Supporting Information: Manipulating Two-Photon-Absorption of Cavity Polaritons by Entangled Light

Bing Gu* and Shaul Mukamel†

Department of Chemistry and Department of Physics and Astronomy, University of California, Irvine, CA 92697, USA

* bingg@uci.edu

† smukamel@uci.edu

CONTENTS

S1. EQ. 4 - ENTANGLED TWO-PHOTON-ABSORPTION

The two-photon absorption (TPA) signal is defined by the transition probability to a final state $|f\rangle$. In the interaction picture using $H_0 = H_\mathrm{p} + H_\mathrm{R}$,

$$P_f(t) = \mathrm{Tr}\left\{|f\rangle\langle f|\,\rho_\mathrm{I}(t)\right\} \tag{S1}$$

where $\rho_\mathrm{I}(t)$ is the density matrix in the interaction picture, and where we have taken into account that $|f\rangle\langle f|$ is time-independent in the interaction picture. The Liouville von-Neumann equation for the joint matter + photon reads

$$i\frac{\mathrm{d}}{\mathrm{d}t}\rho_\mathrm{I}(t) = [H_{\mathrm{RM,\,I}}(t), \rho_\mathrm{I}(t)]. \tag{S2}$$

The formal solution to Eq. (S2) is given by

$$\rho_\mathrm{I}(t) = \mathcal{T}e^{-i\int_{t_0}^{t}\mathcal{L}_{\mathrm{RM,\,I}}(t')\,\mathrm{d}t'}\rho_0 = \mathcal{T}e^{-i\int_{t_0}^{t}H_{\mathrm{RM,\,I}}(t')\,\mathrm{d}t'}\rho_0\bar{\mathcal{T}}e^{i\int_{t_0}^{t}H_{\mathrm{RM,\,I}}(t')\,\mathrm{d}t'}. \tag{S3}$$

where $O_{\rm I}(t) = e^{+iH_0(t-t_0)} O e^{-iH_0(t-t_0)}$ and $\mathcal{T}$ ($\bar{\mathcal{T}}$) is the time-ordering (reverse time-ordering) operator. Here $\mathcal{L}_{\rm RM,\,I}(t)\rho = [H_{\rm RM,\,I}(t), \rho]$ is the Liouvillian superoperator.

Using Eq. (S3) in Eq. (S1) leads to

$$P_f(t) = \mathrm{Tr}\left\{ \bar{\mathcal{T}} e^{i\int_{t_0}^{t} H_{\rm RM}(s)\,\mathrm{d}s} \left|f\right\rangle\left\langle f\right| \mathcal{T} e^{-i\int_{t_0}^{t} H_{\rm RM}(s)\,\mathrm{d}s} \rho_0 \right\}, \tag{S4}$$

where we have used the cyclic invariance of the trace $\mathrm{Tr}\{AB\} = \mathrm{Tr}\{BA\}$. To simplify the notation, we have suppressed the subscript I for interaction picture operators, i.e., $O(t) \equiv O_{\rm I}(t)$. Initially, the system is uncorrelated with the external field, $\rho_0 = \left|g\right\rangle\left\langle g\right| \otimes \rho_{\rm R}(0)$. Expanding the exponentials in Eq. (S4) to second-order in the radiation-matter coupling and retaining the terms leading to two-photon absorption yields

$$P_f(t) = \sum_{\mathbf{p}} \int_{t_0}^{t} dt_2 \int_{t_0}^{t_2} dt_1 \int_{t_0}^{t} dt_2' \int_{t_0}^{t_2'} dt_1' \left\langle g|V_{p_4}(t_1')V_{p_3}(t_2')|f\right\rangle \left\langle f|V_{p_2}^{\dagger}(t_2)V_{p_1}^{\dagger}(t_1)|g\right\rangle G_{\mathbf{p}}^{(2)}(t_1', t_2', t_2, t_1) \tag{S5}$$

where $G_{\mathbf{p}}^{(2)}(t_1', t_2', t_2, t_1) = \left\langle \hat{E}_{p_4}^{\dagger}(t_1')\hat{E}_{p_3}^{\dagger}(t_2')\hat{E}_{p_2}(t_2)\hat{E}_{p_1}(t_1) \right\rangle$ is a field correlation function. Equation (S5) can be represented by the time-loop diagram depicted in Fig. 1c. The subscript $\mathbf{p} = p_4p_3p_2p_1$ denotes the sequence of photons (ω_1/ω_2) that interact with the system along the time-loop clockwise. There are four pathways corresponding to $\mathbf{p} = \{\,1221, 1212, 2121, 2112\,\}$, see Fig. 1c. Since $P_f(t) = 0$ for f-states outside the double-excitation manifold, we can sum over all polariton states, which leads to the final compact expression for the ETPA signal

$$S_{\rm ETPA} = \sum_{\mathbf{p}} \int_{t_0}^{t} dt_2 \int_{t_0}^{t_2} dt_1 \int_{t_0}^{t} dt_2' \int_{t_0}^{t_2'} dt_1' C_{\mathbf{p}}(t_1', t_2', t_2, t_1) G_{\mathbf{p}}^{(2)}(t_1', t_2', t_2, t_1) \tag{S6}$$

where $C_{\mathbf{p}}(t_1', t_2', t_2, t_1) = \left\langle V_{p_4}(t_1')V_{p_3}(t_2')V_{p_2}^{\dagger}(t_2)V_{p_1}^{\dagger}(t_1) \right\rangle$ is the four-point dipole correlation function, and where we have used $I = \sum_f \left|f\right\rangle\left\langle f\right|$.

S2. EQ. 5 - SUM-OVER-STATES EXPRESSION FOR THE TRANSITION AMPLITUDE

For initially pure two-photon state $\rho_{\rm R}(0) = \left|\Phi\right\rangle\left\langle\Phi\right|$, the ETPA signal can be recast as the modulus square of a transition amplitude $S_{\rm ETPA} = \sum_f \left|T_{fg}\right|^2$. The transition amplitude for the entangled two-photon absorption reads

$$T_{fg} = \sum_{p_1,p_2} \int_{t_0}^{t} \mathrm{d}t_2 \int_{t_0}^{t_2} \mathrm{d}t_1 \left\langle f|V_{p_2}^{\dagger}(t_2)V_{p_1}^{\dagger}(t_1)|g\right\rangle \left\langle 0|\hat{E}_{p_2}(t_2)\hat{E}_{p_1}(t_1)|\Phi\right\rangle \tag{S7}$$

Using the many-body eigenstates of the polariton Hamiltonian $\{\ |\,i\rangle, i = 0, 1, \cdots\}$ sorted in ascending order of energy $\{\,\omega_i\,\}$, the raising dipole operator $V_n^{\dagger}$ can be written as [1]

$$V_n^{\dagger}(t) = -\sum_{i<j} e^{i\omega_{ji}t} \boldsymbol{\mu}_{ji} \cdot \mathbf{e}_n \left|j\right\rangle\left\langle i\right|. \tag{S8}$$

where $\boldsymbol{\mu}_{ji} = \langle j|\boldsymbol{\mu}|i\rangle$ is the dipole matrix element. Inserting Eq. (S8) into Eq. (S7) yields Eq. (5) in the main text

$$T_{fg}(t) = \sum_{p_1 \neq p_2} \sum_{e} D^{(e)}_{p_2 p_1} \int_{t_0}^{t} \mathrm{d}t_2 e^{i\omega_{fe} t_2} \int_{t_0}^{t_2} \mathrm{d}t_1 e^{i\omega_{eg} t_1} \Phi_{p_2 p_1}(t_2, t_1) \tag{S9}$$

where $\Phi_{p_2 p_1}(t_2, t_1) = \langle 0|\hat{E}_{p_2}(t_2)\hat{E}_{p_1}(t_1)|\Phi\rangle$ is proportional to the amplitude of detecting photon p_1 at t_1 and photon p_2 at t_2. Intuitively, the matter can be taken as a photon detector with a complex inner structure.

It is useful to have the frequency-domain expression for the transition amplitude. The two-photon amplitude in the time domain can be written as

$$\Phi_{p_2 p_1}(t_2, t_1) = \iint \mathrm{d}\omega_2 \mathrm{d}\omega_1 e^{-i\omega_{p_1} t_1} e^{-i\omega_{p_2} t_2} \Phi_{p_2 p_1}(\omega_{p_2}, \omega_{p_1}) \tag{S10}$$

where $\Phi_{p_2 p_1}(\omega_2, \omega_1) \equiv \langle 0|\hat{E}_{p_2}(\omega_2)\hat{E}_{p_1}(\omega_1)|\Phi\rangle$, $\hat{E}_j(t) = \int \mathrm{d}\omega \hat{E}_j(\omega) e^{-i\omega t}$, and $\hat{E}_j(\omega) = i\sqrt{\frac{\omega}{2\epsilon_0 \mathcal{V}}} b_j(\omega)$. Inserting Eq. (S10) into Eq. (S9) leads to the frequency-domain expression for the transition amplitude (up to a global phase)

$$T_{fg} = \sum_{e} \iint \mathrm{d}\omega_1 \, \mathrm{d}\omega_2 \frac{1}{\omega_{fg} - i\gamma_f - \omega_1 - \omega_2} \left(D^{(e)}_{12} \frac{\left\langle 0 \middle| \hat{E}_1(\omega_1)\hat{E}_2(\omega_2) \middle| \Phi \right\rangle}{\omega_{eg} - \omega_2 - i\gamma_e} + D^{(e)}_{21} \frac{\left\langle 0 \middle| \hat{E}_2(\omega_2)\hat{E}_1(\omega_1) \middle| \Phi \right\rangle}{\omega_{eg} - \omega_1 - i\gamma_e} \right) \tag{S11}$$

S3. THE TWIN-PHOTON WAVEFUNCTION

We consider the following twin-photon wavefunction produced by parametric down conversion (PDC) [2, 3]

$$\phi(\omega_1, \omega_2) = \mathcal{N} A(\omega_1 + \omega_2) \mathrm{sinc}\left(\Delta k L/2\right) \tag{S12}$$

where L is the crystal length, $\Delta k = k_{\mathrm{p}} - (k_1 + k_2)$, $A(\omega_1 + \omega_2) = \left(\frac{1}{\sigma\sqrt{\pi}}\right)^{1/2} \exp\left(-\frac{(\omega_1 + \omega_2 - \omega_{\mathrm{p}})^2}{\sigma^2}\right)$ is the normalized pump pulse envelope with bandwidth σ, $\mathrm{sinc}(x) = \sin(x)/x$, $\mathcal{N}$ the normalization constant. For a narrow-band pump $\sigma \to 0$, the spectral envelope

$$A(\omega_1 + \omega_2) \approx \delta(\omega_1 + \omega_2 - \omega_{\mathrm{p}}) \tag{S13}$$

which reflects energy conservation in the PDC process. In type-II down-conversion where $\mathbf{e}_1$ and $\mathbf{e}_2$ are orthogonal, we can expand the wave vector in a Taylor series around the central frequency

$$k_j(\Delta\omega_j + \omega_j^0) \approx k_j(\omega_j^0) + v_j^{-1} \Delta\omega_j, \tag{S14}$$

and the phase-matching condition may be approximated to linear order as

$$\Delta kL/2 = \frac{1}{2}\left(\Delta\omega_1 T_1 + \Delta\omega_2 T_2\right) \tag{S15}$$

where $\Delta\omega_j = \omega_j - \omega_j^0$, and the transit time difference $T_j = L/v_\mathrm{p} - L/v_j$ for $j = 1, 2$ with $v_j = \nabla_{k_j}\omega_j(k_j^0)$ is the group velocity. With Eqs. (S15) and (S13), The PDC two-photon wavefunction generated from a monochromatic pump becomes Eq. (7)

$$\phi(\omega_1, \omega_2) = \mathcal{N}\delta(\omega_1 + \omega_2 - \omega_\mathrm{p})\mathrm{sinc}\left(\frac{\Delta\omega_1 T}{2}\right) \tag{S16}$$

where $T = T_1 - T_2$ is the entanglement time characterising the arrival time delay between the two photons.

In the time domain, the two-photon wavefunction reads

$$\phi(t_1, t_2) \equiv \int \mathrm{d}\omega_1 \int \mathrm{d}\omega_2 e^{-i\omega_1 t_1 - i\omega_2 t_2}\phi(\omega_1, \omega_2) = \frac{2\pi\mathcal{N}}{T} e^{-i\omega_1^0 t_1 - i\omega_2^0 t_2}\Pi\left(\frac{t_1 - t_2}{T}\right) \tag{S17}$$

where the rectangular function $\Pi(x) = 1$ for $-\frac{1}{2} < x < \frac{1}{2}$ and 0 otherwise and ω_i^0 is the central frequency of the i-th beam. Equation (S17) reflects the time-correlation between the entangled photons: the arrival time of each photon is random, but they must arrive together within the entanglement time. Note that the two photons are not time-ordered (ω_1 can come before or after ω_2) as in the quantum light generated by atomic cascade [4].

S3.A. The correlation amplitude

Here we establish the connection between the two-photon correlation amplitude Φ and the two-photon wavefunction ϕ. The two-photon correlation amplitude can be obtained by

$$\begin{aligned}\Phi_{21}(\omega_2, \omega_1) &= \iint \mathrm{d}\omega_1' \,\mathrm{d}\omega_2' \phi(\omega_1', \omega_2') \langle 0|\hat{E}_2(\omega_2)\hat{E}_1(\omega_1) a_1^\dagger(\omega_1') a_2^\dagger(\omega_2')|0\rangle \\ &= -\frac{\sqrt{\omega_2\omega_1}}{2\epsilon_0\mathcal{V}} \iint \mathrm{d}\omega_1' \,\mathrm{d}\omega_2' \phi(\omega_1', \omega_2') \langle 0|a_2(\omega_2) a_1(\omega_1) a_1^\dagger(\omega_1') a_2^\dagger(\omega_2')|0\rangle\end{aligned} \tag{S18}$$

For distinguishable photons,

$$\langle 0|a_2(\omega_2) a_1(\omega_1) a_1^\dagger(\omega_1') a_2^\dagger(\omega_2')|0\rangle = \delta(\omega_1 - \omega_1')\delta(\omega_2 - \omega_2'). \tag{S19}$$

Then

$$\Phi_{21}(\omega_2, \omega_1) = -\frac{\sqrt{\omega_2\omega_1}}{2\epsilon_0\mathcal{V}}\phi(\omega_1, \omega_2) \tag{S20}$$

and in the time-domain

$$\Phi_{21}(t_2, t_1) \approx -\frac{\sqrt{\omega_2^0\omega_1^0}}{2\epsilon_0\mathcal{V}}\phi(t_1, t_2) \tag{S21}$$

where we have invoked the slowly varying approximation

$$\frac{\sqrt{\omega_2\omega_1}}{2\epsilon_0\mathcal{V}} \approx \frac{\sqrt{\omega_2^0\omega_1^0}}{2\epsilon_0\mathcal{V}}. \tag{S22}$$

Similarly,

$$\Phi_{12}(\omega_2,\omega_1) = -\frac{\sqrt{\omega_2\omega_1}}{2\epsilon_0\mathcal{V}}\phi(\omega_2,\omega_1), \tag{S23}$$

and

$$\Phi_{12}(t_2,t_1) = \iint \mathrm{d}\omega_2\mathrm{d}\omega_1 e^{-i\omega_2 t_1}e^{-i\omega_1 t_2}\Phi_{12}(\omega_1,\omega_2) \approx -\frac{\sqrt{\omega_2^0\omega_1^0}}{2\epsilon_0\mathcal{V}}\phi(t_2,t_1) \tag{S24}$$

These relations allow us to obtain the correlation amplitude from the two-photon wavefunction.

1. Indistinguishable photons

The distinguishing characteristics by polarization or arrival time in the entangled photons can be eliminated such that they become indistinguishable [5].

For indistinguishable photons, we can suppress the photon index such that

$$\langle 0|a(\omega_2)a(\omega_1)a^\dagger(\omega_1')a^\dagger(\omega_2')|0\rangle = \delta(\omega_1-\omega_1')\delta(\omega_2-\omega_2') + \delta(\omega_1-\omega_2')\delta(\omega_2-\omega_1'). \tag{S25}$$

Then

$$\Phi_{21}(\omega_2,\omega_1) = \Phi_{12}(\omega_2,\omega_1) = -\frac{\sqrt{\omega_2\omega_1}}{2\epsilon_0\mathcal{V}}\left(\phi(\omega_1,\omega_2)+\phi(\omega_2,\omega_1)\right). \tag{S26}$$

It follows that $\Phi_{12}(t_2,t_1) = \Phi_{21}(t_2,t_1)$ meaning that the transition amplitudes associated with pathways involving the same intermediate state but a different photon sequences coincide. This implies that matter cannot distinguish the interacting photons.

S3.B. Uncorrelated photons

For uncorrelated single photons, the two-photon wavefunction can be factorized as

$$\phi(\omega_1,\omega_2) = \phi_1(\omega_1)\phi_2(\omega_2), \tag{S27}$$

and so is the detection amplitude $\tilde{\Phi}_{p_2p_1}(t,t') \equiv \langle 0|a_{p_2}(t)a_{p_1}(t')|\Phi\rangle$ representing the probability ampliutude of observing photon p_1 at time t' and photon p_2 at time t,

$$\tilde{\Phi}_{p_2p_1}(t,t') \equiv \langle 0|a_{p_2}(t)|\phi_{p_2}\rangle\,\langle 0|a_{p_1}(t')|\phi_{p_1}\rangle\,. \tag{S28}$$

The detection amplitude is proportional to the correlation amplitude under the approximation in Eq. (S22). The single-photon state reads

$$|\phi_j\rangle = \int \mathrm{d}\omega_j \phi_j(\omega_j) b_j^\dagger(\omega_j) \, |0\rangle \tag{S29}$$

where the vaccum corresponds to the modes associated with j-th photon. Inserting Eq. (S29) into Eq. (S28) leads to

$$\begin{aligned}\tilde{\Phi}_{12}(t_1, t_2) &= \langle 0|b_1(t_1)|\varphi\rangle \, \langle 0|b_2(t_2)|\chi\rangle \\ &= \int \mathrm{d}\omega \int \mathrm{d}\omega_1 e^{-i\omega t_1} \varphi(\omega_1) \, \langle 0|b_1(\omega) a_1^\dagger(\omega_1)|0\rangle \int \mathrm{d}\omega' \int \mathrm{d}\omega_2 \chi(\omega_2) e^{-i\omega' t_2} \, \langle 0|b_2(\omega') a_2^\dagger(\omega_2)|0\rangle \\ &= \phi_1(t_1)\phi_2(t_2)\end{aligned} \tag{S30}$$

where $\phi(t) = \int \mathrm{d}\omega e^{-i\omega t}\phi(\omega)$. Similarly,

$$\tilde{\Phi}_{21}(t_1, t_2) = \phi_1(t_2)\phi_2(t_1) \tag{S31}$$

Insering Eqs. (S30) and (S31) into Eq. (S9) leads to the transition amplitude for uncorrelated photons

$$T_{fg} = \frac{\sqrt{\omega_1^0 \omega_2^0}}{2\mathcal{V}\epsilon_0} \sum_e \iint \mathrm{d}\omega_1 \, \mathrm{d}\omega_2 \frac{\phi_1(\omega_1)\phi_2(\omega_2)}{\omega_1 + \omega_2 - \omega_{fg} + i\gamma_f} \left(\frac{D_{12}^{(e)}}{\omega_{eg} - \omega_2 - i\gamma_e} + \frac{D_{21}^{(e)}}{\omega_{eg} - \omega_1 - i\gamma_e} \right) \tag{S32}$$

If the two photons are narrowband with central frequencies ω_j^0 such that

$$\phi(\omega_1) \approx \phi(\omega_1^0)\delta(\omega_1 - \omega_1^0) \tag{S33}$$

the transition amplitude reduces to

$$T_{fg} = \frac{\sqrt{\omega_1^0 \omega_2^0}}{2\mathcal{V}\epsilon_0} \frac{1}{\omega_1^0 + \omega_2^0 - \omega_{fg} + i\gamma_f} \phi_1(\omega_1^0)\phi_2(\omega_2^0) \sum_e \left(D_{12}^{(e)} \frac{1}{\Delta_e^{(2)} - i\gamma_e} + D_{21}^{(e)} \frac{1}{\Delta_e^{(1)} - i\gamma_e} \right) \tag{S34}$$

S3.C. Coherent states

If the photons are in coherent states corresponding to the semiclassical light, the detection amplitude is given by

$$\phi_{p_2 p_1}(t, t') = \langle \phi_{p_2}|a_{p_2}(t)|\phi_{p_2}\rangle \, \langle \phi_{p_1}|a_{p_1}(t')|\phi_{p_1}\rangle \tag{S35}$$

The difference between the coherent state and the single-photon state is that annihilation of an photon does not change the photon state in the former whereas it projects the photon state to the vacuum for the latter.

Coherent states can be generally defined as

$$|\phi_j\rangle = e^{\alpha A_j^\dagger - \alpha_j^* A_j}\,|0\rangle \tag{S36}$$

where $A_j^\dagger \equiv \int_0^\infty \mathrm{d}\omega \mathcal{A}(\omega) b_j^\dagger(\omega)$ is a single-photon creation operator. For a single photon mode,

$$A_j(t) = b_j(\omega). \tag{S37}$$

This corresponds to a monochromatic light. For a continuum of modes,

$$A_j^\dagger = \int \mathrm{d}\omega \phi_j(\omega) b_j^\dagger(\omega) \tag{S38}$$

where $\phi_j(\omega)$ is the normalized spectral envelope. It follows that Eq. (S35) becomes

$$\phi_{21}(t,t') = \int \mathrm{d}\omega_2 e^{-i\omega_2 t}\alpha_2\phi_2(\omega_2) \int \mathrm{d}\omega_1 e^{-i\omega_1 t'}\alpha_1\phi_1(\omega_1) \tag{S39}$$

Realizing that the expectation value of the electric field operator is given by

$$E_j(\omega) = i\sqrt{\frac{\hbar\omega}{2\epsilon_0 \mathcal{V}}}\alpha_j\phi_j(\omega), \tag{S40}$$

Eq. (S39) becomes

$$\Phi_{21}(t,t') = \int \mathrm{d}\omega_2 e^{-i\omega_2 t} E_2(\omega_2) \int \mathrm{d}\omega_1 e^{-i\omega_1 t'} E_1(\omega_1) = E_2(t)E_1(t'). \tag{S41}$$

Equation (S41) implies that the detection amplitude is simply the product of the electric fields, consistent with a semiclassical picture of photon detection theory [6].

The two-photon transition amplitude can be then obtained by inserting Eq. (S41) into Eq. (S34)

$$T_{fg}(t) = \sum_{p_1\neq p_2}\sum_e D^{(e)}_{p_2p_1} \int_{t_0}^{t} \mathrm{d}t_2 e^{i\omega_{fe}t_2} E_{p_2}(t_2) \int_{t_0}^{t_2} \mathrm{d}t_1 e^{i\omega_{eg}t_1} E_{p_1}(t_1) \tag{S42}$$

The corresponding frequency-domain expression reads

$$T_{fg} = \sum_e \iint \mathrm{d}\omega_1\,\mathrm{d}\omega_2 \frac{E_1(\omega_1)E_2(\omega_2)}{\omega_{fg} - i\gamma_f - \omega_1 - \omega_2}\left(\frac{D^{(e)}_{12}}{\omega_{eg} - \omega_2 - i\gamma_e} + \frac{D^{(e)}_{21}}{\omega_{eg} - \omega_1 - i\gamma_e}\right). \tag{S43}$$

Thus, we have obtained the classical two-photon absorption amplitude from a fully quantum mechanical treatment. For monochromatic fields $E_j(\omega_j) = E_j\delta(\omega_j - \omega_j^0)$, Eq. (S43) reduces to

$$T_{fg} = \sum_e \frac{E_1(\omega_1^0)E_2(\omega_2^0)}{\omega_{fg} - i\gamma_f - \omega_1^0 - \omega_2^0}\left(\frac{D^{(e)}_{12}}{\Delta_e^{(2)} - i\gamma_e} + \frac{D^{(e)}_{21}}{\Delta_e^{(1)} - i\gamma_e}\right). \tag{S44}$$

TABLE S1. Expressions for two-photon-absorption signal with quantum and classical light. The photon indexes $p_2p_1 = \{\,21, 12\,\}$ depending on which photon interacts with the matter first.

Time domain	
classical light	$T_{fg}(t) = \sum_{p_1\neq p_2}\sum_e D^{(e)}_{p_2p_1}\int_{t_0}^{t}\mathrm{d}t_2 e^{i\omega_{fe}t_2}E_{p_2}(t_2)\int_{t_0}^{t_2}\mathrm{d}t_1 e^{i\omega_{eg}t_1}E_{p_1}(t_1)$
quantum light	$T_{fg}(t) = \sum_{p_1\neq p_2}\sum_e D^{(e)}_{p_2p_1}\int_{t_0}^{t}\mathrm{d}t_2 e^{i\omega_{fe}t_2}\int_{t_0}^{t_2}\mathrm{d}t_1 e^{i\omega_{eg}t_1}\Phi_{p_2p_1}(t_2,t_1)$
Frequency domain	
classical light	$T_{fg} = -\sum_{p_1\neq p_2}\sum_e \iint \mathrm{d}\omega_1\,\mathrm{d}\omega_2 \frac{E_1(\omega_1)E_2(\omega_2)}{\omega_{fg}-i\gamma_f-\omega_1-\omega_2}\left(\frac{D^{(e)}_{p_2p_1}}{\omega_{eg}-\omega_{p_1}-i\gamma_e}\right)$
quantum light	$T_{fg} = -\sum_e\sum_{p_2\neq p_1}\iint \mathrm{d}\omega_1\,\mathrm{d}\omega_2 \frac{1}{\omega_{fg}-i\gamma_f-\omega_1-\omega_2}\left(D^{(e)}_{p_2p_1}\frac{\langle 0\,\vert\, E_{p_2}(\omega_{p_2})E_{p_1}(\omega_{p_1})\,\vert\,\Phi\rangle}{\omega_{eg}-\omega_{p_1}-i\gamma_e}\right)$

1. Classical light with the same spectral function with quantum light

If the classical light have the same spectral function as in the quantum light,

$$E_j(\omega_j) = E_j^0\frac{T}{2\pi}\mathrm{sinc}\left(\Delta\omega_j T/2\right). \tag{S45}$$

Using the identity $\int_{-\infty}^{+\infty}\mathrm{sinc}\left(\omega T/2\right)e^{-i\omega t}\,\mathrm{d}\omega = \frac{2\pi}{T}\Pi\left(\frac{t}{T}\right)$, the pulse envelope reads

$$E_j(t) = E_j^0 e^{-i\omega_j^0 t}\Pi\left(\frac{t}{T}\right) \tag{S46}$$

Inserting Eq. (S46) into Eq. (S42) leads to the two-photon transition amplitude with two rectangular pulses ($t_0\to-\infty, t\to\infty$)

$$\begin{aligned}
T_{fg} &= E_2^0E_1^0\sum_{p_1\neq p_2}\sum_e D^{(e)}_{p_2p_1}\int_{-\infty}^{\infty}\mathrm{d}t_2 e^{i(\omega_{fe}-\omega^0_{p_2})t_2}\Pi\left(\frac{t_2}{T}\right)\int_{-\infty}^{t_2}\mathrm{d}t_1 e^{i\left(\omega_{eg}-\omega^0_{p_1}\right)t_1}\Pi\left(\frac{t_1}{T}\right)\\
&= E_2^0E_1^0\sum_{p_1\neq p_2}\sum_e D^{(e)}_{p_2p_1}\int_{-T/2}^{T/2}\mathrm{d}t_2 e^{i(\omega_{fe}-\omega^0_{p_2})t_2}\frac{1}{i\Delta_e^{(p_1)}}\left(e^{i\Delta_e^{(p_1)}t_2}-e^{-i\Delta_e^{(p_1)}T/2}\right)\\
&= -E_2^0E_1^0\sum_{p_1\neq p_2}\sum_e D^{(e)}_{p_2p_1}\left(\frac{2i\mathrm{sinc}\left((\omega_{fg}-\omega_1^0-\omega_2^0)T/2\right)}{\omega_{eg}-\omega^0_{p_1}}+\frac{e^{-i(\omega_{eg}-\omega^0_{p_1})T/2}2i\mathrm{sinc}\left((\omega_{fe}-\omega^0_{p_2})T/2\right)}{\omega_{eg}-\omega^0_{p_1}}\right)
\end{aligned} \tag{S47}$$

We have assumed that the pulse duration is shorter than the lifetime, i.e., $T\ll\gamma_e^{-1}$. The first term contains the two-photon resonance condition and thus represents the TPA process whereas the second term contains two single-photon resonances representing a sequential excitation. As shown, for the uncorrelated light, varying the spectral width $1/T$ does not allow modifying the transition amplitude for each transition pathways.

S4. THE BLOCK DIAGONAL POLARITON HAMILTONIAN

S4.A. Two molecules with different transition frequencies

1. Single-polariton block

For $N = 2$ molecules, the subspace Hamiltonian in single-polariton subspace reads

$$H^{(1)} = \begin{bmatrix} \omega_{\rm c} & g_0 & g_0 \\ g_0 & \omega_{\rm a} & 0 \\ g_0 & 0 & \omega_{\rm b} \end{bmatrix} \tag{S48}$$

where g_0 is the single-molecule coupling strength.

2. Two-polariton block

The two-polariton block Hamiltonian spanned by the basis $|gg2\rangle, |eg1\rangle, |ge1\rangle, |ee0\rangle$ reads

$$H^{(2)} = \begin{bmatrix} 2\omega_{\rm c} & \sqrt{2}g_0 & \sqrt{2}g_0 & 0 \\ \sqrt{2}g_0 & \omega_{\rm a}+\omega_{\rm c} & 0 & g_0 \\ \sqrt{2}g_0 & 0 & \omega_{\rm b}+\omega_{\rm c} & g_0 \\ 0 & g_0 & g_0 & \omega_{\rm a}+\omega_{\rm b} \end{bmatrix} \tag{S49}$$

Solving $\det\left(\omega - H^{(2)}\right) = 0$ yields the polariton energies $\omega = 2\omega_{\rm c} \pm \sqrt{\delta^2 + 6g_0^2}, 2\omega_{\rm c}$.

S4.B. Two-polariton block for N identical molecules

We now consider N identical molecules with transition frequency ω_0 and coupling $g_j = g_0$. To understand the structure of the two-polariton states, it is convenient to introduce the collective exciton operators

$$X_j^\dagger = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{ik_j n} \sigma_n^\dagger, \quad j = 0, 1 \cdots, N-1, \tag{S50}$$

where $k_j = 2\pi j/N, j = 0, 1, \cdots, N-1$. The collective exciton operators satisfy the commutation relations

$$[X_i, X_j^\dagger] = -\frac{1}{N} \sum_n e^{i(k_i - k_j)n} \sigma_n^z = \delta_{ij} - \frac{2}{N} \sum_n e^{i(k_i - k_j)n} \sigma_n^\dagger \sigma_n \tag{S51}$$

Since these are different from the boson commutation relations, the excitons cannot in general be considered as bosons. In the low excitation limit of many molecules, i.e., $\sum_{n=1}^{N}\sigma_n^\dagger\sigma_n \ll N$, Eq. (S51) becomes

$$\left[X_i, X_j^\dagger\right] = \delta_{ij} + \mathcal{O}(N^{-1}) \tag{S52}$$

and the collective excitons are approximately bosons.

The upper and lower polaritons are admixtures of the bright exciton state $|\mathrm{X}_0\rangle = X_0^\dagger|G\rangle$, where $|G\rangle$ is the ground state for all molecules, and the cavity mode, with an enhanced splitting $2g_0\sqrt{N}$. The double-excitation manifold contains $\frac{N(N+1)}{2}+1$ states. The polariton Hamiltonian can be recasted in terms of the collective exciton operators

$$H_\mathrm{p} = \omega_0\sum_{j=0}^{N-1}X_j^\dagger X_j + \omega_\mathrm{c}a^\dagger a + g_0\sqrt{N}\left(X_0^\dagger a + X_0 a^\dagger\right). \tag{S53}$$

The double-excitation space can be decomposed into three subspaces spanned, respectively, by

$$\{\ |2\rangle,\ |\mathrm{X}_0 1\rangle,\ |\mathrm{X}_0\mathrm{X}_0\rangle = \sqrt{\frac{N-1}{N}}\left(X_0^\dagger\right)^2\ |g\rangle\ \}, \tag{S54}$$

$\{\ |\mathrm{X}_j\mathrm{X}_0\rangle,\ |\mathrm{X}_j 1\rangle, j\neq 0\ \}$, and $\{\ |\mathrm{X}_j\mathrm{X}_k\rangle, j,k\neq 0\ \}$. The first block comes from excitations of bright excitons and cavity photons and contains three two-polariton states. The subblock Hamiltonian reads

$$H = \begin{bmatrix} 2\omega_c & g_0\sqrt{2N} & 0 \\ g_0\sqrt{2N} & \omega_0+\omega_\mathrm{c} & g_0N/\sqrt{N-1} \\ 0 & g_0N/\sqrt{N-1} & 2\omega_0 \end{bmatrix}. \tag{S55}$$

Eigenvalues of this Hamiltonian Eq. (S55) leads to a pair of upper and lower two-polaritons and one middle two-polariton

$$|f_\mathrm{M}\rangle = \left[\sqrt{\frac{2(N-1)}{3N-2}}, 0, \sqrt{\frac{N}{3N-2}}\right] \tag{S56}$$

at $2\omega_\mathrm{c}$. The enhanced coupling between $|2\rangle$ and $|\mathrm{X}_0 1\rangle$ due to the presence of cavity photons is responsible for the enhanced upper and lower two-polariton splitting.

In addition to this splitting, there is another polariton pair from the second subspace involving dark exciton excitation and cavity photons. The Hamiltonian in this subblock spanned by states $|X_j 1\rangle$ and $|X_j X_0\rangle$ is given by (for each j)

$$H = \begin{bmatrix} \omega_0+\omega_\mathrm{c} & g\sqrt{\frac{N-2}{N}} \\ g\sqrt{\frac{N-2}{N}} & 2\omega_0 \end{bmatrix} \tag{S57}$$

where $g = g_0\sqrt{N}$. The splitting is slightly reduced compared to the vacuum Rabi splitting by a factor of $\sqrt{\frac{N-2}{N}}$. Such states are not dipole connected to the upper and lower polaritons, and cannot be observed in the TPA. The third block involves only dark exciton excitations.

---

[1] Konstantin E. Dorfman, Frank Schlawin, and Shaul Mukamel, "Nonlinear optical signals and spectroscopy with quantum light," Rev. Mod. Phys. **88** (2016).

[2] C. K. Hong and L. Mandel, "Theory of parametric frequency down conversion of light," Phys. Rev. A **31**, 2409–2418 (1985).

[3] Timothy E. Keller and Morton H. Rubin, "Theory of two-photon entanglement for spontaneous parametric down-conversion driven by a narrow pump pulse," Phys. Rev. A **56**, 1534–1541 (1997).

[4] Ashok Muthukrishnan, Girish S. Agarwal, and Marlan O. Scully, "Inducing Disallowed Two-Atom Transitions with Temporally Entangled Photons," Phys. Rev. Lett. **93**, 093002 (2004).

[5] W. P. Grice, A. B. U'Ren, and I. A. Walmsley, "Eliminating frequency and space-time correlations in multiphoton states," Phys. Rev. A **64**, 063815 (2001).

[6] Roy J. Glauber, "The Quantum Theory of Optical Coherence," Phys. Rev. **130**, 2529–2539 (1963).