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-
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 dramatic-
cally 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 alterna-
tive, 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,

for the very first pump 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 exper-
iment. 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
$\sin^2(A_d[n]/2) = 1/(N - n + 1)$ (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 pop-
ulations in the excited wave packet and the input (target)
state defines an effective area for the pump (dump) pulses.

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 $|\psi_d\rangle$ that would have been
excited from the target state $|t\rangle$, by the time-reversed dump.

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:

$$E_p(\omega) \propto F_d(\omega) A(\omega),$$
$$E_d(\omega) \propto F_p(\omega) A(\omega) \exp[i\phi_d(\omega)],$$

where $A(\omega)$ 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
See text
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 build up. 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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