Chirped-pulse adiabatic control in coherent anti-Stokes Raman scattering for imaging of biological structure and dynamics

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Two novel control methods based on adiabatic passage are proposed to be implemented in coherent anti-Stokes Raman scattering (CARS) microscopy for noninvasive imaging of biological structure and dynamics. Advancements in coherent control of vibrational dynamics lie in the development of novel noninvasive imaging techniques that provide statical and dynamical information about biological species with molecular specificity. Of particular interest is the development of coherent anti-Stokes Raman scattering (CARS) microscopy and spectroscopy, based on a nonlinear optical process utilizing ultrafast laser pulses to generate strong, molecular-specific signals. CARS microscopic imaging techniques use selective excitation of Raman transitions at predetermined frequencies and involve laser pulse manipulation. Ultrafast laser pulses have come into play in biological imaging quite recently.1–3 The picosecond pulse techniques were utilized in CARS microscopy to achieve high chemical selectivity.4 Modern imaging methods use femtosecond pulses and are based on manipulation with the phase function,5 using polarization related properties of the light,6 and spectral phase shaping.7 Femtosecond chirped pulses were applied to vibrational mode selective excitation in the stimulated Raman and CARS spectroscopy.8–10 Implementation of femtosecond pulse techniques to control vibrational motion in CARS microscopy brings new advantages associated with high peak intensity for a given pulse energy.

CARS is a four-wave mixing process that involves interaction of molecular vibrational modes with the pump and Stokes pulse resulting in preparation of a molecular system in a coherent superposition of the ground and the excited vibrational states. This superposition is analyzed by a probe pulse that may be delayed with respect to the pump pulse. When applied, it induces the anti-Stokes transition at frequency 2ωp − ωs. Notably, the amplitude of the generated anti-Stokes field is determined by the coherence between the ground and excited vibrational states induced by the pump and Stokes pulse. In general, molecular vibrational modes may relate to a single molecule or to different molecular species in a complex biological system. By tuning onto a predetermined vibrational frequency one can create a three-dimensional biological image, reveal the known molecular species, and obtain novel microscopic data.

In this Letter we propose two methods implementing linearly chirped femtosecond pulses in CARS to control the excitation of molecular vibrations having close vibrational frequencies. We describe molecular vibrational modes by the two-level system (TLSs) presenting the ground and excited vibrational states (Fig. 1). Transition frequencies of the TLSs are chosen to be very close, δ ≪ ωTLS, in accordance with the dense vibrational frequency spectrum. Electromagnetic fields with central frequencies ωp and ωs are defined as

\[ E_{p,s}(t) = E_{p,s}^{(0)}(t) \cos(\omega_{p,s}(t-t_0) + \alpha_{p,s}(t-t_0)^2/2), \]

where \( E_{p,s}^{(0)}(t) = E_0 \exp(-(t-t_0)^2/2 \tau_0^2) \) are the time-dependent pump and Stokes field envelopes, with the chirp-dependent pulse duration \( \tau = \tau_0[1+\alpha^2/\tau_0^4]^{1/2} \); \( \tau_0 \) is the transform-limited pulse duration. The temporal (α) and spectral (α′) chirps are related as \( \alpha = \alpha/\tau^4/(1 + \alpha^2/\tau_0^4) \). Because the anti-Stokes field amplitude is determined by the vibrational coherence induced in a TLS, it is now reasonable to focus on the first part of the CARS scheme where the TLSs interact with the pump and Stokes pulse.

Fig. 1. (Color online) Schematic of the CARS.
According to the first proposed method, control of coherence in the TLS is achieved by linearly chirped pulses with $\alpha_p = \alpha_s = \alpha$, such that the frequency difference of the pump and Stokes pulse is always in resonance with $\omega_{21}$. The second proposed method implies $\alpha_s$ to be constant, giving monotonous change of the Stokes pulse frequency, and $\alpha_p$ to have same magnitude and opposite sign before the central time $t_0$ and then to flip the sign. At $t_0$ the difference of the pump and Stokes pulse frequencies comes into resonance with the $\omega_{21}$ frequency and stays in resonance for the rest of the time. We call this method the “roof” method in accordance with the temporal shape of the pump–pulse instantaneous frequency.

The Hamiltonian that describes the interaction of the TLS with the external electromagnetic fields is obtained in the rotating wave approximation. After the adiabatic elimination of virtual states (Fig. 1) it reads $H = -\Lambda \hat{\sigma}_z / 2 - \Omega^R(t) \hat{\sigma}_x$, where $\hat{\sigma}_{x,z}$ are the Pauli matrices, $\Lambda = \delta + (\alpha_s - \alpha_p)(t-t_0)$ is an effective detuning (for the resonant TLS $\delta = 0$), $\Omega^R(t) = \mu \tilde{E}^\text{p}(t) E_s(t)$ for the resonant TLS $\delta = 0$, $\Omega^R(t) = \mu \tilde{E}^\text{p}(t) E_s(t)$ for the off-resonant TLS. $\delta$ is the effective detuning, $\mu$ is the dipole moment, $\Delta$ is the detuning from the excited state chosen such that $\Delta \gg \gamma_{p,s}$. The diagonal elements of the Hamiltonian describe bare-state energies in the field interaction representation. They depend on the chirp parameters, $\alpha_{p,s}$, and also on the detuning $\delta$. Notably, there is no dependence of the diagonal elements on the ac Stark shifts caused by the pump and Stokes fields as in Refs. 10 and 11; because they are the same in magnitude they cancel each other. The off-diagonal elements describe coupling of the bare states through the effective Rabi frequency $\Omega^R(t)$. Diagonalization of the Hamiltonian leads to the dressed states having time-dependent energy separation $\Omega(t) = \sqrt{\Lambda^2 + 4 \Omega^2(t) t^2}$, which is also called generalized Rabi frequency. The time evolution of the dressed states is governed by the Hamiltonian $H_d = \Omega(t) \hat{\sigma}_z / 2 + i \Theta(t) \hat{\sigma}_x$, where $\Theta(t)$ is the nonadiabatic coupling parameter defined as $\Theta(t) = (\Lambda \Omega^R(t) - \Omega^R(t))/\Omega^2(t)$.

Calculated in accordance with the two proposed methods, coherence of two TLSs, formed through the pump and Stokes pulse interaction, demonstrates dramatically different behavior depending on the chirp implementation. The first method gives zero diagonal elements in the interaction Hamiltonian for the resonant TLS and $\pm \delta$ for the off-resonant TLS. Chirp dependence takes place in the coupling term—the effective Rabi frequency—and establishes the selectivity of the excitation. Therefore the dynamics of the system is just a well-known Rabi solution. The coherence density plot of the resonant TLS is depicted in Fig. 2(a) as a function of the peak-effective Rabi frequency, $\Omega^R_{21}$, and dimensionless frequency chirp parameter, $\alpha'/\tau_0^2$, for $\tau_0 = 15[\omega^{-1}]$, where $\omega$ is the unit frequency equal to $\omega_{21}$. We assume that initially only ground states $|1\rangle$ and $|3\rangle$ are equally populated. According to the Rabi solution the coherence oscillates as a function of $\Omega^R_{21}$ independently from $\alpha'/\tau_0^2$. The coherence density plot of the off-resonant TLS is shown in Fig. 2(b). The coherence is zero in the large region of chirp parameters, $\alpha'/\tau_0^2$, for any value of $\Omega^R_{21}$. This is due to the adiabatic dynamics in the TLS that gives zero population transfer to the upper level. In the vicinity of zero chirp, the off-resonant Rabi oscillations of the coherence are observed as a function of $\Omega^R_{21}$. Thus control of coherence is achieved by means of the chirps that provide the conditions for adiabaticity in strong fields.

The roof method induces qualitatively different dynamics in the TLSs exposed to the pump and Stokes laser fields. The adiabatic passage takes place in this case and leads to the maximum coherence in the resonant TLS [Fig. 3(a)] and minimum coherence in the off-resonant TLS [Fig. 3(b)] in a broad range of the peak Rabi frequency. The adiabaticity of the dynamics may be well understood from the consideration of the dressed state picture. The energy of the bare and the dressed states in the field interaction representation is shown as a function of time for the resonant TLS in Fig. 4(a). Bare states come to the resonance at central time $t_0$ and further remain un-
changed. Because the nonadiabatic coupling is negligibly small the system evolution takes place within a single dressed state. Initially, the lower dressed state coincides with the populated bare ground state. As time approaches the central time \( t_0 \), both bare states acquire equal probability amplitudes that remain unchanged, and give maximum final coherence \( \rho_{34} \).

Coherence is more sensitive to the field amplitude in the off-resonant TLS and depends on the sign of the chirp in weak fields. For the positive chirp [Fig. 4(b)], the crossing of the bare states takes place far before \( t_0 \), when the field amplitude is rather weak, and therefore dressed states have small energy separation. At this time the nonadiabatic coupling is strong enough to couple them and to promote population to the upper dressed state, leading to nonzero coherence \( \rho_{34} \). For the negative chirp the crossing does not occur and evolution is essentially adiabatic, giving zero population transfer and zero coherence in the off-resonant system. In strong fields, the dressed states have large energy separation for all times, resulting in negligible nonadiabatic coupling leading to complete (zero) population transfer to the upper level and zero coherence for \( \alpha' > 0 \) (\( \alpha' < 0 \)).

The roof method suggests the robust way to obtain noninvasive image of biological structure. For example, various biological tissue contain molecular groups, having CH vibrations that span from 2800 to 3100 cm\(^{-1}\) and may be selectively excited to provide noninvasive image with high chemical sensitivity. Similar to the multiplex CARS method,\(^{12-14}\) we can, for example, fix the pump central frequency and scan the Stokes frequency to obtain the vibrational spectrum of unknown molecular species. However, for each instantaneous magnitude of the Stokes central frequency, the maximum intensity of the CARS signal and the efficient suppression of the background signal will be provided in our method in contract to the multiplex CARS method.

Recently, the somewhat related idea of using chirped pulses in CARS spectroscopy has been demonstrated experimentally,\(^{11}\) where the two equally chirped pulses were used. Time delay between pulses has been utilized as an effective way to tune two-photon detuning into resonance. That allowed the authors to achieve high spectral resolution by using broadband pulses. One can see from present analysis that imposing temporal delay gives rise to ac Stark shifts. In turn, these time-dependent Stark shifts result in an effective nonlinear avoided crossing and substantial nonadiabatic coupling.\(^{10}\) Optimization of the selective excitation of the vibrational coherence under condition of nonlinear avoided crossing could be a challenge even in the adiabatic limit. Therefore the method\(^{11}\) is sensitive to the pulse parameters, and excitation selectivity is limited because of the nonadiabatic coupling induced by the Stark shifts. In contrast, our methods employ full advantage of adiabatic passage technique and provide a clear and simple way of controlling predetermined vibrational coherence. The robustness of the methods should facilitate experimental implementations. To reach adiabatic regime one can use 100 fs transform-limited pulses at a repetition rate ~1 MHz with averaged beam power of 25 mW similar to those used in Ref 4. Assuming dipole moments to be equal to 1 debye, we estimate \( \Omega_0^2 = 200 \) THz, giving the Landau–Zener parameter to be well in the adiabatic range, \((\Omega_0^2/\alpha) \approx 40\).

In summary, we have proposed two methods based on adiabatic passage and resulting in the desired maximum coherence in the predetermined TLS. Choosing totally overlapped pulses, we removed the ac Stark shifts influence on the final quantum yield. Using two equal chirps in the first scheme provides the Rabi oscillation type of coherence control. The roof method implements constant chirp in the pump (Stokes) pulse and the flipping sign of the chirp in the Stokes (pump) pulse. It provides the adiabatic passage type of coherent control and gives a robust solution for a variety of the chirp. Both methods can be used for noninvasive imaging of biological structure and femtosecond dynamics studies and as an efficient tool for suppression of the background signal in the CARS spectroscopy.

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References