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P.M. Whitmore, H.J. Robota, and C.B. Harris

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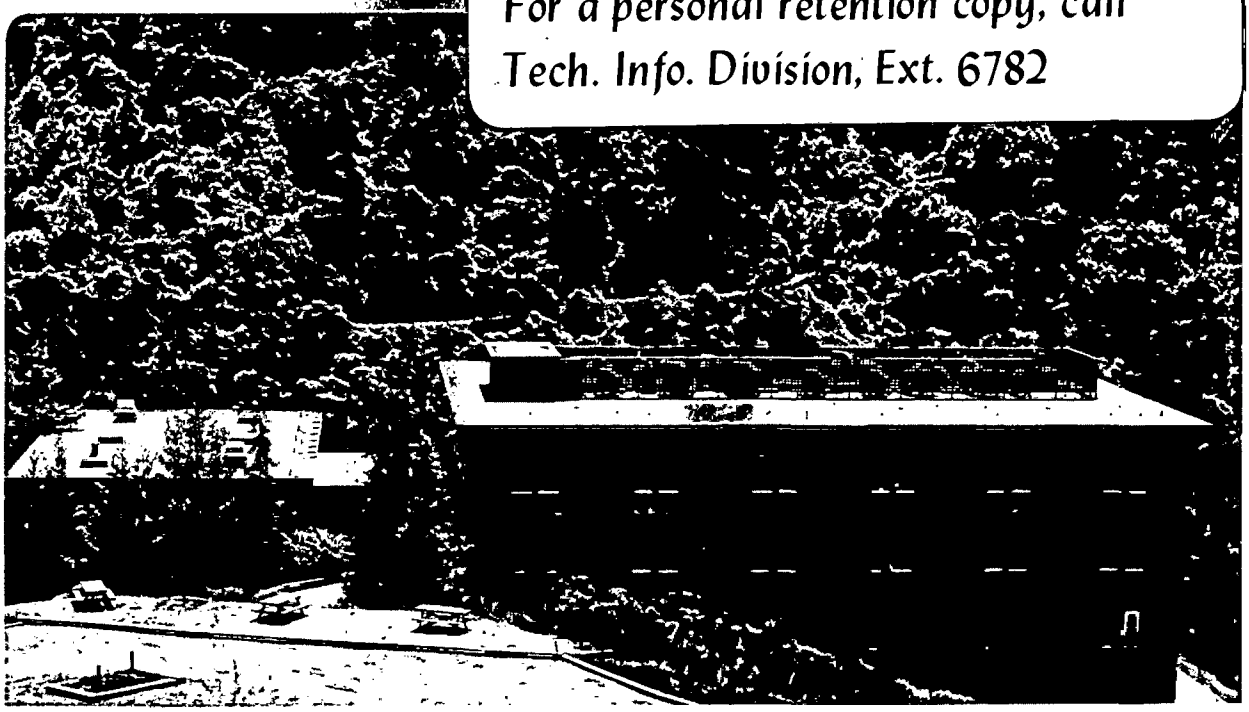

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Electronic Energy Transfer From Pyrazine to a Silver(111) Surface Between 10Å and 400Å.

by

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ABSTRACT

The phosphorescence lifetime of pyrazine molecules above a Ag(111) surface has been measured as a function of molecule-metal separation between 10Å and 400Å. In contrast to the previous work on the pyrazine/Ag system, we find that the lifetime decreases monotonically as the pyrazine approaches the metal surface. The distance dependence of the phosphorescence lifetime is described quantitatively using the classical treatment of non-radiative energy transfer of Chance, Prock, and Silbey.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number W-7405-ENG-48, and by the San Francisco Laser Center, a National Science Foundation Regional Instrumentation Facility, NSF Grant No. CHE79-16250 awarded to the University of California at Berkeley in collaboration with Stanford University.

Significant controversy has arisen regarding the applicability of a rigorous classical theory for the description of electronically excited molecules near a metal surface. The origin of this dispute is the finding of Rossetti and Brus (RB)[1] that the lifetimes of phosphorescing pyrazine molecules at distances less than 100Å from an evaporated silver surface remain approximately constant. This is in complete disagreement with the classical prediction that the excited state lifetime should decrease rapidly as the molecule approaches the surface due to rapid and efficient non-radiative energy transfer[2,3]. Further, all previous experimental work on a variety of substrates and excited species has shown excellent agreement with the classical theory to distances of 5Å to 10Å for a molecule above a metal surface[2,4-8]. The RB result is particularly troublesome in light of the continuing uncertainty as to the origin of anomalously large Raman scattering probabilities for molecules near silver surfaces.

It is the purpose of this communication to report our findings for the distance-dependent phosphorescence lifetime of pyrazine above a Ag (111) single crystal surface at 20K. We find excellent agreement with the predictions of the classical theory for pyrazine surface separations down to 10Å. Another unexpected result reported by Rossetti and Brus was a marked biexponential behavior of the phosphorescence decay for separations smaller than 500Å. As the separation was decreased, they observed a constant long lifetime component which dominated their decay and a short lifetime component which reached a limiting value near 100Å separation. We find that the time-dependent emission is described quite well by a single exponential decay throughout the entire range of surface-molecule spacings. Only for distances less than 50Å is there a suggestion of multi-exponential decay. We believe this is due to variations in the molecule-metal separations resulting from small surface

irregularities or irregularities in the adsorbed pyrazine layer.

Assemblies consisting of a single crystal silver(111) surface, condensed layer of argon, and final monalayer of pyrazine were prepared in an ultrahigh vacuum chamber with typical operating pressure $\lesssim 1 \times 10^{-10}$ torr. The thicknesses of the argon films and the pyrazine layers were monitored with a rotating analyzer ellipsometer at 3000Å incident wavelength. Phosphorescence spectra for such assemblies revealed the maximum absorption of the pyrazine $^1n\pi^*$ 0-0 vibronic band to be near 3270Å, and the emission of the $^3n\pi^*$ 0-0 band occurred at 3870Å. For the time-dependent phosphorescence decay measurements, the pyrazine was excited at 3270Å with a 10 nsec. pulse from the doubled output of a Quanta-Ray Nd:YAG pumped dye laser operating with DCM dye. The phosphorescence was collected within the vacuum chamber by a one inch f/1 lens. Outside the chamber the emission was focussed through Schott UG 375 and Corning CS 7-54 glass filters onto the photocathode of a photomultiplier. Time response of the phosphorescence was measured with a Biomation 8100 transient digitizer. The lifetimes were calculated by fitting each decay curve to a single exponential. The results are shown as the points in Fig. 1.

The theoretical distance dependence of the pyrazine phosphorescence lifetime was calculated from the classical equations of Chance, Prock, and Silbey[2,9]. Numerical integration of these equations yields the solid line shown in Fig. 1. The model used for the calculation places the emitting molecule 3Å above the argon layer and assumes the radiating dipole to be oriented parallel to the surface. This is a reasonable assumption in this case since the phosphorescence emission is polarized along the N-N axis of the molecule, and under our adsorption conditions it is most probable that the

pyrazine molecules were aligned with their rings parallel to the surface. Also, the lifetime is measured through the radiative decay channel, and dipoles parallel to the surface have a radiative decay probability substantially greater than dipoles oriented normal to the surface. The dielectric constants for argon and silver used in the calculation were $\tilde{\epsilon}(Ar) = 1.44$ and $\tilde{\epsilon}(Ag) = -3.6+.15i$ as determined ellipsometrically during the course of the investigation. The emission wavelength is taken as 3800Å with a quantum yield of 0.33. An infinite separation lifetime of 25 msec gives a good fit to the data.

As can be seen from Figure 1 there is excellent agreement between the theoretical and experimental values for separations throughout the range studied (10Å to 400Å). A rigorous, completely classical treatment seems to quantitatively describe the behavior of radiating molecules near a metal surface to very short distances. The question naturally remains at what point quantum corrections will become evident for very small separations. However, since the classical theory predicts such a rapid decrease in the lifetime and probability for photon emission in the very short separation regime, the nature and degree of deviations from classical behavior will be extremely difficult to detect with present methods.

Acknowledgements: This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract Number W-7405-ENG-48. The authors are extremely indebted for the support of the San Francisco Laser Center, a National Science Foundation Regional Instrumentation Facility, NSF Grant No. CHE79-16250 awarded to the University of California at Berkeley in collaboration with Stanford University.

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Figure Caption

Figure 1: Phosphorescence lifetime of $^3n\pi^*$ pyrazine at 20K as a function of distance to the Ag(111) surface. The points are the experimental measurements. The line is the lifetime calculated using the classical model of Chance, Prock, and Silbey (see text for details of the calculation and Ref. 2 and 9 for relevant equations.)

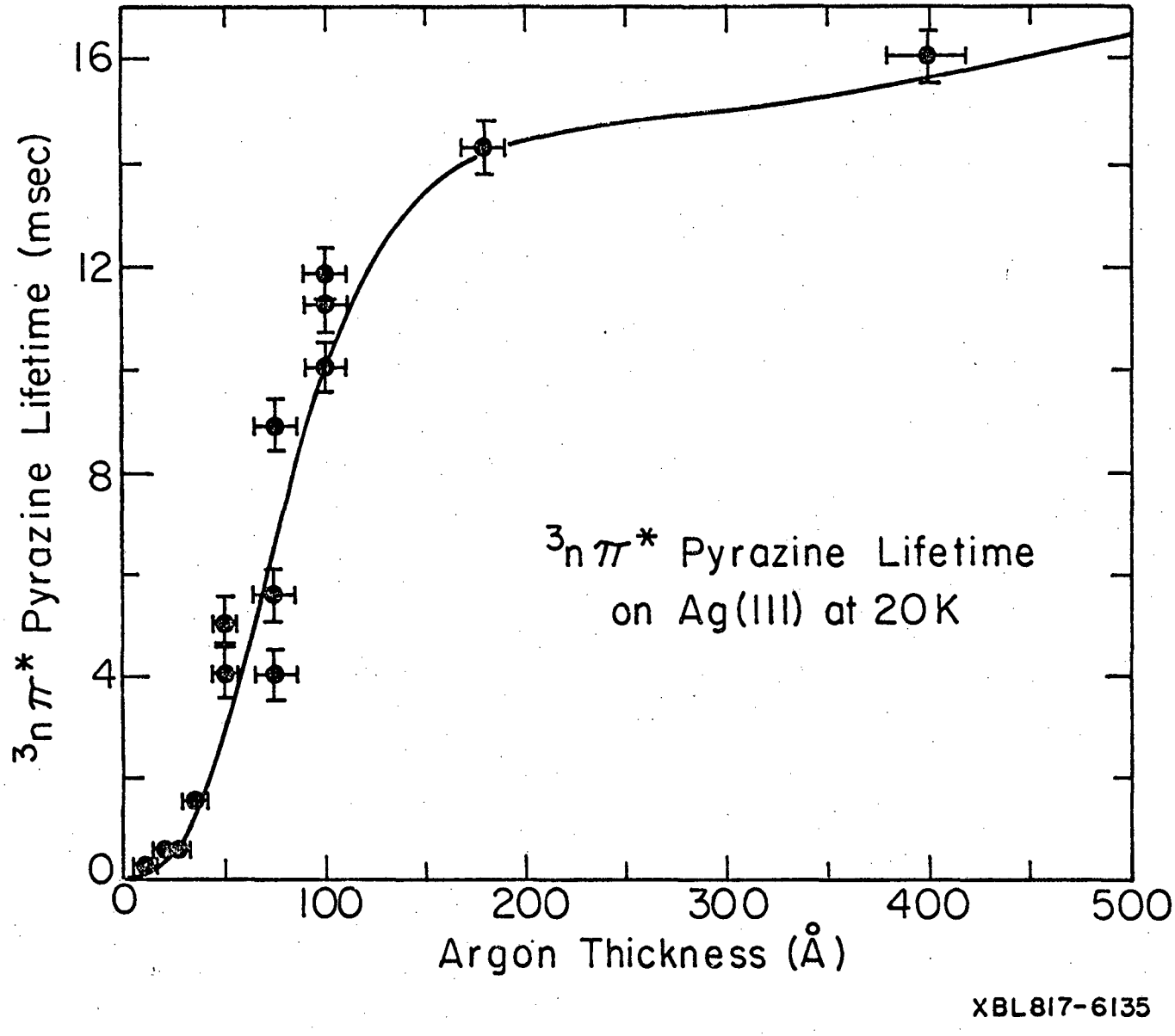
16
12
8
4
0
0
100
200
300
400
500
$^3n\pi^*$ Pyrazine Lifetime (msec)
Argon Thickness (Å)
$^3n\pi^*$ Pyrazine Lifetime
on Ag(111) at 20K
XBL817-6135

Figure 1

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