

## Modeling of Decay Rates for Molecules at an Island Surface

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The decay rates for molecules at rough surfaces are studied via an island surface model, with particular emphasis on the effect due to the *distribution* of surface roughness. Two extreme cases are studied when the surface islands distribute themselves evenly and when they coalesce to form local clusters at the molecule-substrate interface. The optical properties of the interfacial layer in these two cases are described by the Maxwell-Garnett and the fractal-cluster models, respectively. Among other results, it is found that both enhancement and suppression of the surface-induced decay rates are possible due to the presence of roughness, with more dramatic suppression taking place when the surface islands coalesce to form clusters.

### INTRODUCTION

The study of optical phenomena at rough interfaces has remained a topic of constant interest for over a hundred years. Among these, optical absorption and emission from adsorbed molecules have been studied intensively after the discovery of the dramatic surface enhancement of Raman scattering in 1974, for which roughness of the substrate metallic surface is understood to play the most significant role leading to the enhancement of the signal.<sup>1</sup> In particular, both experimental and theoretical studies of fluorescence from molecules at metal surfaces had been carried out in great detail by the late 1970's in the "far-distance regime" with molecule-surface distances ( $d$ ) greater than about 100 Å. Among many theoretical descriptions, the phenomenological approach of Chance, Prock and Silbey (CPS) stood out as one of the simplest models which had been very successful in explaining the observed modified lifetimes and level-shifts for the admolecules fluorescing in the vicinity of a metal surface.<sup>2</sup> It was not until the early 80's when experiments were carried out in the close distance regime ( $d < 100$  Å) that the CPS theory was found inadequate.<sup>3,4</sup> Many theoretical propositions have then been put forward to explain the discrepancy observed in the data and thereby modifying the CPS theory. These include the effects due to surface damping,<sup>4,5</sup> surface roughness,<sup>6,7</sup> and the nonlocal dielectric response of the substrate,<sup>8,9</sup> among others.

While all these effects or different combinations among them are plausible for explaining the data observed in a particular "close-distance experiment", we shall address specifically the effects due to surface roughness in this present work. Previous works have already studied this prob-

lem by modeling the surface as both a randomly-(Gaussian-distributed)<sup>6</sup> or periodically-roughened substrate.<sup>7</sup> Among other results, it was pointed out that the presence of roughness could lead to a suppression of nonradiative decay and hence *enhancement* of fluorescence compared to the flat surface case, due to a re-coupling of the non-radiative surface plasmon to radiative modes.<sup>7</sup> A recent experiment performed by Ahmadi and Rusling<sup>10</sup> has indeed revealed the possibility of observing enhanced fluorescence from pyrene adsorbed at a rough silver electrode. Aside from "extended" surface morphologies, "localized" structures have also been considered in the literature with most of the works adopting the "island surface model". In particular, the cases of an isolated surface island<sup>11,12</sup> as well as a two-dimensional array of islands<sup>13</sup> have all been studied previously. While the single island case has been studied very thoroughly taking into consideration also the nonlocal dielectric response of the substrate,<sup>9</sup> the case for a "two-island" or "many-island" substrate usually becomes quite complicated mathematically. A previous treatment has been limited to a static theory with local dielectric response from the substrate and the islands modeled as a 2D square periodic array of interacting spheres.<sup>13</sup> Detailed numerical results of up to a "five-sphere" substrate were worked out, and it was found that the nonradiative decay rates are quite insensitive to the geometry of the clustering spheres as long as the molecule is not located in the "cavity-site" (i.e. the space between two islands). An alternative and simpler approach would be to apply mean-field theory to calculate an "effective" dielectric response for the two-dimensional island layer at the interface. To this end, the theories of Maxwell-Garnett<sup>14,15</sup> and Bruggeman<sup>16</sup> have often been applied.

These previous investigations have all assumed that

the distribution of the surface islands is uniform throughout the interface layer,<sup>15,17</sup> which may not be very realistic for certain kinds of interfaces. In fact, a recent experiment on the fluorescence of R6G and malachite on porous silica surfaces has revealed fractal nature for the substrate surface.<sup>18</sup> More recently, scanning tunneling microscopy studies of metal-on-metal growth at submonolayer coverages have also revealed formation of fractal-like islands at the interface.<sup>19</sup> Hence, it is of interest to go beyond the "uniform-distribution" assumption for the islands to model the interfacial roughness. It is the purpose of the present work to study the effect of the "distribution of roughness" at the interface on the decay rates of the admolecules. We shall look at the extreme case where the surface islands coalesce to form clusters and compare with the results in the other extreme where they disperse themselves uniformly throughout the interfacial layer.

## THEORETICAL MODELING

For simplicity, we shall assume the admolecule to be a point dipole at a distance  $d$  from and oriented perpendicular to the substrate surface. The roughness at the interface is modeled as a 2D array of spherical islands (of equal radii  $a$ ) with the distribution of these spheres being arbitrary. We shall apply below an effective medium theory to calculate an average dielectric function for this "island layer" of thickness  $2a$ . Thus we have to solve the problem involving an emitting dipole on a "layered system" with the surface roughness now being replaced by a layer with an effective dielectric function ( $\epsilon$ ) calculated in terms of those of the molecular and of the substrate media. According to the phenomenological approach<sup>2</sup> and for a quantum yield of unity, the decay rate of the admolecule normalized to the free decay rate value can be expressed in the form

$$\frac{\gamma}{\gamma_0} = 1 - \frac{3}{2} \text{Im} \int_0^{\infty} \text{Re}^{-2i\pi k \frac{u^3}{l_1}} du, \quad (1)$$

where  $k = \sqrt{\epsilon_1} \omega/c$  is the emission wave number of the molecule and  $l_1 = -i\sqrt{l - u^2}$ .  $R$  is a kind of Fresnel reflection coefficient given by

$$R = \frac{R_{12} + R_{23}e^{-2i\pi k d_1}}{1 + R_{12}R_{23}e^{-2i\pi k d_1}}, \quad (2)$$

with  $R_{ij} = (\epsilon_j - \epsilon_i)/(\epsilon_j + \epsilon_i)$  and  $l_2 = -i\sqrt{\epsilon_2 - u^2}$ .  $\epsilon_1$  and  $\epsilon_2$  are the dielectric functions of the molecular and the substrate media, respectively, the distance  $d_1$  is that from the molecule to the interface and  $d_2 = 2a$  is the thickness of the

layer.

In order to study the effect due to the distribution of roughness at the interface on the decay rates, we have adopted the two models below (labelled as A and B) for the calculation of  $\epsilon$  in terms of  $\epsilon_1$  and  $\epsilon_2$ . We shall limit ourselves to the case of weakly-roughened surfaces so that the concentrations of these surface islands are low.

### Model A: Maxwell-Garnett Model

To model the case when the surface islands are dispersed uniformly throughout the layer, we follow the previous work<sup>15,17</sup> to adopt the Maxwell-Garnett (MG) model to determine the average dielectric function ( $\epsilon$ ) of the interfacial layer. The MG model is an effective medium theory which is accurate for small particle concentration. For spherical particles of dielectric function  $\epsilon_2$  distributed in a host medium  $\epsilon_1$ ,  $\epsilon$  can be obtained as

$$\epsilon = \epsilon_1 \left( 1 + \frac{3f\beta}{1 - f\beta} \right), \quad (3)$$

where  $f$  is the volume fraction of the particles, and  $\beta$  is the depolarizing field factor which takes the following form for spherical particles:

$$\beta = \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1}, \quad (4)$$

Note that  $\epsilon$  in this case does not explicitly depend on the radius of the sphere.

### Model B: 2D Fractal Cluster Model

For the other extreme where the particles coalesce to form local clusters, we have adopted the differential effective medium formalism by Hui and Stroud for the optical properties of fractal clusters.<sup>20</sup> Despite the simplicity of this model, it has been found that the results so obtained agree quite well to a certain extent with those from a more accurate computer simulation approach.<sup>21</sup> To be applicable to our present situation with the islands at the interfacial layer, the original version of the fractal cluster (FC) model must be varied a little. Instead of forming three-dimensional (3D) fractal clusters as in Ref. 20, mainly 2D clusters are formed here when the islands coalesce at the interface.<sup>22</sup> We recapitulate here some results from Refs. 20 and 22 in order to make our presentation clear. Following Ref. 20, we assume at a certain instant during the formation of the 2D (cylindrical) cluster that the size has grown to a radius  $R$  (thickness  $2a$ ), with a dielectric function  $\epsilon(R)$ . Then, for an infinitesimal increment in the size of the cluster, one can apply the effective medium theory to obtain<sup>22</sup>

$$\epsilon(R + dR) = \epsilon(R) - 2\epsilon(R) \frac{f'_c(R)}{f_c(R)} \frac{\epsilon_1 - \epsilon(R)}{\epsilon_m + \epsilon(R)} dR, \quad (5)$$

where  $f_c(R) = df/dR$ , with  $f_c$  being the volume fraction of the islands in the cluster, and for a 2D FC, we have

$$f_c(R) = \left(\frac{R}{a}\right)^{d_f-2}, \quad (6)$$

with  $d_f (< 2)$  being the fractal dimension of the cluster. One can hence obtain a differential equation involving  $\epsilon(R)$  from Eq.(6) which, on integration, yields the following algebraic equation for  $\epsilon(R)$ :

$$\frac{\epsilon(R)}{\epsilon(a)} \left[ \frac{\epsilon_1 - \epsilon(a)}{\epsilon_1 - \epsilon(R)} \right]^2 = [f_c(R)]^{-2}. \quad (7)$$

This result closely resembles that for the 3D cluster given in Ref. 20. Note that  $\epsilon(a) = \epsilon_2$  and is simply the dielectric function of the islands and the substrate. We shall assume here a metallic substrate with a complex dielectric function. Solving Eq. (7) as a quadratic equation for  $\epsilon(R)$  and ignoring the solution with a negative imaginary part,<sup>20</sup> one can obtain a unique result for the dielectric function of one cluster of the spherical particles when they coalesce.

The ultimate dielectric function for the whole "roughened layer" when the islands coalesce to form local fractal clusters is obtained by another application of the effective medium (MG) theory to a collection of these 2D clusters, as indicated briefly below.

Let  $f_v = f/f_c$  be the volume fraction of these 2D clusters in the layer. The average dielectric function for the island layer in the clustering case can then be given by<sup>14</sup>

$$\epsilon = \epsilon_1 \left( 1 + \frac{2f_v\beta_c}{1-f_v\beta_c} \right) \quad (8)$$

where  $\beta_c$  is the depolarizing field factor of the 2D cluster,

$$\beta_c = \frac{\epsilon(R) - \epsilon_1}{\epsilon(R) + \epsilon_1}. \quad (9)$$

Note that the factor 2 (instead of 3) appears in Eq. (8) since the clusters are now cylindrical in shape for the 2D case. With these two models (A and B), we can now study the effect on molecular decay rates due to the distribution of roughness at the interface.

## NUMERICAL RESULTS AND DISCUSSION

We have performed some computation using both Eqs. (7)-(9) and (3) together with (1) for the system studied previously using only the MG model.<sup>15</sup> Thus we have the mole-

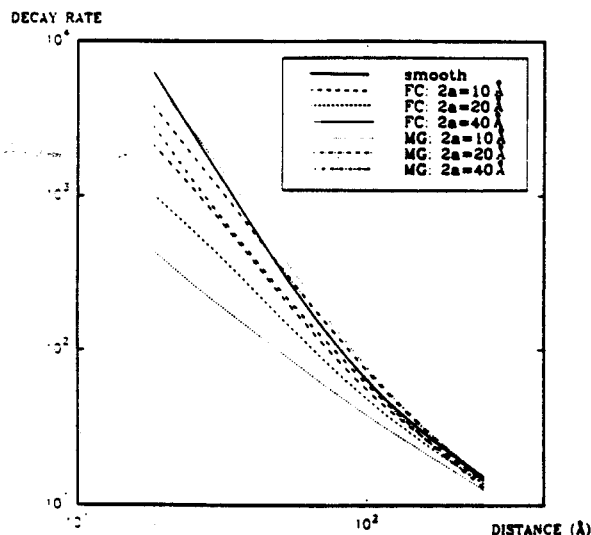


Fig. 1. Plot of normalized induced-decay rates versus molecular-surface distances for different sizes of the islands, with the interfacial roughened layer modeled according to both the Maxwell-Garnett (MG) and the fractal cluster (FC) models. The emission wavelength is fixed at 3800 Å, the volume fraction of the islands at 0.01, the fractal dimension at 1.7 for the FC case, and the size of one 2D cluster at  $R/a = 10$ .

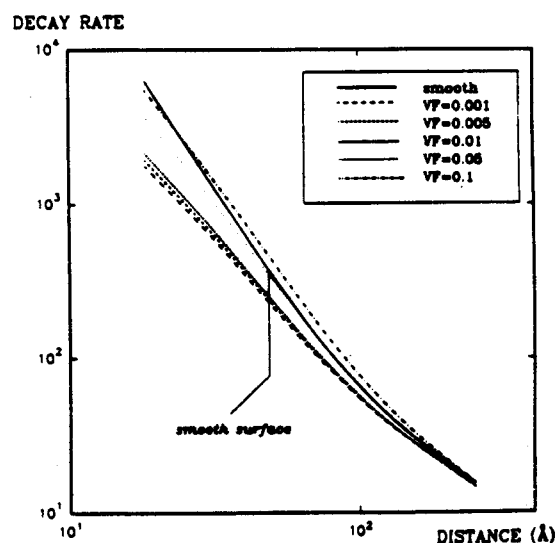


Fig. 2. Same as Fig. 1, except that the island size is fixed at a = 5 Å while the volume fraction is varied from 0.1% to 10%. Only the results from the FC model are shown in the graph.

cule emitting at a wavelength of 3800 Å in a medium with  $\epsilon_1 = 1.7$ , and the substrate is taken to be silver throughout, with the optical constants for silver available from the literature.<sup>23</sup> Fig. 1 shows the results for the normalized decay rates versus molecule-surface distances ( $d$ ) for different values of the surface island radius for both the MG and the FC models. It is clear that the case where the islands are clustered leads to a diminution of the induced-decay rates as compared to the case where they are dispersed throughout the interface layer. Furthermore, while almost all the results obtained in this calculation within the range of the set of the parameters give results smaller than those for the flat-surface case, "crossing" does occur between the flat surface and the MG curves. It can also occur with the FC curves for another set of parameters (see below). Thus it confirms once again that the presence of surface roughness can lead to both the possibilities of enhancing or suppressing the induced-decay rates for the admolecules as observed in various modeling studies.<sup>7,12</sup>

It is also remarkable to see the significant effects due to surface roughness at such close distances even for the slight presence of roughness at the interface (only 1% in volume fraction in this case). Fig. 2 shows similar decay-rate plots (versus  $d$ ) for the FC model for different values of the volume fraction of the islands. While suppression from the flat surface values is seen once again, one can see that as the "amount of metal" increases in the interfacial layer, dis-

sipation leads to larger nonradiative decay and hence less suppression. Crossing between the FC and the flat curves finally take place for  $V_F$  roughly above 5%. We also performed a similar calculation with the MG model and found that just like the case in Fig. 1, most results are greater than those from the FC modeling, and crossing with the flat surface curve occurs at a very low value of volume fraction at

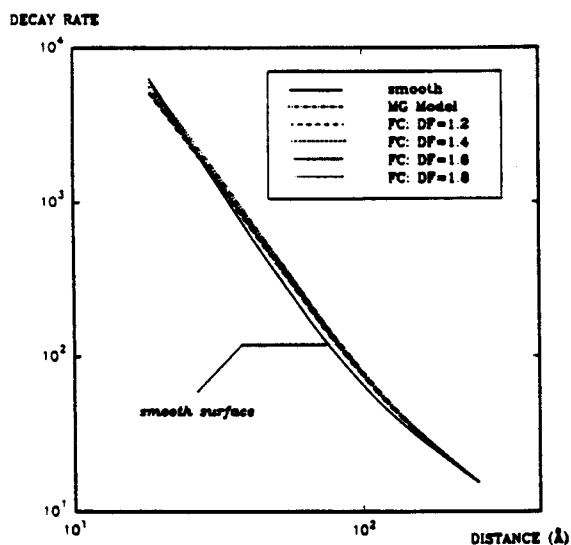


Fig. 3. Same as Fig. 1, except that both the volume fraction and the island size are fixed at 0.01 and 5 Å, respectively. The fractal dimension ( $DF = d_f$ ) is varied from 1.2 to 1.8 in the FC model.

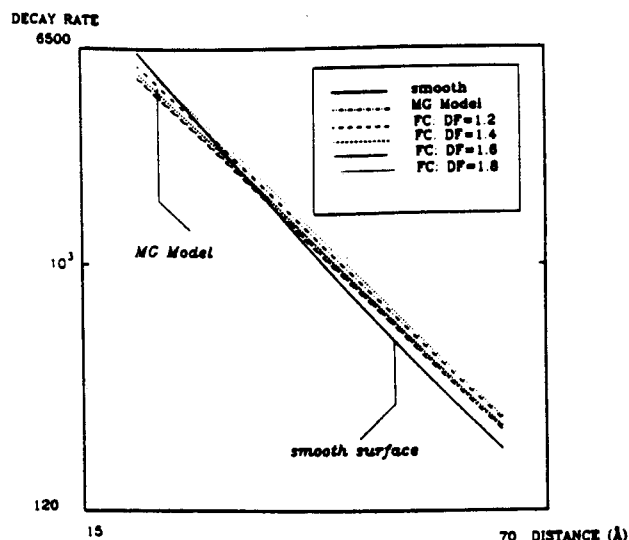


Fig. 4. An enlarged portion of Fig. 3.

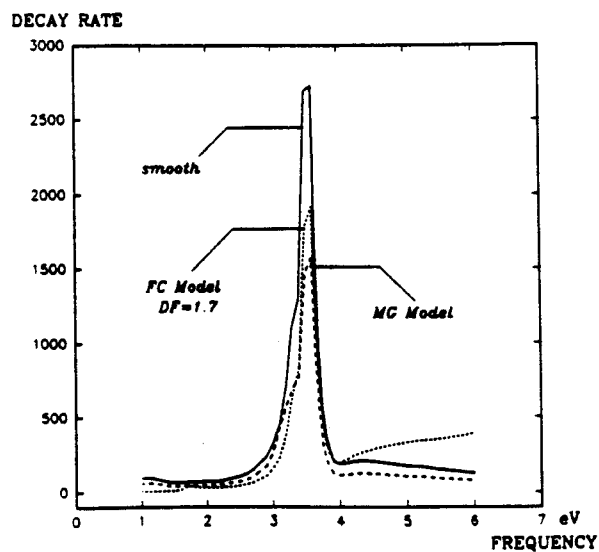


Fig. 5. Normalized induced-decay rate versus emission frequency of the admolecule for the flat-surface case, the MG model, and the FC model, respectively. The molecule-surface distance is fixed at 50 Å, and all other parameters are as in Fig. 3.

roughly something above 0.5%. Figs. 3 and 4 show again similar plots with the FC fractal dimension varied. This shows qualitatively the effect due to different "degree of clustering" among the islands. We see that while the overall results are not very sensitive to this factor, surface-induced damping does increase with the fractal dimension, and beyond a certain critical value of  $d_f$  ( $\sim 1.8$ ), the FC results become greater than those from the MG modeling. We should also mention that aside from being insensitive to the parameter  $d_f$  in the FC model, the results are also completely insensitive to the cluster size. We have varied  $R/a$  from 5 to 50 and seen no appreciable change in the results. Fig. 5 shows a plot of induced-decay rates versus emission frequency of the molecule for a distance fixed at  $d = 50 \text{ \AA}$ . We see that while the different cases (flat, MG, FC) give slightly different values for the decay rates, the resonant positions are almost identical and are all at roughly the flat-surface plasmon resonance frequency for silver ( $\sim 3.5 \text{ eV}$ ). This is consistent with previous results obtained by modeling the island surface as a periodic 2D array of spheres in which it was found that the nonradiative decay rates are quite insensitive to the geometrical structure of the substrate islands.<sup>13</sup> This is so for our calculation since at such a close distance of  $50 \text{ \AA}$ , we expect that the total decay rate is mainly nonradiative in nature.

## CONCLUSION

Within the mean field theory approach, we have studied the effect of surface roughness on the decay rates for admolecules in the vicinity of an island surface, paying particular attention to the role of the distribution of roughness at the interface. We believe that our modeling results can be tested since as mentioned above, fractal-clustering behavior among the islands was indeed observed in metal-on-metal growth processes. In comparison with previous modeling work which treats the surface islands as individual particles without averaging them over the interfacial layer,<sup>13</sup> our approach is highly simplified but limited in the sense that we cannot model the situation where the admolecule falls within the so-called "cavity site" at the interface. Moreover, our approach allows us to study different configurations for the distribution of the surface islands which would be otherwise extremely difficult without resorting to an all-numeric approach via computer simulation. Furthermore, as we have seen, the results obtained within this simple approach are quite consistent with previous results such as the possibility of both enhancing and suppressing flat-surface-induced decay rates due to the presence of roughness,<sup>7,12</sup> as

well as the insensitivity of the decay rates to the details of the island configurations at close molecule-surface distances.<sup>13</sup>

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## Key Words

Admolecule; Fractal cluster; Decay rate; Island surface.

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