jz-2022-008658.R1

Name: Peer Review Information for "Single Photon Scattering Can Account for the Discrepancies Between Entangled Two-Photon Measurement Techniques"

First Round of Reviewer Comments

Reviewer: 1

Comments to the Author
What is the major advance reported in the paper?

This manuscript reports characterization of the spectral and temporal properties of entangled photon pairs (EPPs) transmitted through or scattered from a two-photon absorbing sample (Rh6G in ethanol). They find, as other authors have already reported, that the EPP absorption is not detectable. Based on spectral detection, they claim the EPP absorption rates and is equal to or smaller than the rate of single-photon scattering.

What is the immediate significance of this advance?

The magnitude of the quantum advantage for two photon excitation of molecules using EPPs is currently under debate. The widely varying Results from different experiments have not been reconciled. Measurements that place bounds on the EPP absorption rate by using fiducials such as one-photon scattering events could help clarify the strengths of these signals in a way that could be platform-independent.
Although the instrumentation and measurements are more advanced than those of previous reports, and therefore there is potential for new insight, discussion of their results is somewhat superficial.

Technical suggestions

The authors claim that no two-photon absorption has occurred, yet their paper is entitled “interaction with a virtual state mediated two-photon transition.” Since they do not measure an interaction of this kind, I believe they should rename the manuscript.

1. Page 3 Lines 15-18: To the best of my knowledge there is no early theoretical work suggesting that entangled two photon absorption cross sections can attain values close to one photon absorption cross sections.

2. Page 5 Line 54: I'm under the impression that the authors are referring to the single-pair-per-mode quantum limit. How did they estimate the number of pairs per mode?

3. Page 8 Line 53 to Page 9 Line 6, the statements about entanglement are vague here, and they don't show that the photons are entangled. For example can a classically correlated state produce the same result?

4. Page 9 Line 8: The value of "<20 fs" is a very short entanglement time considering that there is likely some group delay dispersion in the experiment, are the authors considering how GDD affects their entanglement time?

5. Page 11, Figure 4: I don't understand the explanation for the scattering signal plotted in Fig. 4. Why doesn't the scattered spectrum look identical to the SPDC spectrum shown in Figure. S2? For example, why are the scatter peak wavelengths shifted from the SPDC peak wavelengths?

6. In Figure S3, it appears as if there is absorption from ZnTPP at 550nm and beyond, however the authors claim that the lack of absorption in this region is what causes the lack of a 90 degree signal for ZnTPP. Can the authors explain how this is possible? Furthermore, if there is no scatter, what is the signal shown in Figure S6?

7. On page. 12, lines 27-30: The authors mention the cross-section sensitivity of their instrument. The authors do not mention that for Rh6G, their sensitivity is decreased because they have not (to my knowledge) attempted to filter out the scatter. Ideally, the authors should filter out the scatter and then report on the origin of any remaining signal.

8. Page 12, lines 34-37: what is the slope of the fit and why does it have this dependence? If it is scatter, why doesn't it have a linear dependence?

9. Page 13, Figure 5: Since the claim is that the lost photons are scattered, the vertical axis label should not be "absorbed photons," but instead should be, e.g. "Scattered photon rate" or "Difference in transmitted photon rate."

10. SI, pages 3 and 4: It is difficult to follow the math describing the ff wavefunction and probability of coincidences. Also, in some cases it's incomplete. Ideally the form of the joint spectral amplitude or density should be written out mathematically as well.

Reviewer: 2

Comments to the Author
Hickham et al. present a detailed and nicely explained study of entangled two photon absorption (or the lack thereof) in this manuscript. They measure the transmitted light, the fluorescence and the scattered light to create a complete accounting of the photon budget of the material, what is absorbed, emitted and scattered.

While the paper is well written, I found that the cautious nature of the presentation perhaps makes there final conclusion less clear. I would advise the to slightly strengthen their abstract to lead with the fact that, when a variety of methods are considered, ETPA is highly limited in R6G.

The most important measurement appears to be the scattering, which if it was resonant scattering we would expect the spectrum to match the doubled light spectrum rather than the low energy spdc source spectrum. This seems important, but I had some trouble undertstanding what the fundamental expectaion was, vs is what they saw.

I also am not totally clear on what they anticipate in the absorption experiment. If ETPA does exist, then do you expect the spectral components of the interference pattern to change? That seems implied by the manuscript but is not officially stated.

Finally, the primary point appears to be, that scattering can lead to apparent linear response in the absorption as a function of power, without requiring a two photon response. This definitely adds to the need for a standard ways to report and measure ETPA.

In general, the paper is an excellent contribution to the literature, and should be published subject to the minor revisions suggested.

Author's Response to Peer Review Comments:

During revisions, Nathan Harper contributed numerous edits to the SI theory and provided helpful discussions and interpretations vital to understanding the results. We would like to request that his name be added to the manuscript as a contributing author such that the author list reads: *Bryce P. Hickam[1]†, Manni He[1]†, Nathan Harper[1], Szilard Szoke[2], Scott K. Cushing[1]**

Editor:
1. In particular, please make a case for why the paper is a good fit for JPCL instead of JPC, e.g., by stating specific significance in the introduction. Clearly differentiate the work from other recent reports like https://pubs.acs.org/doi/10.1021/acs.jpca.2c00720 .

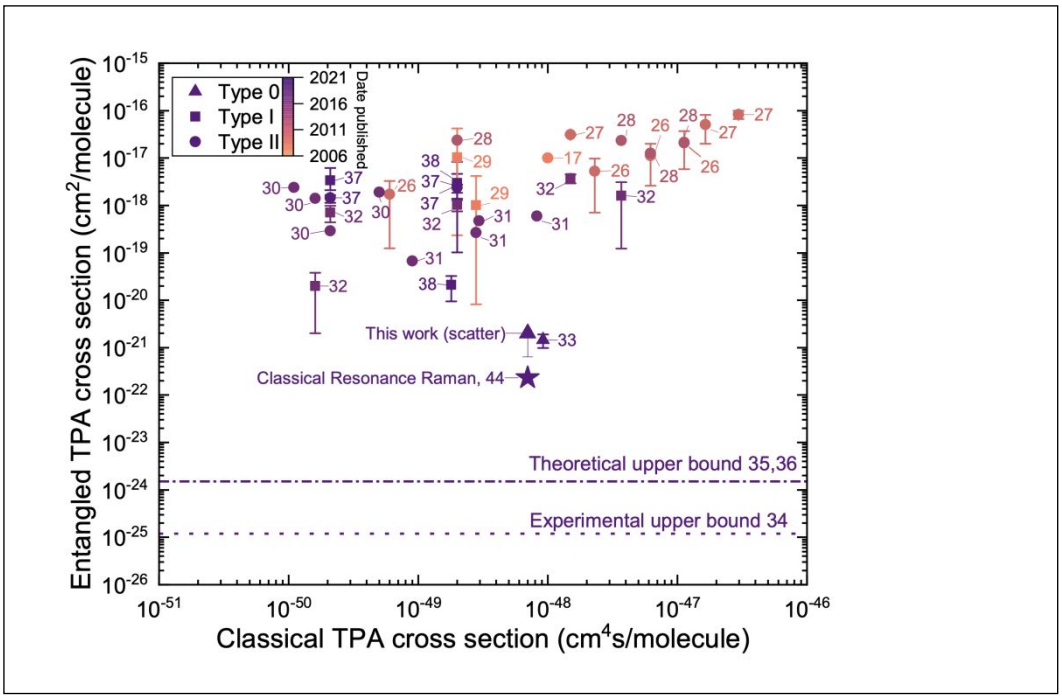
Response:
The significance of our paper is that it is the first report to experimentally explain the discrepancy between the variety of ETPA experiments in literature, such as those in the Figure 1 of the manuscript and the paper the editor cited for comparison. By being the first to characterize the entangled state temporally and spectrally during a possible molecular interaction, we measure classical one photon scattering as a dominant interaction at the low cross sections / high molecular concentrations popular to the field. The one photon scattering is easily mistaken for linearized two photon absorption in methods that rely on intensity changes, even when measuring the change in number count of coincidences. The paper therefore fits the JPCL criteria because it provides 1) an explanation of current discrepancies and 2) a technique to fix these discrepancies so as to unify the growing field and move beyond current cross section-based arguments. Reaching a broad audience through rapid publication is critical given the increasing scientific interest and federal funding aimed at looking at entangled molecular processes, particular for microscopy.

Accordingly, the following text was added to the abstract:
"This result can account for the discrepancies between the wide variety of entangled two-photon absorption cross sections reported from different measurement techniques. The reported instrumentation can unambiguously separate classical and entangled effects and therefore is of importance for the growing field of nonlinear and multiphoton entangled spectroscopy."

And the following text to the introduction:
"The single photon scattering explains the past discrepancies in measured cross sections between different techniques. Moreover, the paper presents a blueprint for a spectrometer that can unambiguously determine entangled photon excited state effects in the rapidly growing field of entangled nonlinear and multiphoton spectroscopy."

2. References: All references should use JPCL formatting (carefully check all references in both the main file and supporting information, if any)
Response: The references have been checked in both the main file and the supporting information and, to our knowledge, all use JPCL formatting.

3. Consider using color in Figure 1
Response: We considered several options to depict Figure 1 in color (see below) and agree with the editor that a color scale is easier to interpret.



3. Provide a full title page for your supporting information

Response: A full title page for the supporting information has been included in the document.

Reviewer 1:

1. The authors claim that no two-photon absorption has occurred, yet their paper is entitled "interaction with a virtual state mediated two-photon transition." Since they do not measure an interaction of this kind, I believe they should rename the manuscript.

Response: We agree with the reviewer, and admittedly struggled with several titles to convey the message of the paper. We have now gone with the more direct title: Single Photon Scattering Can Account for the Discrepancies Between Entangled Two-Photon Measurement Techniques

2. Page 3 Lines 15-18: To the best of my knowledge there is no early theoretical work suggesting that entangled two photon absorption cross sections can attain values close to one photon absorption cross sections.

Response: We have removed the phrase "theory and" to avoid confusion regarding theoretical studies of ETPA cross section values. The sentence now reads: "For example, early experiments purported that entangled photons can linearize two-photon processes to achieve near one-photon absorption cross sections."

3. *Page 5 Line 54: I'm under the impression that the authors are referring to the single-pair-per-mode quantum limit. How did they estimate the number of pairs per mode?*

Response: We have now edited the sentence to read: "The large bandwidth and 10^{-8} conversion efficiency allow for a flux in the sub-μW range without exceeding the single-pair-per-mode quantum limit, as calculated by total photon pairs per second divided by the frequency bandwidth in Hz."

3. Page 8 Line 53 to Page 9 Line 6, the statements about entanglement are vague here, and they don't show that the photons are entangled. For example can a classically correlated state produce the same result?

Response: The reviewer is correct that by randomly adjusting the phase of two classical photons (https://journals.aps.org/pra/pdf/10.1103/PhysRevA.100.013839) the generally held rule that any purity or coincidences better than 50% is a quantum state fails. However, replicating a "quantum" fourth-order interference relies on a direct manipulation of the phase of the classical light, whereas here the SPDC inherently creates an entangled state, so we believe our 95% purity is sufficient justification of two-photon bunching and entanglement.

We have modified the aforementioned text to make this more clear: In a two-photon Michelson interferogram, the degree of entanglement can be qualitatively inferred by examining the amplitude ratio above and below the oscillation baseline. A "top-heavy" feature, for example shown in Fig. 3 top trace, indicates photon bunching. The generally held rule is that a visibility of better than 50% confirms the state is quantum, although it must be remarked that randomization of phase and precise control of classical light can reproduce the "quantum dip". However, given the >95% purity measured here and the fact that SPDC with a CW laser inherently creates an entangled state, we believe we can reasonably confirm that our input source is entangled.

4. Page 9 Line 8: The value of "<20 fs" is a very short entanglement time considering that there is likely some group delay dispersion in the experiment, are the authors considering how GDD affects their entanglement time?

Response: We thank the author for bringing this to our attention as we did not mention a critical experimental detail. In our measurement setup, the entanglement time is measured after the sample interaction and not just estimated from the bandwidth. We have modified the sentence to now read: "The broad bandwidth also results in a ~20 fs correlation time (entanglement time) as measured after the sample. The entanglement time is not transform limited due to the group delay dispersion in the periodically poled chip and further optics. "

5. Page 11, Figure 4: I don't understand the explanation for the scattering signal plotted in Fig. 4. Why doesn't the scattered spectrum look identical to the SPDC spectrum shown in Figure. S2? For example, why are the scatter peak wavelengths shifted from the SPDC peak wavelengths?

Response: We thank the reviewer for bringing this point up. We have not clearly identified the scattering mechanism responsible for the loss in this paper (we plan to in follow up work).

However, the scattered spectrum is going to be some convolution of the molecular scattering cross section that depends on wavelength and the SPDC frequency spectrum, which would lead to a distortion in the measured spectrum. We agree the exact scattering mechanism deserves further follow up in a later paper. For now, we have included the sentence: "The scattered spectrum that is measured is a convolution of the wavelength dependent molecular scattering cross section and the SPDC signal which is why it does not appear identical to Figure S2."

6. In Figure S3, it appears as if there is absorption from ZnTPP at 550nm and beyond, however the authors claim that the lack of absorption in this region is what causes the lack of a 90 degree signal for ZnTPP. Can the authors explain how this is possible? Furthermore, if there is no scatter, what is the signal shown in Figure S6?

Response: The reviewer is correct to point out that there is a small absorption peak near 550nm for ZnTPP. The signal in Figure S6 is purely the dark EMICCD counts, and the oscillation frequency is due to cavity oscillation instead of photon interference. The smaller absorption of ZnTPP compared to R6G in this region would lead to a smaller resonant scattering process. Given the experiments were already done near the noise floor of the EMICCD it is not surprising that no signal was detected. However, our language did not properly convey this at all, so we have made the following additions:

To the text: As a control, zinc tetraphenylporphyrin (ZnTPP) was measured because it has a narrow-band absorption at 400 nm that is ~200 nm from the SPDC spectrum as well as a much weaker absorption near 550 nm (aligned with R6G). No scattered signal was measured for ZnTPP within the sensitivity limit of our spectrometer, which may be expected because ZnTPP has a lower absorption cross section than R6G, but other factors regarding the nature of the scattering process may come into play. All light is transmitted within our error bars and Figure S6 represents the dark count fluctuations of the EMICCD.

In Figure S6 caption: The signal here is purely a result of the noise of the EMICCD camera.

7. On page. 12, lines 27-30: The authors mention the cross-section sensitivity of their instrument. The authors do not mention that for Rh6G, their sensitivity is decreased because they have not (to my knowledge) attempted to filter out the scatter. Ideally, the authors should filter out the scatter and then report on the origin of any remaining signal.

Response: Unfortunately, the scatter and any fluorescence signal overlap so they cannot be separated by filtering. The sensitivity is instead estimated by using the noise floor of the detector relative to the maximum possible photon count before detector saturation. We have added the following explanation to the text: The 10^{-25} cm^2/molecule sensitivity is estimated based on the noise floor of the detector and the maximum possible photon count before detector saturation. At this sensitivity, we estimate the maximum fluorescence count rate, including collection efficiency, to be approximately 5-10 photons/s.

8. Page 12, lines 34-37: what is the slope of the fit and why does it have this dependence? If it is scatter, why doesn't it have a linear dependence?

Response: We have updated the manuscript by replacing Figure 5 with a plot of transmitted photon rate vs input photon rate (shown below). This figure displays the relationship that is to be expected for a linear scattering process, as well as the updated cross section calculated using this technique. The cross section values reported in the paper have been accordingly updated. The previous Figure 5 has been moved to the SI (shown below).

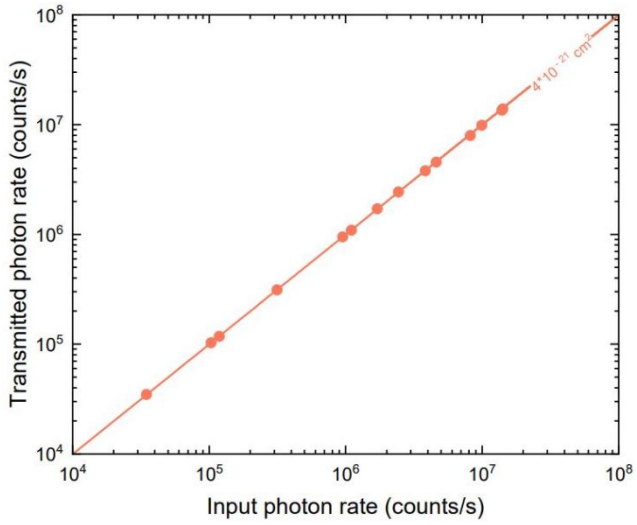


Fig. 5: Measured transmitted photon rate (orange data points) and fit (orange solid line) vs input photon rate for 5mM Rhodamine 6G in water. Using the method standard in literature, the ETPA cross section from the measured absorption rate would be $4\,(\pm 1) * 10^{-21}$ cm^2/molecule. In this manuscript, the linear relationship is determined to not be from ETPA,

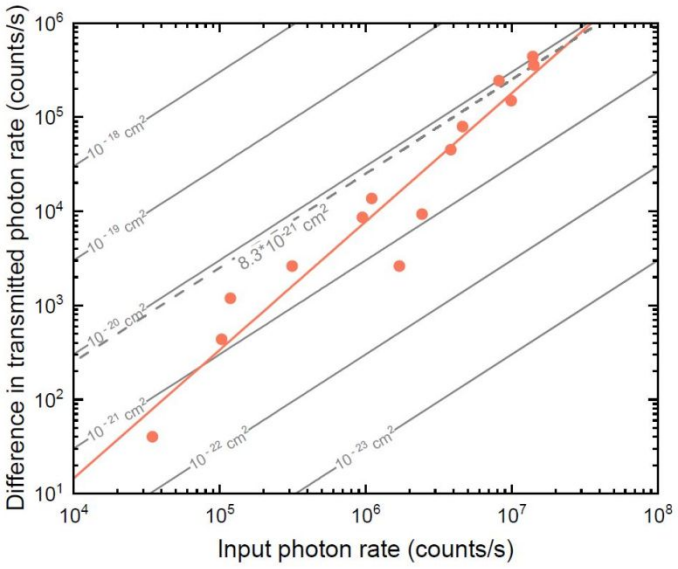


Fig. S9: Measured absorbed photon rate (orange data points, calculated from: $R_{solvent} - R_{sample,}$ a popular method used in literature) and fit (orange solid line) vs input photon rate for 5mM Rhodamine 6G in water. The slope of the line of best fit for this data is 1.3. Using the method standard in literature, the ETPA cross section from the measured absorption rate would be $8\ (\pm 1) * 10^{-21}$ cm²/molecule. In this manuscript, the linear relationship is determined to not

We also added the following text to the SI to further explain the cross section calculation:
The process is repeated for a blank water standard. The absorption cross section reported in Figure 5 is calculated from a plot of the transmitted photon rate vs. the input photon rate using the following steps:

$$A = \varepsilon lc \#(1)$$

$$\varepsilon = \frac{N_A}{\ln 10}\sigma \#(2)$$

$$T = \frac{I_{sample}}{I_{solvent}} = 10^{-A} \#(3)$$

$$\log_{10}\frac{I_{sample}}{I_{solvent}} = \log_{10} 10^{-A} = -A \#(4)$$

$$-\log_{10}\frac{I_{sample}}{I_{solvent}} = \varepsilon(1\ cm)(5mM) \#(5)$$

$$-\log_{10}\frac{I_{sample}}{I_{solvent}} = \frac{\left(6.02 * 10^{23}\frac{molecule}{mole}\right)}{\ln 10} * \sigma * (1\ cm) * \left(\frac{0.005mol}{1000\ cm^3}\right) \#(6)$$

$$-\log_{10}\frac{I_{sample}}{I_{solvent}} = 2.8759 * 10^{19}\frac{molecule}{cm^2}\sigma \#(7)$$

$$\sigma = -\frac{1}{2.8759 * 10^{19} molecule}\frac{cm^2}{}\log_{10}\frac{I_{sample}}{I_{solvent}} \#(8)$$

$$\sigma = -\frac{1}{2.8759 * 10^{19} molecule}\frac{cm^2}{}\log_{10}(0.9725) \#(9)$$

$$\sigma = 4 * 10^{-21}\frac{cm^2}{molecule} \#(10)$$

9. Page 13, Figure 5: Since the claim is that the lost photons are scattered, the vertical axis label should not be "absorbed photons," but instead should be, e.g. "Scattered photon rate" or "Difference in transmitted photon rate."

Response: We thank the reviewer for the suggestion, the vertical axis label has been updated to: Difference in transmitted photon rate.

10. SI, pages 3 and 4: It is difficult to follow the math describing the ff wavefunction and probability of coincidences. Also, in some cases it's incomplete. Ideally the form of the joint spectral amplitude or density should be written out mathematically as well.

Response: We thank the reviewer for pointing this out.. Per the reviewer's suggestion, we have added more details, intermediate steps, and approximations used on the math described under the SI section "Broadband fourth-order interference" (Pages 4-6), as well as given an explicit example of our JSA in the SI on Page 3:

For example, for the single peaks, the JSA takes the form of

$$\phi(\lambda_s,\lambda_p) = \frac{1}{\sigma_{SPDC}\sqrt{2\pi}}\exp\left[-\frac{(\lambda_s - 2\lambda_p)^2}{2{\sigma_{SPDC}}^2}\right] \#(2)$$

where λ_s is the wavelength of the signal, λ_p is the wavelength of the pump, and $\sigma_{SPDC} = \frac{FWHM}{2\sqrt{2ln2}}$ where $FWHM$ is the full width half maximum of the fitted peaks.

Reviewer 2:

1. Hickham et al. present a detailed and nicely explained study of entangled two photon absorption (or the lack thereof) in this manuscript. They measure the transmitted light, the fluorescence and the scattered light to create a complete accounting of the photon budget of the material, what is absorbed, emitted and scattered. While the paper is well written, I found that the cautious nature of the presentation perhaps makes there final conclusion less clear. I would advise the to slightly strengthen their abstract to lead with the fact that, when a variety of methods are considered, ETPA is highly limited in R6G.

Response: We thank the reviewer for this suggestion and agree that we were a bit overly cautious in presentation. The editor had similar remarks. We have added the following to strengthen the claims of the paper

Changed title to: Single Photon Scattering Can Account for the Discrepancies Between Entangled Two-Photon Measurement Techniques

Added to Abstract: This result can account for the discrepancies between the widely varying entangled two-photon absorption cross sections reported from a variety of measurement techniques. The reported instrumentation can unambiguously separate classical and entangled effects and therefore is of importance for the growing field of nonlinear and multiphoton entangled spectroscopy.

Added to Introduction: The single photon scattering explains the past discrepancies in measured cross sections between different techniques. Moreover, the paper presents a blueprint for a spectrometer that can unambiguously determine entangled photon excited state effects for the rapidly growing field of entangled nonlinear and multiphoton spectroscopy.

2. The most important measurement appears to be the scattering, which if it was resonant scattering we would expect the spectrum to match the doubled light spectrum rather than the low energy spdc source spectrum. This seems important, but I had some trouble undertstanding what the fundamental expectaion was, vs is what they saw.

Response: We are slightly confused by the reviewers question, as we do not know if the doubled light spectrum refers to a two-photon scattering from the SPDC or the initial pump photon? Either way, we agree the scattering mechanism requires more understanding, as was also brought up by Reviewer #1. At this point, we are planning another paper to fully explore this concept, although the measured spectral and temporal data definitively indicate some form of one-photon scattering.

We have added the following sentences to help with this point, and agree further investigation is warranted in the future.

At this point, the exact nature of the scattering mechanism is unknown, but the scattered spectrum and its single-photon time dependence are clearly measured.

3. I also am not totally clear on what they anticipate in the absorption experiment. If ETPA does exist, then do you expect the spectral components of the interference pattern to change? That seems implied by the manuscript but is not officially stated.

Response: The reviewer is correct, in that if ETPA is present two things will happen in the transmitted interferogram: 1) the photon bunching feature will diminish and 2) if any fluorescence is collected or a nonuniform absorption process occurs, the classical component will change spectrally. This text has been added to the paper and we agree it helps with clarity.

If ETPA does occur, then the photon bunching feature will diminish and the classical component will change spectrally due to the added fluorescence signal (or a nonuniform single photon absorption process).

4. Finally, the primary point appears to be, that scattering can lead to apparent linear response in the absorption as a function of power, without requiring a two photon response. This definitely adds to the need for a standard ways to report and measure ETPA. In general, the paper is an excellent contribution to the literature, and should be published subject to the minor revisions suggested.

Response: We thank the reviewer for their helpful suggestions to further improve the manuscript.