Generation of Narrowband Inversion with Broadband Laser Pulses

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We show experimentally, here for Na vapor, and theoretically that picosecond frequency-swept laser pulses create in multilevel systems an inversion profile which is far narrower than the pulse spectrum. This selectivity persists even when the Rabi frequency is substantially larger than the spacing between pumped and suppressed transitions.

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Excitation of controlled nonequilibrium distributions is often desirable in optical spectroscopy, and this is most commonly done with narrowband lasers. For example, stabilized continuous-wave (cw) lasers or transform-limited nanosecond pulses are commonly used to excite a single rovibronic line in the crowded spectrum of a molecule [1]. However, the Boltzmann population distribution of even the extremely cold molecules (e.g., 3 K) produced by a supersonic molecular-beam expansion will typically have a width of a few wave numbers, so only a small fraction of the available molecules can be excited by such pulses. In addition, intermolecular and intramolecular processes often occur on a far shorter time scale, and it is often necessary to measure dynamical properties with ultrashort (10^{-14}–10^{-11} s) laser pulses. These pulses inevitably have a far wider bandwidth than nanosecond pulses, thus degrading the selectivity.

In this paper, we demonstrate experimentally in Na vapor that frequency-swept ultrashort laser pulses produce more selective excitation and better population transfer than transform-limited pulses with the same bandwidth. Careful pulse-shape control [2,3] is not needed for this application—the intrinsic *robustness* of the process helps dramatically in experimental applications. In fact, we point out that frequency-modulated laser pulses permit quite selective excitation even when the peak Rabi frequency exceeds the separation between the excited and suppressed transitions.

In our experiments, the enhanced selectivity and robustness results from population inversion via adiabatic rapid passage (ARP) [4–7]. In a two-level system, efficient population transfer results from applying radiation with the carrier frequency starting far below the resonance frequency, sweeping "slowly" through the resonance, and ending far above the resonance. The criterion for adiabaticity is that $|d\theta/dt| \ll (\omega_1^2+\Delta^2)^{1/2}$, where ω_1 is the Rabi frequency, Δ is the frequency detuning of the laser from resonance, and $\theta=\tan^{-1}(\Delta/\omega_1)$. The exact shape of both the pulse amplitude and the frequency sweep are not important—it matters only that the frequency sweep be performed slowly enough to satisfy this criterion. ARP in the optical domain has been previously demonstrated on a nanosecond or longer time scale by ramping a dc Stark field to adiabatically Stark shift a transition through resonance [8,9] and passing a molecular beam transversely across a cw laser near the beam waist [10,11]. Furthermore, nanosecond laser pulses with both arbitrary frequency and amplitude modulation have been generated [12] for the purpose of generating ARP.

This concept of ARP is also applicable to multilevel systems, but, as we show below, the adiabatic criteria are somewhat more complex. Frequency-swept picosecond laser pulses have produced enhanced excitation in multilevel systems [13], but, to our knowledge, selective excitation of allowed transitions using frequency-swept laser fields has not been previously demonstrated [14]. In particular, we focus on selective excitation in terms of the three-level system shown in Fig. 1. Here the initial population begins in the ground state, $|1\rangle$. The excited states $|2\rangle$ and $|3\rangle$ are coupled by the applied laser field. The center frequency is set between the two upper states, and

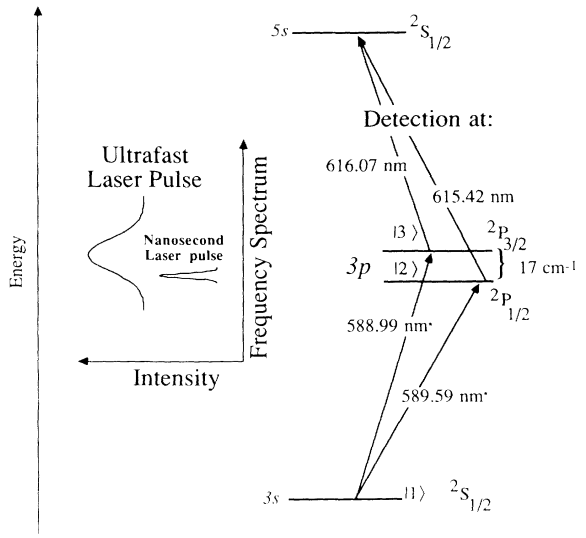

FIG. 1. Energy levels of Na [15]. A narrow bandwidth laser covers one of the two *D* lines of sodium, whereas an ultrafast laser pulse (≤ 1 ps) can encompass both transitions. Wavelengths marked with an asterisk correspond to frequency-swept excitation in our experiments.

the pulse spectrum is sufficiently broad to overlap both of the upper states. A transform-limited (i.e., minimum $\Delta\omega\Delta t$) laser pulse excites states $|2\rangle$ and $|3\rangle$ equally, as long as the pulse spectrum covers both the $|1\rangle \rightarrow |2\rangle$ and $|1\rangle \rightarrow |3\rangle$ transitions. However, if the laser pulse is frequency swept adiabatically through the resonance with the upper-state transitions, then the state excited first by the laser pulse becomes selectively populated, and the selectivity remains largely independent of Rabi frequency. Furthermore, we demonstrate that either of the two upper states may be selectively excited simply by controlling the direction of the sweep.

We performed a two-laser experiment to demonstrate selective excitation in Na vapor using frequency-modulated pulses. The D line resonances around 589 nm are separated by ≈ 17 cm^{-1} [15] and provide a good approximation to a three-level system under the experimental conditions used here. Two dye lasers were pumped with a mode-locked frequency-doubled Nd:YAG laser and amplified with an excimer-pumped three-stage dye cell amplifier. Frequency-swept pump pulses centered at ≈ 589 nm were generated by coupling the output from one of the dye lasers (3 ps, FWHM) into 20 m of single-mode 4-μm silica-core optical fiber. Self-phase modulation and group-velocity dispersion then broadened the pulses to ≈ 15 ps and produced a moderately linear red to blue frequency sweep [16,17] of ≈ 5 cm^{-1}/ps (Fig. 2). The asymmetry observed on the red edge of the pulse spectrum in Fig. 2(a) is due to saturation in the dye amplifier which causes a preferential amplification of the leading edge of the pulse—in this case, the red Fourier components. Note that this is not a particularly clean laser pulse. To reverse the direction of the frequency sweep, amplified pulses were double passed through a diffraction grating pair (1800 lines/mm) separated by 1.5 m. This configuration corresponded to an overcompensated pulse compressor, and typically produced 30-ps blue to red frequency-swept pulses without altering the spectrum. A longer probe pulse (5 ps FWHM, 2.5-cm^{-1} FWHM bandwidth) was tuned to the $5s \leftarrow 3p$ transition (≈ 616 nm) [15] to detect population in either the $^2P_{1/2}$ or $^2P_{3/2}$ state (see Fig. 1). The temporal delay between the pump and probe pulses was set ≈ 1–2 ns.

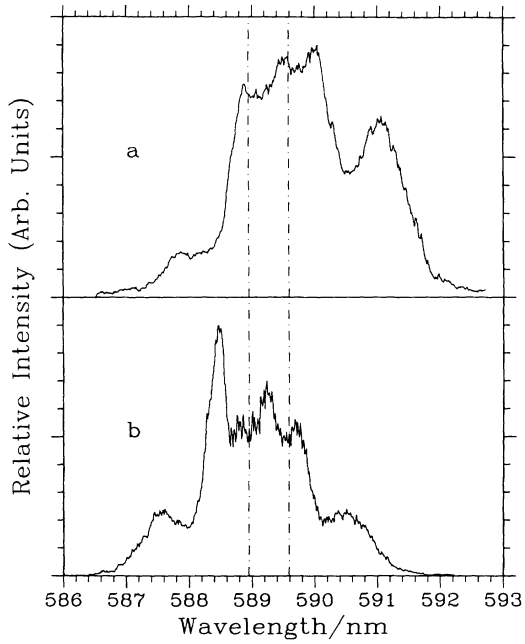

FIG. 2. Spectra of frequency-swept pulses, observed after amplification. Direction of chirp is (a) from red to blue, and (b) from blue to red. The dotted lines correspond to the location of the two D-line transitions of sodium.

An effusive Na beam was generated in a stainless-steel vacuum chamber. The optical density of sodium in the beam plume was minimized by placing a stainless-steel aperture in front of the nozzle, which confined the sodium to ≈ 1 cm in the laser interaction region. Irradiation took place ≈ 1 cm from the tip of the nozzle; fluorescence was detected perpendicular to the laser- and sodium-beam propagation axes. Scatter and fluorescence at 589 nm were suppressed with a Schott RG-610 filter; scatter at 616 nm was minimized by spatial filtering and by delaying acquisition of the fluorescence signal to avoid pulse breakthrough. Figure 3 shows typical results for a red to blue frequency sweep (a) and blue to red sweep (b) through the $5s \leftarrow 3p$ transitions. The Rabi frequencies in the figure were computed by approximating the electric-field envelope of the laser as the function $\exp(-at^4)$, and using a dipole moment of 9 D for the $^2P_{3/2} \leftarrow {}^2S_{1/2}$ transition, calculated from the known oscillator strength [15(b)]. In the low-intensity limit, linear response is realized: The fluorescence excited from the $^2P_{3/2}$ state is twice as strong as the fluorescence excited from the $^2P_{1/2}$ state, as expected from the 2:1 ratio of oscillator strengths for the $^2P_{3/2} \leftarrow {}^2S_{1/2}$ and $^2P_{1/2} \leftarrow {}^2S_{1/2}$ transitions, respectively [18]. As the laser intensity increases, the fluorescence distribution shifts strongly. With the red to blue sweep, the $^2P_{1/2}$ state is preferentially excited (≈ 3:1 ratio), even though its oscillator strength is smaller; with the blue to red sweep, the $^2P_{3/2}$ state is almost exclusively excited. Residual excitation of the suppressed transition may be attributed to the nearly Gaussian inhomogeneous laser-beam profile; in the wings of the laser-beam profile, the lower intensity is not sufficient to cause ARP. The fluorescence ratio was quite sensitive to the spatial alignment of the pump and probe laser beams; slight misalignments of the laser beams degraded selectivity.

The observed selectivity at the highest incident intensities is at first surprising, since the peak Rabi frequencies substantially exceeded the 17-cm^{-1} splitting of the D lines. Off-resonant excitation becomes efficient in two-level systems when $\omega_1 \approx \Delta$, so it might be guessed that the selectivity should be degraded as the Rabi frequency approaches the D-line separation. Contrary to these expectations, we see only slight degradation in selectivity at

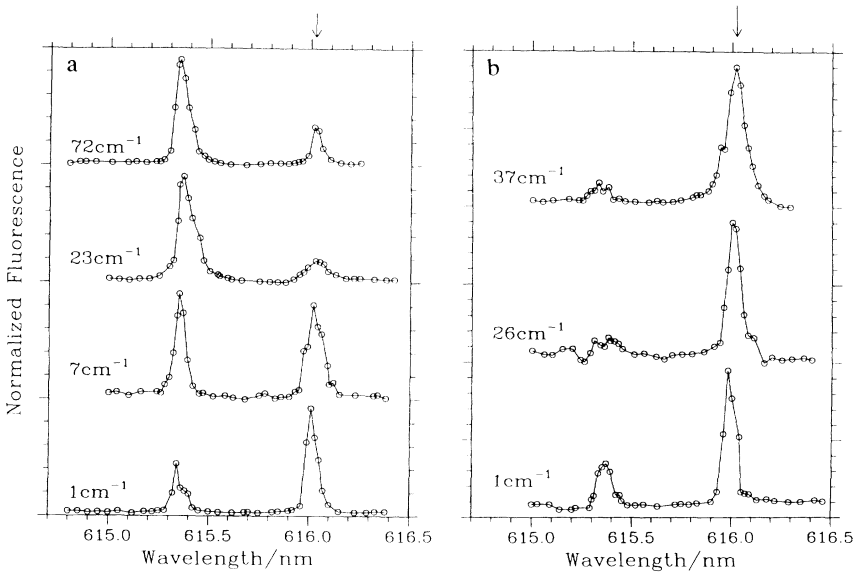

FIG. 3. Normalized relative intensities of fluorescence from the $5s \rightarrow 3p$ transition for the pump-pulse frequency swept (a) from red to blue, and (b) from blue to red. The numbers in cm^{-1} correspond to approximate peak Rabi frequencies ($\pm 10\%$). The arrow at 616 nm corresponds to the fluorescence peak from the $5s \rightarrow {}^2P_{3/2}$ transition, which in turn reflects the population transferred to the ${}^2P_{3/2}$ level by the pump pulse.

our highest powers. Furthermore, the observed selectivity in the high-power limit does not arise simply because the frequency-swept pulse depletes the ground-state populations before the next transition is excited. To illustrate this the time evolution of the density matrix corresponding to the three-level system of Fig. 1 interacting with a linearly swept (5 cm^{-1}/ps, red to blue) 10-ps FWHM pulse was simulated numerically, and is shown in Fig. 4(a). The assumed pulse envelope of $\exp[-a(t-t_0)^4]$ is a reasonable approximation to our experimental envelope; the assumed Rabi frequency is $2\pi(50\ \text{cm}^{-1})$. As the pulse frequency approaches resonance with the D-line transitions, states $|2\rangle$ and $|3\rangle$ both become populated. However, as the pulse sweeps past resonance, all the population is swept into state $|2\rangle$. Simulations with $\omega_{1,\text{peak}} = 2\pi(100\ \text{cm}^{-1})$ still show that 99% of the population is transferred to state $|2\rangle$; with a still smoother (Gaussian) pulse envelope and 10-ps FWHM duration, the D-line separation can be exceeded by several orders of magnitude, and selectivity is still retained.

This selectivity in the excitation profile is best illustrated by a dressed-state picture [19]. Figure 4(b) shows the time evolution of eigenvalues and eigenvectors of the Hamiltonian corresponding to Fig. 1. At the beginning of the laser pulse, each dressed state corresponds nearly to a single bare state (far below resonance $|\alpha\rangle \rightarrow |1\rangle$, $|\beta\rangle \rightarrow |2\rangle$, and $|\gamma\rangle \rightarrow |3\rangle$). As the laser field evolves in time, the dressed states change in composition, becoming linear combinations of the three bare atomic states. After the laser pulse, each dressed state again correlates to a single bare state (far above resonance $|\alpha\rangle \rightarrow |2\rangle$, $|\beta\rangle \rightarrow |3\rangle$, and $|\gamma\rangle \rightarrow |1\rangle$). If the laser field is applied adiabatically, then the system will evolve only along the energy surface corresponding to state $|\alpha\rangle$, and thus after the frequency sweep is completed, $|1\rangle \rightarrow |2\rangle$. This means that the sweep must be slow compared to the square of the energy separations $E_\alpha - E_\beta$ and $E_\alpha - E_\gamma$. Figure 4 illustrates a rather general result, confirmed numerically, which is that the adiabatic condition is easier to meet during the first half of the pulse (as resonance is approached) and more difficult to maintain as the sweep is concluded.

In conclusion, we have shown that experimentally straightforward techniques for generating frequency-modulated pulses provide robust selective excitation of allowed transitions and enhanced population transfer. The frequency sweep need not be perfectly linear, nor even monotonic; as long as the adiabatic condition is satisfied, selective excitation and population inversion will occur. Furthermore, by controlling the direction of the frequency sweep, it is possible to selectively excite different transitions. There is currently much theoretical interest in using highly controlled frequency- and amplitude-modulated laser fields for studies in bond-selective chemistry [20–22]. Robustness will be extremely important for laboratory applications, where complications such as Rabi frequency inhomogeneities make application of (for example) a normal π pulse impossible [23]. The very large insensitivity to experimental complications leads us to believe that ARP with ultrashort frequency-modulated laser pulses will play a central role in transforming theoretical schemes into practical tools for laser-selective chemistry.

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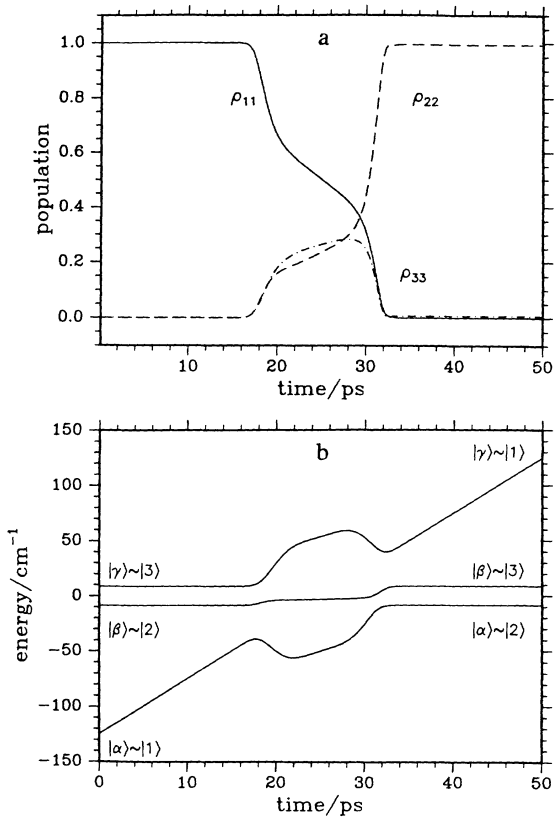

FIG. 4. (a) Populations of the $^2S_{1/2}$ ($|1\rangle$), $^2P_{1/2}$ ($|2\rangle$), and $^2P_{3/2}$ ($|3\rangle$) levels in Na for a frequency-swept pulse whose Rabi frequency [$\omega_1 = 2\pi(50\ \text{cm}^{-1})$] substantially exceeds the 17-cm^{-1} D-line spacing. Note that population is transferred quantitatively into level $|2\rangle$ by the end of the pulse, even though $|3\rangle$ is also populated at intermediate times. (b) Energies of the three dressed states with time, using the same pulse parameters as in (a). The population remains almost completely in the lowest energy level $|\alpha\rangle$ even in this high Rabi frequency limit.

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