Improved efficiency of stimulated Raman adiabatic passage in photoassociation of a Bose-Einstein condensate

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We theoretically examine Raman photoassociation of a Bose-Einstein condensate, revisiting simulated Raman adiabatic passage (STIRAP). Due to collisional mean-field shifts, efficient molecular conversion requires strong coupling and low density, either of which can bring about rogue photodissociation to noncondensate modes. We demonstrate explicitly that rogue transitions are negligible for low excited-state fractions and photodissociation that is slower than the STIRAP timescale. Moreover, we derive a reduced-parameter model of collisions, and thereby find that a gain in the molecular conversion efficiency can be obtained by adjusting the atom-atom scattering length with off-resonant magnetoassociation. This gain saturates when the atom-atom scattering length is tuned to a specific fraction of either the molecule-molecule or atom-molecule scattering length. We conclude that a fully-optimized STIRAP scheme may offer the best chance for achieving coherent conversion from an atomic to a molecular condensate with photoassociation.

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I. INTRODUCTION

Photoassociation occurs when a pair of colliding ultracold atoms absorb a laser photon 1, thereby jumping from the two-atom continuum to a bound molecular state. If the initial atoms are Bose-condensed 2, 3, 4, 5, then the subsequent molecules will also form a Bose-Einstein condensate 6, 7, 8. On the other hand, the process known as the Feshbach resonance 9, which we refer to as magnetoassociation, occurs when two ultracold atoms collide in the presence of a magnetic field, whereby the spin of one of the colliding atoms flips, and the pair might then jump from the two-atom continuum to a bound molecular state 10, 11. As with collective photoassociation, the so-formed molecules will comprise a Bose-Einstein condensate (BEC) if the incident atoms are themselves Bose-condensed 12, 13, 14.

Early theories of collective association accounted only for the condensates, neglecting noncondensate modes 10, 11, 15, 16, 17, 18, 19. Rogue 13, 14, or unwanted 17, 18, 19, transitions to noncondensate modes occur because the dissociation of a zero-momentum BEC molecule need not take the atoms back to the zero-momentum atomic condensate, but may just as well end up creating two noncondensate atoms with equal-and-opposite momenta. Since the collective condensate coupling scales like the square root of the laser intensity (Feshbach-resonance width) and the dissociation rate scales like the intensity (width), rogue dissociation is expected to play a dominant role in strong photoassociation (magnetoassociation) 13, 14, 17, 18, 19.

Pioneering experiments 20 with photoassociation of 87Rb condensate were found to be just on the verge 17 of coherent atom-molecule conversion. Next-generation Na 21 and 7Li 22 experiments were aimed at the strongly interacting regime, and probed the predicted 13, 14, 19 photoassociation rate limit. Meanwhile, groundbreaking experiments in magnetoassociation of a Na condensate demonstrated a tunable scattering length 23, as well strong condensate losses for sweeps of the magnetic field across resonance 24. Subsequent experiments in Feshbach-tuning the scattering length led to the formation of stable 85Rb 25 and 137Cs 26 condensates—which are otherwise incondensable in significant fractions due to uncooperative (zero-field) scattering lengths 27, as well as a controlled collapse of a condensate with bursts of atoms emanating from a remnant condensate 28, a counterintuitive decrease in condensate losses for an increasing interaction time 29, and collective burst-remnant oscillations 30. It turns out that rogue dissociation is at the heart of these magnetoassociation experiments 31, 32, 33, 34. Most recently, short-lived quantum degenerate molecules have been created by sweeping a BEC across a Feshbach resonance 35.

When it comes down to creating a molecular condensate, the catch to photoassociation is that it generally occurs to an electronically-excited state, and the subsequent irreversible losses to spontaneous decay defeat the purpose of molecular coherence. Adding a second laser to drive molecular population to a stable electronic state, stimulated Raman adiabatic passage (STIRAP) 36 in photoassociation 37, 38, 39 of a Bose-Einstein condensate 40, 41, 42, 43 has been proposed as a means for avoiding radiative decay. Likewise, combining STIRAP with near-resonant magnetoassociation is also a viable
means to avoid spontaneous decay when creating a stable molecular BEC, although the laser spectroscopy (bound-bound) is different from the usual photoassociation (free-bound-bound).

The hallmark of STIRAP is the counterintuitive pulse sequence, which in photoassociation of a BEC amounts to adjusting the two lasers so that in the beginning, when the system is mainly atomic condensate, the strongest coupling is between the excited-molecular and stable-molecular condensates, while in the end, when effectively everything is in the target state, the strongest coupling is between the atomic and excited-molecular condensate. As the population is transferred between the atomic and stable-molecular condensates, the state with the larger population is always weakly coupled to the electronically-excited molecular condensate, and the subsequently low (ideally zero) population reduces (eliminates) radiative losses. In principle, STIRAP allows for complete conversion from an atomic to a molecular condensate.

In practice, however, free-bound-bound STIRAP relies on a superposition that includes the atoms and stable molecules but excludes the electronically-excited molecules, and the conversion efficiency is reduced from unity when this so-called dark state is disrupted by collisions between particles. Specifically, mean-field shifts due to collisions between condensate particles (atom-atom, atom-molecule, and molecule-molecule) make it difficult to achieve STIRAP by moving the system off the required two-photon resonance. Such two-photon frequency shifts lead to a larger excited-state fraction, and thus more losses to radiative decay, which of course reduces the molecular conversion efficiency, defeating the purpose of collective conversion. Nevertheless, the collisional interaction strength is directly proportional to density, and the conversion efficiency can be improved by treating the density as an optimization parameter. Another collision-avoidance option is STIRAP in an optical lattice with two particles per site, although this scheme is not many-body coherent.

The purpose of this Article is to re-investigate Raman photoassociation of a nonideal Bose-Einstein condensate, focusing on improving the efficiency of STIRAP from an atomic to a molecular condensate. In Sec. II we introduce the model and briefly review the idea of improving the molecular conversion efficiency by reducing the density. Because this system is in fact strongly coupled, for low density or otherwise, and because rogue photodissociation to noncondensate modes can be prominent for strongly coupled systems, Sec. III explicitly demonstrates that rogue transitions are negligible when the excited-state fraction is low and photodissociation is slow compared to the STIRAP timescale. The main contribution of this work is given in Sec. IV which illustrates that the conversion efficiency can be further improved by tuning the atomic scattering length with off-resonant magnetoassociation. Overall discussion is given in Sec. V.

II. DENSITY TUNING STIRAP

Turning to the situation of Fig. 1 we assume that N atoms have Bose-condensed into the same one-particle state, e.g., a plane wave with wave vector \( \mathbf{k} = 0 \). Photoassociation then removes two atoms from this state \( |1\rangle \), creating a molecule in the excited state \( |2\rangle \). Including a second laser, bound-bound transitions remove excited molecules from state \( |2\rangle \) and create stable molecules in state \( |3\rangle \). In second quantized notation, boson annihilation operators for atoms, primarily photoassociated molecules, and stable molecules are denoted, respectively, by \( a, b, \) and \( g \). The laser-matter interactions that drive the atom-molecule and molecule-molecule transitions are characterized by their respective Rabi frequencies \( \kappa \) and \( \Omega \). The two-photon and intermediate detunings are \( \Delta \) and \( \delta \). The wavy line denotes the irreversible losses that STIRAP is intended to manage.

\[
\begin{align}
\lambda_{11} &= \frac{4\pi \hbar a_{11}}{mV}, \\
\lambda_{13} &= \lambda_{31} = \frac{3\pi \hbar a_{13}}{mV}, \\
\lambda_{33} &= \frac{2\pi \hbar a_{33}}{mV},
\end{align}
\]

where \( a_{ij} \) is the particle-particle scattering length, \( V \) is the quantization volume that is expedient in a particular context (e.g., cubic box or spherical cavity), and \( m \) is the mass of an atom. For the time being, we assume...
that the spontaneous decay rate of the excited-molecular condensate is sufficiently large to justify neglect of the mean-field shifts for the electronically excited molecular state \(1\). For future reference, we define \(\tilde{\lambda}_{ij} = V\lambda_{ij}\).

The three-mode Hamiltonian for this freely-interacting system can be written

\[
\frac{H}{\hbar} = \frac{1}{2} \Delta_0 a^\dagger a + (\delta - \frac{1}{2} i\gamma_s) b^\dagger b
- \frac{1}{2} \left[ \kappa (b^\dagger a a + a^\dagger a b) + \Omega (g^1 b + b^1 g) \right]
+ \frac{1}{2} (\lambda_{11} a^\dagger a^\dagger a a + \lambda_{33} g^1 g^1 g g)
+ \lambda_{13} a^\dagger a^1 a g. \tag{2}
\]

The mean-field equations for collective two-color photoassociation of a freely-interacting gas are obtained from the Heisenberg equations of motion:

\[
\dot{a} = \frac{1}{\hbar} \left( \frac{1}{2} \Delta + \Lambda_{11} |a|^2 + \Lambda_{13} |g|^2 \right) a - \chi a^* b, \tag{3a}
\]

\[
\dot{b} = \frac{1}{\hbar} \left( \delta - \frac{1}{2} i\gamma_s \right) b - \frac{1}{\hbar} (\chi a a + \Omega g), \tag{3b}
\]

\[
\dot{g} = \frac{1}{\hbar} \left( \Lambda_{13} |a|^2 + \Lambda_{33} |g|^2 \right) g - \frac{1}{\hbar} \Omega b. \tag{3c}
\]

Here the effects of Bose enhancement \(\text{[10]}\) have been included by scaling the mean-field amplitudes according to \(x \rightarrow x/\sqrt{N}\) (where \(x = a, b, g\)). The mean-field probability \(|a|^2 \langle b^\dagger a^\dagger a a \rangle\) is then of the order of unity (half), and the coupling strengths have been redefined as \(\chi = \sqrt{N} \kappa\) and \(\lambda_{ij} = N \lambda_{ij} = \rho \lambda_{ij}\).

The transient STIRAP pulses are taken as Gaussian, i.e., \(\chi(t) = \chi_0 \exp\left[-(t - D_1)^2/T^2\right]\) and \(\Omega(t) = \Omega_0 \exp\left[-(t - D_2)^2/T^2\right]\).

Assuming an ideal gas \((\lambda_{ij} = 0)\), it is easy to show from the steady-state limit \((\dot{x} = 0)\) that Eqs. \(4\) reduce to an algebraic system that can be plugged trivially into \textit{Mathematica} \(\text{[11]}\), yielding exact solutions \(\text{[40]}\). Here we scale the atomic (molecular) amplitude(s) as \(a \rightarrow e^{i\Delta t/2} a\) \((b \rightarrow e^{i\Delta t} b, g \rightarrow e^{i\Delta t} g)\), and keep only normalized solutions \(|a|^2 + 2|b|^2 + |g|^2 = 1\) that are real for real values of \(\Omega/\chi \rightarrow (0, \infty)\). The dark state is given as

\[
\Delta_0 = 0, \tag{4a}
\]

\[
a_0 = \frac{1}{2} \sqrt{\frac{\Omega}{\chi}} \left[ \sqrt{8 + \left( \frac{\Omega}{\chi} \right)^2} - \Omega \right], \tag{4b}
\]

\[
b_0 = 0, \tag{4c}
\]

\[
g_0 = -\frac{1}{4} \left[ \sqrt{8 + \left( \frac{\Omega}{\chi} \right)^2} - \Omega \right], \tag{4d}
\]

It is evident from Eqs. \(4\) that, for a two-photon resonance \((\Delta = 0)\), the dark state is an eigenstate of the system with all atoms (stable molecules) for \(\Omega/\chi \rightarrow 0\) \((\Omega/\chi \rightarrow \infty)\), and zero excited molecules; hence, for an initial BEC and adiabatic counternutation pulses, the two-photon-resonant system will follow this eigenstate as it evolves from atoms into stable molecules. The presence of collisions, which introduce a time-dependent shift of the two-photon detuning, means that the system cannot start out in, nor subsequently follow, the dark state, and a nonzero excited-state fraction will ensue.

To illustrate numerically, we concentrate on explicit parameters for a dilute quantum-degenerate gas of \(^{87}\text{Rb}\) atoms \(\text{[12]}\): \(\gamma_s = 7.4 \times 10^7 \text{s}^{-1}\), \(\chi_0 = 2.1 \times 10^9 \sqrt{\rho/\rho_0} \text{s}^{-1}\), \(\rho_0 = 4.3 \times 10^{13} \text{cm}^{-3}\), \(\lambda_{11} = 4.96 \times 10^{-11} \text{cm}^3/\text{s}\), \(\lambda_{13} = -6.44 \times 10^{-11} \text{cm}^3/\text{s}\); although unknown, the stable-molecule mean-field shift \(\lambda_{33} = 2.48 \times 10^{-11} \text{cm}^3/\text{s}\) is estimated by assuming equal atom-atom and molecule-molecule scattering lengths. The effect of collisions is demonstrated explicitly in Fig. \(2\). Setting the mean-field-shift terms to zero, \(\lambda_{ij} = 0\), we see in Fig. \(2\) (a) that STIRAP works exactly as expected for a near-adiabatic pulse sequence, losing only a small fraction of particles to spontaneous decay. Reinstating collisions, Fig. \(2\) (b) shows an order of magnitude increase in the excited-state fraction, and a corresponding decrease in the conversion efficiency of some two orders of magnitude, as spontaneous decay gets the upper hand.

Nevertheless, since the collisional mean-field shifts are directly proportional to the density \((\lambda_{ij} \propto \rho)\), then we expect that reducing the density of the initial BEC could improve the conversion efficiency of STIRAP from an

![FIG. 2: Stimulated Raman adiabatic passage in photoassociation of a nonideal Bose-Einstein condensate. For a given \(\chi_0(\rho)\), the pulse parameters are \(\Omega_0 = \chi_0, T = 5 \times 10^4 \chi_0, D_1 = 4.5T\) and \(D_2 = 2.5T\). The two-photon (intermediate) detuning is \(\Delta = 0\) \((\delta = \chi_0)\). Note that \(|g|^2 = 1/2\) is actually complete conversion, since two atoms are destroyed to create a molecule. (a) For an ideal gas with \(\rho = \rho_0\), STIRAP mostly defeats spontaneous decay, as expected for a moderately adiabatic pulse sequence. (b) Adding collisional interactions shifts the system off resonance, leading to a larger excited-state fraction and, thus, more losses to spontaneous decay. (c) Density-tuning the STIRAP efficiency: Losses to spontaneous decay decrease as collisional mean-field shifts are marginalized for lower densities, but the STIRAP timescale \((\propto 1/\sqrt{\rho})\) increases as well, and spontaneous decay eventually regains its dominance. Here a larger peak bound-bound pulse was used, \(\Omega_0 = 50\chi_0\), as discussed in the text.](image-url)
atomic to a molecular condensate \( \text{43} \). This idea was spawned in our development of Feshbach-stimulated photoproduction of stable molecular condensates \( \text{32} \) (see also related work \( \text{31} \)). Consider for example the density \( \rho = 4.3 \times 10^{12} \text{ cm}^{-3} \), so that \( \chi_0 = 2.1 \times 10^5 \text{ s}^{-1} \), \( \Lambda_{11} = 213 \text{ s}^{-1} \), \( \Lambda_{33} = 107 \text{ s}^{-1} \), and \( \Lambda_{13} = 277 \text{ s}^{-1} \). The mean-field shifts are then roughly three orders of magnitude smaller than the peak Bose-enhanced free-bound coupling \( \chi_0 \), and since \( \chi_0 \) sets the timescale for atom-molecule STIRAP \( \text{40} \), we expect a smaller role for particle interactions compared to when \( \rho = \rho_0 \). This intuition is confirmed in Fig. 2 (c). Note that pulses with asymmetric heights \( \text{41, 42} \) improve the short-pulse efficiency of STIRAP by more than an order of magnitude compared to when \( \rho = \rho_0 \). For across-resonance sweeps \( \text{25} \), as well as the counter-rotating terms \( \text{15, 16, 19} \). Similarly, the losses for rogue dissociation, we have dropped the spontaneous decay term \( \gamma_b b^\dagger b \). Also, anticipating low populations, we have neglected collisions with noncondensate atoms. The corresponding mean-field theory is derived from the Heisenberg equations of motion:

\[
i\dot{a} = \left[ \frac{\Delta}{2} + \Lambda_{11} |a|^2 + \Lambda_{13} |g|^2 \right] a - \chi^* b, \quad (6a)
\]

\[
i\dot{b} = \delta b - \frac{i}{2} \left[ \chi a^2 + \Omega g + \xi \int d\epsilon \sqrt{\epsilon} f(\epsilon) C(\epsilon) \right], \quad (6b)
\]

\[
i\dot{g} = \frac{[\Lambda_{13} |a|^2 + \Lambda_{33} |g|^2]}{2} g - \frac{i}{2} \Omega b, \quad (6c)
\]

\[
i\dot{C}(\epsilon) = \left[ \Delta + \epsilon \right] C(\epsilon) - \frac{\xi}{\sqrt{\epsilon}} f(\epsilon) \frac{[1 + 2P(\epsilon)]}{b}, \quad (6d)
\]

\[
i\dot{P}(\epsilon) = \frac{(2\pi \omega_0)^{3/2}}{\sqrt{\epsilon}} f(\epsilon) [b^* C(\epsilon) - C^*(\epsilon)b]. \quad (6e)
\]

In Eqs. (6), we have taken the continuum limit

\[
\frac{1}{N} \sum_k G_k \rightarrow \frac{1}{4\pi^2 \omega_\rho^{3/2}} \int d\epsilon \ G(\epsilon), \quad (7)
\]

and we also have introduced the rogue and normal densities, \( C(\epsilon) \equiv \sqrt{\epsilon} \left( a_k a_{-k} \right) / (2\pi \omega_\rho^{3/4}) \) and \( P(\epsilon) \equiv \langle a_k^\dagger a_{-k} \rangle \), as well as the rogue coupling \( \xi(t) = \chi(t) / (2\pi \omega_\rho^{3/4}) \).

Before moving on, we discuss basic renormalization. For \( \chi_0 = \Omega_0 = 0 \) and ignoring the normal density, simple Fourier analysis of an initial excited-bound molecular condensate gives the below-threshold binding energy as the real and negative pole of

\[
\omega - \delta - \Sigma(\omega) + i\eta = 0, \quad (8)
\]

where \( \eta = 0^+ \) and the molecular self-energy is defined as

\[
\Sigma(\omega) = \frac{1}{2} \xi^2 \int d\epsilon f^2(\epsilon) \frac{\sqrt{\epsilon}}{\omega - \epsilon - i\eta}. \quad (9)
\]

The simplest energy dependence for the continuum is one that obeys the Wigner threshold law up to some abrupt cutoff: \( f^2(\epsilon) = \Theta(\epsilon_M - \epsilon) \). The detuning (binding energy) then picks up a term \( \Sigma(0) = \xi^2 \sqrt{\epsilon_M} \). In principle, the cutoff is infinite, and therefore so is the continuum.
shift of the molecular binding energy. To account for this divergence, one defines the so-called physical detuning \( \delta = \delta - \xi^2 \sqrt{\epsilon_M} \), which is finite by definition in the limit of an infinite cutoff.

In practice, any numerical procedure employs a finite cutoff, and the finite shift is accounted for in exactly the same manner. Hence, the intermediate detunings in Eqs. (6) are taken as physical (renormalized) detunings. Anticipating low noncondensate fractions, the normal density–Bose enhancement of the noncondensate modes—was neglected. Reminiscent of our original nondegenerate quasicontinuum model of photoassociation [38], we introduce \( N_{qc} = 2 \times 10^3 \) quantum-degenerate quasicontinuum states and a cutoff \( \epsilon_M = 10 \chi_0 \), sufficient to deliver convergence and keep numerical artifacts to a minimum, where convergence is determined by the requirement

\[
|a|^2 + 2 |b|^2 + |g|^2 + \int d\epsilon |C(\epsilon)|^2 = 1. \tag{10}
\]

That said, we report numerical STIRAP solutions of the mean-field theory (9) for rogue transitions to noncondensate modes in Raman free-bound-bound photoassociation of a BEC. The focus is on the lowest density from Fig. 2 (\( \rho = 4.3 \times 10^{10} \text{ cm}^{-3} \)), as an explicit example in Fig. 3 and the key results are summarized in Table I.

In this case, not only is the coupling strong to begin with, but we have an especially low density. Here the rogue coupling is a bit stronger, due to the low density, leading to a slightly larger noncondensate fraction. But, due to the fact that mean-field shifts are effectively eliminated for the lowest density, the bound state fraction is in this case the lowest. In the end, even for this low density, we see that rogue photodissociation to noncondensate modes does not affect the final stable-molecule conversion efficiency. We have confirmed that, for artificially large rogue couplings \( \xi \gtrsim 1 \), i.e., faster photodissociation, rogue noncondensate modes indeed begin to play a more invigorated role. Also, if the timescale for STIRAP is lengthened too much, we expect that rogues should likewise begin to dominate.

### IV. Feshbach Tuning STIRAP

As we have already seen, reducing the density of the initial atomic condensate acts to marginalize collisional mean-field shifts of the two-photon resonance, leading to an improvement in the efficiency of STIRAP from an atomic to a molecular condensate. With this idea in mind, it seems possible that collisional mean-field shifts could be further marginalized by adjusting the atom-atom scattering length via off-resonant magnetoassociation. We address this problem by first rewriting the Hamiltonian (2) in a form that makes the mechanics of the Feshbach-tuned efficiency more transparent.

Neglecting rogue photodissociation to noncondensate modes as per the previous section, consider now the total number of particles, which is given by the operator

\[
N = a^\dagger a + 2(b^\dagger b + g^\dagger g).
\tag{11}
\]

Due to the damping term (\( \propto i \gamma_a \)) in the Hamiltonian (2), it cannot be said that \( N \) is a conserved quantity. Nevertheless, it is certainly true that \( N \) commutes with the Hamiltonian, i.e., \( [H, N] = 0 \), regardless of the non-Hermitian nature of \( H \). It is then reasonable to presume that one may add multiples of \( N \) to the Hamiltonian without altering the essential physics. For example, it is implicitly accepted that the two free Hamiltonians \( H_0/h = \frac{1}{2} \Delta a^\dagger a + \delta b^\dagger b \) and \( H_0/h = -\Delta g^\dagger g + (\delta - \Delta)b^\dagger b \) will give the same physics, and the two are of course related by the addition (subtraction) of the term \( \frac{1}{2} h \Delta N \).
[see also derivation of Eqs. (14)]. Similarly, it is also reasonable to expect that subtracting the term $\frac{1}{2} \hbar \lambda_{11} N^2$ will leave the dynamics unchanged, an operation that results in the Hamiltonian

$$\frac{H}{\hbar} = \frac{1}{2} \Delta a^\dagger a + \delta b^\dagger b + \frac{1}{2} \lambda_{33} g^\dagger g g + \lambda_{13} a^\dagger a g g,$$

$$-\frac{1}{2} [\kappa(b^\dagger a a + a^\dagger a b) + \Omega(g b^\dagger b g)] ,$$  \hspace{1cm} (12)

where the parameters $\lambda_{33} = \lambda_{33} - 4 \Lambda_{11}$ and $\lambda_{13} = \lambda_{13} - 2 \Lambda_{11}$ now characterize the mean-field shifts due to collisional interactions, and we continue to neglect the mean-field shifts associated with electronically-excited molecules.

The reduced-parameter Hamiltonian \cite{12} gives the mean-field equations

$$\dot{a} = \left( \frac{1}{2} \Delta + \Lambda_{13}^a |g|^2 \right) a - \chi a^* b, \hspace{1cm} (13a)$$

$$\dot{b} = (\delta - \frac{1}{2} \kappa \gamma_a) b - \frac{1}{2} \chi a^* a g + \Omega g^\dagger b g, \hspace{1cm} (13b)$$

$$\dot{g} = (\Lambda_{13} a^\dagger a |g|^2) g - \frac{1}{2} \Omega b. \hspace{1cm} (13c)$$

We have made an extensive numerical comparison between the solutions to reduced-parameter mean-field model \cite{13} and the solutions to the conventional mean-field model \cite{6}. As expected, the conventional and reduced-parameter mean-field equations of motion lead to exactly the same physics. Moreover, we have also confirmed that, barring a fluke in the scattering length(s), collisions with the excited-state are safely ignored.

Besides reducing the number of parameters, it seems that $\Lambda_{33}^a = 0$, which corresponds to $a_{11} = a_{33}/8$, is a special case that could further improve the molecular conversion efficiency. Indeed, reducing the scattering length produces another marked gain in the molecular conversion efficiency [Fig. 1(a)]. The gain saturates because $\Delta_{11}$ is steadily decreasing, so that $\chi_{33} \to \lambda_{33}$. Similar saturation is shown in Fig. 4(b) for $\Lambda_{13} = 0$, but any gain here is outweighed by the fact that $a_{11} < 0$ destabilizes the initial BEC against collapse, although a system where $a_{13} > 0$ may prove otherwise. Again, further improvements can be achieved by optimizing the laser parameters \cite{12, 13}.

Before closing, we extend our model to explicitly describe tuning the scattering length via magnetoassociation. Hence, in addition to the primary-photonassociation molecular state, the BEC atoms are coupled to a second molecular state, denoted by the operator $\phi$, with a Feshbach resonance. For well-resolved resonances, light-driven transitions involving the Feshbach state are neglected just as, for example, direct free-bound photoassociation transitions are neglected in Feshbach-stimulated photodestruction of molecular BEC \cite{14, 14}. The Hamiltonian is then appended to read

$$\frac{H}{\hbar} = \ldots + \omega_B \phi^\dagger \phi - \frac{\alpha}{\sqrt{N}} (\phi^\dagger a a + a^\dagger a^\dagger \phi),$$  \hspace{1cm} (14)

where $\omega_B = [\omega_B - i (\Gamma_d + \Gamma_{\rho a})]$. Here $\Gamma_d$ is the rate of magnetodissociation to noncondensate modes and $\Gamma_{\rho}$ is the loss rate due to collision-induced vibrational relaxation; also, the magnetoassociation coupling is $\alpha = \sqrt{2 \pi \rho a_{11} |\Delta_{11} \Delta_B|/m}$, and the energy (detuning) of the magnetoassociation state is $\hbar \omega_B = \text{sgn}(a_{11}) |\Delta_{11} (B - B_0)|$, with $\Delta_{11}$ the difference between the atom pair and molecule magnetic moments and $\Delta_B$ is the width of the resonance. Anticipating lowest-order perturbation theory, we have neglected molecule-molecule collisions.

When the system is off-resonance ($\omega_B \gg \alpha, \Gamma_d, \rho \Gamma_{\rho}$), it is easily shown from the Heisenberg equation of motion for the molecular operator that, to lowest order, off-resonant magnetoassociation can be included simply by making the substitution

$$\Lambda_{11} \to \Lambda_{11} = \Lambda_{11} - \frac{2 \alpha^2}{\omega_B} \left[ 1 + i \left( \frac{\Gamma_d}{\omega_B} + \frac{\rho \Gamma_{\rho}}{\omega_B} \right) \right].$$  \hspace{1cm} (15)

According to Fig. 4 we are looking at about an order of magnitude decrease in the scattering length. For concreteness, we assume $\mathbb{R}[\Lambda_{11}] = \Lambda_{11}/10$, which translates into the magnetic field position $B = B_0 + 0.9 \Delta_B$. The question is then whether this is sufficiently detuned from resonance to justify neglect of dissociative and relaxation losses. The ultracold magnetodissociation rate is $\Gamma_{\rho} = a_{11} \Delta_B / h^2$, where $p$ is the relative atom-pair momentum; hence, using the uncertainty relation $p^{1/2} \rho \sim \hbar/2$, we find $\Gamma_{\rho}/\omega_B \sim a_{11} \hbar^{1/2} \Delta_B / (B - B_0) \sim 10^{-3}$. Estimating $\Gamma_d \sim 10^{-10} \text{cm}^3/\text{s}$ \cite{52}, $\Delta_B \sim 0.1 \text{G}$ and $\Delta_{11} = \mu_B$ (i.e., a Bohr magneton), then the loss term due to vibrational quenching is roughly $\rho \Gamma_{\rho}/\omega_B \sim 10^{-4}$ for $\rho \sim 10^{12} \text{cm}^{-3}$. It should therefore be possible, using one of the more than forty Feshbach resonances found in $^{87}$Rb \cite{52}, to improve the STIRAP efficiency by tuning
the atom-atom scattering length.

V. DISCUSSION

Admittedly, we have neglected an explicit trapping potential for either the atoms or the molecules, a move which we now justify. From Fig. 2(c), the timescale for STIRAP is $T = 5 \times 10^3 / \chi_0 \approx 24$ ms. For $N = 5 \times 10^9$ condensate atoms in a spherically symmetric trap, let us say that the reduction in density from $\rho_0 = 4.3 \times 10^{14}$ cm$^{-3}$ to $\rho \sim 10^{12}$ cm$^{-3}$ is achieved solely by reducing the frequency of the trap from $\nu_1 = 100$ s$^{-1}$ to $\nu_t \sim 1$ s$^{-1}$. The STIRAP timescale is then fast enough to allow inclusion of the trap with an average over a Thomas-Fermi density distribution $\rho$, which should not drastically alter the predicted optimal density.

Also, the Raman-formed molecules can be vibrationally hot [42], and molecule-molecule and atom-molecule collisions may thus foster relaxation to lower-lying vibrational levels. This vibrational quenching is accounted for in exactly the same fashion as already presented in Sec. 4 for the Feshbach molecular state. An exact value for the $^{87}$Rb$_2$ quenching rate (per unit density) is unknown (hence the neglect in Ref. [42]), although the upper bound $\Gamma_\nu < 10^{-10}$ cm$^3$/s has been measured [21]. At this rate, vibrational quenching could well be an issue, even for the optimal density $\rho \sim 10^{12}$ cm$^{-3}$. However, a lower peak bound-bound Rabi coupling ($\Omega_0 / \chi_0 = 50$ compared to $10^3$ [42]) means that, for the same bound-bound laser intensities, it should be possible to target lower-lying levels. Because the vibrational-relaxation rate decreases with decreasing binding energy [34], targeting lower-lying vibrational levels should also lead to slower relaxation rates. In the end, vibrational quenching should be manageable.

The remaining concern is whether the photoassociation laser will overlap with the expanded BEC cloud for user-friendly intensities. If not, then the cloudsize could be reduced by adjusting the number of condensate atoms; additionally, Feshbach-tuning the scattering length will also reduce the cloudsize. In particular, if the density $\rho = 4.6 \times 10^{12}$ cm$^{-3} \approx \hat{\rho}$ is achieved by lowering the number of atoms to $N = 10^4$, the scattering length to $a_{11} = a_{11}/8$, and the trap frequency to $\nu_t = 3$ s$^{-1}$, then we find that the cloudsize is only barely increased from $R_0 = 8.9$ $\mu$m to $R = 11$ $\mu$m. By optimizing the number of atoms, the trap frequency and atomic scattering length, overlap between the BEC cloud and the photoassociation laser should be manageable for user-friendly intensities.

Previously [12], we have argued that experimental Raman photoassociation of a BEC [21] is on the verge of coherent conversion. The experiments in question are performed with continuous-wave lasers and spontaneous decay from the primary photoassociation state is managed with a large intermediate detuning. To enable coherent phenomena, the two-photon Rabi frequency, $\chi \Omega / \delta$, must be of the order of the two-photon spontaneous decay linewidth, $\Omega^2 \gamma_0 / 2\delta^2$, a condition that is not quite satisfied in the Wynar et al. [21] experiments. On the other hand, atom-atom collisions are also an issue in achieving continuous-wave coherence, and avoiding them by increasing the laser intensity and decreasing the density could potentially bring rogue photodissociation and laser-cloud overlap into play. Our opinion remains that coherent continuous-wave conversion can only be achieved by a difficult-to-impossible balance of laser intensity and condensate density. This bottleneck is probably not unique to the $^{87}$Rb system.

The present work has examined transient stimulated Raman adiabatic passage in photoassociation of a freely-interacting condensate in the presence of rogue and radiative decay. We have shown that rogue photodissociation to noncondensate modes is generally negligible, and that radiative decay, enhanced by collisional mean-field shifts, can be managed by adjusting the initial condensate density and the atom-atom scattering length. In conclusion, a fully-optimized STIRAP scheme—i.e., where the detunings, pulse-sequence parameters (heights, widths, spacing, and number of sequences), particle number, trap parameters, and atomic scattering length are optimized—offers probably the best chance for achieving coherent atom-molecule conversion in photoassociation.

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