Precise Control of Molecular Dynamics with a Femtosecond Frequency Comb - A Weak Field Route to Strong Field Coherent Control

Avi Pe’er, Evgeny A. Shapiro, Matthew C. Stowe, Moshe Shapiro, and Jun Ye

1 JILA, National Institute of Standards and Technology and University of Colorado, Boulder, CO 80309-0440
2 Department of Chemistry, University of British Columbia, Vancouver, Canada
3 Department of Chemical Physics, Weizmann Institute of Science, Rehovot 76100, Israel

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. The concept is presented analytically and its feasibility and robustness are verified by simulations of dynamics in Rb2. We consider application of this concept to the formation of stable, deeply bound, ultracold molecules.

PACS numbers: 33.80.-b, 33.80.Ps, 34.30.+h, 42.50.Hz, 42.65.Dr, 33.90.+h

Although mode-locked lasers emit broadband ultrashort pulses, they can be utilized to perform frequency selective excitation just like narrow-band CW lasers due to their precise frequency comb. This spectral selectivity is explained by the very long inter-pulse phase coherence, which allows for coherent accumulation of the excitation amplitudes from multiple pulses in an excited material system, similar to a generalized Ramsey experiment. This idea led to the realization of direct frequency comb spectroscopy in atomic systems. Here we propose to apply the principle of coherent accumulation, combined with weak field coherent control, to precisely control molecular dynamics at high efficiencies.

While analysis of coherent quantum control is relatively simple in the weak field perturbative domain, extension to strong fields is not straightforward. Analytic models exist only for simple cases, and solutions are often found by numerical optimizations. 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 / 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 the Raman transition shown in Fig. 1 from a single vibrational level embedded in a dense environment of other levels near the dissociation limit, to a single deeply bound vibrational level. Loosely bound Feshbach molecules can be generated with high efficiency via adiabatic sweeping through a magnetic Feshbach scattering resonance in an ultracold atomic ensemble. Since molecules are not amenable to standard laser cooling techniques, magneto-photo-association of cold atoms is a major avenue pursued for obtaining cold molecules, which now represents one of the most exciting research fields in cold matter. So far, stable, ultracold ground state molecules have not been produced in high densities, mainly because of the poor wavefunction overlap between the spatially spread continuum states of colliding atoms and the localized molecular states. Feshbach molecules appear therefore to be an important midstage towards deeply bound ultracold molecules.

When the energy level spacing near the input state is small compared to the natural line-width of excited states, the application of CW techniques is not straightforward. Any scheme relying on populating an excited state during the transition is inherently limited because most of the population will be lost to spontaneous decay during the time needed to resolve the input state. Short pump-dump pulses could eliminate spontaneous emission losses, but then the total interaction time is too short. A similar problem is met by stimulated Raman adiabatic passage (STIRAP). For the adiabatic passage to hold, the Rabi frequency Ω must be larger than the decay rate Γ from the intermediate state: Ω ≳ Γ. Since both the power broadened pump line-width and the two-photon line-width of STIRAP are of order Ω, the possibility of population transfer to neighboring levels should be considered. Thus, predictions for using STIRAP to photo-associate an atomic Bose-Einstein condensate depend strongly on modeling of the decay process and the atomic continuum states.

To overcome these difficulties, we employ the scheme illustrated in Fig. 1 which is based on a phase-coherent train of shaped pump-dump pulse pairs. Each pulse pair is weak, i.e., it 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. Therefore, in order 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 $f_{\text{rep}}$ must match a sub-harmonic of the Raman energy difference.

Let us clarify the role of the different amplitudes and phases involved. All pulse pairs share a common temporal (spectral) shape and phase ($E(t)$ or $E(\omega)$), which is 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 to achieve coherent accumulation.

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 to perform the transfer, just like in a Ramsey experiment. In general, the fraction $p$ of population excited (or dumped) is related to the “pulse area” $A$ by $\sin^2(A/2) = p$. As population is accumulated in the target state and depleted from the input state, the dump “area” of the nth pulse $A_d[n]$ should decrease and the pump “area” $A_p[n]$ increase for each pulse pair to transfer the same fraction of population (for $N$ pulses),

$$\sin^2\left(\frac{A_d[n]}{2}\right) = \frac{1}{n}, \quad \sin^2\left(\frac{A_p[n]}{2}\right) = \frac{1}{N - n + 1}. \quad (1)$$

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. In general, for any given pump series, a dump series can be matched according to the ratio fraction of excited population $p/n$. Clearly the very first dump pulses and the last pump pulses are of areas near $\pi$ 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.

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. For weak pulses we can express these two wave-packets, using first order perturbation theory, as

$$|\psi_p\rangle = \sum_{\omega} E_p(\omega) \exp[i\phi_D(\omega)] |\omega\rangle \langle \omega|d_{el}|i\rangle$$

$$|\psi_d\rangle = \sum_{\omega} E_d(\omega)|\omega\rangle \langle \omega|d_{el}|t\rangle, \quad (2)$$

where $|\omega\rangle$ denotes the vibrational states in the excited potential using the detuning $\omega$ from the pulse carrier.
frequency as a vibrational index, $F_p(\omega) = \langle \omega | d_p | t \rangle$ and $F_d(\omega) = \langle \omega | d_d | t \rangle$ are the pump and the dump transition dipole matrix elements, which under the Condon approximation are propotional to the Franck-Condon factors $\langle \omega | i \rangle$, $\langle \omega | t \rangle$. $d_{p,d}$ is the electronic transition dipole moment and $E_p(E_d)$ is the spectral amplitude of the pump (time-reversed dump) field. $\phi_D(\omega)$ 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 \([11]\), 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:

$$E_p(\omega) \propto F_d(\omega) A(\omega)$$

$$E_d(\omega) \propto F_p(\omega) A(\omega) \exp[i\phi_D(\omega)], \quad (3)$$

where $A$ is an arbitrary spectral amplitude, common to both fields. Intuitively, this spectral shaping avoids pumping of what cannot be dumped (due to a node in the dump dipole matrix elements), and vice versa. An example of pump (dump) Franck-Condon factors is shown in Fig. 2(b). The fast oscillation (alternating sign) of the Franck-Condon factors for the dump pulse is canceled by the relative delay of half a vibration between the two pulses, so the pump should only be spectrally shaped according to the slow envelope of $F_d(\omega)$. Such shaping is easily achieved with current ultrafast pulse shapers \([12]\).

It may seem surprising that a broadband pulse can dump a broadband wave-packet to a single state, but since we tailored the wave-packet to the pulse, such that all the transition amplitudes from levels within the wave-packet 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 \([13]\) that solves the time-dependent Schrödinger equation (within the rotating wave approximation) with three wave-packets on three potential surfaces, coupled by two arbitrary pulses. According to Eq. 3, the pulses can be shaped in two stages: differential shaping that ensures overlap of the wave-packets by matching the pulses to the different Franck Condon spectral responses; 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 Franck-Condon function 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. 3, the common spectral amplitude $A(\omega)$ is completely arbitrary, and for weak enough pulses, this is verified by our simulation. Yet, it is desirable to minimize the total number of pulses for both practical reasons (more tolerant phase locks) and fundamental ones (the total interaction time is limited by the coherence time of the input state), so how strong can the pulses be and still qualify as “weak”? The limiting power level is where two-photon (Raman) processes by one pump pulse become pronounced, and here spectral shaping will have an important effect.

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 \([14]\), 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, localized at the zero slope of the ground potential), so population initially excited by the red part of the pulse cannot be later de-excited by the blue part because there are no available levels to de-excite 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 pulse can improve considerably the dumping efficiency for the first dump pulse that is necessarily strong because it dumps to an empty target state.

The common chirping can help resolve vibrational structure around the target state deep in the molecular well, yet it cannot resolve rotational / hyperfine structure, and certainly not the dense environment around the input state. Here, the combination of coherent control and coherent accumulation proves powerful - coherent...
control techniques (pulse shaping, chirping) are used to achieve a precise state 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 $\sim 10$ nm in bandwidth (100 fs transform limited), chirped out to $\sim 1.5$ ps by dispersion of 500,000 fs$^2$. The pump pulses depleted $>90\%$ of the input population, and when the inter-pulse phase was tuned to the Raman condition, $95\%$ of this population reached the target state. The purifying nature of the coherent accumulation process is demonstrated by the obtained final wave-packet practically a single state.

The coherent accumulation process proves to be quite robust against intensity fluctuations. Simulations show that scaling the intensity of the pump or the dump pulse train (or both) by a factor of two leaves the total transfer efficiency constant within a few percent. The exact variation of dump pulse area according to the accumulated population (Eq. (1)) is also not critical. Even if the dump area is kept constant, the transfer efficiency is $>50\%$ over a range of factor of two in intensity.

Due to 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 exactly why CW techniques, such as STIRAP, require caution. Although our comb scheme is no exception, the deleterious effects of this leakage are suppressed for two reasons. First, for a single pulse-pair the leakage is diminished by the use of weak, mainly “one photon” pulses. Second, assuming the comb is not matched to the energy spacing of nearby levels, after a large number of pulses $N$ the leakage process resembles an incoherent random walk, thus scaling as $\sqrt{N}$, whereas the coherent depletion of the input state scales linearly as $N$, causing it to dominate. In our simulation, although the input is depleted by $90\%$ after 40 pulses, it remains $>98\%$ pure.

Although we considered wave-packet dynamics in one excited potential, the scheme is easily generalized to dynamics in a set of coupled potentials (e.g. spin-orbit). The pulses should then be designed according to the (more complex) shape and phase of the transition dipole matrix elements to the set of excited potentials. 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 inter-atomic potential near dissociation, and are usually not well known.

To conclude, 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. Due to the use of weak pulses the process can be analyzed within a perturbative model, thus opening an analytic path to strong field problems that were so far accessible only by numerical optimizations. We believe the scheme is very general and will find applications in many areas of coherent control. Specifically, it can be used to produce deeply bound ultracold molecules.

We thank P. Julienne, P. Zoller, and D. Jin for discussions. Work at JILA is funded by NSF, DOE, and NIST. A. Pe‘er thanks the Fulbright Foundation for support.

[1] Th. Udem, R. Holzworth, and T. W. Hansch, Nature 416, 233 (2002); J. Ye, H. Schnatz, and L. W. Hollberg, IEEE J. Sel. Top. Quant. 9, 1041 (2003); S. T. Cundiff and J. Ye, Rev. Mod. Phys. 75, 325 (2003).
[2] A. Marian et al, Science 306, 2063 (2004); M. C. Stowe, F. C. Cruz, and J. Ye, Phys. Rev. Lett 96, 153001 (2006).
[3] M. Shapiro and P. Brumer, J. Chem. Phys. 84, 4103 (1986); D. J. Tannor and S. A. Rice, J. Chem. Phys.
83, 5013 (1985); M. Shapiro and P. Brumer, Rep. Prog. Phys. 66, 859942 (2003).

[4] U. Gaubatz et al, J. Chem. Phys. 92, 5363 (1990); N. Dudovich et al, Phys. Rev. Lett. 94, 083002 (2005); K. F. Lee et al, Phys. Rev. Lett. 93, 233601 (2004).

[5] N. V. Vitanov et al, Adv. At. Mol. Opt. Phys. 46, 55 (2001).

[6] H. Rabitz et al, Science 288, 824 (2000).

[7] P. S. Julienne, E. Tiesinga, and T. Kohler, J. Mod. Opt. 51, 1787 (2004); C. A. Regal et al, Nature 424, 47 (2003); M. W. Zwierlein et al, Phys. Rev. Lett. 91, 250401 (2003); S. Jochim et al, Science 302, 2101 (2003); T. Bourdel et al, Phys. Rev. Lett. 93, 050401 (2003).

[8] J. M. Sage et al, Phys. Rev. Lett. 94, 203001 (2005); C. M. Dion et al, Phys. Rev. Lett 86, 2253 (2001).

[9] C. P. Koch, R. Kosloff, and F. Masnou-Seeuws, Phys. Rev. A 73, 043409 (2006); E. Luc-Koenig et al, Phys. Rev. A 70, 033414 (2004).

[10] P. D. Drummond et al, Phys. Rev. A 65, 063619 (2002); M. Mackie et al, Phys. Rev. A 63, 043415 (2001).

[11] P. M. Morse, Phys. Rev. 34, 57 (1929); A. Frank, A. L. Rivera, and K. B. Wolf, Phys. Rev. A 61, 054102 (2000).

[12] A. M. Weiner, Rev. Sci. Inst. 71, 1929 (2000).

[13] B. M. Garraway and K. Suominen, Rep. Prog. Phys. 58, 365 (1995).

[14] C. J. Bardeen, Q. Wang, and C. V. Shank, Phys. Rev. Lett 75, 3410 (1995); J. Cao, C. J. Bardeen, and K. R. Wilson, Phys. Rev. Lett 80, 1406 (1998); V. S. Malinovsky and J. L. Krause, Phys. Rev. A 63, 043415 (2001).