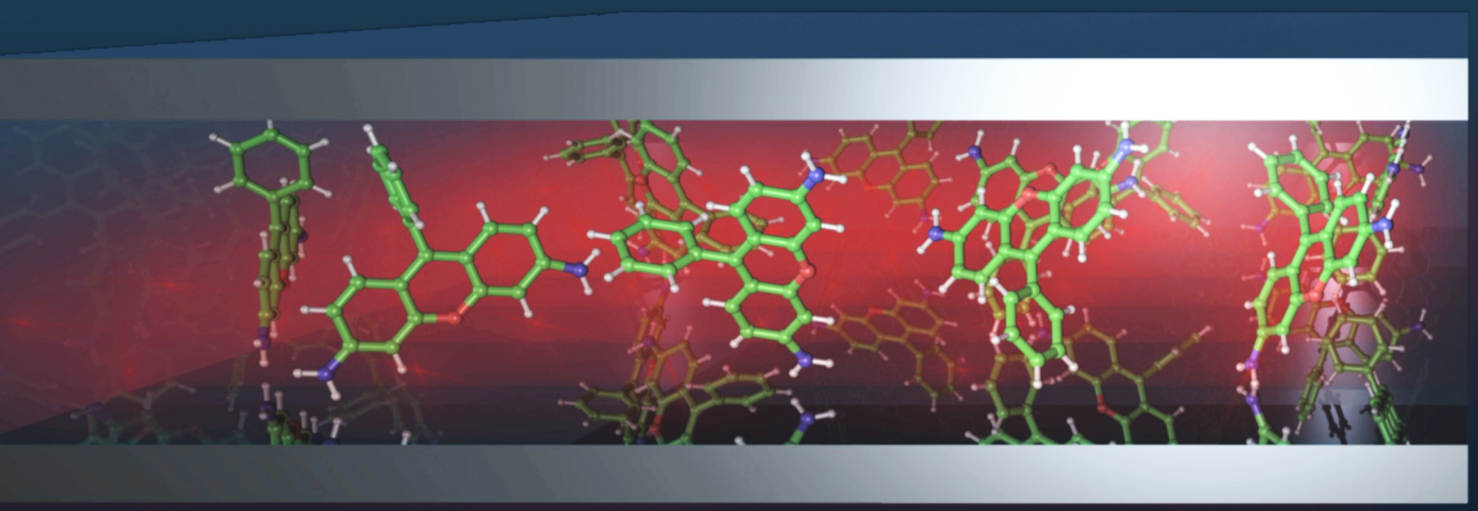
Manipulating molecules with mirrors

Semi-classical molecular dynamics simulations of polaritonic chemistry



$$\Psi = \beta_1(t)|\rangle|0\rangle +$$
$$\beta_2(t)|\rangle|0\rangle +$$
$$\beta_3(t)|\rangle|0\rangle +$$
$$\beta_4(t)|\rangle|0\rangle +$$
$$\beta_5(t)|\rangle|0\rangle +$$
$$\beta_6(t)|\rangle|0\rangle +$$
$$\beta_7(t)|\rangle|0\rangle +$$
$$\beta_8(t)|\rangle|0\rangle +$$
$$\alpha(t)|\rangle|1\rangle$$

Gerrit Groenhof

Department of Chemistry & NanoScience center
University of Jyväskylä
Finland

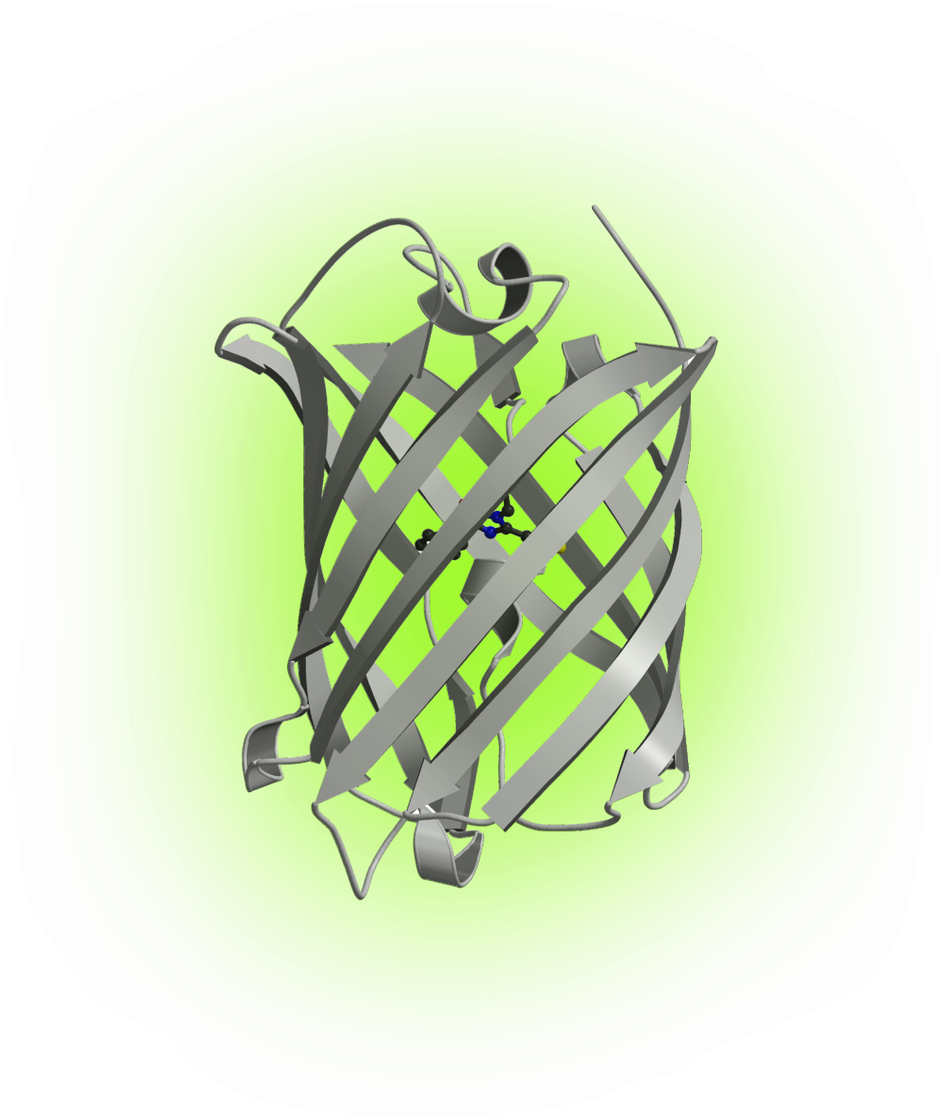
Johannes Feist

Jussi Toppari

Manipulating photo-chemistry

Green Fluorescent Protein (Ser65Thr/His148Asp)

ultra-fast excited-state proton transfer



Stoner-Ma *et al.*, *J. Am. Chem. Soc.* **130** (2008) 1227-1235

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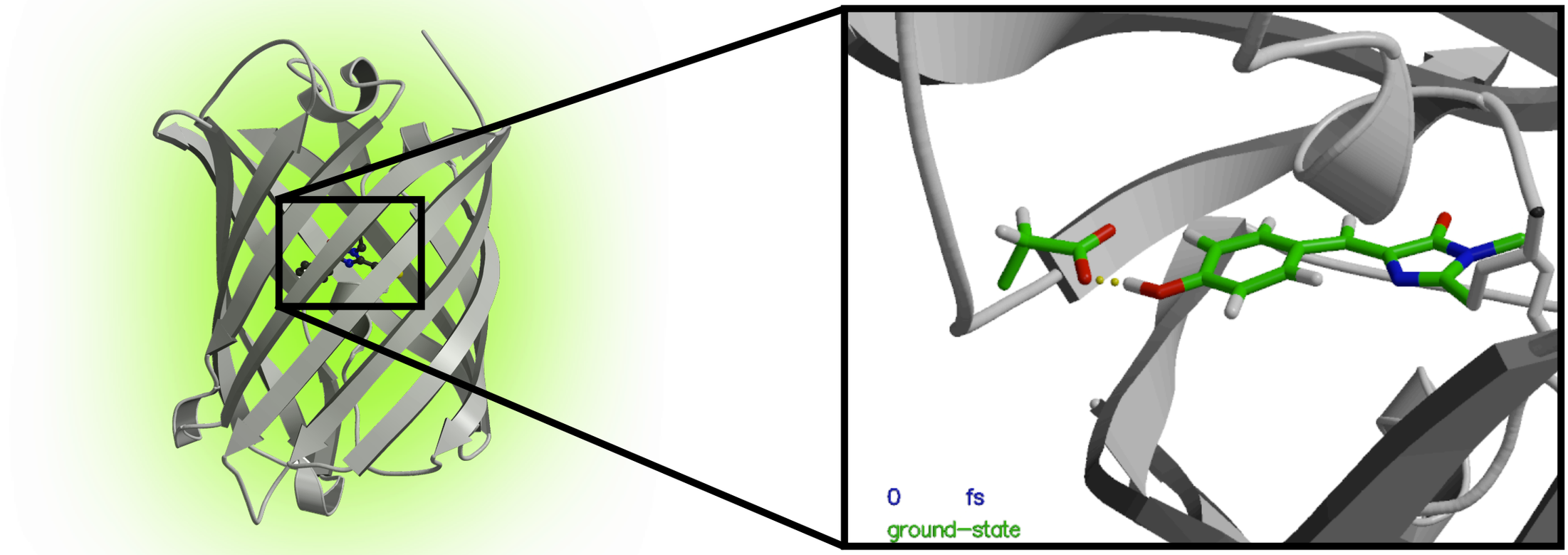
Calvin
Luk



CASSCF(6,6)/3-21G//Amber03

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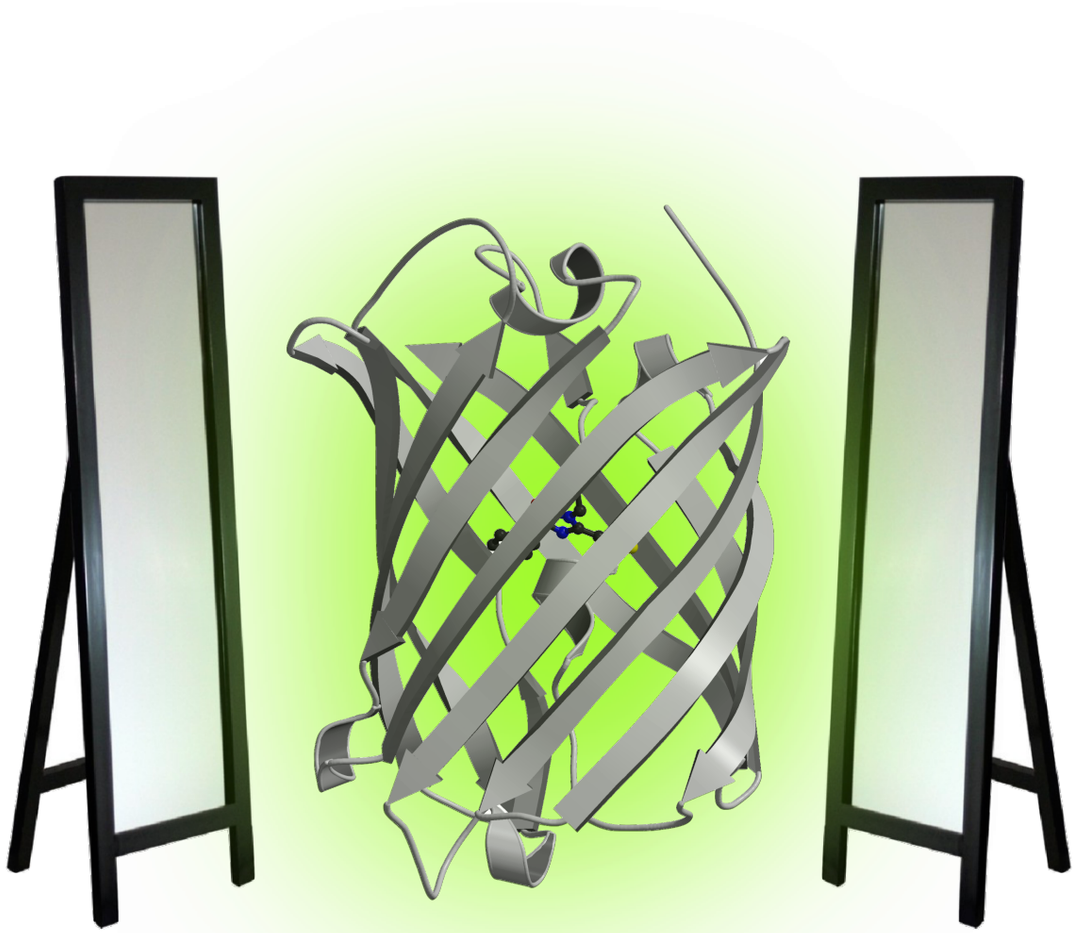

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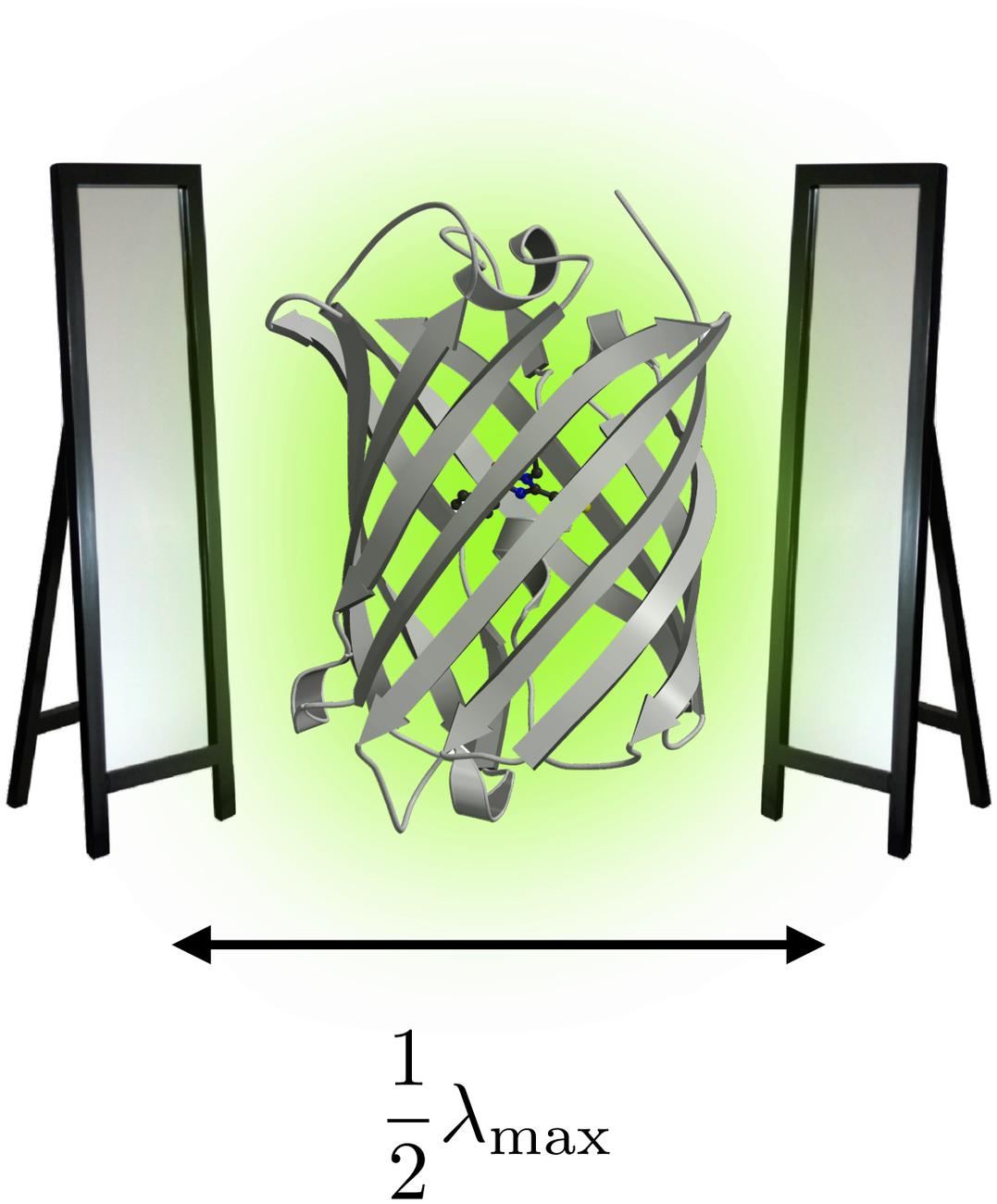

$$\frac{1}{2}\lambda_{\max}$$

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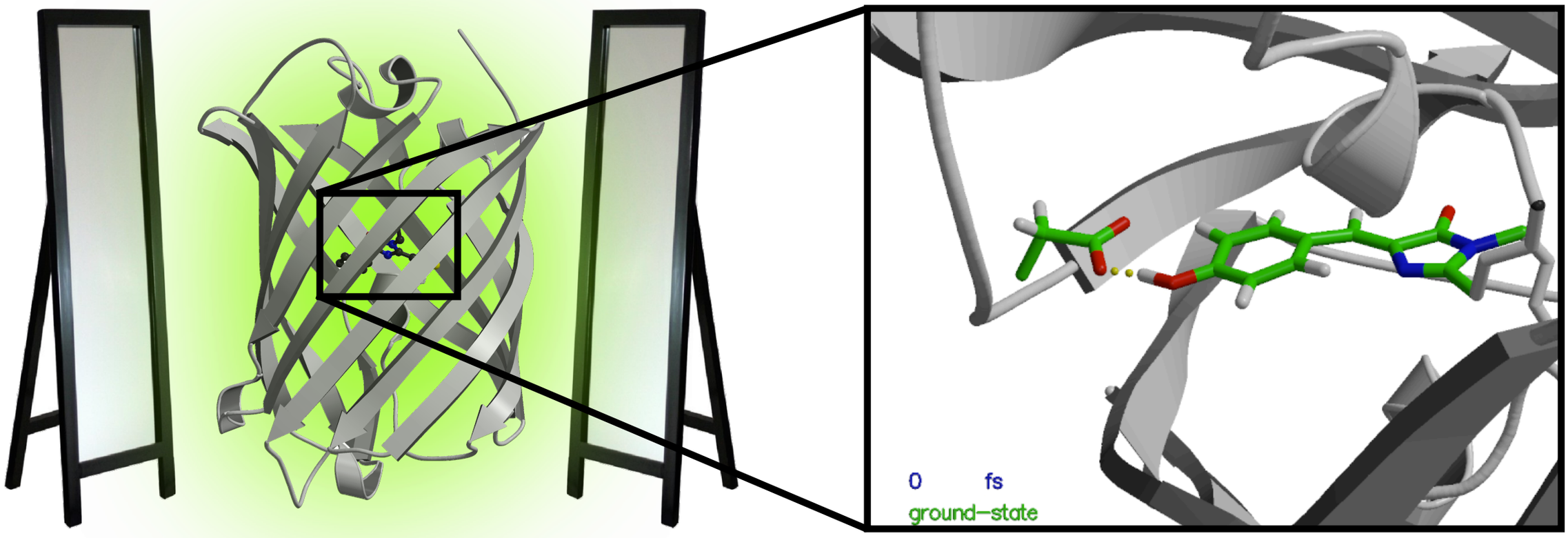

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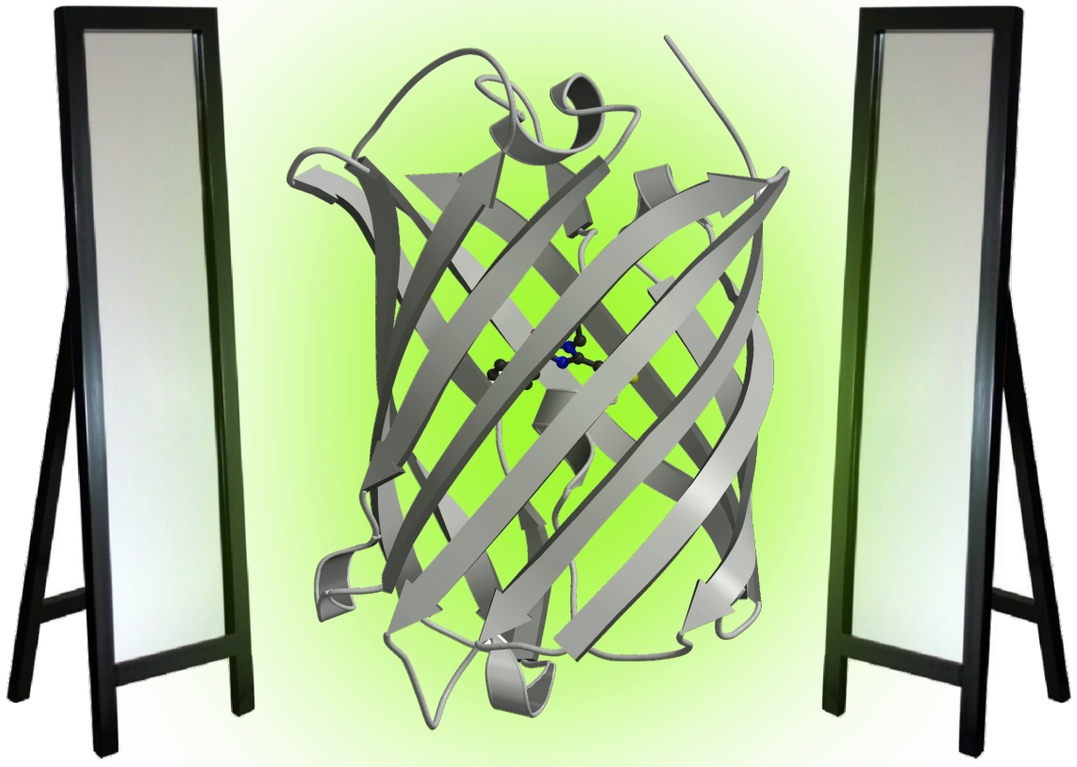
Manipulating photo-chemistry with mirrors

Green Fluorescent Protein

confining light

Fabry-Pèrrot micro-cavities



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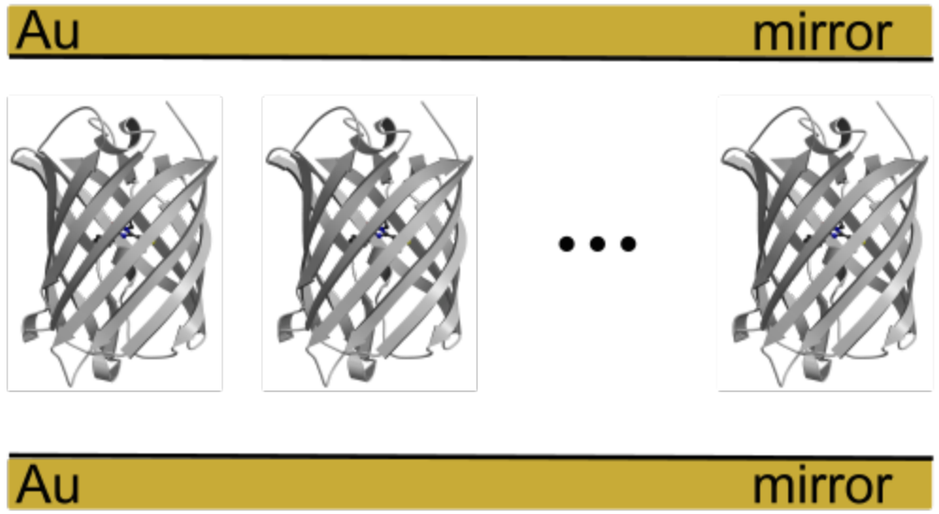
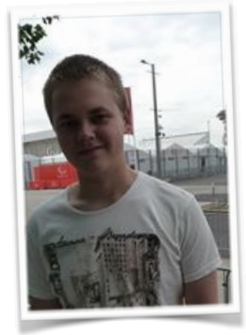




Mikael Kautto

Satu Mustalahti

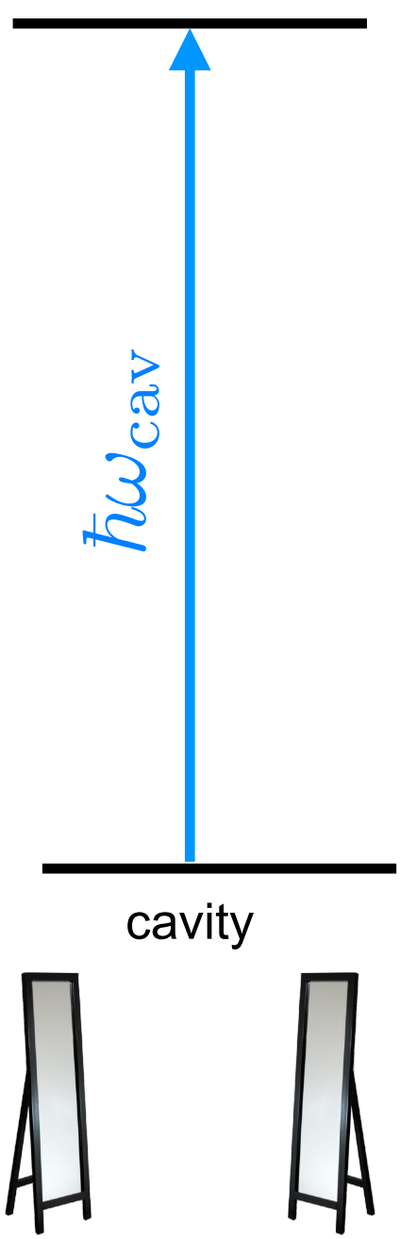
Eero Hulkko

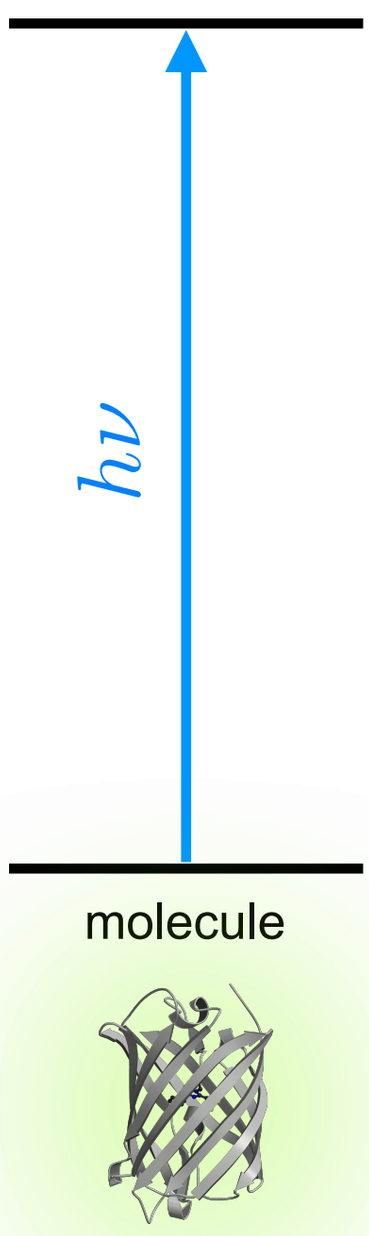
Ossi Hakamaa

Why does the photochemistry change?

strong coupling with confined light (cavity QED)

light-matter hybrid states: polaritons





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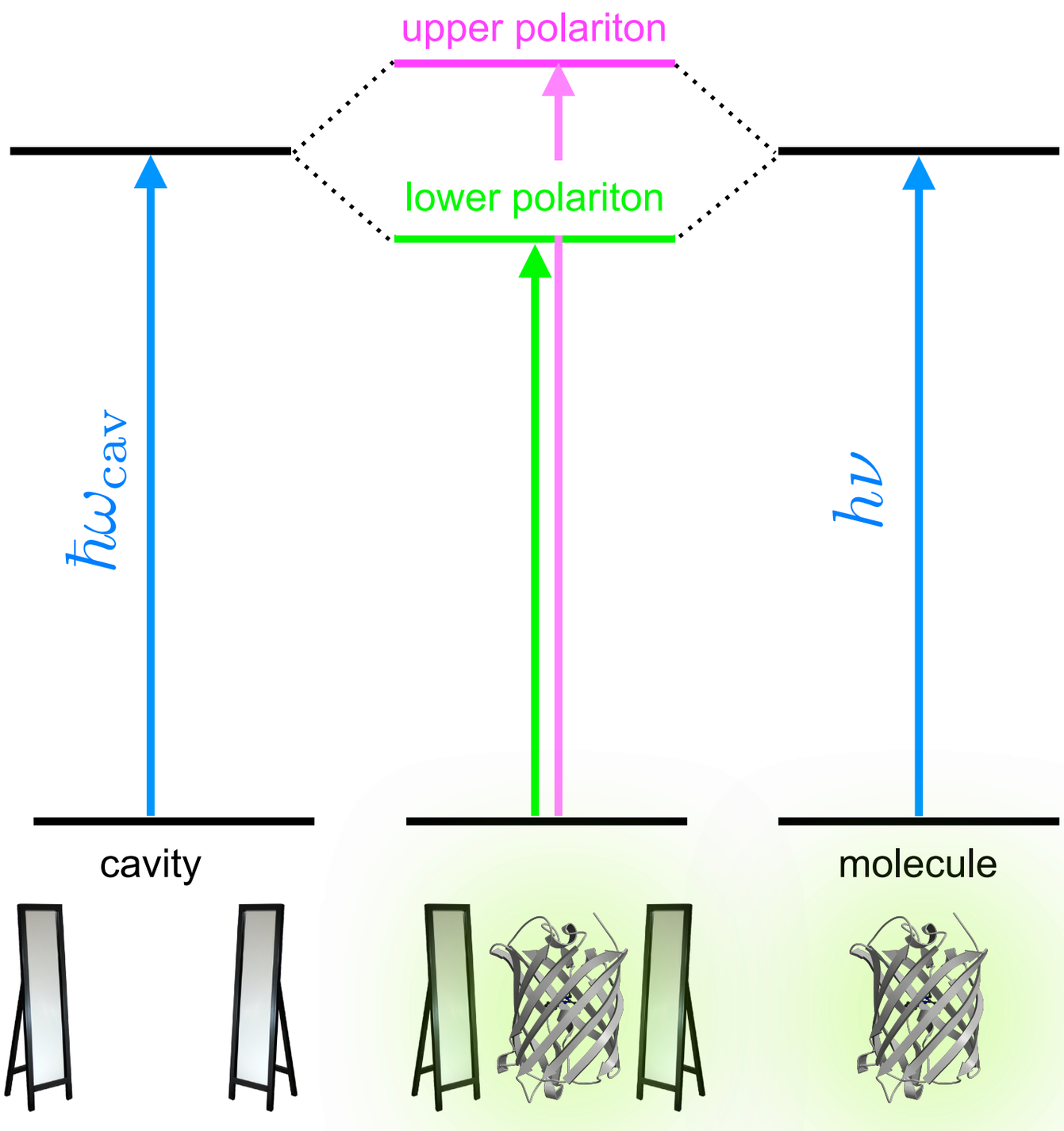

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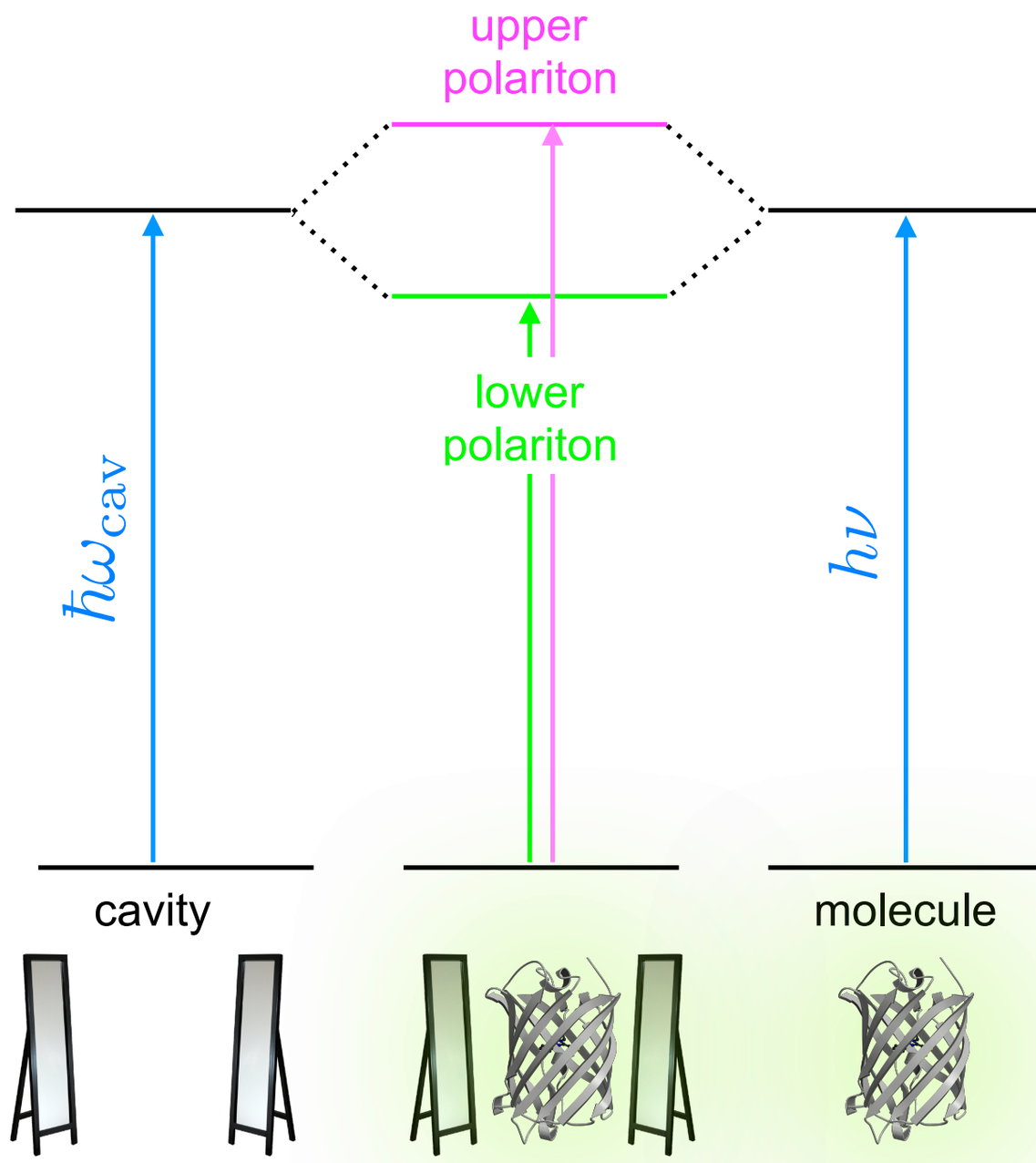
$$\hat{H}_{\mathrm{tot}} = \hat{H}_{\mathrm{mol}} + \hat{H}_{\mathrm{cav}} + \hat{H}_{\mathrm{int}}$$



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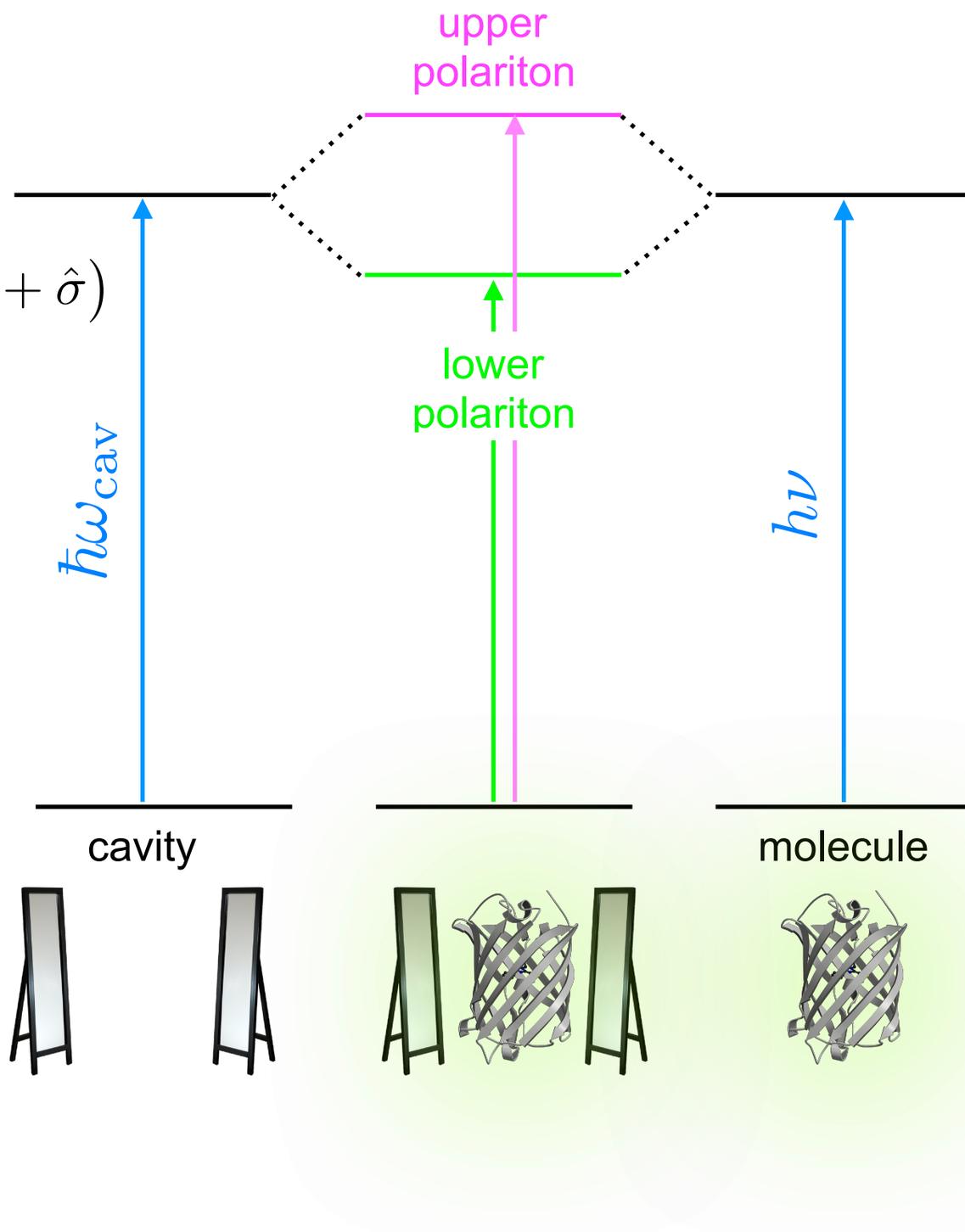
Rabi model

$$\hat{H}_{\mathrm{tot}} = \hbar\omega_{\mathrm{mol}}\hat{\sigma}^{\dagger}\hat{\sigma} + \hbar\omega_{\mathrm{cav}}\hat{a}^{\dagger}\hat{a} + \hbar g\left(\hat{a}^{\dagger} + \hat{a}\right)\left(\hat{\sigma}^{\dagger} + \hat{\sigma}\right)$$



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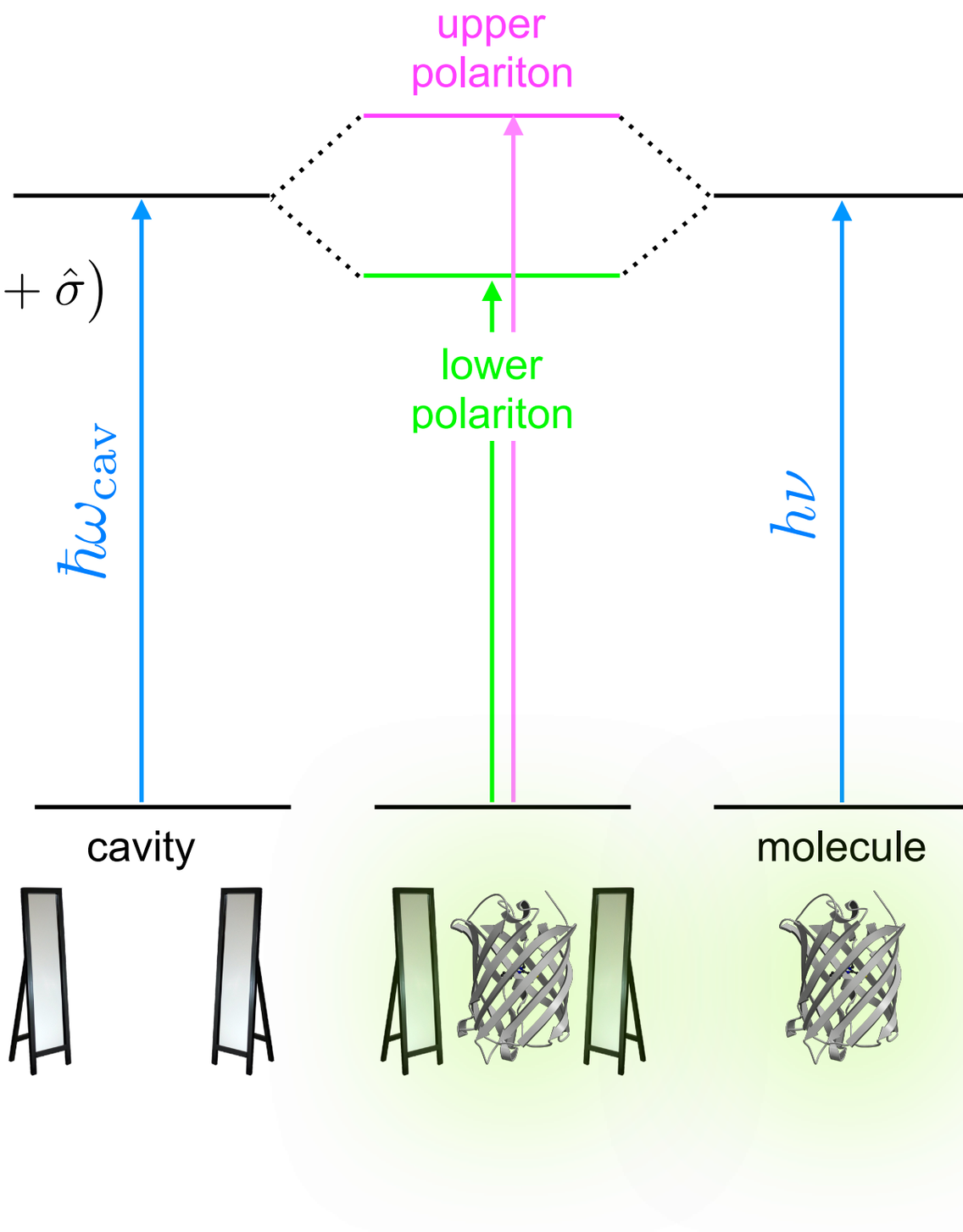
light-matter coupling in cavity

$$\hbar g \approx \boldsymbol{\mu}^{e\to g} \cdot \mathbf{u}_{\mathrm{cav}} \sqrt{\hbar\omega_{\mathrm{cav}}/\epsilon_0 V_{\mathrm{cav}}}$$



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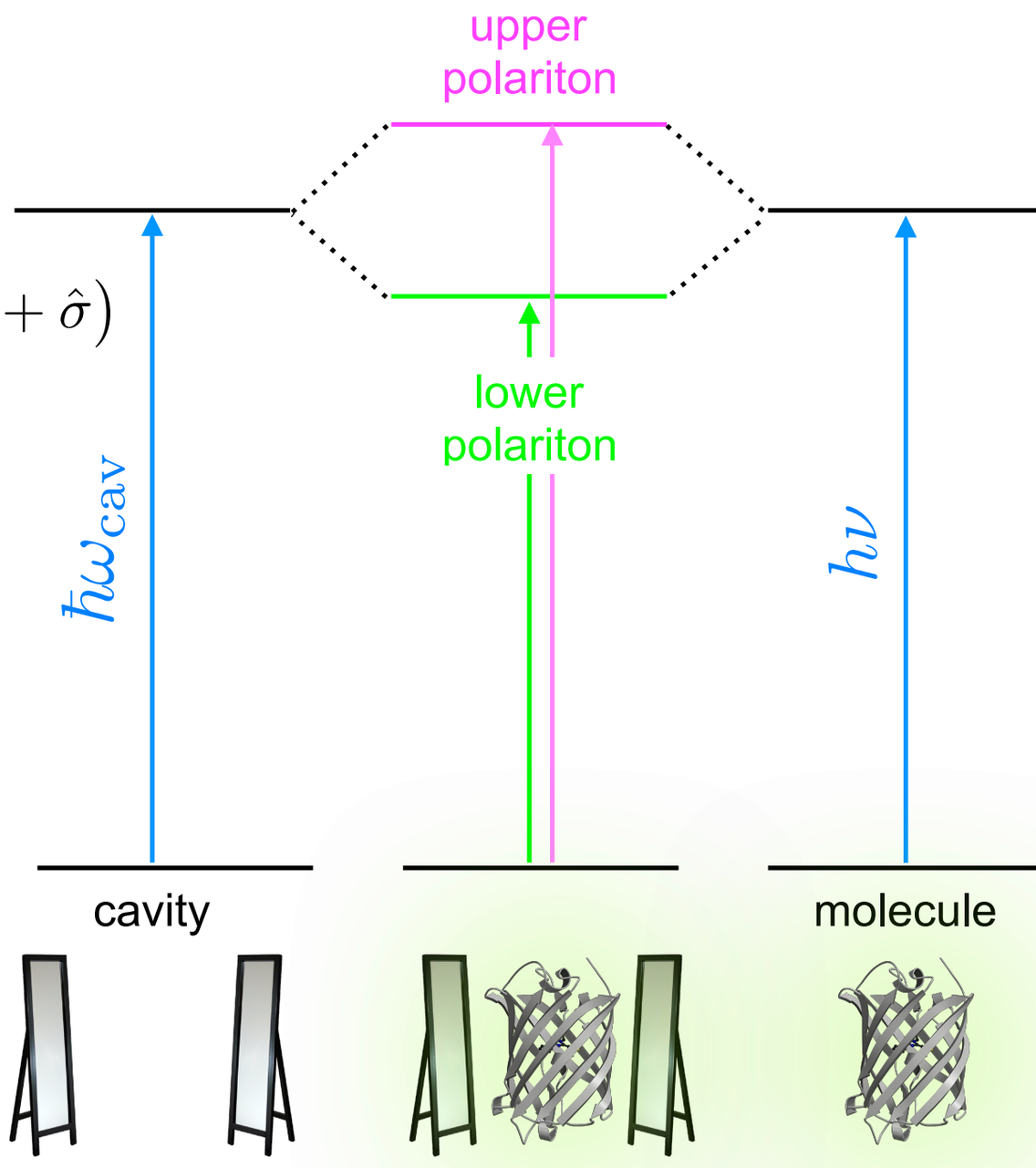
rotating wave approximation

$$\hbar\omega_{\mathrm{mol}} \sim \hbar\omega_{\mathrm{cav}}$$

$$\hat{a}^{\dagger}\hat{\sigma}^{\dagger} \approx \hat{a}\hat{\sigma} \approx 0$$



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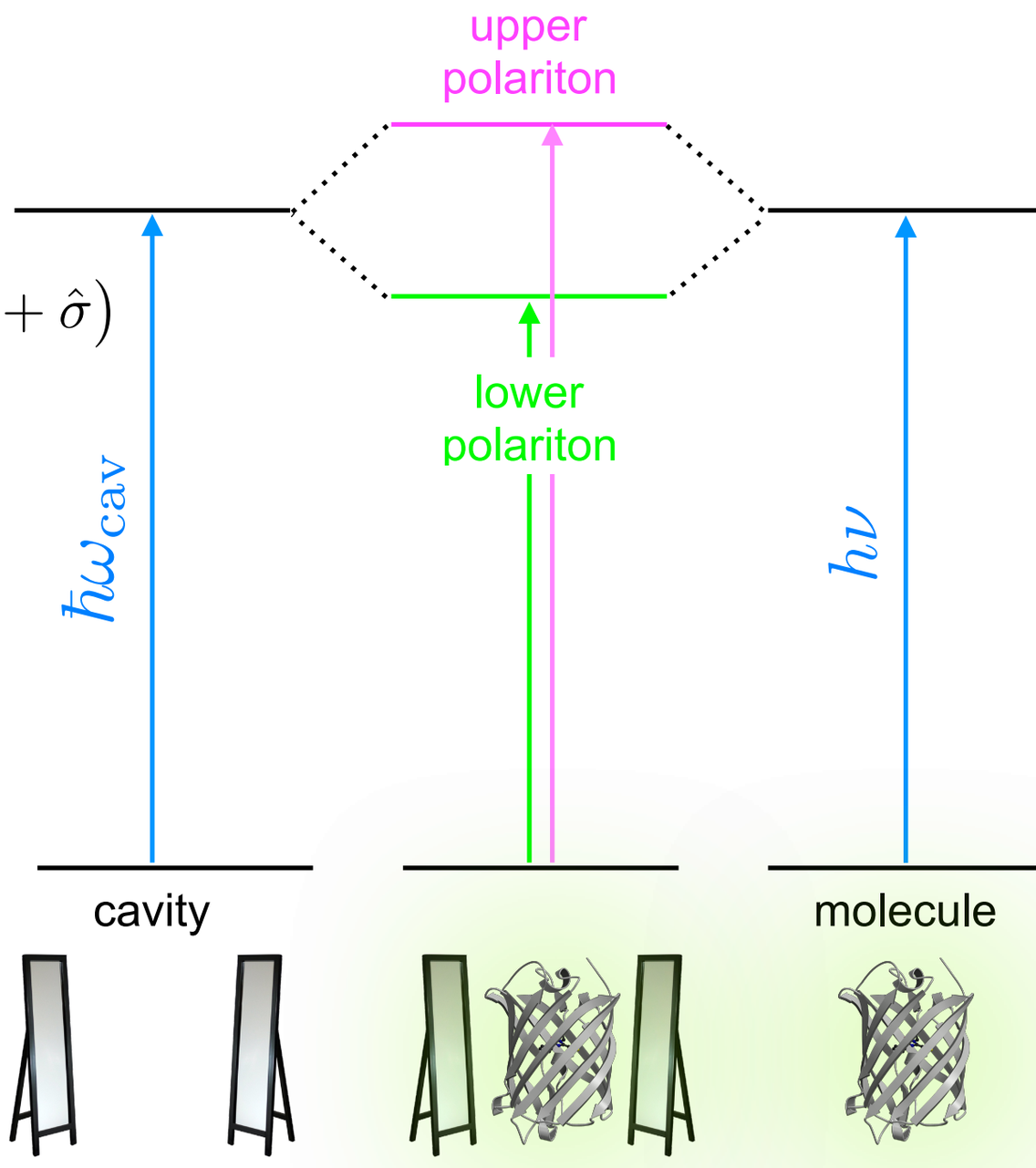


Jaynes-Cummings model (atoms)

$$\hat{H}_{\mathrm{JC}} = \hbar\omega_{\mathrm{mol}}\hat{\sigma}^{\dagger}\hat{\sigma} + \hbar\omega_{\mathrm{cav}}\hat{a}^{\dagger}\hat{a} + \hbar g\left(\hat{a}^{\dagger}\hat{\sigma} + \hat{a}\hat{\sigma}^{\dagger}\right)$$

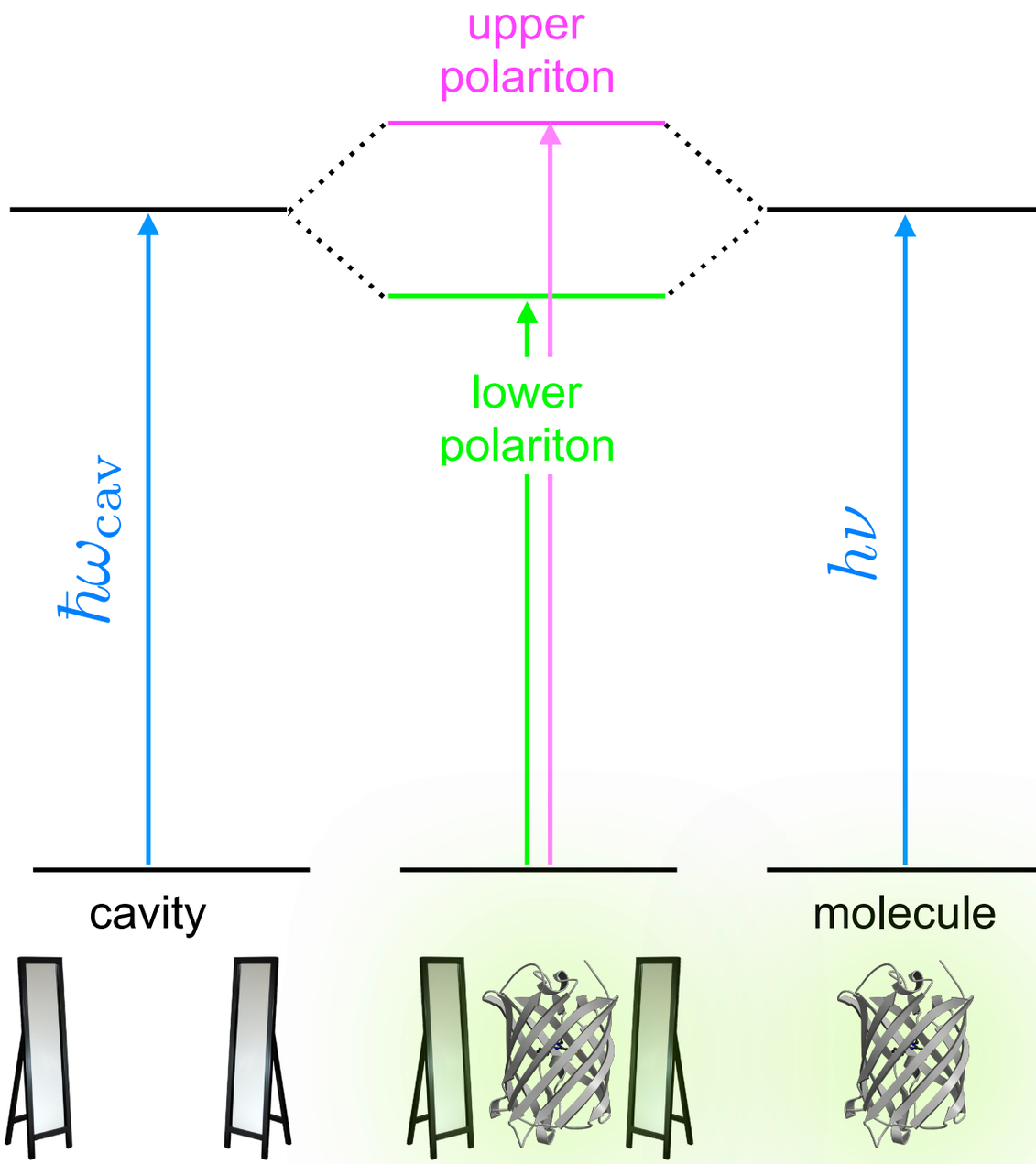
Why does the photochemistry change?

strong coupling with confined light (cavity QED)

light-matter Hamiltonian for one protein (Jaynes-Cummings)

in matrix form

$$\mathbf{H}_{\mathrm{JC}} = \begin{pmatrix} H_{11} & H_{21} \\ H_{12} & H_{22} \end{pmatrix}$$



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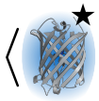
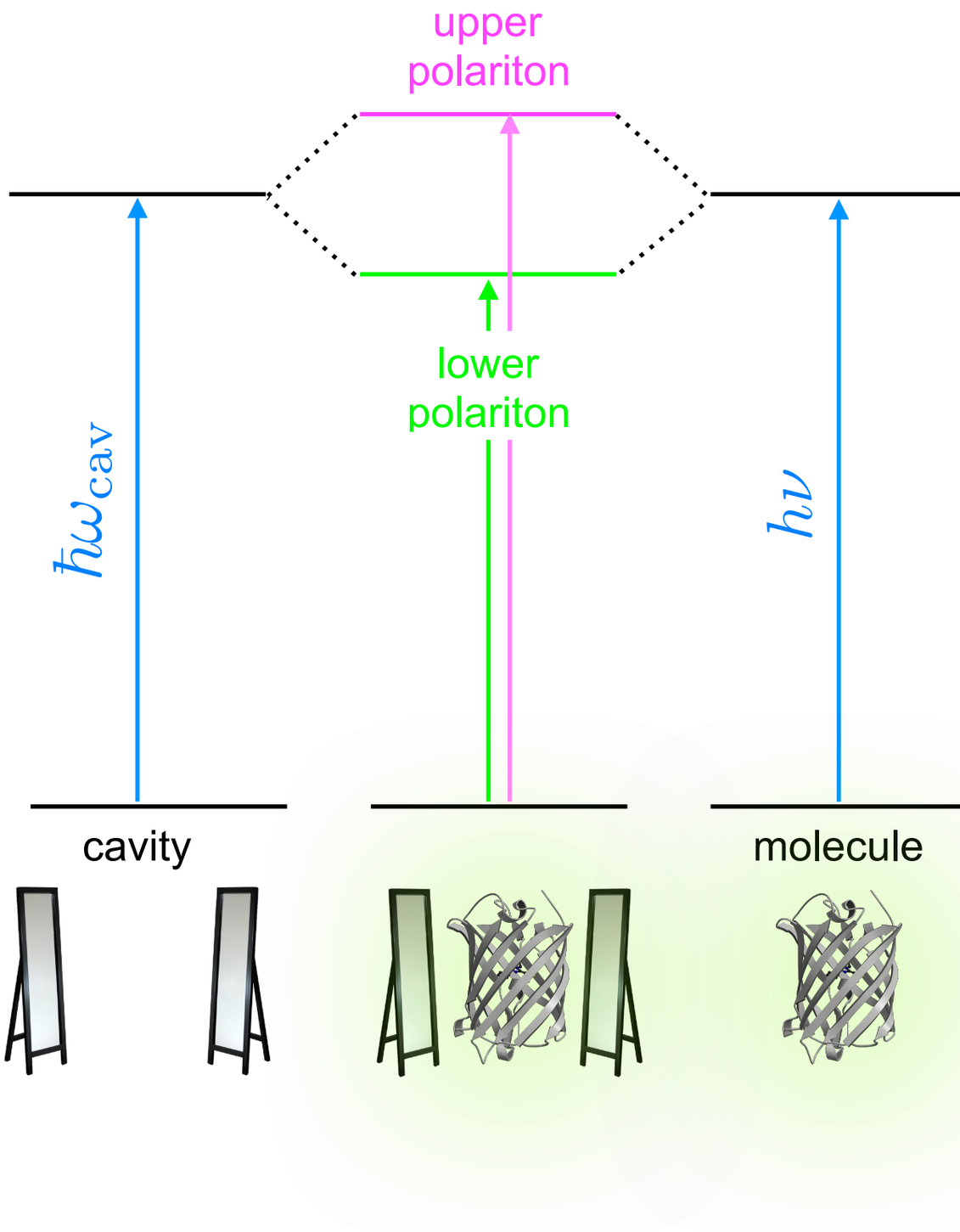
with matrix elements

$$H_{11} = \langle \text{  } | \hat{H} | \text{} \rangle \langle 0|0 \rangle$$

$$H_{22} = \langle \text{  } | \hat{H} | \text{} \rangle \langle 1^{\star}|1^{\star} \rangle + \hbar\omega_{\mathrm{cav}}$$



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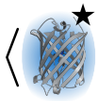
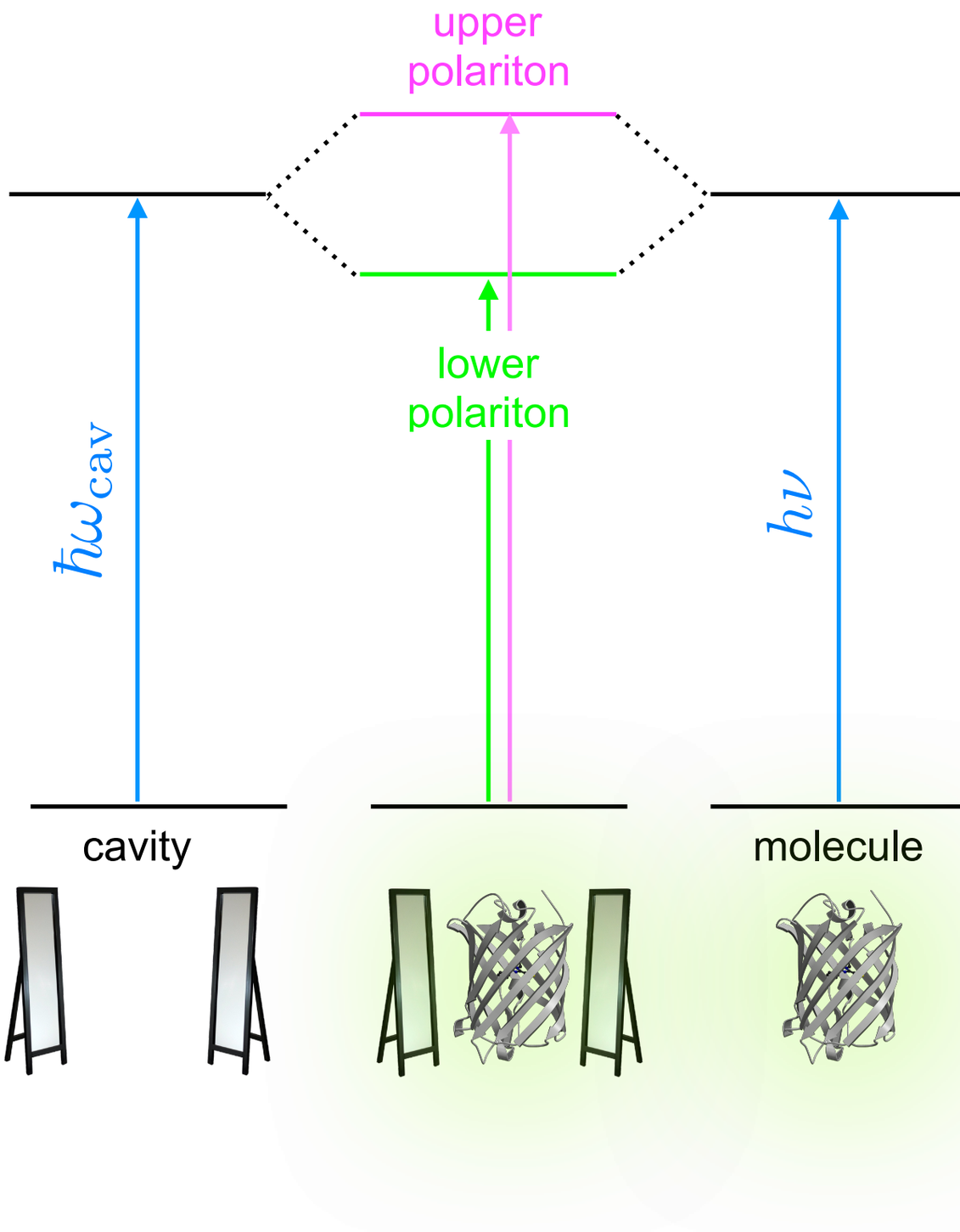
$$H_{11} = \langle \text{  } | \hat{H} | \text{} \rangle \langle 0|0 \rangle$$

$$H_{22} = \langle \text{  } | \hat{H} | \text{} \rangle \langle 1|1 \rangle + \hbar\omega_{\mathrm{cav}}$$

$$H_{12} = H_{21} = |\langle \text{  } | \hat{\mu} | \text{  } \rangle| \sqrt{\hbar\omega_{\mathrm{cav}}/\epsilon_0 V_{\mathrm{cav}}}$$



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$$H_{11} = V_{\mathrm{S}_1}(\mathbf{R})$$

$$H_{22} = V_{\mathrm{S}_0}(\mathbf{R}) + \hbar\omega_{\mathrm{cav}}$$

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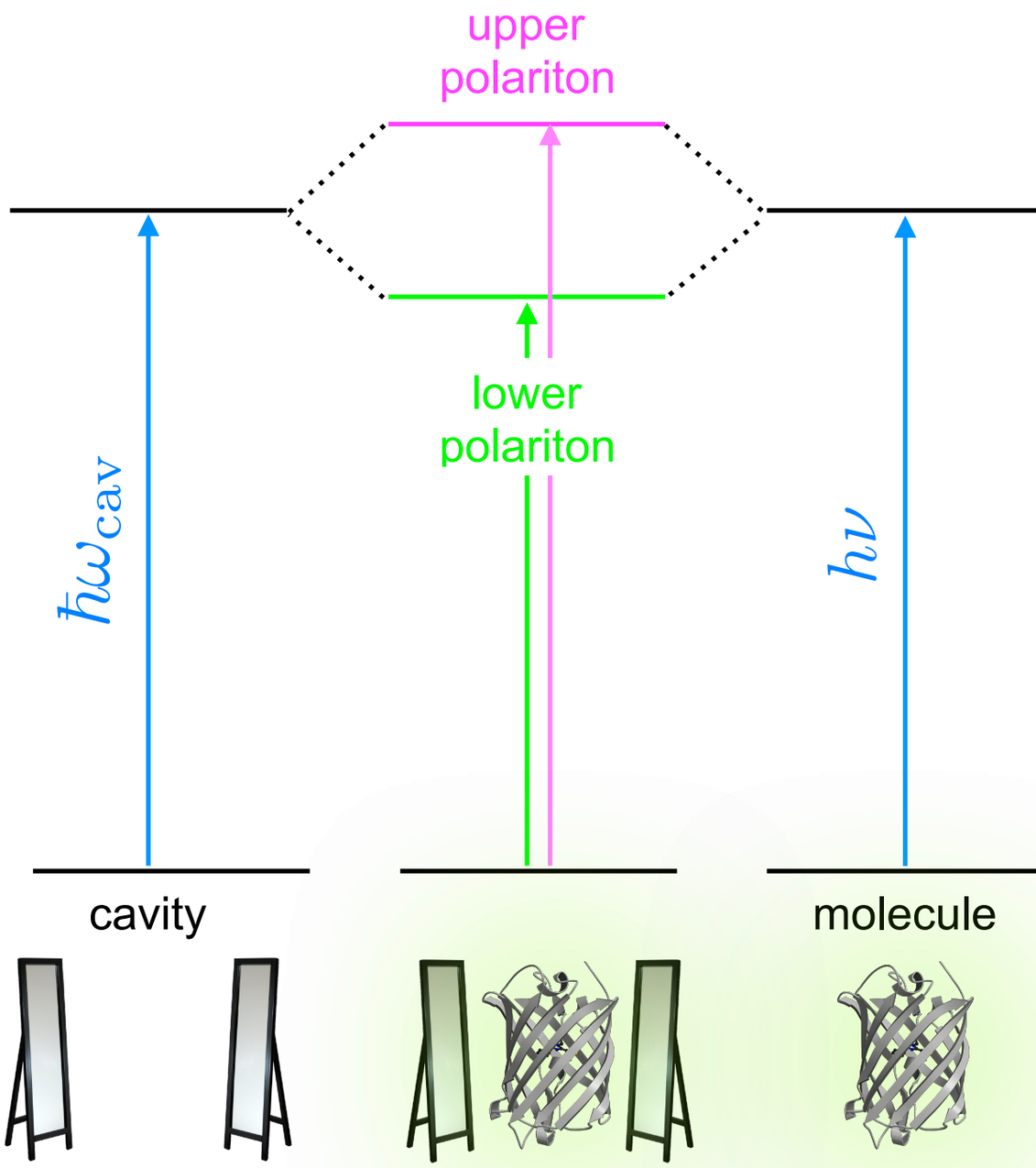

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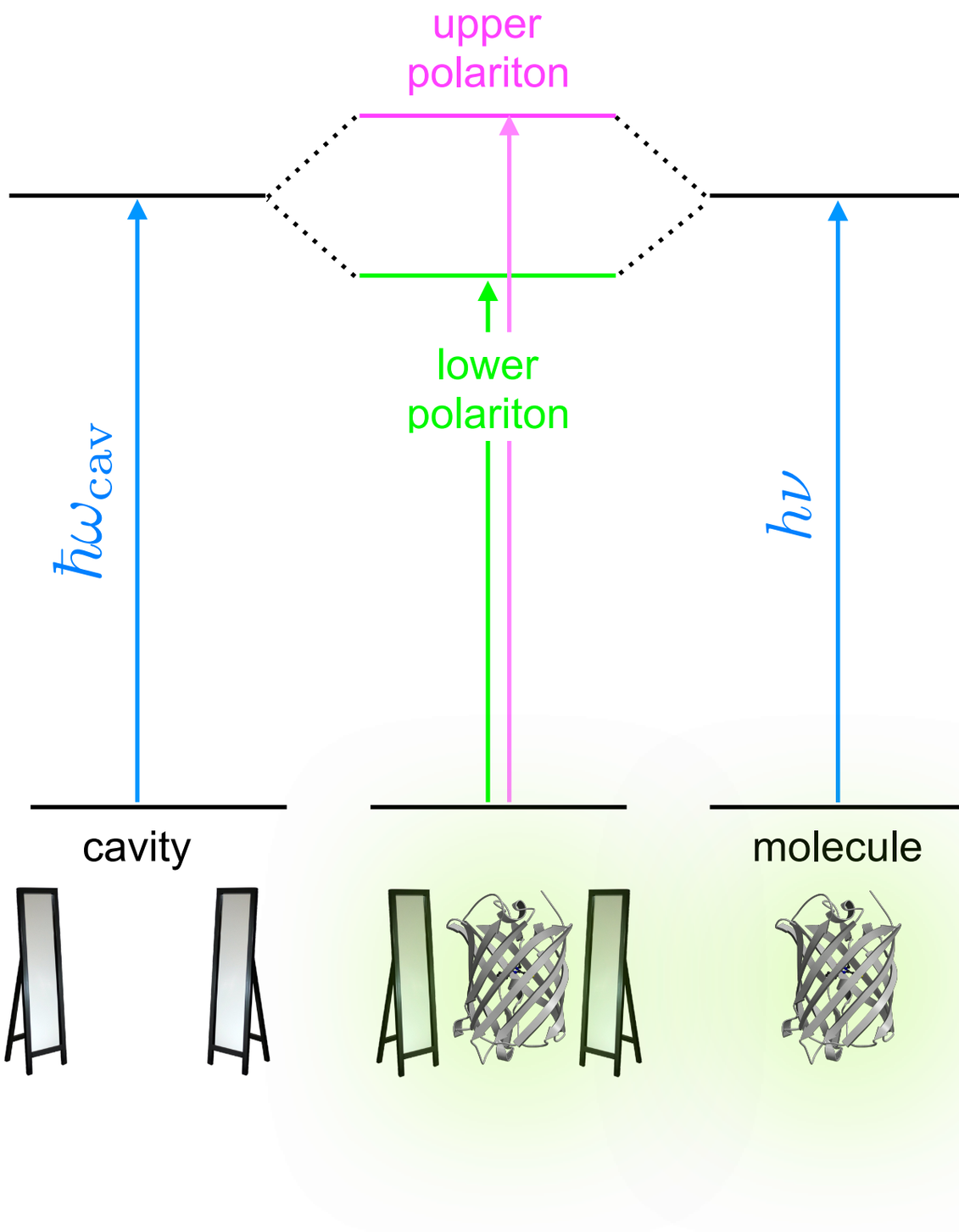
and solution

$$\Psi^K = \beta_1^K|\,\text{  }^{\star}\rangle|0\rangle + \alpha^K|\,\text{  }\rangle|1\rangle^{\star}$$

$$|\beta_1^K|^2 + |\alpha^L|^2 = 1$$



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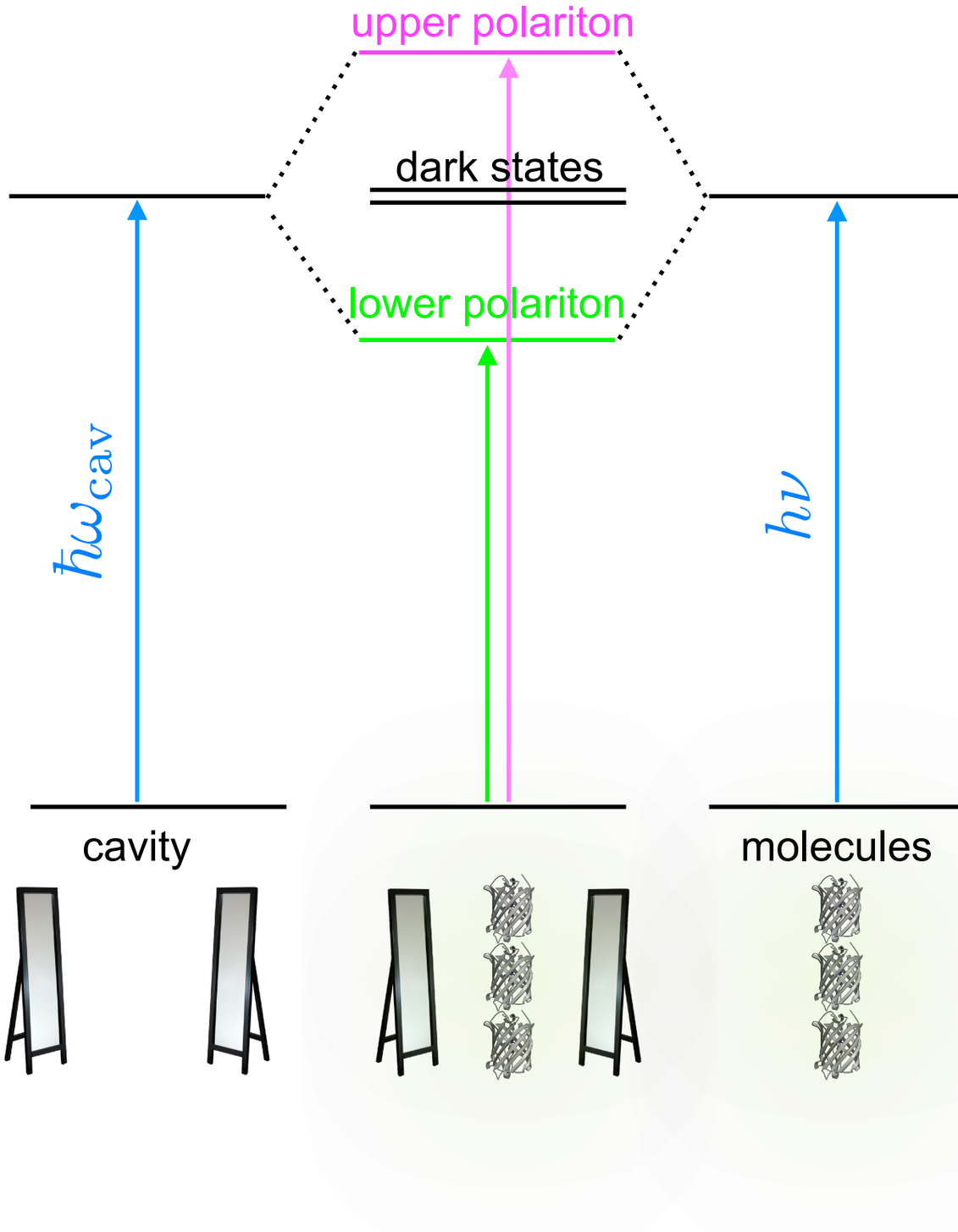
light-matter Hamiltonian for three proteins (Tavis-Cummings)

$$\mathbf{H}_{\mathrm{JC}} = \begin{pmatrix} H_{11} & 0 & 0 & H_{41} \\ 0 & H_{22} & 0 & H_{42} \\ 0 & 0 & H_{33} & H_{43} \\ H_{14} & H_{24} & H_{34} & H_{44} \end{pmatrix}$$



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$$H_{11} = \langle \text{🦠}^{\star}\text{🦠🦠}|\hat{H}|\text{🦠}^{\star}\text{🦠🦠}\rangle\langle 0|0\rangle$$

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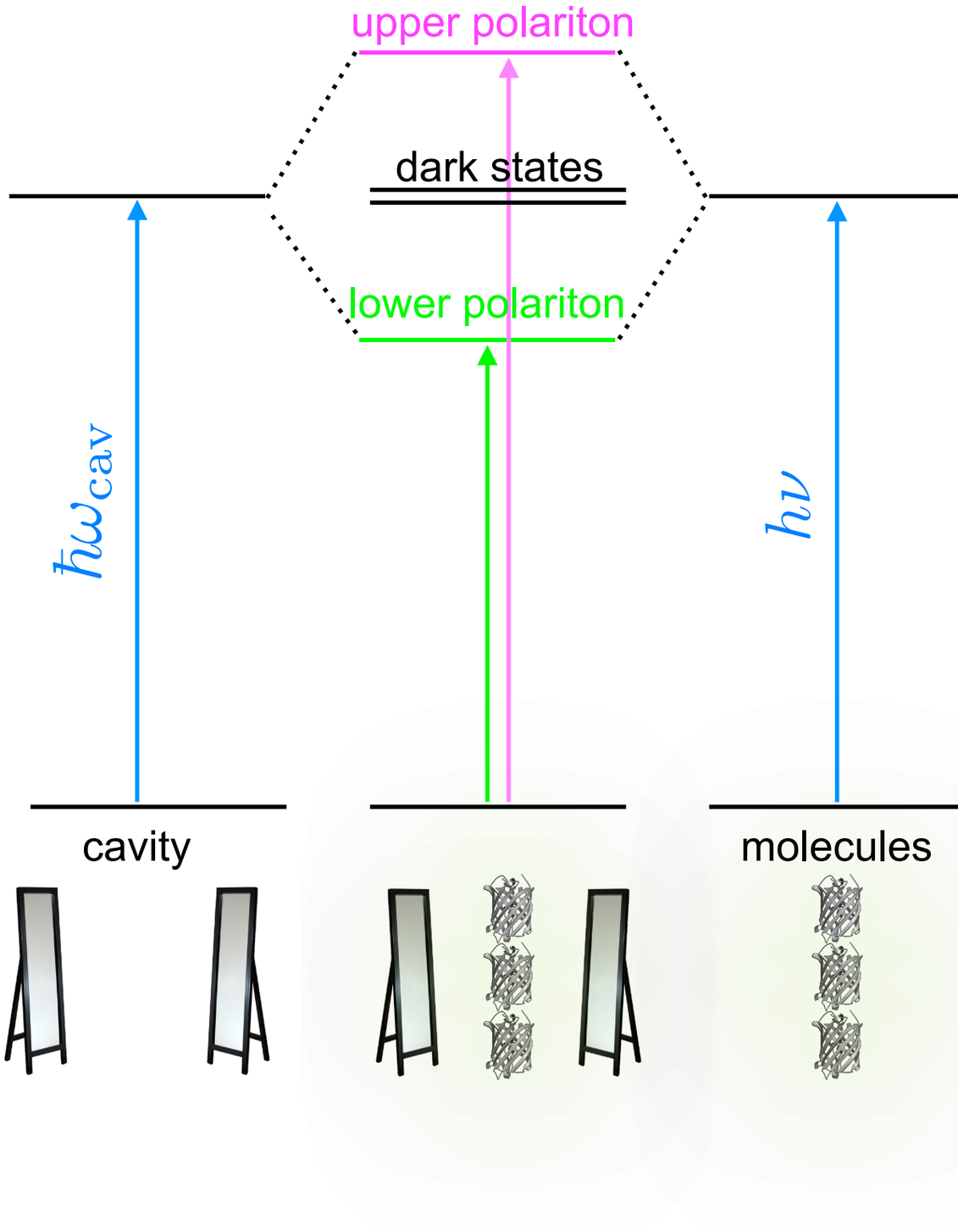

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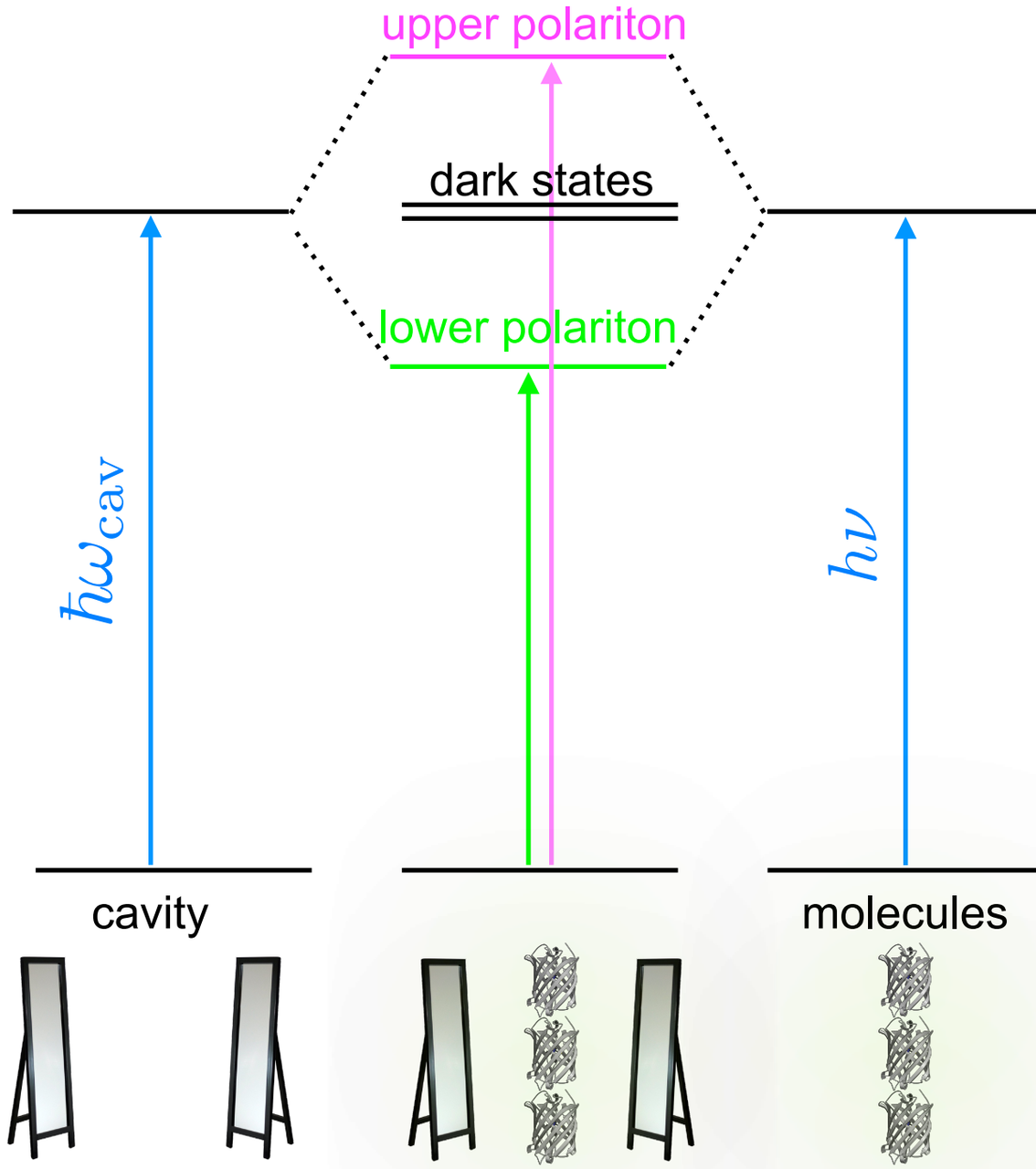
$$H_{4i} = H_{i4} = |\langle \text{🦠}^{\star}|\hat{\mu}|\text{🦠}\rangle|\sqrt{\hbar\omega_{\mathrm{cav}}/\epsilon_0 V_{\mathrm{cav}}}$$



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with matrix elements

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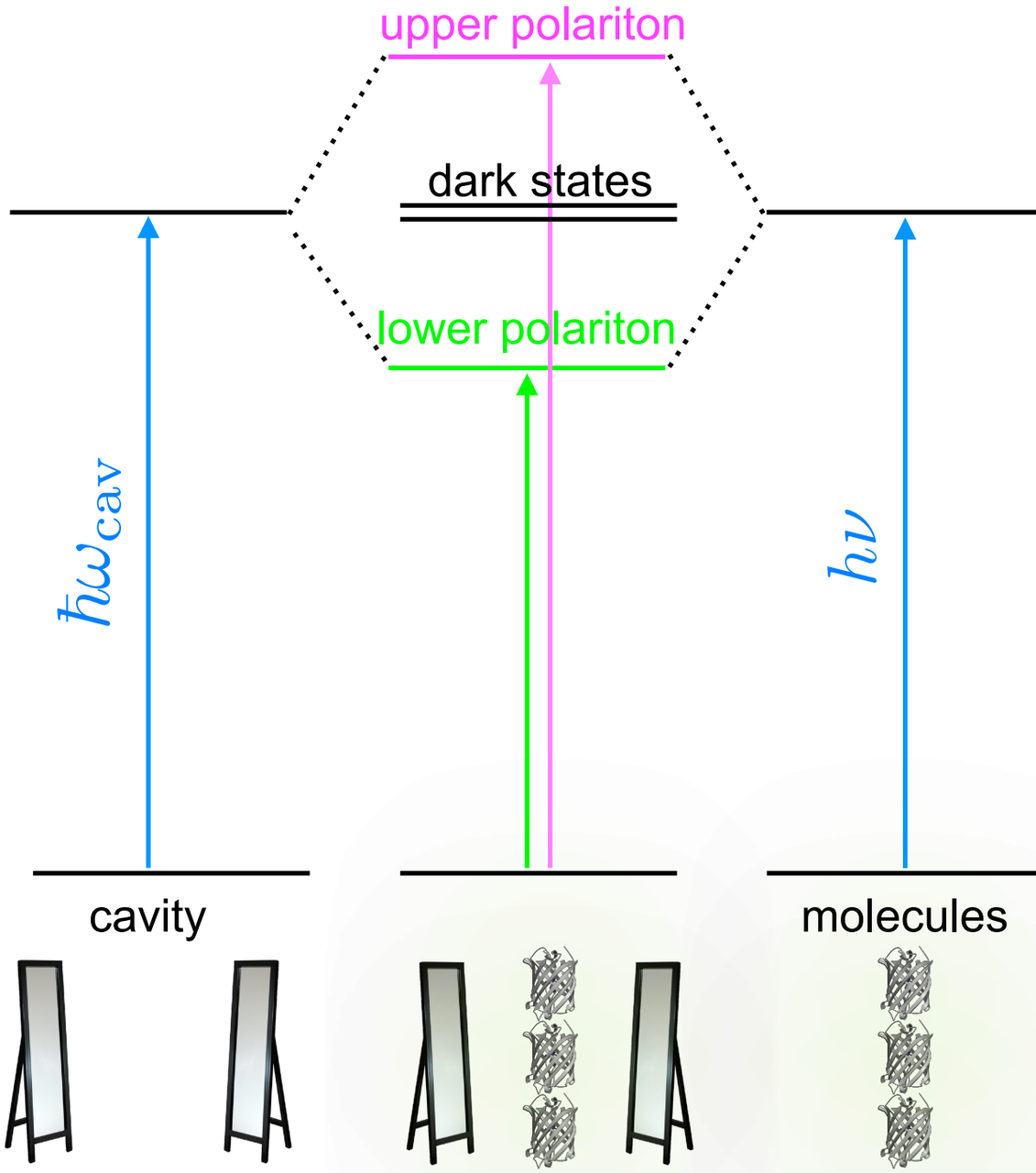

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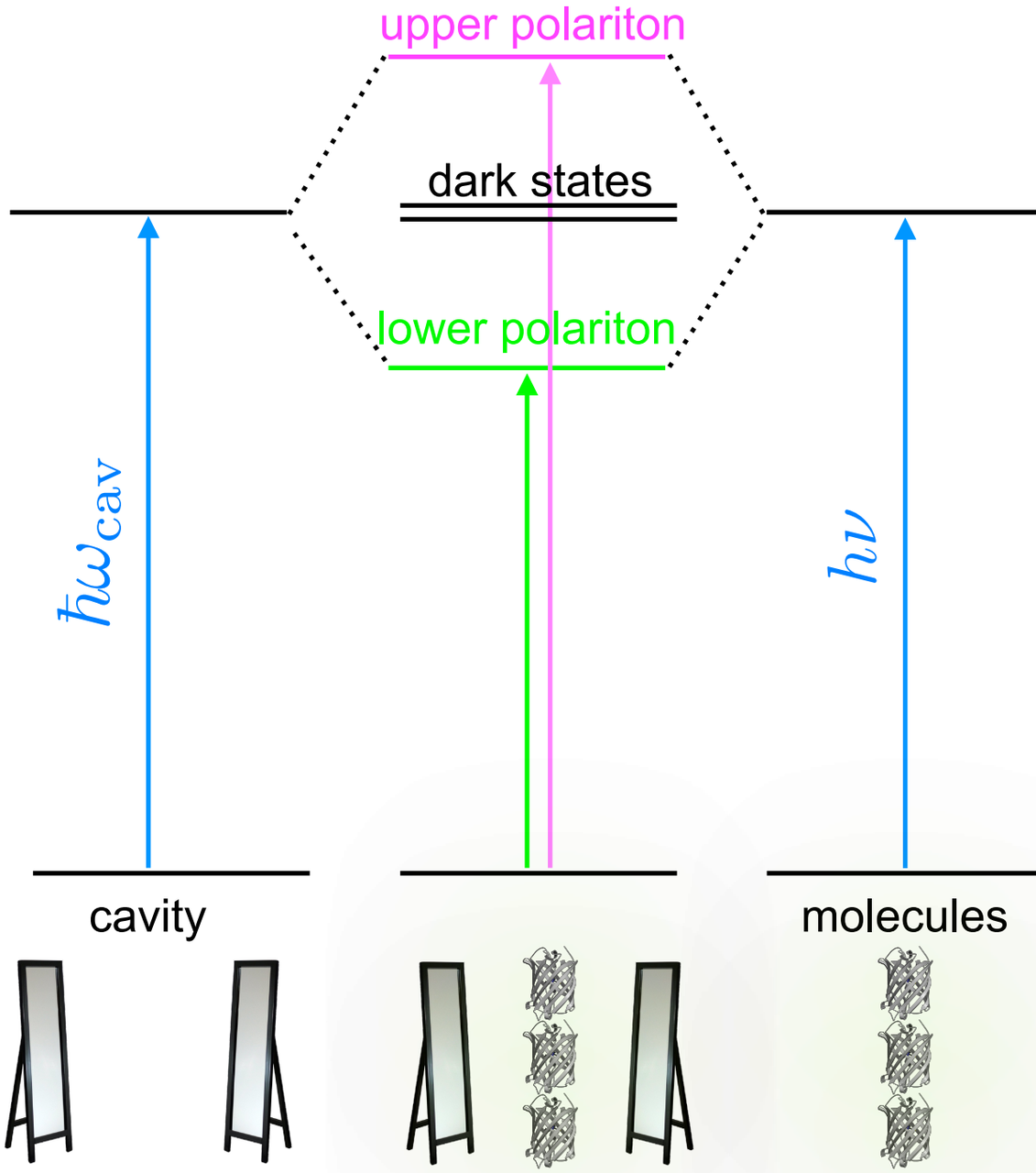

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$$H_{i4} = H_{4i} = |\boldsymbol{\mu}^{\mathrm{TDM}}_{\mathrm{S}_0\rightarrow\mathrm{S}_1}(\mathbf{R}_i)|\sqrt{\hbar\omega_{\mathrm{cav}}/\epsilon_0 V_{\mathrm{cav}}}$$

and solution

$$\Psi^K = \beta_1^K|\,\overset{\star}{\blacksquare}\,\blacksquare\,\blacksquare\,\rangle|0\rangle + \beta_2^K|\,\blacksquare\,\overset{\star}{\blacksquare}\,\blacksquare\,\rangle|0\rangle + \beta_3^K|\,\blacksquare\,\blacksquare\,\overset{\star}{\blacksquare}\,\rangle|0\rangle + \alpha^K|\,\blacksquare\,\blacksquare\,\blacksquare\,\rangle|\overset{\star}{1}\rangle$$

Why does the photochemistry change?

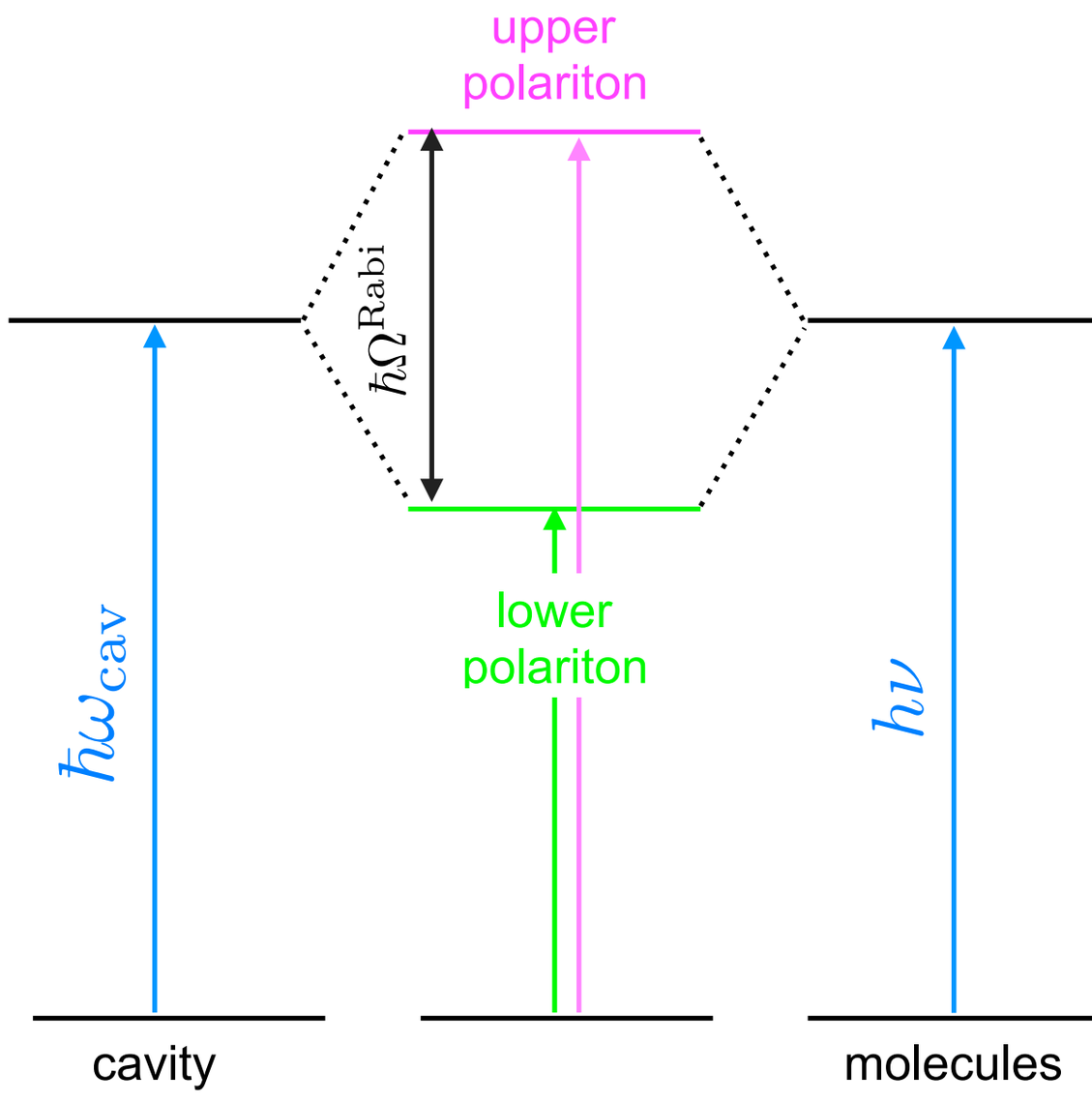
strong coupling with confined light (cavity QED)

two ‘bright’ polaritons

$$\Psi^K = \beta_1^K|\star\rangle|0\rangle + \beta_2^K|\star\rangle|0\rangle + \beta_3^K|\star\rangle|0\rangle + \alpha^K|\rangle|1^\star\rangle$$

Rabi splitting

$$\hbar\Omega^{\mathrm{Rabi}} \propto \sqrt{N/V_{\mathrm{cav}}}$$



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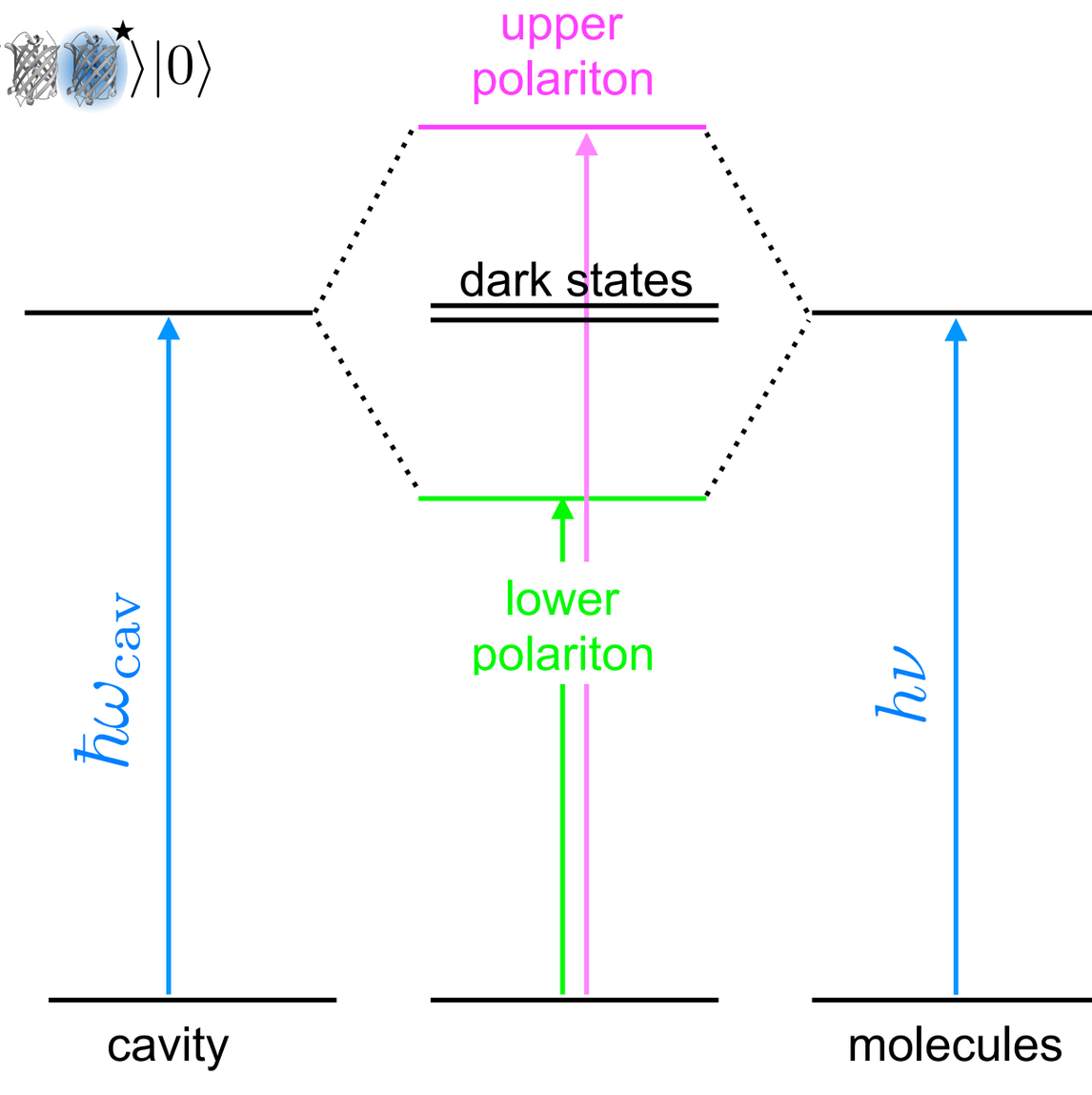
two ‘dark’ states (in general *N*-1)

$$\Psi^K = \beta_1^K|\star\,\,\rangle|0\rangle + \beta_2^K|\,\star\,\rangle|0\rangle + \beta_3^K|\,\,\star\rangle|0\rangle$$



Why does the photochemistry change?

strong coupling with confined light (cavity QED)

Mikael Kautto

two ‘bright’ polaritons

$$\Psi^K = \beta_1^K|\star\,\,\,\rangle|0\rangle + \beta_2^K|\,\star\,\rangle|0\rangle + \beta_3^K|\,\,\star\rangle|0\rangle + \alpha^K|\,\,\,\rangle|1\rangle$$

Eero Hulkko

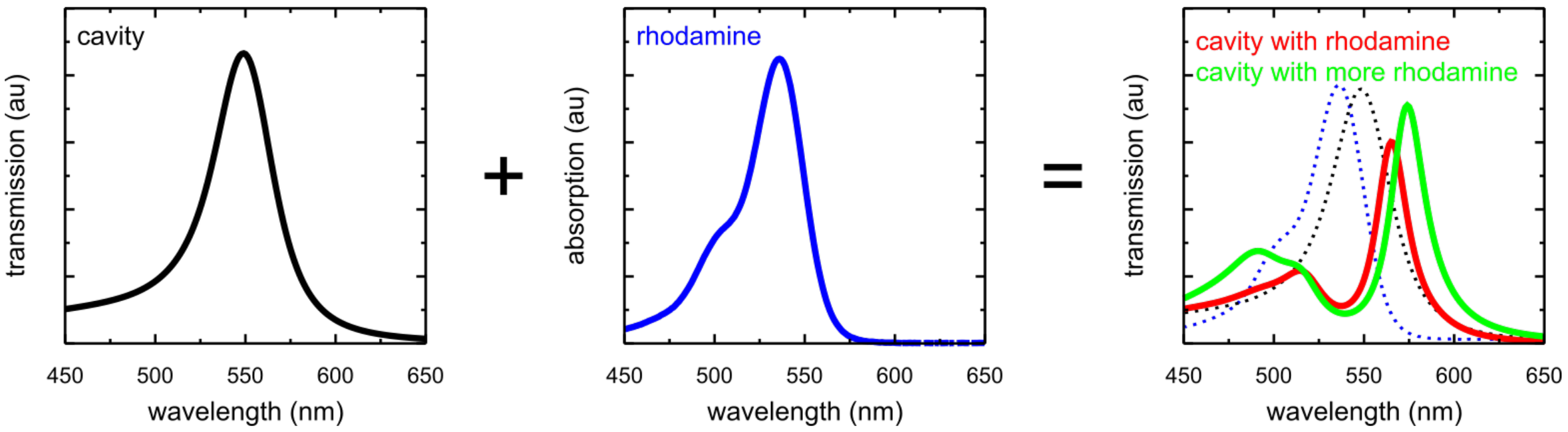
two ‘dark’ states (in general *N*-1)

$$\Psi^K = \beta_1^K|\star\,\,\,\rangle|0\rangle + \beta_2^K|\,\star\,\rangle|0\rangle + \beta_3^K|\,\,\star\rangle|0\rangle$$

Siim Pikker

double peak spectrum

example: cavity with rhodamine 6G



Simulating molecules in cavity

QED matrix elements

independent molecules interacting with cavity photon

$$H_{11} = V_{\mathrm{S}_1}(\mathbf{R}_1) + V_{\mathrm{S}_0}(\mathbf{R}_2) + V_{\mathrm{S}_0}(\mathbf{R}_3)$$

$$H_{22} = V_{\mathrm{S}_0}(\mathbf{R}_1) + V_{\mathrm{S}_1}(\mathbf{R}_2) + V_{\mathrm{S}_0}(\mathbf{R}_3)$$

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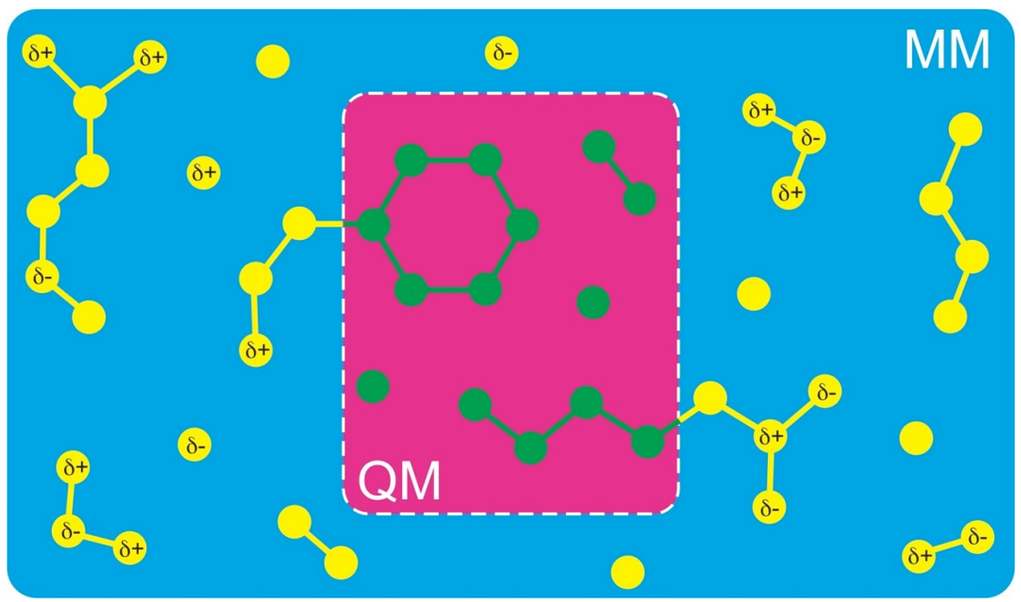
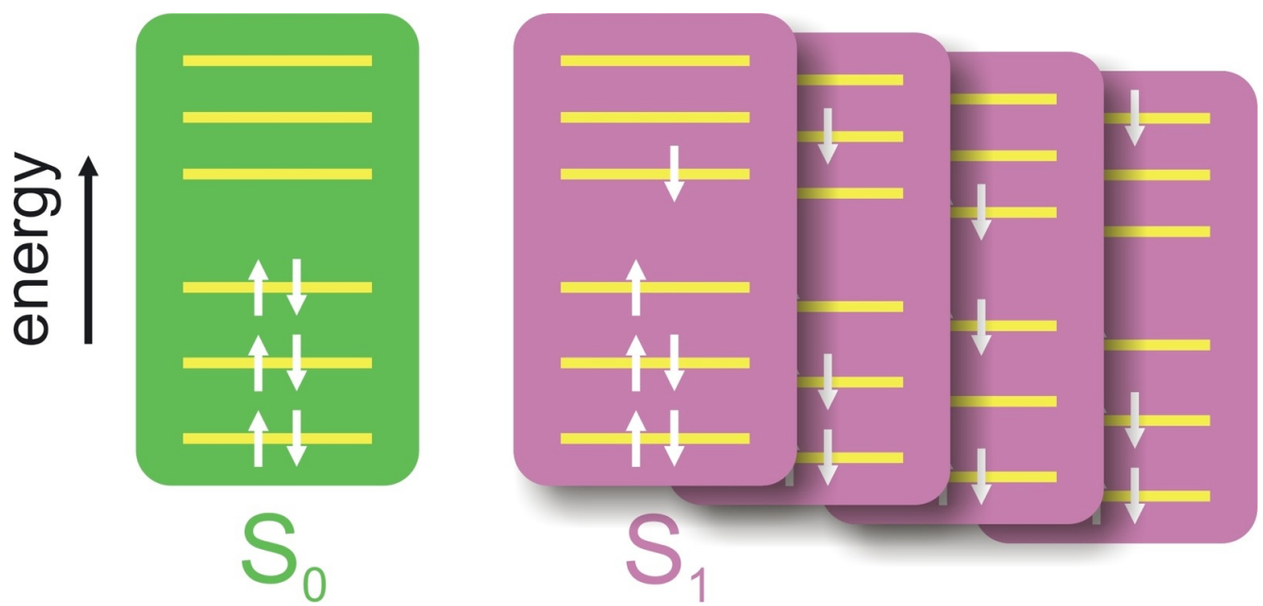
QM/MM energies in ground (S_0) and excited (S_1) states





Boggio-Pasqua *et al*. *Phys. Chem. Chem. Phys.* 14 (2012): 7912

Simulating molecules in cavity

QED matrix elements from QM/MM calculations

independent molecules interacting with cavity photon

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diagonalize

two ‘bright’ <u>delocalised</u> polariton states *N*-1 ‘dark’ states

$$\Psi^K = \beta_1^K|\text{🧊}^\star\text{🧊🧊}\rangle|0\rangle + \beta_2^K|\text{🧊}\,\text{🧊}^\star\text{🧊}\rangle|0\rangle + \beta_3^K|\text{🧊🧊}\,\text{🧊}^\star\rangle|0\rangle + \alpha^K|\text{🧊🧊🧊}\rangle|1^\star\rangle$$

Hellmann-Feyman forces on the atoms: on-the-fly molecular dynamics

$$\mathbf{F}_i^K = -\langle\Psi^K|\nabla_{\mathbf{x}_i}\mathbf{H}^{\mathrm{cav}}|\Psi^K\rangle$$

Simulating molecules in cavity

QED matrix elements from QM/MM calculations

independent molecules interacting with cavity photon

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Hellmann-Feyman forces on the atoms: on-the-fly molecular dynamics

$$\mathbf{F}_i^K = -\langle\Psi^K|\nabla_{\mathbf{x}_i}\mathbf{H}^{\mathrm{cav}}|\Psi^K\rangle$$

transitions between states: surface hopping / Ehrenfest

www.gromacs.org

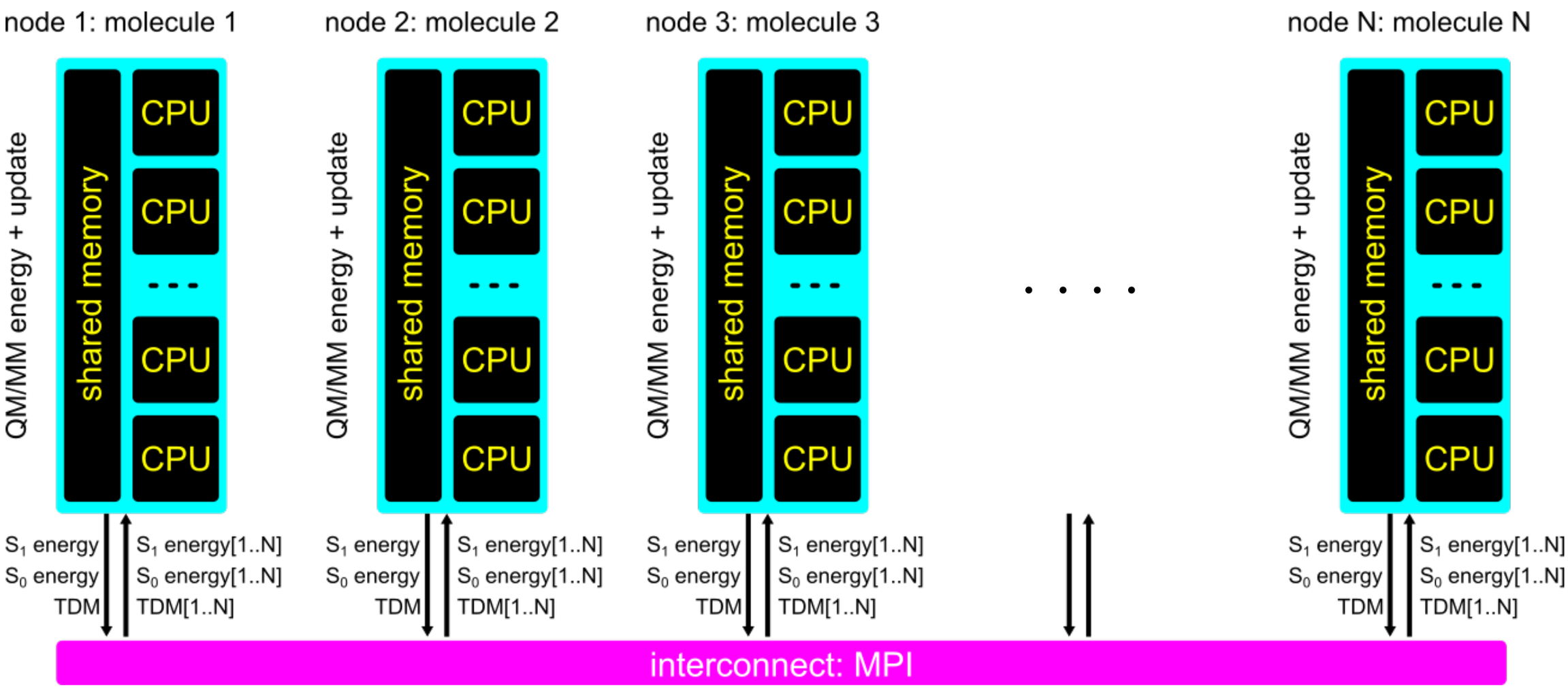
Simulating molecules in cavity

implementation in Gromacs

linear scaling Tavis-Cummings QM/MM model

Gromacs uses as many MPI nodes as there are molecules

Terachem/Gaussian/.. uses all shared memory threads on node



Luk, Feist, Toppari, Groenhof, *J. Chem. Theory Comput.* 13 (2017) 4324

Simulating molecules in cavity

implementation in Gromacs

Sisu.csc.fi: 1688 TFlop/s

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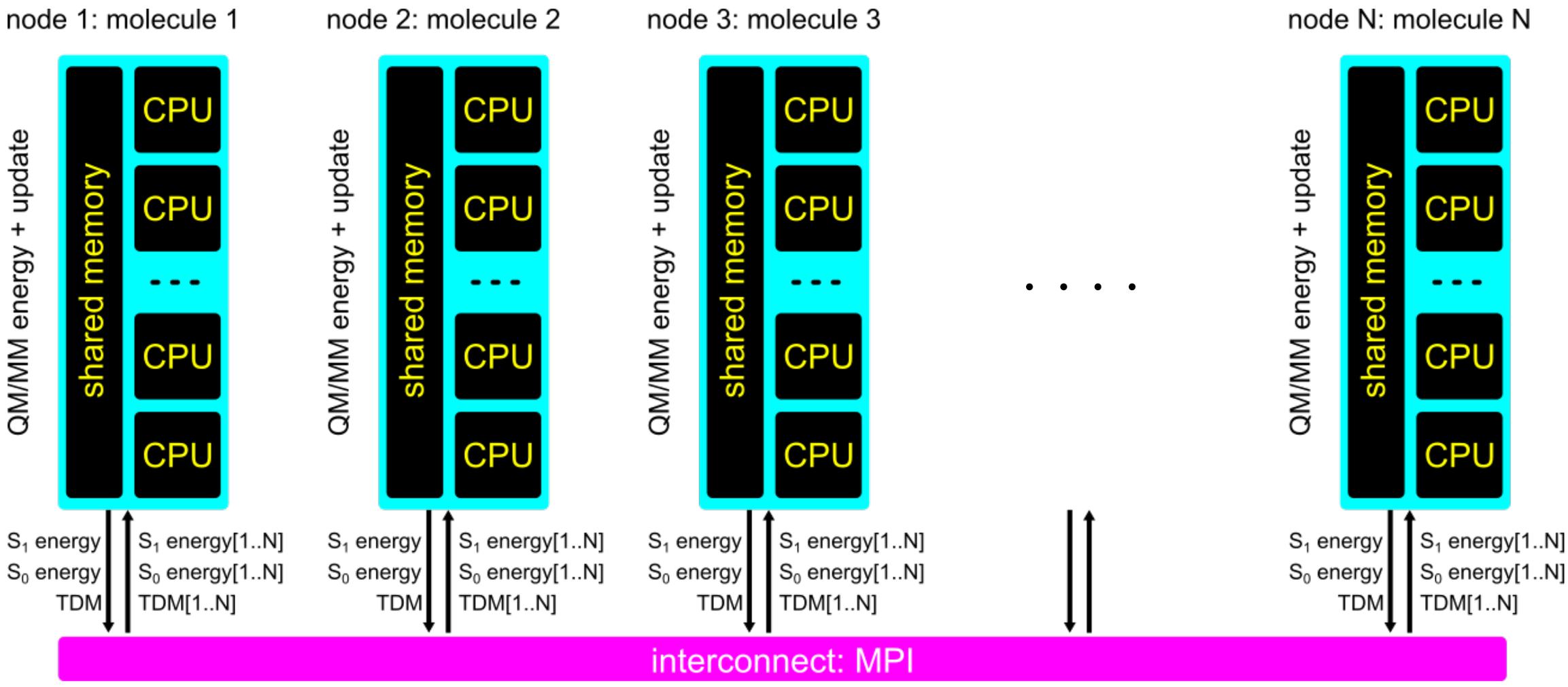


new world record: 1,600 rhodamine dyes in solution?

43,200 QM / 17,700,800 MM atoms on 1,600 nodes (38,400 CPUs)

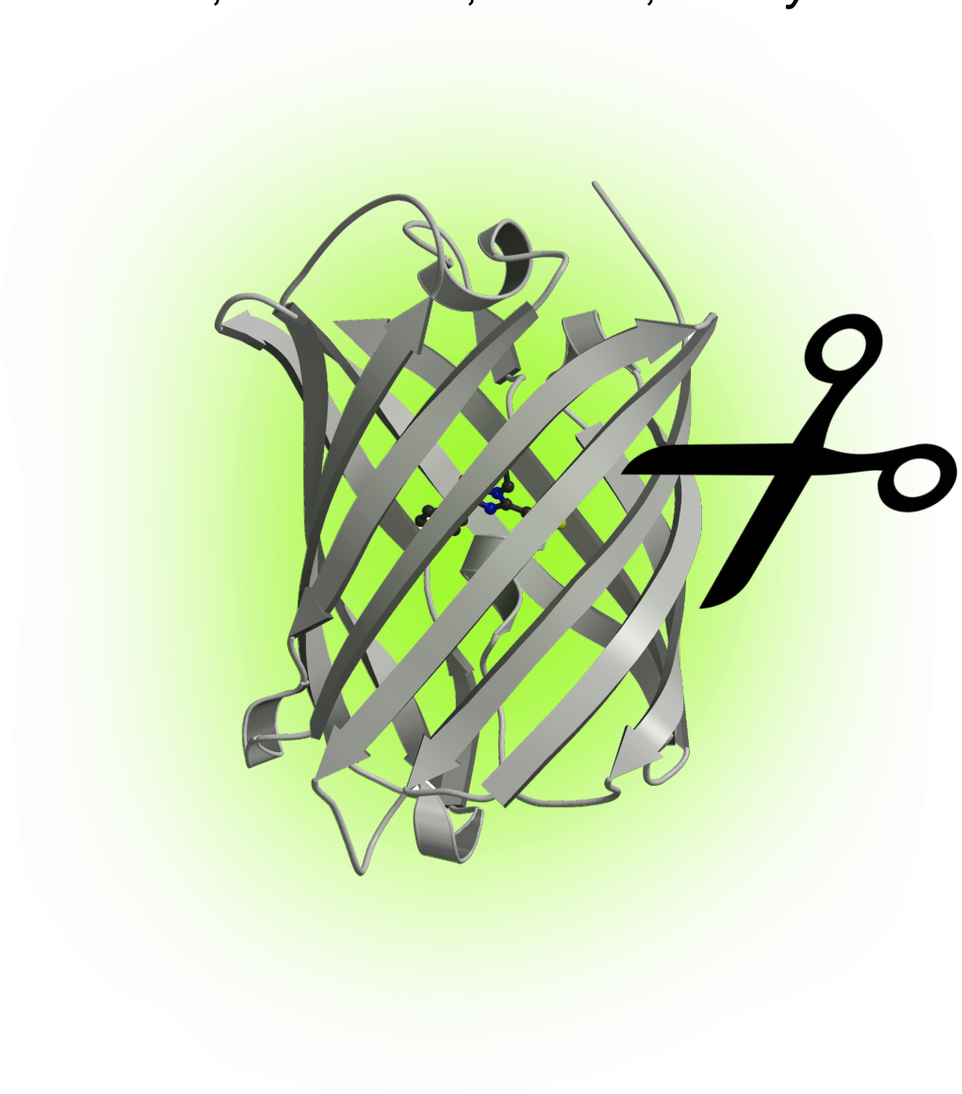
Manipulating photo-chemistry with mirrors

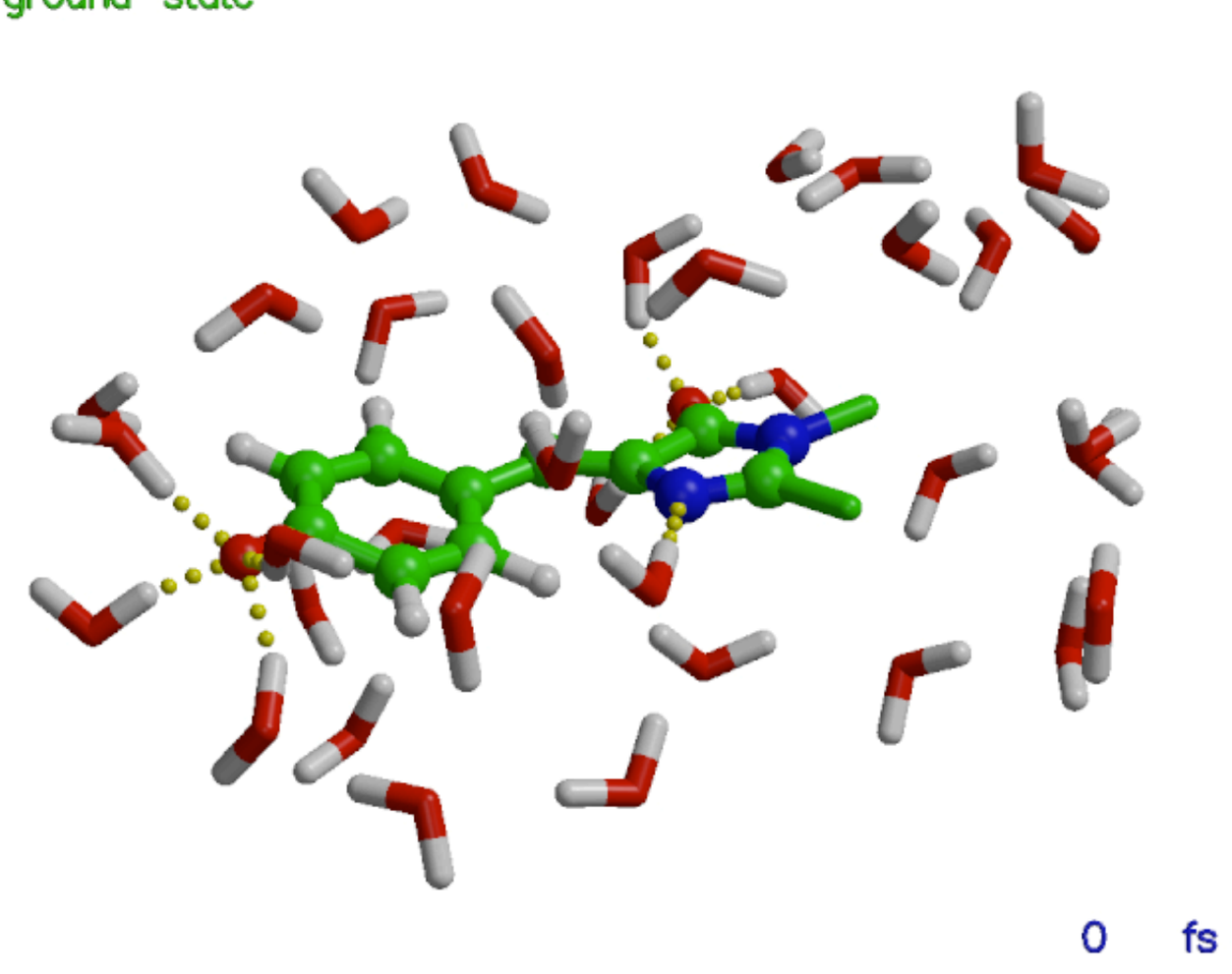
GFP chromophore in water

no fluorescence: dark

Dmitry Morozov

Webber, Litvinenko, Meech, *J. Phys. Chem. B* **105** (2001) 8036





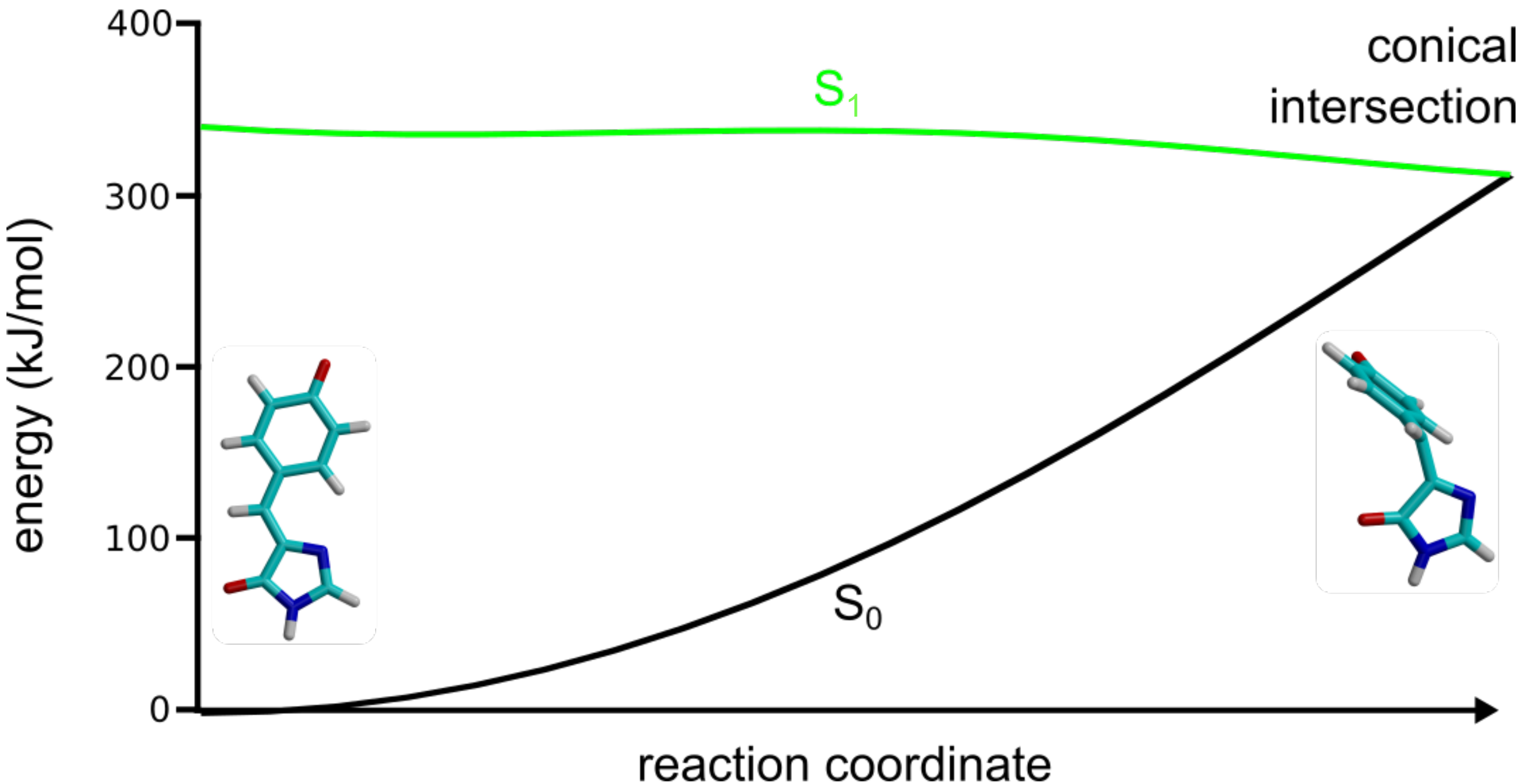
CASSCF(6,6)/3-21G//SPC & CASSCF(12,11)/cc-pVDZ//EFP

Morozov & Groenhof, *Angew. Chem. Int. Ed.* **55** (2016) 576-578

Manipulating photo-chemistry with mirrors

GFP chromophore in water

no fluorescence: dark

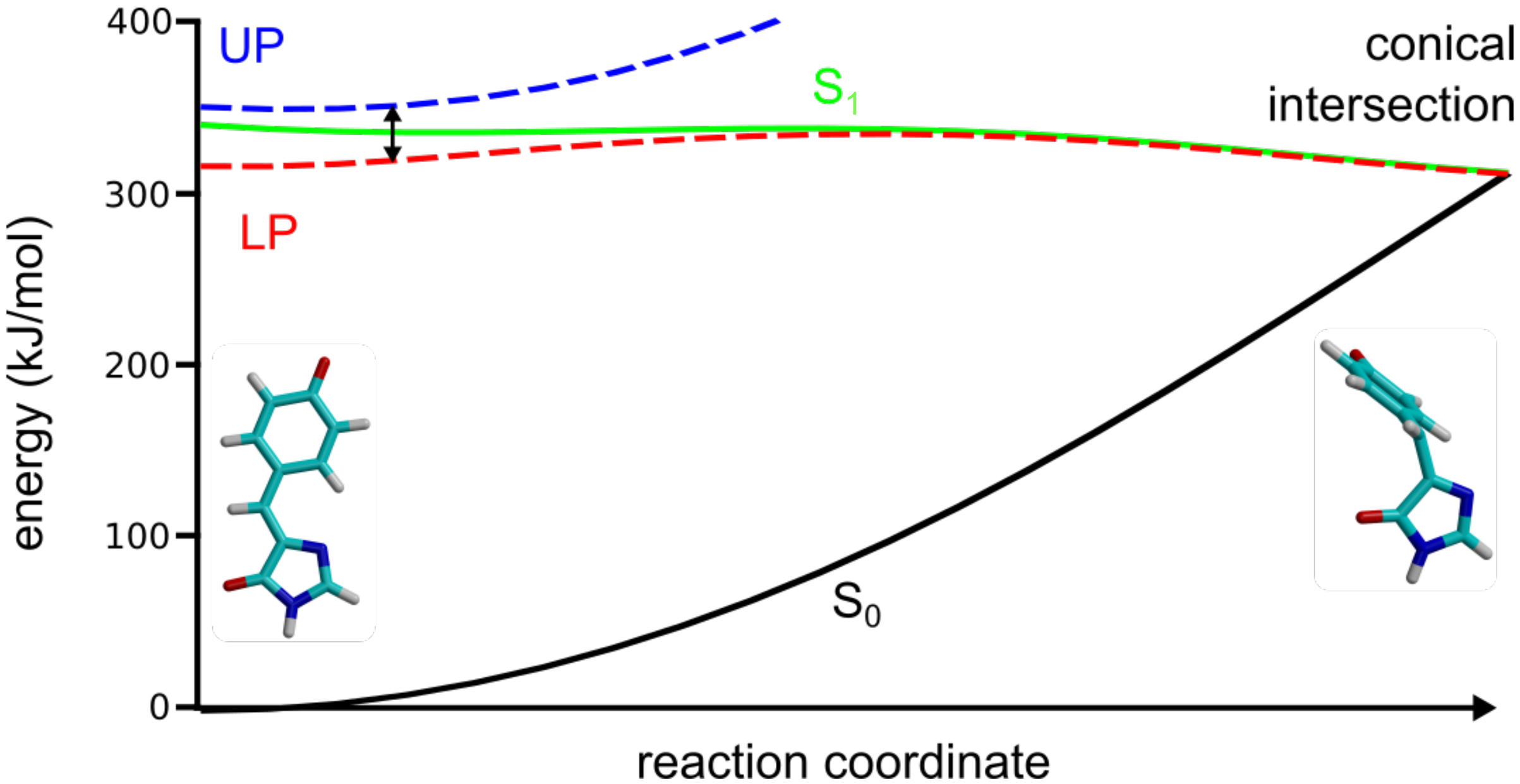


Manipulating photo-chemistry with mirrors

one GFP chromophore in water in a cavity

strong coupling to confined light?

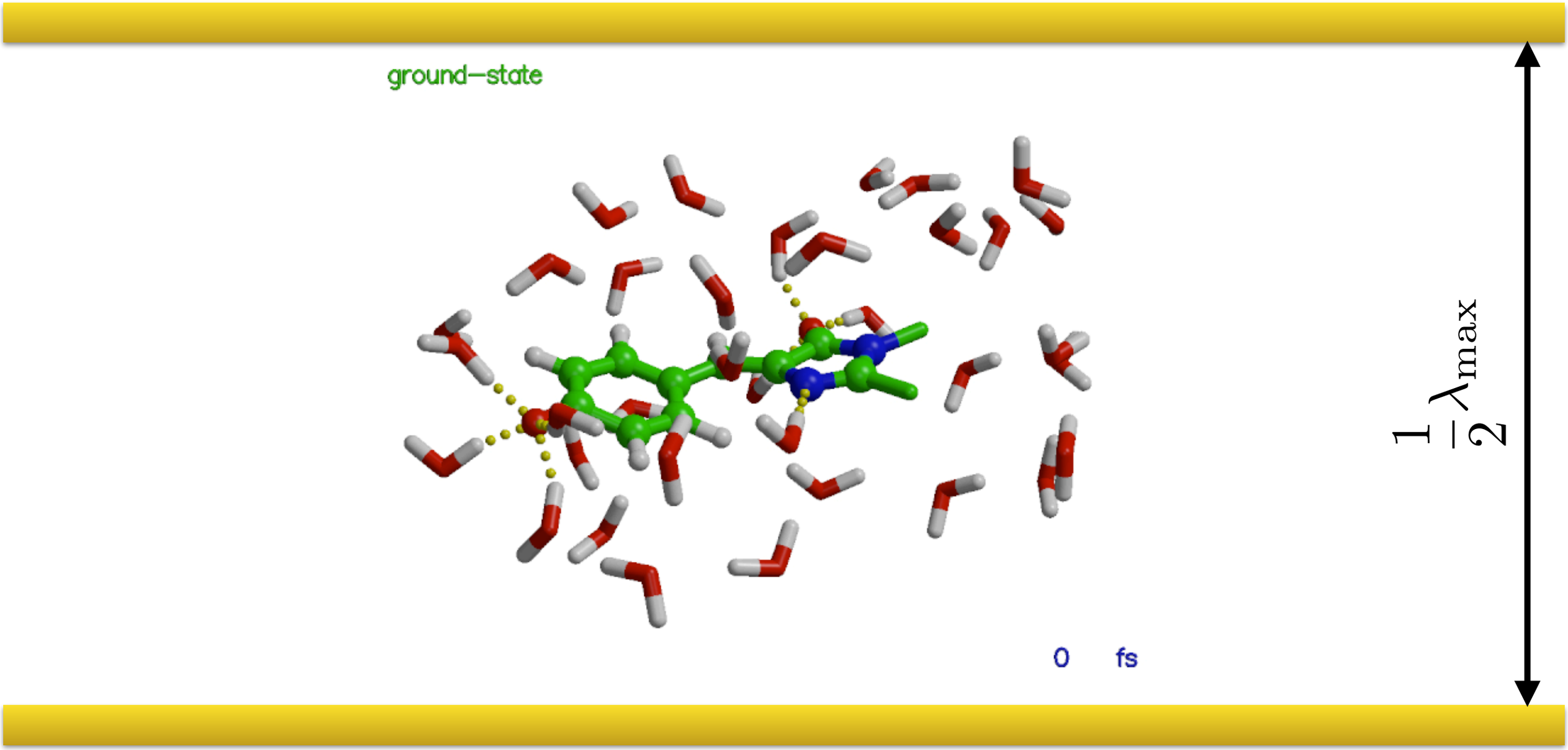
minimum on lower polariton surface



Manipulating photo-chemistry with mirrors

one GFP chromophore in water in a cavity

no fluorescence: dark

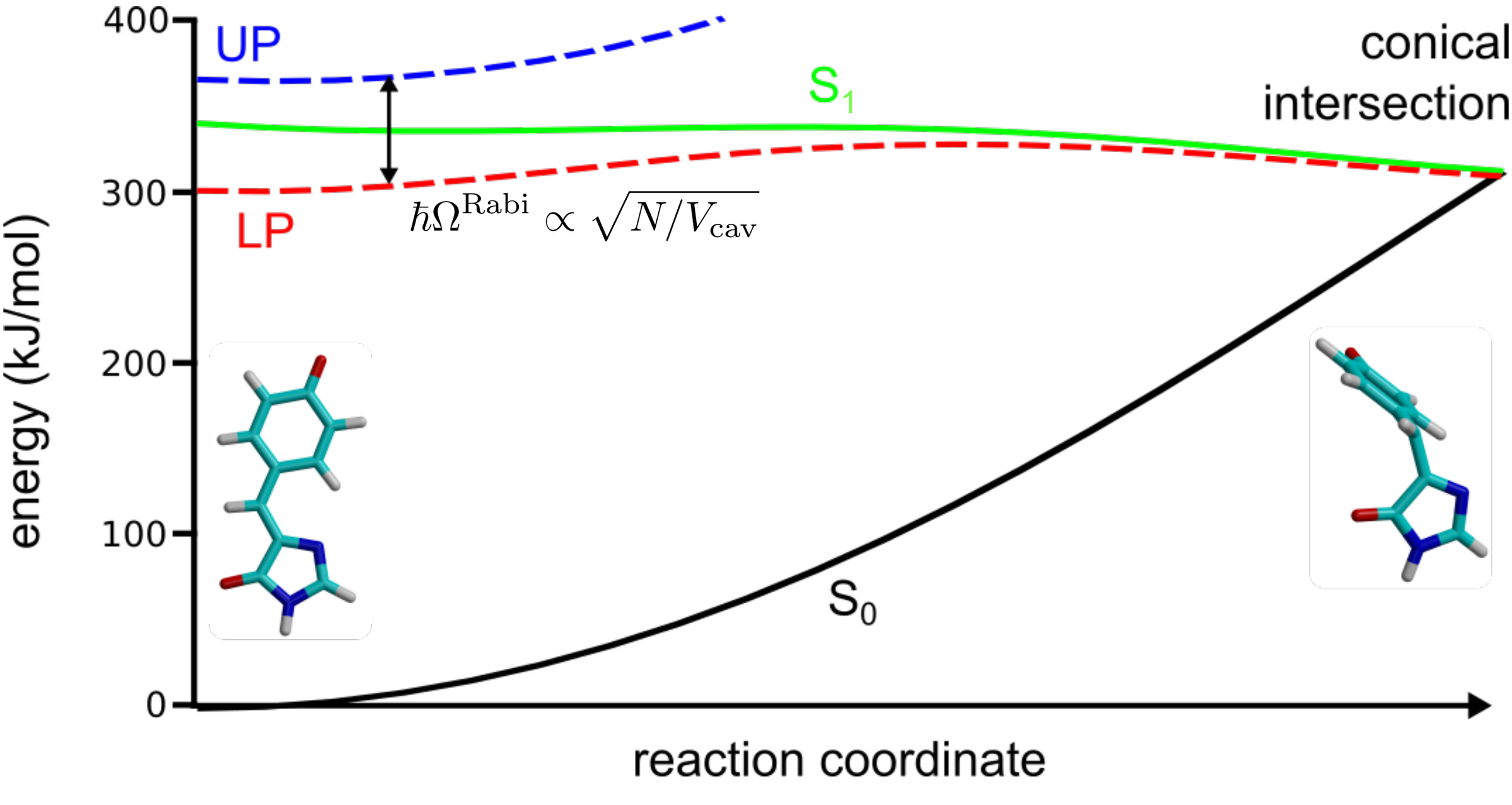


Manipulating photo-chemistry with mirrors

four GFP chromophores in water in a cavity

two times stronger coupling with confined light

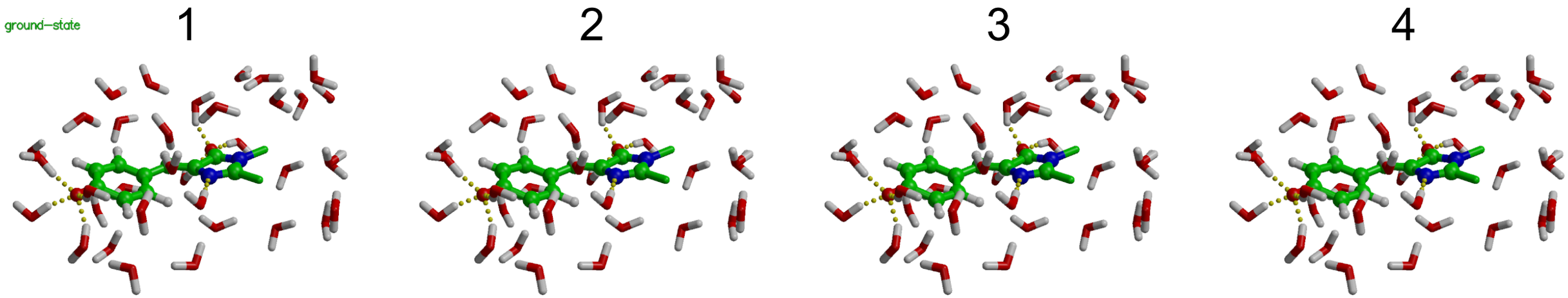
deeper minimum on lower polariton surface



Manipulating photo-chemistry with mirrors

four GFP chromophores in water in a cavity

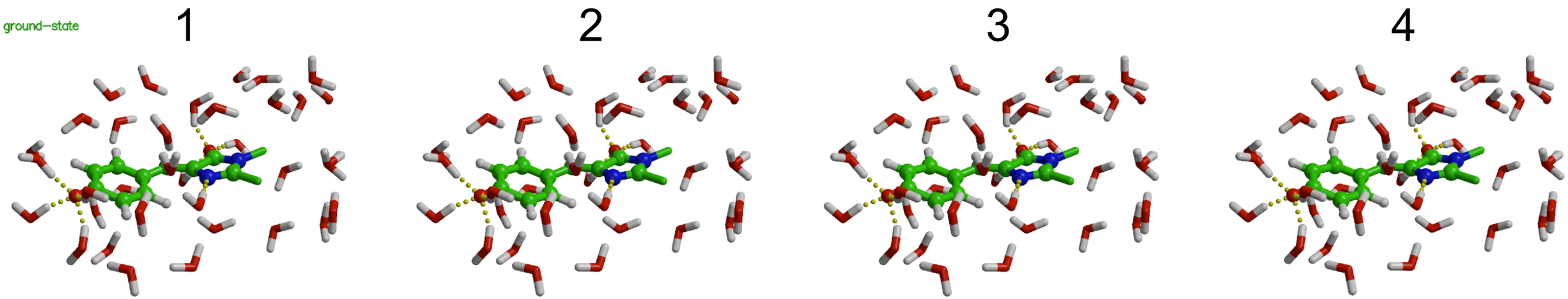
trapped: fluorescence



Manipulating photo-chemistry with mirrors

four GFP chromophores in water in a cavity

trapped: fluorescence



Manipulating photo-chemistry with mirrors

four GFP chromophores in water in a cavity

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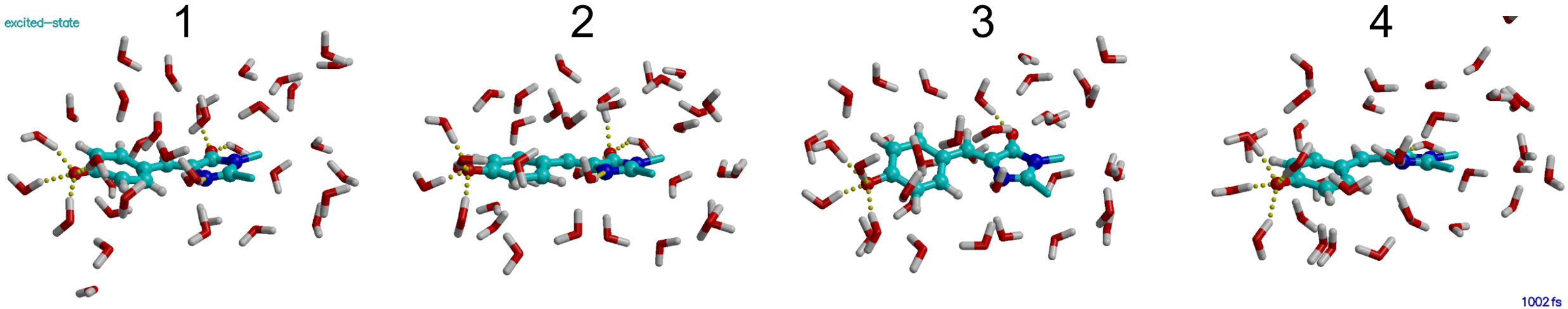
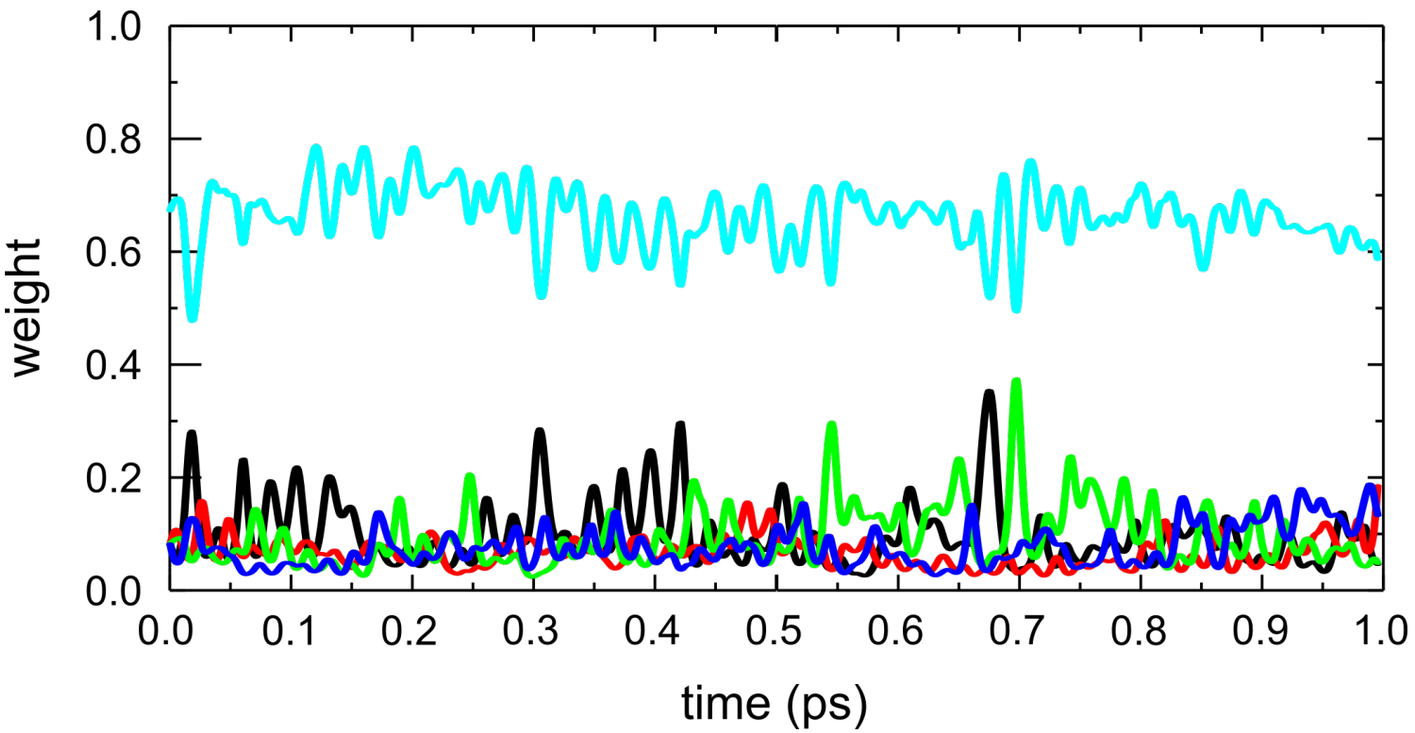


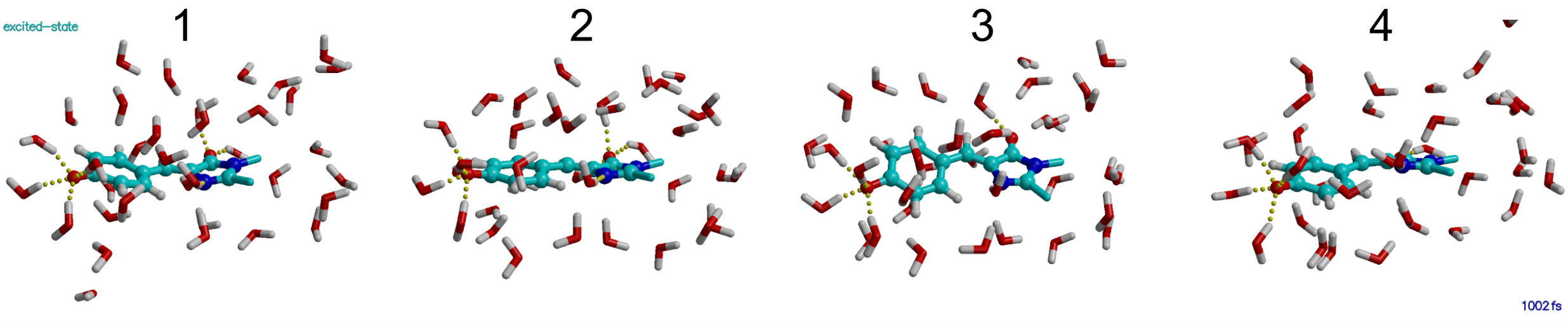


$$\Psi^{\mathrm{LP}} = +\beta_1^{\mathrm{LP}}|1^\star 234\rangle|0\rangle + \beta_2^{\mathrm{LP}}|12^\star 34\rangle|0\rangle + \beta_3^{\mathrm{LP}}|123^\star 4\rangle|0\rangle + \beta_4^{\mathrm{LP}}|1234^\star\rangle|0\rangle + \alpha^{\mathrm{LP}}|1234\rangle|1\rangle$$

Manipulating photo-chemistry with mirrors

four GFP chromophores in water in a cavity

trapped: fluorescence



challenge in real life (AKA experiment …)

cavity mode lifetime

far less than a picosecond …

limits polariton lifetime

dark states

different potential energy surfaces

density of dark states proportional to concentration

Arpan Dutta's poster

Manipulating photo-chemistry with mirrors

polariton lifetime 'paradox' (at least for a chemist…)

slow emission observed in low-finesse cavities

time resolved fluorescence of TBDC J-aggregates

Schwartz *et al. ChemPhysChem* 14 (2013) 125

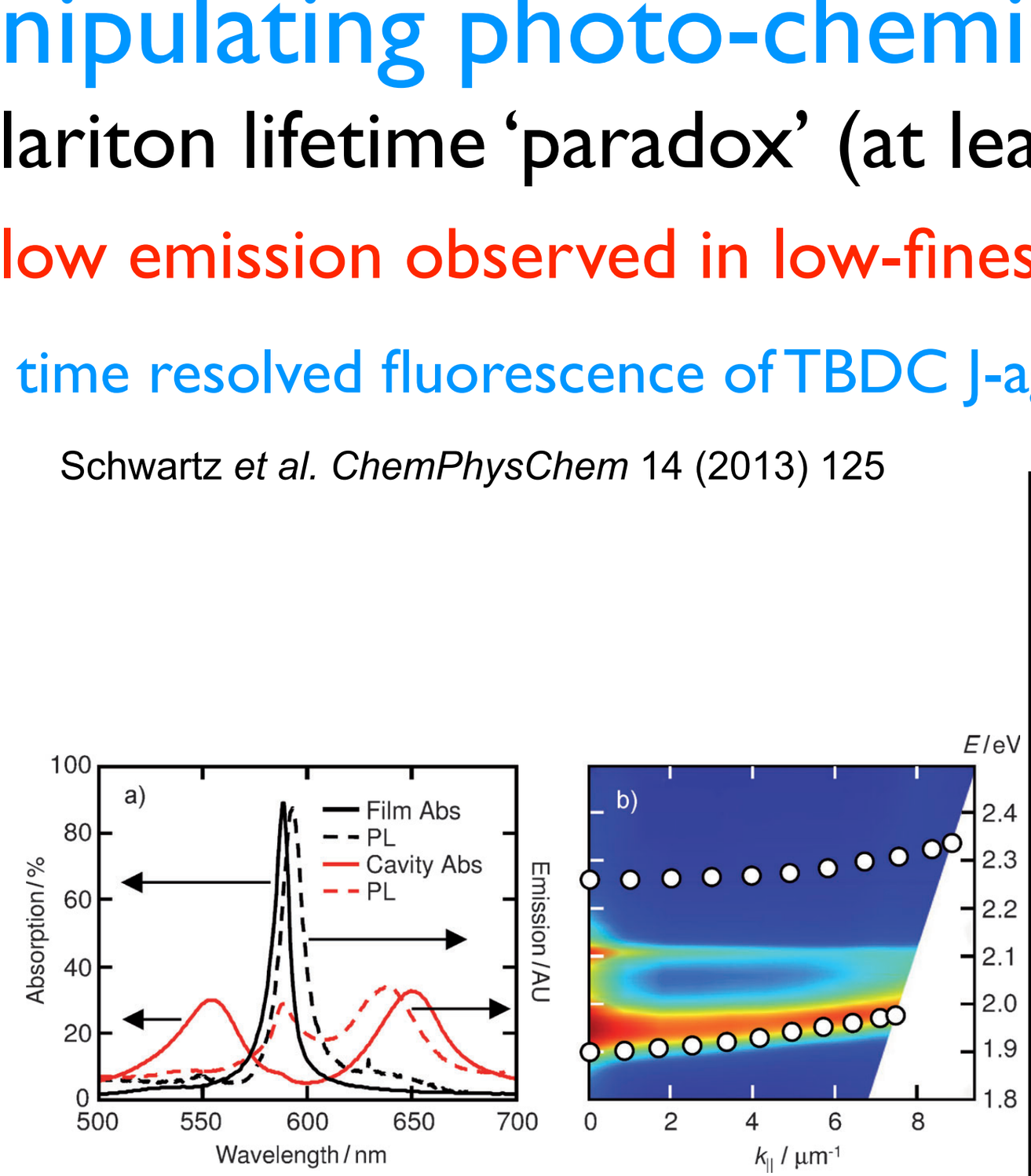


Figure 2. a) Absorption (——) and emission (-----) of the bare molecules and the coupled system upon excitation at 400 nm. b) Dispersion diagram of the coupled system, measured by transmission (white circles) and emission (color) under nonresonant excitation.

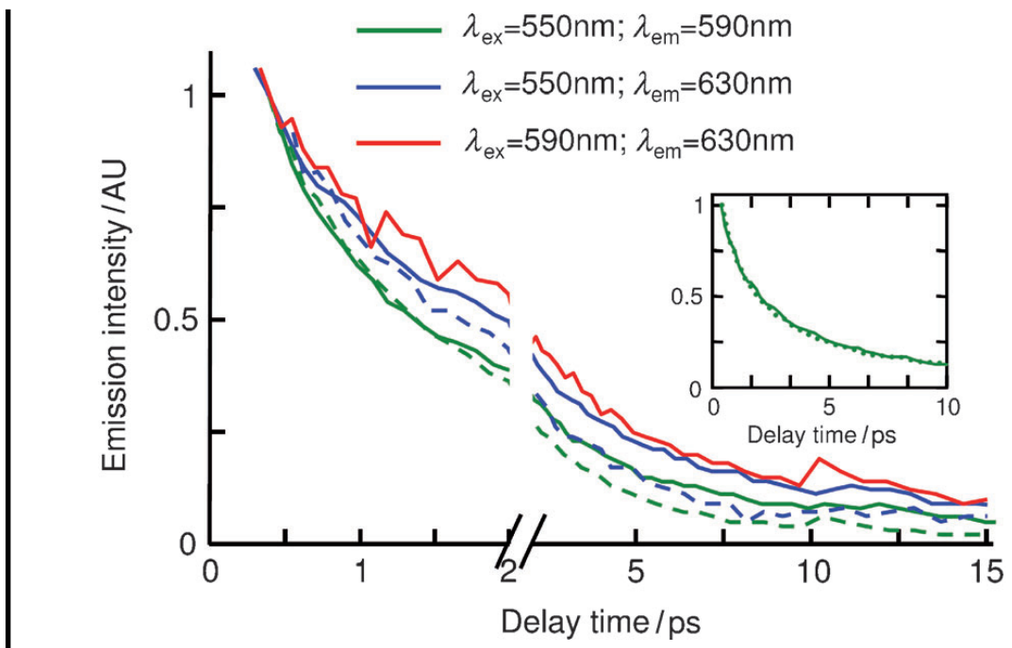


Figure 4. Time-resolved fluorescence measurements for the cavity (——) and a bare molecular film (-----) following a pulsed excitation. The curves are normalized at a delay time of $t = 0.4$ ps. The inset shows the $|P-\rangle$ emission decay with different pump intensities—20 (••••) and 350 μJ cm^{-2} (——) per pulse.

why is that?

Manipulating photo-chemistry with mirrors

polariton lifetime 'paradox' (at least for a chemist…)

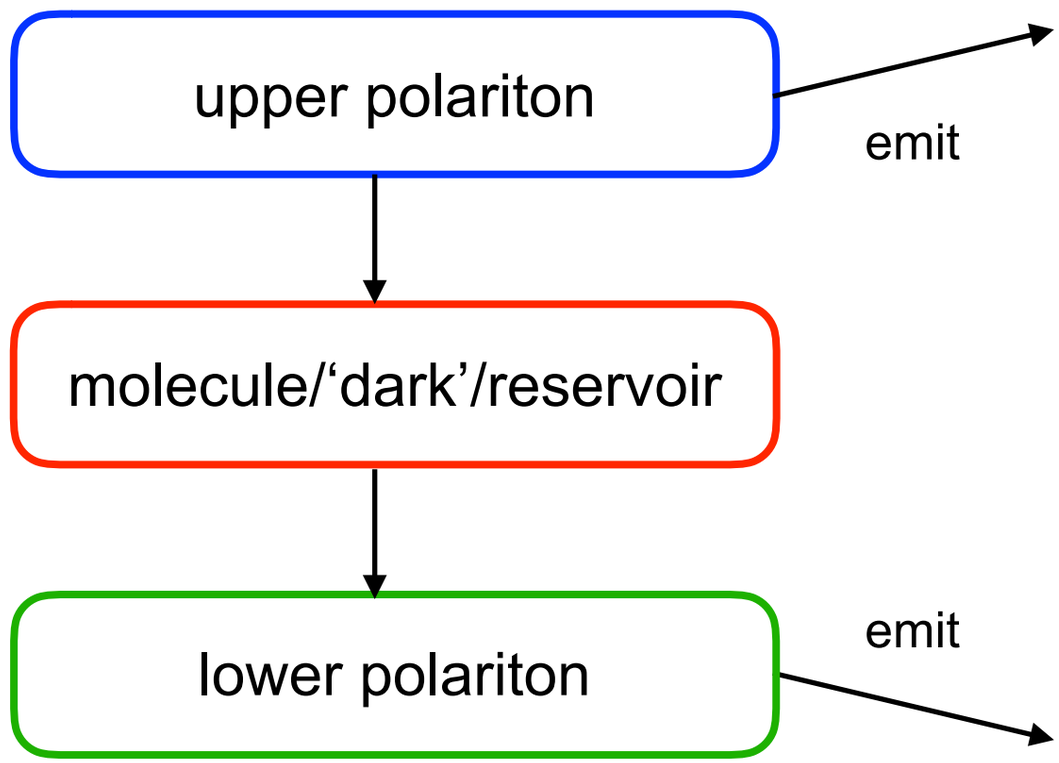
slow emission observed in low-finesse cavities (τ_{cav} ~10 fs)

lower polariton has long lifetime

Schwartz *et al. ChemPhysChem* 14 (2013) 125

George *et al. Faraday Discuss.* 178 (2015) 281

Wang *et al. Adv. Funct. Matter* 26 (2016) 6198



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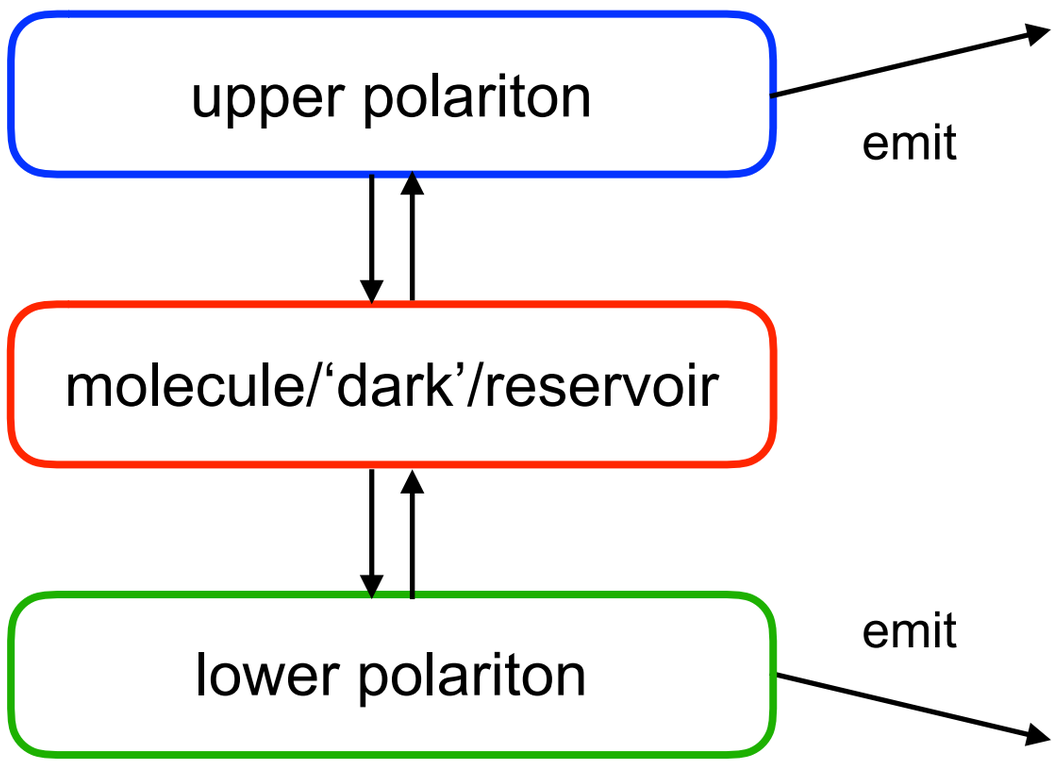
reversible population transfer between bright and dark polaritons

Lidzey *et al. Appl. Phys. Lett.* 82 (1999) 3316

Litinskaya *et al. J. Lumin* 110 (2004) 364

Chovan *et al. Phys. Rev. B* 78 (2008) 045320



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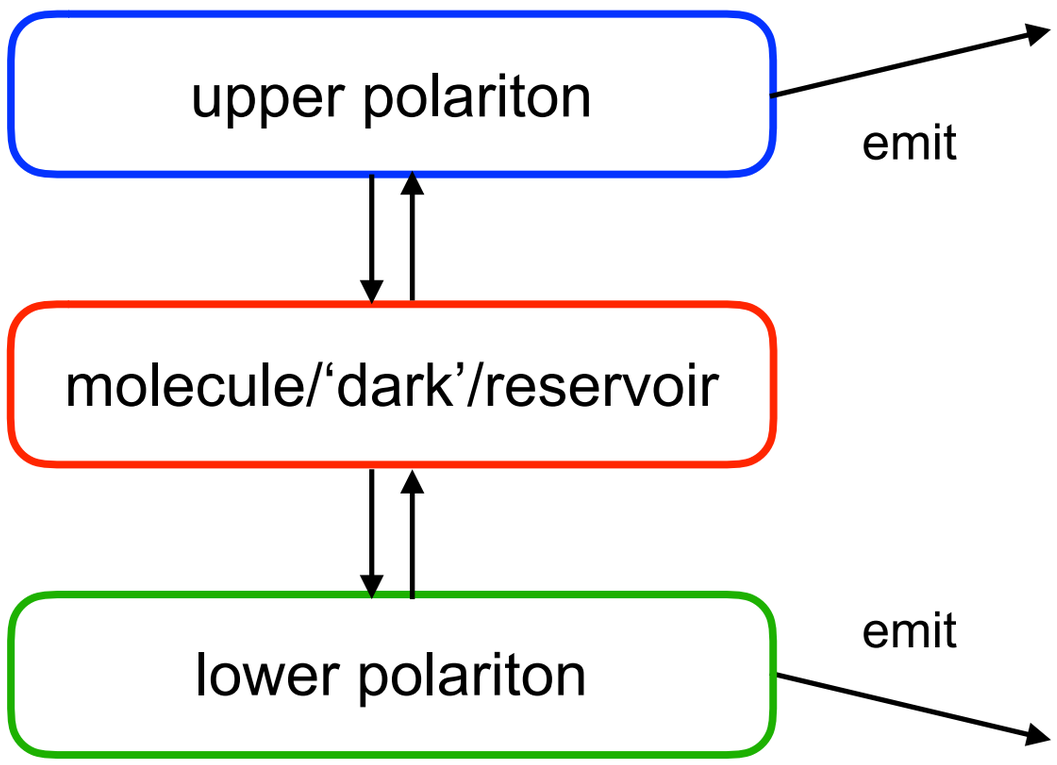
atomistic pump-probe simulations

chromophores in low-finesse cavities

track relaxation dynamics



Manipulating photo-chemistry with mirrors

modelling relaxation dynamics in low-finesse cavities

polaritonic state (basis)

$$\psi^k = \sum_{i=1}^{N} \beta_i^k |g_1 g_2 .. e_i .. g_{N-1} g_N\rangle|0\rangle + \alpha^k |g_1 g_2 .. g_i .. g_{N-1} g_N\rangle|1\rangle$$

Manipulating photo-chemistry with mirrors

modelling relaxation dynamics in low-finesse cavities

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total *time-dependent* polaritonic wave function

$$\Psi(t) = \sum_{k}^{N+1} = c_k(t)\psi^k$$

$$\rho_{jk}(t) = c_j^*(t)c_k(t)$$

propagate expansion coefficients along with classical MD trajectories

Manipulating photo-chemistry with mirrors

modelling relaxation dynamics in low-finesse cavities

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propagate expansion coefficients along with classical MD trajectories

Ehrenfest dynamics (mean field)

$$\mathbf{F}_a = -\sum_{k}^{N+1}\sum_{l}^{N+1} \rho_{kl}(t)\langle\psi^k|\nabla_a \hat{H}|\psi^l\rangle$$

Manipulating photo-chemistry with mirrors

modelling relaxation dynamics in low-finesse cavities

polaritonic state (basis)

$$\psi^k = \sum_{i=1}^{N} \beta_i^k |g_1 g_2 .. e_i .. g_{N-1} g_N\rangle|0\rangle + \alpha^k |g_1 g_2 .. g_i .. g_{N-1} g_N\rangle|1\rangle$$

total *time-dependent* polaritonic wave function

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propagate expansion coefficients along with classical MD trajectories

Ehrenfest dynamics (mean field)

$$\mathbf{F}_a = -\sum_{k}^{N+1}\sum_{l}^{N+1} \rho_{kl}(t)\langle\psi^k|\nabla_a \hat{H}|\psi^l\rangle$$

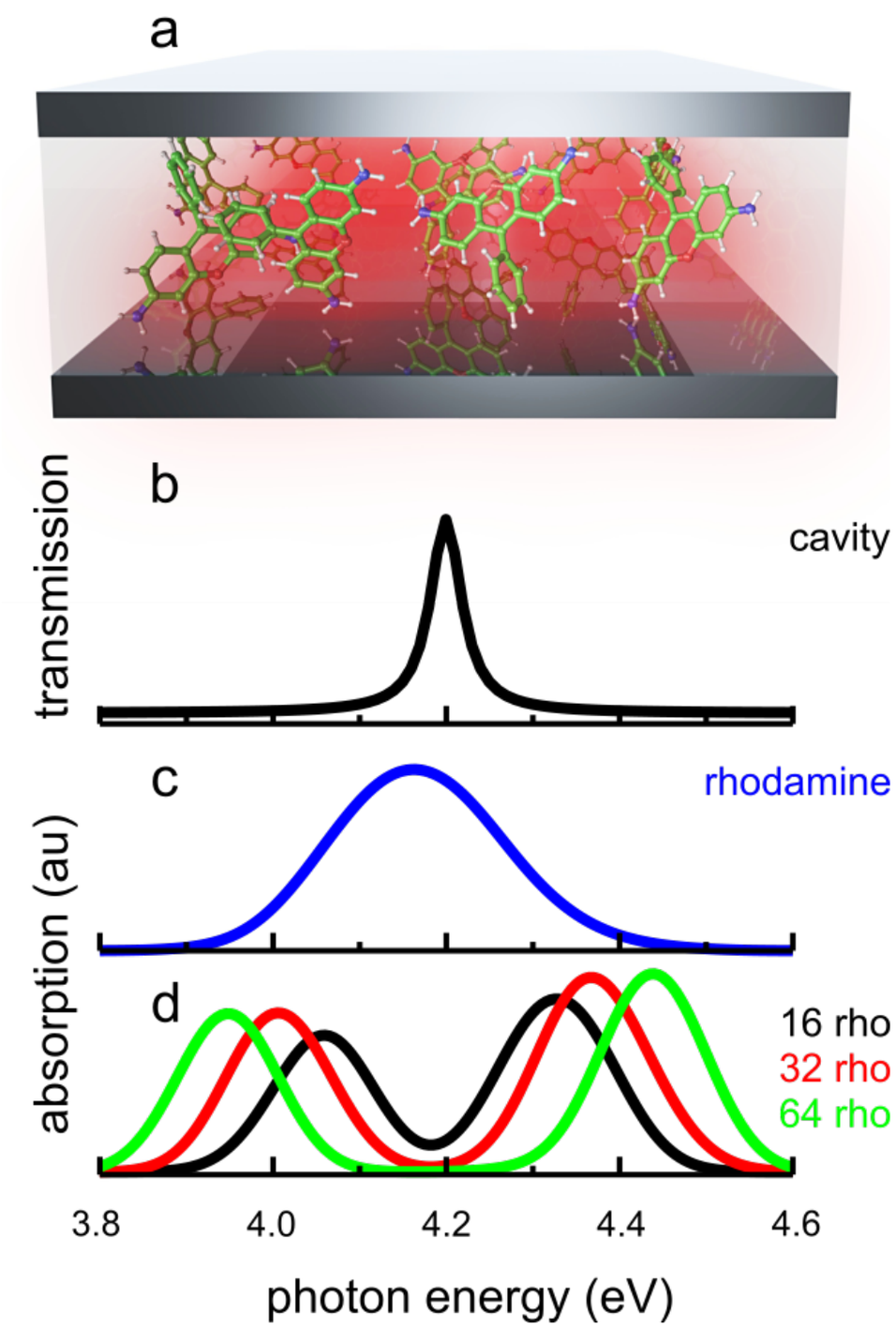
finite lifetime of cavity mode

$$\rho_{kk}(t+\Delta t) = \rho_{kk}(t)\exp\left[-\gamma_{\mathrm{cav}}|\alpha^k(t)|^2\Delta t\right] \qquad \rho_{kk} = c_k^* c_k$$

Manipulating photo-chemistry with mirrors

modelling relaxation dynamics in low-finesse cavities

rhodamine chromophores between thin metal mirrors



molecules plus environment

$$N = 1, 2, 4, 6, .., 500, .., 1000$$

aligned to cavity field

cavity parameters

$$\hbar\omega_{\rm cav} = 4.2 \text{ eV}$$

$$\hbar\gamma_{\rm cav} = 43 \text{ meV} \qquad \tau_{\rm cav} = 15 \text{ fs}$$

various cavity volumes (fields)

atomistic rhodamine model

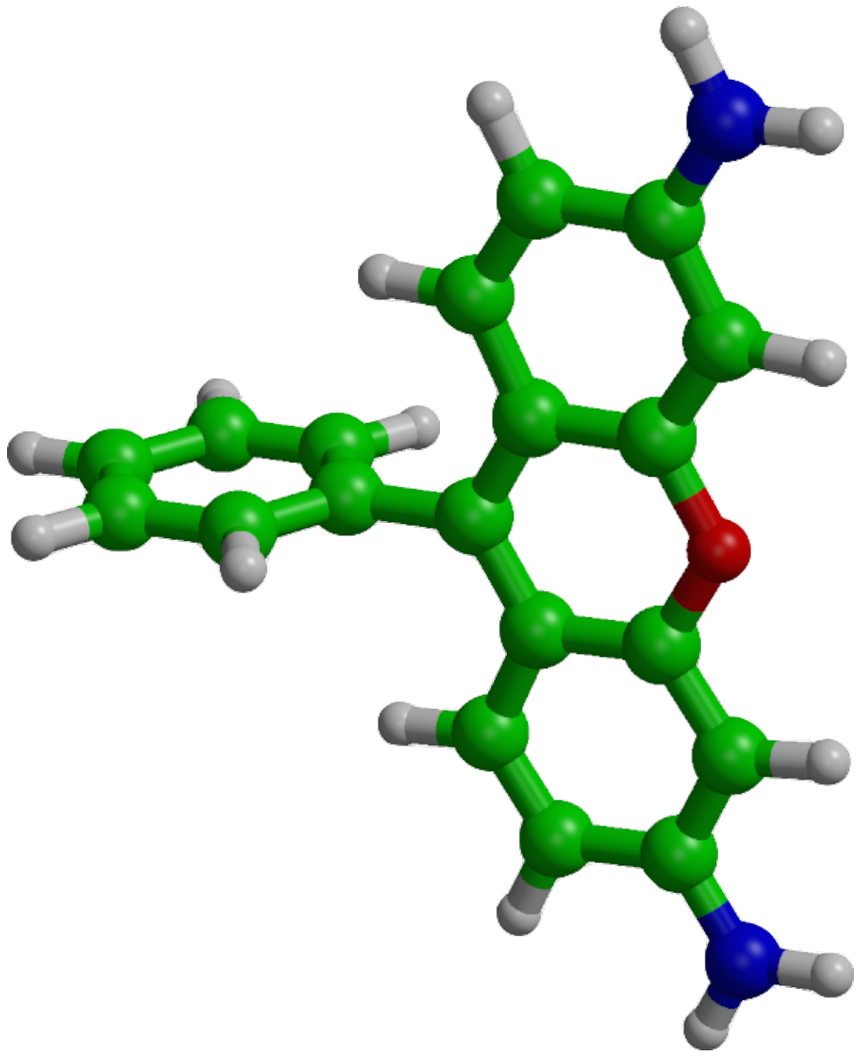
$$h\nu = 4.18 \text{ eV}$$

Manipulating photo-chemistry with mirrors

modelling relaxation dynamics in low-finesse cavities

rhodamine model

bare rhodamine

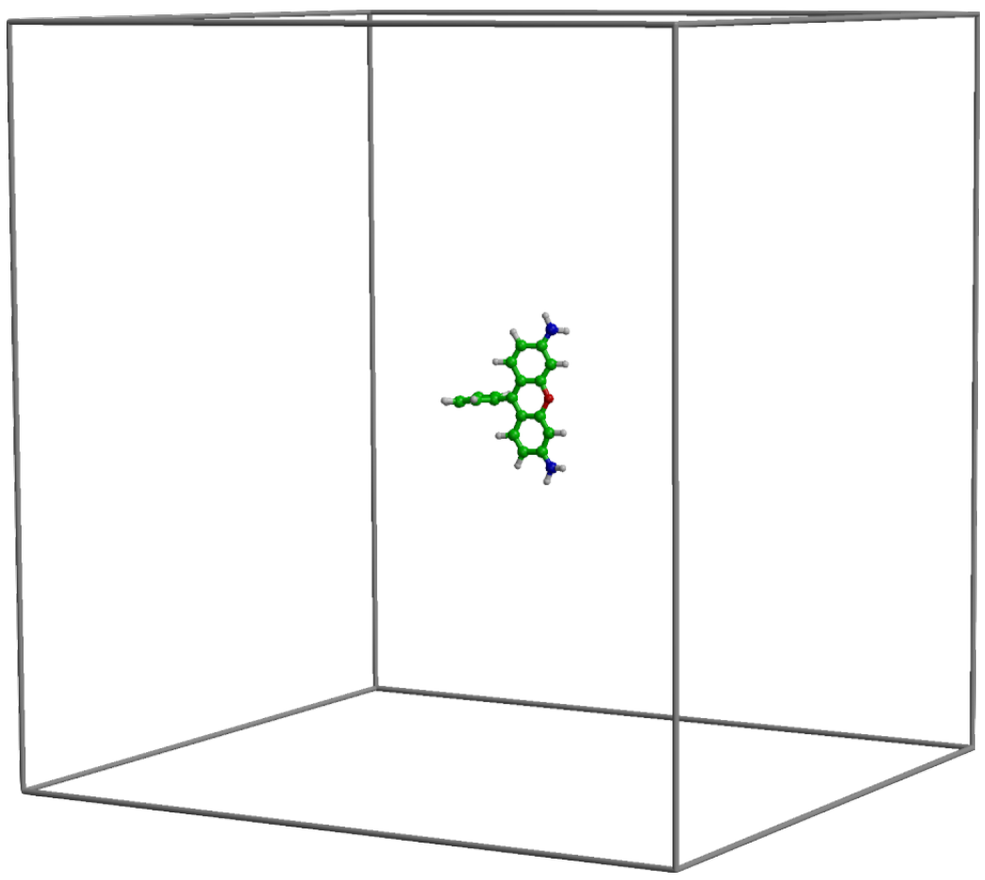


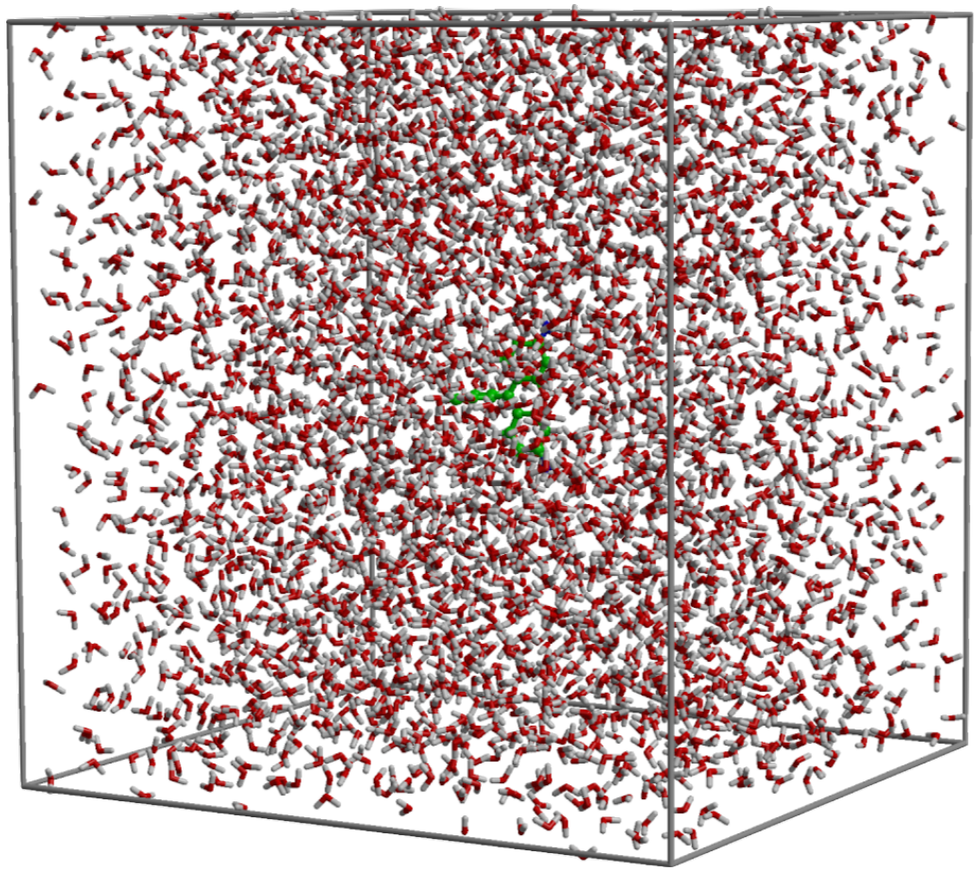
Manipulating photo-chemistry with mirrors

modelling relaxation dynamics in low-finesse cavities

rhodamine model

bare rhodamine in water @ 300 K & 1 bar





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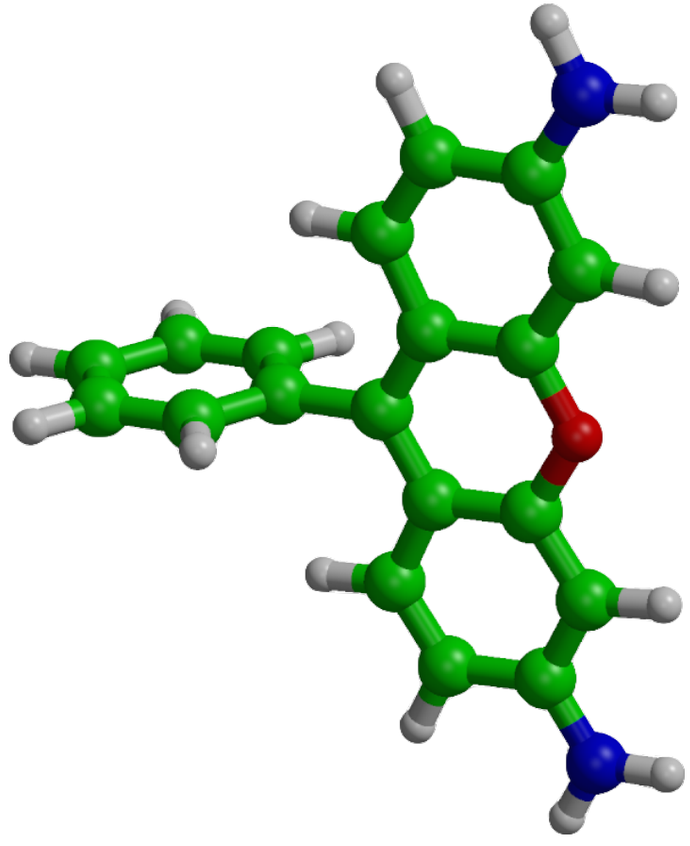
modelling relaxation dynamics in low-finesse cavities

rhodamine model

- bare rhodamine in water @ 300 K & 1 bar
- QM/MM

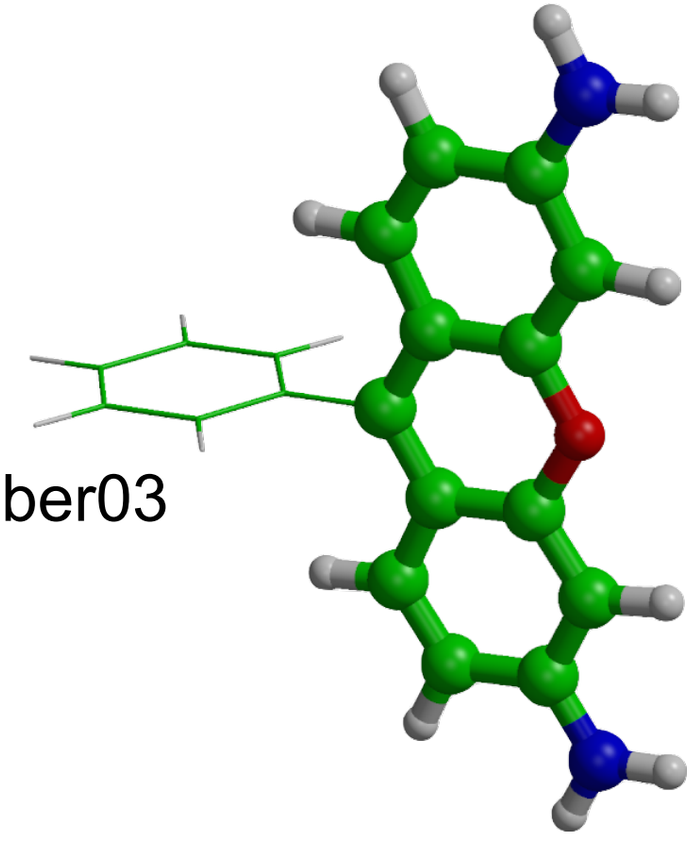


Manipulating photo-chemistry with mirrors

modelling relaxation dynamics in low-finesse cavities

rhodamine model

- bare rhodamine in water @ 300 K & 1 bar
- QM/MM
- electronic ground state (S_0)



Amber03

Hartree-Fock/3-21G

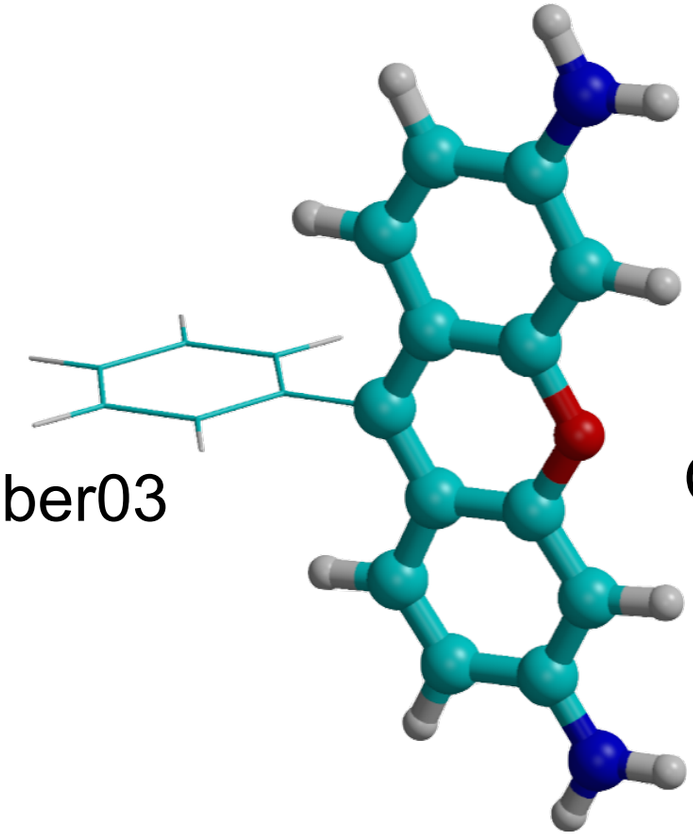
$$\Psi^{S_0}(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_n) = |\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)..\phi_i(\mathbf{r}_i)\phi_j(\mathbf{r}_j)..\phi_{n-1}(\mathbf{r}_{n-1})\phi_n(\mathbf{r}_n)\rangle$$

Manipulating photo-chemistry with mirrors

modelling relaxation dynamics in low-finesse cavities

rhodamine model

- bare rhodamine in water @ 300 K & 1 bar
- QM/MM
- electronic excited state (S_1)



Amber03

Configuration Interaction/3-21G

truncated to one electron excitations

$$\Psi^{S_1}(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_n) = \sum_{ip} C_{ip} |\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)..\phi_p(\mathbf{r}_i)\phi_j(\mathbf{r}_j)..\phi_{n-1}(\mathbf{r}_{n-1})\phi_n(\mathbf{r}_n)\rangle$$

Manipulating photo-chemistry with mirrors

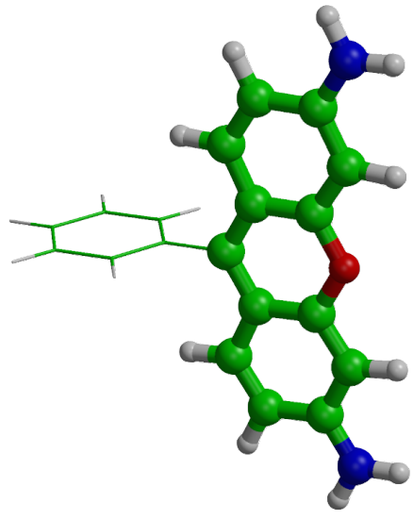
modelling relaxation dynamics in low-finesse cavities

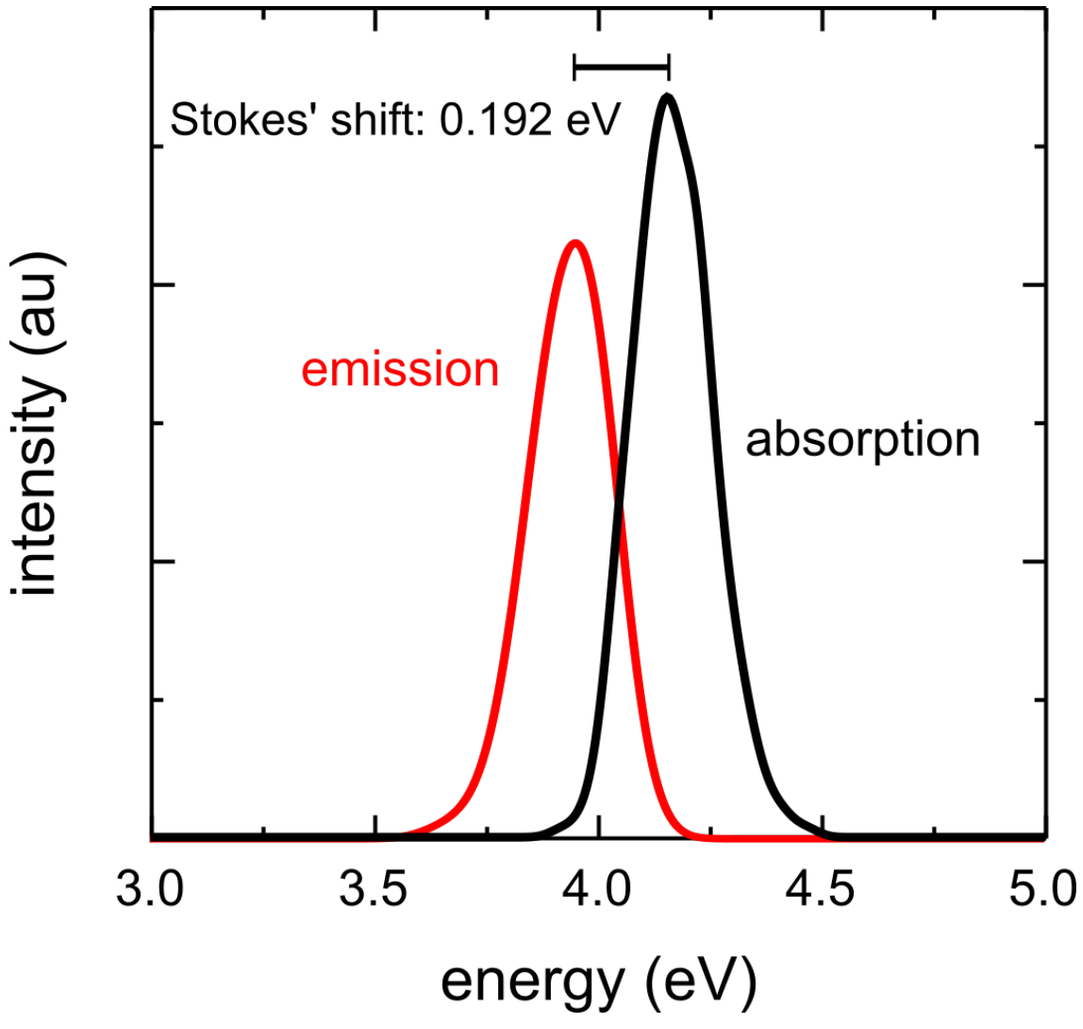
rhodamine model

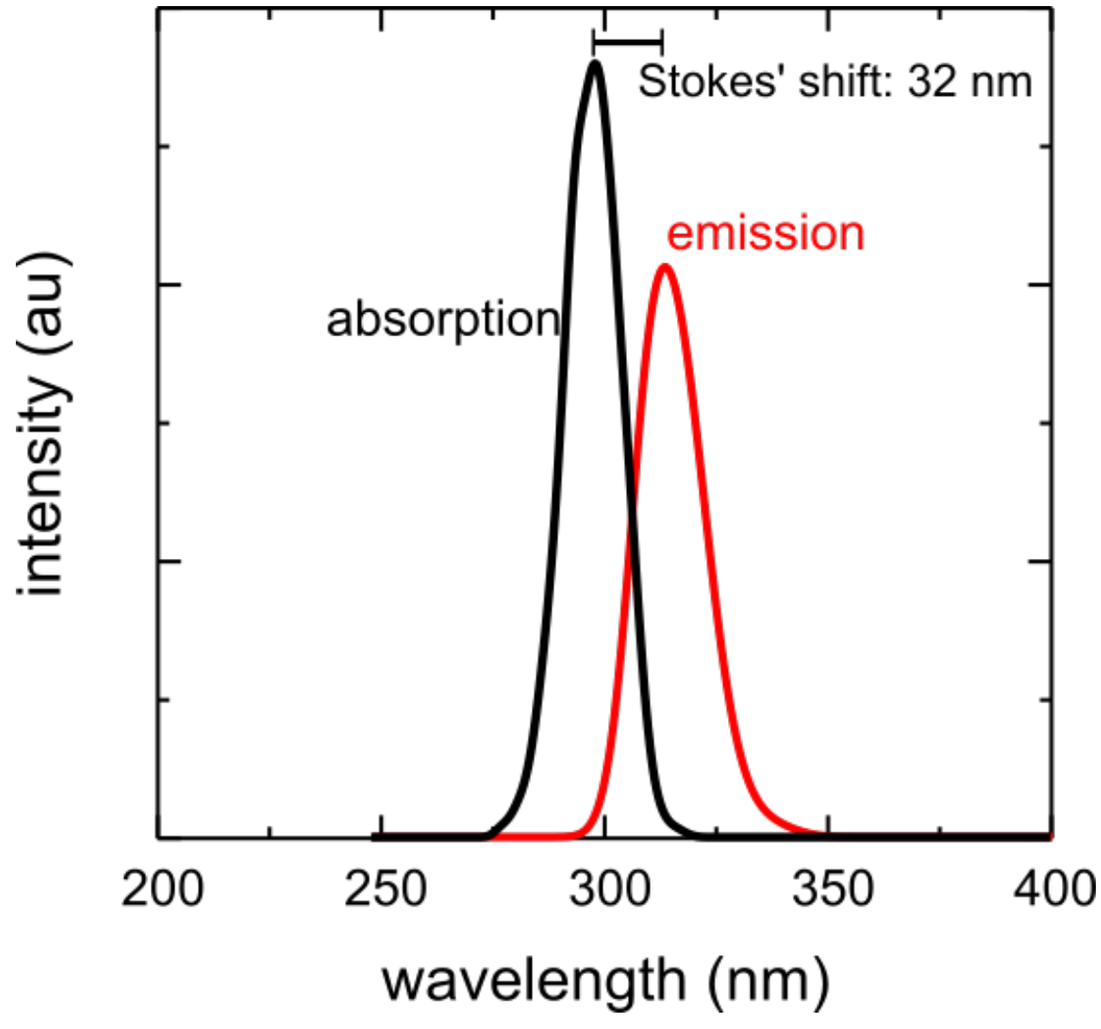
bare rhodamine in water @ 300 K & 1 bar

QM/MM

electronic absorption spectra ($S_0 \rightarrow S_1$)





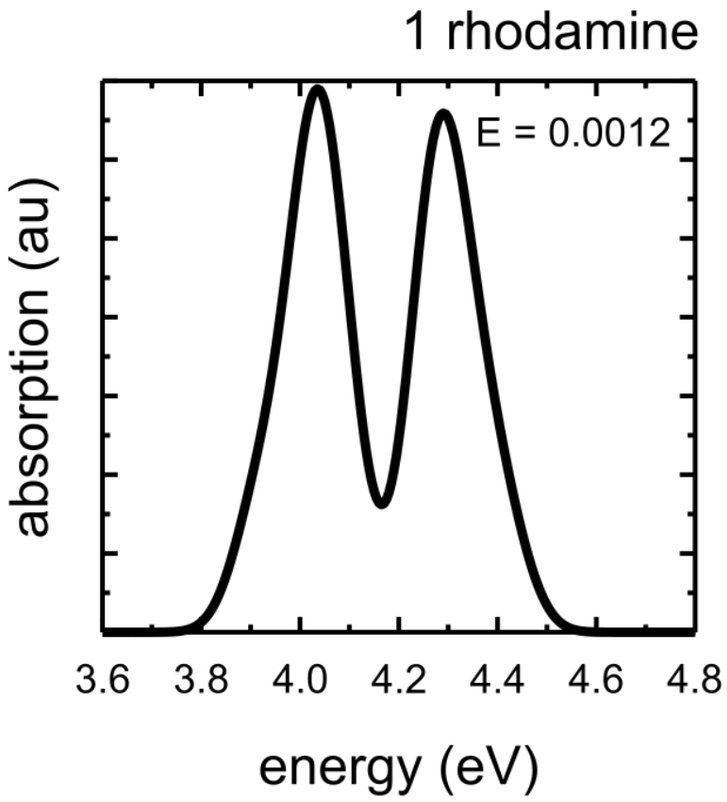


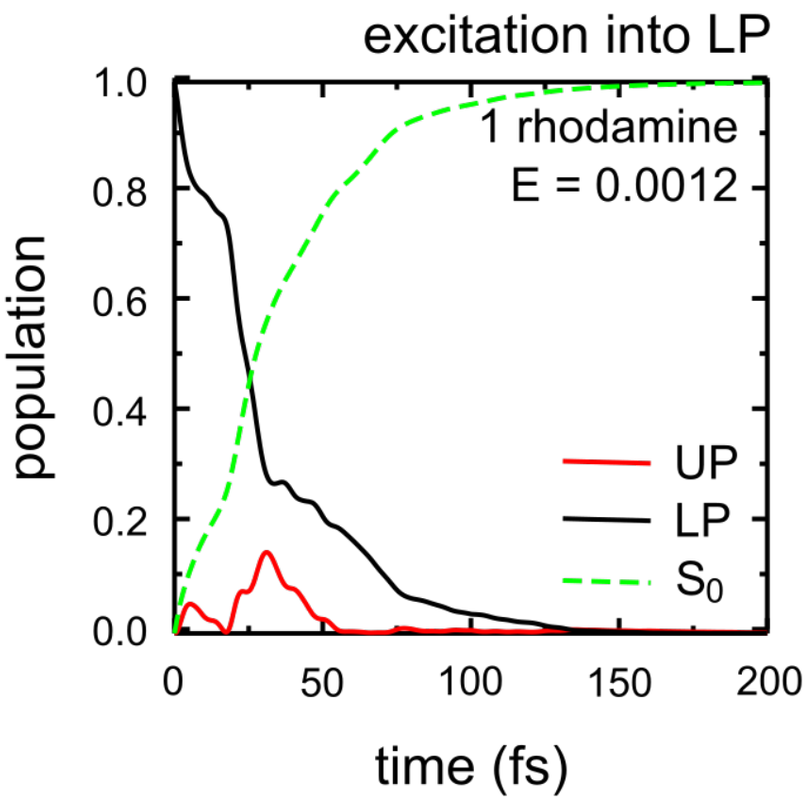
Manipulating photo-chemistry with mirrors

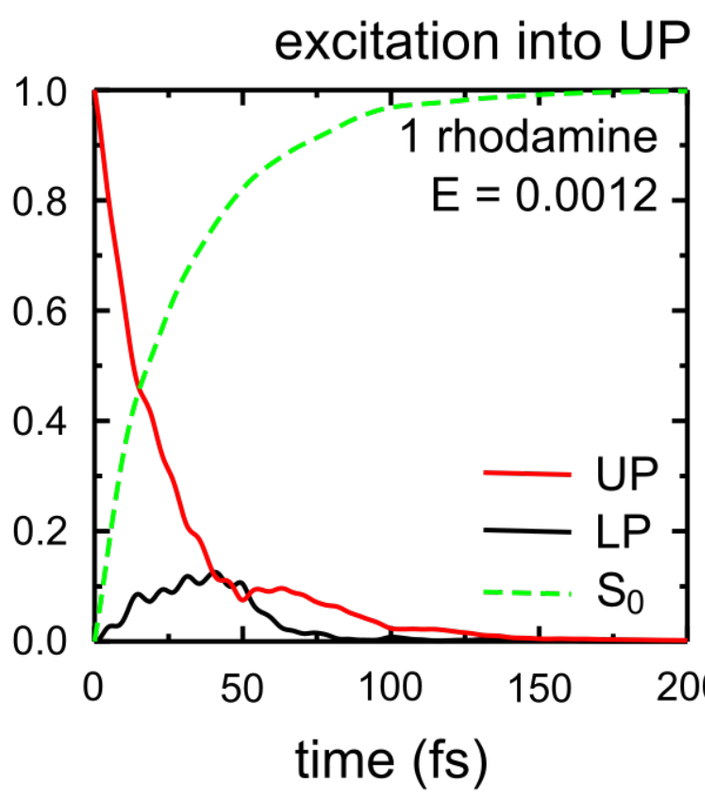
modelling relaxation dynamics in low-finesse cavities

one rhodamines plus environment between two metal mirrors

state populations





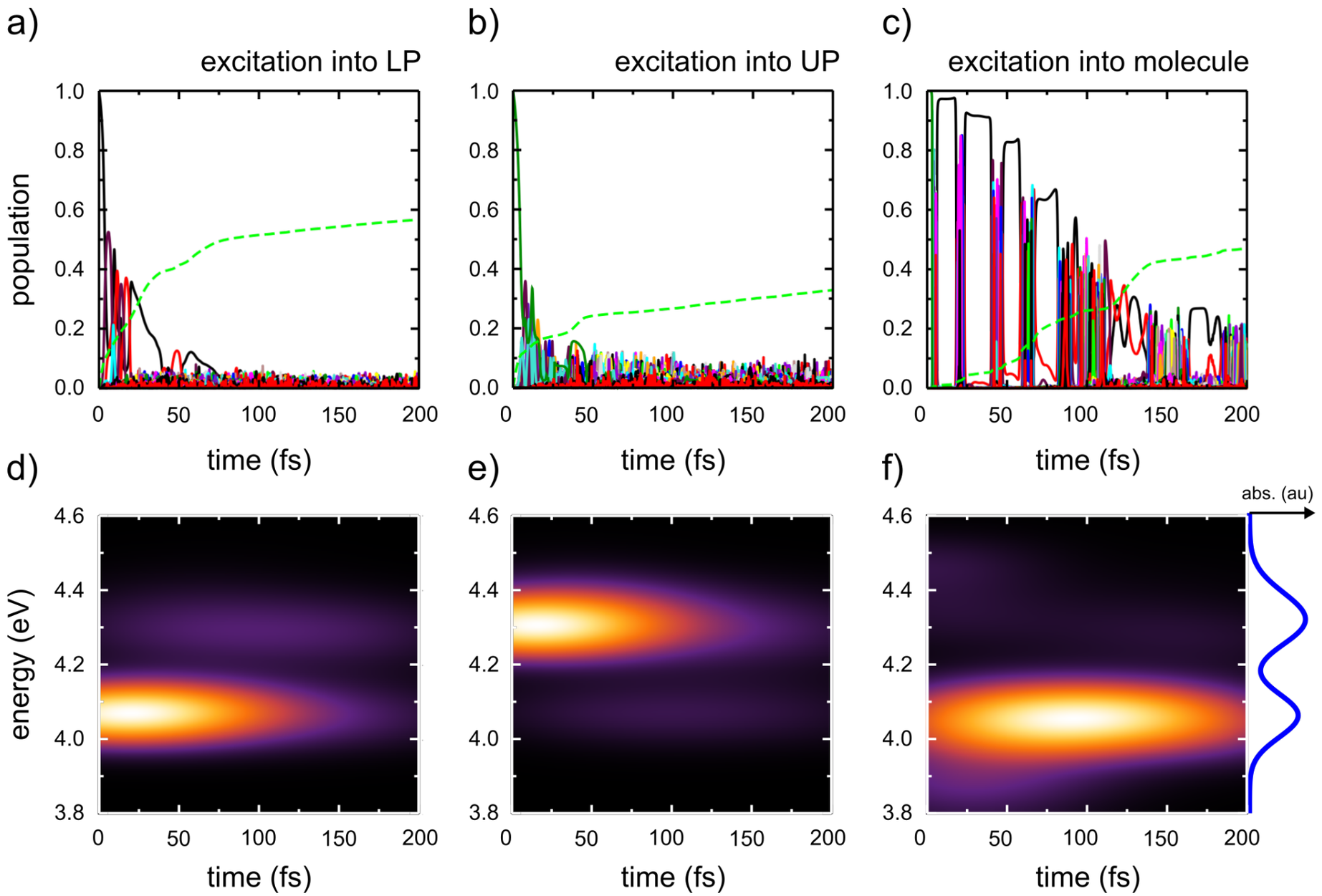


Manipulating photo-chemistry with mirrors

modelling relaxation dynamics in low-finesse cavities

64 rhodamines plus environment between two metal mirrors

state populations & time-resolved fluorescence spectra



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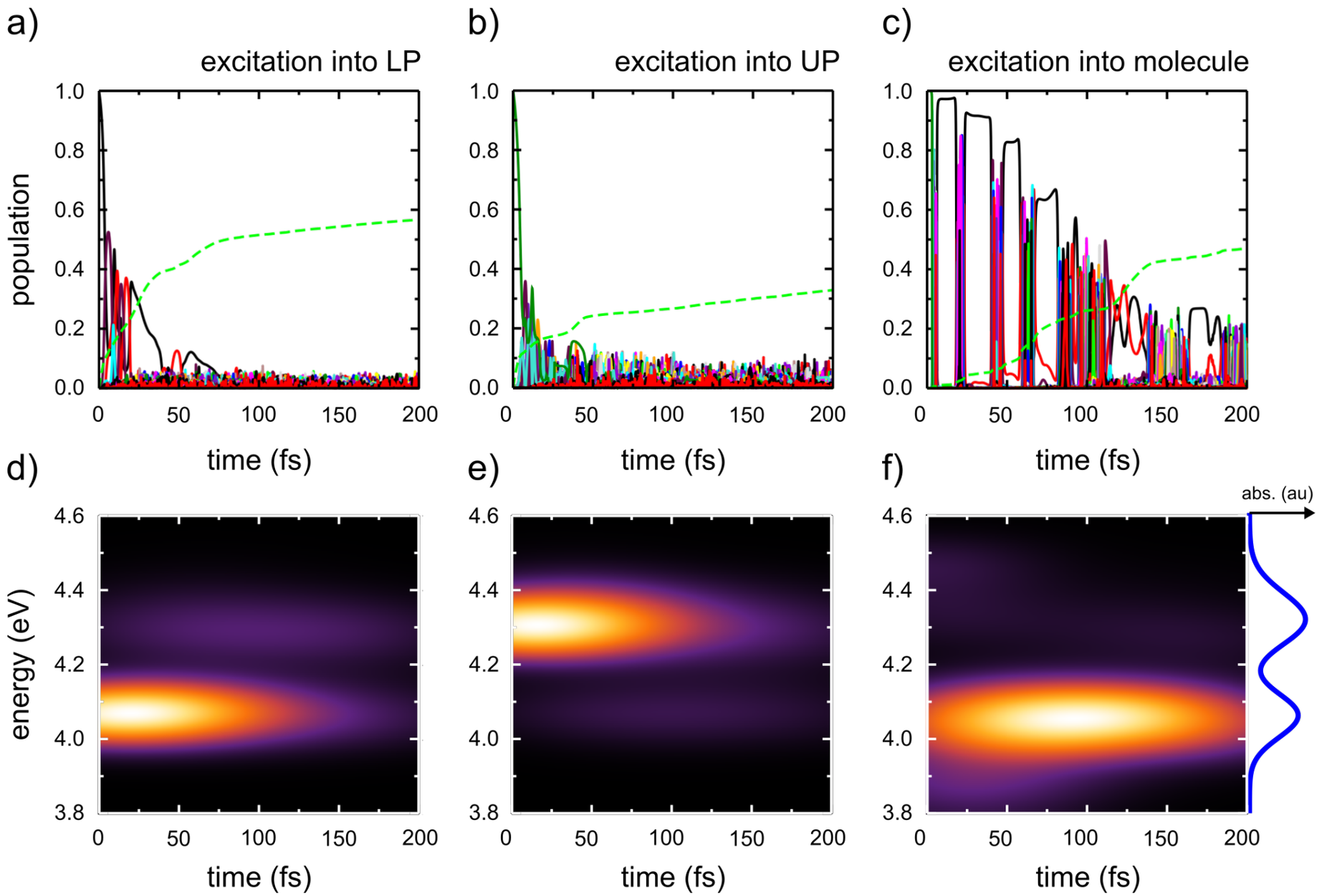


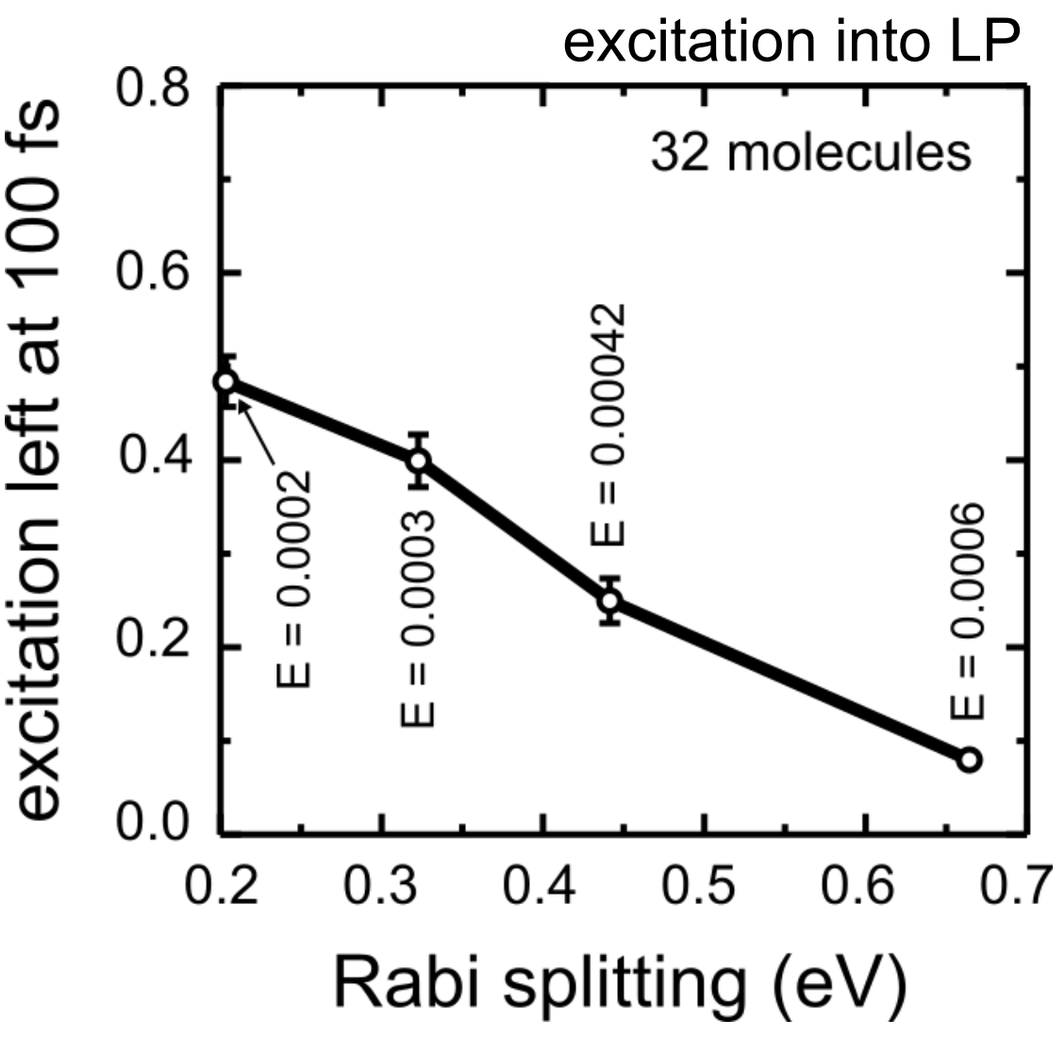
reversible population transfer between bright and dark polaritons

Manipulating photo-chemistry with mirrors

modelling relaxation dynamics in low-finesse cavities

lifetime of molecule-cavity systems

depends on accessibility of dark states



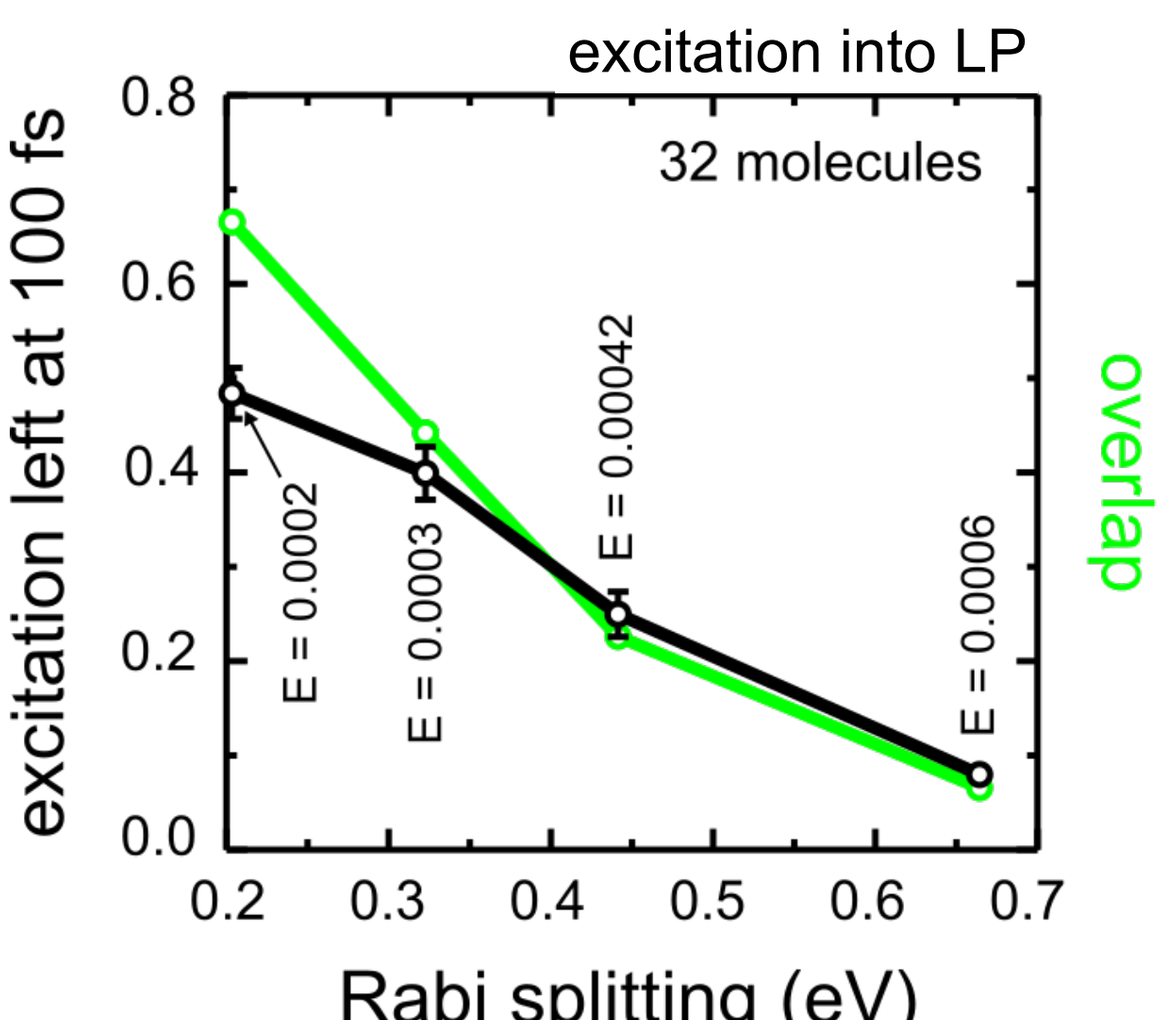
Manipulating photo-chemistry with mirrors

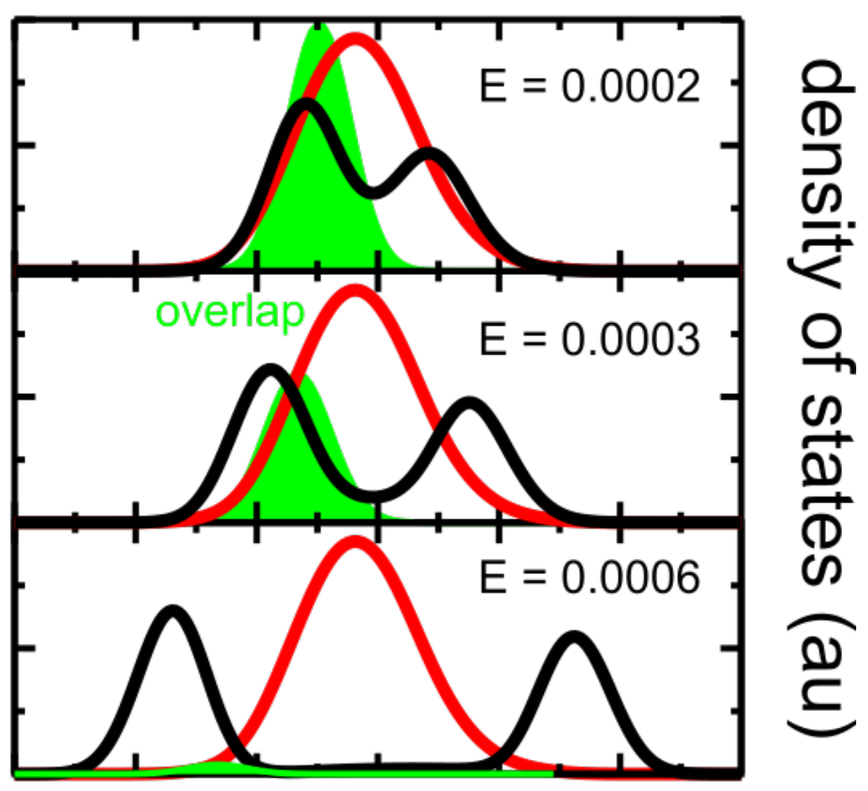
modelling relaxation dynamics in low-finesse cavities

lifetime of molecule-cavity systems

depends on accessibility of dark states

depends on overlap between bright (LP) and dark polaritonic states





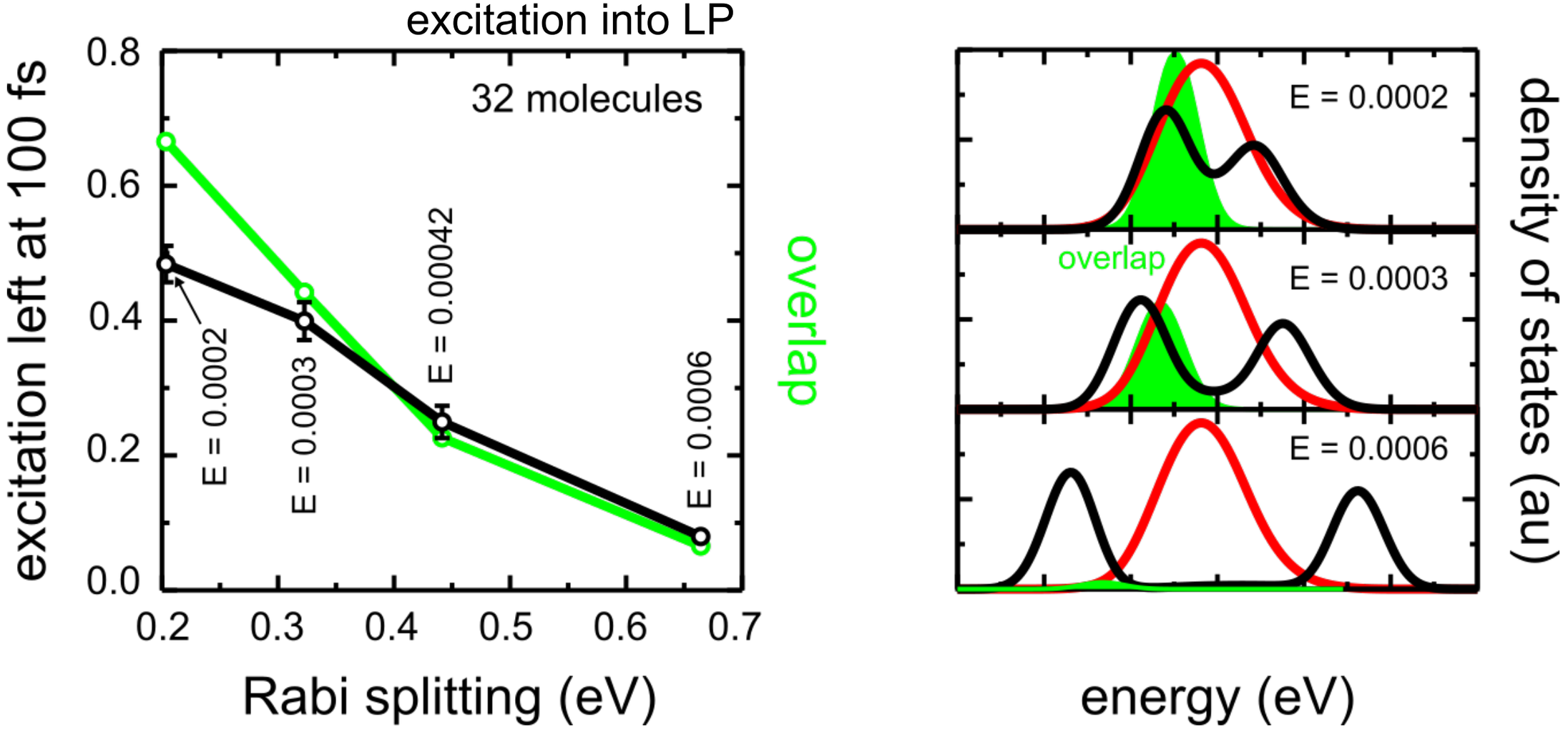
Manipulating photo-chemistry with mirrors

modelling relaxation dynamics in low-finesse cavities

lifetime of molecule-cavity systems

- depends on accessibility of dark states
- depends on overlap between bright (LP) and dark polaritonic states
- density of dark states matches molecular absorption spectrum

Coles *et al. Phys. Rev. B* 84 (2011) 205214



Manipulating photo-chemistry with mirrors

modelling relaxation dynamics in low-finesse cavities

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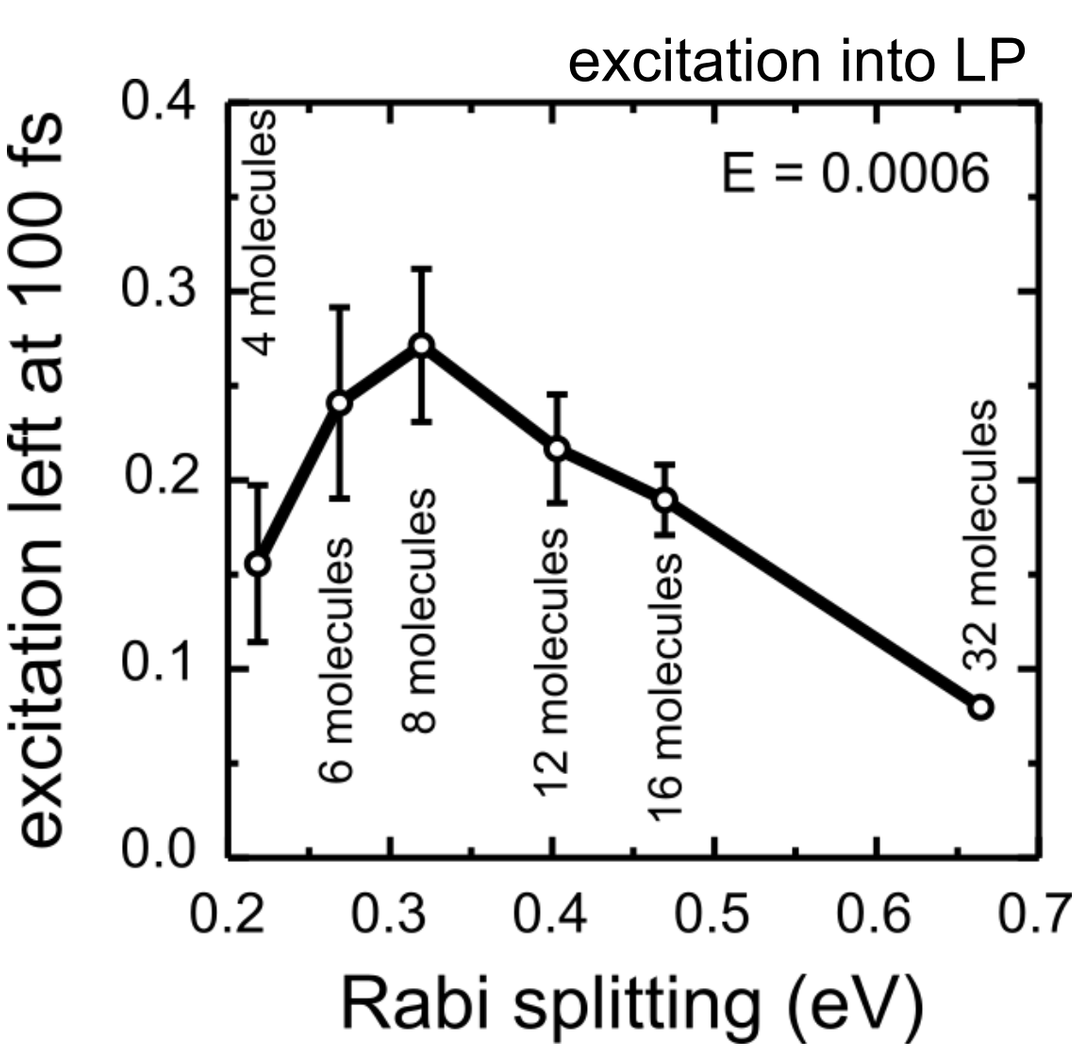

Manipulating photo-chemistry with mirrors

modelling relaxation dynamics in low-finesse cavities

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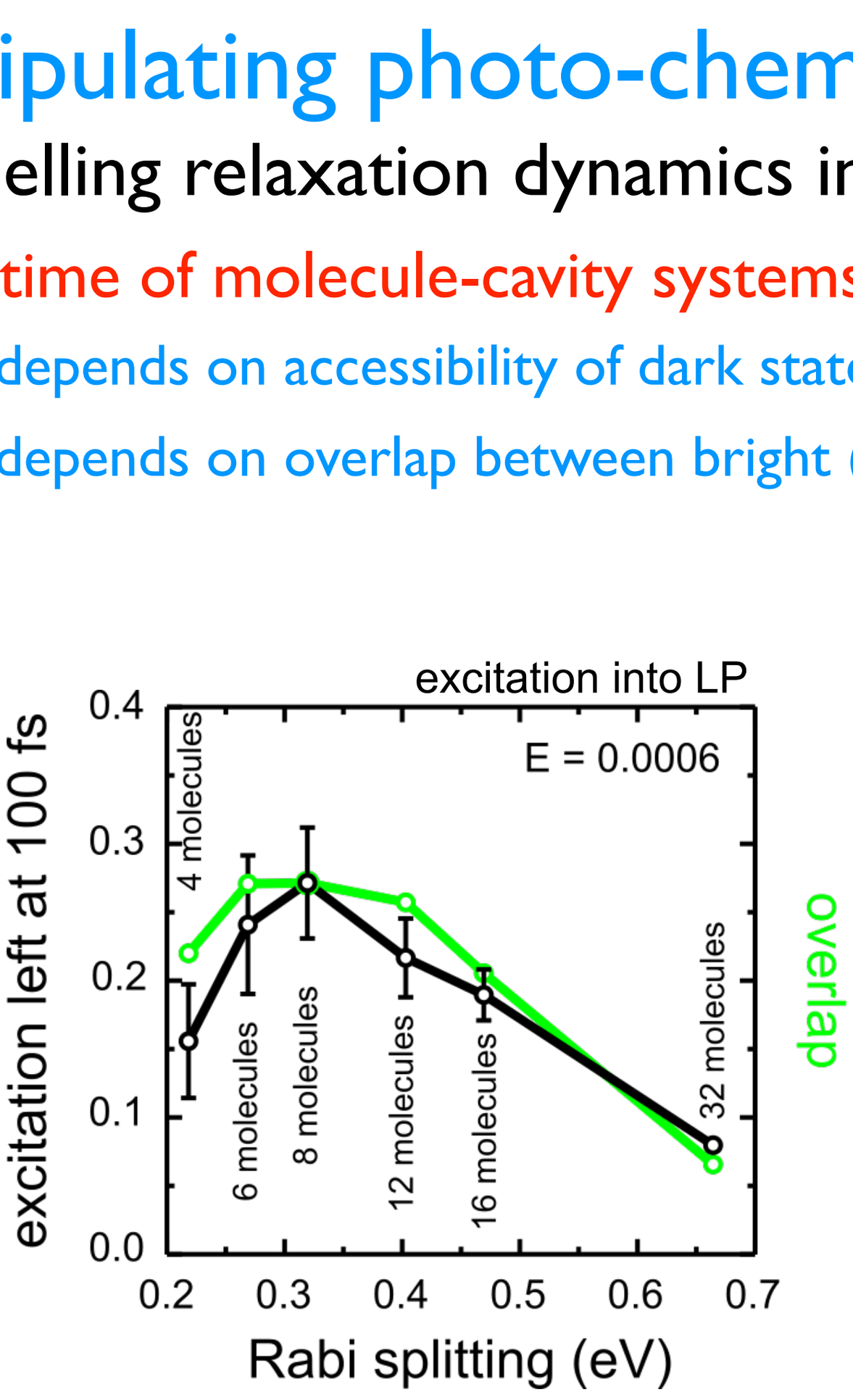

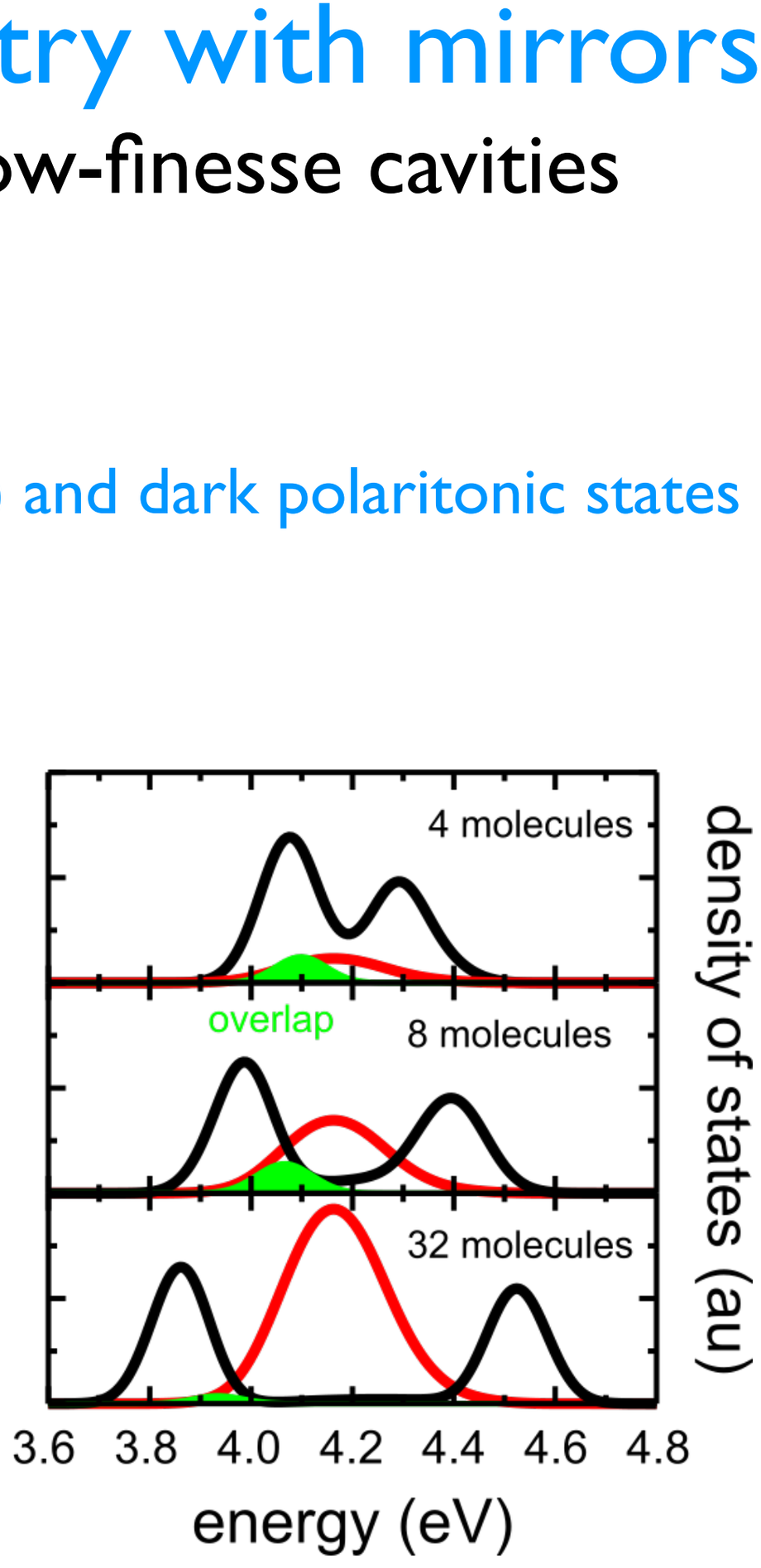

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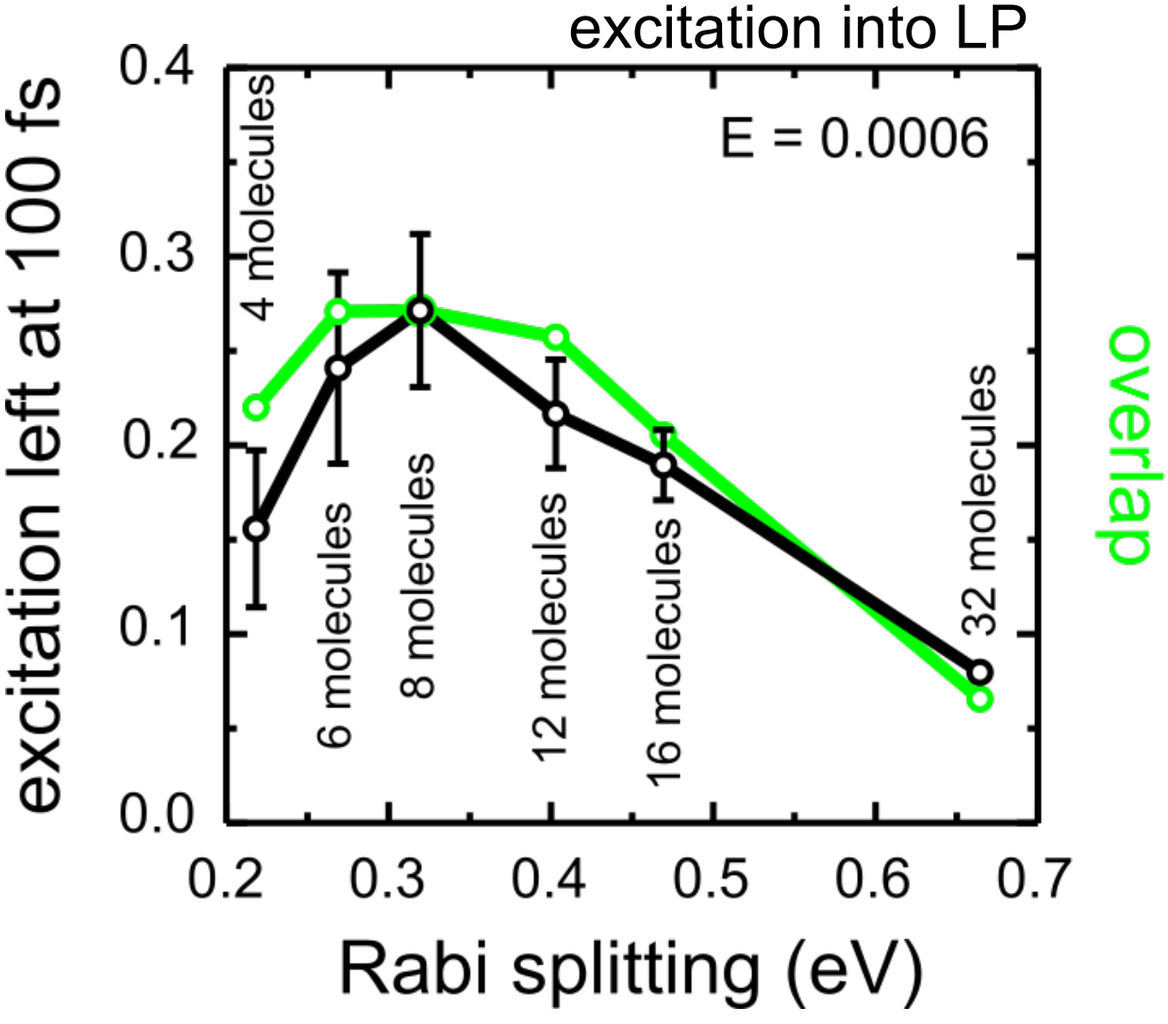
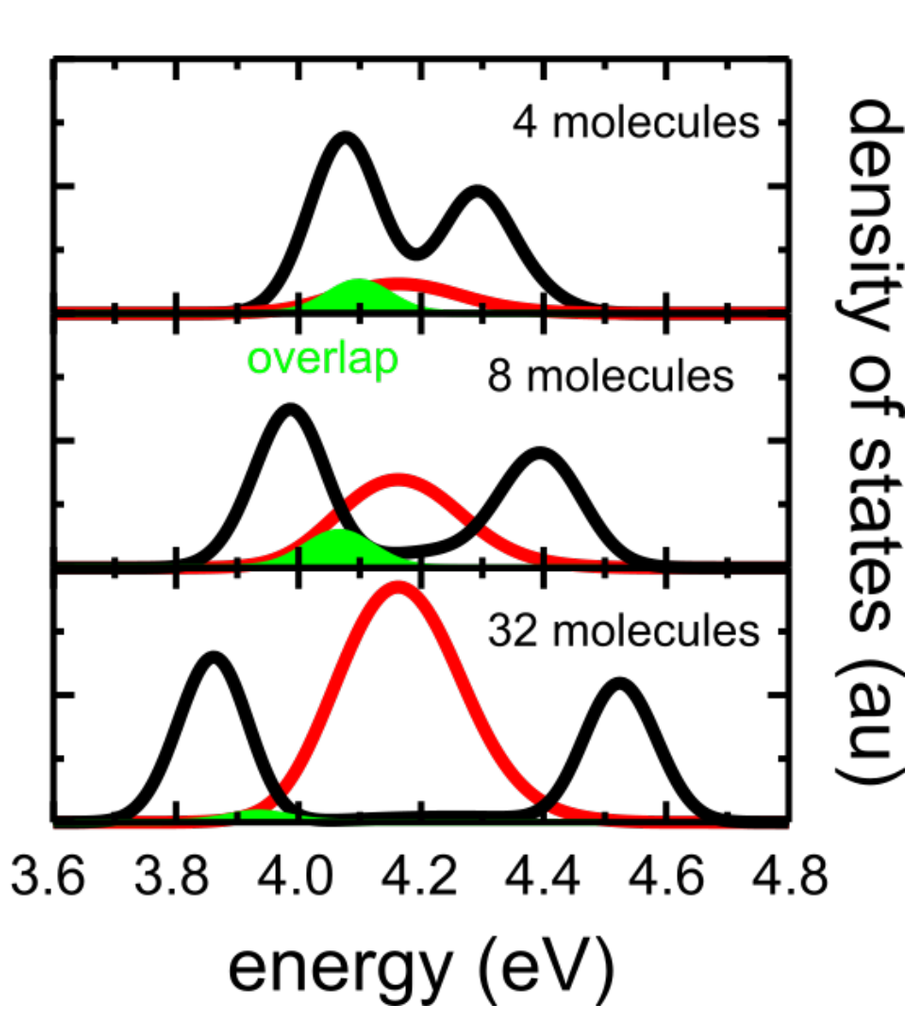


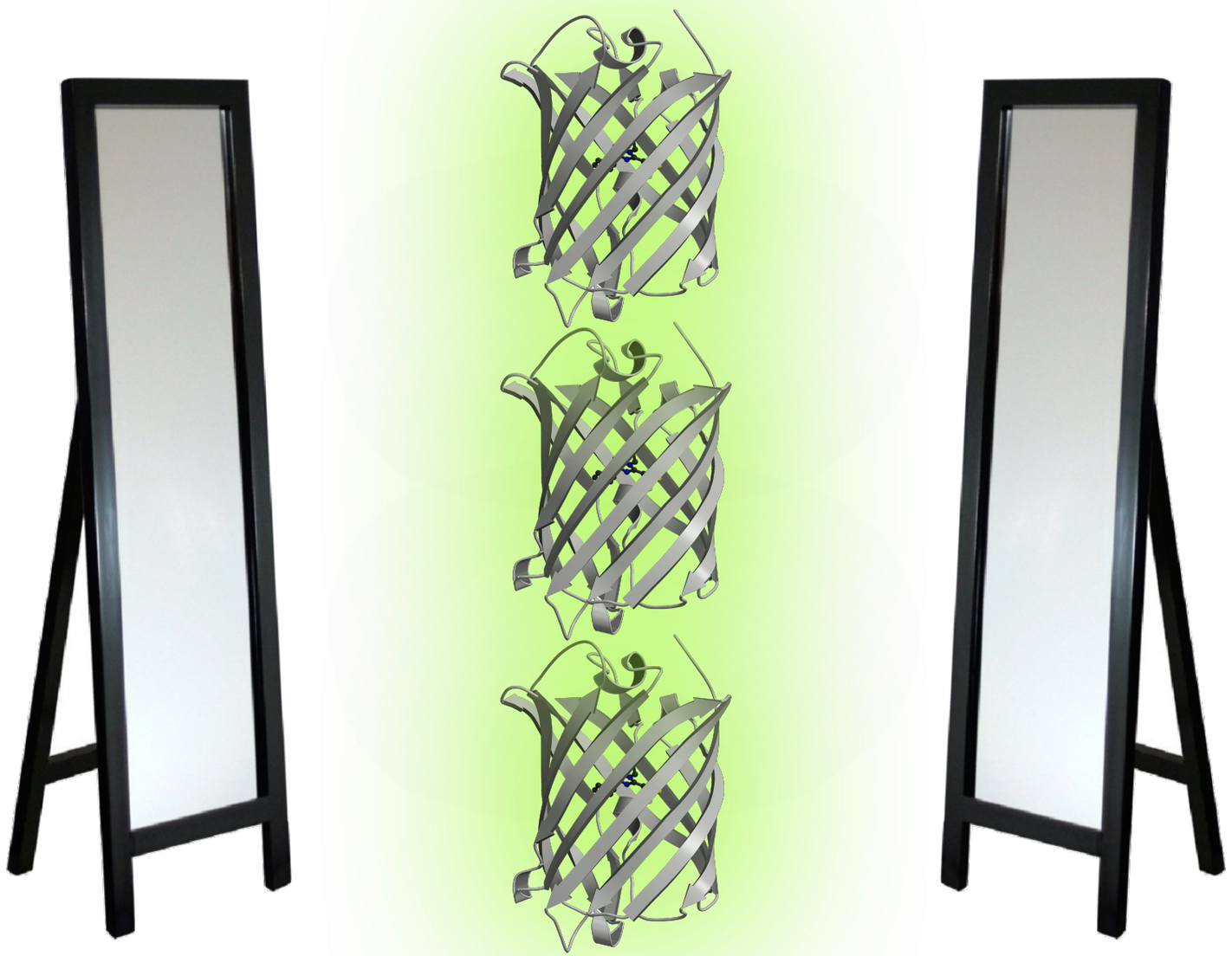


Manipulating photo-chemistry with mirrors

summary

cavity Tavis-Cummings QM/MM model

simulations of molecules under strong coupling with confined light



Manipulating photo-chemistry with mirrors

summary

cavity Tavis-Cummings QM/MM model

simulations of molecules under strong coupling with confined light

new photocatalysis paradigm?

re-shaping potential energy surface (lower polariton)

control of photo-chemical reactions

Ebbesen *et al.*: *Angew. Chem. Int. Ed.* 51 (2012) 1592–1596

Manipulating photo-chemistry with mirrors

summary

- cavity Tavis-Cummings QM/MM model
  - simulations of molecules under strong coupling with confined light

new photocatalysis paradigm?

- re-shaping potential energy surface (lower polariton)
  - control of photo-chemical reactions

suggestions for cavity photocatalysis from this work

- increase intrinsic polariton lifetime
  - very high-finesse cavity
- avoid transfer into dark states
  - LP below absorption spectrum (high Rabi splitting)
    - small cavity volume
    - large molecular concentration

see Arpan Dutta's poster

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Jussi Toppari

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Luis Duarte

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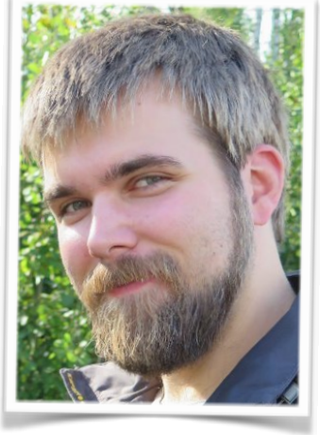

Ossi Hakamaa

Claudia Climent (UAM)

support (Euros, FLOPs & photons)

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