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OPTICAL ABSORPTION SPECTROSCOPY OF MOLECULES ADSORBED ON Ni(111) AND ENERGY TRANSFER FROM THE 3nn* STATE OF PYRAZINE TO Ni(111) AND Ag(111) SURFACES

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OPTICAL ABSORPTION SPECTROSCOPY OF MOLECULES ADSORBED ON Ni(111) AND ENERGY TRANSFER FROM THE $3\eta\pi^*$ STATE OF PYRAZINE TO Ni(111) AND Ag(111) SURFACES

Heinz Juergen Robota
(Ph.D. thesis)

November 1981

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Optical Absorption Spectroscopy of Molecules Adsorbed
on Ni(III) and Energy Transfer from the \(3\Pi\) State of Pyrazine
to Ni(III) and Ag(III) Surfaces

by

Heinz Juergen Robota
(Ph.D. Thesis)
1981

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Office of Basic Energy Sciences, Chemical Sciences Division of the
Optical Absorption Spectroscopy of Molecules Adsorbed on Ni(111) and Energy Transfer from the $^3n\pi^*$ State of Pyrazine to Ni(111) and Ag(111) Surfaces

Heinz Juergen Robota

Abstract

Changes in the optical response of a Ni(111) surface as a result of adsorption of molecules is measured with a spectroscopic rotating analyzer ellipsometer. For the molecules pyridine, pyrazine, and naphthalene condensed onto the nickel surface at low temperature, the changes in optical response can be described with a dielectric model which treats the adsorbed phase as a separate continuous medium of well-defined thickness and complex refractive index. For annealed layers less than 100 Å thick, the absorption coefficient corresponds well with the known optical absorption spectrum of these molecules. When a wide variety of molecules are chemisorbed onto the Ni(111) surface, the modification of the optical response can no longer be described by considering the optical properties of the adsorbate alone. Rather, every molecule studied revealed a single broad absorption maximum at 4.2 eV. This absorption peak is attributed to the selective enhancement of bulk interband excitations resulting from perturbations of the metal orbitals upon chemisorption.

The nonradiative energy transfer from the $^3n\pi^*$ state of pyrazine to Ni(111) and Ag(111) surfaces is studied as a function of the distance between the excited molecule and the metal surface. The relative phosphorescence yield of pyrazine above the Ni(111) surface was measured between 7 Å and 100 Å separation to test the applicability of the classical energy transfer theory of Chance, Prock, and Silbey at very short
distances. The cubic distance dependence predicted by this theory when the metal-molecule separation becomes very small is experimentally verified. For the Ag(111) surface, surface plasmon polariton excitations lead to a more complex distance dependence of the energy transfer rate. The luminescent decay times were measured directly for the phosphorescence of pyrazine between 10 Å and 420 Å above the Ag(111) surface. The experimental distance dependence of the energy transfer rate is found to be in quantitative agreement with the classical theory. The nature of the modes acting as energy acceptors in these two cases is compared in order to explain the differences in the energy transfer characteristics.

Charles B. Harris
10 Nov. 1981
to my parents
ACKNOWLEDGEMENT

The process by which one grows from a curious youngster to a practicing scientist is a complex one, filled with people and events whose influence is often unrecognized and unacknowledged. Even after the decision is made to pursue a scientific career, the growth of attitudes and the development of approaches to problems rests greatly upon the environment in which one is trained. Having completed one phase of my training, I now wish to acknowledge those people who nurtured my interest in science and served as trainers and guides, as well as those who refreshed my spirits when all was not well.

Ms. Rosario Olivares is unquestionably responsible for my desire to become a scientist. As my high school chemistry instructor, she instilled in her students not only the basics of chemistry, but developed inquisitive minds which enthusiastically embraced discovery and mastery of new ideas in all fields of study.

Special thanks go to Professor Charles B. Harris for financial support and for creating a research atmosphere in which students are encouraged to test their own capabilities and expand the limits of their expertise. His belief that lessons learned through personal exertion, in which a student may sample both success and failure, are far more valuable than results obtained by following another's prescription, and results in the development of self-reliant students, unafraid to accept new challenges for which no prescribed course of action exists.

To my fellow students in the Harris Group, an enormous debt is owed for scientific as well as social development. Dirk Zweer and Antonio Gallo, with whom I began the spectroscopic ellipsometry project, provided
a basis for scientific understanding and experimental expertise which I hope I can pass along to others. Tony provided not only professional direction, but as my roommate for several years, exposed me to personal warmth, compassion and far reaching interests that greatly altered my perspective of life. His culinary expertise remains a euphoric treat in the memories of all who shared his table. Alan Campion convinced us all that personal ingenuity was a far more valuable tool than any scientific instrument when confronting unexplored scientific problems. Whether the topic of conversation was scientific, literature, music, football, chess, or the shore birds of California, Paul Cornelius spoke with infectious enthusiasm and enviable authority. To Paul Whitmore I give special thanks for putting up with my lunacy as a most able colleague. His ability to interpret my often incoherent hand gestures and facial contortions has made him a vital consultant and advisor in interpreting our experimental findings. Mrs. Vijaya Narasimhan has been an ever present source of support and assistance as the group secretary. To those not mentioned by name, the legacy of the Harris Group is far reaching and each of you has shared in my growth and enjoyment.

As an undergraduate student, the model provided by the diligent study of James Sutton had a significant impact on my attitude toward success as a student. Jim has also been a trusting friend and wonderful companion on many bicycle rides. David Cafiso has also been a challenging cycling partner who rode with enthusiasm sufficient to pull us both up many a long hill. Lew Lee, Tom Anderson, Jocko, and Bob Nicholls have been lasting friends who were always prepared to lend a hand or attentive ear.
The machine and electronic shops of the Department of Chemistry deserve thanks beyond words for their technical assistance throughout my graduate years. Their patience with students and enthusiasm for new and intricate problems make the novice designer's task immeasurably easier.

Finally, I wish to thank my wonderful wife Susan. She provided me with encouragement when things went poorly, shared in my joy when things went well and in general, put up with antics that would render a weaker woman a hopeless wreck.

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Chapter I

INTRODUCTION

Through the application of ultrahigh vacuum technology and the development of several types of electron spectroscopy, our knowledge of the physical and chemical behavior of metal surfaces and their interaction with gaseous molecules has increased rapidly. In conjunction with experimental progress, theoretical developments in the calculation of electronic band structures at metal surfaces, the determination of detailed structures of adsorbates from LEED intensity data, and the prediction of the angular dependent electron yields in UPS measurements promise to aid in the development of a detailed, integrated model of the steady state properties of adsorbate-surface systems. With the body of knowledge presently available, a number of models for specific surface catalyzed reactions have been proposed. These models have been investigated by new experimental techniques which are at the forefront of a new chapter in surface chemical investigation. These experiments seek to isolate and understand specific dynamic interactions proposed in surface catalytic models. Inherent in such dynamic processes are adsorbates in electronically or vibrationally excited states. This reveals one aspect of adsorbate-metal systems which has received relatively little attention, namely, the nature and dynamics of the electronically excited states of the adsorbed species. A complete conceptual model of surface catalytic activity can not be developed without understanding the electronic structure and dynamics of both the metal substrate and the adsorbed species. The work described in this dissertation represents an attempt to deduce the nature of the electronic excitations associated
with the metal-adsorbate system from which the relative importance of metal and adsorbate orbitals in forming the chemisorption bond can be inferred. The dynamical properties of the metal surface are investigated by examining the role of collective surface electronic excitations in nonradiative energy transfer from an electronically excited molecule near the surface.

In the growth of surface science, many experimental techniques requiring high vacuum have been developed. However, for direct application to catalytic or electrochemical systems, the nonvacuum environment renders these techniques unsuitable. As a result, it is important to develop alternate experimental methods which can be used both in vacuum and as in situ probes of ongoing reaction processes. The optical spectroscopic methods used in the course of this work may provide the foundation for the development of general surface sensitive experimental techniques.

Chapter II of this dissertation describes the use of spectroscopic ellipsometry to determine the optical absorption spectrum of molecules adsorbed on the Ni(111) surface. The absorption coefficient is determined indirectly by measuring the response of the surface to polarized light before and after adsorption of molecules as a function of wavelength. By applying a straightforward dielectric model, the complex refractive index of the adsorbed layer can be determined. Since the imaginary part of the refractive index is related to the optical absorption spectrum, new electronic excitations induced upon adsorption can be detected. An attempt is made to isolate the effects of proximity of the adsorbate to the surface from those resulting from chemical interaction of the two species. Initially, the adsorbates were selected because of their
potential for a variety of surface bonding interactions involving both occupied and vacant one electron orbitals connected in the low energy electronic excitations of these molecules. However, when these molecules were chemisorbed, the results suggested that vigorous reaction led to a very different electronic spectrum whose excitations were either shifted to energies beyond our instrumental capabilities or were so severely broadened as to be unidentifiable. Further, the changes in the optical response suggested the importance of specific one electron orbitals in the nickel for chemisorption on the (111) surface. By comparing changes in the optical response upon chemisorption of molecules more extensively studied by other techniques with the findings from these varying methods, an identification of the substrate electronic levels affected by chemisorption can be made.

For molecules undergoing reactive changes on surfaces, the dynamics of the interacting species must be considered. While no detailed theory for such processes has been developed, the fate of an electronically excited species near a metal substrate has been investigated both theoretically and experimentally. The theory pertaining to the behavior of electronically excited species near a mirror (metal surface) has been derived in detail within the framework of a classical, macroscopic, electrodynamic model. Extensions of the model to include microscopic effects have also been made. The predictions of this theory have profound importance when considering the possibility for reactions on surfaces which involve excited states.

Chapter III describes experiments designed to verify the mechanism of electronic energy transfer from an excited molecule to a metal surface predicted by the classical macroscopic theoretical model. In these
experiments, a layer of electronically excited luminescent molecules is located at the top of an argon layer of known thickness which has been deposited directly onto the metal surface being investigated. The ability of two surfaces, Ni(111) and Ag(111), to act as energy acceptors was investigated in two different but related experiments. The relative luminescence yield from the $^3\pi^*$ state of pyrazine as a function of distance between 7 Å and 100 Å above the Ni(111) surface was determined to specifically test the distance dependence of the energy transfer rate predicted by the classical theory. In the second experiment, the actual lifetime of the luminescence following laser excitation, as a function of distance between 10 Å and 420 Å above the Ag(111) surface, was determined. This allowed a direct quantitative comparison of the experimental energy transfer rate with the theoretical prediction.
Chapter II

SPECTROSCOPY OF MOLECULES ADSORBED ON Ni(111)

A. Introduction

The catalytic activity of metal surfaces provides a wide variety of unexplained physical and chemical phenomena which has become the object of intense and varied research. In the effort to understand catalytic activity, attention has been focussed on initially understanding the extremely complex physical and chemical properties of clean metal surfaces. In order to reduce the number of unknown parameters, experimentalists have concentrated greater and greater effort on discovering the properties of single crystal surfaces. It is hoped that a thorough understanding of such idealized systems will provide a basis for describing and predicting the properties of more general metal surfaces.

Numerous experimental techniques have been developed to investigate the properties of clean as well as adsorbate covered surfaces. Most notably, electron spectroscopies have played a major role in our expanding knowledge of surface behavior. In order to develop a complete description of surface chemical interactions, it is necessary to consider evidence from all available techniques applied to both the clean and adsorbate covered surface. Only in this way is it possible to develop a consistent body of evidence for describing a particular adsorbate-surface combination. Of the electron spectroscopies, the development and continued refinement of angle resolved ultraviolet photoelectron spectroscopy (ARUPS) and high resolution electron energy loss spectroscopy (HREELS) have been perhaps the most significant contributors to our understanding of surface chemistry.
An area which has remained generally undeveloped is the use of optical reflection techniques for investigating the electronic excitations of adsorbate-surface systems. The electronic excitations of clean surfaces as compared to adsorbate covered surfaces offers the potential for determining the important one electron orbitals of both adsorbate and substrate involved in the formation of surface chemical bonds. The identification of excitations which may be considered intrinsic to the adsorbed molecule, intrinsic to the metal surface, as well as charge transfer excitations between adsorbate and substrate would provide important clues for the understanding of surface chemistry. When such information is considered in the context of ARUPS information regarding the occupied states near the Fermi energy and changes in the vibrational frequencies of chemisorbed molecules from HREELS, a truly integrated model for surface bond formation can emerge. Of equal importance, the low lying electronic excitations of surface bound species provide information applicable to the development of models for the dynamical properties of these systems. This is of immense importance in developing models for surface catalytic behavior.

As a final note of introduction, it is valuable to discuss recent advances in the theoretical methods for describing surfaces. Most notable among present methods are the multilayer calculations. By combining several infinite sheets of a slice through a perfect crystal, it has been possible to reproduce bulk band structure results for the inner sheets and determine surface states and resonances as well. These calculations have been instrumental in unambiguously identifying surface states and resonances discovered in ARUPS experiments. Their implications for identifying the orbitals most likely to participate in the formation of
surface bonds is only beginning to receive attention, but some success has already been noted. As a general result of these calculations, it is safe to say that the electronic orbitals of the bulk crystal can have significantly different relative amplitudes in the surface region than in the crystal interior and may be as important as wavefunctions localized on the clean surface in determining both the physical and chemical properties of a metal surface. These findings are profoundly important for the interpretation of surface spectroscopic results as well as in our conceptual formulation of surface bonding models.

In this section of this dissertation, I present the results and interpretation of experiments which probe the changes in the optical response of a Ni(111) single crystal surface upon adsorption of a variety of molecules. The molecules were adsorbed under a variety of conditions which produced adlayers ranging from marginally affected organic condensates to the onset of epitaxially grown oxides. By investigating a range of adlayers it becomes possible to develop a feeling for the relative importance of substrate and overlayer contributions to the final adlayer-substrate optical spectrum.

B. Experimental

Complete details of the experimental chamber, the rotating analyzer ellipsometer and the low temperature sample stage may be found in the Doctoral Dissertation of A. R. Gallo. A sketch of the apparatus and experimental procedure is given here to facilitate a conceptual understanding of the experiment. A schematic diagram of the spectroscopic ellipsometry configuration is shown in Figure 1.
Figure 1. The schematic view of the experimental chamber when configured for spectroscopic ellipsometry. The spherical mirror in the figure has replaced the lens/flat mirror combination described in the text.
SCHEMATIC VIEW OF UHV SPECTROSCOPIC ELLIPSOMETRY CONFIGURATION

75 W Xe ARC LAMP

DOUBLE MONOCHROMATOR

SINGLE CRYSTAL

UHV CHAMBER

VIEW PORT

VIEW PORT

VARIABLE LEAK VALVE

SPLHICAL MIRROR

MgF2 INPUT POLARIZER

INPUT WINDOW

LEED/AUGER OPTICS

LEED/AUGER OPTICS

ARGON ION SPUTTERING GUN

EXIT WINDOW

ROTATING ANALYZER WITH QUARTZ POLARIZER

LIQUID HELIUM CRYOSTAT
1. Apparatus

The stainless steel vacuum chamber used in these experiments is pumped by a titanium sublimation pump and a 400 l/s Varian Vacion pump in the triode configuration. Typical operating pressures are $1-2 \times 10^{-10}$ torr as measured by an uncorrected ionization gauge. The predominant background gases are $\text{H}_2$, Ar, Co, and $\text{CH}_4$, in order of decreasing abundance as measured by a UTI 100 C quadrupole residual gas analyzer. The chamber is configured in two levels. The upper level contains the liquid helium-cooled experimental stage, LEED/Auger optics, quartz entrance and exit windows, an argon ion sputtering gun, variable leak valve to a gas inlet line, and observation ports. The lower level houses the sample heating stage, a tungsten filament, residual gas analyzer, ion gauge, and additional observation ports. The sample is moved between levels with a magnetically coupled linear/rotary motion manipulator.

The nickel single crystal sample was spark cut from a 3/8" diameter rod of 99.999+% purity (Materials Research Corp.). After a preliminary orientation of the surface within $2^\circ$ of the $(111)$ face by Laue X-ray backscattering, the back was ground parallel to the face. The 1/8" thick sample was then electron beam welded to a specially machined 99.99+% purity polycrystalline nickel backing. The sample assembly was then carefully reoriented and polished to within $1^\circ$ of the $(111)$ face. During the final polish in a slurry of .05 $\mu\text{Al}_2\text{O}_3$, the surface was swabbed at 30 minute intervals with a solution containing glacial acetic, nitric, sulfuric and phosphoric acids in relative proportion 5:3:1:1 heated to 80°C. This etching procedure removed surface layers damaged during the stages of coarse polishing.
Once in the vacuum chamber, the crystal was cleaned with several cycles of argon ion sputtering followed by extensive annealing. Typical cleaning involved 15 minutes of 2 K\text{V} argon ion sputtering at an angle near 60° from the surface normal, 15 minutes annealing near 600°C, then an additional 5 minutes sputtering followed by a final anneal for 20-25 minutes. The sample was heated by lowering the crystal-backing assembly into the prongs of an insulated stage which can be raised to 5 K\text{V} above ground potential. A tungsten filament located opposite the stage was heated to produce a high flux of thermally ejected electrons which then cross the gap and strike the crystal backing. Temperature measurements were made using an optical pyrometer. Typical operating conditions were a 4 K\text{V} potential and a current of 7 mA to bring the sample to 600-700°C. After such a cleaning procedure, LEED and Auger analysis showed highly ordered, clean nickel (111) surfaces.

During the experiments the crystal assembly was held in the copper end of a liquid helium cryostat. A secure mount was provided by mating a dovetail machined into the crystal backing with a female dovetail in the copper tip. A small leaf spring pressing on the crystal backing prevented wobbling and produced good thermal contact in the dovetail. Once in the holder, the manipulator was unscrewed from the sample. This arrangement allowed sample cooling to below 10 K, as evidenced by continuous condensation of H\textsubscript{2} at 10^{-8} torr. Two iron-doped gold/chromel thermocouples mounted on the cold tip provided temperature estimates, but absolute measurements were prevented by the heating of secondary junctions at the vacuum feedthrough by the cryostat gas return heater.

A 75 W high pressure Xe arc lamp in conjunction with a Spex Doublemate monochromator equipped with ruled gratings blazed at 2500 Å produced light
of sufficient intensity to 2350 Å free from broadband scattered light. The light exiting the monochromator was collected with a fused silica lens, reflected from a MgF₂ coated aluminum mirror, and passed through a MgF₂ Rochon prism input polarizer onto the sample surface. The reflected light passed through the fused silica analyzer polarizer and was detected by an EMI 9558 Q photomultiplier. The photomultiplier output was presented to a buffer amplifier of typical gain 100 before passing to the analog-to-digital converter for processing.

Two features of this system are considered extremely important. Both entrance and exit windows were specially constructed of UV-grade fused silica components annealed at high temperature to minimize stress-induced birefringence. The fused silica components were then attached to a pyrex graded seal on a standard vacuum flange, and, when mounted and under vacuum, display virtually no birefringence throughout the range of experimental wavelengths. The second feature, believed to be unique, is an optical path passing through holes in the LEED/Auger optics. This was accomplished by electron discharge machining to prevent warpage of the retarding grids. This arrangement allows optical studies of overlayers of known periodicity and composition, thus eliminating errors in surface adsorbate structures examined due to variations in local pressures during adsorption in separate LEED/Auger and optical spectroscopic experiments.

The spectroscopic rotating analyzer ellipsometer used in these experiments was built after a design by Aspnes. Detailed information regarding the operation, calibration, and data analysis involved in using this type of instrument may be found in References 6 and 7. Briefly, the elliptically polarized light that exits the chamber passes through a
polarizer rotating at 31.25 Hz, producing a sinusoidally time-varying flux detected by the photomultiplier. The signal is sent through a buffer amplifier to an ADAC Model 1030 analog-to-digital converter interfaced to a Digital Equipment Corp. PDP11/03 laboratory micro-computer. The analysis of this signal by the computer is triggered by optical encoder circuitry on the analyzer motor. Mounted on the shaft of the rotating analyzer is a nickel-plated, polished disc with 72 parallel cuts machined at equal intervals around the circumference. At one point on the disc, an additional hole is drilled between two cut-outs. Two optical encoders are aligned with this disc to provide 72 trigger points for data collection and a single trigger acting as the origin for the data triggers.

To normalize the spectrum to the intensity of the excitation source, the photomultiplier output is monitored by a Kepco APH-2000M programmable high voltage supply, and the photomultiplier voltage is adjusted so that the average DC signal level stays constant over the entire wavelength region of interest. Signal averaging is achieved by programming the computer to collect data for a specified number of revolutions of the analyzer. The monochromator is then turned to the next wavelength by a computer-controlled stepping motor, and a delay is built into the program to allow for mechanical vibrations to decay and the photomultiplier supply to adjust to the new signal level.

All the ellipsometric spectra were recorded with 0.5 mm slits on the monochromator (10 Å passband) and the data points were taken at 5 Å intervals. Each point was averaged over 200 revolutions of the analyzer. The incident beam was about 60° from the surface normal and linearly polarized at 30° from the plane of incidence.
Condensed layers of gases were prepared by adsorption while the crystal was cooled to 15 K. Thicknesses were monitored ellipsometrically, and in some cases the overlayers were annealed at 150 K and cooled back to 15 K before spectra were taken.

The studies of chemisorbed molecules were all performed at room temperature except where otherwise noted. Gases were deposited at pressures in the $10^{-8}$ torr range for several minutes until saturation occurred as measured by the change in the ellipsometric parameter $\Delta$. Auger and LEED results were obtained after the ellipsometric spectra were recorded to minimize the effects of electron beam damage to the overlayers.

2. Data Acquisition and Reduction

Following the final annealing of the crystal, the sample assembly is moved from the heating stage to the crystal stage. The cryostat assembly is moved into the optical path and the optical components are aligned. Due to the daily movement of the sample, the angle of incidence and beam positions on the input and output windows can vary significantly. The latter is not a problem, but the former is a major difficulty which will be discussed further below. If the experiments are to be performed at low temperatures, the sample is cooled and a final alignment of the optics is often necessary due to contractions in the cryostat. After the system has been calibrated, a spectral scan on the bare surface is performed. The gas of interest is then admitted to the chamber and progress of the adsorption is monitored ellipsometrically at a wavelength where the overlayer is presumably transparent. A second spectral scan is then collected and the two data sets can be analyzed. If further treatments of the sample are to be done, they are all performed without moving any of the system components.
While a detailed systematic discussion of ellipsometry is beyond the scope of this dissertation, a brief introduction should serve as an aid to understanding the experiments and their subsequent interpretation. (A more detailed description may be found in the Appendix, as well as examples of the data analysis methods.) Linearly polarized light may be decomposed into electric field components parallel (p) and perpendicular (s) to the plane of incidence. Upon reflection from a surface, the final polarization state is, in general, elliptic due to changes in the relative amplitude and phase of the two component fields. Ellipsometry relates these changes to the complex dielectric response functions of the reflecting system. Inherent in the interpretation of ellipsometric data are a number of assumptions which for many systems appear to be reasonable. One assumes that the reflecting system can be described as a homogeneous, isotropic, semi-infinite substrate exhibiting a sharp planar boundary, covered by one or more layers of uniform thickness, also homogeneous and isotropic. This system is then embedded in some form of ambient surrounding. The applicability of this model has been challenged, especially in interpreting the behavior of thin molecular layers and sub-monolayer films on atomically clean surfaces. Several attempts have been made at describing the scattering of radiation by atomic and molecular systems in a more rigorous fashion, yet for the general analysis of laboratory data they offer little prospect for routine applicability. Some extensions to anisotropic substrates and overlayers have been made, but they remain difficult to apply, and the bulk of ellipsometric data continues to be interpreted within this simplified framework (see Ref. 8).

The quantities measured in ellipsometry may be expressed as:

\[ \rho = \frac{r_p}{r_s} = \tan \psi e^{i\Delta} \]
where $\tilde{r}_p$ and $\tilde{r}_s$ are the complex amplitude reflection coefficients for the electric field at the interface. In the simplified model described above, $\tilde{r}_p$ and $\tilde{r}_s$ are the Fresnel coefficients and are related to the optical properties of the overlayer, substrate and ambient, as well as the angle of incidence. For this model,

$$
\frac{\tilde{r}_p}{\tilde{r}_s} = \frac{\tilde{n}_1^2 \cos \phi_0 - n_0 (\tilde{n}_1^2 - n_0^2 \sin^2 \phi_0)^{1/2}}{\tilde{n}_1^2 \cos \phi_0 + n_0 (\tilde{n}_1^2 - n_0^2 \sin^2 \phi_0)^{1/2}} \frac{\tilde{n}_0 \cos \phi_0 + (\tilde{n}_1^2 - n_0^2 \sin^2 \phi_0)^{1/2}}{\tilde{n}_0 \cos \phi_0 - (\tilde{n}_1^2 - n_0^2 \sin^2 \phi_0)^{1/2}}
$$

where $\tilde{n}_0$ is the refractive index of the ambient, $\tilde{n}_1$ is the complex refractive index of the substrate, and $\phi_0$ is the angle of incidence with respect to the substrate normal. For the systems to be dealt with here, the three phase (ambient-overlayer-substrate) ellipsometric equation can be expressed as

$$
\rho = \tan \psi e^{i\Delta} = \frac{r_{1p} + r_{2p} e^{-iZ}}{1 + r_{1p} r_{2p} e^{-iZ}} \frac{1 + r_{1s} r_{2s} e^{-iZ}}{r_{1s} + r_{2s} e^{-iZ}}
$$

$$
Z = \left(\frac{4\pi d}{\lambda_0}\right) (\tilde{n}_1^2 - n_0^2 \sin^2 \phi_0)^{1/2}
$$

where $d$ is the thickness of the overlayer and $\lambda_0$ is the vacuum wavelength of light. A more complete discussion is given in the Appendix.

Unlike classical null ellipsometers, rotating analyzer systems of this type measure $\tan \Psi$ and $\cos \Delta$ rather than $\Psi$ and $\Delta$ directly. For the metal systems investigated, the expected values of $\Psi$ and $\Delta$ are such that there is no ambiguity in converting from $(\cos \Delta, \tan \Psi)$ to $(\Delta, \Psi)$ for further analysis. The simplest type of analysis consists of the difference
between bare metal parameters \((\bar{\Delta}, \bar{\Psi})\) and the corresponding values for the covered metal at each point in the spectrum. The difference functions \(\delta \Psi = \Psi - \bar{\Psi}\) and \(\delta \Delta = \Delta - \bar{\Delta}\) (the bar indicating bare metal values) are, in general, complicated functions of the overlayer dielectric properties and thickness. However, experience has shown that most of the spectral features can be gleaned from these simple functions without resorting to sophisticated analyses. Figure 2a shows the result of \(\delta \Delta\) and \(\delta \Psi\) for a 10 Å layer of condensed annealed pyrazine. For comparison, 2b demonstrates the result of analyzing for \(n\) and \(k\). These spectra also demonstrate the sensitivity of the instrument for moderate and strong absorption features in very thin layers. (Notice the resolved vibronic structure in the low energy transition.) As a standard tool, difference spectra are not usually used to interpret spectral data. They are extremely useful, though, in regions where the overlayers are transparent, where \(\delta \Psi = 0\) and \(\delta \Delta = d/\lambda_0\), so that the change in \(\Delta\) can be used as a crude measure of the thickness of the overlayer during an adsorption.

Two factors in these experiments make rigorous analyses of the spectra difficult. The first involves uncertainty in the angle of incidence. For a given dielectric constant and wavelength of light, variations in the angle of incidence by as little as 0.01° have pronounced influence on the values of \(\Psi\) and \(\Delta\). Due to the nature of our sample mount, variations in the angle of incidence as large as 1° arise on a daily basis. Measurements of this angle are subject to errors of approximately \(\pm 0.1°\). Thus, the values of optical constants resulting from the analysis must not be regarded as absolute but used for defining spectral features and as a means of comparison between systems.
Figure 2a. The result of a simple difference spectrum $(\delta \Delta, \delta \Psi)$ for a 10 Å thick, condensed and annealed layer of pyrazine on Ni(111). \( \delta \Psi \) reflects the absorbing properties of the layer while \( \delta \Delta \) is most sensitive to the refractive index.

Figure 2b. Absorbance calculated from an iterative analysis assuming a 10 Å thick layer. Compare the vibronic structure with that of a thick layer in Figure 7.
PYRAZINE / Ni (III)
Condensed, annealed
\( d = 10 \, \text{Å} \)

\( \delta \Delta \) vs. \( \lambda (\text{Å}) \)

\( \delta \psi \) vs. \( \lambda (\text{Å}) \)

XBL8II-3576
PYRAZINE/Ni(III)
Condensed, annealed
\( d = 10 \text{ Å} \)
The second uncertainty in the analysis is in the thickness of the overlayer. Complete characterization of the overlayer requires three parameters: the real and imaginary parts of the refractive index, and the thickness of the layer. Ellipsometric measurements provide only two pieces of information, so a third measurement must be made or inferred. The most common solution is to make an ellipsometric measurement where the overlayer is assumed transparent. The remaining variables, n and d, can be uniquely determined, and the calculated thickness can then be used to calculate both n and k at other wavelengths. A second method involves making measurements of $\Psi$ and $\Delta$ at several thicknesses during the course of a deposition. A series of solutions over a range of n and k values is calculated which make the thickness a purely real quantity. When the solutions for two different thicknesses are plotted in n-k space, the intersections of the curves correspond to the n and k values shared by both measurements. If the assumption is made that these n and k values are constant for all thicknesses, then the thickness of the overlayer at the end of the adsorption run can be calculated and used in the determination of n and k at different wavelengths. This approach has proven to be useful for a number of condensed layer systems, but for very thin layers and chemisorbed systems, this method has been found to be unreliable. The solution to this problem which was finally adopted in our analysis is a cautious comparison of the thickness of the overlayer expected from exposure times and molecular dimensions with that obtained by minimizing the absorption index in a region of expected transparency.
C. Condensed Aromatic Hydrocarbons on Ni(111)

For aromatic molecules condensed onto metal surfaces at low temperature, the dominant attractive forces arise through interaction between static and induced dipole moments. Such weak interaction is expected to leave the electronic structure of both the molecule and metal essentially unchanged from the isolated systems. With additional adsorption leading to multilayers of condensates, the interactions closely resemble those found in the low temperature solid phases of the pure aromatic molecules. Adsorption at low temperatures generally leads to a disordered phase, but by raising the temperature slightly, these layers may anneal, leading to an equilibrium configuration for the condensed molecular layer.

Since the intermolecular interactions are weak, perturbations induced by the layer in direct contact with the metal may lead to phases very different from the pure hydrocarbon. The growth of pseudomorphic condensed phases has been observed for naphthalene on Pt(111). The spectrum of such a crystalline structure may reveal changes in the energies of excited states as well as different vibronic structure due to the new type of environment experienced by molecules in the adlayer.

The molecules studied in condensed layers on Ni(111) have relatively strong electronic transitions in the near UV. Therefore, they may be used as model systems for comparison with the more strongly bound chemisorbed molecules as well as providing a gauge of instrumental sensitivity for detecting new absorption processes.

1. Pyridine

Pyridine is the simplest aza-aromatic hydrocarbon with one nitrogen atom in the six membered aromatic ring. The molecular structure and lowest energy excited electronic states, as found in the gas phase,
are shown in Figure 3. High resolution gas phase absorption spectra reveal only an extremely diffuse spectrum.\textsuperscript{12} This is likely due to interaction between vibronic states of the $1\text{n}^*\pi^*$ configuration with the vibronic states of the $1\pi\pi^*$ configuration.

Upon condensation into solid pyridine at low temperatures, the diffuse nature of the spectrum continues to obscure details of the vibronic levels.\textsuperscript{13} Additionally, the interaction of the excited configurations with their polarizable environment leads to a shift in the electronic absorption energies of the two states. As a consequence of this shift, the weakly absorbing ($f=0.003$) $1\text{n}^*\pi^*$ transition is almost indistinguishable from the edge of the stronger ($f=0.04$) $1\pi\pi^*$ transition.\textsuperscript{13}

For thin annealed layers of pyridine condensed on a Ni(111) surface, the absorption spectrum, shown in Figure 4, closely resembles that of molecular pyridine alone. The diffuse vibronic profile suggests a vibrational progression with energy near 900 cm\textsuperscript{-1} which resembles the gas phase profile with a vibronic spacing of $\sim$1000 cm\textsuperscript{-1}.\textsuperscript{13} A suggestion of the $1\pi\pi^*$ transition is found in the region near 2850 Å. The possibility for determining the importance of adsorbate-substrate interactions in this system is minimal. The absence of well resolved absorption features for even the pure condensed phase makes comparison with the adsorbed layer impossible. However, the strong similarity between the condensed adlayer and the gas phase spectra indicate virtually no perturbation by the presence of the metal.

2. Pyrazine

The diazabenzene pyrazine, with para-substituted nitrogen atoms, has a more complex electronic structure than pyridine. This arises from the interaction of the nominally degenerate nonbonding
Figure 3. Summary of the gas phase ultraviolet electronic transitions of pyridine. The dipole transition moments are shown with respect to the molecular geometry.
Figure 4. The analyzed absorption spectrum for a 65 Å thick condensed, annealed layer of pyridine on Ni(111).
nitrogen orbitals to form molecular orbitals consisting of symmetric and antisymmetric linear combinations, in the lowest order approximation. The lowest energy excited singlet state involves excitation of an electron from the antisymmetric combination of nonbonding orbitals to the lowest lying unoccupied orbital. This $^1\text{B}_3\text{u}$ state has been extensively studied in a wide variety of glassy solutions, substituted crystals, and the pure single crystal state. A sharp spectrum of well resolved vibronic bands follows an intense 0-0 electronic origin and has led to a detailed model of the vibrational potential in the excited electronic state. The dominant vibration is the $v_{6\alpha}$ ring breathing mode which shows very little sensitivity to the molecular environment. This is demonstrated in Figure 5. As in pyridine, the next electronically excited singlet state is of $^1\pi\pi^*$ character and is diffuse with only a broad vibronic envelope. The transition dipole directions and energies of the electronic origins for these two states for single crystal pyrazine at 4.2 K is shown in Figure 6.

For thin, annealed, adlayers of pyrazine, the low resolution absorption spectrum clearly shows the electronic origin of the $^1\text{B}_3\text{u}$ state with well-defined vibronic peaks to higher energy as seen in Figure 7. In the pure crystal, the electronic origin is at 3327 Å which is in close agreement with the value 3307 Å found for annealed adlayers on Ni(111) at 15 K. However, the vibronic spacing, as determined from many spectra, is found to be $525 \pm 25$ cm$^{-1}$. This is substantially smaller than all previously observed energies for the $v_{6\alpha}$ vibration. Presumably, the active mode remains $v_{6\alpha}$, but this can not be determined unambiguously. It is appealing to attribute this affect to the influence of the metal surface, leading to an altered equilibrium crystal structure for such a
Figure 5. Summary of data on $v_6$ mode in $^1n\pi^*$ state of pyrazine.
<table>
<thead>
<tr>
<th>Environment</th>
<th>$\nu_6$ Frequency in $^1B_{3u}$ State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor</td>
<td>$584 \text{ cm}^{-1}$</td>
</tr>
<tr>
<td>Cyclohexane sol'n</td>
<td>582</td>
</tr>
<tr>
<td>Benzene sol'n</td>
<td>586</td>
</tr>
<tr>
<td>Pure crystal (4K)</td>
<td>587</td>
</tr>
</tbody>
</table>

Average - Non-surface environment \[ 585 \text{ cm}^{-1} \]

Surface Nickel (III) \[ 525 \pm 25 \text{ cm}^{-1} \]

XBL 788-5659
Figure 6. Summary of the crystal ultraviolet transitions of pyrazine at 4.2°K. The dipole transition moments are shown with respect to the molecular geometry.
The diagram shows the electronic transitions and energy levels of Pyrazine. The transitions are labeled as follows:

- $^1B_{2u}$ to $^1\pi\pi^*$ at 37,400 cm$^{-1}$
- $^1B_{3u}$ to $^1\pi\pi^*$ at 30,057 cm$^{-1}$

The molecule is represented with nitrogen atoms (N) and the transition is indicated with an arrow. The code XBL 788-5658 is also present.
Figure 7. The analyzed absorption spectrum for a 40 Å thick condensed, annealed pyrazine layer on Ni(111).
thin layer of pyrazine. While much higher resolution spectra, spectra of much thicker layers, or spectra of deuterated pyrazine might resolve this question, no efforts to pursue these methods were made.

The electronic origin of the $^{1}\text{B}_{2u}$ state is observed at 2740 Å in the condensed adlayer. No definitive value for this transition in the pure crystal has been published, but the value of 2674 Å (37400 cm$^{-1}$),$^{18}$ suggested in a two photon laser excitation spectrum, shows a much smaller red shift from the gas phase than the condensed adlayer. Despite the difference in 0-0 energy, the vibronic profile and the suggested 1000 cm$^{-1}$ progression closely resemble those found in the gas phase.$^{17}$

Recently, electron energy loss results for very thin adlayers of pyrazine on a Ag(111) surface at 80 K became available for comparison with the Ni(111) system.$^{19}$ For adsorption on the Ag(111) surface, the 0-0 origin of the $^{1}\text{B}_{2u}$ state appears at a loss energy slightly greater than 4.6 eV. This corresponds well with the estimated value of 37400 cm$^{-1}$ (4.64 eV) for the pure crystal. The vibronic energies in the $^{1}\pi\pi^*$ transition could not be determined due to interference by the large loss from exciting the surface plasmon on the Ag(111) surface at 3.8 eV. Again, despite the energy discrepancy between the adlayer on Ni(111) and Ag(111), the vibronic profile of the $^{1}\text{B}_{2u}$ state is quite similar for the two systems.

A previous attempt to correlate the apparent intensity ratio of the $^{1}\pi\pi^*:^{1}\pi\pi^*$ absorptions for the annealed adlayer suggested that the pyrazine was not lying flat on the Ni(111) surface.$^{20}$ By considering the intensity ratios for pyrazine ground state vibrations on the Ag(111) surface, it was concluded that pyrazine did indeed lie flat on that surface.$^{19}$ A review of the previous calculation for the Ni(111) system detected an
error which greatly affects the calculated absorption intensity ratios. For molecular planes aligned parallel to the surface, the intensity ratio of $^{1}\pi\pi^*$:$^{1}\pi\pi^*$ is expected to be $\sim 4:1$. Any tipping of the molecular plane, either about the N-N axis, or perpendicular to it, rapidly predicts $^{1}\pi\pi^*$:$^{1}\pi\pi^*$ intensity ratios much larger than 4:1. The observed ratios for adlayers range from 4:1 for the thinnest layers (about 2 monolayers) to 3:2 for adlayers approaching 100 Å in thickness. Considering the uncertainty in the absolute absorption coefficients for the adlayer (see Appendix) it would imply that the pyrazine molecules actually stack with their molecular planes parallel to the Ni(111) surface as well.

It appears, then, that thin adlayers of pyrazine on the Ni(111) surface experience a perturbation of their normal crystal structure. This is revealed in the large energy difference in the dominant vibronic progression in the $^{1}B_{3u}$ electronic state as compared to other environments, as well as a greater red shift of the $^{1}B_{2u}$ electronic origin. However, despite these differences, the absorption spectrum remains quite clearly that of molecular pyrazine.

3. Naphthalene

The two electronically excited singlet states of lowest energy in the naphthalene molecule are both of $^{1}\pi\pi^*$ character. Since there are no atoms with nonbonding electrons, the only other excited electronic configurations would require the participation of the ring $\sigma$ orbitals. Such excited states are of much higher energy and are generally unimportant in the low energy absorption spectra of aromatic hydrocarbons. The lower of the two excited configurations encountered here is of $^{1}B_{3u}$ symmetry and the higher of symmetry $^{1}B_{2u}$. In the gas phase, both
excitations are polarized in the molecular plane along the short axis. The crystal structure on naphthalene has two inequivalent molecules per unit cell. These molecules interact and produce linear combinations of individual molecular states which must form representations for the crystalline point group. While this is true for pyridine and pyrazine as well, the effect of this interaction is not discernible in pyridine and not very large in pyrazine. In conjunction with the numerous totally symmetric vibrational modes, these interactions produce a very complex crystal absorption spectrum.

The analyzed absorption spectrum for an 25 Å layer of annealed naphthalene on the Ni(111) surface at 15 K is shown in Figure 8. The weak absorption with origin at 3166 Å is assigned to the $^1B_{3u}$ state with the stronger $^1B_{2u}$ absorption beginning at 2962 Å. These origins are in good agreement with high resolution results on naphthalene single crystals at low temperatures. Both the $^1B_{3u}$ and $^1B_{2u}$ electronic states show numerous peaks following the vibrationless origin. These maxima are tabulated in Table 1 along with the results of McClure and Wolf for single crystal naphthalene. There is very reasonable correspondence between the low resolution spectra for the adlayer and the high resolution neat crystal results.

Of particular interest is the electronic origin of the $^1B_{3u}$ state in the adlayer. In the molecular crystal, the interaction of the two inequivalent molecules in the unit cell gives rise to two electronic states caused by the mixing of the isolated molecular states. This leads to the Davydov splitting in the $^1B_{3u}$ electronic origin of 166 cm$^{-1}$ for crystalline naphthalene. Transitions to only one of these states is electric dipole allowed and thus, only the electronic origin of the
Figure 8. The analyzed absorption spectrum for a 25 Å thick condensed, annealed layer of naphthalene on Ni(111).
Table 1
A Comparison of the Absorption Maxima for Condensed Naphthalene on Ni(111) with Single Crystal Naphthalene Spectra

<table>
<thead>
<tr>
<th>Adsorbed Layer</th>
<th>McClure</th>
<th>Wolf</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>31590 cm(^{-1})</td>
<td>31642 cm(^{-1})</td>
<td>31625 cm(^{-1})</td>
<td>(1^B_{3u}) 0-0</td>
</tr>
<tr>
<td>31955</td>
<td>31976</td>
<td>31960</td>
<td>0-0 + 405</td>
</tr>
<tr>
<td>32295</td>
<td>32236</td>
<td>32230</td>
<td>0-0 + 700 (A)</td>
</tr>
<tr>
<td>32460</td>
<td>32466</td>
<td>32460</td>
<td>A + 500</td>
</tr>
<tr>
<td>32693</td>
<td>32690</td>
<td>32670</td>
<td>A + 710</td>
</tr>
<tr>
<td>33015</td>
<td>32990</td>
<td>32970</td>
<td>A + 1010</td>
</tr>
<tr>
<td>33170</td>
<td>33149</td>
<td>33150</td>
<td>A + 1190</td>
</tr>
<tr>
<td>33448</td>
<td>33456</td>
<td>33450</td>
<td>A + 1490</td>
</tr>
<tr>
<td>33767</td>
<td>33780</td>
<td>33800</td>
<td>(1^B_{2u}) 0-0</td>
</tr>
<tr>
<td>33947</td>
<td>33899</td>
<td>33985</td>
<td>0-0 + 190</td>
</tr>
<tr>
<td>34258</td>
<td>34290</td>
<td>34305</td>
<td>+ 505</td>
</tr>
<tr>
<td>34555</td>
<td></td>
<td>34535</td>
<td>+ 740</td>
</tr>
<tr>
<td>34781</td>
<td>34800</td>
<td>34865</td>
<td>+ 1070</td>
</tr>
<tr>
<td>35146</td>
<td>35180</td>
<td>35170</td>
<td>+ 1370 (B)</td>
</tr>
<tr>
<td>35341</td>
<td></td>
<td>35350</td>
<td>B + 180</td>
</tr>
<tr>
<td>35657</td>
<td>35690</td>
<td>35690</td>
<td>+ 520</td>
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<td>35920</td>
<td>+ 750</td>
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<td>36400</td>
<td></td>
</tr>
<tr>
<td>36641</td>
<td>36580</td>
<td>36580</td>
<td>+ 1410 (C)</td>
</tr>
</tbody>
</table>

The Assignments are those due to Wolf. The experimental resolution of the McClure spectra was very high and only strong peaks in correspondence with the Wolf results are shown. In the \(1^B_{2u}\) spectrum, the results of McClure were untabulated and read from the figure of the spectrum. For the overlayer, the peaks were selected from a single representative spectrum. Although shown to the nearest 1 cm\(^{-1}\), the experimental resolutions is \(~60\) cm\(^{-1}\), and within this range very good agreement with the single crystal spectra is found.
allowed component is observable. The agreement between the single crystal spectra with those of adlayers on Ni(111) indicate an unperturbed molecular layer in its own crystal structure. These observations hold for layers as thin as 20 Å. In thinner layers the weak \( ^1B_{3u} \) origin and associated vibrational bands become obscured by the noise in the analyzed spectrum.

4. Summary

The analyzed absorption coefficients for very thin adlayers of aromatic molecules reveal the sensitivity of the RAE to new absorption processes in adsorbed layers. By comparing the spectra of the annealed adlayers on the Ni(111) surface with those of the pure molecular species, information regarding the influence of the metal substrate on the thin layers can be determined. Both pyridine and naphthalene appear to be generally uninfluenced by the presence of the metal. For naphthalene in particular, the observed Davydov component of the \( ^1B_{3u} \) electronic origin as well as the vibrational energies of both the \( ^1B_{3u} \) and \( ^1B_{2u} \) states indicate a crystalline phase without perturbation by the nickel surface. In contrast to this behavior, pyrazine shows deviations from the pure crystal in both electronic states studied. While the origin of the \( ^1B_{3u} \) state is very close to the pure crystal value, the dominant vibrational progression is shifted to lower energy by about 60 cm\(^{-1}\). This is surprising in light of the insensitivity of this vibrational mode to other environments. Further, while not as definite, the origin of the \( ^1B_{2u} \) state is at a much lower energy than found for pyrazine in solution and suggested for pyrazine in the low temperature single crystal.
D. Chemisorbed Adlayers on Ni(111)

Significant improvement in calculation technique and experimental expertise has led to a greater understanding of the properties of atoms and molecules bound to metal surfaces. Details of the bonding interaction, energies of occupied orbitals, and the geometrical arrangement of adsorbed species can in some cases be deduced from a variety of experimental probes. Recently, the combination of optical spectroscopy with photoemission and band structure calculations has been shown to be a powerful tool for the investigation of the electronic redistribution which occurs upon chemisorption. The success of experiments on small molecules on metal surfaces, particularly those on H₂, O₂, and CO on W²⁴⁻²⁶ and Ni²⁷,²⁸ single crystals, makes the prospect for studying the chemisorption of larger molecules very good.

Because of the importance of these endeavors to such areas as catalysis, studies of the fundamental electronic structures of large hydrocarbons chemisorbed on metal surfaces are now beginning to emerge. Of special interest is the chemisorption behavior of unsaturated and aromatic hydrocarbons. The low-lying electronic excited states of the molecular adsorbate should be very sensitive indicators of the interactions between the molecular π system and the metal. Photoemission experiments on the chemisorption of unsaturated hydrocarbons on Ni(111)²⁹ indicates that the electronic structures of the adsorbates remain essentially unperturbed in the bonding process, even though the molecular orbitals directly involved in the bond formation shift to somewhat higher binding energy and broaden slightly in energy. This result would suggest that the optical spectrum of a chemisorbed monolayer should resemble the free molecule spectrum of the adsorbate, with the changes in peak energy and line width revealing details of the bonding interaction.
We have measured the visible-UV optical response of a series of molecules adsorbed on a single crystal nickel (111) surface. The molecules chosen for the initial investigation ranged from aza-aromatic hydrocarbons, which are capable of interaction through either their π systems or their nitrogen lone pairs, to aromatic hydrocarbons, expected to bond exclusively through their π systems, and finally to small molecules, which are capable of no π interactions and exhibit no strong electronic excitations in this energy region.

We find that the UV-visible absorption spectra for all the chemisorbed species are nearly identical, and there is no evidence of molecular-type transitions. The UV-visible spectrum of all the molecules chemisorbed on Ni(111) consists of a single peak centered at ~4.2 eV which can be attributed to an enhancement of a bulk metal interband transition. The relationship of this transition to the band structure of nickel and the specific metal orbitals perturbed via chemisorption is discussed.

1. Results

Pyrazine, Pyridine, Benzene, and Naphthalene on Ni(111)

Pyrazine, pyridine, benzene, and naphthalene all appear to chemisorb on the Ni(111) surface at room temperature. Saturation of the surface occurs after 3-5 L exposures, with a final 5 of about 0.5°-0.7° at 3500 Å. The adsorption of pyridine leads to a very diffuse LEED pattern visible only at low electron energies (Fig. 9). LEED spots for the chemisorbed pyrazine were very indistinct and subject to very rapid deterioration in the electron beam. Naphthalene on the other hand produces very clear, reproducible patterns which would deteriorate after longer beam exposures. From an initial set of rings surrounding each
Figure 9. The LEED pattern of pyridine chemisorbed on Ni(111) at room temperature. The beam energy is 66 eV. (a) Photograph of the diffraction pattern. (b) Sketch of the pattern. Nickel diffraction spots are indicated by solid circles. Spots due to chemisorbed pyridine are indicated by the open outlines.
clean surface spot, annealing to 350 K produces the pattern seen in Figure 10. Although we make no assignment of these patterns, similar results were obtained on the Pt(111) surface.

The spectrum of each of these chemisorbed molecules is shown in Figures 11-14. Each adsorption spectrum is dominated by one large, broad feature, which is centered at 2850 Å in the case of pyrazine and benzene, and at 3050 Å for chemisorbed pyridine and naphthalene. None of the molecules studied exhibited any absorption features in the visible region of the spectrum.

CO, O₂, Ethanol on Ni(111)

The chemisorption of CO on Ni(111) yielded the familiar LEED pattern after saturation at 3L. The final δ was 0.6° monitored at 3000 Å. The UV absorption spectrum is shown in Figure 15 and consists of a large, broad peak centered at 2800 Å.

Adsorption of O₂ at room temperature appears to undergo a rapid chemisorption phase (δ = 0.2° at 5000 Å, p(2x2) LEED pattern develops after 1.5 L). After this initial stage, a slow oxygen uptake is indicated by the ellipsometer, with a final δ = 2.0° and a LEED pattern characteristic of NiO after 300 L. The analyzed spectrum of chemisorbed O₂ is shown in Figure 16, and again a broad feature at 2900 Å is prominent. Prolonged exposure to form the NiO had two effects on the analyzed spectrum. The magnitude of the analyzed peak was markedly increased and the actual peak position was shifted to higher energy as seen in Figure 17.

At room temperature, exposure of the crystal to ethanol leads to a disordered chemisorbed phase, with δ = 0.3° at 5000 Å. The absorption spectrum of this species is shown in Figure 18 and exhibits a peak at 2750 Å. For comparison, a spectrum of a 100 Å thick layer of ethanol
Figure 10. The LEED pattern of naphthalene chemisorbed on Ni(111) at room temperature after annealing at 80°C. The beam energy is 52 eV. (a) Photograph of the diffraction pattern. (b) Sketch of the pattern. Nickel diffraction spots are indicated by solid circles. Spots due to chemisorbed naphthalene are indicated by solid and open ovals.
Figure 11. The analyzed absorption spectrum for chemisorbed pyrazine on Ni(III).
Figure 12. The analyzed absorption spectrum for chemisorbed pyridine on Ni(111).
PYRIDINE/Ni(III)
Chemisorbed
d = 4.5 Å

Absorbance

λ(Å)

2400 2800 3200 3600

XBL8II-3572
Figure 13. The analyzed absorption spectrum for chemisorbed benzene on Ni(111).
BENZENE/Ni (111)
Chemisorbed
\( d = 5 \text{Å} \)

Absorbance

\( \lambda (\text{Å}) \)

2400 2600 2800 3000 3200 3400 3600 3800

0.0 0.05 0.1 0.15 0.2

XBL 812-9045
Figure 14. The analyzed absorption spectrum for chemisorbed naphthalene on Ni(111).
Figure 15. The analyzed absorption spectrum for chemisorbed CO on Ni(111).
Figure 16. The analyzed absorption spectrum for chemisorbed oxygen on Ni(111).
Figure 17. The analyzed spectrum of epitaxial NiO formed after prolonged exposure of the Ni(111) surface to oxygen.
Epitaxial NiO
\(d = 14 \text{ Å}\)

Refractive index
Absorption coefficient

Absorbance

\(\lambda (\text{Å})\)

XBL8II-3567
Figure 18. The analyzed absorption spectra of chemisorbed ethanol (upper curve) and a 100 Å layer of condensed ethanol (lower curve), shown on the same scale for comparison.
ETHANOL/Ni(III)

Chemisorbed
d = 4 Å

Condensed
d = 100 Å

Absorbance

2400
2800
3200
3600
λ(Å)
condensed on Ni(lll) at 80 K is shown on the same scale. No evidence of an absorption peak is visible in the condensed layer spectrum.

2. Discussion

In contrast to the behavior of the condensed aromatic molecules, the formation of a chemisorption bond has a very pronounced effect on the optical spectrum. All traces of the molecular transitions which appeared for the condensed layers are lost, and a single intense, broad absorption band centered between 2800 Å and 3100 Å (~4.2 eV) dominates the UV spectrum. This absorption appears at approximately the same energy and with the same shape for all the chemisorbed species studied, suggesting that a feature of the chemisorption process, rather than the molecular properties of the adsorbate, is responsible for the observed absorption peak. In light of the strong interband excitations for the bulk nickel in this energy range, it is likely that this spectral feature originates in chemisorption-induced modifications in the optical response of the metal substrate.

Previous reflectance work on H₂, O₂, and CO on W(110) yielded a very similar result: enhanced absorption at the energies of bulk interband transitions, accompanied by removal of lower energy transitions which appear in the clean metal spectrum. This behavior was attributed to a chemisorption-induced quenching of W(110) surface resonances (which were the initial states of the low-energy transitions), accompanied by a rehybridization of bulk bands, thus changing the interband matrix elements slightly and enhancing bulk excitation intensities. This analysis was supported by UPS data and theoretical calculations demonstrating the existence of these surface resonances, and by subsequent studies of the anisotropy of the optical response of the adsorbate-covered surface.
This same mechanism has been used to explain effects of chemisorption on photoemission from Ni(111).\textsuperscript{27,33} Chemisorption of H\textsubscript{2}, O\textsubscript{2}, CO, etc. causes electron emission from an sp\textsubscript{2}-like A\textsubscript{1} surface state (0.25 eV below E\textsubscript{F} on the clean surface) to shift to higher binding energy with increasing coverage and eventually disappear. At the same time electron emission from two sp-like A\textsubscript{1} bulk bands increases. This is interpreted as a mixing of adsorbate orbitals with the tails of bulk bands at the surface (the A\textsubscript{1} bulk bands having significant electron density in the surface region), causing both the removal of the surface state and the rehybridization which increases the interband matrix elements for excitations out of the A\textsubscript{1} bulk states. The d-like A\textsubscript{3} bulk state is affected very little in this process, suggesting little participation of Ni d-orbitals in the chemisorption bonding. Strong interaction of adsorbate orbitals with the Ni s-band would also lead to a highly delocalized adsorbate band spread out many eV in energy, and this is supported by the absence of emission from an adsorbate-like bonding orbital.

We believe that the chemisorption-induced feature which we observe in the optical spectrum at 4.2 eV is a direct result of this same rehybridization of the A\textsubscript{1} s-band that is indicated in the photoelectron spectrum taken at \textasciitilde 20 eV. Although there are many interband contributions to this region of the nickel absorption spectrum, band structure calculations\textsuperscript{34,35} support the assignment of an optical transition at \textasciitilde 4.5 eV to a A\textsubscript{1} \rightarrow A\textsubscript{3} excitation (i.e., out of the lower sp-like state), near the L point in the 3-D Brillouin zone (the [111] direction). This is illustrated in Figure 19. Just as in the photoemission experiments, rehybridization of this A\textsubscript{1} state upon chemisorption would change the A\textsubscript{1} \rightarrow A\textsubscript{3} matrix element, thus enhancing this bulk transition.
Figure 19. Calculated band structure of nickel including electron correlation, taken from Ref. 35 (only the minority spin bands are shown). The lowest $A_1$ band is predominantly s-like, with significant $p_z$ character near the L point (z in the direction of the surface normal). The highest $A_3$ band is mainly d-like. The arrow indicates the interband transition at 4.2 eV which is enhanced upon chemisorption.
Of the many contributions to the bulk nickel spectrum in this region, only the $A_1 + A_3$ transitions near the L point seem to be enhanced upon chemisorption. This can be rationalized in terms of a rehybridization of the $A_1$ (sp$_z$-like) states to increase the $p_z$ character of the state ($z$ direction along the surface normal) near the surface as a chemical bond to an adsorbate is formed. Such an increase in $p$ character might lead to better overlap with the $d$-like $A_3$ final state, thus increasing the intensity of these transitions. Excitations from the sp-like $A_1$ states near the X-point (in the [100] direction), which should occur near 3.5 eV, are not enhanced upon chemisorption, probably because the bond formation does not require significant hybridization in the [100] direction. Thus, the chemisorption process seems to selectively enhance transitions from the nickel sp-like bands along the direction of the surface normal.

Another feature of the optical spectra which is particularly striking in comparing the spectra of the condensed and chemisorbed aromatic hydrocarbons is the disappearance of quite strong molecular transitions upon chemisorption. None of the intense $\pi\pi^*$ absorptions (nor the weaker $n\pi^*$ of pyrazine), which are prominent in the absorption spectra of even very thin condensed layers, can be seen in the spectra of the respective chemisorbed species. In the related photoemission work on Ni(111), Himpsel, Knapp, and Eastman (HKE) claim that there are no resonances from adsorbate valence orbitals in the photoelectron spectra of $H_2$ and $O_2$ on Ni(111) because the adsorbate bonding orbital interacts so strongly with the s-band of the metal that it disperses in energy over the entire width of the s-band (~6 eV wide). However, earlier photoemission results of hydrocarbons chemisorbed on Ni(111) by Demuth and Eastman (DE) were used to demonstrate that the molecular orbitals of the adsorbate, even those
involved with bond formation, remain essentially intact after chemisorption. Those adsorbate bonding orbitals seem to shift to higher binding energy and to broaden slightly. However, our results and those of HKE, which indicate strong s-band contributions to the chemisorption process, seem to be at odds with the DE picture.

We believe that our results and the ARUPS results of HKE are consistent with the data presented by DE, but not with their interpretation of the data. A closer examination of the DE photoelectron spectra shows first the decrease in electron emission just below the Fermi energy which is now known to be due predominantly to the removal of the $\Lambda_1$ surface state on the (111) surface of nickel (although very slight perturbations in the d-band emission might also be represented). In addition to the electron emission from the many low-lying adsorbate levels which seem relatively unperturbed from the gas phase, there is a broad resonance which occurs at $\sim 5$ eV below $E_F$ for all the adsorbates. DE assign this electron emission peak to an adsorbate $\pi$ orbital which, after interaction with the metal, shifts to higher binding energy relative to the gas phase. However, our results and those of HKE, which imply the presence of this resonance even for adsorbates which do not have a nearby valence orbital, strongly suggest that this feature is in fact the enhanced electron emission from the lower $\Lambda_1$ state of the substrate, and not due to a molecular adsorbate level. If this interpretation is correct, then the electron emission from the adsorbate bonding orbital is not represented in the photoelectron spectrum, or is at least so broad as to be unresolved. These bonding orbitals, the $\pi$ levels of the unsaturated hydrocarbons, which would have been the initial states for the lowest energy optical excitations, would thus be broadened greatly so that the
corresponding absorption peaks would not be visible, as is the case for the systems we have studied.

The removal of the $\Lambda_1$ surface state, the enhancement of the $\Lambda_1$ bulk states, and the severe broadening of the adsorbate bonding levels, are all consistent with the picture of nickel bonding mainly through its s-like band states. If our analysis of the photoelectron spectra of unsaturated hydrocarbons on Ni(111) is correct, the adsorbates interact with the metal mainly through their $\pi$ systems (with possible contributions from the nitrogen lone pairs in the heteronuclear aromatics). The s-band participation in the chemisorption process has been proposed previously, especially in comparisons with chemisorption on Pd or Pt, where the d-bands play a much larger role. Bonding of unsaturated hydrocarbons through their $\pi$ systems has also been supported by a wide variety of studies.

Naturally the d-band of Ni must participate to some extent in the chemisorption process even though in the cases studied s-band contributions seem to dominate. The degree of d-band character in the chemisorption bond should vary with different adsorbates, and should be reflected in the optical spectrum. Two features should indicate strong d-band interactions: perturbations of interband excitations from d-like states, and the appearance of molecular transitions in the absorption spectrum, since the adsorbate bonding orbital should not be broadened greatly upon interaction with the d-band. In fact, recent photoemission studies of $\text{H}_2$/Ni(111) indicate that there exists a low-temperature phase in which the nickel d-bands appear to play a larger role in the formation of the chemisorption bond, as determined from large changes in the emission from the d-band states and from the appearance of a resonance
at 9 eV below $E_F$ attributed to the H orbital. Similar d-band contributions have been noted for CO/Ni(111). 31

Such dramatic changes in electronic structure must surely be apparent in the optical spectrum at the appropriate energies. We cannot, unfortunately, probe the spectral regions of interest here because we are limited to working in the visible-near UV. However, Rubloff and Freeouf 40 have investigated CO/Ni(111) at higher energies using surface reflectance and electron loss measurements. In addition to a peak in the ELS at ~4 eV, which we can now assign to an enhanced metal interband transition, there is an absorption near 8 eV which could correspond, as they suggest, to the $X^1\Sigma^+ \rightarrow \Lambda^1\Pi$ of molecular CO (i.e., a $5\sigma \rightarrow 2\pi^*$ excitation). This indicates d-band interaction in addition to s-band contributions, which is consistent with the picture of CO bonding through the $5\sigma$ orbital on carbon with back-bonding from the metal d-states into the $2\pi^*$. Optical investigations of the perturbations of these metal d-states should provide more information on the details of this bonding interaction.

3. Conclusion

We have studied the optical response of molecules chemisorbed on Ni(111) surfaces in the visible-near UV region. The observed absorption peak at 4.2 eV is assigned to a selective enhancement of the $A_1 \rightarrow A_3$ interband excitation near the L-point of the Brillouin zone (i.e., in the direction of the surface normal). Our results suggest that the $\pi$ orbitals of the aromatic hydrocarbons (and perhaps the nitrogen lone pairs in the azabenzenes) interact strongly with the nickel s-band states in forming the chemisorption bond.
ELECTRONIC ENERGY TRANSFER FROM MOLECULES TO SURFACES

A. Introduction

For molecules located near a metal surface, energy transfer to the metal provides a new mechanism for relaxation of an excited state in addition to relaxation mechanisms associated with the immediate molecular environment. This transfer of energy is a result of the response of the essentially free electrons in the metal to the electric fields caused by the oscillating dipole moment of an excited molecule. This new relaxation process is very long range and for molecules near or on the surface, it may compete very favorably with other relaxation mechanisms. When considering the possibility for photochemical reactions or reacting molecules going through intermediate states involving electronically excited configurations on metal surfaces, the prospect for effective damping due to energy transfer must be considered. The intrinsic linewidths arising from lifetime broadening of rapidly relaxing species is also important when interpreting the results of various surface spectroscopic methods.

An electronically excited molecule, viewed as an oscillating dipole, is influenced by the presence of a metal surface through several mechanisms. When the molecule is far from the surface (on the order of the wavelength of the dipole radiation), the lifetime of the excited state is perturbed by the radiation field reflected from the metal surface. This "image dipole" effect causes the lifetime to become shorter, if the reflected field is out of phase with the oscillating dipole, or longer, if it is in phase. At smaller separations, collective excitations
in the metal such as bulk and surface plasmons, and electron hole pair excitations can act as energy acceptors, provided that energy and momentum can be conserved. At very short distances, the excited dipole can transfer energy through its near-field components to the electron gas of the metal which, by various scattering processes, can dissipate the energy into the bulk metal. This "lossy wave" mechanism is very efficient and can shorten the lifetime of an excited molecule by several orders of magnitude.

The most successful general theory of energy transfer to metal surfaces has been developed by Chance, Prock, and Silbey (CPS). Their classical, macroscopic approach explores both the role of the metal dissipative modes and the dependence of the energy transfer rate on the metal-molecule separation. In this model, the molecule is treated as a point dipole located above a metal of (local) dielectric constant $\varepsilon(\omega)$, separated from a dielectric ambient by a sharp boundary. Within this framework, it is possible to separate the total decay rate of the excited molecule into radiative and nonradiative components, the latter representing the rate of energy transfer to the metal.

Experiments on a wide variety of systems have explored the range of applicability of the CPS treatment by measuring the distance dependence of the energy transfer rate. Almost all have found at least qualitative agreement with the predictions of the CPS theory, even for molecule-metal separations as small as 7 Å. In those experiments which could not be explained satisfactorily by the CPS model, the investigators were unable to conclude that the approximations in the theory had become invalid.
Attempts to observe the breakdown of the CPS model have led investigators to systems in which energy transfer to surface plasmons is important. In particular, silver has been investigated extensively because surface plasmons are available as energy acceptors at visible and near-UV wavelengths. Recent results for the pyrazine/silver system, in which the pyrazine $3\pi\pi^*$ excited state (located at 3.3 eV) occurs near the resonant surface plasmon energy (3.8 eV), indicate that the energy transfer rate remains approximately constant for separations from 125 A down to 10 A. This is in direct disagreement with the prediction of the CPS theory for this system at these separations. In another study, the lifetime of the pyrazine $1\pi\pi^*$ state (located at 4.8 eV, above the surface plasmon energy) was indirectly determined for molecules in direct contact with the silver surface. The resulting lifetime was in approximate agreement with the prediction of a CPS treatment.

B. Theory

With the aid of the simple, classical model outlined above, Chance, Prock, and Silbey adapted the methods used by Sommerfeld when he considered radio transmission above the earth. The emitter is now the molecular dipole and the earth is replaced by the metal surface. A complete description of the derivation can be found in Reference 51. A sketch of the important features of the derivation will be given here in order to clarify the consequences of the theoretical predictions on experimentally measurable quantities.

The motion of the dipole, treated as a classical harmonic oscillator, is given by

$$\ddot{u} + \omega^2 u = \frac{e^2}{m} E_r - b_0 \dot{u}$$  \hspace{1cm} (1)
where \( \mu \) is the dipole moment, \( \omega \) the dipole oscillation frequency, \( m \) the effective mass, \( E_r \) the dipole's own reflected electric field acting as a driving force, and \( b_0 \) the damping constant (inverse lifetime) in the absence of the mirror. This can be solved by substituting

\[
\mu = \mu_0 e^{-i(\omega_0 + \delta \omega)t} e^{-bt/2}
\]

and

\[
E_r = E_0 e^{-i(\omega_0 + \delta \omega)t} e^{-bt/2}
\]

into Equation (1). This yields the new damping constant \( b \) and frequency shift \( \delta \omega \) resulting from the dipole interacting with the reflected field

\[
\delta \omega = \frac{b^2}{\delta \omega} + \left[ \frac{e^2}{2\mu_0 m \omega} \right] \text{Re}(E_0)
\]

and

\[
b = b_0 + \left[ \frac{e^2}{2\mu_0 m \omega} \right] \text{Im}(E_0).
\]

The frequency shift is quite small and is not expected to be experimentally observable. However, \( b \), the new damping rate, can be very different from \( b_0 \), even for distances large compared to the emitting wavelength. For \( d \leq 1000 \) Å, the new damping rate increases rapidly due to energy transfer from the dipole to the metal.

The method used to calculate the reflected field is somewhat involved. A Fourier expansion of the exact dipole field in terms of cylindrical eigenfunctions is made, using the reduced wavevector, \( u \) (wavevector normalized to the free photon wavevector) as the expansion variable. This representation yields the Hertz vector for the dipole in...
terms of a superposition of radial waves. A similar representation of
the Hertz vector for the metal response is combined with the dipole
field to match boundary conditions and determine the appropriate reflec-
tion coefficient for the metal response. From this, the reflected
electric field at the dipole may be evaluated leading to a general
expression for the damping rate of the oscillating dipole

\[ b_1 = b_0 - \frac{3}{2} b_0 q \text{ Im} \left[ \int_0^\infty R_\| e^{\frac{-2\lambda_1 d}{\lambda_1}} \frac{u^3}{\lambda_1^3} \, du \right] \]  

(6)

and

\[ b_\| = b_0 + \frac{3}{2} b_0 q \text{ Im} \left[ \int_0^\infty (1-u^2)R_\| + R_\perp \frac{e^{\frac{-2\lambda_1 d}{\lambda_1}}}{\lambda_1^3} \, du \right] \]  

(7)

for dipole orientations perpendicular and parallel to the surface. In
these expressions \( q \) is the free molecule luminescence quantum yield and
\( \lambda_1^3 = 2\pi \varepsilon_1 \frac{d}{\lambda} \) where \( \lambda \) is the vacuum radiation wavelength of the emitter,
\( \varepsilon_1 \) is the ambient dielectric constant and \( d \) the distance of the dipole
from the surface. We therefore find a complex distance dependence of
the total damping rate.

For molecules located very near the surface, \( d/\lambda \ll 1 \), which allows
an approximation in which the integral equations can be solved analytically.
The resulting damping rate

\[ b = \frac{b_0 q}{4d^3} \text{ Im} \left\{ \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} \right\} \]  

(8)

shows a \( d^{-3} \) distance dependence. In the distance regime where the approxi-
mation is valid, the damping rate due to energy transfer will dominate
other decay mechanisms. This is reflected in the expected quantum yield
of the luminescence for radiating molecules close to the surface

\[ \phi = 4d^3 \left[ \text{Im} \left\{ \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} \right\} \right]^{-1}. \]  

(9)

While the CPS theory has been successfully applied in a variety of experiments, we expect the assumptions made in its derivation to become less valid as the separation between the molecule and the metal approaches molecular dimensions. In this case, the description of the oscillating charge density by a point dipole would appear as quite incorrect. Secondly, the use of a local dielectric constant to describe the metal is also incorrect. The response of the metal to applied fields should be in terms of a nonlocal dielectric constant \( \varepsilon(\omega, \mathbf{k}) \), where the \( \mathbf{k} \) dependence reflects the wavelength dependence of the response. This is important, as the electric field near the dipole source has contributions for \( \mathbf{k} \)'s from zero to very large values in the Fourier expansion in Equations (6) and (7). For a jellium surface, Persson \(^43\) calculated the damping rate of the dipole using a model \( \varepsilon_2(\omega, \mathbf{k}) \) and found a new mode of energy transfer due to the excitation of electron-hole pairs, now allowed by the momentum available in the dipolar field. This new process is expected to become important at distances less than 100 Å and to dominate at \( d \leq 10 \) Å. Further improvement can be made by using a microscopic theory which requires a continuous variation of response functions and fields in crossing the metal-ambient boundary. Such a calculation was recently done for a jellium surface and showed reflected fields of a point dipole to be quite different near the interface from those found using macroscopic boundary conditions. \(^52,53\)
C. Experimental

We have devised a new experiment which is capable of studying the entire energy transfer region from several hundred Angstroms to the point where the molecule is in intimate contact with the surface, in contrast to the experiments of Kuhn and Drexhage which were limited to distances greater than about 50 Å.41 In this experiment a luminescent molecule is separated from the surface by a layer of condensed argon, whose thickness may be varied to map the distance dependence of the energy transfer rate at short distances.

This chapter describes two experiments examining the lifetime of the \(^3n\pi^*\) state of pyrazine as the distance to the surface of a metal is decreased. The initial experiment measured the relative phosphorescence yield of pyrazine above a Ni(111) surface in the distance regime where Equation (9) is expected to be valid. A second, more elaborate investigation measured the lifetime of the \(^3n\pi^*\) phosphorescence directly over a wider distance range above a Ag(111) surface. While the relative luminescence yield measurement was done first, it is easiest to describe the more elaborate experimental arrangement first.

The experimental arrangement is shown schematically in Figure 20. Details of the configuration and capabilities of the stainless steel ultrahigh vacuum chamber are described in Chapter II. Typical operating pressures were \(\leq 2 \times 10^{-10}\) torr. Silver samples were spark-cut from a 3/8" rod (Aremco Products, 99.999% purity) and oriented to within 1° of the (111) direction by Laue x-ray backscattering. The silver wafer was electron beam welded to a nickel backing, then mechanically and chemically polished before being placed in the vacuum chamber. At the start of each experiment, the silver surface was cleaned by argon ion bombardment and
Figure 20. A schematic view of the experimental apparatus and experimental geometry. 1) Single crystal Ag(111) surface; 2) Liquid helium cryostat sample mount; 3) f/1 collection lens with conical shroud; 4) External focussing lens; 5) Colored glass filters; 6) Photomultiplier tube in a dry ice cooled housing; 7) Spherical mirror for use in ellipsometry; 8) Ellipsometer MgF$_2$ input polarizer; 9) Ellipsometer alignment apertures; 10) Rotating analyzer polarizer, motor, and photomultiplier; 11) Excitation laser alignment apertures; 12) MgF$_2$ polarizer for polarizing excitation laser.
annealing. The sample was then placed on the liquid helium cold tip, which was pre-cooled to minimize condensation of residual gases on the silver surface.

The argon and pyrazine layers were constructed by condensation on the silver surface held at 20 K. Thicknesses were measured with a rotating analyzer ellipsometer. Details of this instrument are given elsewhere. The ellipsometric parameters ($\Delta, \psi$) were measured continually during the deposition and $\lambda = 3000 \, \text{Å}$. The refractive index of the argon layer was determined by the method of Malin and Vedam. The measured refractive index, $n(Ar) = 1.2 - 0.03i$, remained approximately constant throughout these experiments. These optical constants were used to calculate the thickness of the spacers. We estimate the error in the thickness determination to be 5–10%. A monolayer of pyrazine was condensed on top of the argon layer.

The pyrazine emission was excited at 3250 Å by a linearly polarized, 10 ns pulse from the frequency-doubled output of a Nd:YAG pumped dye laser (Quanta-Ray Corp.) operating with DCM dye. The phosphorescence was collected by a one inch f/1 lens mounted inside the vacuum chamber. Outside the chamber, the emission was isolated with colored glass filters (Schott GG375 and Corning CS 7-54) and focussed onto the photocathode of a photomultiplier (EMI 6256S). The phosphorescence decay was recorded with a transient waveform digitizer (Biomation 8100) interfaced to a laboratory microcomputer (Digital Equipment Corp. PDP 11/03) for signal averaging and storage on floppy diskette. Phosphorescence lifetimes were calculated with a least squares fit of a single exponential to the experimental decay.
The Ni(III) crystal used in the relative luminescence yield measurement was prepared as described in Chapter II. Pyrazine phosphorescence was excited by a filtered medium pressure Hg arc in the position of the alignment laser in Figure 20. The spectral range of the incident light covered the entire $^1\text{nπ*}$ absorption band. The resulting luminescence was collected as in the direct lifetime measurement. The intensity was determined by counting photons for fixed intervals in order to establish an average luminescence flux.

Finally, phosphorescence excitation spectra could be determined by scanning the monochromator in Figure 20 while detecting the phosphorescence in the photon counting configuration. By using either a filtered arc or a laser as an excitation source, a phosphorescence spectrum could be obtained by replacing the filters with a monochromator before the photomultiplier.

D. Phosphorescence of Pyrazine

The photophysics of pyrazine at low temperatures has been studied extensively, resulting in a detailed knowledge of its excited states and their dynamics. For molecules excited into the lowest energy, electronically excited singlet state of $^1\text{nπ*}$ character, the most probable relaxation mechanism involves rapid intersystem crossing to the triplet manifold. Once in the triplet manifold, internal conversion rapidly brings the molecule into the vibrationless $^3\text{nπ*}$ state. At the temperatures used in the energy transfer investigations, the populations of the three zero field split magnetic sublevels are in thermal equilibrium resulting in a single exponential phosphorescence decay time. The radiation is polarized along the N-N axis of the molecule.
Since the pyrazine environment in the energy transfer measurements is quite different from those found in molecular spectroscopy experiments, it is possible that the molecular dynamics will also be altered. In order to assure that the behavior of pyrazine remains essentially unchanged, both phosphorescence excitation and phosphorescence spectra were measured for pyrazine above the metal surface at the argon vacuum interface.

Figure 21 shows the phosphorescence excitation spectrum of a thick (~25 Å) pyrazine layer deposited onto a 200 Å thick argon layer above a Ag(111) surface. The spectrum was collected by isolating the phosphorescence through colored glass filters and counting photons for a set interval before the monochromator was stepped to the next wavelength. No account has been taken of the intensity changes of the excitation source at different wavelengths. The origin and vibronic peaks of the $1_{n\pi^*}$ state are well resolved and closely resemble the absorption spectrum of condensed pyrazine on Ni(111) determined with spectroscopic ellipsometry (Chapter II). This establishes the origin of phosphorescent emission as the excited singlet states.

The use of glass filters, rather than a monochromator, to isolate the phosphorescent emission was based upon the difficulty in properly realigning the monochromator before each experimental point as well as the lower efficiency compared to the glass filters. However, questions regarding the purity of the detected radiation could not be answered without a comparison of the spectral composition of the radiation detected with and without the filters in place. Figure 22 shows the luminescence detected through the collection optics with and without filters. The measurement was made for a pyrazine-argon-Ag(111) system similar to that
Figure 21. The phosphorescence excitation spectrum of a thick (~25 Å) layer for pyrazine on the boundary between vacuum and a 200 Å thick argon layer above a Ag(111) surface. The variation in excitation source intensity has not been taken into account.
Phosphorescence Excitation Spectrum of Pyrazine at the Argon-Vacuum Interface
Figure 22. a) The spectral distribution of light collected when exciting a layer of pyrazine (~25 Å thick) at the boundary between vacuum and a 200 Å thick argon layer above a Ag(111) surface. The small peak at 3280 Å is the scattered light from the exciting laser. The remaining peaks are due to the phosphorescent emission of the pyrazine layer.

b) The spectral distribution of light detected when colored glass filters are introduced in the optical path before the monochromator. Note the absence of the scattered laser light as well as the reduced intensity for phosphorescence of pyrazine at energies lower than the 0-0 peak.
Phosphorescence of the $^3n\pi^*$ State of Pyrazine at the Argon-Vacuum Interface
used in determining the excitation spectrum. The excitation source was the pulsed output of a laser tuned to 3280 Å. Collected radiation was focused onto the slit of a Spex Doublemate monochromator and the spectrum was collected by counting photons.

The phosphorescence spectrum as measured without the glass filters shows some scattered laser radiation. However, the dominant intensity is due to the 0-0 phosphorescence origin, followed by a series of peaks resulting from the final state being vibrationally excited. These vibrational peaks correspond well in both energy and relative intensity to those found in the phosphorescence spectrum of pyrazine in low temperature benzene single crystals. When the isolating glass filters are placed before the monochromator, the effective bandpass is sharply peaked at the phosphorescence origin. Intensity due to vibrationally excited final states is sharply reduced and no trace of the laser peak is found. Thus, the use of glass filters is seen to reduce the detected phosphorescence almost completely to the 0-0 electronic transition.

E. Results

1. Relative Phosphorescence Yield of Pyrazine above the Ni(111) Surface

The phosphorescence intensity was linear in the thickness of adsorbed pyrazine, for a fixed argon spacer thickness, as shown in Figure 23. This observation suggests that rapid resonant energy transfer occurs, bringing the excitation to the pyrazine-argon interface, from which energy transfer to the surface takes place. Consequently, the effective emitter-surface separation is taken to be the thickness of the argon spacer layer.

Figure 24 shows the distance dependence of the emission intensity. The data are plotted as log-log and a least squares fit of the data yields
Figure 24. Pyrazine phosphorescence intensity as a function of argon spacer thickness for a fixed pyrazine overlayer thickness of 5 Å. The ordinate shows the average count rate although longer counting times were used to improve the statistics. The error bars reflect the uncertainty in the thickness of the pyrazine overlayer, which, in a series of separate experiments, we determined to be reproducible to ± 10%. The line shown is a least squares fit to a power law with an exponent of 3.07 ± 0.05.
Pyrazine Phosphorescence Intensity (counts/sec)

\[ \log_{10}(\text{counts/sec}) \]

Argon Thickness \( d \) (Å)

- Pyrazine
- Argon
- Nickel

5 Å Pyrazine Thickness

XBL 7912-5468
a slope of $3.07 \pm 0.05$. At very short distances the pyrazine emission intensity was considerably weaker than the scattered exciting light, even though the filter combinations were carefully chosen to minimize spectral overlap between the excitation and observation passbands. Consequently, it was necessary to measure the light intensity before and after the deposition of pyrazine, taking the difference as the phosphorescence intensity. Even though long counting times were used to improve the statistics, the high background precluded our measuring the quantum yield at smaller separations.

2. Phosphorescence Lifetime of the $^3\pi\pi^*$ State of Pyrazine above Ag(111)

Phosphorescence decays were recorded for pyrazine-silver separations between 420 Å and 10 Å. The 10 Å distance represents only two layers of argon separating the pyrazine from the silver surface. For fixed incident laser power, the phosphorescence intensity decreased with decreasing distance to the Ag surface. Attempts to measure phosphorescence from pyrazine on a single monolayer of argon (5 Å from the silver surface) failed due to low signal levels. An example of a typical decay curve is shown in Figure 25.

The lifetimes calculated from the decays are presented in Table 2. Lifetimes were measured for laser excitation polarized both in and perpendicular to the plane of incidence and the differences between the lifetimes for the two polarizations were within experimental error for all distances. For separations greater than 25 Å, the fit of a single exponential to the measured decay was excellent, although there is some evidence for more rapid decay at very short times following excitation. We believe that this short lifetime component arises from pyrazine
Figure 25. A typical phosphorescence decay curve obtained after averaging 300 laser shots.
Table 2

The Observed Phosphorescence Decay Times at the Distances Indicated for a Monolayer of Pyrazine Separated from the Ag(111) Surface by a Layer of Argon at 20 K

<table>
<thead>
<tr>
<th>d (Å)</th>
<th>τ (msec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.2</td>
</tr>
<tr>
<td>20</td>
<td>0.5</td>
</tr>
<tr>
<td>25</td>
<td>0.5</td>
</tr>
<tr>
<td>35</td>
<td>1.5</td>
</tr>
<tr>
<td>50</td>
<td>4.0 - 4.9</td>
</tr>
<tr>
<td>75</td>
<td>3.9 - 8.9</td>
</tr>
<tr>
<td>100</td>
<td>10.1 - 11.8</td>
</tr>
<tr>
<td>180</td>
<td>14.2</td>
</tr>
<tr>
<td>420</td>
<td>16.0</td>
</tr>
</tbody>
</table>
adsorbed near a small number of surface defects. This is demonstrated in Figure 26. At distances less than 25 Å, the fit of a single exponential is less satisfactory as seen in Figure 27. The nonexponential decay at short distances can be attributed to microscopic irregularities in the Ag surface and the pyrazine layer. These irregularities produce a range of dipole-metal separations, resulting in a distribution of phosphorescence lifetimes.

F. Discussion

The cubic dependence of the relative phosphorescence yield from the $^3n\pi^*$ state of pyrazine above a Ni(111) surface is consistent with the predictions of the Chance, Prock, and Silbey theory. However, we are unable to make a quantitative comparison between the experimental and theoretically predicted absolute luminescence quantum yield.

Energy transfer from the $^3n\pi^*$ state of pyrazine to a nickel surface is almost entirely due to a resistive damping or "lossy wave" mechanism. However, for silver surfaces, energy transfer due to resonant excitation of surface plasmon polariton modes becomes a very important new decay mechanism. While these surface collective excitations are not excitable directly with a radiation field, due to the inability to simultaneously conserve momentum and energy, the nonradiation components of a radiating dipole near the surface couple very effectively to these excitations. As one approaches the surface plasmon resonant energy, the density of these modes increases rapidly, until at resonance, very rapid, long range energy transfer is expected. Since these surface modes are delocalized excitations, the importance of a nonlocal dielectric treatment of the surface response is accentuated. The silver surface plasmon resonance is at 3.8 eV, while the pyrazine phosphorescence is at 3.3 eV, making it
Figure 26. The result of a least squares fit of a single exponential to the experimental decay curve. The fit is excellent except at very short times, where more rapid decay is suggested. This is attributed to pyrazine adsorbed above a small number of surface irregularities.
$^{3}_n\pi^*$ Pyrazine 100 Å above Ag(III)
Figure 27. The result of a least squares fit of a single exponential to the experimental decay curve. The fit is not satisfactory and suggests a distribution of actual decay times throughout the pyrazine layer. This is attributed to the affects of microscopic roughness on the surface or in the adsorbed layers leading to a distribution of molecule-metal distances.
possible to detect the effects of the nonlocal response when the molecule 
is nearly in contact with the surface.

The observed distance dependence of the phosphorescence lifetime can 
be directly compared to the behavior predicted by the CPS theory. The 
model used corresponded to our experimental configuration: a layer of 
pyrazine 3 Å above an argon layer adsorbed on a silver surface. The 
ambient was vacuum (n = 1) and the emission wavelength of pyrazine was 
3800 Å. The optical constants for Ar and Ag at 3800 Å were determined 
ellipsometrically during the experiment. A value of 0.3 for ϕp, the 
phosphorescence quantum yield, was taken from the literature. The 
only adjustable parameter, τ0, was the phosphorescence lifetime of 
pyrazine at an argon-vacuum interface at infinite separation from the 
Ag surface.

The total decay rate for dipoles oriented parallel to the silver 
surface was calculated from the equations in Reference 59:

\[
\frac{b}{b_0} = \frac{\tau_0}{\tau} = 1 + \frac{3}{4} \phi_p \text{ Im} \left[ \int_0^\infty \left( \frac{1-u^2}{u^2} R^\parallel + \frac{1}{u} R^\perp \right) \frac{u^3}{\hat{d}} e^{-2\hat{d} \frac{u}{\ell_1}} du \right]
\]

where the explicit formulas for the reflectivities R and normalized 
distances \( \hat{d} \) may be found. Only the calculation for parallel dipoles is 
shown because, as noted previously, the probability for radiative 
decay of parallel dipoles is much greater than that of perpendicular 
dipoles in this distance regime.

The result of the calculation for τ0 = 25 ms is plotted with the 
experimentally determined lifetimes in Figure 28. The value of 25 ms 
for τ0 is comparable to the phosphorescence lifetime of pyrazine in a 
variety of environments. Excellent agreement is found between 
the observed distance dependence of the lifetime and the prediction of 
the CPS theory.
Figure 28. A comparison between the distance dependence of the relative damping rate as determined experimentally with the theoretical prediction of the CPS model. The lifetime of the pyrazine at infinite separation from the silver surface was taken to be 25 ms. All other parameters were either measured during the experiment or taken from the literature.
$^{3}n\pi^{*}$ Pyrazine above Ag(III)
A detailed analysis of the CPS description can provide insight into the fundamental nature of the energy transfer process. Following Weber and Eagan, the expression for the total decay rate (Eq. (10)) can be separated into three parts which describe the decay of the dipole through separate channels: 1) emission of photons; 2) resonant excitation of surface plasmons; 3) energy transfer to the metal through the driving of "lossy waves". As a measure of the importance of these decay paths in the total decay rate, Figure 29a shows the channels as a function of dipole-metal separation. For distances less than 100 Å, energy transfer through "lossy waves" is the dominant mode of decay. The difficulty in measuring the phosphorescence lifetimes at small separations is a direct consequence of the extremely small probability for photon emission near the surface. The probability for surface plasmon excitation is also very small at short distances due to competition with decay through the "lossy waves". However, at larger separations, between 150 Å and 500 Å, excitation of surface plasmons is the primary energy transfer mechanism.

A similar analysis can be made for the nickel surface. The result of decomposing the decay rate is shown in Figure 29b. As expected by the nickel surface plasmon resonance energy of 8.1 eV, molecular decay through excitation of resonant surface plasmon polaritons is extremely small and may be neglected. Equally striking is the very large contribution of the lossy wave decay at large distances. This is a direct consequence of the very different electronic band structure of nickel and silver. The first interband excitation in silver is in the region of the surface plasmon resonance. In fact, it is the modulation of the Drude free electron dielectric constant by this interband excitation which results in this low energy plasmon resonance. On the basis of the silver electron density alone, the plasmon resonance is expected in the
Figure 29. By dividing the integral over reduced wavevector, $u$, in Equation 10 into three regions corresponding to the decay of the pyrazine molecules through radiation (RD), excitation of surface plasmons (SP), and driving "lossy waves" on the surface (LW), the probability for decay into each of these modes can be determined as a function of distance from the surface.

a) The probability for the decay of the $3\pi^*$ state of pyrazine above a silver surface.

b) The probability for the decay of the $3\pi^*$ state of pyrazine above a nickel surface.

Note the importance of surface plasmon excitation in the silver case compared to the large lossy wave contribution for nickel.
$^3n\pi^*$ Pyrazine 3 Å above Argon Spacer on Ag(III)
$3_n \pi^*$ Pyrazine 3 Å above Argon Spacer on Nickel

Decay Probability

\[ \text{d (Å)} \]

LW
RD
SP
same energy region as in nickel where such a resonance is in fact observed. In contrast, nickel has numerous interband excitations beginning in the near IR and extending throughout the visible-UV energy range. This results in a sizable imaginary component in the nickel dielectric constant. In order for the driven charge density waves on the metal surface to act as energy acceptors, they must be damped by processes in the metal. The damping in silver depends exclusively on the scattering of the free electrons in the metal. However, for nickel, the damping of the driven surface waves is dominated by resonant excitation of single electron-hole interband resonances in the metal interior. Thus, while both nickel and silver act as efficient long range energy acceptors, the microscopic details of the energy transfer mechanism is very different.

In conclusion, the $d^3$ behavior of the relative phosphorescence yield of pyrazine above a Ni(111) surface is in accord with the expectations of the classical, macroscopic theory of Chance, Prock, and Silbey to within two layers of argon from the metal surface. Further, the quantitative agreement between the observed and predicted lifetime of the $^3n\pi^*$ state of pyrazine to the same distance above a Ag(111) surface conclusively confirms the validity of the theoretical model. Our inability to make measurements at smaller molecule-metal separations leaves unanswered the question of the importance of microscopic corrections to the model. However, even the behavior expected on the basis of the simple model suggests that present experimental methods will be unable to detect molecules through their luminescence when nearly in contact with the metal surface. Therefore, new methods must be developed before this small separation limit can be investigated.
APPENDIX A

A BRIEF INTRODUCTION TO SPECTROSCOPIC ELLIPSOMETRY

Ellipsometric measurements and their interpretation play a critical role in experiments described in this dissertation. While ellipsometry has its origin in the work immediately following the appearance of Maxwell's equations, development into a general research technique required the availability of laboratory micro-computers which are capable of automated instrument operation and rapid data manipulation. The rebirth of ellipsometry has led to renewed interest in the optics of surfaces and the development of many ellipsometers designed for laboratory use. Review articles, conference proceedings, and a recent monograph provide an extensive literature for the interested reader. However, in order to appreciate the experiments, data reduction, and conclusions detailed in the body of this dissertation, an introduction to ellipsometry for the general reader is considered a valuable guide.

This appendix is intended to provide both a basic mathematical and conceptual introduction to the rudiments of ellipsometry. With a simple development based on physical models, the mathematical results can be manipulated to provide a starting point for a discussion on the interpretation of ellipsometric measurements in three types of adsorption systems: 1) multilayer adsorption of nonabsorbing adsorbates; 2) multilayer condensation of absorbing adsorbates; 3) chemisorption and reactive adsorption. Since many ellipsometer designs exist, only the principle of the rotating analyzer will be given as an example of measuring the ellipsometric angles \( \Delta \) and \( \Psi \).
A. Reflection of Light at Interfaces

A number of assumptions regarding the physical system being modeled will be important throughout this discussion. We assume all light to be monochromatic plane waves, all dielectric media to be homogeneous, isotropic, nonmagnetic at optical frequencies and to have sharp, planar boundaries. The incident, reflected, and transmitted electric fields at each boundary are considered to be of definite polarization. Referring to Figure 30, we can resolve any polarized plane wave into linearly polarized components with electric field vectors oscillating only in the plane (p polarized) or only perpendicular (s polarized) to the plane of incidence. These component fields can be combined with different relative phase and amplitude to reproduce any polarized beam from linear to circular polarization. Finally, the response of the dielectric media to the incident electromagnetic field is described by a linear response function dependent only upon the frequency of the oscillating field. In this local approximation we may use either the complex dielectric function \( \varepsilon'(\omega) = \varepsilon' - i\varepsilon'' \) or the complex refractive index \( \tilde{n}(\omega) = n - ik \) to describe the dielectric response. For the analysis of absorption coefficients, \( \tilde{n} \) proves to be more convenient as the absorption coefficient \( k \) can be related to molar extinction coefficients and thus provides a useful comparison with other absorption spectra.

Figure 30 shows the incident, reflected, and transmitted fields needed to describe the response of the dielectric medium 1 to the field incident from medium 0. By applying the boundary conditions at the interface which require continuity of \( E \) and \( H \) tangent to the interface, we find that \( \phi_i = \phi_r \) and

\[
\tilde{n}_0 \sin \phi_0 = \tilde{n}_1 \sin \phi_1
\]  

(A-1)
Figure 30. The reflection of light at a dielectric boundary requires the incident, reflected, and transmitted waves to follow Maxwell's equations in the two media. This is shown schematically for light polarized in the plane of incidence (P-polarized) and perpendicular to the plane of incidence (S-polarized).
Reflection of P-Polarized Light at a Dielectric Boundary

Reflection of S-Polarized Light at a Dielectric Boundary

\[ \vec{E}_{ip}, \vec{H}_{ip} \] Medium O

\[ \vec{E}_{rp}, \vec{H}_{rp} \] Medium O

\[ \vec{E}_{tp}, \vec{H}_{tp} \] Medium I

\[ \vec{E}_{ts}, \vec{H}_{ts} \] Medium I
which is Snell's Law. The amplitudes of the incident and reflected fields are complex quantities which can be related to the properties of the reflecting system.

\[
\begin{align*}
\tilde{r}_p &= \frac{\tilde{E}_p}{\tilde{E}_p} = \frac{\tilde{n}_1 \cos \phi_i - \tilde{n}_0 \cos \phi_t}{\tilde{n}_1 \cos \phi_i + \tilde{n}_0 \cos \phi_t} \quad (A-2a) \\
\tilde{r}_s &= \frac{\tilde{E}_s}{\tilde{E}_s} = \frac{\tilde{n}_0 \cos \phi_i - \tilde{n}_1 \cos \phi_t}{\tilde{n}_0 \cos \phi_i + \tilde{n}_1 \cos \phi_t} \quad (A-2b)
\end{align*}
\]

where \( \tilde{r}_p \) and \( \tilde{r}_s \) are the customary Fresnel complex amplitude reflection coefficients. Similar expressions for the transmission coefficients can be found. In these expressions, we have considered the refractive indexes to be complex which requires \( \phi_i \) and \( \phi_t \) also to be complex.

Generally, medium \( 0 \) is a nonabsorbing ambient, thus, \( \tilde{n}_0 \) and \( \phi_i \) are real. Equations A-2 may be simplified by application of Snell's Law so that the system is described by the refractive indexes of each medium and only the real angle of incidence. Making use of trigonometric identities, we find

\[
\cos \phi_t = \left( \tilde{n}_1^2 - \tilde{n}_0^2 \sin^2 \phi_i \right) / \tilde{n}_1
\]  

(A-3)

The subscript on the angle of incidence may now be dropped and \( \phi \) will always refer to the real angle of incidence in medium \( 0 \).

The amplitude reflection coefficients \( \tilde{r}_p \) and \( \tilde{r}_s \) are complex numbers. This represents changes in both the amplitude of the reflected field as well as its phase, with respect to the incident field, brought about by reflection. This can be formalized by expressing \( \tilde{r}_p \) and \( \tilde{r}_s \) in complex polar notation.
While the absolute phase of the plane wave can not be determined, the relative phase and amplitude of the two linearly polarized component fields can be measured. This is expressed in the fundamental equation of ellipsometry

\[ \frac{\tilde{r}_p}{\tilde{r}_s} = \frac{\tilde{r}_p}{|\tilde{r}_s|} e^{i(\delta_p - \delta_s)} = \tan \psi e^{i\Delta} \]  

which defines the ellipsometric angles \( \psi \) and \( \Delta \). By substituting Equations (A-2) into (A-5), we arrive at an expression for \( \tilde{n}_1 \) in terms of \( n_0 \), the angle of incidence \( \phi \), and the quantity \( \tilde{\rho} \)

\[ \tilde{n}_1 = n_0 \sin \phi [1 + (\frac{1 - \tilde{\rho}}{1 + \tilde{\rho}}) \tan^2 \phi] \]  

This is the basis for ellipsometric measurements of the refractive index of condensed dielectric media.

The determination of spectral properties of molecules adsorbed on metal surfaces requires a relation between \( \tilde{\rho} \) and the optical properties of the adsorbate on the metal substrate. Figure 31 gives insight into the development of such an expression. For a wave incident from medium 0 onto medium 1, the initial encounter produces a reflected and transmitted field. The transmitted component then gives rise to a second reflected component at the interface of medium 1 and medium 2 as well as a transmitted component into medium 2. This component field from the 1-2 interface produces an infinite series of reflected and transmitted field
Figure 31. Light incident on a multilayer system produces an infinite train of reflected and transmitted wave components of diminishing amplitude.
Reflection of Light at a Multilayer Interface

Incident Field

Medium 0
\( n_0 \)

Medium 1
\( \tilde{n}_1 = n_1 - ik_1 \)

Medium 2
\( \tilde{n}_2 = n_2 - ik_2 \)

Reflected Field

Transmitted Field
components. It is possible to sum the infinite series analytically and derive an expression for the net amplitude reflection coefficients in terms of the reflection coefficients at the 0-1 ($r_{01p}$, $r_{01s}$) and 1-2 ($r_{12p}$, $r_{12s}$) interfaces, the vacuum wavelength of the incident light, $\lambda$, and the thickness, $\phi$, of medium 1

$$\tilde{R}_p = \frac{r_{02p} + r_{12p} e^{-i2Z}}{1 + r_{01p} r_{12p} e^{-i2Z}}$$  \hspace{1cm} (A-7a)

$$\tilde{R}_s = \frac{r_{01s} + r_{12s} e^{-i2Z}}{1 + r_{01s} r_{12s} e^{-i2Z}}$$  \hspace{1cm} (A-7b)

$$Z = \frac{2\pi d}{\lambda} \left( n_1^2 - n_0^2 \sin^2 \phi \right)^{\frac{1}{2}}$$  \hspace{1cm} (A-7c)

These expressions may now be used to determine the ellipsometric angles for this system

$$\rho = \tan \psi e^{i\Delta} = \frac{\tilde{R}_p}{\tilde{R}_s} = \left( \frac{r_{02p} + r_{12p} e^{-i2Z}}{1 + r_{01p} r_{12p} e^{-i2Z}} \right) \cdot \left( \frac{1 + r_{01s} r_{12s} e^{-i2Z}}{r_{01s} + r_{12s} e^{-i2Z}} \right).$$  \hspace{1cm} (A-8)

This expression represents the second important result of this section. In principle, the number of interfaces and films can be extended indefinitely, with the simple two medium reflection coefficients in Equations (A-2) applying to each boundary, requiring the summation of reflected and transmitted fields for each intermediate medium. However, the three phase system, ambient-overlayer-substrate, will suffice for further discussion.

B. Experimental Determination of $\Delta$ and $\psi$

Within the simple dielectric model we have used to describe
reflecting systems, we have given an expression relating $\Delta$ and $\psi$ to the refractive indexes of the media, the angle of incidence, and the vacuum wavelength of the incident light. This poses the question of how one determines $\Delta$ and $\psi$ experimentally. While many ellipsometer designs exist, this discussion will focus exclusively on the rotating analyzer ellipsometer (RAE) used in our laboratory. An explicit account of the construction and operation of this instrument may be found in Reference 5.

The operating components of the RAE consist of a monochromatic light source, input polarizer, reflecting system, analyzer polarizer rotating on its axis at constant angular velocity, and a photoelectric detector. The input polarizer fixes the incident beam at a specific azimuthal angle, thereby determining the initial relative amplitudes of $\hat{E}_p$ and $\hat{E}_s$.

Since the incident beam is linearly polarized, the relative phase difference of the two components is zero. Upon reflection from the surface, the resulting electric field components have altered relative amplitudes and phase producing, in general, elliptically polarized light. The photodetector experiences a sinusoidal variation in light intensity caused by the reflected beam passing through the rotating analyzer polarizer. Only in the special cases with the incident beam polarized completely in or perpendicular to the plane of incidence, will the reflected field be wholly polarized in or perpendicular to the plane as well.

Under these conditions, the detected intensity will range from zero at extinction to its maximum value as the analyzer rotates. This condition is used in calibrating the instrument in order to accurately determine the polarization axes of the two polarizers as well as system phase shifts and attenuation factors induced by the photoelectric detection electronics. In general, the detected intensity will consist of both...
a dc level and an ac modulation. A complete derivation of calibration and ellipsometric equations for this system are found in Reference 8.

The detected intensity, $I$, can be described as a Fourier series with a singular angular component

$$I = I_0 (1 + \alpha \cos(\Delta - A_0) + \beta \sin(\Delta - A_0)). \quad (A-9)$$

The angle $A_0$ is the azimuthal angle corresponding to the plane of incidence with respect to the angular coordinate system on the analyzer and $\Delta$ is the azimuthal angle at a given time in the same coordinates. Similarly, $P_0$ and $P$ represent the orientation of the input polarizer.

By making intensity measurements at fixed positions around the analyzer axis, we can determine the Fourier coefficients

$$\alpha + i\beta = \sum_\theta I(\theta) e^{i\theta} / \sum_\theta I(\theta) \quad (A-10a)$$

and define

$$Q = \frac{1}{2} \tan^{-1}(\beta/\alpha) \quad (A-10b)$$

$$\zeta = (1 - \zeta)^{1/2}/(1 + \zeta) \quad (A-10c)$$

$$\zeta = (\alpha^2 + \beta^2)^{1/2}. \quad (A-10d)$$

From these quantities the ellipsometric angles can be determined

$$\rho = \tan\psi e^{i\Delta} = \frac{\cot(Q - A_0) - i\alpha}{\tan(P - P_0)}/[1 + i\alpha\cot(Q - A_0)]. \quad (A-11)$$

These expressions are for a perfect system and require modification for real measuring systems caused by component imperfections and the effects of photoelectric detection electronics.
C. Spectroscopy of Adsorbates

As a result of Equation (A-6), the refractive index of a dielectric substrate is uniquely determined by $\Delta$ and $\psi$, provided the refractive index of the ambient is known. For the measurements made with our instrument the ambient is vacuum, and $n_0 = 1.000$, simplifying the system considerably. When considering the ambient-overlayer-substrate problem, we are always able to determine the substrate refractive index before adsorbing the overlayer, thus reducing the problem only to the thickness of the overlayer and the complex refractive index $\tilde{n}_1$. Herein lies a serious problem, as we are able to measure only two quantities, $\Delta$ and $\psi$, yet have three unknowns. The following sections describe methods used to overcome this problem for three distinct adsorbate systems.

1. Nonabsorbing Overlayers at a Single Wavelength

The simplest case is that of a nonabsorbing condensed layer on a substrate whose refractive index is known at a single wavelength. In principle, this problem can now be solved since we have reduced the number of unknowns to two, $n_1$ and $d$. However, experience has shown that real systems require a more general approach due to imperfections and experimental error. We have adapted the method of Malin and Vedam \textsuperscript{10} for these systems.

Beginning with Equation (A-8), we find the thickness of the overlayer to appear only in an exponential factor which we define as

$$\tilde{n} \equiv e^{-i\Delta Z}.$$  \hspace{1cm} (A-12)

Algebraic rearrangement of (A-8) yields an equation quadratic in $\tilde{n}$ which can be solved in terms of the optical constants of the system and the measured value of $\tilde{\beta}$. The value of $\tilde{n}$ may be used to determine the value of $d$ for a given set of optical constants as
For a general set of optical constants, $\tilde{d}$ is seen to be a complex number. In order to be physically meaningful, $d$ must be a real number. Thus, the condition $\text{Im}(\tilde{d}) = 0$ provides a method for determining allowed optical constants of the overlayer.

In order to determine a self-consistent set of values for $\tilde{n}_1$ and $d$, the ellipsometric angles must be determined at a number of film thicknesses. By assuming $\tilde{n}_1$ to be independent of thickness, the following procedure is used to determine $\tilde{n}_1$ and $d$:

1) Establish a grid of $n_1$ and $k_1$ values considered physically acceptable as solutions for $\tilde{n}_1$. Calculate $\tilde{d}$ from the known system parameters $\phi$, $\lambda$, $\tilde{n}_2$, and measured $\tilde{\rho}$ at a given $n_1$ while varying $k_1$. By monitoring $\text{Im}(\tilde{d})$, a change in sign indicates a zero and the corresponding $k_1$ value is interpolated from the $\text{Im}(\tilde{d})$ values at the two $k_1$ values bounding the zero. This point is plotted on the grid. Sweep through the entire range of $n_1$ values in a similar way.

2) Since the equations are quadratic in $\tilde{n}$, repeat 1) for the other root.

3) Perform 1) and 2) for a second value of $\tilde{\rho}$ at a different film thickness.

4) At the intersections of the two curves, we have $\tilde{n}_1$ values for different thicknesses which are physically allowed and consistent for both measured
5)'s. Using the thicknesses, determine a calculated \( \rho \) to compare with the measured \( \tilde{\rho} \).

5) The values of \( \tilde{n}_1 \) and \( d \) which minimize the error between experimental and calculated \( \tilde{\rho} \) is taken as correct. These are typically unambiguous choices.

The application of this method is demonstrated for an argon layer on a Ag(lll) surface at \( \lambda = 3000 \) Å. As can be seen in Figure 32, the family of curves intersects consistently near \( \tilde{n}_1 = 1.2 - 0.036i \). Also note the small absorptive part. This is likely due to imperfections in the layer or surface which lead to preferential scattering of one polarization component of the electric field. This may also account for the small real part of \( \tilde{n}_1 \) which is expected from other measurements to lie between 1.27 and 1.30. If a simpler procedure had been used requiring \( k_1 \) to be identically zero, either very large errors between the measured and calculated \( \rho \) values or thicknesses inconsistent with the deposition rates result. Table Al shows the differences between calculated and measured \( \tilde{\rho} \) values as error = \(? Re(\rho_{cal} - \rho_{measured})| + |Im(\rho_{cal} - \rho_{measured})|\)

2. Absorbing Condensed Layers

The experimental procedure required to obtain ordered layers of condensed adsorbates at low temperature precludes the fairly rigorous methods of the previous section. A different approach must be used which relies on the relative thinness (\( d \ll \lambda \)) of the adsorbed layer. In each case, the data consist of pairs of \( \Delta, \psi \) points for the clean substrate and adsorbate covered substrate at the same wavelength. The spectrum is collected by stepping the monochromator at fixed intervals before collecting each point. All spectral scans are run so that at least \( 100 \) Å is scanned at wavelengths longer than the origin of any overlayer.
Figure 32. The curves 1-7 are the values of $\tilde{\mathbf{R}}_1 = n_1 - ik_1$, which give a real thickness for an argon layer being deposited on a silver substrate with $\lambda = 3000$ Å. The thickest layer is curve 1 and the thinnest is curve 7. The intersection is seen to be in the vicinity of $\tilde{\mathbf{R}}_1 = 1.2 - 0.036i$. This, then is the only value which is consistent throughout the range of thicknesses examined and is taken as the correct value.
Table A1

The calculated thicknesses of an argon layer condensed on a Ag(111) surface at 20 K

<table>
<thead>
<tr>
<th>Curve</th>
<th>$\Delta$</th>
<th>$\psi$</th>
<th>d(A)</th>
<th>Error</th>
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<td>17.633</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
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<td>88.0</td>
<td>4.29 x 10^{-4}</td>
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<tr>
<td>5</td>
<td>114.131</td>
<td>20.270</td>
<td>137</td>
<td>4.22 x 10^{-4}</td>
</tr>
<tr>
<td>4</td>
<td>110.451</td>
<td>21.464</td>
<td>187</td>
<td>5.14 x 10^{-4}</td>
</tr>
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<td>105.669</td>
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<td>1.50 x 10^{-3}</td>
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<tr>
<td>2</td>
<td>104.358</td>
<td>25.329</td>
<td>323</td>
<td>2.10 x 10^{-3}</td>
</tr>
<tr>
<td>1</td>
<td>103.140</td>
<td>28.871</td>
<td>420</td>
<td>1.94 x 10^{-3}</td>
</tr>
</tbody>
</table>

These values were determined with $\phi = 60.37^\circ$, $\lambda = 3000$ Å and $\tilde{\eta}_2 = 2.089 - 1.002i$. The value of the argon refractive index, taken from Figure 32 was $1.20 - 0.036i$. 
electronic transitions. In this region, we expect $k_\perp \rightarrow 0$ which is used in the determination of the overlayer spectrum.

As demonstrated by Aspnes, when $d/\lambda \ll 1$, the exponential factor in (A-8) can be linearized, and approximations to $\delta \Delta = \Delta - \bar{\Delta}$ and $\delta \psi = \psi - \bar{\psi}$ (the bar indicates bare substrate) can be made. In this approximation, $\delta \Delta$ is most strongly influenced by $d$ and $n_\perp$ while $\delta \psi$ is most affected by $k_\perp$. Figure 33a and b shows the $\delta \Delta$ and $\delta \psi$ for an annealed layer of pyrazine on Ni(111). The simple difference $\delta \psi$ clearly shows the absorption peaks associated with the $1\pi\pi^*$ and $1\pi\pi^*$ excitations of pyrazine and the anomalous dispersion of $n_\perp$ in $\delta \Delta$. By first examining $\delta \Delta$ and $\delta \psi$, we have a preview of the spectral features which must appear in a suitable analyzed spectrum.

From the linear approximation, it is possible to develop an analytic solution for the value of $\tilde{n}_\perp$ if we guess at a reasonable value of $d$. By starting our data analysis in a spectral range where $k = 0$, we can try a number of $d$'s until the value of $k_\perp$ is minimized. The analytic solution to $\tilde{n}_\perp$ involves a quartic equation with four roots. Two roots can be immediately eliminated as their structure makes $n_\perp$ complex or gives $k_\perp$ nonimaginary components. In selecting between the remaining two, physical intuition must be used. However, the choice is seldom difficult. Also, when the analysis is complete, the wrong choice leads to absorption peaks of negative magnitude.

This roundabout procedure of guessing $d$ to minimize $k_\perp$ is only needed to provide a starting point for analysis. With this trial solution, a value of $\tilde{\rho}$ is calculated and compared with the measured $\tilde{\rho}$. The agreement is seldom within acceptable bounds. A better solution is generated by considering $\tilde{\rho}$ an analytic function of $\tilde{n}_\perp$. Making a linear
Figure 33. This figure shows the relationship of $\delta \Delta$ and $\delta \psi$ to the final absorption coefficient calculated for the absorbing overlayer. Note the obvious difference between $\delta \psi$ and the absorption coefficient calculated for thicknesses which are too thin and too thick. From this comparison, the final thickness is found to be between 70 Å and 100 Å.

a) $\delta \Delta$ between the covered and bare surface.
b) $\delta \psi$ between the covered and bare surface.
c) The calculated absorption coefficient resulting from a guess of $d = 10$ Å.
d) Same as c except the "wrong root" was selected as a starting value for iteration.
e) The calculated absorption coefficient resulting from a guess of $d = 50$ Å.
f) The calculated absorption coefficient resulting from a guess of $d = 80$ Å.
g) The calculated absorption coefficient resulting from a guess of $d = 100$ Å.
h) The calculated absorption coefficient resulting from a guess of $d = 200$ Å.
Calculation of the Overlayer Absorption Coefficient

\( \delta \Delta \)

\( \delta \psi \)
Taylor expansion of \( \tilde{\rho} \) in \( \tilde{n}_1 \), we can slightly vary \( n_1 \) to develop a better solution for \( n_1 \) and \( k_1 \). This procedure is iterated until the error between calculated and measured \( \tilde{\rho} \) is minimized. For each point after the first, the previous solution of \( \tilde{n}_1 \) is used as the starting value for the iteration loop.

Figures 33c-h shows the calculated absorption coefficient for the pyrazine-Ni(III) system at a number of thicknesses which range from too thin to too thick. This serves to underscore the point that the absolute values of \( k_1 \) are not necessarily quantitatively correct, but do reveal the absorptive properties of the overlayer. Further, a good guess for \( d \) is important and an effort to obtain adsorption conditions in order to estimate \( d \) in experiments must be made.

3. Chemisorbed and Reactive Adsorbates

For molecules engaging in chemisorptive bonding or outright reaction with a metal surface, the simplifying assumptions useful in other situations become invalid. The distinction between overlayer and substrate is obscured if not entirely lost by the role of the surface in the bonding. Even if we consider the adsorbed molecules and the outermost layer of substrate atoms the overlayer, electronic interactions in the bonding process affect the states of the substrates. Therefore, in the absence of clear molecular or atomic resonances, any structure in the spectrum of a system is difficult to interpret.

The use of \( \delta_{\Delta} \) and \( \delta_{\Psi} \) is extremely important in the chemisorbed overlayer spectrum as they require no assumptions or calculation. Only the changes occurring upon chemisorption are noted. In order to develop a more accurate representation of the absorption changes upon chemisorption, the procedure in the previous section is employed in finding
an effective $k_1$ for the "overlayer". However, the thicknesses chosen generally reflect the thickness of the chemisorbed layer and the first layer of substrate atoms. The resulting $k_1$ is thus not expected to approach zero at any point in the spectrum. Never-the-less, the structure in the analyzed $k_1$ spectrum is meaningful and does represent absorptive processes produced by chemisorption. In this light, any absorptive transitions in the substrate removed upon chemisorption are expected to appear as negative peaks in $k_1$. 
APPENDIX B

COMPUTER PROGRAMS USED IN ELLIPSOMETRY

The remainder of this appendix provides a description of the computer programs used in collecting and analyzing ellipsometric data. The purpose, operation, and linking routines are included for each program. The programs are often interactive and the instructions supplied or questions asked during the program, should be clear enough for the uninitiated to use the programs with the additional aid of these descriptions. Names listed here are for the source files, executable images are generally followed by the .SAV extension.

IADAC2.MAC

Purpose: This subroutine monitors the Status Register of the Adac Corporation A/D conversion board and reads the data from the DATA register.

Operation: The routine is called as CALL IADAC2(KBUFF). KBUFF is a 72 element, double precision integer array. The routine recognizes data on ADAC channel 0 and reads the DATA register following completion of the A/D conversion. The 72 data points are counted and the routine returns to the calling program.

CAL.FOR

Purpose: Determine P₀, Al+AF, and ETA in order to calibrate the ellipsometer prior to a spectroscopic run.

Operation: A starting position and rotation direction of the input polarizer must be set manually with the rotation stage controller. By calling IADAC2, the I(θ) is collected for 200 revolutions. The Fourier A and B coefficients are calculated and the residual,
\[ R = 1 - A^2 + B^2 \] is determined. After stepping to the final \( P \) position, \( R \) is fit to a parabola to determine the calibration parameters. A data file, DX:CALIBP.ARM, is created and the calibration values stored. It is customary to repeat calibration cycles until \( P1 \) is as close to zero as possible since the program steps the input polarizer to 1000 steps with the ADAC 14 bit before exiting.

Linking Routines: IADAC2, PARFIT

SCAN.FOR

Purpose: Determine \( \Delta \) and \( \psi \) over a specified range of wavelengths.

Operation: The calibration parameters are read from the file DX:CALIBP.ARM. The program then requests a number of input parameters:

1) the data storage file name; 2) the angle of incidence; 3) the starting wavelength; 4) number of points to be collected; 5) number of averaging cycles; 6) number of \( A \) between data points. The number of \( A \) between points is dependent upon the specific stepping motor-monochromator combination used. The program presently operates with 1 \( A = 1 \) step. The data is collected from IADAC2 and \( \Delta \) and \( \psi \) are calculated. For display on the terminal, \( \Delta \) and \( \psi \) are converted to degrees and \( \varepsilon', \varepsilon'', n, k \) are calculated assuming formulas for a single interface. Only \( \Delta \) and \( \psi \) are stored on diskette in radians. After each point, the stepping motor steps to a new wavelength and a new \( \Delta \) and \( \psi \) pair is collected. The final scan wavelength is entered after the final point.

The data file is unformatted with the number of records = number of points+2 and record length=4 words. The first two records contain control information: 1) angle of incidence, number of data points; 2) starting wavelength, final wavelength. The remaining records contain \( \Delta, \psi \) pairs.
Linking Routines: IADAC2, PULSE

SCRIBE.FOR

Purpose: Plot $\Delta, \psi, \varepsilon', \varepsilon'', n, k, -\text{Im}(1/\varepsilon)$ as a function of wavelength for a data file created by SCAN.

Operation: Upon entering the desired file name, the first two records are read. Once the number of data points is known, the file is re-defined the appropriate length and the $\Delta, \psi$ pairs are read into memory. The wavelength at each value is also determined and stored. The values of $\Delta, \psi, \varepsilon', \varepsilon'', n, k, -\text{Im}(1/\varepsilon)$ can be plotted as a function of wavelength. The plotting routines of P. Cornelius, contained in PACLIB, are used in plotting the data.

Linking Routines: PACLIB, TCSLIB

NOTE: All plotting routines using the PACLIB library must be linked with TCSLIB following PACLIB in the linking sequence!

For the calculation of overlayer spectroscopic values, two data files are required, the bare and adsorbate covered surface files. The analysis takes place with sequential use of COLLECT, ZIPPER, ZAP.

COLLECT.INV (The executable image is COLLECT.NEW)

Purpose: Create a working data file with the control information and $\Delta, \psi, \bar{\Delta}, \bar{\psi}$ values.

Operation: The user supplies a bare surface file name. The control information and $\bar{\Delta}, \bar{\psi}$ values are stored. A new data file, DX1:WORK.DAT is created with number of seconds=number of points+1 and record size=8 words. The user supplies the covered surface file name. After the control information is written onto the first record, values of $\bar{\Delta}, \bar{\psi}, \Delta, \psi$ are written into the remaining records with the
last data points collected written first, thus inverting the spectral sequence. For noninverting collection use COLLECT.SAV from COLLECT.FOR.

ZIPPER.FOR

Purpose: Calculate \( \bar{n} = n - ik \) for the overlayer.

Operation: The principles of this program are given in Section C.2. The control information is read from the first record and the file is redefined the appropriate length. The first \( \Delta, \psi, \Delta, \psi \) values, along with a guess at \( d \) provide starting values for the iteration. As each point is calculated, the values of \( n, k, \) and \( \lambda \) are written over the \( \Delta, \psi \) and \( \Delta \) on DX1:WORK.DAT. If no agreement is found after 100 iteration loops, an error message is printed and no \( n, k \) values are stored—this is a failed analysis.

Linking Routines: POLRT, BENNY

ZAP.FOR

Purpose: Plot \( k \) and \( n \) as a function of wavelength from the result of ZIPPER.

Operation: Again, control information is read first from DX1:WORK.DAT followed by a redefining of the file length. The values \( n, k, \) and \( \lambda \) are read into arrays. Again, plotting is done with PACLIB routines. Capability for a smoothing routine is included.

Linking Routines: PACLIB, TCSLIB

CHANGE.FOR

Purpose: Plot \( \delta \Delta \) and \( \delta \psi \) for two data files created by SCAN.

Operation: The covered file name is supplied and the control values and the \( \Delta, \psi \) values are stored. The bare file name is entered and the values of \( \delta \Delta \) and \( \delta \psi \) are calculated and replace \( \Delta, \psi \) in the storage
array. These are then plotted as a function of wavelength by PACLIB routines.

Linking Routines: PACLIB, TCSLIB

NANDK.FOR

Purpose: Calculate a self-consistent set of n, k and d values for an arbitrary overlayer at a single wavelength.

Operation: The principles of this program are outlined in Section C.1. The user supplies a set of $\Delta, \psi$ values at two different layer thicknesses as well as the angle of incidence and substrate optical constants. A grid of n and k values is established. For n,k pairs giving $\text{Im}(d) = 0$, the point is plotted directly onto the grid during the program. For the first $\Delta, \psi$ pair, the program plots a point, \textquotedblleft .\textquotedblright, and an \textquotedblleft x\textquotedblright for the second pair. Once complete, the same routine is repeated for the second root of the quadratic. Intersections are read directly from the graph and thicknesses can be calculated. A thickness for each root, as well as the magnitudes of $\text{Im}(d)$ and difference between calculated and measured $\delta$ values are displayed.

Linking Routines: BENNY, TCSLIB

Examples of these computer programs in use are given below. The sequence followed is that used in actually performing a spectroscopic ellipsometric scan. A brief statement describing what is taking place is provided before each program. The user specified inputs required to operate these programs are underlined, all other output is under computer control. Following the working examples, the source listings of each of these programs is given.
THIS IS AN OPERATING EXAMPLE OF THE PROGRAMS USED IN ELLIPSOMETRY

CALIBRATE THE ELLIPSOMETER

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<td>0.027089</td>
<td>0.716335</td>
<td>0.331221</td>
<td>0.380191</td>
</tr>
<tr>
<td>P1 17)</td>
<td>0.034097</td>
<td>0.717154</td>
<td>0.316742</td>
<td>0.385647</td>
</tr>
<tr>
<td>P1 18)</td>
<td>0.040724</td>
<td>0.720121</td>
<td>0.298763</td>
<td>0.391808</td>
</tr>
<tr>
<td>P1 19)</td>
<td>0.046542</td>
<td>0.722809</td>
<td>0.281794</td>
<td>0.397138</td>
</tr>
<tr>
<td>P1 20)</td>
<td>0.052360</td>
<td>0.725027</td>
<td>0.266227</td>
<td>0.405477</td>
</tr>
<tr>
<td>P1 21)</td>
<td>0.058178</td>
<td>0.727479</td>
<td>0.250909</td>
<td>0.413845</td>
</tr>
</tbody>
</table>

11 RESIDUALS
ETA= 1.262046  P1= 0.006023  GOODNESS OF FIT= 0.000552
A1: AF= 0.256079  GOODNESS OF FIT= 0.000539

TYPE 1 TO CONTINUE

STOP

AFTER THE FIRST CALIBRATION CYCLE, THE INPUT POLARIZER WAS REJECTED AT PLUS 10 STEPS AS INDICATED BY THE VALUE OF P1. WHEN EXITING THE PROGRAM, THE INPUT POLARIZER IS ROTATED TO 1000 STEPS FOR SCANNING.

SCAN THE ELLIPSOMETER
**RU DXI:SCAN**

**INPUT THE DATA FILE NAME** INCLUDE DXI)...#DXI:NAME

CALCULATE AND STORE EFFECTIVE OPT. CONSTANTS

ENTER ANGLE OF INCIDENCE IN DEGREES, F8.3

50.83

ENTER LAMBDA IN ANGSTROMS: F9.2

5000.

ENTER NUMBER OF DATA POINTS TAKEN: I4

11

ENTER NUMBER OF CYCLES PER DATA POINT: I4

200

ENTER NUMBER OF ANGSTROMS BETWEEN DATA POINTS: F10.2

10.

<table>
<thead>
<tr>
<th>DATA</th>
<th>LAMBDA</th>
<th>DELTA</th>
<th>PHI</th>
<th>E1</th>
<th>E2</th>
<th>INDEX</th>
<th>ABSORP</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>3000.00</td>
<td>124.685</td>
<td>17.448</td>
<td>2.688</td>
<td>3.445</td>
<td>1.878</td>
<td>0.917</td>
</tr>
<tr>
<td>2.</td>
<td>2970.00</td>
<td>124.062</td>
<td>17.846</td>
<td>2.668</td>
<td>3.506</td>
<td>1.881</td>
<td>0.932</td>
</tr>
<tr>
<td>3.</td>
<td>2900.00</td>
<td>125.054</td>
<td>10.330</td>
<td>2.607</td>
<td>3.634</td>
<td>1.891</td>
<td>0.966</td>
</tr>
<tr>
<td>4.</td>
<td>2870.00</td>
<td>125.324</td>
<td>19.854</td>
<td>2.537</td>
<td>3.782</td>
<td>1.893</td>
<td>1.064</td>
</tr>
<tr>
<td>5.</td>
<td>2860.00</td>
<td>125.472</td>
<td>17.373</td>
<td>2.451</td>
<td>3.922</td>
<td>1.893</td>
<td>1.043</td>
</tr>
<tr>
<td>6.</td>
<td>2950.00</td>
<td>125.596</td>
<td>17.024</td>
<td>2.363</td>
<td>4.056</td>
<td>1.878</td>
<td>1.080</td>
</tr>
<tr>
<td>7.</td>
<td>2940.00</td>
<td>125.740</td>
<td>20.731</td>
<td>2.274</td>
<td>4.164</td>
<td>1.879</td>
<td>1.109</td>
</tr>
<tr>
<td>8.</td>
<td>2930.00</td>
<td>125.944</td>
<td>20.639</td>
<td>2.125</td>
<td>4.272</td>
<td>1.874</td>
<td>1.140</td>
</tr>
<tr>
<td>9.</td>
<td>2920.00</td>
<td>125.671</td>
<td>20.731</td>
<td>2.134</td>
<td>4.360</td>
<td>1.869</td>
<td>1.166</td>
</tr>
<tr>
<td>10.</td>
<td>2910.00</td>
<td>125.757</td>
<td>21.411</td>
<td>2.035</td>
<td>4.473</td>
<td>1.864</td>
<td>1.200</td>
</tr>
<tr>
<td>11.</td>
<td>2900.00</td>
<td>125.977</td>
<td>21.819</td>
<td>1.927</td>
<td>4.665</td>
<td>1.855</td>
<td>1.231</td>
</tr>
</tbody>
</table>

ENTER THE FINAL WAVELENGTH: F6.1...2900.

STOP --

*TO VIEW THE RESULT, THE DATA MAY BE PLotted*

**RU DXI:SCRIBE**

ENTER THE DATA FILENAME...#DXI:NAME

*Plotting is controlled by input integers:*

- PHI=1
- DELTA=2
- REAL EPSILON=3
- IMAGINARY EPSILON=4
- REFRACTIVE INDEX=5
- ABSORPTION COEFFICIENT=6
- LOSSFUNCTION=7
- ENTER NUMBER OF TICK SUBDIVISIONS ON X AND Y...S:5
- ENTER THE CONTROL INTEGER...1
- TYPE 1 TO ENTER HARD COPY MODE, OR -1 TO LEAVE
- FOR NEW LIMITS, ENTER 1...
- TO CONTINUE PLOTTING, ENTER 1....

STOP --

*AFTER A BARE AND COVERED SURFACE HAS BEEN SCANNED*

THE OPTICAL CONSTANTS OF THE OVERLAYER CAN BE CALCULATED
TO SEE CHANGES IN DELTA AND PSI BETWEEN TWO FILES, USE THE CHANGE PROGRAM

RU DX2:CHANGE
ENTER THE COVERED METAL FILE NAME...#DX1:PZN4
ENTER BARE METAL FILE NAME...#DX1:AGN4
ENTER THE X AND Y TICK SUBDIVISIONS...-5.5

THE PROGRAM FIRST PLOTS THE CHANGE IN DELTA

TYPE 1 TO ENTER HARD COPY MODE, OR -1 TO LEAVE
ENTER A 1 TO SET NEW LIMITS...0
ENTER 1 TO PLOT DELTA(PSI)...0

STOP --

BEFORE CALCULATING THE OVERLAYER OPTICAL CONSTANTS A WORK FILE USING THE PROGRAM COLLECT MUST BE CREATED

RU DX2:COLLECT
THIS PROGRAM REQUIRES AVAILABLE SPACE ON
DX1: EQUAL TO THE SIZE OF THE INPUT FILES
ENTER THE BARE METAL FILE NAME...#DX1:AGN4
ENTER THE COVERED METAL FILE NAME...#DX1:PZN4

STOP --

RU DX2:ZIPPER
ENTER OVERLAYER THICKNESS, F10.3...80.
TYPE 1 FOR PRINTOUT...0.
JK= 1  N1= 1.024  -0.101
JK= 2  N1= 1.085  -0.664
SELECT THE VALUE OF N1 ABOUT WHICH TO
ITERATE BY PICKING JK.  JK= 1

STOP --

RU DX2:ZAP
ENTER THE TICK SUBDIVISIONS ALONG X,Y...5,5

THE PROGRAM FIRST PLOTS THE ABSORPTION COEFFICIENT

TYPE 1 TO ENTER HARD COPY MODE, OR -1 TO LEAVE
ENTER: 0 TO EXIT, 1 FOR ABSORPTION COEFFICIENT
2 FOR REFRACTIVE INDEX, 3 TO SMOOTH PRESENT CURVE,
4 TO SET NEW LIMITS...0

STOP --
PROGRAM CAL
PROGRAM TO FIND CALIBRATION PARAMETERS
FOR ROTATING ANALYSER ELLIPSOMETER

INTEGER KBUFF
DIMENSION KBUFF(72),P(200),R(200),T(200),A(200)

100 FORMAT(' CALIBRATION PROGRAM')
10 WRITE(5,100)
200 FORMAT(' ENTER INITIAL P IN STEPS, IS')
N=1
READ(5,210) IP
210 FORMAT(I4)
WRITE(5,220)
220 FORMAT(' ENTER FINAL P IN STEPS, IS')
READ(5,230) IF
230 FORMAT(' ENTER INTERVAL IN STEPS, IS')
READ(5,210) INT
IFP=INT(IP-IFP)/INT+1
IFN=200 IFP+IS+16
WRITE(5,240)
240 FORMAT(' BUFFER SPACE EXCEEDED')
GO TO 10
15 WRITE(5,241)
241 FORMAT(' TYPE 1 TO OUTPUT CALIBRATION POINTS')
READ(5,242) KEY
242 FORMAT(I4)

INITIALIZE BUFFERS AND REGISTERS

MSGN=-1
17 IF(IP .GT. IFP) MSGN=1
N=0
C=0
A=0
B=0

THE ROUTINE IADAC3 COLLECTS THE DATA AND STORES THE POINTS
IN KBUFF(J). BEFORE EACH POINT, KBUFF IS INITIALIZED
AFTER EACH POINT, THE 5 BIT OF THE ADAC STATUS REGISTER
IS RESET TO ZERO. NCDF IS THE NUMBER OF CYCLES PER DATA
POINT AND IS ALSO COUNTED IN IADAC3

NCDF=200
CALL IADAC3(KBUFF,NCDF)

CALCULATE A AND B AT THIS POL. ANGLE

S=0
C=0

DO 40 J=1,72
ANG=3.14159*FLOAT(J-1)/36.
S=S+AJFLT(KBUFF(J))*SIN(2.*ANG)
C=C+AJFLT(KBUFF(J))*COS(2.*ANG)
40 D=0

41 CALL IPOKE('176770','400~2>
DO 42 M2=1,150
42 CONTINUE
N=1
DO 69 Z JM=1,500
ZZZZZ=ATAN2(2.3,3.5)
43 CONTINUE
C CURVE FITTING

43 CONTINUE
SIGMA1=FLOAT(N)
SIGMA2=FLOAT(N)
CALL PARFIT(N,P,R,C1,C2,SIGMA1)
P1=-C1/(2.*C2)
ETA=SQRT(1./((1.-C0+((C1**2)/(4.*C2)))))
CALL PARFIT(N,P,R,C1,C2,SIGMA2)
AF=C0+((C1*P1)+(C2*(P1**2)))
WRITE(5,150) N
150 FORMAT(1X,13,' RESIDUALS')
WRITE(5,160) ETA,P1,SIGMA1
160 FORMAT(1X,13,' ETA=','F9.6','P1=','F10.6','SIGMA1=','F10.6')
WRITE(5,170) ETA,P1,SIGMA2
170 FORMAT(1X,13,' ETA=','F9.6','P1=','F10.6','SIGMA2=','F10.6')
55 WRITE(S,500)
500 FORMAT('STEP 1 TO CONTINUE')
READ(S,510) IFIN
510 FORMAT(1I1)
IF(IFIN) 61,61,10
61 CALL ASSIGN('DX1:CALIBF.ARM',14)
DEFINE FILE 1 (1X6.U.IIBM)
WRITE('1'1ETA,P1,AF1)
DO 76 M=1,1000-IFP
CALL IFONE('176770','40032')
DO 77 M2=1,150
77 CONTINUE
CALL IFONE('176770','32')
DO 70 M3=1,50
70 CONTINUE
STOP
END

PROGRAM SCAN
C PROGRAM TO CALCULATE AND STORE DELTA, PSI
C AND EFFECTIVE (NQ-PHASE) OPTICAL CONSTANTS FOR
C SPECTROSCOPIC ELLIPSOMETRY. PROGRAM STEPS WAVELENGTH BETWEEN
C DATA POINTS BY PULSING STEPPING MOTOR ATTACHED TO SOURCE
C MONOCHROMATOR.

INTEGER*4 KBUFF
REAL LAMBDA,LAMDF
COMPLEX RHO, EPS, OCNK
INTEGER JOLT,JILT
DIMENSION KBUFF(72)
CALL IFONE('176770','32')
CALL ASSIGN('DX1:CALIBF.ARM',14)
DEFINE FILE 1 (1X6.U.IIBM)
READ('1'1ETA,P1,AF1)
CALL CLOSE(1)
WRITE(5,90)
90 FORMAT('CALCULATE AND STORE EFFECTIVE OPT. CONSTANTS')
WRITE(S,100)
100 FORMAT('ENTER ANGLE OF INCIDENCE IN DEGREES,F8.3')
READ(S,115) PHID
115 FORMAT(F8.3)
PHI=PHID3.14159/180.
WRITE(S,120)
120 FORMAT('ENTER LAMBD A IN ANGSTROMS, F9.2')
READ(S,120) LAMBDA
125 FORMAT(F9.2)
SWL=LAMDBA
P=5B17759
WRITE(S,161)
161 FORMAT(' ENTER NUMBER OF DATA POINTS TAKEN, I4')
READ(S,162) NDPT
162 FORMAT(I4)
WRITE(S,162) NDPT
163 FORMAT(' ENTER NUMBER OF CYCLES PER DATA POINT, I4')
READ(S,162) NCDP

STEPPING MOTOR ON PRESENT APPARATUS HAS 1 STEP PER ANGSTROM.

WRITE(5,100)
100 FORMAT('ENTER NUMBER OF ANGSTROMS BETWEEN DATA POINTS, F10.2')
READ(5,190) ANGST
190 FORMAT(F10.2)
ANGST=IFIX(ANGST)

THE DATA STORED ON THE DISK FROM THIS EXPERIMENT IS ONLY PSI AND DELTA. THE REMAINING QUANTITIES OF INTEREST ARE EASILY RECOVERED FROM THESE VALUES. THEREFORE, THE OPTICAL CONSTANTS ARE PRINTED OUT SOLELY AS A CONVENIENCE AT RUN TIME.

WRITE(5,200)
200 FORMAT('DATA LAMBDA DELTA PSI
CEI CD INDEX ABSORPTION')
DO 10 I=1,NPT

CLEAR BUFFERS
DO 20 J=1,72
20 CALL JICVT(J,KBUFF(J))
CALL IPOKE('176770',72)
KNUMY=IPEEK('176772')

THE MACRO ROUTINE IADAC3 COLLECTS THE DATA FROM THE ADAC BOARD. IT KEEPS TRACK OF THE NUMBER OF THE NUMBER OF ENTRIES UPON RETURN, KBUFF IS READY TO BE ANALYSED

DO 30 KM=1,NCDP
30 CONTINUE
CALL IPOKE('176770','32')
S=O
C=O
T=O
DO 40 J=1,72
40 ANC=3.14159*FLOAT(1-J)/36.
S=S+IJFLT(KBUFF(J))*SIN(2.*ANC)
C=C+IJFLT(KBUFF(J))*COS(2.*ANC)
D=D+IJFLT(KBUFF(J))
A=2.*ANC

THE DATA IS STORED USING DIRECT ACCESS UNFORMATED STORAGE INTO THE FILE NAME SPECIFIED BY THE USER. IN ORDER FOR MANIPULATION OF THE DATA TO MAKE SENSE, IT MUST BE NOTED THAT THE ANGLES ARE STORED IN RADIANS AND PRINTED ON THE TERMINAL IN DEGREES.

WRITE(5,I5) ICNT,DELTA,PSI
OCNK=SQRT(OCN)
DELTA=DELTA180./3.14159
PSI=PSI180./3.14159
IF(DELTA.GT.0.)GOTO 79
DELTA=DELTA180.
PSI=PSI
79 ICNT=ICNT-2
WRITE(5,210) ICNT,LAMBDA,DELTA,PSI,EP,OCNK
210 FORMAT('13','/F7.2,'/X,6F9.3')

PULSING SEQUENCE TO STEPPING MOTOR USES SUBROUTINE PULSE IN MACRO LANGUAGE WHICH STEPS MOTOR ONE STEP. FOLLOWING DO LOOP SLOWS STEPPING SPEED TO ALLOW MOTOR TO KEEP UP WITH COMPUTER.
PROGRAM SCHEME
REAL IWL,FWL,LAMBDA(1000)
COMPLEX Z,PHI,EPNS
DIMENSION P(1000),F(1000),B(1000)
LOGICAL# FARRAY(10),GARRAY(10)
CALL IN(700)
CALL PULSE
CALL INIT(400)
CALL PULSE
Z=CMPLX(0.0,1.0)
WRITE(*,100)
100 FORMAT('ENTER THE DATA FILENAME...')
CALL ASSIGN(1,BOZO,-1)
DEFINE FILE L (1002+U,JUBUM)
READ(I11)MM,IPNTS
READ(112)111LW,FWL
DO 75 I=1,IPNTS
11=II2
READ(112)D(I),P(I)
75 LAMBDA(I)=IWL-(I-1)*(IWL-FWL)/(IPNTS-1)
CALL CCOPY((F6.1),FARRAY)
CALL SCOPY((F6.1),GARRAY)
NFORM=1
CALL PRED(6,8)
WRITE(*,170)
170 FORMAT('PLOTTING IS CONTROLLED BY INPUT INTEGERS:/'
$'PSI'=1/'DELTA'=2/'REAL EPSILON=3/'IMAGINARY EPSILON=4/'$'
$'REFRACTIVE INDEX=5/'AEROSORPTION COEFFICIENT=6/'LOSS$'
$'FUNCTION=7/')
WRITE(*,100)
100 FORMAT('ENTER NUMBER OF TICK SUBDIVISIONS ON X AND Y...')
READ(5,181)N1,N2
181 FORMAT(2I2)
WRITE(*,190)
190 FORMAT('ENTER THE CONTROL INTEGER...')
READ(5,200)KEY1
200 FORMAT(I1)
IF(KEY1.EQ.1)GOTO 1
IF(KEY1.EQ.2)GOTO 2
IF(KEY1.EQ.3)GOTO 3
1 DO 80 J=1,IPNTS
80 B(I)=180.0+P(I)*180.0/3.14159
GOTO 900
2 DO 25 I=1,IPNTS
25 I(I)=D(I)*180.0/3.14159
GOTO 900
3 DO 35 J=1,IPNTS
RHO=CMPLX(SIN(P(I))/COS(P(I)))*CMPLX(Z*P(I))
EPS=(1.0-RHO)/(1.0+2*RHO)*SIN(PHI)**2/COS(PHI)**2*EPS
OCNK=CMPLX(SQR(T EPS))
IF(KEY1.EQ.3)B(I)=REAL(OCNK)
IF(KEY1.EQ.4)B(I)=AIMAG(OCNK)
IF(KEY1.EQ.5)B(I)=REAL(OCNK)
IF(KEY1.EQ.6)B(I)=AIMAG(OCNK)
IF(KEY1.EQ.7)B(I)=ABS(1.0/EPS)
35 CONTINUE
900 CALL NEWPAG
CALL GRAP(P(IPNTS,LAMBDA,B,-1,NFORM)
CALL HICK(N1,N2,FARRAY,GARRAY,6,8)
CALL HOMC
CALL HARD(HARD)
IF(HARD.EQ.0)GOTO 900
NFORM=1
WRITE(*,205)
205 FORMAT('FOR NEW LIMITS, ENTER 1...')
READ(5,200)KEY
IF(KEY.NE.15)GOTO 905
CALL WINADVJ(X1,X2,Y1,Y2)
FORM=0
GOTO 900

705 WRITE(5,210)
210 FORMAT(2I0,CONTINUE PLOTTING, ENTER 1...)
READ(S,200)KEY
IF(KEY.EQ.1)GOTO 185
STOP
END

PROGRAM COLLECT
DIMENSION P1(1000),D1(1000),P2(1000),D2(1000)
WRITE(5,190)
100 FORMAT('THIS PROGRAM REQUIRES AVAILABLE SPACE ON'/
       '0. DX1: EQUAL TO THE SIZE OF THE INPUT FILES')
WRITE(5,110)
110 FORMAT('ENTER THE BARE METAL FILE NAME...')
CALL ASSIGN(1,'BARE1','RDO')
DEFINE FILE 1 (1002,4,U,IBUM)
READ(1)X1,IPNTS
DO 10 I=1,IPNTS
   11 I=I+2
   READ(1)II,II,III,IV(I,1)
20 CONTINUE
READ(1)II,II,III,IV(I,1)
CALL CLOSE(1)
WRITE(5,140)
40 FORMAT('ENTER THE COVERED METAL FILE NAME...')
CALL ASSIGN(1,'COVER1','RDO')
DEFINE FILE 1 (1002,4,U,IBUM)
DO 30 I=1,IPNTS
   31 I=I+2
   READ(1)II,II,III,IV(I,1),II,IV(I,1)
30 CONTINUE
END

PROGRAM ZIPPER
THIS PROGRAM CALCULATES THE OPTICAL CONSTANTS OF A /
SURFACE OVERLAYER FROM THE PSI AND DELTA VALUES FOR /
THE BARE AND COVERED SURFACE FOR A GIVEN OVERLAYER /
THICKNESS, USING THE LINEAR APPROXIMATION FORMULAS /
FROM THE AACHESON REVIEW (3.31) SPECT. ELLIPSOIDCY OF /
 SOLIDS IN 'OPTICAL PROPERTIES OF SOLIDS: NEW /
 DEVELOPMENT', TO PROVIDE STARTING VALUES FOR AN /
ITERATIVE SOLUTION.
DIMENSION A(5),B(5),R(4),R1(4),X(2)*Z(2)
REAL#N 12
REAL LAMDA=4.085
COMPLEX RAD=0.0001*
COSIG,F,C,N1,Z1,Y2,INT(2),J,Y,
INT(I,XX(4),XZ
LOGICAL#I,IP00(10),IP00(10)
CALL ASSIGN(1,'ZIPPER',B,'RDO')
DEFINE FILE 1 (18+U,IBUM)
READ(1)P1,P2,P3,P4,P5,P6,P7,P8,P9,P10,P11,
CALL CLOSE(1)
CALL ASSIGN(1,'ZIPPER',B)
WRITE(5,120)
120 FORMAT('ENTER OVERLAYER THICKNESS, R10.3...')
READ(S,130)D
130 FORMAT(2F10.3)
WRITE(S,130)
130 FORMAT(2F10.3)
100 FORMAT('TYPE 1 FOR PRINTOUT...')
READ(S,190)KEY
190 FORMAT(II)
J=CMPLX(10.0,1.0)
THE FOLLOWING CODES USE THE INVERTED APPROXIMATION FORMULAS TO CALCULATE N AND K FOR THE OVERLAYER. THE RESULTING QUARTIC EQUATION IS SOLVED USING THE SCIENTIFIC SUBROUTINE POLRT AND NON-MATH SOLUTIONS ARE DISCARDED.

\[ P = (\sqrt{\text{RH}} - \text{RHO})/\text{RH} \]
\[ C = 4.31145 + \text{EPS} - \text{RHO} \]
\[ \text{EPS} = \sin\phi_1^2 \times \cos(\phi_1) \]
\[ \text{RHO} = \text{RHO} \times \text{EPS} \]
\[ \text{RHO} = \text{RHO} \times \text{RH} - \text{RHO} \]
\[ \text{RHO} = \text{RHO} \]
\[ \text{RHO} = \text{RHO} \]

CALL POLRT(A, B, C, D, E)

CONTINUE IF ((N1 < 0) OR (N2 < 0))

N1 = \[ \text{N1} \times \text{RHO} \]
N2 = \[ \text{N2} \times \text{RHO} \]

DO 10 J = 1, 4

If \( \text{ABS}(\text{RHO}) < 0.01 \), go to 10

END
DN=ABCD(AIMAG(RHO:1))-AIMAG(INT(1)))
IF(AN .LT. 0.000001 AND. BN .LT. 0.000001) GO TO 199
1 N1=N1+0.0001
Y=(RHOT Nag INT(1))*0.0001/(INT(2)-INT(1))
N1=N1+Y-0.0001
AN=AB2(AIMAG(RHOT)-REAL(INT(1)))
BN=AB2(AIMAG(RHOT)-AIMAG(INT(1)))
IF(AN .GT. 0.0001 OR. BN .GT. 0.0001) GO TO 5
199 IF(AN .LT. 0.00001) WRITE(5,200) LAMBDAN1
200 FORMAT(1X*10.1SX,'N1='2F10.3)
WRITE(1,III)N1,LAMBDA
100 IF(AN .LT. 100) GO TO 910
10 CONTINUE
STOP
END

PROGRAM ZAP
LOGICAL FARRAY(10),GARRAY(10)
REAL LAMBDAA(100)
DIMENSION B(1000),C(8)
COMPLEX N1(1000)
INTEGER TKX,TRY
CALL ASSIGN1,'DXIW0RN',8;
DEFINE FILE 1 (1.4U.IIBM)
READ(1)*12,1IDF
IFNTS=IDF
CALL CLOSE(1)
N=IDF+1
CALL ASSIGN1,'DXIW0RN',0;
DEFINE FILE 1 (N.5U.IIBM)
GO 77 IFNITS
II=II+1
READ(1)*12,N1(I),LAMDBA(I)
77 CONTINUE
WRITE(5,100)
100 FORMAT('ENTER THE TICK SUBDIVISIONS ALONG X,Y...')
READ(5,110)TKX,TRY
110 FORMAT(22I3)
IFORM=1
CALL SCOPY('F.G.1',FARRAY)
CALL SCOPY('F.G.3',GARRAY)
CALL INITI(4Q)
CALL TREF('6,6')
DO 715 I=1,IFNITS
715 D(I)=-(AIMAG(N1(I)))
72 D(I)-AIMAG(N1(I)))
CALL NEWFAG
CALL GRAPH(IFNTS,LAMDAA.B+1,IFORM)
CALL HICK(TRY,TKX,FARRAY,GARRAY,6,6)
CALL HARD(IHARD)
IF(1HARD.LT.0)GOTO 920
WRITE(5,300)
300 FORMAT('ENTER: 0 FOR NEW LIMITS; 1 FOR ABSORPTION/"
'+'COEFFICIENT;'/"62 FOR REFRACTIVE INDEX; 3 TO/"
'C SMOOTH PRESENT CURVE; 4 TO EXIT...')
IFORM=1
READ(5,310)KEY
310 FORMAT(1)
IF(KEY.0T.0)GOTO 321
CALL WINAJ(X1,X2,Y1,Y2)
NFORM=0
GOTO 920
321 IF(KEY.0T.01)GOTO 323
DO 322 I=1,IFNITS
322 B(I)=-(AIMAG(N1(I)))
GOTO 920
323 IF(KEY.0T.2)GOTO 325
DO 324 I=1,IFNITS
324 B(I)=REAL(N1(I))
GOTO 920
325 IF(KEY.0T.3)GOTO 500
C(3)=(-3.2*(B(1)+B(5))+12.2*(B(2)+B(4))+17.2*D(3))/25.
C(1)=B(1)
C(2)=B(2)
C(4)=(-2.2*(B(1)+B(7))+3.2*(B(2)+B(6))+6.2*(B(3)+B(5)))
C(7)=-B(4)/21.
C(5)=(-21.2*(B(1)+B(7))+14.2*(B(2)+B(5))+39.2*(B(3)+B(7)))
C(6)=(-62.2*(B(2)+B(11))+9.2*(B(2)+B(10)))+44.2*(B(3)+B(9))
C(8)=B(4)*(D(10)+D(4)*(D(5)+D(7)))+0.2*B(6))/420.
C(13)=(-9.2*(B(1)+B(13))+9.2*(B(2)+B(11)))+16.2*(B(3)+B(10))
C(21)=B(5)/(24.*B(6)+B(8)))+25.*B(7)/143.
PROGRAM CHANGE
LOGICAL* FARRAY(10), GARRAY(10)
REAL LAMBDA(1000), DELTA(1000), PSI(1000)
CALL INIT(480)
WRITE(5,100)
100 FORMAT('ENTER THE COVERED METAL FILENAME...
CALL ASSIGN(1,BOZO,-1)
DEFINE FILE 1 (1002,4,U,IBM)
READ(1,1)Z, IPNTS
READ(1,2)SWL,FWL
DO 900 I=1,IPNTS
II=I+2
READ(1,2)DELTA(I), PSI(I)
900 LAMBDA(I)=SWL-(Z-1).*(SWL-FWL)/(IPNTS-1)
CALL CLOSE(1)
WRITE(5,110)
110 FORMAT('ENTER THE BARE METAL FILENAME...
CALL ASSIGN(1,BOZO,-1)
JJ=IPNTS+2
DEFINE FILE 1 (JJ,4,U,IBM)
DO 910 I=1,IPNTS
II=I+2
READ(1,2)X, Y
DELTA(I)=X-DELTA(I)/180.*3.14159
910 PSI(I)=Y-PSI(I)/180.*3.14159
70 WRITE(5,120)
120 FORMAT('ENTER 1 TO PLOT CHANGE IN DELTA, 2 FOR CHANGE IN PSI...
CALL SCOPY('F5.0'), FARRAY)
CALL SCOPY('F6.3'), GARRAY)
CALL PREP(S,6)
IF(KEY.EQ.1)GOTO 90
IF(KEY.EQ.2)GOTO 95
GOTO 99
90 CALL NEWPAG
CALL GRAPH(IPNTS, LAMBDA, DELTA, -1, 1)
CALL HICK(10, 10, FARRAY, GARRAY, S, 6)
CALL HICK(Y, HARD)
IF(IHARD.EQ.1)GOTO 90
GOTO 70
95 CALL NEWPAG
CALL GRAPH(IPNTS, LAMBDA, PSI, -1, 1)
CALL HICK(10, 10, FARRAY, GARRAY, S, 6)
CALL HICK(Y, HARD)
IF(IHARD.EQ.0)GOTO 95
GOTO 70
99 STOP
END
PROGRAM NANDK
LOGICAL F ARRAY(10), G ARRAY(10)
COMPLEX J, RHO(2), N1, N2
REAL DEL(2), PSI(2), NIMIN, NIMAX, INCN1, LAMBDA, PHI, IMD
KIMIN, KIMAX, INCK1
CALL SCOPY('F6.3', F ARRAY)
CALL SCOPY('F6.3', G ARRAY)
J = CMPLX(0.0, 1.0)
WRITE(5, 100)
100 FORMAT('ENTER THE KNOWN SUBSTRATE REFRACTIVE INDEX (N-K)...')
READ(5, 105) N2
105 FORMAT(2F20.5) WRITE(5, 110)
110 FORMAT('ENTER THE WAVELENGTH IN ANGSTROMS AND THE ANGLE OF INCIDENCE IN DEGREES...')
READ(5, 115) LAMBDA, PHI
99 CALL INIT(480)
120 FORMAT(4F20.5)
Z = 3.14159 / 180.
PHI = PHI * Z
C PHI = COS(PHI)
S2 PHI = (SIN(PHI))**2
THE CALCULATION OF THE N AND K GRID NOW TAKES PLACE WITH THE STORAGE OF THE K VALUES WHICH MAKE THE THICKNESS PURELY A REAL QUANTITY

705 WRITE(5, 130)
130 FORMAT('ENTER THE RANGE OF REAL(N1) VALUES AS')
135 FORMAT(3F20.10)
READ(5, 135) N1MIN, N1MAX, INCN1
140 FORMAT('ENTER THE RANGE OF ABS(K1) VALUES AS')
145 FORMAT(3F20.10)
READ(5, 145) K1MIN, K1MAX, INCK1
NMAX = INT((NIMAX - NIMIN)/INCN1) + 1
KMAX = INT((KIMAX - KIMIN)/INCK1) + 1
XMIN = N1MIN
XMAX = N1MAX
YMIN = K1MIN
YMAX = K1MAX
CALL NEWPAG
CALL PREP(4, 6)
CALL DWINO(XMIN, XMAX, YMIN, YMAX)
CALL SEET((10, 10, F ARRAY, G ARRAY, 6, 6)
CALL MVABS(XMIN, YMIN)
CALL DRABS(XMIN, YMAX)
CALL DRABS(XMAX, YMIN)
CALL DRABS(XMAX, YMAX)
DEL(1) = DEL(1) * Z
PSI(1) = PSI(1) * Z
DEL(2) = DEL(2) * Z
PSI(2) = PSI(2) * Z
DO 78 M = 1, 2
RHO(M) = SIN(PSI(M)) * (COS(DEL(M)) + J * SIN(DEL(M))) / COS(PSI(M))
SIGN = 1.
74 DO 900 I = 1, NMAX
Q = FLOAT(I - 1) * INCN1 + NMIN
DO 910 L = 1, 2
CH1 = 0
CH2 = 0
900 DO 920 K = 1, KMAX
R = FLOAT(K - 1) * INCK1 - KMIN
N1 = CMPLX(1, R)
910 IF(N1.EQ.0.0) GOTO 920
920 CALL ETA(N2, N1, LAMBDA, CPHI, S2 PHI, RHO(L), IMD, D, SIGN)
CH2 = CH1
CH1 = IMD
IF(K.EQ.1) GOTO 920
IF(CH1 .GT. 0.0 AND CH2 .GT. 0.0) GOTO 920
IF(CH1 .LT. 0.0 AND CH2 .LT. 0.0) GOTO 920
ZM = CMPLX(CH2 - CH1) / (FLOAT(INCK1))
IF(L.EQ.2)GOTO 79
CALL POINTA(Y,0)
CALL RECOVR
CALL HOME
GOTO 920
79 CALL MOVEA(Q,Y)
CALL DRAWREL(-3,-3)
CALL DRAWREL(-3,-3)
CALL DRAWREL(6,6)
CALL DRAWREL(-3,-3)
CALL DRAWREL(6,6)
CALL DRAWREL(-3,-3)
CALL POINTA(0,Y)
CALL RECOVR
CALL HOME
GOTO 920
920 CONTINUE
910 CONTINUE
900 CONTINUE
IF(SIGN.EQ.-1.)GOTO 75
SIGN=1.
GOTO 74
75 WRITE(S,170)
170 FORMAT('TO CALCULATE A THICKNESS, ENTER A 1...')
READ(S,175)ID
175 FORMAT(I1)
IF(ID.NE.1)GOTO 61
50 WRITE(S,180)
180 FORMAT('ENTER THE BEST N1 (N1+K)...')
READ(S,190)
190 FORMAT('FOR DELTA-PSI NUMBER 1 OR 2...')
READ(S,175)ID
SIGN=1.
GOTO 60
60 CALL ETA(N2+N1,LAMBDA,CPHI,S2PHI,RHO(ID),IMD,D,SIGN)
D=D
CALL BENVY(1.0-N1,N2,LAMBDA,PHI,D,INT)
ERR=ABS(REAL(1.0)-REAL(RHO(ID)))+ABS(AIMAG(1.0)-AIMAG(RHO(ID))
WRITE(S,220)INT,IMD,ERR
220 FORMAT('COMPLEX THICKNESS=2E15.3 ERROR=E12.4')
IF(SIGN.EQ.-1.)GOTO 61
SIGN=1.
GOTO 74
61 WRITE(S,230)
230 FORMAT('YOUR OPTIONS: 1 FOR A NEW N1--/')
2 FOR A NEW DELTA-PSI SET...')
READ(S,175)KEY
IF(KEY.EQ.1)GOTO 77
777
goto 77
STOP
END
SUBROUTINE ETA(N2+N1,LAMBDA,CPHI,S2PHI,RHO,ID,IMD,D,SIGN)
COMPLEX R1S,R2S,R1P,R2P,RHO,ZETA,A,B,C
N1,N2,N12,N22,
X1,X2,N12CF,
REAL LAMBDA,IMD
N1=214N2=22
N12CF=N12CPHI
X2=CSQRT(N22-S2PHI)
X1=CSQRT(N12-S2PHI)
R1S=(CPHI-X1)/(CPHI+X1)
R2S=(X1-X2)/(X1+X2)
R1P=(N12CF-X1)/(N12CF+X1)
R2P=(N12CF+X1-N12CF)/N12CF+X1-N12CF
A=(RHDORR1P-K1S)*R2P*K2S
B=(RHDORR2S-R2P)+(RHDORR2P-R2S)*R1P*R1S
C=A*RHDORR1P*R1S
ZETA=-5*BSIGN*CSQRT(B**2-4.*A*C)/A
IMD=REAL(CLOG(ZETA)/X1)
D=LAMBDA*AIMAG(CLOG(ZETA))/(12.566371*X1)
RETURN
END
REFERENCES


62. The complete proceedings of three international conferences on ellipsometry may be found in: a) Surface Science 96; b) Surface Science 113.


64. A particularly complete discussion may be found in J. A. Stratton, *Electromagnetic Theory*, McGraw-Hill, New York, 1941.

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