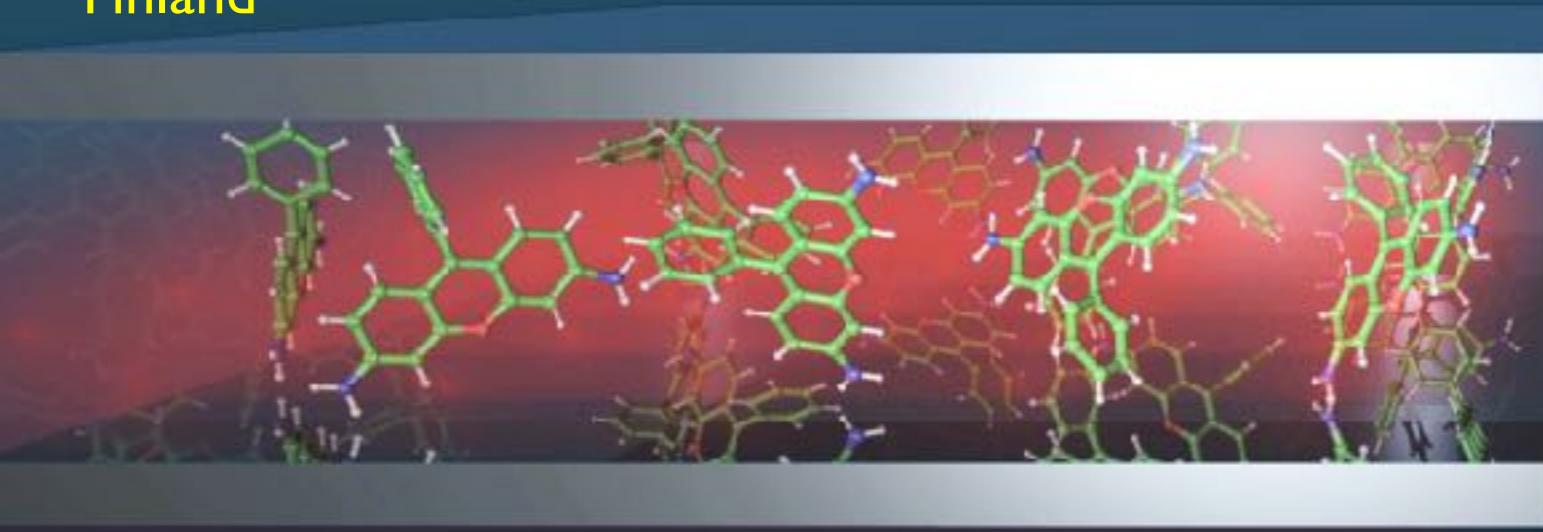


Multi-scale molecular dynamics simulations of polaritonic chemistry

Gerrit Groenhof

Department of Chemistry & Nanoscience center
University of Jyväskylä
Finland



Johannes
Feist (UAM)



Calvin
Luk



Jussi
Toppari

$$\Psi = \beta_1(t) | \text{[molecule 1]} \rangle | 0 \rangle + \\ \beta_2(t) | \text{[molecule 2]} \rangle | 0 \rangle + \\ \beta_3(t) | \text{[molecule 3]} \rangle | 0 \rangle + \\ \beta_4(t) | \text{[molecule 4]} \rangle | 0 \rangle + \\ \beta_5(t) | \text{[molecule 5]} \rangle | 0 \rangle + \\ \beta_6(t) | \text{[molecule 6]} \rangle | 0 \rangle + \\ \beta_7(t) | \text{[molecule 7]} \rangle | 0 \rangle + \\ \beta_8(t) | \text{[molecule 8]} \rangle | 0 \rangle + \\ \alpha(t) | \text{[molecule 9]} \rangle | 1 \rangle$$

Manipulating photo-chemistry

Green Fluorescent Protein (Ser65Thr/His148Asp)

ultra-fast excited-state proton transfer



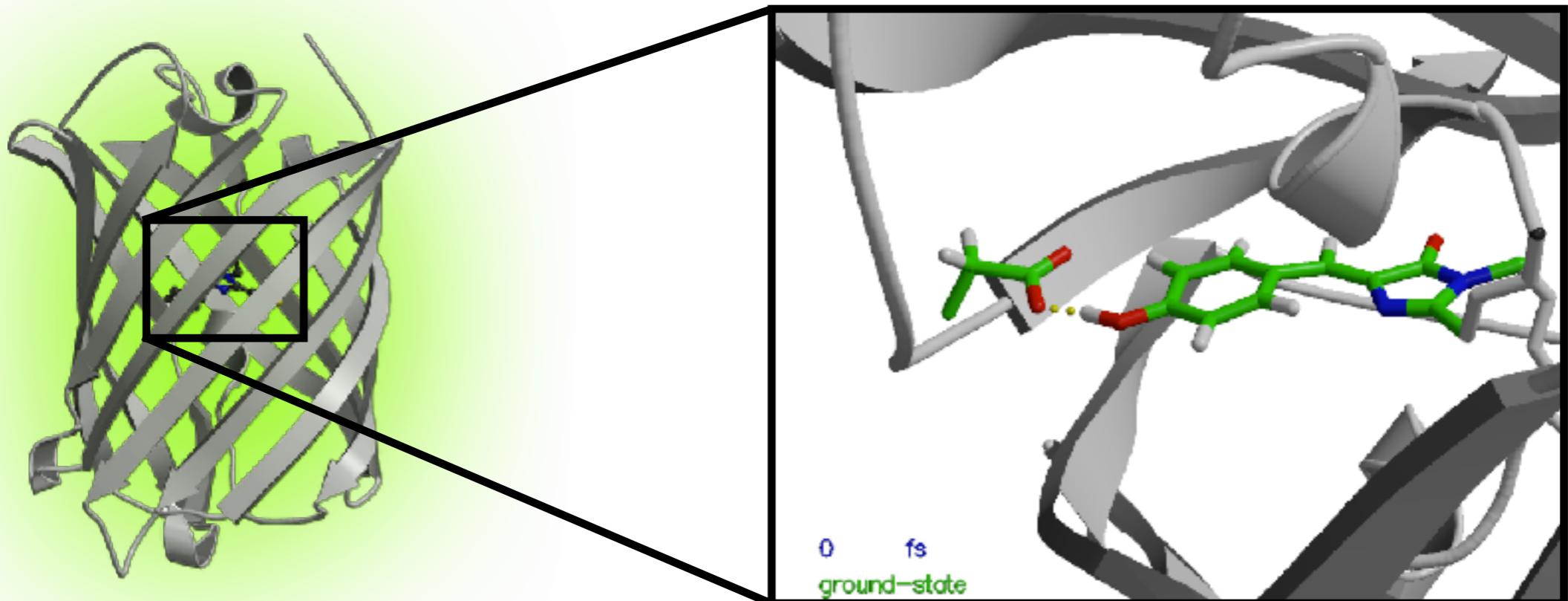
Manipulating photo-chemistry

Green Fluorescent Protein (Ser65Thr/His148Asp)

ultra-fast excited-state proton transfer



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Luk

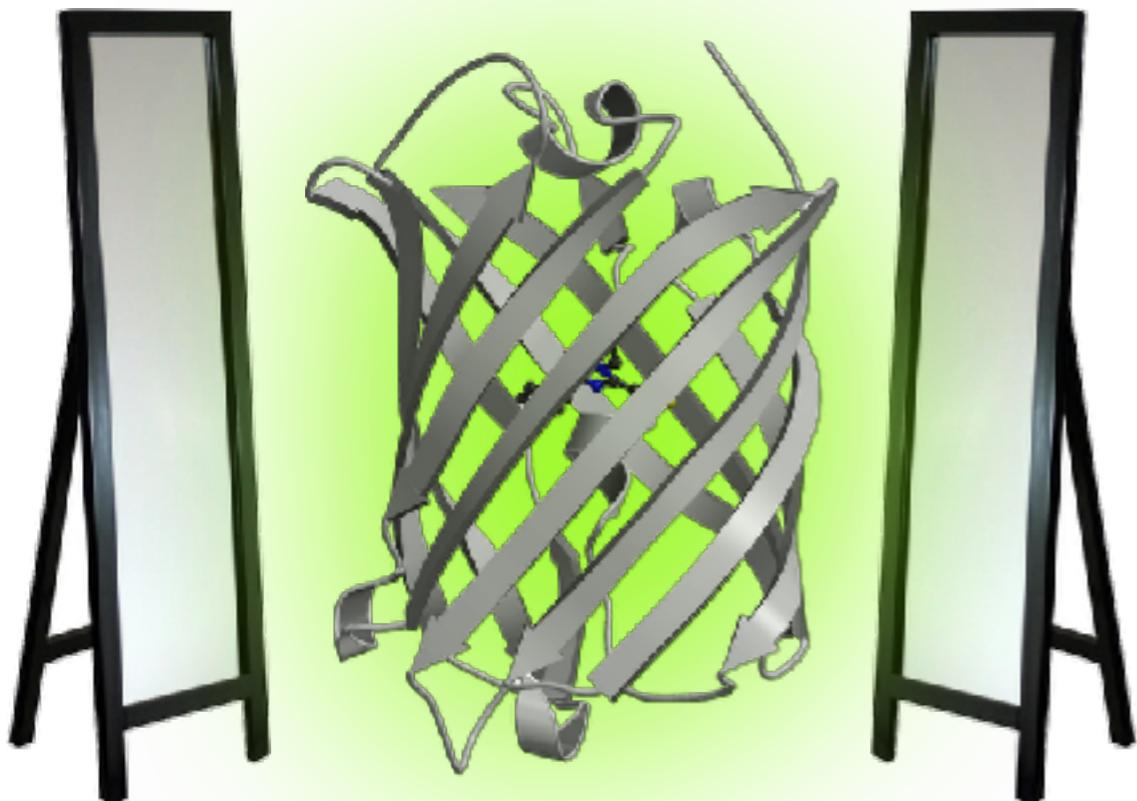


CASSCF(6,6)/3-21G//Amber03

Manipulating photo-chemistry with mirrors

Green Fluorescent Protein (Ser65Thr/His148Asp)

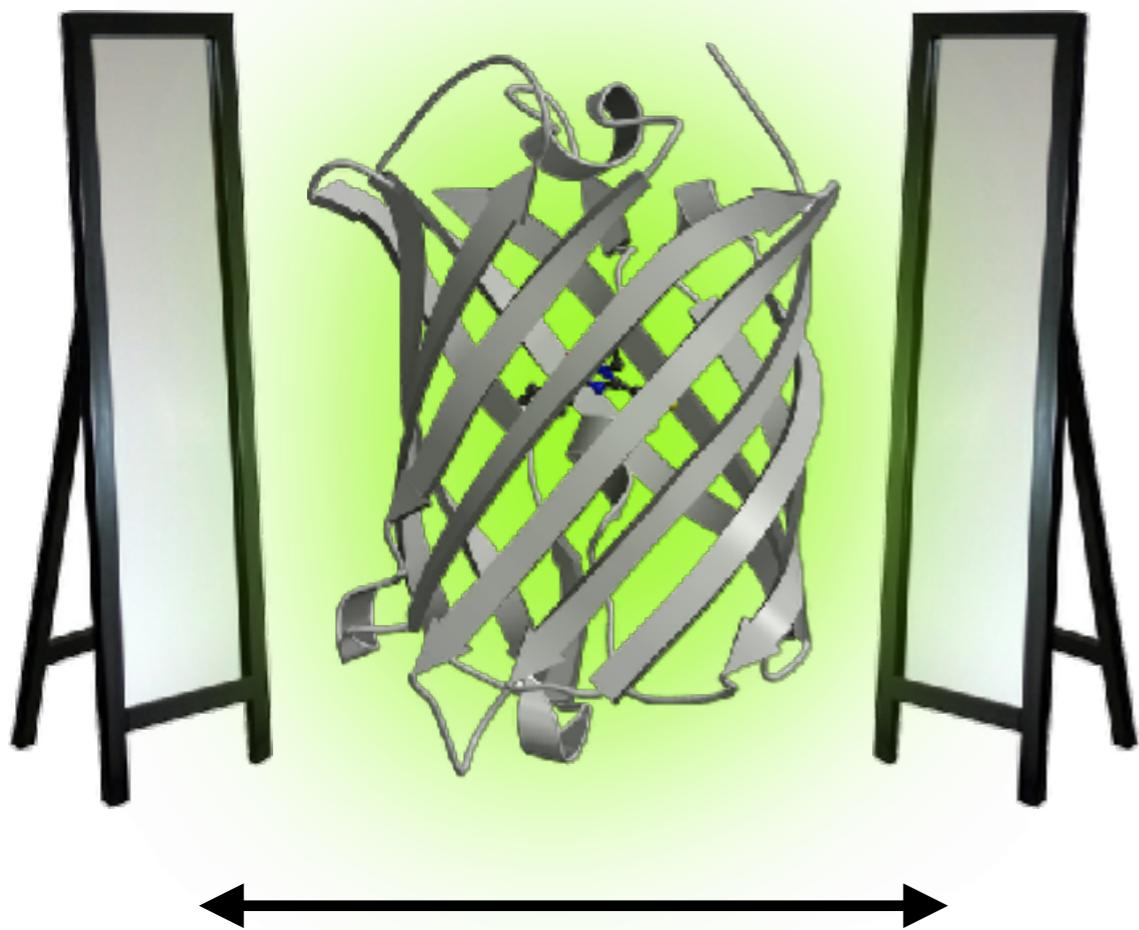
ultra-fast excited-state proton transfer



Manipulating photo-chemistry with mirrors

Green Fluorescent Protein (Ser65Thr/His148Asp)

ultra-fast excited-state proton transfer



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

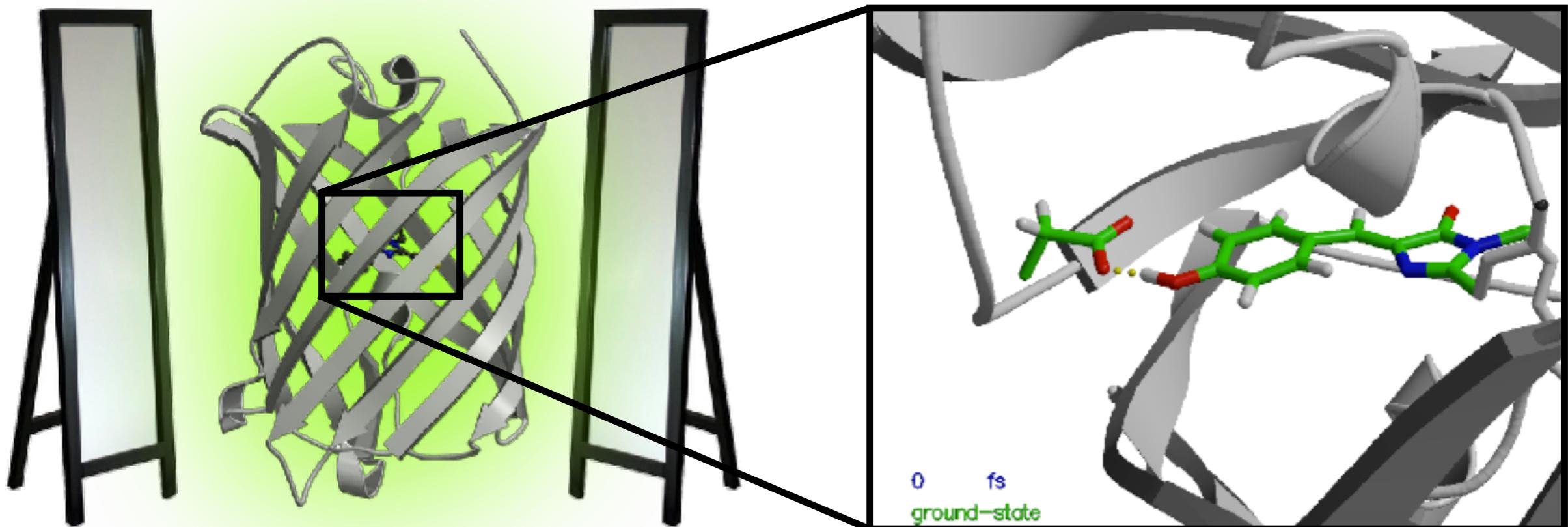
Manipulating photo-chemistry with mirrors

Green Fluorescent Protein (Ser65Thr/His148Asp)

ultra-fast excited-state proton transfer



Calvin
Luk



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

Manipulating photo-chemistry with mirrors

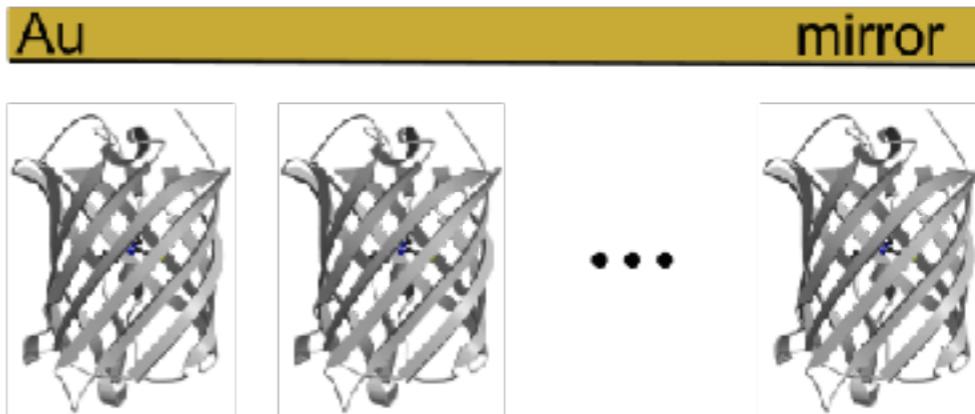
Green Fluorescent Protein

confining light

Fabry-Pèrrot micro-cavities



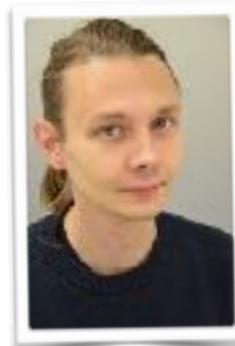
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Mikael
Kautto



Satu
Mustalahti



Eero
Hulkko



Ossi
Hakamaa

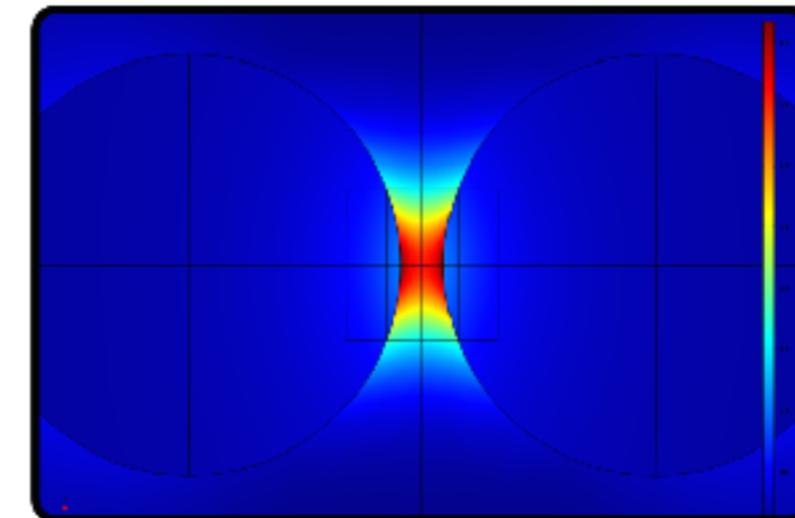
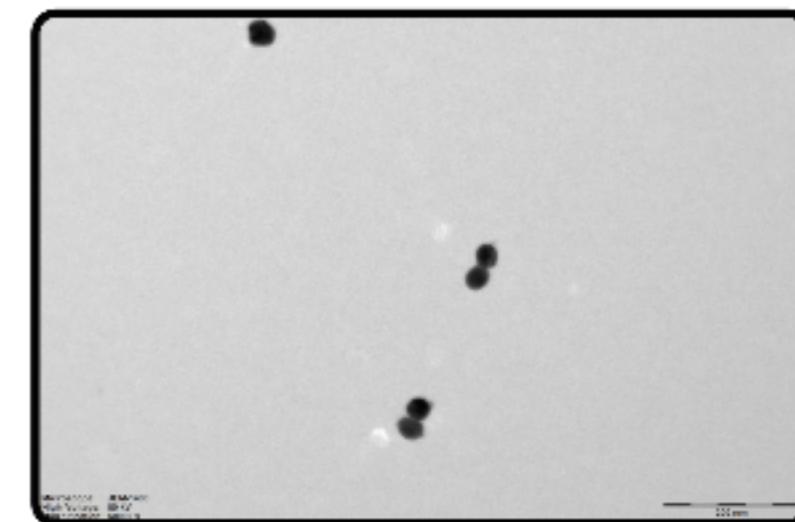
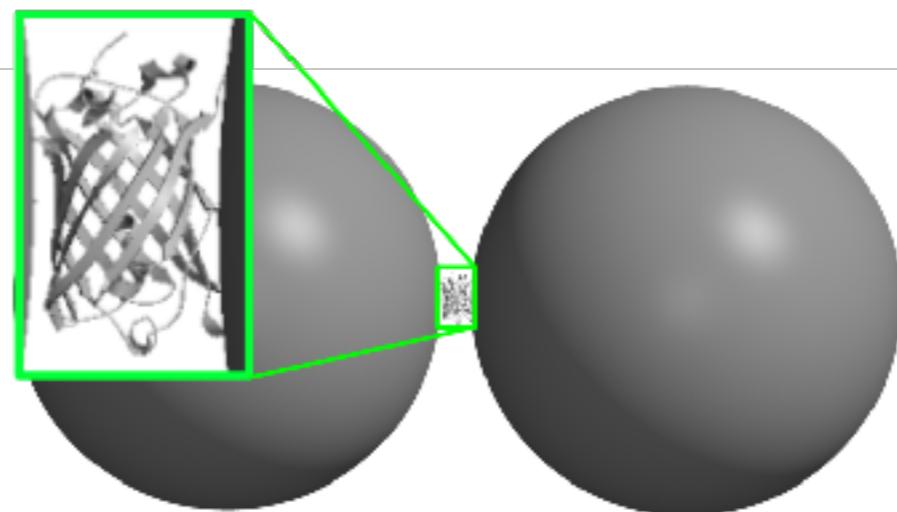
Manipulating photo-chemistry with mirrors

Green Fluorescent Protein

confined light modes
plasmonic nanocavities



=



additional SR144C/D147C mutations



Satu
Mustalahti

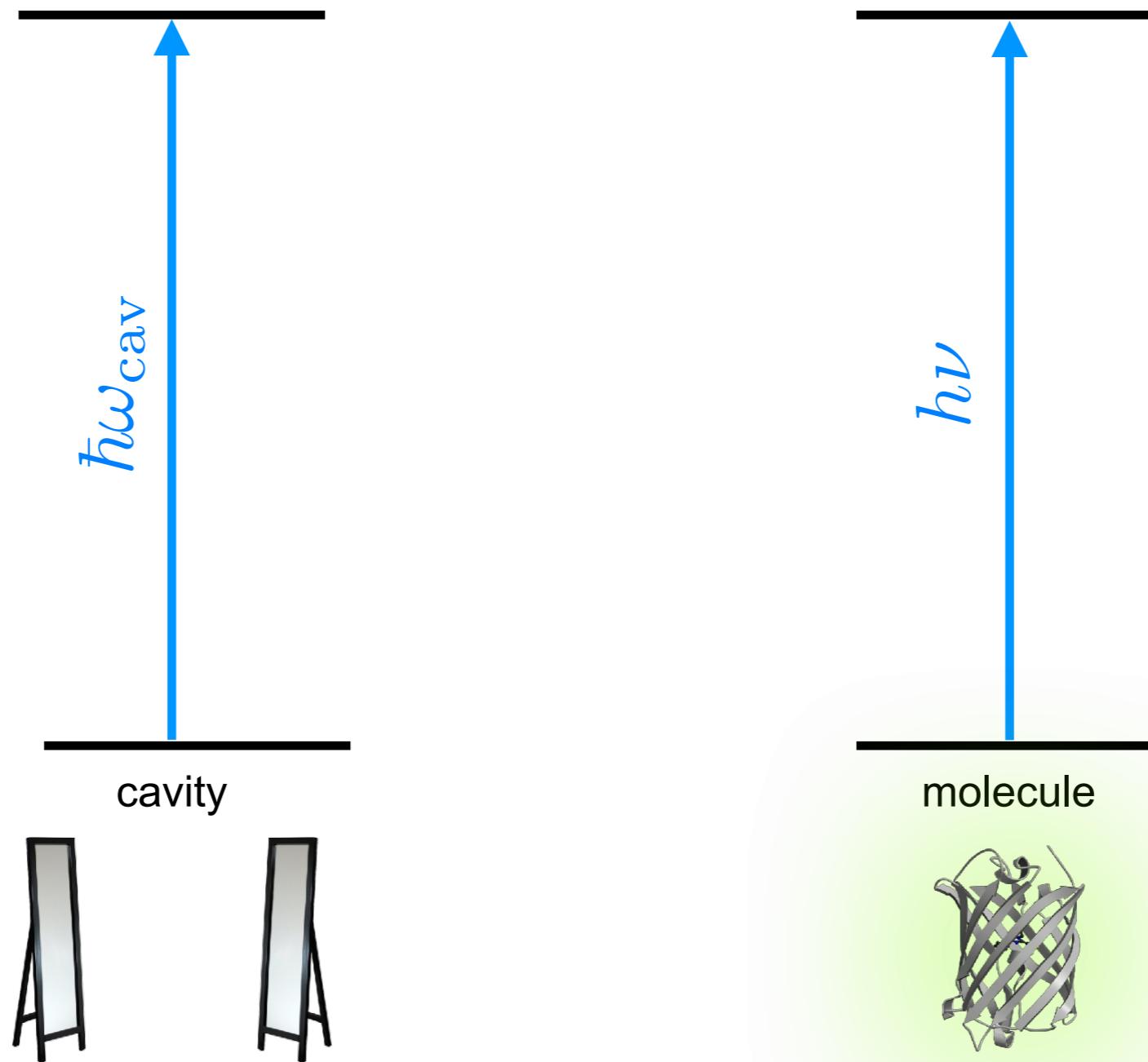


Eero
Hulkko

Why does the photochemistry change?

strong coupling with confined light (cavity QED)

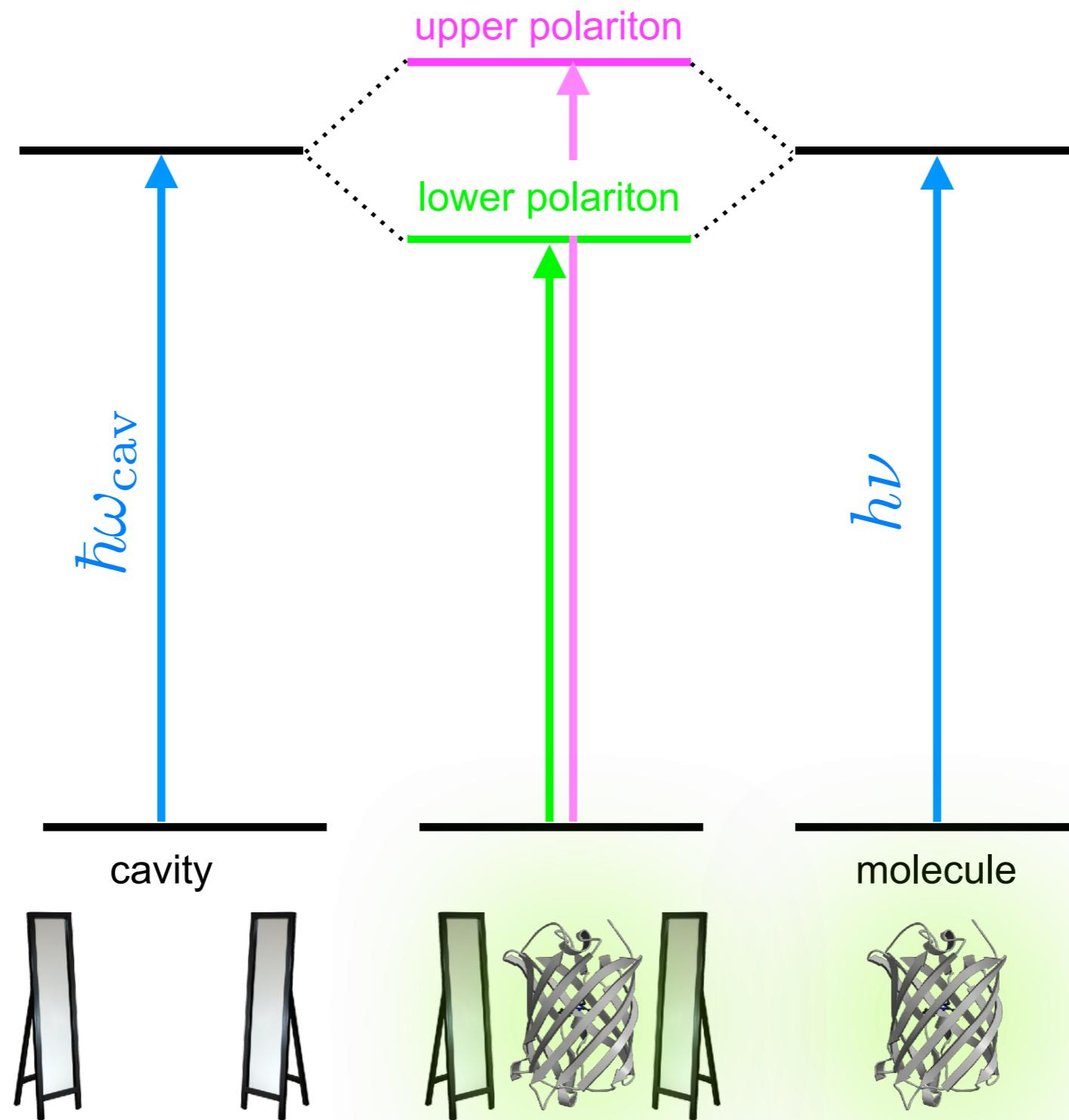
light-matter hybrid states: polaritons



Why does the photochemistry change?

strong coupling with confined light (cavity QED)

light-matter hybrid states: polaritons

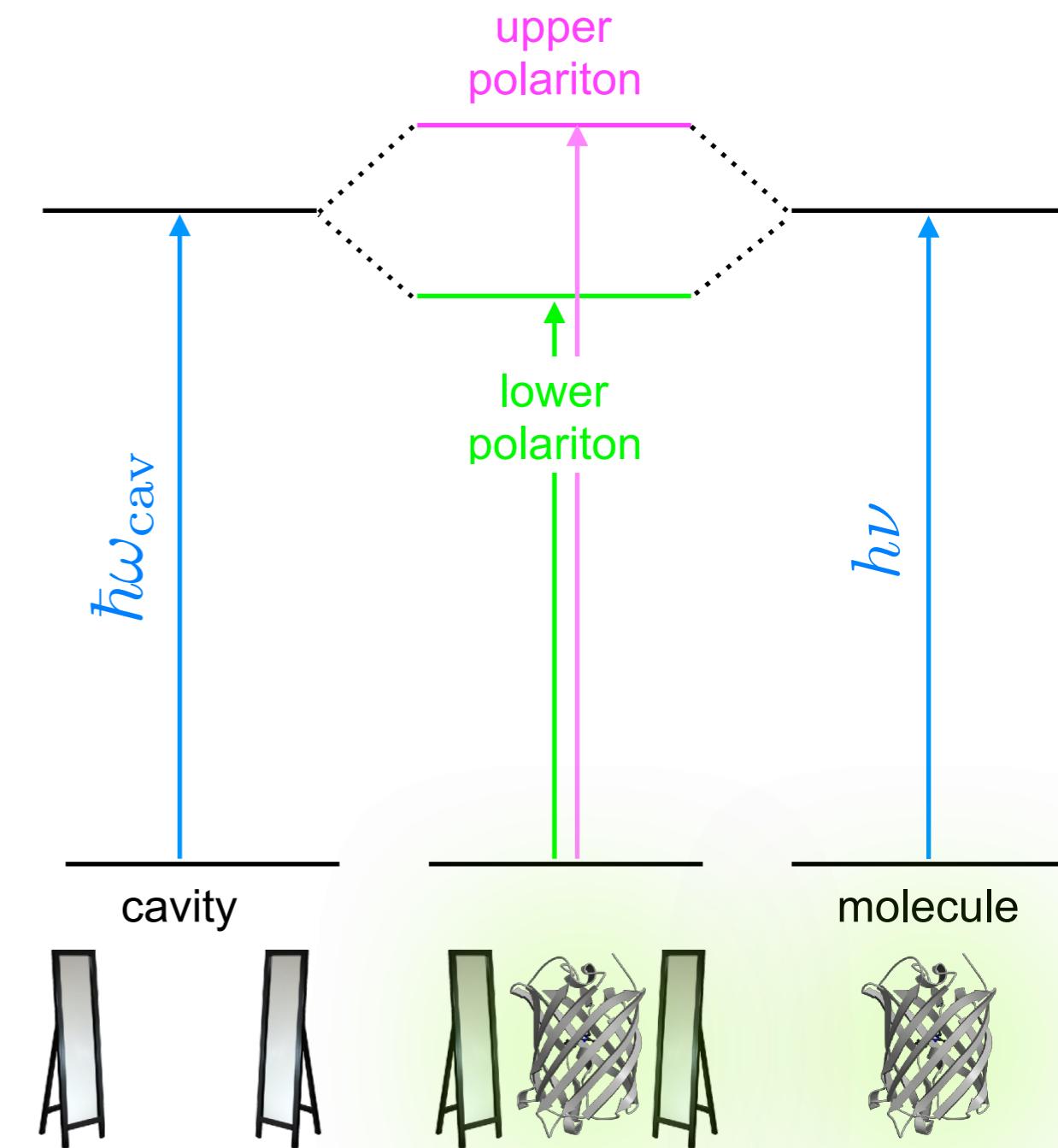


Why does the photochemistry change?

strong coupling with confined light (cavity QED)

light-matter interaction

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



Why does the photochemistry change?

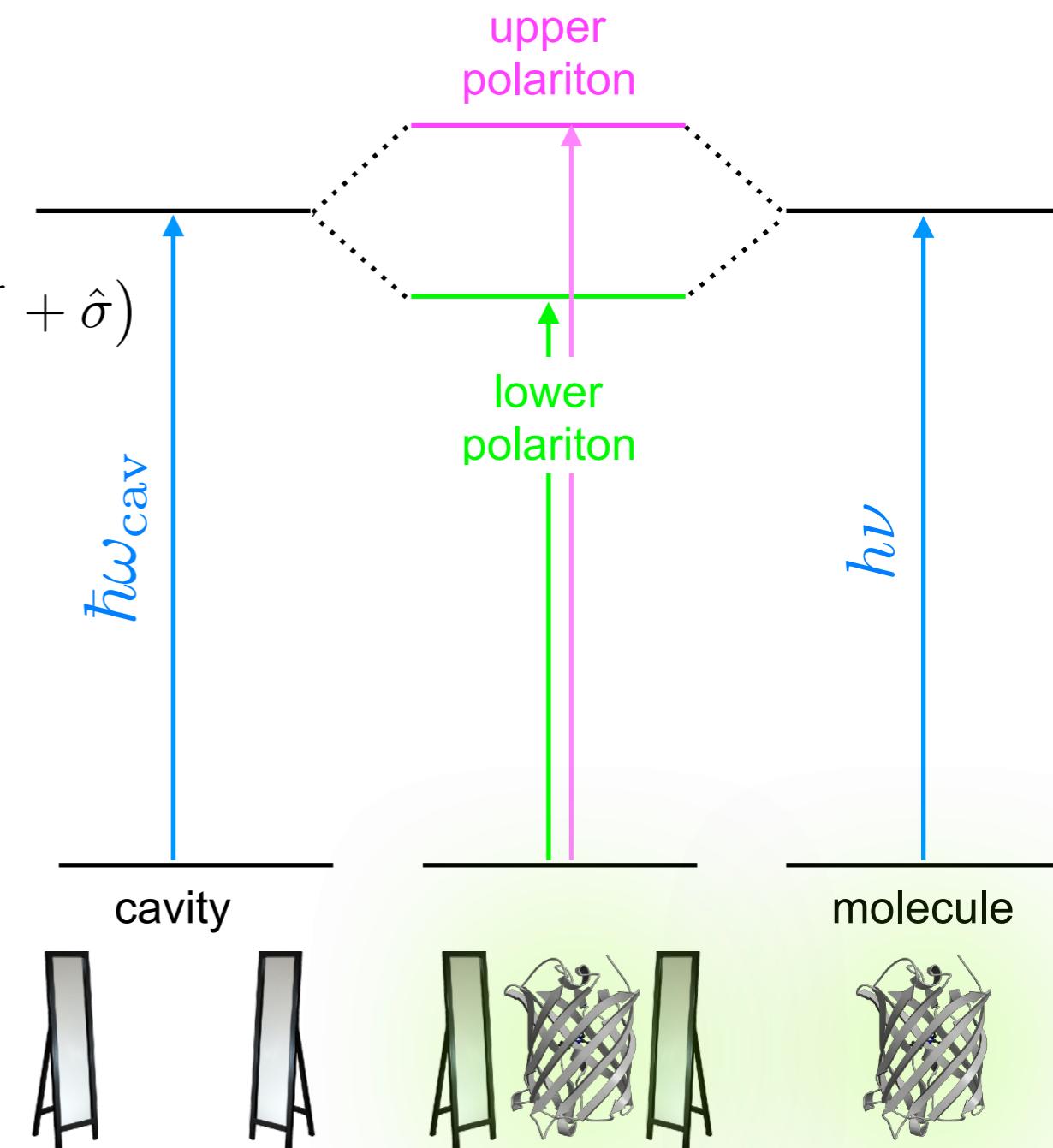
strong coupling with confined light (cavity QED)

light-matter interaction

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

Rabi model

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



Why does the photochemistry change?

strong coupling with confined light (cavity QED)

light-matter interaction

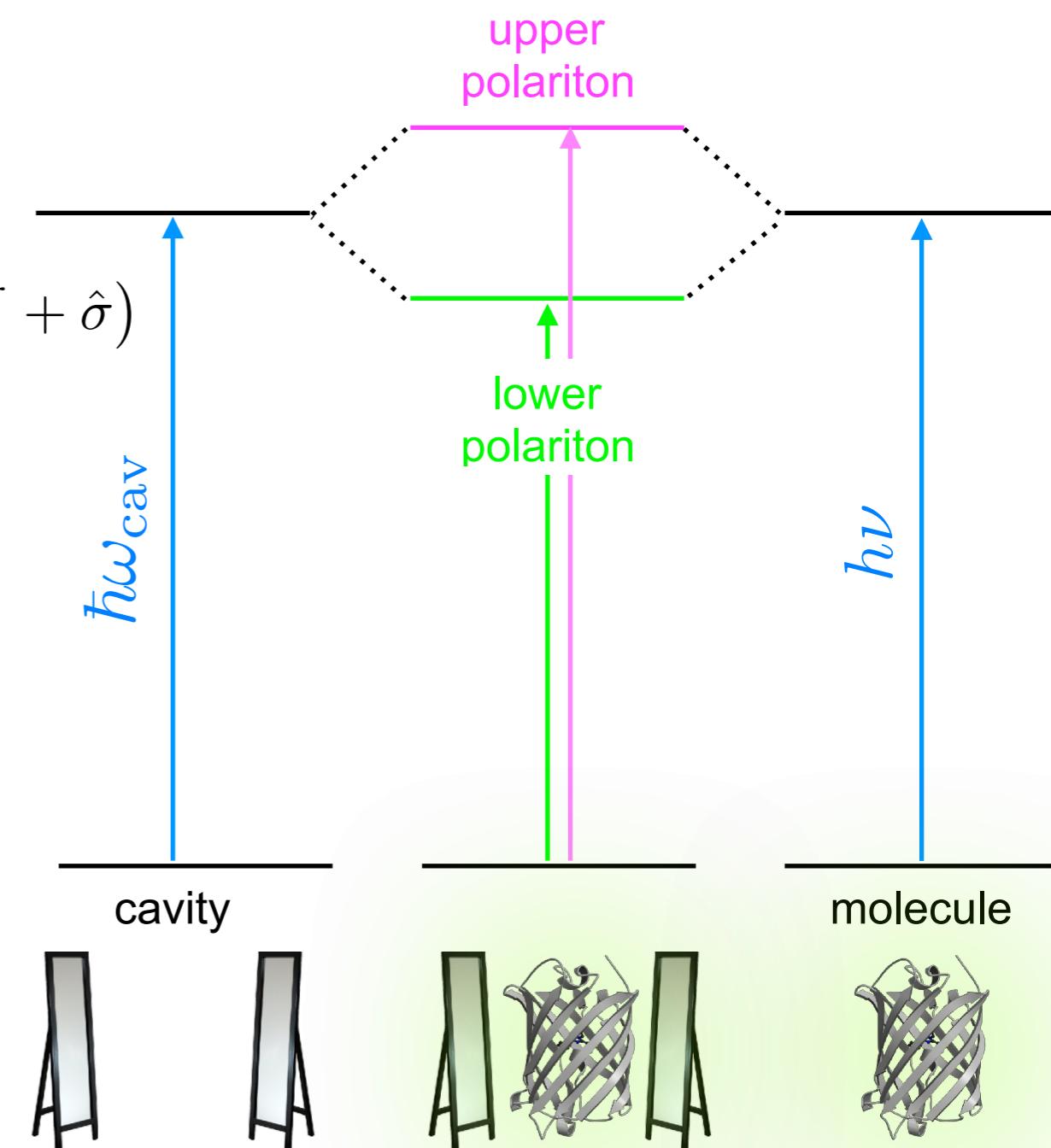
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light-matter coupling in cavity

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



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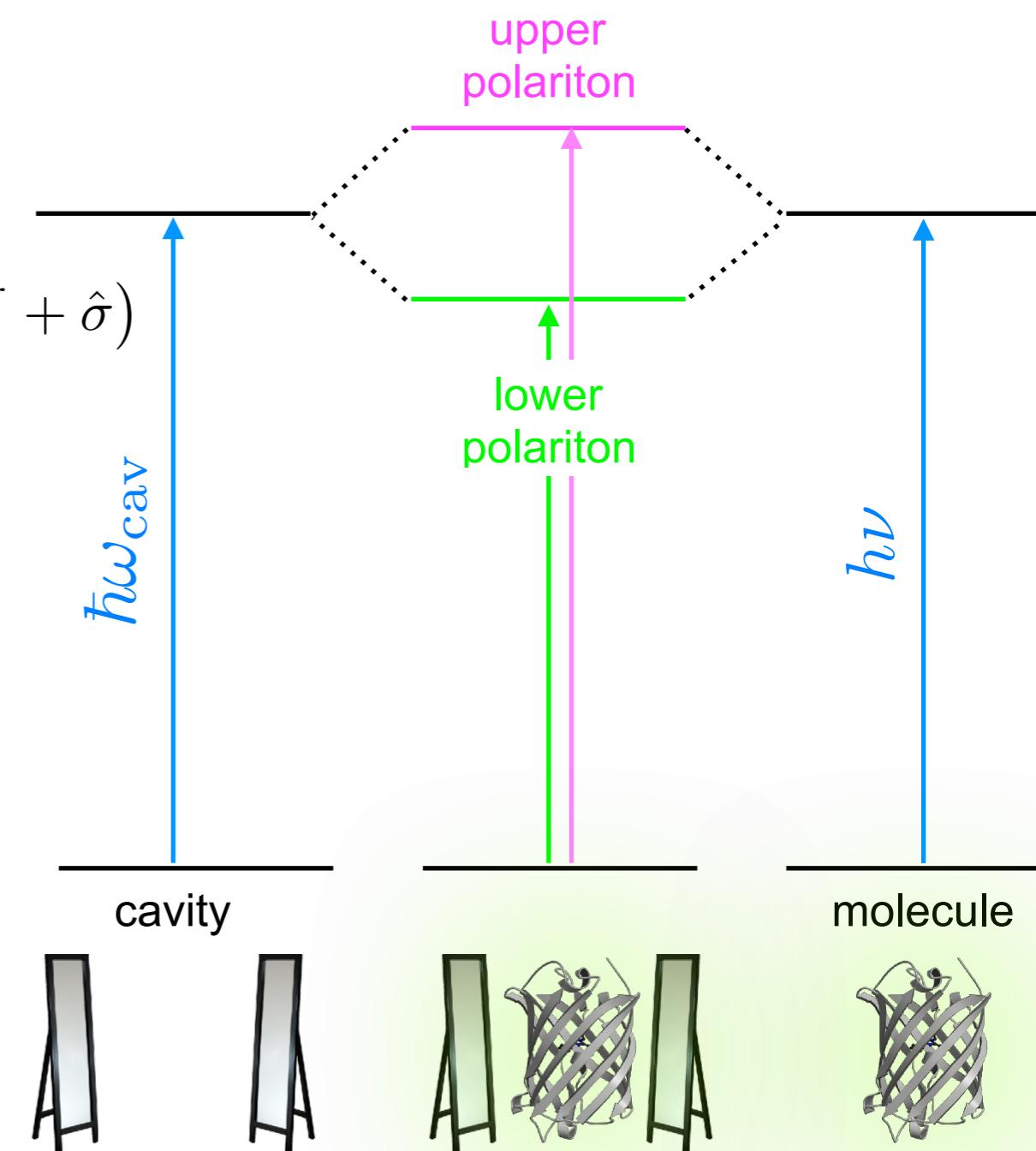
light-matter coupling in cavity

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

rotating wave approximation

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

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



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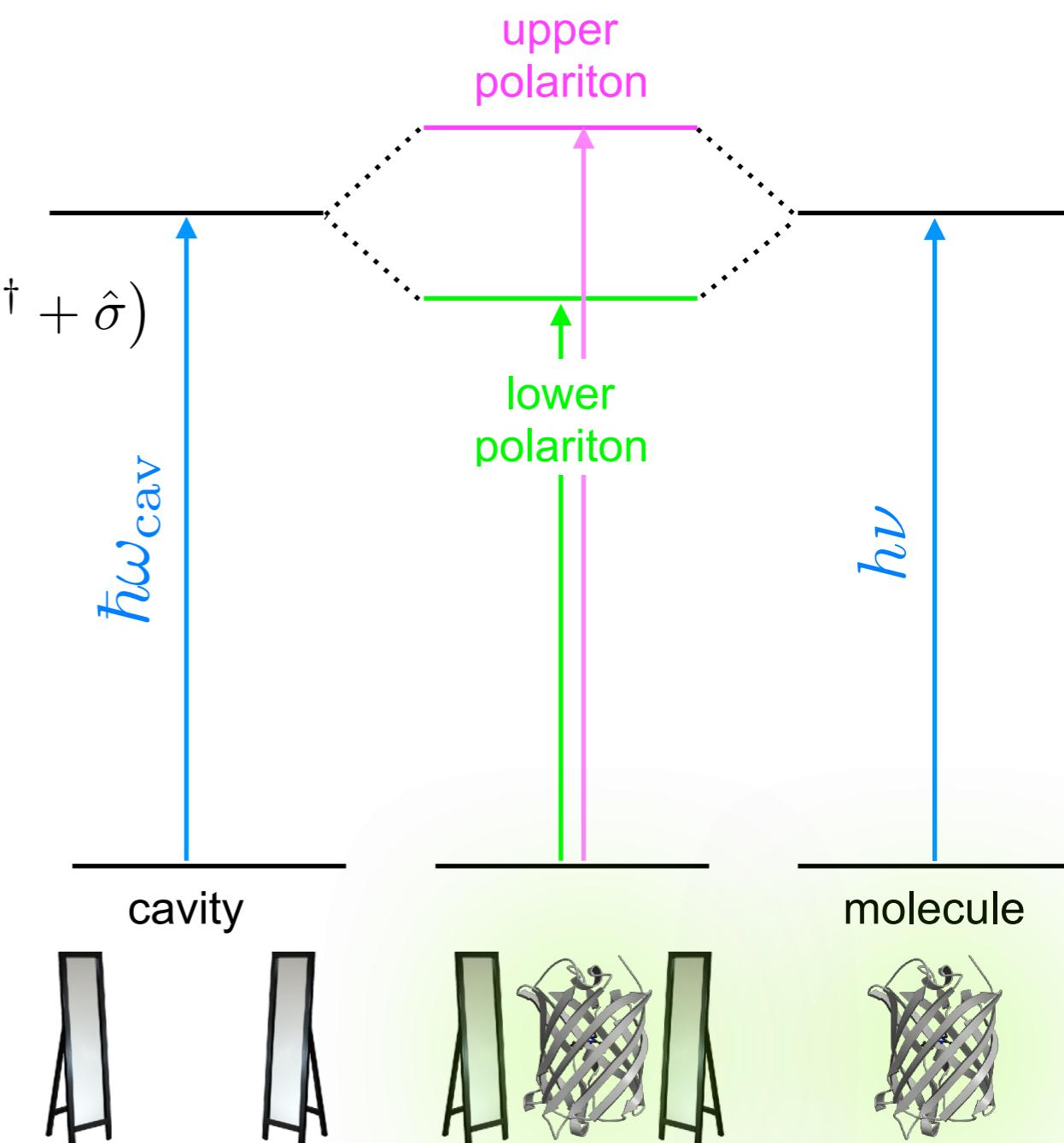
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$$\hat{a}^\dagger\hat{\sigma}^\dagger \approx \hat{a}\hat{\sigma} \approx 0$$

Jaynes-Cummings model (atoms)

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



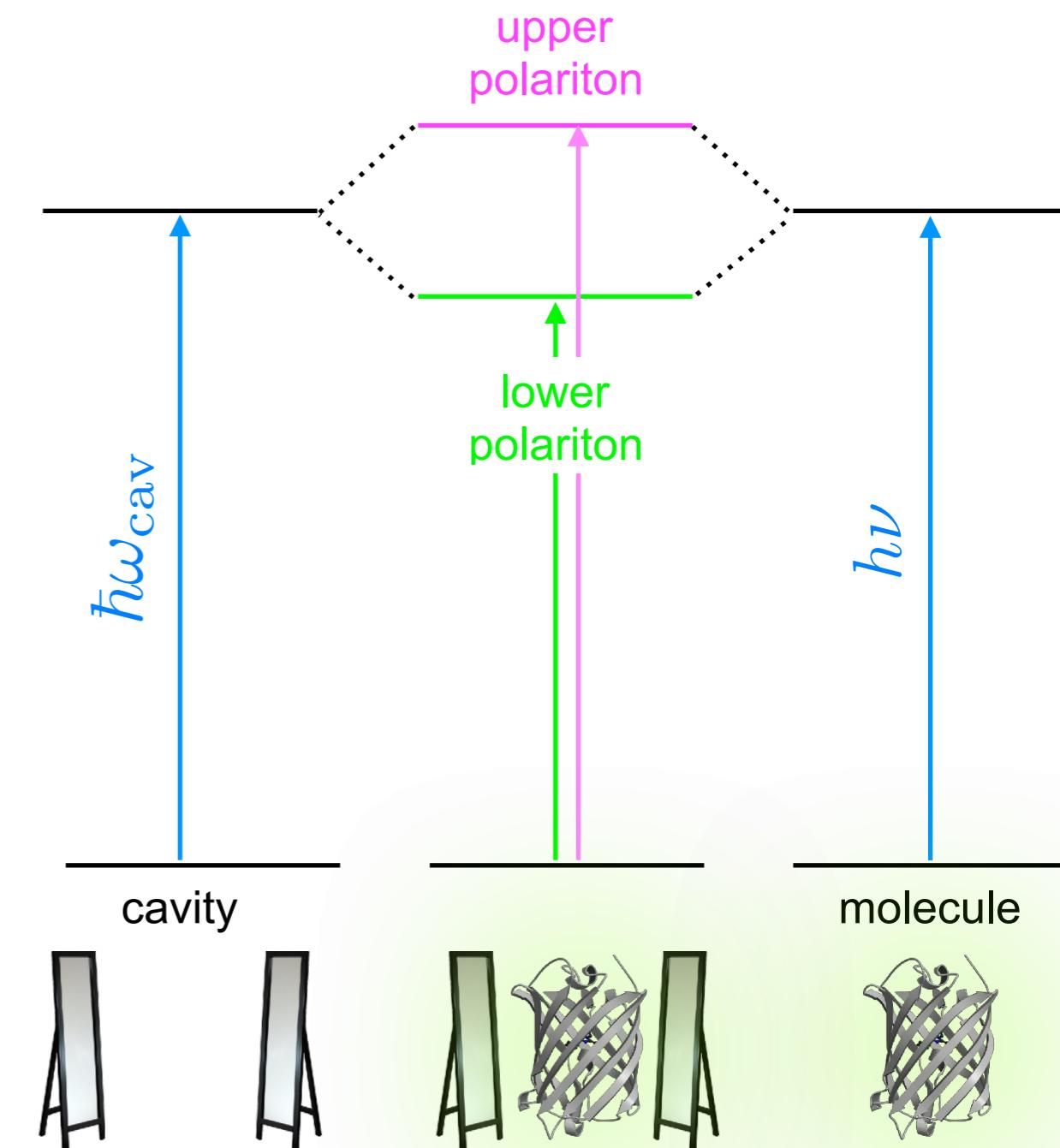
Why does the photochemistry change?

strong coupling with confined light (cavity QED)

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

in matrix form

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



Why does the photochemistry change?

strong coupling with confined light (cavity QED)

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

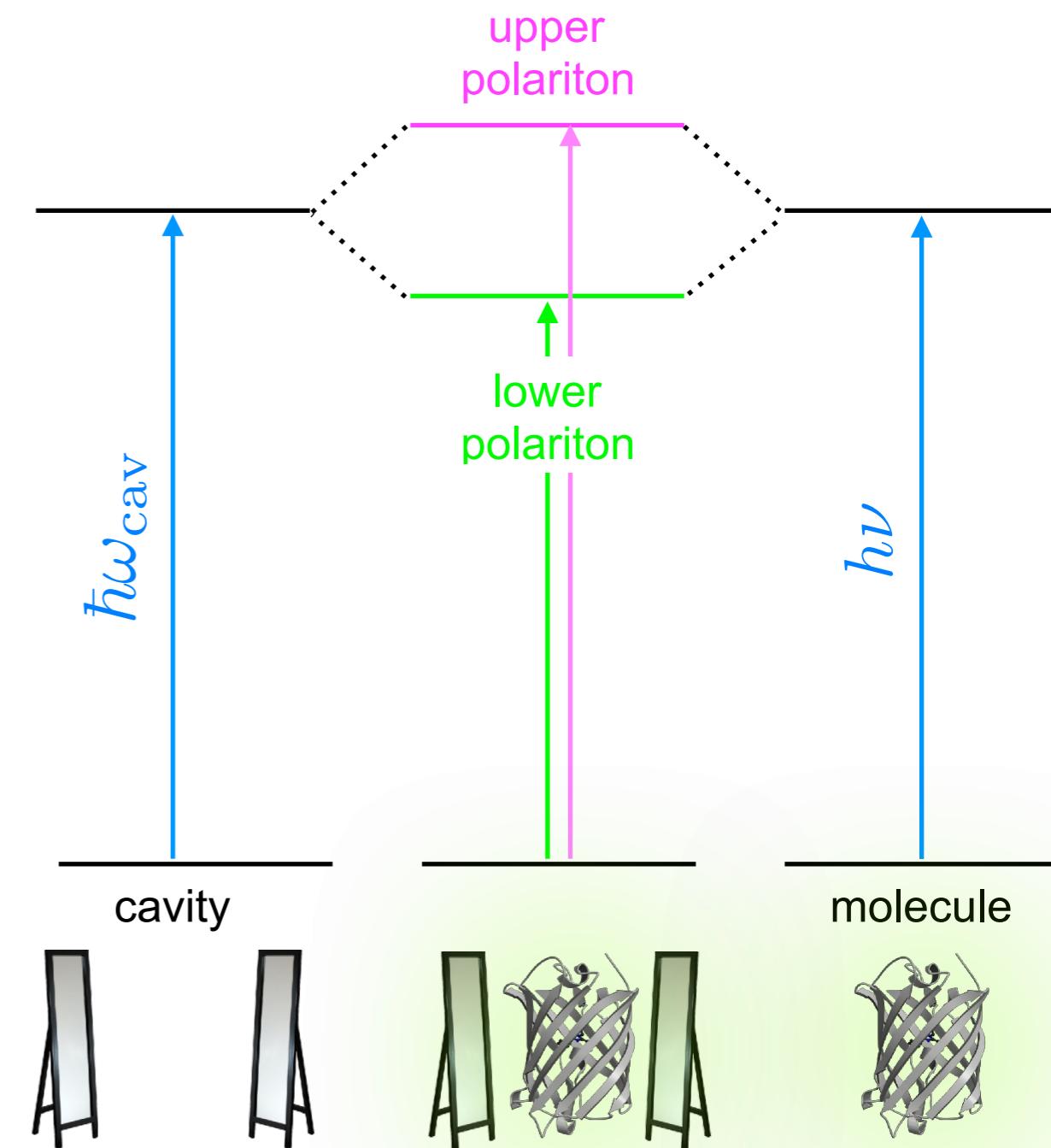
in matrix form

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

with matrix elements

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

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



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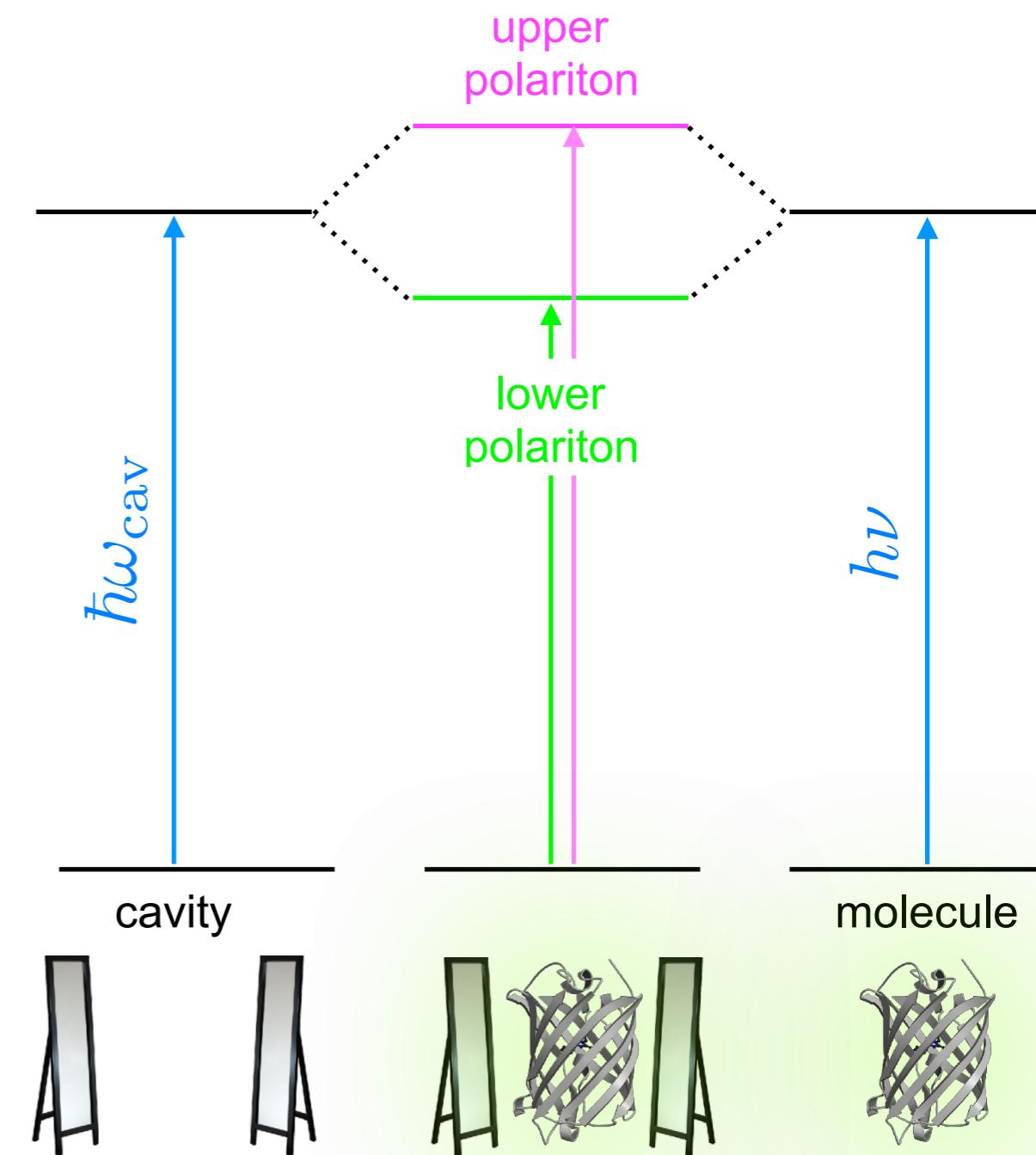
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$$H_{12} = H_{21} = |\langle \text{protein}^\star | \hat{\mu} | \text{protein} \rangle| \sqrt{\hbar\omega_{\text{cav}}/\epsilon_0 V_{\text{cav}}}$$



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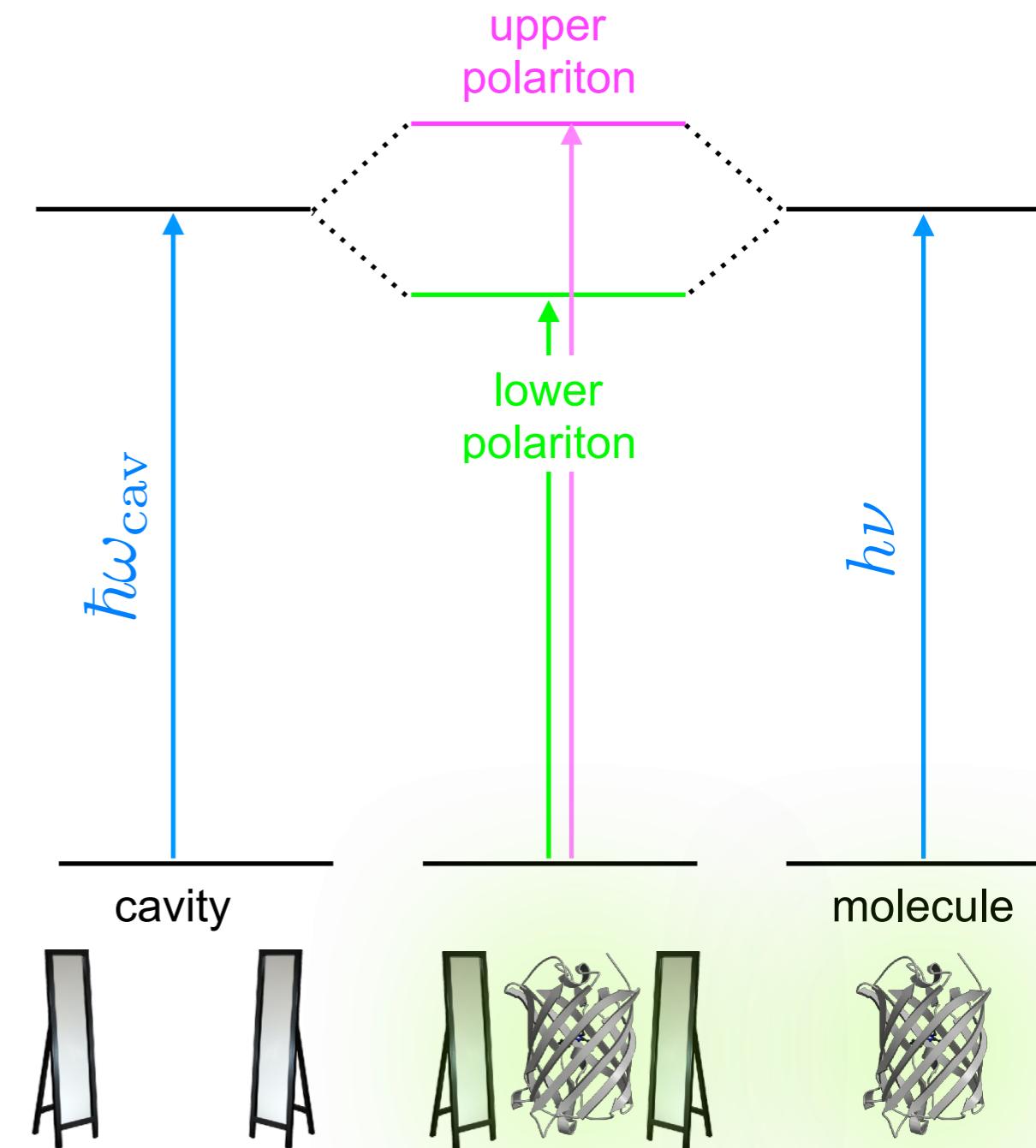
$$\mathbf{H}_{\text{JC}} = \begin{pmatrix} H_{11} & H_{22} \\ H_{12} & H_{22} \end{pmatrix}$$

with matrix elements

$$H_{11} = V_{S_1}(\mathbf{R})$$

$$H_{22} = V_{S_0}(\mathbf{R}) + \hbar\omega_{\text{cav}}$$

$$H_{12} = H_{21} = |\boldsymbol{\mu}_{S_0 \rightarrow S_1}^{\text{TDM}}(\mathbf{R})| \sqrt{\hbar\omega_{\text{cav}}/\epsilon_0 V_{\text{cav}}}$$



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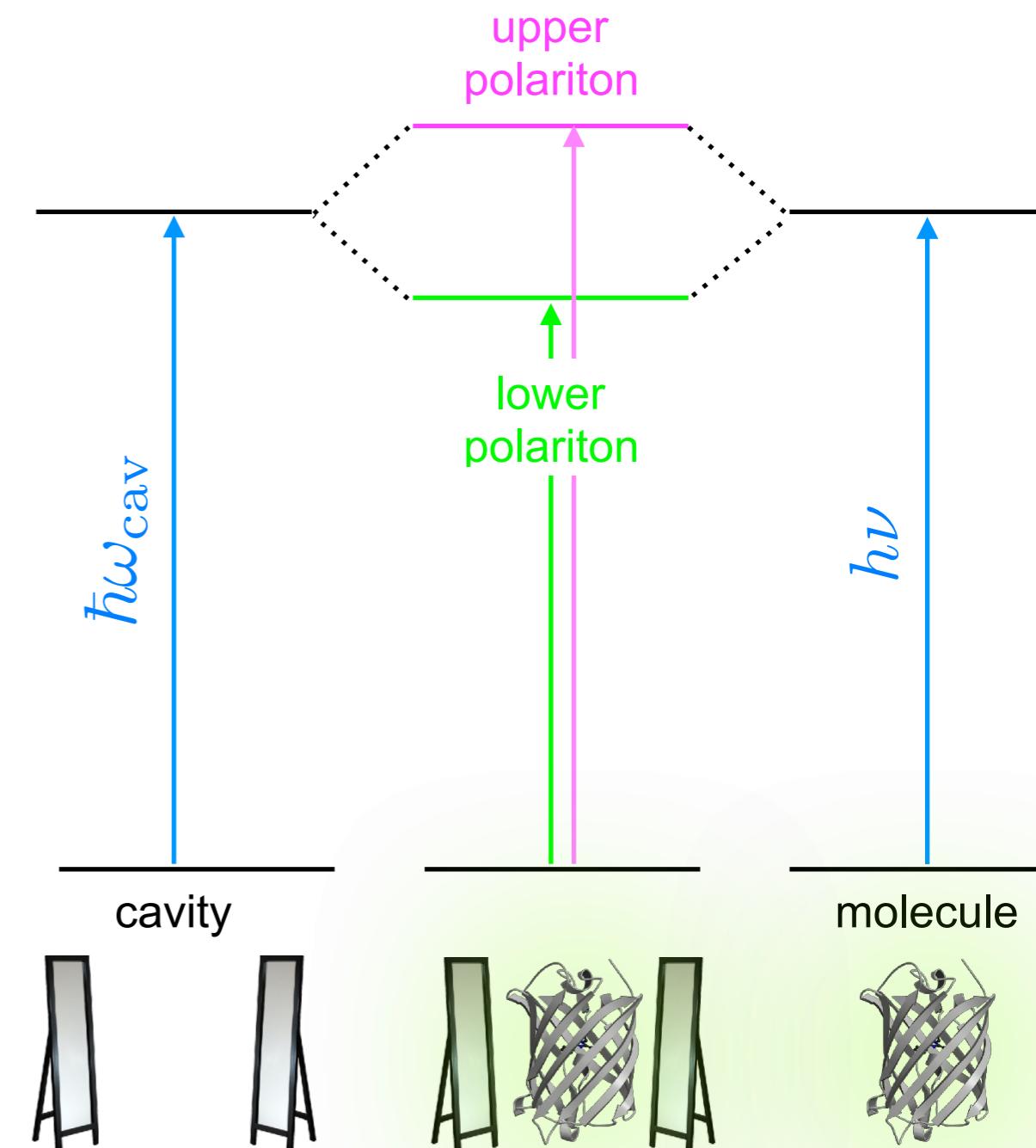
$$H_{22} = V_{S_0}(\mathbf{R}) + \hbar\omega_{\text{cav}}$$

$$H_{12} = H_{21} = |\boldsymbol{\mu}_{S_0 \rightarrow S_1}^{\text{TDM}}(\mathbf{R})| \sqrt{\hbar\omega_{\text{cav}}/\epsilon_0 V_{\text{cav}}}$$

and solution

$$\Psi^K = \beta_1^K | \text{protein}_1^\star \rangle | 0 \rangle + \alpha^K | \text{protein}_1 \rangle | 1^\star \rangle$$

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

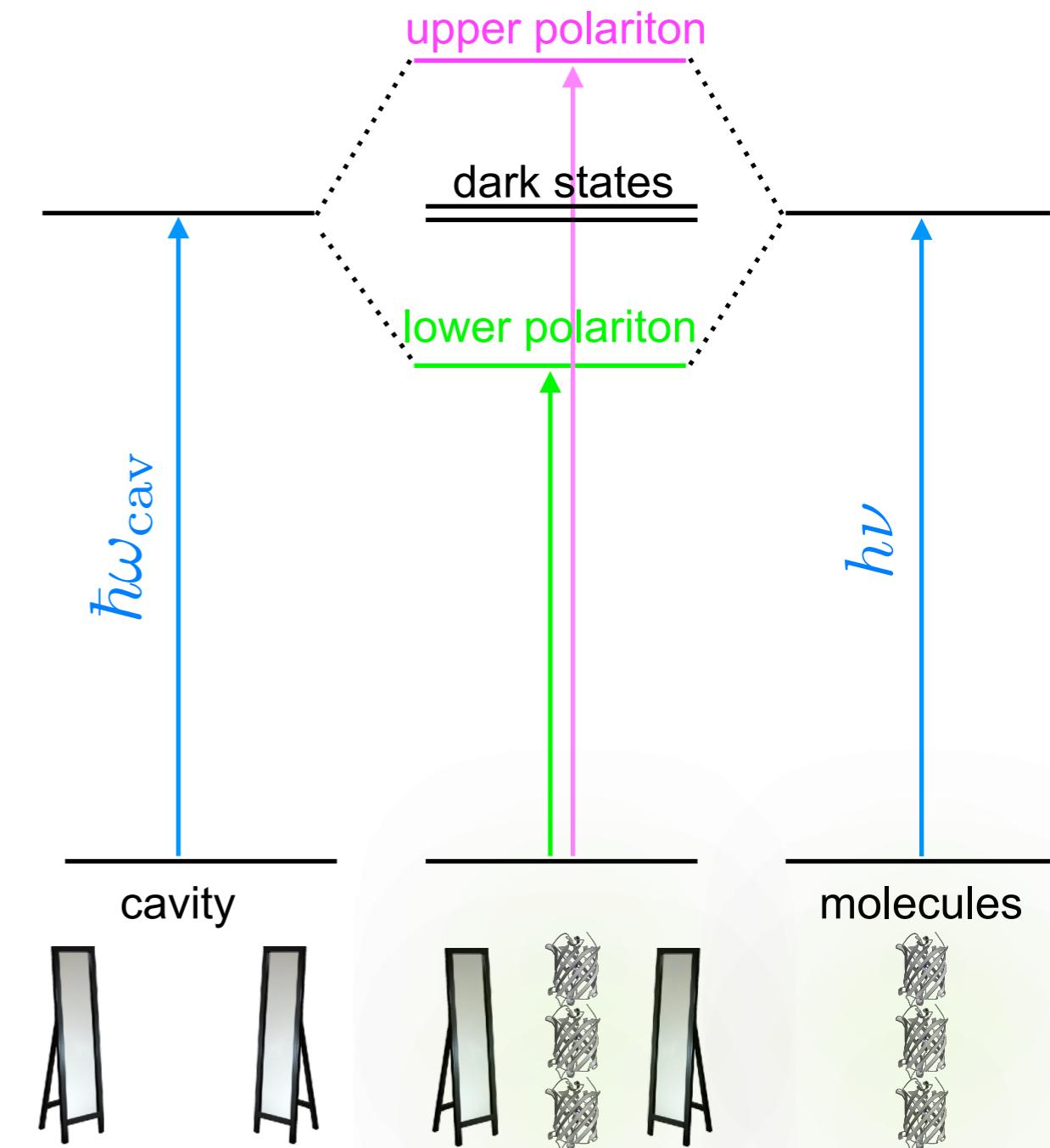


Why does the photochemistry change?

strong coupling with confined light (cavity QED)

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

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



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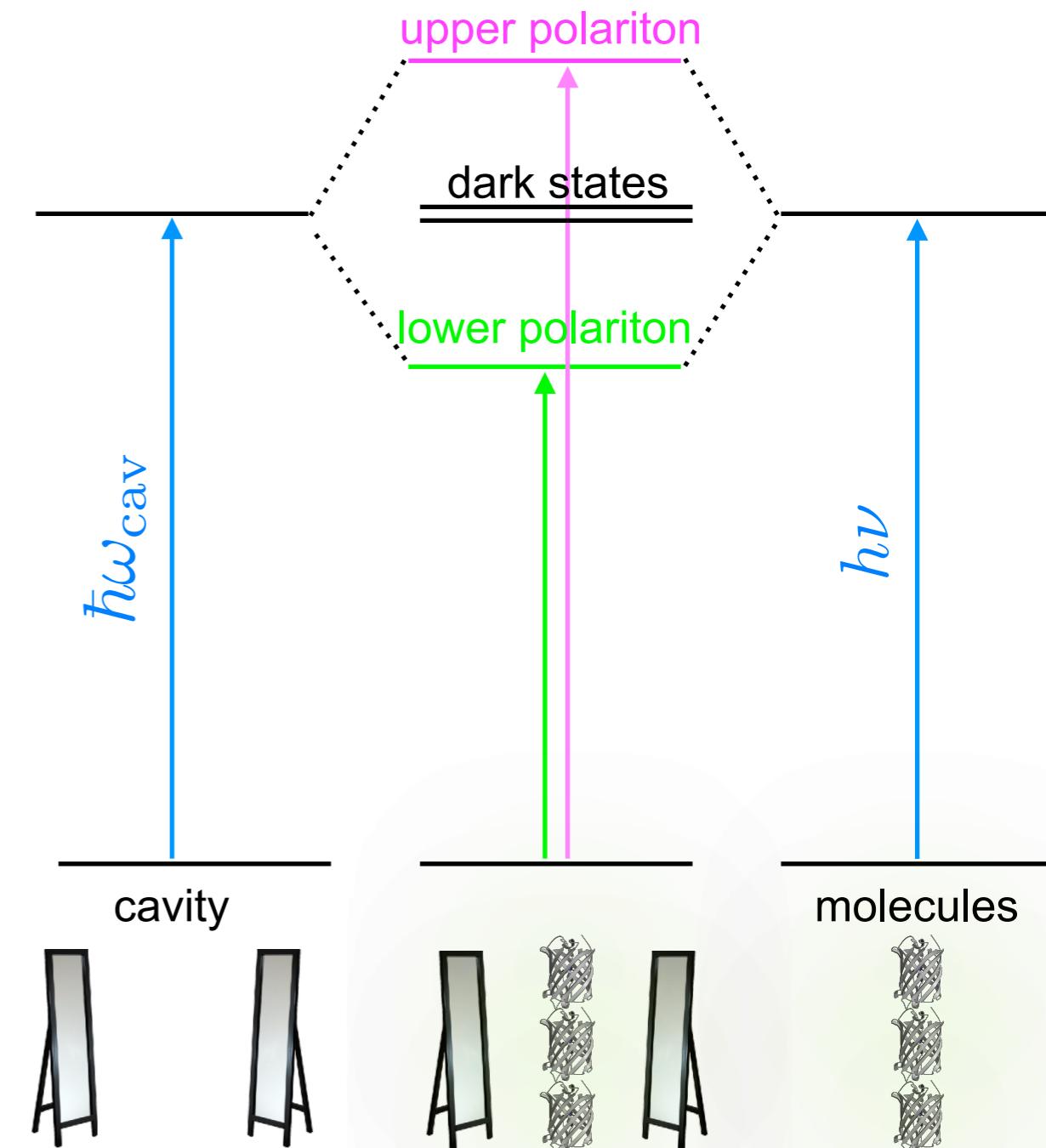
with matrix elements

$$H_{11} = \langle \text{protein}_1 | \hat{H} | \text{protein}_1 \rangle \langle 0 | 0 \rangle$$

$$H_{22} = \langle \text{protein}_2 | \hat{H} | \text{protein}_2 \rangle \langle 0 | 0 \rangle$$

$$H_{33} = \langle \text{protein}_3 | \hat{H} | \text{protein}_3 \rangle \langle 0 | 0 \rangle$$

$$H_{44} = \langle \text{molecules} | \hat{H} | \text{molecules} \rangle \langle 1 | 1 \rangle + \hbar\omega_{\text{cav}}$$



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

with matrix elements

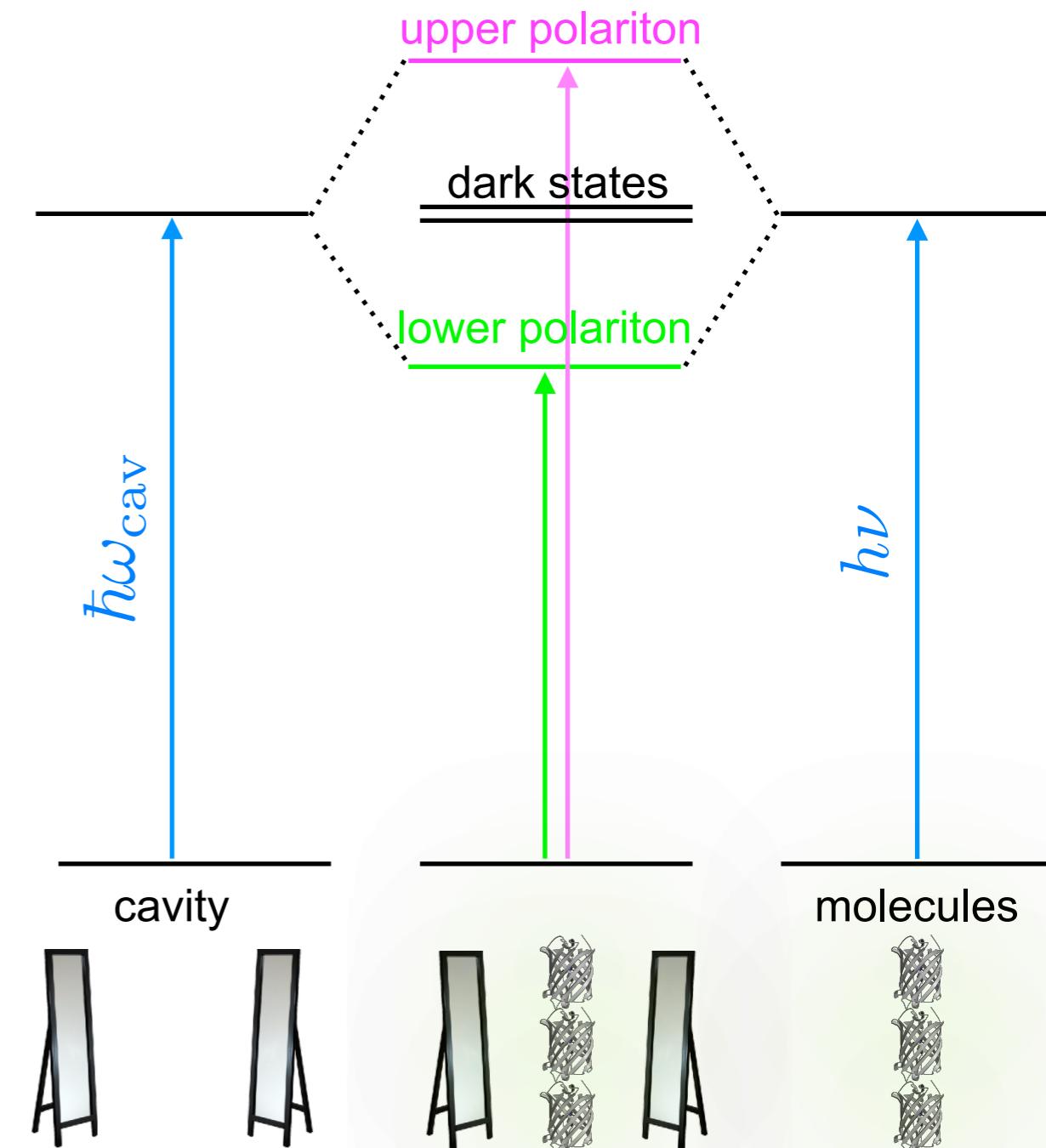
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$$H_{22} = \langle \text{protein}_2 | \hat{H} | \text{protein}_2 \rangle \langle 0 | 0 \rangle$$

$$H_{33} = \langle \text{protein}_3 | \hat{H} | \text{protein}_3 \rangle \langle 0 | 0 \rangle$$

$$H_{44} = \langle \text{molecules} | \hat{H} | \text{molecules} \rangle \langle 1 | 1 \rangle + \hbar\omega_{\text{cav}}$$

$$H_{4i} = H_{i4} = |\langle \text{protein}_i | \hat{\mu} | \text{molecules} \rangle| \sqrt{\hbar\omega_{\text{cav}} / \epsilon_0 V_{\text{cav}}}$$



Why does the photochemistry change?

strong coupling with confined light (cavity QED)

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

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

with matrix elements

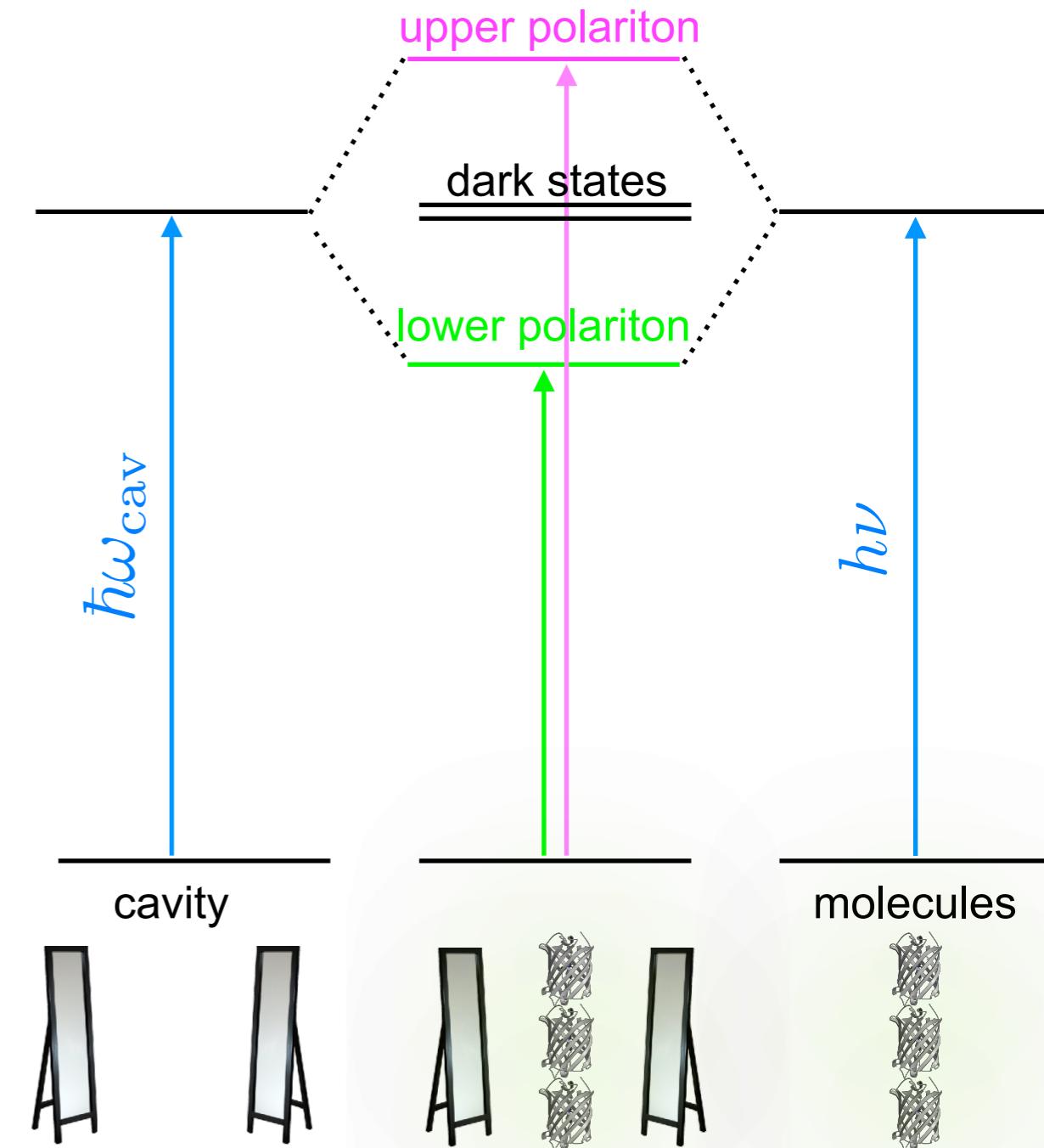
$$H_{11} = V_{S_1}(\mathbf{R}_1) + V_{S_0}(\mathbf{R}_2) + V_{S_0}(\mathbf{R}_3)$$

$$H_{22} = V_{S_0}(\mathbf{R}_1) + V_{S_1}(\mathbf{R}_2) + V_{S_0}(\mathbf{R}_3)$$

$$H_{33} = V_{S_0}(\mathbf{R}_1) + V_{S_0}(\mathbf{R}_2) + V_{S_1}(\mathbf{R}_3)$$

$$H_{44} = V_{S_0}(\mathbf{R}_1) + V_{S_0}(\mathbf{R}_2) + V_{S_0}(\mathbf{R}_3) + \hbar\omega_{\text{cav}}$$

$$H_{i4} = H_{4i} = |\boldsymbol{\mu}_{S_0 \rightarrow S_1}^{\text{TDM}}(\mathbf{R}_i)| \sqrt{\hbar\omega_{\text{cav}}/\epsilon_0 V_{\text{cav}}}$$



Why does the photochemistry change?

strong coupling with confined light (cavity QED)

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

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

with matrix elements

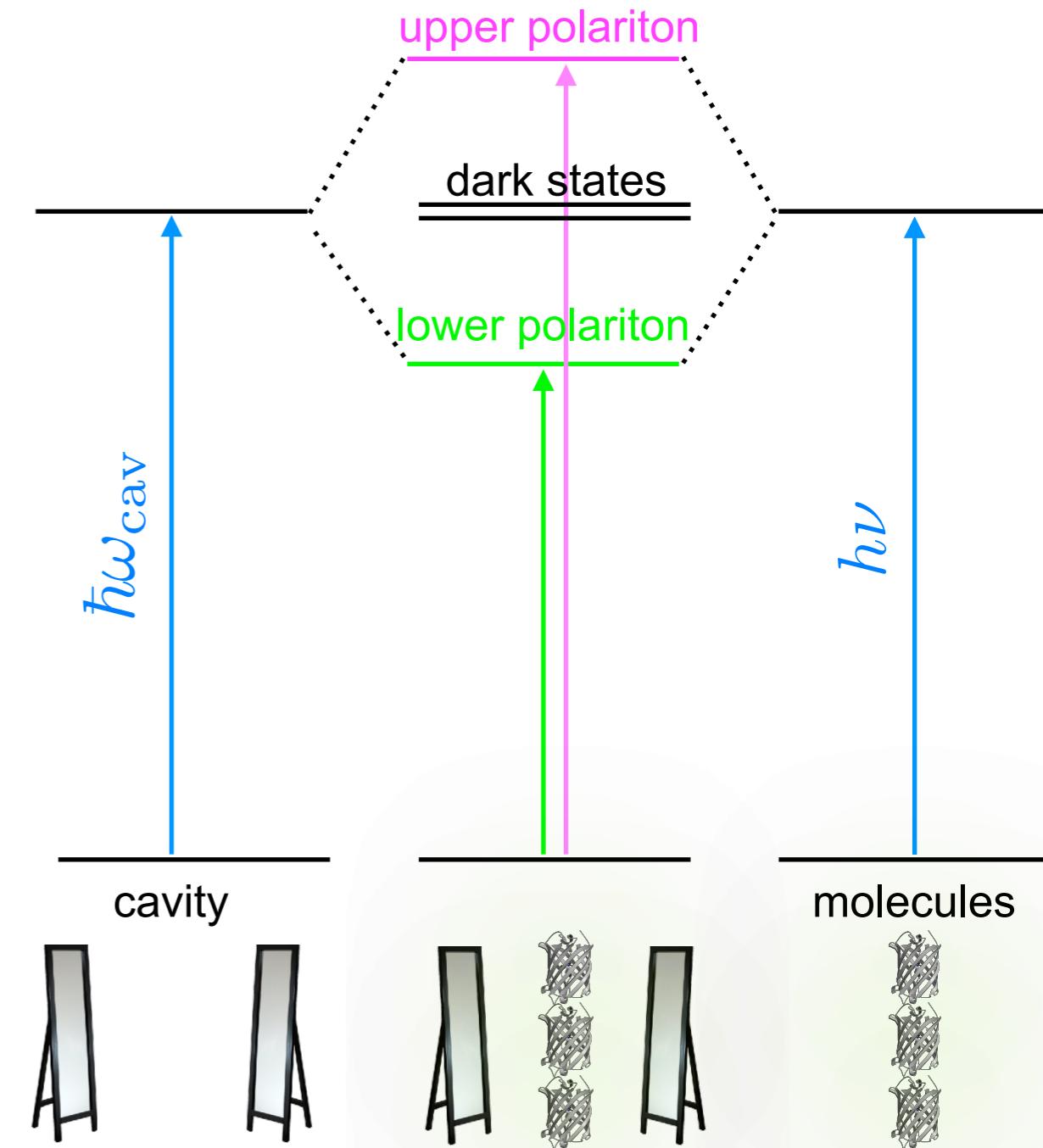
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$$H_{33} = V_{S_0}(\mathbf{R}_1) + V_{S_0}(\mathbf{R}_2) + V_{S_1}(\mathbf{R}_3)$$

$$H_{44} = V_{S_0}(\mathbf{R}_1) + V_{S_0}(\mathbf{R}_2) + V_{S_0}(\mathbf{R}_3) + \hbar\omega_{\text{cav}}$$

$$H_{i4} = H_{4i} = |\boldsymbol{\mu}_{S_0 \rightarrow S_1}^{\text{TDM}}(\mathbf{R}_i)| \sqrt{\hbar\omega_{\text{cav}}/\epsilon_0 V_{\text{cav}}}$$



and solution

$$\Psi^K = \beta_1^K | \text{protein 1}^\star \text{protein 2} \text{protein 3} \rangle |0\rangle + \beta_2^K | \text{protein 1} \text{protein 2}^\star \text{protein 3} \rangle |0\rangle + \beta_3^K | \text{protein 1} \text{protein 2} \text{protein 3}^\star \rangle |0\rangle + \alpha^K | \text{protein 1} \text{protein 2} \text{protein 3} \rangle |1\rangle$$

Why does the photochemistry change?

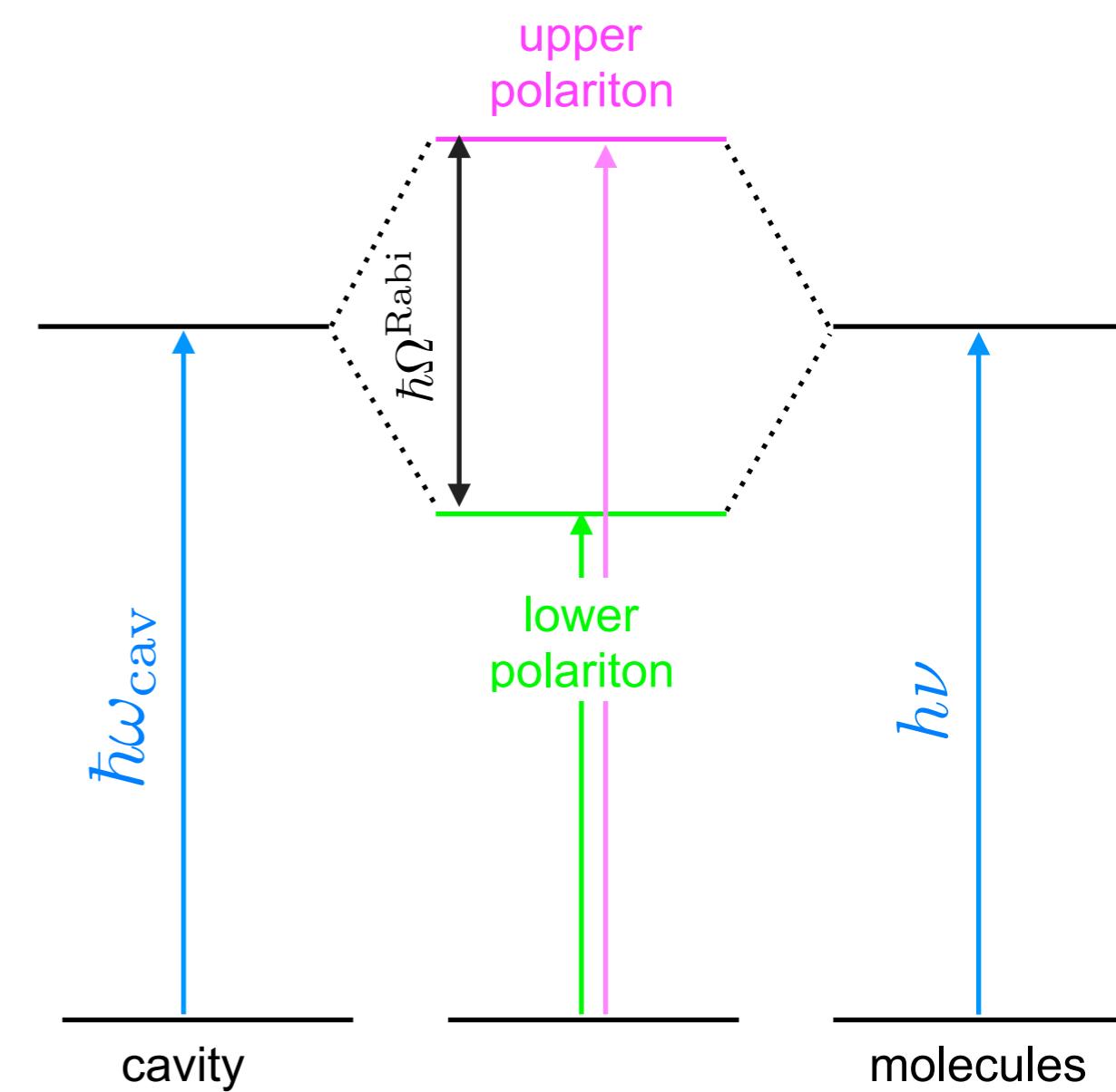
strong coupling with confined light (cavity QED)

two ‘bright’ polaritons

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

Rabi splitting

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



Why does the photochemistry change?

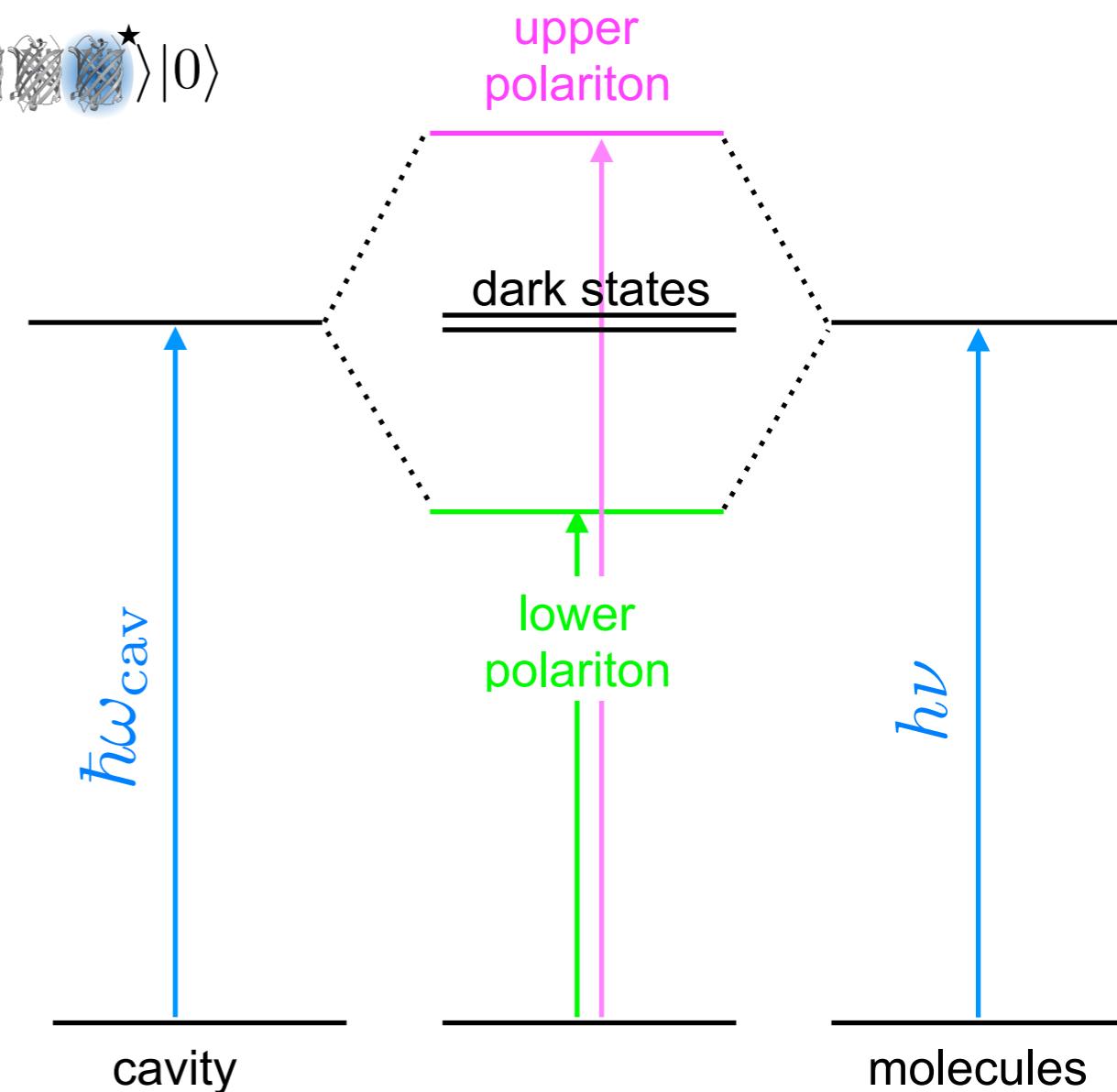
strong coupling with confined light (cavity QED)

two ‘bright’ polaritons

$$\Psi^K = \beta_1^K | \text{diagram with 1 star} \rangle |0\rangle + \beta_2^K | \text{diagram with 2 stars} \rangle |0\rangle + \beta_3^K | \text{diagram with 3 stars} \rangle |0\rangle + \alpha^K | \text{diagram with 4 stars} \rangle |1\rangle$$

two ‘dark’ states (in general $N-1$)

$$\Psi^K = \beta_1^K | \text{diagram with 1 star} \rangle |0\rangle + \beta_2^K | \text{diagram with 2 stars} \rangle |0\rangle + \beta_3^K | \text{diagram with 3 stars} \rangle |0\rangle$$



Why does the photochemistry change?

strong coupling with confined light (cavity QED)

two 'bright' polaritons

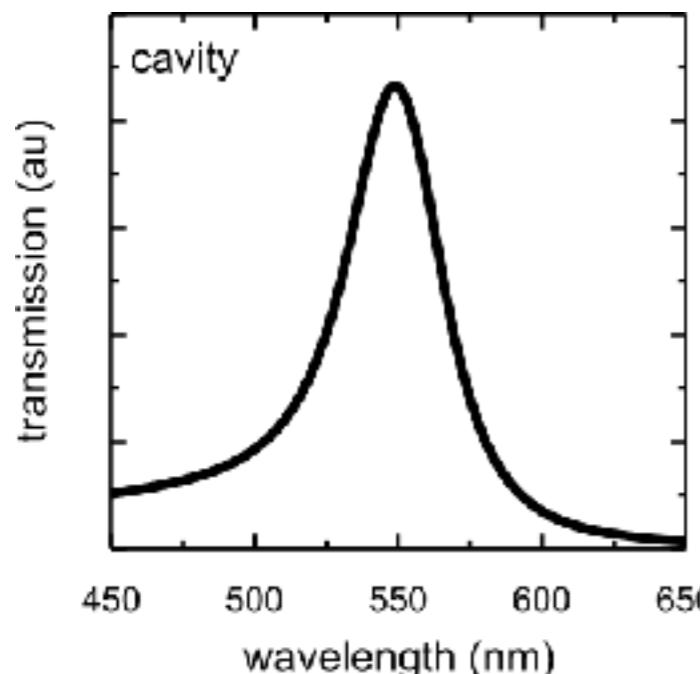
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two 'dark' states (in general $N-1$)

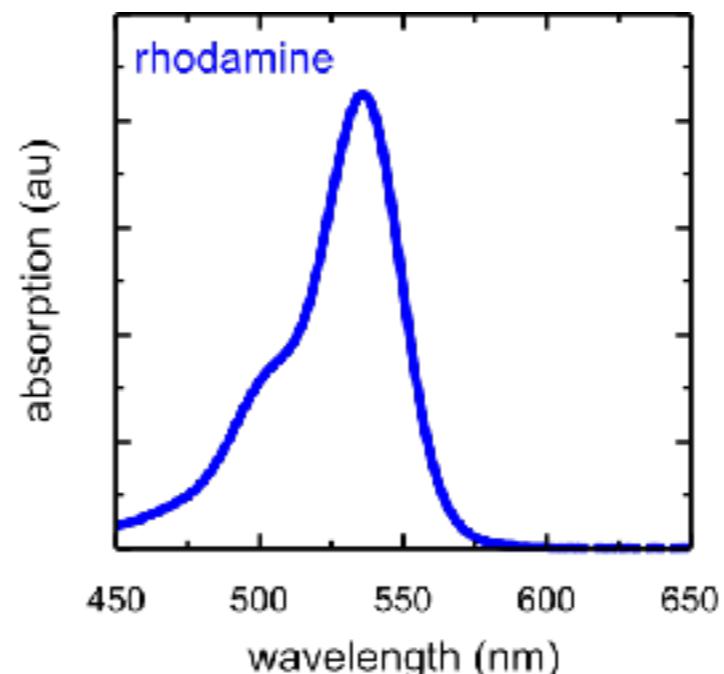
$$\Psi^K = \beta_1^K | \text{diagram with star} \rangle |0\rangle + \beta_2^K | \text{diagram with star} \rangle |0\rangle + \beta_3^K | \text{diagram with star} \rangle |0\rangle$$

double peak spectrum

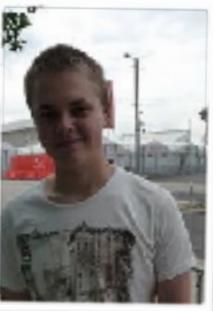
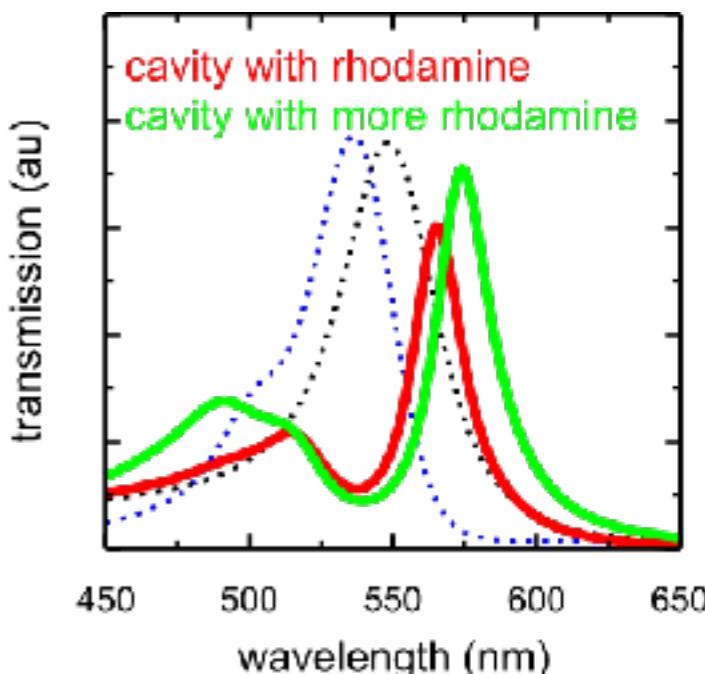
example: cavity with rhodamine 6G



+



=



Mikael
Kautto



Eero
Hulkko



Siim
Pikker

Simulating molecules in cavity

QED matrix elements

independent molecules interacting with cavity photon

$$H_{11} = V_{S_1}(\mathbf{R}_1) + V_{S_0}(\mathbf{R}_2) + V_{S_0}(\mathbf{R}_3)$$

$$H_{22} = V_{S_0}(\mathbf{R}_1) + V_{S_1}(\mathbf{R}_2) + V_{S_0}(\mathbf{R}_3)$$

$$H_{33} = V_{S_0}(\mathbf{R}_1) + V_{S_0}(\mathbf{R}_2) + V_{S_1}(\mathbf{R}_3)$$

$$H_{44} = V_{S_0}(\mathbf{R}_1) + V_{S_0}(\mathbf{R}_2) + V_{S_0}(\mathbf{R}_3)$$

$$H_{i4} = H_{4i} = |\boldsymbol{\mu}_{S_0 \rightarrow S_1}^{\text{TDM}}(\mathbf{R}_i)| \sqrt{\hbar\omega_{\text{cav}}/\epsilon_0 V_{\text{cav}}}$$

Simulating molecules in cavity

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independent molecules interacting with cavity photon

$$H_{11} = V_{S_1}(\mathbf{R}_1) + V_{S_0}(\mathbf{R}_2) + V_{S_0}(\mathbf{R}_3)$$

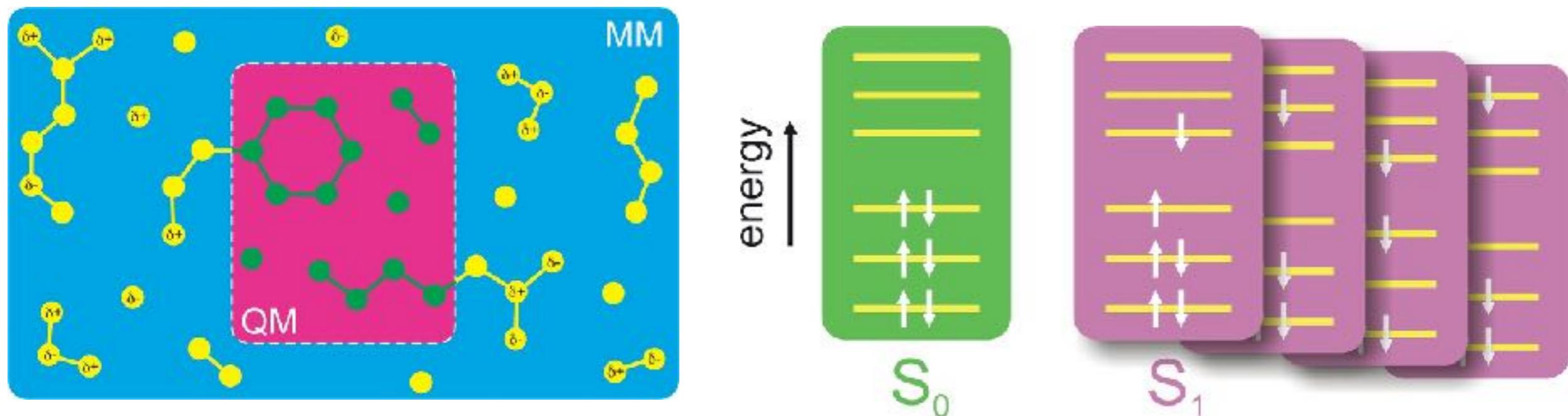
$$H_{22} = V_{S_0}(\mathbf{R}_1) + V_{S_1}(\mathbf{R}_2) + V_{S_0}(\mathbf{R}_3)$$

$$H_{33} = V_{S_0}(\mathbf{R}_1) + V_{S_0}(\mathbf{R}_2) + V_{S_1}(\mathbf{R}_3)$$

$$H_{44} = V_{S_0}(\mathbf{R}_1) + V_{S_0}(\mathbf{R}_2) + V_{S_0}(\mathbf{R}_3)$$

$$H_{i4} = H_{4i} = |\boldsymbol{\mu}_{S_0 \rightarrow S_1}^{\text{TDM}}(\mathbf{R}_i)| \sqrt{\hbar\omega_{\text{cav}}/\epsilon_0 V_{\text{cav}}}$$

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



Back to simulating molecules in cavity

QED matrix elements from QM/MM calculations

independent molecules interacting with cavity photon

$$H_{11} = V_{S_1}(\mathbf{R}_1) + V_{S_0}(\mathbf{R}_2) + V_{S_0}(\mathbf{R}_3)$$

$$H_{22} = V_{S_0}(\mathbf{R}_1) + V_{S_1}(\mathbf{R}_2) + V_{S_0}(\mathbf{R}_3)$$

$$H_{33} = V_{S_0}(\mathbf{R}_1) + V_{S_0}(\mathbf{R}_2) + V_{S_1}(\mathbf{R}_3)$$

$$H_{44} = V_{S_0}(\mathbf{R}_1) + V_{S_0}(\mathbf{R}_2) + V_{S_0}(\mathbf{R}_3)$$

$$H_{i4} = H_{4i} = |\boldsymbol{\mu}_{S_0 \rightarrow S_1}^{\text{TDM}}(\mathbf{R}_i)| \sqrt{\hbar\omega_{\text{cav}}/\epsilon_0 V_{\text{cav}}}$$

diagonalize

two ‘bright’ delocalised polariton states $N-1$ ‘dark’ states

$$\Psi^K = \beta_1^K | \text{Diagram 1} \rangle |0\rangle + \beta_2^K | \text{Diagram 2} \rangle |0\rangle + \beta_3^K | \text{Diagram 3} \rangle |0\rangle + \alpha^K | \text{Diagram 4} \rangle |1\rangle$$

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

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

Simulating molecules in cavity

QED matrix elements

independent molecules interacting with cavity photon

$$H_{11} = V_{S_1}(\mathbf{R}_1) + V_{S_0}(\mathbf{R}_2) + V_{S_0}(\mathbf{R}_3)$$

$$H_{22} = V_{S_0}(\mathbf{R}_1) + V_{S_1}(\mathbf{R}_2) + V_{S_0}(\mathbf{R}_3)$$

$$H_{33} = V_{S_0}(\mathbf{R}_1) + V_{S_0}(\mathbf{R}_2) + V_{S_1}(\mathbf{R}_3)$$

$$H_{44} = V_{S_0}(\mathbf{R}_1) + V_{S_0}(\mathbf{R}_2) + V_{S_0}(\mathbf{R}_3)$$

$$H_{i4} = H_{4i} = |\mu_{S_0 \rightarrow S_1}^{\text{TDM}}(\mathbf{R}_i)| \sqrt{\hbar\omega_{\text{cav}}/\epsilon_0 V_{\text{cav}}}$$

diagonalize

two ‘bright’ delocalised polariton states $N-1$ ‘dark’ states

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

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

transitions between states: surface hopping

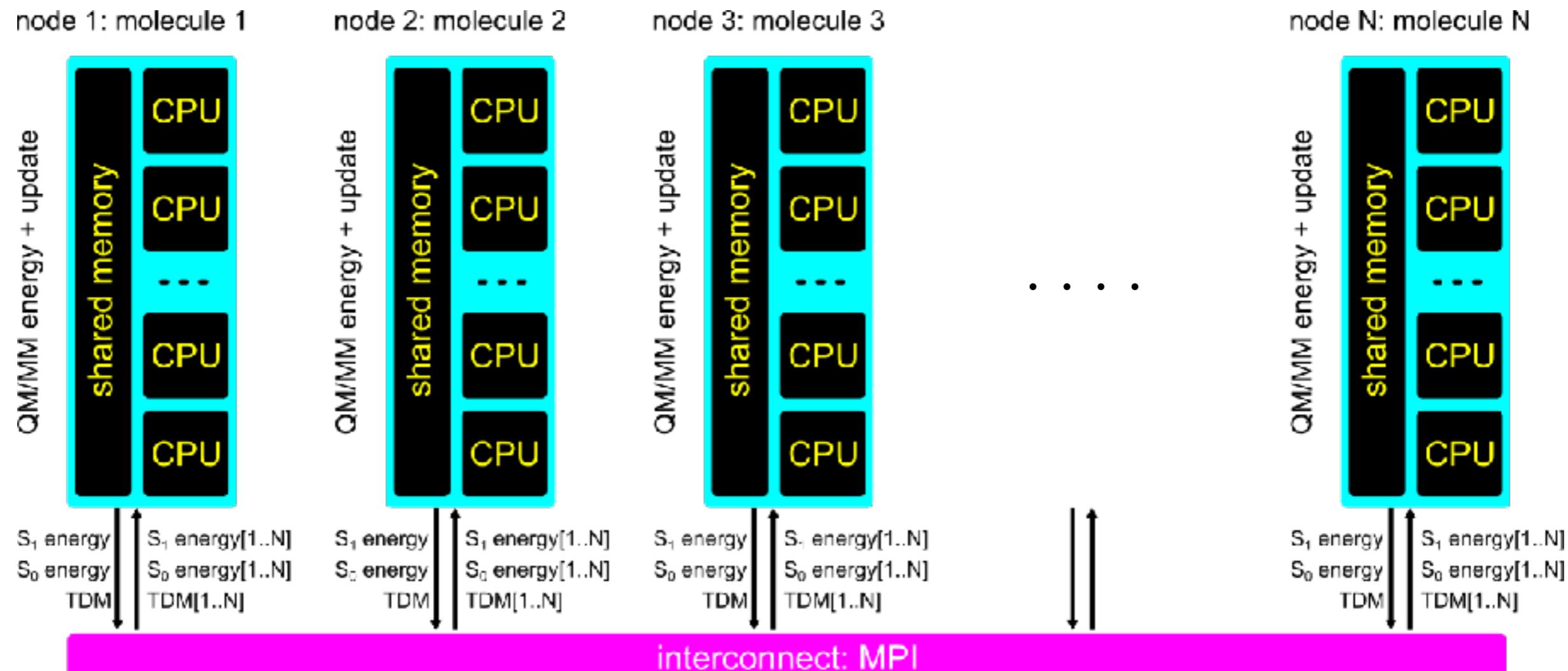
Simulating molecules in cavity

implementation in Gromacs

linear scaling cavity “QED”/MM

Gromacs 4.5 uses as many MPI nodes as there are molecules

Gaussian09 uses all shared memory threads on node



Simulating molecules in cavity

implementation in Gromacs

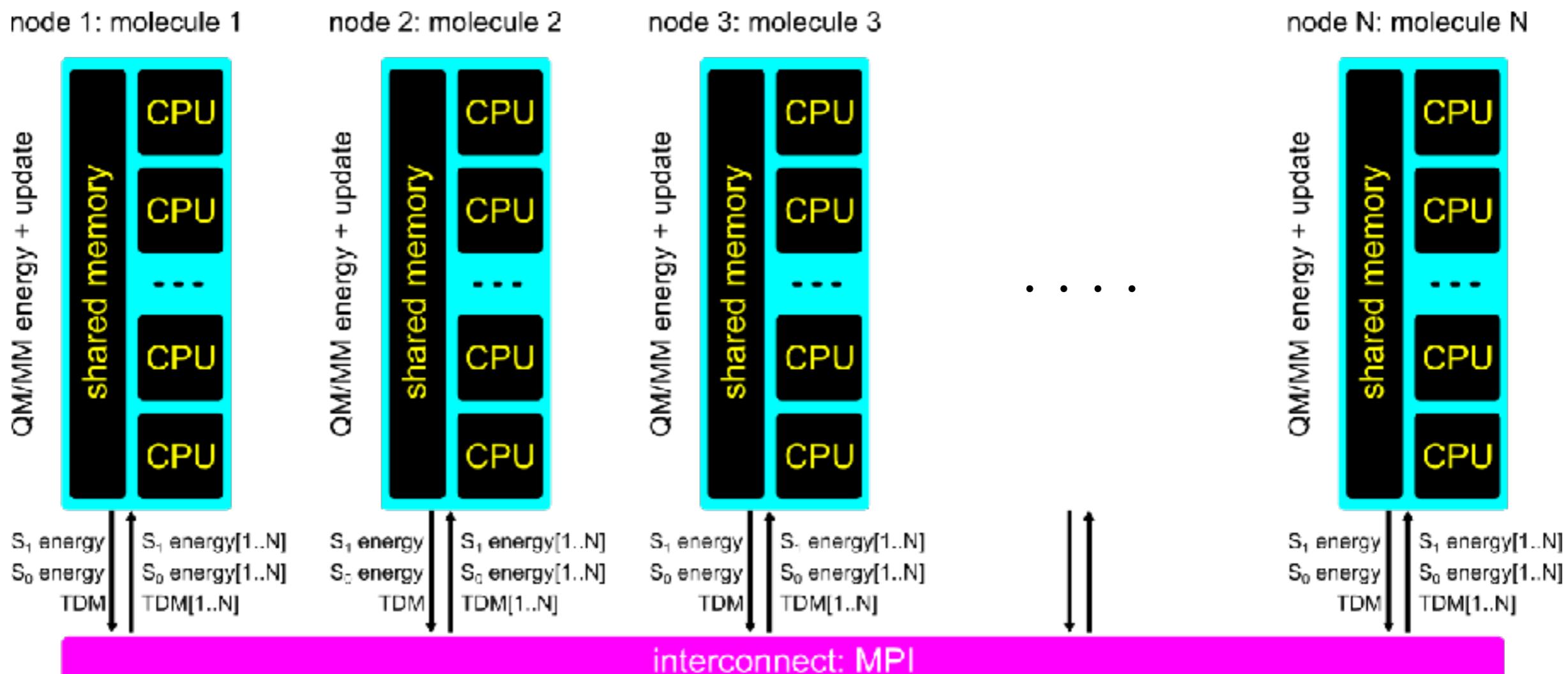
linear scaling cavity “QED”/MM



Sisu.csc.fi: 1688 TFlop/s

Gromacs 4.5 uses as many MPI nodes as there are molecules

Gaussian09 uses all shared memory threads on node



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

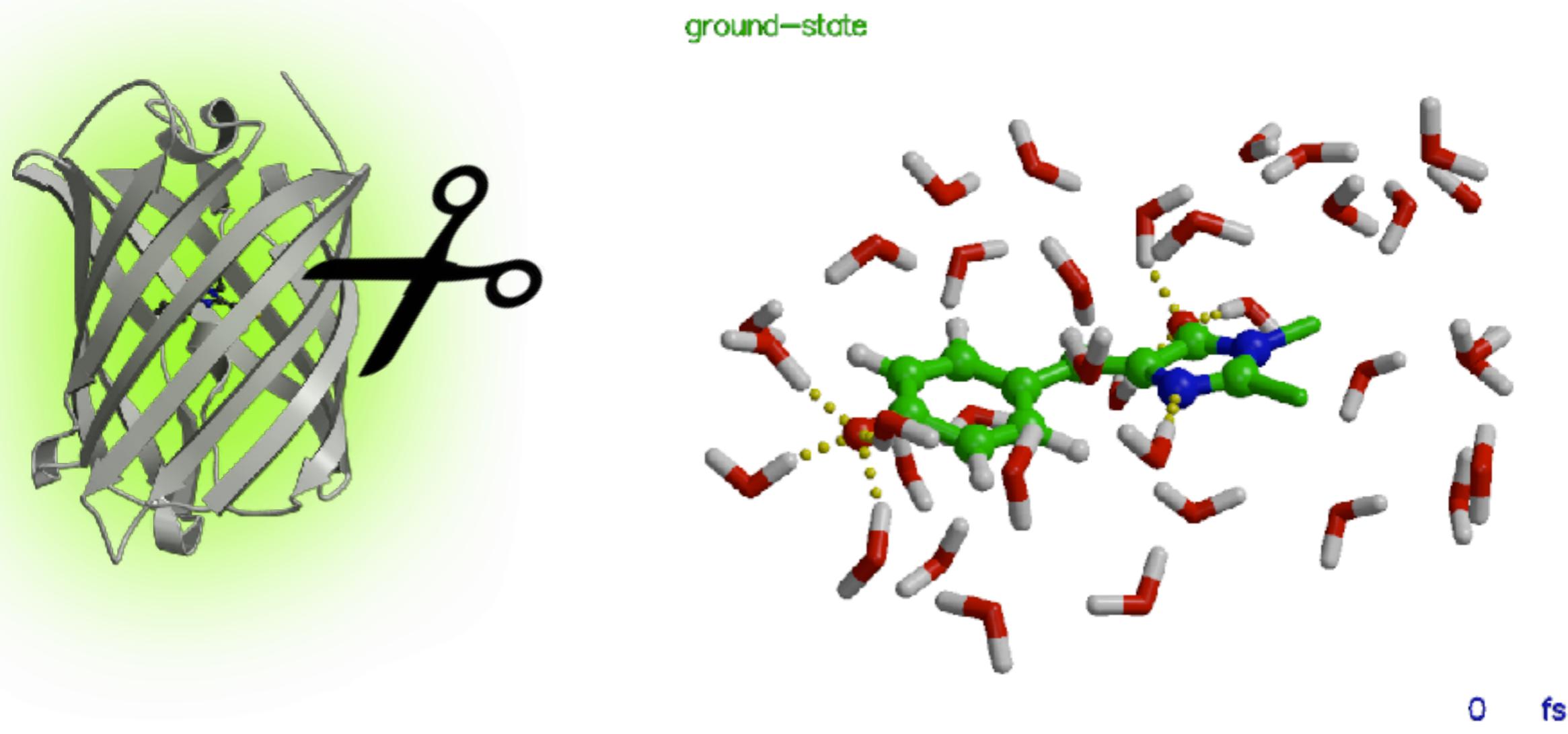
GFP chromophore in water

no fluorescence: dark

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



Dmitry
Morozov

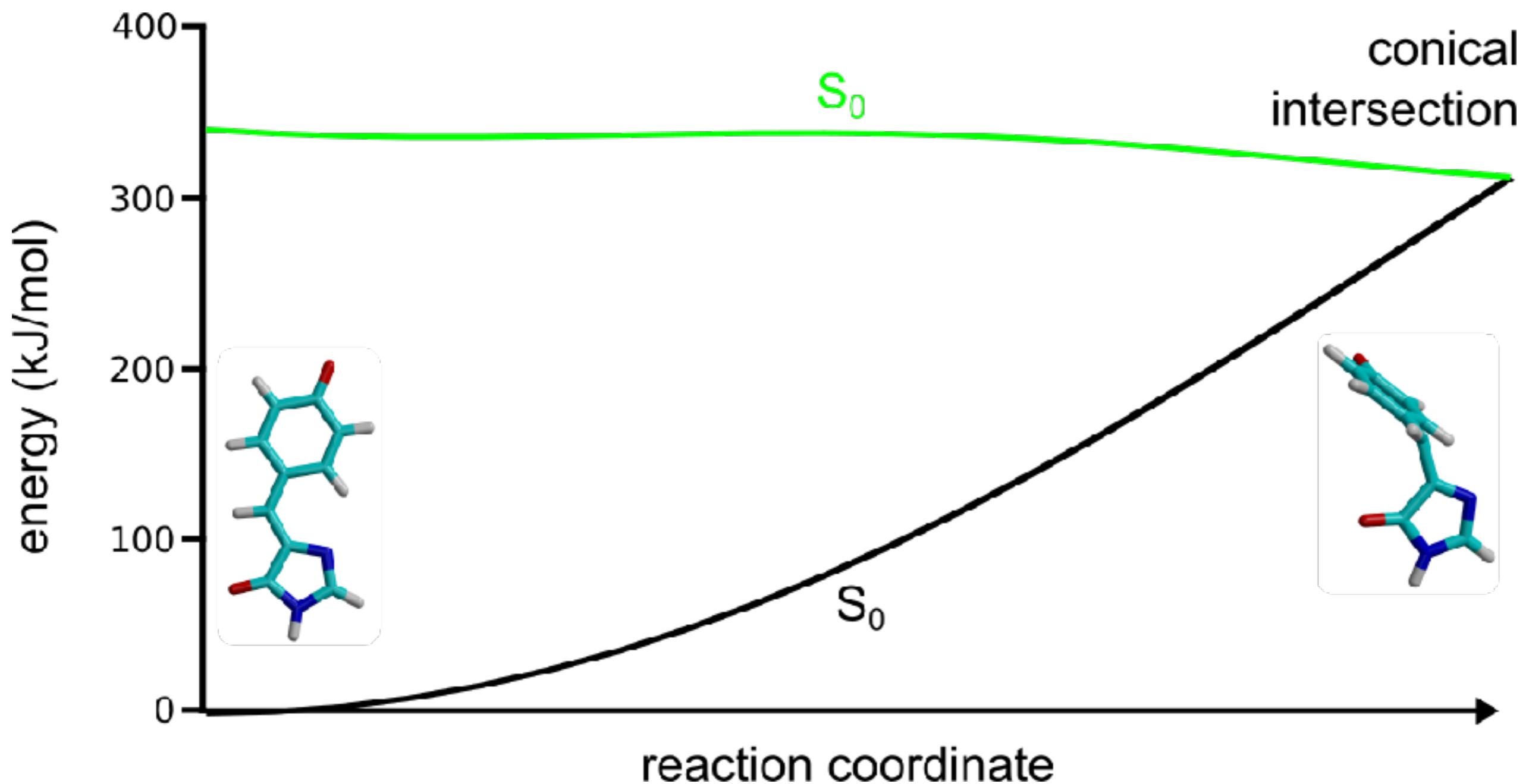


CASSCF(6,6)/3-21G//SPC & CASSCF(12,11)/cc-pVDZ//EFP

Manipulating photo-chemistry with mirrors

GFP chromophore in water

no fluorescence: dark

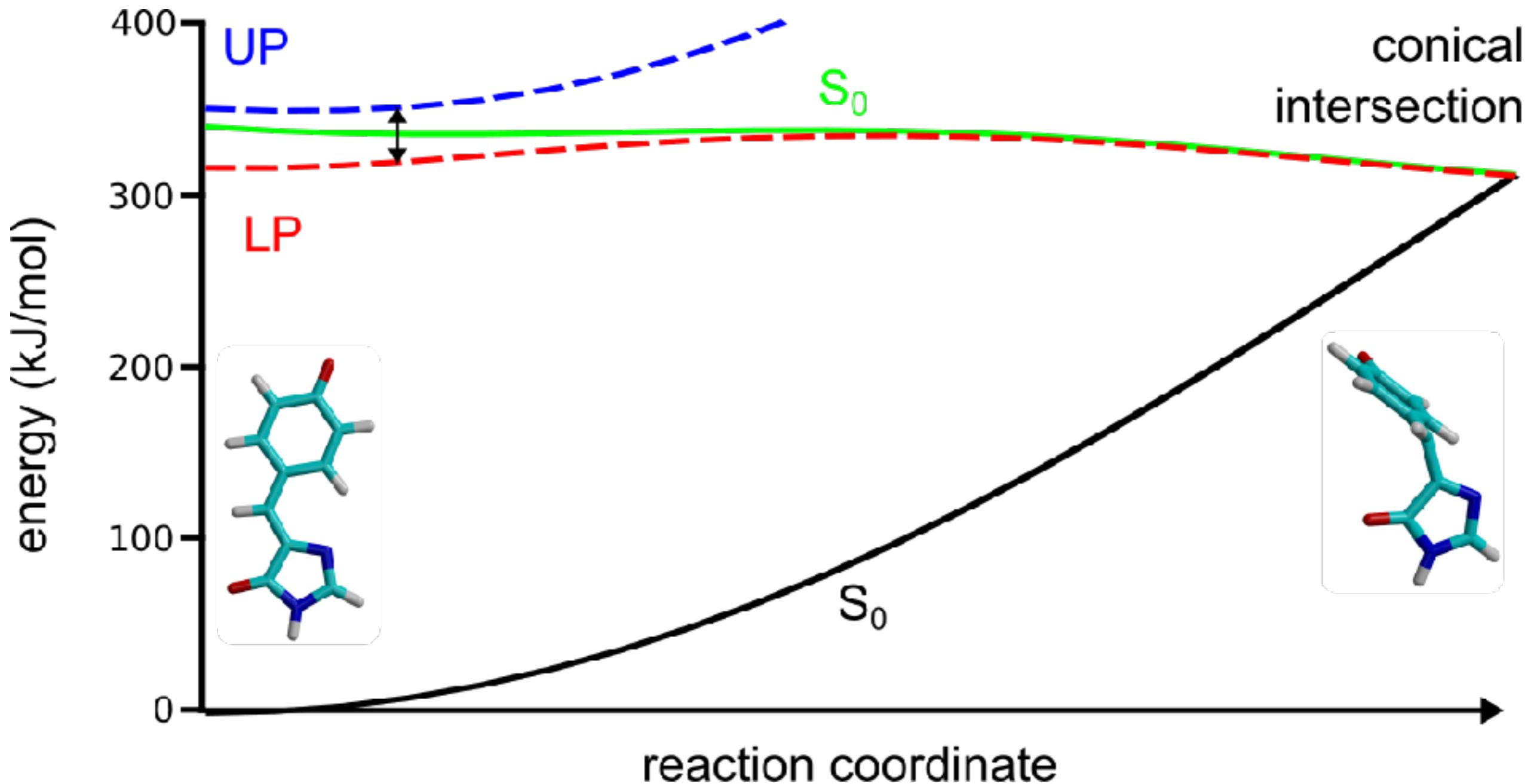


Manipulating photo-chemistry with mirrors

one GFP chromophore in water in a cavity

strong coupling to confined light?

minimum on lower polariton surface

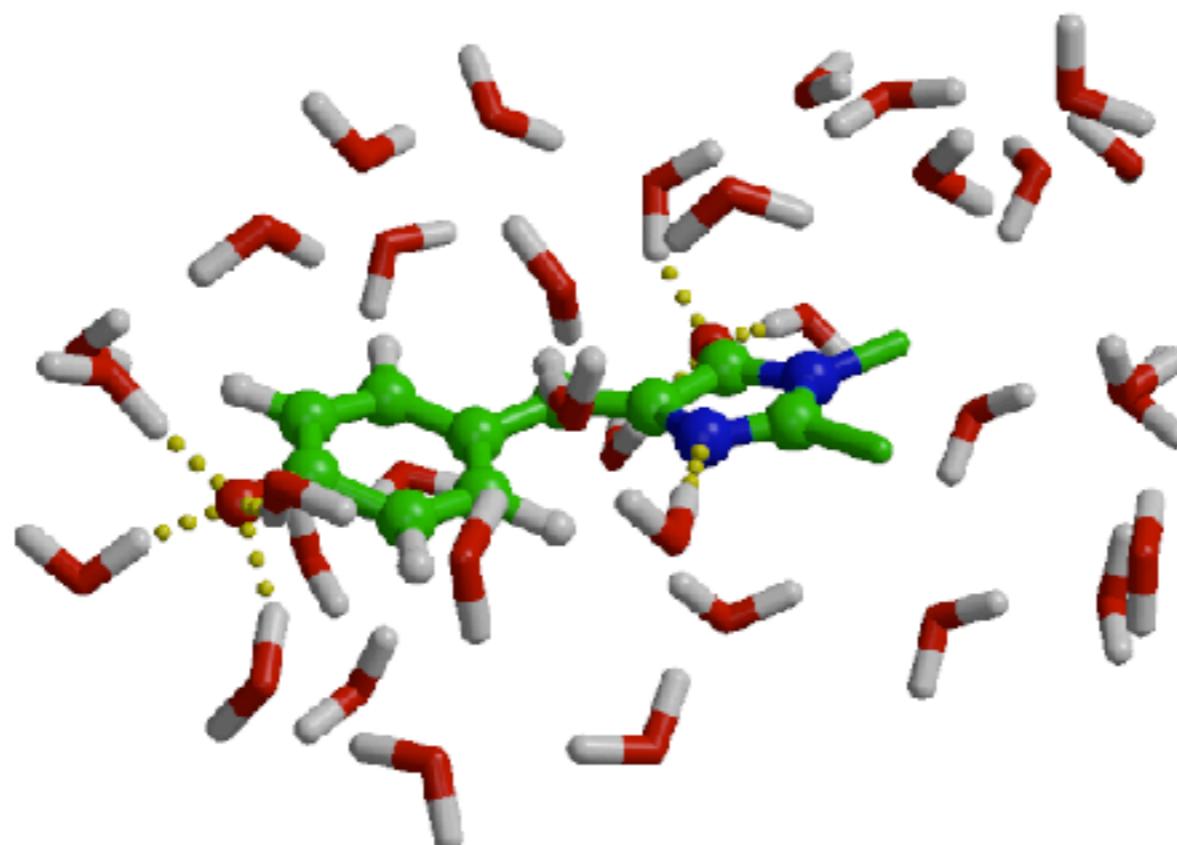


Manipulating photo-chemistry with mirrors

one GFP chromophore in water in a cavity

no fluorescence: dark

ground-state



0 fs

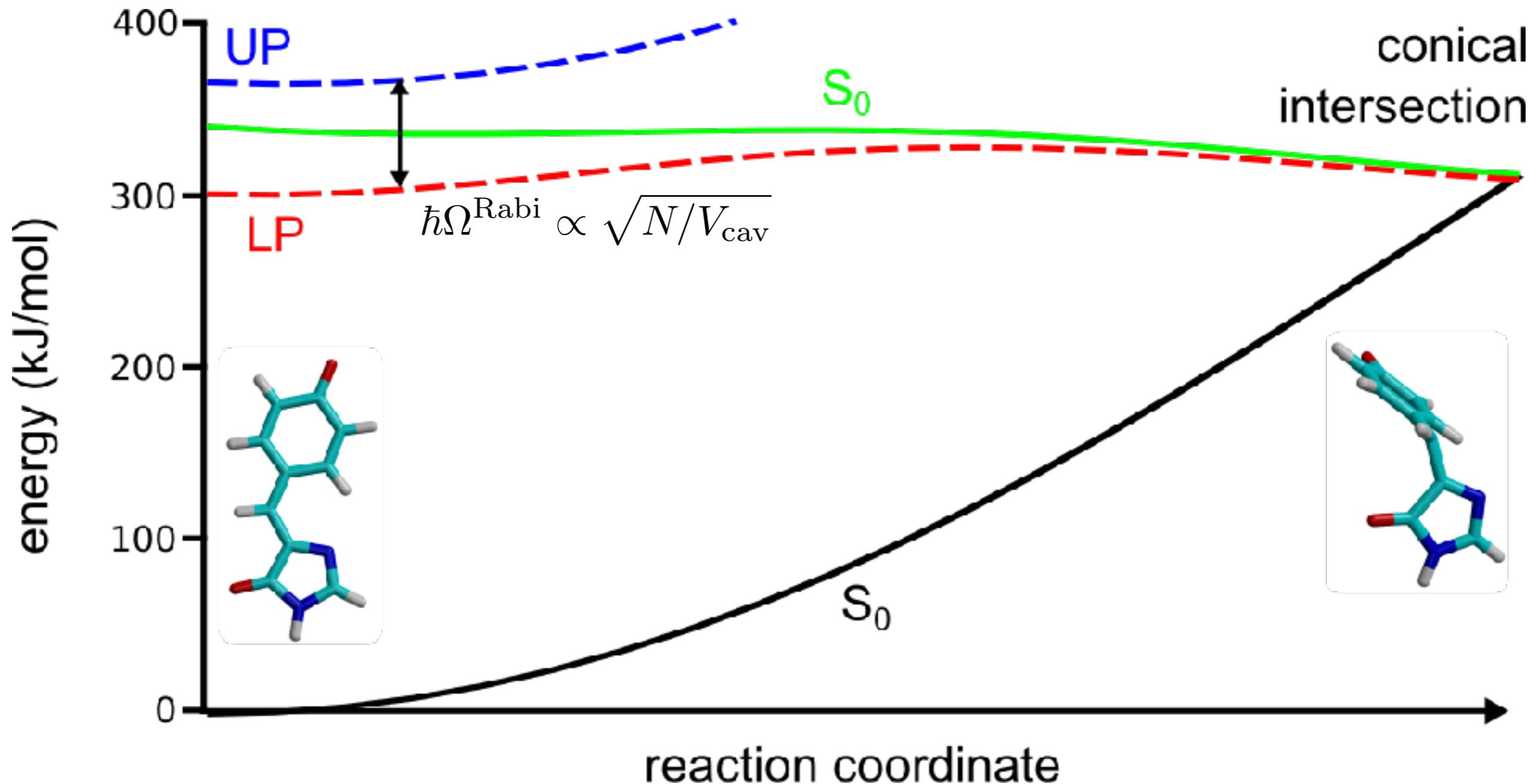
$$\frac{1}{2}\lambda_{\max}$$

Manipulating photo-chemistry with mirrors

four GFP chromophores in water in a cavity

two times stronger coupling with confined light

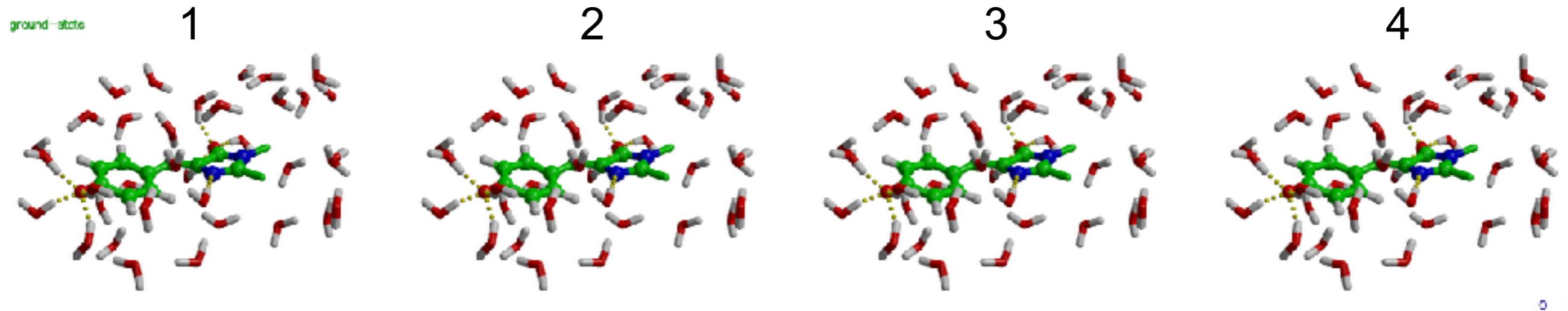
deeper minimum on lower polariton surface



Manipulating photo-chemistry with mirrors

four GFP chromophores in water in a cavity

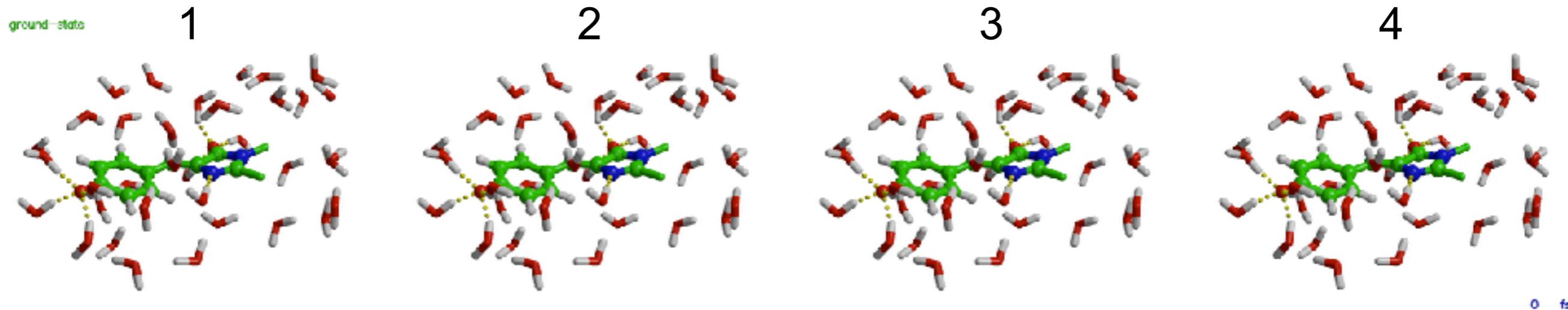
trapped: fluorescence



Manipulating photo-chemistry with mirrors

four GFP chromophores in water in a cavity

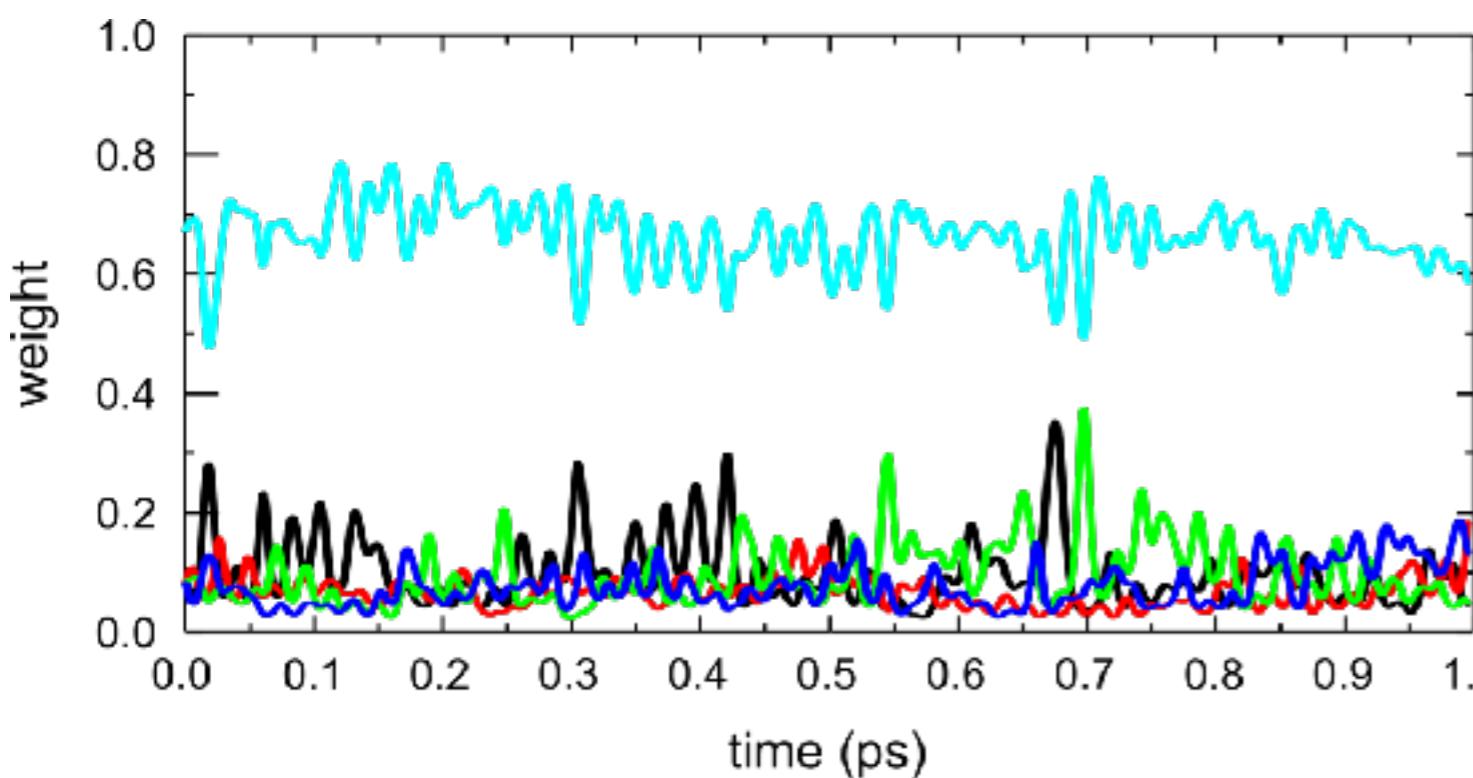
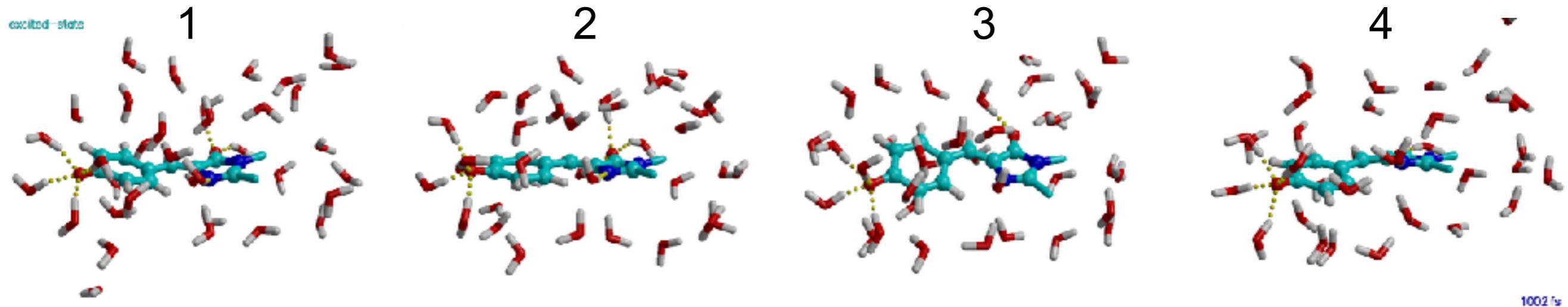
trapped: fluorescence



Manipulating photo-chemistry with mirrors

four GFP chromophores in water in a cavity

trapped: fluorescence

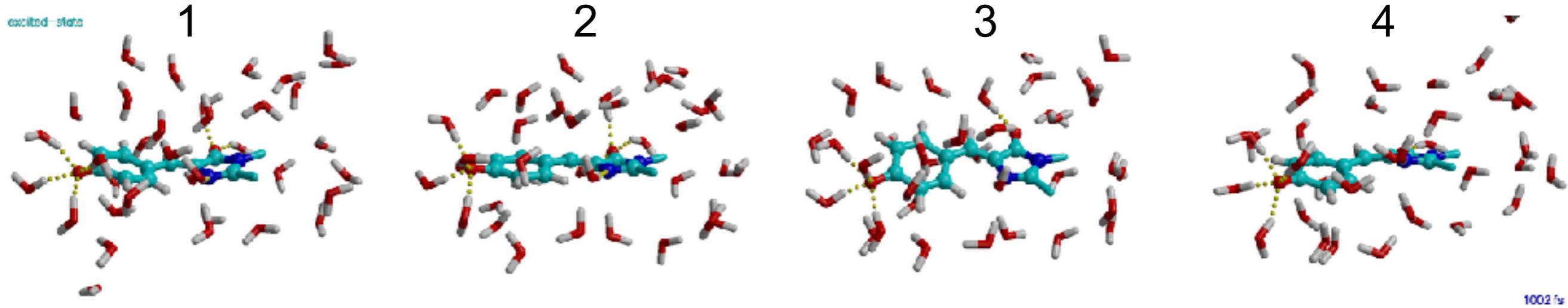


$$\Psi^{\text{LP}} = +\beta_1^{\text{LP}} |1^*234\rangle|0\rangle$$
$$+\beta_2^{\text{LP}} |12^*34\rangle|0\rangle$$
$$+\beta_3^{\text{LP}} |123^*4\rangle|0\rangle$$
$$+\beta_4^{\text{LP}} |1234^*\rangle|0\rangle$$
$$+\alpha^{\text{LP}} |1234\rangle|1\rangle$$

Manipulating photo-chemistry with mirrors

four GFP chromophores in water in a cavity

trapped: fluorescence



challenge/frustration in real life

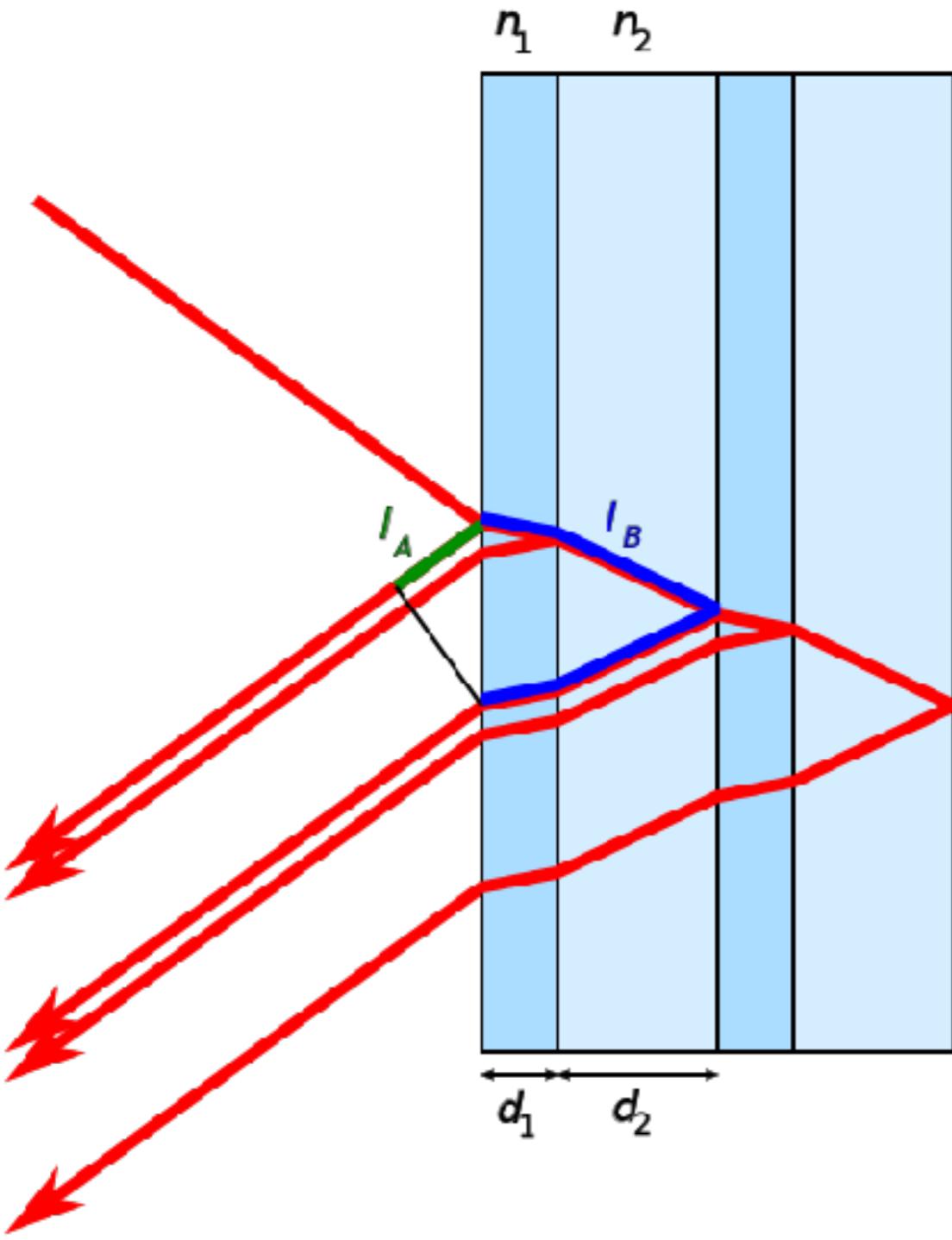
cavity lifetimes

far less than a picosecond ...

we need something else to proof this principle

Manipulating photo-chemistry with mirrors

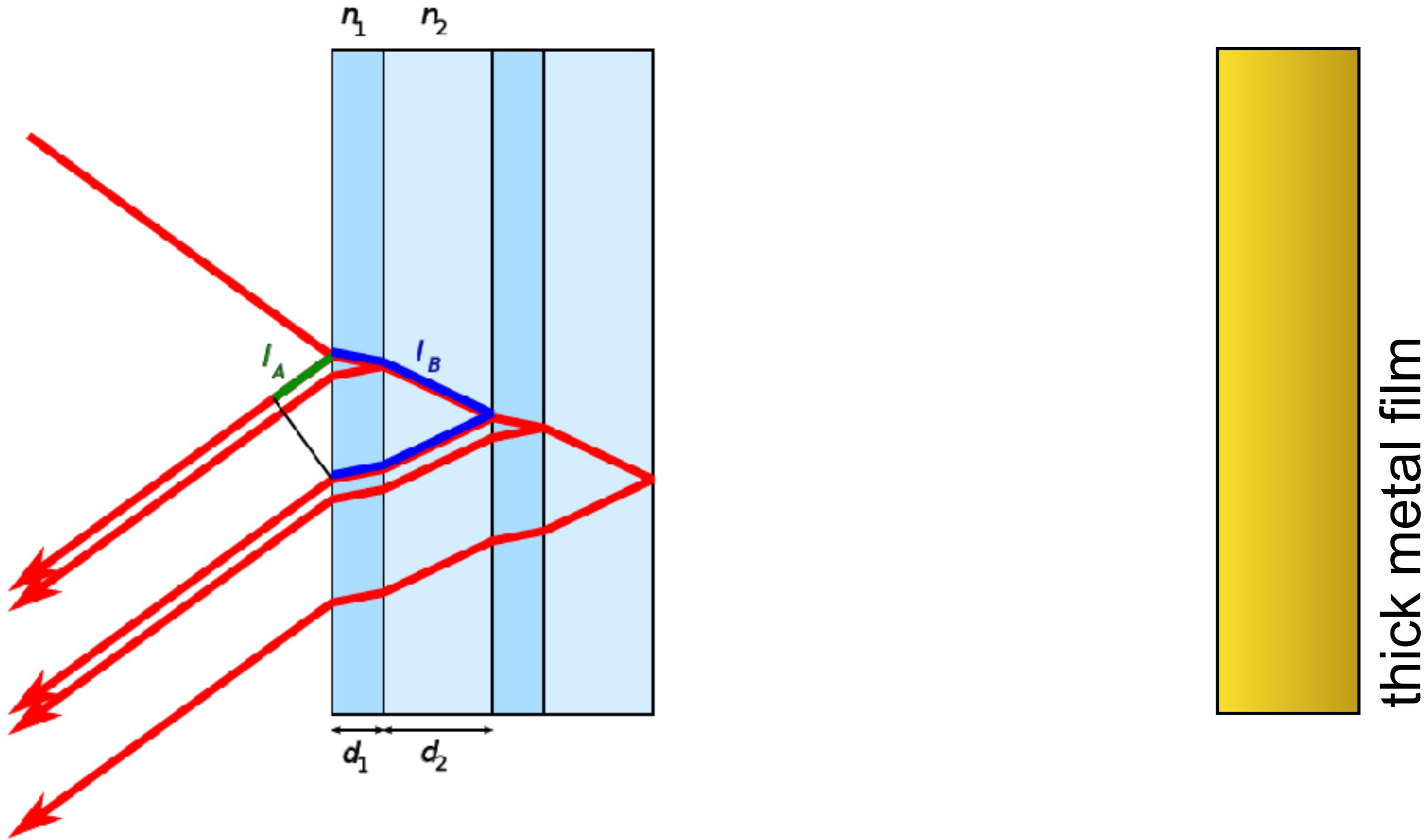
dielectric/distributed Bragg mirror



Manipulating photo-chemistry with mirrors

dielectric/distributed Bragg cavity

cavity lifetimes ~ 100 femtoseconds



Manipulating photo-chemistry with mirrors

dielectric/distributed Bragg cavity

cavity lifetimes \sim 100 femtoseconds

ultra-fast reactions

excited state intra-molecular proton transfer (ESIPT)

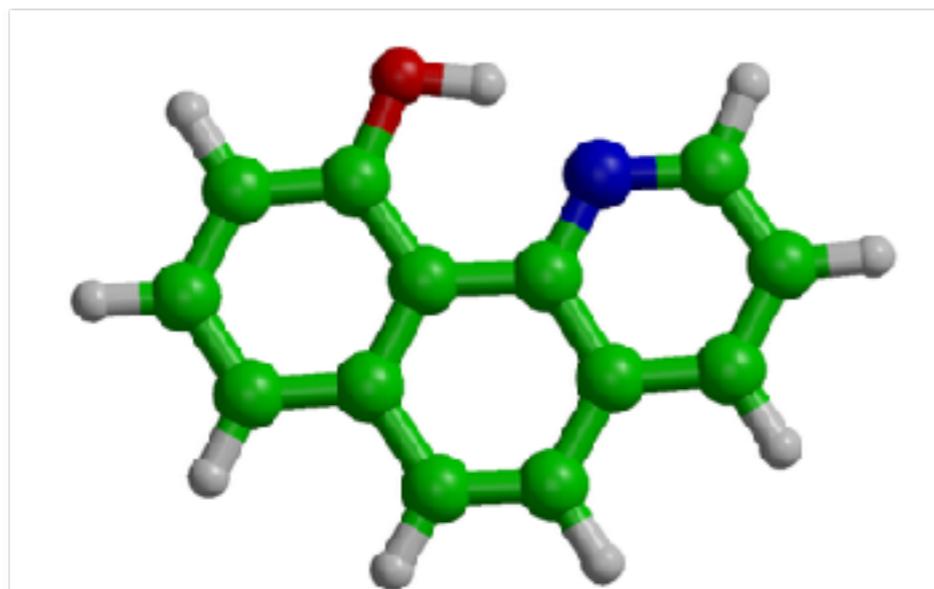
10-hydroxybenzo[*h*]quinolone (HBQ)



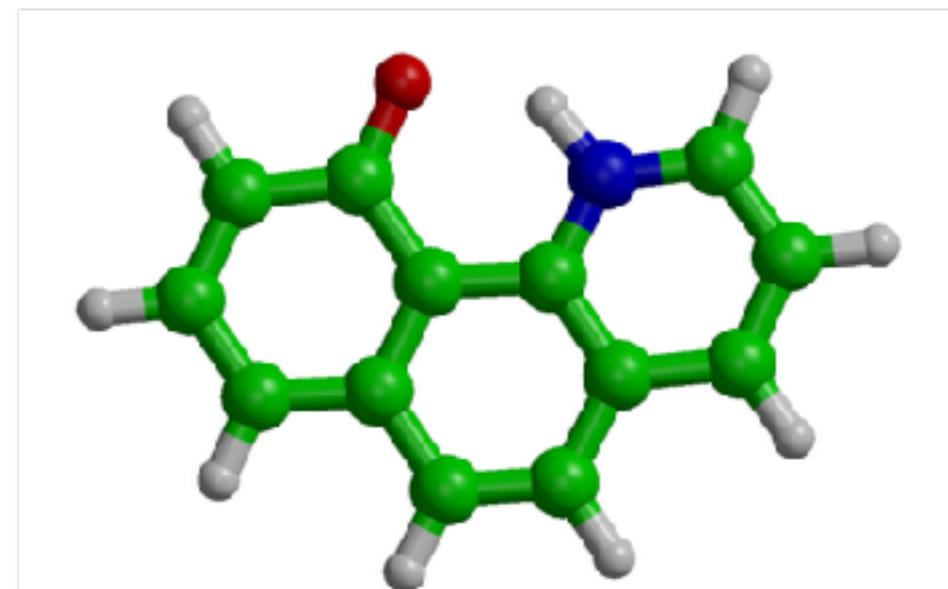
Ossi
Hakamaa



Satu
Mustalahti



\sim 15 fs



$\lambda_{\text{abs}} = 380 \text{ nm}$

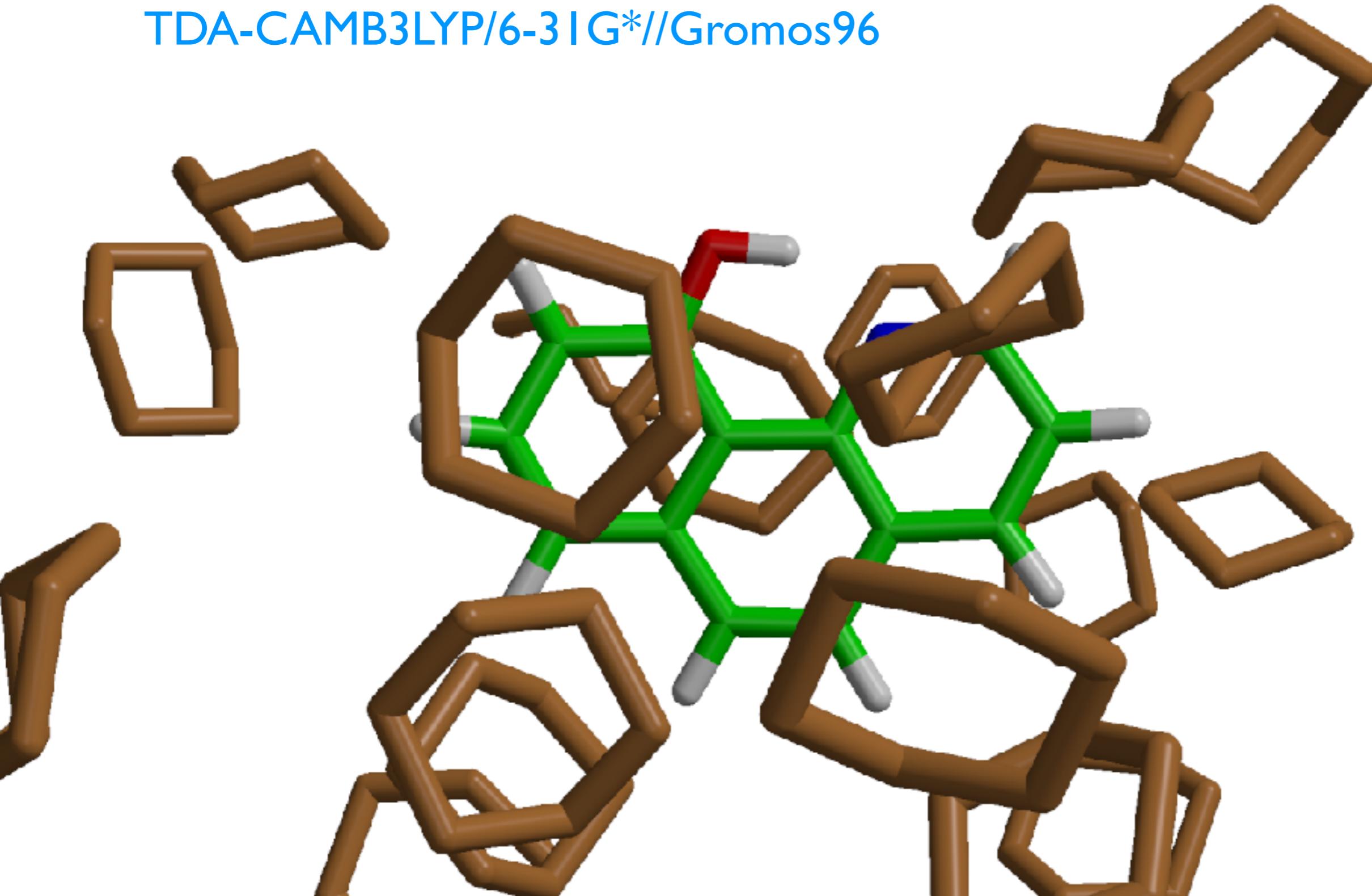
$\lambda_{\text{em}} = 610 \text{ nm}$

Manipulating photo-chemistry with mirrors

excited-state intra-molecular proton transfer

HBQ in cyclohexane solvent outside of cavity

TDA-CAMB3LYP/6-31G*//Gromos96



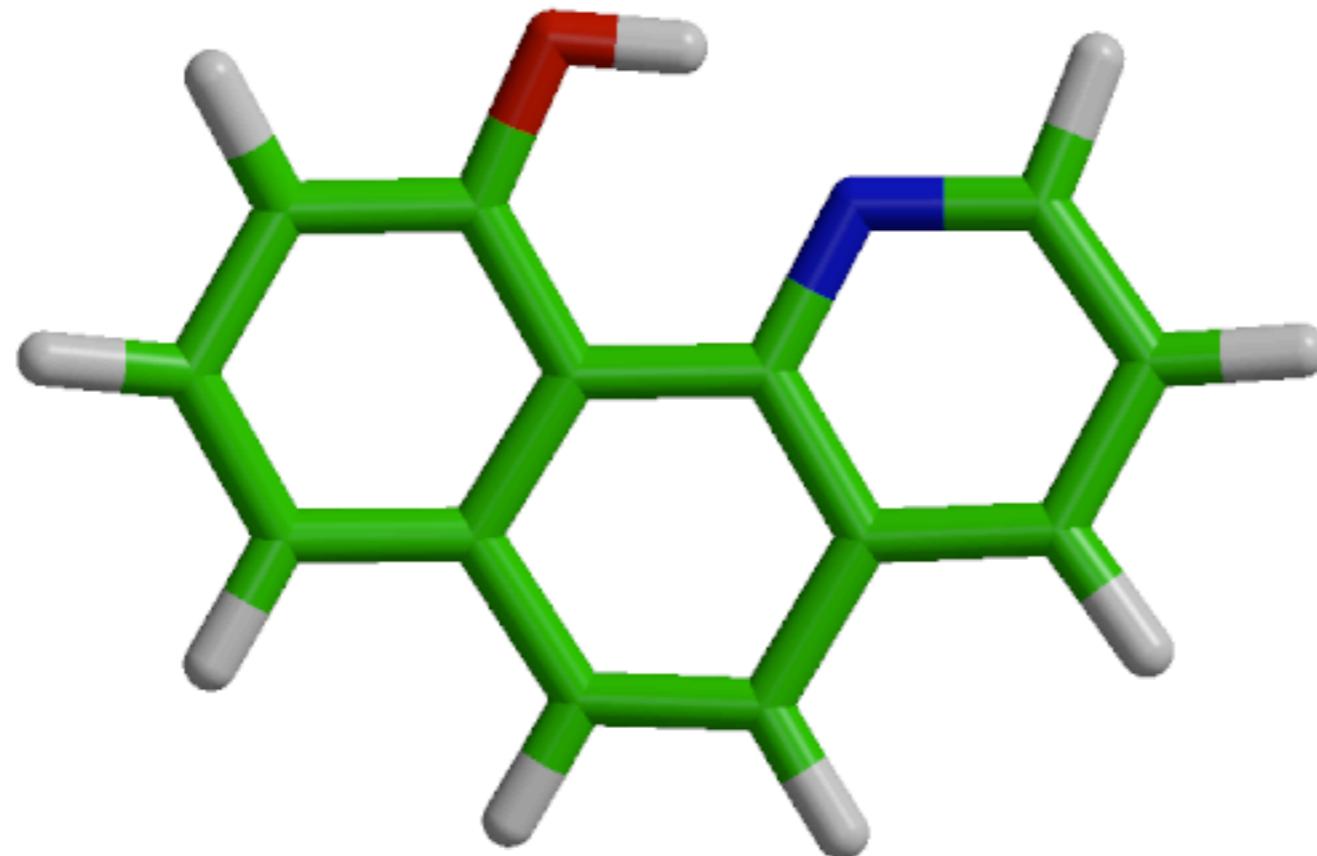
Manipulating photo-chemistry with mirrors

excited-state intra-molecular proton transfer

HBQ in cyclohexane solvent outside of cavity

TDA-CAMB3LYP/6-31G*//Gromos96

0 fs



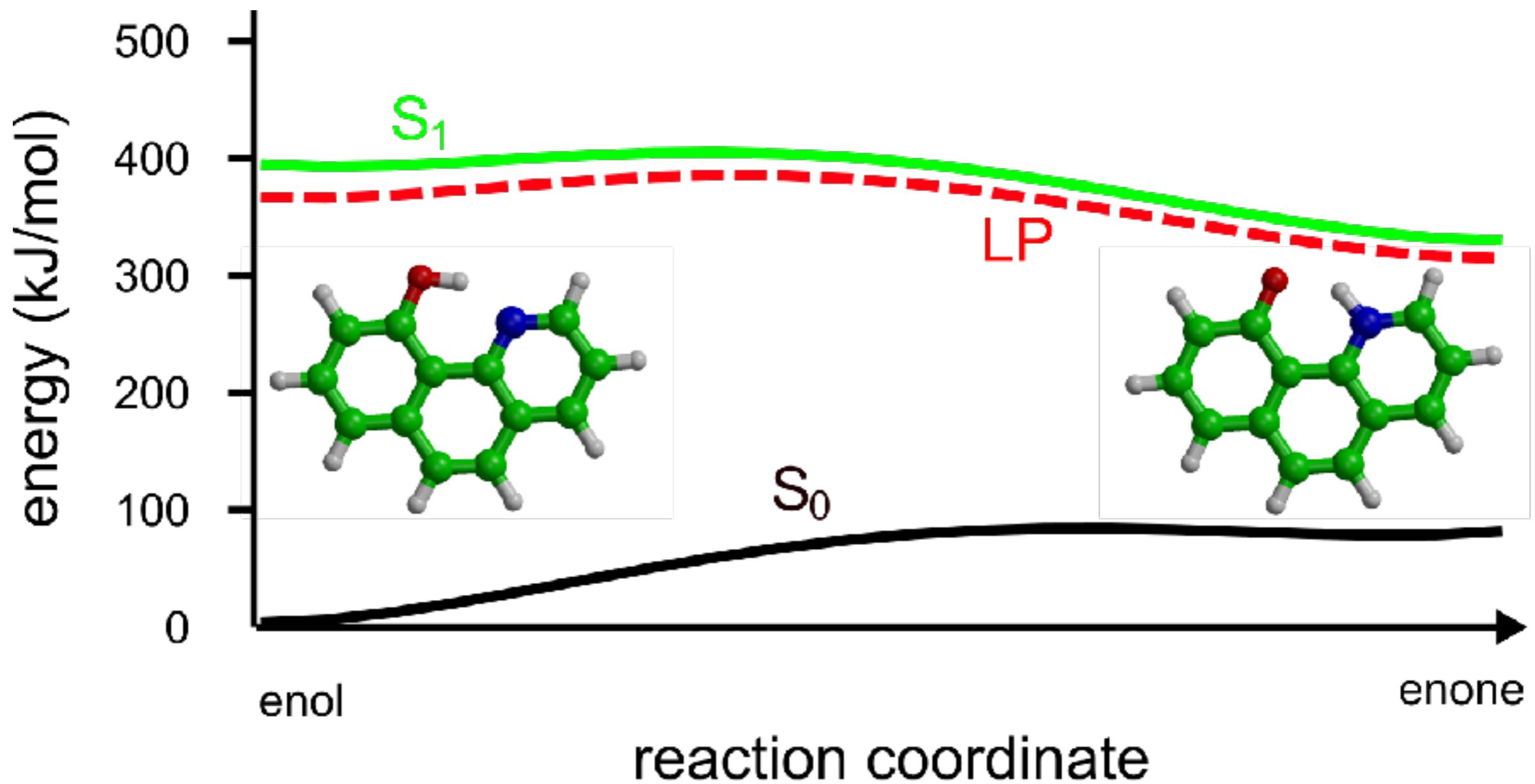
ground-state

Manipulating photo-chemistry with mirrors

excited-state intra-molecular proton transfer

HBQ potential energy profiles

TDA-CAMB3LYP/6-31G*

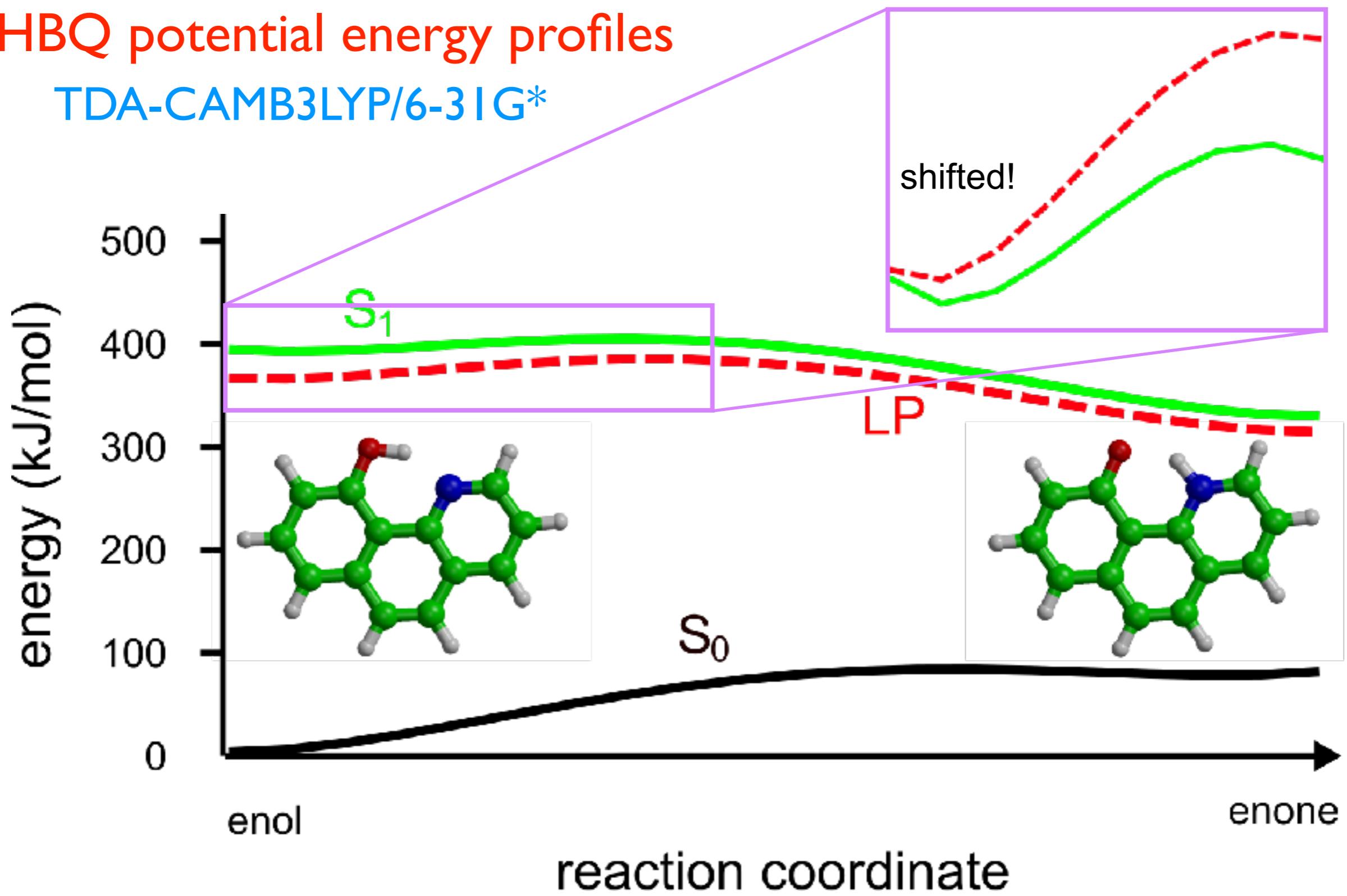


Manipulating photo-chemistry with mirrors

excited-state intra-molecular proton transfer

HBQ potential energy profiles

TDA-CAMB3LYP/6-31G*

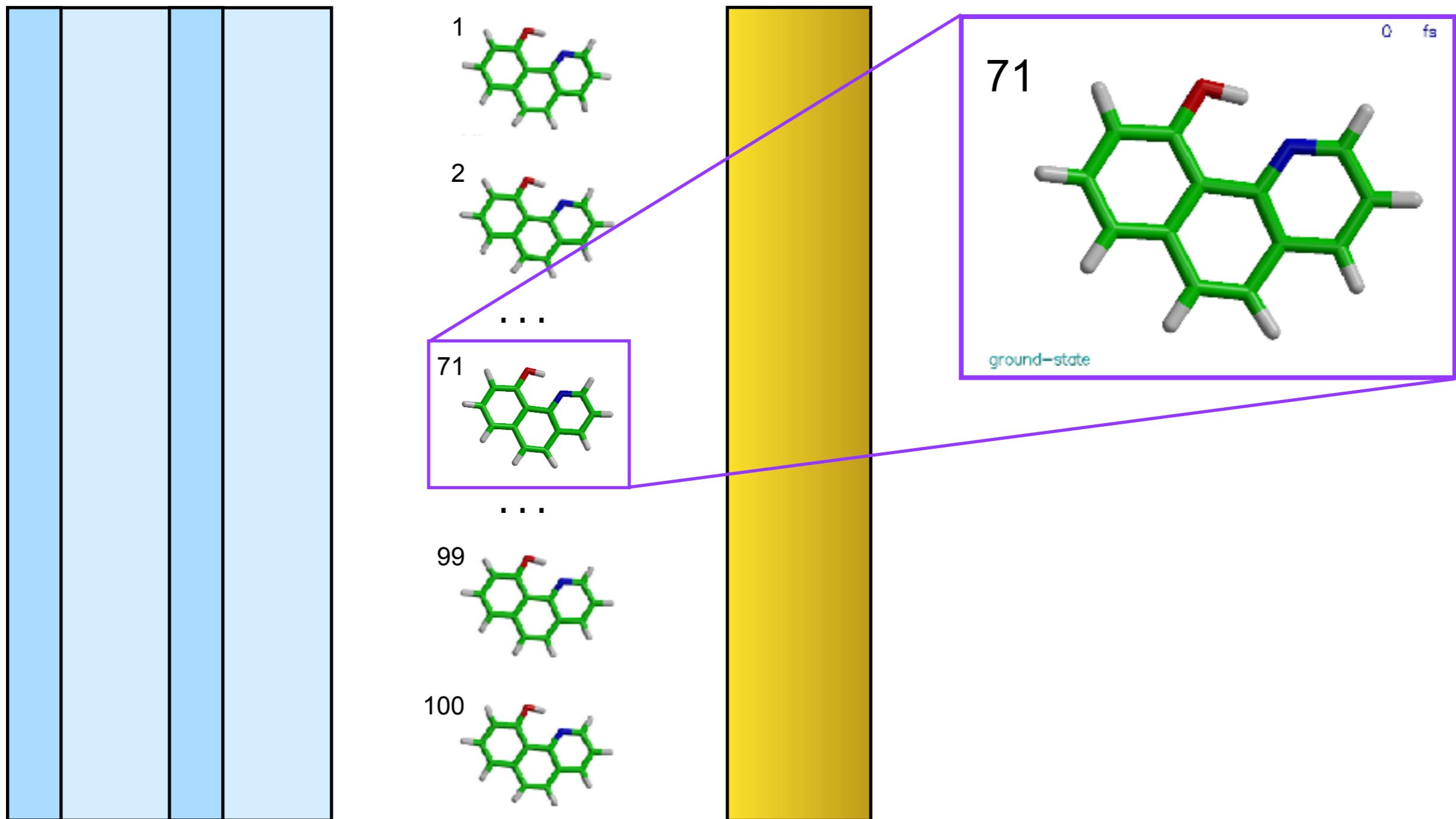


Manipulating photo-chemistry with mirrors

excited-state intra-molecular proton transfer

400 HBQ in cyclohexane solvent inside dielectric cavity

TDA-CAMB3LYP/6-31G*//Gromos96

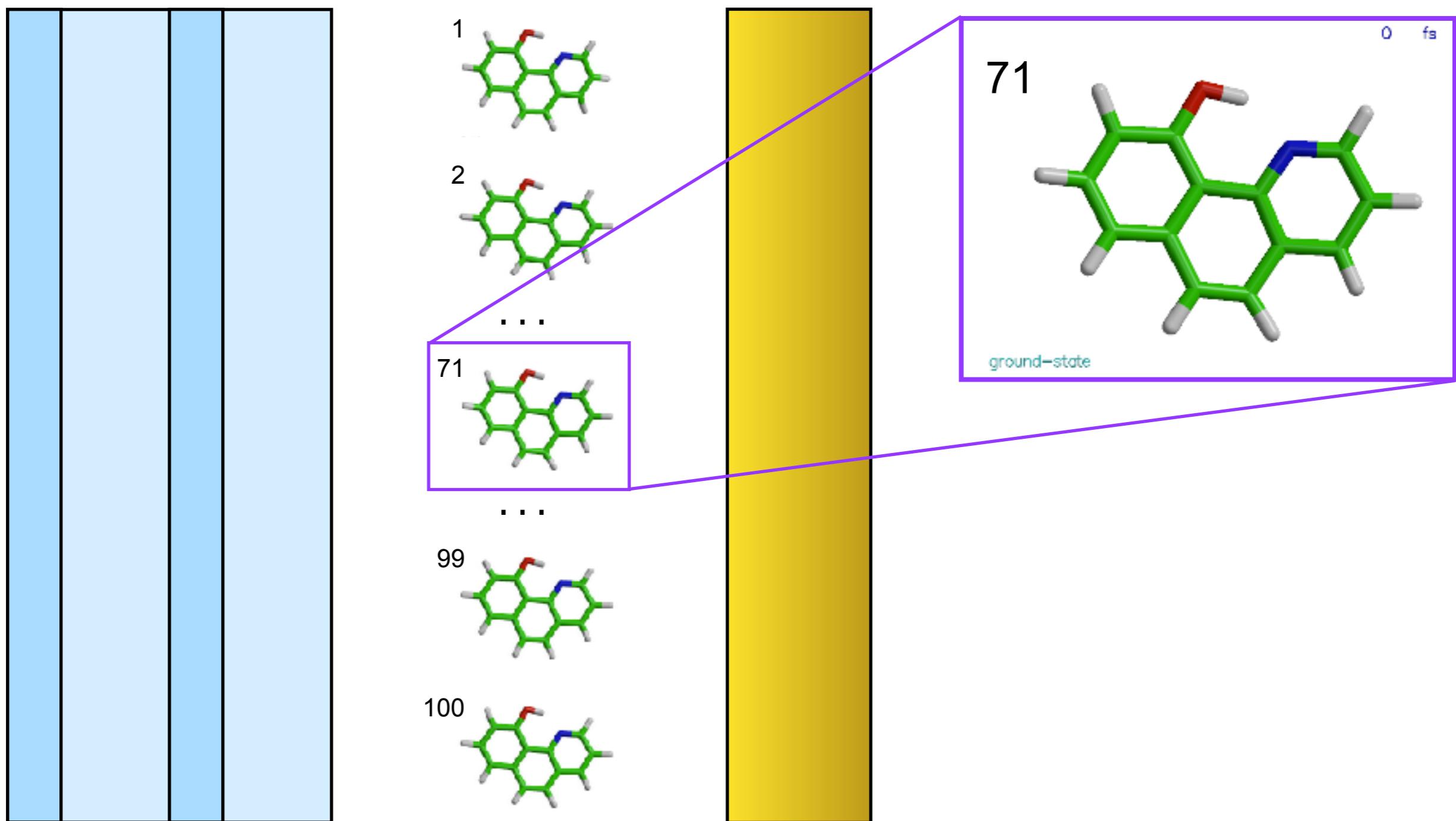


Manipulating photo-chemistry with mirrors

excited-state intra-molecular proton transfer

400 HBQ in cyclohexane solvent inside dielectric cavity

TDA-CAMB3LYP/6-31G*//Gromos96

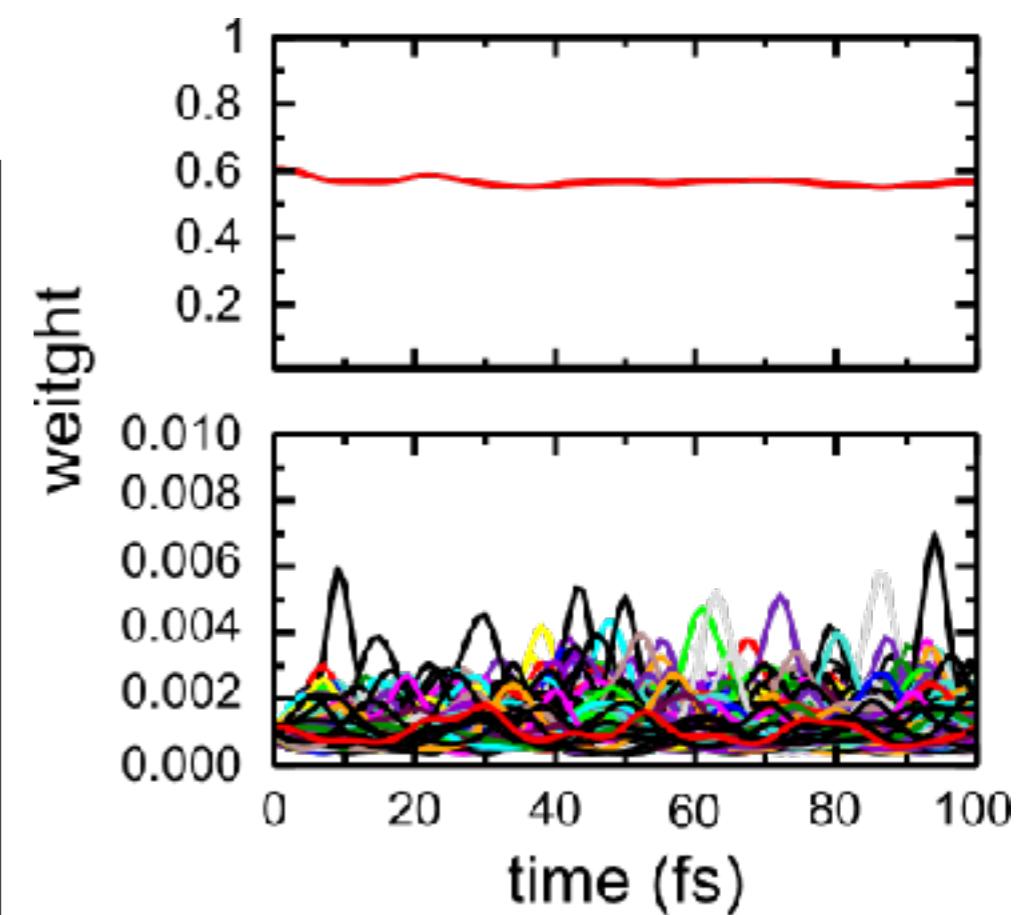
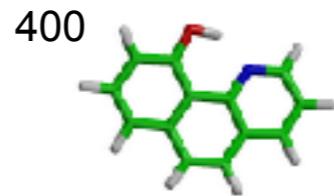
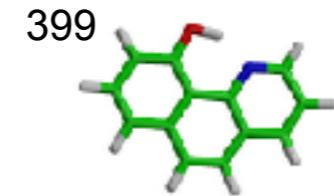
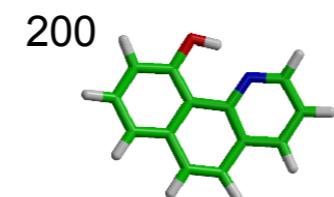
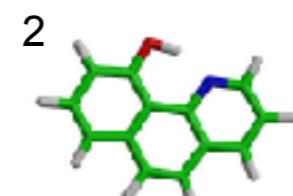
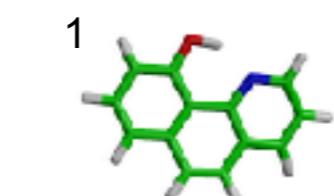
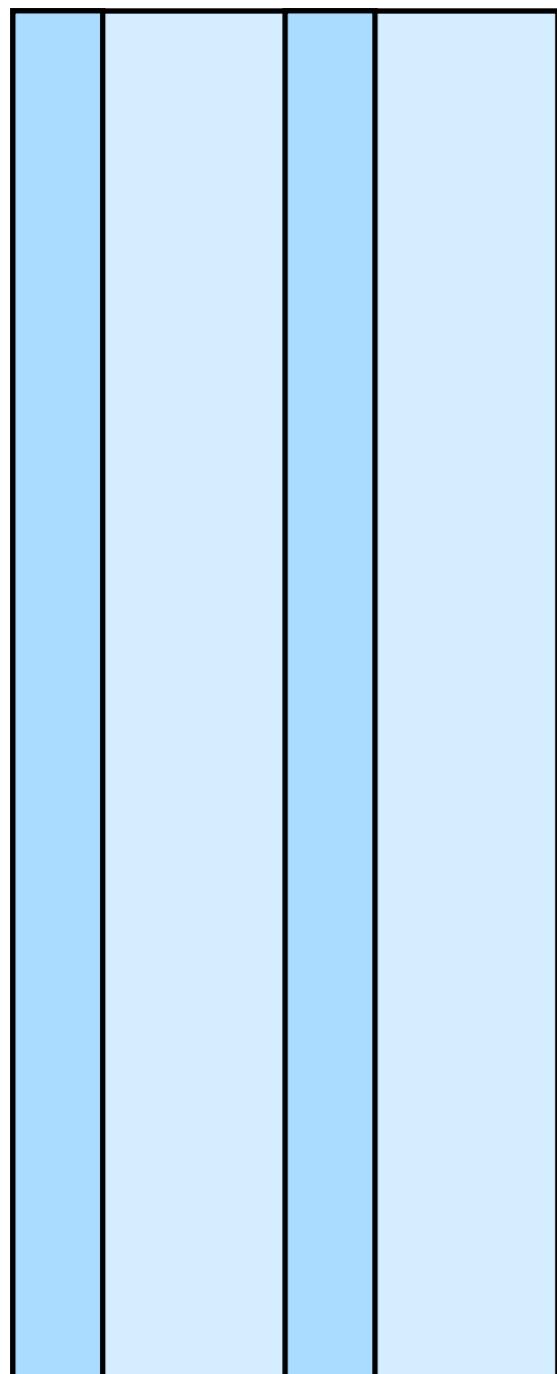


Manipulating photo-chemistry with mirrors

excited-state intra-molecular proton transfer

400 HBQ in cyclohexane solvent inside dielectric cavity

TDA-CAMB3LYP/6-31G*//Gromos96



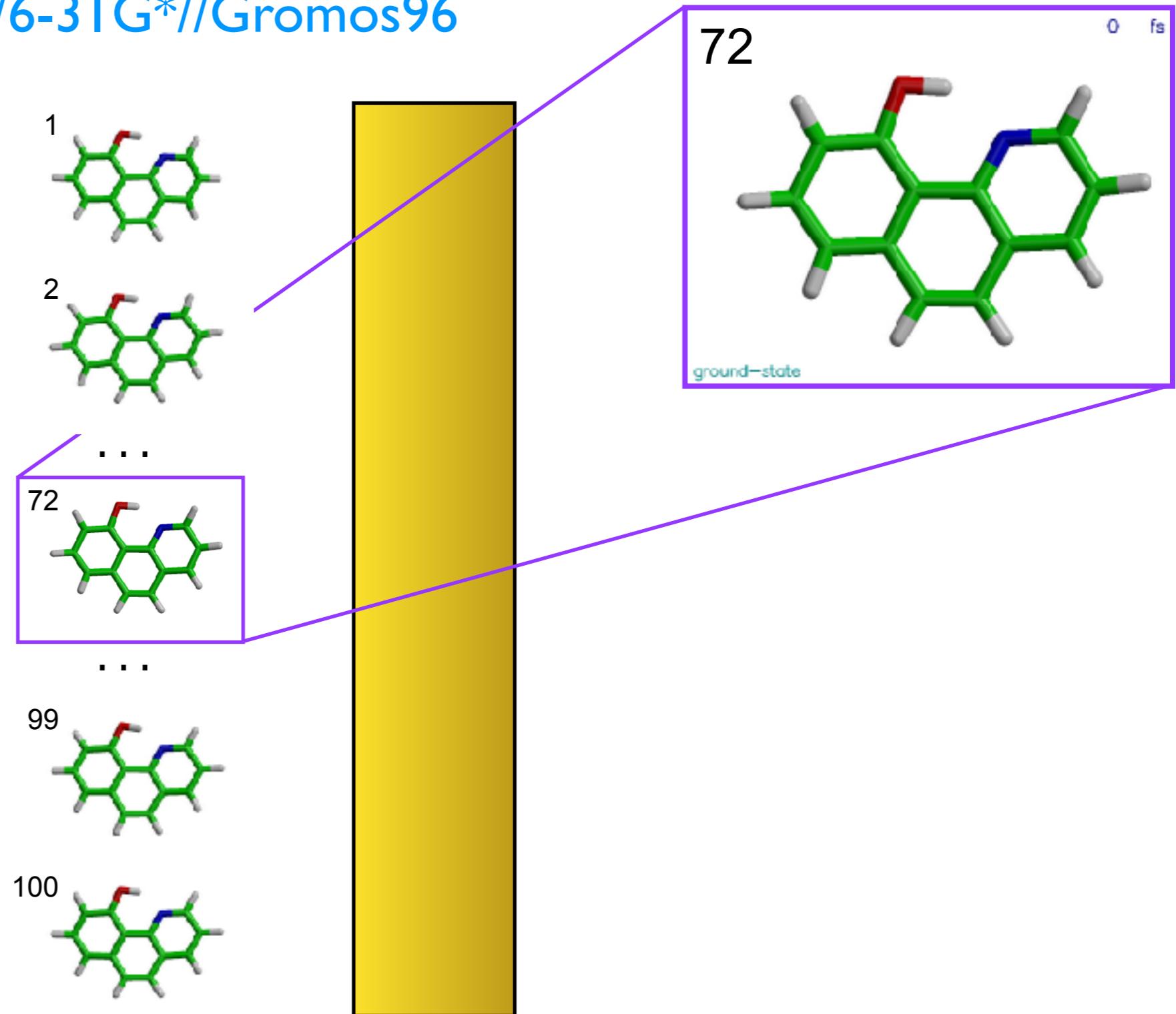
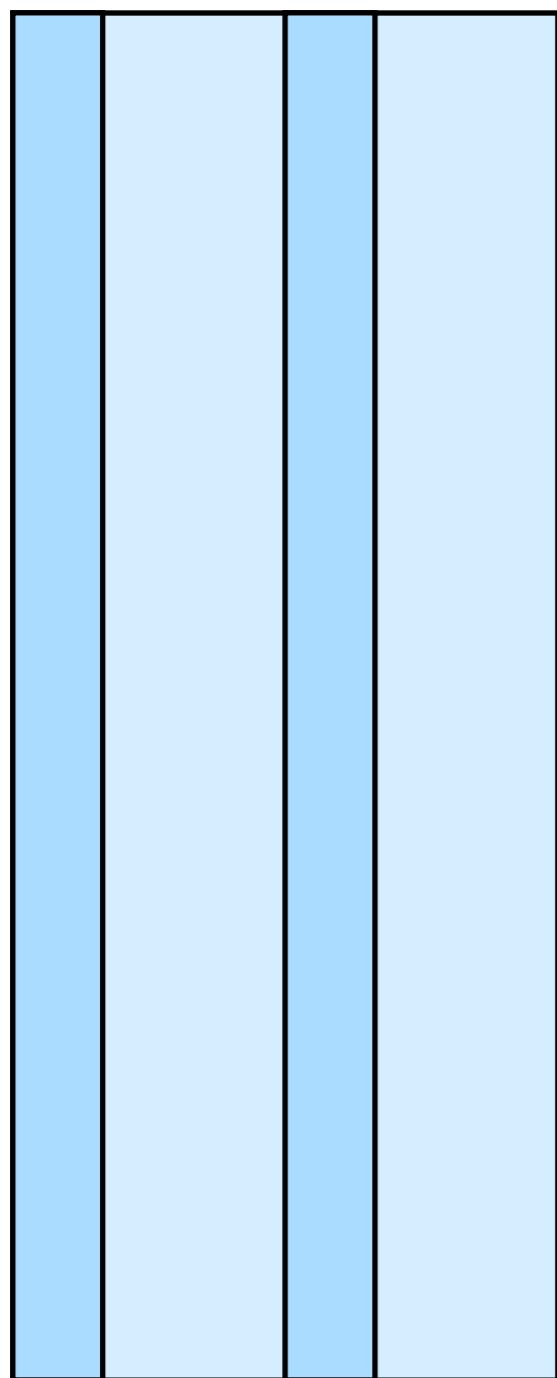
$$\begin{aligned}\Psi^{\text{LP}} = & +|1^*2\dots400\rangle|0\rangle \\ & +|12^*\dots400\rangle|0\rangle \\ & \dots \\ & +|12\dots400^*\rangle|0\rangle \\ & +|12\dots400\rangle|1\rangle\end{aligned}$$

Manipulating photo-chemistry with mirrors

excited-state intra-molecular proton transfer

100 HBQ in cyclohexane solvent inside dielectric cavity

TDA-CAMB3LYP/6-31G*//Gromos96

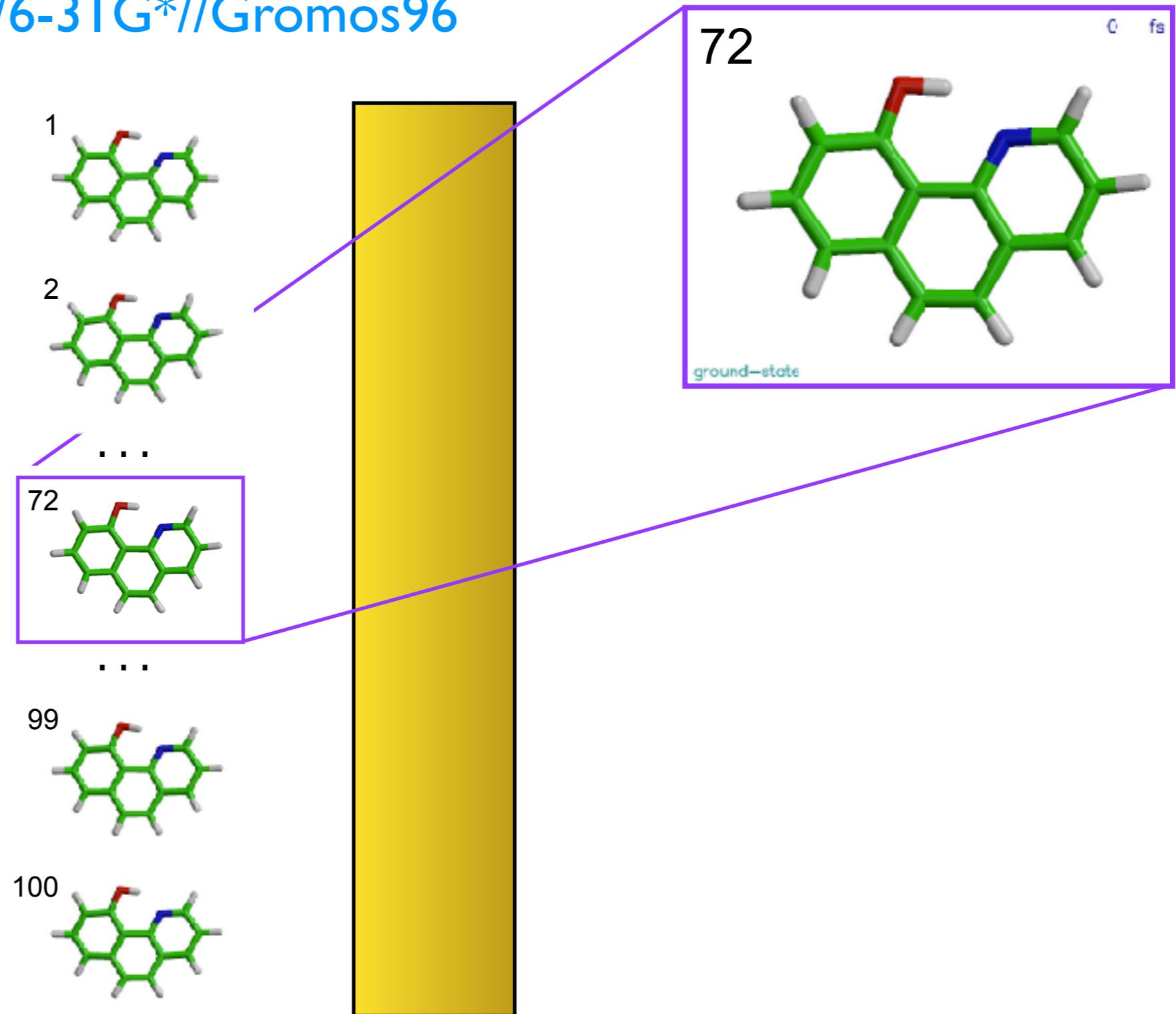
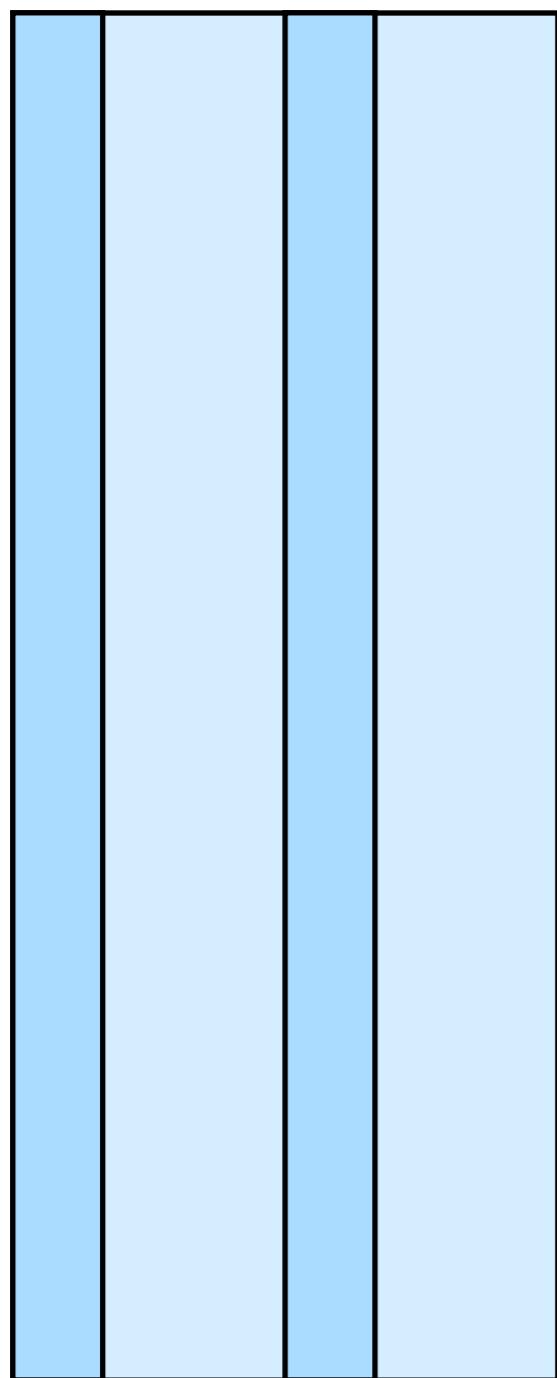


Manipulating photo-chemistry with mirrors

excited-state intra-molecular proton transfer

100 HBQ in cyclohexane solvent inside dielectric cavity

TDA-CAMB3LYP/6-31G*//Gromos96

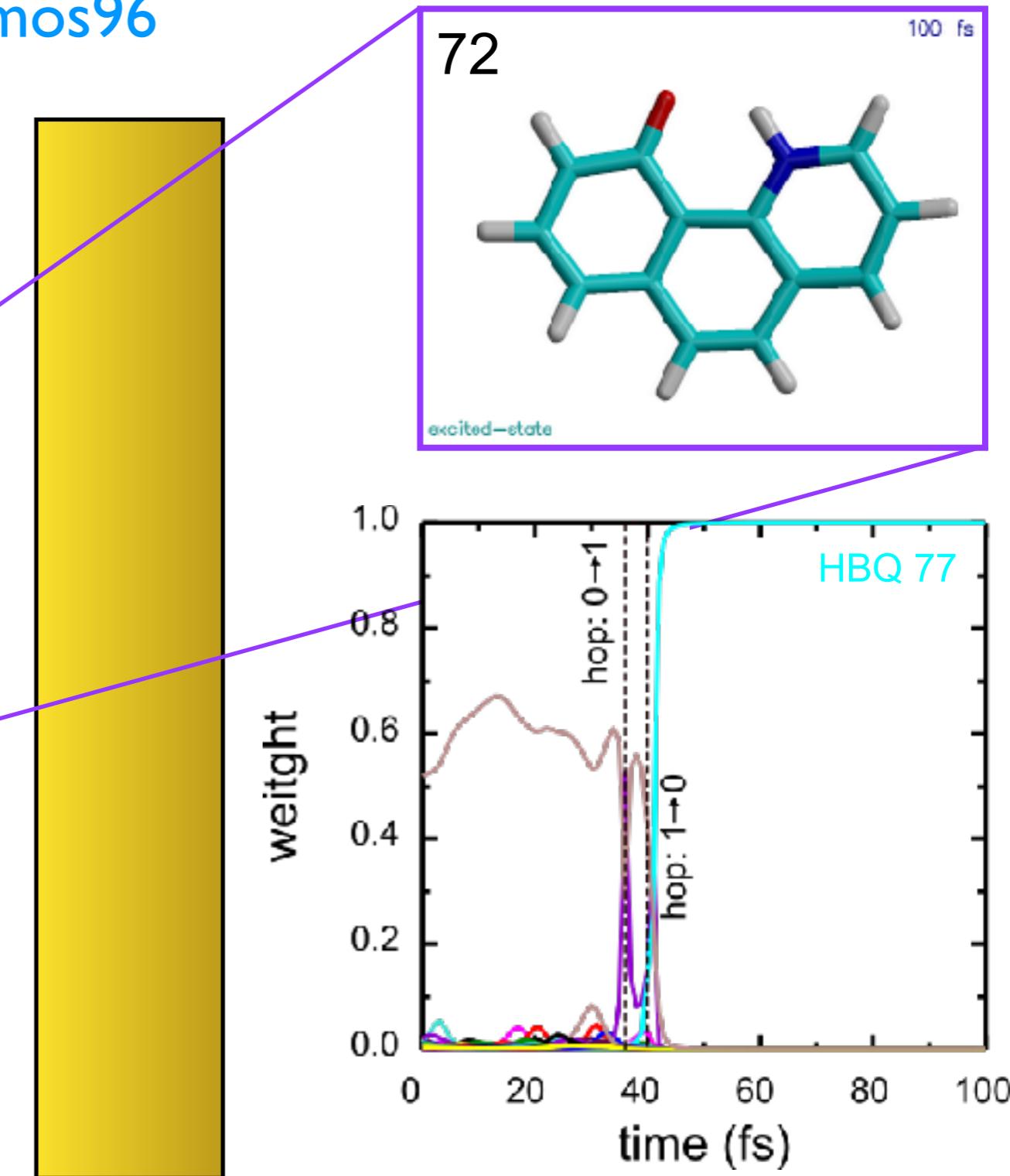
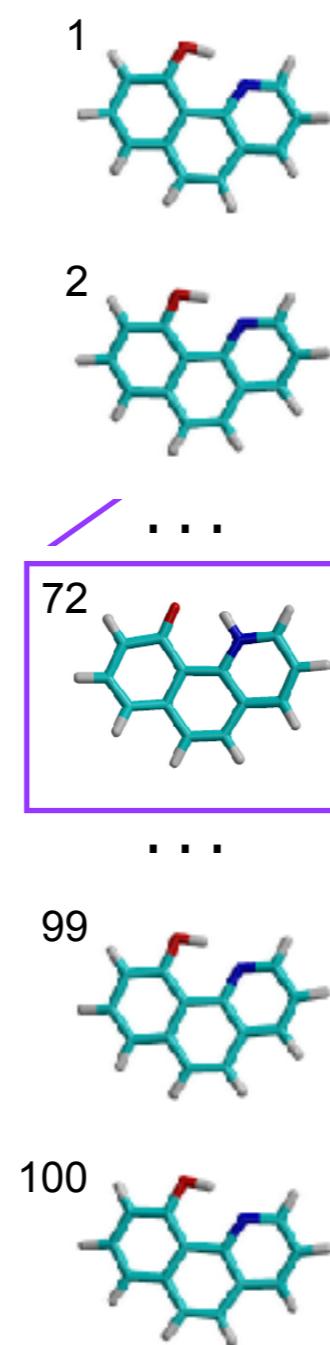
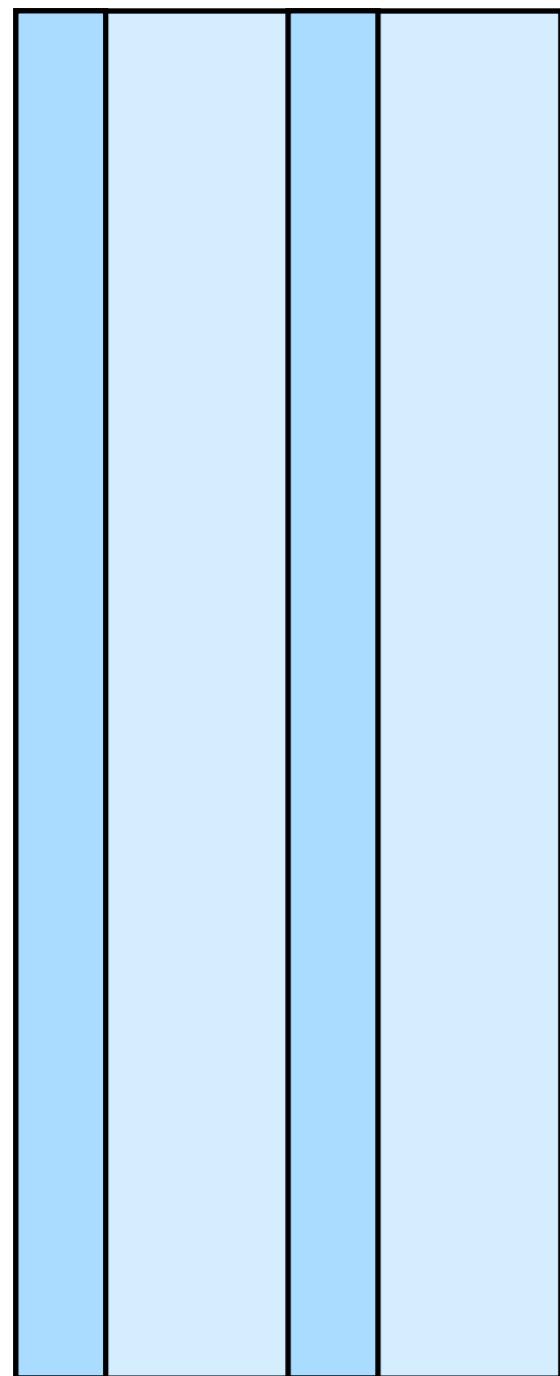


Manipulating photo-chemistry with mirrors

excited-state intra-molecular proton transfer

100 HBQ in cyclohexane solvent inside dielectric cavity

TDA-CAMB3LYP/6-31G*//Gromos96



Manipulating photo-chemistry with mirrors

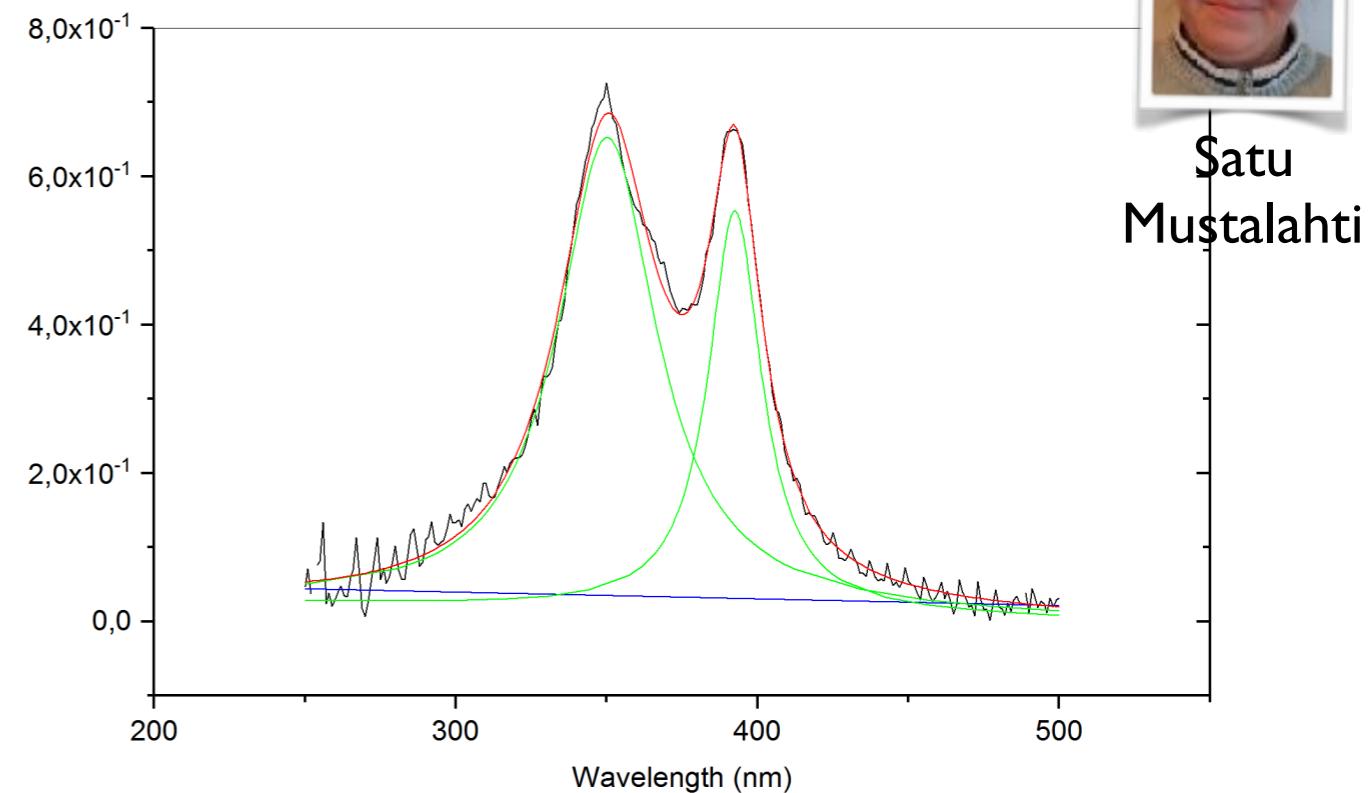
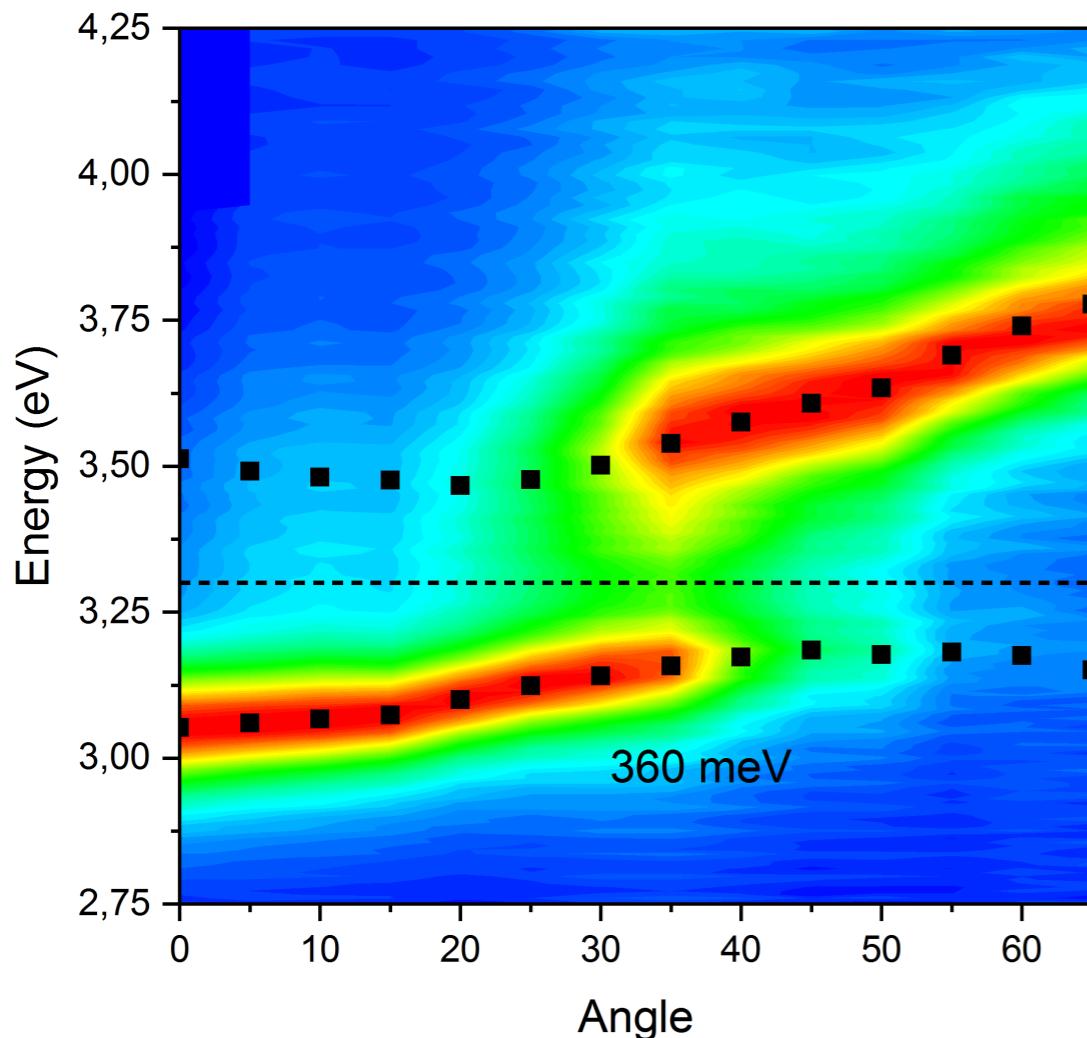
excited-state intra-molecular proton transfer

real HBQ in PMMA inside dielectric cavity

aluminium mirrors



Ossi
Hakamaa



Satu
Mustalahti

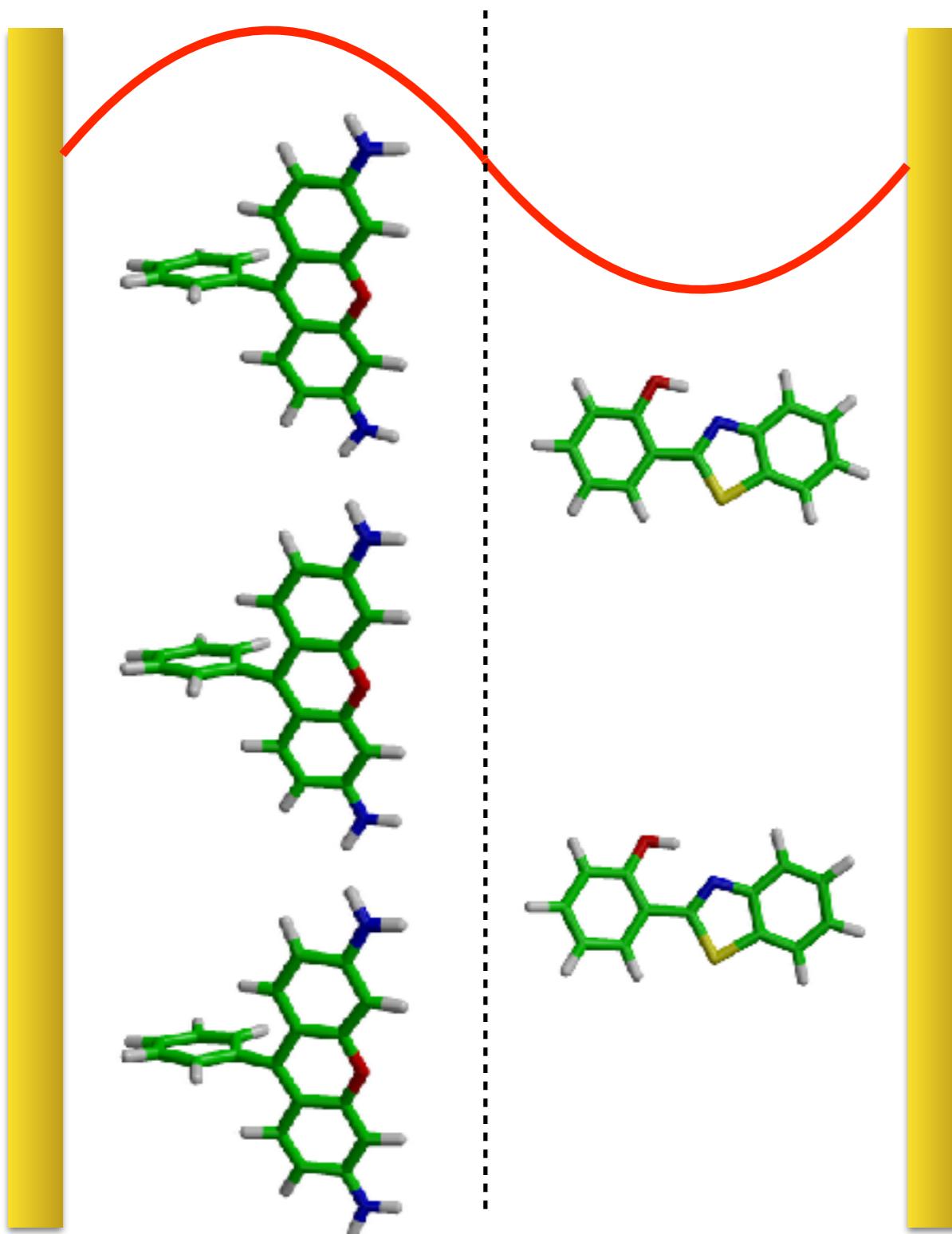
how to detect the effect of strong coupling?

reduced/slower formation of red-shifted emission ...

Manipulating photo-chemistry with mirrors

excitation energy transfer

reactive & un-reactive molecules coupled to same light mode

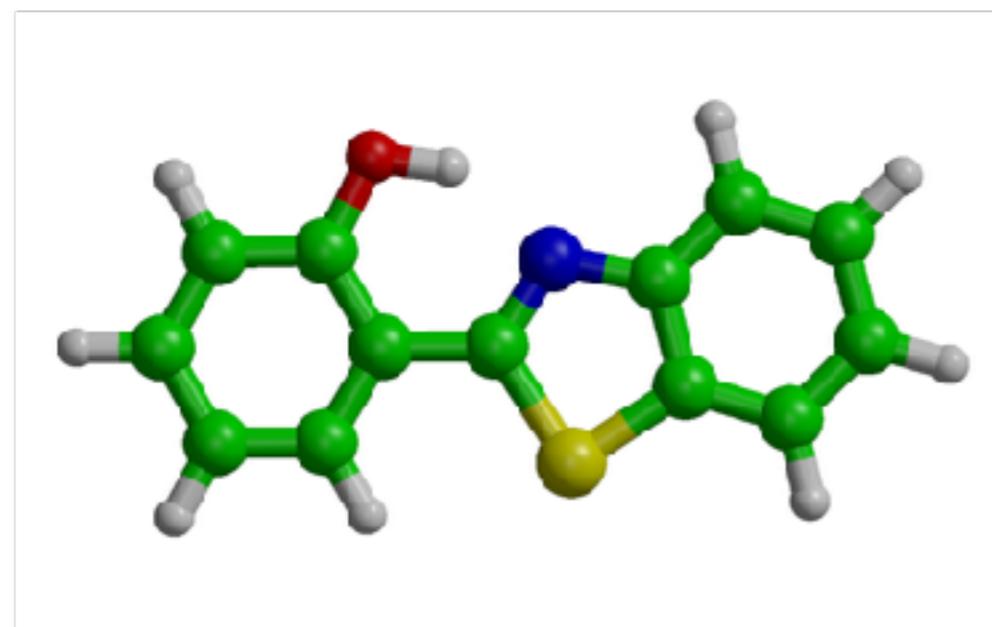


Manipulating photo-chemistry with mirrors

excitation energy transfer

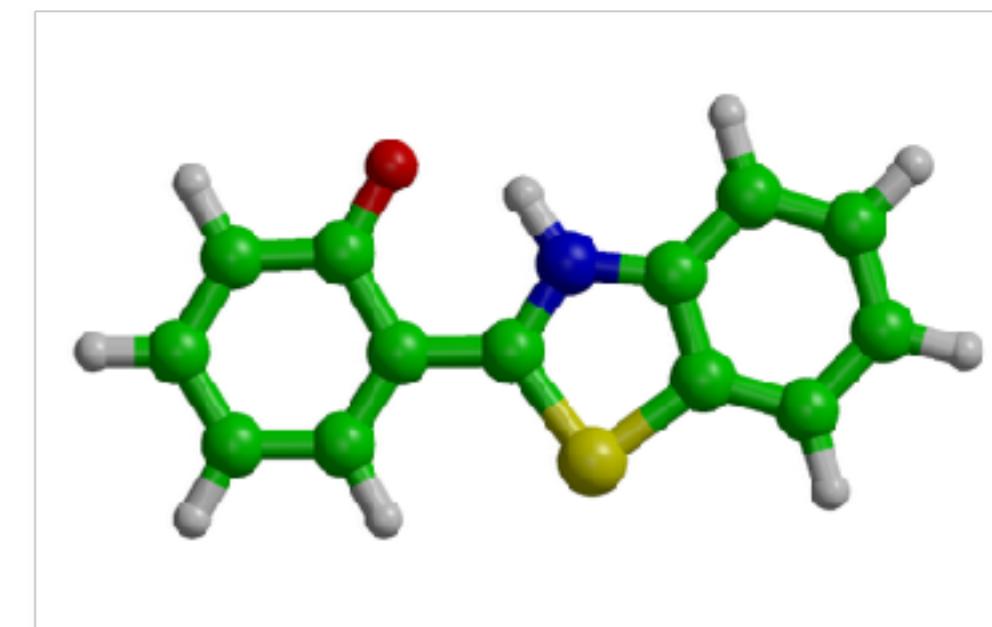
reactive & un-reactive molecules coupled to same light mode

reactive molecules: 2-(2'-hydroxyphenyl)benzothiazole (HBT)



$\lambda_{\text{abs}} = 340 \text{ nm}$

$\sim 30 \text{ fs}$



$\lambda_{\text{em}} = 525 \text{ nm}$

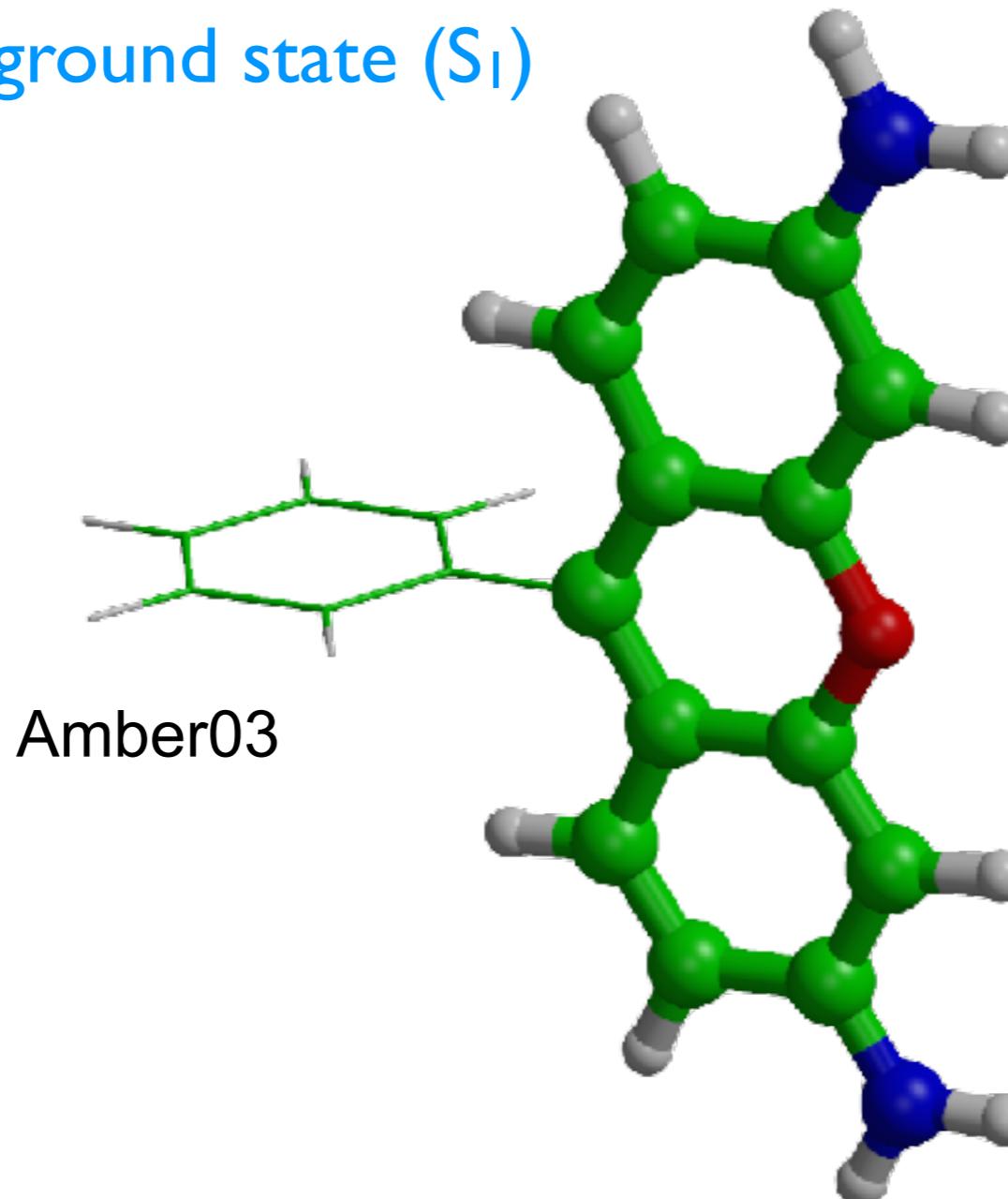
Manipulating photo-chemistry with mirrors

excitation energy transfer

reactive & un-reactive molecules coupled to same light mode

un-reactive molecules: rhodamine (Rho)

electronic ground state (S_1)



Hartree-Fock/3-21G

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

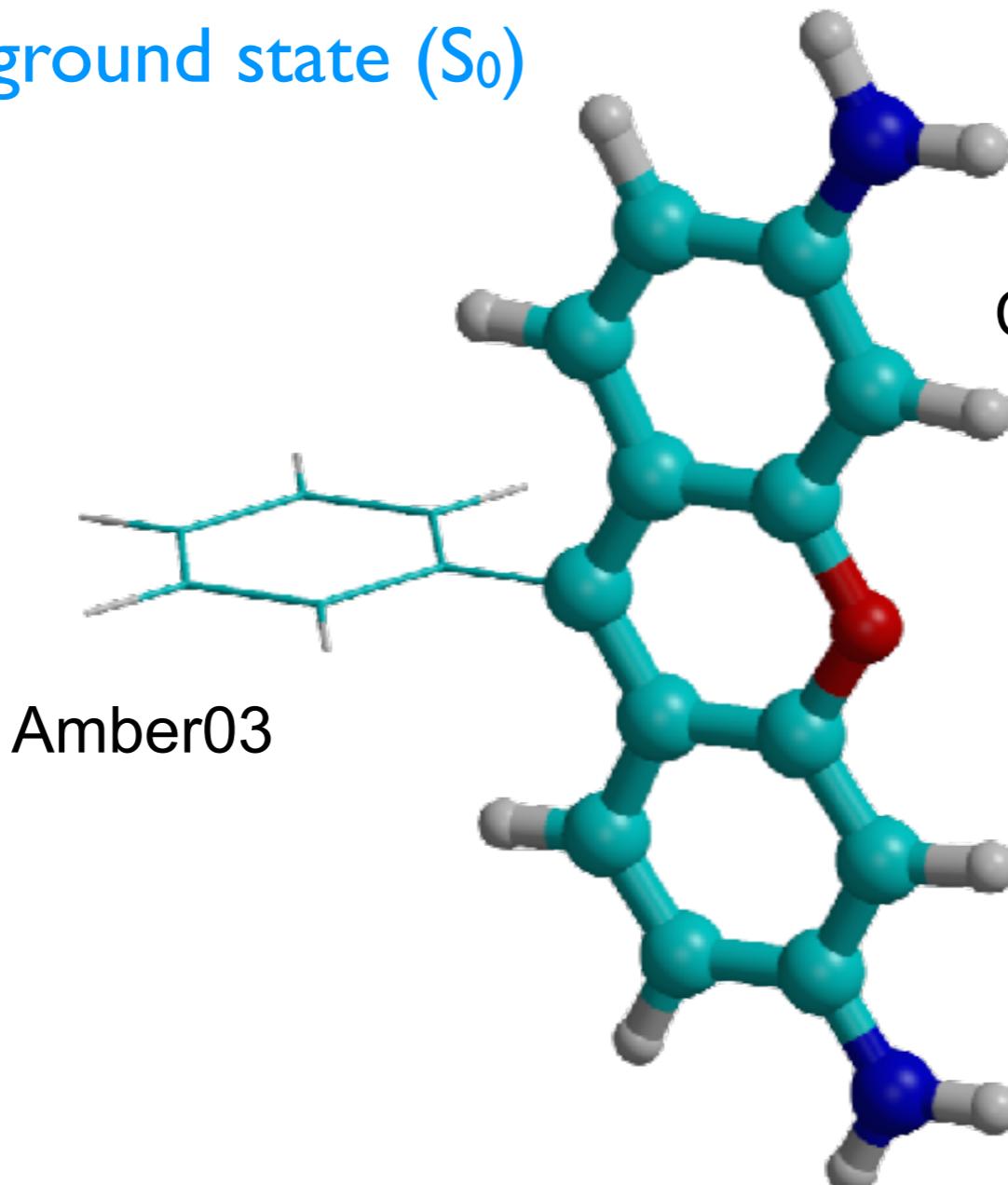
Manipulating photo-chemistry with mirrors

excitation energy transfer

reactive & un-reactive molecules coupled to same light mode

un-reactive molecules: rhodamine (Rho)

electronic ground state (S_0)



Configuration Interaction/3-21G

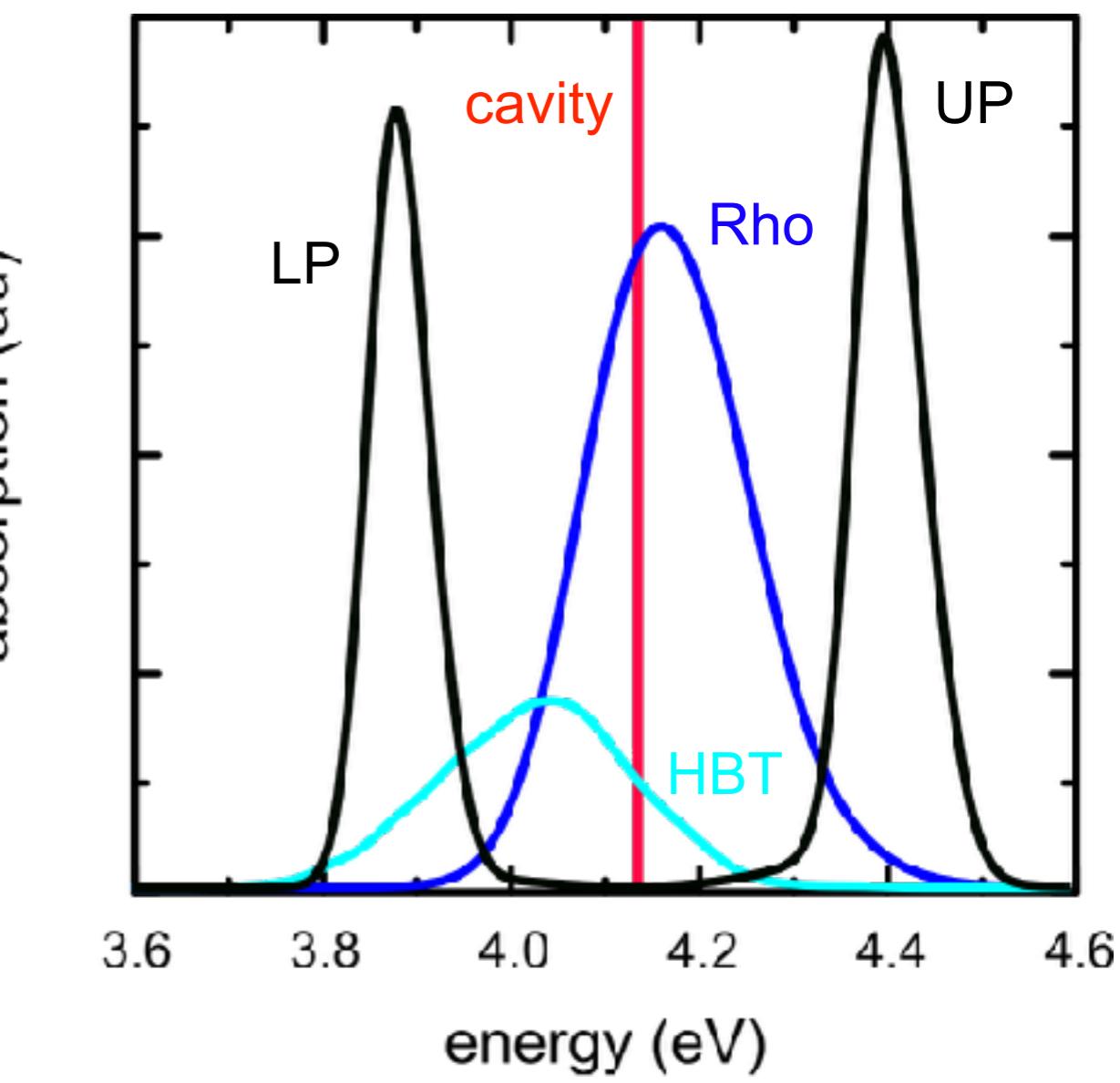
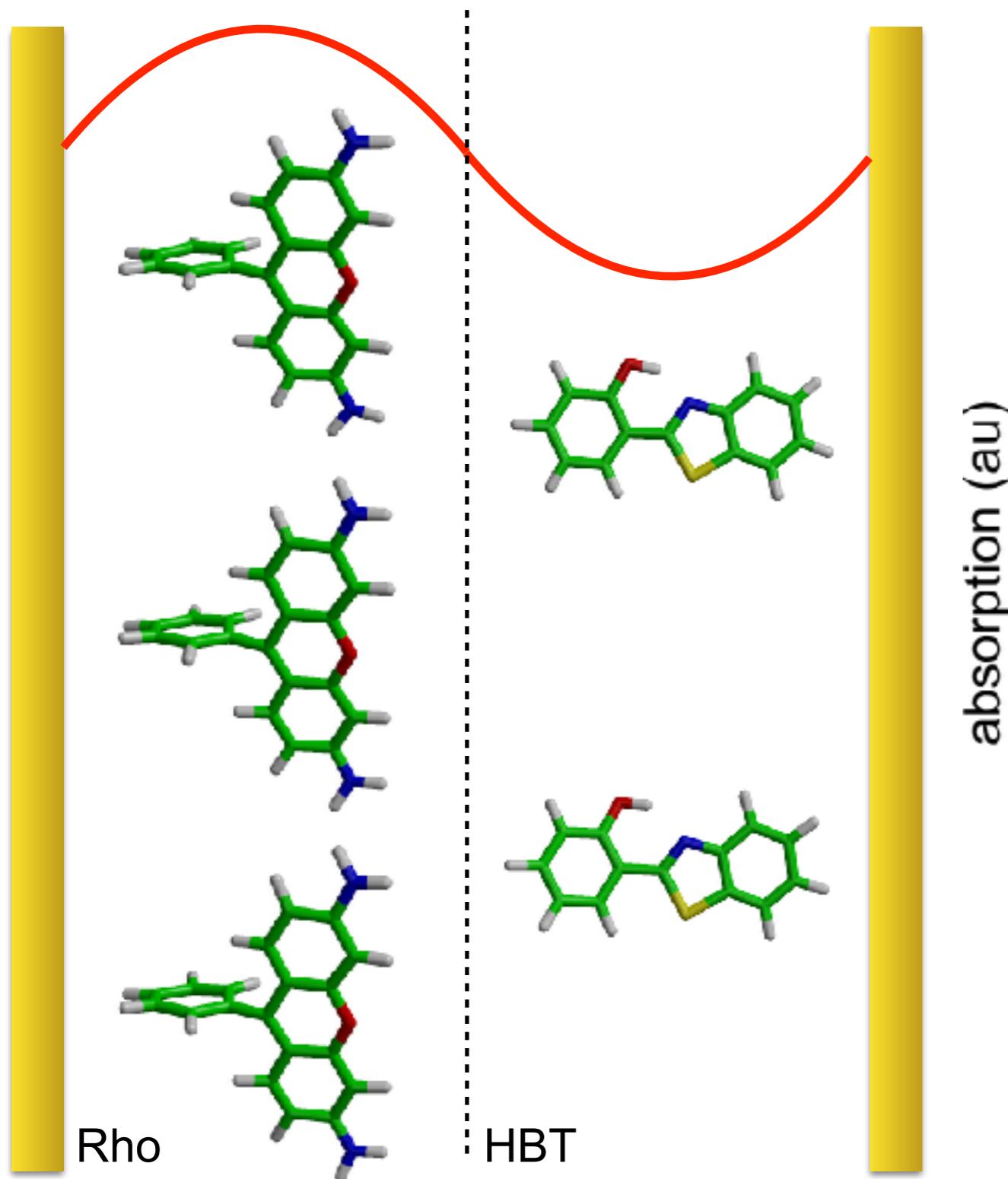
truncated to one electron excitations

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

Manipulating photo-chemistry with mirrors

excitation energy transfer

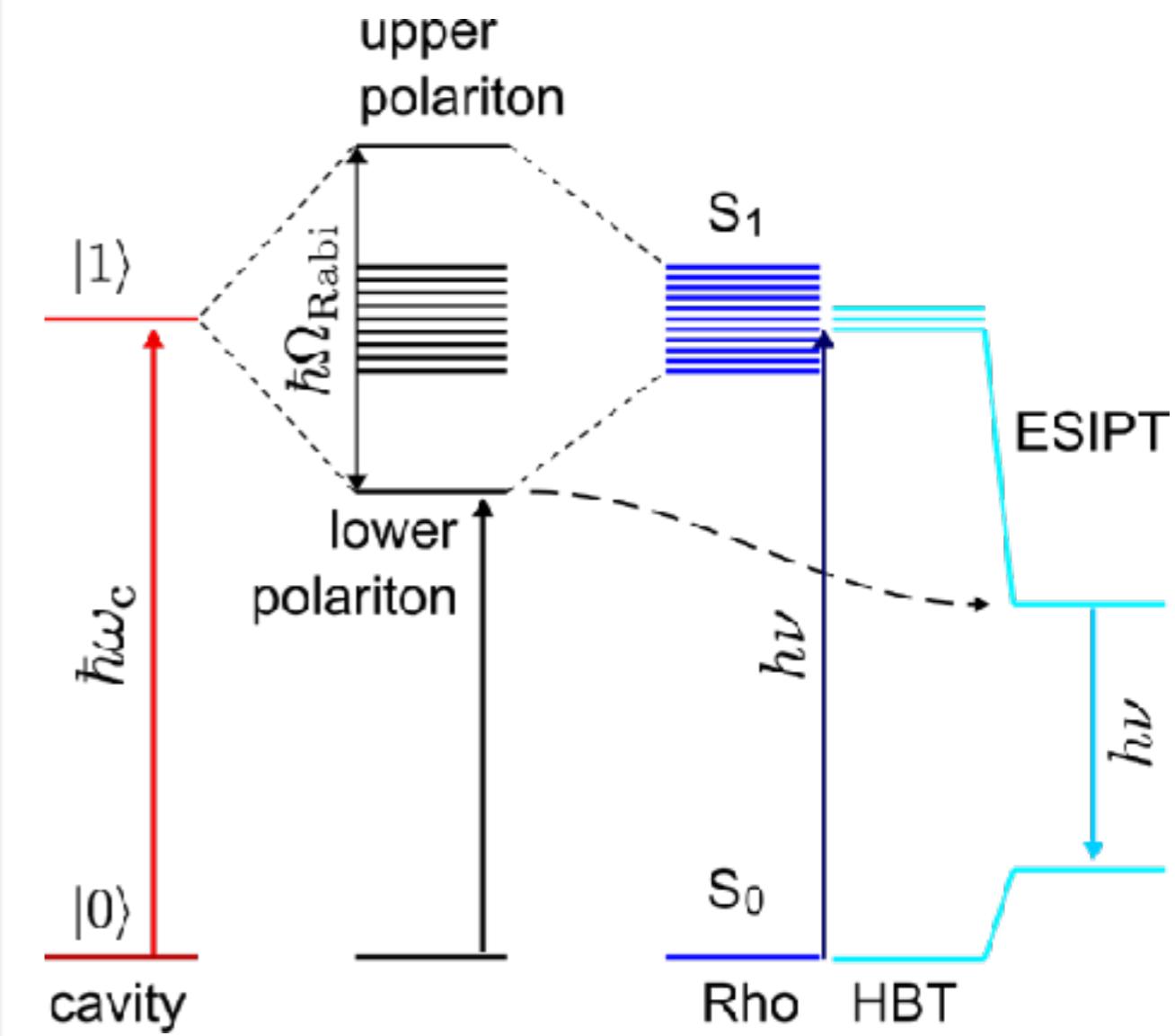
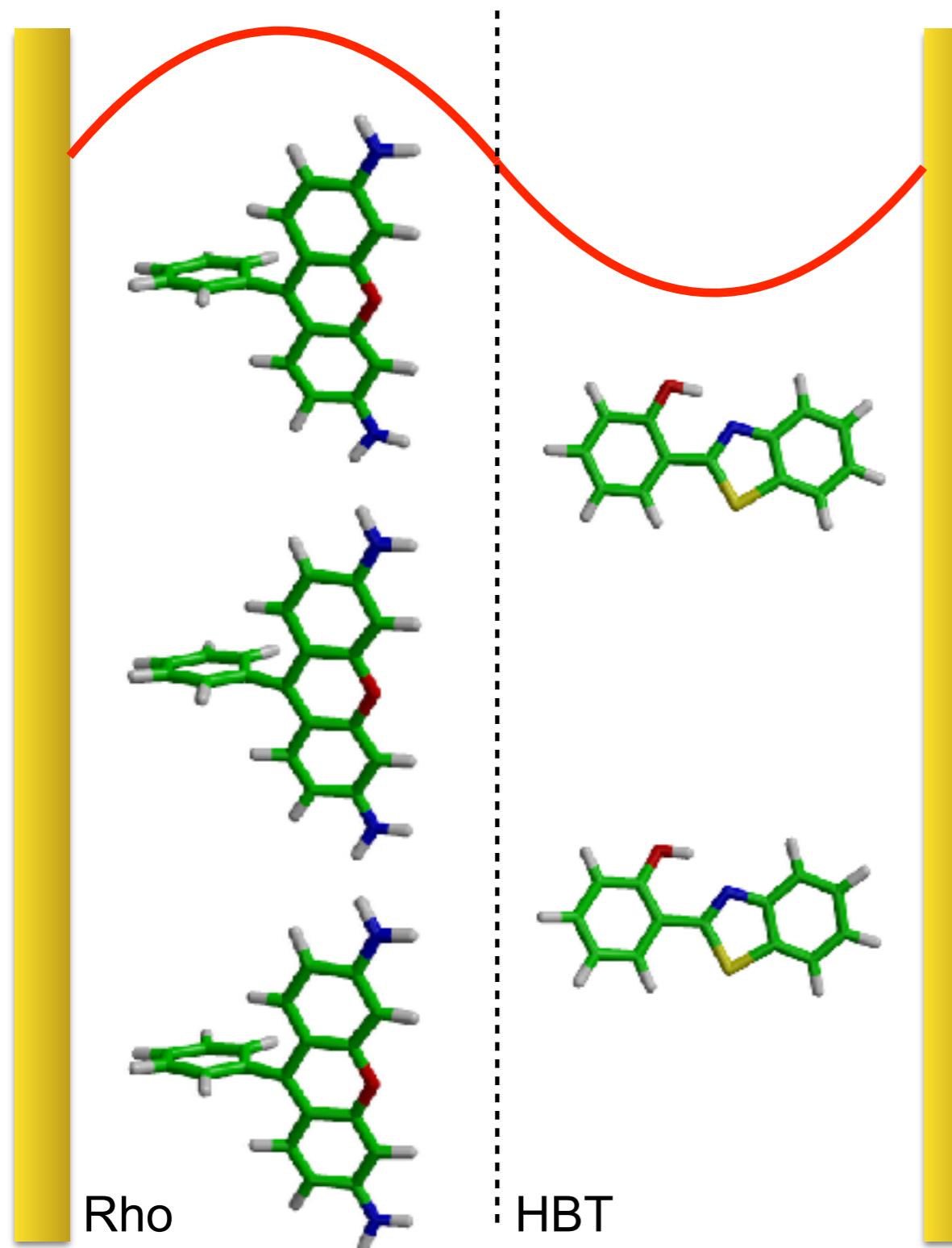
reactive & un-reactive molecules coupled to same light mode



Manipulating photo-chemistry with mirrors

excitation energy transfer

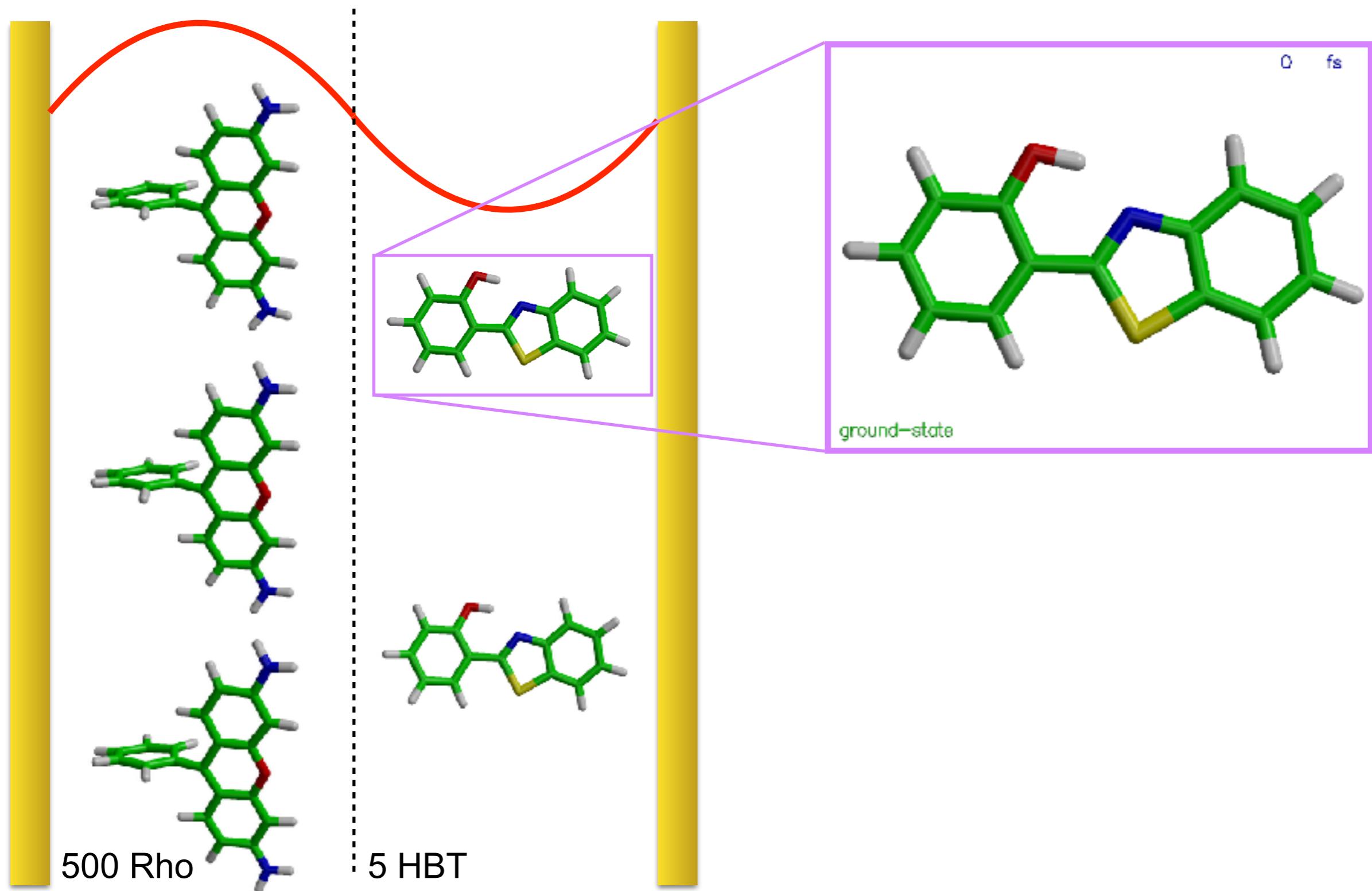
reactive & un-reactive molecules coupled to same light mode



Manipulating photo-chemistry with mirrors

excitation energy transfer

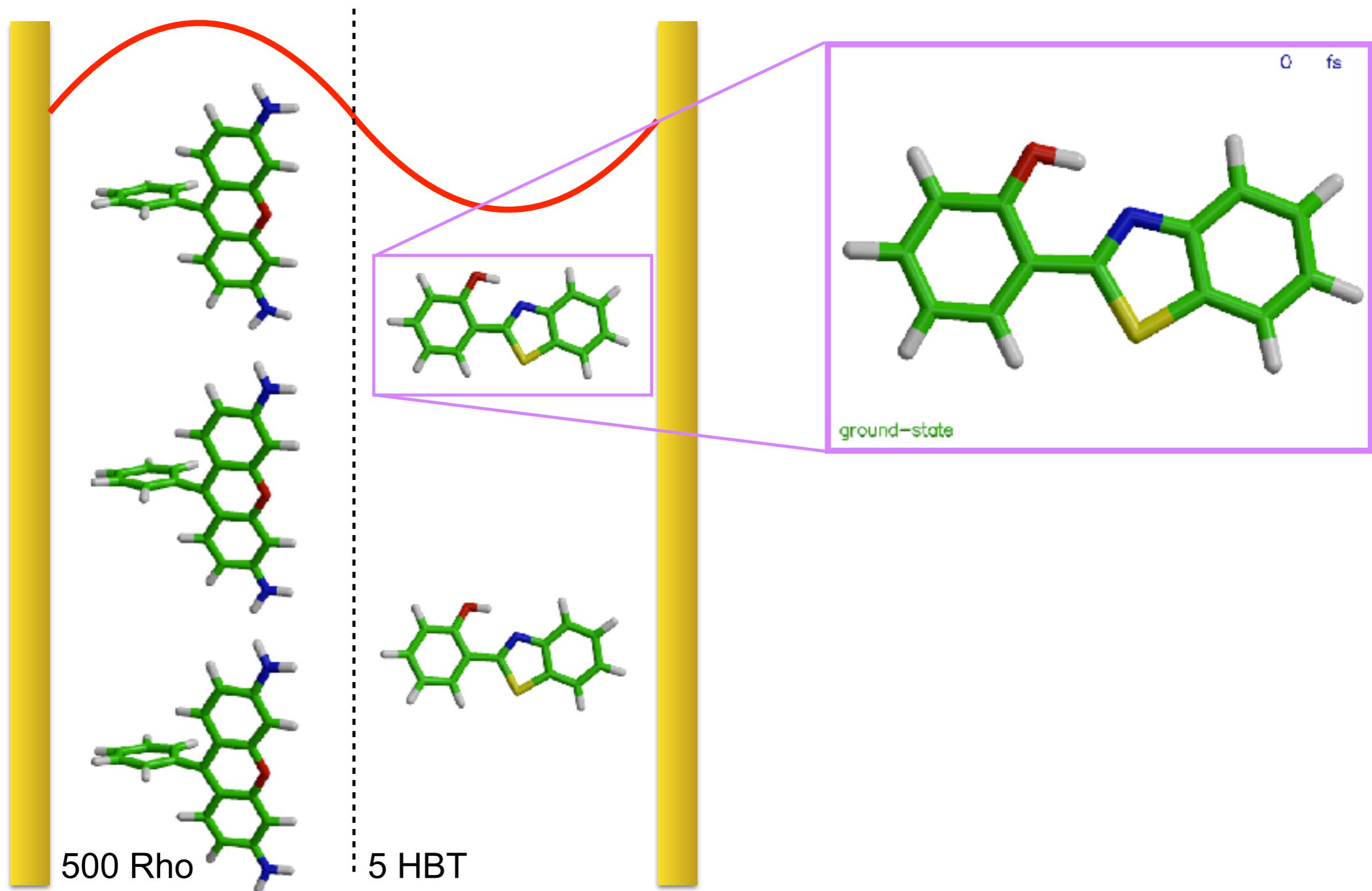
reactive & un-reactive molecules coupled to same light mode



Manipulating photo-chemistry with mirrors

excitation energy transfer

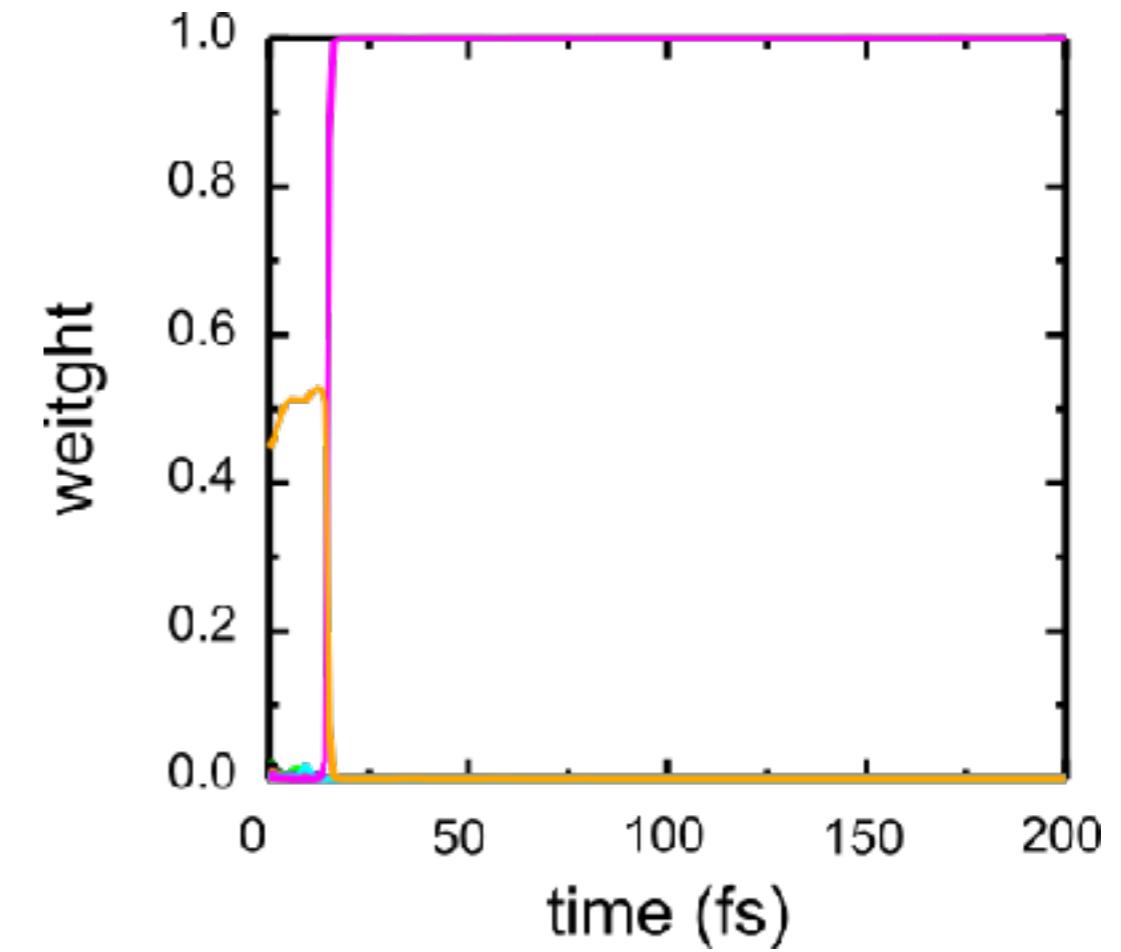
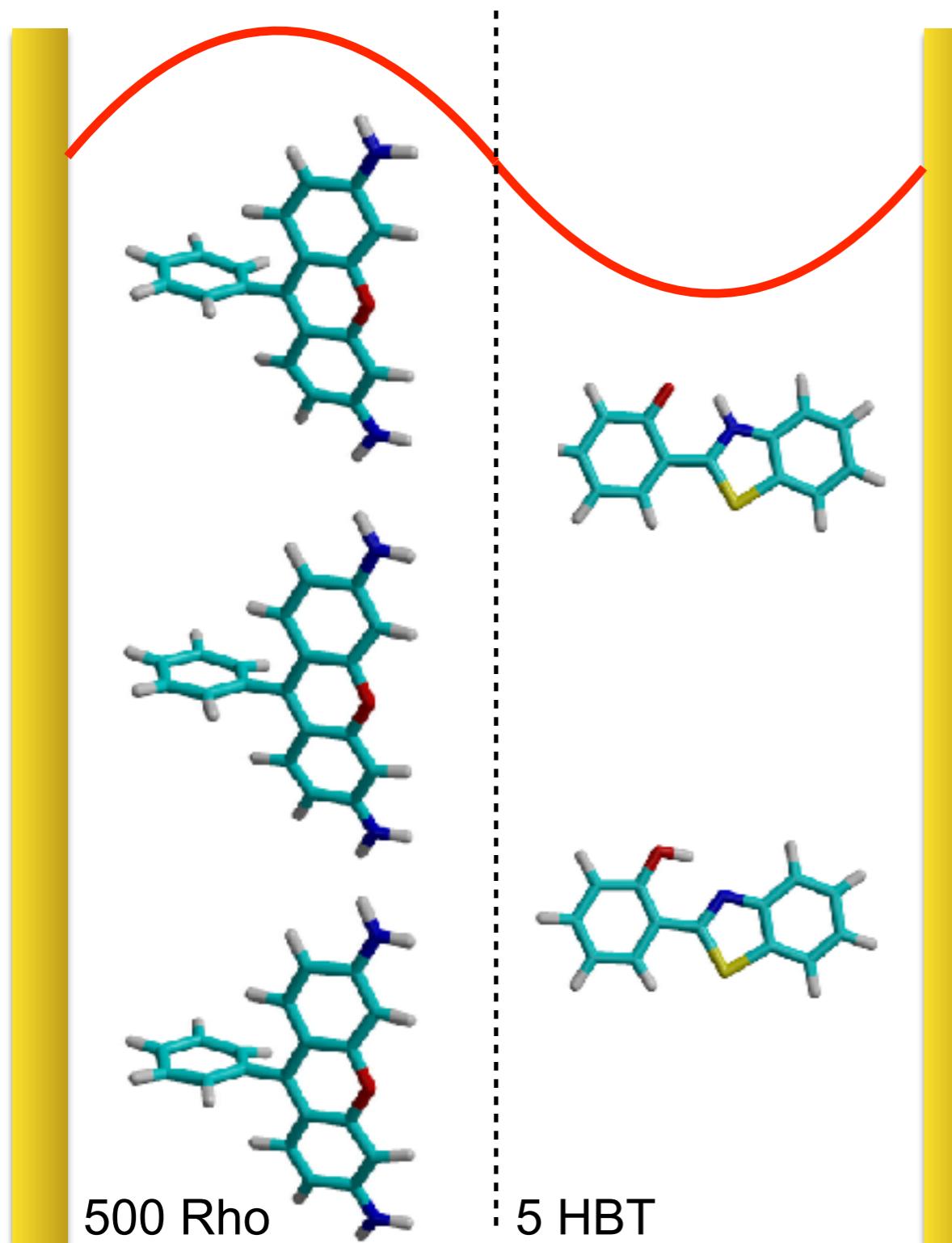
reactive & un-reactive molecules coupled to same light mode



Manipulating photo-chemistry with mirrors

excitation energy transfer

reactive & un-reactive molecules coupled to same light mode



$$\Psi^K = \boxed{+\beta_1^K |Rho_1^* Rho_1 .. Rho_{500} HBT_1 .. HBT_5\rangle|0\rangle}$$

...

$$\boxed{+\beta_{500}^K |Rho_1 Rho_1 .. Rho_{500}^* HBT_1 .. HBT_5\rangle|0\rangle}$$
$$\boxed{+\beta_{501}^K |Rho_1 Rho_1 .. Rho_{500} HBT_1^* .. HBT_5\rangle|0\rangle}$$

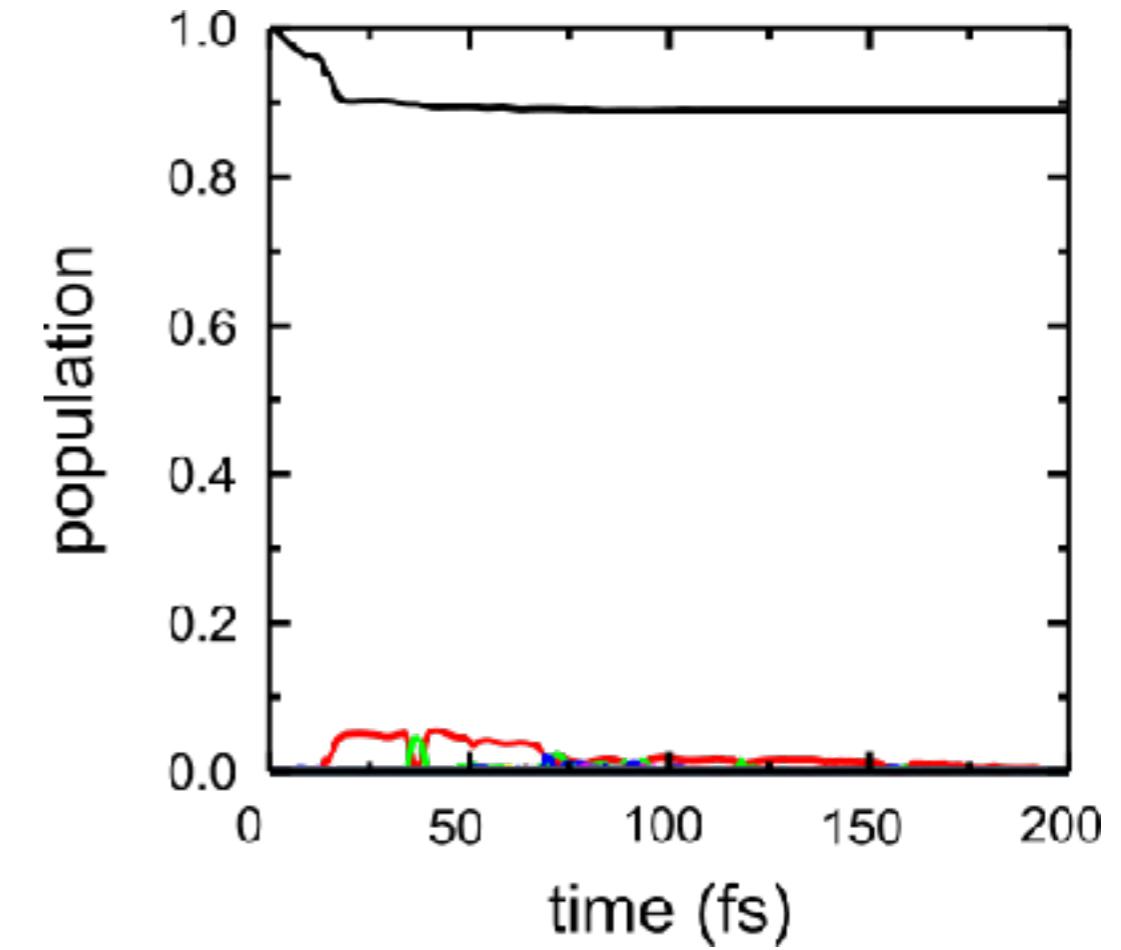
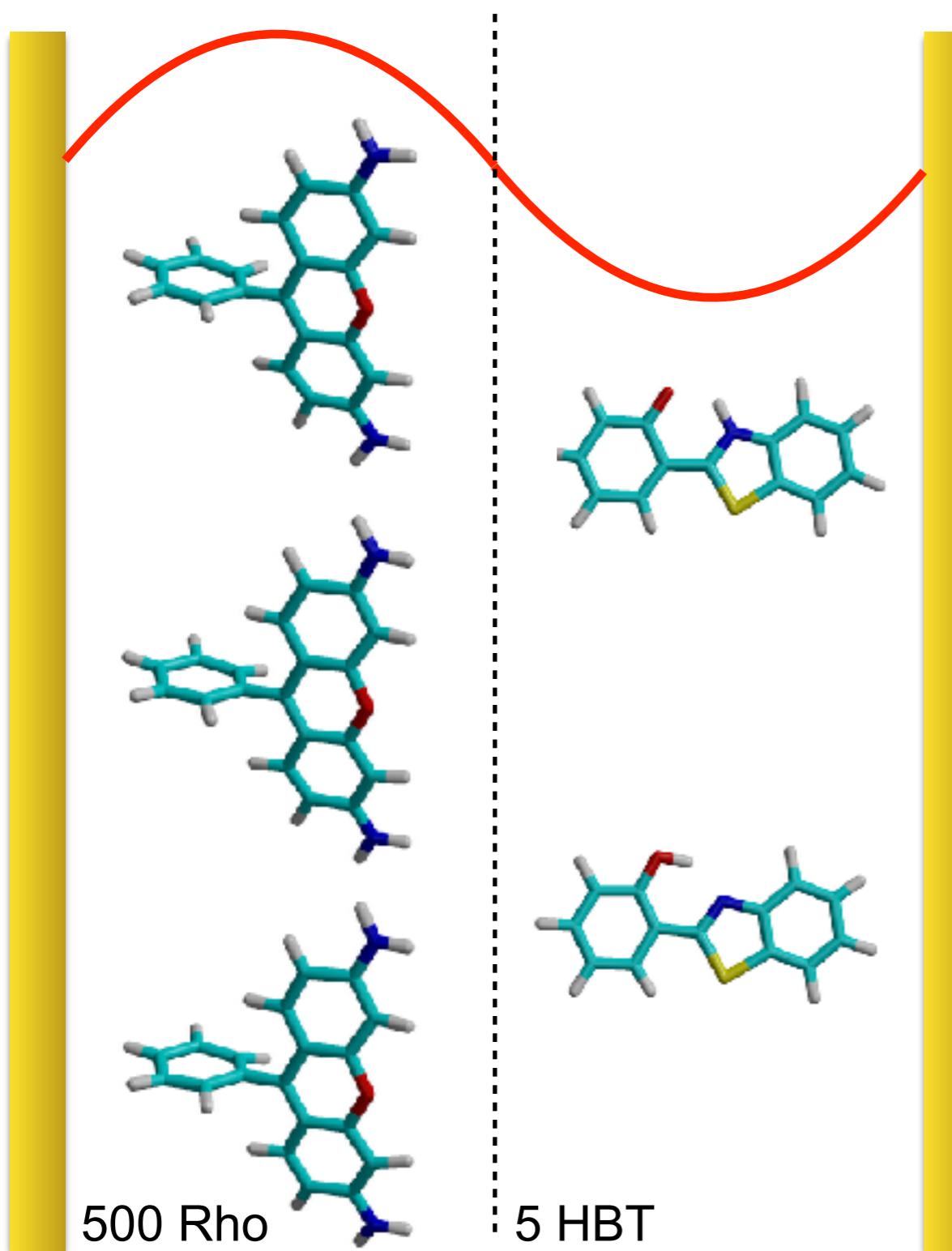
...

$$\boxed{+\beta_{501}^K |Rho_1 Rho_1 .. Rho_{500} HBT_1 .. HBT_5^*\rangle|0\rangle}$$
$$\boxed{+\beta_{501}^K |Rho_1 Rho_1 .. Rho_{500} HBT_1 .. HBT_5\rangle|1\rangle}$$

Manipulating photo-chemistry with mirrors

excitation energy transfer

reactive & un-reactive molecules coupled to same light mode



$$\Phi(t) = \sum_K c_K(t) \Psi^K$$

$$p_1(t) = [c_1(t)]^* c_1(t)$$

$$p_2(t) = [c_2(t)]^* c_2(t)$$

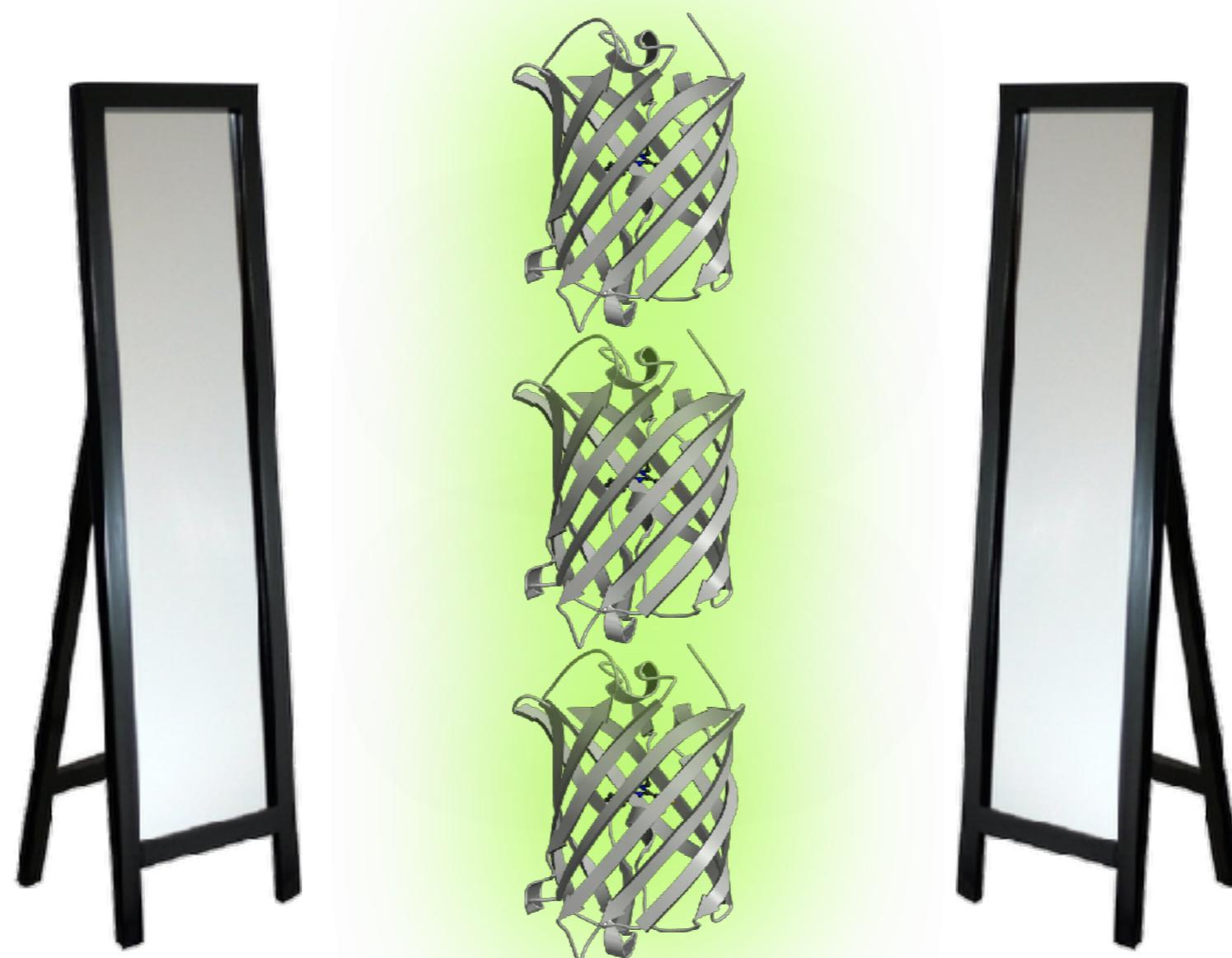
$$p_3(t) = [c_3(t)]^* c_3(t)$$

Manipulating photo-chemistry with mirrors

summary

cavity “QED”/MM

simulations of molecules under strong coupling with confined light



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re-shaping potential energy surface

control of photo-chemical reactions

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Angew. Chem. Int. Ed. 55 (2016) 6202–6206

Angew. Chem. Int. Ed. 56 (2017) 9034–9038

Lidzey & coworkers: *Nature Materials* 13 (2014) 712–719

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validity of the model

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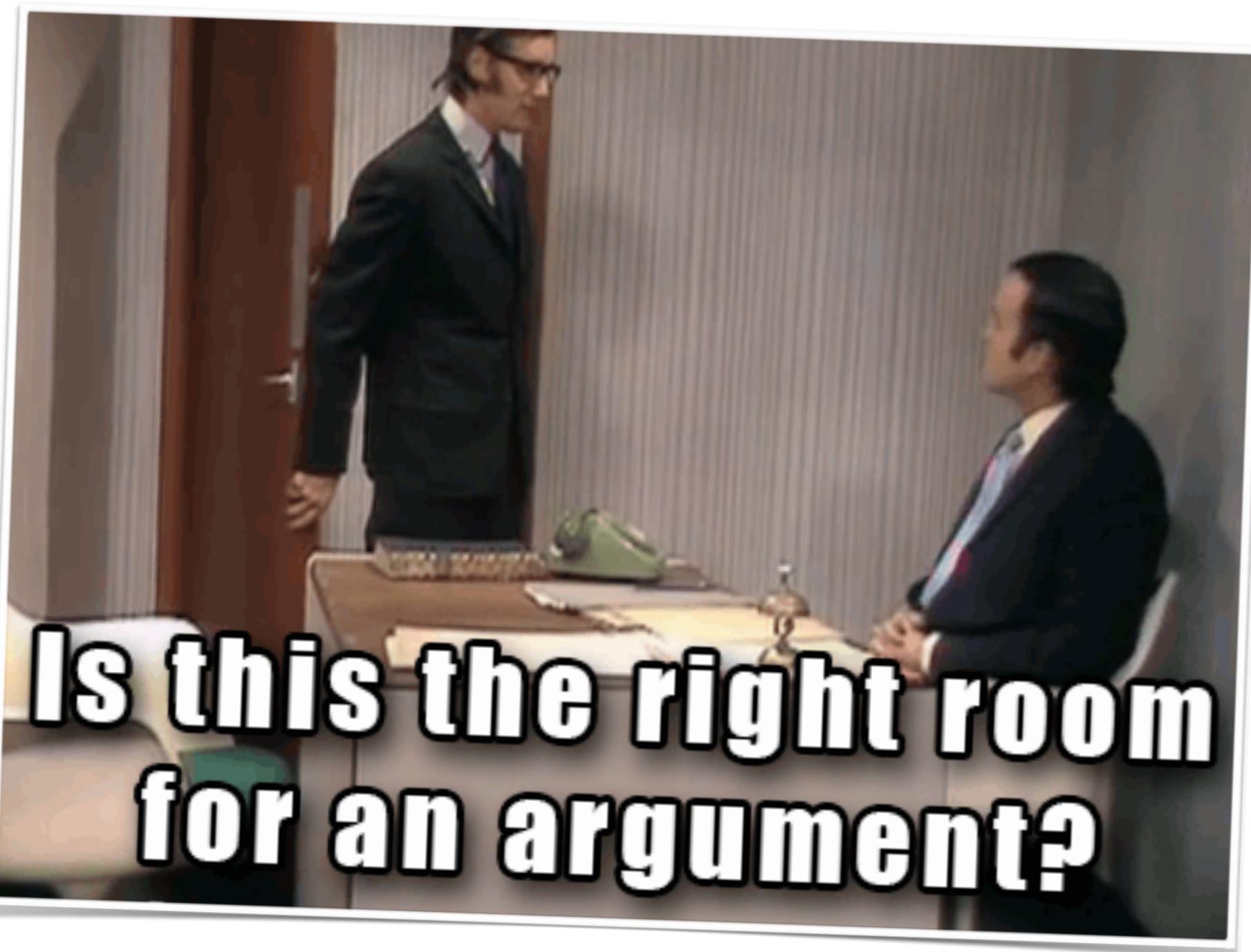
Aili
Asikainen



Ossi
Hakamaa

support (Euros, FLOPs & photons)

Questions?

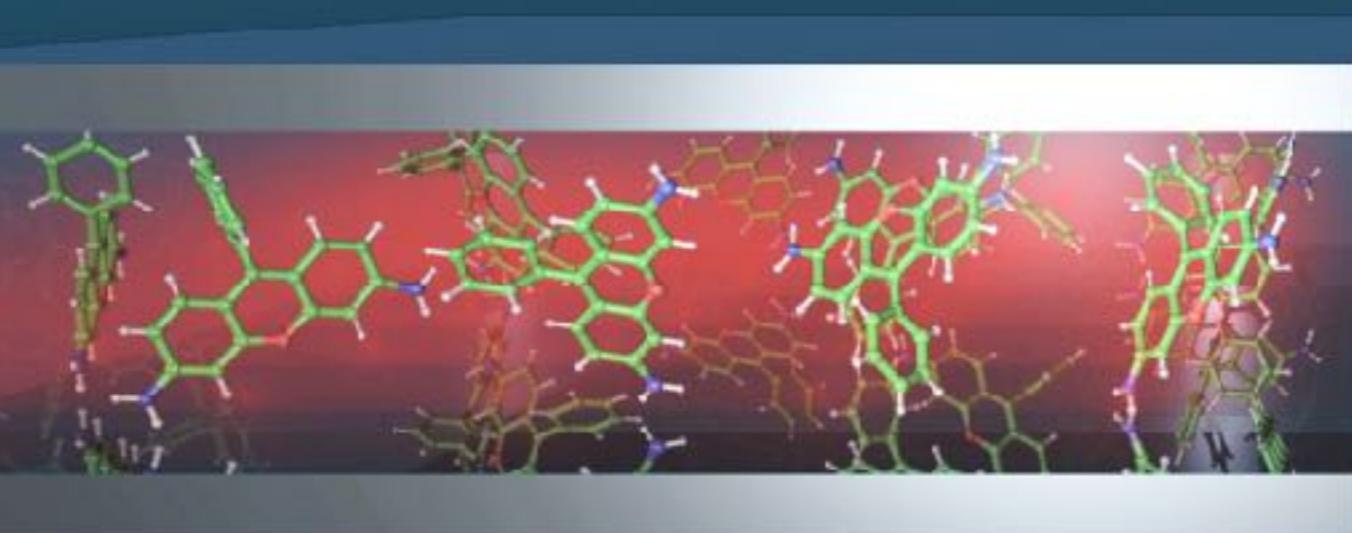


**Is this the right room
for an argument?**

Manipulating chemistry with mirrors

Gerrit Groenhof

Department of Chemistry & Nanoscience center
University of Jyväskylä
Finland



Johannes
Feist (UAM)



Calvin
Luk



Jussi
Toppari

$$\Psi = \beta_1(t) | \text{[molecule 1]} \rangle | 0 \rangle + \\ \beta_2(t) | \text{[molecule 2]} \rangle | 0 \rangle + \\ \beta_3(t) | \text{[molecule 3]} \rangle | 0 \rangle + \\ \beta_4(t) | \text{[molecule 4]} \rangle | 0 \rangle + \\ \beta_5(t) | \text{[molecule 5]} \rangle | 0 \rangle + \\ \beta_6(t) | \text{[molecule 6]} \rangle | 0 \rangle + \\ \beta_7(t) | \text{[molecule 7]} \rangle | 0 \rangle + \\ \beta_8(t) | \text{[molecule 8]} \rangle | 0 \rangle + \\ \alpha(t) | \text{[molecule 9]} \rangle | 1 \rangle$$