Frequency-domain coherent control of femtosecond two-photon absorption: intermediate-field versus weak-field regime

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Abstract
Coherent control of femtosecond two-photon absorption in the intermediate-field regime is analysed in detail in the powerful frequency domain using an extended fourth-order perturbative description. The corresponding absorption is coherently induced by the weak-field non-resonant two-photon transitions as well as by four-photon transitions involving three absorbed photons and one emitted photon. The interferences between these two groups of transitions lead to a difference between the intermediate-field and weak-field absorption dynamics. The corresponding interference nature (constructive or destructive) strongly depends on the detuning direction of the pulse spectrum from one-half of the two-photon transition frequency. The model system of the study is atomic sodium, for which both experimental and theoretical results are obtained. The detailed understanding obtained here serves as a basis for coherent control with rationally-shaped femtosecond pulses in a regime of sizeable absorption yields.

1. Introduction
Femtosecond pulses offer unique ways to coherently control photo-induced quantum dynamics of matter [1–5]. The corresponding key characteristic is their coherence over a broad spectrum. Multiphoton absorption processes in atoms and molecules, which are of fundamental scientific importance as well as applicative importance to the fields of nonlinear spectroscopy and microscopy, are among the processes that have been controlled most effectively by shaped femtosecond pulses [5–19]. The control principle is the coherent manipulation of interferences among the manifold of initial-to-final state-to-state multiphoton pathways that are induced by the pulse. Constructive interferences lead to absorption enhancement (i.e., increased transition probability), while destructive interferences lead to absorption attenuation (i.e., decreased transition probability). The interference manipulation is implemented by shaping the femtosecond pulse [20], i.e., manipulating the spectral phase, amplitude and/or polarization of its different frequency components. Hence, in order to fully utilize the coherent control potential of a given excitation scheme, the ideal line of action is to rationally shape the pulse based on an initial identification of the different multiphoton pathways and their interference mechanism. When such identification is not possible, a practical non-ideal partial solution is to use automatic experimental optimization of the pulse shape using learning algorithms that generally consider the system as a black box [21]. As shown by the many successful coherent control studies of multiphoton absorption conducted in the past [5–15], the ideal line of rational pulse shaping is feasible and very powerful once the photo-excitation picture is available in the frequency domain. This is possible only within the framework of perturbation theory, where a valid perturbative description in the time domain is (Fourier) transformed to the frequency domain. However, so far the frequency domain has been exploited only in the weak-field regime [5–15], where the pulse intensity is low and the N-photon absorption is described by perturbation theory of the lowest non-vanishing order, i.e., the Nth order. Physically, the corresponding
N-photon absorption is coherently induced simultaneously by all the possible initial-to-final state-to-state pathways of N absorbed photons. For two-photon absorption the lowest order is the second one, involving all the pathways of two absorbed photons [5–11].

The advantage of limiting the pulse intensity to the weak-field regime is the relative simplicity of the lowest-order perturbative description. Yet, a major disadvantage of the weak-field regime is the low absorption yields (i.e., population transfers) associated with it. For non-resonant two-photon absorption they are typically below 0.1% population transfer. When higher absorption yields are desired, one needs to use higher pulse intensities that imply deviation from the weak-field regime and the insufficiency of the lowest-order perturbative description. Thus, in order to continue exploiting the powerful frequency domain for rational pulse shaping also beyond the weak-field regime one needs to extend the perturbative description to include a finite number of multiple non-vanishing orders beyond the lowest one. Then, the N-photon absorption is coherently induced by the weak-field pathways of N absorbed photons as well as by additional pathways of M absorbed photons and M − N emitted photons \((M > N)\). The highest order included in the perturbative description sets the maximal value of \(M\). We refer to this regime as the intermediate-field regime. It is distinguished from the strong-field regime where no perturbative description is valid. The strong-field regime is actually the only one that all the past control studies of multiphoton processes beyond the weak-field regime have focused on [16–19].

Studying the intermediate-field regime is the subject of the present work. It extends the powerful frequency-domain picture of femtosecond two-photon absorption to pulse intensities that lead to considerable absorption yields, exceeding the weak-field yields by more than two orders of magnitude. The intensities allow a valid description within the framework of fourth-order perturbation theory, which includes contributions from both the second and fourth orders associated, respectively, with two- and four-photon (interfering) pathways. The two-photon pathways are the weak-field non-resonant pathways of two absorbed photons, while the newly-introduced four-photon pathways are of three absorbed photons and one emitted photon. As shown below, the latter are of resonance-mediated nature with either the initial or final state of the transition playing the role of the intermediate state. Hence, the two-photon absorption has a different physical nature in the intermediate-field regime as compared to the weak-field regime. The relative contribution of the four-photon pathways to the total absorption amplitude, i.e., the magnitude of the fourth-order term relative to the second-order term, increases as the pulse intensity (field strength) increases. The fourth-order term is negligible relative to the second-order term in the weak-field limit and becomes comparable to it (about one-half of it) in the upper intensity limit of the fourth-order intermediate-field regime. At the present study, with the sodium atom (Na) as the model system, the intensity limits of the second-order weak-field regime and of the fourth-order intermediate-field regime are identified, respectively, to be \(5 \times 10^{10} \text{ W cm}^{-2}\) and \(2.5 \times 10^{10} \text{ W cm}^{-2}\) peak intensity of the transform-limited pulse, with a corresponding population transfer below 0.1% and of 10–40% (depending on the specific case), respectively. Using higher intensities requires the inclusion of additional perturbative orders beyond the fourth one.

We systematically investigate in detail the intermediate-field coherent control and the corresponding interference mechanisms, including their dependence on the pulse spectrum and its detuning from one-half of the two-photon transition frequency. The absorption dynamics in the intermediate-field regime is compared with that in the weak-field regime. As a test case for femtosecond phase control the study uses the family of shaped pulses having a \(\pi\) spectral phase step, which in the weak-field regime allows high degree of control over the full accessible range of the non-resonant two-photon absorption. Section 2 presents and elaborates on the extended frequency-domain fourth-order perturbative theoretical description. The Na intermediate-field control results are presented in section 3. They include experimental results, exact non-perturbative results calculated by the numerical propagation of the time-dependent Schrödinger equation and perturbative results calculated numerically using the frequency-domain fourth-order formulation. The formers are used to validate the latter. Then, in section 4, the perturbative results are analysed and discussed based on their corresponding frequency-domain description, which allows the identification of the interference mechanisms leading to the different intermediate-field features.

2. Intermediate-field theoretical description

The atomic femtosecond two-photon absorption process we consider is from an initial ground state \(|g\rangle\) to a final excited state \(|f\rangle\), which are coupled via a manifold states \(|n\rangle\) having the proper symmetry. The spectrum of the pulse is such that all the \(|g\rangle–|n\rangle\) and \(|f\rangle–|n\rangle\) couplings are non-resonant, i.e., the spectral amplitude at all the corresponding transition frequencies is zero: \(|E(\omega_{fn})| = |E(\omega_{fn})| = 0\), except for the \(|f\rangle–|n\rangle\) resonant coupling for which in general \(|E(\omega_{fn})| \neq 0\). The corresponding excitation scheme is shown schematically in figure 1.

Within the present intermediate-field regime, the time-dependent (complex) amplitude \(a_f(t)\) of state \(|f\rangle\) at time \(t\), following irradiation with a (shaped) temporal electric field \(\varepsilon(t)\), can be validly described by fourth-order time-dependent perturbation theory. So, in general, it includes non-vanishing contributions from both the second and fourth perturbative orders:

\[
a_f(t) = a_f^{(2)}(t) + a_f^{(4)}(t),
\]

with

\[
a_f^{(2)}(t) = -\frac{1}{\hbar^2} \sum_m \mu_{fnm} \int_{-\infty}^{t_1} \int_{-\infty}^{t_2} \varepsilon(t_1)\varepsilon(t_2) 
\times \exp[i(\omega_{fn}t_1 + \omega_{mg}t_2)] \, dt_1 \, dt_2,
\]

\[
a_f^{(4)}(t) = \frac{1}{\hbar^4} \sum_m \mu_{fnm} \int_{-\infty}^{t_1} \int_{-\infty}^{t_2} \varepsilon(t_1)\varepsilon(t_2) 
\times \sum_{l_1 l_2} \int_{-\infty}^{t_1} \int_{-\infty}^{t_2} \varepsilon(t_3)\varepsilon(t_4) 
\times \sum_{m_1 m_2} \mu_{m_1m_2} \mu_{m_1m_2} \int_{-\infty}^{t_3} \int_{-\infty}^{t_4} \varepsilon(t_3)\varepsilon(t_4) 
\times \exp[i(\omega_{fnl_1} + \omega_{m_1g}t_2)] \, dt_1 \, dt_2 \, dt_3 \, dt_4,
\]

\[
a_f^{(4)}(t) = \frac{1}{\hbar^4} \sum_m \mu_{fnm} \int_{-\infty}^{t_1} \int_{-\infty}^{t_2} \varepsilon(t_1)\varepsilon(t_2) 
\times \sum_{l_1 l_2} \int_{-\infty}^{t_1} \int_{-\infty}^{t_2} \varepsilon(t_3)\varepsilon(t_4) 
\times \sum_{m_1 m_2} \mu_{m_1m_2} \mu_{m_1m_2} \int_{-\infty}^{t_3} \int_{-\infty}^{t_4} \varepsilon(t_3)\varepsilon(t_4) 
\times \exp[i(\omega_{fnl_1} + \omega_{m_1g}t_2)] \, dt_1 \, dt_2 \, dt_3 \, dt_4,
\]
Figure 1. Excitation scheme of femtosecond two-photon absorption in the intermediate-field regime. The indicated levels correspond to the Na atom (not to scale). Shown are pathway examples of non-resonant two-photon transitions and four-photon transitions from $|g\rangle \equiv 3s$ to $|f\rangle \equiv 4s$. The four-photon transitions involve three absorbed photons and one emitted photon in any possible order, and thus can be decomposed into two parts: a non-resonant two-photon transition and a Raman transition. The border line between these two parts can be either on-resonance or near-resonance with 3p or 4s (with detuning $\delta$). The Raman transition itself can be non-resonant due to the np states (except for 7p) or on/near-resonance with 7p (with detuning $\delta$).

$$a_f^{(5)}(t) = -\frac{1}{\hbar^2} \sum_{k,l,m} \mu_{fk} \mu_{il} \mu_{lm} \mu_{mg}$$
$$\times \int_{-\infty}^{\infty} \int_{-\infty}^{t_1} \int_{-\infty}^{t_2} \int_{-\infty}^{t_3} e(t_1) e(t_2) e(t_3) e(t_4)$$
$$\times \exp[-i(\omega_{12} t_1 + \omega_{23} t_2 + \omega_{34} t_3 + \omega_{45} t_4)] dt_1 dt_2 dt_3 dt_4,$$

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. The second-order term $a_f^{(2)}(t)$ by itself corresponds to the weak-field regime. The intermediate-field final amplitude $A_f \equiv a_f (t \rightarrow \infty)$ of state $|f\rangle$ after the pulse is over (i.e., $t \rightarrow \infty$) can be expressed as

$$A_f = A_f^{(2)} + A_f^{(4)},$$

with $A_f^{(2)} \equiv a_f^{(2)}(t \rightarrow \infty)$ and $A_f^{(4)} \equiv a_f^{(4)}(t \rightarrow \infty)$. The final $|f\rangle$ population $P_f = |A_f|^2 = |\text{Re}(A_f)|^2 + |\text{Im}(A_f)|^2$ of state $|f\rangle$ reflects the degree of two-photon absorption.

This perturbative description allows a transformation into a frequency-domain picture. Within the frequency-domain framework, the spectral field of the pulse $E(\omega) \equiv |E(\omega)| \exp[i\Phi(\omega)]$ is given as the Fourier transform of $\epsilon(t)$, with $|E(\omega)|$ and $\Phi(\omega)$ being, respectively, the spectral amplitude and phase of frequency $\omega$. For the unshaped transform-limited (TL) pulse, $\Phi(\omega) = 0$ for any $\omega$. We also define the normalized spectral field $\tilde{E}(\omega) \equiv E(\omega)/|E_0| \equiv |\tilde{E}(\omega)| \exp[i\Phi(\omega)]$ that represents the pulse shape, where $|E_0|$ is the peak spectral amplitude. This allows us to clearly distinguish in the expressions given below between the dependence on the pulse intensity and the dependence on the pulse shape. The maximal spectral intensity $I_0$ is proportional to $|E_0|^2$ ($I_0 \propto |E_0|^2$). Different values of $I_0$ correspond to different temporal peak intensities $I_{TL}$ of the TL pulse.

As shown before for the weak-field regime [6], the second-order amplitude $A_f^{(2)}$ is given by

$$A_f^{(2)} = -\frac{1}{\hbar^2} |E_0|^2 A_f^{(2)}(\omega_{fg}),$$

$$A_f^{(2)}(\Omega) = \mu_{fg}^2 \int_{-\infty}^{\infty} \tilde{E}(\omega) \tilde{E}(\Omega - \omega) d\omega,$$

where $\omega_{fg}$ is the $|g\rangle - |f\rangle$ transition frequency and $\mu_{fg}$ is the corresponding real effective non-resonant two-photon coupling. It is given by $\mu_{fg}^2 \equiv \sum_n \mu_{fn} \mu_{ng}$, with $\omega_0$ being the carrier frequency of the pulse. Equations (5)–(6) reflect the fact that $A_f^{(2)}$ coherently interferes all the non-resonant two-photon pathways from $|g\rangle$ to $|f\rangle$ of any combination of two absorbed photons with frequencies $\omega$ and $\omega' = \omega_{fg} - \omega$. Several such two-photon pathways are shown schematically in figure 1. The phase associated with each two-photon pathway is $\Phi(\omega) + \Phi(\omega_{fg} - \omega)$. So, with the TL pulse all these pathways acquire zero phase and thus interfere one with the other in a fully constructive way. With a given spectrum $|E(\omega)|$, this leads to the maximal $|A_f^{(2)}|$ and the maximal weak-field non-resonant two-photon absorption.

The fourth-order amplitude term $A_f^{(4)}$ is much more complicated than $A_f^{(2)}$ and we have calculated it to be given by

$$A_f^{(4)} = -\frac{1}{\hbar^4} |E_0|^4 [A_f^{(4,\text{res})} + A_f^{(4,\text{near-res})}],$$

$$A_f^{(4,\text{res})} = i\pi A_f^{(2)}(\omega_{fg}) A_f^{(R)}(0),$$

$$A_f^{(4,\text{near-res})} = -\Phi \int_{-\infty}^{\infty} \frac{1}{\hbar^4} |E_0|^4 A_f^{(2)}(\omega_{fg} - \delta) A_f^{(R)}(\delta),$$

where $A_f^{(R)}(\delta)$ is the pulse shape of the Raman term.
where $A^{(2)}(\Omega)$ is defined in equation (6) and
\[ A^{(R)}(\Delta \Omega) = A^{(\text{non-res})}(\Delta \Omega) + A^{(\text{res})}(\Delta \Omega), \]
\[ A^{(\text{non-res})}(\Delta \Omega) = \left( \mu_{f}^{2} + \mu_{s}^{2} \right) \int_{-\infty}^{\infty} \tilde{E}(\omega + \Delta \Omega) \tilde{E}^{*}(\omega) \, d\omega, \]
\[ A^{(\text{res})}(\Delta \Omega) = |\mu_{fn r}|^{2} \left[ \text{Im} \tilde{E}(\omega_{fn r} + \Delta \Omega) \tilde{E}^{*}(\omega_{fn r}) \right. \]
\[ + \int_{-\infty}^{\infty} \tilde{E}(\omega_{fn r} + \Delta \Omega - \delta) \tilde{E}^{*}(\omega_{fn r} - \delta) \, d\omega \].

This set of equations reflects the fact that $A^{(4)}$ interferes all the four-photon pathways from $|g\rangle$ to $|f\rangle$ of any combination of three absorbed photons and one emitted photon. Several typical four-photon pathways are shown schematically in figure 1.

Each four-photon pathway can actually be divided into two two-photon parts: (i) a non-resonant transition of two absorbed photons $\omega$ and $\omega'$ with a frequency sum of $\Delta \Omega = \omega + \omega' = \omega_{f} - \delta$ and (ii) a Raman transition of two photons $\omega_{fg}$ and $\omega_{fg}'$ with a frequency difference of $\Delta \Omega = \omega_{r} - \omega_{g}'$. The border line between these parts is detuned by $\delta$ from either $|f\rangle$ or $|g\rangle$ according to whether, respectively, part (i) or part (ii) comes first (see figure 1). The $A^{(\text{non-res})}$ and $A^{(\text{res})}$ terms of $A^{(4)}$ (equations (7)–(9)) interfere, respectively, these on-resonant ($\delta = 0$) and near-resonant ($\delta \neq 0$) four-photon pathways. The on-resonant pathways are excluded from $A^{(\text{res})}$ by the Cauchy’s principle value operator $\phi$. The integration taking place in these terms over the corresponding pathways is expressed using the product of two parameterized amplitudes, $A^{(2)}(\Delta \Omega)$ and $A^{(4)}(\Delta \Omega)$, which originate from the different two-photon parts of the four-photon pathways. The amplitude $A^{(2)}(\Delta \Omega)$ interferes all the non-resonant two-photon transitions (parts (i)) with transition frequency $\Omega$, while the amplitude $A^{(R)}(\Delta \Omega)$ interferes all the Raman transitions (parts (ii)) with transition frequency $\Delta \Omega$. As given by equations (10)–(12), $A^{(R)}(\Delta \Omega)$ includes two components. The first component is $A^{(\text{non-res})}(\Delta \Omega)$ interfering all the Raman transitions that are of non-resonant nature, with $\mu_{gs}^{2}$ and $\mu_{gf}^{2}$ being the $|g\rangle-|g\rangle$ and $|f\rangle-|f\rangle$ real effective non-resonant Raman couplings due to all the non-resonantly coupled states $|n\rangle$. They are given by $\mu_{gs}^{2} = \sum_{n \neq n_{f}} |\mu_{n f}|^{2} \left[ \frac{1}{\omega_{n f} - \omega_{g}} + \frac{1}{\omega_{n f} + \omega_{g}} \right]$ and $\mu_{gf}^{2} = \sum_{n \neq n_{f}} |\mu_{n f}|^{2} \left[ \frac{1}{\omega_{n f} - \omega_{f}} + \frac{1}{\omega_{n f} + \omega_{f}} \right]$. Hence, their sum ($\mu_{gs}^{2} + \mu_{gf}^{2}$) (appearing in equation (11)) is either positive or negative, depending on the state and pulse spectrum. The second component of $A^{(R)}(\Delta \Omega)$ is $A^{(\text{res})}(\Delta \Omega)$ interfering all the Raman transitions that are of resonance-mediated nature via $|n_{r}\rangle$, with $\delta'$ being the detuning from $|n_{r}\rangle$ (see figure 1). These on-resonant ($\delta' = 0$) and near-resonant ($\delta' \neq 0$) transitions are interfered separately, respectively, in the first and second terms of $A^{(\text{res})}$ (equation (12)). The Cauchy’s principle value operator $\phi$ excludes the on-resonant transitions from the second term.

For a given physical system and a given pulse shape $\tilde{E}(\omega)$, a nonzero $A^{(2)}$ is proportional to $|E_{0}|^{2}$ while a nonzero $A^{(4)}$ is proportional to $|E_{0}|^{4}$, i.e., their ratio is proportional to $|E_{0}|^{2}$ or, equivalently, to $I_{0}$. For a given $I_{0}$, the relative magnitude and relative sign between the real parts $\text{Re}[A^{(2)}]$ and $\text{Re}[A^{(4)}]$ are generally determined by the pulse shape $\tilde{E}(\omega)$ and by the magnitudes and signs of the different Raman couplings ($\mu_{gs}^{2}$, $\mu_{gf}^{2}$, and $|\mu_{fn r}|^{2}$). The same applies also to the imaginary parts $\text{Im}[A^{(2)}]$ and $\text{Im}[A^{(4)}]$.

In the present work, for a set of intensities $I_{0}$, the final $|f\rangle$ population $P_{f}$ (i.e., the degree of two photon absorption) is controlled via the pulse shape $\tilde{E}(\omega)$. Three different spectra $\tilde{E}(\omega)$ are being considered, with the control knobs being the various spectral phases $\Phi(\omega)$. The three spectra are chosen such that their central spectral frequency $\omega_{0}$ is of no detuning, blue detuning or red detuning from $\omega_{fg}/2$, with $|\tilde{E}(\omega_{fg}/2)| \approx 0.5$ for the detuned cases. This set of spectra generally corresponds to the typical case, where $A^{(4)}$ is negligible relative to $A^{(2)}$ in the weak-field limit and becomes comparable to $A^{(2)}$ (quantitatively, about one-half of it) in the upper intermediate-field limit. These spectral shifts do not change the sign of the various Raman couplings and hardly change their magnitude. They do, however, affect the relative amplitude associated with the different interfering pathways and, thus, their overall interference result. For example, as shown below, in the cases studied here the spectral change from red- to blue-detuning leads to a change in the relative sign between $\text{Im}[A^{(2)}]$ and $\text{Im}[A^{(4)}]$, and thus to a change in the nature of their interference from destructive to constructive.

In general, the dynamics and interference mechanisms discussed in this work involve intra-term as well as (intensity-dependent) inter-term interferences involving the multiphoton pathways of the second- and fourth-order perturbative terms.

3. Results

The physical model system of the study is the sodium (Na) atom [22]. It includes the 3s ground state as $|g\rangle$, the 4s state as $|f\rangle$, the manifold of p states as $|n\rangle$ manifold and the 7p state as $|n_{f}\rangle$. So, $A^{(2)} \equiv A^{(2)}_{fs}$ and $A^{(4)} \equiv A^{(4)}_{fs}$. The transition frequency $\omega_{fg} \equiv \omega_{ds,3s} = 25740$ cm$^{-1}$ corresponds to two 777 nm photons and the transition frequency $\omega_{fn r} \equiv \omega_{dp,4s} = 12801$ cm$^{-1}$ corresponds to one 781.2 nm photon. The atomic sodium is irradiated with phase-shaped linearly-polarized femtosecond pulses having an intensity spectrum of $\sim 5$ nFWHM-bandwidth (~180 fs TL duration) centred around a wavelength $\lambda_{0}$ tunable between 773 nm and 780 nm. As a test case, for three different values of the central wavelength, the present study uses the family of shaped pulses having $\pi$-step spectral phase patterns. In the weak-field regime [6] this family allows high degree of control over the full accessible range of the two-photon absorption, from zero to the maximal level (induced by the TL pulse). Each such pattern is characterized by the $\pi$-step position $\omega_{\text{step}}$, with $\Phi(\omega) \leq \omega_{\text{step}}$, where $\omega_{\text{step}} = \pi/2$ and $\Phi(\omega) > \omega_{\text{step}} = \pi/2$.

The understanding and analysis of the intermediate-field control mechanism is conducted below using the frequency-domain picture given in equations (4)–(12) and the corresponding numerical results for the Na system. However,
Figure 2. Experimental results (squares) and non-perturbative theoretical results (solid lines) for the two-photon absorption in Na induced by the shaped pulses having a \( \pi \)-step spectral phase pattern. The results include an integration over the experimental spatial beam profile. The traces show the final 4s population \( P_{4s} \) as a function of the step position \( \omega_{\text{step}} \). The value of \( P_{4s} \) is normalized by the final population \( P_{4s, \text{TL}} \) excited by the corresponding transform-limited (TL) pulse. Each column corresponds to a different central spectral wavelength \( \lambda_0 = 773, 777 \) and 779.5 nm with a different pulse energy in each row (increasing from top to bottom). Each pulse energy corresponds to a different temporal peak intensity of the transform-limited pulse at the peak of the spatial beam profile \( I_{\text{profile-peak}} \).

prior to the analysis, the extended perturbative picture and results are validated by a comparison to exact non-perturbative results that their own validity is confirmed first by a comparison to experiment. The exact non-perturbative results have been calculated by the numerical propagation of the time-dependent Schrödinger equation (TDSE) using the fourth-order Runge–Kutta method. The theoretically considered manifold of \( p \)-states is from 3p to 8p, including all the (1/2 and 3/2) fine-structure states [22].

3.1. Non-perturbative calculations versus experiment

Experimentally, atomic sodium vapour is produced in a static chamber at 300 °C (Na partial pressure of \( \sim 0.1 \) Torr) with 10 Torr Ar buffer gas. It is irradiated at a 1 kHz repetition rate with shaped femtosecond laser pulses of three different central spectral wavelengths: \( \lambda_0 = 773, 777 \) and 779.5 nm. The corresponding spectral intensity bandwidth (FWHM) is, respectively, 5.5, 4.5 and 5 nm. The 773 nm and 777 nm spectra are Gaussians, while the 779.5 nm spectrum is a modified Gaussian having a slight asymmetry towards short wavelengths. The slight change in the experimental spectral shape between the three cases results from technical limitations and is of no significance to the analysis and discussion presented below. The laser pulses undergo shaping in a 4f optical setup incorporating a pixelated liquid-crystal spatial light phase modulator [20]. The effective spectral shaping resolution is \( \delta \omega_{\text{shaping}} = 2.05 \text{ cm}^{-1} \) (0.125 nm) per pixel. The experiment is conducted with different pulse energies. Upon focusing, the corresponding temporal peak intensity of the TL pulse at the peak of the spatial beam profile \( I_{\text{TL}} \) ranges from \( 5 \times 10^8 \text{ W cm}^{-2} \) to \( 7 \times 10^9 \text{ W cm}^{-2} \). Following the interaction with a pulse, the Na population excited to the 4s state radiatively decays to the lower 3p state. The fluorescence emitted in the decay of the 3p state to the 3s ground state serves as the relative measure for the excited 4s population \( P_f \equiv P_{4s} \). It is optically measured at 90° to the beam propagation direction using a spectrometer coupled to a time-gated camera system. The measured signal results from an integration over the spatial beam profile.

Figure 2 compares the non-perturbative theoretical results (solid lines) with the experimental results (squares) for the two-photon absorption in Na. Each column in the figure corresponds to a different spectral case of \( \lambda_0 = 773, 777 \) or 779.5 nm with different pulse energies, i.e., different \( I_{\text{profile-peak}} \). The pulse energy increases from top to bottom within a single column. The traces show the final 4s population \( P_{4s} \) as a function of the \( \pi \) phase step position \( \omega_{\text{step}} \) each of the traces is normalized by the final 4s population \( P_{4s, \text{TL}} \) excited by the corresponding TL pulse. The weak-field \( \pi \)-traces are given in the first-row panels ((a) panels) of figure 2. The non-perturbative theoretical results shown in figure 2 account for the experimental integration over the spatial beam profile. Each of the presented traces results from an appropriately-weighted integration over a set of calculations conducted each with a different single value of \( I_0 \).

As can be seen, there is an excellent agreement between the experimental results (‘real experiment’) and the non-perturbative results (‘computer experiment’). Hence, the accuracy of the latter is confirmed for the present intermediate-field excitation of Na.

3.2. Perturbative calculations versus non-perturbative calculations

Next, the confirmed non-perturbative calculations are used to validate the intermediate-field perturbative results and to
The weak-field traces are given in the first-row panels (a) panels. For comparison, they are also shown in all the other panels (thin black line). As can be seen from the figure, the perturbative results reproduce the exact non-perturbative results up to the $I_0$ that corresponds to a TL peak intensity of $I_{TL} = 2.5 \times 10^{10} \text{ W cm}^{-2}$ ((c) panels of figure 3). This is the intensity limit of the fourth-order intermediate-field regime for the present Na excitation. As the last-row panels ((d) panels) of figure 3 show, the fourth-order perturbative description is not sufficient above this intensity. The corresponding intensity limit of the weak-field regime, where $A_f \approx A_f^{\pi}$, is $I_{TL} \approx 5 \times 10^8 \text{ W cm}^{-2}$.

3.3. Intermediate-field features of the $\pi$-trace

The prominent features of the intermediate-field $\pi$-traces are presented below. As previously shown [6] and can be seen in figure 3(a) panels), the weak-field TL-normalized $\pi$-trace is symmetric around $\omega_{\text{step}} = \omega_{4s,3s}/2$ (777 nm) and is identical for any $\omega_0$ ($\lambda_0$). Its shape is determined only by the spectral bandwidth of the pulse. Also, since it is TL-normalized, it is independent of the intensity $I_0$ (see equation (5)). However, when deviating from the weak-field regime with the fourth perturbative order playing a role, the TL-normalized $\pi$-trace loses its weak-field symmetry and its shape becomes dependent on both $\omega_0$ and $I_0$. At a given $\omega_0$, the degree of deviation from the weak-field shape depends on $I_0$.
As mentioned above, in the weak-field regime the maximal non-resonant two-photon absorption is induced by the TL pulse. Additionally, as can be seen in the figure, the same maximal weak-field two-photon absorption is also induced by the shaped pulse with \( \omega_{\text{step}} = \omega_{4s,3s}/2 \) (777 nm), i.e., \( P_{\text{4s,step}@\omega_{4s,3s}/2} = P_{\text{TL}} \) or \( R_{\text{step}@\omega_{4s,3s}/2} = P_{\text{4s,step}@\omega_{4s,3s}/2}/P_{\text{TL}} = 1 \). Both pulses induce fully constructive interferences (i.e., zero relative phase) between values that are induced by the TL pulse (i.e., the asymptotes \( \lambda = 777 \) nm (figure 3—column (2)), and hardly noticeable for 780 nm (figure 3—column (3)), weakly noticeable for \( P_{\text{I}} \) dependence of \( \omega \) absorption even exceeds the TL absorption (see figure 3(3c)).

A(\( \omega \)) also displays the weak-field trace (black thin lines; shown also in all the nonzero \( \delta \) cases. Specifically, it applies to the non-detuned case of \( \lambda \). For completeness, the figure displays the intermediate-field features described above, using the intermediate-field trace (grey thick lines), which originates from the different dependence of the second- and fourth-order amplitudes, \( A_{4s}^{(2)} \) and \( A_{4s}^{(4)} \), on the pulse shape.

For a given spectrum \( |E(\omega)| \), the on-resonant term \( A_{4s}^{(4,\text{non-res})} \) of \( A_{4s}^{(4)} \) (equation (8)) is proportional to \( A_{4s}^{(2)} \). It is so since \( A_{\text{TL}}^{(4)}(\Delta \Omega = 0) \) depends only on the spectral intensity: all the corresponding Raman transitions involve two identical photons and their amplitudes in equations (10)–(12) are of the form \( \tilde{E}(\omega)\tilde{E}^*(\omega) = |E(\omega)|^2 \). Thus, the difference in the phase dependence of \( A_{4s}^{(2)} \) and \( A_{4s}^{(4,\text{non-res})} \), originates only from the non-resonant term \( A_{\text{f}}^{(4,\text{near-res})} \) of \( A_{4s}^{(4)} \), which interferes all the near-resonant four-photon pathways of nonzero detunings \( \delta \neq 0 \) from 3s or 4s (see above).

As equation (9) shows, \( A_{\text{f}}^{(4,\text{near-res})} \) is given by a proper \( \varphi \)-integration over all the nonzero \( \delta \) values. Its phase dependence originates from the phase dependence of the integrands \( A_{\varphi}\text{(4)}(\omega_{4s,3s} - \delta) \) and \( A_{\text{R}}^{(4)}(\delta) \). Their dependence on the spectral phase pattern \( \Phi(\omega) \) is reflected in their values for a given \( \delta \) and, more importantly, in their functional dependence on \( \delta \). So, the \( \varphi \)-integration yields different results for different phase patterns. Due to the \( 1/\delta \) weighting (and its sign change for \( \pm \delta \)), the \( \varphi \)-integration result is dominated by the integration over small values of \( \delta \) and is highly sensitive to the degree of symmetry of the integrand \( A_{\varphi}\text{(4)}(\omega_{4s,3s} - \delta)A_{\text{R}}^{(4)}(\delta) \) around \( \delta = 0 \), i.e., how different are its values for \( \pm \delta \). Below, the intermediate-field two-photon absorption is analysed based on the \( \delta \)-dependence of \( A_{\varphi}\text{(4)}(\omega_{4s,3s} - \delta) \) and \( A_{\text{R}}^{(4)}(\delta) \) for several representative cases of the \( \varphi \)-step position \( \omega_{\text{step}} \) with the different \( \lambda \).

The analysis of the amplitude \( A_{\text{R}}^{(4)}(\delta) \), which is contributed by all the Raman parts of the \( \delta \)-detuned four-photon pathways, is simplified by including its component \( A_{\text{non-res}}^{(4)}(\delta) \) (see equation (10)) only for the study of the dip feature at \( \omega_{\text{step}} = \omega_{\text{p,4s}} \) (781.2 nm). As described above, \( A_{\text{non-res}}^{(4)}(\delta) \) interferes those Raman parts that are resonance-mediated via the 7P state. This line of analysis is supported by the discussion given below and by the perturbative results presented in figure 4 for the \( \pi \)-traces at \( I_{\text{TL}} = 2.5 \times 10^{10} \) W cm\(^{-2} \) (i.e., the intermediate-field limit). In addition to the real TL-normalized \( \pi \)-traces (grey thick lines), which are also shown in the (c) panels of figure 3, the figure displays the \( \pi \)-traces (black thick lines) calculated with \( A_{\text{R}}^{(4)}(\delta) = A_{\text{non-res}}^{(4)}(\delta) \), i.e., with artificially setting \( A_{\text{non-res}}^{(4)}(\delta) \) to zero for any \( \delta \). As can be seen, the resonance-mediated Raman transitions via 7P are of significance only for discussing the dip at \( \omega_{\text{step}} = \omega_{\text{p,4s}} \) (781.2 nm). For completeness, the figure also displays the weak-field trace (black thin lines; shown also in figure 3) that originates only from \( A_{\varphi}\text{(4)} \) and, thus, is not affected by changes in the Raman part.

The non-resonant Raman term \( A_{\text{non-res}}^{(4)}(\delta) \) (equation (11)) coherently integrates all the non-resonant
Raman amplitudes $\tilde{E}(\omega + \delta)\tilde{E}^*(\omega)$ contributed by all the possible pairs of photons with a frequency difference of $\delta$ ($\omega$ is scanned across the spectrum). With $\Phi(\omega) = 0$ (TL pulse) or any $\pi$ spectral phase step, the amplitude contributed by any such pair of photons is a real (positive or negative) quantity and, thus, so is the resulting $A^{(2)}(\omega_{4s,3s} - \delta)$. Figure 5 displays, together with the Raman part data, the corresponding $A^{(2)}(\omega_{4s,3s} - \delta)$ (black thick lines) as a function of $\delta/\Delta\omega$ in the different cases. The zone of small $|\delta|$ around $\delta = 0$, which is the most contributing to $A_f^{(\text{inter-res})}$ (see above), is also indicated schematically. As can be seen from the figure, the $\delta$-dependence of $A^{(2)}(\omega_{4s,3s} - \delta)$ around $\delta = 0$ is different from one case to the other and depends on both the spectral phase pattern and $\lambda_0$ ($\omega_0$). Each panel also shows, for comparison, the $A^{(2)}(\omega_{4s,3s} - \delta)$ trace of the corresponding TL pulse (black thin line).

4.2. Intermediate-field two-photon absorption: shaped pulse with $\omega_{\text{step}} = \omega_{4s,3s}/2$ versus TL pulse

The first-row panels ((a) panels) of figure 5 correspond to the TL pulse of the different $\lambda_0$ ($\omega_0$) cases. Since the TL pulse induces fully constructive interferences among all the two-photon pathways that contribute to $A^{(2)}(\Omega)$ for any $\Omega$, the corresponding value $A^{(2)}_{\text{TL}}(\Omega) = \omega_{4s,3s} - \delta$ is actually the maximal one (positive and real) for any given $\delta$. As can be seen from equation (6), $A^{(2)}_{\text{TL}}(\Omega) = \omega_{4s,3s} - \delta$ is actually a convolution of the corresponding spectrum $|\tilde{E}(\omega)|$.

Thus, with a Gaussian spectrum around $\omega_0$, it is peaked at $\Omega_{\text{peak}} = 2\omega_0$, i.e., at $\delta_{\text{peak}} = \omega_{4s,3s} - 2\omega_0$. So, for the different cases of $\omega_0$ one obtains the following behaviour: (i) For $\omega_0 > \omega_{4s,3s}/2$ ($\lambda_0 = 773.5$ nm, figure 5(1a)) $\text{peak} < 0$ and $A^{(2)}(\omega_{4s,3s} - \delta)$ monotonically decreases around $\delta = 0$ as $\delta$ increases from negative to positive values, i.e., $A^{(2)}(\omega_{4s,3s} + |\delta|) > A^{(2)}(\omega_{4s,3s} - |\delta|)$ for small $|\delta|$; (ii) For $\omega_0 < \omega_{4s,3s}/2$ ($\lambda_0 = 780$ nm, figure 5(3a)) $\delta_{\text{peak}} > 0$ and $A^{(2)}(\omega_{4s,3s} - \delta)$ monotonically increases around $\delta = 0$ upon the negative-to-positive increase of $\delta$, i.e., $A^{(2)}(\omega_{4s,3s} - |\delta|) < A^{(2)}(\omega_{4s,3s} + |\delta|)$ for small $|\delta|$; (iii) For $\omega_0 = \omega_{4s,3s}/2$ ($\lambda_0 = 777$ nm, figure 5(2a)) $\delta_{\text{peak}} = 0$ and $A^{(2)}(\omega_{4s,3s} - \delta)$ is symmetric around $\delta = 0$, i.e., $A^{(2)}(\omega_{4s,3s} + |\delta|) = A^{(2)}(\omega_{4s,3s} - |\delta|)$.

The second-row panels ((b) panels) of figure 5 correspond to the shaped pulse with $\omega_{\text{step}} = \omega_{4s,3s}/2$ (777 nm). Generally, when a $\pi$ phase step is positioned at $\omega_{\text{step}}$, the value of $A^{(2)}(\Omega = 2\omega_{\text{step}})$ is equal to the corresponding TL value $A^{(2)}_{\text{TL}}(\Omega = 2\omega_{\text{step}})$ due to fully constructive interferences among all the involving two-photon pathways. As for the TL pulse, the phases associated with these pathways are all zero. However, as $\Omega$ deviates from $2\omega_{\text{step}}$, the value of $A^{(2)}(\Omega)$ gradually reduces with comparable magnitude for positive and negative deviations. Hence, a $\pi$-step at $\omega_{\text{step}} = \omega_{4s,3s}/2$ yields a peak of $A^{(2)}(\omega_{4s,3s} - \delta)$ at $\delta = 0$ (with the TL value). When $\omega_0 = \omega_{4s,3s}/2$ ($\lambda_0 = 777$ nm; figure 5(2b)), this peak is a global one and $A^{(2)}(\omega_{4s,3s} - \delta)$ has a perfect symmetry around $\delta = 0$, i.e., $A^{(2)}(\omega_{4s,3s} - |\delta|) = A^{(2)}(\omega_{4s,3s} + |\delta|)$. When $\omega_0 \neq \omega_{4s,3s}/2$ ($\lambda_0 = 773.5$ and 780 nm; figures 5(1b) and 3b)), this peak is a local one with only an approximate symmetry.
of $A^{(2)}(\omega_{4s,3s} - \delta)$ around $\delta = 0$, i.e., $A^{(2)}(\omega_{4s,3s} - |\delta|) \approx A^{(2)}(\omega_{4s,3s} + |\delta|)$ for small $|\delta|$.

Based on the above analysis of $A^{(\text{non-res} R)}(\delta)$ and $A^{(2)}(\omega_{4s,3s} - \delta)$, considering also the integrand factor $1/\delta$ that is anti-symmetric around $\delta = 0$, the magnitude of $A^{(4s)}_{\text{res}} \text{near-res}$ can be compared between the TL pulse case $A^{4s,\text{TL}}$ and the shaped pulse case of $\omega_{\text{step}} = \omega_{4s,3s}/2$ (777 nm) and $A^{(4s)}_{\text{res}} \text{near-res}$, i.e., in the no-detuning case of $\lambda_0 = 777$ nm - $A^{4s,\text{TL}}(\lambda_0)$ = $A^{4s,\text{step}}(\omega_{4s,3s}/2) = 0$, since the amplitudes contributed to the $g^2$-integral by the four-photon pathways of positive and negative detuning $\pm|\delta|$ are equal and, thus, cancel out each other; (ii) in the red- and blue-detuning cases of $\lambda_0 = 773.5$ nm and 780 nm - $A^{4s,\text{TL}}$ is equal and, thus, cancel out each other for the shaped pulse of $\omega_{\text{step}} = \omega_{4s,3s}/2$ while they are significantly different one from the other for the TL pulse.

As discussed below, important is also the sign of $A^{(4s,\text{near-res}}$ relative to $A^{(4s)}$, which is determined by the pulse spectrum and by the non-resonant Raman couplings sum $(\mu^2_{3s,3s} + \mu^2_{4s,3s})$. The sign of $A^{(2)}_{\text{res}} \text{near-res}$ relative to $A^{(4s,\text{TL}}$ and the sign of $A^{(4s,\text{near-res}}$ relative to $A^{(4s,\text{step}}(\omega_{4s,3s}/2)$ are obtained here to be the same for any $\lambda_0$. However, upon a blue-to-red spectral shift of $\lambda_0$ (i.e., from 773.5 nm to 780 nm) these signs change from positive to negative, with the sign flip occurring when passing via $\lambda_0 = 777$ nm. The sign change results from a change in the relative magnitude of the amplitudes contributed by the negatively-detuned and positively-detuned four-photon pathways, while $(\mu^2_{3s,3s} + \mu^2_{4s,3s})$ keeps its sign and is effectively constant over the whole $\lambda_0$ range considered here.

For comparing the two-photon absorption induced by the TL pulse versus the absorption induced by the shaped pulse of $\omega_{\text{step}} = \omega_{4s,3s}/2$, one needs to consider the coherent amplitude addition of $A^{(2)}_{\text{res}}$ and $A^{(4s)}_{\text{res}}$. For the TL pulse and for any shaped pulse with a $\pi$-step phase pattern, $A^{(2)}_{\text{res}}$ (equation (5)) is an imaginary quantity, i.e., $A^{(2)}_{\text{res}} = \text{Im}[A^{(2)}_{\text{res}}]$, while $A^{(4s)}_{\text{res}}$ is a complex quantity. When only $A^{(\text{non-res} R)}(\delta)$ is included in $A^{(R)}$ (see above), the corresponding $A^{(4s)}_{\text{res}} \text{near-res}$ component is real while the corresponding $A^{(4s)}_{\text{res}} \text{non-res}$ component is imaginary. Due to the $1/|\delta|$ preceding factor of $A^{(4s)}_{\text{res}}$ (equation (7)), they contribute, respectively, solely to the imaginary and real parts of $A^{(4s)}_{\text{res}}$, i.e., $\text{Im}[A^{(4s)}_{\text{res}}] \propto A^{(4s)}_{\text{res}} \text{near-res}$ and $\text{Re}[A^{(4s)}_{\text{res}}] \propto A^{(4s)}_{\text{res}} \text{non-res}$.

Thus, the interferences between the pathways groups of $A^{(4s)}_{\text{res}}$ and of $A^{(4s)}_{\text{res}}$ actually take place between those included in $A^{(4s)}_{\text{res}}$ and those included in $\text{Im}[A^{(4s)}_{\text{res}}]$ i.e., in $A^{(4s)}_{\text{res}}$.

Since the following relations are satisfied here: (i) $A^{(2)}(\omega_{4s,3s}/2, \omega_{\text{step}}(\omega_{4s,3s}/2)) = A^{(2)}_{\text{res}}(\omega_{4s,3s}/2)$, (ii) $P_{\omega_{\text{step}}} = |A^{(2)}_{\text{res}}|^2 = |A^{(4s)}_{\text{res}} + \text{Im}[A^{(4s)}_{\text{res}}]|^2 + |\text{Re}[A^{(4s)}_{\text{res}}]|^2$, (iii) $\text{Re}[A^{(4s)}_{\text{res}}] \propto \text{Im}[A^{(4s)}_{\text{res}}]$ (see equation (8)) and (iv) $A^{(2)}_{\text{res}} \propto \omega_{\text{step}}/\omega_{4s,3s}$ while $A^{(4s)}_{\text{res}} \propto \omega_{\text{step}}/\omega_{4s,3s}$ (see equations (5) and (7)), the TL-normalized $\pi$-trace value $R_{\text{step}}(\omega_{4s,3s}/2)$ (real and positive) corresponding to $\omega_{\text{step}} = \omega_{4s,3s}/2$ is given as

$$R_{\text{step}}(\omega_{4s,3s}/2) = \frac{P_{\omega_{\text{step}}(\omega_{4s,3s}/2)}}{P_{\text{TL}}}. \quad (13)$$
where the pulse shape dependence enters only via the $K$ factors. Accounting for the magnitude of $|A_{4s, \text{TL}}^{(4\text{near-res})}|$ versus $|A_{4s, \text{step}@\omega_{4s, 3s/2}}^{(2)}|$ and for the sign of $A_{4s}^{(4\text{near-res})}$ relative to $A_{4s}^{(2)}$, one obtains the following behaviour for the different $\lambda_0$ cases: (i) for blue detuning of $\omega_0 > \omega_{4s, 3s/2}$ ($\lambda_0 = 773.5$ nm): $K_{\text{step}@\omega_{4s, 3s/2}} > 0$, $K_{\text{TL}} > 0$, $|K_{\text{step}@\omega_{4s, 3s/2}}| < |K_{\text{TL}}|$, and thus $R_{\text{step}@\omega_{4s, 3s/2}} < 1$; (ii) for no detuning of $\omega_0 = \omega_{4s, 3s/2}$ ($\lambda_0 = 777$ nm): $K_{\text{step}@\omega_{4s, 3s/2}} = 0$, $K_{\text{TL}} = 0$, and thus $R_{\text{step}@\omega_{4s, 3s/2}} = 1$; (iii) for red detuning of $\omega_0 < \omega_{4s, 3s/2}$ ($\lambda_0 = 780$ nm): $K_{\text{step}@\omega_{4s, 3s/2}} < 0$, $K_{\text{TL}} < 0$, $|K_{\text{step}@\omega_{4s, 3s/2}}| < |K_{\text{TL}}|$, and thus $R_{\text{step}@\omega_{4s, 3s/2}} > 1$. In other words, the two-photon absorption induced by the shaped pulse of $\omega_{\text{step}} = \omega_{4s, 3s/2}$ is lower, equal or higher than the TL absorption according to whether $\omega_0$ ($\lambda_0$) is blue detuned, non-detuned or red detuned from $\omega_{4s, 3s/2}$, respectively. One can also see that, when $|K_{\text{step}@\omega_{4s, 3s/2}}| \neq 1$, the value of $|R_{\text{step}@\omega_{4s, 3s/2}}|$ increases as $I_0$ increases. This entire intermediate-field behaviour is indeed that observed in the results of figure 3, except for a small deviation of $R_{\text{step}@\omega_{4s, 3s/2}}$ from one of value one in the case of $\lambda_0 = 777$ nm (for example, in figure 3(2c) it reaches a value of 1.15). This deviation originates from the resonance-mediated Raman term $A_{\text{res}}^{(R)}$ that is excluded from $A^{(R)}$ in this part of the analysis and is not symmetric around $\delta = 0$ (as $A_{\text{non-res}}^{(R)}(\delta)$ is).

4.3. Intermediate-field two-photon absorption: shaped pulse with $\omega_{\text{step}} \approx \omega_0$

The third-row panels (panels (1c) and (3c)) of figure 5 correspond to the shaped pulse with $\omega_{\text{step}} = \omega_0$ in the detuned $\lambda_0$ cases of 773.5 nm and 780 nm (the corresponding case with $\lambda_0 = 777$ nm is actually that already considered in section 4.2). It is considered here as the representative case for the region of $\omega_{\text{step}} \approx \omega_0$, where a systematic attenuation or enhancement of the intermediate-field TL-normalized absorption relative to the weak-field TL-normalized absorption occurs (figures 3(1c) and (3c), figures 4(a) and (c)). The attenuation or enhancement correspond, respectively, to the blue ($\lambda_0 = 773.5$ nm) or red detuning ($\lambda_0 = 780$ nm) of $\omega_0$ from $\omega_{4s, 3s/2}$. Detailed analysis of the present case, as conducted above for the TL-pulse and for the shaped pulse with $\omega_{\text{step}} = \omega_{4s, 3s/2}$, leads to the conclusion that the only difference here is that $A_{4s}^{(2)}$ $\neq A_{4s}^{(2)}$. While $A_{4s, \text{step}@\omega_{4s, 3s/2}}^{(2)} = A_{4s, \text{TL}}^{(2)}$. All the other qualitative conclusions regarding the different amplitude components in terms of their magnitude, sign and real/imaginary character are exactly the same for both the $\omega_{\text{step}} = \omega_0$ and $\omega_{\text{step}} = \omega_{4s, 3s/2}$ pulses.

In general, the ratio $RR_{\text{step}@\omega_{\text{step}}}$ between the intermediate-field and weak-field TL-normalized absorption corresponding to the shaped pulse of a given $\omega_{\text{step}}$ is given by

$$RR_{\text{step}@\omega_{\text{step}}} = \frac{K_{\text{step}@\omega_{\text{step}}} |A_{4s, \text{step}@\omega_{\text{step}}}^{(2)}|^2 + |K_{\text{TL}}| |I_0|^2}{|K_{\text{step}@\omega_{\text{step}}}||I_0|^2}$$

$$= \left| 1 + \text{Re}[A_{4s, \text{step}@\omega_{\text{step}}}^{(0)}/A_{4s, \text{TL}}^{(2)}]^2 + \text{Im}[A_{4s, \text{step}@\omega_{\text{step}}}^{(0)}/A_{4s, \text{TL}}^{(2)}]^2 \right|$$

$$= \left| 1 + K_{\text{step}@\omega_{\text{step}}} |I_0|^2 + |K_{\text{TL}}| |I_0|^2 \right|$$

$$= \left| 1 + K_{\text{TL}} |I_0|^2 \right|$$

(14)

where the pulse shape dependence enters only via the $K$ factors. As can be seen, there is a close similarity between this equation and equation (13). So, based on the above analysis conclusions, one gets the observed intermediate-field behaviour for $\omega_{\text{step}} = \omega_0$: (i) for blue detuning of $\omega_0 > \omega_{4s, 3s/2}$ ($\lambda_0 = 773.5$ nm): $K_{\text{step}@\omega_{\text{step}}} > 0$, $K_{\text{TL}} > 0$, $|K_{\text{step}@\omega_{\text{step}}}| < |K_{\text{TL}}|$, and thus $RR_{\text{step}@\omega_{\text{step}}} < 1$ (attenuation); (ii) for red detuning of $\omega_0 < \omega_{4s, 3s/2}$ ($\lambda_0 = 780$ nm): $K_{\text{step}@\omega_{\text{step}}} < 0$, $K_{\text{TL}} < 0$, $|K_{\text{step}@\omega_{\text{step}}}| < |K_{\text{TL}}|$, and thus $RR_{\text{step}@\omega_{\text{step}}} > 1$ (enhancement). Also, for both $\lambda_0$ values, the value of $|RR_{\text{step}@\omega_{\text{step}}}|$ increases as $I_0$ increases. In the red detuning case ($\lambda_0 = 780$ nm), this increase leads eventually to an intermediate-field absorption that exceeds the intermediate-field TL absorption (figure 3(3c)). It worth emphasizing that the intermediate-field attenuation/enhancement effect considered here is relative to the weak-field case of the same shaped pulse, while for the pulse with $\omega_{\text{step}} = \omega_{4s, 3s/2}$ it is considered above relative to the intermediate-field TL absorption.

4.4. Intermediate-field two-photon absorption: shaped pulse with $\omega_{\text{step}} = \omega_p^{\text{4s}}$

As discussed above with regard to figure 4, the intermediate-field dip feature at $\omega_{\text{step}} = \omega_p^{\text{4s}}$ (781.2 nm) originates from the inclusion of the Raman term $A_{\text{res}}^{(R)}$ in the complete Raman term $A^{(R)}$ (equations (10)–(12)). As described above, $A_{\text{res}}^{(R)}$ interferes only those Raman parts that are resonance-mediated via $\hat{p}$. Each of them is either on-resonance or near-resonance with $7p$ ($\delta^*$ is the corresponding detuning). So, overall, each corresponding four-photon pathway is either on- or near-resonance with $4s$ and either on- or near-resonance with $7p$. The higher is the field amplitude $|\tilde{E}(\omega_p^{\text{4s}})|$ at $\omega_p^{\text{4s}}$ the more prominent is the dip. So, here, it is most prominent for $\lambda_0 = 780$ nm (figure 4(c)).

With the inclusion of $A_{\text{res}}^{(R)}$, the terms $A_{4s}^{(4\text{near-res})}$ and $A_{4s}^{(4\text{non-res})}$ become complex quantities, and thus they both contribute to both the imaginary and real parts of $A_{4s}^{(2)}$. So, the analysis of the corresponding interference mechanism is much more complicated as compared to the above, when $A_{\text{res}}^{(R)}$ is excluded. Essentially, the interference mechanism leading to the dip is very similar to that we recently identified in weak-field resonance-mediated (2 + 1) three-photon absorption [14], where a $\pi$-step at $\omega_p^{\text{4s}}$ leads to a strong enhancement in the population transfer to the $7p$ state. Here, for example, a $\pi$-step at $\omega_p^{\text{4s}}$ leads to a constructive add-up within the $g$-integral of $A_{4s}^{(4\text{near-res})}$ (equation (9)) between the amplitudes contributed by the four-photon pathways on-resonant with $7p$ that are of positive detuning $+\delta$ and of negative detuning $-\delta$ from $4s$. The corresponding Raman transition involves the absorption of the photon $\omega_p^{\text{4s}} \pm \delta$ and the emission of the photon $\omega_p^{\text{4s}}$. Since $\tilde{E}(\omega_p^{\text{4s}} + \delta)$ and $\tilde{E}(\omega_p^{\text{4s}} - \delta)$ are of opposite signs for the shaped pulse of $\omega_{\text{step}} = \omega_p^{\text{4s}}$, the sign of the detuning $\delta$ (and of the integrand factor $1/\delta$) becomes correlated with the sign of $\tilde{E}(\omega_p^{\text{4s}} + \delta)$, leading to the constructive add-up and resulting amplitude enhancement. For the TL pulse, the add-up is destructive since the signs of $\tilde{E}(\omega_p^{\text{4s}} - \delta)$ and $\tilde{E}(\omega_p^{\text{4s}} + \delta)$ are the same. Upon a detailed analysis, accounting also
for the $\delta$-dependence of $A^{(2)}(\omega_{4s}, \omega_{3s} - |\delta|)$ when $\omega_{\text{dep}} = \omega_{10} = 4S (781.2 \text{ nm})$ (very similar to that when $\lambda_{\text{dep}} = 780 \text{ nm}$ (figure 5(c))), one obtains that, for the present Na excitation, the sign of the amplitude contributed to $A^{(4)}_{4s}$ by the four-photon pathways with non-resonant Raman parts (i.e., corresponding to $A^{(\text{non-res})}$) is opposite to the sign of the amplitude contributed by those with resonance-mediated Raman parts (i.e., corresponding to $A^{(\text{res})}$). This leads to a dip feature rather than a peak feature.

5. Conclusions

In conclusion, coherent control of femtosecond two-photon absorption in the intermediate-field regime in analysed in detail using a powerful frequency domain description that is based on fourth-order perturbation theory. The two-photon absorption is coherently induced by non-resonant two-photon transitions as well as by four-photon transitions that introduce a resonance-mediated nature to the excitation. Their relative contributions to the total absorption amplitude depend on the field strength. The corresponding interference mechanism is identified to include intra-group and inter-group interferences involving these two groups of multiphoton transitions. The inter-group interferences lead to a difference between the intermediate-field and weak-field absorption dynamics. Their constructive/destructive nature is found to depend on the detuning direction of the pulse spectrum from one-half of the two-photon transition frequency; It changes upon a red- to-blue detuning change. The extended frequency-domain description and its detailed understanding serve as a basis for femtosecond control with rationally-shaped pulses in a regime of significant absorption yields, reaching population transfer in the range of 10–40% (depending on the specific system and excitation scheme). They also serve as a basis for future extensions to molecular systems, to other types of multiphoton processes, to more complicated excitation schemes, and to higher pulse intensities involving higher perturbative orders.

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