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Quantum plasmonics of finite-size particles with coherent anti-Stokes Raman scattering

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We have developed a semianalytical theory to study a quantum plasmonic system composed of a quantum particle and a metallic particle with finite size. The quantum particle is composed of molecules driven by three laser fields and produces a coherent anti-Stokes Raman scattering (CARS) signal which is enhanced by plasmonic resonance of the metallic particle. The enhanced CARS field and the control laser form a Λ scheme that gives highly nonlinear and spatially nonlocal effects. We obtain absorption spectra that show periodic oscillations with radius of the spherical quantum particle, the whispering gallery effect. Plasmonic resonance gives very large and narrow absorption peaks as well as vanishing absorption or Fano dip at specific values of frequency and interparticle distance. The space between the two particles provides a resonant cavity effect which explains the oscillations of absorption power spectra with interparticle distance.

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I. INTRODUCTION

The study of interactions between metallic nanostructures and quantum emitters such as molecules [1] and quantum dots [2–7] has been a subject of active investigations due to its significance in both fundamental and applied sciences. Such a topic is fundamentally interesting as it involves the interactions between elementary excitations (plasmons in metals and excitons in dielectric materials) coupled with photons to form polaritons in the hybrid nanostructure. The coupling between photons, plasmons, and excitons in low-dimensional structures such as metallic nanostructures and quantum emitters like quantum dots or wires often leads to novel and exotic quantum optical effects [8]. Several interesting results from the study of strong coupling [9] between a semiconductor quantum dot and a spherical metallic nanoparticle have been reported. These include nonlinear Fano effect [2,3], exciton-induced transparency [4], nonclassical photon statistics [5], effects of spin coupling in the presence of magnetic fields [6], inhibition of optical excitation and enhancement of Rabi oscillations [7], and coherent control of nanoamplifiers [10]. Besides spherical metallic nanoparticles, systems that involve coupling between a quantum dot and multiple metallic nanoparticles [8,11], metallic nanowires [12], and metallic-dielectric nanoshells [13] have also been studied. Recent studies in quantum nonlinear plasmonics include nonlinear plasmonic effects of metallic nanoparticles on a three-level quantum system (QS) with electromagnetically induced transparency [14], and quantum properties of light in a four-level double Raman configuration in a quantum plasmonic system [15].

This field of research has also found its way through a wide range of applications such as the development of biological markers [16], nanosensors [17,18], and control of emission from semiconductor nanocrystals [19–21]. One of the most remarkable applications of plasmon-exciton coupling is in molecular spectroscopy such as the surface-

enhanced Raman scattering (SERS) [22] technique that provides species-specific molecular fingerprints. The proximity of the system to metallic nanostructures enables local-field enhancement by surface plasmon resonance (SPR) resulting in the amplification of the SERS signal by a factor of 10^3 – 10^{10} [23]. The spectroscopic signal can be further enhanced through coherent nonlinear optical processes such as coherent anti-Stokes Raman scattering (CARS) [24,25]. The surface enhanced CARS signal [26] near hot spot regions of metallic nanostructures can be much higher than that of SERS, enabling single molecule detection [27] by maximizing the scattered CARS signal at the Fano resonance frequency (dip) [28] where absorption vanishes. On the other extreme, large absorption peaks due to excitation of plasmon resonances produce very intense electric fields in a localized region that can cause photodisintegration of biomolecules, and this would be useful for destruction of cancer cells.

In this paper, we investigate the plasmonic effects of a nearby spherical metallic particle (MP) on a quantum system of spherical particles composed of molecules driven by lasers in the CARS scheme, as illustrated in Fig. 1. In particular, we develop a theory to study the effects of size of the particles on the absorption spectra of the hybrid structure. The molecular quantum system is modeled as four discrete energy levels coupled to three laser fields that produce the CARS field through a four-wave mixing process. We know from previous studies that strong-field coupling can cause splitting of spectroscopic peaks and create a Fano dip that would complicate the spectra. It is interesting to explore how these strong-coupling effects are affected by the size of the quantum and metallic particles. Spatial inhomogeneity of the laser fields inside the spherical quantum particle is accounted for by the Mie theory. We compute the absorption power spectra of these particles and study the effects of the radius of the particles ranging from nanometer to micrometer regimes as well as the effects of interparticle distance. For a mesoscopic

FIG. 1. A finite-size particle of a QS composed of molecular energy levels driven by pump (orange), Stokes (red), and control (green) lasers, producing a CARS signal that contributes to the local field in the MP, which in turn scatters the field back to enhance the local field in the QS.

particle with radius larger than $1 \mu\text{m}$, the CARS signal in the QS can be enhanced to a sufficiently high level that it couples strongly with the control laser field to form a Raman transition beyond the electromagnetic induced transparency (EIT) regime, and further contributes to the CARS signal. Together with the plasmonic resonance from the MP and the spatially dependent local field as well as the laser fields, the mesoscopic effects contribute to an exotic plasmonic nonlinear quantum coherence.

II. SCATTERED FIELDS WITH LOCAL-FIELD ENHANCEMENT

In the far-field approximation, the coherent anti-Stokes Raman scattering electric field in frequency domain ω generated by the four-wave mixing process in a particle of volume V is [29,30]

$$\mathbf{E}(\mathbf{R}, \omega) = -\frac{\omega^2}{c^2} \int_V \frac{\mathbf{P}^\perp(\mathbf{r}, \omega) e^{ik(\omega)|\mathbf{R}-\mathbf{r}|}}{4\pi\epsilon_0|\mathbf{R}-\mathbf{r}|} d^3r \quad (1)$$

where $k(\omega) = \omega/c$ and $\mathbf{P}^\perp(\mathbf{r}, \omega) = \hat{\Theta}P_\Theta(\mathbf{r}, \omega) + \hat{\Phi}P_\Phi(\mathbf{r}, \omega)$ is the polarization vector transverse to the radial direction $\hat{\mathbf{R}}$.

In the QS-MP system, the field scattered by one particle becomes the local field at the position inside another particle. Specifically, the electric field at $\mathbf{R}$ scattered by the QS of radius ρ is

$$\mathbf{E}_{\text{QS}}^\perp(\mathbf{R}, \omega) = -\int_{|\mathbf{r}|<\rho} C_{\text{QS}}(\mathbf{R}-\mathbf{r}, \omega) N_{\text{QS}} \tilde{\rho}_{ca}^\perp \tilde{\rho}_{ac}(\mathbf{r}, \omega) d^3r \quad (2)$$

where N_{QS} is the number density of the molecules and $\tilde{\rho}_{ca}^\perp$ is the transverse transition matrix element of the electric dipole moment operator. The coherence of the a - c transition due to

both the CARS and the Λ (Raman) transition coupled by the CARS field and the control laser field is given by

$$\tilde{\rho}_{ac}(\mathbf{r}, \omega) = \tilde{\rho}_{ac}^{\text{NL}}(\mathbf{r}, \omega) + \frac{\tilde{\rho}_{ac}^\Lambda(\mathbf{r}, \omega)}{\epsilon_{\text{QS}}^{\text{eff}}(\mathbf{r}, \omega)}. \quad (3)$$

which is the Fourier transform of $\rho_{ac}(\mathbf{r}, t)$ (in the Schrödinger picture) while the expressions for $\tilde{\rho}_{ac}^{\text{NL}}$ and $\tilde{\rho}_{ac}^\Lambda$ are given in Appendices A and B, respectively. The effective dielectric function,

$$\epsilon_{\text{QS}}^{\text{eff}}(\mathbf{r}, \omega) = \frac{2\epsilon_b + \epsilon_{\text{QS}}^{(1)}(\mathbf{r}, \omega)}{3\epsilon_b}, \quad (4)$$

appears because of the local-field effect, which is exclusively applied only to the linear-response part of the polarization, where ϵ_b is the background dielectric function around the QS and the dielectric function is given by Eq. (B12) in Appendix B. Thus, Eq. (3) provides a semianalytical approach that includes both CARS and Raman, like the case of fluorescence and Raman [31].

The transverse dipole moment in the standard spherical polar coordinates is given by [29]

$$\begin{aligned} \tilde{\rho}_{ca}^\perp &= \rho_{ca,\Theta} \hat{\Theta} + \rho_{ca,\Phi} \hat{\Phi} \\ &= \begin{pmatrix} 0 & 0 & 0 \\ \cos \Theta \cos \Phi & \cos \Theta \sin \Phi & -\sin \Theta \\ -\sin \Phi & \cos \Phi & 0 \end{pmatrix} \begin{pmatrix} \hat{\mathbf{R}} P_x^{\text{NL}} \\ \hat{\mathbf{R}} P_y^{\text{NL}} \\ \hat{\mathbf{R}} P_z^{\text{NL}} \end{pmatrix} \end{aligned} \quad (5)$$

and the nonlocal response function is (assuming $R \gg |\mathbf{r}|$)

$$C_{\text{QS}}(\mathbf{R}-\mathbf{r}, \omega) = \frac{\omega^2}{c^2} \frac{e^{ik(\omega)(R-\hat{\mathbf{R}}\cdot\mathbf{r})}}{4\pi\epsilon_0 R}. \quad (6)$$

Similarly, the electric field at $\mathbf{R}'$ scattered by the MP of radius a is

$$\begin{aligned} \mathbf{E}_{\text{MP}}^\perp(\mathbf{R}', \omega) &= -\int_{|\mathbf{r}'|<a} C_{\text{MP}}(\mathbf{R}'-\mathbf{r}', \omega) \alpha(\mathbf{r}', \omega) \mathbf{E}_{\text{MP}}^{\perp\text{loc}}(\mathbf{r}', \omega) \frac{d^3r'}{V_{\text{MP}}} \\ &= -\int_{|\mathbf{r}'|<a} C_{\text{MP}}(\mathbf{R}'-\mathbf{r}', \omega) \frac{1}{\epsilon_{\text{MP}}^{\text{eff}}(\mathbf{r}', \omega)} \\ &\quad \times [\epsilon_0 \chi_{\text{MP}}(\mathbf{r}', \omega) \mathbf{E}_{\text{MP}}^{\perp\text{loc}}(\mathbf{r}', \omega)] d^3r' \end{aligned} \quad (7)$$

where V_{MP} is the volume of the MP with the nonlocal response function (assuming $R' \gg |\mathbf{r}'|$)

$$C_{\text{MP}}(\mathbf{R}'-\mathbf{r}', \omega) = \frac{\omega^2}{c^2} \frac{e^{ik(\omega)(R'-\hat{\mathbf{R}}'\cdot\mathbf{r}')}}{4\pi\epsilon_0 R'}. \quad (8)$$

Note that the term in the square bracket of Eq. (7) is the linear polarization of the MP. Also, the scattered far-field $\mathbf{E}_{\text{MP}}^\perp(\mathbf{R}', \omega)$ depends on the transversal components of the local fields $E_{\text{MP},\Theta}^{\text{loc}}$ and $E_{\text{MP},\Phi}^{\text{loc}}$, through

$$\mathbf{E}_{\text{MP}}^{\perp\text{loc}}(\mathbf{r}', \omega) = \hat{\Theta} E_{\text{MP},\Theta}^{\text{loc}}(\mathbf{r}', \omega) + \hat{\Phi} E_{\text{MP},\Phi}^{\text{loc}}(\mathbf{r}', \omega). \quad (9)$$

We define the linear susceptibility χ_{MP} , Drude-type dielectric function for metal ϵ_{MP} [32], and effective dielectric

function $\varepsilon_{\text{MP}}^{\text{eff}}$, respectively, as

$$\chi_{\text{MP}}(\mathbf{r}', \omega) = \frac{\varepsilon_{\text{MP}}(\mathbf{r}', \omega) - \varepsilon_b}{\varepsilon_b}, \quad (10)$$

$$\varepsilon_{\text{MP}}(\mathbf{r}', \omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i\Gamma)}, \quad (11)$$

$$\varepsilon_{\text{MP}}^{\text{eff}}(\mathbf{r}', \omega) = \frac{2\varepsilon_b + \varepsilon_{\text{MP}}(\mathbf{r}', \omega)}{3\varepsilon_b}, \quad (12)$$

which are related to the polarizability α and the enhancement factor γ by

$$\alpha(\mathbf{r}', \omega) = V_{\text{MP}} \varepsilon_0 \gamma(\mathbf{r}', \omega), \quad V_{\text{MP}} = \frac{4\pi a^3}{3}, \quad (13)$$

$$\gamma(\mathbf{r}', \omega) = 3 \frac{\varepsilon_{\text{MP}}(\mathbf{r}', \omega) - \varepsilon_b}{\varepsilon_{\text{MP}}(\mathbf{r}', \omega) + 2\varepsilon_b} = \frac{\chi_{\text{MP}}(\mathbf{r}', \omega)}{\varepsilon_{\text{MP}}^{\text{eff}}(\mathbf{r}', \omega)} \quad (14)$$

where ε_∞ is the background dielectric function at frequencies far beyond ω_p due to positive ion cores in noble metals, ω_p is the plasma frequency, and Γ is the electron damping coefficient.

Using the plasmonic resonance condition $2\varepsilon_b + \text{Re}\varepsilon_{\text{MP}}(\omega) = 2\varepsilon_b + \varepsilon_\infty - \frac{\omega_p^2}{(\omega^2 + \Gamma^2)} = 0$ we define the plasmonic resonant frequency $\omega_r = \sqrt{\frac{\omega_p^2}{2\varepsilon_b + \varepsilon_\infty} - \Gamma^2}$. We assume the CARS peak (transition frequency) to be at ω_{ac} , i.e., resonant to the separation between level a and level c . Then, we would have plasmonic resonance by setting $\omega_{ac} = \omega_r$, which gives

$$\omega_{p0} = \sqrt{(\omega_{ac}^2 + \Gamma^2)(2\varepsilon_b + \varepsilon_\infty)}, \quad (15)$$

the plasma frequency that gives plasmonic enhancement at the transition frequency ω_{ac} .

III. LOCAL FIELDS FOR THE METALLIC PARTICLE-QUANTUM SYSTEM

According to Fig. 1 the MP is displaced by $\mathbf{D} = \hat{z}D$ from the QS, so $\mathbf{r}'$ becomes $\mathbf{D} + \mathbf{r}'$.

A. Local field for the MP at $\mathbf{r}'$

The local field $\mathbf{E}_{\text{MP}}^{\text{loc}}(\mathbf{D} + \mathbf{r}', \omega)$ at $\mathbf{D} + \mathbf{r}'$ of the MP consists of the scattered fields from all points $\{\mathbf{s}\}$ inside the QS, which depends on the quantum coherence $\tilde{\rho}_{ac}$, i.e.,

$$\begin{aligned} \mathbf{E}_{\text{MP}}^{\text{loc}}(\mathbf{D} + \mathbf{r}', \omega) \\ = -N_{\text{QS}} \vec{\phi}_{ca}^\perp \int_{\text{QS}, |\mathbf{s}| < \rho} C_{\text{QS}}(\mathbf{D} + \mathbf{r}' - \mathbf{s}, \omega) \tilde{\rho}_{ac}(\mathbf{s}, \omega) d^3s, \end{aligned} \quad (16)$$

$$\begin{aligned} C_{\text{QS}}(\mathbf{D} + \mathbf{r}' - \mathbf{s}, \omega) \\ = \frac{\omega^2}{c^2} \frac{e^{ik(\omega)(|\mathbf{D} + \mathbf{r}'| - \hat{n}'_+ \cdot \mathbf{s})}}{4\pi \varepsilon_0 |\mathbf{D} + \mathbf{r}'|}. \end{aligned} \quad (17)$$

Assuming the z axis is along the interparticle axis (as depicted in Fig. 1),

$$\hat{n}'_+ = \frac{\mathbf{D} + \mathbf{r}'}{|\mathbf{D} + \mathbf{r}'|} \simeq \hat{z}, \quad (18)$$

$$\mathbf{D} + \mathbf{r}' = (\hat{z}D + r'\hat{r}') \quad (19)$$

$$= (r' \sin \theta' \cos \varphi', r' \sin \theta' \sin \varphi', r' \cos \theta' + D), \quad (20)$$

$$\begin{aligned} |\mathbf{D} + \mathbf{r}'| &= \sqrt{r'^2 \sin^2 \theta' + (D + r' \cos \theta')^2} \\ &\simeq D \left\{ 1 + \frac{1}{2} \frac{r'^2 + 2Dr' \cos \theta'}{D^2} \right\}, \end{aligned}$$

$$\hat{n}'_+ \cdot \mathbf{s} = \frac{s(D \cos \theta + r'u)}{|\mathbf{D} + \mathbf{r}'|} \simeq r \cos \theta, \quad (21)$$

$$u(\theta', \varphi', \theta, \varphi) = \hat{r}' \cdot \hat{s} \quad (22)$$

where $\hat{z} \cdot \mathbf{s} = s \cos \theta$, $\hat{r}' = (\sin \theta' \cos \varphi', \sin \theta' \sin \varphi', \cos \theta')$, $\hat{s} = (\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta)$, and $\mathbf{s} = s\hat{s}$. We may not neglect $r'u$ since it may be comparable to $D \cos \theta$ when θ is close to 90° .

B. Local field for the QS at $\mathbf{r}$

The local field $\mathbf{E}_{\text{QS}}^{\text{loc}}(\mathbf{r}, \omega)$ at $\mathbf{r}$ in the QS is composed of the integrated polarization corresponding to scattering by all points $\{\mathbf{D} + \mathbf{r}'\}$ inside the MP, i.e.,

$$\mathbf{E}_{\text{QS}}^{\text{loc}}(\mathbf{r}, \omega) = -\varepsilon_0 \int_{\text{MP}, |\mathbf{r}'| < a} C_{\text{MP}}(\mathbf{r} - (\mathbf{D} + \mathbf{r}'), \omega) \frac{\chi_{\text{MP}}(\mathbf{D} + \mathbf{r}', \omega)}{\varepsilon_{\text{MP}}^{\text{eff}}(\mathbf{D} + \mathbf{r}', \omega)} \mathbf{E}_{\text{MP}}^{\perp \text{loc}}(\mathbf{D} + \mathbf{r}', \omega) d^3r' \quad (23)$$

where $\varepsilon_{\text{MP}}^{\text{eff}}$ [given by Eq. (12)] is due to the local-field enhancement to the linear polarization like the second term in Eq. (3).

We assume that there is no external CARS field or incident laser field which may be quasiresonant with the a - c transition or CARS transition. Inserting Eq. (16) into Eq. (23) we have

$$\mathbf{E}_{\text{QS}}^{\text{loc}}(\mathbf{r}, \omega) = \varepsilon_0 \int_{\text{MP}, |\mathbf{r}'| < a} C_{\text{MP}}(\mathbf{r} - \mathbf{D} - \mathbf{r}', \omega) \frac{\chi_{\text{MP}}(\mathbf{D} + \mathbf{r}', \omega)}{\varepsilon_{\text{MP}}^{\text{eff}}(\mathbf{D} + \mathbf{r}', \omega)} \left[N_{\text{QS}} \vec{\phi}_{ca}^\perp \int_{\text{QS}, |\mathbf{s}| < \rho} C_{\text{QS}}(\mathbf{D} + \mathbf{r}' - \mathbf{s}, \omega) \tilde{\rho}_{ac}(\mathbf{s}, \omega) d^3s \right] d^3r' \quad (24)$$

where

$$C_{\text{MP}}(\mathbf{r} - \mathbf{D} - \mathbf{r}', \omega) = \frac{\omega^2}{c^2} \frac{e^{ik(\omega)(|\mathbf{r} - \mathbf{D}| - \hat{n}_- \cdot \mathbf{r}')}}{4\pi \varepsilon_0 |\mathbf{r} - \mathbf{D}|}, \quad (25)$$

$$\hat{n}_- = \frac{\mathbf{r} - \mathbf{D}}{|\mathbf{r} - \mathbf{D}|} \simeq -\hat{z}, \quad (26)$$

$$\mathbf{r} - \mathbf{D} = (r\hat{r} - \hat{z}D), \quad (27)$$

$$|\mathbf{r} - \mathbf{D}| = \sqrt{r^2 \sin^2 \theta + (D - r \cos \theta)^2}, \quad (28)$$

$$\hat{n}_- \cdot \mathbf{r}' = \frac{r'(ru - D \cos \theta')}{|\mathbf{r} - \mathbf{D}|} \simeq -r' \cos \theta' (\theta' \text{ not } 90^\circ), \quad (29)$$

$$\hat{r} = [r \sin \theta \cos \varphi, r \sin \theta \sin \varphi, r \cos \theta]. \quad (30)$$

For small separation $kD \lesssim 1$ or the near-field regime, the longitudinal field component is present when the contribution of the operator $\nabla \nabla$ is evaluated exactly [33], but this involves more elaborate calculations. To avoid further complication to the theory, we confine our study to the far-field regime $kD > 1$.

Assuming $r' \ll D$ the phase factor in C_{QS} can be expanded as

$$\frac{e^{ik(\omega)(|\mathbf{D}+\mathbf{r}'|-\hat{n}'_+ \cdot \mathbf{s})}}{|\mathbf{D}+\mathbf{r}'|} = \frac{e^{ik(\omega)|\mathbf{D}+\mathbf{r}'|}}{D\{1 + \frac{r'^2+2Dr' \cos \theta'}{2D^2}\}} e^{-ik(\omega)\hat{n}'_+ \cdot \mathbf{s}} \quad (31)$$

$$= \frac{e^{ik(\omega)D}}{D\{1 + \frac{r'^2+2Dr' \cos \theta'}{2D^2}\}} e^{ik(\omega)\hat{z} \cdot \mathbf{r}'} e^{-ik(\omega)\hat{n}'_+ \cdot \mathbf{s}} \quad (32)$$

where we use $|\mathbf{D} + \mathbf{r}'| \approx D + \hat{z} \cdot \mathbf{r}'$ and $\frac{e^{ik(\omega)|\mathbf{D}+\mathbf{r}'|}}{|\mathbf{D}+\mathbf{r}'|} \approx \frac{e^{ik(\omega)D}}{D\{1 + \frac{r'^2+2Dr' \cos \theta'}{2D^2}\}} e^{ik(\omega)\hat{z} \cdot \mathbf{r}'}$.

The product of the two phase factors becomes

$$\frac{e^{ik(\omega)(|\mathbf{r}-\mathbf{D}|-\hat{n}_- \cdot \mathbf{r}')}}{|\mathbf{r}-\mathbf{D}|} \frac{e^{ik(\omega)(|\mathbf{D}+\mathbf{r}'|-\hat{n}'_+ \cdot \mathbf{s})}}{|\mathbf{D}+\mathbf{r}'|} = \frac{e^{ik(\omega)|\mathbf{r}-\mathbf{D}|}}{|\mathbf{r}-\mathbf{D}|} \frac{e^{ik(\omega)D}}{D\{1 + \frac{r'^2+2Dr' \cos \theta'}{2D^2}\}} e^{ik(\omega)(\hat{z}-\hat{n}_-) \cdot \mathbf{r}'} e^{-ik(\omega)\hat{n}'_+ \cdot \mathbf{s}} \quad (33)$$

where we use

$$(\hat{z} - \hat{n}_-) \cdot \mathbf{r}' = r' \cos \theta' - \frac{r'(ru - D \cos \theta')}{|\mathbf{r} - \mathbf{D}|} \simeq 2r' \cos \theta' - \frac{rr'u}{D}, \quad (34)$$

$$\hat{n}'_+ \cdot \mathbf{s} = s \frac{(D \cos \theta + r'u)}{|\mathbf{D} + \mathbf{r}'|} \simeq s \cos \theta + \frac{sr'u}{D}. \quad (35)$$

Inserting the C_{QS} into Eq. (16), the local field at MP becomes

$$\mathbf{E}_{\text{MP}}^{\text{loc}}(\mathbf{D} + \mathbf{r}', \omega) = -\frac{\omega^2}{c^2} \frac{e^{ik(\omega)|\mathbf{D}+\mathbf{r}'|}}{4\pi\epsilon_0|\mathbf{D}+\mathbf{r}'|} N_{\text{QS}} \vec{\delta}_{ca}^{\perp} \Psi(\mathbf{r}', \omega) \quad (36)$$

where we define the integral in $\mathbf{E}_{\text{MP}}^{\text{loc}}$ as

$$\Psi(\mathbf{r}', \omega) = \int_{\text{QS}, |\mathbf{s}| < \rho} e^{-ik(\omega)\hat{n}'_+ \cdot \mathbf{s}} \tilde{\rho}_{ac}(\mathbf{s}, \omega) d^3s \quad (37)$$

$$= \int_{s=0}^{\rho} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} e^{-ik(\omega)s \frac{(D \cos \theta + r'u)}{|\mathbf{D}+\mathbf{r}'|}} \left(\tilde{\rho}_{ac}^{\text{NL}}(\mathbf{s}, \omega) + \frac{\tilde{\rho}_{ac}^{\Lambda}(\mathbf{s}, \omega)}{\epsilon_{\text{QS}}^{\text{eff}}(\mathbf{s}, \omega)} \right) s^2 \sin \theta d\theta ds d\phi. \quad (38)$$

Inserting the C_{MP} and C_{QS} into Eq. (24), the local field in the QS can be expressed as

$$\begin{aligned} \mathbf{E}_{\text{QS}}^{\text{loc}}(\mathbf{r}, \omega) &= A(\mathbf{r}, \omega) \int_{\text{MP}, |\mathbf{r}'| < a} \int_{\text{QS}, |\mathbf{s}| < \rho} \frac{\chi_{\text{MP}}(\mathbf{D} + \mathbf{r}', \omega)}{\epsilon_{\text{MP}}^{\text{eff}}(\mathbf{D} + \mathbf{r}', \omega)} \frac{1}{1 + \frac{r'^2+2Dr' \cos \theta'}{2D^2}} e^{ik(\omega)(\hat{z}-\hat{n}_-) \cdot \mathbf{r}'} e^{-ik(\omega)\hat{n}'_+ \cdot \mathbf{s}} \tilde{\rho}_{ac}(\mathbf{s}, \omega) d^3s d^3r' \\ &= A(\mathbf{r}, \omega) \int_{\text{MP}, |\mathbf{r}'| < a} \frac{\chi_{\text{MP}}(\mathbf{D} + \mathbf{r}', \omega)}{\epsilon_{\text{MP}}^{\text{eff}}(\mathbf{D} + \mathbf{r}', \omega)} \frac{1}{1 + \frac{r'^2+2Dr' \cos \theta'}{2D^2}} e^{ik(\omega)r'[(1 + \frac{D}{|\mathbf{r}-\mathbf{D}|}) \cos \theta' - \frac{ru}{|\mathbf{r}-\mathbf{D}|}]} \Psi(\mathbf{r}', \omega) d^3r' \end{aligned} \quad (39)$$

where

$$A(\mathbf{r}, \omega) = \vec{\delta}_{ca}^{\perp} \epsilon_0 N_{\text{QS}} \left(\frac{\omega^2}{4\pi\epsilon_0 c^2} \right)^2 \frac{e^{ik(\omega)|\mathbf{r}-\mathbf{D}|}}{|\mathbf{r}-\mathbf{D}|} \frac{e^{ik(\omega)D}}{D}. \quad (40)$$

For $\frac{r'}{D} \ll 1$ the $\Psi(\mathbf{r}', \omega)$ becomes $\Psi(\omega)$, almost independent of space as $e^{-ik(\omega)s \frac{(D \cos \theta + r')}{|D+r|}}$ is approximately $e^{-ik(\omega)s \cos \theta}$. If the metallic particle is assumed to have a homogeneous charge density or plasma frequency, $\varepsilon_{\text{MP}}(\omega)$ would be independent of spacetoo. Hence, the local field simplifies to

$$\mathbf{E}_{\text{QS}}^{\text{loc}}(\mathbf{r}, \omega) = A(\mathbf{r}, \omega) \frac{\chi_{\text{MP}}(\omega)}{\varepsilon_{\text{MP}}^{\text{eff}}(\omega)} \Psi(\omega) \mathcal{V}_{\text{MP}}, \quad (41)$$

$$\mathcal{V}_{\text{MP}} = \int_{\text{MP}, |\mathbf{r}'| < a} e^{ik(\omega)(1 + \frac{D}{|\mathbf{r}-\mathbf{D}|})r' \cos \theta'} d^3 r'. \quad (42)$$

IV. NONLINEAR INTEGRAL EQUATION

Equations (38) and (39) form a highly nonlinear and spatially nonlocal problem for $\mathbf{E}_{\text{QS}}^{\text{loc}}$ because the coherence $\tilde{\rho}_{ac}^{\Lambda}$ in the integral also depends on the local field $\mathbf{E}_{\text{QS}}^{\text{loc}}$ as given by Eq. (B1). The $\tilde{\rho}_{ac}^{\text{NL}}$ in Ψ is due to three lasers interacting to produce a nonlinear four-wave mixing CARS field, which contributes partly to the local field $\mathbf{E}_{\text{QS}}^{\text{loc}}$ and at the same time can also be sufficiently strong to drive the a - c transition in the Λ system to produce the coherence $\tilde{\rho}_{ac}^{\Lambda}$ given by Eq. (B1). Phase matching of the CARS is implicitly included in $\tilde{\rho}_{ac}^{\text{NL}}$ [given by Eq. (A1)] through the laser wave vectors contained in the spatial distribution functions of the respective focused laser fields as computed exactly by the Mie theory (Appendix E in Ref. [30]).

Please note that, while $\tilde{\rho}_{ac}^{\Lambda}$ may include the nonlinear dependence on $F(\mathbf{r}, \omega) = \tilde{\rho}_{ca}^{\perp} \cdot \mathbf{E}_{\text{QS}}^{\text{loc}} / \hbar$, the $\varepsilon_{\text{QS}}^{\text{eff}}$, $\varepsilon_{\text{QS}}^{(1)}$, and $\chi^{(1)}$ are defined to be linear-response functions and should not depend on $F(\mathbf{r}, \omega)$. The problem now is that the expression in the integral Eq. (37) depends on $F(\mathbf{r}, \omega)$. Multiplying Eq. (41) by $\tilde{\rho}_{ca}^{\perp} / \hbar$ we have the formidable nonlinear integral equation for $F(\mathbf{r}, \omega)$ to be solved:

$$F(\mathbf{r}, \omega) = C(\mathbf{r}, \omega) \left\{ \Psi^{(3)}(\omega) + \int e^{-ik(\omega)\hat{n}'_+ \cdot \mathbf{s}} \frac{\tilde{\rho}_{ac}^{\Lambda}(\mathbf{s}, \omega)}{\varepsilon_{\text{QS}}^{\text{eff}}(\mathbf{s}, \omega)} d^3 s \right\} \quad (43)$$

$$= F_0(\mathbf{r}, \omega) + C(\mathbf{r}, \omega) \int F(\mathbf{s}, \omega) H(\mathbf{s}, \omega) d^3 s \quad (44)$$

where the first term is (spatially local)

$$F_0(\mathbf{r}, \omega) = C(\mathbf{r}, \omega) \Psi^{(3)}(\omega), \quad (45)$$

$$C(\mathbf{r}, \omega) = \eta \left(\frac{\omega^2}{c^2} \right)^2 \frac{e^{ik(\omega)D}}{4\pi D} \frac{e^{ik(\omega)|\mathbf{r}-\mathbf{D}|}}{4\pi |\mathbf{r}-\mathbf{D}|} \frac{\chi_{\text{MP}}(\omega)}{\varepsilon_{\text{MP}}^{\text{eff}}(\omega)} \mathcal{V}_{\text{MP}}, \quad (46)$$

$$\Psi^{(3)}(\omega) = \int_{r=0}^{\rho} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} e^{-ik(\omega)r \cos \theta} \tilde{\rho}_{ac}^{\text{NL}} \times (\mathbf{r}, \omega) r^2 \sin \theta d\theta dr d\phi \quad (47)$$

and the second term (spatially nonlocal) has the response function given by

$$H(\mathbf{s}, \omega) = \frac{e^{-ik(\omega)\hat{n}'_+ \cdot \mathbf{s}} \tilde{\rho}_{ac}^{\Lambda}(\mathbf{s}, \omega)}{F(\mathbf{s}, \omega) \varepsilon_{\text{QS}}^{\text{eff}}(\mathbf{s}, \omega)} = e^{-ik(\omega)\hat{n}'_+ \cdot \mathbf{s}} \frac{\chi_{\text{QS}}^{\Lambda}(\mathbf{r}, \omega)}{\eta \varepsilon_{\text{QS}}^{\text{eff}}(\mathbf{s}, \omega)} \\ = i \frac{e^{-ik(\omega)\hat{n}'_+ \cdot \mathbf{s}}}{1 + \frac{1}{3} i \eta \frac{A(\mathbf{s}, \omega)}{B(\mathbf{s}, \omega)}} \left(\frac{A(\mathbf{s}, \omega) - n_{ac} |F(\mathbf{s}, \omega)|^2}{B(\mathbf{s}, \omega) + \Upsilon_{ac}^*(\omega) |F(\mathbf{s}, \omega)|^2} \right), \quad (48)$$

$$A(\mathbf{s}, \omega) = n_{ab} I_c - n_{ac} \Upsilon_{ab}(\omega) \Upsilon_{bc}^*(\omega), \quad (49)$$

$$B(\mathbf{s}, \omega) = \{ \Upsilon_{ac}^*(\omega) \Upsilon_{bc}^*(\omega) + I_c \} \Upsilon_{ab}(\omega) \quad (50)$$

where $\eta = \frac{N_{\text{QS}} |\rho_{ca}|^2}{\hbar \varepsilon_0}$. We have used the pieces in Appendix B to express the ratio as

$$\frac{\tilde{\rho}_{ac}^{\Lambda}(\mathbf{s}, \omega)}{\varepsilon_{\text{QS}}^{\text{eff}}(\mathbf{s}, \omega)} = \frac{F(\mathbf{s}, \omega) \chi_{\text{QS}}^{\Lambda}(\mathbf{s}, \omega)}{\eta \varepsilon_{\text{QS}}^{\text{eff}}(\mathbf{s}, \omega)} \\ = i F(\mathbf{s}, \omega) \frac{\Upsilon_{bc}^*(\omega)}{1 + \frac{1}{3} \chi^{(1)}(\mathbf{s}, \omega)} \left(\frac{n_{ab} I_c - n_{ac} J_b(\omega)}{J_c(\omega) J_b(\omega) - I_4 I_c} \right) \quad (51)$$

where I_c, I_4, J_b, J_c , and $\chi^{(1)}$ are defined in Appendix B.

When the CARS field is small the $|F(\mathbf{s}, \omega)|^2$ in Eq. (48) may be neglected, giving

$$F(\mathbf{r}, \omega) = F_0(\mathbf{r}, \omega) + C(\mathbf{r}, \omega) \int F(\mathbf{s}, \omega) H_0(\mathbf{s}, \omega) d^3 s \quad (52)$$

with the kernel

$$H_0(\mathbf{s}, \omega) = i \frac{e^{-ik(\omega)\hat{n}'_+ \cdot \mathbf{s}}}{\frac{B(\mathbf{s}, \omega)}{A(\mathbf{s}, \omega)} + \frac{1}{3} i \eta}. \quad (53)$$

On the other extreme, when the CARS field is large such that $|F(\mathbf{s}, \omega)|^2 \gg I_c, |\Upsilon_{\alpha\beta}|$, we have

$$F(\mathbf{r}, \omega) = F_0(\mathbf{r}, \omega) + C(\mathbf{r}, \omega) \times \left(\frac{n_{ac}}{i \Upsilon_{ac}^*} \right) \int \frac{F(\mathbf{s}, \omega) e^{-ik(\omega)\hat{n}'_+ \cdot \mathbf{s}}}{1 + \frac{1}{3} i \eta \frac{A}{B}} d^3 s. \quad (54)$$

In either case both Eqs. (52) and (54) are the Fredholm equation of the second kind. Note that we may not avoid getting the Fredholm equation simply by reformulating the scattered field Eq. (1) such that the linear polarization is transformed away because the linear dielectric function has spatial dependence.

We may employ the method of Ref. [35] to solve the Fredholm or the so-called Lippmann-Schwinger equation by multiplying Eq. (52) with the kernel $H_0(\mathbf{r}, \omega)$ [Eq. (53)], and, integrating, we have

$$\int F(\mathbf{r}, \omega) H_0(\mathbf{r}, \omega) d^3 r = \int F_0(\mathbf{r}, \omega) H_0(\mathbf{r}, \omega) d^3 r + \int C(\mathbf{r}, \omega) H_0(\mathbf{r}, \omega) d^3 r \int F(\mathbf{s}, \omega) H_0(\mathbf{s}, \omega) d^3 s \quad (55)$$

and the integral to be evaluated is

$$\xi_0 = \int F(\mathbf{r}, \omega) H_0(\mathbf{r}, \omega) d^3 r = \frac{\int F_0(\mathbf{r}, \omega) H_0(\mathbf{r}, \omega) d^3 r}{1 - \int C(\mathbf{r}, \omega) H_0(\mathbf{r}, \omega) d^3 r}. \quad (56)$$

Hence, the (approximate) initial solution obtained by neglecting the $|F|^2$ in the kernel of Eq. (48) is

$$F_i(\mathbf{r}, \omega) = F_0(\mathbf{r}, \omega) + C(\mathbf{r}, \omega) \xi_0, \quad (57)$$

which shows the physics of the field enhancement through the second term. To obtain a better solution, we replace $F(\mathbf{r}, \omega)$ in the kernel of Eq. (48) by $F_i(\mathbf{r}, \omega)$, the approximate solution Eq. (57), giving

$$H(\mathbf{r}, \omega) \simeq H_i(\mathbf{r}, \omega) = i \frac{e^{-ik(\omega)\hat{n}_+ \cdot \mathbf{r}}}{1 + \frac{1}{3}i\eta \frac{A(\mathbf{r}, \omega)}{B(\mathbf{r}, \omega)}} \times \left(\frac{A(\mathbf{r}, \omega) - n_{ac}|F_i(\mathbf{r}, \omega)|^2}{B(\mathbf{r}, \omega) + \Upsilon_{ac}^*(\omega)|F_i(\mathbf{r}, \omega)|^2} \right). \quad (58)$$

Integrating as before,

$$\begin{aligned} & \int F(\mathbf{r}, \omega) H_i(\mathbf{r}, \omega) d^3 r \\ &= \int F_0(\mathbf{r}, \omega) H_i(\mathbf{r}, \omega) d^3 r \\ &+ \int C(\mathbf{r}, \omega) H_i(\mathbf{r}, \omega) d^3 r \int F(\mathbf{s}, \omega) H_i(\mathbf{s}, \omega) d^3 s, \end{aligned} \quad (59)$$

we have

$$\xi_i = \int F(\mathbf{r}, \omega) H_i(\mathbf{r}, \omega) d^3 r = \frac{\int F_0(\mathbf{r}, \omega) H_i(\mathbf{r}, \omega) d^3 r}{1 - \int C(\mathbf{r}, \omega) H_i(\mathbf{r}, \omega) d^3 r}, \quad (60)$$

which is used to compute a more precise solution:

$$F(\mathbf{r}, \omega) = F_0(\omega) + C(\mathbf{r}, \omega) \xi_i. \quad (61)$$

We may iterate the cycle by setting $F(\mathbf{r}, \omega)$ as $F_i(\mathbf{r}, \omega)$ in the kernel and repeat the computation to further obtain a more precise $F(\mathbf{r}, \omega)$. In our computation we repeat the cycle up to two times as further iteration does not yield significantly more different or precise results. We have used more computational points for larger particles since we have to maintain at least ten spatial points within the scale of one laser wavelength for accurate volume integration.

Using the solutions of the local fields we have the absorption power spectral densities of the quantum system and the metallic particle:

$$S_X(\omega) = \frac{\varepsilon_0}{2} \int \text{Im}[\varepsilon_X(\mathbf{r}, \omega)] |\mathbf{E}_X^{\text{loc}}(\mathbf{r}, \omega)|^2 dV, \quad (62)$$

which depends on the imaginary parts of the ε_{QS} and ε_{MP} , where $X = \text{QS}, \text{MP}$. Here, a negative sign would mean emission rate.

In all the figures, we have plotted $S_X(\omega)$ (which has the dimension of joule or watt per hertz), which is actually the absorption power spectral density. Note that $Q_X(\omega) = \omega S_X(\omega)$ also has the unit of power and is essentially $Q_X(\omega) = \text{Re}[-i\omega \mathcal{F}\{U_X\}] = \text{Re}\mathcal{F}\{\frac{dU_X}{dt}\}$, the real part of the Fourier transform ($\mathcal{F}$) of $\frac{dU_X}{dt}$, where $U_X = \frac{\varepsilon_0}{2} \int \mathcal{F}^{-1}\{\varepsilon_X(\mathbf{r}, \omega) |\mathbf{E}_X^{\text{loc}}(\mathbf{r}, \omega)|^2\} dV$, but it does not reflect the actual power. The actual total power is $\bar{Q}_X(\omega) = \int S_X(\omega) d\omega$, the integration of the power spectral density $S_X(\omega)$ (watt per hertz) over the frequency range.

At plasmonic resonance the energy density $u = \frac{1}{2} \frac{d(\omega \varepsilon)}{d\omega} |\mathbf{E}_{\text{QS}}^{\text{loc}}|^2$ becomes very large due to not only the enhanced $\mathbf{E}_{\text{QS}}^{\text{loc}}$ but also the contribution of the dispersion $\frac{d\varepsilon}{d\omega}$. As the field at certain regions of the plasmonic nanoparticle is confined to a smaller volume, the energy density is much higher than in the incident wave, contributing to a large $\nabla \cdot \mathbf{S}$. This is due to the fact that plasmonics is a resonance phenomenon where the system rapidly and coherently accumulates and stores energy from the incident wave coherently during many oscillations and it is the field amplitude that builds up and is enhanced. Thus we may have larger du/dt but the total energy is conserved. The spatial-temporal variation of the energy is described by $du/dt + \nabla \cdot \mathbf{S} = -\mathbf{J} \cdot \mathbf{E}$, which includes the accumulation or dissipation of the energy with time, and spatial localization of the field from the incoming wave is balanced by the absorption and dissipation.

V. RESULTS AND DISCUSSIONS

In our simulations we have used the following parameters (unless stated otherwise): number density of molecules $N_{\text{QS}} = 2 \times 10^{26} \text{ m}^{-3}$; characteristic radiative decay in soft or condensed matter $\gamma_0 = 5 \times 10^{12} \text{ s}^{-1}$; decoherence rates $\gamma_{ab} = \gamma_{dc} = \gamma_{ab} = \gamma_{ac} = \gamma_0$, $\gamma_{bc} = 0.6\gamma_0$; detunings of the fields $\Delta_4 = \Delta_c = \Delta_s = \Delta_p = 0 \text{ s}^{-1}$; transition frequencies $\omega_{ac} = 3.586 \times 10^{15} \text{ s}^{-1}$, $\omega_{ab} = 3.54 \times 10^{15} \text{ s}^{-1}$, $\omega_{db} = 2.96 \times 10^{15} \text{ s}^{-1}$, $\omega_{dc} = 3.006 \times 10^{15} \text{ s}^{-1}$, $\omega_{bc} = 4.6 \times 10^{13} \text{ s}^{-1}$, $\omega_{ac} = \omega_{ab} + \omega_{bc}$, $\omega_{dc} = \omega_{db} + \omega_{bc}$; Rabi frequencies for the pump beam $\Omega_{p0} = 1.5\gamma_{ac}$, for the Stokes beam $\Omega_{s0} = 1.5\gamma_{ac}$, and for control beam $\Omega_{c0} = 2\gamma_{ac}$; and populations $\rho_{dd} = 0$, $\rho_{cc} = 0.95$, $\rho_{bb} = 0.05$, $\rho_{aa} = 0$ with the inversions $n_{dc} = \rho_{dd} - \rho_{cc} = -0.95$, $n_{db} = \rho_{dd} - \rho_{bb} = -0.05$, $n_{ac} = \rho_{aa} - \rho_{cc} = -0.95$, $n_{ab} = \rho_{aa} - \rho_{bb} = -0.05$. The dipole transition matrix elements (aligned along x) are $\wp_{dc,x} = \wp_{db,x} = \wp_{ac,x} = \wp_{ab,x} = 1.6 \times 10^{-29} \text{ C m}$. Also, we have used $\varepsilon_{\infty} = 3.7$, $\Gamma = 2.73 \times 10^{13} \text{ s}^{-1}$, and $\omega_p = \omega_{p0}$ for the plasmonic resonant case and $\omega_p = 0.9\omega_{p0}$ for the nonresonant case, with ω_{p0} given by Eq. (15).

According to Eq. (A1) the CARS process is expected to give rise to absorption peaks mainly around ω_{ac} . The Raman process should give EIT peaks at $\omega_{ac} \pm 2\gamma_{ac}$ but these peaks

do not show up. We also notice that the CARS peaks are complicated by several factors: broadening, spatially inhomogeneous fields in the quantum particle, and mesoscopic resonances as the result of Mie scattering as the size of the QS particle increases. Thus, any variation in the peaks is due to finite-size effect. In the figures we have plotted, S_{QS} and S_{MP} are in units of watts and we set the regime of validity as $D = 3(a + \rho_{\max}) > 3\rho_{\max}$ due to approximations in Eqs. (6) and (8).

A. Spectra versus interparticle separation

Figures 2 and 4 show the variation of the power densities S_{QS} and S_{MP} with frequency, i.e., absorption spectra, for a range of interparticle distance D and several values of particle radii $\rho = a = 10$ nm, 100 nm, and 1 μ m. For small particle size $\rho = a = 10$ nm with interparticle distance in the range $D = 60$ –140 nm, the spectral peaks in S_{MP} are Mollow's triplets, with the principal peak at $\omega = \omega_{ac}$ due to CARS and the lower side peaks near $\omega_{ac} \pm (\Omega_{p0} + \Omega_{s0} + \Omega_{c0}) \simeq \omega_{ac} \pm 5\gamma_{ac}$ due to ac Stark shifts by the laser fields in the Raman (EIT) process. For S_{QS} , the same peaks as in S_{MP} appear, but the side peaks are much lower than the central peaks, actually about 500 times lower than in S_{MP} . The spectra of S_{MP} are not affected by plasmonic resonance while the magnitude of S_{MP} is only slightly increased, so we only show the plots for $\omega_p = 0.9\omega_{p0}$. For S_{QS} with the plasmonic resonance ($\omega_p = \omega_{p0}$) the central peaks are enhanced more than other side peaks, by a factor of nearly 10^3 higher than the peak without plasmonic resonance ($\omega_p = 0.9\omega_{p0}$).

For medium particle size $\rho = a = 100$ nm and interparticle distance in the range $D = 600$ –1400 nm, the peak for S_{QS} is about four times larger than S_{MP} . The side peaks in S_{MP} and S_{QS} almost disappear and are no longer resolved. There is a small dip at $\omega = \omega_{ac}$ which is a prominent feature connected to nonlinear coupling with Fano effect and double resonance [34]. The plasmonic enhancement factor of S_{QS} is as high as a factor of 10^3 with the main and side peaks visible only periodically, but S_{MP} is almost unaffected by the plasmonic effect.

For large particle size $\rho = a = 1$ μ m and interparticle range $D = 6$ –14 μ m, S_{MP} has essentially a single dominant peak around ω_{ac} but the side peak has shifted from $\omega_{ac} + 5\gamma_{ac}$ to $\omega_{ac} + 6\gamma_{ac}$, and similarly for S_{QS} but with a small dip at the central peak. There is an absorption minimum or Fano dip around $\omega_{ac} - 0.1\gamma_{ac}$, a clear sign of the Fano interference effect due to nonlinear coupling. The plasmonic enhancement here is around a factor of 10^3 with the anti-Stokes peaks redshifted from $\omega_{ac} + 4\gamma_{ac}$ to ω_{ac} as D increases and then reappearing at $\omega_{ac} + 4\gamma_{ac}$, showing the effect of configurational resonance of the QS-MP system.

The logarithmic plots for medium and large particle radii show periodic oscillations at intervals of about $\lambda_4/2 = 263$ nm as D varies, where $\lambda_4 = 525.28$ nm. This interference effect happens only in the case of plasmonic resonance where standing waves of the CARS fields fit in between the two particles separated by $n\lambda_4/2$, multiples of the half wavelength of the a - c transition.

B. Stronger laser fields

Optimization of the absorption power can be achieved by controlling the quantum coherence [36] using the pump, Stokes, and control laser fields and this will be a subject of further analysis. We now look at the spectra in Figs. 3 and 4 with stronger laser fields: $\Omega_{p0} = 2\gamma_{ac}$, $\Omega_{s0} = 3\gamma_{ac}$, $\Omega_{c0} = 4\gamma_{ac}$.

For small particles $\rho = a = 10$ nm the spectra of S_{MP} and S_{QS} as hybrids of CARS and Raman coherences show Mollow side peaks near $\omega_{ac} \pm (\Omega_{p0} + \Omega_{s0} + \Omega_{c0}) \simeq \omega_{ac} \pm 9\gamma_{ac}$ besides the central peak at ω_{ac} . Within the spectrum there are oscillations that are regularly spaced with a period of about γ_{ac} due to the beating between Ω_{c0} and Ω_{s0} , modulated by the three main peaks and with a small dip at ω_{ac} . Such oscillations also appear in the case of weaker fields where Ω_{p0} and Ω_{s0} are equal but $0.5\gamma_{ac}$ lower than Ω_{c0} . However, when Rabi frequencies are all equal, these oscillations are absent. Thus, the oscillations are due to the difference between Ω_{c0} and Ω_{p0} or Ω_{s0} . At plasmonic resonance, the central peak of S_{QS} is enhanced by a factor of 10^3 and the side peaks become hardly visible.

For $\rho = a = 100$ nm (Fig. 3), the side peaks in S_{MP} completely disappear. Interestingly, we have *negative absorption* as a dip in S_{QS} at $\omega = \omega_{ac}$ which indicates gain without population inversion since we verify that it is manifested by a finite but small population in level b ($\rho_{bb} = 0.05$, $n_{ab} = -0.05$) coupled to the strong control laser. Unlike the usual lasing without inversion [37], the gain here is unique as it appears at certain values of ρ and medium range of D only. The negative absorption persists even at plasmonic resonance, with enhancement of a factor of 10^3 . Also, the periodic oscillations across D with a period of $\lambda_4/2$ can only be seen in the $\log_{10}$ scale, unlike the previous case of weaker fields.

For larger particles $\rho = a = 1$ μ m, the features in S_{MP} and S_{QS} are quite similar to the weak-field case. At plasmonic resonance $\omega_p = \omega_{p0}$, a series of narrow and high peaks emerges (with width $0.03\gamma_{ac}$ based on numerical check) in S_{QS} redshifted from the frequency range $\omega_{ac} + 5\gamma_{ac}$ to $\omega_{ac} + 0.5\gamma_{ac}$ as D increases and then reappearing at $\omega_{ac} + 5\gamma_{ac}$. The peaks are more prominent for a smaller range of interparticle distance, enhanced by more than a factor of 10^3 by SPR, more than the case of weak fields. We notice that narrow peaks due to plasmonic enhanced Mie resonances in the larger particle case can be computationally challenging. The rate of the oscillations at plasmonic resonance remains the same as the weaker-field case, i.e., with a period of $\lambda_4/2$, the half wavelength of the a - c transition.

The three ranges of D in Figs. 2, 3, and 4 differ by one or two orders of magnitude—60 nm, 600 nm, and 6 μ m—while the peaks decay at a similar rate. This shows that for larger particles the plasmonic resonance not only enhances the power but also gives a long-range interparticle interaction effect similar to the Forster interaction. Spectral peaks associated with the four-level system (Raman and CARS) are shifted by the mesoscopic-size effect, as in the cases of medium and large particle sizes, and also possibly buried by plasmonic effect.

FIG. 2. Absorption power spectrum of the QS vs interparticle distance D for three values of particle radii $\rho = 10$ nm, 100 nm, and $1 \mu\text{m}$ for off-resonant and resonant plasma frequencies ω_p with weaker laser fields: $\Omega_{p0} = 1.5\gamma_{ac}$, $\Omega_{s0} = 1.5\gamma_{ac}$, and $\Omega_{c0} = 2\gamma_{ac}$. Other parameters are described in the discussion section. The $\log_{10}$ plot shows the oscillations due to enhancement effect more clearly. The bottom panels are two-dimensional plots of $\bar{Q}_{QS}$ for the case with plasmonic enhancement showing that power conservation is not violated.

C. Spectra versus particle radius of the QS

The effects of particle radius can be seen from a better perspective in Figs. 5 and 6, which show the variations of

the power spectra S_{QS} and S_{MP} , respectively, with particle radius ρ in three ranges of ρ for $D = 3(a + \rho_{\max})$ with $a = 100$ nm and $\rho_{\max}$ is the highest value for each range. The

FIG. 3. Absorption power spectrum of QS vs interparticle distance D , the same as Fig. 2 except with stronger laser fields: $\Omega_{p0} = 2\gamma_{ac}$, $\Omega_{s0} = 3\gamma_{ac}$, and $\Omega_{c0} = 4\gamma_{ac}$.

ranges are chosen to show the significant rise in the power at around 300, 900, and 1600 nm. The plots of $\log_{10} S_{QS}$ (Fig. 5) for the radius in small range $\rho = 10\text{ nm} - 0.5\text{ }\mu\text{m}$ and $D = 1.8\text{ }\mu\text{m}$ with plasmonic resonance conditions indicate that the power density increases very rapidly with ρ . For larger ρ there is a saturation effect connected to the Mie focusing where the power increases slowly with ρ . Power enhancement is less significant as ρ increases further while the power density oscillates in a periodic manner. There is

also an almost consistent (Fano) dip near ω_{ac} for small values of ρ , below about 800 nm. However, for particle radius larger than around 800 nm there is no noticeable Fano dip at ω_{ac} . Here, the situation is similar to the usual Fano dip except that the mesoscopic size effect washes out the Fano dip. The oscillations over the medium range $\rho = 0.5 - 1.2\text{ }\mu\text{m}$ are quite periodic, which is whispering gallery effect. We estimate the period to be $\rho_{osc} = 76\text{ nm}$ from the two-dimensional (2D) plots, where $2\pi\rho_{osc}$ almost fits an effective wavelength. As

FIG. 4. Same as in Fig. 2 except it is the absorption power spectrum of the MP S_{MP} plotted vs interparticle distance D for $\omega_p = 0.9\omega_{p0}$. The results for plasmonic resonance case $\omega_p = \omega_{p0}$ are quite similar and only slightly higher, so we do not show the plots.

the central peak becomes higher there seems to be a slight narrowing rather than broadening, and this is connected to the intense laser fields formed by the focusing effect of the spherical particle. For large particle size range, at 1350 nm (in the 2D plot versus radius ρ) the oscillations become twice more rapid when a peak starts to have a dip and split into two peaks that look progressively more identical in width of $\rho_{osc}/2$ as ρ increases. This suggests that $2\pi(\rho_{osc}/2)$ almost fits half the wavelength.

The oscillations across ρ are also found in S_{MP} as shown in Fig. 6. The level-splitting effect is complicated by the size effect as we have the asymmetric Mollow sidebands at around $\omega_{ac} \pm 5\gamma_{ac}$ over a wide range of ρ . Even for larger particle size range, $\rho = 1.2\text{--}2\text{ }\mu\text{m}$ with $D = 6.3\text{ }\mu\text{m}$, the side peaks appear to remain asymmetrical throughout the values of ρ .

At plasmonic resonance $\omega_p = \omega_{p0}$, the spectral peaks continue to oscillate as ρ increases. The plasmonic resonance does not affect the qualitative features of either S_{MP} (Fig. 6) or S_{QS} (Fig. 5), i.e., it does not show any different or new feature except the higher peaks corresponding to plasmonic-induced absorption. The plasmonic enhancement factors for the three ranges are roughly the same, about a factor of 10^3 for S_{QS} but only about 30% higher for S_{MP} .

D. Absorption power

For the case of weak field with Rabi frequency of $\Omega_{c0} = 2\gamma_{ac}$ and dipole moment taken to be $1.6 \times 10^{-29}\text{ C m}$ the corresponding electric-field amplitude of the control laser

is $E_{c0} = 6.6 \times 10^7\text{ V/m}$. Hence, the continuous laser power $\bar{Q}_L = 2V \sum_{j=p,s,c} u_j \int \delta(\omega - \nu_j) \omega d\omega = V \sum_{j=p,s,c} \nu_j \epsilon_0 E_{j0}^2$ incident on the QS, and MPs with volume V and radii 10 nm, 100 nm, and $1\text{ }\mu\text{m}$ are about 1.11 mW, 1.11 W, and 1110 W, respectively. The actual absorption power $\bar{Q}_X = \int u_X d\omega dV = \int S_X(\omega) d\omega$, $X = \text{QS, MP}$ is obtained by integrating the spectral power density $S_X(\omega)$ over the frequency. Care has to be taken to use a sufficiently large number of points and not to integrate far beyond the peaks to minimize error and obtain convergence of results. For an actual laser with linewidth γ , $\delta(\omega - \nu_j)$ can be replaced by a Lorentzian $\frac{\gamma/\pi}{(\omega - \nu_j)^2 + \gamma^2}$ that satisfies $\lim_{\gamma \rightarrow 0} \int \frac{\gamma \omega d\omega/\pi}{(\omega - \nu_j)^2 + \gamma^2} = \int \delta(\omega - \nu_j) \omega d\omega = \nu_j$. The integrand, $A = \frac{\gamma \omega/\pi}{(\omega - \nu_j)^2 + \gamma^2}$ [$\rightarrow \delta(\omega - \nu_j) \omega$], is a dimensionless and asymmetric function; with its peak at half width, $A_{1/2}$ can be much larger than unity since we have the constraint $\gamma A_{1/2} \sim \nu_j$, where typically $\gamma/\nu_j < 1$.

Similarly, for $\bar{Q}_X$ the dimensionless function A has been implicitly contained within the spectral power density $S_X(\omega)$ we have plotted. So, although the peaks of $S_X(\omega)$ may be much higher than $V \epsilon_0 E_{j0}^2$, the widths are around γ_{ac} , which is much less than ν_j , such that $\bar{Q}_X < \bar{Q}_L$, i.e., power and energy are conserved. This has been confirmed for all cases and we show $\bar{Q}_{QS}$ in the 2D plots at the bottom panels of Fig. 2 for the weaker fields.

At SPR, very large and narrow peaks, with enhancement of a factor of 10^3 , are the result of plasmonic field amplification. This means that the QS has the capacity to absorb and store a larger amount of power within a narrow range of frequency

FIG. 5. Absorption power spectrum for the QS vs particle radius ρ in three different ranges of ρ for plasmonic off-resonant and resonant plasma frequencies ω_p . Here, the MP particle radius is $a = 100$ nm and $D = 3(a + \rho_{\max})$, where $\rho_{\max}$ is the maximum for each range of ρ . Other parameters are described in the discussion section.

around certain peaks since SPR is a resonance effect. Narrow peaks imply a very fast absorption process in the time domain (which is beyond the present scope that focuses on the spectral domain). Thus, the plasmonic peaks do not violate energy conservation as we have also verified that the total power

obtained after integration over the frequency of the spectra is less than the total incident laser power $\bar{Q}_L = \sum_{j=p,s,c} \bar{Q}_j$ for any particle radius, i.e., $\bar{Q}_L > \bar{Q}_X$.

The QS-MP system is also a plasmonic resonator with the interparticle spacing serving like a cavity with a high- Q

FIG. 6. Absorption power spectrum for the MP vs three different ranges of particle radius ρ for plasmonic off-resonant and resonant plasma frequencies ω_p . Other parameters are the same as Fig. 5. The spectra of Q_{MP} for $\omega_p = \omega_{p0}$ are essentially identical to the spectra for $\omega_p = 0.9\omega_{p0}$, so we do not show the plots for $\omega_p = \omega_{p0}$.

quality factor. At plasmonic resonance the field is enhanced, so the energy density is much higher than in the incident wave. The system continuously accumulates and stores energy from the CARS field (concurrent with and limited by the dissipation) and amplifies the field amplitude coherently during many oscillations, but not the energy. Strong spatial (subwavelength) confinement of the plasmonic field also gives high power within a unit area or high intensity possibly reaching the regimes of multiphoton ionization and tunnel ionization.

In conclusion, we have developed a theory to compute the local CARS fields and absorption power spectrum of spherical QSs and MPs of finite sizes. We find from the $\log_{10}$ scale plots that the spectrum scales very rapidly with ρ and a for small particle sizes. The rapid rise of spectral power density with particle size is the unexpected finding. It is as significant as the enhancement of narrow peaks at plasmonic resonance. We find oscillations in the power as the particle radius increases due to the whispering gallery effect and interestingly becomes two times more rapid above about $1.4 \mu\text{m}$. The mesoscopic size of the particles can deform the spectral peaks and gives rise to a kind of Fano dip and narrow peaks features that are very sensitive to the sizes of the QS and MP. Together with plasmonic resonance, very large and very small absorption at certain frequencies can be achieved for certain particle sizes. We also analyze the variations of the spectral density with interparticle spacing and find that the spectral density in $\log_{20}$ scale that oscillates with the spacing at plasmonic resonance can accommodate a kind of cavity resonance effect. This paper provides a useful theoretical and computational basis for further studies of realistic finite-size quantum plasmonic structures, particularly the challenging endeavors to obtain exact numerical solutions and extend the theory to excitations by pulsed lasers with high intensity as well as few photons.

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APPENDIX A: POLARIZATION DUE TO CARS IN THE QS

The first term of the coherence in Eq. (3) is given by Eq. (D4) of [30]

$$\tilde{\rho}_{ac}^{\text{NL}}(\mathbf{r}, \omega) = \frac{i\Omega_c(\mathbf{r})\tilde{\rho}_{bc}(\mathbf{r}, \omega - \nu_c)}{\Upsilon_{ac}^*(\omega)}, \quad (\text{A1})$$

$$\Upsilon_{ac}^*(\omega) = \gamma_{ac} - i(\omega - \omega_{ac}) \quad (\text{A2})$$

with the ground-state coherence

$$\tilde{\rho}_{bc}(\mathbf{r}, \omega - \nu_c) = \frac{\Omega_p(\mathbf{r})\Omega_s^*(\mathbf{r})}{\Upsilon_{bc}^*(\omega) + \delta_S(\omega)} \left[\frac{n_{dc}}{\Upsilon_{dc}^*(\omega)} + \frac{n_{db}}{\Upsilon_{db}(\omega)} \right], \quad (\text{A3})$$

$$\delta_S(\omega) = \frac{|\Omega_s|^2}{\Upsilon_{dc}^*(\omega)} + \frac{|\Omega_p|^2}{\Upsilon_{db}(\omega)}, \quad (\text{A4})$$

$$\Upsilon_{dc}^*(\omega) = \gamma_{dc} - i\Delta_p - i(\omega - \nu_4), \quad (\text{A5a})$$

$$\Upsilon_{db}(\omega) = \gamma_{db} + i\Delta_s - i(\omega - \nu_4), \quad (\text{A5b})$$

$$\Upsilon_{bc}^*(\omega) = \gamma_{bc} - i(\Delta_p - \Delta_s) - i(\omega - \nu_4) \quad (\text{A5c})$$

where $n_{db} = \rho_{dd} - \rho_{bb}$ and $n_{dc} = \rho_{dd} - \rho_{cc}$ are the population differences; $\Delta_p = \nu_p - \omega_{dc}$ and $\Delta_s = \nu_s - \omega_{db}$ are the laser detunings; ν_4 is the carrier frequency of the CARS signal taken to be ω_{ac} ; Ω_q and ν_q are the Rabi frequencies and carrier frequencies of the pump ($q = p$), Stokes ($q = s$), and control ($q = c$) lasers; and ω_{mn} and γ_{mn} are the atomic transition frequencies and decoherence rates between levels m and n ($m, n = a, b, c, d$).

APPENDIX B: COHERENCE DUE TO THE Λ SCHEME IN THE QS

The second term in Eq. (3) is responsible for the EIT-type or Λ transition and has been defined by Eq. (B5). Assuming the probe pulse comes after the pump and Stokes pulses are

gone, we have the coherence and susceptibility for the EIT case:

$$\tilde{\rho}_{ac}^{\Lambda}(\mathbf{r}, \omega) = iF(\mathbf{r}, \omega) \frac{n_{ab}I_c - n_{ac}J_b(\omega)}{J_b(\omega)\Upsilon_{ac}^* + I_c\Upsilon_{ab}(\omega)} \quad (\text{B1})$$

$$= iF(\mathbf{r}, \omega)\Upsilon_{bc}^*(\omega) \frac{n_{ab}I_c - n_{ac}J_b(\omega)}{J_c(\omega)J_b(\omega) - I_4I_c},$$

$$\chi_{\text{QS}}^{\Lambda}(\mathbf{r}, \omega) = \frac{\eta}{F(\mathbf{r})} \tilde{\rho}_{ac}^{\Lambda}(\mathbf{r}, \omega) = i\eta\Upsilon_{bc}^*(\omega) \frac{n_{ab}I_c - n_{ac}J_b(\omega)}{J_c(\omega)J_b(\omega) - I_4I_c}, \quad (\text{B2})$$

$$J_c(\omega) = \Upsilon_{ac}^*(\omega)\Upsilon_{bc}^*(\omega) + I_c, \quad (\text{B3})$$

$$J_b(\omega) = \Upsilon_{ab}(\omega)\Upsilon_{bc}^*(\omega) + I_4 \quad (\text{B4})$$

where $\eta = \frac{N_{\text{QS}}|\mathcal{D}_{ca}|^2}{\hbar\epsilon_0}$, $I_c(\mathbf{r}) = |\Omega_c(\mathbf{r})|^2$, $I_4(\mathbf{r}) = |F(\mathbf{r})|^2$, $\Upsilon_{ab}(\omega) = \gamma_{ab} + i\Delta_c - i(\omega - \nu_4)$, $\Upsilon_{ac}^* = \gamma_{ac} - i\Delta_4 - i(\omega - \nu_4)$, $\Upsilon_{bc}^* = \gamma_{bc} - i(\Delta_4 - \Delta_c) - i(\omega - \nu_4)$, and $n_{ac} = \rho_{aa} - \rho_{cc}$,

$n_{ab} = \rho_{aa} - \rho_{bb}$. The effective decoherences are $\gamma_{ab} = \frac{\Gamma_c + \Gamma_b}{2} + \gamma_{ab}^d$ and $\gamma_{ac} = \frac{\Gamma_c + \Gamma_b}{2} + \gamma_{ac}^d$ with Γ_b and Γ_c as the spontaneous emission rates, γ_{ac}^d and γ_{ab}^d are dephasing rates, and $\Delta_4 = \nu_4 - \omega_{ac}$ and $\Delta_c = \nu_c - \omega_{ab}$ are the detunings.

The dielectric function $\epsilon_{\text{QS}}^{(1)}$ in Eq. (4), susceptibility $\chi_{\text{QS}}^{(1)}$, and $\tilde{\rho}_{ac}^{(1)}$ of the QS are obtained from $\tilde{\rho}_{ac}^{\Lambda}$ as

$$\begin{aligned} \tilde{\rho}_{ac}^{(1)}(\mathbf{r}, \omega) &= \tilde{\rho}_{ac}^{\Lambda}(\mathbf{r}, \omega)|_{I_4=0} \\ &= iF(\mathbf{r}) \frac{n_{ab}I_c - n_{ac}\Upsilon_{ab}(\omega)\Upsilon_{bc}^*(\omega)}{J_c(\omega)\Upsilon_{ab}(\omega)}, \end{aligned} \quad (\text{B5})$$

$$\begin{aligned} \chi_{\text{QS}}^{(1)}(\mathbf{r}, \omega) &= \chi_{\text{QS}}^{\Lambda}(\mathbf{r}, \omega)|_{I_4=0} \\ &= i\eta \frac{n_{ab}I_c - n_{ac}\Upsilon_{ab}(\omega)\Upsilon_{bc}^*(\omega)}{J_c(\omega)\Upsilon_{ab}(\omega)}, \end{aligned} \quad (\text{B6})$$

$$\epsilon_{\text{QS}}^{(1)}(\mathbf{r}, \omega) = \epsilon_b[1 + \chi_{\text{QS}}^{(1)}(\mathbf{r}, \omega)]. \quad (\text{B7})$$

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