Quantum dynamics of a molecular emitter strongly coupled with surface plasmon polaritons: A macroscopic quantum electrodynamics approach (EP)

Siwei Wang (iD), Gregory D. Scholes (iD), and Liang-Yan Hsu (iD)

COLLECTIONS

Note: This paper is part of a JCP Special Topic on Dynamics of Open Quantum Systems.

(EP)   This paper was selected as an Editor's Pick

View Online   Export Citation   CrossMark

ARTICLES YOU MAY BE INTERESTED IN

Luminescence spatial characteristics of ZnSe:Fe
Journal of Applied Physics **126**, 015702 (2019); https://doi.org/10.1063/1.5094954

Highly-collimated, high-charge and broadband MeV electron beams produced by magnetizing solids irradiated by high-intensity lasers
Matter and Radiation at Extremes **4**, 044401 (2019); https://doi.org/10.1063/1.5082330

Principles of enantio-selective excitation in three-wave mixing spectroscopy of chiral molecules
The Journal of Chemical Physics **151**, 014302 (2019); https://doi.org/10.1063/1.5097406

Quantum dynamics of a molecular emitter strongly coupled with surface plasmon polaritons: A macroscopic quantum electrodynamics approach EP

View Online   Export Citation   CrossMark

Siwei Wang,[1,2] iD Gregory D. Scholes,[1,a)] iD and Liang-Yan Hsu[2,b)] iD

AFFILIATIONS

[1] Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA
[2] Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan

Note: This paper is part of a JCP Special Topic on Dynamics of Open Quantum Systems.
[a)] **Electronic mail:** gscholes@princeton.edu
[b)] **Electronic mail:** lyhsu@gate.sinica.edu.tw

ABSTRACT

We study a molecular emitter above a silver surface in the framework of macroscopic quantum electrodynamics and explore the population dynamics including non-Markovian effects. The theory we present is general for molecular fluorescence in the presence of dielectrics with any space-dependent, frequency-dependent, or complex dielectric functions. Furthermore, the proposed theory allows us to calculate the memory kernel of polaritons using computational electrodynamics packages. In the limit of a high vibration frequency, the different strengths of exciton-polariton couplings lead to distinct characteristics in the population dynamics, e.g., Franck-Condon-Rabi oscillation. (The frequency of Rabi oscillation is dependent on the Franck-Condon factor.) Additionally, in a specific condition, we derive a parameter-free formula that can be used to estimate the exciton-polariton coupling between a molecular emitter and a nanocavity, and the coupling estimated by our theory is in good agreement with the reported experimental results [Chikkaraddy *et al.*, Nature **535**, 127–130 (2016)].

I. INTRODUCTION

Light-matter interactions play a central role in a variety of fields such as photovoltaics,[1,2] surface-enhanced Raman spectroscopy,[3–5] energy transfer in light-harvesting complexes,[6] biosensing,[7] plasmon-coupled resonance energy transfer,[8–10] and molecular fluorescence.[11,12] Since the 1970s, the study of molecular fluorescence altered by dielectric environments has attracted extensive attention in the area of chemical physics.[13–16] In fact, the lifetime of molecular fluorescence near an interface is related to the photonic local density of states.[17] Kuhn, Drexhage, Chance, and Silbey *et al.* clearly demonstrated the oscillation of the molecular spontaneous emission rate as a function of the metal-molecule distance.[18–20] Recently, due to advances in nanotechnology, single molecules in nanoscale metallic cavities have been realized, and extremely strong couplings between molecules and surface plasmon polaritons (SPPs) have been observed.[21] Under such a strong coupling regime, the role of coherent quantum dynamics is supposed to be important, and the rate of molecular fluorescence may not be described by classical electrodynamics.

A quantum emitter coupled to surface plasmon polaritons has been tackled by a number of studies during the past two decades.[22–25] However, most of them concentrate on pure electronic-state systems, and there is still a lack of understanding of the influence of molecular vibrations on a quantum emitter in a complex dielectric environment. Furthermore, from a view point of materials science, it is nontrivial to calculate the magnitude of exciton-polariton couplings in a variety of dielectric materials. The two issues

motivate us to establish a theory of molecular fluorescence which incorporates the effects of both molecular vibrations and plasmon polaritons.

In the present study, we explore the quantum dynamics of a molecular emitter strongly coupled with SPPs. Specifically, we study the population dynamics of a two-level molecule coupled to a high-frequency vibrational mode above a silver surface. Population dynamics is one of the most important characteristics of quantum dynamics, and it has been extensively studied in several systems.[26–30] The remainder of the article is organized as follows. In Sec. II, in the framework of macroscopic quantum electrodynamics,[8–10,22,31,32] by adopting the electric-dipole approximation, the rotating-wave approximation, and the Condon approximation, we derive a set of differential equations describing the quantum dynamics of a two-level molecule coupled to a vibrational mode in arbitrary inhomogeneous, dispersive, and absorbing media. The memory kernels of the differential equations can be separated into the parts of polaritons and molecular vibrations. In Sec. III, in order to clearly demonstrate the role of molecular vibrations, we discuss a molecular emitter with a high vibration frequency, the characteristics of the population dynamics in three conditions, the numerical demonstration of the Franck-Condon-Rabi oscillation, and the relation between the Jaynes-Cummings model and our model. Moreover, we derive a parameter-free formula to estimate exciton-polariton couplings in a hybrid plasmon-exciton system. Experimentally, exciton-polariton couplings can be obtained from the Rabi splitting via optical dark field spectra.[21] Our formula provides a convenient theoretical estimate before performing experiments. In Sec. IV, we review the main results and give a perspective for future work.

II. METHODS

A. Theory and model Hamiltonian

In this paper, we focus on the quantum dynamics of spontaneous emission (fluorescence) radiated by a molecular emitter in the proximity of plasmonic materials (dispersive and absorbing media) without any embedded charges or currents. To describe such a system, we model the total Hamiltonian as $\hat{H}_{\text{tot}} = \hat{H}_{\text{mol}} + \hat{H}_{\text{pol}} + \hat{H}_{\text{int}}$, which incorporates a molecular system $\hat{H}_{\text{mol}}$, polariton fields $\hat{H}_{\text{pol}}$, and their interactions $\hat{H}_{\text{int}}$. Furthermore, to clearly demonstrate the role of molecular vibrations, we consider a molecule having two electronic states (a ground state $|g\rangle$ and an excited state $|e\rangle$) and a vibration mode with the frequency ω_{v} as well as the displacement d, as shown in Fig. 1. As a result, the molecular Hamiltonian can be described as

$$\hat{H}_{\text{mol}} = |g\rangle\Big(\hbar\omega_{\text{v}}\big[b^{\dagger}b - \sqrt{\alpha}(b^{\dagger} + b) + \alpha\big]\Big)\langle g| + |e\rangle\Big(\hbar\omega_{\text{eg}} + \hbar\omega_{\text{v}}b^{\dagger}b\Big)\langle e|,$$

(1)

where $\hbar\omega_{\text{eg}}$ is the energy gap between the electronically excited state and the electronically ground state, and b^{+} and b denote the creation operator and the annihilation operator of a harmonic oscillator (the vibrational mode), respectively. Moreover, for convenience, we define a vibrational state $|M(\alpha)\rangle$ associated with a quantum number M and the Huang-Rhys factor α, and it satisfies $\big[b^{\dagger}b - \sqrt{\alpha}(b^{\dagger} + b) + \alpha\big]|M(\alpha)\rangle = M|M(\alpha)\rangle$.

For the polariton Hamiltonian, we apply the techniques of macroscopic quantum electrodynamics developed by Gruner and Welsch,[33] and the quantization of the electromagnetic field in inhomogeneous, dispersive, and absorbing linear dielectrics is described by

$$\hat{H}_{\text{pol}} = \int d\boldsymbol{r} \int_0^{\infty} d\omega\, \hbar\omega \hat{\boldsymbol{f}}^{\dagger}(\boldsymbol{r}, \omega) \cdot \hat{\boldsymbol{f}}(\boldsymbol{r}, \omega),$$

(2)

where $\hat{\boldsymbol{f}}(\boldsymbol{r}, \omega)$ and $\hat{\boldsymbol{f}}^{\dagger}(\boldsymbol{r}, \omega)$ are the annihilation operator and the creation operator for bosonic vector fields, respectively, i.e., $\hat{f}_i(\boldsymbol{r}, \omega)|\{1_i(\boldsymbol{r}, \omega)\}\rangle = |\{0\}\rangle$ and $\hat{f}_i^{\dagger}(\boldsymbol{r}, \omega)|\{0\}\rangle = |\{1_i(\boldsymbol{r}, \omega)\}\rangle$, where $|\{0\}\rangle$ is a vacuum state and $|\{1_i(\boldsymbol{r}, \omega)\}\rangle$ is a one-polariton state associated with a polariton frequency ω and a certain polarization direction i at position $\boldsymbol{r}$. The two operators satisfy the following
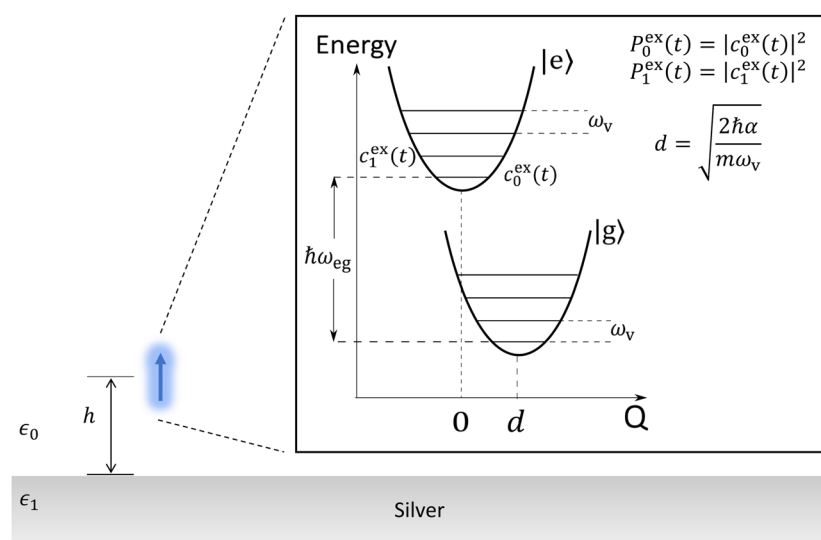

FIG. 1. A molecular emitter above a silver surface. $P_N^{\text{ex}}(t)$ is the population of the molecular excited state with N vibrational quanta. The blue arrow shows the direction of the transition dipole moment of the molecule at a height h above the silver surface. $\epsilon_0(\epsilon_1)$ is the dielectric function of vacuum (sliver). The energy difference between electronically ground state $|g\rangle$ and excited state $|e\rangle$ is $\hbar\omega_{\text{eg}}$. The frequency of the vibrational mode denotes ω_{v}, and the displacement d of the potential energy surface is associated with the Huang-Rhys factor α.

commutation relation:[31]

$$\left[\hat{f}_i(\boldsymbol{r},\omega),\hat{f}_j^\dagger(\boldsymbol{r}',\omega')\right] = \delta_{ij}\delta(\boldsymbol{r}-\boldsymbol{r}')\delta(\omega-\omega'), \qquad (3)$$

where δ_{ij} denotes a Kronecker delta function and the subscripts i (or j) indicate the spatial components x, y, z.

For the interactions between the electromagnetic field (SPPs) and the molecular emitter, we adopt the electric-dipole approximation, the rotating-wave approximation, and the Condon approximation (the details can be found in Appendix A), so the interaction Hamiltonian can be cast into[34]

$$\hat{H}_{\text{int}} = -\left(|e\rangle\langle g|\hat{\boldsymbol{E}}^{(+)}(\boldsymbol{r}_{\text{M}})\cdot\boldsymbol{\mu} + |g\rangle\langle e|\hat{\boldsymbol{E}}^{(-)}(\boldsymbol{r}_{\text{M}})\cdot\boldsymbol{\mu}\right), \quad (4)$$

$$\hat{\boldsymbol{E}}^{(+)}(\boldsymbol{r}_{\text{M}}) = \int_0^\infty d\omega\,\hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{M}},\omega), \qquad (5)$$

where $\boldsymbol{\mu}$ is the transition dipole moment of a molecule, $\hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{M}},\omega)$ is the operator of electromagnetic fields[22] with frequency ω at the position of the molecule $\boldsymbol{r}_{\text{M}}$, $\hat{\boldsymbol{E}}^{(+)}(\boldsymbol{r}_{\text{M}})$ corresponds to the summation of all polariton modes, and $\hat{\boldsymbol{E}}^{(-)}(\boldsymbol{r}_{\text{M}})$ is the Hermitian conjugate of $\hat{\boldsymbol{E}}^{(+)}(\boldsymbol{r}_{\text{M}})$. Furthermore, the operator of electromagnetic fields is associated with bosonic vector fields $\hat{\boldsymbol{f}}(\boldsymbol{r},\omega)$ and the dyadic Green's function $\overleftrightarrow{\boldsymbol{G}}(\boldsymbol{r}_{\text{M}},\boldsymbol{r},\omega)$, and it is expressed as

$$\hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{M}},\omega) = i\sqrt{\frac{\hbar}{\pi\epsilon_0}}\frac{\omega^2}{c^2}\int d\boldsymbol{r}\sqrt{\epsilon_{\text{I}}(\boldsymbol{r},\omega)}\,\overleftrightarrow{\boldsymbol{G}}(\boldsymbol{r}_{\text{M}},\boldsymbol{r},\omega)\cdot\hat{\boldsymbol{f}}(\boldsymbol{r},\omega), \quad (6)$$

where $\epsilon_{\text{I}}(\boldsymbol{r},\omega)$ is the imaginary part of the dielectric function $\epsilon(\boldsymbol{r},\omega)$ of the environment, ϵ_0 is the permittivity of free space, c is the speed of light in a vacuum, and $\overleftrightarrow{\boldsymbol{G}}(\boldsymbol{r}_{\text{M}},\boldsymbol{r},\omega)$ satisfies

$$\left(\frac{\epsilon(\mathbf{r}_{\text{M}},\omega)\omega^2}{c^2} - \nabla\times\nabla\times\right)\overleftrightarrow{\boldsymbol{G}}(\boldsymbol{r}_{\text{M}},\boldsymbol{r},\omega) = -\boldsymbol{\delta}(\mathbf{r}_{\text{M}}-\mathbf{r}). \quad (7)$$

B. Quantum dynamics of an excited molecule

In order to explore the quantum dynamics of a molecular emitter, we start from the time-dependent Schrödinger equation $i\hbar\,\partial|\psi(t)\rangle/\partial t = \hat{H}_{\text{tot}}|\psi(t)\rangle$ and use a wavefunction ansatz based on the Wigner–Weisskopf theory.[35] In this ansatz, the time-dependent state $|\psi(t)\rangle$ of the system can be expanded by a complete set of state vectors formed by electronic states, vibrational states, and polariton states, i.e.,

$$\begin{aligned}
|\psi(t)\rangle = &\sum_{N=0}^\infty C_N^{\text{e}0}(t)e^{-i(\omega_{\text{eg}}+\omega_{\text{v}}N)t}|e\rangle|N(0)\rangle|\{0\}\rangle \\
&+ \sum_{M=0}^\infty \int d\boldsymbol{r}\int_0^\infty d\omega\, C_M^{\text{gi}}(\boldsymbol{r},\omega,t) \\
&\times e^{-i(\omega+\omega_{\text{v}}M)t}|g\rangle|M(\alpha)\rangle|\{1_i(\boldsymbol{r},\omega)\}\rangle,
\end{aligned} \quad (8)$$

where $C_N^{\text{e}0}(t)$ and $C_M^{\text{gi}}(\boldsymbol{r},\omega,t)$ are the coefficients of the electronically excited state (the superscript e) with zero-polariton state (the superscript 0) and the electronically ground state (the superscript g) with one-polariton state having a certain polarization direction (the superscript i), respectively.

Substituting Eq. (8) into $i\hbar\,\partial|\psi(t)\rangle/\partial t = \hat{H}_{\text{tot}}|\psi(t)\rangle$ and after some algebra (see Appendix B), one can derive a set of differential

equations,

$$\dot{C}_K^{\text{e}0}(t) = -\sum_{L=0}^\infty \int_0^t dt'\, K_{\text{pol}}(t,t')K_{\text{vib}}^{K,L}(t,t')C_L^{\text{e}0}(t'), \quad (9)$$

where $K_{\text{pol}}(t,t')$ is the memory kernel of polaritons and $K_{\text{vib}}^{K,L}(t,t')$ is the memory kernel of molecular vibrations between the states K and L. The memory kernel of polaritons is defined as

$$K_{\text{pol}}(t,t') = \sum_{i,j}\frac{\mu_i\mu_j}{\pi\hbar c^2\epsilon_0}\int_0^\infty d\omega\,\omega^2\text{Im}G_{ij}(\boldsymbol{r}_{\text{M}},\boldsymbol{r}_{\text{M}},\omega)e^{-i(\omega-\omega_{\text{eg}})(t-t')}, \quad (10)$$

where $\text{Im}G_{ij}(\boldsymbol{r}_{\text{M}},\boldsymbol{r}_{\text{M}},\omega)$ is the matrix element of the imaginary part of the dyadic Green's function $\overleftrightarrow{\boldsymbol{G}}(\boldsymbol{r}_{\text{M}},\boldsymbol{r}_{\text{M}},\omega)$ and μ_i is the vector component of the transition dipole moment $\boldsymbol{\mu}$ of the molecule. The memory kernel of molecular vibrations is defined as

$$K_{\text{vib}}^{K,L}(t,t') = \sum_{M=0}^\infty \langle K(0)|M(\alpha)\rangle e^{i\omega_{\text{v}}(K-M)t}\langle M(\alpha)|L(0)\rangle e^{i\omega_{\text{v}}(M-L)t'}, \quad (11)$$

where $\langle K(0)|M(\alpha)\rangle$ is related to the Huang-Rhys factor and the associated Legendre polynomials $\mathcal{L}_N^{M-N}(\alpha)$,[36]

$$\langle M(0)|N(\alpha)\rangle = e^{-\frac{\alpha}{2}}\sqrt{\frac{N!}{M!}}\alpha^{(M-N)/2}\mathcal{L}_N^{M-N}(\alpha). \quad (12)$$

Equation (9) is a system of Volterra-type integro-differential equations,[37] including non-Markovian effects, and it can be solved using a trapezoidal rule algorithm.[38] Note that Eq. (9) is general for a two-level molecule coupled to a vibrational mode in the presence of inhomogeneous, dispersive, and absorbing media (not limited to a silver surface).

C. Numerical calculation of the memory kernel of polaritons

The non-Markovian quantum dynamics of a molecular emitter is determined by the two factors: the memory kernel of polaritons $K_{\text{pol}}(t,t')$ and the memory kernel of molecular vibrations $K_{\text{vib}}^{K,L}(t,t')$. The memory kernel of polaritons, i.e., Eq. (10), is governed by the dyadic Green's function, which is related to the photonic local density of states. In numerical simulations, it is nontrivial to calculate the dyadic Green's function in arbitrary media, and most studies restrict their systems in analytically solvable systems such as a spherical surface or an infinite plane.[39–47] However, we find that the polariton kernel $K_{\text{pol}}(t,t')$ given in Eq. (10) can be written in terms of the Purcell factor $F_{\text{P}}(\omega)$ and the spontaneous emission rate of a molecule in a vacuum $A_0(\omega)$, i.e.,

$$K_{\text{pol}}(t,t') = \frac{1}{2\pi}\int_0^\infty d\omega\,A_0(\omega)F_{\text{P}}(\omega)e^{-i(\omega-\omega_{\text{eg}})(t-t')}. \quad (13)$$

The Purcell factor is defined as $F_{\text{P}}(\omega) = A(\omega)/A_0(\omega)$,[17] where $A(\omega)$ is the spontaneous emission rate of a molecule in media, and the two

emission rates $A(\omega)$ and $A_0(\omega)$ are[17]

$$A(\omega) = \frac{2\omega^2}{\hbar c^2 \epsilon_0} \sum_{i,j} \mu_i \mu_j \, \mathrm{Im} \, G_{ij}(\boldsymbol{r}_M, \boldsymbol{r}_M, \omega), \tag{14}$$

$$A_0(\omega) = \frac{\omega^3 |\boldsymbol{\mu}|^2}{3c^3 \hbar \pi \epsilon_0}. \tag{15}$$

Note that $A(\omega)$ and $A_0(\omega)$ are based on Fermi's golden rule (the rates in the incoherent limit). Equation (13) provides two important information. First, the memory kernel of polarions is related to the Purcell factor, indicating that one can analyze the quantum dynamics of a molecular emitter via the behavior of the Purcell factor. Second, nowadays, the Purcell factor has been able to be calculated by computational packages, e.g., Lumerical FDTD Solutions.[48] Lumerical FDTD Solutions is a commercial package which can calculate electric fields and the Purcell factor by solving Maxwell's equations based on the finite-difference time-domain (FDTD) method. Recently, Lumerical FDTD Solutions has been extensively used to calculate the Purcell factor.[21,49–52] That is, one can easily obtain the memory kernel of polaritons by calculating $F_P(\omega)$ instead of using brute-force methods to solve the dyadic Green's function.

In this study, we focus on a molecular emitter above a silver surface. The dielectric function ϵ_1 of silver is adopted from the work of Johnson and Christy,[53] and the corresponding dyadic Green's function can be decomposed into[10,17]

$$\overleftrightarrow{\boldsymbol{G}}(\boldsymbol{r}_M, \boldsymbol{r}_M, \omega) = \overleftrightarrow{\boldsymbol{G}}_0(\boldsymbol{r}_M, \boldsymbol{r}_M, \omega) + \overleftrightarrow{\boldsymbol{G}}_s(\boldsymbol{r}_M, \boldsymbol{r}_M, \omega) + \overleftrightarrow{\boldsymbol{G}}_p(\boldsymbol{r}_M, \boldsymbol{r}_M, \omega), \tag{16}$$

where $\overleftrightarrow{\boldsymbol{G}}_0(\boldsymbol{r}_M, \boldsymbol{r}_M, \omega) = (\omega/6\pi c)\overleftrightarrow{I}$ is the free-space dyadic Green's function ($\overleftrightarrow{I}$ is a 3×3 identity matrix), $\overleftrightarrow{\boldsymbol{G}}_s(\boldsymbol{r}_M, \boldsymbol{r}_M, \omega)$ is the s-polarized dyadic Green's function, and $\overleftrightarrow{\boldsymbol{G}}_p(\boldsymbol{r}_M, \boldsymbol{r}_M, \omega)$ is the p-polarized dyadic Green's function. $\overleftrightarrow{\boldsymbol{G}}_s(\boldsymbol{r}_M, \boldsymbol{r}_M, \omega)$ and $\overleftrightarrow{\boldsymbol{G}}_p(\boldsymbol{r}_M, \boldsymbol{r}_M, \omega)$ can be derived from the integration in the reciprocal space.[10,17]

III. RESULTS AND DISCUSSION

A. High-frequency condition

In general, Eq. (9) can be employed to a two-level molecule coupled to a vibrational mode in an arbitrary dielectric system. To clearly demonstrate the role of molecular vibrations, we only focus on the first excited state of a molecule having a high vibration frequency under the resonance condition.

The Purcell factor $F_P(\omega)$ of the molecule above the silver surface is evaluated based on Eq. (16)[10] at different heights $h = 1.0$, 1.5, and 2.0 nm. In order to obtain the dyadic Green's function, we take the molecule as a point dipole and use the dielectric function ϵ_1 from the work of Johnson and Christy.[53] Our calculations show that the Purcell factors $F_P(\omega)$ behave like a Lorentzian, as depicted in Fig. 2. Therefore, one can approximate the curves of the Purcell factors as a Lorentz function, which corresponds to the mode of SPPs at a frequency ω_{SPP} as follows:

$$F_P(\omega) = F_P(\omega_{SPP}) \frac{\Gamma^2}{(\omega - \omega_{SPP})^2 + \Gamma^2}, \tag{17}$$
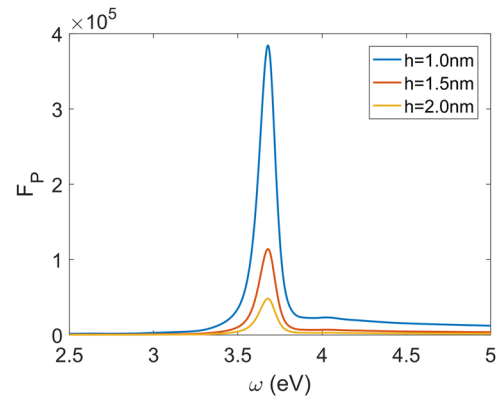

FIG. 2. Purcell factor of a molecule at a height h above a silver surface. The Purcell factor is associated with the memory kernel of plasmon polaritons. Our calculations indicate that the Purcell factor of a molecular emitter above a silver surface can be described by a Lorentz function.

where $F_P(\omega_{SPP})$ is the peak height of the Lorentz function and Γ is the half width at half maximum which corresponds to the photon loss rate in a dielectric environment.[54]

Substituting Eqs. (11), (13), and (17) into Eq. (9), one can obtain

$$\dot{C}_K^{e0}(t) = -\sum_{L=0}^{\infty} \int_0^t dt' \sum_{M=0}^{\infty} \left\{ \frac{F_P(\omega_{SPP})}{2\pi} \int_0^{\infty} d\omega A_0(\omega) \right.$$
$$\left. \times \frac{\Gamma^2}{(\omega - \omega_{SPP})^2 + \Gamma^2} e^{-i(\omega - \omega_{eg} - \omega_v(K-M))(t-t')} \right\}$$
$$\times \left\{ \langle K(0)|M(\alpha)\rangle\langle M(\alpha)|L(0)\rangle e^{-i\omega_v(L-K)t'} \right\} C_L^{e0}(t'). \tag{18}$$

Equation (18) can be further simplified in the resonance condition $\omega_{eg} = \omega_{SPP}$. For the ω dependent integral in Eq. (18), the Lorentz function contributes most around $\omega \approx \omega_{SPP}$, so we can approximate $A_0(\omega) \approx A_0(\omega_{SPP})$, i.e., the flat continuum approximation[25] $(\omega/\omega_{SPP})^3 \approx 1$. Moreover, in the spirit of the rotating-wave approximation, $e^{-i(\omega - \omega_{eg} - \omega_v(K-M))(t-t')}$ makes its main contribution to the ω dependent integral when $\omega - \omega_{eg} - \omega_v(K-M) = 0$. The conditions $\omega \approx \omega_{SPP}$, $\omega - \omega_{eg} - \omega_v(K-M) = 0$, and $\omega_{eg} = \omega_{SPP}$ indicate that the ω dependent integral is nonvanishing only when $K = M$, which gives $\delta_{K,M}$. As a result, Eq. (18) can be reduced to

$$\dot{C}_K^{e0}(t) = -\sum_{L=0}^{\infty} \int_0^t dt' \sum_{M=0}^{\infty} \left\{ \frac{\Gamma}{2} A_0(\omega_{SPP}) F_P(\omega_{SPP}) e^{-\Gamma(t-t')} \delta_{K,M} \right\}$$
$$\times \left\{ \langle K(0)|M(\alpha)\rangle\langle M(\alpha)|L(0)\rangle e^{-i\omega_v(L-K)t'} \right\} C_L^{e0}(t'), \tag{19}$$

where $\delta_{K,M}$ is the Kronecker delta function. Furthermore, in the high-frequency limit ($\omega_v \gg \Gamma$), we can use the rotating-wave approximation for the t' dependent integral, and Eq. (19) can be further reduced to

$$\dot{C}_K^{e0}(t) = -\sum_{L=0}^{\infty} \int_0^t dt' \sum_{M=0}^{\infty} \left\{ \frac{\Gamma}{2} A_0(\omega_{SPP}) F_P(\omega_{SPP}) e^{-\Gamma(t-t')} \delta_{K,M} \right\}$$
$$\times \left\{ \langle K(0)|M(\alpha)\rangle\langle M(\alpha)|L(0)\rangle \delta_{K,L} \right\} C_L^{e0}(t'). \tag{20}$$

Note that the rotating-wave approximation drops all fast oscillating terms $e^{i\omega_v(K-M)(t-t')}$ with $K \neq M$ and $e^{i\omega_v(K-L)t'}$ with $L \neq M$ in

Eq. (18), and finally only the terms which satisfy $L = M = K$ are left. When we focus on the first excited state ($K = 0$), Eq. (20) can be simplified as

$$\dot{C}_0^{e0}(t) = -\frac{A_0(\omega_{SPP})F_P(\omega_{SPP})\Gamma}{2}\langle 0(0)|0(\alpha)\rangle\langle 0(\alpha)|0(0)\rangle$$
$$\times \int_0^t dt'\, e^{-\Gamma(t-t')}C_0^{e0}(t'). \tag{21}$$

Equation (21) is an equation of motion of a two-level molecule coupled to a high-frequency vibrational mode in the resonance condition $\omega_{eg} = \omega_{SPP}$ (the energy gap is equal to the energy of the SPP mode).

B. Characteristics of population dynamics in three conditions

To understand the population dynamics governed by Eq. (21), we differentiate both sides of Eq. (21) with respect to time t, and it becomes a second-order differential equation,

$$\frac{d^2 C_0^{e0}(t)}{dt^2} + \Gamma \frac{dC_0^{e0}(t)}{dt} + \left(\frac{\Omega}{2}\right)^2 C_0^{e0}(t) = 0, \tag{22}$$

where

$$\Omega = |\langle 0(0)|0(\alpha)\rangle|\sqrt{2A_0(\omega_{SPP})F_P(\omega_{SPP})\Gamma}. \tag{23}$$

In the following, we consider an initial condition $C_0^{e0}(0) = 1$ and analyze the population dynamics of $C_0^{e0}(t)$ in the three conditions: (1) $\Omega < \Gamma$, (2) $\Omega = \Gamma$, and (3) $\Omega > \Gamma$.

In the case of $\Omega < \Gamma$, $C_0^{e0}(t)$ can be solved analytically as follows:

$$C_0^{e0}(t) = \frac{\Gamma + \sqrt{\Gamma^2 - \Omega^2}}{2\sqrt{\Gamma^2 - \Omega^2}} e^{\frac{-\Gamma+\sqrt{\Gamma^2-\Omega^2}}{2}t} + \frac{-\Gamma + \sqrt{\Gamma^2 - \Omega^2}}{2\sqrt{\Gamma^2 - \Omega^2}} e^{\frac{-\Gamma-\sqrt{\Gamma^2-\Omega^2}}{2}t}. \tag{24}$$

Apparently, the population of the electronically excited but vibrationally ground state $P_0^{e0}(t) = |C_0^{e0}(t)|^2$ consists of three exponential functions, i.e., $e^{-\Gamma+\sqrt{\Gamma^2-\Omega^2}t}$, $e^{-\Gamma-\sqrt{\Gamma^2-\Omega^2}t}$, and $e^{-\Gamma t}$.

In the case of $\Omega = \Gamma$, $C_0^{e0}(t)$ becomes

$$C_0^{e0}(t) = e^{\frac{-\Gamma}{2}t}\left(1 + \frac{\Gamma}{2}t\right). \tag{25}$$

Equations (24) and (25) convey an important message: fluorescence lifetime cannot be simply described by a single exponential when $\Omega \lesssim \Gamma$.

In the case of $\Omega > \Gamma$, $C_0^{e0}(t)$ oscillates with time, i.e.,

$$C_0^{e0}(t) = e^{-\frac{\Gamma}{2}t}\left[\cos\left(\frac{\sqrt{\Omega^2-\Gamma^2}}{2}t\right) + \frac{\Gamma}{\sqrt{\Omega^2-\Gamma^2}}\sin\left(\frac{\sqrt{\Omega^2-\Gamma^2}}{2}t\right)\right]. \tag{26}$$

Obviously, the population $P_0^{e0}(t)$ oscillates and decays with time. Furthermore, when $\Omega \gg \Gamma$, the population $P_0^{e0}(t) = |C_0^{e0}(t)|^2$ in Eq. (26) is reduced to

$$P_0^{e0}(t) = e^{-\Gamma t}\cos^2\left(\frac{\Omega t}{2}\right) = \frac{e^{-\Gamma t}}{2}(\cos(\Omega t) + 1). \tag{27}$$

Apparently, the population oscillates with a frequency Ω, as shown in Eq. (23). It is intriguing that the frequency of the Rabi-type oscillation depends on the vibrational overlap, and it can be related to the Franck-Condon factor. As a result, we call this phenomenon *Franck-Condon-Rabi oscillation*. Comparing *Franck-Condon-Rabi frequency* Ω with the Rabi frequency under zero vibrational couplings $\Omega_0 = |\langle 0(0)|0(0)\rangle|\sqrt{2A_0(\omega_{SPP})F_P(\omega_{SPP})\Gamma} = \sqrt{2A_0(\omega_{SPP})F_P(\omega_{SPP})\Gamma}$, the ratio can be expressed as a function of the Huang-Rhys factor α, i.e.,

$$\frac{\Omega}{\Omega_0} = |\langle 0(0)|0(\alpha)\rangle| = e^{-\alpha/2}. \tag{28}$$

Equation (28) indicates that vibrational degrees of freedom can play a significant role in the Rabi cycle of molecular fluorescence. In the high-frequency limit, Rabi frequency exponentially decreases with the Huang-Rhys factor.

C. Numerical demonstration of Franck-Condon-Rabi oscillation

To verify the relation in Eq. (28), i.e., the frequency of the Franck-Condon-Rabi oscillation, we consider the Lorentz-type Purcell factor [recall Eq. (17)] and calculate $P_0^{e0}(t)$ numerically using Eq. (18). To demonstrate the phenomenon of the Franck-Condon-Rabi oscillation, we adopt the following parameters: $\hbar\omega_{SPP} = 3.68$ eV, $\Gamma = 10^{-3}\,\omega_{SPP}$, and $F_P(\omega_{SPP}) = 3.927 \times 10^5$. For the part of the molecule, we use $A_0(\omega_{SPP}) = 6.366 \times 10^{-7}\omega_{SPP} = 3.5593$ ns^{-1}, $\alpha = 0.2, 0.6$, and 1.0, and $\omega_v = 1500$ cm^{-1} and 3000 cm^{-1}.

The population dynamics $P_0^{e0}(t)$ are numerically calculated based on Eq. (18), and the corresponding oscillation frequencies Ω are obtained by using the discrete Fourier transform. Both results are shown in Fig. 3. Note that there is no high frequency approximation in Eq. (18). Qualitatively, one can find that the population is independent of the vibration frequency ω_v but related to the Huang-Rhys factor α. Quantitatively, to examine Eq. (28), first, we calculate the value of Ω_0 analytically based on Eq. (23) and obtain $\Omega_0 = 663.69$ cm^{-1}. Second, we derive the values of Ω from the Fourier transform of the population $P_0^{e0}(t)$, as shown in Fig. 3. According to the two values, we can calculate their ratio Ω/Ω_0. The oscillation frequency Ω, the ratio Ω/Ω_0, and the vibrational overlap $|\langle 0(0)|0(\alpha)\rangle| = e^{-\alpha/2}$ are summarized in Table I. The ratios and the vibrational overlaps nearly perfectly match each other, indicating that Eqs. (23) and (26) allow us to precisely describe the population dynamics of a two-level molecule coupled to a high-frequency vibrational mode in the condition $\omega_{eg} = \omega_{SPP}$.

In Fig. 3, we find that the vibrational frequency does not play a role in oscillation frequency. In fact, it can be understood by a simple physical picture. In the condition $\omega_{eg} = \omega_{SPP}$, the vibrational transitions between different electronic states depend on Γ (the distribution of the photonic density of states or the photon loss rate in a dielectric environment). When $\omega_v \gg \Gamma$, the distribution of the photonic density of states only matches the resonant transition, e.g., 0-0 transition, so the off-resonant transitions cannot occur. On the other hand, when $\omega_v \ll \Gamma$, the distribution of the photonic density of states coincides with a large number of off-resonant transitions so the dynamics of molecular vibrations are mixed. In our
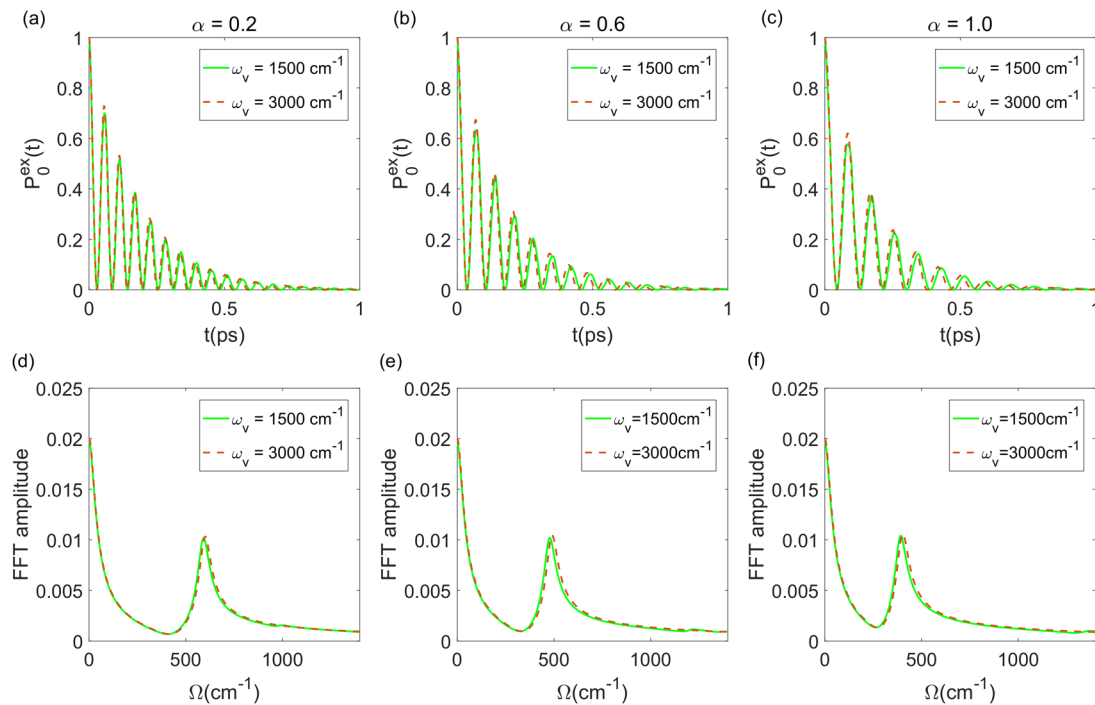
FIG. 3. Population dynamics with different Huang-Rhys factors and the corresponding oscillation frequencies based on Eq. (18). (a)–(c) The population dynamics $P_0^{ex}(t)$ of the molecular excited state with zero vibrational quanta for the Huang-Rhys factors, (a) $\alpha = 0.2$, (b) $\alpha = 0.6$, and (c) $\alpha = 1.0$. (d)–(f) correspond to the Fourier transform of (a)–(c), respectively. The oscillation frequencies are independent of the frequency of the vibrational mode ω_v, but the frequencies decrease with the increasing Huang-Rhys factor α.

study, the vibrational frequency $\omega_v = 1500$ cm^{-1} is much higher than $\Gamma = 10^{-3}\omega_{SPP} \approx 29.68$ cm^{-1}, so only the 0-0 transition is allowed and Franck-Condon-Rabi frequency is independent of ω_v.

D. Correspondence with the Jaynes-Cummings model

The Jaynes-Cummings (J-C) model is a two-level system interacting with a quantized mode of an optical cavity. Originally, the J-C model was used to study a molecule in a cavity,[55] and recently it has been extensively applied to investigate Rabi splitting and the dynamics of hybrid plasmon-exciton systems.[21,23,56] In order to model the loss of photons near the metal, we modified the J-C Hamiltonian as

$$\hat{H}_{JC} = \hbar(\omega_P - i\tilde{\Gamma})\hat{a}^+\hat{a} + \frac{\hbar\omega_t}{2}(\hat{\sigma}_z + \hat{I}) + V(\hat{a}\hat{\sigma}_+ + \hat{a}^+\hat{\sigma}_-), \quad (29)$$

TABLE I. Oscillation frequency Ω, frequency ratio Ω/Ω_0, and vibrational overlap $|\langle 0(0)|0(\alpha)\rangle| = e^{-\alpha/2}$ with respect to different Huang-Rhys factors $\alpha = 0.2$, 0.6, and 1.0. Nearly the same frequency ratios and vibrational overlaps indicate the validity of Eq. (28).

α	0.2	0.6	1.0
Ω (cm^{-1})	600.1	491.4	403.1
Ratio	0.904	0.740	0.607
$e^{-\alpha/2}$	0.905	0.741	0.607

where $\hat{a}^+$ and $\hat{a}$ are photon creation and annihilation operators, respectively; $\hat{\sigma}_+ = |e\rangle\langle g|$ and $\hat{\sigma}_- = |g\rangle\langle e|$ are the raising and lowering operators of the two-level system, respectively; $\hat{\sigma}_z = |e\rangle\langle e| - |g\rangle\langle g|$; ω_P is the frequency of the photonic mode of the cavity; ω_t is the transition frequency of the two-level system; $\tilde{\Gamma}$ is the loss rate of the photon in the cavity; and V is the coupling between the two-level system and the photonic mode of the cavity, i.e., exciton-polariton coupling.

We reduce the Fock space of the J-C model and focus on the two states, $|\psi_t\rangle = |e, \{0\}\rangle$ and $|\psi_P\rangle = |g, \{1\}\rangle$, where $|\psi_t\rangle$ is an electronically excited state coupled to a zero-photon state and $|\psi_P\rangle$ is an electronically ground state coupled to a single-photon state. Furthermore, if we connect the parameters of the J-C model and the parameters of our model, it turns out that ω_t corresponds to ω_{eg} (the gap between the electronically excited state and the ground state), ω_P corresponds to ω_{SPP} (the frequency of the SPP mode), and $\tilde{\Gamma} = \Gamma$ (the loss due to the SPP mode). In the subspace of the two states, the reduced J-C model is equivalent to a 2 by 2 matrix,

$$\tilde{H}_{JC} = \begin{bmatrix} \hbar\omega_t & V \\ V & \hbar(\omega_P - i\tilde{\Gamma}) \end{bmatrix} = \begin{bmatrix} \hbar\omega_{eg} & V \\ V & \hbar(\omega_{SPP} - i\Gamma) \end{bmatrix}. \quad (30)$$

By using the trial wavefunction $|\Psi(t)\rangle = C_t(t)e^{-i\omega_t t}|\psi_t\rangle + C_P(t)e^{-i(\omega_P - i\tilde{\Gamma})t}|\psi_P\rangle$, where $C_{t(p)}(t)$ is the coefficient of the state $|\psi_{t(p)}\rangle$, it is straightforward to derive an equation of motion of $C_t(t)$,

$$\frac{\partial}{\partial t} C_t(t) = -\left(\frac{V}{\hbar}\right)^2 \int_0^t dt' \, e^{-i(\omega_P - \omega_t - i\bar{\Gamma})(t - t')} C_t(t')$$
$$= -\left(\frac{V}{\hbar}\right)^2 \int_0^t dt' \, e^{-i(\omega_{SPP} - \omega_{eg} - i\Gamma)(t - t')} C_t(t'). \quad (31)$$

In the resonance condition $\omega_{eg} \approx \omega_{SPP}$, comparing Eq. (31) with Eq. (21), one derives the exciton-polariton coupling in terms of the spontaneous emission rate $A_0(\omega_{SPP})$, the height of the Purcell factor $F_P(\omega_{SPP})$, the half width of the Purcell factor Γ, and the vibrational overlap $|\langle 0(0)|0(\alpha)\rangle|$,

$$V = \hbar |\langle 0(0)|0(\alpha)\rangle| \sqrt{A_0(\omega_{SPP}) F_P(\omega_{SPP}) \Gamma / 2}. \quad (32)$$

Equation (32) is one of the main results in our work because the exciton-polariton coupling can be deduced from the parameter-free formula. In other words, $A_0(\omega_{SPP})$, $F_P(\omega_{SPP})$, Γ, and $|\langle 0(0)|0(\alpha)\rangle|$ can be derived from experiments or theoretical calculations.

Equation (32) offers a quite good estimate on the exciton-polariton coupling reported in Ref. 21. The work done by Chikkaraddy et al.[21] provides nearly all the parameters required by Eq. (32) (except for the vibrational overlap) for the methylene-blue (MB) molecule and the plasmonic cavity, including the magnitude of the transition dipole moment $\mu_{MB} = 3.8$ D, the transition frequency $\omega_{eg}^{MB} = 665$ nm, the height of the Purcell factor $F_P^{MB}(\omega_{eg}) \approx 3.5 \times 10^6$, and the half width at half maximum $\hbar\Gamma_{MB} \approx 84$ meV. The rate of the molecular spontaneous emission under the resonance condition $\omega_{eg}^{MB} = \omega_{SPP}$ is then calculated as $A_0^{MB}(\omega_{SPP}) \approx 1.54 \cdot 10^{+7} s^{-1}$. For the vibrational overlap $|\langle 0(0)|0(\alpha)\rangle|$ of the MB molecule, we perform a Density-Functioinal Theory (DFT) study on its ground (S_0) and its first singlet excited state (S_1) using Gaussian 16 A.03.[57] The geometry optimization and the harmonic vibrational frequency calculations of both S_0 and S_1 states are performed with the CAM-B3LYP[58] exchange-correlation functional and the 6-311 + G* basis set; the S_0 state is calculated using the spin-restricted density functional theory, and the S_1 state is calculated using time-dependent DFT. Subsequently, we perform the Duschinsky transformation[59] to calculate the Huang-Rhys factors along each normal mode using the DUSHIN code developed by Reimers.[60] All the normal modes with high Huang-Rhys factors are given in Table II.

It is clear that nearly all the vibrational overlaps $|\langle 0(0)|0(\alpha)\rangle|$ are close to 1 especially for high vibrational frequency modes ($\omega_v > 500$ cm^{-1}), so we can take $|\langle 0(0)|0(\alpha)\rangle| \approx 1$ in Eq. (32) and obtain the exciton-polariton coupling of the MB molecule as $V_{MB} \approx 39$ meV and the Rabi splitting $2V_{MB} \approx 78$ meV.

TABLE II. Vibrational frequency ω_v, Huang-Rhys factor α, and vibrational overlap $|\langle 0(0)|0(\alpha)\rangle|$ of the MB molecule. Nearly all the Huang-Rhys factors are small especially for high vibrational frequency modes ($\omega_v > 500$ cm^{-1}), indicating that the vibrational overlaps of MB molecule can be neglected in Eq. (32).

ω_v (cm^{-1})	α	$|\langle 0(0)|0(\alpha)\rangle|$
109	0.06	0.97
245	0.04	0.98
452	0.20	0.90
514	0.09	0.96
792	0.04	0.98
1448	0.02	0.99

It is surprising that the Rabi splitting derived from our method (78 meV) agrees quite well with the experimental result (80–95 meV).[21] The small deviation of the two results may originate from a reason that the Purcell factor in Chikkaraddy's work has a long tail in the high-frequency regime, which may lead to an underestimation of V_{MB}. Although Eq. (32) does not give a perfect match with the experimental value, it indeed provides a handy tool to calculate the exciton-polariton coupling without using any free-tuning parameters. Compared with the work done by Chikkaraddy et al.,[21] in their study the exciton-polariton coupling is calculated based on cavity quantum electrodynamics with a free-tuning parameter (an effective volume). More importantly, Eq. (32) contains a vibrational overlap, which is not considered in most studies on molecular emitters. We hope that our theory will motivate experimental physicists and chemists to explore the influence of vibrational overlaps on exciton-polariton couplings.

IV. CONCLUSIONS

In this study, we have established a theory of molecular fluorescence, which allows us to describe the non-Markovian quantum dynamics of a molecular emitter in a wide variety of nanostructures (not limited to plasmonic materials). Within the electric-dipole approximation, the rotating-wave approximation, and the Condon approximation, we find that the quantum dynamical equation of molecular fluorescence, Eq. (9), can be expressed in terms of the polariton kernel $K_{pol}(t, t')$ (associated with the effect of a dielectric environment) and the vibrational kernel $K_{vib}^{K,L}(t, t')$ (associated with a vibrational overlap). Moreover, we find that the polariton kernel is directly related to the Purcell factor and the molecular spontaneous emission rate in a vacuum, indicating that one can obtain the kernel computationally or experimentally. For a molecule with a high-frequency vibrational mode above a silver surface, Eq. (9) can be further reduced to a second-order linear differential equation, as shown in Eq. (22). According to the relation between Ω and Γ (the half width of a Lorentzian-shaped Purcell factor) in Eq. (22), we clearly demonstrate three different behaviors of the population dynamics of the electronically excited state. When $\Omega \gg \Gamma$, the population dynamics of the excited state behaves as a Rabi-type oscillation and depends on the Franck-Condon factor. As a result, we refer to this phenomenon as Franck-Condon-Rabi oscillation. Note that there is no Franck-Condon-Rabi oscillation in the work done by Chikkaraddy et al.[21] due to $\Omega_{MB} < \Gamma_{MB}$ ($\hbar\Omega_{MB} = 2V_{MB} \approx 78$ meV and $\hbar\Gamma_{MB} \approx 84$ meV). Therefore, the population dynamics of the MB molecule is supposed to exponentially decay. In order to experimentally observe the Franck-Condon-Rabi oscillation, the condition $\Omega > \Gamma$ is required. Furthermore, our main result indicates that the exciton-photon coupling (or exciton-polariton coupling) in the Jaynes-Cummings model can be deduced from a parameter-free formula based on the experimental observables in Eq. (32).

Although we have clearly demonstrated the quantum dynamics of a molecular emitter coupled with SPPs, several issues still remain to be addressed. First, the interaction Hamiltonian $\hat{H}_{int}$ [recall Eq. (4)] is based on the rotating-wave approximation, and it is valid when the energy gap of a molecule is resonant or nearly resonant with the frequency of a polariton mode, i.e., $\omega_{eg} = \omega_{SPP}$. Second, we neglect the vibrational coordinate dependence of the transition dipole moment and simply adopt the Condon

approximation in $\hat{H}_{\text{int}}$. In fact, when the molecule is placed in a vacuum (or a homogeneous medium), the role of vibrational coordinate in electronic transitions has been widely investigated,[61,62] known as the Herzberg-Teller coupling.[63] The influence of polaritons on the Herzberg-Teller coupling deserves further exploration. Third, in the low-frequency limit ($\omega_v \ll \Gamma$), Eq. (21) is not held, and one cannot describe the dynamics of the electronically excited states simply using Eq. (22). These issues will be further explored in our future work. Quantum electrodynamics is a powerful tool to investigate light-matter interactions in molecular sciences,[64–66] and its applications are emerging in nanotechnology and nanosciences.[8–10,32] We hope that this study could motivate more experimental and theoretical investigations into the quantum dynamics of a molecule strongly coupled with SPPs.

APPENDIX A: DERIVATION OF EQ. (4) FROM QUANTUM ELECTRODYNAMICS

In the minimal-coupling scheme, the total Hamiltonian of a molecule in the medium-assisted electromagnetic field can be described as[22]

$$\hat{H}_{\text{tot}} = \hat{H}_{\text{pol}} + \sum_{\alpha} \frac{1}{2m_{\alpha}} |\hat{\boldsymbol{p}}_{\alpha} - q_{\alpha}\hat{\boldsymbol{A}}(\hat{\boldsymbol{r}}_{\alpha})|^2$$
$$+ \frac{1}{2} \int d\boldsymbol{r} \hat{\rho}_{\text{M}}(\boldsymbol{r})\hat{\phi}_{\text{M}}(\boldsymbol{r}) + \int d\boldsymbol{r}\hat{\rho}_{\text{M}}(\boldsymbol{r})\hat{\phi}(\boldsymbol{r}), \quad \text{(A1)}$$

where the first term is the polariton Hamiltonian [recall Eq. (2)], the second term is the kinetic energy of nucleus and electrons in the molecule, the third term is the Coulomb energy of the molecule, and the fourth term is the Coulomb energy of the interaction between the molecule and the electromagnetic field. The symbols of the four terms will be explained in the following.

In the second term, q_{α} and m_{α} are the point charge and mass of charge, respectively. $\hat{\boldsymbol{r}}_{\alpha}$ and $\hat{\boldsymbol{p}}_{\alpha}$ are the position and momentum operators of the point charges, respectively, and $\hat{\boldsymbol{A}}(\hat{\boldsymbol{r}}_{\alpha})$ is the vector potential of the electromagnetic field associated with $\hat{\boldsymbol{E}}(\boldsymbol{r},\omega)$ in Eq. (5),

$$\hat{\boldsymbol{A}}(\hat{\boldsymbol{r}}_{\alpha}) = \int_0^{\infty} d\omega \frac{\hat{\boldsymbol{E}}^{\perp}(\hat{\boldsymbol{r}}_{\alpha},\omega)}{i\omega} + \text{H.c.}, \quad \text{(A2)}$$

$$\hat{\boldsymbol{E}}^{\perp(\parallel)}(\hat{\boldsymbol{r}}_{\alpha},\omega) = \int d\boldsymbol{r} \, \delta^{\perp(\parallel)}(\hat{\boldsymbol{r}}_{\alpha} - \boldsymbol{r}) \cdot \hat{\boldsymbol{E}}(\boldsymbol{r},\omega), \quad \text{(A3)}$$

where $\delta^{\perp}(\boldsymbol{r})$ and $\delta^{\parallel}(\boldsymbol{r})$ are transverse and longitudinal delta functions, respectively.

In the third term of Eq. (A1), $\hat{\rho}_{\text{M}}(\boldsymbol{r})$ and $\hat{\phi}_{\text{M}}(\boldsymbol{r})$ are the charge density operator and electric potential operator of the point charges,

$$\hat{\rho}_{\text{M}}(\boldsymbol{r}) = \sum_{\alpha} q_{\alpha}\delta(\boldsymbol{r} - \hat{\boldsymbol{r}}_{\alpha}), \quad \text{(A4)}$$

$$\hat{\phi}_{\text{M}}(\boldsymbol{r}) = \int d\boldsymbol{r}' \frac{\hat{\rho}_{\text{M}}(\boldsymbol{r}')}{4\pi\epsilon_0|\boldsymbol{r} - \boldsymbol{r}'|}, \quad \text{(A5)}$$

where $\hat{\boldsymbol{r}}_{\alpha}$ and $\hat{\boldsymbol{p}}_{\alpha}$ are the position and momentum operators of the nucleus and electrons composing the molecule, respectively.

In the fourth term, $\hat{\phi}(\boldsymbol{r})$ is the electric scalar potential operator of the medium which satisfies the Maxwell equation,

$$\nabla\hat{\phi}(\boldsymbol{r}) = -\hat{\boldsymbol{E}}^{\parallel}(\boldsymbol{r}), \quad \text{(A6)}$$

where $\hat{\boldsymbol{E}}^{\parallel}(\boldsymbol{r})$ is the summation of all polariton mode of the operator $\hat{\boldsymbol{E}}^{\parallel}(\hat{\boldsymbol{r}},\omega)$ in Eq. (A3),

$$\hat{\boldsymbol{E}}^{\parallel}(\boldsymbol{r}) = \int d\omega \, \hat{\boldsymbol{E}}^{\parallel}(\hat{\boldsymbol{r}},\omega) + \text{H.c..} \quad \text{(A7)}$$

In order to simplify the total Hamiltonian $\hat{H}_{\text{tot}}$, we rearrange Eq. (A1) in the Coulomb gauge ($[\hat{\boldsymbol{p}}_{\alpha}, \hat{\boldsymbol{A}}(\hat{\boldsymbol{r}}_{\alpha})] = 0$),

$$\hat{H}_{\text{tot}} = \hat{H}_{\text{mol}} + \hat{H}_{\text{pol}} + \hat{H}_{\text{int}}, \quad \text{(A8)}$$

$$\hat{H}_{\text{mol}} = \sum_{\alpha} \frac{\hat{\boldsymbol{p}}_{\alpha}^2}{2m_{\alpha}} + \frac{1}{2} \int d\boldsymbol{r}\hat{\rho}_{\text{A}}(\boldsymbol{r})\hat{\phi}_{\text{A}}(\boldsymbol{r})$$
$$= \sum_{\alpha} \frac{\hat{\boldsymbol{p}}_{\alpha}^2}{2m_{\alpha}} + \frac{1}{2} \sum_{\alpha,\beta} \frac{q_{\alpha}q_{\beta}}{4\pi\epsilon_0|\hat{\boldsymbol{r}}_{\alpha} - \hat{\boldsymbol{r}}_{\beta}|}, \quad \text{(A9)}$$

$$\hat{H}_{\text{pol}} = \int d\boldsymbol{r} \int_0^{\infty} d\omega \, \hbar\omega \hat{\boldsymbol{f}}^{\dagger}(\boldsymbol{r},\omega) \cdot \hat{\boldsymbol{f}}(\boldsymbol{r},\omega), \quad \text{(A10)}$$

$$\hat{H}_{\text{int}} = -\sum_{\alpha} \frac{q_{\alpha}}{m_{\alpha}}\hat{\boldsymbol{p}}_{\alpha} \cdot \hat{\boldsymbol{A}}(\hat{\boldsymbol{r}}_{\alpha}) + \sum_{\alpha} \frac{q_{\alpha}^2}{2m_{\alpha}}\hat{\boldsymbol{A}}^2(\hat{\boldsymbol{r}}_{\alpha}) + \int d\boldsymbol{r}\hat{\rho}_{\text{A}}(\boldsymbol{r})\hat{\phi}(\boldsymbol{r}), \quad \text{(A11)}$$

where $\hat{H}_{\text{mol}}$ is the Hamiltonian of a molecule placed in a vacuum, $\hat{\rho}_{\text{A}}(\boldsymbol{r})$ and $\hat{\phi}_{\text{A}}(\boldsymbol{r})$ are the charge density operator and the electric potential operator for the point charges in the molecule, respectively, and the subscript $\alpha(\beta)$ is the index of both nucleus and electrons. To simplify this molecular Hamiltonian, we apply the Born-Oppenheimer approximation and include two electronic states, and one harmonic vibrational mode. Based on such assumption, the exact molecular Hamiltonian $\hat{H}_{\text{mol}}$ in Eq. (A9) can be approximated into the form Eq. (1).

For the interaction Hamiltonian $\hat{H}_{\text{int}}$, we neglect the $\hat{\boldsymbol{A}}^2(\hat{\boldsymbol{r}}_{\alpha})$ term owing to its zero contribution during the molecular spontaneous emission processes.[67] As a result, the interaction Hamiltonian turns to be

$$\hat{H}_{\text{int}} = -\sum_{\alpha} \frac{q_{\alpha}}{m_{\alpha}}\hat{\boldsymbol{p}}_{\alpha} \cdot \hat{\boldsymbol{A}}(\hat{\boldsymbol{r}}_{\alpha}) + \int d\boldsymbol{r}\hat{\rho}_{\text{A}}(\boldsymbol{r})\hat{\phi}(\boldsymbol{r}). \quad \text{(A12)}$$

For simplicity, the first term in Eq. (A12) can be replaced with the molecular dipole operator $\hat{\boldsymbol{\mu}}_M \equiv \sum_\beta q_\beta(\hat{\boldsymbol{r}}_\beta - \boldsymbol{r}_M)$, where $\boldsymbol{r}_M$ is the center of mass of the molecule, and we approximate the first part in Eq. (A12) as

$$-\sum_\alpha \frac{q_\alpha}{m_\alpha}\hat{\boldsymbol{p}}_\alpha \cdot \boldsymbol{A}(\hat{\boldsymbol{r}}_\alpha) = -\sum_\alpha \frac{q_\alpha}{i\hbar}[\hat{\boldsymbol{r}}_\alpha, \hat{H}_{mol}] \cdot \boldsymbol{A}(\hat{\boldsymbol{r}}_\alpha) \qquad (A13)$$

$$\approx -\sum_\alpha \frac{q_\alpha}{i\hbar}[\hat{\boldsymbol{r}}_\alpha, \hat{H}_{mol}] \cdot \boldsymbol{A}(\boldsymbol{r}_M) \qquad (A14)$$

$$= -\sum_\alpha \frac{q_\alpha}{i\hbar}[\hat{\boldsymbol{r}}_\alpha - \boldsymbol{r}_M, \hat{H}_{mol}] \cdot \boldsymbol{A}(\boldsymbol{r}_M) \qquad (A15)$$

$$= -\frac{1}{i\hbar}[\hat{\boldsymbol{\mu}}_M, \hat{H}_{mol}] \cdot \boldsymbol{A}(\boldsymbol{r}_M). \qquad (A16)$$

Note that the derivation of Eq. (A13) requires the canonical commutation relation $[\hat{\boldsymbol{r}}_\alpha, \hat{\boldsymbol{p}}_\alpha] = i\hbar$; the electric-dipole approximation $\boldsymbol{A}(\hat{\boldsymbol{r}}_\alpha) \approx \boldsymbol{A}(\boldsymbol{r}_M)$ results in Eq. (A14); and the charge neutrality condition $\boldsymbol{r}_M\sum_\alpha q_\alpha = 0$ gives Eq. (A15).

Moreover, by substituting $\hat{I} = (|e\rangle\langle e| + |g\rangle\langle g|) \otimes \sum_M |M(0)\rangle\langle M(0)| = (|e\rangle\langle e| + |g\rangle\langle g|) \otimes \sum_N |N(\alpha)\rangle\langle N(\alpha)|$ into $\hat{H}_{mol}$, we can get an alternative expression of $\hat{H}_{mol}$,

$$\hat{H}_{mol} = \sum_N |g\rangle|N(\alpha)\rangle(\hbar\omega_v N)\langle N(\alpha)|\langle g|$$
$$+ \sum_M |e\rangle|M(0)\rangle(\hbar\omega_{eg} + \hbar\omega_v M)\langle M(0)|\langle e|. \qquad (A17)$$

If the permanent dipole moment of the molecule is very small ($\langle e|\hat{\boldsymbol{\mu}}_M|e\rangle = \langle g|\hat{\boldsymbol{\mu}}_M|g\rangle \approx 0$), only the transition dipole moment $\langle e|\hat{\boldsymbol{\mu}}_M|g\rangle = \langle g|\hat{\boldsymbol{\mu}}_M|e\rangle = \boldsymbol{\mu}$ needs to be considered, and the first part of the interaction Hamiltonian Eq. (A12) now can be further reduced to

$$-\frac{[\hat{\boldsymbol{\mu}}_M, \hat{H}_{mol}] \cdot \boldsymbol{A}(\boldsymbol{r}_M)}{i\hbar} = \frac{i}{\hbar}(\hat{I}\hat{\boldsymbol{\mu}}_M\hat{H}_{mol} - \hat{H}_{mol}\hat{\boldsymbol{\mu}}_M\hat{I}) \cdot \boldsymbol{A}(\boldsymbol{r}_M)$$

$$= \frac{i}{\hbar}\left\{|g\rangle\langle e|\boldsymbol{\mu}\left(\hbar\omega_{eg} + \sum_N \hbar\omega_v N(|N(0)\rangle\langle N(0)| - |N(\alpha)\rangle\langle N(\alpha)|)\right) - \text{H.c.}\right\} \cdot \boldsymbol{A}(\boldsymbol{r}_M)$$

$$= \frac{i}{\hbar}\left\{|g\rangle\langle e|\boldsymbol{\mu}\left(\hbar\omega_{eg} + \sum_N \hbar\omega_v(b^\dagger b|N(0)\rangle\langle N(0)| - \bar{b}^\dagger\bar{b}|N(\alpha)\rangle\langle N(\alpha)|)\right) - \text{H.c.}\right\} \cdot \boldsymbol{A}(\boldsymbol{r}_M)$$

$$\approx i\{|g\rangle\langle e|\boldsymbol{\mu}\omega_{eg} - \text{H.c.}\} \cdot \boldsymbol{A}(\boldsymbol{r}_M) \qquad (A18)$$

$$= \{|g\rangle\langle e|\boldsymbol{\mu} - \text{H.c.}\} \cdot \left\{\int_0^\infty d\omega \frac{\omega_{eg}}{\omega}\hat{\boldsymbol{E}}^\perp(\boldsymbol{r}_M, \omega) - \text{H.c.}\right\} \qquad (A19)$$

$$\approx -\left\{|g\rangle\langle e|\boldsymbol{\mu} \cdot \hat{\boldsymbol{E}}^{\perp(-)}(\boldsymbol{r}_M) + |e\rangle\langle g|\boldsymbol{\mu} \cdot \hat{\boldsymbol{E}}^{\perp(+)}(\boldsymbol{r}_M)\right\}, \qquad (A20)$$

where in order to derive Eq. (A18), we implicitly use the Condon approximation so that the transition dipole moment is independent of nuclear coordinates $\left(\sum_N \hbar\omega_v(b^\dagger b|N(0)\rangle\langle N(0)| - \bar{b}^\dagger\bar{b}|N(\alpha)\rangle\langle N(\alpha)|)\right) \approx 0$ and $\bar{b}^\dagger = b^\dagger - \sqrt{\alpha}$). In addition to derive Eq. (A20), $\omega = \omega_{eg}$ is set in the integral because of the pretrace rotating-wave approximation.[68]

In order to cope with the second term in $\hat{H}_{int}$, we expand $\hat{\rho}_M(\boldsymbol{r})$ in a multi-polar form and retain only the first nonvanishing term,

$$\hat{\rho}_M(\boldsymbol{r}) \approx \sum_\alpha q_\alpha \delta(\boldsymbol{r} - \boldsymbol{r}_M) - \nabla \cdot \left(\delta(\boldsymbol{r} - \boldsymbol{r}_M)\sum_\alpha q_\alpha(\hat{\boldsymbol{r}}_\alpha - \boldsymbol{r}_M)\right)$$
$$= -\nabla \cdot \delta(\boldsymbol{r} - \boldsymbol{r}_M)\hat{\boldsymbol{\mu}}_M. \qquad (A21)$$

Plugging Eq. (A21) into the second part of the interaction Hamiltonian Eq. (A12), we can derive

$$\int d\boldsymbol{r}\hat{\rho}_M(\boldsymbol{r})\hat{\phi}(\boldsymbol{r}) = -\int d\boldsymbol{r}\left(\nabla \cdot \delta(\boldsymbol{r} - \boldsymbol{r}_M)\hat{\boldsymbol{\mu}}_M\right)\hat{\phi}(\boldsymbol{r})$$

$$= \int d\boldsymbol{r}\left(\delta(\boldsymbol{r} - \boldsymbol{r}_M)\hat{\boldsymbol{\mu}}_M\right) \cdot \nabla\hat{\phi}(\boldsymbol{r}) = \hat{\boldsymbol{\mu}}_M \cdot \nabla\hat{\phi}(\boldsymbol{r}_M) \qquad (A22)$$

$$= -\hat{\boldsymbol{\mu}}_M \cdot \hat{\boldsymbol{E}}^\parallel(\boldsymbol{r}_M) = -\hat{I}\hat{\boldsymbol{\mu}}_M\hat{I} \cdot \hat{\boldsymbol{E}}^\parallel(\boldsymbol{r}_M) \qquad (A23)$$

$$= -|e\rangle\langle g|\boldsymbol{\mu} \cdot \hat{\boldsymbol{E}}^{\parallel(+)}(\boldsymbol{r}_M) - |g\rangle\langle e|\boldsymbol{\mu} \cdot \hat{\boldsymbol{E}}^{\parallel(-)}(\boldsymbol{r}_M), \qquad (A24)$$

where integration by parts is applied to the derivation of Eq. (A22), and the rotating-wave approximation is again used for deriving Eq. (A24).

Finally, we obtain the approximated interaction Hamiltonian Eq. (4) by combining Eqs. (A24) and (A20),

$$\hat{H}_{int} = -\left(|e\rangle\langle g|\hat{\boldsymbol{E}}^{(+)}(\boldsymbol{r}_M) \cdot \boldsymbol{\mu} + |g\rangle\langle e|\hat{\boldsymbol{E}}^{(-)}(\boldsymbol{r}_M) \cdot \boldsymbol{\mu}\right), \qquad (A25)$$

the Helmholtz decomposition theorem, and the property of the operator $\hat{\boldsymbol{E}}^{(+)}(\boldsymbol{r}_M)$ is applied,[22]

$$\hat{\boldsymbol{E}}^{(\pm)}(\boldsymbol{r}_M) = \hat{\boldsymbol{E}}^{\parallel(\pm)}(\boldsymbol{r}_M) + \hat{\boldsymbol{E}}^{\perp(\pm)}(\boldsymbol{r}_M), \qquad (A26)$$

$$\hat{\boldsymbol{E}}(\boldsymbol{r}_M) = \hat{\boldsymbol{E}}^{(+)}(\boldsymbol{r}_M) + \text{H.c.}. \qquad (A27)$$

APPENDIX B: DERIVATION OF THE DYNAMIC EQUATION (9)

In order to simplify the notation, we use Einstein summation notation and define an auxiliary dyadic Green's function $\bar{\bar{G}}_{ji}(\boldsymbol{r}_M, \boldsymbol{r}, \omega)$,

$$\bar{\bar{G}}_{ji}(\boldsymbol{r}_M, \boldsymbol{r}, \omega) = i\mu_j \frac{\omega^2}{c^2}\sqrt{\frac{\hbar}{\pi\epsilon_0}}\sqrt{\epsilon_I(\boldsymbol{r}, \omega)}G_{ji}(\boldsymbol{r}_M, \boldsymbol{r}, \omega). \qquad (B1)$$

Substituting Eq. (8) into $i\hbar\,\partial|\psi(t)\rangle/\partial t = \hat{H}_{\text{tot}}|\psi(t)\rangle$, the left-hand side of $i\hbar\,\partial|\psi(t)\rangle/\partial t = \hat{H}_{\text{tot}}|\psi(t)\rangle$ turns to be

$$i\hbar\,\partial|\psi(t)\rangle/\partial t = \sum_{N=0}^{\infty}\left\{i\hbar\dot{C}_N^{e0}(t) + \hbar(\omega_{\text{eg}} + \omega_{\text{v}}N)C_N^{e0}(t)\right\}e^{-i(\omega_{\text{eg}}+\omega_{\text{v}}N)t}|e\rangle|N(0)\rangle|\{0\}\rangle$$
$$+ \sum_M \int d\boldsymbol{r} \int_0^{\infty} d\omega\left\{i\hbar\dot{C}_M^{gi}(\boldsymbol{r},\omega,t) + \hbar(\omega + \omega_{\text{v}}M)C_M^{gi}(\boldsymbol{r},\omega,t)\right\}e^{-i(\omega+\omega_{\text{v}}M)t}|g\rangle|M(\alpha)\rangle|\{1_i(\boldsymbol{r},\omega)\}\rangle. \quad \text{(B2)}$$

For the right-hand side of $i\hbar\,\partial|\psi(t)\rangle/\partial t = \hat{H}_{\text{tot}}|\psi(t)\rangle$, $\hat{H}_{\text{tot}}|\psi(t)\rangle$ can be separated into $\hat{H}_{\text{mol}}|\psi(t)\rangle$, $\hat{H}_{\text{pol}}|\psi(t)\rangle$, and $\hat{H}_{\text{int}}|\psi(t)\rangle$, and they are evaluated as follows:

$$\hat{H}_{\text{mol}}|\psi(t)\rangle = \sum_{N=0}^{\infty}(\hbar\omega_{\text{eg}} + \hbar\omega_{\text{v}}N)C_N^{e0}(t)e^{-i(\omega_{\text{eg}}+\omega_{\text{v}}N)t}|e\rangle|N(0)\rangle|\{0\}\rangle$$
$$+ \sum_{M=0}^{\infty}\int d\boldsymbol{r}\int_0^{\infty}d\omega(\hbar\omega_{\text{v}}M)C_M^{gi}(\boldsymbol{r},\omega,t)e^{-i(\omega+\omega_{\text{v}}M)t}|g\rangle|M(\alpha)\rangle|\{1_i(\boldsymbol{r},\omega)\}\rangle, \quad \text{(B3)}$$

$$\hat{H}_{\text{pol}}|\psi(t)\rangle = \sum_{M=0}^{\infty}\int d\boldsymbol{r}\int_0^{\infty}d\omega(\hbar\omega)C_M^{gi}(\boldsymbol{r},\omega,t)e^{-i(\omega+\omega_{\text{v}}M)t}|g\rangle|M(\alpha)\rangle|\{1_i(\boldsymbol{r},\omega)\}\rangle, \quad \text{(B4)}$$

$$\hat{H}_{\text{int}}|\psi(t)\rangle = -\sum_{N=0}^{\infty}(\hat{E}_j^{(-)}(\boldsymbol{r}_{\text{M}})\mu_j)C_N^{e0}(t)e^{-i(\omega_{\text{eg}}+\omega_{\text{v}}N)t}|g\rangle|N(0)\rangle|\{0\}\rangle$$
$$- \sum_{M=0}^{\infty}(\hat{E}_j^{(+)}(\boldsymbol{r}_{\text{M}})\mu_j)\int d\boldsymbol{r}\int_0^{\infty}d\omega C_M^{gi}(\boldsymbol{r},\omega,t)e^{-i(\omega+\omega_{\text{v}}M)t}|e\rangle|M(\alpha)\rangle|\{1_i(\boldsymbol{r},\omega)\}\rangle$$
$$= -\sum_{N=0}^{\infty}\int_0^{\infty}d\omega\,\mu_j(-i)\sqrt{\frac{\hbar}{\pi\epsilon_0}}\frac{\omega^2}{c^2}\int d\boldsymbol{r}\sqrt{\epsilon_{\text{I}}(\boldsymbol{r},\omega)}G_{ji}^*(\boldsymbol{r}_{\text{M}},\boldsymbol{r},\omega)C_N^{e0}(t)e^{-i(\omega_{\text{eg}}+\omega_{\text{v}}N)t}|g\rangle|N(0)\rangle|\{1_i(\boldsymbol{r},\omega)\}\rangle$$
$$- \sum_{M=0}^{\infty}\int_0^{\infty}d\omega\,\mu_j(i)\sqrt{\frac{\hbar}{\pi\epsilon_0}}\frac{\omega^2}{c^2}\int d\boldsymbol{r}\sqrt{\epsilon_{\text{I}}(\boldsymbol{r},\omega)}G_{ji}(\boldsymbol{r}_{\text{M}},\boldsymbol{r},\omega)C_M^{gi}(\boldsymbol{r},\omega,t)e^{-i(\omega+\omega_{\text{v}}M)t}|e\rangle|M(\alpha)\rangle|\{0\}\rangle, \quad \text{(B5)}$$

where $\hat{f}_i(\boldsymbol{r}',\omega')|\{1_k(\boldsymbol{r},\omega)\}\rangle = \delta(\boldsymbol{r}-\boldsymbol{r}')\delta(\omega-\omega')\delta_{i,k}|\{0\}\rangle$ and $\hat{f}_i^+(\boldsymbol{r}',\omega')|\{0\}\rangle = |\{1_i(\boldsymbol{r}',\omega')\}\rangle$ are used. Comparing the left-hand side and the right-hand side of the Schrödinger equation $i\hbar\,\partial|\psi(t)\rangle/\partial t = \hat{H}_{\text{tot}}|\psi(t)\rangle$ and using the notation in Eq. (B1), we can get the following equation:

$$-i\hbar\left\{\sum_N \dot{C}_N^{e0}(t)e^{-i(\omega_{\text{eg}}+\omega_{\text{v}}N)t}|e\rangle|\{0\}\rangle|N(0)\rangle + \sum_M\int d\boldsymbol{r}\int_0^{\infty}d\omega\dot{C}_M^{gi}(\boldsymbol{r},\omega,t)e^{-i(\omega+\omega_{\text{v}}M)t}|g\rangle|M(\alpha)\rangle|\{1_i(\boldsymbol{r},\omega)\}\rangle\right\}$$
$$= \int d\omega\int d\boldsymbol{r}\left\{\sum_N\bar{\bar{G}}_{ji}^*(\boldsymbol{r}_{\text{M}},\boldsymbol{r},\omega)C_N^{e0}(t)e^{-i(\omega_{\text{eg}}+\omega_{\text{v}}N)t}|g\rangle|\{1_i(\boldsymbol{r},\omega)\}\rangle|N(0)\rangle + \sum_M\bar{\bar{G}}_{ji}(\boldsymbol{r}_{\text{M}},\boldsymbol{r},\omega)C_M^{gi}(\boldsymbol{r},\omega,t)e^{-i(\omega+\omega_{\text{v}}M)t}|e\rangle|\{0\}\rangle|M(\alpha)\rangle\right\}. \quad \text{(B6)}$$

Let $\langle e|\langle\{0\}|\langle K(0)|$ and $\langle g|\langle\{1_i(\boldsymbol{r}',\omega')\}|\langle K(0)|$ act on Eq. (B6) sequentially, and we get the following equations:

$$i\hbar\dot{C}_K^{e0}(t)e^{-i(\omega_{\text{eg}}+\omega_{\text{v}}K)t}$$
$$= -\int d\omega\int d\boldsymbol{r}\sum_M\bar{\bar{G}}_{ji}(\boldsymbol{r}_{\text{M}},\boldsymbol{r},\omega)$$
$$\times \langle K(0)|M(\alpha)\rangle C_M^{gi}(\boldsymbol{r},\omega,t)e^{-i(\omega+\omega_{\text{v}}M)t}, \quad \text{(B7)}$$

$$i\hbar\sum_M\dot{C}_M^{gi}(\boldsymbol{r},\omega,t)e^{-i(\omega+\omega_{\text{v}}M)t}\langle K(0)|M(\alpha)\rangle$$
$$= -\bar{\bar{G}}_{ji}^*(\boldsymbol{r}_{\text{M}},\boldsymbol{r},\omega)C_K^{e0}(t)e^{-i(\omega_{\text{eg}}+\omega_{\text{v}}K)t}. \quad \text{(B8)}$$

Using the completeness relation ($\overleftrightarrow{I} = \sum_{n=0}^{\infty}|n(\alpha)\rangle\langle n(\alpha)|$) and the orthogonality relation ($\langle n(\alpha)|m(\alpha)\rangle = \delta_{nm}$), Eq. (B8) becomes

$$\dot{C}_M^{gi}(\boldsymbol{r},\omega,t)e^{-i(\omega+M\omega_v)t}$$
$$= \frac{-\bar{\bar{G}}_{ji}^*(\boldsymbol{r}_{\text{M}},\boldsymbol{r},\omega)}{i\hbar}\sum_{L=0}^{\infty}\langle M(\alpha)|L(0)\rangle C_L^{e0}(t)e^{-i(\omega_{\text{eg}}+L\omega_v)t}, \quad \text{(B9)}$$

with initial conditions $C_M^{gi}(\boldsymbol{r},\omega,0) = 0$, Eq. (B9) can be formally integrated,

$$C_M^{gi}(\boldsymbol{r},\omega,t) = \int_0^t dt'\frac{-\bar{\bar{G}}_{ji}^*(\boldsymbol{r}_{\text{M}},\boldsymbol{r},\omega)}{i\hbar}\sum_{L=0}^{\infty}\langle M(\alpha)|L(0)\rangle$$
$$\times C_L^{e0}(t')e^{-it'[(\omega_{\text{eg}}-\omega)+\omega_v(L-M)]}. \quad \text{(B10)}$$

Substituting this formula into Eq. (B7), one can get the following result:

$$\dot{C}_K^{e0}(t) = \int_0^\infty d\omega \int_0^t dt' \int d\boldsymbol{r} \frac{\bar{\bar{G}}_{ji}(\boldsymbol{r}_M, \boldsymbol{r}, \omega) \bar{\bar{G}}_{ki}^*(\boldsymbol{r}_M, \boldsymbol{r}, \omega)}{-\hbar^2}$$
$$\times \sum_{L=0}^\infty \left\{ \sum_{M=0}^\infty \langle K(0)|M(\alpha)\rangle\langle M(\alpha)|L(0)\rangle e^{-i\omega_v M(t-t')} \right\}$$
$$\times e^{-i(\omega-\omega_{eg})(t-t')} e^{-i\omega_v(Lt'-Kt)} C_L^{e0}(t'). \tag{B11}$$

Using the relationship,[31]

$$\text{Im}\,G_{jk}(\boldsymbol{r}_A, \boldsymbol{r}_B, \omega) = \int d\boldsymbol{r} \frac{\omega^2}{c^2} \epsilon_I(\boldsymbol{r}, \omega) G_{ji}(\boldsymbol{r}_A, \boldsymbol{r}, \omega) G_{ki}^*(\boldsymbol{r}_B, \boldsymbol{r}, \omega), \tag{B12}$$

we obtain Eq. (9) as follows:

$$\dot{C}_K^{e0}(t) = -\frac{\mu_j \mu_k}{\hbar\pi\epsilon_0} \int_0^t dt' \left\{ \int_0^\infty d\omega \frac{\omega^2}{c^2} \text{Im}\,G_{jk}(\boldsymbol{r}_M, \boldsymbol{r}_M, \omega) e^{-i(\omega-\omega_{eg})(t-t')} \right\}$$
$$\times \sum_{L=0}^\infty \left\{ \sum_{M=0}^\infty \langle K(0)|M(\alpha)\rangle\langle M(\alpha)|L(0)\rangle e^{-i\omega_v M(t-t')} \right\}$$
$$\times e^{-i\omega_v(Lt'-Kt)} C_L^{e0}(t'). \tag{B13}$$

REFERENCES

[1] H. A. Atwater and A. Polman, Nat. Mater. **9**, 205 (2010).

[2] B. E. Hardin, E. T. Hoke, P. B. Armstrong, J.-H. Yum, P. Comte, T. Torres, J. M. J. Fréchet, M. K. Nazeeruddin, M. Grätzel, and M. D. McGehee, Nat. Photonics **3**, 406 (2009).

[3] M. Fleischmann, P. J. Hendra, and A. J. McQuillan, Chem. Phys. Lett. **26**, 163 (1974).

[4] J. Gersten and A. Nitzan, J. Chem. Phys. **73**, 3023 (1980).

[5] D. A. Weitz, S. Garoff, J. I. Gersten, and A. Nitzan, J. Chem. Phys. **78**, 5324 (1983).

[6] G. D. Scholes, G. R. Fleming, A. Olaya-Castro, and R. van Grondelle, Nat. Chem. **3**, 763 (2011).

[7] F. Vollmer and Y. Lang, Nanophotonics **1**, 267 (2012).

[8] L.-Y. Hsu, W. Ding, and G. C. Schatz, J. Phys. Chem. Lett. **8**, 2357 (2017).

[9] W. Ding, L.-Y. Hsu, and G. C. Schatz, J. Chem. Phys. **146**, 064109 (2017).

[10] J.-S. Wu, Y.-C. Lin, Y.-L. Sheu, and L.-Y. Hsu, J. Phys. Chem. Lett. **9**, 7032 (2018).

[11] Q. Hu, D. Jin, J. Xiao, S. H. Nam, X. Liu, Y. Liu, X. Zhang, and N. X. Fang, Proc. Natl. Acad. Sci. U. S. A. **114**, 10017 (2017).

[12] S. Fedele, M. Hakami, A. Murphy, R. Pollard, and J. Rice, Appl. Phys. Lett. **108**, 053102 (2016).

[13] K. H. Drexhage, H. Kuhn, and F. P. Schäfer, Ber. Bunsen-Ges. Phys. Chem. **72**, 329 (1968).

[14] M. R. Philpott, J. Chem. Phys. **62**, 1812 (1975).

[15] R. R. Chance, A. Prock, and R. Silbey, Adv. Chem. Phys. **37**, 1 (1978).

[16] H. Morawitz, Phys. Rev. **187**, 1792 (1969).

[17] L. Novotny and B. Hecht, *Principles of Nano-Optics* (Cambridge University Press, 2006).

[18] H. Kuhn, J. Chem. Phys. **53**, 101 (1970).

[19] K. H. Drexhage, J. Lumin. **1-2**, 693 (1970).

[20] R. R. Chance, A. Prock, and R. Silbey, J. Chem. Phys. **60**, 2744 (1974).

[21] R. Chikkaraddy, B. de Nijs, F. Benz, S. J. Barrow, O. A. Scherman, E. Rosta, A. Demetriadou, P. Fox, O. Hess, and J. J. Baumberg, Nature **535**, 127–130 (2016).

[22] H. T. Dung, L. Knöll, and D.-G. Welsch, Phys. Rev. A **62**, 053804 (2000).

[23] A. González-Tudela, P. A. Huidobro, L. Martín-Moreno, C. Tejedor, and F. J. García-Vidal, Phys. Rev. B **89**, 041402 (2014).

[24] R.-Q. Li, D. Hernángomez-Pérez, F. J. García-Vidal, and A. I. Fernández-Domínguez, Phys. Rev. Lett. **117**, 107401 (2016).

[25] I. Thanopulos, V. Yannopapas, and E. Paspalakis, Phys. Rev. B **95**, 075412 (2017).

[26] S. Jang, J. Chem. Phys. **131**, 164101 (2009).

[27] S. Jang, J. Chem. Phys. **135**, 034105 (2011).

[28] A. Nazir, Phys. Rev. Lett. **103**, 146404 (2009).

[29] A. Montoya-Castillo, T. C. Berkelbach, and D. R. Reichman, J. Chem. Phys. **143**, 194108 (2015).

[30] S. J. Jang, J. Phys. Chem. C **123**, 5767 (2019).

[31] H. T. Dung, L. Knöll, and D.-G. Welsch, Phys. Rev. A **57**, 3931 (1998).

[32] W. Ding, L.-Y. Hsu, C. W. Heaps, and G. C. Schatz, J. Phys. Chem. C **122**, 22650 (2018).

[33] T. Gruner and D.-G. Welsch, Phys. Rev. A **53**, 1818 (1996).

[34] P. Schwendimann and E. Sigmund, J. Phys. C: Solid State Phys. **19**, 5975 (1986).

[35] V. Weisskopf and E. Wigner, Z. Phys. **63**, 54 (1930).

[36] A. Wunsche, Quantum Opt. **3**, 359 (1991).

[37] A. Arikoglu and I. Ozkol, Comput. Math. Appl. **56**, 2411 (2008).

[38] J. T. Day, Comput. J. **9**, 394 (1967).

[39] G. X. Li, J. Evers, and C. H. Keitel, Phys. Rev. B **80**, 045102 (2009).

[40] A. Gonzalez-Tudela, F. J. Rodríguez, L. Quiroga, and C. Tejedor, Phys. Rev. B **82**, 115334 (2010).

[41] J. Hakami, L. Wang, and M. S. Zubairy, Phys. Rev. A **89**, 053835 (2014).

[42] P. Yao, C. Van Vlack, A. Reza, M. Patterson, M. M. Dignam, and S. Hughes, Phys. Rev. B **80**, 195106 (2009).

[43] F. Carreño, M. A. Antón, V. Yannopapas, and E. Paspalakis, Phys. Rev. B **95**, 195410 (2017).

[44] G. X. Li, F.-L. Li, and S.-Y. Zhu, Phys. Rev. A **64**, 013819 (2001).

[45] H. T. Dung, L. Knöll, and D.-G. Welsch, Phys. Rev. A **65**, 043813 (2002).

[46] G. P. Wiederrecht, G. A. Wurtz, and J. Hranisavljevic, Nano Lett. **4**, 2121 (2004).

[47] D. E. Chang, A. S. Sørensen, E. A. Demler, and M. D. Lukin, Nat. Phys. **3**, 807 (2007).

[48] See http://www.lumerical.com/tcad-products/fdtd/ for Lumerical Solutions, Inc.

[49] W. Zhou, M. Dridi, J. Y. Suh, C. H. Kim, D. T. Co, M. R. Wasielewski, G. C. Schatz, T. W. Odom et al., Nat. Nanotechnol. **8**, 506 (2013).

[50] P. T. Kristensen, C. Van Vlack, and S. Hughes, Opt. Lett. **37**, 1649 (2012).

[51] C. Ropp, Z. Cummins, S. Nah, J. T. Fourkas, B. Shapiro, and E. Waks, Nat. Commun. **4**, 1447 (2013).

[52] V. Srinivasan and S. S. Ramamurthy, J. Phys. Chem. C **120**, 2908 (2015).

[53] P. B. Johnson and R. W. Christy, Phys. Rev. B **6**, 4370 (1972).

[54] G. C. des Francs, J. Barthes, A. Bouhelier, J. C. Weeber, A. Dereux, A. Cuche, and C. Girard, J. Opt. **18**, 094005 (2016).

[55] E. T. Jaynes and F. W. Cummings, Proc. IEEE **51**, 89 (1963).

[56] R.-C. Ge and S. Hughes, Phys. Rev. B **92**, 205420 (2015).

[57] M. J. Frisch et al., GAUSSIAN 16, Revision A.03, Gaussian, Inc., Wallingford, CT, 2016.

[58] T. Yanai, D. P. Tew, and N. C. Handy, Chem. Phys. Lett. **393**, 51 (2004).

[59] F. Duschinsky, Acta Physicochim. URSS **7**, 551 (1937).

[60] J. R. Reimers, J. Chem. Phys. **115**, 9103 (2001).

[61] G. Orlandi and W. Siebrand, J. Chem. Phys. **58**, 4513 (1973).

[62] S. H. Lin and H. Eyring, Proc. Natl. Acad. Sci. U. S. A. **71**, 3802 (1974).

[63] G. Herzberg and E. Teller, Z. Phys. Chem. **21**, 410 (1933).

[64] D. L. Andrews and B. S. Sherborne, J. Chem. Phys. **86**, 4011 (1987).

[65] D. Andrews, Chem. Phys. **135**, 195 (1989).

[66] A. Salam, J. Phys. Chem. A **123**, 2853 (2019).

[67] G. Fischer, *Vibronic Coupling: The Interaction Between the Electronic and Nuclear Motions, Theoretical Chemistry* (Academic Press, 1984).

[68] C. Fleming, N. I. Cummings, C. Anastopoulos, and B. L. Hu, J. Phys. A: Math. Theor. **43**, 405304 (2010).