

Fluorescent lifetimes of molecules on silver-island films

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Received September 21, 1981

The fluorescence of molecules on silver-island films exhibits nonexponential decay and is several orders of magnitude more rapid than on a silica surface, while the total emission intensity is slightly increased. This behavior results from the electromagnetic coupling between the fluorescing molecules and the plasmon resonances of the silver islands. We obtain good agreement with a model that uses the same theory for the electromagnetic coupling as has been used to account for surface-enhanced Raman scattering.

Fluorescent lifetimes of molecules near metal surfaces are dramatically affected by the electromagnetic interaction between the excited molecules and the metal surface. To date, experimental and theoretical investigations have focused on the effects of a smooth surface.¹⁻³ In this Letter we report the first known study of fluorescent lifetimes of molecules near rough silver surfaces and show that the behavior is significantly different. We quantitatively account for our results by using a model that describes the electromagnetic interaction between molecules and rough metal surfaces.^{4,5} Our results probe the de-excitation process directly and shed new insights on the details of the mechanism that causes surface-enhanced Raman scattering and other anomalous optical properties of molecules near rough metal surfaces.

Numerous experiments^{2,3} have shown that as the distance d between a molecule and a smooth surface is decreased, the fluorescent lifetime decreases as d^3 . This has been successfully explained as a coupling between the molecular dipole and the image dipole induced in the metal.¹ Rapid, nonradiative damping by excitation of surface plasmons and electron-hole pairs shortens the lifetime and quenches the fluorescence. In contrast, we show that the fluorescent lifetimes of molecules near a rough silver surface are shortened dramatically but that their radiation is not substantially quenched. These results are attributed to the electromagnetic coupling between the molecular dipole and the polarization induced in the surface-roughness features. This macroscopic polarization replaces the image dipole used to model the smooth-surface results and can become large at the frequency of the localized electronic plasma resonance. This description of the electromagnetic interaction between a molecular dipole and a rough metal surface has been successfully used to account for an origin of surface-enhanced Raman scattering (SERS).⁴

To provide surfaces with reasonably well-characterized roughness, we use silver-island films, which have

been shown to exhibit SERS⁶ as well as other anomalous optical properties.⁷ High-resolution scanning electron micrographs show that the islands are roughly circular in cross section with mean diameters of ~ 200 Å and cover 30–40% of the surface. A thin layer of europium III thenoyltrifluoroacetate (ETA) is deposited on the island film or on a bare silica substrate by a dipping technique.^{8,9} By comparing the fluorescence signal from a coated silica surface with that from a solution of ETA, we estimate a surface coverage of 3×10^{13} molecules/cm², which corresponds to half-monolayer coverage, assuming a cross section of 150 Å²/molecule. We excite the ETA at 390 nm and monitor the 5D_0 – 7F_2 emission of the Eu^{3+} ion at 613 nm.

The fluorescence decay of the Eu^{3+} ion deposited on a bare silica slide has an exponential decay with a characteristic time of 280 μsec , the same as that of solid ETA, and has a measured quantum efficiency of ~ 0.4 . For substrates dipped under identical conditions to give approximately equal coverages of molecules, we find that the fluorescence has the same spectrum but is increased by a factor of ~ 5 for silver-island films compared with bare silica. However, the time scale of the light emission is decreased by about 3 orders of magnitude, and the decay is no longer a simple exponential, as shown in Fig. 1.

This behavior is a direct manifestation of the electromagnetic coupling between the Eu^{3+} ions and the silver islands. The incident field induces a dipole in the silver islands, which may increase the strength of the local pump field at the molecules. Similarly, the near-field radiation of the fluorescing Eu^{3+} ions induces a response in the form of a macroscopic polarization in the silver islands. This response will be large if the pump frequency corresponds to the plasma resonance frequency of the spheroid and, in such circumstances, will increase both the radiative and nonradiative decay rates of the system. The slight increase in the total emission results from a balance between the increased absorption in the molecules and the increased damping

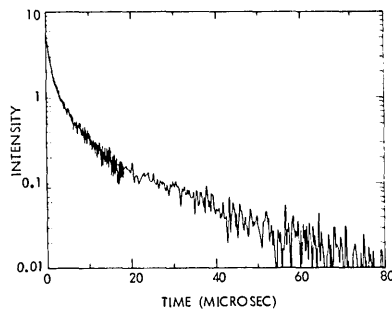


Fig. 1. Fluorescence decay of Eu^{3+} on silver-island films.

of the emission that is due to nonradiative processes in the silver. However, SERS excitation measurements on these films show that the pump frequency is considerably higher than the frequency for the maximum enhancement of the local fields outside the islands.¹⁰ In fact we see no SERS from these films when we excite at 406.7 nm and shorter wavelengths, and we estimate that the increase in the absorption that is due to increased local fields can be at most an order of magnitude. Thus, even allowing for the maximum increase in absorption, the fluorescence is not substantially quenched by this rough surface, and therefore the shortened lifetime is not due to totally nonradiative processes. In contrast to the results obtained on a smooth metal surface, where the decreased lifetime is caused by an increased nonradiative decay rate, our results reflect the fact that the response induced in the silver islands can result in significant radiation.

The electromagnetic coupling to the silver island is strongly dependent on the distance between it and the fluorescing ion. Thus the nonexponential behavior indicates a distribution of decay rates resulting from the contributions of Eu^{3+} ions lying on the bare silica at varying distances from the Ag islands. To show this, we repeated the measurement using an oxidized aluminum substrate instead of silica to quench the fluorescence from the Eu^{3+} ions between the silver islands. Reflection measurements on Ag-Al samples show that the island plasma resonance remains; fluorescence measurements on flat, oxidized Al samples show that the Eu^{3+} emission is strongly quenched by the Al. On the Eu-Ag-Al sample, the signal level is reduced substantially but is approximately exponential. This supports the contention that it is the Eu^{3+} ions between the islands that contribute to the signal at longer times, and it is the distribution of their separation distances from the Ag islands that leads to the nonexponential decay.

To develop a quantitative expression for the observed decay, we use semiclassical radiation theory to obtain expressions for the radiative and nonradiative decay rates of a fluorescing molecule a distance r from the center of a silver spheroid. In the spirit of the mean-field models for island films, we assume that the local field at any ion between the islands is composed of an average contribution from all the islands plus a distance-dependent contribution from the nearest Ag island. Thus the averaging of the signal from the molecules over the island film can be accomplished by

considering a single spheroid of cross-sectional radius b in the center of a disk of molecules. The signal at a time t after the laser pulse is given by

$$S(t) = N \int d^2r \sigma(\mathbf{r}) Y(\mathbf{r}) \Gamma(\mathbf{r}) \exp[-t\Gamma(\mathbf{r})]. \quad (1)$$

Here N is the number of ions per unit area, $Y(\mathbf{r}) = \Gamma_r/\Gamma$ is the quantum yield, and $\sigma(\mathbf{r})$, $\Gamma(\mathbf{r})$, and $\Gamma_r(\mathbf{r})$ are the absorption cross section and the total and radiative decay rates of the system, respectively.

Although in general the fields induced in a metallic spheroid in the near field of the dipole of a fluorescing molecule must be expressed as a sum over many multipole contributions, there are two simple limiting cases determined by the distance between the molecule and the spheroid surface compared with the local radius of curvature.⁵ At short distances, the response is that of a plane surface, with the total decay rate increasing as d^{-3} and the radiative emission being heavily damped. At large distances, the dipolar term dominates, and the interaction approaches that of two point dipoles. Since the Eu^{3+} ions themselves are separated from the silver by the surrounding ligands of the ETA molecule and by an oxide coating on the islands, and since the local radius of curvature of an oblate island can be considerably less than its diameter, we use the dipole approximation for the interaction between the ions on the silica and the Ag island. Although this is certainly an oversimplification, it emphasizes the effects of the roughness and maintains most of the essential physics while keeping the calculations more tractable.

We denote the ratio of the local to the applied fields at a molecule that is due to a dipolar response in the silver spheroid as $A(\omega)$. This same expression also describes the ratio of the emission dipole of the system to the molecular dipole. This ratio can be calculated explicitly for an isolated spheroid.⁵ However, we approximate it as $A_{\parallel} \approx 1 + 2\beta/r^3$ and $A_{\perp} \approx 1 - \beta/r^3$ for fields parallel and perpendicular to the radial direction, respectively. The effective polarizability of the spheroid $\beta(\omega)$ becomes large at the frequency of the plasma resonance and is determined by the exact shape of the island as well as by the effects of the fields from the neighboring islands. The dipolar response of the island to the applied field can increase the absorption rate of the molecule; thus $\sigma = \sigma_F |A(\omega_L)|^2$, where σ_F is the absorption cross section of the free ion and ω_L is the laser frequency.⁵ The radiative decay rate is calculated by using the expression $\Gamma_r = \omega_s^3 |\mu|^2 / 3\hbar c^3$, where ω_s is the Stokes frequency and $|\mu|$ is the system emission dipole, which is determined by the molecular dipole moment and the response induced in the island. Thus $\Gamma_r = \gamma_F |A(\omega_s)|^2$, where γ_F is the radiative decay rate of the free ion. The damping of the emission is calculated from the local joule heating in the island⁵ caused by the out-of-phase portion of the dipolar response. It has an r^{-6} distance dependence and can be represented by the nonradiative decay rate $\Gamma_{nr} \sim \gamma_F (b/r)^6$. We note that the r^{-6} dependence of the dipole-dipole interaction reflects the surface roughness and is in contrast to the d^{-3} dependence characteristic of a smooth surface.

The Eu^{3+} ions on top of the silver islands are all relatively close to the metal. Also, the local radius of curvature on top of the oblate islands is larger than

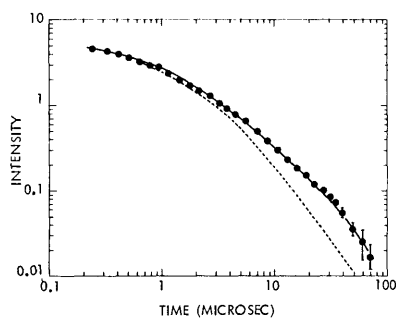


Fig. 2. Comparison of experimental fluorescence decay with calculations of model for molecules on a silver-island film assuming a large polarizability only at the emission frequency (solid line) and also at the excitation frequency (dotted line).

around the edges. Thus the fluorescence of the molecules on top of the islands will be relatively heavily damped and make only a small contribution to the total signal, particularly at longer times. Furthermore, since the islands are separated by approximately their diameters, those molecules at a distance $r \gtrsim 2b$ will be more strongly affected by neighboring islands. Thus we extend the integral over a ring of molecules in the plane of the substrate from b to $2b$. We also average over all possible orientations of the emission dipole in the plane of the substrate, but, because of the substantial anisotropy of β at ω_s , we neglect the contribution of the much smaller out-of-plane polarization in the silver.

We compare two limiting cases with the data in Fig. 2. We assume a large polarizability of the silver islands only at the emission frequency or equally large polarizabilities at both the laser and the emission frequencies. As was discussed earlier, our SERS measurements on these films suggest that the first case is more nearly correct. As is shown in Fig. 2, we do in fact get better agreement with the data by assuming large polarizability only at the emission frequency. This is an explicit example of a case in which the excitation and emission frequencies are sufficiently separated that only one is influenced by the electronic plasma resonances of a rough silver surface. We also note the agreement of the model with the approximately power-law dependence of the measured decay at longer times. From the fit of the rough-surface calculations to the data, we obtain a value of $\sim 2 \mu\text{sec}$ for the ions with the shortest

measurable lifetime. In the case of SERS, the increase in the total emission dipole that is due to the resonant response of the spheroid results in an additional enhancement arising in the emission. Of course, the damping processes will not affect the Raman process as they do the fluorescence.

In conclusion, we report the first known study of the changes in fluorescent lifetimes when molecules are placed on rough silver surfaces. We observe a substantial increase in the total fluorescent decay rate without a concomitant decrease in the emission quantum yield. Our results are in sharp contrast with the observations of molecules near smooth metal surfaces where the increased fluorescent decay rate is associated with virtually complete quenching of the quantum yield. Using the same electrodynamic model that has been used to describe SERS, we are able to account for the observed temporal decay of the fluorescence for molecules on the silver-island films. These results are also the first known example of a surface-enhanced linear optical process in which the excitation and emission frequencies are widely enough separated that only one is strongly affected by the silver resonance.

We would like to thank A. Nitzan and T. Tiedje for useful discussions, R. Stephens for the loan of equipment, and H. Deckman for the electron micrographs.

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