Achieving ‘perfect’ molecular discrimination via coherent control and stimulated emission

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New Journal of Physics 11 (2009) 115007 (11pp)
Received 29 April 2009
Published 5 November 2009
Online at http://www.njp.org/
doi:10.1088/1367-2630/11/11/115007

Abstract. We illustrate how stimulated emission near threshold can turn modest coherent control yields into essentially perfect discrimination between systems. We demonstrate selective two-photon driven superfluorescence in atomic Rb and Na, where the shape of an ultrafast drive laser controls which atoms superfluoresce. Furthermore, we demonstrate high contrast selectivity in driving stimulated emission from dye molecules in solution by tailoring the shape of the ultrafast drive laser pulse. In both cases, we demonstrate discrimination with a control factor of about $10^4$.

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1. Introduction

There have been thousands of coherent control experiments over the past two decades since the field was established [1]–[4]. Early experiments focused on preparing specific target states in atoms and molecules [5]–[11] or on producing a desired reaction product from a single molecule [12]–[15]. Many of these experiments made use of closed-loop learning control in order to optimize the control fields for preparation of the target state of interest [16]. With an eye towards microscopy, standoff detection and other applications, some experiments have focused on discriminating between multiple atomic or molecular systems [17]–[20]. While control over target state preparation and discrimination between excitation of multiple samples has been demonstrated in a wide variety of systems, the control yields are typically modest, with control factors of the order of 10 or less. However, it has been shown that stimulated emission can lead to significant enhancement of single atom or molecule control yields [21]. Here, we show how stimulated emission, in conjunction with coherent control over multi-photon absorption, can lead to almost perfect discrimination between two dye molecules in solution, whereas control over fluorescence in these same molecules yields a control factor of about 2 [17]. As liquid-phase control experiments have proven difficult to interpret [22]–[24], we also present control results on selective two-photon absorption driven superfluorescence (SF) in separate atomic vapors. In the atomic case, the light–matter interaction is well understood [25], and we demonstrate explicitly how the large discrimination in the SF yields is driven by the single atom dynamics.

2. Experiment

We use a Ti:sapphire laser system capable of producing 30 fs pulses at a repetition rate of 1 kHz and an energy of \( \approx 1 \) mJ. The laser central wavelength is tunable from 772 to 784 nm. The amplified pulses from our laser system are shaped in an acousto-optic modulator (AOM)-based pulse shaper [27] under computer control. For feedback learning control experiments, we employ a genetic algorithm (GA) that uses 40 individuals, 20 phase genes, and a differential phase basis [28]. The pulses are characterized via SHG FROG [29].

The shaped laser pulses were split into two arms, with each arm focused to a 400 \( \mu \)m spot size (full-width at half-maximum for the intensity distribution). This yielded a 20 cm Rayleigh range and very little intensity variation over the length of the samples. For the experiments with atomic samples, one arm contained a heated glass cell with rubidium vapor at the focus and the other contained a sodium heat pipe oven at the focus. Both fluorescence and SF were collected from the excited atoms. Fluorescence from the center of the heat pipe/cell was collected at 90° with respect to the beam propagation direction and imaged onto a photomultiplier tube (PMT), as illustrated in figure 1. Interference filters were used to isolate specific transitions (the 3p–3s transition in Na and the 6p–5s transition in Rb). Stimulated emission from the atoms (in the forward direction) was collected with two separate photodiodes (PD) and combined onto one cable using a signal combiner for ease of digitization. All signals were acquired by a digital oscilloscope mounted in a computer. The Na signal was delayed with a long cable in order to distinguish between the two signals on the oscilloscope. The experiments involving dyes

\[ \text{In using the phrase 'single atom or molecule control', we refer to control over an ensemble of atoms or molecules in which each atom or molecule acts independently of the others.} \]
Figure 1. Our experimental setup. 30 fs pulses were shaped by an AOM-based pulse shaper and split into two arms. Each arm was focused into a cell containing either an atomic or molecular sample.

in liquid phase used the same focal geometry with the solutions placed in glass cells at room temperature.

We carried out closed-loop learning control experiments in order to maximize the discrimination between the atom and dye-molecule pairs, as well as parameterized pulse shape scans in order to highlight the relationship between the spontaneous and stimulated emission yields.

3. Results

Earlier work has demonstrated that the forward emission from our ensemble of Na atoms is SF [21]. This was established via measurements of the pulse duration, coherence, delay relative to the drive pulse, the absence of backward emission and comparisons between our measurements and numerical integration of the Maxwell–Bloch equations. In Rb, we also observed an absence of backward emission and performed measurements of the forward scattered intensity as a function of density in order to confirm that the emission was SF. Figure 2 and its inset show the stimulated emission yield on the 6p–5s transition as a function of density. The inset shows an enlargement for low densities where the forward emission varies quadratically with density (a quadratic fit is shown along with the data). Combined with the absence of backwards emission, this suggests the light is neither amplified spontaneous emission (ASE) nor parametric wave mixing in the Rb sample.
Figure 2. Rubidium SF. The outer figure shows rubidium SF (6p–5s) yield as a function of density. The inset shows the SF yield as a function of density for low densities (the region in the dashed box) along with a quadratic fit. We used a pulse energy of approximately 45 µJ for the measurement.

We performed two separate learning control experiments with the atomic samples. We aimed to maximize the Rb/Na SF yield in one experiment and maximize the Na/Rb SF yield in the other. The control factor (explained below) is then the product of these two optimal ratios. The results are shown in figure 3. In figure 3, the signal (both solid and dashed curves) starting at ~ 0 ns is SF from Rb, while the signal just before 250 ns is SF from Na. Here, the solid curve shows the signal for a pulse shape designed to maximize Na/Rb and the dashed curve shows the signal for another pulse shape designed to maximize Rb/Na. The inset shows the relevant atomic structure for both atoms where we measure light from the transition corresponding to the blue line in Rb (6p–5s) and the orange line in Na (3p–3s). The duration of the signals is determined by the capacitance of the large aperture PD, which we used for the measurements in order to digitize them without sampling errors.

For the dye experiments, we used methanol solutions of the same two dyes that were used in earlier control experiments, which used the spontaneous emission yield for feedback: DCM (4-dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-4H-pyran) and ruthenium [Ru(dpb)3](PF6)2 (dpb is 4,4′-diphenyl-2,2′-dipyridine) [17]. The dye solutions were held in cells approximately 5.5 cm long. The normalized single-photon absorption and emission spectra for DCM and [Ru(dpb)3]2+ are shown in figure 4. Both DCM and [Ru(dpb)3]2+ have overlapping absorption spectra from 400 to 600 nm, requiring two photons to be absorbed from our laser centered at 780 nm. Figure 5 shows the stimulated emission spectra for DCM and [Ru(dpb)3]2+. The stimulated emission spectra are very similar to each other, centered at the same wavelength as the emission spectra for the dyes and somewhat narrower than the emission spectra shown above, as expected. We observed some evidence of continuum generation in the
Figure 3. Normalized control results for selectivity between Rb and Na stimulated emission. The solid curve represents a pulse designed to maximize Na/Rb and the dashed curve represents a pulse designed to maximize Rb/Na. The signal starting at $\sim 0$ ns represents Rb and that at $\sim 250$ ns, Na. The insets show the atomic level structure, where the blue line is the lasing we measure in Rb and the orange line is the lasing we measure in Na. The pulse energies were approximately 170 $\mu$J for Na and 45 $\mu$J for Rb.

Figure 4. Single-photon absorption and emission spectra for $[\text{Ru(dpdb)}_3]^{2+}$ (a) and DCM (b). The blue curve represents absorption and the red curve represents emission. Data courtesy of Niels Damrauer.

dye samples, which we suspect seeded the stimulated emission from the two-photon excited dye molecules. This is consistent with previous two-photon driven lasing measurements [30].

Figure 6 shows the results for selective excitation in DCM and $[\text{Ru(dpdb)}_3]^{2+}$. The control goals were to maximize the DCM/$[\text{Ru(dpdb)}_3]^{2+}$ and $[\text{Ru(dpdb)}_3]^{2+}$/DCM stimulated emission.
yields, respectively, where we collect the whole stimulated emission spectrum with the photo diodes. The pump laser light was filtered out with a short pass filter. The solid curve shows the signal for a pulse shape designed to maximize DCM/[Ru(dpb)$_3$$]^{2+}$ and the dashed curve shows the signal for a pulse shape designed to maximize [Ru(dpb)$_3$$]^{2+}$/DCM. The signal starting close to 0 ns represents [Ru(dpb)$_3$$]^{2+}$ and the signal just after 150 ns represents DCM. In the case of a transform limited pulse, both dyes gave a similar stimulated emission yield.

4. Discussion

Shaping the drive pulse in our experiments allows for the production of a strong forward emission from one sample while almost completely suppressing emission from the other. In terms of selectivity between two samples, we feel it is useful to describe the result in terms of a control factor that accounts for selectivity in both directions and gives a measure of the maximum discrimination possible. In both the atomic and molecular cases, the control factor we consider (the product of the stimulated emission yield ratios for the two control experiments—i.e. max(Na/Rb) x max(Rb/Na), or max(DCM/[Ru(dpb)$_3$$]^{2+}$) x max([Ru(dpb)$_3$$]^{2+}$/DCM)) is greater than $10^4$, even though the control factor for the same molecules when optimizing spontaneous emission ratios is $\sim 2$ [17]. The control ratio in either direction in both experiments was about 100 : 1 (limited largely by signal to noise), yielding a control factor of about $10^4$. If
Figure 6. Normalized control results for selectivity between DCM and [Ru(dpb)₃]²⁺. The solid curve represents a pulse designed to maximize DCM/[Ru(dpb)₃]²⁺ and the dashed curve represents a pulse designed to maximize [Ru(dpb)₃]²⁺/DCM. The signal starting at ∼0 ns represents [Ru(dpb)₃]²⁺ and that at ∼150 ns, DCM. The insets show the two chemical structures of the molecules.

we were to simply quote the control ratio possible in either direction, then this could mask a lack of control in the other direction and it would not convey the discrimination possible with two different pulse shapes.

The control we observe in Na versus Rb exploits the different electronic structures of the two atoms. Based on these results alone, one might ask whether an intermediate resonance, such as the 5p state in Rb, is required to exert significant control in competition with another non-resonant two-photon absorbing systems. The experiment with the dyes suggests that this is not the case, since the two absorption spectra are very similar between 400 and 800 nm (with no absorption at all near 780 nm), and we expect near resonant enhancements to play a more important role than states that are far from resonance.

One might also ask whether the control we observe in the dye molecules is a result of selective seeding of the stimulated emission via nonlinear interactions between the pump pulse and the solvent molecules [22, 23]. Our measurements of the stimulated emission spectra suggest that this is not the case, as the two measured spectra for the forward emission (shown in figure 5 for an unshaped pulse) overlap quite closely, making it very difficult to selectively seed one emission while suppressing the other.
Figure 7. Measurements of the fluorescence and SF for both Rb and Na as a function of energy and the phase-offset parameter $\delta$. Panels (a) and (b) show Rb SF and fluorescence, respectively, where the maximum pulse energy is approximately $45 \mu J$. Panels (c) and (d) show Na SF and fluorescence, respectively, where the maximum pulse energy is approximately $170 \mu J$.

In order to demonstrate how the dramatic selectivity is based on control over single atom/molecule dynamics enhanced by stimulated emission, we measured both the spontaneous and stimulated emission from the atomic ensembles as a function of pulse shape for a simple pulse shape parameterization, with a spectral phase given by

$$\Phi(\omega) = \frac{\pi}{2} \sin(\beta \omega + \delta).$$

This periodic spectral phase was chosen because it effectively discriminates between the two samples and has a simple interpretation for the case of sodium, where the two-photon absorption is not resonantly enhanced. In this case, any antisymmetric spectral phase leads to constructive interference between competing pathways to the final state, whereas a symmetric spectral phase leads to destructive interference and a suppression of two-photon absorption \[5\]. The excitation of Rb is affected by the intermediate resonances, which makes the pulse shape dependence of the excitation more complicated \[31\]. (We note here that the spectrum of our laser was not centered at 777 nm, the center of the two-photon resonance in Na, and therefore $\delta = 0$ does not imply the spectral phase is antisymmetric around the two-photon resonance.)

Figure 7 shows fluorescence and SF for both Rb and Na as a function of energy and $\delta$. Panels (a) and (b) show SF and fluorescence, respectively, from Rb; panels (c) and (d) show the SF and fluorescence, respectively, from Na. We note that the SF as a function of energy and $\delta$ for each atom follows the fluorescence closely—i.e. the SF yield is driven by the single atom-field dynamics. In addition to demonstrating that the SF yield follows the single atom excitation, this pulse shape parameterization demonstrates how a modest single-atom discrimination can
lead to a dramatic discrimination in the SF yields. Figure 8 shows the Rb and Na SF yield as a function of $\delta$ at a fixed energy (not the same energy for the two different atoms). The dashed curve represents Na SF and the solid curve Rb SF. Controlling $\delta$ yields a substantial contrast between the SF for one atom versus another.

We measured the optimal pulses for a few of the GA results in atomic Rb and Na, shown in figure 9. Although it is difficult to interpret the dynamics for the optimal pulses because of volume averaging related to spatial intensity variation [25, 32], we note a few features for interested readers. Panels (a) and (b) show measured Wigner distributions [33] for a pulse designed to maximize Na/Rb SF yield and a pulse designed to maximize Rb/Na SF yield, respectively. Panels (c) and (d) represent the pulse intensity and phase in time of (a) and (b). Trying to suppress the Rb SF and keep the Na SF yielded a pulse with a double structure, whereas trying to suppress the Na SF and keep the Rb SF yielded a pulse with just a single peak. Both pulses are of order 100 fs, exhibit a smoothly varying phase, and have a relatively simple temporal structure, indicating that the discrimination is quite sensitive to the drive laser pulse shape.

5. Conclusion

We demonstrate how stimulated emission near threshold can turn modest coherent control yields into essentially perfect discrimination between systems. We demonstrate selective two-photon driven SF in atomic Rb and Na and selective two-photon driven stimulated emission in solvated laser dyes with similar single-photon absorption spectra. The shape of an ultrafast drive laser
controls which atom/molecule the emission is from. In both cases the control factor is greater than $10^4$.

Acknowledgments

We thank Niels Damrauer for providing the molecular samples, the absorption and emission spectra, and helpful discussions. This work was supported by the National Science Foundation under award number 0555214.

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New Journal of Physics 11 (2009) 115007 (http://www.njp.org/)