Quantum Noise in the Collective Abstraction Reaction $A + B_2 \rightarrow AB + B$

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We demonstrate theoretically that the collective abstraction reaction $A + B_2 \rightarrow AB + B$ can be realized efficiently with degenerate bosonic or fermionic matter waves. We show that this is dominated by quantum fluctuations, which are critical in triggering its initial stages with the appearance of macroscopic nonclassical correlations of the atomic and molecular fields as a result. This study opens up a promising new regime of quantum-degenerate matter-wave chemistry.

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The making and probing of ultracold molecular gases has attracted much attention in recent years [1]. Starting from an atomic Bose-Einstein condensate, magnetic Feshbach resonances and/or optical photoassociation [2] can be exploited to create not only diatomic molecules but also more complex molecules, such as evidenced by the recent observations of transient short-lifetime trimers Cs_3 [3] or tetramers Cs_4 (actually the resonances in inelastic processes) [4]. In another development of relevance for the present study, atom-dimer dark states were produced through coherent photoassociation [5], a process sometimes called superchemistry [6].

So far, matter-wave superchemistry has concentrated largely on the coherent combination or decomposition reactions [7] between atoms and homonuclear or heteronuclear [8] molecules. In this Letter we extend these ideas to the coherent abstraction reaction (or bimolecular reactive scattering) $A + B_2 \rightarrow AB + B$. This reaction is an important benchmark system extensively studied for many years in chemical physics, a particularly noteworthy contribution being the study by Shapiro and Brumer of the coherent control of single-molecular photoassociation or bimolecular collisions via interference of reactive pathways [9]. One main result is to demonstrate that the coherent abstraction reaction can be realized and controlled efficiently in degenerate matter waves by exploiting an atom-molecule dark state. An important characteristic of this process is that it is triggered by quantum noise, leading to large shot-to-shot fluctuations that dominate the initial stages of the reaction. From a theoretical point of view, this implies that the mean-field Gross-Pitaevskii equation is not appropriate to describe the early stages of the coherent bimolecular reaction, and can be used only once the product reactant populations become macroscopic. This is in contrast with single-molecular combination reactions such as the atom-dimer [2,6] or atom-trimer conversion [10], and is reminiscent of quantum or atom optics situations such as the laser, superradiance, and matter-wave superradiance; see, e.g., Refs. [11–13].

The basic idea in realizing the collective reaction $A + B_2 \rightarrow AB + B$ in quantum-degenerate gases is to first create highly excited trimers AB_2 via an entrance-channel atom-dimer Feshbach resonance, and to then photodissociate them into a closed-channel bound dimer and an atom. The use of a dynamical two-photon resonance scheme involving an intermediate trimer state permits one to exploit the existence of a coherent population trapping state (CPT) that prevents the trimer population from becoming significant throughout the conversion process. Such a generalized atom-molecule dark state does *not* exist in other schemes that involve, e.g., an intermediate two-species atomic state. Note also that this scheme is different from a purely collision-induced reaction [14] and from the nondegenerate single-pair dynamics of reactive scattering [9]. To our knowledge this is the first proposal for the quantum control of matter-wave abstraction reactions, and as such it represents a promising new step in superchemistry [4,6].

Our model system is illustrated by Fig. 1. Denoting the strength of the $A + B_2 \rightarrow AB_2$ coupling with detuning δ by λ_1', the Rabi frequency of the dissociating laser by Ω_1' and its detuning by Δ, the dynamics of the system is described

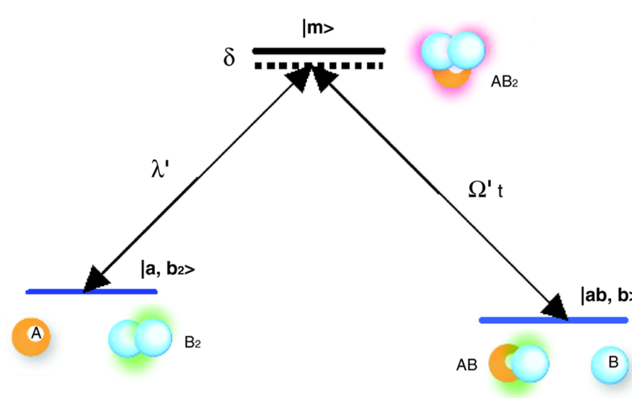

FIG. 1 (color online). Schematic illustration of the coherent abstraction reaction $A + B_2 \rightarrow AB + B$ with degenerate matter waves. Here the atoms A and B can be bosonic or fermionic.

at the simplest level by the model Hamiltonian

$$\begin{aligned}\mathcal{H} = -\int dr\Big\{&\sum_{i,j}\chi'_{i,j}\hat{\psi}_i^\dagger(r)\hat{\psi}_j^\dagger(r)\hat{\psi}_j(r)\hat{\psi}_i(r) + \delta\hat{\psi}_t^\dagger(r)\hat{\psi}_t(r)\\ &+ \lambda'[\hat{\psi}_t^\dagger(r)\hat{\psi}_a(r)\hat{\psi}_{b_2}(r) + \text{H.c.}]\\ &+ (\Delta+\delta)\hat{\psi}_{ab}^\dagger(r)\hat{\psi}_{ab}(r)\\ &- \Omega'[\hat{\psi}_{ab}^\dagger(r)\hat{\psi}_b^\dagger(r)\hat{\psi}_t(r) + \text{H.c.}]\Big\}. \end{aligned} \tag{1}$$

We consider first the case of a bosonic system, in which case the annihilation operators $\hat{\psi}_i$, where the indices i, $j = a$, b, b_2, ab, t stand for atoms (A and B), dimers (B_2 and AB) and trimers, satisfy standard bosonic commutation relations. The terms proportional to $\chi'_{i,j}$ describe s-wave collisions between these species. We remark that trimer formation via an atom-dimer resonance is actively studied in ongoing experiments, and that the Feshbach-resonance-aided photoassociation considered here could also be reformulated as a laser frequency modulation scheme [9,15]. Finally, the Bose-enhanced selectivity of dissociation channels in coherent photodissociation of the heteronuclear trimers ABC was also studied by Moore and Vardi [7].

In the framework of a standard mean-field approach where $\hat{\psi}_i \rightarrow \sqrt{n}\psi_i$ we find readily

$$\begin{aligned}\dot{\psi}_a &= 2i\sum_j \chi_{a,j}|\psi_j|^2\psi_a + i\lambda\psi_{b_2}^*\psi_t;\\ \dot{\psi}_b &= 2i\sum_j \chi_{b,j}|\psi_j|^2\psi_b - i\Omega\psi_{ab}^*\psi_t;\\ \dot{\psi}_{b_2} &= 2i\sum_j \chi_{b_2,j}|\psi_j|^2\psi_{b_2} + i\lambda\psi_a^*\psi_t;\\ \dot{\psi}_{ab} &= 2i\sum_j \chi_{ab,j}|\psi_j|^2\psi_{ab} - i\Omega\psi_b^*\psi_t + i(\Delta+\delta)\psi_{ab},\\ \dot{\psi}_t &= 2i\sum_j \chi_{t,j}|\psi_j|^2\psi_t + (i\delta-\gamma)\psi_t\\ &\quad + i\lambda\psi_a\psi_{b_2} - i\Omega\psi_b\psi_{ab}, \end{aligned} \tag{2}$$

with $\chi_{i,j} = n\chi'_{i,j}$, $\lambda = \lambda'\sqrt{n}$ and $\Omega = \Omega'\sqrt{n}$, and the phenomenological decay rate γ accounts for the loss of intermediate trimers.

For $\psi_b(0) = \psi_{ab}(0) = 0$, Eqs. (2) imply that there is *no growth* in the populations of the atoms B and of the dimers AB. This indicates that the mean-field Gross-Pitaevskii equations cannot describe the short-time behavior of the familiar coherent atom-dimer or atom-trimer conversion [6,10], break down completely in studying the onset of this bimolecular reaction. A similar situation has been previously encountered in a broad range of systems in quantum optics, but also in coupled degenerate atomic and molecular systems such as the matter-wave superradiance in Bose-condensed atoms [11–13]. Following a strategy developed in the study of these systems, we decompose the problem into an initial stage dominated by quantum noise followed by a classical stage that arises once the product components have acquired a macroscopic population. The initial quantum stage is treated in a linearized approach whose main purpose is to establish the statistical properties of the initial fields required for the classical stage [13].

To simplify the description of the initial stages we note that in the collisionless limit an effective second-quantized Hamiltonian can be obtained by adiabatically eliminating the intermediate excited state

$$\hat{\mathcal{H}}_{\text{eff}} = -(G\hat{c}_{ab}^\dagger\hat{c}_b^\dagger\hat{c}_a\hat{c}_{b_2} + \text{H.c.}) + \hat{c}_0, \tag{3}$$

where $\hat{c}_0 = \omega_1\hat{c}_a^\dagger\hat{c}_a\hat{c}_{b_2}^\dagger\hat{c}_{b_2} + \omega_2\hat{c}_{ab}^\dagger\hat{c}_{ab}\hat{c}_b^\dagger\hat{c}_b$,

$$\begin{aligned}G &= (\lambda'\Omega'/\delta)\int dr\phi_{ab}^*(r)\phi_b^*(r)\phi_a(r)\phi_{b_2}(r),\\ \omega_1 &= (\lambda'^2/\delta)\int dr\phi_a^*(r)\phi_a(r)\phi_{b_2}^*(r)\phi_{b_2}(r),\\ \omega_2 &= (\Omega'^2/\delta)\int dr\phi_{ab}^*(r)\phi_{ab}(r)\phi_b^*(r)\phi_b(r),\end{aligned}$$

and $\hat{\psi}_i(r,t) = \phi_i(r)\hat{c}_i(t)$. Equation (3) is reminiscent of the Hamiltonian describing spin-exchange scattering in a two-species two-pseudospin-state Bose condensate [16].

For short enough interaction times, the populations of the products remain small compared to the total particle numbers. In this regime, we can treat the fields $\hat{\psi}_a$ and $\hat{\psi}_{b_2}$ classically, $\hat{c}_{a,b_2} \rightarrow \sqrt{N_{a,b_2}}$, and neglect the term in Eq. (3) describing only the interactions of the modes $\hat{c}_{a,b_2}$. This amounts to linearizing the dynamics of the fields $\hat{c}_{ab}$ and $\hat{c}_b$, with the noise source $\hat{f}_j^\dagger(t)$,

$$\dot{\hat{c}}_{ab,b}(t) = \hat{f}_{b,ab}^\dagger(t) = i\mathcal{G}\hat{c}_{b,ab}^\dagger(t),$$

which is familiar from quantum treatments of the optical parametric oscillator [11] and of the molecular dissociation (pair production) [17]. The noise operators satisfy

$$\langle\hat{f}_i^\dagger(t)\hat{f}_j(t')\rangle = 0, \qquad \langle\hat{f}_i(t)\hat{f}_j^\dagger(t')\rangle = \mathcal{G}^2\delta_{ij}\delta(t-t'),$$

where $\mathcal{G} = G\sqrt{N_aN_{b_2}}$ and i, $j = ab$ or b here and in the following. It is these noise operators that trigger the evolution of the system from initial vacuum fluctuations.

The quantum noise-induced populations of the $\hat{c}_{g_2,b}$ mode and their fluctuations correlation are

$$\begin{aligned}N_j &\equiv \langle\hat{c}_j^\dagger\hat{c}_j\rangle = \sinh^2(\mathcal{G}t) \approx N_aN_{b_2}G^2t^2;\\ \mathcal{C}_{ab} &= \mathcal{C}_b \equiv \frac{\langle\Delta\hat{N}_{ab}\Delta\hat{N}_b\rangle}{\sqrt{N_{ab}N_b}} = 1 + \sinh^2(\mathcal{G}t) > 1,\end{aligned} \tag{5}$$

where $\Delta\hat{N}_j \equiv \hat{N}_j - \langle\hat{N}_j\rangle$. Equation (5) can also be derived by solving Eq. (3) to second order in time. The second factorial moment of the modes $\hat{c}_j$ is typical of chaotic fields $g_j^{(2)} = 2$, but they are entangled, with

$$[g^{(2)}_{ab,b}]^2 - g^{(2)}_{ab} g^{(2)}_b = \sinh^{-2}(\mathcal{G}t) + 4\sinh^{-1}(\mathcal{G}t) > 0, \quad (6)$$

indicative of a violation of the classical Cauchy-Schwartz inequality.

For comparison we comment briefly on the case where atoms A are bosonic and atoms B fermionic. We obtain similar equations of motion in that case, except that the noise operators $(-\hat{f}^\dagger_b, \hat{f}^\dagger_{ab})$ are now different. These equations can be solved via a Bogoliubov transformation, and we find that as a result of the Fermi statistics the vacuum-noise-triggered population is now $N_j = \sin^2(\mathcal{G}t) < 1$ (for the zero-momentum mode [17]), with the dimer-atom pairs correlation becoming $\mathcal{C}_{ab} = \mathcal{C}_b = 1 - \sin^2(\mathcal{G}t) < 1$. The Mandel Q parameters [11] are

$$Q_j = \frac{\langle \hat{N}_j^2\rangle - N_j^2}{N_j} = \begin{cases} (a) & \cosh^2(\mathcal{G}t) > 1, \\ (b) & \cos^2(\mathcal{G}t) < 1, \end{cases} \quad (7)$$

where (a) is for creating bosonic and (b) fermionic matter-wave fields, which exhibit therefore super-Poisson or sub-Poisson statistics [11], respectively.

We conclude the discussion of the short-time dynamics by mentioning that the long-time quantum statistics of the AB and B populations can be calculated by a positive-P representation technique [18] and other methods [16]. Rather than adopting such a full quantum treatment, we proceed in the following by combining the mean-field description of Eqs. (2) with stochastic classical seeds with statistics consistent with the results of the short-time linearized quantum theory [13].

We now turn to the long-time reaction dynamics. We proceed by numerically computing a large number of trajectories (typically about 300) from initial classical seeds that satisfy the short-time statistics of Eq. (5). For each trajectory n, we use Eqs. (2) to calculate the particle populations $N_{i,n}(t)$ where $i = A, B_2, AB$, and B.

Figure 2 shows the standard deviation $\Delta N_i(t)$ of the particle populations $i = A, B, AB$, and B_2 for $\delta = \pm 3$, and the inset shows a range $\pm\Delta N_i$ about their mean, $\bar{N}_i(t) \pm \Delta N_i(t)$ for $\delta = 3$ and in the case of bosonic atoms. As expected, the small product seeds triggered by the initial quantum fluctuations are significantly amplified before reaching a stationary value for $\delta = 3$.

An important feature of the coherent abstraction reaction is that it can be controlled and optimized by exploiting the existence of a CPT dark state [5,10]. Under a dynamical two-photon resonance condition, Eqs. (2) admit a steady-state CPT solution such that the trimer state remains unpopulated at all times [19]

$$N^s_{ab,b} = \frac{2\mathcal{R}}{(1+\mathcal{R})[1 + 2\mathcal{R} + \sqrt{(1-2\mathcal{R})^2 + 8\mathcal{R}\Omega^2/\lambda^2}]}, \quad (8)$$

where we have applied the steady-state ansatz [10] $\psi^s_i = |\psi^s_i| e^{i\theta_i} e^{i\mu_i t}$, $(\theta, \mu)_{b_2,ab} = 2(\theta, \mu)_b$, $(\theta, \mu)_a = (\theta, \mu)_b$ and $\mathcal{R} \equiv N_a(0)/2N_{b_2}(0)$ is introduced to define the initial ratio of the particles numbers. Using $\partial N^s_{ab}/\partial\mathcal{R} = 0$, we can find the maximum value $N^s_{ab}|_{\max} = 1/3$ for $\mathcal{R} = 1/2$.

Figure 3(a) shows the mean particle populations obtained by averaging over $n_T = 300$ trajectories. In this

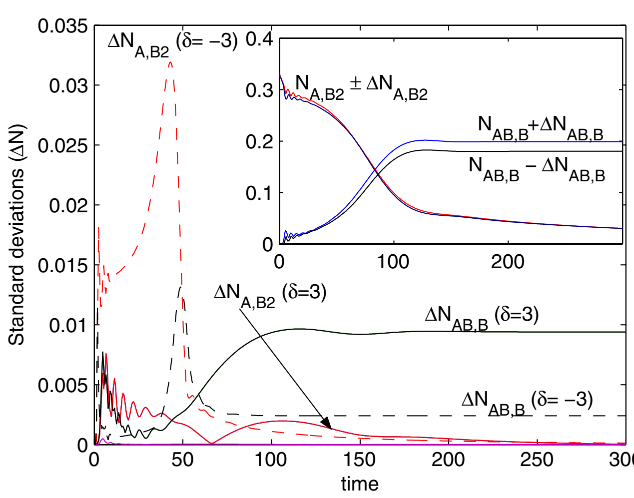

FIG. 2 (color online). Standard deviations of the atom and dimer populations $(\Delta N_j(t) = \langle \Delta\hat{N}_j^2\rangle^{1/2})$ for $\delta = 3$ or $\delta = -3$. Time is in units of λ^{-1}, and $\gamma = 1$. The other parameters are given in the text. The trimer number remains zero at all times due to the CPT condition. Inset: fluctuating range of the populations $\bar{N}_i(t) \pm \Delta N_i(t)$ for $\delta = 3$.

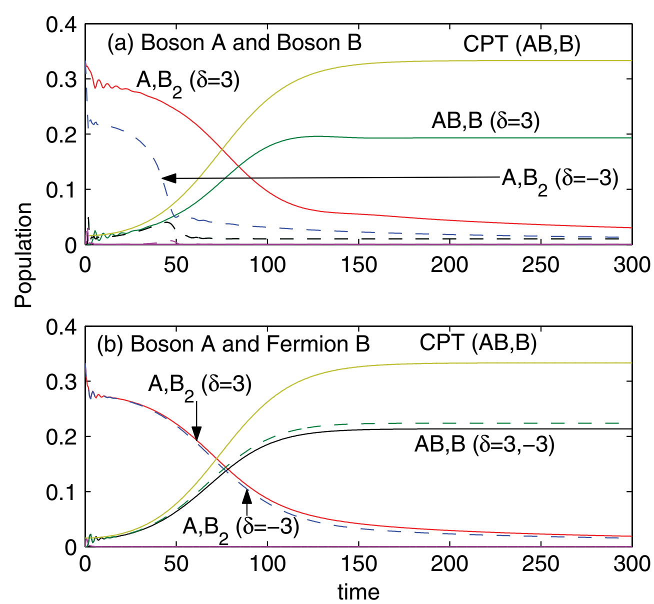

FIG. 3 (color online). Populations of dimers and atoms for $\delta = 3$ or $\delta = -3$ (in units of λ/n) by averaging 300 trajectories. Time is in units of λ^{-1}, and $\gamma = 1$. The trimer number remains zero at all times. The line labeled "CPT" shows the ideal population of products (dimers AB and atoms B).

example atom A is ^{87}Rb and atom B is ^{41}K, $\lambda = 4.718 \times 10^4\ \mathrm{s}^{-1}$, and $\Omega(t) = \Omega_0 \mathrm{sech}(t/\tau)$ with $\Omega_0/\lambda = 20$, $\lambda\tau = 20$ [20]. The collision parameters, in units of λ/n, are $\chi_{aa} = 0.5303$, $\chi_{bb} = 0.3214$, $\chi_{ab} = 0.8731$, and the others are taken as 0.0938 [20]. As the scattering lengths of the various collisions, especially those involving molecular trimers, are not known at this time we have carried out simulations by for a large set of plausible collision parameters for the Rb-K, Rb-Na or other atomic condensate [19]. We found that the stable bimolecular conversion is always possible for appropriate values of the external field detuning δ. The departure of the product populations from the ideal CPT value is due to the fact that only an approximate adiabatic condition exists for the CPT state [15,19]: $\gamma_{\mathrm{nl}}(t) \approx \frac{|\dot{\eta}|}{1+\eta}\frac{1}{4\lambda} \ll 1$, with $\eta = \lambda/\Omega$, which becomes increasingly difficult to satisfy in the last stages ($\eta \gg 1$).

Our proposal relies crucially on the capability to avoid rapid collisional quenching or the formation of an unstable atom-dimer sample. When energetically allowed, collision-induced reactions always occur at some rate, and we need to guarantee that the time scale over which quantum fluctuations dominate the dynamics is short enough for that the dynamics not to be collision dominated. From the condition $|\mathcal{G}t| < 1$ we estimate the maximum permissible collision-induced rate to be of the order of $10^5\ \mathrm{s}^{-1}$ for $|\delta| = 3$ and $\Omega_0 = 20\lambda$. A typical low-temperature inelastic collisions rate coefficient is $10^{-17}\ \mathrm{m}^3/\mathrm{s}$ [18,21], corresponding to a rate of about $10^3\ \mathrm{s}^{-1}$ for a sample density of $10^{14}\ \mathrm{cm}^{-3}$. In that case the fluctuations-induced dynamics will dominate the short-time behavior of the system.

Finally we remark that by using ^{87}Rb for the bosonic atoms A and ^{40}K for the fermionic atoms B we can realize the conversion of bosonic pairs to fermionic pairs. It is likewise described by Eqs. (2) with the substitution $\chi_{j,j}|\psi_j|^2 \rightarrow A_j|\psi_j|^{4/3}$, where $A_j = (6\pi^2)^{2/3}/4M_j$, $j = ab$, b, and M_j denotes the particle mass, provided that we ignore the s-wave collisions of fermionic particles and only consider their kinetic energy [22]. In contrast to the purely bosonic case, molecule formation is now found to be stable for both positive and negative detunings, see Fig. 3(b).

In conclusion, we have shown that in the collective reaction $A + B_2 \rightarrow AB + B$, the initial quantum fluctuations lead to the strongly correlated creation of dimer-atom pairs. This indicates that in the quantum-degenerate regime, elementary bimolecular reactive scattering are significantly different from the familiar single-molecular reaction. It may lead to fascinating new opportunities in degenerate chemistry, such as, e.g., the reaction $2A_2 \rightarrow A_3 + A$.

Future work will also study the unique "superchemistry" effects of ultraselectivity or confinement-induced stability in our system [7]. In addition, a complete analysis of collisional effects [14,23] will need to be considered. While experiments along the lines of this analysis promise to be challenging, recent progress in quantum-degenerate chemistry [5,7,15] and in the control of atom-molecule systems [3,4,24,25] indicates that achieving this goal should become possible in the not too distant future.

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