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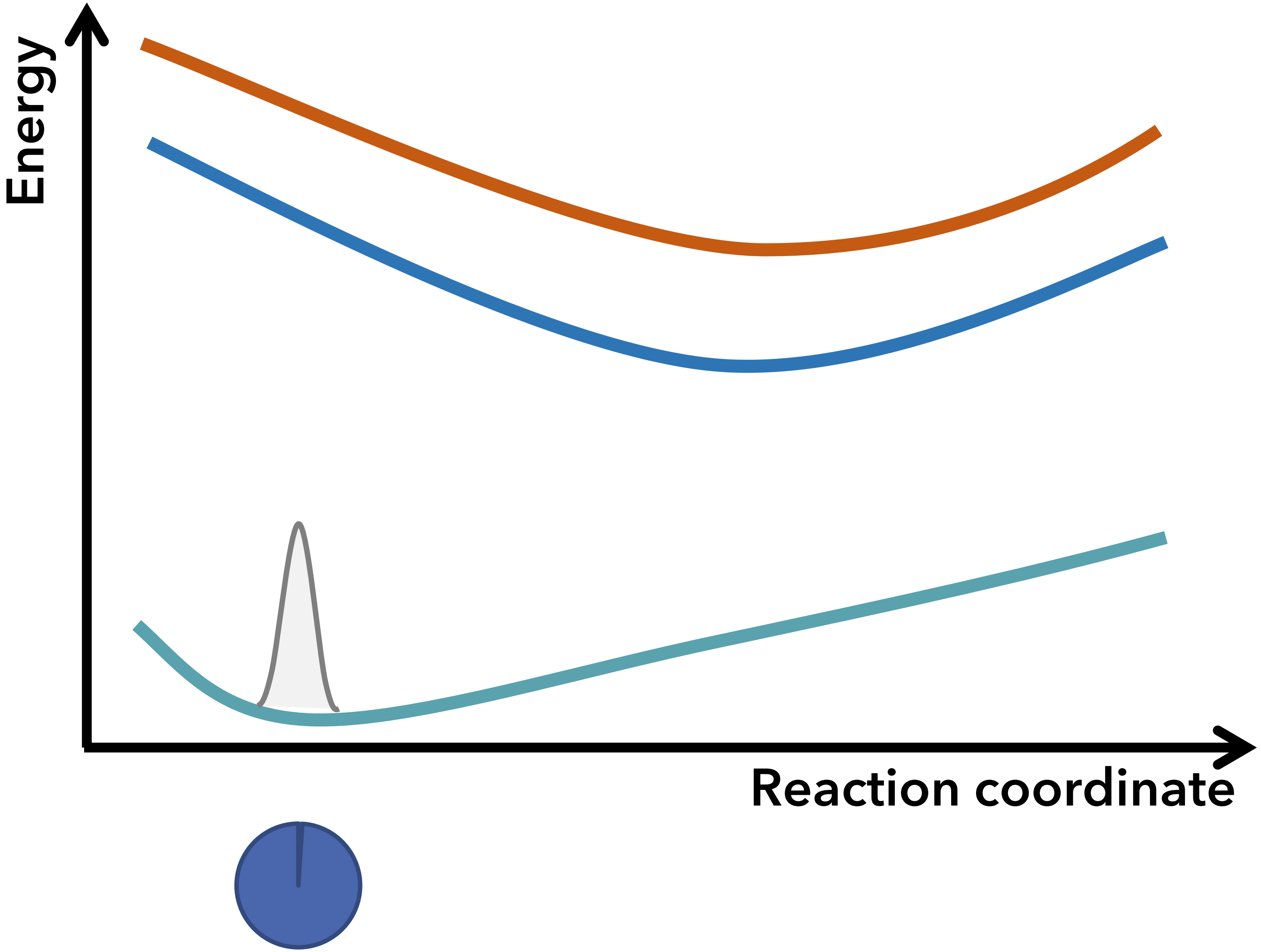
Nonadiabatic Molecular Dynamics: Concepts, Methods, and Emerging Tools

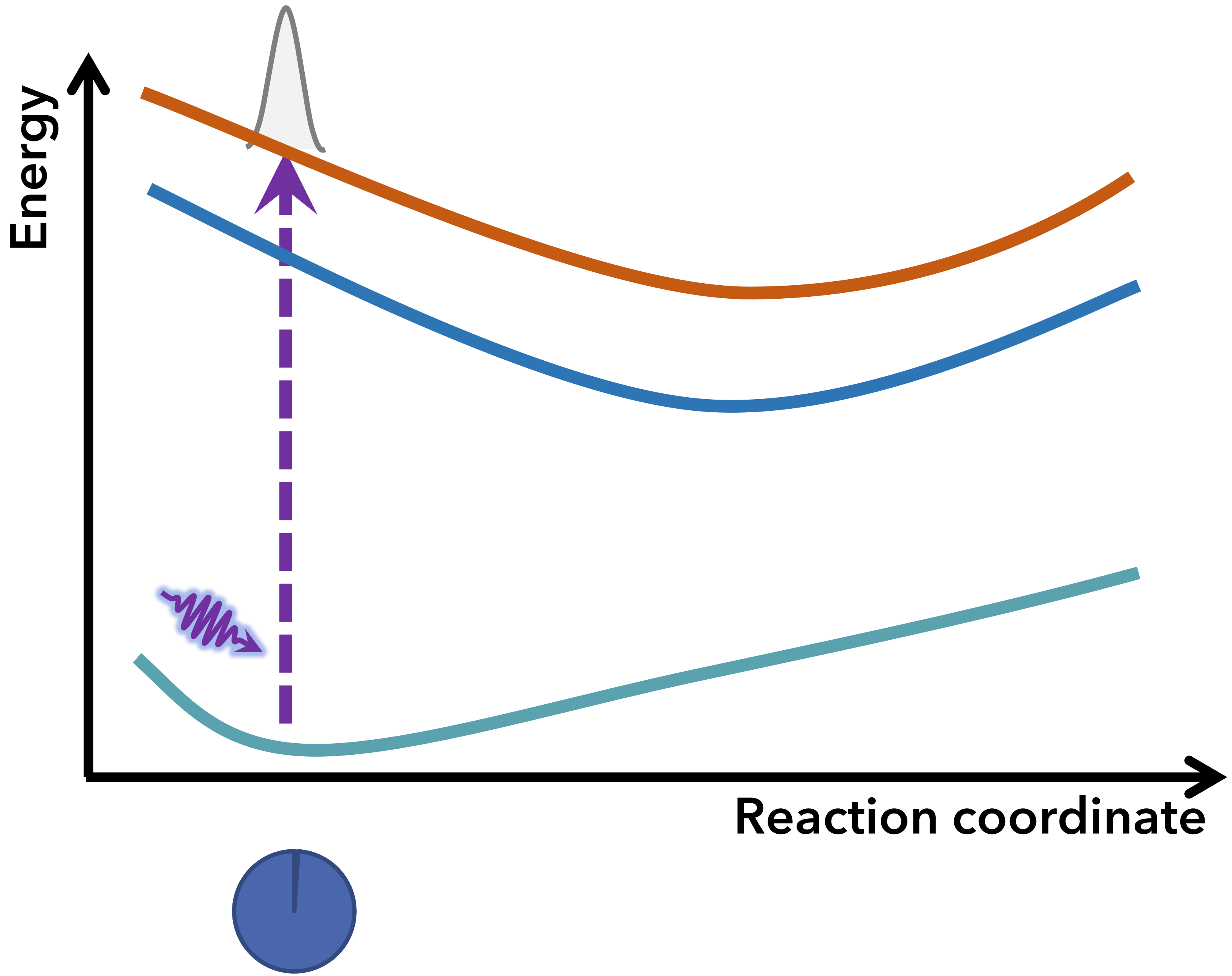
III– Case study: Non-Kasha fluorescence of pyrene

Case study:
Non-Kasha fluorescence of pyrene

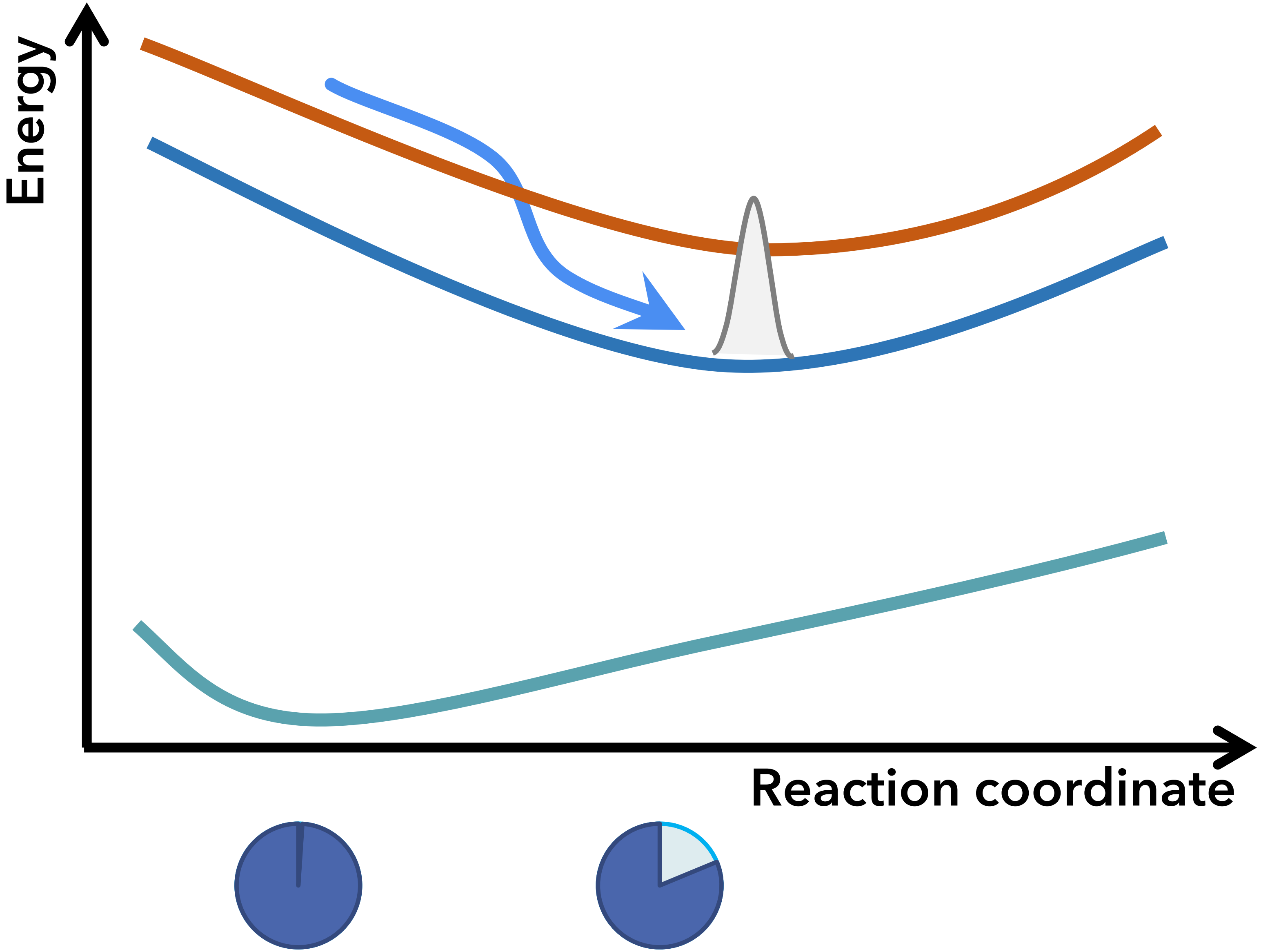
Nonadiabatic dynamics



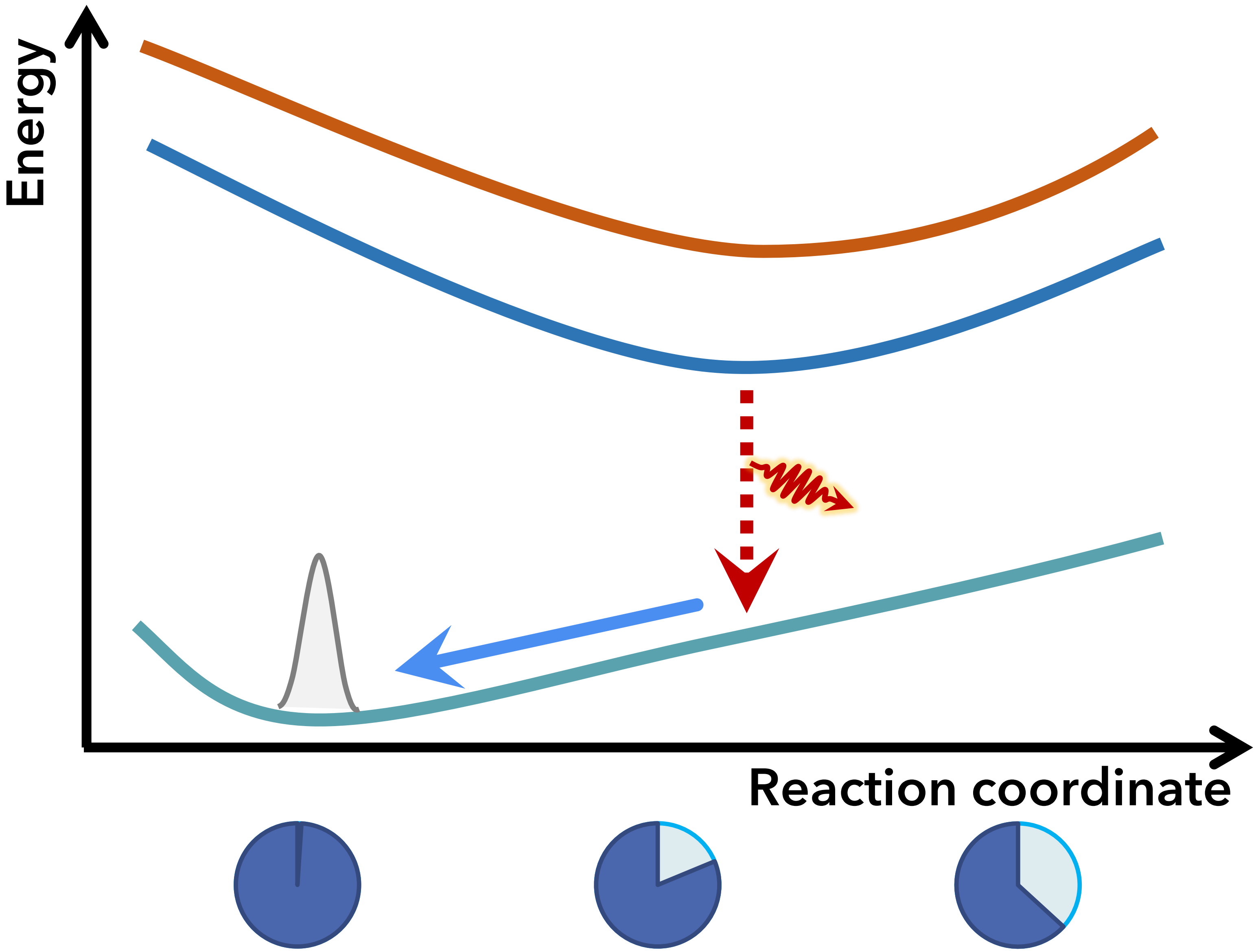
Photoabsorption



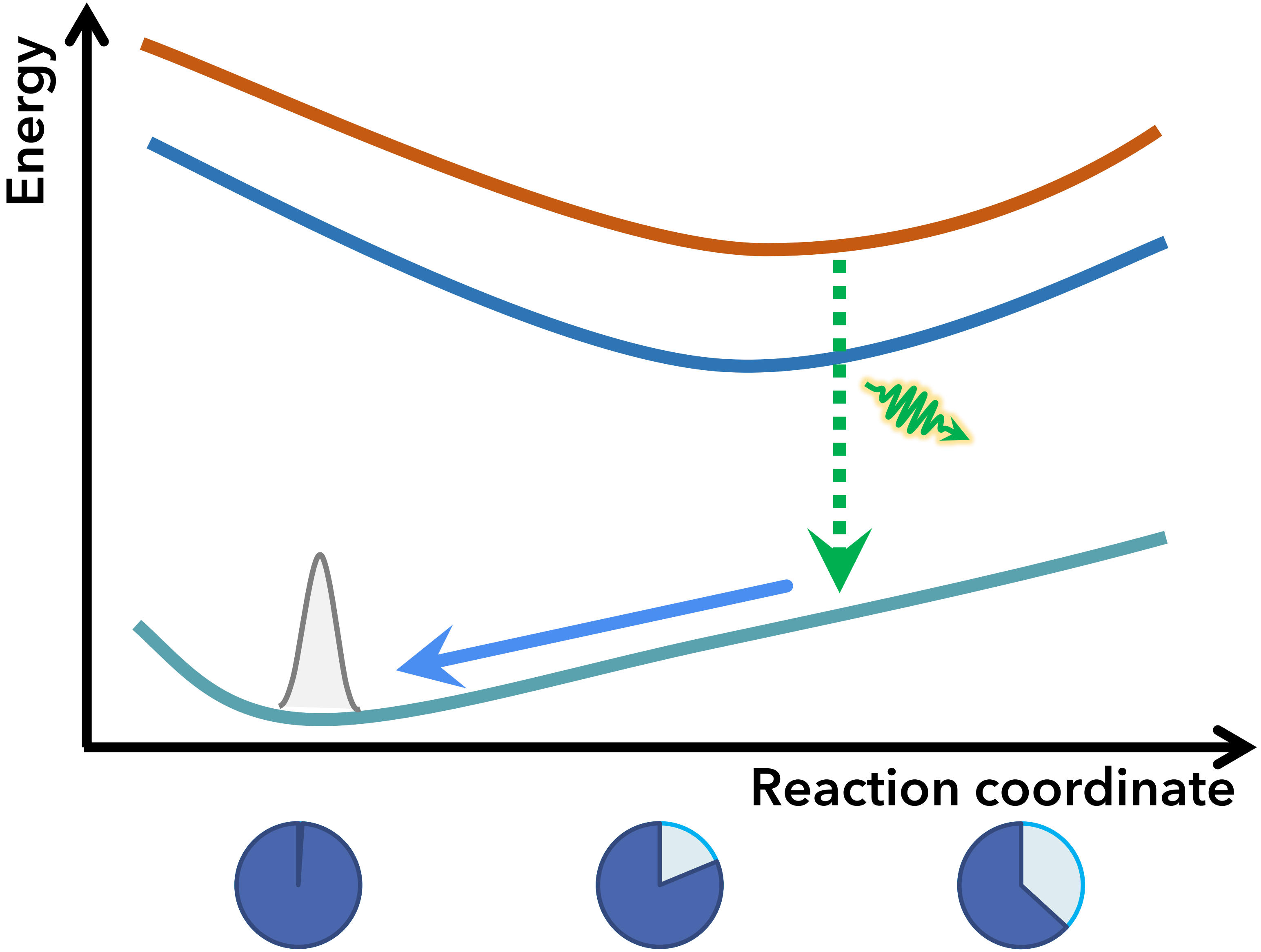
Kasha rule

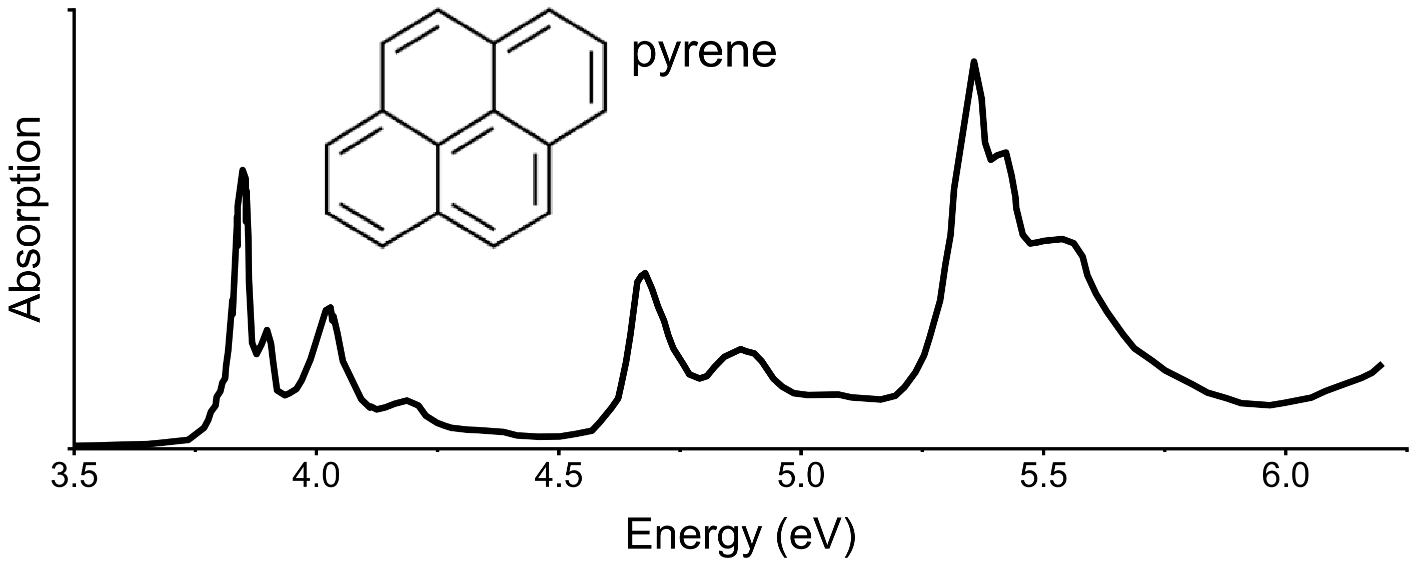


Fluorescence

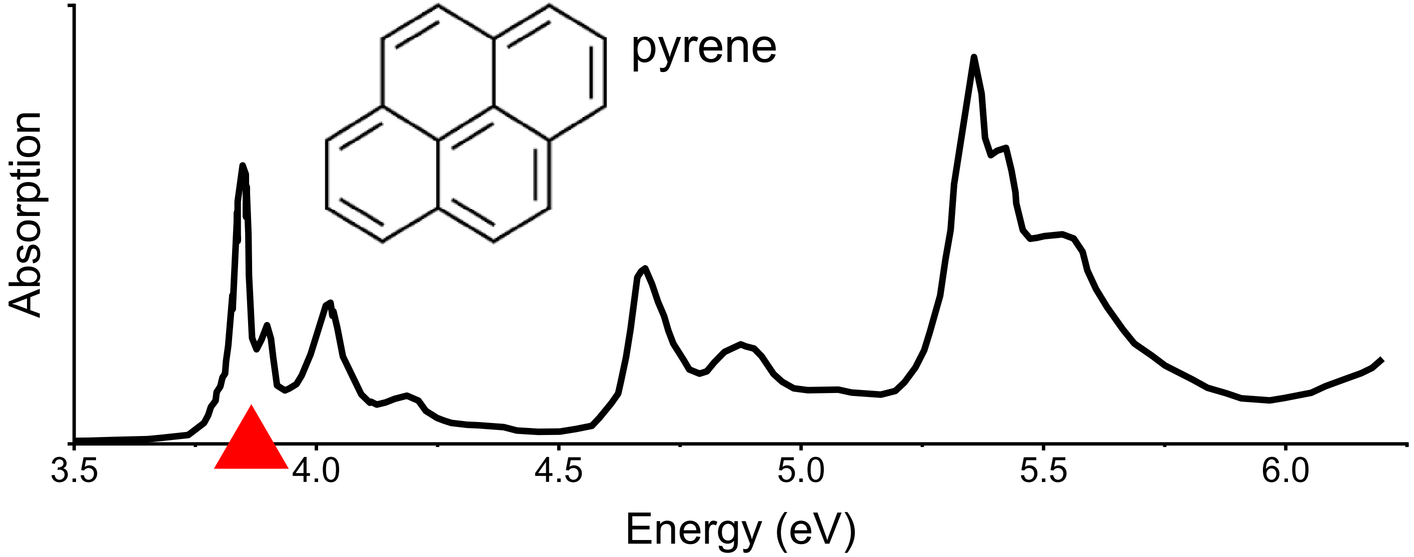


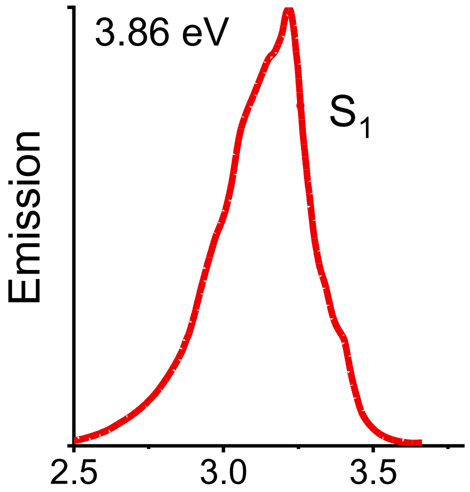
Non-Kasha fluorescence



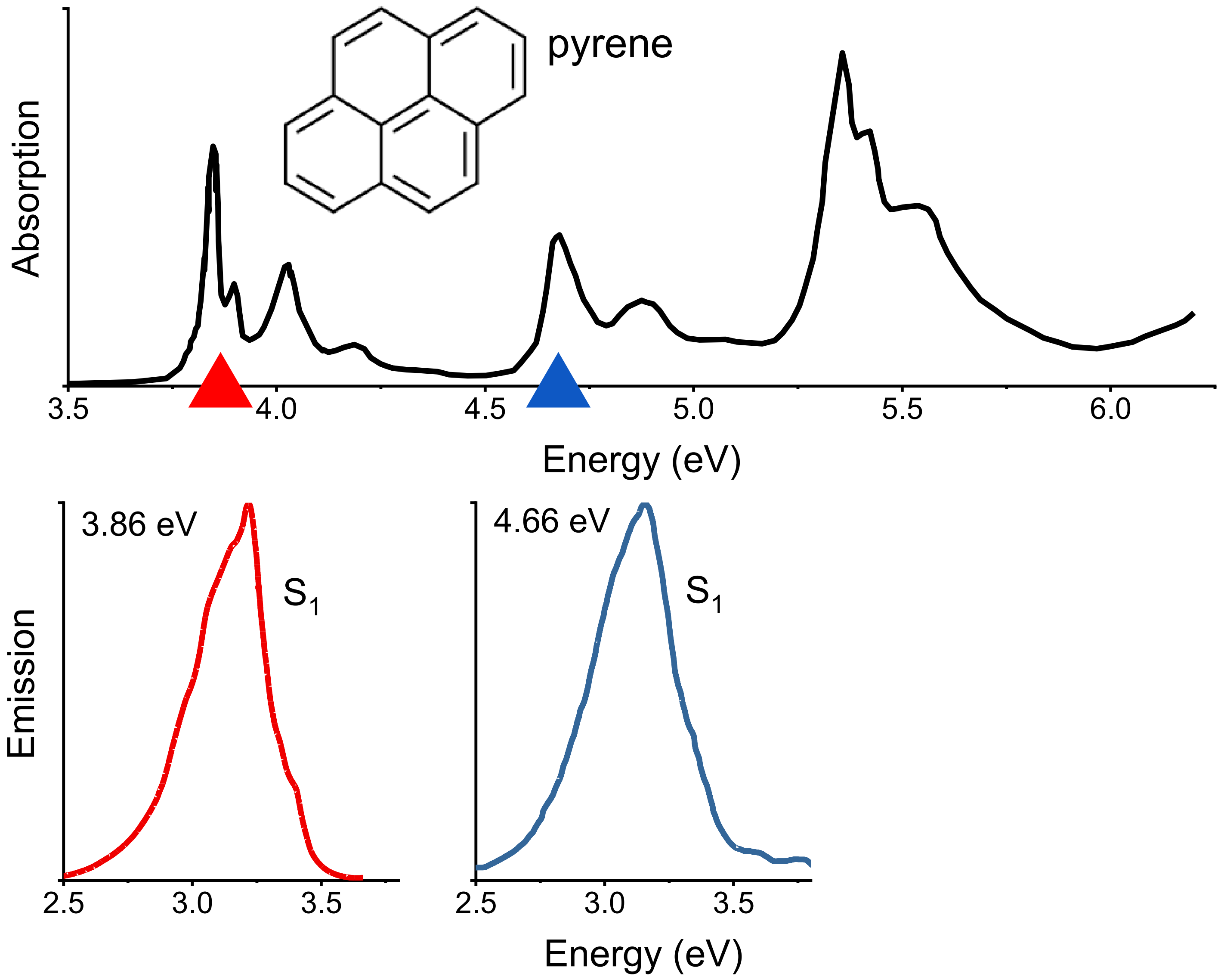


Baba *et al. J Chem Phys* **1971,** *55*, 2433





Baba *et al. J Chem Phys* **1971,** *55*, 2433



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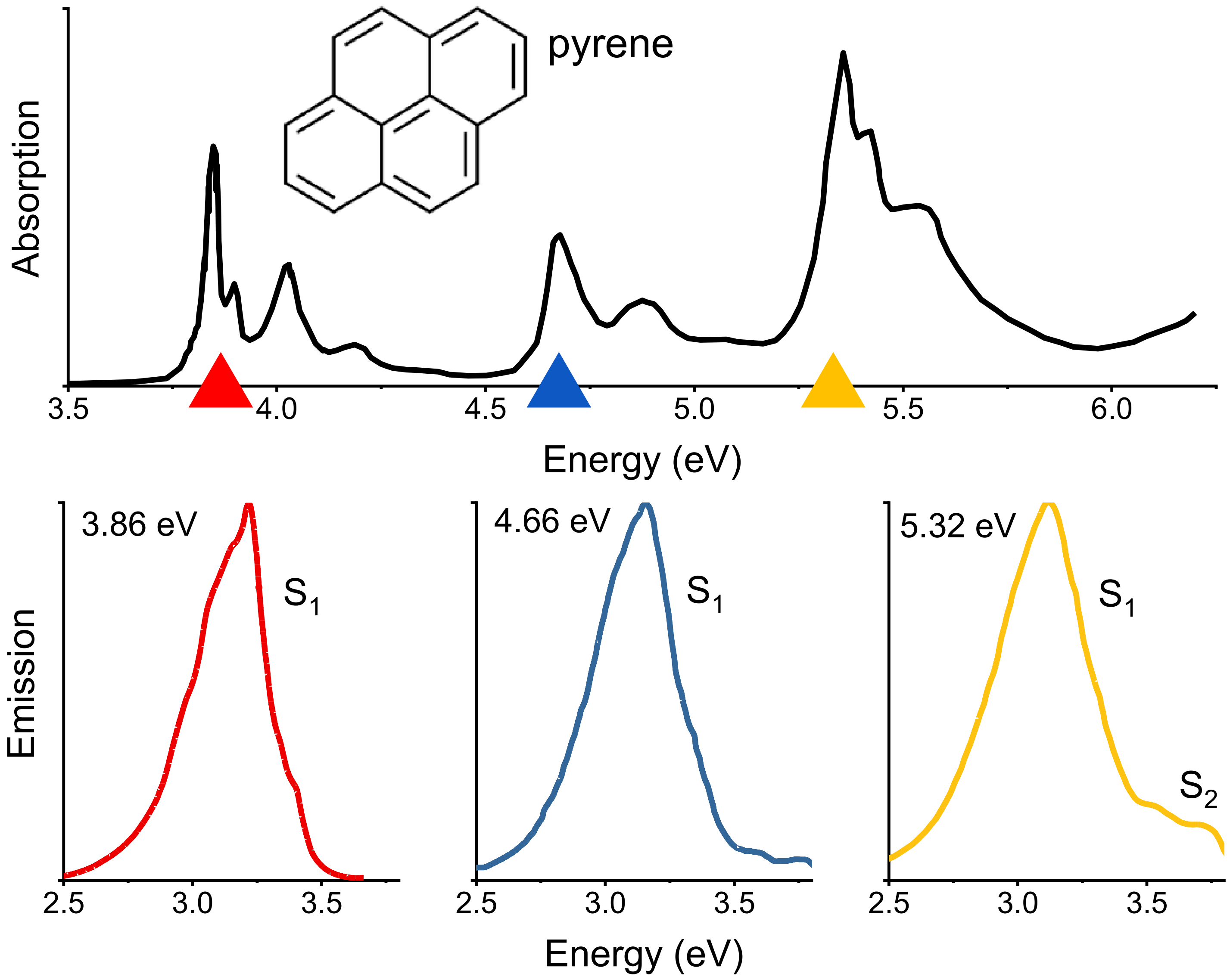
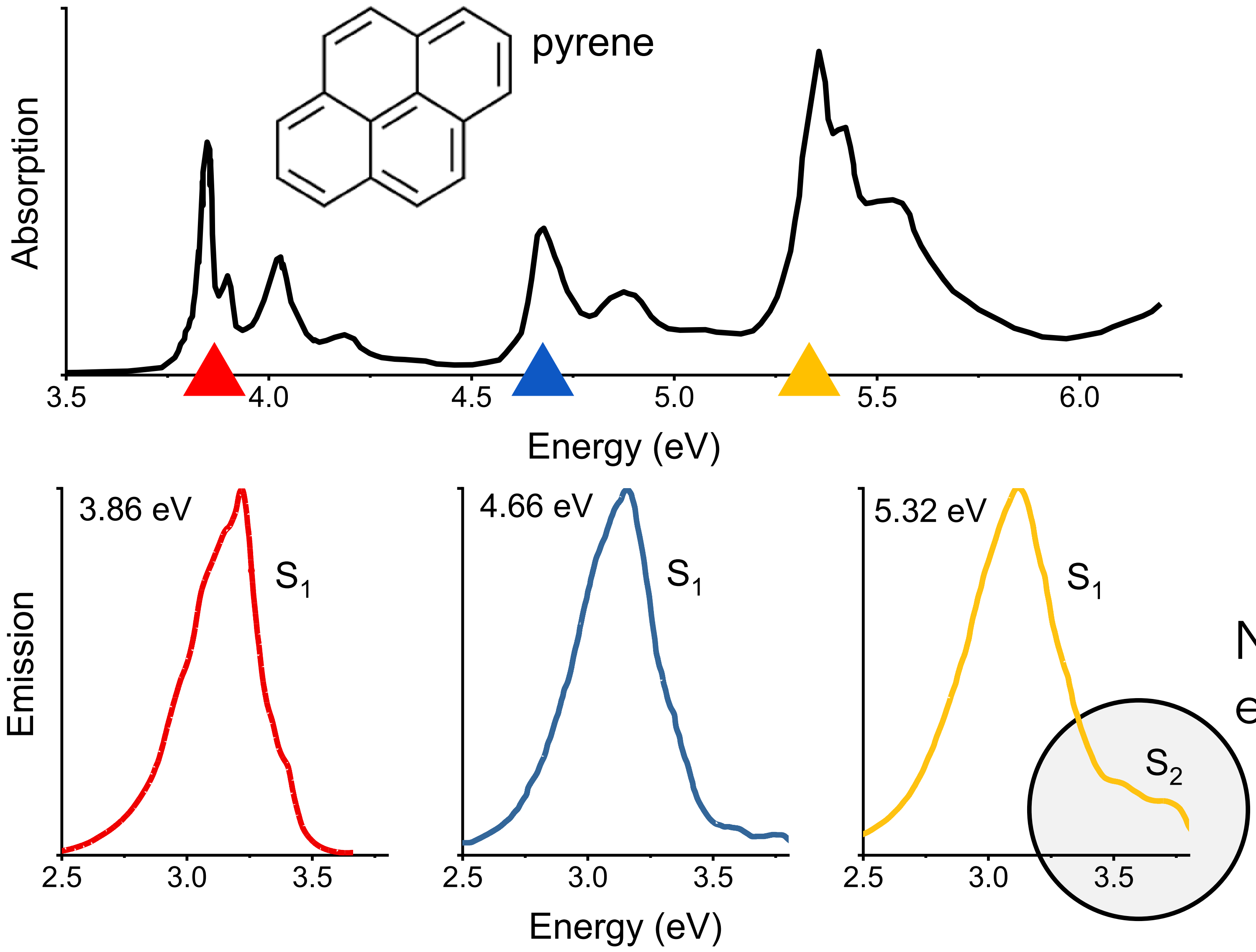


Baba *et al. J Chem Phys* **1971,** *55*, 2433



Non-Kasha emission?

The Journal of Chemical Physics
ARTICLE
scitation.org/journal/jcp

Non-Kasha fluorescence of pyrene emerges from a dynamic equilibrium between excited states

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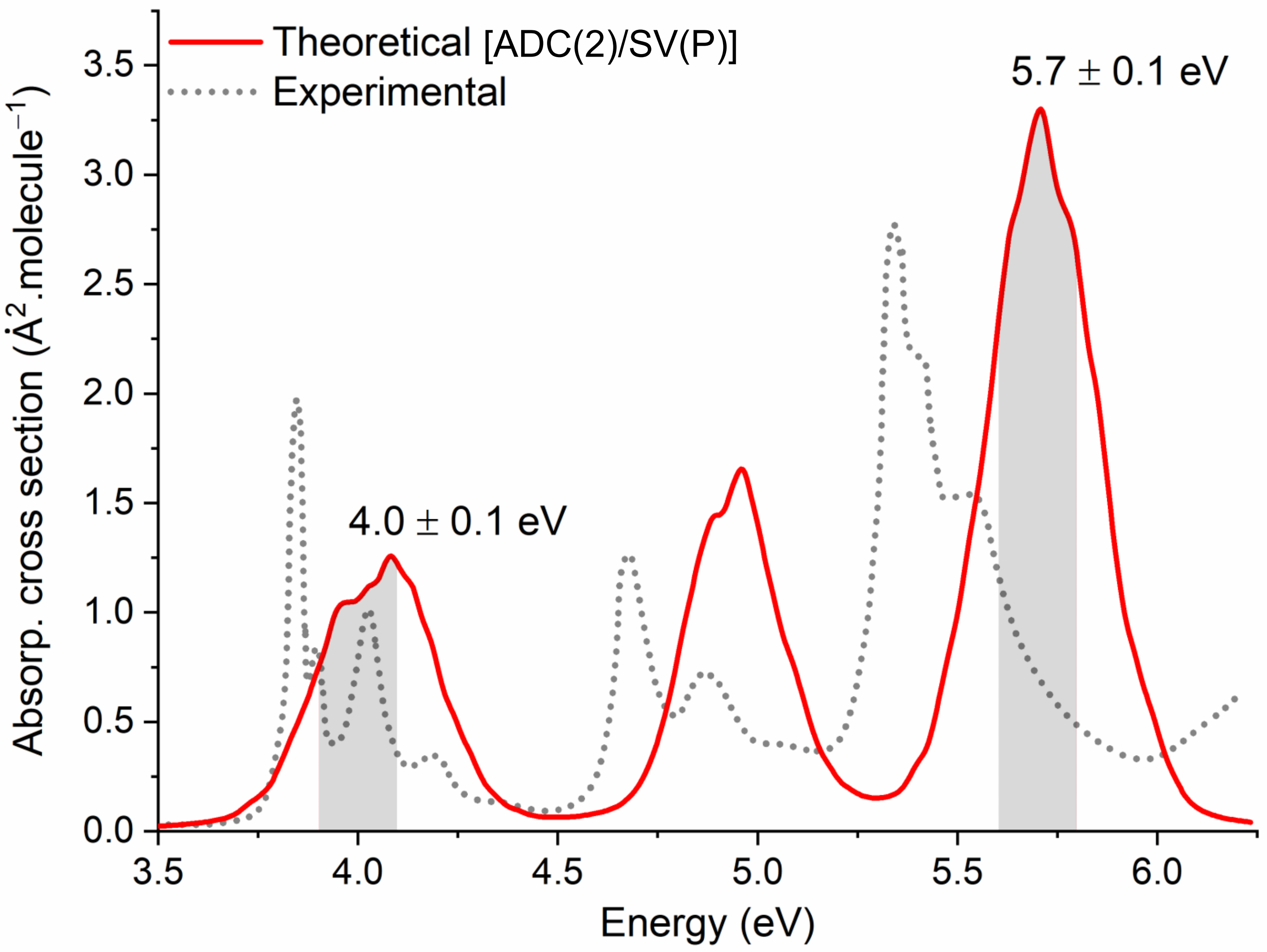
Braun *et al*. *J Chem Phys* **2022**, *157*, 154305

Dynamics from two excitation windows



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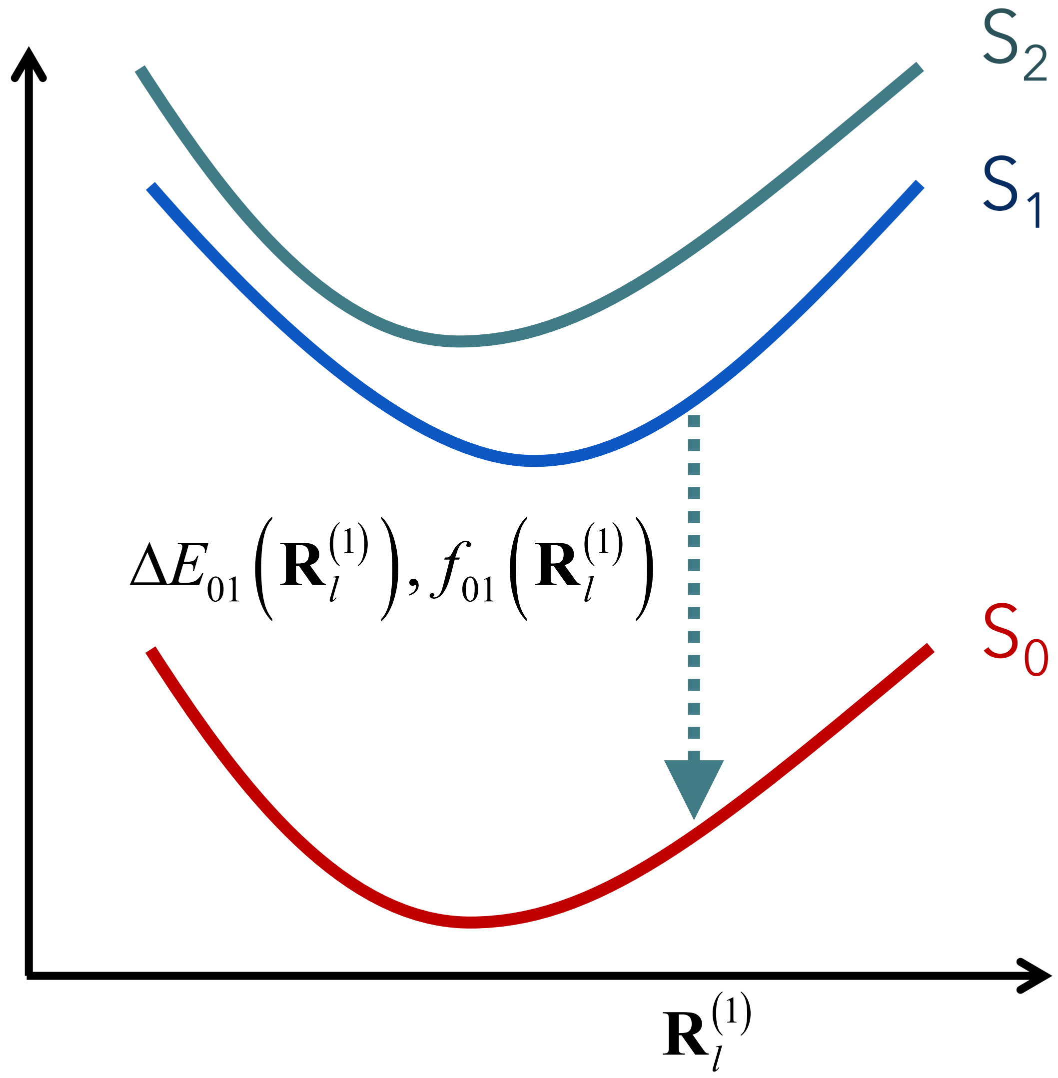
Simulating non-Kasha fluorescence

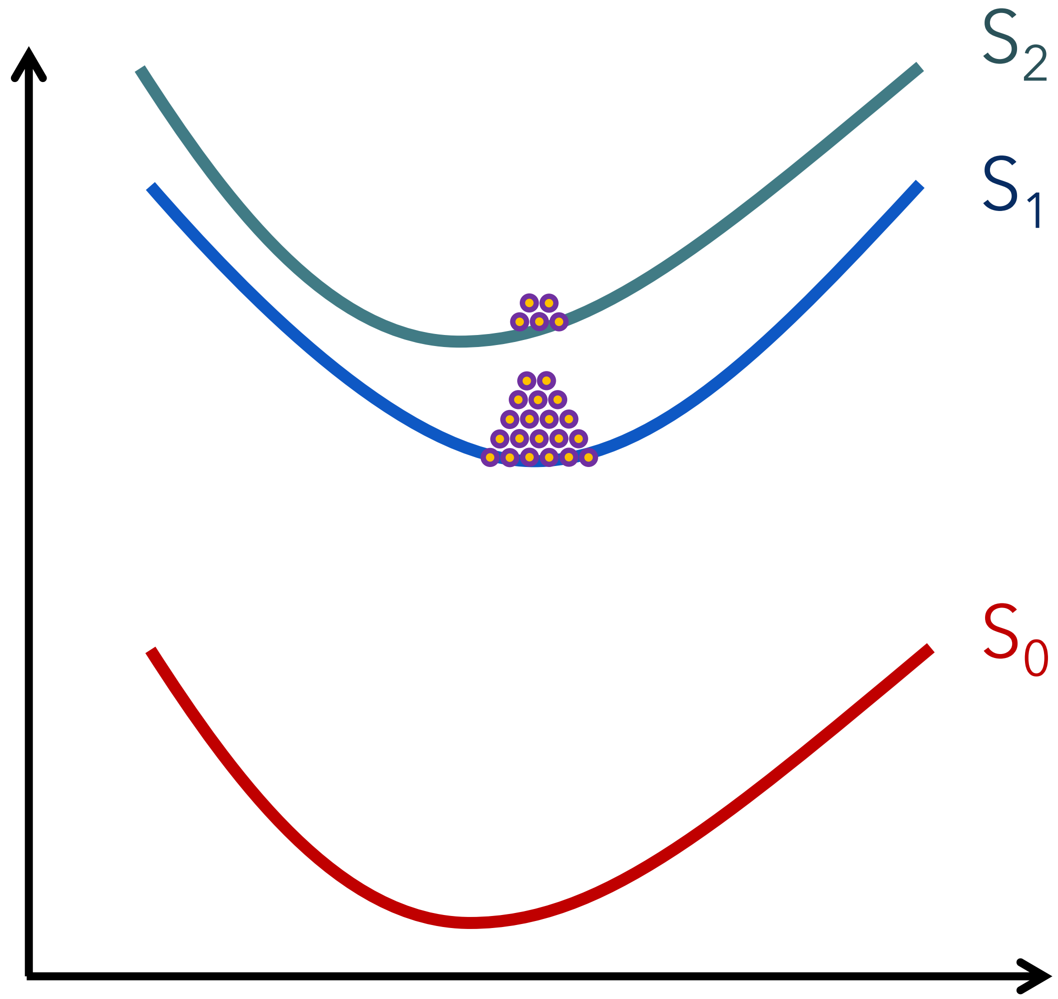
$$\Gamma_{TOT}\left(E\right)=\sum_J \Gamma_{J\to 0}\left(E\right)\rho_{1J}$$

$\sum_J (\ )$	Sum over electronic states *J*
$\Gamma_{J\to 0}\left(E\right)$	Differential emission rate from S_J to S_0
ρ_{1J}	Distribution of excited-state population *J* (relative to S_1)



$$\Gamma_{TOT}(E) = \sum_J \Gamma_{J\to 0}(E)\,\rho_{1J}$$

$$\Gamma_{J\to 0}(E) = \frac{2\alpha^3}{N_p^{(J)}} \sum_l^{N_p^{(J)}} \Delta E_{0J}^2\left(\mathbf{R}_l^{(J)}\right) f_{0J}\left(\mathbf{R}_l^{(J)}\right) \times\left[1 - H\left(E - \varepsilon_a\right)\right] \times G\left(E - \Delta E_{0J}\left(\mathbf{R}_l^{(J)}\right), \delta_J\right)$$



$$\Gamma_{TOT}\left(E\right)=\sum_{J}\Gamma_{J\to 0}\left(E\right)\rho_{1J}$$

$$\rho_{1J}=\frac{N_p^{(J)}}{N_T}$$

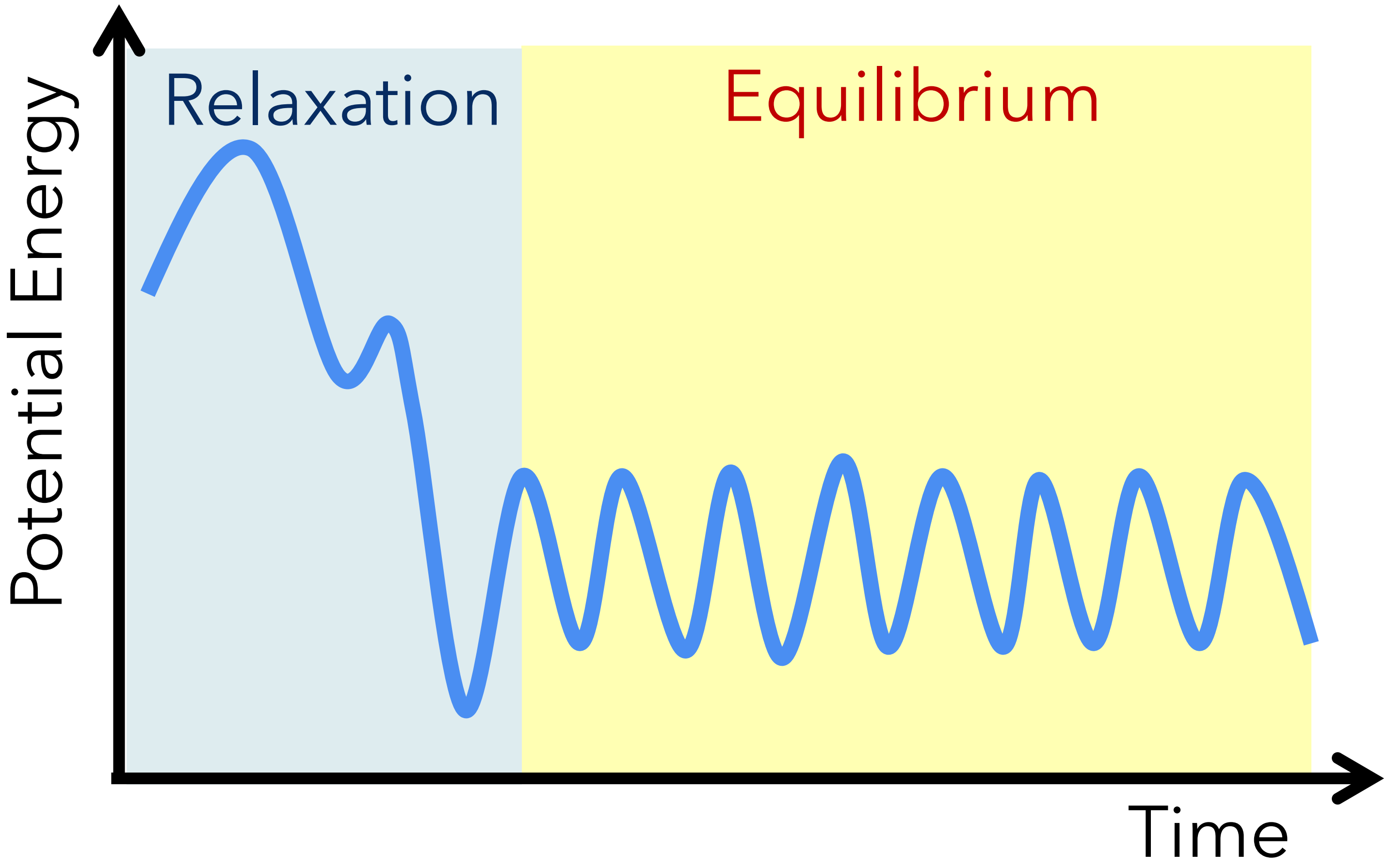
Number of points in state *J* during dynamics

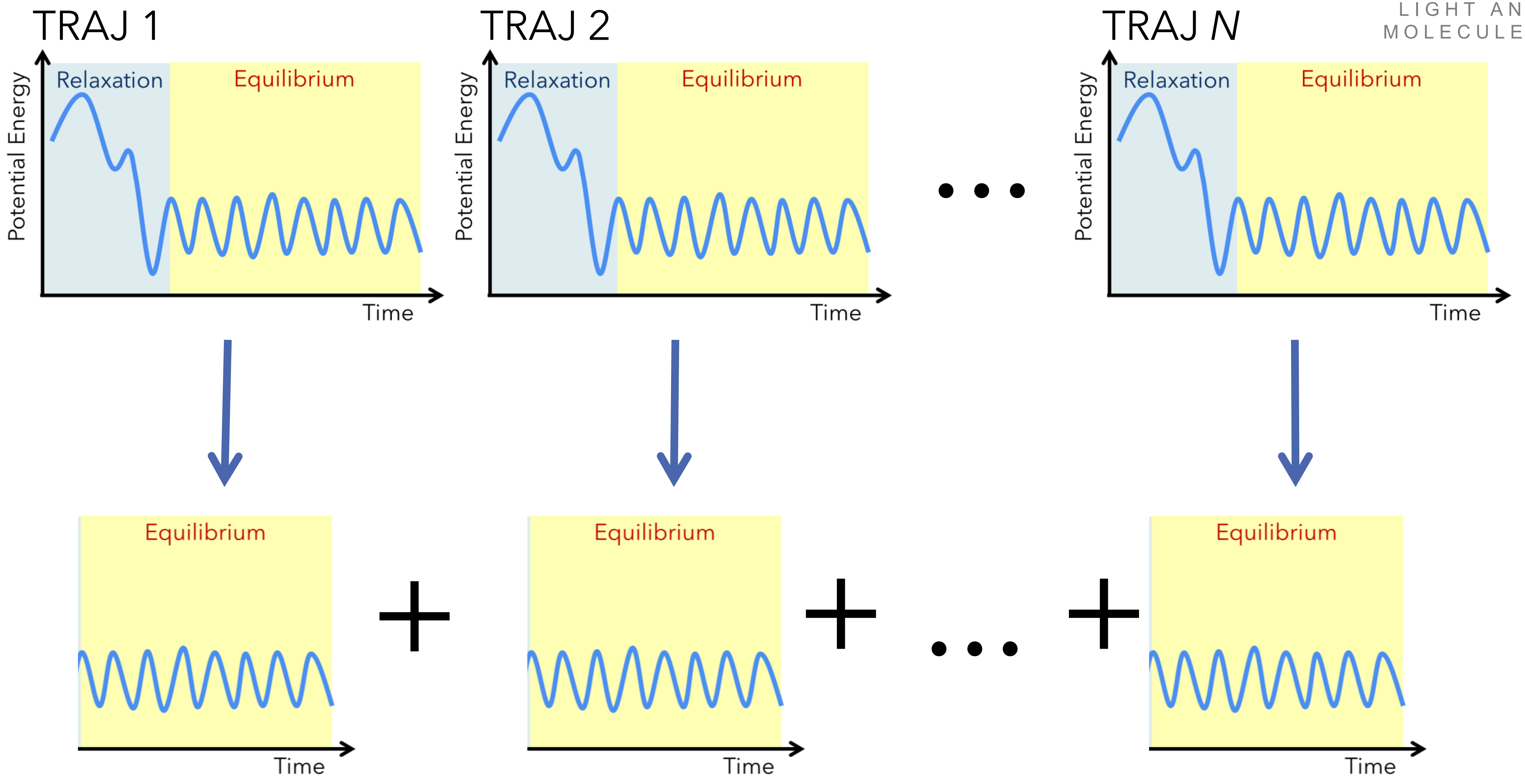
Building the ensemble

Pyrene fluorescence: 100 ns – Dynamics is unaffordable

Ergodic protocol:

- Simulate many short surface hopping trajectories
- Discard initial relaxation
- Build the ensemble with the relaxed part of all trajectories
- Suppose this total cumulative time is representative of phase space occupation


Potential Energy
Relaxation
Equilibrium
Time



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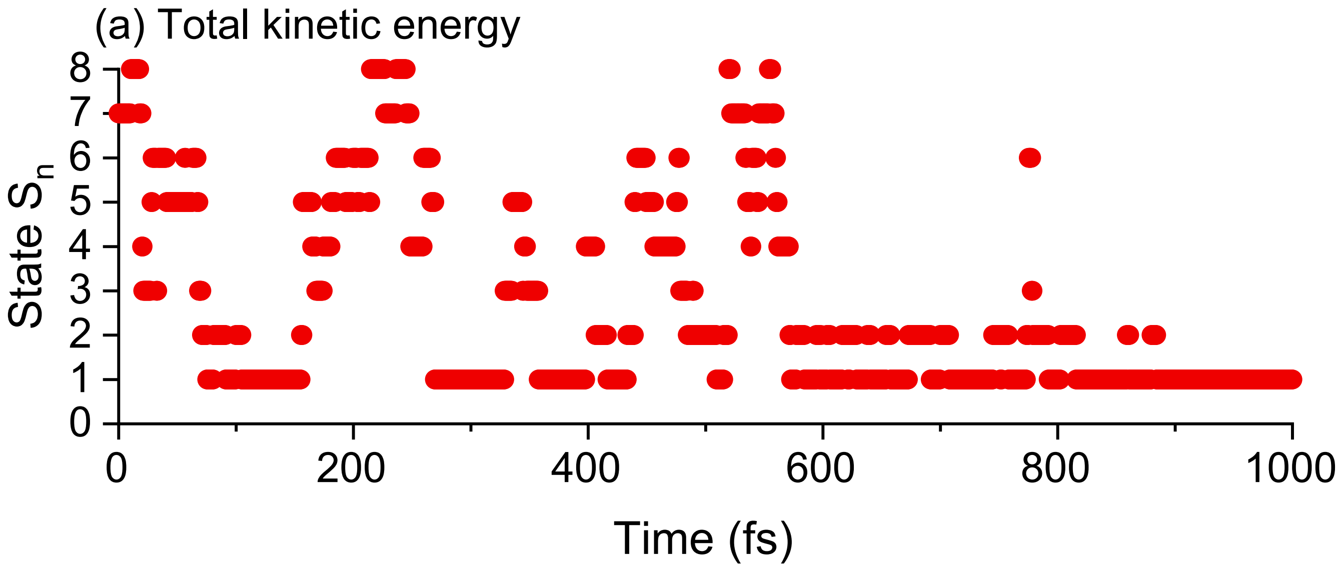
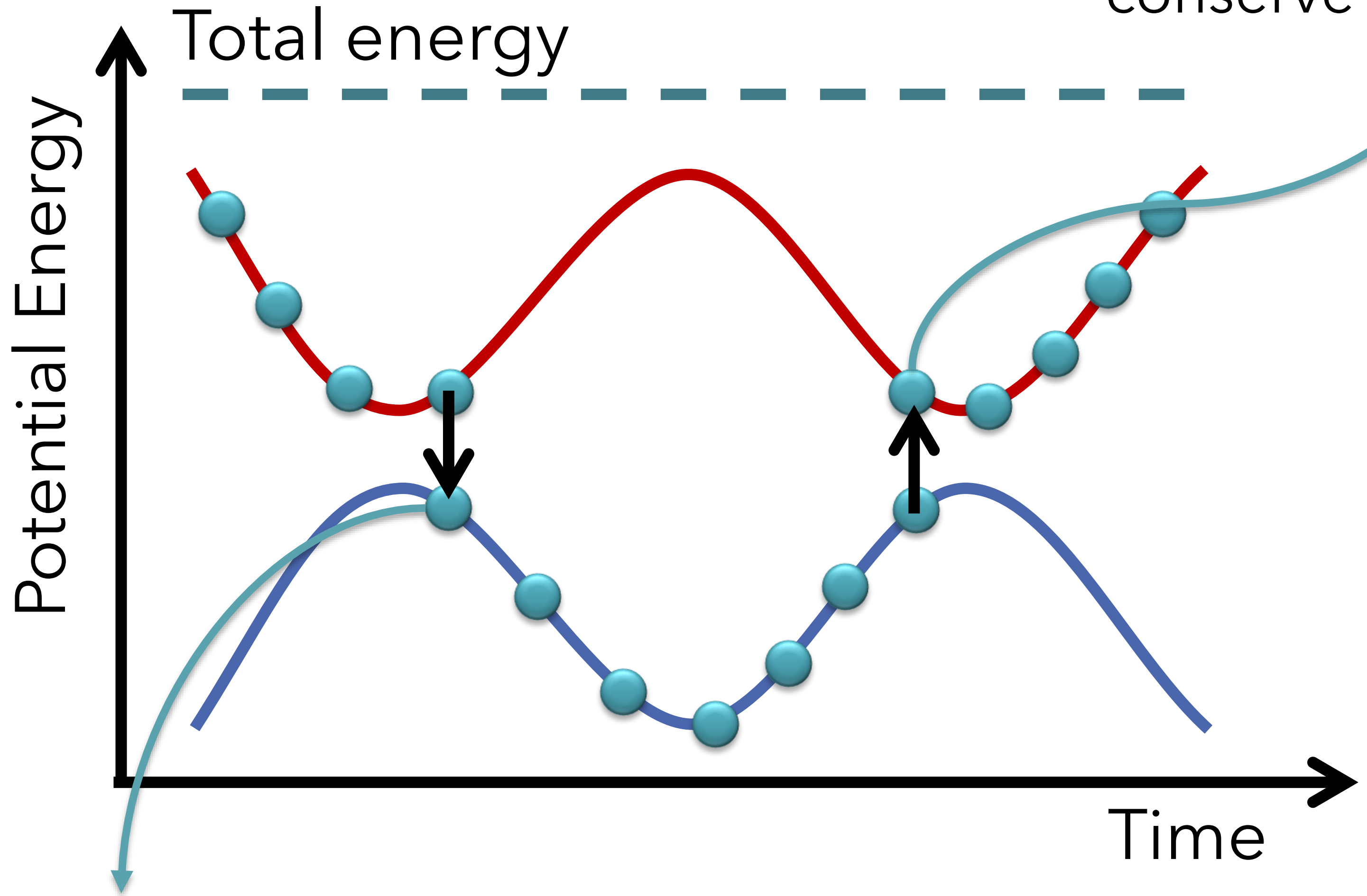
Then, ADC(2) surface hopping...



A parenthesis:
Velocity rescaling in surface hopping

Reduce the velocity to
conserve total energy



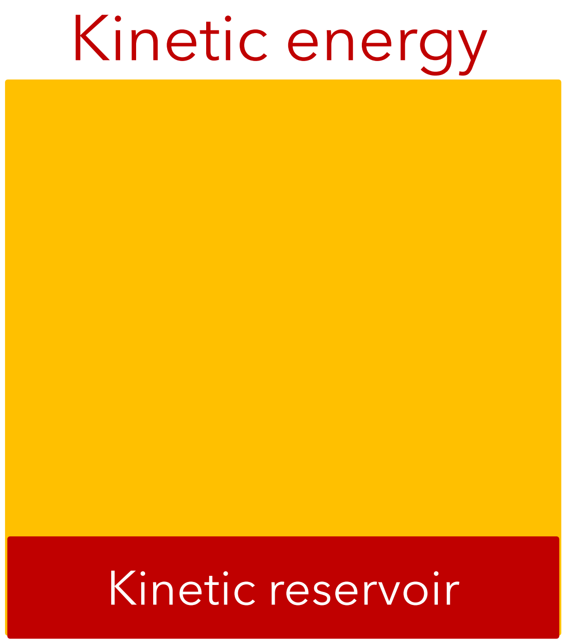
Increase the velocity to
conserve total energy

After hopping from L to J , velocity is rescaled as

$$\mathbf{v}_\alpha^{(J)} = \mathbf{v}_\alpha^{(L)} + \gamma_{LJ} \frac{\mathbf{u}_\alpha}{M_\alpha}$$

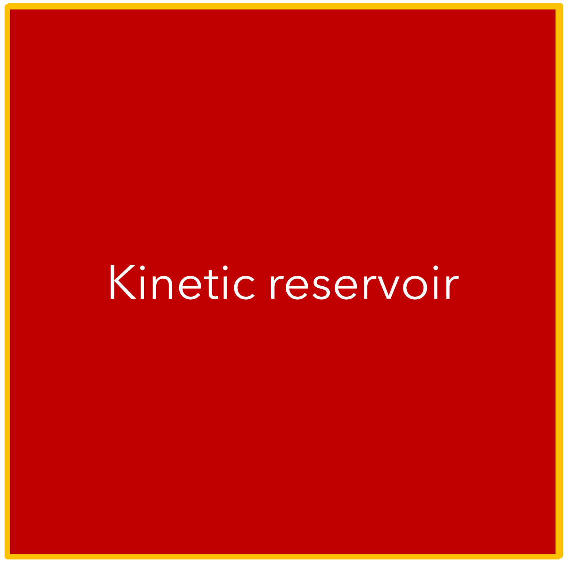
Rescaling is only possible if the kinetic energy removed from the molecule satisfies

$$\left|\Delta K_{LJ}\right| \leq \underbrace{\frac{1}{2\sum_\alpha \frac{u_\alpha^2}{M_\alpha}} \left(\sum_\alpha \mathbf{v}_\alpha^{(L)} \cdot \mathbf{u}_\alpha \right)^2}_{\text{Kinetic energy reservoir}}$$



Rescaling in the NAC direction ($\mathbf{u} = \mathbf{h}_{LJ}$)

$$\left|\Delta K_{LJ}\right| \leq \frac{1}{2\sum_{\alpha}\frac{\left(h_{LJ,\alpha}\right)^2}{M_\alpha}}\left(\sum_{\alpha}\mathbf{v}_{\alpha}^{(L)} \cdot \mathbf{h}_{LJ,\alpha}\right)^2$$

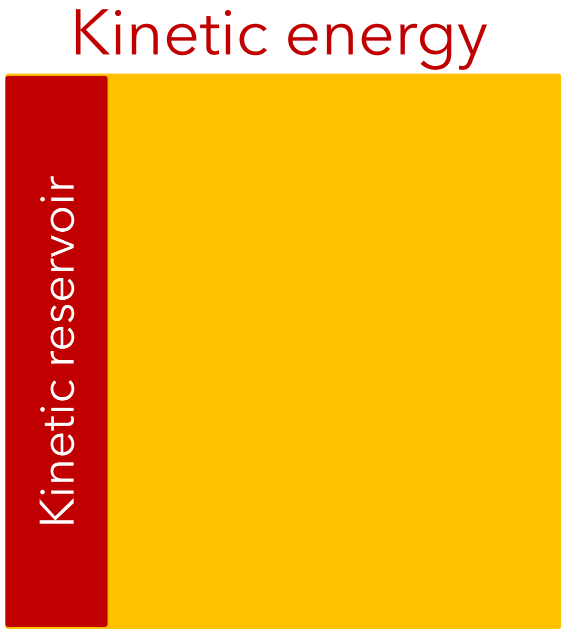


Rescaling in the momentum direction ($\mathbf{u} = \mathbf{p}_{L}$)

$$\left|\Delta K_{LJ}\right| \leq \frac{1}{2\sum_{\alpha}\frac{p_{L,\alpha}^2}{M_\alpha}}\left(\sum_{\alpha}\mathbf{v}_{\alpha}^{(L)} \cdot \mathbf{p}_{L,\alpha}\right)^2 = K_L$$

Rescaling in the momentum direction, with a **reduced kinetic reservoir**

$$\left|\Delta K_{LJ}\right| \leq \frac{K_L}{N}$$



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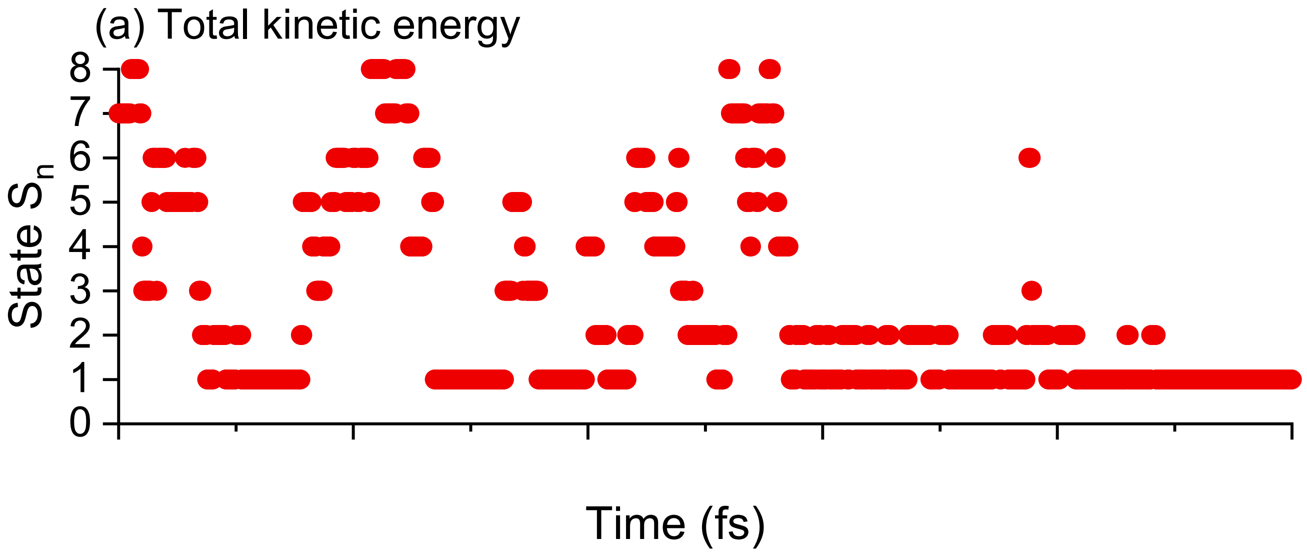
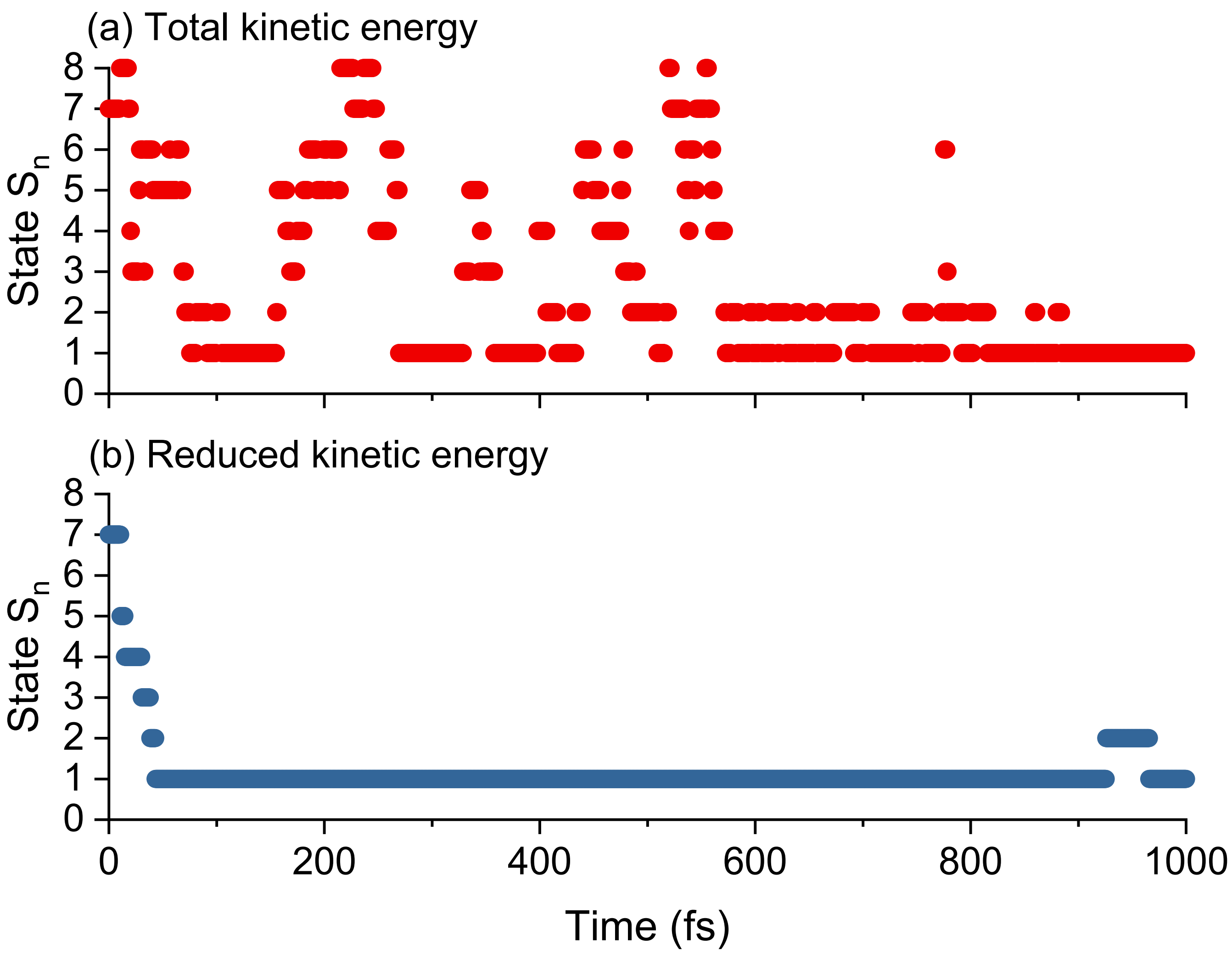
Velocity rescaling!



Velocity rescaling!



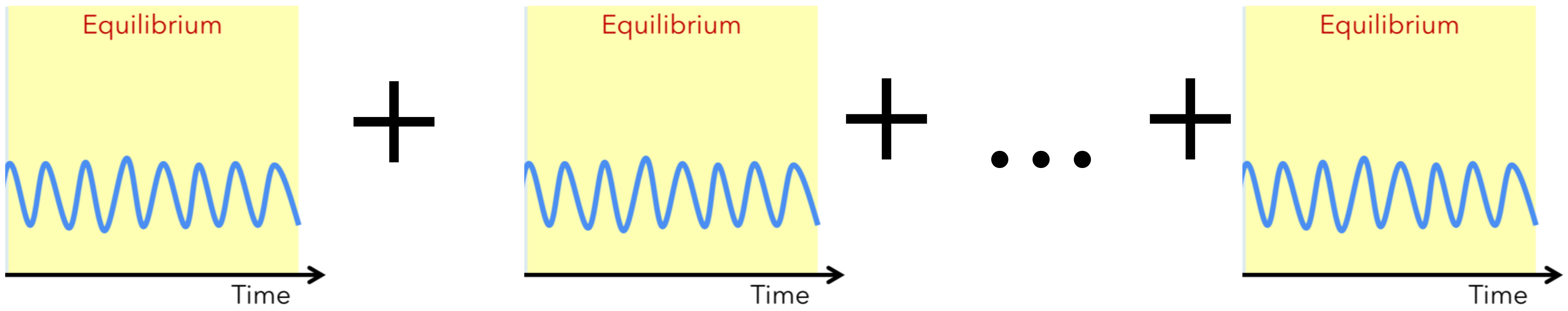
Quick guide to velocity rescaling:

- If possible, rescale along the NAC vector direction
- If NAC vectors are unavailable, adjust in the gradient difference direction
- If gradient differences are unavailable, use a reduced kinetic reservoir

Toldo *et al. JCTC* **2024**, 20, *614*

End of parenthesis

TRAJ 1 TRAJ 2 TRAJ *N*



	Cumulative time
High-energy band	21 ps
Low-energy band	23 ps

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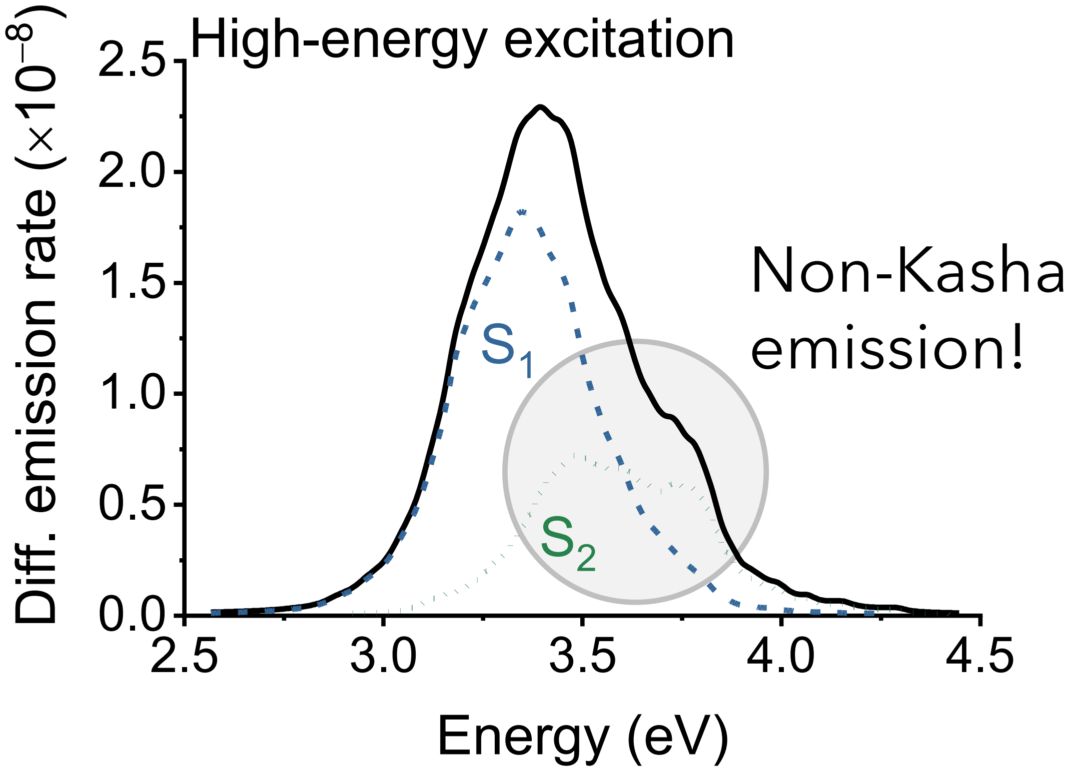

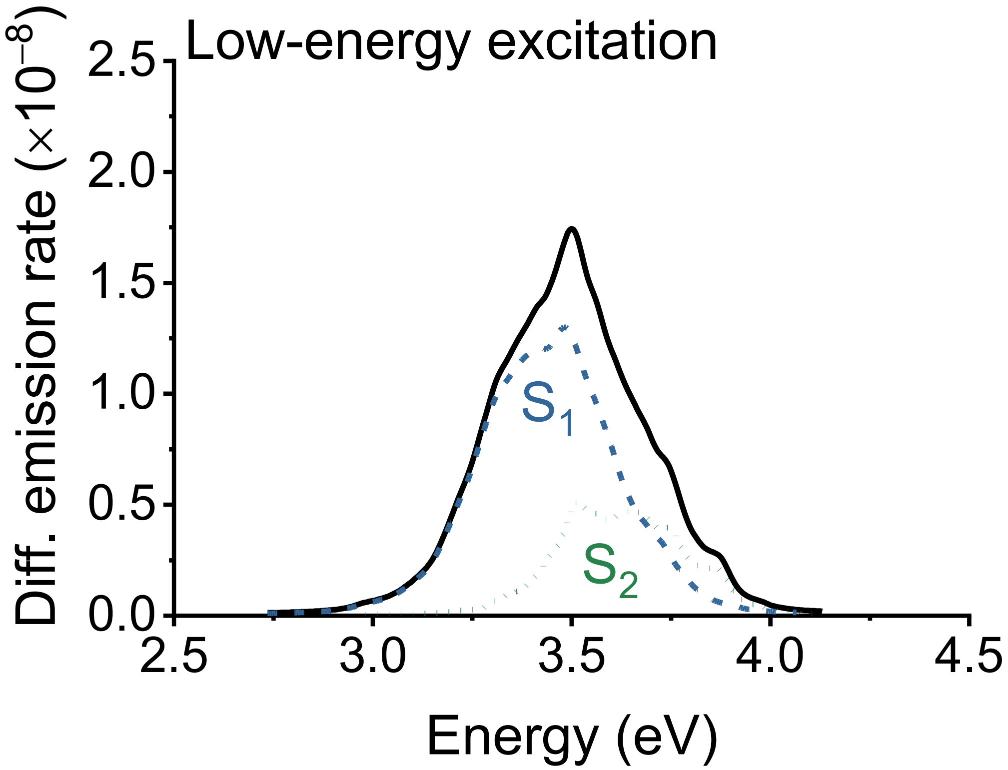

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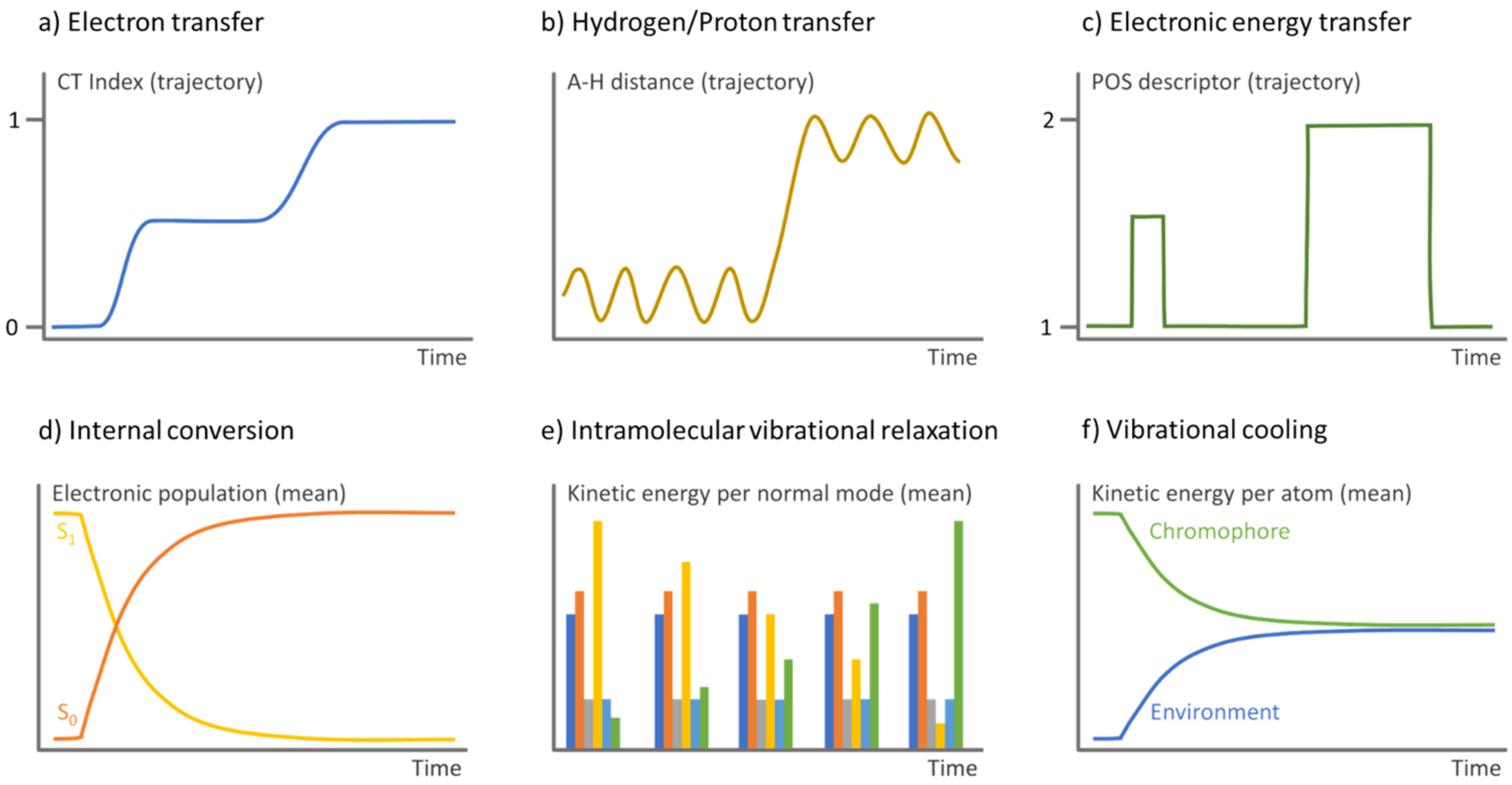
We employed nuclear ensembles and surface hopping to characterize the non-Kasha fluorescence of pyrene.

And we can do much more…

Surface hopping algorithmic flexibility



Toldo *et al.*, *PCCP* **2023,** *25*, 8293

Newton-X offers a complete software platform for surface hopping dynamics, from spectrum simulations to advanced data analysis.

Barbatti *et al.* *JCTC* **2022,** *18*, 6851

To know more:

Pyrene fluorescence:

- Braun *et al*. *J Chem Phys* **2022**, *157*, 154305

Kinetic energy rescaling:

- Toldo *et al. JCTC* **2024**, *20*, 614

Surface hopping flexibility:

- Toldo *et al.*, *PCCP* **2023,** *25*, 8293

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