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Distance Dependence of 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 430 to 20 Å. 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-wave-vector components of the dipole near field.

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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 10 Å, the smallest molecule-metal separation for which data have been obtained.¹⁻⁷ This problem was first modeled by Chance, Prock, and Silbey (CPS)⁷ by calculating the through-space electromagnetic interaction between an oscillating dipole and a surface with a local (i.e., wave-vector 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, or 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 modeling. 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 classical 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 3800 Å (3.3 eV) and this coincides with a large absorption in the gallium arsenide due to the Λ_3 - Λ_1 interband transition.⁹

The low-temperature UHV apparatus employed in the experiments has been described in detail elsewhere.¹ Briefly, polished undoped (carrier concentrations $< 10^{14}/\text{cm}^3$) single-crystalline GaAs(110) wafers (Crystal Specialties, Inc.) were clamped to an aluminum block and cleaned with several argon-ion-bombardment/anneal cycles. Low-energy electron diffraction 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 30 K were obtained. Ammonia spacers were condensed on the gallium arsenide surface, and the spacer layer thicknesses were measured with a rotating-analyzer ellipsometer. Monolayers of pyrazine were then condensed on the ammonia spacers. The pyrazine phosphorescence was excited at 3210 Å with an unpolarized second Stokes pulse (10 ns duration) from an H₂ 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 re-

corder interfaced to a computer. Measurements were made for ammonia spacer thicknesses between 20 and 430 Å, 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 3 Å above the ammonia spacer and oriented parallel to the surface of the gallium arsenide. The dielectric constants were measured ellipsometrically during the ammonia depositions: $\epsilon(\text{GaAs}) = 12.5 + 17.0i$ and $\epsilon(\text{NH}_3) = 1.7$ at $\lambda = 3800$ Å. The energy-transfer rate was calculated with the appropriate equations from Ref. 10 and the result for the lifetime versus spacer thickness is shown as the solid curve in Fig. 1. The best fit to the experimental measurements was obtained by use of a free molecular lifetime of 24 ms 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 main-

ly 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 wave-vector dependence of the energy-transfer rate (i.e., the contribution of each of the different wave-vector 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-wave-vector components of the dipole field, generating electron-hole pairs in the solid. The shoulder which appears just above the photon wave vector ($u = 1$) 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 5000 Å). 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

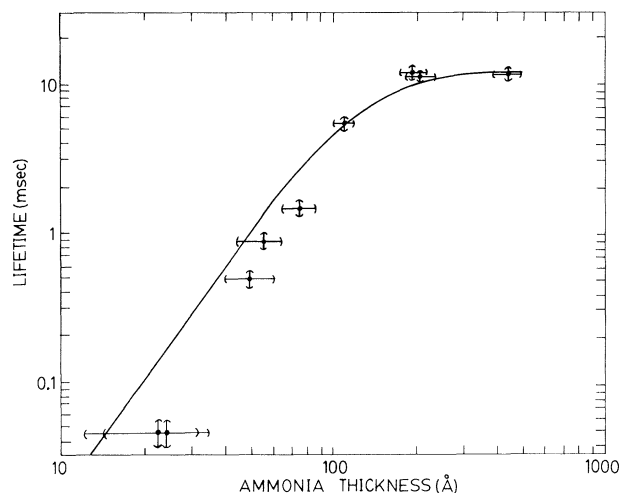


FIG. 1. Logarithmic plot of the lifetime of $^3n\pi^*$ pyrazine above GaAs(110) vs ammonia spacer thickness. The points are experimental values, and the solid curve is the behavior calculated from the Chance-Prock-Silbey model (see text for details).

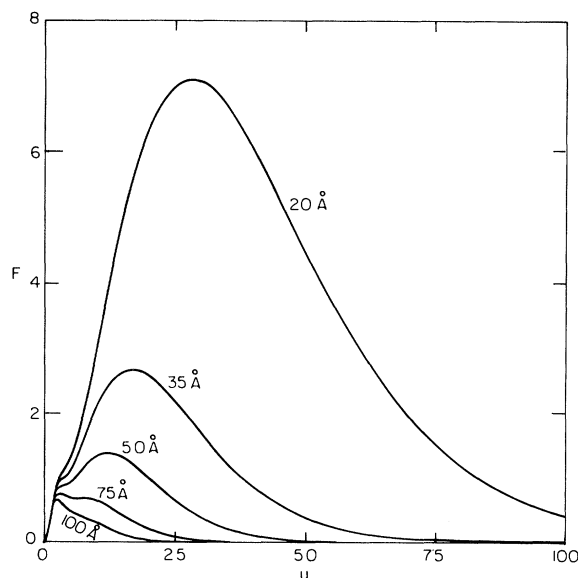


FIG. 2. The wave-vector spectrum of the energy transfer calculated for various spacer thickness (20–100 Å) for the $^3n\pi^*$ pyrazine/ammonia/GaAs(110) system. The wave vector, u , has been normalized to the photon wave vector. The appropriate geometry and optical constants are described in the text.

image-dipole description of electronic energy transfer can be applied to the transfer to GaAs (110) at 3.3 eV down to 20 Å. The dominant decay mechanism is the transfer of energy to interband electron-hole excitations of the semiconductor through the high-wave-vector 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.

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