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Role of Nanocavity Plasmons in Tunneling Electron Induced Light Emission on and near a Molecule

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By using a microscopic quantum model, we study theoretically different roles of nanocavity plasmons in scanning tunneling microscope (STM) induced light emission upon selective initial excitation of molecules or plasmons. The time evolution and spectroscopic properties of the emission from the coupled plasmon-molecule system in each case are studied using time-dependent quantum mater equations. When the STM tip is placed on the molecule to ensure direct carrier injection induced molecular excitation, the major role of the plasmons is to enhance the molecular emission via increasing its radiative decay rate, resulting in sharp molecule-specific emission peaks. On the other hand, when the STM tip is located in close proximity to the edge of the molecule but without direct carrier injection into the molecule, the role of the plasmon-molecule coupling is to cause destructive interferences between the two quantum objects, leading to the occurrence of Fano dips around the energy of the molecular exciton in the plasmonic emission spectra.

Key words: Scanning tunneling microscope induced luminescence, Plasmon enhanced spectroscopy, Fano resonance, Quantum master equation

I. INTRODUCTION

Scanning tunneling microscope (STM) offers a unique platform for characterizing and manipulating light-matter interactions at the atomic scale. By controlling charge injection with sub-nanometer spatial precision and simultaneously recording the frequency-resolved emission spectrum, the electronic and vibrational properties of a single molecule can be revealed [1–3]. It is well recognized that nanocavity plasmons (NCP) play an important role in STM induced molecular emission, including enhancing the emission intensity, reshaping the spectral profile and even generating new emission channels [3–10].

Nevertheless, the role of NCP in the excitation process of molecules is still under debate. For example, while it is proposed that light emission from molecules can be attributed to resonant carrier injections into molecular orbitals [1, 11] and the major role of plasmons is to enhance the emission rate rather than to directly excite the emitter [6–8], it is also argued that the NCP excited by inelastic tunneling electrons can act as a local light source to excite the molecules via their mutual electromagnetic interactions [5, 12]. However, in recent experiments where the STM tip was placed in close proximity to the edge of a single molecule to prevent direct carrier injection into the molecule and therefore only the NCP can be excited by the tunneling electrons initially, only molecule-modified NCP emission with asymmetric Fano dips, rather than sharp molecular peaks, were observed [13, 14]. Consequently, the role of NCP in STM induced light emission from molecular junctions still remains to be further studied.

In this paper, we study theoretically the time evolution and spectral properties of the emission from the coupled plasmon-molecule system using time-dependent quantum master equations. To mimic STM induced luminescence (STML) experiments, a single molecule and a single-mode NCP are assumed to be selectively excited initially, depending on the tip position with respect to the molecule. The effect of NCP on the molecular emission and the effect of individual molecules on the NCP emission will be studied in detail. The influence of the magnitude of the radiative decay rate of molecules on the emission spectral profile will also be discussed briefly. Our model helps to clarify the role of plasmon-molecule interactions in affecting the spectroscopic properties of biased molecular junctions.

II. THEORETICAL MODEL

The master equation describing the dynamics of the coupled plasmon-molecule system can be written as [5,

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7, 8]

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -i\left[H_0 + V_{\text{mol-NCP}}, \rho\right] + \left(\mathcal{L}_{\text{tun}} + \mathcal{L}_{\text{damp}}\right)\rho \quad (1)$$

where H_0=H_{mol}+H_{NCP} is the Hamiltonian for the coupling-free molecule and NCP, ρ=$\rho_{\text{mol}}\otimes\rho_{\text{NCP}}$ is the density operator for the coupled plasmon-molecule system. The interactions between the single molecule and the NCP are considered in the dipole approximation $V_{\text{mol-NCP}}$=$g(\hat{a}^\dagger\hat{\sigma}_-+\hat{\sigma}_+\hat{a})$, where $\hat{a}^\dagger$ ($\hat{a}$) is the creation (destruction) operator for the NCP, $\hat{\sigma}_+$=$|e\rangle\langle g|$ ($\hat{\sigma}_-$=$|g\rangle\langle e|$) is the excitation (de-excitation) operator for the molecular exciton, $|g\rangle$ and $|e\rangle$ are the ground and excited states of the molecule, respectively. For simplicity, only a single-mode NCP is taken into account. $\mathcal{L}_{\text{tun}}$ and $\mathcal{L}_{\text{damp}}$ are Liouvillian operators that account for tunneling currents induced excitation and various damping processes, respectively, which will be detailed below.

The Liouvillian operator $\mathcal{L}_{\text{tun}}$ accounts for the tunneling events with either the molecule or the NCP excited [5, 7, 8]

$$\mathcal{L}_{\text{tun}}\rho = -\sum_{ij}\left(\gamma_{\text{tun}}^{i\to j} s_{ii}\rho s_{ii} - \gamma_{\text{tun}}^{j\to i} s_{ij}\rho s_{ji}\right) \quad (2)$$

where $\gamma_{\text{tun}}^{i\to j}$ is the tunneling electron induced transition rate from the i-th level to the j-th level of the plasmon-molecule system, s_{ij} is a square matrix with the element (i, j) equaling to 1 while all other elements vanish.

The Liouvillian operator $\mathcal{L}_{\text{damp}}$ accounts for various damping processes and takes the standard Lindblad form [5, 7, 8]

$$\mathcal{L}_{\text{damp}}\rho = -\sum_{\alpha=\text{mol,NCP}}\frac{\gamma_\alpha}{2}\left(A_{\alpha,+}A_{\alpha,-}\rho - 2A_{\alpha,-}\rho A_{\alpha,+} + \rho A_{\alpha,+}A_{\alpha,-}\right) \quad (3)$$

where $A_{\text{mol},\pm}$=$\hat{\sigma}_\pm \otimes \mathcal{I}_{\text{sp}}$, $A_{\text{NCP},+}$=$\mathcal{I}_{\text{mol}} \otimes \hat{a}^\dagger$, $A_{\text{NCP},-}$=$\mathcal{I}_{\text{mol}} \otimes \hat{a}$, and $\mathcal{I}$ is a unit operator. γ_{mol} and γ_{NCP} represent the total (radiative plus non-radiative) decay rate of the molecule and the NCP, respectively.

After solving the time-dependent master equation, the density operator $\rho(t)$ that describes the emission properties of the coupled system can be obtained [15]. The populations of the molecular exciton $P_{\text{mol}}(t)$ and the NCP $P_{\text{NCP}}(t)$, corresponding to the diagonal elements of the density matrix, are evaluated as

$$P_{\text{mol}}(t) = \langle 0_{\text{sp}}| \otimes \langle e|\rho(t)|e\rangle \otimes |0_{\text{sp}}\rangle \quad (4)$$

$$P_{\text{NCP}}(t) = \langle 1_{\text{NCP}}| \otimes \langle g|\rho(t)|g\rangle \otimes |1_{\text{NCP}}\rangle \quad (5)$$

Furthermore, to better understand the light emission properties of the coupled plasmon-molecule system, the total emission is artificially decomposed into two parts [16], *i.e.*, the light emission from the single molecule

$$I_{\text{mol}}(\omega) = \int_{-\infty}^{\infty}\langle\hat{\sigma}_+(t)\hat{\sigma}_-(0)\rangle \mathrm{e}^{-i\omega t}\mathrm{d}t \quad (6)$$

and the light emission from the NCP

$$I_{\text{NCP}}(\omega) = \int_{-\infty}^{\infty}\langle\hat{a}^\dagger(t)\hat{a}(0)\rangle \mathrm{e}^{-i\omega t}\mathrm{d}t \quad (7)$$

These two time correlation functions of the molecular and plasmonic operators are calculated via the quantum regression theorem [17].

III. RESULTS AND DISCUSSION

To make the numerical results more realistic, the experimental parameters in Ref.[13] were adopted in the present work. Specifically, the total decay rates of the electronically decoupled molecule and the NCP in STM junctions are estimated to be γ_{mol}≈15 meV and γ_{NCP}≈160 meV, respectively. The plasmon-molecule coupling strength g depends on the lateral distance between the tip apex and the molecule, and a typical value when the tip apex is close to the edge of the molecule reported in Ref.[13] is g≈15 meV. The transition dipole moment of a single molecule used in STML is typically a few Debye, corresponding to a radiative decay rate of $\gamma_{\text{mol}}^{\text{rad}}$≈$10^{-8}$ eV in vacuum [7]. According to the above parameters, the spontaneous emission rate of a molecule in the STM junction has been increased to $\sim 4g^2/\gamma_{\text{NCP}}$≈$5.6\times10^{-3}$ eV. Compared with the radiative decay rate of the same molecule in vacuum (8×10^{-8} eV) [13], such a large enhancement corresponds to a large Purcell factor of $\sim 10^5$, which clearly demonstrates that the spontaneous emission rate of the molecule is enormously enhanced due to its coupling to the NCP. However, it is difficult to obtain the radiative decay rate of the NCP directly from experiments. Nevertheless, Persson and Baratoff [18] have shown theoretically that the quantum efficiency for the emission of localized surface plasmons is ∼0.1 for a spherical nanoparticle with a radius of a few tens of nanometers, so $\gamma_{\text{NCP}}^{\text{rad}}$ is set to be 16 meV.

In the following, we shall discuss time-dependent populations and emission intensities as well as emission spectral properties of the coupled plasmon-molecule system under selective initial excitation of either the molecule or the NCP. In STM induced light emission experiments from a single molecule, the tunneling currents used are typically sub-nanoamperes, corresponding to an average time interval between two successive tunneling electrons on a time scale of nanoseconds [1–3], which is much longer than the lifetime of either the NCP or the molecular exciton near a plasmonic nanocavity on a time scale of sub-picoseconds. Therefore, when evaluating the time-dependent populations of the coupled system, we can start from a specified initial state at t=0 and ignore the tunneling electron induced excitation term (namely, the $\mathcal{L}_{\text{tun}}$ term in Eq.(1)). Specifically, FIG. 1 (b) and (c) are obtained with the initial state $|e\rangle \otimes |0_{\text{NCP}}\rangle$ with only the molecule excited, and

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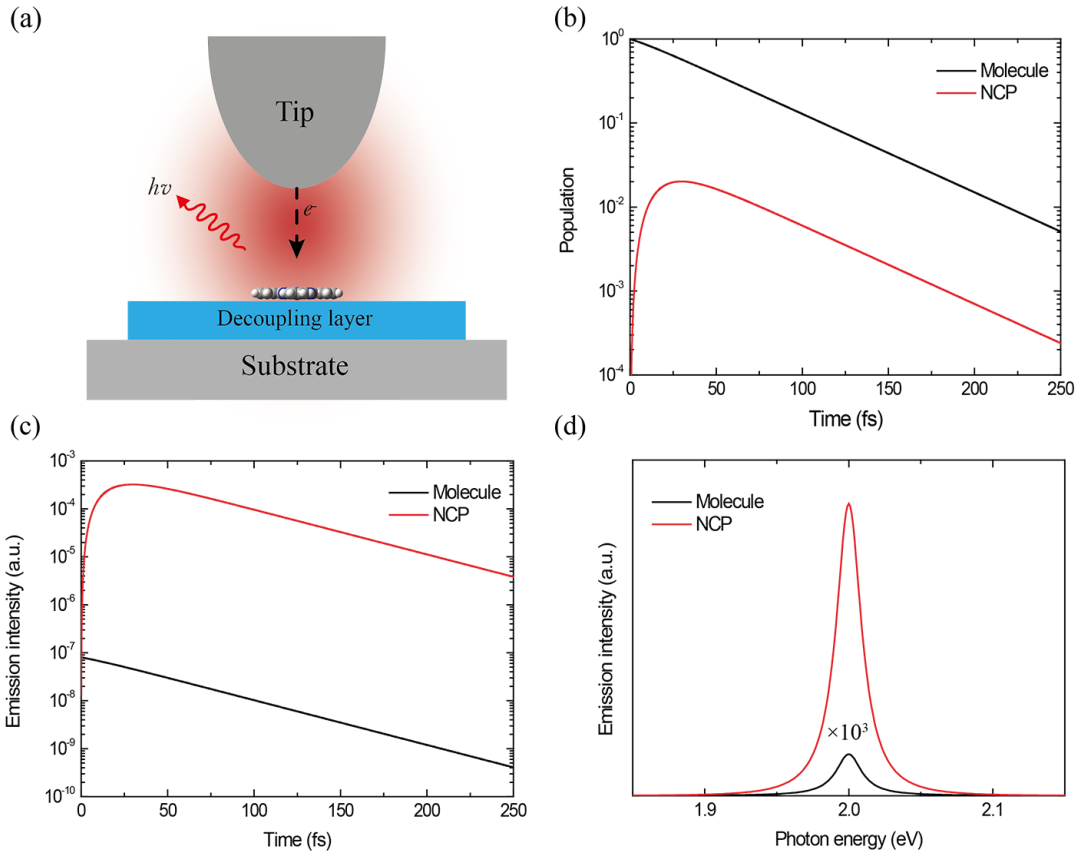

FIG. 1 (a) Schematic of STM induced molecular emission with the tip apex positioned above a molecule that can be directly excited by tunneling electrons. (b) and (c) show the time evolution of the populations (b) and emission intensities (c) of the NCP and the molecule, respectively, after the molecule is initially excited. (d) Emission spectra for the molecule and the NCP when the molecule is selectively excited. The emission energy for both the molecule and the NCP is set to 2 eV.

FIG. 2 (b) and (c) are obtained with the initial state $|g\rangle \otimes |1_{\rm NCP}\rangle$ with only the NCP excited. On the other hand, when evaluating the steady-state emission spectrum in FIG. 1(d) and FIG. 2(d), the tunneling electron induced excitation term in Eq.(1) has also been taken into account, specifically calculated by using Eq.(2).

As shown in FIG. 1(a), when the STM tip is placed on an electronically decoupled molecular emitter, the tunneling electrons may trigger an exciton in the molecule, whose time evolution is subjected to both the plasmon-molecule coupling and the various radiative and non-radiative decay channels. Without the NCP, the radiative emission power will be simply determined by the state population of the molecular exciton as $W_{\rm mol}(t)=P_{\rm mol}(t)\gamma^{\rm rad}_{\rm mol}$. Due to the presence of the NCP, an additional emission channel is established with the energy transferred to NCP and then emitted to far field. That is, although initially only the molecule is excited, the excitation energy will be transferred between the molecule and the NCP due to their mutual interactions. The time-dependent populations of the molecular exciton ($P_{\rm mol}(t)$) and the NCP ($P_{\rm NCP}(t)$) for a given coupling strength are plotted in FIG. 1(b), which shows that the excitation energy is rapidly transferred from the molecular exciton to the NCP whose population quickly increases from $P_{\rm NCP}$=0 at t=0 to a maximum of $P_{\rm NCP}$=0.02 at $t\approx$30 fs. After reaching its maximum, the NCP population then decreases monotonically with time; this is because as time increases, the excitation energy in the molecule is gradually lost and therefore it cannot compensate for the ultrafast NCP dissipation. To quantitatively compare the emission directly from the molecule with that mediated by the NCP, their instantaneous emitting power, determined by the product of the population and the corresponding radiative emission rate, $W_{\rm mol}(t)=P_{\rm mol}(t)\gamma^{\rm rad}_{\rm mol}$ and $W_{\rm NCP}(t)=P_{\rm NCP}(t)\gamma^{\rm rad}_{\rm NCP}$, are plotted in FIG. 1(c). Since the radiative decay rate of the NCP is orders of magnitude larger than that of a single molecule, it has much stronger emission capability after excitation. Therefore, although the molecular exciton is initially excited and the population of the NCP is always much smaller than the exciton, the photon flux emitted by the NCP is significantly larger than that directly from the molecule, as depicted in FIG. 1(c). In other words, it is mainly the dramatic difference in the radiative decay rates between the NCP and the molecule that determines their respective contributions and the total emission behavior.

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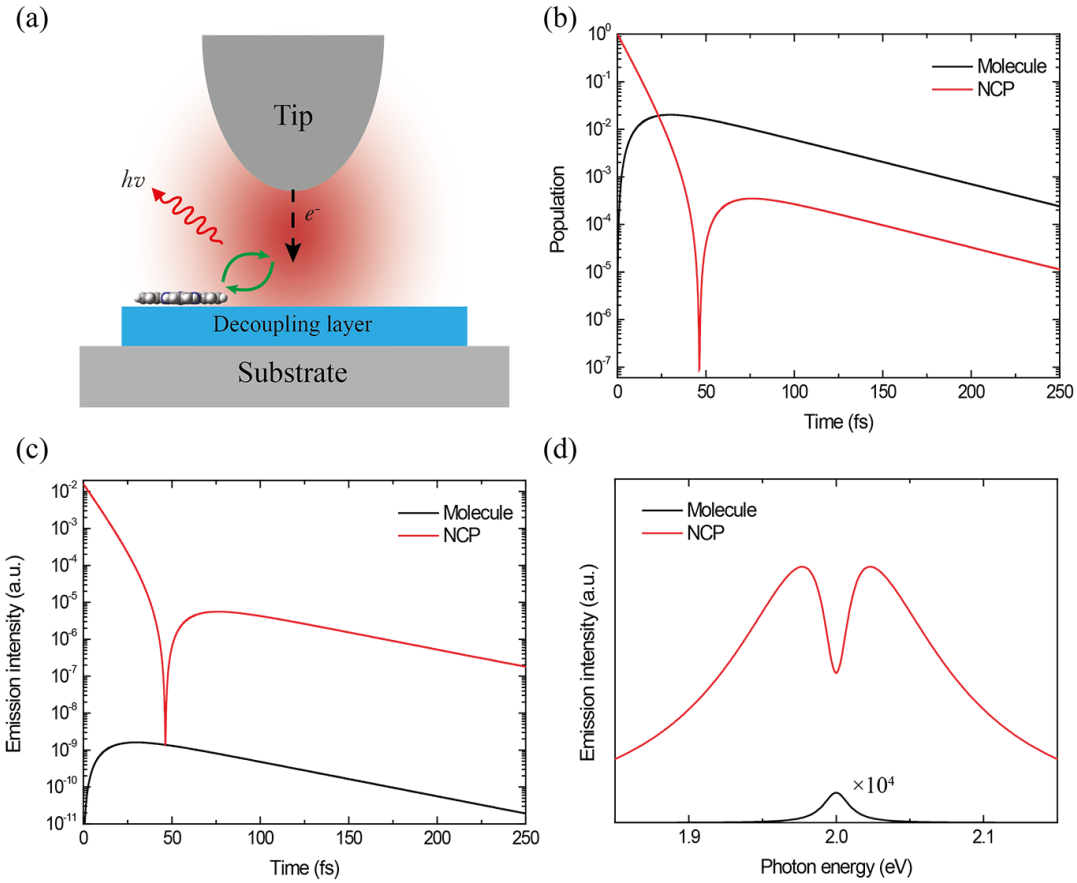

FIG. 2 (a) Schematic of STM induced NCP emission with the STM tip apex located in close proximity to the edge of a molecule. The molecule cannot be directly excited by tunneling electrons. Instead, the localized NCP in the junction can be excited by inelastic tunneling electrons. The time evolution of the populations (b) and emission intensities (c) of the NCP and the molecule after the NCP is initially excited. (d) Emission spectra for the molecule and the NCP when the NCP is selectively excited. The emission energy for both the molecule and the NCP is set to 2 eV.

FIG. 1(d) shows the calculated emission spectra of the coupled system by artificially decomposing into the contribution from the NCP and the molecule. As addressed above, due to its weak emission ability of the molecule with respect to the NCP, the emission directly from a single molecule is negligibly small. The total emission spectrum is almost exactly the same as that from the NCP alone, suggesting an overwhelming contribution from the emission mediated by the NCP. Essentially, during the whole emission process, the NCP serves as an antenna, which first accelerates the de-excitation of the molecule by the Purcell effect, speeds up the energy transfer from the molecule to the NCP, and then scatters the induced emission from the molecule to the far field. Based on this and many previous studies [16, 19], the scattering process described above will most likely go through an elastic scattering, and thus provide a spectrum with a similar line-shape as the emission directly from the molecule. In other words, the role of the NCP in the situation of initial molecular excitation directly by tunneling electrons is to enhance the molecular emission through the increase of the apparent radiative decay rate, leading to the observation of sharp molecule-specific emission peaks.

On the other hand, when the tip is located in close proximity to the edge of a molecule and only the NCP can be directly excited by the tunneling currents, as schematically illustrated in FIG. 2(a), the molecule can be indirectly excited due to the dipolar coupling between the molecule and the NCP. Such coupling could modify both the time evolution and the optical response of the plasmon emission compared with that from a molecule-free tunnel junction. As shown in FIG. 2(b), the population of the molecular exciton $P_{\mathrm{mol}}(t)$, which is 0 at t=0, quickly increases and reaches a maximum of ∼0.02 at t≈30 fs, and then decays monotonically with time. This behavior can be explained in a similar way to the population of NCP in FIG. 1(b): as time increases, the energy in the NCP is rapidly lost and therefore it cannot compensate for the dissipation of the molecular exciton near a plasmonic nanocavity. However, in contrast with the case shown in FIG. 1, here the energy loss of the NCP is so fast that the energy of the molecular exciton will conversely compen-

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sate for the dissipation of the NCP. This can be seen from the population of the NCP $P_{\mathrm{NCP}}(t)$ which quickly decreases to 10^{-7} at $t\approx46$ fs and revives to 3.5×10^{-4} at $t\approx76$ fs due to the energy transferred back from the molecule. Indeed, if without dissipation the energy will be exchanged periodically between the exciton and the NCP. As shown in FIG. 2(c), due to the weak emission capability of a molecule, the light emission from the single molecule after absorbing the energy from the NCP is negligibly small compared with the emission directly from the NCP. Nevertheless, the single molecule does affect the emission properties of the NCP. Since the linewidth of NCP is usually much larger than that of the molecular exciton, the interaction between the exciton and the NCP can be considered as a coherent dipolar coupling between a single discrete mode and a broader continuous mode, which may result in the occurrence of Fano resonance [13, 14, 20]. When the energy is transferred from the NCP to the molecule and back to the NCP again, it may gain additional phase and cause destructive interferences, manifested by a dip in the emission spectrum, as shown in FIG. 2(d). It is worthwhile to note that the dip cannot be simply considered as an incoherent absorption of the NCP emission by the single molecule, since the absorption capability (as its emission capability) is so small that this effect cannot be observed otherwise. Again, the total emission spectrum of the coupled system is essentially the same as the NCP spectrum with Fano dips, and the emission directly from the single molecule is negligibly small. The Fano dip shown in FIG. 2(d) is symmetric for the exact resonant condition between the molecule and NCP, which is different from the asymmetric Fano lineshape observed experimentally [13]. Such discrepancy between the experimental observation and the current model may be attributed to either the symmetric Lorentzian profiles used to describe the molecule and the NCP or the simple dipolar approximation used to model the molecule-NCP coupling, or both [13]. Nevertheless, it should be mentioned that even under the dipolar approximation, when the detuning between the molecule and the NCP is non-zero (*i.e.*, non-resonant), the Fano lineshape superimposed on the plasmon emission spectrum will become asymmetric according to our model, which is in agreement with experimental observations.

We would also like to note that, according to our theoretical model, while molecule-specific emission peaks will usually be observed when the tip is placed on a well-decoupled molecular emitter due to the strong plasmonic enhancement in the radiative decay rate, the appearance of a Fano-dip like spectrum is still possible if the molecule is non-emissive because the destructive interference between the plasmon and molecule may become dominant and will not be buried by the otherwise enhanced emission peak in this case. On the other hand, when the tip is placed in close proximity to the edge of a molecule and only the NCP is initially excited, we will most probably only see Fano dips superimposed on a broad NCP emission spectrum; it is unlikely to observe molecule-characteristic peaks unless the radiative decay rate of the molecule could become comparable to that of the NCP, which is impossible in reality for a single molecule.

IV. CONCLUSION

In summary, we have theoretically studied the time evolution and spectroscopic properties of the light emission from a coupled plasmon-molecule system when the molecule or the NCP can be selectively excited by tunneling electrons in STM junctions. It has been found that when the molecule is selectively excited, the NCP can enormously enhance the molecular emission via enhancing the apparent radiative decay rate of the molecule. On the other hand, when the NCP is selectively excited, the destructive interferences between the NCP and the single emitter generate Fano dips in the NCP emission spectra. Since in reality the intrinsic radiative decay rate of the NCP is orders of magnitude larger than that of a single emitter, it is unlikely to see sharp molecule-characteristic emission peaks if the molecule is excited indirectly through the nanocavity plasmons. The theoretical model presented in this work provides insight into the microscopic mechanism of plasmon-molecule coupling at the nanoscale and helps to understand and predict the light emission properties from such systems.

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