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ABSTRACT

We propose an interferometric pump-probe technique that employs three entangled photons generated by cascaded spontaneous parametric downconversion. A Mach–Zehnder interferometer made of two three-port waveguide arrays is inserted in the optical path. Two independent phases introduced to manipulate the entangled photon state serve as control parameters and can selectively excite matter pathways. Compared to two-photon-absorption of an entangled photon-pair, the three-photon signals are significantly enhanced by frequency-dispersed photon-counting detection.

Quantum light can induce novel nonlinear optical processes, which are not possible with classical light.\textsuperscript{1,2} One notable hallmark of quantum light is entanglement. The most common technique for generating entangled photons is spontaneous parametric downconversion of an input pump laser beam. Energy and momentum (phase matching) conservation gives rise to strong correlations between the generated photons. Entangled photon-pairs (biphotons) have been widely utilized in linear biphoton spectroscopy,\textsuperscript{3–5} pump-probe spectroscopy,\textsuperscript{6–9} and quantum imaging.\textsuperscript{10–12} However, entangled three-photon (also known as triphoton or photon triplets) states in quantum spectroscopy have not been reported yet. The time-energy entanglement of triphoton states demonstrated in recent experiments\textsuperscript{13–15} offers useful control parameters for quantum optical signals.

In this paper, we simulate frequency-dispersed photon-counting third-order two-photon absorption (TPA) spectroscopy signals from a three-level model system. The control parameters in classical pump-probe experiments are the pump frequency and the pump-probe time delay. In recent simulations of pump-probe spectroscopy with entangled photon pairs,\textsuperscript{8,16} the central frequency of input laser pulses generating the biphoton state was scanned and the probe photon was spectrally dispersed. In Ref. 6, it was shown that nonlinear signals with two entangled photons can be manipulated by including a Mach–Zehnder interferometer (MZI) in the optical path to control the degree of entanglement. Using a triphoton state, Mahrlein et al. proposed the complete three-photon Hong–Ou–Mandel (HOM) interference in a three-port waveguide array (WGA),\textsuperscript{17} which is an extension of the celebrated two-photon HOM interference on a two-port beam splitter (BS).\textsuperscript{18} Here, we utilize a MZI with two three-port WGAs to regulate the triphoton state by varying the phases of the two interferometer arms. We show that valuable information about excitation pathways in matter can be revealed using this setup via coincidence photon-counting of the spectrally dispersed probe and idler photons, compared to scanning the central frequency of input laser pulses. The TPA signal with three entangled photons is much stronger than that obtained with entangled photon pairs. Various matter excitation pathways can be enhanced or suppressed by properly choosing the phases introduced in the optical path by the three-port MZI.

We consider the triphoton state generated by cascaded spontaneous parametric downconversion (C-SPDC),\textsuperscript{13–15} as sketched in Fig. 1(a). An input laser pulse with frequency \(\omega_p\) passes through the nonlinear crystal to generate a pair of entangled photons (\(a_1\) and \(a_2\)). The \(a_2\) photon then serves as a pump for a second SPDC process that creates a new pair of entangled photons (\(a_3\) and \(a_4\)). In each SPDC, a pair of orthogonally polarized photons (\(a_1\) and \(a_2\) for SPDC I and \(a_3\) and \(a_4\) for SPDC II) can be separated by a polarizing beam splitter (not shown in Fig. 1) after the SPDC. The details of the experimental setup can be found in Refs. 13 and 14. We assume that the input laser pulse and all output beams (1, 2, and 3) are collinear and propagate along \(z\). At low input pulse intensity, the triphoton state is given by\textsuperscript{16,19} [see Sec. S1 for details]
with the spectral amplitude \(\Omega_{a_{\mu}} = a_{\mu} - a_{\mu}^\dagger\)

\[
F(w_{a_{1}}, w_{a_{2}}, w_{a_{3}}) = N \exp \left[-\gamma(T_{p_{1}a_{1}} + T_{p_{2}a_{2}} + T_{p_{3}a_{3}})^2\right] \\
\times \exp \left[-\frac{\Omega_{a_{1}}^2 + \Omega_{a_{2}}^2 + \Omega_{a_{3}}^2}{2\sigma_p^2}\right] \\
\times \exp \left[-\gamma(T_{a_{2}a_{3}} + T_{a_{3}a_{1}})^2\right].
\]

Here, \(N = \left(\frac{1}{2}\right)^{1/4} \sqrt{\frac{\pi}{2}} |T_{a_{1}} - T_{p_{1}}||T_{a_{2}} - T_{p_{2}}||T_{a_{3}} - T_{p_{3}}|\) is a normalization constant.

To measure the proposed signals, we add a Mach–Zehnder interferometer in the optical path. The MZI for the three-entangled-photon setup is made of two three-port WGAs. Figure 1(b) shows the WGA, which consists of three parallel single-mode-coupled waveguides. The coupling of the 2D waveguides can be tuned by varying their distances. Outer modes 1 and 3 are coupled to inner mode 2 but not to each other, i.e., \(g_{13} = 0\) in Fig. 1(b), because \(g_{13}\) is much smaller than the coupling between neighboring waveguides \((g_{12} \neq g_{23})\) and is neglected. To determine the transformation matrix for the WGA, we consider a three-photon HOM effect. This is an extension of the two-photon HOM effect to the three-photon case, where the probability of detecting one photon in each output port of the WGA is zero. Details of the three-port WGA can be found in Sec. S2 of the supplementary material.

Here, we present the final form of the transformation matrix for the WGA,

\[
M = \begin{pmatrix}
\frac{1}{2} & \frac{i}{2} & -\frac{1}{2} \\
-\frac{i}{2} & \frac{1}{2} & \frac{i}{2} \\
\frac{1}{2} & -\frac{i}{2} & -\frac{1}{2}
\end{pmatrix}.
\]

Figure 1(c) schematically depicts the interferometric pump-probe spectroscopy setup involving the entangled triphoton state. The three entangled photons generated by the C-SPDC pass through the three-port MZI (WGA 1 and WGA 2). Two phases \(\phi_1\) and \(\phi_2\) are introduced to control the triphoton state. The transformation matrix for the three-port MZI is \(C = M^T P M\). Here, \(P = \text{diag}(e^{i\phi_1}, e^{i\phi_2}, 1)\) describes the effect of interferometer phases on the triphoton state. \(M\) and \(M^T\) are the transformation matrices for the first and second WGAs, respectively.

After passing through the three-port MZI, the \(a_1\) photon excites the molecule, which is then probed by the second photon \(a_2\). The third photon \(a_3\) (idler), which does not interact with the sample, is finally detected in coincidence with \(a_2\). The spectrally dispersed two-photon counting signal is given by

\[
S(w_{a_2}, w_{a_3}; \Gamma) = \text{tr} \left[ a_{a_2}^\dagger a_{a_3}^\dagger a_{a_2} a_{a_3} E_{1}^2 V(t - \infty) \right],
\]

where \(\Gamma\) denotes the set of control parameters, such as the entanglement times and the interferometer phases. In Eq. (4), we have taken the trace with respect to the joint field plus molecule density matrix in the interaction picture,

\[
\rho_{\text{int}}(t \to \infty) = \rho_{\text{int}}(-\infty) - \mathcal{F} \int \frac{dt}{\hbar} H_{\text{int}}(t) \rho_{\text{int}}(t),
\]

where \(\mathcal{F}\) represents the superoperator time-ordering, and the superoperator \(H_{\text{int}}\) is defined by \(H_{\text{int}} = O = H_{\text{int}} O - O H_{\text{int}}\). The signal Eq. (5) can be further recast as (see Sec. S3A of the supplementary material)

\[
S(w_{a_2}, w_{a_3}; \Gamma) = \frac{1}{\pi \hbar} \mathcal{F} \int \frac{dt}{\hbar} e^{i\omega_{a_3}} a_{a_2}^\dagger a_{a_3} E_{1}^2 V(t).
\]

Here, \(V\) is the positive frequency part of the dipole operator, and \(E_1(t)\) is the Fourier transform of the photon field \(E_1(t)\) to second order in \(E_1\) and first order in \(E_2\). We then obtain eight terms. Four contribute to a Raman process, where the corresponding matter correlation functions are of the form \(\langle V V' V' V' \rangle\) and will not be considered further. The other four represent the TPA excitation pathways and are depicted in Fig. 2(b). They are denoted as TPA pathways since the system passes through a two-exciton state during the process, which is described by the matter correlation function \(\langle V V' V' V' \rangle\). The triphoton TPA signal is given by (see Sec. SIII B of the supplementary material).
Here, the matter information is imprinted in the signal via the auxiliary function

$$g(\omega_2, \omega_a, \omega_b) = \sum_{\alpha \beta} \left[ \frac{\mu_{\alpha\beta}}{\omega_2 - \omega_{\alpha\beta} + i\eta} \frac{\rho_{\alpha\beta}}{\omega_a - \omega_{\alpha\beta} + i\eta} \right] \times \left[ \frac{\mu_{\alpha\beta}^*}{\omega_b - \omega_{\alpha\beta} + i\eta} \frac{\rho_{\alpha\beta}^*}{\omega_a - \omega_{\alpha\beta} + i\eta} \right] \times \left[ \frac{\mu_{\alpha\beta}}{\omega_2 + \omega_a - \omega_b - \omega_{\alpha\beta} + i\eta} \frac{\rho_{\alpha\beta}}{\omega_2 - \omega_{\alpha\beta} + i\eta} \right] \times \left[ \frac{\mu_{\alpha\beta}^*}{\omega_2 + \omega_a - \omega_b - \omega_{\alpha\beta} + i\eta} \frac{\rho_{\alpha\beta}^*}{\omega_2 - \omega_{\alpha\beta} + i\eta} \right].$$

The normally ordered frequency-domain field correlation function in Eq. (8) is given by Eq. (S39) in Sec. III B of the supplementary material.

We now compare the triphoton signal with its entangled photon-pair counterpart.\(^6,8\) As sketched in Fig. 1(d), the triphoton state is given by diagrams (I) and (II) in Fig. 2(b) and their sum. The two arms. The TPA signal with two entangled photons is given by (Sec. SIV B of the supplementary material)

$$S_{\text{TPA}}^{(3)}(\omega_2, \omega_3; \Gamma) = \frac{\omega_2 \omega_3}{\pi \hbar^2} \frac{1}{4 \pi r e C A} \int d\omega_a \int d\omega_b \times (a_1^* a_2 a_3) \times a_1 (a_2+ a_3 - \omega_b) g(\omega_2, \omega_a, \omega_b).$$

The three-level model system used in our simulations. The dipole moments of all transitions are taken to be the same i.e., $\mu_{\alpha\beta} = \mu_{\alpha\beta}^* = \{\alpha_1, \alpha_2\}$ and $f = \{f_1, f_2\}$. (b) Loop diagrams (I)-(IV) for TPA pathways. Note that there is no time ordering control of the interactions between the left and right branches.

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**FIG. 2.** (a) The three-level model system used in our simulations. The dipole moments of all transitions are taken to be the same i.e., $\mu_{\alpha\beta} = \mu_{\alpha\beta}^* = \{\alpha_1, \alpha_2\}$ and $f = \{f_1, f_2\}$. (b) Loop diagrams (I)-(IV) for TPA pathways. Note that there is no time ordering control of the interactions between the left and right branches.

**FIG. 3.** Frequency correlations $|F(\omega_1, \omega_2, \omega_3)|^2$ [Eq. (2)] between the excitation ($\omega_1$) and probe ($\omega_2$) photons of the triphoton state when the frequency of the idler ($\omega_3$) photon is held constant at (a) $\omega_3 = 9500 \text{ cm}^{-1}$ and (b) $\omega_3 = 8500 \text{ cm}^{-1}$. Other parameters are the input pulse bandwidth $\sigma_p = 200 \text{ cm}^{-1}$, the time delays $T_{p1} = 5 \text{ fs}$, $T_{p2} = 15 \text{ fs}$, $T_{a3} = 5 \text{ fs}$, $T_{a2} = 15 \text{ fs}$, and the central frequencies $15000 \pm 30000 \text{ cm}^{-1}$.
counting detection of the probe and idler photons in the frequency domain.

For comparison, the TPA signals generated by two entangled photons $S^{(2)\text{TPA}}$ are depicted in the bottom row of Figs. 4(d)–4(f). The following parameters for the SPDC: generated photon-pair were used: the input pulse bandwidth $\Delta \omega_0 = 200 \text{ cm}^{-1}$, the time delays $T_{p1} = 5 \text{ fs}$, $T_{p2} = 15 \text{ fs}$, and the central frequencies $\omega_{p0} = \omega_{p2} = \omega_{p0}/2$, which are comparable to those used for $S^{(3)\text{TPA}}$. The signal is plotted in ($\omega_{p0}, \omega_{p2}$) space, where the central frequency of the input laser pulses is scanned and the probe photon $\omega_2$ is spectrally dispersed. The resonances along the $\omega_{p0}$-axis directly reveal the two-exciton states $f_1$ and $f_2$. This is different from the $S^{(3)\text{TPA}}$ signal, where the two-exciton resonances along $\omega_3$ are obtained by the frequency difference $\omega_{p2} - \omega_{p0}$ since we have fixed the central frequency of input pulses and dispersed the idler photon for the measurement of the $S^{(3)\text{TPA}}$ signal.

The triphoton spectrally dispersed TPA signal $S^{(3)\text{TPA}}$ provides the same information about the matter excitations as its biphoton counterpart $S^{(2)\text{TPA}}$. However, the resonance strengths in Fig. 4(c) are 64 times higher than those in Fig. 4(a). We further note that in Fig. 4(c), the resonances at $\omega_3 = 9500 \text{ cm}^{-1}$ (points A–D) are much stronger than those at $\omega_3 = 8500 \text{ cm}^{-1}$ (points E–H), indicating that the $f_1$ state is more favorably excited. This is because, as can be seen in Fig. 3, the marginal distribution of the probe photon ($\omega_2$) at $\omega_3 = 9500 \text{ cm}^{-1}$ is stronger than that at $\omega_3 = 8500 \text{ cm}^{-1}$. We, thus, have a higher probability to detect the $\alpha_2$-photon at $\omega_3 = 9500 \text{ cm}^{-1}$ than that at $\omega_3 = 8500 \text{ cm}^{-1}$, making the corresponding resonances stronger. The eight resonances in the $S^{(2)\text{TPA}}$ signal in Fig. 4(c) have, on the other hand, very similar strengths. Figure 5 displays the marginal distributions of the $\alpha_2$-photon of the biphoton state. Since the probabilities of detecting the $\alpha_2$-photon are very close for the two input pulse central frequencies $\omega_{p0} = 20 500 \text{ cm}^{-1}$ [Fig. 5(a)] and 21 500 cm$^{-1}$ [Fig. 5(b)], the corresponding resonance strengths are very similar.

The above signals reflect the interference of various excitation pathways of the field and matter. For a general interferometric setup, the field correlation function Eq. (S39) [or (S53)] also depends on the phase(s) introduced in the MZI. We next explore the possible manipulations of the doubly excited states ($f_1$ or $f_2$) by varying the phases of the MZI. Figure 6(a) shows the variation of the eight resonances [points A–H in Fig. 4(c)] of $S^{(3)\text{TPA}}$ with the interferometer phase $\phi$. Their strengths are virtually identical in any phase $\phi$. Therefore, the phase $\phi$ introduced to the MZI for the entangled photon-pair cannot select the desired two-exciton state ($f_1$ or $f_2$). However, it is interesting that at $\phi = \pi/2$, the overall biphoton TPA signal $S^{(3)\text{TPA}}$ is suppressed $\sim 10^{-2}$, five orders of magnitude weaker than the signal in Fig. 4(c). Suppression of the TPA can be used to single out other signals.

Figure 6(b) shows the interferometric TPA signal $S^{(3)\text{TPA}}$ with $\phi_1 = 0.62\pi$ and $\phi_2 = 0.32\pi$. Compared to Fig. 4(c), the $\omega_3 = 8500 \text{ cm}^{-1}$ resonances are enhanced, while those at $\omega_3 = 9500 \text{ cm}^{-1}$ are suppressed, indicating that the two-exciton state $f_1$ is efficiently excited.

FIG. 4. Top row: Interferometric TPA signal with three entangled photons $S^{(3)\text{TPA}}$: Eq. (8), with $\phi_1 = 0$ and $\phi_2 = 0$. (a) Contributions of diagrams (I) and (II) in Fig. 2. (b) Contributions of diagrams (III) and (IV). (c) The total signal [sum of (a) and (b)]. Points A–G represent the eight major resonances. Bottom Row: The same as the first row, but for the interferometric TPA signal with two entangled photons $S^{(2)\text{TPA}}$: Eq. (10), with $\phi = 0$.

FIG. 5. Frequency correlations $|F(\omega_1, \omega_2)|^2$ [Eq. (S54) of the supplementary material] between the excitation ($\omega_1$) and probe ($\omega_2$) photons of the entangled photon-pair when the central frequency of input pulses is (a) $\omega_{p0} = 20 500 \text{ cm}^{-1}$ and (b) $\omega_{p0} = 21 500 \text{ cm}^{-1}$. The parameters used for the entangled photon-pair are the input pulse bandwidth $\Delta \omega_0 = 200 \text{ cm}^{-1}$, the time delays $T_{p1} = 5 \text{ fs}$, $T_{p2} = 15 \text{ fs}$, $T_{p2} = 15 \text{ fs}$, and the central frequencies $\omega_{p0} = \omega_{p2} = \omega_{p0}/2$. The above signals reflect the interference of various excitation pathways of the field and matter. For a general interferometric setup, the field correlation function Eq. (S39) [or (S53)] also depends on the phase(s) introduced in the MZI. We next explore the possible manipulations of the doubly excited states ($f_1$ or $f_2$) by varying the phases of the MZI. Figure 6(a) shows the variation of the eight resonances [points A–H in Fig. 4(c)] of $S^{(3)\text{TPA}}$ with the interferometer phase $\phi$. Their strengths are virtually identical in any phase $\phi$. Therefore, the phase $\phi$ introduced to the MZI for the entangled photon-pair cannot select the desired two-exciton state ($f_1$ or $f_2$). However, it is interesting that at $\phi = \pi/2$, the overall biphoton signal $S^{(3)\text{TPA}}$ is suppressed $\sim 10^{-2}$, five orders of magnitude weaker than the signal in Fig. 4(c). Suppression of the TPA can be used to single out other signals.

Figure 6(b) shows the interferometric TPA signal $S^{(3)\text{TPA}}$ with $\phi_1 = 0.62\pi$ and $\phi_2 = 0.32\pi$. Compared to Fig. 4(c), the $\omega_3 = 8500 \text{ cm}^{-1}$ resonances are enhanced, while those at $\omega_3 = 9500 \text{ cm}^{-1}$ are suppressed, indicating that the two-exciton state $f_1$ is efficiently excited.
Furthermore, by adjusting the phases \( \phi_1 \) and \( \phi_2 \), we can also enhance the \( f_1 \) state and suppress the \( f_2 \) state [see Fig. 6(c)] or make their resonance strengths similar [see Fig. 6(d)]. Although the signals with the nonzero phases are weaker, they are still comparable to the biphoton TPA signal in Fig. 4(f). Thus, the two-exciton states can be manipulated by varying the two interferometer phases \( (\phi_1 \) and \( \phi_2) \) introduced in the triphoton state, which is not possible with an entangled photon-pair.

To conclude, we have proposed a pump-probe TPA technique that makes use of three entangled photons. The triphoton state is obtained by a cascaded spontaneous parametric downconversion process at low input pulse intensity, which helps avoid damage to delicate samples. Interferometric TPA signals can be manipulated by adding a three-port MZI in the optical path. The three entangled photons exhibit strong frequency correlations, and the biphoton states \( S^{(2)} \) [see Figs. 4(d)–4(c)] allow us to extract information about the TPA pathways of the matter system with the input laser pulse frequency being fixed. The spectrally dispersed photon-counting signal with the triphoton state is much stronger than the TPA signal with the biphoton state, due to the higher distribution probabilities of the detected photons of the triphoton state. The two interferometer phases offer an effective control tool for selecting the two-exciton pathways.

See the supplementary material for the derivations of the triphoton state generated by cascaded spontaneous parametric downconversion, derivations of the transformation matrix for the three-port waveguide array, and derivations of the two-photon-absorption signals.

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REFERENCES

SUPPLEMENTARY MATERIAL:
Interferometric two-photon absorption spectroscopy with three entangled photons

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S1. DERIVATION OF THE TRIPHOTON STATE

We assume the following form for the classical pump pulse envelope [see Fig. 1(a) of the main text]
\[
E_p^{(+)}(r, t) = \int dq_p \int d\omega_p G(q_p) \alpha_p \mathcal{A}(\omega_p) e^{i q_p \cdot \rho} e^{i k_p z} e^{-i \omega_p t},
\]
(S1)
where \( q_p \) and \( \rho \) are the transverse components of the wavevector and coordinate, respectively. Generating a well-separated triphoton state requires a low pump intensity \( \alpha_p \). The photon field operator for mode \( \mu = 1, 2, 3, a \) is expanded as [1]
\[
E^{(+)}_\mu(r, t) = i \int dq_\mu \int d\omega_\mu \sqrt{\frac{\hbar \omega_\mu}{2 E_0 n_\mu^2(\omega_\mu)}} a_\mu(q_\mu, \omega_\mu) e^{i q_\mu \cdot \rho} e^{i k_\mu z} e^{-i \omega_\mu t}.
\]
(S2)
The two SPDC processes (I and II) are described by the effective interaction Hamiltonians
\[
H_I(t) = \int d r_1 \chi_1^{(2)} E_p^{(+)}(r_1, t) E_1^{(-)}(r_1, t) E_a^{(-)}(r_1, t) + H.c.,
\]
(S3)
\[
H_{II}(t) = \int d r_{II} \chi_{II}^{(2)} E_{a}^{(+)}(r_{II}, t) E_2^{(-)}(r_{II}, t) E_3^{(-)}(r_{II}, t) + H.c..
\]
(S4)
Here, the integrals are taken over their respective interaction volumes. \( \chi_1^{(2)} \) and \( \chi_{II}^{(2)} \) are the second-order susceptibilities of the nonlinear crystals for the first and second SPDC processes, respectively.

We assume that the pump and all output beams (\( \mu = 1, a, 2, \) and 3) are collinear and propagate along \( z \), i.e., \( k_\mu = k_\mu z \). By applying the standard perturbation theory, the triphoton state is give by [1, 2]
\[
|\psi\rangle = \mathcal{C} \int d\omega_3 d\omega_2 d\omega_1 \alpha_p \mathcal{A}(\omega_1 + \omega_2 + \omega_3) \text{sinc} \left[ \frac{T_{a2}}{2} (\omega_2 - \omega_{20}) + \frac{T_{a3}}{2} (\omega_3 - \omega_{30}) \right] \times \text{sinc} \left[ \frac{T_{p1}}{2} (\omega_1 - \omega_{10}) + \frac{T_{pa}}{2} (\omega_2 - \omega_{20} + \omega_3 - \omega_{30}) \right] a_3^\dagger(\omega_3) a_2^\dagger(\omega_2) a_1^\dagger(\omega_1) |0\rangle.
\]
(S5)

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For computational convenience, we approximate the sinc-function by a Gaussian with the same width \([3, 4]\): \( \text{sinc}(x/2) \approx \exp(-\gamma x^2) \), with \( \gamma = 0.0482304 \). The triphoton state can be finally recast as

\[
|\psi\rangle = \int \int \int d\omega_3 d\omega_2 d\omega_1 \alpha_\rho F(\omega_1, \omega_2, \omega_3) a_3^\dagger(\omega_3) a_2^\dagger(\omega_2) a_1^\dagger(\omega_1) |0\rangle,
\]

where \( F(\omega_1, \omega_2, \omega_3) \) is given by Eq. (2) of the main text.

**S2. TRANSFORMATION MATRIX FOR THE THREE-PORT WAVEGUIDE ARRAY**

We examine the three-photon interference at a three-port WGA. A generalization of the HOM effect to three indistinguishable photons was proposed in Ref. 5. A complete destructive interference of three photons can be observed in a three-port device which consists of three parallel single-mode-coupled waveguides [6], as sketched in Fig. 2(a). The three-photon interference is described by the effective Hamiltonian [5]

\[
H = \hbar \left( g_{12} a_1^\dagger a_2 + g_{23} a_2^\dagger a_3 \right) + \text{H.c.}
\]

Here, \( a_1, a_2 \) and \( a_3 \) are annihilation operators of the input modes.

The time evolution of the modes is described by

\[
\frac{d}{dt} A(t) = \frac{d}{dt} \begin{pmatrix} a_1^\dagger(t) \\ a_2^\dagger(t) \\ a_3^\dagger(t) \end{pmatrix} = iM(t)A(t) \equiv i \begin{pmatrix} 0 & g_{12}^* & 0 \\ g_{12} & 0 & g_{23} \\ 0 & g_{23} & 0 \end{pmatrix} A(t),
\]

where we have defined \( A(t) = (a_1^\dagger, a_2^\dagger, a_3^\dagger)^T \), and \( M \) is the coupling matrix. Solving this equation gives

\[
A(t) = e^{iMt}A(0) = V(t)A(0),
\]

where, \( V = e^{iMt} \) is the transformation matrix between the input and output modes.

We assume that the couplings \( g_{12} \) and \( g_{23} \) are real. The eigenvalues of matrix \( M \) are \( \lambda_1 = 0 \), \( \lambda_2 = -\sqrt{g_{12}^2 + g_{23}^2} \), and \( \lambda_3 = \sqrt{g_{12}^2 + g_{23}^2} \), and the corresponding eigenvectors are

\[
v_1 = \begin{pmatrix} g_{23} \\ g_{12} \\ \sqrt{g_{12}^2 + g_{23}^2} \end{pmatrix},
\]

\[
v_2 = \begin{pmatrix} -g_{23} \\ -g_{12} \\ \sqrt{g_{12}^2 + g_{23}^2} \end{pmatrix},
\]

\[
v_3 = \begin{pmatrix} g_{23} \\ g_{12} \\ \sqrt{g_{12}^2 + g_{23}^2} \end{pmatrix}.
\]
The coupling matrix is
\[
M = \begin{pmatrix} v_1 & v_2 & v_3 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} \sqrt{g_{12}^2 + g_{23}^2} & 0 & 0 \\ 0 & \sqrt{g_{12}^2 + g_{23}^2} & 0 \\ 0 & 0 & \sqrt{g_{12}^2 + g_{23}^2} \end{pmatrix} \begin{pmatrix} v_1^T \\ v_2^T \\ v_3^T \end{pmatrix}. \tag{S13}
\]

The transformation matrix then reads
\[
V = e^{iMt} = \begin{pmatrix} \sin^2 \theta + \cos^2 \theta \cos G & i \cos \theta \sin G \cos \theta \sin \theta (\cos G - 1) & i \sin \theta \sin G \\ i \cos \theta \sin G & \cos G & i \sin \theta \sin G \\ \cos \theta \sin \theta (\cos G - 1) & i \sin \theta \sin G & \cos^2 \theta + \sin^2 \theta \cos G \end{pmatrix}, \tag{S14}
\]
where we have defined \( G = \sqrt{g_{12}^2 + g_{23}^2} \), \( \cos \theta = \frac{g_{12}}{\sqrt{g_{12}^2 + g_{23}^2}} \), and \( \sin \theta = \frac{g_{23}}{\sqrt{g_{12}^2 + g_{23}^2}} \). The three-port WGA will transform the input modes \((i = 1, 2, 3)\) as
\[
a_i^\dagger \rightarrow V_{i1}a_1^\dagger + V_{i2}a_2^\dagger + V_{i3}a_3^\dagger. \tag{S15}
\]

We consider the input state
\[
|\psi_{\text{in}}\rangle = |1\rangle_1 |1\rangle_2 |1\rangle_3 = a_1^\dagger a_2^\dagger a_3^\dagger |0\rangle_1 |0\rangle_2 |0\rangle_3. \tag{S16}
\]

The output state after the WGA is
\[
|\psi_{\text{out}}\rangle = (V_{11}a_1^\dagger + V_{12}a_2^\dagger + V_{13}a_3^\dagger) (V_{21}a_1^\dagger + V_{22}a_2^\dagger + V_{23}a_3^\dagger) (V_{31}a_1^\dagger + V_{32}a_2^\dagger + V_{33}a_3^\dagger) |0\rangle_1 |0\rangle_2 |0\rangle_3. \tag{S17}
\]

The three-photon HOM effect is obtained when the probability of finding the output state \(|1\rangle_1 |1\rangle_2 |1\rangle_3\) is zero, i.e.,
\[
V_{11}V_{23}V_{31} + V_{12}V_{23}V_{31} + V_{13}V_{21}V_{32} + V_{11}V_{23}V_{32} + V_{12}V_{21}V_{33} + V_{13}V_{22}V_{33} = 0. \tag{S18}
\]

We thus have [cf. Eq. (S14)]
\[
\cos^4 \left( \frac{G}{2} \right) (3 \cos G - 2) - (3 \cos G + 2) \cos(4\theta) \sin^4 \left( \frac{G}{2} \right) = 0. \tag{S19}
\]

The solutions to Eq. (S19) are shown in Fig. 1. For \( G = \frac{\pi}{2} \) and \( \theta = \frac{\pi}{4} \), then
\[
V = \begin{pmatrix} 1 & i \sqrt{2} & -1 \\ i \sqrt{2} & 0 & i \sqrt{2} \\ -1 & i \sqrt{2} & 1 \end{pmatrix}. \tag{S20}
\]

This will transform the input modes as
\[
a_1^\dagger \rightarrow \frac{1}{2}a_1^\dagger + \frac{i}{\sqrt{2}}a_2^\dagger - \frac{1}{2}a_3^\dagger, \tag{S21}
\]
\[
a_2^\dagger \rightarrow \frac{i}{\sqrt{2}}a_1^\dagger + \frac{i}{\sqrt{2}}a_3^\dagger, \tag{S22}
\]
\[
a_3^\dagger \rightarrow -\frac{1}{2}a_1^\dagger + \frac{i}{\sqrt{2}}a_2^\dagger + \frac{1}{2}a_3^\dagger. \tag{S23}
\]
S3. PUMP-PROBE SPECTROSCOPY WITH THREE ENTANGLED PHOTONS

A. Derivation of the frequency-dispersed photon-counting signal Eq. (7)

Starting from the definition of signal Eq. (5) and using Eq. (6), we have

\[
S(\omega_2, \omega_3; \Gamma) = \langle a_3^\dagger(\omega_3) a_2^\dagger(\omega_2) a_2(\omega_2) a_3(\omega_3) \rangle
\tag{S24}
\]

\[
= \text{tr} \left[ a_3^\dagger(\omega_3) a_2^\dagger(\omega_2) a_2(\omega_2) a_3(\omega_3) \rho_I(t \to \infty) \right]
\tag{S25}
\]

\[
= S_0 - \frac{i}{\hbar} \mathcal{T} \int_{-\infty}^{\infty} dt \text{tr} \left[ a_3^\dagger(\omega_3) a_2^\dagger(\omega_2) a_2(\omega_2) a_3(\omega_3) H_{\text{int},-}(t) \rho_{\text{int}}(t) \right].
\tag{S26}
\]

In Eq. (S26), the first term \( S_0 \) describes the expectation value in the absence of any interaction with the system and thus can be subtracted. The signal can be written as \([7]\)

\[
S(\omega_2, \omega_3; \Gamma) = - \frac{i}{\hbar} \mathcal{T} \int_{-\infty}^{\infty} dt \text{tr} \left[ a_3^\dagger(\omega_3) a_2^\dagger(\omega_2) a_3(\omega_3) a_2(\omega_2), H_{\text{int}}(t) \right] \rho_{\text{int}}(t)
\tag{S27}
\]

\[
= \frac{1}{\pi \hbar} \mathcal{T} \mathcal{S} \int_{-\infty}^{\infty} dt e^{i\omega_2 t} \langle a_3^\dagger(\omega_3) a_2^\dagger(\omega_2) V(t) \rangle,
\tag{S28}
\]

where the commutator in Eq. (S27) is evaluated to

\[
[a_3^\dagger(\omega_3) a_2^\dagger(\omega_2) a_3(\omega_3) a_2(\omega_2), H_{\text{int}}(t)]
\tag{S29}
\]

\[
= a_3^\dagger(\omega_3) a_3(\omega_3) \int \frac{dt_a}{2\pi} \int \frac{dt_b}{2\pi} e^{i\omega_2(t_b-t_a)} [a_2^\dagger(t_a) a_2(t_b), E_2^\dagger(t) V(t) + E_2(t) V^\dagger(t)]
\tag{S30}
\]

\[
= \frac{1}{2\pi} a_3^\dagger(\omega_3) a_2^\dagger(\omega_3) [E_2^\dagger(\omega_2) V(t) e^{i\omega_2 t} - E_2(\omega_2) V^\dagger(t) e^{-i\omega_2 t}].
\tag{S31}
\]
B. Two-photon absorption with three entangled photons

The contributions of diagrams (I) and (II) to Eq. (8) where all interactions are on the ket are

\[
S^{(I)}(\omega_1, \omega_2; \Gamma) + S^{(II)}(\omega_1, \omega_2; \Gamma) \quad (S32)
\]

\[
= \frac{\omega_1 \omega_2}{\pi \hbar} \left( \frac{\hbar}{4\pi \varepsilon_0 c A} \right)^2 \Im \left( \frac{-i}{\hbar} \right)^3 \int_{-\infty}^{t} dt_3 \int_{-\infty}^{t} dt_2 \int_{-\infty}^{t} dt_1 e^{i\omega t} \left\langle V(i) V(\tau_3) V^\dagger(\tau_2) V^\dagger(\tau_1) \right\rangle \\
\left[ \left\langle a_3^\dagger(\omega_3) a_3(\omega_3) a_2^\dagger(\omega_2) a_1^\dagger(\tau_3) a_2(\tau_2) a_1(\tau_1) \right\rangle + \left\langle a_3^\dagger(\omega_3) a_3(\omega_3) a_2^\dagger(\omega_2) a_1^\dagger(\tau_3) a_1(\tau_2) a_2(\tau_1) \right\rangle \right] \\
\quad (S33)
\]

\[
e^{i\omega t_3} e^{-i\omega t_2} e^{-i\omega t_1} e^{i\omega t} \left\langle V(i) V(\tau_3) V^\dagger(\tau_2) V^\dagger(\tau_1) \right\rangle \\
\left[ \left\langle a_3^\dagger(\omega_3) a_2^\dagger(\omega_2) a_1^\dagger(\omega_1) a_3(\omega_3) a_2(\omega_2) a_1(\omega_1) \right\rangle + \left\langle a_3^\dagger(\omega_3) a_2^\dagger(\omega_2) a_1^\dagger(\omega_1) a_3(\omega_3) a_2(\omega_2) a_1(\omega_1) \right\rangle \right] .
\quad (S34)
\]

The contributions of diagrams (III) and (IV) to Eq. (8) with three interactions on the ket and one on the bra are

\[
S^{(III)}(\omega_1, \omega_2; \Gamma) + S^{(IV)}(\omega_1, \omega_2; \Gamma) \quad (S35)
\]

\[
= -\frac{\omega_1 \omega_2}{\pi \hbar} \left( \frac{\hbar}{4\pi \varepsilon_0 c A} \right)^2 \Im \left( \frac{-i}{\hbar} \right)^3 \int_{-\infty}^{t} dt_3 \int_{-\infty}^{t} dt_2 \int_{-\infty}^{t} dt_1 e^{i\omega t} \left\langle V(\tau_3) V(i) V^\dagger(\tau_2) V^\dagger(\tau_1) \right\rangle \\
\left[ \left\langle a_1^\dagger(\tau_3) a_3^\dagger(\omega_3) a_3(\omega_3) a_2^\dagger(\omega_2) a_2(\tau_2) a_1(\tau_1) \right\rangle + \left\langle a_1^\dagger(\tau_3) a_3^\dagger(\omega_3) a_3(\omega_3) a_2^\dagger(\omega_2) a_1(\tau_2) a_2(\tau_1) \right\rangle \right] \\
\quad (S36)
\]

\[
e^{i\omega t_3} e^{-i\omega t_2} e^{-i\omega t_1} e^{i\omega t} \left\langle V(\tau_3) V(i) V^\dagger(\tau_2) V^\dagger(\tau_1) \right\rangle \\
\left[ \left\langle a_3^\dagger(\omega_3) a_2^\dagger(\omega_2) a_1^\dagger(\omega_1) a_3(\omega_3) a_2(\omega_2) a_1(\omega_1) \right\rangle + \left\langle a_3^\dagger(\omega_3) a_2^\dagger(\omega_2) a_1^\dagger(\omega_1) a_3(\omega_3) a_2(\omega_2) a_1(\omega_1) \right\rangle \right] .
\quad (S37)
\]
The field correlation functions for the TPA signals are of the form \( \langle a_3^\dagger a_2^\dagger a_1 a_3 a_2 a_1 \rangle \), and can be expressed as

\[
\begin{align*}
\langle a_3^\dagger (\omega_3) a_2^\dagger (\omega_2) a_1^\dagger (\omega_b) a_3 (\omega_3) a_2 (\omega_b) a_1 (\omega_c) \rangle \\
= & \left[ c_{31} c_{22} c_{13} F^* (\omega_3, \omega_2, \omega_b) + c_{31} c_{23} c_{12} F^* (\omega_3, \omega_a, \omega_2) + c_{32} c_{21} c_{13} F^* (\omega_2, \omega_3, \omega_a) \\
& + c_{32} c_{23} c_{11} F^* (\omega_3, \omega_3, \omega_2) + c_{33} c_{21} c_{12} F^* (\omega_3, \omega_b, \omega_3) + c_{33} c_{22} c_{11} F^* (\omega_a, \omega_3, \omega_3) \right] \\
& \left[ c_{31} c_{22}^* c_{13}^* F (\omega_3, \omega_b, \omega_c) + c_{31} c_{23}^* c_{12}^* F (\omega_3, \omega_c, \omega_b) + c_{32} c_{21}^* c_{13}^* F (\omega_b, \omega_3, \omega_c) \\
& + c_{32} c_{23}^* c_{11}^* F (\omega_3, \omega_3, \omega_b) + c_{33} c_{21}^* c_{12}^* F (\omega_b, \omega_c, \omega_3) + c_{33} c_{22}^* c_{11}^* F (\omega_b, \omega_b, \omega_3) \right],
\end{align*}
\]

where \( c_{ij} \) is the matrix element of the transformation matrix \( C \), and \( F (\omega_a, \omega_2, \omega_3) \) is the spectral amplitude given by Eq. (2) of the main text.

### S4. PUMP-PROBE SPECTROSCOPY WITH ENTANGLED PHOTON-PAIR

#### A. Transformation matrix for the Mach-Zehnder interferometer

The Mach-Zehnder interferometer for the pump-probe experiment with entangled photon-pair consists of two 50:50 beam splitters (BS’s). The transformation matrix for the BS is [8]

\[
M = \begin{pmatrix}
\frac{1}{\sqrt{2}} & i \\
\frac{i}{\sqrt{2}} & \frac{1}{\sqrt{2}}
\end{pmatrix}.
\]

The transformation matrix for the MZI is

\[
C = M^\dagger \text{diag}(e^{i\phi}, 1) M,
\]

which will transform

\[
\begin{align*}
a_1^\dagger & \rightarrow c_{11} a_1^\dagger + c_{12} a_2^\dagger, \\
a_2^\dagger & \rightarrow c_{21} a_1^\dagger + c_{22} a_2^\dagger.
\end{align*}
\]

#### B. Two-photon absorption with entangled photon-pair

The signal is detected by spectrally dispersing the probe photon \( a_2 \) [see Fig. 2(c)]. Similar to the derivation of Eq. (S28), we obtain the expression for the signal with two entangled photons:

\[
S^{(2p)} = \left\langle a_3^\dagger (\omega_2) a_2 (\omega_2) \right\rangle
= \frac{1}{\pi \hbar} \Im \int_{-\infty}^{\infty} dt \text{tr} \left[ E_2^\dagger (\omega_2) e^{i\omega_2 t} V(t) \rho_{\text{int}} (t) \right].
\]

Expanding the density matrix \( \rho_{\text{int}} (t) \) to second order in \( E_1 \) and first order in \( E_2 \), we obtain same diagrams as those in Fig. 3.
The contributions of diagrams (I) and (II) to $S^{(2p)}_{\text{TPA}}$ are

$$
S^{(I)}(\omega_{p0}, \omega_2; \Gamma) + S^{(II)}(\omega_{p0}, \omega_2; \Gamma) = -\frac{\omega_{10}\omega_{20}}{\pi\hbar} \left(\frac{\hbar}{4\pi\varepsilon_0CA}\right)^2 \mathcal{Z} \left(-\frac{i}{\hbar}\right)^3 \int_{-\infty}^{\infty} dt \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \int_{-\infty}^{t''} dt''' e^{i\omega t} \langle V(t) V(\tau_3) V(\tau_2) V'(\tau_1) \rangle \left[ \langle a^+_2(\omega_2) a^+_1(\tau_2) a_2(\tau_1) a_1(\tau_1) \rangle + \langle a^+_2(\omega_2) a^+_1(\tau_2) a_1(\tau_2) a_2(\tau_1) \rangle \right] \right) (S46)
$$

The contributions of diagrams (III) and (IV) to $S^{(2p)}_{\text{TPA}}$ are

$$
S^{(III)}(\omega_{p0}, \omega_2; \Gamma) + S^{(IV)}(\omega_{p0}, \omega_2; \Gamma) = -\frac{\omega_{10}\omega_{20}}{\pi\hbar} \left(\frac{\hbar}{4\pi\varepsilon_0CA}\right)^2 \mathcal{Z} \left(-\frac{i}{\hbar}\right)^3 \int_{-\infty}^{\infty} dt \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \int_{-\infty}^{t''} dt''' e^{i\omega t} \langle V(\tau_3) V(t) V'(\tau_2) V'(\tau_1) \rangle \left[ \langle a^+_1(\tau_3) a^+_2(\omega_2) a_2(\tau_2) a_1(\tau_1) \rangle + \langle a^+_1(\tau_3) a^+_2(\tau_2) a_1(\tau_2) a_2(\tau_1) \rangle \right] \right) (S47)
$$

$$
= -\frac{\omega_{10}\omega_{20}}{\pi\hbar} \left(\frac{\hbar}{4\pi\varepsilon_0CA}\right)^2 \mathcal{Z} \left(-\frac{i}{\hbar}\right)^3 \int_{-\infty}^{\infty} dt \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \int_{-\infty}^{t''} dt''' e^{i\omega t} \langle V(\tau_3) V(t) V'(\tau_2) V'(\tau_1) \rangle \left[ \langle a^+_1(\tau_3) a^+_2(\omega_2) a_2(\tau_2) a_1(\tau_1) \rangle + \langle a^+_1(\tau_3) a^+_2(\tau_2) a_1(\tau_2) a_2(\tau_1) \rangle \right] \right) (S48)
$$

The normally-ordered four-point field correlation function is

$$
\langle a^+_2(\omega_2) a^+_1(\omega_a) a_2(\omega_b) a_1(\omega_c) \rangle = |c_{21}|^2 |c_{12}|^2 F^*(\omega_2, \omega_a) F(\omega_b, \omega_c) + c_{21} c_{12} c_{22} c_{11}^* F^*(\omega_2, \omega_a) F(\omega_c, \omega_b) + c_{22} c_{11} c_{21} c_{12}^* F^*(\omega_a, \omega_2) F(\omega_b, \omega_c) + |c_{22}|^2 |c_{11}|^2 F^*(\omega_a, \omega_2) F(\omega_c, \omega_b). (S50)
$$

Here the two-photon amplitude is [9]

$$
F(\omega_1, \omega_2) = \sqrt{\frac{T_{p1} - T_{p2}}{\pi \sigma_p}} (2\gamma)^{1/4} e^{-\frac{(\omega_1 + \omega_2 - \omega_{\mu0})^2}{2\sigma_p}} e^{\gamma[T_{p1}(\omega_1 - \omega_{\mu0}) + T_{p2}(\omega_2 - \omega_{\mu0})]} (S54)
$$

where $\sigma_p$ is the pump bandwidth, $\omega_{\mu0}$ ($\mu = p, 1$ and 2) is the central frequency of pulse $\mu$, $\gamma = 0.0482304$, and the two time delays are defined similarly to those in Eq. (2) of the main text.