Complete Quantum State Selectivity in Cold Molecular Beams Using Deflection-Resistant Dark States in a STIRAP Configuration

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Complete quantum state selectivity in cold molecular beams using deflection-resistant dark states in a STIRAP configuration.

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One of the main goals of chemical dynamics is the creation of molecular beams composed of a single (vibrational, rotational, and magnetic) quantum state of choice. In this paper we show that it is possible to achieve *complete* quantum state selectivity by producing resistance to electromagnetically induced deflection (EID) and that the state to be selected can be "dialed in" at will. We illustrate the method by showing in detail how to purify thermal beams of the LiRb and IF molecules to yield molecular beams composed of a variety of pre-chosen single internal quantum states and/or superpositions of such states. We expect that this method will be implemented in all subsequent explorations of the fundamentals of chemical reactions and their control, and the use of cold molecules as a vehicle for studying some of the most profound issues of quantum dynamics.

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Ever since their invention, molecular beams have proven invaluable in the study of intermolecular forces, chemical reactions, interaction of matter with electromagnetic fields, scattering of atoms and molecules from surface, and structures of giant molecules [1]. Molecular beams have enhanced our understanding of inter- and intra-molecular dynamics, chemical reactions, interaction of light and matter, scattering of atoms and molecules from surfaces, and the structure of large molecules, including molecules of biological importance [2, 3]. Usually molecular beams are composed of thermal distributions of internal states, and although their temperature can be as low as a few mK, it is clear that the ability to pre-select a *single* internal quantum state of choice [4] would be of tremendous importance as it will allow for the measurement of *state-to-state* differential cross-sections, the most detailed entity that can be observed in the context of molecular collisions [5]. The pre-selection of individual rotational states is also a good starting points for the clean preparation of aligned [6] and oriented [7] molecules. Moreover, since molecular beams are nearly decoherence free, the formation of molecular beams containing "tailor made" *superpositions* of internal states would be highly desirable for quantum encoding and quantum memory storage.

In the past a number of directions of purifying thermal molecular beams have been pursued. These techniques include: hexapole devices to single out one out of two rotational states [8] or the lowest (or highest) of many states [9] and the deflection of ultracold molecules via the use of optically induced dipole forces in far off-resonance traps (FORT) [10]. While the FORT method may be an effective method of preparing molecules in a chosen rotational state, the method cannot induce vibrational selectivity. Thus, the general task of selectively preparing molecular beams composed of a *single* ro-vibrational state of our choice has so far not been achieved.

In this paper we show how, using Coherent Control techniques [4], one can convert thermal molecular beams into beams containing only a *single* pre-selected (ro-vibrational and magnetic) internal state. The method, based on the electromagnetic preparation of "deflection-resistant" states, is best explained via a model composed of three molecular states ($|g\rangle$, $|e\rangle$, $|s\rangle$) interacting with two spatially inhomogeneous electromagnetic fields, the "probe" field $\varepsilon_p(X)$ and the "control" field $\varepsilon_c(X)$, where X is the spatial variable. The $\varepsilon_p(X)$ and $\varepsilon_c(X)$ fields, whose effective strengths are parameterized by the Rabi frequencies $\Omega_p(X) = \varepsilon_p(X) \cdot \mu_{e,g}/2\hbar$ and $\Omega_c(X) = \varepsilon_c(X) \cdot \mu_{s,e}/2\hbar$, where $\mu_{e,g}$ and $\mu_{s,e}$ are the transition dipoles for the $|g\rangle \leftrightarrow |e\rangle$ and $|e\rangle \leftrightarrow |s\rangle$ transitions, are energetically detuned from these one-photon transitions by δ_p and δ_c, respectively.

Relative to the FORT [10] method, our method *reverses* the roles of the state to be selected and the states to be discarded: The discarded states are those that suffer deflection, while the selected state is an electromagnetically generated "deflection-resistant" dark state. Molecules in the discarded states simply experience an effective dipole force due to the lack of the two-photon resonance. At the same time we render our chosen (vib-rotational) state $|g\rangle$, "deflection resistant" by tuning the two fields to be in *two-photon* resonance with the $|g\rangle \leftrightarrow |e\rangle \leftrightarrow |s\rangle$ transition. The chosen state become transparent to the probe field because it evolves into a *dark state* of the same type encountered in *"Coherent Population Trapping"* (CPT) [11, 12], *"Stimulated Raman Adiabatic Passage"* (STIRAP) [13], and *"Electromagnetically Induced Transparency"* (EIT) [14–17]. Such dark states are known to result from the a destructive interference between two overlapping resonances arising from two Autler-Townes [18] split dressed-states that are broadened due to the presence of a continuum [19, 20] (e.g. that of the spontaneously emitted photons from the $|e\rangle$ state). As a result of the interference, a transparency

window in which no absorption of the probe field occurs is formed at $\omega_{e,g} = (E_e - E_g)/\hbar$, justifying the name "dark state". Since the dark state is oblivious to the field, it feels no force whatsoever and sails through the three slits of the setup depicted in Fig. 1 in a straight line, ending up as the only state left in the beam. An approach for deflection of polaritons induced by an EIT dark state [?] differs from the current proposal in the origin of the forces, experimental set-up, and temperature requirement.

We now detail the use of this method for quantum state selectivity: As shown in 1, a supersonic molecular beam collimated by two sequential skimmers is irradiated by a spatially inhomogeneous control field ($\varepsilon_c(X)$) somewhat detuned from the $\omega_{e,s}$ transition frequency. Further down-stream a Gaussian shaped spatially inhomogeneous probe field ($\varepsilon_p(X)$) irradiates the molecular beam. Its frequency is chosen such that the two-photon resonance condition, $\delta_{two} = \delta_p - \delta_c = 0$, is satisfied. By positioning the laser beams such that the molecules are subjected to $\varepsilon_c(X)$ *before* they see $\varepsilon_p(X)$ (the "counter intuitive ordering"[13, 21]), we make sure that the $|g\rangle$ state we wish to select will in fact evolve into a dark state.

The dots of 1 represent dark state molecules that are not subject to any force and sail through the slits in a straight line. The triangles of 1 represent molecules which are in other internal states and thus do not satisfy the two-photon resonance and are subject to a non-zero force. Such molecules are deflected away. We will give a possible set-up as an example. For a 10 micron laser focus and a 1 degree angle between the laser beam and the molecular beam, the effective length of the laser profile seen by the molecular beam is ~ 600 microns; in addition, the Rayleigh length of a 586 nm laser, as used in our numerical simulation, is estimated to be 750 microns given a 10 cm focal length and 6.3 mm aperture diameter. Both of these lengths determines the time scale of the interaction time: a few μs.

In order to demonstrate that the system follows adiabatically a particular field-dressed state, we first obtain the system wave function by expanding it in the bare states basis $|\Psi\rangle = |g\rangle\Psi_g + |e\rangle\Psi_e + |s\rangle\Psi_s$, and solve for the expansion coefficients $\Psi_{g/e/s}(t)$ which satisfy the matrix time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}|\Psi(X,t)\rangle = \underline{\underline{\mathbf{H}}}(X,t) \cdot |\Psi(X,t)\rangle \tag{1}$$

where

$$\begin{aligned}\underline{\underline{\mathbf{H}}}(X,t) &= 2\left[\Omega_p(X,t)|g\rangle\langle e| + \Omega_c(X,t)|s\rangle\langle e|\right.\\ &+ \left.\frac{\delta_p}{2}|e\rangle\langle e| + \frac{\delta_{two}}{2}|s\rangle\langle s| + c.c.\right]\end{aligned} \tag{2}$$

with $\Omega_p = \mu_{e,g}\cdot\varepsilon_p/2\hbar$ and $\Omega_c = \mu_{s,e}\cdot\varepsilon_c/2\hbar$. In addition, for both $\delta_{two} = 0$ and $\delta_{two} \neq 0$, we find the three adiabatic states $\underline{\psi}^{(1,2,3)}$ and their eigenenergies $\mathcal{E}^{(1,2,3)}$. For the target state, $\delta_{two} = 0$ is chosen and one of the eigenenergies is $\mathcal{E}^{(1)} = 0$, i.e., a *dark state*. When the
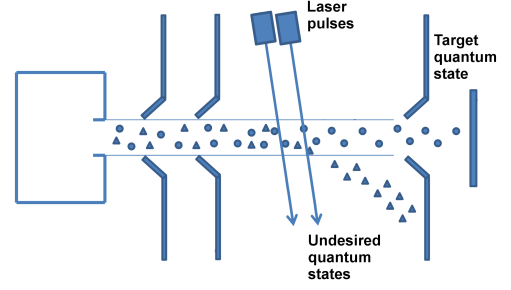

FIG. 1: (Color online) The purification scheme: target state molecules (filled circles) sail through the three slits; molecules in other states (filled triangles) get deflected. Note, the laser beam is focused slightly off axis relative to the molecular beam to maximize the energetic gradient.

molecule encounters $\varepsilon_c(X)$ spatially before $\varepsilon_p(X)$ (the "counter-intuitive ordering"[13]), $\underline{\psi}^{(1)}$, corresponding to $\mathcal{E}^{(1)} = 0$, is the only time-dependent field-dressed state that correlates with the chosen bare state $|g\rangle$, at $t = -\infty$ which, therefore, continues to evolve as a dark state, oblivious to the external fields. For other states, where $\delta_{two} \neq 0$, the system adiabaticly follows a particular field-dressed state, the field-induced potential of which is not homogenous in space. In all of our numerical simulations, the projection of this adiabatic state to the "trapping state" in FORT [10] is extremely close to one. Therefore, these other states, where $\delta_{two} \neq 0$, are subject to deflection forces.
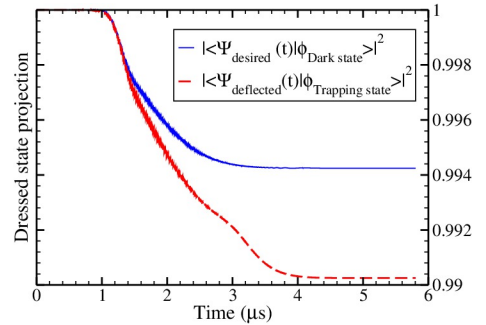

FIG. 2: Adiabatic following of the desired state (LiRb, $\nu_X = 0, J_X = 0$) in solid blue and the deflected state (LiRb, $\nu_X = 0, J_X = 1$) in dashed red.

This much simplified three-level model we described in 1 is adopted to give a straight-forward description of adiabatic following of different field-dressed state, a field-resistant dark state or the deflected trapping state, of the molecules depending on δ_{two}. However, to be more realistic, there are three types of terms that may modify the

Hamiltonian in 1 to disturb or even destroy the adiabatic following due to a finite one-photon detuning and intense laser fields applied: *counter-rotating terms*, coupling to *other intermediate states*, and other field dressing terms due to pulse mixing where the "probe" field can act as "control" field, vice versa. The details of these additional terms will be given in the supplemental material and we will only summarize the conclusion here. In order to test whether our previous conclusion by using a simplified three-level model still holds in the presence of these additional terms, and to evaluate the effective optical potential imposed on a specific state, we incorporate all of these additional terms in our numerical simulations and expand the three-level models to 7-,9- and 11-level models for convergence studies. In the many-level simulations, we project the simulated time-dependent wave packet of the molecules onto the field-dressed states. As shown in 2, we observe that nearly all the molecules are following the field-dressed states, i.e. the desired molecules are adiabatically the field-resistant dark state and the deflected molecules are following the trapping state. The observed nearly perfect adiabatic following proves the validity of the optical potentials, which are later applied to the classical motion study, and that these optical potentials correspond exactly to their equivalents in a simple three level model. Note, due to inevitable scattering of the molecules with the photons and the subsequent spontaneous emission loss, the projection of the total wave function onto the field dressed states is close to but not equal to unity.

By solving the full time dependent Schrödinger equation for the multi-level models, and ascertaining that the molecular system indeed follows one of the adiabatic states , we can then confidently obtain the classical forces acting on the molecules, given as $F(X,t) = -\frac{\partial}{\partial X}\mathcal{E}(X,t)$ and compute the classical trajectories of molecules in different quantum states subject to these forces.

As a first example we consider the purification of a thermal beam of LiRb molecules. In the arrangement depicted in Fig. 1, the average longitudinal velocity of the LiRb beam as it passes through the skimmers is ~ 500 m/s. The sequential-slits arrangement forces the average transverse velocity to be zero, while the supersonic expansion reduces the longitudinal and transverse temperatures to values as low as $\sim 5^o$K. Since the vibrational and rotational temperatures follow the translational temperature, only the ground ($\nu_X = 0$) LiRb vibrational level, where X denotes the $X^1\Sigma$ ground electronic state, is populated at 5^oK, with the higher vibrational states remaining empty. In contrast, the range of the rotational levels that are populated at this temperature is $J_X = 0$ to $J_X = 7$, with a rotational constant $B_e = 0.2158\,\mathrm{cm}^{-1}$.

To demonstrate the ability to purify the system into *any* pre-selected rotational state, we study two cases in which we create a beam composed entirely of the $|\nu_X = 0, J_X = 0\rangle$ state or the $|\nu_X = 0, J_X = 3\rangle$ state. Numerical simulations of classical trajectories under the
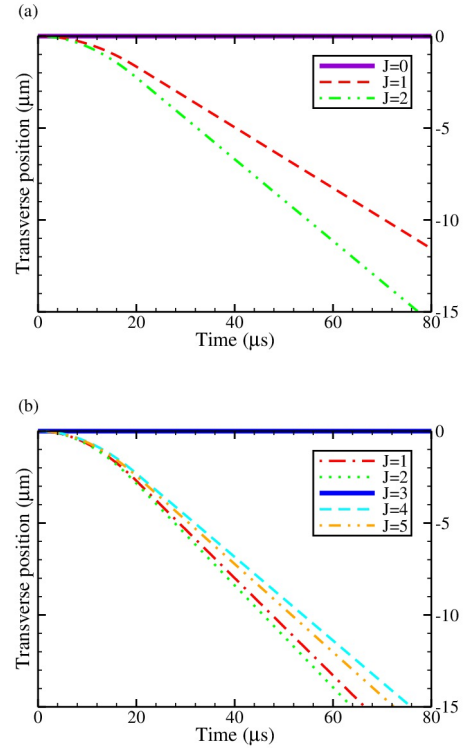

FIG. 3: Molecular beam purification into different rotational states. Shown is the spatial evolution in the transverse direction as a function of time for: **(a)** the $|\nu = 0, J = 0\rangle$ target quantum state (purple solid line); **(b)** the $|\nu = 0, J = 3\rangle$ target quantum state (blue solid line).

action of the optical fields when $|\nu_X = 0, J_X = 0\rangle$ or $|\nu_X = 0, J_X = 3\rangle$ is selected, are presented in 3a and 3b, respectively. Both the ε_p and ε_c electromagnetic fields, have powers of 0.8 W and waist sizes of 10 μm. The one-photon detuning of the probe field, δ_p, is set to be 300 cm^{-1} on the red side of $|\nu_B = 0, J_B = J - 1\rangle$. As shown in 3a (b), the target states ($|\nu = 0, J = 0\rangle$ or $|\nu = 0, J = 3\rangle$), are made to evolve into field-dressed dark states by setting the laser parameters to fulfill the two-photon resonance condition $\delta_{two} = 0$. In contrast, all other states, $|\nu = 0, J \neq 0\rangle$ ($|\nu = 0, J \neq 3\rangle$), do not satisfy this condition and molecules in these undesired states are thus deflected towards the high-field region of the laser waist and move away from the molecular beam. Furthermore, the trajectories of the deflected molecules in various quantum states are slightly different, implying different forces due to different δ_{two}. Regarding the temporal evolution of the wave function of the target molecules, it is well established that keeping both lasers on will conserve the quantum superposition between the two ground states ($|g\rangle = |\nu = 0, J\rangle$ and $|s\rangle = |\nu = 1, J\rangle$). However, if we adiabatically turn off the probe field before the control field, after the separation is complete, we can transfer the population back to the single target state, $|\nu = 0, J\rangle$. The temporal sequencing of the elec-
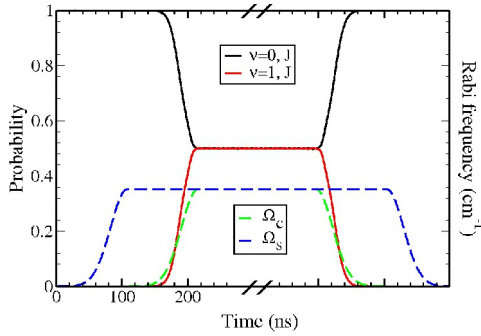
FIG. 4: (Color online) Making just one bare state ($|\nu = 0\rangle$) deflection resistant by forming and unforming a transient superposition with the $|\nu = 1\rangle$ state. Shown is the time dependence of the populations of the two states and that of the laser fields. The turn-off of the fields is the time reversal of their turn-on.

tromagnetic fields during the whole process, on and off of the fields, is presented on 4, where we can see the adiabatic evolution of the population in states $|g\rangle$ and $|s\rangle$.

The thermal spreading should also be considered to demonstrate the applicability of such a separation scheme in reality. For *longitudinal thermal spreading* the main effect is Doppler broadening. For a beam with longitudinal central velocity of 500 m/s, δ_v - the longitudinal velocity spread is on the order of 10% i.e., ~ 50 m/s. This results in relative frequency spread of $\delta_\omega/\omega = 1.6 \times 10^{-7}$ which is negligible relative to both the one-photon detuning and the detuning from two-photon resonance. In the *transverse direction*, for the *deflected molecules* we discard, a strong enough light field guarantees that the light induced deflection potential these molecules experience is greater than the transverse thermal spread in kinetic energy. Our experience is that as long as $\Omega_{max}^2/\delta > 5 \cdot m v_t^2/2$, where v_t is the velocity in the transverse direction, the separation scheme works extremely well. v_t can be controlled to some extent by tuning the ratio between the slit size and the longitudinal distance between the first two slits.

The results presented here display a high degree of selectivity with respect to the two photon resonance condition. For example, if we set $\delta_{two} = 0$ for a Λ system originating in the LiRb $|\nu_X = 0, J_X = 0\rangle$ state, δ_{two} for the $|\nu_X = 0, J_X = 1\rangle$ state will be as small as 0.003 cm^{-1} = 90 MHz. Yet the discrimination between these two states works well! Such great resolution makes it possible to differentiate between hyperfine levels, f, or even various m_f sub-levels. For example, in atomic ^{6}Li subject to moderate magnetic fields, the splitting between the

$|f = 1/2, m_f = 1/2\rangle$ level and the $|f = 1/2, m_f = -1/2\rangle$ level is 75 MHz, enough to allow for the selective preparation of a beam composed of only one of these states by the present method.

One of the merits of such a proposal lies in the robustness against realistic imperfect laser conditions. Such an advantage over methods that *collect* the deflected molecules is that small effects on the trajectories of the deflected molecules are irrelevant because on the *non-deflected* molecules are collected, as long as the deflection is large enough to prohibit the arrival of the deflected molecules to the third slit, as shown in 1. As for the *non-deflected* molecules, their properties are due to the formation of dark states, which are the heart of the STIRAP and EIT experiments, and that it was shown in the past, both theoretically and experimentally, that these processes are robust against laser imperfections such as, intensity fluctuations, frequency drifts, and imperfect laser beam overlaps [13]. More detailed discussions on the robustness can be found in the supplementary material (section E).

The most immediate future application of our method is the selective preparation of beams containing *superposition states,* such as those existing in 4 when the two pulses are on. Such "superposition beams," whose coherence is expected to survive for long times because the decoherence processes inside the beam are extremely slow, would find use in quantum memory and quantum computation devices. Another future direction would involve the use of broad-band, short laser pulses. In the straightforward application of the present technique, the molecular level spacings set a lower limit on the pulse bandwidth to be used, hence on the time scale of the separation process. In order to speed up the process by employing broadband lasers of short (~ 1 ps) durations and enjoy the higher field strengths associated with such lasers, we propose to use Coherent Control pulse-shaping techniques[24] which allow one to home in on a desired two photon transition and render the state of our choice "deflection-resistant" even when the broad laser spectrum covers a number of transitions which satisfy the two photon resonance condition. Another future application would involve the use of different polarizations, or spatially inhomogeneous magnetic fields to deflect away unwanted m_j states. We can also envision the discrimination between states belonging to multiple minima in big molecules [25] and deflecting out minority molecules in a mixture in the presence of majority molecules that absorb in the same spectral region [26].

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