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Abstract

A chirped-pulse quantum control scheme applicable to coherent anti-Stokes Raman scattering spectroscopy, named as C-CARS, is presented aimed at maximizing the vibrational coherence in molecules. It implies chirping of three incoming pulses in the four-wave mixing process of CARS, the pump, the Stokes and the probe, to fulfill the conditions of adiabatic passage. The scheme is derived in the framework of rotating wave approximation and adiabatic elimination of excited state manifold simplifying the four-level model system into a ‘super-effective’ two level system. We demonstrate that the selectivity of excitation of vibrational degrees of freedom can be controlled by carefully choosing the spectral chirp rate of the pulses. The robustness, spectral selectivity and adiabatic nature of this method are advantageous for improving the existing methods of CARS spectroscopy for sensing, imaging and detection.

1. Introduction

Discovery of Raman scattering in the 1920s, which coincided with major developments in quantum mechanics followed by the advancements in laser technology since 1960s, paved new ways for understanding the chemical compounds and structure of molecular systems. Modern Raman spectroscopy, that uses spontaneous Raman scattering at their core, is characterized by a sufficiently low intensity signal, which is incoherent and isotropic. Being one of the leading non-linear optics techniques, coherent anti-Stokes Raman scattering (CARS) spectroscopy makes use of stimulated Raman process resulting in a directional anti-Stokes signal of intensity many orders of magnitude higher than an isotropic spontaneous Raman signal. Because CARS addresses inherent properties of matter, such as vibrational degrees of freedom, it belongs to one of the well-suited and frequently used spectroscopic methods for imaging, sensing and detection without labeling or staining [1–5]. High sensitivity, high resolution and noninversiveness of CARS have been exploited for imaging of chemical and biological samples [6–16], standoff detection [17–20] and combustion thermometry [21, 22]. Recent developments in the applications of CARS in biology include imaging and classification of cancer cells that help early diagnosis [23–25], and rapid and label-free detection of the SARS-CoV-2 pathogens [26]. CARS has also been used recently for observing real-time vibrations of chemical bonds within molecules [27], direct imaging of molecular symmetry [28], graphene imaging [29], and femtosecond spectroscopy [30, 31].

In this work, we present a theoretical description of a general and robust technique of creating maximal-coherence superpositions of quantum states that can be used to optimize the signals in CARS-based applications.

In the four-wave mixing process of CARS, the pump and Stokes pulses having frequencies ω_p and ω_s respectively excite the molecular vibrations to create a coherent superposition which a probe pulse having frequency ω_{pr} then interacts with and generates an anti-Stokes signal. The output signal is blue-shifted and has a frequency of $\omega_{as} = \omega_p - \omega_s + \omega_{pr}$. It is about six orders of magnitude higher in amplitude compared to the spontaneous process and its direction is determined by the phase-matching condition [32–35]. However, one of the main challenges in CARS has been the presence of non-resonant background appearing in the spectra which limits the image contrast and chemical sensitivity. Another coherent, multi-photon Raman process called stimulated Raman scattering (SRS) has an advantage over CARS because of the absence of nonresonant background [36]. In SRS, the frequency difference of pump and Stokes ($\omega_p - \omega_s$) is matched with the vibrational frequency of the molecule to excite the vibrational transitions. However, the detection of compounds using SRS requires a scheme that is more complicated than CARS as the input and output signals in SRS have the same frequencies. In CARS, the signal can be easily extracted by an optical filter due to the anti-Stokes component having a frequency blue-shifted compared to the incoming pulses [37]. To overcome the limitations of CARS, there have been tremendous efforts on removing the background from nonresonant processes and enhancing the signal amplitude [38–47].

In the framework of Maxwell's equations, the amplitude of the anti-Stokes field is related to coherence between the electronic vibrational states of the target molecules. Thus, maximizing coherence is the key to optimizing the intensity of anti-Stokes signal [20, 48]. Chirped pulses have been often used in CARS-based imaging techniques as demonstrated in, e.g. the high spectroscopic resolution experiments [49, 50] and theoretical works on maximizing coherence [51–53]. A method for selective excitation in a multimode system using a transform-limited pump pulse and a linearly chirped Stokes pulse in stimulated Raman scattering is proposed in [54]. The effects of chirped pump and Stokes pulses on the nonadiabatic coupling between vibrational modes are discussed in [55]. A 'roof' method of chirping to maximize coherence is introduced in [56] based on adiabatic passage in an effective two-level system. In this method, the Stokes pulse is linearly chirped at the same rate as that of the pump pulse during the first half of the pulse duration and is oppositely chirped afterwards.

Here, we discuss a chirping scheme in CARS, in which all the incoming pulses are chirped to achieve the maximum coherence and suppress the background via adiabatic passage. The selectivity, robustness and adiabatic nature of this control scheme make it a viable candidate for improving the current methods for imaging, sensing and detection using CARS. We examined in detail the impact of the two-photon detuning on the mechanism of adiabatic passage, and analyzed the controllability of the generation of the maximum coherence depending on the magnitude of the two-photon detuning.

2. Theoretical framework

The variables used in our theory are summarized below.

$E_q(t)$, $q = p, s, pr$	The pump, Stokes and probe fields
$\Omega_{q_0}(t)$, $q = p, s, pr$	The Rabi frequencies of the pump, Stokes and probe fields
α'_q , α_q , $q = p, s, pr$	Spectral and temporal chirp rates of the pump, Stokes and probe fields
τ_0 , τ	Transform-limited pulse duration and chirp-dependent pulse duration
Ω_3 , $\Omega_{3(0)}$	The effective and peak effective Rabi frequencies
$E_i(t)$, $\lambda_i(t)$, $i = 1, 2$	The bare and dressed state energies
$\dot{\theta}(t)$	The non-adiabatic coupling parameter

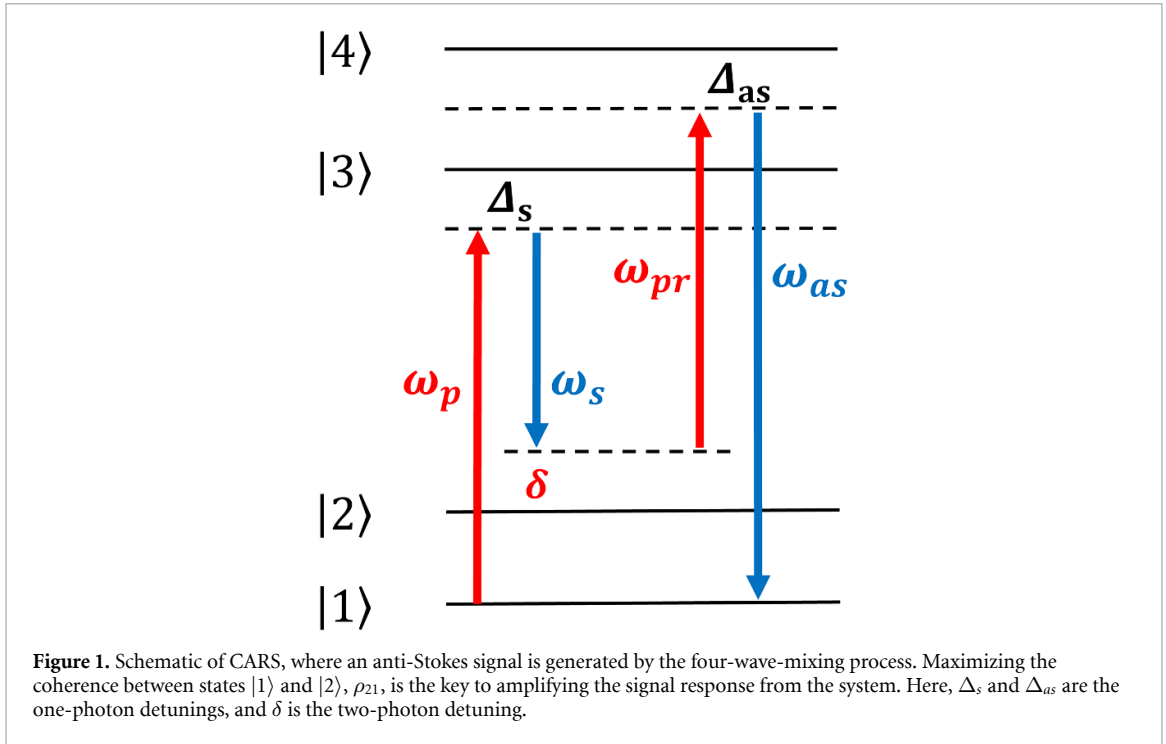
A schematic diagram of the CARS process is given in figure 1. We consider the chirped pump, Stokes and probe pulses with temporal chirp rates α_q , $q = p, s, pr$

$$E_q(t) = E_{q_0}(t) \cos \left[\omega_q(t - t_c) + \frac{\alpha_q}{2}(t - t_c)^2 \right], \quad (1)$$

and having Gaussian envelopes

$$E_{q_0}(t) = \frac{E_{q_0}}{\left(1 + \frac{\alpha_q'^2}{\tau_0^4}\right)^{1/4}} e^{-\frac{(t-t_c)^2}{2\tau^2}}, \quad (2)$$

where τ_0 is the transform-limited pulse duration, τ is the chirp-dependent pulse duration given by $\tau = \tau_0[1 + \alpha_q'^2/\tau_0^4]^{1/2}$ and α_q' is the spectral chirp rate, which is related to the temporal chirp rate as $\alpha_q = \alpha_q'/\tau_0^4(1 + \alpha_q'^2/\tau_0^4)$. The interaction Hamiltonian of the four-level system, after defining the one photon detunings, $\Delta_s = \omega_p - \omega_{31}$ and $\Delta_{as} = \omega_{as} - \omega_{41}$, reads:



$$\mathbf{H}_{\text{int}}(t) = \frac{\hbar}{2} \left[\Omega_p(t) \exp(i\Delta_s t - \frac{i}{2}\alpha_p t^2) |1\rangle\langle 3| + \Omega_s(t) \exp(i\Delta_s t - \frac{i}{2}\alpha_s t^2) |2\rangle\langle 3| \right. \\ \left. + \Omega_{pr}(t) \exp(i\Delta_{as} t - \frac{i}{2}\alpha_{pr} t^2) |2\rangle\langle 4| + \Omega_{as}(t) \exp(i\Delta_{as} t) |1\rangle\langle 4| + h.c. \right], \quad (3)$$

where $\Omega_{q0} = -\mu_{ij}E_{q0}/\hbar$. This Hamiltonian can be simplified to a two-level ‘super-effective’ Hamiltonian by eliminating states $|3\rangle$ and $|4\rangle$ adiabatically under the assumption of large one-photon detunings. The dynamics of the four-level system interacting with the fields in equation (1) is described by the Liouville-von Neumann equation $i\hbar\dot{\rho}(t) = [\mathbf{H}_{\text{int}}(t), \rho(t)]$. We define the two-photon detuning as $\delta = \omega_p - \omega_s - \omega_{21} = \omega_{as} - \omega_{pr} - \omega_{21}$, make the transformations in the interaction frame $\rho_{11} = \tilde{\rho}_{11}$, $\rho_{12} = \tilde{\rho}_{12} e^{-i(\omega_1 - \omega_2)(t-t_c)}$, $\rho_{13} = \tilde{\rho}_{13} e^{i\omega_p(t-t_c)}$, $\rho_{14} = \tilde{\rho}_{14} e^{i\omega_{as}(t-t_c)}$, $\rho_{22} = \tilde{\rho}_{22}$, $\rho_{23} = \tilde{\rho}_{23} e^{-i(\omega_2 - \omega_1 - \omega_p)(t-t_c)}$, $\rho_{24} = \tilde{\rho}_{24} e^{-i(\omega_2 - \omega_1 - \omega_{as})(t-t_c)}$, $\rho_{33} = \tilde{\rho}_{33}$, $\rho_{34} = \tilde{\rho}_{34} e^{-i(\omega_p - \omega_{as})(t-t_c)}$, $\rho_{44} = \tilde{\rho}_{44}$ and obtain a system of differential equations for the density matrix elements:

$$\begin{aligned} i\dot{\rho}_{11} &= \frac{1}{2}\Omega_{p0}(t)e^{\frac{i}{2}\alpha_p(t-t_c)^2}\rho_{31} + \frac{1}{2}\Omega_{as0}(t)\rho_{41} - c.c., \\ i\dot{\rho}_{22} &= \frac{1}{2}\Omega_{s0}(t)e^{-i\delta(t-t_c) + \frac{i}{2}\alpha_s(t-t_c)^2}\rho_{32} + \frac{1}{2}\Omega_{pr0}(t)e^{-i\delta(t-t_c) + \frac{i}{2}\alpha_{pr}(t-t_c)^2}\rho_{42} - c.c., \\ i\dot{\rho}_{33} &= \frac{1}{2}\Omega_{p0}^*(t)e^{-\frac{i}{2}\alpha_p(t-t_c)^2}\rho_{13} + \frac{1}{2}\Omega_{s0}^*(t)e^{i\delta(t-t_c) - \frac{i}{2}\alpha_s(t-t_c)^2}\rho_{23} - c.c., \\ i\dot{\rho}_{44} &= \frac{1}{2}\Omega_{as0}^*(t)\rho_{14} + \frac{1}{2}\Omega_{pr0}^*(t)e^{i\delta(t-t_c) - \frac{i}{2}\alpha_s(t-t_c)^2}\rho_{24} - c.c., \\ i\dot{\rho}_{12} &= \frac{1}{2}\Omega_{p0}(t)e^{\frac{i}{2}\alpha_p(t-t_c)^2}\rho_{32} + \frac{1}{2}\Omega_{as0}(t)\rho_{42} - \frac{1}{2}\Omega_{s0}^*(t)e^{i\delta(t-t_c) - \frac{i}{2}\alpha_s(t-t_c)^2}\rho_{13} \\ &\quad - \frac{1}{2}\Omega_{pr0}^*(t)e^{i\delta(t-t_c) - \frac{i}{2}\alpha_{pr}(t-t_c)^2}\rho_{14}, \\ i\dot{\rho}_{13} &= \Delta_s\rho_{13} + \frac{1}{2}\Omega_{p0}(t)e^{\frac{i}{2}\alpha_p(t-t_c)^2}\rho_{33} + \frac{1}{2}\Omega_{as0}(t)\rho_{43} - \frac{1}{2}\Omega_{p0}(t)e^{\frac{i}{2}\alpha_p(t-t_c)^2}\rho_{11} \\ &\quad - \frac{1}{2}\Omega_{s0}(t)e^{-i\delta(t-t_c) + \frac{i}{2}\alpha_s(t-t_c)^2}\rho_{12}, \\ i\dot{\rho}_{14} &= \Delta_{as}\rho_{14} + \frac{1}{2}\Omega_{p0}(t)e^{\frac{i}{2}\alpha_p(t-t_c)^2}\rho_{34} + \frac{1}{2}\Omega_{as0}(t)\rho_{44} - \frac{1}{2}\Omega_{a0}(t)\rho_{11} \\ &\quad - \frac{1}{2}\Omega_{pr0}(t)e^{-i\delta(t-t_c) + \frac{i}{2}\alpha_{pr}(t-t_c)^2}\rho_{12}, \\ i\dot{\rho}_{23} &= \Delta_s\rho_{23} + \frac{1}{2}\Omega_{s0}(t)e^{-i\delta(t-t_c) + \frac{i}{2}\alpha_s(t-t_c)^2}\rho_{33} + \frac{1}{2}\Omega_{pr0}(t)e^{-i\delta(t-t_c) + \frac{i}{2}\alpha_{pr}(t-t_c)^2}\rho_{43} \\ &\quad - \frac{1}{2}\Omega_{p0}(t)e^{\frac{i}{2}\alpha_p(t-t_c)^2}\rho_{21} - \frac{1}{2}\Omega_{s0}(t)e^{-i\delta(t-t_c) - \frac{i}{2}\alpha_s(t-t_c)^2}\rho_{22}, \\ i\dot{\rho}_{24} &= \Delta_{as}\rho_{24} + \frac{1}{2}\Omega_{s0}(t)e^{-i\delta(t-t_c) + \frac{i}{2}\alpha_s(t-t_c)^2}\rho_{34} + \frac{1}{2}\Omega_{pr0}(t)e^{-i\delta(t-t_c) + \frac{i}{2}\alpha_{pr}(t-t_c)^2}\rho_{44} \\ &\quad - \frac{1}{2}\Omega_{as0}(t)\rho_{21} - \frac{1}{2}\Omega_{pr0}(t)e^{-i\delta(t-t_c) + \frac{i}{2}\alpha_{pr}(t-t_c)^2}\rho_{22}, \\ i\dot{\rho}_{34} &= (\Delta_{as} - \Delta_s)\rho_{34} + \frac{1}{2}\Omega_{p0}^*(t)e^{-\frac{i}{2}\alpha_p(t-t_c)^2}\rho_{14} + \frac{1}{2}\Omega_{s0}^*(t)e^{i\delta(t-t_c) - \frac{i}{2}\alpha_s(t-t_c)^2}\rho_{24} \\ &\quad - \frac{1}{2}\Omega_{as0}(t)\rho_{31} - \frac{1}{2}\Omega_{pr0}(t)e^{-i\delta(t-t_c) + \frac{i}{2}\alpha_{pr}(t-t_c)^2}\rho_{32}. \end{aligned} \quad (4)$$

As the next step, the condition for chirping of the probe pulse such that $\alpha_{pr} = \alpha_s - \alpha_p$ is imposed, which is required to equate the exponentials. The above set of equations is then modified by applying the adiabatic elimination, $\dot{\rho}_{33} = \dot{\rho}_{44} = \dot{\rho}_{34} = 0$ and substituting for $\rho_{14}, \rho_{24}, \rho_{23}$ and ρ_{24} in the equations of $\dot{\rho}_{11}, \dot{\rho}_{22}$ and $\dot{\rho}_{12}$. After defining the new Rabi frequencies:

$$\Omega_1(t) = \frac{|\Omega_{p0}(t)|^2}{4\Delta_s} + \frac{|\Omega_{as0}(t)|^2}{4\Delta_{as}}, \quad \Omega_2(t) = \frac{|\Omega_{s0}(t)|^2}{4\Delta_s} + \frac{|\Omega_{pr0}(t)|^2}{4\Delta_{as}}, \quad (5)$$

and

$$\Omega_3(t) = \frac{\Omega_{p0}(t)\Omega_{s0}^*(t)}{4\Delta_s} + \frac{\Omega_{pr0}^*(t)\Omega_{as0}(t)}{4\Delta_{as}}, \quad (6)$$

the density matrix equations cast into a set of equations describing the dynamics in the super-effective two-level system:

$$\begin{aligned} i\dot{\rho}_{11} &= \Omega_3(t)e^{i\delta(t-t_c) - \frac{i}{2}(\alpha_s - \alpha_p)(t-t_c)^2} \rho_{21} - c.c., \\ i\dot{\rho}_{22} &= \Omega_3^*(t)e^{-i\delta(t-t_c) + \frac{i}{2}(\alpha_s - \alpha_p)(t-t_c)^2} \rho_{12} - c.c., \\ i\dot{\rho}_{12} &= [\Omega_1(t) - \Omega_2(t)]\rho_{12} + \Omega_3(t)e^{i\delta(t-t_c) - \frac{i}{2}(\alpha_s - \alpha_p)(t-t_c)^2} (\rho_{22} - \rho_{11}). \end{aligned} \quad (7)$$

Further transformations of the density matrix elements such as $\rho_{11} = \tilde{\rho}_{11}$, $\rho_{12} = \tilde{\rho}_{12}e^{i\delta(t-t_c) - \frac{i}{2}(\alpha_s - \alpha_p)(t-t_c)^2}$, and $\rho_{22} = \tilde{\rho}_{22}$, and shifting the diagonal elements lead to the following super-effective Hamiltonian for the two-level system in the field-interaction representation:

$$\mathbf{H}_{se}(t) = \frac{\hbar}{2} \begin{pmatrix} \delta - (\alpha_s - \alpha_p)(t-t_c) + \Omega_1(t) - \Omega_2(t) & 2\Omega_3(t) \\ 2\Omega_3^*(t) & -\delta + (\alpha_s - \alpha_p)(t-t_c) - \Omega_1(t) + \Omega_2(t) \end{pmatrix}. \quad (8)$$

The amplitudes of incoming fields are manipulated to make the AC Stark shifts equal, $\Omega_1(t) = \Omega_2(t)$, and cancel out. This condition is satisfied by taking $\Omega_{s0} = \Omega_{pr0} = \Omega_{p0}/\sqrt{2}$, considering the fact that the anti-Stokes signal is absent in the beginning of the process, $\Omega_{as0} = 0$. The effective Rabi frequency $\Omega_3(t)$ reads:

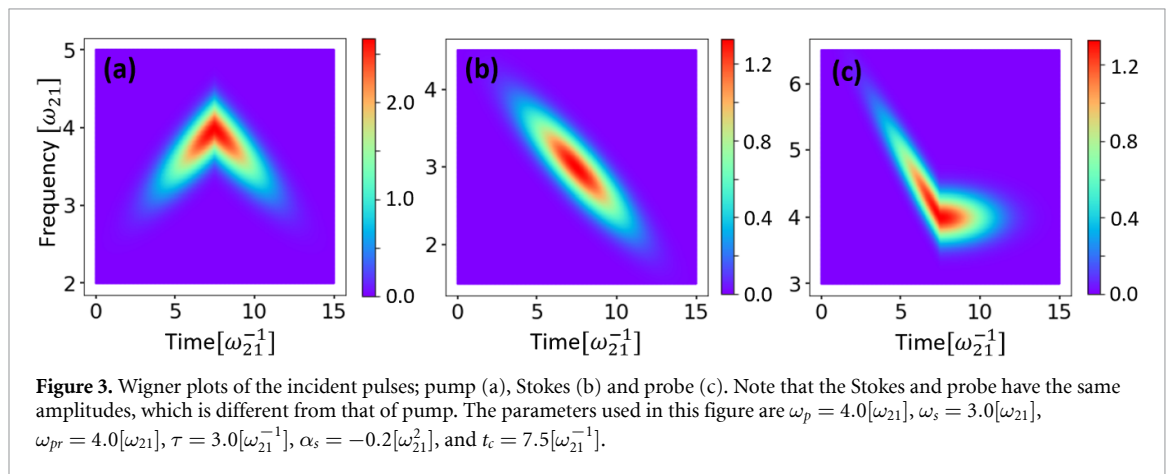
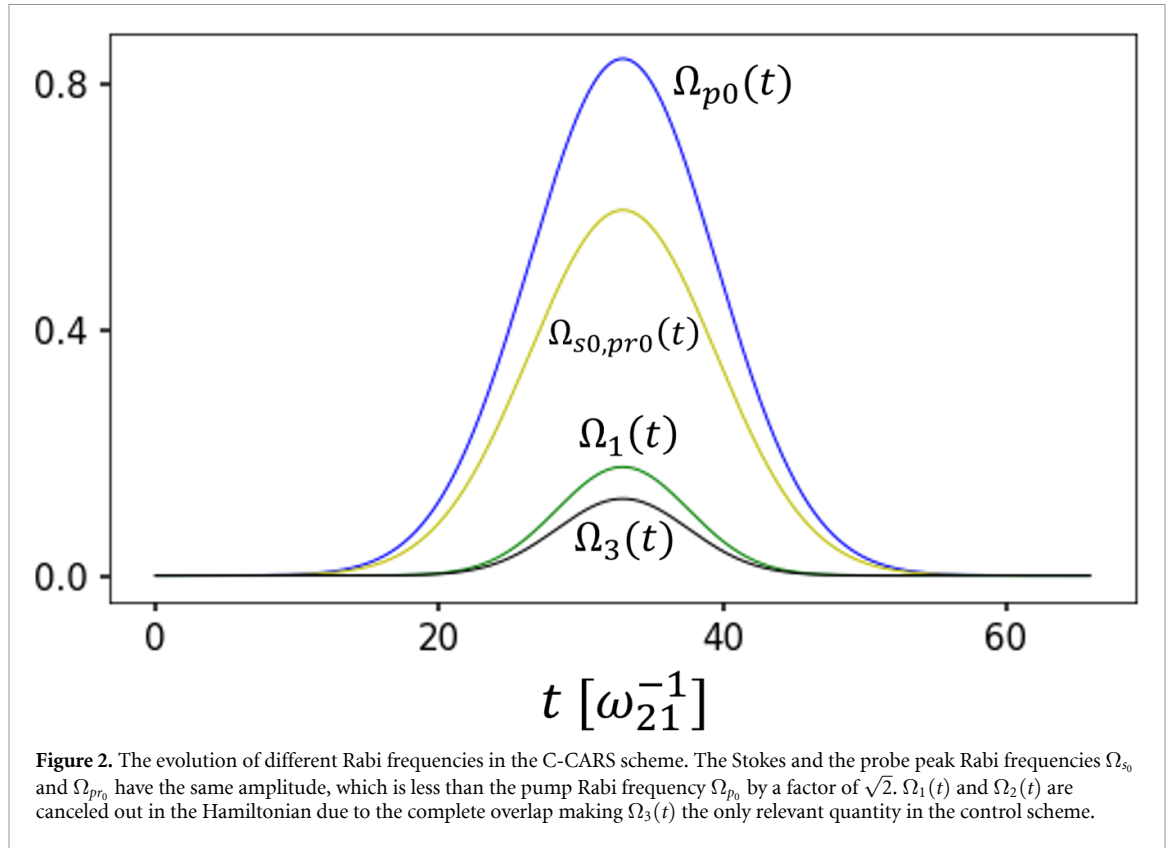
$$\Omega_3(t) = \frac{\Omega_{3(0)}}{\left[\left(1 + \frac{\alpha_p'^2}{\tau_0^2}\right) \left(1 + \frac{\alpha_s'^2}{\tau_0^2}\right) \right]^{1/4}} e^{-\frac{(t-t_c)^2}{\tau^2}}. \quad (9)$$

The peak effective Rabi frequency is given by $\Omega_{3(0)} = \Omega_{p0}^2/(4\sqrt{2}\Delta)$. It is reduced when chirping is applied to the pump and Stokes pulses with the spectral rates α_p' and α_s' respectively. The relative amplitudes of all the Rabi frequencies related to three incoming pulses applied simultaneously are shown in figure 2. In this paper, all the frequency parameters are defined in the units of the frequency ω_{21} and time parameters are defined in the units of ω_{21}^{-1} .

During the interaction, at time $t = t_c + \delta/(\alpha_s - \alpha_p)$, the diagonal elements become equal to zero creating a coherent superposition state having equal populations of states $|1\rangle$ and $|2\rangle$ and, therefore, a maximum value of coherence ρ_{21} . This time can be determined for a fixed value of two-photon detuning, δ . At the two-photon resonance, the system reaches this maximum coherence at the central time t_c . It is further preserved in the state of the maximum coherence by imposing the condition of $(\alpha_s - \alpha_p) = 0$ in the second half of the pulse duration. A smooth realization of this scheme is possible by choosing the temporal chirp rates of the pump and Stokes pulses to be the same in magnitude and opposite in sign before the central time and equal in sign after that, along with the condition imposed for the chirp rate of probe pulse such that $\alpha_{pr} = \alpha_s - \alpha_p$, which was deduced to arrive into the Hamiltonian in equation (8). This chirping scheme, namely C-CARS, is summarized as follows: $\alpha_p = -\alpha_s$ and $\alpha_{pr} = 2\alpha_s$ for $t \leq t_c$, and $\alpha_p = \alpha_s$ and $\alpha_{pr} = 0$ for $t > t_c$. The Wigner-Ville distributions of the incident pulses are found to be

$$W_{E_q}(t, \omega) = \frac{\tau\sqrt{\pi}}{2} E_{q0}^2 e^{-(t-t_c)^2/\tau^2} \left[e^{-\tau^2[\omega - \omega_q - \alpha_q(t-t_c)]^2} + e^{-\tau^2[\omega + \omega_q + \alpha_q(t-t_c)]^2} \right]. \quad (10)$$

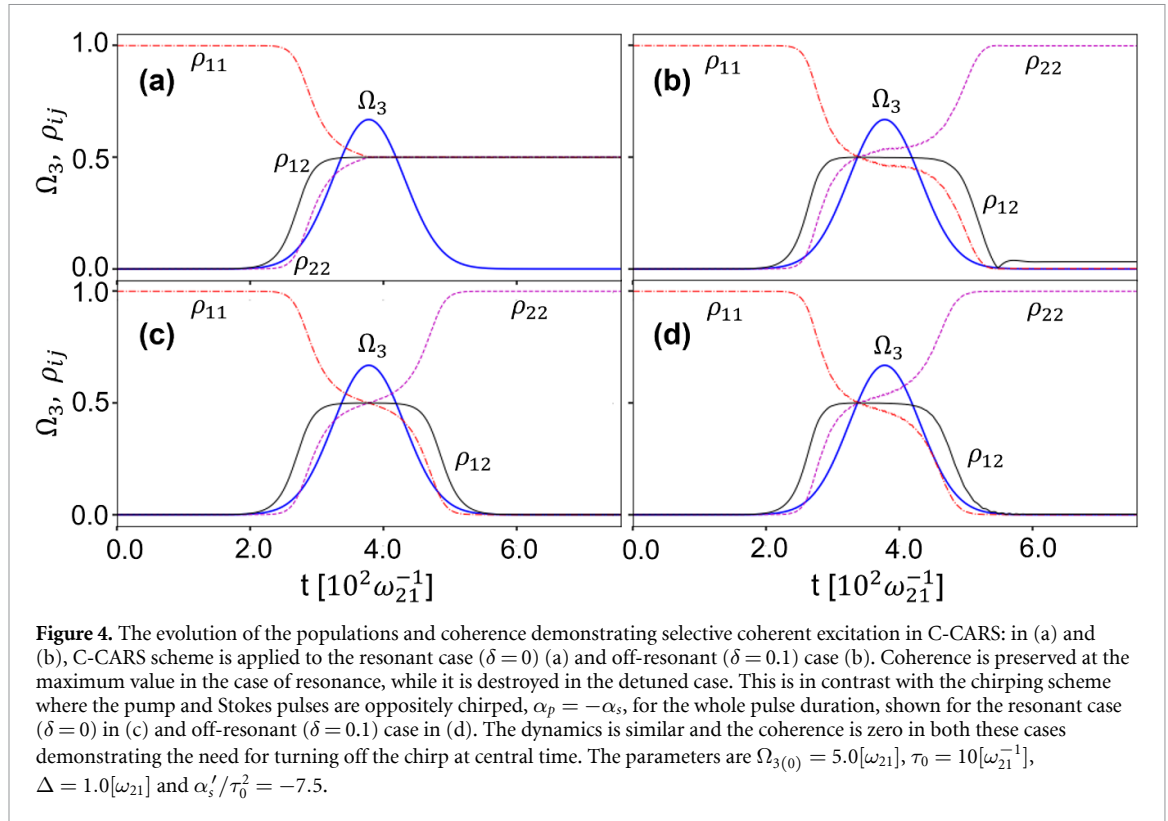
The positive solutions of these equations are depicted in figure 3. The ‘turning off’ of chirping in the second half of the pulse duration is the essence of this scheme, resulting in a selective excitation of the molecules and suppressing any off-resonant background. If α_p is not reversed, the coherence is not preserved leading to population inversion between states $|1\rangle$ and $|2\rangle$.



3. Numerical results

3.1. Super-effective two-level system

To demonstrate the selective excitation of molecules using C-CARS, the time evolution of populations ρ_{11} and ρ_{22} and coherence ρ_{12} is presented in figure 4 for four different cases described below. The C-CARS control scheme is applied for the resonant ($\delta = 0$) and off-resonant ($\delta \neq 0$) case respectively in figures 4(a) and (b). The coherence reaches maximum at the central time in the resonant case, and is preserved till the end of dynamics owing to the zero net chirp rate attained by reversing the sign of α_p . On the contrary, the time of the maximum coherence does not coincide with the central time in the non-resonant case, which results in a population transfer to the upper state and zero coherence. To emphasize the significance of reversing the sign of α_p in C-CARS control scheme we compare it with the scheme when the pump and Stokes are oppositely chirped for the whole pulse duration, $\alpha_p = -\alpha_s$. For this case the dynamics of the system is plotted in figures 4(c) and (d) for $\delta = 0$ and $\delta = 0.1$ respectively. In (c), even though the system reaches a perfect coherence at $t = t_c$, it decreases to zero because population is further adiabatically transferred to state $|2\rangle$. Coherence in (d) behaves similar to that of (b).



3.2. Exact four-level system

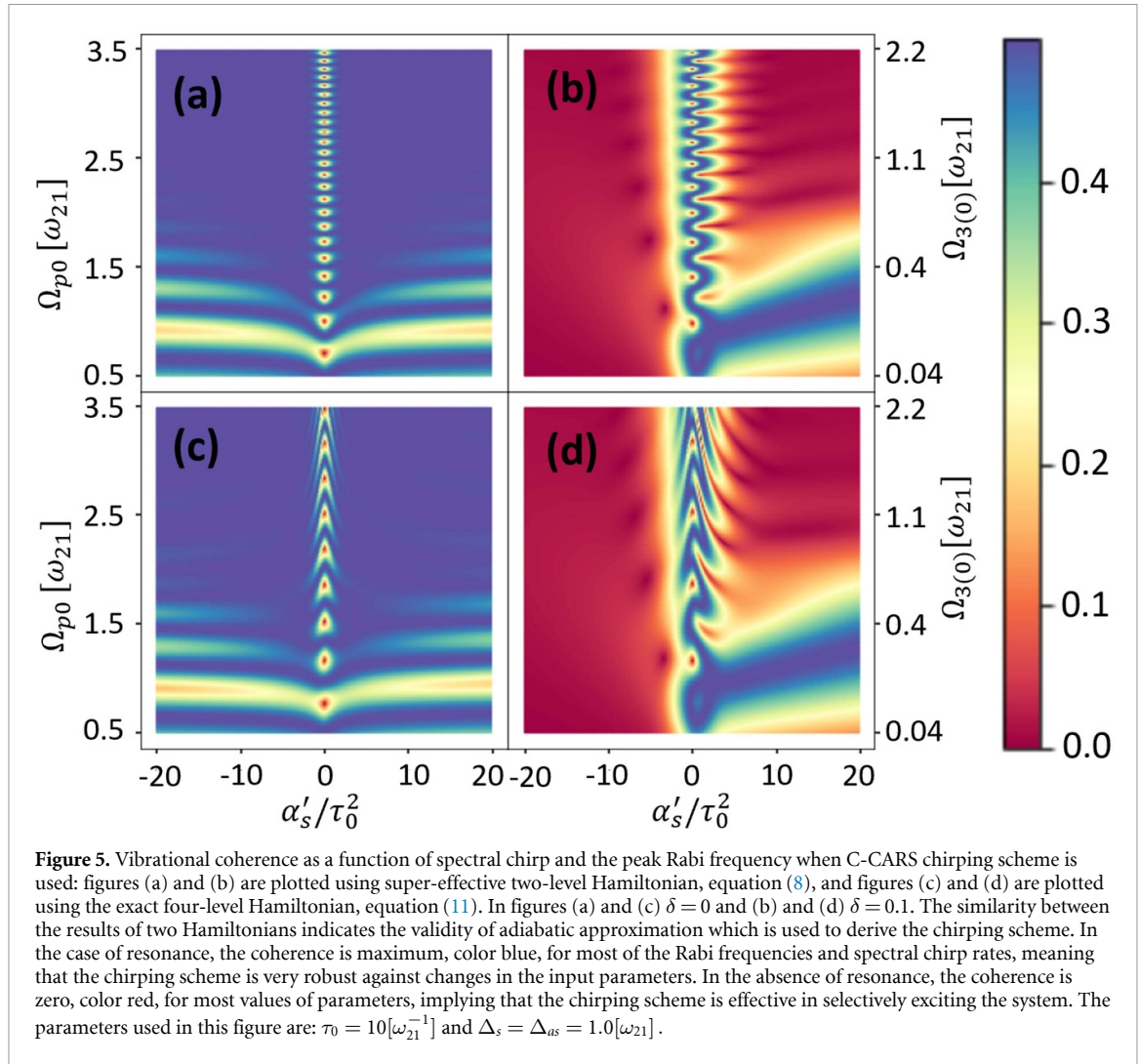
The validity of adiabatic approximation, which led to the derivation of the super-effective Hamiltonian, can be tested by comparing the results of the super-effective two-level system with the exact solution using the Liouville von Neumann equation for the four-level system. To this end, the condition for chirping of the probe pulse $\alpha_{pr} = \alpha_s - \alpha_p$ is applied to the field-interaction Hamiltonian of the four level system:

$$\mathbf{H}_{ex}(t) = \frac{\hbar}{2} \begin{pmatrix} 2\alpha_p(t-t_c) & 0 & \Omega_{p_0}(t) & \Omega_{as_0}(t) \\ 0 & 2[\alpha_s(t-t_c) - \delta] & \Omega_{s_0}(t) & \Omega_{pr_0}(t) \\ \Omega_{p_0}(t) & \Omega_{s_0}(t) & -2\Delta_s & 0 \\ \Omega_{as_0}(t) & \Omega_{pr_0}(t) & 0 & 2[\alpha_p(t-t_c) - \Delta_{as}] \end{pmatrix}. \quad (11)$$

Figure 5 shows the contour-plot of vibrational coherence ρ_{12} at the end of dynamics as a function of the peak Rabi frequency $\Omega_{3(0)}(t)$ and dimensionless spectral chirp rate α'_s/τ_0^2 . Figures (a) and (b) represent the $\delta = 0$ and $\delta = 0.1$ cases, respectively, of the super-effective two level system, and (c) and (d) represent the same cases obtained by the exact solution of the four-level system using the same set of parameters. In all the figures, the one-photon detuning is $\Delta_s = \Delta_{as} = \Delta = 1.0$. Around the region where $\alpha'_s/\tau_0^2 = 0$, adiabatic passage breaks down and the approximate solution disagrees with the exact solution. As the magnitude of spectral chirp rate increases, the adiabatic approximation coincides with the exact one because the Landau-Zener parameter is well in the adiabatic range, $\Omega_{3(0)}^2/|\alpha_p| \gg 1$. In the resonant cases (a) and (c), the coherence is at the maximum, (blue color), for the most part, indicating the robustness of C-CARS chirping scheme in preparing the system in a coherent superposition. In the off-resonant case, zero coherence, (red color), is observed for the most part, which is in a stark contrast with the resonant case, revealing the selective nature of coherent excitation using the C-CARS control scheme.

3.3. Analysis of dressed states and adiabatic passage

When the electromagnetic field interacts with any quantum system, the eigenstates undergo a rearrangement resulting in a set of quantum states that are said to be ‘dressed’ by the light. These states are called dressed states and the initial states that were ‘untouched’ by the light are called bare states [57]. The robustness of the C-CARS control scheme stems from the adiabatic nature of the light–matter interaction, which can be demonstrated by analyzing the evolution of dressed state energies in the super-effective two-level system. To this end, the density matrix $\rho(t)$ is transformed to a dressed density matrix using the transformation $\rho_d(t) = \mathbf{T}(t)\rho(t)\mathbf{T}^\dagger(t)$, where $\mathbf{T}(t)$ is an orthogonal matrix given by:



$$\mathbf{T}(t) = \begin{pmatrix} \cos \theta(t) & -\sin \theta(t) \\ \sin \theta(t) & \cos \theta(t) \end{pmatrix}. \quad (12)$$

The Liouville-von Neumann equation for the dressed density matrix is derived from the bare state density matrix equation and reads

$$i\hbar \frac{d}{dt} \rho(t) = i\hbar \frac{d}{dt} (\mathbf{T}^\dagger(t) \rho_d(t) \mathbf{T}(t)) = [\mathbf{H}_{se}(t), \mathbf{T}^\dagger(t) \rho_d(t) \mathbf{T}(t)]. \quad (13)$$

After expanding this equation and using $\dot{\mathbf{T}}(t) \mathbf{T}^\dagger(t) = -\mathbf{T}(t) \dot{\mathbf{T}}^\dagger(t)$, we arrive at

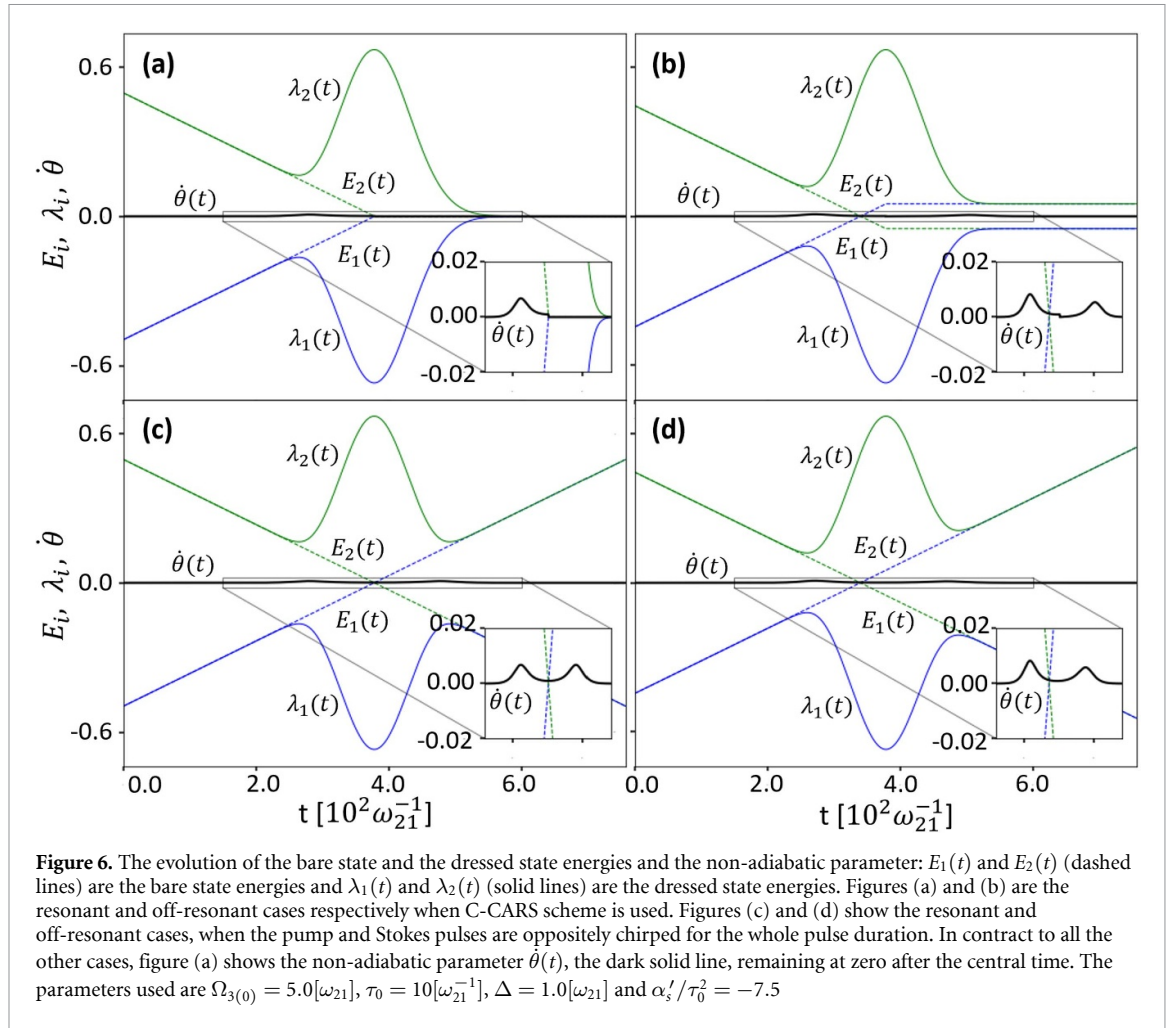
$$i\hbar \dot{\rho}_d(t) = [\mathbf{T}(t) \mathbf{H}_{se}(t) \mathbf{T}^\dagger(t) - i\hbar \mathbf{T}(t) \dot{\mathbf{T}}^\dagger(t), \rho_d(t)] = [\mathbf{H}_d(t), \rho_d(t)], \quad (14)$$

where $\mathbf{T}(t) \mathbf{H}_{se}(t) \mathbf{T}^\dagger(t)$ is a diagonal matrix. For adiabatic passage to occur, the dressed state Hamiltonian $\mathbf{H}_d(t)$ should give the dressed state energies separation greater than $\mathbf{T}(t) \dot{\mathbf{T}}^\dagger(t)$ to avoid coupling between dressed states [57–59]. The dressed state Hamiltonian is found to be

$$\mathbf{H}_d(t) = \frac{\hbar}{2} \begin{pmatrix} -\sqrt{(-\delta + \alpha_{pr}(t-t_c))^2 + (2\Omega_3(t))^2} & -i\dot{\theta}(t) \\ i\dot{\theta}(t) & \sqrt{(-\delta + \alpha_{pr}(t-t_c))^2 + (2\Omega_3(t))^2} \end{pmatrix}, \quad (15)$$

where the non-adiabatic parameter $\dot{\theta}(t)$, which comes from the matrix $\mathbf{T}(t) \dot{\mathbf{T}}^\dagger(t)$, is given by

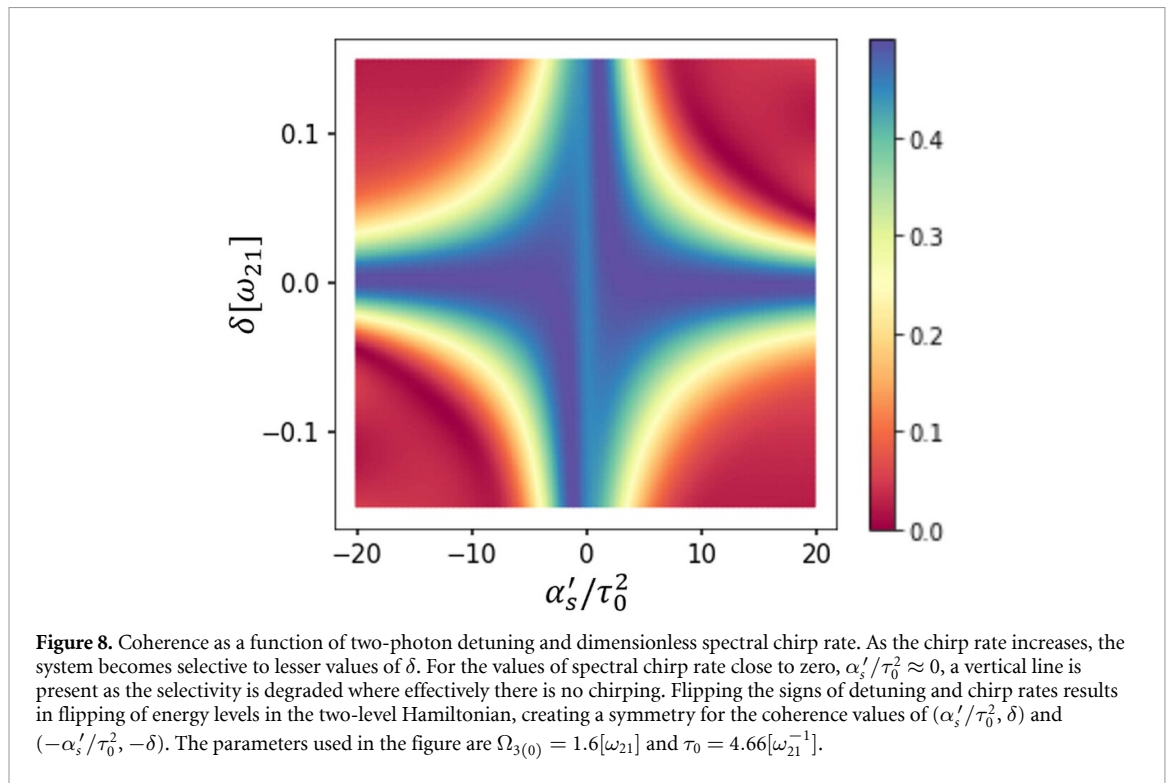
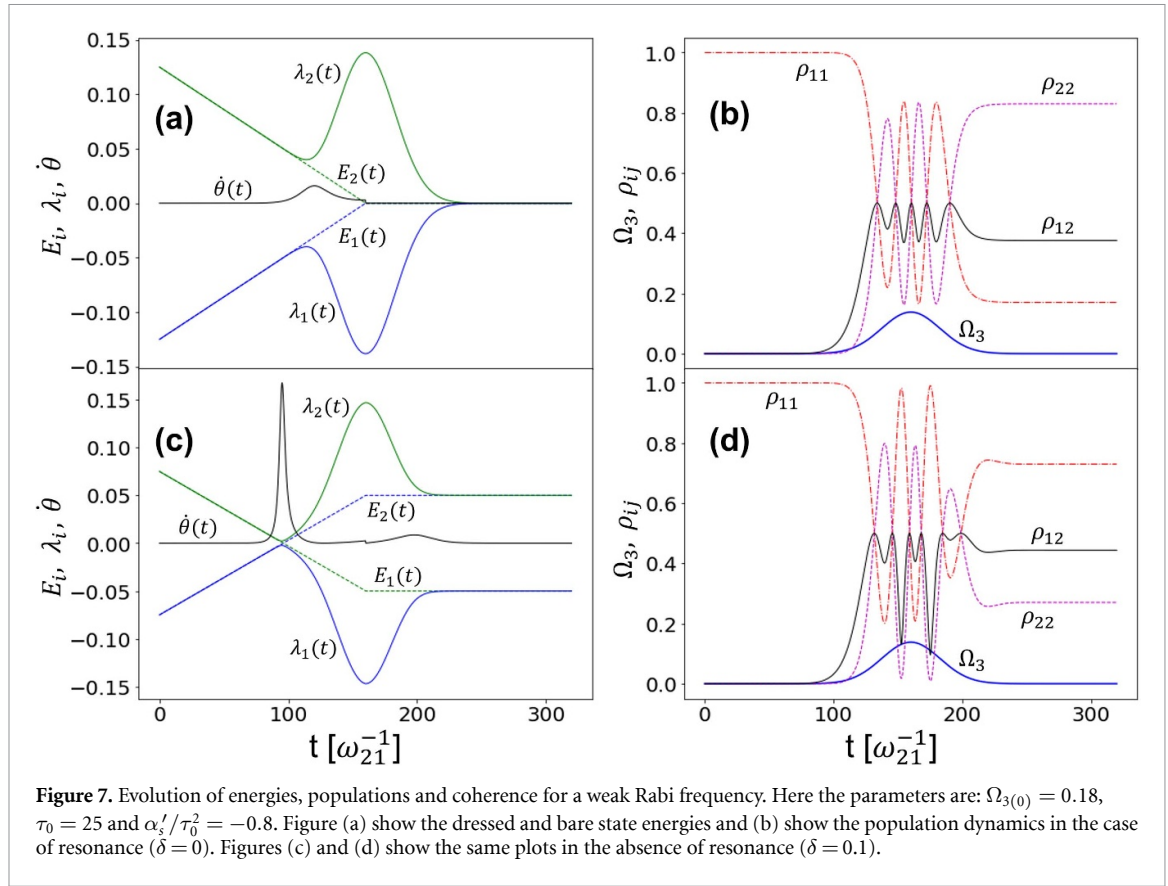
$$\dot{\theta}(t) = \frac{(-\delta + \alpha_{pr}(t-t_c))\dot{\Omega}_3(t) - 2\Omega_3(t)\alpha_{pr}}{(-\delta + \alpha_{pr}(t-t_c))^2 + 4\Omega_3(t)^2}. \quad (16)$$



Analyzing the equation for $\dot{\theta}(t)$ reveals the selective nature of adiabatic passage in the case of resonance. In the resonant case, the C-CARS chirping scheme ensures the process to be adiabatic in the second half of the pulse by keeping the non-adiabatic coupling parameter $\dot{\theta}(t)$ at zero during this time period. But adiabaticity is not guaranteed in the off-resonant case due to the non-zero factor δ in the equation. This is demonstrated in figure 6, where the bare state energies are given by $E_1(t) = H_{se_{11}}(t)$ and $E_2(t) = H_{se_{22}}(t)$ and the dressed state energies are given by $\lambda_1(t) = H_{d_{11}}(t)$ and $\lambda_2(t) = H_{d_{22}}(t)$. The figures (a) and (b) represent resonant ($\delta = 0$) and off-resonant ($\delta \neq 0$) cases when C-CARS control scheme is used. Clearly, the $\dot{\theta}(t)$, dark solid line, has non-zero values in the second half when the system is detuned. The perfectly adiabatic nature of interaction in figure 6(a) corresponds to the maximum coherence in figure 4(a) and the non-adiabatic nature in figure 6(b) corresponds to the population inversion in figure 4(b). The parameters used in figure 6 are the same as that used in figure 4. In figures 6(c) and (d), the same quantities are plotted for $\delta = 0$ and $\delta \neq 0$ respectively for the scheme when the pump and Stokes are chirped oppositely for the whole pulse duration. The process is perfectly adiabatic only in the second half of (a) since a smooth realization of $\dot{\theta}(t) = 0$ was made possible owing to the developed C-CARS control scheme. The dynamics is much different and the selective excitation does not happen when the effective Rabi frequency, $\Omega_3(t)$, is not strong enough as shown in figure 7 where $\Omega_3(0) = 0.18$, $\alpha'_s/\tau_0^2 = -0.8$ and $\tau_0 = 25[\omega_{21}^{-1}]$. In both (a), $\delta = 0$ and (b), $\delta = 0.1$ cases, the non-adiabatic coupling parameter is much greater compared to figure 6. In the off-resonant case (d), the coherence oscillates much stronger compared to the resonant case (c) showing the absence of adiabatic passage.

3.4. The dependence of state selectivity on the chirp rate

To investigate how the value of two-photon detuning and spectral chirp rate are related to the selectivity in C-CARS method, the end-of-pulse vibrational coherence is plotted as a function of δ and α'_s/τ_0^2 in figure 8. At the two-photon resonance, coherence is at the maximum for all the values of chirp rate. If the detuning is large, a small chirp rate can selectively excite the system while for smaller values of detuning, the chirp rate needs to be increased in order to suppress excitation of close vibrational frequencies and the non-resonant



background. This provides a way to control the selectivity by adjusting the values of chirp rate. The plot is symmetric across the diagonal lines as flipping the signs of both α_s and δ will not change the dynamics; it would only result in switching of the diagonal elements in Hamiltonian (8). The plot is also nearly symmetric across the $\delta = 0$ line, indicating that the selectivity holds for both red and blue detunings. When the chirp rate is close to zero, the pulses are transform-limited, implying that the maximum coherence and selectivity

provided by the chirping scheme is absent in this region. This explains the vertical line present at the 0 of abscissa.

4. Conclusion

We presented a control scheme to prepare the ground electronic-vibrational states in the four-level system of CARS in a maximally coherent superposition. We derived the Hamiltonian for a ‘super-effective’ two-level system employing the adiabatic approximation. This two-level Hamiltonian is used to derive the conditions for adiabatic passage necessary for the implementation of the selective excitation of spectrally close vibrations. The amplitudes of the Stokes and probe pulses have to be equal and should be $1/\sqrt{2}$ times that of the pump pulse. The pump pulse should be chirped at the same rate as the Stokes pulse before the central time and at the opposite rate after that. The probe pulse has to be chirped at a rate equal the difference between the chirp rates of the Stokes and the pump pulses for the whole pulse duration. The solutions of Liouville-von Neumann equation show that vibrational coherence is preserved until the end of dynamics in the resonant case due to the adiabatic nature of the interaction. At two-photon resonance, vibrational coherence is at the maximum, 0.5, for a wide range of field parameters revealing the robustness of the method. Conversely, coherence is almost zero in the two-photon off-resonant case for most of the peak Rabi frequency values and the chirp parameters. A comparison of coherence in the four-level and the two-level systems reveals that the adiabatic approximation is valid except for when the chirp rate is almost equal to zero. A dressed-state analysis reveals the details of the mechanism of adiabatic passage using C-CARS control scheme.

Notably, the proposed chirping scheme for maximum coherence is not exclusive to CARS; it can be applied to other coherent Raman techniques such as SRS. However, the amplitudes of the interacting fields must satisfy the condition that the AC Stark shifts cancel out in equation (8). In SRS, for example, equal amplitudes for the pump and the Stokes fields will satisfy this condition.

The presented C-CARS method can find important applications in sensing and imaging of molecular species because it creates a maximally coherent superposition of vibrational states in coherent anti-Stokes Raman scattering allowing the system to emit an optimized signal suitable for detection. The robustness of this method against changes in Rabi frequencies and chirp rates is helpful in experiments. The method permits suppressing the background species and excite only the desired ones; the resolution needed for this distinction can be controlled by the chirp parameter.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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