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P.M. Whitmore, A.P. Alivisatos, and C.B. Harris

February 1983

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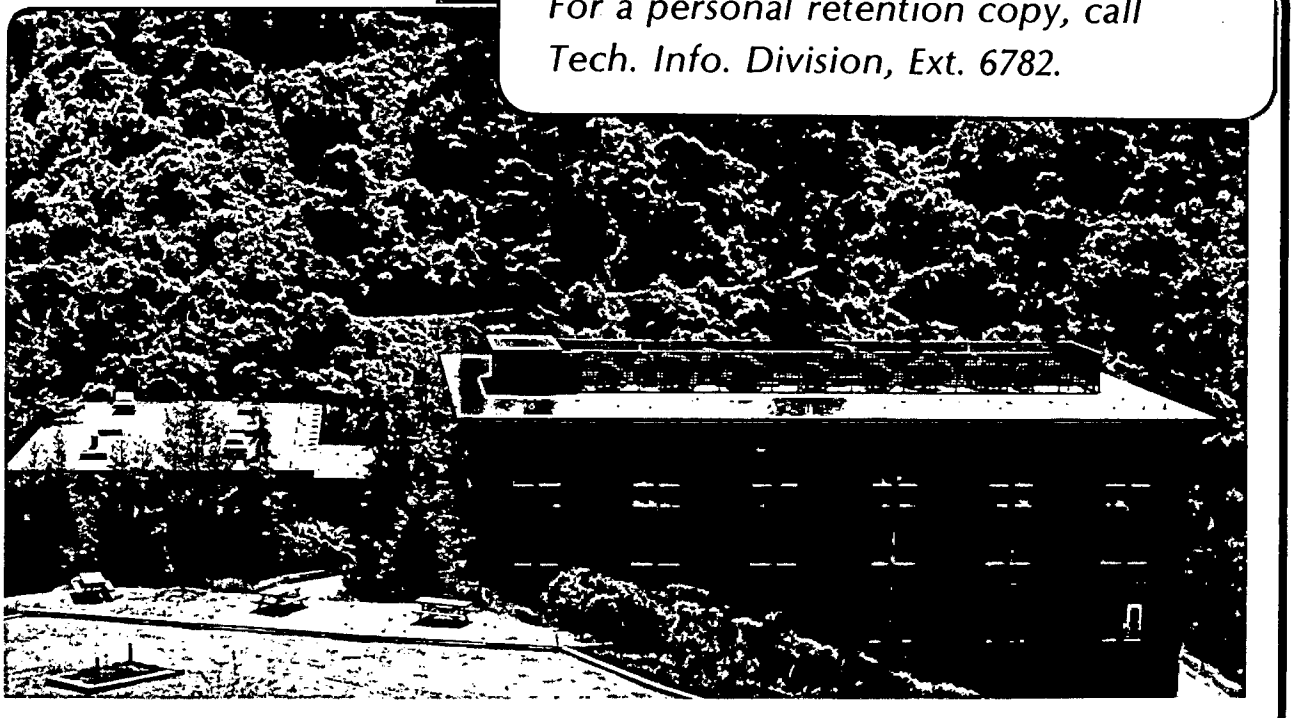

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Electronic Energy Transfer to Semiconductor Surfaces: $^3n\pi^*$ pyrazine/GaAs(110)

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Energy transfer from $^3n\pi^*$ pyrazine to GaAs(110) has been studied. Within experimental error, a classical dielectric model quantitatively reproduces measurements of the distance dependent lifetime for emitter-surface separations from 430Å to 20Å. Analysis of the energy transfer shows that the molecular electronic excitation is dissipated through the creation of electron-hole pairs in the solid by the high wavevector components of the dipole near field.

PACS numbers: 82.65Nz, 68.54-v, 82.20Rp

All direct experimental tests to date on electronic energy transfer from an excited atom or molecule to a metal surface indicate that a simple, classical image dipole theory is adequate to describe the phenomenon down to 10Å, the smallest molecule-metal separartion for which data has been obtained.[1-7] This problem was first modelled by Chance, Prock, and Silbey

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(CPS)[7] by calculating the through-space electromagnetic interaction between an oscillating dipole and a surface with a local (i.e., wavevector independent) dielectric response using an approach developed by Sommerfeld.[8] The success of the CPS formalism for a wide variety of molecule-metal systems supports the view that an excited atom or molecule can be treated as a point dipole over a semi-infinite isotropic dielectric medium, where the dominant modes of energy dissipation in the metal are included in the local (optical) dielectric response of the metal. That is, the dipole field drives surface currents in the free electrons which in turn lose energy by scattering from electrons phonons, impurities, or by resonantly exciting electron-hole pairs.

The transfer of energy from molecules to metal surfaces occurs through the free electrons of the solid, and is in general very efficient, and also amenable to relatively simple theoretical modelling. In insulating materials and intrinsic semiconductors at low temperature, however, the dielectric response, which reflects the acceptor modes for the excitation energy, is dominated by the contribution of the bound electrons and the band structure of the electronic states in the crystal lattice. Consequently, it is not at all clear whether an energy transfer theory which uses a classcal model of the dielectric response function would be as successful for semiconductor surfaces as it has proven to be for metals.

In this letter we report the first experimental and theoretical investigation of electronic energy transfer from a molecule to the surface of an intrinsic semiconductor. The system chosen for this initial investigation was triplet $n\pi^*$ pyrazine(1,4-diazabenzene)/GaAs(110). The phosphorescence lifetime of the molecular triplet state was measured as a function of molecule-semiconductor separation, which was controlled by means of a variable thickness frozen ammonia spacer layer. The pyrazine emission occurs at

3800Å(3.3eV) and this coincides with a large absorption in the gallium arsenide due to the $\Lambda_3 - \Lambda_1$ interband transition.[9]

The low temperature UHV appparatus employed in the experiments has been described in detail elsewhere.[1] Briefly, polished undoped (carrier concentrations $<10^{14}$ /cm^3) single crystalline GaAs(110) wafers (Crystal Specialties,Inc.) were clamped to an aluminum block and cleaned with several argon ion bombardment/anneal cycles. LEED and Auger tests showed that this procedure yields reasonably clean, well-ordered surfaces, although trace amounts of residual surface carbon often remain. The aluminum holder was then mounted in a liquid helium cold tip, and ultimate temperatures of about 30K were obtained. Ammonia spacers were condensed on the gallium arsenide surface, and the spacer layer thicknesses were meaured with a rotating analyzer ellipsometer. Monolayers of pyrazine were then condensed on the ammonia spacers. The pyrazine phosphorescence was excited at 3120Å with an unpolarized second Stokes pulse (10ns duration) from an H_2 Raman-shifted KrF excimer laser (Lambda Physik EMG101). The emission was isolated with colored glass filters, detected by a photomultiplier, and time-resolved and stored with a transient recorder interfaced to a computer. Measurements were made for ammonia spacer thicknesses between 20Å and 430Å, and phosphorescence lifetimes were calculated by fitting the luminescence decay with a single exponential. The results are shown as points in Fig.1.

The observed distance dependence of the pyrazine phosphorescence lifetime was compared to the predictions of the CPS theory. The model used in the calculation placed the pyrazine 3Å above the ammonia spacer and oriented parallel to the surface of the gallium arsenide. The dielectric constants were measured ellipsometrically during the ammonia depositions: $\varepsilon(GaAs)=12.5+17.0i$ and $\varepsilon(NH_3)=1.7$ at $\lambda=3800$Å. The energy transfer rate was calculated using the

appropriate equations from ref.10 and the result for the lifetime vs. spacer thickness is shown as the solid curve in Fig.1. The best fit to the experimental measurements was obtained by using a free molecular lifetime of 24ms and a quantum yield of 0.7 for the molecular emission.

The CPS model reproduces, within experimental error, the qualitative dependence of the phosphorescence lifetime on molecule-semiconductor separation. The lifetime is observed to decrease monotonically with decreasing separation, and an approximate cubic distance dependence is measured, as predicted by CPS theory. The calculation also reproduces the absolute lifetime measurements to within experimental error (due mainly to uncertainty in the spacer thickness measurements); yet the discrepancies at short distances are quite large, and the possibility of a distance dependence slightly greater than d^3 cannot be entirely discounted without more accurate measurement.

The success of the CPS theory suggests that the dominant mechanisms for energy transfer in the pyrazine/GaAs system are included in the local dielectric constant of the solid. Calculations of the wavevector dependence of the energy transfer rate (i.e., the contribution of each of the different wavevector components of the dipole near field to the energy transfer), illustrated in Fig. 2., show that almost all of the energy is transferred through the high wavevector components of the dipole field, generating electron-hole pairs in the solid. The shoulder which appears just above the photon wavevector (u=1) corresponds to polariton excitation in the bulk. This decay mechanism is important for the transfer of energy to semiconductors below the onset of strong interband absorptions (for example, in GaAs at 5000Å). However, the polariton modes are unimportant for the energy transfer in the pyrazine/GaAs(110) system, since they are short-lived and decay quickly into interband excitations.

In conclusion, we have shown that the classical image dipole description of electronic energy transfer can be applied to the transfer to GaAs(110) at 3.3eV down to 20Å. The dominant decay mechanism is the transfer of energy to interband electron-hole excitations of the semiconductor through the high wavevector components of the dipole near field. Experiments are now underway to explore the energy transfer at very short molecule-semiconductor separations, and to study the energy and free carrier concentration dependence of the energy transfer behavior.

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 No.DE-AC03-76F00098. The laser was borrowed from the San Francisco Laser Center, supported by the National Science Foundation under Grant No.CHE79-16250 awarded to the University of California at Berkeley in collaboration with Stanford University.

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FIGURE CAPTIONS:

FIG. 1. Logarithm plot of the lifetime of $^3n\pi^*$ 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).

Fig. 2. The wavevector spectrum of the energy transfer calculated for the $^3n\pi^*$ pyrazine/ammonia/GaAs(110) system. The wavevector, u, has been normalized to the photon wavevector. The appropriate geometry and optical constants are described in the text.

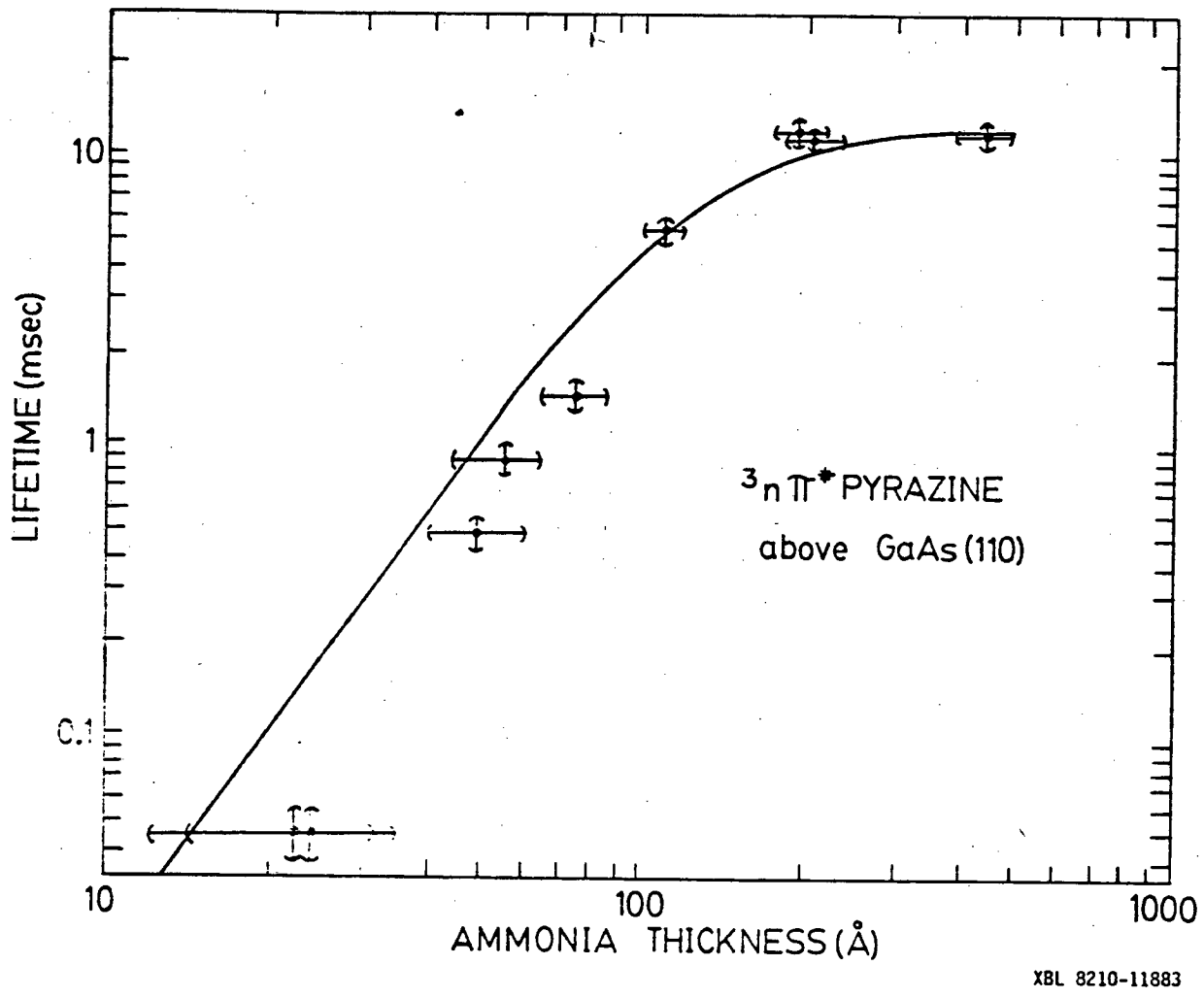
LIFETIME (msec)
10
1
0.1
10
100
1000
AMMONIA THICKNESS (Å)
$^3n\pi^*$ PYRAZINE
above GaAs (110)
XBL 8210-11883

Figure 1

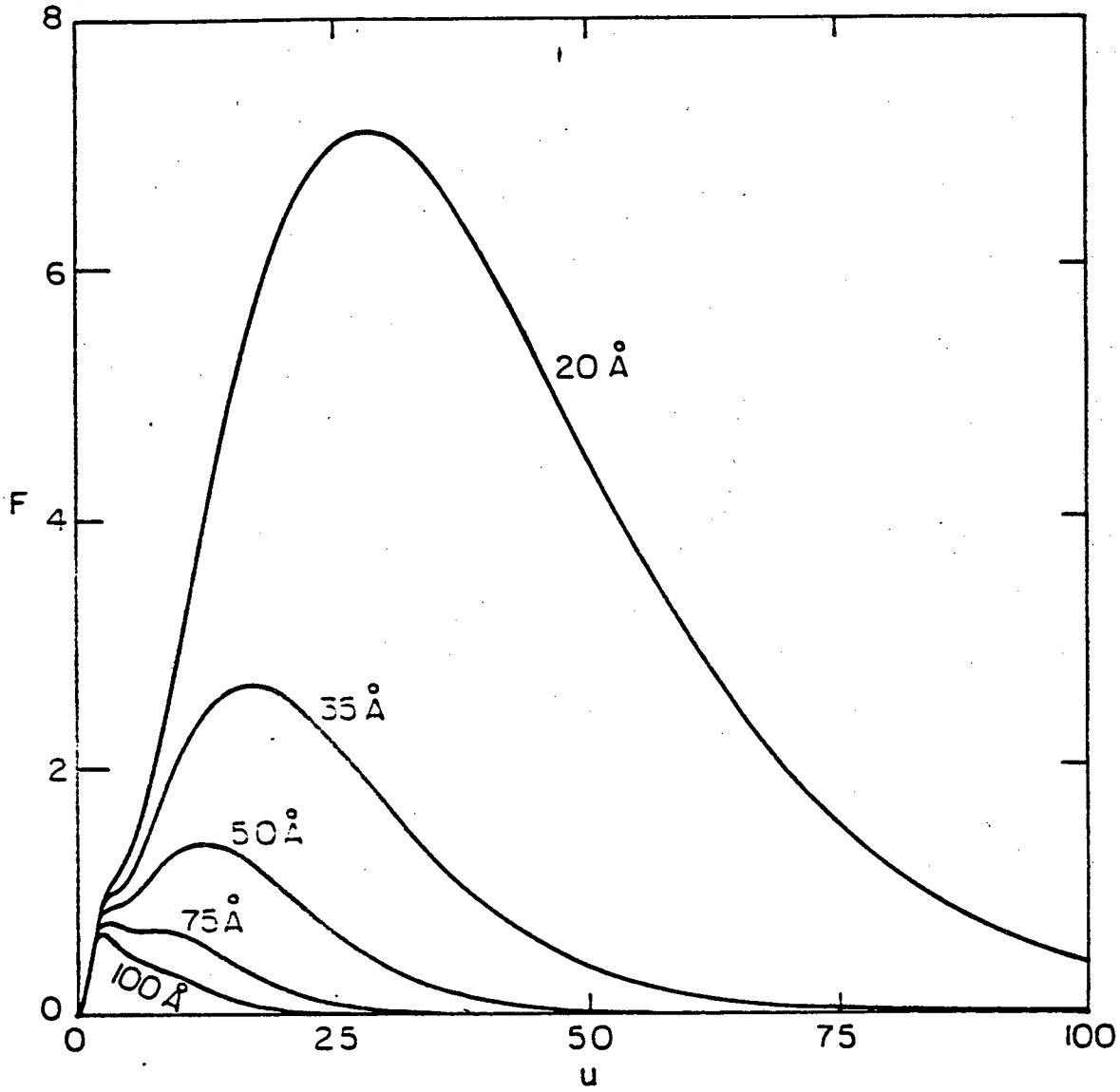

Figure 2

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