

Nonlocal electrodynamic modeling of frequency shifts for molecules at rough surfaces

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The problem of frequency shifts for admolecules at distances very close to a metallic substrate surface protrusion is considered. The molecule is modeled as an oscillating point dipole and the morphology of the substrate is represented by a spherical island. Nonlocal electrodynamic effects are taken into account within the hydrodynamic description of the surface electrons. The results show that the nonlocal effects will tend to suppress the frequency shifts from local theory, and to create blue-shifted higher-order dispersion resonances in the frequency shift spectrum. Possible experimental observation for such effects is discussed.

The study of the spectroscopic properties of admolecules at rough metal surfaces has received considerable attention for the past decade¹⁻³ since the first discovery of the surface enhanced Raman scattering (SERS) (Ref. 4). It is expected that the understanding of such properties will lead to new spectroscopic tools as well as novel photochemistry.⁵ While experimental studies could be carried out with the surface morphology subject to controlled variation to a certain extent (e.g., by imposing a kind of grating⁶ or island structure⁷); a viable theoretical modeling of the phenomenon is the phenomenological classical electrodynamic approach, in which the admolecule is modeled as an emitting point dipole, and the surface structure is represented by a spheroidal island.⁸ Previous works based on this modeling have had some success, such as in predicting the double resonance structure in the photoabsorption spectrum⁹ and the correct order of magnitude for the enhancement factor in the SERS experiment.³ However, since this model assumes a sharp surface boundary and the substrate is characterized by the bulk dielectric function, which is independent of the wave vector, the previous results^{6,8} could only be valid for relatively large molecule-surface distances within such a local electrodynamic description. Several works in the literature have also studied the nonlocal (microscopic) effects due to the surface electrons for the case of a flat¹⁰ as well as a spherical island^{11,12} surface; but their interest has been mostly in the line-broadening (inverse lifetime) effects for the fluorescent admolecules, and the microscopic approach based on the time-dependent density functional theory¹¹ is highly computational in nature. In the present work, we present a study of such nonlocal effects on the level (frequency) shifts of the admolecules at structured surfaces within the phenomenological approach, this will be a generalization of our recent work¹³ in which such effects were ignored. It may also be of interest to note that Ruppin¹⁴ has also studied similar nonlocal effects on the photoabsorption of microspheres in the vicinity of the boundary of a substrate

which is described by a local dielectric function.¹ In the present treatment, we have the nonlocal response coming from the substrate with the admolecule being "pointlike," and our motivation is somewhat different as discussed in the above.

Consider a surface structure modeled as a spherical island of radius a and an oscillating molecular point dipole (frequency ω) located at a distance d above the island surface. We shall follow Ref. 11 by adopting atomic units for our description of the molecular quantities. According to the phenomenological approach, the frequency shift of the molecule is given by:¹⁵

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

where q is the intrinsic quantum yield, $k=2\pi/\lambda$ is the emission wave number, and G is the Green dyadic function defined by the reflected electric field at the dipole site per unit dipole moment:

$$G(\omega) = \frac{E_r(\omega)}{p}. \quad (2)$$

Note that γ_0 in Eq. (1) is the spontaneous decay rate for the "free molecule" (i.e., infinitely away from the surface) and could be given by Einstein's A coefficient as ($\hbar=1$):

$$\gamma_0 = \frac{4k^3}{3} |\mathbf{p}|^2, \quad (3)$$

where \mathbf{p} stands for the transition dipole moment of the fluorescent molecule. Combining Eqs. (1) and (3), we obtain

$$\Delta\omega = -q |\mathbf{p}|^2 \operatorname{Re} G(\omega). \quad (4)$$

In our following model calculation, we shall assume for simplicity that $q=1$ and $|\mathbf{p}|=1$ a.u.

Since our interest here is in the nonlocal effect which is important only at small molecule-surface distances (d), we shall adopt the long-wavelength limit in the calculation of

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E_r (Ref. 16). In this case, E_r could be calculated from the electrostatic solution of the dipole-sphere problem and we obtain¹²

$$G_{\perp}(\omega) = \sum_{n=1}^{\infty} \alpha_n(\omega) \frac{(n+1)^2}{(d+a)^{2(n+2)}}, \quad (5)$$

$$G_{\parallel}(\omega) = \sum_{n=1}^{\infty} \alpha_n(\omega) \frac{n(n+1)}{2(d+a)^{2(n+2)}}, \quad (6)$$

where \perp and \parallel denote the cases for the radially and tangentially oriented molecular dipole moments, respectively. In Eqs. (5) and (6), $\alpha_n(\omega)$ stands for the n th polarizability of the substrate sphere and is given by

$$\alpha_n(\omega) = \frac{n(\epsilon-1)}{n(\epsilon+1)+1} a^{2n+1}, \quad (7)$$

where $\epsilon(\omega)$ is the bulk complex dielectric function of the sphere in the local description.

To account for the nonlocal effects of the substrate island, we adopt the model of Fuchs and Claro¹⁷ for α_n which could be expressed as follows:

$$\alpha_n(\omega) = \frac{n(\xi_n-1)}{n(\xi_n+1)+1} a^{2n+1}, \quad (8)$$

with

$$\xi_n(\omega) = \left[\frac{2}{\pi} (2n+1)a \int_0^{\infty} \frac{j_n^2(ka)}{\epsilon(\mathbf{k},\omega)} dk \right]^{-1}, \quad (9)$$

where j_n is the spherical Bessel function. The simplest kind of nonlocal dielectric function $\epsilon(\mathbf{k},\omega)$ is the hydrodynamic model which accounts for the effect to the lowest order of the wave vector:¹⁸

$$\epsilon(\mathbf{k},\omega) = 1 - \frac{\omega_p^2}{\omega(\omega+i\Gamma) - \beta^2 k^2}, \quad (10)$$

where ω_p is the bulk plasmon frequency and β is given in terms of the Fermi velocity of the metal, respectively. Using this, the Fuchs-Claro model yields¹⁷

$$\xi_n(\omega) = \left[\frac{1}{\epsilon} + (2n+1) \left[\frac{a\omega_p}{\beta u} \right]^2 I_{n+1/2}(u) K_{n+1/2}(u) \right]^{-1}, \quad (11)$$

with ϵ being the Drude function [$k=0$ in Eq. (10)], u a function of ω and Γ (Ref. 17), while I_n and K_n are the modified Bessel functions.

We have performed some numerical studies for different metallic systems and some of the results are shown in Figs. 1–4. The radius of the substrate is taken as 50 a.u. for all the figures and the parameters for the different metals are summarized in Table I.

Figures 1 and 2 show the results for the frequency shifts vs the emission frequency of the admolecule for a noble metal (Ag) and simple metal (Na) substrate, respectively. Results are shown for two locations ($d=3$ a.u. and $d=11$ a.u.) and a radial molecular dipole has been assumed. The case for a parallel (tangential) dipole has also been studied which is found to show similar but generally smaller results than those for a radial dipole at these close

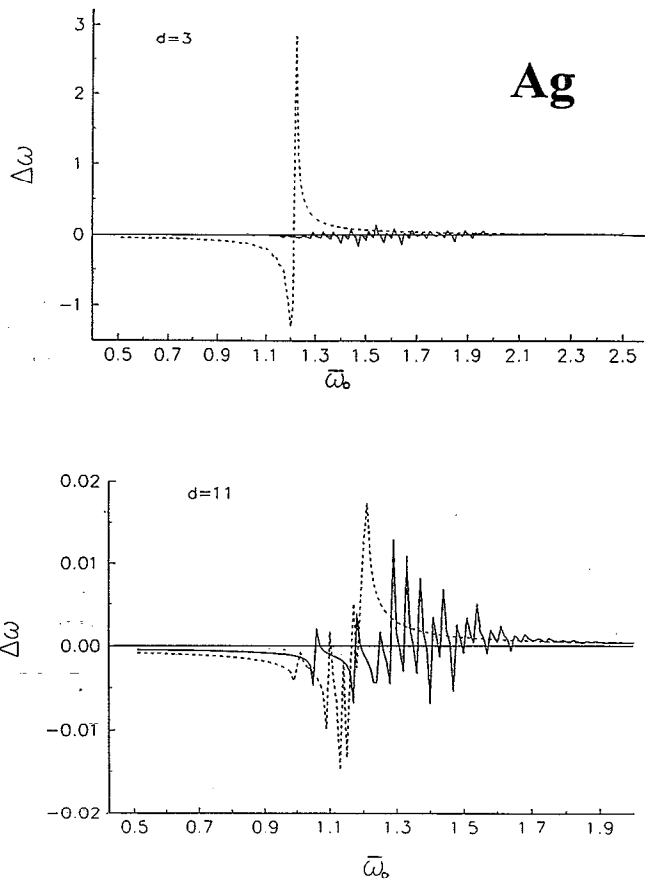


FIG. 1. Frequency shift in (a.u.) vs normalized emission frequency [$\bar{\omega}_0 = \omega_0/\omega_{sp} = \sqrt{3}(\omega_0/\omega_p)$] for a radially oriented admolecule at a Ag sphere for two molecule-substrate distances ($d=3$ and $d=11$ a.u.). The dotted line indicates the local theory results and the solid line the nonlocal results.

distances, due roughly to the antiparallel orientation of the “image dipole” for the tangential case.¹⁹ From Figs. 1 and 2, we observe that even in the local approximation, the dipole-sphere system already exhibits a deviation from a pure “anomalous dispersion” behavior as one would expect to appear in the case for a dipole with a flat substrate.¹⁵ This is most obvious in the large distance ($d=11$ a.u.) case and is due to the multipolar resonance structure in the dipole-sphere system.^{11,12} We also see that for close distances ($d=3$ a.u.), the local results resemble more the flat surface results as expected. When the nonlocal effects are further taken into account, we see that the induced frequency shifts are generally reduced (with respect to the local results^{3,10}), with higher-order (multipolar) “dispersion resonances” being resolved. Here “dispersion resonances” refer to the similar kind of anomalous dispersion observed for the flat surface case¹⁵ which manifests itself at the same resonance frequency in the decay rate spectrum (i.e., at $\omega_{sp} \approx \omega_p/\sqrt{2}$ in the local description for flat surfaces). These dispersion resonances are blue-shifted in position, which is consistent with what was observed before from the decay-rate calculations.¹² Note that in the local theory, the position of these resonances could be given

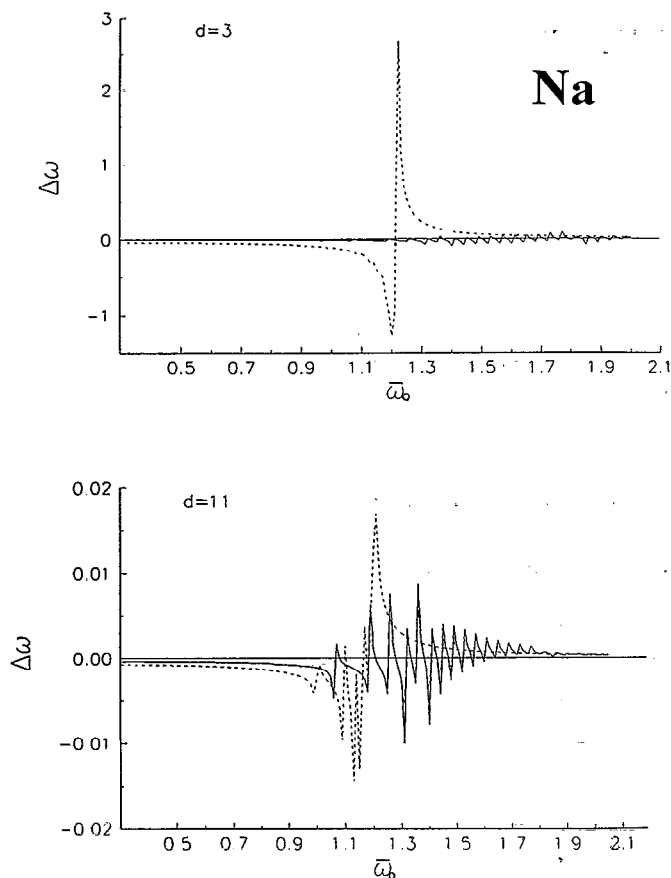


FIG. 2. Same as in Fig. 1, except that the results are for a Na sphere substrate.

approximately by the multipolar surface plasmon frequencies (i.e., $\omega_{sp}^{(l)} \approx \sqrt{[l/(2l+1)]\omega_p}$), which are crowded at the neighborhood of $\omega_0 \approx 1$). In the nonlocal case, the expression for $\omega_{sp}^{(l)}$ is modified with new resonance positions spread out and blue-shifted. Note that the "oscillations" shown by the solid curves are not exactly periodic, and are dependent on these new resonance positions, which could be given approximately by the singularities of Eq. (8) just like one derives $\omega_{sp}^{(l)}$ from Eq. (7) in the local case. It is also worthwhile to point out that the local results can be unreasonably large at close distances; this is the case especially at resonant emission frequencies and with small sizes substrate spheres. Furthermore, the oscillation modes at higher emission frequencies should be quite intrinsic to the properties of the substrate spheres and may be related to the blue-shifted multipolar surface plasmon resonances recently observed from EELS probe of simple metal surfaces.²⁰ It is also well known that quantum size effects do lead to blue-shifted oscillation frequencies for microspheres.²¹ We also notice that the surface plasmon effects are in general somewhat more pronounced in the case for a noble metal (as compared to simple metal) as one would expect. Figure 3 shows the level shifts for an Na sphere as a function of molecule-surface distance at emission frequencies both below and above the surface plasmon reso-

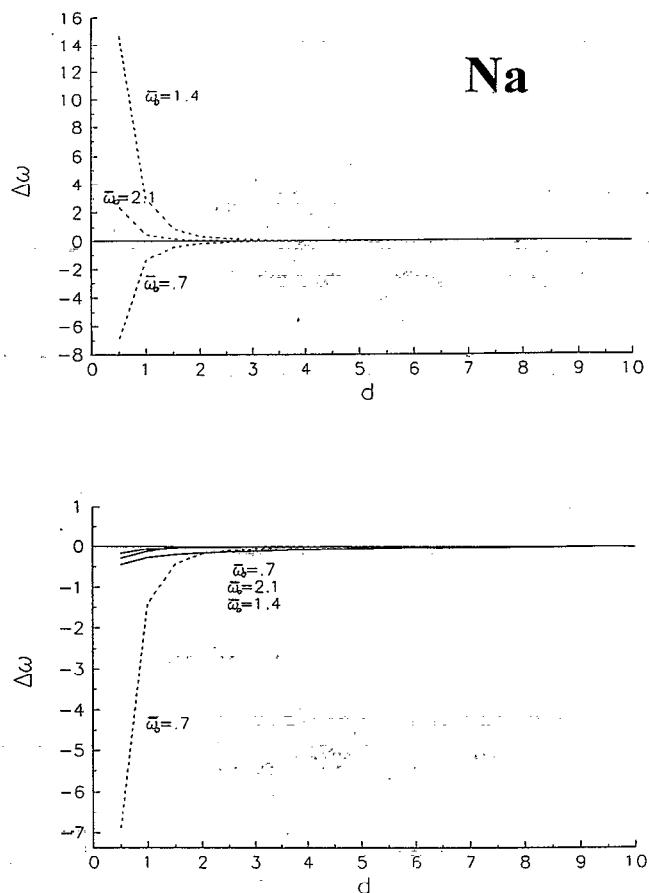


FIG. 3. Frequency shift vs molecule-substrate distance at different normalized emission frequencies of an admolecule at a Na sphere. All units are in a.u. Note that the convergence of the local and nonlocal results at large d is also shown for $\bar{\omega}_0 = 0.7$. The emission frequency values for the solid nonlocal curves are shown in respective order from top to bottom.

nance frequency of the substrate. While the local and the nonlocal results do converge to each other at large distances in general as expected^{11,12,17} (this is indicated for the $\bar{\omega}_0 = 0.7$ case), one most interesting feature we notice is that the nonlocal model could give completely different results, even qualitatively, at very close distances when the emission frequency is above the surface plasmon frequency of the metal. In this case, a blue shift in the molecular level according to the local description can become a red shift in the nonlocal model. We have also studied the effect of the size of the substrate sphere with the molecular parameters ($\bar{\omega}_0$ and d) fixed. It is found that the nonlocal model is more sensitive to the change of the sphere radius than is the local one. This is expected since the nonlocal response takes into account all the electrons spread over the sphere. Figure 4 shows a three-dimensional plot for the result of a tin (Sn) sphere¹⁷ as the substrate. The result contains similar qualitative features as for the other two metals, with the surface plasmon effect again found being slightly smaller than that for Ag and comparable with that for Na. Finally, we would like to comment briefly on the experimental possibility of observing these nonlocal effects as revealed from the present calculation. There are at least

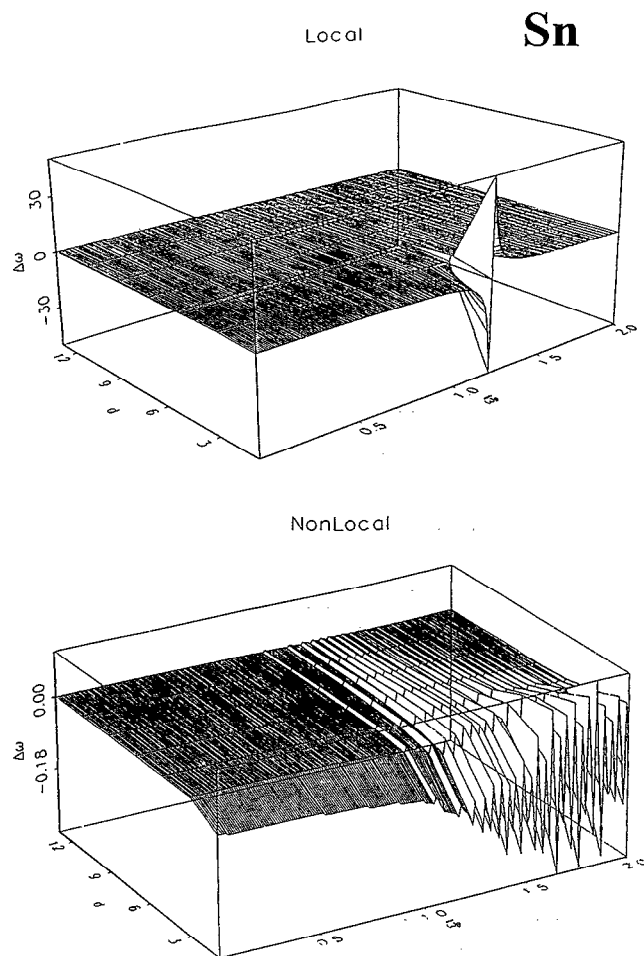


FIG. 4. A three-dimensional plot for the frequency shift vs both the emission frequency and the molecule-substrate distance for a radial dipole at a tin sphere. The distinction between the local and nonlocal results can be clearly seen.

two techniques published in the literature for the monitoring of dipolar frequency shifts at metal surfaces, namely, inelastic electron tunneling spectroscopy for vibrational level shifts,²² and reflectance spectrum analysis where the admolecules are simulated by very fine metallic spherical particles.²³ In the later case, the "admolecule" can no longer be regarded as "pointlike" and the present theoretical model must be modified to take into account the finite size of the "admolecule."²⁴ To study the effects obtained from the present work, the required modification to the above approaches^{22,23} is the preparation of the substrate. A recent publication⁷ has discussed a method of preparing a substrate surface consisting of spherical islands of control-

TABLE I. Numerical parameters used in the present calculation.

	Bulk plasmon frequency	Fermi velocity	Drude model Damping constant
	ω_p in s^{-1}	v_F in $au s^{-1}$	Γ , in s^{-1}
Na (Ref. 11)	8.97×10^{15}	2.02×10^{16}	1.52×10^{13}
Sn (Ref. 17)	1.17×10^{16}	2.34×10^{16}	3.6×10^{13}
Ag (Ref. 25)	1.36×10^{16}	2.62×10^{16}	2.56×10^{13}

lable sizes. We would expect that the present calculation results could be verifiable by combining the techniques described in the above works (Refs. 7, 22, and 23).

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- ¹H. Metiu, *Prog. Surf. Sci.* **153**, 17 (1984).
- ²G. W. Ford and W. H. Weber, *Phys. Rep.* **113**, 195 (1984); P. T. Leung and T. F. George, *Spectroscopy* **4**, 35 (1989).
- ³M. Moskovits, *Rev. Mod. Phys.* **57**, 783 (1985).
- ⁴M. Fleischmann, P. J. Handra, and A. J. McQuillan, *Chem. Phys. Lett.* **26**, 163 (1974).
- ⁵D. A. Jelski, P. T. Leung, and T. F. George, *Int. Rev. Phys. Chem.* (1988).
- ⁶See, e.g., J. C. Tsang, J. R. Kirtley, and J. A. Bradley, *Phys. Rev. Lett.* **11**, 772 (1979); J. R. Kirtley, S. S. Jha, and J. C. Tsang, *Solid State Commun.* **35**, 509 (1980); S. S. Jha, J. R. Kirtley, and J. C. Tsang, *Phys. Rev. B* **22**, 3973 (1980).
- ⁷See, e.g., R. Koh, S. Hayashi, and K. Yamamoto, *Solid State Commun.* **64**, 375 (1987).
- ⁸A. Nitzan and L. E. Brus, *J. Chem. Phys.* **74**, 5321 (1981); **75**, 2205 (1981); J. I. Gersten and A. Nitzan, *Surf. Sci.* **158**, 165 (1985); Y. S. Kim, P. T. Leung, and T. F. George, *Surf. Sci.* **195**, 1 (1988).
- ⁹See the papers by A. Nitzan and L. E. Brus in Ref. 8.
- ¹⁰W. H. Weber and G. W. Ford, *Phys. Rev. Lett.* **44**, 1774 (1980).
- ¹¹W. Ekardt and Z. Penzar, *Phys. Rev. B* **34**, 8444 (1986).
- ¹²P. T. Leung, *Phys. Rev. B* **42**, 7622 (1990).
- ¹³M. H. Hider and P. T. Leung, *Phys. Rev. B* **44**, 3262 (1991).
- ¹⁴R. Ruppin, *Phys. Rev. B* **45**, 11209 (1992).
- ¹⁵R. R. Chance, A. Prock, and R. Silbey, *Phys. Rev. A* **12**, 1448 (1975); *Adv. Chem. Phys.* **37**, 1 (1978).
- ¹⁶P. T. Leung and T. F. George, *J. Chem. Phys.* **87**, 6722 (1987).
- ¹⁷R. Fuchs and F. Claro, *Phys. Rev. B* **35**, 3722 (1987).
- ¹⁸See, e.g., F. Forstmann and R. R. Gerhardts, *Metal Optics Near the Plasma Frequency* (Springer-Verlag, Berlin, 1986).
- ¹⁹See the paper by Y. S. Kim, P. T. Leung, and T. F. George in Ref. 8.
- ²⁰K. D. Tsuei, E. W. Plummer, A. Leibs, K. Kempa, and P. Bakshi, *Phys. Rev. Lett.* **64**, 44 (1990).
- ²¹See, e.g., D. Ugarte, C. Colliex, and P. Trebbia, *Phys. Rev. B* **45**, 4332 (1992), and references therein.
- ²²J. Kirtley and P. K. Hansma, *Phys. Rev. B* **13**, 2910 (1976).
- ²³W. R. Holland and D. G. Hall, *Phys. Rev. Lett.* **52**, 1041 (1984).
- ²⁴See, e.g., W. H. Weber and G. W. Ford, *Surf. Sci.* **109**, 451 (1981).
- ²⁵C. Girard and F. Hache, *Chem. Phys.* **118**, 249 (1987).

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