Research paper

Creation of the maximum coherence via adiabatic passage in the four-wave mixing process of coherent anti-Stokes Raman scattering

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HIGHLIGHTS

- A quantum control method for creation of a maximum vibrational coherence is proposed.
- The method implies linearly chirped ultrafast pulses in the four-wave mixing in CARS.
- The probe pulse must be chirped at the same effective rate as pump and Stokes pulse.

ABSTRACT

Coherent anti-Stokes Raman scattering has been broadly used as an efficient method for molecular identification and specification, utilizing nonlinear optics response of a medium based on inherent and unique properties of its compounds. CARS implies the four-wave mixing process with three beams incident on the molecules and the fourth generated in the medium as a nonlinear response. Here we present a novel method for optimizing this response by maximizing the vibrational coherence in the target molecules. We demonstrate that all three incident fields must be chirped subject to quantum control conditions in order to achieve adiabatic passage between four states in the CARS scheme leading to a maximum vibrational coherence.

Introduction. Coherent anti-Stokes Raman scattering (CARS) is a technique used for analyzing molecular compounds of a medium by addressing the inherent molecular properties using propagating beams of electromagnetic radiation. It belongs to the frontiers of nonlinear optics methods having broad applications in bio-imaging, biochemical and environmental analysis [1], and remote detection [2,3]. A principal step in the advancement of modern CARS based techniques is bringing them to the quantum-enabled level aiming at enhanced sensitivity, chemical specificity and spectral resolution. This is envisioned through the use of the cutting edge photonics techniques [4,5] as well as through incorporating quantum control approaches in the design of CARS schemes [6]. It is known that one of the key parameters in the four-wave mixing in CARS is the coherence between a pair of electronic vibrational states - vibronic states - of the target molecule [7,8], the maximum value of which results in enhanced CARS signal. In this paper, a novel quantum control scheme is presented, which implements specific chirping of three incident ultrafast laser pulses in the four-wave mixing process to significantly enhance CARS signal and suppress the background. It is designed to create the maximum vibrational coherence in a predetermined molecular fragment. Chirped pump and probe pulses in combination with the transform-limited broadband Stokes pulse have been previously used to improve spectroscopic resolution in CARS microscopy [9,10]. Here, we explain why it is beneficial to use the probe pulse chirped at the same rate as an effective chirp of the combination of the pump and Stokes pulses. We demonstrate that the probe pulse must be chirped in a predetermined way in order to perform adiabatic passage between vibrational states maximizing vibrational coherence in the target molecules leading to the enhancement of the CARS signal.

Theoretical framework. To investigate CARS process, we introduce a four-level quantum system representing vibronic states of Raman active modes in target molecules interacting with the electromagnetic fields as shown in Fig. 1. The incident radiation fields are the pump $E_p(t)$, the Stokes $E_s(t)$, and the probe $E_{pr}(t)$, having Gaussian envelopes

$$E_p(t) = E_0(1 + \frac{\omega_0^2}{3})e^{-\frac{(\omega_0^2)}{72}}$$

with the peak envelope value $E_0$ at central time $t_c$, the carrier frequencies $\omega_0$, the temporal linear chirp rates $\gamma_i$, and their spectral counterparts $\alpha_i$, $i = p, s, pr$. The pump and the Stokes pulses build up coherence $\rho_{21}$ between vibronic states $|1\rangle$ and $|2\rangle$ via two-photon excitation involving state $|3\rangle$. The probe pulse sends the
Fig. 1. A schematic of the pump, the Stokes, and the probe incident fields interaction with four vibronic states in a molecule modeling the coherent anti-Stokes Raman scattering process (CARS). Here, $\Delta_s$ and $\Delta_{as}$ are the one-photon detunings, and $\delta$ is the two-photon detuning.

The variables $\Omega_i(t)$, $\Delta_s$, $\Delta_{as}$ and $\alpha_s$ used in this Hamiltonian are defined above.

We use the Hamiltonian in Eq. (1) in the time-dependent Schrödinger equation to study the time evolution of the four-level system via coupled differential equations for probability amplitudes $a_i$, $i = 1, 4$, of the total wave function $\Psi(t) = \sum_{i=1}^{N} a_i |i\rangle$, $N = 4$. Then assuming very large one-photon detunings, which are relevant for Raman vibrational spectroscopy with femtosecond pulses, we adiabatically eliminate two excited states by making $a_3 = a_4 = 0$. These procedures led to an effective two-level system described by two coupled differential equations as follows

\begin{align}
\dot{a}_1 &= (\Omega_1(t))a_1 + (i(\Omega_{13}(t)e^{\omega_1(t-t_0)} \Delta + \Omega_{14}(t)e^{\omega_4(t-t_0)} \delta + \Omega_{12}(t)e^{\omega_2(t-t_0)} \omega_3))a_2, \\
\dot{a}_2 &= (i(\Omega_{23}(t)e^{\omega_2(t-t_0)} \Delta + \Omega_{24}(t)e^{\omega_4(t-t_0)} \delta + \Omega_{21}(t)e^{\omega_1(t-t_0)} \omega_3))a_1.
\end{align}

Then, we define $\Omega_{14} + \Omega_{23} = \Omega_1$, and take the chirp rate of the probe pulse to be equal to the difference of the chirps of the pump and Stokes pulses, $\alpha_3 = \alpha_2 - \alpha_1$. This condition for the chirp rate of the probe pulse is the key to obtain the two-level Hamiltonian suitable for adiabatic passage based on Eq. 2. After simple manipulation with equations, we obtain this Hamiltonian in the field interaction representation, which reads

\begin{align}
H &= \hbar \left( \begin{array}{cc}
-\delta + (\alpha_2 - \alpha_1)(t - t_c) & -\Omega_1(t) \\
\Omega_1(t) & \Omega_1(t)
\end{array} \right) \\
&= \hbar \left( \begin{array}{cc}
-\Omega_1(t) & -\Omega_1(t) \\
\delta & \delta + (\alpha_2 - \alpha_1)(t - t_c) + \Omega_1(t) - \Omega_1(t)
\end{array} \right).
\end{align}

If we manipulate with the fields in such a way that the ac Stark shifts become equal, $\Omega_1(t) = \Omega_2(t)$, then they cancel out in the diagonal matrix elements of the Hamiltonian. It means that there will be no light-induced energy shifts of the vibronic states. Then, the adiabatic passage between them can be easily achieved. To this end, the chirp rate of the applied pump, Stokes and probe fields, chosen to satisfy the adiabaticity condition $\alpha_2 - \alpha_1 = \alpha_3$, provides a smooth transfer of the population from the lower to the upper state, bypassing the energy levels from the ground and the excited vibrational states giving the maximum coherence between them, the change in the frequency difference of the pump and Stokes pulses $\omega_3(t) - \omega_1(t)$ has to be stopped as soon as the resonance is reached. This can be done either by turning off the chirping or by reversing the chirp sign of one of the pulses. This is the essence of the control scheme to maximize coherence between vibronic states: for $t < t_c$ of the Gaussian envelope $e^{-\left[(t-t_0)^2\sigma_t^2\right]}$, the pump and the Stokes chirped pulses must have the temporal chirp rates $\alpha_3 = -\alpha_1$ , giving the effective chirp rate equal to $2\alpha_1$, which induces population transfer just at a double rate. The probe pulse must be chirped as well following the condition that its chirp rate $\alpha_3 = \alpha_2 - \alpha_1$. Later at $t = t_c$, the condition for the chirp rates changes to $\alpha_3 = \alpha_1$, giving $\alpha_3 = 0$. This results in freezing further dynamics between two
In the adiabatic regime, the coupling parameter $\Theta$ in Eq. (4) must be much less than the energy difference of the dressed states represented by the diagonal elements of the $H_d$, $\lambda_{12} = \pm \sqrt{\lambda_1^2 + (\delta + \omega_1(t - t_c))^2}$. Then, the population dynamics occurs within a single dressed state adiabatically. The ratio of $\delta$ to $\lambda / |\Theta|$ is known as the Massey parameter $M(t) \{7,13\}$, with $M(t) \approx 1$ indicating the adiabatic regime of interaction. For the proposed control scheme such that for $t < t_c$, $\sigma = -\sigma_c = \sigma_d = \sigma_i$ and for $t > t_c$, $\sigma_i = \sigma_d = \sigma_c = 0$, $\Theta$ behaves essentially differently in the resonant and the detuned case, shown in Fig. 4(a,b) by green curves. In the case when $\delta = 0$, $\Theta = 0$ is in the second half of the scheme when $t > t_c$. However in the same time interval $\Theta \neq 0$ when $\delta \neq 0$. These observations follow from the expression for $\Theta$ in the Eq. (4). Thus, the exact adiabatic condition is created for the resonant case only. For the first part of the control scheme when $t \leq t_c$, $\sigma = -\sigma_c = \sigma_d = \sigma_i$ and for $t > t_c$, $\sigma_i = \sigma_d = \sigma_c = 0$, $\Theta$ behaves essentially differently in the resonant and the detuned case, shown in Fig. 4(a,b) by solid and dashed lines. This leads to a weak coupling as
The maximum coherence $\rho_{12}$ in the four-level system is present for a broad range of the spectral chirp and the peak Rabi frequency analogously to the adiabatic solution shown in Fig. 3. However, the two-photon detuning imposed in the system breaks adiabatic nature of the population dynamics to the excited state resulting in a creation of a superposition state with various probability amplitudes of the ground and the excited states. A small value or zero vibrational coherence $\rho_{12}$ desired to achieve selectivity of close Raman active vibrational modes is obtained for only a low Rabi frequency range, $\Omega_R < 1/|\omega_{12}|$, shown in Fig. 5. This figure is essentially different from the adiabatic approximation solution shown in Fig. 3. This difference in the quantum yield of the detuned four-level system is due to essentially non-adiabatic processes of four-wave mixing under the condition of the absence of the two-photon resonance in CARS.

In summary, a quantum control method for the creation of the maximum vibrational coherence of Raman active modes is proposed based on a semiclassical description of the four-wave mixing process in coherent anti-Stokes Raman scattering. The method makes use of correlated chirping of three incident fields, the pump, the Stokes and the probe. The Wigner plots presented in Fig. (2) demonstrate the regularity of linear chirping of these fields. According to the control scheme, the Gaussian envelopes of the pulses must overlap; the pump and the Stokes frequencies must be equally chirped in the opposite directions to arrive into the two-photon resonance with the target vibration at the peak field intensity. After that, the chirping must be switched off or forwarded in the same direction to preserve the resonance. Importantly, in order for the adiabatic passage to occur in the four-wave mixing process, the probe pulse must be also chirped with the chirp rate same as the effective chirp rate of the pump and Stokes pulses. When the applied laser fields do not provide the two-photon resonance, the maximum coherence may be also created by carefully tuning the chirp rate so that the ratio of the two-photon detuning to the chirp rate would be less than the pulse duration, $\delta/|\omega_{12}| < \Omega_R$.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References


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