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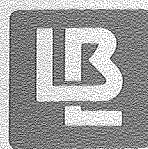
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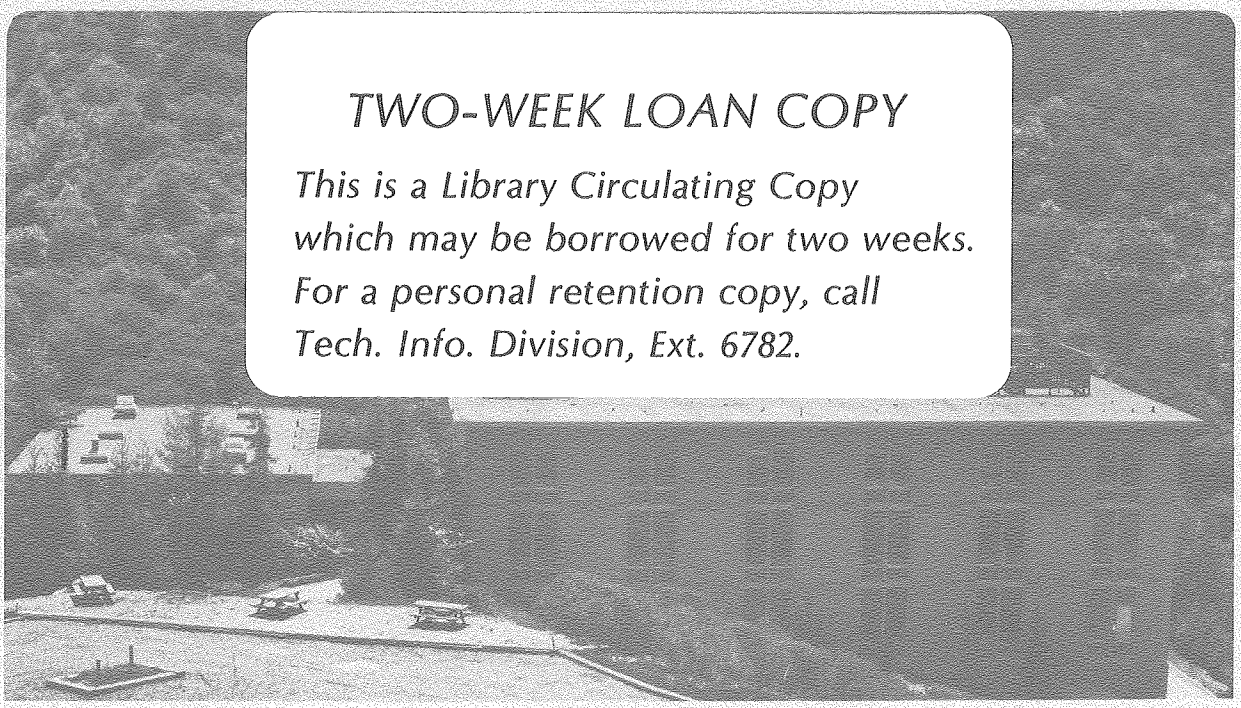
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C. B. Harris, A. Campion, A. R. Gallo,  
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Electronic Energy Transfer to Metal Surfaces: A Test of  
Classical Image Dipole Theory at Short Distances

by

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Abstract

We have measured electronic energy transfer from molecules to metal surfaces at distances less than  $50\text{\AA}$ . A monolayer of a luminescent molecule is separated from a single crystal metal surface by a layer of physisorbed argon. The luminescence quantum yield is measured as a function of the argon spacer thickness. A cubic distance dependence is observed over five orders of magnitude in the emission and is in agreement with classical image dipole theory even for molecule-surface separations as short as  $7\text{\AA}$ .

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There is considerable interest in the optical properties of metal surfaces and molecules adsorbed on them because it provides a way of determining the physical and chemical changes the surface environment induces on the molecular and electronic structure of the adlayer. Energy transfer occurring near interfaces is also of great importance since it ultimately determines the photochemical routes (if any) available to molecules on metal surfaces.

From a more fundamental point of view, measurements of optical properties of molecules near metal surfaces allow one to ascertain the correct microscopic description of an oscillating charge distribution near a conducting plane. This difficult problem is beginning to receive theoretical attention<sup>1</sup>. A classical<sup>2</sup> or semiclassical approach based on Maxwell's equations might be expected to break down at very short distances since they do not correctly describe the distance dependence of the electric fields. There are three potential difficulties with the classical approach.

The first problem is that the field does not change discontinuously as required by a sharp geometric boundary condition. In reality at short distances the fields change continuously and can even behave in an oscillatory fashion<sup>3</sup>. The second difficulty is that classical theories use a long wavelength approximation for the dielectric function of the metal, which implies that the function is local. Finally, classical theories usually represent a molecule on or near a surface in the presence of an incident radiation field as a point dipole<sup>4</sup>, when in fact, the finite spacial extent of the charge distribution can be of the same dimension as the distance to the surface. Therefore, it is important to test the validity of classical

theory for distances on the order of molecular dimensions in order to determine if these difficulties will produce observable deviations from predicted behavior.

In this letter we report a series of experiments on a single crystal Ni(111) surfaces which test the validity of classical theory to 7Å above the surface.

The distance dependence of the fluorescence quantum yield of a molecule near a metal surface is well understood for distances between 50Å and several thousand Angstroms and is based entirely on classical considerations<sup>5-8</sup>. A series of experiments by Kuhn and Drexhage using the Langmuir-Blodgett technique<sup>9</sup> has shown that at large distances, the quantum yield is reduced from the free molecule value by radiative transfer to the absorbing metal. There are also oscillations in the quantum yield which arise from interference between directly emitted photons and those that are reflected from the surface. At distances shorter than about 200Å the quantum yield begins to fall rapidly as non-radiative energy transfer to the surface plasma or other modes of the metal begins to occur.

A complete, classical theory of this energy transfer problem has been published recently by Chance, Prock and Silbey<sup>8</sup>. The key assumptions of the classical theory are: (1) that the molecule may be represented as a point-dipole oscillation, (2) that the dielectric constant of the metal is  $\vec{k}$ -independent, (3) that all the boundaries are infinitely sharp. With these assumptions, the expression for the energy transfer rate at distances such that  $d \ll \lambda$  is

$$W_{ET} = \frac{W_R}{4\pi d^3} \operatorname{Im} \left\{ \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} \right\}$$

where  $w_R$  is the radiative rate constant,  $\hat{d} = 2\pi d/\lambda$ ,  $\epsilon_2$  is the complex dielectric constant of the metal, and  $\epsilon_1$  the dielectric constant of the spacer layer, both at the molecular emission wavelength  $\lambda$ . Therefore, the quantum yield is

$$\phi = 4\hat{d}^3 \left( \text{Im} \left\{ \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} \right\} \right)^{-1}$$

The important functionality to be noted is the cubic dependence on distance,  $d$ , when  $d \ll \lambda$ . When proper boundary conditions are imposed, the CPS theory analytically agrees with the experiments of Kuhn and Drexhage down to  $25\text{\AA}^{10}$ , which is the minimum separation obtained with the Langmuir-Blodgett technique.

In the remainder of this letter we wish to address the question: *Is classical theory valid for energy transfer as the molecule-surface separation approaches molecular dimensions (<50Å)?* To answer this, we have tested the theory under well-defined UHV conditions on Ni(111) from  $100\text{\AA}$  to  $7\text{\AA}$  by measuring the emission from the  $^3n\pi^*$  state of pyrazine (1,4 diazobenzene) as a function of its distance from the Ni surface.

A nickel (111) single crystal was mounted on a variable temperature (10-300<sup>o</sup>K) cold tip modified for UHV use (base pressure  $\sim 2 \times 10^{-10}$  torr). The crystal could be removed from the variable temperature tip for annealing at higher temperatures and was cleaned by consecutive argon ion sputtering and annealing cycles. The surface cleanliness and order were checked using Auger electron spectroscopy and low-energy electron diffraction, respectively. The surface was atomically well-ordered as evidenced by sharp LEED spots and a low background intensity and oxygen, carbon and nitrogen impurities were below 1% as determined by Auger analysis.

Pyrazine phosphorescence from the Ni surface was excited by a filtered medium pressure Hg arc, using unpolarized radiation incident at  $60^\circ$  to the surface normal. The phosphorescence was collected normal to the surface using  $f/1.5$  collection optics. The emission was isolated using glass filters and its intensity recorded using photon counting. Care was taken to ensure that only radiation from the central portion of the crystal was imaged onto the photomultiplier, to avoid complications arising from emission from the sample mount or crystal edges. Since the electronic structure of pyrazine on Ni(111) in the physisorbed state was determined,<sup>11</sup> it was possible to show that the emission monitored in the experiment is from the triplet manifold. Figure 1(a) illustrates the electronic structure of the  $S_0 \rightarrow S_1$  transition characteristic of a  $9\text{\AA}$  layer of pyrazine physisorbed on Ni(111). The spectrum was obtained using ellipsometric spectroscopy<sup>12</sup>. The excitation spectrum illustrated in figure 1(b) demonstrates that the phosphorescence monitored in the  ${}^3n\pi^*$  region originates from the singlet state via intersystem crossing even when the pyrazine is in close proximity to the nickel surface as a physisorbed thin film.

In order to measure the distance dependence of the quantum yield a layer of condensed argon was used to separate the pyrazine from the surface. The deposition of the argon onto the cold ( $10^\circ\text{K}$ ) surface was monitored and controlled by an automated ellipsometer. After depositing the desired thickness of argon, a  $5\text{\AA}$  thick layer of pyrazine, which is slightly more than a monolayer was deposited.

Figure 2 shows the dependence of the phosphorescence emission intensity as a function of the argon spacer distance. The data are plotted as log-log and the least squares slope of the resulting line is 3.07. This cubic dependence of the transfer rate upon distance is consistent with



the predictions of the classical treatment and confirms the classical image dipole theory down to the shortest (7Å) distance that we could measure. This distance corresponds to only two argon layers.

Several points should be noted here. First, in the pyrazine-Ni(111) case studied above, the coupling of the molecular dipole to the Nickel surface plasmon states is expected to be weak since the peak in the Nickel plasmon density of states function is at 8.1 eV<sup>13</sup> while the pyrazine emission is at 3.3 eV.<sup>14, 15</sup> Indeed, it is this feature that allows us to measure the distance dependent quantum yield to such close distances. Recently, it came to our attention that the effect of the surface plasmon dispersion has been partially tested<sup>16</sup> by studying the  $^2D \rightarrow ^4S$  emission in N<sub>2</sub> thin films on sapphire, silver and potassium. The results of these experiments also confirm classical theory. However, the authors could only study the decay at distances greater than 30Å.

In conclusion it should be noted that the method we have outlined should be generally applicable to the study of energy transfer processes occurring near surfaces. Moreover with a suitable choice of molecule and metal and with greater excitation intensities it should be possible to follow the energy transfer processes down to the point where the molecule is in intimate contact with the surface in either a physisorbed or chemisorbed state.

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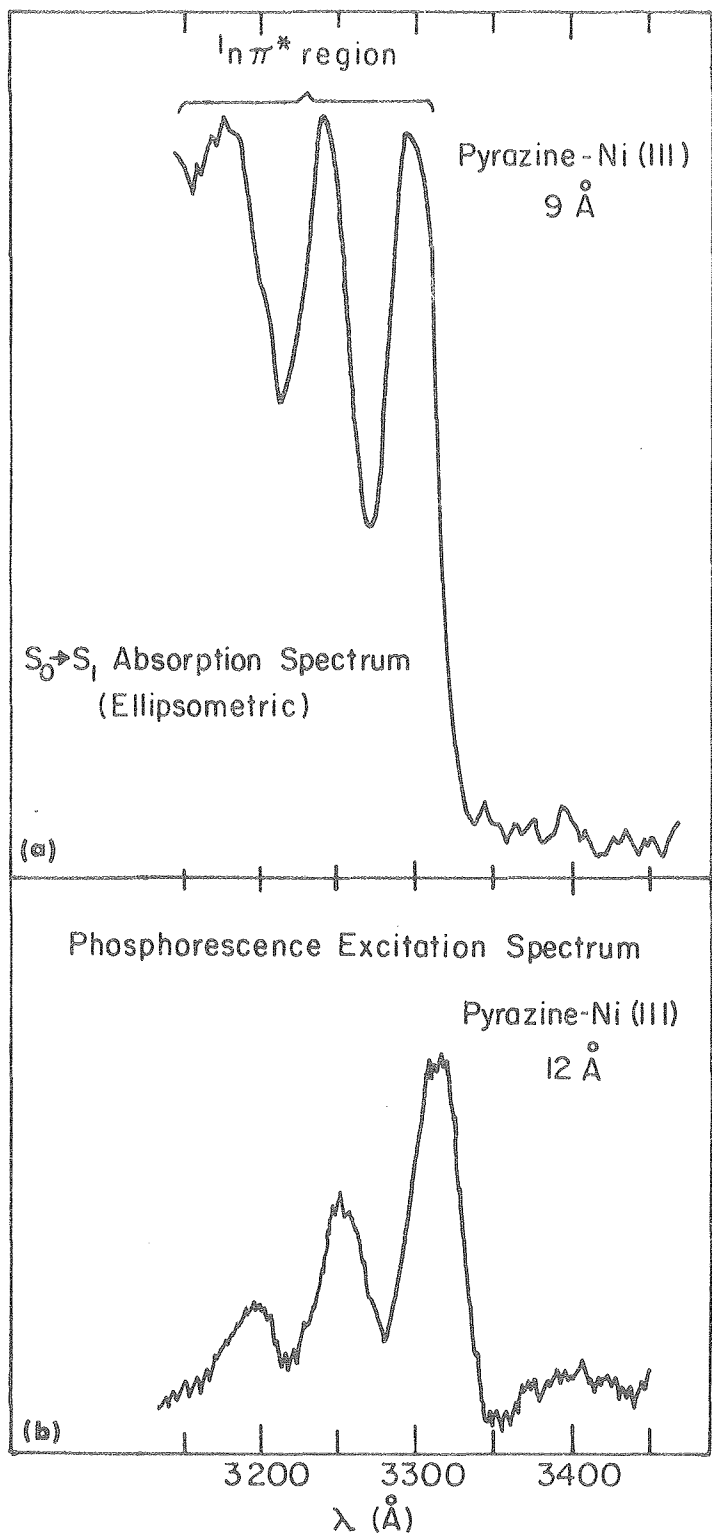
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Figure Captions

Figure 1(a): Resolved vibronic structure of the  $S_0 \rightarrow S_1$  transition in a  $9\text{\AA}$  layer of pyrazine condensed on a Ni(111) surface. (b) The phosphorescence excitation spectrum of a  $12\text{\AA}$  layer of pyrazine condensed on Ni(111).

Figure 2: The observed pyrazine phosphorescence intensity demonstrating the  $d^3$  dependence on the argon spacer layer thickness.



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Figure 1

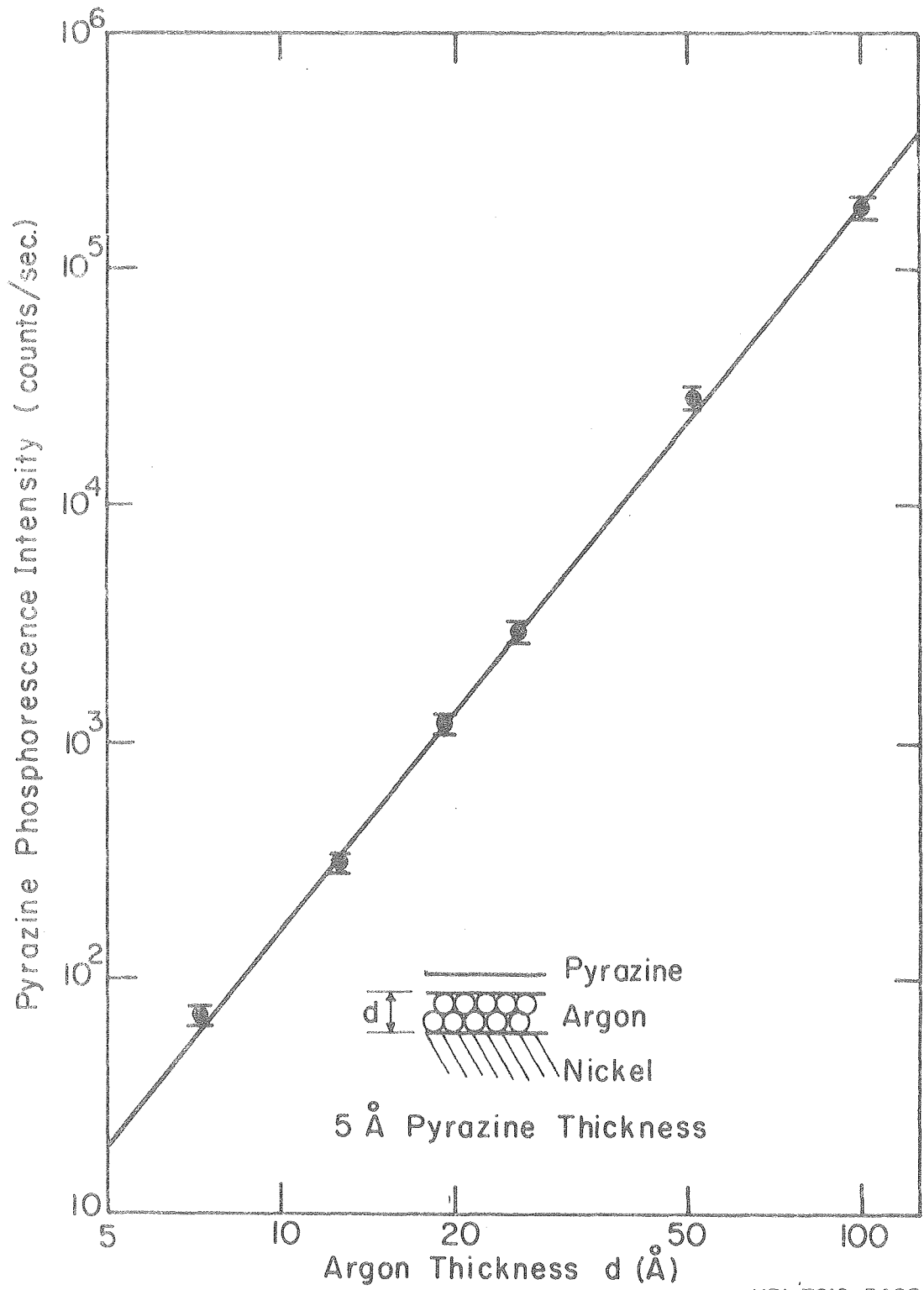


Figure 2