

Rate Limit for Photoassociation of a Bose-Einstein Condensate

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We simulate numerically the photodissociation of molecules into noncondensate atom pairs that accompanies photoassociation of an atomic Bose-Einstein condensate into a molecular condensate. Such rogue photodissociation sets a limit on the achievable rate of photoassociation. Given the atom density ρ and mass m , the limit is approximately $6\hbar\rho^{2/3}/m$.

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Photoassociation of a Bose-Einstein condensate [1,2] has been predicted to feature examples of quantum-coherent transients, such as Rabi oscillations between atomic and molecular condensates [2,3], rapid [2] and Raman [4] adiabatic passage from an atomic condensate to a molecular condensate, and a superposition of macroscopic numbers of atoms and molecules [5]. The Feshbach resonance in a magnetic field is mathematically equivalent to photoassociation, and should give rise to analogous phenomena [6]. Spontaneous-emission decay of the photoassociated molecules causes experimental problems [7], and so far experiments on photoassociation of a Bose-Einstein condensate [8,9] have not demonstrated coherent matter transients. Nonetheless, the prospect of a molecular condensate continues to motivate further work.

Many of the past theoretical studies of coherent photoassociation have taken into account only the atomic and molecular condensates. Notably ignored is the photodissociation of a molecule into a pair of atoms, neither of which belongs to the atomic condensate. We have investigated such “rogue” photodissociation [2,7] using essentially dimensional arguments, and suggested that there is a shortest possible time scale and a corresponding fastest possible Rabi frequency for coherent photoassociation. Given the laser intensity I , the Rabi frequency Ω is proportional to the laser field strength, $\Omega \propto \sqrt{I}$, whereas the rate of rogue photodissociation scales as $\Gamma \propto I$. The equality $\Omega = \Gamma$ occurs when both of these frequencies are approximately equal to

$$\frac{1}{\tau_\rho} = \omega_\rho = \frac{\hbar\rho^{2/3}}{2\mu}. \quad (1)$$

Here $\rho = \rho_A + 2\rho_M$ is an invariant density derived from the densities of the atoms and the molecules, and μ is the reduced mass of a pair of atoms. In an attempt to speed up coherent photoassociation beyond this limit by increasing the laser intensity, damping due to rogue photodissociation overtakes coherent photoassociation [2,7]. There have also been numerical case studies on the effects of noncondensate modes on photoassociation [10,11], but these do not spell out time or frequency scales comparable to Eq. (1).

In the present paper we formulate a minimal yet realistic, microscopic model for rogue photodissociation, and solve

it numerically. The results demonstrate that there is a maximum achievable photoassociation rate, of the order $6\omega_\rho$. The existence of the rate limit is at variance with the wave picture of condensate atoms.

We take a plane-wave laser field with photon momentum \mathbf{q} to drive photoassociation and photodissociation. Initially there is only a condensate of N zero-momentum atoms present. By momentum conservation, only molecules with momentum \mathbf{q} will be generated in the primary photoassociation. In photodissociation such a molecule breaks up into a pair of atoms with opposite momenta. Processes in which both atoms return to the condensate are the subject of our earlier work on coherent photoassociation [2,7], whereas here the focus is on processes in which the molecules break up into pairs of noncondensate atoms.

Our description starts from our generic Hamiltonian for photoassociation and dissociation [2,7]. We write the Heisenberg equations of motion for the boson operators $a_{\mathbf{k}}$ ($b_{\mathbf{k}}$) characterizing atoms (molecules) with momentum \mathbf{k} , and implement two main approximations. First, in the classical approximation analogous to the use of the Gross-Pitaevskii equation, we treat the atomic and molecular condensate operators $a \equiv a_0$ and $b = b_{\mathbf{q}}$ as c numbers. Second, we take into account all pairs of noncondensate atoms with opposite momenta, but no further photoassociation of noncondensate atoms to any molecular states except back to the molecular condensate. It then turns out that the equations of motion for the c -number atomic amplitude $\alpha = a/\sqrt{N}$, molecular amplitude $\beta = \sqrt{2/N}b$, and noncondensate atom pair amplitudes $c_{\mathbf{k}} = \langle a_{\mathbf{k}}a_{-\mathbf{k}} \rangle$ close. As usual, we discuss s -wave photoassociation and dissociation, so that we may uniquely label the two-atom modes with their energy $\hbar\epsilon$. The equations of motion may be cast in the form

$$\dot{\alpha} = i\frac{\Omega}{\sqrt{2}}\alpha^*\beta, \quad (2a)$$

$$\dot{\beta} = i\delta\beta + i\frac{\Omega^*}{\sqrt{2}}\alpha^2 + i\int d\epsilon \xi(\epsilon)c_\epsilon, \quad (2b)$$

$$\dot{c}_\epsilon = -i\epsilon c_\epsilon + i\xi^*(\epsilon)\beta. \quad (2c)$$

To explain the notation, we first consider the model in the absence of the coupling between condensate atoms and

molecules $\propto \Omega$. The quantity δ is the detuning of the laser above the photodissociation threshold of the molecules (corrected for photon recoil energy [2,7]), and $\xi(\epsilon)$ is the coupling strength for photodissociation of a molecule to an atom pair with energy $\hbar\epsilon$. Using the Fermi golden rule, we find the photodissociation rate for molecules $\Gamma(\delta) = 2\pi|\xi(\delta)|^2$. In our modeling we turn the tables, and assert the equality

$$\xi(\epsilon) = \sqrt{\Gamma(\epsilon)/2\pi}, \quad (3)$$

relating the matrix element $\xi(\epsilon)$ and the on-shell photodissociation rate $\Gamma(\epsilon)$ to an atom pair with energy $\hbar\epsilon$. Second, we know from our theory of coherent photoassociation [2,7] that the Rabi frequency Ω is related to the rate of photodissociation by

$$\Omega = \lim_{\epsilon \rightarrow 0} \sqrt{\frac{\sqrt{2}\pi\hbar^{3/2}\rho}{\mu^{3/2}} \frac{\Gamma(\epsilon)}{\sqrt{\epsilon}}}. \quad (4)$$

Third, in order for Eq. (4) to make sense, for low energies $\Gamma(\epsilon) \propto \sqrt{\epsilon}$ must hold true. This, in fact, is known as the Wigner threshold law. In our modeling we take the threshold law to hold for all relevant energies. Finally, for notational convenience, we write the continuum amplitude in terms of a dimensionless quantity $C(x) \equiv c_{x\Omega}\Omega^{-1/2}$. Our final equations of motion for the amplitudes read

$$\dot{\alpha} = i\frac{\Omega}{\sqrt{2}}\alpha^*\beta, \quad (5a)$$

$$\dot{\beta} = i\delta\beta + i\frac{\Omega}{\sqrt{2}}\alpha^2 + i\gamma^{1/2}\Omega \int dx \sqrt{x} C(x), \quad (5b)$$

$$\dot{C}(x) = -i\Omega x C(x) + i\Omega\gamma^{1/2}\sqrt{x}\beta. \quad (5c)$$

The parameter

$$\gamma = \frac{\Gamma(\Omega)}{2\pi\Omega} = \frac{1}{8\pi^2} \left(\frac{\Omega}{\omega_\rho} \right)^{3/2} \quad (6)$$

characterizes the relative importance of rogue photodissociation and coherent photoassociation. In Eqs. (5) we could readily absorb the frequency Ω into the unit of time, but we will not do so as this would cause contorted discussions below.

Coupling to the noncondensate modes introduces the frequency ω_ρ . The presence of this frequency could have been anticipated (and, in fact, was anticipated [2,7]) from dimensional arguments alone. First, inasmuch as one is permitted to ignore the internal state, the only manifest parameter having to do with the motion of an individual atom is its mass m . Second, consider a zero-temperature non-interacting gas of atoms. At zero temperature there is no energy scale, and the absent interaction will introduce no dimensional scales either. The only parameter in evidence is then the density of the gas ρ . Finally, if quantum mechanics is involved, \hbar is implied. Now, up to a numerical factor, the only parameter with the dimension of frequency that can be constructed out of m , ρ , and \hbar is ω_ρ .

We study Eqs. (5) numerically by discretizing the dissociation continuum. We also cut off the continuum at

a maximum frequency ϵ_M . Basically, the vector made of the amplitudes α , β , and $C(x_n)$, ψ , satisfies a Schrödinger equation of the form $i\dot{\psi} = H(\psi)\psi$. As Eqs. (5) are nonlinear, the Hamiltonian H depends on the vector ψ itself. However, if this dependence is ignored, the resulting linear Schrödinger equation may be solved using the norm conserving algorithm described in Ref. [12]. Moreover, the matrix of the Hamiltonian is such that the run time scales linearly with the number of the continuum states n_c . We take care of the nonlinearity with a predictor-corrector method. To execute a time step $t \rightarrow t + h$, we first integrate the Schrödinger equation for the constant Hamiltonian $H[\psi(t)]$ to obtain the ‘‘predicted’’ wave function $\tilde{\psi}(t + h)$, and then ‘‘correct’’ by integrating the Schrödinger equation anew using the Hamiltonian $\frac{1}{2}\{H[\psi(t)] + H[\tilde{\psi}(t + h)]\}$. The algorithm is norm conserving, the error for integrating over a fixed time interval scales with the step size at least as $\mathcal{O}(h^2)$ (empirically often better), and the run time is linear in the number of continuum states. Typically we discretize the continuum in $n_c = 10^4$ steps with the maximum frequency $\epsilon_M = 100\Omega$, but when needed for convergence we do not hesitate to resort to use, say, $n_c = 10^6$ and $\epsilon_M = 10^3\Omega$.

Coupling to the dissociation continuum also shifts the molecular level [13,14]. We correct for the shift by adding to the detuning the Stark shift calculated using perturbation theory for on-threshold photodissociation, namely, $\Gamma(\epsilon_M)/\pi$. The shift may be very large; in fact, if we did not truncate the continuum, it would be infinite. This is our version of the renormalization problem discussed in Ref. [11]. In the limit of a large dissociation rate, perturbation theory becomes unreliable. Correspondingly, it gets difficult to tell exactly what the detuning is with respect to the photodissociation threshold. This problem is not unique to our model, but would emerge in real experiments as well.

For demonstration, Fig. 1 gives the quantities $P_A = |\alpha|^2$ and $P_M = |\beta|^2$, the respective probabilities that an arbitrary atom in the system is part of the atomic or the molecular condensate, as a function of time, given that the system started as an atomic condensate. In Fig. 1(a) we set $\gamma = 0$, and thereby disregard rogue photodissociation. For this (renormalized) detuning $\delta = \Omega$, the conversion between atoms (dotted line) and molecules (dashed line) oscillates in such a way that half of the atomic condensate is periodically converted into a molecular condensate. In Fig. 1(b) we add rogue photodissociation, setting $\Gamma(\Omega) = \Omega$ and hence $\gamma = 1/(2\pi)$. After a few damped oscillations, the probabilities settle down. The total probability that an atom is part of either condensate (solid line) drops to 0.8, indicating that in the process 20% of the atoms are lost to rogue photodissociation. Although the couplings between the condensates and from the molecular condensate to the noncondensate atoms remain, the atomic and the molecular condensates lock up in a superposition immune to rogue photodissociation. It is known from the past work on decay of a discrete state to a shaped continuum

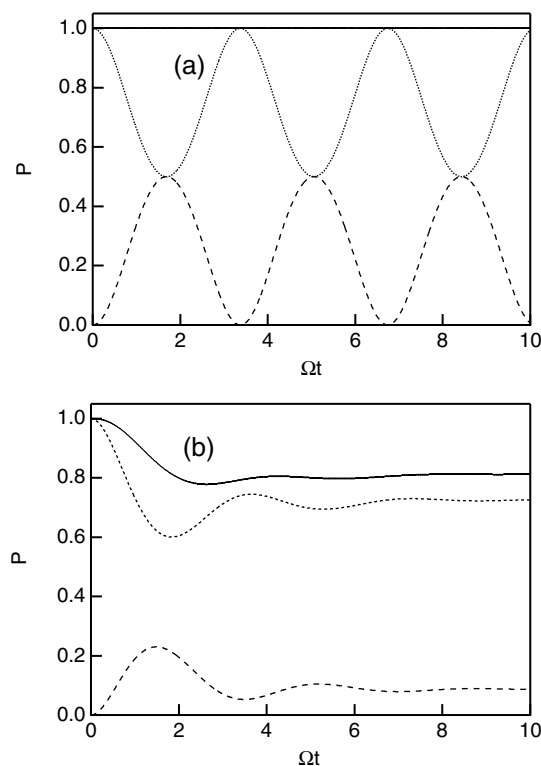


FIG. 1. Atomic (P_A , dotted line) and molecular (P_M , dashed line) probabilities, as well as the total probability that an atom is part of either condensate ($P_A + P_M$, solid line) as a function of time. In (a) there is no rogue photodissociation, $\gamma = 0$, while in (b) we set $\gamma = 1/(2\pi)$. The (renormalized) detuning is fixed at $\delta = \Omega$.

(e.g., photodissociation of a negative ion [15]) that, given a threshold to the continuum, some of the population may stay permanently trapped in the bound state. Curiously, the same applies here to a superposition of atomic and molecular amplitudes, even though the condensate system is nonlinear and the superposition principle does not hold.

Our main subject is limitations on conversion from atoms to molecules due to rogue photodissociation. In the traditional perturbation theory one would study the photoassociation rate as a function of the problem parameters. However, as is obvious from Fig. 1, atom-molecule conversion is not governed by a simple exponential time dependence. A clearcut photoassociation rate generally does not exist. Because of level shifts, it may also be difficult to know the true value of the detuning. To circumvent these problems, we have developed a protocol that mimics conceivable experiments. We first fix an interaction time, call it τ , once and for all. Our basic numerical operation is to calculate the loss of condensate atoms, $1 - P_A(\Omega, \gamma, \delta; \tau)$, as a function of the Rabi frequency Ω , rogue photodissociation amplitude γ , and detuning δ , starting from a pure atomic condensate. We vary the detuning δ , and find what we interpret as the maximal photoassociation probability with the other parameters fixed, $1 - P_A(\Omega, \gamma; \tau)$. The optimal rate for photoassociation is then defined as $R(\Omega, \gamma; \tau) = [1 - P_A(\Omega, \gamma; \tau)]/\tau$.

To get a quantitative handle on the variation of the effective rate R we divide it by ω_ρ , and plot in Fig. 2 the result as a function of the variable $1/(\tau\omega_\rho)$ for four different Rabi frequencies, $\Omega = 1/\tau$ (dotted line), $2/\tau$ (dash-dotted line), $4/\tau$ (dashed line), and $8/\tau$ (solid line). It appears that there is a maximum rate for photoassociation of the order of $6\omega_\rho$.

We emphasize once more that our maximal photoassociation rate measures how many atoms one can remove in a fixed interaction time. There really does not have to be a rate at all. We demonstrate this fact by plotting in Fig. 3 the time dependences of the molecular probability P_M (dotted line), the probability for condensate atoms P_A (dashed line), and the total condensate probability $P_A + P_M$ (solid line) as a function of time. The fixed parameters $\Omega = 4/\tau$, $\delta = -9.27\Omega$, and $\gamma = 1.27$ are chosen in such a way that this is the time evolution used to obtain the maximum of the curve labeled $\Omega = 4/\tau$ in Fig. 2. The laser is tuned well *below* the photoassociation threshold. There is very little molecular probability, so that the molecules are a virtual intermediate state. Instead, we have a slowly damped two-photon flopping between the atomic condensate and noncondensate atom pairs. It is doubtful that such flopping survives the various sources of incoherence left out from our model, such as photoassociation of noncondensate atoms to noncondensate molecules or collisions of noncondensate atoms. But we surmise that added loss mechanisms further hinder photoassociation, and our upper limit for the rate $6\omega_\rho$ would probably hold in a more complete model.

So far we have discussed the case when the molecular state is not damped by spontaneous emission. Our modeling is therefore most appropriate for two-color photoassociation in the Raman configuration. However, we have

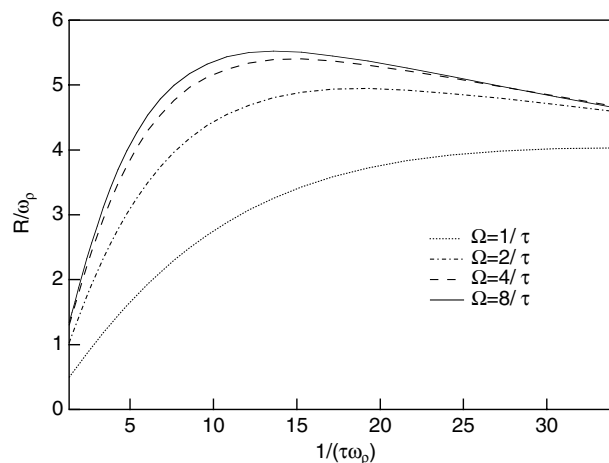


FIG. 2. Maximum rate of photoassociation R for a fixed interaction time τ scaled to the density dependent frequency parameter ω_ρ as a function of $1/(\tau\omega_\rho)$. The lines are for various Rabi frequencies Ω , as indicated in the legend. Physically, in order to follow a line of fixed Rabi frequency toward increasing $1/(\tau\omega_\rho)$, one must at the same time increase the laser intensity and decrease the condensate density, so that rogue photodissociation becomes more prominent.

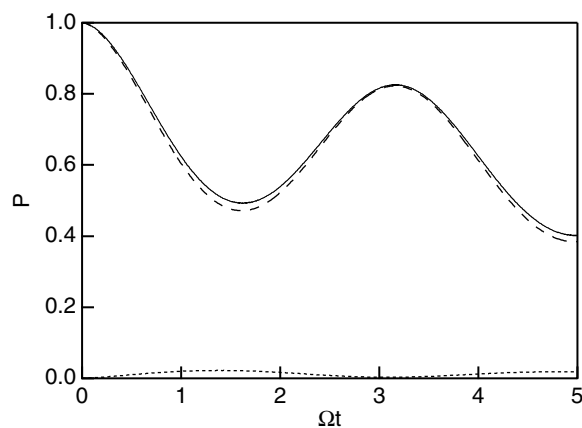


FIG. 3. Time dependences of the three probabilities P_M (dotted line), P_A (dashed line), and total condensate probability $P_A + P_M$ (solid line) as a function of time. The fixed parameters are $\Omega = 4/\tau$, $\delta = -9.27 \Omega$, $\gamma = 1.27$. A true photoassociation rate does not exist for these parameters.

also carried out realistic simulations of one-color photoassociation, in which the spontaneous decay rate of the photoassociated molecules is the largest frequency parameter in the problem. Photoassociation once more does not proceed exponentially and there is some ambiguity in the definition of the rate, but the conclusion is that the maximum achievable rate for photoassociation very nearly equals ω_ρ [16].

If one is to think of atoms as particles, there must be a limit to photoassociation rate. In order to photoassociate, two atoms have to drift close to one another. This process takes longer, the more dilute the gas is; it cannot be sped up arbitrarily by increasing the light intensity. On the other hand, within the two-mode approximation, a gas can be photoassociated arbitrarily fast; just set $\gamma = 0$ in Eqs. (5) and let $\Omega \rightarrow \infty$ by increasing the laser intensity. In the two-mode approximation the atoms are waves, simultaneously everywhere in the atomic condensate. The existence of a maximum to the photoassociation rate thus is a question of particle versus wave nature of the atoms.

The existence of a rate limit also contrasts in an interesting way with scattering theory. When the temperature of the gas is of the order of the critical temperature for Bose-Einstein condensation, the maximum cross section for collisions between atoms as per quantum mechanics, the unitarity limit, gives a collision rate that equals our rogue-photodissociation limit for the rate of photoassociation. At lower temperatures the newly found particle nature dominates, and the rogue-photodissociation limit is more stringent than the unitarity limit.

The two-atom position correlation function straddles particle and wave pictures. Photoassociation evidently depletes two-body correlations at short distances, and the motion of the atoms has to replete them. Though we have not been able to make an explicit connection, we surmise that Ref. [11] focusing on atom-atom correlations boils down essentially to the same physics as our rogue photodissociation. In Ref. [10] the Gross-Pitaevskii equations

were actually integrated numerically in the momentum representation. The phenomenon thus found seems to be what we call modulational instability [17], not rogue photodissociation.

In summary, we have proposed and numerically solved a minimal but realistic model for the photodissociation of molecules to noncondensate atoms that invariably accompanies coherent photoassociation of a Bose-Einstein condensate. The results support the notion that, as the atoms need time to collide, there is a maximum achievable rate to photoassociation of a condensate. What is dimensionally obvious but might be physically surprising is that the maximum rate in a noninteracting, zero-temperature condensate should be of the order of the only frequency parameter that can be constructed out of the density of the condensate. Apart from the fact that rogue photodissociation sets experimental constraints on coherent photoassociation, experiments would also be interesting because they bear on the wave versus particle nature of atoms.

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