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How large is the quantum enhancement of two-photon absorption by time-frequency entanglement of photon pairs?

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We present a theoretical proof that the "quantum enhancement" of two-photon absorption, thought to be a means to improve molecular spectroscopy and imaging, is tightly bounded by the physics of photonic entanglement and nonlinear response.

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A rapidly growing body of research in chemistry, physics, and bioimaging explores the potential use of time-frequency entangled photon pairs (EPPs) in spectroscopic applications that promise increased sensitivity at ultralow photon fluxes and improved simultaneous spectral and temporal resolving power [1–3]. However, in spite of existing experimental evidence pointing to the efficacy of such techniques [4,5], several recent efforts to reproduce these findings have, rather, called into question their validity [6–8]. In light of this emerging controversy, this paper presents a rigorous theoretical proof that the sought-after "quantum enhancement" of two-photon absorption (TPA) is tightly bounded by the physics of photonic entanglement and nonlinear response. The resulting bounds indicate that some of the results observed in the literature cannot be explained by a perturbative treatment of TPA alone, even accounting for enhancement by time-frequency entanglement.

Many of the proposed applications rely on TPA using EPPs, a process called entangled TPA (ETPA). When a low flux of time-frequency EPPs illuminates a two-photon transition in an atom, molecule, or semiconductor, the rate of TPA can be enhanced considerably—in comparison to the rate using the same flux of classical light—by virtue of the quantum nature of photon-number correlations and frequency correlations. Given the extremely small TPA cross sections of typical molecules that are of chemical and biological interest, along with realistically attainable generation rates of EPP, it is clear that many orders of magnitude of quantum enhancement are needed in order to detect TPA signals at the sufficiently low fluxes where the techniques are expected to be most useful. Thus, the essential question is, how many orders of magnitude of TPA enhancement can be provided by time-frequency entanglement of photon pairs?

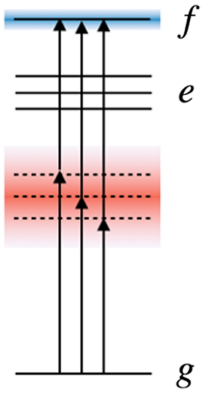

Fig. 1. Frequency anticorrelations of spectrally broad time-frequency EPPs (red) lead to efficient two-photon excitation of spectrally narrow transition from ground state g to final state f.

The first effect, stemming from photon-number correlations, is known both theoretically and experimentally: when time-frequency EPPs illuminate a two-photon transition at low enough flux that different pairs do not overlap in time, the rate of TPA scales linearly with flux because the temporally correlated photons arrive together [9–11]. This scaling is in contrast to the case of a coherent state wherein photons arrive randomly. The interval within which EPPs are correlated is the 'entanglement time' T_e, which is roughly the inverse of the EPP optical bandwidth. The second effect, spectral enhancement stemming from frequency anticorrelation of the EPP, illustrated in Fig. 1, can lead to further enhancement of the TPA probability in the case of a narrow TPA transition that is resonant with the sum of the frequencies [12]. These correlations are present in EPP generated by spontaneous parametric down conversion (SPDC) using a narrow-band pump field.

Linear flux scaling of ETPA is often described in terms of a phenomenological TPA rate, $R = \sigma_e I$, where I ($\mathrm{m^{-2}s^{-1}}$) is the photon flux density, and σ_e (m^2) is the so-called ETPA cross section. This quantity is parametrized through the expression $\sigma_e = (\sigma^{(2)}/A_e T_p)\Pi_e$, where $\sigma^{(2)}$ is the conventional (unenhanced) TPA cross section [13]. T_p is the duration of the EPP

pulse impinging on the TPA sample. A_e is the area within which the EPP are spatially correlated (entangled), which, in experiments where the EPP are tightly focused, is roughly equal to the diffraction-limited focal area, denoted as A_0. The unitless enhancement factor, Π_e, incorporates any enhancement that results from time-frequency entanglement of the incident photon pairs.

In this paper, we show theoretically that in cases in which TPA occurs only via far-off-resonant (virtual) intermediate states, the value of Π_e is bounded to a maximum given by T_p/T_e. Thus, small values of T_e can lead to considerable enhancement of the ETPA rate. Nevertheless, we find that the extremely large quantum enhancement that would be needed to observe TPA signals at low photon flux is not present in molecules with typical two-photon cross sections. A sketch of the derivation follows and is detailed in a separate paper [14].

Well-established perturbation theory using density-matrix formalism shows that the probability to excite a two-photon transition from ground state $|g\rangle$ to final state $|f\rangle$ via far-off-resonant intermediate states $|e\rangle$, $|e'\rangle$ equals

$$P^{\mathrm{TPA}} = \sigma^{(2)} \frac{\gamma_{fg}}{A_0^2} \times \mathrm{Re} \int \frac{\mathrm{d}\omega'}{2\pi} \int \frac{\mathrm{d}\omega}{2\pi} \int \frac{\mathrm{d}\tilde{\omega}}{2\pi} \frac{\left\langle \hat{a}^\dagger(\omega')\hat{a}^\dagger(\tilde{\omega}')\hat{a}(\omega)\hat{a}(\tilde{\omega}) \right\rangle}{\gamma_{fg} - i\omega_{fg} + i\omega + i\tilde{\omega}},$$

where the conventional TPA cross section is

$$\sigma^{(2)} = \left(\frac{\omega_0}{\hbar \varepsilon_0 n c} \right)^2 \frac{1}{2\gamma_{fg}} \left| \sum_e \frac{d_{ef} d_{ge}}{\omega_{eg} - \omega_0} \right|^2.$$

Here, ω_0 is the center frequency of the EPP spectrum, ω_{jk} is the frequency, and γ_{jk} is the dephasing rate between two states j and k. The electric-dipole matrix elements are d_{jk}, and we abbreviate $\tilde{\omega}' \equiv \omega + \tilde{\omega} - \omega'$. A_0 is the beam area at the molecule's location, n is the medium's refractive index, ε_0 is the vacuum permittivity, and c is the vacuum speed of light.

The expectation value of photon creation and annihilation operators $\hat{a}^\dagger$, $\hat{a}$ is evaluated using the well-known theory of type-I SPDC in a nonlinear optical crystal. To bound the probability, we assume a joint spectral amplitude of the EPP state that is diagonal in the two photon's frequencies having no detrimental phase structure, which yields the highest possible enhancement. Using the Cauchy–Schwartz inequality, we prove the following: given a finite spectral region centered at ω_0 and having width 2Ω that fully contains the EPP spectrum, the TPA rate is maximized when the EPP spectrum fills this region uniformly. Then, the maximum TPA cross section is found to equal $\sigma_e = \sigma^{(2)}(\Omega/\pi A_0)$, which corresponds to an enhancement factor $\Pi_e = T_p(2\Omega/2\pi)$, where $2\Omega/2\pi$ is the EPP bandwidth in units of hertz (Hz). Thus, equating $T_e = 2\pi/2\Omega$, we arrive at $\Pi_e = T_p/T_e$.

As an example of molecular TPA with typical parameters, an EPP beam centered at 1064 nm with 40 nm bandwidth is focused to a waist radius of 5 μm into a 1-cm-long solution of rhodamine 6G (R6G) dye, which has a TPA cross section at this wavelength equal to 9×10^{-58} $\mathrm{m^4 s}$. The EPP bandwidth, $2\Omega/2\pi$, is realistically about 10^{13} Hz. The probability of a single R6G molecule absorbing an EPP, including effects of quantum enhancement, is then 1.5×10^{-24}. The probability of an EPP being absorbed in the solution is 1.1×10^{-14} per millimole (mmol), which is far too small a fractional absorbance to be measured via transmittance, regardless of the concentration, EPP rate, or detection scheme. Fluorescence detection of TPA using a continuous EPP rate of 10^{13} $\mathrm{s^{-1}}$ (the boundary between isolated EPPs and overlapping EPPs) yields a predicted TPA rate of 10^{-3} $\mathrm{s^{-1}}$ per mmol of dye concentration. Given realistic concentrations and optical collection and detection efficiencies, this value lies in the undetectable regime.

This result points to the need to examine effects not described by time-frequency entanglement alone to explain differences between TPA excited by coherent-state light and by entangled photons, as reported in some published experimental studies. Understanding these effects will lead to a further examination of current techniques as well as potentially inspire new avenues for developing time-frequency EPPs as a useful resource for quantum-enhanced spectroscopy and imaging.

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