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 reactions 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:

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

Here $m_i$ is the mass, $V_i(x)$ 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 $U_{ij}(x)$, and nonconserving collisions mediated by an effective potential $\chi_{ij}(x)$. 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 $U_{ij}(x)$ by an effective pseudopotential $U_{ij}\delta(x)$. This describes low-energy S-wave scattering only. Similarly, the potential $\chi$ 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

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

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

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 $V_i(x)$ is harmonic: $V_i(x) = (m_i/2)\omega_i^2|x|^2$, where $\omega_i$ represents the rotationally symmetric trap-oscillation frequency for the $i$th species.

The new feature introduced here is the particle number nonconserving potential $\chi$. 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 $i + j \rightarrow k$ is nonresonant. The exception, for which $E_i = E_j + E_f$, corresponds to a Feshbach resonance [10]. Alternatively, energy conserving transitions are possible if $\chi_{ijk}$ has a harmonic time dependence. In this paper, we consider stimulated Raman coupling induced by two laser fields $E_{L1}$ and $E_{L2}$ of frequencies $\omega_{L1}$ and $\omega_{L2}$, 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 species $\phi_1$, together with a corresponding molecular dimer species $\phi_2$:

$$i\hbar \dot{\phi}_1 = -\frac{\hbar^2}{2m_1} \nabla^2 \phi_1 + V_i(x) \phi_1 + U_{11} |\phi_1|^2 \phi_1$$

$$+ U_{12} |\phi_2|^2 \phi_1 + \chi \phi_1^* \phi_2,$$

$$i\hbar \dot{\phi}_2 = -\frac{\hbar^2}{2m_2} \nabla^2 \phi_2 + V_2(x) \phi_2 - \hbar \delta \phi_2$$

$$+ U_{22} |\phi_2|^2 \phi_2 + U_{21} |\phi_1|^2 \phi_2 + \frac{1}{2} \chi^2 \phi_1^2 .$$

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 $\chi$ 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 $V_e(R)$. 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 $E_{L1} = E_0 \cos(\omega_{L1} t)$ ($i = 1, 2$) couple the ground electronic state to a single electronically excited state described by a potential $V_e(R)$, with Rabi frequencies $\Omega_i = |d_M| E_0 / \hbar$ where $d_M$ is the electric dipole matrix element connecting these two states. The excited state has vibrational levels $|\nu\rangle$ with energy $E_\nu$ and radial wave functions $u_{\nu, e}(R)$. The excited levels decay by spontaneous emission at a rate $\gamma_M$. All bound levels are normalized so that $\int dR |u_{\nu, e}(R)|^2 = 1$.

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
Here we introduce the atomic excited state decay rates, denoted as $D_i$. The decay rate $D_i$ is the transition dipole moment, and $\gamma_A$ is the atomic excited state population decay rate. The Raman detuning at trap center for an atomic condensate is $\delta = \gamma_A - \omega_A - \omega_{1/2}$, where $\omega_A$ is the atomic resonance frequency and $\omega_{1/2}$ is the resonance frequency of the excited state.

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 $U_{11}$, $\chi$, $\Gamma_1$, $\beta_1$, and $\alpha$ for a $V_g(R)$ which closely approximates the $^{87}\text{Rb}_2$ ground $^3\Sigma^+_g$ potential, and a $V_f(R)$ which closely approximates the $^{87}\text{Rb}_2$ $^2\Sigma^+_g$ symmetry potential that connects to the $^5\Sigma^+_2 + ^5\Pi^+_2$ dissociation limit. Free-bound Raman coupling of similar states in $^{85}\text{Rb}_2$ has been explored experimentally [13]. In this calculation, $\gamma$ is the bound state of $V_g$ corresponding to the vibrational quantum number $n = 29$, with a binding energy of $-160.7$ GHz with respect to $2E_1$, and we take $\gamma_A = 3.7 \times 10^7$ s$^{-1}$, $\gamma_M = 2\gamma_A$, $\Omega_1 = 2 \times 10^9$ s$^{-1}$, $\Omega_2 = 6.324 \times 10^9$ s$^{-1}$, and $\Omega_A^f = \Omega_i/\sqrt{2}$. We also choose $\omega_{1/2} = \omega_0 - 15.485$ cm$^{-1}$, where $\omega_0$ is the resonance frequency of the $^5\Sigma^+_2 + ^5\Pi^+_2$ atomic transition. For these parameters, we find that $\chi/\bar{n} \approx 7.6 \times 10^{-7}$ m$^3$/s, $\Gamma_1 = 1.629 \times 10^{-23}$ m$^3$/s, $\Gamma_2 = 304.4$ s$^{-1}$, $\beta_1 = 2.108 \times 10^7$ s$^{-1}$, $\beta_2 = 3.344 \times 10^6$ s$^{-1}$, and $\alpha = 134.06$ s$^{-1}$. For realizable BEC densities of $n \approx 4 \times 10^{20}$ m$^{-3}$, we find that $\chi/\bar{n} \gg \Gamma_1/\bar{n}$, as required for coherent dynamics.
FIG. 2. Densities $|\phi(x,t)|^2$ for the atomic (a) and molecular (b) species as depending on time and radial distance $r = |x|$ from the trap center, for $\delta = 3.879 \times 10^7 s^{-1}$ (so that $\delta + \beta_2 - 2\beta_1 = -2.8 \times 10^4 s^{-1}$).

FIG. 3. (a) Occupation numbers $N_j = \int d x |\phi_j(x,t)|^2$ 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 $\delta$.

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 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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