

Precise Control of Molecular Dynamics with a Femtosecond Frequency Comb

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We present a general and highly efficient scheme for performing narrow-band Raman transitions between molecular vibrational levels using a coherent train of weak pump-dump pairs of shaped ultrashort pulses. The use of weak pulses permits an analytic description within the framework of coherent control in the perturbative regime, while coherent accumulation of many pulse pairs enables near unity transfer efficiency with a high spectral selectivity, thus forming a powerful combination of pump-dump control schemes and the precision of the frequency comb. Simulations verify the feasibility and robustness of this concept, with the aim to form deeply bound, ultracold molecules.

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Although mode-locked lasers emit broadband ultrashort pulses, they can perform frequency selective excitation just like narrow-band cw lasers due to their precise frequency comb [1]. This spectral selectivity arises from the long interpulse phase coherence, permitting coherent accumulation of excitation amplitudes from multiple pulses in a material system, similar to a generalized Ramsey experiment. This idea led to the realization of direct frequency comb spectroscopy in atomic systems [2]. Here we propose to apply the principle of coherent accumulation, combined with weak field coherent control, to precisely control molecular dynamics with high efficiency.

While analysis of coherent quantum control is relatively simple in the weak field perturbative domain [3], extension to strong fields is not straightforward. Analytic models exist only for simple cases [4,5] and solutions are often found by numerical optimizations [6]. The core of our approach is to exploit analytic perturbative models to design “ideal” weak pulses and to achieve the high overall efficiency by coherently accumulating many such pulses. This avoids the complication of strong field design while gaining high spectral selectivity offered by the frequency comb. Since the maximal number of accumulated pulses is inherently limited by the coherence time of the material ensemble, we expect our approach to be applicable particularly well to ultracold atomic or molecular ensembles, where coherence times are long.

Motivated by the goal to produce deeply bound ultracold polar molecules from loosely bound Feshbach molecules, we consider a Raman transition from a vibrational level near the dissociation limit, to a deeply bound vibrational level, as shown in Fig. 1. Feshbach molecules can be generated with high efficiency via adiabatic sweeping through a magnetic Feshbach resonance in an ultracold atomic ensemble [7]. Magneto-photo-association of cold atoms is a major avenue currently pursued for obtaining cold molecules [8]. So far, stable, ultracold ground state molecules have not been produced in high densities [9],

mainly due to the poor wave function overlap between the spatially spread continuum states of colliding atoms and the localized molecular states. Feshbach molecules thus appear to be an important midstage towards deeply bound ultracold molecules.

Any scheme aimed at efficiently performing a Raman transition is challenged when the input channel is embedded among other states with energy spacings smaller than the natural width of the intermediate state. For example, in stimulated Raman adiabatic passage (STIRAP), the transfer efficiency generally decreases when multiple, closely spaced input states are involved [5] since the effective Raman linewidth covers multiple states. Thus, it is complicated to use STIRAP for photoassociation of pairs of atoms (even for a Bose-Einstein condensate) when con-

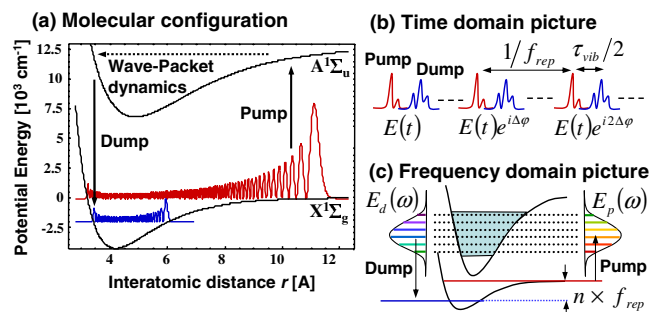


FIG. 1 (color online). Basic Raman control scheme. (a) Morse electronic potentials and vibrational levels (fit to Rb_2). Population is transferred from the input vibrational level near the dissociation limit ($v' = 130$) to a deeply bound level ($v = 45$), mediated via a broadband wave packet in the excited electronic potential. (b) Time-domain picture. A train of phase-coherent pump-dump pulse pairs is shaped to achieve efficient population transfer. The intrapair time is half the vibration time (τ_{vib}) of the intermediate wave packet. (c) Frequency domain picture, showing a tooth-to-tooth match between the pump and the dump frequency combs, with f_{rep} equal to a subharmonic of the net Raman energy difference.

tinuum states are involved [10]. For Feshbach molecules, the energy splitting is large enough to justify a closed three-level model and STIRAP has been recently applied to transfer the population one vibrational level down in the ground potential of Rb_2 [11]. To drive the population further down the vibration ladder would require dramatically enhanced STIRAP intensities and would amplify the already observed loss [11]. Another technique using strong Raman coupling (Rabi oscillations) between atom pairs and molecules in an optical lattice was recently reported [12]. A large detuning from the intermediate state is used to avoid spontaneous loss, however, the use of single Rabi pulse will be less robust than STIRAP. In a third alternative, short, shaped pulses can also eliminate spontaneous emission losses from the intermediate state [13], however, the pulse duration is too short to have the required energy resolution (even after pulse shapers).

To overcome these difficulties, we employ the scheme illustrated in Fig. 1, based on a phase-coherent train of shaped pump-dump pulse pairs. Each pulse pair is weak, i.e., transfers only a small fraction of the input population to the target state. Coherent accumulation then enables a high overall transfer efficiency. In the time domain, each pump pulse excites a wave packet that starts to oscillate in the excited electronic potential. After half a vibration, this wave packet reaches the inner turning point where the dump pulse drives it to the target state. Since population appears on the excited potential only for half a vibration, this scheme eliminates spontaneous emission losses. In between pulse pairs the system is left in a coherent superposition of the input and target states that evolves freely. To enable coherent accumulation of population at the target state, the temporal phase difference between pulse pairs $\Delta\varphi$ should match the phase of the free evolving Raman coherence. In the frequency domain, the combs of the pump and the dump pulses must overlap tooth to tooth and the repetition rate f_{rep} must be a subharmonic of the Raman energy difference. To clarify, all pulse pairs share a common temporal (spectral) shape and phase [$E(t)$ or $E(\omega)$], designed to maximize the transfer efficiency for a single-pulse pair. The relative phase between successive pulse pairs, $\Delta\varphi$, is then controlled via stabilization of the frequency comb.

For the very first dump pulse to drive all the excited population to the *empty* target state its “pulse area” should be $\sim\pi$. After the second pump pulse however, the excited population is about equal to the population already in the target state, so now only a $\pi/2$ “area” dump pulse of the appropriate phase is required, just like in a Ramsey experiment. Similarly, as the input state is depleted, the pump area should slowly increase to excite the same population every time, reaching $\sim\pi$ for the very last pump pulse. In general, the fraction of population excited (or dumped) by a pulse of area A is $\sin^2(A/2)$. Consequently, the dump area of the n th pulse $A_d[n]$ should decrease according to $\sin^2(A_d[n]/2) = 1/n$ and the pump area increase by

$\sin^2(A_p[n]/2) = 1/(N - n + 1)$ (for N pulses). Another equally valid solution is to fix the pump area and vary the dump according to the evolving population distribution.

The pulse area is not a well-defined quantity outside the context of a two-level system. However, the ratio of populations in the excited wave packet and the input (target) state defines an effective area for the pump (dump) pulses. This concept proves useful mainly for weak pulses, where the excitation is predominantly a one-photon process. Clearly the very first dump pulses and the last pump pulses are of areas near π and cannot be considered weak, but for a large N , the majority of the population is transferred by the accumulative effect of all pulses, which are mostly weak. Consequently, even if the first (last) pulses do not have the required area or are complicated by multiphoton effects, the overall process can remain efficient. Experimentally, current intensity modulators can easily meet the required pulse area variation for standard pulse repetition times of 1–10 ns.

For an efficient pump-dump process it is required that the wave packet $|\psi_p\rangle$, excited by the pump from the input state $|i\rangle$ and propagated for half a vibration, will overlap perfectly with the wave packet $|\psi_d^r\rangle$ that would have been excited from the target state $|t\rangle$, by the time-reversed dump. For weak pulses we can express these two wave packets, using first order perturbation theory, as

$$\begin{aligned} |\psi_p\rangle &\propto \sum_{\omega} E_p(\omega) \exp[i\phi_D(\omega)] |\omega\rangle \langle d_e | i \rangle, \\ |\psi_d^r\rangle &\propto \sum_{\omega} E_d^r(\omega) |\omega\rangle \langle d_e | t \rangle, \end{aligned} \quad (1)$$

where $|\omega\rangle$ denotes the vibrational states in the excited potential using the detuning ω from the pulse carrier as a vibrational index, $F_p(\omega) = \langle \omega | d | i \rangle$ ($F_d(\omega) = \langle \omega | d | t \rangle$) is the pump (dump) transition dipole matrix elements (d the dipole operator). $E_p(E_d^r)$ is the spectral amplitude of the pump (time-reversed dump) field and $\phi_D(\omega)$ is the spectral phase acquired by the wave packet between the pulses, which reflects both the delay of half a vibration and the dispersion of the wave packet as it oscillates in the anharmonic excited potential. For the Morse potential fit, used later in the simulations, analytic expressions exist for the vibrational states and energies [14], so both the dipole matrix elements and $\phi_D(\omega)$ are known.

As a result, perfect overlap of the two wave packets can be achieved by shaping the pump field according to the dump dipole matrix elements and vice versa:

$$\begin{aligned} E_p(\omega) &\propto F_d(\omega) A(\omega), \\ E_d(\omega) &\propto F_p(\omega) A(\omega) \exp[i\phi_D(\omega)], \end{aligned} \quad (2)$$

where A is an arbitrary spectral amplitude, common to both fields. Intuitively, this spectral shaping avoids pumping of what cannot be dumped (due to nodes in the dump dipole matrix elements), and vice versa. An example of pump

(dump) dipole matrix elements within the Franck-Condon approximation is shown in Figs. 2(a) and 2(b). The fast oscillation (alternating sign) of the dipole matrix elements for the dump pulse is canceled by the relative delay of half a vibration between the two pulses, so the pump should only be shaped according to the slow envelope of $F_d(\omega)$. Such shaping is easily achieved with current ultrafast pulse shapers [15]. It may seem surprising that a broadband pulse can dump a broadband wave packet to a single state, but since the pulse is tailored to the wave packet, such that all the transition amplitudes interfere constructively only at the target state, this is no contradiction. While the shaped pump-dump pulse pairs achieve spectral selection of a single vibrational level, coherent accumulation is key to further refine the spectral resolution to address rotation and hyperfine levels, as well as to accomplish near unity transfer efficiency.

To check the viability of our scheme, we numerically simulated the molecular dynamics driven by a train of pulses as discussed. The simulation is based on a split-operator code [16] that solves the time-dependent Schrödinger equation with three wave packets on three potential surfaces, coupled by two arbitrary pulses (within the rotating wave approximation). As the molecular potential we used the Morse fit for Rb_2 . Although the Morse fit is not quantitatively accurate for an actual molecule, it includes the qualitative ingredients required for demonstrating our method. According to Eq. (2), the pulses can be shaped in two stages: differential shaping that ensures overlap of the wave packets by matching the pulses to the spectral shape of the dipole matrix elements; and common shaping, which affects the overall shape of both wave-packets (e.g., common chirping). First, the desired effect of differential shaping was verified. Indeed, with weak pulses ($\leq \pi/10$) shaped according to the spectral dipole elements shown in Fig. 2, the overlap of the pumped and dumped wave packets was practically unity (>0.999). We then explored the effect of common shaping on the pump-dump process. Within the perturbative discussion relevant to Eq. (2), the common spectral amplitude $A(\omega)$ is completely arbitrary, and for weak enough pulses, this is verified by our simulation. However, for both practical (accumulated phase noise) and fundamental reasons (limited interaction time due to input state coherence), it is

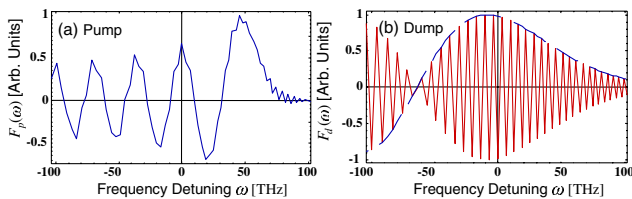


FIG. 2 (color online). Dipole matrix elements ($F(\omega)$) vs frequency detuning from the wave packet carrier; (a) for excitation from level $|v = 130\rangle$ in the ground potential to levels centered around $|\omega = 162\rangle$ in the excited potential and (b) for deexcitation of these levels to $|v = 45\rangle$ in the ground potential.

desirable to increase single-pulse energy to minimize the total number of pulses. Here, common spectral shaping will be important to control deleterious multiphoton effects.

In many cases of molecular dynamics, positively chirped (red to blue) excitation pulses can strongly suppress Raman processes that adversely affect the input wave packet during the pulse [17], leaving the excitation, although strong, essentially one-photon. The reason is that within the Franck-Condon window, the excited potential is usually steeper than the ground potential (e.g., excitation from the ground vibrational level at the zero slope of the ground potential), so population initially excited by the red part of the pulse cannot be later deexcited by the blue because there are no available levels to deexcite to. It is clearly shown in simulation that when the pulses are positively chirped to be longer than the vibration time of both the input and the target states, over 50% of population can be selectively transferred between two deeply bound vibrational levels with one pump-dump pair. Thus, chirping the pulses can improve the dumping efficiency for the first dump pulse that is necessarily strong because it dumps to an empty target state.

Common chirping helps to resolve vibrational structure around the target state deep in the molecular well, yet it cannot resolve rotational or hyperfine structure nor the dense environment around the input state. Here, the combination of coherent control and coherent accumulation proves powerful—coherent control techniques (shaping, chirping) achieve a precise match between specific initial and target states, while coherent accumulation allows high spectral selectivity and total transfer efficiency.

We simulated the full coherent accumulation process in various scenarios. Figure 3 shows simulation results for the interaction of a train of 40 pulse pairs with the molecule at a repetition time of 10 ns, assuming a 30 ns radiative lifetime for the excited states. The pump pulse area was fixed to $\pi/6.6$, exciting about 5.7% of the input population each time, and the dump area was varied to match with the accumulation progress. The pulses were ~ 10 nm in bandwidth (100 fs transform limited), chirped out to ~ 1.5 ps by dispersion of 5×10^5 fs². The pump pulses depleted $>90\%$ of the input population, and when the interpulse phase was tuned to the Raman condition, 95% of this population reached the target. During accumulation, the target population increased and its wave packet was quickly purified to practically a single state.

The coherent accumulation proves to be quite robust against intensity fluctuations. Scaling the intensity of the pump or dump pulse train (or both) by a factor of 2 in simulation leaves the total transfer efficiency constant within a few percent. The exact variation of dump pulse area according to the accumulated population is also not critical. Even if the dump area is kept constant, the transfer efficiency is $>50\%$ over a range of factor of 2 in intensity. The reason for this robustness is that even when not all population is dumped, the anharmonicity of the excited

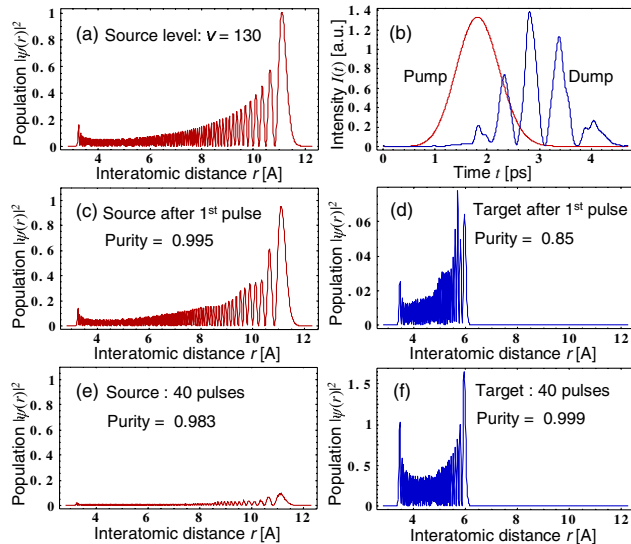


FIG. 3 (color online). Simulation results for the coherent accumulation process. (a) the input state population density, (b) the intensity temporal profile of the shaped, strongly chirped pulses. (c) and (d) are the input and target wave packet population densities after one pulse pair, and (e) and (f) are the corresponding results after 40 pulses. Purity is the normalized overlap between the wave packet and the target (input) state.

potential scrambles the lingering wave packet between pulses, such that the interference with the next pumped wave packet is neither constructive, nor destructive, but averages out (with background population decaying at $1/f_{\text{rep}}$ time scales). Therefore, pulse area errors do not coherently add from pulse to pulse.

Because of the high density of levels near the input state, it is inherently impossible to avoid leakage of population to nearby levels through two-photon Raman processes, which is why also cw techniques, such as STIRAP, require caution. In our scheme this leakage appears as a dark wave packet created on the input state by every pump pulse. However, by the use of weak, mainly “one-photon” pulses, the leakage per pulse is diminished and by assuring that the comb is not matched to the energy spacing to nearby levels, the leakage does not coherently buildup. In our simulation, although the input is depleted by 90% after 40 pulses, it remains $>98\%$ pure.

The selection of the target state in our simulation was guided by the requirement of good overlap. To complete the transfer of population to the absolute rovibrational ground, one can employ the same method again, or use standard cw techniques. Although we considered wave packet dynamics in one excited potential, the scheme is easily generalized to a set of coupled potentials (e.g., spin orbit [13]). The pulses should then be designed according to the (more complex) spectral shape and phase of the transition dipole matrix elements. In addition, since ultrashort pulses are used, the excited wave packets are broad and deeply bound within the excited potential, so their

dynamics is fast. Consequently, the scheme is immune to small perturbations, such as hyperfine interactions, that affect the interatomic potential near dissociation, and are usually not well known.

The presented scheme is a unique and powerful combination of frequency domain control (comb) and time-domain control (molecular dynamics). As such, it enables performance of coherent control tasks with both high efficiency and unprecedented spectral resolution. We believe the scheme is general and will find applications in areas such as control of molecular rovibrational dynamics and photoassociation or dissociation. Specifically, it can be used to produce deeply bound ultracold molecules.

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