

JYX



This is a self-archived version of an original article. This version may differ from the original in pagination and typographic details.

Author(s): Groenhof, Gerrit; Climent, Clàudia; Feist, Johannes; Morozov, Dmitry; Toppari, J. Jussi

Title: Tracking Polariton Relaxation with Multiscale Molecular Dynamics Simulations

Year: 2019

Version: Accepted version (Final draft)

Copyright: © 2019 American Chemical Society

Rights: In Copyright

Rights url: <http://rightsstatements.org/page/InC/1.0/?language=en>

Please cite the original version:

Groenhof, G., Climent, C., Feist, J., Morozov, D., & Toppari, J. J. (2019). Tracking Polariton Relaxation with Multiscale Molecular Dynamics Simulations. *Journal of Physical Chemistry Letters*, 10(18), 5476-5483. <https://doi.org/10.1021/acs.jpcllett.9b02192>

Tracking Polariton Relaxation with Multi-Scale Molecular Dynamics Simulations

Gerrit Groenhof, Clàudia Climent, Johannes Feist, Dmitry Morozov, and J. Jussi Toppari

J. Phys. Chem. Lett., **Just Accepted Manuscript** • DOI: 10.1021/acs.jpcllett.9b02192 • Publication Date (Web): 27 Aug 2019

Downloaded from pubs.acs.org on August 28, 2019

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

Tracking Polariton Relaxation with Multi-Scale Molecular Dynamics Simulations

Gerrit Groenhof,^{* †} Clàudia Climent,[‡] Johannes Feist,[‡] Dmitry Morozov,
[†] and J. Jussi Toppari[¶]

[†] *Nanoscience Center and Department of Chemistry, University of Jyväskylä, P.O. Box 35,
40014 Jyväskylä, Finland.*

[‡] *Departamento de Física Teórica de la Materia Condensada and Condensed Matter Physics
Center (IFIMAC), Universidad Autónoma de Madrid, Madrid, Spain.*

[¶] *Nanoscience Center and Department of Physics, University of Jyväskylä, P.O. Box 35, 40014
Jyväskylä, Finland.*

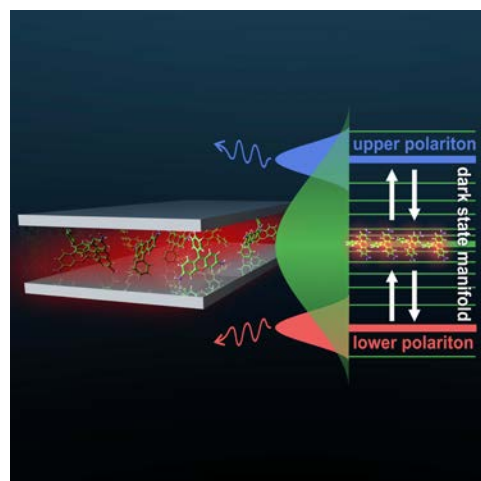
E-mail: gerrit.x.groenhof@jyu.fi

Abstract

When photoactive molecules interact strongly with confined light modes in optical cavities, new hybrid light-matter states form. They are known as polaritons and correspond to coherent superpositions of excitations of the molecules and of the cavity photon. The polariton energies and thus potential energy surfaces are changed with respect to the bare molecules, such that polariton formation is considered a promising paradigm for controlling photo-chemical reactions. To effectively manipulate photo-chemistry with confined light, the molecules need to remain in the polaritonic state long enough for the reaction on the modified potential energy surface to take place. To understand what determines this lifetime, we have performed atomistic molecular dynamics simulations of room-temperature ensembles of rhodamine chromophores strongly coupled to a single confined light mode with a 15 fs lifetime. We investigated three

1
2
3 popular experimental scenarios and followed the relaxation after optically pumping (i) the
4 lower polariton, (ii) the upper polariton or (iii) uncoupled molecular states. The results of the
5 simulations suggest that the lifetime of the optically accessible lower and upper polaritons
6 are limited by (i) ultra-fast photo-emission due to the low cavity lifetime and (ii) reversible
7 population transfer into the 'dark' state manifold. Dark states are superpositions of molecular
8 excitations but with much smaller contributions from the cavity photon, decreasing their
9 emission rates and hence increasing their lifetimes. We find that population transfer between
10 polaritonic modes and dark states is determined by the overlap between the polaritonic and
11 molecular absorption spectra. Importantly, excitation can also be transferred "upwards" from
12 the lower polariton into the dark-state reservoir due to the broad absorption spectra of the
13 chromophores, contrary to the common conception of these processes as a "one-way" relaxation
14 from the dark states down to the lower polariton. Our results thus suggest that polaritonic
15 chemistry relying on modified dynamics taking place within the lower polariton manifold
16 requires cavities with sufficiently long lifetimes and, at the same time, strong light-matter
17 coupling strengths to prevent the back-transfer of excitation into the dark states.
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32

33 TOC GRAPHIC



1
2
3 In general, molecules cannot be treated in isolation, but have to be understood as embedded
4 in and coupled to the electromagnetic field surrounding them. This applies even when the field is
5 in its vacuum state, and leads to properties such as the Lamb shift or spontaneous emission from
6 excited states. In free space these are typically small corrections and can be neglected in many
7 cases (*e.g.*, emission lifetimes are normally on the order of nanoseconds, much slower than the
8 electronic and nuclear dynamics determining most photo-chemical reactions). The situation is
9 different when molecules are placed inside optical or plasmonic cavities,^{1,2} because these photonic
10 structures can modify the vacuum field to such an extent that photonic degrees of freedom also
11 become important.^{3,4} These structures not only confine the light to smaller volumes, increasing the
12 coupling strength, they also restrict the number of photonic modes available to interact with the
13 molecules. The confinement furthermore enhances the light-matter interaction, which can become
14 strong enough for the photonic and molecular degrees of freedom to hybridize into new light-matter
15 states, known as polaritons.^{2,5}
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

We summarize the main consequences of strong light-matter coupling from a molecular standpoint here, with more detailed descriptions available in the literature.^{6,7} Within the single-excitation subspace accessed under weak driving, strong coupling between N molecules and a single confined light mode leads to the formation of $N + 1$ coherent superpositions of excitations in each of the molecules and of the confined light mode:^{8,9}

$$|\psi^k\rangle = \sum_i^N \beta_i^k |g_1 g_2 \dots e_i \dots g_N\rangle |0\rangle + \alpha^k |g_1 g_2 \dots g_i \dots g_N\rangle |1\rangle \quad (1)$$

Here $|g_i\rangle$ and $|e_i\rangle$ are the electronic ground and excited states of molecule i , while $|1\rangle$ or $|0\rangle$ indicates if the confined light mode is excited or not. The β_i^k and α^k are expansion coefficients ($\sum_i |\beta_i^k|^2 + |\alpha^k|^2 = 1$) and the index k labels the $N + 1$ single-excitation eigenstates of the strongly coupled molecule-cavity system. If the excitation energy of the molecules ($h\nu_i$) is similar to the frequency of the confined light mode ($n\omega_{\text{cav}}$), the energy gap, or Rabi splitting ($n\Omega^{\text{Rabi}}$), between the lowest ($k = 1$, *i.e.*, the lower polariton, LP) and the highest ($k = N + 1$, *i.e.*, the upper polariton, UP) hybrid light-matter states is proportional to the square root of the number of molecules (N) that are strongly interacting with the confined light mode of the cavity:

$$n\Omega^{\text{Rabi}} = 2|\mu_{\text{mol}}^{\text{TDM}}| \sqrt{N n \omega_{\text{cav}} / 2 \epsilon_0 V_{\text{cav}}} \quad (2)$$

where $\mu_{\text{mol}}^{\text{TDM}}$ is the transition dipole moment of the molecular excitation, ϵ_0 is the vacuum permittivity, and V_{cav} is the effective mode volume of the confined photon with energy $n\omega_{\text{cav}}$. Note that we have assumed perfect alignment between the molecular dipole moments and the cavity electric field ($E_{\text{cav}} = \sqrt{n\omega_{\text{cav}} / 2 \epsilon_0 V_{\text{cav}}}$) here for simplicity. The lower and upper polariton have the highest contribution of the cavity mode. Since the cavity typically dominates the response under external driving, the absorption spectrum of the cavity-molecule system then contains two peaks corresponding to the lower and upper polaritons, located below and above the absorption maxima of the molecules and the cavity (Figure 1). Due to their smaller cavity contribution, the other $N - 1$ levels are typically far less visible and are thus referred to as ‘dark’ states.

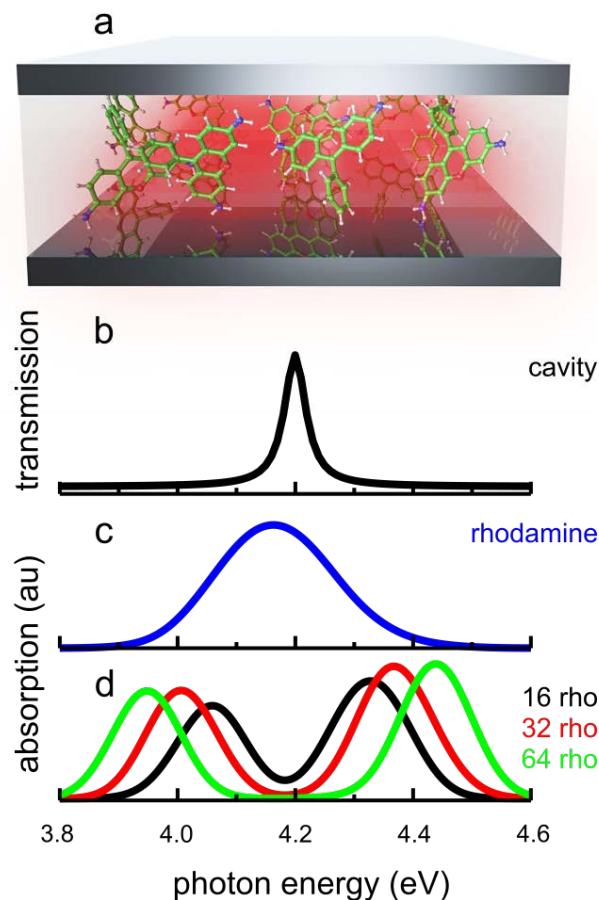


Figure 1: (a) Schematic depiction of the cavity-molecule systems studied in this work. Note that although a typical Fabry-Pérot cavity is illustrated here, the cavities in our simulations more closely resemble a plasmonic nano-cavity, in particular when there are only a few molecules. (b) Cavity transmission spectrum. (c) Absorption spectrum of the rhodamine model in water outside of the cavity. (d) Absorption spectrum of the cavity with 16 (black), 32 (red) and 64 (green) solvated rhodamine molecules in the cavity volume.

The hybridization of light and matter into polaritons not only delocalizes the excitation over many molecules (Equation 1), it also changes the molecular potential energy surface, and thus provides a new way to control photochemistry^{10–19} and photo-physics.^{20–23} To manipulate reactivity with confined light, however, the polariton lifetime should exceed the time it takes for the molecules to react on the modified potential energy surface. As polariton lifetimes are mostly determined by the cavity quality factor (Q-factor), one may thus expect that very high-finesse cavities would be

1
2
3 required, in particular for slower photo-chemical reactions. However, results of recent time-resolved
4 pump-probe experiments on various strongly coupled systems suggest that the lower polariton
5 inherits the excited state lifetime of the molecules, rather than that of the cavity.^{24–26}
6
7

8
9 While this finding could have major implications for the feasibility of polaritonic catalysis,^{7,27–29}
10 an alternative explanation for the slow emission from the lower polaritonic state in these experiments
11 is that the strongly coupled system undergoes transitions into the hybrid ‘dark’ states, which act
12 as a reservoir that slowly replenishes the polariton modes.^{28,30–39} Because these dark states lack
13 a strong contribution from the cavity photon (α^k in Equation 1), their decay is dominated by the
14 excited-state lifetimes of the molecules, which are typically much longer. Results from time-
15 dependent quantum dynamics simulations on simplified molecule-cavity systems, in which the
16 nuclear degrees of freedom were modeled as one or many harmonic oscillators and treated to
17 various levels of approximation, support this notion.^{39–44} Although the vibrational structure of the
18 molecules was included, the harmonic approximation, which was necessary to solve the Schrödinger
19 equation, restricts these simulations to non-reactive systems. To overcome this limitation and model
20 the effects of strong light-matter coupling on the dynamics of even larger ensembles of realistic
21 molecules, we recently proposed a multi-scale molecular dynamics approach based on hybrid
22 Quantum Mechanics / Molecular Mechanics (QM/MM) simulations.⁶ Here, we apply that approach
23 to model the relaxation dynamics of up to a thousand rhodamine molecules strongly coupled to a
24 confined light mode with a lifetime of 15 fs.
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40

41 Because the number of polaritonic states equals the number of molecules in the cavity plus
42 one (Equation 1) and the energy gaps between these states are very small, the dynamics have to be
43 simulated in a dense manifold of coupled states.^{7,45} While Tully’s fewest switches surface hopping
44 (FSSH) algorithm⁴⁶ has been highly successful for modeling non-adiabatic dynamics in systems with
45 few electronic states,⁴⁷ the number of semi-classical simulations required to achieve convergence
46 when there are hundreds to thousands of near-degenerate states precludes FSSH for modeling the
47 dynamics of the large ensembles of strongly coupled molecules in this work. We therefore rely on
48 Ehrenfest, or mean-field, dynamics instead,⁴⁸ and integrate the time-dependent polaritonic wave
49
50
51
52
53
54
55
56
57
58
59
60

function, expanded in the basis of the time-independent polaritonic states (Equation 1):

$$|\Psi(t)\rangle = \sum_k^{N+1} c_k(t) |\psi^k\rangle \quad (3)$$

along the N classical molecular dynamics (MD) trajectories evolving on the mean-field potential energy surface. The force on atom a is then

$$\mathbf{F}_a = - \langle \Psi(t) | \nabla_a \hat{H} | \Psi(t) \rangle = - \sum_k^{N+1} c_k^*(t) c_l(t) \langle \psi^k | \nabla_a \hat{H} | \psi^l \rangle \quad (4)$$

and we use the unitary propagator in a local diabatic basis to integrate the coefficients, $c_k(t)$.⁴⁹ The complete description of our Ehrenfest dynamics simulations is available as supporting information (SI).

We have simulated ensembles of up to 1,000 rhodamine molecules including the solvent environment and a confined light mode with a resonance frequency of $\omega_{\text{cav}} = 4.2$ eV, tuned near the absorption maximum of the rhodamine molecules (Figure 1), which is 4.18 eV at the CIS/3-21G//Amber level of QM/MM theory (SI). The cavity photon lifetime is taken as 15 fs, corresponding to a decay rate of $\gamma_{\text{cav}} = 66.7$ ps⁻¹ (line-width $\hbar\gamma_{\text{cav}} = 0.04$ eV), in line with previous experiments.²⁶ This lifetime depends on the accuracy of the nano-fabrication process, the thickness of the mirrors, and the cavity material.¹ In the simulations, the dissipation of the cavity photon is modelled *ad hoc* as a first-order decay process of polaritonic states with a contribution from the confined light mode:⁶

$$\rho_k(t + \Delta t) = \rho_k(t) \exp[-\gamma_{\text{cav}} |\alpha^k(t)|^2 \Delta t] \quad (5)$$

where $\rho_k(t) = |c_k(t)|^2$ is the population of polaritonic state ψ_k at time t , α^k the contribution of the photonic mode to that state (Equation 1) and Δt the time step of the classical MD simulation (0.1 fs; see SI for further details). The cavity lifetime is illustrated by the finite line width of the cavity transmission peak in Figure 1b.

Two types of ensembles were investigated. In the first, all molecules started from the same initial coordinates, but with different nuclear velocities selected randomly from a Maxwell-Boltzmann distribution at a temperature of 300 K. In the second set of simulations, both initial coordinates and velocities were selected randomly from QM/MM trajectories of a single Rhodamine molecule in water. Assuming instantaneous and resonant photo-excitation, the simulations were started in either the upper or lower polaritonic states. While for the ensembles with the same initial coordinates, the lower and upper polaritons can be identified without ambiguity as the eigenstates with the lowest and highest eigenvalue of the cavity-molecule Hamiltonian, the identification is more complicated for the heterogeneous room temperature ensembles, where the excitation energies form a distribution due to structural heterogeneity (Figure 1c). Because in this situation there are multiple states with a significant contribution of the cavity photon, the initial state of the simulation was a superposition of all polaritonic states below (LP) or above (UP) the transmission maximum of the cavity, weighted by their photonic contributions (*i.e.*, $|\alpha^k|^2$ in Equation 1).

Irrespective of the cavity mode volume (V_{cav}) or the number of molecules (N), the results of our molecular dynamics simulations, shown in Figures 2, 3 and S6-S8 (SI), suggest a relaxation process that involves transient population of 'dark' states, if these are available. After pumping the upper or lower polariton in ensembles of molecules with the same starting coordinates (*i.e.*, same excitation energies), but different velocities, the relaxation initially occurs through direct photo-emission, as evidenced by the rapid build-up of ground state population (dashed green line in Figure 2) and the concomitant decline of the initial polaritonic states. Because the upper and lower polaritons are approximately equal mixtures of the molecular excitations and the confined light mode at the start of the simulations, the initial rate of this radiative decay process is approximately the product of the cavity decay rate (γ_{cav} , Equation 5) and the photonic component of the polariton ($|\alpha^{\text{LP/UP}}|^2 \approx 0.5$, Equation 1). As shown in the insets of Figure 2a-b, the rise of the ground state population in the first few femtoseconds indeed follows a simple exponential function with a decay constant of $0.5\gamma_{\text{cav}}$. However, while the system relaxes, non-adiabatic coupling with the 'dark' states triggers population transfer from both the upper and lower polaritons into these states. As the dark states have a much

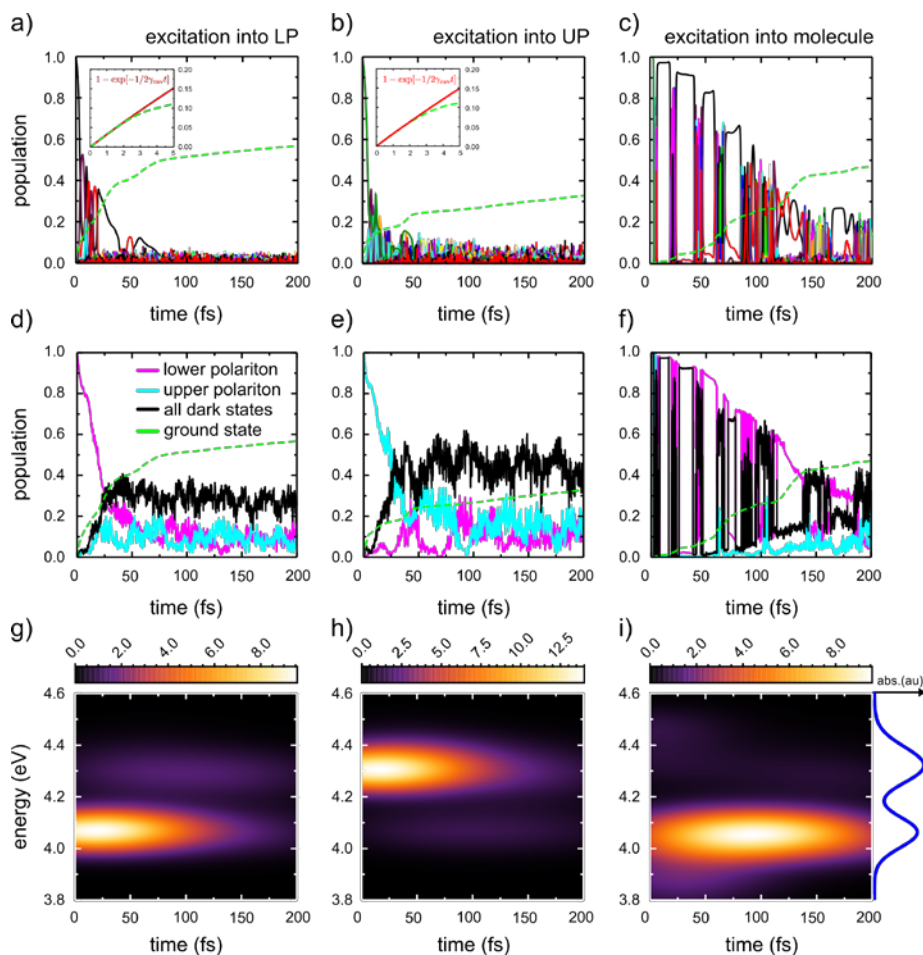


Figure 2: Top panels: populations of the polaritonic states ($|c_k(t)|^2$, Equation 3, all colors) in simulations of 64 molecules in a nano-cavity with single-photon field strength $E_{\text{cav}} = n\omega_{\text{cav}}/2E_0V_{\text{cav}} =$

0.00014 atomic units (0.7 MVcm^{-1}), corresponding to a mode volume of $7,275 \text{ nm}^3$ (leading to a Rabi splitting on resonance of 260 meV , Equation 2), after excitation into the lower polariton (LP, a, d); into the upper polariton (UP, b, e); and into a molecular excited state that is 156 meV above the UP (c, f). The population of the ground state with no photon present (*i.e.*, $|g_1g_2\dots g_i\dots g_M\rangle|0\rangle$) is plotted as green dashed lines. The insets in a and b show the ground state population for the first 5 fs and an exponential fit (red line). Middle panels: populations of the bright lower (magenta) and upper (cyan) polaritons and the sum of the dark states (black). States are considered bright (dark) if the contribution of the cavity photon ($|\alpha^k|^2$) is above (below) 0.05. Bottom panels: time-resolved emission spectra (sunset color scheme) after photo excitation into LP (g), into UP (h) and into a state above the UP (i). The photo-absorption spectrum of this cavity-molecule system is shown at the right of panel i.

smaller contribution of the cavity photon, direct emission is reduced significantly and the rate at which the ground state population builds up decreases. Nevertheless, because population transfer is reversible and also occurs from the dark states back into the bright upper and lower polaritons,

radiative decay continues, albeit at a much lower rate (lower panels in Figure 2).

The observation that the population transfers from upper polariton into 'dark' states and eventually into the lower polariton, is in good qualitative agreement with experiments that probed prolonged photo-luminescence from strongly coupled cavity-molecule systems after pumping the upper polariton,^{24,26,33,35,50} while more recently population transfer from the lower polariton into the 'dark' state manifold has also been suggested on the basis of anti-Stokes emission measured after pumping the lower polariton.⁵¹ Thus, the results of our simulations do not support the conjecture that the polaritons inherit the excited-state lifetime of the molecules,^{24–26} but rather suggest that non-radiative scattering into dark states, which are sometimes referred to as the 'exciton reservoir',^{31,32,36} controls the polariton relaxation, in agreement also with previous calculations on simpler molecular models.^{39,42,45}

To mimic experiments in which a molecular electronic state lying *above* the upper polariton is pumped,^{24,26,52} we added a structure from the equilibration trajectory that has a geometry in which the $S_0 \rightarrow S_1$ excitation energy (4.48 eV) is higher than the upper polariton (4.32 eV), to the cavity. Because of the larger excitation energy, the highest electronic state in these cavities is localized on this molecule. After excitation into that state, the initial decay process is slower than when the UP or LP are pumped directly (Figure 2c). We attribute this difference to the much lower photonic contribution to this state in the cavity. However, due to non-adiabatic transitions, both upper and lower polaritonic states as well as the other dark states become transiently populated. Because only states with a significant photonic contribution can emit efficiently, as evidenced by the photo-luminescence spectra in Figure 2f, the transient population of upper and lower polariton increases the decay rate. The results of these simulations confirm that excitation of uncoupled states leads to transient population of the optically accessible polariton states, in particular the lower polariton (Figure 2f). However, as with excitation directly into the UP or LP,^{33,51} the total lifetime of the polaritonic photoluminescence is controlled by the competition between, on the one hand, direct photo-emission determined by the cavity decay rate, and, on the other hand, transient population of the dark states, and thus exceeds the cavity lifetime (bottom panels in Figure 2).

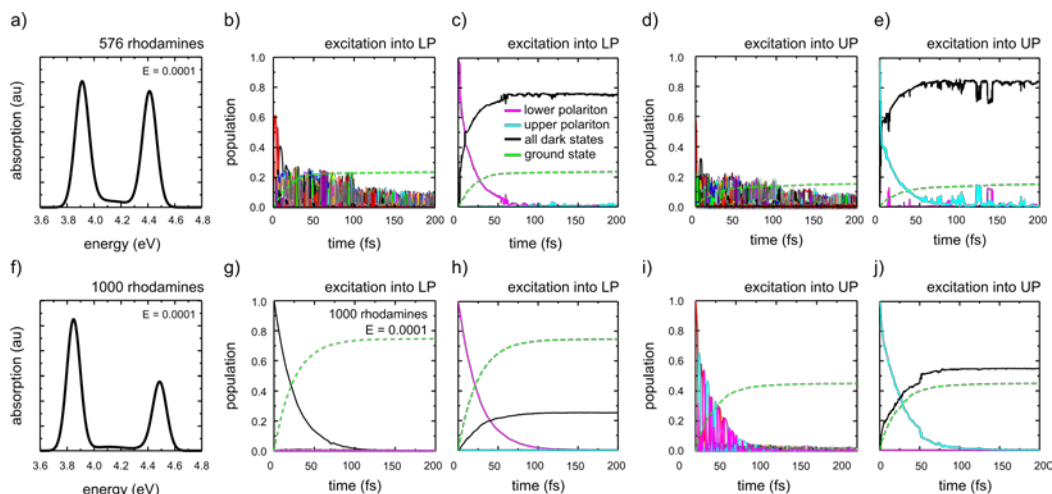


Figure 3: Absorption spectra (first column) and state populations after excitation into the lower polariton (second and third columns) and upper polariton (fourth and fifth columns). The dashed green line is the ground state population. Two systems are shown: 576 (top panels) and 1,000 molecules (bottom panels) in a nano-cavity with single-photon field strength of $E_{\text{cav}} = 0.0001$ atomic units (0.5 MVcm^{-1}), corresponding to a mode volume of $14,259 \text{ nm}^3$. In panels b, d, g and i the populations of all adiabatic polaritonic states are plotted (*i.e.*, $|c_k(t)|^2$, Equation 3, all colors). In panels c, e, h and j the populations of bright lower and upper polaritons are shown in magenta and cyan, respectively, while the total dark state population is plotted as a single black line. States are considered bright (dark) if the contribution of the cavity photon ($|\alpha^k|^2$) is above (below) 0.05.

To investigate the effect of structural disorder among the chromophores we randomly selected initial coordinates and velocities from equilibrium QM/MM trajectories of uncoupled rhodamine. In Figure 3, we plot the time evolution of the populations with 576 and 1,000 rhodamine molecules in the cavity. In line with the results obtained when the molecules have the same starting coordinates, there is competition between direct photo-emission (dashed green line) and transitions into the dark states, when these are available (Figure 3). In the case of 576 and 1,000 molecules, the single-molecule coupling is held constant, so that the Rabi splitting increases by a factor $\sqrt{1000/576} \approx 1.3$, with the effect that for the 1,000 molecule ensemble, the polariton lies outside the absorption band of the uncoupled molecules. The simulation shows that decay through photo-emission is most efficient

in this case. Additionally, this direct radiative decay channel is more efficient for the LP than the UP, as illustrated by the faster build-up of ground state population when the LP state is pumped. The reason for this difference is that from the UP, ‘dark’ states are more accessible, and hence these non-radiative ‘dark’ states become populated to a much larger extent (compare figures 3h and j).

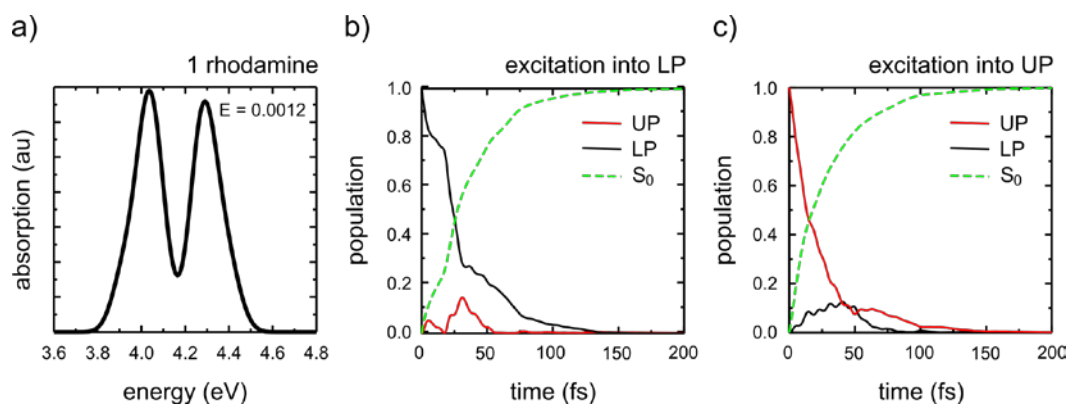


Figure 4: Absorption spectrum (left panel) and state populations after excitation into the lower polariton (middle panel) and upper polariton (right panel) of a single molecule strongly coupled to a nano-cavity with a mode volume of 99 nm^3 , corresponding to a single photon field strength of $E_{\text{cav}} = 0.0012$ Atomic Units (6.2 MVcm^{-1}). The dashed green line is the ground state population.

When there is only a single molecule inside the cavity (Figure 4), which has been realized experimentally for example by Baumberg and co-workers,⁵³ there is non-adiabatic population transfer between the upper and lower polaritons in addition to direct photo-emission. However, because the cavity is tuned near the excitation maximum of the molecule, both states have strong photonic character ($|\alpha^k|^2 \approx 0.5$) and the system rapidly decays to the ground state (green dashed line) from both polaritonic states, with a rate controlled by the cavity lifetime γ_{cav} . The transient population of the lower polariton after pumping the upper polariton (Figure 4c) was also observed in recent tensor network simulations of a single strongly coupled molecule by del Pino and co-workers,³⁹ as were the oscillatory features due to the activation of coherent vibrations of Franck-Condon active modes upon photo-excitation.

Comparing the relaxation process between simulations with the same number of molecules but different cavity mode volumes (Figure S6-S8), or equivalently, different single-photon field

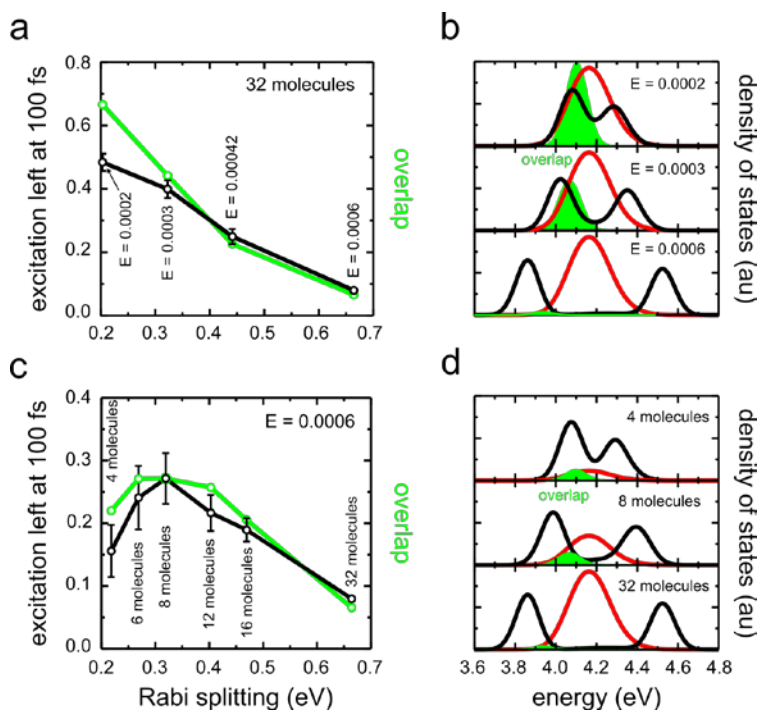


Figure 5: Total population remaining in the excited state manifold, $\sum_k^{N+1} |c_k(t = 100\text{fs})|^2$, containing the LP, $N - 1$ dark states and UP, at 100 fs after photo-excitation into the lower polariton as a function of Rabi splitting (black lines in a and c). In panel a, there are 32 rhodamine molecules in cavities with various single-photon field strengths (E , in atomic units). In c, the number of molecules in the cavity is varied from 4 to 32, while keeping the cavity field strength constant at 0.0006 au (3.1 MVcm^{-1} , 396 nm^3 mode volume). Error bars are estimated from five independent simulations. The green peaks in panels b and d show the overlap between the LP (left dark peak) and the dark states (red peak). The trend of this overlap is shown as green line in panels a and c.

strengths E_{cav} , we observe that decay through direct photo-emission increases if the cavity mode volume decreases. In Figure 5 we plot the total population that remains excited at 100 fs after photo-excitation into the LP as a function of the Rabi splitting. Because non-adiabatic population transfer into the dark states competes with direct photo-emission from the lower polariton, the overall decay rate is determined by the accessibility of the dark states. As the non-adiabatic coupling between states is inversely proportional to the energy gap, the most accessible states are the ones at or near resonance with the lower polariton.

1
2
3 The distribution of the dark states, *i.e.*, their density of states (DOS), is very similar to that of the
4 uncoupled molecules (red curve in Figure 5b) and hence, closely matches the absorption spectrum
5 of the bare molecule (Figure 1c).⁵² Indeed, the overlap, evaluated as the integral between the DOS
6 of the lower polariton (left black peak in Figure 5b) and the DOS of the bare molecules (red; see SI
7 for details of this calculation) shows the same trend as the excited-state survival rate, estimated as
8 the excitation remaining in the system at 100 fs after photo-excitation (Figure 5a). This observation
9 suggests that the rate of population transfer into the dark states is controlled by the DOS of the
10 dark states at the polariton energy level, as suggested by Coles *et al.*⁵² Thus, our results suggest
11 that the efficiency of remaining in the lower polaritonic state, which is essential for manipulating
12 photochemistry,^{7,12,29,54} can be estimated directly from the overlap between the polaritonic and
13 molecular absorption spectra. In other words, the simple picture of photochemistry occurring on
14 polaritonic potential energy surfaces under strong coupling only applies (in the many-molecule
15 case) if the Rabi splitting is large enough for the polaritons to be energetically well-separated from
16 the bare-molecule states, extending similar observations for the absorption spectra in extremely
17 simplified model molecules.³

18
19 To further verify the validity of this overlap argument, we have also varied the number of
20 molecules, while keeping the cavity mode volume, or quantized field strength, constant. In Figure 5c
21 we plot the total excited population remaining at 100 fs after pumping the lower polariton, as a
22 function of Rabi splitting. Again, the trend follows the overlap between the DOS of the lower
23 polariton on the one hand and the DOS of the molecules on the other hand (Figure 5d). Since the
24 energy level of the LP is determined by the square root of the number of rhodamine molecules
25 (Equation 2), while the DOS of the dark states scales linearly with the number of molecules, the
26 overlap has a maximum when there are 8 molecules in our cavity. Indeed, with 8 molecules inside
27 the cavity, the population of dark states at 100 fs is the highest, confirming that the accessibility of
28 these states is determined by their overlap with the optically active lower polariton.

29
30 Because vibronic progression cannot be modelled in classical MD simulations, the molecular
31 spectra appear as a single heterogeneously broadened peak without vibrational structure (Figure 1c).

1
2
3 Because vibronic progression extends the spectrum towards higher energies on the blue side of the
4 absorption maximum, we could thus underestimate the overlap between the upper polariton and
5 the dark states. In contrast, because the lower polariton is situated below the (vertical) absorption
6 maximum, the effects of vibronic progression on the overlap should be much smaller, possibly even
7 negligible.
8
9
10
11
12

13 The observation that the overlap between the bright and dark polaritonic states governs the life-
14 time of the molecule-cavity system is supported by experiments that probed the photo-luminescence
15 in strongly coupled systems after pumping the lower polariton. For molecules with very narrow
16 absorption bands, such as J-aggregates, there is minimal overlap between the dark states and lower
17 polariton already at moderate Rabi splittings. Without involvement of dark states the relaxation
18 process after pumping the lower polariton is thus dominated by ultra-fast radiative emission. In
19 low-finesse cavities, this decay is difficult to detect, both in stationary and transient measurements,
20 in line with experimental observations.²⁴⁻²⁶ In contrast, for molecules with a broad absorption
21 band, there is significant overlap between the bright and dark polaritonic states even for large Rabi
22 splittings. Because in addition to ultra-fast direct photo-emission from the LP, there is also popula-
23 tion transfer into the long-lived dark state manifold due to this overlap, the apparent lifetime of the
24 LP emission is prolonged and hence detectable.^{26,51,52} The results of our simulations furthermore
25 suggest occupation of polaritonic states above the LP due to a redistribution of the thermal energy.
26 This thermal population of polaritonic states can not only account for the observation of anti-Stokes
27 emission after pumping the LP,⁵¹ but also for the temperature dependent emission from the UP.⁵²
28 We believe that our findings could be relevant for designing molecule-cavity systems for polaritonic
29 chemistry, in which access to dark states may compromise the control of photoreactivity due to
30 modifications of the lower polaritonic potential energy surface.^{7,12-14,27,28,54}
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48

49 In summary, we have performed MD simulations of ensembles of rhodamine molecules strongly
50 coupled to a single confined light mode. The results of the simulations suggest that relaxation of the
51 optically active polaritons involves both direct photo-emission with a rate controlled by the cavity
52 lifetime, as well as transitions into the 'dark' state manifold, or 'exciton reservoir'.^{31,32} Because
53
54
55
56
57
58
59
60

1
2
3 the transient population of the dark states, which lack a strong photonic contribution, delays the
4 photo-emission, the molecule-cavity system has a much longer lifetime than the cavity alone, in line
5 with previous experiments^{24–26,33} and theoretical work.^{37,39,42,45} Furthermore, our simulations also
6 suggest that the efficiency of transitions into the dark states is determined by the overlap between the
7 densities of the dark and bright polaritonic states, which can be inferred directly from the absorption
8 spectra. Because both radiative decay and radiationless transitions into the dark state manifold
9 compete with the dynamics on the polaritonic energy landscape,⁵⁴ controlling photochemistry with
10 cavities requires both a long-lived cavity mode and a large Rabi splitting. In follow-up work, we
11 will further address these issues for *photo-reactive* molecules in a cavity.
12
13
14
15
16
17
18
19
20
21
22

23 **Associated content**

24 **Supporting Information**

25
26
27 The Supporting Information is available free of charge on the ACS Publications website. Complete
28 description of the Ehrenfest molecular dynamics simulation protocol, calculation of absorption and
29 emission spectra, calculation of density of states (DOS) and plots of the populations versus time in
30 all simulations.
31
32
33
34
35
36
37
38
39

40 **Author Information**

41 **Corresponding Author**

42
43
44 Email: gerrit.x.groenhof@jyu.fi
45
46
47
48
49

50 **ORCID**

51
52
53 J. J. Toppari: 0000-0002-1698-5591
54
55 G. Groenhof: 0000-0001-8148-5334
56
57
58
59
60

1
2
3 C. Climent: 0000-0002-5302-1660
4

5 J. Feist: 0000-0002-7972-0646
6

7 D. Morozov: 0000-0001-9524-948X
8
9

10 11 **Funding** 12

13
14 This work was supported by the Academy of Finland (Grants 289947 to JJT; 290677 and to GG) as
15 well as the European Research Council (ERC-2016-StG-714870 to JF) and the Spanish Ministry for
16 Science, Innovation, and Universities – AEI (RTI2018-099737-B-I00 to JF).
17
18
19
20

21 **Notes** 22

23
24 The authors declare no competing financial interests.
25
26
27
28

29 **Acknowledgements** 30

31
32 We thank the Center for Scientific Computing (CSC-IT Center for Science) for computational
33 resources and Fredrik Robertsén in particular for his help with running our simulations on GPUs.
34 We also acknowledge PRACE for awarding us access to resource Curie based in France at GENCI.
35
36
37
38
39

40 **References** 41

- 42
43 (1) Vahala, K. J. Optical Microcavities. *Nature* **2003**, *424*, 839–846.
44
45
46 (2) Törmä, P.; Barnes, W. L. Strong coupling between surface plasmon polaritons and emitters: a
47 review. *Rep. Prog. Phys.* **2015**, *78*, 013901.
48
49
50
51 (3) Galego, J.; Garcia-Vidal, F. J.; Feist, J. Cavity-Induced Modifications of Molecular Structure
52 in the Strong-Coupling Regime. *Phys. Rev. X* **2015**, *5*, 041022.
53
54
55
56
57
58
59
60

- 1
2
3
4 (4) Flick, J.; Ruggenthaler, M.; Appel, H.; Rubio, A. Atoms and Molecules in Cavities: From
5 Weak to Strong Coupling in QED Chemistry. *Proc. Natl. Acad. Sci. USA* **2017**, *114*, 3026–
6 3034.
7
8
9
10 (5) Dovzhenko, D. S.; Ryabchuk, S. V.; Rakovich, Y. P.; Nabiev, I. R. Light-matter interaction
11 in the strong coupling regime: configurations, conditions, applications. *Nanoscale* **2018**, *10*,
12 3589–3605.
13
14
15
16 (6) Luk, H.-L.; Feist, J.; Toppari, J. J.; Groenhof, G. Multiscale Molecular Dynamics Simulations
17 of Polaritonic Chemistry. *J. Chem. Theory Comput.* **2017**, *13*, 4324–4335.
18
19
20
21 (7) Feist, J.; Galego, J.; Garcia-Vidal, F. J. Polaritonic chemistry with organic molecules. *ACS*
22 *Photonics* **2018**, *5*, 205–216.
23
24
25
26 (8) Jaynes, E. T.; Cummings, F. W. Comparison of quantum and semiclassical radiation theories
27 with to the beam maser. *Proc. IEEE* **1963**, *51*, 89–109.
28
29
30
31 (9) Tavis, M.; Cummings, F. W. Approximate solutions for an N-molecule radiation-field Hamil-
32 tonian. *Phys. Rev.* **1969**, *188*, 692–695.
33
34
35
36 (10) Hutchison, J. A.; Schwartz, T.; Genet, C.; Devaux, E.; Ebbesen, T. W. Modifying Chemical
37 Landscapes by Coupling to Vacuum Fields. *Angew. Chem. Int. Ed.* **2012**, *51*, 1592–1596.
38
39
40
41 (11) Herrera, F.; Spano, F. C. Cavity-controlled chemistry in molecular ensembles. *Phys. Rev. Lett.*
42 **2016**, *116*, 238301.
43
44
45
46 (12) Galego, J.; Garcia-Vidal, F. J.; Feist, J. Suppressing photochemical reactions with quantized
47 light fields. *Nat. Comm.* **2016**, *7*, 13841.
48
49
50
51 (13) Kowalewski, M.; Bennett, K.; Mukamel, S. Cavity Femtochemistry: Manipulating Nonadia-
52 batic Dynamics at Avoided Crossings. *J. Phys. Chem. Lett.* **2016**, *7*, 2050–2054.
53
54
55
56 (14) Galego, J.; Garcia-Vidal, F. J.; Feist, J. Many-Molecule Reaction Triggered by a Single Photon
57 in Polaritonic Chemistry. *Phys. Rev. Lett.* **2017**, *119*, 136001.
58
59
60

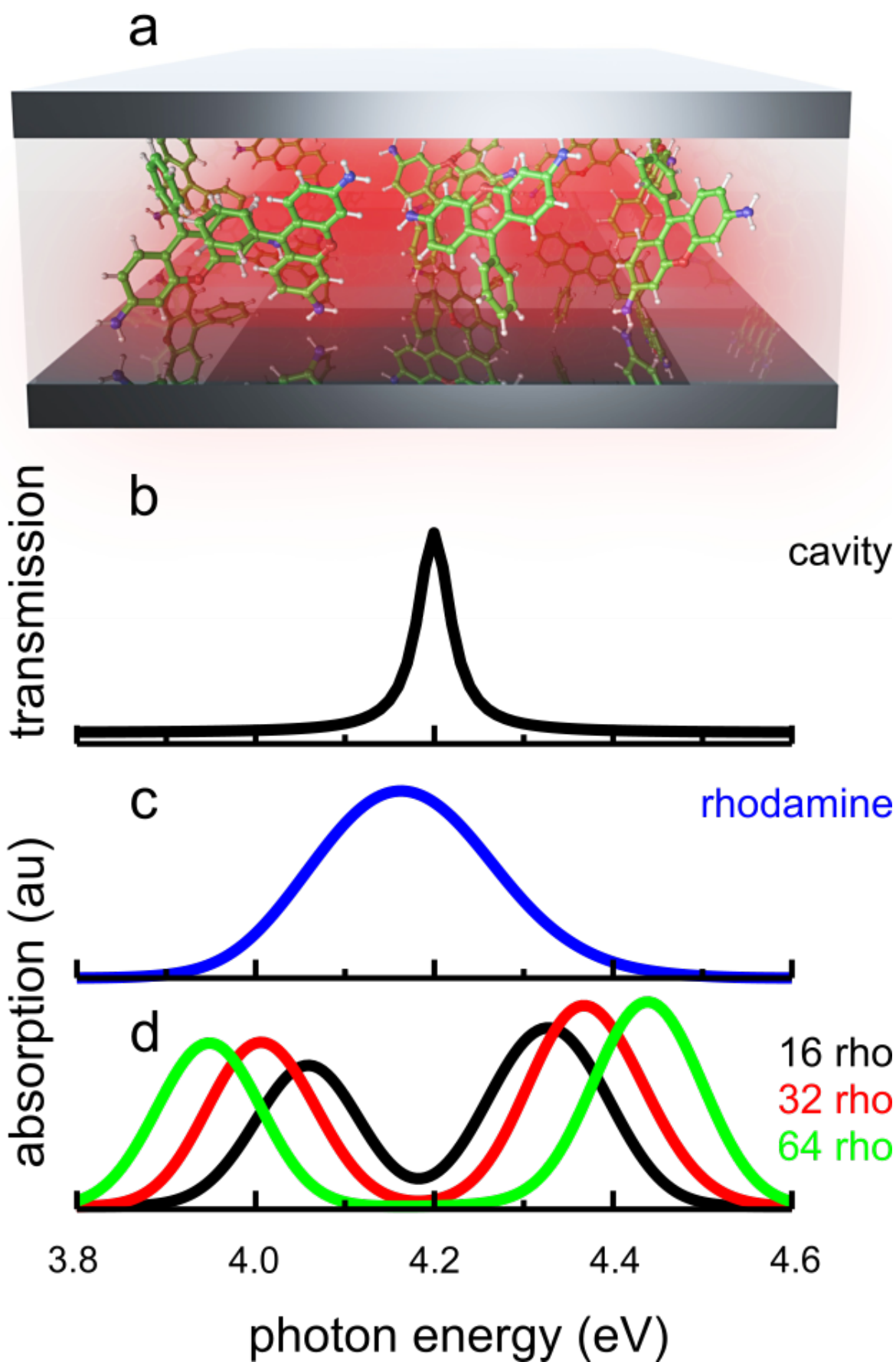
- 1
2
3 (15) Csehi, A.; Halás, G. J.; Cederbaum, L.; Vibók, Á. Competition between Light-Induced and
4 Intrinsic Nonadiabatic Phenomena in Diatomics. *J. Chem. Phys. Lett.* **2017**, *8*, 1624–1630.
5
6
7
8 (16) Vendrell, O. Coherent dynamics in cavity femtochemistry: Application of the multi-
9 configuration time-dependent Hartree method. *Chem. Phys.* **2018**, *509*, 55–65.
10
11
12 (17) Szidarovsky, T.; Halász, G. J.; Császár, A. G.; Cederbaum, L. S.; Vibók, A. Conical Intersec-
13 tions Induced by Quantum Light: Field-Dressed Spectra from the Weak to the Ultrastrong
14 Coupling Regimes. *J. Chem. Phys. Lett.* **2018**, *9*, 6215–6223.
15
16
17
18 (18) Triana, J. F.; Peláez, D.; Sanz-Vicaro, J. L. Entangled Photonic-Nuclear Molecular Dynamics
19 of LiF in Quantum Optical Cavities. *J. Phys. Chem. A* **2018**, *122*, 2266–2278.
20
21
22
23 (19) Munkhbat, B.; Wersäll, M.; Baranov, D. G.; Antosiewicz, T. J.; Shegai, T. Suppression of
24 photo-oxidation of organic chromophores by strong coupling to plasmonic nanoantennas. *Sci.*
25 *Adv.* **2018**, *4*, eaas9552.
26
27
28
29 (20) Zhong, X.; Chervy, T.; Wang, S.; George, J.; Thomas, A.; Hutchison, J. A.; Devaux, E.;
30 Genet, C.; Ebbesen, T. W. Non-Radiative Energy Transfer Mediated by Hybrid Light-Matter
31 States. *Angew. Chem. Int. Ed.* **2016**, *55*, 6202–6206.
32
33
34
35 (21) Zhong, X.; Chervy, T.; Zhang, L.; Thomas, A.; George, J.; Genet, C.; Hutchison, J. A.;
36 Ebbesen, T. W. Energy Transfer between Spatially Separated Entangled Molecules. *Angew.*
37 *Chem. Int. Ed.* **2017**, *56*, 9034–9038.
38
39
40
41 (22) Coles, D. M.; Somaschi, N.; Michetti, P.; Clark, C.; Lagoudakis, P. G.; Savvidis, P. G.;
42 Lidzey, D. G. Polariton-mediated energy transfer between organic dyes in a strongly coupled
43 optical microcavity. *Nature Materials* **2014**, *13*, 712–719.
44
45
46
47 (23) Stranius, K.; Herzog, M.; Börjesson, K. Selective manipulation of electronically excited states
48 through strong light-matter interactions. *Nat. Comm.* **2018**, *9*, 2273.
49
50
51
52
53
54
55
56
57
58
59
60

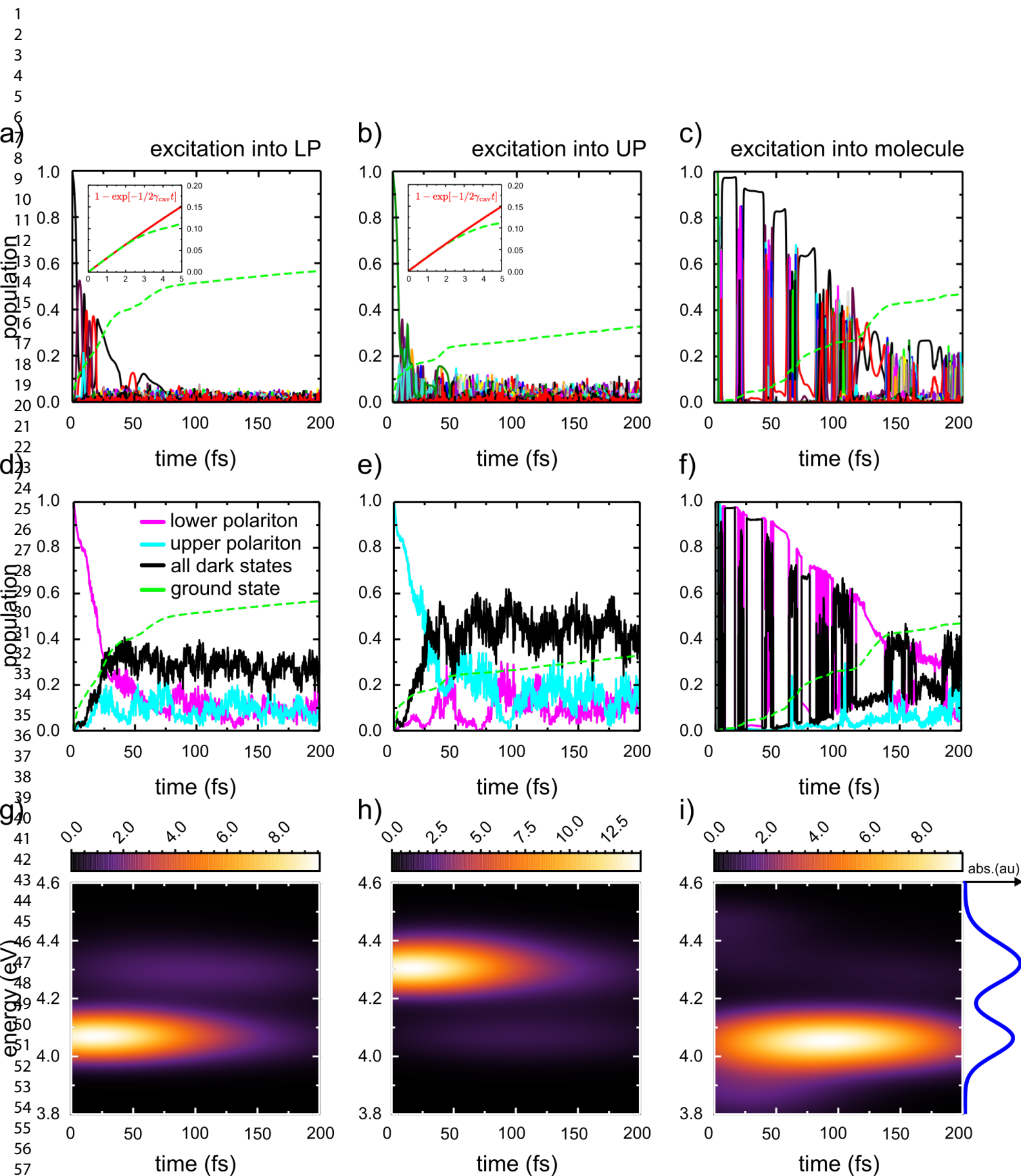
- 1
2
3 (24) Schwartz, T.; Hutchison, J. A.; Leonard, J.; Genet, C.; Haacke, S.; Ebbesen, T. W. Polariton
4 Dynamics under Strong Light-Molecule Coupling. *ChemPhysChem* **2013**, *14*, 125–131.
5
6
7
8 (25) Wang, H.; Wang, H.-Y.; Bozzola, A.; Toma, A.; Panaro, S.; Raja, W.; Alabastri, A.; Wang, L.;
9 Chen, Q.-D.; Xu, H.-L.; Angelis, F. D.; Sun, H.-B.; Zaccaria, R. P. Dynamics of Strong
10 Coupling between J-Aggregates and Surface Plasmon Polaritons in Subwavelength Hole
11 Arrays. *Adv. Funct. Matter.* **2016**, *26*, 6198–6205.
12
13
14
15
16 (26) George, J.; Wang, S.; Chervy, T.; Canaguier-Durand, A.; Schaeffer, G.; Lehn, J.-M.; Hutchi-
17 son, J. A.; Genet, C.; Ebbesen, T. W. Ultra-strong coupling of molecular materials: spec-
18 troscopy and dynamics. *Faraday Discuss.* **2015**, *178*, 281–294.
19
20
21
22
23 (27) Hertzog, M.; Wang, M.; Mony, J.; Börjesson, K. Strong light–matter interactions: a new
24 direction within chemistry. *Chem. Soc. Rev.* **2019**, *48*, 937–961.
25
26
27
28 (28) Ribeiro, R. F.; Martínéz-Martínéz, L. A.; Du, M.; Campos-Gonzalez-Angule, J.; Yuen-Zhou, J.
29 Polariton chemistry: controlling molecular dynamics with optical cavities. *Chem. Sci.* **2018**, *9*,
30 6325–6339.
31
32
33
34
35 (29) Ebbesen, T. W. Hybrid Light-Matter States in a Molecular and Material Science Perspective.
36 *Acc. Chem. Res.* **2016**, *49*, 2403–2412.
37
38
39
40 (30) Somaschi, N.; Mouchliadis, L.; Coles, D.; Perakis, I. E.; Lidzey, D. G.; Lagoudakis, P. G.;
41 Savvidis, P. G. Ultrafast polariton population build-up mediated by molecular phonons in
42 organic microcavities. *Appl. Phys. Lett.* **2011**, *99*, 143303.
43
44
45
46 (31) Agranovich, V. M.; Litinskaia, M.; Lidzey, D. G. Cavity polaritons in microcavities containing
47 disordered organic semiconductors. *Phys. Rev. B* **2003**, *67*, 085311.
48
49
50
51 (32) Litinskaya, M.; Reineker, P.; Agranovich, V. M. Fast polariton relaxation in strongly coupled
52 organic microcavities. *J. Lumin.* **2004**, *110*, 364–372.
53
54
55
56
57
58
59
60

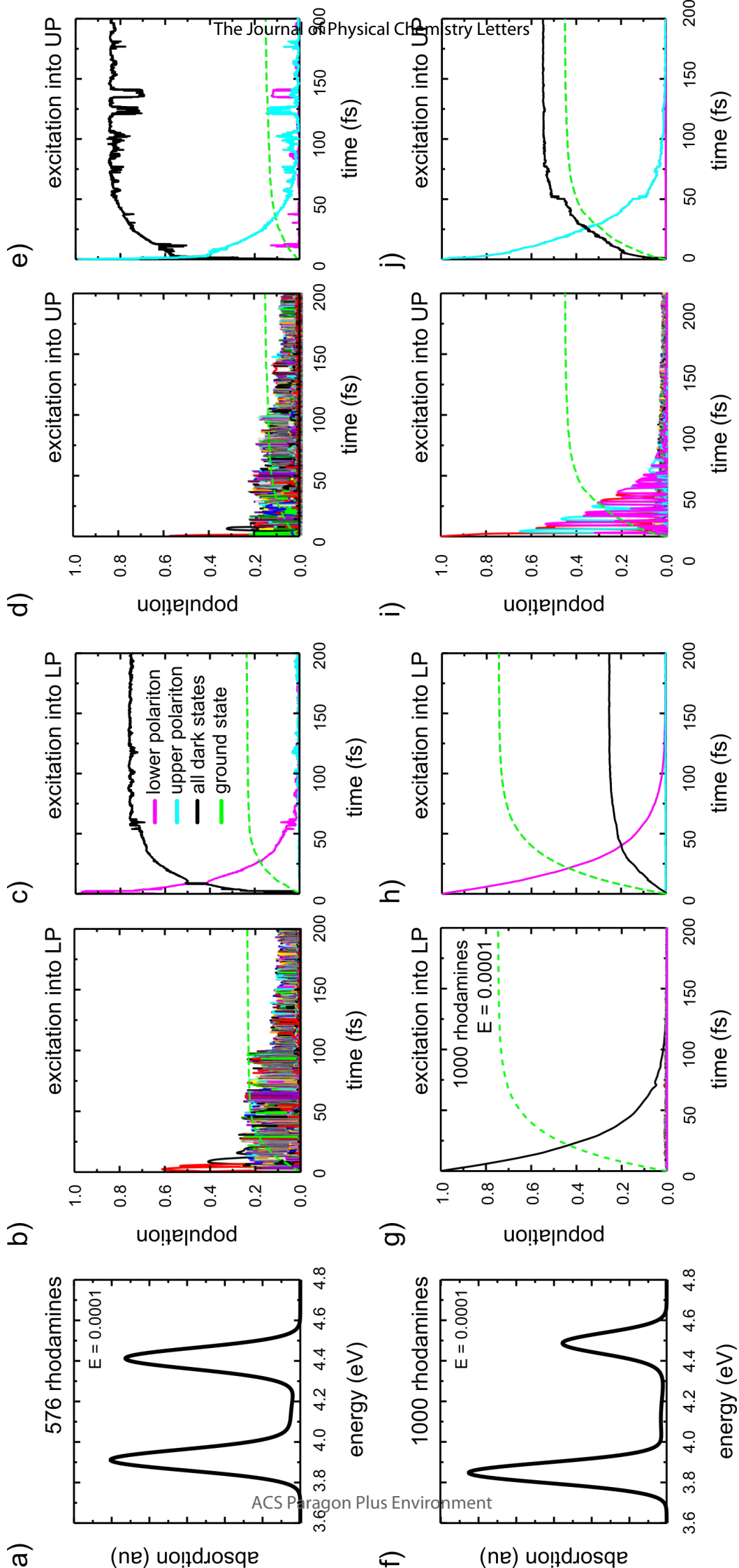
- 1
2
3 (33) Virgili, T.; Coles, D.; Adawi, A. M.; Clark, C.; Michetti, P.; Rajendran, S. K.; Brida, D.;
4 Polli, D.; Cerullo, G.; Lidzey, D. G. Ultrafast polariton relaxation dynamics in an organic
5 semiconductor microcavity. *Phys. Rev. B* **2011**, *83*, 245309.
6
7
8
9
10 (34) Lidzey, D. G.; Bradley, D. D. C.; Virgili, T.; Armitage, A.; Skolnick, M.; Walker, S. Room
11 Temperature Polariton Emission from Strongly Coupled Organic Semiconductor Microcavities.
12 *Appl. Phys. Lett.* **1999**, *82*, 3316–3319.
13
14
15
16
17 (35) Coles, D. M.; Grant, R.; Lidzey, D. G.; Clark, C.; Lagoudakis, P. G. Imaging the polariton
18 relaxation bottleneck in strongly coupled organic semiconductor microcavities. *Phys. Rev. B*
19 **2013**, *88*, 121303.
20
21
22
23
24 (36) Chovan, J.; Perakis, I. E.; Ceccarelli, S.; Lidzey, D. G. Controlling the interactions between
25 polaritons and molecular vibrations in strongly coupled organic semiconductor microcavities.
26 *Phys. Rev. B* **2008**, *78*, 045320.
27
28
29
30
31 (37) del Pino, J.; Feist, J.; Garcia-Vidal, F. J. Quantum Theory of Collective Strong Coupling of
32 Molecular Vibrations with a Microcavity Mode. *New J. Phys.* **2015**, *17*, 053040.
33
34
35
36 (38) Neuman, T.; Aizpurua, J. Origin of the Asymmetric Light Emission from Molecular Exciton-
37 Polaritons. *Optica* **2018**, *5*, 1247.
38
39
40
41 (39) del Pino, J.; Schröder, F. A. Y. N.; Chin, A. W.; Feist, J.; Garcia-Vidal, F. J. Tensor Network
42 Simulation of Non-Markovian Dynamics in Organic Polaritons. *Phys. Rev. Lett.* **2018**, *121*,
43 227401.
44
45
46
47 (40) Michetti, P.; La Rocca, G. C. Polariton-polariton scattering in organic microcavities at high
48 excitation densities. *Phys. Rev. B* **2010**, *82*, 115327.
49
50
51
52 (41) Michetti, P.; La Rocca, G. C. Simulation of J-aggregate microcavity photoluminescence. *Phys.*
53 *Rev. B* **2008**, *77*, 195301.
54
55
56
57
58
59
60

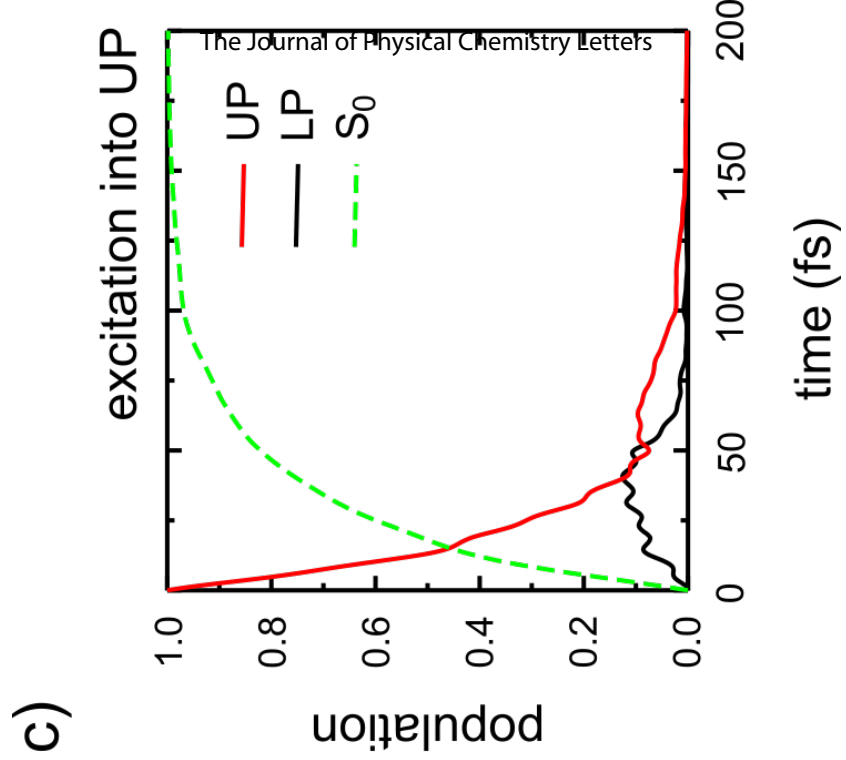
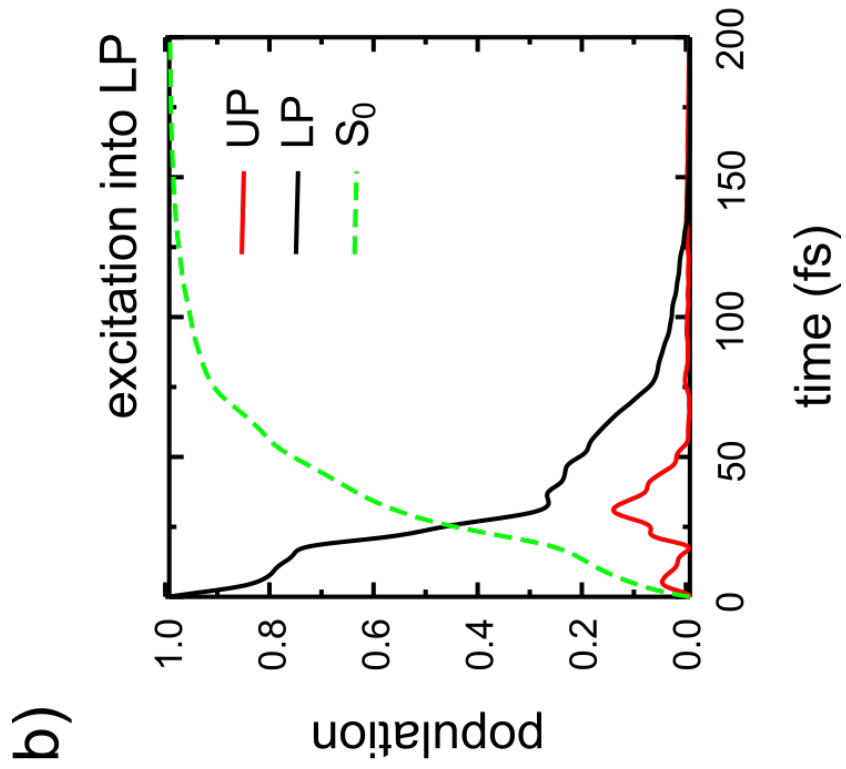
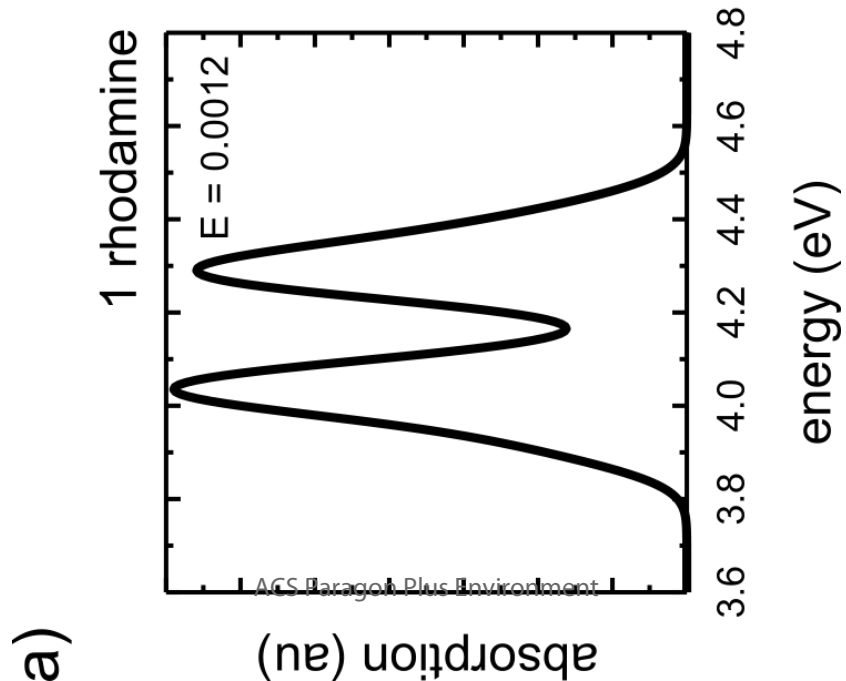
- 1
2
3
4 (42) Herrera, F.; Spano, F. C. Theory of nanoscale organic cavities: The essential role of vibration-
5 photon dressed states. *ACS Photonics* **2018**, *5*, 65–79.
6
7
8 (43) Herrera, F.; Spano, F. C. Dark Vibronic Polaritons and the Spectroscopy of Organic Microcav-
9 ities. *Phys. Rev. Lett.* **2017**, *118*, 223601.
10
11
12 (44) Herrera, F.; Spano, F. C. Absorption and Photoluminescence in Organic Cavity QED. *Phys.*
13 *Rev. A* **2017**, *95*, 053867.
14
15
16 (45) Vendrell, O. Collective Jahn-Teller Interactions through Light-Matter Coupling in a Cavity.
17 *Phys. Rev. Lett.* **2018**, *121*, 253001.
18
19
20 (46) Tully, J. C. Molecular dynamics with electronic transitions. *J. Chem. Phys.* **1990**, *93*, 1061–
21 1071.
22
23
24 (47) Crespo-Otero, R.; Barbatti, M. Recent Advances and Perspectives on Nonadiabatic Mixed
25 Quantum-Classical Dynamics. *Chem. Rev.* **2018**, *118*, 7026–7068.
26
27
28 (48) Ehrenfest, P. Bemerkung über die angenäherte Gültigkeit der klassischen Mechanik innerhalb
29 der Quantenmechanik. *Z. Phys.* **1927**, *45*, 445–457.
30
31
32 (49) Granucci, G.; Persico, M.; Toniolo, A. Direct semiclassical simulation of photochemical
33 processes with semiempirical wave functions. *J. Chem. Phys.* **2001**, *114*, 10608–10615.
34
35
36 (50) Wersäll, M.; Cuadra, J.; Antosiewicz, T. J.; Balci, S.; Shegai, T. Observation of Mode Splitting
37 in Photoluminescence of Individual Plasmonic Nanoparticles Strongly Coupled to Molecular
38 Excitons. *NanoLett.* **2016**, *17*, 551–558.
39
40
41 (51) Georgiou, K.; Jayaprakash, R.; Askitopoulos, A.; Coles, D. M.; Lagoudakis, P. G.; Lidzey, D. G.
42 Generation of Anti-Stokes Fluorescence in a Strongly Coupled Organic Semiconductor Micro-
43 cavity. *ACS Photonics* **2018**, *5*, 4343–4351.
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

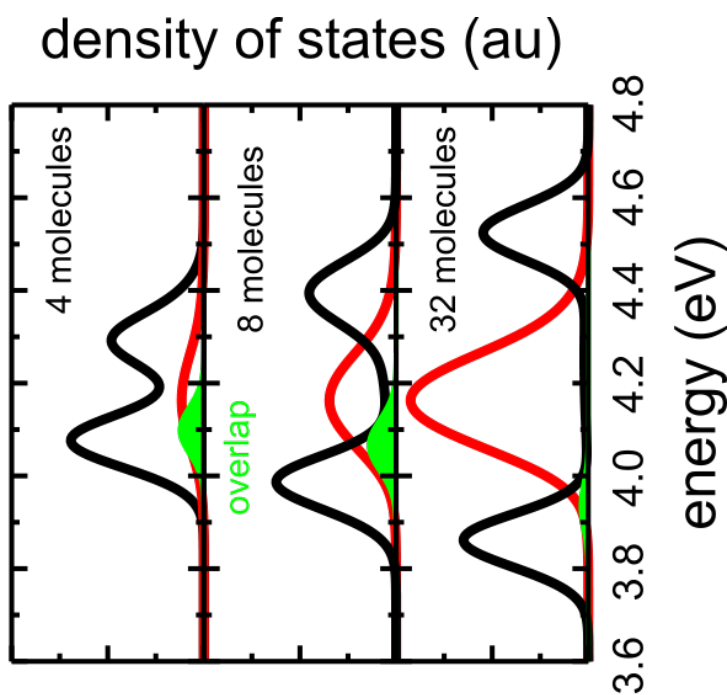
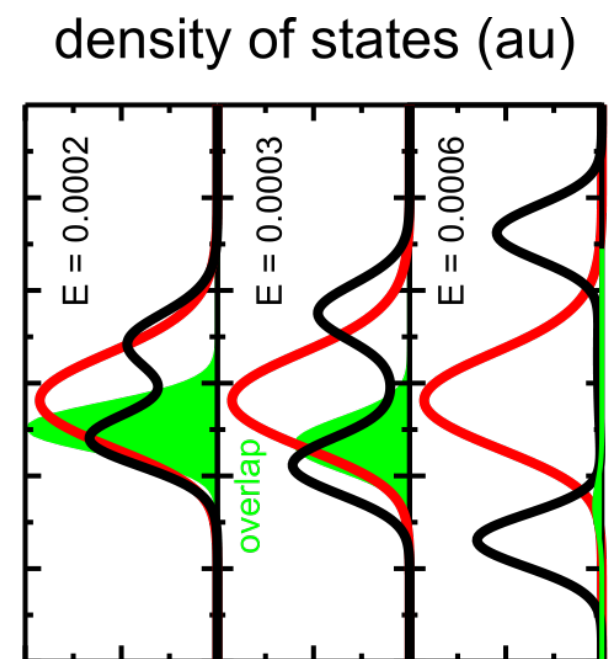
- 1
2
3 (52) Coles, D. M.; Michetti, P.; Clark, C.; Adawi, A. M.; Lidzey, D. G. Temperature dependence of
4 the upper-branch polariton population in an organic semiconductor microcavity. *Phys. Rev. B*
5 **2011**, *84*, 205214.
6
7
8
9
10 (53) Chikkaraddy, R.; de Nijs, B.; Benz, F.; Barrow, S. J.; Scherman, O. A.; Rosta, E.; Deme-
11 triadou, A.; Fox, P.; Hess, O.; Baumberg, J. J. Single-molecule strong coupling at room
12 temperature in plasmonic nanocavities. *Nature* **2016**, *535*, 127–130.
13
14
15
16
17 (54) Eizner, E.; Martínez-Martínez, L. A.; Yuen-Shou, J.; Kéna-Cohen, S. Inverting Singlet and
18 Triplet Excited States using Strong Light-Matter Coupling. *Arxiv* **2016**, *1903.09251v1*, 1–29.
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60



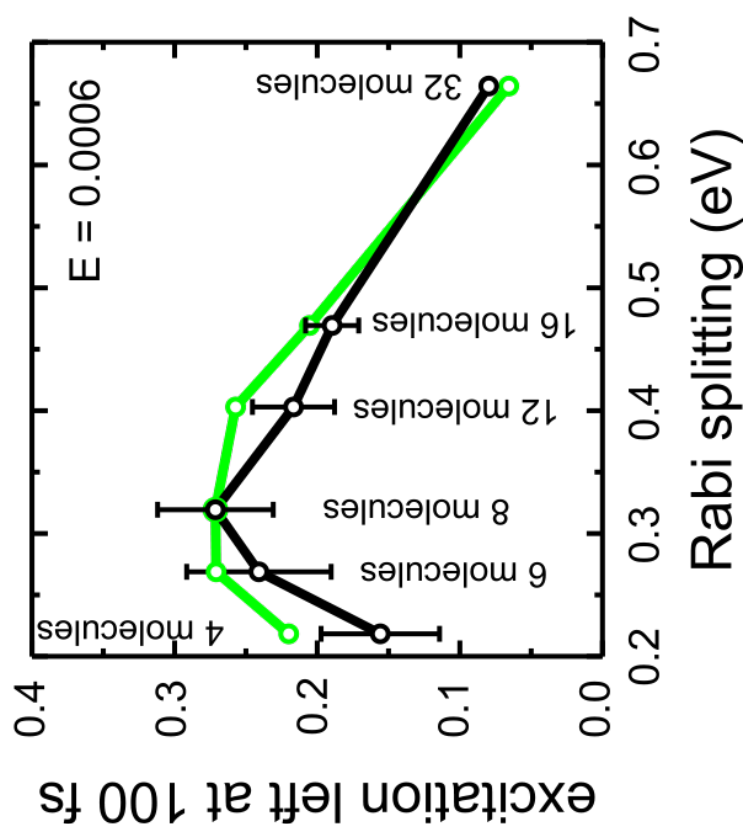
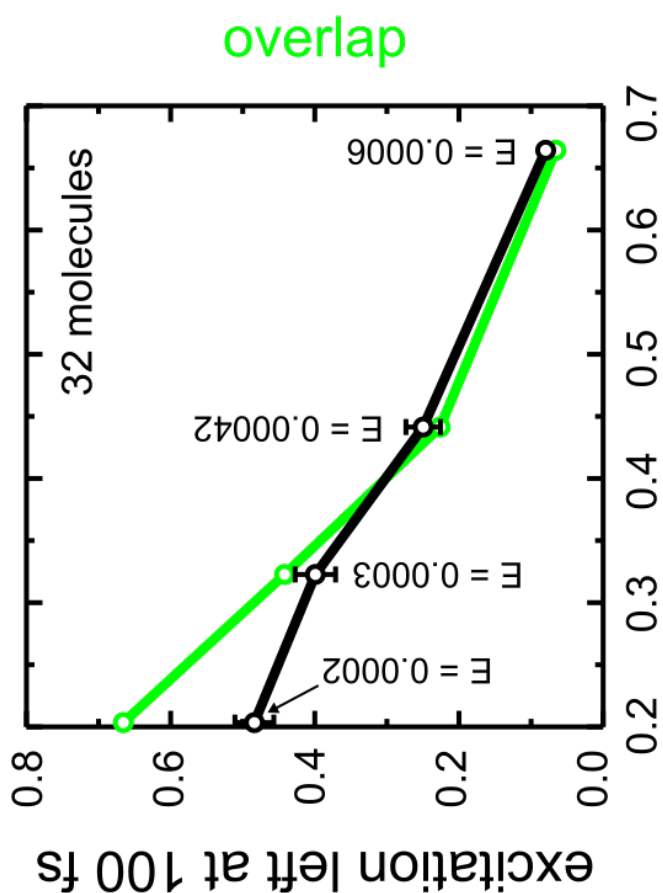


1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60



d



c

