

## Frequency shifts of molecules at rough metal surfaces

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The frequency shifts for dipolar transitions of molecules at rough metallic surfaces are studied in a phenomenological model following the approach of our previous work [Phys. Rev. B **36**, 4664 (1987)], with the surface roughness modeled by a shallow grating profile in most cases. The main findings here are as follows: (1) Such surface-induced shifts are indeed observable for molecular frequencies away from the surface-plasmon resonance frequency of the metal; (2) the presence of surface roughness can either enhance or suppress the flat-surface-induced shifts, leading to extra morphology-dependent resonances originated from the radiative coupling between the molecular emission and the substrate surface plasmon; and (3) the effects in the perfectly reflecting limit can be worked out analytically with numerical results showing interesting features that are unique for this case. Correlations are made with respect to previous experiments on vibrational shifts as well as to recent calculations from a microscopic approach.

### INTRODUCTION

The spectroscopic properties of molecules in the vicinity of a metal surface have been investigated intensively over the past decade, albeit in many cases a surface of perfect flatness has been assumed. Extensive reviews on this topic are available in the literature.<sup>1</sup> More recently, the effects due to corrugations at the metal-dielectric interface have also been studied, motivated partly by the recognition of the importance of surface roughness in processes such as surface-enhanced Raman scattering, and partly by the deviation of experimental results from theories based on a flat interface.<sup>2</sup> Moreover, most of these studies have dealt exclusively with the line-broadening effects which can be studied very accurately by measuring the lifetimes of fluorescent admolecules down to tens of angstroms molecule-surface distances ( $d$ ), by employing the Langmuir-Blodgett spacer technique. It is understood now, for the conditions when  $d$  lies beyond the chemisorption range ( $d \gtrsim 10 \text{ \AA}$ ) and when the molecular transition can be modeled as an oscillating dipole, that the classical electrodynamic phenomenological description is the simplest approach which has sufficient accuracy. For example, previous work in this approach on the lifetimes of these admolecules has clarified the importance of the dynamics in the energy-transfer process between the molecule and the substrate and in particular, the possibility of morphology-induced resonance in the decay rate spectrum has been revealed.<sup>3,4</sup>

A related, and relatively less often studied, problem accompanied with the above surface-induced line-broadening effect is the level shifts for the admolecules. Previous theoretical study<sup>5,6</sup> (with flat interfaces) has concluded that such level shifts (especially for electronic transitions) will hardly be observable, being overshadowed by the aforementioned line-broadening effects.

However, there were other theoretical as well as experimental studies on vibrational transitions which showed the possibility of observing these level shifts. For example, the vibrational mode shifts of benzoic acid in the vicinity of both metallic and superconducting electrodes have been measured to range from about 0.2 to 20 meV (Ref. 7) and model calculations showed that for systems such as CO on a *flat* Cu surface, the line-broadening effects are completely insignificant compared to the shifts in the vibrational levels.<sup>8</sup> Our present work here is to revisit the problem of these surface-induced level shifts, with particular interest in the effects due to the roughness of the surface which, to our knowledge, have not been considered before in the literature. We shall adopt a phenomenological approach which we had followed previously in the study of the admolecular decay rates and shall make comparison with various previous results<sup>5-8</sup> for a flat substrate surface, including some very recent microscopic results.<sup>9,10</sup>

### THEORY

Let us consider a molecule modeled as a point dipole in vacuum oriented normal ( $\parallel \hat{z}$ ) to a substrate surface which is characterized by a local and complex dielectric function  $\epsilon(\omega)$ . The morphology of the surface is described by a profile function  $z = \delta(x, y)$ . Previously, we have worked out a general perturbation theory for the interaction between such a dipole and the surface<sup>3</sup> by applying the theories of Maradudin, Mills, and Agarwal<sup>11,12</sup> to generalize the theory of Chance, Prock, and Silbey<sup>6</sup> to the case with a rough substrate surface. In order to be clear and self-contained in our present application of the previous theory, we have recapitulated some of the previous results in the following.

Consider a two-level molecule with characteristic frequency  $\omega_0$  and level width  $\gamma_0$  sitting on the surface

$z = \delta(x, y)$ . By modeling it as a damped oscillator being driven by the reflected fields from the surface, the level shift and line broadening (normalized with respect to  $\gamma_0$ ) are given approximately by

$$\frac{\Delta\omega}{\gamma_0} = -\frac{3q}{4k^3} \operatorname{Re}(G^{\text{flat}} + G^{\text{rough}}), \quad (1)$$

$$\frac{\gamma}{\gamma_0} = 1 + \frac{3q}{2k^3} \operatorname{Im}(G^{\text{flat}} + G^{\text{rough}}), \quad (2)$$

where  $q$  is the intrinsic quantum yield and  $k = 2\pi/\lambda$  is

the emission wave number. Equations (1) and (2) are valid provided that  $\gamma_0 \ll \omega_0$  and the molecule is not too close to the surface. The dyadic function  $G$  is defined as the reflected field per unit dipole moment acted on the molecule, and can be expressed as the sum of the contributions from the flat and rough part of the surface in the perturbative approach.<sup>3</sup> By solving the Helmholtz equation in the electrodynamic approach and for a dipole oriented along  $\hat{z}$ , one finally obtains to first order in roughness<sup>3,4</sup>

$$G(\omega) = \frac{E_z^{\text{rel}}}{\mu} = -k^3 \int_0^\infty du R \frac{u^3}{\alpha_1} e^{-2k\alpha_1 d} - ik^3 \frac{\epsilon - 1}{4\pi^2} \int dk_x \int dk_y \hat{\delta}(k_x, k_y) \frac{(k_x^2 + k_y^2) e^{ik_2 d}}{k_1 - \epsilon k_2} \int_0^\infty du (1 - R) \frac{u^3}{\alpha_1} e^{-k\alpha_1 d}, \quad (3)$$

where  $d$  is the molecule-surface distance,  $\hat{\delta}(k_x, k_y)$  is the Fourier transform of the profile function,  $k$  is the wave number of the emission from the molecule, the functions  $k_1, k_2, \alpha_1$ , and  $R$  are defined as

$$\begin{aligned} k_1 &= -[\epsilon(\omega)k^2 - (k_x^2 + k_y^2)]^{1/2}, \\ k_2 &= \begin{cases} [k^2 - (k_x^2 + k_y^2)]^{1/2} & \text{for } k^2 > k_x^2 + k_y^2 \\ i[k_x^2 + k_y^2 - k^2]^{1/2} & \text{for } k^2 < k_x^2 + k_y^2, \end{cases} \\ \alpha_1 &= -i(1 - u^2)^{1/2}, \quad R = \frac{\alpha_2 - \epsilon\alpha_1}{\alpha_2 + \epsilon\alpha_1}, \end{aligned} \quad (4)$$

with  $\alpha_2 = -i(\epsilon - u^2)^{1/2}$ . For a sinusoidal grating profile of the form  $z = \delta e^{iQx}$ , we finally obtain

$$\begin{aligned} G(\omega) &= -k^3 \int_0^\infty du R \frac{u^3}{\alpha_1} e^{-2k\alpha_1 d} \\ &\quad - ik^3 \delta \frac{\epsilon - 1}{k_1 - \epsilon k_2} Q^2 e^{ik_2 d} \\ &\quad \times \int_0^\infty du (1 - R) \frac{u^3}{\alpha_1} e^{-k\alpha_1 d}, \end{aligned} \quad (5)$$

with  $k_1 = -[\epsilon(\omega)k^2 - Q^2]^{1/2}$ ,  $k_2 = (k^2 - Q^2)^{1/2}$  for  $k > Q$ ; and  $k_2 = i(Q^2 - k^2)^{1/2}$  for  $k < Q$ . In the limiting case when the substrate becomes perfectly reflecting (conducting), we have  $R = -1$  (Ref. 6) and obtain

$$\begin{aligned} G(\omega) &= \left[ -\frac{ik}{2d^2} + \frac{1}{4d^3} \right] e^{2ikd} \\ &\quad - 4\delta \frac{\epsilon - 1}{k_1 - \epsilon k_2} Q^2 \left[ \frac{1}{d^3} - \frac{ik}{d^2} \right] e^{i(k+k_2)d}. \end{aligned} \quad (6)$$

In the following, we shall use the results in Eqs. (5) and (6) to study the effects on the frequency shifts for such molecule-grating system according to Eq. (1).

#### NUMERICAL RESULTS AND DISCUSSIONS

We have carried out a numerical study of the surface corrugation effects on Eq. (1) in the shallow roughness

limit with  $Q\delta \lesssim 0.03$  for most of the cases. Except for the perfect conducting case, we have taken the substrate to be silver whose optical constants are available in the literature.<sup>13</sup> All the frequency spectra have the molecule-surface distance fixed at 50 Å. Figure 1 shows a plot of the decay rate and frequency shift, normalized to the free molecule decay rate  $\gamma_0$ , versus the emission frequency of the molecule. The roughness parameters in this case only lead to small deviations by either lowering or enhancing the flat-surface values. In particular, with reference to the observability of the frequency shifts, previous work with flat surfaces has concluded that such shifts are hardly observable, being always overshadowed by the induced line broadening.<sup>5</sup> This is, as we can see from Fig. 1, only true when  $\omega_0 \sim \omega_{sp} \sim 3.7$  eV for silver, which is the case for many electronic transitions with uv or visible frequencies. For  $\omega_0 \ll \omega_{sp}$ , however, we can see that an appreciable down shift of  $\omega_0$  is indeed observable while  $\gamma$  becomes very small. This can be understood physically as follows: while the interaction potential energy between a static dipole and its image is always attractive, the time lag between an oscillating (dynamic) dipole and its image response will lead to more "repulsive components," due to misalignment between the two dipoles, and hence the overall interaction in this case is less attractive. Hence, this "retardation effect" will lower by a lesser amount in the energy of the excited state of the molecule and hence a smaller amount in the down shift of the transition frequency. In fact, one would expect  $\Delta\omega \rightarrow 0$  when  $\omega_0 \rightarrow \infty$ . In addition, we observe that a kind of anomalous dispersion appears in the region when  $\omega_0 \sim \omega_{sp}$ . As a matter of fact, these down shifts, when  $\omega_0 \ll \omega_{sp}$ , had indeed been observed in the literature for vibrational transitions of organic molecules in the vicinity of metals and superconductors.<sup>7</sup>

Figure 2 shows the morphology-induced resonance effects on the frequency-shift spectrum. As can be seen, the positions of these peaks are very sensitive to the value of  $Q$  and such peaks disappear in the flat-surface case. The resonances actually occur at emission frequencies with  $k \sim Q$ , and such a phenomenon can only be de-

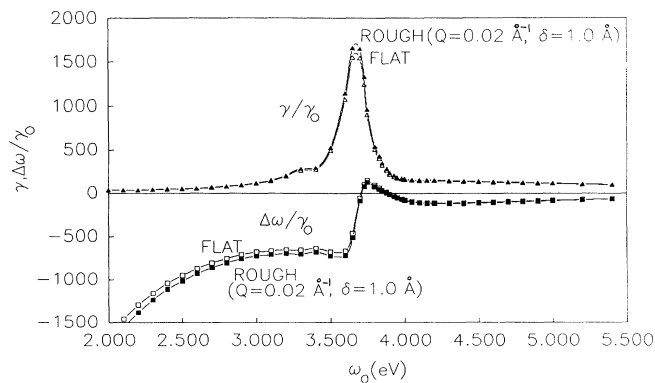


FIG. 1. Normalized decay rate and frequency shift as a function of emission frequency for both the flat and rough surface with the grating parameters as shown.

scribed when the fully dynamical theory is used, rather than the static image theory,<sup>4</sup> due to the fact that the origin of these peaks comes from the radiative coupling of the surface plasmon in the presence of surface roughness. Thus far, we could only exhibit these resonances for  $\omega_0 > \omega_{sp}$ . Furthermore, for a given resonance, the magnitude and sign of these morphology-induced shifts are very sensitive to the values of  $Q$ . As can be seen from Fig. 3, one can have an up shift changed to a down shift by varying  $Q$  by as little as 0.5%.

Let us now turn to the case of a perfectly reflecting (conducting) substrate, in which the phenomenological theory for flat surfaces had been applied before in the literature, in the analysis of molecular frequency shifts near a superconducting electrode.<sup>7</sup> In this case, the effects of the surface roughness can simply be studied by using Eq. (6) in Eqs. (1) and (2).

In Fig. 4 we show the decay-rate spectrum for  $R = -1$  in which we see that for the flat ( $Q=0$ ) case, there is no surface-plasmon-induced resonance and  $\gamma/\gamma_0$  stays more or less constant at the value of about 2 for the range of  $\omega_0$

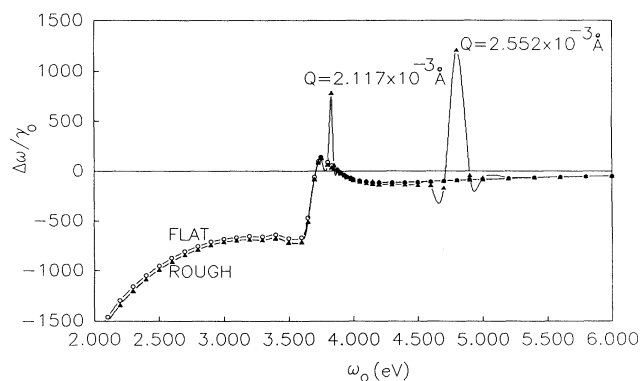


FIG. 2. Normalized frequency shift as a function of emission frequency for different grating parameters. Note the morphology-induced resonance peaks.

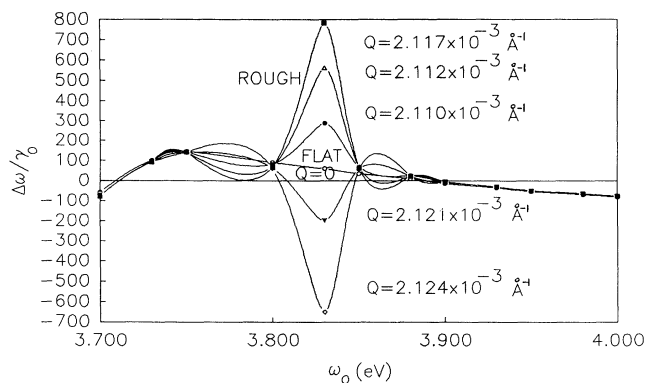


FIG. 3. Same as in Fig. 2, except that the sensitivity of the morphology-induced peaks to small variation of the grating period is shown here.

being considered. This is due to the fact that there is no dissipation into the metal in this case and hence no non-radiative transfer can take place. The value of 2 can be accounted for from the radiative transfer by the molecular dipole and its identical image. However, as in Fig. 2, when there is surface structure ( $Q \neq 0$ ), radiative coupling to the surface plasmon can then occur and lead to the morphology-induced peaks as shown. A similar phenomenon can also be observed in the frequency-shift spectrum (Fig. 5). As  $\omega \rightarrow \infty$ , we expect  $\gamma/\gamma_0 \rightarrow 1$  and  $\Delta\omega/\gamma_0 \rightarrow 0$  as expected, whether the substrate is perfect conducting or not.

Figure 6 explores the distance dependence of the frequency shifts according to the present dipolar-transition model, which is supposed to be valid only when the molecule is not too close to the surface (with  $d \geq 10 \text{ \AA}$ ). Again, the surface effects will lead to a down shift which increases with decrease in  $d$  due to the induced attractive interaction as explained before. When  $d$  becomes very small, one has to look into the details of the interaction between the constituents of the molecule and the surface

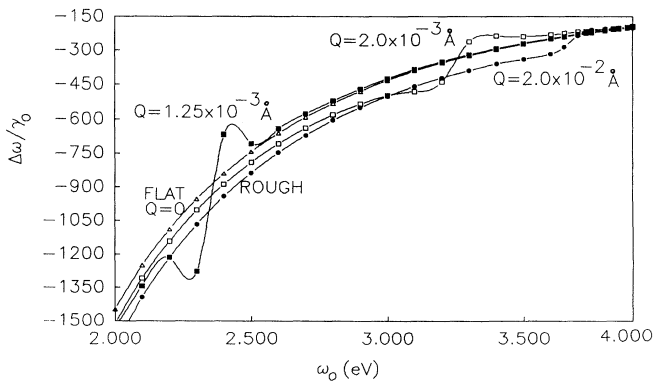


FIG. 4. Normalized decay rate vs emission frequency for a perfect reflecting substrate with different roughness parameters. Note the logarithmic scale used for the decay rates.

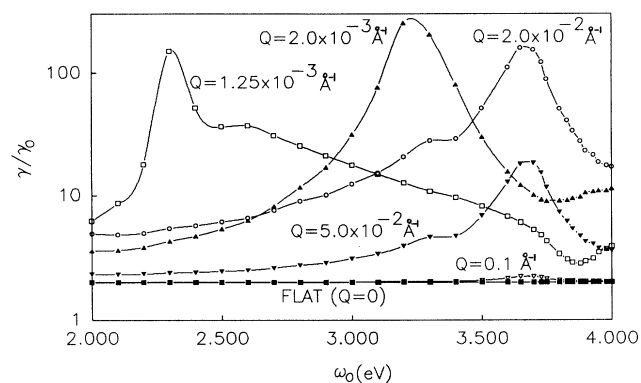


FIG. 5. Same as in Fig. 4, but for normalized frequency shift vs emission frequency, on a semilogarithmic scale.

electrons. A recent microscopic analysis<sup>9</sup> which calculates the quantum-mechanical transition probabilities for hydrogenlike systems near jellium metal surfaces finds that in the close distance regime ( $d \lesssim 10 \text{ \AA}$ ), the overall interaction becomes repulsive and leads to an up shift of the emission frequencies of the adsorbate. In the same work, it is also confirmed that at large distances, the overall interaction will become attractive leading to down shifts in the emission frequencies which are then consistent with the present finding from our phenomenological dipolar emission model. A more recent investigation from a second quantization approach<sup>10</sup> concludes that the phenomenological model may generally give the correct qualitative behavior of the results. Nevertheless, it would be extremely difficult, if not impossible, for the quantized theories to treat the case of rough surfaces. Our present analysis for rough surfaces, though phenomenological, is very feasible and should at least have some merit in understanding qualitatively the roughness effects.

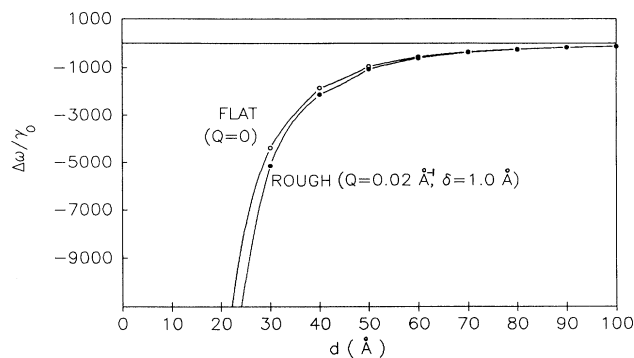


FIG. 6. Normalized frequency shift vs molecule-surface distance for a silver surface with emission frequency fixed at 2.5 eV.

## CONCLUSION

Within a simple phenomenological model, we have explored the effects of surface roughness on the frequency shifts of ad molecules in the vicinity of a metal surface with a shallow grating profile. It would be interesting if experiments such as those for studying vibrational shifts<sup>7</sup> can be designed to verify the present results from modeling, especially the morphology-dependent resonances in the case or both ordinary and superconducting substrates.

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