

LUMINESCENT AND PHOTOCHEMICAL PROPERTIES OF MOLECULES NEAR ROUGH METAL SURFACES

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The unusual luminescent and photochemical properties of molecules near rough metal surfaces have been measured and used to elucidate the electro-dynamics at these interfaces.

The luminescent properties of molecules near rough surfaces of some metals are radically different than these properties near flat surfaces of the same metal. In both cases, the luminescence is an excellent probe of the electro-dynamic interaction among the optical fields, the adsorbates, and the electronic excitations in the surfaces. New excitations in rough surfaces not only induce different luminescent properties but also profoundly affect Raman scattering and many other optical processes at rough metal surfaces¹⁻³. Thus, our studies of the luminescent processes on rough metal surfaces not only provide information on the electro-dynamics at these surfaces but also the origins of their many unusual optical properties. In this paper, we describe detailed measurements of the photochemical and photophysical properties of an adsorbate on discontinuous metal island films. Our goal is to present a unified analysis of all our observations. We use Ruthenium tris-bipyridine (RuTBP) in all our measurements. The discontinuous structure of these films creates an inherent variation in distances between adsorbates and roughness features of the surface. We exploit this structure to probe the distance dependence of the electro-dynamic interactions on this rough surface.

Our experimental procedures used to produce and characterize the discontinuous island films, to apply adsorbates to the film, and to measure fluorescence lifetimes and spectra and photochemical reaction rates are reported in detail elsewhere^{2,3,4}. The fluorescence spectra from RuTBP at the same adsorbate coverage on different substrates exhibit a systematic shift to longer wavelength in the following order: silver-islands on continuous aluminum (Ag/Al, Fig. 1) to silver-islands on silica (Ag/SiO₂) to bare silica (SiO₂, Fig. 2). The emission intensity from Ag/SiO₂ is 1.7 times the intensity on SiO₂. This enhancement is intermediate between the enhancement of fluorescence found for very high and very low quantum efficiency adsorbed molecules and indicates that the emission in this case arises from RuTBP molecules both near islands and on the silica between islands. The rate of

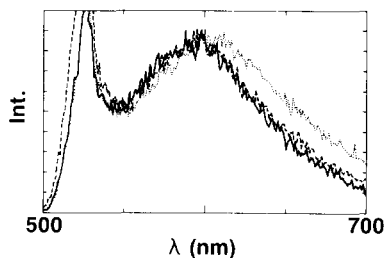


Fig. 1. Normalized spectrum: (—) 0-1.5 nsec after pulsed excitation on Ag/SiO₂; (---) CW excitation on Ag/Al; (···) CW excitation after photochemical degradation on Ag/SiO₂.

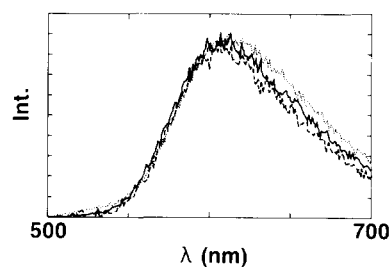


Fig. 2. Normalized spectrum: (—) 6.4-∞ nsec after pulsed excitation on Ag/SiO₂; (---) removed by photochemical degradation on Ag/SiO₂; (···) CW excitation on bare SiO₂.

photochemical reaction of RuTBP is slower on Ag/SiO₂ than on SiO₂. The photochemical degradation of the sample alters the adsorbate emission and the spectra show a systematic shift to longer wavelength in the following order: after photo-induced reaction (Fig. 1) to before reaction to spectrum of the emission removed by the photochemical reaction (Fig. 2).

The temporal decay of the fluorescence from RuTBP on island films is shown in Fig. 3. In contrast to the emission of RuTBP in solution where the decay is exponential with a lifetime of ≈ 500 nsec, on island films, the decay of the emission is nonexponential and much more rapid. Unlike on a flat metal surface where the emission of an adsorbate is also speeded up, the emission on the island film is not quenched. Two spectra in the temporal evolution of the emission spectrum after pulsed excitation are shown in Figs. 1 and 2. As the time between excitation and spectral measurement is increased, the ratio of resonance Raman scattering to fluorescence decreases and the fluorescent emission shifts to longer wavelength.

All our results can be understood using a model of the electrodynamic interactions on island films^{2,5}. The plasma resonances in the islands affect the optical processes in two ways. First, the local fields in and around the islands are increased, pumping optical processes more rapidly. Second, the excited state dipole of the adsorbate induces a macroscopic polarization in the islands. The dipolar component of the polarization increases the total emission dipole of the adsorbate-island system and therefore enhances the radiative decay rate. Lossy modes in the polarization lead to nonradiative decay. The balance between each of these surface-induced electrodynamic effects determines the characteristics of the photophysical and photochemical

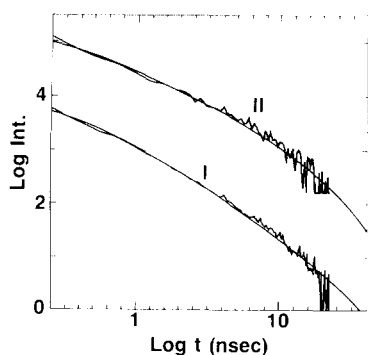


Fig. 3. Temporal decay of fluorescence of RuTBP on (I) silver-island film and (II) gold-island film. (—) Theory for each case.

processes of the adsorbate. Each of the parts of the electrodynamic interactions has a strong dependence on the separation between the adsorbate and the island. The subset of molecules nearest islands are most strongly coupled to the plasma resonance and their photophysical properties are most strongly altered. Adsorbates between islands are less strongly coupled and show behavior more like free molecules.

Our model which incorporates these various electrodynamic interactions and their distance dependence can explain all our experimental results. The agreement between the model and the fluorescent decay curves is excellent (Fig. 3) and can even account for the more subtle differences in tuning of the plasma

resonances on gold and silver-island films to the molecular resonances. The results of our three spectral measurements also support the predictions of our model. Excited molecules nearest islands do decay most rapidly due to strong coupling to the ultrafast decay processes of the plasma resonances in the islands. This subset of molecules has a spectrum shifted to higher energy compared to the spectrum of the more weakly coupled molecules between islands. This systematic shift of emission spectra is not only seen as each experimental method probes the different subsets of molecules but also as different experimental methods probe the same subset of molecules (Figs. 1 and 2). There is a clear equivalence between molecules near islands, those removed most rapidly from the photochemical reactive state by surface-induced decay channels, and those with most rapid decay from the fluorescent emitting state. There is a similar equivalence between molecules between islands, those remaining in the photochemically reactive state longer, and those with slower decay from the fluorescent emitting state.

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