

Supporting Information for

**Intrinsic Limitations on the $|E|^4$ Dependence of the Enhancement Factor
for Surface Enhanced Raman Scattering**

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The purpose of the Supporting Information is to include several well known aspects of the surface enhanced Raman scattering (SERS) phenomenon in the discussion without interrupting the flow of the article.

Orientation and distance dependence of the adsorbate molecule in SERS

The distance and angular dependence of an interacting molecule on a conductor surface can be considered using a model consisting of an effective transition dipole (polarization) inside the conductor. For thin films the dipole oscillates across the film and is known as the screened bulk plasma frequency (SBPP). For nanoparticles and nanostructures the collective oscillation of dipoles is called the localized surface plasmon resonance (LSPR). On a spherical particle surface, the field due to the LSPR decreases with distance as d^3/r^3 , where d is the particle radius and r is the distance from a molecule to the center of particle. The probability of absorption by the molecule, which leads to Raman scattering, is a function of the $\cos^2(\theta)$, where θ is the angle between the transition

dipole on the nanoparticle and transition dipole on the particle. This dependence has leads to the surface selection rule. On a single spherical particle orientation averaging of $\langle \cos^2(\theta) \rangle$ for a molecule with a perpendicular orientation (e.g. pyridine on Ag in a end-on bonding geometry) leads to a decrease in the intensity enhancement by a factor of 1/3 as shown in Figure S1. The averaging for a molecule with a parallel orientation relative to the surface corresponds to $\langle \cos^2(\phi) \sin^2(\theta) \rangle$, which is also gives a factor of 1/3 (Figure S1). Since there are two intensity interactions (one for ω_i and one for ω_s) there is additional factor of 1/3 for emission from an isotropic sample. Furthermore, one must average over the solid angle for emission of the Raman fields at ω_s . In the simplest model this leads to a decrease by a factor 2 since there is a probability of 1/2 that Raman photon will be emitted in the hemisphere that coincides with the nanoparticle surface. Only a photon emitted in the direction of the nanoparticle can be amplified by coupling to nanoparticle Mie scattering. Thus, orientational factors will reduce the enhancement by a factor of 18. The calculations in the text assume that the molecule is on the surface of the nanoparticle. In that case, $d = r$ and the distance factor plays no role in the calculation, $d^3/r^3 = 1$.

The nanoparticle critical radius for Mie scattering

The absorption cross section, σ_{abs} , and scattering cross section, σ_{sca} , depend on particle radius, d as $1/d^3$ and $1/d^6$, respectively. Thus, there is a critical minimum radius required for Mie scattering to be observed. When $\sigma_{\text{sca}}/\sigma_{\text{abs}} < 1$ most of the incident light is absorbed and there can be no intensity enhancement due to Mie scattering and hence no electromagnetic enhancement. Figure S2 shows the ratio of the Raman scattering cross section, σ_{sca} , and absorption cross section, σ_{abs} , of the nanoparticle (Eqn. 10)

calculated at the ratio $d/\lambda = 0.1$, where d is the particle radius and λ is the wavelength of the incident radiation. Since $\sigma_{\text{sca}}/\sigma_{\text{abs}} \gg 1$ in the example, the plot shows that the enhancements given in Figure S2 that would apply for a 50 nm nanoparticle when excited with a common laser source at ~ 500 nm (e.g. Argon ion or Nd:Yag). According to the d^3/λ^3 dependence in Eqns. 10 and 11 the intensity would be decreased by a factor of 1000 for a 5 nm particle and no electromagnetic enhancement would be observed. At this point it is crucial to recognize that the absence of Mie scattering does not rule out resonant Raman scattering from the nanoparticle or a complex of a molecule with the nanoparticle. Enhancement by the chemical or molecular resonant mechanism can still be observed when $\sigma_{\text{sca}}/\sigma_{\text{abs}} < 1$.

The influence of ellipticity and medium dielectric constant on the SERS magnitude

The effect of radius of curvature (ζ) and dielectric constant of the medium (ϵ_s) can increase the SERS enhancement. The dependence of the SERS enhancement as a function of shape factor and medium dielectric constant is shown for the ratio $\omega_p/\Gamma = 100$ in Figure S3 over the entire useful range of $1/6 < \zeta < 1/3$ and $1.0 < \epsilon_s < 3.0$. Figure S3 demonstrates that geometry affects both ω_{sp} and $|g(\omega_{\text{sp}})|^2$ due to the depolarization factor, ζ . An increase in the intensity enhancement term $|g(\omega_{\text{sp}})|^2$ shifts the position of ω_{sp} to lower energy. For example, Figure 5 shows that an additional factor of 2 in enhancement is possible when $\epsilon_s = 1.75$ (i.e. in water) if the aspect ratio of the conductor changes from $\zeta = 1/3$ to $\zeta = 1/5$. However, at the same time the position of the surface plasmon shifts from $\omega_{\text{sp}}/\omega_p = 0.365$ to $\omega_{\text{sp}}/\omega_p = 0.300$. If we assume $\omega_p = 50,000 \text{ cm}^{-1}$ for sake of comparison this corresponds to a shift from $18,200 \text{ cm}^{-1}$ (550 nm) to $14,000 \text{ cm}^{-1}$ (717

nm). Thus, predictions of enhancements made using specific geometries must also account for the both narrow bandwidth and relatively large shifts of surface plasmon.

The connection between the Drude model and empirical dielectric functions

One way to compare the experimental dielectric functions is to consider the effect of an absorptive transition added to the Drude model. The model dielectric function obtained in this manner can be used to calculate enhancement factors using the Clausius-Mosotti local field. The point of such a comparison is to understand how the imaginary part of the dielectric function affects the intensity enhancement line shape for comparison with the experimental dielectric functions of Au and Ag. The results of a model calculation of this type using the parameters $\omega_0 = 30,000 \text{ cm}^{-1}$, $\Gamma_0 = 10,000 \text{ cm}^{-1}$ and $\epsilon_0 = 4$ are shown in Figures S4 and S5 using Eqn. S1. The contribution to $\epsilon_2(\omega)$ is smaller than in Au, which has a number of band-to-band transitions in the visible.³⁶ Figure S4 shows that the predicted absorption band is asymmetric and reduced in intensity relative and broadened dispersion to the free electron model absorption using the same ω_p and Γ shown in Figure 1. This result also corresponds to the case experimental for Au, which has a less intense plasma band and less sharp SPP than Ag. The local field factor is significantly smaller for the model that includes an absorptive transition. The Lorentzian model is:

$$\epsilon_1(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + \Gamma^2} , \quad \epsilon_2(\omega) = \frac{\Gamma \omega_p^2}{\omega(\omega^2 + \Gamma^2)} + \frac{\epsilon_0 \Gamma_0^2}{4(\omega^2 - \omega_0^2) + \Gamma_0^2} \quad (\text{S1})$$

In Eqn. S1, a Lorentzian line shape is added to the imaginary part of the dielectric function, $\epsilon_2(\omega)$, to simulate an absorptive process such as the d-band to conduction band transition of the noble metals, Au and Ag. The effect of an absorption can be seen by

comparing the calculations of $|g(\omega)|^2$ in Figures 2 and S5. The absorptive transition decreases the intensity enhancement factor by more than 100, which provides a model for the reduction of enhancement in Au relative to Ag.

Figure Captions

Figure S1. Two geometries for a surface-adsorbed molecule on a spherical nanoparticle. The angles in spherical polar coordinates are indicated and the orientation averaging is shown in each case to lead to a factor of 1/3.

Figure S2. Calculation of the cross section for scattering relative to absorption for a Drude conductor. The calculation based on the parameters used in Figures 1 and 2 in Eqn. 9 using the ratio $d/\lambda = 0.1$ is shown with the same incident and scattered photon energies indicated in Figure 2.

Figure S3. The effect of ζ and ϵ_s on the maximum value of $|g(\omega)|^2$ for a given ω_p/Γ is plotted as function of reduced units of the plasma frequency ω_{sp}/ω_p . The curves were calculated using Eqns. 12 and 13.

Figure S4. The calculated plasma absorption (solid) and dispersion curves (dotted) are shown for $\omega_p/\Gamma = 200, 100, 40, 20$ and 10 . The dielectric function used in this calculation contained an additional term that represents the bound electrons in noble metals. The dielectric function used was Eqn. S1 with parameters given in the text. In this calculation $\epsilon_s = 1.0$ and $\epsilon_\infty = 4.0$.

Figure S5. The calculated intensity enhancement $|g(\omega)|^2$ for a sphere (Eqn. 6 with $\zeta = 1/3$, $\epsilon_s = 1.0$ and $\epsilon_\infty = 4.0$) in the limit that the diameter $d \ll \lambda$ is shown. The calculated enhancement is shown for five relative values of $\omega_p/\Gamma = 200, 100, 40,$ and 20 using the modified dielectric function given in Eqn. S1.

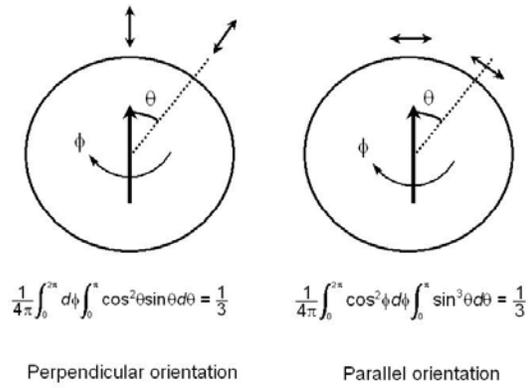


Figure S1.

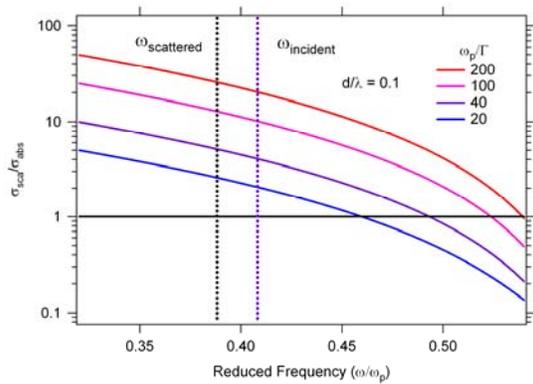


Figure S2.

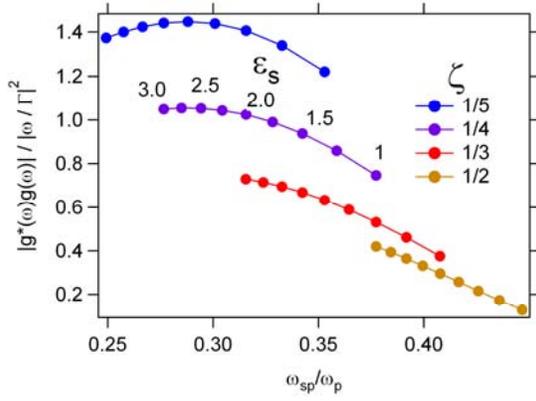


Figure S3.

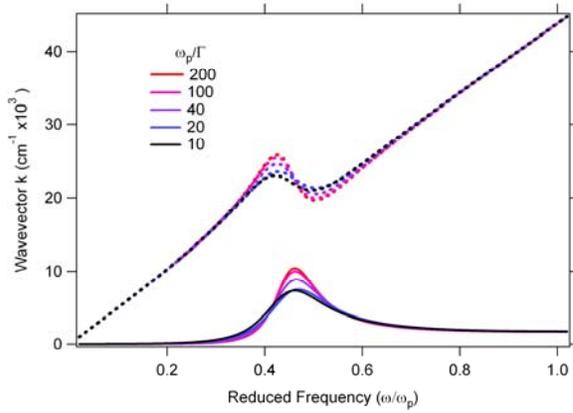


Figure S4.

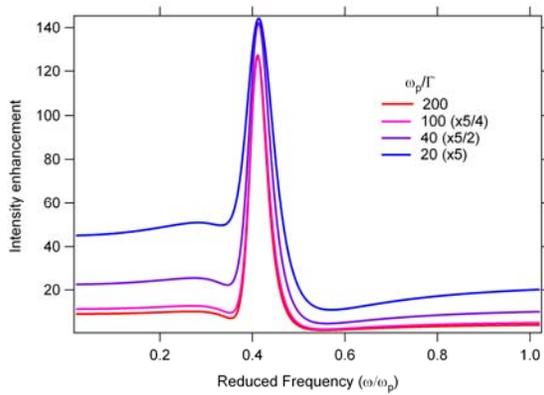


Figure S5.

