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Suppression of coherent scattering by coherent population trapping on molecular vibrational levels

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Abstract: Raman scattering has been studied in molecular media. The role of rotational levels has been investigated. It is shown that the molecular vibrational coherence strongly depends on the effect of coherent population trapping for rotational levels. The obtained results are important for application of Raman spectroscopy to molecular detection for engineering, chemical, and biological applications.

Keywords: coherent anti-Stokes Raman scattering, four wave mixing

1 Introduction

Raman spectroscopy [1] is one among many powerful techniques that has been widely used in engineering, chemical, and biological applications. The sensitivity of coherent Raman scattering can be improved by applying femtosecond adaptive technique to excite maximal vibrational coherence to perform real time identification of bacterial spores [2–6], and this technique has a potential to identify biomolecules as well. It was theoretically shown that chirped laser pulses, even a single linearly chirped laser pulse, can be used for an efficient manipulation of atomic population in ultracold Rb atoms [7, 8].

There are several methods of spectroscopy that analyze energy, one of which is Raman Spectroscopy. This method is used to observe vibrational, rotational, and other low-frequency modes in a given system. It is used in several fields of study, such as identifying molecules in chemistry, measuring temperature in solid-state physics, and non-invasive monitoring of muscle tissue, among other things. The Raman effect takes place when light enters a molecule and interacts with its electrons, exciting them to a higher state. The molecules then relax to a level different than the original state, emitting a photon with a different frequency than what originally entered the system. Specifically, Coherent Anti-Stokes Raman Spectroscopy (CARS) is a process which enhances the Raman signal for greater resolution and allows us to better identify the vibrational frequency.

It is the quantum coherent effects that are able to enhance the Raman scattering. Quantum coherence effects, such as coherent population trapping (CPT) [9] and electromagnetically induced transparency (EIT) [10–13], have been the focus of broad research activity for the last two decades, as they drastically change optical properties of media. For example, for EIT in CW and pulsed regimes [11–15], absorption practically vanishes. The medium with excited quantum coherence, phaseonium [10], can be used to make a ultra-dispersive prism [16] that has several orders of magnitude higher angular spectral dispersion. The bending of light has been also demonstrated using transverse dragging effect [17]. The corresponding steep dispersion results in the ultra-slow or fast propagation of light pulses, [18–22] which can produce huge optical delays [22] and can be used for drastic modification of the phase-matching conditions for Brillouin scattering [23], four-wave mixing [24], controllable switching between bunching and anti-bunching [25], storage and retrieval of pulses [27], freezing of a light pulse [28], and ultrahigh enhancement in absolute and relative rotation sensing using fast and slow light [29].

In this paper, we show how the application of pulse shaping techniques to stimulated Raman scattering can enhance its sensitivity, and extend the technique to media with strong light scattering. Recently, it was shown that the optical 0π-pulses [30] under the condition of electromagnetically induced transparency (EIT) [31, 32] are very sensitive to resonant interaction, and have advantages to be used in Raman spectroscopy. Moreover, the femtosecond 0π-pulses were successfully used for detection of two-photon absorption in non-radiative media. [33]
2 Model

Now, let us consider a $\Lambda$-type dielectric medium. A strong field of frequency $\omega_{p}$ is the coupling field and a weak field of frequency $\omega_{d}$ is the probe field. The probe and coupling fields can be represented as

$$E_{p,d} = E_{p,d}^{0} \exp[i k_{p,d} z - \omega_{p,d} t]$$  \hspace{1cm} (1)

where $E_{p,d}^{0}$ is the amplitudes of fields at $z = 0$. The interaction Hamiltonian in the rotating wave approximation can be written as

$$H = \hbar \left[ \Omega_{p} e^{i \delta_{p} t} |b\rangle \langle a| + \Omega_{d} e^{i \delta_{d} t} |c\rangle \langle a| + a \text{d} j \right]$$

where $|b\rangle \langle a|$ and $|c\rangle \langle a|$ are the atomic projection operators, $\Omega_{p} = \varphi_{ab} E_{p}/\hbar$ and $\Omega_{d} = \varphi_{ac} E_{d}/\hbar$ are the probe and coupling Rabi frequencies, $\Delta_{p} = \omega_{ab} - \omega_{p}$ and $\Delta_{d} = \omega_{ab} - \omega_{d}$ are detunings for probe and coupling laser beams, and $\varphi_{ab}$ and $\varphi_{ac}$ are the dipole momenta of the transitions. The coupling field is resonant with the $|a\rangle \rightarrow |c\rangle$ transition ($\Delta_{d} = 0$).

The density matrix equations are given by

$$\frac{\partial \sigma}{\partial t} = \frac{i}{\hbar} [\sigma, H] - \frac{1}{2} (\Gamma' \sigma + \sigma \Gamma)$$  \hspace{1cm} (2)

where $\Gamma$ is the matrix of relaxation rates for all components of the density matrix $\sigma$.

The set of density matrix equations can be solved in terms of $n_{ab} = n_{a} - n_{b} = \rho_{aa} - \rho_{bb}$. The steady-state solution is given by

$$\Gamma_{ab} \rho_{ab} = i \Omega n_{ab}$$  \hspace{1cm} (3)

$$\gamma_{a} n_{a} = i \Omega (\rho_{ab} - \rho_{ba}^{*}) = -2 \Omega \text{Im} (\rho_{ab})$$  \hspace{1cm} (4)

$$\gamma_{a} n_{a} = 2 |\Omega|^{2} \text{Re} \left( \frac{1}{\Gamma_{ab}} \right) (n_{a} - n_{b})$$  \hspace{1cm} (5)

$$n_{a} = \frac{\mathcal{R}}{\mathcal{R} + \gamma_{a}} n_{b}$$  \hspace{1cm} (6)

$$\rho_{ab} = i \frac{n_{ab}}{\Gamma_{ab}} \Omega$$  \hspace{1cm} (7)

where $\mathcal{R} = 2 |\Omega|^{2} \text{Re} \left( \frac{1}{\Gamma_{ab}} \right)$.

Similarly, for three-level atoms, the set of density matrix equations can be solved in terms of $n_{ab} = n_{a} - n_{b} = \rho_{aa} - \rho_{bb}$, $n_{ca} = n_{c} - n_{a} = \rho_{aa} - \rho_{cc}$, and the steady-state equations are given by

$$\Gamma_{ab} \rho_{ab} = i \Omega n_{ab} - i \Omega_{d} \rho_{cb}$$  \hspace{1cm} (8)

$$\Gamma_{ca} \rho_{ca} = \Gamma_{ab} n_{ca} + i \Omega \rho_{cb}$$  \hspace{1cm} (9)

$$\Gamma_{cb} \rho_{cb} = i \Omega \rho_{ca} - i \Omega_{d} \rho_{ab}$$  \hspace{1cm} (10)

$$\rho_{ab} = i \Omega \frac{n_{ab}}{\Gamma_{ab}} - i \Omega_{d} \frac{\rho_{cb}}{\Gamma_{cb}}$$  \hspace{1cm} (11)

$$\rho_{ca} = \Omega \frac{n_{ca}}{\Gamma_{ca}} + i \Omega \frac{\rho_{cb}}{\Gamma_{cb}}$$  \hspace{1cm} (12)

$$\rho_{cb} = \frac{\Omega \frac{n_{ab}}{\Gamma_{ab}} - \frac{n_{ca}}{\Gamma_{ca}}}{\Gamma_{cb} + |\Omega|^{2} \frac{1}{\Gamma_{ab}} + |\Omega|^{2} \frac{1}{\Gamma_{ca}}}$$  \hspace{1cm} (13)

and

$$\dot{n}_{b} = \gamma_{b} n_{a} + i \Omega (\rho_{ba} - \rho_{ab}) = 0$$  \hspace{1cm} (14)

$$\dot{n}_{c} = \gamma_{c} n_{a} + i \Omega (\rho_{ca} - \rho_{ac}) = 0$$  \hspace{1cm} (15)

Figure 1: (Left) Molecular levels: excited electronic states, vibrational and rotational levels. (Center) Three-level model can be used for describing vibrational excitation. (Right) To take into account effects of rotational and vibrational excitation simultaneously, the model should include four levels.
Then, the steady-state solution is given by

\[ A_{ab} = 2|\Omega|^2 \Re \left( \frac{\Gamma_{cb}\Gamma_{ca} + |\Omega|^2}{\Gamma_{cb} + |\Omega|^2 + |\Omega|^2} \right) \]  

(17)

\[ A_{ca} = 2|\Omega|^2 \Re \left( \frac{|\Omega|^2}{\Gamma_{ab}\Gamma_{ca}} \right) \]  

(18)

\[ B_{ca} = 2|\Omega|^2 \Re \left( \frac{\Gamma_{cb}\Gamma_{ab} + |\Omega|^2}{\Gamma_{ab}\Gamma_{ca}} \right) \]  

(19)

\[ B_{ab} = 2|\Omega|^2 \Re \left( \frac{|\Omega|^2}{\Gamma_{ab}\Gamma_{ca}} \right) \]  

(20)

The analytical solution is very complicated to be analyzed easily. Thus, for the four-level atoms, we believe that the analytical solutions are too complicated to be analyzed, and we prefer to perform simulations to study the four-level model.

The temporal and spatial evolution of fields is determined by the propagation equations

\[
\frac{\partial \Omega_p}{\partial z} = -i\eta \sigma_{ab} \quad \frac{\partial \Omega}{\partial z} = i\eta \sigma_{ca},
\]

(21)

where \( \eta = \frac{3\lambda^3 N}{16\pi^2} \), \( \Gamma_{ca} = \gamma_{ca} - i(\omega_{ac} - \omega_d) \), \( \Gamma_{cb} = \gamma_{cb} + i(\omega_{bc} - \omega_p + \omega_d) \), and \( \Omega_{ab} = \gamma_{ab} + i(\omega_{ab} - \omega_p) \). The Doppler broadening is important to take into account by averaging the index of refraction over velocity distribution [34].

The parameters, which are close to molecular gases and Rb vapors, are chosen for simulations: \( \Delta_p = 0 \), \( \Omega_d = 3.5 \times 10^5 \text{ s}^{-1} \), \( \gamma_r = 2 \times 10^7 \text{ s}^{-1} \), \( \gamma_{ab} = \gamma_r + \Delta_p \), \( \gamma_{cb} = 3 \times 10^3 \text{ s}^{-1} \), the density of Rb atoms is \( 10^{13} \text{ cm}^{-3} \). Simulations perform without Doppler broadening (\( \Delta_p = 0 \)) as well as with taking the Doppler broadening into account (\( \Delta_p = 0.991 \times 10^9 \text{ s}^{-1} \)).

### 3 Role of CPT for excitation of rotation and vibration coherence

Usually, with weak laser field, the three-level atom is a good approximation. But, in order to achieve higher sensitivity in detection, a stronger laser field is needed. This, however, has its limitations, because once the Rabi frequency becomes comparable with rotational frequency, new coherent effects start influence the Raman processes.
namely, once the dark state with rotational levels is formed, the excitation of vibrational coherence start decreasing.

Indeed, we have performed simulations for three-level atoms and four-level atoms. The results are shown in Figure 2. For three-level atoms, we show efficient excitation of vibrational coherence as shown in Figure 2(A). Also, one can see excitation of rotational coherence in Figure 2(B). Once, for four-level atoms, the excitation of rotational coherence prevents the excitation of vibrational coherence (see in Figure 2(C)).

Similar behavior can be observed for more sophisticated effects such as STIRAP and CHIRAP where by adjusting properly the pulse shapes, we can demonstrate very efficient population transfer from ground state to excited vibrational state as it is shown in Figure 3. Also, we have shown that with increasing laser fields, both the STIRAP and CHIRAP processes of adiabatic population transfer are strongly modified as shown in Figure 4.

**Figure 3:** Adiabatic passage population transfer achieved with STIRAP and CHIRPED pulses

**Figure 4:** The effect of STIRAP modified by the presence of the rotational levels.

### 4 Conclusions

In this paper, we consider a model that takes into account molecular rotational motion. We study the role of the rotational levels on electromagnetically induced transparency, on coherent population trapping. Strong modification of coherent effects have been found due to formation of the rotational dark states. We have been using the parameters for relaxation rates in the molecular and atomic systems from experimental works [16, 19, 22], we have demonstrated that the studied effects have strong influence on the propagation of optical beams and on population transfer.

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