Collective Dissipative Molecule Formation in a Cavity

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We propose a mechanism to realize high-yield molecular formation from ultra-cold atoms. Atom pairs are continuously excited by a laser, and a collective decay into the molecular ground state is induced by a coupling to a lossy cavity-mode. Using a combination of analytical and numerical techniques, we demonstrate that the molecular yield can be improved by simply increasing the number of atoms, and can overcome efficiencies of state-of-the-art association schemes. We discuss realistic experimental setups for diatomic polar and nonpolar molecules. This work exemplifies the opportunities for state engineering in cold molecules using collective cavity-couplings, especially in the presence of strong dissipation.

There is considerable interest in preparing and manipulating ultra-cold ensembles of molecules for quantum simulations, metrology and the study of chemical reactions in the ultra-cold regime [1–5]. Diatomic molecules in their electronic and ro-vibrational ground-state are routinely produced using the coherent stimulated Raman adiabatic passage (STIRAP) technique [6–10]. Alternatively, continuous formation of ground-state molecules can be realized by photoassociation via a weakly bound excited molecular state [11–16]. While more sophisticated methods such as photoassociation followed by pulsed population transfer [17] or re-pumping of vibrationally excited molecules [18, 19] have been experimentally demonstrated, efficiencies of ground-state molecular formation are usually lower than those achieved with STIRAP and without rotational state selectivity. It has recently been proposed to overcome some of these limitations by coupling molecular transitions to a cavity mode [20] or a photonic waveguide [21]. Common to all these schemes is the use of formation processes based on single molecules.

Here, we propose a mechanism to exploit collective effects to perform continuous high-yield molecular formation from ultra-cold atoms in a cavity. Our scheme is based on photo-association to a collective excited bound-state followed by superradiant-type decay to the molecular ground-state. We consider the regime of large dissipation, where both the number of photons in the cavity and the number of electronic excitations is negligible, and derive an effective master equation for the internal dynamics of a two-atom initial state (e.g., a low-energy scattering pair as a four-level system with states |
\[ n \alpha \rangle, |n \beta \rangle, |n \gamma \rangle, |n \delta \rangle\] corresponding to the system Hamiltonian and \( (\hbar = 1) \)

\[ \hat{H}_{LA} = \frac{\Omega}{\sqrt{N}} \left( \hat{S}_{1e} + \hat{S}_{1\epsilon} \right) \]  

\[ \hat{H}_{C} = g \sqrt{N} \left( \hat{a}^\dagger \hat{S}_{1g} + \hat{S}_{1g} \hat{a} \right). \]

Here, \( \hat{H}_{LA} \) and \( \hat{H}_{C} \) represent the coupling of the transition dipole moments of the transitions \( |i\rangle_n \leftrightarrow |e\rangle_n \) and \( |e\rangle_n \leftrightarrow |g\rangle_n \) to the laser and cavity fields with Rabi frequency \( \Omega \) and vacuum Rabi frequency \( g \), respectively. \( \hat{S}_{\alpha\beta} = \sum_n \delta_{\alpha\beta} \sqrt{n}/\sqrt{N} \) are collective operators that couple the internal states of each pair \( n \) via \( \delta_{\alpha\beta} = \langle \alpha | \beta \rangle_n \) \( (\alpha, \beta = i, e, g, x) \). \( \hat{H} \) is defined in a rotating frame [22] with the detunings of the laser and the
cavity, $\Delta = \omega_{\text{cavity}} - \omega_L$ and $\delta = \omega_C - \omega_L - \omega_{\text{gi}}$, respectively. These are included in $H_0 = \Delta \hat{N}_c + \delta \hat{a} \hat{a}$. Then, $\hat{N}_\alpha = \sum_n \hat{a}_\alpha^{(n)}$ is the total number of atoms, $\hat{a}$ is the cavity photon annihilation operator, while $\omega_L$, $\omega_C$ and $\omega_{\text{gi}}$ are the frequencies of the laser, the cavity and the transitions, respectively. Two eigenstates of Eq. (2) are polaritons, and we define polariton operators as $\hat{P}_\pm \equiv (\hat{a} \pm \hat{S}_{\text{ge}})/\sqrt{2}$.

Dissipative terms are described by the super-operator

$$\mathcal{D}\hat{\rho} = \mathcal{L}[\hat{\chi}]\hat{\rho} + \sum_{n=1}^N \left( \mathcal{L}[\hat{L}_{\gamma_n}] + \mathcal{L}[\hat{L}_{\delta_n}] + \mathcal{L}[\hat{L}_{\gamma_x}] \right) \hat{\rho}$$

with $3N + 1$ decay channels, each governed by a Lindblad term $\mathcal{L}[L]\hat{\rho} = -[L, \hat{\rho}] + 2L \rho L^\dagger$. Here we include cavity decay with rate $2\kappa$, $\hat{L}_C = \sqrt{\kappa} \hat{a}$, spontaneous emission from the excited state $|e\rangle_n$ for each pair $n$, $\hat{L}_{\gamma_n} = \sqrt{\gamma_n} \hat{a}_\alpha^{(n)}$ with rates $2\gamma_n$ for $\alpha = i, g, x$. We define $\Gamma = \sum_\alpha \gamma_\alpha$ and the complex detunings $\tilde{\Delta} = \Delta - i\Gamma$ and $\tilde{\delta} = \delta - i\kappa$.

In the regime of strong dissipation with $(\tilde{N}_c + \hat{a} \hat{a}^\dagger) \ll 1$, both the excited states and the cavity mode are weakly populated and can be adiabatically eliminated [23, 24]. Then, the dynamics reduces to an effective master equation for the sub-systems $\{|i\rangle_n, |g\rangle_n, |x\rangle_n\}$ [see Fig. 1(c)].

We find that the new effective Lindblad operators read

$$\hat{L}_{\text{eff}} = \sqrt{\lambda_n \xi \hat{S}_{gi} \delta_n} \hat{L}_{\text{eff}}^{(n)} = \sqrt{\lambda_n \xi \hat{S}_{gi} \delta_n} \hat{A}_n$$

The terms $\hat{L}_{\text{eff}}^{(n)}$ in Eq. (4) give rise to a virtual excitation of the states $|e\rangle_n$ being lost via the cavity or via spontaneous emission, respectively. Here, $\lambda_n = \Omega^2 \kappa/g^2$ and $\lambda_n^\prime = \Omega^2 \gamma_\alpha/\tilde{\Delta}^2$ are the respective rates, while $\xi = \sqrt{N} g^2 (N g g - \tilde{\Delta})^{-1}$ is a collective dimensionless loss operator stemming from the excited state propagator, which captures the effects of virtually excited superradiant states [in the weak light-matter coupling regime $Ng \ll 1$ or $C = g^2/\epsilon \Omega$ the cavity cooperativity] or virtually excited polaritons (in the strong coupling regime $Ng \gg 1$), as we will see below. Thus, Eq. (4) gives rise to collective, dissipative, and uni-directional population transfer from the states $|i\rangle_n$ to the desired molecular bound states $|g\rangle_n$ and the loss states $|x\rangle_n$ [see sketch in Fig. 1(c)], with rates that depend on state populations via $\xi \hat{S}_{gi}$.

We find a new effective Hamiltonian with general form

$$\hat{H}_\text{eff} = -\frac{\Omega^2}{2\Delta} \left( \hat{N}_i + \sqrt{N} \hat{S}_{gi} \xi \hat{S}_{gi} \right) + \text{h.c.}$$

The first term $-\Omega^2 \hat{N}_i/(2\tilde{\Delta})$ in Eq. (5) corresponds to the usual AC Stark shift for a small coupling $\Omega$. The second term corresponds to the self energy due to a molecule being virtually excited by the laser and exchanging this excitation with the cavity. Since $[\hat{N}_\alpha, \hat{H}_\text{eff}] = 0$, $\hat{H}_\text{eff}$ cannot drive any coherent population transfer and thus we find that all interesting dynamics is driven by dissipation. In the following, we simulate the effective equations of motion first on bare resonance $\Delta = \delta = 0$, then on resonance with a (virtual) polariton.

Numerically, the master equation evolution with terms from Eqs. (4) and (5) can be efficiently simulated by exploiting the permutation symmetry among the $N$ three level systems, which allows for utilizing a collective spin basis [25]. In practice we furthermore employ a quantum trajectory method [24–26]. In the numerical simulations, the initial state is the product $\otimes_n |i\rangle_n$.

For $\Delta = 0$, we choose typical parameters for RbCs describing a transfer of Feshbach molecules prepared in state $|i\rangle$ [27] to the absolute ground state $|g\rangle$ [28] via the excited state $|e\rangle = (\gamma^2 + \gamma_3 \gamma_1) |\Delta\rangle$ $\gamma_3 = 38$ [see also Fig. 1(b)] [7, 28]. We consider up to $N = 10^5$ molecules trapped in a three-dimensional optical lattice created by a laser with wavelength $\lambda_{\text{latt}} = 1064.5 \, \text{nm}$. Two lattice beams are placed
at angles $\pm \theta$ ($\theta = \arccos[\lambda_{\text{latt}}/(2\lambda_{\text{eg}})] = 57^\circ$) with respect to the cavity axis in order to match a desired cavity mode [Fig. 1(a) and below]. The excited state has a half linewidth $\Gamma/2\pi = 2.65$ MHz. The branching ratios $f_x = \gamma_x/\Gamma$ for the decay from $|e\rangle$ into the states $|x\rangle$, $|g\rangle$, and $|i\rangle$ are $f_x \approx 0.999$, $f_g = 1.3 \times 10^{-3}$, and $f_i = 1.3 \times 10^{-4}$, respectively, such that photoassociation without a cavity leads to a maximal asymptotic value of $(N_g/N)(t \to \infty) \equiv (N_g/N)(t \to \infty) \approx N_\infty \equiv f_g/(f_g + f_x) \approx 1.3 \times 10^{-3}$. The photoassociation laser (wavelength of $\lambda_{\text{PA}} = 1557$ nm) has a Rabi frequency $\Omega/2\pi = 70$ kHz in the weak coupling regime. We assume a cavity of length $L = 280 \mu$m, free spectral range $c/2L = 535$ GHz, mode waist $\omega_0 = 12 \mu$m, and half linewidth $\kappa/2\pi = 5.4$ MHz, which is tuned in resonance with the $\lambda_{\text{eg}} = 977$ nm transition $|e\rangle \leftrightarrow |g\rangle$, resulting in a peak vacuum Rabi frequency $g/2\pi = d_{el}\sqrt{f_g\omega_0^2/2\hbar^2N}/2\pi \approx 770$ kHz with the mode volume $V = \pi\omega_0^2L/4$ and the electronic transition dipole moment $d_{el} = 0.1$ a.u. [28].

For $\Delta = \delta = 0$, we find $\hat{H}_{\text{eff}} = 0$ and the dynamics is governed by dissipative Lindblad terms only, with $\xi = \sqrt{N}/(\Gamma + N_\delta C)^{-1}$. Figure 1(d) shows exemplary results for the time evolution of the molecular ground-state fraction $N_g/N$ as a function of $N$, with $1 \leq N \leq 10^5$. For $N = 1$ the figure shows that the presence of a cavity (here $C \approx 0.04$) induces an enhancement of $N_\infty g/N$ from $\sim 0.1\%$ (no cavity, dashed red line) to $\sim 4\%$, due to increased state-selectivity [20]. Strikingly, with increasing $N$, we observe an enhancement towards $N_\infty g/N \rightarrow 1$, at the cost of an increased transfer time. Figure 2(a) is a contour plot of the long-time population fraction $N_\infty g/N$ in the loss state $|x\rangle$ as a function of $N$ and $C$. The plot shows that, for increasing collective cooperativity $NC$, $N_\infty g/N$ rapidly decreases from its bare (no-cavity) value $\sim 1$ towards 0 [upper right corner in Fig. 2(a)].

To gain further insight, we obtain an analytical solution of the dynamics in the limit of large collective cooperativity $NC \gg 1$ and large but finite molecule number $N_g \gg 1$. In the quantum trajectories picture, the decay rate of a state $|\psi\rangle$ is given by $\langle \psi | - 2 \sum \hat{L}^\dagger_{\text{eff}} \hat{L}_{\text{eff}} | \psi \rangle$. With these assumptions, we can restrict the discussion to the symmetric Dicke states, assume $(N_g + 1)C \gg 1$, and neglect fluctuations by approximating operators by their expectation values $N_x \equiv (N_x)$. We then obtain the following rates for the decays via the different channels

$$2 \langle \hat{L}^\dagger_{\text{eff}} \hat{L}_{\text{eff}} \rangle \approx \frac{2}{\tau} \frac{N_i}{(N_g + 1)C} \equiv \zeta_i$$

$$2 \sum_n \langle \hat{L}^\dagger_{\text{eff}}(n) \hat{L}_{\text{eff}}(n) \rangle \approx \frac{2f_x}{\tau} \frac{N_i}{(N_g + 1)^2C^2} \equiv \zeta_n.$$  

Note that for $(N_g + 1)C \gg 1$, the decay via the cavity [Eq. (6)] dominates over spontaneous emission [Eq. (7)]. Dynamics is then governed by non-linear rate equations

$$\dot{N}_i = - \zeta_x - \zeta_g - \zeta_n$$

$$\dot{N}_x = \zeta_x$$

$$\dot{N}_g = \zeta_g + \zeta_n,$$

for which we provide analytical solutions in Ref. [24] for the time-dependence of the populations, $N_x(t)$. For large $N_\infty g$, we find for the loss state fraction

$$\frac{N_\infty g}{N} \approx \frac{f_x \ln(N)}{NC} \approx 0.$$

The half time $T_1/2 = - \int_{N_\infty g}^{N_\infty g} dN/N$ for population transfer out of state $|i\rangle$ is well approximated by

$$T_1/2 \approx NC\tau.$$  

This scaling is observed as straight contours for large $NC$ in the numerical simulations in Fig. 2(b). The demonstration of increased molecular yield in the ground state due to collective dissipative effects, at the cost of decreased transfer rates, is one of the central results of this work.

We find that the slowdown of $T_1/2$ in Eq. (12) is due to terms $\propto 1/[\Gamma(N_g + 1)C$ in Eqs. (6) and (7), caused by polariton formation. The latter is captured by Fig. 3(a), which is a contour plot of $N_i$ of Eq. (8) as a function of $N_g$ and $\Delta$, with $\delta = \Delta$. For $\Delta = 0$, the figure shows that $N_i$ decreases rapidly with increasing $N_g$. The rate $N_i$ is instead maximized for an optimal choice of detuning

$$\Delta_{\text{opt}}^\pm = \pm \left[ \max \left( 0, (N_g + 1)g^2 - \frac{T^2 + \kappa^2}{2} \right) \right]^{1/2}.$$  

This reflects the formation of two polaritons with energy $E^\pm \sim \Delta_{\text{opt}}^\pm$ for large enough $N_g \gtrsim (\Gamma^2 + \kappa^2)/2g^2$. To circumvent the slowdown, we propose to chirp the
laser detuning to stay resonant with the polariton energy, which depends on the (time dependent) expectation value $N_g(t)$. This adjustment can be adiabatic since the dynamics of $N_g(t)$ is slow compared to $\Gamma (O(\Omega^2/\Gamma))$, and thus it is sufficient to consider a time dependent $\Delta(t)$ and $\delta(t) = \Delta(t)$ in Eqs. (4) and (5).

For $\kappa \leq \gamma + \Gamma \leq \sqrt{N_g + 1}\gamma$, the decay rates of the different channels assume the simple form [24][29]

$$2 \left\langle \hat{L}_{\kappa}^\dagger \hat{L}_{\kappa} \right\rangle \approx \frac{2\Omega^2\kappa}{(\kappa + \Gamma)^2} N_i \equiv \zeta_\kappa$$

(14)

$$2 \sum_n \left\langle \hat{L}_{\kappa(n)}^\dagger \hat{L}_{\kappa(n)} \right\rangle \approx \frac{2\Omega^2\gamma_n}{(\kappa + \Gamma)^2} N_i \equiv \zeta_\gamma_n$$

(15)

and rate equations Eqs. (8) to (10) have a simple analytical solution, with exponential form

$$\frac{N_g(t)}{N} = \exp \left[ -\frac{2\Omega^2(\kappa + \gamma + \gamma_x)t}{(\kappa + \Gamma)^2} \right]$$

(16)

$$\frac{N_g(t)}{N} = \frac{\kappa + \gamma}{\kappa + \gamma_x + \gamma_x} \left[ 1 - \exp \left( -\frac{2\Omega^2(\kappa + \gamma + \gamma_x)t}{(\kappa + \Gamma)^2} \right) \right]$$

(17)

These equations are formally equivalent to those of a single three-level system in the weak driving limit with decay rates $\gamma_i$, $\gamma_x$, and $\gamma_g + \kappa$. While collective effects are present in the polariton formation, the final rate is here independent of $N$. For $\kappa \gg \gamma_x$, the ground-state population approaches $N$ as $N_g/N \approx 1 - \gamma_x/\kappa$, at the cost of an increasing time-scale $\sim \kappa/\Omega^2$.

Figure 3(b) shows numerical results for the increase of $N_g/N$ as a function of time $t$, for different values of $\kappa$, in agreement with the discussion above. We find that the $\gamma_g$ decay channel pumps molecules out of the completely symmetric state into so-called “dark states” that do not couple to the cavity. These dark states decay with a slower rate $2\Omega^2(\gamma_y + \gamma_x)/(N_g g^2)$ [24] and are responsible for the long-time dynamics [inset of Fig. 3(b)].

Whether higher molecular yields are reached by staying on bare resonance or chirping the laser depends on what limits state selectivity. If transfer times are not a concern, staying on bare resonance ($\Delta = 0$) provides the highest yield. For a reasonable lattice lifetime of 1 s, we obtain a peak ground state population $N_g/N \approx 92\%$ after 55 ms with a transfer half time $T_2 \approx 3.2\text{ ms}$ (98\% for infinite lattice lifetime). These results are essentially unchanged by considering locally different coupling strengths $g_n = g(x_n) = g \exp[-(x_n^2 + y_n^2)/\omega_0^2] \cos(2\pi z_n/\lambda_{eg})$, due to the finite cavity mode waist $\omega_0$ and the different lattice positions, with $z_n (x_n, y_n)$ oriented along the cavity axis (in the perpendicular planes) [see Fig. 1(a)]. For example, for a $20 \times 20 \times 25$ lattice at angle $\theta = 57^\circ$ and assuming perfect matching of lattice and cavity modes with $\cos(2\pi z_n/\lambda_{eg}) = 1$ [30], we find a peak $N_g/N \sim 92\%$, a transfer time 48 ms and $T_2 \sim 2.7\text{ ms}$, with infinite lattice lifetime final fraction 97\%. Thus, ground state populations comparable to STIRAP ($\sim 90\%$) [7, 8] can be achieved without the need of a time-dependent laser pulse. These results are robust against reasonable lattice mismatches. Even in a worst case scenario of complete positional disorder [i.e., uniform and Gaussian ($\sigma_{xy} = 5 \mu m$) distributions in the $z$ and $x-y$ directions, respectively] we find a peak $N_g/N \sim 71\%$ (73\% for infinite lattice lifetime) after 21 ms and $T_2 \sim 0.4\text{ ms}$.

For a scenario with $10^4$ Rb$_2$ Feshbach molecules (see parameters above), the system is closer to the first scenario and we find that staying on bare resonance ($\Delta = 0$) provides the highest yield. For a reasonable lattice lifetime of 1 s, we obtain a peak ground state population $N_g/N \approx 92\%$ after 55 ms with a transfer half time $T_2 \approx 3.2\text{ ms}$ (98\% for infinite lattice lifetime). These results are essentially unchanged by considering locally different coupling strengths $g_n = g(x_n) = g \exp[-(x_n^2 + y_n^2)/\omega_0^2] \cos(2\pi z_n/\lambda_{eg})$, due to the finite cavity mode waist $\omega_0$ and the different lattice positions, with $z_n (x_n, y_n)$ oriented along the cavity axis (in the perpendicular planes) [see Fig. 1(a)]. For example, for a $20 \times 20 \times 25$ lattice at angle $\theta = 57^\circ$ and assuming perfect matching of lattice and cavity modes with $\cos(2\pi z_n/\lambda_{eg}) = 1$ [30], we find a peak $N_g/N \sim 92\%$, a transfer time 48 ms and $T_2 \sim 2.7\text{ ms}$, with infinite lattice lifetime final fraction 97\%. Thus, ground state populations comparable to STIRAP ($\sim 90\%$) [7, 8] can be achieved without the need of a time-dependent laser pulse. These results are robust against reasonable lattice mismatches. Even in a worst case scenario of complete positional disorder [i.e., uniform and Gaussian ($\sigma_{xy} = 5 \mu m$) distributions in the $z$ and $x-y$ directions, respectively] we find a peak $N_g/N \sim 71\%$ (73\% for infinite lattice lifetime) after 21 ms and $T_2 \sim 0.4\text{ ms}$.

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In summary, we proposed two novel methods for high-yield state selective preparation of ultra-cold molecules in a cavity. Both schemes rely on collective, dissipative effects. It is an exciting prospect to investigate how similar collective effects could be used to engineer generic state-transfer schemes even outside of the ultra-cold regime [31, 32].

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Supplemental Materials: Collective Dissipative Molecule Formation in a Cavity

Adiabatic Elimination

In order to adiabatically eliminate the cavity and the excited states, we follow the formalism of Reiter and Sørensen [23]. First, we split the system into an excited state manifold with fast dynamics and a ground state manifold with slow dynamics, both of which are weakly coupled. We define the ground state manifold by \( \hat{N}_e + \hat{a} \hat{a}^\dagger = 0 \), so that there are neither molecular excitations nor photons. The excited state manifold contains all remaining states \( (\hat{N}_e + \hat{a} \hat{a}^\dagger \geq 1) \), but as we use the interaction as a perturbation, it is sufficient to restrict the analysis to the single excitation limit \( \hat{N}_e + \hat{a} \hat{a}^\dagger = 1 \). The condition for the adiabatic elimination to be valid is that the interaction is much slower than the excited state dynamics, e.g., because \( \sqrt{N} \Omega \ll \Gamma \). This assumption corresponds to the situations analyzed in the main paper. Following the notation of Reiter and Sørensen, we arrive at:

\[
\hat{H}_e = \hat{H}_0 + \hat{H}_C = \Delta \hat{N}_e + \delta \hat{a} \hat{a}^\dagger + g \sqrt{N} \left( \hat{a} \hat{S}_{ge} + \hat{S}_{eg} \hat{a}^\dagger \right) \quad (S1)
\]

\[
\hat{H}_g = 0 \quad (S2)
\]

\[
\hat{V}^+ = \sqrt{N} \Omega \hat{S}_{ei} \quad (S3)
\]

\[
\hat{V}^- = \sqrt{N} \Omega \hat{S}_{te} \quad (S4)
\]

The Lindblad operators \( \hat{L}_k \) are defined in the main paper.

Next, we calculate the non-hermitian Hamiltonian \( \hat{H}_{\text{NH}} = \hat{H}_e - i \sum \hat{L}_k^\dagger \hat{L}_k \). Note that the factor 2 compared to Reiter and Sørensen [23] arises due to a different definition of the Lindblad operators:

\[
\hat{H}_{\text{NH}} = \hat{\Delta} \hat{N}_e + \hat{\delta} \hat{a} \hat{a}^\dagger + g \sqrt{N} \left( \hat{a} \hat{S}_{ge} + \hat{S}_{eg} \hat{a}^\dagger \right) \quad (S5)
\]

with \( \hat{\Delta} = \Delta - i \Gamma \) and \( \hat{\delta} = \delta - i \kappa \). In the single excitation limit \( \hat{H}_{\text{NH}} \) can be inverted. It is straightforward to confirm that:

\[
\hat{H}_{\text{NH}}^{-1} = \left[ \hat{\Delta}^2 - \hat{\Delta}(\hat{N}_g + \hat{N}_e)g^2 \right]^{-1} \left\{ \hat{\Delta}^2 \hat{a} \hat{a}^\dagger - g \sqrt{N} \hat{\Delta} \left( \hat{S}_{eg} \hat{a} + \hat{S}_{ge} \hat{a}^\dagger \right) + \left[ \hat{\Delta} \hat{\delta} - \left( \hat{N}_g + 1 \right) g^2 \right] \hat{N}_e + Ng^2 \hat{S}_{eg} \hat{S}_{ge} \right\} \quad (S6)
\]

The effective operators are now given by:

\[
\hat{H}_{\text{eff}} = -\frac{1}{2} \hat{V}^+ \left[ \hat{H}_{\text{NH}}^{-1} + \left( \hat{H}_{\text{NH}}^{-1} \right)^\dagger \right] \hat{V}^+ + \hat{H}_g \quad (S7)
\]

\[
\hat{L}_{\text{eff}}^k = \hat{L}_k \hat{H}_{\text{NH}}^{-1} \hat{V}^+ \quad (S8)
\]

We find:

\[
\hat{H}_{\text{eff}} = -\frac{\Omega^2}{2 \Delta} \left( \hat{N}_i + \sqrt{N} \hat{S}_{g\delta} \hat{\xi} \hat{S}_{gi} \right) + \text{h.c.} \quad (S9)
\]

\[
\hat{L}_{\text{eff}}^k = \frac{\Omega \sqrt{\kappa}}{g} \hat{\xi} \hat{S}_{gi} \quad (S10)
\]

\[
\hat{L}_{\text{eff}}^\alpha(n) = \frac{\Omega \sqrt{\gamma}}{\Delta} \left( \hat{\alpha}^{(n)}_n - \hat{\alpha}^{(n)}_e \hat{\xi} \hat{S}_{gi} \right) \quad (S11)
\]

with \( \hat{\xi} = \sqrt{N} g^2 \left( \hat{N}_g g^2 - \hat{\Delta} \hat{\delta} \right)^{-1} \).

The adiabatic elimination as discussed above is valid in the single excitation limit, which can be assumed if \( \langle \hat{N}_e + \hat{a} \hat{a}^\dagger \rangle \ll 1 \). The number of excitation \( \langle \hat{N}_e + \hat{a} \hat{a}^\dagger \rangle \) can be estimated by comparing the pumping rate \( \sqrt{N} \Omega \) to the total excitation decay \( \Gamma_{\text{tot}} \) and the total detuning \( \Delta_{\text{tot}} \):

\[
\langle \hat{N}_e + \hat{a} \hat{a}^\dagger \rangle \approx \frac{N \Omega^2}{\Gamma_{\text{tot}}^2 + \Delta_{\text{tot}}^2} \ll 1. \quad (S12)
\]
We first consider the scheme on bare resonance. The short times dynamics is best described in terms of bare excitons so that \( N_t \approx N \), \( \Gamma_{\text{tot}} = \Gamma \), and \( \Delta_{\text{tot}} = 0 \). In this case we can rewrite Eq. (S12) to find \( N \ll \Gamma^2/\Omega^2 \approx 1400 \) for the RbCs parameters. In contrast, the long time dynamics is best described by polaritons and dark states. As the latter are populated only very slowly, we restrict the analysis of the long time dynamics to polaritons. We find for the RbCs parameters. In contrast, the long time dynamics is best described by polaritons and dark states. As analogous to the one used by Zhang et al. \( [25] \). We describe the dynamics of the two level systems in the Dicke basis \( |J,M\rangle \) \([33–36]\]. Note that both steps are exact.

For the first step we use that molecules that enter state \(|x\rangle\) as molecule loss and we only need to treat the dynamics of the remaining two level systems.

In order to simulate \( N \) identical two level systems with particle loss, we employ a quantum trajectories algorithm analogous to the one used by Zhang et al. \( [25] \). We describe the dynamics of the two level systems in the Dicke basis \( |J,M\rangle \) \([33]\), while keeping track of the molecule number \( N \) \([25]\). The result are equations for a matrix of the form \( [N,J,M] \langle N,J,M| \). The contributions to the equations of motion for the diagonal matrix elements \( [N,J,M] \langle N,J,M| \) are given in Tab. I.

As there are no off-diagonal elements generated in the equations in Tab. I and the initial state is given by the diagonal element \( [N,N/2,N/2] \langle N,N/2,N/2| \), the diagonal elements are sufficient to describe the system dynamics. This motivates the description using a quantum trajectory algorithm, which becomes a simple Monte Carlo Markov chain of jumps between the matrix elements, due to the trivial Hamiltonian contribution.

### Numerical Simulations

In order to develop an efficient algorithm, we use two steps: In a first step we go from \( N \) three level molecules (with states \(|i\rangle\), \(|g\rangle\), and \(|x\rangle\)) to two level molecules (with states \(|i\rangle\) and \(|g\rangle\)) with variable molecule number. In a second step we take advantage of the permutation symmetry of the system to reduce \( N \) spin-1/2 (two level) systems (dimension \( \sim 2^N \)) to one spin-\( N/2 \) system (dimension \( \sim N^2 \)) \([25,33–36]\). Note that both steps are exact.

For the first step we use that molecules that enter state \(|x\rangle\) have no coherence with the rest of the system (decay only via local dissipation) and have no influence on the dynamics of the system. This allows us to treat decay into state \(|x\rangle\) as molecule loss and we only need to treat the dynamics of the remaining two level systems.

In order to simulate \( N \) identical two level systems with particle loss, we employ a quantum trajectories algorithm analogous to the one used by Zhang et al. \( [25] \). We describe the dynamics of the two level systems in the Dicke basis \( |J,M\rangle \) \([33]\), while keeping track of the molecule number \( N \) \([25]\). The result are equations for a matrix of the form \( [N,J,M] \langle N,J,M| \). The contributions to the equations of motion for the diagonal matrix elements \( [N,J,M] \langle N,J,M| \) are given in Tab. I.

As there are no off-diagonal elements generated in the equations in Tab. I and the initial state is given by the diagonal element \( [N,N/2,N/2] \langle N,N/2,N/2| \), the diagonal elements are sufficient to describe the system dynamics. This motivates the description using a quantum trajectory algorithm, which becomes a simple Monte Carlo Markov chain of jumps between the matrix elements, due to the trivial Hamiltonian contribution.

### Derivation of Rate Equations

In order to consider the effects of the different decay channels, we need to separate the decay rates given in the second row of Tab. I into the different decay channels. For no detuning \( \Delta = \delta = 0 \), this yields:

\[
-\left\{ \hat{L}_{\text{eff}}^{\alpha} \right\}_{\alpha}^{\kappa} \left[ |N,J,M\rangle \langle N,J,M| \right] = -\frac{2\Omega^2 (J + M)(J - M + 1)}{CT} \left( \frac{N}{2} - M + 1 + \frac{1}{C} \right)^2 |N,J,M\rangle \langle N,J,M| \tag{S13}
\]

\[
-\left\{ \sum_{\alpha} \hat{L}_{\text{eff}}^{\alpha(n)} \right\}_{\alpha}^{\kappa} \left[ |N,J,M\rangle \langle N,J,M| \right] = -\frac{2\Omega^2 \gamma_0}{\Gamma} \left( \frac{N}{2} - M + 1 + \frac{1}{C} \right)^2 \left[ \frac{N}{2} + M - 2 \frac{(J + M)(J - M + 1)}{\frac{N}{2} - M + 1 + \frac{1}{C}} + \frac{(J + M)(J - M + 1)(\frac{N}{2} - M + 1)}{(\frac{N}{2} - M + 1 + \frac{1}{C})^2} \right] \tag{S14}
\]

where \( \alpha = i, g, x \).

To simplify these equations, we make two assumptions: (i) We assume that the dynamics is taking place in the completely symmetric state, for which \( J = N/2 \), and (ii) we assume \( N \gg 1 \). The first assumption is justified
| Term | Value |
|------|-------|
| $-i[H_{\text{eff}}, |N, J, M\rangle \langle N, J, M|]$ | 0 |
| $-\{\sum_k \hat{L}_{\text{eff}}^k |N, J, M\rangle \langle N, J, M|\}$ | $-\frac{2\hbar^2}{\Delta_\hbar} |N, J, M\rangle \langle N, J, M|(J + M)(J - M + 1)|\xi|^2$ |
| $\hat{L}_{\text{eff}}^\dagger |N, J, M\rangle \langle N, J, M| \hat{L}_{\text{eff}}$ | $\frac{\Omega_{\gamma_{\gamma}}^2}{\Delta^2} |N, J, M\rangle \langle N, J, M| - M - 2(J + M)(J - M + 1) \text{Re}(|\xi|^2) + (J + M)(J - M + 1)(\frac{N}{2} - M + 1)|\xi|^2$ |
| $\sum_{\alpha} \hat{L}_{\text{eff}}^{\alpha(n)}(n) |N, J, M\rangle \langle N, J, M| L_{\text{eff}}^{\alpha(n)\dagger}$ | $\frac{\Omega_{\gamma_{\gamma}}^2}{\Delta^2} |N, J, M\rangle \langle N, J, M|\beta_{\alpha_{\alpha}}^2(J + M - 1)$ |
| $\sum_{\alpha} \hat{L}_{\text{eff}}^{\alpha(n)}(n) |N, J, M\rangle \langle N, J, M| \hat{L}_{\text{eff}}^{\alpha(n)}$ | $\frac{\Omega_{\gamma_{\gamma}}^2}{\Delta^2} |N, J, M\rangle \langle N, J, M|\alpha_{\alpha}^2(J + M - 1)(J - M + 1) \text{Re}(|\xi|^2) + (J + M)(J - M + 1)|\xi|^2$ |
| $\sum_{\alpha} \hat{L}_{\text{eff}}^{\alpha(n)}(n) |N, J, M\rangle \langle N, J, M| L_{\text{eff}}^{\alpha(n)\dagger}$ | $\frac{\Omega_{\gamma_{\gamma}}^2}{\Delta^2} |N, J, M\rangle \langle N, J, M|\delta_{\alpha_{\alpha}}^2(J + M - 1)$ |

TABLE I. Different contributions to the time evolution of density matrix element $|N, J, M\rangle \langle N, J, M|$. Notation: $\xi = \frac{g^2}{(N/2 - M + 1)^2 + \Delta^2}$ (a factor of $\sqrt{N}$ different from the operator $\hat{\xi}$). $\alpha_{\alpha}^2 = (N + 2)/(4J(J + 1))$, $\beta_{\alpha_{\alpha}}^2 = (N + 2J + 2)(J + M)(J - M + 1)|\xi|^2/(4J(2J + 1))$, $\delta_{\alpha_{\alpha}}^2 = (N - 2)(J - M + 1)|\xi|^2/(4J(2J + 1))$. Further below. The second assumption is justified for large collective cooperativity $NC$ and not too small $C$ (e.g., $C \sim 10^{-3}$ is fine for $N \sim 10^5$, but not thermodynamic limit with $N \to \infty$ and $C \to 0$). In this way, only the initial dynamics with $N_g \ll N$ is ignored, which we empirically find to be a good approximation. Using $N_g = N/2 - M$ and $N_i = N/2 + M$, we simplify:

\[
\begin{align*}
-\{\hat{L}_{\text{eff}}^\alpha |N, J, M\rangle \langle N, J, M| \hat{L}_{\text{eff}}^\dagger & \approx \frac{2\Omega^2}{\Gamma} \frac{N_i(N_g + 1)}{(N_g + 1 + \frac{1}{C})^2} \\
\sum_{\alpha} \hat{L}_{\text{eff}}^{\alpha(n)\dagger} \hat{L}_{\text{eff}}^{\alpha(n)} & \approx \frac{2\Omega^2}{\Gamma} \frac{N_i}{(N_g + 1)^2 C^2} .
\end{align*}
\]

Now we can justify assumption (i): For $N_g C \gg 1$ the cavity decay channel is dominant, for which $J$ does not change. As $J = N/2$ for the initial state, we can thus expect $J$ to remain close to this value. In fact, the dominant spontaneous emission rate $\gamma_c$ can only decrease $N - 2J$, pushing the system back into the superradiant state $J = N/2$ if it moves out of that state during the initial dynamics. This corresponds to the results of numerical simulation, where initially $N - 2J$ grows, but then quickly decays back towards zero.

Note that the Eqs. (S15) to (S16) are still state dependent. In order to get rate equations we need to take the expectation value of the right hand side. For $N \gg 1$, the fluctuations of the particle numbers $N_i$ and $N_g$ around their
mean values are typically small compared to their expectation values. Therefore, the expectation values of the right hand side are well approximated by taking the expectation value of $N_g$, directly in the denominator, recovering the rate equations given in the paper. Note that by comparing simulations of the rate equations to simulations of the full master equation, we find that up to a prefactor for the loss state population $N_x$ they give a good approximation to the dynamics.

Solution of Rate Equations

For large $N_gC$, we note that $N_x \ll N$, as $\hat{N}_x \ll \hat{N}_g$. Thus, to first order $N_g = N - N_t$. For large $N$, we can thus write down a differential equation for the initial state population:

$$\dot{n}_i \equiv \dot{\hat{N}}_i/N \approx -\frac{2}{N C \tau} \frac{n_i}{1 - n_i}$$  

(S17)

with $\tau = \Gamma/\Omega^2$. This equation can be integrated to find for the time $T$ to reach a population fraction $n_i$ in the initial state:

$$T(n_i) = \int_1^{n_i} \frac{dn'_i}{n'_i} = \frac{NC\tau}{2} \ln \left( \frac{e^{n_i-1}}{n_i} \right)$$  

(S18)

or inverted to get the time evolution of $n_i$

$$n_i(t) = -W\left[-\exp\left(-1 - \frac{2t}{NC\tau}\right)\right]$$  

(S19)

where $W(x)$ is the product logarithm or Lambert $W$ function, which is defined as the inverse of $x = we^w$.

Rate Equations with Detuning

In order to compute rate equations for the chirped pulse, we replace $\Delta = \delta = \Delta_{opt}$ with

$$\Delta_{opt} = \left\{ \max \left[ 0, (N_g + 1)g^2 - \frac{\Gamma^2 + \kappa^2}{2} \right] \right\}^{1/2}.$$  

(S20)

If we assume $(N_g + 1)g^2 > (\kappa^2 + \Gamma^2)/2$, the cavity decay dominates and we can restrict the analysis to the completely symmetric Dicke state, for which one can replace $\hat{S}_{ig}\hat{S}_{gi} = \hat{N}_i(\hat{N}_g + 1)/N$. This leads to:

$$\hat{L}_{\text{eff}}^{\kappa\dagger}\hat{L}_{\text{eff}}^{\kappa} = \Omega^2 g \omega \kappa \left[ \left( \hat{N}_g - N_g \right)g^2 - \frac{(\kappa - \Gamma)^2}{2} \right]^2 + (\kappa + \Gamma)^2 \left( (N_g + 1)g^2 - \frac{\Gamma^2 + \kappa^2}{2} \right)$$

$$\approx \frac{\Omega^2 \kappa}{(\Gamma + \kappa)^2} \hat{N}_i$$  

(S21)

$$\hat{L}_{\text{eff}}^{\alpha\dagger}\hat{L}_{\text{eff}}^{\alpha} = \frac{\Omega^2 \gamma}{\Gamma^2 + (N_g + 1)g^2} \left[ \hat{N}_i - \frac{2\hat{N}_i}{(N_g + 1)g^2} \left[ (\hat{N}_g - N_g \right)g^2 - \frac{(\kappa - \Gamma)^2}{2} \right]^2 + (\kappa + \Gamma)^2 \left( (N_g + 1)g^2 - \frac{\Gamma^2 + \kappa^2}{2} \right) \right]$$

$$\approx \frac{\Omega^2 \gamma}{(\Gamma + \kappa)^2} \hat{N}_i$$  

(S22)

where we approximated by replacing operators with their expectation values and neglecting higher order terms in $(\Gamma + \kappa)/\sqrt{N_g + 1}g$.

However, in numerical simulations the noise term $\hat{N}_g - N_g$ turns out to be important as well. Firstly, for $\Delta N_g \sim \sqrt{N_g}$, we find that the noise term looks like $N_g g^2$. This is only negligible if $N^{1/4}g \ll \kappa + \Gamma$. Secondly, we can end up in a negative feedback loop, running out of resonance: Consider a state for which $\langle \hat{N}_g(t) \rangle < N_g(t_1)$. In this case
\[ \partial_t \langle \hat{N}_g \rangle \sim \langle \hat{L}_g^{\dagger} \hat{L}_g^{\text{eff}} \rangle < \partial_t N_g \sim \langle \hat{L}_g^{\dagger} \hat{L}_g^{\text{eff}} \rangle |_{\hat{N}_g = N_g}. \] This leads to \((\hat{N}_g - N_g)(t_2) < (\hat{N}_g - N_g)(t_1)\) for \(t_2 > t_1\), running further out of resonance. In practice this can be solved by keeping \(\Delta\) a bit smaller than \(\Delta_{\text{opt}}\). We choose

\[ \Delta = \left\{ \max \left[ 0, N \left( \frac{N_g(t)}{N} \right)^{1.5} g^2 - \frac{\Gamma^2 + \kappa^2}{2} \right] \right\}^{1/2} \tag{S23} \]

with \(N_g(t)/N\) plugged in according to an empiric estimate

\[
\frac{N_g(t)}{N} = \frac{(\kappa + \gamma_g)(\kappa + \gamma_x)\left\{ 1 - \exp \left[ -\frac{2\Omega^2(\kappa + \gamma_g + \gamma_x)t}{(\kappa + \Gamma)^2} \right] \right\}}{\left( \kappa + \gamma_g + \gamma_x \right)(\gamma_g + \gamma_x)} \left\{ 1 - \exp \left[ \frac{2\Omega^2(\gamma_g + \gamma_x)t}{N g^2 - \frac{\Gamma^2}{2} + \frac{\kappa^2}{2}} \right] \right\} \tag{S24} \]

This choice yields very good results, and a further optimization is beyond the scope of this paper.

### Dark States

As discussed above and shown in Tab. I, only spontaneous emission towards \(|i\rangle\) and \(|g\rangle\) might lead to a decrease of \(J - N/2\). These states with lowered \(J\) can still decay via the cavity until \(M = -J\), or reformulated \(N_i = N/2 - J\). The remaining states are dark states and will decay with a lower rate. Note that the dark states do not have shifted energies with respect to the bare excited states. Thus the laser is detuned with respect to the ground state – dark state transition by about \(\Delta^2 \sim N g^2\). This leads to a significantly lowered decay rate. To estimate the number of molecules that will decay via the dark states, we assume that every spontaneous emission towards \(|g\rangle\) reduces \(J\), whereas spontaneous emission towards \(|i\rangle\) leaves \(J\) unchanged. This rough approximation is empirically justified for \(J \approx N/2\) and by comparison of the final results to simulation of the full dynamics. With this assumption the dark state fraction becomes \(\gamma_g/(\kappa + \gamma_g + \gamma_x)\). The decay rate of this dark states is given by \(2\Omega^2(\gamma_g + \gamma_x)/(\Delta^2 + \Gamma^2) \approx 2\Omega^2(\gamma_g + \gamma_x)/(N g^2 - \kappa^2/2 + \Gamma^2/2)\).

### Comparison between both Schemes

For given \(g\), we find that the chirped pulse scheme gives a loss state population of:

\[
\frac{N_x^\infty}{N} \text{ (chirp)} \approx \frac{\gamma_x}{\sqrt{N}g} \gg \frac{\gamma_x}{\sqrt{N}g} \frac{\kappa}{\sqrt{N}g} = \frac{f_x}{NC} \approx \frac{N_x^\infty}{N \ln(N)} \text{ (no chirp)} \tag{S25} \]

Thus for \(\ln(N) < N g^2/\kappa^2\) the scheme without a chirp yields higher state selectivity. In contrast, for given half time we find:

\[
\frac{N_x^\infty}{N} \text{ (no chirp)} \approx \frac{f_x \tau \ln(N)}{5T^2_\tau} \tag{S26} \]

\[
T^2_\tau \text{ (chirp)} \approx \frac{\ln(2)\kappa}{\Omega^2} \approx \frac{\ln(2)\tau\kappa}{\Gamma} \tag{S27} \]

\[
\frac{N_x^\infty}{N} \text{ (chirp)} \approx \frac{f_x \tau \ln(2)}{T^2_\tau} \tag{S28} \]

Thus, for \(N \gtrsim 30\), the state selectivity with the second scheme is higher. For a typical number of \(N \sim 1000\) molecules we find that the state selectivity with the chirped pulse is higher by a factor of 2. Note also that the first scheme does not decay exponentially, but the long time dynamics exhibits a stronger collective slowdown so that considering the total transfer time instead of the half time favors the chirped scheme even more.
In order to model local cavity coupling constants for large molecule numbers, we use an effective model. We define a threshold cooperativity \( C_{\text{thr}} \), and assume that molecules with local coupling \( C_n = g_n^2/(\kappa \Gamma) < C_{\text{thr}} \) do not couple to the cavity \( g_n \to 0 \), whereas molecules with \( C_n > C_{\text{thr}} \) couple with average cooperativity \( C_n \to C_{\text{eff}} = (\sum C_n)/N' \). By employing this binary decision model, we arrive at a situation with particle permutation symmetry, which can be simulated as described above. \( C_{\text{thr}} = C_{\text{thr}}(N) \) is chosen such that, if \( N \) molecules couple with \( C_{\text{thr}} \) to a cavity, the \( |x\rangle \) state fraction is half of its no cavity value [red dashed line in Fig. S1(a)]. Errors are given by or smaller than the line width.

In order to derive an expression for \( C_{\text{eff}} \), we analyze the limit for which the cavity decay is dominant. We first derive an expression for the states after \( k \) decay processes via the cavity. Then, we calculate the cavity decay rate and the spontaneous emission rates for these states. Comparing the rates of decay for the different decay channels we can estimate the final ground state population and the half time.

For a local cavity coupling constant, we find effective operators for the master equation after adiabatic elimination

\[
\hat{H}_{\text{eff}} = 0 \quad (S29)
\]

\[
\hat{L}_{\text{eff}}^a(n) = \sqrt{\lambda_2} \left( \sigma^{a(n)}_{\alpha i} - \sigma^{\alpha(n)}_{\alpha i} \right) \hat{\xi} \hat{g}_{\text{gi}} \quad (S30)
\]

\[
\hat{L}_{\text{eff}}^\alpha(n) = \sqrt{\lambda_2} \left( \sigma^{\alpha(n)}_{\alpha i} - \sigma^{\alpha(n)}_{\alpha i} \right) \hat{\xi} \hat{g}_{\text{gi}} \quad (S31)
\]

with \( \hat{S}_{\text{gi}} = \sum_n (g_n/g_0) \sigma^{(n)}_{\text{gi}} \) and \( \hat{\xi} = \sqrt{N_0 g_0^2 \left( \sum_n g_n^2 \sigma^{(n)}_{\text{gi}} + \kappa \Gamma \right)}^{-1} = \sqrt{N C (\bar{C} + 1)}^{-1} \), where \( g_0 \) is the peak cavity coupling constant, \( \bar{C} \) is the average cooperativity and \( C \) is the peak cooperativity.

Taking the initial state as \( \left| \psi^{(0)} \right\rangle = \bigotimes_n |i\rangle_n \), the state after \( k \) decay processes via the cavity decay channel \( \hat{L}_{\text{eff}}^a(n) \) is given by

\[
\left| \psi^{(k)} \right\rangle = \frac{1}{\mathcal{N}_k} \left( \hat{L}_{\text{eff}}^a(n) \right)^k \left| \psi^{(0)} \right\rangle = \frac{1}{\mathcal{N}_k^2} \sum_{I,G} \bigotimes \bigotimes_{i \in I} g_i |i\rangle \bigotimes_{m \in G} |g\rangle_m \quad (S32)
\]

for some normalization constants \( \mathcal{N}_k \) and \( \mathcal{N}_k^2 \). \( I \) denotes the set of atom pairs in state \( |i\rangle \) and \( G \) denotes the set of molecules in state \( |g\rangle \). The sum runs over all possible choices of sets \( I \) and \( G \) such that \( |G| = k \), \( |I| = N - k \), and \( I \cap G = \emptyset \). This can be easily confirmed by checking \( \left| \psi^{(0)} \right\rangle = \bigotimes_n |i\rangle_n \) and \( \hat{L}_{\text{eff}}^\alpha(n) \left| \psi^{(k)} \right\rangle \propto \left| \psi^{(k+1)} \right\rangle \). In these states we get to leading order in \( 1/(N_0 \bar{C}) \):

\[
\zeta_{\alpha} \approx \frac{2 f_\alpha N_i}{\tau (N_0 + 1)^2 \bar{C}^2} \quad (S33)
\]

\[
\zeta_{\alpha} \approx \frac{2 f_\alpha N_i}{\tau (N_0 + 1)^2 \bar{C}^2} \quad (S34)
\]
This also justifies in hindsight to look at the cavity dominated limit, as cavity decay dominates for $N_g \bar{C} \gg f_\alpha$. From these we get the equations of motion:

\[
\begin{align*}
\dot{N}_i &\approx -\frac{2}{\tau} \frac{N_i}{(N_g + 1) \bar{C}} \\
\dot{N}_g &\approx \frac{2}{\tau} \frac{N_i}{(N_g + 1) \bar{C}} \\
\dot{N}_x &\approx \frac{2 f_x}{\tau} \frac{N_i}{(N_g + 1)^2 \bar{C}^2}
\end{align*}
\] (S35, S36, S37)

These equations are equivalent to Eqs. (6) to (10) of the main paper for no disorder with the replacement $C \rightarrow \bar{C}$. This motivates the choice:

\[
C_{\text{eff}} = \frac{\sum_n C_n}{N'}
\] (S38)

where the sum over molecules with $C_n > C_{\text{thr}}$ and $N'$ is the number of these molecules.

Fig. S1(b) and (c) show a comparison of the effective model and a full simulation for 10 molecules and different disorder strengths. We find a good correspondence.