

How to use the dispersion in the $\chi^{(3)}$ tensor for broadband generation of polarization-entangled photons

Valeria Vento ^{1,2} Francesco Ciccarello ^{1,2} Sakthi Priya Amirtharaj ^{1,*} and Christophe Galland ^{1,2,†}

¹*Institute of Physics, Swiss Federal Institute of Technology Lausanne (EPFL), CH-1015 Lausanne, Switzerland*

²*Center of Quantum Science and Engineering, Swiss Federal Institute of Technology Lausanne (EPFL), CH-1015 Lausanne, Switzerland*



(Received 9 August 2024; accepted 28 March 2025; published 16 April 2025)

Polarization-entangled photon pairs are a widely used resource in quantum optics and technologies and are often produced using a nonlinear process. Most sources based on spontaneous parametric down-conversion have relatively narrow optical bandwidths because the pump, signal, and idler frequencies must satisfy a phase-matching condition. Extending the bandwidth—for example, to achieve spectral multiplexing—requires changing some experimental parameters such as temperature, crystal angle, poling period, etc. Here we demonstrate broadband (tens of THz for each photon) generation of polarization-entangled photon pairs by spontaneous four-wave mixing in a diamond crystal, with a simple colinear geometry requiring no further optical engineering. Our approach leverages the quantum interference between electronic and vibrational contributions to the $\chi^{(3)}$ tensor. Entanglement is characterized by a single realization of a Bell test over the entire bandwidth using fiber dispersion spectroscopy and fast single-photon detectors. The results agree with the biphoton wave function predicted from the knowledge of the $\chi^{(3)}$ and Raman tensors and demonstrate the general applicability of our approach to other crystalline materials.

DOI: [10.1103/PhysRevResearch.7.L022017](https://doi.org/10.1103/PhysRevResearch.7.L022017)

Introduction. Nonlinear optical processes play a pivotal role in producing and engineering quantum states of light. Spontaneous parametric down-conversion (PDC) and four-wave mixing (FWM), which rely, respectively, on the $\chi^{(2)}$ and $\chi^{(3)}$ susceptibility of materials, have been employed for generating a variety of photonic quantum states [1]—entangled photon pairs generated in the low-gain regime being the most popular class. PDC sources generally offer the highest brightness because, for noncentrosymmetric crystals, the efficiency of $\chi^{(2)}$ processes is much larger than that of $\chi^{(3)}$ processes. A challenge with PDC is the large frequency difference between the pump and the signal (or idler) fields that restricts the spectral bandwidth over which phase matching can be achieved without modifying the experimental conditions or implementing delicate dispersion engineering in periodically poled waveguides [2]. Moreover, materials such as silicon and diamond have no $\chi^{(2)}$ nonlinearity while being popular platforms for integrated quantum photonics at telecom and visible wavelengths, respectively [3]; it motivates the use of FWM for generating entangled photons.

Among the photonic degrees of freedom that can be entangled, polarization is often the easiest to manipulate and measure. However, generating polarization entanglement usually requires careful engineering of the source, since parametric nonlinear processes more naturally generate photon pairs that are entangled in the temporal and spatial degrees of freedom due to energy and momentum conservation, respectively. There are relatively few demonstrations of polarization-entangled photon pairs produced by spontaneous FWM, with the most established methods relying on the $\chi^{(3)}$ nonlinearity of optical fibers [4–7] or silicon waveguides [8,9] that are themselves embedded within a Sagnac loop. The photon pairs produced by FWM in glass fibers or silicon waveguides are typically copolarized, and or entanglement is generated from two orthogonal sources after erasing distinguishing information in all other degrees of freedom (spatial and temporal). This erasure has also been achieved using a fully integrated silicon photonic circuit comprising a polarization rotator between TE and TM modes [10]. To simplify such FWM sources, researchers leveraged the tensorial nature of the $\chi^{(3)}$ nonlinear response and engineered the polarization mode dispersion to achieve polarization entanglement directly out of silicon [11] and AlGaAs [12] waveguides.

When FWM is used to generate photon pairs, vibrational Raman scattering is mostly known as a source of noise degrading the purity of the joint quantum state [13,14]. This problem is particularly pronounced in amorphous media such as optical fibers because the Raman scattered light has a broad spectrum [15]. In crystalline materials such as silicon, AlGaAs, and diamond, the Raman peak is very sharp (few wave numbers), so Raman noise is more easily avoided by choosing

*Present address: Centre for Quantum Information, Communication and Computing, Indian Institute of Technology Madras, Chennai, Tamil Nadu 600036, India.

†Contact author: chris.galland@epfl.ch

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an appropriate detuning from the pump. Interestingly, a recent work by Freitas *et al.* showed that polarization entanglement can be generated from bulk diamond for pairs detuned by $\pm 900 \text{ cm}^{-1}$ from the degenerate two-photon pump [16], a result qualitatively attributed to the interference of electronic and vibrational (Raman) microscopic pathways leading to photon pair creation.

In this Letter, inspired by Ref. [16], we establish a theory of polarization-entangled photon pair generation using FWM in diamond (also applicable to silicon and other crystals for which the $\chi^{(3)}$ and Raman tensors are known) and validate our predictions by performing coincidence measurements and Bell tests over a large optical bandwidth of 2200 cm^{-1} (65 THz) on either side of the pump frequency (spanning 130 THz in total). Moreover, we achieve this characterization in a single set of polarization measurements by employing fiber spectroscopy [17], where the frequency information of individual photons is mapped onto detection time through the natural dispersion of optical fibers. The relaxed phase-matching condition for FWM enables statistically significant violation of the Clauser-Horne-Shimony-Holt (CHSH) inequality [18] for the Ψ^+ Bell state across a considerable bandwidth at all measured frequency shifts below 1250 cm^{-1} (37.4 THz)—a bandwidth on par with that of state-of-the-art single-photon sources in optimized photonic platforms [19,20]. We find that our results agree with the theoretical predictions accounting for the frequency dependence of $\chi^{(3)}$ that is due to the sharp vibrational Raman resonance at 1332 cm^{-1} .

We notice that the term “broadband” is sometimes used in the literature to indicate correlated photon-pair sources capable of establishing entanglement between far-detuned photons—typically to bridge visible and telecom ranges—while keeping a narrow linewidth [21]. On the contrary, we generate a broad bandwidth of entangled photon pairs at once with a single pump laser of fixed frequency, similar to a recent demonstration on a CMOS platform [22]. In this sense, our technique also offers an advantage over coherent anti-Stokes Raman scattering (CARS) for probing third-order nonlinearities. Indeed, the dispersion features we analyze could be obtained with CARS only by employing an additional broadly tunable (170 nm) visible pump. In analogy to CARS, a recent work [23] used a tunable THz source to evidence third-harmonic enhancement and suppression in diamond, qualitatively explained in terms of the same $\chi^{(3)}$ dispersion.

Results. Figure 1(a) illustrates the concept of the experiment in the frequency domain. Two vertically polarized pump photons at frequency ω_p can generate pairs of correlated photon pairs at ω_S (Stokes) and $\omega_A \equiv 2\omega_p - \omega_S$ (anti-Stokes) frequencies, satisfying energy conservation. The polarization state of the correlated pair is determined by the third-order susceptibility tensor of diamond, as we will explicate below. Quite generally, the existence of a Raman-active optical phonon mode at frequency Ω_v causes a resonant contribution to the $\chi^{(3)}$ tensor when photon pairs satisfy $\omega_{A/S} = \omega_p \pm \Omega_v$ [24]. Our results are, therefore, applicable to other crystalline materials and optical media in general.

Figure 1(b) shows the experimental setup. A mode-locked titanium:sapphire oscillator (Tsunami, Spectra Physics) generates 200-fs pulses at 781 nm with a repetition rate of

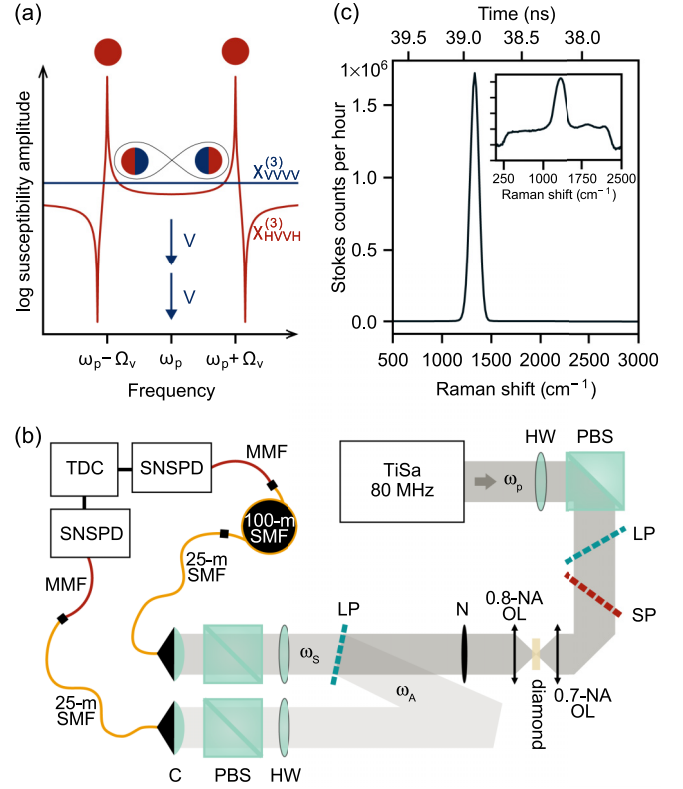


FIG. 1. (a) Sketched amplitude of the two relevant $\chi^{(3)}$ tensor elements in diamond under vertically polarized pump (blue arrows) at ω_p ; Ω_v is the Raman-active optical phonon frequency. Circles of matching colors represent correlated photons at Stokes (ω_S) and anti-Stokes (ω_A) frequencies, with the generation of the $\Psi^\pm$ Bell states expected where $|\chi_{HVHV}^{(3)}| \simeq |\chi_{VVVV}^{(3)}|$. (b) Experimental setup. HW: Half-wave plate. PBS: Polarizing beam splitter. OL: Objective lens. LP: Tunable long-pass filter. SP: Tunable short-pass filter. N: Notch. C: Coupler. SMF: Single-mode fiber. MMF: Multimode fiber. SNSPD: Superconducting nanowire single-photon detector (Eos 210 CS, Single Quantum), TDC: Time-to-digital converter (ID900, ID Quantique). The sample is a 300- μm -thick synthetic diamond crystal cut perpendicular to the [100] crystal axis. (c) Stokes spectrum measured by single-photon fiber spectroscopy (logarithmic scale in inset).

80 MHz. To resolve the sharp spectral dependence of the susceptibility sketched in Fig. 1(a), the pump pulse duration should be of the same order of magnitude as the phonon coherence time, which is around 8 ps in diamond [25]. We use tunable long-pass (LP) and short-pass (SP) filters to increase the pulse duration to 1.1 ps by reducing the spectral width to 0.8 nm. The average power on the sample is 48 mW (600 pJ pulse energy), below the onset of single-beam stimulated processes [26].

The collected Stokes and anti-Stokes signals are split into two different paths by a long-pass interference filter placed almost perpendicular to the beam to minimize the polarization-dependent response between *s* and *p* components. Next, each signal is spectrally dispersed through 25 m of single-mode fibers (SMFs). Since losses also increase with the fiber length, we add 100 m SMF only to the Stokes path.

Knowing the dispersion parameters of the fibers, we can convert photon detection times into detuning from the pump in wave numbers [27]. Superconducting nanowire single-photon detectors (SNSPDs) allow us to achieve a temporal resolution of around 30 ps per detector (time jitter). Figure 1(c) shows the Stokes spectrum obtained—the laser synchronization pulse is used as the start signal and the detection of a H polarized Stokes photon as the stop signal.

Fiber spectroscopy has been employed to measure various spectral properties of photon pairs generated by PDC, like the joint spectral amplitude [28] and the second-order correlation function [29]. Reference [30] measured the spectrum of PDC-generated polarization-entangled photons, but the spectral variation of the quantum state was not addressed. Our work reveals the frequency evolution of the degree of purity, polarization entanglement, and nonlocality of the biphoton state generated by FWM. Our measurement technique can also be used to characterize sources of polarization-entangled photons implemented in flat optical systems [31–33], including metamaterials [34,35] and nanoresonators [36,37].

Since diamond is centrosymmetric, the third-order susceptibility mediates the lowest-order nonlinear optical processes. It is a complex rank-3 tensor that depends on the frequencies and polarizations of the four fields involved: $\chi_{ijkl}^{(3)}(\omega_A, \omega_p, \omega_s)$, where the indices i, j, k, l specify the polarization directions of the fields at the four frequencies listed in the same order in the parenthesis. In a stimulated scattering experiment, two incoming beams at ω_p and ω_s can generate light at ω_A through the following third-order nonlinear processes: (i) stimulated Raman scattering, when $\omega_p - \omega_s = \Omega_v$, which is the optical phonon frequency; (ii) two-photon absorption, when $2\omega_p$ corresponds to an electronic transition; and (iii) any nonresonant FWM process mediated by far-detuned electronic levels. In 1974, Levenson and Bloembergen performed stimulated FWM spectroscopy on diamond, and from the independent knowledge of the Raman tensor and Raman gain, they extracted all components of its $\chi^{(3)}$ tensor [38].

In our experiment, we employ a single pump beam with frequency ω_p far from any electronic resonance. We can therefore neglect two-photon absorption and write $\chi^{(3)} = \chi^{(3)E} + \chi^{(3)R}$, where $\chi^{(3)E}$ is the nonresonant—hence real—electronic FWM contribution and $\chi^{(3)R}$ is the (complex) vibrational Raman scattering contribution featuring a resonance at $\omega_{A/S} = \omega_p \pm \Omega_v$ [24], where Ω_v is the frequency of the optical phonon at 1332 cm^{-1} . The pump propagates along the [100] crystallographic axis and the diamond is rotated to align the [001] axis with the pump polarization, which is vertical in the laboratory frame [27]. In this configuration, Raman scattering ($\chi^{(3)R}$) only generates horizontally polarized pairs [16,38]. Figure 2(a) shows the amplitude and phase of the nonzero components of the susceptibility tensor contributing in this case,

$$\chi_{VVVV}^{(3)} = \chi_{VVVV}^{(3)E} \equiv F \chi_{HVHH}^{(3)E}, \quad (1)$$

$$\chi_{HVHH}^{(3)} = \chi_{HVHH}^{(3)E} + \chi^{(3)R} = \chi_{HVHH}^{(3)E} \left(1 + \frac{\Delta}{\Omega_v - \omega + i\Gamma_v} \right), \quad (2)$$

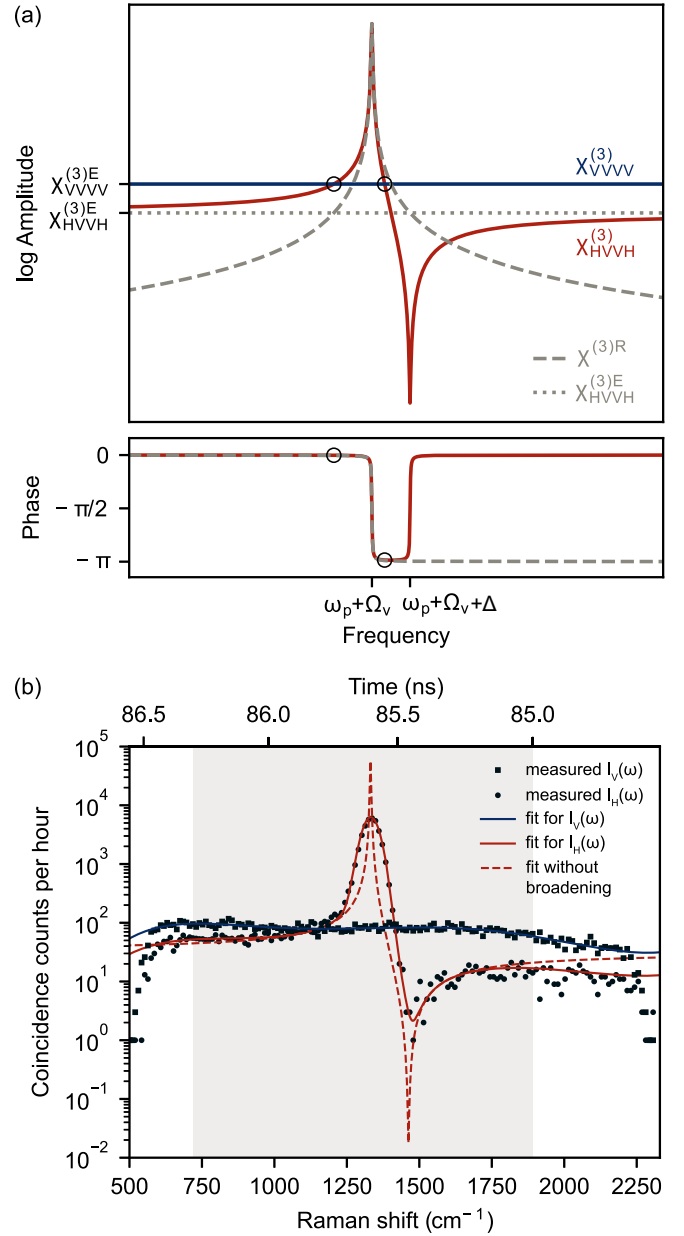


FIG. 2. (a) Theoretical amplitude and phase of $\chi_{VVVV}^{(3)}$ (solid blue) and $\chi_{HVHH}^{(3)}$ (solid red). The Raman and the electronic contributions to the latter are shown as dashed and dotted gray lines, respectively. At the frequencies where $\chi_{VVVV}^{(3)}$ and $\chi_{HVHH}^{(3)}$ have the same amplitude (Eq. (5)), the maximally entangled states $|\Psi_{\pm}\rangle$ are generated [Eq. (5)]. (b) Frequency-resolved anti-Stokes–Stokes coincidences measured after selecting V (black squares) or H (black circles) polarization in the two detection paths. The data are acquired in 1 h. The solid blue curve is a polynomial fit that reflects the setup polarization response function since no resonances are expected in this configuration. The solid red curve represents the fit function $A \log(I_H(\omega) * G(\omega)) + b$ multiplied by the setup response, where the free parameters $\Delta = 130.59 \text{ cm}^{-1}$, $\sigma_G = 24.80 \text{ cm}^{-1}$, $A = 0.82$, $b = 1.51$ are extracted by fitting within the gray region. The dashed red line shows the fit function without convolution, corresponding to the red line in (a).

where $\omega = \omega_p - \omega_s = \omega_A - \omega_p$, and $\Gamma_v = 2\pi c\gamma_v$ is the vibrational decay rate with $\gamma_v \simeq 1 \text{ cm}^{-1}$ the Raman linewidth.

Following Ref. [38], we define $\Delta = \frac{|\alpha^R|^2 N}{24\hbar\chi_{HVVH}^{(3)E}}$, where α^R is proportional to the Raman tensor and N is the volumic density of unit cells. The value of Δ corresponds to the angular frequency difference between the maximum and minimum of $|\chi_{HVVH}^{(3)}|$, i.e., between the points of maximum constructive and destructive interference of $\chi^{(3)E}$ and $\chi^{(3)R}$ (Fig. 2).

The measured rate of photon pairs for V and H polarizations follow the proportionality relations $I_V(\omega) \propto |\chi_{VVVV}^{(3)}|^2$ and $I_H(\omega) \propto |\chi_{HVVH}^{(3)}|^2$, respectively. We measure them by counting the coincidences between anti-Stokes and Stokes photons after they pass through parallel polarizers, as displayed in Fig. 2(b). Since $\chi_{VVVV}^{(3)}$ is theoretically constant in frequency, we use the measured $I_V(\omega)$ as a characterization of the setup spectral response, which we assume to be polarization independent (the polarization of photons is largely scrambled by the time they impinge on the SNSPD). To account for the spectral broadening due to the finite pump bandwidth and the temporal jitter of the detectors, the theoretical H -polarized intensity $|\chi_{HVVH}^{(3)}|^2$ is convoluted with a Gaussian $G(\omega)$ of variance σ_G^2 centered at Ω_v . After multiplying by the setup response extracted above, the resulting model [red line in Fig. 2(b)] accurately reproduces our data.

In the Appendix, we give the general biphoton polarization state generated under arbitrary pump polarization. For a vertical pump polarization, the wave function reduces to

$$|\psi(\omega)\rangle = \chi_{HVVH}^{(3)E} \left[F |VV\rangle + \left(1 + \frac{\Delta}{\Omega_v - \omega + i\Gamma_v} \right) |HH\rangle \right]. \quad (3)$$

As is customary for spontaneous PDC and FWM in the low gain regime, this biphoton wave function should be understood as the one-photon-pair component of the full two-mode squeezed state. It is an excellent description of the results obtained by coincidence measurements (which are not sensitive to the vacuum component) as long as the probability of photon pair emission is much smaller than one per pulse, so double-pair emission is a negligible process. The probability $P_{\theta_1, \theta_2}(\omega)$ to measure a coincidence when Stokes and anti-Stokes polarizers are set at angles θ_1 and θ_2 is expressed in the Appendix; from Eq. (A6), we extract the correlation parameter $E_{\theta_1, \theta_2}(\omega) = P_{\theta_1, \theta_2}(\omega) + P_{\theta_1 + \pi/2, \theta_2 + \pi/2}(\omega) - P_{\theta_1, \theta_2 + \pi/2}(\omega) - P_{\theta_1 + \pi/2, \theta_2}(\omega)$ and the CHSH parameters [18]

$$S^{\Psi\pm}(\omega) = E_{0, \theta}(\omega) + E_{0, -\theta}(\omega) \pm E_{2\theta, \theta}(\omega) \mp E_{2\theta, -\theta}(\omega), \quad (4)$$

where $\theta = \pi/8$. The corresponding Bell inequalities $S^{\Psi\pm}(\omega) \leq 2$ are maximally violated by the Bell states

$$|\Psi_{\pm}\rangle = \frac{|HH\rangle \pm |VV\rangle}{\sqrt{2}}, \quad (5)$$

respectively. As shown in Figs. 3(a) and 3(b), we extract the parameters $S^{\Psi\pm}(\omega)$ for $\phi = \xi = 0$ from the direct measurement of $n_{\theta_1, \theta_2}(\omega)$ and compare them with the values theoretically computed from Eqs. (A7)–(4) with Δ and σ_G fixed by the measurement of $I_V(\omega)$ and $I_H(\omega)$ in Fig. 2(b). The F parameter is set to 2 to best reproduce the data within a range of values constrained by the material's anisotropy [27]. The measured and theoretical values demonstrate good agreement. The Bell inequality for $S^{\Psi+}(\omega)$ is violated by up

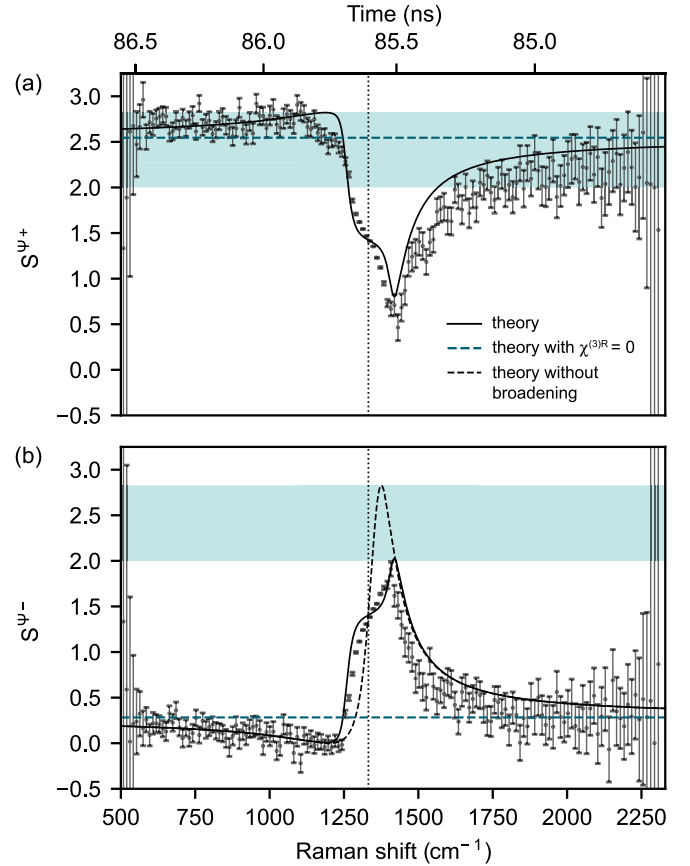


FIG. 3. (a), (b) Symbols represent the measured CHSH parameters $S^{\Psi+}(\omega)$ (a) and $S^{\Psi-}(\omega)$ (b) extracted from a set of 16 coincidence measurements of 1 h each (four measurements for each of the four correlation parameters $E_{\theta_1, \theta_2}(\omega)$ appearing in Eq. (4), see also Ref. [27]). The error bars are calculated by propagating the standard deviation of the coincidence counts in the region $[630, 890] \text{ cm}^{-1}$. The shaded domain is delimited by the upper classical bound of 2 and the upper quantum bound of $2\sqrt{2}$. The dotted black vertical line indicates the Raman resonance, solid lines are theoretical curves computed from Eqs. (A7)–(4); dashed blue lines are computed from Eq. (3) without the Raman contribution. In (b), the dashed black curve is computed without accounting for the setup response.

to 8.7 standard deviations over a broad spectral range below 1250 cm^{-1} . The measured and theoretical values of $S^{\Psi-}(\omega)$ display no violation of the corresponding Bell inequality. This is a consequence of the suboptimal spectral resolution of the measurement. In the ideal case, before the convolution with the Gaussian $G(\omega)$ (dashed black curve), the inequality is violated in a narrow spectral region around 1375 cm^{-1} , where the biphoton state is $|\psi(\omega)\rangle \approx |\Psi_{-}\rangle$.

Conclusion. In summary, we built on the recent observation of a polarization entangled photon from a nonlinear process in diamond [16] to establish a complete theory of the biphoton wave function resulting from spontaneous four-wave mixing in the presence of electronic and vibrational contributions to the third-order nonlinearity, validating our predictions with a fiber-assisted spectrally resolved Bell test. In our experiment, the coincidence detection rate of polarization-entangled photon pairs per unit bandwidth is of $\sim 0.25 \text{ Hz/nm}$ for a

pump power of 48 mW, with an overall detection efficiency not better than a few percent (including total internal reflection inside the diamond, fiber coupling losses, propagation losses, and detector efficiency). The pair generation rate is therefore on the order of 10 Hz/nm for an interaction length of $\sim 3 \mu\text{m}$ determined by the depth of focus. How much could the brightness of the source be improved? As detailed in the Appendix, based on the results from Ref. [39], we estimate that a centimeter-long diamond waveguide pumped under similar conditions would generate pairs at a rate of 10 to 100 kHz/nm, which would further increase quadratically with pump power and be enhanced using photonic resonators. Our results, therefore, motivate the further development of diamond photonic integrated circuits tailored to produce broadband polarization-entangled photons around any center wavelength in the material's transparency window.

Note added in proof. Related results have been independently obtained in Ref. [40].

Acknowledgments. We acknowledge Professor A. Jorio and his team for insightful discussions. This work received funding from the European Union's Horizon 2020 research and innovation program under Grant Agreement No. 820196 (ERC CoG QTONE) and from the Swiss National Science Foundation (Projects No. 214993 and No. 198898).

V.V. and F.C. performed the measurements, V.V. and S.P.A. implemented the fiber spectroscopy setup, V.V. analyzed the

data and developed the model, V.V. and C.G. wrote the paper, C.G. led the project.

The authors declare no competing interests.

Data availability. The data that support the findings of this study will be deposited in a Zenodo repository [41].

Appendix: derivation of the general biphoton wave function

1. Arbitrary pump polarization. We consider a pump field with arbitrary polarization represented by the normalized amplitudes $a_V = \cos \phi$ and $a_H = \sin \phi e^{i\xi}$, where $\phi \in [0, \frac{\pi}{4}]$ and $\xi \in [0, \frac{\pi}{2}]$. In addition to Eqs. (1) and (2), we must consider

$$\chi_{VVHH}^{(3)} = \chi_{HVHV}^{(3)E} F' \left(1 + \frac{1}{2F'} \frac{\Delta}{\Omega_v - \omega + i\Gamma_v} \right), \quad (\text{A1})$$

where $F' \equiv \chi_{VVHH}^{(3)E} / \chi_{HVHV}^{(3)E}$ is related to F by the material's anisotropy [27] and the following identities hold:

$$\chi_{VVVV}^{(3)} = \chi_{HHHH}^{(3)}, \quad (\text{A2})$$

$$\chi_{HVHH}^{(3)} = \chi_{VHHV}^{(3)}, \quad (\text{A3})$$

$$\chi_{VVHH}^{(3)} = \chi_{HHVV}^{(3)} = \chi_{HVHV}^{(3)} = \chi_{VHVH}^{(3)}. \quad (\text{A4})$$

Following Eqs. (1)–(A4), we can write the non-normalized biphoton wave function generated by the nonlinear interaction for an arbitrary pump polarization:

$$\begin{aligned} |\psi(\omega)\rangle = & \chi_{HVHV}^{(3)E} \left[\left(a_V^2 F + a_H^2 \left(1 + \frac{\Delta}{\Omega_v - \omega + i\Gamma_v} \right) \right) |VV\rangle + \left(a_H^2 F + a_V^2 \left(1 + \frac{\Delta}{\Omega_v - \omega + i\Gamma_v} \right) \right) |HH\rangle \right. \\ & \left. + 2a_V a_H F' \left(1 + \frac{1}{2F'} \frac{\Delta}{\Omega_v - \omega + i\Gamma_v} \right) (|HV\rangle + |VH\rangle) \right]. \end{aligned} \quad (\text{A5})$$

When the Stokes and anti-Stokes polarizers are set at angles θ_1 and θ_2 , respectively, from the vertical, the coincidence detection probability is computed as

$$P_{\theta_1, \theta_2}(\omega) = \frac{n_{\theta_1, \theta_2}(\omega)}{n_{\theta_1, \theta_2}(\omega) + n_{\theta_1 + \pi/2, \theta_2 + \pi/2}(\omega) + n_{\theta_1, \theta_2 + \pi/2}(\omega) + n_{\theta_1 + \pi/2, \theta_2}(\omega)}, \quad (\text{A6})$$

where

$$n_{\theta_1, \theta_2}(\omega) = P_{\theta_1, \theta_2}^{\text{th}}(\omega) * G(\omega) \quad (\text{A7})$$

is the expected measured coincidence counts obtained by spectral convolution of the non-normalized theoretical joint detection probability $P_{\theta_1, \theta_2}^{\text{th}}(\omega)$ with the Gaussian modeling the setup response. Note that $I_V(\omega) \propto P_{0,0}^{\text{th}}(\omega)$ and $I_H(\omega) \propto P_{\pi/2, \pi/2}^{\text{th}}(\omega)$ for $\phi = \xi = 0$.

In Fig. 4, we compare CHSH parameters computed for different pump polarizations to demonstrate that our measurement configuration ($\phi = \xi = 0$) exhibits the maximum and broadest violation of Bell inequalities. Indeed, rotating the linear pump polarization from $\phi = 0$ (vertical) to $\phi = \pi/4$ gradually degrades the CHSH parameter $S^{\Psi+}(\omega)$ in the off-resonance regions. To further validate our model,

we experimentally implement a Bell test for the worst case, $\phi = \pi/4$. In this configuration, the mixed terms of Eq. (A5) (proportional to $|VH\rangle$ and $|HV\rangle$) are nonzero. The measured $S^{\Psi+}(\omega)$ values shown in Fig. 4 manifest good agreement with the theoretical curve. We notice that a circular pump polarization ($\phi = \frac{\pi}{2}$, $\xi = \frac{\pi}{4}$) would also generate entangled photon pairs, albeit within a narrower spectral range than in the linear vertical case. Indeed, the computed CHSH parameter

$$S^{\Phi-}(\omega) = -E_{0,\theta}(\omega) - E_{0,-\theta}(\omega) + E_{2\theta,\theta}(\omega) - E_{2\theta,-\theta}(\omega) \quad (\text{A8})$$

for circular polarization shows maximum violation of the corresponding Bell inequality ($S^{\Phi-}(\omega) \leq 2$) at low Raman shifts, where the Bell state $|\Phi_{-}\rangle = \frac{|HV\rangle - |VH\rangle}{\sqrt{2}}$ can be generated.

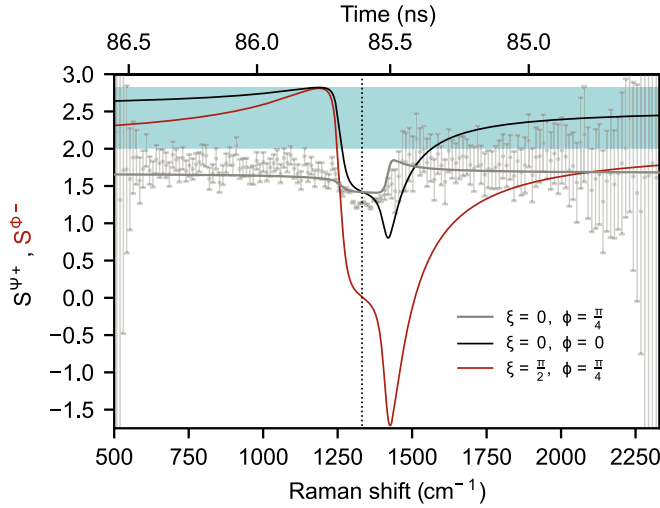


FIG. 4. Bell test for different pump polarizations. Shaded gray circles represent the measured CHSH parameter $S^{\psi+}(\omega)$ for linear pump polarization at $\phi = \frac{\pi}{4}$. The gray line is the corresponding theoretical curve. The black line represents the theoretical $S^{\psi+}(\omega)$ for linear pump polarization at $\phi = 0$ (vertical) as in Fig. 3(b). The red line represents the theoretical CHSH parameter $S^{\psi-}(\omega)$ for circular pump polarization, i.e., $\phi = \frac{\pi}{4}$ and $\xi = \frac{\pi}{2}$. The dotted black vertical line indicates the Raman resonance. The blue region spans between the classical upper bound of 2 and the quantum upper bound of $2\sqrt{2}$.

2. *Improving the photon pair generation rate.* We estimate here the photon pair generation rates that could be achieved using diamond waveguides. First, the wave-vector mismatch, defined as $\Delta k_L = 2k_p - k_S - k_A$, where $k_{p/S/A}$ are the pump, Stokes, and anti-Stokes wave vectors, fixes an intrinsic coherence length of $L_{\text{coh}} = \frac{2\pi}{\Delta k_L} \gtrsim 700 \text{ } \mu\text{m}$ for diamond's dispersion around 780 nm. Second, Ref. [39] shows that the coherence length can be increased at will by suitably engineered diamond waveguides. Indeed, FWM in waveguides requires satisfying the phase-matching condition $\Delta k = 2\gamma P_p - \Delta k_L \approx 0$, where P_p is the pump power and $\gamma = \omega_p n_2 / c A_{\text{eff}}$ is the effective nonlinearity of the waveguide, with n_2 the nonlinear refractive index ($\approx 1.23 \times 10^{-19} \text{ m}^2/\text{W}$) and A_{eff} the effective mode area. The waveguide can be engineered to have $\Delta k_L > 0$, i.e., an anomalous (positive) group velocity dispersion D around the pump wavelength. As a consequence, a pump power of $P_p = \Delta k_L / 2\gamma$ gives, in principle, an infinite coherence length over some bandwidth. Simulations show that $D \approx 500 \text{ ps}/(\text{nm Km})$ at an excitation wavelength of 800 nm for $A_{\text{eff}} \approx 400 \times 500 \text{ nm}^2$ [39]. Since $\Delta k_L = D\omega_p^2 2\pi c (\omega_p - \omega_s)^2 / \omega_p^2$, we calculate an optimal pump power of $P_p < 1 \text{ kW}$ that has the same order of magnitude as the peak power we employ in our experiment (which is $\sim 600 \text{ W}$). For a centimeter-long waveguide pumped in these conditions, the estimated photon pair generation rate is on the order of 10 to 100 kHz/nm. Of course, in such a realization, the TE/TM birefringence of the waveguide should also be minimized.

- [1] Y. Wang, K. D. Jöns, and Z. Sun, Integrated photon-pair sources with nonlinear optics, *Appl. Phys. Rev.* **8**, 011314 (2021).
- [2] U. A. Javid, J. Ling, J. Staffa, M. Li, Y. He, and Q. Lin, Ultrabroadband entangled photons on a nanophotonic chip, *Phys. Rev. Lett.* **127**, 183601 (2021).
- [3] G. Moody, V. J. Sorger, D. J. Blumenthal, P. W. Juodawlakis, W. Loh, C. Sorace-Agaskar, A. E. Jones, K. C. Balram, J. C. F. Matthews, A. Laing, M. Davanco, L. Chang, J. E. Bowers, N. Quack, C. Galland, I. Aharonovich, M. A. Wolff, C. Schuck, N. Sinclair, M. Lončar *et al.*, 2022 roadmap on integrated quantum photonics, *J. Phys.: Photonics* **4**, 012501 (2022).
- [4] H. Takesue and K. Inoue, Generation of polarization-entangled photon pairs and violation of Bell's inequality using spontaneous four-wave mixing in a fiber loop, *Phys. Rev. A* **70**, 031802(R) (2004).
- [5] X. Li, P. L. Voss, J. E. Sharping, and P. Kumar, Optical-fiber source of polarization-entangled photons in the 1550 nm telecom band, *Phys. Rev. Lett.* **94**, 053601 (2005).
- [6] J. Fan, M. D. Eisaman, and A. Migdall, Bright phase-stable broadband fiber-based source of polarization-entangled photon pairs, *Phys. Rev. A* **76**, 043836 (2007).
- [7] B. Fang, M. Liscidini, J. E. Sipe, and V. O. Lorenz, Multidimensional characterization of an entangled photon-pair source via stimulated emission tomography, *Opt. Express* **24**, 10013 (2016).
- [8] H. Takesue, H. Fukuda, T. Tsuchizawa, T. Watanabe, K. Yamada, Y. Tokura, and S. ichi Itabashi, Generation of polarization entangled photon pairs using silicon wire waveguide, *Opt. Express* **16**, 5721 (2008).
- [9] Y.-H. Li, Z.-Y. Zhou, L.-T. Feng, W.-T. Fang, S.-L. Liu, S.-K. Liu, K. Wang, X.-F. Ren, D.-S. Ding, L.-X. Xu, and B.-S. Shi, On-chip multiplexed multiple entanglement sources in a single silicon nanowire, *Phys. Rev. Appl.* **7**, 064005 (2017).
- [10] N. Matsuda, H. Le Jeannic, H. Fukuda, T. Tsuchizawa, W. J. Munro, K. Shimizu, K. Yamada, Y. Tokura, and H. Takesue, A monolithically integrated polarization entangled photon pair source on a silicon chip, *Sci. Rep.* **2**, 817 (2012).
- [11] N. Lv, W. Zhang, Y. Guo, Q. Zhou, Y. Huang, and J. Peng, 15 μm polarization entanglement generation based on birefringence in silicon wire waveguides, *Opt. Lett.* **38**, 2873 (2013).
- [12] P. Kultavewuti, E. Y. Zhu, X. Xing, L. Qian, V. Pusino, M. Sorel, and J. S. Aitchison, Polarization-entangled photon pair sources based on spontaneous four wave mixing assisted by polarization mode dispersion, *Sci. Rep.* **7**, 5785 (2017).
- [13] K. Inoue and K. Shimizu, Generation of quantum-correlated photon pairs in optical fiber: Influence of spontaneous raman scattering, *Jpn. J. Appl. Phys.* **43**, 8048 (2004).
- [14] J. Fan and A. Migdall, A broadband high spectral brightness fiber-based two-photon source, *Opt. Express* **15**, 2915 (2007).
- [15] G. Agrawal, *Nonlinear Fiber Optics*, Electronics and Electrical (Elsevier Science, London, 2007).
- [16] T. A. Freitas, P. Machado, L. Valente, D. Sier, R. Corrêa, R. Saito, C. Galland, M. F. Santos, C. H. Monken,

- and A. Jorio, Microscopic origin of polarization-entangled Stokes–anti-Stokes photons in diamond, *Phys. Rev. A* **108**, L051501 (2023).
- [17] M. Avenhaus, A. Eckstein, P. J. Mosley, and C. Silberhorn, Fiber-assisted single-photon spectrograph, *Opt. Lett.* **34**, 2873 (2009).
- [18] J. F. Clauser, M. A. Horne, A. Shimony, and R. A. Holt, Proposed experiment to test local hidden-variable theories, *Phys. Rev. Lett.* **23**, 880 (1969).
- [19] H. C. Lim, A. Yoshizawa, H. Tsuchida, and K. Kikuchi, Broadband source of telecom-band polarization-entangled photon-pairs for wavelength-multiplexed entanglement distribution, *Opt. Express* **16**, 16052 (2008).
- [20] M. Alshowkan, J. M. Lukens, H.-H. Lu, B. T. Kirby, B. P. Williams, W. P. Grice, and N. A. Peters, Broadband polarization-entangled source for C + L-band flex-grid quantum networks, *Opt. Lett.* **47**, 6480 (2022).
- [21] L. Duan, T. J. Steiner, P. Pintus, L. Thiel, J. E. Castro, J. E. Bowers, and G. Moody, Broadband entangled-photon pair generation with integrated photonics: Guidelines and a materials comparison [arXiv:2407.04792](https://arxiv.org/abs/2407.04792).
- [22] A. Miloshevsky, L. M. Cohen, K. V. Myilswamy, M. Alshowkan, S. Fatema, H.-H. Lu, A. M. Weiner, and J. M. Lukens, Cmos photonic integrated source of broadband polarization-entangled photons, *Optica Quantum* **2**, 254 (2024).
- [23] J. Zheng, G. Khalsa, and J. Moses, Phonon-mediated third-harmonic generation in diamond, *Phys. Rev. Appl.* **22**, 014066 (2024).
- [24] R. W. Boyd, in *Nonlinear Optics*, 3rd ed., edited by R. W. Boyd (Academic Press, Burlington, 2008), pp. 473–509.
- [25] S. T. Velez, V. Sudhir, N. Sangouard, and C. Galland, Bell correlations between light and vibration at ambient conditions, *Sci. Adv.* **6**, eabb0260 (2020).
- [26] V. Vento, S. Tarrago Velez, A. Pogrebna, and C. Galland, Measurement-induced collective vibrational quantum coherence under spontaneous Raman scattering in a liquid, *Nat. Commun.* **14**, 2818 (2023).
- [27] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevResearch.7.L022017> for details on fiber spectroscopy calibration, diamond orientation and anisotropic $\chi^{(3)}$ response, Bell test measurements, and coincidence to accidental ratio.
- [28] K. Zielnicki, K. Garay-Palmett, D. Cruz-Delgado, H. Cruz-Ramirez, M. F. O’Boyle, B. Fang, V. O. Lorenz, A. B. U’Ren, and P. G. Kwiat, Joint spectral characterization of photon-pair sources, *J. Mod. Opt.* **65**, 1141 (2018).
- [29] C. Okoth, A. Cavanna, T. Santiago-Cruz, and M. V. Chekhova, Microscale generation of entangled photons without momentum conservation, *Phys. Rev. Lett.* **123**, 263602 (2019).
- [30] M. A. Weissflog, A. Fedotova, Y. Tang, E. A. Santos, B. Laudert, S. Shinde, F. Abtahi, M. Afsharnia, I. Pérez Pérez, S. Ritter *et al.*, A tunable transition metal dichalcogenide entangled photon-pair source, *Nat. Commun.* **15**, 7600 (2024).
- [31] V. Sultanov, T. Santiago-Cruz, and M. V. Chekhova, Flat-optics generation of broadband photon pairs with tunable polarization entanglement, *Opt. Lett.* **47**, 3872 (2022).
- [32] P. R. Sharapova, S. S. Kruk, and A. S. Solntsev, Nonlinear dielectric nanoresonators and metasurfaces: Toward efficient generation of entangled photons, *Laser Photon. Rev.* **17**, 2200408 (2023).
- [33] E. A. Santos, M. A. Weissflog, T. Pertsch, F. Setzpfandt, and S. Saravi, Entangled photon-pair generation in nonlinear thin-films, *Nanophotonics* **13**, 3545 (2024).
- [34] T. Santiago-Cruz, S. D. Gennaro, O. Mitrofanov, S. Addamane, J. Reno, I. Brener, and M. V. Chekhova, Resonant metasurfaces for generating complex quantum states, *Science* **377**, 991 (2022).
- [35] J. Ma, J. Zhang, Y. Jiang, T. Fan, M. Parry, D. N. Neshev, and A. A. Sukhorukov, Polarization engineering of entangled photons from a lithium niobate nonlinear metasurface, *Nano Lett.* **23**, 8091 (2023).
- [36] K. F. Lee, Y. Tian, H. Yang, K. Mustonen, A. Martinez, Q. Dai, E. I. Kauppinen, J. Malowicki, P. Kumar, and Z. Sun, Photon-pair generation with a 100 nm thick carbon nanotube film, *Adv. Mater.* **29**, 1605978 (2017).
- [37] M. A. Weissflog, R. Dezert, V. Vinel, C. Gigli, G. Leo, T. Pertsch, F. Setzpfandt, A. Borne, and S. Saravi, Nonlinear nanoresonators for Bell state generation, *Appl. Phys. Rev.* **11**, 011403 (2024).
- [38] M. D. Levenson and N. Bloembergen, Dispersion of the nonlinear optical susceptibility tensor in centrosymmetric media, *Phys. Rev. B* **10**, 4447 (1974).
- [39] B. J. M. Hausmann, I. Bulu, V. Venkataraman, P. Deotare, and M. Lončar, Diamond nonlinear photonics, *Nat. Photon.* **8**, 369 (2014).
- [40] D. Sier, L. Valente, T. A. Freitas, M. F. Santos, C. H. Monken, R. Corrêa, and A. Jorio, Emergent broadband polarization entanglement from electronic and phononic four-wave mixing indistinguishability, [arXiv:2408.11602](https://arxiv.org/abs/2408.11602).
- [41] [10.5281/zenodo.15156784](https://doi.org/10.5281/zenodo.15156784).