PHYSICAL REVIEW A **72**, 051803(R) (2005)

ac Stark-mediated quantum control with femtosecond two-color laser pulses

Carles Serrat
Departament de Física i Enginyeria Nuclear, Universitat Politècnica de Catalunya, Colom 11, 08222 Terrassa, Spain
(Received 19 July 2005; published 21 November 2005)

A critical dependence of the quantum interference on the optical Stark spectral shift produced when two-color laser pulses interact with a two-level medium is observed. The four-wave mixing of two ultrashort phase-locked ω-3ω laser pulses propagating coherently in a two-level system depends on the pulses' relative phase. The phase dominating the efficiency of the coupling to the anti-Stokes Raman component is found to be determined by the sign of the total ac Stark shift induced in the system, in such a way that the phase sensitivity disappears precisely where the ac Stark effect due to both pulses is compensated. A coherent control scheme based on this phenomenon can be contemplated as the basis for nonlinear optical spectroscopy techniques.

DOI: 10.1103/PhysRevA.72.051803 PACS number(s): 42.65.Dr, 42.65.Re, 32.80.Qk

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, photoionization or molecular dissociation, and in biological applications such as spectroscopy and imaging, among others [1–8]. 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 can be modified [1].

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 ω and 3ω propagating in a two-level atom (TLA) was recently reported [9]. It was shown how the nonlinear $\chi^{(3)}$ coupling to the anti-Stokes Raman field at frequency 5ω depends critically on the initial relative phase ϕ of the propagating pulses. The study was centered to intense pulses in the visible and ultraviolet spectral regions, with field central frequencies at resonance or lower than the atomic transition. The phenomena observed in [9] can, however, be scaled to various laser and material parameters. In the mid-infrared (MIR) spectral range, in particular, experiments on ultrafast molecular dynamics are frequently performed by help of two-color pump-probe nonlinear spectroscopy techniques. In these studies, nonlinear effects such as stimulated Raman processes may become important due to the high intensities inherent to ultrashort pulses, and those nonlinear effects are often utilized as a complementary tool to gain information [10].

In this paper, a critical dependence of the quantum interference on the optical Stark effect induced in the medium is observed. To demonstrate the basic physics, I consider the simplest case of the excitation of a two-level system in the MIR by ω-3ω pulses, with pulse durations of 300 fs (spectral width of $\approx 35\ \mathrm{cm}^{-1}$) and peak intensities $\sim 10^8\ \mathrm{W/cm}^2$, which are typically considered in nonlinear spectroscopy setups [10]. I examine the influence of frequency detuning by considering the field at 3ω above resonance with respect to the atomic transition, in regions where a near Raman resonance is achieved. Under these conditions, I demonstrate that the quantum interference is governed by the total optical Stark shift induced in the system. I further observe that the relative spectral amplitude of the anti-Stokes fields produced by phase-locked pulses cancels for frequencies that compensate the ac Stark effect. This interference phenomenon might be considered as the basis for an ultrafast spectroscopy tool based on coherent control, which I name coherent Stark nonlinear spectroscopy (CSNS) for use later below.

The pulse propagation is modeled by means of the full set of Maxwell-Bloch equations beyond the rotating-wave approximation, which allow the resonant as well as the nonresonant regimes of the system to be considered [1,11]. The equations are written as

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

$$\frac{\partial E}{\partial t} = -\frac{1}{\epsilon_0}\frac{\partial H}{\partial z} - \frac{N_{at}\mu}{\epsilon_0 T_2}(\rho_1 - T_2\omega_{12}\rho_2),$$

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

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

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

where $H(z,t)$ and $E(z,t)$ represent the magnetic and electric fields propagating along the z direction, respectively, μ_0 and ϵ_0 are the magnetic permeability and electric permittivity of free space, $N_{at}=2\times10^{24}\ \mathrm{m}^{-3}$ is the density of polarizable atoms, $\mu=4.2\times10^{-29}$ cm is the effective dipole coupling coefficient, $T_1=T_2=1$ ps are the excited-state lifetime and dephasing time, respectively, ρ_1 and ρ_2 are the real and imaginary components of the polarization, and ω_{12} is the transition resonance angular frequency of the two-level medium, which is considered in the MIR spectral region (see Fig. 1). The population difference is ρ_3, and ρ_{30} represents its initial value. An hyperbolic secant two-color pulse, which can be expressed as

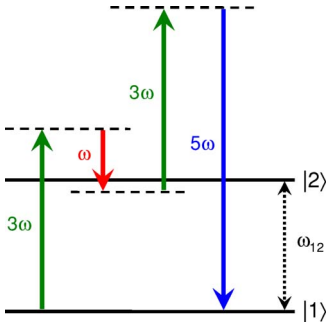

FIG. 1. (Color online) Schematic energy level diagram. The resonance wavelength is considered in the MIR at $\lambda_{(\omega_{12})}=3000$ nm.

$$E(t) = E_\omega(t) + E_{3\omega}(t) = E_0\,\mathrm{sech}[(t-t_0)/t_p] \times\{\cos[\omega(t-t_0)] + \cos[3\omega(t-t_0)+\phi]\}, \quad (2)$$

is externally injected to the system. E_ω and $E_{3\omega}$ represent the fields with central angular frequencies ω and 3ω, respectively. The peak input electric field amplitude E_0 is chosen the same for both pulses and results in an intensity of 4.0×10^8 W/cm^2. The duration of the pulses is given by $t_p=\tau_p/1.763$, with $\tau_p=300$ 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 ϕ is the relative phase. The propagating system has been resolved numerically by means of a standard finite difference time domain method described elsewhere [9,11].

Figure 2 shows the field spectra at different propagation lengths in the case where 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, and the succeeding plots show the evolution of the spectrum as the pulses propagate through the medium. Spectral components at 5ω, 7ω, and 9ω are produced as a result of the coupling through the third-order nonlinearity $\chi^{(3)}$ of the medium. Clearly, the conversion to the anti-Stokes Raman component $E_{5\omega}$ depends on the relative phase between the pulses. For the parameter values in Fig. 2, the coupling to $E_{5\omega}$ is more efficient for $\phi=0$ than for $\phi=\pi$. As mentioned above, these results can be compared to those in Ref. [9], and they corroborate the relative phase dependence in the important case of MIR transitions. It is worth noting that the interference effect involves the anti-Stokes spectral Raman component 5ω only, not the 7ω nor the 9ω, which remain insensitive to the initial relative phase of the pulses. To lowest order, this is conceivable since in the coupling to 5ω two primary paths are available, namely $3\omega+3\omega-\omega$ and $3\omega+\omega+\omega$, while this is not given for 7ω and 9ω.

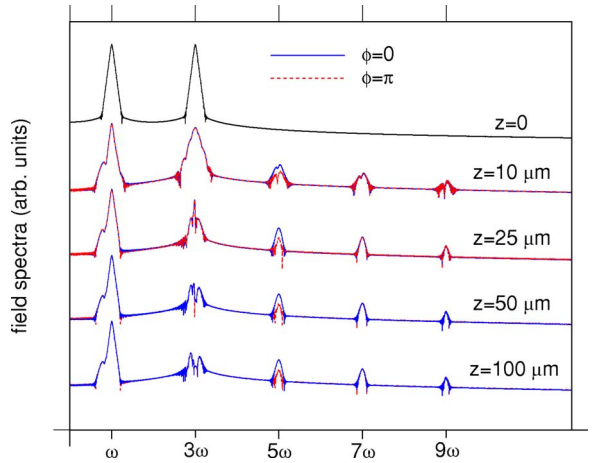

FIG. 2. (Color online) Spectra of the total field at different propagation lengths as indicated. In the case shown, the central pulse frequency 3ω is at resonance with the atomic transition. Each spectrum is plotted in the logarithmic scale. The relative spectral amplitude of the anti-Stokes 5ω components is shown quantitatively in Fig. 3 (case with $\eta=9.0$).

I now jump to the study of the frequency detuning of the fields with respect to the atomic transition, which is the key part of the present investigation. I will show that there is a central pulse frequency ω at which the relative phase dependence of the coupling to the anti-Stokes Raman component disappears. I will demonstrate that this can occur because the different ac Stark shifts produced in the medium by the fields E_ω and $E_{3\omega}$ can be compensated for certain frequencies in the case that $\omega<\omega_{12}<3\omega$. I will conclude that the optical Stark shift governs the relative phase dependence and therefore the quantum interferences in the nonlinear coupling.

Indeed, the ac Stark frequency shift $\Delta\omega$ produced by a field of frequency ω that is not near resonance with a transition of frequency ω_{12} can be expressed as [12]

$$\Delta\omega = -\frac{\omega_{12}-\omega}{2} \pm \frac{1}{2}\left[(\omega_{12}-\omega)^2 + 4\beta^2\left(1+\frac{\omega_{12}-\omega}{\omega_{12}+\omega}\right)\right]^{1/2}, \quad (3)$$

where $+$ is for $\omega<\omega_{12}$ and $-$ is for $\omega\gtrsim\omega_{12}$. In (3), $\beta=\mu|E|/(2\hbar)$, where $|E|$ is taken in our study as the peak amplitude of the pulses, ω_{12} is the frequency of the atomic transition, and ω is the field angular frequency. Note that the conditions
$\beta/\omega\ll1$ and $\beta/\omega_{12}\ll1$ must be met for Eq. (3) to be valid [12]. Far from resonance, where

$$\frac{(\omega_{12}-\omega)^2}{\beta^2} \gg \frac{8\omega_{12}}{\omega_{12}+\omega}, \quad (4)$$

Eq. (3) becomes

$$\Delta\omega \approx \beta^2\left[\frac{1}{\omega_{12}-\omega} + \frac{1}{\omega_{12}+\omega}\right]. \quad (5)$$

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 hence the separation in frequency of the atomic 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 present case, the main contributions to the ac Stark effect come from the two components of the propagating pulses at frequencies ω and 3ω. Requiring that the combined ac Stark effect is null

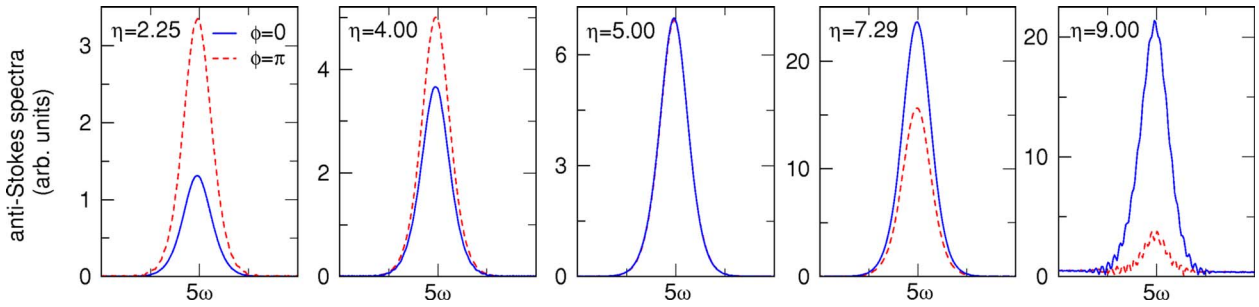

FIG. 3. (Color online) Spectra for differents values of η showing the anti-Stokes 5ω frequency component of the field at the propagation distance $z=25$ μm, for $\phi=0$ (solid lines) and $\phi=\pi$ (dashed lines). At $\eta=5$ (center plot) the dependence on the relative phase disappears.

$$0=\frac{1}{\omega_{12}-\omega}+\frac{1}{\omega_{12}+\omega}+\frac{1}{\omega_{12}-3\omega}+\frac{1}{\omega_{12}+3\omega}, \qquad (6)$$

we obtain $\omega=\omega_{12}/\sqrt{5}$. It is worth noting that the ac Stark cancellation condition (6) does not depend on the pulse duration and therefore in that sense the result is general. I will show next that this is the frequency at which the four-wave mixing relative phase dependence effect is suppressed.

The ac Stark cancellation frequency $\omega=\omega_{12}/\sqrt{5}$ is indeed observed with accuracy from the numerical simulations. In Fig. 3, the spectral amplitude of the anti-Stokes 5ω component is shown for different values of the detuning of the fields. The spectra corresponding to $\phi=0$ is shown by solid lines, 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 5ω anti-Stokes component. To quantify this behavior, it is useful to define the parameter $\eta=(\omega_{12}/\omega)^2$, which sets the value of the detuning of the E_ω and $E_{3\omega}$ fields. For $\eta<5$, the ac Stark shift due to E_ω 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 5ω anti-Stokes field is enhanced for $\phi=\pi$, as it can be observed in Fig. 3 (plots on the left). Contrarily, for $\eta>5$, when the ac Stark shift due to $E_{3\omega}$ dominates over the shift induced by E_ω, the coupling to the 5ω anti-Stokes Raman component is enhanced for $\phi=0$ (plots on the right 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. (6). As already noticed above, for the numerical simulations to agree with the theory, the ac Stark effect needs to be considered beyond the rotating wave approximation (see, e.g., Eq. (33) in Ref. [12]).

Going forward, I compute the relative spectral amplitude of the anti-stokes Raman fields, which is defined as

$$\Delta E_{5\omega}(z)=\frac{E^0_{5\omega}(z)-E^\pi_{5\omega}(z)}{E^0_{5\omega}(z)+E^\pi_{5\omega}(z)}, \qquad (7)$$

where $E^0_{5\omega}(z)$ is the spectral amplitude at the generated anti-Stokes 5ω frequency for $\phi=0$ (see Fig. 3), and $E^\pi_{5\omega}(z)$ is the spectral amplitude at 5ω in the case that $\phi=\pi$. Figure 4 shows the results obtained from the numerical simulations for $z=25$ μm. Relative differences in amplitudes as $|\Delta E_{5\omega}|\gtrsim 0.5$ can readily be produced in the cases considered in the simulations, and, importantly, the relative phase dependence at $\eta=5.0$ remains suppressed for propagation distances at least as long as $z=100$ μm. This makes sense since for the ac Stark-shift cancellation to prevail during propagation, i.e., for Eq. (6) to be consistent, the peak amplitudes of E_ω and $E_{3\omega}$ must remain equivalent, and therefore they have to contribute equally to the coupling to $E_{5\omega}$, which is indeed observed at $\eta=5$. Contrarily, for $\eta<5$ the power at $E_{5\omega}$ is mainly due to E_ω, while for $\eta>5$ it is mainly shifted from $E_{3\omega}$. Also important, as noted above, is that the simulations have been performed near the Raman resonance, since for large values of the detuning (i.e., for very small or very large η), the nonlinear coupling to 5ω is not efficient.

To conclude, I have shown that considering the coherent propagation of two-color phase-locked femtosecond pulses in a two-level medium, with central angular frequencies ω and 3ω, one can find an angular frequency ω at which the ac Stark effect produced by the propagating pulses is cancelled. At this frequency value, which requires the pulse with central frequency 3ω 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 quantum interference effect has not been reported before. In the present paper, I have considered atomic frequencies that lie in the MIR spectral region, which are of the most interest for applications in nonlinear spectroscopy. It has to be stressed, however, that the phenomena

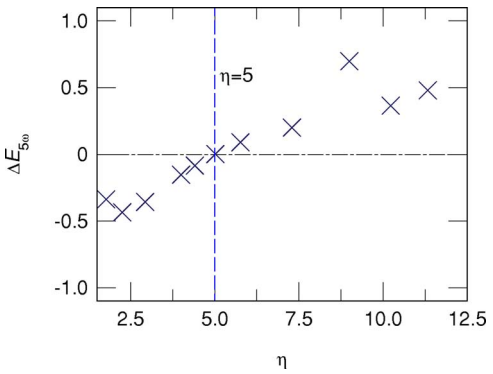

FIG. 4. (Color online) Relative spectral amplitude of the anti-stokes Raman fields [as defined in Eq. (7)] as a function of the parameter η for $z=25$ μm. The dashed lines are a guide to the eye.

reported here can be scaled to several material and pulse parameters, and therefore straightforward applications can be conceived for different nonlinear spectroscopy methods based on coherent control. Indeed, the production of phase-related ω-3ω pulses is frequently accomplished by some frequency tripling mechanism or by frequency difference, with the subsequent variation of the phase of one of the pulses in order to obtain experimental control over the relative phase. Although the present 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 quasicontinuous energy bands as in semiconductors [13,14]. In this area, CSNS can be utilized to extract information of different physical parameters characterizing the material transitions being probed, by, e.g., measuring the relative spectral amplitude of the anti-Stokes Raman fields. The ac Stark mediated coherent control scenario reported in this paper has therefore a broad interest and might be the basis for further studies in more complex systems.

Support from the *Programa Ramón y Cajal* of the Spanish Ministry of Science and Technology and from project FIS2004-02587 is acknowledged.

[1] See, e.g., S. Mukamel, *Nonlinear Optical Spectroscopy* (Oxford University Press, New York, 1995); M. Shapiro and P. Brumer, *Principles of the Quantum Control of Molecular Processes* (Wiley Inter-Science, Hoboken, NJ, 2003).

[2] E. Charron, A. Giusti-Suzor, and F. H. Mies, Phys. Rev. Lett. **71**, 692 (1993).

[3] S. Watanabe, K. Kondo, Y. Nabekawa, A. Sagisaka, and Y. Kobayashi, Phys. Rev. Lett. **73**, 2692 (1994).

[4] D. W. Schumacher, F. Weihe, H. G. Muller, and P. H. Bucksbaum, Phys. Rev. Lett. **73**, 1344 (1994).

[5] A. D. Bandrauk and N. H. Shon, Phys. Rev. A **66**, 031401(R) (2002).

[6] A. Brown, W. J. Meath, and A. E. Kondo, Phys. Rev. A **65**, 060702(R) (2002).

[7] X. Song, S. Gong, S. Jin, and Z. Xu, Phys. Lett. A **319**, 150 (2003).

[8] T. Hornung, R. Meier, R. de Vivie-Riedle, and M. Motzkus, Chem. Phys. **267**, 261 (2001).

[9] C. Serrat, Phys. Rev. A **72**, 023808 (2005).

[10] G. Seifert, T. Patzlaff, H. Graener, Vib. Spectrosc. **23**, 219 (2000); M. Heid, T. Chen, U. Schmitt, and W. Kiefer, Chem. Phys. Lett. **334**, 119 (2001); D. Oron, N. Dudovich, D. Yelin, and Y. Silberberg, Phys. Rev. A **65**, 043408 (2002); J. A. Gruetzmacher, J. Chem. Phys. **119**, 1590 (2003); Soo-Y. Lee, D. Zhang, D. W. McCamant, P. Kukura, and R. A. Mathies, *ibid.* **121**, 3632 (2004); J.-X. Cheng and X. S. Xie, J. Phys. Chem. B **108**, 827 (2004).

[11] R. W. Ziolkowski, J. M. Arnold, and D. M. Gogny, Phys. Rev. A **52**, 3082 (1995).

[12] S. H. Autler and C. H. Townes, Phys. Rev. **100**, 703 (1955).

[13] L. Allen and J. H. Eberly, *Optical Resonance and Two-Level Atoms* (Dover Publications, New York, 1975).

[14] See, e.g., V. P. Kalosha, M. Muller, and J. Herrmann, J. Opt. Soc. Am. B **16**, 323 (1999).