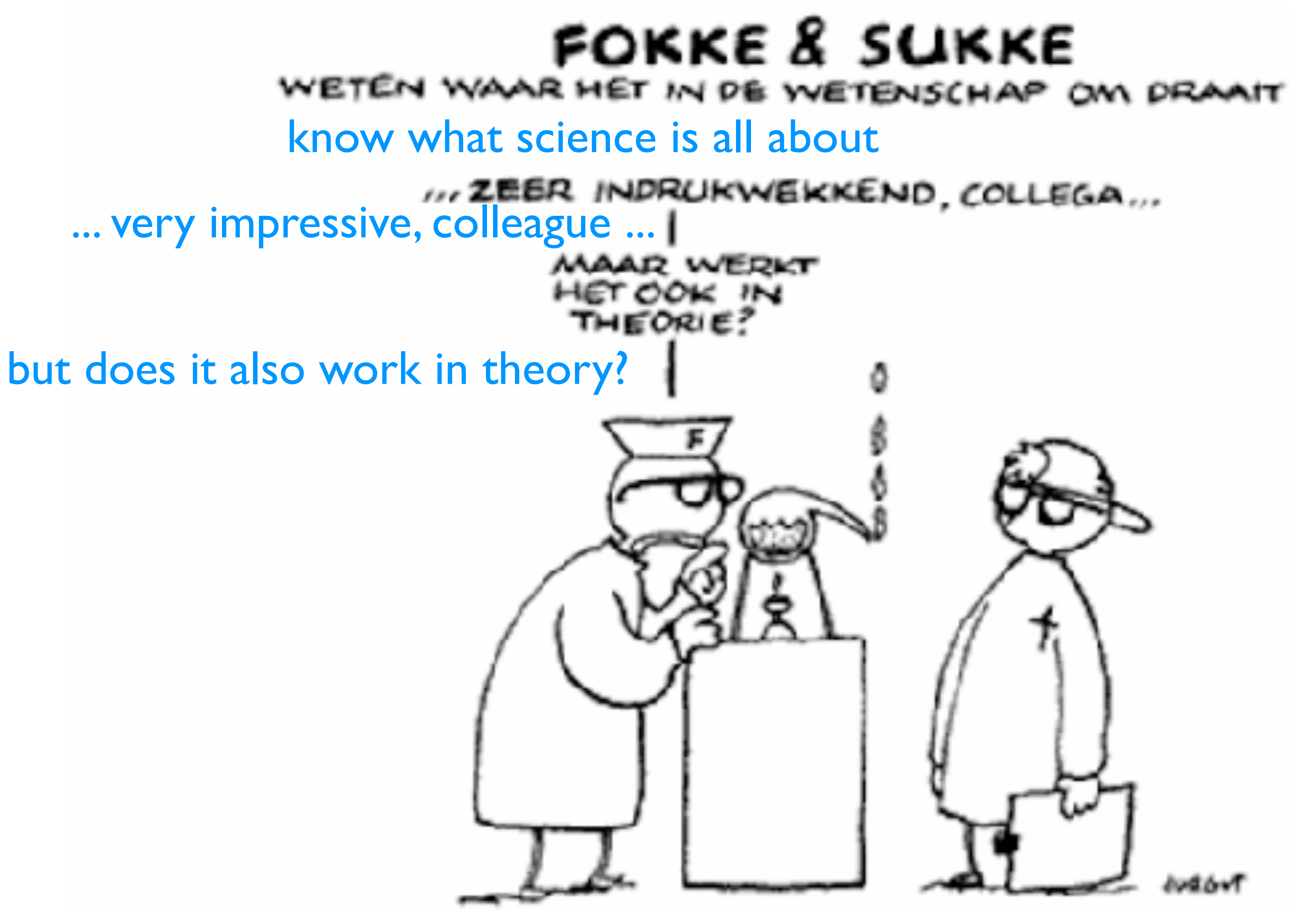
Observe while it happens: catching photochemistry in the act with computer simulations

Gerrit Groenhof

Department of Chemistry & Nanoscience Center
University of Jyväskylä
Finland



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Computational
Biomolecular
Chemistry

Why observe while it happens?

"Everything that living things do can be understood in terms of the jiggling and wiggling of atoms."

Richard Feynman

argumentum ad verecundiam

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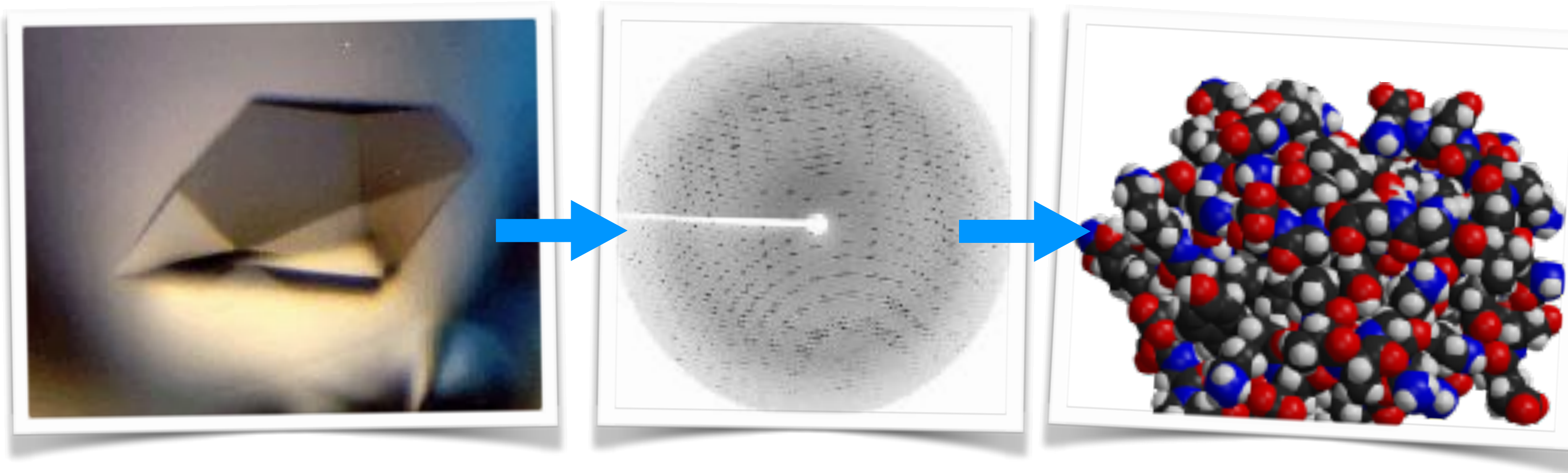
Why is that so difficult?

experiment cannot access the relevant length- and timescales simultaneously

spacial resolution: Å (10^{-10} m)



x-ray crystallography

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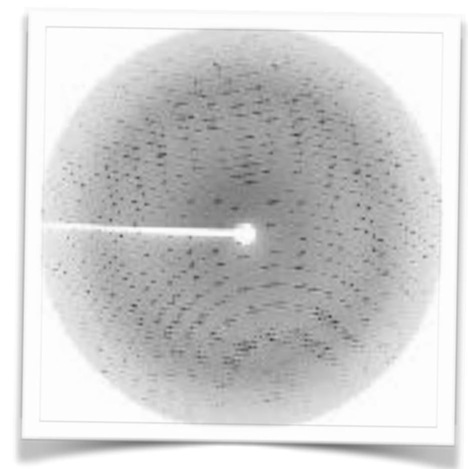

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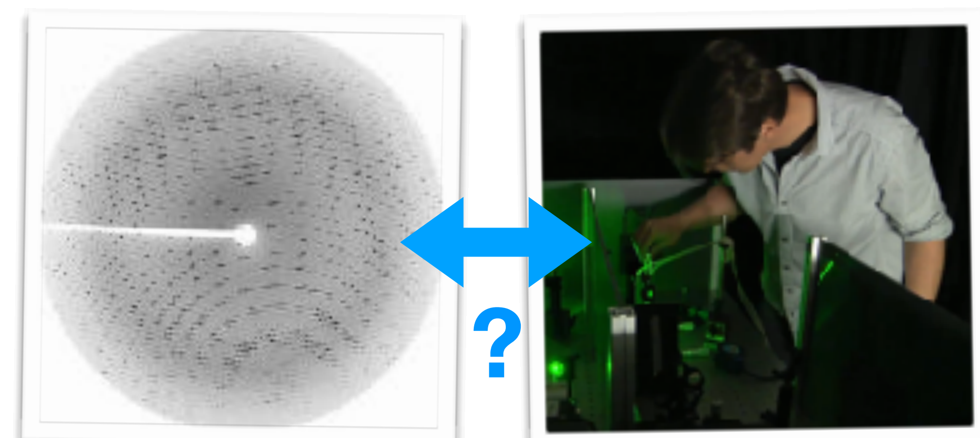

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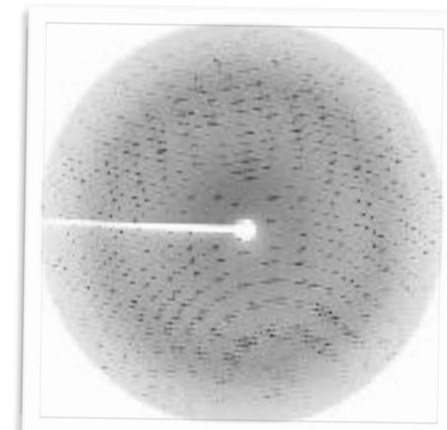


x-ray crystallography

transient spectroscopy

What can we do instead?

molecular dynamics computer simulations

Sisu.csc.fi: 1688 TFlop/s

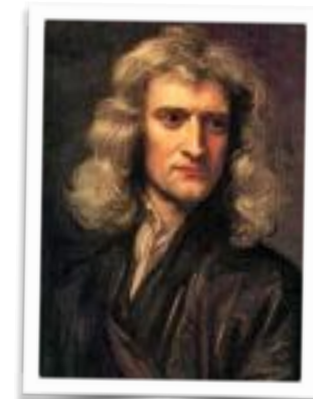
Molecular dynamics simulations


Isaac Newton

classical nuclei

$$\mathbf{F}_i = -\nabla_{\mathbf{R}_i} V(\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_N) = m_i \frac{d^2}{dt^2}\mathbf{R}_i$$

Molecular dynamics simulations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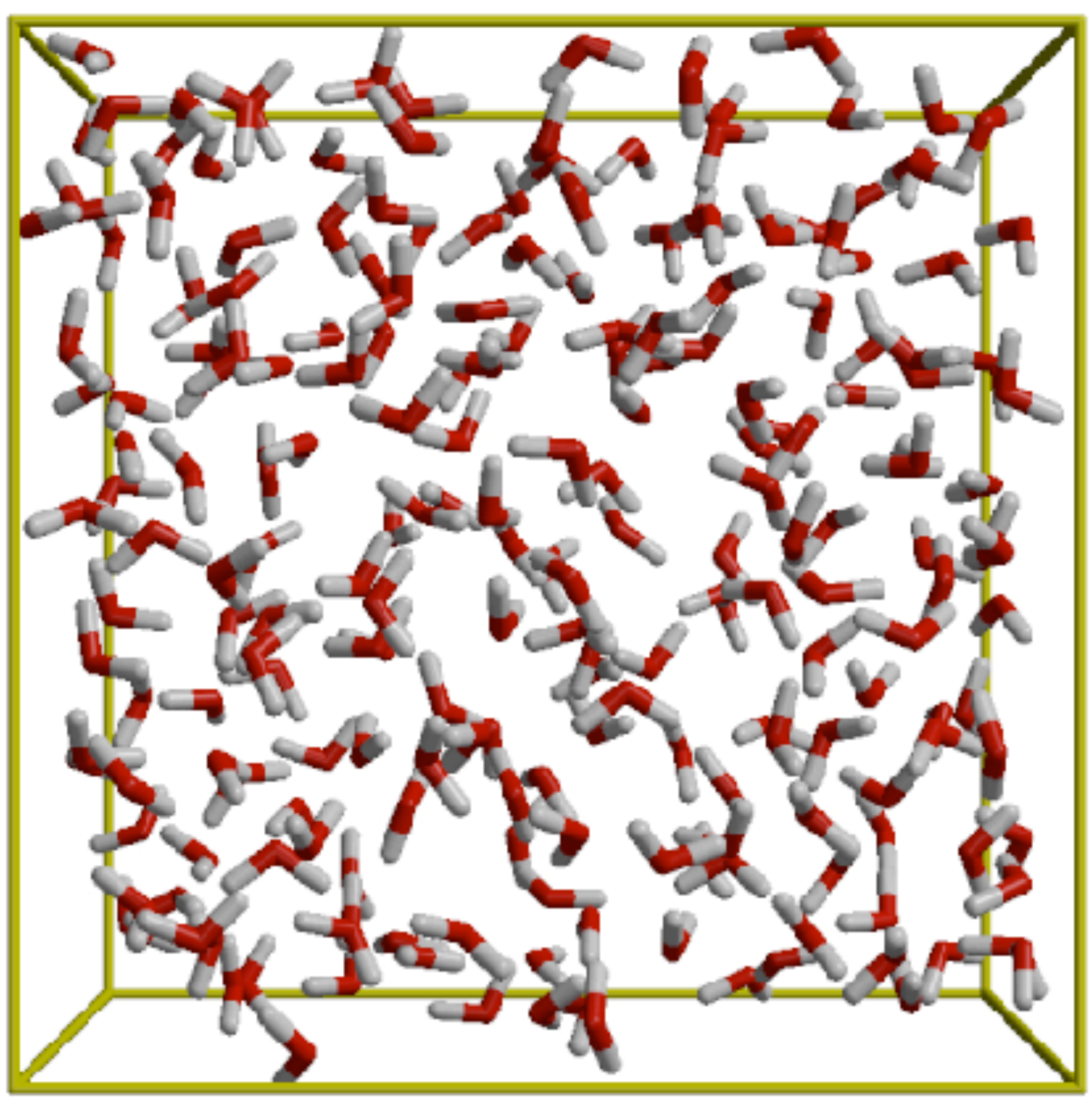
trajectory

jiggling & wiggling



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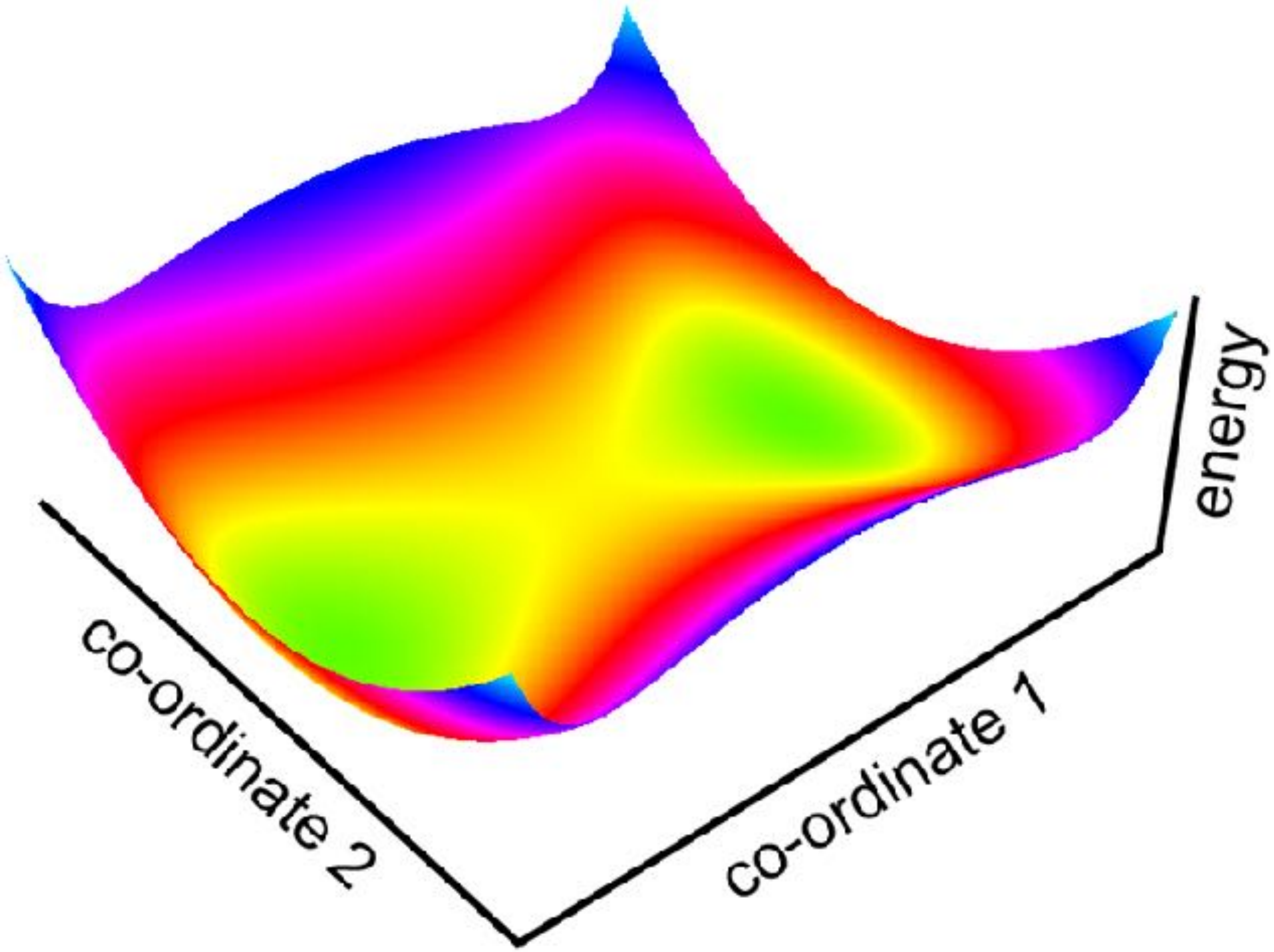
potential energy surface



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potential energy surface

quantum mechanics (QM)

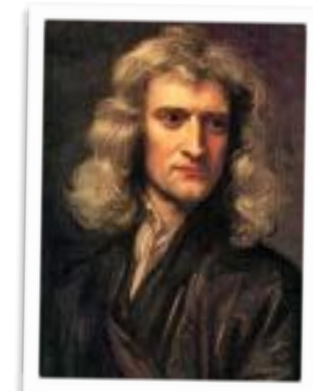
explicit electrons

$$V^{\mathrm{QM}}(\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_N) =$$


Erwin Schrödinger

$$\langle \Psi_e(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_n) | \hat{H}_e(\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_N) | \Psi_e(\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_n) \rangle$$

Molecular dynamics simulations



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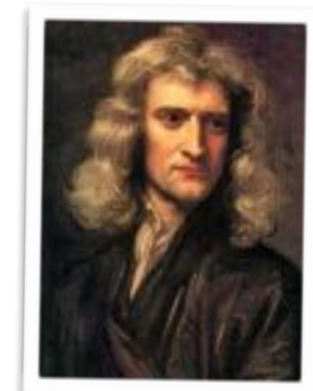
molecular mechanics (MM)

approximate the effect of electrons by empirical functions with parameters

$$V^{\mathrm{MM}}(R_1, R_2, ..., R_N) = \sum_k v_k(R_i, R_j, R_k, R_l; \{p_k\})$$

or combination of both

Molecular dynamics simulations



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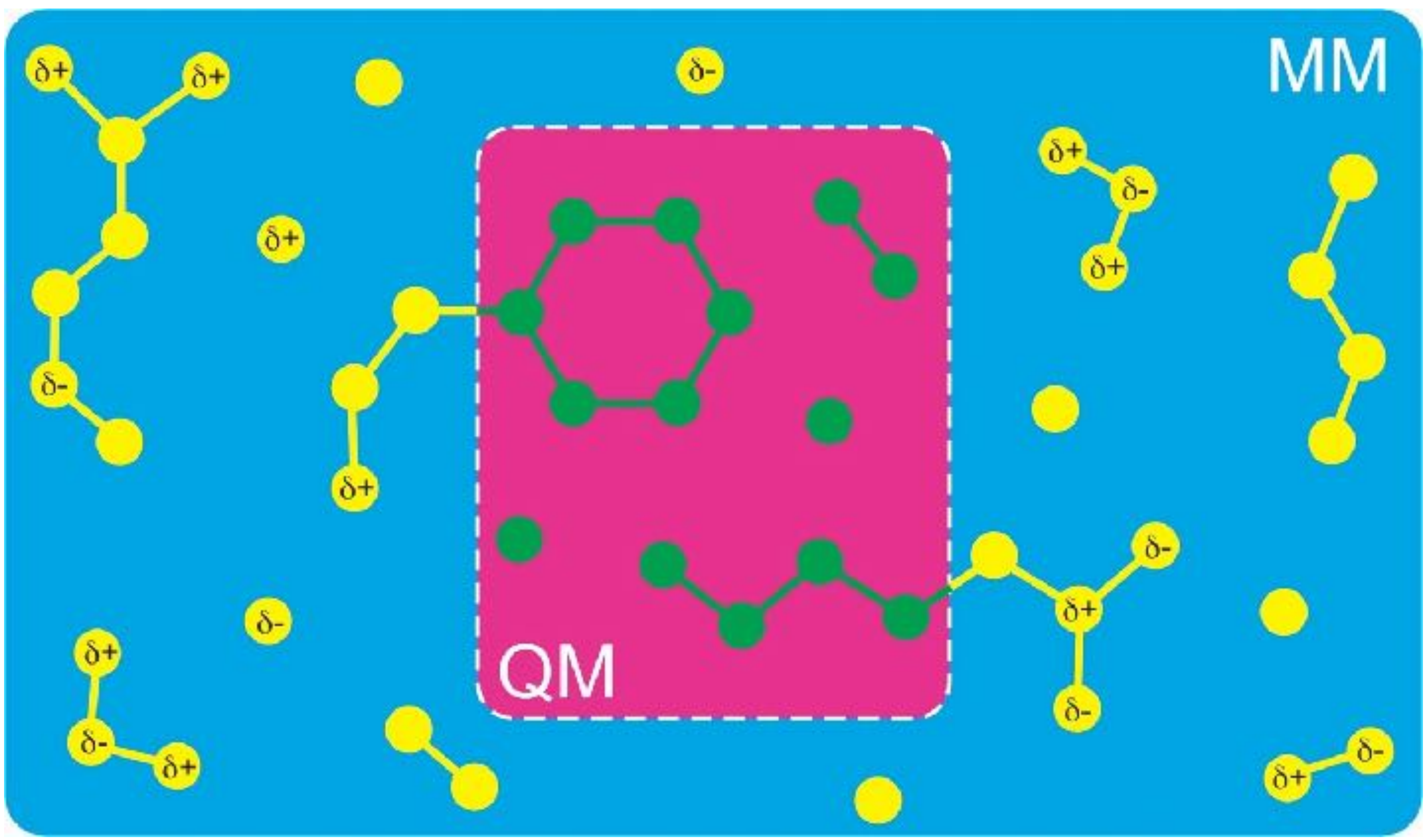
quantum mechanics/molecular mechanics (QM/MM)



Arieh Warshel

Michael Levitt

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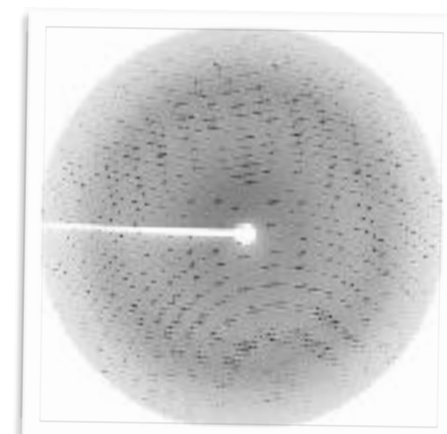
- time resolution: femtoseconds(10^{-15} s) ✓
- fs time & Å spacial resolution ✗



x-ray crystallography

transient spectroscopy

What can we do instead?

molecular dynamics computer simulations

- time resolution: femtoseconds ✓
- spacial resolution: Å (10^{-10} m) ✓
- accuracy? ⚠

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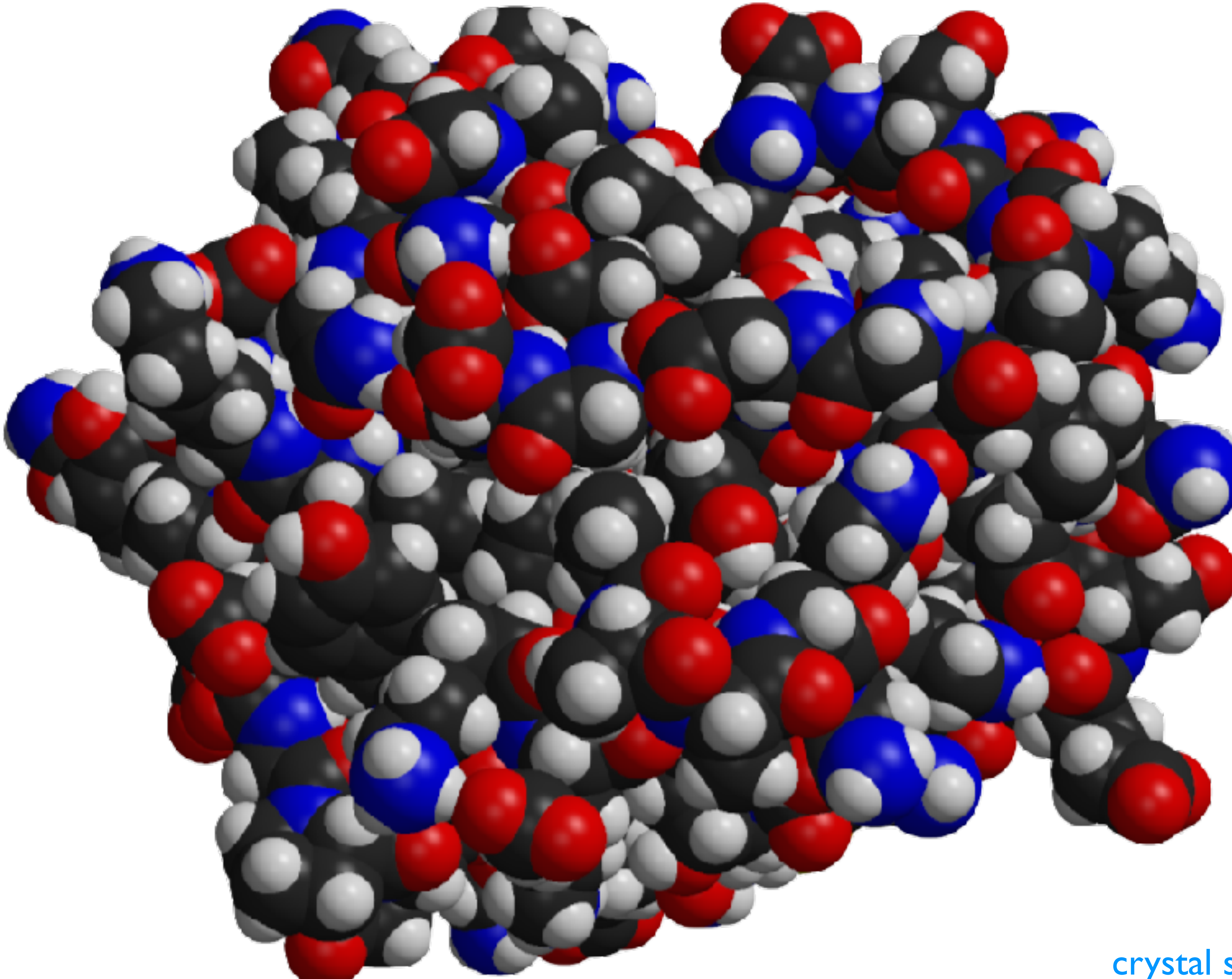
Observe while it happens until 2015

MD simulation of photoactive yellow protein



crystal structure: 2PHY

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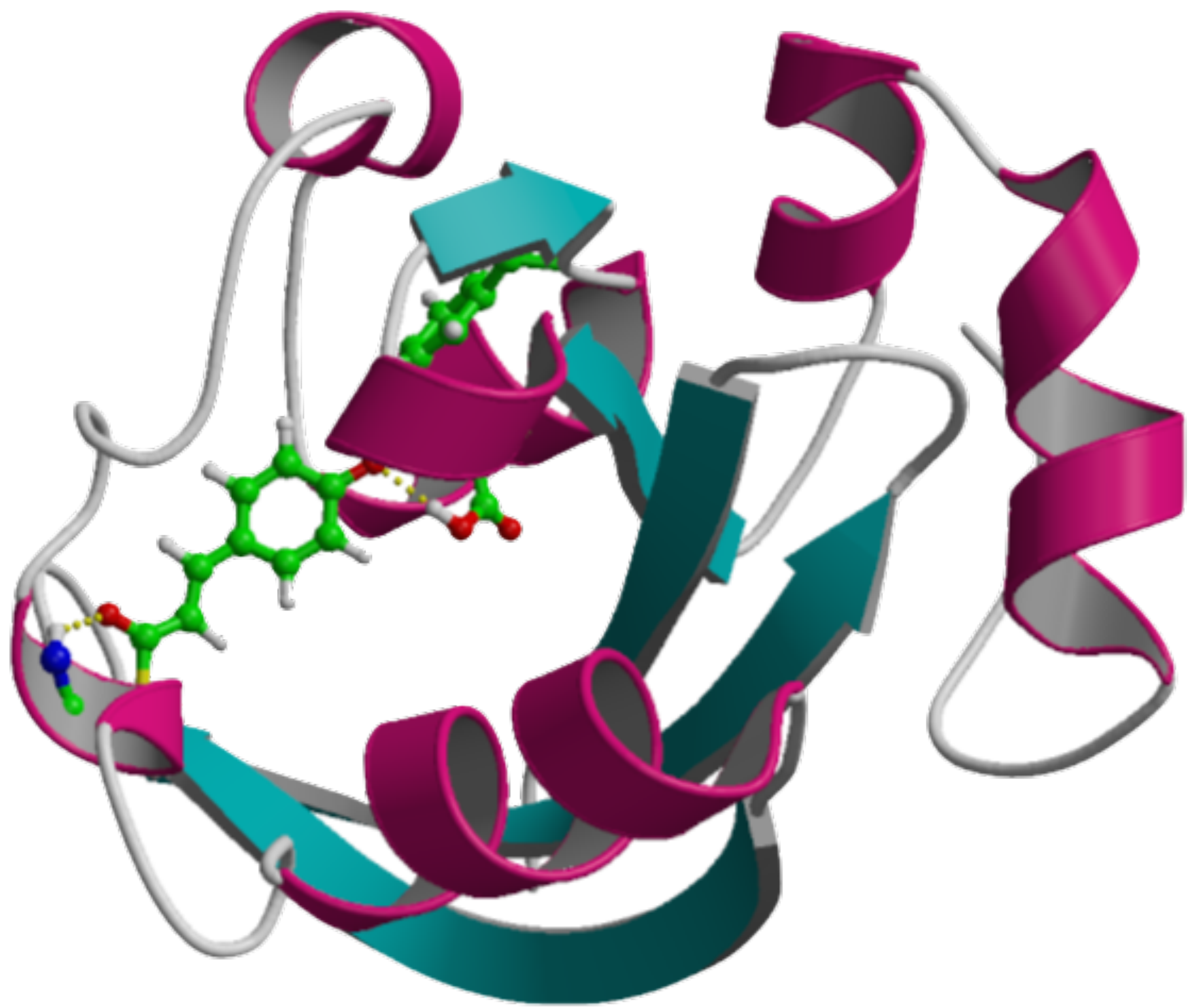

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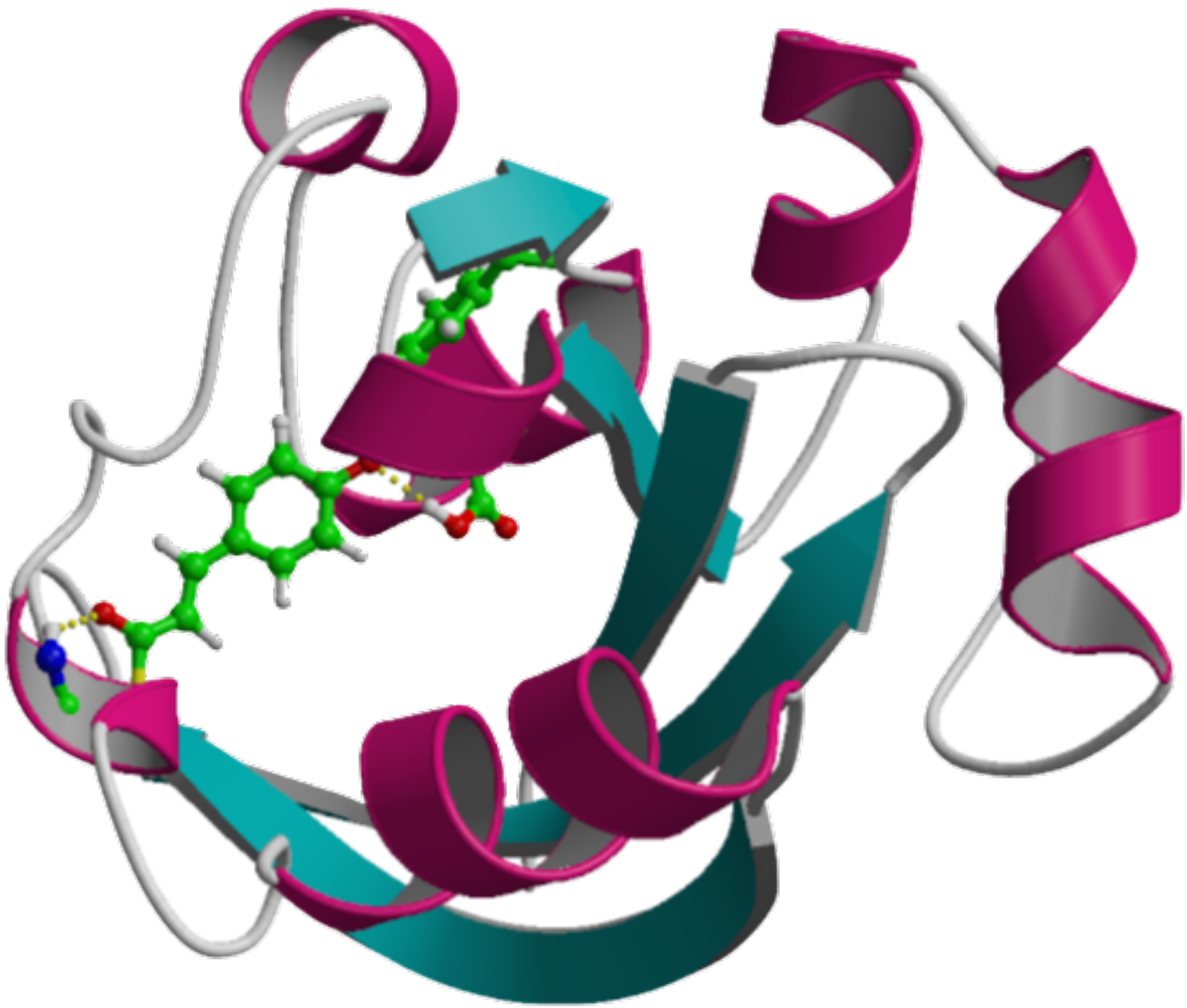
photoreceptor ("eye") in *halorhodospira halophila*

detect and respond to blue light



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K. J. Hellingwerf *et al.*, *J. Phys Chem. A* **107** (2003) 1082-1094

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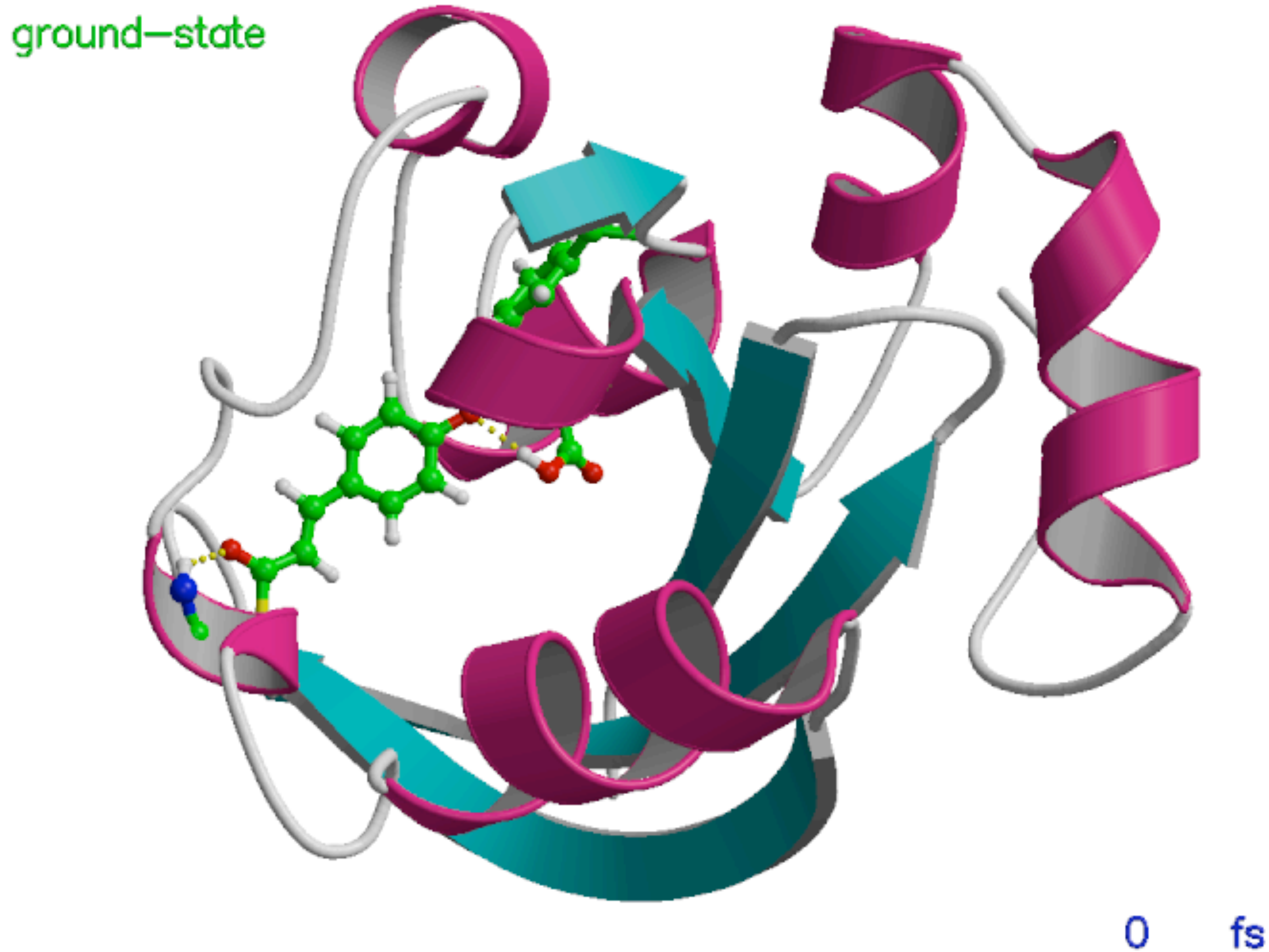
all atom simulation of photoactive yellow protein



G. Groenhof *et al.*, *JACS* **126** (2004) 4228-4232

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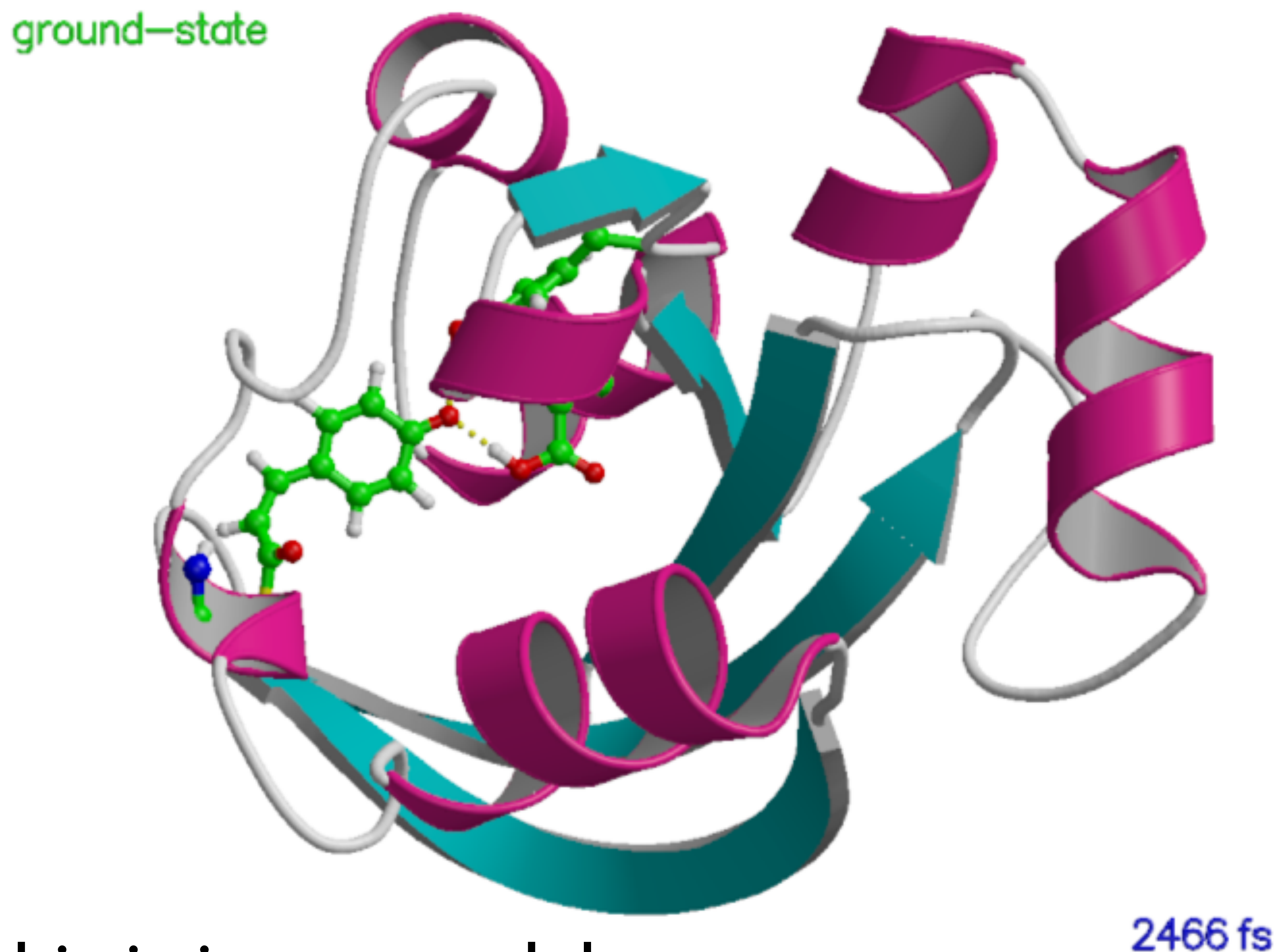


but hey, this is just a model…

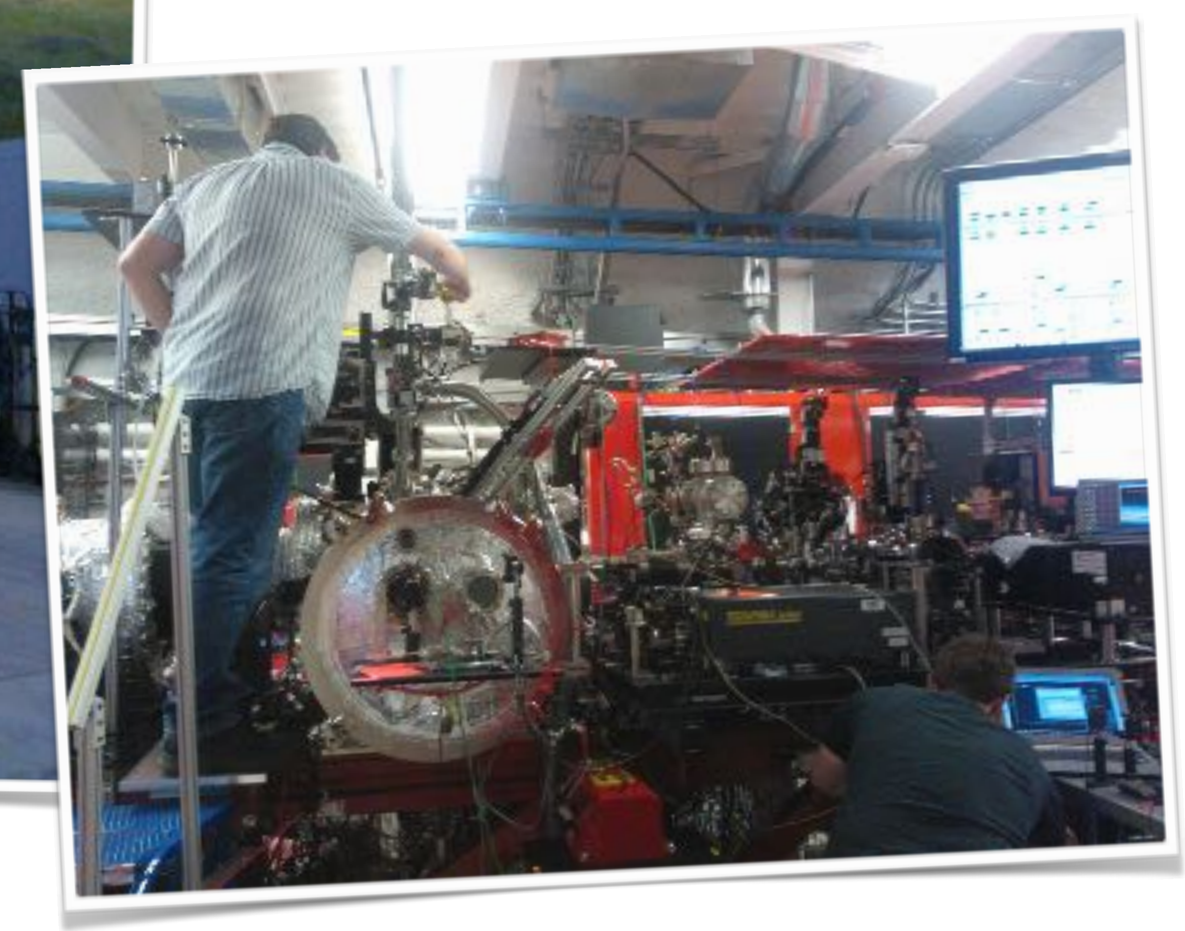
difficult to verify validity, until now

Femtosecond time-resolved x-ray diffraction

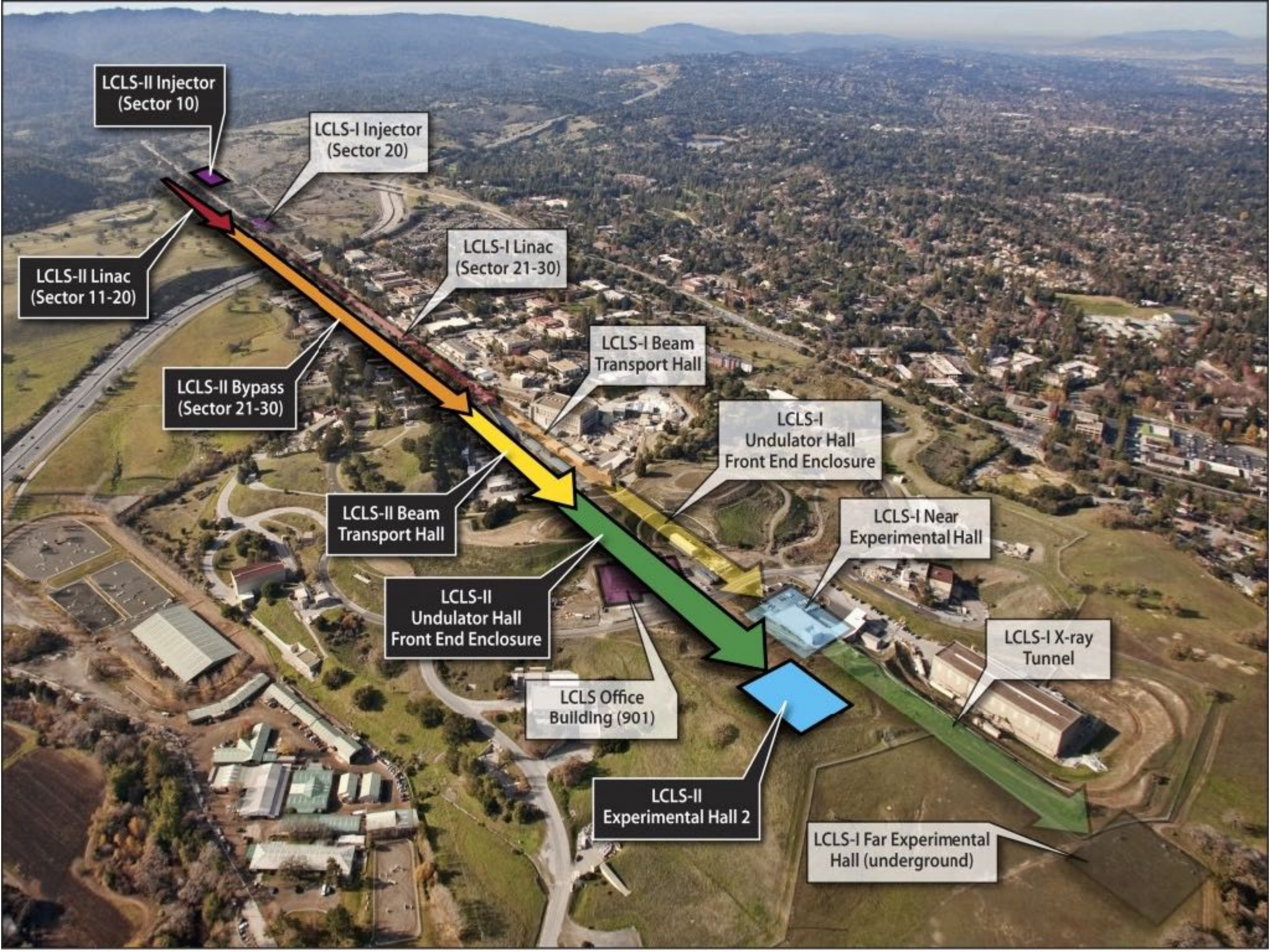
free electron lasers

Linear Coherent Light Source in Stanford

Coherent X-ray Imaging (CXI)

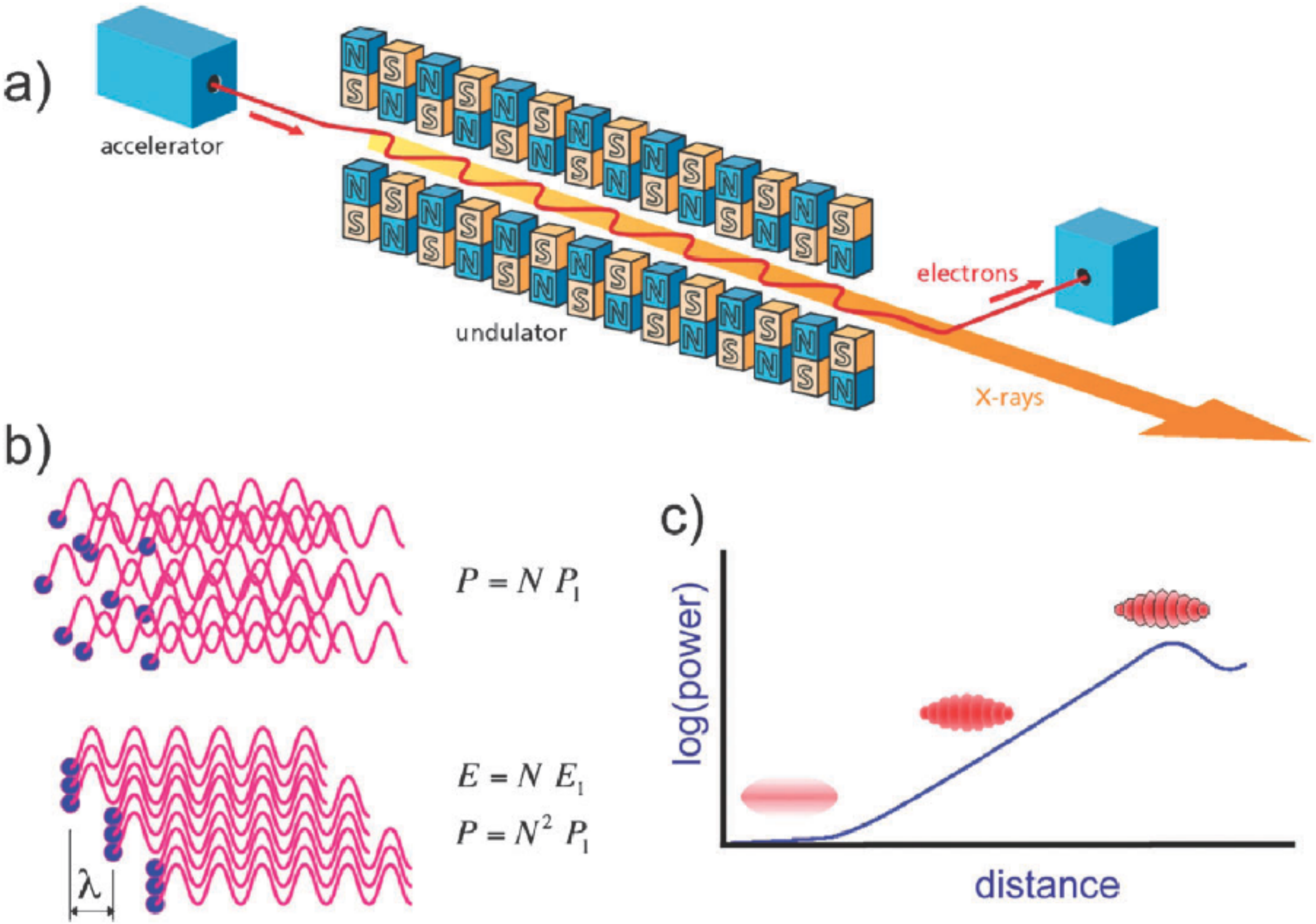


P. Emma *et al.*, *Nature Photonics* **4** (2010) 641-647



LCLS-II Injector (Sector 10)
LCLS-I Injector (Sector 20)
LCLS-II Linac (Sector 11-20)
LCLS-I Linac (Sector 21-30)
LCLS-II Bypass (Sector 21-30)
LCLS-I Beam Transport Hall
LCLS-I Undulator Hall Front End Enclosure
LCLS-II Beam Transport Hall
LCLS-I Near Experimental Hall
LCLS-II Undulator Hall Front End Enclosure
LCLS-I X-ray Tunnel
LCLS Office Building (901)
LCLS-II Experimental Hall 2
LCLS-I Far Experimental Hall (underground)

Free electron laser



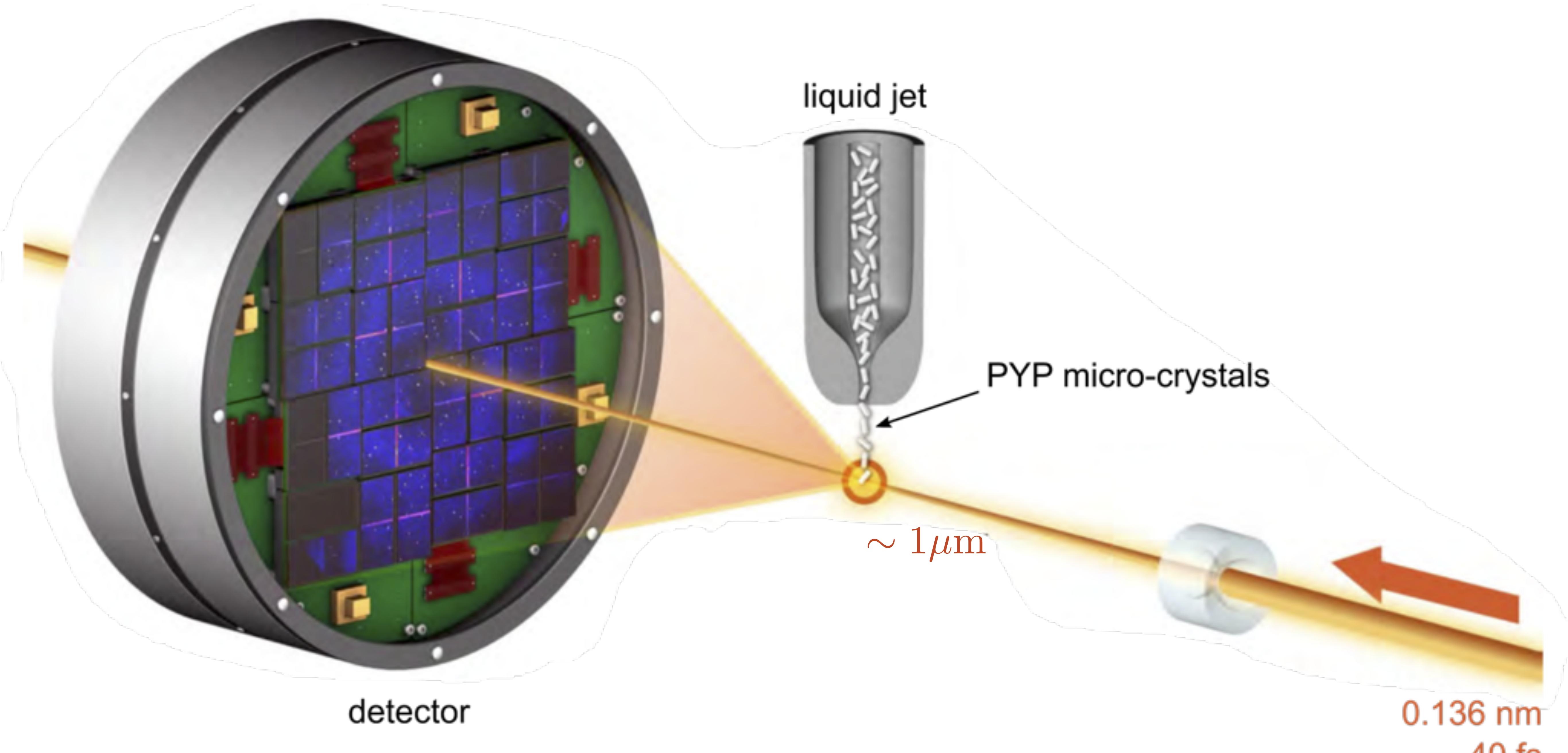
B. D. Patterson & R. Abela, *PCCP* **12** (2010) 5647-5652

Serial femtosecond x-ray crystallography

diffract and destroy

outrun radiation damage

nano crystals



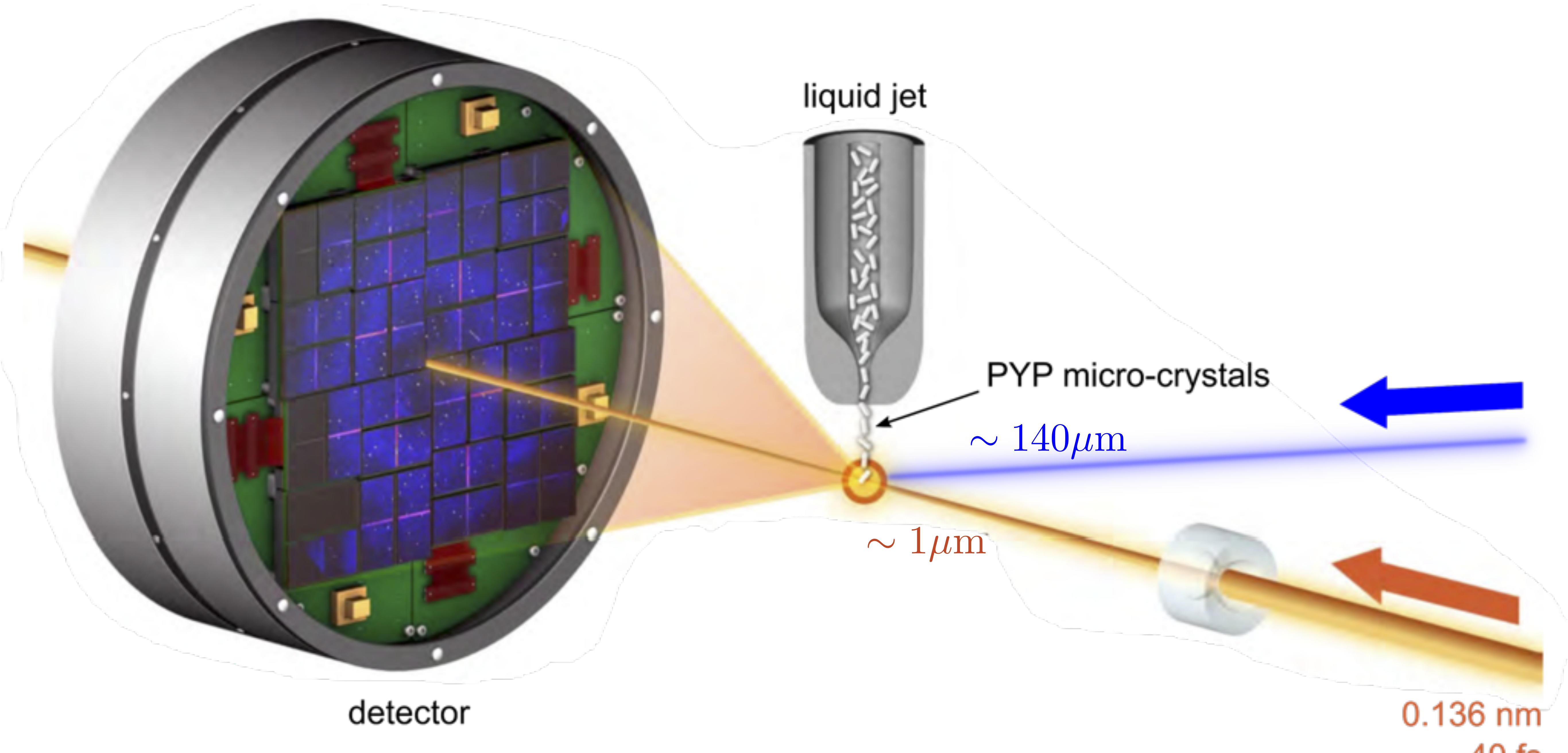
H. N. Chapman *et al.*, *Nature* **470** (2011) 73-77

Serial femtosecond x-ray crystallography

diffract and destroy

time-resolved: pump-probe

synchronization: timing tool



M. Harmand *et al.*, *Nature Photonics* **7** (2013) 215-218

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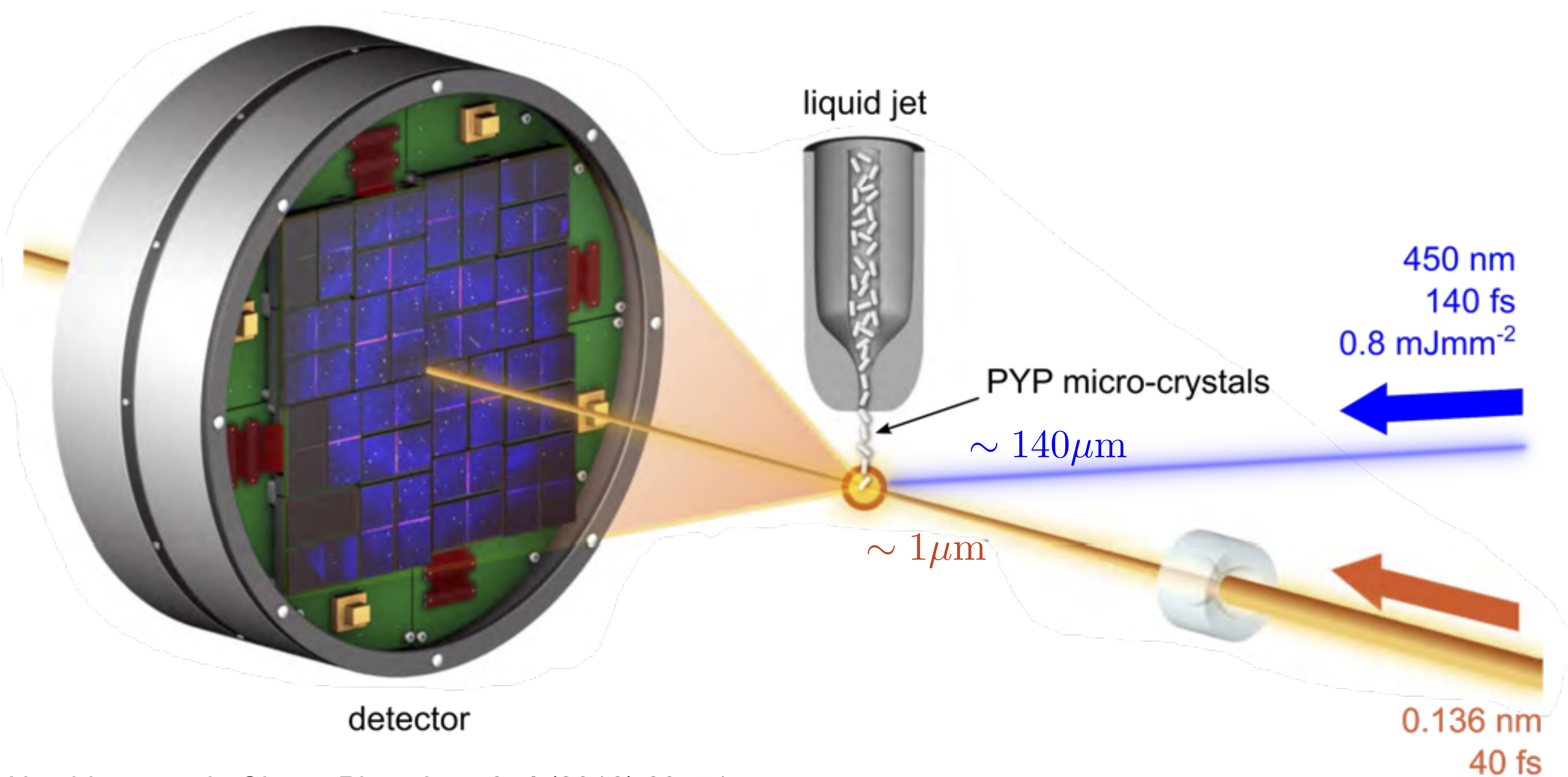

Hutchison *et al.*, *Chem. Phys. Lett*. **654** (2016) 63–71

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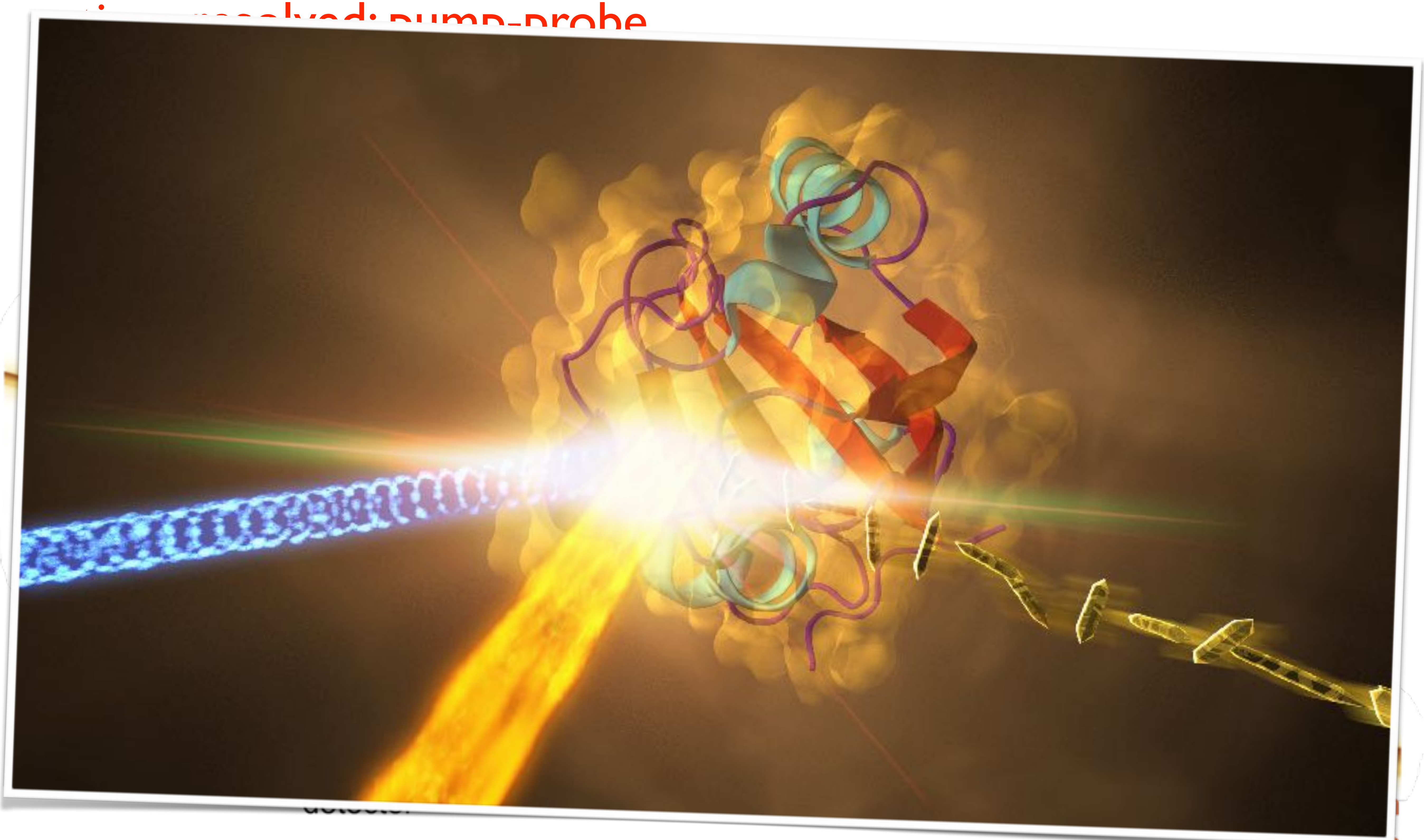
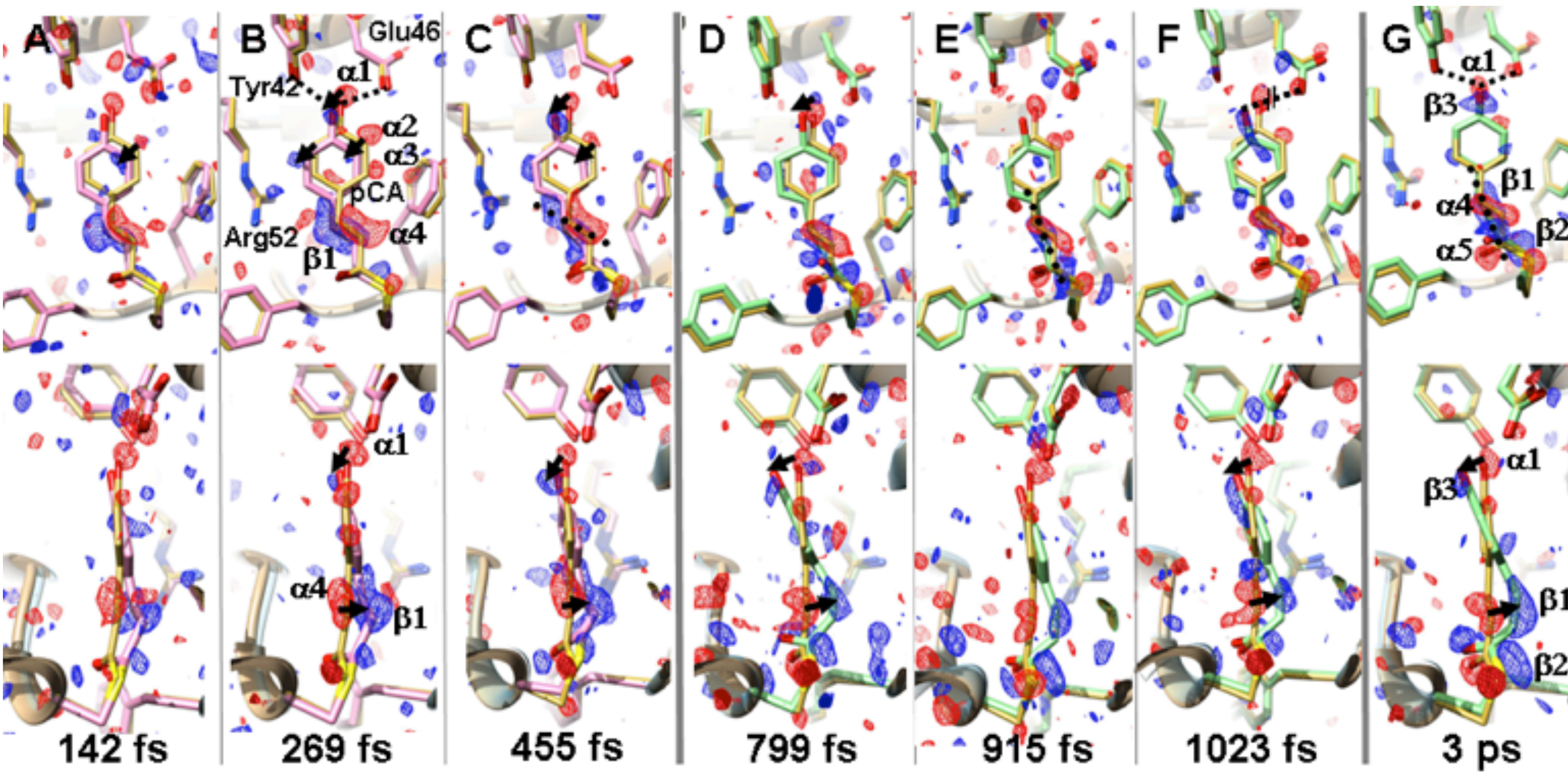


Serial femtosecond x-ray crystallography

indexing, timing tool sorting, merging & refinement

seven difference density maps from 100 femto- to 3 picosecond



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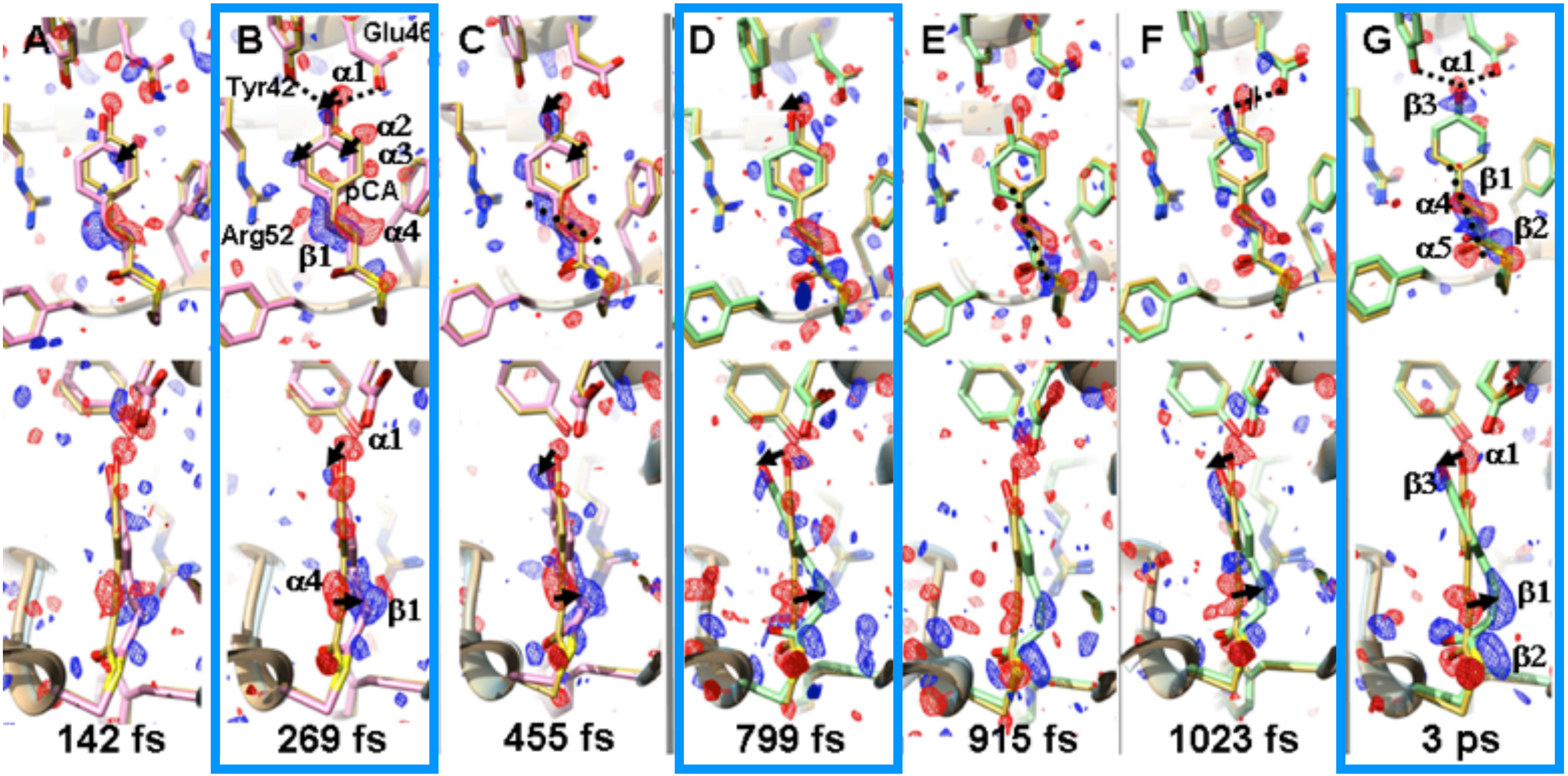

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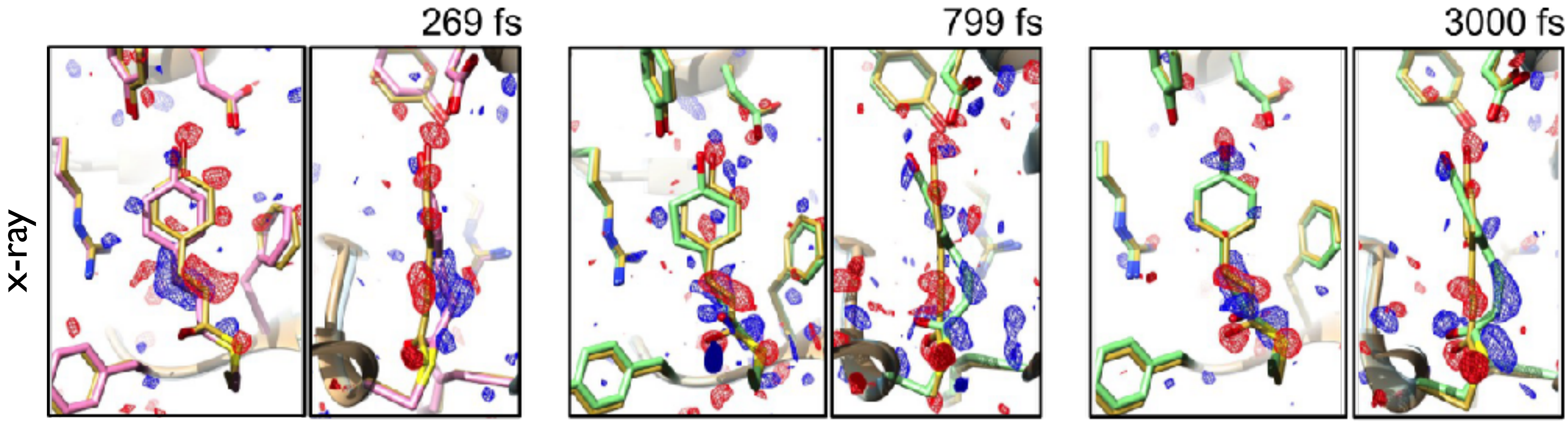

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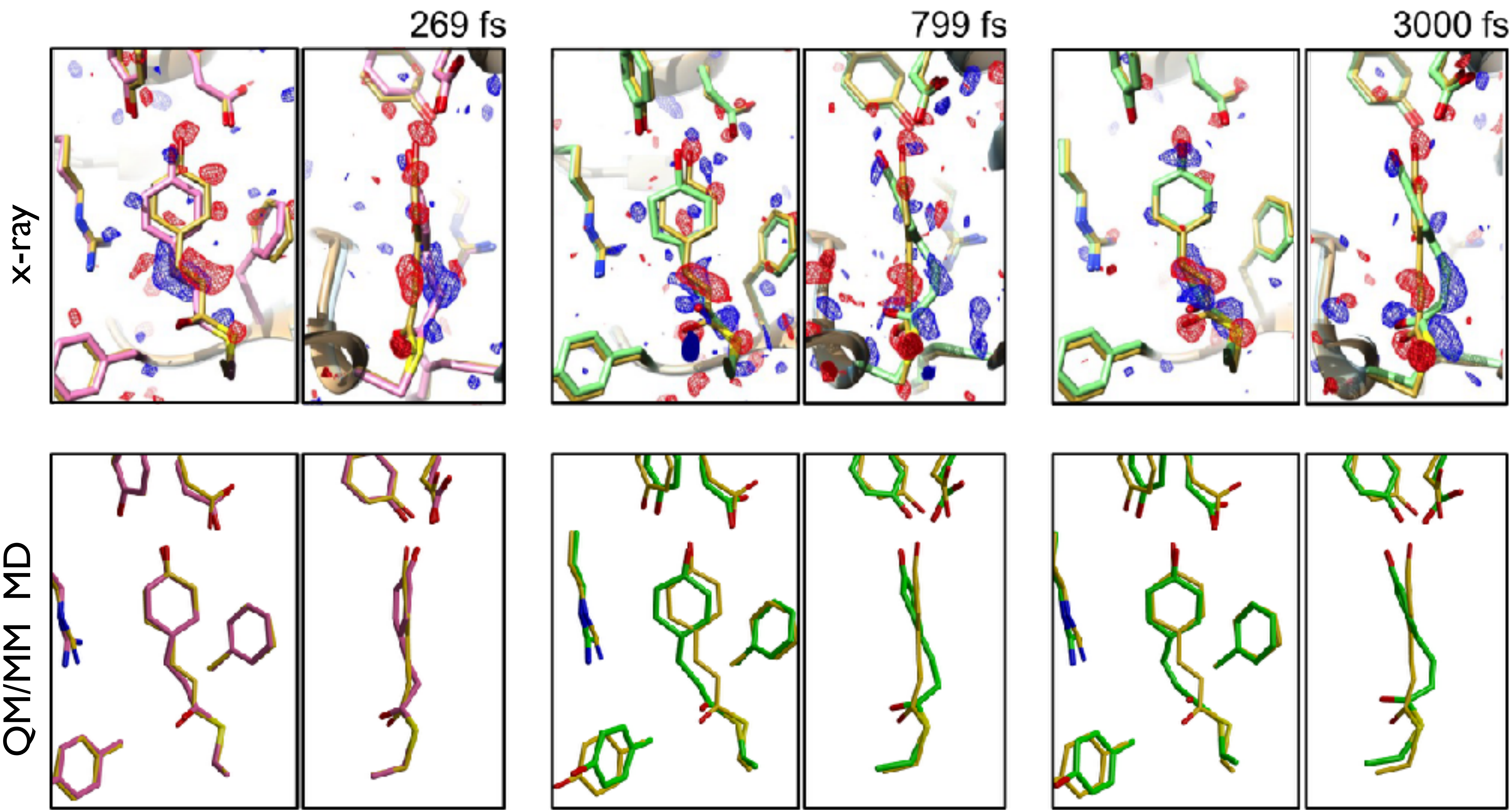


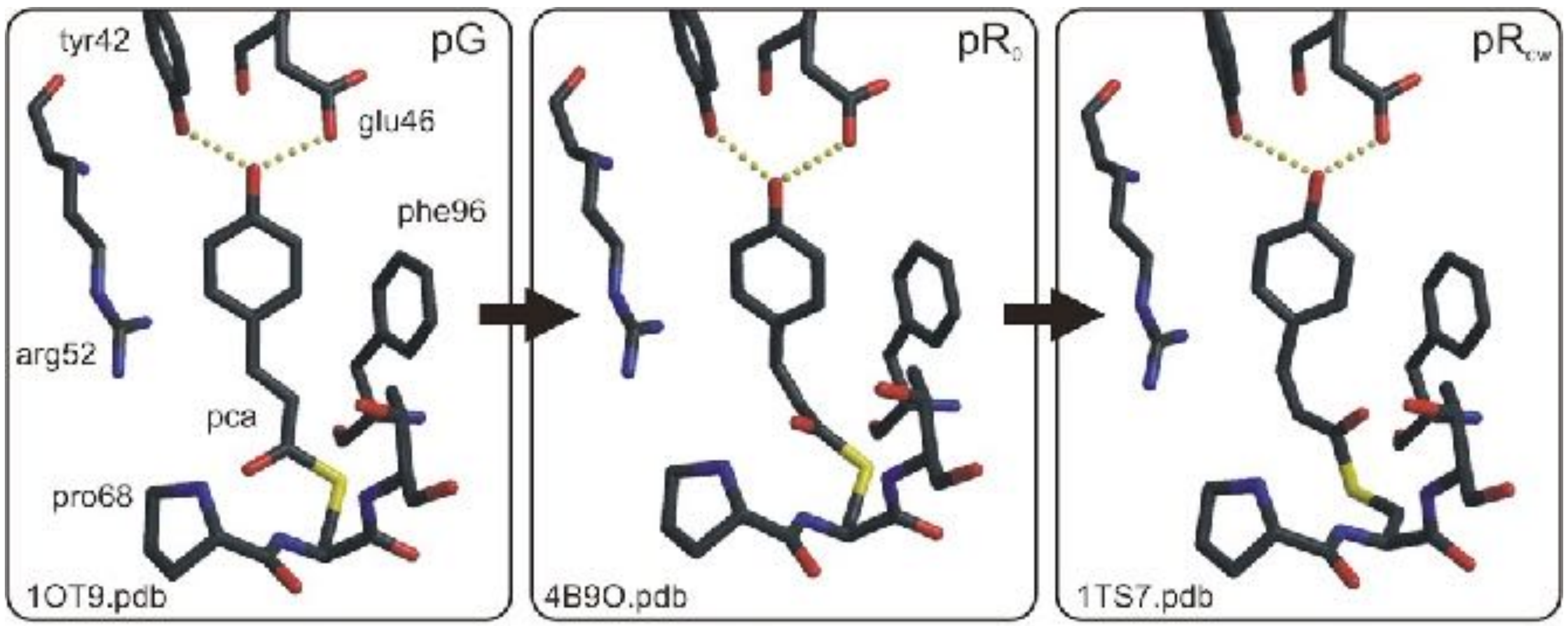
Pande, Hutchison, Groenhof *et* very many *al*., *Science* **352** (2016) 725-729

From picosecond to nanoscecond

previous x-ray diffraction studies @ synchrotrons

100 ps

1 ns



Schotte et al.

PNAS **107** (2012) 76

Ihee et al.

PNAS **102** (2005) 7145

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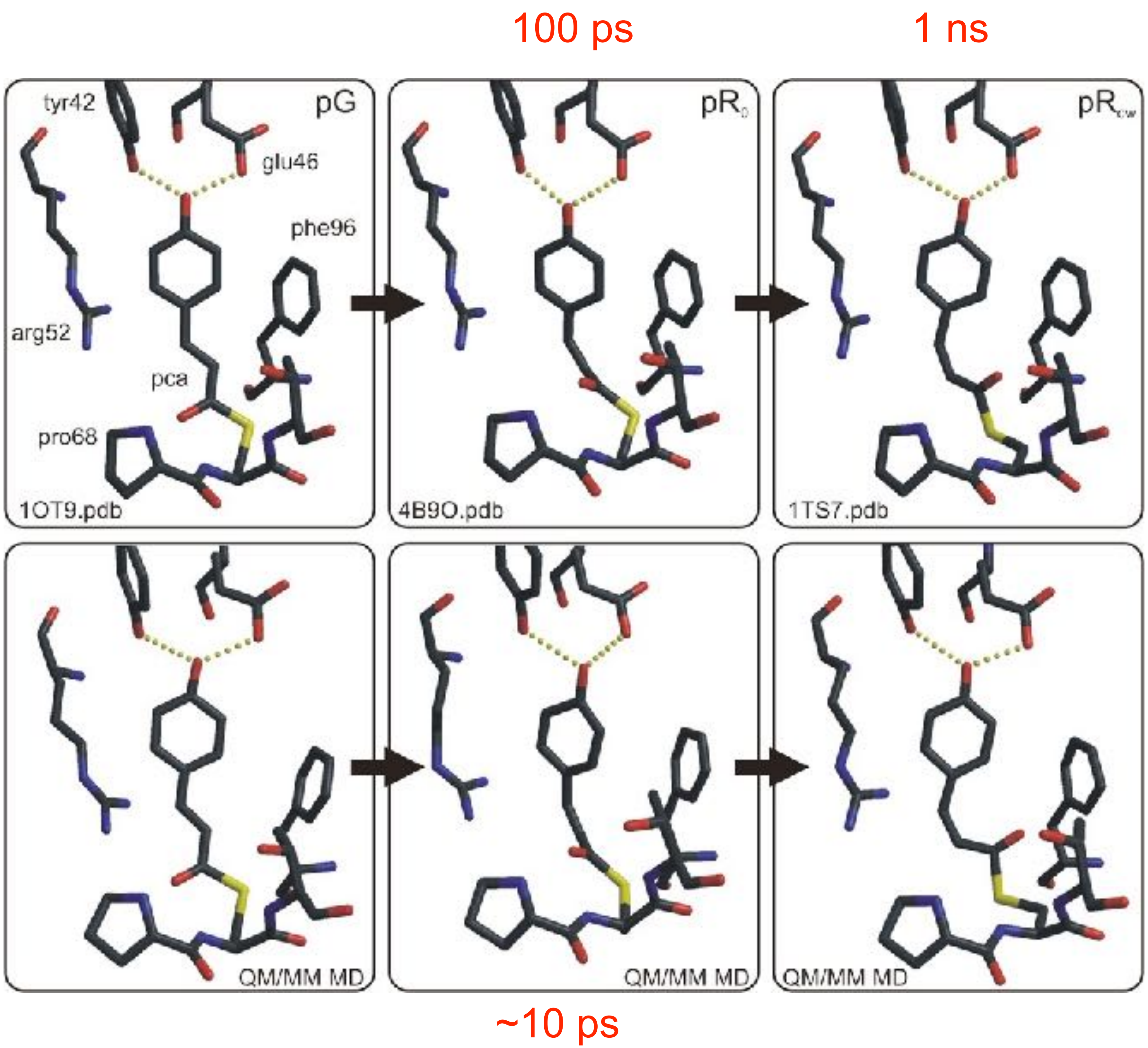

Schotte et al.

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CAS(10,9)/6-31G*/Amber03

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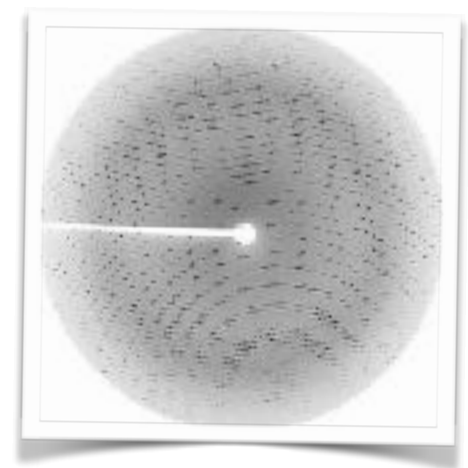
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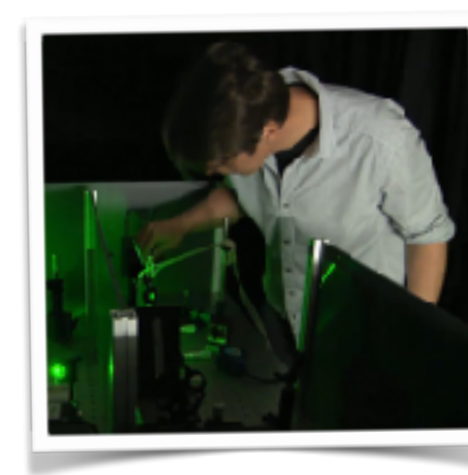
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time resolution: femtoseconds

spacial resolution: Å (10^{-10} m)

accuracy?


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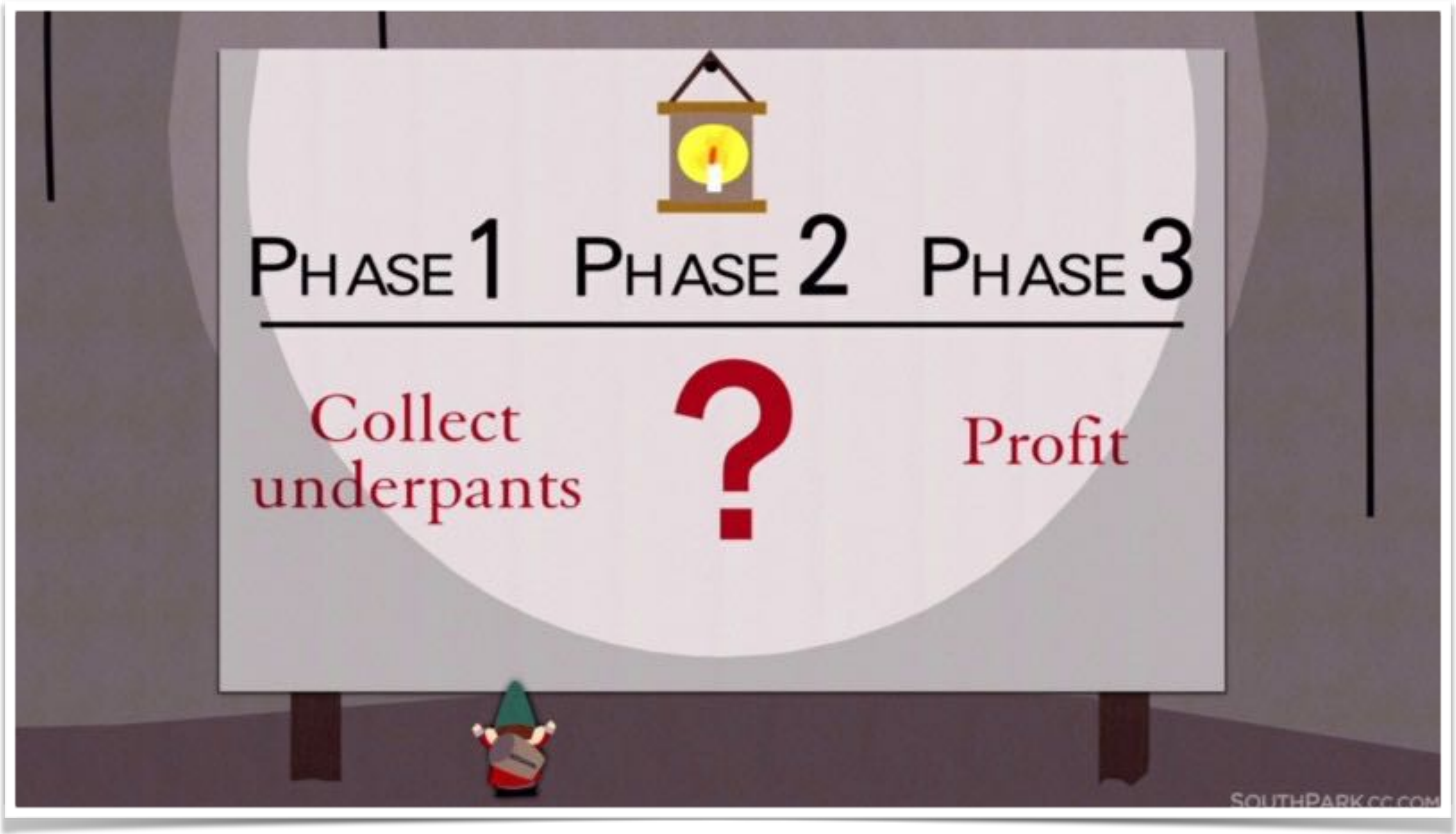
The bigger picture $$$

South Park's Underpants Gnomes' Profit Plan



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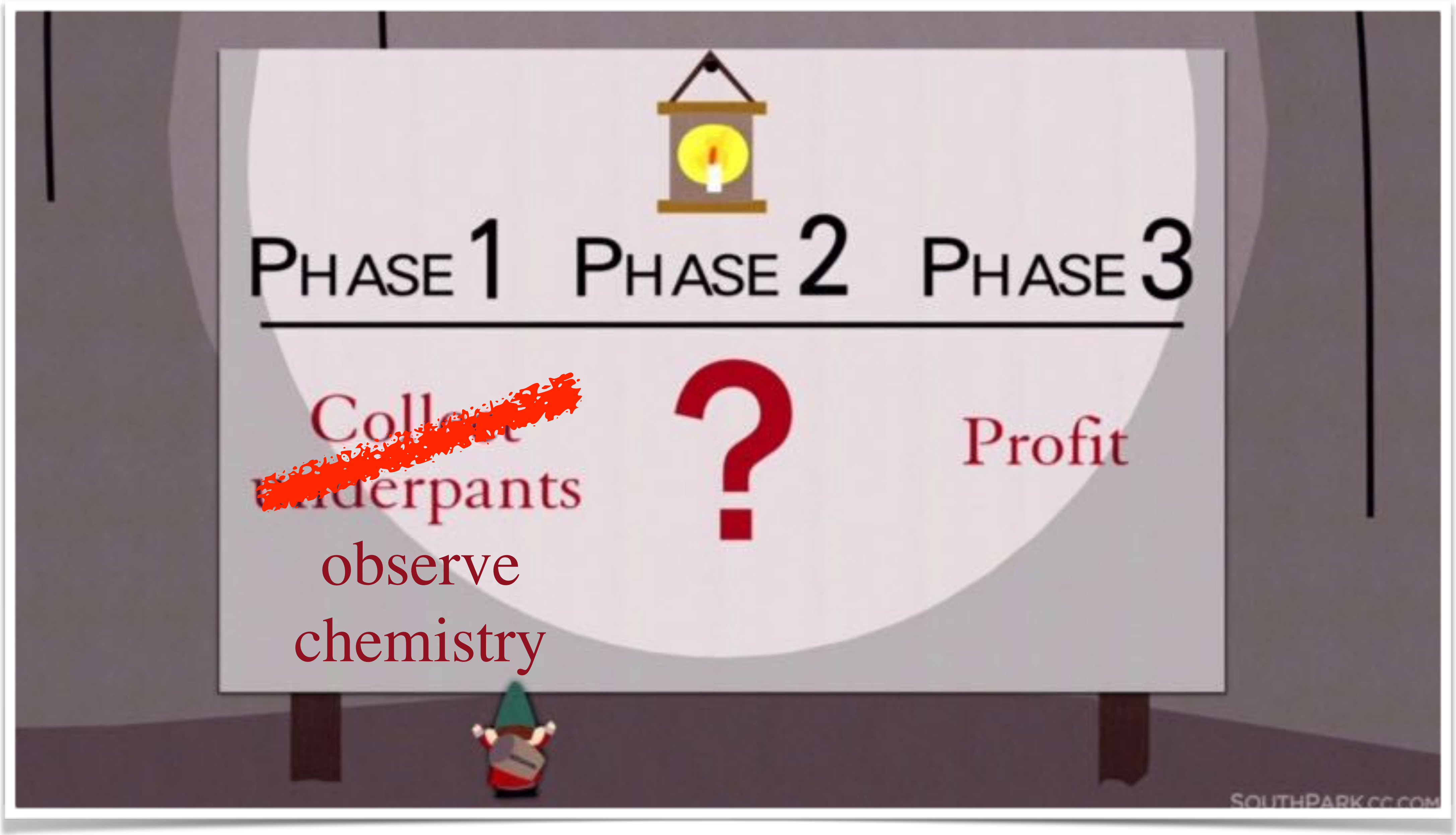

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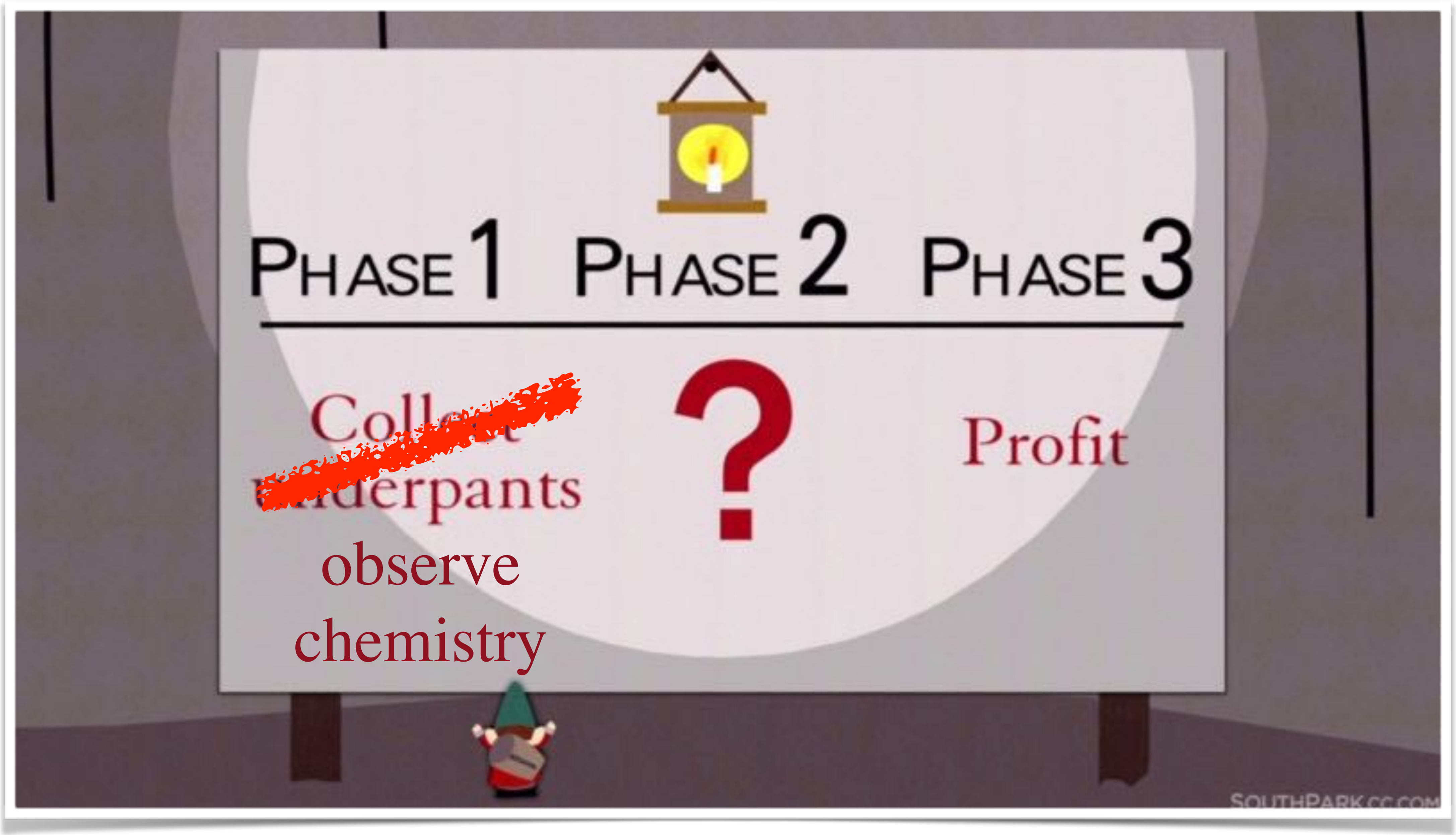


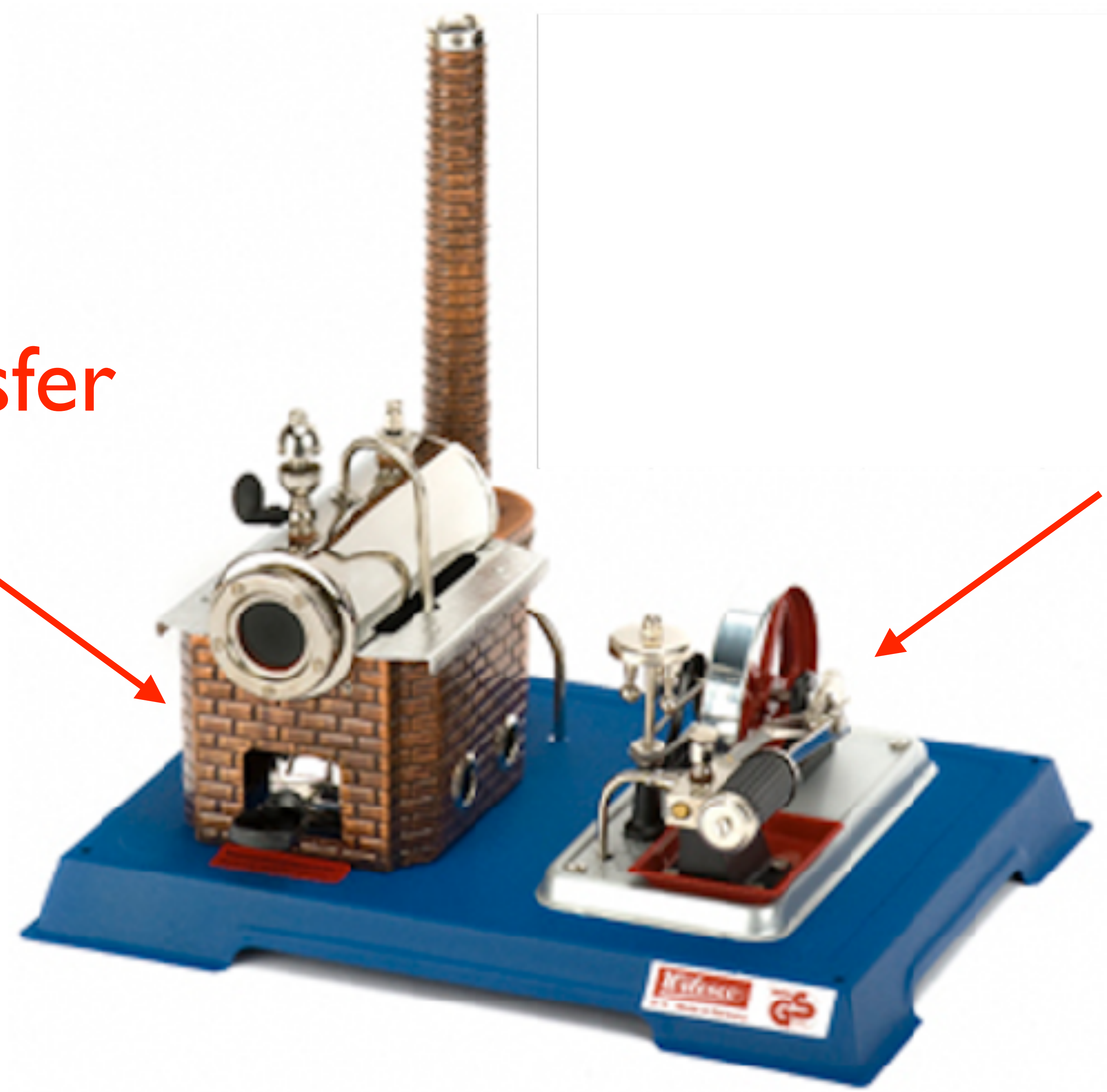
our Phase 2 strategy

manipulate chemistry

Our ultimate goal

light-fuelled artificial molecular machines

energy transfer



isomerization

Our ultimate goal

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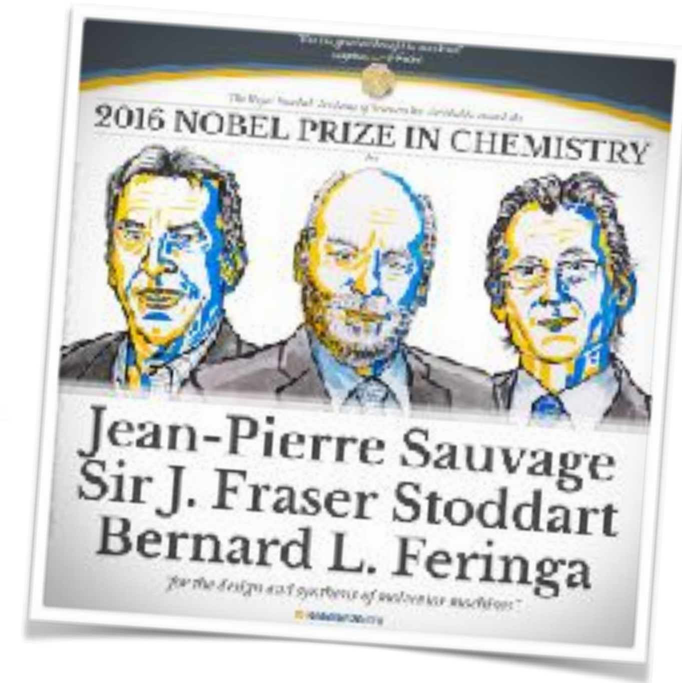

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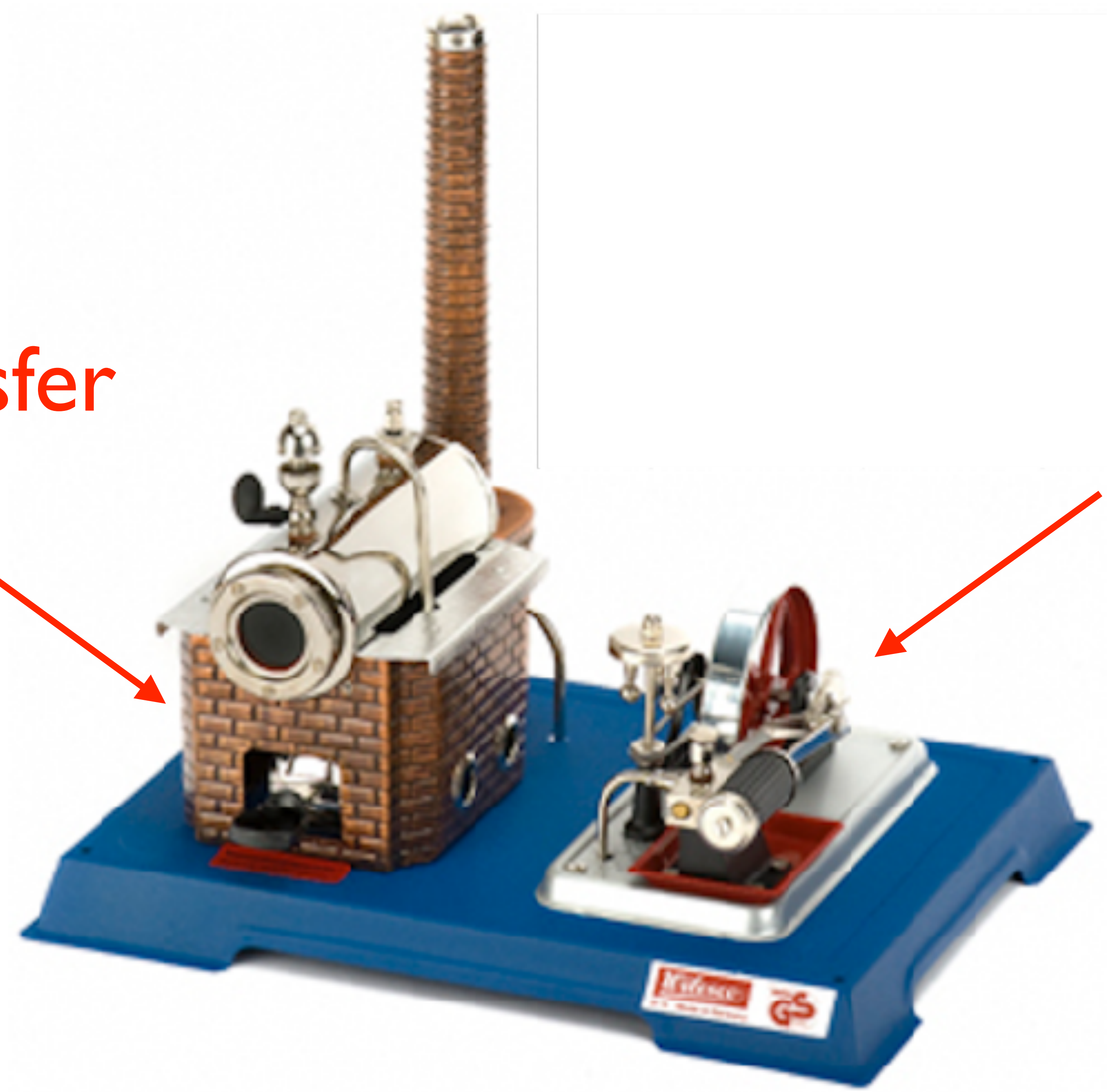

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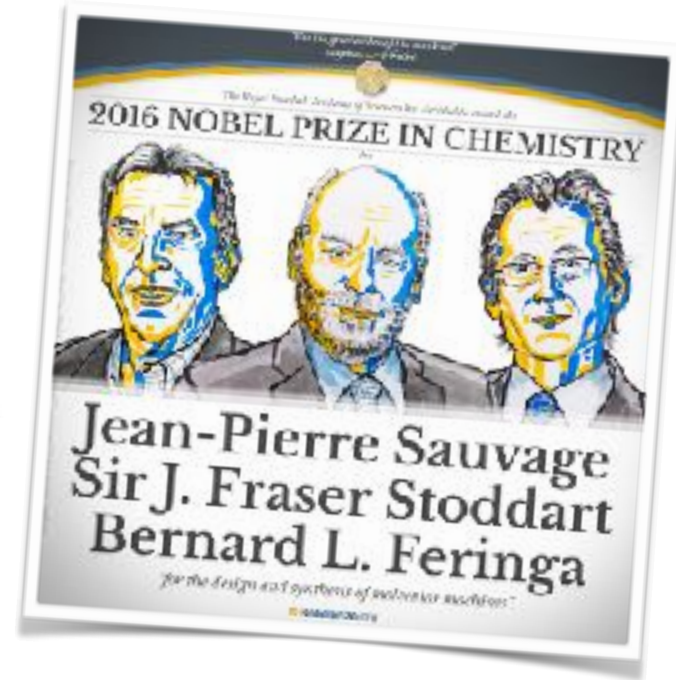
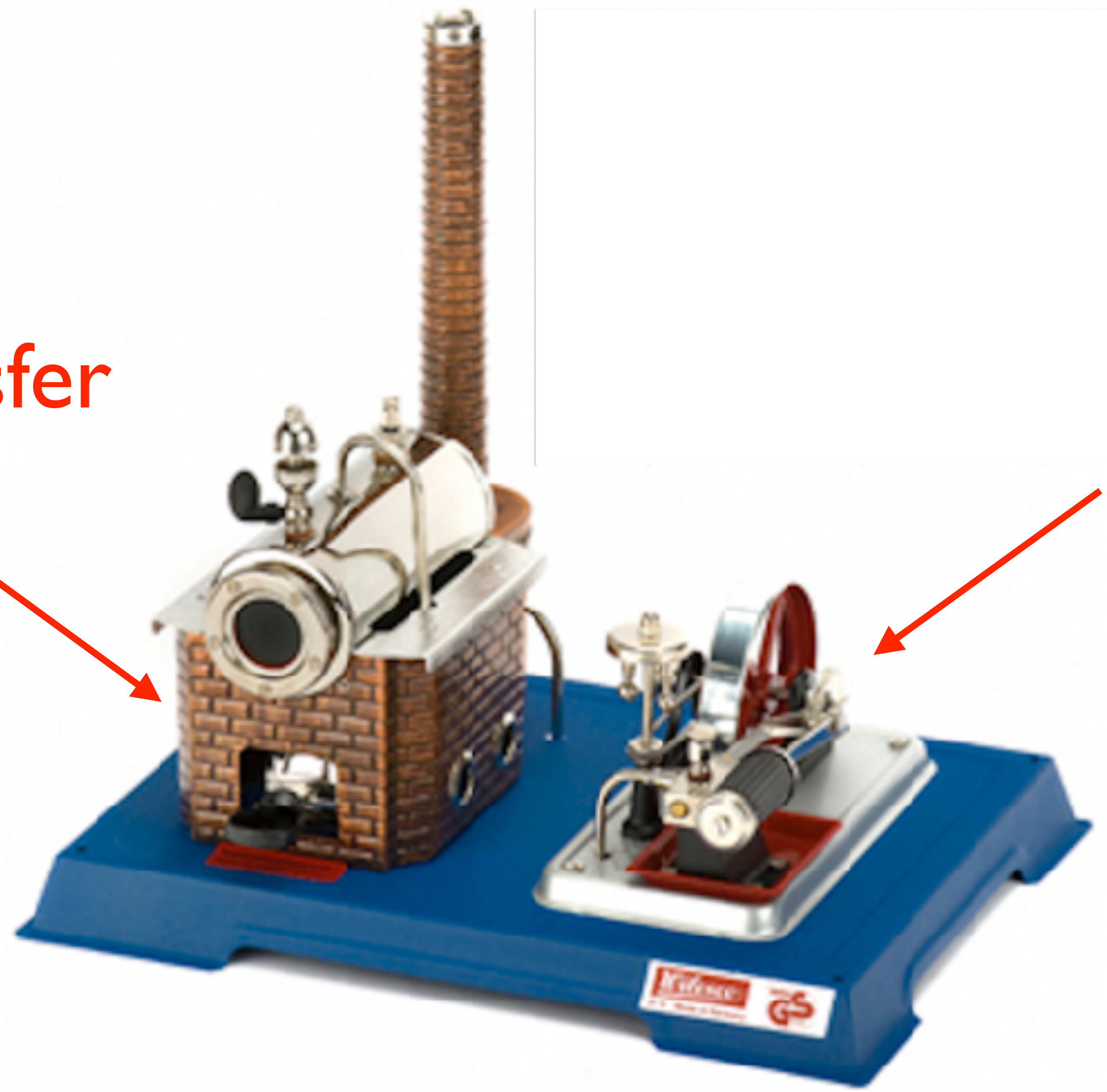


energy transfer

isomerization



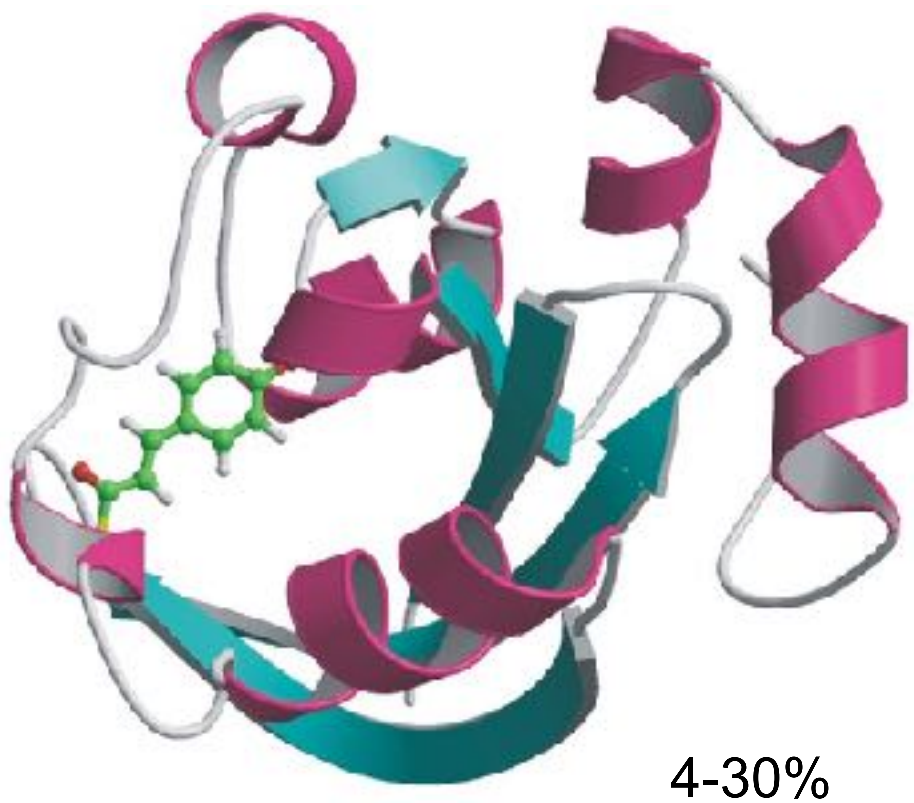
complete understanding of photochemistry required

control & design

Get inspired by nature

e.g. photo-isomerization in photoactive yellow protein

learn & mimic the effect of the protein environment



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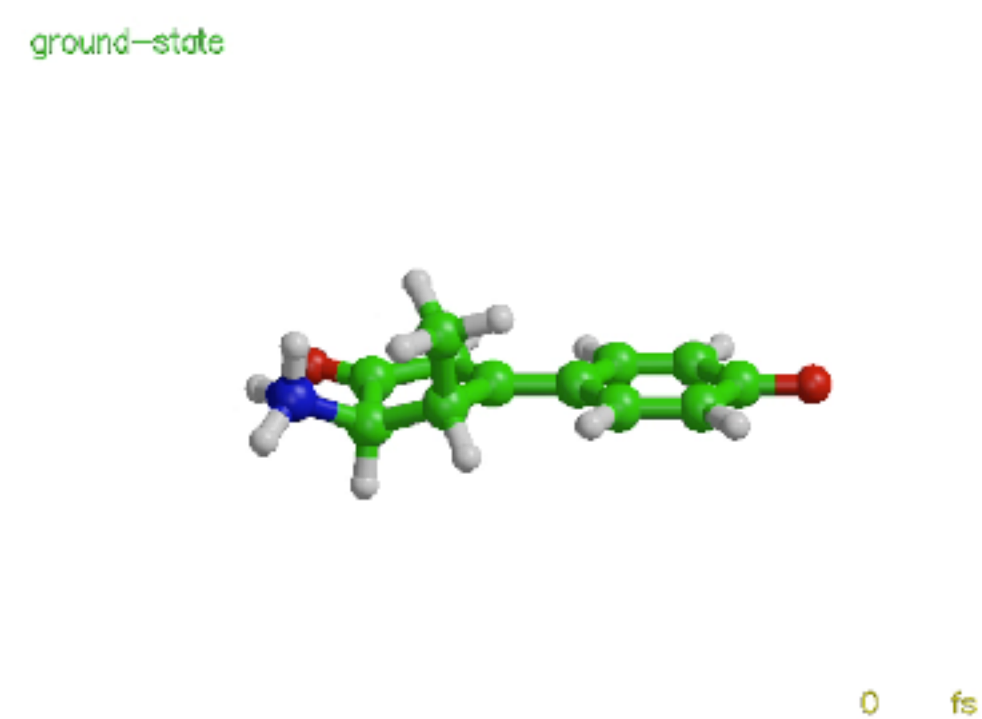

4-30%

~70%

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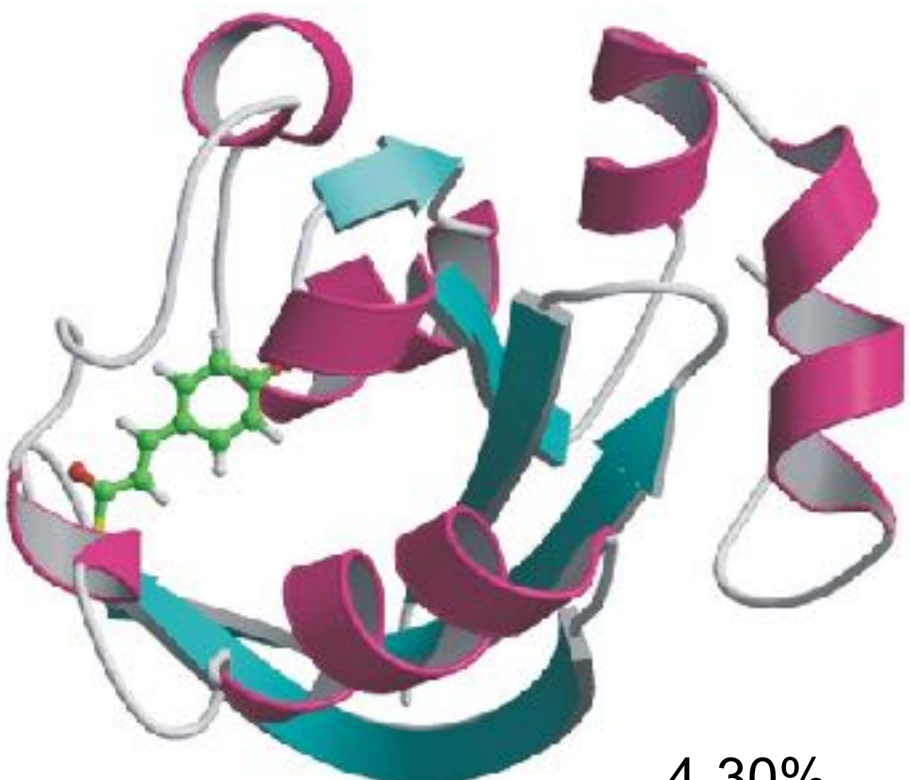

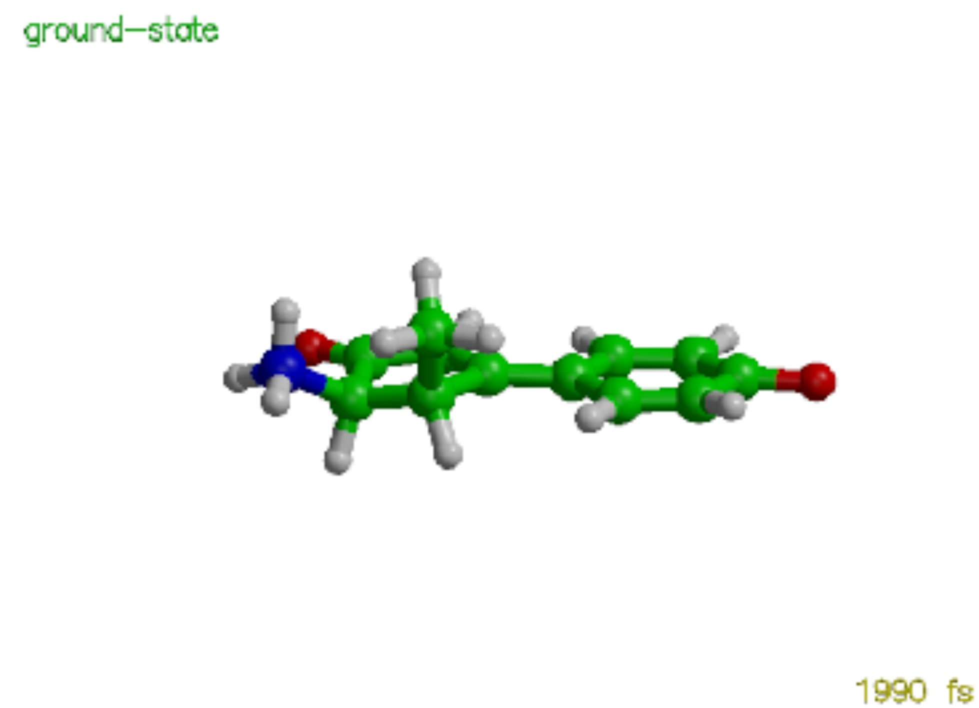

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seemed like a good idea at first, but ….

difficult to improve functionality

difficult to transfer functionality

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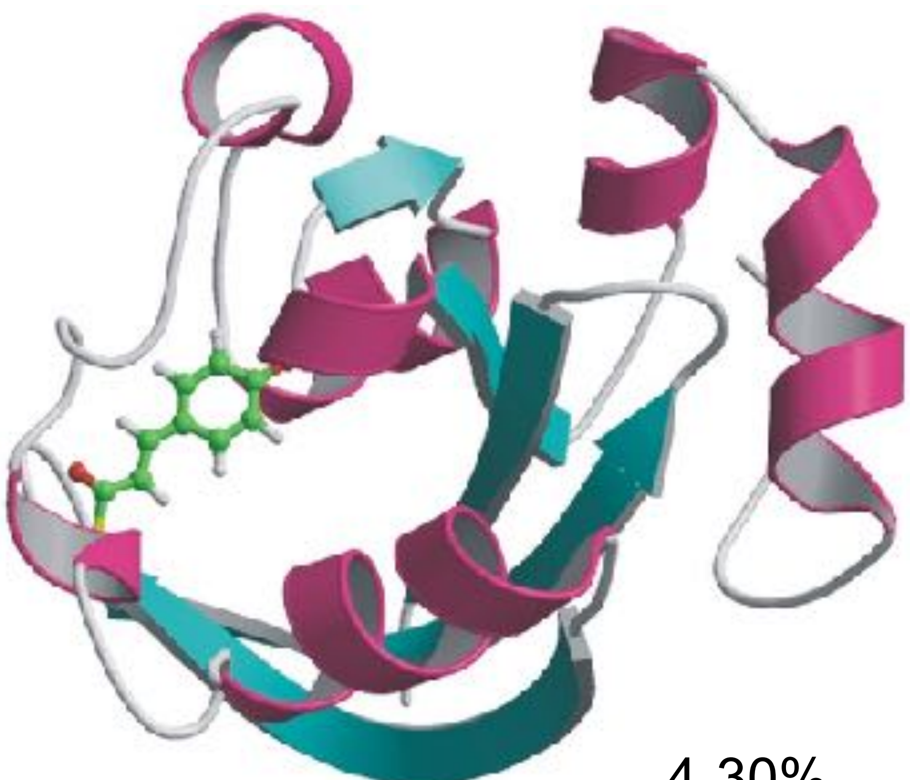

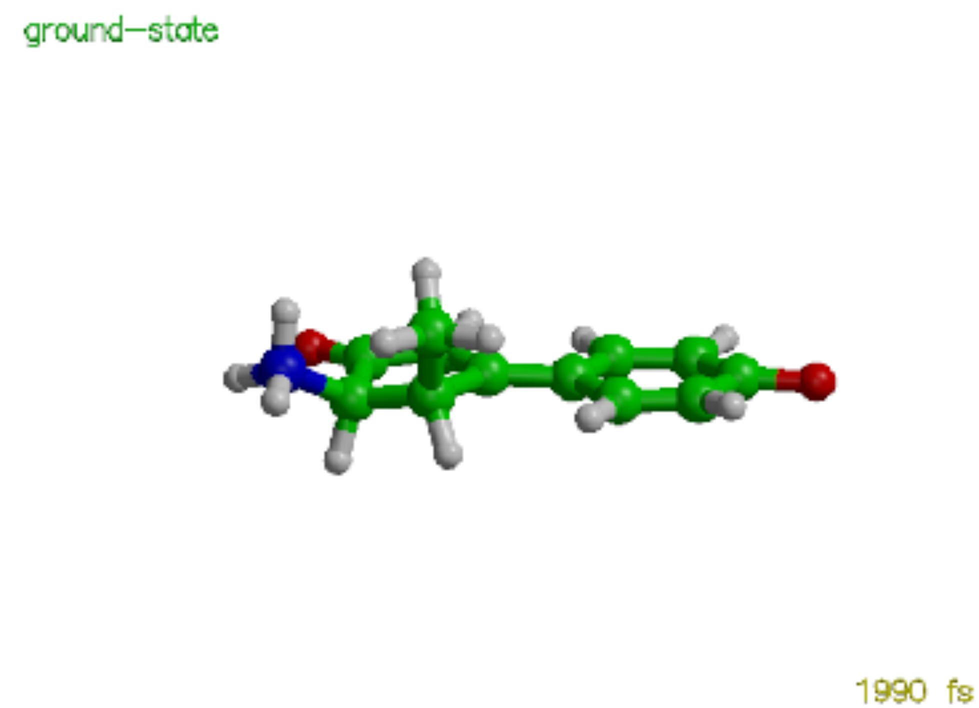

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~70%

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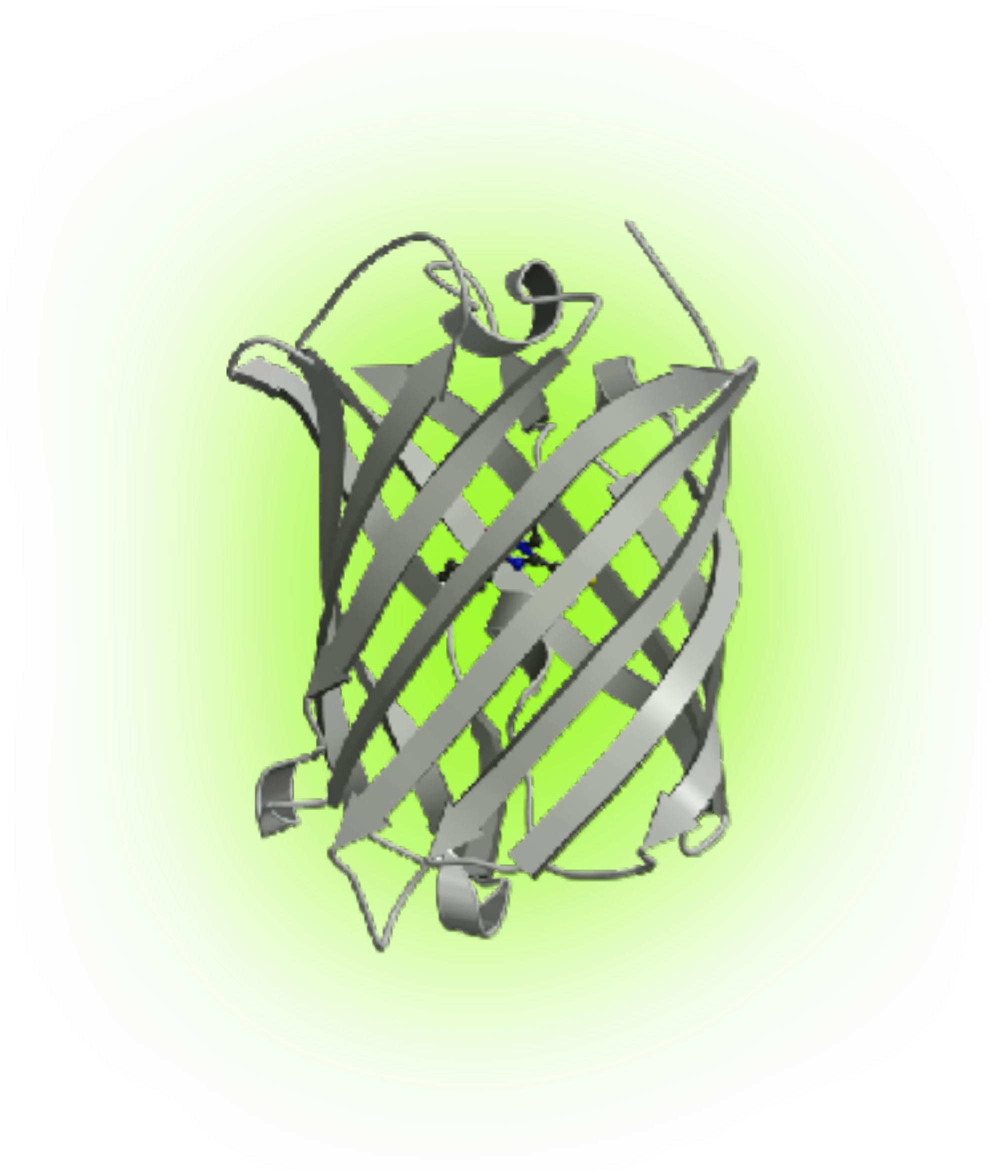
try something else instead!

with Jussi Toppari

Manipulating photo-chemistry

Green Fluorescent Protein (Ser65Thr/His148Asp)

ultra-fast excited-state proton transfer



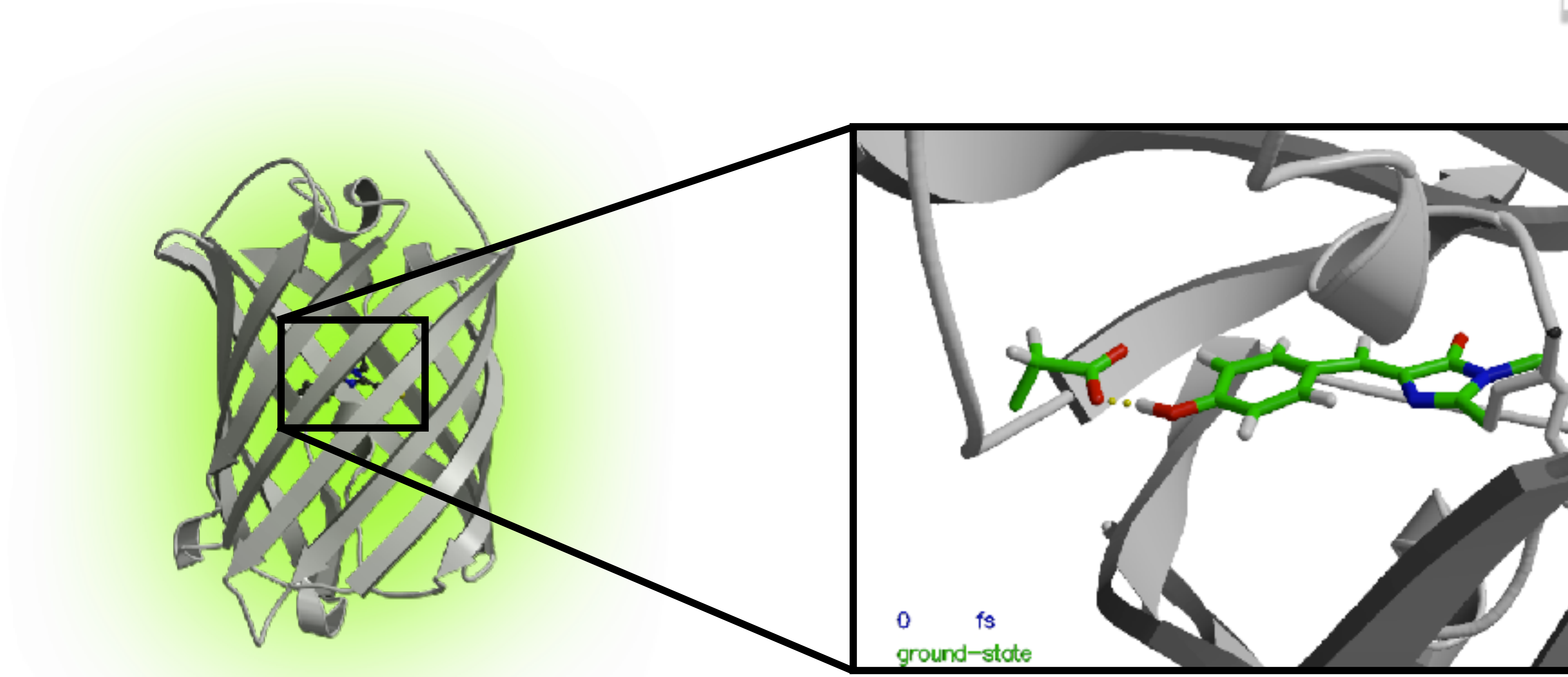
Stoner-Ma *et al.*, *J. Am. Chem. Soc.* **130** (2008) 1227-1235

Manipulating photo-chemistry

Green Fluorescent Protein (Ser65Thr/His148Asp)

ultra-fast excited-state proton transfer

Calvin Luk



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

Manipulating photo-chemistry with mirrors

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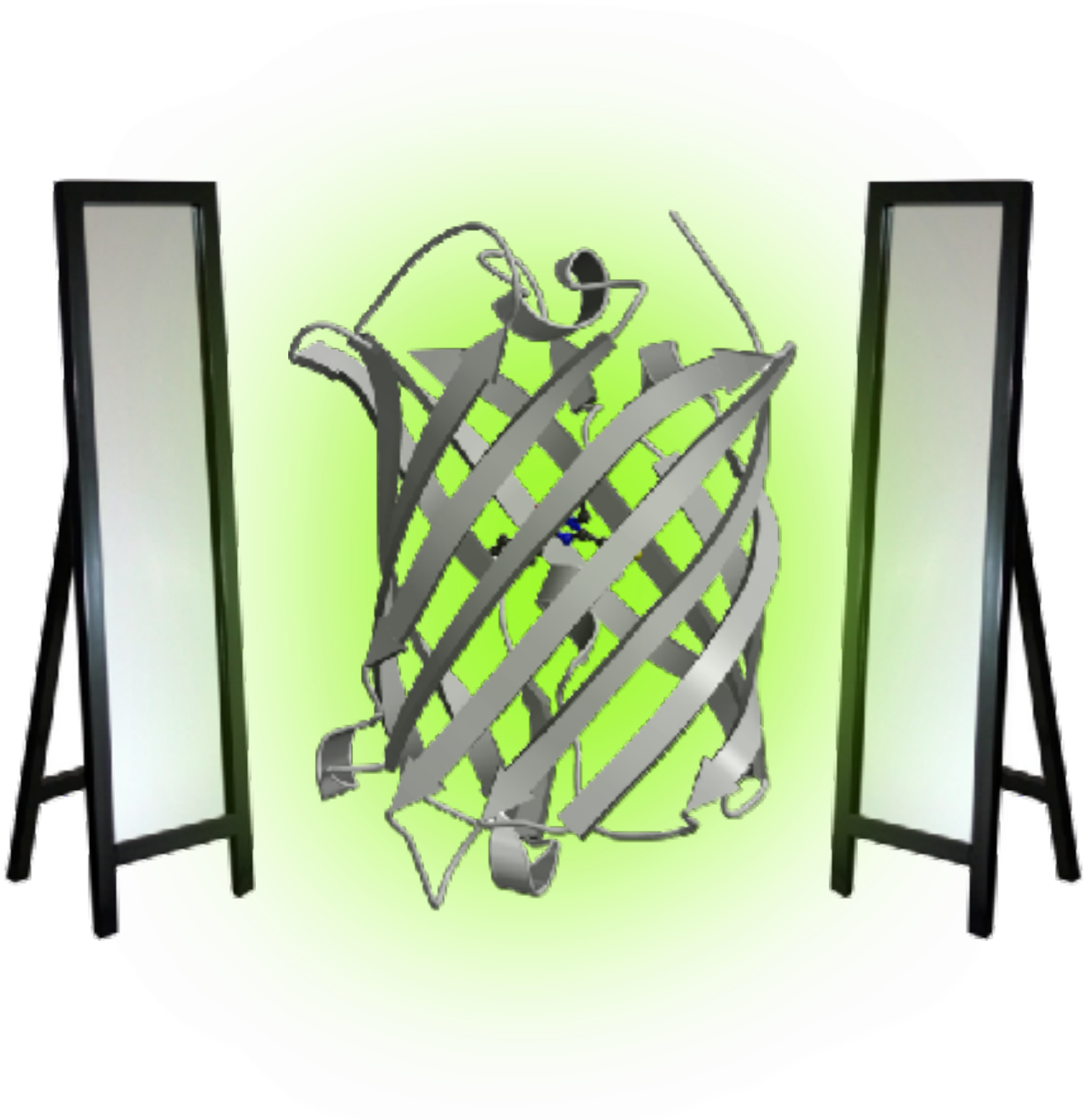

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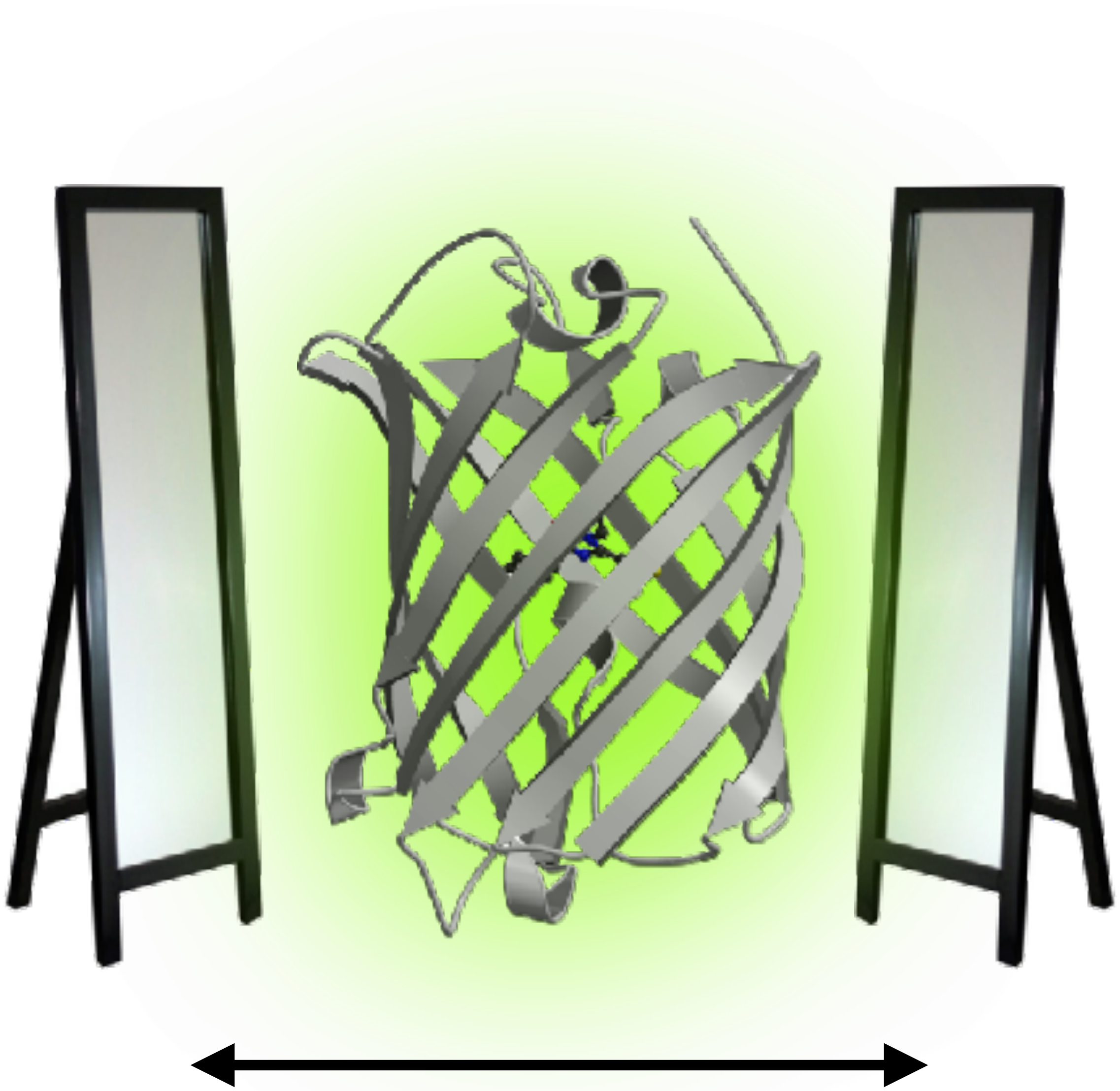

$$\frac{1}{2}\lambda_{\max}$$

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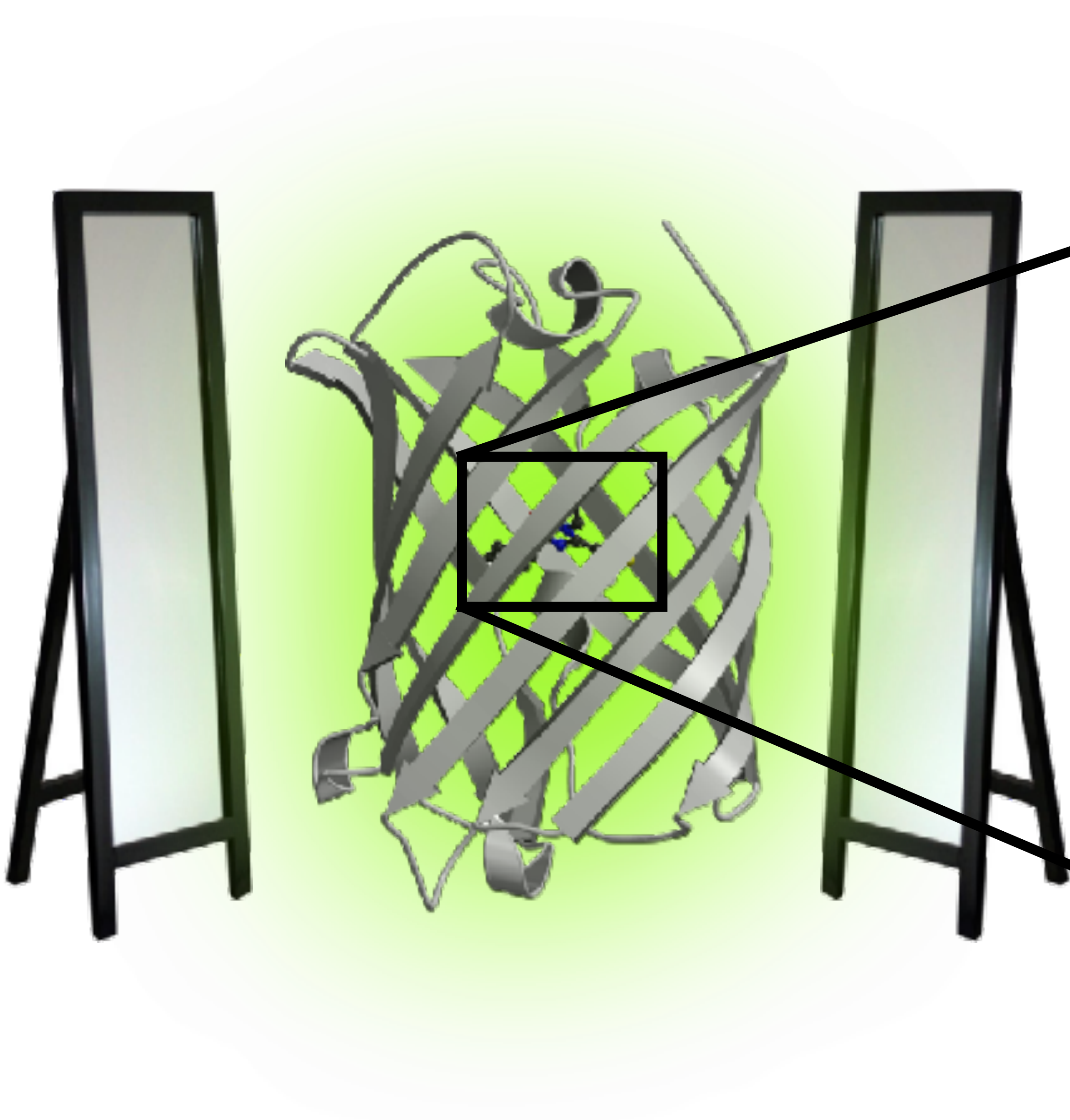

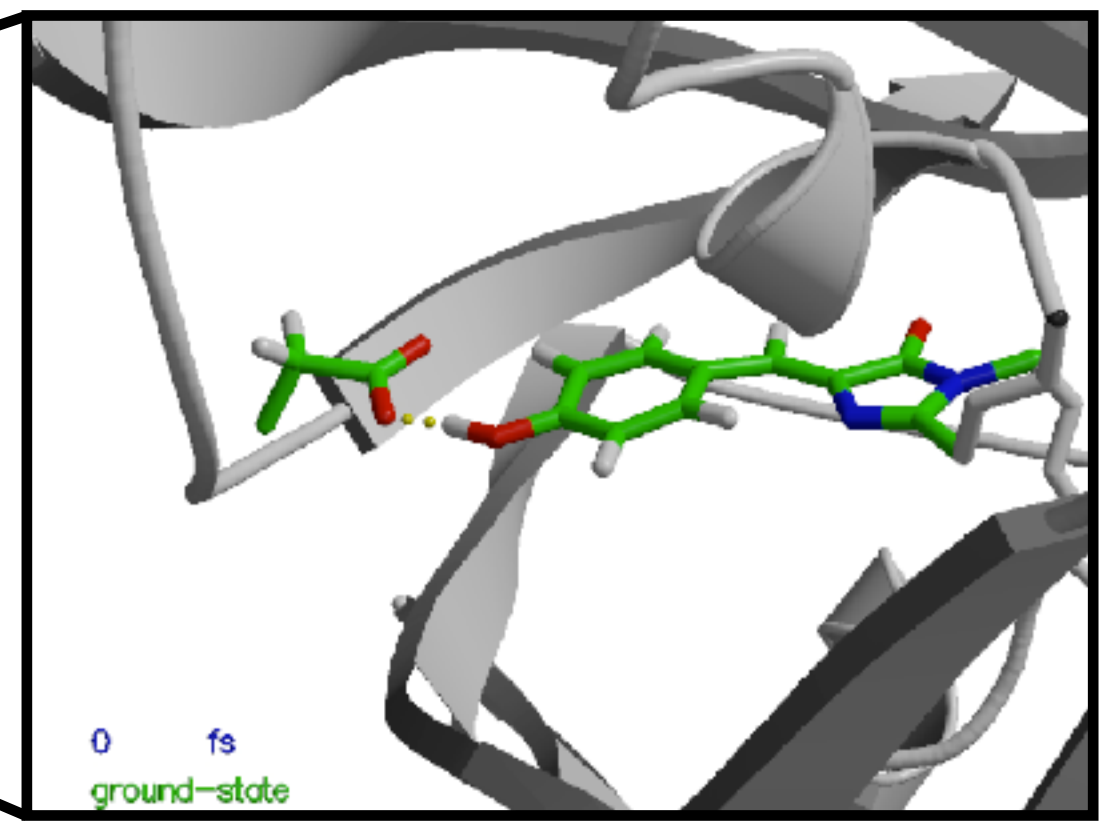

CASSCF(6,6)/3-21G//Amber03

Manipulating photo-chemistry with mirrors

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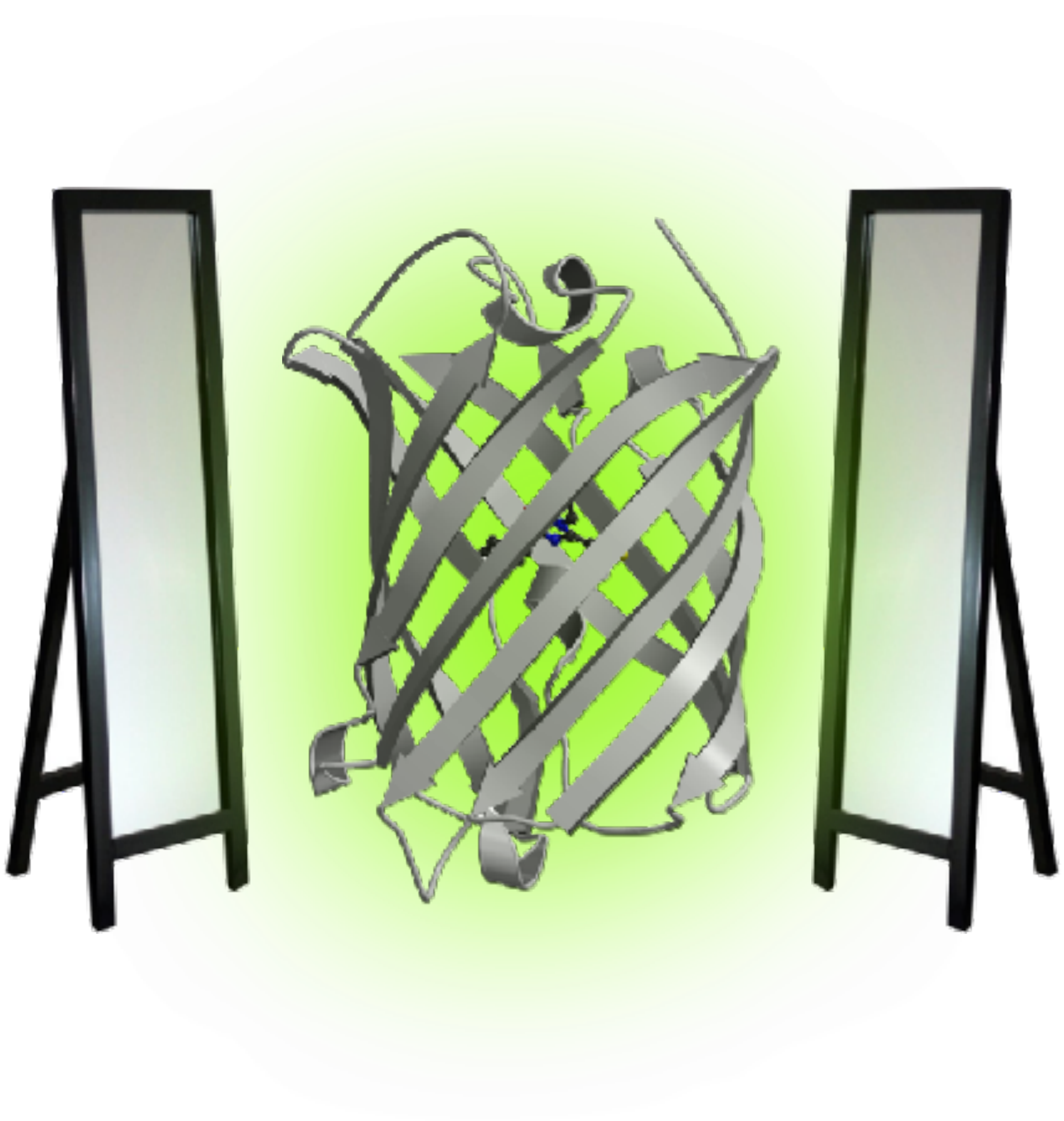

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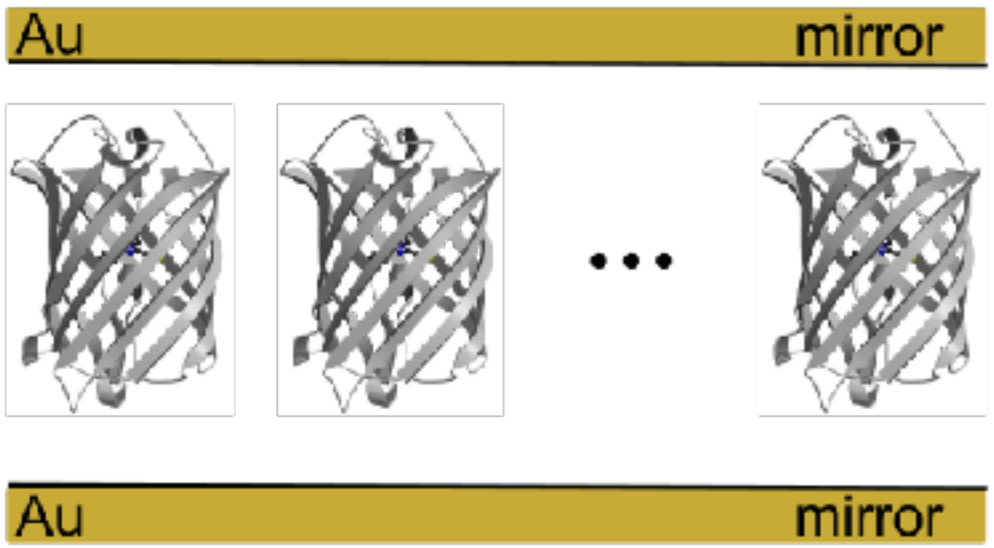


Mikael Kautto

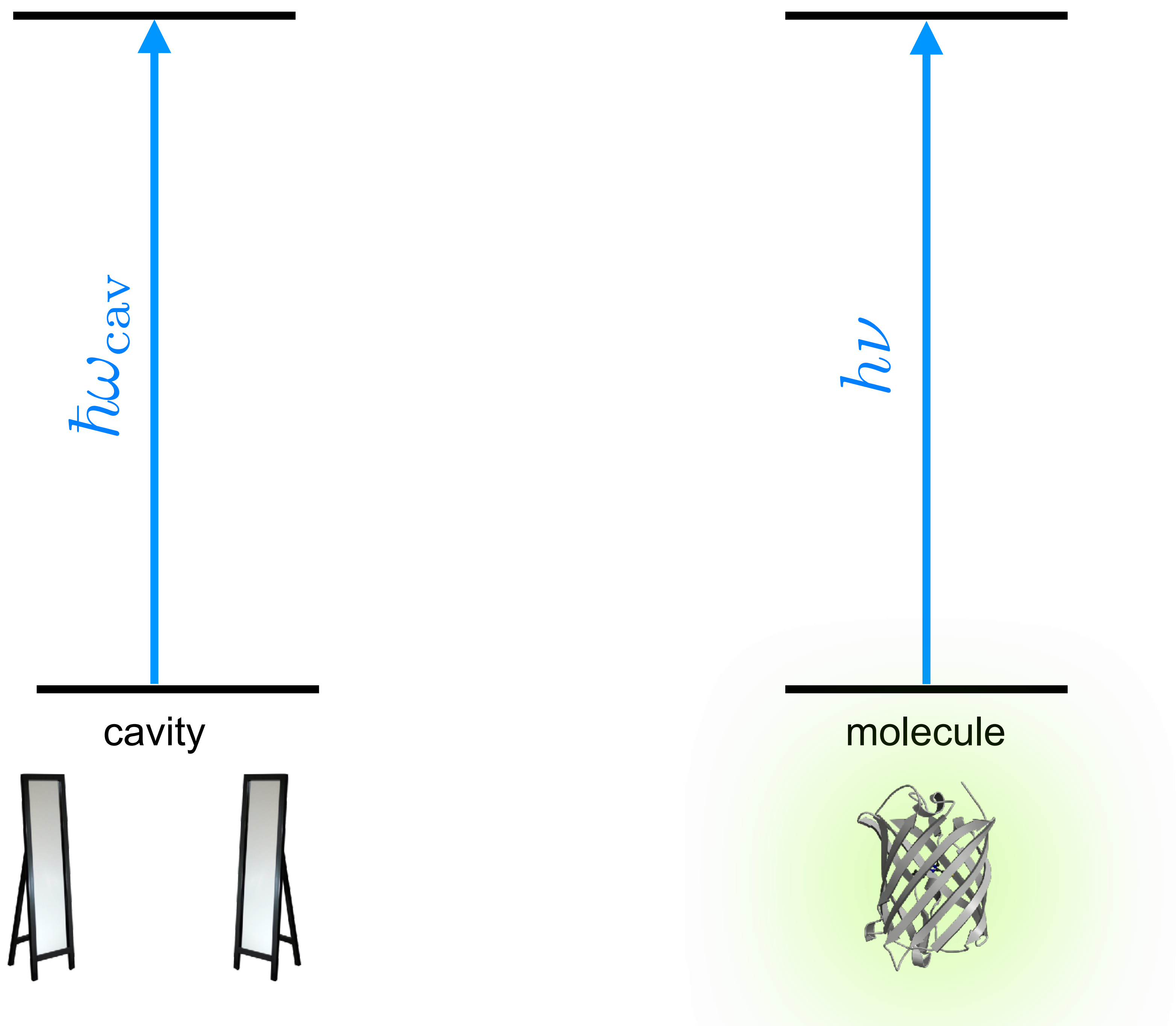
Satu Mustalahti

Eero Hulkko

Why does the photochemistry change?

strong coupling with confined light (cavity QED)

light-matter hybrid states: polaritons



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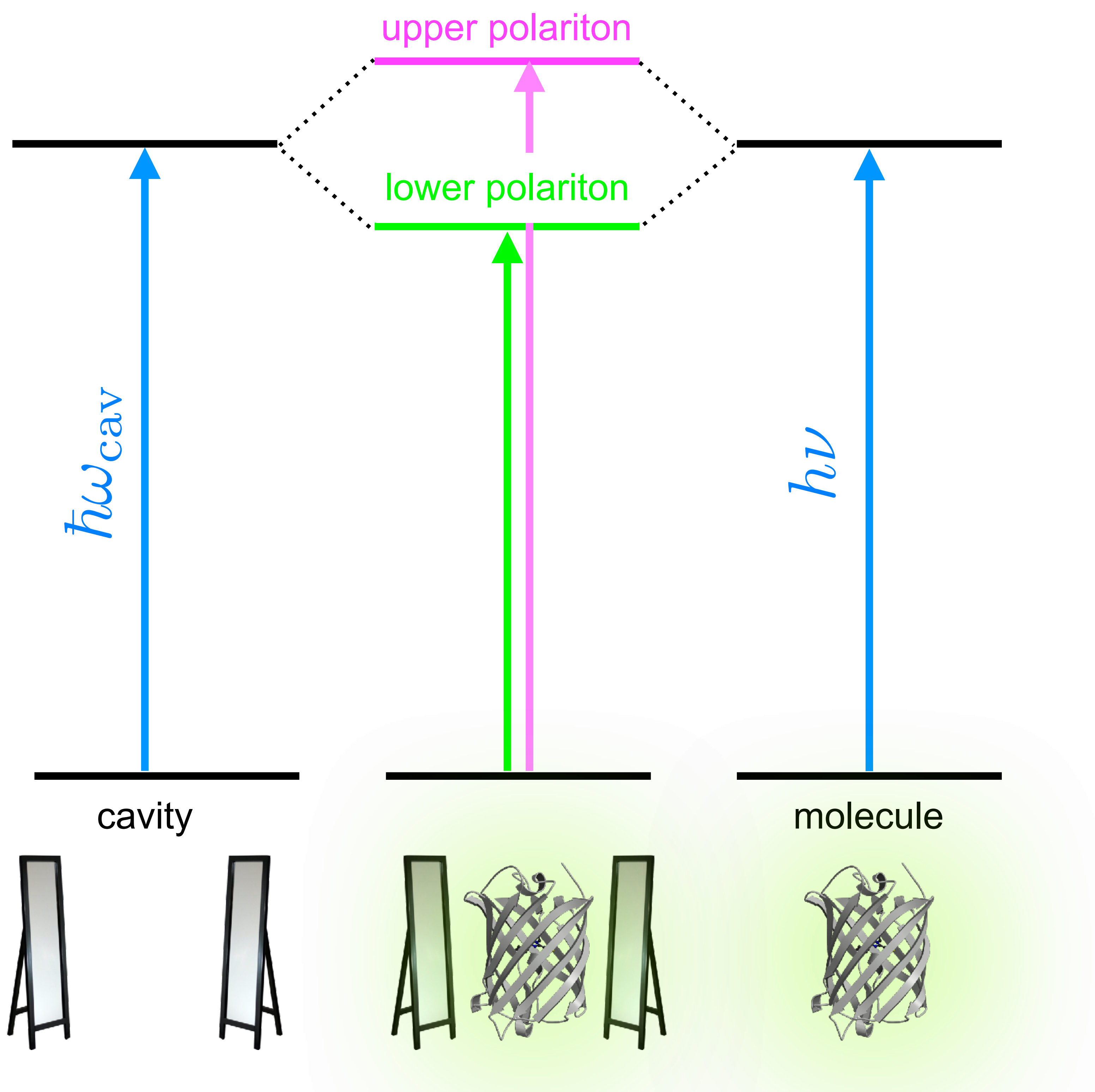

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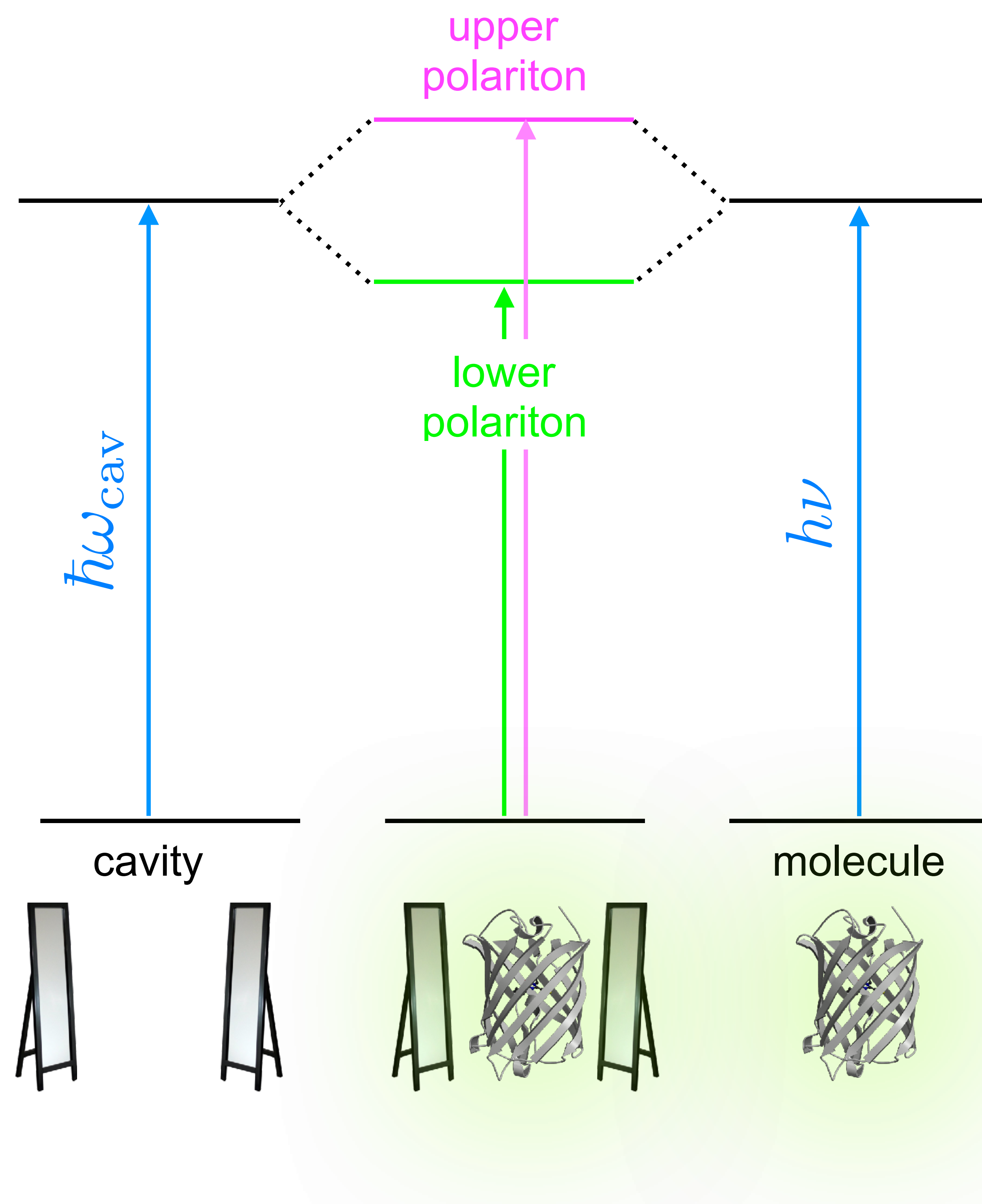

Jaynes & Cummings, *Proc. IEEE* **51** (1963) 89−109

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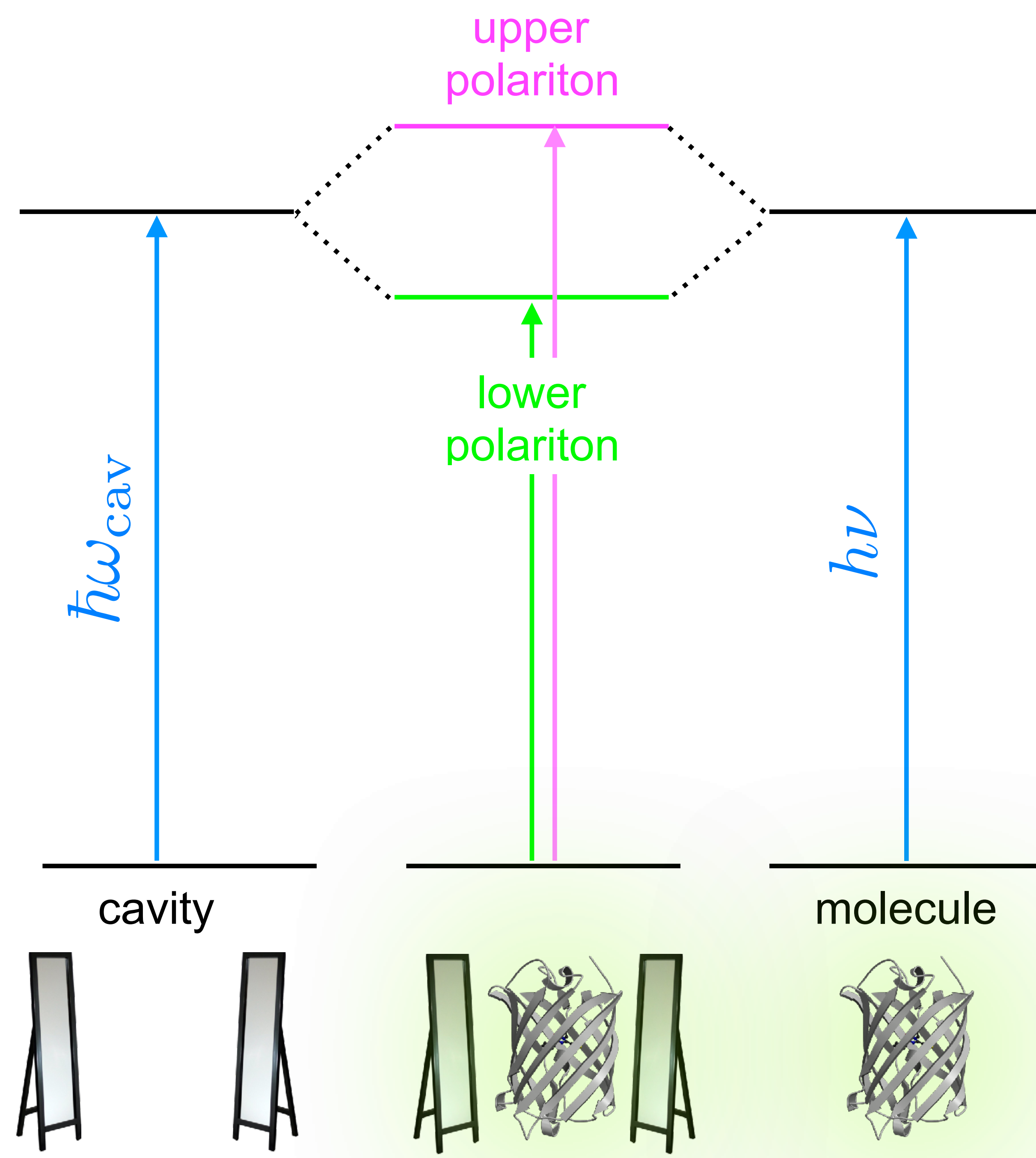

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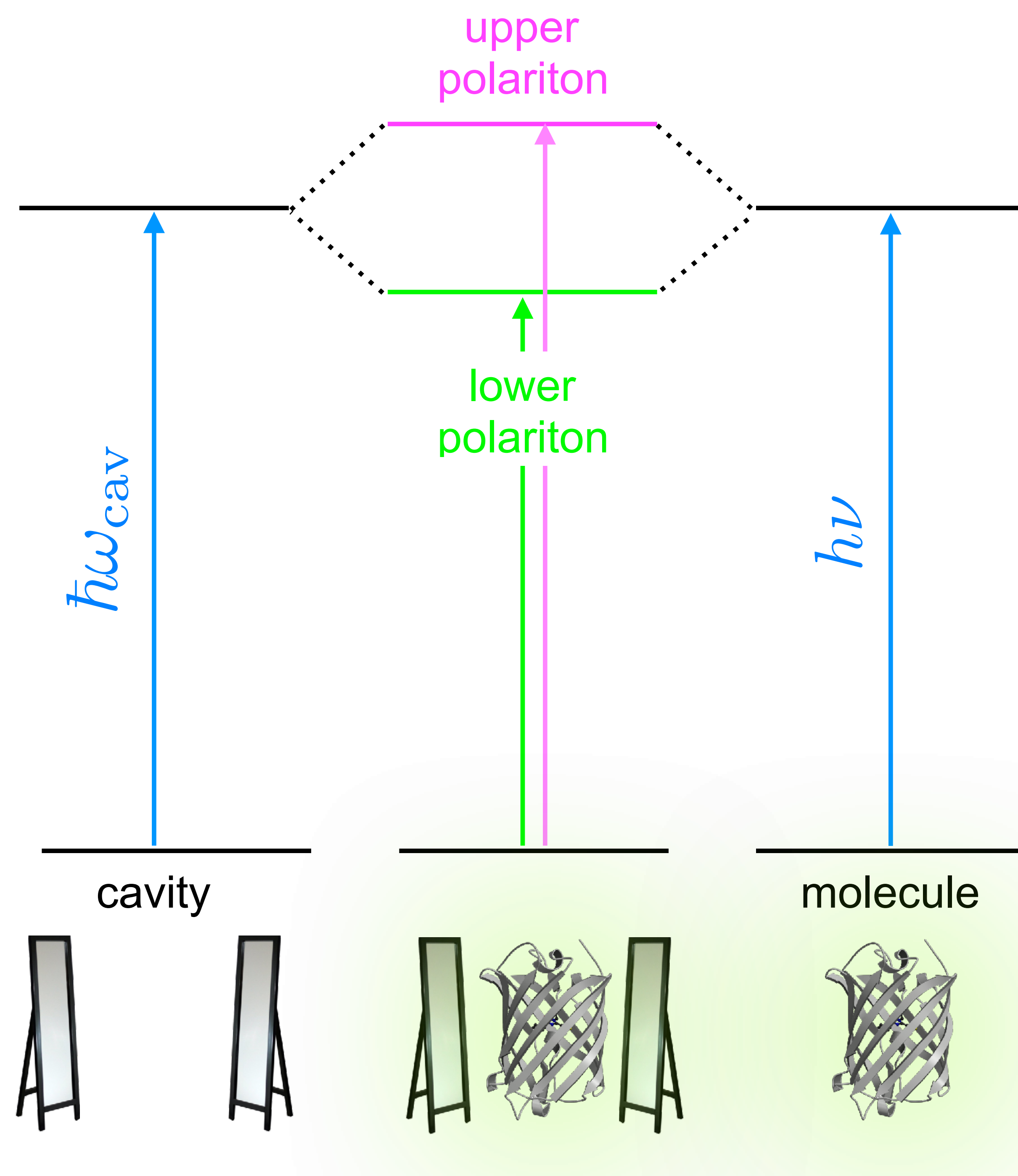

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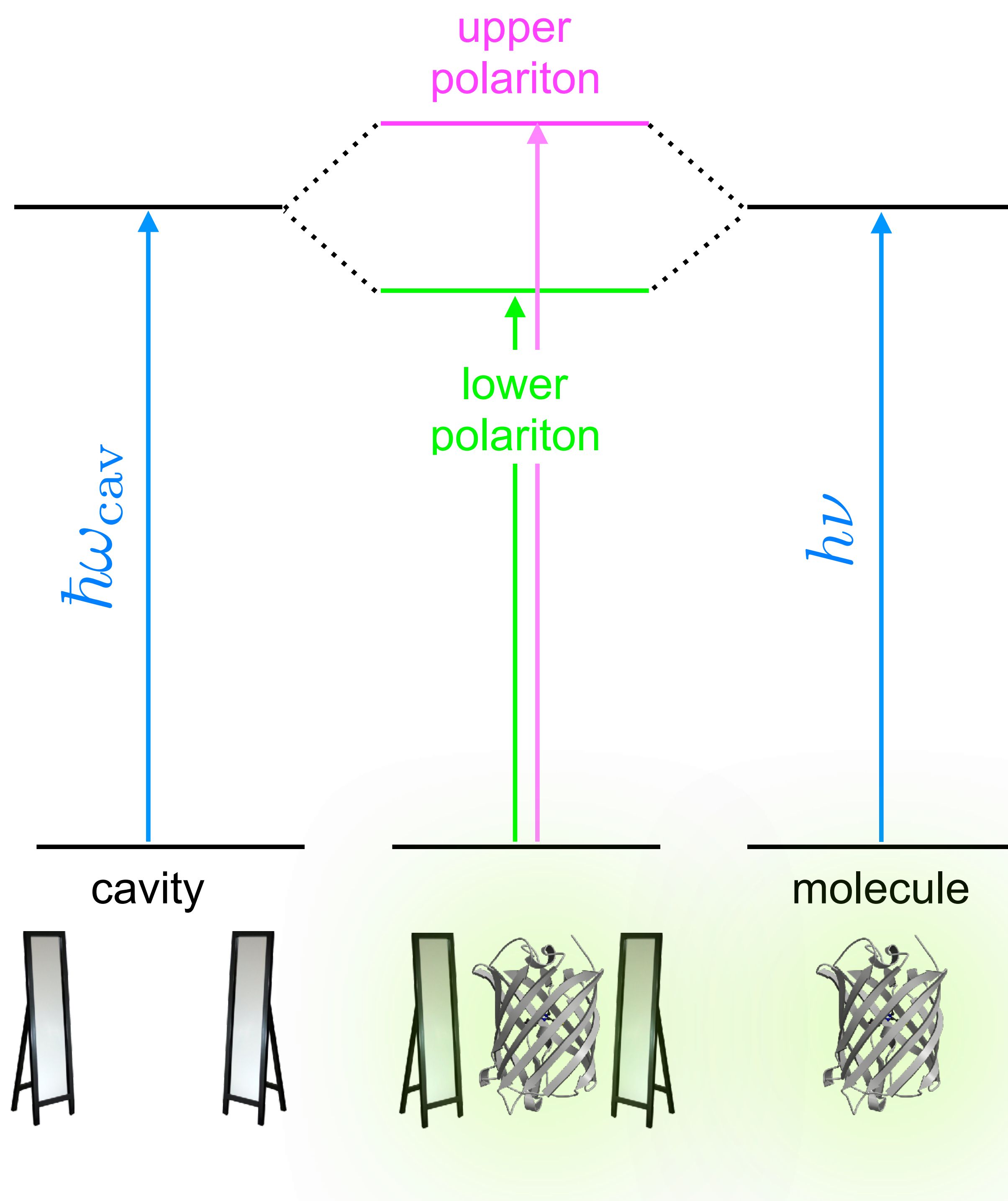

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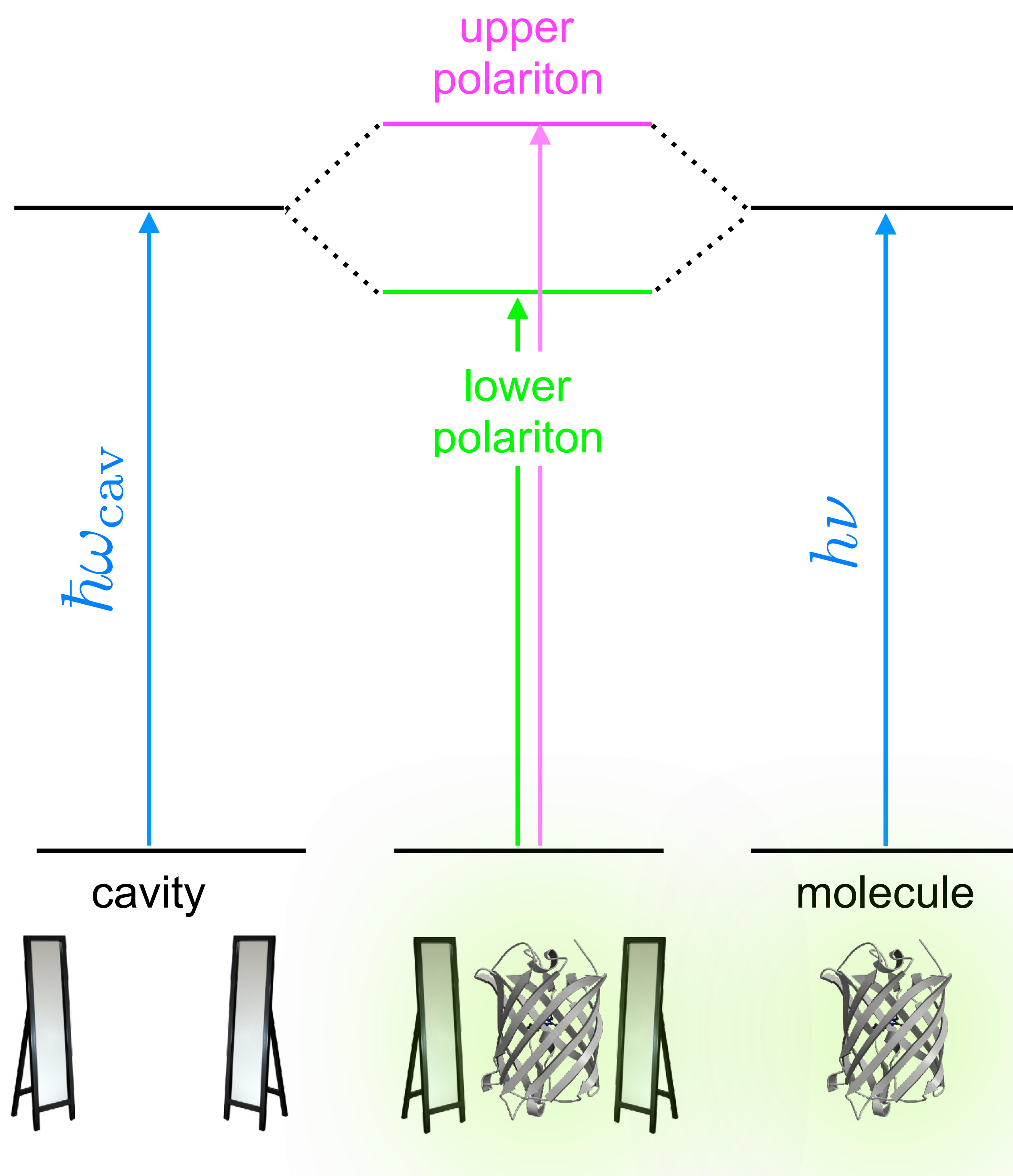
and solution

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

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



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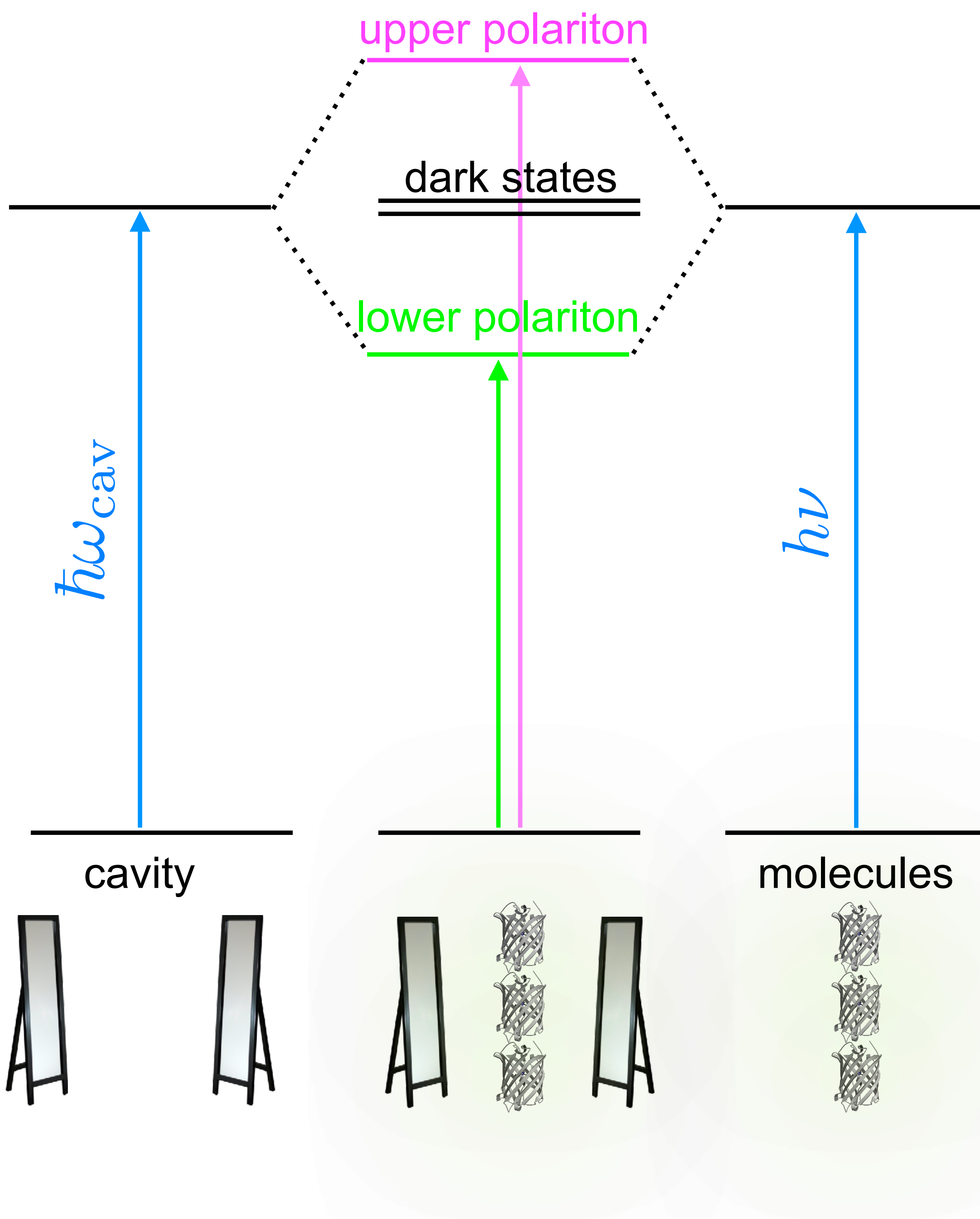

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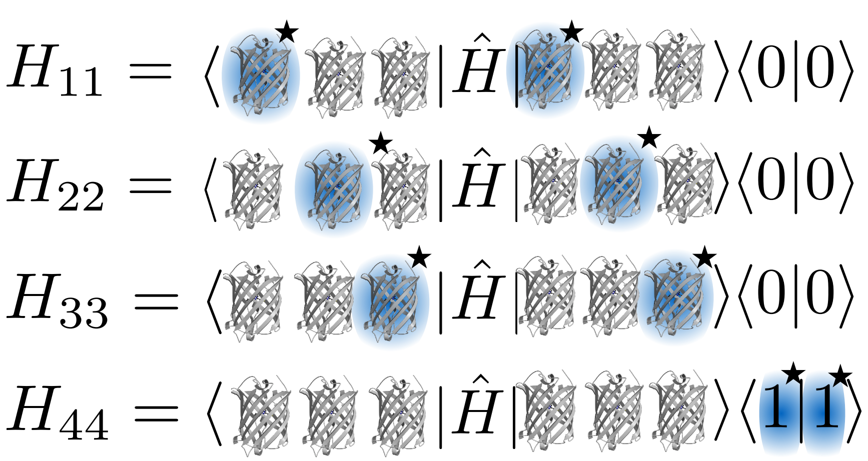

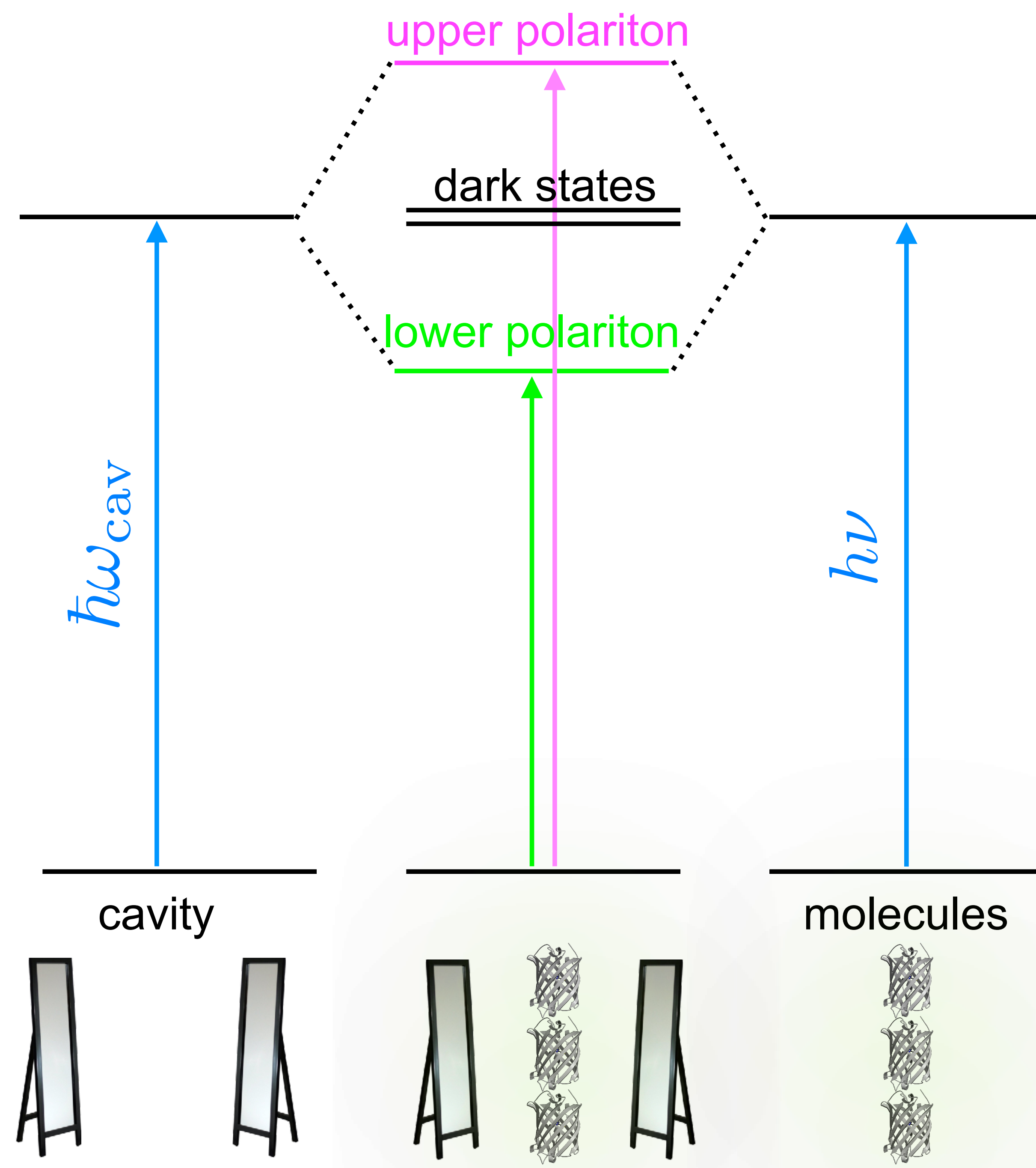

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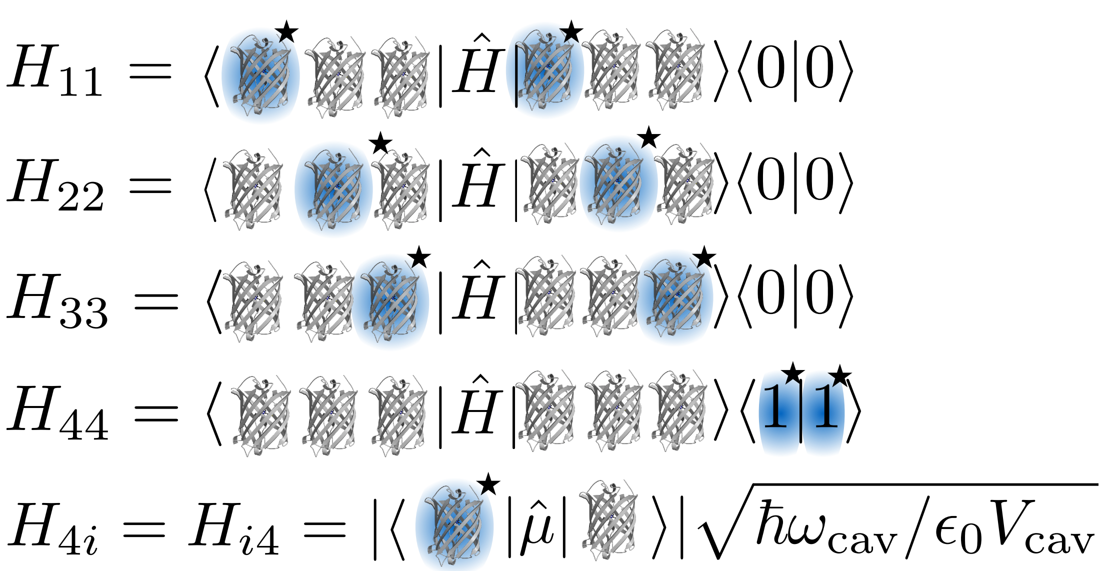

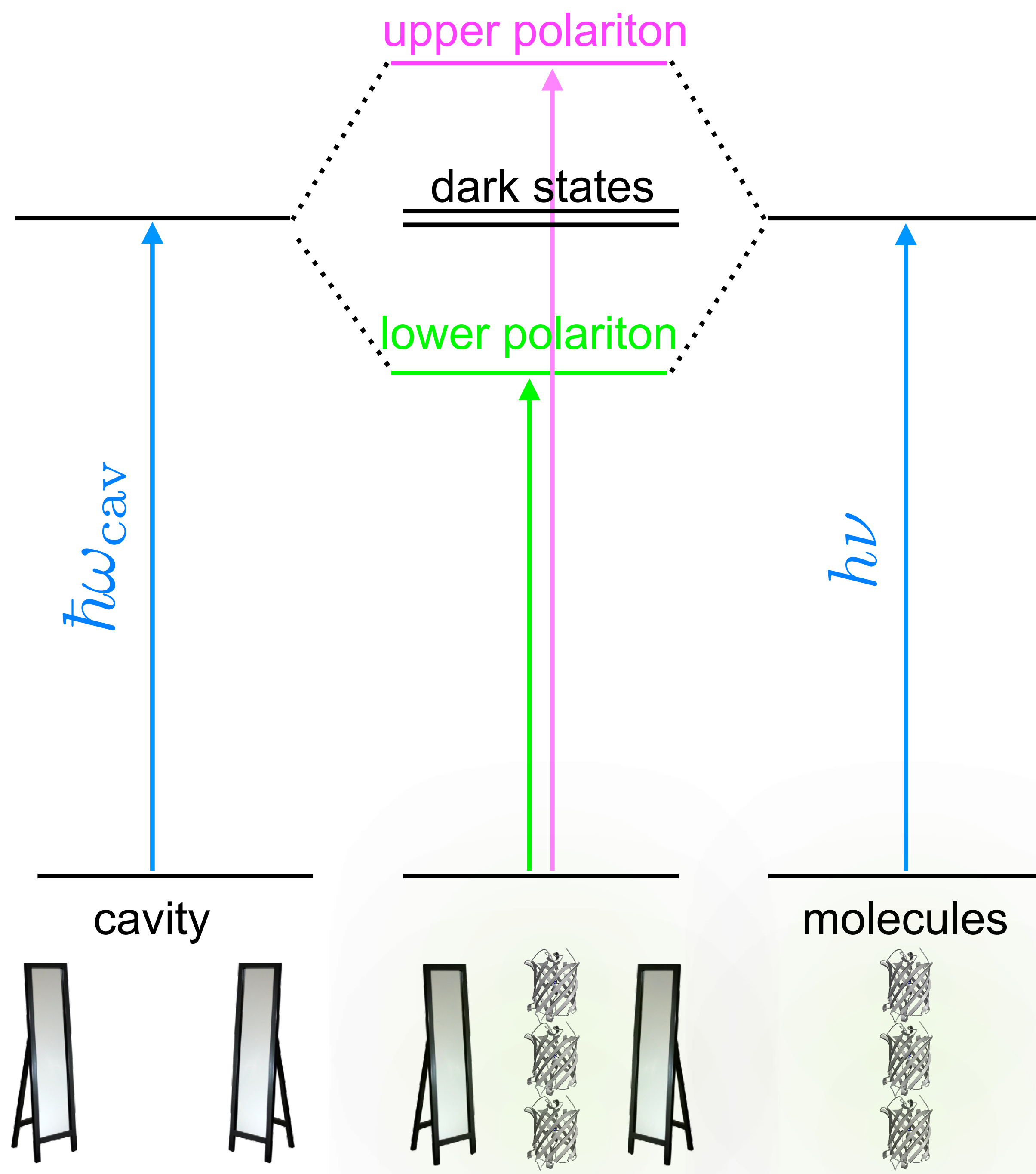

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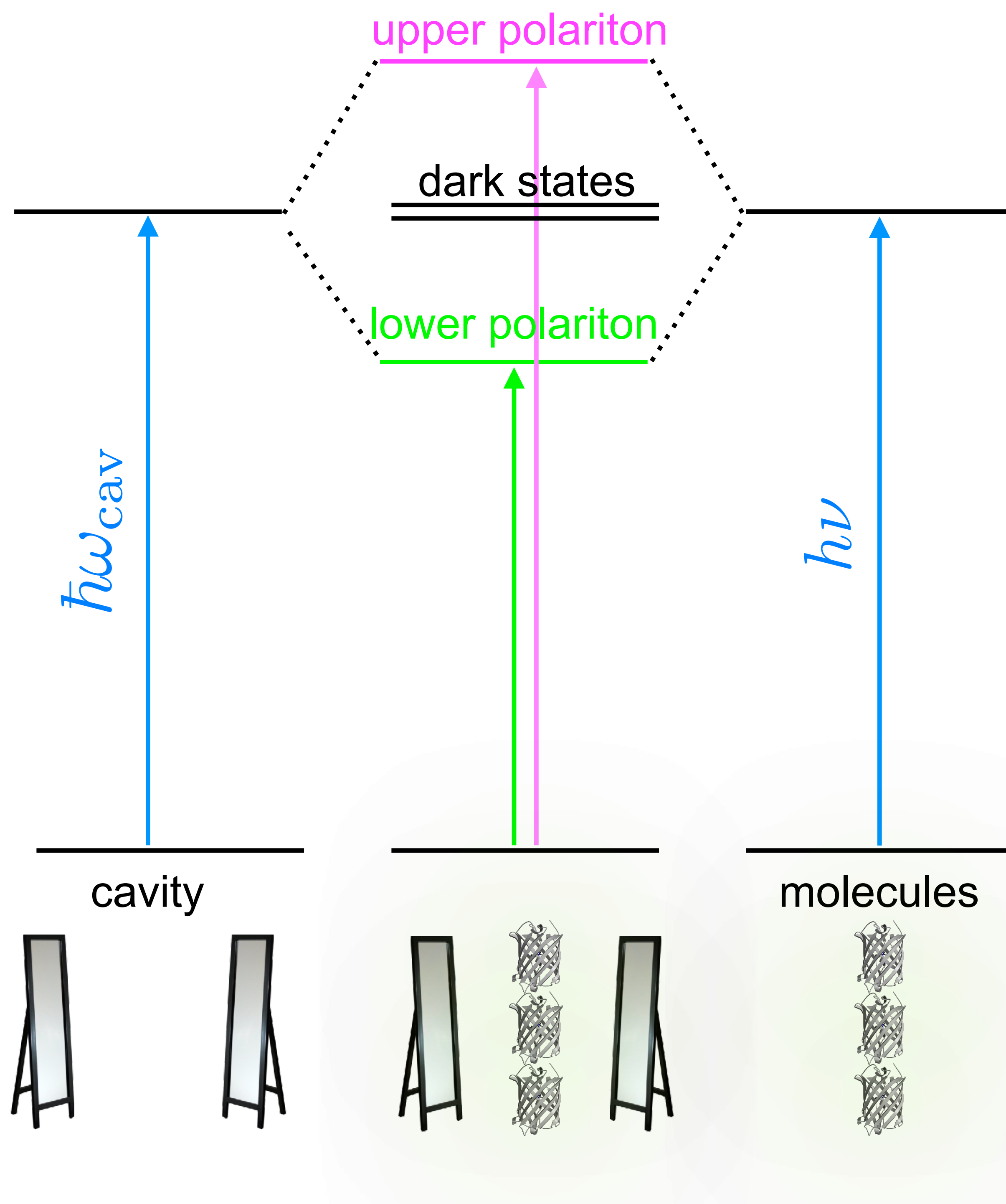

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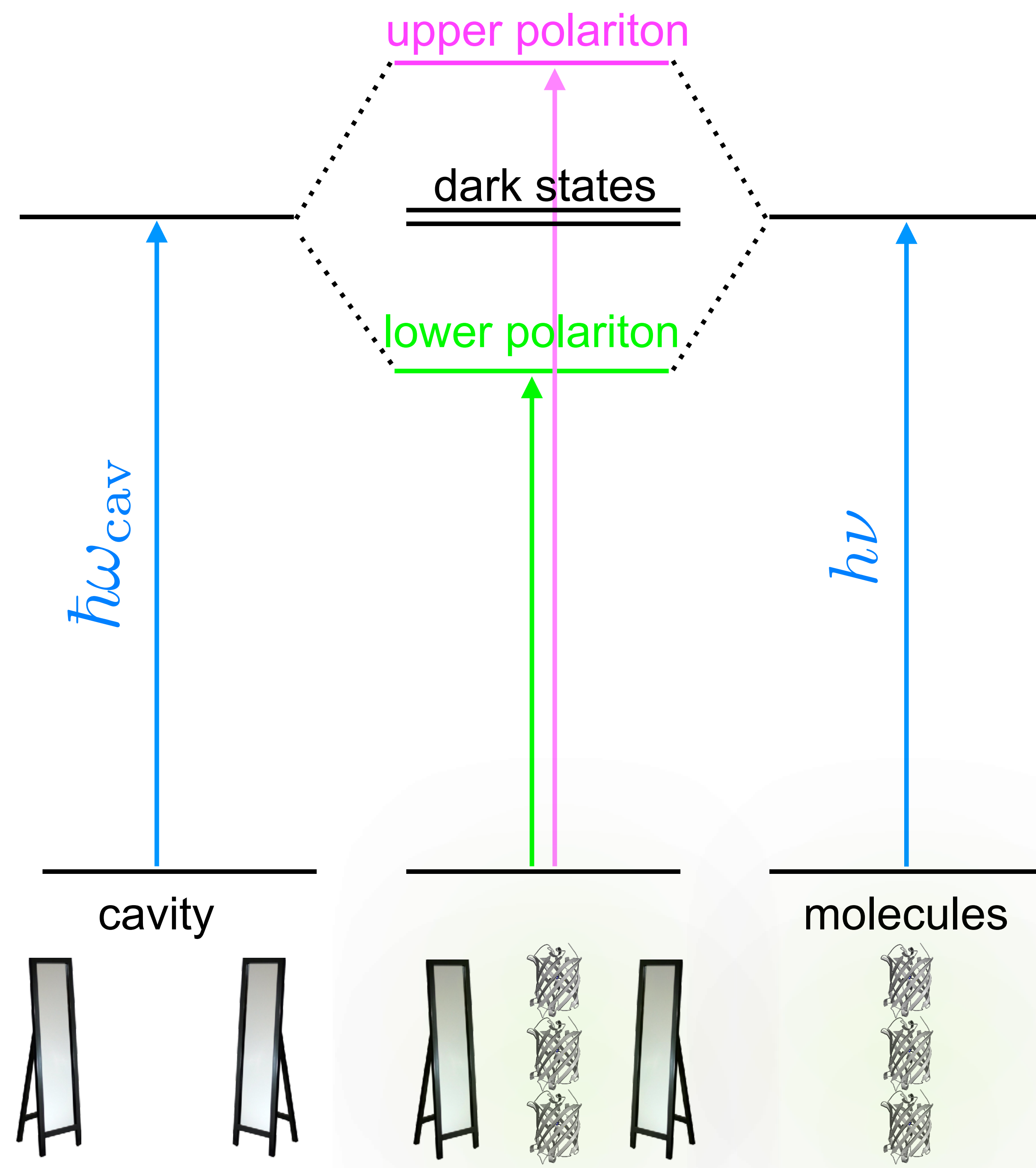

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Why does the photochemistry change?

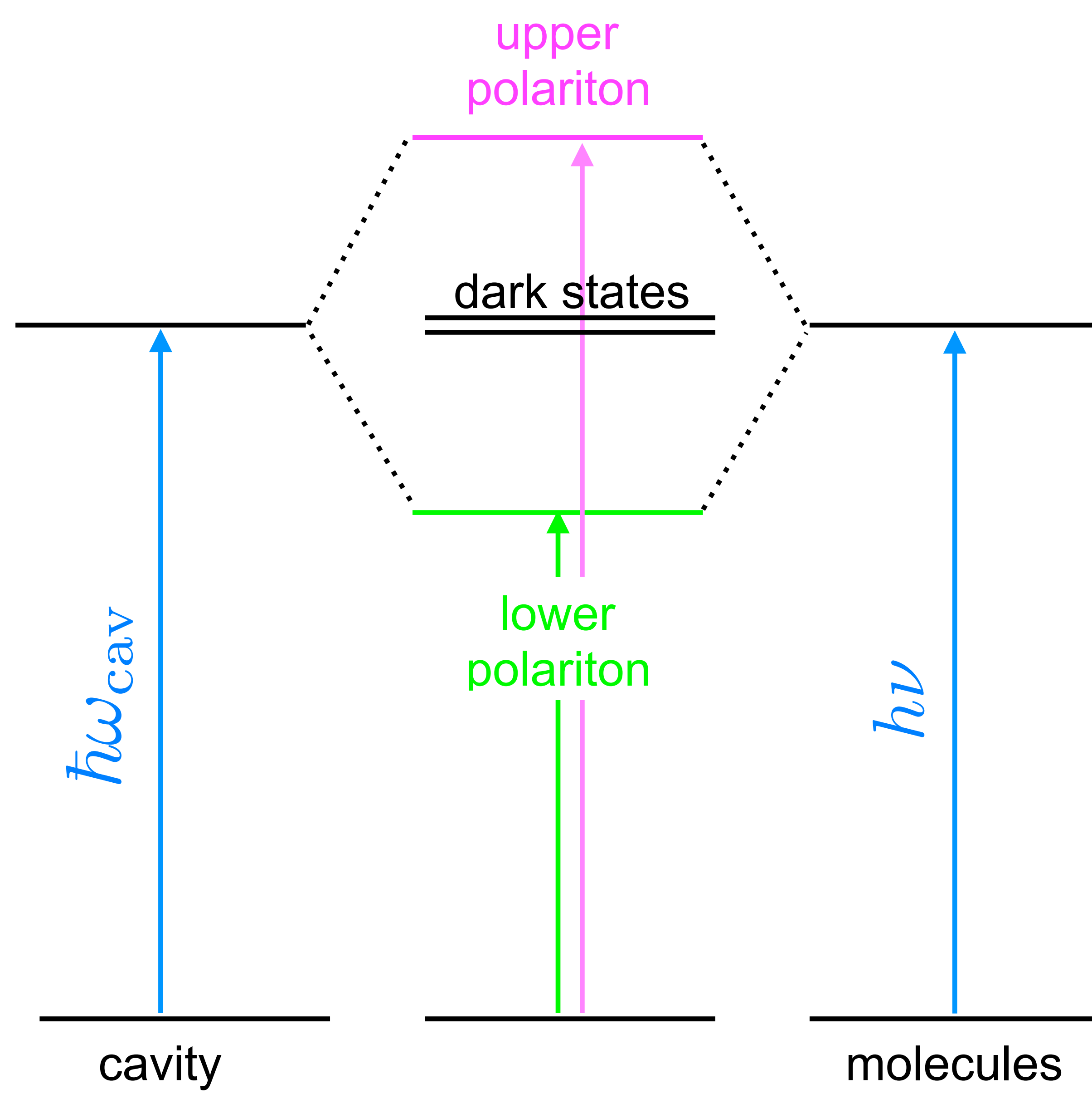
strong coupling with confined light (cavity QED)

two bright polaritons

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

Rabi splitting

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



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

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two bright polaritons

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

two dark states (in general *N*-1)

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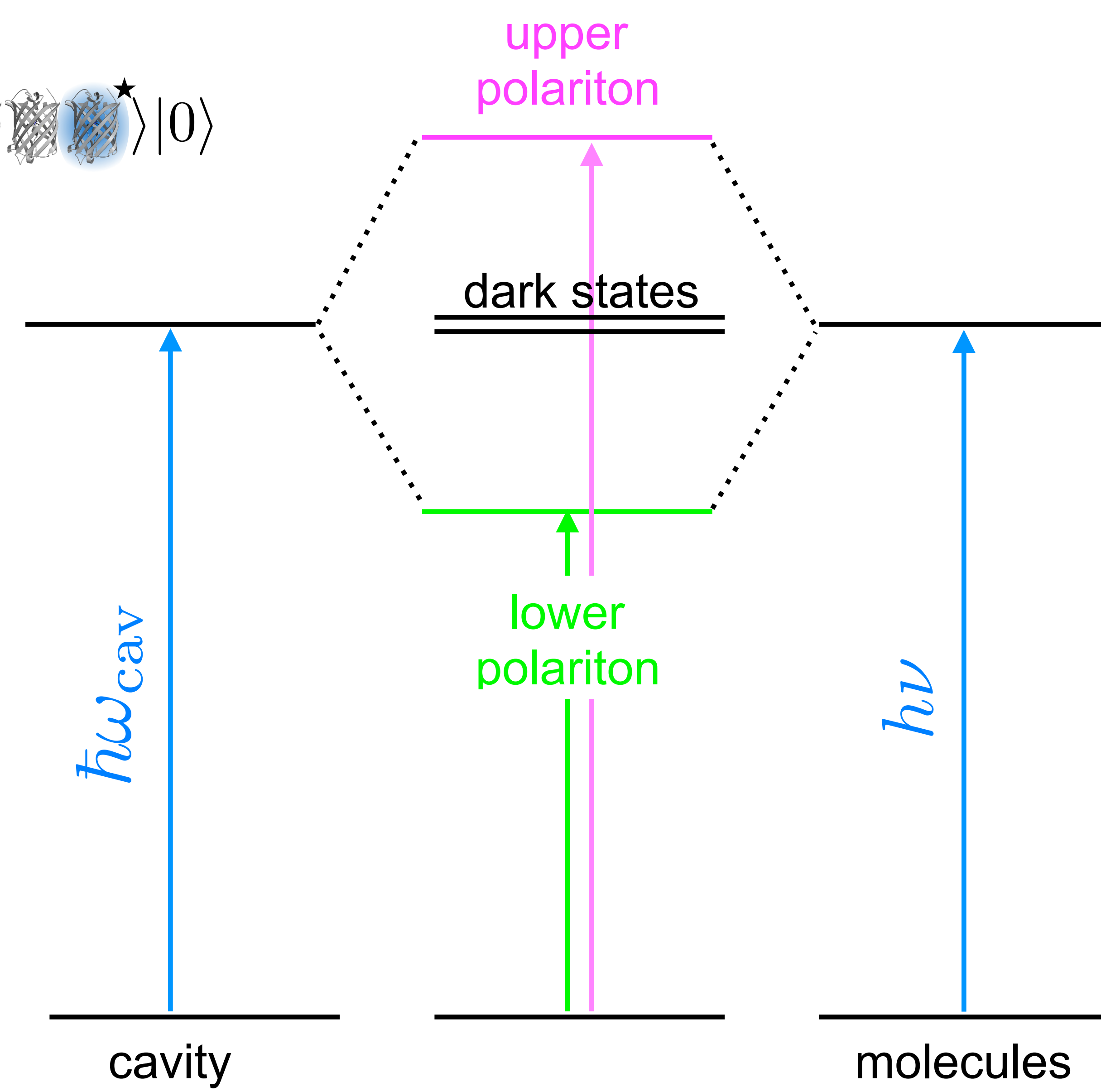

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strong coupling with confined light (cavity QED)

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Eero
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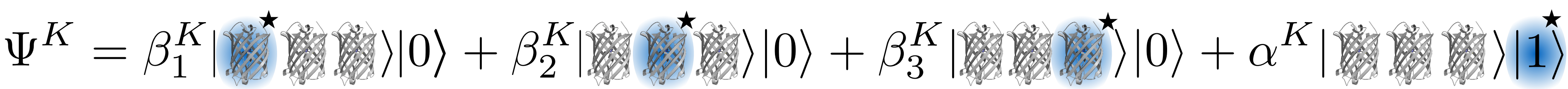
two bright polaritons



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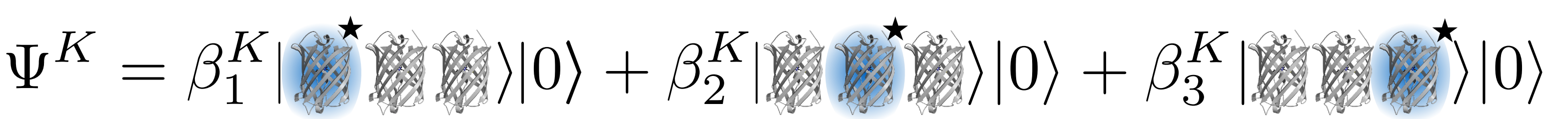
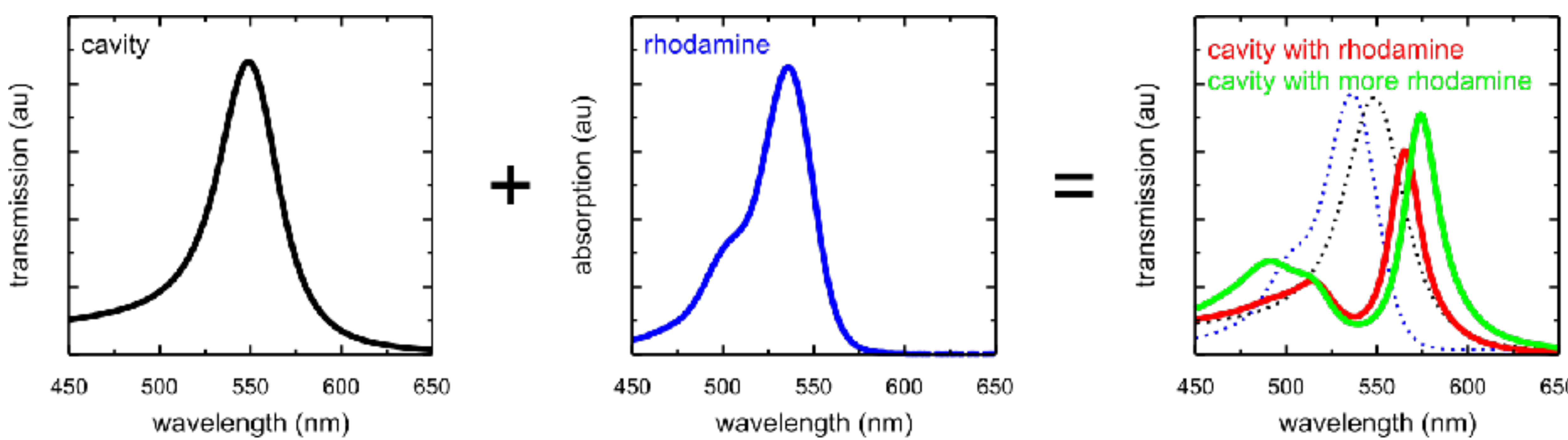


double peak spectrum

example: cavity with rhodamine 6G

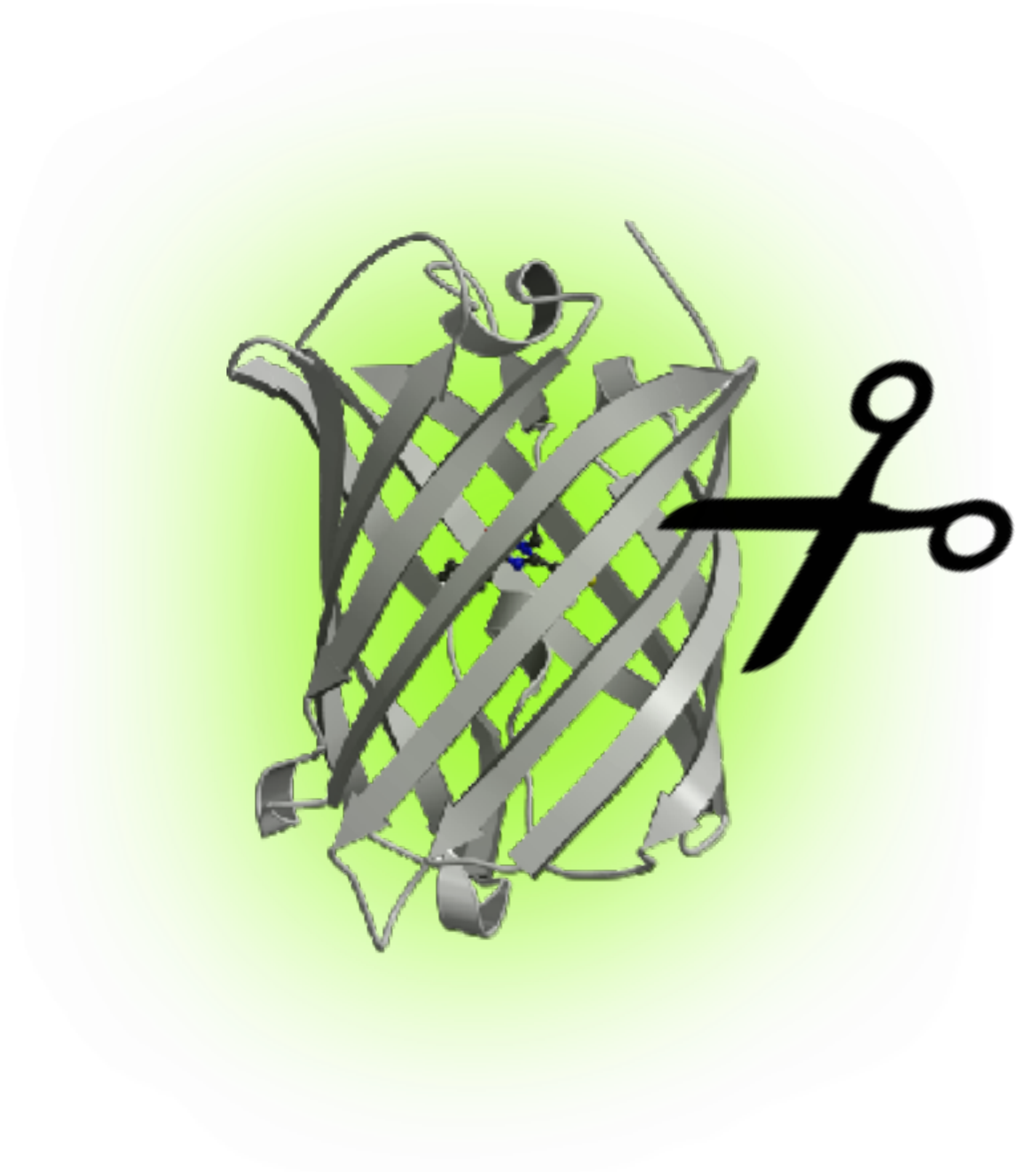


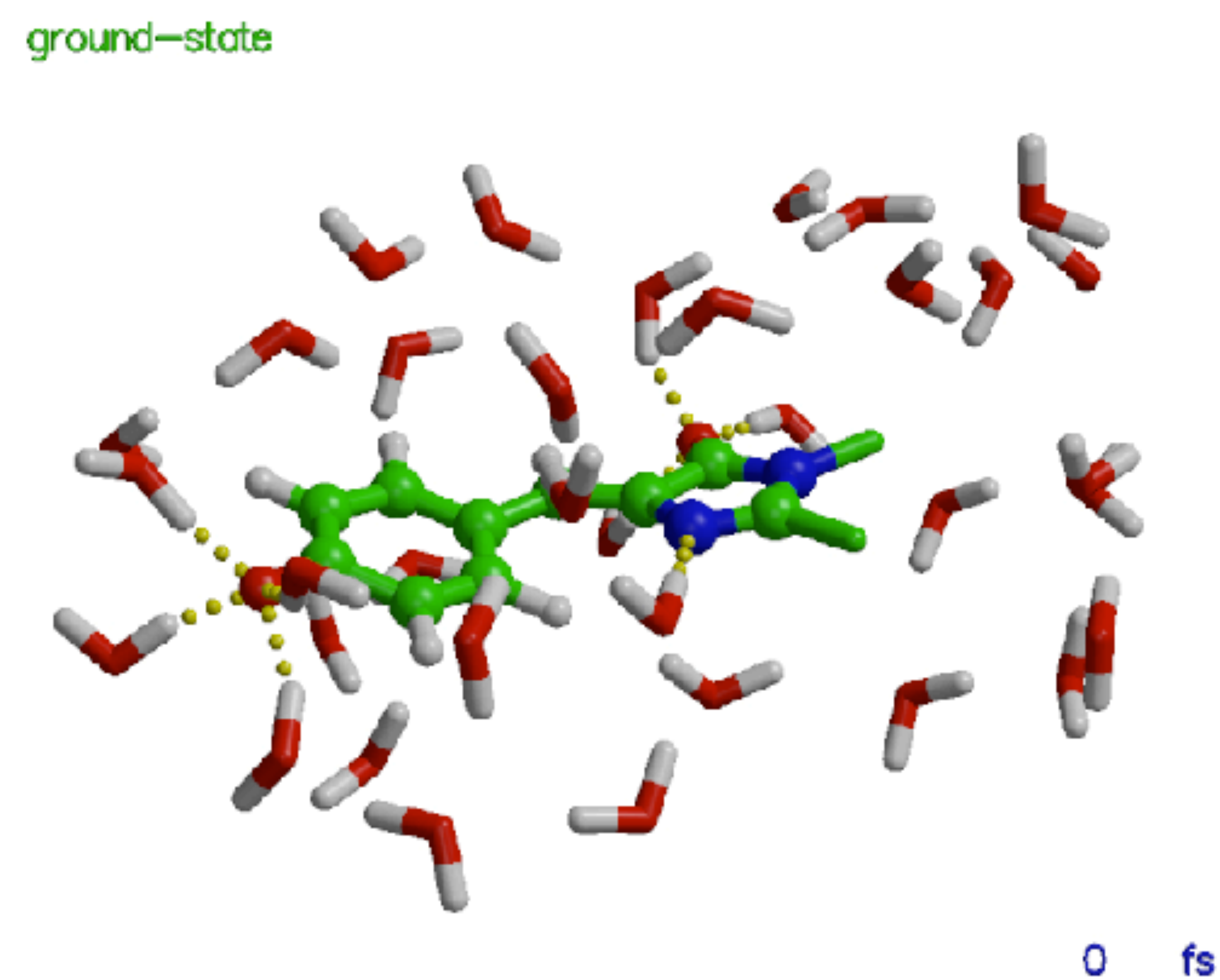
Manipulating photo-chemistry with mirrors

GFP chromophore in water

no fluorescence: dark

Dmitry Morozov





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

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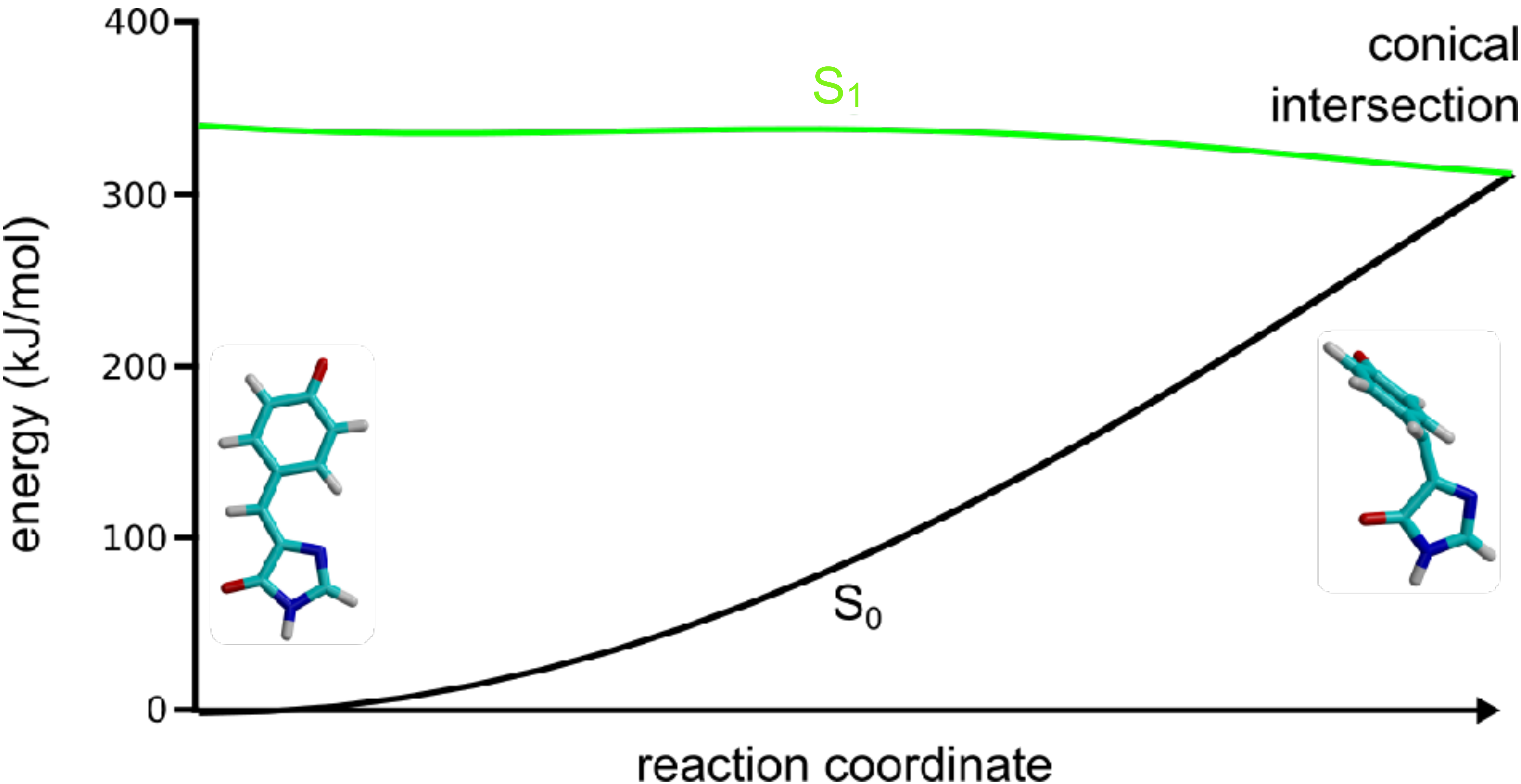
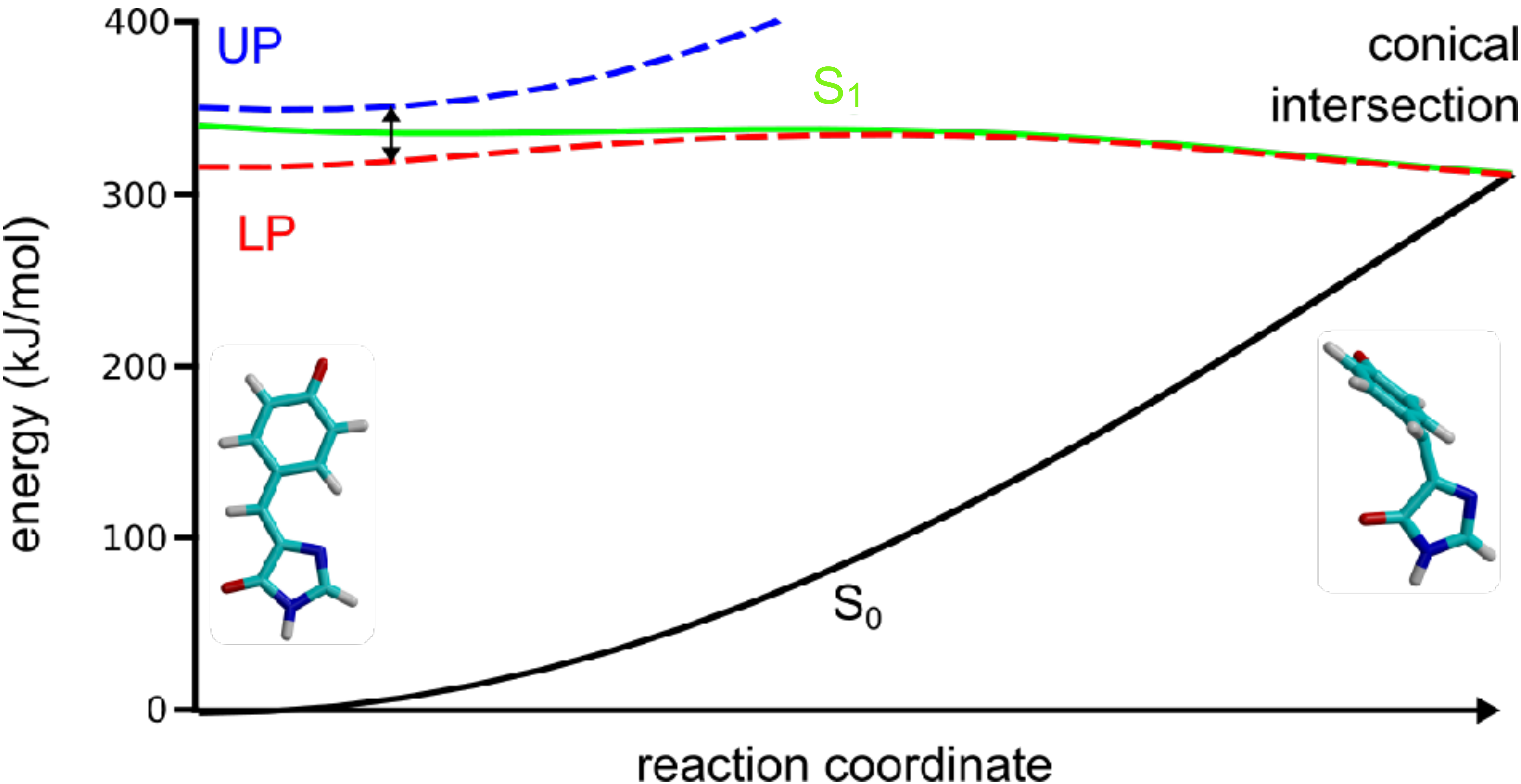


Manipulating photo-chemistry with mirrors

one GFP chromophore in water in a cavity

strong coupling to confined light?

minimum on lower polariton surface



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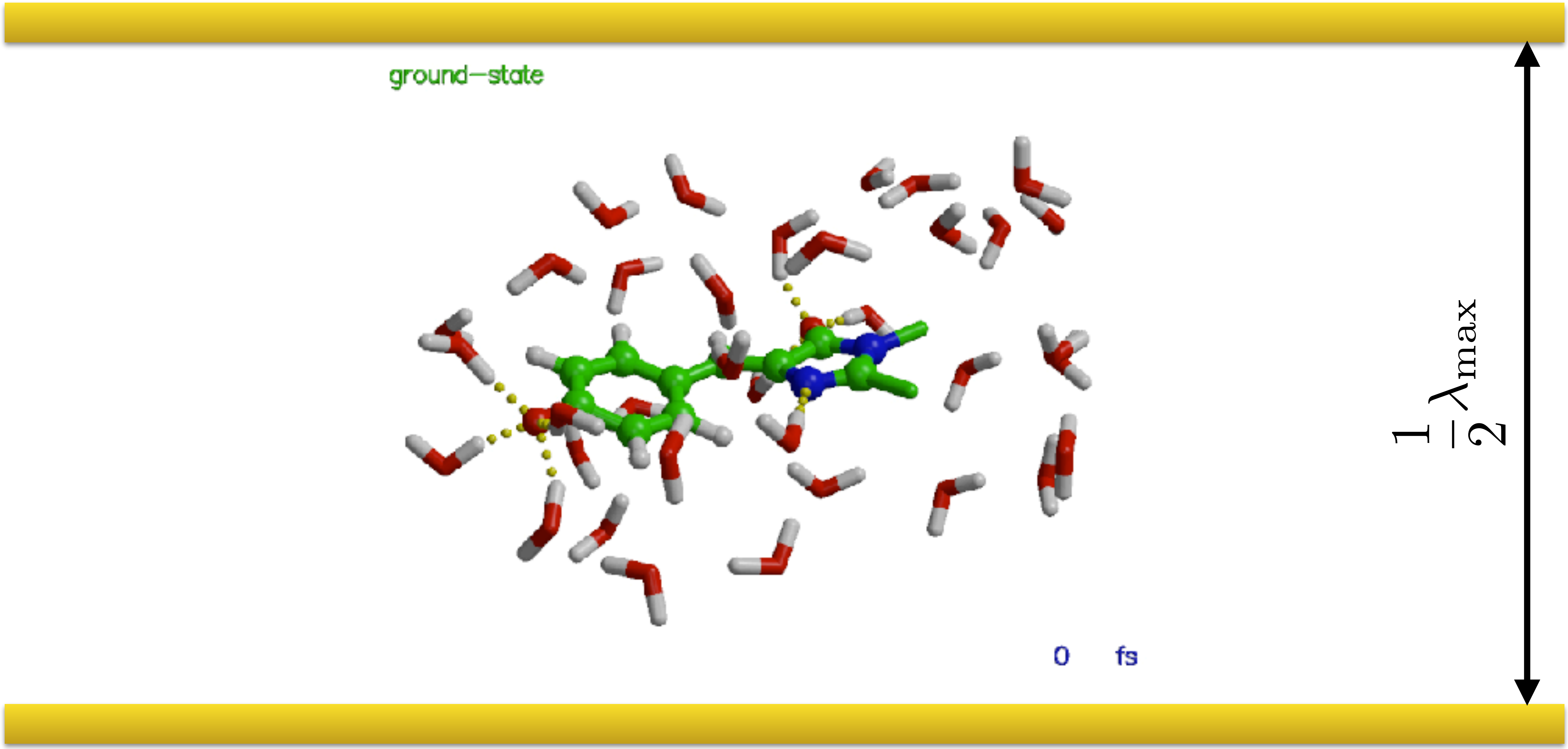
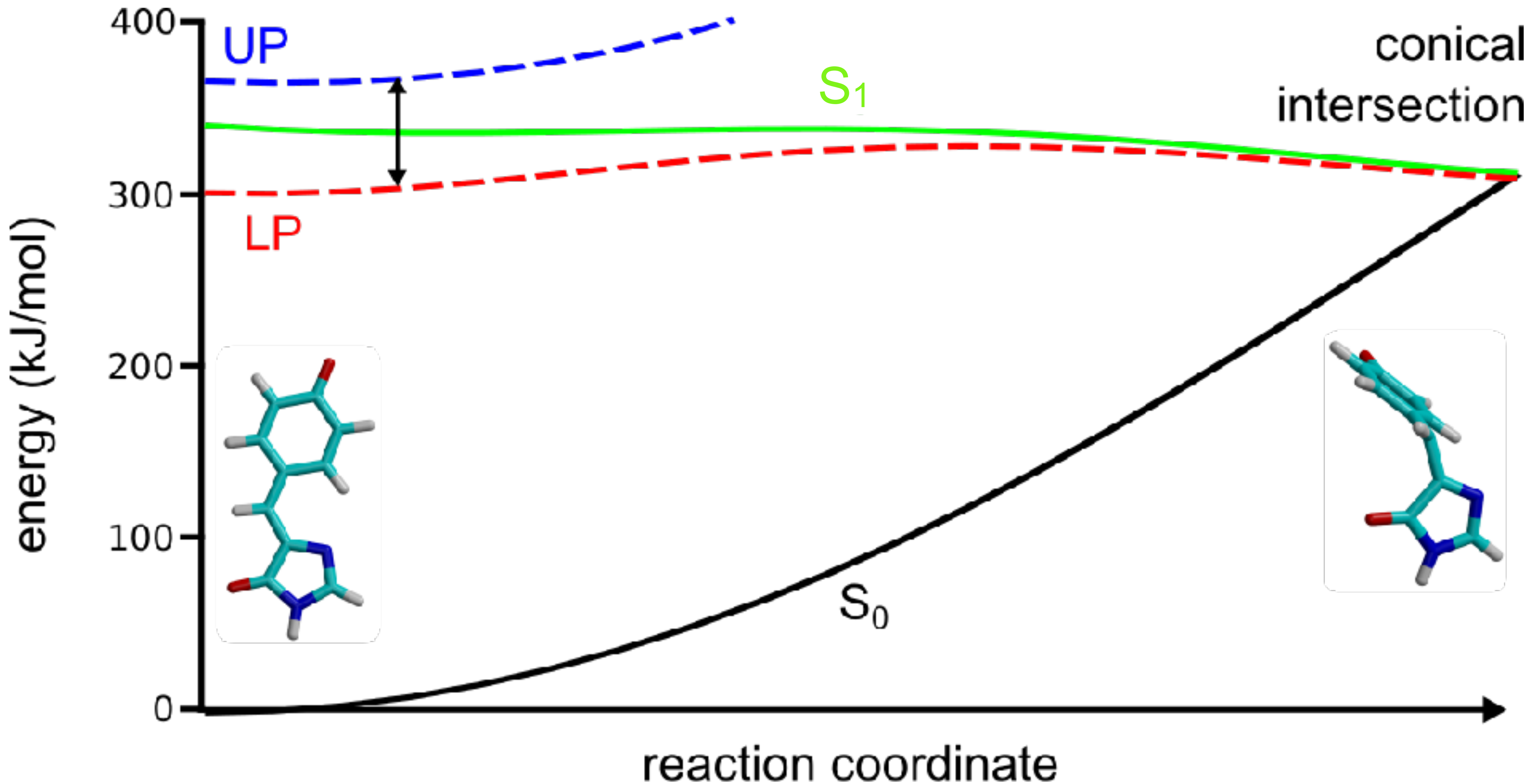


Manipulating photo-chemistry with mirrors

four GFP chromophores in water in a cavity

two times stronger coupling with confined light

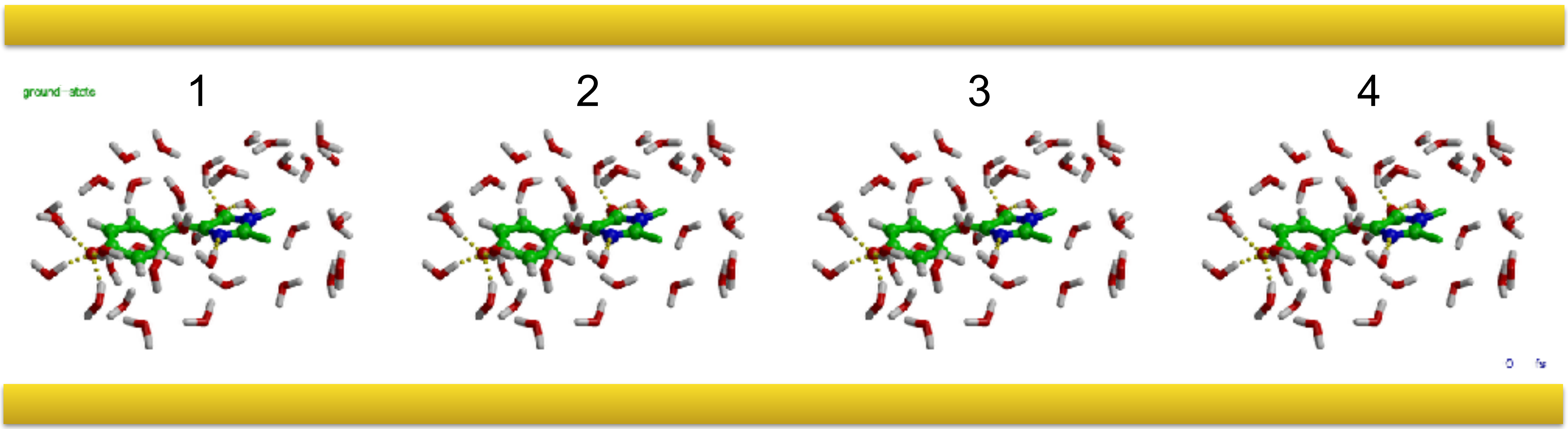
deeper minimum on lower polariton surface



Manipulating photo-chemistry with mirrors

four GFP chromophores in water in a cavity

trapped: fluorescence



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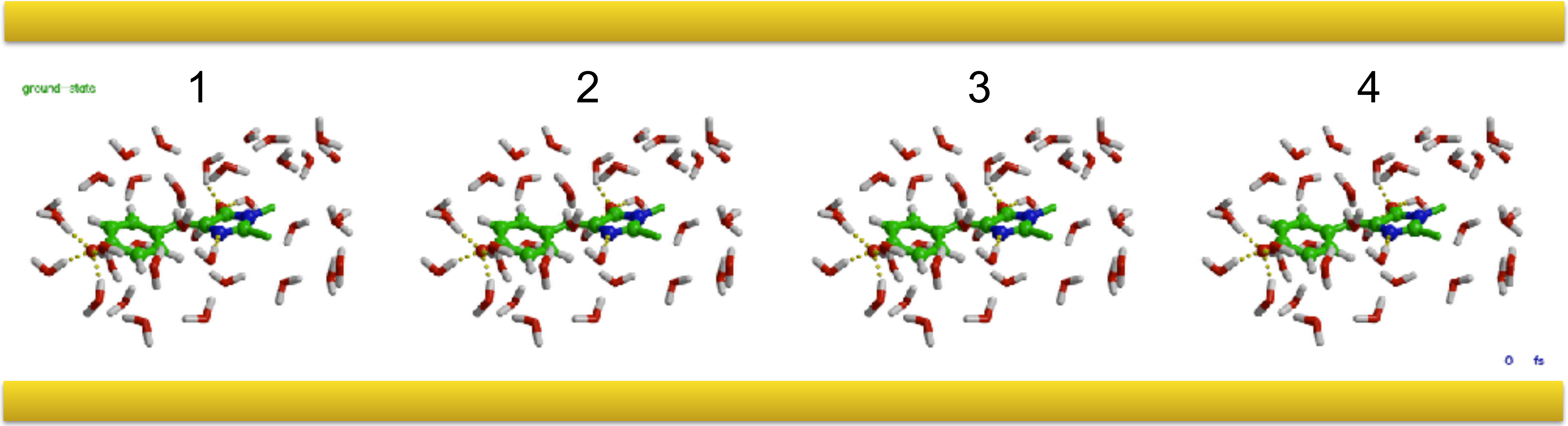

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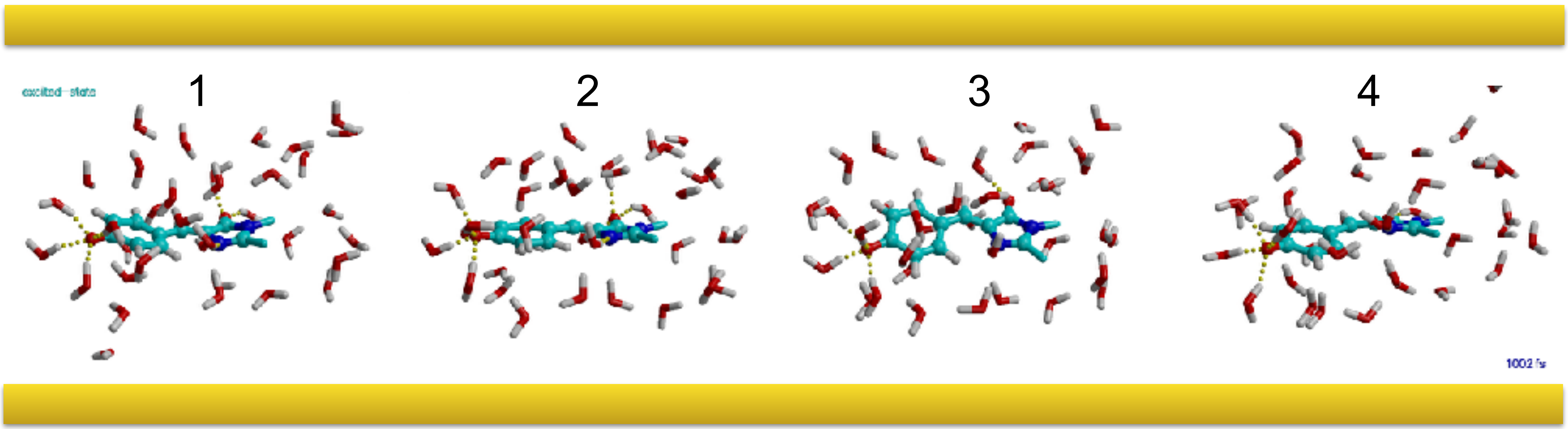
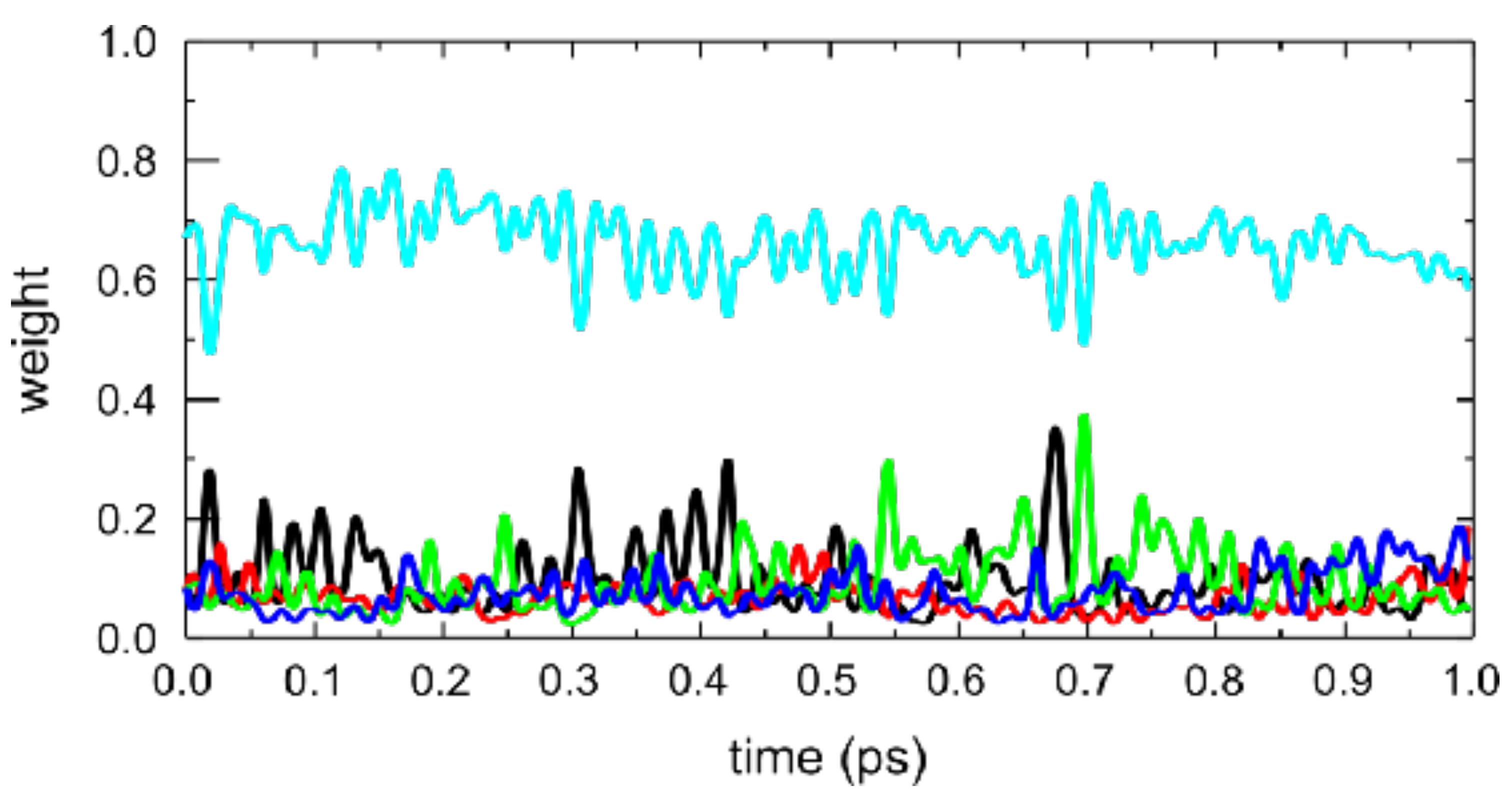




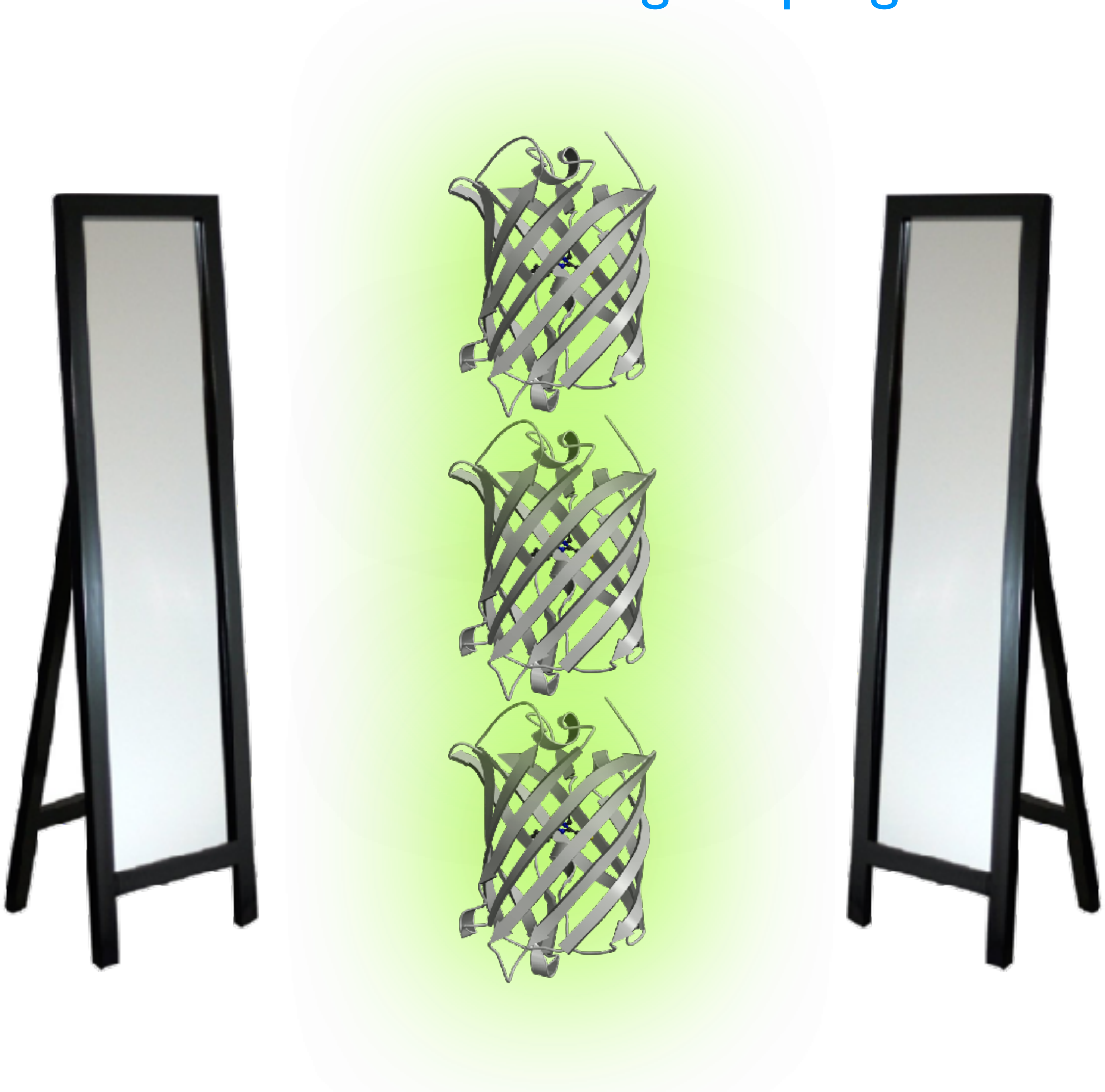
$$
\begin{aligned}
\Psi^{\mathrm{LP}} \quad = \quad & \boxed{+\beta_1^{\mathrm{LP}}|1^\star 234\rangle|0\rangle} \\
& \boxed{+\beta_2^{\mathrm{LP}}|12^\star 34\rangle|0\rangle} \\
& \boxed{+\beta_3^{\mathrm{LP}}|123^\star 4\rangle|0\rangle} \\
& \boxed{+\beta_4^{\mathrm{LP}}|1234^\star\rangle|0\rangle}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

Manipulating photo-chemistry with mirrors

summary

cavity “QED”/MM

simulations of molecules under strong coupling with confined light



Manipulating photo-chemistry with mirrors

- summary
  - cavity “QED”/MM
    - simulations of molecules under strong coupling with confined light
- new photocatalysis paradigm?
  - re-shaping potential energy surface
    - control of photo-chemical reactions

Ebbesen & coworkers: *Angew. Chem. Int. Ed.* 51 (2012) 1592–1596

Manipulating photo-chemistry with mirrors

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  - coherent transfer of energy: light harvesting

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Angew. Chem. Int. Ed. 55 (2016) 6202–6206
Nature Materials 14 (2015) 1123–1129
Coles *et al.* *Nature Materials* 13 (2014) 712–719

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  - cavity lifetimes
    - dielectric mirrors
  - interpretation of cavity spectra
    - optical filtering

Acknowledgements

Dmitry Morozov

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Oleg Blyednov

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Jussi Toppari

Siim Pikker

Eero Hulkko

Aili Asikainen

Vaibhav Modi

Tero Heikkilä

support (Euros, FLOPs & photons)

SUOMEN AKATEMIA

CSC CSC – IT CENTER FOR SCIENCE

laser lab NSC

SLAC NATIONAL ACCELERATOR LABORATORY

Simulating molecules in cavity

QED matrix elements

independent molecules interacting with cavity photon

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

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$$H_{44} = V_{\mathrm{S}_0}(\mathbf{R}_1) + V_{\mathrm{S}_0}(\mathbf{R}_2) + V_{\mathrm{S}_0}(\mathbf{R}_3)$$

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

Free electron laser

SLAC

laser parameters

Table 1 | Design and typical measured parameters for both hard (8.3 keV) and soft (0.8–2.0 keV) X-rays. The 'design' and 'hard' values are shown only at 8.3 keV. Stability levels are measured over a few minutes.

Parameter	Design	Hard	Soft	Unit
Electrons				
Charge per bunch	1	0.25	0.25	nC
Single bunch repetition rate	120	30	30	Hz
Final linac e^- energy	13.6	13.6	3.5–6.7	GeV
Slice† emittance (injected)	1.2	0.4	0.4	μm
Final projected† emittance	1.5	0.5–1.2	0.5–1.6	μm
Final peak current	3.4	2.5–3.5	0.5–3.5	kA
Timing stability (r.m.s.)	120	50	50	fs
Peak current stability (r.m.s.)	12	8–12	5–10	%
X-rays				
FEL gain length	4.4	3.5	~1.5	m
Radiation wavelength	1.5	1.5	6–22	Å
Photons per pulse	2.0	1.0–2.3	10–20	10^{12}
Energy in X-ray pulse	1.5	1.5–3.0	1–2.5	mJ
Peak X-ray power	10	15–40	3–35	GW
Pulse length (FWHM)	200	70–100	70–500	fs
Bandwidth (FWHM)	0.1	0.2–0.5	0.2–1.0	%
Peak brightness (estimated)	8	20	0.3	10^{32} *
Wavelength stability (r.m.s.)	0.2	0.1	0.2	%
Power stability (r.m.s.)	20	5–12	3–10	%

*Brightness is photons per phase space volume, or photons s^{-1} mm^{-2} $mrad^{-2}$ per 0.1% spectral bandwidth.
†'Slice' refers to femtosecond-scale time slices and 'projected' to the full time-projected (that is, integrated) emittance of the bunch.

P. Emma *et al.*, *Nature Photonics* **4** (2010) 641-647

Simulating molecules in cavity

QED matrix elements

independent molecules interacting with cavity photon

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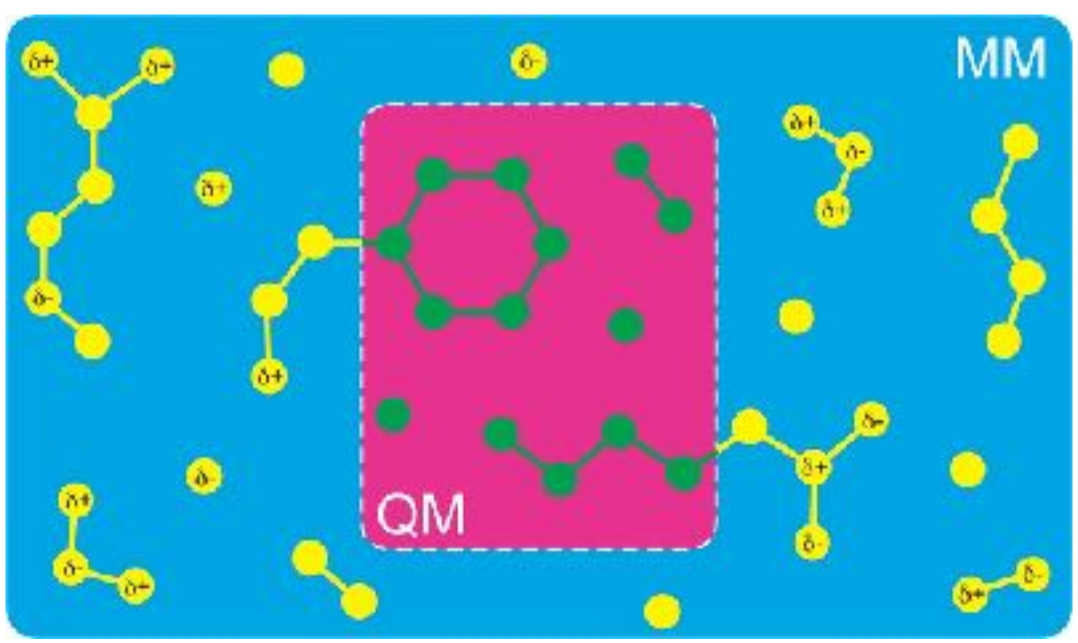
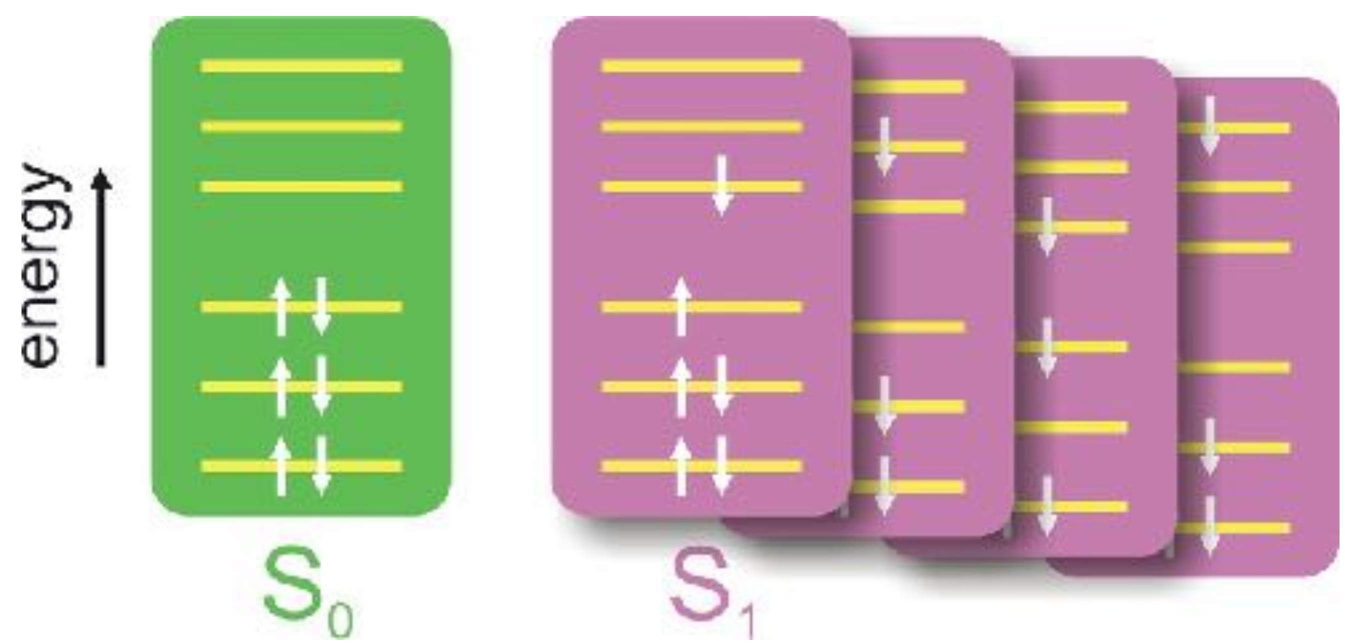
QM/MM energies in ground (S_0) and excited (S_1) states





Boggio-Pasqua, Burmeister, Robb, Groenhof *Phys. Chem. Chem. Phys.* **14** (2012) 7912

Simulating molecules in cavity

QED matrix elements

Calvin Luk

independent molecules interacting with cavity photon

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

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Jussi Toppari

Johannes Feist

diagonalize

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

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

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

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

transitions between states: surface hopping

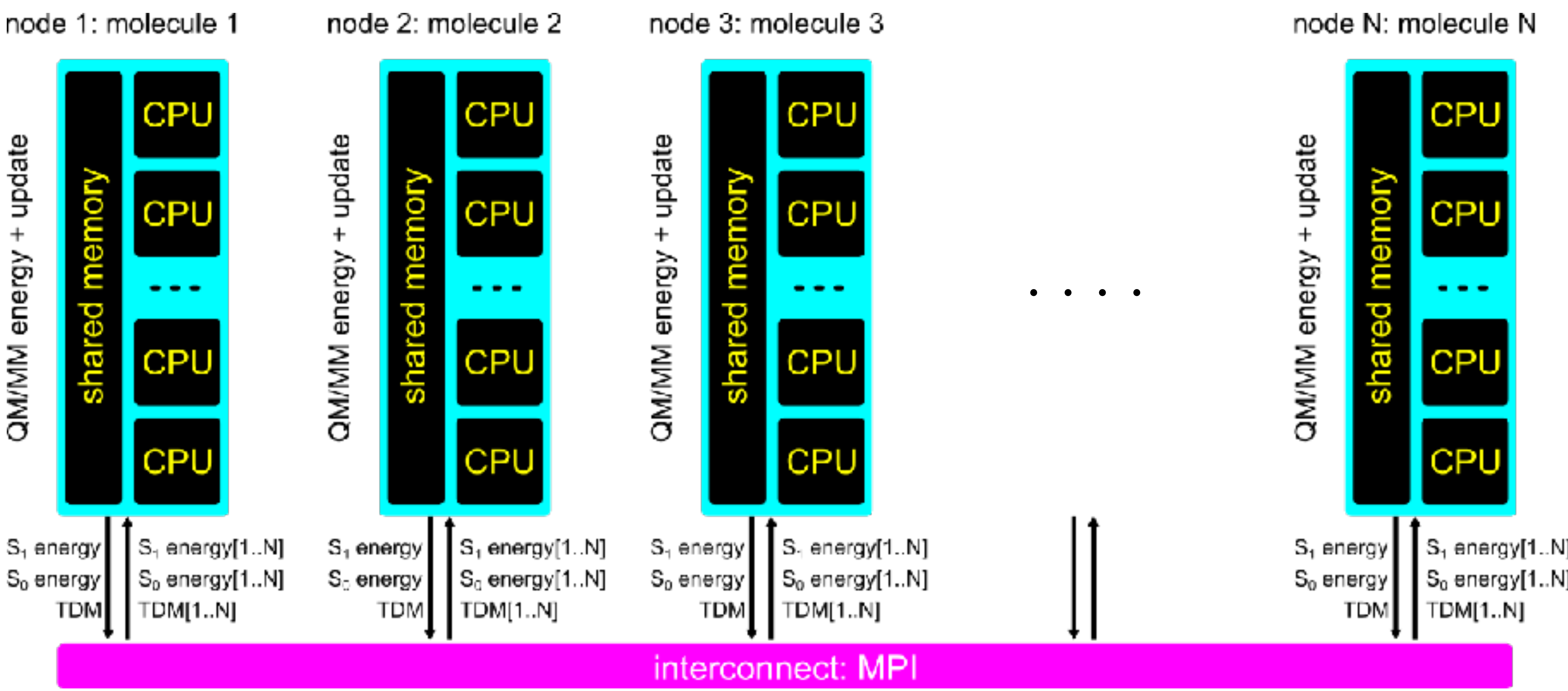
J. Chem. Theory Comput. 13 (2017) 4324

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



www.gromacs.org

Simulating molecules in cavity

implementation in Gromacs

Sisu.csc.fi: 1688 TFlop/s

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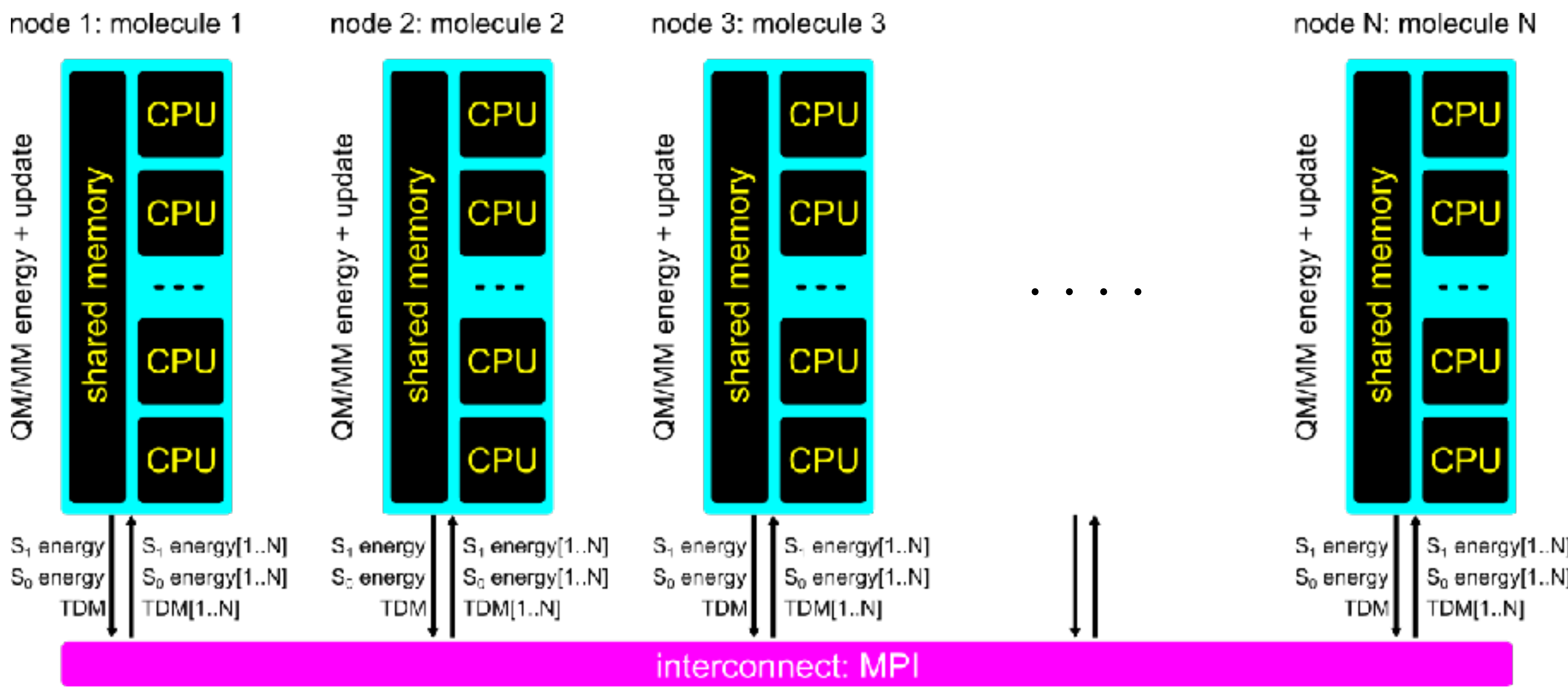


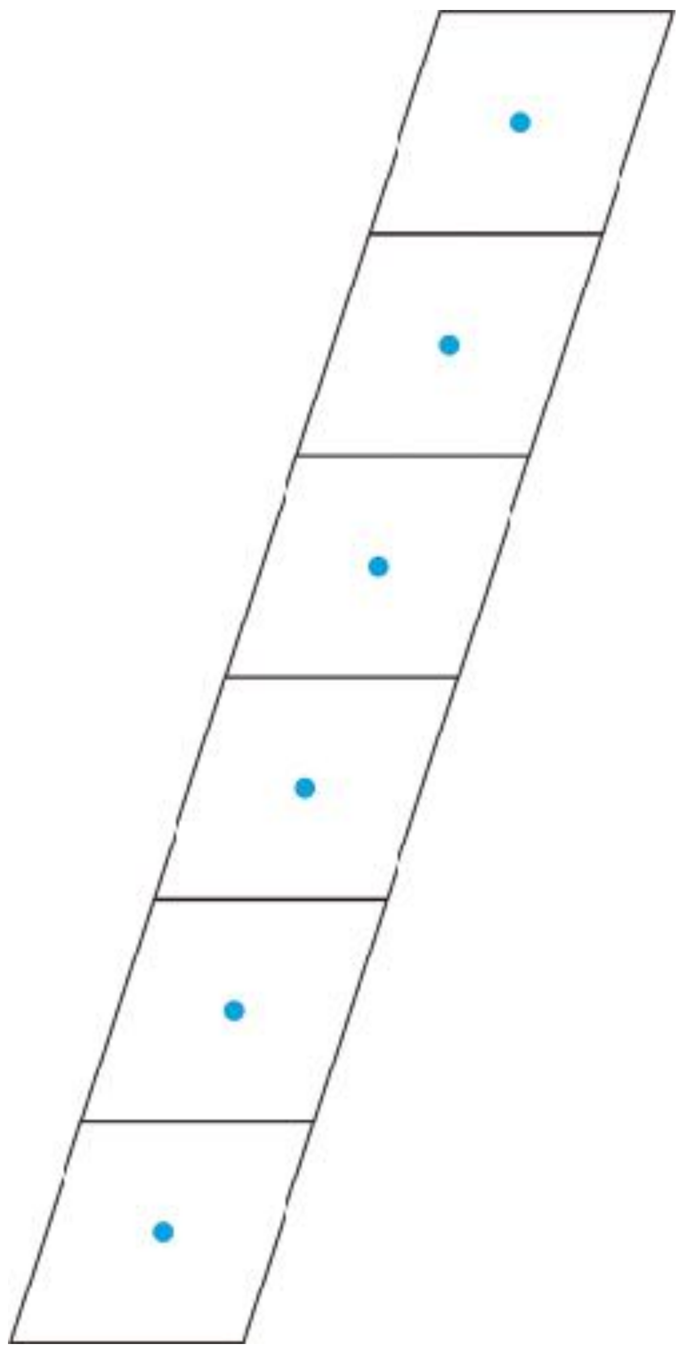
new world record?

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

X-ray crystallography

scattering from one atom in the unitcell

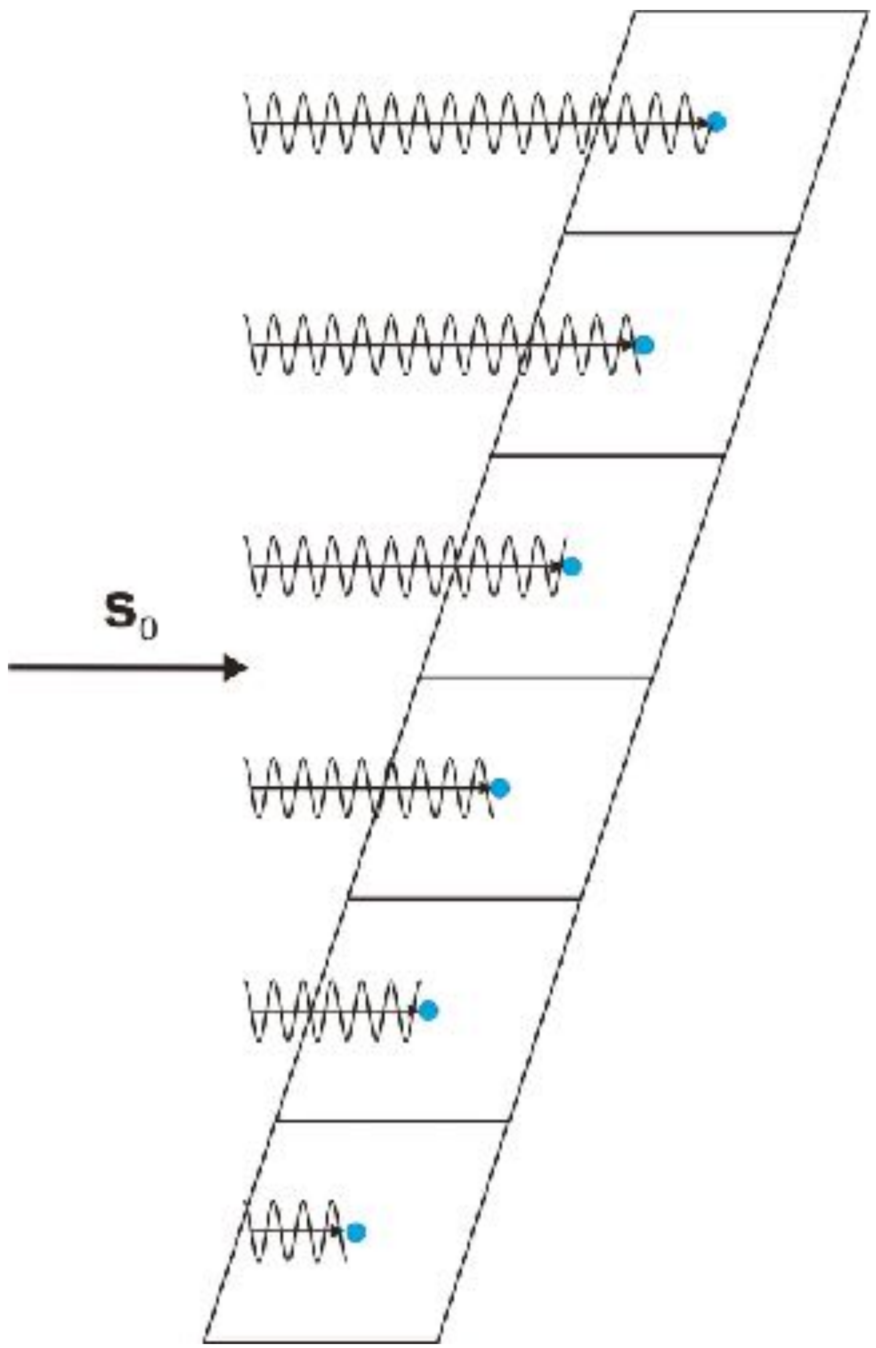
crystal (i.e lattice of unitcells)



X-ray crystallography

scattering with one atom in the unitcell

crystal (i.e lattice of unitcells)



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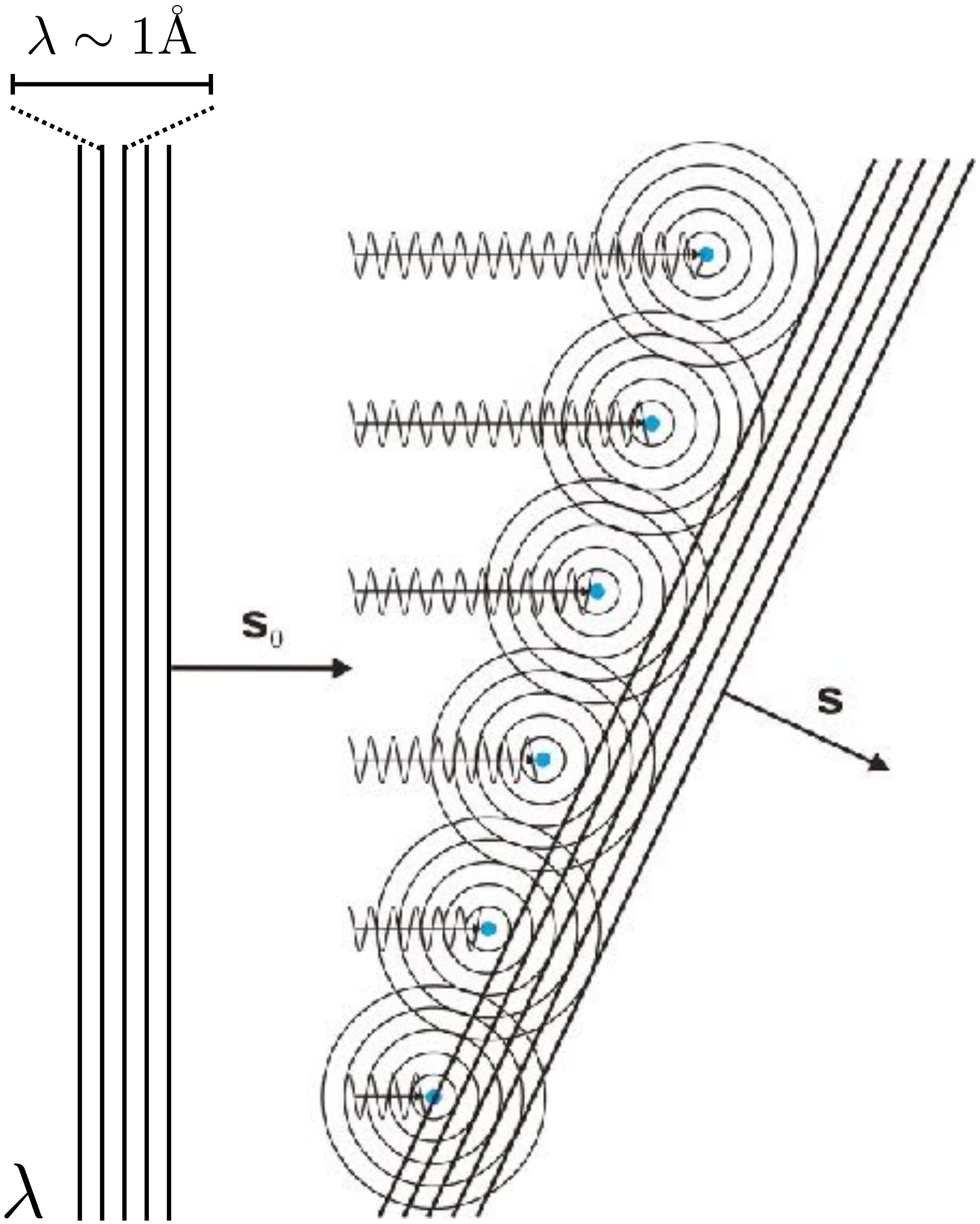

scattering vector

$$\mathbf{S} \equiv (\mathbf{s} - \mathbf{s}_0)/\lambda$$

X-ray crystallography

scattering with one atom in the unitcell

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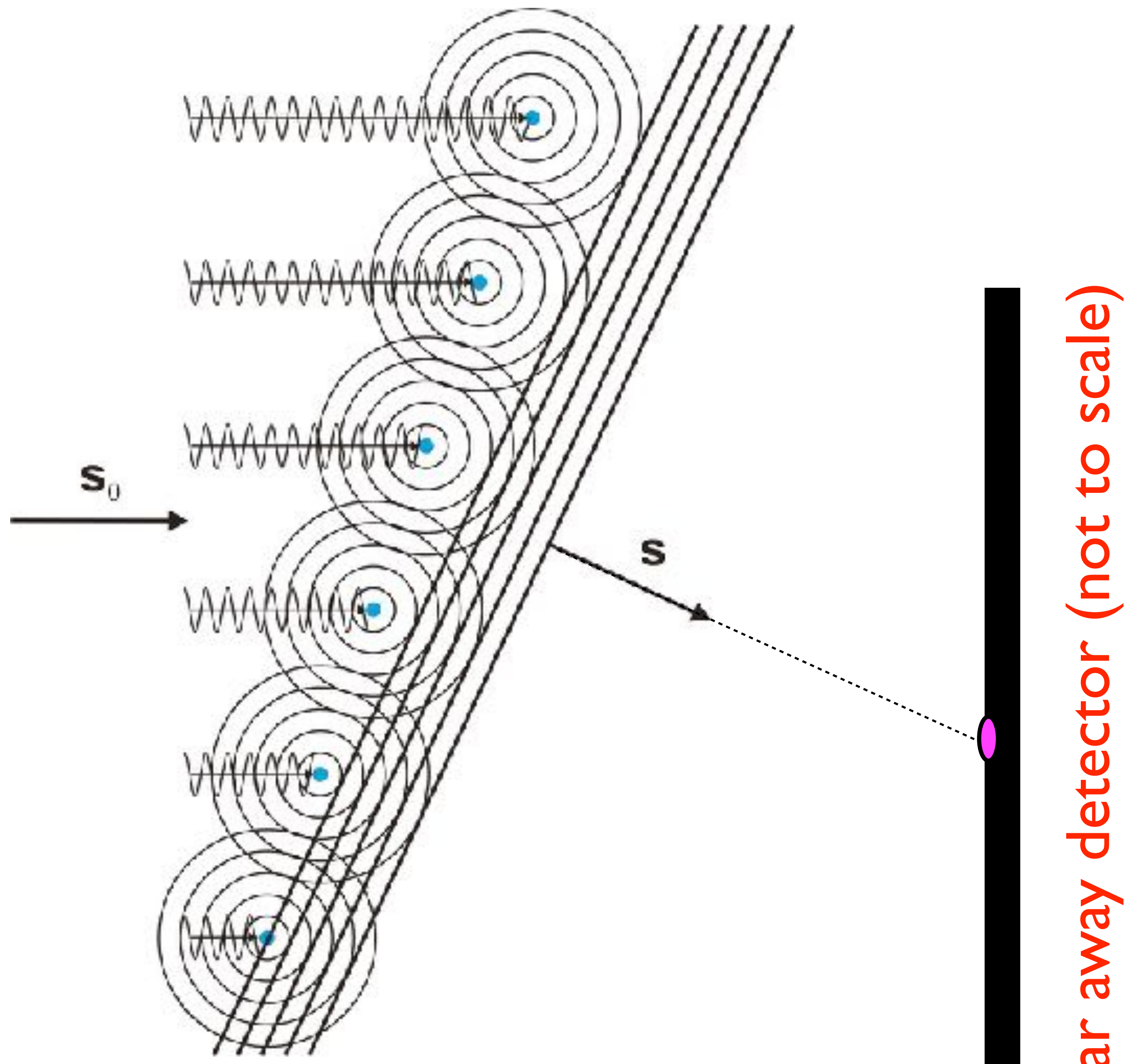

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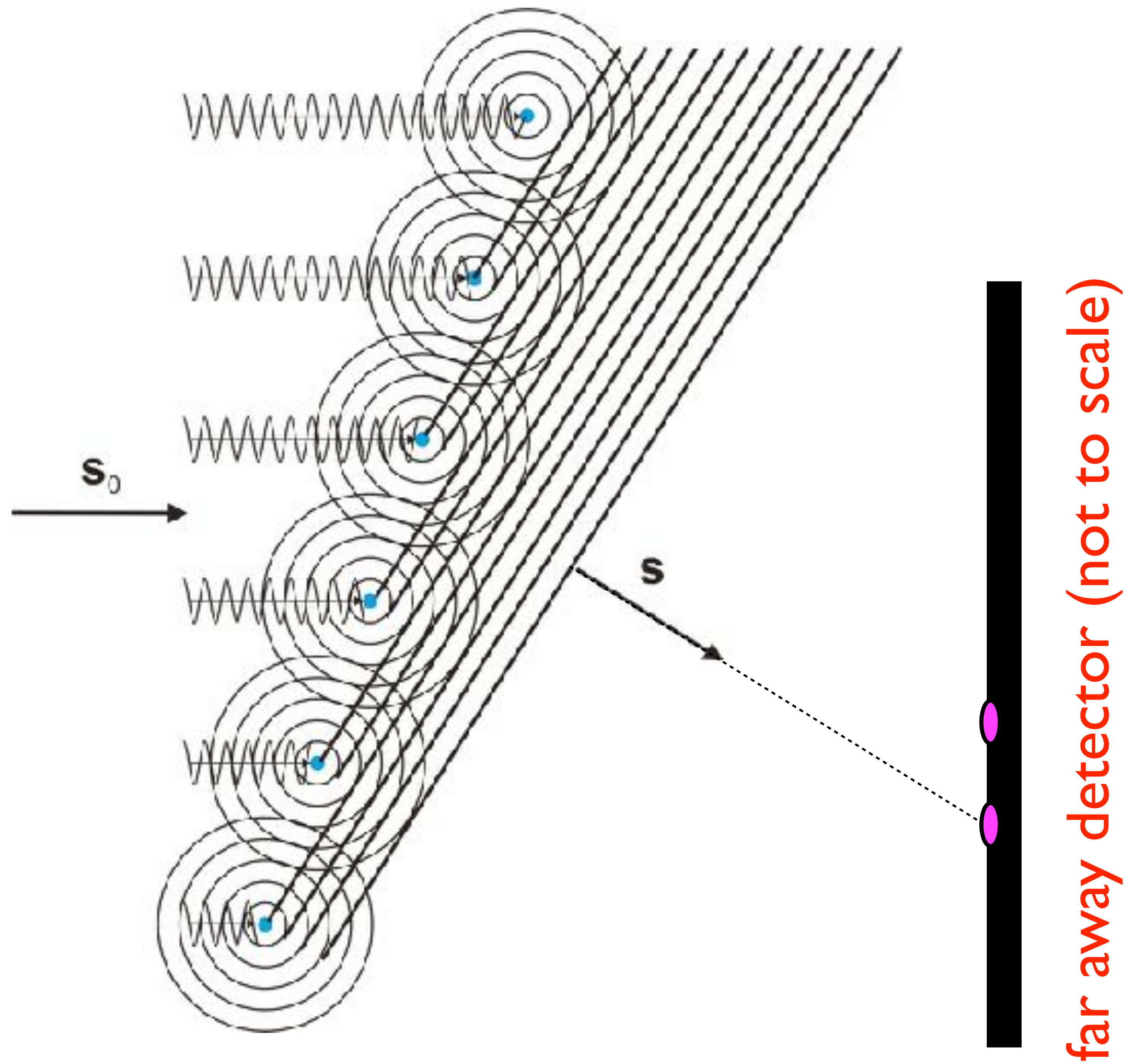

scattering vector

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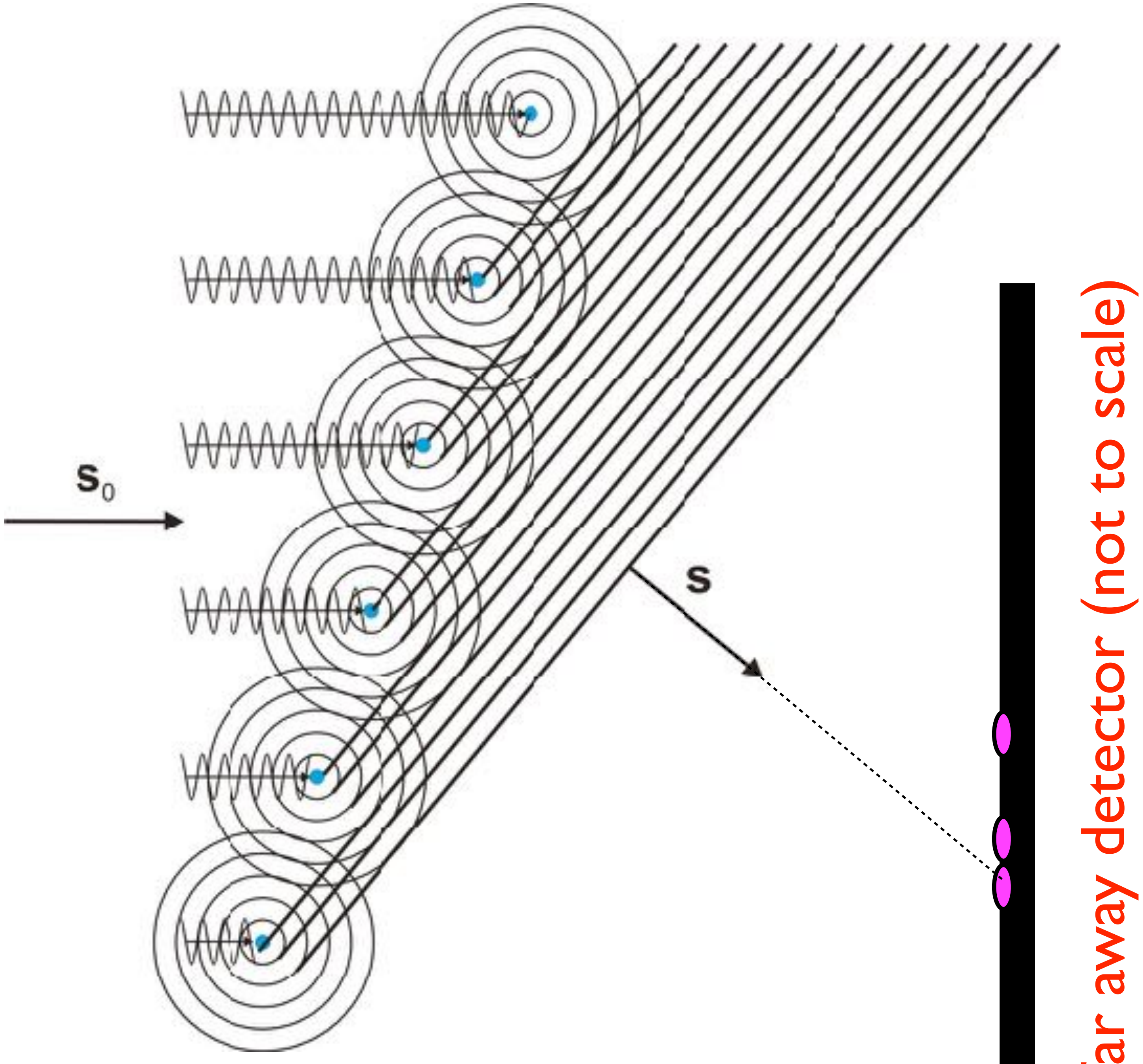
X-ray crystallography

scattering with one atom in the unitcell

crystal (i.e lattice of unitcells)

discrete scattering spots: diffraction

reflections



scattering vector

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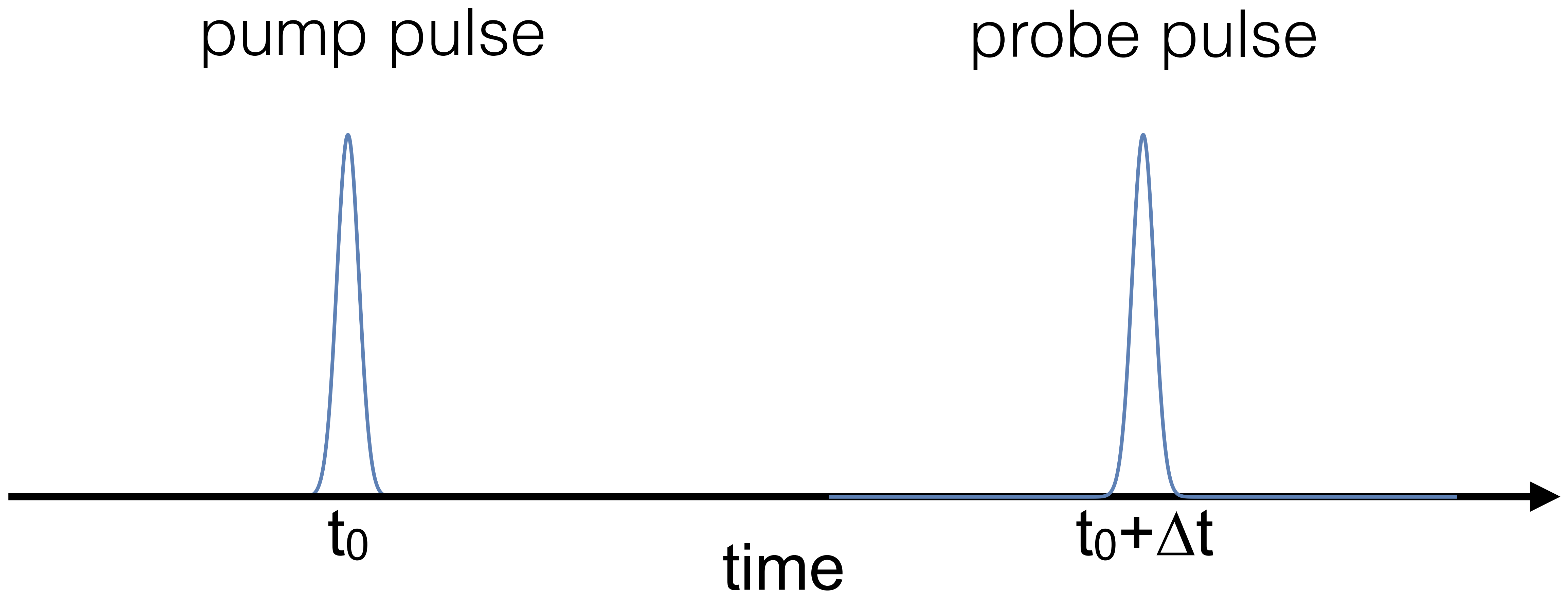
Time-resolved spectroscopy

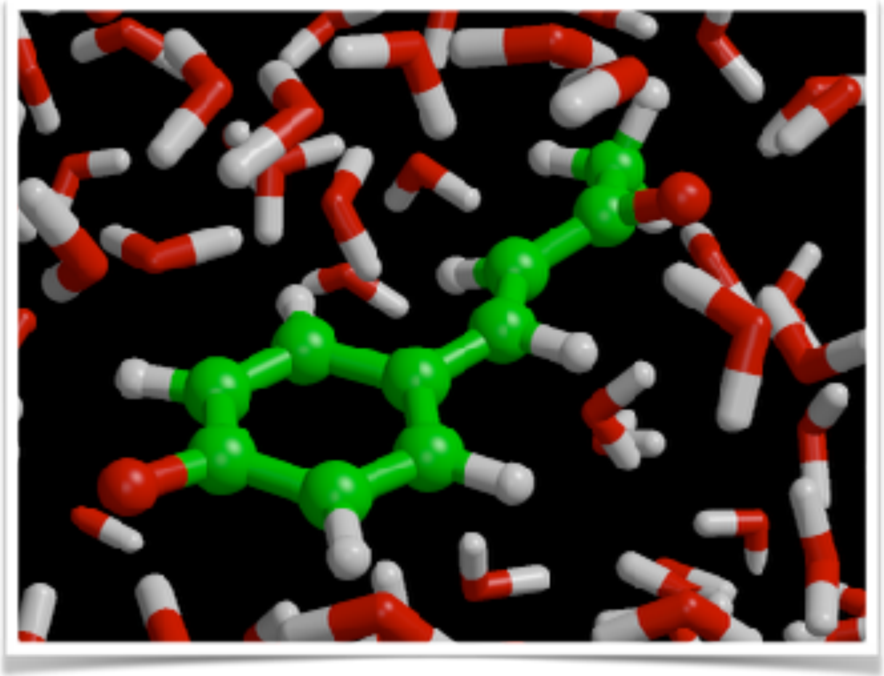
linear pump-probe spectroscopy



Time-resolved spectroscopy

linear pump-probe spectroscopy

idealised example: PCK in water

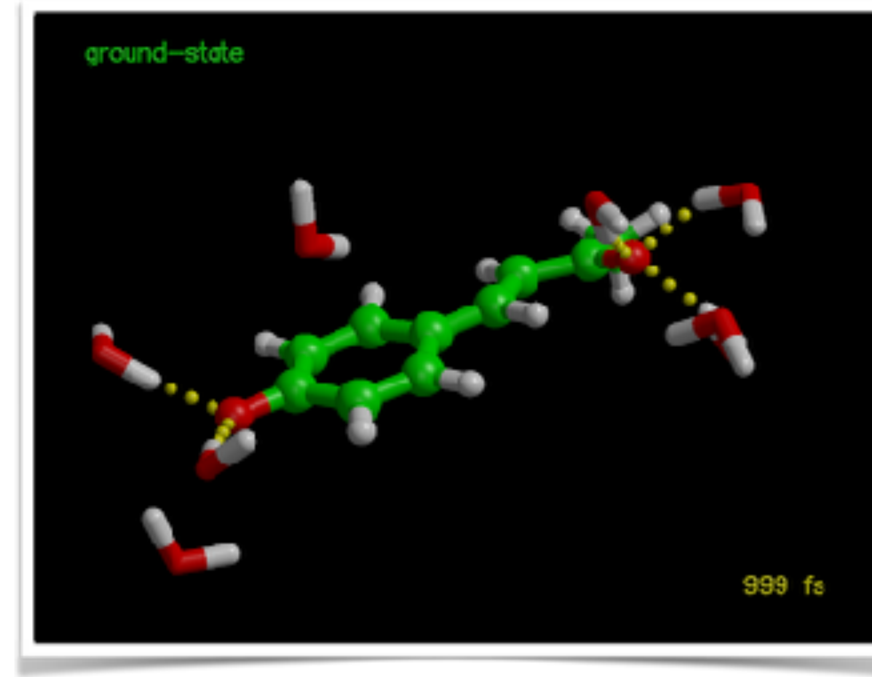


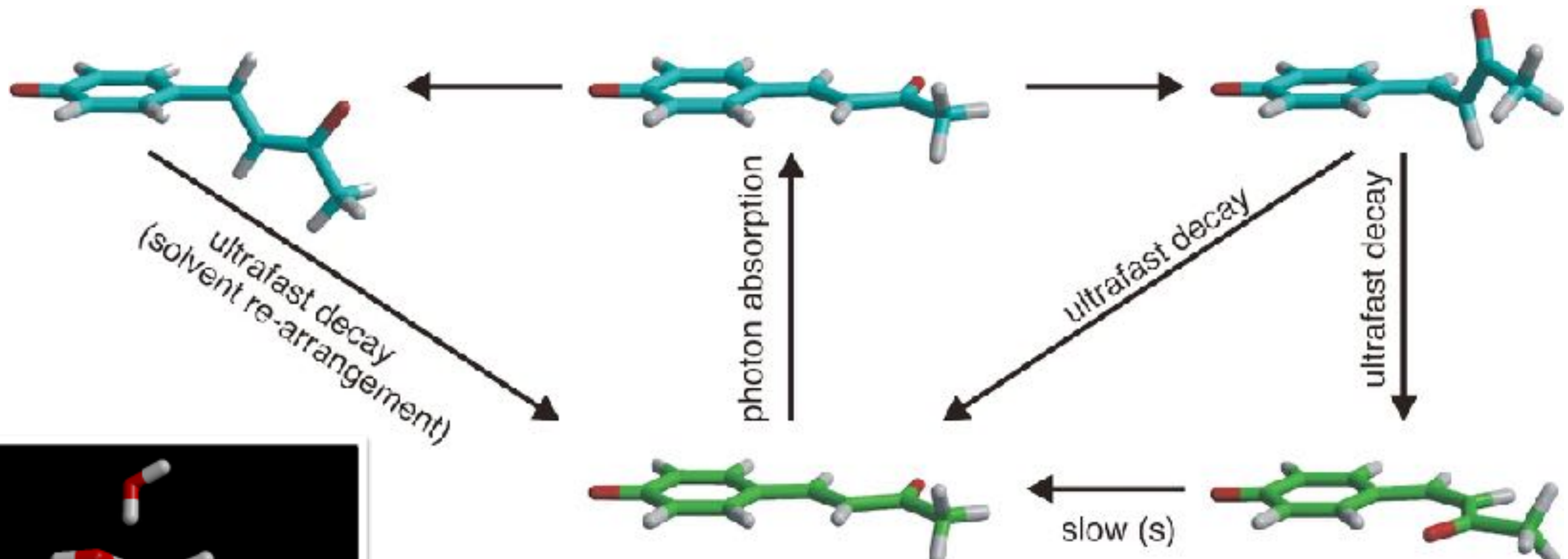
Time-resolved spectroscopy

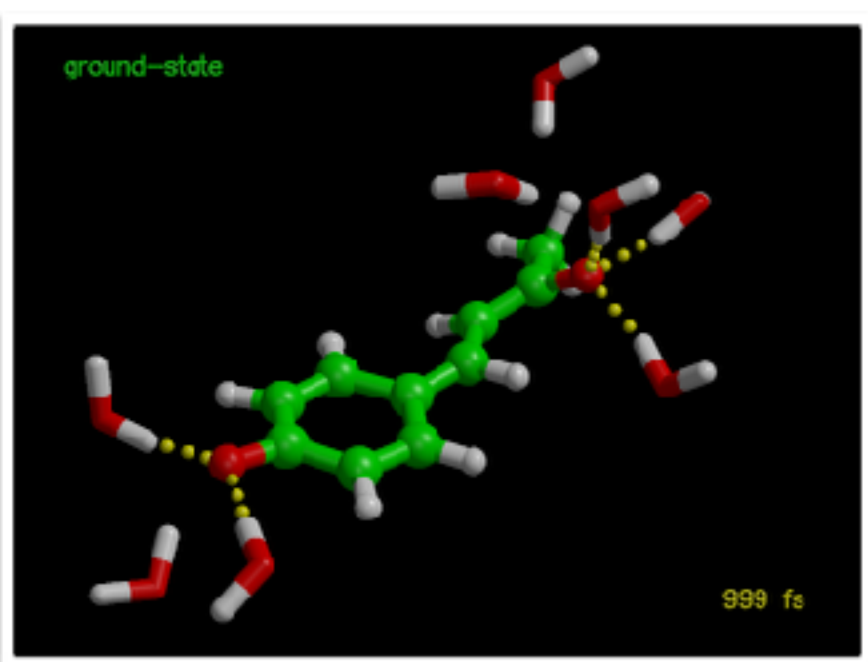
linear pump-probe spectroscopy

idealised example: PCK in water

assuming our simulations are correct ;-)



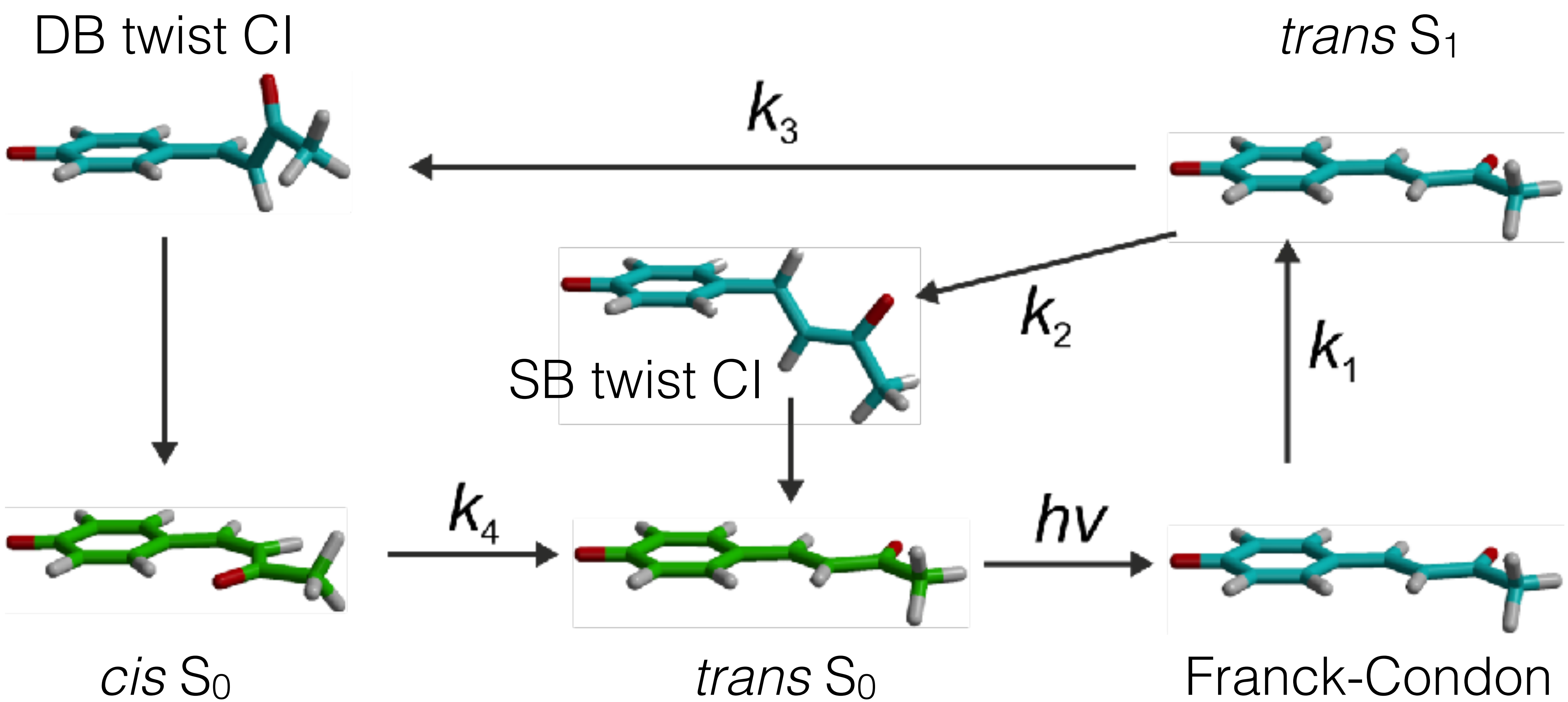




Time-resolved spectroscopy

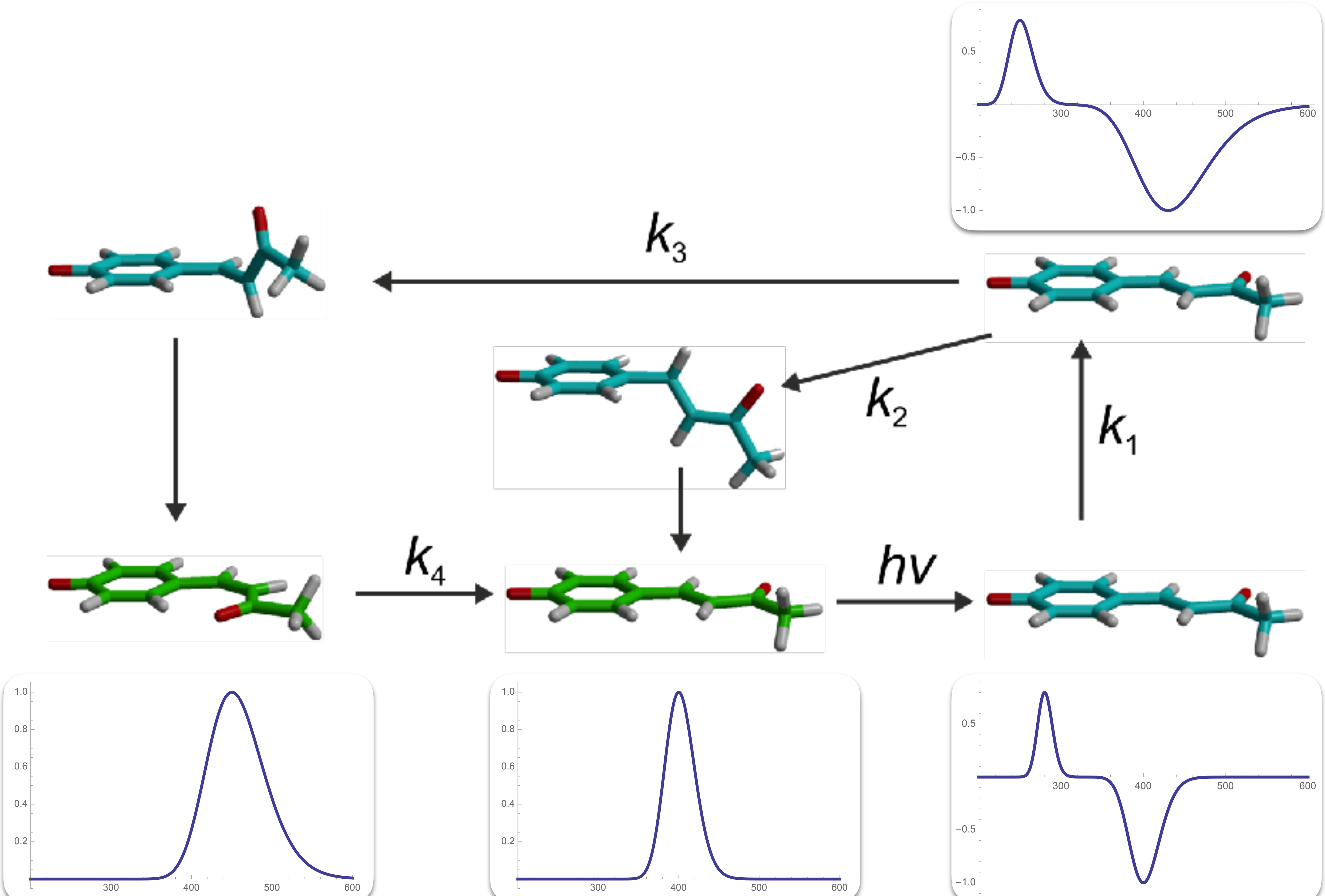
note: different orientation of reaction scheme!

horizontal excitation ;-)



Time-resolved spectroscopy

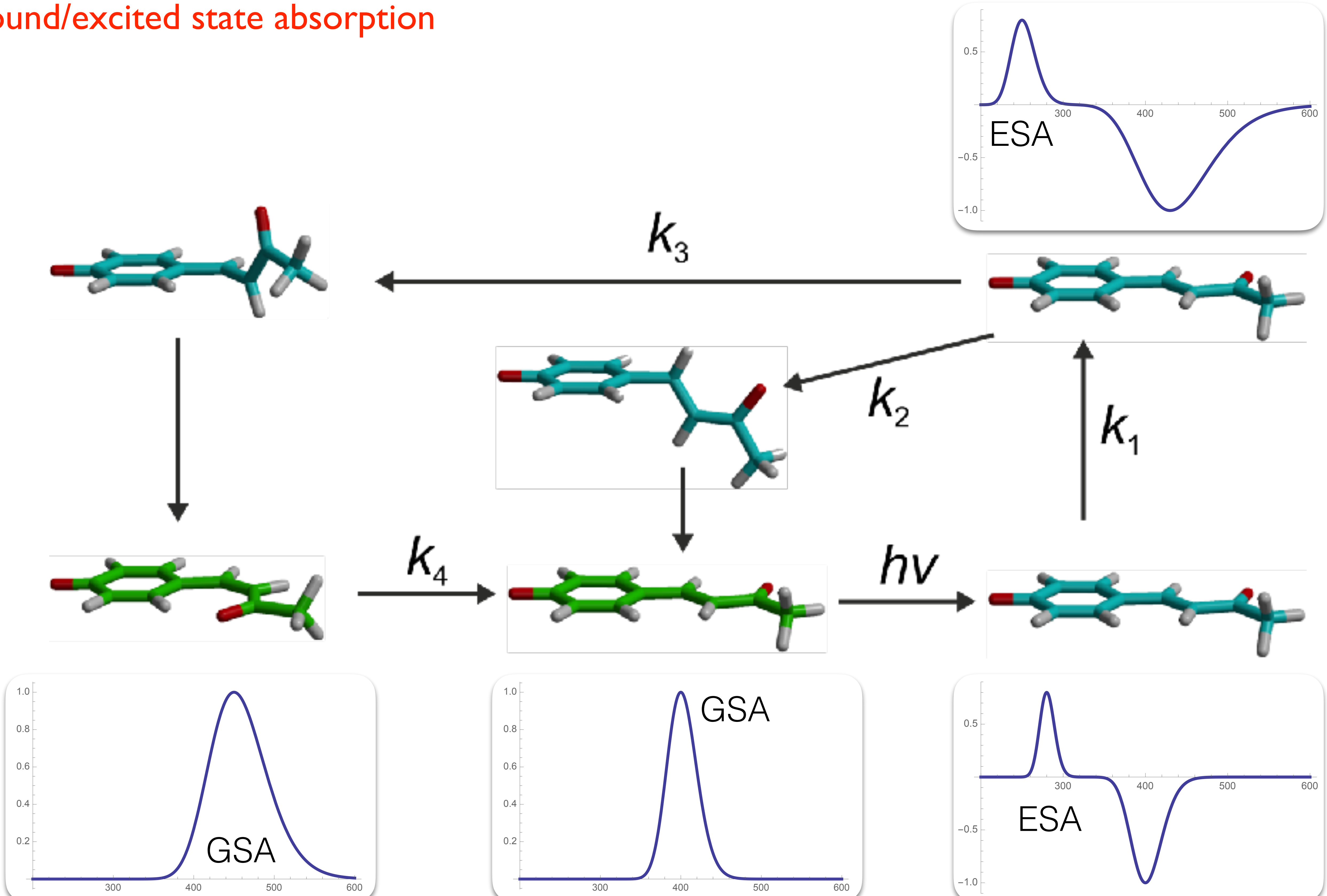
intermediates are species with own spectrum:



Time-resolved spectroscopy

intermediates are species with own spectrum:

ground/excited state absorption

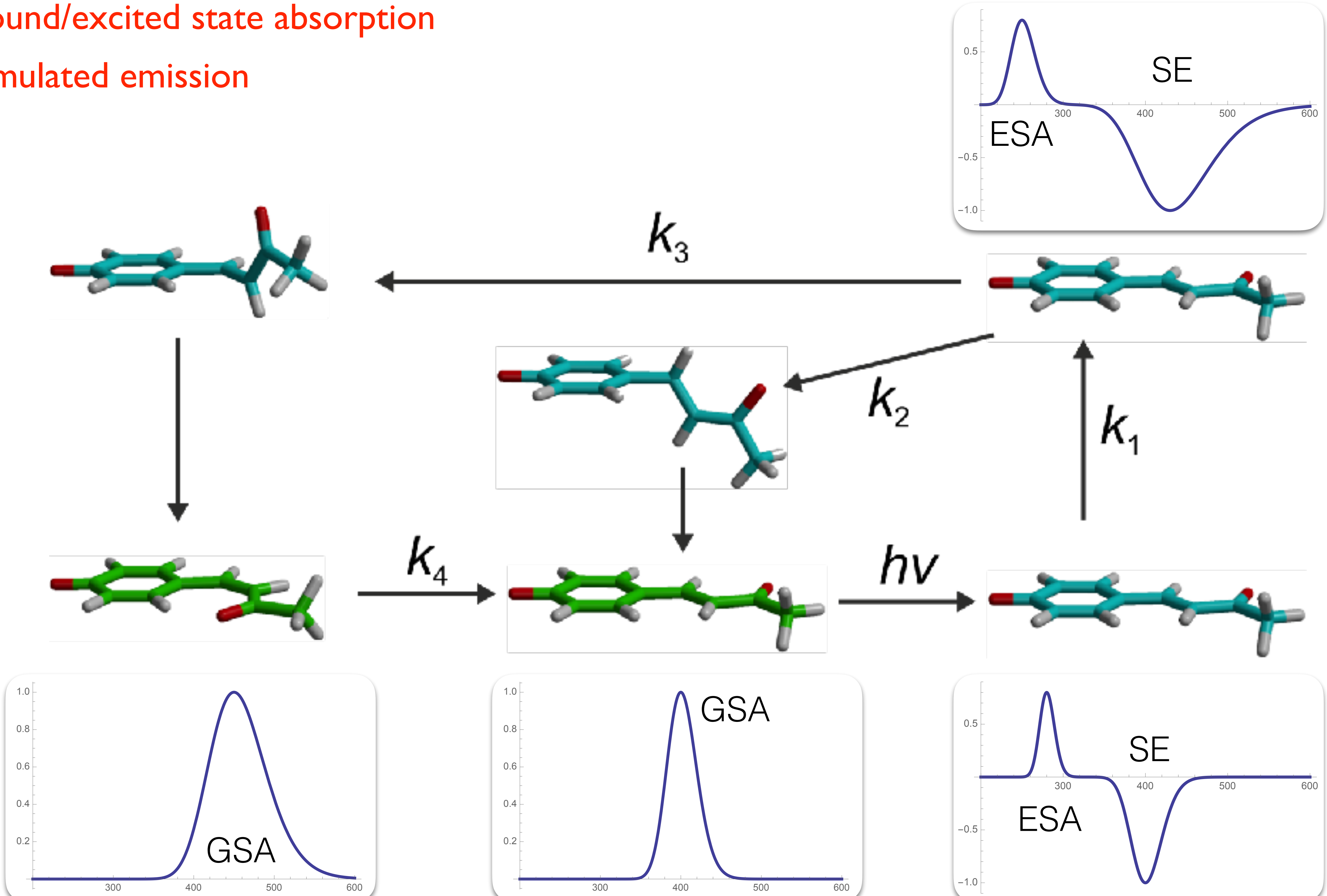


Time-resolved spectroscopy

intermediates are species with own spectrum:

ground/excited state absorption

stimulated emission



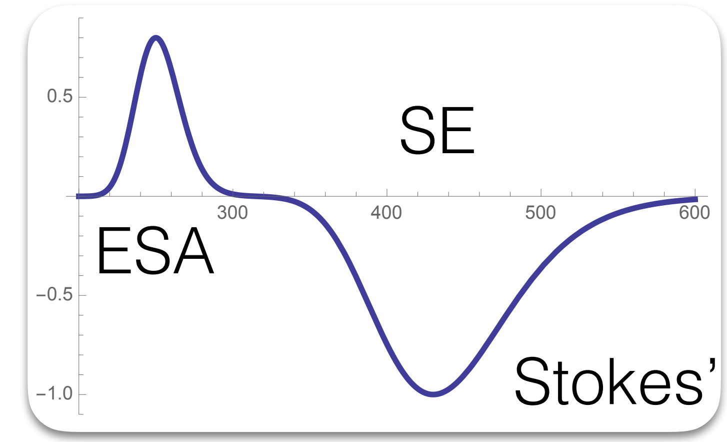
Time-resolved spectroscopy

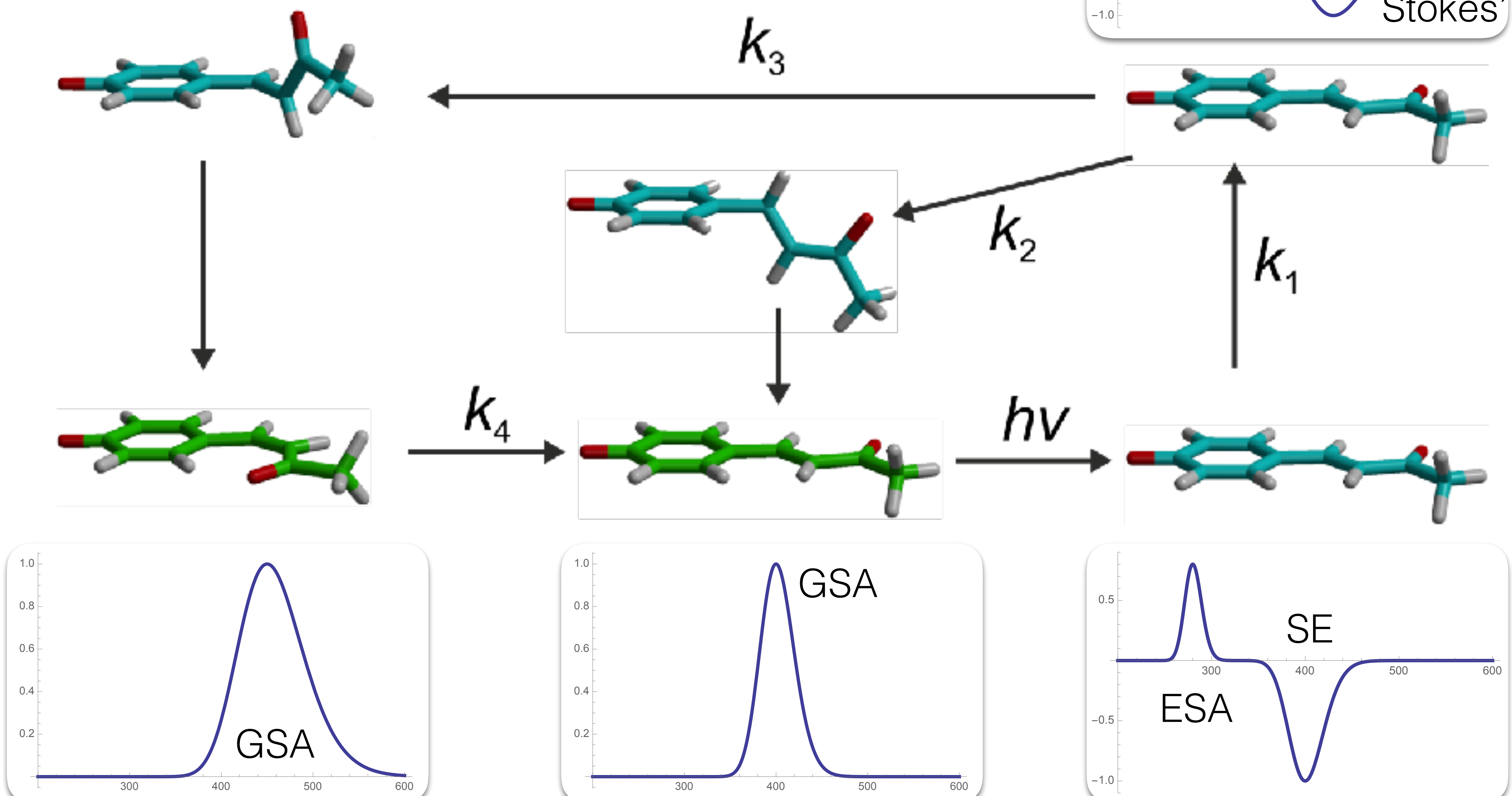
intermediates are species with own spectrum:

ground/excited state absorption

stimulated emission

Stokes' shift



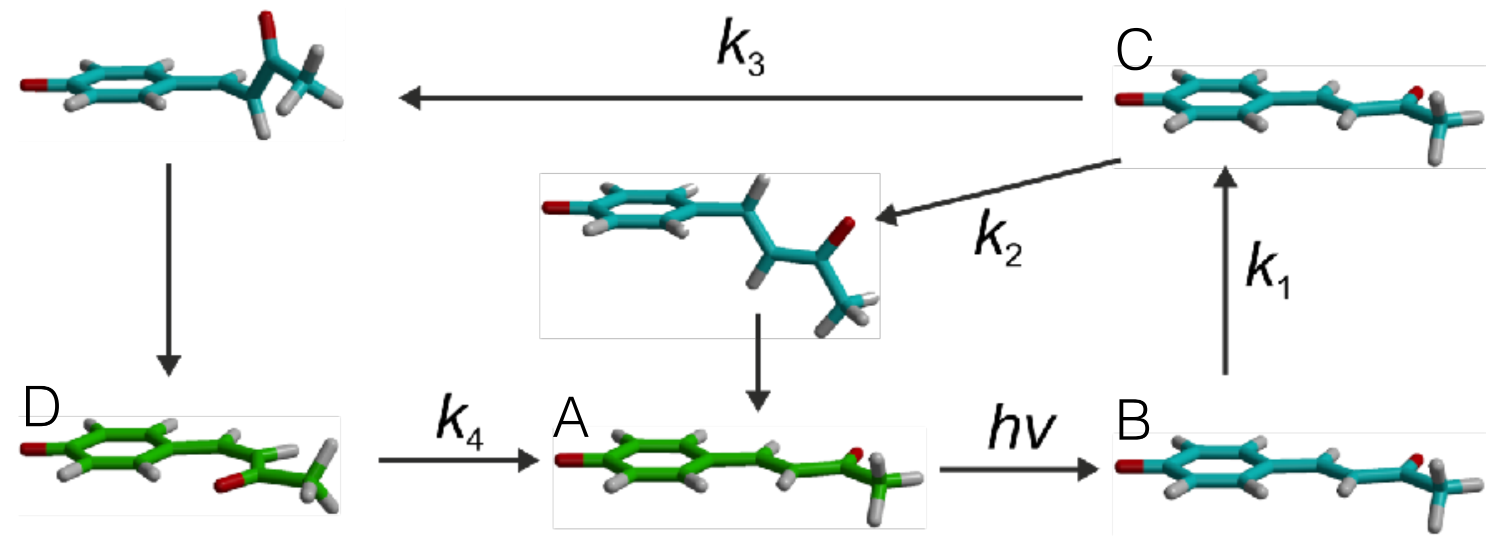


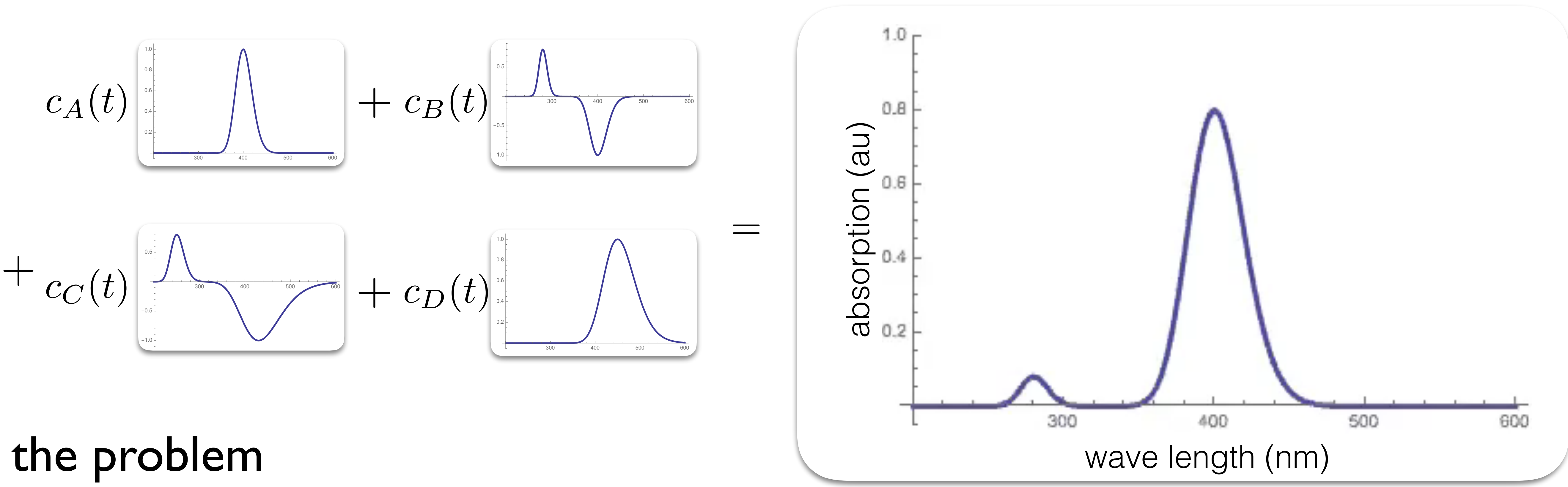
Time-resolved spectroscopy

time-dependent spectrum

linear superposition of SAS

$$S(\lambda, t) = \sum_i c_i(t) s_i(\lambda)$$





the problem

from atomistic model to spectral signal: easy

from spectral signal to atomistic model: difficult

heavily underdetermined optimisation problem