Formation of deeply bound molecules via chainwise adiabatic passage

Elena Kuznetsova,1,2 Philippe Pellegrini,1 Robin Côté,1 M. D. Lukin,3 and S. F. Yelin1,2

1Department of Physics, University of Connecticut, Storrs, CT 06269
2ITAMP, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138
3Physics Department, Harvard University, Oxford St., Cambridge, MA 02138

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We suggest and analyze a novel technique for efficient and robust creation of dense ultracold molecular ensembles in their ground rovibrational state. In our approach a molecule is brought to the ground state through a series of intermediate vibrational states via a multistate chainwise Stimulated Raman Adiabatic Passage (c-STIRAP) technique. We study the influence of the intermediate states decay on the transfer process and suggest an approach that minimizes the population of these states, resulting in a maximal transfer efficiency. As an example, we analyze the formation of 87Rb2 starting from an initial Feshbach molecular state and taking into account major decay mechanisms due to inelastic atom-molecule and molecule-molecule collisions. Numerical analysis suggests a transfer efficiency > 90%, even in the presence of strong collisional relaxation as are present in a high density atomic gas.

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Ultracold molecular gases open possibilities for studying new exciting physical phenomena and their applications. For example, ultracold molecules can find use in testing fundamental symmetries [1, 2], in precision spectroscopy [3, 4] and ultracold chemistry [5]. Dipolar ultra-cold quantum gases promise to show new phenomena due to strong anisotropic dipole-dipole interactions. Dipolar molecules in optical lattices can be employed as quantum simulators of condensed matter systems [6]. Ultracold polar molecules also represent an attractive platform for quantum computation [7].

Dense samples of molecules in their ground rovibrational state \( v = 0, J = 0 \) are required for many of these applications. In this state, they have a large permanent electric dipole moment and are stable with respect to collisions and spontaneous emission. Currently translationally ultracold (100 nK - 1 mK) molecules are produced by magneto- [8] and photoassociation [9] techniques. In both of these techniques the molecules are translationally cold, but vibrationally hot, since they are formed in high vibrational states near the dissociation limit of the electronic ground state. Therefore, once created, molecules have to be rapidly transferred to the ground rovibrational state.

One of the most efficient ways to transfer population between two states is based on the Stimulated Raman Adiabatic Passage (STIRAP) technique [10, 11, 12, 13]. STIRAP provides a lossless robust transfer between an initial and a final state of a three-level system using a Raman transition with two counterintuitively ordered laser pulses. The main difficulty with a two-pulse STIRAP in molecules is to find an intermediate vibrational state of the excited electronic potential with a good Franck-Condon overlap with both a highly delocalized initial high vibrational state and a tightly localized \( v = 0 \) state [14]. It was therefore proposed in [15] to transfer population in several steps down the ladder of vibrational states using a sequence of stimulated optical Raman transitions. In this case the initial and final vibrational levels of each step do not differ significantly, and it is easier to find a suitable intermediate vibrational level in the excited electronic state. In this step-wise approach population is transferred through a number of vibrational levels in the ground electronic state. In a dense gas, molecules in such states are subject to inelastic collisions with background atoms or other molecules. The released kinetic energy greatly exceeds the trap depth resulting in loss of both molecules and atoms from the trap. This process is expected to limit the efficiency of creation of dense ultracold molecular samples. In this work we present a technique allowing an efficient transfer of a molecule from a high-lying to the ground vibrational state which minimizes population loss due to inelastic collisions in intermediate levels. Our technique is based on generalized chainwise STIRAP, which in principle allows for lossless transfer to the ground vibrational state. We note that serial STIRAP as in [13, 15] and pump-dump technique with a train of short pulses [16] should also allow lossless transfer if pulses are shorter than the collisional relaxation time.

The idea of this work can be described using a simple five-level model molecular system with states chainwise coupled by optical fields as illustrated in Fig.1

The states \( |g_1⟩, |g_2⟩ \) and \( |g_3⟩ \) are vibrational levels of the ground electronic molecular state, while \( |e_1⟩ \) and \( |e_2⟩ \) are vibrational states of an excited electronic molecular state. Molecules are formed in a high vibrational state \( |g_1⟩ \), which in the following is assumed to be a molecular Feshbach state. The state \( |g_3⟩ \) is the deepest bound vibrational state \( v = 0 \), and \( |g_2⟩ \) is an intermediate vibrational state. The goal is to efficiently transfer population from the state \( |g_1⟩ \) to state \( |g_3⟩ \). At least two vibrational levels \( |e_1⟩ \) and \( |e_2⟩ \) in an excited electronic state are required, one having a good Franck-Condon overlap with \( |g_3⟩ \), and the other with the initial Feshbach molecular state \( |g_1⟩ \).
The states $|e_1\rangle$ and $|e_2\rangle$, molecules decay due to spontaneous emission and collisions, and in the states $|g_1\rangle$ (for bosonic molecules) and $|g_2\rangle$ they experience fast inelastic collisions with background atoms leading to loss of molecules from a trap. It means that populating the states $|e_1\rangle$, $|e_2\rangle$ and $|g_2\rangle$ has to be avoided when a background atomic gas is present, or the transfer process has to be faster than the collisional relaxation time.

This can be achieved via chainwise STIRAP. The wave function of the system is $|\Psi\rangle = \sum_i C_i \exp(-i\phi_i(t))|i\rangle$, where $i = g_1, e_1, g_2, e_2, g_3$; $\phi_{g_1} = 0$, $\phi_{e_1} = \nu_1 t$, $\phi_{g_2} = (\nu_2 - \nu_1)t$, $\phi_{e_2} = (\nu_3 + \nu_2 - \nu_1)t$, $\phi_{g_3} = (\nu_4 - \nu_3 + \nu_2 - \nu_1)t$; $\nu_i$ is the frequency of the $i$th optical field. The evolution is then governed by the Schrödinger equation

$$i\hbar \frac{\partial |\Psi\rangle}{\partial t} = H(t) |\Psi\rangle,$$

where the time-dependent Hamiltonian is given by

$$H = \begin{pmatrix}
0 & -\Omega_4 & 0 & 0 & 0 \\
-\Omega_4 & -\Delta_2 & -\Omega_3 & 0 & 0 \\
0 & -\Omega_3 & -\Omega_2 & 0 & 0 \\
0 & 0 & -\Omega_2 & \Delta_1 & -\Omega_1 \\
0 & 0 & 0 & -\Omega_1 & 0
\end{pmatrix}.$$

The Hamiltonian Eq. (2) has a dark state, a specific superposition of states uncoupled from applied laser fields, given by the expression

$$|\Phi^0\rangle = \frac{\Omega_2\Omega_4 |g_1\rangle - \Omega_4\Omega_1 |g_2\rangle + \Omega_1\Omega_3 |g_3\rangle}{\sqrt{\Omega_2^2 + \Omega_4^2 + \Omega_1^2 + \Omega_3^2}}.$$
$W^T \mathcal{L} W$, and the Hamiltonian $H^a$ is diagonal; $W$ is the rotation matrix. The Liouville operator $\mathcal{L}$ consists of the usual decays, where only population decays ($\propto T_1^{-1}$) into other vibrational states or the continuum are considered (see Fig.1). Since at $t = -\infty$ all population is assumed to be in state $|g_1\rangle$, initial conditions for Eq. (5) read as $\rho_{00}^a = 1$, $\rho_{nm}^a = 0$ for $nm \neq 00$, where $\rho_{00}^a$ denotes the dark state population.

The decay of the dark state due to the population loss from the $|g_1\rangle$ and $|g_2\rangle$ states is then described by the equation (keeping only terms up to the $\Omega^2/\Omega_0^2$ order)

$$\frac{\rho_{00}^a}{\rho_{00}^a} \approx -(\Gamma_2 + \Gamma_1 \cos^2 \theta) \left(\frac{\Omega}{2\Omega_0} \sin 2\theta\right)^2 - \Gamma_1 \cos^2 \theta \tag{6}$$

Equation (6) shows that the intermediate state decay can be neglected during the transfer time $T_{tr}$ if $(\Gamma_1 + \Gamma_2)T_{tr} (\sin 2\Theta/2\Omega_0)^2 \ll 1$. From this expression one can see that the intermediate state decay rate is reduced by a factor $(\Omega/\Omega_0)^2 \ll 1$ in this regime. It also follows from Eq. (6) that decay from $|g_1\rangle$ is not suppressed, so that the transfer process has to be faster than this decay.

Magnetoo- and photoassociation techniques produce molecules mostly from ultracold Bose, two-spin component Fermi and mixture of alkali metal atomic gases. In traps with high initial atomic density, weakly bound Feshbach molecules rapidly decay due to inelastic atom-molecule collisions, which were found to be the major limiting factor of molecule lifetime. Depending on the quantum statistics of the constituent atoms, the alkali dimers show different behavior with respect to inelastic atom-molecule and molecule-molecule collisions. Fermionic alkali dimers in the Feshbach state are very stable with respect to collisions, especially close to the resonance, where the scattering length is large. Lifetimes of the Feshbach molecules of the order of 1 s have been observed experimentally [19, 20]. In contrast, bosonic and mixed dimers experience fast vibrational quenching due to inelastic atom-molecule collisions, even in their Feshbach state. An atomic density in a trap is typically in the range $n_{at} \sim 10^{11} - 10^{14}$ cm$^{-3}$, then the Feshbach state relaxation rate is in the range $\Gamma_1 \sim 10^{-1} - 10^4$ s$^{-1}$ (calculated from the corresponding inelastic atom-molecule collision coefficient $k_{inel} \sim 10^{-10}$ cm$^3$s$^{-1}$ [21, 22, 23]). At the same atomic densities the vibrational relaxation rate $\Gamma_2$ of intermediate vibrational states for bosonic molecules is in the range $\Gamma_2 \sim 10^2 - 10^5$ s$^{-1}$ (calculated from $k_{inel} \sim 6 \cdot 10^{-10}$ cm$^3$s$^{-1}$ for $^{7}$Li$^2$ [24] and the same range of atomic densities). Inelastic molecule-molecule collisional relaxation rates are about two orders of magnitude smaller due to typically smaller molecular density.

We next illustrate the technique for a sample seven-state bosonic $^{87}$Rb$_2$ molecular system (see the inset to Fig.2). In the first step, the Feshbach state can be coupled to the electronically excited pure long range molecular state $|0_g^a(v, J = 0)\rangle$, located close to the $5S_{1/2} - 5P_{3/2}$ dissociation asymptote. For example, following [11], the $v = 31$ vibrational level can be chosen 6.87 cm$^{-1}$ below the dissociation limit. The second STIRAP step can be to $v = 116$ in the ground electronic state. The authors of Ref. [11] mention that the Franck-Condon factors from the excited $|0_g^a(v, J = 31)\rangle$ state to the ground state vibrational levels down to the $X^1\Sigma_g^+ (v = 116)$ are similar to the second-to-last vibrational state used in the STIRAP experiment in [11]. The ground state $v = 00$ state can then be reached in four steps, using e.g. the path given in Table I. We note that in Rb$_2$ the $v = 0$ state cannot be reached from the $v = 116$ in two steps due to unfavorable Franck-Condon factors, a minimum of four steps is therefore required, resulting in a seven-state system. A four-step path from the Feshbach to the $v = 00$ state can be realized in Cs$_2$ [25], and therefore in other alkali dimers as well.

The transitions $|e_1\rangle - |g_2\rangle$, $|g_2\rangle - |e_2\rangle$, $|e_2\rangle - |g_3\rangle$ and $|g_3\rangle - |e_3\rangle$ are coupled by CW laser fields, the first transition $|g_1\rangle - |e_1\rangle$ and the last transition $|e_3\rangle - |g_4\rangle$ in the chain are coupled by the fields $\Omega_1 = \Omega_{1\max} (1 + \tanh (t - \tau/2)/2)$ and $\Omega_6 = \Omega_{6\max} (1 - \tanh (t + \tau/2)/2)$, respectively. In the above scheme we picked the $|e_3\rangle - |g_4\rangle$ transition with a large transition dipole moment, and intermediate transitions coupled by CW fields with close and reasonably large moments. In this case the Stokes pulse intensity can be minimized, and CW fields, provided, e.g., by laser diodes, can have the same intensity to optimize the transfer efficiency. The wavelengths of the transitions in Table I are covered by Ti:Sapphire and diode lasers. To provide the phase coherence between the laser fields required to carry out STIRAP, lasers can be phase-locked to spectral components of a frequency comb [26].

The results of the numerical simulation are given in Fig. 2. We assumed that the CW fields have the same amplitude of the electric field $E_0$, resulting in a Rabi frequency $\Omega_{0i} = D_{v',v} |E_0|/2\hbar$ for ith transition. The Rabi frequencies of STIRAP fields were chosen to satisfy a condition that $\Omega$ is less than the binding energy of the Feshbach molecular state to minimize Raman dissociation of weakly bound molecules. The pulse duration $T$ and delay $\tau$ were varied to obtain the maximal transfer efficiency. To estimate the decay rate of intermediate vibrational states, the highest atomic density $n_{at} \sim 10^{14}$ cm$^{-3}$ available experimentally was used along with the

### Table I: Possible chainwise transfer path from the Feshbach to the ground rovibrational state in the Rb$_2$ molecule. Shown also the corresponding transition dipole moments and wavelengths.

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|---|---|---|
| $v - v'$ transition | $D_{v,v'} \lambda$ | Debye mm |
| 1 | $|\text{Feshbach}\rangle - |0_g, v = 31, J = 0\rangle$ | 0.4 | 780.7 |
| 2 | $|0_g, v = 31, J = 0\rangle - X^1\Sigma_g^+ (v = 116, J = 0)$ | 0.8 | 780.4 |
| 3 | $X^1\Sigma_g^+ (v = 116, J = 0) - A^3\Sigma_g^+ (v' = 152, J = 1)$ | 0.55 | 846 |
| 4 | $A^3\Sigma_g^+ (v' = 152, J = 1) - B^3\Sigma_u^+ (v' = 50, J = 0)$ | 0.64 | 907.4 |
| 5 | $B^3\Sigma_u^+ (v' = 50, J = 0) - A^3\Sigma_u^+ (v' = 21, J = 1)$ | 0.53 | 990 |
| 6 | $A^3\Sigma_u^+ (v' = 21, J = 1) - X^1\Sigma_u^+ (v = 0, J = 0)$ | 2.37 | 856.4 |
incalst collision coefficient for intermediate vibrational states $k_{inel} \sim 6 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$, giving $\Gamma_2,3 = 6 \times 10^4 \text{ s}^{-1}$. A Decay rate of the Feshbach state $\Gamma_1 = 10^4 \text{ s}^{-1}$ was used. Numerical analysis shows that $> 90\%$ of the population can be transferred to $v = 0$ at high initial atomic density even in the presence of collisional decay from the initial Feshbach state. As can be seen from Fig.2, the population of the intermediate ground vibrational states does not exceed $7\%$ during the transfer process and only for a short time, reducing the molecular loss due to collisions in this states.

We now estimate intensities of CW and pulsed fields corresponding to Rabi frequencies used in our calculations. Taking the peak Rabi frequency of the pump and Stokes fields $\Omega_{max} = 3 \times 10^7 \text{ s}^{-1}$, the corresponding intensities are $I_{p,\max} = c^2 \varepsilon_0^2 / 8 \pi = c(\Omega_{max}^2 / D_v \nu) / 8 \pi$, resulting in $I_1 \sim 3 \text{ W/cm}^2$ and $I_6 \sim 0.1 \text{ W/cm}^2$; for CW fields with a Rabi frequency $\Omega_{max} \sim 6 \times 10^7 \text{ s}^{-1}$ the corresponding intensity is $I_{2,3,4,5} \sim 5 \text{ W/cm}^2$.

In summary, we propose a method of vibrational cooling of ultracold molecules, based on the multistate chainwise STIRAP technique. Molecules which are formed in high-lying vibrational states are transferred into a ground rovibrational state $v = 0$, $J = 0$ using Raman transitions via several intermediate vibrational states in the ground electronic state. Our technique provides $100\%$ vibrational as well as rotational selectivity using selection rules $\Delta J = 0, \pm 1$ for rotational transitions. Numerical analysis of the transfer process for a typical bosonic Rb$_2$ molecular system in a trap with a high atomic density $n_{lat} \sim 10^{14} \text{ cm}^{-3}$ shows that transfer efficiencies $\sim 90\%$ are possible even in the presence of fast collisional relaxation of the Feshbach molecular state.

The multistate chainwise STIRAP technique allows one to use various transitions, coupled by, e.g., rf fields and DC interactions. It can therefore be combined with the recently demonstrated resonant association method [27]. Another possibility is to use the magnetic field dependent DC interchannel coupling between an entrance and a closed channel state as a first transition in the STIRAP chain [28] followed by optical transitions to the ground vibrational state. The chainwise STIRAP can be applied to resonant photoassociation as well, then the first transition in the STIRAP chain will couple the continuum states to a high energy vibrational state in the ground electronic state [29].

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