Bose-Stimulated Raman Adiabatic Passage in Photoassociation

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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 raises an interest because STIRAP has been predicted to be absent in the nondegenerate case [Javanainen and Mackie, Phys. Rev. A **58**, R789 (1998)]. Nevertheless, we find that 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 Bose-Einstein condensation (BEC) in dilute gases continues to develop, candidate systems for BEC are appearing on a regular basis. Besides the original alkalis [1], there is the observation [2] of BEC in hydrogen [3]. Meanwhile, a spin-polarized helium condensate is not out of the question, and the latest theoretical work has also shown that coherent photoassociation might be used to produce a degenerate molecular gas (MBEC) from an already Bose-condensed sample of atoms [4–6].

Photoassociation (PA) occurs when an atom pair interacts with a photon, thereby making a transition from the two-atom continuum to a bound state of the molecule. Quantizing the molecular dissociation continuum allows one to describe such free-bound transitions using standard few-level quantum optics [7–9]. Beyond providing a few-level framework, the quasicontinuum approach has also led to a matter-quantized formulation of photoassociation analogous to the theory of second-harmonic generation of light [5,10]. In this context of nonlinear matter optics [11], atom-molecule conversion displays coherent BEC-MBEC oscillations, adiabatic following, and nonclassical collapse and revivals [5,9].

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 or spontaneous decay, tend to negate the benefits of the coherence. In this Letter we therefore develop coherent two-color free-bound-bound photoassociation, where the primary photoassociated molecules are transferred with another laser field to a stable molecular state. We consider pulsed free-bound and bound-bound couplings that occur in the counterintuitive order [12], and so correspond to stimulated Raman adiabatic passage (STIRAP) from atoms to molecules. The hope is to draw from the feature of STIRAP that, ideally, there is never any population in the intermediate state to suffer from irreversible losses.

Besides its nonlinear character, this problem is of particular interest since we have previously argued for the *absence* of free-bound-bound STIRAP [7]. There is, of course, no doubt as to the production of ultracold molecules with such near-resonant two-color schemes [13]. However, at this time there is no evidence that in a nondegenerate thermal gas the experimental hallmark of STIRAP, counterintuitive pulse order, will either protect the primary photoassociated molecules from decay or enhance the yield of stable molecules. In contrast, the present work illustrates that, in the case of a condensate, STIRAP is feasible and works analogously to the usual three-level scheme. All told, Bose enhancement of the dipole matrix element, owing to many atoms in the condensate state, is what allows for the difference.

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 semiclassical approach to identify the nonlinear counterpart of the dark state [14] that contains no primary photoassociated molecules. Given that Bose enhancement enables a counterintuitive 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 stable 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 have condensed into the same one-particle state, say, 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, we denote the boson annihilation operators for atoms, primarily photoassociated molecules, and stable molecules, respectively, by a, b, and g. Although we do not discuss them explicitly, all effects of photon recoil are correctly incorporated into our formalism [5,9,15].

The laser-matter interactions that drive the atom-molecule and molecule-molecule transitions are written in terms of their respective Rabi frequencies, $\kappa = d_1 E_1/2\hbar$

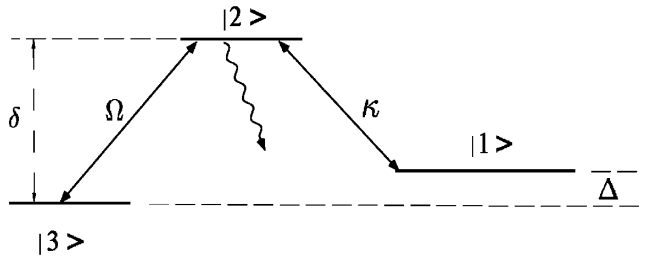

FIG. 1. Three-level illustration of coherent free-bound-bound photoassociation, where N atoms have assumedly Bose condensed into state $|1\rangle$. The free-bound and bound-bound Rabi frequencies are κ and Ω, respectively. Similarly, the two-photon and intermediate detunings are Δ and δ. The wavy line denotes the irreversible losses that STIRAP is expected to combat. The difference from the usual three-level scheme is that the Hamiltonian for photoassociation is trilinear; thus, in the same sense as for "chi-two" processes in nonlinear optics, two atoms are needed to produce one molecule.

and $\Omega = d_2 E_2/\hbar$. 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, Δ and δ. Analogously to Ref. [5], the Hamiltonian for the system is

$$\frac{H}{\hbar} = \frac{H_0}{\hbar} - \tfrac{1}{2}\kappa(aab^\dagger + a^\dagger a^\dagger b) - \tfrac{1}{2}\Omega(bg^\dagger + b^\dagger g), \tag{1}$$

where $H_0/\hbar = (\Delta/2)a^\dagger a + \delta b^\dagger b$.

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

$$i\dot{a} = \tfrac{1}{2}\Delta a - \kappa a^\dagger b, \tag{2a}$$

$$i\dot{b} = \delta b - \tfrac{1}{2}(\kappa aa + \Omega g), \tag{2b}$$

$$i\dot{g} = -\tfrac{1}{2}\Omega b. \tag{2c}$$

Now, since the number of particles is conserved,

$$a^\dagger a + 2(b^\dagger b + g^\dagger g) = N, \tag{3}$$

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

$$i\dot{a} = \tfrac{1}{2}\Delta a - \chi a^\dagger b, \tag{4a}$$

$$i\dot{b} = \delta b - \tfrac{1}{2}(\chi aa + \Omega g), \tag{4b}$$

$$i\dot{g} = -\tfrac{1}{2}\Omega b. \tag{4c}$$

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 κ is scaled by the factor $\sqrt{N}$, while that for the bound-bound transition, Ω, is unchanged. To see why, we recall photoassociation in terms of our quasicontinuum model [7–9]. We introduced a quantization volume V, which rendered the two-atom states discrete. In fact, the dipole matrix element d_1 is computed between such a (box normalized) dissociation state and a bound molecular state [15], with the result that both the matrix element and the Rabi frequency κ scale with the quantization volume as $1/\sqrt{V}$. The continuum limit $V \to \infty$ then finds that $\kappa \to 0$. In contrast, d_2 is the ordinary bound-bound matrix element for a molecule, and the Rabi frequency Ω is independent of the quantization volume V. While $\kappa \to 0$ does not condemn photoassociation of a nondegenerate gas in the thermodynamic limit [7–9], $V \to \infty$ and $N \to \infty$ with $\rho = N/V$ constant, it does imply that $\kappa(t) \ll \Omega(t)$ for all t. Hence, a counterintuitive 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.

This is the essence of our argument for the absence of STIRAP in free-bound-bound photoassociation of a nondegenerate thermal gas [7,9]. More specifically, the indication is that, *a priori*, a counterintuitive pulse sequence will present no benefit over an ordinary scheme. However, as shown above, in a condensate the bare Rabi frequency of a nondegenerate gas κ is scaled by the Bose-enhancement factor $\sqrt{N}$, which leads to a finite value even in the thermodynamic limit [5,9]; $\chi \sim \sqrt{N/V} \sim \sqrt{\rho}$. 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

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

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

$$i\dot{a} = (\tfrac{1}{2}\Delta - \mu)a - \kappa a^\dagger b, \tag{6a}$$

$$i\dot{b} = (\delta - 2\mu)b - \tfrac{1}{2}(\kappa aa + \Omega g), \tag{6b}$$

$$i\dot{g} = -(2\mu g + \tfrac{1}{2}\Omega b). \tag{6c}$$

From this point onward we also resort to the semiclassical approach analogous to the Gross-Pitaevskii approximation used to describe an alkali condensate [16]. Accordingly, the symbols a, b, and g in Eqs. (6) hereafter refer to c numbers, rather than operators.

We are looking for adiabatic solutions to the time-evolution equations (6) for transient couplings $\chi(t)$ and $\Omega(t)$. Denoting the characteristic Rabi frequency 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 χ as the frequency scale 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. In particular, for counterintuitive pulses the limits $t \to (-\infty, +\infty)$ correspond to the limits $\bar{\Omega} \to (\infty, 0)$; thus, we neglect any solution which is not real for *all* values of $\bar{\Omega}$ from 0 to ∞. Discarding also solutions differing only by redundant signs, there remain three properly normalized [$|a|^2 + 2(|b|^2 + |g|^2) = 1$] stationary solutions to Eqs. (6):

$$\mu_0 = 0\,, \tag{7a}$$

$$a_0 = \sqrt{\bar{\Omega}(\sqrt{2 + \bar{\Omega}^2} - \bar{\Omega})}\,, \tag{7b}$$

$$b_0 = 0\,, \tag{7c}$$

$$g_0 = -\frac{1}{2}(\sqrt{2 + \bar{\Omega}^2} - \bar{\Omega})\,; \tag{7d}$$

$$\mu_\pm = \pm\frac{\bar{\Omega}^2 + \bar{\delta}(\bar{\delta} \pm \sqrt{\bar{\Omega}^2 + \bar{\delta}^2})}{2\sqrt{\bar{\Omega}^2 + \bar{\delta}^2}}\,\chi\,, \tag{8a}$$

$$a_\pm = 0\,, \tag{8b}$$

$$b_\pm = \frac{1}{2}\sqrt{1 \pm \frac{\bar{\delta}}{\sqrt{\bar{\Omega}^2 + \bar{\delta}^2}}}\,, \tag{8c}$$

$$g_\pm = -b_\pm\left[\frac{\bar{\Omega}^2 + \bar{\delta}(-\bar{\delta} \pm \sqrt{\bar{\Omega}^2 + \bar{\delta}^2})}{\bar{\Omega}\sqrt{\bar{\Omega}^2 + \bar{\delta}^2}}\right]. \tag{8d}$$

It is easy to see that the above results are the nonlinear counterparts of those obtained from the standard STIRAP analysis; see Ref. [12], whose notation we have adopted. The solution (7) is the dark state [14]. For a counterintuitive 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 ($a_0 \to 1, g_0 \to 0$), while the final dark state is all molecules ($a_0 \to 0, g_0 \to 1/\sqrt{2}$). 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 stable molecular condensate without any loss from the intermediate state.

These results are checked with an exact numerical solution to the equations of motion (6). In Fig. 2, Gaussian pulses of the form $\chi(t) = R\exp[-(t - D_1)^2/T^2]$ and $\Omega(t) = R\exp[-(t - D_2)^2/T^2]$ illustrate that pulses with areas (RT) much greater than unity readily decouple 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 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.

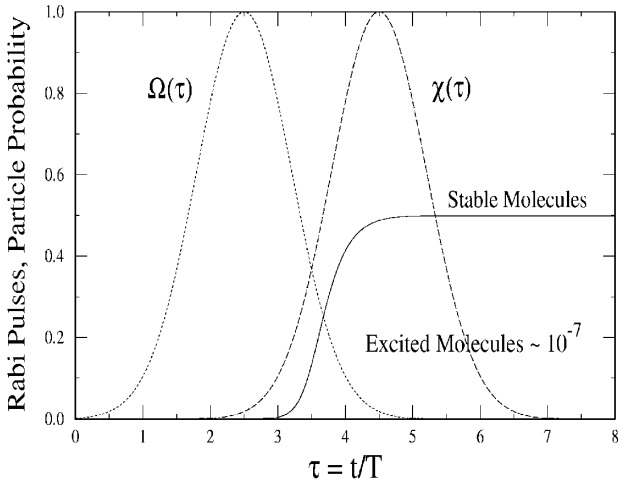

FIG. 2. Bose-stimulated Raman adiabatic passage in photoassociation. The pulses are of equal height, $\chi_0 = \Omega_0 = R$, so that $R = 1$ sets the unit of frequency. The intermediate detuning is $\delta = 1$, the pulse delays are $D_1 = 4.5\,T$ and $D_2 = 2.5\,T$, and the pulse width is $T = 10^4$. Noting that N atoms give $N/2$ molecules at best, we see that $|g|^2 \to 1/2$ and the initial BEC is converted into a stable MBEC.

To improve upon our discussion of the adiabatic approximation, we focus specifically on the effect of pulse overlap. We apply the textbook criterion [17] for adiabaticity to the (real) 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, $|\psi_\pm^T\dot{\psi}_0| \ll |\mu_0 - \mu_\pm|$. Furthermore, we restrict our analysis to zero intermediate detuning ($\bar{\delta} = 0$), and introduce the arbitrary pulse shapes $\chi(t) = Rf_1(\tau)$ and $\Omega(t) = Rf_2(\tau)$, 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

$$F = \frac{|\dot{f}_1(\tau)/f_1(\tau) - \dot{f}_2(\tau)/f_2(\tau)|}{2\sqrt{2f_1^2(\tau) + f_2^2(\tau)}} \times |f_2(\tau)/f_1(\tau) - \sqrt{2 + f_2^2(\tau)/f_1^2(\tau)}|\,. \tag{9}$$

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. (9) 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 $\tau \simeq (D_1 + D_2)/2T$, we determine the maximum value of $F(\tau)$, F_m, 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_m at this point defines the

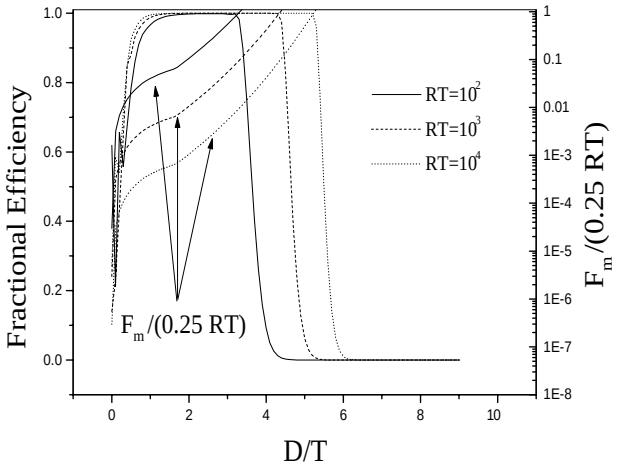

FIG. 3. Efficiency of Bose STIRAP in photoassociation and the nonlinear adiabatic factor as a function of the pulse separation, $D = D_1 - D_2$. In the region of pulse overlap, $\tau \simeq (D_1 + D_2)/2T$, we determine the maximum value of $F(\tau)$, F_m, and compare it to the numerical results for the fractional efficiency, $2|g|^2$. For $RT = (10^2, 10^3, 10^4)$, it is clear that $F_m/(0.25\,RT) = 1$ exactly marks the fall of adiabaticity.

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 $F_m(D) \lesssim 0.25RT$. Incidentally, the same result applies to peaked-exponential pulse shapes, $f_{1,2}(\tau) = \exp(-|t - D_{1,2}|/T)$.

It remains to discuss a few items that we are neglecting. First, we emphasize that our approach is, without *ab initio* justification, semiclassical. However, in the analogous case of rapid adiabatic passage [5], a comparison to the full quantum theory shows that the semiclassical result is already accurate on a 1% level for an atom number as small as 100 [15], and agreement is therefore also expected for STIRAP. The second item regards the explicit role of photodissociation, which amounts to irreversible decay from the intermediate state to the atomic continuum [7–9]. As such, if there is no intermediate-state population, there is no photodissociation. Third, our results are, of course, valid regardless of whether the atoms and molecules are trapped, 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. Lastly, 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.

In conclusion, we hold the line on the absence of STIRAP in nondegenerate free-bound-bound transitions, while at the same time proposing the counterintuitive pulse scheme as a possible mechanism for creating a stable molecular condensate from an initial BEC. This dichotomy arises because, for a condensate, all N atoms are in the same quantum state, and the subsequent Bose enhancement of the free-bound dipole matrix element enables the benefits of the counterintuitive scheme. Our numerical trials have confirmed that Bose STIRAP should take place in two-color photoassociation, and validated a simple quantitative criterion for adiabatic BEC-MBEC conversion.

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