Frequency shifts of an electric-dipole transition near a partially reflecting surface

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The classical theory of dipole radiation is used to calculate the change in frequency of an electric-dipole-allowed transition due to the presence of a nearby reflecting surface. The result is compared to that for a perfect reflector.

I. INTRODUCTION

An atom or molecule in an excited and electric-dipole-allowed state emits at a particular frequency ω_0 and usually has a Lorentzian line shape with width γ_0. The width is related to the spontaneous emission rate, b_∞. When such an emitter is placed near a partially reflecting surface, both the emission rate and the frequency change in a manner dependent on the distance of the atom to the surface, the dielectric properties of the surface, and the medium in which the emitter is embedded.

In recent years, the change in the emission *rate* has been discussed by Morawitz,[1a] Kuhn,[2] Drexhage,[3] Tews *et al.*,[4] Chance *et al.*,[5] and Morawitz and Philpott.[1b] The lifetime measurements of this by Drexhage[6] and Tews[7] are now completely understood[4,5,7] within the framework of the classical theory. The early work[1a,2,3] treated the absorption in the surface approximately, while the later work[1b,4,5] treated this exactly within the classical theory. The exact classical theory[4,5a,5b] using the known dielectric constant of silver gave good agreement with the lifetime experiments of Drexhage[6] and Tews.[7] There was still some discrepancy between theory and experiment, because of the neglect of the second surface which was present in the experiment. This discrepancy has been completely removed by including this surface in the theory.[5f]

The change in frequency has also been discussed by Morawitz,[1a,1c] Kuhn,[2] Chance *et al.*[5] as well as Agarwal,[8] and Barton.[9] There are no experimental measurements of this shift. Agarwal[8] suggested, on the basis of his quantum-electrodynamical calculation (with a model two-level atom), that the frequency shift should have a logarithmic dependence on the distance from atom to surface. This has been criticized by Barton,[9b] who showed that a correct calculation gives the classical shift as the leading term for all distances. He also pointed out that this term for short distances was given first by Lennard-Jones.[10]

In this article, we discuss the exact classical calculation of this shift *removing the restriction of a perfectly reflecting surface* which has characterized most preceding treatments. Those calculations which have attempted to treat nonperfect reflection are approximate and fail to give correct results in the small-distance limit.[1,2] We find that the frequency shift can be much larger than that calculated assuming perfect reflection, and reaches its maximum near the surface plasmon frequency of the metal interface.

II. CLASSICAL THEORY

The line broadening and frequency shift of an electric-dipole emitter in the vicinity of a partially reflecting surface is a result of the coupling with its own reflected field, E_R. The line broadening $\Delta\omega_b$ or shortened lifetime τ_d of the emitter and the frequency shift $\Delta\omega_s$ have their roots in the same interaction with E_R, but with a different phase dependence. In the classical model, where the dipole is a Drude oscillator, the in-phase (real) and the out-of-phase (imaginary) parts of E_R determine $\Delta\omega_s$ and b_d $(=\tau_d^{-1}=\Delta\omega_b)$, respectively, according to

$$\frac{b_d}{b_\infty}\equiv\frac{\tau_\infty}{\tau_d}=1+\frac{3}{2}q\,\mathrm{Im}\left(\frac{\epsilon_1 E_R}{k_1^3\mu_0}\right) \tag{1a}$$

and

$$\frac{\omega_s(d)-\omega_s(\infty)}{b_\infty}\equiv\frac{\Delta\omega_s}{b_\infty}=\frac{-b_\infty}{8\omega}-\frac{3}{4}q\,\mathrm{Re}\left(\frac{\epsilon_1 E_R}{k_1^3\mu_0}\right), \tag{1b}$$

where subscripts d and ∞ refer to distance between dipole and mirror, and b_d/b_∞ is, therefore, the decay rate normalized to the absence of an interface; ϵ_1 and k_1 are the dielectric function and wave vector for the (nonabsorbing) medium containing the dipole of moment μ_0; q is quantum yield of radiation from the luminescent state. The term $b_\infty/8\omega$ is negligible for systems of interest in this paper and will be dropped.

The decay rate b_d has been computed in a series of papers[1c,4,5,7] mentioned above. Classical electromagnetic theory is now used to calculate $\Delta\omega_s$ in terms of the same parameters that occur in calculations of decay rate: dielectric function of the media, dipole geometry, q, and τ_∞.

In this paper we present calculated results for $\Delta\omega_s$ for a dipole emitter near single mirrors of varying thickness, and between two identical thick mirrors.[5c,11,12] Results for the single thick mirror are compared with those for a Drude quasi-free-electron-gas model for the reflector.

A. Single mirrors

We consider first the case of a thick mirror where the geometry is given in Fig. 1. On calculating E_R by the standard method,[13] we can express $\Delta\omega_s$ for a dipole oriented perpendicular or parallel to the single interface as follows[5]:

$$\frac{\Delta\omega_s^\perp}{b_\infty}=\tfrac{3}{4}q\,\mathrm{Re}\left(\int_0^\infty R^{\parallel}e^{-2l\hat{d}}\frac{\tau^3 d\tau}{l}\right), \tag{2a}$$

$$\frac{\Delta\omega_s^\parallel}{b_\infty}=-\tfrac{3}{8}q\,\mathrm{Re}\left(\int_0^\infty [R^\perp+(1-\tau^2)R^\parallel]e^{-2l\hat{d}}\frac{\tau d\tau}{l}\right), \tag{2b}$$

where

$$l=-i(1-\tau^2)^{1/2},$$
$$m=-i(\epsilon_2/\epsilon_1-\tau^2)^{1/2},$$
$$\hat{d}=k_1 d,$$

and $R^\parallel$ and $R^\perp$ are the Fresnel coefficients for a ray whose electric vector with respect to the incidence plane is parallel or perpendicular, respectively,

$$R''=\frac{\epsilon_1 m-\epsilon_2 l}{\epsilon_1 m+\epsilon_2 l},\quad R^\perp=\frac{l-m}{l+m}.$$

Numerical calculations show that $\Delta\omega_s$ varies as d^{-3} over a large distance range and is only of modest size even for the smallest values of d encountered in experiments using the monolayer assembly technique of Kuhn *et al.*,[2] about 30 Å. Therefore, for this paper we will be interested only in the short distance behavior of $\Delta\omega_s$, and will extract the leading term in d^{-3} for all cases. In doing so we find

$$\frac{\Delta\omega_s^{\perp,\parallel}}{b_\infty}=-\frac{q}{\hat{d}^3}\gamma^{\perp,\parallel}, \tag{3}$$

where

$$\gamma^\perp=\tfrac{3}{16}\,\mathrm{Re}\left(\frac{\epsilon_2-\epsilon_1}{\epsilon_2+\epsilon_1}\right)=2\gamma^\parallel.$$

Note the relationship between the values for the dipole oriented parallel to the surface and those for the dipole oriented perpendicular to the surface. Thus, we need calculate only one of these if we are concerned with the short-distance behavior. In this paper we will only explicitly compute $\Delta\omega^\perp$; to find $\Delta\omega^\parallel$ multiply by $\frac{1}{2}$. We also note that for a perfect reflector, ϵ_2 approaches $-\infty$, and $\gamma^\perp=\frac{3}{16}$. This is in agreement with Eq. (1), for at short distances the term $\epsilon_1 E_R/k_1^3\mu_0$ is $2/(2d)^3$, the electric-dipole image term.

Calculated results are shown in Fig. 2(a) for the fatty-acid/silver-mirror system where the index of refraction of the fatty acid is 1.50, and the complex refractive indices for silver are from Johnson and Christy,[14] and q is taken as unity. The horizontal dashed line is the response curve for a perfect reflector. This graph is to be compared to Fig. 2(b), which is a calculation based on the Drude quasi-free-electron description of a silver mirror. In this case, the real and imaginary parts of the dielectric function, ϵ_2' and ϵ_2'', are

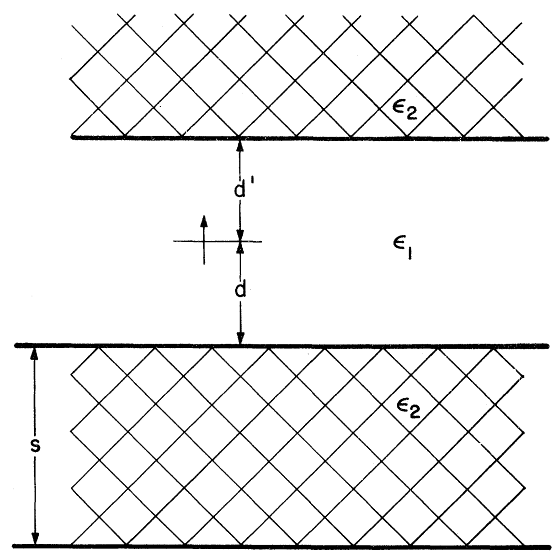

FIG. 1. Geometry of the mirror problems treated herein. The distance from the dipole to the lower partially reflecting surface is d; the thickness of this mirror is s; the distance from the dipole to the upper surface is d'. The first problem is a single thick mirror ($d'=\infty, s=\infty$); the second is a single thin mirror ($d'=\infty$, s finite); the third problem is for double thick mirrors ($d'=d, s=\infty$).

$$\epsilon_2' = 1 - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2}\,, \qquad \epsilon_2'' = \frac{\omega_p^2 \tau^2}{\omega} \frac{1}{1 + \omega^2 \tau^2}\,, \tag{4}$$

where, for a silver mirror, a fit to the long-wavelength dependence of the dielectric function yields $\omega_p = 13.9 \times 10^{15}\ \mathrm{sec}^{-1}$ and $\tau = (31 \pm 12) \times 10^{-15}$ sec. The plasma frequency ω_p is much larger than the experimental plasma frequency for silver because of the presence of interband transitions.[14] The result is that for the real mirror the characteristic frequency-shift dispersion curve is displaced to longer wavelengths and broadened. But although the maximum is an order of magnitude smaller than predicted from the Drude model, it is still an order of magnitude larger than expected for a perfect reflector. However, $\Delta\omega_s$ is still small and would be hard to measure using the fatty-acid monolayer method unless q were large and b_∞ were 10^7 to $10^8\ \mathrm{sec}^{-1}$. For then, since one layer of fatty acid corresponds to $\hat{d} = 0.05$, we calculate for $\Delta\omega_s^\perp$ the range 10^{11}–$10^{12}\ \mathrm{sec}^{-1}$, or 1–10 cm^{-1}.

We note that line broadening $\Delta\omega_b$ will be comparable with $\Delta\omega_s$ near the surface plasmon frequency[1b,5d] around 360 nm for the fatty acid/silver mirror. When written as $\beta/\hat{d}^3$, we have found that β is around 1.4; this is to be compared with a peak in γ of around 2.0. The figure also shows that the region of large β is very narrow; therefore $\Delta\omega_b$ will be very small outside this region.

Finite mirror thickness affects $\Delta\omega_s$ in a way which can be calculated with Eq. (1). We take the real part of Eq. (4.7) of Ref. 5(d) and extract the $\hat{d}^{-3}$ dependence. The result is

$$\frac{\Delta\omega_s^\perp}{b_\infty} = -\frac{3}{2}\frac{q}{\hat{d}^3}\left\{-\frac{1}{8} + \mathrm{Re}\left[\frac{\epsilon_2}{\epsilon_1 + \epsilon_2}\int_0^\infty dx\, x^2 e^{-2x}\left(\frac{1 - l^{-\hat{s}\hat{d}^x} p}{1 - l^{-\hat{s}\hat{d}^x} p^2}\right)\right]\right\}\,, \tag{5}$$

where

$$p = (\epsilon_2 - \epsilon_1)/(\epsilon_1 + \epsilon_2)$$

and

$$\hat{s} = k_1 s,$$

where s is the mirror thickness (see Fig. 1.).

Calculated results are shown in Fig. 3 for four wavelengths, one near the peak of response, one at 612 nm [the EuIII emission wavelength], and two intermediate. This figure should be contrasted with Fig. 6 in Ref. 5(d), where decay rate (logarithmic scale) is the ordinate. No sharp peak in γ is seen to develop, and for thick films γ spans a range of only one order of magnitude. It appears from Fig. 6 in Ref. 5d that no advantage is gained by use of a thin film in a search for an appropriate system for studying frequency shifts.

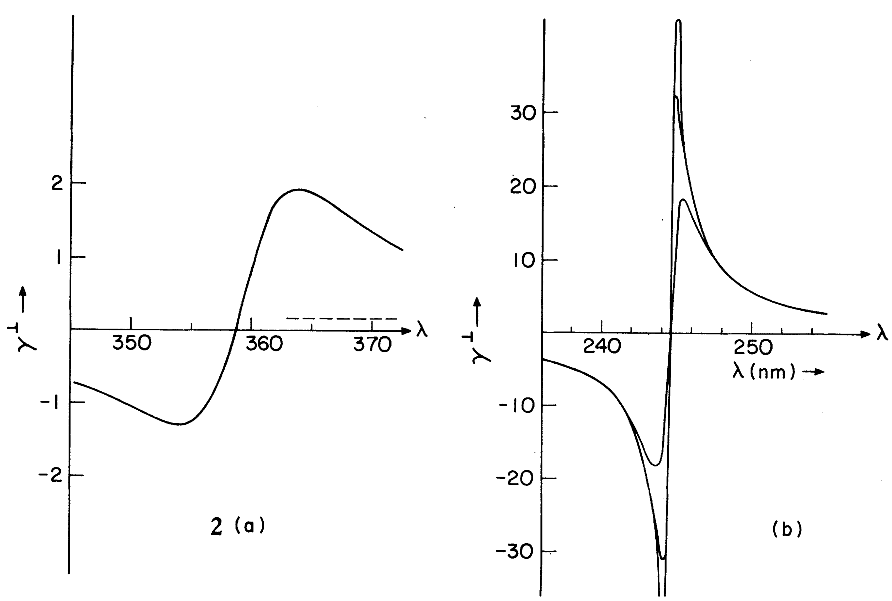

FIG. 2. Frequency-shift parameter $\gamma^\perp$ for a dipole oriented perpendicular to a silver mirror and in a dielectric of refractive index 1.50: (a) dielectric function of Ag taken from Ref. 12; (b) dielectric function of Ag based on Drude model with $\omega_p = 13.9 \times 10^{15}$ sec^{-1} and $\tau = 19$, 31, 43 $\times 10^{-15}$ sec (the larger the τ the lower the peak in γ). Note the difference in wavelength. $\gamma^{\parallel}$ can be found from $\gamma^\perp$ by dividing by 2.

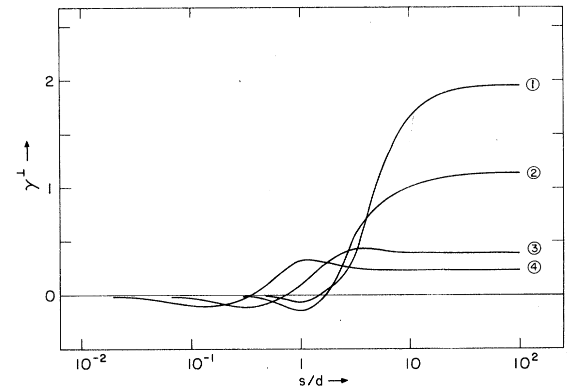

FIG. 3. Frequency shift $\gamma^{\perp}$ of a dipole oriented perpendicular to a silver mirror of thickness s. The dipole is a distance d to the mirror. [See Eq. (5).] The curves are for the following values of real and imaginary parts of the refractive index: (1) $n = 0.075$, $\kappa = 1.585$ ($\lambda = 364$ nm); (2) $n = 0.06$, $\kappa = 1.76$ ($\lambda = 375$ nm); (3) $n = 0.06$, $\kappa = 2.50$; (4) $n = 0.06$, $\kappa = 4.11$ ($\lambda = 612$ nm); $\gamma^{\parallel}$ can be found from $\gamma^{\perp}$ by dividing by 2.

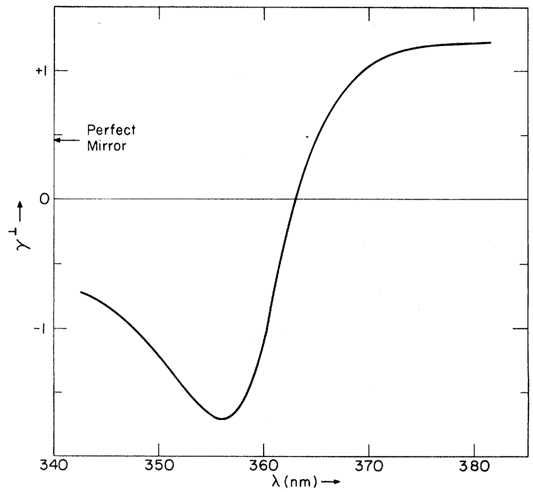

FIG. 4. Frequency-shift parameter $\gamma^{\perp}$ of a perpendicular dipole embedded in a dielectric of refractive index 1.50, and centered between two silver mirrors.

B. Double mirrors

We next consider a pair of identical thick mirrors with a perpendicular dipole centered between them.[5c,11,12] We take the real part of E_R, and extract the leading term, which depends on $\hat{d}^{-3}$. The result is

$$\frac{\Delta\omega_s^{\perp}}{b_\infty} = -\frac{3}{2}\frac{q}{\hat{d}^3}\,\mathrm{Re}\left(\int_0^\infty \frac{pe^{-2x}}{1-pe^{-2x}}x^2\,dx\right) \equiv -q\frac{\gamma'}{\hat{d}^3}, \tag{6}$$

where p is defined in Eq. (5).

Figure 4 shows the frequency dependence of γ' for a silver mirror, where the medium between is a fatty acid of refractive index 1.50, and q is unity. Qualitatively, this is similar to Fig. 2 for a single mirror. The parameter γ' is related to that of Eq. (3) as shown by expanding the integrand of Eq. (6), namely,

$$\gamma' = \tfrac{3}{8}\,\mathrm{Re}\,(p + p^2/2^3 + p^3/3^3 + \cdots), \tag{7}$$

then γ is seen to be one-half the first term in the series for γ'. For a perfect mirror the series is recognized as arising from the multiple images of the central dipole. The "perfect" mirror result is shown by the arrow $[=\frac{3}{8}(1.20205\ldots)]$.

In this description of the perfect mirror, the form of the series is a result of the small-distance approximation. For finite values of $\hat{d}$, phase changes arise owing to the finite length of path traveled by a "ray." However, this effect is not great where only a few layers of fatty acid lie between

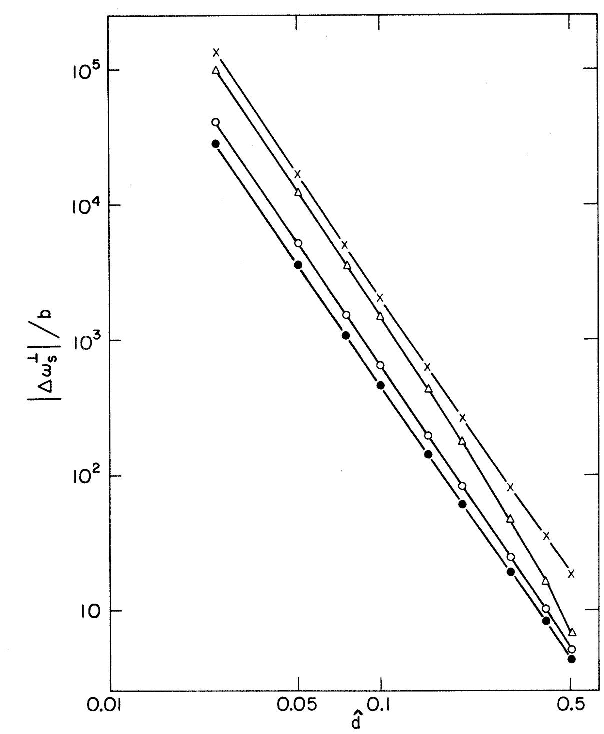

FIG. 5. Frequency shift ($\Delta\omega_s^{\perp}/b$) vs distance ($\hat{d}$) in the small-distance region for a perpendicular dipole centered between two mirrors and embedded in a dielectric of $n_1 = 1.50$. The curves are for different values of the refractive indices of the metal: (×) $\hat{n} = 0.09 + i1.476$; (●) perfect mirror; (△) $\hat{n} = 0.05 + i1.864$; (○) $\hat{n} = 0.06 + i4.11$.

the emitter and the mirror. This is shown in Fig. 5, where for a single layer $\hat{d}$ is 0.05. The dependence on distance of $\Delta\omega^{\perp}/b_{\infty}$ is seen to be nearly inverse cubic up to thickness of a few layers.

III. DISCUSSION

Classical electromagnetic theory has been used to compute the shifts in spectral lines near interfaces, in particular the silver/fatty-acid interface which has been treated experimentally[3,6] and theoretically[1-7] for the related problem of line broadening (or spontaneous emission rate). This theory gives the leading terms of the quantum-electrodynamical theory[9] and thus will be the dominant contribution to the experimental value.

The major conclusion of this work is that the frequency shift depends markedly on frequency (a conclusion also discussed by Morawitz,[1c] who used a Drude model for the dielectric function of the metal) and that this dependence is marked near the surface plasmon frequency ω_{SP}. The frequency shift exhibits a dispersionlike curve near ω_{SP}, while the spontaneous emission rate shows a resonance behavior near ω_{SP}.[1b,5d] The width of the resonance and dispersion is very dependent on the dielectric function of the metal, and so could be used to probe the frequency dependence of the dielectric function.

From our calculations, it appears that it will be very difficult to observe these frequency shifts because they are small and also because of the increased broadening at the small distances necessary to see larger shifts.

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