

Limitations of entangled two-photon absorption detection

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We introduce a method for determining the sensitivity of any given entangled two-photon absorption (ETPA) measurement. By modeling all signal and noise contributions to the measurement, we derive a single numerical value that describes the sensitivity of the ETPA measurement in Göppert-Mayer units. This allows us to directly compare vastly different experimental approaches and determine whether ETPA will be detectable under the given conditions. Therefore we can quantify the effect of any change to a given experimental apparatus and identify the ideal optimization pathway.

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I. INTRODUCTION

Two-photon absorption (TPA) is a valuable tool for a variety of spectroscopy and imaging schemes, creating contrast and improving resolution via nonlinear processes [1–4]. However, since any TPA process requires two photons to interact simultaneously with one absorber, the overall interaction cross sections are prohibitively small. This limitation is typically overcome by vastly increasing the photon flux with high-power pulsed lasers or high-finesse cavities [2,3,5–7]. While quantum correlations could also be exploited in a variety of spectroscopic applications, increasing sensitivity by reducing measured noise in absorption spectroscopy [8–10], or to translate the measured signal to a different spectral range [11,12], here we use quantum correlations to increase the instantaneous photon pair flux, thereby increasing the TPA rate.

Molecular TPA requires the simultaneous arrival of two photons and sets strict limits on their combined energy. Thus, time-frequency entangled photon pairs promise a significant advantage in absorption yield. Furthermore, it has been proposed that the quantum correlations embedded in the photon pair provide access to molecular information inaccessible with classical light sources [1,13]. However, these correlations could just as well decrease the TPA yields in an unfortunate experimental configuration [14,15]. To measure the effect of quantum correlations on TPA yields, the high-power laser is replaced by a parametric down conversion (PDC) source that produces time-frequency entangled photon pairs. However, the increase in absorption efficiency is now counteracted by the decrease in power driving the TPA. Therefore observing

molecular TPA driven by entangled pairs (ETPA) in the laboratory is very challenging, primarily due to the prohibitively low overall ETPA rate [16–24].

There are two approaches to detecting molecular absorption: measuring attenuation of the transmitted field and measuring fluorescence emitted by the absorber. In this work we focus on direct fluorescence detection as described in Refs. [16–20]. However, our approach can also be applied to the transmission approach, as presented in Refs. [22,23,25–27]. Although a fluorescence event is always tied to a molecule reaching an excited state, any information about the excitation pathway is lost. Here we consider three excitation pathways: ETPA, TPA, and single-photon or hot band absorption (HBA) [28]. Therefore, detecting only a fluorescence signal when exciting with PDC light is insufficient for measuring ETPA. Furthermore, technical imperfections, most notably detector dark counts, significantly contribute to any recorded signal.

Since the overall goal is to investigate the effect of the quantum correlations on the absorption yield, only the strength of the quantum correlations must be varied in the experiment, while all other parameters have to remain constant. This modulation can be achieved by either separating the correlated photons [21,22,29] or by introducing losses [16–20,23].

These different methods and the dependence of the ETPA signature on all properties of the excitation beam make comparisons between published (null-) results nontrivial. Therefore, we developed a unifying framework that allows us to directly compare different ETPA measurements. By treating the absorber as a black box and focusing on the measurement system, we developed an analytical model that enables us to predict whether observations are possible by calculating the expected signal and noise levels for any given set of experimental parameters. Our aim is to clear up the intense ongoing controversies and “null-results” currently plaguing the ETPA community by creating a universal benchmark. Furthermore, we can directly calculate the impact of each experimental parameter on the final sensitivity, thus

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providing a clear path for improvement of any given ETPA experiment.

II. MODEL

Our model is based on calculating signal-to-noise ratios, analogous to the detection threshold derived in Ref. [26]. By modeling both the signal and the noise, and then comparing them, we obtain a lower bound for the detectable ETPA strength in a given experimental configuration.

In the experiment, a total of N_{rec} potential ETPA fluorescence events will be recorded. As previously mentioned, this will be the sum of all possible excitation pathways,

$$N_{\text{rec}} = N_{\text{ent}} + N_c + N_h + N_{\text{dark}}, \quad (1)$$

the desired ETPA contribution N_{ent} , an unavoidable classical TPA contribution N_c caused by two uncorrelated photons getting absorbed, as well as direct single-photon absorption N_h [28]. In the experiment the recorded number of events N_{rec} will also include a nonfluorescence contribution consisting of detector dark counts N_{dark} .

Thus in any ETPA experiment, the amount of correlated pairs interacting with the absorber must be varied while keeping the total number of photons at the absorber—and therefore the resulting non-ETPA contribution—constant. This results in at least two data points: one with maximal correlations of the light field and the largest total fluorescence yield, from now on called signal (S), and one background (B) measurement recorded with minimal (spoiled) correlations. An ETPA signature can then be detected if the difference between the two data points is greater than the measurement uncertainty:

$$S - B \geq u(S) + u(B), \quad (2)$$

with $u(S)$ ($u(B)$) being the measurement uncertainty of S (B). To investigate the best possible case, we assume Poissonian statistics for all measured quantities:

$$u(S) = n_\sigma \sqrt{S} \text{ and } u(B) = n_\sigma \sqrt{B}, \quad (3)$$

with the accuracy n_σ . Given a sufficient set of experimental parameters, all contributions to S and B are known. Therefore, Eq. (2) allows us to make quantitative predictions about the detectability of an ETPA signature.

Rate estimations

To calculate the TPA rates the pair ϕ_{pair} and single-photon $\phi_{s,i}$ fluxes at the absorber are needed. Therefore we assume an ideal (nondegenerate) PDC source that produces N_P correlated photon pairs per pump pulse. Since any experiment will involve optical losses between the source and the absorber, which will break the pair correlations, we describe these losses using the transmission coefficients $\eta_{s,i}$ of signal and idler beams, respectively. Using the photon creation $\hat{a}_{s,i}^\dagger$ and annihilation operators $\hat{a}_{s,i}$ for the signal and idler beam at the sample position, the single-photon flux can be written as

$$\phi_{s,i} = \frac{\langle \hat{a}_{s,i}^\dagger \hat{a}_{s,i} \rangle}{A_{s,i} T_{s,i}} = \frac{\eta_{s,i} N_P}{A_{s,i} T_{s,i}}, \quad (4)$$

with $A_{s,i}$ and $T_{s,i}$ denoting the cross-sectional area and temporal duration of the wave packets at the sample position.

As previously mentioned, the absorber can be excited by two uncorrelated photons [18]. This classical TPA rate can be written as

$$f_c = \sigma_c N_t \phi_s \phi_i = \sigma_c N_t \frac{\eta_s \eta_i N_P^2}{A^2 T^2}, \quad (5)$$

with the number of illuminated molecules N_t and the classical TPA cross section σ_c , assuming both beams have the same spatial $A_s = A_i = A$ and temporal $T_s = T_i = T$ shape, ensuring maximal overlap and therefore maximizing the TPA yield.

In PDC, the photon pair is defined by the properties of the pump beam and phase matching of the nonlinear medium, resulting in spatial, spectral, and temporal correlations between the signal and idler photons. We model these quantum correlations by introducing the entanglement area A_e and the entanglement time T_e . These represent the conditioned spatial and temporal distributions of the idler photon, upon the detection of the signal photon [19,30–33]. In the absence of coupling between spatial and spectral degrees of freedom and strong two-photon entanglement, the total number of modes of the PDC light can be approximated to $M = AT/A_e T_e$ [34–36].

The photon number n in every mode of a multimode two-mode squeezed vacuum state is given by a thermal distribution $P(n)$ [37]. Assuming a uniform distribution of the nonlinear gain over all modes, the number of pairs at the absorber is $\langle n \rangle = \eta_s \eta_i N_P / M$. Since every signal photon in a given mode forms a potential pair with every idler photon in the same mode and thereby can cause ETPA, the pair flux must include these higher photon number effects:

$$\phi_{\text{pair}} = \sum_{i=0}^M \sum_{n=0}^{\infty} \frac{P(n) n^2}{A A_e T T_e} = \frac{\eta_s \eta_i N_P}{A A_e T T_e} + 2 \frac{\eta_s^2 \eta_i^2 N_P^2}{A^2 T^2}. \quad (6)$$

The ETPA rate can then be written as follows [36]:

$$f_{\text{ent}} = \sigma_c N_t \phi_{\text{pair}} = \sigma_c N_t \left(\frac{\eta_s \eta_i N_P}{A_e T_e A T} + 2 \frac{\eta_s^2 \eta_i^2 N_P^2}{A^2 T^2} \right). \quad (7)$$

Note that the ETPA rate does not depend on an entangled cross section σ_e but only on the classical cross section σ_c as the “nonclassicality” is fully transferred to the optical field [38,39].

In the low-gain case $\langle n \rangle < 1$, the quantum enhancement observed in the experiment is described by the number of modes M and is completely given by the optical fields, consistent with the arguments made in Refs. [23,38,39]. Any additional enhancement, as discussed in [15,39], could be included as an increased effective mode number without changing the arguments made here.

In the high-gain case, $\langle n \rangle > 1$, Eq. (7) scales quadratically, making ETPA detection much easier [18,40], with an enhancement given by the value of the second-order correlation function $g^{(2)}$ [19,41,42].

Even for excitation far off resonance, one photon absorption can occur, leading to a linearly scaling fluorescence signal [28]. This HBA rate can be expressed using the signal (idler) flux $\phi_{s,i}$ at the absorber as

$$f_h = \frac{N_t}{A T} (\sigma_{h,s} \eta_s + \sigma_{h,i} \eta_i) N_P, \quad (8)$$

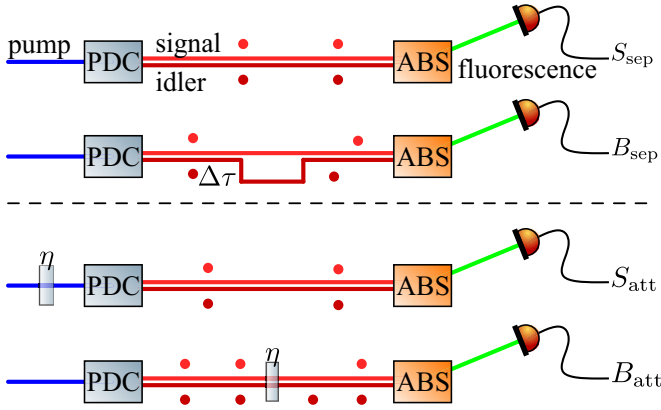


FIG. 1. Experimental configuration for signal and background measurements in both schemes discussed here. Entangled photon pairs are created by pumping a PDC crystal and are sent to a two-photon resonant absorber (ABS). The resulting fluorescence is then detected by a single-photon-sensitive detector. A setup for measuring the signal S_{sep} in the separation scheme is shown in (a1). The background measurement B_{sep} is obtained by delaying the idler beam by $\Delta\tau$ (a2). In the attenuation scheme, an attenuator η is placed either in the pump beam to obtain the signal measurement S_{att} (b1) or in the signal and idler beams to measure the background B_{att} (b2).

with the wavelength-dependent hot band cross section $\sigma_{h,s,i}$. Since all experiments we analyze in this work utilize frequency-degenerate photon pairs, $\sigma_{h,s} = \sigma_{h,i} = \sigma_h$.

III. SENSITIVITY CALCULATION

Since TPA and HBA processes are always present, even for an ideal stream of entangled pairs, and cannot be fully suppressed by clever design, their impact on any ETPA measurement must be considered. Using Eq. (2) we analyze two different measurement schemes (shown in Fig. 1) by calculating the expected number of detected events and the corresponding uncertainties in an ETPA measurement.

So far, all derivations have been made for a single pump pulse. Therefore, to find the actual measured values, the repetition rate of the pump f_{rep} and the integration time T_{int} have to be considered. In the case of a continuous wave pump, we use the coherence time of the pump ($1/\text{Bandwidth}$) as the pulse duration T and set $f_{\text{rep}} = 1/T$.

A. Separation

In this conceptually straightforward approach, one measurement S_{sep} is taken with pairs that are as strongly correlated in time and space as possible, and the second measurement (B_{sep}) is taken with the pairs separated in time (space) by more than the entanglement time (area), rendering ETPA impossible. We assume that the delay matches the time between pump pulses $\Delta\tau = 1/f_{\text{rep}}$, as to not change the single-photon flux at the absorber. An experimental realization of the method in the spatial domain can be found in [22]. Based on the considerations in Sec. II A and Eq. (1), the expected signal and background can be written as follows:

$$S_{\text{sep}} = \eta_s \eta_i \eta_d T_{\text{int}} f_{\text{rep}} \frac{N_t}{A} \left(\underbrace{\frac{N_p \sigma_c}{A_e T_e}}_{\text{ETPA}} + 2 \underbrace{\frac{\eta_s \eta_i N_p^2 \sigma_c}{AT}}_{\text{CTPA}} + \underbrace{\frac{N_p^2 \sigma_c}{AT}}_{\text{CTPA}} + \underbrace{\frac{(\eta_s + \eta_i) N_p \sigma_h}{\eta_s \eta_i}}_{\text{HBA}} \right) + \underbrace{T_{\text{int}} f_{\text{dark}}}_{\text{Dark counts}}, \quad (9)$$

$$B_{\text{sep}} = \eta_s \eta_i \eta_d T_{\text{int}} f_{\text{rep}} \frac{N_t}{A} \left(\frac{N_p^2 \sigma_c}{AT} + \frac{(\eta_s + \eta_i) N_p \sigma_h}{\eta_s \eta_i} \right) + T_{\text{int}} f_{\text{dark}}. \quad (10)$$

In addition to integrating over the acquisition time (T_{int}) we also included the detection efficiency η_d and the detector dark count rate f_{dark} . Note that the ETPA term is missing from (10) since signal and idler are separated far enough to break all correlations. Inserting into (2) and isolating the TPA cross section σ_c yields

$$\sigma_c \geq \frac{n_o^2 A^2 T}{T_{\text{int}} f_{\text{rep}} \eta_s \eta_i \eta_d N_t} \frac{1}{X} \left\{ \frac{1}{N_p} + \frac{2}{X} + 2 \sqrt{\frac{1}{X^2} + \frac{1}{N_p X} + \frac{T_{\text{int}}}{n_o^2} \left(\frac{f_{\text{rep}} N_t}{AN_p} \eta_d (\eta_s + \eta_i) \sigma_h + \frac{f_{\text{dark}}}{N_p^2} \right)} \right\}, \quad (11)$$

with

$$X = M + 2\eta_s \eta_i N_p. \quad (12)$$

As mentioned earlier, successful ETPA detection is only possible if the inequality (2) and therefore (11) is fulfilled. Thus we found a lower bound for the detectable TPA cross section and therefore the sensitivity of the measurement.

A quick analysis of (11) shows that increasing T_{int} is beneficial in any case, while (12) can be utilized to identify the low- and high-gain regime. In the low-gain single-pair regime, $M > 2\eta_s \eta_i N_p$, the sensitivity-bound scales at most with $1/N_p$, as the ETPA contribution to the recorded signal (11) also grows linear. In the high-gain regime of multiple

pairs per mode ($M < 2\eta_s \eta_i N_p$) the scaling becomes at most $1/N_p^2$, as the ETPA contribution increases quadratically with the number of photon pairs. However, in this semiclassical case, the quantum advantage is reduced to a small factor given by the value of the $g^{(2)}$ function of the light, as the number of modes M becomes insignificant [19,41,42].

A more thorough discussion of the implications for ETPA experiment design can be found in Sec. IV.

B. Attenuation

Next we apply our model to the method introduced by Dayan *et al.* [43], which is most prevalent in the current

TABLE I. Experimental parameters used throughout the text if not stated otherwise.

	(a) Geneva	(b) Oregon	(c) Oregon CW	(d) Oregon BSV	(e) Boulder FS	(f) Boulder Fibre	Figure 2
source	[16]	[17]	[18]	[18]	[19]	[20]	This work
T_{int}	5.56 h	0.5 h	8.33 h	1.0 h	0.75 h	13.0 h	3.0 h
$\eta_{s,i}$	71.0%	70.0%	85.3%	85.3%	76.0%	50.0%	70.0%
η_d	5.18%	1.9%	8.15%	8.15%	4.5%	1.61%	7.15%
A	15.9 μm^2	12.57 μm^2	15.9 μm^2	15.9 μm^2	1256.64 μm^2	18.0 μm^2	12.57 μm^2
T	200.0 ns	200.0 ns	200.0 ns	8.0 ps	110.0 fs	110.0 fs	100.0 ns
A_e	15.9 μm^2	12.57 μm^2	15.9 μm^2	15.9 μm^2	1.7 μm^2	2.1 μm^2	12.57 μm^2
T_e	140.0 fs	100.0 fs	110.0 fs	110.0 fs	1620.0 fs	1070.0 fs	100.0 fs
$T_{e,\text{min}}$	56.0 fs	42.0 fs	56.0 fs	56.0 fs	17.0 fs	22.0 fs	100.0 fs
N_P	1.9×10^5 PpP	2.5×10^4 PpP	2.4×10^5 PpP	1.6×10^7 PpP	147.0 PpP	2.0 PpP	1.0×10^9 PpP
f_{rep}	5.0 MHz	5.0 MHz	5.0 MHz	0.0 MHz	80.0 MHz	80.0 MHz	10.0 MHz
f_{dark}	215 Hz	125 Hz	3 Hz	3 Hz	50 Hz	100 Hz	10 Hz
σ_{HBA}	4.5×10^{-40} cm ²	4.5×10^{-40} cm ²	4.5×10^{-40} cm ²	4.5×10^{-40} cm ²	1.0×10^{-40} cm ²	1.0×10^{-40} cm ²	1.0×10^{-40} cm ²
N_t	1.6×10^{-15} mol	4.0×10^{-16} mol	1.6×10^{-15} mol	1.6×10^{-15} mol	2.8×10^{-12} mol	1.5×10^{-11} mol	2.0×10^{-16} mol
η	53.0%	50.0%	54.0%	70.0%	68.0%	63.0%	70.0%
σ_c att	1.2×10^4 GM	1.2×10^6 GM	2.8×10^2 GM	2.2×10^{-3} GM	1.7×10^4 GM	1.4×10^4 GM	9.6×10^{-4} GM
σ_c split	2.8×10^3 GM	3.0×10^5 GM	6.6×10^1 GM	5.5×10^{-4} GM	4.2×10^3 GM	3.3×10^3 GM	2.4×10^{-4} GM
Target σ_c	9.9 GM	9.9 GM	9.9 GM	9.9 GM	390.0 GM	390.0 GM	9.9 GM

literature [16–20,24,30,40]. In this method an attenuator is used to vary the strength of the correlation for the signal and background measurements while ensuring that the single-photon flux remains constant. The background B_{att} is recorded by placing an attenuator with transmittance η in the signal and idler beams as shown in Fig. 1(b2). This re-

sults in a linear reduction of single photons and a quadratic reduction of entangled pairs. To record the signal S_{att} , the same amount of attenuation is now introduced to the PDC pump [see Fig. 1(b1)], linearly reducing the amount of single photons and entangled pairs. Thus, the signal and background become

$$S_{\text{att}} = \eta_s \eta_i \eta_d T_{\text{int}} f_{\text{rep}} \frac{N_t}{A} \left(\eta \frac{N_P \sigma_c}{A_e T_e} + 2\eta^2 \frac{\eta_s \eta_i N_P^2 \sigma_c}{AT} + \eta^2 \frac{N_P^2 \sigma_c}{AT} + \eta \frac{(\eta_s + \eta_i) N_P \sigma_h}{\eta_s \eta_i} \right) + T_{\text{int}} f_{\text{dark}}, \quad (13)$$

$$B_{\text{att}} = \eta_s \eta_i \eta_d T_{\text{int}} f_{\text{rep}} \frac{N_t}{A} \left(\eta^2 \frac{N_P \sigma_c}{A_e T_e} + 2\eta^4 \frac{\eta_s \eta_i N_P^2 \sigma_c}{AT} + \eta^2 \frac{N_P^2 \sigma_c}{AT} + \eta \frac{(\eta_s + \eta_i) N_P \sigma_h}{\eta_s \eta_i} \right) + T_{\text{int}} f_{\text{dark}}. \quad (14)$$

Inserting into (2) and isolating the TPA cross section σ_c yields

$$\sigma_c(\eta) \geq \frac{n_\sigma^2 A^2 T}{T_{\text{int}} f_{\text{rep}} \eta_s \eta_i \eta_d N_t} \frac{1}{\eta Y} \left\{ \frac{1}{N_P} + \frac{2M}{N_P Y} + \frac{2\eta(1 + 2\eta_s \eta_i)}{Y} \right. \\ \left. + 2\sqrt{\frac{M^2 + MY}{N_P^2 Y^2} + \frac{M(1 + \eta)(1 + 2\eta_s \eta_i)}{\eta N_P Y^2} + \frac{(1 + 2\eta_s \eta_i)(1 + 2\eta_s \eta_i \eta^2)}{Y^2} + \frac{T_{\text{int}}}{n_\sigma^2} \left(\frac{f_{\text{rep}} N_t}{2AN_P} \eta \eta_d (\eta_s + \eta_i) \sigma_h + \frac{f_{\text{dark}}}{N_P^2} \right)} \right\}, \quad (15)$$

with

$$Y = M(\eta - 1) + 2\eta_s \eta_i N_P \eta (\eta^2 - 1). \quad (16)$$

The scaling dynamics at low and high gain are analogous to Eq. (11) while the crossover point is now modulated by η , as can be seen in Eq. (16).

To achieve optimal sensitivity with this method, the optimal attenuation value η_{opt} must be found. In the low-gain regime η_{opt} is primarily affected by the dark counts and takes values between approximately 0.25 for no dark counts and 0.5 for a large number of dark counts. In the high-gain regime, η_{opt} takes values between 0.5 and approximately 0.7, primarily influenced by the HBA strength and detector dark counts.

The sensitivity gain due to finding the optimal attenuation is only up to 25% in the high-gain regime and up to 30% in the low-gain regime. Nevertheless, the experimental simplicity of this optimization makes it valuable for any attenuation-based ETPA experiment. Unless stated otherwise, we will always use η_{opt} in the following discussion.

IV. RESULTS

Figure 2 shows the minimal detectable value of σ_c or ETPA sensitivity for the two methods over the photon pair flux per mode N_P/M . In this figure we assume Rhodamine 6G as the absorber and broadband frequency-degenerate

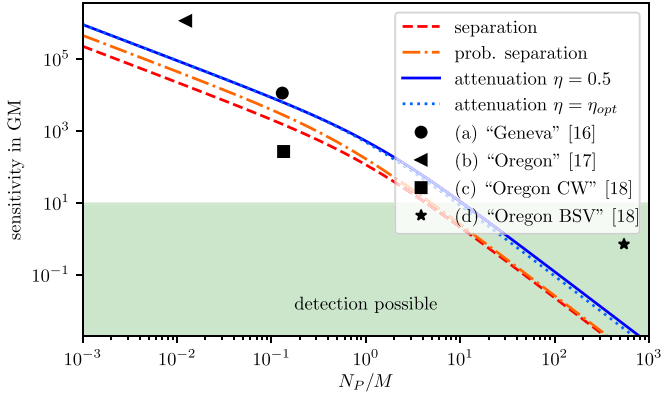


FIG. 2. Comparing the attenuation method (15) (blue) with different attenuation values η to the separation method (11). The shaded area indicates possible ETPA detection using Rhodamine 6G at 1064 nm as the target. The separation method outperforms the attenuation method in all cases, while the attenuation method can be improved by optimized attenuation in the high-flux regime for the parameters chosen here. The markers represent the parameter sets used in the attenuation method measurements published in Refs. [16–18]. The full set of parameters can be found in Table I.

PDC light centered at 1064 nm. While implementing the attenuation method is relatively straightforward, deterministically splitting the degenerate beam into signal and idler is more challenging. One possible approach is to use a dichroic mirror with a transmission edge at the central wavelength to create a short-wavelength signal and a long-wavelength idler. Then, the idler beam can be delayed by $\Delta\tau$ before recombining the two beams on another dichroic mirror, thus making only ETPA impossible without changing any other property of the exciting beam. We also applied our method to probabilistic splitting of the degenerate PDC light, see Appendix A.

To compare the different methods, we make the strong assumption, that all further experimental parameters will remain constant when the measurement method is changed. However, since this may require a significant reconfiguration of the experimental setup, it is likely that the parameters will change and any parameter estimation on our part would be speculative. The exact parameters we used can be found in Table I.

As expected, the separation method outperforms the attenuation method in all cases due to the total suppression of ETPA in the background measurement, given equal parameters. However, due to the increased complexity, losses $\eta_{s,i}$ will probably increase, leading to an underestimation of the detectable σ_c .

We also plot our predicted ETPA sensitivity for four published experiments using Rhodamine 6G and degenerate PDC centered at 1064 nm [16–18] as black markers in Fig. 2. Since only the marker for the bright squeezed vacuum (BSV) experiment shown by Landes *et al.*, (d) “Oregon BSV,” lies in the green shaded region, we only predict ETPA detection for this experiment, consistent with the observations made by the authors. In this high-gain experiment, a 1.8 times increase in fluorescence efficiency of the BSV over a coherent state was observed [18].

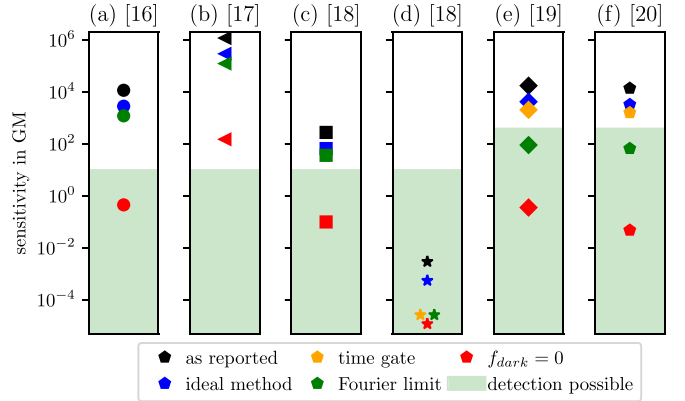


FIG. 3. Our model applied to published experimental data (black). Only experiment (d) reaches the required sensitivity. We optimized the sensitivity by selecting the optimal method (blue) and, in the cases of pulsed excitation, introduced time-gated detection (yellow). Additionally, we assume Fourier-limited Gaussian photon pairs (green), reaching the sensitivity goal in cases (e) and (f). Finally, we eliminate detector dark counts (red) and also reach the goal in cases (a) and (c). Case (b) however does not reach the sensitivity goal.

However, we would like to stress that our treatment of the absorber as a black box might be insufficient to reproduce the experimental results. Moreover, it also seems challenging to determine the exact experimental parameters for these types of experiments.

Nevertheless, we can use our model to evaluate possible improvements to future ETPA measurements. We use the six distinct experimental configurations presented in [16–20] as case studies, with all used parameters listed in Table I. We plot the ETPA sensitivity according to our model for all six experiments as black markers in Fig. 3 and indicate the goal σ_c of the particular absorber used as a green shaded area.

First, we determine the ideal method for each experiment under the strong assumption that the experimental parameters are unaffected by the change in method. While the exact parameters of these experiments vary, they could all improve their sensitivity and reach a lower detectable σ_c by using the separation method as indicated by the blue marker.

As the next step we incorporate time-gated fluorescence detection, as described in Appendix B for the experiments using pulsed pump beams (shown in yellow in Fig. 3), yielding a 21 times improvement in sensitivity in experiment (d) “Oregon BSV.” For continuous wave pump beams we introduced a very fast chopper, but the decrease in effective acquisition time negated any gain due to time-gating. Additionally, time gates could be a valuable tool for identifying and eliminating nonfluorescence two-photon effects such as second harmonic generation.

Subsequently, we eliminate any group dispersion of the photon pairs and assume Fourier-limited Gaussian pulses, depicted in green. As experiments (e) “Boulder FS” and (f) “Boulder Fibre” suffer from significant group velocity dispersion, this change is especially effective here and is sufficient to reach the desired sensitivity.

Lastly, we completely eliminate detector dark counts by setting $f_{\text{dark}} = 0$. This yields improvements of multiple orders

of magnitude, as shown in red, in all but one case (d) “Oregon BSV”. By following these steps we reach the desired sensitivity in five out of six cases.

V. CONCLUSION

We present a pragmatic approach to determining the sensitivity of ETPA measurements based on signal-to-noise ratio calculations. By treating the absorber as a black box and applying a simple probabilistic TPA model, we can calculate the expected signal and noise contributions in a given ETPA experiment. We derive our ETPA sensitivity from this calculation as the minimal detectable TPA cross-section.

By comparing this value to the TPA cross-section of the absorber in use, we can determine whether the measurement is expected to be successful. Therefore, our model allows us to directly compare vastly different experiments. We can directly compare published ETPA results and are able to reproduce most of them.

Exploring different methods shows, that most experiments could be improved by switching to the separation method discussed here and in [22]. However, since our assumptions on the resulting new experimental setup are quite crude, a more thorough characterization of the resulting experimental setup would be needed to determine the actual enhancement in sensitivity.

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DATA AVAILABILITY

All data is contained within the manuscript.

APPENDIX A: PROBABILISTIC SEPARATION

If deterministic splitting of the signal and idler beams is not feasible, a modified version of the separation ansatz discussed in Sec. III A can be used [21,24]. Here, the correlations in the background measurement are spoiled by delaying half of both beams by more than the entanglement time T_e . Again, assuming the delay matches the time between pump pulses $\Delta\tau = \frac{1}{f_{\text{rep}}}$ ensures that the single-photon flux at the absorber remains unchanged.

We proceed analogous to the deterministic case as the signal S_{sep} (9) remains unchanged, while the background B_{prob} is modified. Since the ETPA term is not fully suppressed, we now find

$$S_{\text{sep}} = \eta_s \eta_i \eta_d T_{\text{int}} f_{\text{rep}} \frac{N_t}{A} \left(\frac{N_p \sigma_c}{A_e T_e} + 2 \frac{\eta_s \eta_i N_p^2 \sigma_c}{AT} + \frac{N_p^2 \sigma_c}{AT} + \frac{(\eta_s + \eta_i) N_p \sigma_h}{\eta_s \eta_i} \right) + T_{\text{int}} f_{\text{dark}}, \quad (\text{A1})$$

$$B_{\text{prob}} = \eta_s \eta_i \eta_d T_{\text{int}} f_{\text{rep}} \frac{N_t}{A} \left(\frac{N_p \sigma_c}{2A_e T_e} + \frac{\eta_s \eta_i N_p^2 \sigma_c}{4AT} + \frac{N_p^2 \sigma_c}{AT} + \frac{(\eta_s + \eta_i) N_p \sigma_h}{\eta_s \eta_i} \right) + T_{\text{int}} f_{\text{dark}}. \quad (\text{A2})$$

Again, inserting into (2) and isolating the TPA cross section σ_c yields

$$\sigma_c \geq \frac{n_\sigma^2 A^2 T}{T_{\text{int}} f_{\text{rep}} \eta_s \eta_i \eta_d N_t} \frac{1}{Z} \left\{ \frac{3}{N_p} + \frac{4(2 - 3\eta_s \eta_i)}{Z} + 4 \sqrt{\frac{M}{N_p Z} + \frac{2M(3 - \eta_s \eta_i)}{N_p Z^2} + \frac{(4 + \eta_s \eta_i)(1 + 2\eta_s \eta_i)}{Z^2} + \frac{T_{\text{int}}}{4n_\sigma^2} \left(\frac{f_{\text{rep}} N_t}{AN_p} \eta_d (\eta_s + \eta_i) \sigma_h + \frac{f_{\text{dark}}}{N_p^2} \right)} \right\}, \quad (\text{A3})$$

$$Z = 2M + 7\eta_s \eta_i N_p. \quad (\text{A4})$$

As expected, (A3) and (11) are very similar, with the deterministic approach outperforming the probabilistic method with equal parameters. While the difference between the two methods decreases in the high-gain case (see Fig. 2).

APPENDIX B: TIME-GATING

We assume pure exponential decay of the fluorescence rate with the decay time τ and that the dark counts are distributed uniformly. Furthermore, we assume $T \ll \tau$ and approximate the excitation pulse as a Dirac delta function. Thus time-gating linearly decreases dark counts to $f_{\text{dark, gate}} = g f_{\text{dark}}$ with the relative width of the gate g , and nonlinearly decreases

fluorescence counts. Integrating the normalized temporal fluorescence event distribution of one excitation pulse over all subsequent time gates and multiplying by the detection efficiency η_d yields the decreased detection efficiency

$$\eta_{d, \text{gate}} = \eta_d \frac{1 - e^{-\frac{g}{f_{\text{rep}} \tau}}}{1 - e^{-\frac{1}{f_{\text{rep}} \tau}}}. \quad (\text{B1})$$

If the assumption $T \ll \tau$ does not hold, we numerically integrate the pump pulse shape to determine $\eta_{d, \text{gate}}$. We then use these modified parameters in our model to determine the ideal time-gate width and quantify the increase in sensitivity.

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