Surface-enhanced Raman scattering (SERS) can offer an increased cross section in the presence of metal surfaces with nanometer-scale features \(^1\) and the prospect of single molecule spectroscopy. \(^5\) Two aspects of the enhanced Raman dipole moment have been considered: chemical, where the molecule itself is modified in some way through proximity to the nanostructure \(^1\) (particularly relevant for metal nanoparticles containing just a few atoms \(^3\)), and electromagnetic, where fields associated with the physical geometry of the nanostructure bring about the enhancement. \(^1\) It is widely accepted that a significant SERS effect can be induced by an enhancement in the electric field near metal surfaces, notably in dimers. \(^2\) The prevailing physical interpretation of this electromagnetic enhancement stems from a quasi-static model that applies when all relevant particle dimensions are sufficiently small. Here, we report a mechanism for large average field enhancement over relatively large distances in recessed regions with metal boundaries, which involves resonance in a propagating waveguide mode that occurs in nanometer-scale metal–insulator–metal structures. Such propagating modes exist, for example, between dimer particles. The enhancement is then related to the cavity quality factor \((Q)\). The physical description and the underlying analytical model we present provide opportunities for building new structures with large SERS, for control of the enhanced field regions, and for achieving SERS at desirable wavelengths.

While there have been rather extensive simulations showing enhanced fields in metallic particle systems using quasi-static (electrostatic, with the real part of the dielectric constant at the appropriate wavelength) \(^3\) and electromagnetic models, \(^3\) it is the electrostatic description that has provided the underlying physical understanding to date. The basic concept is that polarization charge in the metal supports a large field in a gap, as would occur in a dimer consisting of two spherical metal particles with small separation. \(^3\) The increased electric field can then enhance the Raman dipole moment of the material in this region of space. Low power and equal enhancement of both the pump and the Raman fields results in a field to the fourth power SERS enhancement factor. \(^1\) With sufficiently small geometries relative to the wavelength, an electrostatic description becomes appropriate. Therefore, with normalization to the local, incident field, calculations based on this description should provide an accurate measure of the enhancement. Also, in the low-frequency limit is the geometry-independent small particle Mie resonance, where the particle (scattering) cross-section peaks \(^1\) and much of the work on the metal nanoshells, which have more degrees of freedom than solid spheres, \(^6\) is done. Three-dimensional (3D) dimers and other related systems have propagating fields in the regions where enhancement occurs. This propagating field can be treated as a waveguide eigenmode problem. With appropriate geometries, the propagating field resonates, and the \(Q\) of the cavity resonance then dictates the field enhancement. With a small uniform gap width, the resonance is associated with a single propagating mode, and this waveguide mode propagates for arbitrarily small gaps. This understanding provides an alternative basis for SERS and leads to new structures that have large enhanced fields over significant length scales. As the waveguide wavelength reduces with decreasing gap width, resonance can occur with a cavity length that is small compared with the free space wavelength. An electrostatic model is applicable when the length is small relative to this waveguide mode wavelength. Returning to the polarization charge in the metal, the waveguide cavity analysis explains why the charge density is large in certain interstitial regions with metal boundaries.

We assume that the bulk complex dielectric constant \((\varepsilon)\) for the metal applies, and we consider the case of Ag. \(^9\) With sufficiently small geometries, a model that accounts for spatially dependent screening in the metal is required. We first consider the two-dimensional (2D) nanoparticle dimer of Fig. 1 in free space. The geometry in Fig. 1 can be viewed as a metal nanoparticle with a uniform waveguide (Region 1) having a propagating mode in the \(z\) direction, and it could also represent two elements in a nanoparticle chain waveguide with a guided wave propagating along the chain in the \(x\) direction. \(^6\) The lowest-order waveguide mode in the slot can resonate in the \(z\) direction with the correct value of \(t\), given the other parameters (notably \(w\)), thereby resulting in field enhancement.
Figure 2 shows finite-element solutions of the Helmholtz wave equation with a TM (using the geometry of Fig. 1 and waveguide nomenclature, and solving for $H_y$) plane-wave incident normally from the top of the dimer, with a free space wavelength of $\lambda_0 = 582$ nm. Figures 2(a) and 2(b) show $|E_x|$ and (b) $|H_y|$ for the first slot resonance, with $t = 54.4$ nm; (c) $|E_x|$ and (d) $|H_y|$ for the second slot resonance, with $t = 118.2$ nm. The geometry is shown by the dashed lines.

Figure 2 shows finite-element solutions of the Helmholtz wave equation with a TM (using the geometry of Fig. 1 and waveguide nomenclature, and solving for $H_y$) plane-wave incident normally from the top of the dimer, with a free space wavelength of $\lambda_0 = 582$ nm. Figures 2(a) and 2(b) show $|E_x(x,z)|$ and $|H_y(x,z)|$, respectively, for the first resonant length (adjusting $t$ in Fig. 1) with a slot width of $w = 4$ nm. The case for the second resonance is given in Figs. 2(c) and 2(d). Note how large the electric field becomes on resonance. For wavelengths further removed from the metal bulk plasma resonance, where the dissipative loss is reduced, the enhancement can be even greater. The first resonance has $E_x$ minimum at the center $(z=0)$, and the second has a maximum at this point.

Figure 3(a) shows the average electric field magnitude in the region between the two nanoparticles, $\langle |E| \rangle$, as the thickness $t$ is adjusted. Note the significant change in field enhancement as the cavity length is varied and also the periodic peaks, which suggest a single, dominant, propagating waveguide mode in the slot. With TM polarization, there is a waveguide mode that propagates for arbitrarily small slot width $w$. The mode responsible for the resonance in the 2D slot has fields that decay away from both sides of both slot interfaces (in the $x$ direction in Fig. 1) and propagates in the $z$ direction. Solving the eigenvalue problem for this mode yields a half-wavelength that precisely matches the distance between peaks in Fig. 3(a), confirming the resonant character of the enhancement mechanism. The electrostatic solution [shown in Fig. 3(a) for the smallest slot width (4 nm) as a dotted–dashed curve] was obtained from Laplace’s equation, $\nabla \cdot \epsilon \nabla \phi = 0$, where $\phi$ is the potential, with an incident field of $E = \hat{x}E_i = -\nabla \phi$. Note the agreement with the electromagnetic solution only for very small slot length, as expected. The resonant enhancement allows for a large average field over relatively large distances. The identification of this resonance was possible through a waveguide mode electromagnetic analysis, and armed with this understanding, it becomes possible to iden-
tify new geometries for SERS. The field enhancement, i.e., the cavity \( Q \), reduces with increasing slot width, as Fig. 3(a) shows. The calculated wavelength-dependent responses are given in Fig. 3(b). The wavelengths where the peaks occur correspond to resonant slot lengths for the lowest-order propagating waveguide mode.

From Fig. 3, wider or lower \( Q \) resonant gaps will provide less field enhancement but with a view to Raman spectroscopy will more closely provide equal enhancement over a broader energy range than those with higher \( Q \). Given the \( Q \), significant energy deviations from the pump will not yield equal enhancement for the pump and Stokes fields, and hence in this range, the SERS enhancement will be less than the fourth power of the (pump) field.\(^{13}\) Short and nonresonant gaps [small relative to the propagating mode wavelength in the gap, say less than about 10 nm in Fig. 3(a)] will yield significant field enhancement over this length scale. If resonance occurs due to other physical aspects of the overall structure, these other parameters, in addition to those of the gap, will dictate the \( Q \). Therefore, in the case of a nonresonant gap, one might expect the \( Q \) and the field enhancement to be independent.

A 2D circular dimer can be represented by a staircase geometry with sufficiently fine steps and hence a cascaded set of uniform waveguides. The concept of a resonant waveguide field can be applied. A 3D rectangular or spherical dimer has the same propagating waveguide mode and hence the same resonance phenomenon, only in this case, the resonance is in two dimensions (\( z \) and \( y \), with \( y \) normal to the page, referring to Fig. 1). Regardless of how close the dimer particles are, there will always be a propagating mode, although the impact of material loss increases with reducing separation.\(^{21}\) As the field enhancement is greater with reduced average separation, this can be best achieved over a length scale equal to the particle diameter by using a uniform slot or a rectangular dimer. Local fields associated with the near surfaces of a spherical dimer, or indeed corners with an included angle less than 180°,\(^{22}\) can of course be large over small length scales.

We have shown that a slot structure in a metal nanoparticle, which can be viewed as Fig. 1 without complete slot penetration (which forms a dimer), also provides large resonant field enhancement.\(^{13}\) The field enhancement for the first resonance of the slot structure is larger than that for the dimer, i.e., the quality factor is higher, but this is reversed for the second resonance.

The enhanced field concept we have described is associated with the negative dielectric constant and a resonant polariton surface mode from two interacting surfaces. With appropriate design, a variety of 3D structures can provide resonant SERS. Through this mechanism, it is possible to have a large average electric field over significant length scales, relative to that possible with tips or other geometries that can be described using a quasi-static field approximation. The relationship between the cavity dimensions and those of the molecule will likely be important. Also, introduction of the molecule will impact the dimer gap cavity field solution to some degree. For the simple geometry we considered, the slot waveguide modes constituting these fields can be solved by means of a transcendental equation. The principles we have outlined could be used to achieve large SERS at desirable wavelengths, which should be useful in various experimental settings.

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