes. This was the process used to make sample 1 (see Table 9). During the entire preparation period, the amount of oxygen (chamber pressure) was not as stable as described above. The oxygen dose value of $10^7$ L (Langmuir, $1L=10^{-6}$ Torr sec) listed in Table 9 was only an estimate. However, what we really needed was a qualitative comparison among BTA on cuprous oxides and BTA on clean copper. As long as we could tell the qualitative difference among them, the exact amount of oxygen dose was not important.

To make Sample 2 (Table 9), we followed similar steps but started to heat the sample in $10^{-6}$ torr (oxygen pressure) and remained in this range for a longer period. The maximum temperature was about 70°C but dropped very fast upon higher oxygen exposure due to oxidation of the tungsten heating wire. The estimated preparation conditions are listed in Table 9 also. The oxidation of Sample 3 was well-controlled. The leak valve held the pressure (oxygen) at $10^{-6}$ Torr for 10 minutes. The preparation conditions are given in Table 9. The UPS EDCs of Sample 1 and Sample 2 will be shown and discussed in the chapter on results and discussion.
Table 9. Preparation of clean copper and cuprous oxide

<table>
<thead>
<tr>
<th>Preparation condition</th>
<th>work function (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1 oxygen dose (99.99%)</td>
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</tr>
<tr>
<td>~10^7 L, room temperature</td>
<td></td>
</tr>
<tr>
<td>Sample 2 oxygen dose (99.99%)</td>
<td>5.1</td>
</tr>
<tr>
<td>&lt;10^7 L at ~50°C</td>
<td></td>
</tr>
<tr>
<td>Sample 3 oxygen dose (99%)</td>
<td>~4.7</td>
</tr>
<tr>
<td>600L, room temperature</td>
<td></td>
</tr>
<tr>
<td>Sample 4 copper evaporation</td>
<td>4.5</td>
</tr>
<tr>
<td>(99.99% copper wire)</td>
<td></td>
</tr>
<tr>
<td>&lt;1.6x10^-9 Torr, room temperature, ~70Å thick</td>
<td></td>
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</tbody>
</table>
C. Benzotriazole Adsorption

Benzotriazole was evaporated through a capillary of length 6.35 cm and inner diameter 0.24 cm. It is made of OFHC copper and capable of keeping a pressure difference between the main chamber and the BTA evaporator. The design purpose was to maintain $10^{-9}$ Torr at the chamber ($P_c$) and $10^{-5}$ Torr at BTA evaporator ($P_b$). For the low pressure case, we have

$$C(P_b - P_c) = CP_b = S_cP_c$$

where $C$ is a conductance of this capillary and $S_c$ is the pumping speed in the chamber side, which equals 350 l/s.

Therefore, $C = 0.035$ l/s. Assuming that this capillary is operated in the free molecular flow regime, a more accurate, but complicated formula relating conductance to the capillary tube's geometry is,

$$C = \frac{1}{[1 + (3/8)(L/R)](\pi R^2)}$$

at 300°K, for air

where $R$ is the radius and $L$ is the length, both in cm, $C$ is in l/s.
Another simplified formula is,

\[ C = \frac{96R^3}{[1+(4/3)D]} \approx \frac{96R^3}{L} \]

when \( L \gg R \)

For convenience, we chose \( 2R=2/32 \text{in.}=0.24 \text{cm} \) and \( L=2 \text{in.}=6.35 \text{cm} \). We substitute the values of \( R \) and \( L \) back into the second equation to calculate the value of \( C \), \( C=0.0254 \text{ l/s} \). According to the first equation, the chamber pressure should be \( 7.2 \times 10^{-10} \text{ Torr} \) if the BTA evaporator pressure is \( 1 \times 10^{-5} \text{ Torr} \). In practice, when the gate valve between the evaporator and the chamber was opened before evaporation, the chamber pressure dropped from \( 7 \times 10^{-10} \text{ Torr} \) to \( 3 \times 10^{-9} \text{ Torr} \).

To evaporate benzotriazole, the pyrex tube was warmed to melt the BTA powder (the BTA melting point is at \( 98.5^\circ \text{C} \)). Additional heating would cause the chamber pressure to rise so we knew that BTA was evaporating. During evaporation, the sample position and orientation were shown in Figure 5(h). A liquid nitrogen cold finger was attached to the sample holder and the thickness monitor housing through two copper braids. The sample's lowest temperature was about \(-90^\circ \text{C} \). It was low enough for the formation of the condensed phase of BTA, but high enough for preventing CO and H\(_2\)O contamination. Since the thickness monitor showed no frequency shifts upon BTA evaporation, we were not able to describe the film thickness quantitatively.
IV. RESULTS AND DISCUSSION

Benzotriazole adsorption on one clean copper film (evaporated) and three oxidized copper films with different oxygen doses are chosen for discussion. The sample preparation conditions and their work functions are listed in Table 12 for copper oxides. Different thicknesses of benzotriazole were evaporated onto each sample at, or below, room temperature. The EDCs always showed the chemisorbed phase for thin layers of benzotriazole, whether the samples were cooled or at room temperature upon preparation. When the thickness increased, the spectra gradually changed from that characteristic of the chemisorbed phase to that of the condensed phase, i.e., bulk benzotriazole in cooled samples. The co-existence of chemisorbed and condensed phases was also observed before reaching the pure condensed phase. It means that the molecular solid benzotriazole is piling up on top of the chemisorbed Cu-BTA complex. This co-existence phase became mostly the chemisorbed phase after the temperature was raised to -30°C. No detectable work function change was found in the chemisorbed and co-existence phases. However, the whole spectrum was shifted to higher binding energy if the thickness was increased after the pure condensed phase had been reached.

In the following discussion, we will describe the method for distinguishing cuprous and cupric oxides first. The relaxation energy shift and hydrogen bond, the gas phase
and condensed phase of BTA, the nature of BTA chemisorption on copper (oxides) and a new model for CuBTA chemisorption structure will be the subsequent topics.

A. Identification of Oxidation State by Means of UPS

Cuprous and cupric oxides can be distinguished in two ways\(^{56}\):

1. The cuprous oxide has a red color and cupric oxide a black color.

2. The He(I) EDC from CuO reveals a broad emission from overlapping oxygen-induced 2p and Cu 3d states (broad maximum 2-7eV below Fermi level), and shake-up satellites 10-12eV below \(E_F\). However, the observation of shake-up features during the interaction of oxygen with Cu surfaces, as pointed out by Stone\(^{57}\), does not necessarily imply the formation of CuO. Figure 14 shows the EDC of Sample 1 measured at 21eV photon energy. The Cu 3d band is at -2.9eV. An oxygen peak was found at -6.0eV and a shoulder at -7.2eV. The sharp peak was seen at -1.4eV just above the d-band associated with an antibonding combination of Cu 3d and O 2p orbitals\(^{58}\). A satellite-like broadened feature is observed 9-12eV below \(E_F\). Even though there was no way to determine the color of this oxide inside the chamber, the clear separation of the Cu
Figure 14. EDC of Cu\textsubscript{2}O at 21 eV.
3d band and the oxygen peak characterized it to be a cuprous oxide (Cu₂O). Moreover, this spectrum is in excellent agreement with He(I) data from polycrystalline Cu₂O obtained by Evans. The other oxides (Sample 2 and Sample 3) are Cu₂O also.

B. Relaxation Energy Shift and Hydrogen Bond

The power of electron spectron spectroscopy for solving problems in surface science and catalysis has led to many applications of photoemission to adsorbed species on metallic substrates. Adsorption occurs, when the atom or molecule, called the 'adsorbate', stays on the surface of the solid, called the 'substrate' (or 'adsorbent'). If the atoms of the adsorbate form chemical bonds with the surface of the substrate, we say it is chemisorbed. Electrons are shared between these atoms and substrate. The electron donor-acceptor (charge-transfer) interaction has been discussed in Chapter I to point out the molecular orbital energy shift due to chemisorption. The orbitals involved in the chemical bonding are called bonding orbitals. Others are called nonbonding orbitals. If the adsorbate interacts with the surface of the substrate by means of the Van der Waals force, we say it is physisorbed. (It only exists at low temperatures.) No charge transfer is possible. All orbitals in physisorbed molecules are called nonbonding orbitals and no energy shift would be
observed. To avoid confusion, the terms bonding and nonbonding are used only for considerations of adsorbate-substrate interaction. For the adsorbate-adsorbate interaction, the intermolecular force is mainly Van der Waals, but it can be a hydrogen bond interaction for those hydrogen bonded molecular solids such as H$_2$O, NH$_3$ and benzotriazole, etc.... If the hydrogen bond is very strong, the molecular orbitals involved in this kind of interaction would have orbital energy shifts.

An energy shift means that the binding energy of an orbital is different from that of the corresponding orbital in the free molecule. The total binding energy shift of any orbital may have contribution from three sources: two mentioned previously are (1) chemisorption (adsorbate-substrate interaction) (2) hydrogen bond (adsorbate-adsorbate interaction) and the remaining one is (3) the relaxation effect (induced by the photoionization process). In photoemission experiments, any molecular orbital experiences an additional relaxation shift, no matter whether it is bonding, nonbonding or hydrogen bonded. We will discuss the relaxation shift first and then the hydrogen bond.

1. Relaxation energy shift

In photoemission experiments, the binding energy of orbitals in a free molecule, $E_b$, are given by the Einstein relation:
\[ E_D = E_K - h\nu \]

where \( h\nu \) is the photon energy and \( E_K \) the kinetic energy of the photoelectron.

In the case of adsorbed gases on metals, the binding energies are defined as

\[ E_D' = (E - E_F) + \phi \]

where \( (E-E_F) \) is the energy difference between an observed peak and the Fermi level, and is \( \phi \) the work function of the sample.

We now consider a physisorbed, nonhydrogen-bonded system, in which the orbital binding energy shifts are only contributed by the relaxation effect. The adsorbate photoemission peaks have the same structure observed in the free atom or molecule. The binding energy of each peak is lowered relative to the gas-phase value by an additional relaxation energy that arises through polarization of the substrate valence electrons to screen the adsorbate hole state. The relaxation energy \( E_R \) is the difference between \( E_D \) and \( E_D' \) (\( E_R = E_D - E_D' \)), which reflects differences in the initial and final state energies of the gaseous and adsorbed molecule. Examination of the photoemission spectra of adsorbates showed that strongly bound
σ-orbitals show larger relaxation shifts than more weakly bound π-orbitals. However, many people tentatively assumed the relaxation shifts of the σ- and π-orbital ionization energies from their gas phase values are equal. This assumption (from Demuth and Eastman) stems from the observations that (a) the relaxation shifts of both π and various σ orbitals are seen to be identical for the condensed (physisorbed) species, and that (b) chemisorption bonding is observed to be a weak perturbation on the molecule - no strong changes in the molecular configuration are observed between condensed and chemisorbed phases.

In a physisorbed, but hydrogen bonded system, all molecular orbitals are either (1) nonbonding and not hydrogen bonded or (2) nonbonding and hydrogen bonded. We can calculate the relaxation energies from type (1) orbitals (π and σ) and compare them to the energy shifts of type (2) orbitals (π's to π, σ's to σ). The additional energy shifts are due to the hydrogen bond interaction. In chemisorbed system, the situation would be more complicated. However, a nonbonding and nonhydrogen-bonded orbital is still the key to separate the relaxation energy shift and chemical energy shift.

2. Hydrogen bond

Hydrogen bonding was first recognized some 70 years ago by Huggins and others. The first theory of the hydrogen bond
was formulated by Pauling. He used the Pauli principle and an electrostatic model to visualize the formation of a hydrogen bond, AX-H...YB. He argued that since the 1s hydrogen orbital is already used in chemical bonding with the X atom the additional interaction with Y can only come about by electrostatic forces. However, if one accepts that the hydrogen bond arises from short-range interactions, a view supported by the fact that the hydrogen bond distance, RX-H...Y is always smaller than the sum of the van der Waals radii, then one expects not only electrostatic interactions to be present but also exchange and charge-transfer interactions as well. Many theoretical studies came to the conclusion that for shorter distances the electron delocalization (charge-transfer) contribution to the hydrogen bond becomes extremely important. The suggestion that the charge-transfer transition band should appear in the vacuum ultraviolet region has been confirmed by Nagakura who discovered the charge-transfer band associated with the intermolecular hydrogen bond complex of acetic acid with triethylamine at 165nm in the vapor phase. The band is shifted to 170nm in n-heptane and in acetonitrile.

The charge-transfer effect due to hydrogen bonding was also observed in a UPS study. Campbell et al. have performed a 40.81eV UPS study of the molecular solids NH₃ and H₂O. The energy separation of the two uppermost bands of solid ammonia are not significantly different from the 3a₁ (nitrogen lone
pair) and le ($\pi_{NH_2}$) molecular orbitals of gaseous NH$_3$. The hydrogen bond interaction in solid NH$_3$ can not perturb the molecular orbitals. By contrast, the hydrogen bond has produced a significant change in the electronic structure of the valence bands of solid H$_2$O. The three uppermost valence bands were measured. They corresponded to $1b_1$ (No, oxygen lone pair, $\pi$ orbital), $3a_1$ (No, oxygen lone pair, $\sigma$ orbital, responsible for hydrogen bonding), and $1b_2$ ($\sigma_{OH}$) of gaseous H$_2$O. In their solid state measurement, the $3a_1$ band was severely perturbed to the extent that it had almost lost its identity. The energy separation of the $1b_1$ band and the $1b_2$ band was about 6.2eV which is 0.3eV larger than that in the gaseous molecule. The hydrogen bond interaction in solid H$_2$O reveals the charge-transfer characteristic, which results in the relative energy shift in molecular orbitals. The difference in the hydrogen bond effect on solid NH$_3$ and H$_2$O was related directly to the much smaller hydrogen bond length in H$_2$O (1.75Å), compared with that in NH$_3$ (2.347Å).

C. The Gas Phase and Condensed Phase of BTA

The ionization potentials and orbital assignments of the molecular orbitals are the crucial information needed to understand the chemisorption interaction between the adsorbate and substrate. However, gas phase orbitals become broadened in solid state spectra; two or several nearest orbitals may
overlap to form one band. This Van der Waals interaction creates difficulty in directly comparing the chemisorbed spectrum to the gas phase spectrum. Most of the time, it is more convenient to reference to the condensed phase spectrum (physisorption). Figure 15(c) shows a replica of the HeI and HeII spectra of gas-phase benzotriazole from Palmer and Kennedy’s work. The X-coordinate is the ionization potential in eV. They also did a calculation of the molecular orbital energies and the assignment of structures in the gas phase photoelectron spectrum. The lines shown below the spectrum represent the energy positions of the calculated molecular orbitals. The corresponding experimental ionization potential and orbital assignments are listed in Table 10.

Figure 15(a) and (b) shows typical photoelectron spectra of solid benzotriazole in (a) the condensed phase on an oxidized copper surface measured at 28eV photon energy from Sample 3. (b) the condensed phase on a clean copper surface measured at 24eV photon energy from Sample 4. The EDC of Sample 3 (oxide) is shown in Figure 15 (dots) and the EDC of Sample 4 (clean copper) will be shown in Figure 22 (dots).

Following Palmer’s assignment, we have measured five S (σ) orbitals, five P (π) orbitals, one N+ (symmetric nitrogen lone pair) orbital and one N- (antisymmetric nitrogen lone pair) orbital. All the orbital energy positions are marked on these condensed phase spectra in Figure 15(a) and (b). Their relative energy positions are according to the experimental
values of ionization potential measured in the gas phase. See Table 10. The X-axis of the condensed phase spectrum shows the binding energy with respect to the Fermi level of oxidized copper and clean copper, respectively.

Compare these two condensed spectra. They are similar except: (1) In Figure 15(b), the measurement started from a kinetic energy of 2eV. In Figure 15(a), the measurement started from 6eV. There are more secondary electrons in the former spectrum. They almost buried the molecular orbital contributions $S_1$ and $S_2$. (2) The copper 3d band above $p_7$ can still be viewed in Figure 15(b) but not in (a). This indicates that the benzotriazole film is thicker on the cuprous oxide surface than on the clean copper surface and will be discussed later. All the condensed phase spectra of BTA should have similar structures regardless of the substrate, because they are free from the adsorbate-substrate interaction, and are only affected by intermolecular forces: Van der Waals and hydrogen bond interactions. These intermolecular forces will make the gas molecular orbital peak broaden and possibly shift (if the hydrogen bonding is strong in molecular solids) upon condensation.

Compared to the gas phase spectrum, the N-band energy shifts downwards about 0.2-0.3eV in the two condensed solid benzotriazole spectra. Benzotriazole is a well-known hydrogen bonded solid. From the study of Escande et al., among four BTA molecules, there are six hydrogen bonds. The two shortest
Figure 15. EDCs of condensed BTA and gas BTA

(a) EDC of BTA condensed phase on copper oxide, Sample 3 at 28eV
(b) EDC of BTA condensed phase on clean copper, Sample 4 at 24eV
(c) EDC of BTA gas phase at He(I) and He(II)
Table 10. Benzotriazole orbital energies (eV)

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</tr>
<tr>
<td>$S_1$</td>
<td>20.10</td>
<td>$\sigma$</td>
</tr>
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</table>
Figure 16. Sample 3 at 28eV

... EDC of copper oxide

— EDC of BTA chemisorbed on copper oxide
hydrogen bond lengths are 1.80Å\(^0\) and 1.85Å\(^0\) and a little bit longer than the 0...H bond (1.75Å\(^0\)) in solid H\(_2\)O\(^6\). Other weaker hydrogen bond lengths are 2.21Å\(^0\), 2.27Å\(^0\), 2.28Å\(^0\) and 2.51Å\(^0\). According to Campbell's study, the N- energy shift is very possibly due to a strong hydrogen bond effect.

D. The Nature of BTA Chemisorption on Cu (Oxides)

Figure 17 shows the EDC of Sample 1 measured at 28eV photon energy (dots). This copper oxide was Cu\(_2\)O as discussed before. The Cu 3d band is at -3.1eV. Oxygen 2p levels have a flat maximum but still cover the same energy region (5-8eV below \(E_F\)). The difference in 28eV (photon) and 21eV (photon) spectra is due to final state effects and is a characteristic in UPS studies. Since there is no relation between copper BTA chemisorption and this effect, we will not discuss it further. Benzotriazole (BTA) was evaporated on Sample 1 at -10°C. While evaporating, the pressure in the main chamber rose from 2\(\times\)10\(^{-9}\) to 4\(\times\)10\(^{-9}\) Torr. The typical structure of chemisorbed CuBTA is shown as a solid line in Figure 17. This spectrum was taken after Sample 1 warmed up to room temperature. The Cu 3d band lost considerable intensity due to chemisorption. The benzotriazole spectrum changed dramatically compared to its condensed phase. However, the \(P_1\) band has the character of solid benzotriazole. Its energy position showed no detectable shift during the increase in BTA thickness until the pure
Figure 17. Sample 1 at 28eV

--- EDC of Cu$_2$O

--- EDC of BTA chemisorption on Cu$_2$O
condensed phase were reached. Its intensity always increased as more BTA was evaporated on the sample. These phenomena indicate that $P_1$ has no bonding to the copper oxide substrate. It is at 9.6eV below $E_p$.

1. **Identification of the bonding and nonbonding orbitals**

We will separate the relaxation and chemical effects in order to identify the bonding and nonbonding orbitals. For convenience, we assume that all $\sigma$-orbitals and $\pi$-orbitals have the same relaxation energy shift and will discuss the possible case if $\sigma$-orbitals have larger energy shifts. Referencing to the energy position of the nonbonding orbital $P_1$, other gas-phase molecular orbitals have been located in Figure 17. Three new peaks are marked A, B and C. The binding energy of $P_1$ has 14.7eV in the chemisorbed state and 15.0eV in the free molecular state. Therefore, the relaxation energy shift is 0.3eV.

Before we really identify the bonding and nonbonding orbitals for this chemisorbed structure, we would like to point out the fact that the CuBTA chemisorbed structure is unique for different amounts of preadsorbed oxygen by showing the chemisorbed CuBTA EDC of Sample 2 at 19eV and 28eV and of Sample 3 at 28eV. To have a more clear comparison, we follow the equal relaxation shift (for $\sigma$ and $\pi$ orbitals) assumption to position the gas molecular orbitals on Figures 18, 19 and 15.
Figure 18 shows the EDC of Sample 2 measured at 28eV photon energy (dots) also. The clear separation between oxygen 2p and Cu 3d identifies the Cu$_2$O character. The Cu 3d band is at -3.1eV as that of Sample 1. The oxygen 2p has a different appearance but it still covers the same energy range (5-8eV). Benzotriazole was evaporated at room temperature. The evaporating pressure was similar to that for Sample 1. This chemisorption structure is basically the same as the one in Figure 18. The broader peaks may be due to the thinner layer of benzotriazole so that the background electrons from the oxygen peaks contribute more to the spectrum. The high temperature surface oxygen was less reactive towards methanol and other molecules and seems to be responsible for this thinner adsorbed layer. Despite the broadening, most of the peak positions can be assigned to the same energy positions as those in Sample 1. New peak B was not so pronounced as that in Sample 1 but definitely still a shoulder on P$_1$ whose energy was at -9.6eV also. We only point out that the chemisorbed CuBTA structure on Sample 3 (Figure 15) is the same as those on heavily oxidized copper surfaces, without further discussion.

Figure 19 shows the EDC of Sample 2 measured at 19eV photon energy (dots). The Cu 3d band is at -2.9eV and oxygen 2p -5.8eV. This oxide spectrum is not the same as the one in Figure 20 measured at 28eV. We observe the final state effect again. However, the observed chemisorption features (B, P$_1$, C
Figure 18. Sample 2 at 28eV

... EDC of Cu$_2$O

—— EDC of BTA chemisorption on Cu$_2$O
Figure 19. Sample 2 at 19eV

... EDC of Cu$_2$O

— EDC of BTA chemisorption on Cu$_2$O
and \( P_3 \) show no structural differences by comparing to those measured at 28eV photon energy (Figures 17 and 18). The rising tail left of peak B is the right side of the secondary electron peak.

Now we go back to Figure 17 and identify the bonding or nonbonding orbitals by following this order: \( \pi \)-orbitals, nitrogen lone pairs, \( \sigma \)-orbitals and then a summary.

1) Significantly, \( P_3 \) shows no chemical shift because its relative energy position does not change with respect to \( P_1 \). Therefore, \( P_3 \) is a nonbonding orbital. We have difficulty in observing \( P_2, P_4 \) and \( P_5 \). \( P_2 \) may be buried by a new feature C, \( P_4 \) and \( P_5 \) may be located under the Cu 3d band. A direct subtraction technique (chemisorption EDC - clean metal EDC) was used to discover the remnant of the \( \pi \) level of ethylene occurring on the top of the emission from the silver d band\(^6\). This technique has been used widely in chemisorption studies,\(^{73,74,75}\) especially when the attenuation of the metal d band is small. While the d band attenuation is large, a small contribution from the adsorbate may be smeared out due to the very large intensity difference between the clean metal d band and the chemisorption d band. Therefore, we use a normalization method. We multiplied the intensity of the \( \text{Cu}_2\text{O} \) EDC by a factor to normalize the Cu 3d peaks of \( \text{Cu}_2\text{O} \) and of Cu-BTA (at -3.1eV), then do the subtraction. Figure
Figure 20. Sample 2 at 19 eV

- normalization subtraction

... direct subtraction
20 shows the results from the direct subtraction (dots) and from the normalization subtraction (solid line). They are subtracted from Figure 19. Only $P_1$, $P_4$ and $P_5$ are positioned to show the fact that $P_4$ and $P_5$ do not have chemical shift. They are nonbonding orbitals. $P_2$ is, therefore, assumed to be nonbonding orbital based on the following arguments: (a) $P_2$ can not be assigned to peak $C$ as a chemisorption effect because the binding energy of peak $C$ is lower than that of $P_2$. (b) Since $\pi$ orbital electrons are highly delocalized, wherever $\pi$ electrons interact with other systems, the weaker $\pi$ orbitals should be more easily affected. The fact that $P_3$, $P_4$ and $P_5$ show nonbonding character implies that $P_2$ is nonbonding also. Therefore, we conclude no $\pi$-3d interaction between BTA and the copper oxide surface.

(2) $N^-$ disappears. Even though we can not determine the energy positions of the chemisorbed $N^+$ and $N^-$ right now, it is still reasonable to say that the nitrogen lone pairs are bonding orbitals.

(3) Refer to Figure 17. $S_3$ and $S_4$ disappear and new peaks $A$ and $B$ appear. $S_1$ and $S_2$ may shift a little bit towards the lower binding energy side. We can not determine where $S_5$ locates; even though we assume that the $\sigma$-orbitals have a larger relaxation shift than the $\pi$-orbitals do. These $\sigma$-orbitals still show a relative energy shift. The situation is not going to change. Therefore, we keep the assumption
of equal relaxation energy shift and suggest several possible causes:

(a) Electron charge back donation from Cu 3d to the LUMO (Lowest Unoccupied Molecular Orbital) of BTA may enlarge the triazole and benzene rings. Since $S_4$ electrons mainly distribute along C-N-N-N-C chain, the triazole ring stretching may lower the binding energy of $S_4$ and it shifts to peak B.

(b) Another possible cause is hydrogen dissociation. The adsorption of ammonia on evaporated clean copper and preoxidized copper films was studied by X-ray photoelectron spectroscopy at 295K by Matloob and Roberts\textsuperscript{76}. With atomically clean copper, no adsorption was observed at low pressures of ammonia ($\lesssim 10^{-5}$Torr), however, at higher pressures ($\sim 10^{-4}$Torr), a broad (FWHM=3eV) N 1s signal was observed centered at about 398eV. This is not characteristic of molecularly adsorbed ammonia, which has a characteristic N 1s value at 400eV\textsuperscript{77}. They suggested that the adsorbed ammonia is at least partially dissociated on clean copper at 295K. After exposing a preoxidized copper surface to ammonia at about $10^{-4}$Torr for 10 minutes at 295K, the O 1s signal almost disappeared and a strong N 1s peak developed at 398eV. Ammonia evidently has dissociated on adsorption, giving rise to hydrogen adatoms which have removed the surface
oxide as water. The binding energy (398 eV) is ~1 eV higher than that of typical N adatoms (397 eV). The stoichiometry of the surface process was suggested as follows:

\[ \text{NH}_3 + O \rightarrow \text{NH} + \text{H}_2\text{O}_{(g)} \]

In other investigations, people found that H\textsubscript{2}O\textsuperscript{78,79}, HNCO\textsuperscript{80,81}, C\textsubscript{2}H\textsubscript{4}\textsuperscript{82} and HCN\textsuperscript{83} did not adsorb on a clean Cu(111) surface at 300K (e.g., exposure to 10-1000L HCN), but the presence of adsorbed oxygen greatly promoted its interaction with the copper surface and caused the dissociative adsorption (very probably due to the weak bonding between hydrogen and copper\textsuperscript{83}). The driving force of the hydrogen dissociation is the formation of the strong O-H bond. The OH group, however, is not necessarily stable on a Cu surfaces, as indicated by Solymosi\textsuperscript{83} in his HCN study. The subsequent procedures are given by

\[ \text{Cu-OH} + \text{Cu-OH} \rightarrow \text{Cu-O} + \text{Cu} + \text{H}_2\text{O}_{(g)} \]

\[ \text{Cu-OH} + \text{HCN} + \text{Cu} \rightarrow \text{Cu} + \text{H}_2\text{O}_{(g)} + \text{Cu-CN} \]

This process proceeds simultaneously with the adsorption of HCN, producing thereby free adsorption sites. Based on these studies, we believe that hydrogen
dissociation did occur in our benzotriazole vapor adsorption on copper oxides. It was through the weak bonding between hydrogen and copper (reference 83 and NH$_3$ case), but highly promoted by the strong oxygen-hydrogen bond. According to many studies of benzotriazole adsorption (on copper), we prefer that hydrogen is from the more labile N-H group. Among the $\sigma$-orbitals, $S_1$, $S_2$ and $S_3$ involve the N-H atomic bond. The dissociation, therefore, causes the energy shifts of these orbitals. Following the assumption of equal relaxation shifts for $\sigma$ and $\pi$-orbitals, $S_3$ moved to the higher binding energy side and $S_1$ and $S_2$ shifted to opposite direction, but left a tail under $S_1$.

(c) The third possibility is polymerization. UPS measurements on H$_2$CO (formaldehyde) have been made by Sexton et al.$^{72}$ and Bowker and Madix.$^{84}$ Sexton interpreted the spectrum taken at 200K to be a polymer paraformaldehyde. (The unit cell includes one H$_2$CO and one Cu. Oxygen is the bridge which interacts with Cu by a lone pair orbital and one covalent bond to the C atom of CH$_2$. The polymer was connected by the other covalent bond to the C atom of CH$_2$ of the next unit cell.) The paraformaldehyde and molecular formaldehyde structures were separated by EELS (Electron Energy Loss Spectroscopy) but not UPS. In their interpretation of the UPS spectrum (paraformaldehyde), the highest $\pi$ orbital ($1b_1$
corresponding to \( \Pi c = 0 \) did not shift, but the oxygen lone pair (\( 2b_2 \)) shifted to the higher binding energy side because of the chemisorption effect, two lower lying bands shifted to be closer to each other. All the peaks were broadened compared to the condensed phase. Lacking EELS information on benzotriazole (on copper (oxides)), we cannot tell whether the \( \sigma \)-orbital shift means polymerization or not. However, this phenomenon (polymeric CuBTA) stemmed from many studies (see Introduction). We, therefore, suggest that polymerization is another possible cause of the \( \sigma \)-orbital shift, especially peak A (result from \( S_1 \), \( S_2 \), \( S_3 \)).

(4) To understand the UPS spectra of Cu(I)BTA, we have discussed:

(a) Benzotriazole bonded to copper through the nitrogen lone pair. This stemmed from the disappearance of the N-orbital. Peak C was suggested to be the result of the chemical shift of the nitrogen lone pair. However, its broadness produced difficulty in observing the behavior of the N\(^+\) orbital and we hesitated to assign peak C to be from N\(^-\),N\(^+\), or both.

(b) There was no \( \pi \)-d interaction between benzotriazole and copper. This stemmed from the results of our subtraction technique which showed no relative shift between all \( \pi \)-orbitals in comparison to the condensed phase spectrum.
(c) Hydrogen dissociation and polymerization are suggested as being responsible for the σ-orbitals' dramatic displacement (S₁, S₂, S₃ to peak A). Back donation from copper to benzotriazole probably resulted in peak B (shift from S₄).

2. Further discussion on BTA and Cu interaction

In the discussion below, we will give more evidence for the lack of π-δ interaction at first. Then, we will assign the new energy positions of N- and N+ after the chemical shift.

(1) Benzotriazole is N (nitrogen lone pair) bonded on copper oxide surfaces, and it does not lie flat on the surface.

Based on a consideration of the C 1s and N 1s binding energies, it was suggested that pyridine adsorbed on iron and nickel⁸⁵ and on palladium⁸⁶ at room temperature by "π-bonding", while pyridine on copper⁸⁶ and pre-oxidized nickel⁸⁷ showed "N-bonding". Pyridine adsorbed on Pd⁸⁷ at 165K was N-bonded also. In the pyridine condensed phase, the binding energies of C 1s and N 1s are 286.2eV and 400.1eV, respectively. All N-bonding modes have only small shifts of the C 1s and N 1s binding energies. For example, the C 1s and N 1s binding energies are 285.5eV and 399.9eV on evaporated Pd (165K), 285.9eV and 400.2eV on evaporated Cu (295K) and 286.0eV and 400.2eV on pre-oxidized Ni.
The energy range for the C 1s shift is from -0.2eV to -0.7eV, and from 0.1eV to -0.2eV for the N 1s shift. The N-bonded mode has pyridine standing perpendicular to the metal substrate surface. In the UPS study, pyridine has been proposed as being N-bonded and to stand up on the copper surface on the basis of angle-resolved measurements. In their study, there was no relative energy shift among all the π-orbitals, and the nitrogen lone pair peak shifted to higher binding energy.

π-bonded pyridine does not necessarily mean that the aromatic ring is strictly parallel to the surface. The aromatic ring may incline at some angle as a result of an additional interaction with the surface via the nitrogen lone-pair orbital. However, all π-bonded pyridine showed strong binding energy shifts upon adsorption. The C 1s and N 1s have shifted to 284.6eV and 398.7eV for evaporated Ni (290K) and 284.7eV and 398.5eV for evaporated Pd (295K). Compared to the condensed molecule, the binding energy shifts are about -1.6eV for C 1s and -1.4eV for N 1s.

According to XPS studies of benzotriazole adsorption on copper oxide from Roberts, the N 1s binding energy of BTA was 400.2eV (3.2eV FWHM). Upon adsorption on copper(I) oxide, the N 1s binding energy was 399.9eV (2.3eV FWHM). Even though there was no report on the binding energy shift of C 1s, the bonding mode studies of pyridene adsorption strongly support that benzotriazole is mainly
N-bonded upon adsorption on cuprous oxides. That means benzotriazole does not lie down on the copper oxide surface also.

(2) A tentative assignment of the nitrogen lone pair orbitals is that the chemisorbed N- overlaps with P3 and the chemisorbed N+ is peak C. According to this assignment, the binding energy shifts upon BTA adsorption are about -1.4±0.2eV for N- and -0.6±0.1eV for N+. We explain the reason below.

Figure 21 shows the coexistence of the chemisorbed phase and condensed phase EDC (solid line), which was measured at about -70°C after several BTA evaporations on Sample 1. The EDC for the mainly chemisorbed phase is shown by dots. It was measured right after the temperature rose to -30°C. After the copper oxide surface had been covered by chemisorbed benzotriazole, the molecular solid benzotriazole would deposit on top of the chemisorbed film. The intensity of the spectrum from the chemisorbed BTA was reduced (mean free path effect) and that of condensed-phase spectrum increased. When the temperature rose high enough to desorb the condensed benzotriazole, we can observe that the intensity of the Cu 3d band (chemisorbed structure) increased compared to the solid and dotted -spectra. In the P4 and P5 region, no significant change occurred. This can be explained by the decreasing intensity of the nonbonding P4, P5 and the
Figure 21. Sample 1 at 28ev

— EDC of coexistence phase on \( \text{Cu}_2\text{O} \) at \(-70^\circ\text{C}\)

... EDC of chemisorption phase on \( \text{Cu}_2\text{O} \) at room temperature
increasing intensity of the Cu 3d band.

For the nonbonding $P_1$ the intensity dropped after the sample temperature increased. Peak C showed the opposite response because of its chemisorbed character. The shoulder marked by $P_3$ had a very similar character to the $P_4$ and $P_5$ region -- no significant change. This suggested that the shoulder probably not only included the nonbonding structure ($P_3$), but also involved some chemisorbed structure, such as N-. Compared to the condensed-phase spectrum, this shoulder is really broader. Therefore, we assign the peak from chemisorbed N- to this shoulder and the chemisorbed N+ structure to peak C.

3. Benzotriazole chemisorbed on a clean copper surface at room temperature

In benzotriazole adsorption studies, no atomically clean copper surfaces have previously been used. Infrared spectroscopy is not sensitive to just a thin surface layer. XPS only observed small amounts of the benzotriazole adsorption characteristic on electrochemically clean copper (copper substrate still in solution upon benzotriazole treatment). Therefore, the role of the copper atom on benzotriazole adsorption has never been discussed. Figure 22 shows an EDC for a clean copper (Sample 4) measured at 24eV photon (dots). Two Cu 3d features are located at -2.6eV and -3.5eV with a shoulder at about -4.6eV. During evaporation of
Figure 22. Sample 4 at 24 eV

... EDC of clean copper

— EDC of BTA chemisorbed on clean copper
benzotriazole the copper sample temperature was about -10°C, the main chamber pressure rose from 2x10^{-9} Torr to 4x10^{-9} Torr. The spectrum (Solid line) clearly showed the same chemisorption characteristic as that on cuprous oxides. Still assuming the equal relaxation shift of all σ-orbitals and π-orbitals, we marked P S, N+ and N- energy positions as we did in the study of BTA ON Cu_2O. Here, P_1 located at -10.1eV and gave a 0.4eV relaxation shift. Peaks A, B and C appeared at the same relative energy positions as found in the cuprous oxide case. Figure 23 shows the results of the subtraction techniques for the difference between BTA-clean Cu and clean copper EDCS. The top curve is from the normalizing subtraction and it reveals no chemical shifts of P_4 and P_5 with respect to P_1. The bottom one is from direct subtraction only for reference. The condensed phase spectrum has been shown in Figure 15 (b) and appeared no different from the condensed phase measured on the Cu_2O substrate, except for secondary electron effects. Right after taking the spectrum at Figure 15(b), we stopped adding liquid nitrogen and took the spectrum again when the sample warmed up to room temperature. The results are shown in Figure 24. This spectrum is basically the same as the chemisorbed spectrum (solid line) of Figure 20. The Cu 3d band is relatively lower than these benzotriazole peaks in Figure 22 and it is reversed in Figure 20. This phenomenon agrees with the fact that more benzotriazole molecules are available and the higher temperatures is in favor of the
Figure 23. Sample 4 at 24eV

--- normalization subtraction

... direct subtraction
Figure 24. Sample 4 at 24eV
Chemisorbed BTA after warming up to room temperature
chemisorption reaction. All the discussion made for the BTA-Cu₂O case are still true for the case of BTA on clean Cu, except that no oxygen-promoting hydrogen desorption is possible in the latter case. However, the spectra are almost the same. This implies that the Cu 3d band plays the main role upon benzotriazole adsorption. The study of pyridine adsorbed on clean copper at room temperature \(^{88}\) supports our normalization subtraction result and the shift of the nitrogen lone pairs, which suggests the N-bonding and a vertical molecular plane. Actually, no benzene adsorption on a clean copper surface at room temperature has been found\(^ {89}\). This shows that the π-3d interaction or the breaking of the C-H bond in the benzene ring are not preferred on clean copper surfaces. On the other hand, the study of ammonia adsorption on clean copper surfaces at room temperature suggests that N-H bond-breaking is possible due to copper backdonation, eventhough copper is known to be a weak backdonator. Our measurement (BTA on clean copper) gives another possible example.

E. A New Model of CuBTA Chemisorption Structure

We have pointed out the disadvantages of the two Cu(I)BTA structures shown in Figure 2 before. We now construct a new model for the Cu(I)BTA structure based on our results and those from XPS studies. Several assumptions are made:
The adsorption of BTA molecules on copper surfaces was carried out with the blocking of two surface atoms of Cu by each BTA, according to the study of Angely et al.\textsuperscript{33}. This was the only stoichiometry experiment on a BTA vapor treated copper (oxide) system. Other stoichiometric studies, which gave the ratio of 1:1 to BTA and Cu (except the short time immersion study from Fox et al.\textsuperscript{30}), were all performed in solutions including BTA\textsuperscript{−} and Cu\textsuperscript{+} ions.

The benzotriazole would clean off (part of) the oxygen by forming H\textsubscript{2}O\textsubscript{(g)}. This suggested that oxygen did not incorporate into Cu(I)BTA's structure.

The evaporated copper film would be more like a Cu(111) single crystal in order to have more compact structure. Polycrystalline films often have preferred axes for the crystallite normal axes, corresponding to normals to close-packed planes. The distance between two nearest atoms is 2.55\textgreek{A}\textsuperscript{0} in the Cu(111) surface plane. This distance can be found in Cu(100) and Cu(110) surface planes also. Therefore, we set up a Cu(I)BTA structure on a Cu(111) surface.

According to our study, benzotriazole stood up on the copper surface and bonded through nitrogen lone pairs.

The typical C-N bond length is about 2\textgreek{A}\textsuperscript{0}, based on studies of many copper derivatives\textsuperscript{90}.

All the values of bond lengths and angles of the benzotriazoles molecule were from Escande's study\textsuperscript{52}. 
Two possible linear chains of Cu-BTA are shown in Figure 25(a) and (b) (according to Roberts XPS data, three nitrogen atoms have equivalent charge distributions). The copper surface is perpendicular to the benzotriazole molecular planes. In Figure 25(a), we can see that the free nitrogen atom N₁ (not bonded to a copper atom) is close to a hydrogen atom H₅ (refer to Figure 3(b)), which projects out from the neighbor benzotriazole molecule. The distance is about 0.7Å and it may be too short for bonding. However, the benzotriazole molecules are not necessarily exactly normal to the copper surface. If two neighboring molecules are off normal by +9° and -9°, respectively, the distance between N₁ and H₅ is about 1.2Å (the covalent bond length of N-H is about 1Å). This geometry indicates a very strong charge transfer between the N₁ and the H₅ atoms, and suggests that the polymeric chain is connected through very strong charge transfer interactions between benzotriazole molecules (C₅-H₅...N₁, hydrogen bond). In Figure 25(b), we will have C₈-H₈...N₃ to achieve the polymerization. Now we apply this model to explain the results from three experiments.

1. We review our UPS spectra for the Cu-BTA chemisorbed species (BTA on Cu and BTA on Cu₂O). S₁ and S₂ only shifted a little bit towards the lower binding energy side and became broader. Among S₁, S₂ and S₃ orbitals, S₁ provides the biggest contribution to N₁-H₁ bonding. S₂ involved a small amount of N₁-H₁ bonding. It is very
Figure 25. The structure of CuBTA chemisorption film with two possible orientations (a) and (b)
interesting that $S_3$ involved both $N_1-H_1$, $C_5-H_5$ and $C_8-H_8$ bonds. Referring to our model, $N_1$ (or $N_3$) interacts with a hydrogen atom $H_5$ (or $H_8$) closely after $H_1$ dissociation. These interactions ($N_1-H_5$ and $N_3-H_8$) are enforced by the copper lattice. The new bond length is longer than the older one by only a small amount. This could explain the reason why $S_1$ and $S_2$ did not reveal a large change after $H_1$ desorption, but shifted to the lower binding energy side only a little bit (because the N-H bond length is longer). The model shows that $S_3$ is responsible for polymerization. Upon polymerization, the bond energy increases$^{92}$ and may cause $S_3$ to shift towards the higher binding energy side.

(2) Cotton and Scholes$^4$ have done solubility and tarnish resistance tests on five different molecules (benzotriazole, indazole, benzimidazole, indole and 1-Methyl benzotriazole) as mentioned in Introduction. The results were listed in Table 2. Their Cu(I)BTA polymeric model could not explain these results as pointed out before. Now we use our model to explain the results in Table 2. First, we must mention that polymerization would increase the insolubility$^{92}$. Second, the less active sites of the copper surface would show better tarnish resistance. There is no doubt that benzotriazole has very low solubility and good tarnish resistance because of the polymeric chain and the fact that all surface copper atoms
are able to bond to nitrogen atoms. Because it lacks one nitrogen atom, indazole (Figure 1(b)) cannot polymerize. It is, therefore, soluble in organic reagents, but it passed the tarnish resistance tests because one indazole is still bonded to two copper atoms and no active Cu sites were available. The possible geometry of benzimidazole (Figure 1(c)) adsorbed on the copper surface is shown in Figure 26(a) (assuming N-bonding). Polymerization is still possible due to one free nitrogen atom on the top. This explains the insolubility of benzimidazole. However, we can see that not all copper atoms are able to bond with nitrogen atoms. More active copper surface atoms explains why this molecule fails the tarnish resistance test. The indole molecule is shown in Figure 1(d). Its geometry after adsorption onto a copper surface is shown in Figure 26(b). No polymerization is possible because of the lack of free nitrogen lone pairs. Many active sites of copper atoms are exposed also. These features explain the results that no insoluble complex formed and the indole-covered samples failed the tarnish resistance test. The 1-Methyl benzotriazole molecule is shown in Figure 1(e). Its geometry after adsorption on the copper surface is similar to that of indazole. However, the methyl group (-CH₃) is too big and it probably pushes the neighbor molecules further away. This would create many active copper atom site and led to the failure in tarnish resistance. The
Figure 26. The possible structures of benzimidazole and indole on copper surfaces (a) Benzimidazole (b) Indole
lack of polymerization and longer distance between molecules than those in indazole may be the cause of the failure to form any insoluble complex.

(3) Mayanna and Setty\textsuperscript{17} have reported the effect of BTA on the corrosion rates of copper single crystal (110), (100) and (111) planes in dilute sulphuric acid. The inhibition efficiency in the crystal planes was in the order (100)>(110)>(111) at all concentrations of benzotriazole. Before explaining these results, we have to point out two things: First, the increasing degree of polymerization would increase the hydrogen bond strength\textsuperscript{92}. Pauling gave a very good example from the study of the polymer (HCN)$_n$. The energy of the hydrogen bond in the dimer, H-C≡N...H-C≡N, was evaluated as 3.28 Kcal/mole, and the sum of the energies of the two bonds in the trimer, H-C≡N...H-C≡N...H-C≡N, as 8.72 Kcal/mole. Secondarily, compactness is one of the important concerns in inhibition efficiency. In the Cu(111) plane, there are three possible directions for growing polymeric Cu-BTA chains. However, too many degrees of freedom would result in disorder and very short polymeric chains. Both should lower the stabilization of the Cu-BTA film and the copper surface is more easily attacked by other corrosive materials. Following this argument, the Cu(110) plane should show better inhibition than the Cu(100) plane does. The reverse results may come
from the fact that the Cu-BTA film is less compact on the Cu(110) plane.
V. CONCLUSION

The new model of CuBTA chemisorption structure elucidates the inhibition mechanism of the CuBTA protective film as below:

(1) All the copper atoms are able to bond to BTA nitrogen atoms. The lack of active surface sites prevents the attack from corrosive ions.

(2) The benzotriazole molecule stands up on the copper surface and, therefore, a more compact protective surface film can be grown. This would give better protection to the underlying copper surface.

(3) The surface protective films are composed of infinite chains in which the CuBTA complexes are connected by strong charge-transfer interactions between benzotriazole molecules (through C-H...N hydrogen bonding). These strong polymeric chains stabilize the protective films (i.e., decrease the solubility) in other corrosive or organic solutions.

Hydrogen dissociation plays a very important role in benzotriazole adsorption on copper (oxide) surfaces. Combined with the stoichiometry study and the knowledge of the Cu crystal lattice, the new model of CuBTA chemisorption structure was constructed. With the existence of an oxide layer, the O-H formation gives a reasonable cause of the hydrogen dissociation. The hydrogen dissociation on clean
copper surfaces stems from the fact that the adsorption of ammonia is at least partially dissociative on copper at 295K° as reported by Matloob and Roberts. No structural difference can be observed in our photoemission studies of both BTA-clean copper and BTA-cuprous oxide surface film and it gives another example to assert the major role of copper atom upon BTA adsorption. However, it is hard to come up with a very good description for this dissociation process. In chemisorption studies, the bond cleavage is attributed to the charge backdonation from substrate levels. The process requires the overlapping of the adsorbate anti-bonding orbital with the substrate backdonating level. This would be backdonation from the copper 3d band to a σ anti-bonding vertical located between N and H atoms. However, the lowest unoccupied molecular orbital (LUMO) is the π* orbital which does not have any distribution in the N-H bond. Therefore, more theoretical or experimental studies are needed to understand this hydrogen dissociation process.
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47. The ray tracing program is from B. Tonner, University of Pennsylvania.


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