Measurement of Entangled State Before, During, and After a Proposed Entangled Two-Photon Molecular Excitation

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Abstract

Entangled photon pairs are predicted to linearize and increase the efficiency of multiphoton absorption, allowing continuous wave laser diodes to drive ultrafast time-resolved spectroscopy, nonlinear photonics, and nonlinear biological microscopy at low fluxes. However, despite a range of theoretical studies and experimental measurements of entangled two-photon absorption cross sections in molecular systems, inconsistencies persist about the value of the linearized and enhanced cross section. We present an entangled two-photon spectrometer that is capable of characterizing entangled photon states before, during, and after a proposed two-photon excitation event. The spectrometer uses a custom <100 nW, 20 fs, broadband entangled photon source that theoretically optimizes any possible entangled two-photon absorption. The spectrometer is then used to measure Rhodamine 6G, a common fluorescent molecular dye with a virtual-state-mediated two-photon absorption. The proposed entangled two-photon interaction is found to be equal to or lower than that of a classical single photon scattering event, providing further bounds for proposed theoretical and experimental measurements. The entangled linearization of nonlinear, multi-photon, and ultrafast spectroscopies could have broad scientific aspects, but the results of this paper suggest that molecules with near-resonant, real intermediate states are necessary for technologically significant applications.

Introduction

It is well known that the inherent correlations between entangled photons lead to spectroscopic enhancements in signal-to-noise1–4 and diffraction limits5 as well as measurement techniques such as ghost imaging.6–12 A new and quickly growing field of entangled two-photon spectroscopy exploits these correlations in a different approach: examining changes in excited state interactions when entangled photon pairs create real or virtual populations in a sample.13–16 The theory and experiments that launched this field purported to demonstrate that entangled photons can linearize two-photon processes to achieve near one-photon absorption cross sections.17 This finding would have far-reaching implications in optics and photonics as low power, continuous wave (CW) laser systems could replace pulsed lasers in spectroscopic techniques such as nonlinear bioimaging and ultrafast spectroscopy.18–20 Combined with nanophotonic platforms that are capable of generating and manipulating entangled photon pairs,21,22 ultrafast measurements could achieve unprecedented accessibility and availability.

While the entangled photons’ linearization of two-photon processes is easy to derive theoretically,23–25 debate has recently arisen over the enhancement factor that entangled photons can provide, as represented by the entangled two-photon absorption (ETPA) cross section. Fig. 1 depicts the range of ETPA cross sections that have been experimentally measured to date, as well
as some theoretical and experimental upper bounds.\textsuperscript{17,26–31,19,32–38} One issue complicating this debate is that disparate measurement techniques based on transmission, coincidence counting, and fluorescence have all been used to quantify the ETPA cross section but with disagreement. Moreover, in almost all cases, an intensity counting method is used, and the entangled state is not fully characterized. In this paper, we therefore construct a spectrometer that temporally and spectrally measures the entangled photon state before, during, and after a proposed entangled two-photon event so as to remove ambiguity about potential single photon loss channels. This spectrometer is used to measure the proposed entangled two-photon excitation of a prototypical molecular dye, Rhodamine 6G (R6G), which has a well characterized, virtual state-mediated classical two-photon absorption starting at $\sim$750 nm.\textsuperscript{39,40} To enhance the chances of measuring a two-photon fluorescence signal, the spectrometer uses a custom, high-flux 20 nW, $10^{-8}$ efficiency entangled photon source with tunable bandwidth and correlation time down to 20 fs.\textsuperscript{41} By measuring the temporal and spectral characteristics of the transmitted and 90-degree signals, we determine that any entangled enhancement to the two-photon absorption is less than the cross section of a single photon (resonant) scattering ($\sim 10^{-21}$ cm$^2$/molecule) process. The conclusion is based on the facts that: 1) the entangled state is identical before and after transmission, with only an amplitude loss, and 2) the scattered signal temporally follows a one-photon interference pattern instead of an entangled two-photon interference, with spectral components far from the fluorescence spectrum of the dye. The paper presents a blueprint for a spectrometer that can unambiguously determine entangled photon excited state effects. The scattering limited cross section for R6G bolsters current theories that suggest real intermediate states are necessary for entangled two-photon excitation events with high cross sections.\textsuperscript{42,43}

Figure 1: Reported experimental ETPA cross sections vs classical TPA cross sections compiled from all ETPA studies conducted prior to January 2022.\textsuperscript{17,26–31,19,32–38} The shape of the data point reflects the polarization type of the entangled photons. Reported ETPA cross sections for the same compound at varying concentrations are represented as an average with vertical error bars indicating the highest and lowest reported bounds. The dashed lines represent ETPA upper bounds that were previously reported.\textsuperscript{34–36} The shading of the points indicates the year in which the results were published, with darker colors representing more recent data. Classical resonance Raman cross section is also included.\textsuperscript{44}
Experimental Details

The entangled photons are generated from a periodically poled 8% MgO doped congruent lithium tantalate (CLT) bulk crystal. The design and spectral characterization of the entangled photon source have previously been reported. The crystal is optimized for Type 0 energy-time entanglement by spontaneous parametric down-conversion (SPDC). A bandwidth of ~200 nm is produced by down-conversion of a 406 nm CW diode laser. The large bandwidth allows for a flux in the sub-uW range without exceeding the single-photon-per-mode quantum limit. Here, a 400 mW laser diode is used to create 20 nW as compared with ~pW powers in most previous experiments. The broad bandwidth also results in a ~20 fs correlation time (entanglement time) from the CW laser diode. The entangled photon bandwidth can be varied by tuning the temperature of the bulk crystal. For experiments in this paper, two distinct entangled photon bandwidths centered at 812 nm were utilized: a non-degenerate “split” SPDC spectrum spanning ~200 nm in wavelength and a degenerate “unsplit” SPDC spectrum (more details in the Supplementary Information). The two SPDC spectra are used to emphasize the scattering that can happen both close to and far from resonance of a molecule's absorption. The high flux and tunable correlation times, from tens of femtoseconds to picoseconds, increase the likelihood of measuring any entangled event.

Rhodamine 6G was selected for studies due to its absorption properties in the visible wavelength regime, its purely virtual two-photon classical absorption, as well as its high fluorescence quantum yield. There are also several measurements of the proposed ETPA to use as reference. A concentration of 5 mM R6G in ethanol was used for experiments; the fluorescence spectrum for this concentration is depicted in Fig. 4. Solvent effects and molecular dimerization at high sample concentration accounts for the redshifted spectrum. Previously reported one-photon absorption cross sections for R6G in ethanol are on the order of $10^{-16}–10^{-17}$ cm$^2$/molecule and the two-photon absorption cross section is $70 \times 10^{-50}$ cm$^4$/ photon. A higher 110 mM sample was also tested with the same results.

A custom two-photon Michelson-type interferometer, shown in Fig. 2, is used to characterize the fourth-order interference and entanglement (coherence) time of the broadband entangled photons. The configuration allows the broad SPDC bandwidth to be characterized and directed onto the sample in a collinear geometry. For these 90-degree measurements, the photon pairs exiting the Michelson interferometer are focused (500 µm beam waist) onto the center of the cuvette. A complete mathematical description of the interferometer output can be found in the Supplementary Information. The measurement protocol is as follows: first, a cuvette containing pure ethanol is placed at the output of the Michelson interferometer. Second, the fourth-order interference is measured by collecting coincidences as a function of an optical time delay. The coincidence counting detection setup consists of a broadband 50:50 beamsplitter and two single photon avalanche photodiodes (SPADs, Laser Components). The fourth-order interference measurements are then repeated with the cuvette filled with R6G solution. Simultaneous to the coincidence counting measurement, a single photon counting EMICCD spectrometer (Princeton Instruments) is placed at 90 degrees relative to the excitation beam to measure any scatter or fluorescence. The collection efficiency of the collection optics plus spectrometer is ~$10^{-4}$, calculated from measured classical single photon fluorescence and quantum yield of R6G. Monitoring the timescale and spectral features of the 90-degree signal differentiate one photon events, such as scattering, from an entangled two-photon absorption or fluorescence event.
Figure 2: Experimental setup used to measure the proposed entangled two-photon absorption and 90-degree signal. The entangled photon source consists of a continuous wave diode laser pumping a periodically poled lithium tantalate crystal. The resultant entangled photon cone is collimated before the two-photon Michelson interferometer. The fourth-order interference of the entangled photon pairs is measured with a coincidence counting configuration and the time-resolved 90-degree signal was imaged onto a spectrometer/EMICCD. ND: continuous neutral density filter wheel, HWP: half-wave plate, L: lens, ppLT: periodically poled lithium tantalate chip, LP: 500 nm longpass filter, IF: interference filter, OAP: off-axis parabolic mirror, C1: cylindrical lens, QWP: quarter-wave plate, BS1 and BS2: 50:50 plate beamsplitters, M1 and M2: mirrors, D1 and D2: multimode fiber coupled single photon avalanche diodes connected to a coincidence circuit, Spec/EMICCD: Spectrometer and electron multiplying intensified charge coupled device.

Results and Discussion

Fig. 3 shows the fourth-order interference of the entangled photon state before and after interacting with 5mM R6G/ethanol as well as the signal collected at 90-degrees to the excitation pathway. The top trace is measured through a cuvette filled with pure ethanol for reference. In a two-photon Michelson interferogram, the degree of entanglement (visibility) is related to the amplitude ratio above and below the baseline. For this experiment, the corresponding entanglement time is <20fs with a visibility of 0.94. When the cuvette is filled with R6G (middle trace in Fig. 3), the visibility of the interference slightly decreases to 0.86, but the interferogram retains the spectral and temporal features shown with ethanol. Namely, no modulation of the transmitted quantum state is measured. The bottom trace in Fig. 3 shows the summed spectrum collected at 90-degrees by the EMICCD. The interferogram follows that of a one-photon event. If the collected signal originated from an entangled two-photon event, it would follow the amplitude of the input state, as the molecule would act similar to a coincidence counter.49
Figure 3: Photon counts versus time delay for broadband entangled photons traveling through a two-photon Michelson interferometer. The top trace is transmitted coincidence counts through ethanol, the middle trace is transmitted coincidence counts through R6G in ethanol, and the bottom trace is summed EMICCD counts of the 90-degree signal. The y axis has been scaled and shifted for visualization.

The one-photon nature of the scattered signal is further confirmed by looking at the wavelength spectrum collected at 90-degrees (Fig. 4). The measured single photon fluorescence of R6G is shown for reference in purple. When the non-degenerate entangled photon spectrum is used (Fig. SI1), a scattered spectrum is measured away from the expected fluorescence that instead correlates with the wings of the non-degenerate SPDC spectrum. When a degenerate spectrum is used, a reduced amplitude scattering is measured at the central 800 nm wavelength of the SPDC, as would be expected since it is farther from the R6G absorption tail. As a control, zinc tetraphenylporphyrin (ZnTPP), which has a narrow-band absorption at 400 nm, far from the SPDC spectrum, was also measured. No scattered signal was measured for ZnTPP in our spectrometer because the overlap of the absorption is too far from the SPDC spectrum to allow significant resonant scattering. All light is therefore transmitted within our error bars.
Figure 4: One photon fluorescence (purple trace) and the measured scatter spectra from 5mM R6G in ethanol for non-degenerate (pink trace) and degenerate (orange trace) entangled photons. The spectra have been normalized and scaled such that they can be displayed on similar scales. The scattered signal matches the entangled photon spectrum.

The scattered cross section can be calculated using the equation:\textsuperscript{33}

\[ F_E = \gamma N_E c \times 10^{-6} \times l N_A \sigma_E \]

where \( F_E \) is the collected signal, \( \gamma \) is the collection efficiency, \( N_E \) is the incident entangled photon flux, \( \phi_F \) is the fluorescence quantum yield, \( c \) is the concentration in mM, \( l \) is the pathlength in cm, \( N_A \) is Avogadro’s number, and \( \sigma_E \) is the entangled two-photon absorption cross section.

The resulting scatter cross section is \( 2 \pm 1 \times 10^{-21} \) cm\(^2\)/molecule. For comparison, the standard method of the field, the measured attenuation cross section using the transmission spectrum (Fig. 5) is \( 8 \pm 1 \times 10^{-21} \) cm\(^2\)/molecule (See SI for more information on the measurement). The agreement between measured scatter cross section and attenuation cross section further confirms that no entanglement enhanced two-photon absorption or fluorescence is detected in our setup. Indeed, the measured values are above the theoretical maximum ETPA cross section for R6G (\( 3 \times 10^{-24} \) cm\(^2\)/molecule, dashed line in Fig. 1) that was previously calculated\textsuperscript{36} and extrapolated from measurements of second-harmonic generation.\textsuperscript{35} Note that our spectrometer is capable of measuring cross sections down to the \( 10^{-25} \) cm\(^2\)/molecule range, based on signal-to-noise analysis. The results are also in line with the measurements of Parzuchowski et al,\textsuperscript{34} where no signal was measured after extensive filtering and an ETPA cross section upper limit of \( 1.5 \times 10^{-21} \) cm\(^2\)/molecule was established for R6G. An entangled event could be occurring, but it is weaker than any single-photon scattering processes inherent to R6G. Scattering, or other single photon processes such as hot band absorption,\textsuperscript{50} can therefore lead to an inflated absorption cross section measured in transmission-only experiments or fluorescence experiments. Scattered photons can also leak through filters put in place to block the SPDC light or original pump beam. This may be the cause of discrepancies between different measurement types and theories in replicating reported cross sections.
Recently, theoretical and experimental measurements have emphasized the importance of resonant or near resonant real states to achieve high two-photon entangled interactions, as compared to the purely virtual interactions measured here.\textsuperscript{42,43} The results of this paper indicate that caution must be taken when measuring entangled two-photon events because the single-photon scattering and other single-photon processes will replicate a linear absorption at low power. The results reported here emphasize the importance of characterizing the actual quantum state instead of relying on pure intensity measurements. As the field of excited state entangled interactions continues to be explored and molecules are synthesized to maximize entangled enhancements, a standardized spectrometer such as presented here is vital.

Figure 5: Measured absorbed photon rate (orange data points), fit (orange solid line), and calculated ETPA cross sections (gray solid lines) vs input photon rate for 5mM Rhodamine 6G in water. The gray solid lines indicate the absorbed photon rate for ETPA cross sections, which are noted along the lines. The ETPA cross section from the measured absorption rate is $8 \times 10^{-21} \text{cm}^2/$molecule and is included as a dashed gray line.

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