Efficient Coherent Population Transfer in NO Molecules Using Pulsed Lasers

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Highly efficient and selective population transfer in NO molecules in the electronic ground state ($X^2\Pi_{1/2}$) from the vibrational level v''=0 to the level v''=6 is demonstrated. It shows, for the first time with pulsed lasers, that a rather generally applicable scheme for complete control over the level population in atoms and molecules is now available. The efficiency relies on a counterintuitive interaction sequence of two lasers with the molecule in a process of stimulated Raman scattering involving adiabatic passage.

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Coherent light-matter interaction is a source of fascinating phenomena. Surprising observations are not uncommon and often result in important new applications. One example is the meanwhile well known phenomenon of dark resonances, created by a coherent superposition of quantum states, which leads to the suppression of spontaneous decay. A specific superposition of this kind, induced by an appropriately timed sequence of coherent laser pulses in a multilevel system, is a crucial element of new techniques for the transfer of population. Such techniques allow efficient and selective preparation of highly excited states [1,2], which play a significant role in many nonequilibrium systems. They also allow efficient transfer of photon momenta to atoms for improved performance of mirrors and beam splitters in atomic interferometry [3]. Those techniques rely on a specific (so-called counterintuitive) sequence of interactions with two radiation fields [1,2,4], on a controlled chirp of the laser frequency [5,6] or on a specifically tailored time dependence of the electric field of the radiation [7].

The first of these techniques seems to be the only one of those relying on laser coherence, which has already been successfully applied in a collision dynamics study. In that experiment [8] complete transfer of the population of a single rovibronic thermally populated level of a molecule to a single level in a vibrationally excited state has been achieved in a Raman-type process [Fig. 1, right-hand side (r.h.s.)] using cw lasers. The frequencies of the pump and Stokes lasers are tuned to their respective resonances with an intermediate level 2. The interaction begins with the Stokes laser, connecting levels 2 and 3, and ends with the pump laser, connecting levels 1 and 2. As experimentally demonstrated in Ref. [2] as well as in Ref. [3] in the context of momentum transfer, loss of population from the intermediate level by spontaneous decay does not occur, even if the interaction time with the radiation fields is much longer than the intermediate level lifetime [2]. Our present work demonstrates that this technique can be carried an important step further by using, for the first time, pulsed lasers. It is applied to achieve efficient and selective vibrational excitation of NO in its electronic ground state. The successful implementation proves that this concept can eventually be applied to a large class of species, including molecules such as O_2 and H_2. We first explain why this is not simply a straightforward extension of previous work.

The surprising result obtained with cw lasers can be rationalized by realizing that there exists a so-called trapped state [9] $|a_0\rangle$ among the three eigenstates of the strongly coupled system of molecular levels and radiation fields. The coupling strength is given by the Rabi frequencies $\Omega_{s,p} = \mu E_{s,p}/\hbar$, where the indices s and p refer to the Stokes and pump laser, respectively. This eigenstate

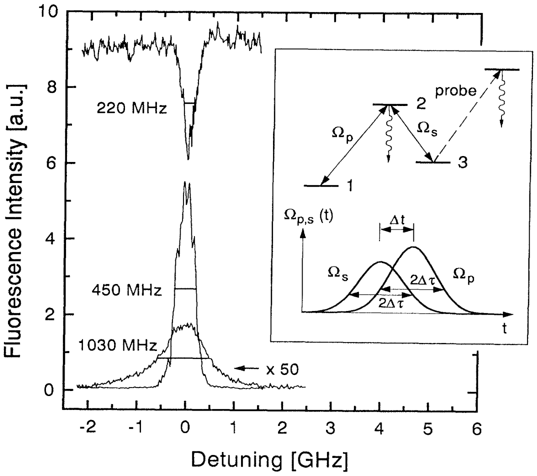

FIG. 1. Open three level system (r.h.s.) coupled by two radiation fields. The time evolution of the Rabi frequencies $\Omega_{s,p}(t)$ and a probe laser transition are also shown. The upper trace on the l.h.s. shows the variation of the fluorescence induced by the pump laser tuned to resonance with the 1 → 2 transition as the Stokes laser is tuned across the resonance of the 2 → 3 transition. The lower two traces show the fluorescence out of level 3 induced by the probe laser for a delay of the Stokes pulse of $\Delta t = -4\,\text{ns}$. For the narrower one, the Stokes laser frequency is tuned across the 2 → 3 transition, while the pump laser is kept at the one-photon resonance. For the broader one, the pump laser is tuned across the 1 → 2 transition and Stokes laser turned off.

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$$|a_0\rangle = N^{-1}(\Omega_s|1\rangle - \Omega_p|3\rangle), \quad N = (\Omega_p^2 + \Omega_s^2)^{1/2} \tag{1}$$

is a superposition of the eigenfunctions of the initial and final level. It has no contribution of the radiatively decaying level 2, provided the two-photon resonance is maintained [10]. If the particles interact first with the Stokes laser, which couples the initially unpopulated levels (see r.h.s of Fig. 1), the coefficient $N^{-1}\Omega_s$ decreases from unity at very early times to zero at very late times while $N^{-1}\Omega_p$ increases from zero to unity. Assuming negligible phase fluctuations of the radiation fields during the interaction time, the condition [2]

$$\Omega\,\Delta\tau \gg 1 \tag{2}$$

has been derived for complete transfer, i.e., for adiabatic evolution of the system according to Eq. (1). For Gaussian pulses, $\Delta\tau$ is the half width at $1/e$ of $E(t)$. The name STIRAP has been introduced for this method [2], because it combines features of stimulated Raman scattering, when applied to a lambda-type level system, and the adiabatic passage phenomenon.

Neglect of phase fluctuations is justified for single-mode cw lasers if the interaction time of particles with the radiation fields is short compared to the inverse of the laser linewidth. Narrow band single-mode radiation is available in the visible range of the spectrum. However, only few molecules have low lying electronic states within reach of visible cw laser radiation, while many molecules have their first absorption band at a wavelength $\lambda < 400\,\text{nm}$. In this range, only pulsed lasers provide adequate power. Unfortunately, the coherence properties of pulsed lasers are inferior to those of cw lasers. Evaluation of the conditions for adiabatic evolution in the presence of phase fluctuations leads to a modified adiabaticity condition, best written in terms of the pulse energy [11]

$$\Omega^2\,\Delta\tau > (\Delta\tau)^{-1}(1+R^2)B\,, \tag{3}$$

where R is the ratio of the actual laser bandwidth to the transform limited bandwidth for the given pulse length. The factor B is of the order of 100 and depends on the pulse length as well as on the spectrum of the pulse. Obviously, the condition given by Eq. (3) strongly suggests the use of pulsed laser radiation with a nearly transform limited bandwidth, $R \approx 1$.

In our experiment, the cw radiation of two single-mode dye lasers is amplified in two pulsed dye amplifiers. These are simultaneously pumped by the second harmonic of a single-mode injection seeded Nd:YAG laser, yielding 4 ns pulses in the UV after doubling and mixing. The output of one amplifier is frequency doubled in a KDP crystal to $\lambda = 300\,\text{nm}$ and used as the Stokes laser. The output of the other amplifier is frequency doubled and mixed in KDP crystals with the fundamental frequency of the Nd:YAG laser. It yields $\lambda = 226\,\text{nm}$ required for the pump transition in the STIRAP process.

An optical delay line is used to vary the relative time delay of the pulses before they are coaxially combined and cross an uncollimated pulsed supersonic beam, 20 mm downstream of the nozzle. The pulse energies at the molecular beam are typically 0.1 mJ for the pump and 1 mJ for the Stokes laser. They were adjusted to yield Rabi frequencies of the order of a few $10 \times 10^9\ \text{s}^{-1}$ for both the pump and Stokes transition with laser beam diameters of 2 and 4 mm, respectively.

The mean rotational energy of the molecules in the pulsed beam of 10% NO seeded in argon (total pressure 1 bar, nozzle diameter 0.5 mm) corresponds to a temperature of about 2 K. The population is concentrated in the rotational levels $J''{=}1/2$ and $3/2$ of the vibrational ground state $v''{=}0$ in the lower fine structure state $X^2\Pi_{1/2}$. About 25% of the NO molecules are found in the lambda component with negative parity of the $X^2\Pi_{1/2}(v''{=}0,J''{=}1/2)$ state. The aim is to transfer all molecules out of this state into the $X^2\Pi_{1/2}(v''{=}6, J''{=}1/2)$ level via the intermediate state (level 2 of Fig. 1) $A^2\Sigma(v'{=}0,\ J'{=}1/2)$. Molecules in level $v''{=}6$ are excited to the level $A^2\Sigma^+(v'{=}4)$ by the probe laser, an excimer pumped dye laser operating at $\lambda = 235\,\text{nm}$. The subsequent fluorescence intensity is proportional to the population in level $v''{=}6$ (level 3 of Fig. 1, r.h.s.). The probe laser pulse is delayed by 1 μs with respect to the pump and Stokes laser pulses.

Figure 1 (l.h.s.) shows the variation of the population in $v''{=}6$ as the Stokes laser frequency is tuned across the two-photon resonance while the pump laser frequency is in resonance with the transition between levels 1 and 2. It furthermore shows the reduction of the fluorescence out of level 2. This fluorescence induced by the pump laser should disappear when the conditions for complete population transfer, Eq. (3) and two-photon resonance, are satisfied. However, fluorescence from the spatial wings of the pump laser, where the maximum Rabi frequency is too low for the STIRAP process but high enough to populate level 2, prevents us from detecting a larger decrease of the fluorescence intensity.

The observed linewidth is about 220 MHz. From this result we conclude that the linewidth of the pump and Stokes laser radiation is about 160 MHz. This is less than twice the transform limited bandwidth of 110 MHz for a 4 ns pulse. The high transfer efficiency of the STIRAP process is evident because the probe laser induced fluorescence exceeds by 2 orders of magnitude the signal obtained with the Stokes laser blocked. In this latter case, population in level 3 is established by spontaneous emission from level 2 only [Franck-Condon pumping (FCP)].

The determination of the *absolute* transfer efficiency T with narrow band pulsed lasers is more difficult compared to coherent population transfer with cw lasers. In the cw case it is straightforward to calibrate the transfer efficiency by normalizing the population in level 3 to the one resulting from spontaneous emission induced by the pump laser alone (FCP) [2]. This procedure relies on the known branching ratios for spontaneous emission and on the fact that the interaction time of the molecules with the laser fields is long enough to fully deplete the population of level 1. In the present case, however, the pulse length is short compared to the spontaneous emission lifetime of 200 ns [12] and the population left in level 2 after the pump pulse depends critically on the pulse area $A = \int \Omega(t)dt$. For $A = 2n\pi$ all molecules return to level 1, while area $A = (2n+1)\pi$ leaves all molecules in level 2, from which they decay by spontaneous emission. Under our experimental conditions, the molecules undergo of the order of $2n = 10$ Rabi cycles during the 4 ns pump pulse. Therefore, if the average over a number of pulses with small pulse-to-pulse fluctuations of the pulse energy is taken, 50% of the molecules will be found in level 2 and the population established in level 3 by spontaneous emission will be the same as that expected from a rate equation treatment.

The determination of the *absolute* transfer efficiency given by $T = 2\gamma F S_{\mathrm{STI}}/S_{\mathrm{FCP}}$ requires a careful analysis of the sources contributing to the fluorescence signals. Here F is the branching ratio of radiative decay (given by the relevant Franck-Condon factor and rotational linestrength factor) from level 2 to level 3. S_{FCP} and S_{STI} are the probe laser induced fluorescence intensities observed with the pump laser alone and after the STIRAP process, respectively. The factor 2 accounts for the fact that FCP places only half of the molecules which are initially in level 1 into level 2. The factor γ can be estimated. It accounts for the differences in the size of the detected sample of molecules contributing to the signals S_{FCP} and S_{STI}. In particular, the velocity range of molecules accessible by FCP is determined by the saturation broadened linewidth, while partial compensation of the Doppler shift occurs in the two-photon STIRAP process. A factor $\gamma < 1$ accounts for this difference.

Careful analysis of all contributions to γ leads to a transfer efficiency T of the order of unity. The uncertainty is mainly related to the uncertainty in the determination of γ. It is therefore important to confirm the high transfer efficiency independently. In fact, the characteristic signature of the highly efficient STIRAP process is convincingly demonstrated by comparison of experimental and calculated results for the variation of the transfer efficiency T with the relative delay Δt of the pump pulse with respect to the Stokes pulse (see Fig. 1, r.h.s.). Results from numerical solutions of the Schrödinger equation for pulses with transform limited bandwidth are shown in Fig. 2(a). If the Stokes laser precedes the pump laser ($\Delta t < 0$) by more than twice the pulse width, T is relatively small. If the delay is about half the pulse width (STIRAP regime), T reaches a value of unity and is strikingly insensitive to small variations of the delay as well as to small variations of the laser intensities. In this regime, the coherent nature of the radiation is essential. The plateau, $T \approx 1$, extends deeper into the negative delay region for increasing Rabi frequencies.

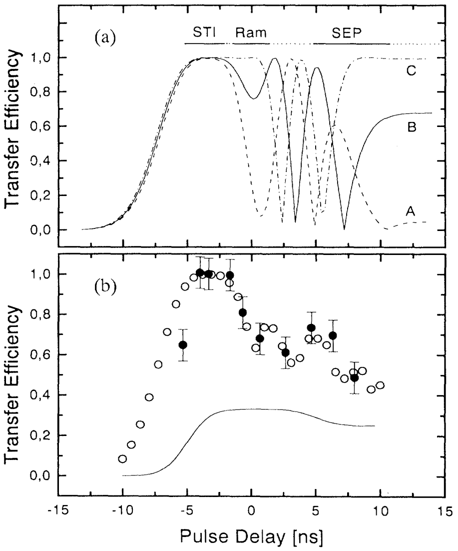

FIG. 2. (a) Calculated transfer efficiency T as the Stokes laser delay is varied for three different pairs of Rabi frequencies $\Omega = \Omega_p = \Omega_s$ (A: 4.4×10^9 s^{-1}; B: 4.7×10^9 s^{-1}; C: 5.0×10^9 s^{-1}). (b) Comparison of the experimentally determined transfer efficiency T with the calculated data. The latter results from an average over 80 laser pulses per data point, for $\Delta\tau = 3.8$ ns, mean Rabi frequencies $\overline{\Omega}_{p,s} = 4.7 \times 10^9$ s^{-1}, and pulse energy fluctuations according to a Gaussian distribution with $\sigma = 0.15\overline{\Omega}_{p,s}$. The experimental data have been normalized to the calculated ones at $\Delta t = -3.3$ ns. For comparison the transfer efficiency expected for stimulated emission pumping, calculated using rate equations and assuming pulse energies large enough to saturate the transitions, is also shown.

The evolution of the population is determined by Rabi oscillations, when the pulses overlap (Raman regime, $\Delta t \approx 0$) or when the pump pulse precedes the Stokes pulse in the regime of stimulated emission pumping (SEP) [13], $\Delta t > \Delta\tau$. In these latter configurations T varies between nearly zero and nearly unity for only small variations of the pulse energies. Thus, for $\Delta t \gtrsim \Delta\tau$ a high degree of laser coherence is undesirable since it leads to large fluctuations in the transfer efficiency.

In Fig. 2(b) experimental and numerical results are compared. The calculated transfer efficiencies represent an average over 80 pulse sequences with varied pulse energies. The distribution of energies is chosen to resemble the experimentally determined fluctuations. The oscillations of T with Δt vanish as a result of this averaging procedure. In the experiment, the Rabi frequency was lower by a factor of 2 for the data point taken at $\Delta t = -5.3$ ns. The good agreement of experimental and theoretical variation of T with Δt confirms that the predicted complete population transfer under STIRAP conditions is in fact achieved in the experiment.

For comparison the transfer efficiency expected for stimulated emission pumping, calculated using rate equations, is also shown. The maximum transfer efficiency is substantially smaller and the variation of T with the delay Δt of the laser pulses is characteristically different.

A brief comparison of our approach with coherent population transfer relying on frequency chirp, reported recently in Refs. [5,6], is in order. Boers *et al.*, [6] demonstrate efficient population transfer in rubidium atoms, induced by a frequency chirped picosecond pulse in a ladder configuration of levels. In that case, the frequency evolves such that the laser couples levels 3 and 2 first, then all three levels and levels 2 and 1 last. This scheme is not applicable for the lambda-type level configuration, Ref. [14]. Warren and co-workers [5] emphasize that selective population of a single level in a group of many in an electronically excited state is possible with a chirped pulse. Sequential application of this concept with two lasers would also lead to efficient and selective population transfer between levels in the electronic ground state, provided the electronic lifetime of level 2 is long compared to the pulse duration. No such restriction applies for the STIRAP concept. It is particularly important to recognize that according to Eq. (3) the energy required for complete coherent population transfer in a given atom or molecule is much less for pulses of nanosecond duration as compared to picosecond pulses.

In summary, we have demonstrated a *practical* way to efficiently and selectively transfer population, for the first time with pulsed lasers, via a stimulated Raman process involving adiabatic passage (STIRAP). Optimum utilization of the coherence of the radiation fields is achieved by suitable delay of the pulses. This is an important step in the effort to put a technique at our disposal which is applicable to a large class of atomic and molecular systems.

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