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Stimulated deceleration of diatomic molecules on multiple rovibrational transitions with coherent pulse trains

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Abstract

We propose a method of stimulated laser decelerating of diatomic molecules by counter-propagating π -trains of ultrashort laser pulses. The decelerating cycles occur on the rovibrational transitions inside the same ground electronic manifold, thus avoiding the common problem of radiative branching in Doppler cooling of molecules. By matching the frequency comb spectrum of the pulse trains to the spectrum of the *R*-branch rovibrational transitions we show that stimulated deceleration can be carried out on several rovibrational transitions simultaneously. This enables an increase in the number of cooled molecules with only a single laser source. The exerted optical force does not rely on the decay rates in a system and can be orders of magnitude larger than the typical values of scattering force obtained in conventional Doppler laser cooling schemes.

1. Introduction

While laser cooling is one of the key techniques of modern atomic physics [1–3], neutral molecules are notoriously challenging to cool to ultracold temperatures. To accomplish this feat one must exercise precise control over a multitude of internal degrees of freedom. A breakthrough in molecular cooling and slowing techniques—even for diatomic molecules—is anticipated to enable substantial progress in quantum information processing [4], matter–wave interferometric sensors [5], quantum-controlled chemical reactions [6] and precision measurements [7–9].

To date, the coldest samples of diatomic molecules were obtained by assembling them from ultracold atoms via photo—or magneto—association. This approach produced a gas of ground-state polar molecules near quantum degeneracy [10, 11]. However, so far only bialkali molecules have been produced in this way, and the number of molecules produced is fairly small ($\sim 10^4$). Deceleration of ensembles of cold molecules in electrostatic Stark decelerators has been demonstrated [12, 13], as well as 'Sisyphus cooling' of polyatomic molecules [14].

Direct laser cooling of molecules could yield substantially larger samples for a wider range of species. In traditional Doppler cooling, the radiative force originates from momentum transfer to atoms from a laser field and subsequent spontaneous emission in random directions. Repeating this optical cycle tens of thousands of times can slow down thermal beams and cool atomic samples down to the Doppler limit (typically mK). Unfortunately, most atoms and all molecules can radiatively decay to a multitude of states. Exciting population from all these lower-energy states requires a large number of lasers, which makes the conventional scheme impractical. Only for a narrow class of molecules with highly-diagonal Franck–Condon overlaps (i.e., 'near-cycling' electronic transitions) and appropriate rotational structure, this branching problem can be mitigated [15–17]. This has been successfully implemented with multiple diatomic molecular species, and magneto-optical trapping of molecules has been demonstrated [18–20]. However, the range of species to which this technique may be applied is expected to be limited.

Here we explore an alternative: employ absorption and *stimulated* emission on weak transitions inside the same molecular electronic manifold. The appeal of this concept is readily apparent: it should be applicable to essentially all polar species. This enables its application to a wide range of molecules which would not be

amenable to laser cooling, including polyatomic molecules, where rapid non-radiative decay processes including radiationless decomposition processes—often dominate the decay from excited electronic states [21].

The concept of stimulated forces was put forward by Kazantsev [22] in 1974; he proposed illuminating a two-level atom with a sequence of alternatively directed and oppositely detuned π -pulses. For an atom initially in the ground state, a π -pulse impinging from the left would drive the population upward, while the π -pulse from the right cycles the population back to the ground state. The net change of atomic momentum is twice the photon recoil momentum $p_r = \hbar k_c$, where k_c is the laser wave-vector. The advantage of this scheme over Doppler cooling is that the momentum transfer can occur much faster than the radiative decay; this is crucial for the use of rovibrational transitions, for which Doppler cooling is impractical due to the very long radiative lifetimes. Stimulated forces with counter-propagating π -pulses was explored in a number of works [23–25].

Closely related is the 'bichromatic force', or 'BCF' [26–33]. Here the trains of Kazantsev's π -pulses effectively arise from the beating of two counter-propagating CW lasers of different frequencies. While BCF experiments to date have been limited to atoms, BCF deceleration of diatomic molecules on near-cycling electronic transitions was recently proposed [34].

In this work we explore molecular slowing with coherent pulse trains. Pulse trains offer several advantages. First, the broadband structure of mode-locked lasers allows one to address multiple rotational levels simultaneously. Secondly, it simplifies stabilization of the multiple frequencies involved, even for species for which building reference cells is impractical [35]. Finally, by manipulating the phases of successive pulse trains, as shown below, the capture range of velocities addressed can be tuned. This manipulation of phase is crucial to correct for imperfect π -pulses, which will be an inevitable consequence of beam profiles and technical noise.

2. Qualitative considerations

We focus on the transitions between the rovibrational levels (v, J) inside the ground electronic potential. The frequencies $\nu_{J,J+1}^{v,v'}$ of the *R*-branch $(J \rightarrow J' = J + 1)$ electric-dipole-allowed transitions between rovibrational manifolds read

$$\nu_{J,J+1}^{\nu,\nu'} \approx \nu_{0,1}^{\nu,\nu'} + \left(3B_{\nu'} - B_{\nu}\right)J + \left(B_{\nu'} - B_{\nu}\right)J^2,\tag{1}$$

where $\nu_{0,1}^{v,v'}$ is the frequency of the $X(v, J=0) \rightarrow X(v', J'=1)$ transition and B_v are the rotational constants for the *v*th vibrational level [36]. This pattern matches the frequency comb (FC) spectrum of pulsed lasers which consists of a series of sharp equidistant peaks (teeth) located at

$$\nu_n = \nu_c + \nu_{\rm rep} \times n - \frac{\Phi}{2\pi T},\tag{2}$$

where *n* is an integer number, ν_c is the carrier frequency, the teeth-spacing $\nu_{rep} = 1/T$ is defined in terms of pulse repetition period *T*, and Φ is the carrier-envelope-offset (CEO) phase. We will focus on the $v = 0 \rightarrow v' = 1$ transitions. The molecular and the comb spectra could be matched by choosing $\nu_c = \nu_{0,1}^{0,1}$ and $\nu_{rep} = (3B_1 - B_0)/n'$, with *n'* being an integer. The *R*-branch spectrum (1) becomes Doppler-shifted for moving molecules; we will adjust Φ to follow the Doppler shift of the band-head frequency.

As an example, consider the LiCl molecule; here $\nu_c \approx 19.29$ THz with T = 0.95 ns for the number of teeth between nearby rovibrational transitions n' = 40. For the PbO molecule, $\nu_c \approx 21.63$ THz with T = 0.98 ns for n' = 15.

Based on these observations we propose the following scheme of stimulated deceleration of molecules with pulse trains. As illustrated in figure 1(a), the essential idea is to replace each of the Kazantsev's π -pulses by a train of N pulses, each of pulse area $\theta = \pi/N$. Interference of molecular transition probability amplitudes induced by the pulses leads to a frequency-dependence of the force resembling the FC spectrum. This will occur simultaneously on several rovibrational transitions. The elementary cycle will consist of two subsequent counter-propagating π -trains. Each cycle will transfer twice the recoil momentum $p_r = \hbar k_c$. To maximize the optical force we assume that the time delay between trains is negligible.

For a moving molecule, Doppler shifts due to the co- and counter-propagating trains have opposite signs. The counter-propagating/upward-stimulating train must be tuned below the resonance and the co-propagating train above the resonance. This can be attained by keeping the carrier frequencies of the two trains the same but having two different CEO phases.

Before proceeding to the full analysis, note that the spectrum given in equation (1) is for the *R*-branch. To avoid driving *P*-branch transitions, one would need to eliminate the low-frequency (n < 0) half of the comb spectrum in equation (2), thus reducing the problem to a collection of (separate) two-level systems. This truncation may be accomplished by installing a dispersive element and a static mask at the output of the cavity;



the mask would cut out a predefined spectral window. Such a technique has been used by the Orsay group [37] in pulsed laser cooling of the vibrational state distribution of Cs_2 molecules.

Furthermore, we would like to avoid driving the $v = 1 \rightarrow v = 2$ transitions, see figure 1(b). Fortunately, due to anharmonicity, $\nu_{0,1}^{1,2} < \nu_{0,1}^{0,1}$, so the $\nu_{1,2}^{1,2}$ bandhead is shifted to lower frequencies, already masked-out. Thereby only the higher-*J* rotational transitions will overlap with the truncated comb spectrum. The lowest *J* of the $v = 1 \rightarrow 2$ band overlapping with the comb spectrum could be estimated as $J_{\text{max}} = (\nu_{0,1}^{1,2} - \nu_{0,1}^{0,1})/(B_2 + B_1) \approx \omega_e x_e/B_e$, where we used the conventional spectroscopic notation [36]. For LiCl and PbO, this limits us to $v = 0 \rightarrow 1$ transitions with J < 6 and J < 10 correspondingly. This limitation to low *J*

is consistent with our neglect of higher-order non-rigid-rotor terms in equation (1). This limitation is of little consequence: at temperatures below 300 K, the majority of the molecular population is in these low-*J* levels. Another peculiarity is that dipole matrix elements vary across rovibrational transitions, while the trains must execute the full π rotation for all transitions simultaneously; to meet this requirement pulse shapers would need to be used so that the Rabi frequency of various transitions remains the same.

3. Formalism

Since the FC fields couple only pairs of molecular levels, the problem is reduced to finding the time evolution and optical force on a two-level system. Due to the rapid nanosecond time-scale of π -train cycles we may neglect slow radiative decay of the vibrational levels (relevant lifetimes are on the order of a millisecond). We also approximate short non-overlapping laser pulses by δ -functions. In this limit, the pulses are fully characterized by the pulse area θ and phase Φ .

In the interaction picture, the propagator U_{train} for a train of N pulses may be decomposed into a product of propagators due to individual pulses U_p : $U_{\text{train}} = U_N \dots U_2 U_1$. The pre-train $(t = t_0^-)$ and post-train $(t = t_0^+ + NT)$ values of the density matrix are related as $\rho(t_0^+ + NT) = U_{\text{train}} \rho(t_0^-) U_{\text{train}}^+$. The propagator across the *p*th pulse may be found analytically [38]: $U_p = \mathbf{I} \cos(\theta/2) + \mathbf{i}\sigma_p \sin(\theta/2)$, with $\sigma_p = \sigma_x \cos\eta_{\text{L},\text{R}}(t_p) - \sigma_y \sin\eta_{\text{L},\text{R}}(t_p)$, where $\sigma_{x,y}$ are the Pauli matrices. Here t_p is the arrival time of the *p*th pulse and L (left) and R (right) label the co- and counter-propagating π -trains in figure 1(a). The phase $\eta_{\text{L},\text{R}}(t) = \delta t \mp k_c z(t) - \Phi^{\text{L},\text{R}}(t)$ is the cumulative phase of the laser field experienced by the moving molecule, $z(t) \approx vt$. Focusing on a target velocity v_0 , we may redefine $\Phi^{\text{L},\text{R}}(t) = \delta t \mp k_c z_0(t) + \Phi_c^{\text{L},\text{R}}(t)$, where $z_0(t)$ is the spacial coordinate of the molecules which initially were at the center of velocity distribution, $\Phi_c^{\text{L},\text{R}}(t)$ is the control phase that we will tune to optimize the deceleration process. Then

$$\eta_{\rm L,R}(t) = \mp k_c \left(z(t) - z_0(t) \right) - \Phi_c^{\rm L,R}(t).$$
(3)

At this point we have a prescription for evolving the density matrix over time. The last needed ingredient is the expression for the mechanical momentum transferred to the two-level system. The fractional momentum kick due to a single train may be expressed in terms of the excited state population difference at the end and at the beginning of the train $-\Delta p_{\text{train}}/p_r = \rho_{ee}(t_0^+ + NT) - \rho_{ee}(t_0^-)$ [38].



Figure 2. Dependence of the fractional momentum kick per deceleration cycle on the Doppler defect phase. Here $N_c = 500$ and π -trains are composed of four $\pi/4$ pulses. The overview plot in panel (a) was generated while the velocities were kept constant and control phases $\Phi_c^{L,R} = 0$. Panel (b) zooms in onto the central tooth of panel (a).

For the elementary cycle

$$\frac{\Delta p_{\text{cycle}}}{p_{r}} = \rho_{ee} \left(t_{0}^{+} + 2NT \right) + \rho_{ee} \left(t_{0}^{-} \right) - 2\rho_{ee} \left(t_{0}^{+} + NT \right).$$
(4)

Based on the described formalism we developed a Mathematica package to simulate stimulated deceleration by coherent pulse trains. We start by discussing our computed dependence of momentum kick per cycle on the Doppler 'defect' phase $k_c(v - v_0(t))T$, shown in figure 2(a). First of all, Δp is a periodic function, reflecting the underlying periodicity of the FC spectrum. The transferred momentum spikes at values of the phase which are multiples of 2π . At these points the maximum transferred momentum is limited to twice the recoil momentum, as expected from equation (4). This happens only when during the cycle the system starts and ends in the ground state, with a full transfer of the population to the excited state by the first train, i.e., when the π -train conditions are satisfied. Qualitatively, at such values of the phase the probability amplitudes transferred by subsequent pulses interfere constructively.

The detailed profile of the momentum transfer shown in figure 2(b) depends on the number of pulses inside π -trains and the number of cycles. For a fixed number of pulses the calculated profile displays a very complicated substructure resulting from intricate interferences of probability amplitudes driven by the multitude of pulses. In accordance with the time-frequency uncertainty principle, as the number of pulses grows larger, the peaks become narrower effectively reducing the capture velocity range to zero. Because of this effect, it is natural to wonder how to increase the number of decelerated molecules at the end of the process. This goal can be attained by imposing the following phase relation between the last and the first pulses of two subsequent π -trains:

$$\Phi_c^{\mathrm{R,L}}\left(t_{M+1,1}\right) = -\Phi_c^{\mathrm{L,R}}\left(t_{M,N}\right) + \pi.$$
(5)

Here $t_{M,n}$ is the arrival time of the *n*th pulse of the *M*th train. The origin of the phase relation (5) may be readily understood using the Bloch sphere visualization method.

This method maps the quantum state vector of a two-level system onto a surface of a sphere. The south/ north poles correspond to the pure ground/excited states, respectively. Other points are uniquely associated with various superposition states. The interaction with *n*th pulse of the *M*th train leads to an instantaneous clockwise rotation of the Bloch vector about the axis $\mathbf{O}_{M,n}$ on angle equal to the pulse area θ . The $\mathbf{O}_{M,n}$ direction is determined by rotating the *y*-axis about the *x*-axis on angle $\eta_{L,R}(t_{M,n})$, (see the equation (3) in the main text), the cumulative phase of the laser field as seen by the moving molecule. The axes $\mathbf{O}_{M,n}$ lie in the *x*-*y* plane and their directions can be controlled by choosing the $\boldsymbol{\Phi}_{c}^{R,L}$ phases.

To begin with, assume that $v = v_0$ and the control phase $\Phi_c = 0$. Then the phases $\eta_{L,R} = 0$ and the rotation axes $O_{M,n}$ coincide with the *y*-axis. The right π -train rotates the Bloch vector from the south to the north pole of the sphere and the left π -train brings it back to the south pole. If the molecular velocity *v* is somewhat different from v_0 , the phase $\eta_{L,R} = \mp k_c (v - v_0) T$ is no longer zero. This leads to 'skewed' rotation axes (see figure 3(a)) and at the end of the train the Bloch vector, marked by the letter 'c' in 3 (a), no longer points to a pure excited state. The phase mismatch will accumulate further due to the interaction with the left train. This results in momentum kick per cycle much smaller than $2p_c$ or even of the opposite sign.

The phase mismatch problem can be largely mitigated by flipping the direction of the rotation axis for the subsequent π -train: $\mathbf{O}_{M+1,1} = -\mathbf{O}_{M,N}$ (this translates into the equation (5)). Then for $\nu = \nu_0$ the Bloch vector when acted upon by the right train exactly retraces the 'left-train' trajectory in the opposite direction. For $\nu \neq \nu_0$,





the retracing will not be perfect, but the phase mismatch will be less pronounced compared to the 'uncorrected' scenario.

In addition to increasing the velocity capture range, the phase relation (5) makes our scheme insensitive to laser intensity variations in which the total pulse area of the train differs from π . Indeed, with the phase reversal (5), as long as the pulse areas of the left and right trains are the same, the Bloch vector in figure 3 exactly retraces the original trajectory (driven by the left train), ending up in the ground state, independent of the value of the pulse area. This is essential in any real experiment, where the intensity of the beam will vary across its spatial profile, and lasers often exhibit intensity fluctuations. With this scheme, ensuring accurate cycling is simply a question of aligning the counterpropagating beams and employing a laser with short-term (pulse-to-pulse) intensity stability. Deviations from these conditions are addressed in section 4. While our paper was in preparation, a similar mechanism has been elucidated for bichromatic optical forces [39]. During the preparation of this manuscript, we became aware of the work of [40], which also proposes using stimulated emission to slow molecular beams. [40] propose solving the problem of incomplete π -pulses using adiabatic rapid passage, rather than phase reversals as in the current work.

As the molecules slow down, the phases have to track $v_0(t)$ as proposed in [38]; a typical rate of phase-tuning is $d\Phi/dt \approx p_r^2/(\hbar m)/N$, where *m* is the molecular mass. Experimentally the required phase-tuning can be attained with electro-optical modulators.

In figure 4(a) we investigate the time evolution of the velocity distribution for LiCl molecules. We consider the case of a cryogenically cooled molecular beam with a 140 m s⁻¹ forward velocity and a rotational temperature of ≈ 1 K [41]. The forward velocity distribution is modeled as a Gaussian with half-width equal to 20 m s⁻¹. Initially all molecules are in the ground vibrational manifold with ($J \leq J_{max}$) and they enter the interaction volume at the same moment of time (t=0). The laser phase follows the time evolution of v_0 , so the maximum of the optical force is always at $v_0(t)$. To maximize the velocity capture range, the control phase changes as equation (5). The strongly peaked force (figure 2) leads to the compression of velocity distribution near its maximum. However since the force profile narrows with increasing number of cycles N_c , the width of the maximum of velocity distribution starts to decrease too. The area under the maximum also decreases, that means that the effective number of cooled molecules grows smaller. This is caused by a build-up of destructive interferences at the wings of the force profile.

To improve the final number of decelerated molecules one could simply stop the trains and wait until all the molecules radiatively decay into the ground ro-vibrational manifold and then restart the deceleration process. This would clear out all the unwanted superpositions. However the required time-scales are too long. Instead, one could employ the much faster radiative decay of the upper electronic states, as shown schematically in figure 1(c). In this process additional broad-band laser pulses would drive the transitions: $X(v, J) \rightarrow A(v', J')$, with the lower-frequency transitions $X(v = 0, J < J_{max}) \rightarrow A(v', J')$ filtered out. Due to the spontaneous decay of the A(v', J') levels, most of the population after several absorption-radiative decay cycles gravitates towards the manifold $X(v = 0, J < J_{max})$ used as a starting point for stimulated deceleration. We simulated such a reset/stimulated deceleration scheme in figure 4(b). Here the stimulated deceleration process is the same as in figure 4(a), with the addition of resetting pulses applied every 10 000 cycles. We observe that while the peak of velocity distribution becomes narrower over time, its height increases so that the area (i.e., the number of molecules) increases.

So far we have neglected fine (or hyperfine) structure of molecular states. These could complicate the analysis as the pulses could couple several levels. Still one could isolate two-level transitions using chiral pulse

5



Figure 4. Time evolution of the forward velocity distribution of an ensemble of decelerated LiCl molecules. All molecules are initially thermally distributed over the rotational states of ground vibrational state of the ground electronic state. The initial velocity distribution is modeled by a gaussian, as discussed in the text. The single pulse area was $\theta = \pi/4$, with a pulse repetition period of T = 1 ns. Each cycle takes 8 ns, and $N_c = 10^4$ corresponds to 80 μ s of deceleration. (a) Velocity distributions for the stimulated deceleration scheme with Doppler phase tracking and train-to-train phase correction. (b) The same as in (a) but with additional population reset applied every 10 000 cycles.

trains. For example, for the singlet ground state diatomic molecule one could use the σ^+ (σ^-) circularlypolarized trains. Then a subset of two-level transitions ($v = 0, J, F = I + J, M_F = I + J$) \Leftrightarrow ($v = 1, J' = J + 1, F' = I + J + 1, M_{F'} = I + J + 1$) becomes isolated.

4. Corrections for spatially extended source and pulse imperfections

The above calculations consider a single molecular trajectory, beginning at position z_0 and velocity v_0 , and included the effects of a spread in v around v_0 . In actual experiments, molecules are produced in pulses of finite spatial spread as well as velocity spread. Unfortunately, this means that our deceleration scheme will not apply equally well to all molecules. Molecules at different positions along the beam axis will see different relative phases for the left-going and right-going pulses, so our π -phase reversal will only be perfect for a vanishing subset of the original pulse.

For $v \neq v_0$ and $z(0) \neq z_0(0)$ the retracing will not be perfect, and the phase reversal error will be changing from one cycle to another as $|\delta \phi| = |\text{Mod}[\eta_L(t_{N_c,1}) - \eta_L(t_{N_c,N}), \pi]| = |\text{Mod}[2(kz(0) + (2N_c - 1)(N - 1)kT(v - v_0)), \pi]|$. Although the perfect phase reversal can not be realized for all molecules simultaneously, introducing the π - phase offset leads to improving the deceleration force profile as compared to the 'uncorrected' scenario. As an illustration of this effect is shown in figure 5. We compare the deceleration force velocity dependence profiles calculated for $N_c = 1000$ cycles with and without introducing the π -phase offset between the right and left π -trains, including molecules starting their trajectories from different *z*-positions.

As seen in figure 5, imperfect areas and spread in *z* introduces a significant degradation in the performance. However, simulations of a spatially extended molecule pulse indicate that the scheme is surprisingly robust for molecules which begin their trajectories near the ideal one. As shown in figure 6, a large fraction of the molecules within $\pm \lambda/4$ of the ideal trajectory (modulo one wavelength) will follow a similar deceleration path.

5. Technical considerations

A practical realization of our proposed deceleration scheme requires the generation of phase-coherent pulse trains, with controllable phase relationships, of sufficient power to decelerate molecules in reasonable distances.



Figure 5. The velocity dependencies of an average momentum kick per cycle after a 1000 cycles for the LiCl molecules stating their trajectories from different z-positions. The pulse repetition period is T = 1 ns. The red and blue curves were obtained with and without introducing the π -phase offset between the left and right pulse trains. The pulse area variations were considered as $\theta_{Ncl}^{right} = \pi/4(1 - \varepsilon_c)$, $\theta_{Ncl}^{left} = \theta_{Ncl}^{right}(1 - \varepsilon_{lr})$, where ε_c , ε_{lr} are the random values: the left pannels ((a)–(c)) ε_c varies from –0.01 to 0.01, ε_{lr} varies from -10^{-4} to 10^{-4} .

Fortunately, it is now commonplace to generate phase-coherent pulse trains, thanks to modern FCs generated by mode-locked lasers [42–45].

Moreover, high-fidelity, line-by-line spectral shaping has been demonstrated for individual FC frequency components while preserving phase stability [46, 47]. One can now consider addressing vibrational transitions directly with coherent pulse trains due to the development of new light-sources in the mid-infrared (IR) spectral regions [48]. Driven by interest in molecular spectroscopy, there has been significant work on the development of mid-IR FCs, and the capabilities of light sources capable of addressing vibrational transitions is rapidly advancing. Early mid-IR comb sources were generated by down-conversion of near-IR mode-locked lasers through difference frequency generation; greater efficiency can be obtained with optical parametric oscillators [43–45]. More recently, direct generation of mid-IR combs has been enabled by technologies such as fiber lasers and quantum cascade lasers [49]. Present FC's can generate average output powers in excess of 1 W in the mid-IR [43]. Increases in both power and spectral coverage are expected [50].

For a beam of area *S*, a molecular transition dipole moment of *D* and gaussian pulses of temporal width τ_p , the expected average beam power requirements are $P \approx \frac{\hbar^2 c c_0 S}{2D^2 T \tau_p} \cdot \left(\frac{\pi}{N}\right)^2$, where *N* is the number of pulses per π train.

We consider the case of a cryogenic beam of LiH molecules with initial velocity of 140 m s⁻¹. Due to its small mass, LiH is potentially one of the easier molecules to decelerate, although its ${}^{1}\Sigma$ electronic ground state makes it ill suited for Stark deceleration or Zeeman deceleration techniques. The $v'' = 0 \rightarrow v' = 1$ transition lies at a wavelength of 7 microns [51], with a transition dipole of 0.12 Debye [52]. As a hydride, only the lowest rotational state would have significant population in a cryogenic beam [53]. We take a $T \sim 1$ ns repetition period with $n_t \sim 10^2$ comb teeth, for $\tau_p = T/n_t \sim 10^{-11}$ s. With a beam area of $S \sim 1$ mm² and $N = 10^2$, we



Figure 6. The same time evolution as shown in figure 4, but for an ensemble of molecules which begin their trajectory at arbitrary positions within the intervals $-\lambda/4 + m\lambda < z < \lambda/4 + m\lambda$, m = 0, 1, ... Additionally, errors between the pulse area of the left- and right-going pulse trains were introduced at the level of $\delta\theta = \pi \cdot 10^{-4}$. In (b), there are additional population resets applied every 7500 cycles.

find a power requirement of 10 W. As LiH will require roughly $2 \times 10^4 \hbar k$ to decelerate to rest, the deceleration process will take roughly 2 ms, in which time the molecules will move less than 0.2 m, well within the Rayleigh range of a beam of this wavelength and diameter.

Now we discuss another technical issue: the imperfect polarization of laser pulses. As an example, consider driving stimulated transitions with linearly polarized pulses and denote \mathcal{A} as the degree of unwanted circular polarization. Ideally the pulses would drive the $|J, M\rangle \leftrightarrow |J + 1, M\rangle$ transitions. However, because of the admixture of circular polarization, one would also drive the transitions to the $|J + 1, M - 1\rangle$ and $|J + 1, M + 1\rangle$ magnetic substates. This is problematic, because the states $|J + 1, M + 1\rangle$ and $|J + 1, M - 1\rangle$ are dark states for linear polarization. The unwanted fraction of the population transferred due to a single cycle is $\sim \mathcal{A}$.

Commercial polarization optics routinely achieve polarization extinction ratios in excess of 10^5 . For the electric fields amplitudes, this is a factor of 300 suppression for the circular polarization relative to the linear. Naively, one might expect molecules to be pumped into the dark state over the course of 300 successive π trains. However, *because* the dark state population does not participate in the slowing, we should not expect coherent population accumulation in this dark state: population transferred to the dark state in successive pulses will no longer be in phase with population transferred in earlier pulses. Consequently, we would expect to be able to undergo $\sim 10^5 \pi$ -train sequences before being transferred to the dark state, which is larger than the $N_c = 10^4$ cycles we are nominally proposing before repumping. Similar arguments apply to misalignment of the linear polarization of two counter-propagating pulse trains, where we also expect to align polarizations to levels given by extinction ratios of 10^5 .

Transverse losses play a role in any deceleration scheme. Traditional Stark decelerators typically suffer significant losses at low velocities due to transverse motion [54, 55]. These losses can be ameliorated by designs that provide continuous transverse confinement [56]. Schemes for laser deceleration of atomic beams, such as the Zeeman decelerator, typically exhibit an increase in their angular divergence for two reasons: a decrease in their longitudinal velocity and an increase in their transverse temperature due to spontaneous emission events [57]. The scheme detailed in this work will exhibit an increase in angular divergence for the former reason, but not the latter, as stimulated emission will leave the transverse velocities unchanged. Possible extensions to our technique could use either transverse cooling or transverse confinement to reduce or eliminate this transverse divergence.

6. Conclusions

We have proposed a method of stimulated deceleration of the ensembles of diatomic molecules by the coherent trains of ultrashort shaped laser pulses. The deceleration is based on the stimulated transitions driven within each of the several pairs of rovibrational states in the ground electronic potential. Since all the transitions are within the ground electronic potential (where the lifetimes of the levels are long), the radiative decay induced loss of the population to the unwanted states is avoided. The resulting scattering force is based on the stimulated transitions and is not limited by the small radiative decay rates of the involved levels. Using the pulse shaping allows one to match the positions of individual FC teeth with the frequencies of chosen molecular transitions. Manipulating the carrier envelope phase offset between the subsequent pulses allows the FC to remain on resonance with a given velocity group of the ensemble and makes the scheme robust to laser intensity variations. Manipulating the intensities of individual FC modes allows to keep the pulse area constant for the different rovibrational transitions compensating the difference of corresponding dipole matrix elements. The evolution of the velocity distribution of cryogenic molecular beam decelerated according to the proposed scheme has been calculated, and appears promising.

The technical demands for laser power strain the capabilities of current mid-IR lasers, but laser technology at these wavelengths is expected to evolve rapidly. Additionally, similar ideas to those proposed here can potentially be applied to visible transitions, which offer greater dipole moments and larger laser powers. There, larger spontaneous emission rates will be a technical challenge, but potentially an aid in providing population resets.

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