Hot-Band Absorption Can Mimic Entangled Two-Photon Absorption

Ryan N. Wilson, Alexander Mikhaylov, Kristen M. Parzuchowski, Michael D. Mazurek, Charles H. Camp Jr, Martin J. Stevens, Ralph Jimenez

Abstract: While searching for entangled two-photon absorption in LDS798, we instead observe fluorescence signals originating from hot-band absorption. This process could lead to overestimating entangled two-photon absorption cross sections by several orders of magnitude.

1. Introduction

For decades there has been an effort to develop sensitive spectroscopic techniques that utilize non-classical light sources. Recently, attention has been given to imaging techniques taking advantage of spontaneous parametric down-conversion (SPDC), with numerous publications reporting entangled two-photon absorption (E2PA) and entangled two-photon excited fluorescence (E2PEF) for many different chromophores with large excitation efficiencies compared to classical two-photon absorption (C2PA). The resulting E2PA cross sections, $\sigma_{E2PA}$, may be as large as $10^{-17}$ cm$^2$, which is on the same order of magnitude as a moderately-strong one-photon absorption (1PA) transition. More recently, however, a number of studies have reported conflicting results that cast doubt on the large enhancements claimed in those reports.

For example, three different groups employed E2PEF measurements to determine the $\sigma_{E2PA}$ of Rhodamine 6G (Rh6G) [1, 2, 3]. Tabakaev et al. reported that $\sigma_{E2PA}$ was $(0.99 - 1.9) \times 10^{-21}$ cm$^2$ for a range of fluorophore concentrations [1]. However, the null result of Parzuchowski et al., supported by results from a study by Landes et al. [3], reported an upper bound on the cross section of Rh6G of $\sigma_{E2PA} \leq 1.2 \times 10^{-25}$ cm$^2$ [2]. The origin of the $\approx 10,000$-fold variation in reported $\sigma_{E2PA}$ values is unclear.

In earlier reports, the fluorescence signal’s linear dependence on the pump power alone was taken as proof that the signals originated from E2PA. However, this signature is also consistent with many one-photon mechanisms [2]. One such mechanism, hot-band absorption (HBA), has been shown to play a crucial role in C2PA measurements [4], but has not been discussed in the E2PA literature. Since HBA is a 1PA process, it scales linearly with excitation power similar to the predicted scaling of the E2PA rate. This amalgamation of signals would lead to misleading conclusions regarding the efficiency of E2PA and its dependence on molecular properties and on the quantum state of the light.

2. Experimental Setup

We perform experiments with two excitation sources, a fiber laser and an SPDC source. The fiber laser provides CW 1060 nm radiation for the classical two-photon excited fluorescence (C2PEF) measurements. The SPDC beam is generated by a CW pump laser at 532 nm and its spectrum is measured to have a roughly 150 nm bandwidth.

The 1060 nm laser and SPDC beams are independently focused with a lens into the sample, which is contained in a 2x10 mm spectroscopic quartz cuvette. Fluorescence is collected perpendicular to the beam propagation direction. More details about the experimental setup can be found in Ref. [5]. C2PEF measurements on Rh6G are used to ensure the proper alignment of the optical system and characterize its sensitivity before repeating the C2PEF measurement with LDS798. The C2PEF power dependence is roughly quadratic in the 50-500 mW range, consistent with C2PA [5]. However, this dependence transitions to linear for powers below 1 mW, which is consistent with a 1PA process. Although a transition of this type is rather uncommon in C2PEF experiments, there are several reports of similar behavior indicating the presence of the HBA process [4].
3. Results and Discussion

For LDS798 under SPDC excitation, we measure a strong fluorescence signal (Fig. 1a). To assess whether the signal is E2PEF, we test for a unique signature of the process by independently varying the SPDC pump power and attenuating the SPDC beam. Varying the SPDC pump power, we observe that the fluorescence follows a linear dependence. Attenuation of the SPDC beam power also results in a linear dependence. The latter result clearly indicates that the fluorescence signal is not related to E2PA, which should result in a quadratic dependence.

To confirm the presence of HBA, a set of experiments are performed to characterize the temperature dependence of the fluorescence signal on LDS798 encapsulated in a poly-dimethylsiloxane (PDMS) matrix. The fluorescence signal increases nearly four-fold when increasing temperature from 283 K to 323 K, and is well fit by a Boltzmann function (Fig. 1b). The experiment was repeated with SPDC excitation, both the full spectrum and with a 1055 nm short-pass filter in place (Fig. 1c, black and blue respectively). The short-pass filter blocks all idler photons from the SPDC pairs to eliminate the possibility of E2PA. With SPDC excitation, the fluorescence signal is nearly unchanged when the short-pass filter is inserted into the beam, implying that E2PA is not the cause of the measured fluorescence. The signals also scale with temperature identically to the classically excited signal.

Several important points can be concluded from this study. We have shown that even when the excitation wavelengths are detuned hundreds of nanometers from the 1PA peaks of a chromophore, excitation from thermally populated vibronic states is possible via HBA. Although this effect is known from previous reports on C2PEF, it has not been discussed in previous studies of E2PA. Explaining the origin of inconsistency among different experiments is the most significant challenge currently facing the development of E2PA spectroscopy and its applications. As shown here for LDS798, the HBA signal can partially mimic the power scaling of E2PA. It seems likely that this mechanism could be contributing to E2PA measurements on other chromophores. Potential HBA contributions should be carefully quantified since they could lead to a significant over-estimate of any quantum enhancement for the 2PA efficiency. Our results underline a critical need to perform stringent tests for unique signatures of E2PA in measured signals with SPDC excitation to distinguish one-photon processes from E2PA. The proper validation procedure is to vary the incident power from the entangled photon source both by attenuating the power input to the SPDC crystal and also by attenuating the power after the crystal. To demonstrate E2PEF, these two methods of varying the incident power must show linear and quadratic fluorescence power dependencies, respectively.

References

[1] D. Tabakaev et al. “Energy-Time-Entangled Two-Photon Molecular Absorption”. In: Phys. Rev. A 103.3 (2021), p. 033701.
[2] Kristen M. Parzuchowski et al. “Setting Bounds on Entangled Two-Photon Absorption Cross Sections in Common Fluorophores”. In: Phys. Rev. App. 15.4 (2021), p. 044012.
[3] Tiemo Landes et al. “Experimental feasibility of molecular two-photon absorption with isolated time-frequency-entangled photon pairs”. In: phys. Rev. Research 3 (3 Aug. 2021), p. 033154.
[4] M. Drozbizhev et al. “Photon Energy Upconversion in Porphyrins: One-Photon Hot-Band Absorption Versus Two-Photon Absorption”. In: Chem. Phys. Lett. 370 (2003), pp. 690–699.
[5] Alexander Mikhailov et al. “Hot-Band Absorption Can Mimic Entangled Two-Photon Absorption”. In: (2021). arXiv: 2111.05946 [quant-ph].