# REMARK ON THE MORPHOLOGY-DEPENDENT RESONANCE IN THE DECAY RATE SPECTRUM FOR MOLECULES NEAR A SPHERICAL SURFACE

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It is known that in the decay rate spectrum for molecules near a spherical surface, an extra morphology-dependent resonance structure appears in addition to the usual surface plasmon resonance ($\omega_{\mathrm{sp}} \approx \omega_{\mathrm{p}}^{\mathrm{bulk}}/\sqrt{3}$). Here an alternative but more physical interpretation of these peaks is given, where it is seen that the morphology-dependent peak can be described only in a dynamic retarded theory.

## 1. Introduction

It is well known that morphological effects play a very important role in surface spectroscopic studies [1], and in particular, decay rates for molecules located near a sphere (which serves as a prototype surface structure) have been reported extensively in the literature [2–6]. Previously, the behavior of the decay rates as functions of the molecule–surface distance and molecular orientation has been studied. In addition, it has been observed that the simple nonretarded image theory can be very inaccurate for large molecule–surface distances or highly conducting spheres [5]. In this work, we study further the decay rate spectrum as a function of emission frequency within the context of the dynamic energy transfer theory (ET) [3–6] and compare it with the results obtained from the static image theory (IT) [2]. We see that the morphology-dependent peak obtained previously by Ruppin [3] can be interpreted as the radiative energy transfer resonance between the molecule and the sphere, and that such peak can be described only in the context of the dynamic theory.

## 2. Brief summary of previous results

Let us consider the simplest case of a radial dipole located at $(d, 0, 0)$ above a sphere of radius $a$. By assuming a quantum yield of unity, the total (T) and radiative (R) normalized decay rates have been obtained previously within ET in the form [6]

$$\frac{\gamma_{\mathrm{T}}^{\mathrm{ET}}}{\gamma_0} = 1 + \tfrac{3}{2} \operatorname{Re} \sum_{n=1}^{\infty} (2n+1) n(n+1) B_n \left( \frac{h_n^{(1)}(kd)}{kd} \right)^2 , \quad (1)$$

$$\frac{\gamma_{\mathrm{R}}^{\mathrm{ET}}}{\gamma_0} = \tfrac{3}{2} \sum_{n=1}^{\infty} n(n+1)(2n+1) \times \left| \frac{j_n(kd) + B_n h_n^{(1)}(kd)}{kd} \right|^2 , \quad (2)$$

where $j_n$ and $h_n^{(1)}$ are the spherical Bessel and Henkel functions, and $k = \omega/c$ is the wave number of the molecular emission. $B_n$ is a kind of "Mie coefficient" defined by

$$B_n = \frac{j_n(ka)\psi_n'(\sqrt{\epsilon}ka) - \epsilon j_n(\sqrt{\epsilon}ka)\psi_n'(ka)}{\epsilon j_n(\sqrt{\epsilon}ka)\zeta_n'(ka) - h_n^{(1)}(ka)\psi_n'(\sqrt{\epsilon}ka)} , \quad (3)$$

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with $\psi_n(x) \equiv xj_n(x)$, $\zeta_n(x) \equiv xh_n^{(1)}(x)$, and $\epsilon(\omega)$ is the complex dielectric function of the substrate sphere. The non-radiative (NR) rate can then be obtained as a difference between (1) and (2). On the other hand, upon adopting the simpler non-retarded IT, one obtains [5]

$$\frac{\gamma_T^{IT}}{\gamma_0} = 1 + \frac{3}{2k^3} \operatorname{Im} \sum_{n=1}^{\infty} \alpha_n(\omega) \frac{(n+1)^2}{d^{2(n+2)}}, \tag{4}$$

where the $n$-pole polarizability $\alpha_n(\omega)$ is given by

$$\alpha_n(\omega) = \frac{n(\epsilon-1)}{n(\epsilon+1)+1} a^{2n+1}. \tag{5}$$

Strictly speaking, we cannot have radiative transfer in IT since the dipole cannot radiate in the static limit [7]. Nevertheless, Gersten and Nitzan (GN) [2] have devised a simple model to include the radiative transfer within IT, and their result for a radial dipole is obtained as

$$\frac{\gamma_R^{IT}}{\gamma_0} = \left| 1 + 2\left(\frac{a}{d}\right)^3 \frac{\epsilon-1}{\epsilon+2} \right|^2. \tag{6}$$

Previously, we have studied in detail the different distance behaviors of expressions (1) and (2) as compared to those of (4) and (6) [5-7]. Here we want to compare the two theories by studying the decay rate spectrum as a function of the emission frequency $\omega$. Before we present our numerical results, it is interesting to point out that the "resonance structure" implied from ET is very different from that obtained within IT. While in ET resonance arises from the singular behavior of $B_n$, which depends on *both* the dielectric ($\epsilon$) and geometrical ($a$) properties of the sphere (the "Mie resonances"), the situation in IT is quite different and depends only on the dielectric property of the sphere. We illustrate these features through numerical computations in section 3.

## 3. Numerical results

Fig. 1 shows the total decay rates according to both ET and IT for a radial dipole located at $(d, 0, 0)$ with $d = 1000$ Å above a silver sphere for three different values of the radius $a$ (with the actual molecule–surface distance $d-a$ ranging from 50 to 500 Å). It can be seen that IT (dotted curves) becomes more inaccurate as the molecule is located farther from the sphere (note the log scale for $\gamma_T/\gamma_0$) [5]. But what is of more interest is the appearance of an extra resonance structure in ET (solid curves) in addition to the ordinary surface plasmon peak with $\omega_{sp} \approx \omega_p^{bulk}/\sqrt{3}$ [3]. At the low-frequency end, this extra peak appears in ET with its position and magnitude varying according to the size of the sphere, while only the ordinary plasmon peak shows up in IT. While Ruppin [3] explained the origin of these peaks in terms of the dipole ($l = 1$) and higher multipole contributions ($l > 1$), here we present a slightly different interpretation. In fig. 2, we show the separate contributions from the radiative (dotted) and non-radiative (dashed) transfers to the total rate according to ET. It is clear that this new peak arises from the resonance behavior of the radiative transfer which of course is absent in the non-retarded IT. This peak may grow to overshadow the ordinary plasmon peak, to appear like a peak shift in the decay rate spectrum (fig. 1c). A similar peak-shift phenomenon has been observed before in surface-enhanced Raman scattering [8]. In fig. 3 we show the same calculation for the configuration of fig. 2 using IT and the GN model

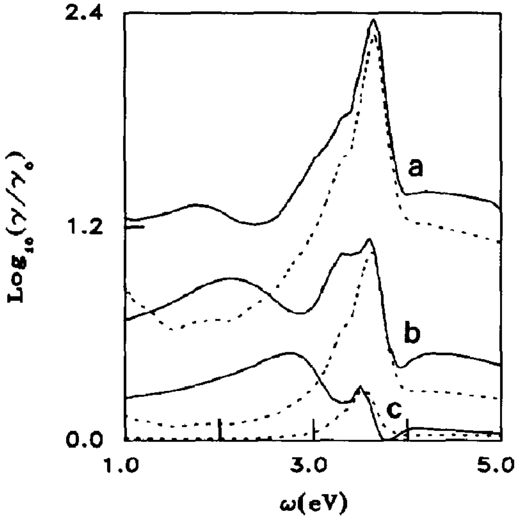

Fig. 1. Decay rate spectrum for a molecule located at $d = 1000$ Å from the center of a Ag sphere for various values of the radius $a$: (a) 950 Å, (b) 750 Å, (c) 500 Å. The solid curves represent the results from the dynamic theory (ET) and the dotted curves the results from the image theory (IT).

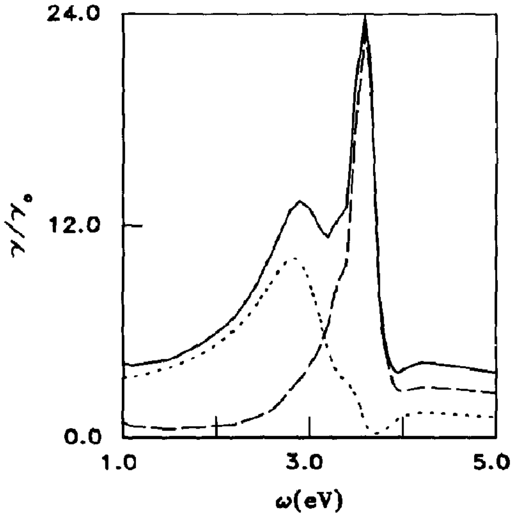

Fig. 2. Decay rate spectrum for a molecule located at $d=700$ Å from the center of a Ag sphere of radius $a=500$ Å according to the dynamic theory. The solid, dotted and dashed curves denote the total, radiative and non-radiative rates, respectively.

for the radiative rate (eq. (6)). From the comparison of figs. 2 and 3, we see clearly that IT describes the non-radiative transfers quite accurately and the GN model for the radiative rate within IT is inaccurate. Furthermore, the peak for $\gamma_R^{IT}$ according to the GN model cannot move according to different sizes of the sphere, since it is completely determined by the dielectric property of the sphere as revealed in eq. (6). This, of course, contradicts the exact result as shown in fig. 1.

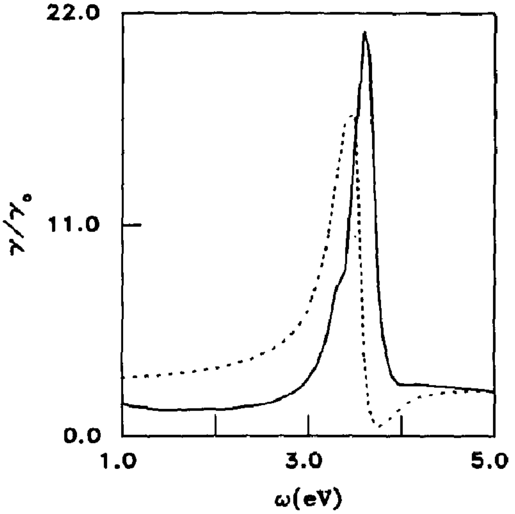

Fig. 3. Same as fig. 2, except that the image theory is applied. The solid and dotted curves denote the total and radiative rates, respectively.

## 4. Discussion and conclusion

Since the exact dynamics for any dipole–substrate system generally presents a rather complicated mathematical problem, it has been a wide belief [2,9,10] that under ordinary experimental situations where the molecule–surface distance ($s \approx 10^2$ Å) is much smaller than the emission wavelength ($\gamma \approx 10^3$ Å), the simpler non-retarded theory (IT) can be applied instead. Previously, we have pointed out that this is only true if the conductivity of the substrate is relatively low so that $s$ is much smaller than $\delta$, the skin depth of the substrate [11]. In this present work, we have observed further that for a rough surface (a sphere in this case), the condition $s \ll \lambda$ is not sufficient if the emission frequency is within the resonance peak of the radiative transfer (see fig. 1a, where $s=50$ Å $\ll \lambda \approx 10^3$ Å). The decay rate spectrum for a molecule near a rough surface according to the dynamic theory should have a multipeak structure in general, and a "shift" in the ordinary peak may seem to occur as explained above. This should shed some light on the earlier controversy as to whether surface roughness may lead to a peak shift in the energy loss spectrum as observed in an experiment of electron scattering upon a Mo surface [12]. This multipeak phenomenon does not happen for the case of a flat surface (where the conditions $s \ll \lambda$ and $s \ll \delta$ are sufficient for IT to be valid), since the surface plasmon mode cannot couple to the radiative mode without the presence of roughness. However, the phenomenon of the morphology-dependent peaks should be very general and should occur for any kind of rough surfaces. In fact, we have recently observed a similar multipeak phenomenon for the case of a grating surface [13]. Hence we conclude that the exact dynamic theory for the classical decay rates of molecules at rough surfaces contains much richer features which the simpler image theory (or the GN type approach to radiative decay) cannot adequately describe, irrespective of the usual situation where the molecule–surface distance is much smaller than the emission wavelength.

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## References

[1] H. Metiu, Progr. Surface Sci. 17 (1984) 153;
M. Moskovits, Rev. Mod. Phys. 57 (1985) 783.

[2] J.I. Gersten and A. Nitzan, Surface Sci. 158 (1985) 165, and references therein.

[3] R. Ruppin, J. Chem. Phys. 76 (1982) 1681.

[4] H. Chew, J. Chem. Phys. 87 (1987) 1355.

[5] P.T. Leung and T.F. George, J. Chem. Phys. 87 (1987) 6722.

[6] Y.S. Kim, P.T. Leung and T.F. George, Surface Sci. 195 (1988) 1.

[7] P.T. Leung, Y.S. Kim and T.F. George, J. Phys. Chem., to be published.

[8] K. Ohtaka and M. Inoue, J. Phys. C 15 (1982) 6463.

[9] L.E. Brus, J. Chem. Phys. 73 (1980) 940; 74 (1981) 737.

[10] N. Liver, A. Nitzan and K.F. Freed, J. Chem. Phys. 82 (1985) 3831.

[11] P.T. Leung, T.F. George and Y.C. Lee, J. Chem. Phys. 86 (1987) 7227.

[12] J. Lecante, Y. Ballu and D.M. Newns, Phys. Rev. Letters 38 (1977) 36;
T. Rahman and A.A. Maradudin, Phys. Rev. B 21 (1980) 504.

[13] P.T. Leung, Y.S. Kim and T.F. George, Phys. Rev. B, to be published.