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Emission frequency of single molecules at a metallic aperture: the applicability of the image theory

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Abstract

The simple classical image theory is applied to describe the shift in emission frequencies for single molecules at a metallic aperture. The validity of this approach is further clarified using well known results for the case of molecules at flat surfaces. For molecules oriented parallel to the plane of the aperture, a numerical example shows that aside from the general small red shift, the two orthogonal "in-plane" directions behave quite differently in their emission frequencies as they are scanned from the center to the edge of the tip, suggesting a possible way of distinguishing the two orientations through observation of their emission frequencies.

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1. Introduction

Recent successes in applying the near field scanning optical microscope (NSOM) to the imaging and spectroscopic studies of single molecules in condense phase [1–3] have stimulated lots of effort in the theoretical understanding of the molecular emission characteristics as perturbed by the tip of the NSOM. Due to the morphological complexity of the tip, most of the existing theoretical approaches in solving this "molecule–tip" boundary value problem are numerical in nature. For example, techniques such as the "finite difference time domain" [4,5], "multiple-multipole" [6] and "discretized Green function" [7] methods have all been applied [8]. Moreover, it would be desirable if at least in certain situations, simple analytical results can be available to provide guidelines for judging the acceptability of the corresponding (presumably more accurate) numerical results. It is the purpose of this communication to show that the emission frequencies of these single molecules probed by a NSOM tip can reasonably be estimated using simple classical electrostatic theory. To introduce and to justify the approach, we shall first give a brief review for the case of fluorescing molecules at a metal surface, in which we shall critically examine and justify the limitations of the simple electrostatic theory as applied to the computation of fluorescence properties of the molecules. It turns out as a little surprise, that such a simple theory is more accurate for frequency shifts calculations under most experimental conditions and more limited for the corresponding computations of decay rates (inverse lifetimes). After this clarification, we shall apply the electrostatic method to the calculation of the frequency shifts of the molecular dipoles at a metallic aperture.

2. Brief review on fluorescence at metal surfaces

Molecular fluorescence in the presence of a metallic substrate boundary has been studied intensively for the past three decades [9,10]. Most significantly, aside from

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other spectroscopic properties, it is important to know how the emission frequencies and the lifetimes of the molecule are modified due to its interaction with the metallic vicinity. One simple theoretical approach for the description of this phenomenon is a classical phenomenological (CP) model in which the fluorescing molecule is modeled as a radiating dipole which interacts electromagnetically with the metal. Ignoring quantum effects, this description has enough accuracy for most situations when the molecule is located farther than a few nanometers from the metal boundaries [11]. In this approach, the frequency shifts and decay rates normalized to the decay rate of the free molecule can be expressed as [9]:

$$\frac{\Delta\omega}{\gamma_0} = -\frac{3n^2}{4\mu k^3}\mathrm{Re}(E_0), \qquad (1)$$

$$\frac{\gamma}{\gamma_0} = 1 + \frac{3n^2}{2\mu k^3}\mathrm{Im}(E_0), \qquad (2)$$

where μ and E_0 are the amplitudes of the molecular dipole moment and reflected field at the dipole site, respectively, with E_0 being complex in general. We have assumed the system to have an intrinsic quantum yield of unity. n is the refractive index of the medium in which the molecule is located and k is the emission wavelength in the medium.

Even within this CP approach, however, the exact solution for the electrodynamics of the dipole–substrate interaction is not always easy due to the possibly complicated geometry of the boundary. Hence the much simpler approximated static image theory (IT) has often been applied, with the understanding that, as long as the molecule–surface distance (d) is much smaller than the emission wavelength (λ) of the molecule, which is generally valid in various experimental situations ($d \lesssim 100$ nm and $\lambda \approx 500$ nm), IT will be accurate enough since the electrodynamical effects can be well ignored in this situation. Moreover, we have previously pointed out that one must be very careful in applying IT to the calculation of lifetimes of the admolecules [12]. For metallic substrates, in addition to the condition $d \ll \lambda$, one must also require $d \ll \delta$, the skin depth of the metal. In addition, IT is valid only if the emission frequency is not close to that for resonant radiative transfer between the molecule and the metal in case of non-planar geometry [13].

In the following section, we shall show that in spite of these many restrictions for IT to be applicable for decay rate calculations, it turns out to be relatively much more accurate for the corresponding frequency-shifts calculations. We shall then apply it to study the dipole-aperture problem which will shed some light on the frequency shifts of the single molecules as perturbed by the NSOM tip.

3. Applicability of the image theory

To demonstrate the disparity in the accuracy of IT for frequency shift and decay rate calculations, we consider the simple case of a dipole oriented parallel to a metal surface which is of perfect flatness. In this case, the full electrodynamics is solvable and E_0 in Eqs. (1) and (2) can be obtained as follows [9]:

$$E_0 = \frac{\mu k^3}{2\varepsilon_1}\int_0^\infty \mathrm{d}u\left[(1-u^2)R^{\parallel} + R^{\perp}\right]\mathrm{e}^{-2l_1 kd}\frac{u}{l_1}, \qquad (3)$$

where $R^{\parallel} = (\varepsilon_1 l_2 - \varepsilon_2 l_1)/(\varepsilon_1 l_2 + \varepsilon_2 l_1)$ and $R^{\perp} = (l_1 - l_2)/(l_1 + l_2)$ are the Fresnel coefficients with $l_j = -\mathrm{i}(\varepsilon_j/\varepsilon_1 - u^2)^{1/2}$, $\varepsilon_1 = n^2$ and ε_2 the complex dielectric function of the substrate. On the other hand, if one applies the simpler electrostatic image theory, one obtains:

$$E_0 = -\frac{\mu}{8\varepsilon_1 d^3}\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2}. \qquad (4)$$

Fig. 1 shows a comparison between the results for normal-

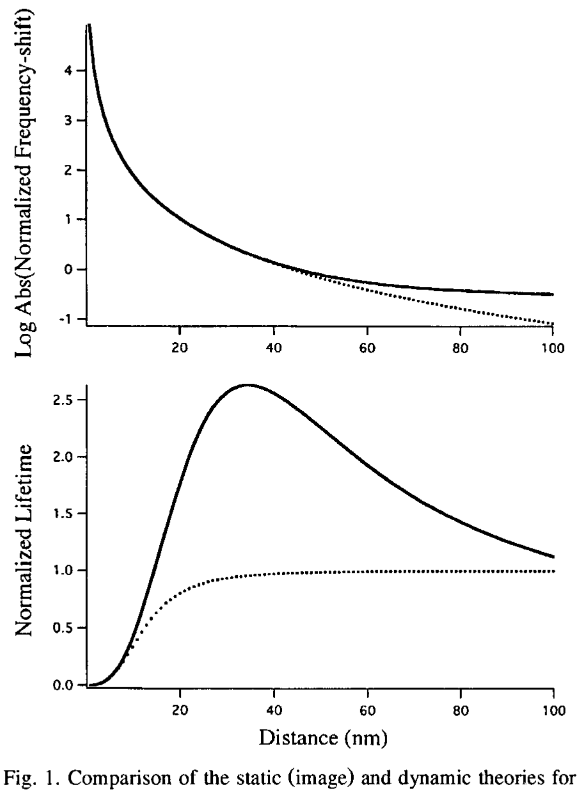

Fig. 1. Comparison of the static (image) and dynamic theories for the calculation of frequency shifts and lifetimes (inverse decay rates). The solid and dotted lines show the results as a function of molecule–surface distance obtained from the dynamic and static theories, respectively.

ized frequency shifts and lifetimes (inverse decay rates) calculated using both the dynamic (Eq. (3)) and static (Eq. (4)) theories for a molecule with emission wavelength $\lambda = 600$ nm located parallel to an aluminum surface [14]. As can be seen, IT fails badly for lifetime calculations at far distances ($d \gtrsim 10$ nm), a result consistent with previous observations [12]; whereas it remains relatively accurate for frequency shifts calculations for a much greater distance range, up to 50 nm!

To understand the physical origin for such disparity in the validity of the static theory, we first reformulate Eqs. (1) and (2) using real field amplitudes as follows [5]:

$$\frac{\Delta\omega}{\gamma_0} = -\frac{3n^2}{4\mu k^3}\tilde{E}_0 \cos\phi, \tag{5}$$

$$\frac{\gamma}{\gamma_0} = 1 + \frac{3n^2}{2\mu k^3}\tilde{E}_0 \sin\phi, \tag{6}$$

where

$$\tilde{E}_0 = \left[(\text{Re}\, E_0)^2 + (\text{Im}\, E_0)^2\right]^{1/2}, \tag{7}$$

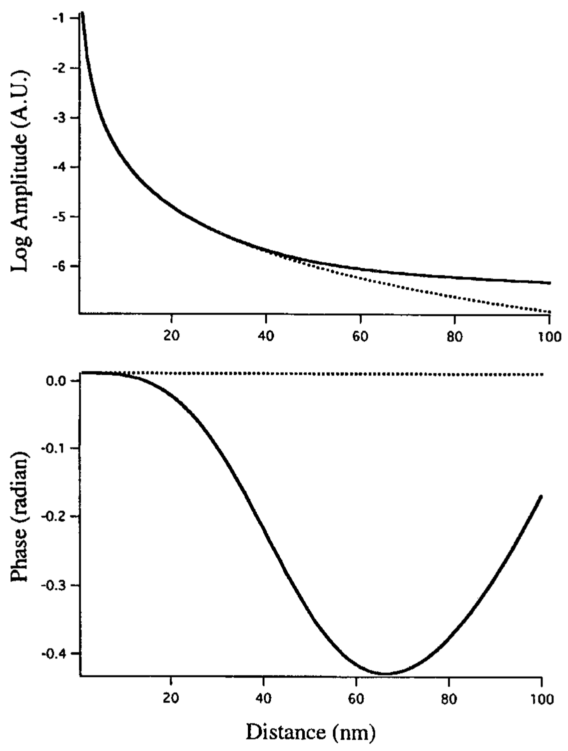

Fig. 2. Results from the model with a real driving field showing the amplitude and phase of the reflected field at the dipole site. The problem and notations are the same as those in Fig. 1.

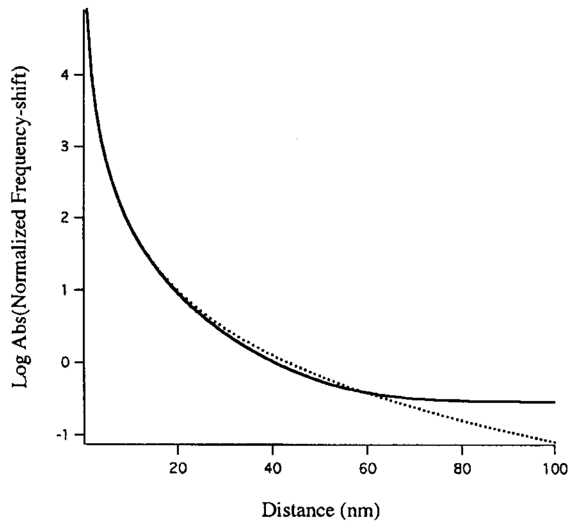

Fig. 3. Results for frequency shifts from both theories for a perfect conducting substrate. Notations are the same as in Fig. 1. Note that in this case the static theory leads to null results for the decay rate calculation, thus no comparison can be made with the dynamic theory.

and ϕ is the phase difference between the reflected field at the dipole site and the oscillating dipole and is given by:

$$\tan\phi = \frac{\text{Im}\, E_0}{\text{Re}\, E_0}. \tag{8}$$

Since the difference in the static and dynamic theories lies mainly in the ignorance of the time-retardation effect in the former by having the reflected field acted instantly on the dipole, we expect the main discrepancy between the two as applied to Eqs. (5) and (6) to come from the calculation of the phase ϕ. In fact, IT implies that ϕ is independent of d which is obviously unphysical and inconsistent with the dynamic theory. Fig. 2 demonstrates this by comparing $\tilde{E}_0$ and ϕ in Eqs. (7) and (8) as calculated from the two theories for the same problem as in Fig. 1. Now it is clear from Eqs. (5) and (6) that the different functional dependence on ϕ for the decay rate and the frequency shift will determine the sensitivity on the inaccuracy of the image theory. Eq. (5) indicates that an error in ϕ will lead to an error $\sim \sin\phi\, |\Delta\phi|$ whereas that for Eq. (6) will be $\sim \cos\phi\, |\Delta\phi|$. For distances $d \lesssim \lambda$, we expect $|\phi|$ to be small and hence the error that occurs in Eq. (6) for decay rate calculations is much greater. The physics behind this is that due to the predominance of the radiative transfer rate at far distances and its sensitive dependence on the phase difference ϕ, IT becomes very inaccurate for calculating the decay rates since it cannot handle any radiative transfers [13]. In fact, one can look at the extreme case of a perfect conducting substrate in which case IT leads to null results for the surface-induced decay, while still gives reasonably accurate results for the frequency shifts as illustrated in Fig. 3.

4. The dipole-aperture problem

Having confirmed the validity of the static IT for frequency shifts calculations, we shall now study the emission frequency shifts of a single molecule at a NSOM tip by modeling it as a dipole interacting with a metallic aperture with dimension of the fiber end of the tip. In accord with previous experiments [3], we assume the dipole to be oriented parallel to the x–y plane of the aperture along the x-axis. For simplicity, we shall assume the molecule to lie right on the plane (i.e. $z = 0$) and the results should be close to the realistic case of near field imaging with small z. Furthermore, we shall idealize the metal to be a perfect conductor. Under these simplified assumptions, the image field at the dipole site can be obtained in cylindrical coordinates using the method of inversion as follows [15]:

$$E_\rho = \frac{\mu_\rho}{\pi a^3}\left\{\frac{2}{(1-r^2)(1+r^2)^2} + \frac{1}{r^2(1+r^2)} - \frac{\tan^{-1}[2r/(1-r^2)]}{2r^3}\right\}, \tag{9}$$

$$E_\psi = \frac{\mu_\psi}{\pi a^3}\left\{\frac{r^2-1}{2r^2(1+r^2)^2} + \frac{\tan^{-1}[2r/(1-r^2)]}{4r^3}\right\}, \tag{10}$$

where a is the radius of the aperture, $r = \rho/a$, and μ_ρ, μ_ψ are the cylindrical components of the molecular dipole moment. Note that we have opposite signs in the above results compared to those obtained in Ref. [15].

Using Eqs. (9) and (10) into Eq. (1), we have calculated the frequency shifts of a molecule oriented parallel to an aperture of radius of 50 nm. The results for the two orthogonal "in plane" (i.e. x and y) dipole orientations are shown in Fig. 4. It is seen that aside from the relatively small red-shifts as previously mentioned in the literature [8], the two orthogonally oriented dipoles are affected very differently as they are scanned from the center to the edge of the aperture. The "radial" oriented dipole shows up with "edge effects" while the "tangential" one does not. Hence it may be possible to distinguish these two orientations by observing their change in emission frequencies as the NSOM tip scans over the molecule.

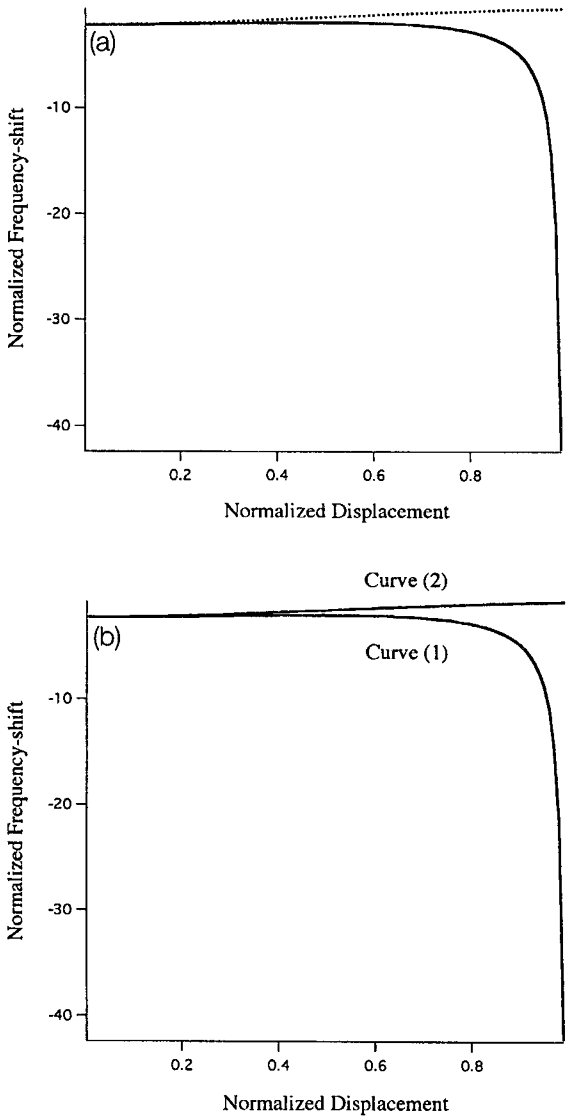

Fig. 4. Frequency shift calculations for a molecular dipole at an aperture oriented parallel and located on the plane of the aperture. The results show the normalized shifts as a function of the displacement (normalized to the aperture radius) from the center of the aperture. Curve 1 and 2 show the two cases with the dipole lying along the "radial" and "azimuthal" directions, respectively.

5. Discussion and conclusion

As mentioned at the beginning, a simple theoretical description for the interaction between a molecule and an environment of irregular geometry is most of the time impossible without resort to highly involved numerical methods. Unfortunately, even numerical approaches are limited to the finite computation power of various machines, and various approximations are often required. For example, in numerical simulation of the NSOM problem, it is well known that a true 3D modeling is many times more involved compared to a 2D simulation [4–8]. However, though the 2D approach can sometimes give qualitatively reasonable results, it can be quantitatively far from accurate. Hence it is always desirable if one can have more analytical results to compare with. In fact, the red-shifts obtained here in Fig. 4 turn out to be much smaller than those obtained previously in a numerical approach [5]. While our analytical results here are obtained after many idealizations, we believe that the previous 2D results should be reevaluated using a 3D simulation for better quantitative accuracy. In addition, the previous calculation for the radiative and nonradiative decay rates [5] can only be justified in a true 3D approach.

We thus conclude that simple analytical solutions, even under many idealizations, are useful as guidance for numerical modeling. Here we have justified and obtained a simple result for the emission frequencies of dipoles at an aperture [16]. One certainly hopes that a similar simple result can be obtained for the induced decay rates (hence the lifetimes) which are the only quantities so far measured in various experiments [2,3]. However, in such a case, one must assume a real metal in place of a perfect conductor and one has to worry about the limitation of the static theory as explained in the above sections.

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