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Nonradiative lifetime of excited states near a small metal particle

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The nonradiative lifetime of excited states near a small ($\lesssim 2$ nm) metal particle is investigated within a purely electromagnetic model. The excited state is described as a point dipole, and the metal particle is characterized by its self-consistently obtained nonlocal density-density correlation function. *Resonant* coupling, between excited states of adsorbates and various electronic excitations of the metal particle, is shown to be an important lifetime-determining decay channel.

I. INTRODUCTION

The lifetime of excited molecular levels in contact with metal surfaces plays a crucial role for, e.g., the accurate determination of enhancement factors pertinent to various problems related to surface-enhanced Raman scattering (SERS).[1] Because of the roughness sensitivity of SERS it is not surprising that the simple problem of a molecule in contact with a dielectric or metallic sphere (or spheroid) was studied very often[2–8] in order to obtain deeper insight in the various aspects of the electromagnetic contribution to SERS at rough surfaces.

In all of these studies the dielectric properties of the metal particle were described either by a simple Drude model or by a *local bulk* dielectric constant whose frequency dependence was taken from experimental data. Hence *both* nonlocal size effects *and* nonlocal surface-response properties were completely neglected. As a result of these approximations, the electromagnetic coupling of molecules to metal particles is dominated by the classical surface plasmons of the underlying local-response model. However, as we know from our earlier studies of related problems,[9–13] the dynamical properties of *very* small metal particles (typically in the range of 2 nm and less) are governed *both* by collective modes *and* by electron-hole pair excitations. Depending on the experimental conditions, the role played by the collective modes is sometimes completely negligible, and all the information is obtained from the coupling to single electron-hole pairs. For instance, in Ref. 12 it was shown that the inelastic scattering of electrons from small metal particles is, at large scattering angles, completely determined by its coupling to electron-hole pairs. The reason for this "anomalous" behavior is simply that at larger wave vector transfer, the collective modes (the higher multipole surface plasmons) carry less and less oscillator strength. This result is very similar to what has been found for planar surfaces by Inglesfield and Wikborg.[14]

In a purely electromagnetic framework the lifetime of excited molecular states will be determined by the coupling matrix elements of the fluctuating electric field set up by the oscillating dipole in front of the metal sphere. Hence, on the basis of a multipole expansion, the transition rate can be shown to consist of both low-l multipole contributions and higher-l contributions as well (see below). Because classical macroscopic electrodynamics is not valid for larger wave vectors (which means higher l values in spherical geometry), we conclude that classically obtained results become less and less meaningful for experimental conditions under which the high-l part of the coupling is dominant. As we shall see below, this is (obviously) the case in the immediate neighborhood of the spherical surface. It is for this reason that we have reexamined some results on the lifetime of molecular states in contact with a metal sphere.

There are two recent papers directly related to the problem under discussion—namely, the work by Gersten and Nitzan,[3] and the work by Ruppin.[5] Both works consider rather *large* distances of the molecular states to the sphere. Hence their results are more or less consistent with the application of classical electrodynamics. However, for reasons we have discussed above, their results cannot be used to understand experimental findings for molecules which are a few atomic units away from the spherical surface. It is this region we are investigating in this paper.

II. THEORY

An oscillating point dipole at any point $\mathbf{r}_1$ in space sets up a "bare" electrostatic potential of the following form:

$$\phi_{\text{dip}}(\mathbf{r},\mathbf{r}_1)=\mathbf{p}\cdot\nabla_{\mathbf{r}_1}\frac{1}{|\mathbf{r}-\mathbf{r}_1|} . \tag{1}$$

Here, $\mathbf{p}$ has—in our context—the meaning of a dynamical molecular dipole transition-matrix element from the ground state of the molecule to a certain excited state (vibronic or electronic) and $\mathbf{r}$ is any point in $\mathbf{r}$ space. ϕ_{dip} acts as an "external" perturbation on the ground state of the metal particle under discussion. Consequently, the perturbation Hamiltonian H' is given as follows:

$$H'=\int d\mathbf{r}\,\rho(\mathbf{r})\phi_{\text{dip}}(\mathbf{r},\mathbf{r}_1) . \tag{2}$$

Here, $\rho(\mathbf{r})$ is the operator of the electronic charge of the metal particle. Within linear-response theory, application of Fermi's golden rule leads to the following expression for the transition rate Γ (in Rydberg atomic units):

$$\Gamma=8\mathbf{p}\cdot\nabla_{\mathbf{r}_1}\mathbf{p}\cdot\nabla_{\mathbf{r}_2}\big|_{\mathbf{r}_2=\mathbf{r}_1}\sum_{l=0}^{\infty}\frac{4\pi}{2l+1}\int d\mathbf{r}\,B_l(r,r_1)\sum_{m=-l}^{l}Y_{l,m}(\Omega_1)Y^*_{l,m}(\Omega)$$
$$\times\sum_{\tilde{l}=0}^{\infty}\frac{4\pi}{2\tilde{l}+1}\int d\mathbf{r}'(-1)\mathrm{Im}\chi(\mathbf{r},\mathbf{r}';\omega)B_{\tilde{l}}(r',r_2)\sum_{\tilde{m}=-\tilde{l}}^{\tilde{l}}Y^*_{\tilde{l}\tilde{m}}(\Omega_2)Y_{\tilde{l}\tilde{m}}(\Omega')\ . \quad (3)$$

In Eq. (3), Imχ means the imaginary part of the retarded density-density response function of the metal sphere[10,11] and $B_l(r,r_1)$ is short for

$$B_l(r,r_1)=\frac{r^l}{r_1^{l+1}}\Theta(r_1-r)+\frac{r_1^l}{r^{l+1}}\Theta(r-r_1) \quad (4)$$

with $\Theta(x)$ the Heaviside step function. Of course, for a spherically symmetric particle only the diagonal elements of Eq. (3) with $l=\tilde{l}$ contribute to Γ.

If the point dipole at $\mathbf{r}_1$ is well outside the electronic charge being polarized, the expression for Γ is considerably simplified. In this limiting case evaluation of the right-hand side of Eq. (3) gives

$$\Gamma=4\sum_{l=1}^{\infty}\mathrm{Im}\alpha_l(\omega)/R^{2l+1}(R/r_1)^{2l+1}p^2/r_1^3[(l+1)^2\cos^2\theta+P_l'(x)\,|_{x=1}\sin^2\theta]\ . \quad (5)$$

In this expression $\alpha_l(\omega)$ is the dynamical l-pole polarizability of the sphere, R is the radius of the sphere, θ means the angle between the dipolar axis and the line connecting the point dipole with the center of the sphere, and P_l' is the derivative of the lth Legendre polynomial P_l. Of course, on the basis of the results we have obtained for χ in our earlier work,[9–11,15] we could use the exact formulation (3) and study more complicated situations (e.g., the dipole *embedded* in the electronic surface). However, as we know from the corresponding work of Hellsing and Persson[16–18] for a flat surface, in this situation it might be necessary to study the modification of the electronic wave function in the presence of the dipole in a nonlinear way. We think that in this latter case we face a complicated chemisorption problem which is definitely beyond the scope of the present work and which has not yet been addressed in the existing literature.

If the Drude dielectric constant $\epsilon(\omega)$ is used in the formula for the classical l-pole polarizability of a metallic sphere of radius R, namely

$$\alpha_l(\omega)=\frac{\epsilon(\omega)-1}{\epsilon(\omega)+(l+1)/l}R^{2l+1}\ , \quad (6)$$

we see immediately that Eq. (5) transforms to an expression derived by Ohtaka and Inoue.[8,19] The difference from their expression is that we see how it originates from the general microscopic expression for the nonradiative lifetime, Eq. (3), and that we are using the microscopically obtained polarizabilities $\alpha_l(\omega)$. As a consequence, our near-surface results deviate considerably from theirs.

III. RESULTS AND DISCUSSION

Experimentally, the answers to the following three questions are of utmost interest.

First, how does Γ depend on the frequency ω with the position $\mathbf{r}_1$ of the dipole held fixed?

Second, how does Γ depend on $\mathbf{r}_1$ with the frequency ω held constant?

Third, what is the dipole contribution to Γ and what is the contribution of the remaining multipoles?

The answer to the second question is also of some interest for flat surfaces, as in this way one should be able to disentangle surface and bulk contributions, respectively, to Γ.[20] For the present case this latter problem is of minor importance, simply because everything is mixed up.

However, there is a related problem, and this is, in fact, problem 3. For a dipole far away from the metal particle only the $l=1$ part of the coupling should be important. This is a consequence of the long range of the Coulomb coupling. On the other hand, for a dipole near the surface rather large-l components come into play. Because for low l $\alpha_l(\omega)$ is governed by the collective mode[10,11] whereas for large l the single-pair excitations gain more and more oscillator strength,[11] we obtain a *true* change in the character of Γ when the dipole approaches the surface. This is a completely new result which is necessarily missing in any classical investigation.

As an example we study in the following a spherical jellium particle corresponding to 92 valence electrons of Na ($r_s=4a_0$). Hence the particle has a radius of $R=92^{1/3}\times 4a_0=18.057a_0$. The self-consistent calculation of the response functions $\alpha_l(\omega)$ was described in full detail in our previous work.[10,11] Therefore this discussion will not be repeated here, and the interested reader is referred to the already published work.

In order to see more clearly the importance of the self-consistent nonlocal properties of small metal particles (in comparison to their classical counterparts) we calculate, in addition, results following from the use of the classical $\alpha_l(\omega)$, Eq. (6), with an $\epsilon(\omega)$ given by a Drude-like dielectric constant

$$\epsilon(\omega)=1-\omega_p^2/(\omega^2+i\omega\gamma)\ . \quad (7)$$

Here, $\omega_p^2=4\pi ne^2/m$ is the bulk plasma frequency of Na, $r_s=4a_0$, and γ is set equal to 10 meV. For a discussion of this "numerical damping" see Ref. 10.

We are now in a position to discuss our results. Figure 1 shows Γ (in Ry a.u. $=2.068\times 10^{16}$ s^{-1}) for a dipole with

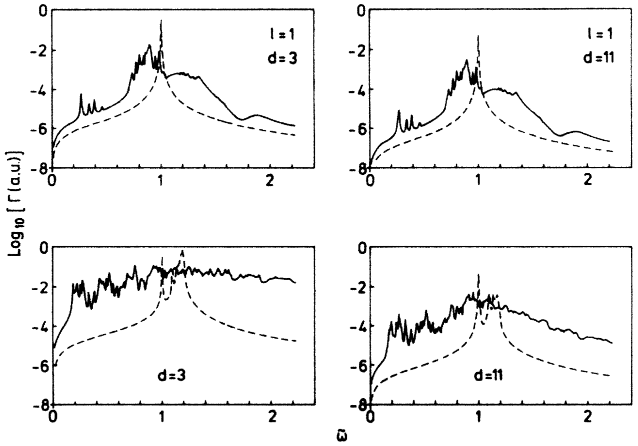

FIG. 1. Frequency dependence of the transition rate Γ as defined by Eq. (5) of the text. The parameters describing the metal particle correspond to 92 valence electrons of Na. The dipole moment assumed was $p = 1ea_0$ (e being the electronic charge, a_0 the Bohr radius) and two dipole positions r_1 are considered. In both cases the upper panel shows the dipole contribution $l = 1$ to the total Γ. The angle θ was set equal to zero. The frequency ω is given in units of the classical dipolar surface plasmon frequency of Na, $\tilde{\omega} \equiv \omega/(\omega_p^{\text{Na}}/\sqrt{3})$, $d = r_1 - R$ [see Eq. (5)], and $\log_{10}\Gamma$ is given with Γ in Ry a.u. Continuous line: microscopical result, obtained with $\alpha_l(\omega)$ of Ref. 11. Dashed line: classical result, obtained with the use of $\alpha_l(\omega)$ of Eq. (6) in calculating the transition rate Γ in Eq. (5). Note the pronounced resonant character of the coupling. For other p values Γ is easy to calculate because Γ scales with p^2 [see Eq. (5) of the text].

a dipole moment p of $p = 1ea_0$ at two different distances d from the spherical jellium edge, namely at $d = r_1 - R = 3a_0$ and at $d = 11a_0$. The first value of d is on the borderline of the applicability of formula (5), because r_1 is *not* well outside the induced charge. However, a glance at the induced charge density at various frequencies, obtained especially in Refs. 10 and 11, shows that $r_1 - R = 3a_0$ might be acceptable ($r_1 - R = 0$ definitely would not). For each value of r_1 the $l = 1$ result is separately given. By comparing this contribution with the full-l result we are able to estimate the importance of a complete theory if r_1 approaches the surface of the particle. Not surprisingly, a pure dipole theory ($l = 1$ part of Γ only) breaks down near the surface.

The resonant character of the coupling can very nicely be seen from the figure. Whenever ω approaches a particle-hole pair frequency, Γ is drastically enhanced. Near the surface, $r_1 - R = 3a_0$, Γ is dominated by the coupling to electron-hole pairs whereas further away, $r_1 - R = 11a_0$, the coupling is smoothly transformed to a purely collective low-l coupling.

Generally, these curves correspond to similar results obtained by Ruppin,[21] but in contrast to his work our result is based on the truly microscopic (model) response functions of Ref. 11. Hence all nonlocal and size-dependent effects are included from the very beginning, and there is no need to use a local *bulk* dielectric constant as in Ref. 5.

The classical results, shown as dashed lines in Fig. 1, are governed by the l-pole surface plasmons. The relative importance of the $l = 1$ dipolar surface plasmon can nicely be seen by comparing the $r_1 - R = 3a_0$ result with the $r_1 - R = 11a_0$ result.

Both classically and microscopically Γ is sensitively dependent on whether or not the frequency ω of the oscillating dipole is in resonance with the various elementary excitations of the metal particle. Classically, there are only *collective* l-pole resonances, whereas quantum mechanically all the l-pole particle-hole pairs come into play.

Figure 2 gives the distance dependence of Γ at three characteristic frequencies ω. Once again, the $l = 1$ contribution is separately shown in each case. The first frequency, $\tilde{\omega} = 0.07$ in the units used in the figure (see caption to Fig. 1), corresponds to $\omega = 250$ meV and is off

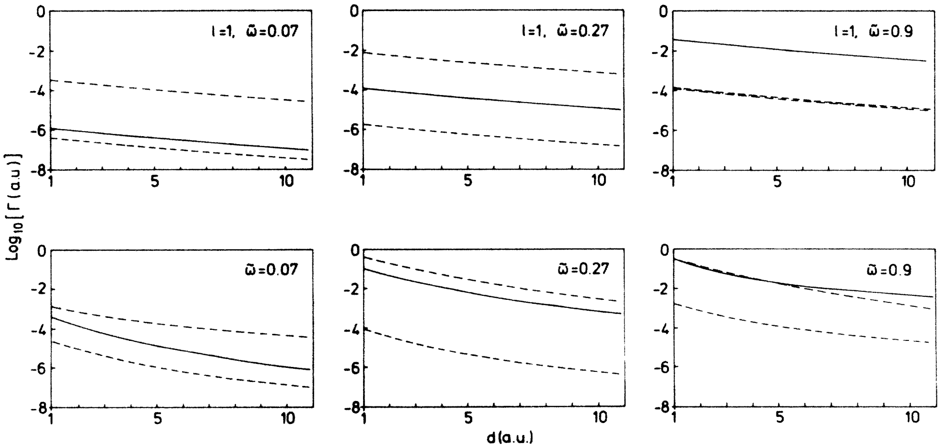

FIG. 2. Distance dependence of Γ for three different frequencies corresponding to off-resonant ($\tilde{\omega} = 0.07$), resonant electron-hole pair ($\tilde{\omega} = 0.27$), and resonant collective ($\tilde{\omega} = 0.90$) coupling, respectively. The distance d from the spherical jellium edge, $d = r_1 - R$, is given in Bohr. In addition to the microscopic result (continuous line) and the classical result (dashed line) we give the independent electron result (dashed-dotted line). This latter curve is obtained from the use of unscreened $\alpha_l^0(\omega)$ in Eq. (5). For a discussion of $\alpha_l^0(\omega)$ in comparison to $\alpha_l(\omega)$ see Ref. 11.

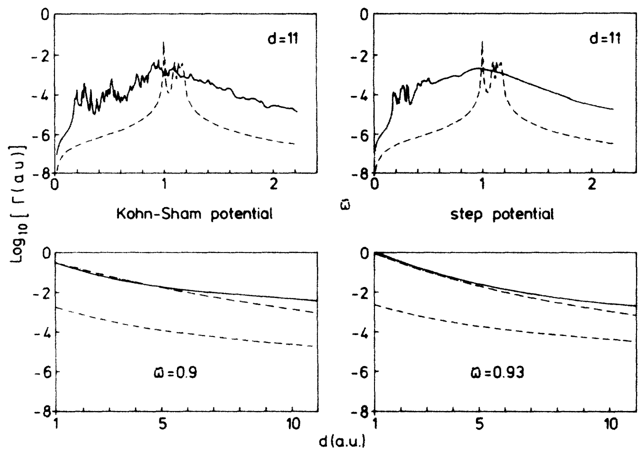

FIG. 3. Comparison of the frequency dependence (upper panel) and the distance dependence (lower panel) of Γ for the Kohn-Sham potential barrier (Refs. 10 and 11) and the energy-minimizing step-potential barrier (Ref. 15). The frequencies $\tilde{\omega}=0.90$ (for Kohn-Sham) and $\tilde{\omega}=0.93$ (for the step potential) are those pertaining to the collective dipolar surface plasmon frequencies of the two different models. It is due to these slightly different frequencies that the classical curves on the left-hand side of the figure do not exactly agree with those of the right-hand side.

resonant to all the electron-hole pairs in the metal particle under discussion. Consequently, the transition rate Γ is rather low. The second frequency, $\tilde{\omega}=0.27$, corresponds to a resonant coupling to the lowest $l=1$ electron-hole pair excitation frequency (see Fig. 1, $l=1$ result). As a result, Γ is enhanced dramatically by approximately 3 orders of magnitude (note that the $\log_{10}\Gamma$ is given on the ordinate). Finally, the third frequency $\tilde{\omega}=0.9$ corresponds to the *collective* $l=1$ resonance frequency. This results in a further enhancement of Γ which, however, is not as large as one might think. The reason is simply that the resonant character at $\tilde{\omega}=0.27$ is already very pronounced.

For theoretical reasons, we show in Fig. 2 as a dotted-dashed line microscopic results obtained *without* electron-electron interaction. That means, in the calculation of Γ [Eq. (5)] we have used the independent electron polarizability $\alpha_l^0(\omega)$ instead of the correct $\alpha_l(\omega)$ pertaining to the system of interacting electrons.[22] The relative importance of self-consistency at low frequencies can nicely be seen. Interestingly enough, at $\tilde{\omega}=0.9$ the difference between the two results is not very large (for the full-l result).

In Fig. 3 a comparison is given for Γ obtained on the one hand for the Kohn-Sham potential and on the other hand for the total-energy minimizing step potential of Ref. 15. In both cases the lower panel shows Γ at the value $\tilde{\omega}$ corresponding to the $l=1$ surface plasmon frequency, which is $\tilde{\omega}=0.90$ for the Kohn-Sham barrier and $\tilde{\omega}=0.93$ for the step potential. Except for the more pronounced electron-hole pair structure in the Kohn-Sham potential[15] the results are rather similar. Note that the small difference in the classical result corresponding to the dashed lines in the lower panel of the figure is caused by the different values of $\tilde{\omega}$.

Finally, we want to comment on absolute numbers for Γ as compared to Γ values at flat surfaces. First of all, we have to assume values for p, d, and for ω. For $p=0.1ea_0\approx0.25$ D, $d=3a_0$, and $\tilde{\omega}=0.07$ [these numbers correspond to the C-O stretch mode on Cu(100)] we obtain for the spherical case $\Gamma=6\times10^{-7}$ a.u.$\approx1.2\times10^{10}$ s^{-1} which is smaller by approximately 1 order of magnitude than for the planar case[23] (and for $r_s=2.67a_0$). The reason is clearly that $\tilde{\omega}=0.07$ is off resonant to every electron-hole pair excitation of the spherical particle under discussion. If $\tilde{\omega}=0.27$ is assumed to be typical for the resonant coupling, we would end up with $\Gamma=2.3\times10^{-4}$ a.u.$\approx4.6\times10^{12}$ s^{-1}, which means an enhancement of 3 orders of magnitude. This is larger by a factor of 45 compared to the planar case. Hence we see that it depends sensitively on the frequency ω whether or not Γ_{sphere} is reduced or enhanced as compared to Γ_{plane}. We think that is a *natural* consequence of the *resonant* character of the coupling in the case of very small metal clusters.

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