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Superchemistry: Dynamics of Coupled Atomic and Molecular Bose-Einstein Condensates

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We analyze the dynamics of a dilute, trapped Bose-condensed atomic gas coupled to a diatomic molecular Bose gas by coherent Raman transitions. This system is shown to result in a new type of “superchemistry,” in which giant collective oscillations between the atomic and the molecular gas can occur. The phenomenon is caused by stimulated emission of bosonic atoms or molecules into their condensate phases.

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The experimental observation of dilute gas Bose-Einstein condensation (BEC) is revolutionizing low-temperature physics [1]. BEC represents the ultimate limit for the cooling of a gas, since nearly all of the atoms may occupy the condensate ground state. Rather than being identifiable as single particles, these atoms coherently populate a matter wave field, and can be coupled out of the condensate to produce an “atom laser” [2]. This suggests the possibility of nonlinear atom optics. Because of atomic interactions, even a single-species condensate may exhibit nonlinear wave behavior analogous to self-phase modulation in optics [3]. Here, we propose that a more general type of nonlinearity may occur through atom-molecule coupling, and show that this coupling may result in the formation of a molecular Bose condensate through stimulated emission of molecular bosons.

More generally, we define “superchemistry” as *the coherent stimulation of chemical reactions via macroscopic occupation of a quantum state by a bosonic chemical species*. In other words, superchemistry results in greatly enhanced, non-Arrhenius chemical kinetics at ultralow temperatures. In the simplest case of $A + B \rightarrow C$ reactions, there are three possibilities for the quantum statistics of the components: $bb \rightarrow b$, $bf \rightarrow f$, and $ff \rightarrow b$, where b stands for bosonic and f for fermionic. In all three cases stimulated emission can occur. Interestingly, the latter two of these cases correspond to well-known quantum-field theories, the Lee-Van Hove

model of meson theory, and the Friedberg-Lee model of high- T_C superconductivity [4]. In this Letter we consider a chemical system of the first type where bosonic enhancement of the chemical dynamics is the strongest. We develop the theory of coherently interacting atomic and molecular condensates needed to describe this process, and consider a specific coupling mechanism based on stimulated free-bound Raman transitions [5].

We begin with the usual quantum-field theory Hamiltonian for a noninteracting (atomic or molecular) species (i), in a well-defined internal state:

$$\hat{H}^{(0)} = \sum_i \int d^3\mathbf{x} \left[\frac{\hbar^2}{2m_i} |\nabla \hat{\Phi}_i(\mathbf{x})|^2 + [V_i(\mathbf{x}) + E_i] \hat{\Phi}_i^\dagger(\mathbf{x}) \hat{\Phi}_i(\mathbf{x}) \right]. \quad (1)$$

Here m_i is the mass, $V_i(\mathbf{x})$ is the trapping potential, and E_i is the internal energy of species i . The particles also interact through collisions. We consider particle number-conserving collisions mediated by an interspecies potential $U_{ij}(\mathbf{x})$, and nonconserving collisions mediated by an effective potential $\chi_{ijk}(\mathbf{x})$. The first of these nonlinear terms describes the well-known intraspecies repulsion or attraction, as well as interspecies couplings [6]. It is desirable to introduce a momentum cutoff to simplify the field theory [7], and to replace $U_{ij}(\mathbf{x})$ by an effective pseudopotential $U_{ij}\delta(\mathbf{x})$. This describes low-energy S -wave scattering only. Similarly, the potential χ can be replaced by

an equivalent S -wave pseudopotential, again with the proviso that a momentum cutoff is introduced at the level of $k_m \sim a^{-1}$, where a is the longest scattering length in the problem. The result is an effective quantum field theory [8] in which

$$\hat{H}_{\text{eff}}^{(c)} = \frac{1}{2} \sum_{ij} \int d^3\mathbf{x} [\hat{\Phi}_i^\dagger(\mathbf{x}) \hat{\Phi}_j^\dagger(\mathbf{x}) U_{ij} \hat{\Phi}_j(\mathbf{x}) \hat{\Phi}_i(\mathbf{x})],$$

$$\hat{H}_{\text{eff}}^{(nc)} = \frac{1}{2} \sum_{ijk} \int d^3\mathbf{x} [\hat{\Phi}_i^\dagger(\mathbf{x}) \hat{\Phi}_j^\dagger(\mathbf{x}) \chi_{ijk} \hat{\Phi}_k(\mathbf{x}) + \text{H.c.}]. \quad (2)$$

In the diagonal case, $U_{ii} = 4\pi\hbar^2 a_i/m_i$, where a_i is the i th species scattering length. In the present work, we assume that the trap potential $V_i(\mathbf{x})$ is harmonic: $V_i(\mathbf{x}) = (m_i/2)\omega_i^2|\mathbf{x}|^2$, where ω_i represents the rotationally symmetric trap-oscillation frequency for the i th species.

The new feature introduced here is the particle number nonconserving potential χ . Terms like this occur in nonlinear optics, where they describe parametric processes of subharmonic and second-harmonic generation, which change the photon number [9]. While matter is clearly not created or destroyed in low temperature experiments, an analogous effect can occur where two atoms are converted into one molecule. Inside a Bose condensate, this chemical conversion is dominated by coherent stimulated emission, in which transitions are enhanced by the number of molecules already occupying the ground state. This is completely different from the usual chemical kinetics, which predicts that the rates of chemical reactions do not depend on the number of particles in the product mode, and go to zero at low temperatures according to the Arrhenius law. This type of classical (Boltzmann) kinetic theory is inapplicable in BECs, where the particle wavelength exceeds the interparticle spacing.

In general, the conversion process $i + j \leftrightarrow k$ will be nonresonant. The exception, for which $E_k = E_i + E_j$, corresponds to a Feshbach resonance [10]. Alternatively, energy conserving transitions are possible if χ_{ijk} has a harmonic time dependence. In this paper, we consider stimulated Raman coupling induced by two laser fields \mathbf{E}_{L1} and \mathbf{E}_{L2} of frequencies ω_{L1} and ω_{L2} , as illustrated in Fig. 1. This coupling becomes resonant when the Raman detuning $\delta = (2E_1 - E_2)/\hbar - (\omega_{L2} - \omega_{L1})$ goes to zero. This allows coupling to a single molecular state, which can be selected by the Raman laser frequencies.

The implication of these new terms is seen most easily by considering the corresponding mean field equations, in which the operators are replaced by their mean values, and a factorization is assumed. Elsewhere [8], using a variational technique, we have shown that this gives a good estimate of the ground-state energy at high density—relative to the spatially uncorrelated behavior that can occur at low densities (corresponding to a Bose gas of dressed dimers). In the present case the relevant equations are obtained, in a rotating frame, for the simplest case of one atomic

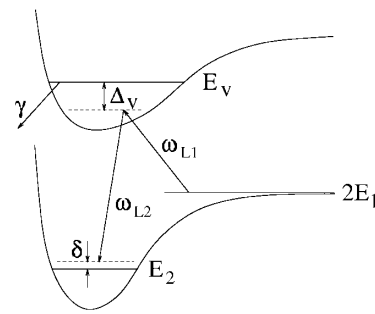


FIG. 1. Schematic diagram of the Raman photoassociation.

species ϕ_1 , together with a corresponding molecular dimer species ϕ_2 :

$$i\hbar\dot{\phi}_1 = -\frac{\hbar^2}{2m_1}\nabla^2\phi_1 + V_1(\mathbf{x})\phi_1 + U_{11}|\phi_1|^2\phi_1 + U_{12}|\phi_2|^2\phi_1 + \chi\phi_1^*\phi_2, \quad (3)$$

$$i\hbar\dot{\phi}_2 = -\frac{\hbar^2}{2m_2}\nabla^2\phi_2 + V_2(\mathbf{x})\phi_2 - \hbar\delta\phi_2 + U_{22}|\phi_2|^2\phi_2 + U_{21}|\phi_1|^2\phi_2 + \frac{1}{2}\chi^*\phi_1^2. \quad (4)$$

Here we assume that $U_{12} = U_{21}$ is the only number-conserving scattering process, while $\chi \equiv \chi_{112}$ describes conversion of atoms into molecules by stimulated Raman transitions. Many interesting dynamical properties of these types of equations, including nonlinear oscillations, nonequilibrium phase transitions, and soliton formation, have been explored in nonlinear optics [11]. A novel feature here is the presence of the trap potential which localizes the interaction volume.

We derive the Raman coupling coefficient χ for a simplified model of the two-body interaction, in which the atoms interact in their electronic ground state through a single Born-Oppenheimer potential $V_g(R)$. Molecules are formed in a single bound vibrational state of energy E_2 with radial wave function $u_2(R)$. Two free atoms with zero relative kinetic energy have a total energy $2E_1$, and a relative radial wave function $u_1(R)$, normalized so that asymptotically $u_1 \sim \sqrt{4\pi}(R - a_1)$. We assume that the two laser fields $\mathbf{E}_{Li} = \mathbf{E}_{0i} \cos(\omega_{Li}t)$ ($i = 1, 2$) couple the ground electronic state to a single electronically excited state described by a potential $V_e(R)$, with Rabi frequencies $\Omega_i = |\mathbf{d}_M \cdot \mathbf{E}_{0i}|/\hbar$ where \mathbf{d}_M is the electric dipole matrix element connecting these two states. The excited state has vibrational levels $|v\rangle$ with energy E_v and radial wave functions $u_{e,v}(R)$. The excited levels decay by spontaneous emission at a rate γ_M . All bound levels are normalized so that $\int dR |u_{e,v(2)}|^2 = 1$.

To proceed further, we first notice that the effective Hamiltonian in first-order perturbation theory should reproduce the known behavior of two atoms in a relative

S-wave scattering process in the presence of an external radiation field [12]. Here we recall that the effective field theory has a momentum cutoff (otherwise the perturbation theory would diverge for higher order terms). From these requirements we obtain

$$\frac{U_{11}}{\hbar} = \frac{U_0}{\hbar} - \sum_v \left[\frac{(\Omega_1)^2}{4\Delta_v} + \frac{(\Omega_2)^2}{4\Delta_v^{(1)}} \right] |I_{1,v}|^2, \quad (5)$$

$$\frac{\chi}{\hbar} = -\frac{\Omega_1\Omega_2}{2\sqrt{2}} \sum_v \frac{I_{1,v}I_{2,v}^*}{\Delta_v}. \quad (6)$$

Here $U_0/\hbar = 4\pi\hbar a_1/m_1$, $\Delta_v = (E_v - 2E_1)/\hbar - \omega_{L1}$, $\Delta_v^{(1)} = (E_v - 2E_1)/\hbar - \omega_{L2}$, and $I_{j,v}$ are the overlap integrals $I_{j,v} = \int dR u_{e,v}(R)u_j^*(R)$. In addition, the molecular spontaneous emission leads to the incoherent production of molecules in different states, together with atomic excited state decays. Treating these as loss processes, we obtain additional terms of form

$$\begin{aligned} \dot{\phi}_1 &= -\alpha\phi_1 + i\beta_1\phi_1 - \Gamma_1|\phi_1|^2\phi_1, \\ \dot{\phi}_2 &= -\Gamma_2\phi_2 + i\beta_2\phi_2, \end{aligned} \quad (7)$$

where the induced decay rates are

$$\Gamma_j = \frac{\gamma_M}{8} \sum_v \left[\frac{(\Omega_j)^2}{\Delta_v^2} + \frac{(\Omega_{3-j})^2}{(\Delta_v^{(j)})^2} \right] |I_{j,v}|^2 \quad (j = 1, 2), \quad (8)$$

$$\alpha = \frac{\gamma_A}{8} \sum_{i=1,2} \frac{(\Omega_i^A)^2}{D_i^2}, \quad (9)$$

and $i\beta_j\phi_j$ is a light shift term, with

$$\beta_1 = \sum_{i=1,2} \frac{(\Omega_i^A)^2}{4D_i}, \quad (10)$$

$$\beta_2 = \sum_v \left[\frac{(\Omega_2)^2}{4\Delta_v} + \frac{(\Omega_1)^2}{4\Delta_v^{(2)}} \right] |I_{2,v}|^2. \quad (11)$$

Here we have introduced $\Delta_v^{(2)} = (E_v - E_2)/\hbar - \omega_{L1}$, $D_i = \omega_0 - \omega_{Li}$, where ω_0 is the resonance frequency of the atomic transition between the dissociation limits of the excited and ground potentials. Also, $\Omega_j^A = |\mathbf{d}_A \cdot \mathbf{E}_{0j}|/\hbar$ is the atomic Rabi frequency, \mathbf{d}_A is the transition dipole moment, and γ_A is the atomic excited state population decay rate. The Raman detuning at trap center for an atomic BEC is $\tilde{\delta} \equiv \delta + \beta_2 - 2\beta_1 + 2(U_{11}/\hbar)|\phi_1(0,0)|^2$.

Rotationally or vibrationally inelastic atom-molecule collisions may also give rise to losses. The magnitude of these rates is presently unknown, and we neglect them here. We note that these rates should decrease rapidly with increasing molecular binding energy and go to zero in the molecular ground state.

We have calculated U_{11} , χ , Γ_i , β_i , and α for a $V_g(R)$ which closely approximates the $^{87}\text{Rb}_2$ ground $^3\Sigma_u^+$ potential, and a $V_e(R)$ which closely approximates the $^{87}\text{Rb}_2$ 0_g^- symmetry potential that connects to the

$5^2S_{1/2} + 5^2P_{3/2}$ dissociation limit. Free-bound Raman coupling of similar states in $^{85}\text{Rb}_2$ has previously been explored experimentally [13]. In this calculation, $|2\rangle$ is the bound state of V_g corresponding to the vibrational quantum number $v = 29$, with a binding energy of -160.7 GHz with respect to $2E_1$, and we take $\gamma_A = 3.7 \times 10^7 \text{ s}^{-1}$, $\gamma_M = 2\gamma_A$, $\Omega_1 = 2 \times 10^{10} \text{ s}^{-1}$, $\Omega_2 = 6.324 \times 10^9 \text{ s}^{-1}$, and $\Omega_i^A = \Omega_i/\sqrt{2}$. We also choose $\omega_{L1} = \omega_0 - 15.485 \text{ cm}^{-1}$, where ω_0 is the resonance frequency of the $5^2S_{1/2} \leftrightarrow 5^2P_{3/2}$ atomic transition. For these parameters, we find that $\chi/\hbar \approx 7.6 \times 10^{-7} \text{ m}^3/2\text{s}$, $\Gamma_1 \approx 1.629 \times 10^{-23} \text{ m}^3/\text{s}$, $\Gamma_2 \approx 304.4 \text{ s}^{-1}$, $\beta_1 \approx 2.108 \times 10^7 \text{ s}^{-1}$, $\beta_2 \approx 3.344 \times 10^6 \text{ s}^{-1}$, and $\alpha = 134.06 \text{ s}^{-1}$. For realizable BEC densities of $n \sim 4 \times 10^{20} \text{ m}^{-3}$, we find that $\chi n^{1/2} \gg \Gamma_2, \Gamma_1 n$, as required for coherent dynamics.

Based on these results, we have carried out simulations of Eqs. (3) and (4), using $a = 5.4 \text{ nm}$ [14], $U_{11}/\hbar \approx 4.96 \times 10^{-17} \text{ m}^3/\text{s}$, and additional terms given by Eqs. (7). The atom-molecule (U_{12}) and molecule-molecule (U_{22}) scattering rates are neglected. Provided they are not too strong, the effect of these terms will simply be to change the condensate self-energies, and hence to modify the optimum Raman detuning. We also choose $\omega_1/2\pi = \omega_2/2\pi = 100 \text{ Hz}$, and an initial number of atoms $N = 5 \times 10^5$. We assume an initial condition of a pure atomic BEC, with no molecules present, as given by the steady state of the standard Gross-Pitaevskii equation in a trap.

The results are shown in Fig. 2. We observe giant oscillations between atomic and molecular condensates, which take place on short time scales. The integrated atomic and molecular numbers, shown in Fig. 3(a), do not show complete atom-molecule conversion, because the oscillation frequency is higher in the center of the trap, due to the inhomogeneous atomic density. The total number shows a small decay due to spontaneous emission.

The pronounced oscillation between an atomic and a molecular condensate provides clear evidence of a long-range coherence effect. In contrast, stimulated Raman photoassociation in a thermal cloud of atoms would not produce similar collective oscillations, because the phases associated with the individual atom/molecule conversion processes are random in a thermal cloud. The effect is also very different from stimulated transitions between two spin states of Bose-condensed atoms [15]. That conversion is linear in the atomic amplitudes, and therefore the stimulated transition rate is equal to the single particle rate and independent of the density [16]. In contrast, stimulated atom-molecule conversion in a condensate is nonlinear in the atomic and molecular amplitudes, and the conversion rate scales with density as $\dot{n}_i \propto \chi n_1 \sqrt{n_2}$.

Figure 3(b) shows the result of the calculation for a reduced atom number and two times smaller density, but with the same effective initial Raman detuning. The density dependence of the superchemistry transitions is evident in the

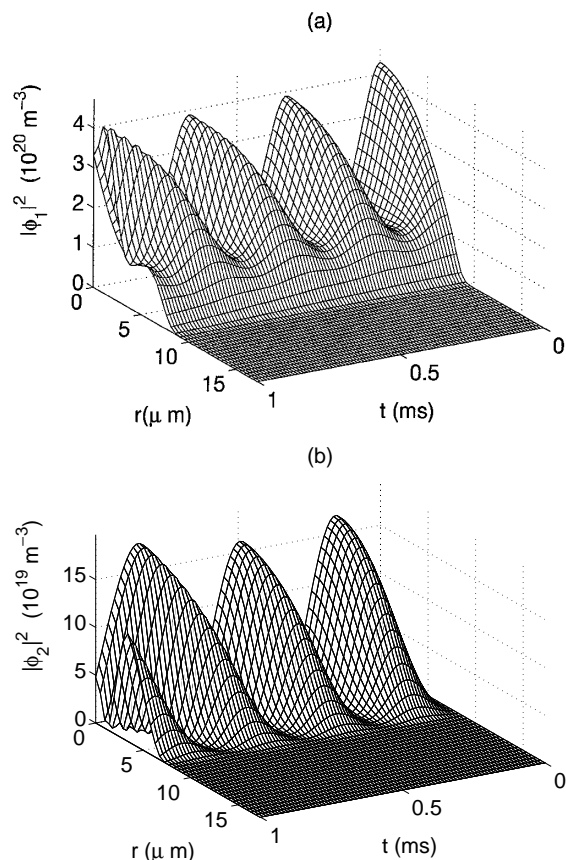


FIG. 2. Densities $|\phi_i(\mathbf{x}, t)|^2$ for the atomic (a) and molecular (b) species as depending on time and radial distance $r = |\mathbf{x}|$ from the trap center, for $\delta = 3.879 \times 10^7 \text{ s}^{-1}$ (so that $\delta + \beta_2 - 2\beta_1 = -2.8 \times 10^4 \text{ s}^{-1}$).

comparison of Figs. 3(a) and 3(b), which shows that the higher density cloud oscillates faster. This effect could be studied by optically imaging the atomic cloud at a succession of times. Observation of an essentially pure atomic condensate during one of the atom number maxima would imply that the molecular gas which exists at a prior time must be coherent. Important signatures of the coherent stimulation are a reaction rate that initially increases with time [see inset, Fig. 3(a)], and the density dependence of the nonlinear oscillation period.

In summary, number-nonconserving interactions between bosonic atomic and molecular condensates at ultralow temperatures are predicted to result in a form of superchemistry—in which Bose-enhanced coherent quantum dynamics replaces the usual chemical kinetics, giving a completely new type of behavior. We find that giant collective oscillations can occur between atomic and molecular Bose condensates. The phenomenon is the matter wave analog to optical frequency doubling and parametric down conversion. Interesting quantum behavior may also result, ranging from squeezed-state generation [17] to quantum soliton formation [8], or even quantum chaos. Quantum effects may change short-distance correlations, and need to be included in any treatment going beyond the mean field theory. In

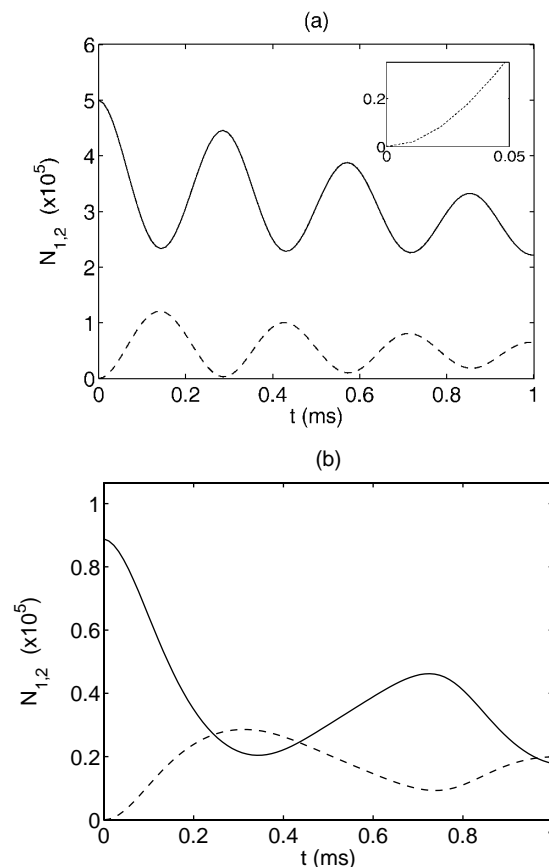


FIG. 3. (a) Occupation numbers $N_i = \int d\mathbf{x} |\phi_i(\mathbf{x}, t)|^2$ of the atomic (solid line) and molecular (dashed line) fields, as a function of time t , for the parameter values of Fig. 2; (b) same as in (a) but for the half the initial atomic density and the same initial effective detuning $\tilde{\delta}$.

the future, the highly specific nature of these proposed Bose-enhanced reactions could open the way for new types of quantum-controlled chemical synthesis, or other novel and unexpected quantum-phase dependent phenomena.

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