**ELECTRONIC ENERGY TRANSFER FROM MOLECULES TO METAL AND
SEMICONDUCTOR SURFACES, AND CHEMISORPTION-INDUCED CHANGES
IN OPTICAL RESPONSE OF THE NICKEL (111) SURFACE**

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Ph.D. Thesis

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Electronic Energy Transfer
from Molecules to Metal and Semiconductor Surfaces,
and Chemisorption-induced Changes in Optical Response
of the Nickel (111) Surface

Paul Michael Whitmore

Abstract

The evolution of molecular excited states near solid surfaces is investigated. The mechanisms through which energy is transferred to the surface are described within a classical image dipole picture of the interaction. More sophisticated models for the dielectric response of the solid surface add important new decay channels for the energy dissipation. The predictions and applicability of three of these refined theories are discussed.

These theories were tested by measuring the distance dependence of the energy transfer from an electronically excited molecule to two metal surfaces, Ni(111) and Ag(111). In the first experiment, the total phosphorescence quantum yield of pyrazine on Ni(111) was measured as a function of thickness of an argon spacer layer. The observed distance dependence is found to be in agreement with the behavior predicted by the simple image dipole model down to 7 Å separation. The second experiment measured the energy transfer rate directly by following the pyrazine phosphorescence lifetime as a function of distance to a Ag(111) surface. Quantitative agreement is found between the experimental lifetimes and those predicted by the simple classical theory down to 10 Å separation. Within this model, the dominant modes for energy disposal in these two metals are compared. It is shown that surface plasmons act as important acceptors in the energy transfer to silver in the near-UV

region.

The first attempt to extend this picture of molecule-surface energy transfer to semiconductors is reported. The phosphorescence lifetime of pyrazine was measured as a function of ammonia spacer thickness on an undoped GaAs(110) surface. The observed distance dependence of the energy transfer agrees with the prediction of the classical theory to within experimental error, although the experimental results may indicate slightly faster energy transfer rates than the theoretical predictions. According to this simple model, the energy transfer to intrinsic semiconductors occurs through the bound electron dielectric response. Thus, electronic excitation energy is transferred to bulk polariton modes and interband electronic excitations of the solid, if any.

The implications of molecule-surface energy transfer on the spectroscopy of adsorbed species are discussed, with particular emphasis on recent ELS work of Demuth and Avouris, who studied molecules chemisorbed on silver surfaces. The impact of these energy transfer studies on the optical spectroscopy of electronic excited states of molecules chemisorbed on Ni(111) is also described, and becomes an important consideration in analyzing the results of the last chapter of this dissertation.

In the final investigation of the electronic excited states of molecule-metal systems, the adsorption of a series of molecules on a Ni(111) surface was studied by UV-visible spectroscopic ellipsometry. The changes in the optical response of the surface were analyzed within a simple dielectric model for the reflection. Chemisorption of molecules on the Ni(111) surface produces a peak in the overlayer

optical response at 4.2eV. This absorption is attributed to an enhancement of bulk interband excitations resulting from perturbations of the metal orbitals upon chemisorption. These perturbations are described in terms of the metal band structure and the interaction of the molecules with specific metal surface states, leading to chemical bond formation.

Charles B. Harris 10/8/82.

to my family

TABLE OF CONTENTS

I. OVERVIEW.....	1
II. ENERGY TRANSFER FROM ELECTRONICALLY EXCITED MOLECULES TO METAL AND SEMICONDUCTOR SURFACES	
A. Introduction.....	6
B. Theory	
1. Chance, Prock, and Silbey (CPS) Theory.....	11
2. Refinements of CPS Theory.....	25
C. Electronic Energy Transfer to Metals: $^3_{n\pi}$ pyrazine/ Ni(111) and Ag(111)	
1. General Considerations.....	43
2. Experimental.....	50
3. Results	
a. Phosphorescence excitation and emission spectra of pyrazine at an argon/vacuum interface at 20K.....	58
b. Relative phosphorescence intensity of pyrazine above Ni(111).....	64
c. Phosphorescence lifetime of pyrazine above Ag(111).....	69
4. Discussion.....	76
5. Conclusions.....	90
D. Energy Transfer to Semiconductors: $^3_{n\pi}$ pyrazine/ GaAs(110)	
1. General Considerations.....	91
2. Experimental.....	110
3. Results.....	111
4. Discussion.....	117
5. Conclusions.....	120
E. Implications of Energy Transfer.....	121

TABLE OF CONTENTS (continued)

III. CHEMISORPTION-INDUCED CHANGES IN THE OPTICAL RESPONSE OF THE NICKEL(111) SURFACE	
A. Introduction.....	125
B. Experimental	
1. Apparatus.....	127
2. Data acquisition and reduction.....	133
C. Results	
1. Pyrazine, pyridine, and naphthalene on Ni(111).....	142
2. CO, O ₂ , and ethanol on Ni(111).....	143
D. Discussion.....	164
E. Conclusion.....	184
ACKNOWLEDGEMENTS.....	186
REFERENCES.....	188

Chapter I

OVERVIEW

The wide range of physical and chemical processes which occur at the gas (or liquid)/solid interface forms an area of science which can excite and challenge those who seek to understand it. These surface phenomena surround us, whether in the form of a rusting automobile chassis or ion transport across cellular membranes, and yet the activity of atoms and molecules in the two-dimensional world of a surface is foreign to most people whose only experience is in three dimensions. As with the exploration of any uncharted world, this unfamiliarity can be a double-edged sword: although substantial experience must be acquired in order to understand and predict the behavior of molecules at surfaces, the very novelty of the effects can instill a sense of wonder and discovery in those studying them even after many years of struggle.

The presence of a surface between a bulk solid and the gas (or liquid) surrounding it leads to significant changes in the behavior of both the bulk material and of the adjacent molecules. The interruption of the bulk electronic structure by the surface creates surface electronic states, either delocalized electron densities in the band picture or localized "dangling bonds" in the valence description. These surface states become the source of the high physical and chemical activity of the solid surface, such as its adhesive or catalytic properties. In very special circumstances, even novel physical effects which are observed in the solid state, such as nonlinear optical phenomena, are greatly enhanced at the surface of some materials.

Just as for bulk properties, the behavior of isolated atoms and molecules is altered drastically when a solid surface is present. Not only can molecule-surface reactions occur, but molecule-molecule reactions can be accelerated by the lowering of potential barriers or by the caging of reactants on the surface. As with the solid materials, some physical properties of molecules, such as their polarizability, can be enhanced when placed on certain metal surfaces.

One of the ultimate goals of scientific research in this area is to describe these fundamental molecule-surface interactions. This very description of interfacial behavior, though, lies on the interface between two rather disparate disciplines, the worlds of molecular and solid state physics, and as such presents a formidable challenge to both theoreticians and experimentalists. The theoretical frameworks of these two disciplines are each inadequate to properly deal with the coupling between a molecule and a solid, and it is the theoretician's task to choose a judicious combination of the molecular and solid state viewpoints. Experimentalists studying surfaces also face problems which are not often encountered in gas-phase or solid state investigations. For example, optical spectroscopies, which form the mainstay of analytical work on gas, liquid, or solid state systems, become very difficult and complicated experiments when applied to surface species. The low number densities of molecules on a surface require a highly surface-sensitive technique for their study, but the reflection properties of many materials are such that this sensitivity is very low. Such new experimental obstacles are by no means insurmountable-- in fact this dissertation deals with optical studies of molecules at surfaces-- but the introduction of a surface forces the adjustment and

adaptation of experimental methods.

Many investigations of adsorbed molecules seek to measure or calculate the static properties of the molecule-surface system, such as the equilibrium geometries of adsorbate and surface atoms, and the energies of occupied electronic orbitals. These studies certainly add to the understanding of the chemical changes that take place upon adsorption, the nature of the bonding species in their ground states.

However, much can be learned about dynamical processes on surfaces by studying nonequilibrium situations, specifically, excited states of the molecule-surface system. Knowledge of these excited states can not only add insight into the equilibrium chemical interactions between adsorbate and surface, but also the evolution of these adsorbed species, their desorption/adsorption kinetics, their surface diffusion, their inter- and intramolecular chemical reactions, are all intimately linked to these excited electronic and vibrational states.

The work which is described in this dissertation is such a study of the excited states of the molecule-surface system, and is divided into two parts. Chapter II is devoted to the more fundamental of the investigations, in which the evolution of a molecular excited state on a surface is explored. In particular, the details of the electromagnetic coupling between the molecule and the surface, and the nature and relative importance of the various energy dissipation channels (the acceptor modes in the solid) are modeled theoretically. These predictions are compared to experimental measurements of energy transfer from a molecule ($^3\pi^*$ pyrazine) to metal (Ni and Ag) and semiconductor (GaAs) surfaces. In the nickel experiment, the pyrazine was separated from the surface with an inert argon spacing layer, and the relative

phosphorescence yield was measured as a function of this spacer thickness. Similarly, energy transfer from pyrazine to silver was monitored by measuring the pyrazine phosphorescence lifetime directly at varying spacer thicknesses. An identical phosphorescence lifetime experiment was performed for pyrazine on an ammonia spacer on GaAs. These results are evaluated in terms of a classical image dipole model, and the mechanisms for the energy transfer in each system are discussed and compared. The implications of these energy transfer studies for other surface phenomena are outlined, and the particular application to surface optical spectroscopies lays the foundation for the experiments described in the subsequent chapter.

The second half of this work, described in Chapter III, illustrates the use of an optical technique, spectroscopic ellipsometry, to measure the absorption spectrum of the electronic states of a molecule-metal system. This technique measures the change of polarization state of light upon reflection from a surface, and, when analysed within a simple model, the optical dielectric properties of the reflecting system can be deduced. Originally designed to investigate the electronic absorption spectrum of adsorbed molecules, the transitions of the molecular adsorbates on the nickel (111) surface only appear in the spectrum of weakly interacting (i.e., physisorbed and condensed) layers. Upon chemisorption, the optical dielectric properties of the surface are found to change in a way that reflects the perturbations of the metal electronic structure during the bond formation. The analysis of these perturbations in terms of the nickel bulk and surface electronic states is facilitated by additional insight gained from photoemission experiments and band structure calculations. This particular

combination of experimental and theoretical probes promises to be a powerful tool in the investigation of chemisorption phenomena.

Chapter II

ENERGY TRANSFER FROM ELECTRONICALLY EXCITED MOLECULES TO METAL AND SEMICONDUCTOR SURFACES

A. Introduction

A proper description of the ways in which internal excitation energy is transferred between molecules and surfaces through electromagnetic field interactions, particularly in the short distance regime, is crucial to the understanding of a wide variety of molecule-surface interactions. For energy transfer processes which occur over very short distances (on the order of atomic dimensions), a complete description necessitates a quantum mechanical approach. However, because of the large number of atoms which must be included to properly treat the surface response, this method is extremely cumbersome and not generally useful. It has been demonstrated though that an approximate, classical treatment can qualitatively describe the energy transfer over a large range of molecule-surface separations. The simplicity of this classical model and the physical insight it provides into the mechanisms of the energy transfer made it attractive for use in many classes of problems. Thus it becomes very important to determine in each case the distance regime over which this simple model can be used to describe the energy transfer.

As a prelude to the discussion of molecule-surface interactions, let us consider the case of the interaction of an electronically excited molecule with another nearby molecule, a problem treated first by

Forster,¹ and later quantified by Dexter.² In this picture, the excited molecule sets up around it an oscillating electromagnetic field which, to lowest order, is a dipole field associated with a harmonically bound charge oscillating with the frequency of the electronic excitation. This electromagnetic field mediates the interaction between the electrons of the excited and ground state molecules, leading to a finite probability for the excitation to be transferred from one molecule to another. (It should be emphasized that the dipole field is very long range and leads to the energy transfer at a distance. The interaction of two molecules at very short distances, where the electron densities actually overlap, is not treated in this description and is similarly ignored in the extension to molecule-surface energy transfer. Such considerations become most germane to treatments of chemisorption which will be discussed in Chapter III of this work.) This interaction of two dipoles at a distance is the same electric field mediated interaction which leads to the van der Waals attraction between (induced) dipoles. The distance dependence of the dipole near field is $1/r^3$, so the interaction energy is proportional to $1/r^6$, and the Forster transfer rate also goes like $1/r^6$. Another noteworthy feature of this process is the so-called Forster transfer radius, or "critical interaction length"; that is, the distance at which the probability for energy transfer is $1/2$ (Crudely speaking, then, molecules which are closer than this critical distance probably will transfer the excitation, molecules farther away probably will not.) The Forster transfer radius in molecular systems is typically on the order of tens of Angstroms (25-75Å). The corresponding transfer radius and distance dependence of the energy transfer rate between molecules and surfaces (which can be viewed

as energy transfer from one dipole to a distribution of dipoles in the surface) demonstrate that this process is much longer range than Forster-Dexter transfer-- the rate of molecule-surface energy transfer depends on the inverse cube of the separation, and the "critical interaction length" is on the order of hundreds of Angstroms.

The extension of the treatment of this electromagnetic interaction to the case of an oscillating dipole over a surface must include some important new considerations. First of all, the extent of the plane surface makes the spatial variation of the dipole field much more important. The interaction of the dipole with delocalized states at the surface brings a new restriction to bear on the energy transfer, namely the matching of wavevector (momentum) components parallel to the surface. The rate of energy transfer to the various surface modes will be determined by the strength of the coupling between these modes and the dipole field components which can match both momentum parallel to the surface and energy.

There are several mechanisms through which an electronically excited molecule can be influenced by the presence of a solid surface. For molecules located far from the surface (on the order of the dipole emission wavelength), the excited molecule will be perturbed by the radiation field reflected from the interface. This "image effect", or interference effect, causes the excited state lifetime to decrease, if the reflected field is out of phase with the oscillating dipole, or increase, if it is in phase. This oscillation of the excited state lifetime with varying distance to the surface has been observed by Drexhage and quantitatively described in terms of this interference phenomenon.³ The dissipation of excitation energy, however, takes place

through internal losses in the radiating dipole and is dependent only on the reflection properties of the surface. This effect does not involve direct transfer of energy from the molecule to the solid, and thus it is not of primary interest in this discussion.

At smaller molecule-surface separations additional interactions become important. The excited dipole can transfer its energy to collective excitations of the solid, such as surface plasmons, or to electron-hole pair excitations, which can act as energy acceptors provided that energy and momentum can both be conserved. The excited molecule can also begin to transfer energy through the near field components of its dipole field to the free carriers of the crystal, which, through scattering from phonons, lattice imperfections (including the surface), or interband transitions, can dissipate the energy into the bulk. This "lossy surface 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 surfaces is the classical, macroscopic approach developed by Chance, Prock, and Silbey (CPS).⁴ This treatment explores both the role of the dissipative modes in the solid and the dependence of the energy transfer rate on the molecule-surface separation. The model treats the excited molecule as a point dipole located above a solid of local dielectric constant $\tilde{\epsilon}(\omega)$, which is separated from a dielectric ambient at an infinitely sharp boundary. Within this framework, the total decay rate of the excited molecule can be separated into radiative and nonradiative components, the latter representing the rate of energy transfer into the surface.

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.⁵⁻⁸ All have found at least qualitative agreement with the predictions of the CPS theory, even for molecule-surface separations as small as 7Å. (An experiment by Rossetti and Brus which had indicated a deviation from the CPS behavior has since been repeated by those workers under better vacuum conditions and been found to be in accord with those predictions down to 35Å of the surface⁸).

Despite the apparent success of this classical model, one expects that at some point a more exact treatment must be required to quantitatively describe the energy transfer process. The delocalized nature of the electronic states of the solid, the correlation of those electrons (including screening effects and collective excitations), and the possibility of high wavevector excitations in the electron gas (specifically, electron-hole pair production), can only be properly accounted for by including in the theory nonlocal dielectric behavior and the finite spatial extent of the molecular dipole. Further, a correct description of the surface region must reflect the smoothly varying electron density across the surface. Recently, theories have been developed incorporating some of these details, and deviations from the CPS behavior are predicted at distances below 7Å.⁹⁻¹⁴

The purpose of this research effort has been twofold. First, experiments were designed and performed to test the applicability of the CPS model in the description of the energy transfer from an electronically excited molecule to a variety of surfaces in the very short separation regime. Then, after the results of the experiments had justified the use of the CPS model for these systems, calculations were performed to analyze the physical mechanisms for the energy transfer and

the efficiency of the various pathways for energy degradation.

In this chapter, I describe first the CPS model and the development of the equations used in the analysis of the experiments. A brief discussion of the approximations inherent in this approach is included, as well as a qualitative evaluation of some of these approximations. The next section is devoted to the studies of energy transfer to metals: specifically, the distance dependence, mechanisms, and efficiencies, of the energy transfer from $^3n\pi^*$ pyrazine (1,4-diazabenzene) to nickel(111) and to silver(111) are measured and compared. Following this is a preliminary report of the extension of this work to semiconductor surfaces. The results of an experimental study of the energy transfer from $^3n\pi^*$ pyrazine to gallium arsenide (110) are analyzed, and the efficiencies of the energy transfer to silicon, germanium, and gallium arsenide are compared within the CPS model. Finally, the implications of these relaxation channels for excited adsorbed molecules on surface spectroscopies are discussed, with particular emphasis on surface optical absorption measurements, which are the subject of Chapter III.

B. Theory

1. Chance, Prock, and Silbey (CPS) Theory

Attention was first drawn to the effect of a nearby surface on molecular fluorescence by the work of Kuhn and co-workers, who used a fatty acid spacer technique to study the distance dependence of energy transfer.¹⁵ Kuhn's theoretical treatment of this problem was limited to

weakly absorbing surfaces, and successfully explained only the oscillations of the fluorescence lifetime with distance to the surface. In an extension of this description, Chance, Prock, and Silbey developed a formalism, exact within classical electromagnetic theory, which is applicable to strongly absorbing solids as well, and consequently the observed fluorescence quenching at short distances was quite accurately modeled.⁴

Following Chance, et al., an oscillating point dipole near a surface will be driven by its own electromagnetic field which has been reflected from the interface. The equation of motion for the dipole is

$$\ddot{\mu} + b_0 \dot{\mu} + \omega^2 \mu = (e^2/m) E_R \quad (1)$$

where ω is the natural oscillation frequency of the undamped dipole, b_0 is the decay rate for the dipole in the absence of the reflecting surface, m is the effective mass of the dipole, and E_R is the reflected electric field at the dipole position. The reflected field will clearly oscillate with the same frequency and lifetime as the driven dipole. If one then assumes a functional form

$$\mu = \mu_0 e^{-i(\omega+\Delta\omega)t} e^{-bt/2} \quad (2)$$

$$E_R = E_0 e^{-i(\omega+\Delta\omega)t} e^{-bt/2} \quad (3)$$

and substitutes into the equation of motion, the frequency shift $\Delta\omega$ and new decay rate b can be calculated. The frequency shift

$$\Delta\omega = b^2/8\omega + (e^2/2\mu_0\omega) \operatorname{Re}(E_0) \quad (4)$$

is found to be very small for the cases of interest here (although they are predicted to be quite large for short-lived excited states very near the surface--see Section E of this Chapter). The decay rate for the dipole becomes

$$b = b_0 + (e^2/\mu_0\omega) \operatorname{Im}(E_0) \quad (5)$$

or, in terms of the classical expression for the quantum yield ($q=b_r/b$), the normalized decay rate is

$$\hat{b} = b/b_0 = 1 + (3q\tilde{\epsilon}_1/2\mu_0k_1^3) \operatorname{Im}(E_0) \quad (6)$$

where $\tilde{\epsilon}_1$ is the dielectric constant of the medium in which the dipole is imbedded, and k_1 is the propagation constant in that medium ($k_1 = \omega\tilde{\epsilon}_1^{1/2}/c$). The calculation of the decay rate of the dipole in the presence of the surface thus becomes a problem of determining the reflected field at the dipole.

The calculation of the electric field at a dipole near an interface has been treated by a number of authors.^{1,11-19} Chance, et al., followed the derivation of Sommerfeld.¹⁶ The details of the calculation depend upon the geometry of the dielectric interfaces and dipole orientation, and thus only the general procedure for the solution will be described here. Sommerfeld's treatment calculates the electric field from the Hertz vectors associated with the dipole (i.e., the electromagnetic vector potentials). In order to describe the spatial

variation of the field, the dipole field is Fourier analyzed in terms of different wavevector components. In other words, the Hertz vectors are constructed as a superposition of eigenfunctions (with associated eigenvalues u , the normalized wavevector) which will reproduce the spatial variation of the dipole field. Once this superposition has been created, the effect of the reflecting surface on the dipole field can be included by matching the Maxwell boundary conditions for each Fourier (wavevector) component at the interface.

It is at this point in the evaluation of the reflection of the electric field at the surface that the classical theory employs some key simplifying approximations. All the interfaces are assumed to be smooth (no roughness) and represent sharp discontinuities in the bulk dielectric functions. These dielectric responses are taken to be local; that is, the response of charges at a particular point depends only upon the external field applied at that point. Thus the dielectric constant is not a function of separation (wavevector), but only of frequency, $\tilde{\epsilon}(\omega)$. The only energy dissipation channels are those incorporated in the imaginary part of $\tilde{\epsilon}(\omega)$, and, since this value is usually taken from optical measurements, only those mechanisms which are represented in (or can be inferred from) optical studies can be included. In the next section the limitations of these approximations will be explored, and it will be shown how the removal of some of these approximations can incorporate new channels for the energy transfer into the theory.

The general result for the reflected electric field at the dipole is an integral over all wavevector components of the form

$$E_0 = \int_0^\infty [BR^p + CR^s] e^{-2l_1 \hat{d}_1} \frac{u^3}{l_1} du \quad (7)$$

where R^P, R^S are the complex Fresnel reflection coefficients for waves polarized parallel to and perpendicular to the plane of incidence, $\hat{d}_1$ is the (normalized) distance from the dipole to the surface, and $l_1 = -i(1-u^2)^{1/2}$. The coefficients B and C are determined from the geometry and dipole orientation in a specific case.²⁰ The term in brackets represents the amplitude change (contained in the appropriate reflection coefficients) and the exponential is the phase change for each wavevector component of the electric field after reflection back to the dipole. Inserting this form for the reflected field into the expression for the decay rate yields

$$\hat{b} = 1 + Aq \operatorname{Im} \int_0^\infty [BR^P + CR^S] e^{-2l_1 \hat{d}_1} \frac{u^3}{l_1} du \quad (8)$$

where q is the free molecule quantum yield, and the coefficients A, B, and C for various special cases are tabulated in Table 1.

The second term of Eq.(8) thus describes the modification of the total decay rate of an excited dipole due to its proximity to a surface. The imaginary part of the integrand describes the coupling of the various wavevector components of the dipole field to the decay channels available. As noted previously, the integral over all wavevector components in Eq.(8) can be separated into contributions corresponding to the different decay mechanisms. A rigorous separation into radiative and nonradiative decay can be achieved, but it can also easily be rationalized in terms of a physical picture of the interaction of the dipole field with a surface. Figure 1(a) shows the radiation field associated with a dipole at one instant during its oscillation.

Table 1

Parameters for Equation (8)

<u>Orientation</u>	<u>A</u>	<u>B</u>	<u>C</u>
z	-3/2	1	0
x, y	3/4	$\frac{1-u^2}{u^2}$	$\frac{1}{u^2}$
Isotropic	1/2	$\frac{1-2u^2}{u^2}$	$\frac{1}{u^2}$

Figure 1. The electric field lines associated with a dipole near a surface at one instant during its oscillation. (a) The surface charge induced by the radiation field of the dipole. The periodic charge density oscillation has wavelengths greater than that of the radiation pattern (i.e., $k < k_{\text{photon}}$). (b) The surface charge induced by near field components of the dipole. Here the wavelengths of the surface dipoles are shorter than that of the radiation field ($k > k_{\text{photon}}$). The surface charge oscillation whose wavelength matches that of the surface plasmon at this energy (λ_{sp}) will propagate away from the dipole (surface plasmon excitation). The other high wavevector field components dissipate energy through coupling to bulk scattering processes (lossy waves).

Radiation Field Pattern

$$\lambda \approx \lambda_p$$

$$k \approx k_0$$

$$u \approx 1$$

$$\lambda > \lambda_p$$

$$k < k_0$$

$$u < 1$$

(a)

XBL 821-5064

(b)

XBL 821-5000

The dipole field induces a surface polarization on the solid, and the dipoles associated with this oscillating surface current set up their own radiation field pattern (not shown on Fig. 1a). The interference of this reflected radiation field with the directly emitted dipole radiation leads to the modulation of the radiative decay rate at large distances, described by Drexhage.³ It is clear from the radiation field pattern in Fig. 1(a) that those surface dipoles with wavelength larger than the dipole emission wavelength (i.e., with wavevector smaller than the photon wavevector) will participate in modifying the decay rate of the dipole through its radiation field. Thus, the integral of Eq.(8) over normalized wavevector $0 < u < 1$ represents this modification of the radiative decay rate of the dipole.

The energy transfer to the solid surface, however, takes place through the "static" and "induction" fields of the dipole. Figure 1(b) shows (on a much smaller scale than Fig. 1a) the near field of a dipole at one instant during its oscillation. The electric field of the dipole again induces a surface charge separation, but here the associated surface dipoles all have wavelengths less than that of the radiation field pattern. Thus, these dipole field components which will dissipate energy into the metal through some loss mechanisms all have wavevectors greater than the photon wavevector. The integral in Eq.(8) from $1 < u < \infty$ represents this total energy transfer rate into the surface. Also shown in Fig. 1(b) is the oscillating surface dipole whose wavevector exactly matches the wavevector of a discrete excitation of the surface at the dipole frequency. Pictured here is the excitation of a surface plasmon, a surface charge oscillation which can propagate far from the dipole position before decaying into bulk excitations. This decay channel is

found to be very important in electronic energy transfer to metals, particularly to silver at visible and near ultraviolet frequencies (see the next section).

This separation of the total decay rate into radiative and nonradiative components has been established rigorously by Chance, Prock, and Silbey, but the breakdown of the energy transfer rate (i.e., the nonradiative contribution) into different physical mechanisms has yet to be realized within this model. Still, an approximate division of the energy transfer rate is possible by following the example of Weber and Eagen,²¹ who associated features of the integrand of Eq.(8) with specific physical transfer mechanisms. This approach requires an insight into and an intuition about the response of a material to an external electromagnetic field, and in this sense the analysis is circular-- only the physics expected will be included. However, this treatment has proven enlightening in demonstrating the relative importance of the various possible decay channels for a specific molecule-surface system.

As an example of this separation of energy transfer mechanisms, Figure 2 shows the wavevector dependence of the integrand of Eq.(8) evaluated for the case of a dipole emitting at 6328Å located at various distances d above a silver surface. The integral of this function from $0 < u < \infty$ is the total decay rate of the excited dipole. This integral can now be divided into various decay channels corresponding to the possible physical mechanisms described qualitatively above. In attempting this separation, one must identify the features of the integrand with one of the possible decay mechanisms. The plot in Fig. 2 shows three distinguishable features of each curve: for $0 < u < 1$ the function

Figure 2. The imaginary part of the integrand of Eq. (8) vs. normalized wavevector u , calculated for a perpendicular dipole emitting at $6328\text{\AA}$ located at various distances above a silver surface with local dielectric response (CPS model). Optical constants for silver at this wavelength were taken from Ref. 34.

XBL 8210-11886

increases smoothly before becoming discontinuous at $u=1$; there is a sharp peak at $u=1$ (in this case at $u=1.3$); and finally, there is a broad peak at large wavevector which grows and shifts to larger u as the dipole-surface separation decreases. In the analysis of Chance, Prock, and Silbey, it was shown that the contribution to the integral from $0 < u < 1$ represented the radiative decay rate, i.e., the rate of decay through photon emission. Thus, the rest of the integral, from $1 < u < \infty$, must represent the rate of energy transfer through all the other possible mechanisms. The occurrence of the sharp peak in the function at the surface plasmon wavevector at this energy ($u=1.3$) allows the identification of this feature with the rate of surface plasmon excitation by the dipole. The remainder of the integral, the contribution to the dipole decay rate through the high wavevector field components, must represent the energy transfer to the solid via the driving of "lossy surface waves". As noted before, in this level of approximation the mechanisms for the dissipation of energy through these "lossy" waves are limited to those which can be included in the local (optical) dielectric constant of the solid. In particular, the dielectric losses in this CPS model are those due to electron scattering mechanisms, mainly scattering from phonons, crystal imperfections, and direct ($k=0$) interband transitions. For the specific case of silver at visible frequencies, there are no direct interband transitions; thus the lossy wave mechanism dissipates the energy through the scattering of the nearly free conduction electrons.

Once the identification of the features of the function with specific physical decay mechanisms has been effected, one can calculate the relative contribution of each mechanism (i.e., the branching ratio

into the possible decay channels) as a function of molecule-surface separation, or energy, or both. This application will be illustrated for the specific comparisons of the systems which were studied experimentally.

2. Refinements of CPS Theory

It will be seen that the experimental results obtained in this study are quantitatively described by the CPS theory; thus, this model seems to include the physics necessary to treat the energy transfer in these molecule-surface systems. However, inherent in this model are limitations which neglect energy transfer processes which must become important for certain systems. These approximations in the CPS theory have been described qualitatively above, and it is appropriate at this point to analyze them in order to predict qualitatively how the removal of these restrictions would affect the theoretical decay rates and, if possible, predict where the more accurate descriptions should become necessary to correctly describe the energy transfer. To this end, the last portion of this Theory section is devoted to a discussion of three important theoretical approaches which relax some of the restrictions of the CPS theory, and thus predict different energy transfer rates for certain molecule-surface systems.

Of the approximations included in the classical theory, the most important is the use of a local dielectric constant to describe the response of the electrons of the solid to external fields. Not only does this simplification preclude an important energy acceptor mode of the solid, viz., the excitation of electron-hole pairs in the conduction

electron gas (a $k \neq 0$ process), but other basic physical interactions, such as electron screening and correlation, are also ignored. (The term "electron-hole pair" in this context refers to the excitation in a free electron gas and should not be confused with the electrons and holes created in interband transitions, which will be discussed in more detail later.) As a result of this unphysical modeling of the electron response, the CPS theory produces a prediction of unphysical behavior. In Fig. 2 the wavevector dependence of the dipole-silver coupling is plotted for several different molecule-surface separations. The broad peak at large wavevector, which is attributed to the dipole decay through "lossy" electron scattering, grows and shifts to higher wavevector at short distances. That is, at short separation the electron gas of the solid responds to the near field of the dipole which varies more and more rapidly as the dipole approaches the surface. In this approximate treatment there is no limit to the spatial variations of the fields which can drive the electrons. Thus, when the dipole is in direct contact with the surface ($d=0$), the energy transfer through these high wavevector lossy waves becomes infinite.

This singularity can be removed with the introduction of a more realistic description of the response of the conduction electron gas. The possibility for electron-hole excitation can be incorporated into the theory by using a nonlocal description for the electron gas response, and this has been a major thrust of the recent refinements of the theory. This modification affects essentially high wavevector loss mechanisms, both by adding new decay channels (electron-hole excitations) and by forbidding others (due to energy and momentum conservation). For this reason, the correction should be most important

to the description of the energy transfer from dipoles very close to the surface, and the effects should also be largest for those surfaces with many possible electron-hole pair excitations (i.e., for nearly free electron materials). The predicted decay rates for these systems would then be slightly faster than the CPS predictions at short distances, except for dipoles right on the surface, where the transfer rate should be finite (in contrast to the infinite rate predicted by CPS at zero separation).

The most straightforward incorporation of nonlocal dielectric behavior into the energy transfer theory has been the work of Ford and Weber (FW).^{9,10} As their model they took a point dipole placed above a solid with a smooth, sharp boundary. The electrons in the solid are taken to be confined to the half-space bounded by an infinite potential barrier. The effect of this potential on the response of the electron gas has been described in detail by Kliever and Fuchs within their specular scattering model.^{22,23} Basically, this approximation reproduces the essential features of the electromagnetic fields calculated by self-consistent methods, such as Feibelman's treatment.²⁴ However, it has recently been shown that electric field singularities which arise in this model are due solely to the discontinuity of the dielectric function at the surface-- thus the optical response in very close proximity to the surface (within a few Å) is not accurately described. This treatment then is only useful for illustrating the gross effects of the nonlocal dielectric behavior of the solid and should not be taken to be a quantitative theory at close distances to the surface.

The important refinement which FW introduced to the CPS model then

is their inclusion of the nonlocal (i.e., wavevector-dependent) dielectric response of the solid. This was effected by using a Lindhard form for the dielectric constant $\tilde{\epsilon}(\omega, k)$, modified to account for the finite relaxation time of the electrons.^{25,26} This dielectric function describes the response of an electron gas to an external potential, including the Coulomb interaction between electrons (and thus, screening effects) in a perturbative manner, and also including the constraints imposed by the Pauli principle (which places limits on the possible electron-hole pair excitations). This Lindhard dielectric function takes the form

$$\epsilon_1(k, \omega) = \epsilon_b(\omega) + \frac{3\omega_p^2 p^2 f_1(z, p)}{(\omega + i\nu)(\omega + i\nu [f_1(z, p)/f_1(z, 0)])} \quad (9)$$

$$\epsilon_t(k, \omega) = \epsilon_b(\omega) - \frac{\omega_p^2 f_t(z, p)}{\omega(\omega + i\nu)} \quad (10)$$

where

$$f_1(z, p) = 1/2 + \frac{1}{8z} \{ [1 - (z-p)^2] \log \frac{z-p+1}{z-p-1} + [1 - (z+p)^2] \log \frac{z+p+1}{z+p-1} \} \quad (11)$$

$$f_t(z, p) = \frac{3}{8} (z^2 + 3p^2 + 1) - \frac{3}{32z} \{ [1 - (z-p)^2]^2 \log \frac{z-p+1}{z-p-1} + [1 - (z+p)^2]^2 \log \frac{z+p+1}{z+p-1} \} \quad (12)$$

Here,

$$z = k/2k_F \quad (13)$$

and

$$p = (\omega + i\nu)/kv_F \quad (14)$$

with k_F the Fermi wavevector, v_F the Fermi velocity, and ν the collision frequency of the conduction electrons. The plasma frequency is $\omega_p = (4\pi n e^2 / m)^{1/2}$ and $\epsilon_b(\omega)$ is the bound electron contribution, which includes such effects as interband absorptions in a phenomenological manner.

These expressions for the dielectric constants are used to calculate the surface impedances for p- and s-polarized incident electromagnetic fields

$$Z^P(u, \omega) = \frac{8i}{\omega} \int_0^\infty dq \frac{1}{k^2} \left(\frac{u^2}{\epsilon_1(k, \omega)} + \frac{q^2}{\epsilon_t(k, \omega) - c^2 k^2 / \omega^2} \right) \quad (15)$$

$$Z^S(u, \omega) = \frac{8i}{\omega} \int_0^\infty dq \frac{1}{\epsilon_t(k, \omega) - c^2 k^2 / \omega^2} \quad (16)$$

where $k^2 = u^2 + q^2$. (That is, u is the normal component of the incident wavevector k parallel to the surface, and q is the component of k normal to the surface. The surface impedances, then, sum the response of the surface to all possible waves with a particular parallel component u .) The surface impedances are related to the amplitude reflection coefficients by

$$r_{12}^s = \frac{(c^2 q_1 / 4\pi\omega) Z^S - 1}{(c^2 q_1 / 4\pi\omega) Z^S + 1} \quad (17)$$

$$r_{12}^p = \frac{1 - (\omega \epsilon_1 / 4\pi q_1) Z^P}{1 + (\omega \epsilon_1 / 4\pi q_1) Z^P} \quad (18)$$

In order to obtain numerical results for a specific material, in this case, silver, the parameters in the Lindhard dielectric must be determined. This is accomplished first by fitting the $q=0$ form of the

dielectric constant to the local (optical) dielectric $\tilde{\epsilon}(\omega)$:

$$\tilde{\epsilon}(\omega, 0) = \epsilon_b(\omega) - \frac{\omega_p^2}{\omega(\omega + i\nu)} \quad (19)$$

For silver in the region 450-700nm, FW were able to fit the measured optical data using $\omega_p = 9.33\text{eV}$, $\nu = 0.058\text{eV}$, and $\epsilon_b = 3.6$. The remaining parameters were determined using one electron per atom and the free electron mass, yielding $k_F = (3n)^{1/3} = 1.2 \times 10^8 \text{ cm}^{-1}$, and $v_F = \hbar k_F / 2m = 1.4 \times 10^8 \text{ cm/sec}$.

The wavevector-dependent reflection coefficients can now be used in the expression describing the Fourier spectrum of the energy transfer to the surface in Eq.(8). The resulting plot of the integrand as a function of wavevector is shown in Figure 3 for a dipole emitting at $6328\text{\AA}$, oriented perpendicular to and at various distances above a silver surface. The wavevector dependence of the energy transfer shows the same gross features as the corresponding Fourier spectrum calculated within the CPS model, and in fact at small wavevectors (or for large dipole-surface separations) the local and nonlocal calculations are identical. The nonlocal results show the same increase from $0 < u < 1$ associated with radiative decay, and the same peak at $u = 1.3$ related to the excitation of surface plasmons. The broad peak at large wavevector which represented the energy transfer due to scattering of driven surface modes in the local picture is altered in the nonlocal calculation, being somewhat larger and also exhibiting a high wavevector cutoff at very short separation. This lossy wave mechanism in the nonlocal description represents an entirely new energy dissipation channel, namely the excitation of electron-hole pairs.

Figure 3. The imaginary part of the integrand of Eq. (8) vs. normalized wavevector u , calculated for a perpendicular dipole emitting at $6328\text{\AA}$ located at various distances above a silver surface with nonlocal dielectric response (FW model). Parameters for the Lindhard dielectric function were obtained as described in the text. Also shown is the maximum wavevector for the excitation of bulk and surface electron-hole pairs.

XBL 8210-11887

The wavevector dependence of this new excited state of the electron gas can be understood by considering the details of the electron-hole creation. For an electron gas in its ground state at absolute zero temperature, the electrons fill the lowest states available, one electron per state according to the Pauli principle. Thus the filled states form a sphere in k -space, centered at $k=0$. When a given amount of energy is supplied to the electron gas, an electron can be excited to a new k -state subject to energy and momentum conservation provided that this final state was formerly unoccupied, that is, was located outside the filled Fermi sphere. The constraints on the possible excitations imposed by energy conservation, momentum conservation, and the Pauli principle, require that for a given energy the accompanying wavevector change must lie in the range

$$(\mathbf{k}_F^2 + 4\pi m\omega/\hbar)^{1/2} - k_F < \Delta k < (\mathbf{k}_F^2 + 4\pi m\omega/\hbar)^{1/2} + k_F \quad (20)$$

The resulting spectrum of possible electron-hole excitations in the bulk is depicted in Figure 4(a), which also shows the dispersion curves for excitation of bulk plasmons and photons. The corresponding spectrum of surface excitations is derived from the projection of the bulk excitation spectrum onto the surface, and this is shown in Figure 4(b) (which also includes the discrete surface plasmon mode). The surface electron-hole excitations are allowed for all parallel wavevectors

$$0 < u < (\mathbf{k}_F^2 + 4\pi m\omega/\hbar)^{1/2} + k_F \quad (21)$$

and phase space factors will weight large wavevectors, thus producing a

Figure 4. Schematic excitation spectrum for a free electron gas, after Ford and Weber (Ref. 10). (a) Dispersion curves for bulk excitations. The bulk plasmon frequency $\omega' = \epsilon_b^{-1/2} \omega_p$. (b) Dispersion curves for surface excitations. Projection of bulk plasmon dispersion curve is not shown, but the discrete surface plasmon excitations are illustrated. The energy of the surface plasmon resonance is $\omega' = (\epsilon_b + 1)^{-1/2} \omega_p$, for a surface embedded in vacuum. The thin horizontal line in (b) corresponds to the abscissa in Fig. 3.

(a) BULK EXCITATIONS

(b) SURFACE EXCITATIONS

peak in the excitation spectrum near the upper end of its range. For the excitation energy of 1.96eV in the example of Fig. 3, the horizontal line in Fig. 4b is the abscissa in Fig. 3, and the high wavevector cutoff occurs at $2.8 \times 10^8 \text{ cm}^{-1}$, or 2860 in normalized units. This cutoff wavevector is evident in the energy transfer spectrum of Fig. 3.

The nonlocal description thus provides a more realistic modeling of the energy transfer to an electron gas by including the possibility of electron-hole excitation. In fact, this becomes the dominant energy dissipation mechanism at short distances, and the energy transfer rate is found to be quite insensitive to the electron scattering rate, which was the dominant loss channel in the local description. As was expected on physical grounds, the nonlocal description deviates from the local picture when the energy transfer occurs predominantly at large $u \sim k_F$. In the case of silver in the visible, this becomes important for separations below about $25 \text{ \AA}$. At very short distances in fact ($d < 2 \text{ \AA}$), the high wavevector cutoff of the electron-hole excitations removes the unphysical singularity of the energy transfer rate predicted by CPS theory (see Fig. 2).

Despite the apparent improvements of the FW theory, it must be emphasized that the quantitative predictions from this approach should still be viewed with some skepticism. The applicability of the Lindhard dielectric function is obviously limited to those solids whose optical response is due mainly to free electron contributions and not to interband transitions or conduction electrons which interact strongly with the lattice potential. Also, it has been noted that the deviations from CPS behavior occur at very short distances, where the other approximations in the theory such as point dipoles and infinitely sharp

smooth surfaces, probably become tenuous.

(It should be added in passing that Ford and Weber attempted to describe the effect of the finite molecular size in the context of another problem, that of the surface enhanced Raman effect. They treated the molecule as either a harmonic oscillator, a spherical potential well, or as a dielectric sphere. In each case the multipole polarizabilities were computed, and from these the effective enhancement of the Raman signal. Their calculations indicate a significant difference in the Raman gain between point dipole and finite multipole models. However, in treating the energy transfer problem, FW oddly revert to using the point dipole approximation "since the wavelength of visible radiation is much larger than typical molecular sizes." This obvious but irrelevant justification only skirts the issue-- for molecules very close to the surface the near field is changing rapidly over molecular dimensions, and the energy transfer is determined by the solid's response to this near field, much as the Raman gain is derived from the induced image of the (finite) molecular multipole. Thus one expects that the molecular size should have an effect on the energy transfer rates from molecules in very close proximity to the surface. Unfortunately, this particular theoretical refinement has yet to be included into the theory.)

The advantage of the FW treatment lies in its straightforward incorporation of nonlocal dielectric behavior into the CPS formalism. In essence, this correction only alters the calculation of the amplitude reflection coefficients; the remainder of the CPS analysis is left intact. However, while the ease of computation is preserved with the FW approach, the physical interpretation of the energy transfer process is

made no more clear. That is, the two distinct loss mechanisms, electron-hole excitation and dielectric heating, have been combined in the analysis, with no clear distinction to allow a separation of the two contributions or an assessment of their relative importance. Clearly a more sophisticated treatment of the electron gas response is required to resolve the physics of these decay channels.

One such involved yet elegant theory is that of Persson.¹¹ This formalism operates within the same general bounds as that of CPS and FW, using as a model a point dipole above an infinite potential barrier, the dielectric response taking the Lindhard form to include nonlocality. (Although in the infinite barrier model the electron gas is confined to the half-space of the solid, a later paper by Persson, et al.,¹² relaxes this restriction, using a semi-infinite barrier. An electron propagator method within this model yields much the same result as the earlier work.) The basic approach to the energy transfer problem is standard: The dipole field is decomposed into plane waves with real wavevectors (radiation field components) and complex wavevectors (evanescent waves representing the near field). The reflection properties of these waves are calculated from the linear response of the electron gas the the fields inside the metal (a refinement over the "Maxwell equations with boundary conditions" approach of FW). Given the field at the surface, the Poynting vector can be determined to get the energy flow into the solid.

The physical insight is provided by the novel description of the electric vector field using three scalar fields:

$$\vec{E} = \vec{P} A + \vec{K} B + \vec{P} \times \vec{K} C \quad (22)$$

where $\vec{P} = -i\vec{V}$, $\vec{K} = \vec{n} \times \vec{P}$, and $\vec{n}$ is the surface normal pointing into the solid. Each of the scalar fields A, B, and C represents a different type of electric field. The B and C fields denote (modified) photon fields of s- and p-polarization, respectively. The A field describes the field due to the charge density of the solid, having separate components to describe bulk plasmons and electron-hole pairs. The linear response of the nonlocal electron gas to an external photon field (with the appropriate harmonic transformations) leads to an analytic decoupling, for each incident wave, of the different energy dissipation mechanisms, including excitation of bulk plasmons, surface plasmons, and electron-hole pairs, and losses through scattering from phonons and impurities. A Fourier decomposition of the dipole field into these plane waves then gives the rate of energy transfer into each of these modes.

Although the numerical analysis of the exact equations is cumbersome, Persson has presented the results of some limiting cases as well as some applications to particular illustrative systems. Using aluminum as an example of a free electron material, Persson was able to reproduce some well-known results for the energy transfer from electronically and vibrationally excited dipoles. The energy transfer through electronic scattering processes was found to vary as d^{-3} , the distance dependence predicted in the local approximation of CPS theory. The excitation of surface plasmons goes as $e^{-\alpha d}$, also as predicted in the local picture and in the quantum treatment of Philpott.²⁷

In addition to this classical behavior, the Persson approach

predicts a d^{-4} dependence of the energy transfer to electron-hole excitations. This decay channel is in fact the dominant one for dipoles very close to the surface of a free electron material. For dipole excitation energies at optical frequencies, the creation of electron-hole pairs through the near field components is only important at distances less than about 5Å. However, for vibrationally excited dipoles, the d^{-4} dependence of the energy transfer rate is expected for $d < 100\text{Å}$. This is in fact very surprising, for the near field of the dipole can only excite electron-hole pairs for $d < 30\text{Å}$ over aluminum. The excitation of electron-hole pairs occurs at greater separation because the necessary momentum is supplied not by the dipole near field, but by the scattering from the surface itself. This electron-hole excitation using the surface as a momentum source is a completely new decay mechanism, and one which is predicted to be very important in the total energy transfer from a vibrating dipole. For free electron materials with long electron mean free paths (i.e., at energies below interband transitions), this decay channel (with its d^{-4} dependence) should dominate the electron scattering losses (and their d^{-3} dependence) for $d < 100\text{Å}$, and the deviation from CPS behavior should be measurable.

Both the FW model and the Persson model are valuable refinements in that they demonstrate the modification to the predicted energy transfer behavior brought about by the inclusion of nonlocal behavior (i.e., through using Lindhard dielectric functions). A less transparent but more realistic approach has been developed by Metiu, et al.¹³ Metiu's model removes the simplification of the Lindhard formulation and includes nonlocality by using a self-consistent jellium within the random phase approximation. In addition to providing a more fundamental

description of the electron gas response, this model also removes another approximation in the other treatments described above: namely, the self-consistent jellium model allows the dielectric properties of the electron gas to vary smoothly across the surface region. This improvement removes the singularity in the fields calculated at the surface. In the application of this treatment to the energy transfer from a dipole to a metal, Metiu still uses an infinite potential barrier to confine the electron gas to the solid. This approximation, made only because of financial constraints, will affect the magnitude of the induced surface polarization charge, but the general conclusions of this work will probably remain unchanged. (It should be noted in passing that a finite potential barrier for a self-consistent jellium model has been used in the work of Feibelman.²⁴ His work, however, being mainly concerned with the refraction of radiation at a surface, only describes the corrections to the classical treatment for large dipole-surface separations-- that is, no near field dipole components have been included. Thus Feibelman's model does not describe short-range energy transfer as accurately as Metiu's work.)

Rather than calculate explicitly the distance dependence of the energy transfer rate, Metiu instead calculates the electric field induced at the dipole position and compares these to the fields calculated from other models. Although the experimental observables are not dealt with directly, the fields are simply related to them by the general equations (4) and (5); that is, the real part of the electric field is related to the frequency shift and the imaginary part to the corrected lifetime (and energy transfer rate).

The determination of the electric field in this treatment begins

with the dipole field, which is taken as an external perturbation. Within linear response theory, this potential induces a charge polarization in the jellium. A Green's function Π describes the response of the electron gas to the external field, and this polarization can be calculated with the random phase approximation. The computational task is to determine the response function Π , which is simply related to the polarization induced by a dipole field. Maxwell's equations then allow the calculation of the electric field from this charge density.

The results of numerical calculations using this formalism illustrate the higher level of accuracy of this refined model. Metiu compares the calculations of the electric field using the phenomenological image theory (CPS model), a model which includes spatial dispersion but an abrupt discontinuity of the dielectric function at the surface (FW model), and finally his own theory which includes nonlocality and a smoothly varying dielectric function at the surface. As shown before, the addition of the nonlocal dielectric behavior adds to the imaginary part of the field (that is, the energy transfer rate) by introducing a new energy dissipation mode, electron-hole excitations. The singularity in the d^{-3} dependence of the energy transfer rate is removed because of the conservation laws described above. However, the discontinuity in the dielectric function, which has the bulk value up to the sharp surface, causes a cusp in the electric field at the surface. The Metiu model removes this cusp by allowing the dielectric function to change smoothly (i.e., there is no induced charge density at the surface). Because the singularity in the electric field is removed in the Metiu result, the field is smaller very near the

surface, and even slower energy transfer rates are expected near the surface.

Although Metiu's approach utilizes a jellium which cannot accurately model most real solids, one important conclusion from his work is worth noting. For his calculations, which were mainly concerned with dipoles excited at visible or UV frequencies, the electric fields outside the surface converge to the classical field at distances of about $6\text{\AA}$. Thus, the energy transfer behavior at these energies and for larger distances will be virtually identical to the CPS predictions even in this model.

C. Electronic Energy Transfer to Metals: $^3n\pi^*$ pyrazine/Ni(111) and
 $^3n\pi^*$ pyrazine/Ag(111)

1. General Considerations

The discussion of the various theoretical models in the previous section provides the basis for predicting the behavior of the transfer of energy from an electronically excited molecule to a metal surface. The optical properties of metals in the visible and near-UV is dominated by the conduction electron response, and to the extent that these electrons behave as a nearly free electron gas, the energy transfer models of the previous section should be directly applicable. Thus, all the models would predict energy transfer according to the CPS results down to very short molecule-metal separations ($d < 7\text{\AA}$), below which nonlocal dielectric behavior might display an observable effect. In addition, departure from the CPS prediction might arise if other

features of the electron response which were treated phenomenologically in the CPS formalism, such as interband transitions or surface plasmons, become important in the energy dissipation. To summarize, then, the considerations of the previous section indicate that the energy transfer from electronically excited molecules to real metals should proceed according to the predictions of CPS theory: namely, the energy transfer should occur mainly through lossy waves (except where discrete energy acceptors such as surface plasmons are available), and this transfer through electron scattering should display a d^{-3} distance dependence close to the surface.

The molecular system chosen as a monitor of the energy transfer to metals was $^3n\pi^*$ pyrazine (1,4 diazabenzene), a molecule whose relatively long phosphorescence lifetime (~ 20 msec) and high radiative quantum yield (0.3) lend themselves to convenient spectroscopic measurement. The photophysical properties of this aromatic compound have been extensively investigated.²⁸ The phosphorescence occurs from the lowest triplet state, the $^3B_{3u}(n\pi^*)$, which can be populated in an optical process as illustrated in Figure 5. Excitation from the ground state to the singlet manifold is followed by internal conversion to the zero vibrational level of the $^1B_{3u}(n\pi^*)$ state. Intersystem crossing to the $^3B_{2u}(\pi\pi^*)$ and further internal conversion populate the $^3B_{3u}(n\pi^*)$ level. These internal conversion and intersystem crossing processes occur with unity quantum yield and at rates much faster (10^{11} sec^{-1}) than the triplet state phosphorescence (10^2 sec^{-1}), so the phosphorescence decay is a reflection of the evolution of this lowest triplet state. In these experiments, then, the pyrazine was excited at 3.8eV into the $^1n\pi^*$ manifold, and the decay of the $^3n\pi^*$ state at 3.3eV

Figure 5. Jablonski diagram showing the energy levels of the low-lying singlet and triplet states of pyrazine, including the spin-orbit splitting of the triplets. Also shown is the excitation scheme for populating the lowest $^3n\pi^*$ state ($^3B_{3u}$) which was used to monitor the energy transfer to the surface.

XBL 8210-11884

above the ground state is followed by observing the phosphorescence.

(In reality this triplet state is split into three sublevels by spin-orbit coupling.²⁹ These sublevels have very different natural lifetimes, and emission from only one of them is dipole-allowed, the transition being polarized along the N-N axis. However, at temperatures above 10K the populations of these sublevels are in thermal equilibrium, and the observed phosphorescence decay becomes a single exponential representing the population-weighted average of the individual sublevel lifetimes. Since all of the experiments reported here were performed at temperatures above 10K, the phosphorescence lifetimes measured were then averages over all three sublevel lifetimes. The proximity of a surface should shorten the individual spin sublevel lifetimes by the same multiplicative factor because they are all at nearly the same energy, so the averaged lifetime should also be shortened by this same factor. Consequently, one can treat the triplet state as a single level exhibiting a single exponential decay which will be perturbed by the proximity of a surface.)

The occurrence of this molecular excited state at 3.3eV allows an interesting comparison to be made between the energy transfer to two metal surfaces, nickel(111) and silver(111). The excitation energy of the molecular dipole is very near the surface plasmon resonance of silver (at 3.6eV), and very far from that of nickel (at 8.1eV). Thus the density of surface plasmons which can accept the energy is very high on the silver surface, and very low on nickel (see Figure 6). Therefore, one expects that the energy transfer from ${}^3\Pi^*$ pyrazine via surface plasmon excitation should be much more efficient on silver than on nickel.

Figure 6. Energy level diagram showing the relationship of the donor π^* pyrazine level to the acceptor surface plasmon modes of silver and nickel.

XBL 2210-11885

On the other hand, the optical properties of the two metals indicate that electron scattering should be a much more important energy dissipation route for nickel than silver. The optical constants of nickel at 3.3eV (3800Å) show a large absorptive part ($\epsilon_2=8.53$ at $\lambda=3800\text{\AA}$) reflecting the existence of strong interband electronic transitions in this energy region. Energy transfer to nickel will occur through lossy surface waves which dissipate the energy by exciting these interband transitions in the bulk. Silver, by contrast, still responds like a nearly free electron gas in this region, its first interband excitation occurring at slightly higher energy. The energy loss through driven surface modes on silver occurs through impurity and phonon scattering with very low efficiency ($\epsilon_2=0.15$ at $\lambda=3800\text{\AA}$). Thus the lossy wave mechanism should be a much more effective energy transfer channel for nickel than for silver in the near-UV.

2. Experimental

An experiment was designed to measure the distance dependence of the energy transfer from a molecule to a metal surface. By ensuring surface cleanliness with an ultrahigh vacuum environment and modern surface preparation techniques, and by spacing the emitting molecules a known distance from the surface with precisely measured argon layers, the energy transfer could be studied over a wide range of molecule-metal separations, even to the point of direct contact of the molecule with the surface. Since only the energy transfer behavior was of interest here, attention was focussed on the separations shorter than 500Å, and in particular, on the very short separations where the approximations of

CPS theory might become invalid.

The experimental probes of the energy transfer to nickel(111) and to silver(111) were of two types. For the pyrazine/argon/nickel system, the energy transfer was monitored by measuring the relative phosphorescence yield (related to the energy transfer rate) as a function of argon spacer thickness. In the pyrazine/argon/silver case, a direct measurement of the triplet state lifetime (and thus, the energy transfer rate) was made possible through the use of pulsed laser excitation and time-resolved phosphorescence detection techniques.

The apparatus used in these studies is shown schematically in Figure 7. Typical operating pressures were 2×10^{-10} torr. Preliminary studies of the surface chemistry of the metal crystals were performed in a slightly more versatile configuration, the details of which will be deferred until the next chapter. The metal samples were spark cut from a 3/8 in. rod (nickel: Materials Research Corp., 99.999% purity; silver: Aremco Products, 99.999% purity), oriented to within 1° of the (111) direction by Laue backscattering, and mechanically and chemically polished. At the start of each experiment the sample was cleaned by argon ion bombardment and annealing (the exact cleaning procedure having been determined during the preliminary experiments), then placed on a liquid helium cold tip which was pre-cooled to minimize condensation of residual gases on the sample surface.

The argon and pyrazine layers were constructed by condensation on the metal surface held at 20K. Thicknesses were measured with a rotating analyzer ellipsometer, also shown in Fig. 7, which will be described more fully in Chapter III. The ellipsometric parameters (Δ, ψ) were measured at $\lambda = 3000\text{\AA}$ during the depositions. The refractive index

Figure 7. A schematic view of the experimental apparatus and experimental geometry: (1) Single crystal metal surface; (2) liquid helium cryostat sample mount; (3) $f/1$ collection optics with conical shroud; (4) external focussing lens; (5) colored glass filters; (6) photomultiplier tube in dry ice-cooled housing; (7) spherical mirror for use in ellipsometry and excitation spectra; (8) ellipsometer MgF_2 input polarizer; (9) ellipsometer alignment apertures; (10) rotating analyzer polarizer, motor, and photomultiplier; (11) excitation laser alignment apertures; and (12) MgF_2 polarizer for polarizing excitation laser.

XBL 819-6594

of the argon layer was determined by depositing gas until the value of Δ , which began decreasing upon initial adsorption, turned over and monotonically increased. This turning point occurs when the optical path length of the beam in the argon layer is one-half a wavelength. By fitting the (Δ, ψ) value at the turning point, one obtained a value of the refractive index of the argon layer which, assuming the index remains constant, should reproduce the (Δ, ψ) pairs during the entire deposition. Using this $\bar{n}(\text{Ar})$ measured from several calibration runs, the thickness of the layer can be calculated.

An alternative method of determining the refractive index of the spacer layer involved finding the one spacer index which reproduced all the (Δ, ψ) pairs during the deposition. This method was developed by Malin and Veda³⁰ and is illustrated in Figure 8. Each curve represents the set of complex refractive indices (n, k) which, for a purely real overlayer thickness, will reproduce a (Δ, ψ) value measured at one point during the deposition. The intersection of these curves is then the actual refractive index of the argon layer (again, assuming a constant index for all thicknesses). The results of the measurements in these experiments, $\bar{n}(\text{Ar}) = 1.2 - 0.03i$, remained approximately constant and agreed well with the value derived from fitting the turning point for Δ . This refractive index of argon was used to calculate the thickness of the spacer layers, with errors estimated to be 5%-10% for all but the thinnest layers, where the error was probably about $5\text{\AA}$, the thickness of one argon layer. A monolayer of pyrazine was then condensed on top of the argon layer.

After the construction of these sandwich matrices, the optical components of the ellipsometer were removed and the phosphorescence

Figure 8. A plot of the (n,k) values which, for purely real layer thicknesses, reproduce the measured (Δ,ψ) parameters at seven points during the deposition. The intersection is the (constant) refractive index of the argon spacer.

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measurements were performed. For the nickel study, pyrazine phosphorescence was excited by an unpolarized, filtered, medium pressure Hg arc lamp whose output covered the entire pyrazine $^1n\pi^*$ manifold. The excitation source was placed in the position of the alignment laser in Fig.7, and phosphorescence was collected normal to the surface using $f/1.5$ optics. The emission was isolated using colored glass filters, and its intensity was recorded using photon counting. At very short distances the pyrazine emission intensity was much weaker than the scattered excitation light, even though filter combinations were carefully chosen to minimize the spectral overlap between the excitation and observation passbands. Consequently, it was necessary to measure the light intensity before and after pyrazine deposition, taking the difference as the phosphorescence intensity. Measurements of this relative luminescence intensity were made as functions of argon spacer thickness, to get the distance dependence of the energy transfer, and of pyrazine thickness, to verify that the argon thickness was in fact the effective emitter-surface separation.

In the silver experiment, the phosphorescence lifetime of the pyrazine was measured directly. The pyrazine emission was excited at $3250\text{\AA}$ by a linearly polarized 10 nsec pulse from the frequency-doubled output of a Nd:YAG pumped dye laser (Quanta-Ray Corp.) operating with DCM dye. The phosphorescence was collected along the surface normal with a 1 in. $f/1$ lens mounted inside the vacuum chamber. Outside the chamber, the emission was isolated with colored glass filters (Schott GG375 and Corning CS7-54) 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. PDP11/03) for signal averaging and storage on floppy disks. Phosphorescence lifetimes were calculated with a least-squares fit of a single exponential to the experimental decay. As for nickel, the lifetime measurements were performed as a function of argon spacer thickness to map out the distance dependence of the energy transfer.

In order to justify these particular choices of excitation and detection schemes, it was necessary to verify that the spectroscopy of the pyrazine excited states was not drastically altered in the unusual environment of an argon/vacuum interface. To this end, phosphorescence excitation spectra were performed by scanning the ellipsometer light source and detecting the phosphorescence with the photon counter. Once the excitation maximum had been determined, the pyrazine was excited at that wavelength (with either a laser or an arc lamp), and a phosphorescence emission spectrum was recorded by dispersing and detecting the output from the collection viewport using a monochromator and photon counter. The results of these preliminary experiments predicated the choices of the particular excitation and emission passbands employed in the energy transfer measurements.

3. Results

a. Phosphorescence excitation and emission spectra of pyrazine at an argon/vacuum interface at 20K

The phosphorescence excitation spectrum of a thick (25Å) layer of pyrazine deposited on a 200Å argon spacer over a Ag(111) surface is

shown in Figure 9. The measured intensity of the phosphorescence has not been corrected for the variation in lamp flux across the spectral range. There are two peaks in the excitation spectrum with onsets near 3300Å and 2750Å, each exhibiting resolved vibronic structure. The peak positions and vibrational progressions correspond well with the $^1n\pi^*$ and $^1\pi\pi^*$ transitions, respectively, observed in the electronic absorption spectra of pyrazine condensed on metal surfaces. (For details of these absorption spectra, see the results of the spectroscopic ellipsometry studies described in Chapter III.) The pyrazine emission from the $^3n\pi^*$ state thus originates from the excitation into the singlet manifold, just as in the molecular crystal studies. The maximum phosphorescence intensity occurs upon excitation of the 0-0 band of the $^1n\pi^*$ transition at 3280Å, so this wavelength was chosen to excite the pyrazine emission in the subsequent experiments.

Using a pulsed dye laser tuned to 3280Å, the spectrum of the phosphorescence from this same pyrazine/argon/silver(111) system was measured. Figure 10 shows the spectral distribution of emission collected without (Fig. 10a) and with (Fig. 10b) colored glass filters. The unfiltered emission shows a 0-0 band at 3850Å with a regular progression of peaks to longer wavelength, corresponding to decay of the triplet state to excited vibrational levels of the ground state. The small peak observed at 3280Å is due to excitation light which is diffusely scattered off the surface into the collection optics. The energies and relative intensities of these emission peaks correspond very well with the phosphorescence of crystalline pyrazine at low temperatures.³¹ When the colored glass filters are placed before the monochromator, only emission in a narrow wavelength window (3750Å-4000Å)

Figure 9. The phosphorescence excitation spectrum of a 25Å layer of pyrazine above a 200Å argon spacer on a Ag(111) surface.

1966

Figure 10. The phosphorescence emission spectrum of a 25Å layer of pyrazine above a 200Å argon spacer on a Ag(111) surface (a) without, and (b) with colored glass filters on the output of the collection optics. The small peak at 3280Å in (a) is due to scattered excitation light and is eliminated in (b) by the filters, which also reduce the relative intensities of the lower energy vibronic bands of the pyrazine emission.

XBL 819-6640

is allowed to pass to the detector. As a result, Fig. 10(b) shows that the emission to the vibrationally excited ground state (i.e., the long wavelength peaks) are filtered from the signal, leaving a phosphorescence signal peaked at the 0-0 band origin at 3850Å (with small contributions from the first and second vibronic features). Also, the narrow passband eliminates the scattered laser excitation (and, with the proper filter choice, also eliminates fluorescence from the filters themselves), thus providing a pure phosphorescence signal for intensity or time-resolved analysis.

b. Relative phosphorescence intensity of pyrazine above nickel(111)

The phosphorescence intensity of pyrazine was linear in the thickness of adsorbed pyrazine for a fixed spacer of argon (72Å) on Ni(111), as shown in Figure 11. This linear dependence suggests that rapid resonant energy transfer (of the Forster-Dexter type) occurs within the pyrazine layer, the excitation only being transferred to the metal from the molecules at the pyrazine/argon interface. Therefore, the argon spacer thickness can be taken as the effective emitter-surface separation for the energy transfer.

The distance dependence of the emission intensity is shown in Figure 12. The data are displayed on a logarithm plot, and a best fit least-square line has a slope of 3.07 ± 0.05 . That is, the phosphorescence yield shows an approximate d^3 dependence on the argon spacer thickness down to 7Å above the surface, in accord with CPS theory. However, even though long counting times were used to improve the statistics, the high background and low signal levels precluded

Figure 11. Pyrazine phosphorescence intensity vs. thickness of the pyrazine layer above a 72Å argon spacer on Ni(111).

XBL 7912-5469

Figure 12. Pyrazine phosphorescence intensity for a 5Å pyrazine layer above a Ni(111) surface as a function of argon spacer thickness. The ordinate shows the average count rate, although longer counting times were used to improve the statistics. The line shown is a least-squares fit to a power law with an exponent of 3.07 ± 0.05 .

XBL 7912-5468

measurement of the relative quantum yield at separations smaller than 7Å.

c. Phosphorescence lifetime of pyrazine over silver(111)

Phosphorescence decays were recorded for pyrazine-silver separations between 420Å and 10Å. The 10Å distance represents only two layers of argon separating the pyrazine from the silver surface. An example of a typical phosphorescence decay curve is shown in Figure 13. For fixed incident laser power, the phosphorescence intensity decreased with decreasing distance to the surface. Attempts to measure phosphorescence from pyrazine on a single monolayer of argon (5Å above the silver surface) failed due to extremely low signal levels.

The phosphorescence decays were recorded for laser excitation polarized both in and perpendicular to the plane of incidence, and, to within experimental error, the results for the two polarizations were identical. Although this observation could be evidence for all the pyrazine molecules having the same orientation with respect to the silver surface, it is more likely that the molecules adsorb with a distribution of these orientations. Dipoles parallel to the surface would be selectively detected, because at these separations their radiative probability is 2-20 times greater than that of perpendicular dipoles.⁸

Phosphorescence lifetimes were calculated by fitting the decays to a single exponential, and the results are presented in Table 2. For all the separations studied, the fit of a single exponential to the measured decay was excellent, although there is some evidence for more rapid

Figure 13. A typical phosphorescence decay curve for $^3n\pi^*$ pyrazine above an argon spacer on Ag(111). This signal level was obtained after integrating 300 laser shots.

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Table 2

The observed phosphorescence decay times for a layer of pyrazine separated from a Ag(111) surface by an argon layer of thickness d

<u>$d(\text{\AA})$</u>	<u>$\tau(\text{msec})$</u>
10	0.2
20	0.5
25	0.5
35	1.5
50	4.0 - 4.9
75	3.9 - 8.9
100	10.1 - 11.8
180	14.2
420	16.0

decay at very short times following excitation (see Fig.14). This short lifetime component is probably due to phosphorescence from pyrazine adsorbed near a small number of surface defects.

The observed distance dependence of the pyrazine phosphorescence lifetime was compared to the behavior predicted by CPS theory. The model used corresponded to the experimental configuration: a layer of pyrazine placed 3Å above an argon layer adsorbed on a silver surface. The ambient was vacuum ($\epsilon=1$), and the optical constants of the silver and argon were measured ellipsometrically during the experiment ($\tilde{\epsilon}(\text{Ag}) = -3.6 + 0.15i$ at 3800Å). The emission wavelength of pyrazine was 3800Å, and a value of 0.3 for ϕ_p , the phosphorescence quantum yield, was taken from the literature.³² The only adjustable parameter was τ_0 , the phosphorescence lifetime of pyrazine at an argon/vacuum interface at infinite separation from the silver surface.

The total decay rate for dipoles oriented parallel to the silver surface was calculated from Eq.(8), using the coefficients and reflectivities appropriate to this experimental geometry:

$$\frac{b}{b_0} = \frac{\tau_0}{\tau} = 1 + \frac{3}{4} \phi_p \text{Im} \int_0^\infty \left[\left(\frac{1-u^2}{u^2} \right) R^P + \frac{1}{u^2} R^S \right] \times e^{-2\hat{d}_1 \frac{u^3}{1}} du \quad (23)$$

where

$$R^{P,S} = \frac{r_{12}^{P,S} + r_{23}^{P,S} e^{-2\hat{d}_2}}{1 + r_{12}^{P,S} r_{23}^{P,S} e^{-2\hat{d}_2}} \quad (24)$$

$$r_{ij}^P = \frac{\epsilon_{ij}^{1j} - \epsilon_{ji}^{1i}}{\epsilon_{ij}^{1j} + \epsilon_{ji}^{1i}} \quad (25)$$

Figure 14. The logarithm of the phosphorescence intensity of $^3n\pi^*$ pyrazine 100Å above Ag(111) vs. time. The line is the best least-squares exponential ($\tau = 10.8$ msec).

$$r_{ij}^S = \frac{l_i - l_j}{l_i + l_j} \quad (26)$$

$$l_j = -i (\epsilon_j / \epsilon_1 - u^2)^{1/2} \quad (27)$$

$$\hat{d}_i = 2\pi\epsilon_1^{1/2} d_i / \lambda \quad (28)$$

Here d_1 is the distance from the pyrazine to the top of the argon spacer ($d_1=3\text{\AA}$), and d_2 is the argon spacer thickness. Only this calculation for the parallel dipole is shown because, as noted previously, in this distance regime the probability for radiative decay of parallel dipoles is much greater than that of perpendicular dipoles.

Figure 15 shows the result of the calculation for $\tau_0 = 25$ msec, plotted with the experimentally determined lifetimes. The value of 25 msec 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 CPS theory.

4. Discussion

The results of the above experiments verify the applicability of the CPS description of the energy transfer process to nickel and silver in the near-UV, at least down to $10\text{\AA}$ distance above the surface. Unfortunately, tests of the various refinements of the CPS theory could not be performed, since experimental limitations prevented measurements at shorter distances, where deviations from CPS behavior are

Figure 15. The lifetime of $^3\pi\pi^*$ pyrazine above Ag(111) vs. argon spacer thickness. The points are experimental values, and the solid curve is the behavior calculated from the Chance, Prock, and Silbey model (see the text for details).

XBL 819-6591

predicted. Nevertheless, the fact that the CPS theory seems to apply down to about $10\text{\AA}$ separation implies that the classical image dipole treatment includes most of the important physics of the energy transfer to these metals.

Given that the CPS model correctly describes the electronic energy transfer down to short distances, an analysis of this formalism can provide valuable insight into the fundamental physical interactions involved in the transfer process. As noted before, the nonradiative energy transfer takes place through the near field of the dipole, i.e., those components having wavelengths larger than the radiation field (photon) wavelength at that energy. Figure 16 is a plot of the imaginary part of the integral of Eq.(23) evaluated for the $^3_{n\pi^*}$ pyrazine/argon/nickel and $^3_{n\pi^*}$ pyrazine/argon/silver systems which were studied in this work. The area under each curve is proportional to the total energy transfer rate at a particular argon spacer thickness, and each curve represents the contribution of the various wavevector components of the field to the energy transfer.

As was illustrated before in the Theory section, these curves display two features which derive from distinct energy transfer mechanisms. The sharp peak near $u=1$ is associated with energy transfer through excitation of resonant surface plasmons. As expected from the density of surface plasmons on the two surfaces at this energy, the energy transfer to these plasmons is much larger on silver than on nickel. The broad peak at high wavevector arises from the dissipation of energy through lossy surface waves. Because of the strong interband electronic transitions in nickel at this energy, the scattering of these driven surface modes is a much larger contributor to the energy transfer

Figure 16. The imaginary part of the integrand of Eq. (23) vs. normalized wavevector u , showing the surface plasmon contribution (at u_{sp}) and lossy wave contribution (at large u) to the energy transfer from pyrazine to (a) Ni(111), and (b) Ag(111) at several distances. The pyrazine is taken to be $3\text{\AA}$ above the argon spacer and lying parallel to the surface. The dielectric constants used are $\epsilon(\text{Ag}) = -3.6 + 0.15i$ and $\epsilon(\text{Ar}) = 1.44$ at $\lambda = 3800\text{\AA}$. Optical constants for nickel at this wavelength were taken from Ref. 33.

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rate for nickel than silver.

The plots of these wavevector contributions at different emitter-surface separations show the relative importance of these two energy transfer mechanisms as the dipole approaches the surface. An even more illustrative comparison can be obtained by performing the integrations under the various features separately, thereby calculating the actual rate of energy transfer through these different physical mechanisms. Normalizing these individual rates to the total decay rate yields an effective branching ratio for the dipole deactivation, and when calculated as a function of distance a very clear picture of the dipole-surface interaction emerges. The relative decay probabilities versus distance for the experimental nickel and silver configurations are shown in Figure 17. The three decay channels are: (1) the emission of photons (RD); (2) the excitation of resonant surface plasmons (SP); and (3) dielectric heating of the surface through lossy waves (LW).

In both the nickel and silver systems (and in fact for any surface where nonradiative energy transfer can take place), the decay of the excited dipole by photon emission is the most probable of the three energy disposal routes when the dipole is very far from the surface (ignoring of course the intramolecular nonradiative relaxation processes implied by a quantum yield less than unity). As the molecule approaches the surface and energy transfer becomes a competitive decay channel, the probability for photon emission decreases monotonically. For this reason, the attempts to monitor the energy transfer by detecting pyrazine phosphorescence were unsuccessful below $10\text{\AA}$ separation.

Below about $400\text{\AA}$ nonradiative energy transfer to the surface dominates the dipole decay, but the separation of the decay probability

Figure 17. Calculated probability for decay of $^3\pi\pi^*$ pyrazine on (a) Ni(111) and (b) Ag(111) as a function of argon spacer thickness. The decay occurs through photon emission (RD), resonant surface plasmon excitation (SP), and dielectric losses (LW). Geometries and optical constants are the same as in Fig. 16. Phosphorescence quantum yield of $^3\pi\pi^*$ pyrazine $\phi_p = 0.3$.

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in Fig. 17 illustrates the differences in the mechanisms for the transfer to nickel and silver. For the nickel surface at this energy, resonant surface plasmon excitation is an unimportant decay channel at all molecule-metal separations. The dominant energy transfer mechanism for nickel, and the most probable deactivation pathway below 400Å separation, is the dissipation through lossy surface waves. The energy transfer to the surface is a very long range effect, the so-called "critical transfer distance," or distance where the energy transfer probability is $1/2$, occurring at about 200Å. This can be compared to the corresponding critical length for Forster energy transfer in molecular systems, which is typically about 50Å.

For the silver surface, too, the energy transfer competes with photon emission at large distances, dominating the dipole decay at separations closer than 500Å. Here, however, surface plasmon excitation is a very important decay channel and is the most probable relaxation route between 100Å and 500Å. Below 100Å, the lossy wave mechanism again acts as the primary energy dissipation channel.

A further illustration of the importance of surface plasmons in the energy transfer to silver is provided in Figure 18. which is a plot of the ratio of the energy transfer rates to silver and nickel as a function of distance for various dipole-excitation energies. When the value of this ratio becomes greater than one, the energy transfer process is faster on silver than on nickel. At very low energy (near 2.0eV), energy transfer to silver is faster than to nickel only at separations around 2000Å. Presumably transfer to resonant surface plasmons on silver is most efficient at this distance and is responsible for the larger transfer rate. As the excitation energy increases toward

Figure 18. Calculated ratio of energy transfer rates from perpendicular dipoles to silver and to nickel as a function of distance (in Å) for different energies. Values of optical constants taken from Refs. 33 and 34.

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the surface plasmon resonance in silver (at 3.6eV), more surface plasmons become available to act as energy acceptors. Thus the maximum of the ratio of the energy transfer rates increases and also moves to shorter separation where the plasmon excitation probability is greatest. (This distance for optimum transfer to surface plasmons probably decreases because the wavevectors of these plasmons are increasing to higher energy. Thus more near field components are necessary to match wavevectors, and these field components only become available at short distance.) When the energy being transferred is almost equal to the silver surface plasmon resonance, the transfer rate is greater on silver than nickel for all distances shorter than 500Å. At this energy, the silver surface has available a large number of surface plasmons to receive the excitation energy, and these plasmons happen to be strongly coupled to bulk scattering mechanisms (interband transitions) which make the energy transfer very efficient. As a function of energy, the maximum of the ratio of the silver to nickel transfer rates seems to reflect the density of states of the surface plasmons on silver, suggesting that it is only through plasmon excitation that the energy transfer to silver becomes more rapid than the transfer to nickel.

5. Conclusions

The distance dependence of the energy transfer rate has been measured for $^3\pi\pi^*$ pyrazine on nickel(111) and silver(111) down to very short separations (7Å and 10Å, respectively). A monotonic increase in the energy transfer rate is observed as the dipole-metal separation

decreases, and the dependence is in quantitative agreement with the predictions of the Chance, Prock, and Silbey theory. Attempts to measure energy transfer rates at smaller separation were unsuccessful. Analysis of the decay pathways within the CPS model demonstrates the important role played by surface plasmons in the energy transfer to silver in the near-UV.

D. Energy Transfer to Semiconductors: $^3n\pi^*$ pyrazine/GaAs(110)

1. General Considerations

The study of energy transfer to surfaces has until recently been restricted to metal surfaces, such as the work on nickel and silver described in the previous section. The reasons for this focus of attention are simple. First of all, metal surfaces are the most chemically interesting of the common materials. Their catalytic properties have found widespread application, yet are still poorly understood from a fundamental standpoint. Thus, dynamical questions such as the interaction of molecular excited states with the surface form one of the main thrusts in the effort to unravel the complex chemical processes which can occur.

In addition to this practical rationale for pursuing energy transfer studies on metals, there is also a more esthetic motivation for these experiments, viz., the desire to critically test the theoretical descriptions of the energy transfer process on surfaces. As has been demonstrated earlier, these theoretical treatments are all faced with the task of describing the enormously complicated response of a real

solid to an electromagnetic field. In order to render this burden manageable, most models have resorted to either simplifying the solid (e.g., by using a jellium model), or by applying phenomenological equations to try to include complicated physics in a gross fashion. In either case, it has been found that calculations involving a free electron gas are the easiest, and more complex physics can be incorporated with additional parameters in the electron gas response (e.g., relaxation times to include the effect of electron scattering and interband transitions, Lindhard or hydrodynamic dielectric functions to describe electron-hole excitations, etc.). Thus, the ease of using a jellium model has directed the bulk of experimental testing to free electron materials, i.e., to metals.

It is the purpose of this study to extend the testing of energy transfer theories to a new class of materials, namely, semiconductors. Prompted by the widespread interest in semiconductors for their unusual physical properties, it has become increasingly clear that the chemical properties of these materials, which are not well characterized, are of prime importance in the manufacture and use of these materials. Energy transfer studies will hopefully form a basis for the understanding of the surface chemistry and chemical dynamics on these solids.

From a more fundamental view, semiconductors should also lead to more rigorous tests of energy transfer theories. In the first place, the dominant features of the optical response of semiconductors are derived from such effects as interband transitions. This strong electron-lattice interaction is typical of the interactions which were treated only phenomenologically in most theories, through the use of electron relaxation rates or dielectric constants due to bound

electrons. Thus a study of energy transfer through these excitations in semiconductors, which, unlike metals, do not have the obscuring effects of the free electron gas response, should lead to more critical testing of these approximations in the theory. Further, the relative contributions of free carrier and bound electron properties to the energy transfer rates can be explored with semiconductors by studying different energy regions or by varying the concentrations of dopants.

As in the case of metals, the energy dissipation channels available to semiconductor surfaces are determined by the electronic structure of the solid, so it is useful to begin with a discussion of the properties of electron states in these materials. Metallic systems are characterized by a partial filling of the highest occupied electronic states, the so-called conduction band. The filled states in this band have unfilled states very close in energy, and the free electron gas nature of the metal electrons is derived from the ease of scattering of electrons within this conduction band. By contrast, at absolute zero temperature, the highest occupied electronic states in semiconductors (the valence band) are separated from the lowest unoccupied states (the conduction band) by a small energy gap, which usually lies in the range 0.1eV-4eV. It is only through thermal excitation, impurity carriers, lattice defects, or non-stoichiometric composition, that mobile electrons can occupy the conduction band, and the electronic properties of semiconductors are derived from these various processes for creating mobile carriers. In contrast to the high free carrier concentrations in metals ($10^{23}/\text{cm}^3$), where the behavior of the electron gas must obey Fermi statistics and the Pauli principle, the concentration of mobile carriers in semiconductors is much smaller (10^{14} - $10^{17}/\text{cm}^3$), so that the

electron gas behaves according to classical Boltzmann statistics (and consequently exhibits properties with very strong temperature dependence).

The difference in the electronic structures of metals and semiconductors leads to important differences in the response of these materials to applied electromagnetic fields. The free electrons in a good conductor like a metal dominate the optical behavior, moving in response to the applied field and (for all but very high frequency fields) effectively screening the interior of the solid from the external field. This free electron response is characterized by a (real) dielectric constant $\epsilon < 0$, reflecting the ability of the electron gas to cancel these fields inside the bulk. By contrast, intrinsic semiconductors respond as dielectrics, their optical properties deriving from the response of their bound electrons. These electrons, bound to the atomic sites, cannot move freely to completely screen the external fields but can only move slightly, polarizing the material with the induced dipoles. This polarization is manifested in the dielectric constant of the material, which for semiconductors is $\epsilon > 1$ for optical frequencies where there are no absorptions. Because these bound electrons cannot completely shield the applied field, electromagnetic waves can not only penetrate the solid but in certain cases can propagate in the material. This photon field which travels in the bulk (and which also couples to bulk phonon modes at low energies) is called a polariton. This excitation in the dielectric, as well as other excitations of the bound electrons such as interband transitions, will be seen to play a role in the deactivation of a dipole above a semiconductor surface.

The optical response of a pure semiconductor can be separated into three energy regimes.³⁵ Figure 19 illustrates this separation for a typical semiconductor, in this case gallium arsenide. Shown in this figure are the spectral dependences of the reflectance R , the real and imaginary dielectric constants ϵ_1 and ϵ_2 , and the energy loss function, $-\text{Im}(\epsilon)^{-1}$. Neglecting the long wavelength absorptions in doped semiconductors due to the electron-phonon scattering of the free carriers, the optical response in Region 1 (0-10eV) is dominated by many strong absorption features derived from direct interband (valence to conduction) transitions. Also in this region, near the fundamental edge (the onset of the direct interband absorptions), would also be found structure due to exciton states, impurity states, and indirect (non-vertical) phonon-assisted interband transitions, if any. At higher energy (10-20eV) in Region 2, the so-called "metallic" region, the reflectance drops off sharply as the valence electrons, above the interband transition energy, respond essentially as unbound electrons. These valence electrons can in fact perform collective oscillations (bulk plasmons), and the excitation of these plasmons is indicated by the peak in the loss function in this region. At even higher energy (20-25eV) in Region 3, a small, broad absorption peak is seen for those materials having d-band states below the valence band. The absorption in this region is due to another interband transition (d-band to conduction band), but the main effect of this absorption is merely to shift the level of the zero frequency dispersion (according to the Kramers-Kronig relations).

Assuming that all the important energy dissipation modes are accounted for in the optical dielectric response, one expects

Figure 19. The spectral dependence of the reflectance R , the real and imaginary parts of the dielectric constant, ϵ_1 and ϵ_2 , and the energy loss function, $-\text{Im}(\epsilon)^{-1}$, for gallium arsenide (taken from Ref. 35).

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qualitative differences in the energy transfer from dipoles to semiconductors as compared to metals, except in that region of the semiconductor spectrum where metal-like plasmon behavior is observed. At energies typical of many low-lying electronic states of molecules (Region 1), the optical response of metals is due mainly to free electron contributions and interband transitions. These free carriers act as mediators for the energy transfer from dipoles, dissipating energy through scattering, surface plasmon excitation, or electron-hole excitations in the electron gas. Interband electronic transitions can also be created by the driving of the mobile carriers in the metal which scatter into bulk excitations through interaction with the crystal potential.

Energy transfer mechanisms in semiconductors, however, cannot involve participation of free electrons, for their dielectric response is dominated by the bound electrons. Thus, deactivation of electronically excited dipoles cannot occur through surface plasmon or electron-hole (intraband) excitations, and free carriers are not available to dissipate energy into the bulk through scattering processes. Instead, energy transfer must occur through the interaction of the dipole field with the bound electrons of the semiconductor.

Insight into the physical mechanisms for energy transfer in this case can again be obtained from an analysis of the wavevector spectrum of the energy transfer rate, calculated in the local approximation of the CPS formalism. A comparison of the energy transfer behavior of silicon, germanium, and gallium arsenide, helps identify and assess the importance of the different energy dissipation modes in the solid. The low energy optical properties of these three materials is shown in

Figure 20, and the excitation energy of the dipole is taken to be 2.5eV, which is located below, above, and near the onset of, the interband transition energies of silicon, germanium, and gallium arsenide, respectively. Participation of these bulk excitations in the energy transfer should thus decrease in going from germanium to gallium arsenide to silicon. Also of note in the optical spectra of these semiconductors is the large value of ϵ_1 , the real part of the dielectric constant, indicative of the optical response of the bound electrons.

Figure 21 shows the wavevector dependence of the integrand of Eq.(8) evaluated for dipoles at several distances above these three surfaces. Just as in the case of nickel and silver, these plots represent the contribution to the energy transfer rate from the different wavevector components of the dipole field. The broad peak at large wavevector, which in metals derived from "lossy wave" dielectric heating and scattering into bulk excitations, can again be associated with the loss of energy to interband excitations in the semiconductors, since the relative efficiency of this mechanism decreases in going from germanium to gallium arsenide to silicon, as expected from the optical data. In these cases, as noted before, the interband transitions must be excited directly because there are no "lossy wave" modes as such.

The other feature of these plots is the sharp peak which occurs at low wavevector for silicon and gallium arsenide. In silver and nickel a sharp peak in this region was associated with the surface plasmon excitation mechanism, but at this energy there are no plasmon modes on the semiconductor surfaces. An expanded view of this region, shown in Figure 22, reveals that this low wavevector peak is quite broad compared to the surface plasmon peak on silver, and there also appears to be a

Figure 20. The dielectric constants of silicon, germanium, and gallium arsenide from 0eV to 5eV. The relation of the hypothetical dipole excitation energy (2.5eV) to the interband absorption features is indicated by the dashed lines.

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Figure 21. The imaginary part of the integrand of Eq. (8) vs. normalized wavevector u , calculated for a dipole emitting at 2.5eV and oriented normal to the surfaces of silicon, germanium, and gallium arsenide. Optical properties of these materials are shown in Fig. 20.

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Figure 22. Detail of the wavevector spectrum of Fig. 21, showing the low-wavevector contribution of polariton excitation to the energy transfer. (For germanium, the polariton channel is strongly coupled to the pair excitations, so a distinct feature due to polariton production is not evident.)

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cutoff at normalized wavevector $u \sim 4$.

These facts and the absence of this peak for germanium at this energy lead to the identification of this feature with the excitation of bulk polariton modes in the semiconductors. These polariton modes (at energies far above phonon energies) are essentially photon-like, with normalized wavevectors $k \sim [\epsilon(\infty)]^{1/2}$, which for these materials occurs at $k \sim 4$. Since these bulk modes can propagate in any direction in the solid, the component of the wavevector parallel to the surface (the variable u of Fig. 22) can take on any value up to this bulk value. The strong coupling of this mode to bulk interband excitations in germanium causes the polaritons to become poorly defined entities which very quickly decay into bulk interband transitions (just as for the surface plasmons on nickel in the near UV).

Finally, the relative importance of these decay mechanisms as a function of dipole-semiconductor separation is illustrated in Figure 23. As was seen for energy transfer to metals, at large distances from the semiconductor surface (a few hundred Å for these systems) energy transfer is not a very important effect, the excited dipole decaying mainly through photon emission or intramolecular energy degradation. Closer to the surface (50-150 Å) polariton excitation becomes a significant decay pathway. (In the case of germanium, dipole decay through wavevectors $1 < u < 4$ has still been attributed to "polariton creation," even though these modes quickly transfer energy to bulk interband excitations and should be included in the "pair production" contribution.) For all these semiconductors, the deactivation of an excited dipole at short distances ($d < 50-100$ Å) occurs through "pair production," i.e., excitation of interband transitions in the bulk.

Figure 23. Calculated probability for dipole decay to silicon, germanium, and gallium arsenide at 2.5 eV as a function of distance to the surface. The decay channels available to the dipole are photon emission, interband electron-hole pair production, and bulk polariton excitation. A radiative quantum yield of 0.3 was used in the calculation.

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Implicit in this analysis of energy transfer to semiconductor surfaces is the assumption that CPS theory applies to these systems. The differences in the fundamental physics of the transfer to metals and semiconductors does not allow a priori extension of the results of the tests of classical theory on metals to semiconductor systems. In fact, the mechanisms for energy transfer to semiconductors, which involve interaction with bound electrons and details of the band structure of the solid, are treated only phenomenologically in the CPS formalism. Furthermore, the applicability of classical energy transfer theory may differ from one semiconductor material (or type of material) to another because of the vast differences in electronic properties which can be obtained for these solids. Thus, it seems much more important for semiconductors than for metals that each material be carefully examined, and perhaps after a large data base has been accumulated it may be possible to identify some trends in the energy transfer behavior (e.g., the effects of free carrier concentration, the type of bands involved in the bulk transition, etc.).

As a first step in this direction, the applicability of CPS theory was tested by measuring the distance dependence of the rate of energy transfer from $^3\text{Hn}^*$ pyrazine to undoped gallium arsenide (110). In addition to its novel electrical properties such as its very high carrier mobility, gallium arsenide also exhibits interesting chemical behavior, due in large part to the polar character of some of its low Miller index surfaces.³⁶ For these energy transfer studies, however, the (110) surface was chosen because it is stable to faceting and is relatively unreactive. This particular face also can be easily prepared by cleaving, which facilitates the manufacture of clean single crystal

surfaces. Undoped gallium arsenide has a very low carrier concentration ($<10^{15}/\text{cm}^3$), so the participation of free electrons in the energy transfer is minimized. Finally, this material has several strong interband absorptions in the region of the $^3_{\text{nm}}^*$ pyrazine emission,³⁵ again allowing the use of this molecular excited state as a probe of the energy transfer to these bulk transitions.

2. Experimental

The distance dependence of the phosphorescence lifetime over gallium arsenide was measured in the same manner as the pyrazine/silver experiment described in the previous section (see Fig. 7). Polished undoped GaAs(110) wafers (Crystal Specialties, Inc.) were clamped to an aluminum block and cleaned with several argon ion bombardment/anneal cycles as prescribed in the literature.³⁷ (Preliminary experiments using LEED/Auger show that this cleaning procedure gives reasonably clean, well-ordered surfaces, although trace amounts of residual surface carbon often remain.) After cleaning, this aluminum holder was mounted in the liquid helium cold tip, but the thermal contact to the surface was poor enough that minimum temperatures of only about 30K could be achieved. For this reason, sandwich matrices were constructed on the surface using ammonia spacers because argon, the spacer material in the silver experiment, could not be condensed consistently. (Those measurements on GaAs which were made successfully using argon spacers, however, gave results very similar to the lifetimes measured using ammonia spacers of the same thickness.)

Phosphorescence excitation spectra of pyrazine on GaAs(110) were

essentially identical with the results for pyrazine on silver, showing $1_{n\pi^*}$ and $1_{\pi\pi^*}$ absorption profiles. However, the unavailability of a Nd:YAG laser necessitated excitation of the pyrazine emission at $3120\text{\AA}$ using the unpolarized second Stokes beam of a Raman shifted KrF excimer laser (Lambda Physik EMG 101). Because the laser excitation was not located at the maximum of the excitation profile as it was in the silver work, the signal-to-noise of the phosphorescence decay was poorer in the GaAs experiment. Consequently, lifetime measurements could only be performed down to about $20\text{\AA}$ separation.

Besides the use of a different spacer material and laser excitation wavelength, the phosphorescence lifetime measurements were made in the same way as for the silver studies. Spacer thicknesses were measured ellipsometrically as described before, and single exponentials were fit to the observed phosphorescence decays to obtain the lifetime of the pyrazine triplet state.

3. Results

Lifetime measurements for the pyrazine triplet state were made for emitters on ammonia spacers of thicknesses between $20\text{\AA}$ and $430\text{\AA}$. The determination of these spacer thicknesses was less reliable and accurate than those of the energy transfer experiments on metals. The ellipsometer design (especially the 60° angle of incidence and the absence of a compensator) is not optimal for measurements on dielectrics. The preparation of the GaAs surface is also less systematic than that of metal surfaces, so the GaAs surface was slightly rougher (and perhaps not chemically stoichiometric). The neglect of

this imperfect surface layer introduces a systematic error into the distance calibrations which seemed slightly greater for the semiconductor experiments. These intrinsic errors were all estimated and incorporated into the uncertainty in the thickness measurements, but other more subtle questions, such as the exact structure of the ammonia layer, could not be answered.

These phosphorescence measurements on gallium arsenide demonstrated a strong temperature dependence of the emission decay. As the temperature of the layer was raised (to approximately 50K) the phosphorescence decay became shorter. This effect was apparently reversible, but the lack of accurate temperature control and measurement prevented a more systematic examination. This temperature dependence is probably not unique to the pyrazine/ammonia/GaAs system, but the low sublimation temperature of argon limited the range of temperatures at which measurements in the silver experiment could be made. Since the shortening of the phosphorescence decay with increasing temperature could be reversed, the effect was probably not due to diffusion of pyrazine into the spacer but rather to some phonon-assisted deactivation of the pyrazine triplet. In any event, the measurements reported here were all done at the lowest temperatures possible ($\sim 30\text{K}$), and presumably the influence of this thermal quenching process is minimized (or at least is constant for all the measurements).

Phosphorescence lifetimes for the pyrazine triplet were calculated by fitting the decay to a single exponential, and the results for unpolarized excitation (which are identical to the results for polarized excitation, to within experimental error) are listed in Table 3. The exponential fits are in general quite good, although the phosphorescence

Table 3

The observed phosphorescence decay times for a layer of pyrazine separated from a GaAs(110) surface by an ammonia spacer of thickness d

<u>$d(\text{\AA})$</u>	<u>$\tau(\text{msec})$</u>
20	0.04
50	0.48 - 0.87
75	1.4
110	5.6
200	11.6 - 12.0
425	12.4

decay did show a more rapid component at very short times following excitation. As in the case of silver, this short time behavior is attributed to pyrazine adsorbed near defect sites. The slight deviations from non-exponential decay (ignoring the initial rapid decay) and the signal-to-noise for each measurement were included in the estimate of the errors in the phosphorescence lifetimes.

The observed distance dependence of the pyrazine phosphorescence lifetime was compared to the predictions of CPS theory. The same model was used as for the pyrazine/argon/silver experiment: the pyrazine was placed $3\text{\AA}$ above and parallel to an ammonia spacer on GaAs(110). The optical constants were measured ellipsometrically during the experiment: $\tilde{\epsilon}(\text{GaAs}) = 12.5 + 17.0i$ and $\epsilon(\text{NH}_3) = 1.3$ at $\lambda=3800\text{\AA}$. The energy transfer rate was calculated using Eqns. (23)-(28). The best fit to the experimental measurements was achieved with a free pyrazine phosphorescence lifetime of 24 msec and a quantum yield of 0.7. The free molecular lifetime used compares well with literature values and with the value needed to fit the silver data. However, the phosphorescence quantum yield of 0.3 which was used in the silver work gives a poor fit to the absolute energy transfer rates on gallium arsenide while reproducing the distance dependence very well. (The predicted rates using this value of the quantum yield are significantly shorter than the experimentally determined rates on gallium arsenide.) The value of $\phi_p = 0.7$ needed to match the absolute lifetimes is nevertheless not inconsistent with other literature values for this quantity.^{29,38} The plot of the calculated distance dependence of the phosphorescence lifetime is shown with the experimental measurements in Figure 24.

Figure 24. Logarithm plot of the lifetime of $^3\pi\pi^*$ pyrazine above GaAs(110) vs. ammonia spacer thickness. The points are experimental values, and the solid curve is the behavior calculated from the Chance, Prock, and Silbey model (see text for details).

XBL 8210-11863

4. Discussion

The excellent agreement between the experimental and theoretical distance dependence of the energy transfer rate indicates that the essential molecule-semiconductor interactions are included in the simple model of the CPS theory. This model incorporates polariton excitation as well as the excitation of bulk interband transitions, and the relative contributions of these energy transfer mechanisms and photon emission are shown as functions of distance in Figure 25. (At these energies, however, the polariton modes are strongly coupled to the bulk interband excitations, just as in the case of germanium at 2.5eV (see Fig. 22). Thus, for gallium arsenide at the pyrazine emission energy, there are no discrete polariton modes, and the separation of the energy transfer to interband electron-hole excitations is rather artificial.)

The correct prediction of the distance dependence of the energy transfer rate indicates that the transfer to semiconductors occurs through the dipole near field. However, the inability of the theory to reproduce the exact transfer rates for the same lifetime and quantum yield of pyrazine used in the silver experiment could be an indication of a failure of the CPS model. If the coupling of the near field to the interband transitions were more efficient than CPS theory allows, that is, if the optical constants did not include all the interactions by neglecting some decay channel such as non-vertical interband excitations, then the actual decay of the dipole would be much faster than the theoretical predictions even though the measured distance dependence would be approximately in accord with theory. This

Figure 25. Calculated decay probability vs. distance for $^3_{n\pi^*}$ pyrazine on an ammonia spacer over GaAs(110).

XBL 8210-11889

possibility, that high wavevector components of the dipole field may be involved in exciting non-vertical interband transitions, can only be explored theoretically by treating the energy transfer interaction in a nonlocal picture, including the details of the semiconductor band structure.

Before a reliable comparison of the absolute experimental and theoretical energy transfer rates can be made, however, more accurate experimental measurements must be obtained. Increased signal-to-noise and temperature stability to avoid thermal quenching effects will yield better values for the phosphorescence lifetimes. Improvements in the sensitivity of the ellipsometer and more systematic surface preparation should also allow better determination of the spacer thicknesses.

The photophysical properties of pyrazine at an ammonia/vacuum interface should also be characterized so that the theoretical predictions for the energy transfer rate are uniquely determined. As was mentioned before, the value of the phosphorescence quantum yield for pyrazine which provided a good fit to the results on gallium arsenide ($\phi_p=0.7$) was not inconsistent with other literature values, which range from 0.3 to 1.0. If the photophysics of pyrazine actually is different for molecules on the argon/vacuum interface at 20K (as was the case in the silver experiment) than for those on the ammonia/vacuum interface at 30K (as in the GaAs work), then the CPS theory does demonstrate quantitative agreement with experiment.

5. Conclusion

The distance dependence of the phosphorescence lifetime of $^3n\pi^*$

pyrazine on GaAs(110) has been measured. The CPS theory correctly predicts the observed distance dependence, but quantitative agreement with the absolute transfer rates is only achieved by assuming a large (but realistic) value for the phosphorescence quantum yield. Thus the energy transfer seems to occur through the dipole near field, but the applicability of the CPS model to the description of the excitation of interband transitions by the dipole cannot be assessed without additional experimental work.

E. Implications of Energy Transfer

The electromagnetic interaction between molecules and surfaces has thus far been discussed within the context of energy transfer, but this coupling also has important consequences for the spectroscopic and dynamical properties of adsorbed molecules. For example, the enhancement of the Raman cross-section observed for molecules adsorbed on certain metal surfaces has been attributed, at least in part, to the coupling of the molecular polarizability to surface plasmon modes and to the metal electron gas through the image dipole field.³⁹ Surface photochemical reactions, too, are to a great degree dependent upon this dipolar coupling to the surface, for the evolution of a molecular excited state along a reactive pathway must compete with the quenching of the excited state through energy transfer to the surface.

Of greater importance to the discussion which follows in the next chapter of this dissertation are the implications of molecule-metal energy transfer to the spectroscopy of excited electronic states of adsorbed molecules. The classical image dipole theory predicts both a

frequency shift and a lifetime broadening of electronic states due to the interaction of the dipole with its own reflected field (see Eqns. (4) and (6)). These perturbations of the electronic absorption profiles could drastically alter the appearance of the spectrum by changing the energy ordering of the peaks and by obscuring fine structure (or the entire peak) through broadening effects. The complications in the detection and assignment of spectral features for chemisorbed layers could severely limit the utility of spectroscopic studies of these species.

The classical image dipole formulas of Eqns. (4) and (6) make specific predictions for the frequency shifts and lifetime shortening of electronic excited states based upon the optical dielectric response of the surface. Clearly the magnitudes of these changes will increase with the efficiency of the energy transfer, so the effects on the absorption spectrum should be greatest when molecules are very close to the surface or are excited to an energy coincident with good acceptor modes of the solid, such as the surface plasmon resonance energy.

As a direct test of these formulas for electronic excited states, electronic absorption spectra of aromatic molecules on silver (111) were measured by Demuth and Avouris using electron-energy-loss techniques.^{40,41} Here, the energies of the excited states were very close to the surface plasmon resonance of silver, and very large frequency shifts and broadenings were expected. However, the results of this study show at best ambiguous behavior when compared to the theoretical predictions. The excited state lifetimes, inferred from a lineshape analysis of the absorption profiles, were in approximate agreement with expectations based upon classical theory. In fact, the

observed maxima for the absorption peaks are all within 0.2eV of the corresponding absorptions in the gas phase-- much smaller than the predicted shifts. These apparently contradictory results of the test of image dipole theory could be, as the authors of that work argued, a demonstration of the failure of the image dipole model at short distances. As was described before, the calculation of energy transfer rates at short distances overestimates the contribution from high wavevector components of the dipole field when local dielectric constants are used. Thus the predicted energy shifts could conceivably be too large, a nonlocal dielectric description becoming necessary to correctly treat the problem. While the use of a nonlocal dielectric function would reduce the effect of very high wavevector loss mechanisms, presumably the introduction of the electron-hole dissipation channel would decrease the excited state lifetimes enough to produce a coincidental agreement with the lifetimes predicted by the local image dipole theory.

The discrepancy between the classical theory and experiment raises the whole issue of the applicability of any of the previously described energy transfer models to the discussion of chemisorbed molecules. Even the inclusion of some of the corrections to the local image dipole (CPS) formulation leaves serious doubt about the validity of the entire approach. All of the approximations involved will certainly negate any direct extension of the predictions to chemisorbed species. In addition to the obvious need for a microscopic treatment of the surface response, including the effects of the band structure of the solid, the concepts of a discrete dipole and the dipole-surface separation become meaningless when the valence electron cloud of the molecule penetrates

the electron gas of the surface upon chemical bond formation. The coupling between the chemically bonded entities will certainly not be pure electromagnetic field interaction but will have some through-bond component. Thus, the quantum description of the molecule-metal moiety seems essential to the prediction of "molecular" excited state energies and lifetimes.

The next chapter of this dissertation reports the results of optical studies of molecules chemisorbed on the nickel (111) surface. From the above discussion, clearly only qualitative predictions can be made about the effects of energy transfer on the spectra of chemisorbed species. One would expect the energy transfer rates to be quite large for molecules very near the nickel surface at near-UV frequencies, so the linewidths for "molecular" excited states of chemisorbed molecules may be broadened significantly. The bonding interaction for nickel is very strong, however, much stronger than for silver; thus, line broadening due to interaction with the dispersive band states of nickel could dominate any contribution from these dynamical effects.

To summarize, then, energy transfer from excited molecules can have profound effects on the outcome of many surface spectroscopic and photochemical studies. However, the approximate descriptions of this energy transfer at short distances have already been challenged, and at best will only be applicable where the direct interaction with the metal surface is not very strong (e.g., for physisorbed molecules). For chemisorbed layers, the entire foundation of the energy transfer formalism becomes tenuous, and the effects of this process on the observed spectrum become unpredictable or even insignificant when compared with the spectral changes caused by chemical bond formation.

Chapter III

CHEMISORPTION-INDUCED CHANGES IN THE OPTICAL RESPONSE OF THE NICKEL(111) SURFACE

A. Introduction

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.⁴²⁻⁴⁴ The success of experiments on small molecules on metal surfaces, particularly those on H₂, O₂, and CO on W⁴²⁻⁴⁴ and Ni^{45,46} 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)⁴⁷ indicate 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 linewidth revealing the details of the bonding interaction (rather than energy transfer effects, for example).

In this work, the visible-UV optical response of a series of molecules adsorbed on a single crystal nickel (111) surface has been measured. 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.

The results reported here indicate 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 $\sim 4.2\text{eV}$, which can be attributed to an enhancement of a bulk metal interband transition. The relationship of this transition to the bulk structure of nickel and the specific metal orbitals perturbed via chemisorption will be discussed.

B. Experimental

1. Apparatus

Full descriptions of the ultrahigh vacuum chamber and electronic circuitry are included in the doctoral dissertations of A. R. Gallo and D. A. Zwemer. A schematic diagram of the apparatus is shown in Figure 26. Briefly, the stainless steel vacuum chamber used in these experiments is pumped by 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 ion gauge. The predominant background gases are H_2 , Ar, CO, and CH_4 , in order of decreasing abundance as measured by a UTI 100C quadrupole residual gas analyzer. The chamber is configured in two levels. The upper level contains the liquid helium-cooled experimental stage, LEED/Auger optics, fused silica entrance and exit windows, and 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 in. diameter rod (Materials Research Corp., 99.999% purity). After a preliminary orientation of the surface within 2° of the (111) face by Laue x-ray backscattering, the back was ground parallel to the face. The 1/8 in. 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° of the (111) face. During the final polish in a slurry of $0.05 \mu Al_2O_3$, the

Figure 26. Schematic diagram of the ultrahigh vacuum chamber configured for spectroscopic ellipsometry. The spherical mirror depicted in the figure has replaced the lens/planar mirror combination described in the text.

SCHEMATIC VIEW OF UHV SPECTROSCOPIC ELLIPSOMETRY CONFIGURATION

XBL 819-6 642

surface was swabbed at 30 min. intervals with a solution containing glacial acetic, nitric, sulfuric, and phosphoric acids, in relative proportions 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 min. of 2 kV argon ion sputtering at an angle near 60° from the surface normal, 15 min. annealing near 600°C, then an additional 5 min. sputtering, followed by a final anneal for 20-25 min. The sample was heated by lowering the crystal-backing assembly into the prongs of an insulated stage, which can be raised to 5 kV 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 kV 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 10K, as evidenced by continuous condensation of H_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 2500Å, produced light of sufficient intensity to 2350Å free from broadband scattered light. The light exiting the monochromator was collected with a fused silica lens, reflected from a MgF_2 coated aluminum mirror, and passed through a MgF_2 Rochon prism input polarizer onto the sample surface. The reflected light passed through the quartz analyzer polarizer and was detected by an EMI 9558Q 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 the 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 the design of Aspnes. Detailed information regarding the operation, calibration, and data analysis involved in using this type of instrument may be found in Refs. 48 and 49. 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 analog-to-digital converter (ADAC Corp., Model 1030) interfaced to a laboratory microcomputer (Digital Equipment Corp., PDP11/03). 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 disk with 72 parallel cuts machined at equal intervals around the circumference. At one point on the disk, an additional hole is drilled between two cut-outs. Two optical encoders are aligned with this disk 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 0.5mm slits on the monochromator (10Å passband), and the data points were taken at 5Å intervals. Each point was averaged over 200 revolutions of the analyzer.

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 Δ . Auger and LEED results were obtained after the ellipsometric spectra were recorded to minimize the effects of electron beam damage to the overlayers.

Condensed layers of gases were prepared by adsorption while the crystal was cooled to 15K. Thicknesses were monitored ellipsometrically, and in some cases the overlayers were annealed at 150K and cooled back to 15K before spectra were taken.

2. Data acquisition and reduction

Following the final anneal 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 of 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 into the chamber, and progress of the adsorption is monitored ellipsometrically at a wavelength where the overlayer is presumably transparent. A second 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.

As an aid in understanding these experiments and their interpretation, a brief introduction to ellipsometry is presented here. The interested reader is referred to the extensive reviews of the subject^{50,51} and to the excellent summary of the theory and computer programs in the doctoral dissertation of H. J. Robota. 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, elliptical, due to the 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. In the simplest model, the reflecting system is 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 submonolayer 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. 51).

The quantities measured in ellipsometry may be expressed as

$$\rho = \frac{\tilde{r}_p}{\tilde{r}_s} = \tan \psi e^{i\Delta} \quad (1)$$

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

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

where n_0 is the refractive index of the ambient, $\tilde{n}_1$ is the complex refractive index of the substrate, and ϕ_0 is the angle of incidence with respect to the substrate normal. For any layered system, the Fresnel coefficients for a given layer j can be determined to be

$$\tilde{r}_{jp} = \frac{\tilde{n}_j \cos \phi_{j-1} - \tilde{n}_{j-1} \cos \phi_j}{\tilde{n}_j \cos \phi_{j-1} + \tilde{n}_{j-1} \cos \phi_j} \quad (3)$$

$$\tilde{r}_{js} = \frac{\tilde{n}_{j-1} \cos \phi_{j-1} - \tilde{n}_j \cos \phi_j}{\tilde{n}_{j-1} \cos \phi_{j-1} + \tilde{n}_j \cos \phi_j} \quad (4)$$

where now all refractive indices and angles are, in general, complex.

For the systems to be dealt with here, the three phase (ambient-overlayer-substrate) ellipsometric equation can be expressed as

$$\rho = \tan \psi e^{i\Delta} = \frac{r_{1p} + r_{2p} e^{-iZ}}{1 + r_{1p} r_{2p} e^{-iZ}} \times \left(\frac{1 + r_{1s} r_{2s} e^{-iZ}}{r_{1s} + r_{2s} e^{-iZ}} \right) \quad (5)$$

$$Z = (4\pi d / \lambda_0) (\tilde{n}_1^2 - n_0^2 \sin^2 \phi_0)^{1/2} \quad (6)$$

where d is the thickness of the overlayer and λ_0 is the vacuum wavelength of light. For all of the results presented here, the incident beam was about 60° from the surface normal and linearly polarized at 30° from the plane of incidence.

Unlike classical null ellipsometers, rotating analyzer systems of this type measure $\tan \psi$ and $\cos \Delta$, rather than ψ and Δ directly. For the metal systems investigated, the expected values of ψ and Δ are such that there is no ambiguity in converting from $(\cos \Delta, \tan \psi)$ to (Δ, ψ) 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 27(a) shows the result of $\delta\Delta$ and $\delta\psi$ for a $10\text{\AA}$ layer of condensed annealed pyrazine. For comparison, Figure 27(b) 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 $\delta\psi \approx 0$ and $\delta\Delta \approx d/\lambda_0$, so that the change in Δ 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 ψ and Δ . Due to the nature of the sample mount in this experiment, 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 $\pm 0.1^\circ$. 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.

The second uncertainty in the analysis is in the thickness of the overlayer. Complete characterization of the overlayer requires three

Figure 27. (a) The result of a simple difference spectrum ($\delta\Delta, \delta\psi$) for a 10Å 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. (b) Absorbance calculated from an iterative analysis assuming a 10Å thick layer. Compare the vibronic structure with that of a thick layer in Fig. 28.

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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 method³⁰ is that of Malin and Vedam, which was discussed in the energy transfer experiments of the preceding chapter. Measurements of ψ and Δ are made at several thicknesses during the course of the deposition, and 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 was 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.

The frequency-dependent complex refractive index represents the desired information about the response of the adsorbed overlayer, and

the method used to obtain these values is straightforward. Each experimental spectrum terminates in a region where the overlayer is expected to be transparent. The values of ψ and Δ measured for the bare and covered surface are used in a linear approximation expansion of the exact ellipsometric equations, which are applicable to layers where $d \ll \lambda$.⁵¹ An initial guess is made for d and the complex refractive index is calculated. Successive values for d are examined until k is minimized. This value of the complex refractive index and thickness are then used in an iteration scheme based on a Taylor expansion of ρ in the complex refractive index. Iterations are performed until the deviation of the calculated ρ value from measured ρ value is within expected experimental error. This represents the first value of the overlayer refractive index. The next point in the spectrum is analyzed in the same way, using the best fit refractive index from the previous point as the starting value for the iteration. The complex index is calculated at each point in the spectrum, and the final results are plotted as n and k vs. λ . Experience has shown that while the absolute values of n and k have a strong dependence on the chosen film thickness, the features in the spectrum remain undistorted until obviously erroneous thicknesses are used.

C. Results

1. Pyrazine, pyridine, benzene, and naphthalene on Ni(111)

The analyzed ellipsometric spectra of annealed condensed layers of pyrazine, pyridine, and naphthalene on Ni(111) at 15K are shown in

Figures 28-30. Intense absorption peaks with vibronic structure are evident. The spectrum of a thick layer of condensed benzene showed no absorption maxima in this wavelength region, only the apparent onset of a large peak at higher energies. These spectra establish the positions of the molecular absorptions in the adsorbed layer and will be useful in interpreting the spectra of the corresponding chemisorbed species.

Pyrazine, pyridine, benzene, and naphthalene all appear to chemisorb on Ni(111) at room temperature. Saturation of the surface occurs after 3-5 L exposures, with a final δA of about 0.5° - 0.7° at 3500Å. The adsorption of pyridine leads to a very diffuse LEED pattern visible only at low electron energies (Figure 31). 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 clean surface spot, annealing to 350K produces the pattern seen in Figure 32. Although no assignment of these patterns is attempted here, similar results were obtained on the Pt(111) surface.^{52,53}

The spectrum of each of these chemisorbed molecules is shown in Figures 33-36. Each absorption spectrum is dominated by one large, broad feature, which is centered at 2850Å in the case of pyrazine and benzene, and at 3050Å for chemisorbed pyridine and naphthalene. None of the molecules studied exhibited any absorption features in the visible region of the spectrum.

2. CO, O₂, and ethanol on Ni(111)

Figure 28. The analyzed absorption spectrum for a 40Å thick condensed, annealed pyrazine layer on Ni(111).

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Figure 29. The analyzed absorption spectrum for a 65Å thick condensed, annealed layer of pyridine on Ni(111).

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Figure 30. The analyzed absorption spectrum for a 25Å thick condensed, annealed layer of naphthalene on Ni(111).

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Figure 31. The LEED pattern of pyridine chemisorbed on Ni(111) at room temperature. The beam energy is 66eV. (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.

(b)

XBL 811-7806

Figure 32. The LEED pattern of naphthalene chemisorbed on Ni(111) at room temperature after annealing at 350K. The beam energy is 52eV. (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.

(a)

(b)

XBL 811-7805

Figure 33. The analyzed absorption spectrum of pyrazine chemisorbed on Ni(111).

Figure 34. The analyzed absorption spectrum of pyridine chemisorbed on Ni(111).

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Figure 35. The analyzed absorption spectrum of benzene chemisorbed on Ni(111).

Figure 36. The analyzed absorption spectrum of naphthalene chemisorbed on Ni(111).

XBL811-3570

The chemisorption of CO on Ni(111) yielded the familiar LEED pattern⁵⁴ after saturation at 3 L. The final $\delta\Delta$ was 0.6° monitored at 3000Å. The UV absorption spectrum is shown in Figure 37 and consists of a large, broad peak centered at 2800Å.

Adsorption of O₂ at room temperature appears to undergo a rapid chemisorption phase ($\delta\Delta=0.2^\circ$ at 5000Å, 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 $\delta\Delta=2.0^\circ$ and a LEED pattern characteristic of NiO after 300 L. The analyzed spectrum of chemisorbed O₂ is shown in Figure 38, and again a broad feature at 2900Å 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 39.

At room temperature, exposure of the crystal to ethanol leads to a disordered chemisorbed phase, with $\delta\Delta=0.3^\circ$ at 5000Å. The absorption spectrum of this species is shown in Figure 40 and exhibits a peak at 2750Å. For comparison, a spectrum of a 100Å thick layer of ethanol condensed on Ni(111) at 80K is shown on the same scale. No evidence of an absorption peak is visible in the condensed layer spectrum.

D. Discussion

The electronic absorption spectra of thick, annealed layers of pyrazine, pyridine, and naphthalene condensed on Ni(111) show intense peaks with sharp vibronic structure. As previously reported for pyrazine on Ni(111),⁵⁵ the peak energies and vibrational spacings agree

Figure 37. The analyzed absorption spectrum of CO chemisorbed on Ni(111).

Figure 38. The analyzed absorption spectrum on oxygen chemisorbed on Ni(111).

Figure 39. The analyzed absorption spectrum of epitaxial NiO formed after prolonged exposure of the Ni(111) surface to oxygen.

Figure 40. The analyzed absorption spectrum of chemisorbed ethanol (upper curve) and a 100Å layer of condensed ethanol (lower curve), shown on the same scale for comparison.

XBL8II-3568

well with those reported for the respective bulk crystals. (For a complete discussion of the assignments of these condensed layer spectra, see the doctoral dissertation of H. J. Robota.) The intense absorption peaks which occur near 2700Å in the spectra of pyrazine and pyridine are attributed to $\pi\pi^*$ excitations ($^1B_{2u}$ and 1B_2 , respectively).⁵⁶

Similarly, the absorption band in the spectrum of naphthalene is derived from two $\pi\pi^*$ transitions $^1B_{3u}$ and $^1B_{2u}$.⁵⁷ The additional feature in the condensed pyrazine spectrum at 3300Å corresponds to an $n\pi^*$ excitation out of a nitrogen lone pair molecular orbital. This good agreement with bulk crystal transition energies and vibrational spacings indicates that, for the case of weak interaction with the metal, the adsorbed molecules retain their molecular electronic structure and are only slightly perturbed by the metal surface.

In contrast to this behavior, the formation of a chemisorption bond has a very pronounced effect on the optical spectrum. All traces of the molecular transitions are lost, and a single intense, broad absorption band centered between 2800 and 3100Å (~4.2eV) 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 view of the strong interband excitations for the bulk nickel in this energy range,⁵⁸ it is likely that this spectral feature originates in chemisorption-induced modifications in the optical response of the metal substrate.

A physical mechanism for this effect is provided in a self-consistent calculation of hydrogen chemisorption to Pd(111),⁵⁹ which can

be taken as a prototype for Ni(111) chemisorption. The calculation of the electronic structure of the clean surface,⁶⁰ which reproduces experimental work function and photoemission results, exhibits eleven surface states and surface resonances (bulk orbitals with high electron density at the surface) throughout the projected two-dimensional Brillouin zone (see Figure 41). In particular, an sp-like surface state occurs in a gap along $\bar{\Gamma}$ (the [111] direction), and s-like surface states are found in energy gaps along $\bar{\Gamma}$ and $\bar{K}$ (the [110] direction). (In palladium, only the latter d-like surface states are filled. For nickel, in addition to these bands, the sp-like surface state is also occupied.)

Upon chemisorption, the intrinsic surface states on clean Pd(111) are all affected: some disappear, some move to lower energy, and some change their orbital character. Physically, the adsorbate orbital (in this case, the H atom) interacts with the metal orbitals at the surface (i.e., the surface states and resonances) to form bonding and antibonding combinations. The metal states involved in the bonding shift to lower energy (higher binding energy). If an intrinsic surface state, which can only exist in an energy gap, is shifted out of this gap, it rehybridizes with the bulk wavefunctions, effectively distributing its electron density into the interior of the solid. This disappearance of the surface state upon bonding is often called "quenching" of the surface state.

Accompanying these changes in the surface electronic structure of the metal are strong perturbations in the electronic orbital of the adsorbate. The details of the bonding/antibonding interactions will determine whether the bonding/antibonding metal-adsorbate "molecular"

Figure 41. Calculated two-dimensional band structure for the (111) surface of Group VIII metals (taken from Ref. 60). The surface states and resonances (indicated by the solid lines) occur in energy gaps and regions of low density of bulk states.

XBL 8210-11890

orbitals will be broadened through strong coupling to highly dispersive bulk bands. For hydrogen chemisorption on Pd(111), the hydrogen interacts with the d-like surface states. The strength of the interaction is much larger than the width of the d-band, so little broadening occurs. The bonding orbital for the adsorbate, being located far from the s-band, undergoes no further broadening and remains well-defined. The antibonding resonance, however, is degenerate with (unoccupied) s-like bands and is consequently highly dispersive. In this case then, a hydrogen resonance should be observable in photoemission, but no $\sigma\sigma^*$ transition should appear in the optical spectrum.

Experiments have clearly demonstrated these chemisorption-induced perturbations in the surface electronic structure. Reflectance studies of H_2 , O_2 , and CO on W(110)⁴² produced results very similar to the optical studies on nickel reported here. Enhanced absorption at the energies of bulk interband transitions was observed, accompanied by the 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), and concurrent rehybridization of the bulk bands leading to an increase of bulk interband excitation probabilities. This analysis was supported by UPS data and theoretical calculations demonstrating the existence of these surface resonances,⁴² and by subsequent studies of the anisotropy of the optical response of the adsorbate-covered surface.⁴³

This same mechanism can be used to explain the enhanced absorption in the Ni(111) optical spectrum at 4.2eV which accompanies chemisorption

in the experiments described in this work. According to this scheme, the increased oscillator strength of bulk transitions at this energy is derived from the rehybridization of (i.e., the quenching of) intrinsic surface states on Ni(111). Angle-integrated photoemission experiments performed at relatively low energy^{45,61} show the existence of a Λ_1 surface state near the L point (the [111] direction) which, for H_2 , O_2 , and CO adsorption at room temperature shifts to lower energy upon chemisorption and is ultimately quenched after very short exposures. Concurrent with the disappearance of this surface state, the bulk band which lies at the bottom of the energy gap, which also has Λ_1 symmetry, displays an increase in emission due to the rehybridization with the surface state.

Further support for this assignment of bands involved in the changes in the optical response comes from band structure calculations. In particular, the empirical band calculations of Smith, et al.,⁶³ adjust a first-principles band calculation so that good agreement is achieved with experimental values for the d-band position, d-band width, and the exchange splitting between the majority- and minority-spin s-bands. Computation of the optical response from this empirical band structure yields excellent agreement with measured peak positions and intensities, and the features in the optical spectrum can be attributed to transitions between specific pairs of bands.

Of special interest is the absorption at 4.7eV, the most intense feature in the theoretical spectrum. This peak is derived from transitions between one pair of bands (1+6), with major contributions to the joint density of states occurring at three points in the Brillouin zone (see Figure 42): along Σ (the Γ -K line) near the K point (the

Figure 42. Empirical bulk band structure of nickel showing the interband transitions responsible for the absorption features in the metal spectrum above 4eV (taken from Ref. 62).

XBL 8210-11891

[110] direction, along Δ (the Γ -X line) near the X point (the [100] direction), and along Q (the L-W line) near the L point (the [111] direction). Thus, there is an optical transition at 4.2eV which involves the lower sp-like band near the L point (which correlates to the A_1 bulk state). This and the photoemission results support the identification of the $A_1 \rightarrow A_3$ transition near the L point with the chemisorption-induced enhanced absorption in the optical spectrum.

Another feature of the optical spectra of aromatic hydrocarbons on Ni(111) which can provide some information as to the nature of the surface chemical bond is the disappearance of very 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),⁴⁵ no resonances from the adsorbate valence orbitals are observed in the photoelectron spectra of H_2 and O_2 on Ni(111). Presumably the adsorbate bonding orbital interacts so strongly with the s-band of the metal that it disperses over the entire width of the s-band (~6eV wide).

(Earlier photoemission results for hydrocarbons chemisorbed to Ni(111)⁴⁷ were used by those authors to demonstrate that the molecular orbitals of the adsorbate, even those involved with the bond formation, remain essentially intact after chemisorption. In this interpretation the adsorbate bonding orbitals seem to shift to higher binding energy and to broaden slightly. This broad resonance, however, occurred at ~5eV below E_F for all the adsorbates studied and could in fact be due to the same enhanced A_1 bulk band emission observed upon the chemisorption

of small molecules. Thus the conclusions which were drawn concerning the bonding to Ni(111) in that work must be questioned since they are based upon this assignment of the broad resonance to an adsorbate orbital.)

The removal of the Λ_1 surface state, the enhancement of the Λ_1 bulk states, and the apparently severe broadening of the adsorbate bonding levels, are all consistent with the picture of nickel bonding mainly through its s-like band states. This s-band participation in the chemisorption process has been proposed previously,^{45,63,64} especially in comparisons with chemisorption on Pd or Pt, where the d-bands play a much larger role. The difference in chemisorption behavior between nickel and palladium probably derives from two factors. First, as has been noted before,⁴⁵ the 3d orbitals of nickel are more tightly bound than the 4d or 5d orbitals of palladium and platinum, respectively, and thus the bonding through these d wavefunctions might be expected to be less favorable for nickel than for palladium. Second, the surface band calculations⁶⁰ indicate that the sp-like surface state on Pd(111) is empty, so interaction with the d-like surface states is the dominant bonding scheme. For Ni(111) the sp-like surface state is occupied and can interact with adsorbates to form a chemical bond.

Even though reaction through the s-bands seems to dominate the adsorption characteristics of Ni(111), one would expect that to some extent the d-like surface states predicted to exist would participate in the chemisorption process. Strong d-band interactions should be indicated by two features in the optical spectrum: the 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. (This presumes of course that the final state for the molecular transition is also not dispersed by interaction with metal s-bands. In the H/Pd(111) calculation,⁵⁹ the antibonding orbital was broadened greatly, so that no molecular-type excitation would be expected to be observable even though the bonding takes place mainly through non-dispersive d-band states.)

Recent photoemission studies of H/Ni(111) by Eberhardt, Greuter, and Plummer (EGP)⁴⁶ indicate that there is a low-temperature phase in which the nickel d-bands play a larger role in the formation of the chemisorption bond. Large changes in the emission from d-band states are observed, and a resonance attributed to the hydrogen orbital appears at 9eV below E_F . (Very similar d-band participation has also been noted for CO/Ni(111).⁵⁴) EGP suggest that at low temperatures the hydrogen atom sits in a three-fold site at the surface, bonding through nickel d-like surface states. At higher temperatures, the atom diffuses to a low-energy site below the surface layers. In this location, the atom can still interact with the nickel s-like surface states which penetrate deeper into the bulk than the d-like surface states.

Clearly this mechanism poses some problems in attempting to explain the room temperature chemisorption of large molecules. The optical spectra as well as photoemission results of these species suggest strong s-band interactions, but the probability is low that a large molecule like benzene interacts with s-like surface states by diffusing below the surface layer.

An alternative explanation is provided if one presumes separate bonding schemes for small atoms and large molecular adsorbates. The

proposal of EGP satisfactorily accounts for the different chemisorption phases of hydrogen on nickel. For larger molecules like naphthalene, which can interact with many surface atoms through its delocalized π system, it is conceivable that the overlap of the diffuse molecular orbitals with delocalized s-like metal surface states is much better than with the localized d-like states. Thus, although the details of the chemical bonding for hydrogen and benzene would be quite different, the resulting interaction with the same s-like surface state would lead to very similar perturbations in the optical and photoelectron spectra.

It is clear that without further experimental data the proposed explanation of the chemisorption behavior of nickel is far from conclusive. However, this type of analysis points out the utility of this combination of experimental and theoretical probes in attempting to elucidate details of chemisorptive bonding. Future efforts in this direction should include optical spectra over very wide energy ranges (to identify the initial surface state transitions before chemisorption, as was done in the tungsten reflectance studies), and angle-resolved photoemission of large molecules at different temperatures. These investigations combined with improved surface electronic structure calculations will ultimately provide a complete picture of the nature of the surface chemical bond.

E. Conclusion

The optical response of molecules chemisorbed on Ni(111) has been measured in the visible-near UV region. The observed absorption peak at 4.2eV is assigned to an enhancement of the $A_1 + A_2$ interband excitation

near the L point of the Brillouin zone (i.e., in the direction of the surface normal). These results suggest that the adsorbates interact strongly with the nickel s-band states in forming the chemisorption bond.

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