Effect of Surface Dynamical Fluctuations on Light Scattering by a Nearby Dipole

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We introduce a model which accounts for surface-generated dynamical fluctuations, and we evaluate the corresponding absorption and resonance fluorescence spectra. Our results provide the first semiquantitative agreement with a recent experiment.

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The scattering and emission of light from a molecule near a metallic surface are substantially modified by the surface's response to the molecule's electromagnetic fields. This process is of general relevance since the same response affects other phenomena such as chemical properties of molecules near, and optical properties of, a surface. Drexhage's[1] pioneering experiments demonstrated such an effect in the form of strong variation of a molecule's lifetime as a function of its distance from a metallic surface. His data were subsequently explained by Chance, Prock, and Silbey[2] in the framework of a simple model: The excited molecule is treated as a classical dipole, driven by its own radiation field which reflects back from the surface. The model attributes the observed lifetime variation at short distances, typically on the order of 10 nm, to the response of the surface plasmon (SP) modes.

The central point of this Letter is to *complement* the classical dipole antenna (CDA) model by including surface-generated dynamical fluctuations. Such fluctuations arise, for instance, in association with Ohmic losses.[3] They induce a fluctuating component in the motion of the nearby probe dipole. There was no need to consider fluctuations in previous work[1,2] since only the dipole's lifetime was observed. On the other hand, the fluctuating component does affect the dipole-dipole correlation function, which is directly responsible for the absorption[4] and resonance fluorescence (RF) spectra.[5]

Very recent experiments by Holland and Hall[6] have yielded data with unexplained features for which these fluctuations appear to be particularly relevant. We present here predictions of both the absorption spectrum and the weak-field RF spectrum pertaining to a molecule near a surface.

Our model consists of a perfectly flat semi-infinite metallic surface, treated as a lossless jellium,[7] and a pointlike immobile dipole located at a distance d. The dipole is coupled to the SP and reflected-wave modes of the surface-electromagnetic field system. The dynamical fluctuations are introduced in the SP equation of motion since the SP field extends a few tenths of a nanometer into the bulk,[8] where the SP collective charge oscillations act as an ac current in the far-ultraviolet frequency domain. Consequently, in keeping with Drude's model of metallic conductivity, random currents are formed by SP electrons undergoing inelastic collisions from lattice imperfections. Whatever their actual origin, it is these random currents that induce a finite lifetime *and* give a fluctuating component to the SP charge oscillations.[9]

The coupled equations of motion for the complex dipole amplitude $B(t)$ and a typical SP mode amplitude $a_{\parallel}(t)$, specified by momentum $\mathbf{k}_{\parallel}$ parallel to the surface, are

$$da_{\parallel}(t)/dt = -i(\omega_{\parallel} - i\gamma_{\parallel})a_{\parallel}(t) - i\Omega_{\parallel}B(t) + F(\mathbf{k}_{\parallel},t), \tag{1a}$$

$$dB(t)/dt = -i(\omega_D - \Delta_{\mathrm{RW}} - i\gamma_{\mathrm{RW}})B(t) - i\Omega_L e^{-i\omega t} - i\sum_{\parallel}\Omega^*_{\parallel}a_{\parallel}(t). \tag{1b}$$

The symbols in (1) signify the following: $\omega_{\parallel}$ and $\gamma_{\parallel}$ are the frequency and width of a SP mode specified by $\mathbf{k}_{\parallel}$. The dipole-SP coupling is $\Omega_{\parallel}$. The triad ω_D, Δ_{RW}, and γ_{RW} denote the dipole's natural frequency, frequency shift, and width, respectively, the latter two due to the coupling with the reflected-wave modes. The system is driven by a weak monchromatic laser field of strength Ω_L and frequency ω.

The new term in (1a) is the noise term $F(\mathbf{k}_{\parallel},t)$, the statistical properties of which embody the physical origin of the fluctuations. We assume (δ^3 denotes a discrete δ function) the following properties:

$$\langle F(\mathbf{k}_{\parallel},t)\rangle = 0, \quad \langle F(\mathbf{k}_{\parallel},t)F^*(\mathbf{q}_{\parallel},t')\rangle = \delta^3(\mathbf{k}_{\parallel} - \mathbf{q}_{\parallel})|A_{\mathbf{k}_{\parallel}}|^2 \exp[-i\omega_{\parallel}(t-t')]\exp[-(t-t')/\tau_c]. \tag{2}$$

The assumptions (2) are motivated by the reservoir theory *Ansatz*[10]

$$F(\mathbf{k}_{\parallel},t) = \sum_{\beta} g_{\parallel,\beta}\sqrt{n_{\beta}}\exp(-i\omega_{\beta}t),$$

where β denotes the relevant statistical bath modes (random currents) with equilibrium populations n_{β} and frequency ω_{β}, respectively, and $g_{\parallel,\beta}$ is the coupling of the $\mathbf{k}_{\parallel}$ SP mode to the bath mode β. The physical origin of the fluctuations implies that the coupling $g_{\parallel,\beta}$ is appreciable only in a frequency band $|\omega_{\parallel} - \omega_{\beta}| \lesssim \tau_c^{-1}$, where

$\Delta E \simeq \hbar/\tau_c$ is a typical energy transfer in an inelastic scattering event. A Lorentzian model for $|g_{\|,\beta}|^2$ yields Eq. (2).

Upon elimination of the SP amplitude from (1b), the $\Omega_\| B(t)$ term in (1a) contributes to the dipole's lifetime ($\gamma_{RW} \rightarrow \gamma_S = \gamma_{RW} + \gamma_{SP}$) because of the additional decay to SP modes. The $F(\mathbf{k}_\|, t)$ term in (1a) induces a dipole noise term in (1b) given by

$$-i \sum_\| \Omega_\|^* \int_0^t d\tau \exp[-i(\omega_\| - i\gamma_\|)(t-\tau)] F(\mathbf{k}_\|, \tau).$$

The former is included in the CDA model; the latter is not. Note also that since typically $\omega_\| > \tau_c^{-1} \sim 10^{14}$ Hz the noise term in the dipole equation of motion, after elimination of the SP degrees of freedom, has a correlation time τ_c.

The absorption spectrum is given by[4]

$$S_{AB}(\omega) = \lim_{t\rightarrow\infty} |\Omega_L|^2 \int_{-\infty}^{\infty} d\tau \exp^{i\omega\tau} \langle B(t+\tau) B^*(t) \rangle, \tag{3}$$

where frequency and d-dependent prefactors have been omitted. A considerable simplification of the expression for $S_{AB}(\omega)$ results from employment of the divergence of the SP density of states at $\omega_{SP} = \omega_p/\sqrt{2}$,[11] where ω_p is the plasma frequency and $d\omega_\|/dk_\| \rightarrow 0$ for $k_\| \rightarrow \infty$. Accordingly, upon insertion of the solution of (1b) into (3), the summations associated with the correlation given in (2) can be approximated by a single term:

$$\sum_\| |\Omega_\||^2 |A_{\mathbf{k}_\|}|^2 [(\omega_\| - \omega)^2 + \tau_c - 2)]^{-1} \simeq |A|^2 \left(\sum_\| |\Omega_\||^2\right) [(\omega_{SP} - \omega)^2 + \tau_c^{-2})]^{-1}, \tag{4}$$

where $|A|^2 = \lim_{k_\| \rightarrow \infty} |A_{k_\|}|^2$. Thus in conjunction with expression (3) the fluctuations are specified by $|A|^2$ and τ_c only.

The expression for the absorption spectrum is easily obtained with use of (4):

$$S_{AB}(\omega) = |\Omega_L|^2 \{ \sum_m |\Omega_m|^2 \delta(\omega_m - \omega_D) [(\omega_D - \omega)^2 + \gamma_S^2]^{-1} + C(d) [(\omega_D - \omega)^2 + \gamma_S^2]^{-1} [(\omega_{SP} - \omega)^2 + \tau_c^{-2}]^{-1} \}, \tag{5}$$

where

$$C(d) = (\tau_c^2 |A|^2 \pi \tau_c) [\sum_\| |\Omega_\|(d)|^2].$$

Expression (5) ignores a narrow peak[12] and a small shift in the ω_D resonance.[6] The d dependences (which are critical for comparison with experiment) occur in the total dipole width $\gamma_S = \gamma_{RW} + \gamma_{SP}$, in the dipole couplings Ω_m, where m refers to the reflected-wave modes, and in Ω_L.[13]

The first term in (5) is the usual Lorentzian line shape associated with the absorption of a free dipole. The second term in (5) is the surface term, involving a product of two Lorentzians centered around ω_D and ω_{SP}. This form can also be derived from a general theorem[14] about the resonance fluorescence spectrum of a dipole driven by a weak laser with arbitrary spectral distribution.

Obviously the surface term's signature is a two-peaked line shape. Typically $\tau_c^{-1} \sim |\omega_D - \omega_{SP}|$, and so if $\gamma_S \sim \tau_c^{-1}$ the two peaks will be broad humps and not well resolved. This condition is realized in a recent experiment by Holland and Hall.[6] They used metallic islands (which act as dipoles with huge radiative widths—10^{15} Hz) above a Ag surface.

Figure 1(a) is a replot of the Au-island data,[6] tacitly identifying the deviations of the normalized normal-incidence reflectivity from unity with the absorption spectrum. Figure 1(b) gives the results of the calculation. In keeping with expression (5) the double-hump line shape is observed for the smallest reported distance and the location of the maxima are at ω_D ($\lambda_D = 540$ nm, corresponding to the island's SP frequency) and ω_{SP} ($\lambda_{SP} = 350$ nm for a Ag surface). At larger distances the ω_{SP} peak fades away, since $C(d)$ decays exponentially[7] with d. The detailed distance dependence shown in Fig. 1(b) depends on three parameters, i.e., $\gamma_S(d)$, τ_c, and $|\alpha|^2 = \tau_c^2 |A|^2$. We compute $\gamma_S(d)$ from the Holland-Hall value $\gamma_0 = 10^{15}$ Hz for the free dipole's radiative linewidth, together with the ratio $\gamma_S(d)/\gamma_0$, which is calculated from the expressions of Chance, Prock, and Silbey[2] evaluated at $\lambda_D = 540$ nm with a realistic dielectric constant.[15] The other parameters are varied in the ranges 10^{-14} sec $\geq \tau_c \geq 5 \times 10^{-15}$ sec, $0.05 \geq |\alpha|^2 \geq 0.01$, yielding fits of the quality of Fig. 1(b). The deficiencies of the fit are that the calculated ω_{SP}-peak height and width are too small, and the observed ω_D-peak d dependence is only qualitatively reproduced.

With regard to the ω_{SP} peak, note that the data are normalized to the surface reflection. The latter, due to residual surface roughness, is strongly frequency dependent near ω_{SP}.[16] When the resulting distortion is removed from the data, or alternatively, the model is extended to include surface roughness,[17] the ω_{SP} peak will be broadened and increased. The d dependence of the ω_D peak is controlled mainly by the delicate competition between the d dependences of the γ_S (denom-

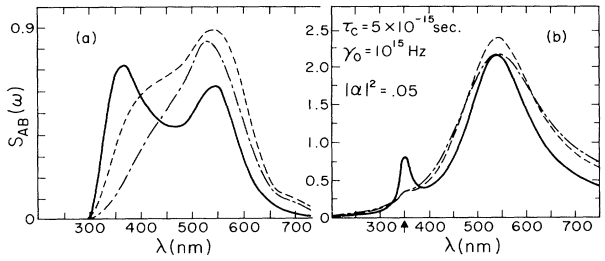

FIG. 1. The measured and calculated absorption spectra for gold islands. The solid, broken, and dash-dotted curves correspond to $d = 21$, 41, and $d = 51$ nm, respectively. (a) Replot of the data from Ref. 6; (b) calculated curve according to Eq. (5) with use of the indicated parameters. The solid-line calculated curve is normalized to the data at the arrow-marked wavelength.

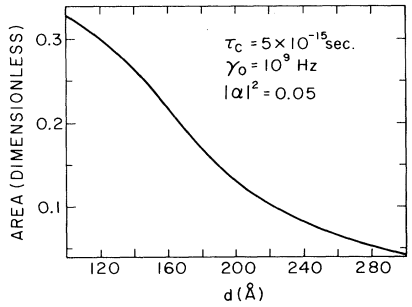

FIG. 2. The area (dimensionless) under the RF peak for a dipole with $\lambda_D = 540$ nm. The surface-term parameters are indicated.

inator)[18] and $|\Omega_L|^2$, $\sum_m |\Omega_m|^2 \delta(\omega_m - \omega_D)$ (numerator); see Eq. (5).

We now mention briefly the resonance fluorescence of a molecule near the surface. The quantum operator counterpart of Eqs. (1) must be used to obtain the RF spectrum.[17] It consists of an infinitely sharp Rayleigh peak[5] and the same surface term as in Eq. (5). Since $\gamma_S << \tau_c^{-1}, |\omega_D - \omega_{SP}|$ for a molecule, the surface term modifies only the height (area) of the ω_D peak. Figure 2 gives the area of the RF peak (dimensionless) with use of the same parameters of Fig. 1(b), except for $\gamma_0 = 10^9$ Hz. By comparison, the Rayleigh peak area is $(\Omega_L/\gamma_S)^2 \lesssim 0.25$ in the weak-field limit. Our results thus predict a significant RF signal and its distance dependence.

In summary, we have proposed a simple model which complements the CDA model by accounting for dynamical surface-generated fluctuations. These fluctuations modify in a particular manner the scattering of light by a nearby dipole. The model provides the first dynamical explanation for the main qualitative features of the Holland-Hall data, including some of the distance dependences. We have also calculated the branching ratio of the total resonance-fluorescence light flux to the Rayleigh-peak light flux for a molecule near a metallic surface. This prediction appears open to experimental test.

We recognize that the agreement between our theory and the data is imperfect. The use of a point dipole model for a nearly macroscopic metallic island may be thought to be inappropriate, and thus account for the discrepancies. However, recent calculations[19] indicate that such an island responds as a point dipole, provided that it is far enough from the surface, a condition amply satisfied by the data.[19] We speculate that the remaining discrepancies may arise from the relatively great density of such islands in the experiment, indicating the need for multidipole contributions in the theory and the dielectric constant of the space layer. The important point is that the double-peak character of the spectrum can be expected on the basis of underlying fluctuations.

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perimposed on top of the peak of width τ_c^{-1} both centered at $\omega = \omega_{SP}$. Since $\gamma_{\parallel} \sim 10^{12}$ Hz $\ll \tau_c^{-1}$ the narrow peak is not resolved in the data of Ref. 6. The RF spectrum considered below is also insensitive to the existence of this narrow peak.

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