

# Theory of entangled two-photon emission/absorption [E2P-EA] between molecules

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(Dated: 4 July 2023)

This paper presents a comprehensive study of the theory of entangled two-photon emission/absorption (E2P-EA) between a many-level cascade donor and a many-level acceptor (which could be quantum dots or molecules) using second order perturbation theory, and where the donor-acceptor pair are in a homogeneous but dispersive medium. To understand the mechanism of E2P-EA, we analyze how dipole orientation, radiative lifetime, energy detuning between intermediate states, separation distance, and entanglement time impact the E2P-EA rate. Our study shows that there are quantum interference effects in the E2P-EA rate expression that lead to oscillations in the rate as a function of the entanglement time. Furthermore, we find that the E2P-EA rate for a representative system consisting of two quantum dots can be comparable to one-photon emission/absorption (OP-EA) when donor and acceptor are within a few nm. However the E2P-EA rate falls off much more quickly with separation distance than does OP-EA.

## I. INTRODUCTION

Resonance energy transfer (RET) has been widely studied in the past few years due to its promising potential in bioimaging,<sup>1,2</sup> photovoltaics,<sup>3-5</sup> and photosynthesis.<sup>6-8</sup> Generally, for a donor-acceptor distance smaller than the excitation wavelength, i.e.,  $R \ll \lambda$ , the RET rate described by Förster theory has a distance dependence proportional to  $R^{-6}$ , which indicates its limitation to a very short distance. To overcome this limitation, plasmonic nanoparticles are used to transfer the excitation and thereby to increase the distance of RET.<sup>9,10</sup> In order to simulate RET in a plasmonic environment, several theoretical works<sup>11-15</sup> have developed new methodologies and insights to study plasmon-mediated RET. To date, these studies have focused on one-photon RET (OP-RET). Little is known about the mechanism of RET when two entangled photons are involved in the energy transfer. A simple and effective approach for investigating the topic is to consider the emission and absorption of a real entangled two-photon pair between the donor and acceptor, which is a process we call entangled two-photon emission/absorption (E2P-EA). An earlier study from our group Ref. [16], developed a related theory involving a donor and two separate acceptors. However, this did not consider the case (which turns out to be more interesting) where a single acceptor absorbs both photons.

Entangled photons are of great interest as promising candidates for numerous technologies. This motivates their study using fundamental physics,<sup>17</sup> where non-local correlation of the entangled photons can involve various degrees of freedom such as spatial,<sup>18,19</sup> time-frequency<sup>20</sup> and polarization<sup>21</sup>. These features make entangled photons useful in applications involving quantum information,<sup>22,23</sup> quantum communication<sup>24,25</sup> and quantum sensing.<sup>26-28</sup> The most commonly used source of entangled photons is based on spontaneous parametric downconversion (SPDC).<sup>29</sup> SPDC is a nonlinear optical process, where one pump photon of fre-

quency  $\omega_p$  is converted into a pair of lower frequency photons, which are denoted the signal  $\omega_s$  and idler  $\omega_i$  photons. Typically, the generated photon pair demonstrates time-frequency and polarization entanglement. The resulting temporal correlation particularly can enhance the probability of two-photon absorption. This phenomenon is known as entangled two-photon absorption (ETPA). Several studies<sup>30-32</sup> have shown that the rate of ETPA is linearly proportional to the input photon flux, showing that ETPA is advantageous for probing chemical and biological systems compared with the higher intensities that are needed for classical two-photon absorption.

In addition to SPDC, another entangled photon source involves semiconductor quantum dots (QDs).<sup>33-35</sup> QDs can be regarded as a cascade emitter. The energy levels can be modeled as a four-level system, which consists of the ground state ( $|g\rangle$ ), two degenerate intermediate exciton states with different spin configurations ( $|X_{H(V)}\rangle$ ) and the biexciton state ( $|XX\rangle$ ). Often this energy level structure is simplified to three levels, and if the rate of emission of the first photon (starting in the biexciton state) is slow compared to the second, the resulting photons can be highly entangled. The cascade emitter is a point-like source in this treatment, emitting light from a single location. In contrast, SPDC uses a nonlinear crystal as the emitter, leading to photons that are plane waves. This difference in the emission process results in different properties including the two-photon wavefunction, the entanglement time and entanglement area. While recent studies have largely focused on the physical processes involved in SPDC light, the processes involved in cascade emitters remain unclear. In Ref. [36], the entangled photon properties such as Schmidt numbers and heralding were studied for quantum dot emitters that were modeled as a cascade source. In Ref. [37], quantum dot emitters in polarized cavities were considered.

In this paper, we present a formulation to understand entangled two-photon emission/absorption (E2P-EA) for a cascade emitter treated as a many-level system that excites an absorber that can have any number of energy levels. In Section II, we

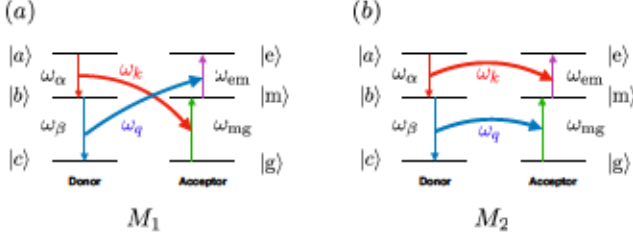


FIG. 1. Schematic of the entangled two-photon emission/absorption between the three-level donor and the three-level acceptor. (a) The pathway where the first emitted photon  $\omega_k$  is absorbed by the donor first and the second emitted photon  $\omega_q$  is absorbed second. (b) The pathway where the second emitted photon  $\omega_q$  is absorbed by the donor first and the first emitted photon  $\omega_k$  is absorbed second.

derive an expression for the E2P-EA rate using second order perturbation theory. In Section III, we analyze how the dipole orientation, radiative lifetime, energy detuning, distance and entanglement time impact the E2P-EA rate. In Section IV, we summarize the article.

## II. METHODS

To fully capture the essential physics of RET when entangled two-photons are involved, we need to consider a perturbative expansion to fourth order, as has been done in the past for determining Casimir-van der Waals interactions.<sup>38</sup> However, by simplifying the process as separate but linked emission and absorption events involving a pair of entangled photons, we can gain some insights into the underlying physics. Indeed, if we derive the analogous expression for one-photon emission/absorption (OP-EA) within the rotating-wave approximation (details are in Appendix A), we show that this rate is equivalent to the fully retarded version of Förster theory. This gives us a starting point for deriving an expression for the rate of entangled two-photon emission/absorption (E2P-EA), and the resulting expression allows us to understand the influence of time-frequency entanglement on the process. Nevertheless, it is necessary to keep in mind that the rotating-wave approximation and the neglect of virtual photons can lead to the omission of contributions that are present in the 4th order theory. We also note that our E2P-EA expression assumes that the ground and two-photon excited states have zero probability for one-photon excitation, as is rigorously true for molecules with inversion symmetry but often found in other situations.

We consider the emission/absorption mediated by a pair of entangled photons between a single cascade donor and a single acceptor in a homogeneous dispersive medium. The emitter, acceptor and the field are treated fully quantum mechanically. The Hamiltonian for the acceptor, under the dipole and

rotating-wave approximations, can be expressed as

$$\begin{aligned} H &= H_0 + V_{\text{int}}(t) \\ &= \sum_m \hbar \omega_{\text{mg}} \hat{b}_{\text{mg}}^\dagger \hat{b}_{\text{mg}} + \sum_m \hbar \omega_{\text{em}} \hat{b}_{\text{em}}^\dagger \hat{b}_{\text{em}} \\ &\quad + \hbar \sum_{\lambda} \sum_l \omega_l \hat{a}_l^{\lambda\dagger} \hat{a}_l^{\lambda} + V_{\text{int}}(t), \end{aligned} \quad (1)$$

where  $g$ ,  $m$  and  $e$  denote the ground, intermediate, and final states, including the possibility of many intermediates (see FIG. 1). Also  $\hat{b}_{\text{mg}} = |g\rangle\langle m|$ ,  $\hat{b}_{\text{em}} = |m\rangle\langle e|$  and  $\hat{a}_l^{\lambda}$  is the annihilation operator for a photon of frequency  $\omega_l$  and polarization  $\lambda$ . Here  $\omega_{\text{mg}}$  describes the transition frequency from the ground state to the intermediate state;  $\omega_{\text{em}}$  describes the transition frequency from the intermediate state to the excited state. The light-matter coupling in the interaction picture is given by

$$\begin{aligned} V_{\text{int}}(t) &= \sum_m \hbar \hat{b}_{\text{mg}}^\dagger(t) \sum_{\lambda} \sum_l \mathcal{E}_{\text{mg}}^{\lambda}(\omega_l) e^{i\mathbf{k}_l \cdot \mathbf{R}} \hat{a}_l^{\lambda}(t) + \text{H.c.} \\ &\quad + \sum_m \hbar \hat{b}_{\text{em}}^\dagger(t) \sum_{\lambda} \sum_l \mathcal{E}_{\text{em}}^{\lambda}(\omega_l) e^{i\mathbf{k}_l \cdot \mathbf{R}} \hat{a}_l^{\lambda}(t) + \text{H.c.} \end{aligned} \quad (2)$$

where  $\hat{b}_{\text{mg(em)}}(t) = \hat{b}_{\text{mg(em)}} \exp(-i\omega_{\text{mg(em)}}t)$ ,  $\hat{a}_l^{\lambda}(t) = \hat{a}_l^{\lambda} \exp(-i\omega_l t)$ ,  $\mathcal{E}_{\text{mg(em)}}^{\lambda}(\omega_l) = -\boldsymbol{\mu}_{\text{mg(em)}} \cdot \hat{\mathbf{e}}_{\mathbf{k}_l}^{\lambda} \sqrt{\frac{\omega_l}{2\hbar\epsilon V}}$ . Here,  $\mathbf{k}_l$  is the wave vector of the field;  $\mathbf{R}$  is the spatial displacement vector between the donor and the acceptor;  $\boldsymbol{\mu}_{\text{mg(em)}}$  is the transition dipole of the acceptor;  $\hat{\mathbf{e}}_{\mathbf{k}_l}^{\lambda}$  is the polarization vector;  $\epsilon$  is the permittivity;  $V$  is the volume. Since the medium is dispersive, the permittivity is a function of frequency.

We then consider the entangled two-photon state generated by an arbitrary cascade emitter. Initially, the cascade emitter is in the excited state  $|a\rangle$ . Sequential decay goes to intermediate state  $|b_s\rangle$  and then to state  $|c\rangle$ , leading to emission of the entangled photon pair. To include for many intermediate states of the emitter, we use  $s$  to label all the possible intermediate states  $|b_s\rangle$  of the emitter. We assume that the time  $t$  is larger than the decay lifetime of the emissions such that  $t \gg \gamma_{\alpha s}^{-1}, \gamma_{\beta s}^{-1}$  to make sure the photon pair has reached the acceptor. As shown in Appendix B, based on work presented in Ref. [39], the initial state of the system can be expressed as

$$\begin{aligned} |i\rangle &= \sum_s \sum_{\mathbf{k}, \mathbf{q}} \sum_{\lambda_{\mathbf{k}}, \lambda_{\mathbf{q}}} \frac{g_{\alpha s, \mathbf{k}}^{\lambda_{\mathbf{k}}} g_{\beta s, \mathbf{q}}^{\lambda_{\mathbf{q}}}}{(\omega_q - \omega_{\beta s} + i\gamma_{\beta s})(\omega_k + \omega_q - \omega_{\alpha s} - \omega_{\beta s} + i\gamma_{\alpha s})} \\ &\quad \times |1_{\mathbf{k}}^{\lambda_{\mathbf{k}}}, 1_{\mathbf{q}}^{\lambda_{\mathbf{q}}}; g\rangle, \end{aligned} \quad (3)$$

where  $g_{\alpha s, \mathbf{k}}^{\lambda_{\mathbf{k}}} = -\boldsymbol{\mu}_{\alpha s} \cdot \hat{\mathbf{e}}_{\mathbf{k}}^{\lambda_{\mathbf{k}}} \sqrt{\frac{\omega_k}{2\hbar\epsilon V}}$  and  $g_{\beta s, \mathbf{q}}^{\lambda_{\mathbf{q}}} = -\boldsymbol{\mu}_{\beta s} \cdot \hat{\mathbf{e}}_{\mathbf{q}}^{\lambda_{\mathbf{q}}} \sqrt{\frac{\omega_q}{2\hbar\epsilon V}}$ . Here,  $\boldsymbol{\mu}_{\alpha s}$  and  $\boldsymbol{\mu}_{\beta s}$  describe the transition dipoles of the donor from state  $|a\rangle$  to state  $|b_s\rangle$  and from state  $|b_s\rangle$  to state  $|c\rangle$ , respectively;  $\omega_{\alpha s}$  and  $\omega_{\beta s}$  describe the transition frequencies of the donor from state  $|a\rangle$  to state  $|b_s\rangle$  and from state  $|b_s\rangle$  to state  $|c\rangle$ , respectively. Because Eq. (3) cannot be factorized into the product of  $|1_{\mathbf{k}}^{\lambda_{\mathbf{k}}}\rangle$  and  $|1_{\mathbf{q}}^{\lambda_{\mathbf{q}}}\rangle$ , the state is entangled in frequency. The entanglement of the state is maximized when  $\gamma_{\beta s} \gg \gamma_{\alpha s}$ . Note that the long-time limit,

i.e.,  $t \gg \gamma_{\alpha s}^{-1}, \gamma_{\beta s}^{-1}$ , allows us to discard some terms in Eq. (3), which are proportional to  $\exp(-i\gamma_{\alpha s}t)$  and  $\exp(-i\gamma_{\beta s}t)$ . These terms primarily matter in the transient dynamics and in the non-resonance cases, which are not our present concern.

When second-order perturbation theory is applied to the evolution of the acceptor while interacting with the entangled photons, the excitation probability amplitude is described as

$$M = -\frac{1}{\hbar^2} \langle f | \int_0^t dt_2 \int_0^{t_2} dt_1 V_{\text{int}}(t_2) V_{\text{int}}(t_1) | i \rangle \quad (4)$$

In Eq. (4),  $|i\rangle$  corresponds to the initial state of the sys-

tem, given by Eq. (3);  $|f\rangle$  corresponds to the final state of the system, which is given by  $|f\rangle = |0; e\rangle$ . This means that the initial state corresponds to the acceptor being in the ground state and the field being in a two-photon state; the final state corresponds to the acceptor being in the excited state and the field being in the vacuum state. Since there are two possible pathways for the two-photon emission/absorption, we have to consider two time orderings for the interactions. Then, the excitation probability amplitude is

$$\begin{aligned} M &= M_1 + M_2 \\ &= \sum_{\mathbf{k}, \mathbf{q}} \sum_{\lambda_k, \lambda_q} \sum_{s, m} \left\{ \int_0^t dt_2 \int_0^{t_2} dt_1 \frac{g_{\alpha s, \mathbf{k}}^{\lambda_k} g_{\beta s, \mathbf{q}}^{\lambda_q}}{(\omega_q - \omega_{\beta s} + i\gamma_{\beta s})(\omega_k + \omega_q - \omega_{\alpha s} - \omega_{\beta s} + i\gamma_{\alpha s})} \right. \\ &\quad \times \left( \langle f | V_{\text{int}}(t_2) | 0_{\mathbf{k}}^{\lambda_k}, 1_{\mathbf{q}}^{\lambda_q}; m \rangle \langle m; 0_{\mathbf{k}}^{\lambda_k}, 1_{\mathbf{q}}^{\lambda_q} | V_{\text{int}}(t_1) | 1_{\mathbf{k}}^{\lambda_k}, 1_{\mathbf{q}}^{\lambda_q}; g \rangle \right. \\ &\quad \left. \left. + \langle f | V_{\text{int}}(t_2) | 1_{\mathbf{k}}^{\lambda_k}, 0_{\mathbf{q}}^{\lambda_q}; m \rangle \langle m; 1_{\mathbf{k}}^{\lambda_k}, 0_{\mathbf{q}}^{\lambda_q} | V_{\text{int}}(t_1) | 1_{\mathbf{k}}^{\lambda_k}, 1_{\mathbf{q}}^{\lambda_q}; g \rangle \right) \right\}, \end{aligned} \quad (5)$$

where for completeness, we let the summation index  $m$  include all the possible intermediate states of the acceptor rather than just one state. As shown in FIG. 1, the two terms,  $M_1$  and  $M_2$ , correspond to the time-ordered pathways where (i) the first emitted photon  $\omega_k$  is absorbed first, and (ii) the first emitted photon  $\omega_k$  is absorbed second, respectively.

Assuming the frequency of the field is continuous, which is true in unbounded space, the summation over  $\mathbf{k}, \mathbf{q}$  can be

replaced by an integral,

$$\sum_{\mathbf{k}, \mathbf{q}} \rightarrow \left( \frac{V}{(2\pi)^3} \right)^2 \int d^3\mathbf{k} \int d^3\mathbf{q}, \quad (6)$$

where  $V$  is the volume. To evaluate the integral over  $\mathbf{k}$  and  $\mathbf{q}$ , the dispersion relation between the wavenumber and the frequency is required. Since we assume the donor and acceptor are in dispersive medium, not vacuum, we have  $k \approx k_\alpha + \frac{dk}{d\omega}(\omega_k - \omega_\alpha) = k_\alpha + \frac{\omega_k - \omega_\alpha}{v_\alpha}$ , where  $v_\alpha$  is the group velocity and  $\omega_\alpha$  is the averaged frequency of the photon. Because it is a group velocity, the index  $s$  is left out and the group velocity represents an average over the possible intermediate states. As shown in Appendix C, we can derive

$$\begin{aligned} M_1 &\approx \frac{e^{i\phi}}{\hbar^2} \sum_{s, m} \left\{ \left( \mu_{\alpha s} \cdot \overleftrightarrow{\theta}(\omega_{\alpha s}, \mathbf{R}) \cdot \mu_{\text{mg}} \right) \left( \mu_{\beta s} \cdot \overleftrightarrow{\theta}(\omega_{\beta s}, \mathbf{R}) \cdot \mu_{\text{em}} \right) \right. \\ &\quad \times \int_0^t dt_2 \int_0^{t_2} dt_1 e^{i(\omega_{\text{em}} t_2 + \omega_{\text{mg}} t_1)} e^{-i(\omega_{\alpha s} + i\gamma_{\alpha s})(t_1 - \frac{R}{v_\alpha})} \Theta[t_1 - \frac{R}{v_\alpha}] e^{-i(\omega_{\beta s} + \gamma_{\beta s})(t_2 - \frac{R}{v_\beta} - t_1 + \frac{R}{v_\alpha})} \Theta[t_2 - \frac{R}{v_\beta} - t_1 + \frac{R}{v_\alpha}] \left. \right\}, \end{aligned} \quad (7)$$

where  $\phi = (k_\alpha - \omega_\alpha/v_\alpha)(q_\beta - \omega_\beta/v_\beta)R^2$  is a constant phase factor,  $\Theta$  is a unit step function,  $v_\alpha$  and  $v_\beta$  are the group velocities of the photons with frequencies  $\omega_\alpha$  and  $\omega_\beta$ , respec-

tively. Here,  $\overleftrightarrow{\theta}(\omega_{\alpha(\beta)s}, \mathbf{R})$  is the electric dipole-dipole coupling tensor,<sup>40–45</sup> where the matrix element is described as

$$\theta_{ij}(\omega_{\alpha s}, \mathbf{R}) = \frac{\omega_{\alpha s}^3 e^{i\omega_{\alpha s} R / c_{\alpha s}}}{4\pi\epsilon(\omega_{\alpha s})c_{\alpha s}^3} \left[ (\delta_{ij} - 3\mathbf{e}_R \mathbf{e}_R) \left( \frac{c_{\alpha s}^3}{\omega_{\alpha s}^3 R^3} - \frac{ic_{\alpha s}^2}{\omega_{\alpha s}^2 R^2} \right) - (\delta_{ij} - \mathbf{e}_R \mathbf{e}_R) \frac{c_{\alpha s}}{\omega_{\alpha s} R} \right], \quad (8)$$

where  $c_{\alpha s}$  is the speed of light in the dispersive medium,  $c_{\alpha s} =$

$c/\sqrt{\epsilon(\omega_{\alpha s})/\epsilon_0}$ . When  $v_\alpha < v_\beta$ , the time integration yields

$$M_1 \approx -\frac{e^{i\phi}}{\hbar^2} \sum_{s,m} \left( \mu_{\alpha s} \cdot \overleftrightarrow{\theta}(\omega_{\alpha s}, \mathbf{R}) \cdot \mu_{\text{mg}} \right) \left( \mu_{\beta s} \cdot \overleftrightarrow{\theta}(\omega_{\beta s}, \mathbf{R}) \cdot \mu_{\text{em}} \right) e^{i(\omega_{\text{em}} \frac{R}{v_\beta} + \omega_{\text{mg}} \frac{R}{v_\alpha})} \frac{e^{-(i\omega_{\beta s} - i\omega_{\text{em}} + \gamma_{\beta s})T_e}}{i(\omega_{\alpha s} - \omega_{\text{mg}}) + (\gamma_{\alpha s} - \gamma_{\beta s})} \frac{1 - e^{-(i\delta + \gamma_{\alpha s})(t - \frac{R}{v_\alpha})}}{i\delta + \gamma_{\alpha s}}, \quad (9)$$

where the detuning is defined as  $\delta \equiv \omega_{\alpha s} + \omega_{\beta s} - \omega_{\text{mg}} - \omega_{\text{em}}$ . Since the detuning is determined by the initial and final states of the emitter and acceptor, it is independent of  $s$  and  $m$ . Here, we define  $T_e$ , the entanglement time, similar to Ref. [46] as follows

$$T_e \equiv \frac{R}{v_\alpha} - \frac{R}{v_\beta}. \quad (10)$$

Even though Eq. (10) has the same expression as the entanglement time used for a SPDC source of photons, there is a subtle difference between them. For SPDC, the entanglement

time is the maximum time difference between detection of the two photons. On the other hand, for a cascade emitter, the entanglement time is the minimum time difference between detection of the two photons. The discrepancy arises from the different ways in which two emission processes occur. The entanglement time is determined by the distance between the donor and acceptor, and the group velocity of the two photons. Experimentally, one can adjust the entanglement time by changing the distance between the donor and acceptor, or by altering the dispersive medium.

Likewise, we have

$$M_2 \approx \frac{e^{i\phi}}{\hbar^2} \sum_{s,m} \left( \mu_{\alpha s} \cdot \overleftrightarrow{\theta}(\omega_{\alpha s}, \mathbf{R}) \cdot \mu_{\text{em}} \right) \left( \mu_{\beta s} \cdot \overleftrightarrow{\theta}(\omega_{\beta s}, \mathbf{R}) \cdot \mu_{\text{mg}} \right) e^{i(\omega_{\text{em}} \frac{R}{v_\alpha} + \omega_{\text{mg}} \frac{R}{v_\beta})} \frac{1 - e^{-(i\omega_{\beta s} - i\omega_{\text{mg}} + \gamma_{\beta s})T_e}}{i(\omega_{\beta s} - \omega_{\text{mg}}) + \gamma_{\beta s}} \frac{1 - e^{-(i\delta + \gamma_{\alpha s})(t - \frac{R}{v_\alpha})}}{i\delta + \gamma_{\alpha s}}. \quad (11)$$

If we assume the difference between the two terms,  $\omega_{\text{em}} \frac{R}{v_\alpha} + \omega_{\text{mg}} \frac{R}{v_\beta}$  and  $\omega_{\text{em}} \frac{R}{v_\beta} + \omega_{\text{mg}} \frac{R}{v_\alpha}$  is negligible, then the excitation

probability is given by

$$\begin{aligned} P_{\text{E2P}}(t) &= |M_1 + M_2|^2 \\ &= \left| \sum_{s,m} \left\{ \frac{\left( \mu_{\alpha s} \cdot \overleftrightarrow{\theta}(\omega_{\alpha s}, \mathbf{R}) \cdot \mu_{\text{mg}} \right) \left( \mu_{\beta s} \cdot \overleftrightarrow{\theta}(\omega_{\beta s}, \mathbf{R}) \cdot \mu_{\text{em}} \right) e^{-(i\omega_{\beta s} - i\omega_{\text{em}} + \gamma_{\beta s})T_e}}{i\hbar(\omega_{\alpha s} - \omega_{\text{mg}}) + \hbar(\gamma_{\alpha s} - \gamma_{\beta s})} \right. \right. \\ &\quad \left. \left. + \frac{\left( \mu_{\alpha s} \cdot \overleftrightarrow{\theta}(\omega_{\alpha s}, \mathbf{R}) \cdot \mu_{\text{em}} \right) \left( \mu_{\beta s} \cdot \overleftrightarrow{\theta}(\omega_{\beta s}, \mathbf{R}) \cdot \mu_{\text{mg}} \right) (1 - e^{-(i\omega_{\beta s} - i\omega_{\text{mg}} + \gamma_{\beta s})T_e})}{i\hbar(\omega_{\beta s} - \omega_{\text{mg}}) + \hbar\gamma_{\beta s}} \right\} \times \frac{1 - e^{-(i\delta + \gamma_{\alpha s})(t - \frac{R}{v_\alpha})}}{i\hbar\delta + \hbar\gamma_{\alpha s}} \right|^2 \end{aligned} \quad (12)$$

We assume  $\gamma_{\beta s} \gg \gamma_{\alpha s}$ , which corresponds to the condition

where the photons are highly entangled. As  $\gamma_{\alpha s} \ll \delta$ , we de-

rive the following expression for the rate of E2P-EA

$$\begin{aligned}
 K &= \lim_{t \rightarrow \infty} \frac{P_{\text{E2P}}(t)}{t} \\
 &= \frac{2\pi}{\hbar} \left| \sum_{s,m} \left\{ \frac{(\boldsymbol{\mu}_{\alpha s} \cdot \overleftrightarrow{\boldsymbol{\theta}}(\omega_{\alpha s}, \mathbf{R}) \cdot \boldsymbol{\mu}_{\text{mg}})(\boldsymbol{\mu}_{\beta s} \cdot \overleftrightarrow{\boldsymbol{\theta}}(\omega_{\beta s}, \mathbf{R}) \cdot \boldsymbol{\mu}_{\text{em}}) e^{-(i\omega_{\beta s} - i\omega_{\text{em}} + \gamma_{\beta s})T_e}}{i\hbar(\omega_{\alpha s} - \omega_{\text{mg}}) - \hbar\gamma_{\beta s}} \right. \right. \\
 &\quad \left. \left. + \frac{(\boldsymbol{\mu}_{\alpha s} \cdot \overleftrightarrow{\boldsymbol{\theta}}(\omega_{\alpha s}, \mathbf{R}) \cdot \boldsymbol{\mu}_{\text{em}})(\boldsymbol{\mu}_{\beta s} \cdot \overleftrightarrow{\boldsymbol{\theta}}(\omega_{\beta s}, \mathbf{R}) \cdot \boldsymbol{\mu}_{\text{mg}})(1 - e^{-(i\omega_{\beta s} - i\omega_{\text{mg}} + \gamma_{\beta s})T_e})}{i\hbar(\omega_{\beta s} - \omega_{\text{mg}}) + \hbar\gamma_{\beta s}} \right\} \right|^2 \delta(E_{\delta}). \quad (13)
 \end{aligned}$$

Note that since we assume  $\gamma_{\alpha s} \ll \delta$ , the index  $s$  drops out in the expression involving the Dirac delta function, which means that energy conservation is not dependent on the intermediate states.

To compute Eq. (13) numerically, we replace the Dirac delta function  $\delta(E_{\delta})$  with the ETPA line shape function,  $g_e(\omega_f)$ , as previously derived<sup>47</sup>. In this function, the ETPA linewidth is determined by the spontaneous radiative lifetime from the Fermi's golden rule, and this leads to a resonant line-shape given by:

$$g_e(\omega_f) = \tau_r = \left[ \sum_{j < f} \frac{1}{3\pi\epsilon\hbar} \left( \frac{|\omega_{jf}|}{c} \right)^3 |\mu_{jf}|^2 \right]^{-1}. \quad (14)$$

Eq. (13) in combination with Eq. (14) provide the governing equations describing the entangled two-photon emission/absorption rate between a single many-level cascade donor and a single acceptor. Our formula gives a convenient way to analyze the effects of entanglement, energy detuning, and entanglement time on the emission/absorption rate, using input from electronic structure calculations. In addition, we would like to emphasize that our model can be applied to any molecule as acceptor, and is not limited to a three-level system.

### III. RESULTS AND DISCUSSION

Let us first focus our attention on the excitation probability for entangled photons generated by a cascade emitter ( $P_{\text{E2P}}$ ) in comparison to the excitation probability for uncorrelated photons generated by two separate emitters ( $P_{\text{S2P}}$ ). For simplicity, we only consider one intermediate state in the emitter. Thus, the index  $s$  is left out throughout this section. Here,  $P_{\text{E2P}}$  is calculated according to Eq. (12);  $P_{\text{S2P}}$  is given as follows (see

Appendix D)

$$\begin{aligned}
 P_{\text{S2P}} &= \sum_m \left| \frac{(\boldsymbol{\mu}_{\alpha} \cdot \overleftrightarrow{\boldsymbol{\theta}}(\omega_{\alpha}, \mathbf{R}) \cdot \boldsymbol{\mu}_{\text{mg}})(\boldsymbol{\mu}_{\beta} \cdot \overleftrightarrow{\boldsymbol{\theta}}(\omega_{\beta}, \mathbf{R}) \cdot \boldsymbol{\mu}_{\text{em}})}{i\hbar(\omega_{\alpha} - \omega_{\text{mg}}) + \hbar\gamma_{\alpha}} \right. \\
 &\quad \left. + \frac{(\boldsymbol{\mu}_{\alpha} \cdot \overleftrightarrow{\boldsymbol{\theta}}(\omega_{\alpha}, \mathbf{R}) \cdot \boldsymbol{\mu}_{\text{em}})(\boldsymbol{\mu}_{\beta} \cdot \overleftrightarrow{\boldsymbol{\theta}}(\omega_{\beta}, \mathbf{R}) \cdot \boldsymbol{\mu}_{\text{mg}})}{i\hbar(\omega_{\beta} - \omega_{\text{mg}}) + \hbar\gamma_{\beta}} \right|^2 \\
 &\quad \times \left| \frac{1 - e^{-(i\delta + \gamma_{\alpha} + \gamma_{\beta})(t - \frac{R}{v_{\alpha}})}}{i\hbar\delta + \hbar(\gamma_{\alpha} + \gamma_{\beta})} \right|^2. \quad (15)
 \end{aligned}$$

One of the notable differences between  $P_{\text{E2P}}$  and  $P_{\text{S2P}}$  is that in terms of the time-dependent part,  $P_{\text{E2P}}$  is proportional to  $1/\gamma_{\alpha}^2$  and  $P_{\text{S2P}}$  is proportional to  $1/(\gamma_{\alpha} + \gamma_{\beta})^2$ . In the case  $\gamma_{\beta} \gg \gamma_{\alpha}$  where the entangled photons are highly correlated in the time domain,  $P_{\text{E2P}}$  is larger than  $P_{\text{S2P}}$ . That is, the excitation using entangled photons is more likely to occur than excitation using uncorrelated photons. To demonstrate the difference, we analyze the ratio of  $P_{\text{E2P}}$  and  $P_{\text{S2P}}$  as a function of  $\gamma_{\beta}$  and  $\Delta \equiv \omega_{\alpha} - \omega_{\text{mg}}$ , as shown in Fig. 2. For simplicity, we consider a three-level quantum dot as donor and another three-level quantum dot as acceptor. The parameters are chosen using a InAs quantum dot embedded in a GaAs/AlAs planar microcavity<sup>48–50</sup> as the donor. This leads to the parameters  $\omega_{\alpha} = 1.398$  eV,  $\omega_{\beta} = 1.42$  eV,  $\delta = \omega_{\alpha} + \omega_{\beta} - \omega_{\text{mg}} - \omega_{\text{em}} = 0$  eV,  $\boldsymbol{\mu}_{\alpha} = \boldsymbol{\mu}_{\beta} = \boldsymbol{\mu}_{\text{em}} = \boldsymbol{\mu}_{\text{mg}} = (0, 0, 10)$  D,  $\mathbf{R} = (10, 0, 0)$  nm,  $\gamma_{\alpha} = 0.005$  eV,  $T_e = 0$  fs and  $t = \infty$ . Figure 2 shows that  $P_{\text{E2P}}$  can be three orders of magnitude larger than  $P_{\text{S2P}}$ . In addition, the ratio  $P_{\text{E2P}}/P_{\text{S2P}}$  becomes larger when  $\gamma_{\beta}$  and  $\Delta$  are larger.

To further analyze Eqs. (12) and (15), we consider the case where the emitter only has one intermediate state and the condition,  $\gamma_{\alpha} \gg \gamma_{\beta}$ , where the two photons are minimally entangled. In other words, the second photon is emitted a long time after the first photon. Also, we choose a value of the entanglement time so that  $\exp[-(i\omega_{\beta} - i\omega_{\text{em}} + \gamma_{\beta})T_e] = 1 - \exp[-(i\omega_{\beta} - i\omega_{\text{mg}} + \gamma_{\beta})T_e]$  as this makes the two pathways contribute equally to the rate. In this limit, Eq. (12) can

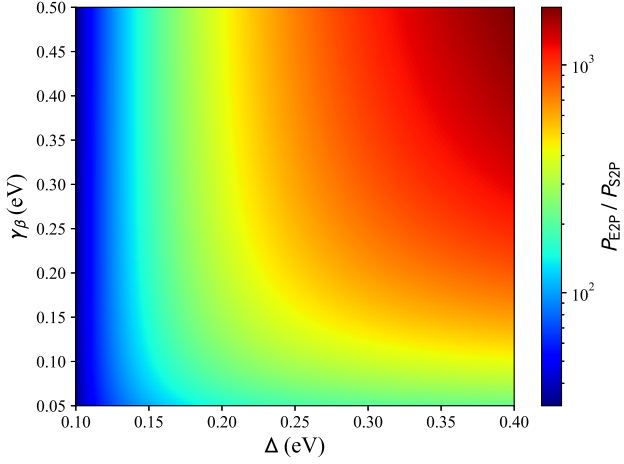


FIG. 2. The ratio of the excitation probability for entangled two-photon emission/absorption ( $P_{E2P}$ ) to the uncorrelated two-photon emission/absorption result ( $P_{S2P}$ ). Here,  $\gamma_\beta$  is the decay rate of the donor from state  $|b\rangle$  to  $|c\rangle$  and  $\Delta \equiv \omega_\alpha - \omega_{mg}$ .

be approximated as

$$P_{E2P} \approx \sum_m \left| \frac{(\mu_\alpha \cdot \vec{\theta}(\omega_\alpha, \mathbf{R}) \cdot \mu_{mg})(\mu_\beta \cdot \vec{\theta}(\omega_\beta, \mathbf{R}) \cdot \mu_{em})}{i\hbar(\omega_\alpha - \omega_{mg}) + \hbar\gamma_\alpha} + \frac{(\mu_\alpha \cdot \vec{\theta}(\omega_\alpha, \mathbf{R}) \cdot \mu_{em})(\mu_\beta \cdot \vec{\theta}(\omega_\beta, \mathbf{R}) \cdot \mu_{mg})}{i\hbar(\omega_\beta - \omega_{mg}) + \hbar\gamma_\beta} \right|^2 \times \left| \frac{1 - e^{-(i\delta + \gamma_\alpha)(t - \frac{R}{v_\alpha})}}{i\hbar\delta + \hbar\gamma_\alpha} \right|^2. \quad (16)$$

Eq. (16) is approximately the same as Eq. (15) as  $\gamma_\alpha \gg \gamma_\beta$ , which means the excitation probability using entangled and unentangled photons are equivalent under such condition. This makes sense because minimally entangled photons can be regarded as uncorrelated photons.

Let us now further examine the main result of our work, Eq. (13). In many respects, Eq. (13) resembles the usual one-photon emission/absorption rate (Appendix A). First, factors related to the orientation of the transition dipole moment are determined by the electric dipole-dipole coupling tensor, Eq. (8), as in OP-EA. However, two pairs of dipoles are involved in the emission/absorption process, rather than a single pair as in OP-EA. Also, the rate is smaller when the photon energy is detuned from resonance, i.e., when  $\omega_\alpha - \omega_{mg}$  and  $\omega_\beta - \omega_{mg}$  are nonzero. In addition, there is a significant difference between Eq. (13) and the usual one-photon emission/absorption rate, concerning the exponential term containing the entanglement time,  $T_e$ . In Eq. (13),  $T_e$  determines which pathway dominates during the emission/absorption. The entanglement time,  $T_e$ , is the difference between the transit times of the two photons from donor to acceptor, i.e.,  $\frac{R}{v_\alpha} - \frac{R}{v_\beta}$ . When  $T_e$  is small, the transit time of the first emitted photon is almost the same as the second emitted photon.

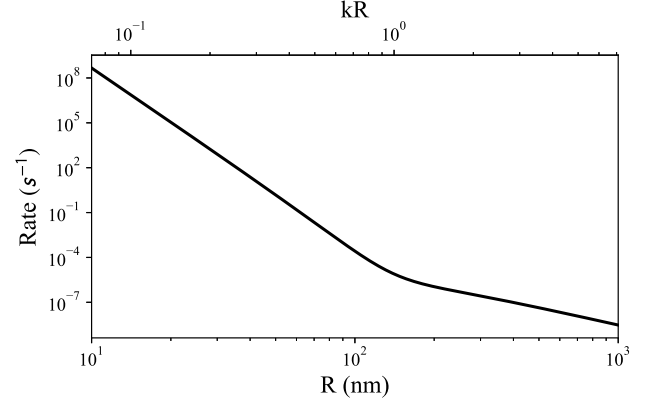


FIG. 3. Log-log plot showing E2T-EA rate as a function of distance  $R$ . We consider  $\mu_\alpha = \mu_\beta = \mu_{em} = \mu_{mg} = 10$  D and the transition moments are all aligned in the same direction. Here,  $\omega_\alpha = 1.398$  eV,  $\omega_\beta = 1.42$  eV,  $\omega_{em} = 1.398$  eV,  $\omega_{mg} = 1.42$  eV,  $\gamma_\alpha = 0.005$  eV,  $\gamma_\beta = 0.05$  eV and  $T_e = 0$  fs.

Hence, the first emitted photon is more likely to arrive at the acceptor first, which means  $M_1$  (FIG. 1 (a)) dominates in the emission/absorption. When  $T_e$  is large, the transit time of the first emitted photon is longer than the second, in which case the first emitted photon is more likely to arrive at the acceptor second, and  $M_2$  (FIG. 1 (b)) dominates in the emission/absorption. Thus we see that the entanglement time,  $T_e$ , plays a crucial role in determining which pathway dominates during the E2P-EA process. Furthermore, the exponential terms containing  $T_e$  cause quantum interference.

In order to gain insight into how E2P-EA varies with donor-acceptor separation, we show a log-log plot of the E2P-EA rate as a function of  $R$  between 10 nm and 1  $\mu$ m in FIG. 3. The slope is about  $-12$  between 10 nm and 100 nm, then it changes to about  $-4$  between 200 nm and 1  $\mu$ m. This shows that the E2P-EA rate is proportional to  $R^{-12}$  in the near-zone ( $\omega R/c \ll 1$ ) and proportional to  $R^{-4}$  in the far-zone ( $\omega R/c \gg 1$ ), which is consistent with OP-EA where the exponents are half of these values. The slope of the line in FIG. 3 changes around  $R = 150$  nm. Since the frequency we used here is around 1.4 eV (885 nm), we expect the transition point occurs at  $\omega R/c \approx 1$ , where the corresponding distance is  $885/2\pi \approx 140$  nm. The result is in good agreement with our prediction. Since E2P-EA decays a lot faster than OP-EA, it will be difficult to observe E2P-EA in long distance. Our calculation (FIG. 3) suggests that E2P-EA is most likely to occur when  $R \lesssim 10$  nm. In Appendix E, we show the formulation of E2P-EA for a one-dimensional system where the donor and acceptor are placed in a waveguide. In that case the E2P-EA rate is independent of the distance, which suggests that confining E2P-EA to one dimension provides a way to simplify the observation of E2P-EA.

It is of particular importance to evaluate the OP-EA and E2P-EA rates for the same system so that we can understand which process dominates in the near-zone. In FIG. 4, we show the comparison of OP-EA and E2P-EA rates as a function



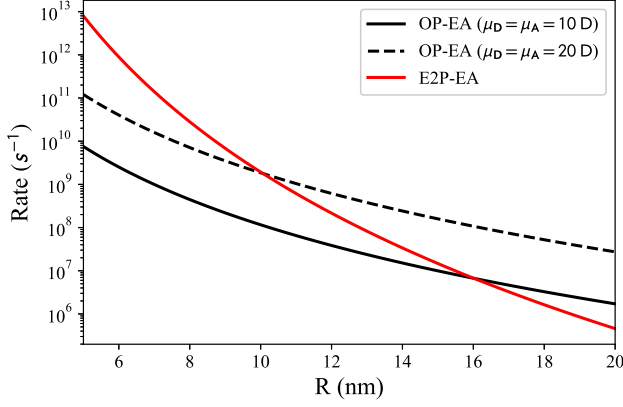


FIG. 4. Comparison of one-photon emission/absorption (OP-EA) and entangled two-photon emission/absorption (E2P-EA) rates as a function of distance  $R$ . For OP-EA,  $\omega_D = \omega_A = 2.8$  eV. Here,  $\mu_D = \mu_A = 10$  D in the solid black line;  $\mu_D = \mu_A = 20$  D in the dashed black line. For E2P-EA, we consider  $\mu_\alpha = \mu_\beta = \mu_{em} = \mu_{mg} = 10$  D and they are all aligned in the same direction. Here,  $\omega_\alpha = 1.4$  eV,  $\omega_\beta = 1.4$  eV,  $\omega_{em} = 1.4$  eV,  $\omega_{mg} = 1.4$  eV,  $\gamma_\alpha = 0.005$  eV,  $\gamma_\beta = 0.05$  eV and  $T_e = 0$  fs.

of distance  $R$  between 5 nm and 20 nm. These results are based on the following parameters. For E2P-EA, we consider a three-level quantum dot as emitter and a three-level quantum dot as acceptor. The parameters are  $\mu_\alpha = \mu_\beta = \mu_{em} = \mu_{mg} = 10$  D with all transition moments being aligned in the same direction. Here,  $\omega_\alpha = 1.4$  eV,  $\omega_\beta = 1.4$  eV,  $\omega_{em} = 1.4$  eV,  $\omega_{mg} = 1.4$  eV,  $\gamma_\alpha = 0.005$  eV,  $\gamma_\beta = 0.05$  eV and  $T_e = 0$  fs. For OP-EA,  $\omega_D = \omega_A = 2.8$  eV, where  $\omega_{D(A)}$  is the one-photon transition frequency of the donor (acceptor). Two sets of the transition dipole moments are considered, where (i)  $\mu_D$  and  $\mu_A$  are the same as the ones used in E2P-EA and (ii)  $\mu_D$  and  $\mu_A$  are twice as large as the ones used in E2P-EA. The figure shows that the E2P-EA rate is comparable to the OP-EA rate in the near-zone. Indeed, when  $R < 8$  nm, the E2P-EA rate can be greater than the OP-EA rate. Note that the E2P-EA rate reaches  $10^{13} \text{ s}^{-1}$  when  $R = 5$  nm. The rate of  $10^{13} \text{ s}^{-1}$  is possible, but it is close to the limit where the perturbation theory would break down.

Next, we study the entangled two-photon emission/absorption rate as a function of  $T_e$  (x-axis) and  $\gamma_\beta$  (y-axis). For simplicity, we use a three-level quantum dot as donor and as acceptor. To explore how the energy arrangement of the three-level models affect the emission/absorption rate, we consider two cases, where (i) the energy levels of the two quantum dots are perfectly aligned and (ii) the energy levels of the two quantum dots are mismatched. The results are shown as colormaps in Fig. 5. Here, we use the parameters  $\omega_\alpha = 1.398$  eV,  $\omega_\beta = 1.42$  eV,  $\delta = \omega_\alpha + \omega_\beta - \omega_{mg} - \omega_{em} = 0$  eV,  $\mu_\alpha = \mu_\beta = \mu_{em} = \mu_{mg} = (0, 0, 10)$  D,  $\mathbf{R} = (10, 0, 0)$  nm,  $\gamma_\alpha = 0.005$  eV. In Fig. 5 (a), we have  $\omega_{em} = 1.398$  eV and  $\omega_{mg} = 1.42$  eV, which corresponds to the case where the energy levels are perfectly aligned. In Fig. 5 (b), we have  $\omega_{em} = 1.898$  eV and  $\omega_{mg} = 0.92$  eV, which corresponds to

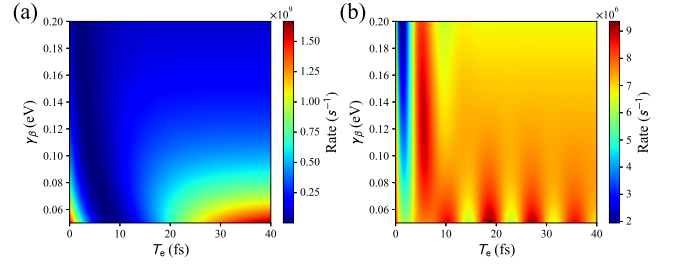


FIG. 5. Entangled two-photon emission/absorption rate as a function of  $T_e$  (x-axis) and  $\gamma_\beta$  (y-axis). We consider  $\mu_\alpha = \mu_\beta = \mu_{em} = \mu_{mg} = 10$  D and all transition moments are aligned in the same direction. The distance between the donor and the acceptor is 10 nm, and  $\gamma_\alpha = 0.005$  eV. (a) Here,  $\omega_\alpha = 1.398$  eV,  $\omega_\beta = 1.42$  eV,  $\omega_{em} = 1.398$  eV and  $\omega_{mg} = 1.42$  eV. (b) Here,  $\omega_\alpha = 1.398$  eV,  $\omega_\beta = 1.42$  eV,  $\omega_{em} = 1.898$  eV and  $\omega_{mg} = 0.92$  eV.

the case where the energy levels mismatch.

Fig. 5 (a) shows that for the case where energy levels are perfectly aligned, there are two areas which give relatively large emission/absorption rates. In particular, the emission/absorption rate is greater (i) when the entanglement time is close to zero and (ii) when the entanglement time is large. This feature demonstrates the fact discussed earlier that the entanglement time determines which pathway dominates in the emission/absorption process. When  $T_e \rightarrow 0$ ,  $\exp[-(i\omega_\beta - i\omega_{em} + \gamma_\beta)T_e] \rightarrow 1$  and the first term in Eq. (13) dominates, whereas when  $T_e \rightarrow \infty$ ,  $\exp[-(i\omega_\beta - i\omega_{em} + \gamma_\beta)T_e] \rightarrow 0$ , and the second term in Eq. (13) dominates. Between the two areas, the emission/absorption rate is relatively small due to destructive interference between the two pathways. Furthermore, the rate has an inverse dependence on  $\gamma_\beta$ . This is due to the fact that according to the earlier equation, Eq. (3), the spectrum of the entangled two-photon state becomes broader when  $\gamma_\beta$  gets larger. This results in a smaller amplitude for the resonant frequency in the entangled two-photon state. Note that in Fig. 5 (a), there is no oscillation with respect to the entanglement time due to interference. The reason is that the energy levels are perfectly aligned and the two photons are nearly degenerate. Thus,  $\omega_\beta - \omega_{em}$  and  $\omega_\beta - \omega_{mg}$  are very small, and very large  $T_e$  is required to see oscillations. Besides,  $\exp(-\gamma_\beta T_e)$  introduces dephasing into the expression, so the oscillation is washed out for large  $T_e$ .

Fig. 5 (b) shows that there is a clear oscillating pattern with respect to the entanglement time for the case where energy levels mismatch. The oscillation arises from the exponential term in the numerator of Eq. (13). The period of the oscillation is about 8 fs. The energy difference between the donor and the acceptor is 0.5 eV ( $\sim 8.3$  fs), which gives a good account of the period. Furthermore, we can see interference of the two pathways when  $T_e \sim 4$  fs. The interference is destructive when  $0 < T_e < 4$  fs; the interference is constructive when  $4 < T_e < 8$  fs. In general, the rate has an inverse dependence on  $\gamma_\beta$ . However, when constructive interference dominates, the rate peaks at a certain value of  $\gamma_\beta$ , which is around 0.12 eV.

#### IV. CONCLUSION

In summary, we have derived a new formulation for the entangled two-photon resonance emission/absorption (E2P-EA) rate between a donor and an acceptor using second-order perturbation theory for the cascade emission that is coupled to second-order perturbation theory for the absorption. With this result, we have demonstrated several characteristics of E2P-EA using a temporally entangled two-photon state. First, we have shown that the probability of E2P-EA can be enhanced by orders of magnitude compared to the one with two unentangled photons. The higher the entanglement of the two photons is, the larger the enhancement is. Second, we have shown how the rate is affected by the two possible pathways for the emission/absorption, and that the entanglement time determines which pathway dominates during the emission/absorption, and when there might be interference between the two pathways. Finally, we have shown that the E2P-EA rate is comparable to one-photon emission/absorption (OP-EA) in the near-zone, for the specific choices of energy levels and transition moments that we considered. Moreover, E2P-EA could dominate when excitation of the acceptor species by one photon is forbidden but two-photons are allowed. This suggests that some experiments that were previously thought to involve OP-EA are actually E2P-EA.

#### ACKNOWLEDGMENTS

This research was supported by NSF Grant CHE-2055565. We thank K. Nasiri Avanaki for useful discussions.

#### AUTHOR DECLARATIONS

##### Conflict of Interest

The authors have no conflicts to disclose.

#### DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

#### Appendix A: One-Photon Emission/Absorption

For one-photon emission/absorption, the initial state after the emission is given as

$$|i\rangle = \sum_{\mathbf{k}} \sum_{\lambda_{\mathbf{k}}} \frac{g_{\mathbf{k}}^{\lambda_{\mathbf{k}}}}{(\omega_{\mathbf{k}} - \omega_{\mathbf{D}}) + i\gamma} |1_{\mathbf{k}}^{\lambda_{\mathbf{k}}}, g\rangle \quad (\text{A1})$$

, where  $\omega_{\mathbf{D}}$  is the transition frequency from the ground state to the excited state of the donor and  $\gamma$  is the decay rate of the

excited state of the donor. According to first-order perturbation theory, the excitation probability amplitude is described as

$$\begin{aligned} M &= \frac{1}{\hbar} \langle f | \int_0^t dt_1 V_{\text{int}}(t_1) | i \rangle \\ &= \sum_{\mathbf{k}} \sum_{\lambda_{\mathbf{k}}} \int_0^t dt_1 \frac{g_{\mathbf{k}}^{\lambda_{\mathbf{k}}}}{(\omega_{\mathbf{k}} - \omega_{\mathbf{D}}) + i\gamma} \langle 0 : e | V_{\text{int}}(t_1) | 1_{\mathbf{k}}; g \rangle \\ &= \frac{1}{\hbar} (\mu_{\mathbf{D}} \cdot \overleftrightarrow{\boldsymbol{\theta}}(\omega_{\mathbf{D}}, R) \cdot \mu_{\mathbf{A}}) \int_0^t dt_1 e^{(i\omega_{\mathbf{A}} - i\omega_{\mathbf{D}} + \gamma)(t_1 - R/c)} \\ &= \frac{1}{\hbar} (\mu_{\mathbf{D}} \cdot \overleftrightarrow{\boldsymbol{\theta}}(\omega_{\mathbf{D}}, R) \cdot \mu_{\mathbf{A}}) \left( \frac{1 - e^{(i\omega_{\mathbf{A}} - i\omega_{\mathbf{D}} + \gamma)(t - R/c)}}{i(\omega_{\mathbf{A}} - \omega_{\mathbf{D}}) + \gamma} \right) \end{aligned} \quad (\text{A2})$$

As  $\gamma \ll |\omega_{\mathbf{D}} - \omega_{\mathbf{A}}|$ , we derive the following expression for the rate of the OPEA

$$K = \frac{2\pi}{\hbar} (\mu_{\mathbf{D}} \cdot \overleftrightarrow{\boldsymbol{\theta}}(\omega_{\mathbf{D}}, R) \cdot \mu_{\mathbf{A}})^2 \delta(\omega_{\mathbf{A}} - \omega_{\mathbf{D}}) \quad (\text{A3})$$

#### Appendix B: Entangled two-photon state

The entangled two-photon state is derived in the same way as Ref. [39]. The state of the molecule-field system is given by

$$|\psi(t)\rangle = c_a(t) |a, 0\rangle + \sum_s \sum_{\mathbf{k}} c_{b_s, \mathbf{k}} |b_s, 1_{\mathbf{k}}\rangle + \sum_{\mathbf{k}, \mathbf{q}} c_{c, \mathbf{k}, \mathbf{q}} |c, 1_{\mathbf{k}}, 1_{\mathbf{q}}\rangle \quad (\text{B1})$$

According to the Schrödinger equation  $|\dot{\psi}(t)\rangle = -\frac{i}{\hbar} V_{\text{int}}(t) |\psi(t)\rangle$ , we obtain the equation of motions of  $c_a$ ,  $c_{b_s, \mathbf{k}}$  and  $c_{c, \mathbf{k}, \mathbf{q}}$  as follows

$$\dot{c}_a = -i \sum_s \sum_{\mathbf{k}} \sum_{\lambda_{\mathbf{k}}} g_{\alpha s, \mathbf{k}}^{\lambda_{\mathbf{k}}} c_{b_s, \mathbf{k}} e^{i(\omega_{\alpha s} - \omega_{\mathbf{k}})t} \quad (\text{B2})$$

$$\begin{aligned} \dot{c}_{b_s, \mathbf{k}} &= -i \sum_s \sum_{\lambda_{\mathbf{k}}} g_{\alpha s, \mathbf{k}}^{\lambda_{\mathbf{k}}} c_a e^{-i(\omega_{\alpha s} - \omega_{\mathbf{k}})t} \\ &\quad - i \sum_s \sum_{\mathbf{q}} \sum_{\lambda_{\mathbf{q}}} g_{\beta s, \mathbf{q}}^{\lambda_{\mathbf{q}}} c_{c, \mathbf{k}, \mathbf{q}} e^{i(\omega_{\beta s} - \omega_{\mathbf{q}})t} \end{aligned} \quad (\text{B3})$$

$$\dot{c}_{c, \mathbf{k}, \mathbf{q}} = -i \sum_s \sum_{\lambda_{\mathbf{q}}} g_{\beta s, \mathbf{q}}^{\lambda_{\mathbf{q}}} c_{b_s, \mathbf{k}} e^{-i(\omega_{\beta s} - \omega_{\mathbf{q}})t} \quad (\text{B4})$$

Using the Weisskopf-Wigner approximation and solving the differential equations, we have

$$\begin{aligned} c_{c, \mathbf{k}, \mathbf{q}}(t = \infty) &= \sum_s \sum_{\mathbf{k}, \mathbf{q}} \sum_{\lambda_{\mathbf{k}}, \lambda_{\mathbf{q}}} \frac{g_{\alpha s, \mathbf{k}}^{\lambda_{\mathbf{k}}} g_{\beta s, \mathbf{q}}^{\lambda_{\mathbf{q}}}}{(\omega_{\mathbf{q}} - \omega_{\beta s} + i\gamma_{\beta s})(\omega_{\mathbf{k}} + \omega_{\mathbf{q}} - \omega_{\alpha s} - \omega_{\beta s} + i\gamma_{\alpha s})} \end{aligned} \quad (\text{B5})$$

, which is the coefficient of the entangled two-photon state.



### Appendix C: Derivation of Eq. (7)

Replacing the summation over  $\mathbf{k}$  and  $\mathbf{q}$  by integrals, we obtain

$$M_1 = \left( \frac{V}{(2\pi)^3} \right)^2 \sum_{\lambda_{\mathbf{k}}, \lambda_{\mathbf{q}}} \sum_{s,m} \left( \int_0^t dt_2 \int_0^{t_2} dt_1 \int d^3\mathbf{k} \int d^3\mathbf{q} \right. \\ \times \frac{g_{\alpha s, \mathbf{k}}^{\lambda_{\mathbf{k}}} g_{\beta s, \mathbf{q}}^{\lambda_{\mathbf{q}}}}{(\omega_q - \omega_{\beta s} + i\gamma_{\beta s})(\omega_k + \omega_q - \omega_{\alpha s} - \omega_{\beta s} + i\gamma_{\alpha s})} \\ \times \langle f | V_{\text{int}}(t_2) | 0_{\mathbf{k}}^{\lambda_{\mathbf{k}}}, 1_{\mathbf{q}}^{\lambda_{\mathbf{q}}}; m \rangle \langle m; 0_{\mathbf{k}}^{\lambda_{\mathbf{k}}}, 1_{\mathbf{q}}^{\lambda_{\mathbf{q}}} | V_{\text{int}}(t_1) | 1_{\mathbf{k}}^{\lambda_{\mathbf{k}}}, 1_{\mathbf{q}}^{\lambda_{\mathbf{q}}}; g \rangle \Big) \quad (\text{C1})$$

Inserting all the coupling terms and evaluating the two brackets, we have

$$M_1 = \left( \frac{1}{16\pi^3 \hbar \epsilon} \right)^2 \sum_{s,m} \left\{ \int_0^t dt_2 \int_0^{t_2} dt_1 \int_0^\infty k^2 dk \int d\Omega_k \right. \\ \times \int_0^\infty q^2 dq \int d\Omega_q e^{i(\omega_{\text{em}} t_2 + \omega_{\text{mg}} t_1)} e^{-i(\omega_k t_2 + \omega_q t_1)} \\ \times \frac{\omega_k \omega_q e^{i(\mathbf{k} \cdot \mathbf{R} + \mathbf{q} \cdot \mathbf{R}')}}{(\omega_q - \omega_{\beta s} + i\gamma_{\beta s})(\omega_k + \omega_q - \omega_{\alpha s} - \omega_{\beta s} + i\gamma_{\alpha s})} \\ \times \sum_{\lambda_{\mathbf{k}}} \left[ (\mu_{\alpha s} \cdot \hat{\mathbf{e}}_{\mathbf{k}}^{\lambda_{\mathbf{k}}})(\mu_{\text{em}} \cdot \hat{\mathbf{e}}_{\mathbf{k}}^{\lambda_{\mathbf{k}}}) \right] \sum_{\lambda_{\mathbf{q}}} \left[ (\mu_{\beta s} \cdot \hat{\mathbf{e}}_{\mathbf{q}}^{\lambda_{\mathbf{q}}})(\mu_{\text{mg}} \cdot \hat{\mathbf{e}}_{\mathbf{q}}^{\lambda_{\mathbf{q}}}) \right] \Big\} \quad (\text{C2})$$

Using the identity of the polarization sum,

$$\sum_{\lambda_{\mathbf{k}}} \hat{\mathbf{e}}_{\mathbf{k}i}^{\lambda_{\mathbf{k}}} \hat{\mathbf{e}}_{\mathbf{k}j}^{\lambda_{\mathbf{k}}} = \delta_{ij} - \hat{k}_i \hat{k}_j \quad (\text{C3})$$

and the relation,

$$-\int \hat{k}_i \hat{k}_j e^{\pm i \mathbf{k} \cdot \mathbf{R}} d\Omega_k = \frac{1}{k^2} \nabla_i \nabla_j \int e^{\pm i \mathbf{k} \cdot \mathbf{R}} d\Omega_k \quad (\text{C4})$$

and integrating over  $\Omega_k, \Omega_q$ , we can rewrite  $M_1$  as

$$M_1 = \left( \frac{1}{8\pi^2 \hbar \epsilon} \right)^2 \sum_{s,m} \left\{ \sum_{i,j \in \{1,2,3\}} \sum_{i',j' \in \{1,2,3\}} \mu_{\alpha s}^i \mu_{\text{em}}^j \mu_{\beta s}^{i'} \mu_{\text{mg}}^{j'} \int_0^t dt_2 \int_0^{t_2} dt_1 e^{i(\omega_{\text{em}} t_2 + \omega_{\text{mg}} t_1)} \right. \\ \times \int_0^\infty dk \int_0^\infty dq \left[ (-\nabla^2 \delta_{ij} + \nabla_i \nabla_j) \frac{i(e^{ikR} - e^{-ikR})}{R} \right] \left[ (-\nabla'^2 \delta_{i'j'} + \nabla'_{i'} \nabla'_{j'}) \frac{i(e^{iqR'} - e^{-iqR'})}{R'} \right] \\ \times \frac{\omega_k \omega_q e^{-i(\omega_k t_2 + \omega_q t_1)}}{(\omega_q - \omega_{\beta s} + i\gamma_{\beta s})(\omega_k + \omega_q - \omega_{\alpha s} - \omega_{\beta s} + i\gamma_{\alpha s})} \Big\}, \quad (\text{C5})$$

where  $\mu_{\alpha s}^i$  is the  $i$ th component of the transition dipole mo-

ment of the donor;  $\mu_{\text{em}}^j$  is the  $j$ th component of the transition dipole moment of the acceptor. Discarding the unphysical incoming wave,  $e^{-ikR}$  and  $e^{-iqR'}$ , we have

$$M_1 = \left( \frac{1}{8\pi^2 \hbar \epsilon} \right)^2 \sum_{s,m} \left\{ \sum_{i,j \in \{1,2,3\}} \sum_{i',j' \in \{1,2,3\}} \mu_{\alpha s}^i \mu_{\text{em}}^j \mu_{\beta s}^{i'} \mu_{\text{mg}}^{j'} \int_0^t dt_2 \int_0^{t_2} dt_1 e^{i(\omega_{\text{em}} t_2 + \omega_{\text{mg}} t_1)} \right. \\ \times \int_0^\infty dk \int_0^\infty dq \frac{e^{ikR}}{R^3} \left[ (1 - ikR)(\delta_{ij} - 3\hat{\mathbf{e}}_{\mathbf{R}i} \hat{\mathbf{e}}_{\mathbf{R}j}) - k^2 R^2 (\delta_{ij} - \hat{\mathbf{e}}_{\mathbf{R}i} \hat{\mathbf{e}}_{\mathbf{R}j}) \right] \\ \times \frac{e^{iqR'}}{R'^3} \left[ (1 - iqR')(\delta_{i'j'} - 3\hat{\mathbf{e}}_{\mathbf{R}'i'} \hat{\mathbf{e}}_{\mathbf{R}'j'}) - q^2 R'^2 (\delta_{i'j'} - \hat{\mathbf{e}}_{\mathbf{R}'i'} \hat{\mathbf{e}}_{\mathbf{R}'j'}) \right] \\ \times \frac{\omega_k \omega_q e^{-i(\omega_k t_2 + \omega_q t_1)}}{(\omega_q - \omega_{\beta s} + i\gamma_{\beta s})(\omega_k + \omega_q - \omega_{\alpha s} - \omega_{\beta s} + i\gamma_{\alpha s})} \Big\} \quad (\text{C6})$$

Since the emitted photons are centered around the transition

frequencies, we can replace  $k, k^2$  by  $k_\alpha, k_\alpha^2$  and  $q, q^2$  by

$q_\beta$ ,  $q_\beta^2$ . We can assume  $R = R'$  because the distance be-

tween the donor and acceptor barely changes during emission/absorption. Inserting the dispersion relation,  $k = k_\alpha + \frac{\omega_k - \omega_\alpha}{v_\alpha}$ , yields

$$M_1 = \left(\frac{1}{2\pi\hbar}\right)^2 \sum_{s,m} \left\{ \left( \mu_{\alpha s} \cdot \overleftrightarrow{\theta}(\omega_{\alpha s}, \mathbf{R}) \cdot \mu_{\text{mg}} \right) \left( \mu_{\beta s} \cdot \overleftrightarrow{\theta}(\omega_{\beta s}, \mathbf{R}) \cdot \mu_{\text{em}} \right) \int_0^t dt_2 \int_0^{t_2} dt_1 e^{i(\omega_{\text{em}} t_2 + \omega_{\text{mg}} t_1)} \right. \\ \left. \times e^{i\phi} \int_0^\infty d\omega_k \int_0^\infty d\omega_q \frac{e^{-i\omega_k(t_2 - R/v_\alpha)} e^{-i\omega_q(t_1 - R'/v_\beta)}}{(\omega_q - \omega_{\beta s} + i\gamma_{\beta s})(\omega_k + \omega_q - \omega_{\alpha s} - \omega_{\beta s} + i\gamma_{\alpha s})} \right\}, \quad (\text{C7})$$

where  $\phi = (k_\alpha - \omega_\alpha/v_\alpha)(q_\beta - \omega/v_\beta)R^2$  and

$$\theta_{ij}(\omega_{\alpha s}, \mathbf{R}) = \frac{\omega_{\alpha s}^3 e^{i\omega_{\alpha s} R/c_{\alpha s}}}{4\pi\epsilon c_{\alpha s}^3} \left[ (\delta_{ij} - 3e_{\mathbf{R}i}e_{\mathbf{R}j}) \left( \frac{c_{\alpha s}^3}{\omega_{\alpha s}^3 R^3} - \frac{ic_{\alpha s}^2}{\omega_{\alpha s}^2 R^2} \right) - (\delta_{ij} - e_{\mathbf{R}i}e_{\mathbf{R}j}) \frac{c_{\alpha s}}{\omega_{\alpha s} R} \right]. \quad (\text{C8})$$

Lowering the limit in the  $\omega_k$  and  $\omega_q$  integration to  $-\infty$  and

performing the definite integral, we can derive

$$M_1 \approx \frac{e^{i\phi}}{\hbar^2} \sum_{s,m} \left\{ \left( \mu_{\alpha s} \cdot \overleftrightarrow{\theta}(\omega_{\alpha s}, \mathbf{R}) \cdot \mu_{\text{mg}} \right) \left( \mu_{\beta s} \cdot \overleftrightarrow{\theta}(\omega_{\beta s}, \mathbf{R}) \cdot \mu_{\text{em}} \right) \right. \\ \left. \times \int_0^t dt_2 \int_0^{t_2} dt_1 e^{i(\omega_{\text{em}} t_2 + \omega_{\text{mg}} t_1)} e^{-(i\omega_{\alpha s} + i\omega_{\beta s} + \gamma_{\alpha s})(t_1 - \frac{R}{v_\alpha})} \Theta[t_1 - \frac{R}{v_\alpha}] e^{-(i\omega_{\beta s} + \gamma_{\beta s})(t_2 - \frac{R}{v_\beta} - t_1 + \frac{R}{v_\alpha})} \Theta[t_2 - \frac{R}{v_\beta} - t_1 + \frac{R}{v_\alpha}] \right\}. \quad (\text{C9})$$

#### Appendix D: S2P-EA

As a result, the excitation probability is

To derive the excitation probability for separated two photons, we define the initial state as follows

$$|i_{\text{S2P}}\rangle = \sum_k g_{\alpha,k}^{\lambda_k} \left\{ \frac{1}{\omega_k - \omega_\alpha + i\gamma_\alpha} \right\} |1_k\rangle \\ \otimes \sum_q g_{\beta,q}^{\lambda_q} \left\{ \frac{1}{\omega_q - \omega_\beta + i\gamma_\beta} \right\} |1_q\rangle. \quad (\text{D1})$$

According to second-order perturbation theory, the excitation amplitude is

$$M = -\frac{1}{\hbar^2} \langle f | \int_0^t dt_2 \int_0^{t_2} dt_1 V_{\text{int}}(t_2) V_{\text{int}}(t_1) | i_{\text{S2P}} \rangle. \quad (\text{D2})$$

$$P_{\text{S2P}} = \sum_m \left| \frac{\left( \mu_\alpha \cdot \overleftrightarrow{\theta}(\omega_\alpha, \mathbf{R}) \cdot \mu_{\text{mg}} \right) \left( \mu_\beta \cdot \overleftrightarrow{\theta}(\omega_\beta, \mathbf{R}) \cdot \mu_{\text{em}} \right)}{i\hbar(\omega_\alpha - \omega_{\text{mg}}) + \hbar\gamma_\alpha} \right. \\ \left. + \frac{\left( \mu_\alpha \cdot \overleftrightarrow{\theta}(\omega_\alpha, \mathbf{R}) \cdot \mu_{\text{em}} \right) \left( \mu_\beta \cdot \overleftrightarrow{\theta}(\omega_\beta, \mathbf{R}) \cdot \mu_{\text{mg}} \right)}{i\hbar(\omega_\beta - \omega_{\text{mg}}) + \hbar\gamma_\beta} \right|^2 \\ \times \left| \frac{1 - e^{-(i\delta + \gamma_\alpha + \gamma_\beta)(t - \frac{R}{v_\alpha})}}{i\hbar\delta + \hbar(\gamma_\alpha + \gamma_\beta)} \right|^2. \quad (\text{D3})$$

## Appendix E: One-dimensional E2P-EA

In the one-dimensional case, the two photons propagate along one axis. The excitation amplitude is given by

$$M = \left(\frac{L}{2\pi}\right)^2 \sum_{s,m} \left\{ \int dk \int dq \int_0^t dt_2 \int_0^{t_2} dt_1 \frac{g_{\alpha s, k} g_{\beta s, q}}{(\omega_q - \omega_{\beta s} + i\gamma_{\beta s})} \right. \\ \times \frac{1}{(\omega_k + \omega_q - \omega_{\alpha s} - \omega_{\beta s} + i\gamma_{\alpha s})} \\ \times \left\{ \langle f | V_{\text{int}}(t_2) | 0_k, 1_q; m \rangle \langle m; 0_k, 1_q | V_{\text{int}}(t_1) | 1_k, 1_q; g \rangle \right. \\ \left. + \langle f | V_{\text{int}}(t_2) | 1_k, 0_q; m \rangle \langle m; 1_k, 0_q | V_{\text{int}}(t_1) | 1_k, 1_q; g \rangle \right\} \left. \right\} \quad (\text{E1})$$

Following steps as in the three-dimensional case, we obtain

$$K = \frac{2\pi}{\hbar} \sum_{s,m} \left\{ \left| \frac{|\mu_{\alpha s}| |\mu_{\beta s}| |\mu_{\text{mg}}| |\mu_{\text{em}}|}{\epsilon^2 \hbar^2 A^2 \nu_{\alpha} \nu_{\beta}} \right|^2 \right. \\ \times \left| \frac{(\omega_{\alpha s} + i\gamma_{\beta s})(\omega_{\beta s} - i\gamma_{\beta s})}{i\hbar(\omega_{\beta s} - \omega_{\text{mg}}) + \hbar\gamma_{\beta s}} \left( 1 - e^{-(i\omega_{\beta s} - i\omega_{\text{mg}} + \gamma_{\beta s})T_e} \right) \right. \\ \left. + \frac{(\omega_{\alpha s} + i\gamma_{\beta s})(\omega_{\beta s} - i\gamma_{\beta s})}{i\hbar(\omega_{\alpha s} - \omega_{\text{mg}}) - \hbar\gamma_{\beta s}} e^{-(i\omega_{\beta s} - i\omega_{\text{em}} + \gamma_{\beta s})T_e} \right|^2 \delta(E_{\delta}) \left. \right\}. \quad (\text{E2})$$

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