

**ELECTROMAGNETICALLY INDUCED CHANGES  
IN INTENSITIES, SPECTRA, AND TEMPORAL  
BEHAVIOR OF LIGHT SCATTERING FROM  
MOLECULES ON SILVER-ISLAND FILMS**

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## ELECTROMAGNETICALLY INDUCED CHANGES IN INTENSITIES, SPECTRA, AND TEMPORAL BEHAVIOR OF LIGHT SCATTERING FROM MOLECULES ON SILVER-ISLAND FILMS

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Résumé - Les interactions électrodynamiques conduisant à la diffusion Raman exaltée de surface (SERS) conduisent aussi à des modifications dramatiques des intensités, des spectres et du comportement en fonction du temps de l'émission de fluorescence des adsorbats sur des surfaces métalliques rugueuses. Des déplacements spectraux de la fluorescence d'adsorbats sur des couches granulaires ont été observés par différentes méthodes. On peut rendre compte des modifications observées dans le cadre de la théorie électromagnétique du SERS, généralisée pour inclure les détails des résonances moléculaires et des processus d'émission relaxée.

Abstract The electrodynamic interactions which lead to surface-enhanced Raman scattering (SERS) also lead to dramatic changes in the intensities, spectra, and temporal behavior of the fluorescent emission of adsorbates on rough metal surfaces. Spectral shifts of the fluorescence of adsorbates on island films have been observed (a) by examining the emission from adsorbates on different substrates, (b) by a "photochemical holeburning" method, and (c) by measuring the temporal evolution of the fluorescent spectrum at very short times after laser excitation. The observed changes can be accounted for within the framework of the electromagnetic theory of SERS generalized to include the details of molecular resonances and relaxed emission processes.

Beyond the initially observed enhancement of normal Raman scattering, a number of other optical properties of molecules absorbed on rough metal surfaces also exhibit unusual behavior: absorption<sup>2</sup>, resonance Raman scattering<sup>3</sup>, fluorescence<sup>3,4,5,6</sup>, and photochemistry<sup>7,8</sup>. The dominant mechanism underlying these phenomena is the electrodynamic interaction among the optical fields, the vibrational and electronic states of the adsorbate, and the plasma resonances localized on the roughness features of the surface. A model based on these electrodynamic interactions has been used to explain many observations of the optical behavior of adsorbates on island films including: the hierarchy of enhancements of normal Raman, resonance Raman and relaxed fluorescence<sup>3</sup>; excitation profiles of Raman scattering<sup>9</sup>; phosphorescent lifetimes<sup>4</sup>; and photochemical degradation rates<sup>8</sup>.

In this paper, we discuss the intensity, spectral, and temporal characteristics of fluorescent emission from adsorbates on island films. Our measurements show that the molecules with the strongest electromagnetic coupling to islands have altered emission characteristics compared to their characteristics in an electromagnetically inert environment. The emission rate of these molecules is substantially increased; their photochemical degradation rate is substantially decreased; and both the peak wavelength and shape of the fluorescent emission spectrum are shifted. Each of these effects can be understood when the details of the molecular resonance and of relaxed emission processes are included in the picture of the electrodynamic coupling with the islands. Furthermore, the observed changes can be used to probe the

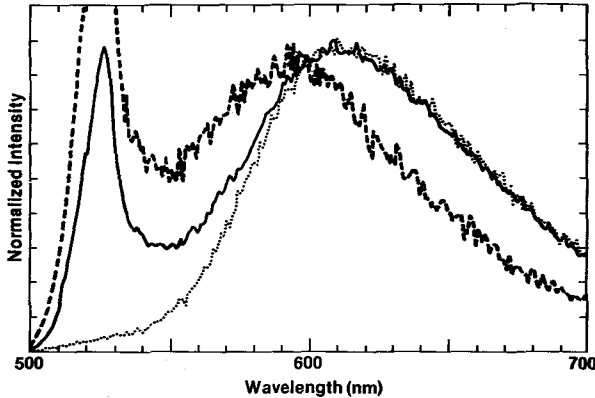


Figure 1. Normalized fluorescence spectrum from RuTBp on (—) Ag/SiO<sub>2</sub>, (---) Ag/Al, (.....) SiO<sub>2</sub>.

rescence spectra and photochemical degradation rates<sup>3,8</sup> are reported in detail elsewhere. The adsorbate used in the present study is ruthenium tris-bipyridine (RuTBp). We use silver and gold island films with islands about 200Å in diameter and separated by similar distances. Lifetime measurements are made using a time-correlated photon counting technique<sup>10</sup>, and temporally resolved spectra are measured using a variation of a technique which has been suggested for fluorescence rejection for Raman spectroscopy.<sup>11</sup>

The fluorescence spectra from RuTBp at the same adsorbate coverages on different substrates is shown in Figure 1. These normalized spectra show a progressive shift of the emission to longer wavelength in the following sequence: silver-islands on aluminum (Ag/Al) to silver-islands on silica (Ag/SiO<sub>2</sub>) to bare silica (SiO<sub>2</sub>). The intensity of the emission from Ag/SiO<sub>2</sub> is enhanced by 1.7 over the intensity from SiO<sub>2</sub>. This result is intermediate between the enhancement of fluorescence found for very high and very low quantum efficiency adsorbates<sup>3</sup> and suggests that the total emission for RuTBp on Ag/SiO<sub>2</sub> is made up of emission from molecules both near the islands and on the silica between the islands. Our photochemical results for RuTBp are similar to those found for another adsorbate, Rhodamine 6G<sup>8</sup>. The rate of photochemical degradation of molecules on Ag/SiO<sub>2</sub> is slower than on SiO<sub>2</sub> and the spectra again show a progressive shifting to longer wavelength in the following sequence: after degradation to before degradation to spectrum of emission remove by the photochemical process (equal to the spectrum before degradation minus the spectrum after degradation).

The fluorescent decay curves of RuTBp on silver and gold island films are shown in Figure 2. In solution, RuTBp emission has an exponential time dependence with a lifetime of  $\approx 200$  nsec. In contrast, the decay on island films is much more rapid and has a nonexponential character. The temporal evolution of the emission spectrum of RuTBp on island films after pulsed excitation is shown in Figure 3. As the delay time between the excitation pulse and the observed fluorescence is increased, the ratio of Raman scattering to fluorescence decreases, and the fluorescent emission shifts to longer wavelength.

Our results can be understood in terms of a model based on the electrodynamic interactions on island films<sup>3</sup>. The influence of the resonances affects the optical processes in two ways. First, the local fields in and around the islands are enhanced and therefore the pumping of the optical process is increased. Second, the oscillating dipole of the adsorbed, excited molecule induces a macroscopic polarization in the islands. The dipolar component of this response increases the total emission dipole of the coupled molecule-island system and thus increases the radiative decay

spatial dependence of the electromagnetic interactions of the inhomogeneous environment inherent in the structure of island films. We find that the temporal and spectral behavior complement each other as a probe of the spatial dependence, and both are consistent with results of experiments which employ different substrates to emphasize fluorescence from molecules in various positions on the films.

Experimental procedures used to prepare and characterize island films,<sup>3,4,9</sup> apply molecular coatings,<sup>3,8</sup> and measure fluo-

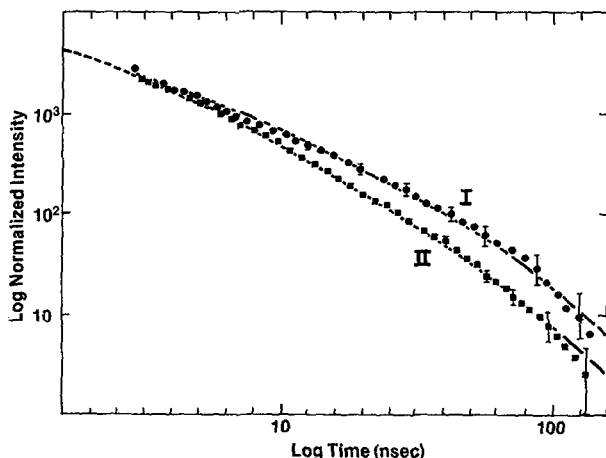


Figure 2. Temporal decay of fluorescence of RuTBP (I) Silver-island film with excitation at 438 nm, (II) Gold-island film with excitation at 458 nm. Emission detected at 600 nm. (----) Theory for each case<sup>4</sup>.

rate of the system. Also, nonradiative decay channels are opened to the excited molecule by coupling to lossy modes in the island. The balance between these new surface-induced radiative and nonradiative decay channels as well as those channels intrinsic to the molecule determine the radiative yield of the system. Each of the portions of the electrodynamic coupling is a sensitive function of the separation between the molecule and the island. The subset of molecules on the film closest to islands are most strongly coupled to the plasma resonance of the island and thus exhibit fastest decay of the adsorbate. Molecules between islands exhibit decay more like the free molecule.

The effects of the increased radiative rate and inhomogeneous nature of an island film are seen directly in the decay curves in Figure 2. The inhomogeneity of couplings across the film causes different molecules to experience different surface-induced increases in their radiative rates and thus produces the observed nonexponential behavior. In curve I, both the excitation and emission wavelength are tuned to the silver island film resonance. However, in curve II, only the emission wavelength is tuned to the resonance of the gold island film. This difference leads to differently shaped decay curves in the two cases. As shown by the dashed lines in Figure 2, the electrodynamic picture applied to describe fluorescence decay on island films<sup>4</sup> accounts both for this difference in shapes of the curves as well as the shape of each individual curve.

The results of our three spectral measurements confirm that molecules nearest islands do decay most rapidly and that this subset of molecules has a spectrum shifted to shorter wavelength compared to the spectrum of the weakly coupled molecules between the islands. Not only does each individual experiment indicate a spectral shift as it probes the inhomogeneous environment of the island film but spectra from different experiments exhibit striking resemblances. Thus, emission (a) from molecules on Ag/Al, (b) from molecules most resistant to photochemical degradation on Ag/SiO<sub>2</sub>, and (c) from molecules with the fastest fluorescent decay rates on Ag/SiO<sub>2</sub> all show similar spectra. These molecules are spatially near islands and, having very rapid surface-induced decay rates, spend less time in photochemically reactive and other excited states. In contrast, emission (a) from molecules on SiO<sub>2</sub>, (b) from molecules least resistant to photochemical degradation on Ag/SiO<sub>2</sub>, and (c) from molecules with longer fluorescent decay rates on Ag/SiO<sub>2</sub> all show similar spectra but at a longer wavelength than those discussed above. These molecules are far from islands and, having only weak coupling to surface-induced modes, have residence times in photochemically reactive and other excited states more like the free molecule.

Our experimental methods have allowed us to probe the inhomogeneity of the island film and have also revealed a dramatic spectral shift of the emission from molecules nearest the islands. This shift is induced by the electrodynamic coupling of the excited states of the adsorbate to the plasma resonances in the film. For the most

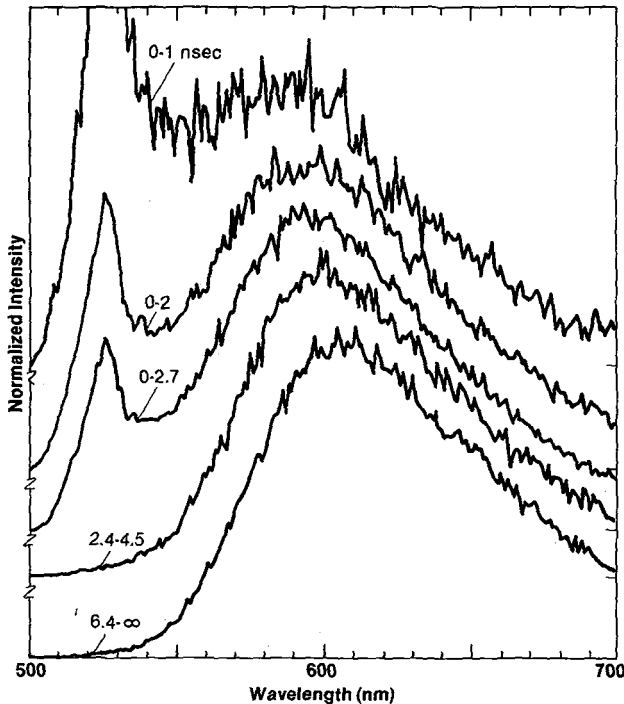


Figure 3. Temporal evolution of normalized spectrum of RuTBp on silver-island film. Times marked on each curve represent the temporal window after pulsed excitation during which fluorescence is collected.

strongly coupled molecules, the surface-induced decay rate may be so fast that it can compete successfully with the very fast inter- and intramolecular processes which relax the excited state of the molecule before it emits in a free state such as on  $\text{SiO}_2$ . Thus, a molecule strongly coupled to the plasma resonance may emit before this relaxation occurs and with a spectrum shifted compared to the free case. In addition, while the spectral shape of the free molecule emission is determined by the Frank-Condon factors connecting the ground and excited states; when the molecule is strongly coupled to the plasma resonance, the frequency dependence of the radiative yield of surface-induced decay channels will also affect the overall radiative efficiency of each transition of the adsorbed molecule. This would also cause strongly coupled molecules to emit with a different spectrum than weakly coupled or free molecules.

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