We theoretically investigated the biphoton state generated by spontaneous four wave mixing (SpFWM) in ultrathin nonlinear films. The expression of the biphoton state is obtained by perturbation method, in which the longitudinal phase mismatch term is eliminated due to the ultra-small nonlinear interactive length. As a result of the relaxation of the longitudinal phase match condition, frequency bandwidth of the biphoton state could be very large. The correlation function of the biphoton state is analyzed, showing that the space and time in the biphoton correlation of this state are factorable. The calculations of the frequency purity further indicate that the temporal and spatial degrees of freedom in this biphoton state are separable. The spatial Schmidt numbers of the biphoton state are also calculated, showing that this state supports high dimensional transverse entanglement. These results show that SpFWM in ultrathin nonlinear films is promising in generating biphoton states for applications involving hyper-entanglement and high-dimensional entanglement.

I. Introduction

Spontaneous parametric nonlinear optical processes, including spontaneous parametric down conversion (SPDC) [1, 2] and spontaneous four wave mixing (SpFWM) [3-5], are important ways to generate correlated biphoton states, which have been widely investigated and applied in various experiments of quantum information processing [6] and quantum communications [7, 8] involving photons. In these processes, the energy and momentum conservations between the annihilated and generated photons determine the properties of quantum correlation in the biphoton states [9-19]. The momentum conservation can be expressed by the phase matching conditions, which is largely determined by the geometrical structure of the nonlinear media.

Usually, nonlinear optical bulk crystals [13] or periodically poled waveguides [20] with length of ~mm are employed in SPDC. Due to the considerable interaction length, the longitudinal phase mismatch becomes remarkable and brings some limits to the generated biphoton states. For example, in these states the temporal and spatial degrees of freedom are not separable, limiting their applications in realization of hyper-entanglements [21]. It also leads to the difficulty on the definitions of temporal and spatial coherences in these states. Instead, the coherence of these states is defined in an “X” trajectory in the spatial and temporal dimensions [10, 15-16].

On the other hand, the longitudinal phase mismatch also limits the frequency and spatial frequency bandwidths of the biphoton states [12], which are important for quantum metrology techniques based on biphoton interferences [22, 23]. For the biphoton state generation by SpFWM, usually the third order nonlinear waveguides, such as optical fibers [3] and silicon waveguides [4], are employed. Long waveguide lengths are required (several hundreds meters for optical fibers and several millimeters for silicon waveguides) to compensate the low third order nonlinearity in these materials. Hence, the longitudinal phase mismatch is also important. It mainly impacts on the frequency bandwidth of the biphoton states if the processes are stimulated only in a specific waveguide mode, or among several known modes [24].

Recently, nonlinear optical effects in nonlinear thin films attracted much attention. The thicknesses of these nonlinear films are very small, which relax the requirement of longitudinal phase matching. It has been demonstrated by four wave mixing in thin metallic films and graphite thin films [25, 26]. It also has been proposed that the longitudinal phase matching factor can be eliminated in biphoton states generated by SPDC in thin films [27]. However, properties of the biphoton state generated in the nonlinear films by either SPDC or SpFWM have not been investigated. Ref. [28] pointed out that the spatial mode analysis of biphoton states generated by SPDC would have problems of divergence if the phase matching factor disappears. It can be expected that similar problems also exist in analyzing other properties of the biphoton states generated by SpFWM in ultrathin nonlinear optical processes in thin films, such as correlation function and transverse entanglement.

In this work, we theoretically investigated the properties of biphoton states generated by SpFWM in ultrathin nonlinear optical processes comprehensively. The expression of the biphoton state is obtained by perturbation method, showing that the ultrathin film structure relaxes the requirement of phase matching in the SpFWM process. Then, the correlation function of the biphoton state is deduced, showing that the relaxation of phase match leads to the time-space factorability in the correlation function. It also leads to the spatiotemporal separatability of the biphoton state, which is analyzed by the frequency purity when the spatial and polarization degrees of freedom are traced out. On the other hand, the spatial Schmidt numbers are calculated to show that high-dimensional transverse entanglement can be realized by this state. Finally, the feasibility of experimental observation of this biphoton state is evaluated numerically using different nonlinear ultrathin materials.

II. EXPRESSION OF BIPHOTON STATES GENERATED BY SpFWM IN ULTRATHIN FILM

The sketch of the biphoton state generation by SpFWM in a ultrathin film is shown in Fig. 1 (a). The film is made by a medium with high third order nonlinearity, which has a thickness of \( d \). A linearly polarized pulsed pump light, which is shown by the red beam, illuminates the film at a
The polarization direction of the pump beam is defined as x-axis and the surface of the ultrathin film is the x-y plane. Due to the ultrathin property of the nonlinear film and the polarization of the pump beam, only the components $\chi^{(3)}_{xx}$ and $\chi^{(3)}_{xyy}$ in the nonlinear susceptibility tensor are effective in SpFWM. The signal and idler photons generated by SpFWM would emit from the spot.

To analyze the generated biphoton state, the Schrödinger equation of SpFWM process can be solved by perturbation method under low parametric gain [3, 9]. The solution provides the expression of the biphoton state $|\psi_{s, i}\rangle$

$$|\psi_{s, i}\rangle = \sum_{j_s, j_i=0,1} \sum_{l_s, l_i=0,1} \int dS \psi(S, j_s, j_i, l_s, l_i) a_s^\dagger(S, j_s, l_s)(0_j_S, 0_j_S) a_i^\dagger(S, j_i, l_i)(0_j_I, 0_j_I),$$

where $a_s^\dagger(S, j_s, l_s)$ ( $a_i^\dagger(S, j_i, l_i)$ ) is the creation (annihilation) operator for a mode with indices $S_{j_s} = [\omega_{j_s}, k_{j_s}]$, $j_s = 0, 1$ and $l_s = 0, 1$. $\omega_{j_s}$ and $k_{j_s}$ are frequency and transverse wavevector (in plane component of the wave vector of the mode) of the signal/idler photons, respectively. $j_s = 0$ ( $j_s = 1$ ) presents the modes propagating upwardly (downwardly) respect to the x-y plane. Here and henceforth, the “$|$” in the subscript means the variable is transverse. The electric fields of these modes are all linearly polarized, $l_s$ indicate two polarization directions. The modes with polarizations parallel with the x-y plane are indicated by $l_s = 0$ and $l_s = 1$ indicates that the modes polarized along the plane spanned by the propagating direction and z-axis. In the following discussion, the two polarization directions are represented as “TE” and “TM”, respectively. $k_{j_s}$ can be expressed by the spatial frequency $k_{j_s} = |k_{j_s}|$ and angle $\phi_{k_{j_s}}$, which are shown in Fig. 1 (b). The notation $|\ast|$ means the magnitude of a vector or the modulus of a complex expression. The integral variable $S = [S_x, S_z]$ in Eq. (1) is a six-dimensional vector. $\psi(S, j_s, j_i, l_s, l_i)$ is the probability amplitude function for the signal and idler photons.

To simplify the calculation, we assume that the pump light is a series of Gaussian pulses with central frequency of $\omega_{p0}$ and temporal duration of $\tau_p$. Its spatial distribution is Gaussian, and its waist is on the ultrathin film with a radius of $r_p$. The peak power of the pump pulses is $P_p$. We also define two angular frequency detunings as $\Omega_{ji} = \omega_{j_i} - \omega_{i0}$. Here, $\omega_{j_i}$ is the central angular frequency of the signal or idler fields, which determined by the optical filters for the signal/idler photon collections and satisfied $\omega_{j_i} + \omega_{j_i} = 2\omega_{p0}$. In this case $\psi(S, j_s, j_i, l_s, l_i)$ has an explicit expression (See the detailed derivation in Appendix A)

$$\psi(\Omega_{j_s}, \Omega_{j_i}, k_{j_s}, k_{j_i}, j_s, j_i, l_s, l_i) = \beta(\gamma P_p, d_{eff})(\pi r_p) (\sqrt{2}\pi r_p) \times G_{s}(\Omega_{j_s}, \Omega_{j_i}) G_{i}(k_{j_s}, k_{j_i}) \Phi(\phi_{j_s}, \phi_{j_i}, l_s, l_i) \times \Theta(\Omega_{j_s}, k_{j_s}, j_s, l_s) \Theta(\Omega_{j_i}, k_{j_i}, j_i, l_i) U(\Omega_{j_s}, k_{j_s}) U(\Omega_{j_i}, k_{j_i}),$$

where $\gamma$ is the third order nonlinear coefficient proportional to $\chi^{(3)}_{xx}$, but inverse proportional to $r_p^2$. Here, $\beta$ is a constant, and the explicit expressions of $\beta$ and $\gamma$ can be found in Appendix A. The constant $d_{eff}$ is the effective nonlinear interaction length when the absorption of pump light, signal and idler photons in film are taken into consideration. In Appendix F, the method to calculate $d_{eff}$ for different types of material will be given. The terms $G_{s}(\Omega_{j_s}, \Omega_{j_i})$ and $G_{i}(k_{j_s}, k_{j_i})$ in Eq. (2) are

$$G_{s}(\Omega_{j_s}, \Omega_{j_i}) = e^{-r_p^2(\Omega_{j_s}, \Omega_{j_i})^2/4},$$

$$G_{i}(k_{j_s}, k_{j_i}) = e^{-2|k_{j_s}|^2|k_{j_i}|^2/4},$$

and they originate from the energy and transverse momentum conservations in the SpFWM, respectively. The terms $\Phi(\phi_{j_s}, \phi_{j_i}, l_s, l_i)$ and $\Theta(\Omega_{j_s}, k_{j_s}, j_s, l_s)$ have forms of

$$\Phi(\phi_{j_s}, \phi_{j_i}, l_s, l_i) = \sum_{m=0}^{\infty} \left(\gamma x^\ast\right)^m \cos(\phi_{j_s} + \frac{l_s - m}{2} \pi) \cos(\phi_{j_i} + \frac{l_i - m}{2} \pi),$$

$$\Theta(\Omega_{j_s}, k_{j_s}, j_s, l_s) = \cos^{l_s}(\theta_{j_s}(\Omega_{j_s}, k_{j_s}, j_s)),$$

where $\theta_{j_s}(\Omega_{j_s}, k_{j_s}, j_s) = (-1)^{l_s} \arcsin[k_{j_s} / k_{j_s}(\Omega_{j_s})]$ is the angle between the wavevector of a mode and the z-axis, with $k_{j_s}(\Omega_{j_s})$ being the angular wavenumber at $\omega_{j_s}$ . The parameter $\gamma x^\ast = \chi^{(3)}_{xx} / \chi^{(3)}_{xx}$, indicating the anisotropy of the nonlinear susceptibility. The terms $U(\Omega_{j_s}, k_{j_s}) = u(k_{j_s}(\Omega_{j_s}) - k_{j_s})$ in Eq. (2) are unit step functions. The angular wavenumbers $k_{j_s}(\Omega_{j_s})$ are related to the angular frequency detuning $\Omega_{j_s}$ via the dispersion relationship. In all the relevant numerical calculations in this paper, a linear dispersion relationship $k_{j_s} = (\omega_{j_s} + \omega_{j_s}) n_{j_s} / c$ is utilized, where $n_{j_s}$ is the refractive index of the ultrathin film.

Compared with expressions of biphoton states generated by SPDC in bulk crystals [9, 10], Eq. (2) has two differences. Firstly, there is no sinc-type factor in Eq. (2) since the phase mismatching effect is neglected in the integral along the longitudinal direction. Secondly, it has
two unit step functions, which are from that we truncate \( k_{s,i} \) to only keep the spatial modes propagating along the longitudinal direction, and dropped all the evanescent modes along this direction. It is reasonable since usually the collection of signal/idler photons is in far field. By this way, the problem of divergence mentioned in Ref. [28] can be overcome.

For a specific signal (idler) mode with transverse wavevector \( \mathbf{k}_{s,i} \) (\( \mathbf{k}_{s,i} \)), the joint spectral intensity [29] of the biphoton state shown in Eq. (2) can be explicitly expressed as
\[
F(\Omega_s, \Omega_i) = e^{-i(\Omega_s + \Omega_i) + \Omega_s^2 / 2},
\]
which extends homogeneously along the axis of \( \Omega_s = -\Omega_i \) until that \( k_s(\Omega_s) \geq k_{s||} \) and \( k_i(\Omega_i) \geq k_{i||} \) are not satisfied. It is clearly different from the \( F(\Omega_s, \Omega_i) \) of the biphoton states generated by SPDC in thick nonlinear media, in which the phase mismatching term makes \( F(\Omega_s, \Omega_i) \) decay along the axis of \( \Omega_s = -\Omega_i \) [29]. This difference means that the frequency bandwidth of the biphoton state generated by SpFWM in an ultrathin film could be much larger than that generated by SPDC in thick nonlinear crystals.

### III. CORRELATION FUNCTION OF THE BIPHOTON STATE

The spatiotemporal structure of two photon correlation could be demonstrated by coincidence measurement of signal and idler photons under different time delay and spatial shift [16], which is in proportion to the modulus of correlation function of idler photons under different time delay and spatial shift [16], [17].

The correlation function of the biphoton state [15]. When the collection and detection processes of signal and idler photons are taken into consideration, the correlation function of the biphoton state described in Eq. (1) can be calculated by
\[
C(t_s,t_i,\mathbf{r}_s,\mathbf{r}_i) = \langle 0\vert \hat{a}_s(t_s,\mathbf{r}_s)\hat{a}_i(t_i,\mathbf{r}_i)\vert \psi\rangle
\]
where \( \hat{a}_{s,i}(t_{s,i},\mathbf{r}_{s,i}) \) (see the explicit expressions of them in Appendix B) is the annihilation operator/signal/idler photons at time \( t_{s,i} \) and positions \( \mathbf{r}_{s,i} = r_{s,i}[\cos\varphi_{s,i},\sin\varphi_{s,i}] \). In the collection configuration for deriving Eq. (5), only the photons propagating upwardly with respect to \( x-y \) plane are collected, and this results in the term \( \psi(S,j_s = 0, l_j = 0, l_i) \) inside the integral in Eq. (5). The terms \( F_{s,i}(\Omega_{s,i}) \) and \( F_s(k_{s,i}) \) are introduced to represent the filtering processes on the frequency and spatial frequency in the collection and detection after the biphoton generation, and in the calculation they have forms of
\[
F_{s,i}(\Omega_{s,i}) = e^{-i\Omega_{s,i} + \Omega_{s,i}^2 / 2}, \quad F_s(k_{s,i}) = \begin{cases}
1, & Y_{s,i} k_{s,i} < 1/2 \\
0, & \text{others}
\end{cases}.
\]

In Eq. (6.1), the signal and idler channels have the same filtering bandwidth \( \Omega_s \). The filtering function shown in Eq. (6.2) corresponds to a lens which only collect the signal (idler) photons in modes with \( k_{s,i} < 1/2 Y_s \).

When \( t_s \) and \( \mathbf{r}_s \) are set as the origins of temporal and spatial coordinate, an explicit expression of Eq. (5) can be obtained as
\[
C(\Delta t,\mathbf{r}) = C_s \sum_{k_{s,i} - 0, l_j = 0, l_i} d\Omega_s F_s(\Omega_s) F_i(\Omega_i) e^{-i\Delta t} \sum_{j_s = 0, l_j = 0, l_i} d\mathbf{r}_s d\mathbf{r}_i g_s(k_{s,i}) g_i(k_{s,i}) l_i \left( \frac{r_s^2 k_{s,i}^2}{2} \right) J(k_{s,i},\Delta t,\varphi_i) \times \Theta(\Omega_s, k_{s,i}, 0, l_j) \Theta(\Omega_i, k_{i,j}, 0, l_i) U(\Omega_s, k_{s,i}) U(\Omega_i, k_{i,j}),
\]
where \( \Delta t \) is the time delay and \( \Delta r = \Delta r e^{i\varphi_i} \) is the spatial shift between the idler and signal photons. In Eq. (7), \( g_s(k_{s,i}) = e^{-i(k_{s,i}^2 + \Delta k^2) / 4} \) and \( I_0(\ast) \) is the modified 1st-order Bessel function. The explicit expression of the constant \( C_s \) can be found in Appendix B. The expression of \( J(k_{s,i},\Delta t,\varphi_i) \) is
\[
J(k_{s,i},\Delta t,\varphi_i) = -\frac{1}{2} \left( 1 + r_{s,j} \right) J_0(\Delta r) \cos \left( \frac{\pi}{2} (m_s - m_i) \right) + \frac{1}{2} \left( 1 - r_{s,j} \right) J_0(\Delta r) \cos \left( \frac{\pi}{2} (m_s + m_i) + 2\varphi_i \right).
\]

This equation is similar with the correlation function of the biphoton state generated in SPDC in bulk nonlinear crystal.
pumped by plane wave, except two differences. Firstly, the kernel function in the Hankel transformation is different. Secondly, Eq. (10) can be factored to two parts only depending on \( \Delta \tau \) and \( \Delta r \), respectively, while the correlation function in Ref. [30] does not have this property. Since the \( \Delta \tau \)-dependent part is the same for all the four \( C_{ij}(\Delta \tau, \Delta r) \), the correlation function \( C(\Delta \tau, \Delta r) \) of the biphoton state generated by SpFWM in ultrathin film can also be factored to temporal and spatial correlation functions. This means that the space and time in the biphoton state is factorable. Although this conclusion is obtained under the condition that \( (\omega_{i0}\omega_0-\Omega_r)n_z/c>1/\gamma_c \), in Fig.2 we will show that it could be valid even when this condition is not satisfied well.

Fig. 2 The numerical calculations of the correlation function. (a)-(d) are \[ C(0, \Delta r)\] and \[ C(\Delta \tau, \Delta r) \] versus \( \Delta \tau \) and \( \Delta r \), respectively. The vertical coordinates in (a)-(d) are the same, and the colorbar next to (d) is for all of (a)-(d).

According to Eq. (9), we calculated all the four \( C_{ij}(0, \Delta r) \) under \( \Omega_r=2\pi \times 50 \text{ THz} \), \( \gamma_c=1 \mu \text{m} \), and \( r_p=1/3 \), i.e., \( (\omega_i-\omega_0-\Omega) n_z/c>>1/\gamma_c \) is not satisfied. The normalized results are shown in Figs. 2 (a) to (d). It is obvious that all the four terms are azimuthally anisotropic. This is different from the isotropic correlation function in Ref. [30], and the reason is that the anisotropy of the nonlinear susceptibility is considered in our model. Moreover, \( |C_{00}(0, \Delta r)| \) and \( |C_{11}(0, \Delta r)| \) are much larger than \( |C_{01}(0, \Delta r)| \) and \( |C_{10}(0, \Delta r)| \), and therefore the former two are dominant in the calculation of \( |C(0, \Delta r)| \). It is obvious that the orientations of \( |C_{00}(0, \Delta r)| \) and \( |C_{11}(0, \Delta r)| \) is along \( \phi=0 \) and \( \phi=\pi \), respectively, and this makes \( |C(0, \Delta r)| \) nearly orient along \( \phi=\pi/4 \), which is calculated according to Eq. (9) and shown in the Fig. 2 (e). In Fig. 2 (f), \( |C(\Delta \tau, \Delta r)|/|C(0, 0)| \) versus \( \Delta \tau \) and \( \Delta r \) are shown with \( \phi \) fixed at \( \pi/4 \) and \( \Delta r=\Delta r_{p}e^{\pm \pi/4} \). When \( \Delta \tau (\Delta r) \) is fixed at arbitrary position, \( |C(\Delta \tau, \Delta r)| \) always shows Airy disk section (Gaussian) profile with variable of \( \Delta r (\Delta \tau) \), which corresponds to the profiles of the Hankel (Fourier) transformation of the filtering function in Eq. (6.1) (Eq. (6.2)). These results show that biphoton correlation of the state in Eq. (1) is factorable in temporal and spatial domains even under larger filtering bandwidths in frequency and spatial frequency. This property is much different from the biphoton state generated by SpDC in bulk nonlinear crystals. Their spatiotemporal structure of the biphoton correlation has nonfactorable \( \lambda \)-geometry [30]. Such nonfactorability is determined by the requirement of phase match of SpDC in bulk crystals. On the other hand, for the biphoton state generated by SpFWM in ultrathin films, the factorability in the biphoton correlation revealed in Fig. 2 is due to the relaxation of the requirement of longitudinal phase match.

In the calculations for Fig. 2 (f), the pump beam is approximated by monochromatic plane wave. By numerically calculating the Eq. (7), we can study whether the biphoton correlation is factorable under Gaussian pump. The Monte Carlo method is employed to numerically compute the integrals in Eq. (7), when \( r_p=1 \mu \text{m} \), \( r_{0}=10 \mu \text{m} \) and other parameters are the same to those used in the calculation for Fig. 2 (f). The calculated results are shown in Figs. 2 (g) and (h). In Fig. 2 (g), the calculated normalized correlation function \( |C(\Delta \tau, \Delta r)|/|C(0, 0)| \) versus \( \Delta \tau \) is shown under different \( \Delta r \). It can be seen that varying \( \Delta \tau \) does not change the Airy disk section profile of the calculated curves and its full width at half maxima (FWHM), which is the correlation length of the biphoton state. It only leads to the variation of magnitude of the curves. Figure 2 (h) shows the calculated \( |C(\Delta \tau, \Delta r)|/|C(0, 0)| \) versus \( \Delta r \), when \( \Delta \tau \) is set at different values. It can be seen that all the curves under different \( \Delta \tau \) have Gaussian profile. Their widths indicate the correlation time of the biphoton state, which are almost unchanged under different \( \Delta r \). Only the magnitudes of these curves decreases with increasing \( \Delta r \). The two figures indicate that the biphoton correlation is still factorable in temporal and spatial domains even that Gaussian spatial distribution of the pump light is considered.

IV. SPATIOTEMPORAL SEPARABILITY OF THE
BIPHOTON STATE

As shown in Fig. 2, the correlation function of the biphonton generated in ultrathin film has factorable spatiotemporal structure. Since the correlation function is calculated based on the expression of the biphonton state, the temporal and spatial degrees of freedom in the biphonton state itself would be separable. The separability of a quantum state in two degrees of freedom can be evaluated by the purity of quantum state when one of the degrees of freedom is traced out [21]. To explore the spatio-temporal separability of the biphonton state shown in Eq. (1), we calculate the frequency purity \( \text{Tr}(\rho_{\Omega_{s},\Omega_{c}}^{2}) \) by tracing out the both of the spatial and polarization degrees of freedom. The result is (See the detailed derivation in Appendix C) are

\[
\text{Tr}(\rho_{\Omega_{s},\Omega_{c}}^{2}) = \frac{B}{N^{2}},
\]

where

\[
N = \frac{1}{4} \sum_{l_{1},l_{2},j_{1},j_{2}} \int d\Omega_{s} \int d\Omega_{c} \int d\Omega_{s} \int d\Omega_{c} \int d\omega_{s} \int d\omega_{c} \int d\omega_{s} \int d\omega_{c} \\
\times G_{\Omega_{s}}^{2}(k_{s_{1}},k_{s_{2}})G_{\Omega_{c}}^{2}(k_{c_{1}},k_{c_{2}})F_{\Omega_{s}}^{2}(\Omega_{s})F_{\Omega_{c}}^{2}(\Omega_{c})F_{\Omega_{s}}^{2}(\Omega_{s})F_{\Omega_{c}}^{2}(\Omega_{c}) \\
\times I(k_{s_{1}},k_{s_{2}},l_{1},l_{1})\Theta^{2}(\Omega_{s},k_{s_{1}},0,l_{1})\Theta^{2}(\Omega_{c},k_{c_{1}},0,l_{2}) \\
\times U(\Omega_{s},k_{s})U(\Omega_{c},k_{c}),
\]

and

\[
B = \sum_{l_{1},l_{2},j_{1},j_{2}} \sum_{l_{1},l_{2}} \sum_{j_{1},j_{2}} \int d\omega_{s} \int d\omega_{s} \int d\omega_{s} \int d\omega_{s} \int d\omega_{s} \int d\omega_{s} \int d\omega_{s} \int d\omega_{s} \\
\times \left[ k_{s_{1}}dk_{s_{2}}dk_{s_{2}}dk_{s_{2}}dk_{c_{1}}dk_{c_{1}}dk_{c_{1}}dk_{c_{1}} \right] \\
\times \left[ \prod_{m=1}^{2} G_{\Omega_{m}}^{2}(\Omega_{m},\Omega_{m})G_{\Omega_{m}}^{2}(\Omega_{m},\Omega_{m})F_{\Omega_{m}}^{2}(\Omega_{m})F_{\Omega_{m}}^{2}(\Omega_{m}) \right] \\
\times F_{\Omega_{m}}^{2}(k_{m})F_{\Omega_{m}}^{2}(k_{m})I(k_{m},k_{m},l_{m},l_{m}) \\
\times \left[ \prod_{m=1}^{2} \Theta^{2}(\Omega_{m},k_{m},0,l_{m}) \right] \\
\times \Theta^{2}(\Omega_{m},k_{m},0,l_{m})U(\Omega_{m},k_{m},l_{m})U(\Omega_{m},k_{m},l_{m}),
\]

In Eqs. (12) and (13), the term \( I(k_{s_{1}},k_{s_{2}},l_{1},l_{1}) \) is defined as

\[
I(k_{s_{1}},k_{s_{2}},l_{1},l_{1}) = (1 + r_{p}^{2})I_{0}(r_{p}^{2}k_{s_{1}}k_{s_{2}}) \\
+ (1 + r_{x}^{2}) \cos((l_{x} - l_{y})\pi)J_{2}(r_{p}^{2}k_{s_{1}}k_{s_{2}}).
\]

Compared with the denominator in Eq. (11), the numerator has eight additional terms, four cosine and four unit step functions in the integral. All the eight terms are smaller than 1 and this guarantees \( \text{Tr}(\rho_{\Omega_{s},\Omega_{c}}^{2}) \leq 1 \) according to Eq. (11). When \( \Omega_{c} \) is in small and \( \gamma_{c} \) is relatively large, i.e., the detection process is narrowband in both of the frequencies and spatial frequencies, all of the eight additional terms are nearly zero. In such case, the denominator and numerator in Eq. (10) is equal, leading to \( \text{Tr}(\rho_{\Omega_{s},\Omega_{c}}^{2}) = 1 \). It shows that the biphonton state are separable in its temporal and spatial degrees of freedoms. This conclusion is consistent with the limit case shown in Ref. [21], where the two degrees of freedoms are separable in the biphonton state generated by SPDC in bulk crystal when the filtering bandwidth of the frequency is nearly 0 or that of the spatial frequency is very small.

When the bandwidths of the frequency and spatial frequency filtering processes increases, Eq. (10) cannot be simplified in the way mentioned above. We calculate the evolution of the frequency purity with increasing \( \gamma_{c} \) and under different \( \Omega_{c} \), numerically according to Eqs. (10), (11), and (12), and show the results in Fig. 3. The multi-dimensional integrals in Eq. (11) and (12) are implemented by the Monte Carlo methods. In the calculations, the rectangular filtering function in Eqs. (6.2) and (11) is replaced by \( F_{\Omega}(\Omega) = e^{-\frac{1}{4}r_{p}^{2}/\Omega^{2}} \), to make the comparison between our results and the results of similar calculation for biphoton state generated by SPDC in bulk crystal [21] reasonable, in which the filtering function of spatial frequency is Gaussian.

![Fig. 3 The numerical calculations of the frequency purity Tr(\( \rho_{\Omega_{s},\Omega_{c}}^{2} \)).](image)

(a) \( \Omega_{p} = 6\pi/\tau_{p} \) (b) \( \Omega_{p} = 30\pi/\tau_{p} \) (c) \( \Omega_{p} = 60\pi/\tau_{p} \)

Figure 3 (a) is the result under different \( \gamma_{c} \) when the frequency filtering bandwidth is set 3THz. The shadow band shows the results of 50 times of numerical computations involving Monte Carlo integrals for each case, the dashed dot line is their average. It can be seen that the calculated purity \( \text{Tr}(\rho_{\Omega_{s},\Omega_{c}}^{2}) \) is always close to 1 under varying \( \gamma_{c} \). Figure 3 (b) and (c) show the results when the frequency filtering bandwidth increases to 30THz and 60 THz, respectively. It can be seen that the purity is still close to 1 with broader \( \Omega_{c} \). These results indicate that the temporal and spatial degrees of freedoms of the biphonton state studied here are separable, even under such large temporal and spatial filtering bandwidths. As a comparison, previous works of the analysis on biphonton states generated by SPDC in bulk crystals [11] shows that for the biphonton state generated in a crystal with a length of 1mm, the state purity would drop to near 0.2 when \( \Omega_{c}/2\pi = 4.7\text{THz} \) and \( \gamma_{c} = 100\mu\text{m} \). Hence, it is concluded that the biphonton states generated by SpFWM in ultrathin film are spatiotemporally separable even under large photon collection/detection frequency and spatial frequency bandwidths, thanks to the relaxation of the
requirement on longitudinal phase match. Since the separability between different degrees of freedom is important for the demonstration of hyper-entanglement, therefore ultrathin film is a type of promising material for realizing biphoton hyper-entanglement [21].

V. HIGH DIMENSIONAL TRANSVERSE ENTANGLEMENT IN BIPHOTON STATE

Above analysis shows that the requirement of longitudinal phase match relaxes in SpFWM in ultrathin films. On the other hand, the transverse phase match in this process still is required. It leads to the property of high dimensional transverse entanglement, which can be indicated by the spatial Schmidt number. Larger spatial Schmidt number means higher entanglement dimension [28]. The spatial Schmidt number can be obtained by Schmidt decomposition of the biphoton state under the bases of plane wave modes [28,31]. Here, we calculated the spatial Schmidt number to show the high dimensional transverse entanglement in the biphoton state generated by SpFWM in an ultrathin film.

Firstly, the spatial Schmidt number is obtained by $K_s = 1/\text{Tr}[\rho(k_s, k_s)]$, in which $\rho(k_s, k_s)$ is the density matrix of the biphoton state in the subspace spanned by $k_{s1}$ and $k_{s2}$ [11]. Under the assumption that only the upwardly propagating photons with specific signal and idler frequencies are collected, the explicit expression of $K_s$ can be deduced (see the detailed derivation in Appendix D) from the expression of the biphoton state in Eq. (2), and it has form of

$$K_s = \frac{N_s}{T},$$

(15)

where

$$N_s = \sum_{i_0=0,1} \sum_{i_1=0,1} \sum_{j_0=0,1} \sum_{j_1=0,1} \int dk_{s1} \int dk_{s2} |\psi(k_{s1}, k_{s2}, i_0, i_1, j_0, j_1)|^2,$$

(16)

and

$$T = \sum_{i_0=0,1} \sum_{i_1=0,1} \sum_{j_0=0,1} \sum_{j_1=0,1} \int dk_{s1} \int dk_{s2} \int dk_{s1} \int dk_{s2} \times |\psi(k_{s1}, k_{s2}, i_0, i_1, j_0, j_1)|^2 \times |\psi(k_{s1}, k_{s2}, i_0, i_1, j_0, j_1)|^2 \times |\psi(k_{s1}, k_{s2}, i_0, i_1, j_0, j_1)|^2.$$

(17)

The $\psi(k_{s1}, k_{s2}, i_0, i_1, j_0, j_1)$ in Eqs. (15) and (16) is the $\psi(\Omega_s, \Omega_s, k_{s1}, k_{s2}, i_0, i_1, j_0, j_1)$ in Eq. (3) with fixed $\Omega_s, \Omega_s, j_0, j_1$ and $f_{i_0, i_1} = 1$. Though the implementation of the integrals about $\varphi_{k_s}$ and $\varphi_{k_s}$ in Eqs. (15) and (16) can give expressions (the Eqs. (D9-D18) in Appendix D) appropriate for calculating $K_s$ numerically, they are too complex to give intuitionistic physical picture. To get this, we take two assumptions. First, only the photon pairs with “HH” polarizations are collected. Second, $r_p$ is relatively large so that the term $G_{k_{s0}}(k_{s0}, k_{s0})$ in $\psi(k_{s0}, k_{s0}, i_0, i_1, j_0, j_1)$ can be approximated by $4\pi \delta(k_{s0}, k_{s0})/r_p^2$.

Under the two assumptions, we get an approximation of $K_s$ as (See detailed derivation in Appendix D)

$$K_s = \frac{1}{8} \int \frac{dk_{s0}}{2\pi} \frac{U(\Omega_s, k_{s0})U(\Omega_s, k_{s0})}{r_p^2}. $$

(18)

An approximated expression of the spatial Schmidt number of the biphoton state generated by SpDC in thick crystal can be obtained as (See detailed derivation in Appendix D)

$$K_s = \frac{3}{8} \int \frac{dk_{s0}}{2\pi} \text{sinc}^2(\Delta k)LU(\Omega_s, k_{s0})U(\Omega_s, k_{s0}), $$

(19)

where $\Delta k$ and $L$ is the longitudinal phase mismatch in the SpDC and the thickness of the second order nonlinear crystal. The comparison between Eqs. (18) and (19) shows clear physics. In Eq. (18), the numerator has contributions of all the modes propagating along the longitudinal direction, while in Eq. (19), the numerator only has contributions of the modes satisfying the longitudinal phase matching condition. The denominators in Eqs. (18) and (19) are same and define the correlation volume [31]. Since the numerator in Eq. (19) is much smaller than that in Eq. (18), $K_s$ is much larger than $K_s$ under the same $r_p$. Therefore, the dimension of the transverse entanglement in the biphoton state generated by SpFWM in ultrathin films could be much higher than that of the state generated by SpDC in bulk crystal, due to the disappearance of the longitudinal phase mismatch. This conclusion is based on the two assumptions leading to Eq. (18), but in Fig. 4 it will be further verified by numerical calculations based on the Eq. (D9-D18) in Appendix D without any approximation.

![Fig. 4 The numerical calculations of the spatial Schmidt number $K_s$ of the biphoton state generated by SpFWM in ultrathin film](image)

The inset shows $K_s$ for biphoton state generated by SpDC in a nonlinear crystal with a length of 1mm. In the calculations of SpFWM, $\lambda_p = 1530\text{nm}$, $\lambda_i = 1580\text{nm}$ and $n_s = 2.6$. In the calculations of SpDC, $\lambda_p = 405\text{nm}$ and $\lambda_i = 810\text{nm}$, and $n_s = n_i = 1.7$.

According to Eq. (15-17), the spatial Schmidt number $K_F$ is calculated numerically and the results are shown in Fig. 4. It can be seen that $K_F$ increases with increasing $r_p$. According to Eq. (18), $K_F$ can be considered as the ratio
between a certain volume and the correlation volume determined by \( r_p \). Larger \( r_p \) gives lower correlation volume and leads to higher \( K_F \). The spatial Schmidt number \( K_F \) versus \( r_p \) for the biphoton state generated by SPDC in a nonlinear crystal with a length of \( L=1\text{mm} \) is also calculated according to the Eq. (23) in Ref. [11], and shown in Fig. 4 for comparison. The comparison between the two curves also show that even with smaller \( r_p \), \( K_F \) could be much higher than \( K_S \).

VI. DISCUSSION ON EXPERIMENTAL DEMONSTRATION

Coincidence photon counting measurement is the way to experimentally investigate the properties of biphoton states generated by SpFWM in ultrathin films. Since the nonlinear interaction length in an ultrathin film is very small, the key to demonstrate the biphoton state generation is whether sufficient coincidence photon counts can be recorded using proper materials and reasonable pump conditions. Several types of films, such as Au films and layered materials, have proven their high third-order nonlinearity [25, 32, 33]. In the following discussions, we will estimate the coincidence photon count rates of the photon pairs generated by SpFWM in some typical ultrathin films.

Consider that a pulsed pump light illuminates the ultrathin film in the vertical direction. It is a Gaussian beam with a Gaussian temporal pulse profile. Its waist locates on the film. The generated signal and idler photons are collected by a multimode collection system. Specifically, they are collected by lens with angular aperture of \( \theta_c \), pass the corresponding frequency filters with unified angular frequency bandwidth of \( \Omega_c \), and finally detected by two single photon detection devices with effective area of \( \pi r_p^2 \). When \( \theta_c \) and \( \Omega_c \) are not too large, the coincidence photon count rate per pulse can be estimated by the following equation (see the detailed derivation in Appendix E)

\[
n_c \approx \alpha_c \eta_c \eta_i (\gamma P_p d_{ph})^2 \Omega_c \tau_p \sin^2 \frac{\theta_c}{2 \lambda_{p0}} \left[ \frac{1}{2} (1+\gamma c^2) + \frac{1}{2} (1-\gamma c^2) \right],
\]

where \( \alpha_c = n_{ph} \sigma^2 / 9 \), \( \eta_c \) (\( \eta_i \)) and \( \lambda_{p0} \) are the detection efficiency of the signal (idler) photons and the central wavelength of the pump light, respectively.

According to Eq. (20), the coincidence count rate \( n_c \) is calculated when graphene, Bi\(_2\)Se\(_3\) and Au films are considered. In Fig. 5 (a), \( n_c \) are plotted with the increasing material thickness \( d \). In the calculation, the pump pulse width \( \tau_p \) and peak power \( P_p \) are 200fs and 80W, respectively. Graphene and Bi\(_2\)Se\(_3\) are treated as layered materials in the calculations, and therefore their thicknesses increase discretely.

It is obvious in Fig.5 (a) that for the three ultrathin films, the coincidence count rate due to SpFWM are much higher. It can be seen that \( n_c \) for graphene and Bi\(_2\)Se\(_3\) is much higher than that for Au films. It is partly due to the higher nonlinear refractive index of graphene and Bi\(_2\)Se\(_3\), and partly due to the stronger absorption in Au films. According to Eqs. (F2) and (F3) in Appendix F, \( d_{ph} \) will increases first increases and then decreases when the thickness of Au film or the layers of graphene and Bi\(_2\)Se\(_3\) increase. This results from the strong absorptions in the materials, and leads to the maximum in the curves of \( n_c \) in Fig.5 (a) for all of the three materials.

The Fig. 5 (b), (c) and (d) show \( n_c \) under increasing pump power \( P_p \) for different materials. Here, the layer numbers of both graphene and Bi\(_2\)Se\(_3\) are \( N_c=15 \), and the thickness of Au film is 20nm. It can be seen that the coincidence count rate for graphene exceeds 0.01 per pulse when \( P_p \) is 500W. For Bi\(_2\)Se\(_3\) film, \( n_c \) approximates 0.1 per pulse when \( P_p \) is 400W. For Au film, although the nonlinearity is lower than the former two materials, it can be compensated by higher \( P_p \). It can be seen that \( n_c \geq 0.01 \) can be obtained under \( P_p = 19.3\text{kHz} \) in Fig.5 (d). In the calculations about Figs. 5 (a-d), \( r_p \) and \( \tau_p \) are always kept at 5\( \mu \text{m} \) and 200fs, respectively. The damage thresholds of graphene and Au film are around 14\( \mu \text{J/cm}^2 \) [34] and 100\( \mu \text{J/cm}^2 \) [35], respectively, which correspond to \( P_p = 55\text{kW} \) and \( P_p = 393\text{kW} \), respectively, with \( r_p \) and \( \tau_p \) mentioned above. In Ref. [33], even when the peak intensity of the incident laser pulses reaches 10.4GW/cm\(^2\), corresponding to \( P_p = 8.16\text{kW} \) with \( r_p = 5\mu \text{m} \), Bi\(_2\)Se\(_3\) shows no damage. Therefore, the peak powers of pump light used in estimating \( n_c \) in Figs. 5 (a-d) are far away from the damage thresholds of the materials. These calculations indicate that the biphoton state generated by SpFWM in ultrathin films could be demonstrated by proper material selection and
reasonable pumping condition, with considerable coincidence count rates for applications on quantum optics and quantum information involving high-dimensional entanglement.

Under the pump power levels used in the calculation in Fig. 5 (b), (c) and (d), Kerr effect might become significant and its influence should be taken into consideration. Since the longitudinal phase mismatching term in the expression of the biphoton state disappears in ultra-thin materials, the change of the refractive index due to Kerr effect may influence the biphoton state only via the unit step functions presenting the truncation of the transverse wavevectors. However, in the numerical calculations of correlation functions in Fig. 2 and frequency purities in Fig. 3, as well as the evaluations of coincidence count in Fig. 5, the unit step function is always within filtering bandwidths. Hence, the Kerr effect has little impact on the results shown in the three figures. Also, it can be calculated that the changes of the refractive index in Au film, graphene and Bi2Se3 are 0.017, 0.005 and 0.05 when the pump powers are set at 2kW, 500w and 400W, respectively, for the three materials. Substituting these refractive index changes into the calculations of Eq. (18), it can be seen that the changes of the refractive index in Au film, graphene and Bi2Se3 are all smaller than 4%. Hence, the Kerr effect also has little impact on the results of Fig. 4.

In conclusion, we have theoretically investigated the biphoton state generated by SpFWM in ultrathin nonlinear films. The expression of the biphoton state is obtained by perturbation method under low parametric gain. Thanks to the ultrathin film structure, the requirement of longitudinal phase coincidence count in Fig. 5, the unit step function is always 1.

**APPENDIX A: DERIVATION OF THE EXPRESSION OF THE BIPHOTON STATE**

In the interaction, the pump is treated as classical electromagnetic waves. For simplicity, we assume the pump field has Gaussian-shape dependence on time \( t \) and spatial coordinates \( x \) and \( y \) in the transverse plane of the thin film. It is linearly polarized and the polarization is parallel to the electrical field in the domains of frequency and spatial frequencies as

\[ \mathbf{E}_p(t,x,y,z) = \hat{x} E_p^{(+)}(t,x,y,z) + \hat{y} E_p^{(-)}(t,x,y,z) \]

Under these assumptions, the electrical field intensity of the pump can be expressed as:

\[ \mathbf{E}_p(t,x,y,z) = \hat{x} E_p^{(+)}(t,x,y,z) + \hat{y} E_p^{(-)}(t,x,y,z) \]

\[ = \hat{x} E_p^{(+)0} e^{-\frac{1}{2} \left( r_p^2 \right)} e^{i(k_{2pr} - \omega_{pr} t)} + \hat{y} E_p^{(-)0} e^{-\frac{1}{2} \left( r_p^2 \right)} e^{i(k_{2pr} + \omega_{pr} t)} \],

where \( \omega_{pr}, r_p \) and \( r_p \) are the central angular frequency, temporal duration and the transverse radius of the pump beam. Here, \( \hat{x} \) is the unit vector along \( x \) axis. After implementing the Fourier transformation for \( t, x \) and \( y \), we express the electrical field in the domains of frequency and spatial frequencies as

\[ \mathbf{E}_p(\omega_p, k_{pr}, k_{pr}, z) = \hat{x} E_p^{(+)}(\omega_p, k_{pr}, k_{pr}, z) + \hat{y} E_p^{(-)}(\omega_p, k_{pr}, k_{pr}, z) \]

\[ = \hat{x} E_p^{(+)0} e^{\frac{1}{2} \left( r_p^2 \right)} e^{i(k_{2pr} - \omega_{pr} t)} + \hat{y} E_p^{(-)0} e^{\frac{1}{2} \left( r_p^2 \right)} e^{i(k_{2pr} + \omega_{pr} t)} \]

where \( \omega_{pr}, k_{pr} \) and \( k_{pr} \) are frequency, the component of the transverse wavevector of the pump field, respectively. The quantized signal and idler fields generated in the SpFWM have expressions [36] of

\[ \hat{E}_s(t,x,y,z) = \hat{E}_s^{(+)}(t,x,y,z) + \hat{E}_s^{(-)}(t,x,y,z) \]

\[ = (2\pi)^\frac{3}{2} \int \frac{d\omega_p}{2\sqrt{c_0^2}} \int d k_{pr} \sum_{j=0, l=0} \hat{a}_s(\omega_p, k_{pr}, k_{pr}, j, l) e^{i(k_{2pr} + k_{j+l})} e^{(-i\omega_{pr} t)} u[k_s(\omega_p) - k_{j+l}] \]

\[ - (2\pi)^\frac{3}{2} \int \frac{d\omega_p}{2\sqrt{c_0^2}} \int d k_{pr} \sum_{j=0, l=0} \hat{a}_s(\omega_p, k_{pr}, k_{pr}, j, l) e^{-i(k_{2pr} + k_{j+l})} e^{(+i\omega_{pr} t)} u[k_s(\omega_p) - k_{j+l}] \],

\[ \hat{E}_i(t,x,y,z) = \hat{E}_i^{(+)}(t,x,y,z) + \hat{E}_i^{(-)}(t,x,y,z) \]
\[
\begin{align*}
&= (2\pi)^{\frac{3}{2}} \int d\omega \int d\omega \int d\omega \sum_{j,k,l=0,1} \hat{\epsilon}_{i,j} \hat{\epsilon}_{i,j} \hat{a}^\dagger(\omega, k_x, k_y, j, l) e^{i(k_x x + k_y y)} e^{-i(\omega t - k_z z)} u[k(\omega) - k_{ij}] \\
&- (2\pi)^{\frac{3}{2}} \int d\omega \int d\omega \int d\omega \sum_{j,k,l=0,1} \hat{\epsilon}_{i,j} \hat{\epsilon}_{i,j} \hat{a}^\dagger(\omega, k_x, k_y, j, l) e^{i(k_x x + k_y y)} e^{-i(\omega t - k_z z - \omega t)} u[k(\omega) - k_{ij}],
\end{align*}
\]

where \(\omega_0 \ (\omega_1)\), \(k_x\) \((k_y)\) and \(k_y\) \((k_y)\) are the frequency, the \(x\)-component and \(y\)-component of the transverse wavevectors of the signal (idler) field, respectively. The meaning of \(j_{ij}\) and \(l_{ij}\) have been given in the paragraph below Eq. (1) in Sec. II. The four indices \(\omega_{x,i}, k_{x,i}, k_{y,i}\) and \(j_{i}, l_{i}\) can determine the wavevector of a mode uniquely. For instance, if a mode has indices \(\omega_x, k_x\) and \(k_y\), its wavevector can be represented as \((k_x, k_y, (1)\sqrt{k_x^2 + k_y^2})\) in the Cartesian coordinate for the upwardly and downwardly propagating modes, respectively, where \(k_z\) is the total angular wavenumber and depend on \(\omega\) via the dispersion relationship \(k_z(\omega)\). In the summation in Eq. (A3) and (A4), \(l_{ij}=0,1\) presents the “TE” and “TM” polarizations, respectively. The vector \(\hat{e}_{x,i}\) and \(\hat{e}_{y,i}\) are unit vectors along the “TE” and “TM” polarization direction for signal (idler) photons. The operators of \(\hat{a}^\dagger(\omega, k_x, k_y, j, l)\) and \((\hat{a}(\omega, k_x, k_y, j, l))\) are the annihilation and creation operators of the signal (idler) fields, respectively. It is notable that the dimensions of \(\hat{a}^\dagger(\omega, k_x, k_y, j, l)\) are the photon number within unit volume in the space spanned by \(\omega, k_x, k_y\) and \(k_{z,i}\) \(\omega, k_x, k_y\). In Eq. (A3) and (A4), \(u(k(\omega) - k_{ij})\) is a unit step function, in which \(k_{ij}=\sqrt{k_x^2 + k_y^2} \ (k_{ij}=\sqrt{k_x^2 + k_y^2})\) is the total transverse angular wavenumber of the signal (idler) field. By the two unit step functions, only the modes propagating along the \(z\) axis are kept in the calculation.

We can use the polar coordinate variables \((k_{ij}, \varphi_{x,i})\) and \((k_{ij}, \varphi_{y,i})\) to replace the Cartesian variables \((k_x, k_y)\) and \((k_x, k_y)\). The relationship between the variables are \(k_x=k_{ij} \cos \varphi_{x,i}, k_y=k_{ij} \sin \varphi_{x,i} \) and \(k_y=\sin \varphi_{y,i}, \) as shown in Fig. 1 (b). Also, an angle \(\theta(x, k_x, k_y,j)\) and \(\theta(x, k_x, k_y,j)\) \((j=1,2)\) is defined to characterize the angle between \(z\) axis and the wavevector of a mode, and they can be calculated by \(\sin \theta_{x,i}(\omega_x, k_x, k_y,j_i)\) \((-1)^{j_i} k_x/ k_{ij}(\omega_x)\). With these variables, we can get

\[
\hat{\epsilon}_{x,0} = -\sin \varphi_{x,i} \hat{\epsilon}_x + \cos \varphi_{x,i} \hat{\epsilon}_y
\]
\[
\hat{\epsilon}_{y,0} = -\sin \varphi_{y,i} \hat{\epsilon}_x + \cos \varphi_{y,i} \hat{\epsilon}_y
\]
\[
\hat{\epsilon}_{x,1} = \sin \theta \hat{\epsilon}_x - \cos \theta \hat{\epsilon}_y, \cos \theta \sin \varphi_{x,i} \hat{\epsilon}_x - \cos \theta \sin \varphi_{y,i} \hat{\epsilon}_y
\]
\[
\hat{\epsilon}_{y,1} = \sin \theta \hat{\epsilon}_x - \cos \theta \hat{\epsilon}_y, \cos \theta \sin \varphi_{x,i} \hat{\epsilon}_x - \cos \theta \sin \varphi_{y,i} \hat{\epsilon}_y
\]

The different polarization components of pump, signal and idler fields are coupled by different components in the nonlinear susceptibility tensor in the SpFWM. Considering that the polarizations of the pump fields are along \(x\) directions and assume that the materials has spatial inversion symmetry, only the tensor components \(\chi^{(3)}_{xxy}\) and \(\chi^{(3)}_{xxz}\) are effective in the SpFWM process. Then, the positive frequency part of the idler polarizations can be obtained as

\[
\hat{P}^{(s)}(x, y, z, t) = \chi^{(3)}_{xxy}[E^{(+)}(x, y, z, t)]^2 \sum_{j_{ij}, k_{ij}} \hat{E}^{(-)}(x, j_{ij}) + \hat{E}^{(+)}(x, j_{ij}) \hat{E}^{(-)}(x, j_{ij})] + \hat{E}^{(+)}(x, y, z, t),
\]

where

\[
\hat{P}^{(s)}(x, y, z, t) = -\chi^{(3)}_{xxy}[E^{(+)}(x, y, z, t)]^2 \sum_{j_{ij}, k_{ij}} \sin \varphi_{x,i} \hat{a}^\dagger(\omega_x, k_x, k_y, j_i, 0) \cos \theta \sin \varphi_{y,i} e^{i(k_x x + k_y y)} e^{-i(\omega t - k_z z)} E^{(+)}(x, y, z, t),
\]

and

\[
\hat{P}^{(s)}(x, y, z, t) = \chi^{(3)}_{xxy}[E^{(+)}(x, y, z, t)]^2 \sum_{j_{ij}, k_{ij}} \sin \varphi_{x,i} \hat{a}^\dagger(\omega_x, k_x, k_y, j_i, 0) \cos \theta \sin \varphi_{y,i} e^{i(k_x x + k_y y)} e^{-i(\omega t - k_z z)} E^{(+)}(x, y, z, t),
\]
Then, the interaction Hamiltonian for the FWM parametric process takes the form of

\[ \hat{H}_i = \omega_i \left[ \int_{\mathbb{R}^2} dx \int_{\mathbb{R}^2} dy \int_{\mathbb{R}^2} dz \left[ \hat{P}^{(+)}(x,y,z,t) \cdot \hat{\mathbf{E}}^{(-)}(t,x,y,z) + h.c. \right] \right] \]  

(A9)

where "\( \ast \)" presents the dot product. In Eq. (A8), \( L_x \) and \( L_y \) are the size of the film along \( x \) (y) direction. Substituting Eqs. (A3), (A4) and (A5) into (A8) and implementing the integrals with variables \( x, y \) and \( z \), we can get the explicit expression of \( \hat{H}_i \) as

\[ \hat{H}_i = -\hbar \chi_{\text{eff}}^{(3)} \frac{\langle \rho_p \rangle^2}{2} - 2\pi \epsilon_0 \sum_{j=0,1} \sum_{l=0,1} \sum_{m=0,1} \int d\omega_i \int d\omega_j \int d\omega_p \int d\omega_{p_2} \int d\omega_{p_2'} \int d\omega_{p_3} \int d\omega_{p_3'} \int d\omega_{p_4} \frac{\epsilon_i^{\ast} \epsilon_j^{\ast} \epsilon_p \epsilon_{p_2} \epsilon_{p_2'} \epsilon_{p_3} \epsilon_{p_3'} \epsilon_{p_4}}{2} e^{-i\omega_0 \epsilon_{p_0} \epsilon_{p_4} e^{-i\omega_0 \epsilon_{p_4}}} \]

\[ \times \left[ \int d\mathbf{k}_{i,j,l} \int d\mathbf{k}_{p,j,l} \int d\mathbf{k}_{p_2,j,l} \int d\mathbf{k}_{p_2',j,l} \int d\mathbf{k}_{p_3,j,l} \int d\mathbf{k}_{p_3',j,l} \int d\mathbf{k}_{p_4,j,l} \right] \cos \left[ \theta (\omega, k_{i,j,l}) \right] \cos \left[ \theta (\omega, k_{i,j,l}) \right] \]

\[ \times \sum_{n=0} \left( r_x \right)^n \cos \left( \phi_{i,j,l} + \frac{l_j - m}{2} \pi \right) \cos \left( \phi_{i,j,l} + \frac{l_j - m}{2} \pi \right) \alpha_i^{\ast} \left( \omega, k_{i,j,l} \right) \alpha_j^{\ast} \left( \omega, k_{i,j,l} \right) \]

(A10)

where \( \Delta \omega = \omega_p - \omega_{p_2} - \omega_{p_3} - \omega_{p_4} \), \( \Delta k_i = k_{p_2} + k_{p_3} - k_{i,j,l} \) and \( \Delta k_j = k_{p_2} + k_{p_3} - k_{i,j,l} \). To simplify the calculation, the dependence of \( \chi_{\text{eff}}^{(3)} \) on the angular frequencies of pump, signal and idler fields are neglected in the derivation of Eq. (A9). Similar with the treatment for SPDC [36], we consider that the size of the ultrathin film in the \( x \)-y plane is much larger than the transverse size of pump beam, and the terms \( L_x \times \text{sinc}(\Delta k_i L_x / 2) \) and \( L_y \times \text{sinc}(\Delta k_j L_y / 2) \) can be replaced by \( 2\pi \delta(\Delta k_i) \) and \( 2\pi \delta(\Delta k_j) \). Also, since the film is ultrathin along \( z \) axis, the term \( \text{sinc}(\Delta k_{i,j,l}) \) can be approximated by 1, i.e., the longitudinal phase mismatch can be neglected. Under the two approximations, Eq. (A9) can be simplified as

\[ \hat{H}_i = -(2\pi)^3 n_p / 6 \int d\mathbf{k}_{i,j,l} \int d\mathbf{k}_{p,j,l} \int d\mathbf{k}_{p_2,j,l} \int d\mathbf{k}_{p_2',j,l} \int d\mathbf{k}_{p_3,j,l} \int d\mathbf{k}_{p_3',j,l} \int d\mathbf{k}_{p_4,j,l} \frac{\epsilon_i^{\ast} \epsilon_j^{\ast} \epsilon_p \epsilon_{p_2} \epsilon_{p_2'} \epsilon_{p_3} \epsilon_{p_3'} \epsilon_{p_4}}{2} e^{-i\omega_0 \epsilon_{p_0} \epsilon_{p_4} e^{-i\omega_0 \epsilon_{p_4}}} \]

\[ \times \left[ \int d\mathbf{k}_{i,j,l} \int d\mathbf{k}_{p,j,l} \int d\mathbf{k}_{p_2,j,l} \int d\mathbf{k}_{p_2',j,l} \int d\mathbf{k}_{p_3,j,l} \int d\mathbf{k}_{p_3',j,l} \int d\mathbf{k}_{p_4,j,l} \right] \cos \left[ \theta (\omega, k_{i,j,l}) \right] \cos \left[ \theta (\omega, k_{i,j,l}) \right] \]

\[ \times \sum_{n=0} \left( r_x \right)^n \cos \left( \phi_{i,j,l} + \frac{l_j - m}{2} \pi \right) \cos \left( \phi_{i,j,l} + \frac{l_j - m}{2} \pi \right) \alpha_i^{\ast} \left( \omega, k_{i,j,l} \right) \alpha_j^{\ast} \left( \omega, k_{i,j,l} \right) \]

(A11)

where \( \gamma = n_p / (\pi r_p^2) \) with \( n_p \) is the nonlinear coefficient in the SpFWM, and \( P_p = 2(2\pi)^2 n_p \epsilon_0 c E_0^2 \) is the peak power of the pump pulses. Here, \( n_p \) is the linear refractive index of the film at the central frequency of the pulsed pump light. In the introduction of \( P_p, E_0 \) is assumed to be real to simplify the calculations. A ratio \( r_x = \chi_{\text{eff}}^{(3)} / \chi_{\text{eff}}^{(3)} \) is defined to indicate the anisotropy of the nonlinear susceptibility in the ultrathin film.

The initial states of the signal and idler fields are vacuum states and they evolve according to Schrödinger equation. For SpFWM, a perturbative solution of this equation is \( \left| \psi \right\rangle \approx -\left( i / \hbar \right) \int_0^\infty dt \hat{H}_i \left| 0 \right\rangle \left| 0 \right\rangle \) [9]. Substituting Eq. (A10) into this solution, we can get

\[ \left| \psi \right\rangle \approx \beta \left( i / \hbar \right) \int_0^\infty dt \hat{H}_i \left| 0 \right\rangle \left| 0 \right\rangle \sum_{j=0,1} \sum_{l=0,1} \sum_{m=0,1} \int d\omega_i \int d\omega_j \int d\omega_p \int d\omega_{p_2} \int d\omega_{p_3} \int d\omega_{p_3'} \int d\omega_{p_4} \]

\[ \times \left[ \int d\mathbf{k}_{i,j,l} \int d\mathbf{k}_{p,j,l} \int d\mathbf{k}_{p_2,j,l} \int d\mathbf{k}_{p_2',j,l} \int d\mathbf{k}_{p_3,j,l} \int d\mathbf{k}_{p_3',j,l} \int d\mathbf{k}_{p_4,j,l} \right] \cos \left[ \theta (\omega, k_{i,j,l}) \right] \cos \left[ \theta (\omega, k_{i,j,l}) \right] \]

\[ \times \sum_{n=0} \left( r_x \right)^n \cos \left( \phi_{i,j,l} + \frac{l_j - m}{2} \pi \right) \cos \left( \phi_{i,j,l} + \frac{l_j - m}{2} \pi \right) \alpha_i^{\ast} \left( \omega, k_{i,j,l} \right) \alpha_j^{\ast} \left( \omega, k_{i,j,l} \right) \]

(A12)

where the parameter \( \beta = i(2\pi)^3 n_p / 3 \). In the derivation of Eq. (A11), \( |\omega_{i,j} - \omega_{p_0}| \ll \omega_{p_0} \) is assumed. The Eq. (A11) can be written in a compact form as

\[ \left| \psi \right\rangle = \sum_{j=0,1} \sum_{l=0,1} \sum_{m=0,1} \int d^3 S \psi (S_j, l_i, j_i, l_i) \alpha_i^{\ast} (S_j, l_i) \alpha_i (S_j, l_i) \left| 0 \right\rangle \left| 0 \right\rangle \]

(A13)

which is the Eq. (1) in Sec. II. The meanings of \( S_{x,y} \) and \( k_{x,y|j|} = [k_{x,y,k_{x,y|j|}}] \) can be found in the explanation of Eq. (1)
in Sec. II. $\psi(S, j, l, j, l)$ is the biphoton probability amplitude function and its expression is shown in Eq. (2) in Sec. II.

**APPENDIX B: CALCULATION OF CORRELATION FUNCTION**

In the case that only the photons propagating upwardly with respect to $x$-$y$ plane are collected, two spatiotemporally varying annihilation operators can be constructed as

\[ \hat{a}_i(t_i, r_i) = (2\pi)^{-3/2} \sum_{j_i=0, l_i=0} \int d\Omega_i \int d^2k_{ij} \hat{a}_i(\Omega_i, k_{ij}, 0, l_i) F_{\Omega_i}(\Omega_i) F_{\delta}(k_{ij}) e^{i(k_{ij} \cdot r_i - \Omega_i t_i)}, \quad (B1) \]

\[ \hat{a}_j(t_j, r_j) = (2\pi)^{-3/2} \sum_{j_j=0, l_j=0} \int d\Omega_j \int d^2k_{jj} \hat{a}_j(\Omega_j, k_{jj}, 0, l_j) F_{\Omega_j}(\Omega_j) F_{\delta}(k_{jj}) e^{i(k_{jj} \cdot r_j - \Omega_j t_j)}, \quad (B2) \]

where $F_{\Omega_i}(\Omega_i)$ and $F_{\delta}(k_{ij})$ are the frequency and spatial frequency filtering functions in the collection and detection of signal and idler photons. The filtering functions in our calculations are shown in the Eqs. (6.1) and (6.2) in Sec. III.

The correlation function can be calculated by [30]

\[ C(t_i, r_i, t_j, r_j) = \langle 0 | \langle 0 | \hat{a}_i(t_i, r_i) \hat{a}_j(t_j, r_j) | \psi' \rangle_{t_i = t_j} \rangle. \quad (B3) \]

After substituting Eqs. (A12), (B1) and (B2) into (B3), and utilizing the commutation relationships

\[ [\hat{a}_i(\Omega_i, k_{ij}, j_i, l_i), \hat{a}_j(\Omega_j, k_{jj}, j_j, l_j)] = \delta(\Omega_i - \Omega_j) \delta(k_{ij} - k_{jj}) \delta(j_i, j_j), \quad (B4) \]

\[ [\hat{a}_i(\Omega_i, k_{ij}, j_i, l_i), \hat{a}_j^†(\Omega_j, k_{jj}, j_j, l_j)] = \delta(\Omega_i - \Omega_j) \delta(k_{ij} - k_{jj}) \delta(j_i, j_j^†), \quad (B5) \]

\[ [\hat{a}_i(\Omega_i, k_{ij}, j_i, l_i), \hat{a}_j^†(\Omega_j, k_{jj}, j_j, l_j)] = [\hat{a}_i(\Omega_i, k_{ij}, j_i, l_i), \hat{a}_j^†(\Omega_j', k_{j}', j_i^', l_i^')] = 0, \quad (B6) \]

we get the expression of $C(t_i, r_i, t_j, r_j)$ as

\[ C(t_i, r_i, t_j, r_j) = \langle 0 | \langle 0 | \hat{a}_i(t_i, r_i) \hat{a}_j^†(t_j, r_j) | \psi' \rangle_{t_i = t_j} \rangle = (2\pi)^{-3} \sum_{j_i=0, l_i=0} \int d\Omega_i \int d^2k_{ij} \int d\phi_i \int d\phi_j G_{\Omega_i}(\Omega_i, \phi_i) G_{\delta}(k_{ij}, \phi_j) \Phi(\phi_i, \phi_j, j_i, l_i) \times \Theta(\Omega_i, k_{ij}, 0, l_i) \Theta(\Omega_i, k_{ij}, 0, l_i) U(\Omega_j, k_{ij}) U(\Omega_j, k_{ij}) F_{\Omega_j}(\Omega_j) F_{\delta}(k_{ij}) e^{i\Omega_i (t_i + t_j)} e^{-i(k_{ij} \cdot r_i + k_{ij} \cdot r_j)} \quad (B7) \]

After substituting Eq. (2) into Eq. (B7), we can get

\[ C(t_i, r_i, t_j, r_j) = C_c \sum_{j_i=0, l_i=0} \int d\Omega_i \int d^2k_{ij} \int d\phi_i \int d\phi_j G_{\Omega_i}(\Omega_i, \phi_i) G_{\delta}(k_{ij}, \phi_j) \Phi(\phi_i, \phi_j, j_i, l_i) \times \Theta(\Omega_i, k_{ij}, 0, l_i) \Theta(\Omega_i, k_{ij}, 0, l_i) U(\Omega_j, k_{ij}) U(\Omega_j, k_{ij}) F_{\Omega_j}(\Omega_j) F_{\delta}(k_{ij}) e^{i\Omega_i (t_i + t_j)} e^{-i(k_{ij} \cdot r_i + k_{ij} \cdot r_j)} \quad (B8) \]

where $C_c = (2\pi)^{-3} \beta \gamma P_d d_{\text{eff}} (\pi r_p^2) (\sqrt{\pi} r_p)$.

Considering the following equations

\[ k_{ij} \cdot r_i = k_{ij} r_i \cos \phi_i \cos \phi_{j} + k_{ij} r_i \sin \phi_i \sin \phi_{j} = k_{ij} r_i \cos (\phi_{ij} - \phi_i), \quad (B9) \]

\[ k_{ij} \cdot r_j = k_{ij} r_j \cos \phi_i \cos \phi_{j} + k_{ij} r_j \sin \phi_i \sin \phi_{j} = k_{ij} r_j \cos (\phi_{ij} - \phi_j), \quad (B10) \]

\[ e^{i(k_{ij} \cdot r_i - \phi_i)} = \sum_{n=-\infty}^{\infty} i^n J_n(k_{ij} r_i) e^{i\phi_i}, \quad (B11) \]

\[ e^{i(k_{ij} \cdot r_j - \phi_j)} = \sum_{n=-\infty}^{\infty} i^n J_n(k_{ij} r_j) e^{i\phi_j}, \quad (B12) \]

we can finish the integrals about $\phi_{ij}$ and $\phi_{ij}$ in Eq. (B8) and get

\[ C(\Delta t, \Delta r) = C_c \sum_{j_i=0, l_i=0} \int d\Omega_i \int d\Omega_j \int d^2k_{ij} \int d^2k_{ij} G_{\Omega_i}(\Omega_i, \phi_i) G_{\delta}(k_{ij}, \phi_j) \times \Theta(\Omega_i, k_{ij}, 0, l_i) \Theta(\Omega_i, k_{ij}, 0, l_i) U(\Omega_j, k_{ij}) U(\Omega_j, k_{ij}) F_{\Omega_j}(\Omega_j) F_{\delta}(k_{ij}) e^{i\Omega_i (t_i + t_j)} e^{-i(k_{ij} \cdot r_i + k_{ij} \cdot r_j)} \]

\[ \times \left[ k_{ij} \delta_{ij} \int k_{ij} dk_{ij} g_{ij}(k_{ij}, k_{ij}) J_{n=0}(k_{ij} r_i) e^{-i(k_{ij} \cdot r_i)} \right] \times \Theta(\Omega_i, k_{ij}, 0, l_i) \Theta(\Omega_i, k_{ij}, 0, l_i) U(\Omega_j, k_{ij}) U(\Omega_j, k_{ij}), \quad (B13) \]

where $g_{ij}(k_{ij}, k_{ij}) = e^{-i(k_{ij}^2 + k_{ij}^2) / 4}$. The expression of $J(k_{ij}, r_i, \phi_i)$ is

\[ J(k_{ij}, r_i, \phi_i) = \frac{1}{4} \sum_{n=-\infty}^{\infty} \int \left[ J_{n+1}(k_{ij} r_i) e^{i(n+1)\phi_i} \right] \left[ (1 - r_j) J_{n+1}(k_{ij} r_j) e^{-i(n+1)\phi_j} e^{-i(k_{ij}^2 / 2) \phi_i} \right. \]

\[ \left. - (1 + r_j) J_{n+1}(k_{ij} r_i) e^{-i(n+1)\phi_i} e^{i(k_{ij}^2 / 2) \phi_i} \right] \]

\[ \times \left[ J_{n+1}(k_{ij} r_j) e^{i(n+1)\phi_j} \right] \left. \left[ (1 - r_j) J_{n+1}(k_{ij} r_j) e^{-i(n+1)\phi_j} e^{-i(k_{ij}^2 / 2) \phi_j} \right. \right] \]

\[ \left. - (1 + r_j) J_{n+1}(k_{ij} r_j) e^{-i(n+1)\phi_j} e^{i(k_{ij}^2 / 2) \phi_j} \right] \]
\[-(1 + r_x) J_{n-1}(k_{ij} r_p^2) e^{-i(k_{ij} r_p^2)} e^{i(n+1) \phi} e^{\frac{-(n+1) \phi}{2}} \] ,

(B14)

where \( L_n(*) \), \( J_{n-1}(*) \), and \( J_{n-1}(*) \) are the \( n \)th-order modified Bessel function, \((n+1)\)th-order Bessel function, and \((n-1)\)th-order Bessel function, respectively.

When \( r_x \) is set at origin, i.e., \( r_x = 0 \), Eq. (14) is simplified to

\[ J(k_{ij} r_p^2) = \frac{1}{2} \left[ (1 + r_x) J_0(k_{ij} r_p^2) \cos\left(\frac{n}{2}(l_i - l_j)\right) - (1 - r_x) J_2(k_{ij} r_p^2) \cos\left(\frac{n}{2}(l_i + l_j) + 2 \phi_i\right) \right] \] .

(B15)

Equations (B13) and (B15) are the Eqs. (7) and (8) in Sec. III, respectively.

**APPENDIX C: CALCULATION OF PURITY OF REDUCED DENSITY MATRIX**

With the collection and detection configuration in the derivation of Eq. (5), we can get an effective biphoton probability amplitude function as [21]

\[ |\psi(e_s, \Omega_s, \Omega_s, k_{ij}, l_i, l_j)|^2 = |\psi(eq, \Omega_s, \Omega_s, k_{ij}, l_i, l_j)|^2 \] (C1)

Then an effective biphoton state can be written as

\[ \sum_{l_i, l_j = 0}^\infty \int d\Omega_s \int d\Omega_f \int d k_{ij} \int d k_{ij} \int d \Omega_{f, i} \int d \Omega_{f, j} |\psi(eq, \Omega_s, \Omega_s, k_{ij}, l_i, l_j)|^2 \] (C2)

To get its density matrix, this effective biphoton state should be normalized [11]. The normalized constant \(|N_e|\) would be obtained by

\[ \sum_{l_i, l_j = 0}^\infty \int d\Omega_s \int d\Omega_f \int d k_{ij} \int d \Omega_{f, i} \int d \Omega_{f, j} |\psi(eq, \Omega_s, \Omega_s, k_{ij}, l_i, l_j)|^2 = 1 \] (C3)

The part within the bracket in Eq. (C3) can be expanded into

\[ \sum_{l_i, l_j = 0}^\infty \int d\Omega_s \int d\Omega_f \int d k_{ij} \int \int d \Omega_{f, i} \int d \Omega_{f, j} |\psi(eq, \Omega_s, \Omega_s, k_{ij}, l_i, l_j)|^2 \]

Substituting the equation

\[ e^{-i (k_{ij} r_p^2 \cos(\phi_i - \phi_j))} = \sum_{n_{\infty}}^\infty (-1)^n L_n(k_{ij} r_p^2 \cos(\phi_i - \phi_j)) \] (C5)

into Eq. (C4) and implementing the integrals about \( \phi_{k_{ij}} \) and \( \phi_{l_i} \), we get

\[ \sum_{l_i, l_j = 0}^\infty \int d\Omega_s \int d\Omega_f \int d k_{ij} \int d \Omega_{f, i} \int d \Omega_{f, j} |\psi(eq, \Omega_s, \Omega_s, k_{ij}, l_i, l_j)|^2 \]

\[ \frac{1}{4} \sum_{l_i, l_j = 0}^\infty \int d\Omega_s \int d\Omega_f \int d k_{ij} \int d \Omega_{f, i} \int d \Omega_{f, j} \]

\[ \times G_{0} (\Omega_s, \Omega_f) g_{0}^2 (k_{ij}, k_{ij}) F_{0}^2 (\Omega_f) F_{0}^2 (k_{ij}) F_{0}^2 (k_{ij}) \]

\[ \times I(k_{ij}, k_{ij}, l_i, l_j) \Theta^2 (\Omega_s, k_{ij}, 0, l_i) U(\Omega_s, k_{ij}) U(\Omega_s, k_{ij}) \] (C6)

where \( I(k_{ij}, k_{ij}, l_i, l_j) = (1 + r_x^2) J_0(r_p^2 k_{ij} r_p^2) + (1 - r_x^2) \cos(l_i - l_j) r_p^2 J_2(r_p^2 k_{ij} r_p^2) \). Then the explicit expression of the normalized constant \( N_e \) is obtained by \(|N_e| = (\sum_{l_i, l_j = 0}^\infty \int d\Omega_s \int d\Omega_f \int d k_{ij} \int d \Omega_{f, i} \int d \Omega_{f, j} |\psi(eq, \Omega_s, \Omega_s, k_{ij}, l_i, l_j)|^2)^{1/2} \) .

The normalized effective biphoton state is

\[ |\psi|_{Ne} = N_e |\psi|_e \] (C7)

We can get the density matrix of this state as

\[ \rho = \sum_{l_i, l_j = 0}^\infty \sum_{l_i, l_j = 0}^\infty \sum_{l_i, l_j = 0}^\infty \int d\Omega_s \int d\Omega_f \int d k_{ij} \int d \Omega_{f, i} \int d \Omega_{f, j} \int d k_{ij} \int d k_{ij} \int d k_{ij} \]
\[
\begin{align*}
\langle \psi, \Omega_{a1}, \Omega_{i1}, k_{s1}, \Omega_{r2}, \Omega_{r1}, k_{r2}, \Omega_{r1}, k_{r1}, I_{s1}, l_{s1}, l_{r1} \rangle \psi, \Omega_{a2}, \Omega_{i2}, k_{s2}, \Omega_{r2}, \Omega_{r1}, k_{r2}, \Omega_{r1}, k_{r1}, I_{s2}, l_{s2}, l_{r2} \rangle
\times a_{j}^{\dagger}(\Omega_{a1}, k_{s1}, l_{s1}, l_{r1}) a_{j}^{\dagger}(\Omega_{a2}, k_{s2}, l_{s2}, l_{r2}) a_{j}(\Omega_{i1}, k_{r1}, l_{r1}) a_{j}(\Omega_{i2}, k_{r2}, l_{r2}) = \mathcal{D}^{2}.
\end{align*}
\]

Tracing out the parameters \(k_{s1,2}, k_{r1,2}, I_{s1,2}\) can reduce the density matrix \(\rho\) to \(\rho_{a_{1},a_{2}}\) which describes the temporal biphoton state. This process can be presented by the following equation
\[
\rho_{a_{1},a_{2}} = \frac{1}{N_{a}} \sum_{I_{s1}=I_{s2}=0}^{1} \sum_{l_{s1}=l_{s2}=0}^{1} \int d k_{s1} \int d k_{s2} a_{j}^{\dagger}(\Omega_{a1}, k_{s1}, l_{s1}, l_{r1}) a_{j}(\Omega_{a2}, k_{s2}, l_{s2}, l_{r2}) a_{j}(\Omega_{i1}, k_{r1}, l_{r1}) a_{j}(\Omega_{i2}, k_{r2}, l_{r2}) .
\]

After that Eq. (C8) is substituted into Eq. (C9) and the commutations
\[
\begin{align*}
a_{j}(\Omega_{a1}, k_{s1}, l_{s1}, l_{r1}) a_{j}(\Omega_{a2}, k_{s2}, l_{s2}, l_{r2}) & = a_{j}(\Omega_{a1}, k_{s1}, l_{s1}, l_{r1}) \delta(\Omega_{a1} - \Omega_{a2}) \delta(\Omega_{r1} - \Omega_{r2}) + a_{j}(\Omega_{a2}, k_{s2}, l_{s2}, l_{r2}) a_{j}(\Omega_{i1}, k_{r1}, l_{r1}) \\
ad_{j}(\Omega_{a1}, k_{s1}, l_{s1}, l_{r1}) a_{j}(\Omega_{a2}, k_{s2}, l_{s2}, l_{r2}) & = a_{j}(\Omega_{a1}, k_{s1}, l_{s1}, l_{r1}) \delta(\Omega_{a1} - \Omega_{a2}) \delta(\Omega_{r1} - \Omega_{r2}) + a_{j}(\Omega_{a2}, k_{s2}, l_{s2}, l_{r2}) a_{j}(\Omega_{i1}, k_{r1}, l_{r1})
\end{align*}
\]
are used, the explicit expression of \(\rho_{a_{1},a_{2}}\) can be calculated as
\[
\begin{align*}
\rho_{a_{1},a_{2}} & = \frac{1}{N_{a}} \sum_{I_{s1}=I_{s2}=0}^{1} \sum_{l_{s1}=l_{s2}=0}^{1} \int d k_{s1} \int d k_{s2} a_{j}^{\dagger}(\Omega_{a1}, k_{s1}, l_{s1}, l_{r1}) a_{j}(\Omega_{a2}, k_{s2}, l_{s2}, l_{r2}) a_{j}(\Omega_{i1}, k_{r1}, l_{r1}) a_{j}(\Omega_{i2}, k_{r2}, l_{r2}) \psi(\Omega_{a1}, \Omega_{i1}, k_{s1}, \Omega_{r2}, \Omega_{r1}, k_{r2}, \Omega_{r1}, k_{r1}, I_{s1}, l_{s1}, l_{r1}) a_{j}^{\dagger}(\Omega_{a2}, \Omega_{i2}, k_{s2}, \Omega_{r2}, \Omega_{r1}, k_{r2}, \Omega_{r1}, k_{r1}, I_{s2}, l_{s2}, l_{r2})
\end{align*}
\]

Next, the purity \(\text{Tr}(\rho_{a_{1},a_{2}}^{2})\) can be obtained as
\[
\begin{align*}
\text{Tr}(\rho_{a_{1},a_{2}}^{2}) & = \int d \Omega_{a} \int d \Omega_{i} a_{j}(\Omega_{a}) a_{j}(\Omega_{a}) \rho_{a_{1},a_{2}} a_{j}(\Omega_{a}) a_{j}(\Omega_{a})
= \frac{1}{N_{a}} \sum_{l_{s1}=l_{s2}=0}^{1} \sum_{l_{s1}=l_{s2}=0}^{1} \int d k_{s1} \int d k_{s2} a_{j}(\Omega_{a1}, k_{s1}, l_{s1}, l_{r1}) a_{j}(\Omega_{a2}, k_{s2}, l_{s2}, l_{r2}) a_{j}(\Omega_{i1}, k_{r1}, l_{r1}) a_{j}(\Omega_{i2}, k_{r2}, l_{r2}) | | \psi(\Omega_{a1}, \Omega_{i1}, k_{s1}, \Omega_{r2}, \Omega_{r1}, k_{r2}, \Omega_{r1}, k_{r1}, I_{s1}, l_{s1}, l_{r1}) | |^{2}
\end{align*}
\]

The Eq. (C13) is the Eq. (11) in Sec. IV and the Eq. (13) is a compact form of Eq. (C14)

**APPENDIX D: CALCULATION OF SPATIAL SCHMIDT NUMBER**

To calculate the spatial Schmidt number, the frequency detunings of the signal and idler photons are fixed at \(\Omega_{s}\) and \(\Omega_{i}\), respectively. If only the upwardly propagating photons are collected, a spatial biphoton state can be obtained as
\[
| N_{k}^{2} = \frac{1}{N_{a}} \sum_{l_{s1}=l_{s2}=0}^{1} \sum_{l_{s1}=l_{s2}=0}^{1} \int d k_{s1} \int d k_{s2} | | \psi(\Omega_{a1}, \Omega_{i1}, k_{s1}, \Omega_{r2}, \Omega_{r1}, k_{r2}, \Omega_{r1}, k_{r1}, I_{s1}, l_{s1}, l_{r1}) | |^{2} | | \psi(\Omega_{a2}, \Omega_{i2}, k_{s2}, \Omega_{r2}, \Omega_{r1}, k_{r2}, \Omega_{r1}, k_{r1}, I_{s2}, l_{s2}, l_{r2}) | |^{2}.
\]

The Eq. (C13) is the Eq. (11) in Sec. IV and the Eq. (13) is a compact form of Eq. (C14)

\[
\begin{align*}
\text{Tr}(\rho_{a_{1},a_{2}}^{2}) & = \frac{B}{| N_{a}^{2} |}.
\end{align*}
\]
expressed as
\[ \sum_{l_0=0}^{2} \sum_{l_0=-1}^{1} \int d\mathbf{k}_{\parallel} \int d\mathbf{k}_{\parallel} \left| \psi(\mathbf{k}_{\parallel}, \mathbf{k}_{\parallel}, l_0, l_0) \right|^2 = \frac{1}{4} C_0^2 G_{\mathbf{k}_{\parallel}}^2 (\Omega_{\mathbf{k}_{\parallel}}, \Omega_{\mathbf{k}_{\parallel}}) \sum_{l_0=0}^{2} \sum_{l_0=-1}^{1} \int d\mathbf{k}_{\parallel} \int d\mathbf{k}_{\parallel} g_\mathbf{k}_{\parallel}^2 (\mathbf{k}_{\parallel}, \mathbf{k}_{\parallel}) \]
\[ \times \left( \mathbf{k}_{\parallel}, \mathbf{k}_{\parallel}, l_0, l_0 \right) \Theta^2 (\Omega_{\mathbf{k}_{\parallel}}, \mathbf{k}_{\parallel}, 0, l_0) \Theta^2 (\Omega_{\mathbf{k}_{\parallel}}, \mathbf{k}_{\parallel}, 0, l_0) \mathcal{U} (\Omega_{\mathbf{k}_{\parallel}}, \mathbf{k}_{\parallel}) \mathcal{U} (\Omega_{\mathbf{k}_{\parallel}}, \mathbf{k}_{\parallel}) \]. \quad (D3)

where \( C_0 \) is the same with that in Eq. (C4) in Appendix C. This expression can give the expression of density matrix of the normalized \( \left| \psi \right\rangle_\mathbf{k} \) as
\[ \rho_k = N_k^{-1} \sum_{l_0=0}^{2} \sum_{l_0=-1}^{1} \int d\mathbf{k}_{\parallel} \int d\mathbf{k}_{\parallel} \int d\mathbf{k}_{\parallel} \int d\mathbf{k}_{\parallel} \left| \psi(\mathbf{k}_{\parallel}, \mathbf{k}_{\parallel}, l_0, l_0) \right|^2 \psi^* (\mathbf{k}_{\parallel}, \mathbf{k}_{\parallel}, l_0, l_0) \psi^* (\mathbf{k}_{\parallel}, \mathbf{k}_{\parallel}, l_0, l_0) \]
\[ \times a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) \]
\[ \times a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) \]
\[ \times a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) \]. \quad (D4)

Then, the dimensions of \( l_0 \) and \( l_0 \) in \( \rho_k \) can be traced to get a reduced density matrix \( \rho_{k_0} \), and the result is
\[ \rho_{k_0} = N_k^{-1} \sum_{l_0=0}^{2} \sum_{l_0=-1}^{1} \int d\mathbf{k}_{\parallel} \int d\mathbf{k}_{\parallel} \int d\mathbf{k}_{\parallel} \int d\mathbf{k}_{\parallel} \left| \psi(\mathbf{k}_{\parallel}, \mathbf{k}_{\parallel}, l_0, l_0) \right|^2 \psi^* (\mathbf{k}_{\parallel}, \mathbf{k}_{\parallel}, l_0, l_0) \psi^* (\mathbf{k}_{\parallel}, \mathbf{k}_{\parallel}, l_0, l_0) \]
\[ \times a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) \]
\[ \times a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) \]
\[ \times a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) \]. \quad (D5)

The purity of \( \rho_{k_0} \) is \( \text{Tr}(\rho_{k_0}^2) \) and can be calculated as
\[ \text{Tr}(\rho_{k_0}^2) = \int d\mathbf{k}_{\parallel} a_\mathbf{k}_{\parallel}(\mathbf{k}_{\parallel}) \rho_{k_0}^2 (\mathbf{k}_{\parallel}) . \quad (D6) \]

After that Eq. (D5) is substituted into Eq. (D6), \( \text{Tr}(\rho_{k_0}^2) \) can be expressed as
\[ \text{Tr}(\rho_{k_0}^2) = \frac{T}{N_k^2} , \quad (D7) \]

where \( N_k = 1/N_k \) and \( T = \sum_{l_0=0}^{2} \sum_{l_0=-1}^{1} \int d\mathbf{k}_{\parallel} \int d\mathbf{k}_{\parallel} \int d\mathbf{k}_{\parallel} \int d\mathbf{k}_{\parallel} \left| \psi(\mathbf{k}_{\parallel}, \mathbf{k}_{\parallel}, l_0, l_0) \right|^2 \psi^* (\mathbf{k}_{\parallel}, \mathbf{k}_{\parallel}, l_0, l_0) \psi^* (\mathbf{k}_{\parallel}, \mathbf{k}_{\parallel}, l_0, l_0) \]
\[ \times a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) \]
\[ \times a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) \]
\[ \times a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) \]. \quad (D8)

Then, it is easy to get the spatial Schmidt number as
\[ K_F = 1/\text{Tr}(\rho_{k_0}^2) = N_k^2 / T . \quad (D9) \]

According to Eq. (3) in Sec. II, the explicit expression of \( \psi(\mathbf{k}_{\parallel}, \mathbf{k}_{\parallel}, l_0, l_0) \) can be obtained. After it is substituted into (D8), and the integrals about \( \varphi_{\mathbf{k}_{\parallel}} \) and \( \varphi_{\mathbf{k}_{\parallel}} \) is implemented, Eq. (D8) can be expressed as
\[ T = \sum_{l_0=0}^{2} \sum_{l_0=-1}^{1} \int d\mathbf{k}_{\parallel} \int d\mathbf{k}_{\parallel} \int d\mathbf{k}_{\parallel} \int d\mathbf{k}_{\parallel} \left| \psi(\mathbf{k}_{\parallel}, \mathbf{k}_{\parallel}, l_0, l_0) \right|^2 \psi^* (\mathbf{k}_{\parallel}, \mathbf{k}_{\parallel}, l_0, l_0) \psi^* (\mathbf{k}_{\parallel}, \mathbf{k}_{\parallel}, l_0, l_0) \]
\[ \times a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) \]
\[ \times a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) \]
\[ \times a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) \]
\[ \times a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) a_\mathbf{k}_{\parallel} (\mathbf{k}_{\parallel}, l_0) \]. \quad (D10)

where
\[ F_1 = \frac{1}{16} \cos \left( \frac{l_1 - l_2 + m_1 - m_2}{2} \pi \right) \cos \left( \frac{l_1 - l_2 + m_1 - m_2}{2} \pi \right) \cos \left( \frac{m_1 - m_2}{2} \pi \right) \]
\[ \times \cos \left( \frac{m_1 - m_2}{2} \pi \right) \sum_{n=-\infty}^{\infty} I_n \left( \frac{r_1^2 k_{\parallel} k_{\parallel}}{2} \right) \int_{l_0}^{l_0} \left( \frac{r_1^2 k_{\parallel} k_{\parallel}}{2} \right) \int_{l_0}^{l_0} \left( \frac{r_1^2 k_{\parallel} k_{\parallel}}{2} \right) \int_{l_0}^{l_0} \left( \frac{r_1^2 k_{\parallel} k_{\parallel}}{2} \right) \], \quad (D11)

\[ F_2 = \frac{1}{128} \cos \left( \frac{l_1 - l_2 + m_1 - m_2}{2} \pi \right) \]
\[ \times \sum_{n=-\infty}^{\infty} I_n \left( \frac{r_1^2 k_{\parallel} k_{\parallel}}{2} \right) \int_{l_0}^{l_0} \left( \frac{r_1^2 k_{\parallel} k_{\parallel}}{2} \right) \int_{l_0}^{l_0} \left( \frac{r_1^2 k_{\parallel} k_{\parallel}}{2} \right) \int_{l_0}^{l_0} \left( \frac{r_1^2 k_{\parallel} k_{\parallel}}{2} \right) \], \quad (D12)

\[ F_3 = \frac{1}{128} \cos \left( \frac{l_1 - l_2 + l_1 - l_2}{2} \pi \right) \]
Utilizing Eqs. (D2) and (D9-D18), the spatial Schmidt number of the biphoton state described by Eq. (2) can be calculated numerically. However, a simpler form of (D9) can be derived under two assumptions. Firstly, we only collect the photon pairs with “TE/TE” polarizations. Secondly, pump beam has relatively large transverse radius, so that the signal and idler photon pairs generated in the SpFWM have $\|k_s\| \approx \|k_i\|$. (With this assumption, the term of $22^2 ||(,)||/4$ in Eq. (3) can be simplified as $2^2 ||(,)||$.) After these two assumptions, Eq. (D8) can be simplified to
\[
N_k = \frac{1}{8} \int \frac{2\pi}{r_p^2} \int d\Omega |U(\Omega, k)| |
\]
According to $N_k = |N_k|^2$ and Eq. (D2), a simplified form of $N_k$ can be obtained as
\[
N_k = \frac{2\pi}{r_p^2} \int d\Omega |U(\Omega, k)| |
\]
with longitudinal thickness of $L$, and the term $\text{sinc}(\Delta kL / 2)e^{i\Delta l / 2}$ originates from the longitudinal phase mismatch. After substituting Eq. (A2) into Eq. (D22), and restricting the signal and idler fields to the propagating fields along $z$ axis, we can obtain

$$
\Psi(k_{s,i},k_{s,i}) = C_s e^{\frac{i \omega_i k_{s,i} + i \omega_i k_{s,i}}{2}} \sin(\frac{\Delta kL}{2}) e^{\frac{i \Delta l}{2}} U(\Omega_{s,i}, k_{s,i}) U(\Omega_{s,i}, k_{s,i})
$$

(D23)

Taking the same process leading to Eqs. (D2), (D8) and (D9), we can get the spatial Schmit number of the SPDC process in thick crystal as

$$
K_S = \frac{N_s^2}{T} \int d\mathbf{k}_{s,i} \sin^2(\Delta kL)U(\Omega_{s,i}, k_{s,i}) U(\Omega_{s,i}, k_{s,i})
$$

(D22)

which is the Eq. (19) in Sec. IV.

**APPENDIX E: ESTIMATING THE COINCIDENCE COUNT RATE OF PHOTON PAIR GENERATION**

The filtering functions of the signal/idler frequency filters are the same to that shown in Eq. (6.1) in Sec. III, and the filtering functions [38] of the collection system can be approximated by Gaussian functions

$$
F_{s,i}(k_{s,i}) = e^{-\frac{k_{s,i}^2}{2\kappa_{s,i}^2}}, \quad F_{i}(k_{s,i}) = e^{-\frac{k_{s,i}^2}{2\kappa_{i}^2}},
$$

(E1)

where $k_{s,i} = \omega_i / c$ and $k_{s,i} = \omega_i / c$ are the wavenumbers of the signal and idler fields in vacuum. When the frequency filtering bandwidth is not too large, and the central angular frequencies of the signal/idler frequency filters are not far away from $\omega_{p,j}$, the filtering functions in Eq. (E1) can be approximated by

$$
F_{s,i}(k_{s,i}) \approx e^{-\frac{k_{s,i}^2}{2\kappa_{s,i}^2}}, \quad F_{i}(k_{s,i}) \approx e^{-\frac{k_{s,i}^2}{2\kappa_{i}^2}}
$$

(E2)

Then, the following operators are constructed

$$
a_{s,i}^\dagger(t_s, r_s) = (2\pi)^{-\frac{3}{2}} \sum_{l_s,j_s=0} d\Omega_{s,i} d\mathbf{k}_{s,i} a_{s,i}^\dagger(\Omega_{s,i}, k_{s,i}, 0, l_s) F_{s,i}(\Omega_{s,i}) F_{s,i}(\mathbf{k}_{s,i}) e^{i(k_{s,i} r_s - \Omega_{s,i} t_s)},
$$

(E3)

$$
a(t_s, r_s) = (2\pi)^{-\frac{3}{2}} \sum_{l_s,j_s=0} d\Omega_{s,i} d\mathbf{k}_{s,i} a_{s,i}(\Omega_{s,i}, k_{s,i}, 0, l_s) F_{s,i}(\Omega_{s,i}) F_{s,i}(\mathbf{k}_{s,i}) e^{i(k_{s,i} r_s - \Omega_{s,i} t_s)}.
$$

(E4)

Since there is no other source of photons at the signal/idler frequencies in the model shown in Fig. 1 (a), except the photon pairs generated in SpFWM, the signal/idler photon generation rate is equal to the photon pair generation rate[2]. When both of the frequency and spatial frequency filtering functions are uniform for the signal and idler photons, we can get the coincidence count rate by $\eta R_s$, where $R_s$ is the single side count rate of signal photon. The expression of $R_s$ is [2]

$$
R_s = \eta \int d\mathbf{r}_s D(\mathbf{r}_s) \langle \Psi | a_{s,i}^\dagger(t_s, \mathbf{r}_s) a(t_s, \mathbf{r}_s) | \Psi \rangle_{x=1},
$$

(E5)

where $D(\mathbf{r}_s) = 1$ ($r_s < r_s$) and $D(\mathbf{r}_s) = 0$ ($r_s > r_s$) are due to the assumption that the single photon detectors have circle aperture with radius $r_s$.

Substituting the expression of $|\Psi\rangle_{x=1}$ in Eqs. (2) and (3) into Eq. (E5), we can get

$$
R_s = (2\pi)^{-\frac{3}{2}} |\beta|^4 \int_{(x_p, y_p, z_p)^2} (\sqrt{\pi r_s^2})^2 \eta \int d\mathbf{r}_s D(\mathbf{r}_s)
$$

$$
\times \langle 0 | \sum_{l_s,m_s=0} \sum_{l_i,m_i=0} d\mathbf{k}_{s,i} d\Omega_{s,i} d\mathbf{k}_{i,i} G_{s,i}(\Omega_{s,i}, \mathbf{k}_{s,i}) G_{i,i}(\mathbf{k}_{i,i}, \mathbf{k}_{i,i})
$$

$$
\times \Phi(\varphi_{s,i}, \varphi_{s,i}, l_s, l_i) \Phi(\varphi_{i,i}, \varphi_{i,i}, 0, l_i) F_{s,i}(\Omega_{s,i}) F_{i,i}(\mathbf{k}_{s,i}) e^{i(k_{s,i} r_s - \Omega_{s,i} t_s)}
$$

$$
\times \sum_{l_s=0} \int d\Omega_{i,i} d\mathbf{k}_{i,i} a_{s,i}(\Omega_{s,i}, \mathbf{k}_{s,i}, 0, l_i) F_{s,i}(\Omega_{s,i}) F_{i,i}(\mathbf{k}_{s,i}) e^{i(k_{s,i} r_s - \Omega_{s,i} t_s)}
$$

$$
\times \sum_{l_i=0} \int d\Omega_{s,i} d\mathbf{k}_{s,i} a_{s,i}(\Omega_{s,i}, \mathbf{k}_{s,i}, 0, l_i) F_{s,i}(\Omega_{s,i}) F_{i,i}(\mathbf{k}_{s,i}) e^{i(k_{s,i} r_s - \Omega_{s,i} t_s)}
$$

$$
\times \sum_{l_s,m_s=0} \sum_{l_i,m_i=0} d\mathbf{k}_{s,i} d\Omega_{s,i} d\mathbf{k}_{i,i} G_{s,i}(\Omega_{s,i}, \mathbf{k}_{s,i}) G_{i,i}(\mathbf{k}_{i,i}, \mathbf{k}_{i,i})
$$

$$
\times \Phi(\varphi_{s,i}, \varphi_{s,i}, l_s, l_i) \Phi(\varphi_{i,i}, \varphi_{i,i}, 0, l_i) F_{s,i}(\Omega_{s,i}) F_{i,i}(\mathbf{k}_{s,i}) e^{i(k_{s,i} r_s - \Omega_{s,i} t_s)}
$$

$$
\times \sum_{l_i=0} \int d\Omega_{s,i} d\mathbf{k}_{s,i} a_{s,i}(\Omega_{s,i}, \mathbf{k}_{s,i}, 0, l_i) F_{s,i}(\Omega_{s,i}) F_{i,i}(\mathbf{k}_{s,i}) e^{i(k_{s,i} r_s - \Omega_{s,i} t_s)}
$$

$$
\times \sum_{l_s,m_s=0} \sum_{l_i,m_i=0} d\mathbf{k}_{s,i} d\Omega_{s,i} d\mathbf{k}_{i,i} G_{s,i}(\Omega_{s,i}, \mathbf{k}_{s,i}) G_{i,i}(\mathbf{k}_{i,i}, \mathbf{k}_{i,i})
$$

$$
\times \Phi(\varphi_{s,i}, \varphi_{s,i}, l_s, l_i) \Phi(\varphi_{i,i}, \varphi_{i,i}, 0, l_i) F_{s,i}(\Omega_{s,i}) F_{i,i}(\mathbf{k}_{s,i}) e^{i(k_{s,i} r_s - \Omega_{s,i} t_s)}
$$

\( \times \sum_{l_i=0} \int d\Omega_{s,i} d\mathbf{k}_{s,i} a_{s,i}(\Omega_{s,i}, \mathbf{k}_{s,i}, 0, l_i) F_{s,i}(\Omega_{s,i}) F_{i,i}(\mathbf{k}_{s,i}) e^{i(k_{s,i} r_s - \Omega_{s,i} t_s)} \).
\[ \times \Theta(\Omega_z, k_{z1}, 0, l_{z1}) \Theta(\Omega_z, k_{z2}, 0, l_{z2}) U(\Omega_z, k_{z2}) U(\Omega_z, k_{z2}) a_{p, \Omega_z, k_{z1}}^+ (\Omega_z, k_{z1}, 0, l_{z1}) a_{p, \Omega_z, k_{z2}}^+ (\Omega_z, k_{z2}, 0, l_{z2}) |0\rangle |0\rangle . \] (E6)

With the commutations
\[
\begin{align*}
[a_i(\Omega, k_i, 0, l_i), a^+_i(\Omega', k_i', 0, l_i')] &= \delta(\Omega - \Omega') \delta(k_i - k_i') \delta_{l_i, l_i'} , \\
[a_i(\Omega, k_i, 0, l_i), a_i^+(\Omega', k_i', 0, l_i')] &= \delta(\Omega' - \Omega) \delta(k_i' - k_i) \delta_{l_i, l_i'} , \\
[a_i(\Omega, k_i, 0, l_i), a_i^+(\Omega', k_i', 0, l_i')] &= \delta(\Omega - \Omega') \delta(k_i - k_i') \delta_{l_i, l_i'} .
\end{align*}
\] (E7)

Eq. (E6) can be simplified into
\[
R_s = (2\pi)^3 |\beta|^2 (\gamma P_d d_{eff})^2 \int d\Omega d\Omega' d(k_i, k_i') \int d\Omega \int d\Omega' \int d(k_i, k_i') \int d(k_i, k_i') \int d(k_i, k_i') \int d(k_i, k_i') 
\times G_{\Omega, \Omega'}(\Omega, \Omega') \Theta(\Omega, k_i, 0, l_i) \Theta(\Omega', k_i, 0, l_i) U(\Omega, k_i) U(\Omega, k_i') \Phi(\varphi_{ki}, \varphi_{kl}, \theta_{kl}, l) U(\Omega', k_i) U(\Omega', k_i') \Phi(\varphi_{ki}, \varphi_{kl}, \theta_{kl}, l) 
\times F_{\Omega, \Omega'}(\Omega, \Omega') F_{\Omega, \Omega'}(\Omega, \Omega') F_{\Omega, \Omega'}(\Omega, \Omega') F_{\Omega, \Omega'}(\Omega, \Omega') \delta^{(4)}(k_{i}, k_{i}' - \Omega - \Omega') e^{i(\Omega - \Omega') \Delta}. \] (E8)

When \( r_p \) and \( \tau_p \) are relatively large, the functions \( G_{\Omega, \Omega'}(\Omega, \Omega') = e^{-(\Omega - \Omega')^2 / 4} \) and \( G_{\Omega, \Omega'}(\Omega, \Omega') = e^{-(\Omega - \Omega')^2 / 4} \) can be approximated by \( G_{\Omega, \Omega'}(\Omega, \Omega') = 2\sqrt{\pi} \delta(\Omega - \Omega') / \tau_p \) and \( G_{\Omega, \Omega'}(\Omega, \Omega') = 4\pi \delta(\Omega - \Omega') / r_p^2 \), respectively. When these approximations are used, Eq. (E8) can be simplified to
\[
R_s = 8\pi^3 |\beta|^2 (\gamma P_d d_{eff})^2 \int d\Omega d\Omega' d(k_i, k_i') \int d\Omega \int d\Omega' \int d(k_i, k_i') \int d(k_i, k_i') \int d(k_i, k_i') 
\times \Theta(\Omega, k_i, 0, l_i) \Theta(\Omega, k_i, 0, l_i) \Theta(\Omega, k_i, 0, l_i) U(\Omega, k_i) U(\Omega, k_i) \Phi(\varphi_{ki}, \varphi_{kl}, \theta_{kl}, l) U(\Omega, k_i) U(\Omega, k_i) \Phi(\varphi_{ki}, \varphi_{kl}, \theta_{kl}, l) 
\times F_{\Omega, \Omega'}(\Omega, \Omega') F_{\Omega, \Omega'}(\Omega, \Omega') F_{\Omega, \Omega'}(\Omega, \Omega') F_{\Omega, \Omega'}(\Omega, \Omega') \delta^{(4)}(k_{i}, k_{i}' - \Omega - \Omega') e^{i(\Omega - \Omega') \Delta}. \] (E9)

According to Eq. (4.2) and the expression of \( U(\Omega_z, k_z) \), the terms \( \Theta(\Omega_z, k_z, 0, l_z) \), \( \Theta(\Omega_z, k_z, 0, l_z) \), \( \Theta(\Omega_z, k_z, 0, l_z) \), \( U(\Omega_z, k_z) \) and \( U(\Omega_z, k_z) \) are all nearly unit when the bandwidths of frequency and spatial frequency filtering processes are not very large. In such case, after the expressions of \( F_{\Omega, \Omega'}(\Omega, \Omega') \) and \( F_{\Omega, \Omega'}(\Omega, \Omega') \) in Eq. (6.1) and Eq. (E2) are substituted into Eq. (9), this equation can be simplified to
\[
R_s = 8\pi^3 |\beta|^2 (\gamma P_d d_{eff})^2 \int d\Omega d\Omega' d(k_i, k_i') \int d\Omega \int d\Omega' \int d(k_i, k_i') \int d(k_i, k_i') \int d(k_i, k_i') 
\times \Theta(\Omega, k_i, 0, l_i) \Theta(\Omega, k_i, 0, l_i) \Theta(\Omega, k_i, 0, l_i) U(\Omega, k_i) U(\Omega, k_i) \Phi(\varphi_{ki}, \varphi_{kl}, \theta_{kl}, l) U(\Omega, k_i) U(\Omega, k_i) \Phi(\varphi_{ki}, \varphi_{kl}, \theta_{kl}, l) 
\times F_{\Omega, \Omega'}(\Omega, \Omega') F_{\Omega, \Omega'}(\Omega, \Omega') F_{\Omega, \Omega'}(\Omega, \Omega') F_{\Omega, \Omega'}(\Omega, \Omega') \delta^{(4)}(k_{i}, k_{i}' - \Omega - \Omega') e^{i(\Omega - \Omega') \Delta}. \] (E10)

With Eq. (E10), the coincidence count per pump pulse can be obtained as \( n_c = \eta_s (\sqrt{\pi \tau_p}) R_s \), which is the Eq. (20) in Sec. V.

**APPENDIX F: PARAMETERS FOR ESTIMATING THE COINCIDENCE COUNT RATE**

Firstly, let us see how to acquire the effective nonlinear interaction length \( d_{eff} \). The losses of the pump light and signal/idler photons along \( z \) direction make \( d_{eff} \) less than the film thickness. These losses are from the material absorptions, and in the following paragraphs the \( d_{eff} \) in different materials will be acquired according to different absorption models.

In Au film, the peak power of the pump light variation along the \( z \) direction obeys the equation
\[
\frac{dP_p(z)}{dz} = -\alpha_0 - \alpha_T A_{\text{eff}},
\] (F1)

where \( \alpha_0 \) is the linear absorption coefficient and \( \alpha_T \) is the two photon absorption (TPA) coefficient, and \( A_{\text{eff}} \) is the effective area of the pump light. In Eq. (2), we can see that the biphoton probability amplitude is proportional to \( P_p d_{eff} \), in which \( P_p \) is the peak power of the pump light before it enters the film. Also, since the signal and idler are weak fields, their decays along \( z \) can be described simply by a factor \( e^{-\alpha_0 z} \) when \( \alpha_0 \) for signal and idler photons are assumed to be the same. Thus, we can define the effective nonlinear interaction length as
\[
d_{eff} = \left[ \frac{1}{d_{eff}^2} \right] d z e^{-\alpha_0 d_{eff}^2} P_p(z)/P_p,
\] (F2)

in which \( P_p(z) \) can be obtained by numerically solving Eq. (F1).

For layered materials, such as graphene and Bi2Se3, the \( d_{eff} \) can be defined according to Ref. [38] and has form of
\[ d_{\text{eff}} = d_L \frac{N_L}{(1 + \frac{N_L}{2} e^{-\alpha_{\text{lut}} d_L})^2 (1 + \frac{N_L}{2} e^{-\alpha_{\text{lut}} d_L}) (1 + \frac{N_L}{2} e^{-\alpha_{\text{lut}} d_L})}, \]  

(F3)

where \( d_L \), \( N \), and \( \alpha_{\text{pl}} \) (\( \alpha_{\text{lut}}, \alpha_{\text{sat}} \)) are the thickness of monolayer, number of layers, and the absorption coefficient of the pump (signal/idler) light in monolayer. The absorption of pump light includes the linear absorption, TPA and saturation absorption (SA).

In graphene, the linear absorption coefficient, TPA coefficient, and the SA threshold of light with wavelength around 1.5 \( \mu m \) are \( \alpha_0 = 5.64 \times 10^{17} / m \), \( \alpha_T = 0.9 \times 10^{16} \text{cm} / \text{GW} \) and \( I_{\text{sat}} = 3 \text{GW} / \text{cm}^2 \) [39]. In Sec. V, \( r_p \) is set as 5 \( \mu m \) and the effective area of the pump light is \( A_{\text{eff}} = \pi r_p^2 \). Under the pump powers used in the calculations about graphene in Sec. V, \( \alpha_T P_p / A_{\text{eff}} \) is much less than \( \alpha_0 \) and the pump light intensity \( P_p / A_{\text{eff}} \) is lower than \( I_{\text{sat}} \). Hence, the TPA and SA effects can be neglected in the calculation of \( d_{\text{eff}} \) for graphene. In Bi\(_2\)Se\(_3\), according to Ref. [33], even when the incident irradiance at 800nm is \( I_{\text{sat}} = 10.4 \text{GW} / \text{cm}^2 \), which corresponds to \( P_p = 8.16 \text{kW} \) with \( r_p = 5 \mu m \), TPA does not occur. Moreover, the SA threshold of Bi\(_2\)Se\(_3\) at 800nm is \( 10.12 \text{GW} / \text{cm}^2 \) and corresponds to \( P_p = 7.9 \text{kW} \) with \( r_p = 5 \mu m \), which is much higher than the power used in the calculations about Bi\(_2\)Se\(_3\) in Sec. V. Thus, in the calculations about Bi\(_2\)Se\(_3\), the TPA and SA effects also can be neglected. Based on these analysis, Eq. (F3) can be simplified to

\[ d_{\text{eff}} = d_L \frac{N}{(1 + \frac{N}{2} e^{-\alpha_{\text{lut}} d_L})^4}, \]

(F4)

where \( \alpha_0 \) is the linear absorption coefficient of graphene/ Bi\(_2\)Se\(_3\). In the derivation of Eq. (F4), \( \alpha_{\text{lut}} \) and \( \alpha_{\text{sat}} \) are assumed to be the same.

Secondly, other parameters used in estimating \( n_\phi \) in different materials are listed in the following table.

| Table F1 Some parameters used in the calculations for Figs. 5 (a-d) |
|---------------------------------|-----------------|-----------------|
| Au film                        | Graphene        | Bi\(_2\)Se\(_3\) |
| \( \lambda_p=600\text{nm} \)   | \( d_L=0.3\text{nm} \) | \( d_L=1\text{nm} \) |
| \( \lambda_s=700\text{nm} \)   | \( \lambda_p=1530\text{nm} \) | \( \lambda_p=800\text{nm} \) |
| \( \Omega/2\pi=1\text{THz} \)  | \( \Omega/2\pi=1\text{THz} \) | \( \Omega/2\pi=1\text{THz} \) |
| \( \theta_r=6' \)              | \( \theta_r=6' \) | \( \theta_r=6' \) |
| \( r_c=1\text{mm} \)           | \( r_c=1\text{mm} \) | \( r_c=1\text{mm} \) |
| \( \chi^{(1)}_{\text{max}}=(10^{-17}+i10^{-18})\text{m}^2/\text{V}^2 \) | \( \chi^{(1)}_{\text{max}}=10^{-15}\text{m}^2/\text{V}^2 \) | \( \chi^{(1)}_{\text{max}}=10^{-15}\text{m}^2/\text{V}^2 \) |
| \( n_{p0}=0.24+i3.07 \)        | \( n_{p0}=2.6 \) | \( n_{p0}=5.5 \) |
| \( \alpha_0=4.45\times10^7/\text{m} \) | \( \alpha_0=5.64\times10^7/\text{m} \) | \( \alpha_0=1.38\times10^7/\text{m} \) |
| \( r_\chi=1 \)                 | \( r_\chi=1/3 \) | \( r_\chi=1/3 \) |

[1] D. N. Klyshko, Photons and Nonlinear Optics (Gordon and Breach, New York, 1988).
[2] C. K. Hong and L. Mandel, Phys. Rev. A 31, 2409 (1985).
[3] J. Chen, X. Li, and P. Kumar, Phys. Rev. A 72, 033801 (2005).
[4] J. Sharpeing, K. Lee, M. Foster, A. Turner, B. Schmidt, M. Lipson, A. Gaeta, and P. Kumar, Opt. Express 14, 12388 (2006).
[5] Y. Guo, W. Zhang, S. Dong, Y. D. Huang, and J. D. Peng, Opt. Lett. 39, 2526-2529 (2014).
[6] J. Zeuner , A. N. Sharma , M. Tillmann , R. Heilmann, M. Gräfe, A. Moqanaki, A. Szameit and P. Walther, Nature 13 1 (2018).
[7] R. Ursin, F. Tiefenbacher, T. Schmitt-Manderbach, and etc., Nature Phys. 3, 481-486 (2007).
[8] Q. C. Sun, Y., L., Mao, S. J. Chen and etc., Nat. Photonics 10, 671 (2016).
[9] M. H. Rubin, D. N. Klyshko, Y. H. Shih, and A. V. Sergienko, Phys. Rev. A 50, 5122 (1994).
[10] A. Gatti, T. Corti, E. Brambilla, and D. B. Horoshko, Phys. Chem. Phys. A 86, 053803 (2012).
[11] Y. Zhang and F. S. Roux, Phys. Rev. A 89, 063802 (2014).
[12] J. Peña, Jr., Phys. Rev. A 93, 013852 (2016).
[13] G. Molina-Terriza, S. Minardi, Y. Deyanova, C. I. Osorio, M. Hendrych, and J. P. Torres, Phys. Rev. A 72, 065802 (2005).
[14] O. Jedrkiewicz, M. Clerici, A. Picozzi, D. Faccio, and P. Di Trapani, Phys. Rev. A 76, 033823 (2007).
[15] A. Gatti, E. Brambilla, L. Caspani, O. Jedrkiewicz, and L. A. Lugliato, Phys. Rev. Lett. 102, 223601 (2009).
