PHOTONICS Research

Quantum versus optical interaction contribution to giant spectral splitting in a strongly coupled plasmon–molecules system

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Vacuum Rabi splitting, which stems from a single photon interaction with a quantum emitter (a single atom, molecule, or quantum dot), is a fundamental quantum phenomenon. Many reports have claimed that using J aggregate coupling to highly localized plasmon can produce giant Rabi splitting (in scattering spectra) that is proportional to $\sqrt{N}$, where N is the number of excitons in J aggregates, and this splitting originates purely from quantum interaction between excitons and plasmons. In this work, we show that the scattering spectra are very sensitive to the surrounding matter, and the giant spectral splitting stems both from the quantum interaction of a single molecule with plasmons (Rabi splitting) and from the classical optical interaction of multiple molecules with plasmons. We develop a Lorentzian model to describe molecules and plasmon and find that the collective optical interaction is dominant in generating the giant splitting (in scattering spectra), which is also proportional to $\sqrt{N}$, upon the quantum interaction of single-molecule Rabi splitting. Simply speaking, the observed giant spectral splitting is not a pure quantum Rabi splitting effect, but rather a mixture contribution from the large spectral modulation by the collective optical interaction of all molecules with plasmons and the modest quantum Rabi splitting of a single molecule strongly coupled with plasmons.

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1. INTRODUCTION

The radiation of light from quantum emitters such as atoms, molecules, and quantum dots (QDs) can reflect both the intrinsic and extrinsic properties of quantum emitters, as it depends not only on the intrinsic quantum energy states of emitters themselves but also on their extrinsic background electromagnetic properties. The background material and structure can accelerate, decelerate, or even inhibit the spontaneous emission of quantum emitters [1]. They can also cause strong coupling of emitting light with the quantum emitter and lead to Rabi splitting in the radiation spectrum in some special situations, such as micro/nanocavity with high-quality factor (high-Q) and small modal volume [2]. The strong light–matter interactions at the single-photon level, which are described by the cavity quantum electrodynamics (QED), offer a promising means to explore quantum optical application such as single-photon switches, coherent control, and entanglement of distinguishable quantum systems [3–5]. The interactions are rooted in the strong coupling between a quantum emitter and a radiation field mode with the condition $g \gg \kappa, \gamma$, where g, κ, and γ are the coupling coefficient, cavity loss, and decay rate of the quantum emitter, respectively [6,7]. When a two-level atom is strongly coupled to a single-mode vacuum field, the excited state will split into two states and electrons travel circularly between them via the process of releasing and capturing photons [8]. This will induce two splitting peaks (so-called Rabi splitting) in photoluminescence spectra, and the interval between two peaks is called vacuum Rabi frequency Ω_R. Ideally, the best way to observe Rabi splitting is to use an atomic system, since their behaviors and characteristics are easily understood as quantum level [9–11]. However, it is hard to fix an atom in a macroscopic cavity QED system. Even if a relatively stationary trapped atom can be achieved, a decrease in the coupling strength g is inevitable, since it needs a big room for trapping [12,13]. Moreover, the dipole moment μ of atom is too small so that it needs to further decrease the mode volume V and increase the quality factor (Q) in order to observe single-atom Rabi splitting to happen in a sufficiently large optical energy density.

Recently, strong coupling has been reported for quantum well (QW) [14], QD [15–18], and J aggregates [19–22] as quantum emitters in two types of systems; one is a traditional cavity system [15–18] such as photonic crystal cavity [16,17], and the other is a plasmonic nanocavity system [19–31].

The first report of Rabi splitting in a semiconductor is based on a single QW grown in the vertical cavity surface-emitting laser with narrow absorption linewidths [14]. However, the effect has been disputed for many years as to whether it is really a QW cavity strong-coupling phenomenon or a semiclassical nonperturbative normal-mode coupling phenomenon [9,32]. A single QD, which represents an artificial two discrete energy-level system and can be located precisely in a high-Q photonic crystal cavity, shows a vacuum Rabi splitting in all directions in the photoluminescence spectra and the obvious spectral anticrossing that represents a unanimous signature of a strong-coupling regime [17]. In contrast to a single atom, the transition dipole moment of a single QD μ is very large, so it can produce giant vacuum Rabi splitting by conveniently increasing the size of the QD.

In order to further decrease the mode volume V beyond the photonic crystal cavity and operate strong coupling at room temperature, a plasmonic nanocavity offers an efficient means to transport and localize the energy of light into some nanoscale regions called hot spots, where the electromagnetic field intensity is enhanced by many orders of magnitude upon the incident light [33–38]. Then single-photon energy can produce a sufficiently large energy density and allow the possibility of strong coupling to occur. Since it is hard to match the size of a single QD in a plasmonic nanocavity, molecules are considered instead as an excellent kind of quantum emitter [39]. In experiment, it is far more difficult to get strong coupling at the single-molecule level, as molecules will be easy to aggregate (so-called J aggregates with high transition dipole moment). Recently, many works about strong exciton-plasmon coupling between J aggregates and various types of surface plasmon have appeared [19–22]. Using open silver nanoprisms coupling to molecular aggregates of TDBC dye (a cyanine dye), some authors reported that they could obtain a coupling rate $g = 140$ meV and estimated the number of molecules that were regarded as contributing to Rabi splitting in quantum level is ≈1000 [20]. To avoid molecular aggregates, some researchers have placed methylene-blue molecules into cucurbit (7) uril, which can accommodate only one molecule. When the plasmonic nanocavity system of nanoparticle-on-mirror (NPoM) is partially filled with these composite molecules, they claimed to see the Rabi splitting of $\Omega_R = 380$ meV and achieve single-molecule Rabi splitting of $\Omega_R = 80-95$ meV by statistically estimating a method based on the dipole moment $\mu = 3.8$ D of molecules [22]. All these works estimate Rabi splitting of a single molecule based on $g = \sqrt{N}\mu E_{\text{vac}}$ [N is the number of dipoles (molecules); E_{vac} is the vacuum field], but it is not clear whether one can directly translate the spectral splitting into the Rabi splitting in quantum energy level of electrons in molecules. In this work, we will reconsider this interesting problem by deeply examining all relevant physical processes and mechanisms of plasmon–molecule interaction in these practical experimental systems. Eventually we hope to answer several interesting questions as to whether the observed spectral splitting is equal to Rabi splitting in the internal energy level, what mechanisms contribute to the spectral splitting, and what their specific contributions are.

2. RESULTS AND DISCUSSION

A. Analysis of Scattering and Fluorescence

Note that in all the above experiments [19–22], researchers have adopted a model where the observed spectral splitting in scattering, reflection, absorption, or transmission spectra is equivalent to the quantum Rabi splitting, and then tried to use classical technique [40] to describe quantum behavior. Intrinsically, quantum Rabi splitting stems from energy-level splitting of a single atom or molecule (more rigorously, their outer electron energy state). As indicated by the upper panel of Fig. 1(a), when the atom interacts with the vacuum field, the atomic excited state will split up and down by $\hbar\Omega_R/2$ so that it forms the splitting states $|e,+\rangle$ and $|e,-\rangle$, respectively. This energy splitting will be reflected by the famous anticrossing feature in the plot of eigenenergy of the atom against the detuning of probe light energy, as illustrated in the lower panel of Fig. 1(a). Extrinsically, the quantum phenomenon will be exhibited from a single Lorentzian peak to two adjacent splitting peaks in the photoluminescence spectra, as depicted in Fig. 1(b). Importantly, photoluminescence spectra can exactly reflect the energy-level splitting of a single atom and be immune to the environmental variety. In addition, the splitting will be small or modest [12,13], e.g., on the scale of μeV, due to the small dipole moment of the single atom. However, for such J aggregate–plasmon experiments [19–22], it is not appropriate to use spectral splitting to represent the quantum Rabi splitting, since these systems will be much more complex than was initially thought. In fact, the optical spectrum, such as the scattering-light spectrum, will be easily modulated by the geometric and physical characteristics of the background matter surrounding the atom or molecule, and it will carry both quantum and optical interaction information for this complex system. For plasmon coupling to a J aggregate that contains many excitons, the system is so complicated that it is very difficult, or even impossible, to use only the scattering light spectrum to faithfully probe the pure internal quantum state of an atom or molecule that the well-established photoluminescence

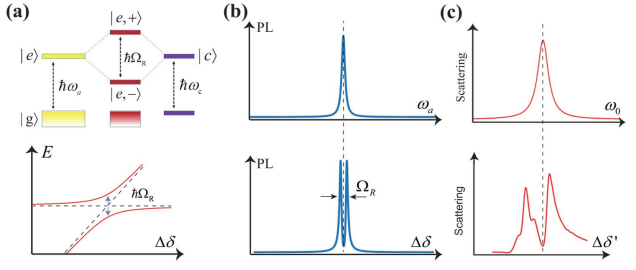

Fig. 1. Schematic illustration of energy level and spectra in emitter-field coupling system. (a) Upper panel, energy-level splitting in single atom interacting with optical field. Here ω_a is the transition frequency of the atom and ω_c is the resonance frequency of the field; $\hbar$ is the reduced Planck constant; $|e\rangle$ and $|g\rangle$ mean the atom is in the excited state and ground state, respectively; $|c\rangle$ means cavity resonance state. Lower panel, anticrossing for Rabi splitting. $\Delta\delta$ is the frequency detuning between atom and field. (b) Quantum Rabi splitting of single atom in photoluminescence spectra; (c) spectral splitting in the system, which consists of plasmon interacting with the J aggregate. ω_0 is the transition frequency of the molecular emitter, and $\Delta\delta'$ is the frequency detuning between the J aggregate and the field.

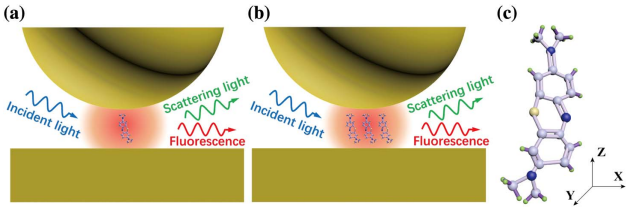

Fig. 2. Schematic illustration of methylene blue molecules embedded in the nanogap of an NPoM structure and their quantum and optical interaction with plasmons excited by incident light. (a) A single methylene blue molecule placed in the hot spot (with the maximum electric field enhancement) of the nanogap, as depicted by the red circle. The Rabi splitting due to plasmon–molecules strong coupling can be reflected by the scattering light and fluorescence, but the weak fluorescence will be absorbed by plasmonic structure and become hard to detect. (b) In multi-molecule level, the real Rabi splitting can only be reflected by fluorescence, while the scattering light involves not only the Rabi splitting but also complex optical interaction. (c) Chemical structure of methylene blue molecule.

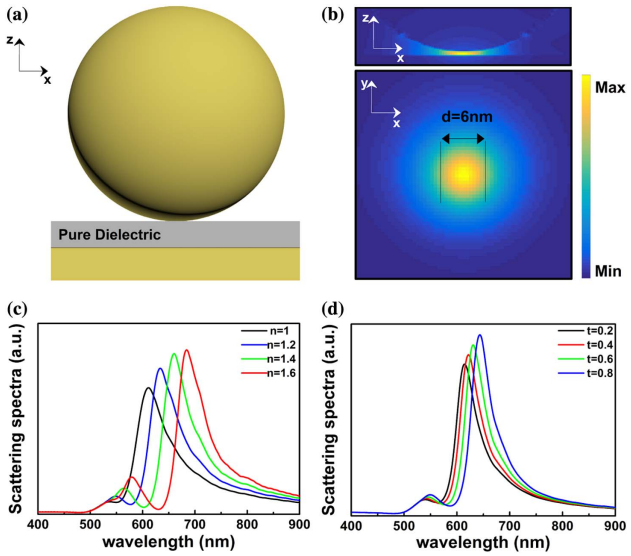

Fig. 3. Engineering plasmonic resonance in an NPoM structure by changing the physical and geometric properties. (a) Schematic diagram of the NPoM structure; (b) electric field intensity distributions of NPoM in the vertical $x-z$ plane (top) and horizontal $x-y$ plane (bottom), respectively. The diameter of the hot spot is 6 nm as shown by the $x-y$ plane field pattern. (c) Simulated scattering spectra when the plasmonic nanogaps are filled with pure dielectric films whose refractive index varies from 1.0 to 1.6. The plasmonic resonance peak redshifts from 610 to 684 nm (from 2.03 to 1.81 eV in energy). (d) Simulated scattering spectra with the thickness of pure dielectric film changing from 0.8 to 0.2 nm, showing plasmon resonance peak blueshifting from 643 to 614 nm (from 1.93 to 2.02 eV in energy).

spectra can carry. Unfortunately, as illustrated in Fig. 1(c), many research works have regarded such a giant spectral splitting that stems from a J aggregate interacting with plasmon in the scattering spectrum as quantum Rabi splitting.

Specifically, the plasmon–exciton Rabi splitting is observed by measuring the scattering (including either reflection, or absorption, or transmission) spectrum and examining the spectral modulation feature (in particular, spectral peak shift and splitting). As illustrated in Fig. 2, when shining an incident light upon the plasmon–molecules system, several physical processes will take place simultaneously. The first process is the direct elastic scattering of light from both the molecules as a whole and the plasmonic nanogap as a whole. The second process is the strong coupling of the plasmon nanogap mode with the molecular exciton (modeled as a two-level quantum emitter) and the associated secondary inelastic scattering of light. The third process is the fluorescence of molecule (absorption of pump light and re-emission at lower frequency). The fluorescence is a sign of molecular internal state and thus can exactly represent the molecular energy-level splitting. In this regard, fluorescence is an excellent tool to examine vacuum Rabi splitting. On the other hand, the scattering light is the feedback from the molecular external state in response to the incident light, and thus can also reflect the Rabi splitting at the single-molecule level. Therefore, the single-molecular Rabi splitting can be reflected by either fluorescence or scattering light [Fig. 2(a)].

Yet, things become much more complicated when multiple molecules interact with plasmons. In the multi-molecule level [Fig. 2(b)], the potential barrier for internal electrons, which contribute to forming molecular excitons, between molecules is so high that every molecule should be regarded as an independent individual and would not affect each other at the quantum level. It means the energy level splitting would not further expand even when adding more and more molecules [9]. In other words, the fluorescence of a multi-molecule is almost the same as that of a single molecule, except peak power. In contrast, because scattering light is far more sensitive to the surrounding matter of molecules, adding molecules will alter the scattering pattern due to the strong optical interaction and coupling between molecules and surrounding plasmons [33]. So far, many reports have regarded the scattering spectra of a multi-molecule system as the faithful signature of quantum strong coupling, and overwhelmingly ascribed the giant splitting in the scattering spectra to quantum Rabi splitting. However, as there exist many physical processes simultaneously in the plasmon–molecules coupling system, and they all can make a contribution to the spectrum variation of scattering light, it is too early to translate the observed spectral splitting phenomena into a pure quantum mechanism. Therefore, it remains a largely unresolved and controversial issue whether the plasmon–molecules system can realize strong light–matter interaction in a quantum optics level, whether the observed giant Rabi splitting purely originates from this quantum strong coupling effect, and how to understand and extract the exact equivocal number of excitons in J aggregates contributing to the giant splitting [20].

As the first step to examine and analyze the major physics underlying the plasmon–molecules coupling system, we investigate how the surrounding matter in the nanogap affects plasmonic resonance in scattering spectra by performing three-dimensional finite-difference time-domain (3D-FDTD) simulations. When the gap of NPoM is filled with 1 nm thickness of the pure dielectric, which is not strongly dispersive material [Fig. 3(a)], the plasmon resonance peak varies from

610 to 684 nm, with the refractive index of the dielectric changing from 1.0 to 1.6 [Fig. 3(c)], respectively. This means that the changing of the physical properties of the nanogap will greatly affect plasmon resonance. If we alter the thickness of the pure dielectric (refractive index is 1.4) from 0.8 to 0.2 nm, the plasmon resonance peak varies from 643 to 614 nm [Fig. 3(d)]. This illustrates that plasmon is sensitive to the geometric properties of matter. Moreover, if the dielectric contains the characteristics of resonance, which means that it is strongly dispersive, the interaction between dielectric and plasmon will be greatly enhanced. Previous study showed that it is feasible to dramatically modify the scattering spectra of a spherical metallic nanoparticle by precisely placing a single QD in its proximity [41]. One can control the far-field scattering spectra through manipulating the near-field coupling between plasmon and a single QD so that a double-peak feature appears in the scattering spectra. When there are several independent scattering individuals that contain properties of resonance in hot spots of NPoM [Fig. 3(b)], the optical signals stemming from the interaction system not only reflect the individual scattering of the molecules but also involve the multiple scattering between them and plasmons. The former has a dominant contribution from the molecule–plasmon quantum interaction, while the latter has a pure optical interaction origin. In other words, the giant splitting of the molecules–plasmon system in scattering spectra not only contains quantum interaction, which points to single-molecular Rabi splitting, but also contains multi-molecule-level optical interaction. Such a physical insight suggests we should be more careful and conservative when looking at the observed giant spectral splitting and ascribing it to quantum Rabi splitting. Keeping this in mind, in the following, we will quantitatively clarify the quantum and optical interaction for the spectral splitting of the system consisting of single molecule/N molecules and plasmon, respectively. This issue is of enormous importance for clarifying the true physics behind a strongly coupled plasmon–molecule system and paving a right path for quantum optics applications, such as quantum information and single-photon devices [42,43].

B. Quantum Interaction

To address the plasmon–molecule quantum interaction, let us consider the model case that a two-level atom (here referring to a molecular exciton) is in a completely closed box. If the box is small enough, there are some discrete electromagnetic modes that are far apart so that the transition frequency of the two-level atom can only match one of the discrete modes. When the atom interacts with the single-mode field, the Hamiltonian of the coupled light–atom system is well established [44] and reads

$$H = H_0 + H_1 = \frac{1}{2}\hbar\omega_a\sigma_z + \hbar\omega_c\alpha^\dagger\alpha + \hbar g(\sigma^+\alpha + \sigma^-\alpha^\dagger). \tag{1}$$

Here ω_c and ω_a are the mode frequency of the quantized field and the transition frequency of the atom, respectively; $\alpha^\dagger$ and α are the creation and annihilation operator of the photon, respectively; σ_z is the Pauli operator; σ^+ and σ^- are the raising operator and lowering operator of the atom, respectively; and g is the coupling strength between the atom and mode field.

In Eq. (1), the first two terms reflect the free atom and the mode-field Hamiltonian, respectively, and the last term $H_1 = \hbar g(\sigma^+\alpha + \sigma^-\alpha^\dagger)$ is the interaction Hamiltonian between atom and field. The interaction Hamiltonian in the interaction picture is $H_1' = e^{iH_0t/\hbar}H_1e^{-iH_0t/\hbar}$. Considering the wave function [45] $|\varphi(t)\rangle = \sum_n\{C_{a,n}(t)|a,n\rangle + C_{b,n}|b,n\rangle\}$ and combining it with a Schrödinger equation, we can get the Rabi oscillating frequency from $C_a(t)$ or $C_b(t)$ as

$$\Omega_{\text{quantum}} = \sqrt{\delta^2 + 4g^2(n+1)}. \tag{2}$$

Here n (0, 1, 2, …) is the number of photons, which exhibit the Jaynes–Cumming ladder [8], and $\delta = \omega_c - \omega_a$ is the detuning of atom and field. When the detuning $\delta = 0$ and the box is in vacuum (which means $n = 0$), the vacuum Rabi splitting is $\Omega_R = 2g$, where $g = \mu E_{\text{vac}}$ is proportional to the transition dipole moment of atom $\mu \sim \langle a|x|b\rangle$ and the vacuum field. It means the size of the atom/molecule and the energy density of the field determine the splitting. Actually, Ω_R represents the quantum interaction strength between a single atom and a single-mode field. To show how strong an interaction a full-size molecule can produce, 3D-FDTD simulations are performed on the NPoM structure [22,35] and a 1 nm methylene blue molecule [22]. The optical response of the molecule can be described by the Lorentzian model $\varepsilon(\omega) = \varepsilon_\infty + f\omega_0^2/(\omega_0^2 - \omega^2 - i\gamma_0\omega)$, where $f = 0.27$ is the reduced oscillator strength [22,46], $\omega_0 = 2.03$ eV is the molecular transition energy, $\varepsilon_\infty = 1.96$ is the high-frequency component, and $\gamma_0 = 85$ meV is the molecular linewidth [22]. The molecule is schematically shown in Fig. 2(c). By constructing the coupled molecule–plasmon system, we use Au nanosphere of 40 nm diameter on an Au nanofilm of 80 nm thickness, separated by a 1 nm single molecule [Fig. 2(a)]. When the single molecule is in optical resonance with the plasmon, a coupled hybrid system exhibiting mode splitting into upper ($\omega_+ = 605$ nm) and lower ($\omega_- = 630$ nm) hybrid plasmon–molecule branches is formed [Fig. 4(a)]. This yields a Rabi frequency of $\Omega_R = 2g = 79.4$ meV in the scattering spectra.

In order to obtain a clearer physical picture and determine whether the plasmon–molecule system is strongly coupled

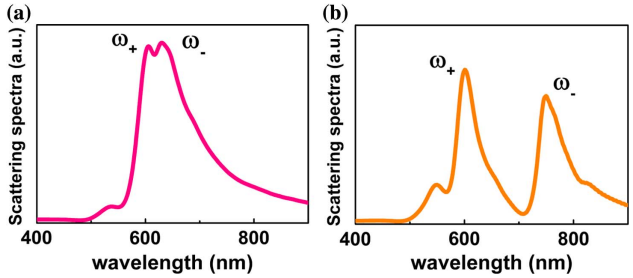

Fig. 4. Vacuum Rabi splitting in a single molecule–plasmon system, when a methylene blue molecule is in resonance with plasmon (detuning $\delta = 0$). (a) Scattering spectrum of plasmon coupling to a single molecule with radius of 0.5 nm. The hybrid plasmon–exciton branches, ω_+ and ω_- are separated by 79.4 meV. (b) Scattering spectrum of plasmon coupling to a huge molecule with diameter of 6 nm. The interval of two peaks splitting is 395 meV.

quantum mechanically, we describe the molecule–field interaction by the dressed-states method. If the box is in vacuum, the eigenvalues of this system are

$$\omega_{\pm,\text{quantum}} = \frac{1}{2}(\omega_0 + \omega_c) \pm \sqrt{g^2 + \frac{\delta^2}{4}}. \quad (3)$$

Since plasmon is sensitive to the surrounding matter, we can calculate the plasmon resonance ω_c and plasmon linewidth γ_c from Eq. (3). The strong-coupling regime can be defined as the situation when the linewidth of coupled states is much smaller than the splitting so that it is actually experimentally visible and can produce a remarkable anticrossing feature. It needs to satisfy the condition of $\Omega_R/\gamma_c > 1$. We find Ω_R/γ_c ($\gamma_c = 49.3$ meV) ~1.61—a very high number for the plasmonic system, which is a rather strict criterion confirming whether the system satisfies the strong-coupling condition [20]. Moreover, we can directly calculate the coupling strength $g = \mu_m E_{\text{vac}}$ by estimating the molecular dipole moment μ_m and the single-photon vacuum field amplitude $E_{\text{vac}} = \sqrt{\hbar\omega/(2n^2\varepsilon_0 V)}$, where ω is the resonance frequency of plasmonic nanocavity, and n is the effective refractive index of the cavity. In the theoretical calculation of the coupling strength, we have assumed that the transition dipole moment of the methylene blue molecule orients parallel to the electromagnetic field vector, and also parallel to the orientation direction of the molecule. Here the mode volume is calculated to be $V = 23$ nm^3. Following Refs. [20,47], the dipole moment can be described as $\mu_m = \sqrt{3\hbar\sigma_m\gamma_0\varepsilon_0\lambda/4\pi^2}$, where $\hbar$ is the Planck constant, γ_0 is the decay rate of the molecule, and λ is the wavelength of the molecule. The absorption cross section of the molecule is calculated by the 3D-FDTD simulation, which shows $\sigma_m = 2.55991 \times 10^{-20}$ m^2. Substituting all the parameters into the formula, we can get the dipole moment $\mu_m = 3.59$ D, which is close to the experimental result [22,46]. We then find the theoretical value of Rabi frequency is $\Omega_R = 2g = 85$ meV, which is also very close to the data assessed from the scattering spectra [Fig. 4(a)]. Based on these results, we find $\Omega_R/\gamma_c \sim 1.7$ and thus can determine the system is going well into the strong-coupling regime.

In the above, we consider a single molecule with a modestly large exciton dipole moment that has already been comparable with a traditional semiconductor QD. If one wishes to further promote the response intensity, a natural way is to adopt an even larger molecule (huge molecule) with a very large exciton size and strength. However, in practice this is not an easy thing. Up to now, achieving strong coupling between a true single molecule and plasmon in experiment is very difficult since it is hard to avoid molecule aggregation and also hard to trap a single molecule in hot spots. Many researchers use a system that consists of highly localized plasmon and J aggregates (consisting of several or tens of molecules in aggregation, and each molecule has an exciton in response to light) to demonstrate strong coupling. In these experiments they have indeed successfully observed giant spectral splitting in scattering light, popularly called giant Rabi splitting, and then managed to estimate how many excitons in J aggregates contribute to this Rabi splitting. However, it is worthwhile to study the situation more carefully and deeply before a final judgment can be cast to settle the issue in the history of quantum physics.

Although the physics underlying the spectral splitting for a single atom/molecule/QD coupling with a dielectric/plasmonic nanocavity mode field has been quite clear and is ascribed to Rabi splitting (a pure quantum interaction effect), things become problematic when one further adds molecules into the system with the hope of expanding the energy level splitting in molecular internal states (and thus the optical spectral splitting) but still ascribes the spectral splitting to the quantum mechanism. When such splitting occurs in a many-atom system, analogous behaviors are classical, since removing one atom has little effect [9]. This is the regime of nonperturbative coupling, rather than the strong-coupling regime [32]. To distinguish between the classical behavior of a many-atom system and the genuine quantum behavior of a single-atom system, it is necessary to perform nonlinear experiments. The situation is the same for a many-molecule system. In practical molecule aggregates, there is no or only very weak quantum interaction between different molecules. Actually, J aggregates are similar to QDs in a sense. However, J aggregates consist of a number of small excitons, and each exciton is described by a dipole moment μ_m (in response to excited light). From the popular viewpoint of the strong-coupling research community, the J aggregate is looked upon as a huge effective molecule that is expected to realize giant Rabi splitting, with the overall optical response to excited light described by a total dipole moment μ_h.

Following such a picture, we take a model where a huge molecule is used to correspond to J aggregates. The molecule is similar to a round cake with a 3 nm radius and 1 nm thickness, and has a transition frequency $\omega_0 = 1.86$ eV. When the huge molecule is placed into the plasmonic nanogap, a coupled hybrid system would exhibit significant splitting mode with upper ($\omega_+ = 604$ nm) and lower ($\omega_- = 748$ nm) branches [Fig. 4(b)]. This yields a Rabi frequency of $\Omega_{\text{huge-mole}} = 2g = 395$ meV. This simulation result approximates to the experimental data as presented in Ref. [22], but the underlying physical interpretation is different. By calculating the absorption cross section of the huge molecule as $\sigma_h = 4.58204 \times 10^{-19}$ m^2, we can obtain the dipole moment as $\mu_h = 15.8$ D. Based on these two parameters, we can extract the theoretical value of Rabi frequency as $\Omega_{\text{huge-mole}} = 2g = 398$ meV, which is close to the simulation result displayed in Fig. 4(b). This means that the model of the huge dipole moment μ_h can indeed interpret the experimental observation of giant spectral splitting in Ref. [22], where it was called Rabi splitting and obviously ascribed to the pure quantum mechanical interaction of molecules with plasmon. Unfortunately, such a huge molecule exhibiting a single huge exciton response to a single photon is hard to be found in practice, even though in theory it can exhibit a pure quantum behavior. On the other hand, our further calculation shows that this increase of Rabi splitting could not go on without limit by continuing to increase the size of the molecule, due to the finite size of the hot spot compared with the big molecule, as shown in Fig. 3(b). In practice, however, the smaller the big molecule, the more likely it will exhibit quantized-field effects [9].

C. Optical Interaction

To date, the optical interaction between molecules in a plasmon environment has not been considered in the regime of strong-coupling physics. The spectral splitting was merely ascribed to the quantum interaction effect of Rabi splitting in many past works, since experimental observations in these works seemed to agree well with the model that each exciton in J aggregates makes a quantum contribution to the Rabi splitting. Such a model originates from well-known Tavis–Cummings model, which deals with many-emitter systems; however, the climb ladder of many-emitters is not the same as that of the single-emitter in many rungs. According to this theory, the original state in the second rung will split into three states, and this corresponds to adding one photon into a QED system [32]. Therefore, such a quantum theory is far away from the original physical scene of quantum Rabi splitting. More remarkably, all these quantum theories cannot handle the propagation of radiation photons in the highly complicated plasmonic nanostructures and the corresponding spectral splitting observed by an external experimenter, which in principle can only be fully understood by combining quantum mechanics for light–atom interaction with classical electrodynamics and optics for light propagation. These insights suggest that one should try other more reasonable alternative physical models to explain experimental observation of giant spectral splitting (not necessarily Rabi splitting).

The optical interaction model is a natural choice, where each J-aggregate molecule is modeled as an exciton in quantum optical interaction with plasmon, and multiple J-aggregate molecules are naturally modeled as multiple individual excitons that are classically optical coupling not only with plasmon but also with each other. This collective coupling with plasmon is responsible for the overall optical scattering spectrum observed experimentally. Like the plasmon hybridization where the plasmon response of a metal nanostructure can be seen as the result of an interacting system that collects all individual plasmons coming from simpler geometries [34,38,48], the collective optical interaction in the plasmon–molecules strongly coupling system is a kind of scattering hybridization that comes from the interacting system collecting all individual molecule–plasmon scattering units optically.

To be more quantitative, we describe this optical interaction by a simplified model regarding plasmon resonance and molecules as two kinds of Lorentzian oscillators interacting with each other. It is then important to first determine the optical response of these two kinds of oscillators. Assuming the electromagnetic field is harmonic at frequency ω, the polarizability of an oscillator can be described by [49] $\alpha = \frac{fe^2}{m(\omega_\hbar^2 - \omega^2 + i\gamma\omega)}$. Here γ is the decay rate, $\omega_\hbar$ is the frequency of the harmonic oscillator, and $f = 2m\omega_\hbar\mu^2/3\hbar e^2$ is the oscillator strength, where $\mu = \langle\psi_2|x|\psi_1\rangle$ is the dipole moment. Suppose a unit volume comprises N dipole moments (harmonic oscillators); then the total polarization of the medium is $N\alpha E = \varepsilon_0\chi E$, where E is the electric field. The linear susceptibility of this multi-oscillator polarization system can be obtained as $\chi = \frac{fNe^2}{m\varepsilon_0(\omega_\hbar^2 - \omega^2 + i\gamma\omega)}$.

Now, we model the plasmon with resonance frequency ω_1 and linewidth γ_1 as another harmonic oscillator that can be described by the Lorentzian model; then the susceptibility of plasmon is given by

$$\chi_1(\omega) = \frac{e^2}{m\varepsilon_0(\omega_1^2 - \omega^2 + i\gamma_1\omega)}. \tag{4}$$

In Eq. (4), $f = 1$, since the oscillator is not a two-level system. As to molecules, we use N harmonic oscillators with frequency ω_0 and linewidth γ_0 to represent N molecules. Their optical response is described by the following Lorentzian model of susceptibility as

$$\chi_2(\omega) = \frac{f_0Ne^2}{m\varepsilon_0(\omega_0^2 - \omega^2 + i\gamma_0\omega)}. \tag{5}$$

When these two kinds of oscillators interact with each other in the plasmon–molecules system of NPoM, they should meet the surface plasmon dispersion condition,

$$k^2 = k_0^2\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1 + \varepsilon_2}. \tag{6}$$

Here k is the surface plasmon wave vector at the molecule–metal interface, which is used to approximately describe the molecule–NPoM system. Based on the relation of $\varepsilon = 1 + \chi(\omega)$, we can obtain

$$\kappa = \chi_1(\omega) + \chi_2(\omega) + \chi_1(\omega)\chi_2(\omega), \tag{7}$$

where $\kappa = (|\varepsilon_1 + \varepsilon_2|k^2 - k_0^2)/k_0^2$ is independent of frequency ω, since $\varepsilon_1 + \varepsilon_2$ is close to a constant within the range of ω. In Eq. (7), the first two terms are two kinds of oscillators in free evolution, and the last term $\chi_1(\omega)\chi_2(\omega)$ reflects their interaction. Based on the condition of $\gamma \ll \omega$ and considering ω and ω_1 being close to ω_0, we can obtain

$$\kappa = \frac{C}{2\omega_0(\omega_1 - \omega)} + \frac{NCf_0}{2\omega_0(\omega_0 - \omega)} + \frac{NC^2f_0}{4\omega_0^2(\omega_0 - \omega)(\omega_1 - \omega)}, \tag{8}$$

where $C = e^2/m\varepsilon_0$ is a constant term. Notice that $\omega_0 \gg C$; if the N is large enough, the solution to Eq. (8) is

$$\omega_{\pm,\text{optical}} = \frac{\omega_0 + \omega_1}{2} \pm \sqrt{\frac{N\omega_0\mu^2}{3\kappa\varepsilon_0\hbar} + \frac{(\omega_0 + \omega_1)^2}{4}}. \tag{9}$$

Furthermore, if the molecules and plasmon are in resonance, the spectral splitting is

$$\Omega_{\text{optical}} = \sqrt{\frac{4N\omega_0\mu^2}{3\kappa\varepsilon_0\hbar}}. \tag{10}$$

The splitting is proportional to $\sqrt{N}$ and to the dipole moment μ. This law of spectral splitting is in good accordance with the prediction of $\Omega_{\text{quantum}} = 2\sqrt{N}\mu E_{\text{vac}}$ as made by the popular quantum strong-coupling theory [20,22]. On the other hand, notice that Eq. (7) is similar to Eq. (1). However, these two equations have different physical pictures. The last term of Eq. (1), $\hbar g(\sigma^+\alpha + \sigma^-\alpha^\dagger)$, which exhibits the cyclical process of spontaneous radiation of a single atom/molecule/QD in single-mode field system, is quantum interaction, while in Eq. (7) the term $\chi_1(\omega)\chi_2(\omega)$, which reflects the process whereby molecules scatter the incident light in a plasmonic system, is optical interaction. In Eq. (10), the formula $\sqrt{N}$ indicates that there is an optical coherent interaction between

molecules so that they respond to a plasmonic field collectively and constructively. In other words, when a group of N molecules interacts with a common light field, the field will correlate the behaviors between dipole moments. These dipole moments working in coordination with plasmon will enlarge the spectral splitting (for simplicity still called Rabi splitting) into $\sqrt{N}\Omega_R$, where Ω_R is single molecule spectral splitting (a true Rabi splitting).

The collective scattering effect is similar to superradiance [50], which is the radiation enhancement effect causing the group of N molecules to emit light as a high-intensity pulse with rate $\propto N^2$. The difference is that optical interaction enlarges the spectral splitting, while superradiance increases the spectral power. In order to demonstrate this concept, we use identical methylene blue molecules with 1 nm diameter and set two molecules, five molecules, and thirteen molecules into the NPoM [Figs. 5(d)–5(f)], respectively. In this case, each molecule should be seen as a single individual emitter. Compared to the single molecular Rabi splitting of $\Omega_{\text{quantum}} = 79.4$ meV, the spectral splitting Ω_{optical} will enlarge with the number of molecules increasing [Figs. 5(a)–5(c)]. In Fig. 5(g), the simulation splitting data are very close to theoretical curve $\Omega_{\text{optical}} = \sqrt{N}\Omega_R$, where Ω_R is the Rabi splitting of a single molecule. Furthermore, we find that the larger the N, the more accurate the splitting is proportional to $\sqrt{N}$. In contrast, the splitting in the molecular fluorescence spectrum is the real Rabi splitting and would not change with the number of the molecules [see red horizontal line in Fig. 5(g)]. By increasing the size of the molecule, the splitting will further enlarge in accordance with Eq. (10), as the big molecule, with a larger dipole moment μ in Eq. (10), will be stronger in response to the incident light and heighten the scattering effect. The larger the molecule, the stronger the optical interaction. This condition cannot apply to the situation of quantum optics, because the smaller the dipole moment, the stronger the quantum effect [9].

The above analysis clearly indicates that an apparent spectral splitting appearing in experimental data of scattering spectrum observation could be interpreted equally well by taking different physical models (quantum interaction versus optical interaction) and making theoretical calculations. The giant Rabi splitting, or more precisely the giant spectral splitting, which is popularly ascribed to the huge quantum interaction rooted in the strong coupling between plasmon and multiple J-aggregate molecules, could actually find its physical origin in both quantum mechanical interaction and classical optical interaction. A pure quantum mechanical interaction that governs the well-established single atom/molecule Rabi splitting is hard to directly translate into a multiple-molecule system, since these molecules could not form a single giant quantum emitter like semiconductor QDs, because the very hard potential barrier would prohibit tunneling and free movement of electrons among all these molecules and forming a huge single exciton to enable the observed giant spectral splitting. A more reasonable and solid physical model would be that quantum mechanical interaction with a plasmon would still govern the single-molecule optical response and create a small or modest Rabi splitting, while classical optical multiple scattering among

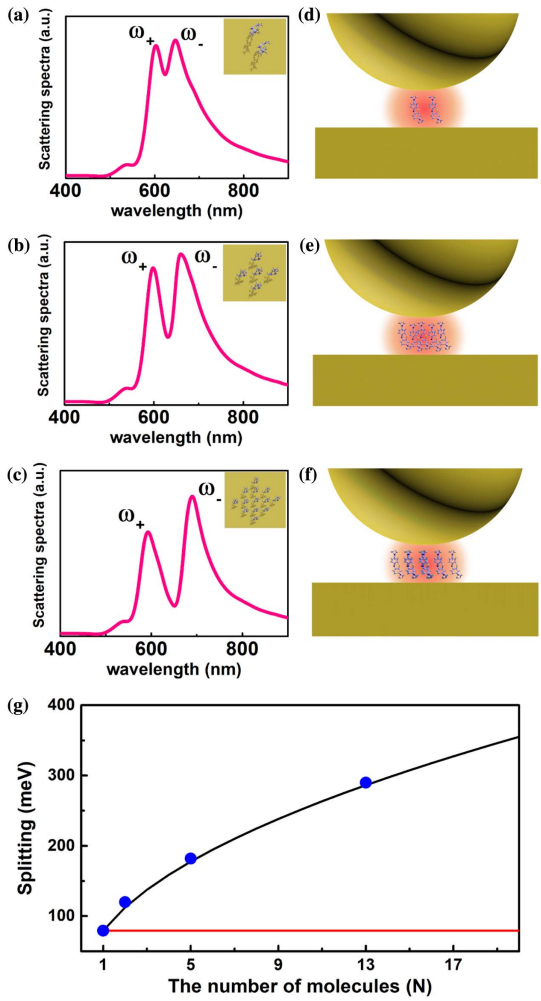

Fig. 5. Scattering spectra of an optical interaction system that consists of multiple methylene blue molecules coupling to plasmon. (a) Two molecules, the interval of the splitting peaks $\Delta = 120$ meV ($\omega_+ = 602.6$ nm and $\omega_- = 640$ nm); (b) five molecules, $\Delta = 182$ meV ($\omega_+ = 597.6$ nm and $\omega_- = 655$ nm); (c) thirteen molecules, $\Delta = 290$ meV ($\omega_+ = 591$ nm and $\omega_- = 686$ nm); (d)–(f) schematic diagram of placing two molecules, five molecules, and thirteen molecules into the NPoM, respectively; (g) calculated spectral splitting in dependence on the number of molecules (blue dots) as compared with the theoretical curve (black line) of optical interaction, which points to splitting with the number of molecules increasing $\Omega_{\text{optical}} = \sqrt{N}\Omega_R$. Red horizontal line represents the real Rabi splitting when considering only the molecular fluorescence spectra.

different molecules and their collective strong coupling with plasmon would induce a giant spectral splitting in the scattering spectrum. In this regard, the popularly observed and so-called giant Rabi splitting is the mixture of quantum and optical effect.

Strictly speaking, the vacuum Rabi splitting, a signature of internal energy-level splitting of atom/molecule, is a fundamental quantum phenomenon. In a quantum strong-coupling mechanism, fluorescence (or photoluminescence for semiconductor QDs) will be circularly released and absorbed by a single molecule. Since adding molecules would not enlarge the energy-level splitting, it is expected that the splitting will be

the same as the single molecular splitting in fluorescence spectra [Fig. 5(g), red horizontal line]. Fluorescence or photoluminescence is the best choice to reveal the quantum mechanical energy-level splitting, as it is more stable and robust and immune to environmental impact. Unfortunately, it is difficult to make such an experimental observation in practice due to the strong absorption of light signals by plasmonic structures.

3. CONCLUSIONS

In conclusion, we have analyzed the physical mechanism underlying the giant spectral splitting observed in many experiments for strongly coupled molecule–plasmon systems. We show that at the single-molecule level, the quantum strong-coupling regime is reached, and Rabi splitting is responsible for the spectral splitting. Yet, at the multi-molecule level, the giant splitting in scattering spectra is not a pure quantum interaction effect, but rather a mixture of single-molecule quantum interaction effect and multiple-molecule optical interaction effect, with the latter dominating the former. We have constructed an approximate physical model by regarding plasmon and molecules as two kinds of harmonic oscillators described by the Lorentzian model for optical interaction. The explicit solution shows the spectral splitting is proportional to $\sqrt{N}$ and to the dipole moment μ, in agreement with experiment and also with the quantum mechanical Rabi splitting model predicted for a huge molecule made up of multiple molecules. This study clearly indicates that in a strongly coupled system of complicated quantum emitters like molecule and nanoscale plasmons with complicated geometric configurations, and under practical optical excitation condition and configuration, there may exist simultaneously more than one physical effect of equal importance in contribution to an apparent experimental phenomenon like the so-called giant Rabi splitting in a molecule–plasmon system. As a consequence, it is a general rule-of-thumb that in these strongly coupling plasmon–molecule systems, the observed spectral splitting is not equal to the Rabi splitting in the internal quantum energy level of electrons in molecules. These studies indicate that nature behaves more complicatedly than it hints at a first glance, and therefore, one should develop a broad vision when looking into light–matter interaction at nanoscale in order to get deep physical insight and find the most important key to a seemingly simple optical phenomenon.

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