Transform-limited pulses are not optimal for resonant multiphoton transitions

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Maximizing nonlinear light-matter interactions is a primary motive for compressing laser pulses to achieve ultrashort transform limited pulses. Here we show how, by appropriately shaping the pulses, resonant multiphoton transitions can be enhanced significantly beyond the level achieved by maximizing the pulse's peak intensity. We demonstrate the counterintuitive nature of this effect with an experiment in a resonant two-photon absorption, in which, by selectively removing certain spectral bands, the peak intensity of the pulse is reduced by a factor of 40, yet the absorption rate is doubled. Furthermore, by suitably designing the spectral phase of the pulse, we increase the absorption rate by a factor of 7.

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The ability to steer quantum systems by coherently manipulating the interacting light (coherent quantum control), has been proposed [1, 2, 3, 4] and recently demonstrated [5, 6, 7, 8, 9, 10] for manipulating both simple and complex systems such as atoms, molecules and semiconductors. Weiner et al. [11] demonstrated selectivity among Raman transitions excited by shaped pulses. They showed that by splitting an initially transform limited pulse into a pulse sequence with a specific repetition rate, a certain vibrational mode of a molecular crystal was excited. Meshulach and Silberberg [12, 13] demonstrated that by manipulating the spectral phase of the exciting laser pulse, one could reduce and even annihilate the two photon absorption (TPA) rate. Nevertheless, it has been established [13] that these processes are maximized by transform-limited pulses, and cannot be enhanced beyond that level by shaping the pulses. Here we show that for transitions that involve an intermediate resonant state, this limit is no longer valid. By shaping the pulses in a way that exploits the spectral response of the interaction around the resonance we enhanced the resonant TPA rate in Rb vapor by a factor of 7, even though their peak intensity was reduced. In another experiment we enhanced the TPA rate by 100% simply by blocking all the red-detuned frequencies of the pulse, although the peak intensity of the pulse was reduced by a factor of 40.

Consider a TPA in an atomic system, induced by a weak femtosecond laser pulse with an electric field $\varepsilon(t)$. The amplitude of the excited state is predicted by the second order time dependent perturbation theory:

$$a_f(t) = -\frac{1}{\hbar^2}\sum_n \mu_{fn}\mu_{ng}\int_{-\infty}^{t}\int_{-\infty}^{t_1}\varepsilon(t_1)\varepsilon(t_2) \times exp(i\omega_{fn}t_1)\exp(i\omega_{ng}t_2)dt_2dt_1\,, \qquad (1)$$

where μ_{fn} and μ_{ng} are the dipole moment matrix elements, with $|g\rangle$,$|n\rangle$ and $|f\rangle$ the ground, intermediate, and final levels, $\omega_{ij} \equiv (E_i - E_j)/\hbar$, and the summation is performed over all possible intermediate states of the unperturbed atom. The pulse duration is assumed here to be considerably shorter than all lifetimes involved. In a nonresonant TPA, all the intermediate levels of the atom are considerably far from the pulse frequency spectrum. The nonresonant excited state amplitude can then be approximated by [13]:

$$a_f^{nr} \approx -\frac{1}{i\hbar^2}\sum_n \frac{\mu_{fn}\mu_{ng}}{\omega_{ng}-\omega_{fg}/2} \times \int_{-\infty}^{\infty} E(\omega)E(\omega_{fg}-\omega)d\omega\,. \qquad (2)$$

where $E(\omega)$ is the Fourier transform of $\varepsilon(t)$, and the pulse spectrum is taken to be centered on $\omega_{fg}/2$. Equation (2) reflects the fact that two-photon transitions occur for all pairs of photons with frequencies that additively give the final transition energy. As is evident from Eq. (2), the nonresonant TPA rate is maximized by a transform limited pulse, where all the spectral elements of $E(\omega)$ have the same phase, and therefore add constructively.

In the case of a resonant TPA, some intermediate (resonant) levels are within the spectral range of the pulse. The contribution to the excited state amplitude due to a transition through an intermediate resonant level $|i\rangle$ is given by:

$$a_f^{r} \approx -\frac{1}{i\hbar^2}\mu_{fi}\mu_{ig}\left[i\pi E(\omega_{ig})E(\omega_{fg}-\omega_{ig}) + \wp\int_{-\infty}^{\infty}\frac{E(\omega)E(\omega_{fg}-\omega)}{\omega_{ig}-\omega}d\omega\right]. \qquad (3)$$

where $\wp$ is the principle value of Couchy, and ω_{ig}, $\omega_{fg}-\omega_{ig}=\omega_{fi}$ are the resonance frequencies. As is evident from Eq. (3), the resonant process exhibits

a different spectral behavior from that of the nonresonant one. In cases where a single resonant level exists close to the two-photon frequency $\omega_{fg}/2$ (compared to the spectral bandwidth of the pulse), the contribution of the nonresonant process is negligible, therefore Eq. (3) describes the total TPA rate.

The first term in Eq. (3) depends only on the spectral components of the pulse at the resonance frequencies, whereas the second term integrates over the contributions of all other spectral components of the pulse. The broad spectral dependence of the second term originates from the short time ($\sim 10^{-13}$ sec) the atom spends at the intermediate level before absorbing the second photon, which according to the uncertainty principle allows for some detuning between the exciting photons and the resonance frequencies. Nevertheless, the larger the detuning, the lower the probability the atom will stay at the intermediate level long enough to absorb a second photon, hence the $\frac{1}{\omega_{ig}-\omega}$ factor. Due to the considerably longer time the atom remains at the final level, the frequencies of all the photon pairs must sum to ω_{fg}, and hence the dependence on $E(\omega)E(\omega_{fg}-\omega)$ in Eqs. (2) and (3). As expected for a harmonically driven system, the first term (the on-resonance contribution) is shifted by $\pi/2$ compared with the second term(the off-resonance contributions). Also, the spectral components below and above the resonance excite the system in-phase and π out-of-phase, respectively. We shall utilize these phase relations to enhance the nonlinear response.

Using the above derivation, we can predict the TPA rate for various pulses with different spectra. When the atom is subjected to a transform limited pulse, the second term in Eq. (3) integrates over both negative and positive contributions, and becomes negligible as the spectral width of the exciting pulse grows larger than $|\omega_{ig}-\omega_{fg}/2|$. In other words, a transform limited pulse induces a destructive quantum interference between the events in which the first exciting photon is red detuned and those in which it is blue detuned. A simple, although counterintuitive, way to enhance the transition probability is to prevent this destructive interference by blocking all red (or blue) detuned photons, despite the fact that this will reduce the pulse's peak intensity (due to both attenuation of the power and broadening of the pulse). Larger enhancement can be achieved by applying a phase function that inverts the sign of $E(\omega)E(\omega_{fg}-\omega)$ about the resonance, so that all photon pairs interfere constructively, and the transition probability is maximized. Since the integrand in Eq. (3) approaches its maximum absolute value around the singular point at ω_{ig}, this enhancement depends on the actual spectral resolution of the phase function, which limits the sharpness of the sign inversion around ω_{ig}.

To demonstrate these enhancements experimentally, we considered the resonant TPA in Rubidium gas between the 5S and the 5D states, which is dominated by resonant transitions through the 5P level (Fig. 1a). The TPA was induced by pulses with a bandwidth of 18 nm (corresponding to 50 fs transform limited pulses), produced by a mode-locked Ti:sapphire laser with an average power of 150 mW and repetition rate of 80 MHz. The spectrum, centered on the two-photon transition frequency $\omega_{fg}/2$ (778 nm), overlapped with the 5S-5P and the 5P-5D resonant transitions at ω_{ig} and ω_{fi} corresponding to 780 nm and 776 nm, respectively. As excited atoms decay spontaneously to the ground level through the 6P level, the TPA intensity is evaluated by measuring the fluorescence at 420 nm. We adjusted the spectral phase of the pulse with a programmable pulse shaper, which includes a liquid crystal spatial light modulator (SLM) at its Fourier plane [14, 15, 16]. The shaper enables both cancellation of dispersion, as well as the application of any desired additional spectral phase mask by applying different phase shifts to the spatially separated spectral components of the pulse. Our setup (Fig. 1b) was almost identical to the one in [12], except that the input laser beam was expanded in order to improve the spectral resolution to less than 0.3 nm.

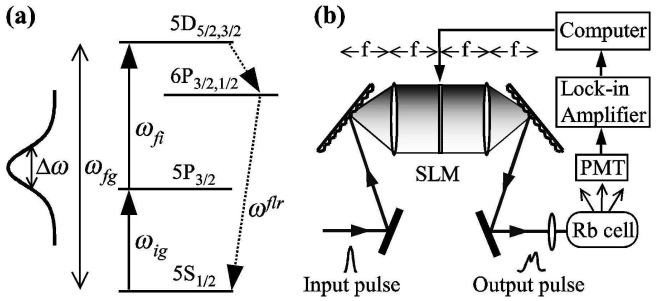

FIG. 1: (a) Energy levels diagram of a resonant TPA in Rb. The frequencies of the 5S-5P (ω_{ig}) and 5P-5D (ω_{fi}) resonant transitions correspond to 780.2 nm and 776.0 nm, respectively. The pulse spectrum is centered on the two-photon transition frequency ($\omega_{fg}/2$) at 778.1 nm, with a bandwidth of $\triangle\omega$ =18 nm (FWHM). The excited atoms spontaneously decay to the ground level through the 6P, emitting a fluorescence signal at ω^{flr} ($\approx$ 420 nm). (b) The experimental setup. Femtosecond laser pulses were modified in a computer-controlled 4-f pulse shaper. The pulse shaper is composed of a pair of diffraction gratings and a pair of achromat lenses. A programmable SLM with 128 computer controlled discrete elements is placed at the Fourier plane and is used to apply phase masks to the spectrum of the pulse. The shaped pulses were focused into the Rb cell, and the fluorescence signal was measured with a photomultiplier tube and a lock-in amplifier.

In the first experiment we demonstrate enhancement of the TPA rate by blocking parts of the spectrum of the exciting pulse. To achieve that, we placed an adjustable slit at the shaper's Fourier plane, and used it to block spectral bands of the pulse symmetrically around $\omega_{fg}/2$ (Fig. 2a). The SLM was used here only for dispersion

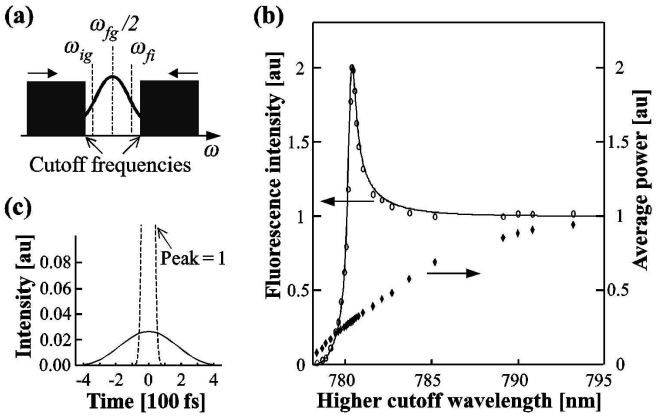

FIG. 2: Experimental and calculated results for enhancement of resonant TPA in Rb by selectively blocking parts of the spectrum. (a) An adjustable slit was used to block spectral bands of the exciting pulse symmetrically around $\omega_{fg}/2$. (b) The average power transmitted through the slit (diamonds) together with the experimental (circles) and calculated (line) normalized fluorescence intensity as a function of the higher cutoff wavelength. When the cutoff wavelengths approached the resonant transitions wavelengths (to within the spectral resolution of our setup), the average power was reduced by 71%, whereas the TPA rate was doubled. (c) Calculated temporal intensities of the optimal shaped pulse (solid) and the initial 50 fs FWHM transform limited pulse (dashed). The optimal pulse is wider by almost a factor of 8 (390 fs FWHM), and its peak intensity is reduced by a factor of 38.

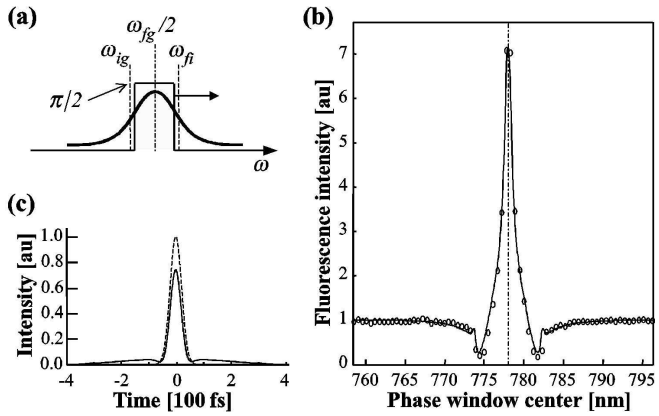

FIG. 3: Experimental and calculated results for enhancement of resonant TPA in Rb by scanning a 4 nm $\pi/2$ phase window over the spectrum of the pulse. (a) The applied phase mask at its optimal position, centered on $\omega_{fg}/2$, its leading and trailing edges close to the resonance frequencies. (b) Experimental (circles) and calculated (line) normalized fluorescence intensity as function of the spectral position of the phase window. Maximum enhancement of 600% occurred when the window was centered on $\omega_{fg}/2$ (778.1 nm, dashed line), as described in (a), performing the desired sign inversion about ω_{ig}. (c) Calculated temporal intensities of the optimal shaped pulse (solid) and the initial transform-limited pulse (dashed), showing a 26% reduction of the peak intensity due to the broadening of the pulse.

cancellation in order to produce transform-limited pulses at the Rubidium gas cell. We measured both the fluorescence signal and the average power transmitted through the slit as a function of the "cutoff wavelengths" (i.e. the shortest and longest wavelengths that passed the slit; see Fig. 2a).

The experimental results are presented in Fig. 2b together with the theoretical curve calculated by Eq. (3). When the cutoff frequencies approached the frequencies of the resonant transitions, we observed a steep enhancement of the fluorescence signal, reaching a factor of 2, while the power of the pulse at that point was reduced by 71%. The maximum signal was achieved when the cutoff frequency was shifted from ω_{ig} by the spectral resolution of the system. Closing the slit further decreased the fluorescence rapidly, which approached zero when the slit closed completely.

Figure 2c illustrates the calculated temporal intensities of the optimal shaped pulse and the initial, unshaped transform-limited pulse, showing both the drastic reduction of the intensity and the broadening of the pulse. These results demonstrate the counterintuitive nature of this enhancement. The 71% reduction in the average power and the 8-fold broadening of the pulse (to 390 fs) result in a reduction of the peak intensity by a factor of 38, yet the TPA rate was increased by 100%.

The goal of the next experiment was to achieve maximum enhancement of the TPA rate by inverting the sign of $E(\omega)E(\omega_{fg}-\omega)$ about the resonance. Therefore we used the SLM as a phase filter to apply a phase shift of $\pi/2$ to a 4 nm spectral window, and scanned that window over the pulse's spectrum. The 4 nm width of the phase window was chosen to fit the difference between resonant transitions at 780 nm and 776 nm, respectively. Figure 3b shows the measured fluorescence intensity vs. the spectral position of the phase window, together with a theoretical curve calculated by Eq. (3). Maximum enhancement by a factor of 7 was achieved when the phase window was centered on $\omega_{fg}/2$, its leading and trailing edges close to the frequencies of the resonant transitions (Fig. 3a). Substituting the phase window at that position in Eq. (3) will show that it performs the desired sign inversion about the resonance for a spectral region of 8 nm around ω_{ig}, thus inducing a constructive instead of a destructive interference in that region. Figure 3c shows the calculated temporal intensities of the optimal shaped pulse and the initial, unshaped transform-limited pulse.

The same enhancement factor (and a similar phase window) was achieved when we performed an adaptive optimization [17, 18, 19, 20] of the phase function, using the fluorescence intensity as a feedback signal.

In conclusion, we have shown that resonant multiphoton transitions can be significantly enhanced by exploiting the general spectral response of the interaction around resonance. When the interaction involves an intermediate resonant state, maximizing the peak intensity by obtaining a transform-limited pulse does not maximize the transition rate (as is the case with nonresonant interactions), and pulses with significantly lower intensities can be more effective. By properly designing the spectral amplitude and phase of the exciting pulse, we have demonstrated large enhancements of resonant TPA, in excellent agreement with the theory. Unlike other experiments in coherent quantum control, where selectivity between a few processes is the primary goal, we achieved an enhancement of the absolute rate of a single, simple nonlinear process. Since this enhancement is based on the general behavior of any system around resonance, we believe this mechanism may have played a role in enhancing more complex nonlinear interactions [18, 19], and could be applied to enhance other resonant nonlinear processes.

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