

PHOTOCHEMISTRY OF MOLECULES ADSORBED ON SILVER-ISLAND FILMS: EFFECTS OF THE SPATIALLY INHOMOGENEOUS ENVIRONMENT

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We have examined how the photochemical reaction rate of molecules adsorbed at rough silver surfaces is affected by the same strong electrodynamic interactions which lead to surface-enhanced Raman scattering. We probe the effects of the spatial variation of the electrodynamic interactions across the island film.

Since the first observations of surface-enhanced Raman scattering (SERS) [1,2], the investigations of the optical properties of adsorbates on rough metal surfaces have expanded to include a wide variety of optical processes such as absorption [3], resonant Raman scattering [4], and fluorescence [5,6]. While the complete description of these optical processes depends on the details of the interface in question, the electrodynamic effects of the plasma resonances localized on the roughness features of the metal surface play a dominant and pervasive role in these processes. The electrodynamic influence of the plasma resonances of the island film affect the optical behavior of the adsorbates by two processes [7]. Field intensities in and around the islands are increased and therefore pumping rates for inelastic scattering and photochemical reaction by the adsorbate are enhanced. Second, the oscillating dipole of the excited adsorbate induces a large response in the roughness features of the film and therefore increases the radiative emission rate and non-radiative damping rate of the excitation. The surface-induced enhancement of any optical process depends on the balance between the enhanced pumping and the rates of decay in the various deexcitation channels. Since the strength of the surface-induced interaction varies around and between the roughness features of the surface [8,9], intensities of optical processes on island films are weighted averages of this balance across the surface. This balance leads to a hierarchy of enhancements for normal Raman

scattering, resonant Raman scattering, and fluorescence [10,11].

The observation of SERS has also led to speculation concerning the effects of these electrodynamic interactions on photochemical reactions at rough metal interfaces [12], and novel chemistry has, in fact, been observed [13]. The very large increase in the local field, produced by excitation of the localized electronic plasma resonances, might be expected to increase the rate of photochemical reactions. However, just as for inelastic optical scattering processes, when the excitation energy must be stored for some finite time in the molecule, the rapid, surface-induced deexcitation of the excited state may counterbalance the increased excitation rate. We have measured the effects of these electrodynamic interactions on the photochemical reactions of a dye molecule, rhodamine 6G (R6G), adsorbed on a silver-island film. In a manner analogous to the probing of spectral inhomogeneities by photochemical hole burning in bulk materials [14], we use the photochemical processes occurring on the film to probe the spectral and spatial inhomogeneities of the surface. We find that molecules between the islands on the film have photochemical rates and emission spectra similar to molecules on bare silica. However, molecules near the islands have slower photochemical rates and altered emission spectra.

Silver-island films are produced on both silica and thermally oxidized aluminum substrates by thermal evaporation of silver at $\approx 1 \text{ \AA/s}$ to a mass thickness of

50 Å. These films are composed of roughly circular islands ≈ 200 Å in diameter and separated by distances comparable to their size. On silica substrates, they exhibit optical absorption resonances peaking at ≈ 4350 Å and characteristic of the localized plasma resonances occurring in the film [15]. Reflectivity studies indicate that the plasma resonance remains for island films on aluminum substrates. Submonolayer R6G films are applied to all substrates with a dipping technique which produces coverages approximately independent of the substrate [16]. The coverage used in these experiments is $\approx 10^{12}$ molecules/cm² [16] and is low enough that the electromagnetic resonances in the film are unaltered by the dye molecules [3]. Furthermore at these coverages, concentration quenching effects are negligible and the radiative quantum efficiency of R6G molecules on silica is very near unity. While the precise photochemical degradation mechanism of R6G is not completely known and depends on the excitation wavelength and local chemical environment, the degradation does proceed from an excited state of the molecule and leads to products with quantum yields lower than those of undegraded R6G [17]. The excitation for all experiments is at 4579 Å and spectra are obtained using ≈ 0.1 W/cm² laser intensity, which causes negligible photochemical reaction. Photochemical degradation is induced using ≈ 10 higher intensity.

Before any photochemical degradation has occurred, fluorescence spectra are obtained from an equal coating of R6G on bare silica and a silver-island film. The fluorescent intensity on the island film is actually decreased by a factor of ≈ 2.5 due to the additional damping of the silver island, and, in fact, most of the observed intensity originates from those molecules adsorbed directly on the bare silica, between the islands. To obtain an unambiguous spectrum of those molecules adsorbed directly on the silver island, the fluorescence from the island films on aluminum is examined. On such films, the fluorescence of molecules between the islands is totally quenched and the small remaining signal (≈ 0.02 of the signal from the coated silica substrate) originates from the molecules directly on the silver islands.

When the laser intensity is increased to induce photochemical degradation, not only is the rate of decay noticeably different on the island film on silica compared to the bare silica; but a dramatic change is observed in the spectral shape of the emission from

the R6G on the island film. The fluorescent emission on bare silica decreases by 77% for a total fluence of $\approx 3 \times 10^{20}$ photons on $\approx 10^{10}$ R6G molecules, and no change in the spectral shape occurs. In contrast, for the same laser conditions, the spectrum from the island film after exposure to the intense laser irradiation exhibits a marked shift to shorter wavelengths compared to undegraded spectrum (fig. 1). While the intensity at the 5540 Å has decreased by 71% — a rate similar to that found for bare silica, emission at shorter wavelengths has decreased by only $\approx 15\%$. The original emission spectrum of the molecules which have been photochemically altered on the island film can be determined by subtracting the spectra before and after exposure to the intense laser radiation. As shown in fig. 2, these molecules produce emission very similar to that from R6G on bare silica. In contrast, as shown in fig. 3, the spectrum of the molecules remaining on the island film after photochemical burning is very similar to the spectrum of fresh R6G on silver islands on aluminum.

This temporal and spectral behavior of the photochemical process occurs for reasons similar to those accounting for other delayed, deexcitation processes on island films. The surface-induced increases in the radiative and non-radiative decay rates can remove energy from the molecule faster than the photochemical reaction rate. The strength of these rates and their balance with the enhanced pumping rates experienced

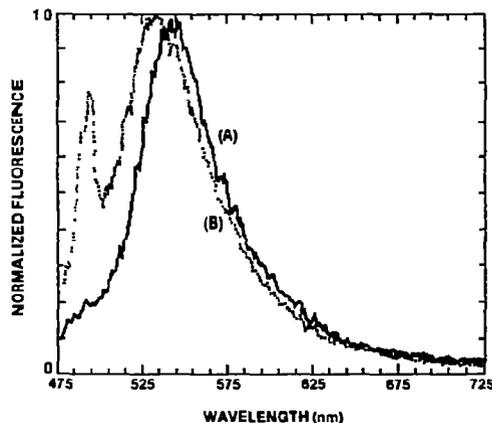


Fig. 1. Normalized emission spectra of R6G on silver islands on silica (A) before (solid line) and (B) after (dotted line) photochemical burning.

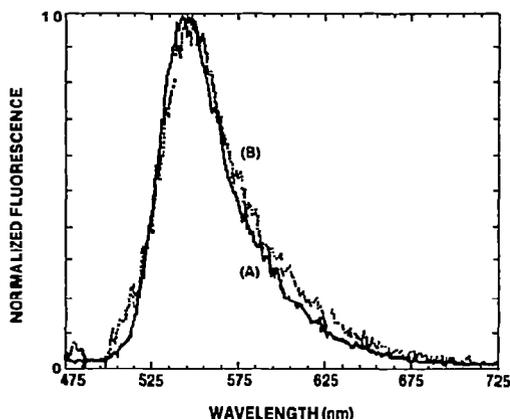


Fig. 2. Normalized emission spectra of (A) the molecules degraded by photochemical burning of R6G on silver-island films and (B) R6G on bare silica (dotted line).

by the adsorbates varies across the film surface. We observe that those molecules on the island film which have faster photochemical rates give emission spectra similar to molecules on bare silica substrates. For these molecules which are on silica between the islands, the observed photochemical decay rate on the island film is similar to that on the bare silica substrate. Since the photochemical decay of R6G has a slow rate compared to all other decay channels of the free molecule, this type of decay mechanism would be more susceptible to change due to surface-induced increases in the radia-

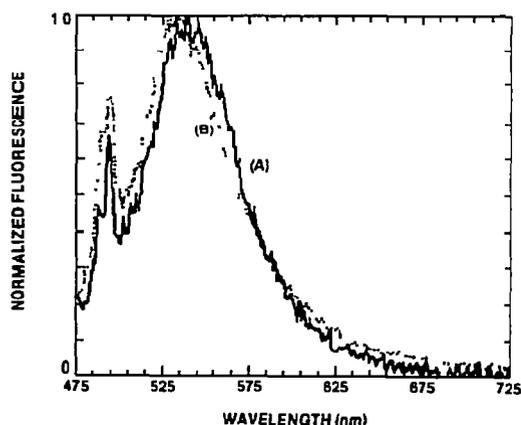


Fig. 3. Normalized emission spectrum of (A) R6G on an island film on aluminum (solid line) and (B) R6G on an island film on silica after photochemical burning (dotted line).

tive and non-radiative decay rates of the molecule. Still, the coupling to the islands does not substantially affect the photochemical rate either through the changes in the deexcitation rates or through an enhanced excitation rate. In contrast, our spectral studies show that some molecules on the film undergo much slower photochemical rates than those between the islands. These molecules produce emission spectra similar to that of R6G on silver islands on aluminum where emission is observed only from molecules very near the islands. Here, despite the enhanced excitation rate of the adsorbate, the surface-induced decay processes dominate the deexcitation of the adsorbate and the photochemical reaction rate is significantly slower than for molecules between the islands.

The slow photochemical rate of the molecules near the islands is consistent with the picture of the electro-dynamics of silver-islands films which has been provided by measurement of the enhancements of other optical processes [11]. As indicated by the 10^5 enhancement measured for normal Raman scattering from molecules on island films, the enhancement of the local field intensity near an island is ≈ 300 . However, the smaller enhancement (10^3) measured for resonant Raman scattering from adsorbates shows that the surface-induced broadening of the vibrational level to which the system is initially pumped reduces the effects of the local field enhancement by a factor of 10, resulting in a net enhancement of excitation rate of the molecular system of ≈ 30 . In addition, the new surface-induced decay channels of the excited vibrational state reduce the efficiency for populating the thermalized excited electronic level by a factor of 10 below the efficiency for the molecule on the electromagnetically inert silica surface. Thus, the rate of preparation of the thermalized, potentially photochemically reactive state, is only enhanced by a factor of ≈ 3 for molecules very near the islands compared to the rate on bare silica. Furthermore, comparison of the relative enhancement of fluorescence suggests that the additional surface-induced damping decreases the radiation emission quantum yield from the thermalized excited state from 1 to $\approx 10^{-3}$. This occurs despite the fact that the radiation emission rate, unlike the photochemical degradation rate, is substantially increased due to the electrodynamic interaction with the islands [9]. The net result is that, for molecules near the islands, the rapid, sur-

face-induced non-radiative damping dominates the photochemical decay and can easily counterbalance the small enhancement in the pumping rate of the photochemically reactive state. Thus, in agreement with our observation, the photochemical degradation rate of molecules near the islands is greatly reduced.

The changes in the photochemical degradation rate, as well as the change in the spectral shape of the emission, have allowed us to probe the spatial inhomogeneities of the electrodynamic of a silver-island film. Since branching into the photochemical channel of the relatively stable R6G is small, this branching is most susceptible to change by the surface-induced processes. Yet, the photochemistry of the molecules between the islands on silica is not substantially altered by the presence of the islands. Although the excitation rate of R6G molecules adsorbed very near silver islands can be enhanced, the rate of photochemical degradation is actually dramatically decreased. In analogy to the use of photochemical hole burning to probe the effects of spectral inhomogeneities induced by local variations in crystalline properties in the bulk, we have used the photochemical degradation to observe the spectral shift in the fluorescent emission of those molecules whose emission is most strongly affected by the silver islands. The origin of this shift is unclear. The different chemical environment for the molecules adsorbed directly to the silver compared to that of the molecules adsorbed on the silica may result in this shift. Alternatively, it is also possible that purely electromagnetic effects may cause the shift, with the large increase in the emission rate emphasizing somewhat higher-frequency fluorescent emission which occurs before complete excited-state thermalization of the R6G molecule

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