

Supplemental Material for “Ultrafast Reversal of a Fano Resonance in a Plasmon-Exciton System”

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I. CAVITY-QUANTUM-ELECTRODYNAMICS MODEL

We employ a cavity quantum electrodynamics (CQED) model for the optical response of a metal nanoparticle system interacting with a quantum dot that is similar to the models discussed in Refs. [1] and [2]. Note that we use SI (MKS) units throughout.

A. Hamiltonian Operator

The system is composed of a quantum dot placed near a metal nanoparticle or system of metal nanoparticles, all in some homogeneous medium of dielectric constant ϵ_{med} . We are interested in the optical response of the system when exposed to an arbitrary light pulse.

The quantum dot is assumed to be a two-state system described by $|q\rangle$, with $q = 0$ and 1 corresponding to ground and excited electronic states, respectively. We consider only a single, dipolar surface-plasmon mode in the metal-nanoparticle system with polarization state along the direction of the polarization of the incident light. The surface-plasmon states are given by $|s\rangle$, $s = 0, 1, 2, \dots, N_s$, where s denotes the number of (bosonic) surface-plasmon quanta in the dipolar mode, and N_s is an effective upper occupancy limit. The Hamiltonian operator is taken to be

$$\hat{H} = \hat{H}_q + \hat{H}_s + \hat{H}_d + \hat{H}_i, \quad (1.1)$$

with various terms defined as follows.

The isolated quantum-dot and surface-plasmon Hamiltonian operators are

$$\hat{H}_q = \hbar\omega_q\sigma^+\sigma, \quad \hat{H}_s = \hbar\omega_sb^+b, \quad (1.2)$$

with $\hat{H}_q|q\rangle = q\hbar\omega_q|q\rangle$ and $\hat{H}_s|s\rangle = s\hbar\omega_s|s\rangle$. For convenience, we have taken the zero-point energy to be the zero of energy. In terms of the isolated QD and plasmon states, one has $\sigma^+ = |q=1\rangle\langle q=0|$, $\sigma = |q=0\rangle\langle q=1|$, $b^+|s\rangle = \sqrt{s+1}|s+1\rangle$, and $b|s\rangle = \sqrt{s}|s-1\rangle$.

Transition dipole operators are defined as $\hat{\mu}_q = d_q(\sigma + \sigma^+)$ and $\hat{\mu}_s = d_s(b + b^+)$, with d_q and d_s being the dipole transition moments associated with the quantum dot and surface plasmon, respectively. The total dipole operator is thus

$$\hat{\mu} = d_q(\sigma + \sigma^+) + d_s(b + b^+) . \quad (1.3)$$

The driving term due to the external electric field, $E(t)$, is given by the usual semiclassical expression for radiation-matter interaction in the dipole approximation:

$$\hat{H}_d = -\hat{\mu}_s E(t) . \quad (1.4)$$

Finally, the quantum dot/surface plasmon interaction term is

$$\hat{H}_i = -\hbar g(\sigma^+ b + \sigma b^+) . \quad (1.5)$$

One way of viewing the origin of this latter term is to consider the interaction energy between two classical point dipoles, μ_q^{CL} and μ_s^{CL} , separated by a distance R and oriented head-to-tail: $V^{CL} = -J \mu_q^{CL} \mu_s^{CL}$, $J = 2/(4\pi\epsilon_0 R^3)$. The corresponding quantum interaction operator is $-\hbar g(\sigma^+ + \sigma)(b^+ + b)$, where we have identified $\hbar g = J d_q d_s$. If $\hbar\omega_q \approx \hbar\omega_s$, $\sigma^+ b$ and σb^+ couple quantum-dot and plasmon states of nearly equal energy, whereas $\sigma^+ b^+$ and σb couple much more energetically separated states. Neglecting these latter, energetically unfavorable coupling terms, gives Eq. (1.5).

The parameters defining the system Hamiltonian operator are thus: the quantum dot and plasmon transition energies $\hbar\omega_q$ and $\hbar\omega_s$, the transition dipole strengths d_q and d_s , and the coupling energy $\hbar g$.

B. Master Equation

At any time, t , the system is described by a quantum-mechanical density operator, $\hat{\rho}$, given by

$$\hat{\rho}(t) = \sum_{q, s} \sum_{q', s'} \rho_{q, s, q', s'}(t) |q\rangle |s\rangle \langle q'| \langle s'| , \quad (1.6)$$

where the complex density matrix elements are denoted by $\rho_{q, s, q', s'}$. It is assumed that this reduced density operator is the result of tracing the full density operator over environmental degrees of freedom.

The equation of motion for $\hat{\rho}$ is taken to be a master equation of the form

$$\frac{d\hat{\rho}}{dt} = \frac{-i}{\hbar} [\hat{H}, \hat{\rho}] + \hat{L}(\hat{\rho}) , \quad (1.7)$$

where the Hamiltonian operator, \hat{H} , is given by Eq. (1.1), and the Lindblad superoperator \hat{L} accounts for environmental effects such as dephasing, damping, and spontaneous emission. The matrix representation of Eq. (1.7), $\langle q|\langle s|d\hat{\rho}/dt|q'\rangle|s'\rangle = d\rho_{q,s,q',s'}/dt$, is a set of $2N_s \times 2N_s$ first-order differential equations to be solved for the time evolution of the density matrix elements.

Following Waks and Sridharan [1], the Lindblad superoperator is decomposed as $\hat{L} = \hat{L}_q + \hat{L}_s$, where

$$\begin{aligned} \hat{L}_q(\hat{\rho}) = & -\frac{\gamma_{q1}}{2}(\sigma^+ \sigma \hat{\rho} + \hat{\rho} \sigma^+ \sigma - 2\sigma \hat{\rho} \sigma^+) \\ & - \gamma_{q2}(\sigma^+ \sigma \hat{\rho} + \hat{\rho} \sigma^+ \sigma - 2\sigma^+ \sigma \hat{\rho} \sigma^+) \end{aligned} \quad (1.8)$$

and

$$\hat{L}_s(\hat{\rho}) = -\frac{\gamma_s}{2}(b^+ b \hat{\rho} + \hat{\rho} b^+ b - 2b \hat{\rho} b^+) \quad (1.9)$$

In Eq. (1.8), the spontaneous emission rate for the quantum dot is $\gamma_{q1} = 1/T_1$ and its dephasing rate is $\gamma_{q2} = 1/T_2$. In Eq. (1.9), γ_s is the surface-plasmon damping rate. The Lindblad formalism leads to a density matrix time evolution, given by Eq. (1.7), that preserves the trace of the density matrix (total probability) and the non-negativity of the diagonal terms (individual state probabilities).

While Eqs. (1.8) and (1.9) are non-intuitive to anyone unacquainted with the Lindblad formalism, use of Eq. (1.6) shows that their contributions to specific $d\rho_{q,s,q',s'}/dt$ terms resulting from Eq. (1.7) can often be straightforwardly interpreted. For example, Eq. (1.8) leads to

$$\begin{aligned} \langle q|\langle s| \hat{L}_q |q'\rangle|s'\rangle = & -\frac{\gamma_{q1}}{2}(q+q') \rho_{q,s,q',s'} + \gamma_{q1} \rho_{q=1,s,q'=1,s'} \delta_{q,0} \delta_{q',0} \\ & - \gamma_{q2}(q+q'-2qq') \rho_{q,s,q',s'} \end{aligned} \quad (1.10)$$

When $q = q' = 1$, Eq. (1.10) represents loss from the excited state of the quantum dot due to spontaneous emission; when $q = q' = 0$, Eq. (10) represents the matching gain into the quantum-dot ground state; when $q = 0$, $q' = 1$, or vice versa, Eq. (1.10) represents dephasing with rate $\gamma_{q2} + \gamma_{q1}/2$. Similarly, Eq. (1.9) leads to

$$\begin{aligned} \langle q|\langle s| \hat{L}_s |q'\rangle|s'\rangle = & -\frac{\gamma_s}{2}(s+s') \rho_{q,s,q',s'} + \\ & \gamma_s \sqrt{(s+1)(s'+1)} \rho_{q,s+1,q',s'+1} \end{aligned} \quad (1.11)$$

The first term on the right-hand side of Eq. (1.11) corresponds to surface-plasmon population loss due to damping when $s = s'$. Each such loss is matched by an equal and

opposite gain given by the second term on the right-hand side. The gain and loss rates are proportionate to $s\gamma_s$, reflective of the bosonic character of the surface plasmons. The $s \neq s'$ terms in Eq. (1.11) correspond to dephasing.

C. Matrix Elements and Rotating Wave Approximation

Using the raising and lowering operator relations given below Eq. (1.2), it is straightforward to evaluate the explicit time derivatives of the complex density matrix elements of Eq. (1.7), $d\rho_{q,s,q',s'}/dt$. Introducing a rotating wave approximation (RWA) greatly simplifies the computational effort, and we have verified by comparison with full numerical solutions in specific cases that it is very accurate.

We now outline how the RWA is implemented. For simplicity, let us denote the density matrix elements as $\rho_{k,k'}$ with the introduction of a collective state index k such that the arrays $q(k)$, $s(k)$ define the specific quantum-dot and plasmon quantum numbers associated with each state k . We define new density-matrix elements $\bar{\rho}_{k,k'}$ via

$$\rho_{k,k'}(t) = \bar{\rho}_{k,k'}(t) \exp(-if_{k,k'}t) \quad , \quad (1.12)$$

where

$$f_{k,k'} = \omega[q(k) + s(k) - q(k') - s(k')] \quad . \quad (1.13)$$

In this expression, ω is the central frequency of the electric field, $E(t)$, interacting with the system. If $\omega \approx \omega_q \approx \omega_s$, $f_{k,k'}$ is proportional to the energy difference between states k and k' .

From Eq. (1.7), one can show that

$$\frac{d\bar{\rho}_{k,k'}}{dt} = \frac{-i}{\hbar} [\bar{H}, \bar{\rho}]_{k,k'} + if_{k,k'} \bar{\rho}_{k,k'} + L(\bar{\rho})_{k,k'} \quad (1.14)$$

where

$$\bar{H}_{k,k'} = H_{k,k'} \exp(if_{k,k'}t) \quad . \quad (1.15)$$

In general, $\bar{H}_{k,k'}$ breaks down into contributions from the four terms in Eq. (1.1). Both \hat{H}_q and \hat{H}_s lead only to diagonal ($k = k'$) matrix elements; therefore, $\exp(if_{kk}t) = 1$, and their contributions do not depend on time. Similarly, the quantum-dot/plasmon interaction, \hat{H}_i , has non-zero matrix elements only if $q(k) + s(k) = q(k') + s(k')$, and thus $f_{kk'} = 0$ as well. The Hamiltonian operator for the optical driving term, \hat{H}_d , already has a fast time-dependence via the electric field, $E(t)$. We take this to be

$$\begin{aligned} E(t) &= E_0 G(t) \cos(\omega t) \\ &= \frac{E_0}{2} G(t) [\exp(i\omega t) + \exp(-i\omega t)] \quad , \end{aligned} \quad (1.16)$$

where ω is the central frequency of the pulse and $G(t)$ is some appropriate envelope function. Eqs. (1.4), (1.15) and (1.16) lead to the matrix elements

$$\langle k | \hat{H}_d | k' \rangle = - \left[d_q \langle q | (\sigma^+ + \sigma) | q' \rangle \delta_{s,s'} + d_s \langle s | (b^+ + b) | s' \rangle \delta_{q,q'} \right] \times \frac{E_0}{2} G(t) \left\{ \exp[i(\omega + f_{k,k'})t] + \exp[i(-\omega + f_{k,k'})t] \right\}, \quad (1.17)$$

where, for simplicity, we have denoted $q = q(k)$, $s = s(k)$, $q' = q(k')$ and $s' = s(k')$. These matrix elements are non-zero only if $|q - q'| = 1$ and $s = s'$ (field driving the quantum dot) or $q = q'$ and $|s - s'| = 1$ (field driving the surface plasmon). In each such case, one of the two exponential terms in the braces of Eq. (1.17) is unity, and the other term is high frequency and is neglected in the RWA.

D. Purcell Effect

Consider only three $|q, s\rangle$ states, $|0, 0\rangle$, $|1, 0\rangle$ and $|0, 1\rangle$, corresponding to the ground state, the excited state of the quantum dot with the plasmon not excited, and the plasmon excited in its $s = 1$ state with the quantum dot in its ground state. Furthermore, consider the case that there is no incident radiation, $E_0 = 0$. An initial state of $|1, 0\rangle$ decays due to coupling of the QD to free space and to the plasmon mode. The decay rate is significantly faster than in the absence of the plasmon mode, a phenomenon known as the Purcell effect [3, 4].

The relevant density matrix elements are $\rho_{00,00}$, $\rho_{10,10}$, $\rho_{01,01}$ and $\rho_{10,01}$. For simplicity, we write $G = \rho_{00,00}$, $Q = \rho_{10,10}$, $S = \rho_{01,01}$ and $C = \text{Im}[\rho_{10,01}]$. The relevant equations of motion inferred from Sec. 1B are

$$\begin{aligned} \dot{G}(t) &= \gamma_s S(t) + \gamma_1 Q(t) \\ \dot{S}(t) &= -2gC(t) - \gamma_s S(t) \\ \dot{Q}(t) &= 2gC(t) - \gamma_1 Q(t) \\ \dot{C}(t) &= g(S(t) - Q(t)) - \Gamma C(t) \end{aligned}, \quad (1.18)$$

where $\Gamma = \gamma_2 + (\gamma_1 + \gamma_s)/2$. The equations for $\dot{S}(t)$, $\dot{Q}(t)$, and $\dot{C}(t)$ are self-contained and can be solved exactly.

A simple and accurate approximate solution can be obtained by drawing a parallel to elementary chemical kinetics. One can view S , Q and $-C$ as being “concentrations” of species. Starting out with $Q(0) = 1$, $S(0) = C(0) = 0$, the magnitudes of the various rate coefficients are such that little “accumulation” in C and S can occur over the course of time. They thus act as low concentration “intermediates,” justifying a steady-state approximation $\dot{C} = \dot{S} = 0$. This leads to the effective equation

$$\begin{aligned}
\dot{Q}(t) &= -\left(\gamma_1 + \frac{4g^2}{4g^2/\gamma_s + \gamma_1 + 2\gamma_2 + \gamma_s}\right) Q(t) \\
&\approx -\left(\gamma_1 + \frac{4g^2}{\gamma_s}\right) Q(t) = -\gamma_1^{\text{eff}} Q(t)
\end{aligned} \tag{1.19}$$

where we have assumed $g_s \gg g_1, g_2, g$.

E. Numerical Aspects

Consider first the case $G(t) = 1$, *i.e.* a sinusoidal electric field. In this case, we seek the steady-state solution to Eq. (1.14), such that $d\bar{\rho}/dt = 0$. While one could try to find this solution by numerically integrating Eq. (14) until such a steady state is achieved, this approach can suffer from numerical errors. However, the effect of the RWA discussed in Sec. 1C above is to remove any explicit time-dependence from Eq. (1.14) when $G(t) = 1$. Because the right-hand side of Eq. (1.14) is equivalent to $A\bar{\rho}$, where A is a time-independent matrix, the steady-state condition becomes the homogeneous equation

$$\frac{d\bar{\rho}}{dt} = A\bar{\rho} = 0 \tag{1.20}$$

Singular-value decomposition (SVD) [5] can be used to extract the non-trivial solutions to Eq. (1.22) for which $\bar{\rho}$ is non-zero.

In practice, we re-express Eq. (1.20) as a real matrix-vector equation of the form

$$\frac{dy}{dt} = By = 0 \tag{1.21}$$

where y is a real vector of dimension $N_y = 8N_s^2$ containing the real and imaginary components of $\bar{\rho}$, and B is an $N_y \times N_y$ real matrix. SVD, based on the algorithm of Ref. [5], is carried out on the matrix B . Typically, two possible non-trivial solutions are obtained from the analysis, and one of them is non-physical; *i.e.*, it cannot be scaled by an overall constant such that $\text{Tr}\bar{\rho} = 1$ with $\bar{\rho}_{k,k} \geq 0$.

When considering a more general pulse, Eq. (1.14) retains a time dependence owing to the envelope function $G(t)$. In this case, we re-cast the equations into a set of $8N_s^2$ equations for the time derivatives of the real and imaginary parts of $\bar{\rho}$, and we use a reliable ordinary-differential-equation integrator [5] to evolve the density matrix elements.

For both the steady-state and time-dependent solutions, we choose a value of N_s high enough that the solution is independent of this choice (that is, using a larger value of N_s gives the same result). For the system and pulse parameters studied in this work, modest plasmon numbers, $N_s \leq 10$, are required for relatively low intensities, in the steady-state calculations ($\leq 1 \text{ MW/cm}^2$), or relatively low fluences, in the pulsed calculations ($\leq 5 \text{ nJ/cm}^2$). Such calculations can be run within a few minutes on a personal computer using a simple serial implementation of the methods described above. Significantly higher

intensities or fluences can be more challenging. For steady-state calculations, the memory requirements for singular value decomposition places an approximate limit of $N_s \leq 30$. For pulsed calculations, obtaining the optical response at the highest fluence reported ($5 \mu\text{J}/\text{cm}^2$) required $N_s = 250$, which required over 2 days of computing time on a single processor. More sophisticated numerical implementations that exploit sparsity in the underlying equations, or parallelization of the calculations, are necessary to make high-field calculations more computationally tractable.

II. SEMICLASSICAL MODEL

A. Full Model

The full semiclassical model describes the plasmon dipole as a forced, damped harmonic oscillator coupled to the quantum-dot dipole, $\mu_q(t) = d_q y_1(t)$:

$$\ddot{\mu}_s(t) + \omega_s^2 \mu_s(t) + \gamma_s \dot{\mu}_s(t) = A_s [E_0 \cos(\omega t) + J \mu_q(t)] . \quad (2.1)$$

Evolution of the quantum-dot dipole is described by the Bloch equations:

$$\begin{pmatrix} \dot{y}_1(t) \\ \dot{y}_2(t) \\ \dot{y}_3(t) \end{pmatrix} = \begin{pmatrix} 0 & \omega_q & 0 \\ -\omega_q & 0 & -\frac{2d_q}{\hbar} [E(t) + J\mu_s(t)] \\ 0 & \frac{2d_q}{\hbar} [E(t) + J\mu_s(t)] & 0 \end{pmatrix} \begin{pmatrix} y_1(t) \\ y_2(t) \\ y_3(t) \end{pmatrix} - \gamma_2 [y_1(t) + y_2(t)] - \gamma_1^{\text{eff}} (y_3(t) + 1) . \quad (2.2)$$

As in Section I, $E(t)$ represents the applied electric field. In terms of the two-state density matrix elements associated with the driven quantum dot, $y_1 = 2\text{Re}\rho_{01}$, $y_2 = -2\text{Im}\rho_{01}$ and $y_3 = \rho_{11} - \rho_{00}$. The parameters d_q and g_2 are as in the CQED model, and γ_1^{eff} is the Purcell-corrected population loss rate coefficient of the quantum dot. (See Section I.D.) The relation of the parameters A_s and J to the CQED model is given in Section II.C, below.

In Eqs. (2.1) and (2.2), $E(t) + J\mu_q(t)$ represents the local electric field experienced by the plasmon due to the presence of the quantum dot, and $E(t) + J\mu_s(t)$ represents the local field experience by the quantum dot due to the presence of the plasmon. Eqs. (2.1) and (2.2) represent five real ordinary first-order differential equations.

B. Rotating Wave Approximation

Eqs. (2.1) and (2.2) can be solved directly without additional approximation, as discussed in Section II.E, below. However, a rotating wave approximation (RWA) similar to that

used for the CQED calculations can also be developed, and the calculations within this approximation yield results that are very close to the full solutions. For continuous-wave excitation, $G(t) = 1$, one uses the following *Ansatz* for $\mu_s(t)$:

$$\mu_s(t) = X_s(t)\exp(-i\omega t) + X_s^*(t)\exp(i\omega t) . \quad (2.3)$$

One then introduces the slow variables $\sigma_{01}(t)$ and $\sigma_{10}(t) = \sigma_{01}^*(t)$ according to

$$\rho_{01}(t) = \sigma_{01}\exp(i\omega t), \quad \rho_{10}(t) = \sigma_{10}\exp(-i\omega t) . \quad (2.4)$$

The equations of motion for $\sigma_{01}(t)$ and the slow variable $y_3(t) = \rho_{11}(t) - \rho_{00}(t)$, neglecting high-frequency oscillatory terms, are readily found to be

$$\begin{aligned} \dot{\sigma}_{01}(t) &= i\sigma_{01}(t)(\omega_q - \omega) + i\frac{d_q}{\hbar}\left(\frac{E_0}{2} + JX_s^*\right)y_3(t) - \gamma_2\sigma_{01}(t) \\ \dot{y}_3(t) &= -\frac{2d_q E_0}{\hbar}\left[\text{Im}\{\sigma_{01}(t)\} + 2J\text{Im}\{X_s\sigma_{01}(t)\}\right] - \gamma_1^{\text{eff}}(y_3(t) + 1) \end{aligned} \quad (2.5)$$

In order to obtain steady-state solutions, we can substitute Eq. (2.3) into Eq. (2.1) and set $\dot{X}_s(t) = \ddot{X}_s(t) = 0$, giving

$$X_s = \frac{A_s(E_0/2 + Jd_q\sigma_{10})}{(\omega_s^2 - \omega^2 - i\gamma_s\omega)} . \quad (2.6)$$

Inserting Eq. (2.6) into Eq. (2.5) leads to three real first-order differential equations. Numerical integration of these equations leads very quickly to a steady-state solution and we have verified that such solutions, for the parameters and intensities of relevance here, do not significantly deviate from the full solutions of Eqs. (2.1) and (2.2).

When considering pulsed excitation, one simply retains the RWA limiting form for the equation of motion for $\ddot{X}_s(t)$, which is equivalent to two complex or four real first-order differential equations, along with Eqs. (2.5), and replace E_0 by $E_0G(t)$. The result is a system equivalent to seven real first-order differential equations, which can also be readily solved numerically.

C. Relation of Parameters to the CQED model

We have written the semiclassical model in terms of an intuitive, coupled-dipole picture. (See Section II.A.) However, for quantitative comparison with the results of CQED calculations, it is necessary to relate the parameters of the semiclassical model to those of the CQED picture. One approach would be to “derive” the semiclassical equations from the CQED model [1]. This involves writing the CQED in terms of Heisenberg equations of motion, taking expectation values, and closing the equations by assuming that the expectation values of certain operator products are equal to the products of the individual operators.

We will take a different approach here. We first consider an isolated plasmon driven by continuous-wave excitation, $E(t) = E_0 \cos(\omega t)$. In the limit of low E_0 , one expects the quantum and classical models to give the same result. In particular, we solve for the steady state of the classical equation Eq. (2.1), with $J = 0$, by replacing $\mu_s(t)$ with the complex phasor $\mu_s^0 \exp(-i\omega t)$. Neglecting high-frequency oscillatory terms, we obtain

$$\mu_s^0 = \frac{E_0}{2} \frac{A_s}{(\omega_s^2 - \omega^2 - i\gamma_s \omega)} . \quad (2.7)$$

The real, time-dependent dipole is given by $\mu_s(t) = \text{Re}[\mu_s^0 \exp(-i\omega t)]$. Evaluating this latter expression on resonance ($\omega = \omega_s$) gives

$$SC: \quad \mu_s(t) = \frac{E_0 A_s}{2\omega_s \gamma_s} \sin(\omega_s t) . \quad (2.8)$$

For solution of the CQED equations, it suffices to consider only the plasmon states $s = 0$ and $s = 1$. The corresponding steady-state solution is then [6]

$$QM: \quad \mu_s(t) = \frac{2E_0 d_s^2}{\hbar \gamma_s} \sin(\omega_s t) . \quad (2.9)$$

Comparing Eqs. (2.8) and (2.9) shows that

$$A_s = \frac{4\omega_s d_s^2}{\hbar} . \quad (2.10)$$

We have already shown that $\hbar g = J d_q d_s$, which fixes J given the quantum parameters g , d_q , and d_s . Here we will further show that this choice is consistent with Eq. (2.1). First, we note that Eq. (2.1) may be rewritten in terms of a coordinate variable x_s :

$$m_s \ddot{x}_s(t) + m_s \omega_s^2 x_s(t) + m_s \gamma_s \dot{x}_s(t) = e_s [E_0 \cos(\omega t) + J e_q x_q(t)] , \quad (2.11)$$

where we have defined $\mu_i(t) = e_i x_i(t)$. The classical interaction energy between the two dipoles may then be written as $V(x_q, x_s) = -J e_q x_q e_s x_s$. This potential will lead to a contribution to the force on the plasmon of $-\partial V / \partial x_s = J e_s e_q x_q$. This is equivalent to the last term of Eq. (2.1).

E. Numerical Aspects

For determination of steady-state cross-sections, solution of Eqs. (2.5) is numerically both more efficient and more stable than solution of the oscillatory Eqs. (2.1) and (2.2). A key reason is the large difference in time scales between the optical frequency and the exciton decay parameters γ_1 and γ_2 ; integrating the equations over many picoseconds to

achieve a true steady state allows small numerical artifacts to appear. The approach of Section II.B was therefore used to calculate steady-state SC results. By contrast, direct integration of (2.1) and (2.2) is possible using standard numerical libraries [5] and provides the advantage of allowing for arbitrary electric-field waveforms and parameter choices that cannot be solved using the RWA. We therefore used this approach to calculate results for pulsed excitation in the SC model.

However, both the full model and the model invoking the RWA agree closely in all cases explored in this work. Testing the full model in the naïve SC case requires a further step, since integration over many nanoseconds would be needed to achieve steady state starting from the system in its ground state. We therefore seed the exciton population near its terminal value by performing a sequence of integrations over a few picoseconds and using a binary search to find the equilibrium value for the exciton population.

III. CROSS-SECTIONS

In the steady-state limit, the dipole may be written as $\mu(t) = \text{Re}[\mu(\omega)\exp(-i\omega t)]$, where $\mu(t)$ is either the total real dipole that results from the semiclassical model or the corresponding quantum mechanical dipole, $\text{Tr}[\rho(t)\hat{\mu}]$. The complex phasor $\mu(\omega)$ is thus

$$\mu(\omega) = \frac{2}{\tau} \int_0^\tau \exp(i\omega t) \mu(t) dt, \quad (3.1)$$

where $\tau = 2\pi c/\omega$. The absorption cross section is [7] $\sigma_{abs}(\omega) = P_{abs}/S_0$, where $P_{abs} = (\omega/2) \text{Im}[\mu E_0^*]$ is the average power absorbed by the dipole. The complex polarizability is

$$\alpha(\omega) = \frac{\mu(\omega)}{\epsilon_{med} E_0}, \quad (3.2)$$

and the incident flux is

$$S_0 = \sqrt{\epsilon_{med}} c \epsilon_0 E_0^2 / 2. \quad (3.3)$$

The absorption cross section is thus

$$\sigma_{abs}(\omega) = (k_{med}/\epsilon_0) \text{Im}[\alpha(\omega)], \quad (3.4)$$

where $k_{med} = \sqrt{\epsilon_{med}} \omega / c$.

Eq. (3.4) is the appropriate form for a dipole in a medium with dielectric constant ϵ_{med} [9,10]. An entirely different route for obtaining Eq. (3.4) is to use the asymptotic form for light radiated by a dipole along with the optical theorem [10]; this approach gives the absorption and not the extinction that might naively be expected [9].

The average total power radiated by the dipole is [9]

$$P_{rad} = \frac{\sqrt{\epsilon_{med}} |\mu(\omega)|^2 \omega^4}{12\pi\epsilon_0 c^3} . \quad (3.5)$$

Dividing this by the incident flux, S_0 , gives the scattering cross section:

$$\sigma_{sca}(\omega) = \frac{|\mu(\omega)|^2}{6\pi|\epsilon_0 E_0|^2} \left(\frac{\omega}{c}\right)^4 . \quad (3.6)$$

Transient cross sections corresponding to the system interacting with a finite-duration pulse are readily defined as generalizations of Eqs. (3.4) and (3.6). One simply replaces $\mu(\omega)$ and E_0 in these equations with

$$\int_{-\infty}^{\infty} \exp(i\omega t) \mu(t) dt \quad \text{and} \quad \int_{-\infty}^{\infty} \exp(i\omega t) E(t) dt , \quad (3.7)$$

respectively. The mathematical process of Fourier-transforming the dipole moment and incident electric fields to obtain cross sections is analogous to the physical process of passing transmitted or scattered light through a monochromator and normalizing the signal by the incident spectrum.

IV. COUPLED-OSCILLATOR MODEL

The semiclassical model can be further simplified by treating the quantum dot as an oscillator, in the same way as the plasmon is treated, rather than using the Bloch equations. This description is accurate only in the linear limit of weak applied fields. The resulting equations of motion, for continuous-wave excitation, are similar to the two-oscillator model developed in Ref. [7]:

$$\begin{aligned} \ddot{\mu}_s(t) + \omega_s^2 \mu_s(t) + \gamma_s \dot{\mu}_s(t) &= A_s [E_0 \cos(\omega t) + J \mu_q(t)] \\ \ddot{\mu}_q(t) + \omega_q^2 \mu_q(t) + \gamma_q \dot{\mu}_q(t) &= A_q [E_0 \cos(\omega t) + J \mu_s(t)] \end{aligned} . \quad (4.1)$$

We assume $A_s \gg A_q$, so that the quantum-dot driving term proportional to $A_q E_0 \cos(\omega t)$ can be neglected. Complexification via $\mu_s(t) = \mu_s^0 \exp(-i\omega t)$, $\mu_q(t) = \mu_q^0 \exp(-i\omega t)$, and neglect of high-frequency time-oscillatory terms then leads to

$$\mu_s^0 = \frac{A_s E_0}{2} \frac{(\omega_q^2 - \omega^2 - i\gamma_q \omega)}{(\omega_q^2 - \omega^2 - i\gamma_q \omega)(\omega_s^2 - \omega^2 - i\gamma_s \omega) - A_s A_q J^2} . \quad (4.2)$$

Under our assumptions, the contribution of the quantum-dot dipole to the total dipole can be neglected. From Eq. (3.4), the absorption cross section is then

$$\sigma_{abs}(\omega) \propto \omega \operatorname{Im}(\mu_s^0) \quad . \quad (4.3)$$

Assuming $\omega_s = \omega_q = \omega_0$ and considering frequencies near resonance gives

$$\sigma_{abs}(\omega \approx \omega_0) \propto \frac{\gamma_q}{\gamma_q \gamma_s + A_s A_q J^2} \quad . \quad (4.4)$$

Finally, relating A_s to the quantum parameters according to Eq. (2.10) and using an analogous form for A_q [8] leads to

$$\sigma_{abs}(\omega \approx \omega_0) \propto \frac{\gamma_q}{\gamma_q \gamma_s + (4g)^2} = \frac{1}{\gamma_s} \left(\frac{\gamma_q \gamma_s}{\gamma_q \gamma_s + (4g)^2} \right) \quad , \quad (4.5)$$

where g is the coupling parameter of the quantum model. For $\gamma_s \gg \gamma_q$ Eq. (4.5) shows that one can achieve transparency dip of 50% or more, relative to the uncoupled maximum, if $g > \sqrt{\gamma_q \gamma_s}/4$.

V. DISCRETE-DIPOLE-APPROXIMATION CALCULATIONS

Rigorous classical electrodynamics simulations using the discrete dipole approximation (DDA) are performed using the production package DDSCAT, version 7.2.2 [11]. Two Au prolate spheroids with semi-major and semi-minor axes of 15 nm and 10 nm, respectively, are arranged coaxially with a gap of 6 nm. A CdSe QD with a diameter of 4 nm is placed in the center of this gap. The system is embedded in a typical polymer medium with dielectric constant $\epsilon_{\text{med}} = 2.25$ and is illuminated by a plane wave polarized along the axis connecting the particles. The Au and CdSe components are assigned a regular grid of dipoles, 3.2×10^6 in total. The Au is assigned the complex-valued dielectric constant based on the measurements of Johnson and Christy [12]. The CdSe QD is given an excitonic feature by assigning it a Lorentzian dielectric function [7]:

$$\epsilon(\omega) = \epsilon_\infty - f \frac{\omega_L^2}{\omega^2 - \omega_L^2 + i\gamma_L \omega} \quad , \quad (5.1)$$

where $\epsilon_\infty = 5.8$ is the high-frequency dielectric constant of CdSe and f is the oscillator strength of the transition. As in Ref. [7], we take $f = 0.1$ and $\hbar\gamma_L = 2$ meV.

The plasmon parameters are obtained by performing a DDA simulation of the system with $f = 0$. The resulting absorption spectrum then includes the red-shift caused by the influence of the nearby high-index QD material, but otherwise is the isolated plasmon

spectrum. Fitting this spectrum to either of the predictions of the CQED and SC models in the low field limit gives $\hbar\omega_s = 2.042$ eV, $\hbar\gamma_s = 150.2$ meV, and $d_s = 2994$ D.

The corresponding absorption spectrum of an isolated QD in the polymer medium is used to obtain the QD model system parameters. In order to study the case of resonant coupling cleanly, ω_L is chosen such that the resulting resonance position is very close to ω_s . Because the QD is sufficiently small that the quasistatic approximation is good, one can simply use $\sigma_{abs}(\omega) \propto \text{Im}\left[\left(\epsilon(\omega) - \epsilon_{med}\right)/\left(\epsilon(\omega) + 2\epsilon_{med}\right)\right]$, which gives $\hbar\omega_L = 2.0322$ eV. For numerical consistency, we then run a DDA simulation of the isolated QD system using 8500 dipoles and fit the CQED or SC model parameters. We find $\hbar\omega_q = 2.042$ (as desired), $g_2 = 1.265$ meV, and $d_q = 13.91$ D. (Note that the spontaneous emission rate, g_1 , is simply fixed in our calculations at a value much smaller than g_2 ; it does not appreciably contribute to the isolated QD absorption spectrum.)

Having obtained the isolated plasmon and QD parameters, a third DDA simulation is performed for the full system. We find that coupling parameter $\hbar g = 10.841$ eV yields model CQED and SC spectra in the low-field limit that are almost superimposable for photon energies from 2.015 eV to 2.065 eV, and are in good agreement with the DDA results (see Fig. 1b, main text).

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