Symmetry-Based Selective Femtosecond Coherent Control of Transient Two-Photon Absorption

Andrey Gandman, Leonid Rybak, Michal Bronstein, Naser Shakour, and Zohar Amitay

Schulich Faculty of Chemistry, Technion - Israel Institute of Technology, Haifa 32000, Israel

We present and implement a new scheme for independent control of both the final and the transient population utilizing the symmetry properties of the system. By proper pulse shaping, utilizing the invariance of the two-photon absorption to specific phase transformations of the pulse, different time evolutions of the transient population are photo-induced for a given (fixed) final state population. The model system is the Na atom. The work is conducted in the weak-field regime for which the transient two-photon excitation is described by second-order perturbation theory. One most attractive case is the extended family of third-order chirp pulses which control the population build-up duration independently of the final population.

The general concept of coherent control is to steer a system towards a desired outcome by utilizing a manifold of interference pathways induced by a broad femtosecond pulse [1, 2, 3, 4]. Till now, this desired objective was mainly to control the transition probability to at least one of the given (fixed) final states. Such control was experimentally demonstrated in various atomic and molecular systems [5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21]. However, we believe that complete control over the transient as well as final population is of major importance to any forthcoming application involving multiphoton processes and fast decoherence or relaxation rates. Despite the great progress in coherent control of state-to-state transition probability, little work was done in controlling the transient population build-up. Most of the experimental advances in this area concentrated on experimental observation [22] and control [23, 24] of coherent transients in a two-level atomic system, using one photon absorption process which does not allow control over the final population of the system, but only over its transient. Moreover, several important applications were also demonstrated, including femtosecond spectral electric field reconstruction [25], high precision calibration of pulse-shaping setups [26], and most importantly, time resolved quantum state holography [27].

In this Letter we present for the first time experimental observation and full coherent control of transient state population excited via nonresonant two-photon transition by shaped femtosecond pulses. The control scheme extends the frequency-domain picture [6] to describe the transient evolution of the population build-up. Then, by a proper pulse shaping, utilizing the invariance of the two-photon absorption to specific phase transformations of the pulse [21], different transient evolutions of the population are photo-induced independently of a desired (fixed) final state population. The intuitive theoretical framework is also verified experimentally. Moreover, extended family of chirp pulses were found to be very robust in controlling separately the final and transient populations on a picosecond timescale using combination of frequency and time domain descriptions. The work is conducted in the weak-field regime for which the transient two-photon absorption is described by second-order perturbation theory, which is the lowest order perturbation for final state phase control. The model system is the Na atom. In general, the essence of the present work is to provide a rational intuitive way to the full control over the state's population evolution as well as its final value on both, short and long timescales.

We consider an atomic two-photon absorption process from an initial ground state $|g\rangle$ to a final excited state $|f\rangle$, which is coupled via a manifold of states $|v\rangle$ that are far from resonance and have the proper symmetry. The light-matter interaction with a shaped temporal electric field $\varepsilon(t)$ is described by second-order time-dependent perturbation theory. Thus, the time-dependent ampli-
tude $a_f(t)$ of state $|f\rangle$ at time $t$, is given by
\begin{equation}
    a_f(t) = -\frac{1}{\hbar^2} \sum_{ij} \mu_{ij} \mu_{ijg} \int_{-\infty}^{t} \int_{-\infty}^{t_1} \varepsilon(t_1) \varepsilon(t_2) \times \exp[i(\omega_{ij} t_1 + \omega_{ijg} t_2)] dt_1 dt_2,
\end{equation}
where $\mu_{ij} = \langle i | \mu | j \rangle$ is the dipole matrix element between a pair of states and $\omega_{ij} = (E_i - E_j)/\hbar$ is the corresponding transition frequency. Within the frequency-domain framework, the spectral field $E(\omega) \equiv |E(\omega)| \exp[i\Phi(\omega)]$ is given as the Fourier transform of $\varepsilon(t)$, with $|E(\omega)|$ and $\Phi(\omega)$ being the spectral amplitude and phase at frequency $\omega$. The transient amplitude $A_{tr}^{(2)}(t)$ can be written as
\begin{equation}
    A_{tr}^{(2)}(t) = \frac{\mu^2_{fg}}{2\pi \hbar^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} E(\omega) E(\omega') \times \exp[i(\omega_{fg} - \omega + \omega')] dt,
\end{equation}
where $\omega_{fg}$ and $\mu^2_{fg}$ are, respectively, the $|g\rangle$-$|f\rangle$ transition frequency and effective non-resonant two-photon coupling. The contribution to the transient amplitude can be separated into two channels of excitation:
\begin{equation}
    A_{tr}^{(2)}(t) = \frac{\mu^2_{fg}}{2\pi \hbar^2} \left[ A_{on-res}^{(2)} + A_{near-res}^{(2)}(t) \right],
\end{equation}
with
\begin{equation}
    A_{on-res}^{(2)} = i\pi A^{(2)}(\omega_{fg}),
\end{equation}
\begin{equation}
    A_{near-res}^{(2)}(t) = -\gamma \int_{-\infty}^{1} \frac{1}{\delta} A^{(2)}(\omega_{fg} - \delta) \exp(-i\delta t) d\delta,
\end{equation}
with
\begin{equation}
    A^{(2)}(\Omega) = \int_{-\infty}^{\infty} E(\omega) E(\Omega - \omega) d\omega.
\end{equation}

The above frequency domain description allows intuitively to identify the interfering pathways that coherently contribute to the transient two-photon transition amplitude (see Fig. 1). The time independent amplitude $A_{on-res}^{(2)}$ coherently interferes all the possible two-photon pathways from $|g\rangle$ to $|f\rangle$ ($\delta = 0$), i.e., coherently integrates over all their corresponding amplitudes. Each such pathway is composed of two absorbed photons of frequencies $\omega$ and $\omega_{fg} - \omega$. As opposed to the time dependent amplitude $A_{near-res}^{(2)}(t)$ which coherently interferes all the possible near-resonance two-photon pathways having a corresponding detuning ($\delta \neq 0$). It involves a non-resonant absorption of two photons with a two-photon transition frequency $\omega_{fg} - \delta$ with a $1/\delta$ amplitude weighting and a time dependent phase term $\exp(-i\delta t)$. The nonresonant pathways are excluded from $A_{near-res}^{(2)}(t)$ by the Cauchy’s principal value operator $\gamma$. The different amplitudes are expressed using the parameterized amplitude $A^{(2)}(\Omega)$ interfering all the possible two-photon pathways with transition frequency $\Omega$: $A_{on-res}^{(2)}$ is proportional to $A^{(2)}(\omega_{fg})$, while $A_{near-res}^{(2)}(t)$ integrates all $A^{(2)}(\omega_{fg} - \delta)$ with $\delta \neq 0$. The transient two-photon transition probability is given by $P_{tr}^{(2)}(t) = \{ A_{on-res}^{(2)} + A_{near-res}^{(2)}(t) \}^2$.

In accordance with previous studies, by evaluating Eq. (3) for time $t \to \infty$ (i.e., after the pulse is over), one obtains $A_{near-res}^{(2)}(t \to \infty) = A_{on-res}^{(2)}$ for finite amplitude of state $|f\rangle$, and the transition probability becomes $P_{tr}^{(2)}(t \to \infty) = 2A_{on-res}^{(2)}$. Utilizing the symmetry property of $A^{(2)}(\omega_{fg})$ that is invariant to any antisymmetric phase transformation, the two channels of excitation (i.e., the on-resonance independent channel $A_{on-res}^{(2)}$ and the near-resonance transient channel $A_{near-res}^{(2)}(t)$) can be selectively controlled. Any phase $\Phi_{\text{add}}^{(\text{add})}$ antisymmetric around $\omega_{fg}/2$ keeps the value of $A^{(2)}(\omega_{fg})$ unchanged, while it generally changes the value of $A^{(2)}(\omega_{fg} - \delta)$ for $\delta \neq 0$. Hence, it alters $A_{near-res}^{(2)}(t)$ while keeping $A_{on-res}^{(2)}$ invariant. The effect of antisymmetric phase addition is explained in details in [21]. $A_{on-res}^{(2)}$, on the other hand, can be controlled from a zero till to its maximal value (TL-level) using a simple $\pi$-step spectral base phase $\Phi_{\text{base}}(\omega)$. The total phase pattern $\Phi(\omega) = \Phi_{\text{base}}(\omega) + \Phi_{\text{add}}^{(\text{add})}$ is presented schematically in Fig. 1.

The physical model system of the study is the sodium (Na) atom, with the 3$s$ ground state as $|g\rangle$ and the 4$s$ final state state as $|f\rangle$, (see Fig. 1). The transition frequency $\omega_{fg} \equiv \omega_{3s,4s} = 25740 \text{ cm}^{-1}$ corresponds to two 777-nm photons. The 3$s$-4$s$ two-photon coupling is nonresonant via the $p$ states. The Na atom interacts with phase-shaped linearly-polarized femtosecond pulses having a one-side blocked at 779 nm (12837 cm$^{-1}$) Gaussian intensity spectrum centered around 790 nm (12658 cm$^{-1}$) with 4 nm (66-cm$^{-1}$) effective bandwidth (~200-fs TL duration), (see Fig. 1).

The sodium vapor in a heated cell is irradiated with such laser pulses, after they undergo shaping in an optical setup incorporating a pixelated liquid-crystal spatial light phase modulator [28]. The effective spectral shaping resolution is $\omega_{\text{shaping}} = 2.05 \text{ cm}^{-1}$ (0.125 nm) per pixel. The peak intensity of the TL pulse is below $10^9 \text{ W/cm}^2$, corresponding to the weak-field regime. To demonstrate the $|f\rangle$ state transient population $P_{tr}^{(2)}(t)$, the 4$s$ state is probed to the 7$p$ state by weak unshaped linearly-polarized femtosecond pulses having a Gaussian intensity spectrum centered around 790 nm (12658 cm$^{-1}$) with 12-nm (300-cm$^{-1}$) bandwidth (~80-fs TL duration), at time delay $\tau_p$. The experimental setup is presented schematically in Fig. 1. The 4$s$-7$p$ transition frequency $\omega_{7p,4s} = 12801 \text{ cm}^{-1}$ corresponding to a one 781.2 nm photon is included in the probe pulse however, it is excluded in the pump pulse by blocking this part of the
spectrum at the Fourier plane of the pulse shaper. The probe beam, which remains a TL pulse, is spatially overlapped with the pump beam in the heated sodium cell. We evaluate the transient population $P_{\text{tr}}^{(2)}(t)$ of the $4s$ state by probing the third harmonic generation signal at the $7p-3s$ transition frequency $\omega_{7p,3s} = 28541 \text{ cm}^{-1}$ corresponding to a one 259.5 nm UV-photon \cite{29}. We assume that the probe pulse is sufficiently weak and short compared to the shaped pump pulse. The UV signal is measured within the beam propagation direction using a spectrometer coupled to a time-gated camera system.

Figure 2 demonstrates experimentally the transient selective coherent control strategy. It presents experimental (circles) and numerical-theoretical (lines) results (Eqs. 3-6) for coherent control of transient two-photon absorption. All the data is normalized by the final population $P_{\text{TL}}^{(2)}(t \to \infty)$ excited by the transform-limited pulse. The data is presented as a function of the probe pulse delay. Panels (a) and (b) show different transient population build-ups resulting in the same TL-level final population. While panel (a) shows the transient population for a TL pulse, i.e., both $\Phi_{\text{base}}(\omega) = 0$ and $\Phi_{\text{antisy}}(\omega) = 0$ for any $\omega$, panel (b) presents the transient population of a modified pulse based on the symmetry properties of the system for which $\Phi_{\text{base}}(\omega) = 0$ remains zero for any $\omega$, however $\Phi_{\text{antisy}}(\omega)$ is not. It has a shape of an antisymmetric step (see Fig. 1) with $\Delta = 0.55 \text{ nm}$ and $\alpha_{\text{amp}}^{\text{antisy}} = \pi$. Although the final population is not affected by this phase addition the transient population build-up is very different as compared to the TL pulse. As long as for the former (a), the population transfer is a smooth line from zero population before the pulse to TL-level at the end of the pulse, for the later (b), it is much longer in time and has a kink in the vicinity of zero probe delay.

As another example Fig. 3 (c) and (d) present the same scenario of selective transient coherent control for zero final population. Panel (c) shows the transient population evolution which eventually results in zero population transfer, i.e., so called a dark-pulse \cite{6}. It utilizes non-zero base phase with a $\pi$-step at $\omega_{\text{base}}^{\pi,\text{dark}} = 778.2 \text{ nm}$ which assures zero final population. The antisymmetric addition $\Phi_{\text{antisy}}^{\text{add}}(\omega) = 0$ remains zero for any $\omega$. First, the transient population is gradually accumulated in the final state until it reaches a value of 20% of the TL-level when the probe delay is zero. Then, all the accumulated population is transferred back to the ground state. In panel (c), while, the base phase with a $\pi$-step at $\omega_{\text{base}}^{\pi,\text{dark}} = 772.2 \text{ nm}$ assures a zero final population, the antisymmetric addition $\Phi_{\text{antisy}}^{\text{add}}(\omega)$ with $\Delta = 0.55 \text{ nm}$ and $\alpha_{\text{amp}}^{\text{antisy}} = \pi$ alters completely the transient population evolution without changing the zero final population. It has two peaks across the evolution with a deep around zero probe delay, and as in the case of TL-level final population, in panels (a) and (b), the modified pulse induces much longer evolution of the transient population. It worth mentioning that all the experimental results are in excellent agreement with the theoretical calculations.

The presented symmetry based control scheme can be applied to independent control of the duration of the transient population evolution regardless of the desired final population. The left column presents the results for TL-level final population with increasing cubic spectral phase from $\varphi_3 = 0$ for the first row, $\varphi_3 = 3 \text{ ps}^3$ for the second row, $\varphi_3 = 5 \text{ ps}^3$ for the third, and $\varphi_3 = 7 \text{ ps}^3$ for the forth. The same cubic phase additions were applied in the middle, and right rows respectively for half of the TL-level final population and zero final population. The data is presented as a function of the probe pulse delay.

![Figure 2](image1.png)

**FIG. 2:** (a)-(d) Experimental (circles) and numerical-theoretical (lines) results for coherent control of transient two-photon absorption. Panels (a) and (b) show different transient population build-ups resulting in the same, TL-level final population. Panels (c) and (d) show different transient population resulting in zero final population, (see text). All the data is normalized by $P_{\text{TL}}^{(2)}(t \to \infty)$ excited by the transform-limited pulse. The data is presented as a function of the probe pulse delay.

![Figure 3](image2.png)

**FIG. 3:** Experimental (circles) and numerical-theoretical (lines) results for symmetry based independent control of the duration of the transient population evolution regardless of the desired final population. The left column presents the results for TL-level final population with increasing cubic spectral phase from $\varphi_3 = 0$ for the first row, $\varphi_3 = 3 \text{ ps}^3$ for the second row, $\varphi_3 = 5 \text{ ps}^3$ for the third, and $\varphi_3 = 7 \text{ ps}^3$ for the forth. The same cubic phase additions were applied in the middle, and right rows respectively for half of the TL-level final population and zero final population. The data is presented as a function of the probe pulse delay.
\[ \Phi_{\text{base}}(\omega) \] in a form of a simple \( \pi \)-step by setting the step at different position \( \omega_{\text{step}} \). The duration of the transient population evolution is controlled using quadratic chirp spectral phase addition \( \Phi_{\text{add}}^{(\text{antisym})}(\omega) = \varphi_3 (\omega - \omega_{fg}/2)^3 \), where \( \varphi_3 \) is a third-order coefficient. This phase addition is antisymmetric around the half of the two-photon transition frequency \( \omega_{fg}/2 \). Being so, it will not influence the final population set by the base phase.

The left column in Fig. 3 presents the results for TL-level final population with increasing cubic spectral phase from \( \varphi_3 = 0 \) for the first row, \( \varphi_3 = 3 \) ps\(^3\) for the second row, \( \varphi_3 = 5 \) ps\(^3\) for the third, and \( \varphi_3 = 7 \) ps\(^3\) for the forth. The same cubic phase additions were applied in the middle, and right rows respectively for half of the TL-level final population and zero final population. As Fig. 3 clearly indicates, the duration of the transient population evolution is highly correlated to the magnitude of the quadratic chirp addition, regardless of the final population. As we increase the magnitude of the quadratic chirp, the duration of transients also increase. This transient elongation is very intuitive as it is well known that quadratic chirp produce beats in the intensity vs. time, causing oscillations after the main pulse. Those oscillations become more and more pronounce as we incense the coefficient \( \varphi_3 \), effectively elongating the pulse. It worth mentioning that linear chirp addition is not applicable for the current scenario as it is symmetric around \( \omega_{fg}/2 \) so it will alter the final population together with the transient duration. Although, in general all the experimental results are in excellent agreement with the theoretical calculations, some discrepancies that do appear, can be accounted for finite pulse shaper resolution [28] and the high sensitivity of the signal [26]. The effect is clearly more pronounced for high chirp values as we get close to the sampling limitation of the shaper.

To emphasize the robustness of the selective transient coherent control which allows independent control of transient population evolution for a given final population, duration of such evolution is presented as a function of the quadratic chirp coefficient \( \varphi_3 \) for different final populations. The calculated data for a Gaussian pulse corresponding to 100 fs unshaped duration is presented in Fig. 4. The transient duration is calculated by looking at 5% (relative to TL-level) deviation of the population from the initial and final levels. The results clearly indicate the possibility of transient duration control independent of the final population. The discrepancies between the curves for deferent final levels are accounted for the duration calculation procedure which does not take into account the relativity of the final population. The common feature for all the curves in Fig. 4 appear to have little correlation for small values of the chirp and a very pronounced linear dependence for high chirp values. As for the first region, both \( \Phi_{\text{base}}(\omega) \) in a form of a simple \( \pi \)-step and the \( \Phi_{\text{add}}^{(\text{antisym})}(\omega) \) have similar relative effect on the pulse duration, thus influencing the transient duration in the same manner. As for the linear region, the \( \pi \)-step influence on the pulse duration is negligible relative to the applied chirp, thus resulting in little impact on the duration of the transient, which is controlled solely by chirp magnitude. Despite its reduced correlation to the duration of the transient evolution, the basic part \( \Phi_{\text{base}}(\omega) \) of the applied phase is vital for control of the final population by setting the proper interference pattern. Such combination of frequency domain picture given in Eqs. [30] with the time domain perspective gives a simple intuitive way to draw the control scenario for independent selective control of both the transient and final populations. While the frequency domain formulation allows us to identify the interfering pathways selectively contributing to the final and transient populations, the time domain picture sets the general limits on the duration of the transient evolution.

In conclusion, full selective coherent control of transient population is presented for the first time in which both transient and final populations are controlled independently. The control scheme is very robust, intuitive and general, and can be applied to any system, once its symmetry properties are identified. The duration of the transient build-up can be controlled from 100 fs to several picoseconds for any desired final population. Moreover, the presented control scheme can be extended to basically any structure of transient evolution by employing a semirational however automatic phase optimization based on closed-loop learning algorithms [30, 31, 32, 33].

\[ \varphi_3 = 5 \text{ ps}^3 \]

\[ \varphi_3 = 7 \text{ ps}^3 \]

\[ \varphi_3 = 0 \]

\[ \varphi_3 = 3 \text{ ps}^3 \]

\[ \omega_{fg}/2 \]

* Electronic address: amitayz@tx.technion.ac.il

[1] D. J. Tannor, R. Kosloff, and S. A. Rice, J. Chem. Phys. 85, 5805 (1986).

[2] M. Shapiro and P. Brumer, Principles of the quantum control of molecular processes (Wiley, New Jersey, 2003).

[3] W. S. Warren, H. Rabitz, and D. Mahleh, Science 259,
[4] H. Rabitz, R. de Vivie-Riedle, M. Motzkus, and K. Kompa, Science 288, 824 (2000).
[5] M. Dantus and V. V. Lozovoy, Chem. Rev. 104, 1813 (2004); ChemPhysChem 6, 1970 (2005).
[6] D. Meshulach and Y. Silberberg, Nature (London) 396, 239 (1998); Phys. Rev. A 60, 1287 (1999).
[7] K. A. Walowicz et al., J. Phys. Chem. A 106, 9369 (2002); V. V. Lozovoy et al., J. Chem. Phys. 118, 3187 (2003).
[8] A. Prákel et al., Phys. Rev. A 70, 063407 (2004).
[9] N. Dudovich et al., Phys. Rev. Lett. 86, 47 (2001).
[10] B. Chatel, J. Degert, and B. Girard, Phys. Rev. A 70, 053414 (2004).
[11] H. U. Stauffer et al., J. Chem. Phys. 116, 946 (2002); X. Dai, E. W. Lerch, and S. R. Leone, Phys. Rev. A 73, 023404 (2006).
[12] S. Lim, A. G. Caster, and S. R. Leone, Phys. Rev. A 72, 041803 (2005).
[13] N. Dudovich, D. Oron, and Y. Silberberg, Phys. Rev. Lett. 92, 103003 (2004).
[14] D. Oron et al., Phys. Rev. A 65, 043408 (2002); N. Dudovich, D. Oron, and Y. Silberberg, Nature (London) 418, 512 (2002); J. Chem. Phys. 118, 9208 (2003).
[15] M. Wollenhaupt et al., Phys. Rev. A 68, 015401 (2003); Chem. Phys. Lett. 419, 184 (2006).
[16] A. Gandman et al., Phys. Rev. A 75, 031401 (R) (2007); Phys. Rev. A 76, 053419 (2007).
[17] L. Chuntonov et al., J. Phys. B 41, 035504 (2008); Phys. Rev. A 77, 021403 (R) (2008).
[18] N. Dudovich et al., Phys. Rev. Lett. 94, 083002 (2005).
[19] C. Trallero-Herrero et al., Phys. Rev. Lett. 96, 063603 (2006).
[20] A. S. Meijer et al., Phys. Rev. A 78, 053403 (2008).
[21] Z. Amitay et al., Phys. Rev. Lett. 100, 193002 (2008).
[22] S. Zamith et al., Phys. Rev. Lett. 87, 033001 (2001).
[23] J. Degert et al., Phys. Rev. Lett. 87, 203003 (2002).
[24] N. Dudovich et al., Phys. Rev. Lett. 88, 123004 (2002).
[25] A. Monmayrant et al., Opt. Lett. 31, 410 (2006).
[26] W. Wohlleben et al., Apl. Phys. B 79, 435 (2004).
[27] A. Monmayrant et al., Phys. Rev. Lett. 96, 103002 (2006).
[28] A. M. Weiner, Rev. Sci. Inst. 71, 1929 (2000); T. Brixner and G. Gerber, Opt. Lett. 26, 557 (2001); T. Brixner et al., Appl. Phys. B 74, S133 (2002).
[29] L. Rybak et al., Opt. Exp. 16, 21738 (2008).
[30] R. Judson and H. Rabitz, Phys. Rev. Lett. 68, 1500 (1992).
[31] T. Brixner and G. Gerber, ChemPhysChem 4, 418 (2003).
[32] R. Levis, G. Menkir, and H. Rabitz, Science 292, 709 (2001).
[33] J. Herek et al., Nature (London) 417, 533 (2002).