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## Cavity-controlled formation of ultracold molecules

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### Abstract

Ultracold ground-state molecules can be formed from ultracold atoms via photoassociation followed by a spontaneous emission process. Typically, the molecular products are distributed over a range of final states. Here, we propose to use an optical cavity with high cooperativity to selectively enhance the population of a pre-determined final state by controlling the spontaneous emission. During this process, a photon will be emitted into the cavity mode. Detection of this photon heralds a single reaction. We discuss the efficiency and the dynamics of cavity-assisted molecule formation in the frame of realistic parameters that can be achieved in current ultracold-atom setups. In particular, we consider the production of Rb<sub>2</sub> molecules in the  $a^3\Sigma_u$  triplet ground state. Moreover, when working with more than two atoms in the cavity, collective enhancement effects in chemistry should be observable.

### Introduction

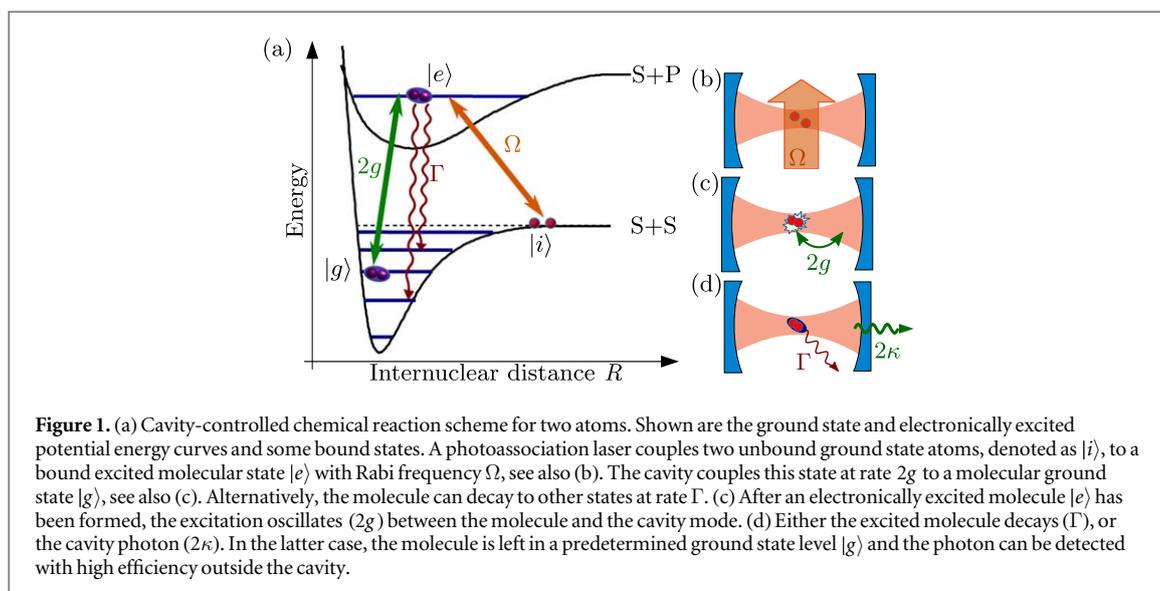
In recent years, the control and manipulation of ultracold atomic samples has enabled studies of chemical reactions in the ultracold regime. Here, the internal and external quantum states of the collision partners can be very well controlled, allowing for precise studies of reactions and observations of possible quantum interference effects. Furthermore, it might be possible to gain absolute control over chemical reactions (reviews: [1, 2]). In ultracold chemistry, one important reaction type is photoassociation (PA) where laser light can fuse together colliding atoms into a well-defined excited molecular bound state [3, 4]. Typically, the excited molecule can decay spontaneously into a number of ro-vibrational levels in the electronic ground state.

Here, we propose a way to control the chemical reaction. For this, we combine concepts of cavity quantum electrodynamics (CQED) in a high-finesse optical cavity with ultracold molecule formation. We make use of the fact that strong confinement of the electromagnetic field modes around a molecule can control its spontaneous emission and thus its final quantum state. Our scheme is related to previous proposals for a molecular matter-wave amplifier in an optical cavity [5] or for coupling atoms to broadband photonic crystal waveguides [6].

For transferring an atom pair to a molecular quantum state also other two-photon schemes are in principle available, such as stimulated Raman adiabatic passage (STIRAP) or pump-dump. In order to achieve high efficiency, however, these schemes require application of well-controlled laser pulses, a large Rabi-frequency  $\Omega$  for the transition between the atom pair and the excited level and long coherence times between the two lasers (for STIRAP). Furthermore, a repetitive application of these schemes does not increase the transfer efficiency.

The cavity-based scheme discussed here overcomes these constraints. Due to the built-in dissipation of the cavity, incoherent and weak pumping into the molecular ground state is possible, making the scheme robust with respect to fluctuations in  $\Omega$ . Furthermore, the scheme can be repeated, e.g. to increase the particle number of the molecular cloud by subsequently feeding it from several atomic samples. Finally, working with the cavity also has the additional advantage of allowing for photon-heralded detection of single reactions.

High-finesse optical microcavities already have a history of very successful quantum optics experiments with single cold atoms (for a review, see e.g. [7]). The strong confinement of the electromagnetic field in such cavities enables fast coherent transfer of atomic excitation into the cavity mode before the atom can decay by



spontaneous emission. Instead, the cavity photon is emitted into a single external mode with high probability while the atom is prepared in a desired ground state. Important applications include deterministic single-photon sources [8]. Introducing microcavities technologies to the realm of ultracold chemistry will enable us to control and instantly detect single reactions with a high efficiency. Furthermore, it will allow for a detailed study of the dynamics and statistics of reactions, in particular where collective effects come into play.

We note that even outside the field of ultracold temperatures, strong light–matter coupling with molecules is a recent hot topic. Possible applications might range from quantum information processing to the modification of chemical reaction landscapes. In these contexts, coherent coupling of single dye molecules [9], ensembles of polymers [10] and even of living bacteria [11] to a cavity have recently been observed.

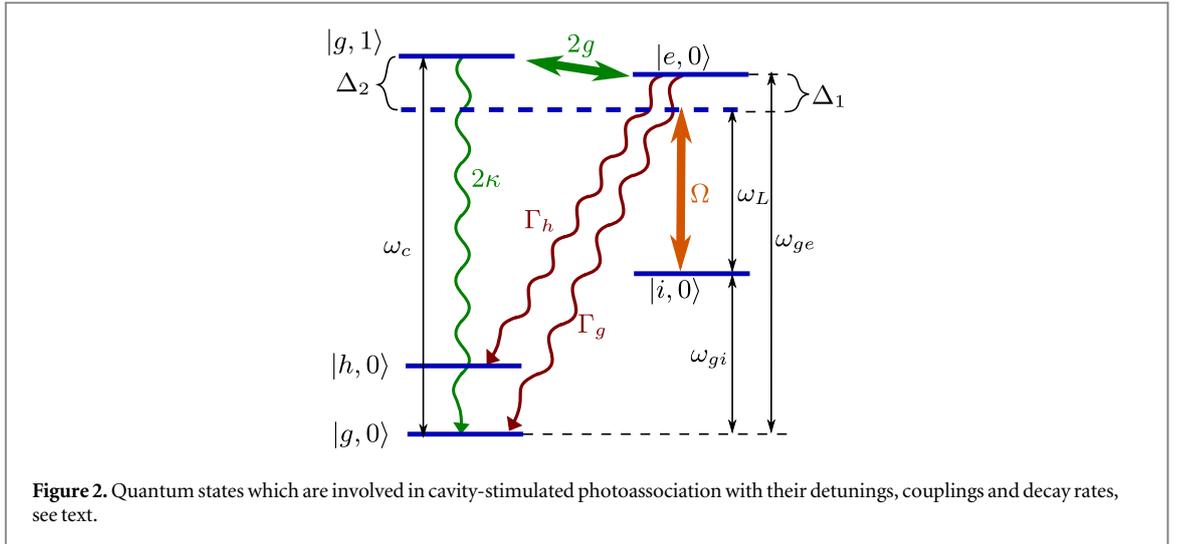
The implementation of CQED concepts with molecules is even more challenging than for atoms: due to the lack of closed electronic transitions in molecules and due to Franck–Condon factors which are in general small, smaller cavity mode volumes than for atoms are required to reach the regime of high cooperativity. Nevertheless, recent advances in cavity design and fabrication (e.g. fiber-based microcavities [12]) have enabled much smaller mode volumes, higher coupling strengths and better integrability compared to traditional cavities formed by bulky mirrors. Therefore, CQED technologies can now be applied to ultracold chemistry.

After presenting the basic scheme for cavity-chemistry, we estimate realistic parameters for an experimental set-up with ultracold rubidium atoms. Afterwards, we simulate the reaction dynamics and efficiency for a square-shaped PA pulse. Finally, we discuss collective effects when several molecules are produced.

### Single-molecule scheme

We start out by presenting a somewhat simplified version of the cavity-controlled PA scheme. We consider an unbound atom pair  $|i\rangle$  which is trapped in between the cavity mirrors. We assume the atoms to be in the vibrational ground state of one potential well of an optical lattice.

A bound state  $|e\rangle$  of the electronically excited molecular potential (asymptotically, e.g.  $S + P$ ) is excited from  $|i\rangle$  by a PA laser with Rabi frequency  $\Omega$ , see figure 1(a). The laser illuminates the atoms from the open side of the cavity, see figure 1(b). Subsequently, the level  $|e\rangle$  can spontaneously decay to the molecular ground state manifold ( $S + S$ ), typically within a few ns, as determined by the inverse linewidth  $1/\Gamma$  of the excited molecular level. In principle, there are many molecular ground state levels available for this decay. However, the cavity can be used to enhance the spontaneous decay into a particular level  $|g\rangle$ , and can therefore control the chemical reaction. For this, the cavity is tuned such that a cavity mode is resonant with the emitted photon. Under this condition, the molecule can undergo a transition from  $|e\rangle$  to  $|g\rangle$  while creating a photon in the cavity mode [5, 13, 14]. The rate of this coherent (reversible) energy exchange is denoted by  $2g$ , see figures 1(a) and (c). In addition, decoherence takes place: the excited state decays at rate  $\Gamma$  and the cavity field at rate  $\kappa$ , see also figure 1(d). In the regime of high cooperativity  $C \equiv g^2/(\kappa\Gamma) \gg 1$ , the electronic excitation can be transferred to the cavity mode faster than it can spontaneously decay into other free space modes. This means, the probability to get a ground-state molecule in a desired (ro-vibrational) quantum state can then be Purcell-enhanced. Since the photon decays from the cavity into a single external spatial mode, it can be detected with high efficiency, thus heralding every single reaction event by a photon click.



### Model Hamiltonian

When driving the  $|i\rangle \leftrightarrow |e\rangle$  transition for a *single* atom pair with the PA laser, at most one electronic or photonic excitation can be brought into the system at a time. We can then model the system effectively by five quantum states denoted by  $|m, n\rangle$ , where  $m$  denotes the atomic/molecular quantum state and  $n$  the cavity photon number, see figure 2. Furthermore, we assume tight confinement in the Lamb-Dicke regime ( $\hbar\omega_{\text{trap}} \gg E_{\text{recoil}}$ ), and therefore, we need not consider the external motion of the particles. The total energy of the atom pair, including the inter-particle interaction, is on the order of the  $\hbar\omega_{\text{trap}}$  which is much smaller than the linewidth  $\Gamma$  of  $|e\rangle$ .

The couplings, detunings and decay rates of the five states are also shown in figure 2. The PA laser field (frequency  $\omega_L$ ) couples the asymptotic two-atom-state  $|i, 0\rangle$  and the excited molecular state  $|e, 0\rangle$  with Rabi frequency  $\Omega$  and detuning  $\Delta_1 = \omega_{ge} - \omega_L - \omega_{gi}$ . The  $|e, 0\rangle$ -state is coupled coherently at rate  $2g$  to the state  $|g, 1\rangle$ , which can decay to  $|g, 0\rangle$  at rate  $2\kappa$ . The two-photon detuning  $\Delta_2 = \omega_c - \omega_L - \omega_{gi}$  is the frequency mismatch between emitted photon and cavity frequency  $\omega_c$ . The  $|e, 0\rangle$ -state can also decay spontaneously at rates  $\Gamma_g$  and  $\Gamma_h$  to the states  $|g, 0\rangle$  and  $|h, 0\rangle$ , respectively ( $\Gamma = \Gamma_g + \Gamma_h$ ). Here,  $|g, 0\rangle$  represents the desired final state, while  $|h, 0\rangle$  represents all other possible states.

The Hamiltonian of the coherently-coupled sub-system  $|i, 0\rangle, |e, 0\rangle, |g, 1\rangle$  in a frame rotating with the laser frequency reads in the rotating-wave approximation

$$\hat{H} = \hbar\Delta_1|e, 0\rangle\langle e, 0| + \hbar\Delta_2|g, 1\rangle\langle g, 1| + \hbar\frac{\Omega}{2}|e, 0\rangle\langle i, 0| + \hbar g|g, 1\rangle\langle e, 0| + \text{h.c.}$$

To take into account the molecular and cavity decay processes, we solve the corresponding master equation in Lindblad form (see [appendix](#)). The system is initialized in  $|i, 0\rangle$  at  $t = 0$ . The goal is to transfer the population from this state as fast, efficiently and coherently as possible to the state  $|g, 0\rangle$  of the ground state molecule. We therefore define the efficiency  $\eta$  of the scheme by the probability to produce a ground-state molecule  $|g, 0\rangle$  via cavity decay,

$$\eta = 2\kappa \int_{t=0}^{\infty} \rho_{g1g1}(t) dt,$$

where  $\rho_{g1g1}(t)$  is the population of the  $|g, 1\rangle$  state.

We can derive an analytical expression for  $\eta$  in the weak-driving limit, ( $\Omega \ll \Gamma, g^2/\kappa$ ), which, as we will later see, exhibits optimal achievable efficiency for time-independent control parameters. In the weak-driving limit, the coherent couplings of the laser  $\Omega$  and the cavity  $g$  slowly keep populating the spontaneously decaying states  $|e, 0\rangle$  and  $|g, 1\rangle$ . As a consequence, a quasi-steady superposition state  $|D\rangle$  forms, which slowly decays in an exponential manner. As derived in the [appendix](#),

$$|D\rangle \approx |i, 0\rangle + \frac{\Omega}{2g^2 + \Gamma(\kappa - i\Delta_2)} [(i\kappa + \Delta_2)|e, 0\rangle - g|g, 1\rangle], \quad (1)$$

when ignoring the slow exponential decay and assuming resonant drive,  $\Delta_1 = 0$ . The decay takes place through the small populations in  $|e, 0\rangle$  and  $|g, 1\rangle$  which decay via  $\Gamma$  and  $\kappa$ , respectively. This yields the transfer efficiency,

$$\eta_{\text{wd}} = \frac{2\kappa\rho_{g1g1}}{2\kappa\rho_{g1g1} + \Gamma\rho_{e0e0}} = \frac{2C}{2C + 1 + (\Delta_2/\kappa)^2}, \quad (2)$$

where  $\rho_{jj}$  are components of the density matrix  $\rho_{\text{wd}} = |D\rangle\langle D|$ . The efficiency  $\eta_{\text{wd}}$  is maximal on two-photon resonance,  $\Delta_2 = 0$ , which we consider from now on. One can also interpret  $\eta_{\text{wd}}$  as the ratio of cavity-induced decay rate  $\Gamma_\kappa = 2g^2/\kappa$  of  $|e, 0\rangle$  (via green arrows in figure 2) and the total decay rate  $\Gamma_\kappa + \Gamma$  of  $|e, 0\rangle$  (for  $\Delta_2 = 0$ ). To obtain significant cavity-stimulated PA, i.e. a large fraction in the  $|g, 0\rangle$  state, we therefore aim at  $C \gg 1$ . For example, a moderate cooperativity  $C \gtrsim 5$  will already result in an efficiency of  $\eta_{\text{wd}} > 0.9$  for producing the chosen molecular quantum state.

As already mentioned the weak-driving limit gives optimal results in terms of transfer efficiency. This can be made plausible as follows. For vanishing  $\Delta_2$  and  $\kappa$ , the states  $|i, 0\rangle$ ,  $|e, 0\rangle$ ,  $|g, 1\rangle$  form a  $\Lambda$ -system which exhibits a dark state  $|D\rangle \propto 2g|i, 0\rangle + \Omega|g, 1\rangle$ . This state is long-lived with no spontaneous decay via  $\Gamma$ , because  $|e, 0\rangle$  is not populated. If we now allow for a small but finite  $\kappa \ll g^2/\Gamma$  to populate the desired final state  $|g, 0\rangle$ , the dark state  $|D\rangle$  will become a little bit lossy due to population of  $|e, 0\rangle$  ( $\propto \kappa^2$ , see equation (1)) and subsequent decay via  $\Gamma$ . These unwanted losses, however, are much smaller than the wanted decay flux from  $|g, 1\rangle \rightarrow |g, 0\rangle$  which is proportional to  $\kappa$ . In addition, in the weak driving limit,  $\Omega \rightarrow 0$ , the dark state  $|D\rangle$  mainly consists of state  $|i, 0\rangle$ . Since this is precisely the initially prepared state the weak driving limit is optimal for efficient transfer from  $|i, 0\rangle$  to the molecular state  $|g, 0\rangle$ .

### Realistic experimental parameters

Compared to a single atom, a molecule often exhibits a reduced dipole matrix element of the electronic transition and thus a reduced coupling strength  $g$  and cooperativity  $C$ . The reduction is to first approximation determined by the Franck–Condon-factor  $f_{\text{FC}} = \Gamma_g/\Gamma$  for the specific ro-vibrational transition in a molecule,

$$g = g_{\text{max}} \sqrt{f_{\text{FC}}} \quad \text{and} \quad C = C_{\text{max}} f_{\text{FC}},$$

where the coupling strength and cooperativity for a closed two-level system ( $f_{\text{FC}} = 1$ ) are given by

$$g_{\text{max}} = d_{\text{el}} \sqrt{\frac{\omega_{ge}}{2\hbar\epsilon_0 V}} \quad \text{and} \quad C_{\text{max}} = \frac{g_{\text{max}}^2}{\kappa\Gamma}, \quad (3)$$

respectively. Here,  $V$  is the volume of the cavity mode and  $d_{\text{el}}$  the dipole moment of the electronic molecular  $|g\rangle \leftrightarrow |e\rangle$  transition with frequency  $\omega_{ge}$  (for a CQED review, we refer the reader to e.g. [7]). In a diatomic molecule,  $d_{\text{el}}$  depends in general on the internuclear distance  $R$ , and the decay rate  $\Gamma$  is about 2 times larger as compared to an atomic excited state (due to a Dicke superradiance effect [15]). In a rubidium dimer ( $\text{Rb}_2$ ), there are strong transitions between ro-vibrational states  $\nu'$  of the shallow well of the  $(1)^3\Pi_g$  potential (which asymptotically correlates to the atomic states  $5S_{1/2} + 5P_{3/2}$ ) and the states  $\nu''$  of the  $a^3\Sigma_u$  potential ( $5S_{1/2} + 5S_{1/2}$ ). In particular, the transition from  $1_g, \nu' = 8$  to  $\nu'' = 0$  at a wavelength of 744 nm has the largest  $f_{\text{FC,max}} = 0.37$ , see [16]. Apart from the transition dipole moment and Franck–Condon factor, the coupling strength  $g$  depends also on the mode volume as  $g \propto 1/\sqrt{V}$ , thus  $V$  should be minimized. For the fundamental  $\text{TEM}_{00}$  mode of a Fabry–Perot resonator,  $V = \pi w_0^2 L/4$ , where  $L$  is the cavity length and  $w_0$  the mode waist. Similar as in [17], we consider the dipole trap beams to enter from the side without being clipped by the mirror substrates, which puts a lower limit on  $L$ . The mode waist  $w_0$  is typically limited by the numerical aperture of the in-/outcoupling optics. According to equation (3), in order to maximise  $C$ ,  $\kappa$  should be minimized. However, as we will discuss in the next section a small  $\kappa$  might lead to unacceptably long transfer times. Furthermore, the transmission through the mirror coatings should dominate over unavoidable absorption and scattering losses in the coatings. In table 1, we give an example for realistic CQED parameters for the above mentioned molecular transition in  $\text{Rb}_2$ . For those parameters, an efficiency of  $\eta_{\text{wd}} > 0.9$  could be achieved for vibrational transitions with  $f_{\text{FC}} \gtrsim 0.05$ .

### System dynamics

Ideally, the transfer from the atom pair  $|i, 0\rangle$  to the molecular state  $|g, 0\rangle$  should be efficient and fast. In the weak driving limit the transfer efficiency is nearly optimal but can be very slow as the transfer time is  $\propto \kappa^{-1}$ . In fact, it can be shown that the transfer rate, which is the exponential decay rate of  $|D\rangle$ , is given by

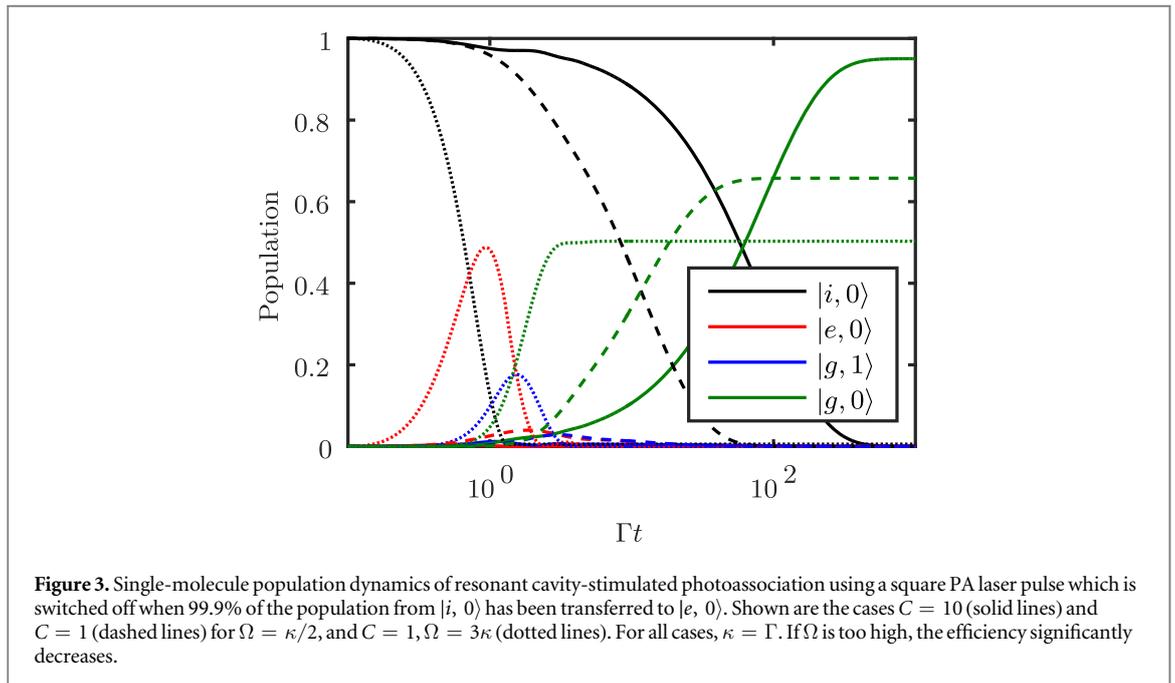
$$R_{\text{wd}} = \frac{\Omega^2}{\Gamma(2C + 1)} \stackrel{C \gg 1}{\approx} \kappa \frac{\Omega^2}{2g^2}, \quad (4)$$

if  $\Delta_1 = 0$ . Clearly, too slow a transfer can be problematic for many reasons, e.g. when the transfer time is on the order of the particle lifetime in the trap.

We therefore now consider the limit of strong driving where a short  $\pi$ -pulse (short compared to all timescales determined by rates) quasi instantaneously transfers the population from  $|i, 0\rangle$  to  $|e, 0\rangle$  at  $t = 0$ . From there, it partially decays into  $|g, 0\rangle$  via the cavity mode but it also partially decays via  $\Gamma$  into  $|h, 0\rangle$ . The efficiency  $\eta_\pi$  of the short- $\pi$ -pulse scheme is then reduced as compared to  $\eta_{\text{wd}}$  of the weak-driving limit,

**Table 1.** Example of a set of realistic CQED parameters. The parameters  $g_{\max}$ ,  $\Gamma$ ,  $C_{\max}$  are derived for the transitions between vibrational states of the  $(1)^3\Pi_g$  and  $a^3\Sigma_u$  potentials in  $\text{Rb}_2$ . Here,  $d_{\text{el}} \approx 3 \times 10^{-29}$  C m, see [6, 18].

Parameter	Symbol	Value
Cavity length	$L$	280 $\mu\text{m}$
Cavity mode waist	$w_0$	4.8 $\mu\text{m}$
Cavity finesse	$\mathcal{F}$	$5 \times 10^4$
Coupling strength for $f_{\text{FC}} = 1$	$g_{\max}$	$2\pi \times 80$ MHz
Cavity field decay rate	$\kappa$	$2\pi \times 5.4$ MHz
Excited state decay rate	$\Gamma$	$2\pi \times 12$ MHz
Cooperativity for $f_{\text{FC}} = 1$	$C_{\max}$	100
Max. Franck–Condon factor	$f_{\text{FC,max}}$	0.37 [16]



**Figure 3.** Single-molecule population dynamics of resonant cavity-stimulated photoassociation using a square PA laser pulse which is switched off when 99.9% of the population from  $|i, 0\rangle$  has been transferred to  $|e, 0\rangle$ . Shown are the cases  $C = 10$  (solid lines) and  $C = 1$  (dashed lines) for  $\Omega = \kappa/2$ , and  $C = 1, \Omega = 3\kappa$  (dotted lines). For all cases,  $\kappa = \Gamma$ . If  $\Omega$  is too high, the efficiency significantly decreases.

$$\eta_{\pi} = \frac{2\kappa}{2\kappa + \Gamma} \eta_{\text{wd}}, \quad (5)$$

where we set  $\omega_c = \omega_{ge}$ . Besides the decay, the dynamics exhibit a damped oscillation of the population between  $|e, 0\rangle$  and  $|g, 1\rangle$ . The oscillation can be understood as a beat of the two eigenstates

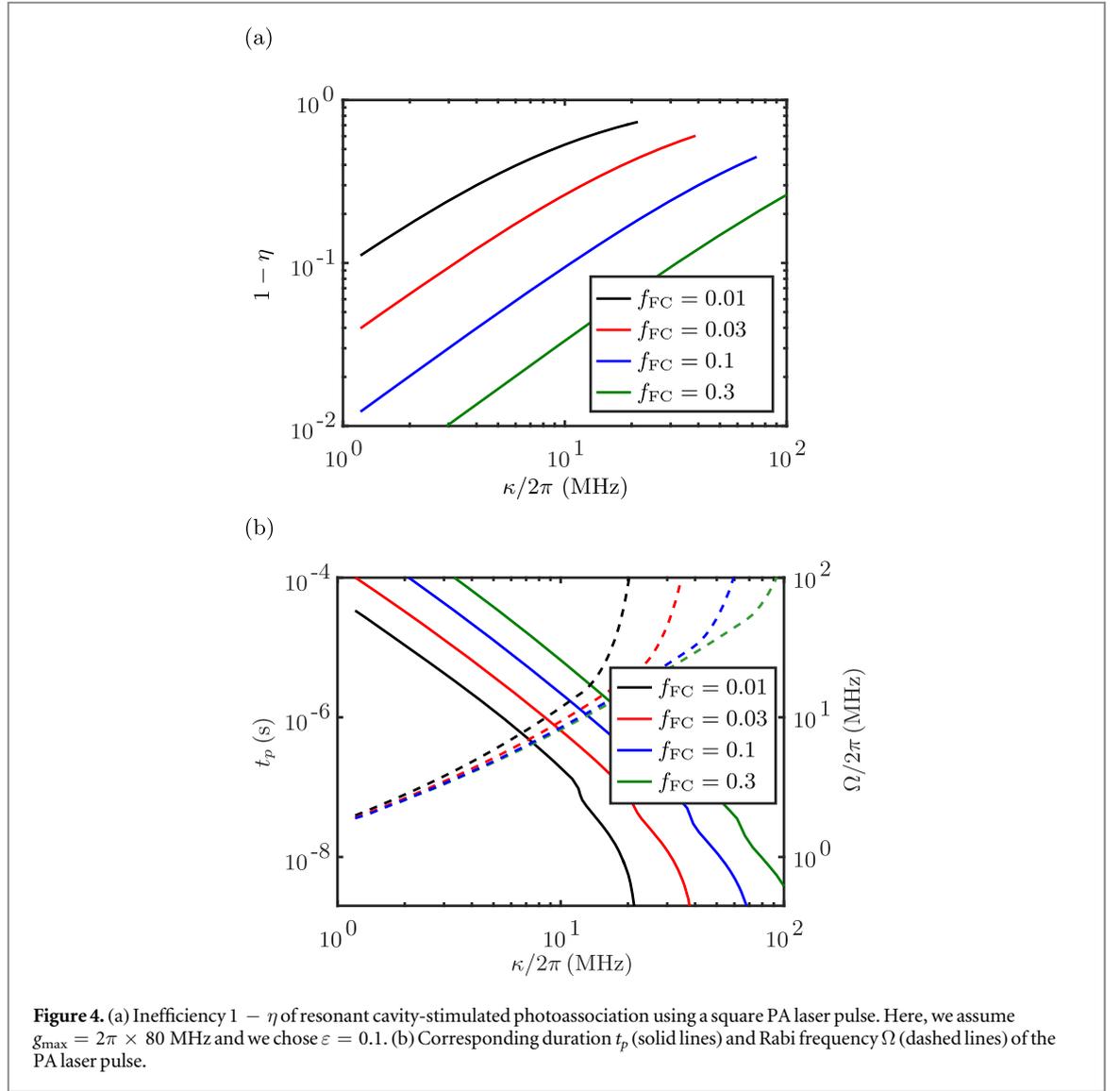
$$|B_{\pm}\rangle \approx \frac{1}{\sqrt{2}}(|e, 0\rangle \pm |g, 1\rangle)$$

of the coupled system, which are populated at  $t = 0$  by the  $\pi$ -pulse as an equal superposition state. In order for  $\eta_{\pi}$  to reach the weak-driving efficiency  $\eta_{\text{wd}}$ , we need  $\kappa \gg \Gamma$ , according to equation (5). However, for a large  $\eta_{\text{wd}}$  we need  $\kappa \ll g^2/\Gamma$ . Both conditions can be simultaneously met only when  $g \gg \Gamma^1$ . According to our parameters in table 1 and even when using a relatively large Franck–Condon factor of  $f_{\text{FC}} > 0.3$ , this condition is not easily reached. Assuming a more typical  $f_{\text{FC}} = 0.1$ , we obtain  $\eta_{\pi} \approx 0.77$  compared to  $\eta_{\text{wd}} \approx 0.95$ . Therefore, in general, the short  $\pi$ -pulse does not seem to be ideal for the transfer.

Therefore, the question arises, how quickly the optical pumping can be done without substantial loss of efficiency compared to the weak-driving limit? To answer this question, we investigate how the transfer efficiency to the ground state  $|g, 0\rangle$  can be optimized when employing a resonant square pulse of duration  $t_p$  and Rabi frequency  $\Omega^2$ .

<sup>1</sup> It turns out, that for a given  $g$  the optimal  $\eta_{\pi}$  is reached for  $\kappa = g \gg \Gamma$ .

<sup>2</sup> We note that there are more efficient schemes than using resonant square laser pulses to transfer electronic excitation into the cavity. Some of them are based on vacuum stimulated rapid adiabatic passages [19, 20] and use specially designed laser pulses  $\Omega(t)$  to transfer the system adiabatically from  $|i, 0\rangle$  to  $|g, 0\rangle$  without populating the excited state  $|e, 0\rangle$ , i.e. by keeping it in a dark state. Those schemes are, however, beyond the scope of the present work.



For this, we solve the time-dependent master equation of the five-level system numerically. In figure 3, some examples of the time-dependent populations are plotted. For  $\Omega = \kappa/2$ , we almost reach the weak-driving efficiencies  $\eta_{\text{wd}} = \frac{20}{21}$  ( $\eta_{\text{wd}} = \frac{2}{3}$ ) for  $C = 10$  ( $C = 1$ ), respectively. Using  $\Gamma = 2\pi \times 12$  MHz, one reaches 95% of the respective asymptotic value within  $t \approx 3 \mu\text{s}$  ( $t \approx 0.5 \mu\text{s}$ ). For a higher Rabi frequency (here,  $\Omega = 3\kappa$ ), the transfer works faster but the efficiency is already significantly reduced.

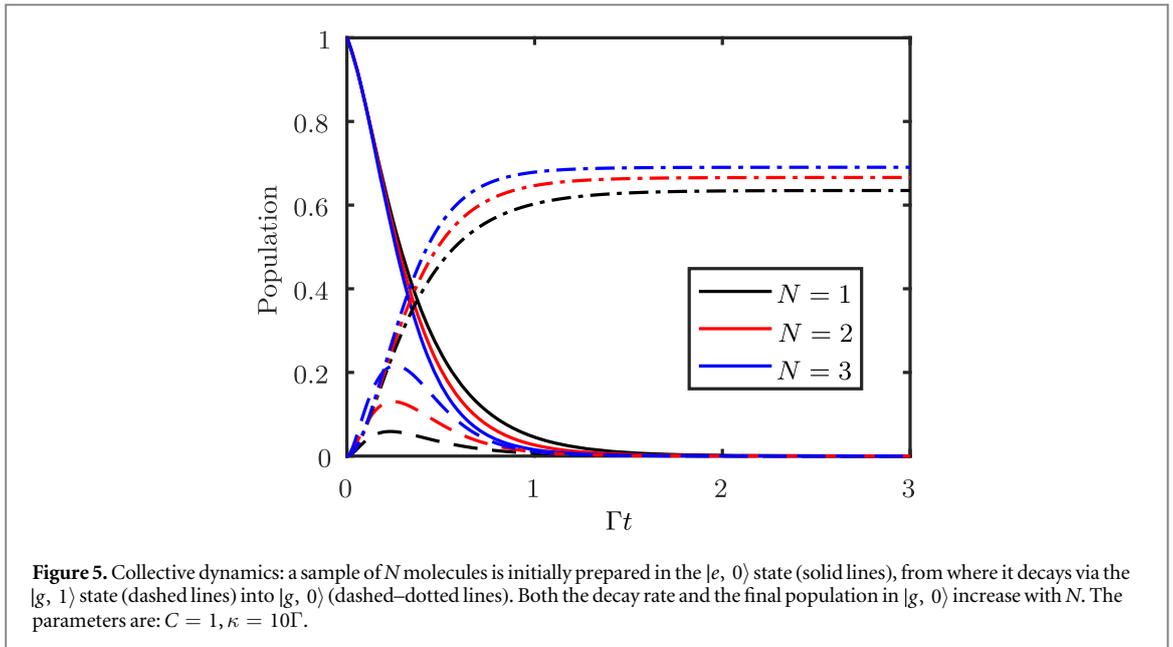
In an optimization, we determine the highest Rabi frequency  $\Omega$  and shortest pulse duration  $t_p$  for which the inefficiency  $1 - \eta$  of this pulsed scheme does not significantly increase compared to the weak-driving limit. In particular, we allow for an inefficiency

$$1 - \eta = (1 + \varepsilon)(1 - \eta_{\text{wd}}),$$

where  $\varepsilon$  is the tolerance, which can be arbitrarily chosen. According to equation (2)  $\eta_{\text{wd}}$  depends only on the cooperativity  $C = g^2/(\kappa\Gamma)$ . However, because  $\Gamma$  is fixed and  $g_{\max} = 2\pi \times 80$  MHz is also an estimated upper limit (see table 1),  $\eta_{\text{wd}}$  essentially depends on  $\kappa$  and the Franck-Condon factors, since  $g = g_{\max} \sqrt{f_{FC}}$ . In figure 4(a), we plot  $1 - \eta$  for four different values of  $f_{FC}$  as a function of  $\kappa$ , where we set  $\varepsilon = 0.1$ . Figure 4(a) can be used to determine  $\kappa$  for a desired  $\eta$  and a given  $f_{FC}$ . Using this  $\kappa$  we can then read off the minimum pulse duration  $t_p$  and the maximal Rabi frequency  $\Omega$  from figure 4(b). It is noteworthy that in the range  $\kappa/2\pi \lesssim 10$  MHz,  $\Omega \approx \kappa$ , almost independent of  $f_{FC}$  and that  $t_p \propto f_{FC}/\kappa^2$ . (For larger values of  $\kappa$ ,  $\Omega$  diverges and  $t_p$  vanishes, see also appendix 'Condition for short  $\pi$ -pulses'.)

For clarity, we finally discuss an example: if an efficiency of  $\eta = 0.97$  is desired on a transition with  $f_{FC} = 0.1$ , we require  $\kappa = 2\pi \times 3$  MHz, see figure 4(a). From figure 4(b) it follows that the pulse length of the PA laser should be at least  $t_p = 4 \times 10^{-5}$  s and its Rabi frequency should be at most  $\Omega = 2\pi \times 3$  MHz.

Using the measured data in [16] we can estimate what Rabi frequencies  $\Omega$  for PA can be realistically reached in an experiment. For this, we take into account that a tightly trapped atom pair in a lattice site has a density of



about  $\sim 10^{15} \text{ cm}^{-3}$ . To reach the Rabi frequency of  $\Omega = 2\pi \times 3 \text{ MHz}$  of our example, a laser power of about 700 mW would be needed when the atom pair is located in a laser focus with  $10 \mu\text{m}$  waist.

If only a smaller Rabi frequency is experimentally available, e.g. due to a smaller laser power, still the same targeted efficiency of  $\eta = 0.97$  can be achieved by simply increasing the laser pulse length which should roughly scale as  $t_p \propto 1/\Omega^2$ , see equation (4).

### Collective effects

So far, we have only considered the coupling of a single molecule to the cavity mode. However, in a typical experiment, there can be up to  $N \approx 10^3$  atom pairs or molecules that couple simultaneously to the cavity mode (see appendix). Coherence can build up among the molecules which modifies their spontaneous emission, thus they should not be treated as independent, giving rise to effects like Dicke-superradiance [15]. For example, if several of them are prepared in  $|e, 0\rangle$  at  $t = 0$ , both the decay rate from this state and the probability to end up in the final state  $|g, 0\rangle$  are collectively increased, see figure 5. Here, the time-dependent master equation has been solved for  $N = 1 \dots 3$  individual four-level molecules coupled to the same cavity mode. Our calculations show that for only up to three atom pairs enhancement effects are already present, but not very strong yet. We expect the enhancement to strongly increase with larger particle numbers. However, for the corresponding calculations other numerical methods than the one used here would be required.

The collective enhancement is most effective in the ‘fast cavity regime’ where  $\kappa > g > \Gamma$ . Although the transfer for single atom pairs in this regime is plagued by relatively low efficiencies  $\eta$ , the collective enhancement can strongly compensate for this. Furthermore, the collective enhancement is particularly suitable to enhance transitions with rather small Franck–Condon factors.

### Conclusions and outlook

In summary, we have shown that ultracold molecule formation in a well-defined quantum state can be strongly enhanced by an optical cavity. We have estimated that preparation of a molecule in certain quantum states can be efficient ( $>90\%$ ) for transitions with moderate Franck–Condon factors ( $f_{\text{FC}} \gtrsim 0.05$ ) in medium high finesse cavities ( $\mathcal{F} \approx 5 \times 10^4$ ). In contrast to existing coherent two-photon schemes for PA of ultracold molecules, our scheme can be regarded as a method to pump (cool) molecules into a desired (ground) state since the necessary dissipation is already build in via the cavity losses. Moreover, the photons dissipated into a single spatial mode can be detected with high efficiency.

The scheme could potentially be extended to cascaded reactions, e.g.  $A \rightarrow B^* \rightarrow C^* \rightarrow D$ , where  $B^*$  is, e.g. produced in a collision. Here, one could use the cavity to observe and control the spontaneous transition between  $B^* \rightarrow C^*$ .

Finally, the coupling of several atom pairs or molecules to the cavity will give rise to interesting collective effects for reactions, which have not been discussed or demonstrated yet. The collective enhancement of the rate and efficiency of molecule formation would be the basis for ‘superradiant chemistry’.

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## Appendix

### Master equation

In order to take into account the incoherent decay processes of the excited molecular state and the cavity photon, we use a master equation in Lindblad form,

$$\frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}] + 2\kappa\mathcal{D}[\hat{a}, \hat{\rho}] + \Gamma_g\mathcal{D}[|g\rangle\langle e|, \hat{\rho}] + \Gamma_h\mathcal{D}[|h\rangle\langle e|, \hat{\rho}],$$

$$\text{where } \mathcal{D}[\hat{b}, \hat{\rho}] = \hat{b}\hat{\rho}\hat{b}^\dagger - \frac{1}{2}\hat{b}^\dagger\hat{b}\hat{\rho} - \frac{1}{2}\hat{\rho}\hat{b}^\dagger\hat{b}.$$

Here,  $\hat{\rho}$  denotes the density operator and  $\hat{a}$  is the annihilation operator of the cavity field.

### Efficiency in the weak-driving limit

In the limit of weak driving ( $\Omega \ll \Gamma, g^2/\kappa$ ), we can derive an analytical expression for the efficiency  $\eta_{\text{wd}}$ , equation (2). It is given by the ratio of the decay rates from  $|g, 1\rangle$  and  $|e, 0\rangle$  in ‘quasi steady-state’,

$$\eta_{\text{wd}} = \frac{2\kappa\rho_{g1g1}^{\text{ss}}}{2\kappa\rho_{g1g1}^{\text{ss}} + \Gamma\rho_{e0e0}^{\text{ss}}} = \left[ 1 + \frac{\Gamma}{2\kappa} \frac{\rho_{e0e0}^{\text{ss}}}{\rho_{g1g1}^{\text{ss}}} \right]^{-1}.$$

Here,  $\rho_{e0e0}^{\text{ss}}$  and  $\rho_{g1g1}^{\text{ss}}$  are components of the steady-state density matrix  $\rho^{\text{ss}}$  which we calculate as follows. We formally close the system in figure 2 by introducing an artificial ‘repump’ rate  $\zeta$  from the states  $|g, 0\rangle$  and  $|h, 0\rangle$  back to state  $|i, 0\rangle$ , which can be, in principle, arbitrarily slow ( $\zeta \rightarrow 0$ ). It turns out, however, that the population ratio  $\rho_{e0e0}^{\text{ss}}/\rho_{g1g1}^{\text{ss}}$  is independent of  $\zeta$ , turning the system effectively into a three-level system, since the populations of the levels  $|g, 0\rangle$  and  $|h, 0\rangle$  are not relevant. The solution for the density matrix  $\rho^{\text{ss}} = |D^{\text{ss}}\rangle\langle D^{\text{ss}}|$  in the weak-driving regime is, to first order in  $\Omega$ ,

$$|D^{\text{ss}}\rangle \approx |i, 0\rangle + \Omega \frac{(i\kappa + \Delta_2)|e, 0\rangle - g|g, 1\rangle}{2g^2 + (\Gamma - 2i\Delta_1)(\kappa - i\Delta_2)},$$

If the system is open, i.e.  $\zeta = 0$ , this state slowly decays exponentially, which can be described by

$$|D\rangle = \exp\left\{-\frac{R_{\text{wd}}}{2}t\right\}|D_{\text{ss}}\rangle,$$

where  $R_{\text{wd}}$  is given, for  $\Delta_1 = \Delta_2 = 0$ , by equation (4).

### Condition for short $\pi$ -pulses

For a chosen  $\varepsilon$ , short  $\pi$ -pulses (as discussed before) are efficient enough if

$$(1 - \eta_\pi) \leq (1 + \varepsilon)(1 - \eta_{\text{wd}}).$$

Using equations (2) and (5), this is equivalent to the following condition

$$\frac{\kappa}{\Gamma} \geq \sqrt{\frac{g^2}{\varepsilon\Gamma^2} + \frac{1}{16}} - \frac{1}{4},$$

which can be approximated by  $\kappa \gtrsim g/\sqrt{\varepsilon}$  for  $g \gg \Gamma\sqrt{\varepsilon}$ .

### Number of atom pairs

The estimated number of pairs  $N \approx 10^3$  in the optical cavity for typical experimental conditions corresponds to a thermal cloud of approx.  $10^6$  atoms with diameter  $2\sigma \approx 40 \mu\text{m}$  in a three-dimensional cubic optical lattice with laser wavelength  $\lambda_{\text{latt}} \approx 1 \mu\text{m}$ , which overlaps with the fundamental cavity mode with waist  $w_0 \approx 5 \mu\text{m}$ .

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