Modeling super-resolution SERS using a T-matrix method to elucidate molecule-nanoparticle coupling and the origins of localization errors

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A computational method to model diffraction-limited images from super-resolution surface-enhanced Raman scattering microscopy is introduced. Despite significant experimental progress in plasmon-based super-resolution imaging, theoretical predictions of the diffraction limited images remain a challenge. The method is used to calculate localization errors and image intensities for a single spherical gold nanoparticle-molecule system. The light scattering is calculated using a modification of generalized Mie (T-matrix) theory with a point dipole source and diffraction limited images are calculated using vectorial diffraction theory. The calculation produces the multipole expansion for each emitter and the coherent superposition of all fields. Imaging the constituent fields in addition to the total field provides new insight into the strong coupling between the molecule and the nanoparticle. Regardless of whether the molecular dipole moment is oriented parallel or perpendicular to the nanoparticle surface, the anisotropic excitation distorts the center of the nanoparticle as measured by the point spread function by approximately fifty percent of the particle radius toward to the molecule. Inspection of the nanoparticle multipoles reveals that distortion arises from a weak quadrupole resonance interfering with the dipole field in the nanoparticle. When the nanoparticle-molecule fields are in-phase, the distorted nanoparticle field dominates the observed image. When out-of-phase, the nanoparticle and molecule are of comparable intensity and interference between the two emitters dominates the observed image. The method is also applied to different wavelengths and particle radii. At off-resonant wavelengths, the method predicts images closer to the molecule not because of relative intensities but because of greater distortion in the nanoparticle. The method is a promising approach to improving the understanding of plasmon-enhanced super-resolution experiments. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4984120>]

I. INTRODUCTION

Super-resolution surface-enhanced Raman scattering (SERS) microscopy enables the spatial localization of plasmonic hot spots below the diffraction limit of light.^{1–5} When irradiated with visible light, noble metal nanoparticles produce strong local electromagnetic fields due to plasmon resonances.^{6–8} If a molecule is in the region of a strong electromagnetic field, or hot spot, the Raman signal of the molecule will be increased by many orders of magnitude.^{9–13} In super-resolution SERS, structural information about the SERS active system is determined from diffraction limited microscopy images. Employing super-resolution imaging with SERS enables sensitive and precise optical mapping of hot spots and molecule localization. However, the accuracy is limited by systematic errors in localization caused by strong nanoparticle-molecule coupling.

Conventional super-resolution microscopy localizes the position of an emitter by fitting the diffraction limited image, or point spread function (PSF), to a two-dimensional Gaussian. These methods have been tremendously successful in the optical determination of structures beyond the diffraction limit of light.^{14–19} However, precise localization is based on the

premise that the location of the emitter is also the most intense point on the PSF. It has been shown that, even for a single dipole emitter, errors in localization arise from factors such as dipole orientations and dielectric interfaces.^{20–26} Although these errors are present in super-resolution SERS, they are generally much smaller than the effects of nanoparticle-molecule interactions.

In plasmon-enhanced super-resolution microscopy, PSF images are accumulated from repeated measurements of fluorescent or Raman-active molecules enhanced by the nanoparticle hot spot. If the emission center is taken to be at the molecule, the PSF centers may be used to map the nanoparticle structure. While these methods correctly predict the shape of the nanoparticle, they systematically underestimate the size of the structure. The localization error characterizes the extent to which the predicted and true structures differ.^{1,4,27–44} The localization is often quantified as the distance between a free dipole at the molecule location and the observed image that has been distorted by the nanoparticle. The strong coupling between a molecule and nanoparticle in plasmon-enhanced super-resolution microscopy is also fundamental in the development of nano-antennas.^{45–47}

In SERS, the molecule is necessarily close to a plasmonically active structure that scatters light efficiently. Consequently, the assumption that the image is centered at the emitter (molecule) is no longer appropriate. Furthermore,

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since the polarizability of a nanoparticle is proportional to its volume, it is reasonable to expect the nanoparticle to dominate the far-field emissions for average size nanoparticles.^{48,49} Nevertheless, super-resolution SERS often measures PSFs shifted tens of nanometers from the nanoparticle center. The magnitude of the PSF distortion is not consistent with the expected intensity difference between a molecule and a nanoparticle.

Localizing the molecule position from the PSF remains a challenge because of the complex near-field interactions that determine the scattered field. Often, finite-difference time domain (FDTD) calculations predict localization errors in plasmon-enhanced fluorescence from far-field emission patterns which reasonably agree with experiments.^{32,33,36–40,42} Although FDTD calculations often agree with experiments, they provide limited near-field information regarding the origin of the errors. Ropp *et al.* proposed an image-dipole interaction model that correlates the PSF error to the relative phases of the molecule and nanoparticle.³² Using parallel and orthogonal dipoles, they demonstrate that the plasmon-enhanced emission may be shifted either toward or away from the nanostructure depending on the dipole-dipole interference.

Here we introduce a theoretical method for modeling super-resolution SERS that uses a multipole expansion of the scattered field combined with a vectorial treatment of the light focusing to simulate the PSF. An extension of the T-matrix method, where a plane wave is used for the incident radiation and then a point dipole source is used for the scattered radiation, is used to simulate SERS.^{48,50–55} This multipole formalism provides an analytical form for the scattered field and is capable of calculating accurate fields for arbitrary arrangements of spherical particles efficiently. Modeling SERS using a point dipole source assumes the single-molecule limit and neglects the feedback between the nanoparticle and molecule. Both of these conditions are reasonably satisfied in experimental conditions. The scattered far-field is propagated using vectorial diffraction theory, and the model PSF is calculated using the Debye-Wolf integral.^{24,56–58} The Debye-Wolf integral provides a rigorous description of high numerical aperture (NA) microscopy imaging.

The multipole expansion of the field used in our approach enables the structure analysis not possible with FDTD. In particular, the T-matrix method writes the total field as the sum of the fields from each individual scatterer in the calculation. While the experimental, or observed, field is the sum of all scatterers, inspection of the underlying constituent fields provides unique insight into the scattering process. The nanoparticle fields may be further decomposed into the respective multipole components to precisely identify contributions to localization errors.

In this work, the field decomposition is employed to propose a second mechanism for the significant PSF distortions observed in super-resolution imaging. Using multipole theory, the response of a single nanoparticle to a radiating point dipole is calculated. Inspection of the nanoparticle reveals significant anisotropy in the scattered field that shifts the nanoparticle PSF significantly toward the molecule. Within

the multipole expansion of the nanoparticle field, we identify significant interference between the dipole and quadrupole resonances, which significantly shifts the nanoparticle PSF. Similar interference has been observed in nano-antennas, where strong nanoparticle-coupling is fundamental to directed light emission.^{47,59,60} The nanoparticle and molecule (point dipole) coefficients are then summed and imaged. A comparison of the nanoparticle and total PSFs distinguishes the localization error from anisotropic nanoparticle excitation and multipole-dipole interference. In the most intense case (in-phase), the anisotropic excitation accounts for approximately 80% of the displacement of the PSF from the nanoparticle center while the interference effects contribute approximately 20%.

Calculations are also presented for off-resonant frequencies and for nanoparticles of different sizes. Recently, it has been shown that decoupling the molecule and nanoparticle by changing the molecule fluorescence wavelength leads to improved localization accuracy.^{37,38,42,43} We investigate this trend using the constituent field decomposition at different wavelengths. An investigation of the nanoparticle size reveals that even in nanoparticles too small to support a quadrupole plasmon resonance, multipole interference significantly shifts the nanoparticle PSF.

In Sec. II, the theory for the SERS-modified T-matrix calculations and diffraction-limited imaging is presented. Section III presents calculations for the single nanoparticle-molecule system. First, calculations using a dipole oriented along the each Cartesian axis are presented in Sec. III B. In Sec. III C, the case of a Raman scattering molecule using a dipole determined from the local electric field is treated. We investigate the spatial mapping of the nanoparticle structure in Sec. III C 1, the constituent fields in Sec. III C 2, the nanoparticle multipoles in Sec. III C 3, off-resonant wavelengths in Sec. III C 4, and size variation in Sec. III C 5. Concluding remarks are presented in Sec. IV.

II. THEORY

A. Electrodynamics calculations

We calculate the scattered electric fields using a modified version of the T-matrix method, which is a generalization of Mie theory for light scattering from multiple spheres.^{49–52} As in Mie theory, the electric field is expanded on the basis of vector spherical harmonics

$$\mathbf{E}_{\text{inc}} = \sum_{l=1}^{\infty} \sum_{m=-l}^l \left[p_{lm} \mathbf{N}_{lm}^{(1)}(k\mathbf{r}) + q_{lm} \mathbf{M}_{lm}^{(1)}(k\mathbf{r}) \right], \quad (1)$$

$$\mathbf{E}_{\text{sc}} = \sum_{l=1}^{\infty} \sum_{m=-l}^l \left[a_{lm} \mathbf{N}_{lm}^{(3)}(k\mathbf{r}) + b_{lm} \mathbf{M}_{lm}^{(3)}(k\mathbf{r}) \right], \quad (2)$$

where $k = 2\pi n_0/\lambda$ is the wavenumber, n_0 is refractive index of the medium, and $k\mathbf{r} = \{kr, \theta, \phi\}$ is the spherical coordinate system centered at the nanoparticle. A nondimensional radial coordinate, kr , is used throughout. $\mathbf{M}_{lm}^{(\sigma)}$ and $\mathbf{N}_{lm}^{(\sigma)}$ are the vector

spherical harmonic basis functions and are given by

$$\begin{aligned}\mathbf{M}_{lm}^{(\sigma)}(k\mathbf{r}) &= \gamma_{lm} \nabla \times [\hat{\mathbf{r}} \cdot \mathbf{u}_{lm}^{(\sigma)}(k\mathbf{r})], \\ \mathbf{N}_{lm}^{(\sigma)}(k\mathbf{r}) &= \frac{1}{k} \nabla \times \mathbf{M}_{lm}^{(\sigma)}(k\mathbf{r}),\end{aligned}\quad (3)$$

where $u_{lm}^{(\sigma)}(k\mathbf{r})$ satisfies the scalar Helmholtz equation

$$u_{lm}^{(\sigma)}(k\mathbf{r}) = z_l^{(\sigma)}(kr) P_l^m(\cos(\theta)) e^{im\phi}, \quad (4)$$

where P_l^m are the associated Legendre polynomials and $z_l^{(\sigma)}$ defines the radial behavior of the scalar spherical harmonic. When $(\sigma) = (1)$ or $(\sigma) = (3)$, $z_l^{(\sigma)}$ is the spherical Bessel function or the spherical Hankel function, respectively. The normalization of the vector spherical harmonics employed in this work is

$$\gamma_{lm} = \left[\frac{2l+1}{l(l+1)} \frac{(l-m)!}{(l+m)!} \right]^{1/2}. \quad (5)$$

In the T-matrix method, the total scattered field for N_s particles may be written as the sum of the scattered fields for each particle. The scattered field for particle i may be written as an expansion of the vector spherical harmonics about its respective origin by a set of scattered coefficients (a_{lm}^i, b_{lm}^i) . The coefficients at each particle depend on all other particles and may be determined by constructing a system of equations. The coefficients for particle i may be written explicitly as

$$a_{lm}^i = \alpha_{lm}^i \left(p_{lm}^i - \sum_{j \neq i} \sum_{l'=1}^{N_s} \sum_{m'=-l'}^{l'} \left[a_{l'm'}^j A_{lm,l'm'}^{(3)}(k\mathbf{r}_{ij}) + b_{l'm'}^j B_{lm,l'm'}^{(3)}(k\mathbf{r}_{ij}) \right] \right), \quad (6)$$

$$b_{lm}^i = \beta_{lm}^i \left(q_{lm}^i - \sum_{j \neq i} \sum_{l'=1}^{N_s} \sum_{m'=-l'}^{l'} \left[b_{l'm'}^j A_{lm,l'm'}^{(3)}(k\mathbf{r}_{ij}) + a_{l'm'}^j B_{lm,l'm'}^{(3)}(k\mathbf{r}_{ij}) \right] \right), \quad (7)$$

where $A_{lm,l'm'}^{(3)}, B_{lm,l'm'}^{(3)}$ are vector addition coefficients and $(\alpha_{lm}^i, \beta_{lm}^i)$ are the single-sphere Mie coefficients.^{50,51,61} The vector addition coefficients are determined by the distance and direction, $\mathbf{r}_{ij} = \{r_{ij}, \theta_{ij}, \phi_{ij}\}$, required to translate origin j to origin i . The primed indices refer to the vector spherical harmonics for particle j . In general, all orders of $(l'm')$ from sphere j may contribute to each (lm) at sphere i .

SERS is modeled by replacing the typical plane wave incident coefficients (p_{lm}^i, q_{lm}^i) with coefficients from a point dipole.^{48,53,55} In Raman scattering, the induced dipole moment ($\mathbf{p}$) of a molecule located at $\mathbf{r}_0$ is determined by the Raman polarizability tensor (α_R) and the primary electric field ($\mathbf{E}_p$)

using

$$\mathbf{p} = \alpha_R \cdot \mathbf{E}_p(\mathbf{r}_0; \lambda_0), \quad (8)$$

$$\mathbf{E}_p(\mathbf{r}_0; \lambda_0) = \mathbf{E}_{\text{inc,PW}}(\mathbf{r}_0; \lambda_0) + \mathbf{E}_{\text{sc,PW}}(\mathbf{r}_0; \lambda_0).$$

The field at the incident wavelength, λ_0 , is defined by the incident plane wave (inc,PW) and the scattered field from the nanoparticle (sc,PW). The field radiated from the molecule is at the new wavelength, λ_R with wavenumber $k_R = 2\pi/\lambda_R$. In this work, Raman scattering occurs at zero Stokes shift such that $\lambda_R = \lambda_0$.

The electric field, $\mathbf{E}_{\text{dp}}(\mathbf{r})$, at an arbitrary point, $\mathbf{r} = \mathbf{r}'$, due to a dipole at $\mathbf{r}_0$ may be calculated as the dot product of the dipole moment with the free-space Green's dyadic, $\overline{\overline{G}}(k_R \mathbf{r}', k_R \mathbf{r}_0)$,²⁴

$$\mathbf{E}_{\text{dp}}(k_R \mathbf{r}') = \frac{4\pi k_R^2}{n_0^2} \overline{\overline{G}}(k_R \mathbf{r}', k_R \mathbf{r}_0) \cdot \mathbf{p}. \quad (9)$$

In the vector spherical harmonic basis, there are two sets of coefficients depending on whether $r_0 < r'$ or $r_0 > r'$.⁴⁸ The incident coefficients are calculated from the center of each particle such that for each particle, $\mathbf{r}'$ is the origin and $r_0 > r'$. In this case, Green's dyadic in the vector spherical harmonics is

$$\begin{aligned}\overline{\overline{G}}(k_R \mathbf{r}', k_R \mathbf{r}_0) &= \frac{ik_R}{\pi} \sum_{l=1}^{N_{\text{max}}} \sum_{m=-l}^l (-1)^m \left[\mathbf{N}_{lm}^{(1)}(k_R \mathbf{r}') \mathbf{N}_{l(-m)}^{(3)}(k_R \mathbf{r}_0) \right. \\ &\quad \left. + \mathbf{M}_{lm}^{(1)}(k_R \mathbf{r}') \mathbf{M}_{l(-m)}^{(3)}(k_R \mathbf{r}_0) \right].\end{aligned} \quad (10)$$

The coefficients for the incident field are given by

$$\begin{aligned}p_{lm} &= (-1)^m \left(\frac{ik_R^3}{n_0^2} \right) \mathbf{N}_{l(-m)}^{(3)}(k_R \mathbf{r}_0) \cdot \mathbf{p}, \\ q_{lm} &= (-1)^m \left(\frac{ik_R^3}{n_0^2} \right) \mathbf{M}_{l(-m)}^{(3)}(k_R \mathbf{r}_0) \cdot \mathbf{p}.\end{aligned} \quad (11)$$

Although $l = 1$ is the dipole term in a multipole expansion, the coefficients (p_{lm}, q_{lm}) are non-zero for some finite expansions $l = N_{\text{max}} > 1$. The additional terms are required to describe a point dipole located away from the origin of the spherical coordinate system. The far-field ($r_0 \ll r'$) coefficients, required for super-resolution modeling, are determined by replacing $\mathbf{N}^{(3)}$ with $\mathbf{N}^{(1)}$ and $\mathbf{M}^{(3)}$ with $\mathbf{M}^{(1)}$ in Eq. (11). In order to calculate the PSF for the system, the vector addition coefficients are used to write the individual scattered fields about a common origin, the center of mass. Following the evaluation of Eq. (11) in the new coordinate system, the individual vector spherical harmonic expansions may be summed to produce a scattered field amenable for imaging.

B. Calculating the PSF

The PSF is calculated by propagating the multipole field through an infinity-corrected lens system followed by the calculation of the Debye-Wolf integral using the angular spectrum representation. The diffraction integrals in the multipole basis are adopted from the work of Hoang *et al.*⁶² In the far-field, the radial component of the scattered electric field, $\mathbf{E}^{\text{sc}}(k\mathbf{r})$, is negligible and only E_{θ}^{sc} and E_{ϕ}^{sc} remain.

In this formulation, the z -axis of the scattering problem corresponds to the optical axis in the imaging setup. If required, the vector addition theorems may be used to transform the nanoparticle scattered field to the optical axis.

The propagation of the scattered field is broken down into three parts: refraction at the objective lens, refraction at the focal lens, and focusing at the detector. The amount of light collected at the objective is defined by the half-angle $\theta_{\max}^{\text{sc}}$ and is determined by the numerical aperture (NA) and refractive index of the scattering medium, $\theta_{\max}^{\text{sc}} = \arcsin(\text{NA}/n_0)$. The superscripts denote coordinates in the scattering (“sc”) and detector or image (“img”) regions. At the focusing lens, the angle is determined by $\sin(\theta^{\text{sc}}) = M \sin(\theta^{\text{img}})$, where M is the magnification. Consequently, the small angle approximation may be invoked at the focusing lens. Following propagation through the two lenses, the electric field in the image space $\mathbf{E}^{\text{img}}(\theta^{\text{img}}, \phi^{\text{img}})$ is given by

$$\mathbf{E}^{\text{img}}(\theta^{\text{img}}, \phi^{\text{img}}) = \frac{\sqrt{\cos(\theta^{\text{img}})}}{\sqrt{n_0 \cos(\theta^{\text{sc}})}} \left[E_{\theta}^{\text{sc}} \begin{pmatrix} \cos(\phi^{\text{sc}}) \cos(\theta^{\text{sc}}) \\ \sin(\phi^{\text{sc}}) \cos(\theta^{\text{sc}}) \\ -\sin(\theta^{\text{sc}}) \end{pmatrix} \hat{\theta}^{\text{img}} + E_{\phi}^{\text{sc}} \begin{pmatrix} -\sin(\phi^{\text{sc}}) \\ \cos(\phi^{\text{sc}}) \\ 0 \end{pmatrix} \hat{\phi}^{\text{img}} \right], \quad (12)$$

where the apodization factor $\sqrt{\cos(\theta)}$ accounts for energy conservation.

The PSF for an arbitrary field can be calculated using the Debye-Wolf integral

$$\mathbf{E}(\rho, \varphi, z) = \frac{ikfe^{-ikf}}{2\pi} \int_0^{\theta_{\max}} \sin(\theta) \int_0^{2\pi} \mathbf{E}^{\text{img}}(\theta, \phi) \times \exp(ik[\rho \sin(\theta) \cos(\phi - \varphi) + z \cos(\theta)]) d\theta d\phi, \quad (13)$$

where k is the wavenumber in the image space and f is the focal length of the focusing lens. The image coordinates are used in the Debye-Wolf integral and the “img” superscript has been omitted for clarity. The field is evaluated in cylindrical coordinates (ρ, φ, z) , where $z = 0$ is the focal plane and ρ is the radial distance from the origin. The term $\exp(ikz \cos(\theta))$ describes defocusing. The pixel resolution is determined by the density of points in ρ and φ . At each value of ρ and φ , the integral over θ is performed numerically.

The vector spherical harmonic field near the focal plane expressed in Cartesian components is calculated using

$$\mathbf{E}(x, y, z) = \sum_{l=1}^N \sum_{m=-l}^l \begin{pmatrix} I_l^{m-1}(\rho, \varphi, z) + I_l^{m+1}(\rho, \varphi, z) \\ i(I_l^{m-1}(\rho, \varphi, z) - I_l^{m+1}(\rho, \varphi, z)) \\ -2I_l^m(\rho, \varphi, z) \end{pmatrix}, \quad (14)$$

where

$$\begin{aligned} I_l^{m+1}(\rho, \varphi, z) &= -\frac{ikfe^{ikf}}{2} i^{m+1} e^{i(m+1)\varphi} \\ &\times \int_0^{\alpha_m} J_{m+1}(k\rho \sin(\theta)) [U_l^m(\theta) \cos(\theta) \\ &+ iV_l^m(\theta)] e^{ikz \cos(\theta)} \sin(\theta) d\theta, \\ I_l^{m-1}(\rho, \varphi, z) &= -\frac{ikfe^{ikf}}{2} i^{m-1} e^{i(m-1)\varphi} \\ &\times \int_0^{\alpha_m} J_{m-1}(k\rho \sin(\theta)) [U_l^m(\theta) \cos(\theta) \\ &- iV_l^m(\theta)] e^{ikz \cos(\theta)} \sin(\theta) d\theta, \\ I_l^m(\rho, \varphi, z) &= -\frac{ikfe^{ikf}}{2} i^m e^{im\varphi} \\ &\times \int_0^{\alpha_m} J_m(k\rho \sin(\theta)) U_l^m(\theta) \sin(\theta) \\ &\times e^{ikz \cos(\theta)} \sin(\theta) d\theta. \end{aligned} \quad (15)$$

The U_l^m and V_l^m terms are the theta-dependent parts of the propagated E_{θ}^{sc} and E_{ϕ}^{sc} field components, respectively, and may be found in Ref. 62. J is the Bessel function. The integration over ϕ is performed analytically.²⁴ The PSF images used in the results are calculated using the intensity of the electric field at the focal plane, $|\mathbf{E}(x, y, 0)|^2$.

III. RESULTS

A. Computational details

All calculations are run on a single, spherical, gold nanoparticle in air using the dielectric data of Johnson and Christy.⁶³ In the SERS calculations, an x-polarized plane wave is used to determine the primary electric field, and a diagonal, isotropic molecular polarizability, $\alpha_{xx} = \alpha_{yy} = \alpha_{zz} = 1$, is used for the molecule. All calculations place the molecule 1 nm from the nanoparticle. Additional nanoparticle-molecule spacings are presented in the [supplementary material](#). The plane wave and Raman calculations are performed at the same frequency. Experimentally, the super-resolution SERS image is collected at a shifted frequency where the Rayleigh scattered light may be removed from the signal. Performing the calculation at the same frequency is a valid approximation if the nanoparticle dielectric function is nearly constant between the two wavelengths. Computationally, the two processes are distinguished by selecting the incident radiation to either be a plane wave source or a dipole source, Eq. (9). All PSFs calculated in this work use the dipole source to calculate the scattered field.

Two coordinate systems are referenced in the calculation: the source (scattering) and the image regions. First, we specify the scattering geometry in the source region. In the present work, the nanoparticle is located at the origin of the scattering coordinate system, the focal point of the objective lens, and the molecule is located in the x-y plane of the nanoparticle. The objective lens is placed in the far-field on the positive z -axis. The optical axis is defined as the z -axis in both the scattering and imaging coordinates. The PSF is calculated in the focal plane of the focusing lens, which is defined as $z = 0$ in the image region.

FIG. 1. The Gaussian-fitted centers of the PSFs for the nanoparticle, molecule, and total scattered fields for the molecule (point dipole) oriented along each Cartesian axis. The nanoparticle is 100 nm in diameter and the molecule is 1 nm away on the x-axis. The molecule orientation is along the x, y, and z axes in (a)–(c), respectively. The total, nanoparticle, and molecule fields are marked by a red “x,” green diamond, and blue circle, respectively.

The calculated PSFs are fit to a two-dimensional Gaussian to determine the PSF center and intensity. Throughout the paper, we compare the specified coordinates of the nanoparticle and molecule in the scattered region to the Gaussian-fit PSF parameters calculated in the image region. Imaging the plane wave excited nanoparticle or the free dipole produces a 1:1 correlation between the (x, y) coordinates in the scattering region and the (x, y) coordinates in the image region.

The magnification is 100 $\times$ and NA = 0.95. The PSF is calculated in the focal region on a square grid of $x = [-1000, 1000] \times y = [-1000, 1000]$ nm with pixel size 40 $\times$ 40 nm. All distances are presented in nanometers. The absolute intensity is proportional to the molecular polarizability and the scattering calculation normalization, so the values calculated are used to investigate relative intensities and are reported as arbitrary units (a.u.). Throughout the results, the point dipole source is labeled as the molecule. Although the PSFs of the molecule are those of a free dipole, the label “dipole” is reserved for the $l = 1$ term in the multipole expansion of the scattered nanoparticle field.

B. Point spread functions for Cartesian-oriented molecular dipole moments

First, we investigate a molecule with a dipole moment along each Cartesian axis. A molecule is placed on the x-axis 1 nm away from a 100 nm diameter gold nanoparticle and imaged at 532 nm. The dipole moment for the three orientations are $\mathbf{p} = (p_x = 1, p_y = 0, p_z = 0)$, $\mathbf{p} = (p_x = 0, p_y = 1, p_z = 0)$, and $\mathbf{p} = (p_x = 0, p_y = 0, p_z = 1)$ for the x-, y-, and z-oriented molecules, respectively. The x-oriented molecule is aligned vertically on the nanoparticle surface. The y and z orientations are both aligned parallel to the nanoparticle but produce different PSFs since the light is collected over a finite solid angle.

The generalized Mie calculation provides multipole coefficients for each nanoparticle and the molecule, in addition to the single basis set expansion for the total field. These constituent fields may be imaged individually to understand each emitter’s contribution to the observed PSF. The molecule (point-dipole) coefficients, $\{p_{lm}, q_{lm}\}$, are used as the incident radiation in the scattering calculation and correspond to imaging a dipole in free space with arbitrary position and dipole moment. The coefficients for the nanoparticle are obtained from solving the system of equations in the T-matrix method. These coefficients provide a unique perspective on the response of the nanoparticle to point source excitation.

The PSF centers and intensities of the constituent fields for the three dipole orientations are presented in Fig. 1 and Table I, respectively. While the molecule position is predicted exactly for Cartesian orientations, the nanoparticle and total fields are significantly affected by the dipole orientation. When the molecular dipole orientation is vertical to the nanoparticle surface, the molecule and nanoparticle fields are in phase. As a result, the nanoparticle and molecule fields constructively interfere for the x-oriented dipole moment. The total PSF is more intense than the two constituent PSFs (nanoparticle and molecule) and centered between the constituent PSFs. In contrast, when the dipole is parallel to the surface, the total intensity is less intense than the nanoparticle and the total PSF center is not between the constituent field centers. These differences arise from the destructive interference between the molecule and the nanoparticle.

Despite significant variance in the predicted PSF center and intensity for the three orientations, in all three cases, the nanoparticle PSF center (green diamond in Fig. 1) is displaced significantly from the center of the nanoparticle (the origin). In contrast, the PSF for the plane wave excitation of a nanoparticle is centered at the origin. The molecule field is less intense in all three cases, but the excitation from a point source profoundly alters the nanoparticle far-field emission.

The localization error, or the difference between the molecule PSF and the total PSF, varies dramatically for the three cases. The x, y, and z orientations predict errors of

TABLE I. Intensities for Gaussian-fit PSFs of the total, nanoparticle, and molecule fields associated with the positions in Fig. 1. The molecule is fixed on the x-axis for all three orientations. The experimentally observed (total) PSF is an order of magnitude greater for the x-oriented molecule than either the y or z orientation. For the y and z orientations, the nanoparticle PSF is more intense than the total due to the destructive interference.

Molecule orientation	Field imaged	Intensity (a.u.)
x-axis	Total	6.20×10^7
	Nanoparticle	4.65×10^7
	Molecule	2.17×10^6
y-axis	Total	2.68×10^6
	Nanoparticle	6.55×10^6
	Molecule	2.17×10^6
z-axis	Total	1.16×10^6
	Nanoparticle	2.41×10^6
	Molecule	7.20×10^5

23, 47, and 11 nm, respectively. The dramatic difference in errors reflects the sensitivity in the far-field emission to dipole orientation and the challenge to localize emitters in plasmon-enhanced microscopy. The origin of the localization errors for the x- and y-oriented molecules is investigated more thoroughly in Secs. III C 1–III C 5.

C. Super-resolution SERS of a molecule in the x-y plane

In this section, the PSF positions and intensities are investigated for the SERS model. In contrast to Sec. III B, the molecular dipole orientation is determined from the electric field from a plane wave scattering calculation according to Eq. (8). Therefore, the local electric field dictates the molecular dipole orientation and strength.

1. Size and shape prediction of a spherical nanoparticle

The SERS model is applied to a molecule in the x-y plane 1 nm away from a 100 nm diameter gold nanoparticle. The plane wave scattered field of the nanoparticle is calculated using the 532 nm x-polarized light. At different positions in the x-y plane, the molecule experiences different local electric fields and therefore interacts with the nanoparticle uniquely at each location. Using a series of molecule positions in the x-y plane, a two-dimensional map of the nanoparticle structure is formed. If the coupled emission is localized at the dipole, the series of measurements should predict the shape and size of the nanoparticle. Since the molecule is at a fixed radius in the x-y plane, it is convenient to define the coordinates using Fig. 2, where ϕ measures the azimuthal angle in the x-y plane.

The calculated PSF centers and intensities are presented in Fig. 3. The relative strength and orientation of the molecular dipole moments at each location are plotted in Fig. 4. The scattered field of a nanoparticle incident with an x-polarized plane wave resembles an x-dipole. As a result, when the molecular is near the x-axis, the dipole moment is the greatest in magnitude and the orientation is aligned vertically to the nanoparticle surface. Near the y-axis, the dipole moments

FIG. 2. A diagram of the nanoparticle-molecule system studied in this work. The molecule is located in the x-y plane for all calculations, so the geometry may be reduced to two dimensions. r_{np} is the radius of the nanoparticle, and r_{mol} is the distance of the molecule from the nanoparticle center. The angle ϕ defines the angle between the vector $\mathbf{r}_{mol}$ and the x-axis. The precise orientation of the molecular dipole may be found in Fig. 4. Note that ϕ coincides with the azimuthal angle in the scattering calculation.

FIG. 3. (a) The specified position of the molecule in the scattering calculation (blue circles) and the Gaussian-fit PSF center (red squares) of the total field for a molecule 1 nm away from a 100 nm gold sphere at 532 nm. (b) The PSF intensity as a function of ϕ , defined in Fig. 2. Additional points are sampled from 80° – 90° to highlight the interference effects. Since the molecule is 1 nm away, the blue circle effectively outlines the nanoparticle circumference.

are significantly weaker and the orientation is parallel to the nanoparticle surface.

As in the Cartesian dipole moments, the vertical orientation induces an in-phase scattered field from the nanoparticle

FIG. 4. A field map indicating the orientation and relative intensities of the molecular dipole moment at the points sampled in Fig. 3. The orientation is vertical to the nanoparticle surface until the molecule is near the y-axis, where it rapidly shifts to a parallel orientation. The dashed black line represents the edge of the nanoparticle. The z-component of the dipole moment is omitted in the arrows despite being included in the calculation. The z-component constitutes less than 10% of the total dipole moment for all geometries, so the two-dimensional plot qualitatively conveys the dipole moments used in the calculation.

FIG. 5. The localization error for a molecule 1 nm away from a 100 nm gold nanoparticle. The error is calculated using the radial distance rather than the Cartesian coordinates to emphasize the increased error near the y-axis.

that enhances the total field, while the horizontal orientation destructively interferes. In the region of constructive interference, the predicted shape in Fig. 3(a) is spherical, but the size is considerably underestimated. In contrast, in the destructive interference region, the total PSF bears no resemblance to the underlying spherical structure of the nanoparticle. Near-field electric field maps and simulated PSFs for the molecule on the x- and y-axis are included in the [supplementary material](#). The two perspectives help illustrating the effects from near-field coupling and far-field interference.

Experimental observations are likely dominated by the most intense orientations, which are two orders of magnitude greater than the weakest images. The dramatic difference in the localization error between the two regimes is clear in the plot of localization error using the radial coordinate, $\text{Error} = \sqrt{x_{\text{dp}}^2 + y_{\text{dp}}^2} - \sqrt{x_{\text{PSF}}^2 + y_{\text{PSF}}^2}$, in Fig. 5. The error is effectively constant for all molecule locations, where the orientation is roughly vertical to the nanoparticle surface. The error increases rapidly when the molecule is near the y-axis, accompanied by a decrease in the intensity. Consequently, the most intense images predict a spherical structure whose radius is approximately three-fifth the true radius of the nanoparticle. These predictions are qualitatively consistent with experimental structure mapping from super-resolution fluorescence measurements.^{37,40–42}

2. Constituent fields

Similar to Sec. III B, we may calculate the constituent PSFs for the SERS system at each molecule location. The calculated PSF centers for three molecule positions, on the x-axis, y-axis, and an oblique angle ($\phi = 45^\circ$), are presented in Fig. 6. The intensities for the constituent field intensities at all of the geometries are given in Fig. 7. The dipole moments in

FIG. 7. The intensity of the constituent fields as a function of ϕ . Near the x-axis, the nanoparticle is many times more intense than the molecule. The nanoparticle intensity changes much more as a function of ϕ than the molecule. The inset focuses on angles near the y-axis where the total field becomes less intense than the nanoparticle alone.

Fig. 4 suggest that the molecule on the x-axis and at $\phi = 45^\circ$ are effectively vertically oriented, while the molecule at the y-axis is horizontally oriented. Consistent with this interpretation, the constituent fields for the SERS case closely resemble the x- and y-axis dipoles in Fig. 1.

When the two fields are in phase, the PSF for the combined field (red “x”) is centered much closer to the nanoparticle (green diamond) than the molecule (blue circle). The image intensities at $\phi = 0^\circ$ reveal that the nanoparticle is twenty times more intense than the molecule. The proximity of the total field to the nanoparticle reflects the disparate intensities between the nanoparticle and molecule and suggests that the nanoparticle dominates the experimentally observed field. The difference between the nanoparticle and total fields represents the contribution from multipole-dipole interference. While the in-phase fields do enhance the intensity and shift the total field toward the molecule, the effect is much smaller than the nanoparticle field distortion. Note that the molecule image location is inside the nanoparticle because of the localization error introduced from the complex dipole moment produced by the primary electric field.^{20,21,23,24} Therefore, the error should not be attributed to a “pulling” effect from the nanoparticle.

The y-axis molecule illustrates the effects of destructive interference between out-of-phase emitters. Similar to the x-axis and oblique cases, the nanoparticle field is distorted toward the molecule. However, now the nanoparticle scattered field is of comparable intensity to the molecule, Fig. 7 (inset). Since the intensities are comparable, multipole-dipole interference contributes significantly more to the observed PSF position. The out-of-phase fields produce a PSF that appears close to the nanoparticle center. The individual fields reveal

FIG. 6. The locations of the constituent field PSFs mapped onto the nanoparticle structure for the (a) x-axis, (b) oblique ($\phi = 45^\circ$), and (c) y-axis molecule locations. The PSF centers for the nanoparticle, molecule, and total fields are marked by a green diamond, blue circle, and red “x,” respectively.

TABLE II. The PSF x-coordinates (nm) and intensities (a.u.) for different order expansions of the vector spherical harmonic basis of the 100 nm nanoparticle at 532 nm. $l_{\max} = 8$ is the full expansion. The $l = 2$ image is calculated by setting the $l = 1$ coefficients to zero.

Expansion order	x-coordinate	Intensity
$l_{\max} = 1$	1.68	1.32×10^9
$l_{\max} = 2$	23.27	1.35×10^9
$l = 2$	23.94	8.29×10^6
$l_{\max} = 8$	23.73	1.35×10^9

that this is not because of weak emission from the molecule but instead because of competing effects of anisotropic excitation and the multipole-dipole interference.

It is surprising that the two fields are comparably intense along the y-axis. When $\phi = 90^\circ$, the nanoparticle and molecule images are 170 and 24 times less intense than at $\phi = 0^\circ$, respectively. The reduction in molecule intensity is consistent with the weaker primary field near the y-axis. The greater reduction in the nanoparticle field indicates that the excitation is sensitive to the phase of the incident source, not just the intensity. Despite the reduction in intensity, the nanoparticle emission is still strongly affected by the molecule. In all three scattering geometries, the nanoparticle PSF is displaced greater than 20 nm toward the molecule. The key distinction is that the nanoparticle field is much weaker on the y-axis, allowing interference effects to play a more prominent role.

3. Multipole decomposition of the nanoparticle for a molecule on the x-axis

In Eq. (2), the scattered field for the nanoparticle is written as a finite sum of multipoles. The expansion is truncated at a maximum value $l = N_{\max} = 8$ in this work, sufficient to converge the physics. Following the calculation, we may extract any individual or set of multipoles from the scattered field expansion. In this section, we calculate the PSF for the dipole ($l_{\max} = 1$), quadrupole ($l = 2$), and dipole with quadrupole ($l_{\max} = 2$) multipoles. Imaging the multipoles separately reveals that the quadrupole contribution is essential to describe the shift in the nanoparticle field.

Table II presents the PSF centers and intensities for the different multipoles of the nanoparticle. The intensity of the dipole is very similar to the total imaged field, suggesting the dipole term dominates the observed field. However, the PSF for the nanoparticle dipole mode is displaced less than 2 nm away from the origin, in disagreement with the total field at $x = 23.73$ nm. In contrast, the quadrupole mode is centered very close to the total expansion despite being over two orders of magnitude

weaker than the dipole term. Although the quadrupole is considerably weaker, the contribution is essential in predicting the observed localization position. The coherent superposition of the individual multipoles produces interference that shifts the far-field emission of the nanoparticle. See the [supplementary material](#) for the individual multipole PSF images.

4. Dependence on incident wavelength

Recent experimental and theoretical efforts have investigated the wavelength dependence of the localization error for plasmon-enhanced super-resolution fluorescence.^{37,38,42,43} Using the constituent fields, we investigate the hypothesis that spectrally decoupled fluorophores improve the super-resolution localization because of the weaker nanoparticle response. Calculations are run at 450, 750, and 950 nm on a 100 nm gold nanoparticle with a molecule 1 nm away on the x-axis. The plasmon resonance for the nanoparticle is at approximately 540 nm.

Figure 8 maps the positions for the constituent fields with the molecule on the x-axis at the three wavelengths. The data for the constituent fields at different geometries may be found in the [supplementary material](#). In all cases, the red “x” for the total field is located closer to the sphere edge than Fig. 6(a). Consequently, our calculations agree with the experiments that observe improved accuracy for off-resonant wavelengths. However, the respective intensities in Table III indicate that the nanoparticle is more intense at all of the wavelengths, in conflict with the proposal that spectral decoupling produces the improved localization accuracy. Rather, the PSF shift may be attributed to the altered response of the nanoparticle. Similar to the on-resonance case, the total image (red “x”) is located very close to the nanoparticle image (green diamond).

5. PSF error as a function of nanoparticle size

It is important to understand the role of the nanoparticle size in correlating super-resolution images to the nanoparticle structure. Additionally, calculations on a range of nanoparticle sizes distinguish between the quadrupole resonance that is expected in larger nanoparticles and an effect induced by the point source excitation. We investigate a single gold nanoparticle with a molecule 1 nm away on the x-axis for diameters from 10 to 300 nm. Since the dipole plasmon resonance shifts to longer wavelengths, each PSF calculation is performed at the maximum $|\mathbf{E}_p(\mathbf{r}_0; \lambda)|^4$ wavelength, which approximates the maximum SERS enhancement. At constant wavelength, large particles exhibit significant deviations from the dipole plasmon resonance (see [supplementary material](#)). The minimum and maximum wavelengths for the set of nanoparticles are

FIG. 8. The PSF centers of the nanoparticle, molecule, and total fields at wavelengths away from the plasmon resonance. A 100 nm gold nanoparticle is used, and the molecule is on the x-axis. The nanoparticle, molecule, and total fields are marked by a green diamond, blue circle, and red “x,” respectively. In all three cases, the nanoparticle emission is displaced further from the origin than in the on-resonance wavelength (532 nm).

TABLE III. Intensities for the off-resonant constituent fields in Fig. 8. Despite improved localization, the nanoparticle field is more intense at all three wavelengths. The relative intensities suggest that the emission of the molecule and nanoparticle are still strongly coupled even away from the plasmon resonance.

Wavelength	Field imaged	Intensity (a.u.)
450	Total	9.73×10^8
	Nanoparticle	6.40×10^8
	Molecule	8.95×10^7
750	Total	2.64×10^7
	Nanoparticle	1.41×10^7
	Molecule	1.92×10^6
950	Total	2.56×10^6
	Nanoparticle	1.25×10^6
	Molecule	2.32×10^5

529 nm and 1162 nm for the 10 nm and 300 nm nanoparticles, respectively.

Figure 9(a) plots the ratio of the error and particle radius for the constituent fields. The errors measure the difference between the Gaussian-fit PSF and the “true,” or expected, position for each contribution. The “true” positions are determined from the geometry specified in the scattering calculation. Therefore, the “true” nanoparticle position is at the origin and the “true” molecule position is at the nanoparticle radius + 1 nm. Since the localization error is calculated with respect to the free dipole, the molecule position is used to calculate the

FIG. 9. Data for the constituent fields as a function of the particle radius calculated at maximum $|\mathbf{E}(\mathbf{r}_0, \lambda)|^4$ wavelength. (a) plots the error of the respective PSFs divided by the radius and (b) the intensities. The errors are defined using the total PSF and true molecule locations ($\text{total} = x_{\text{mol}}^{\text{true}} - x_{\text{mol}}^{\text{PSF}}$), the molecule PSF and true molecule locations ($\text{molecule} = x_{\text{mol}}^{\text{true}} - x_{\text{mol}}^{\text{PSF}}$), and the nanoparticle PSF location and nanoparticle center ($\text{nanoparticle} = x_{\text{np}}^{\text{PSF}} - x_{\text{np}}^{\text{true}}$, where the PSF and true coordinates are switched to produce a positive error).

error for the total field. That is to say, the total error corresponds to the localization error of the molecule in the plasmon-coupled system, the molecule error is the mislocalization of the free dipole, and the nanoparticle error is the distortion induced by the point source. Since the errors grow for particle size, the data are divided by the particle radius to provide a unitless measure of the PSF displacement. Plotting the data in this way demonstrates that the multipolar interference is not simply a consequence of using large nanoparticles that may inherently support quadrupole resonances. If the behavior was caused by the multipole resonances usually observed in large nanoparticles, the error in the nanoparticle PSF should approach zero for small particles.

The nanoparticle error/radius [green diamonds in Fig. 9(a)] for the 10 nm radius particle is 0.66. Since the nanoparticle is centered at the origin, this indicates that the nanoparticle PSF is centered at $x = 6.6$ nm. A multipole analysis of the nanoparticle field as in Sec. III C 3 places the dipole field at $x = 0.6$ nm and the quadrupole field at $x = 6.6$ nm. In this case, the nanoparticle quadrupole contribution is over 4000 times less intense than the dipole contribution, but still displaces the image over fifty percent of the nanoparticle radius. The presence of significant shifts in the smallest structures supports the hypothesis that the behavior is fundamental to the molecule (point dipole) excitation and not a consequence of studying a particle that may sustain a quadrupole resonance.

The constituent intensities are plotted in Fig. 9(b). For all particle sizes, the nanoparticle dominates the total PSF, in agreement with the 100 nm case. The data suggest that the most intense super-resolution SERS images on spherical gold nanoparticles should be observed for structures about 100 nm in diameter. Interestingly, the minimum error in the nanoparticle occurs for slightly larger particles. There is a clear inverse relationship between the accuracy of the total PSF localizing the molecule and the distortion of the nanoparticle from the origin. This relationship is consistent with the notion that the nanoparticle dominates the image and therefore the farther the nanoparticle field is from the origin, the less error there is in localizing the molecule.

IV. CONCLUSIONS

In this paper, we have introduced a method based on a multipole expansion of electric fields to model diffraction limited images from SERS. Although super-resolution SERS is a powerful technique for imaging plasmonic structures, understanding the structure-image correlation remains a significant challenge. The calculated images here predict PSF positions and intensities consistent with the published plasmon-enhanced super-resolution experiments. The method permits a multipole decomposition of the scattered field into contributions from each scatterer. Using the decomposition, it is proposed that the dominant contribution to super-resolution SERS images is a highly asymmetric scattered field from the nanoparticle. The mechanism that distorts the super-resolution SERS image from the nanoparticle center is interference within the multipole fields of the nanoparticle caused by the point dipole source. This is in contrast to the dipole-dipole interference model previously proposed. One could envision developing

a dipole-dipole model where the center and intensity of the nanoparticle dipole account for the shifts from the nanoparticle center. However, given the intensity differences, the most important contribution to a super-resolution SERS model is the altered nanoparticle scattered field. An analysis of the incident frequency and nanoparticle size illustrate the sensitivity of the diffraction-limited image to the scattering structure.

While the predicted localization errors in this work are consistent with the published data, the calculations offer a new perspective on plasmon-enhanced imaging that may be helpful in explaining experiments. It is intuitively clear that a plasmonically active nanoparticle will scatter light efficiently and significantly distort a single-molecule emission pattern. Using multipole theory, we offer unique insight into the structure of experimentally observed PSFs. Physically, super-resolution microscopy may be more aptly described as measuring the distortion of the nanoparticle emission by a molecule, rather than the converse. In the most intense images, the nanoparticle dominates the observed far-field, but reasonable localization accuracy is still obtained because of the dramatic scattered field distortion from the point source excitation.

In future work, the method will be used to predict shifts in PSFs for experimental samples and will be applied to nanoparticle aggregates, here, taking advantage of the generalized Mie formalism that allows straightforward and accurate field calculations for arbitrary aggregates of spherical nanoparticles. Plasmonic hot spots in aggregates are often many orders of magnitude greater in intensity than single nanoparticles, so understanding super-resolution SERS for these structures is essential for experiments in single-molecule chemistry.^{4,5} We think the method introduced here will be effective at predicting diffraction-limited images for the experiments using nanoparticle aggregates.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for additional data including nanoparticle-molecule separation dependence, additional fixed dipole calculations, expanded data sets for wavelength and particle size dependence, and near-field electric field intensity maps with the corresponding simulated PSF.

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