FLUORESCENT LIFETIMES AND YIELDS OF
MOLECULES ADSORBED ON SILVER-ISLAND FILMS

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When molecules are adsorbed on silver island films, their
fluorescent lifetimes are found to be shortened by about three
orders of magnitude and their decay is found to be non-
exponential in time. This behavior is a result of the electro-
magnetic interaction between the molecules and the silver
islands. The emission process of the molecule-island system
can be quite efficient, and the increased radiative rate can
lead to an improved effective quantum yield for adsorbates on
silver-island films.

Recently, much interest has been focused on the optical properties of molecules
near rough metal surfaces. This interest has been stimulated by the observation
of surface-enhanced Raman scattering (SERS)[1,2] as well as other unusual optical
properties of adsorbed molecules.[3,4] It is generally believed that on rough
surfaces localized electronic resonances, or Mie resonances, play a large role in
causing the anomalous optical properties of adsorbed molecules.[5] In this paper,
we discuss the dramatic changes that occur in the fluorescent properties of mole-
cules adsorbed at rough silver surfaces, and show that these effects can be
understood in the context of an electromagnetic interaction between the molecules
and the localized electronic plasma resonances. By measuring the change in the
fluorescent lifetime, we study the dynamics of the interaction, and by measuring
the change in the fluorescent yield, we study the radiative efficiency of the
rough-silver/molecule system.

As our rough surfaces, we use silver-island films, prepared by a slow
($\sim$0.5 Å/sec) thermal evaporation of $\sim$50 Å mass thickness onto a silica
substrate. The electronic resonances localized on the individual islands of the
film cause a sharp peak in the absorption spectrum of the film.The fluorescent
decay rate is a sensitive probe of the interaction of a molecule with its
environment. To measure the effect of a rough metal surface on this rate, we
deposit a thin layer of Europium III thenoyltrifluoroacetonate on both a bare
silica substrate and on a silver-island film. We excite the Eu^{3+} ions at 390 nm
and monitor the $^5D_0$-$^7F_2$ emission at 613 nm. On the bare silica substrate, the
fluorescent decay is exponential with a decay time of 240 μsec. By comparison
with the quantum efficiency (QE) and lifetime in solution, we estimate the QE of
the Eu^{3+} ion on the silica surface to be $\sim$0.4. On a silver island film, the
decay is no longer exponential in time and is about three orders of magnitude
faster. However, the total amount of fluorescence increases by a factor of $\sim$3
over that emitted from the same coverage on a bare silica substrate.

This behavior is a direct result of the electromagnetic interaction between the
fluorescing molecules and the plasma resonances of the silver islands.[6] If the
laser frequency is near a plasma resonance frequency, the dipole induced in the
island will result in a large increase in the local field at the molecule and
will lead to an increased absorption rate. Similarly, the emitting dipole of a

fluorescing molecule will induce a response in the silver, which will be large if the emitted field is on resonance with the localized plasmon. The increase in the net emitting dipole will increase the total emission rate. Thus the observed increased decay rate is a direct result of the increase in the total emitting dipole of the molecule/silver system. The slight increase in the total emitted light results from a balance between the increased absorption due to the increased local field at the pump frequency and the increase in the damping of the emitting dipole at the emission frequency due to energy absorption in the silver.

The electromagnetic coupling between the molecules and the silver is very sensitive to the distance separating the Eu^{3+} ion and the silver island. Since more than half of the ions lie on the bare silica between the islands, there is a distribution of separation distances. This will lead to a distribution of decay rates, resulting in the apparent nonexponential decay.

We have developed a simple model to account for the fluorescence decay in more detail.[6] At a time, t, after a laser pulse, the total fluorescent emission will be the sum of the emission from all the ions, each of which is decaying exponentially with a characteristic time dependent on its position on the film. Thus, the signal will be

$$S(t) = N \int d\vec{r}\ \sigma(\vec{r})\ Y\ (\vec{r})\ \Gamma\ (\vec{r})\ e^{-\Gamma(\vec{r})t} \qquad (1).$$

Here N is the number of ions per unit area (assumed constant) and σ is the probability of excitation, Γ is the total decay rate of the excited ion, and the yield, $Y = \Gamma_r/\Gamma$, where Γ_r is the radiative decay rate. Each quantity is dependent on the position of the ion, and the integral is carried out over the area of ions contributing.

In the spirit of the mean field treatments of the properties of island films,[7] we assume that the local field at any ion is composed of a constant contribution from all of the islands, plus a distance dependent contribution from the island nearest each ion. For the latter, we use the same treatment for the fields of a single spheroid as has been used to account for SERS,[5] and obtain a function, $A(\omega,\vec{r})$ describing the distance-dependent enhancement of the local field and emission dipole of the molecule/island system.[6] Both the dipole, as well as higher order multipoles induced by the molecule in the silver island will be damped by the metal, leading to an increased nonradiative decay rate, Γ_{nr}. We consider only the dipolar damping term, which can also be expressed in terms of $A(\omega,\vec{r})$. As shown in Fig. 1, we obtain good agreement with the data if we assume that $A(\omega,\vec{r})$ at the emission frequency is much larger than at the excitation frequency. If we assume $A(\omega,\vec{r})$ is large at both frequencies, the agreement is not as good. In fact, measurements of the excitation frequency dependence of SERS from these films also suggest that $A(\omega,\vec{r})$ peaks near the emission frequency and is substantially reduced at the pump frequency. From the fit to the data, we obtain a value for the most rapid decay rate of the ions of $\Gamma \sim 0.5 \times 10^6$ Hz. This presumably corresponds to those ions nearest the silver islands, where the electromagnetic coupling is the strongest. To check this, and confirm our modeling, we repeated the experiment using an oxidized aluminum substrate rather than a silica substrate. Reflectivity measurements show that the silver electronic plasma resonance remains; but the bare oxidized Al strongly quenches the fluorescence from the Eu^{3+} ions. Thus we expect only those ions very near the islands to contribute to the observed signal. This appears to be the case: we regain the nearly exponential decay expected for ions at a constant separation from the silver islands. The measured decay rate of ~1.3 $\times$ 10^6 Hz is in reasonable agreement with the decay rate of the Eu^{3+} ions nearest the silver islands on the silica. The Al substrate results and the prediction of our model for this case are also shown in Fig. 1.
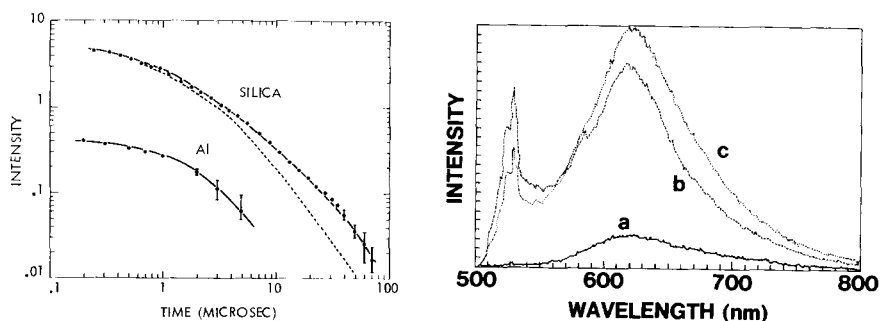
Fig. 1. (left) Decay of fluorescence from Eu^{3+} on silver-island films on silica
         and Al substrates, compared with the theoretical prediction assuming
         enhancement only at the emission frequency (solid line) and at both the
         emission and excitation frequencies (dashed line).

Fig. 2. (right) Fluorescence spectrum of basic fuchsin on (a) bare silica,
         (b) silver-island film on silica, and (c) silver-island film on oxidized
         Al.

Our modeling and the SERS data suggest that the absorption rate of the Eu^{3+} is
not significantly enhanced by the electronic resonance of the silver islands, yet
the total fluorescence from the silver island films is greater than from the same
coverage of Eu^{3+} on bare silica. This implies that the radiative emission
process on the silver island films is fairly efficient. These results have an
important consequence: they suggest that the effective quantum yield of a weakly
fluorescing molecule may be increased when it is placed near the silver
islands. The radiative emission rate may be increased enough by the electro-
magnetic interaction with of the silver islands to compete successfully with the
molecular nonradiative processes that otherwise lower the QE for fluorescence
from the isolated molecule.

To demonstrate the enhancement of the quantum yield, we study the fluorescence
from basic fuchsin, a dye molecule with a very low QE on bare silica. A fluor-
escence spectrum of a thin layer of basic fuchsin on bare silica is shown in Fig.
2(a). For a silver-island film with the same coverage of dye, the total fluor-
escence observed is increased by a factor of ~7, as shown in Fig. 2(b). The
sharp peak in the spectrum at lower wavelengths is SERS from the dye molecules.
When we repeat this experiment using a silver-island film on an oxidized Al
substrate, we observe essentially the same total fluorescence as on the silver-
island film on silica, as shown in Fig. 2(c). Since the oxidized Al totally
quenches any fluorescence from molecules between the islands, the observed fluor-
escence from both the silver-island coated Al- and silica-substrate samples must
originate from dye molecules directly on the silver islands. Electron micro-
graphs of the island films indicate that the silver covers 30-40% of the
surface. Thus the effective enhancement of the total emission per contributing
molecule on the silver islands is at least a factor of ~20 over those on bare
silica.

Evidence supporting an improved QE and not just enhanced absorption is obtained
by comparing the Raman scattering and the fluorescence intensities in Fig. 2.
For the silver island films, we can express the scattered intensities from the

contributing molecules as

$$I_{F\ell} \quad \alpha \quad \sigma_F |A(\omega_L)|^2 \quad \frac{\gamma_F |A(\omega_s)|^2}{\gamma_F |A(\omega_s)|^2 + \Gamma_{nr}} \tag{2}$$

for the fluorescence[6], and

$$I_{RS} \quad \alpha \quad |A(\omega_L)|^2 \; |A(\omega_s)|^2 \tag{3}$$

for the Raman scattering.[5] Here ω_L and ω_s are the laser and shifted frequencies respectively, σ_F and γ_F are the absorption cross section and radiative decay rate of the free molecule, and Γ_{nr} is the nonradiative decay rate of the molecule on the silver-island film. The expression for the fluorescence has the form of $I_{F\ell} \propto \sigma Y$, with the second term representing the yield on silver. The term Γ_{nr} includes both the molecular relaxation rate as well as the *increased damping rate* due to any additional absorption by the silver. The oxidized Al substrate changes the silver plasma resonance and thus the values of $|A(\omega)|^2$. Both for the data shown, and for results from all other samples we have tried, changing from a silica to an oxidized Al substrate causes a larger change in the total SERS intensity than in the total fluorescence. This suggests that the total decay rate in the dominator of the yield term in the expression for the fluorescence (Eq. 2) is not be dominated by the nonradiative decay rate Γ_{nr}. Thus, these results suggest that the *effective quantum yield* of the basic fuchsin on the silver islands has been *increased* over that of the free molecule.

In conclusion, we have presented a study of the effect of a silver-island film on both the lifetime and yield of fluorescing, adsorbed molecules. The lifetime is shortened dramatically and, because of the distribution of island-molecule spacings, the decay becomes nonexponential. A comparison of the SERS and fluorescence from a dye with a low quantum efficiency suggests that the emission process on the silver islands can be reasonably efficient, competing successfully with the molecular and electronic nonradiative damping. This can lead to an increase in the effective quantum yield of fluorescence and therefore be a useful way of improving the signal in fluorescence spectroscopy.

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