Extending SERS into the infrared with gold nanosphere dimers

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Methods

1. Model Dielectric Function

The raw data of Johnson and Christy has been fit to an analytic model by Etchegoin *et al* [Etchegoin, 2006]. The main advantages of using an analytic model of the dielectric function are smooth functions for $Q_{\mathrm{LSP}} = -\varepsilon'/\varepsilon''$ and $\mathrm{d}\varepsilon_1/\mathrm{d}\omega$ which will be discussed below. The original article by Etchegoin *et al* slightly overestimates the local surface plasmon metric, leading to an overestimation of peak field enhancement. In 2007, an errata was published [Etchegoin, 2007], increasing the Drude scattering frequency (reduce the scattering wavelength, λ_γ) from the original value of 17000 nm to 14500 nm. Here, the scattering wavelength is reduced further to 14000 nm such that the calculated peak field enhancements present a lower bound compared to expected experimental values. A comparison of the raw data and the fit used here is presented in Figure 1.

The use of optical constants by other authors, e.g. [Weaver and Frederikse, 2002] results in larger field enhancements than those reported here (up to 10^{12}).

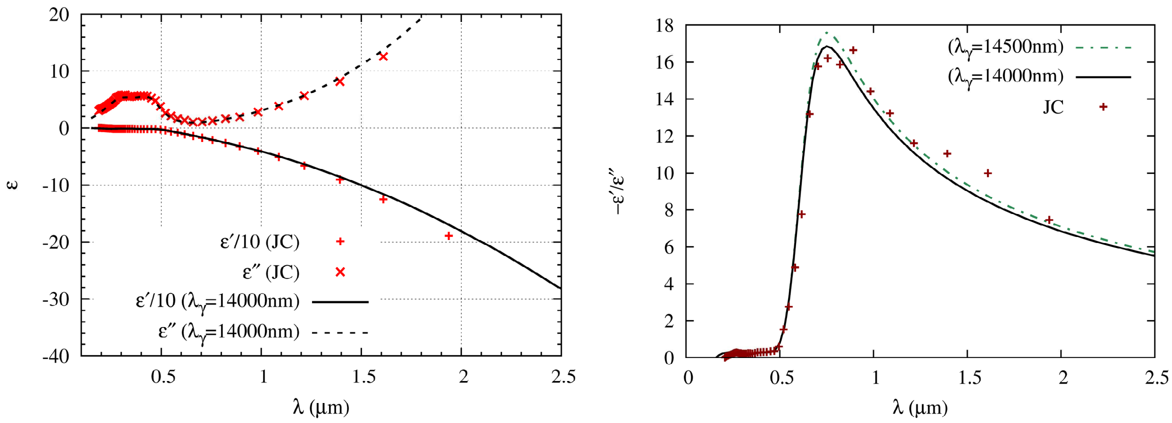

Figure 1. (Left) Model dielectric function of Etchegoin *et al* (using the scattering wavelength of 14000 nm) and the experimental data of Johnson and Christy [Johnson, 1972]. (Right) A comparison of the local surface plasmon metric calculated using the model function of Etchegoin *et al, 2007* (lines) and the experimental data of Johnson and Christy (crosses).

2. Convergence behavior of the Field Enhancement

Depending on the medium index and particle size, vector spherical harmonics (VSH) up to order 45 are required in the expansion of the fields. Because low medium index is associated with larger particles, low *m* calculations required the largest number of VSHs. The convergence rate of the field enhancement with the number of VSHs is presented in Figure 2.

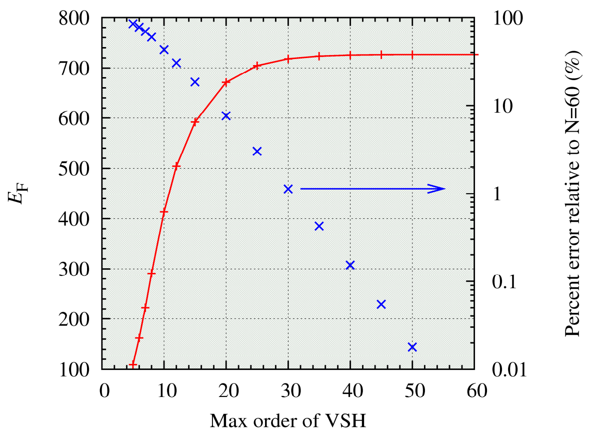

Figure 2. Field enhancement as a function of the number of VSHs included in the exapansion of the fields for m=1.50, r=24.5 nm, λ=719 nm. The relative error for N=45 is less than 0.1 %.

Data

1. Simulation parameters for Peak Fields

Table 1. Simulation parameters that give maximum peak field enhancements for each medium index.

m	r (nm)	λ_p (nm)	Q_{ext}	E_F (Peak)
1.00	41.0	631	7.06	664
1.25	30.5	672	8.06	721
1.50	24.5	719	8.59	726
1.75	21.0	774	8.68	690
2.00	19.0	837	8.44	627
2.25	18.4	913	8.05	578
2.50	20.0	1020	7.62	538
2.75	20.0	1110	7.26	503

2. Simulation parameters for Average Fields

For comparison with the peak fields, the average fields are presented in Figure 3 and Table 2. The fourth power of the field enhancement is calculated for 1369 positions situated 0.5 nm from the surface. After taking the spatial average, the fourth root is taken for comparison with the peak field enhancement.

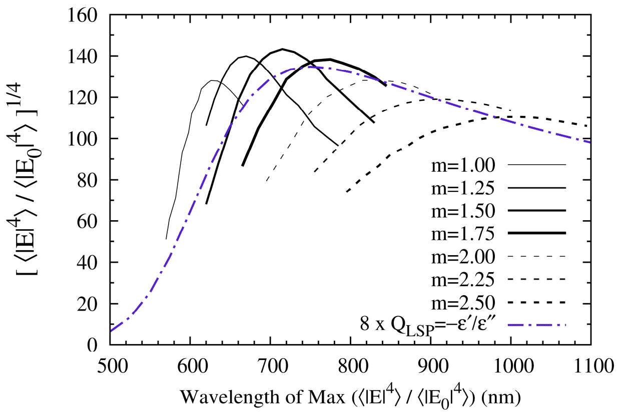

Figure 3. For each background medium refractive index (m), spectra are calculated for a series of sphere radii and the average field enhancement is selected. These field maxima are presented in the figure as a function of their respective resonance position λ_p.

Table 2. Simulation parameters that give maximum peak field enhancements for each medium index.

m	r (nm)	λ_p (nm)	$\left\langle \mathbf{E}(\omega_L)^4 / \mathbf{E}_0(\omega_L)^4 \right\rangle^{\frac{1}{4}}$
1.00	40	626	128
1.25	30	670	140
1.50	24	716	143
1.75	21	775	138
2.00	19	835	128
2.25	18	916	119
2.50	19	1010	110

Derivations

In the following the dielectric function takes the form $\varepsilon = \varepsilon_1 + i\varepsilon_2$. Three topics are discussed, as referenced to in the main text:

1. General surface plasmon metrics applicable to sphere dimers.
2. Explanation of Γ_ω
3. Proof that $\Delta\varepsilon_1 / \varepsilon_2 = 2$
4. FWHM across the extinction efficiency, Q_{ext}

1. General surface plasmon metrics applicable to dimers

Here we show that the generic surface plasmon metric is essentially a description of the maximum polarizability of the system on resonance. Two metrics are derived assuming a dielectric function of the form $\varepsilon = \varepsilon_1 + i\varepsilon_2$, the first applicable to spheres and shells:

$$Q_{\text{LSP}} = -\varepsilon_1 / \varepsilon_2 ,$$

and the second for ellipsoids:

$$Q'_{\text{LSP}} = \varepsilon_1^2 / \varepsilon_2 .$$

Finally, we show that $Q_{\text{LSP}} = -\varepsilon_1 / \varepsilon_2$ provides a good approximation to the field enhancement of a dimer of spheres.

Derivation of $Q_{\text{LSP}} = -\varepsilon_1 / \varepsilon_2$

The polarizability of a sphere in a background medium with dielectric constant ε_m is:

$$\frac{\alpha}{V} = \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \qquad (1.1)$$

In the quasistatic limit, the extinction is $C_{\text{ext}} = \frac{2\pi}{\lambda}\text{Im}(\alpha)$, and so we select the imaginary part of the polarizability (1.1):

$$\frac{\alpha(\varepsilon)}{V} = i\frac{3\varepsilon_2\varepsilon_m}{\varepsilon_2^2 + (\varepsilon_1 + 2\varepsilon_m)^2} \tag{1.2}$$

There are two equivalent resonance conditions for (1.2), either the frequency is changed such that $\varepsilon_1(\omega) = -2\varepsilon_m$, or alternatively, the background medium index is varied to coincide with the real part of the dielectric function at a given frequency:

$$\varepsilon_m = -\frac{\varepsilon_1(\omega)}{2} \tag{1.3}$$

Substituting (1.3) into (1.2) gives:

$$\frac{\alpha(\varepsilon)}{V} = -i\frac{3\varepsilon_1}{2\varepsilon_2} \tag{1.4}$$

Resulting in a frequency dependent metric for the localized resonance on a sphere. A similar derivation can be performed for shells (see e.g. [Arnold, 2009]).

Derivation of $Q'_{\mathrm{LSP}} = \varepsilon_1^2 / \varepsilon_2$

The polarizability of a prolate ellipsoid is given by:

$$\alpha_{\mathrm{ellipsoid}} = V\frac{\varepsilon - \varepsilon_{\mathrm{m}}}{\varepsilon_{\mathrm{m}} + L(\varepsilon - \varepsilon_{\mathrm{m}})} \tag{1.5}$$

Where L is a depolarization factor that depends on the aspect ratio of the ellipsoid (length/width). The depolarization factor is described by [Bohren, 2004]:

$$L = \frac{1-e^2}{e^2}\left(-1 + \frac{1}{2e}\ln\frac{1+e}{1-e}\right) \tag{1.6}$$

Where e is the eccentricity of the particle (a is the radius of the long axis, b is the radius of the short axis:

$$e = \sqrt{1-(b^2/a^2)} \tag{1.7}$$

Following the same argument as above, we select the imaginary part of the polarizability:

$$\frac{\alpha_{\mathrm{ellipsoid}}}{V} = i\frac{\varepsilon_2\varepsilon_{\mathrm{m}}}{\varepsilon_2^2 L^2 + (\varepsilon_{\mathrm{m}} + L(\varepsilon - \varepsilon_{\mathrm{m}}))^2} \tag{1.8}$$

By setting the denominator in (1.8) to zero and solving for L, we get:

$$L = -\frac{\varepsilon_{\mathrm{m}}}{\varepsilon_1 + i\varepsilon_2 + \varepsilon_{\mathrm{m}}} \tag{1.9a}$$

Through the definitions (1.6) and (1.7), L is a real quantity, and so we omit ε_2 from the resonance condition:

$$L = -\frac{\varepsilon_{\mathrm{m}}}{\varepsilon_1 + \varepsilon_{\mathrm{m}}} \tag{1.9b}$$

Substituting (1.9b) into (1.8) gives:

$$\frac{\alpha_{\mathrm{ellipsoid}}}{V} = i\frac{(\varepsilon_1 - \varepsilon_{\mathrm{m}})^2}{\varepsilon_2\varepsilon_{\mathrm{m}}} \tag{1.10}$$

By removing the dependence on the medium refractive index, we can define a local surface plasmon metric applicable to ellipsoids:

$$Q'_{\mathrm{LSP}} = \varepsilon_1^2 / \varepsilon_2 \tag{1.11}$$

From equation 1.10, it is clear that increasing the medium index for ellipsoids reduces the polarizability. But because the depolarization can be made arbitrarily small by increasing the length of the ellipsoid, this additional tuning mechanism is unnecessary.

Generalization to sphere dimers

The polarizability for a sphere dimer can be written down in terms of two unknown geometry dependent coefficients, namely a dipole strength coefficient, *A*, and a depolarization factor *L* (see [Arnold, 2010; Raether, 1988]):

$$\alpha_{\mathrm{dimer}} = AV\frac{\varepsilon - \varepsilon_{\mathrm{m}}}{\varepsilon_{\mathrm{m}} + L(\varepsilon - \varepsilon_{\mathrm{m}})}. \tag{1.12}$$

The value of *A* varies between 0 and 1 depending on the gap fraction (given by $g/2r$, where g is the gap.) The depolarization factor is also proportional to the gap fraction of the sphere dimer and governs the position of the resonance.

Treating (1.12) in the same fashion as the ellipsoid indicates that for very small gaps, or very large particles, the resonance wavelength will shift continuously to the red, and the resonance strength will grow rapidly. However, for small gaps, non-locality in Maxwell's equations causes the field enhancement to be reduced. And, for large particles, radiative damping reduces the field enhancement.

To avoid non-local effects, we constrain the gap to 1nm, limiting the values that the depolarization factor can take. For the case of *m*=1.00 the gap fraction takes values between 1/40 and 1/120, corresponding to spheres of radius 20 nm and 60 nm respectively. The limits of the depolarization factor can be determined empirically by recording the value of the permittivity at the resonance frequency via:

$$L = \frac{-\varepsilon_m}{\varepsilon_1 - \varepsilon_m}, \tag{1.13}$$

where $\varepsilon_m = 1.00$. This function is plotted for gap fractions between 1/40 and 1/120 in Figure 4.

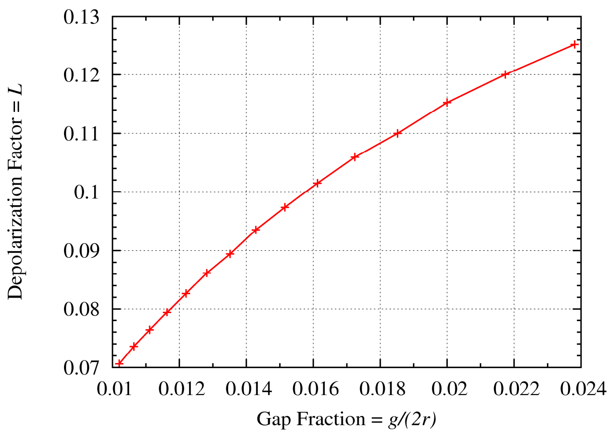

Figure 4. Relationship between the depolarization factor and the gap fraction for sphere dimers in a background medium with *m*=1.00 and *g*=1.00. The position of the resonance was extracted from the peaks in the inset of Figure 1 in the main text. Radius decreases from left to right.

Given a range of values for the depolarization factor, we determine the resonance condition for (1.12) by assuming that the medium index can be matched to the depolarization factor:

$$\varepsilon_{\mathrm{m}} = \frac{\varepsilon_1 L}{L-1} \tag{1.14}$$

Substituting (1.14) into (1.12) and selecting the imaginary part gives:

$$\frac{\alpha_{\mathrm{dimer}}}{V} = -i\frac{\varepsilon_1}{\varepsilon_2(1-L)L} \tag{1.15}$$

For bound values of the depolarization factor, (1.15) reduces to $Q_{\mathrm{LSP}} = -\varepsilon_1 / \varepsilon_2$. Of course, L varies depending on the medium index, and hence it also varies as a function of wavelength. As such, the discrepancy between the exact values of Q_{LSP} and the field enhancement values in Figure 1 of the main article varies by more than a multiplicative constant. However, the trend is clear.

2. Explanation of $\Gamma_\omega = \frac{\Delta\varepsilon_1}{\varepsilon''}\varepsilon''\left[\frac{\mathrm{d}\varepsilon'}{\mathrm{d}\omega}\right]^{-1}$

In the quasistatic limit, the resonance condition for the polarizability of a sphere / ellipsoid / shell is wavelength independent. As such, the width of the resonance can be written in terms of the difference across the FWHM of the real part of the dielectric function. The LSPR frequency is ω_R, and the frequencies corresponding to the low and high frequency bounds of the FWHM are ω_a and ω_b respectively. In order to determine the width in frequency, we assume that the derivative of the permittivity varies slowly with frequency:

$$\frac{\Delta\varepsilon_1}{\Delta\omega} \equiv \frac{\varepsilon_1(\omega_b) - \varepsilon_1(\omega_a)}{\omega_b - \omega_a} \equiv \frac{\Delta\varepsilon_1}{\Gamma_\omega} \approx \left.\frac{\mathrm{d}\varepsilon_1}{\mathrm{d}\omega}\right|_{\omega=\omega_R} \tag{2.1}$$

Which rearranges to give:

$$\Gamma_\omega \approx \Delta\varepsilon_1\left[\frac{\mathrm{d}\varepsilon_1}{\mathrm{d}\omega}\right]^{-1} \tag{2.2}$$

Although the derivative is easily determined from experimental optical constants, the value of Γ_{ε_1} is not constant, and depends on the value of the imaginary part of the dielectric function. We show below that $\Gamma_{\varepsilon_1} / \varepsilon_2$ is constant, and therefore introduce this term into the above equation:

$$\Gamma_\omega \approx \frac{\Delta\varepsilon_1}{\varepsilon_2}\varepsilon_2\left[\frac{\mathrm{d}\varepsilon_1}{\mathrm{d}\omega}\right]^{-1} \tag{2.3}$$

Now, assuming knowledge of $\Gamma_{\varepsilon_1} / \varepsilon_2$ (see below), the quasistatic linewidth can be determined without reference to particle geometry or any specific model for the dielectric function:

$$\Gamma_\omega \approx 2\varepsilon_2\left[\frac{\mathrm{d}\varepsilon_1}{\mathrm{d}\omega}\right]^{-1} \tag{2.4}$$

A figure showing the validity of this expression is given in section 3.

3. Proof that $\frac{\Delta\varepsilon_1}{\varepsilon_2} = 2$.

Figure 5 presents the FWHM across the extinction efficiency for sphere dimers in a series of different medium refractive indices. It is essentially the same as Figure 2 in the manuscript, except that the FWHM is measured across the extinction efficiency instead of the field enhancement.

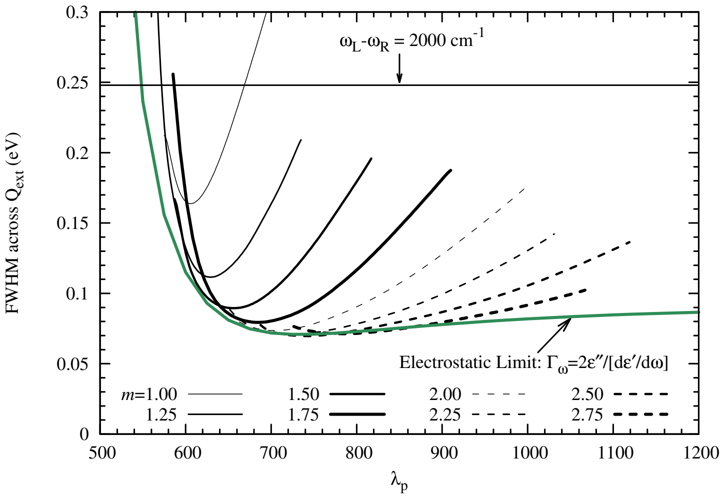

Figure 5. FWHM across the extinction efficiency of sphere dimmers.

In order to justify the use of $\Delta\varepsilon_1/\varepsilon_2 = 2$ we start from equation (1.2) and use the resonance condition for a sphere, $\varepsilon_1 = -2\varepsilon_m$. The polarizability can now be written:

$$\frac{\alpha(\varepsilon)}{iV} = \frac{3\varepsilon_2\varepsilon_m}{\varepsilon_2^2} \tag{3.1}$$

Because the polarizability is symmetric (in terms of ε_1) around $\varepsilon_1 = -2\varepsilon_m$, the FWHM across the real part of the dielectric function is:

$$\Delta\varepsilon_1 = 2abs(\varepsilon_1 - \varepsilon_{1b}) \tag{3.2}$$

Where ε_b is the value of the dielectric function which gives half the polarizability on resonance:

$$\frac{1}{2}\frac{\alpha(\varepsilon)}{iV} = \frac{\alpha(\varepsilon_b)}{iV} \tag{3.3}$$

Or, in full (via Equation 1.2):

$$\frac{1}{2}\frac{3\varepsilon_2\varepsilon_m}{\varepsilon_2^2} = \frac{3\varepsilon_{2b}\varepsilon_m}{\varepsilon_{2b}^2 + (\varepsilon_{1b} + 2\varepsilon_m)^2} \tag{3.4}$$

Solving for ε_{1b} gives:

$$\varepsilon_{1b} = \sqrt{2\varepsilon_2\varepsilon_{2b} - \varepsilon_{2b}^2} - 2\varepsilon_m \tag{3.5}$$

For “good” metals, where the plasma frequency is much larger than the phenomenological scattering rate, the derivative of ε_2 with respect to frequency is much smaller than the derivative of ε_1, and so we assume $\varepsilon_{2b} = \varepsilon_2$. Substituting this into (3.5) gives:

$$\varepsilon_{1b} = \varepsilon_2 - 2\varepsilon_m \tag{3.6}$$

Substituting (3.6) into (3.2) gives:

$$\Delta\varepsilon_1 = 2abs(\varepsilon_1 - \varepsilon_2 + 2\varepsilon_m) \tag{3.7}$$

Substituting in the resonance condition, $\varepsilon_1 = -2\varepsilon_m$, gives:

$$\frac{\Delta\varepsilon_1}{\varepsilon_2} = 2 \qquad (3.8)$$

This methodology gives the same result for the polarizability of an ellipsoid.

References

- M. D. Arnold and M. G. Blaber, *Optics Express*, 2009, **17**, 3835-3847.
- M. D. Arnold, M. G. Blaber, M. J. Ford and N. Harris, *Opt. Express*, 2010, **18**, 7528-7542.
- C. F. Bohren and D. R. Huffman, *Absorption and scattering of light by small particles*, Wiley, Weinheim, 2004.
- P. G. Etchegoin, E. C. Le Ru and M. Meyer, *The Journal of Chemical Physics*, 2006, **125**, 164705-164703.
- P. G. Etchegoin, E. C. Le Ru and M. Meyer, *The Journal of Chemical Physics*, 2007, 127, 189901-189901
- P. B. Johnson and R. W. Christy, *Physical Review B*, 1972, **6**, 4370.
- J. H. Weaver and H. P. R. Frederikse, *Optical properties of selected elements 82 ed.*, CRC Press, Boca Raton, FL, 2001.