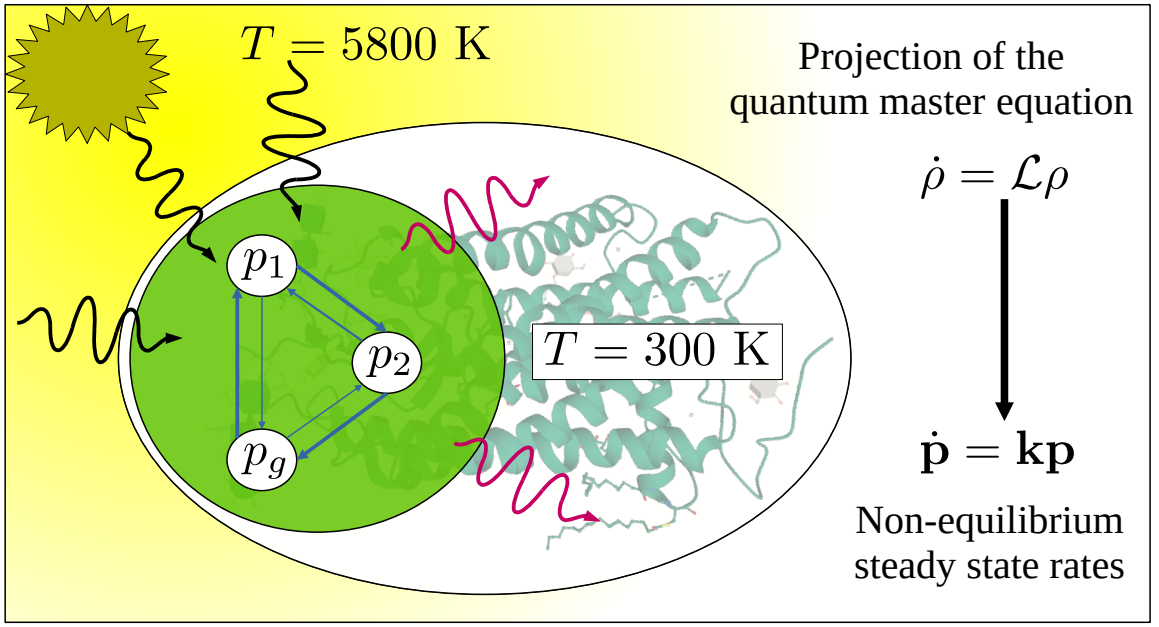
Université Gustave Eiffel

MSME Laboratoire Modélisation et Simulation Multi Echelle

cnrs dépasser les frontières

Reaction Timescales for Non-Adiabatic Processes in Non-Equilibrium Steady States

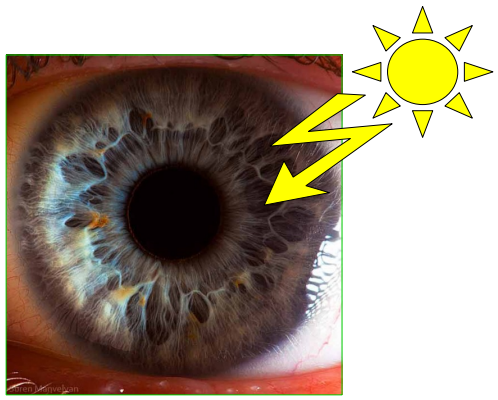


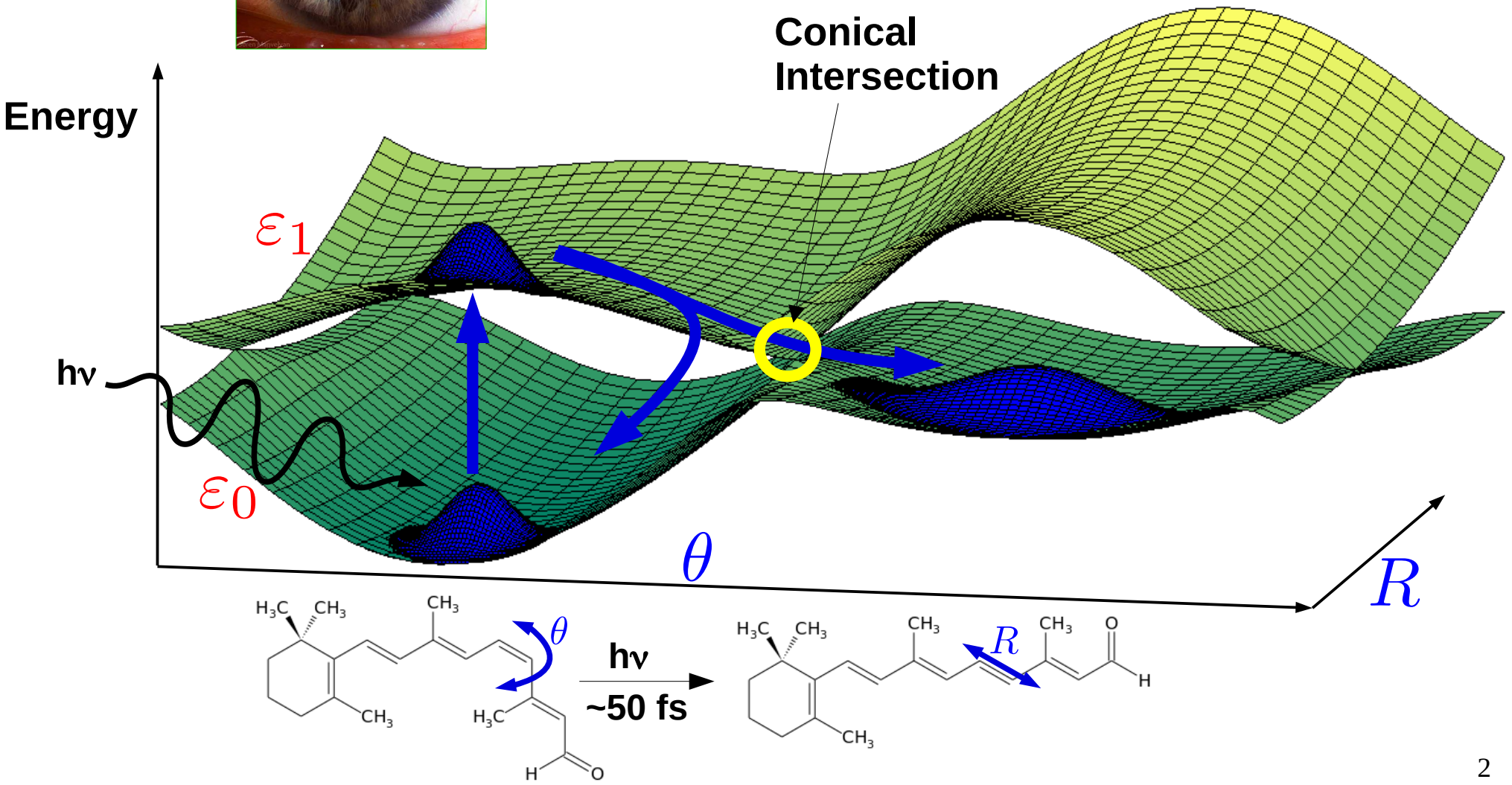
Loïc Joubert-Doriol[a], Kenneth A. Jung[b], Artur F. Izmaylov[b] & Paul Brumer[b]

[a]MSME, Université Gustave Eiffel, France
[b]CPTG, University of Toronto, Canada

Online VISTA Seminar – Oct. 28, 2026

Example from the vision process





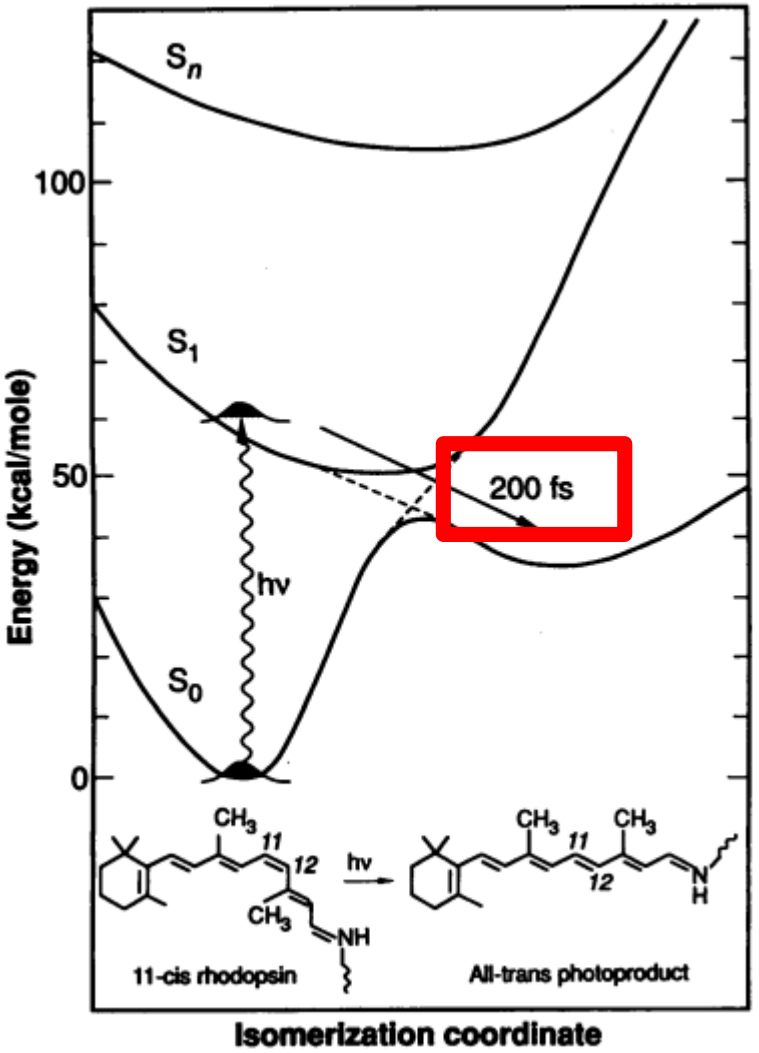
D. Polli *et al*. *Nature* 467, 440 (2010)
P. J. M. Johnson *et al. J. Phys. Chem. B* 121, 4040 (2017)

Evidence for the ultra-fast isomerization

The First Step in Vision: Femtosecond Isomerization of Rhodopsin

R. W. SCHOENLEIN, L. A. PETEANU, R. A. MATHIES, C. V. SHANK

The kinetics of the primary event in vision have been resolved with the use of femtosecond optical measurement techniques. The 11-*cis* retinal prosthetic group of rhodopsin is excited with a 35-femtosecond pump pulse at 500 nanometers, and the transient changes in absorption are measured between 450 and 580 nanometers with a 10-femtosecond probe pulse. Within 200 femtoseconds, an increased absorption is observed between 540 and 580 nanometers, indicating the formation of photoproduct on this time scale. These measurements demonstrate that the first step in vision, the 11-*cis*→11-*trans* torsional isomerization of the rhodopsin chromophore, is essentially complete in only 200 femtoseconds.



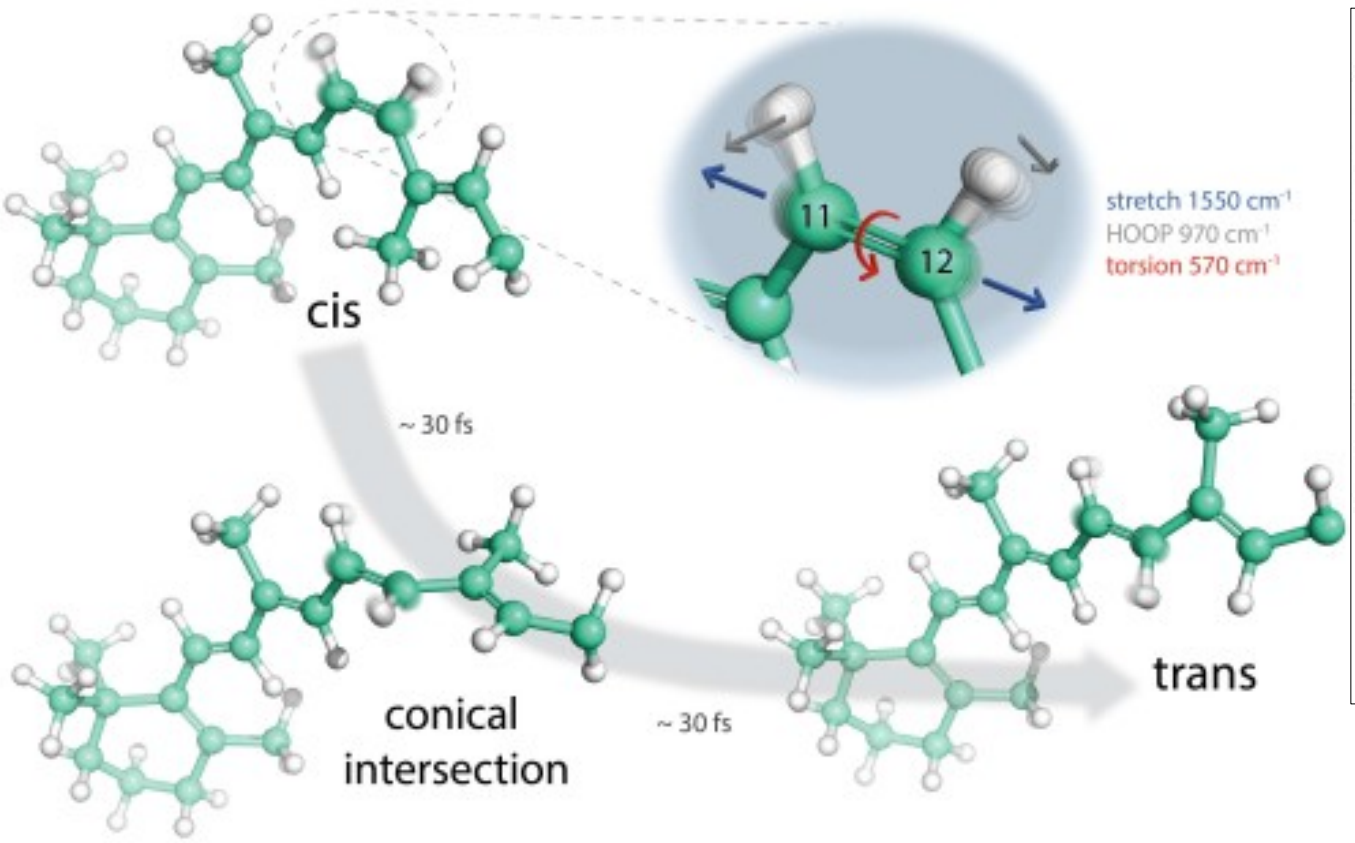
R. W. Schoenlein, L. A. Peteanu, R. A. Mathies, & C. V. Shank, *Science* 254, 412 (1991)

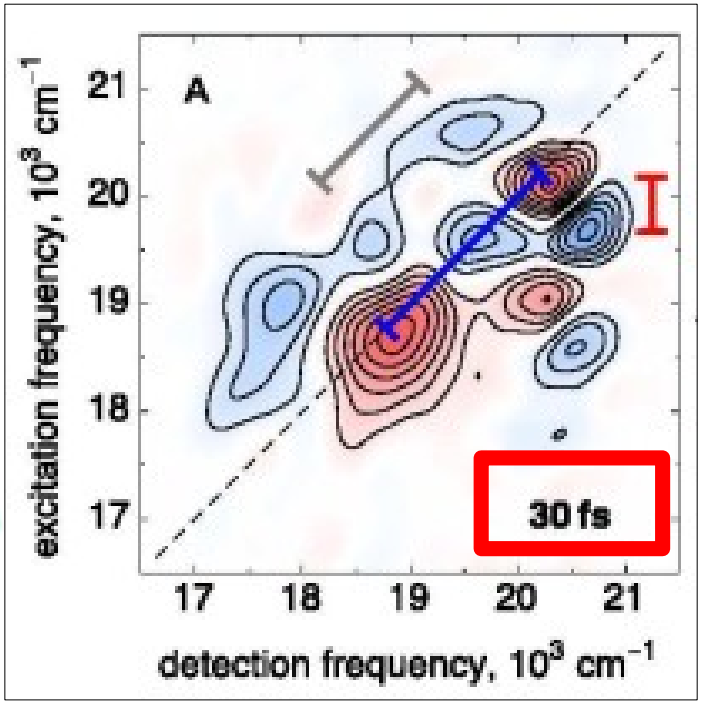
… and even faster isomerization

THE JOURNAL OF PHYSICAL CHEMISTRY B
Article
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The Primary Photochemistry of Vision Occurs at the Molecular Speed Limit

Philip J. M. Johnson,[†] Marwa H. Farag,[‡,§] Alexei Halpin,[†] Takefumi Morizumi,[∥] Valentyn I. Prokhorenko,[§] Jasper Knoester,[‡] Thomas L. C. Jansen,[‡] Oliver P. Ernst,[∥,⊥] and R. J. Dwayne Miller*[,†,§]

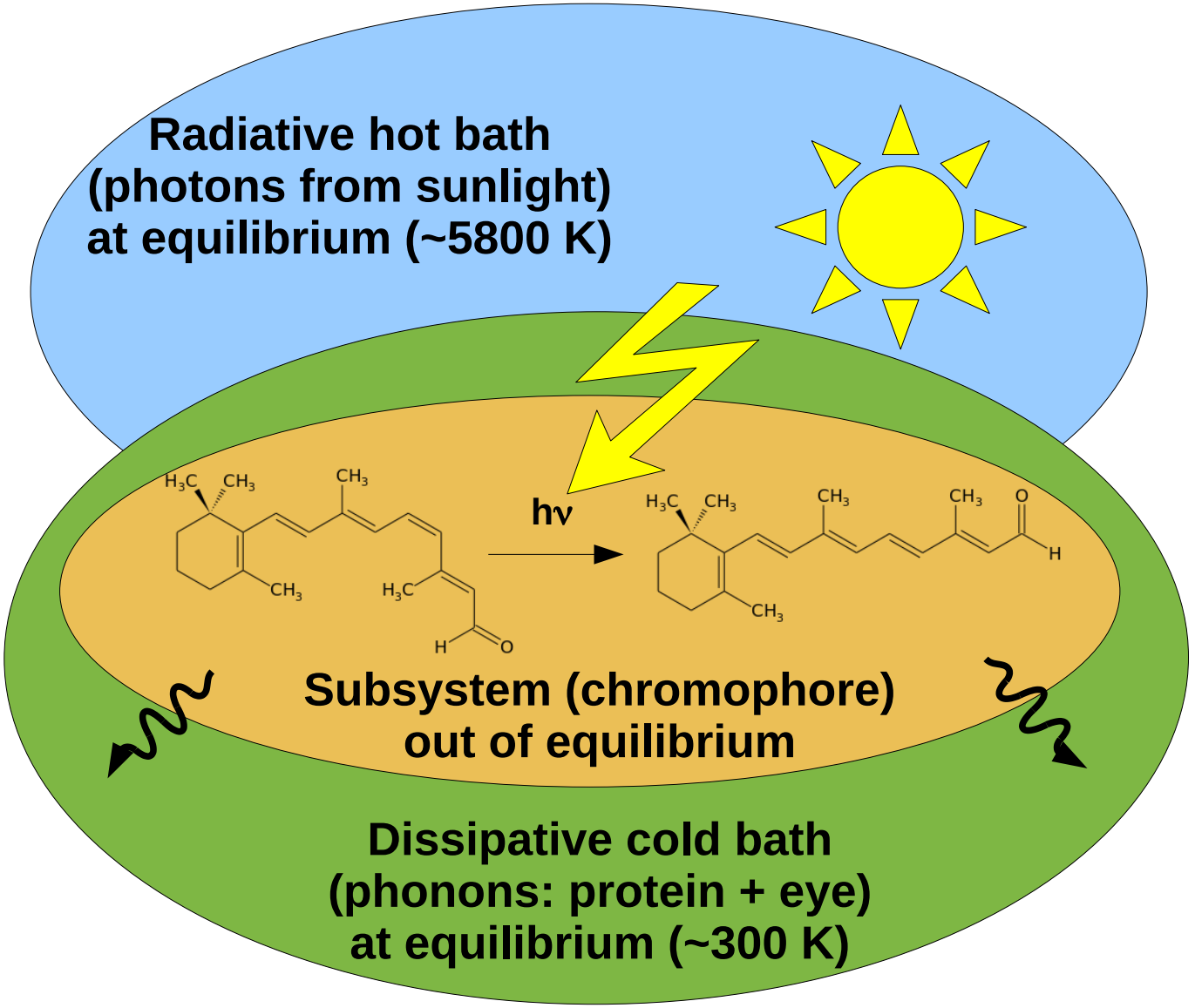




Pump = 11 fs

P. J. M. Johnson et al. *J. Phys. Chem. B* 121, 4040 (2017)

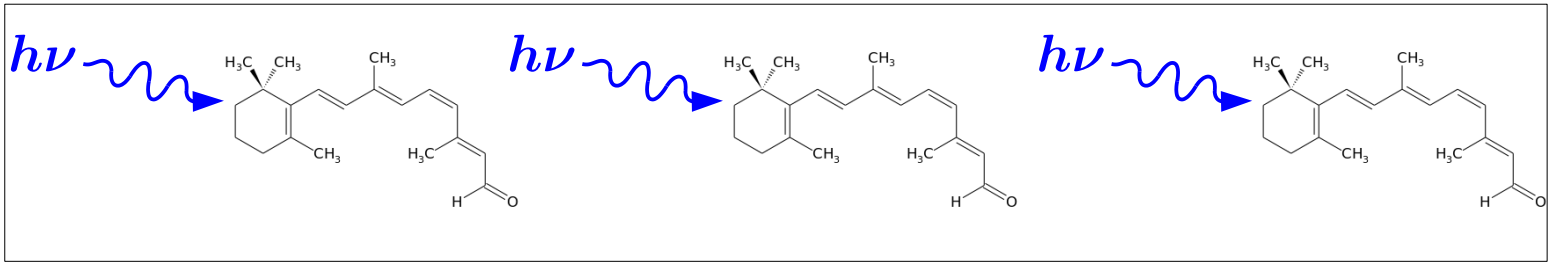
Two baths at different temperatures



Coherent Vs incoherent light excitation

Ultrafast spectroscopy : Schrödinger + light pulse

$$|\Psi_e(t)\rangle = -i\int_0^t \mathrm{d}\tau \mathrm{e}^{-i\hat{H}(t-\tau)}(\hat{\mu}\cdot E(\tau))\mathrm{e}^{-i\hat{H}\tau}|g\rangle$$

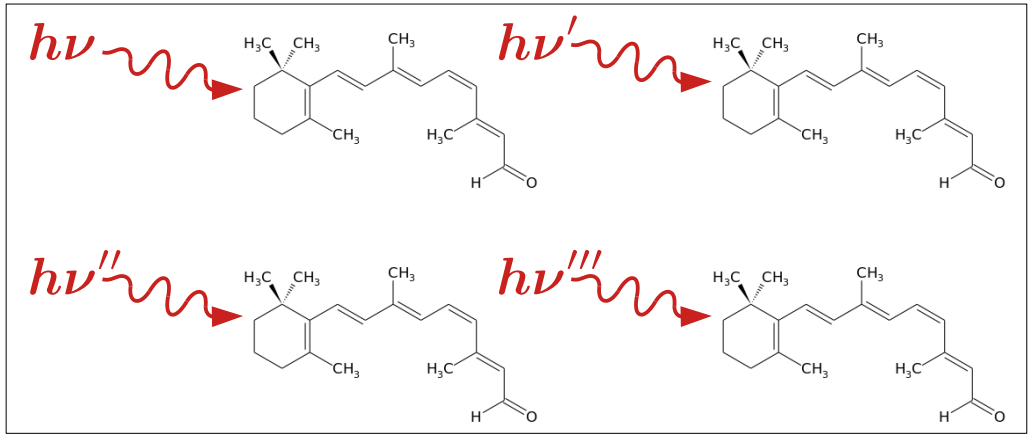


Same light over the ensemble

Sunlight : Ensemble average

$$\overline{|\Psi_e(t)\rangle\langle\Psi_e(t)|} = \sum_{\alpha\beta}\int_0^t \mathrm{d}\tau \int_0^t \mathrm{d}\tau' \mathrm{e}^{-i\hat{H}(t-\tau)}\hat{\mu}_\alpha \mathrm{e}^{-i\hat{H}\tau}|g\rangle\langle g| \times \mathrm{e}^{i\hat{H}\tau'}\hat{\mu}_\beta \mathrm{e}^{i\hat{H}(t-\tau')}\underbrace{\langle E_\alpha(\tau)E_\beta(\tau')\rangle}$$

blackbody radiation correlation function



Different light over the ensemble

T. Grinev & P. Brumer, *J. Chem. Phys.* 143, 244313 (2015)

Description of an open system (subsystem + environment)

$$|\Psi_{tot}\rangle = \sum_k |\Phi_k\rangle|\chi_k\rangle$$

States of the subsystem
What we are interested in

States of the environment
What we cannot know exactly

Coupling with environment
→ Population transfers between different $|\Phi_k\rangle$

Schrödinger equation (unitary) → no transfer

$$|\dot{\Phi}_k\rangle = -i\hat{H}|\Phi_k\rangle$$

Solution: quantum master equation (non unitary)

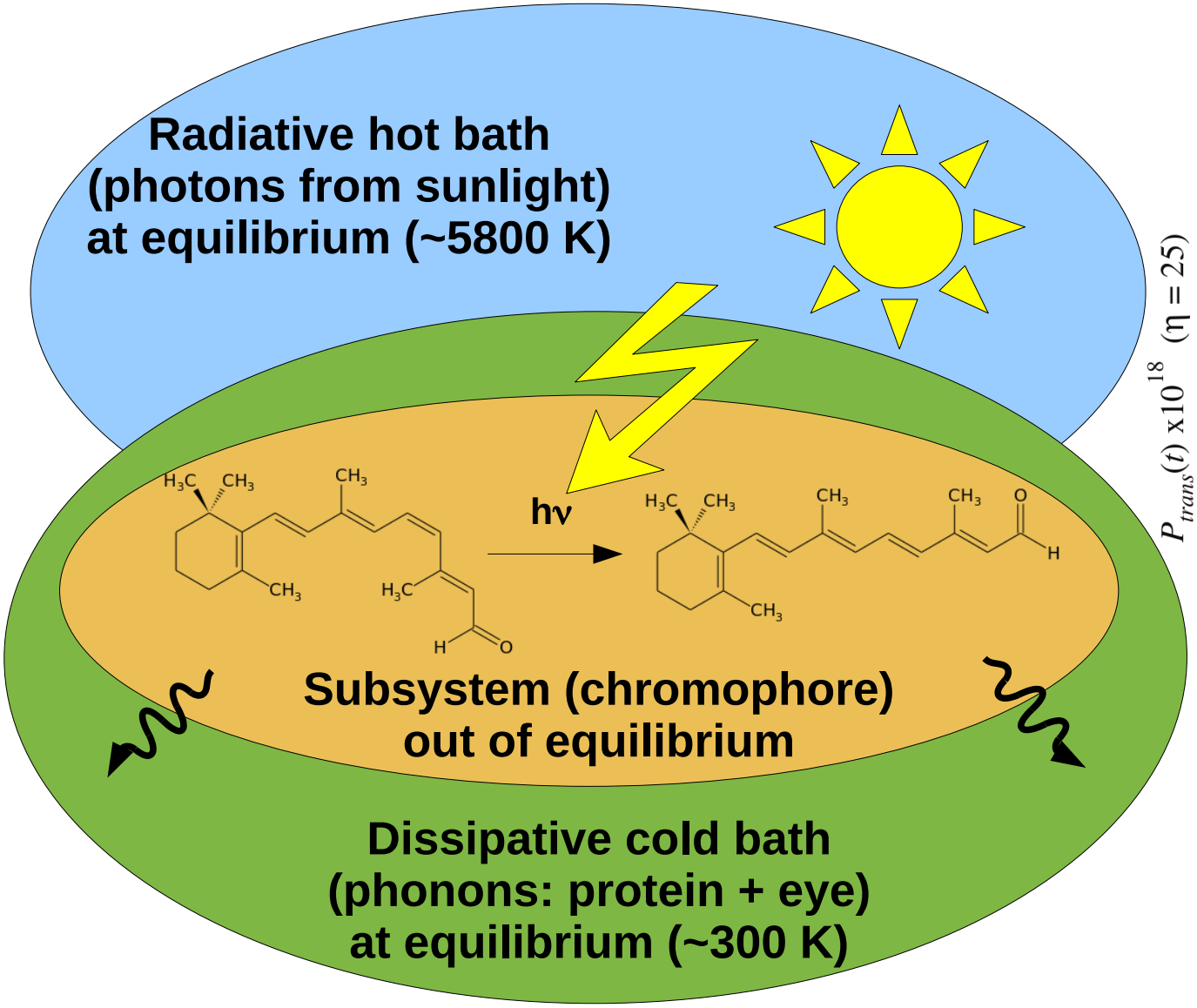
$$\dot{\hat{\rho}} = \mathcal{L}[\hat{\rho}; \Psi(0), t] \qquad \hat{\rho} = \sum_{kl} |\Phi_k\rangle \rho_{kl} \langle\Phi_l|$$

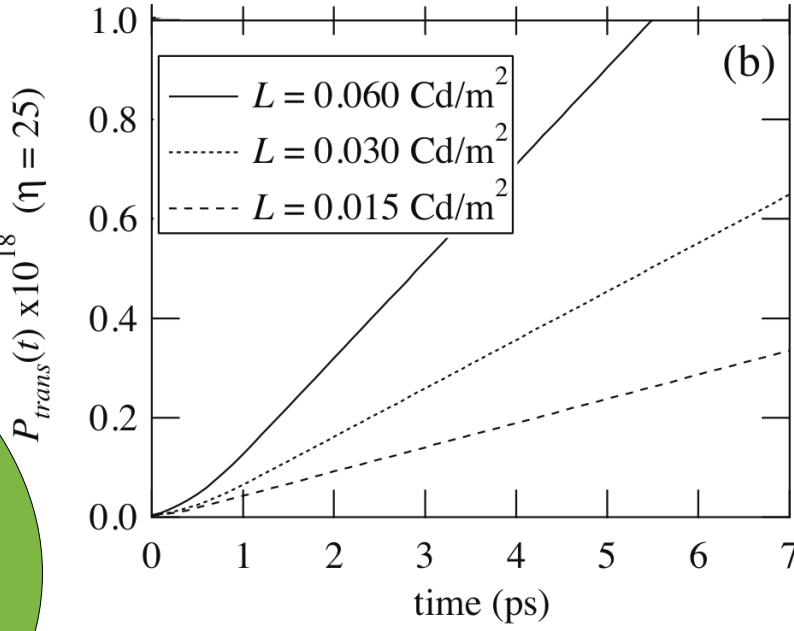
(Reduced) density matrix of the subsystem

Liouvillian: non-unitary generator

Two baths at different temperatures

Quantum master equation : $\dot{\hat{\rho}} = \mathcal{L}\hat{\rho} \equiv -i[\hat{H}, \hat{\rho}] + \mathcal{L}_C[\hat{\rho}] + \mathcal{L}_H[\hat{\rho}]$

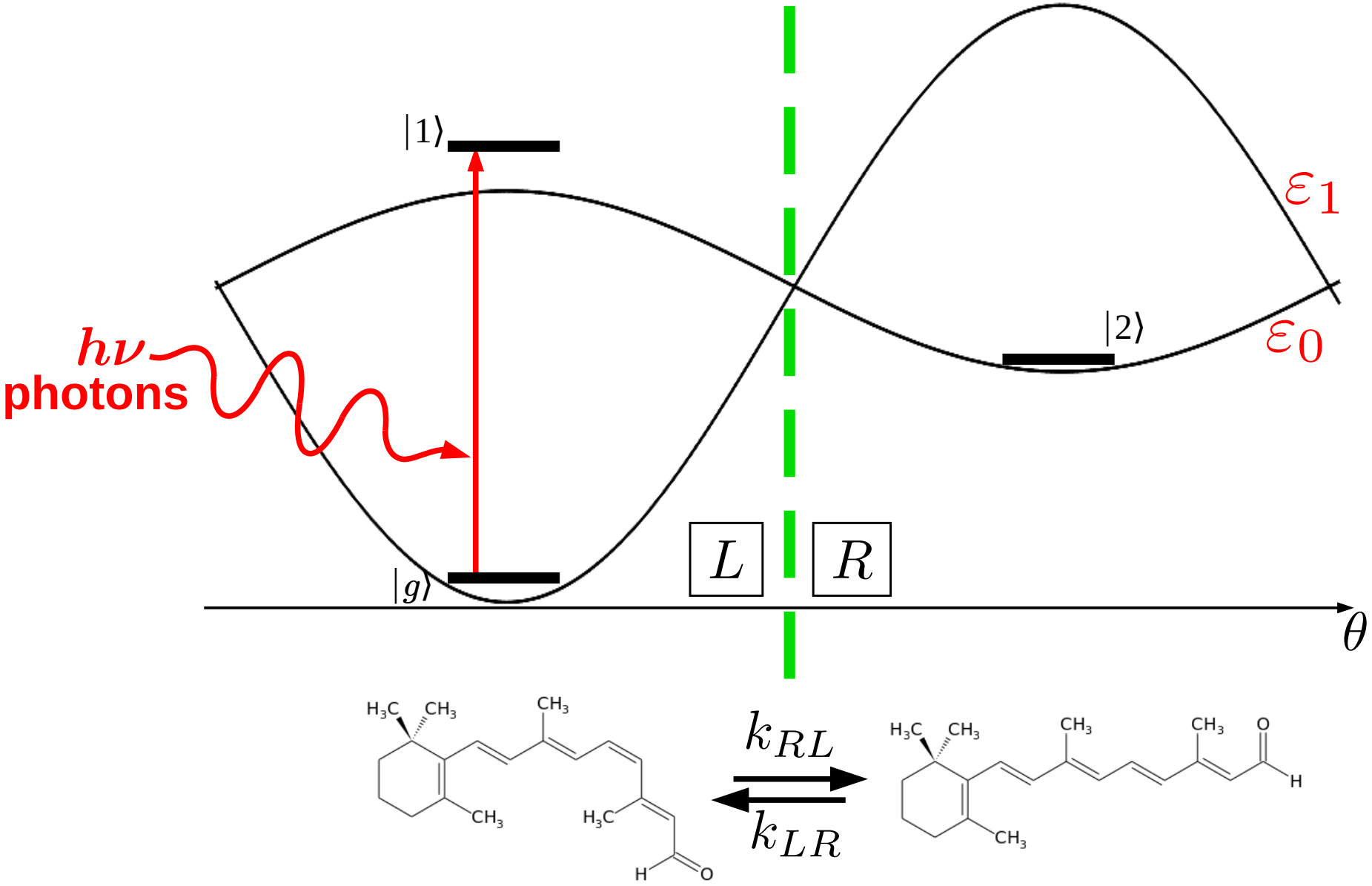




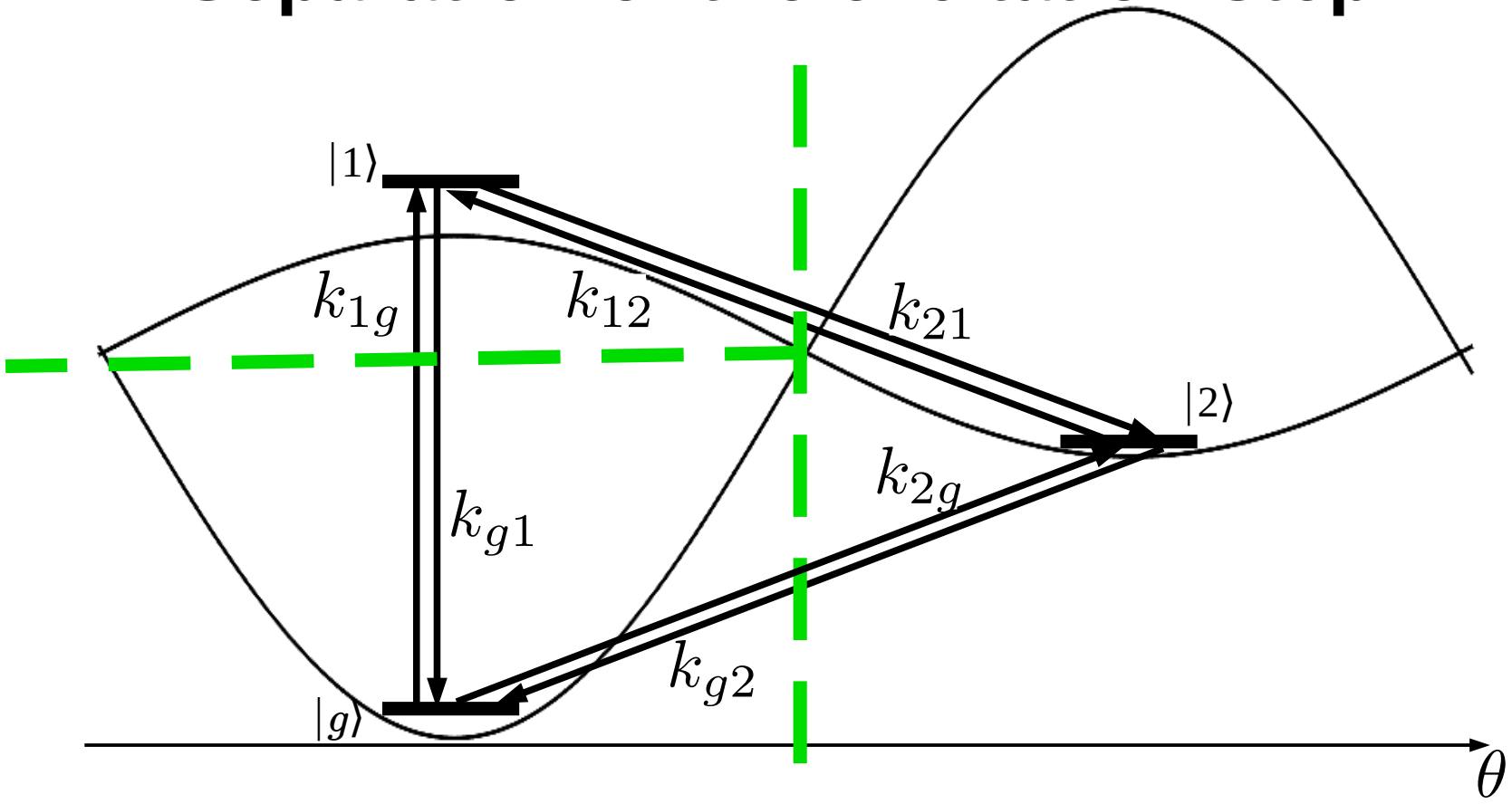
Time scale depends on the light intensity

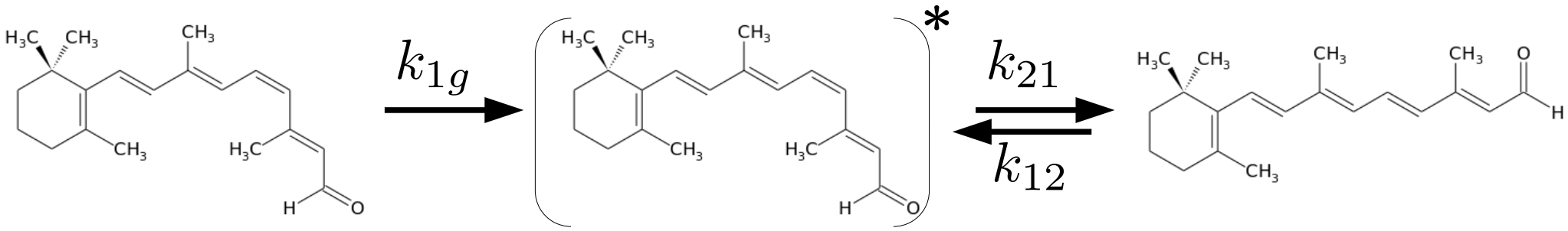
K. Hoki & P. Brumer, *Procedia Chem.* 3, 122 (2011)

Schematic view: a 3-state toy model



Separation of the excitation step

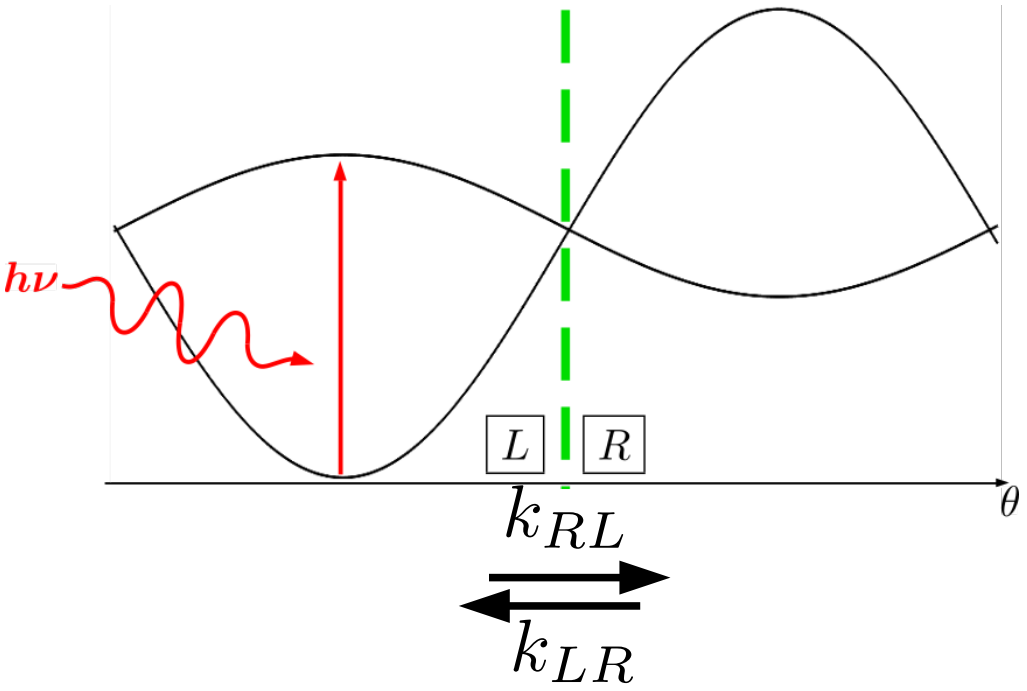




Rate independent of light type → k_{21}

How to estimate this rate?

Rate theory at equilibrium



Kinetic model:

$$\dot{p}_L = k_{LR}p_R - k_{RL}p_L$$
$$\dot{p}_R = k_{RL}p_L - k_{LR}p_R$$

To be fitted from dynamics:

1) asymmetric perturbation of **equilibrium**
2) equilibration dynamics

Approximate treatment:

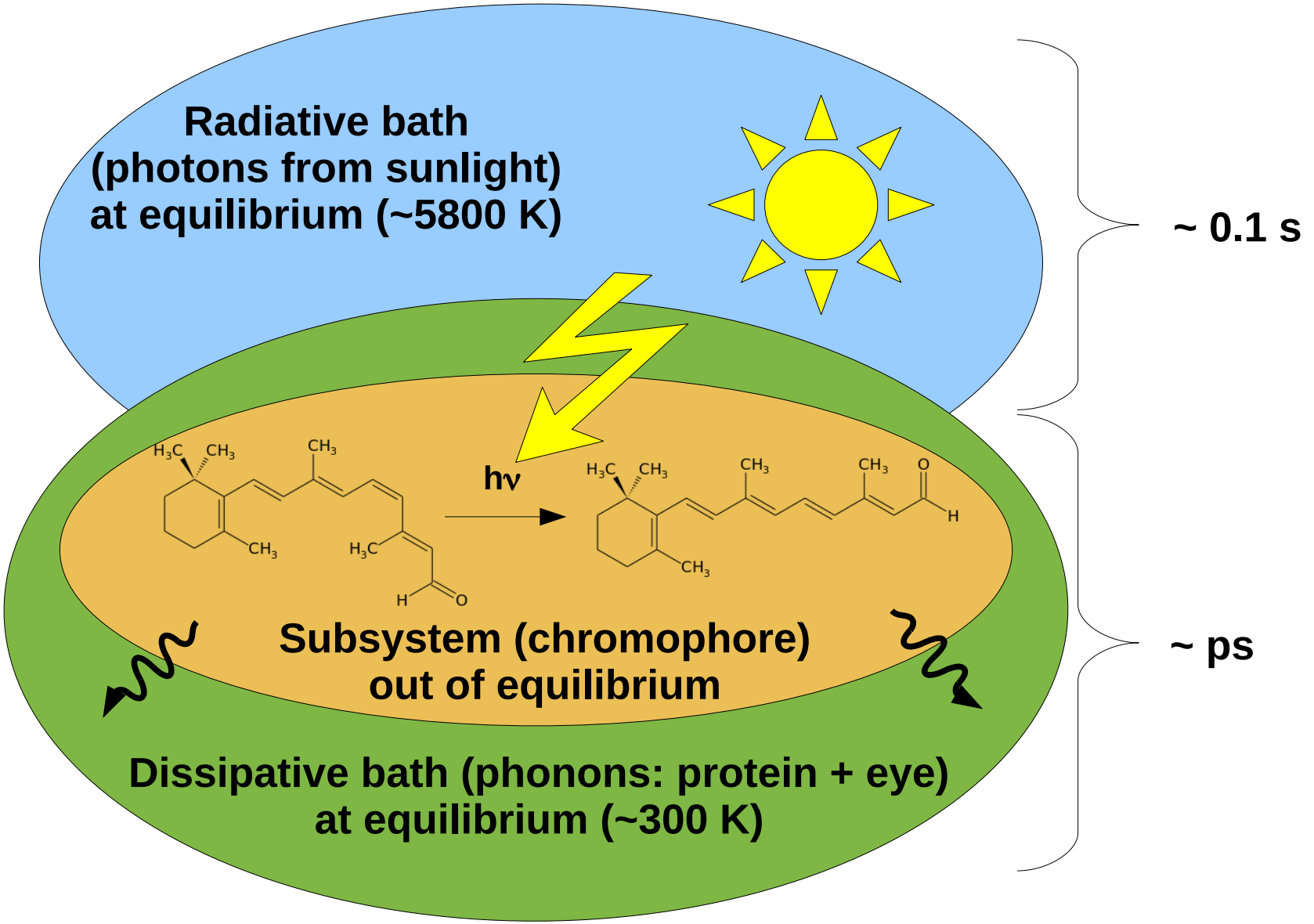
1) initial state from **PT1** + dynamics + population evaluation → linear response
(perturbation = step function)

2) **decaying exponential assumption** → rate given by time derivative

→ flux-flux correlation function = **fluctuation-dissipation theorem**

W. H. Miller, *J. Phys. Chem. A* 121, 793 (1998)

Real process: long timescale ~ seconds



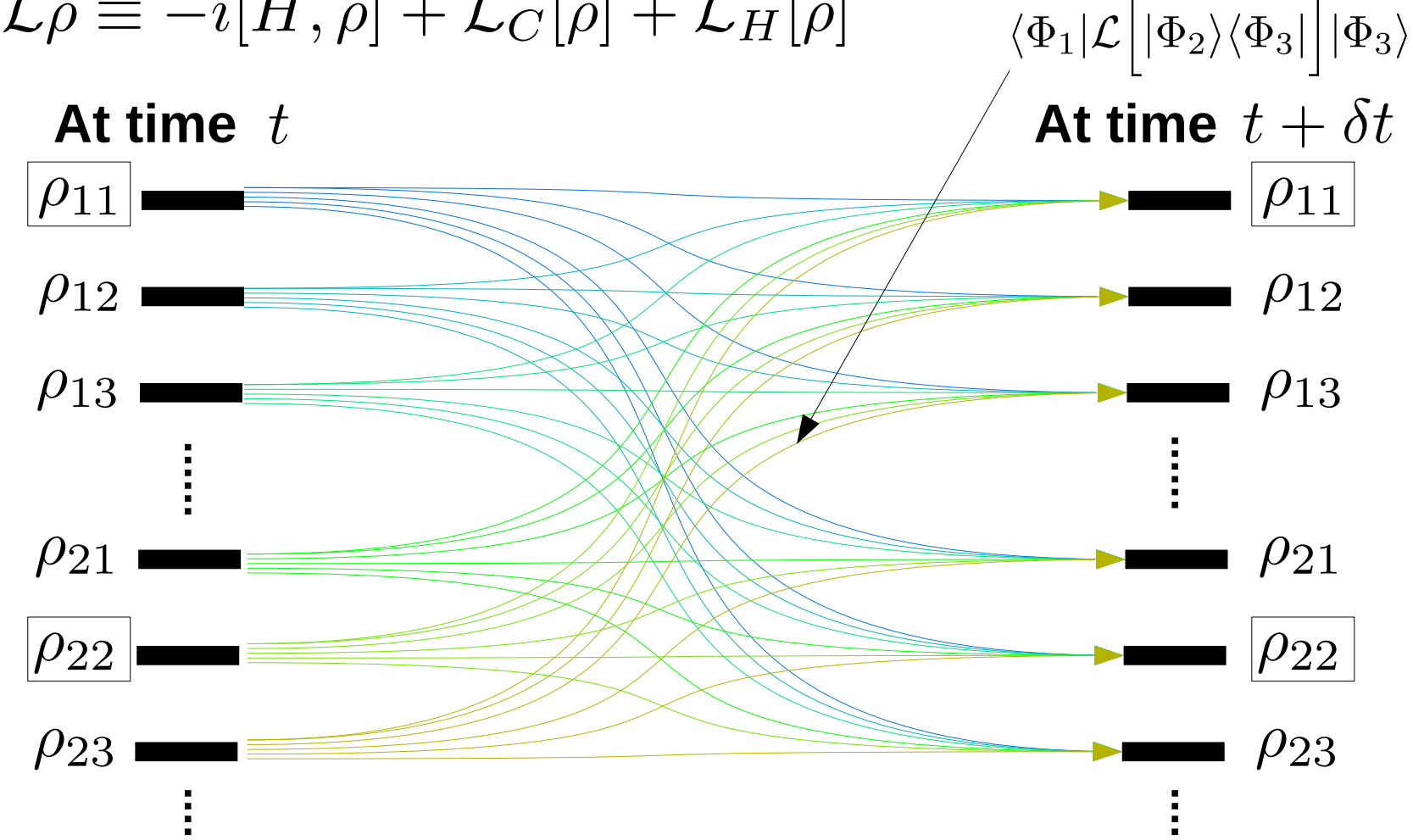
Non-Equilibrium Steady State (NESS)

Markovian quantum master equation with unique NESS

B. Brumer, *J. Phys. Chem. Lett.* 9, 2946 (2018)

Liouvillian: a quantum network

$$\dot{\hat{\rho}} = \mathcal{L}\hat{\rho} \equiv -i[\hat{H}, \hat{\rho}] + \mathcal{L}_C[\hat{\rho}] + \mathcal{L}_H[\hat{\rho}]$$



Feshbach projection technique[1]

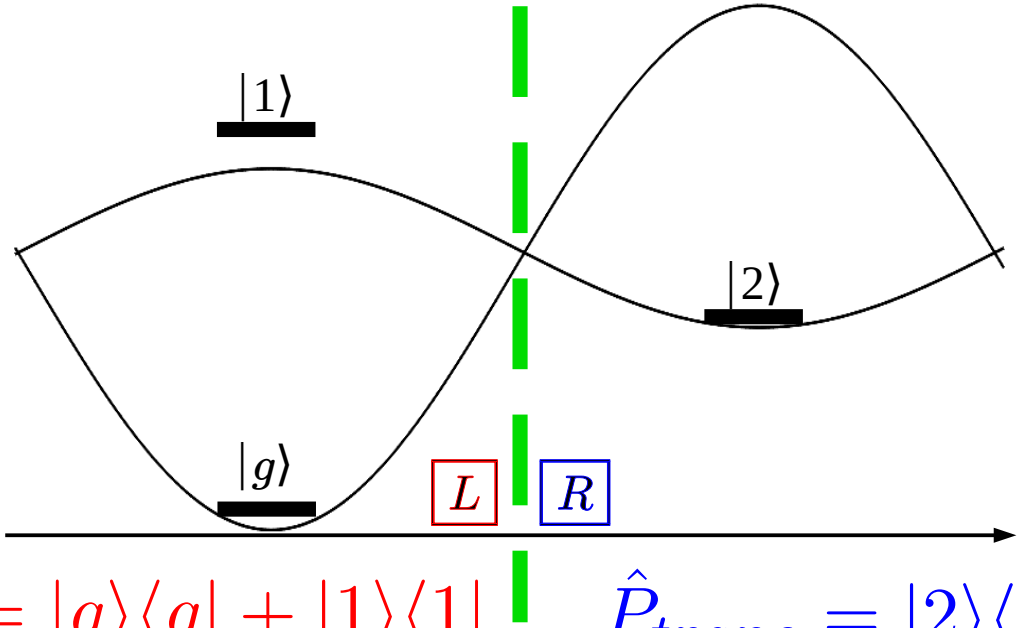
$$\left.\begin{aligned}\dot{\rho}_p &= \mathbf{L}_{pp}\rho_p + \mathbf{L}_{pc}\rho_c \\ \dot{\rho}_c &= \mathbf{L}_{cp}\rho_p + \mathbf{L}_{cc}\rho_c\end{aligned}\right\}$$ Equation for **populations only**

1) J. Wu & J. Cao, *J. Chem. Phys.* 139, 044102 (2013)

How to group states?

$$\dot{\hat{\rho}} = \mathcal{L}[\hat{\rho}]$$

“Coarse-graining”



$$\hat{P}_{cis} = |g\rangle\langle g| + |1\rangle\langle 1| \qquad \hat{P}_{trans} = |2\rangle\langle 2|$$

$$p_L = \mathrm{tr}\{\hat{P}_{cis}\hat{\rho}\} \qquad p_R = \mathrm{tr}\{\hat{P}_{trans}\hat{\rho}\}$$

$$\dot{p}_L = k_{LR}p_R - k_{RL}p_L$$
$$\dot{p}_R = k_{RL}p_L - k_{LR}p_R$$

Extract an equation for cis and $trans$ **populations only** and **valid in the steady state → Feshbach projection**

The Feshbach-Fano projection technique: Definitions

Quantum Master Equation in the **Liouville space**

$\dot{\hat{\rho}} = \mathcal{L}[\hat{\rho}]$ **~ "Hilbert space squared"**

Need for Liouville space projectors (acting on operators)

→ $\Pi_m = \hat{\varrho}_m \mathrm{tr}\{\hat{P}_m \bullet\}$ with $p_m = \mathrm{tr}\{\Pi_m[\hat{\rho}]\}$ $\hat{\varrho}_m = \frac{\hat{P}_m \hat{\rho}_s \hat{P}_m}{\mathrm{tr}\{\hat{P}_m \hat{\rho}_s\}}$

Projector in Hilbert space ($\hat{P}_{cis}, \hat{P}_{trans}$) Steady state

→ $\mathcal{Q} = 1 - \sum_m \Pi_m$ Projector on the complementary space

I. Navrotskaya & S. J. Hammes-Schiffer. *Chem. Phys.* 131, 024112 (2009)

The “coarse-grained” stationary equation

$$\dot{\hat{\rho}} = \mathcal{L}\hat{\rho} \equiv -i[\hat{H}, \hat{\rho}] + \mathcal{L}_C[\hat{\rho}] + \mathcal{L}_H[\hat{\rho}]$$

Projection Complete set of projectors: $\Pi + \mathcal{Q} = 1$, $\Pi = \sum_n \Pi_n$

$$\Pi\dot{\hat{\rho}} = \Pi\mathcal{L}\Pi\hat{\rho} + \Pi\mathcal{L}\mathcal{Q}\hat{\rho} \qquad \mathcal{Q}\dot{\hat{\rho}} = \mathcal{Q}\mathcal{L}\Pi\hat{\rho} + \mathcal{Q}\mathcal{L}\mathcal{Q}\hat{\rho}$$

Solving for $\mathcal{Q}\hat{\rho}$ in the steady-state $\mathcal{Q}\dot{\hat{\rho}} = 0$

$$\mathcal{Q}\hat{\rho} = -(\mathcal{Q}\mathcal{L}\mathcal{Q})^{-1}\mathcal{Q}\mathcal{L}\Pi\hat{\rho}$$

Tracing for the populations

$$\dot{p}_m = \sum_n \underbrace{\mathrm{tr}\{\hat{P}_m(1 - \mathcal{L}(\mathcal{Q}\mathcal{L}\mathcal{Q})^{-1}\mathcal{Q})\mathcal{L}\hat{\varrho}_n\}}_{k_{mn}} p_n$$

Population master equation (only valid in steady-state)

L. Joubert-Doriol *et al*. *J. Chem. Theory Comput.* 19, 1130 (2023)

The “coarse-grained” dynamical equation

k_{mn} → decay-time $t^{(1)}$

$$\dot{p}_m = \sum_n \mathrm{tr}\{\hat{P}_m(1-\mathcal{L}(\mathcal{Q}\mathcal{L}\mathcal{Q})^{-1}\mathcal{Q})\mathcal{L}\hat{\varrho}_n\}p_n \quad = M_1$$

$$+ tr\{\hat{P}_m\mathcal{L}\mathrm{e}^{\mathcal{Q}\mathcal{L}\mathcal{Q}t}\mathcal{Q}[\hat{\rho}(0)]\}$$

$$+ \sum_n \int_0^t \mathrm{d}\tau tr\{\hat{P}_m\mathcal{L}\mathrm{e}^{\mathcal{Q}\mathcal{L}\mathcal{Q}(t-\tau)}\mathcal{Q}\mathcal{L}[\hat{\varrho}_n]\}p_n(\tau)$$

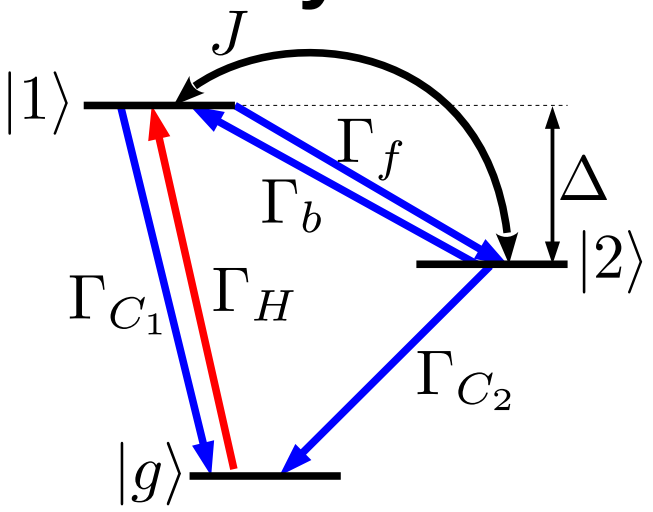
$$+ \sum_n tr\{\hat{P}_m\mathcal{L}(\mathcal{Q}\mathcal{L}\mathcal{Q})^{-1}\mathcal{Q}\mathcal{L}[\hat{\varrho}_n]\}p_n \quad = M_2$$

Non-Markovian: decay-time $t^{(2)}$ dictated by $\mathcal{Q}\mathcal{L}\mathcal{Q}$

Dynamics governed by rates for $t^{(2)} << t < t^{(1)}$

L. Joubert-Doriol *et al*. *J. Chem. Theory Comput.* 19, 1130 (2023)

Dynamics in the three states model



Quantum Master Equation: Lindblad

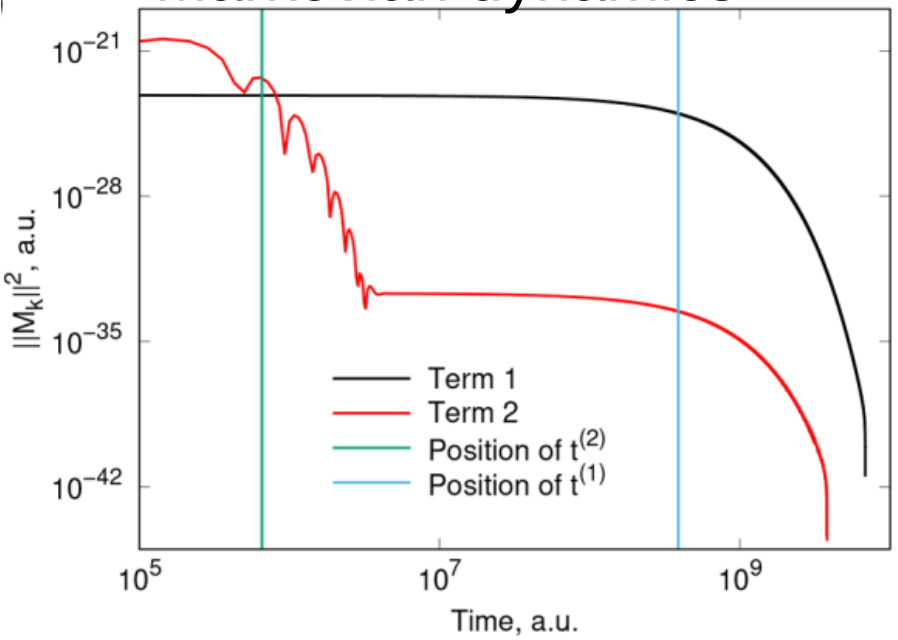
$$\dot{\hat{\rho}} = -i[\hat{H}, \hat{\rho}] + \mathcal{L}_C[\hat{\rho}] + \mathcal{L}_H[\hat{\rho}]$$

Hamiltonian + Cold bath + Hot bath

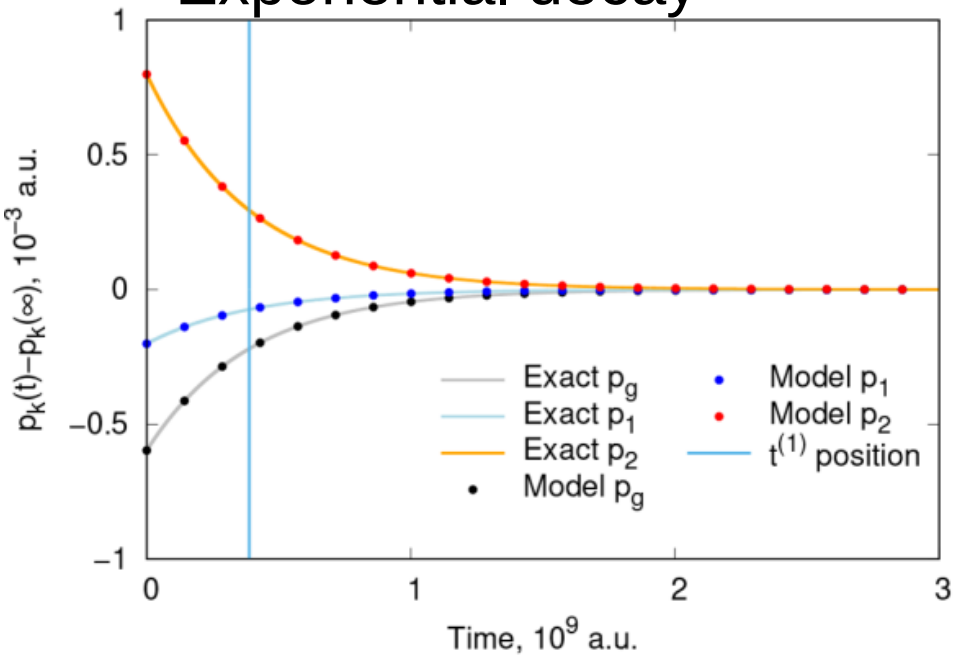
(3-state) (Jump operators)

J = 2 x 10^{-5} a.u.

Markovian dynamics

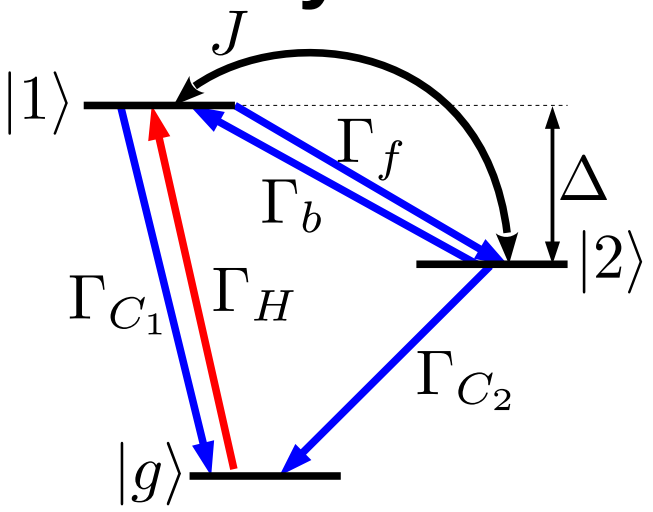


Exponential decay



L. Joubert-Doriol *et al*. *J. Chem. Theory Comput.* 19, 1130 (2023)

Dynamics in the three states model



Quantum Master Equation: Lindblad

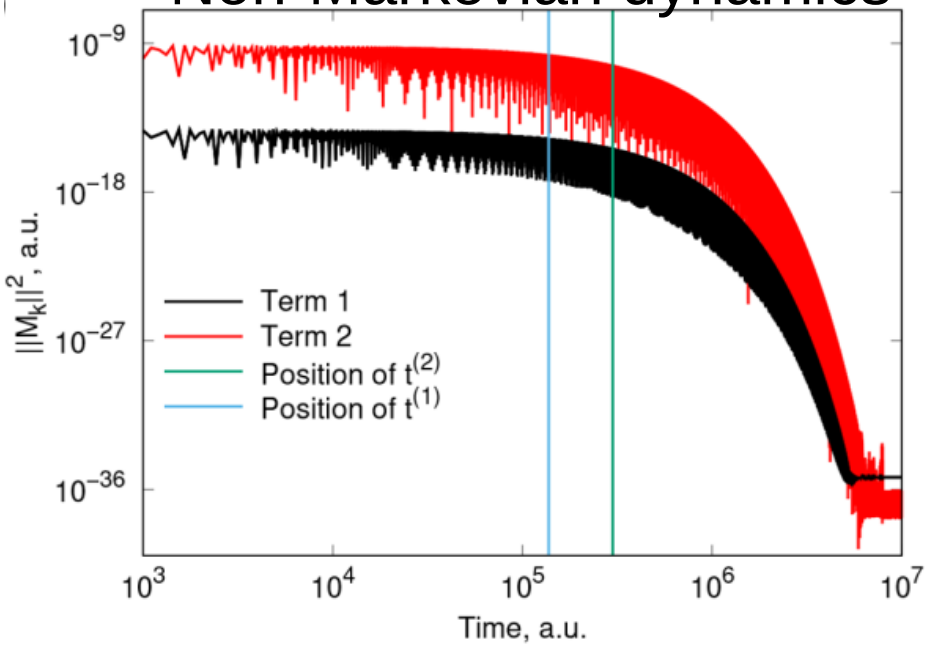
$$\dot{\hat{\rho}} = -i[\hat{H}, \hat{\rho}] + \mathcal{L}_C[\hat{\rho}] + \mathcal{L}_H[\hat{\rho}]$$

Hamiltonian + Cold bath + Hot bath

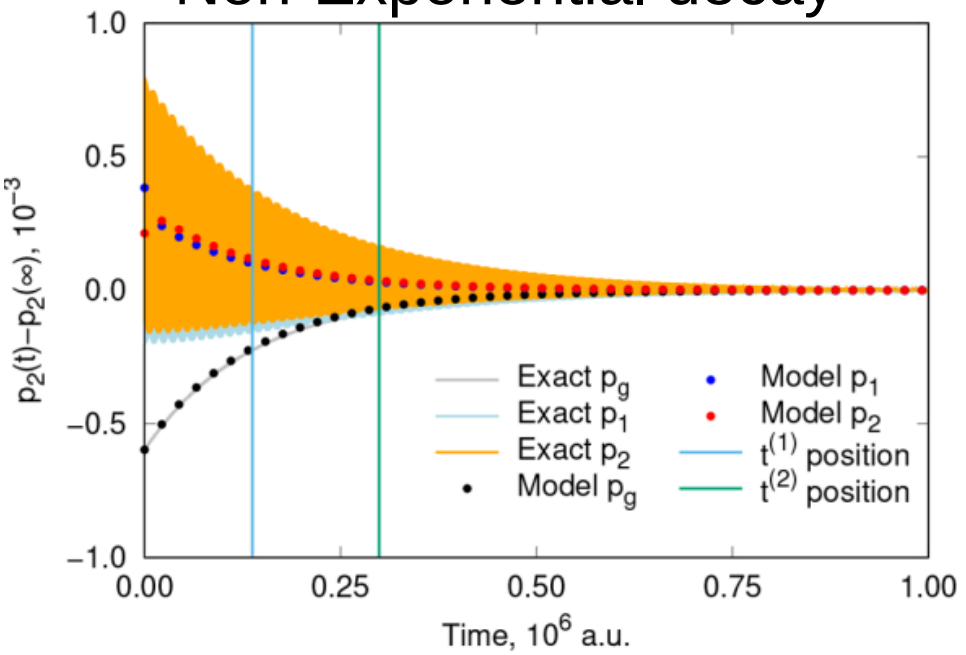
(3-state) (Jump operators)

J = 0.02 a.u.

Non-Markovian dynamics

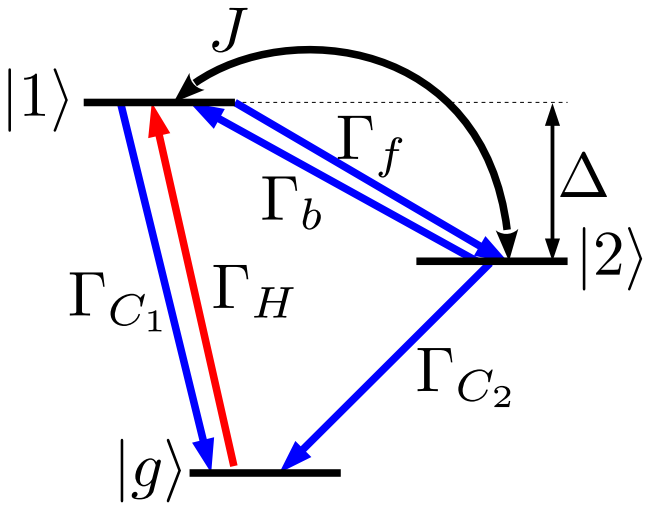


Non-Exponential decay



L. Joubert-Doriol *et al*. *J. Chem. Theory Comput.* 19, 1130 (2023)

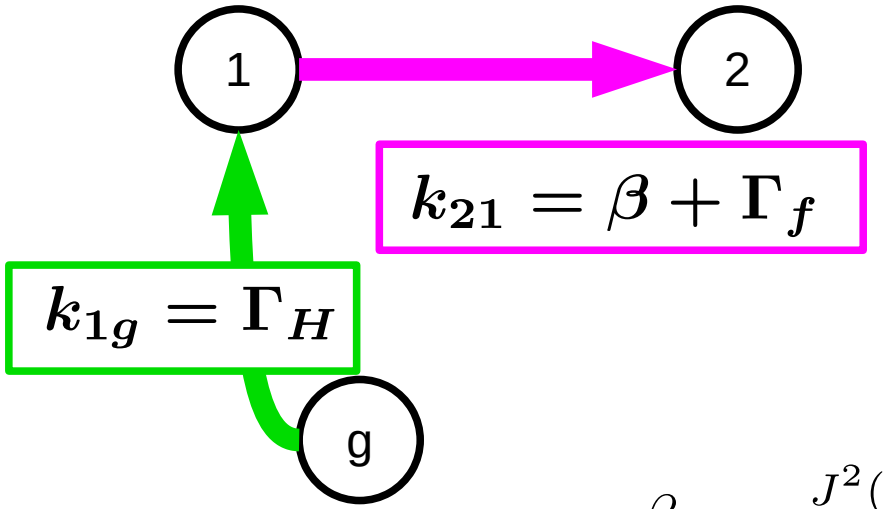
NESS rates in the three states model: 3 groups

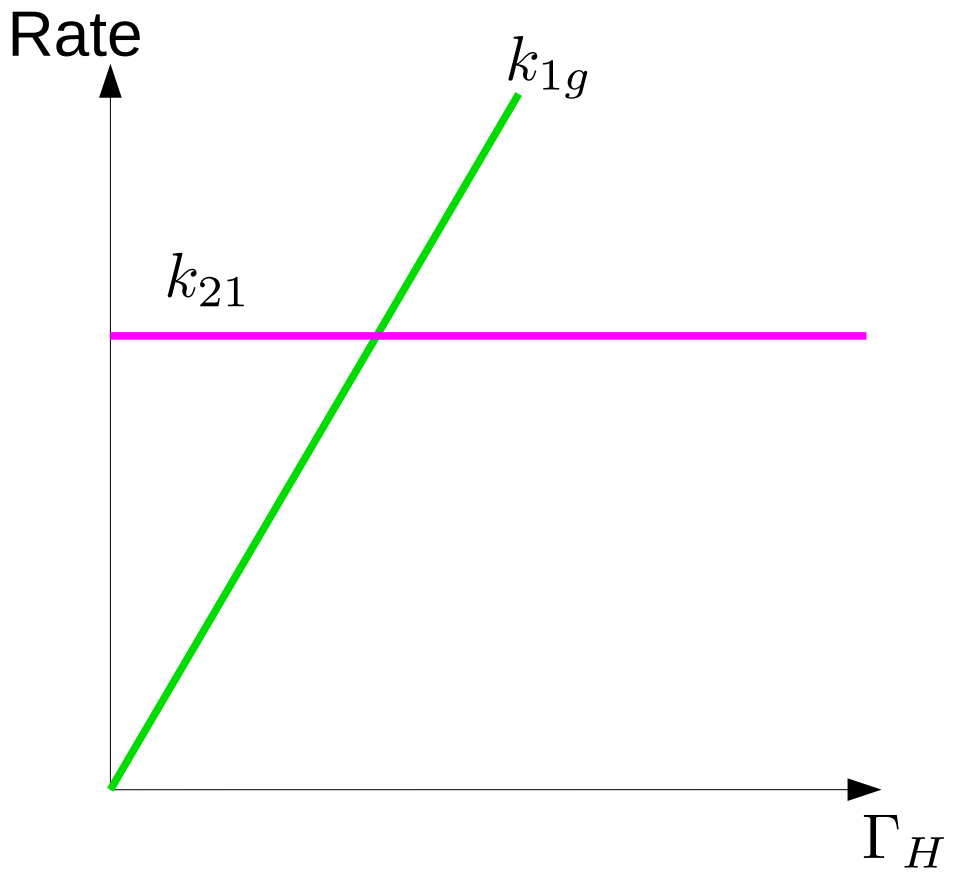


Quantum Master Equation: Lindblad

$$\dot{\hat{\rho}} = -i[\hat{H}, \hat{\rho}] + \mathcal{L}_C[\hat{\rho}] + \mathcal{L}_H[\hat{\rho}]$$

Hamiltonian + Cold bath + Hot bath

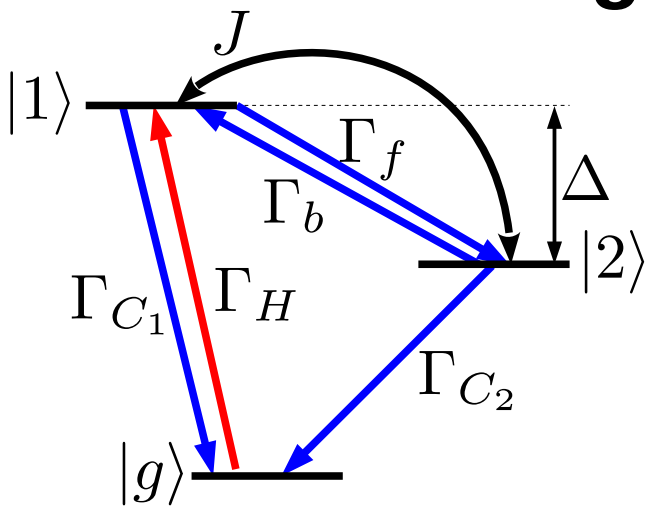




$$\beta = \frac{J^2(\sum_{\text{blue}} \Gamma_j)}{(\sum_{\text{blue}} \Gamma_j)^2 + \Delta^2}$$

L. Joubert-Doriol *et al*. *J. Chem. Theory Comput.* 19, 1130 (2023)

3 groups Vs 2 groups

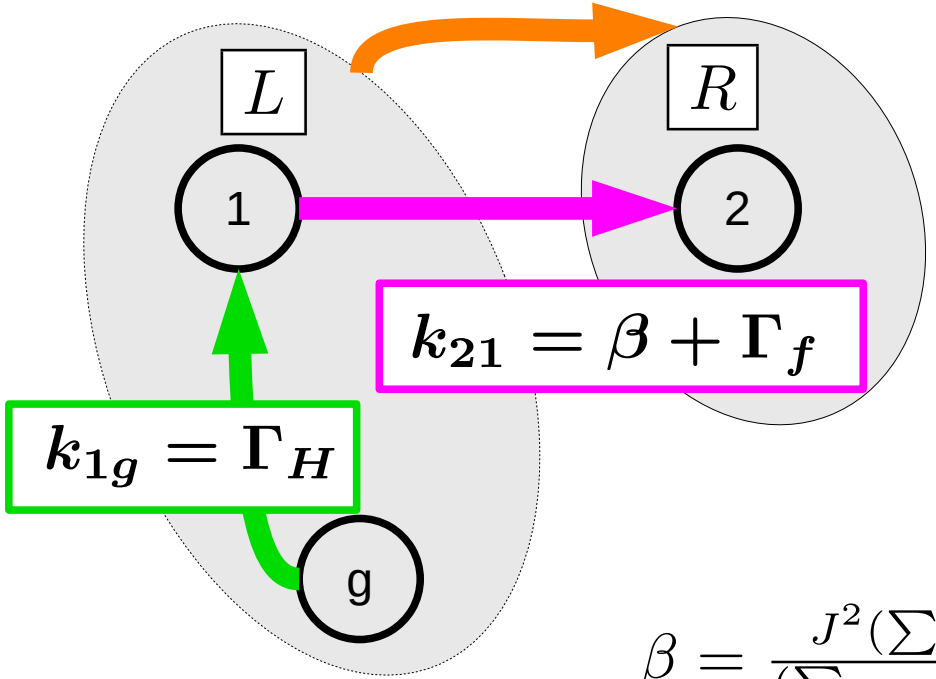


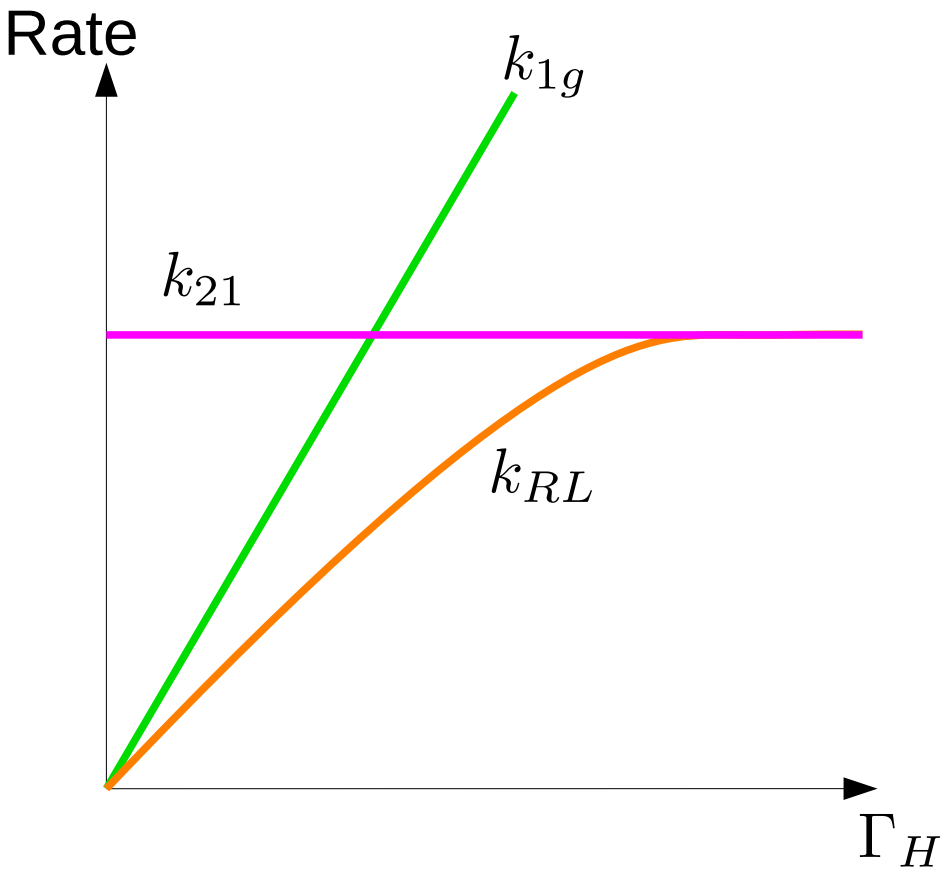
Quantum Master Equation: Lindblad

$$\dot{\hat{\rho}} = -i[\hat{H}, \hat{\rho}] + \mathcal{L}_C[\hat{\rho}] + \mathcal{L}_H[\hat{\rho}]$$

Hamiltonian + Cold bath + Hot bath

$$k_{RL} = \frac{\Gamma_H(\beta+\Gamma_f)}{r(\beta+\Gamma_f)+\Gamma_H+\Gamma_{C_1}}$$



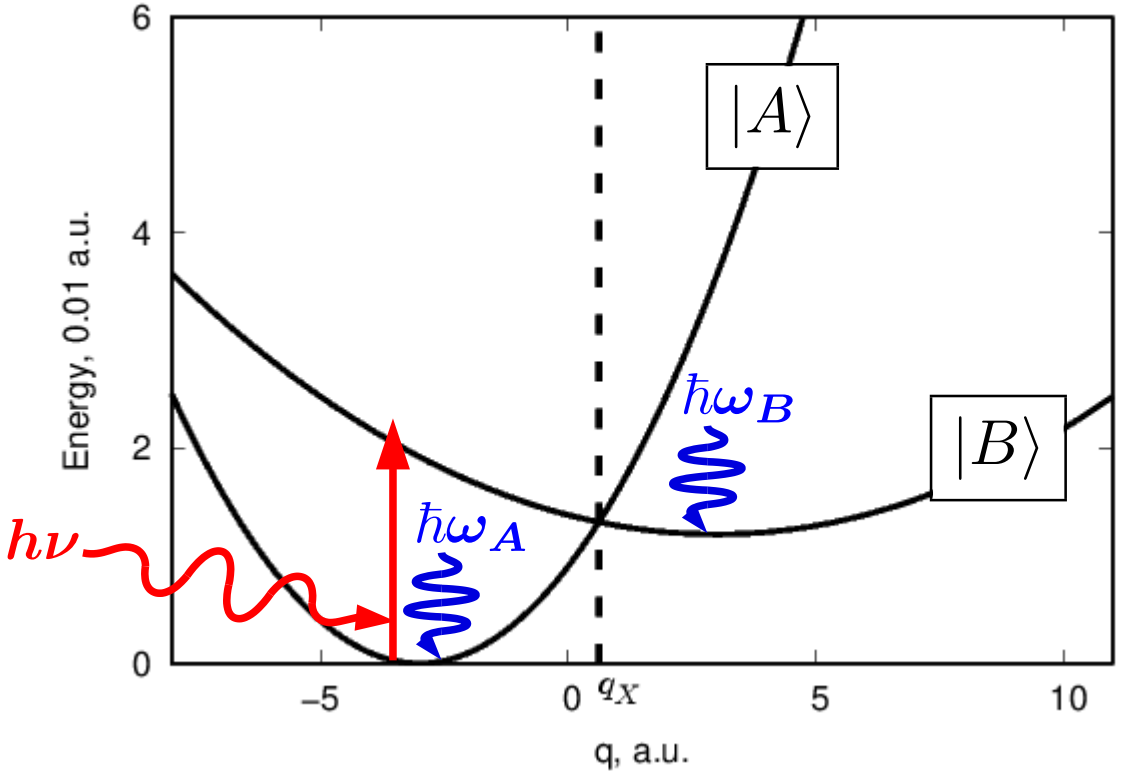


$$\beta = \frac{J^2(\sum_{\text{blue}}\Gamma_j)}{(\sum_{\text{blue}}\Gamma_j)^2+\Delta^2} \qquad r = \frac{\rho_{gg}}{\rho_{gg}+\rho_{11}}$$

L. Joubert-Doriol *et al*. *J. Chem. Theory Comput.* 19, 1130 (2023)

A more realistic spin-boson model

(2-state – 1-dimensional harmonic oscillator)



$$\dot{\hat{\rho}} = -i[\hat{H}, \hat{\rho}] + \mathcal{L}_H[\hat{\rho}] + \mathcal{L}_C^{(A)}[\hat{\rho}] + \mathcal{L}_C^{(B)}[\hat{\rho}]$$

$$\hat{H} = \begin{pmatrix} \hat{H}_A & \lambda \\ \lambda & \hat{H}_B \end{pmatrix}$$

Harmonic oscillators + Lindblad baths

$$\mathcal{L}_H[\hat{\rho}] = \Gamma_H(1+n_H)\left(\hat{\mu}\hat{\rho}\hat{\mu}^\dagger - \tfrac{1}{2}\hat{\mu}^\dagger\hat{\mu}\hat{\rho} - \tfrac{1}{2}\hat{\rho}\hat{\mu}^\dagger\hat{\mu}\right) + \Gamma_H n_H\left(\hat{\mu}^\dagger\hat{\rho}\hat{\mu} - \tfrac{1}{2}\hat{\mu}\hat{\mu}^\dagger\hat{\rho} - \tfrac{1}{2}\hat{\rho}\hat{\mu}\hat{\mu}^\dagger\right)$$

Excitation number, T=5800K

$\hat{\mu} = |A\rangle\langle B|$

Photon absorption rate $\sim \mu s^{-1}$

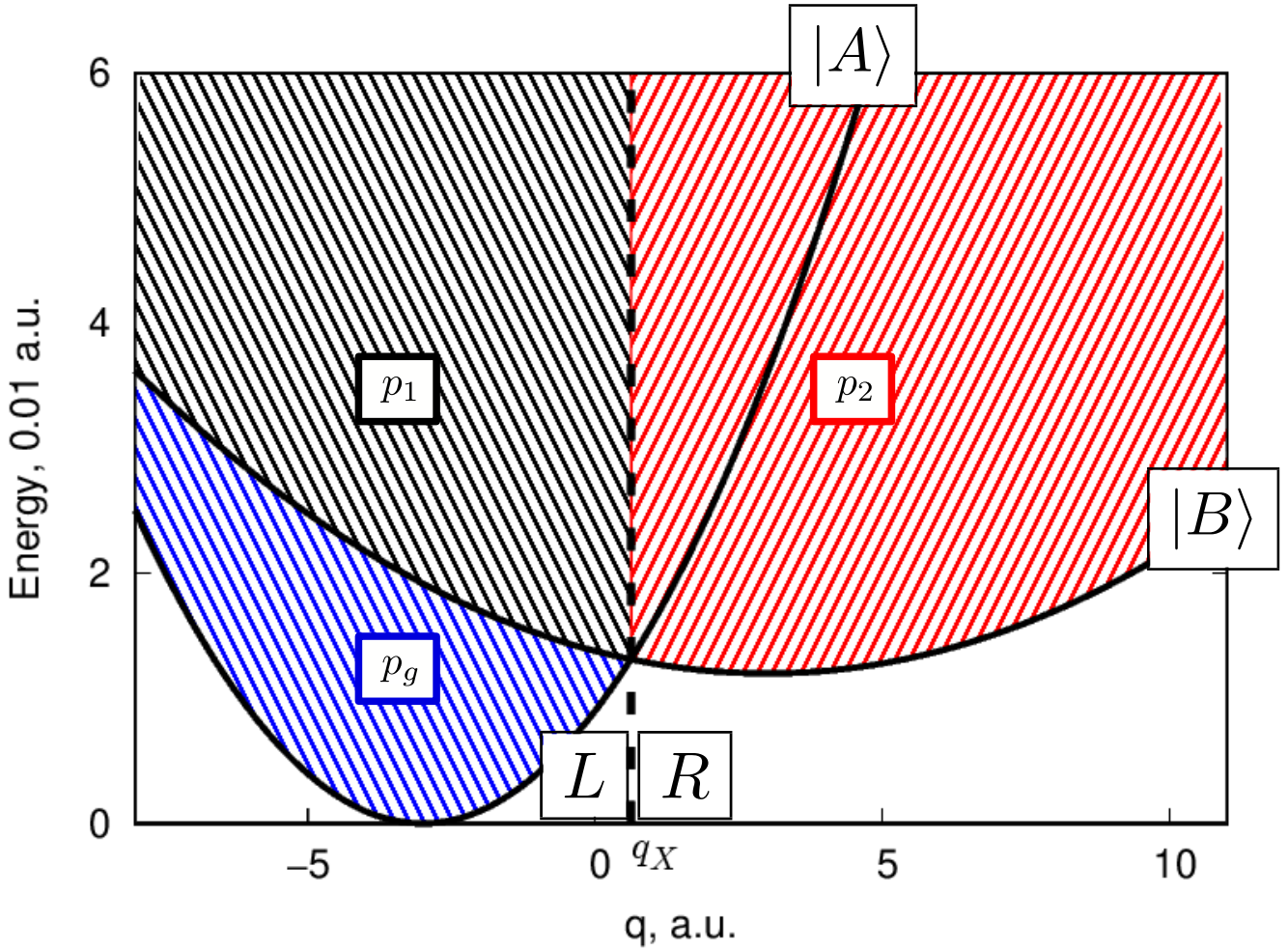
$$\mathcal{L}_C^{(\alpha)}[\hat{\rho}] = \Gamma_C(1+n_C^{(\alpha)})\left(\hat{a}_\alpha\hat{\rho}\hat{a}_\alpha^\dagger - \tfrac{1}{2}\hat{a}_\alpha^\dagger\hat{a}_\alpha\hat{\rho} - \tfrac{1}{2}\hat{\rho}\hat{a}_\alpha^\dagger\hat{a}_\alpha\right) + \Gamma_C n_H^{(\alpha)}\left(\hat{a}_\alpha^\dagger\hat{\rho}\hat{a}_\alpha - \tfrac{1}{2}\hat{a}_\alpha\hat{a}_\alpha^\dagger\hat{\rho} - \tfrac{1}{2}\hat{\rho}\hat{a}_\alpha\hat{a}_\alpha^\dagger\right)$$

Excitation number, T=300K

Annihilation

Phonon absorption rate $\sim ps^{-1}$

“Coarse-graining” of the model



First choice of projectors:

$$\hat{P}_L = \int_{-\infty}^{q_X} \mathrm{d}q \; |q\rangle \langle q|$$

$$\hat{P}_R = \int_{q_X}^{+\infty} \mathrm{d}q \; |q\rangle \langle q|$$

Rate of interest: k_{RL}

Second choice:

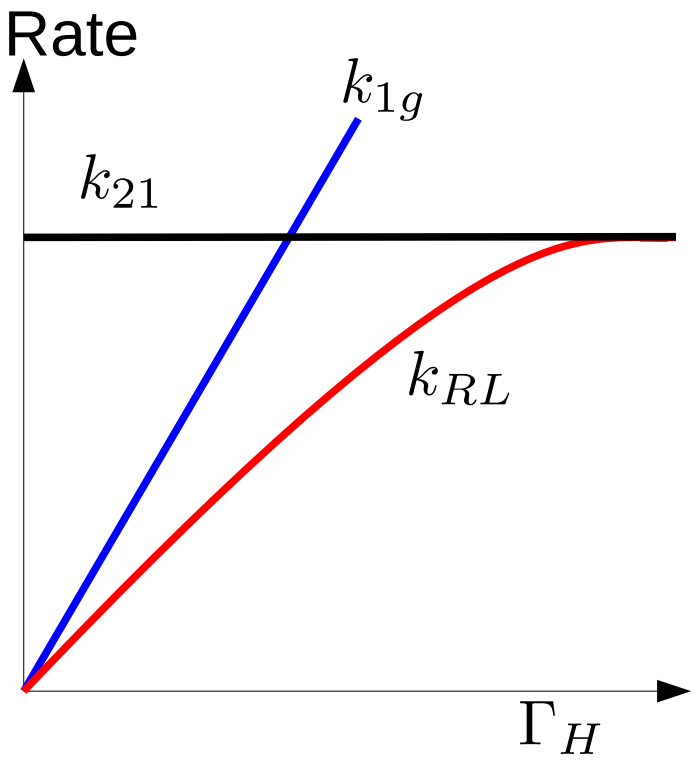
$$\hat{P}_g = |A\rangle \langle A| \, \hat{P}_L$$

$$\hat{P}_1 = |B\rangle \langle B| \, \hat{P}_L$$

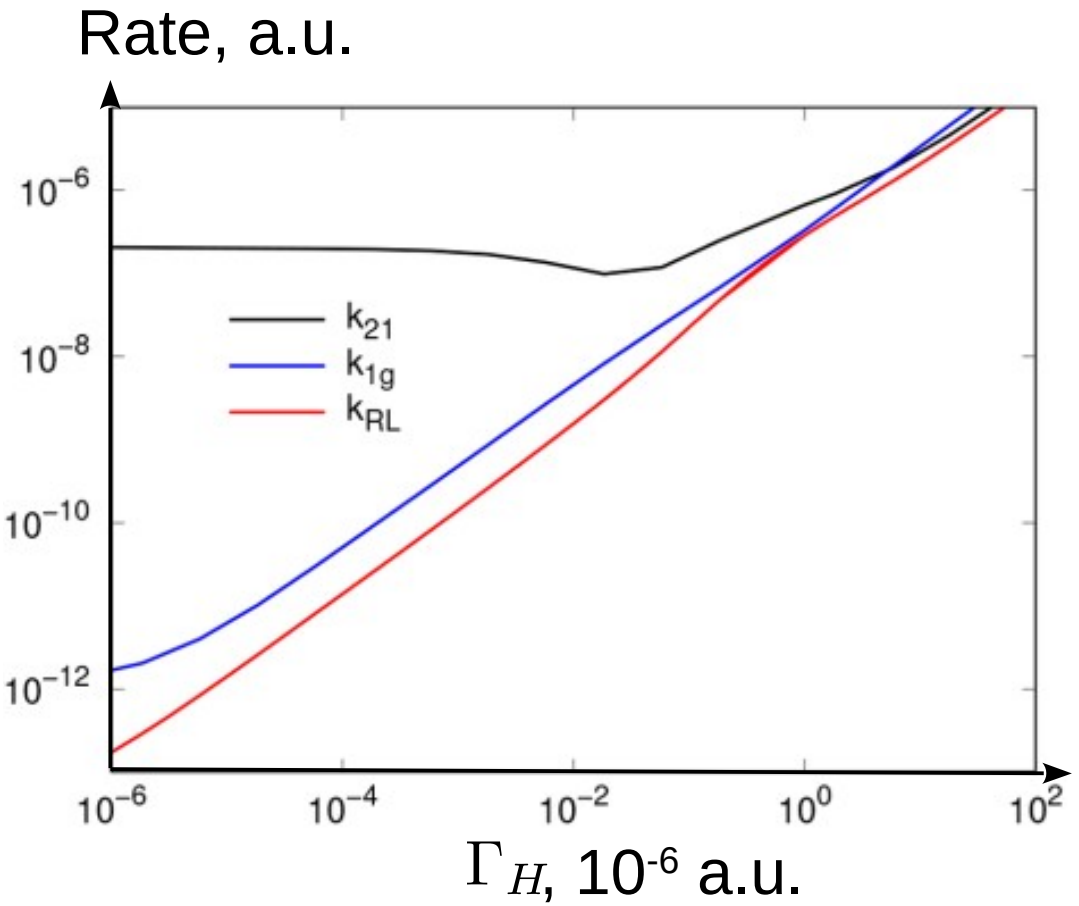
$$\hat{P}_2 = \hat{P}_R$$

Rates of interest: k_{1g}
k_{21}

Comparison between the models



3-state model, analytic results

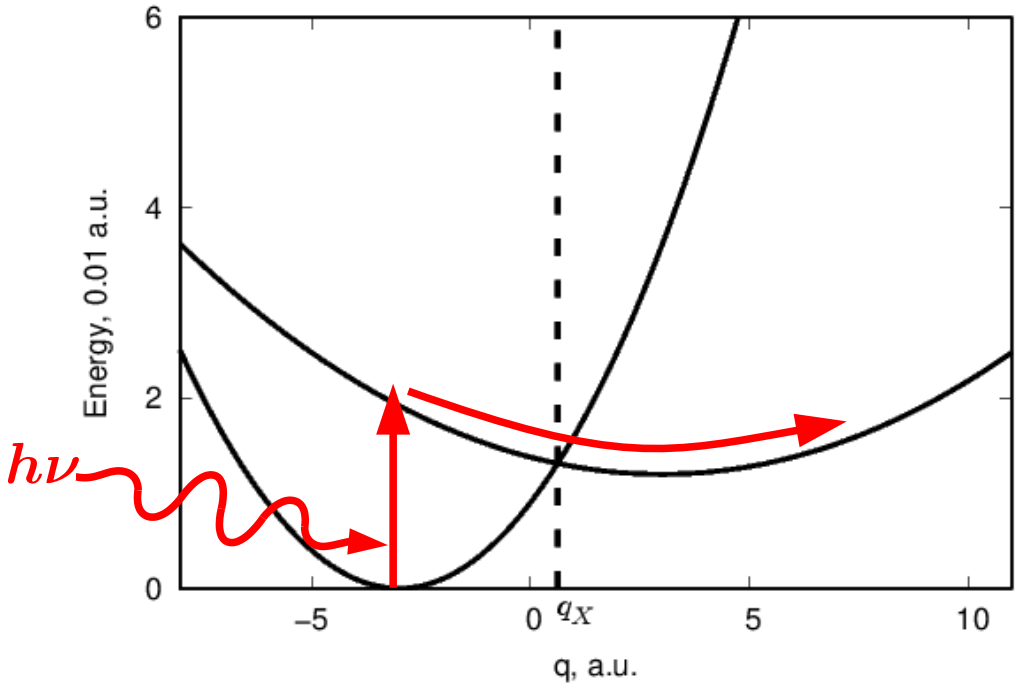


Spin-boson model, Numerical results

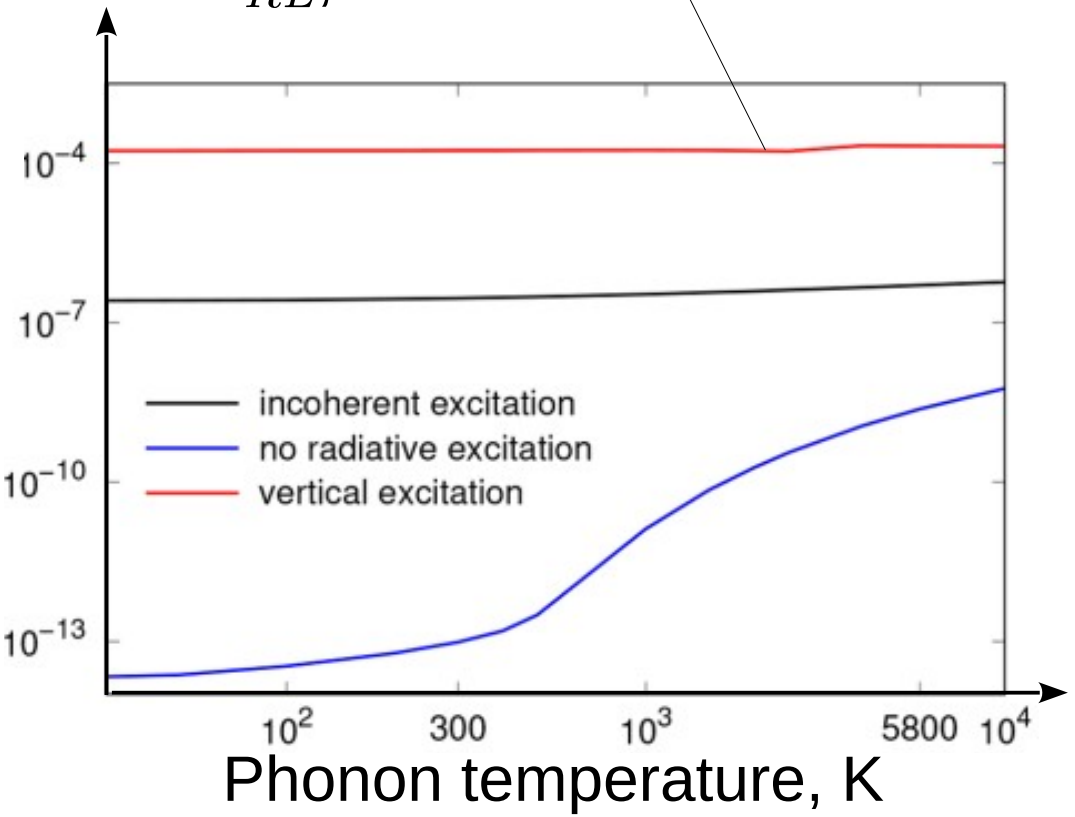
Similar behavior at low Γ_H: k_{21} is constant while k_{RL} increases linearly

L. Joubert-Doriol *et al*. *J. Chem. Theory Comput.* 19, 1130 (2023)

Comparison with an ultra-fast vertical excitation



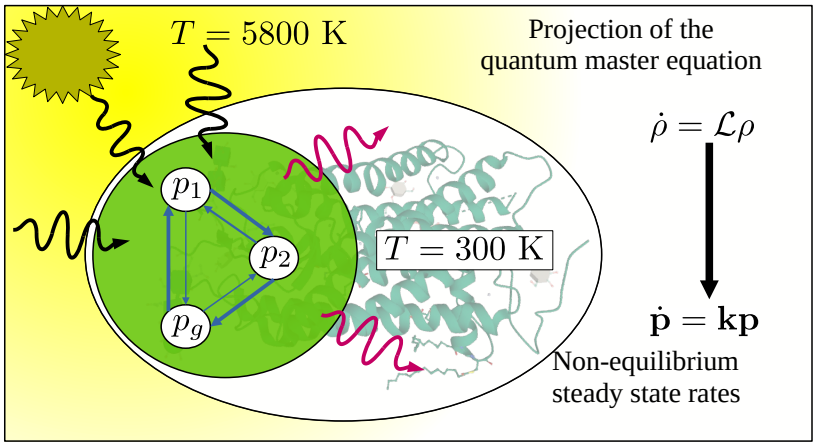
Vertical excitation rate:
Inverse average time of first passage



The ultra-fast process is several orders of magnitude faster

L. Joubert-Doriol *et al*. *J. Chem. Theory Comput.* 19, 1130 (2023)

Conclusion & future work



1) Steady-state rates[1]

$$k_{mn} = \mathrm{tr}\{\hat{P}_m(1 - \mathcal{L}(\mathcal{Q}\mathcal{L}\mathcal{Q})^{-1}\mathcal{Q})\mathcal{L}\hat{\varrho}_n\}$$

→ satisfies **global balance**

→ but **non-unique** $\hat{\varrho}_n$

$$\Pi_m = \hat{\varrho}_m \mathrm{tr}\{\hat{P}_m \bullet\}$$

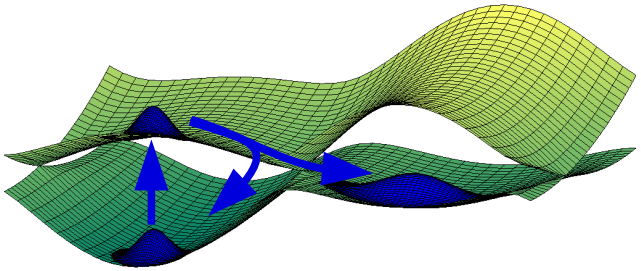
Currently: measurement $\hat{\varrho}_m = \frac{\hat{P}_m \hat{\rho}_s \hat{P}_m}{\mathrm{tr}\{\hat{P}_m \hat{\rho}_s\}}$

In the Secular limit: -conserves detailed balance
-uniqueness of the rates

To do: uniquely define projectors that satisfy physically relevant properties

2) **Major differences** between timescales from ultrasfast excitation and incoherent excitation

To do: test the method on a retinal model[2]



1) L. Joubert-Doriol *et al*. *J. Chem. Theory Comput.* 19, 1130 (2023)
2) S. Hahn & G. Stock, *J. Phys. Chem. B* 104, 1146 (2000)

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Thank you!