On memory effects and molecular switches

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Collaboration: Giovanni Spaventa and Martin Plenio – arXiv:2103.14534

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- **Motivation**: Light induced reactions in chemistry/biology
- Ultrashort recap on **resource theories**
- Application: **Photo-isomers, optimal yield and memory**
- **Lessons/prospects**

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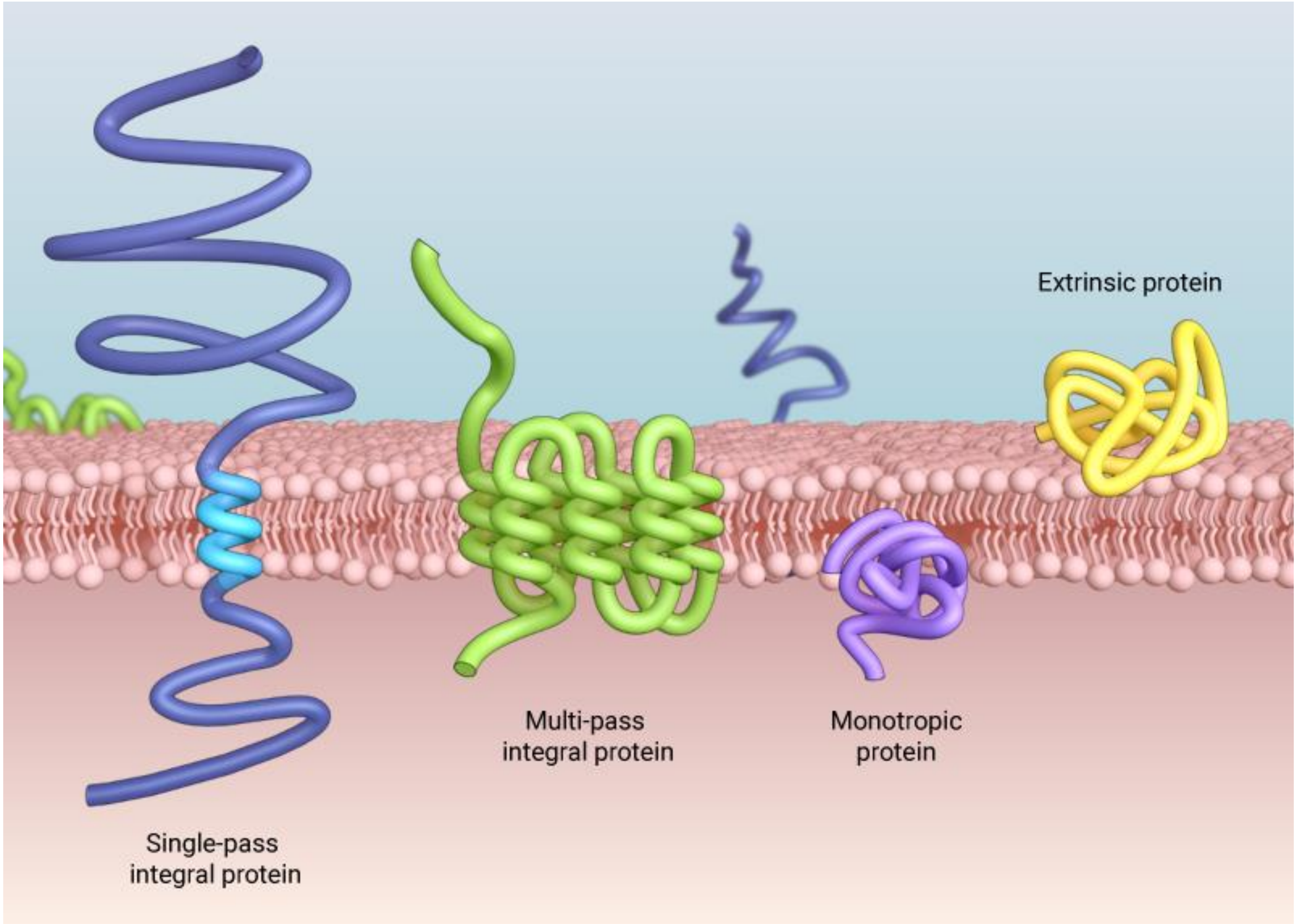
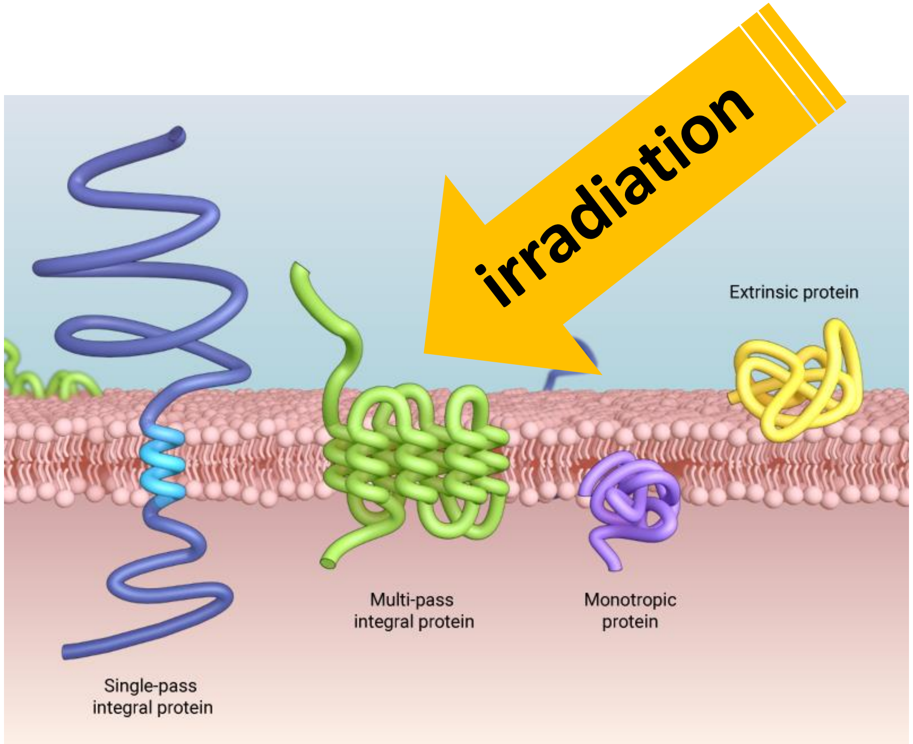
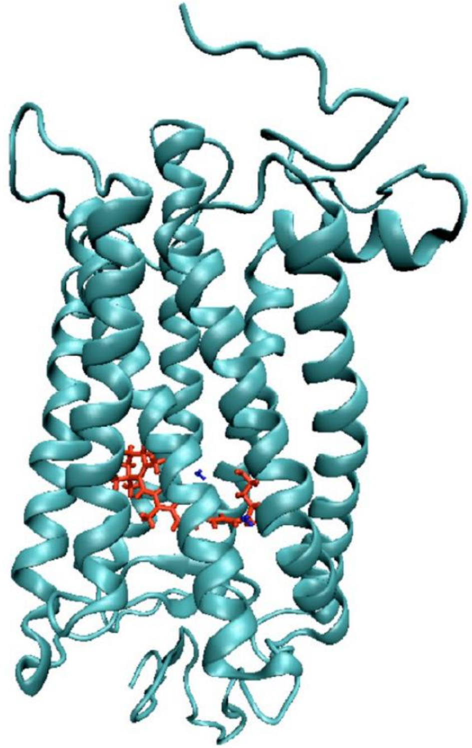

Extrinsic protein
Multi-pass
integral protein
Monotropic
protein
Single-pass
integral protein



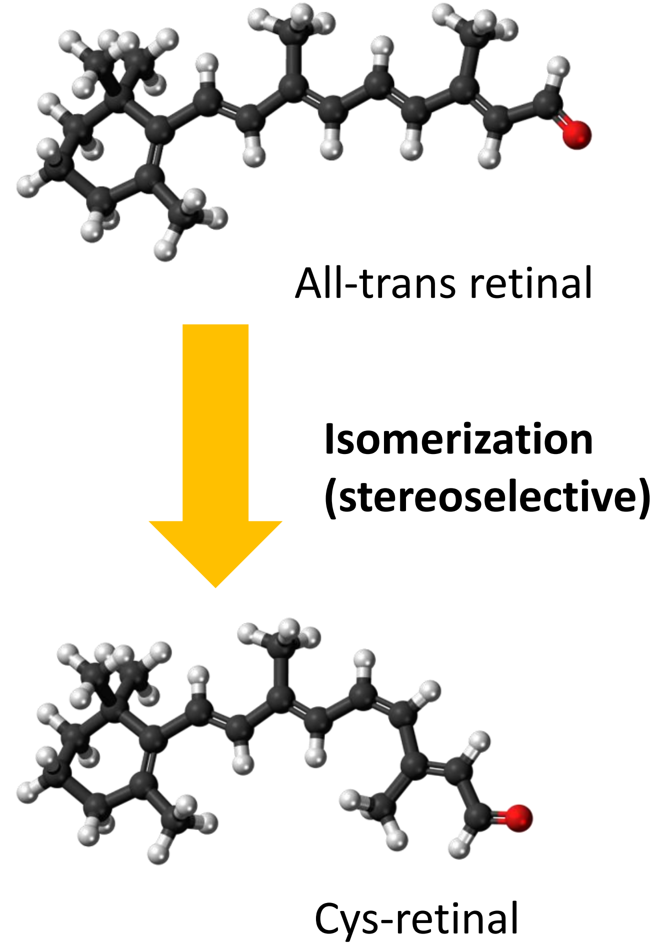
Ligth induced radiations in membrane proteins

Photosynthesis in plants, algae and bacteria
Radical pair formation (magnetic compass, bird navigation)
Retinal isomerization (vision)

Ultrafast processes
High quantum yield

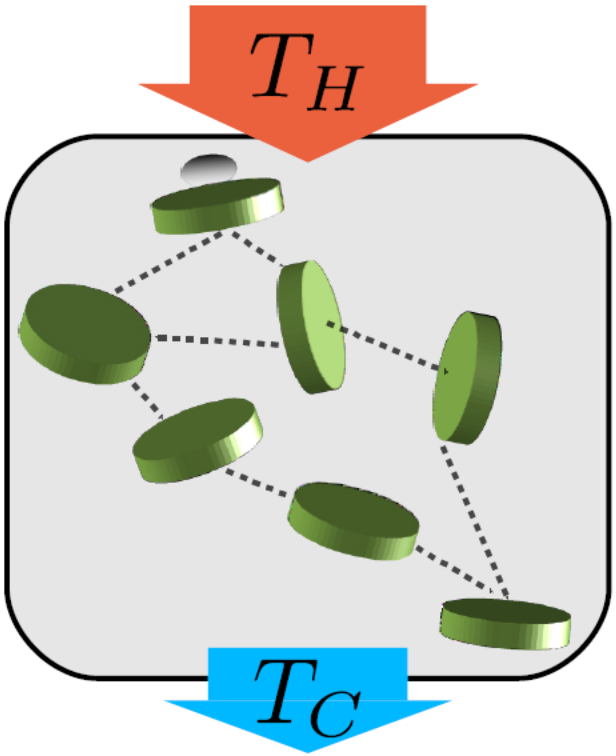


Crystal structure of Rh
(Protein Data Bank record 1U19, chain A)

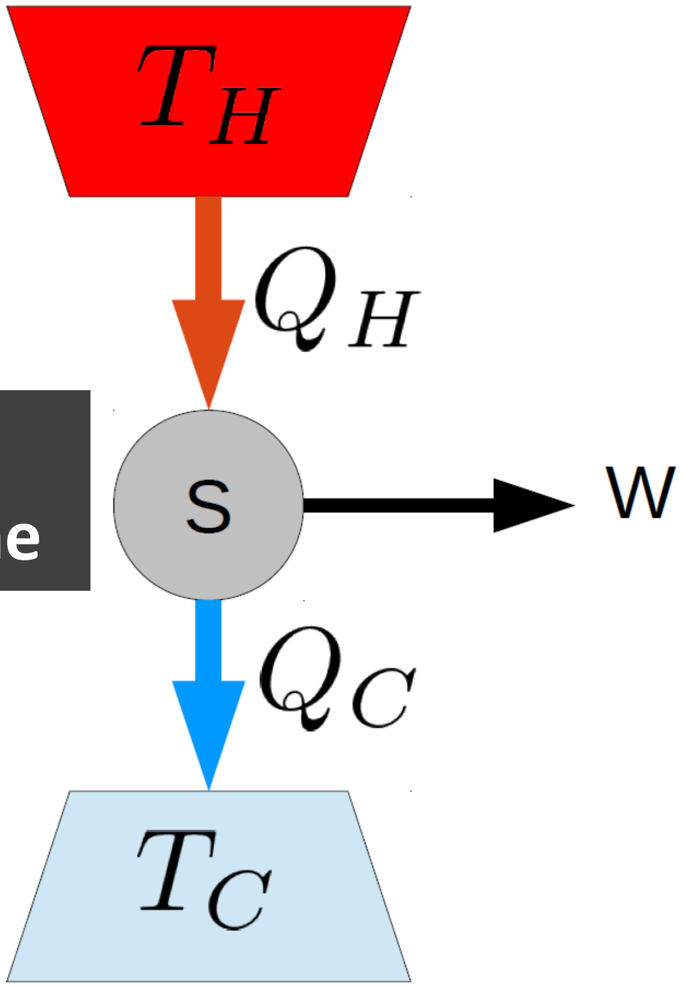


Yield is 67% versus a few percent (non selective) in solution

How does the protein environment *steer* this ultrafast single-product, high yield process?



Quantum Heat Engine



Scovil and Schultz-Dubois, PRL 2, 262 (1959)
Scully, PRL 104, 207701 (2010)
Creatore et al, PRL 111, 253601 (2013)

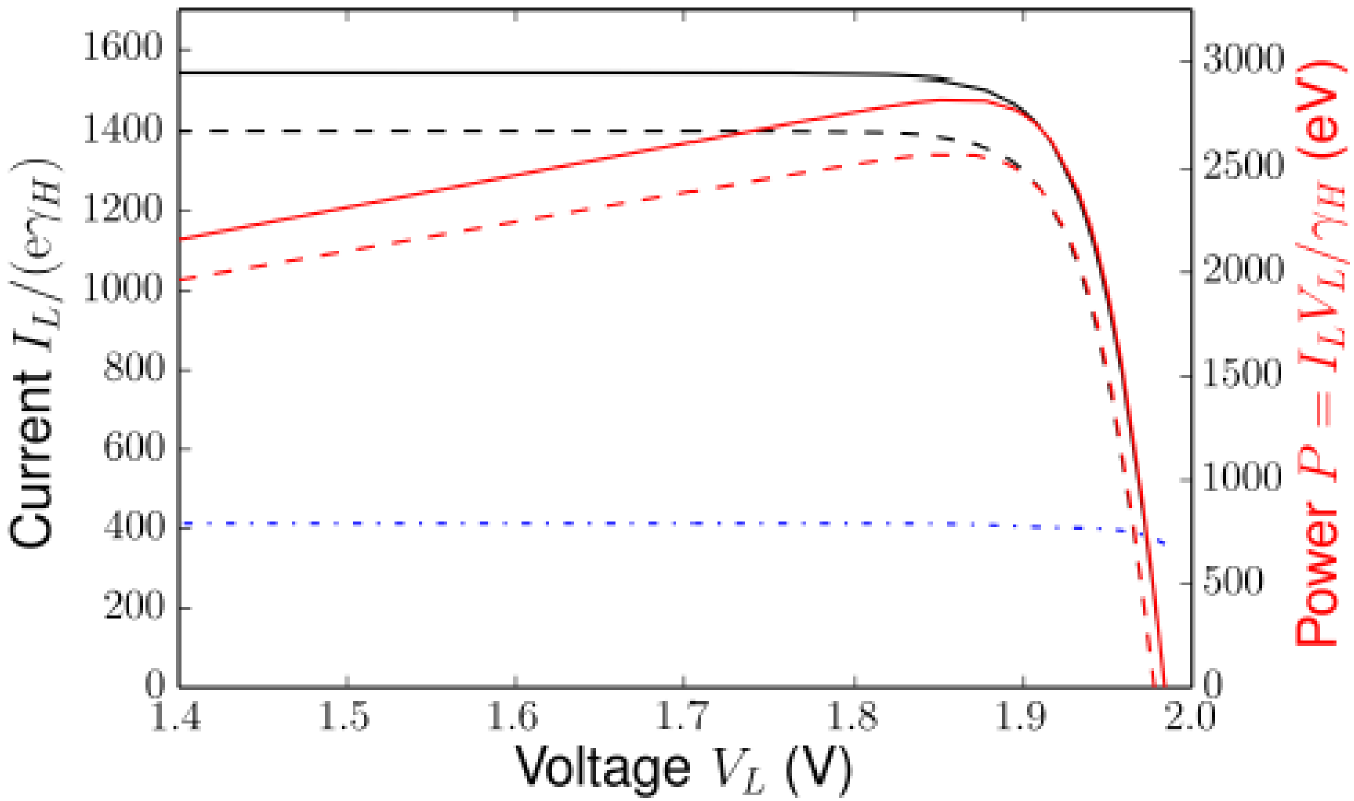


FIG. 4. Numerical I-V characteristic (upper black curve pair) and power (middle red curve pair) of the PC645-based system with (solid lines) and without (dashed lines) coherent mode coupling. The lower blue dash-dotted curve represents the magnitude of $I_{\rm coh}$ up to n=5. The power enhancement is 10.6% when vibrational coupling is included.

$$I_L = \frac{1}{\varepsilon_{30}}\left[\varepsilon_{10} I_H - \sum_{\varepsilon_i > \varepsilon_j} \varepsilon_{ij} I_C^{i\to j} + \varepsilon_{12}(-I_{\rm coh})\right]$$

Killoran, Huelga, Plenio, J. Chem. Phys. 143, 155102 (2015)

Getting rid of specific dynamics: *Quantum resource theories*

Some states and/or operations

States and/or operations out of the free set can become resources for non-free accessible tasks

Canonical example: resource theory of entanglement

Colloquium: *Quantum coherence as a resource*
Alexander Streltsov, Gerardo Adesso, and Martin B. Plenio
Rev. Mod. Phys. **89**, 041003 (2017)

Thermodynamics as a resource theory

- Free access to thermal baths $\tau := e^{-\beta H_B}/Z_B$
- Implement global energy-conserving unitaries
- Trace out subsystems

Thermal operation (TO)

$$\rho_S \xrightarrow[\text{TO}]{\mathcal{T}} \mathrm{Tr}_B \left[U \, \rho_S \otimes \tau \, U^\dagger\right]$$

$$[U, H_S + H_B] = 0$$

On *quasiclassical* states, action of TO characterized by a Gibbs stochastic matrix

$$\rho \xrightarrow{\text{TO}} \sigma \iff \exists G \in \mathsf{GS}_n \text{ s.t. } q = Gp$$

Resource Theory of Quantum Thermodynamics: Thermal Operations and Second Laws
N. Ng and M. P. Woods, in *Thermodynamics in the Quantum Regime. Fundamental Aspects and New Directions*
Felix Binder, Luis A. Correa, Christian Gogolin, and Janet Anders Eds. Springer 2018
An introductory review of the resource theory approach to thermodynamics
Matteo Lostaglio, Rep. Prog. Phys. **82**, 114001 (2019)

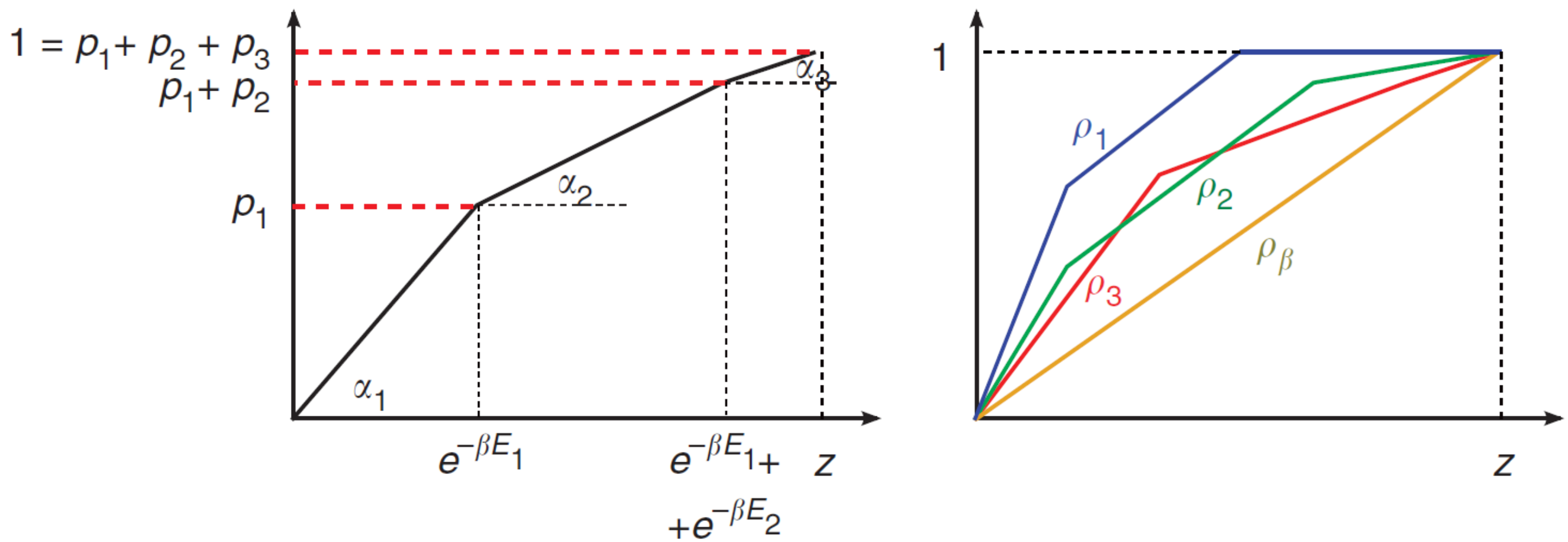
Thermomajorization: $\rho \xrightarrow{\text{TO}} \sigma \iff \rho \succ_{\text{th}} \sigma$

$p(E, g)$

$$p(E_1, g_1)e^{\beta E_1} \geq p(E_2, g_2)e^{\beta E_2} \geq p(E_3, g_3)e^{\beta E_3}...$$

$$e^{\beta E_1}q(E_1, g_1) \geq e^{\beta E_2}q(E_2, g_2) \geq e^{\beta E_3}q(E_3, g_3)....$$

Thermomajorization curves



M. Horodecki and J. Oppenheim, Nat.Comm. **4**, 2059 (2013)
F.G.L.S. Brandao et al, PNAS **112**, 3275 (2015)

PHYSICAL REVIEW A **101**, 042116 (2020)

Editors' Suggestion

Fundamental limitations on photoisomerization from thermodynamic resource theories

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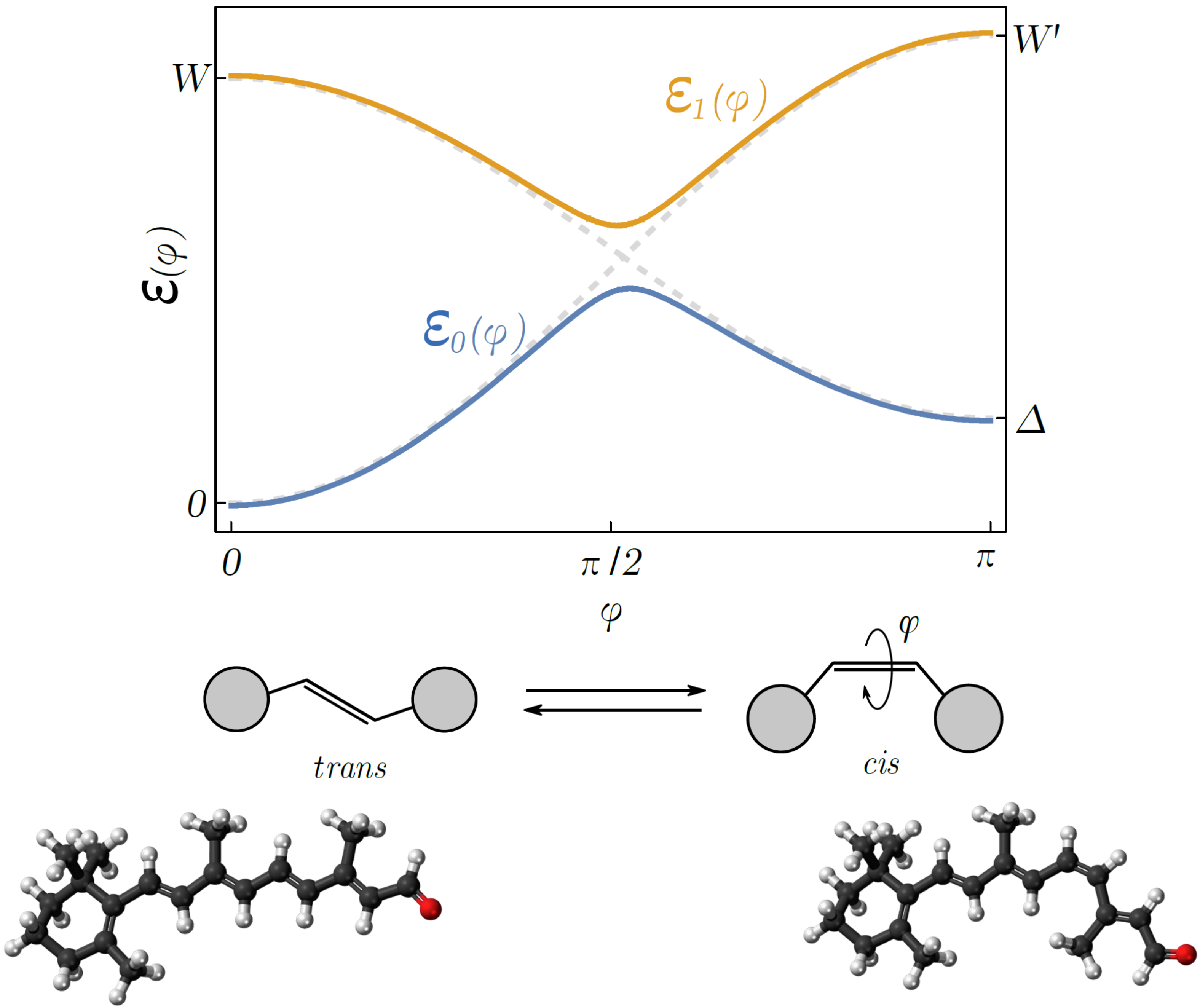
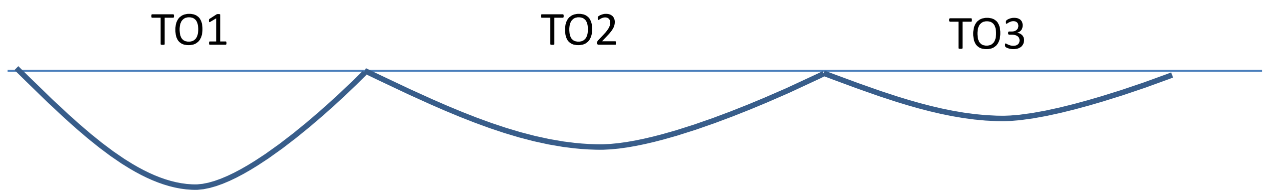
(Received 9 December 2019; revised manuscript received 9 March 2020; accepted 13 March 2020; published 17 April 2020)

Small, out-of-equilibrium, and quantum systems defy simple thermodynamic expressions. Such systems are exemplified by molecular switches, which exchange heat with a bath. These molecules can photoisomerize, or change conformation, or switch, on absorbing light. The photoisomerization probability depends on kinetic details that couple the molecule's energetics to its dissipation. Therefore, a simple, general, thermodynamic-style bound on the photoisomerization probability seems out of reach. We derive such a bound using a resource theory. The resource-theory framework is a set of mathematical tools, developed in quantum information theory, used to generalize thermodynamics to small and quantum settings. From this toolkit has been derived a generalization of the second law, the thermomajorization preorder. We use thermomajorization to upper-bound the photoisomerization probability. Then, we compare the bound with an equilibrium prediction and with a Lindbladian model. We identify a realistic parameter regime in which the Lindbladian evolution saturates the thermomajorization bound. We also quantify the energy coherence in the electronic degree of freedom, and we argue that this coherence cannot promote photoisomerization. This work illustrates how quantum-information-theoretic thermodynamics can elucidate complex quantum processes in nature, experiments, and synthetics.

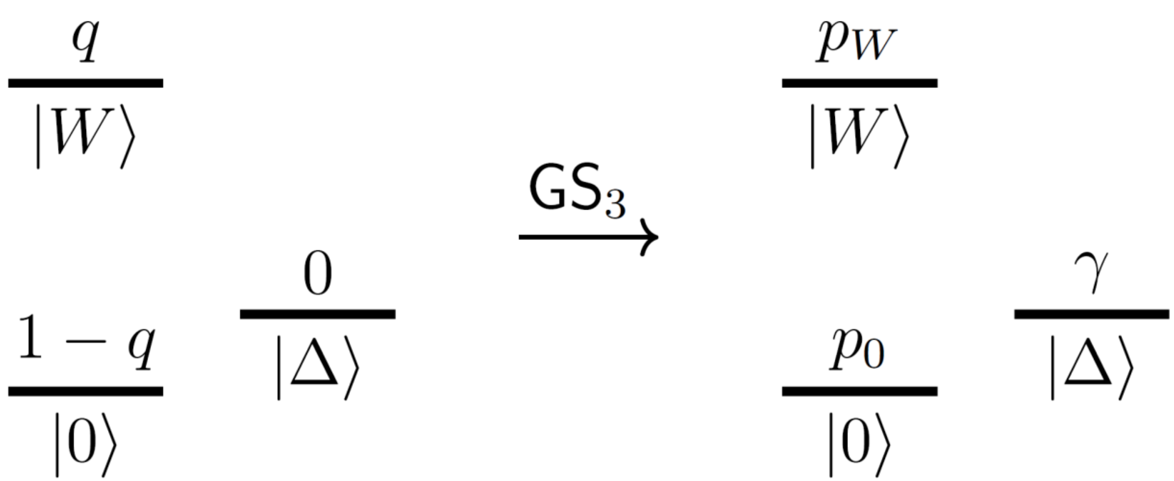


W
W′
$\mathcal{E}_1(\varphi)$
$\mathcal{E}(\varphi)$
$\mathcal{E}_0(\varphi)$
Δ
0
0
π/2
π
φ
φ
trans
cis



Concatenation of thermal operations: Photoexcitation, rotation, thermalization

$$\{|0\rangle, |\Delta\rangle, |W\rangle\} \qquad (p_0, p_\Delta, p_W)$$



$$\gamma := \langle \mathcal{E}_0(\pi)| \, \rho_f \, |\mathcal{E}_0(\pi)\rangle$$

$$\gamma^* := \sup_{G \in \mathsf{GS}_3} \gamma(G)$$

Optimal yield achievable under thermal operations

$$G = \begin{pmatrix} 1 - g_1 e^{-\Delta} - g_2 e^{-W} & g_1 & g_2 \\ (1-g_3)e^{-\Delta} - g_4 e^{-W} & g_3 & g_4 \\ (g_2+g_4)e^{-W} - (1-g_1-g_3)e^{-\Delta} & 1-g_1-g_3 & 1-g_2-g_4 \end{pmatrix}$$

$$\gamma(g_3, g_4) = \left[(1-q)e^{-\Delta}\right](1-g_3) + \left[(1+e^{-W})q - e^{-W}\right] g_4$$

$$\gamma^* = \begin{cases} q + (1-q)\left(e^{-\Delta} - e^{-W}\right) & \text{if } q \geq \tilde{q}\,, \\ (1-q)e^{-\Delta} & \text{if } q < \tilde{q}\,, \end{cases}$$

where we have defined $\tilde{q} = 1/(1+e^W)$.

Next step: Optimal yield cannot be achieved without memory

Non-Markovianity boosts the efficiency of bio-molecular switches, **arXiv2103.14534**

From operations to processes:

$$\rho_i \xrightarrow{\mathcal{T}} \rho_f \iff \exists\ \mathcal{E}_{(t,t_0)} \text{ CPTP s.t. } \rho_f = \mathcal{E}_{(t,t_0)}(\rho_i)$$

Definition IV.1 (Embeddable thermal operations)**.** A thermal operation $\mathcal{T} \in \mathsf{TO}$ is said to be *time-independent Markovian* (or *embeddable*) if there exists a Lindblad generator $\mathcal{L}$ such that $\mathcal{T} = \exp(\mathcal{L})$. The set of embeddable thermal operations on n-dimensional systems is denoted by ETO_n.

Definition IV.2 (Markovian thermal operations)**.** A thermal operation $\mathcal{T} \in \mathsf{TO}$ is said to be *Markovian* (or *memoryless*) if for any $\epsilon > 0$, there exists a sequence of thermal operations $\mathcal{T}_i$ such that $\|\mathcal{T}_i - \mathbb{1}\| < \epsilon$ and $\mathcal{T} = \prod_i \mathcal{T}_i$. The set of Markovian thermal operations on n-dimensional systems is denoted by MTO_n.

Adopted notion of Markovianity relies on divisibility (Rivas et al PRL 2010)
Definition of MTO uses concept of infinitely divisible process (Wolf and Cirac, Comm.Math.Phys. 2008)

Equivalent classification on Gibbs stochastic matrices

⇨ sets EGS_n and MGS_n

Definition I.1 (Continuous thermomajorization)**.** A state ρ continuously thermomajorizes a state σ, denoted $\rho \ggcurly_{\rm th} \sigma$, if there exists a continuous path of states $r(t)$, with $r(0) = \rho$ and $r(1) = \sigma$, such that $\forall t' > t$ one has $r(t) \succ_{\rm th} r(t')$.

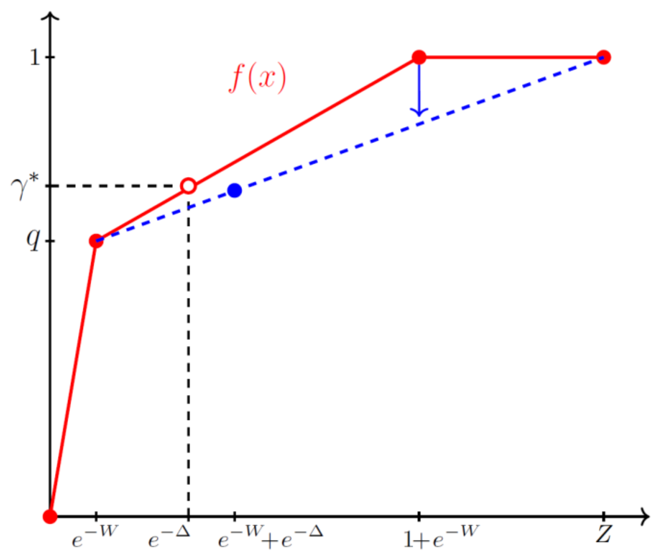
Theorem V.1. *Consider two quasiclassical states ρ, σ. Then, one has $\rho \xrightarrow{\mathsf{MTO}} \sigma$ if and only if $\rho \ggcurly_{\rm th} \sigma$.*

K. Korzekwa and M. Lostaglio, *Quantum advantage in simulating stochastic processes*, arXiv:2005.02403 V1

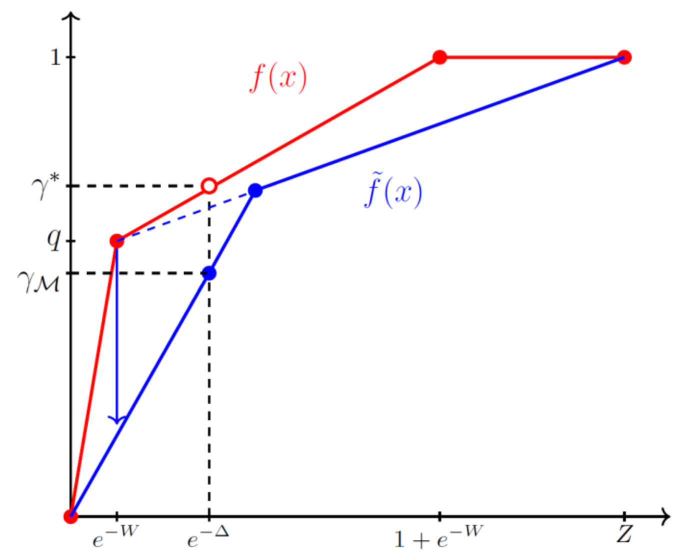
Theorem V.2 (Optimal Markovian yield)**.** *The optimal yield γ^* is not achievable under Markovian thermal operations. Furthermore, the optimal Markovian yield is given by*

$$\gamma_{\mathcal{M}} = \begin{cases} \left[q + (1-q)\frac{e^{-\Delta}}{1+e^{-\Delta}}\right]\frac{e^{-\Delta}}{e^{-\Delta}+e^{-W}} & \text{if } q \geq \tilde{q}\,, \\ \left[1 - q\frac{e^{-W}}{e^{-W}+e^{-\Delta}}\right]\frac{e^{-\Delta}}{1+e^{-\Delta}} & \text{if } q < \tilde{q}\,. \end{cases} \tag{9}$$

$$\tilde{q} = 1/(1+e^{W})$$



(a) The dashed blue curve is the result of the first full thermalization between levels Δ and 0. The second and third segments are brought down, and the new elbow point is at $x = e^{-\Delta} + e^{-W}$.



(b) After the second full thermalization the first and the second segments are brought down. The solid blue curve $\tilde{f}(x)$ is obtained.

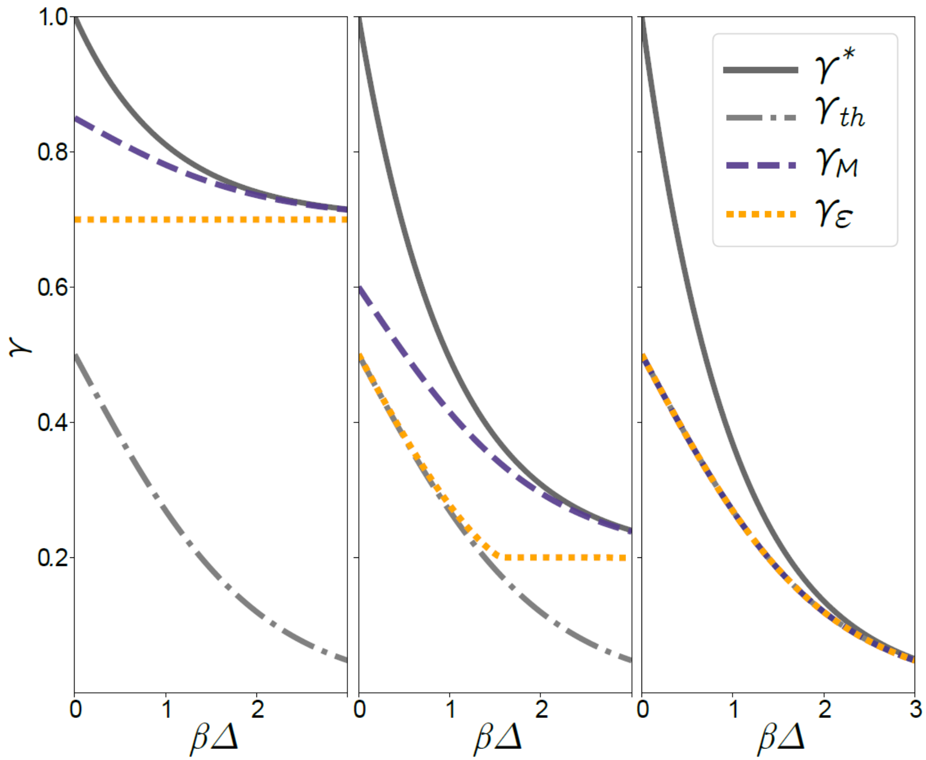
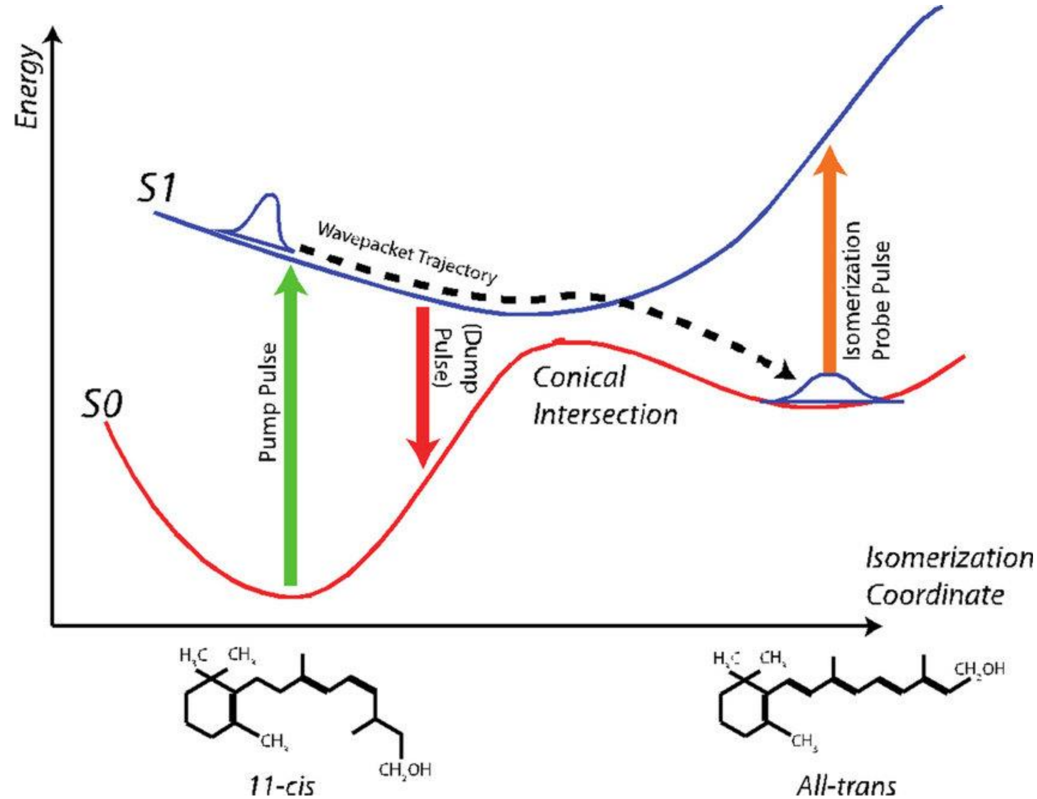


FIG. 3. Comparison between the optimal yield γ^*, the optimal Markovian yield $\gamma_{\mathcal{M}}$ and the optimal embeddable yield $\gamma_{\mathcal{E}}$ obtained via numerical optimization. The results are shown for three different values of q (see Eq.2). The equilibrium value for the yield is denoted by γ_{th}.



M. Mewly et al, Struct. Dyn. **4**, 061707 (2017)

Experimental results
Cerullo et al., Nature **467,** 440 (2010)
Nogly et al., Science **361**, 145 (2018)

Conclusions/Prospects/Open questions

- Resource theories (continuum formulation) can be useful to bound the capabilities of classes of processes
- Design of artificial systems with enhanced capabilities
- Sources of memory. Coherence revisited.
- Beyond thermal operations: phase-covariance is removed. Trade off between NPC and Memory effects

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Giovanni Spaventa, SH and Martin Plenio
Non-Markovianity boosts the efficiency of bio-molecular switches, arXiv2103.14534