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To cite this article: R de J León-Montiel and Juan P Torres 2012 New J. Phys. 14 013018

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New Journal of Physics 14 (2012) 013018 (11pp)
Received 29 June 2011
Published 12 January 2012
Online at http://www.njp.org/
doi:10.1088/1367-2630/14/1/013018

Abstract. We show that the sensitivity and robustness of a label-free optical imaging technique based on stimulated Raman scattering (SRS) can be enhanced by using resonant optical transitions in a Raman adiabatic passage scheme. Our approach is based on the consideration that any enhancement of the flow of energy between two light beams involved in the SRS process is related to an increase in atomic population transfer between the energy levels of interest. One can thus profit from techniques developed in quantum optics to maximize such atomic population transfer for enhancing the sensitivity and robustness of optical imaging techniques.

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1. Introduction

Label-free optical imaging with molecular specificity addresses the question of detecting the presence of a particular chemical substance embedded among many others without the use of any auxiliary alien substances, such as fluorophores. What is needed is an efficient and highly selective technique that samples only specific vibrations of the atoms of interest, and this can be provided by resonance Raman spectroscopy [1].

Recently, a new optical label-free imaging technique based on stimulated Raman scattering (SRS) has been demonstrated [2]. When the difference frequency between two pulses (pump and Stokes) match the atomic frequency transition between two energy levels, the pump beam is depleted (stimulated Raman loss) and the Stokes beam is amplified (stimulated Raman gain (SRG)). Using a high-frequency phase-sensitive detection technique, Freudiger et al managed to measure pump losses $\Delta E_p/E_p \sim 10^{-7}$, where $E_p$ is the initial energy of the pump pulse and $\Delta E_p$ is the loss experienced by the pump pulse, corresponding to a concentration of some 50 $\mu$M (molecule number density of $10^{16}$ cm$^{-3}$) for retinol.

Here we put forward a technique which combines this optical imaging scheme with a quantum optics process that enhances the transfer of atomic populations. In principle, it allows us to go beyond the current level of sensitivity, i.e. lowering the minimum concentration of molecules that can be detected, while at the same time enhancing the robustness of the system against variations in the laser parameters: intensities, detunings, pulse shapes, pulse widths and pulse delays. A higher sensitivity could also be employed for detecting a larger number of molecules with a shorter acquisition time, which is of importance in applications such as in-vivo optical imaging, that require primarily higher speed.

The first step to enhance the sensitivity is to use pump and Stokes pulses that are resonant with auxiliary atomic transitions. If we designate by $|1\rangle$ and $|3\rangle$ the two levels of interest involved in the SRS process, one can make use of a third level $|2\rangle$, so that the pump beam is resonant with the $|1\rangle \rightarrow |2\rangle$ transition and the Stokes beam with the $|3\rangle \rightarrow |2\rangle$ transition. The use of light beams resonant with atomic interactions can greatly enhance the generation efficiency of nonlinear signals [3], allowing the observation of lower concentrations of molecules.

The rapid development of sources with increasingly tuning ranges has overcome any previous limitations that might have impeded the development of resonant Raman spectroscopy [1]. Nowadays, laser sources in combination with optical parametric oscillators can deliver unprecedented tuning range from UV to far infrared [4].

Secondly, in SRS, we measure the gain (loss) in the number of photons of the Stokes (pump) pulses after the interaction. Since these changes are associated with changes in the atomic populations of the two energy levels of interest, $|1\rangle$ and $|3\rangle$, any technique that maximizes the transfer of atomic population from $|1\rangle$ to $|3\rangle$ should also maximize the gain (loss) of the Stokes (pump) pulses.

In quantum optics, several techniques to control the dynamics of atomic populations have been developed over the years [5]. For instance, $\pi$-pulse techniques (Rabi oscillations) can be used [6], but they require precise control of the pulse characteristics (pulse duration and/or intensity) in real experiments. SRS involving adiabatic passage (STIRAP) is an alternative technique that allows precise control of the population transfer between specific quantum states [7, 8]. Indeed, transfer efficiencies close to 100% have been demonstrated [9]. Since

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4 The Spectra Physics Inspire ultrafast optical parametric oscillator (OPO) family provides a tuning range from 345 nm to 2.5 $\mu$m gap-free with no change of intracavity optics or crystals.
STIRAP is an adiabatic process, it is robust against small variations of the main laser parameters [10], which makes STIRAP a realistic and robust way for efficient population transfer between multiple states.

Although STIRAP has been considered extensively as a means for the efficient control of atomic populations in quantum optics applications, the key enabling role that it can play for enhancing the sensitivity and robustness of label-free optical imaging systems based on SRS is not fully appreciated. Previous work has been restricted to considering the enhancement of the generated nonlinear signal produced by using non-overlapping pump and Stokes pulses over overlapping ones [11].

Two important aspects have not been considered yet. Firstly, since real experiments show small fluctuations in the laser parameters, one should look for a scheme where the enhancement of the sensitivity is not compromised when these are taken into account. Secondly, since molecules might be present in extended areas, SRS-based optical imaging cannot neglect in this case the spatiotemporal evolution of the pump and Stokes pulses that propagate and interact with the molecules.

In this paper, our main interest is to show that the use of non-overlapping pump and Stokes pulses in a STIRAP configuration can help increase the sensitivity, while at the same time enhance the robustness of the system. Notwithstanding, it is worth remarking that, because of the high intensity of the pulses involved in the STIRAP process, the spatial resolution of the system might be affected due to intensity-induced local variations in the refractive index of the sample. Indeed, in a similar process, namely electromagnetically induced transparency, changes in the refractive index of the sample are induced by the transverse intensity variation across the coupling beam waist in the region of the focus, giving rise to undesirable effects such as defocusing [12, 13]. However, in our analysis, we consider that pulses propagate very short distances (hundreds of nm) within the sample, which are much shorter than the Rayleigh range of the beams and where such effects are expected to be weak.

2. Basic equations

Let us consider a system of identical atoms, ions or molecules with concentration $N$, where each atom can be described as a three-state system in a $\Lambda$ configuration (figure 1). Each of the states is non-degenerate and there is no direct coupling between states $|1\rangle$ and $|3\rangle$. The atoms interact with two light pulses. The pump pulse, with central frequency $\omega_p$, couples the state $|1\rangle$ with the intermediate state $|2\rangle$, and the Stokes pulse, with central frequency $\omega_s$, couples the state
corresponding Rabi frequencies, as those that describe the evolution of the pump and Stokes fields can be written, in terms of the sample. If we make use of the slowly varying envelope approximation, the wave equations requires considering the changes of the pump and Stokes pulses while they propagate through the medium is homogeneous (the atoms in the ensemble are identical and uniformly distributed) and that the atomic motion is negligible. Equations (2), (4a) and (4b) constitute the mathematical description of the system under study.

\[
\hat{H}(t) = \frac{\hbar}{2} \begin{bmatrix}
0 & \Omega_p^a(t) & 0 \\
\Omega_p(t) & 2\Delta_p & \Omega_s(t) \\
0 & \Omega_s^a(t) & 2(\Delta_p - \Delta_s)
\end{bmatrix},
\]

where \(\Omega_p(t) = -\mu_{12} \cdot \mathbf{E}_p/\hbar\) and \(\Omega_s(t) = -\mu_{32} \cdot \mathbf{E}_s/\hbar\) are the Rabi frequencies of the pump and Stokes pulses, respectively, and \(\mu_{12}\) and \(\mu_{32}\) are the dipole moments for each transition. The detunings of the pump and Stokes laser frequencies can be written as \(\Delta_p = \omega_{21} - \omega_p\) and \(\Delta_s = \omega_{23} - \omega_s\).

Following Ivanov et al [15], the effects of spontaneous decay from level \(|2\rangle\) to levels \(|1\rangle\) and \(|3\rangle\) may be modeled via the Liouville equation

\[
\frac{i\hbar}{\hbar} \frac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}] + \hat{D},
\]

where \(\hat{\rho}\) is the density matrix, and \(\hat{D}\) is a term that is introduced phenomenologically and describes the spontaneous emission within the three-level system,

\[
\hat{D} = \begin{bmatrix}
-2\Gamma_1\rho_{22} & (\Gamma_1 + \Gamma_3)\rho_{12} & 0 \\
(\Gamma_1 + \Gamma_3)\rho_{21} & 2(\Gamma_1 + \Gamma_3)\rho_{22} & (\Gamma_1 + \Gamma_3)\rho_{23} \\
0 & (\Gamma_1 + \Gamma_3)\rho_{32} & -2\Gamma_3\rho_{22}
\end{bmatrix}.
\]

\(\Gamma_1\) and \(\Gamma_3\) are the decay rates from state \(|2\rangle\) to states \(|1\rangle\) and \(|3\rangle\), respectively.

As stated before, the measurement of atom (molecule) concentrations in an extended area requires considering the changes of the pump and Stokes pulses while they propagate through the sample. If we make use of the slowly varying envelope approximation, the wave equations that describe the evolution of the pump and Stokes fields can be written, in terms of the corresponding Rabi frequencies, as [16]

\[
\left( \frac{\partial}{\partial t} + c \frac{\partial}{\partial z} \right) \Omega_p(z, t) = -i\alpha_p \rho_{12}^*,
\]

\[
\left( \frac{\partial}{\partial t} + c \frac{\partial}{\partial z} \right) \Omega_s(z, t) = -i\alpha_s \rho_{32}^*,
\]

where \(c\) is the speed of light and \(\rho_{ij}(i, j = 1, 2, 3)\) are the elements of the density matrix. The effect of the atomic medium on the pump and Stokes pulses propagation depends on the two absorption coefficients: \(\alpha_p = \omega_p N |\mu_{21}|^2/\epsilon_0 \hbar\) and \(\alpha_s = \omega_s N |\mu_{23}|^2/\epsilon_0 \hbar\). In writing equations (4a) and (4b) we have considered that the fields propagate parallel to the \(z\)-direction, the medium is homogeneous (the atoms in the ensemble are identical and uniformly distributed) and that the atomic motion is negligible. Equations (2), (4a) and (4b) constitute the mathematical description of the system under study.
3. Use of stimulated Raman scattering involving adiabatic passage for molecular imaging

Equations (2), (4a) and (4b) are solved in a moving frame defined by the variables $t' = t - z/c$ and $z' = z$. We consider that the initial pump and Stokes pulses show a Gaussian shape given by

$$\Omega_{p,s}(t) = \Omega_0 \exp\left\{-4 \ln 2 \left[ (t \pm \tau/2)/T \right]^2 \right\},$$

where $T$ is the full pulse width at half maximum, $\Omega_0$ is the peak Rabi frequency and $\tau$ is the temporal delay between the pulses. Additionally, the initial condition for the atoms is that all population is in the state $|1\rangle$,

$$\rho_{11}(-\infty) = 1, \quad \rho_{ij}(-\infty) = 0, \quad (i j \neq 1).$$

Even though in our simulations we have considered different types of atoms and molecules, for the sake of clarity we will restrict ourselves to two particular cases. Firstly, ensembles of $^{40}$Ca$^+$ ions, which we will use as a benchmark case to show the robustness and high efficiency that STIRAP can offer to label-free imaging systems. Secondly, since we are interested in molecular imaging, we will consider ensembles of neocyanine molecules. This molecule is of great chemical interest due to its intense absorption (180,000 M$^{-1}$ cm$^{-1}$) and short excited lifetimes ($\sim 120$ ps) [17]. Because of these properties, neocyanine has already been considered as a test molecule in experimental realizations of label-free imaging [3, 18].

For the case of $^{40}$Ca$^+$ ion ensembles, the considered levels are $4^2S_{1/2}(|1\rangle)$, $4^2P_{1/2}(|2\rangle)$ and $3^2D_{3/2}(|3\rangle)$. The transition lifetimes from level $|2\rangle$ to levels $|1\rangle$ and $|3\rangle$ are 7.7 and 94.3 ns, respectively. In order to reduce the harmful effects of the spontaneous decay, we need to employ light pulses with a duration much shorter than the lifetime of each transition.

STIRAP can achieve complete population transfer between states $|1\rangle$ and $|3\rangle$ if the quantum state of the atom can follow adiabatically one particular time-dependent eigenstate of the Hamiltonian given by equation (1), the so-called dark state [8]. Two conditions must be satisfied for trapping the system in the dark state [7]. Firstly, the tune of the frequencies to the two-photon resonance regime: ($\Delta_p = \Delta_s$). Figure 2 shows the fraction of population transferred to the state $|3\rangle$ as a function of the detunings of the pump and Stokes pulses. Figure 2(a) shows

Figure 2. Contour plot of the fraction of population transferred to level $|3\rangle$ as a function of the detuning from the atomic resonances of the pump ($\Delta_p$) and the Stokes ($\Delta_s$) pulses for (a) STIRAP and (b) overlapping pulses.
that the one-photon resonance $\Delta_p = \Delta_s = 0$ is not a requisite for achieving an efficient transfer of population when using a STIRAP scheme. Notwithstanding, figure 2(b) clearly shows that in SRS with initially overlapping pulses, the amount of atomic population transferred to the state $|3\rangle$ do in fact depend on whether there is one-photon resonance or not. For the sake of comparison, in the following we will restrict ourselves to the case of one-photon resonance.

The second and most distinguishing condition is that the evolution of the fields must be adiabatic, following a somehow counterintuitive ordering of the pulses [19]. The system starts with all the population in the ground state $|1\rangle$ and the Stokes field $\Omega_s$ is applied first. In this case, the initial state of the system corresponds exactly to the dark state. Afterwards, $\Omega_p$ is adiabatically increased, while at the same time, $\Omega_s$ is decreased, until the condition $\Omega_p \gg \Omega_s$ is reached. Now all the population has been transferred to the state $|3\rangle$.

We can produce nearly complete population transfer between states $|1\rangle$ and $|3\rangle$ when the pump and Stokes pulses overlap. However, SRS with overlapping pulses is not so robust against changes in the shape or intensity of the pulses, a feature that might change due to variations of laser parameters, or after propagation of the pulses in extended atomic ensembles. Figure 3 shows the fraction of atoms that reach state $|3\rangle$ as a function of the integrated Rabi frequency, i.e. $A = \int \Omega(t) dt$, for the case of overlapping pulses ($\tau = 0$) and the STIRAP configuration with temporal delay $\tau = 0.55$ T. As an example, let us select $\Omega_0$ so that $A = 13$, which corresponds to a nearly 100% population transfer for both cases. Additionally, for the STIRAP configuration, the delay between pulses is set to 5.5 ps. For the case of overlapping pulses, increases of 10% in the integrated Rabi frequency of the pulses diminish the population transfer to $\sim 50\%$, while decreases of 10% produce a population transfer of $\sim 70\%$. On the contrary, in the STIRAP regime, a nearly complete transfer of population is produced within the same range of variations.

Information about the number of atoms or molecules present in the sample is retrieved by measuring the SRG, or alternatively, the stimulated Raman loss. As previously stated, the integrated Rabi frequency is $A = 13$, which maximizes the transfer of population for both SRS with overlapping and non-overlapping pulses, as shown in figure 4(a).

Figure 4(b) shows the change of SRG ($\Delta E_s / E_s$, where $\Delta E_s$ is the gain in energy of the Stokes pulse and $E_s$ is the energy carried by the initial Stokes pulse) as a function of the distance traversed by the pulses through a sample with an ion number density of $10^{18}$ cm$^{-3}$. Figure 4(c) shows the effective molar amplification coefficient $\epsilon$ (in units of M$^{-1}$ cm$^{-1}$) as a function of
the distance [20]. In the initial stages of the propagation, the pulses undergo small changes that still do not affect $\epsilon$. However, as the pulses continue to propagate, their shapes and temporal delays start to change (see figure 4(d)). The magnitude of the changes are comparable (see figure 4(e)), but despite these changes, $\epsilon$ remains practically unchanged for STIRAP, while it decreases for the case of overlapping pulses. We observe that when considering a sufficiently high-concentration sample, the SRG is higher with STIRAP. However, as we will show below, in the case of low concentrations, variations in the SRG are no longer due to propagation through the sample, but to the precise preparation of the initial pulses.

Optical imaging based on SRS is especially suited for detecting very low concentrations of atoms or molecules. Figure 5(a) shows that, in this case, both SRS configurations yield the same linear dependence between concentration and SRG, with an effective molar
amplification coefficient of $\epsilon = 440,000 \text{M}^{-1} \text{cm}^{-1}$. This value of the molar amplification coefficient represents a sensitivity enhancement that would allow us to detect concentrations of up to $\sim 10^{13} \text{cm}^{-3}$. Note that SRS with STIRAP always achieves a higher sensitivity than SRS with overlapping pulses (figure 5(b)). Furthermore, figure 5(c) shows that fractional changes of up to 20% of the initial integrated Rabi frequency do not substantially modify the gain in the fluency of the Stokes pulse in the STIRAP configuration, while for the case of overlapping pulses the gain severely decreases. Nevertheless, $\epsilon$ in STIRAP still changes since we are comparing pulses with a different energy ($E_s$).

So far, we have shown the robustness and the high efficiency that STIRAP can offer to label-free imaging systems by using atomic ensembles as model system. However, since our interest resides in molecular systems, we now turn our attention to ensembles of neocyanine molecules. As stated before, we have selected this molecule because of its great chemical interest and also because it has been considered as a test molecule in experimental realizations of label-free imaging.

The level configuration for neocyanine is shown in figure 6(a). Transitions $|1\rangle \rightarrow |2\rangle$ and $|3\rangle \rightarrow |2\rangle$ are excited by laser pulses with central wavelength of 770 and 850 nm, respectively. We illuminate the sample with 15 fs pulses and a time delay of 9.33 fs between them (STIRAP configuration). The laser is set to have 4 mW average power and 80 MHz repetition rate. For the sake of comparison with [3, 18], we have assumed that the pulses have a transversal section...
Figure 6. (a) Scheme of the neocyanine three-level configuration. (b) SRG as a function of the concentration of neocyanine. Propagation distance: 100 nm. (c) Molar amplification coefficient as a function of the propagation distance. The neocyanine molecule in this figure was created using PyMOL [21].

$S \sim 1 \mu m^2$ and that they propagate 100 nm within the sample. From these parameters, we have that the volume in the laser focus is $10^{-19} m^3$ ($10^{-16} L$).

Figure 6(b) shows the SRG as a function of the neocyanine concentration. Note that by using a STIRAP configuration we obtain an effective molar amplification coefficient of $\epsilon = 11350 M^{-1} cm^{-1}$. This value of the molar amplification coefficient represents a sensitivity enhancement that would allow one to detect concentrations of up to $\sim 0.5 \mu M$.

4. Conclusions

We have presented a new technique to enhance the robustness and sensitivity of an optical label-free imaging technique based on SRS. The technique is based on the interaction of coherent resonant pulses with atoms, ions or molecules via the stimulated Raman adiabatic passage. In principle, in combination with a high-frequency phase-sensitive detection scheme, it allows one to detect amazingly small concentrations of atoms and molecules, where the SRG is found to be linear on the concentration and the propagation. For instance, with an effective molar amplification coefficient of $440000 M^{-1} cm^{-1}$ and $SRG > 10^{-7}$, it is possible to detect $n \sim 10^{-7} S/(2.303 \epsilon)$ ions, which for $S \sim 10 \mu m^2$ yields $n \sim 5$ ions.

In the case of molecular ensembles, we have shown that when using a STIRAP configuration we obtain an effective molar amplification coefficient of $11350 M^{-1} cm^{-1}$, which
for an SRG $> 10^{-7}$ and $S \sim 1 \mu m^2$ corresponds to the detection of $n \sim 20$ molecules. This result can also be understood in terms of the enhanced effective cross section ($\sigma = 0.435 \text{ Å}^2$) of the molecules, which is a consequence of the highly efficient STIRAP process.

We have shown that when using a STIRAP configuration, the SRG remains to be linear on the concentration of molecules and on the propagation distance traveled by the pulses, which allows straightforward quantitative analysis. Finally, we have shown that STIRAP is less sensitive to changes in the energy or shape of the initial pulses, which would make its implementation easier under realistic experimental conditions.

Acknowledgments

This work was supported by projects Consolider Ingenio CSD2006-00019, FIS2010-14831 and FET-Open grant number 255914 (PHORBITECH). This work has also been partially supported by FONCICYT project 94142 and Fundación Privada Cellex Barcelona.

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