

Two-Dimensional Electronic Spectroscopy with Intense Entangled-Photon Beams

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(Received 18 April 2025; revised 14 October 2025; accepted 3 November 2025; published 25 November 2025)

Entangled photons carry nontrivial quantum correlations that defy classical physics and provide new tools for monitoring quantum dynamics in molecules. The use of low-flux entangled photons in molecular spectroscopy has been proposed in the past to probe excited-state dynamics with enhanced temporal and spectral resolutions. However, these techniques have been challenging to implement experimentally since the resulting signal has a low signal-to-noise ratio. The signal strength can be boosted by using intense entangled-photon beams, where multiple pairs of entangled photons are present in the environment. This allows the molecule under study to interact with both entangled and unentangled photons, where the classical component of the spectroscopic signal stemming from the latter can mask the spectral features associated with the former. In this Letter, we show how the signal arising from unentangled photons can be eliminated when intense entangled-photon beams are used in two-dimensional electronic spectroscopy (2DES), and demonstrate the advantage of photonic entanglement.

DOI: [10.1103/bscm-ndnk](https://doi.org/10.1103/bscm-ndnk)

Entanglement [1,2] is a unique quantum phenomenon that can correlate two particles separated by large distances in a nontrivial manner [3]. Particles in an entangled pair behave as a single system, and the states of the two particles cannot be defined independently. There has been an active quest for utilizing the entanglement between photons belonging to an entangled-photon pair (EPP) [4] in molecular spectroscopy [5–9]. The observation of an enhanced two-photon absorption (TPA) rate in atoms [10] with EPPs suggests their potential advantage in probing dynamic processes in molecules, thus leading to multiple theoretical studies exploring the advantage of EPPs in spectroscopy [11–13]. For example, the frequency entanglement between photons has been used to probe excited-state dynamics in molecules with simultaneously high temporal and spectral resolution [14,15], which is not possible with classical light due to the Fourier uncertainty between the time and frequency conjugate variables.

Advantages of entanglement in nonlinear spectroscopies [16–18] have not been realized in an experiment yet, and

the utilization of EPPs remains challenging. Most theoretical studies rely on low-flux EPPs to guarantee that the molecule interacts with a single EPP at a time [19–22], as it provides the clearest visualization of entanglement effects. However, this generates a signal that is too weak to be observed due to a low signal-to-noise ratio [23], and prohibits the experimental realization of earlier proposed 2D [24–28] and pump-probe [29,30] spectroscopies. One way to overcome this hurdle is to use intense entangled-photon beams that carry a large number of EPPs. However, this allows the molecule to interact with both entangled and unentangled photons [31,32], and the signal stemming from the latter can obscure the signal from the former [33,34].

In this Letter, we employ intense entangled beams in 2D electronic spectroscopy (2DES) [35,36] and investigate respective contributions of entangled and unentangled photons to the resulting 2DES signal. Furthermore, we develop a protocol that eliminates the signal component arising from unentangled photons using different pulse sequences, thereby enabling the utilization of entanglement in 2DES with an improved signal-to-noise ratio. The formalism presented here provides a foundation for the development of multidimensional spectroscopic methods employing arbitrarily intense entangled beams [37].

2DES is a four-wave mixing technique that can be used to investigate ultrafast dynamics in chemical [38–41] and biological systems [42–45]. In 2DES, three light pulses

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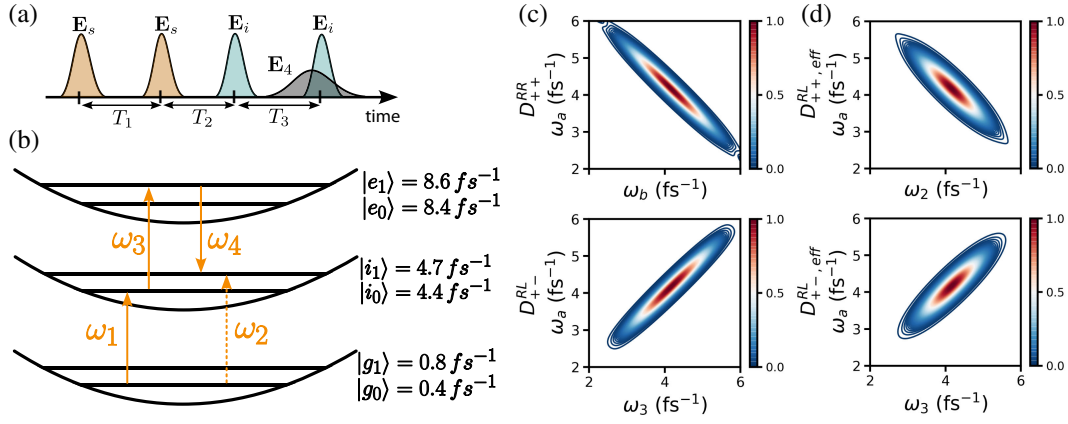


FIG. 1. Overview of 2DES with intense entangled-photon beams. (a) The pulse ordering of entangled beams for 2DES. The interaction of the sample with the first three pulses results in the emission of the $\mathbf{E}_4$ field, which is heterodyned by the $\mathbf{E}_i$ field. (b) The level diagram consisting of three electronic states (ground $|g\rangle$, intermediate $|i\rangle$, and excited $|e\rangle$ states) for the used model system. Vertical arrows represent transitions in the ESA pathway that probe vibrational coherence in the intermediate state. Solid arrows represent field interaction on the left and the dotted arrow represents the field interaction on the right of the density matrix. Frequency-dispersed intermode and intramode correlation functions are shown in (c), top and (c), bottom, respectively, whereas “effective” intermode and intramode correlation functions are shown in (d), top and (d), bottom, respectively.

interact with a sample to induce a nonlinear polarization, which subsequently emits a coherent light field. Because the emitted signal is generally weak, heterodyne detection, where a local-oscillator (LO) field is mixed with the signal field, is employed to record the 2DES signal. The three incoming pulses propagate along wave vectors $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$, and interact with the sample at times t_1 , t_2 , and t_3 , respectively. This results in the emission of a signal light pulse in the phase-matching direction $\mathbf{k}_4 = \pm\mathbf{k}_1 \pm \mathbf{k}_2 \pm \mathbf{k}_3$ at time t_4 , where $t_1 < t_2 < t_3 < t_4$. There are three possible phase matchings in the current four-wave mixing technique: Rephasing (RP) ($\mathbf{k}_4 = \mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_1$), nonrephasing (NRP) ($\mathbf{k}_4 = \mathbf{k}_3 - \mathbf{k}_2 + \mathbf{k}_1$), and double quantum coherence (DQC) ($\mathbf{k}_4 = -\mathbf{k}_3 + \mathbf{k}_2 + \mathbf{k}_1$). Each phase-matched signal is emitted in a unique direction and carries characteristic spectral features that can be used to investigate excited-state dynamics in a molecule. Here, we focus on the NRP phase-matched signal to demonstrate the workings of the proposed method, and the remaining phase-matched signals can be studied in a similar manner. Each phase-matched signal is composed of multiple light-matter interaction (Liouville) pathways that govern the dynamics of the density matrix of the sample. The three Liouville pathways associated with the NRP phase matching are excited-state absorption (ESA), excited-state emission (ESE), and ground-state bleach (GSB), where ESE and

ESA help probe the dynamics in an excited electronic state, and GSB shows ground-state dynamics.

High-gain parametric-down conversion (PDC) [46,47] is used to generate intense signal (“s”) and idler (“i”) beams that are entangled in energy and carry distinct linear polarizations. The entangled beams used in this Letter belong to the family of bright squeezed vacuum states, and such non-classical states of light have enabled exciting applications in quantum imaging [48]. The *s* beam is divided into three parts using beam splitters, where two parts are used for light-matter interactions, while one part is used in the coincidence-detection measurement. Similarly, the *i* beam is split into two parts, where one part is used for the light-matter interaction, while the other part is used as a LO pulse. Figure 1(a) shows the time ordering of the light fields interacting with the sample, along with the LO beam. $\mathbf{E}_s$ ($\mathbf{E}_i$) represents the field corresponding to the *s* beam (*i* beam), and $\mathbf{E}_4$ represents the final output signal field. T_1 , T_2 , and T_3 represent the relative delays between the various *s* and *i* beams used in 2DES.

The signal is obtained by recording the heterodyned output field propagating along $\mathbf{k}_4$ in coincidence with the third part of the *s* beam propagating along $\mathbf{k}_2$. Detectors D_a and D_b placed at $\mathbf{r}_a$ and $\mathbf{r}_b$ are used to detect fields along $\mathbf{k}_4$ and $\mathbf{k}_2$, respectively. The coincidence detection of two fields is given by [49]

$$S = \int d\tau_a \int d\tau_b \langle \hat{\mathbf{E}}_R^{(+)}(\tau_a, \mathbf{r}_a) \hat{\mathbf{E}}_R^{(+)}(\tau_b, \mathbf{r}_b) \hat{\mathbf{E}}_L^{(-)}(\tau_b, \mathbf{r}_b) \hat{\mathbf{E}}_L^{(-)}(\tau_a, \mathbf{r}_a) \rangle_H \quad (1)$$

where the indices R and L represent the right and left superoperators, respectively [50], and represent the direction of operation on the total density matrix, $\rho = \rho_M \rho_F$, where ρ_M is the matter density matrix and ρ_F is the field density matrix. $\langle \cdots \rangle_H = \langle \cdots \rho \rangle_H$ denotes the expectation value over the total Hamiltonian (see End Matter). We have used position vectors in Eq. (1) to account for the positions of the two detectors, but we shall not consider them explicitly in the following. Equation (1) is evaluated by transforming into the interaction picture with respect to the light-matter interaction Hamiltonian, which gives rise to field and matter correlation functions [51] that can be found in the End Matter. Electric fields corresponding to the entangled beams inside the PDC crystal are spatially evolved along the length of the crystal. The

interaction of the pump pulse and the entangled fields with the PDC crystal is treated nonperturbatively, and the details can be found in the Supplemental Material.

The key difference between the conventional multidimensional spectroscopy with classical pulses and the one with the quantum light is the presence of field correlations in the latter case. For the classical (coherent) light, the field correlation function is simply the product of electric field amplitudes of involved light pulses, which is not the case with the quantum light since the field modes are correlated. For example, the effective field-correlation function that exhibits entanglement between field modes and couples them with the molecule for the ESA pathway for the NRP phase-matched signal reads

$$C_{F,\text{eff}}(\omega_a, \omega_4, \omega_3, \omega_2, \omega_1) = D_{+-}^{LL}(\omega_a; \omega_4) [D_{+-,\text{eff}}^{RL}(\omega_a; \omega_3) D_{+-}^{RL}(\omega_2; \omega_1) + D_{+-}^{RL}(\omega_a; \omega_3) D_{+-}^{RL}(\omega_2; \omega_1) + D_{+-}^{RL}(\omega_a; \omega_3) \times D_{+-,\text{eff}}^{LR}(\omega_1; \omega_2) + D_{++,\text{eff}}^{RR}(\omega_a; \omega_2) D_{--}^{LL}(\omega_3; \omega_1) + D_{++}^{RR}(\omega_a; \omega_2) D_{--}^{LL}(\omega_3; \omega_1) + D_{++}^{RR}(\omega_a; \omega_2) D_{--,\text{eff}}^{LL}(\omega_1; \omega_3)], \quad (2)$$

where $D_{+-,\text{eff}}^{\alpha\beta}(\omega_1, \omega_2) = \int d\omega_b D_{++}^{\alpha\gamma}(\omega_1, \omega_b) D_{--}^{\gamma\beta}(\omega_b, \omega_2)$ is the effective two-point field correlation function, with $D_{++}^{\alpha\gamma}(\omega_1, \omega_b) = \langle \hat{\mathbf{E}}_a^{(+)}(\omega_1) \hat{\mathbf{E}}_\gamma^{(+)}(\omega_b) \rangle$ and $D_{--}^{\gamma\beta}(\omega_b, \omega_2) = \langle \hat{\mathbf{E}}_\gamma^{(-)}(\omega_b) \hat{\mathbf{E}}_\beta^{(-)}(\omega_2) \rangle$ being two-point field-correlation functions that are computed numerically, and $\alpha, \beta, \gamma \in \{R, L\}$. The pulse interacting with the sample at time t_n has frequency ω_n , and ω_a is the frequency of the detected heterodyned field mode. The correlation function $D_{+-}^{LL}(\omega_a; \omega_4)$ yields $\delta(\omega_a - \omega_4)$ as it represents the signal mode that is initially in the vacuum, indicating that the mode frequency of the LO pulse is identical to that of the emitted signal field. The effective field correlation function in Eq. (2) is obtained by using Wick's theorem for boson fields since the entangled fields generated via high-gain PDC show Gaussian statistics. Two-point correlators D_{++} and D_{--} are denoted as intermode correlation functions since they are nonvanishing only when the involved field modes belong to two different beams and are entangled, as shown in Fig. 1(c), top. On the other hand, D_{+-} and D_{-+} are denoted as intramode correlation functions since they are nonvanishing only when the involved modes belong to the same beam and are classically correlated, as shown in Fig. 1(c), bottom. Top and bottom panels in Fig. 1(d) show frequency-dispersed effective intermode and intramode correlation functions, respectively. Intramode terms in Eq. (2) correlate modes ω_1 (ω_3) and ω_2 (ω_a) classically, and are collectively denoted as the classical field contribution. Intermode terms in Eq. (2) anticorrelate the modes ω_1 (ω_2) and ω_3 (ω_a), and are collectively denoted as the quantum field contribution.

The model system shown in Fig. 1(b) is used to compute 2DES spectra, and it consists of three electronic states, with

each state containing two vibrational levels. The electronic states are separated by 4 fs⁻¹, and the vibrational frequencies of the ground ($|g\rangle$), intermediate ($|i\rangle$), and excited ($|e\rangle$) states are 0.4 fs⁻¹, 0.3 fs⁻¹, and 0.2 fs⁻¹, respectively. Frequency-dispersed spectra are obtained by Fourier transforming the delay-dependent signal over the delays T_1 and T_3 , with the conjugate frequencies Ω_1 and Ω_3 , respectively. Peaks dispersed over Ω_1 correspond to the electronic coherence created by the first pulse, and thus, are directly related to the mode frequency ω_1 . Similarly, Ω_3 peaks correspond to the electronic coherence created by the first three light pulses, and are directly related to the mode frequency of the output signal field, ω_4 . The left and right panels in Fig. 2 show the classical and quantum contributions, respectively, to the NRP phase-matched signal. Signal contributions to the ESA, ESE, and GSB pathways are shown in the top, middle, and bottom panels, respectively. Peaks are marked using colored circles, with population (coherence) peaks denoted by P (C) in the legend. The classical field-component gives rise to vibrational population peaks for the intermediate electronic state in the 2DES signal, as can be seen for the three pathways in Figs. 2(a)–2(c). The quantum field component, on the other hand, gives rise to distinct peaks for vibrational populations and coherences for the intermediate state in the 2DES signal, as shown in Figs. 2(d)–2(f). Spectral peaks concerning vibrational populations and coherences can be distinguished in 2DES by monitoring their intensity modulations over the delay T_2 . However, peaks corresponding to vibrational populations and coherences can be identified here from the mode frequencies since each mode is correlated with two others.

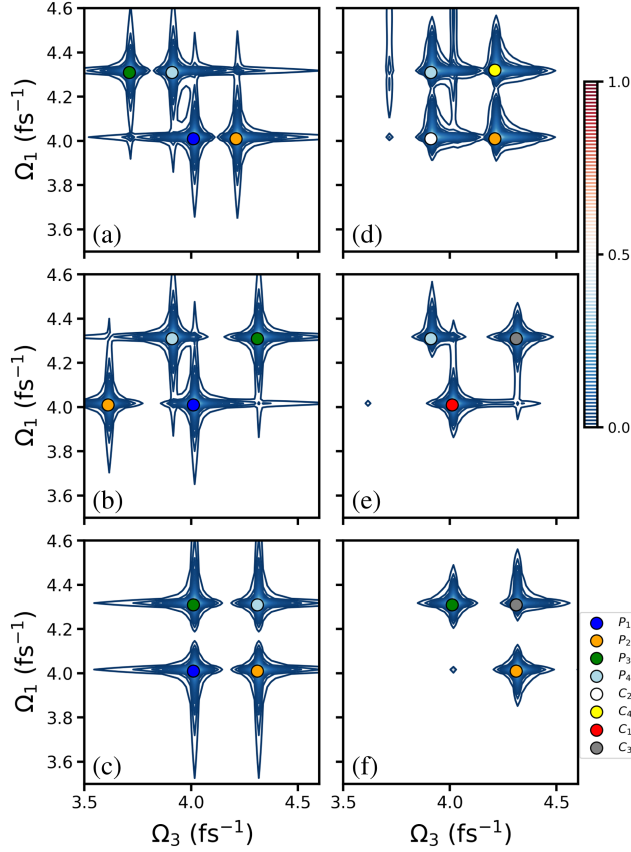


FIG. 2. Frequency-dispersed (Ω_1 - Ω_3) NRP-2DES spectra. (a)–(c) ESA, ESE, and GSB spectra for the classical field-component, respectively. (d)–(f) ESA, ESE, and GSB spectra for the quantum field component, respectively. The delay T_2 is set at 20 fs for all the spectra. Peaks are marked using colored circles, with population (coherence) peaks denoted by P (C). Entangled field parameters: Pump center frequency $\bar{\omega}_p = 8.3$ fs $^{-1}$, signal and idler center frequencies $\bar{\omega}_s = \bar{\omega}_i = 4.15$ fs $^{-1}$, pump bandwidth $\sigma_p = 0.08$ fs $^{-1}$, entanglement time $T_e = 4$ fs, and crystal length $l = 0.2$ μ m.

In the classical field contribution, frequency modes of the first two pulses are classically correlated such that the signal amplitude is maximal for $\omega_1 \approx \omega_2$ and $\omega_a \approx \omega_3$, as can be seen in Fig. 1(d), bottom. This suggests that interactions with the first two beams favor the creation of a vibrational population over the coherence. Thus, the classical field-component generates strong peaks corresponding to vibrational populations, and very weak peaks corresponding to vibrational coherences. In the quantum field contribution, frequency modes of the first two pulses are uncorrelated, and the creation of both population and coherence is equally favored. However, the modes ω_1 (ω_2) and ω_3 (ω_a) are entangled, and transitions to states that satisfy the condition, $\omega_1 + \omega_3 = \omega_p$ and $\omega_2 + \omega_a = \omega_p$, are favored. Since ω_1 and ω_a are associated, respectively, with Ω_1 and Ω_3 , frequencies ω_2 and ω_3 are constrained by $\omega_2 = \omega_p - \Omega_3$ and $\omega_3 = \omega_p - \Omega_1$. Therefore, the peaks

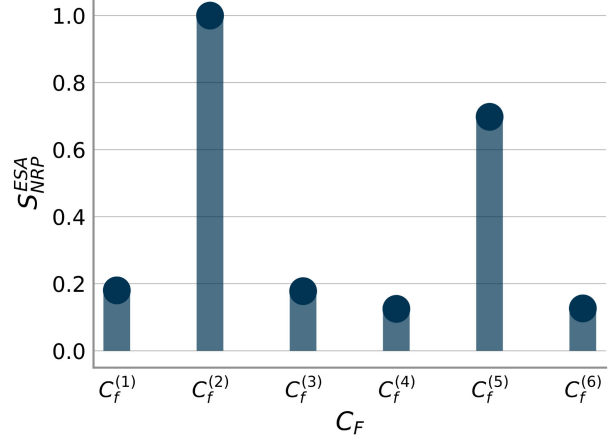


FIG. 3. Relative weights of contributions from the six terms in Eq. (2) to the NRP-ESA signal.

that satisfy $\Omega_1 + \Omega_3 \approx \omega_p$ are associated with vibrational populations since $\omega_1 \approx \omega_2$, and the remaining peaks represent vibrational coherence contributions. However, for sufficiently large pump intensities, s and i beams show a weaker entanglement, which may lead to additional peaks in the signal [52], but this can be corrected by reducing the bandwidth of the pump pulse, which increases the anti-correlation. For our model system, the mode frequencies for all the peaks are mapped out and presented in a table in the End Matter. Having identified classical and quantum contributions to the signal, we now discuss their relative strengths. Hereafter, we focus on the ESA pathway for the NRP phase-matched signal, and the conclusions drawn can be extended to other Liouville pathways in a straightforward manner.

Figure 3 compares peak intensities of the signal stemming from each term, $C_f^{(n)}$, $n = 1, 2, \dots, 6$, of the field correlation function in Eq. (2). The intensities are normalized with respect to the strongest field contribution ($C_f^{(2)}$).

Terms $C_f^{(n)}$, $n \leq 3$, collectively represent the classical field contribution, and terms $C_f^{(n)}$, $n > 3$, collectively represent the quantum field contribution. As can be seen in Fig. 3, the classical field contribution to the signal is stronger than the quantum field contribution, and can hide spectral features arising from entanglement, especially for ESE and GSB pathways where population and coherence peaks overlap. Thus, it is necessary to eliminate the classical field contribution to fully utilize the entanglement in 2DES.

We achieve this elimination by using 2DES signals from two additional pulse sequences: A quantum pulse ordering that uses both s and i entangled beams [Fig. 4(a)], and a classical pulse ordering that utilizes only one of the two entangled beams [Fig. 4(b)]. Both the quantum pulse orderings correlate pairs of modes ($\{\omega_a, \omega_2\}$) and ($\{\omega_1, \omega_3\}$) quantum mechanically, but the classically correlated modes are different. In the first pulse ordering,

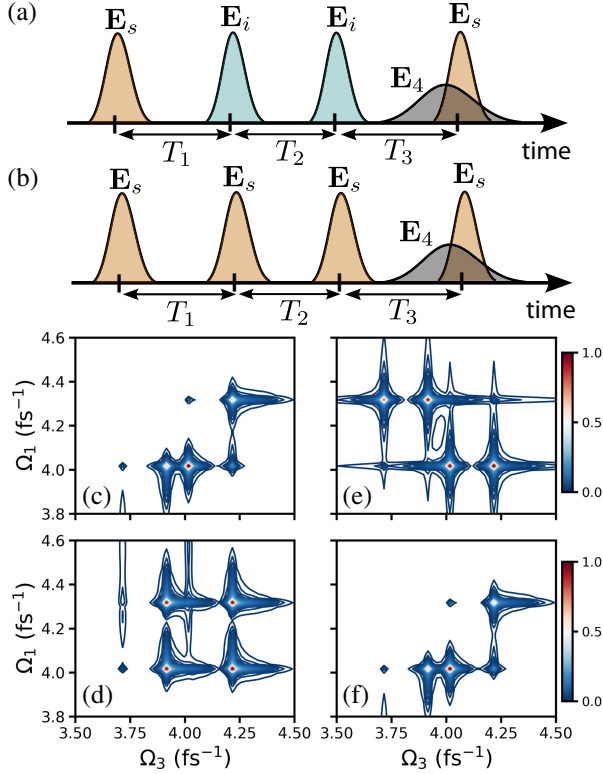


FIG. 4. 2DES for the additional time ordering of beams. (a) An alternate pulse ordering of s and i beams used in 2DES is shown. (b) A classical pulse ordering that uses only the s beam in 2DES is shown. Classical and quantum contributions to the 2DES signal computed for the second pulse ordering are shown in (c) and (d), respectively. Two distinct classical contributions to the 2DES signal for the classical pulse orderings are shown in (e) and (f).

Fig. 1(a), the mode pairs $(\{\omega_a, \omega_3\})$ and $(\{\omega_1, \omega_2\})$ are classically correlated while in the second pulse ordering, mode pairs $(\{\omega_a, \omega_1\})$ and $(\{\omega_2, \omega_3\})$ are classically connected.

Figures 4(c) and 4(d) illustrate the classical and quantum contributions to the NRP-ESA signal, respectively, computed using the second pulse ordering. As expected, the quantum signal in Fig. 4(d) is identical to the quantum signal in Fig. 2(b) obtained for the first pulse ordering shown in Fig. 1(a). Additionally, the two quantum schemes generate different signals for the classical component, as can be seen by comparing Figs. 2(a) and 4(c).

Since the classical signal contributions for both quantum pulse orderings originate from purely classical field correlation functions, one can use the pulse sequence shown in Fig. 4(b) for eliminating the classical contributions. The pulse scheme shown in Fig. 4(b) uses only the s beam for light-matter interaction, while the i beam is used for coincidence detection. Similar to the two prior schemes, using only s beams for light-matter interaction results in a field correlation function with six terms, but each term contains only intramode field correlation functions that are classical in nature (see Supplemental Material [53] for the

expression). This indicates that the earlier proposed quantum spectroscopies that employed one photon from an EPP for light-matter interaction and the other for reference in coincidence detection effectively utilized classical correlation, not the quantum entanglement between the photons [54]. The classical pulse ordering correlates four pairs of field modes classically: $\{\omega_a, \omega_3\}$, $\{\omega_1, \omega_2\}$, $\{\omega_a, \omega_1\}$ and $\{\omega_2, \omega_3\}$, and the correlated modes are identical to the classically correlated modes in both the quantum pulse orderings. The 2DES signal stemming from the first two correlated mode pairs shown in Fig. 4(e) is identical to the classical component of the 2DES signal for the first quantum pulse ordering shown in Fig. 2(a). Similarly, the 2DES signal stemming from the latter two correlated mode pairs shown in Fig. 4(f) is identical to the classical component of the 2DES signal for the second quantum pulse shown in Fig. 4(c). Thus, summing the signals from the two quantum-pulse orderings and subtracting from it the signal obtained using the classical-pulse ordering results in a 2DES signal that only contains features originating from the field entanglement. Note that we use s and i beams generated via a type-II PDC process in order to control the pulse ordering, but one can use pulses generated collinearly in a type-I PDC process for 2DES. However, this allows each light-matter interaction to be mediated via both s and i modes, which results in a signal stemming from the convolution of all possible pulse orderings, and the relevant protocol to eliminate classical contributions can be developed by following the approach discussed above for each possible pulse ordering.

Acknowledgments—D. J. gratefully acknowledges the support from the Swedish Research Council under Grant No. VR 2025-00505. U. H. acknowledges support from the Science and Engineering Research Board, India, under Grant No. CRG/2020/0011100 and the Fulbright-Nehru Academic and Excellence Fellowship, 2023-24, sponsored by the U.S. Department of State and the United State-India Education Foundation. V. Y. C. and S. M. gratefully acknowledge the support of the US Department of Energy, Office of Science, Basic Energy Sciences Award No. DES0022134. S. M. gratefully acknowledges the support of the National Science Foundation through Grant No. CHE-2246379. S. M. gratefully acknowledges support from the US Department of Energy, Office of Science, Basic Energy Sciences Award through Grant No. DES0023233.

Data availability—The data that support the findings of this article are openly available [55].

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End Matter

The total Hamiltonian of the entire system is given by

$$\hat{H} = \hat{H}_0 + \hat{H}_M + \hat{H}_{\text{int}}, \quad \hat{H}_{\text{int}} = -\hat{\mu} \cdot \hat{\mathbf{E}}(\mathbf{r}_M),$$

$$\hat{H}_0 = \hat{H}_A - \int d\mathbf{r} \mathbf{P}(\mathbf{r}, t) \cdot \hat{\mathbf{E}}(\mathbf{r}) \quad (\text{A1})$$

where $\hat{H}_M$ is the molecular Hamiltonian, $\hat{H}_0$ is a sum of the auxiliary Hamiltonian and the source Hamiltonian. The source Hamiltonian represents the coupling of the classical field (pump pulse) with the source via the polarization $\mathbf{P}$. The auxiliary Hamiltonian, $\hat{H}_A$, represents the coupling of the electric field with materials such as, mirrors, the PDC crystal, beam splitters, etc. $\hat{\mu} = \sum_{i,j,i \neq j} (|i\rangle\langle j| + |j\rangle\langle i|)$ is the transition dipole moment (TDM) corresponding to the vibronic transitions in the model system, $\mathbf{r}_M$ is the position vector to the center of charge of molecules, and $\hat{\mathbf{E}}$ is the electric field expressed as

$$\hat{\mathbf{E}}(\mathbf{r}, t) = \hat{\mathbf{E}}^{(+)}(\mathbf{r}, t) + \hat{\mathbf{E}}^{(-)}(\mathbf{r}, t),$$

$$\hat{\mathbf{E}}^{(+)}(\mathbf{r}, t) = [\hat{\mathbf{E}}^{(-)}(\mathbf{r}, t)]^* = \mathbf{e} \int d\omega \hat{\mathbf{E}}^{(+)}(\omega) e^{i\omega t} e^{-i\mathbf{k} \cdot \mathbf{r}} \quad (\text{A2})$$

where $\mathbf{e}$ is the unit vector along the polarization of the field, and $\mathbf{k}$ is the wave vector.

The signal is obtained by the perturbative treatment of the light-matter interaction in Eq. (1). Here we focus on the NRP-ESA signal expression since ESA spectra are primarily discussed throughout the Letter as they contain the most information compared to the remaining pathways. A complete derivation of the NRP-ESA signal can be found in the Supplemental Material [53] along with corresponding time- and frequency-domain Feynman diagrams. The delay-dependent NRP-ESA expression reads

$$S_{\text{NRP}}^{\text{ESA}}(T_1, T_2, T_3) = -\mathcal{N}_{\text{NRP}}^{\text{ESA}} \Re \int d\omega_a \int d\omega_b \int d\omega_4 \int d\omega_3 \int d\omega_2 \int d\omega_1 e^{-i\omega_a(T_3+T_2+T_1)} e^{i\omega_3(T_2+T_1)} e^{-i\omega_2 T_1} C_M C_F, \quad (\text{A3})$$

$\mathcal{N}_{\text{NRP}}^{\text{ESA}}$ is a normalization constant, C_M is the matter correlation function given by

$$C_M = \delta(\omega_a - \omega_3 + \omega_2 - \omega_1) \langle \mu_L \mathcal{G}(\omega_3 - \omega_2 + \omega_1) \mu_L \mathcal{G}(\omega_1 - \omega_2) \mu_R \mathcal{G}(\omega_1) \mu_L \rangle_{H_M}, \quad (\text{A4})$$

where $\mathcal{G}(\omega)$ is the frequency-domain Liouville space propagator, R, L represent the direction of operation of the respective superoperators on a density matrix, and $\langle \cdots \rangle_{H_M}$ denotes the expectation value over the matter Hamiltonian, $\hat{H}_M$. C_F represents the eight-point field correlation function, which is evaluated using Wick's theorem that allows reducing a multipoint correlation function into a sum of products of two-point correlation functions, and can be written as

$$\begin{aligned} C_F(\omega_a, \omega_b, \omega_4, \omega_3, \omega_2, \omega_1) = & D_{-+}^{LL}(\omega_a; \omega_4) [D_{++}^{RR}(\omega_a; \omega_b) D_{--}^{LL}(\omega_b; \omega_3) D_{+-}^{RL}(\omega_2; \omega_1) \\ & + D_{+-}^{RL}(\omega_a; \omega_3) D_{++}^{RL}(\omega_b; \omega_b) D_{+-}^{RL}(\omega_2; \omega_1) + D_{+-}^{RL}(\omega_a; \omega_3) D_{+-}^{RL}(\omega_b; \omega_1) D_{-+}^{LR}(\omega_b; \omega_2) \\ & + D_{++}^{RR}(\omega_a; \omega_b) D_{-+}^{LR}(\omega_b; \omega_2) D_{--}^{LL}(\omega_3; \omega_1) + D_{++}^{RR}(\omega_a; \omega_2) D_{+-}^{RL}(\omega_b; \omega_b) D_{--}^{LL}(\omega_3; \omega_1) \\ & + D_{++}^{RR}(\omega_a; \omega_2) D_{+-}^{RL}(\omega_b; \omega_1) D_{--}^{LL}(\omega_b; \omega_3)] \end{aligned} \quad (\text{A5})$$

where $D_{++}^{RR}(\omega_a, \omega_b) = \langle \hat{\mathbf{E}}_R^{(+)}(\omega_a) \hat{\mathbf{E}}_R^{(+)}(\omega_b) \rangle$, $D_{--}^{LL}(\omega_a, \omega_b) = \langle \hat{\mathbf{E}}_L^{(-)}(\omega_a) \hat{\mathbf{E}}_L^{(-)}(\omega_b) \rangle$, etc., are two-point field correlation functions with $\hat{\mathbf{E}}^{(-)}$ and $\hat{\mathbf{E}}^{(+)}$ being the negative and positive frequency components of the electric field operator. Note that the subscripts denoting s and i are omitted since the classical and quantum field components are identified by two-point field correlation functions, which renders the notation obsolete. Time evolutions of matter and field correlation functions are governed by Hamiltonians $\hat{H}_M$ and $\hat{H}_0$, respectively. Two-point field correlation functions in Eq. (A5) are calculated numerically by the spatial evolution of the entangled fields inside the PDC crystal along its length. Note that the signal is defined as the real part of the integral in Eq. (A3), which

results in the loss of the imaginary part. The imaginary part of the integral can be recovered by changing the phase of the LO pulse. Therefore, the spectra shown in this Letter are absolute values of the integral in the 2DES signal expressions.

Each term in the field correlation function in Eq. (A5) consists of three two-point correlation functions involving entangled fields. Since the matter correlation function does not depend on the frequency ω_b , one can obtain an effective field-correlation function that consists of photon modes coupled to the matter by integrating over ω_b . The effective field-correlation function for the NRP-ESA pathway then reads

$$\begin{aligned} C_{F,\text{eff}}(\omega_a, \omega_4, \omega_3, \omega_2, \omega_1) = & D_{-+}^{LL}(\omega_a; \omega_4) [D_{+-,\text{eff}}^{RL}(\omega_a; \omega_3) D_{+-}^{RL}(\omega_2; \omega_1) + D_{+-}^{RL}(\omega_a; \omega_3) \\ & \times D_{+-}^{RL}(\omega_2; \omega_1) + D_{+-}^{RL}(\omega_a; \omega_3) D_{-+,\text{eff}}^{LR}(\omega_1; \omega_2) + D_{++,\text{eff}}^{RR}(\omega_a; \omega_2) D_{--}^{LL}(\omega_3; \omega_1) \\ & + D_{++}^{RR}(\omega_a; \omega_2) D_{--}^{LL}(\omega_3; \omega_1) + D_{++}^{RR}(\omega_a; \omega_2) D_{-+,\text{eff}}^{LR}(\omega_1; \omega_3)] \end{aligned} \quad (\text{A6})$$

TABLE I. Mode frequencies that are resonant with the vibronic transitions in the molecule are shown for the four light pulses interacting with the sample. Transitions that are favored by entangled modes are in bold.

Pathways	ESA								ESE								GSB							
	Coherence				Population				Coherence				Population				Coherence				Population			
Peaks	C_1	C_2	C_3	C_4	P_1	P_2	P_3	P_4	C_1	C_2	C_3	C_4	P_1	P_2	P_3	P_4	C_1	C_2	C_3	C_4	P_1	P_2	P_3	P_4
ω_1	4	4	4.3	4.3	4	4	4.3	4.3	4	4	4.3	4.3	4	4	4.3	4.3	4	4	4.3	4.3	4	4	4.3	4.3
ω_2	4.3	4.3	4	4	4	4	4.3	4.3	4.3	4.3	4	4	4	4	4.3	4.3	3.6	3.6	3.9	3.9	4	4	4.3	4.3
ω_3	4	4.2	3.7	3.9	4	4.2	3.7	3.9	4.3	3.9	4	3.6	4	3.6	4.3	3.9	3.6	3.9	3.9	3.6	4	4.3	4	4.3
ω_4	3.7	3.9	4	4.2	4	4.2	3.7	3.9	4	3.6	4.3	3.9	4	3.6	4.3	3.9	4	4.3	4.3	4	4	4.3	4	4.3
$\omega_1 + \omega_3$	8	8.2	8	8.2	8	8.2	8	8.2	8.3	7.9	8.3	7.9	8	7.6	8.6	8.2	7.6	7.9	8.2	7.9	8	8.3	8.3	8.6

where $D_{\alpha\beta,\text{eff}}^{+-}(\omega_1, \omega_2) = \int d\omega_b D_{\alpha\gamma}^{++}(\omega_1, \omega_b) D_{\gamma\beta}^{--}(\omega_b, \omega_2)$ is the effective two-point field correlation function, with $\alpha, \beta, \gamma \in \{R, L\}$. Note that the mode ω_1 (ω_a) is correlated with the ω_2 (ω_3) mode in the classical field component, while it is correlated with mode ω_3 (ω_2) in the quantum field component.

The appearance of different kinds of peaks for quantum and classical components of the probe field can be traced

with the help of Table I for the three pathways, which depicts frequencies resonant with the vibronic transitions in the model system for each mode belonging to the light pulses interacting with the sample. Modes ω_1 , ω_2 , ω_3 , and ω_4 belong to pulses interacting with the sample at times t_1 , t_2 , t_3 , and t_4 , respectively. Transitions that are closest to satisfy the entanglement condition are in bold in Table I.