

## A COMPARISON OF RAMAN SCATTERING, RESONANCE RAMAN SCATTERING, AND FLUORESCENCE FROM MOLECULES ADSORBED ON SILVER ISLAND FILMS

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### ABSTRACT

The enhancement of Raman scattering (RS), resonance Raman scattering (RRS), and fluorescence from molecules adsorbed on silver-island films is reported. A hierarchy of enhancements is found:  $10^2$  for RS,  $10^3$  for RRS, and 0.1-10 for fluorescence, depending on the quantum yield of the free molecule. Using the framework of the electromagnetic theory of surface-enhanced Raman scattering, generalized to treat molecular resonance phenomena, we develop a unified picture of the role of the surface plasmon resonances, and the surface-induced damping, in the light scattering processes. The observed hierarchy of enhancements is shown to have important spectroscopic consequences.

### I. INTRODUCTION

There is little doubt that a major part of the enhancement of the Raman scattering cross-section of molecules adsorbed on some rough metal surfaces<sup>1</sup> arises from electromagnetic interactions between the incident radiation, the molecule and the electronic plasma resonances excited on the roughness features of the metal surface.<sup>2</sup> Such interactions also give rise to modification of other electromagnetic properties of adsorbed molecules, including lifetimes,<sup>3</sup> emission yields,<sup>4</sup> and multiphoton excitations.<sup>5</sup> Modifications of photochemical reactions has also been predicted<sup>6</sup> and recently observed.<sup>7</sup>

Of these optical properties, Raman scattering (RS) stands unique in being a non-resonance (from the molecular standpoint) phenomenon. This makes an important difference on the effect caused by the surface: while RS is affected primarily by the increased local electromagnetic field near the surface, resonance properties are also influenced by the effect of the surface of the widths, both of dephasing and lifetime origin, of the excited molecular levels. This difference between RS and resonance processes such as resonance

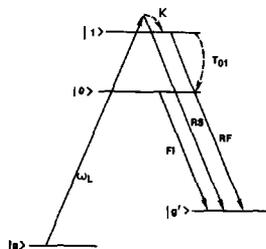
Raman scattering (RRS), resonance fluorescence (RF) (also termed hot luminescence), and ordinary, relaxed fluorescence (OF) results in substantial differences in the surface-induced enhancement factors associated with these phenomena.

In this paper we examine the relative surface enhancements for RS, RRS, RF, and OF, and present a unified picture of the effects of surface electromagnetic interactions on all of these inelastic scattering processes. Our theoretical considerations are based on a simple four-level model which accounts for all the observed trends. The experiments reported here are carried out using silver-island films coated with molecular layers. Our experiments shown that there is a heirarchy of enhancement factors with RS enhanced by  $\sim 10^5$  while RRS + RF (these two components cannot be resolved under our experimental conditions) are enhanced by  $\sim 10^3$ . The enhancement of OF depends on the quantum efficiency (QE) of the isolated molecule. The fluorecence from molecules with low QE is enhanced by one order of magnitude while that from molecules with high QE is actually decreased on the silver island film.

## II. THEORETICAL CONSIDERATIONS

Our theoretical discussion of the light scattering processes is based on the four-level model depicted in Fig. 1. The model includes an initial vibronic level  $|g\rangle$ , a final level  $|g'\rangle$  (in most circumstances these are two vibrational levels of the ground electronic state) and two intermediate levels  $|0\rangle$  and  $|1\rangle$  which represent different vibrational levels of an excited electronic manifold. This is the simplest model that can be used for a unified treatment of RS, RRS, RF, and OF, and the solid arrows in Fig. 1 represent each of these emission processes. We also consider two kinds of relaxation processes, which are represented by the dashed lines: (a) population decay arising from both the emission of radiation and from nonradiative processes like internal conversion and intersystem crossing and (b) pure dephasing arising from interactions with the thermal environment.

Fig. 1 Energy levels and scattering processes for the four-level model. Dashed lines represent non-radiative processes and solid lines represent radiative transitions.



Mathematically, processes of the first kind are accounted for by adding imaginary parts to the energies  $E_0$  and  $E_1$ . Those of the second kind may be taken into account by several available formalisms designed to treat the interaction of quantum systems with thermal baths.<sup>8</sup> A detailed treatment of the model is presented elsewhere<sup>9</sup>, and here we simply list the result obtained for the integrated intensities of the different emission components.

$$I_{RS} = \frac{\Gamma_1^{(R)}}{\gamma_1} \sigma_a |E_L|^2 \quad (1)$$

$$I_{RF} = \frac{\Gamma_1^{(R)}}{\Gamma_1 + \tau} \frac{\kappa}{\gamma_1} \sigma_a |E_L|^2 \quad (2)$$

$$I_{OF} = \frac{\Gamma_0^{(R)}}{\Gamma_0} \frac{\tau}{\Gamma_1 + \tau} \sigma_a |E_L|^2 \quad (3)$$

Here  $\kappa$ , is the "pure" dephasing rate of level  $|1\rangle$  due to intramolecular and thermal bath interactions,  $\tau$  is the population transfer rate from  $|1\rangle$  to  $|0\rangle$  (we ignore the reverse rate) and  $E_L$  is the local electric field. The excited state population decay rate is

$$\Gamma_1 = \Gamma_1^{(R)} + \Gamma_1^{(NR)} \quad (\Gamma_1 = 1,0) \quad (4)$$

and is the sum of the radiative and nonradiative components. The absorption cross-section is

$$\sigma_a = |\mu|^2 \chi \frac{\gamma_1/(2\pi)}{(\Delta\omega)^2 + (\gamma_1/2)^2} \quad (5)$$

where  $\mu$  is the electronic transition matrix, element,  $\chi$  is the appropriate Franck-Condon factor,  $\Delta\omega = \omega_L - \omega_1$  is the energy separation between the energy of level  $|1\rangle$ ,  $\omega_1$ , and the laser energy,  $\omega_L$ , and  $\gamma_1 = \Gamma_1 + \kappa + \tau$  is the total width of level  $|1\rangle$ . We use Eq. (2) both for normal RS and for RRS by taking  $\Delta\omega \gg \gamma_1$  or  $\Delta\omega \ll \gamma_1$  respectively in Eq. (5). Furthermore, since we cannot resolve RRS and RF in our experiments, we consider the combined intensity which we label

$$I_{RRS} = \frac{\Gamma_1^{(R)}}{\Gamma_1 + \tau} \sigma_a |E_L|^2 \quad (6)$$

We now generalize Eqns. (2)-(4) and (8) to include the effects of the surface. We assume that the intramolecular radiationless relaxation rates as well as the thermal dephasing and relaxation rates do not appreciably change upon adsorption. The effects of the surface that we do include are those arising from the local field enhancement, and the increased surface-induced radiative and nonradiative damping rates. Thus,

$$E_L(\omega_L) = E_I(\omega_L)A(\omega_L) \quad (7)$$

where  $E_I(\omega_L)$  is the incident field strength. The surface-induced damping is accounted for by adding an additional term,

$$\Gamma_1(S) = \Gamma_1(R,S) + \Gamma_1(NR,S) \quad (8)$$

to the inherent molecular damping rates,  $\Gamma_1$ . In particular the surface-induced emission rate is<sup>3</sup>

$$\Gamma_1(R,S) = \Gamma_1(R) |A(\omega')|^2 \quad (9)$$

Incorporating these effects in Eqns. (2), (4) and (7), we can express the enhancement ratios for each process as

$$R_{RS} = |A(\omega)|^2 |A(\omega')|^2 \quad (10)$$

$$R_{RRS} = |A(\omega)|^2 |A(\omega')|^2 \frac{\Gamma_1 + \Gamma}{\Gamma_1 + \Gamma + \Gamma_1(S)} \frac{\gamma_1}{\gamma_1 + \Gamma_1(S)} \quad (11)$$

$$R_{QF} = |A(\omega)|^2 |A(\omega')|^2 \frac{\Gamma_0}{\Gamma_0 + \Gamma_0(S)} \frac{\Gamma_1 + \Gamma}{\Gamma_1 + \Gamma + \Gamma_1(S)} \frac{\gamma_1}{\gamma_1 + \Gamma_1(S)} \quad (12)$$

We have approximated  $\Delta\omega \ll \gamma_1$  for the resonant processes.

The factor  $|A(\omega)|^2 |A(\omega')|^2$  is the usual SERS enhancement factor and is essentially molecule independent. The remaining terms depend on the molecular properties. Since the surface-induced broadening always adds to the molecular level width, the additional ratios in Eq. (11) ensure that the relative electromagnetic enhancement of RS is always less than that of RRS. For reasonable numbers ( $\gamma_1 \sim 1-10\text{cm}^{-1}$  and  $\Gamma_1(S) \sim 10-100\text{cm}^{-1}$ ) this reduction will be as much as 2-3 orders of magnitude. The ratios in Eq. (12) reflect the fact that the additional surface-induced damping mitigates the enhanced excitation rate because of the broadening of level  $|1\rangle$ , and decreases the

effective emission yield by adding additional non-radiative decay channels. The enhancement of OF is decreased even further because of the additional ratio in Eq. (13). In fact, since

$$\frac{|A(\omega')|^2 \Gamma_0}{\Gamma_0 + \Gamma(S)} = \frac{|A(\omega')|^2 (\Gamma_0^{(R)} + \Gamma_0^{(NR)})}{\Gamma_0^{(NR)} + |A(\omega')|^2 \Gamma_0^{(R)} + \Gamma^{(NR,S)}},$$

we see that for molecules with high QE ( $\Gamma_0^{(R)} \gg \Gamma_0^{(NR)}$ ) the increased emission rate cannot lead to any enhancement, and we might actually expect a net decrease in the fluorescence. In contrast, for molecules with low QE, the increased radiative emission rate may compete successfully with the molecular non-radiative decay rate, increasing the net enhancement.

### III. EXPERIMENTAL RESULTS

All the enhancement measurements are made by comparing the scattering from molecules adsorbed on silver-island films to that from an equivalent or known number of molecules in an inert environment. The molecules are deposited on the film using a dipping technique with the coverage controlled by the concentration of adsorbate in the dipping solution. For RS, we use p-nitrobenzoate (PNB), while for both RRS and OF we use Rhodamine 6G (R6G) and Basic Fuchsin (BF). The optical properties and electromagnetic behavior of the island films are well characterized by their absorption spectra.<sup>10</sup> The fabrication technique and the adsorbate coverage are controlled so as to use optically identical films allowing comparison of each of the scattering processes. Full details of the film preparation and characterization as well as the experimental techniques are discussed elsewhere.<sup>9,10</sup>

As shown in Fig. 2, the RS intensity from PNB increases monotonically at low concentration in the dipping solvent, but saturates at higher concentration. Because the adsorbate is chemisorbed, we attribute the saturation to the formation of a monolayer coverage, which we take as approximately  $6 \times 10^{14}$  molecules/cm<sup>2</sup> (Ref. 11). The measured enhancement of the 1600 cm<sup>-1</sup> band is  $\sim 10^5$ /molecule, when compared to a 0.25 M solution of PNB in basic ethanol. The excitation wavelength used is 514.5 nm, which is at the peak of the electromagnetic enhancement, as shown in Fig. 3.

The enhancement measurements for the resonant scattering processes are performed by comparing the signal from an island film to that of an equivalent coverage of molecules on a bare silica substrate. A separate set of experiments confirmed that the two surfaces had roughly equal coverages when

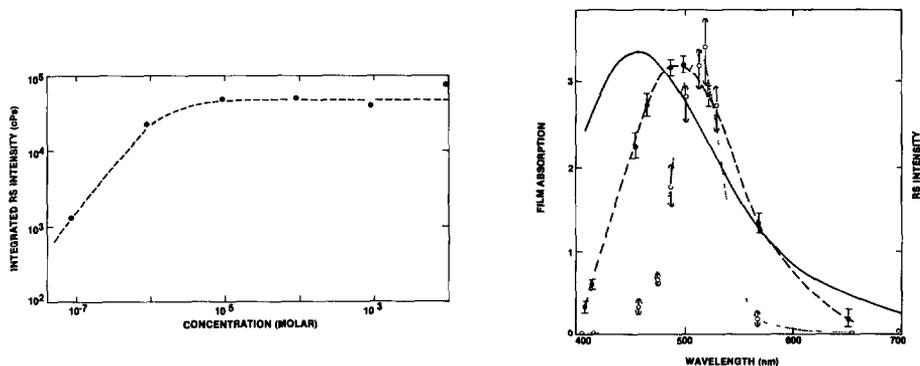


FIGURE 2. (LEFT) SERS intensity of the  $1596\text{ cm}^{-1}$  band of p-nitrobenzoate on an island film as a function of the concentration of p-nitrobenzoic acid in the ethanolic dipping solution.

FIGURE 3. (RIGHT) Silver-Island film excitation spectra of normal RS from p-nitrobenzoate (solid dots, dashed lines) and RRS from R6G (circles, dotted line), compared to the absorption spectrum of the film (solid line).

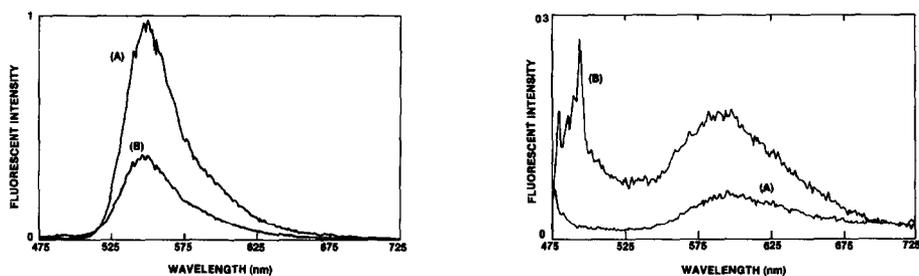


FIGURE 4. (LEFT) Fluorescence spectra of R6G (high QE) excited at 458 nm on (A) silica, and (B) silver-island film.

FIGURE 5. (RIGHT) Fluorescence spectra of BF (low QE) excited at 458 nm on (A) silica, and (B) silver-island film. The spectra are normalized to the peak intensity of R6G on silica in Fig. 4(A).

they were dipped under identical conditions.<sup>9</sup> The electromagnetic enhancement of RRS from the C=C stretch of the Xanthene skeleton of R6G ( $1650\text{ cm}^{-1}$ ) and BF ( $1590\text{ cm}^{-1}$ ) is  $\sim 10^3$ . The excitation wavelength used is 488.0 nm, which is near the peak of the electromagnetic contribution to the enhancement.<sup>9</sup>

Two sets of measurements are performed for OF. At low coverages on a bare silica substrate, R6G has a very high QE ( $\sim 1$ ) while that of BF is very low ( $< 0.01$ ). However, the absorption cross section and spectrum of each molecule is roughly the same. As shown in Fig. 4, the total fluorescence from the high QE R6G is decreased on the island film to  $\sim 0.3$  of its value on bare silica. In contrast, the fluorescence from the low QE BF is increased by nearly a factor of 4 on the island film compared to bare silica, as shown in Fig. 5. These measurements are made using 457.9 nm excitation, but similar results are found at other excitation wavelengths.

These experimental observations establish a clear hierarchy of enhancements;  $10^5$  for RS,  $10^3$  for RRS and  $\sim 0.1 - 10$  for OF depending on the QE of the molecule. These observations are correctly accounted for by the theoretical model.

#### IV. DISCUSSION AND CONCLUSIONS

The four level model used in section II is a grossly oversimplified approximation of the actual molecular system. The observed intensities arise from the superposition of many intermediate levels. However each of these levels is subjected to the same basic processes introduced in the four level model, namely dephasing and population relaxation. Thus the predictions of this model are expected to be qualitatively valid.

An additional complication that arises in a quantitative comparison of the model with the experiment is the necessity of accounting for the behavior of the adsorbates on a very inhomogeneous surface. Thus the use of the isolated spheroid model calculation is avoided, and the enhancement factors,  $A(\omega)$  as well as the surface-induced decay rates,  $\Gamma_1(S)$ , are taken to represent averages over all the molecules contributing to the signal. When this is done, consistent agreement with the experiment is obtained.<sup>9</sup>

Besides the advantage of the enhancement itself for surface spectroscopy studies, the observed hierarchy of enhancements has its own obvious importance. In particular the increase fluorescence intensity may be useful in fluorescence spectroscopy of molecules with low QE. The enhancement of RRS combined with the decrease in fluorescence for molecules with high QE makes resonance Raman spectroscopy feasible in cases where it would otherwise be

obscured by fluorescence.<sup>9</sup> This should have important applications in surface studies of strongly fluorescing molecules and of molecules of biological interest.

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