Quantum control of optical four-wave mixing with femtosecond $\omega-3\omega$ laser pulses: coherent ac Stark nonlinear spectroscopy

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The four-wave mixing produced with two ultrashort phase-locked $\omega-3\omega$ laser pulses propagating coherently in a two-level system in the infrared spectral region is shown to depend on the pulses relative phase. The Maxwell-Bloch equations are solved beyond the rotating-wave approximation to account for field frequencies which are largely detuned from the atomic resonance. The relative phase dominating the efficiency of the coupling to the $5\omega$ anti-Stokes Raman component is determined by sign of the total ac Stark shift induced in the system, in such a way that the phase influence disappears precisely where the ac Stark effect due to both pulses is compensated. This fundamental quantum interference effect can be the basis for nonlinear ultrafast optical spectroscopy techniques.

Phenomena arising from the coherent control of nonlinear interactions are of importance in fields as diverse as optoelectronics and materials research, in high harmonic generation, in photoionization or molecular dissociation, and in biological applications such as spectroscopy and imaging, among others [1, 2, 3, 4, 5, 6, 7]. Optical quantum coherent control is based on the fact that the phases of interfering transition amplitudes in light-matter interactions can be controlled through the optical phase of coherent light sources that drive the interaction, in such a way that the transition rates to final states and the dynamics at various stages of the process can be modified [7].

In a recent paper [8], a theoretical investigation on the quantum coherent control of the optical transient four-wave mixing of two intense phase-locked femtosecond laser pulses of central angular frequencies $\omega$ and $3\omega$ propagating in a two-level atom (TLA) was reported. It was shown how the nonlinear $(\chi^{(3)})$ coupling to the anti-Stokes Raman field at frequency $5\omega$ depends critically on the initial relative phase $\phi$ of the propagating pulses. In Ref. [8], the study was centered to intense pulses in the visible and ultraviolet spectral regions, with frequencies at resonance or lower than the atomic transition. The phenomena observed in [8], however, can be scaled to various laser and material parameters. In the infrared spectral range, for instance, experiments on ultrafast molecular dynamics are frequently performed by help of two-color pump probe nonlinear spectroscopy techniques. In this type of studies, due to the high intensities inherent to ultrashort (subpicosecond) pulses, nonlinear effects such as stimulated Raman processes may become important and are often utilized as a complementary tool to gain information [9].

In this Letter, we address the conditions for quantum coherent control of four-wave mixing interactions with two phase-locked $\omega-3\omega$ femtosecond laser pulses in the mid-IR spectral region. Our purpose is to reveal the basic physics for a strict two-level medium and to this end the Maxwell-Bloch TLA will be considered. We will study pulses with a duration of 300 fs (with a spectral width of $\approx 35 \text{ cm}^{-1}$) and peak intensities as $\sim 10^8 \text{ W/cm}^2$, which are typically used in infrared nonlinear spectroscopy experiments [10]. We will examine the influence of frequency detuning by considering the field at $3\omega$ above resonance with respect to the atomic transition, something that was not considered in [8]. Under these conditions, we will show that the quantum interferences leading to a dominating efficiency of the nonlinear coupling to the anti-Stokes Raman component are governed by the ac Stark shift induced in the system. Furthermore, we will demonstrate that the relative spectral amplitude of the anti-Stokes fields produced by phase-locked pulses cancels for frequency detunings that compensate the ac Stark effect. This fundamental interference effect might be the basis for a novel ultrafast spectroscopy tool based on coherent control, which we name coherent ac Stark nonlinear spectroscopy (CSNS) for use later below.

The pulse propagation is modeled by means of the Maxwell-Bloch equations beyond the rotating-wave approximation, allowing the resonant as well as the nonresonant regimes of the system to be described [11]. The equations are written as

$$\frac{\partial H}{\partial t} = -\frac{1}{\mu_0} \frac{\partial E}{\partial z},$$

FIG. 1: (Color online) Schematic energy level diagram. The resonance wavelength is considered in the mid-IR at $\lambda_{(12)} = 3000 \text{ nm}$
\[ \frac{\partial E}{\partial t} = -\frac{1}{\varepsilon_0} \frac{\partial H}{\partial z} - \frac{N_{\text{at}} \mu}{\varepsilon_0 T_2} (\rho_1 - T_2 \omega_{12} \rho_2) , \]

\[ \frac{\partial \rho_1}{\partial t} = -\frac{1}{T_2} \rho_1 + \omega_{12} \rho_2 , \]

\[ \frac{\partial \rho_2}{\partial t} = -\frac{1}{T_2} \rho_2 + \frac{2 \mu}{\hbar} E \rho_3 - \omega_{12} \rho_1 , \]

\[ \frac{\partial \rho_3}{\partial t} = -\frac{1}{T_1} (\rho_3 - \rho_{30}) - \frac{2 \mu}{\hbar} E \rho_2 , \]

where \( H(z,t) \) and \( E(z,t) \) represent the magnetic and electric fields propagating along the \( z \) direction, respectively, \( \mu_0 \) and \( \varepsilon_0 \) are the magnetic permeability and electric permittivity of free space, respectively, \( N_{\text{at}} = 2 \times 10^{24} \text{ m}^{-3} \) is the density of polarizable atoms, \( \mu = 4.2 \times 10^{-29} \text{ C m} \) is the effective dipole coupling coefficient, \( T_1 = T_2 = 1 \text{ ps} \) are the excited-state lifetime and dephasing time, respectively, \( \rho_1 \) and \( \rho_2 \) are the real and imaginary components of the polarization, and \( \omega_{12} \) is the transition resonance angular frequency of the two level medium, considered in the present simulations in the mid-IR region at 3000 nm (see Fig. 1). The population difference \( \rho_3 \), and \( \rho_{30} \) represents its initial value. An hyperbolic secant two-color pulse that can be expressed as

\[ E(t) = E_{3\omega}(t) + E_{\omega}(t) = E_0 \text{sech}(t-t_0)/t_p \times \]

\[ [\cos(\omega(t-t_0)) + \cos(3\omega(t-t_0) + \phi)] \]  

(2)

is externally injected to the system. The peak input electric field amplitude \( E_0 \) is chosen the same for both pulses and results in an intensity of \( 4 \times 10^8 \text{ W/cm}^2 \). The duration of the pulses is given by \( t_p = t_{\text{rp}}/1.763 \), with \( t_{\text{rp}} = 300 \text{ fs} \) being the full width at half maximum (FWHM) of the pulse intensity envelope. \( t_0 \) gives the offset position of the pulse center at \( t = 0 \), and it is the reference value for the phase of the pulses. The central angular frequencies of the pulses are \( \omega \) and \( 3\omega \), and \( \phi \) is the relative phase. The propagating system has been resolved numerically by means of a standard finite difference time domain method described elsewhere [8].

Figure 2 shows the field spectra at different propagation lengths in the case that the central angular frequency of the field \( E_{3\omega} \) is at resonance with the atomic transition (\( 3\omega = \omega_{12} \)). The spectrum on the top is for the initial pulses. The succeeding plots show the evolution of the spectrum as the pulses propagate through the medium. In this case, we can observe the effect of the absorption of the pulse at \( 3\omega \), together with the appearance of other spectral contributions at \( 5\omega, 7\omega, \) and \( 9\omega \), which are produced as a result of the coupling of the fields through the third order nonlinearity \( (\chi^{(3)}) \) of the medium. It is clear that the conversion to the anti-Stokes Raman component \( (5\omega) \) depends on the relative phase between the pulses. For the parameter values of the results shown in Fig. 2 the coupling to the fifth harmonic \( (5\omega) \) is more efficient for \( \phi = 0 \) than for \( \phi = \pi \), an scenario that was already reported in Ref. 8 for a transition in the visible region.

Hence here we confirm that observed in Ref. 8 for a different system, particularly, considering a mid-IR atomic transition. It is important to note that this phase dependence effect involves the anti-Stokes Raman component \( (5\omega) \) only, not the \( 7\omega \) nor the \( 9\omega \) spectral components, which remain insensitive to the initial relative phase of the pulses.

We now turn to the study of the frequency detuning of the fields with respect to the atomic transition. We will show that there is a central pulse frequency \( \omega \) at which the relative phase dependence of the coupling to the anti-Stokes Raman component, which has been previously discussed in Fig. 2 disappears. We will observe that this effect can occur because the ac Stark shifts produced in the medium by the fields \( E_\omega \) and \( E_{3\omega} \) can be compensated when \( \omega < \omega_{12} < 3\omega \). We will then conclude that the ac Stark shift in the medium governs the relative phase dependence of the coherent four-wave coupling.

Indeed, the ac Stark frequency shift \( \Delta \omega \) produced by a field of frequency \( \omega \) which is not near resonance in a transition of frequency \( \omega_{12} \) can be expressed as

\[ \Delta \omega = \frac{-\omega_{12} - \omega}{2} \]

\[ \pm \frac{1}{2} \left[ (\omega_{12} - \omega)^2 + 4\beta^2 (1 + \frac{\omega_{12} - \omega}{\omega_{12} + \omega}) \right]^{1/2}, \]

where \( + \) is for \( \omega < \omega_{12} \) and \( - \) is for \( \omega \geq \omega_{12} \). \( \beta = \mu |E|/(2\hbar) \), with \( |E| \) being the amplitude of the field, \( \omega_{12} \) the frequency of the atomic transition, and \( \omega \) the field angular frequency. The conditions \( \beta/|E| << 1 \) and

FIG. 2: (Color online) Spectra of the total field at different propagation lengths as indicated. In the case shown, the central pulse frequency \( 3\omega \) is in resonance with the atomic transition. Each spectrum is plotted in logarithmic scale. The relative spectral amplitude of the anti-Stokes \( 5\omega \) components is shown quantitatively for \( z = 25 \mu m \) in Fig. 2 (case with \( \eta = 9.0 \)).
From resonance, where \( \beta/\omega_{12} \ll 1 \) must be met for Eq. 3 to be valid. Far from resonance, where

\[
\frac{(\omega_{12} - \omega)^2}{\beta^2} > \frac{8\omega_{12}}{\omega_{12} + \omega},
\]

Eq. 3 becomes

\[
\Delta \omega \approx \beta^2 \left[ \frac{1}{\omega_{12} - \omega} + \frac{1}{\omega_{12} + \omega} \right].
\]

Note that the last term inside the brackets in Eq. 5 is important far from resonance, where the rotating wave approximation does not apply. Clearly from Eq. 5, when \( \omega > \omega_{12} \) we have \( \Delta \omega < 0 \), and the separation in frequency of the states \( (\omega_{12} + \Delta \omega) \) appears to be less than in the absence of the field. Contrarily, for \( \omega < \omega_{12} \), the ac Stark frequency shift is positive.

In the case of the present investigation, the main contributions to the ac Stark effect come from the two components of the propagating pulses \( E_\omega \) and \( E_{3\omega} \), which have central angular frequencies \( \omega \) and \( 3\omega \), respectively, and the conditions for Eq. 5 are clearly met for the parameter values of our study. Therefore, requiring that the combined ac Stark effect is null

\[
0 = \frac{1}{\omega_{12} - \omega} + \frac{1}{\omega_{12} + \omega} + \frac{1}{\omega_{12} - 3\omega} + \frac{1}{\omega_{12} + 3\omega},
\]

we obtain \( \omega = \omega_{12}/\sqrt{5} \).

We will next show that the ac Stark cancellation frequency \( \omega = \omega_{12}/\sqrt{5} \) is indeed observed with accuracy from numerical simulations. In Figure 3 the spectral amplitude of the anti-Stokes \( 5\omega \) component is shown for different values of the detuning between the fields and the atomic transition at a propagation length such as \( z = 25 \mu m \). It is useful to define the parameter \( \eta = (\omega_{12}/\omega)^2 \), which sets the value of the detuning of the \( E_\omega \) and \( E_{3\omega} \) fields. The spectra corresponding to \( \phi = 0 \) is shown by solid lines in Fig. 3, while the spectra for \( \phi = \pi \) is represented by the dashed lines. Clearly, there is a switch in the tendency to dominate the conversion to the \( 5\omega \) anti-Stokes component. For \( \eta < 5 \), the ac Stark shift due to \( E_\omega \) dominates over the shift induced by \( E_{3\omega} \), and therefore the resulting separation of the states due to the combined Stark effect appears to be larger than in the absence of fields. In this situation, the coupling to the \( 5\omega \) anti-Stokes field is enhanced for \( \phi = \pi \), as it can be observed in Fig. 3 left plots. Contrarily, for \( \eta > 5 \), when the ac Stark shift due to \( E_{3\omega} \) dominates over the shift induced by \( E_\omega \), the coupling to the \( 5\omega \) anti-Stokes Raman component is enhanced for \( \phi = 0 \) (right plots in Fig. 3). In this last case the resulting separation in frequency of the states due to the total Stark effect is less than in the absence of fields. Furthermore, as shown in Fig. 3, the switching occurs at \( \eta = 5 \), where the total ac Stark shift is cancelled, as expected from Eq. 5. Note that for the numerical simulations to agree with the prediction of the analytical theory, the expression for the Stark effect beyond the rotating wave approximation needs to be considered (see Eq. (33) in Ref. [11]).

We now look at the relative spectral amplitude of the anti-stokes Raman fields, which we define as

\[
\Delta E_{5\omega}(z) = \frac{E^0_{5\omega}(z) - E^\pi_{5\omega}(z)}{E^0_{5\omega}(z) + E^\pi_{5\omega}(z)},
\]

with \( E^0_{5\omega}(z) \) being the spectral amplitude at the generated anti-Stokes \( (5\omega) \) frequency in the case that the initial relative phase is \( \phi = 0 \) (see Fig. 3), and \( E^\pi_{5\omega}(z) \) being the spectral amplitude at \( 5\omega \) in the case that the initial relative phase between the pulses is \( \phi = \pi \). Figure 4 shows the results obtained from the numerical simulations for \( z = 25 \mu m \). Relative differences in amplitudes as \( |\Delta E_{5\omega}| \gg 0.5 \) can readily be produced in the cases considered in our simulations. Moreover, we have checked that the relative phase dependence at \( \eta = 5.0 \) remains null for propagation distances as long as \( z = 100 \mu m \).

We have therefore demonstrated that considering the coherent propagation of two-color phase-locked femtosecond pulses in a two-level medium, with central angular frequencies \( \omega \) and \( 3\omega \), one can find an angular frequency \( \omega \) at which the ac Stark effect produced by the
propagating pulses is cancelled. At this frequency value, which requires the pulse with central frequency \(3\omega\) to be above resonance with respect to the atomic transition, the phase dependence of the transient four-wave coupling through the \(\chi^{(3)}\) nonlinear susceptibility of the medium disappears. This is a fundamental quantum interference effect that to the best of our knowledge has not been reported before.

In the present Letter, we have considered atomic frequencies which lie in the mid-IR region, which are of interest for applications e.g. in infrared nonlinear spectroscopic techniques. It has to be stressed however that the phenomena that we report can be scaled to several material and pulse parameters. We can hence imagine straightforward applications for nonlinear ultrafast spectroscopic techniques based on the coherent control of subpicosecond two-color \(\omega-3\omega\) propagating laser pulses. Indeed, the production of phase related \(\omega-3\omega\) pulses is frequently accomplished by some frequency tripling mechanism with the subsequent variation of the phase of one of the pulses in order to obtain experimental control over the relative phase. Although our analysis has obviously been simplified by considering two well isolated levels as a first approach, the switching effect discussed here is of a fundamental level, and in that sense it should be observed experimentally in particular media where the two-level approximation is met. For instance, some gaseous atoms have well isolated resonances (as e.g. rubidium in the visible region). Also, the two-level approximation can be used for studying coherent effects in materials with a broad distribution of transitions, such as inhomogeneously broadened resonance lines in gases and in condensed matter, and even for inhomogeneous quasi-continuous energy bands as in semiconductors \[12\] [13]. CSNS can hence provide information on the transitions being probed by measuring the relative spectral amplitude of the anti-Stokes Raman fields with a simple scan of the laser frequency. The ac Stark mediated coherent control scenario reported in this Letter has therefore a broad interest and may be the basis for future studies on more complex systems.

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\[\begin{align*}
\text{FIG. 4: (Color online) Relative spectral amplitude of the} \quad \text{anti-stokes Raman fields [as defined in Eq. (7)] as a function} \\
\text{of the parameter } \eta \text{ for } z = 25 \mu \text{m. The vertical dashed line is} \\
\eta = 5 \text{ as indicated. The dashed curve is a guide to the eye.}
\end{align*}\]