On the role of entanglement in entangled two-photon absorption molecular spectroscopy

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Entangled two-photon absorption (ETPA) is a process characterized by a linear dependence of the absorption rate of entangled pairs on their flux density, leading to tens of orders of magnitude lower flux densities required than in conventional two-photon absorption (TPA) schemes. However, the role of different entangled degrees of freedom in ETPA was unclear following recent experimental studies, when compared to earlier theoretical works. Here, we clarify this situation by investigating ETPA in Rhodamine 6G (Rh6G). We first demonstrate a linear dependence of the ETPA absorption rate with the photon-pair flux, a clear signature of ETPA, and estimate the first values for the concentration-dependent ETPA cross-section for Rh6G. We then investigate the signature of energy-time entanglement and polarization dependence in the ETPA fluorescence rate and demonstrate a strong dependence of the signal on the inter-photon delay that reflects the coherence time of the entangled two-photon wave-packet. In contrast, we show that there is no significant dependence on the polarization.

Building on Marie Goeppert-Mayer’s discovery of two-photon absorption (TPA) in 1931, non-linear spectroscopic techniques have become invaluable tools for both fundamental and applied research, providing the opportunity to study atomic and molecular transition levels that would be unattainable with linear spectroscopy [1]. However, these techniques typically use relatively high peak power pico- or femtosecond pulsed lasers to compensate for the low probability of two photons arriving simultaneously at the same atom or molecule, thus imposing a practical limitation for photosensitive samples, such as those found in biological systems [2, 3].

A promising solution to address this photo-sensitive limitation is to exploit the concept of entangled two-photon absorption (ETPA) [4]. Consider a simple model for two photon absorption [4] where one photon is excited from the ground state (g) to a virtual level and the other photon further excites this to the final state (f), as illustrated in the energy level diagram on the right of Fig. 1. In the case of classical TPA, the absorption rate of two photons is a product of two independent single-photon absorption rates, resulting in a quadratic dependence on the photon flux density $\phi$, $R_c = \delta_c \phi^2 [1/s]$ [4-6]. Here, $\delta_c$ is the classical TPA cross-section in units of cm$^4$s. However, if the photons are produced in the form of entangled pairs, they act more like a single object, resulting in a linear absorption rate, $R_e = \sigma_e \phi [1/s]$, where $\phi$ is now the photon-pair flux density and $\sigma_e [cm^2]$ is the ETPA cross-section [4]. We can then write the overall two-photon absorption rate as $R_2 = \delta_r \phi^2 + \sigma_e \phi$.

The linear dependence of the absorption rate on the photon-pair flux is a signature that the process is due to ETPA [4, 6-13]. It results in an absorption probability much closer to the values for single photon absorption (SPA). If we consider the energy-level diagram on the right of Fig. 1 in the case of TPA, the transition from the ground state is due to absorption of two photons with bandwidths $\Delta_3$ and $\Delta_2$, which are comparable in value to the bandwidth of the final state $\Delta_f$. In contrast, due to the energy-time entanglement, the ETPA transition behaves like it is induced by a (SPDC) pump photon with bandwidth $\Delta_p \ll \Delta_f$, similarly to SPA.

The ETPA process dominates at low flux, before the classical, quadratic, TPA takes over at $\tilde{\phi} = \sigma_e/\delta_r$. To give an idea of the advantage provided by ETPA in terms of the required flux, the typical values for classical TPA are around $\delta_r \sim 10^{-47} cm^4s$ [14], while for ETPA, values as high as $\sigma_e \sim 10^{-17} cm^2$ have been obtained [8, 9, 11]. Motivated by this, there have been numerous theoretical studies to develop spectroscopic techniques based on ETPA to investigate a wide range of molecular systems [7].

Recently, several experiments emphasized the role of polarization entanglement [8-13], while the original theoretical works [4, 5] and other experiments [15, 17] focused on energy-time entanglement [16]. In this work we clarify this situation by analyzing the ETPA-induced fluorescence intensity of Rh6G as a function of the entangled degrees of freedom of the pairs. This choice for the molecule is motivated by strong absorption properties of Rh6G in the desired wavelength range 510-540 nm and its high quantum yield [19]. The measurements we performed, allow us to demonstrate that the presence of energy-time entanglement is a necessary and sufficient condition to observe ETPA.

**Experimental setup** – The experimental setup is based on a periodically-poled Lithium niobate (PPLN) Type-0 SPDC source for generating entangled photon pairs and three different elements as shown in Fig. 1. Boxes a)-c). This type of source allows us to avoid any ambiguity about the nature of ETPA, by minimizing the entangled degrees of freedom. As shown below, it allowed us to observe the dependence of ETPA-induced fluorescence rate as a function of the photon-pair flux, and the relative signal-idler delay and polarization. This photon-pair source also allows us to improve the photon-pair flux, and hence to have a greater measurement dynamic compared to previous studies [9, 10, 13].

Calibration of the pair-source is done by sending the pairs to a standard coincidence detection scheme comprised of two single-photon detectors and a time-to-digital converter (TDC), see box a). We measured an average coincidence detection rate of around 1100 s$^{-1}$ for 5.1 mW of pump power. Taking into account losses, the beamsplitter (BS), and the detection efficiencies of around 3% at 1064 nm, this corresponds to around $2.6 \times 10^4$ s$^{-1}$ fiber-coupled pairs. This calibration was done in a low flux regime to avoid saturating the single photon
detectors.

Once the calibration was done, the SPDC pairs were sent to the box b) (Fig. 1), where they were focused into the cuvette with the Rh6G molecules in an ethanol solution. The cuvette was placed inside a two-inch integrating sphere, with a (17.6 mm x 13.52 mm sensor) CCD-camera attached to one of its half-inch ports to detect the fluorescence induced by SPDC-pairs to maximize the collection of fluorescence photons. Another port of the sphere was left open, opposite the input, to allow the unabsorbed pairs to pass through - this minimized the chances of spurious detection events due to residual 1064 nm photons, which is further reduced by a short-pass filter installed before the camera.

The role of energy-time entanglement and polarization dependence in the ETPA-induced fluorescence was investigated by inserting a Michelson interferometer before the fluorescence detection setup as shown in box c). In one arm of the interferometer a variable path-length can be controlled to introduce a delay between the photons, and hence, the arrival time difference of the photons sent to the cuvette. Additionally, a λ/4 waveplate is introduced in one path of the interferometer to rotate the polarization of one photon with respect to the other to test the polarization dependence.

**ETPA linearity and cross-section** – The measurement of the ETPA-induced fluorescence dependence on the photon pair flux density represents the first step to demonstrate the linear signature of ETPA and its dependence on entangled properties of the pair. The combination of an integrating sphere and camera was used to improve the collection efficiency, however, the large camera sensor area also introduces a high background noise rate. Measurements at such low levels of flux and a relatively low signal-to-noise ratio require careful calibration of the system. To achieve this, a series of measurements was made to quantify all contributions to the detected signal (see Fig. 2). To obtain the true signal we extracted the background camera counts from measurements with a sample of pure ethanol \(N_E\) from those with Rh6G \(N_{PM}\). Importantly, we also ensured that there were no events due to leakage of the 532 nm pump \(N_{N_{PM}}\) due to its higher single-photon-absorption cross-section and linear response to pump power. This was achieved by tuning the temperature away from the phase-matching condition, such that no pairs were produced. \(N_D\) corresponds to the camera’s dark counts when the laser was turned off. These tests ensure that the detected signal is only due to the fluorescence of Rh6G induced by 1064 nm photon-pairs.

Figure 3 shows the measurements of the fluorescence \(R_g\) rate for three different Rh6G concentrations, \(C = \{110 \text{ mmol/l}, 4.5 \text{ mmol/l}, 38 \mu\text{mol/l}\}\) as a function of the number of SPDC-pairs sent to the sample. These measurements are the first ETPA absorption measurements with Rh6G and clearly demonstrate a linear dependence of the fluorescence rate on the photon-pair flux density. The pump power was varied over 0.25-1.5 W, which corresponds to \(10^8 - 10^9\) pairs per second sent to the Rh6G solution through the fiber. However, taking into account the dispersion in the fiber (2 m, connecting source and sample) and the width of the down-converted spectrum, only 10% of the overall flux, corresponding to 1063-1065 nm range, arrived within the (140 fs) coherence time of the SPDC two-photon wave-packet. Thus, the laser pump powers correspond to varying the effective photon-pair flux incident to the Rh6G solution from \(2.0 \times 10^7\) to \(1.2 \times 10^8\) s\(^{-1}\).

To determine the ETPA cross-section we need to connect the fluorescence and absorption rates. The measured fluorescence rate \(R_g\) can be described by:

\[
R_g = \frac{N_{PM} - N_E}{t_{\text{exp}}} \frac{G}{\eta_{\text{coll}} \eta_{\text{cam}}} \quad (1)
\]
where \( t_{\text{exp}} \) is the integration time and the fluorescence rate is weighted by the gain factor of the camera \( G \), the collection efficiency \( \eta_{\text{col}} \) and the camera quantum efficiency \( \eta_{\text{cam}} \).

The ETPA rate is related to the fluorescence rate through the quantum yield \( Y \) that is concentration- and solvent-dependent:

\[
R_R = Y R_{\text{abs}} = Y C V N_A \sigma_e \phi .
\]  

(2)

Here, \( C \) [mol/l] is the concentration, \( V = 5.6 \times 10^{-9} \) l is the active volume, \( N_A \) is Avogadro’s number and \( \sigma_e \phi = R_e \) is the ”single-molecule” ETPA absorption rate as discussed in the introduction.

In Eq. (1), the factors \( G \), \( \eta_{\text{col}} \) and \( \eta_{\text{cam}} \) are in general difficult to quantify individually. We therefore make a relative measurement using the 532 nm pump laser for SPA and estimate them all together. To do this, we send the 532 nm pump laser through the system and replace the high-pass filters IF \( H \) with a short-pass filter (Thorlabs FESH0650). The pump beam was attenuated to SPDC-intensity levels, such that \( 10^6 \) photons per second were focused in the cuvette. We then use Eq. (1), Eq. (2) and our knowledge of the SPA cross-section to determine \( G/(\eta_{\text{col}} \eta_{\text{cam}}) = 4.5 \pm 0.9 \) (counts)\(^{-1}\).

Table I shows the values obtained for \( \sigma_e \) for low concentrations, where the quantum yield \( Y = 0.95 \) is known for Rh6G in an ethanol solution [19]. This would suggest values of \( \sigma_e \sim 10^{21} \) cm\(^2\), which can be compared to SPA cross-sections of around \( 10^{-17} \) cm\(^2\) and TPA of around \( 10^{-47} \) cm\(^4\) s photons\(^{-1} \) [14]. This clearly demonstrates a significant quantum advantage with respect to the necessary photon flux rates compared to the TPA cross-section. For concentrations as high as 110 mmol/l our current measurement scheme does not allow us to extract the value of \( \sigma_e \), but only the product \( Y \sigma_e = (1.5 \pm 0.8) \times 10^{-23} \) cm\(^2\).

**TABLE I. Results for the ETPA cross-section for two different Rh6G concentrations.**

| \( C \) [mmol/l] | \( \sigma_e \) [cm\(^2\)] |
|-----------------|--------------------------|
| 4.5             | \( (9.9 \pm 4.9) \times 10^{-22} \) |
| 0.038           | \( (1.9 \pm 0.9) \times 10^{-21} \) |

**ETPA polarization and temporal dependence** – We now investigate the dependence of ETPA-induced fluorescence on the polarization of the pairs, which is probed by rotating the \( \lambda/4 \) wave-plate in one of the interferometer arms (Fig. 1 box c)). The polarization of one photon is rotated relative to the other to change the two-photon state from \( |HH\rangle \) to a mixture of states \{\( HH, HV, VV, VH \)\}. In other words, we scan between both photons having the same polarization to photons having orthogonal polarizations. Figure 3 shows the resulting fluorescence rate as a function of the polarization angle where the values vary by less than 1%. This absence of any polarization dependence could be due to the rotation and movement of dye molecules in an isotropic environment, e.g. a liquid solution, where the measurements are also integrated over relatively long times.

A simple way to test the role of energy-time correlations of the photons arriving to the unit of absorbing media on the ETPA-rate is to vary the time delay between the photons on the scale of their coherence time (see Fig. 1 c)). Figure 4 shows the fluorescence rate as a function of the time delay between photons from an entangled pair for a fixed Rh6G concentration and photon-pair flux. The solid line is given by the expected non-resonant ETPA-rate dependence on the inter-photon delay [5] with only the amplitude as a free parameter. The observed signal has a full width at half maximum that corresponds to the coherence time of the photon pairs - approximately 140 fs. The small non-zero experimental background is due to photons that take the same path in the interferometer and hence do not have any time delay de-
dependence, and the “shoulders” are from pairs that have their (fiber) dispersion cancelled by the time delay.

**Conclusion** – We have performed a detailed study of ETPA in a molecular solution of Rh6G in ethanol and extracted the first values for the concentration-dependent ETPA cross-section. We demonstrated the main signature of ETPA, i.e. a linear dependence of the absorption rate with the photon-pair flux. We also demonstrated a strong dependence of the signal on the inter-photon delay that reflects the coherence time of the entangled two-photon wave-packet. Essentially a molecule, absorbing an entangled pair, could be seen as a fs-sensitive coincidence scheme, analogous to a HOM experiment [20], revealing the form of the wavepacket. We investigated the dependence of ETPA on polarization and energy-time entanglement, demonstrating that polarization entanglement is not a necessary condition to observe ETPA, especially in non-polarization sensitive materials, thus proving the fundamental role of energy-time entanglement for ETPA.

Besides its fundamental interest, this work also demonstrates the maturity of quantum technologies, such as SPDC sources, for ETPA studies. This will be of particular interest for sensing in general [21], for photo-sensitive samples, in-vivo studies and microscopy, or alternatively extending recent studies of isomerization phase sensitivity [22] in classical TPA, to the entangled photon pair regime. There is also a growing interest in studying the vision process, where recent studies have reported classical TPA in humans [23] or even as a novel technique for studying the human vision process and whether humans can see single or entangled photons [24-26].

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**References**

[1] R. W. Boyd, *Nonlinear optics* (Elsevier, 2003).
[2] H. B. Bebb and A. Gold, Phys. Rev. 143, 1 (1966).
[3] B. Mollow, Phys. Rev. 175, 1555 (1968).
[4] H.-B. Fei, B. M. Jost, S. Popescu, B. E. A. Saleh, and M. C. Teich, Phys. Rev. Lett. 78, 1679 (1997).
[5] B. Dayan, Phys. Rev. A 76, 043813 (2007).
[6] F. Schlauer, J. Phys. B 50, 203001 (2017).
[7] K. E. Dorfman, F. Schlauer, and S. Mukamel, Rev. Mod. Phys. 88, 045008 (2016).
[8] J. P. Villabona-Monsalve, O. Calderon-Losada, M. Nuñez Portela, and A. Valencia, J. Phys. Chem. A 121, 7869 (2017).
[9] D.-I. Lee and T. Goodson, J. Phys. Chem. B 110, 25582 (2006).
[10] D.-I. Lee and T. Goodson, Proc. SPIE 6653 Lin. and Nonlin. Opt. Org. Mat. VII 6653 (2007), 10.1117/12.745492.
[11] M. R. Harpham, O. Süzerc, C.-Q. Ma, P. Bäuerlec, and T. Goodson III, J. Am. Chem. Soc. 131, 973 (2009).
[12] L. Upton, M. Harpham, O. Suzuki, M. Richter, S. Mukamel, and T. Goodson III, J. Phys. Chem. Lett. 4, 2046 (2013).
[13] O. Varnavski, B. Pinsky, and T. Goodson III, J. Phys. Chem. Lett. 8, 388 (2017).
[14] P. Sperber and A. Penzkofer, Opt. Quant. Eelectron. 18, 381 (1986).
[15] B. Dayan, A. Pe’er, A. A. Friesem, and Y. Silberberg, Phys. Rev. Lett. 93, 023005 (2004).
[16] B. Dayan, A. Pe’er, A. A. Friesem, and Y. Silberberg, Phys. Rev. Lett. 94, 043602 (2005).
[17] A. Pe’er, B. Dayan, A. A. Friesem, and Y. Silberberg, Phys. Rev. Lett. 94, 073601 (2005).
[18] J. D. Franson, Phys. Rev. Lett. 62, 2205 (1989).
[19] R. F. Kubin and A. N. Fletcher, J. Lumin. 27, 455 (1982).
[20] C.-K. Hong, Z.-Y. Ou, and L. Mandel, Phys. Rev. Lett. 59, 2044 (1987).
[21] K. Nasiri Avanaki and G. C. Schatz, J. Phys. Chem. Lett. (2019).
[22] V. I. Prokhorenko, A. M. Nagy, S. A. Waschuk, L. S. Brown, R. R. Birge, and R. J. D. Miller, *Science* **313**, 1257 (2006).

[23] G. Palczewska, F. Vinberg, P. Stremplewski, M. P. Bircher, D. Salom, K. Komar, J. Zhang, M. Cascella, M. Wojtkowski, V. J. Kefalov, and K. Palczewski, *Proc. Natl. Acad. Sci. U.S.A.* **111**, E5445 (2014).

[24] V. C. Vivoli, P. Sekatski, and N. Sangouard, *Optica* **3**, 473 (2016).

[25] J. N. Tinsley, M. I. Molodtsov, R. Prevedel, D. Wartmann, J. Espigulé-Pons, M. Lauwers, and A. Vaziri, *Nat. Commun.* **7**, 12172 (2016).

[26] R. M. Holmes, M. M. Victora, R. F. Wang, and P. G. Kwiat, *Proc. SPIE 10659 Adv. Phot. Count. Tech. XII* **1065903** (2018), 10.1117/12.2306092.