Bose-Enhanced Chemistry: Amplification of Selectivity in the Dissociation of Molecular Bose-Einstein Condensates

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We study the photodissociation chemistry of a quantum degenerate gas of bosonic triatomic ABC molecules, assuming two open rearrangement channels ($AB + C$ or $A + BC$). The equations of motion are equivalent to those of a parametric multimode laser, resulting in an exponential buildup of macroscopic mode populations. By exponentially amplifying a small differential in the single-particle rate coefficients, Bose stimulation leads to a nearly complete selectivity of the collective N-body process, indicating a novel type of ultraselective quantum degenerate chemistry.

A significant effort is currently under way with the goal of producing a stable Bose-Einstein condensate (BEC) in a vapor of molecules. Several groups are pursuing schemes in which atomic BECs are converted to molecular BECs via photoassociation [1] and/or Feshbach resonance [2–4]. Progress is also being made towards forming a molecular BEC by direct evaporation of molecules in a magnetic trap. In this case sympathetic buffer-gas cooling is used to load the trap [5], as opposed to the optical techniques used in the alkali-metal atomic vapors.

Once the technical problems are solved, the realization of molecular condensates will open a new field of quantum-degenerate coherent chemistry. The most striking new feature of the resulting molecular dynamics would be the unprecedented role of nonlinear collective effects, i.e., Bose enhancement and Pauli blocking, induced by the N-body quantum statistics. The probability of any single boson to undergo a transition is enhanced by the number of identical particles occupying the final state, whereas fermions would be subject to Pauli blocking of the output channels. Thus any process which retains a critical phase-space density would greatly differ from that of the isolated single-particle process which dominates "thermal" gas-phase chemistry [6].

The role of Bose stimulation in the association and dissociation of a molecular BEC has already been studied theoretically in the regime where a single atomic mode is coupled to a single molecular mode [7–10]. In this situation the entire condensate is theoretically predicted to undergo large amplitude coherent oscillations between atoms and molecules. The Bose-enhanced oscillation frequency is $\sqrt{N}\,\Omega$, where Ω is the single-particle atom-molecule coupling frequency and N is the total number of condensate particles. While this prediction is significantly modified by the inclusion of quantum-field effects [11–14], the collective evolution remains strikingly different from the single-pair (nondegenerate) dynamics.

The purpose of this Letter is to extend these ideas to the case where more complicated molecules are dissociated into a multiplicity of output channels. In such multichannel quantum-degenerate processes there are two important competing effects: Bose stimulation, which leads to exponential growth of the output channel populations, and condensate depletion, in which the finite number of initial molecules leads to competition between output channels. If certain channels have a slight advantage in coupling strength, they will deplete the condensate before other channels attain a macroscopic population. Related effects have been experimentally observed in the phenomenon of superradiant Rayleigh scattering of laser light from an elongated BEC [15,16], indicating that there are no overwhelming obstacles to obtaining winner-takes-all scenarios in BEC systems.

Studying the simplest example of the dissociation of a triatomic ABC molecule into $AB + C$ or $A + BC$ pairs, we show that the combined effects of Bose stimulation and competition between output channels for a finite initial number of molecules leads to an *amplification of selectivity* which can dramatically enhance any nondegenerate control scheme. Relatively small controllability of the single-particle process translates to near complete controllability of the Bose-stimulated N-body process. Thus, collective amplification and mode competition effects can be employed to achieve the central goal of the fields of optimal and coherent control [17–19].

We consider a BEC of triatomic ABC molecules. The ground-state molecules are resonantly coupled by a stimulated Raman transition to two open dissociation channels: $AB + C$ (AB molecules and C atoms) and $A + BC$ (A atoms and BC molecules), as depicted in Fig. 1. After adiabatic elimination of the intermediate ABC^* state, the N-body second-quantized Hamiltonian in the interaction representation and the rotating wave approximation reads

$$\hat{H} = \hbar\hat{\Phi}(\mathbf{r})[\Omega_1\hat{\Psi}_{AB}^\dagger(\mathbf{r})\hat{\Psi}_C^\dagger(\mathbf{r}) + \Omega_2\hat{\Psi}_A^\dagger(\mathbf{r})\hat{\Psi}_{BC}^\dagger(\mathbf{r})] + \text{H.c.,} \quad (1)$$

where Ω_1, Ω_2 are the coupling frequencies into the $AB + C$ and $A + BC$ dissociation channels, respectively, and $\hat{\Phi}$,
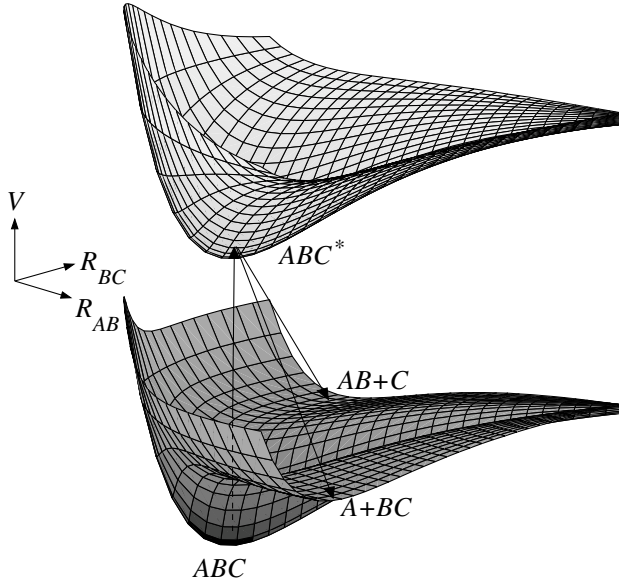
FIG. 1. Stimulated Raman photodissociation of ABC molecules.

$\hat{\Psi}_{AB}$, $\hat{\Psi}_C$, $\hat{\Psi}_A$, $\hat{\Psi}_{BC}$ are the bosonic field operators for ABC, AB, C, A, BC, respectively.

Using the Hamiltonian (1), the Heisenberg equations of motion for these operators are

$$i \frac{d}{dt} \hat{\Phi} = \Omega_1 \hat{\Psi}_{AB} \hat{\Psi}_C + \Omega_2 \hat{\Psi}_A \hat{\Psi}_{BC}, \quad (2a)$$

$$i \frac{d}{dt} \hat{\Psi}_{AB} = \Omega_1 \hat{\Phi} \hat{\Psi}_C^\dagger, \quad (2b)$$

$$i \frac{d}{dt} \hat{\Psi}_C^\dagger = \Omega_1^* \hat{\Phi}^\dagger \hat{\Psi}_{AB}, \quad (2c)$$

$$i \frac{d}{dt} \hat{\Psi}_A = \Omega_2 \hat{\Phi} \hat{\Psi}_{BC}^\dagger, \quad (2d)$$

$$i \frac{d}{dt} \hat{\Psi}_{BC}^\dagger = \Omega_2^* \hat{\Phi}^\dagger \hat{\Psi}_A. \quad (2e)$$

Equations (2) are closely related to the quantum equations of motion of a multimode laser [20], in that the $AB + C$ dissociation channel [Eqs. (2b),(2c)] is only coupled to the $A + BC$ channel [Eqs. (2d),(2e)] via the molecular reservoir $\hat{\Phi}$. In order to demonstrate the collective amplification of selectivity, we use a five-mode model, neglecting the spatial variation of the various fields. This approximation, which assumes there is only one available state per specie, is valid for a zero temperature ABC condensate at exact resonance with the dissociation threshold of the $AB + C$ and $A + BC$ channels. The field operators of Eqs. (2) are thus taken to represent the particle creation and annihilation operators of the respective modes. In the undepleted pump approximation [12,14], the intense $\hat{\Phi}$ field is replaced by a constant c-number $\Phi \sim \sqrt{N}$. Assuming without loss of generality that $\Omega_1 = \Omega_1^*$ and $\Omega_2 = \Omega_2^*$, the initial time evolution of the operators $\hat{\Psi}_{AB}$, $\hat{\Psi}_C$, $\hat{\Psi}_A$, and $\hat{\Psi}_{BC}$ is thus given as

$$\hat{\Psi}_{AB}(t) = \hat{\Psi}_{AB}(0) \cosh \omega_1 t - i \hat{\Psi}_C^\dagger(0) \sinh \omega_1 t, \quad (3a)$$

$$\hat{\Psi}_C^\dagger(t) = \hat{\Psi}_C^\dagger(0) \cosh \omega_1 t + i \hat{\Psi}_{AB}(0) \sinh \omega_1 t, \quad (3b)$$

$$\hat{\Psi}_A(t) = \hat{\Psi}_A(0) \cosh \omega_2 t - i \hat{\Psi}_{BC}^\dagger(0) \sinh \omega_2 t, \quad (3c)$$

$$\hat{\Psi}_{BC}^\dagger(t) = \hat{\Psi}_{BC}^\dagger(0) \cosh \omega_2 t + i \hat{\Psi}_A(0) \sinh \omega_2 t, \quad (3d)$$

where $\omega_1 = \sqrt{N} \, \Omega_1$ and $\omega_2 = \sqrt{N} \, \Omega_2$. Assuming $\langle \hat{\Psi}_{AB}(0) \rangle = \langle \hat{\Psi}_C(0) \rangle = \langle \hat{\Psi}_A(0) \rangle = \langle \hat{\Psi}_{BC}(0) \rangle = 0$ (no initial product coherence), the average numbers of particles $\langle n_j \rangle = \langle \Psi_j^\dagger \Psi_j \rangle$ in the modes $j = AB, C, A, BC$, are given, respectively, as

$$\langle n_{AB}(t) \rangle = \langle n_{AB}(0) \rangle \cosh^2 \omega_1 t + (1 + \langle n_C(0) \rangle) \sinh^2 \omega_1 t, \quad (4a)$$

$$\langle n_C(t) \rangle = \langle n_C(0) \rangle \cosh^2 \omega_1 t + (1 + \langle n_{AB}(0) \rangle) \sinh^2 \omega_1 t, \quad (4b)$$

$$\langle n_A(t) \rangle = \langle n_A(0) \rangle \cosh^2 \omega_2 t + (1 + \langle n_{BC}(0) \rangle) \sinh^2 \omega_2 t, \quad (4c)$$

$$\langle n_{BC}(t) \rangle = \langle n_{BC}(0) \rangle \cosh^2 \omega_2 t + (1 + \langle n_A(0) \rangle) \sinh^2 \omega_2 t. \quad (4d)$$

Starting with a pure ABC condensate $\langle n_{AB}(0) \rangle = \langle n_C(0) \rangle = \langle n_A(0) \rangle = \langle n_{BC}(0) \rangle = 0$, the average product populations grow as

$$N_{1(t)} \equiv \langle n_{AB}(t) \rangle = \langle n_C(t) \rangle = \sinh^2 \sqrt{N} \, \Omega_1 t, \quad (5a)$$

$$N_{2(t)} \equiv \langle n_A(t) \rangle = \langle n_{BC}(t) \rangle = \sinh^2 \sqrt{N} \, \Omega_2 t. \quad (5b)$$

The initial time evolution of Eqs. (5) corresponds to an initial nonexponential (quadratic rather than linear in time) spontaneous dissociation process, followed by an exponential stimulated process [14]. We note that exactly the same equations have been routinely used for over three decades, to describe the phenomenon of parametric superfluorescence [21,22], i.e., the parametric amplification of noise photons, in quantum optics. The feature which produces the striking selectivity of Bose-enhanced chemistry is that any small difference between the two rate coefficients, $\Omega_2 \neq \Omega_1$, is exponentially amplified by the stimulated dissociation, so that

$$N_2(t)/N_1(t) \approx e^{2\sqrt{N}(\Omega_2 - \Omega_1)t}. \quad (6)$$

The linearized model of Eqs. (3) is valid only as long as the population of the triatomic mode $\langle \hat{\Phi}^\dagger \hat{\Phi} \rangle$ is large and the effect of its depletion on the products population growth is negligible. In order to go beyond this approximation we solve the full N-body problem numerically. Starting with no products and fixing the total number of particles N, the accessible Hilbert space is restricted to Fock states of the type $|n_{ABC}, n_{AB}, n_C, n_A, n_{BC}\rangle$ with $n_{AB} = n_C$, $n_A = n_{BC}$, and $n_{ABC} = N - (n_A + n_C)$. Using these states to represent the Hamiltonian (1) we solve numerically the N-body Schrödinger equation,

$$i \frac{d}{dt} c_{n_1,n_2} = \Omega_1 \sqrt{N - (n_1 + n_2)}(n_1 + 1) c_{n_1+1,n_2}$$

$$+ \Omega_1^* \sqrt{N - (n_1 + n_2) + 1}\, n_1 c_{n_1-1,n_2}^*$$

$$+ \Omega_2 \sqrt{N - (n_1 + n_2)}(n_2 + 1) c_{n_1,n_2+1} + \Omega_2^* \sqrt{N - (n_1 + n_2) + 1}\, n_1 c_{n_1,n_2-1}^*, \qquad (7)$$

for the dynamics of the probability amplitudes

$$c_{n_1,n_2}(t) = \langle N - (n_1 + n_2), n_1, n_1, n_2, n_2 | \Psi \rangle. \quad (8)$$

In Fig. 2, we plot the expectation values $\langle n_C \rangle$, $\langle n_A \rangle$, corresponding to the populations in the $AB + C$ channel and the $A + BC$ channel, respectively, as a function of time, for $\Omega_2 = 2\Omega_1$. When $N = 1$ [Fig. 2(a)] the ratio between the two channel populations is, as expected for the single-particle process, $\langle n_A \rangle / \langle n_C \rangle = |\Omega_2/\Omega_1|^2 = 4$. However, for $N = 1000$ [Fig. 2(b)], the Bose stimulated population ratio is $\langle n_A \rangle / \langle n_C \rangle > 40$. Thus, the reaction outcome is highly dependent on the total number of particles, becoming more selective as N increases.

Our numerical calculations are limited by available computation power to $N \leq 1000$. However, the number of particles in current BEC experiments in trapped dilute alkali gases is sometimes as high as 10^7, suggesting a far greater selectivity enhancement. In Fig. 3 we plot the channel population ratio when the leading channel population reaches a maximum, as a function of N for various
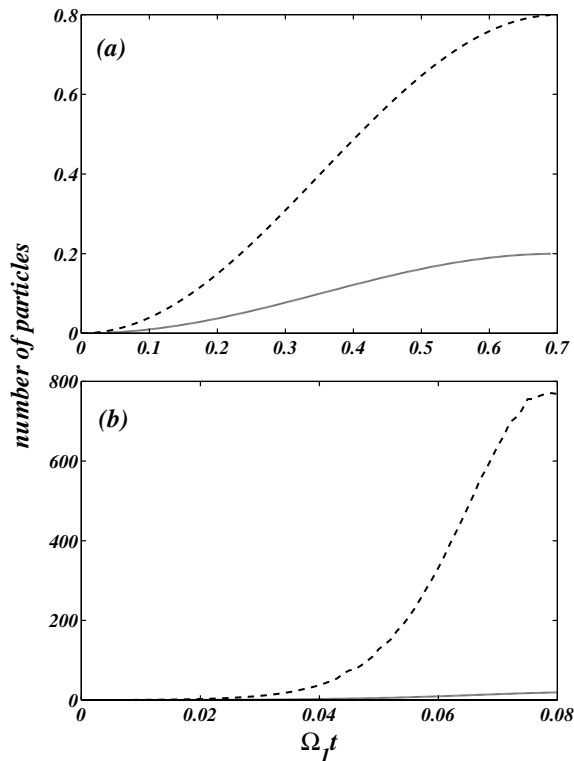
values of Ω_2/Ω_1. The curves are linear fits to the numerical data, demonstrating a power-law dependence of the selectivity as $\sim N^\alpha$. The power α increases with the rate coefficient ratio Ω_2/Ω_1, as shown in Fig. 4.

In order to analytically estimate the dependence of the selectivity on the total particle number, we take a perturbative approach where we first obtain the time t_d at which the leading channel depletes the condensate, and then evaluate the channel population ratio at t_d. Assuming a purely exponential growth, the depletion time is $t_d = \log N / 2\sqrt{N}\,\Omega_2$. Substituting into Eq. (6), we find that the selectivity is enhanced as N^α, where

$$\alpha = 1 - \Omega_1/\Omega_2, \qquad (9)$$

so that $\log[N_2(t_d)/N_1(t_d)] \approx \alpha \log N$. This result is confirmed by the numerical calculations in Fig. 3, giving α values of 0.17, 0.32, and 0.49 for $\Omega_2/\Omega_1 = 1.25$, $\Omega_2/\Omega_1 = 1.5$, and $\Omega_2/\Omega_1 = 2$, in good agreement with the predicted values of 0.2, 0.33, and 0.5, respectively. Extrapolating to $N = 10^6$, we find population ratios that are greater than 13, 100, and 1200 for $\Omega_2/\Omega_1 = 1.25$, $\Omega_2/\Omega_1 = 1.5$, and $\Omega_2/\Omega_1 = 2$, respectively (as compared to single particle ratios of 1.56, 2.25, and 4, respectively).

The dependence of the selectivity amplification constant α on the rate coefficient ratio Ω_2/Ω_1 is plotted in Fig. 4. The solid line depicts the estimate of Eq. (9). At the limit of a high rate coefficient ratio the selectivity is enhanced as

FIG. 2. Expectation values of the $AB + C$ $(- \cdot -)$ and $A + BC$ $(- - -)$ channel populations as a function of time for (a) $N = 1$ and (b) $N = 1000$. The coupling rate ratio is $\Omega_2 = 2\Omega_1$.
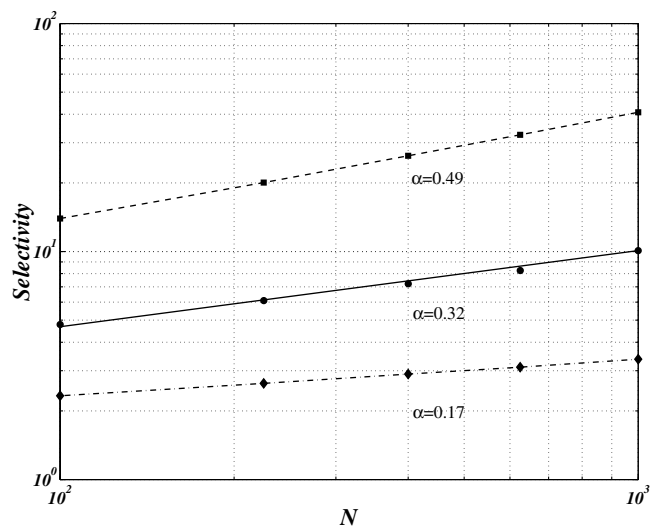

FIG. 3. Channel population ratio $\langle n_A \rangle / \langle n_C \rangle$ when $\langle n_A \rangle = \langle n_A \rangle_{\max}$ as a function of N for $\Omega_2 = 1.25\Omega_1$ (dash-dotted), $\Omega_2 = 1.5\Omega_1$ (solid), and $\Omega_2 = 2\Omega_1$ (dashed).
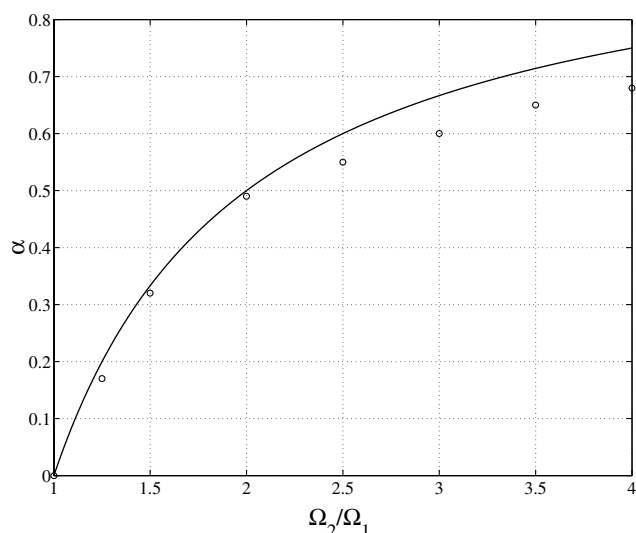
FIG. 4.   The variation of the selectivity amplification constant α with the rate coefficient ratio Ω_2/Ω_1. The solid line corresponds to the estimate of Eq. (9), whereas the circles are obtained from the numerical quantum solutions.

N, implying that all the particles would dissociate into the preferred channel. We note that since the linearized model underestimates the condensate depletion time, the numerical values of α are consistently lower than the theoretical estimate of Eq. (9).

While the five-mode model is sufficient to produce Bose-enhanced gain, it neglects various spatial effects. In particular, channel losses due to the relative translational motion of the products are not accounted for under the assumption that energy conservation forces the reaction products to be at rest. In fact, by imparting additional momentum via the laser fields, such losses could be used to increase selectivity by setting a threshold for amplification. The population in each rearrangement channel would be stimulated only if the respective pump rate $\sqrt{N}\,\Omega_j$ is faster than the channel depletion. Thus, if the motion in the $AB + C$ channel is faster than in the $A + BC$ channel it will be possible to tune the laser intensity so that only one pathway is Bose stimulated. In particular, if A and B are atoms of similar mass $m_A \sim m_B$, and C is a much lighter atom $m_C \ll m_A, m_B$, the $A + BC$ channel will be enhanced at much lower pump intensities than the $AB + C$ channel. Consequently, selectivity could be attained even for $\Omega_1 = \Omega_2$, an issue currently under active investigation.

By drawing an analogy from the phenomena of BEC superradiance [15,16] to multichannel reactive scattering in molecular condensates, we have shown that the selectivity of reactive processes carried out in a quantum-degenerate gas can be greatly amplified by collective enhancement effects. This selectivity is the result of interplay between Bose enhancement, which leads to exponential growth, and competition between modes for a finite number of initial molecules. The effect was demonstrated using the simple model system of two-channel photodissociation, where, due to a small difference between the two channel rate coefficients, population was shown to be directed by the N-body stimulated process into the favored channel, approaching a nearly complete selectivity in the limit of large N. In the quantum degenerate regime, it is therefore only necessary to exert slight control over the reaction rates in order to achieve near-total control over the reaction output. Future work would address the question of complementary Pauli-blocking effects when a molecular BEC is dissociated into fermionic constituents.

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