Bose-Stimulated Raman Adiabatic Passage in Photoassociation

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Abstract

We analyze coherent two-color photoassociation of a Bose-Einstein condensate, focusing on stimulated Raman adiabatic passage (STIRAP) in free-bound-bound transitions from atoms to molecules. This problem is of particular interest since STIRAP is predicted to be necessarily absent in the nondegenerate case [Javanainen and Mackie, Phys. Rev. A 58, R789 (1998)]. However, Bose-stimulation enhances the free-bound dipole matrix element for an atomic condensate, and photoassociative STIRAP turns out to be a viable mechanism for converting an atomic condensate to a molecular condensate with near-unit efficiency.

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As the field of Bose-Einstein condensation (BEC) in dilute gases continues to develop, candidate systems for BEC are being discovered on a regular basis. Besides the original alkalis [1], there is the recent observation [2] of BEC in hydrogen [3]. Meanwhile, a spin-polarized helium condensate is not out of the question [4], and recent theoretical work has shown that coherent photoassociation might be used to produce a degenerate molecular gas (MBEC) from an already-Bose-condensed sample of atoms [5,6]. Here we consider the formation of MBEC using coherent photoassociation.

Photoassociation (PA) is the process in which a pair of atoms interacts with a photon, thereby making a transition from the two-atom continuum to a bound state of the molecule. Quantization of the molecular dissociation continuum allows one to describe such free-bound transitions using the standard techniques of few-level quantum optics [7,8]. Beyond providing a few-level framework, such a quasicontinuum approach has also led to a matter-quantized formulation of photoassociation analogous to the analysis of second-harmonic generation of light [9,6]. In this context of nonlinear matter optics [10], atom-molecule conversion displays coherent BEC-MBEC oscillations, adiabatic following, and non-classical collapse and revivals [6,11].

Nonetheless, one-color free-bound photoassociation generally occurs to an excited electronic state of the molecule, and the subsequent irreversible losses, whether due to photodissociation (PD) or spontaneous decay, tend to negate the benefits of the coherence. In this Letter we develop coherent two-color free-bound-bound photoassociation, where the primary photoassociated molecules are transferred with another laser field to a stable molecular state. The goal is to state-selectively convert a BEC into an MBEC, while averting irreversible losses from electronically excited molecules. We consider pulsed free-bound and bound-bound couplings that occur in the counter-intuitive order [12], and so correspond to stimulated Raman adiabatic passage (STIRAP) from atoms to molecules. Beyond its distinctly nonlinear character, this problem is of particular interest since we have previously argued for the absence of free-bound-bound STIRAP [6]. However, the present work illustrates that such transitions are possible in the case of a condensate, since the free-bound...
dipole matrix element is Bose-enhanced due to the fact that many atoms are in the same quantum state. A similar statistical effect may also increase hot pion production in nuclear physics \([13]\), and speed up the decay rate of the inflation field in cosmology \([14]\).

The development herein is outlined as follows. First, we review the many-body enhancement for the PA dipole matrix element of a condensate, and discuss the implications for coherent free-bound-bound STIRAP. Next we take a semi-classical approach to identify the nonlinear counterpart of the dark state \([15]\) that contains no primary photoassociated molecules. Given that Bose-enhancement allows a counter-intuitive pulse scheme, the limit \(t \to -\infty\) finds the dark state with all atoms, while in the limit \(t \to +\infty\) the dark state contains only molecules. It then appears possible that free-bound-bound STIRAP of an atomic condensate will produce a similarly degenerate gas of molecules. The remaining work establishes conditions that allow such adiabatic following to occur.

Turning to the situation of Fig. 1, we assume that \(N\) identical atoms of mass \(m\) have condensed into the same one-particle state, say, a plane wave state with wave vector \(k = 0\). Photoassociation removes two atoms from this state \(|1\rangle\) and creates an excited molecule in state \(|2\rangle\), with the translational energy due to the recoil momentum of the free-bound photon equal to \(\hbar^2 q_1^2/4m\). Including a second laser frequency, bound-bound transitions remove excited molecules from state \(|2\rangle\) and create stable molecules in state \(|3\rangle\). The translational energy per stable molecule arises from the combined recoil momenta of two photons, and equals \(\hbar^2(q_1 - q_2)^2/4m\). In second-quantized notation, we denote the Boson annihilation operators for atoms, primarily photoassociated molecules, and stable molecules, respectively, by \(a, b,\) and \(g\).

The laser-matter interactions that drive the atom-molecule and molecule-molecule transitions are written in terms of their respective Rabi frequencies, \(\kappa = d_1 E_1/2\hbar\) and \(\Omega = d_2 E_2/2\hbar\). Here the amplitude of the electric field driving a given transition is \(E_i\), and \(d_i\) is the corresponding dipole matrix element \((i = 1, 2)\). Lastly, we define the two-photon and intermediate detunings, \(\Delta\) and \(\delta\), both with due inclusion of photon recoil energies. Analogously to Ref. \([5]\), the Hamiltonian for the system is
\[
\frac{H}{\hbar} = \frac{1}{2} \Delta a^\dagger a + \delta b^\dagger b - \frac{1}{2} \kappa \left( a a^\dagger b^\dagger + a^\dagger a^\dagger b \right) - \Omega \left( b g^\dagger + b^\dagger g \right).
\]  

(1)

The Bose-enhancement of the free-bound dipole matrix element demonstrated as follows. First we consider the Heisenberg equations of motion, which determine the time evolution of the system according to

\[
\dot{a} = -i \left( \frac{1}{2} \Delta a - \kappa a^\dagger b \right),
\]  

(2a)

\[
\dot{b} = -i \left( \delta b - \frac{1}{2} \kappa a a^\dagger - \Omega g \right),
\]  

(2b)

\[
\dot{g} = i \Omega b.
\]  

(2c)

Now, since the number of particles is conserved,

\[
a^\dagger a + 2(b^\dagger b + g^\dagger g) = N,
\]  

(3)

it is clear that \(a, b, g \sim \sqrt{N}\). Hence, we define scaled boson operators of order unity as \(x \rightarrow x' = x/\sqrt{N}\), with \(x = a, b, g\). Dropping the primes, the conserved quantity (3) is normalized to unity, and the equations of motion are given by

\[
\dot{a} = -i \left( \frac{1}{2} \Delta a - \chi a^\dagger b \right),
\]  

(4a)

\[
\dot{b} = -i \left( \delta b - \frac{1}{2} \chi a a^\dagger - \Omega g \right),
\]  

(4b)

\[
\dot{g} = i \Omega b.
\]  

(4c)

From Eqs. (4), the many-body Bose-enhancement of the free-bound dipole matrix element is evident in the scaled Rabi frequency \(\chi = \sqrt{N}\kappa\).

As it happens, the present STIRAP analysis depends crucially on the fact that the bare free-bound coupling \(\kappa\) is scaled by the factor \(\sqrt{N}\), while that for the bound-bound transition, \(\Omega\), is unchanged. To see why, we recall photoassociation in terms of our quasicontinuum model \([7,8]\), which represents the dissociation continuum of the molecule as an infinite number of discrete energy levels separated equally by \(\hbar \epsilon\). The correct free-atom results are recovered by taking the limit \(\epsilon \rightarrow 0\). But, the bare free-bound coupling is given in terms of the frequency spacing as \(\kappa \sim \sqrt{\epsilon}\), or in terms of the corresponding quantization volume
as \( \kappa \sim 1/\sqrt{V} \). In the free-atom limit (\( \epsilon \to 0 \) or \( V \to \infty \)) we then find that \( \kappa \to 0 \). While this observation does not condemn photoassociation of a nondegenerate gas in the thermodynamic limit \( [7,8] \), \( V \to \infty \) and \( N \to \infty \) with \( \rho = N/V \) constant, it does imply that \( \kappa(t) \ll \Omega(t) \) for all \( t \). Hence, a counter-intuitive reversal of the coupling strengths of the pulses \( [12] \), \( \Omega(t) \gg \kappa(t) \) for \( t \to -\infty \) and \( \kappa(t) \gg \Omega(t) \) for \( t \to +\infty \), cannot be achieved. It is therefore the absence of STIRAP that has been predicted for nondegenerate free-bound-bound transitions \( [7] \). However, as shown above, in a condensate the bare Rabi frequency of a nondegenerate gas \( \kappa \) is scaled by the Bose enhancement factor \( \sqrt{N} \), which leads to a finite value even in the thermodynamic limit \( [3] \): \( \chi \sim \sqrt{N/V} \sim \sqrt{\rho} \). This observation will open the door to using STIRAP as a means to create a stable molecular condensate.

In order to facilitate an analytical solution, we define the “Kamiltonian” for the system by adding a multiple of the conserved particle number to the Hamiltonian

\[
K = H - \hbar \mu \left[ a^\dagger a + 2 \left( b^\dagger b + g^\dagger g \right) \right], \tag{5}
\]

where the real constant \( \hbar \mu \) is identified as the chemical potential per atom. The Heisenberg equations of motion for the unit-scaled operators become

\[
\dot{a} = i \left( \mu - \frac{1}{2} \Delta \right) a + \chi a^\dagger b, \tag{6a}
\]

\[
\dot{b} = i \left( 2\mu - \delta \right) b + \frac{1}{2} \chi a a + \Omega g, \tag{6b}
\]

\[
\dot{g} = i \left( 2\mu g + \Omega b \right). \tag{6c}
\]

From this point onward we also resort to the semi-classical approach analogous to the Gross-Pitaevskii approximation used to describe an alkali condensate. Accordingly, the quantities \( a, b, \) and \( g \) are now \( c \)-numbers, rather than operators.

We are looking for adiabatic solutions to the time-evolution equations \( [3] \) for transient couplings \( \chi(t) \) and \( \Omega(t) \). Denoting the characteristic Rabi frequency scale for the light pulses by \( R \) and the characteristic pulse width by \( T \), the adiabatic approximation \( (\dot{x} \approx 0, x = a, b, g) \) should be valid when the evolution time scale of the system is short compared to the time scale of the pulses; for instance when \( RT \gg 1 \). We return to the adiabatic condition in a
moment, and for the time being simply assume time scales for the problem such that \( \dot{x} \approx 0 \) is valid.

Besides the steady state, we now specify exact two-photon resonance (\( \Delta = 0 \)). To economize the ensuing expressions, we also choose the Bose-enhanced Rabi coupling \( \chi \) as the scale for our frequencies by writing \( \Omega = \bar{\Omega} \chi, \delta = \bar{\delta} \chi \). Now, we have already assumed the Rabi frequencies to be real. Without sacrificing generality, this will allow us to consider the amplitudes \( a, b, \) and \( g \) as strictly real. Additionally, for counter-intuitive pulses the limits \( t \to (-\infty, +\infty) \) correspond to the limits \( \bar{\Omega} \to (\infty, 0) \). Thus we neglect any solution which is not similarly real for all values of \( \bar{\Omega} \) from 0 to \( \infty \). Discarding also solutions differing only by redundant signs, there simply remains

\[
\begin{align*}
\mu_0 &= 0, & (7a) \\
a_0 &= \sqrt{\bar{\Omega} \left( \sqrt{2 + \bar{\Omega}^2} - \bar{\Omega} \right)}, & (7b) \\
b_0 &= 0, & (7c) \\
g_0 &= -\frac{1}{2} \left( \sqrt{2 + \bar{\Omega}^2} - \bar{\Omega} \right); & (7d)
\end{align*}
\]

\[
\begin{align*}
\mu_\pm &= \pm \frac{\bar{\Omega}^2 + \bar{\delta} \left( \bar{\delta} \pm \sqrt{\bar{\Omega}^2 + \bar{\delta}^2} \right)}{2 \sqrt{\bar{\Omega}^2 + \bar{\delta}^2}} \chi, & (8a) \\
a_\pm &= 0, & (8b) \\
b_\pm &= \frac{1}{2} \sqrt{1 \pm \frac{\bar{\delta}}{\sqrt{\chi^2 + \bar{\delta}^2}}}, & (8c) \\
g_\pm &= -\frac{1}{2} \sqrt{1 \pm \frac{\bar{\delta}}{\sqrt{\bar{\Omega}^2 + \bar{\delta}^2}}} \\
&\quad \times \left[ \frac{\bar{\Omega}^2 + \bar{\delta} \left( -\bar{\delta} \pm \sqrt{\bar{\Omega}^2 + \bar{\delta}^2} \right)}{\bar{\Omega} \sqrt{\bar{\Omega}^2 + \bar{\delta}^2}} \right]. & (8d)
\end{align*}
\]

It is easy to see that the above results are the nonlinear counterparts of those obtained from the standard STIRAP analysis [12]. The solution (7) is the dark state. For a counter-intuitive pulse sequence, \( \bar{\Omega} \gg 1 \) for \( t \to -\infty \) and \( \bar{\Omega} \ll 1 \) for \( t \to +\infty \), the dark state (7)
initially consists of atoms \((a_0 \rightarrow 1, g_0 \rightarrow 0)\), while the final dark state is all molecules \((a_0 \rightarrow 0, g_0 \rightarrow 1/\sqrt{2})\). At no intervening time is there any population in the intermediate molecular state \((b_0 \equiv 0)\). If the laser pulses allow for adiabatic evolution, an atomic condensate is converted to a molecular condensate without any loss from the intermediate state.

We have checked these results with an exact numerical solution to the equations of motion (8), examining the intuitive adiabatic condition \(RT \gg 1\) as well. In Fig. 2, Gaussian pulses of the form \(\chi(t) = R \exp \left[-(t - D_1)^2/T^2\right]\) and \(\Omega(t) = R \exp \left[-(t - D_2)^2/T^2\right]\) illustrate that an insufficient pulse area \((RT)\) results in a significantly populated intermediate state. On the other hand, a pulse area much greater than unity readily decouples the nonadiabatic states (8), allowing the system to adiabatically follow the dark state as it moves from the initial BEC to MBEC. In particular, Fig. 2(b) gives the probability of creating excited molecules as \(|b|^2 \sim 10^{-7}\), so that irreversible losses from either photodissociation or spontaneous decay should be negligible. Coherent free-bound-bound STIRAP is thereby confirmed.

To improve upon our discussion of the adiabatic approximation, we focus specifically on the effect of pulse overlap. We apply the textbook criterion [16] for adiabaticity to the eigenvector \(\psi = (a, b, g)^T\). From Eqs. (7) and (8), the coupling between the nonadiabatic states, \(\psi_\pm\), and the rate of change of the adiabatic state, \(\dot{\psi}_0\), must therefore be much less than the spacing between the respective chemical potentials, \(|\psi^T_\pm \dot{\psi}_0| \ll |\mu_0 - \mu_\pm|\). Furthermore, we restrict our analysis to zero intermediate detuning \((\delta = 0)\), and introduce the arbitrary pulse shapes \(\chi(t) = R f_1(\tau)\) and \(\Omega(t) = R f_2(\tau)\), where \(\tau = t/T\) is a dimensionless time. The adiabatic condition is then \(F \ll RT\), where the (dimensionless) nonlinear adiabatic factor, \(F\), is given as

\[
F = \frac{|\dot{f}_1(\tau)/f_1(\tau) - \dot{f}_2(\tau)/f_2(\tau)|}{2 \sqrt{2 f_1^2(\tau) + f_2^2(\tau)}} \\
\times \left| f_2(\tau)/f_1(\tau) - \sqrt{2 + f_2^2(\tau)/f_1^2(\tau)} \right|.
\]

We find a dependence on pulse overlap that is qualitatively similar to the results in Ref. [12] for ordinary STIRAP. In particular, if the two pulses vanish concurrently (such that
their ratio is finite), the fraction in Eq. (3) diverges, and the adiabatic condition, $F \ll RT$, is violated. Additionally, an increase in pulse area $RT$ may provide adiabaticity despite a poor pulse overlap. Using Gaussian pulse shapes, these observations may be quantified as follows. In the vicinity of pulse overlap, at dimensionless times $\tau \approx (D_1 + D_2)/2T$, we determine the maximum value of $F(\tau)$, $F_{\text{max}}$, as a function of the delay between the pulses, $D = D_1 - D_2$. Numerically, breakdown of adiabaticity occurs at a specific pulse separation when the fractional efficiency, $2|g|^2$, is no longer of order unity; hence, the value of $F_{\text{max}}$ at this point defines the adiabatic condition in terms of $D$. The results for $RT = (10^2, 10^3, 10^4)$ are shown in Fig. [3]. We find that the adiabatic approximation is valid for pulse overlaps satisfying $F_{\text{max}}(D) \lesssim 0.25 RT$. Incidentally, we find exactly the same result for peaked-exponential pulse shapes, $f_{1,2}(\tau) = \exp(-|t - D_{1,2}|/T)$.

It remains to discuss a few items that we have so far ignored. The first regards the explicit role of photodissociation (PD). Consistent with the quasicontinuum model [7,8,11], we consider PD as irreversible decay from the intermediate state to the atomic continuum. Hence, if there is no intermediate-state population, there is no photodissociation. Second, our results are of course valid regardless of trapping of the atoms and molecules, provided that the time scale for coherent free-bound-bound STIRAP is shorter than the time scale for the motion of the atoms and/or molecules in the trap. Third, if laser intensities permit STIRAP during a time much shorter than the time scales for collisions between atoms and molecules, collisions are negligible as well. Fourth, we have not mentioned the divergence of the adiabatic factor in the wings of the pulses [12]. This is an artifact due to the mathematical shape of the pulse, and can be avoided if, in the region of interest, the shapes satisfy $d(\log \bar{\Omega})/d\tau = 0$. In fact, this is the case for the peaked exponentials mentioned above.

In conclusion, we hold the line on the absence of STIRAP in non-degenerate free-bound-bound transitions, while at the same time proposing the counter-intuitive pulse scheme as a possible mechanism for creating a molecular condensate from an initial BEC. This dichotomy arises because, for the case of a condensate, all $N$ atoms are in the same quantum state, and the subsequent Bose-enhancement of the free-bound dipole matrix element enables a counter-
intuitive reversal of the Rabi frequencies associated with the light pulses. Our numerical trials have confirmed that STIRAP should take place in two-color photoassociation, and validated a simple quantitative criterion for adiabatic atom-molecule conversion.

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FIG. 1. Three-level illustration of coherent free-bound-bound photoassociation, where $N$ atoms have assumedly Bose-condensed into state $|1\rangle$. The free-bound and bound-bound Rabi frequencies are $\kappa$ and $\Omega$, respectively. Similarly, the two-photon and intermediate detunings are $\Delta$ and $\delta$. Irreversible losses are due to either photodissociation, at the rate $\Gamma$, or spontaneous decay, at the rate $\Gamma_S$. The difference from the familiar three-level scheme is that the free-bound interaction involves three particles, and is therefore nonlinear.
FIG. 2. Transient free-bound-bound photoassociation of a BEC for a counterintuitive pulse order. The pulses are of equal height, $\chi_0 = \Omega_0 = R$, so that $R = 1$ sets the unit of frequency. The intermediate detuning is $\delta = 1$, and the pulse delays are $D_1 = 4.5T$ and $D_2 = 2.5T$. Also, recall that $N$ atoms gives a maximum of $N/2$ molecules, so that $|g|^2 = 1/2$ represents complete conversion of the initial condensate. (a) $T = 10$ results in a pulse area insufficient to provide adiabaticity. (b) As expected, at $T = 10^4$ the initial BEC is converted entirely into MBEC.
FIG. 3. Efficiency of free-bound-bound STIRAP and the nonlinear adiabatic factor $F$ plotted as a function of the pulse separation $D = D_1 - D_2$. In the region of pulse overlap, $\tau \approx (D_1 + D_2)/2T$, we determine the maximum value of $F(\tau)$, $F_{\text{max}}$, and compare it to the numerical results for the fractional efficiency, $2|g|^2$. For $R = 1$ and $T = (10^2, 10^3, 10^4)$, it is clear that $F_{\text{max}}/(0.25 RT) = 1$ exactly marks the breakdown of adiabaticity.