Luminescence of dye molecules adsorbed at a Ag surface

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The quenching of the luminescence of molecules adsorbed at a smooth Ag surface is offset by the enhancement of the incident and emitted em fields when they are adsorbed at a Ag island film. The observed spectra which exhibit hot and relaxed luminescence components are analyzed in terms of the relevant electronic processes.

The luminescence of molecules near a metal surface has been studied for systems where the luminescent molecules and the metal surface are separated by an intermediate, dielectric layer (e.g., fatty acid, solid argon).¹⁻³ These studies were largely concerned with the dependence of the luminescence intensity and lifetime on the metal-molecule separation. Our own work has focused on the luminescence of molecules adsorbed directly at the metal surface.⁴⁻⁶

The luminescence and resonant Raman scattering by dye molecules (e.g., fluorescein isothiocyanate, rhodamine 6G), which are not readily detectable when the molecules are adsorbed at a smooth Ag film, were first observed by Ritchie *et al.*^{4,5} for molecules adsorbed at a Ag island film. Other investigators have recently reported the enhancement of the optical absorption as well as the luminescence by molecules adsorbed at noblemetal island films.⁷⁻⁹

We report here results of measurements of the luminescence of dye molecules adsorbed at a "smooth" (continuous) Ag surface; adsorbed at a Ag island film and, for comparison purposes, adsorbed on glass, together with an analysis of the relevant electronic processes which are operative in each case. In the experiments carried out thus far we have used molecules such as fluorescein isothiocyanate⁴ and rhodamine 6G (R6G) which absorb and fluoresce in the visible. We find that the luminescence, which is readily observable when a monolayer of the dye molecules is adsorbed on glass, is strongly quenched and not detectable when the molecules are adsorbed at a smooth evaporated Ag film. On the other hand, when the molecules are adsorbed at a Ag island film, a sizable luminescence which includes both "hot" as well as "relaxed" luminescence components is observed. For molecules adsorbed at a 40-Å (mass thickness)

silver island film, the luminescence is an order of magnitude more intense than that for the molecules adsorbed on glass. Moreover, the molecules adsorbed at the Ag island film exhibit Raman scattering whose intensity is comparable to that of the luminescence. The Raman scattering by the optically absorbing molecules was not discernible when the molecules were adsorbed at the smooth silver surface. The observability of the luminescence and Raman scattering by the molecules adsorbed at a Ag island film is attributed to the enhancement of the incident and emitted em fields by the transverse localized surface-plasmon modes of the Ag island film.¹⁰

The monolayers of adsorbed dye molecules were prepared by immersing a clean glass slide for 30 min in a 10^{-4} M solution of the dye in ethanol. The slides were then rinsed under a stream of pure ethanol and blown dry with compressed Freon. The optical-absorption spectrum of a monolayer of R6G on glass, obtained by measuring the transmission through ten slides in tandem, exhibits a broad



FIG. 1. Normal-incidence transmission spectra for Ag island films of differing mass thicknesses which were deposited onto glass slides having adsorbed monolayers of R6G. The spectra do not perceptibly differ from those obtained for Ag island films deposited onto glass slides without the R6G monolayer.

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band at 5300 Å. The corresponding luminescence spectrum exhibits a broad peak at 5700 Å. Using the data on the integrated absorption by the R6G monolayer, we estimate the coverage to be 0.4. The Ag island films, which ranged in mass thickness from 5 to 150 Å, were prepared by vacuum deposition of Ag at a rate of 1 Å /sec from a boat 350 cm from the glass slide. The normal incidence transmission spectra (Fig. 1) for the R6G monolayers overlaid with Ag island films of various thicknesses exhibit a broad transmission minimum due to the excitation of the transverse localized surface-plasmon resonances of the silver island films, which shift to longer wavelengths with increase in mass thickness. The spectra differ only imperceptibly from the spectra for the Ag island films without the R6G monolayers. Glass et al.,⁷ however, reported splitting and broadening of the plasma resonance of Ag island films with adsorbed rhodamine B and nile blue dyes. We surmise from the transmission spectra for their films, which differ markedly from the corresponding spectra for the Ag island films without the dyes, that the thickness of their dye layer was appreciably greater than a monolayer.

Figure 2 shows the inelastically scattered light



FIG. 2. Curve (a)—the luminescence spectrum of a R6G monolayer on glass; curve (b)—luminescence and Raman scattering spectrum by a R6G monolayer overlaid with a 40-Å Ag island film; dashed curve—inelastically scattered light spectrum for a 40-Å Ag island film without the R6G monolayer. The spectra were obtained using 5 mW of 4765-Å argon laser light as the excitation source.

spectra for a R6G monolayer on glass, before and after deposition of a 40-Å Ag island film overlayer, and for a 40-Å Ag island film on glass without a R6G monolayer, which were obtained using 5 mW of p-polarized 4765-Å cw argon laser excitation. No luminescence or Raman scattering by the R6G molecules was detectable when the R6G monolayer was overlaid with a continuous silver film (thickness > 500 Å). We estimate that the R6G luminescence intensity was quenched by a factor of at least 10³ relative to the luminescence intensity of R6G on glass. The luminescence spectrum for the R6G monolayer overlaid with the Ag island film, which has a maximum at 5550 Å, is 6 times more intense than that for the R6G monolayer without the Ag island film. The spectrum also exhibits peaks at 1170, 1340, 1570, and 1650 cm^{-1} due to Raman scattering by the vibration modes of the adsorbed R6G molecules.¹¹ Moreover, there is an appreciable scattered light intensity at wavelengths close to the laser line, which we interpret as corresponding to hot luminescence¹² by the R6G molecules.

We have more recently obtained (in collaboration with R. B. Stephens) preliminary results for the luminescence for R6G molecules adsorbed at a Ag surface with submicroscopic, axially symmetric bumps.⁶ In this configuration all of the molecules are directly adsorbed at the Ag surface. This differs from the Ag island configuration in which a small fraction of the molecules are not in direct contact with Ag. The features of the observed spectra (i.e., Raman scattering, hot and relaxed luminescence) and their relative intensities are similar to those for the Ag island film overlayer configuration. The observation of the hot and relaxed luminescence and Raman scattering by the R6G monolayers overlaid with the Ag island films is attributed to the enhancement of the incident and emitted em fields arising from the excitation of the transverse localized surface-plasmon resonances of the Ag island films. Data on the dependence of the luminescence intensity on the mass thickness of the Ag island film indicated that a 40-Å film, whose broad adsorption band at 5500 Å overlaps the absorption and emission bands of the adsorbed R6G molecules, yielded the largest intensities of luminescence and Raman scattering by the R6G molecules.

The investigation of the phosphorescence of molecules near a metal surface has shown that for $d \leq 100$ Å the intensity and lifetime of the luminescence decrease with decreasing molecule—metal

separation. These effects are attributed to the deexcitation of the molecules by nonradiative energy transfer from the molecules to the metal.^{13,14} Three major processes have been identified: (a) the excitation of surface-em modes (sem) [which varies as $e^{-\alpha d}$ (where α is the attenuation constant for the sem field in the medium adjacent to the metal)]; (b) the generation of electronic currents in the metal (which varies as d^{-3}); and (c) the excitation of electron-hole pairs in the metal (which varies as d^{-4}).^{14,15}

When the molecules are adsorbed at the metal surface, there is an appreciable broadening and shifting of the molecular energy levels.¹⁶ As a consequence of the large widths of the electronic levels and of the appreciable broadening of the electronic excitations of the adsorbed molecules, the vibronic structure in the absorption and emission spectra will be smeared out. Finally, we note that when the excited electronic level of the adsorbed molecule lies above the Fermi level of the metal, the deexcitation of the molecules can also take place by charge transfer from the excited molecules to the metal.¹⁷

We now proceed to consider in detail the electronic processes that are involved in the luminescence of molecules adsorbed at a metal surface. The incident radiation induces a transition of the electron in the ground state to a vibrational level in the excited electronic state. (We note, however, that there may be sizable "indirect" excitation of the molecules via the transfer of energy from electron-hole pair excitations that are generated in the metal by the incident radiation. This will be particularly important for phosphorescent molecules whose transitions between the ground and excited electronic levels are normally forbidden, and would constitute a "substrate-sensitized luminescence."18) Following excitation, the electrons in the initially excited state dephase and (i) return to the ground state either radiatively (hot luminescence) or nonradiatively, or (ii) undergo thermal relaxation to lower-energy vibrational levels of the excited state from which they can make transitions to the ground state either radiatively (relaxed luminescence) or nonradiatively.¹²

The intensities of the hot and the relaxed luminescence are determined by the respective populations of the dephased initial and thermalized excited states, together with their respective matrix elements for radiative transitions from these states to the ground state. Under steady-state conditions the intensity of the (hot) luminescent emission from the initially excited level *i* is

$$I_{i} \propto h \nu_{i0} N_{i} \Gamma_{i0}^{R} ;$$

$$N_{i} = \Gamma_{0i}^{R} N_{0} \tau_{i} = \Gamma_{0i}^{R} N_{0} (\Gamma_{ij}^{T} + \Gamma_{i0}^{R} + \Gamma_{i0}^{NR})^{-1} , \quad (1)$$

where v_{i0} is the frequency of the emitted light, N_i is the number of molecules in the initially excited level *i*, Γ_{0i}^R is the rate of excitation by the incident radiation per molecule per second, N_0 is the number of molecules in the ground state, τ_i is the lifetime of the *i*th vibrational level, Γ_{ij}^T is the rate of "thermalization" of the level *i* to lower vibrational levels *j*, and Γ_{i0}^R and Γ_{i0}^{NR} are the rates of radiative transitions and nonradiative transitions from the *initially* excited level to the ground electronic state, respectively. We are omitting the effects of intermolecular energy transfer between neighboring molecules. Correspondingly, the intensity of the relaxed luminescence emission from the *thermally relaxed* excited state is

$$I_r \propto h v_{r0} N_r \Gamma_{r0}^R;$$

$$N_r = N_i Q_{ir} \Gamma_{ij}^T \tau_r = N_i Q_{ir} \Gamma_{ij}^T (\Gamma_{r0}^R + \Gamma_{r0}^{NR})^{-1}, \quad (2)$$

where N_r is the number of the molecules in the relaxed state r, Q_{ir} is the probability that a molecule in level i will thermalize to the state r [i.e., $Q_{ir}\Gamma_{ij}^{T}$ is the generation rate (by thermalization) of level rfrom level i], and Γ_{r0}^{R} and Γ_{r0}^{NR} are the rates of radiative and nonradiative transitions from the *relaxed* state to the ground state. [We note that in general $Q_{ir} < 1$ because of deexcitation transitions that take place during the thermalization process. However, when $\Gamma_{jj'}^{T} >> \Gamma_{j0}^{NR} + \Gamma_{j0}^{R}$ (for all intermediate levels j and j' between i and r), as is the case for R6G in dilute solution, then $Q_{ir} \approx 1$ and the rate of generation of the relaxed level r is equal to the rate of thermalization from the excited level i.] The ratio of the relaxed luminescence intensity to that of the hot luminescence is given by

$$\frac{I_r}{I_i} = \frac{\nu_{r0} Q_{ir} \Gamma_{ij}^T \Gamma_{r0}^R}{\nu_{i0} (\Gamma_{r0}^R + \Gamma_{r0}^{NR}) \Gamma_{i0}^R} .$$
(3)

Available data for R6G in dilute solution indicate that $\Gamma_{ij}^T >> \Gamma_{r0}^R >> \Gamma_{r0}^{NR}$ (and therefore, that $Q_{ir} = 1$), and that $\Gamma_{ij}^T \approx 10^{12} \sec^{-1}$ and $\tau_r \approx 10^{-9}$ sec, where the initially excited level *i* is within the first excited singlet electronic state and the state *r* corresponds to the thermally relaxed distribution of vibrational levels within that excited state.¹⁹ We shall assume that the relative magnitudes of these values also apply for the R6G molecules adsorbed on glass. If we make the further assumption that $\Gamma_{r0}^R \approx \Gamma_{i0}^R$ we obtain $I_r/I_i \approx 10^3$ for the R6G molecules on glass. This is consistent with the absence of any hot luminoscence component in the spectrum for R6G adsorbed on glass (Fig. 2).

When the R6G molecules are adsorbed on a continuous silver film, there is strong nonradiative transfer of energy from the excited molecules to the metal. The magnitude of Γ_{j0}^{NR} (j=i...r) is therefore very much greater than that for the molecules on glass and, in fact, is considerably greater than Γ_{i0}^{R} . As one important consequence, the excitedlevel lifetime τ_r is greatly decreased,²⁰ which is primarily responsible for the observed strong quenching of the relaxed luminescence. We also expect an increase in $\Gamma_{ii'}^{T}$ due to energy transfer from the vibrational excitations of the excited state to the metal. However, we do not expect the intensity of the hot luminescence to be as strongly affected by adsorption on the metal as that of the relaxed luminescence, since τ_i for the R6G molecules on glass is already very small.

When the molecules are adsorbed at the silver island film, the enhancements of the local incident and emitted em fields (due to excitation of the localized surface plasmons) increase both the molecu-

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lar radiative excitation rate Γ_{0i}^{R} and the radiative emission rate Γ_{i0}^{R} . The fact that the relaxed luminescence and hot luminescence are comparable in intensity suggests, on the basis of Eq. (3), that $\tau_r \approx (Q_{ir} \Gamma_{ij}^T)^{-1}$. Since the thermalization rate is large $(\Gamma_{ij}^T > 10^{12} \text{ sec}^{-1})$, this in turn suggests that the lifetime of the relaxed excited state may be as much as several orders of magnitude smaller than that for the molecules adsorbed on glass. A sizable relaxed luminescence is nevertheless observed because of the enhancements of the magnitudes of Γ_{0i}^{R} and Γ_{j0}^{R} , which offset the quenching effect of the large nonradiative deexcitation rate, and also lead to an increase in the intensity of the hot luminescence by at least 3 orders of magnitude compared to that for R6G molecules adsorbed on a smooth silver surface. Similar enhancements of the luminescence should also be observed for dye molecules adsorbed on colloidal Ag particles and on an electrochemically processed Ag electrode.

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