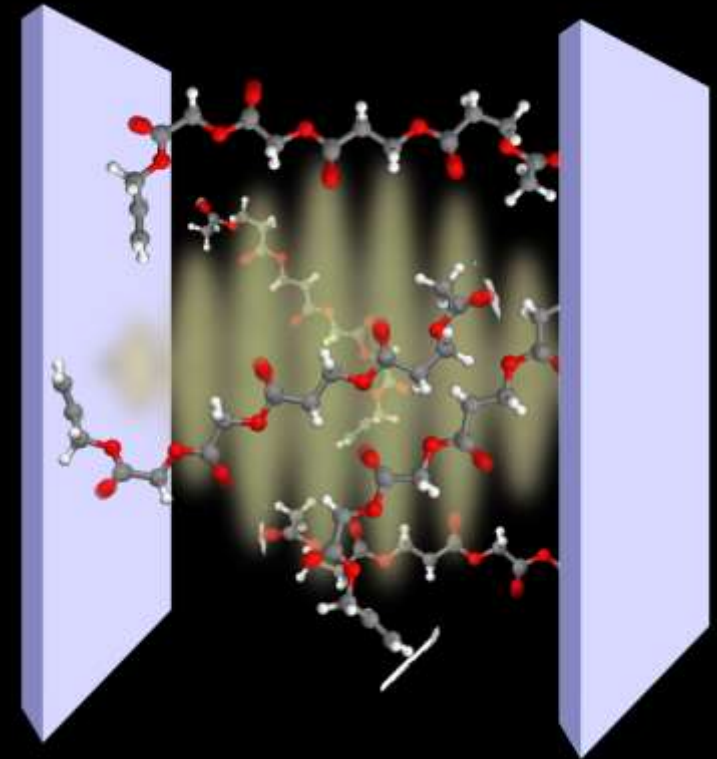


Polariton chemistry: molecules in optical cavities



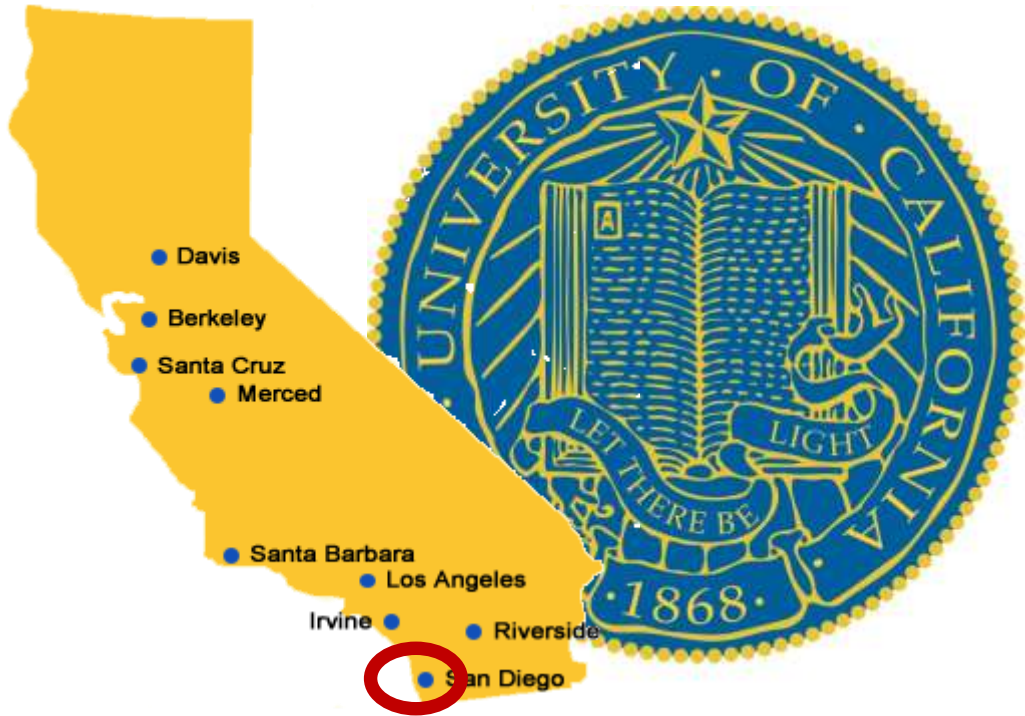
JOEL YUEN-ZHOU
University of California San Diego
Department of Chemistry and Biochemistry

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Research group in theoretical chemical physics at UC San Diego (UCSD) since 2015.



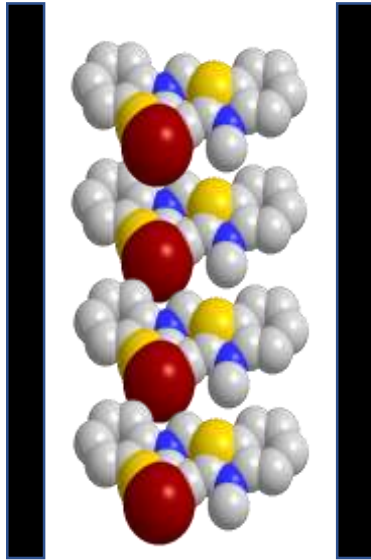
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Our group

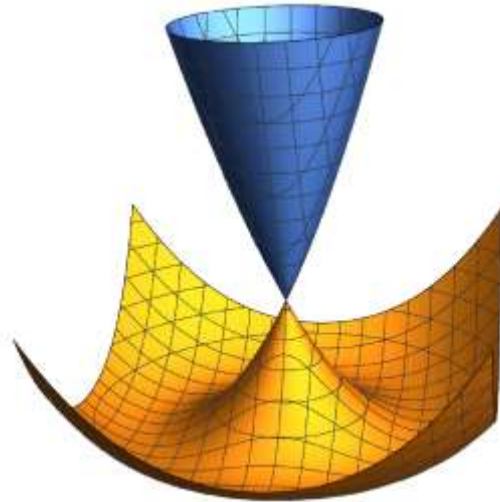


December 2018

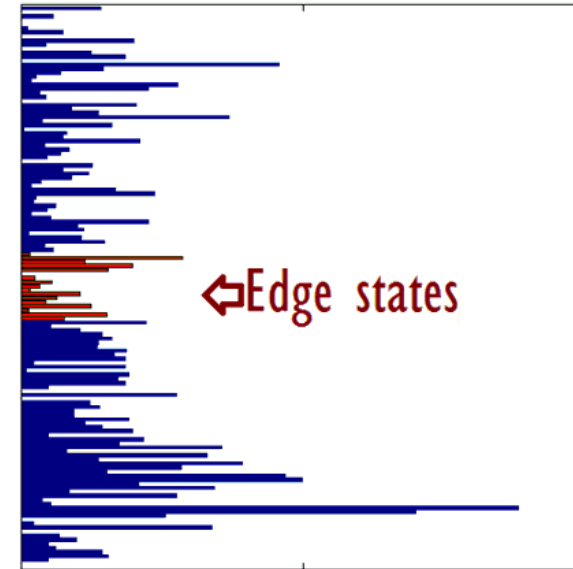
Research on theoretical molecular photonics



Quantum
optics



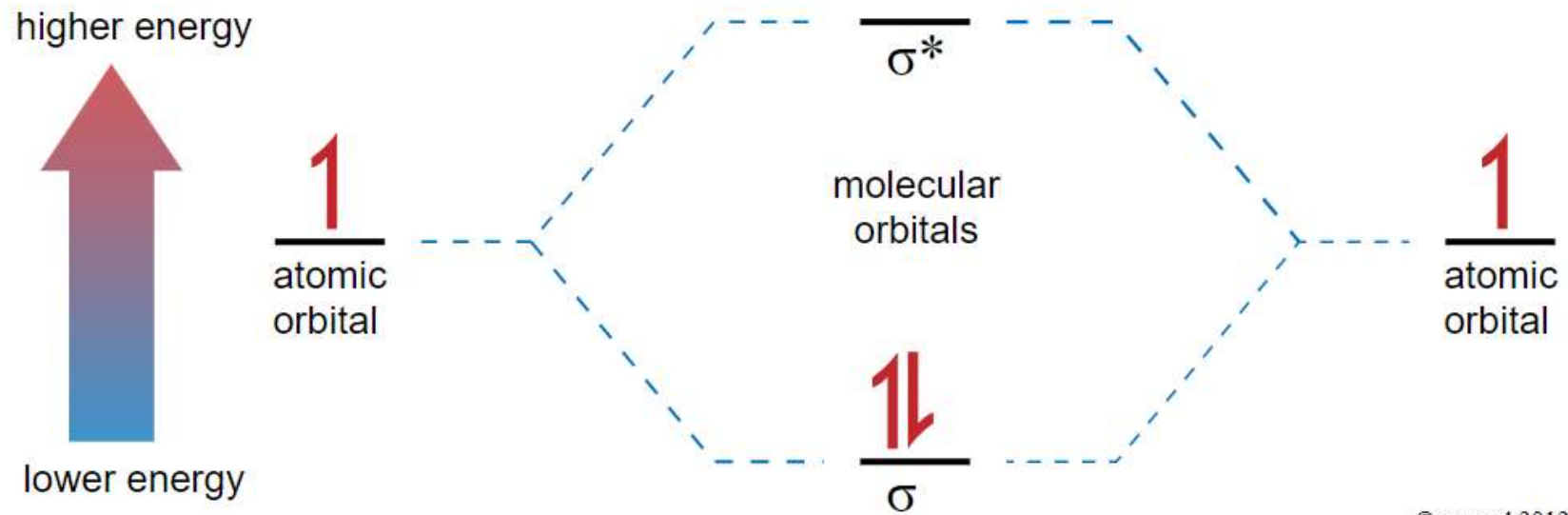
Physical
chemistry



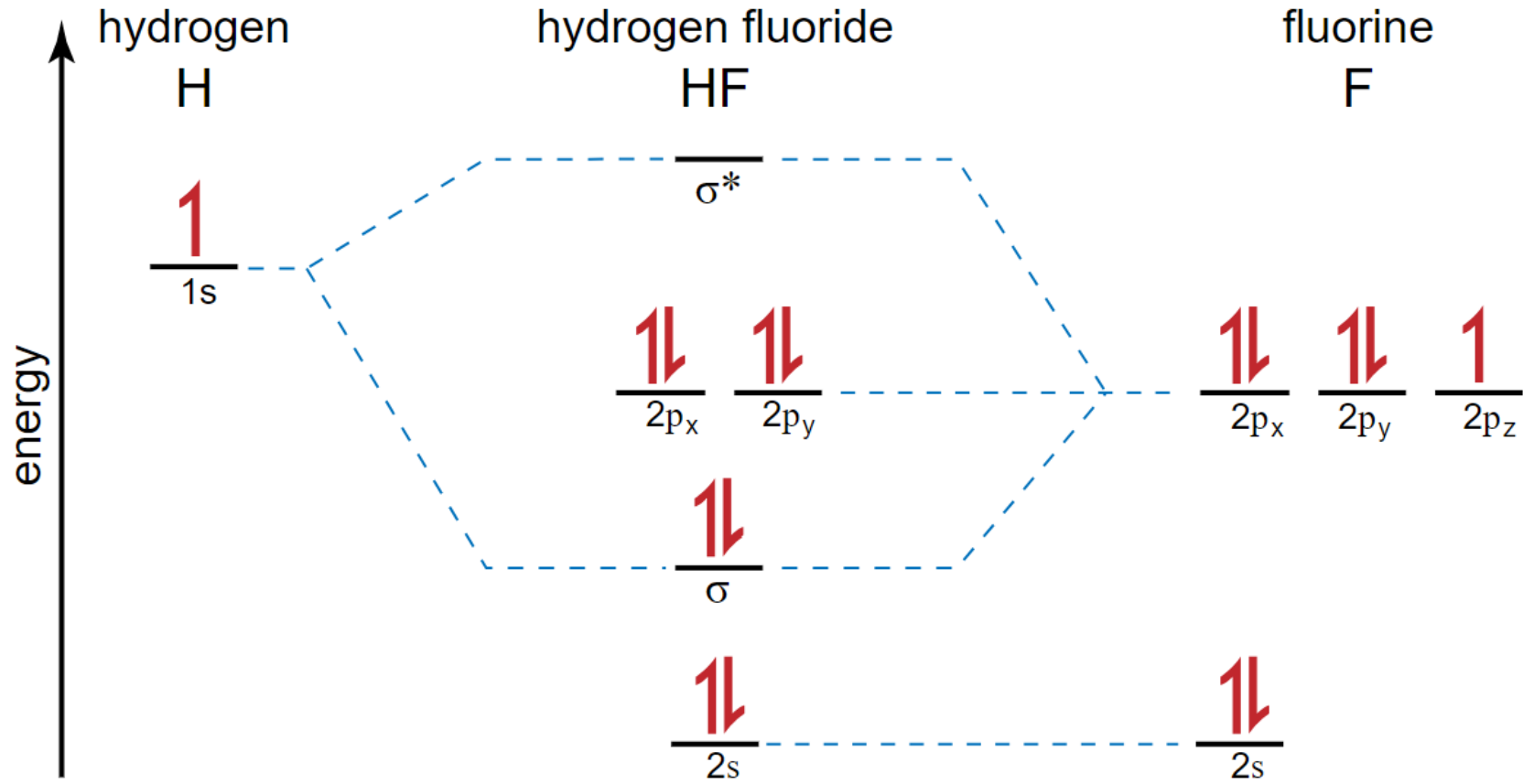
Condensed
matter

Introduction

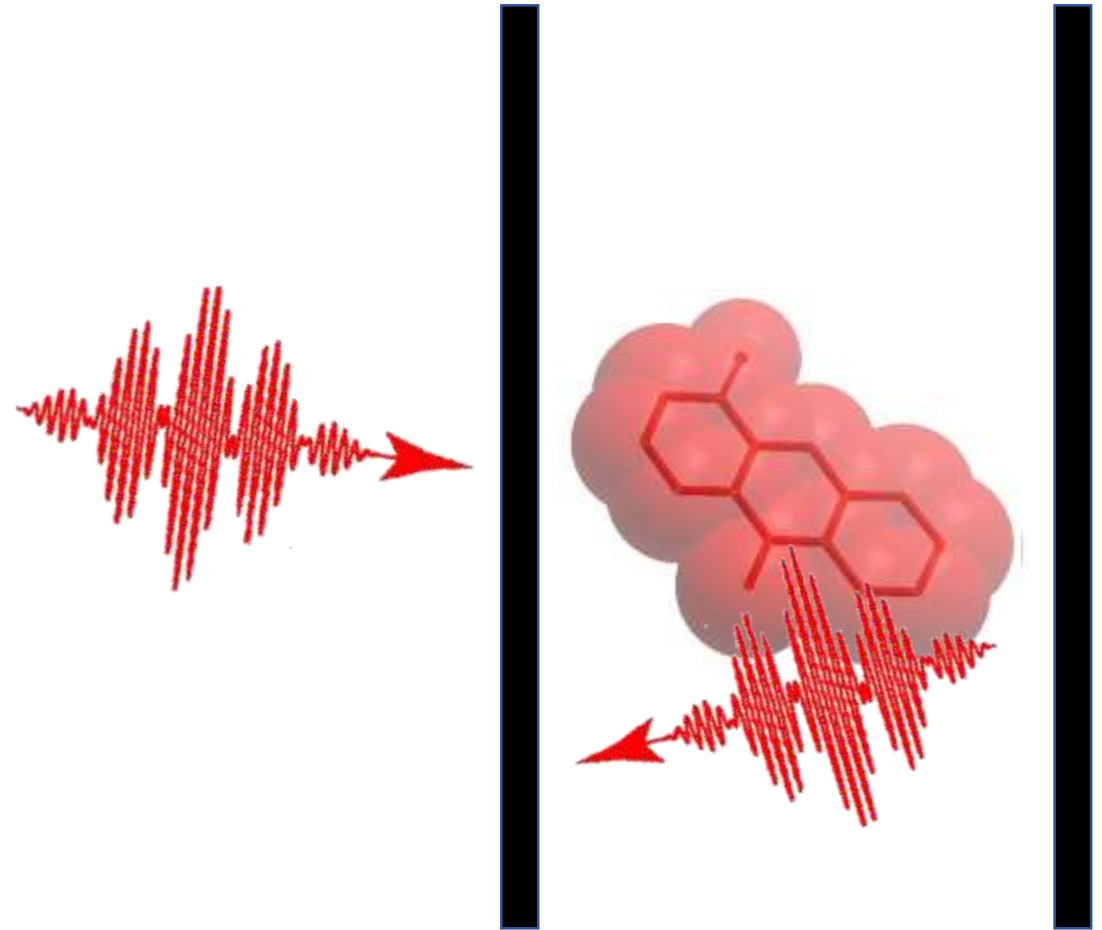
MO diagram for H₂



MO diagram for HF



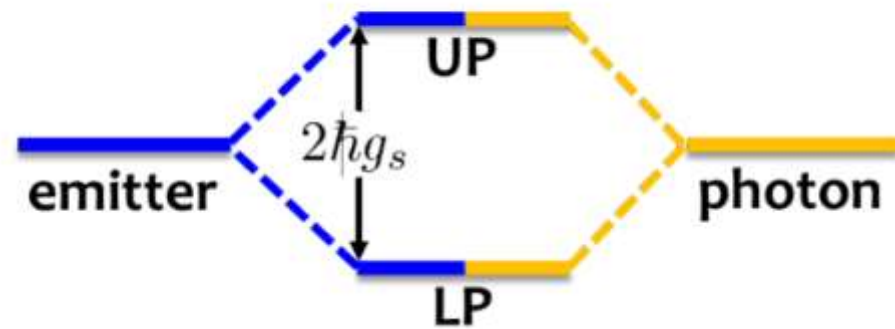
One molecule in a cavity: Jaynes-Cummings



One molecule in a cavity: Jaynes-Cummings

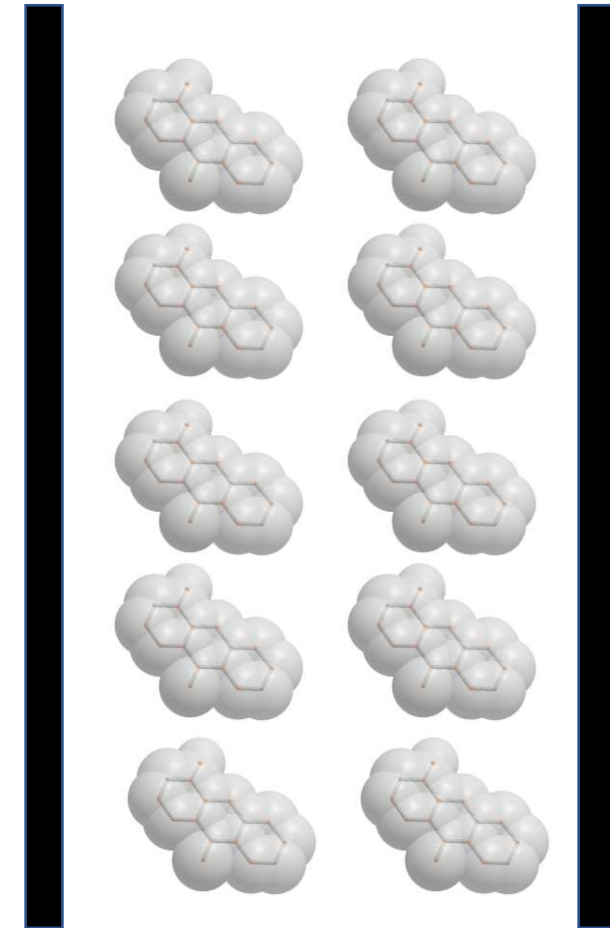
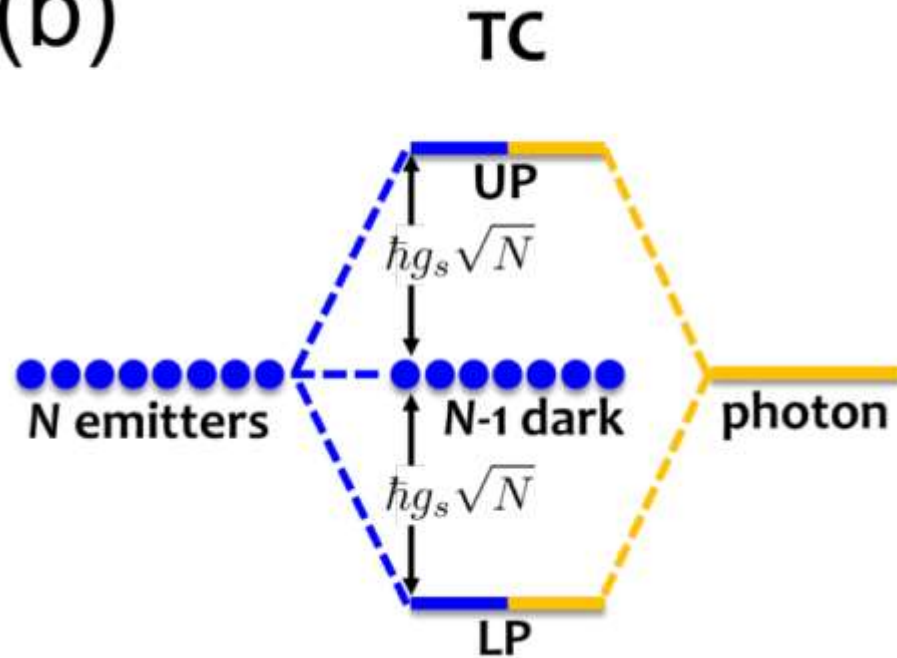
(a)

JC



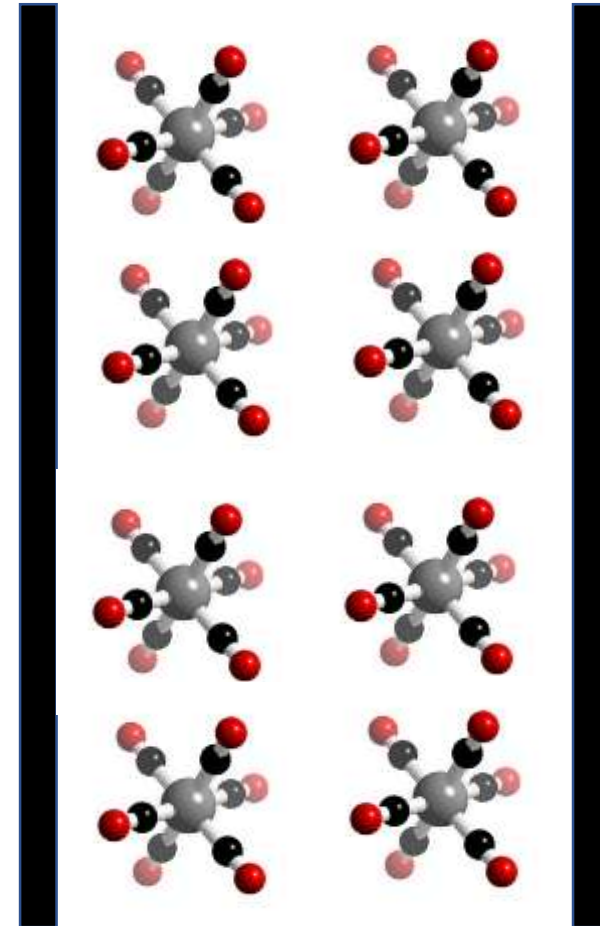
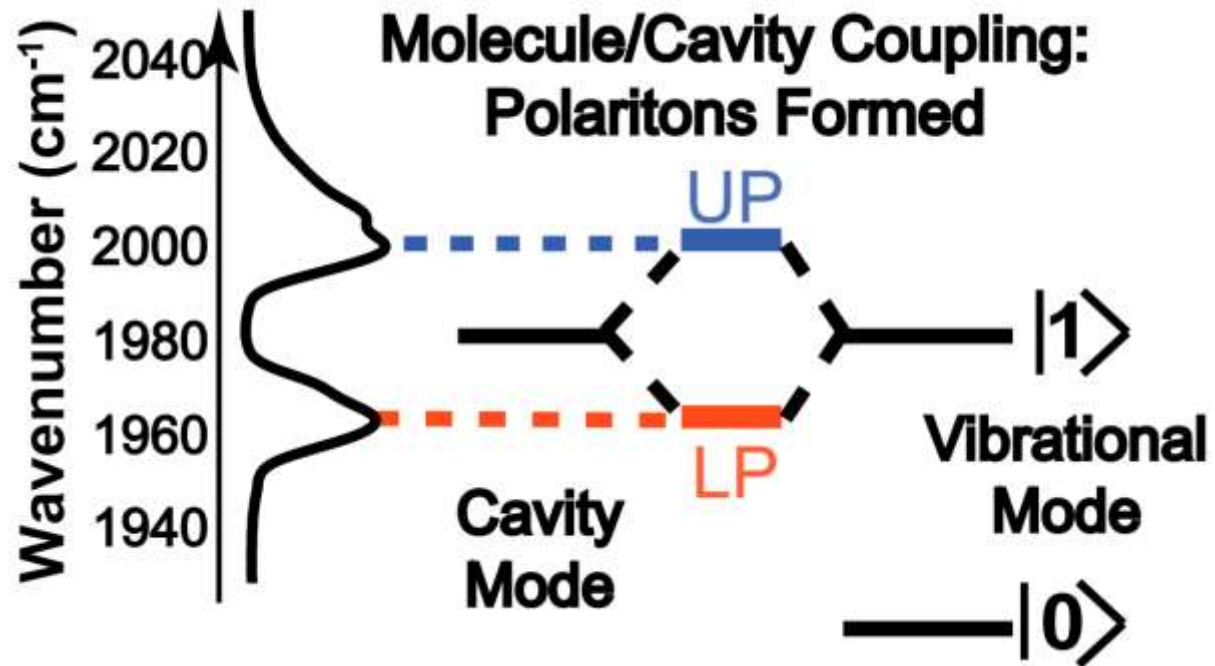
Many molecules in a cavity: Tavis-Cummings

(b)



Rabi splitting $\Omega = 2\sqrt{N}\hbar g_s$ where $N = 10^6 - 10^{10}$

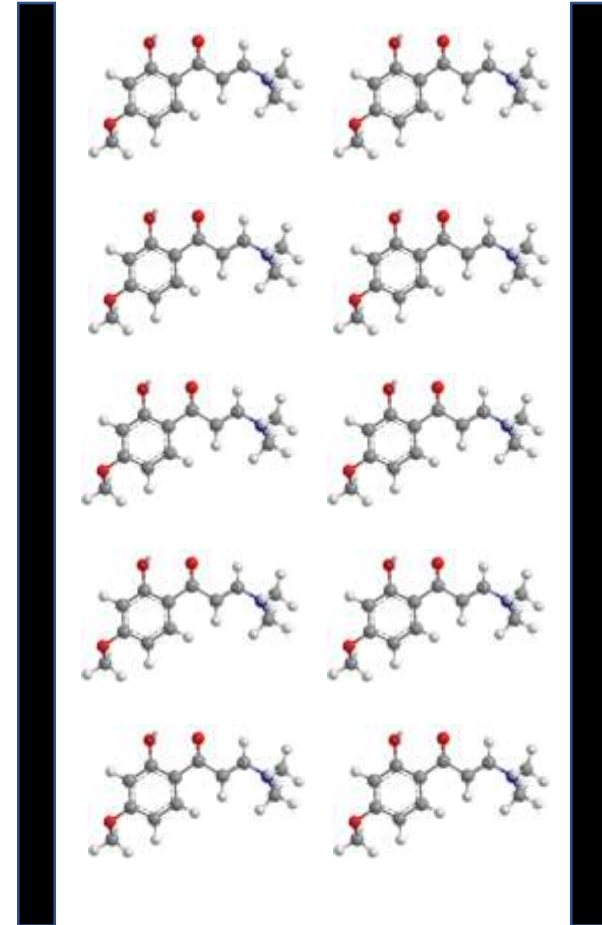
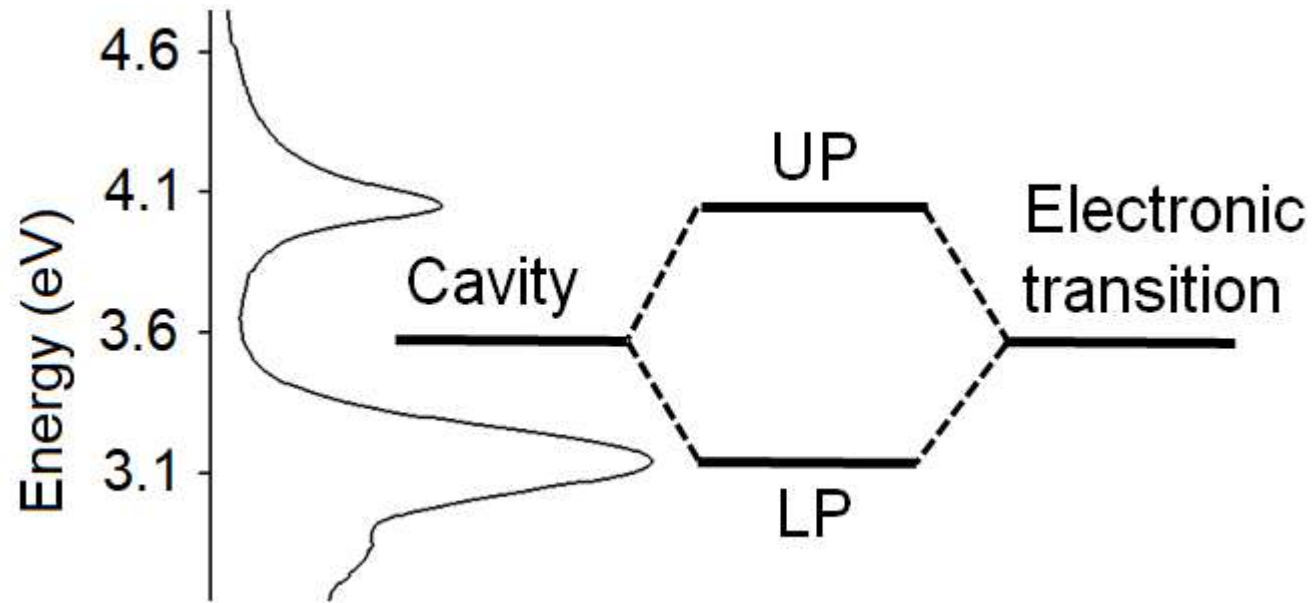
Many molecules in a cavity: Tavis-Cummings



B. Xiang, R. F. Ribeiro, A. D. Dunkelberger, J. C. Owrutsky, B. S. Simpkins, J. Yuen-Zhou, and W. Xiong, PNAS 115, 19 (2018).

$$W(CO)_6$$
$$\omega_{10} = 1983 \text{ cm}^{-1}$$

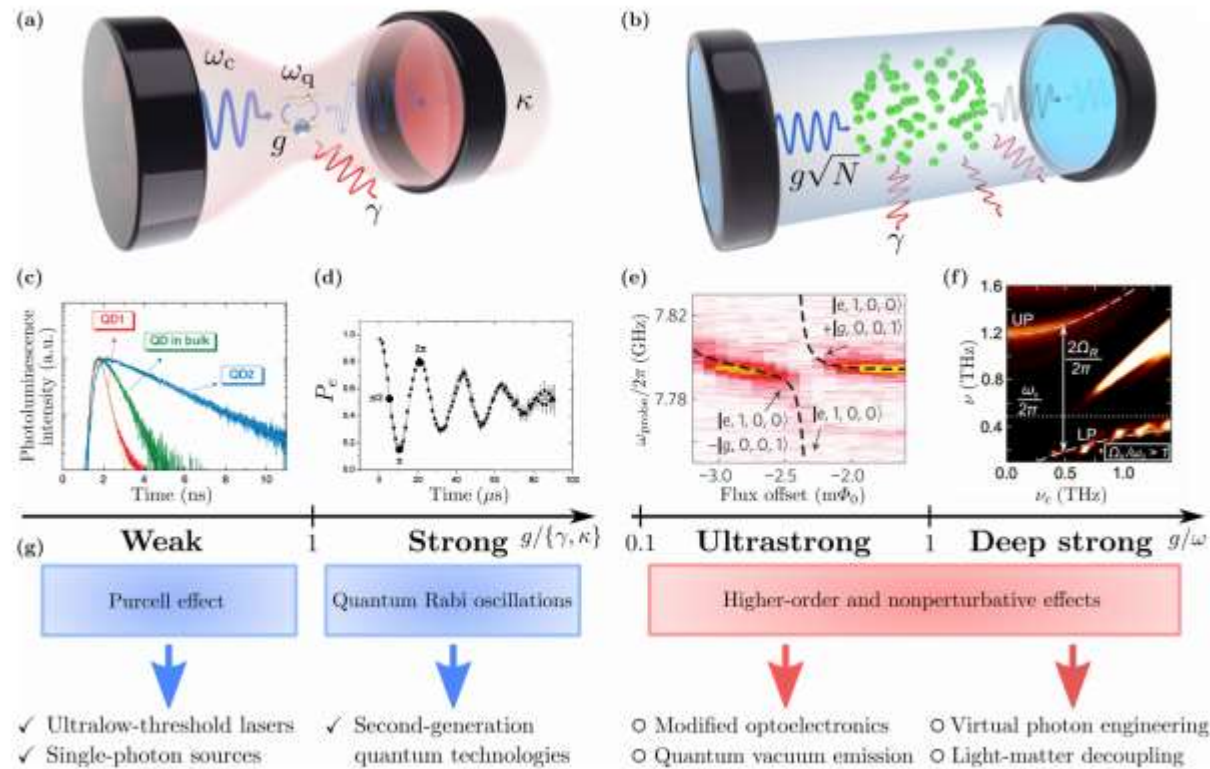
Many molecules in a cavity: Tavis-Cummings



D.P. Kizhmuri, R. Desmukh, L. Martínez, J. Yuen-Zhou, E. Hohenstein, G. John, V. Menon, *in preparation*.

HMPP
 $\omega_{10} = 3.6 \text{ eV}$

The various regimes of light-matter coupling

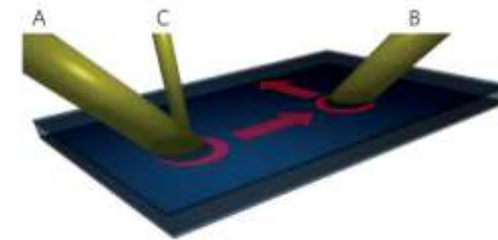
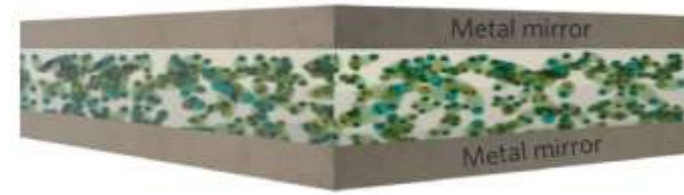


Kockum, Anton Frisk, et al. "Ultrastrong coupling between light and matter." *Nature Reviews Physics* 1.1 (2019): 19.

MOTIVATION: Why molecular polaritons?

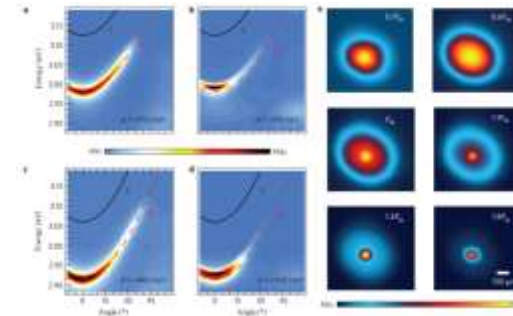
Polariton devices

D. Ballarini, et al., *Nature Commun.* 4, 1778 (2013)



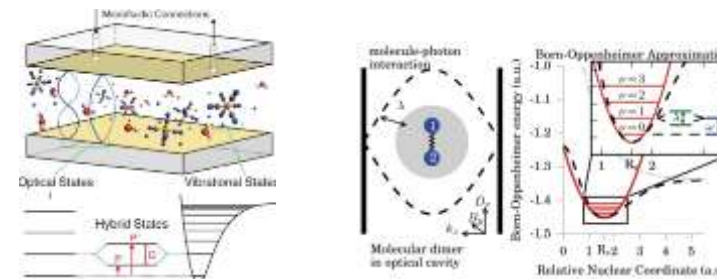
Polariton condensates

E.R. Bittner and C. Silva, *J. Chem. Phys.* 136.3 (2012): 034510.
K. S. Daskalakis, et. al., *Nat. Mater.* 13, 271-278 (2014)



Polariton chemistry

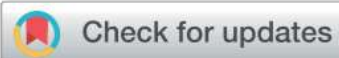
T.W. Ebbesen, *Acc. Chem. Res.* 49(11):2403-12;
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J. Galego, et al, *PRX* 5.4 (2015) 041022;
F. Herrera and F. Spano, *PRL* 116 23 (2016).
M. Kowalewski, K. Bennett, and S. Mukamel, *J. Phys. Chem. Lett.* 7 11 (2016) 2050-2054.




MINIREVIEW

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rsc.li/chemical-science

Polariton chemistry: controlling molecular dynamics with optical cavities

Raphael F. Ribeiro,  Luis A. Martínez-Martínez,  Matthew Du, Jorge Campos-Gonzalez-Angulo  and Joel Yuen-Zhou*

Molecular polaritons are the optical excitations which emerge when molecular transitions interact strongly with confined electromagnetic fields. Increasing interest in the hybrid molecular-photonics materials that host these excitations stems from recent observations of their novel and tunable chemistry. Some of the remarkable functionalities exhibited by polaritons include the ability to induce long-range excitation energy transfer, enhance charge conductivity, and inhibit or accelerate chemical reactions. In this review, we explain the effective theories of molecular polaritons which form a basis for the interpretation and guidance of experiments at the strong coupling limit. The theoretical discussion is illustrated with the analysis of innovative applications of strongly coupled molecular-photonics systems to chemical phenomena of fundamental importance to future technologies.

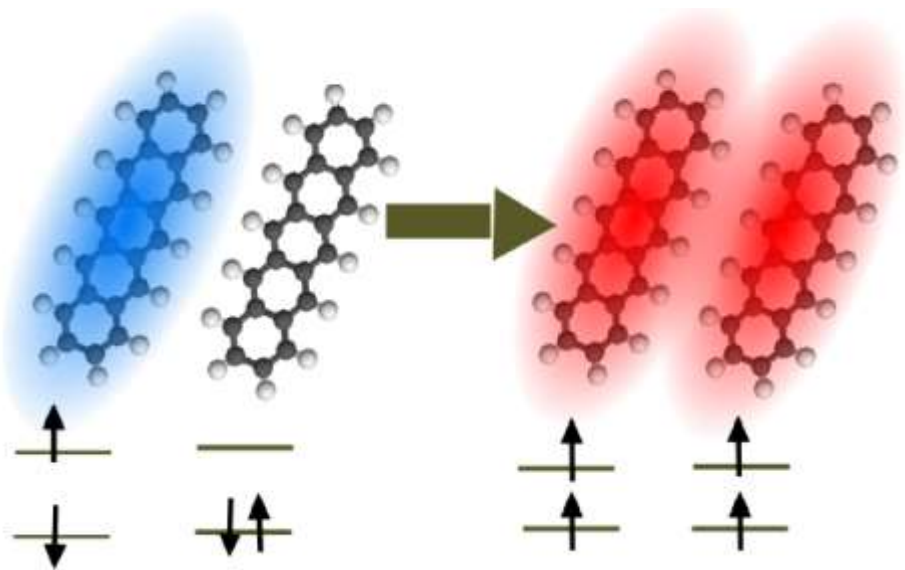
Some of our work: Photophysics

Polariton-Assisted Singlet Fission in Acene Aggregates

Luis A. Martínez-Martínez,[†] Matthew Du,[†] Raphael F. Ribeiro,[†] Stéphane Kéna-Cohen,[‡] and Joel Yuen-Zhou^{*,†}

[†]Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, California 92093, United States

[‡]Department of Engineering Physics, École Polytechnique de Montréal, Montréal H3C 3A7, Quebec, Canada



Anisotropy and Controllable Band Structure in Suprawavelength Polaritonic Metasurfaces

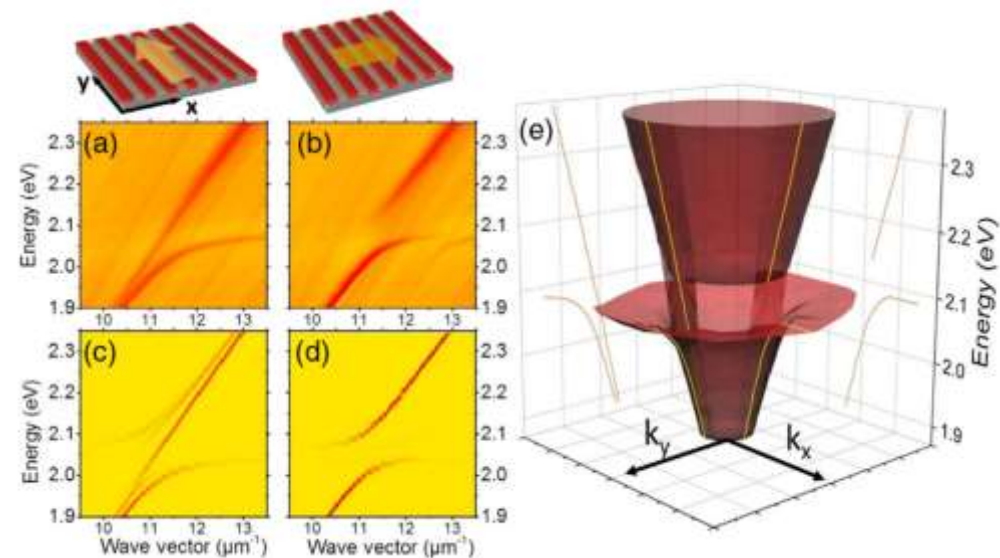
K. Chevrier,¹ J. M. Benoit,¹ C. Symonds,¹ S. K. Saikin,^{2,3} J. Yuen-Zhou,⁴ and J. Bellessa^{1,*}

¹Université Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622, Lyon, France

²Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, USA

³Institute of Physics, Kazan Federal University, Kazan 420008, Russian Federation

⁴Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, California 92093, USA



Some of our work: Ultrastrong coupling, Drexhage problem revisited



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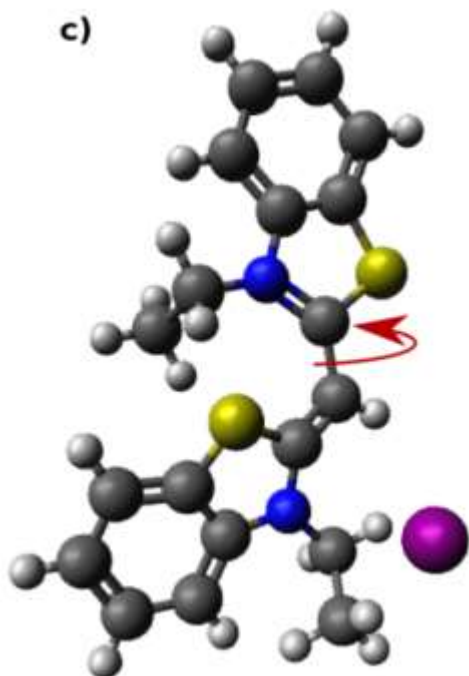
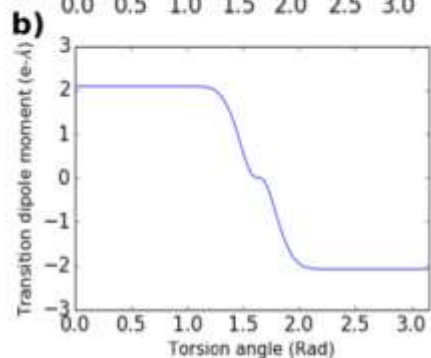
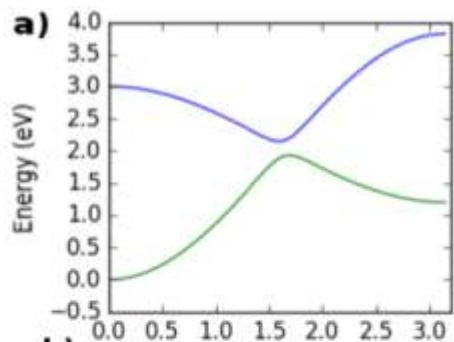
pubs.acs.org/journal/apchd5

Article

Can Ultrastrong Coupling Change Ground-State Chemical Reactions?

Luis A. Martínez-Martínez,¹ Raphael F. Ribeiro,² Jorge Campos-González-Angulo,³ and Joel Yuen-Zhou^{1*}

Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, California 92093, United States



Cite This: J. Phys. Chem. Lett. 2018, 9, 6511-6516

pubs.acs.org/JPC

Letter

Molecular Emission near Metal Interfaces: The Polaritonic Regime

Joel Yuen-Zhou,^{1*} Semion K. Saikin,^{2,3} and Vinod M. Menon⁴

¹Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, California 92093, United States

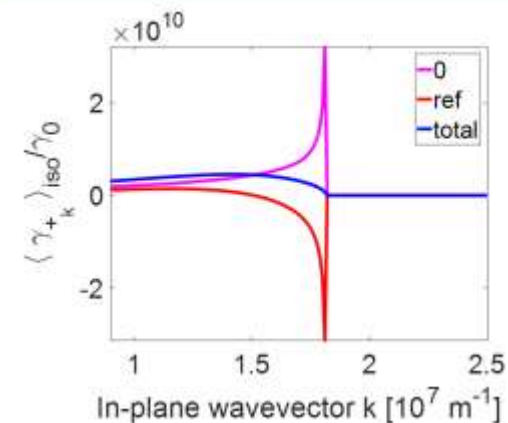
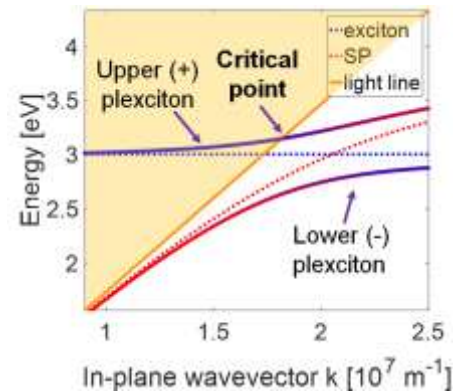
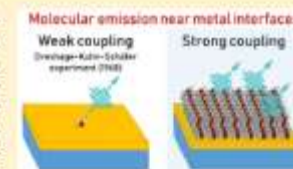
²Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, United States

³Institute of Physics, Kazan Federal University, Kazan 420008, Russian Federation

⁴Department of Physics, Graduate Center and City College of New York, City University of New York, New York, New York 10016, United States

Supporting Information

ABSTRACT: The strong coupling of a dense layer of molecular excitons with surface-plasmon modes in a metal gives rise to polaritons (hybrid light-matter states) called plexcitons. Surface plasmons cannot directly emit into (or be excited by) free-space photons due to the fact that energy and momentum conservation cannot be simultaneously satisfied in photoluminescence. Most plexcitons are also formally nonemissive, even though they can radiate via molecules upon localization due to disorder and decoherence. However, a fraction of them are bright even in the presence of such deleterious processes. In this Letter, we theoretically discuss the superradiant emission properties of these bright plexcitons, which belong to the upper energy branch and reveal huge photoluminescence enhancements compared to bare excitons, due to near-divergences in the density of photonic modes available to them. Our study generalizes the well-known problem of molecular emission next to a metal interface to the polaritonic regime.

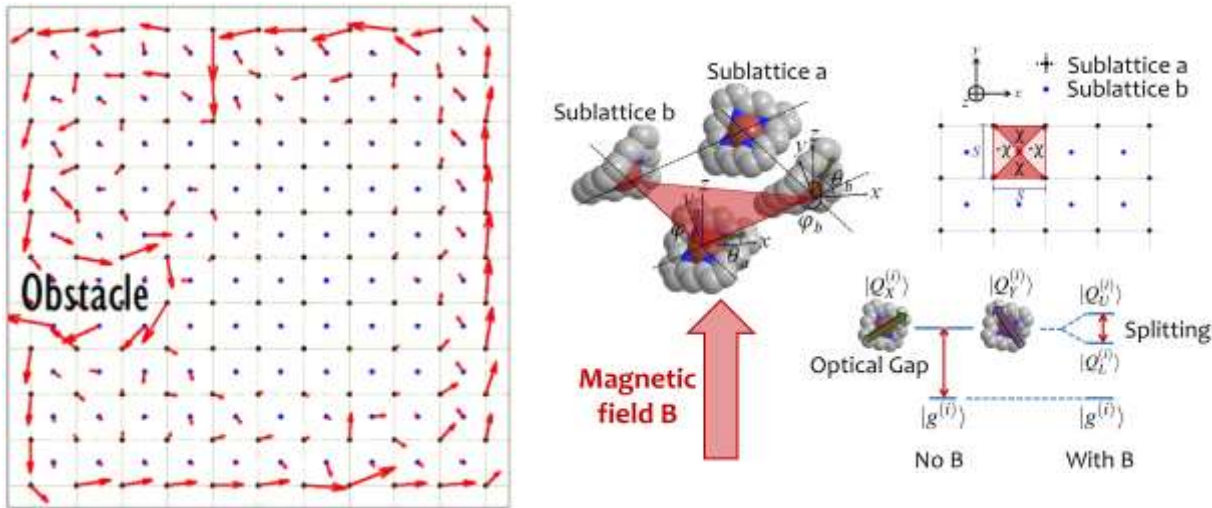


Some of our work: Topological excitons and polaritons



Topologically protected excitons in porphyrin thin films

Joel Yuen-Zhou^{1*}, Semion K. Saikin^{1,2}, Norman Y. Yao³ and Alán Aspuru-Guzik^{1,2}



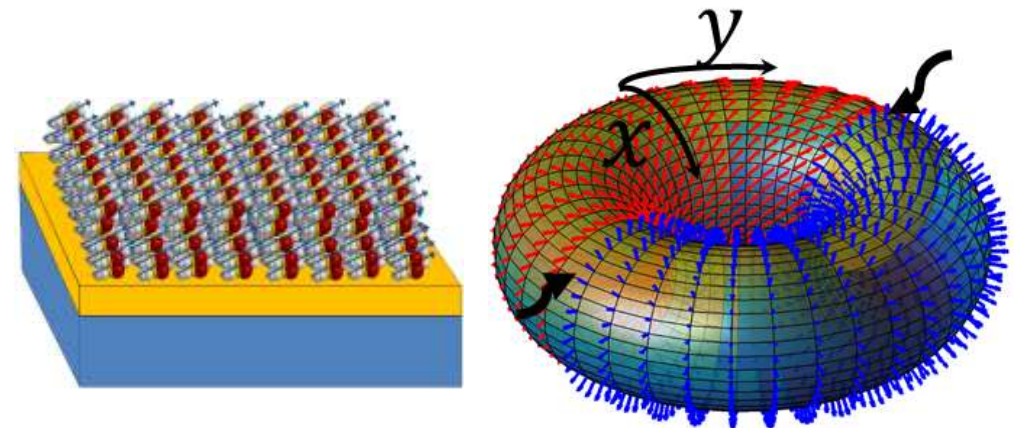
ARTICLE

Received 23 Oct 2015 | Accepted 28 Apr 2016 | Published 9 Jun 2016

DOI: 10.1038/ncomms11783 OPEN

Plexciton Dirac points and topological modes

Joel Yuen-Zhou¹, Semion K. Saikin^{2,3}, Tony Zhu^{4,5}, Mehmet C. Onbasli⁶, Caroline A. Ross⁶, Vladimir Bulovic^{5,7} & Marc A. Baldo^{5,7}



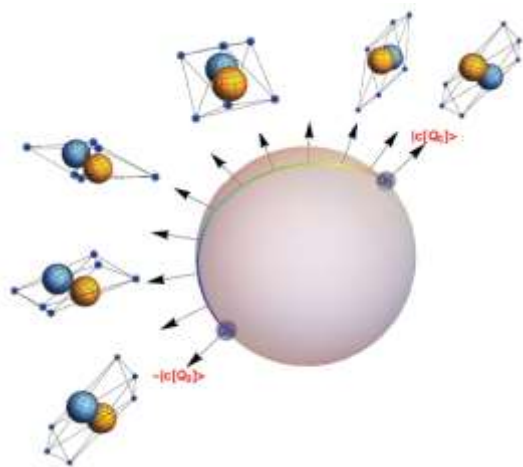
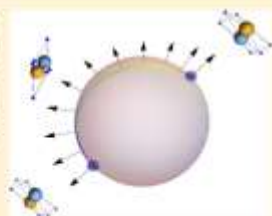
Other works: Topological effects in Born-Oppenheimer dynamics

Vibronic Ground-State Degeneracies and the Berry Phase: A Continuous Symmetry Perspective

Raphael F. Ribeiro* and Joel Yuen-Zhou*

Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, California 92093, United States

ABSTRACT: We develop a geometric construction to prove the inevitability of the electronic ground-state (adiabatic) Berry phase for a class of Jahn–Teller (JT) models with maximal continuous symmetries and $N > 2$ intersecting electronic states. Given that vibronic ground-state degeneracy in JT models may be seen as a consequence of the electronic Berry phase and that any JT problem may be obtained from the subset that we investigate in this Letter by symmetry-breaking, our arguments reveal the fundamental origin of the vibronic ground-state degeneracy of JT models.

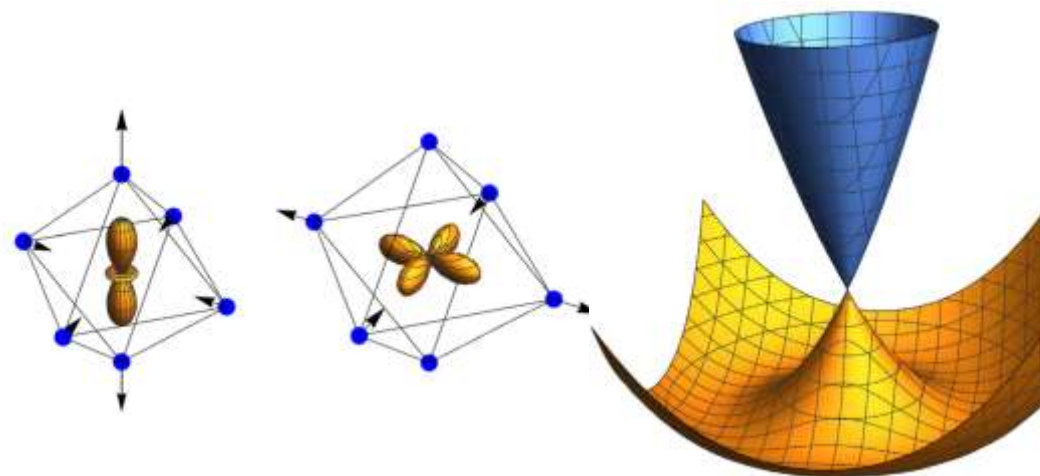


Topical Review

Continuous vibronic symmetries in Jahn–Teller models

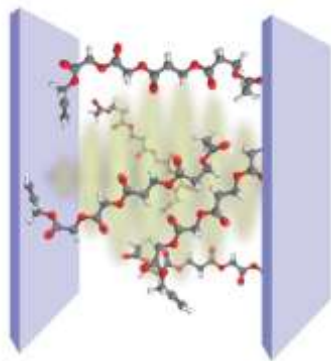
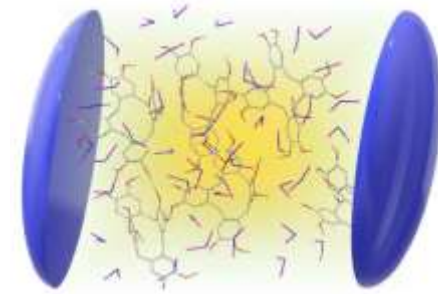
Raphael F Ribeiro* and Joel Yuen-Zhou*

Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, CA 92093, United States of America



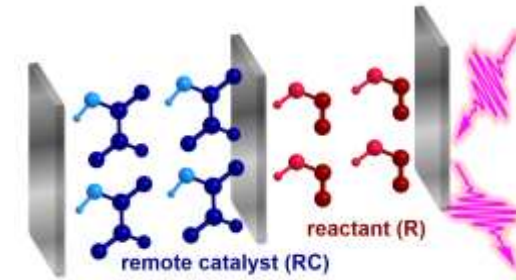
Outline of talk

Ground-state
reactivity



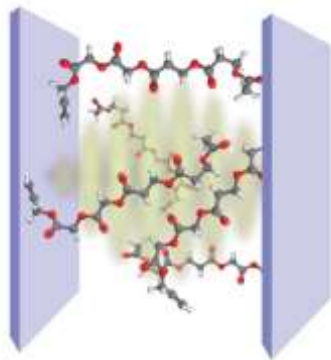
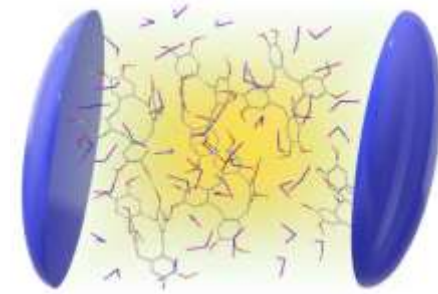
Vibrational
polaritons

Remote control



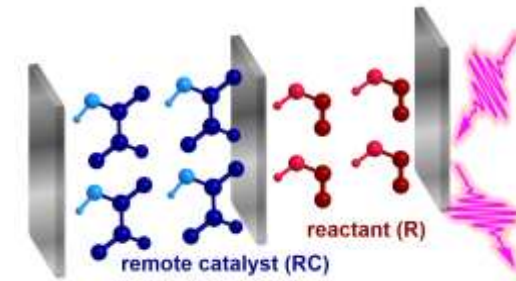
Outline of talk

Ground-state
reactivity



Vibrational
polaritons

Remote control



Polariton chemistry in the dark?



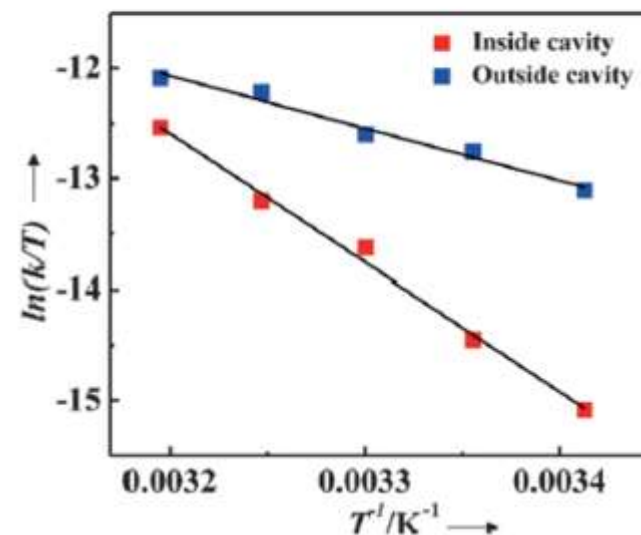
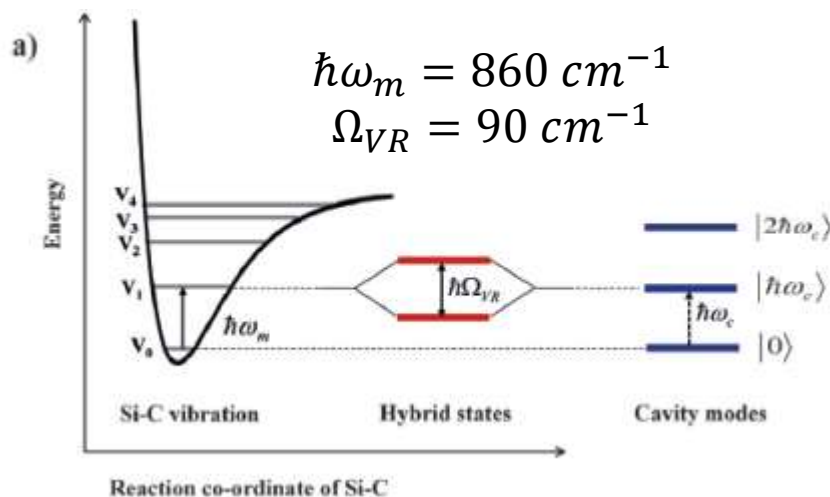
Kinetics Hot Paper

International Edition: DOI: 10.1002/anie.201605504

German Edition: DOI: 10.1002/ange.201605504

Ground-State Chemical Reactivity under Vibrational Coupling to the Vacuum Electromagnetic Field

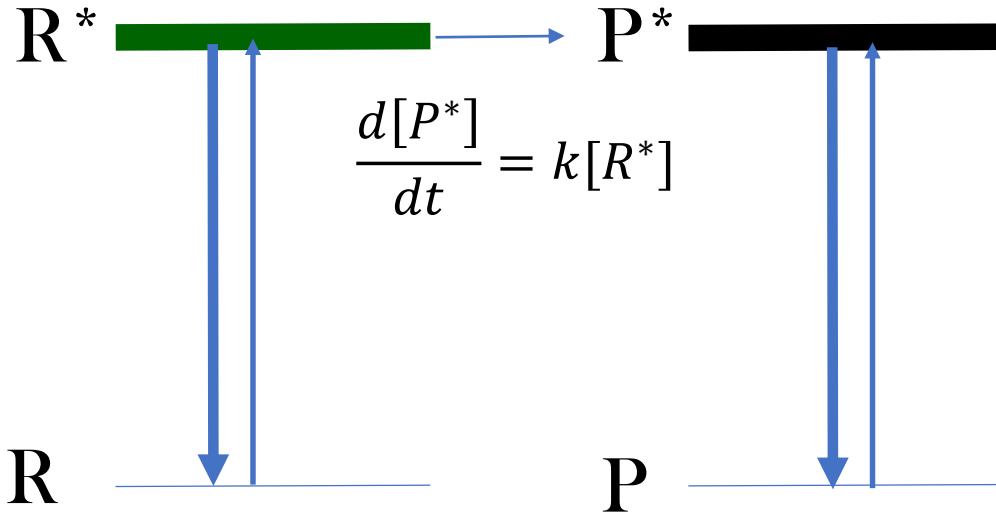
Anoop Thomas⁺, Jino George⁺, Atef Shalabney, Marian Dryzhakov, Sreejith J. Varma, Joseph Moran, Thibault Chervy, Xiaolan Zhong, Eloïse Devaux, Cyriaque Genet, James A. Hutchison, and Thomas W. Ebbesen*



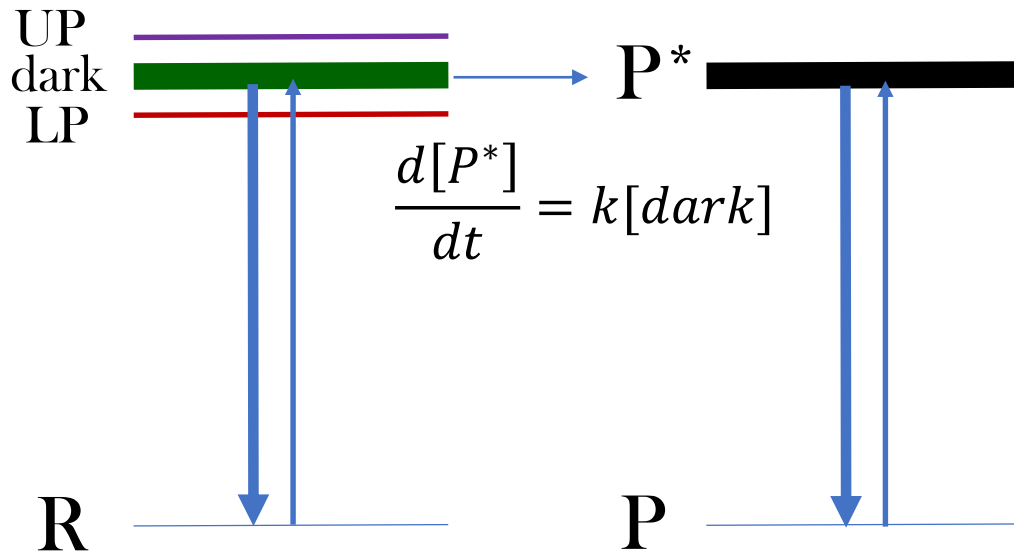
Polariton chemistry in the dark? Our thoughts a year ago

(Koreatown - LA, February 2018)

Outside of the cavity



Inside of the cavity

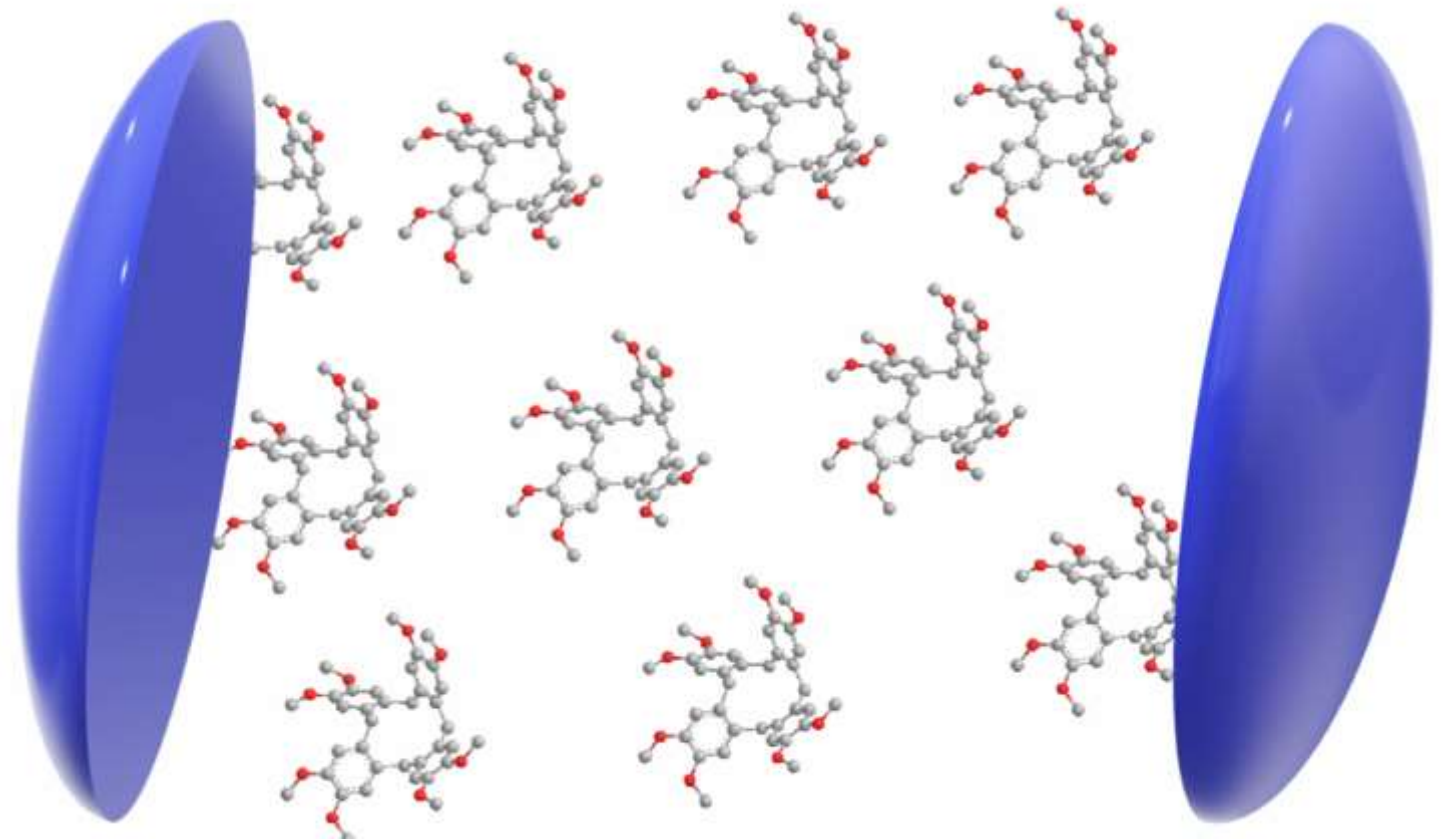


$$\frac{[*dark*]}{[LP]} = 10^{10} \text{ at } 298 \text{ K} \Rightarrow [R^*] \approx [*dark*].$$

Dark states behave like bare molecular excitations.
 Reactivity in cavity should be equal to reactivity out of the cavity.

Polariton chemistry in the dark? Our present thoughts

We have theoretically developed the first model where vibrational strong coupling (VSC) can lead to electron transfer catalysis.



Polariton chemistry in the dark? Our present thoughts

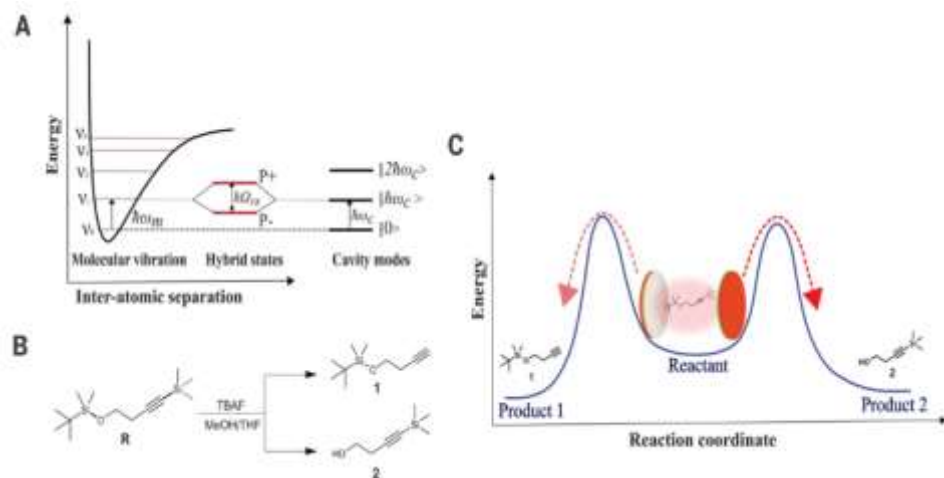
RESEARCH

Science **363**, 615–619 (2019)

CHEMISTRY

Tilting a ground-state reactivity landscape by vibrational strong coupling

A. Thomas^{1*}, L. Lethuillier-Karl^{1*}, K. Nagarajan¹, R. M. A. Vergauwe¹, J. George^{1†}, T. Chervy^{1‡}, A. Shalabney², E. Devaux¹, C. Genet¹, J. Moran^{1§}, T. W. Ebbesen^{1§}



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FIRST REACTIONS

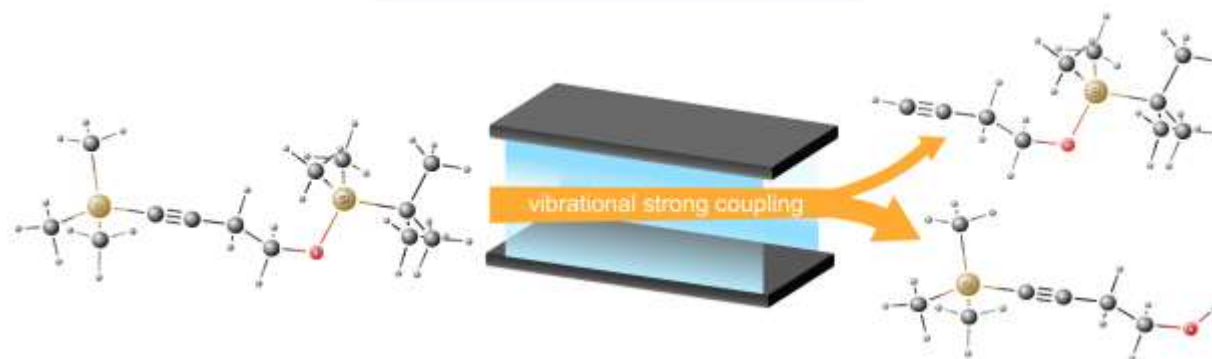
Polariton Chemistry: Action in the Dark

Stéphane Kéna-Cohen^{*†} and Joel Yuen-Zhou^{*‡}

[†]Department of Engineering Physics, École Polytechnique de Montréal, Montréal H3C 3A7 Quebec, Canada

[‡]Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, California 92093, United States

The findings of Ebbesen, Moran, and co-workers could revive the mode-selective chemistry program within the contemporary context of molecules in optical cavities or "polariton chemistry".

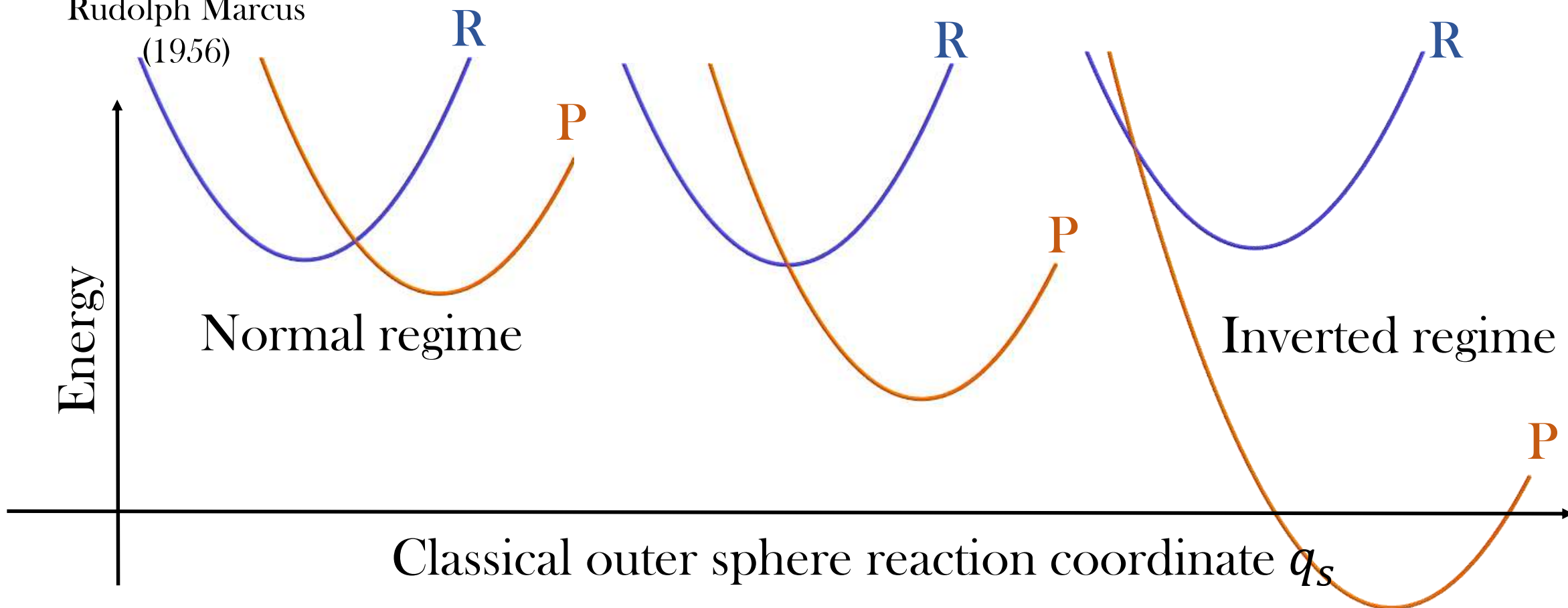


Background: Marcus theory

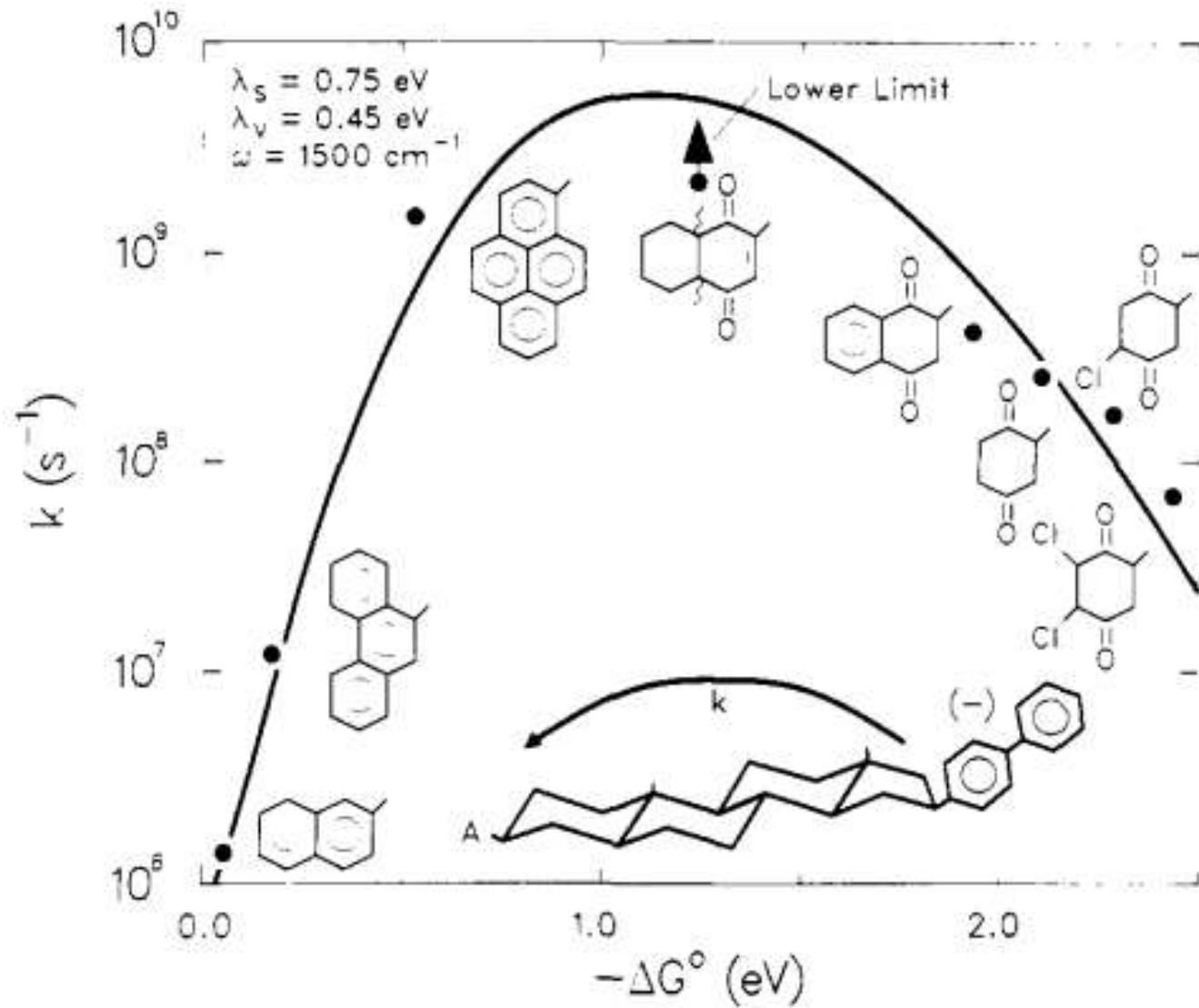


Rudolph Marcus
(1956)

As the reaction becomes more exergonic (larger $-\Delta G$), the reaction can become slower!



Background: Marcus theory

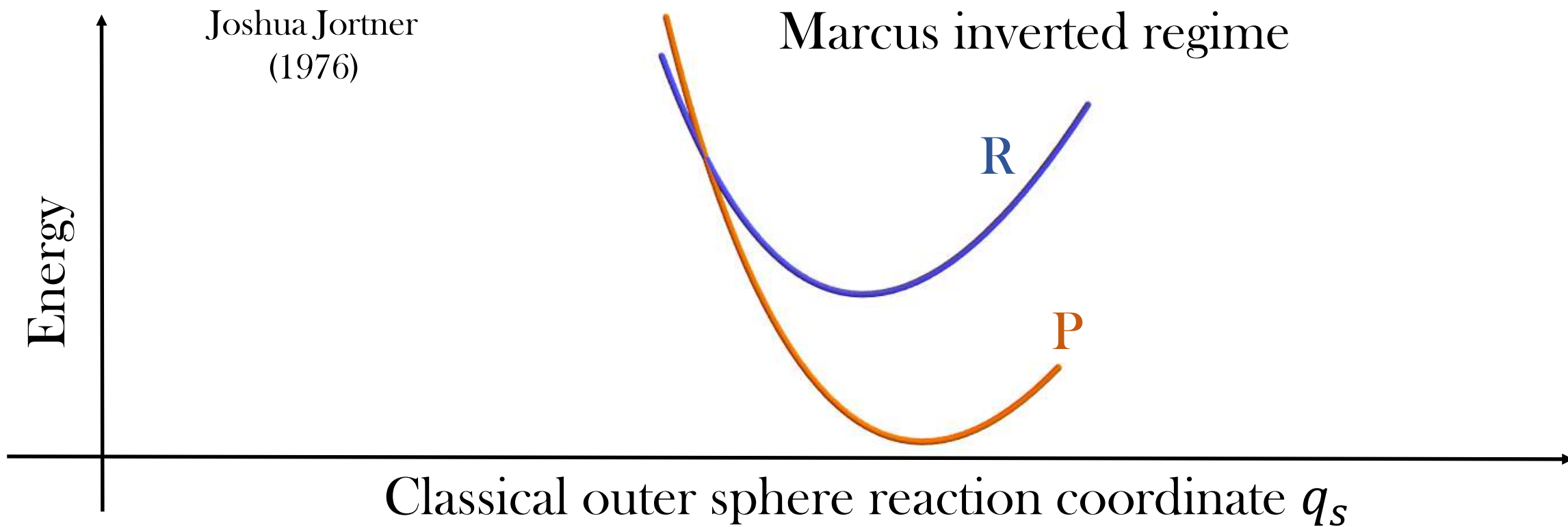


Gerhard Closs
(1984)

Background: Marcus theory - a caveat due to Jortner



Joshua Jortner
(1976)

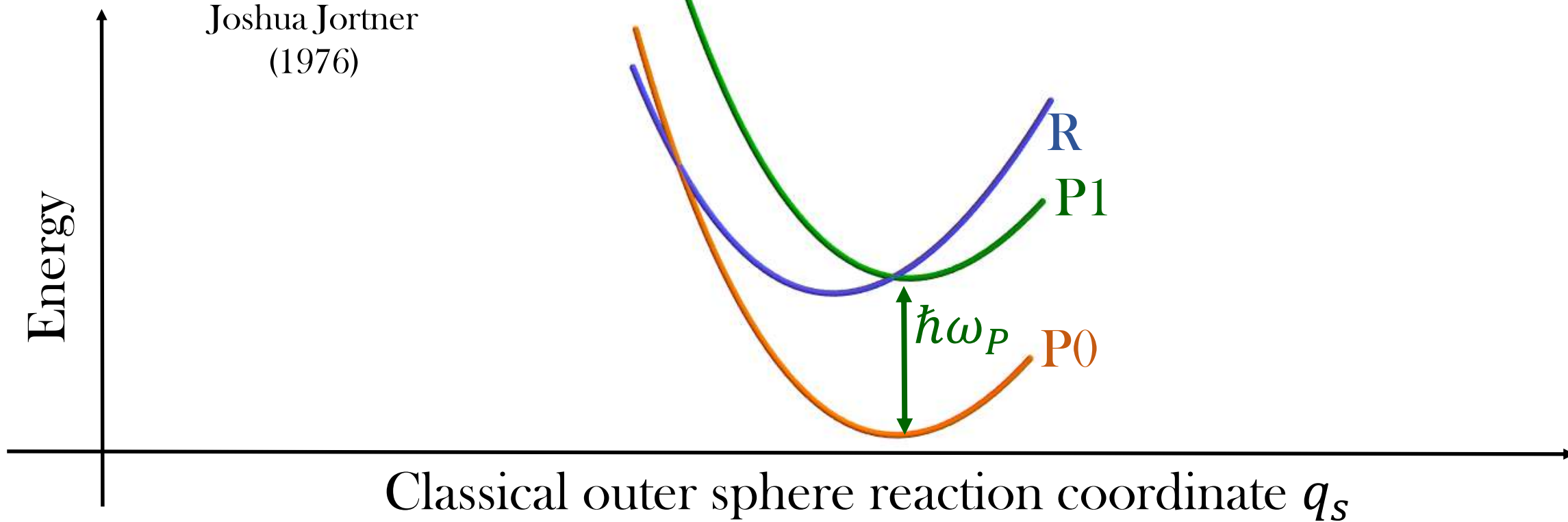


Background: Marcus theory - a caveat due to Jortner



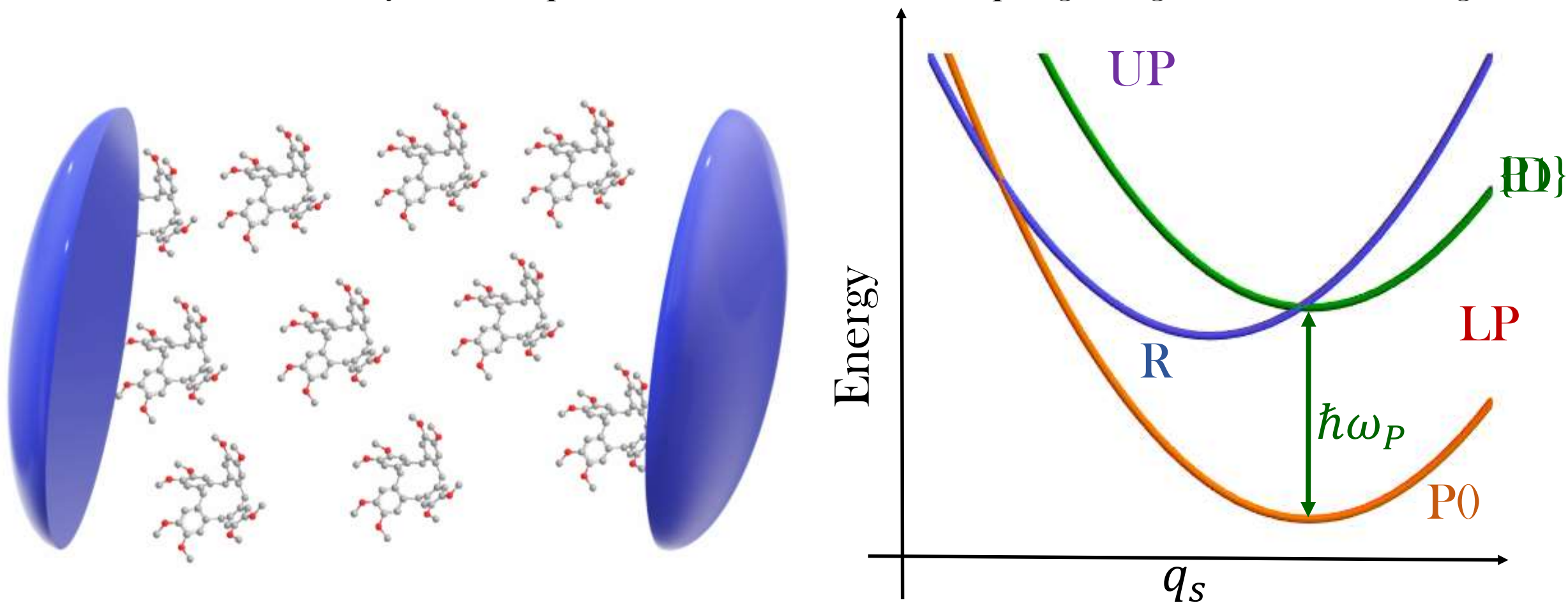
Joshua Jortner
(1976)

A slow rate in the Marcus inverted regime can be accelerated by creating a high-frequency ω_P vibrational excitation in the acceptor.

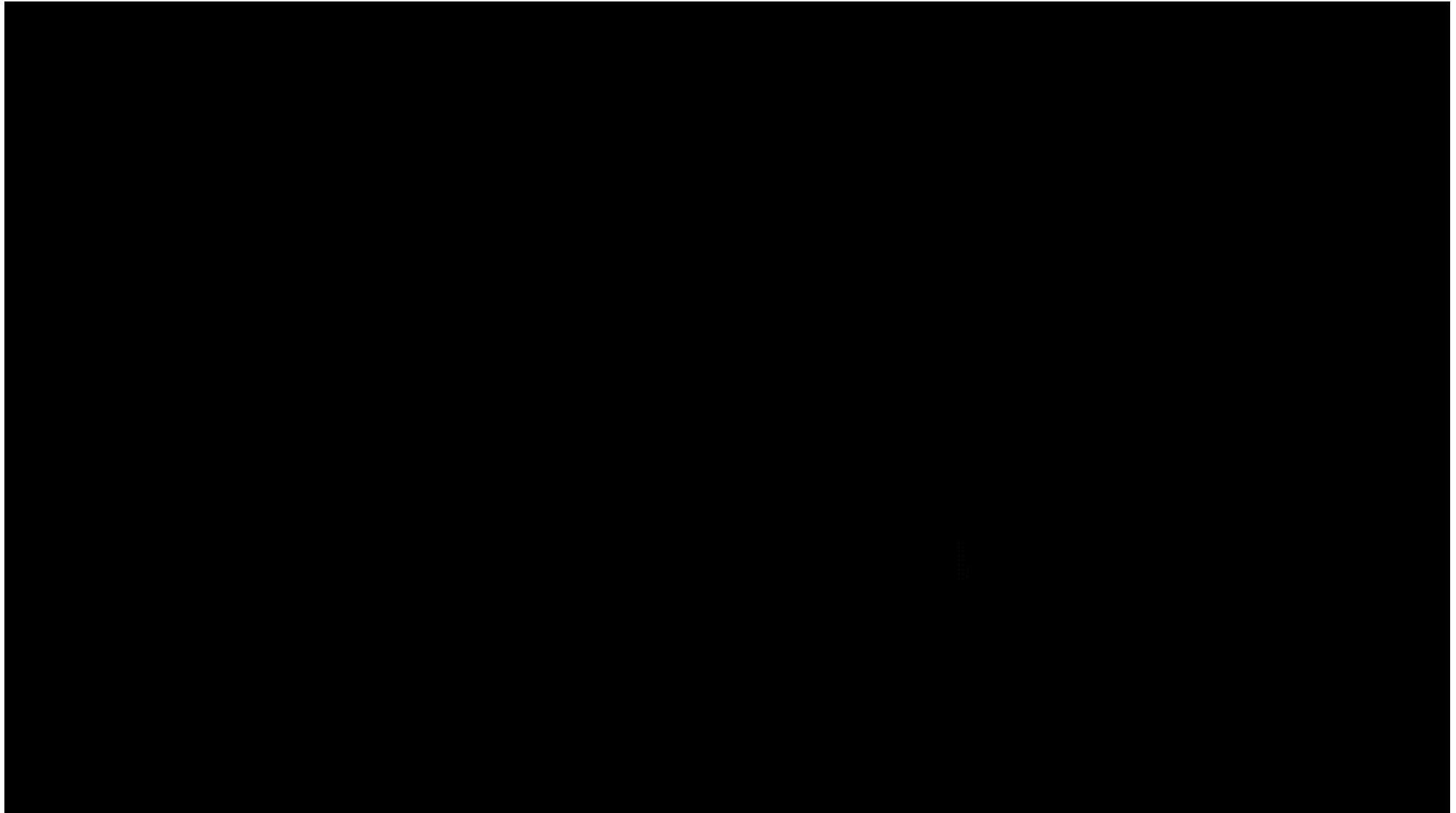


Catalysis of Marcus-Jortner ET with an IR cavity

Let cavity couple to the high-frequency modes of molecules undergoing ET. Place $M = 10^{10}$ reactants in cavity. As rxn proceeds from R to P, coupling to light becomes stronger!

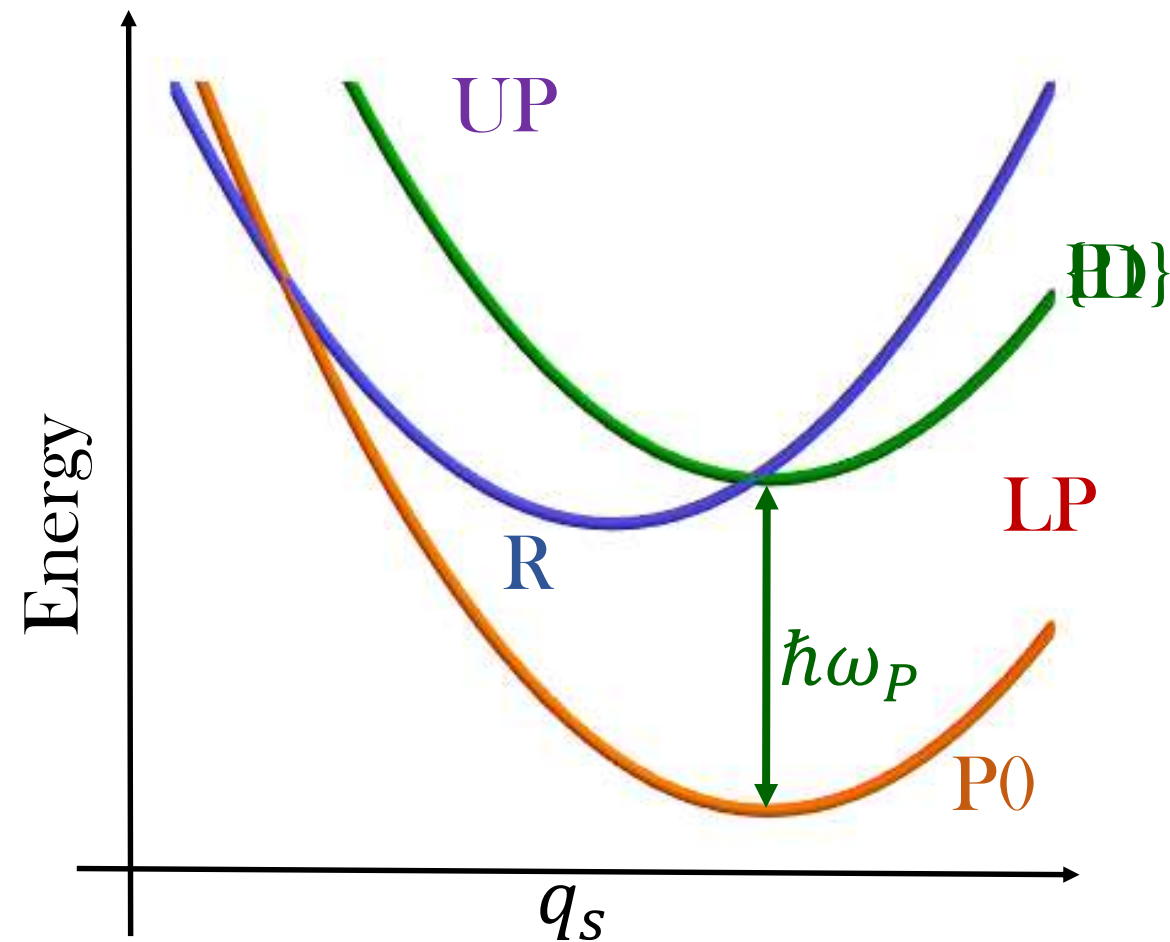
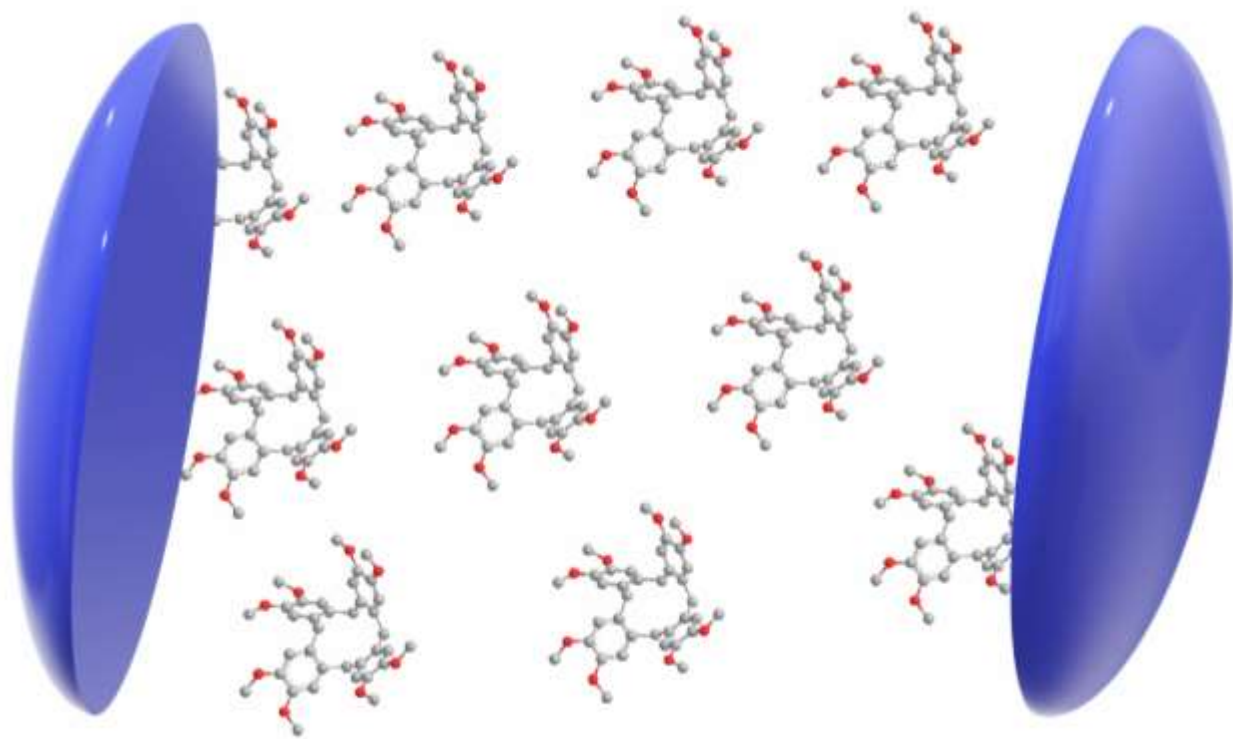


Anomalous kinetics a.k.a. leadership



Catalysis of Marcus-Jortner ET with an IR cavity

Place $M = 10^{10}$ reactants that undergo ET inside of a cavity. Let cavity couple to the high-frequency modes of P. As rxn proceeds from R to P, coupling to light becomes stronger!



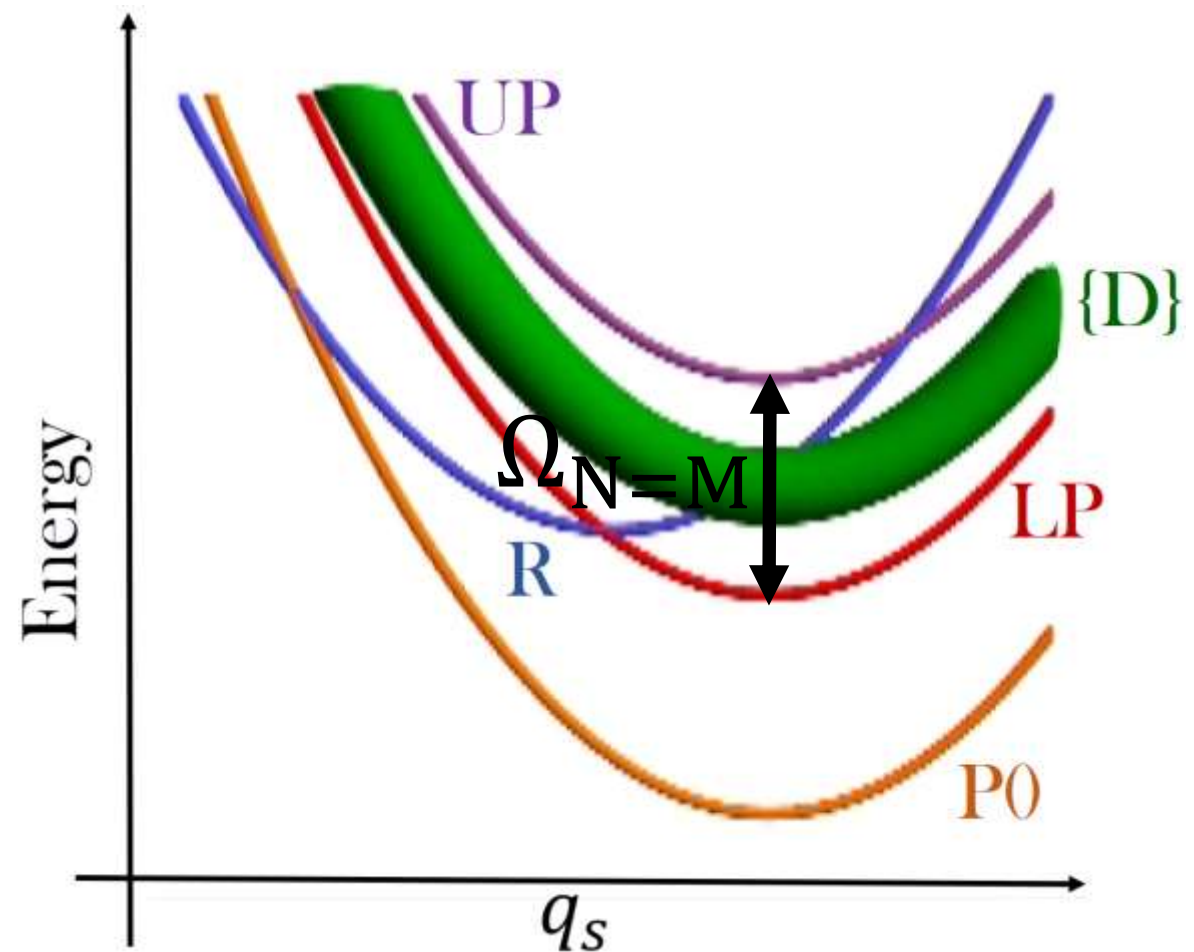
Catalysis of Marcus-Jortner ET with an IR cavity

$N = \#$ P molecules formed.
 $N \leq M = 10^{10}$ total # molecules.
 If we want:

$$k_{R \rightarrow LP}(N) > k_{R \rightarrow \{D\}} \\ \Rightarrow k_{in} > k_{out}$$

We need:

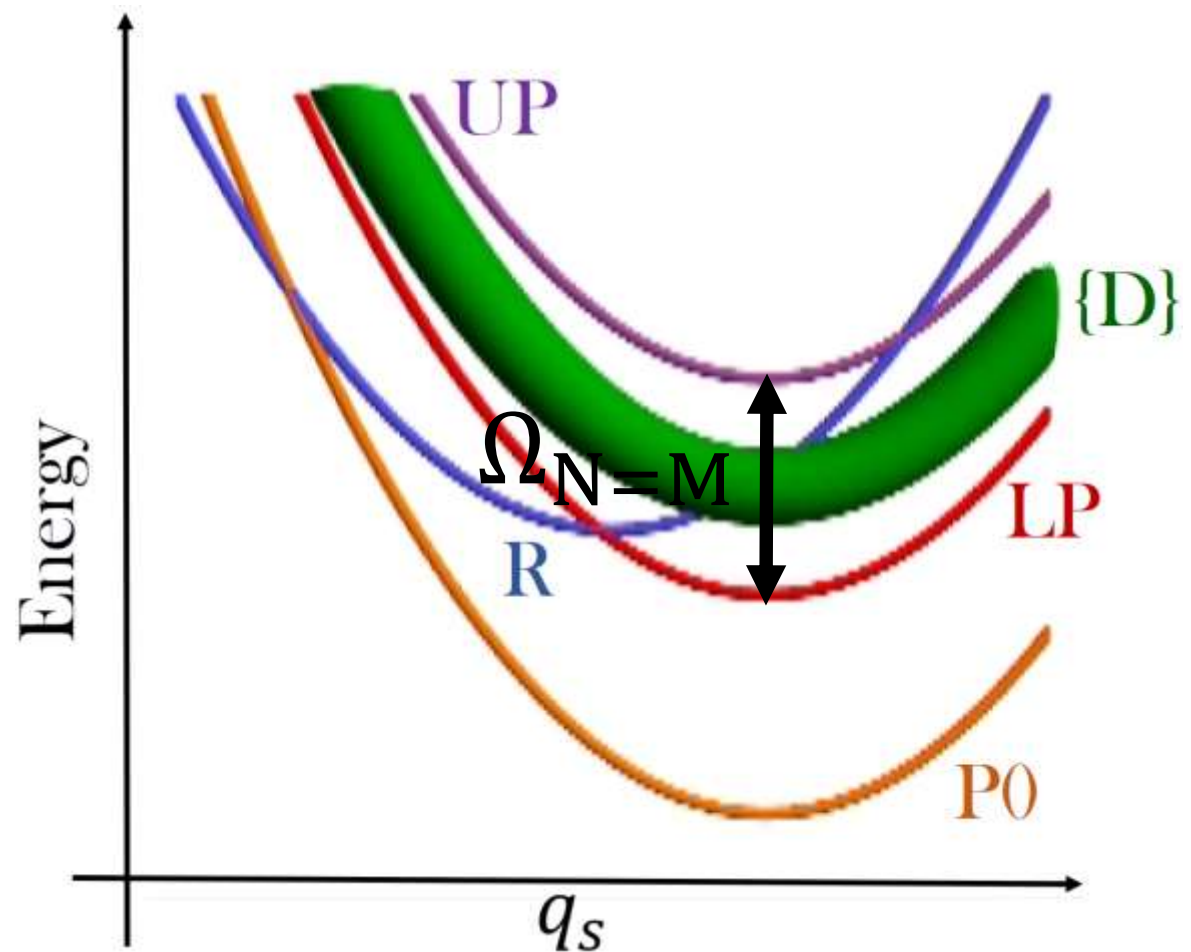
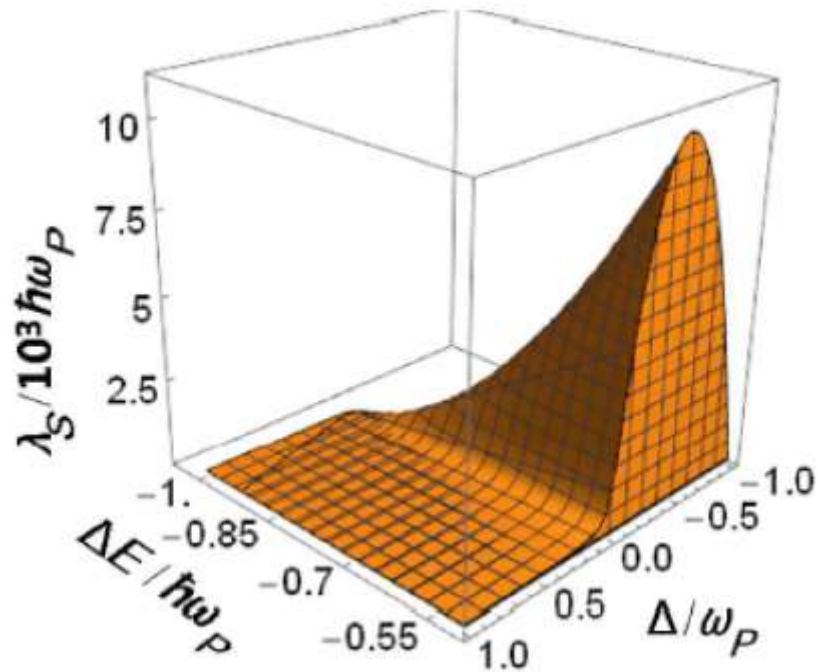
$$\frac{N}{\cos^2 \theta} < \exp \left(\frac{\hbar(\Omega_N - \Delta)}{4\lambda_S k_B T} \right) \\ \times \left[\Delta E + \lambda_S + \hbar\omega_P + \frac{\hbar(\Delta - \Omega_N)}{4} \right]$$



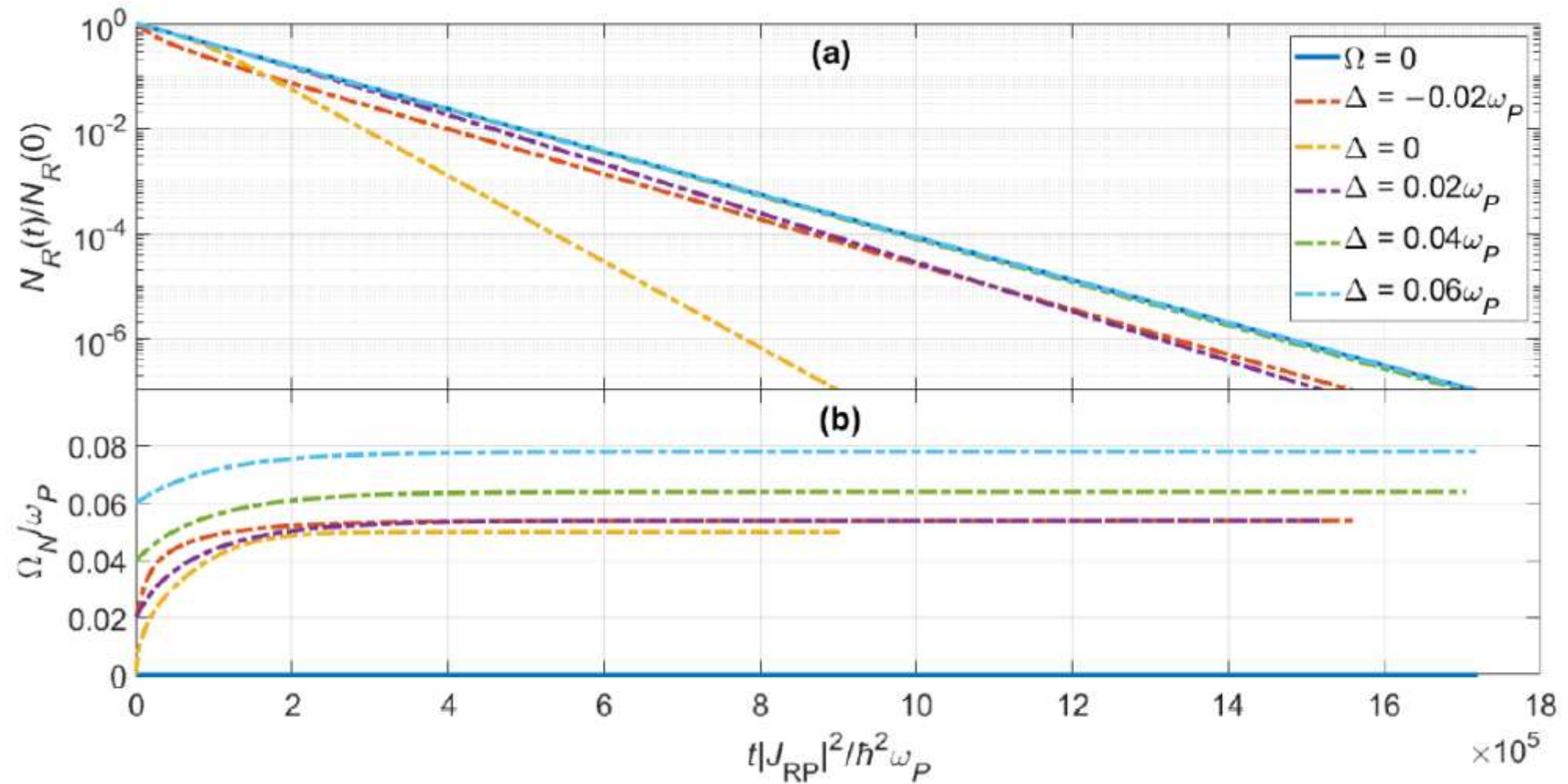
Activation energy reduction due to **LP** can outcompete large activation entropy of **{D}**!!!

Catalysis of Marcus-Jortner ET with an IR cavity

Activation energy reduction due to **LP** can outcompete large activation entropy of **{D}**!!!

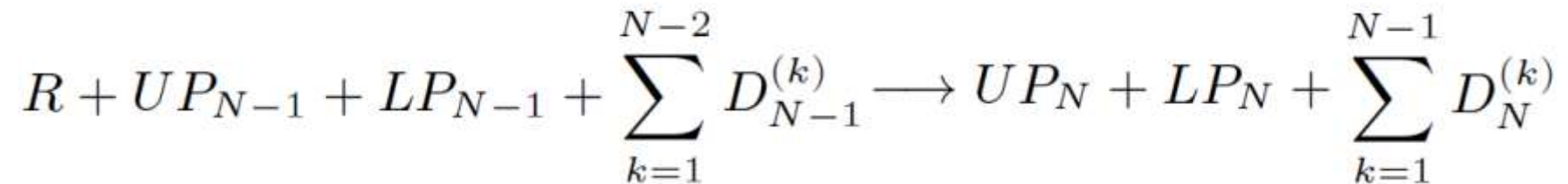


Catalysis of Marcus-Jortner ET with an IR cavity

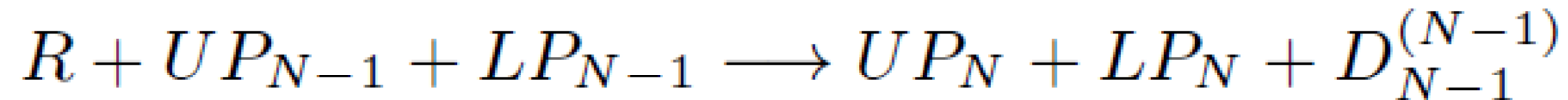


Catalysis of Marcus-Jortner ET with an IR cavity

The reaction that we are interested is in principle $N + 1$ body,



but can be reduced to an effective 3-body process,



Catalysis of Marcus-Jortner ET with an IR cavity

leading to a Marcus-Jortner-type expression of the form,



Jorge Campos

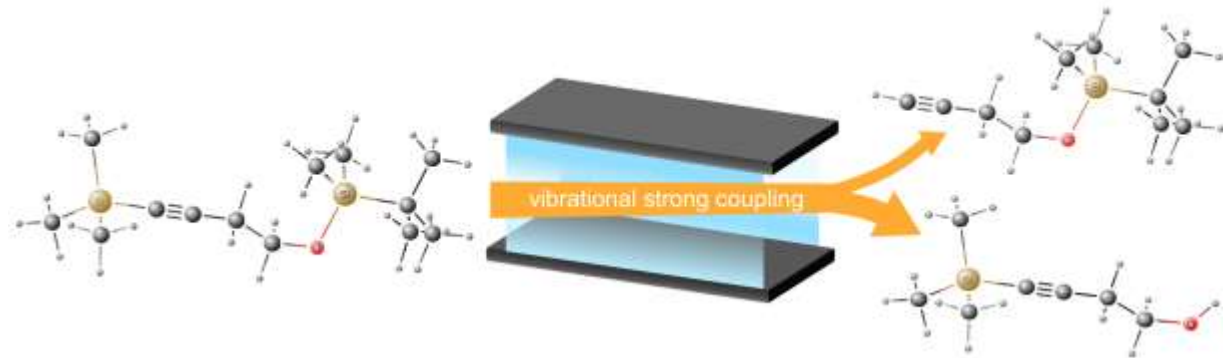
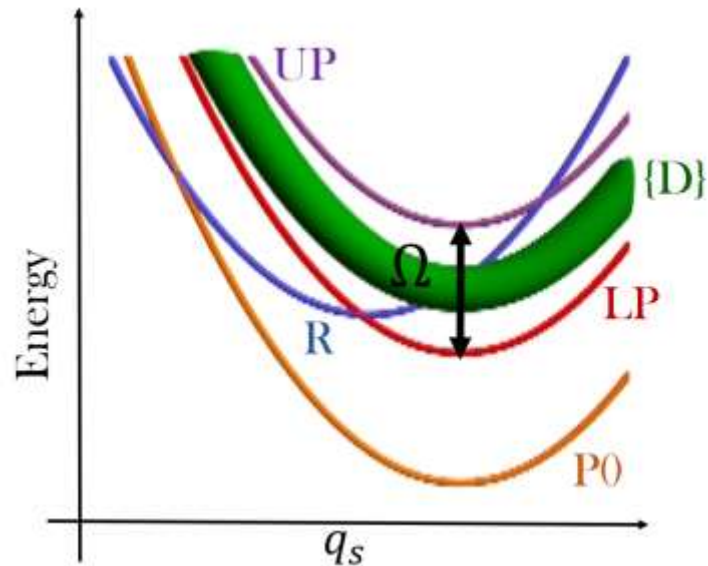
$$k_{R \rightarrow P}^{VSC} = \sqrt{\frac{\pi}{\lambda_S k_B T}} \frac{|J_{RP}|^2}{\hbar} \sum_{v_+=0}^{\infty} \sum_{v_-=0}^{\infty} \sum_{v_D=0}^{\infty} W_{v_+, v_-, v_D}$$

$$W_{v_+, v_-, v_D} = |F_{v_+, v_-, v_D}|^2 \exp\left(-\frac{E_{v_+, v_-, v_D}^\ddagger}{k_B T}\right)$$

$$\begin{aligned} |F_{v_+, v_-, v_D}|^2 &= |\langle 0_{+(N-1)} 0_{-(N-1)} 0_R | v_+ v_- v_D \rangle|^2 \\ &= \left(\frac{\sin^2 \theta_N}{N}\right)^{v_+} \left(\frac{\cos^2 \theta_N}{N}\right)^{v_-} \left(\frac{N-1}{N}\right)^{v_D} \\ &\quad \times \binom{v_+ + v_- + v_D}{v_+, v_-, v_D} |\langle 0' | v_+ + v_- + v_D \rangle|^2, \end{aligned}$$

Summary #1

- ❖ VSC can in fact lead to catalysis of thermally-activated ground state reactions.
- ❖ The elucidated mechanism operates for reactions with large activation energy barriers.
- ❖ It does not lead to (direct) suppression of reactions.
- ❖ Is quantum mechanics important for VSC rxns?

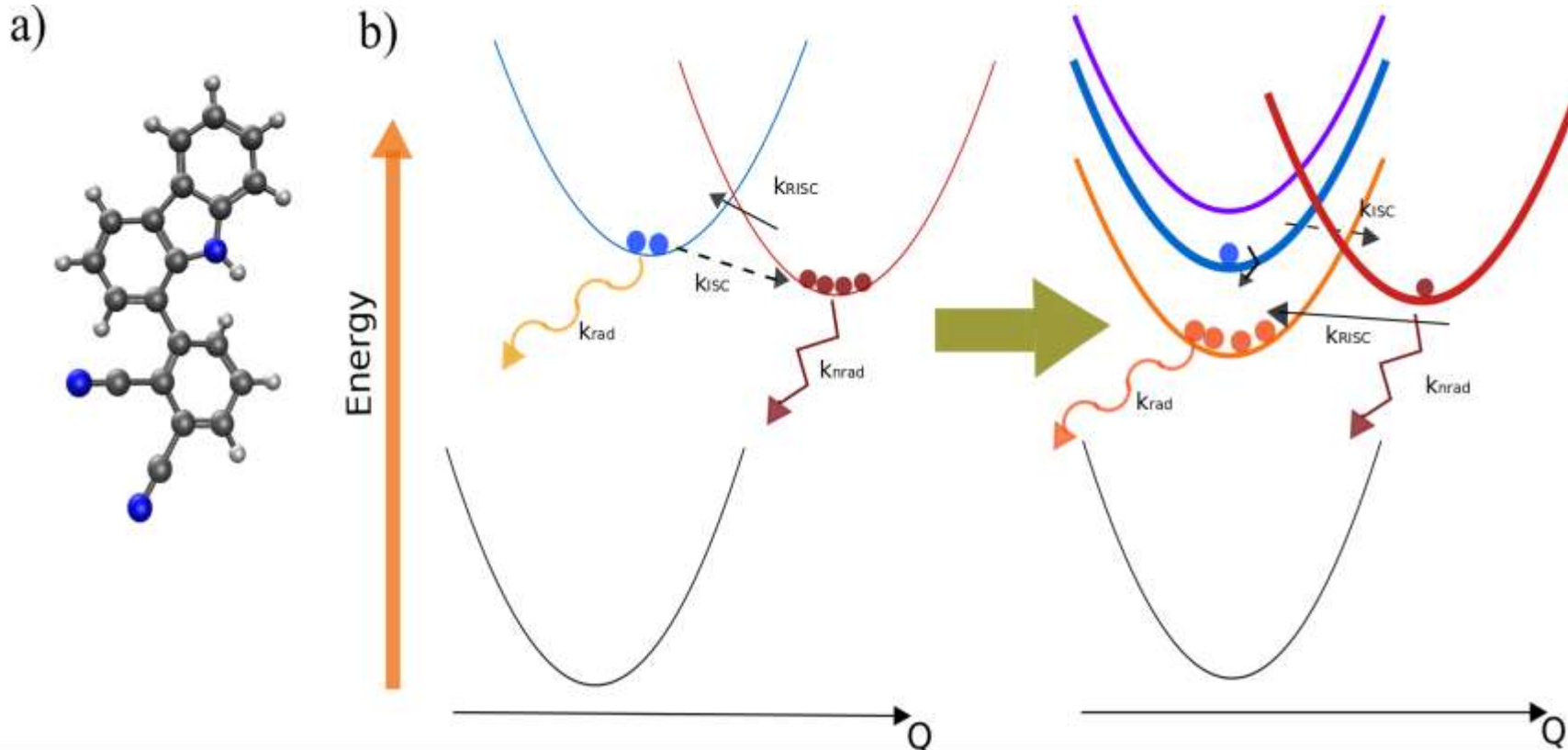


S. Kena-Cohen and J. Yuen-Zhou, ACS Cent. Sci., First reactions, 2019.

J. Campos-González-Angulo, R.F. Ribeiro, J. Yuen-Zhou, arXiv:1902.10264.

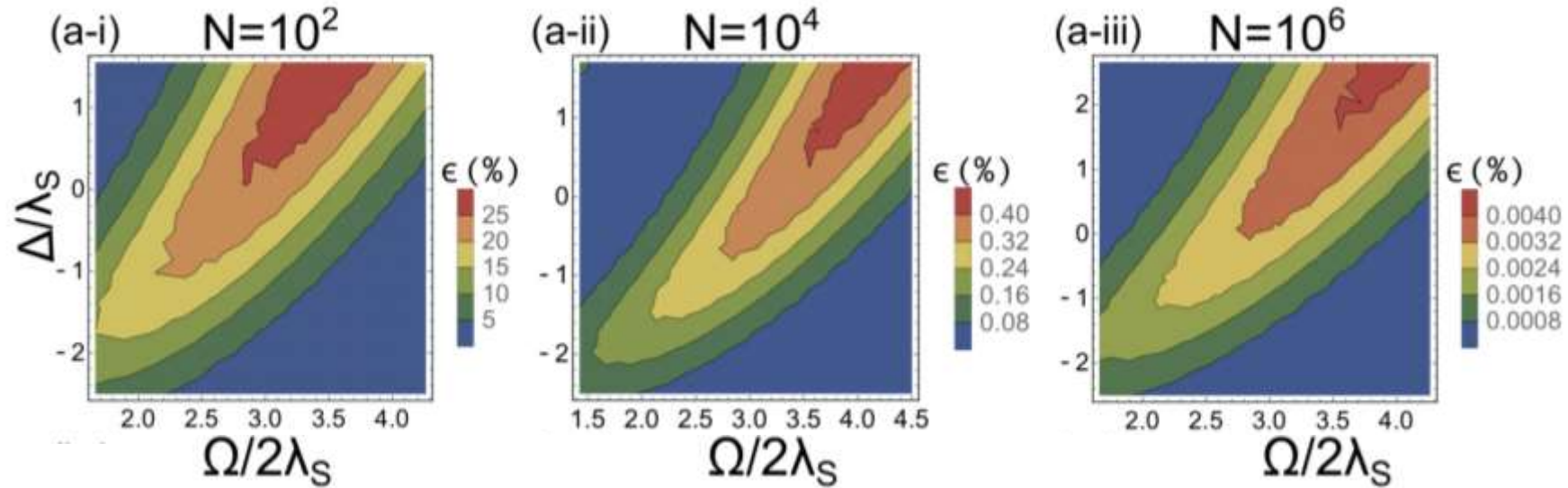
SIMILAR PROBLEM: Harvesting of triplets: the idea

Electrical injection of excitons statistically generates 3 triplets per singlet. Triplets don't give rise to PL.



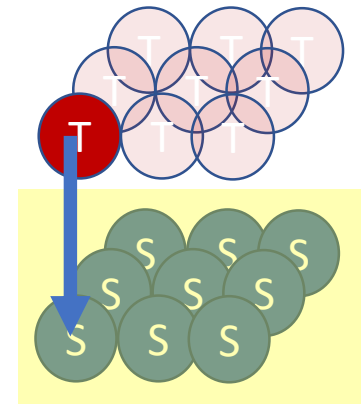
L.A. Martínez-Martínez, E. Eizner, S. Kena-Cohen, J. Yuen-Zhou, J. Chem. Phys., in press
E. Eizner, L.A. Martínez-Martínez, J. Yuen-Zhou, S. Kena-Cohen, arXiv:1903.09251

SIMILAR PROBLEM: Harvesting of triplets: gets worse with larger N



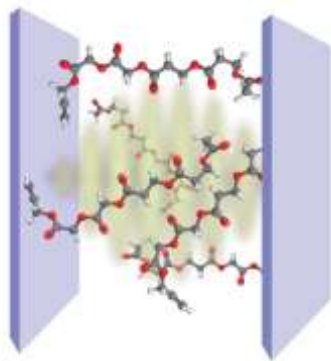
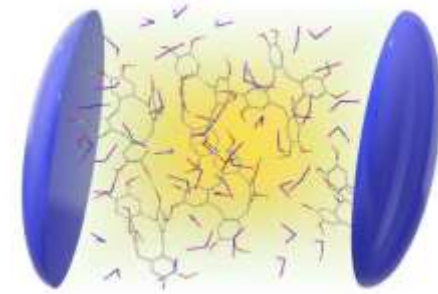
As the number of molecules N in the cavity becomes larger, the fluorescence efficiency decreases. The maximum rate is bounded at

$$k_{T \rightarrow LP} \leq \frac{|V_{ST}|^2}{2\hbar N} \sqrt{\frac{\pi}{\lambda_{T,LP} k_B T}}$$



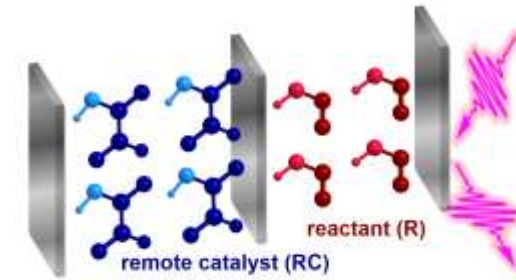
Outline of talk

Ground-state
reactivity



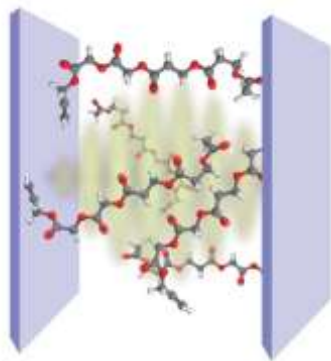
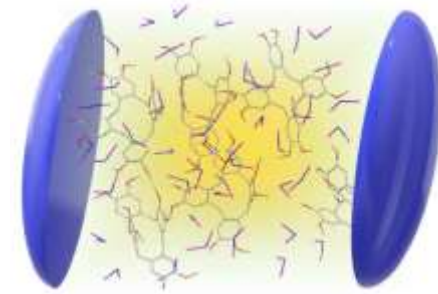
Vibrational
polaritons

Remote control



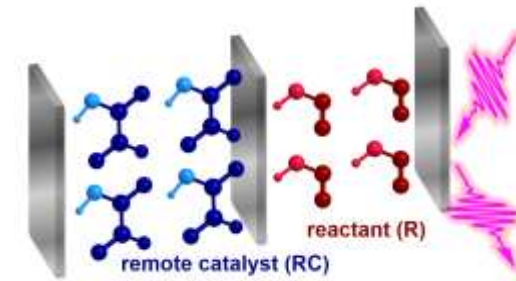
Outline of talk

Ground-state
reactivity



Vibrational
polaritons

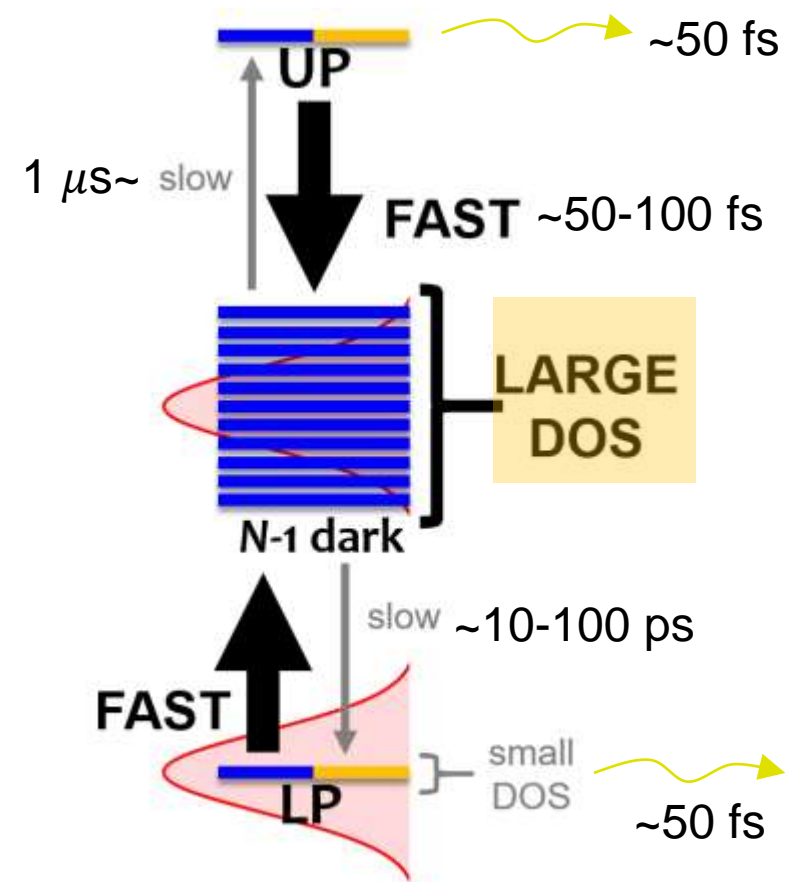
Remote control



Some timescales to keep in mind

In condensed phases, vibrational couplings V lead to relaxation mechanisms.

$$\gamma_{F \leftarrow I} = \frac{2\pi}{\hbar} \sum_f \sum_i p_i |\langle f | V | i \rangle|^2 \rho(\hbar\omega_{f,i})$$

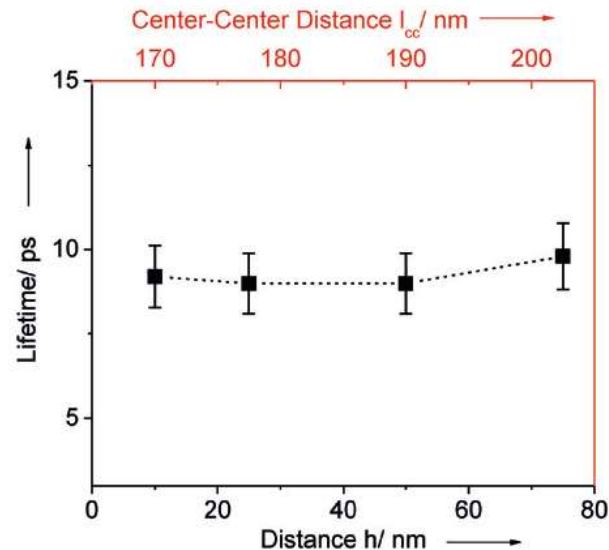
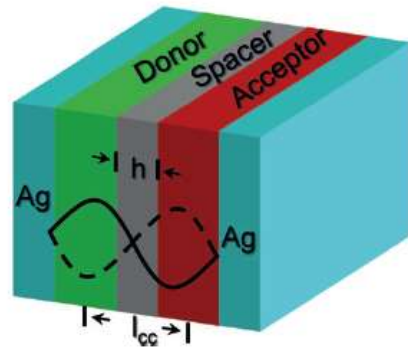


Ribeiro RF, Martínez-Martínez LA, Du M, Campos-Gonzalez-Angulo J, Yuen-Zhou J. Polariton Chemistry: controlling molecular dynamics with optical cavities, *Chem. Sci.*, 9, 6325-6339 (2018).

Polariton assisted remote energy transfer (PARET)

Energy Transfer between Spatially Separated Entangled Molecules

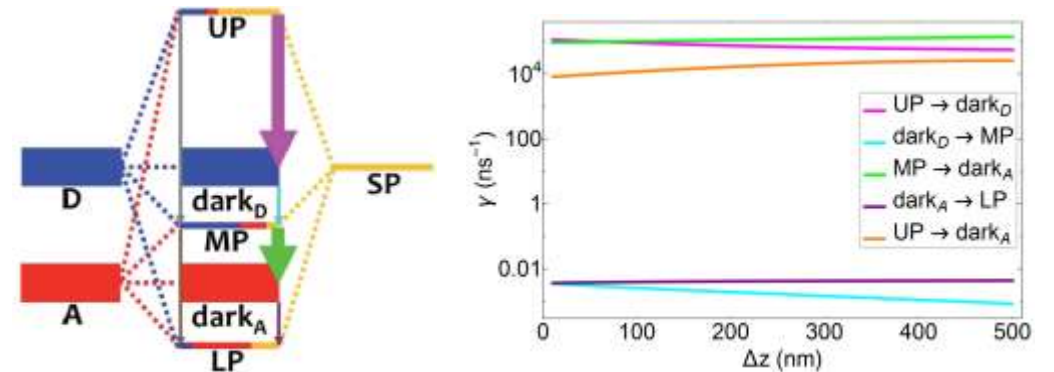
Xiaolan Zhong, Thibault Chervy, Lei Zhang, Anoop Thomas, Jino George, Cyriaque Genet, James A. Hutchison, and Thomas W. Ebbesen*



Zhong et al., *Angew. Chem., Int. Ed.*, 2017, 56, 9034–9038.

Theory for polariton-assisted remote energy transfer†

Matthew Du,^a Luis A. Martínez-Martínez,^a Raphael F. Ribeiro,^a Zixuan Hu,^{b,c} Vinod M. Menon,^{d,e} and Joel Yuen-Zhou^{a*}



M. Du, L.A. Martínez-Martínez, R.F. Ribeiro, V.M. Menon, J. Yuen-Zhou, *Chem. Sci.* 9, 6659–6669 (2018).

Acknowledgements



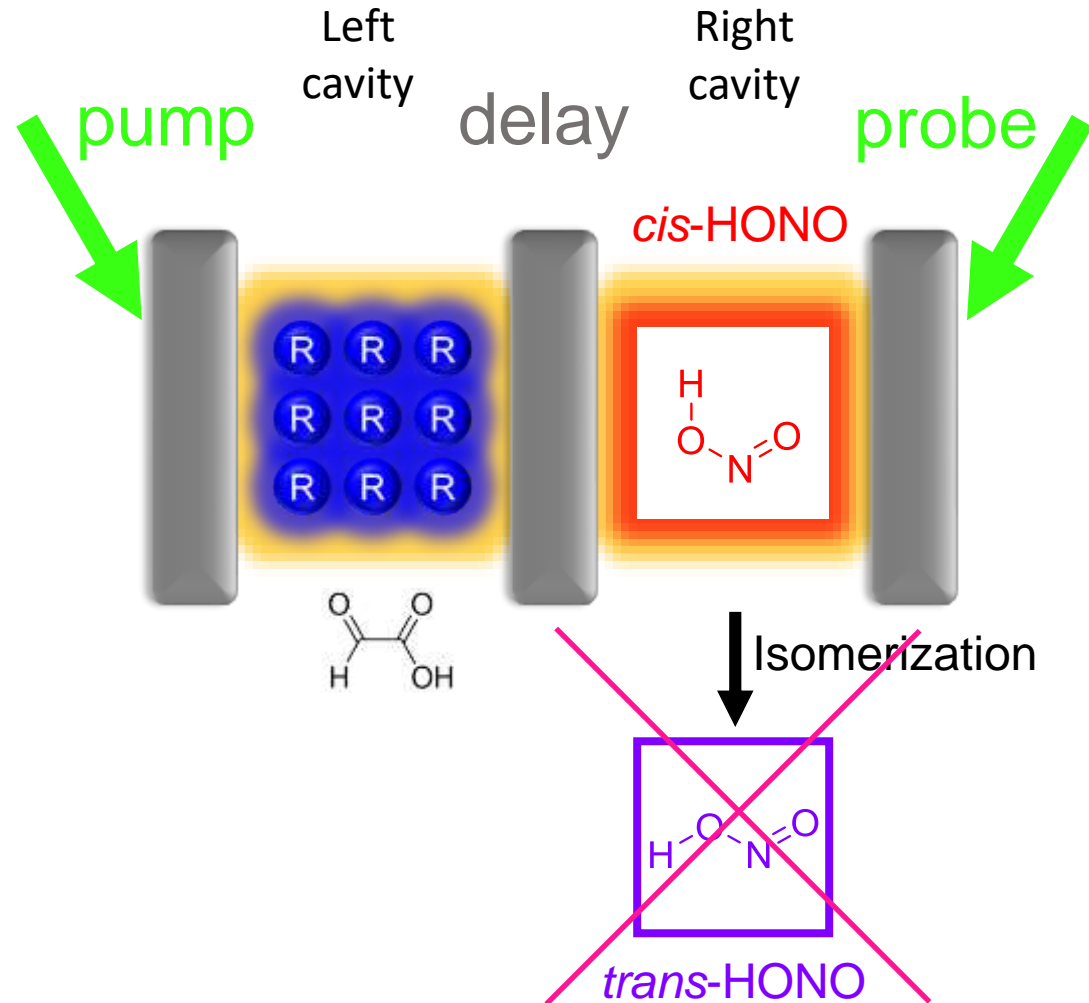
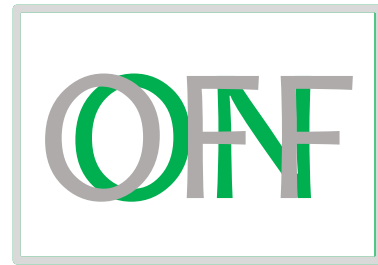
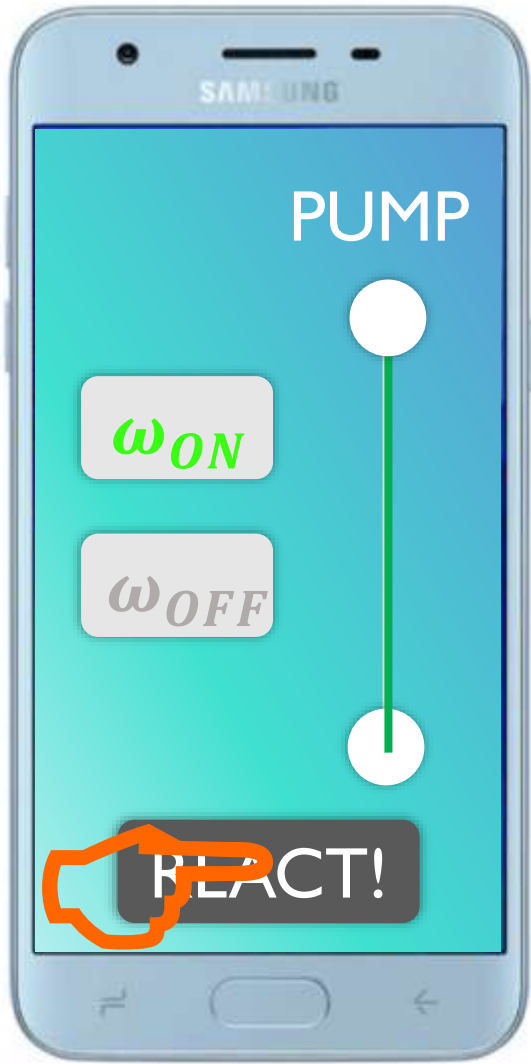
Matthew Du



Raphael Ribeiro

Is remote control of chemistry possible?

From PARET to remote control of chemistry



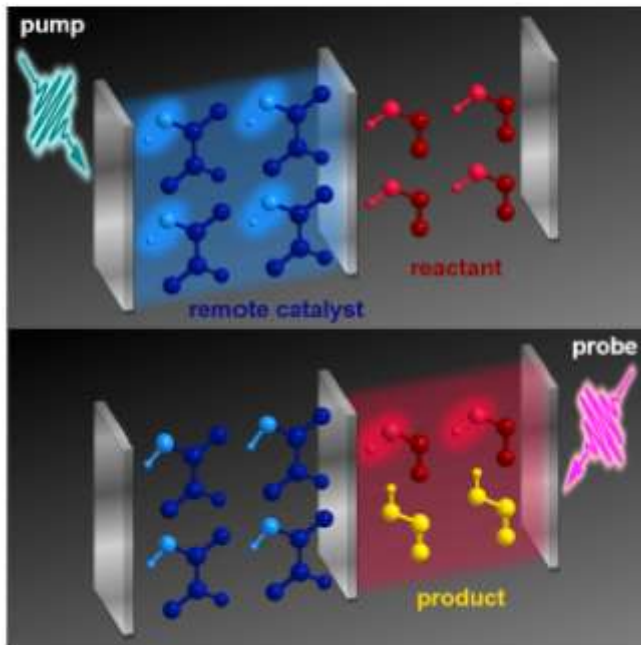
From PARET to remote control of chemistry

Chem

CellPress

Article

Remote Control of Chemistry in Optical Cavities



Traditionally, the catalyst binds to its substrate to enhance chemical reactivity. Here, we theoretically design an optical-cavity-based quantum device that allows the photoexcitation of a "remote catalyst" in one cavity to influence the photochemistry of reactant in another cavity. This non-local effect relies on strong light-matter interaction provided by the cavities. Applying the device to the isomerization of nitrous acid, we demonstrate that increasing the photoexcitation of the "catalyst" can boost reaction efficiency by an order of magnitude.

Matthew Du, Raphael F. Ribeiro,
Joel Yuen-Zhou

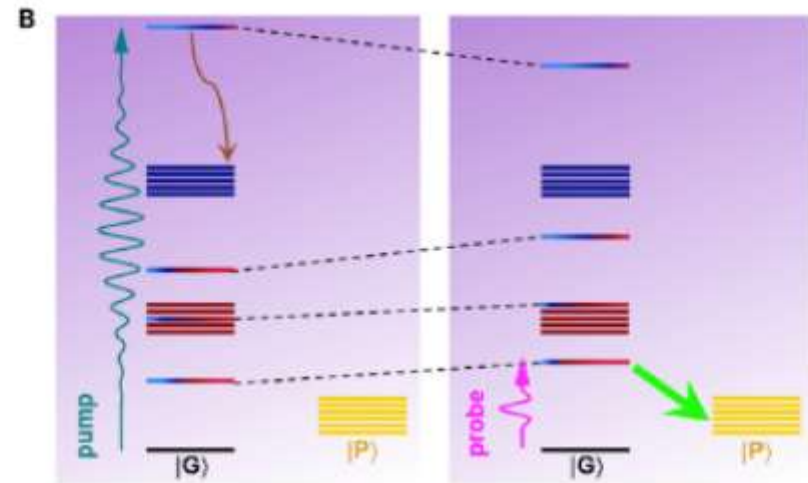
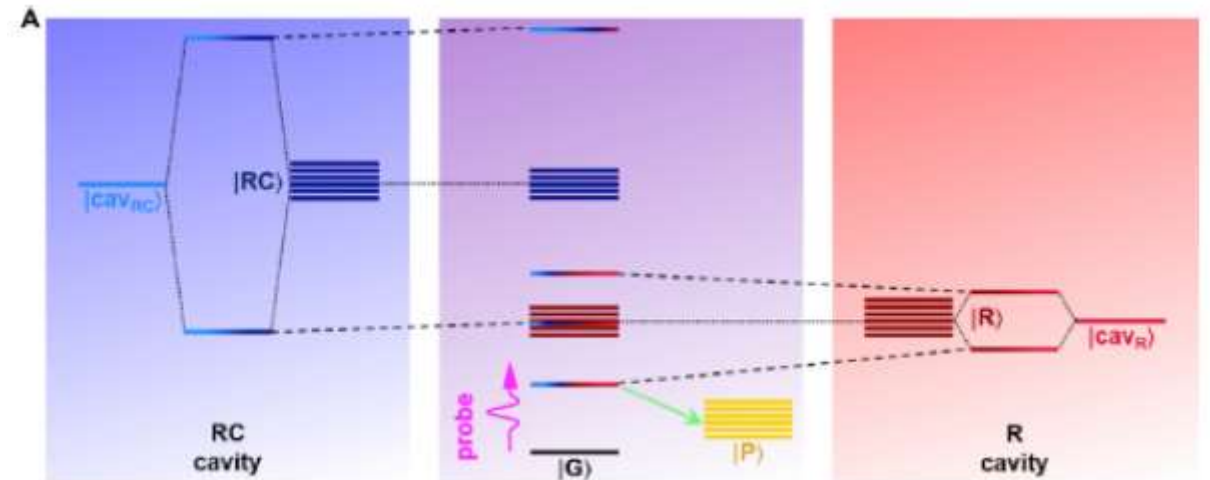
ryuen@ucsd.edu

HIGHLIGHTS

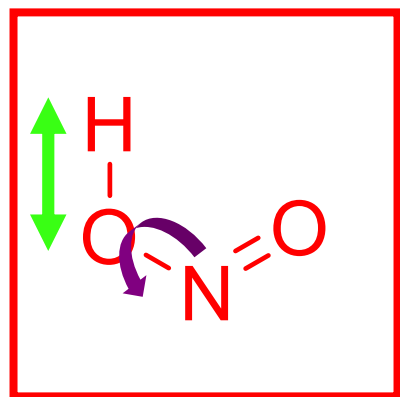
Proposed quantum device
employs optical cavities to enable
remote control of chemistry

A molecule in one vessel affects
the reactivity of a molecule in
another vessel.

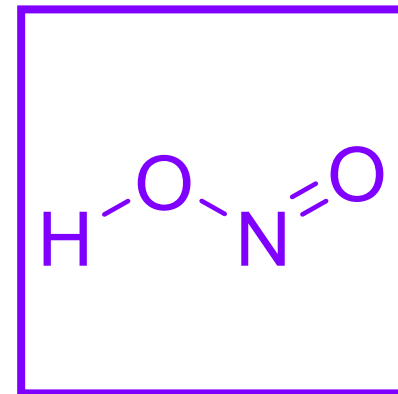
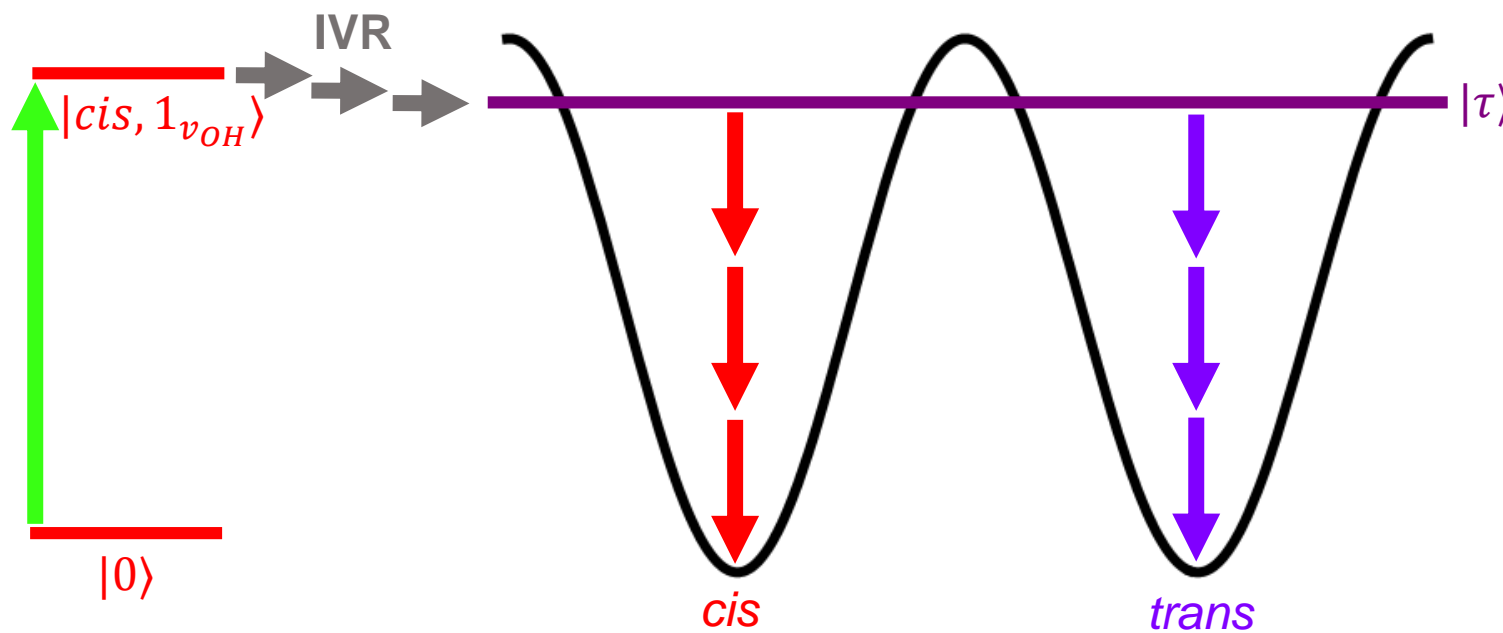
Reaction efficiency can be
enhanced by an order of
magnitude



IR-induced, vibrationally-selective chemistry: *cis*→*trans* isomerization of HONO



cis

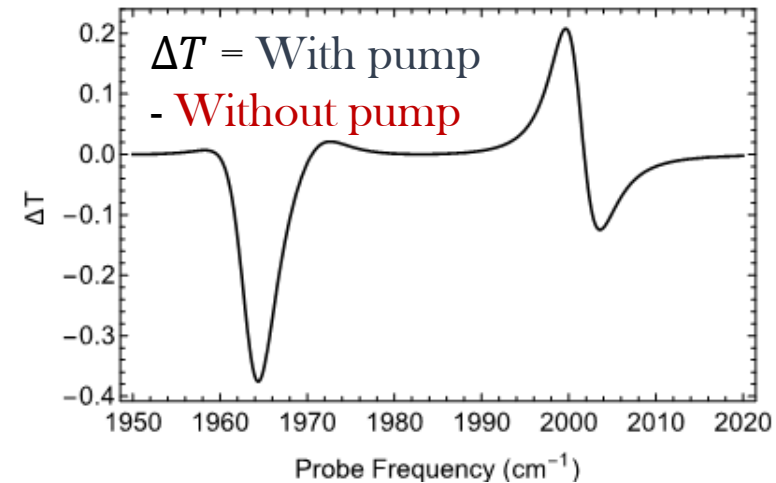
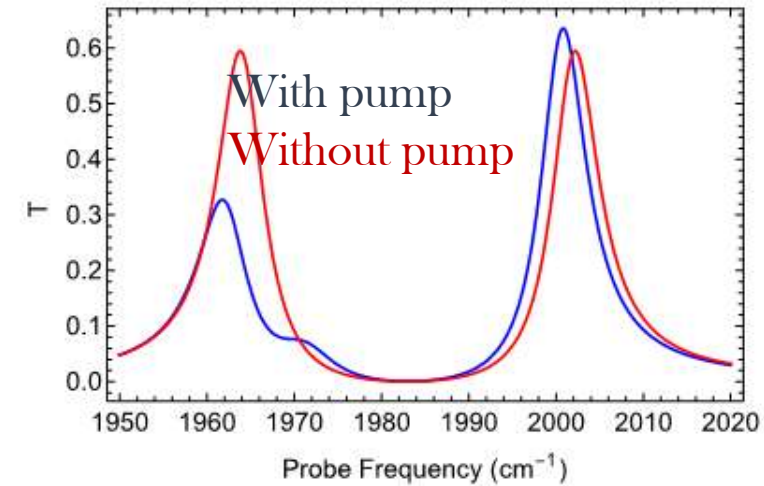
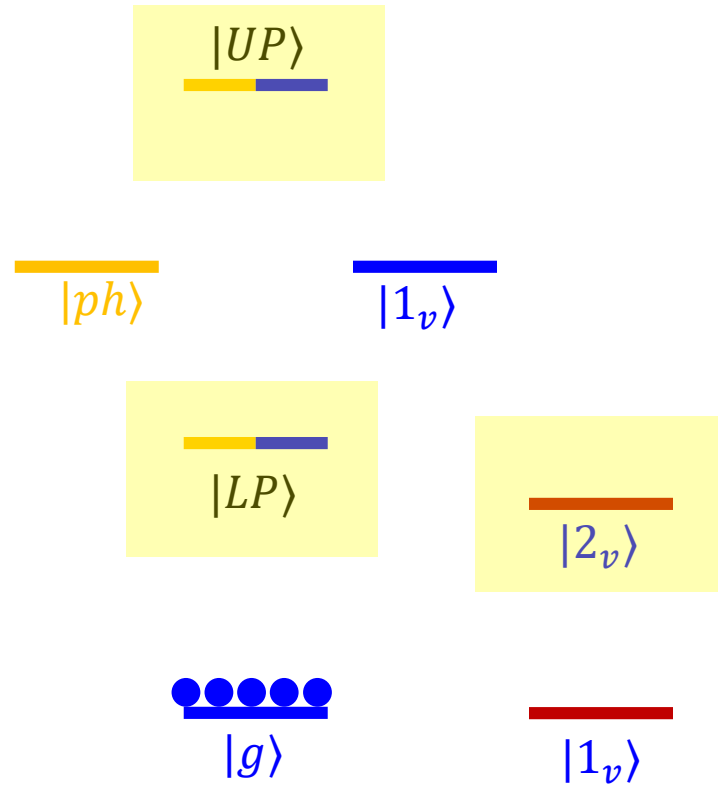


trans

R. T. Hall and G. C. Pimentel, *JCP*, 1963, **38**, 1889.

R. Schanz, V. Botan, and P. Hamm, *JCP*, 2005, **122**, 044509.

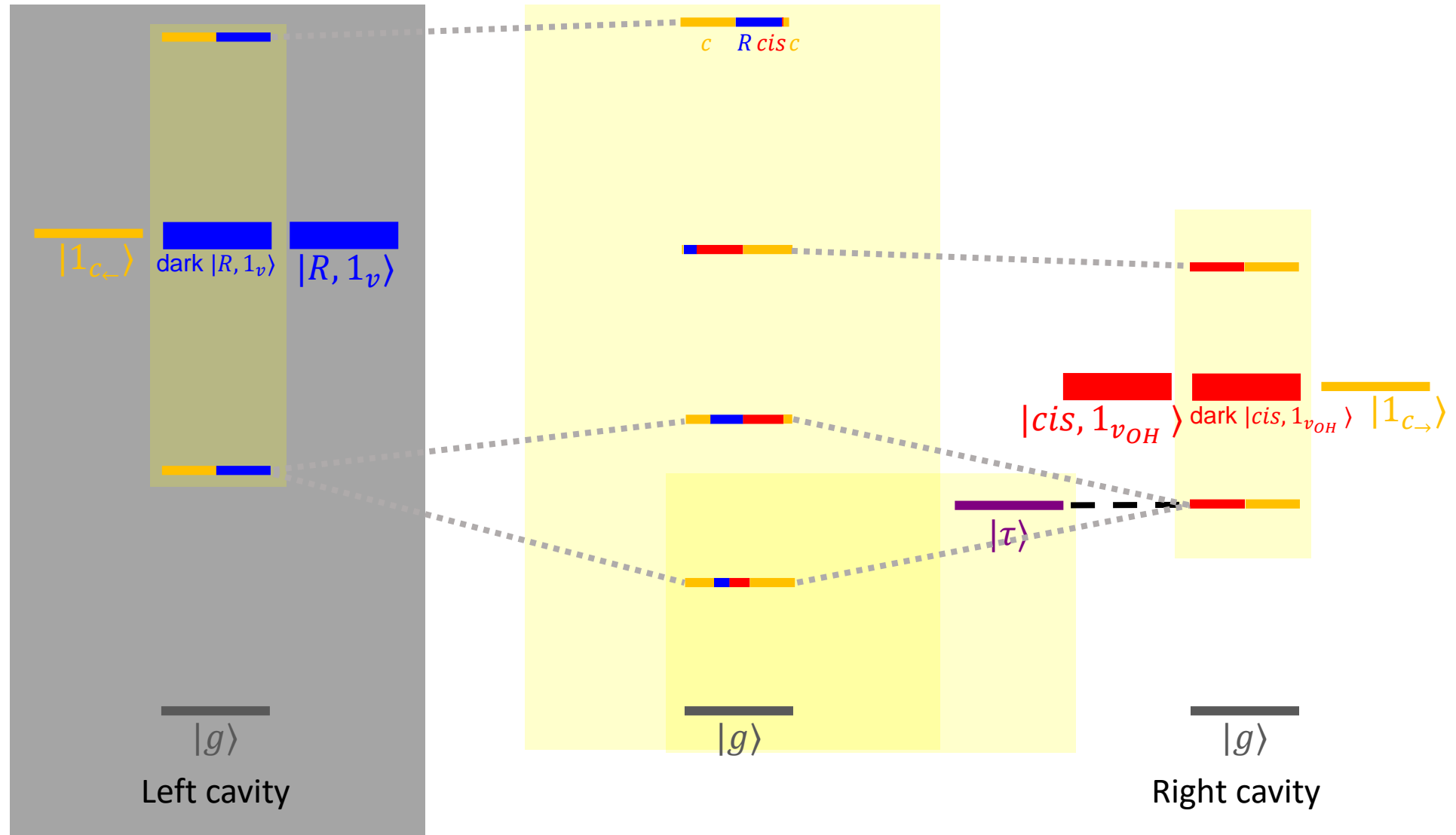
Ultrafast switching of polaritons via saturation of molecular absorption



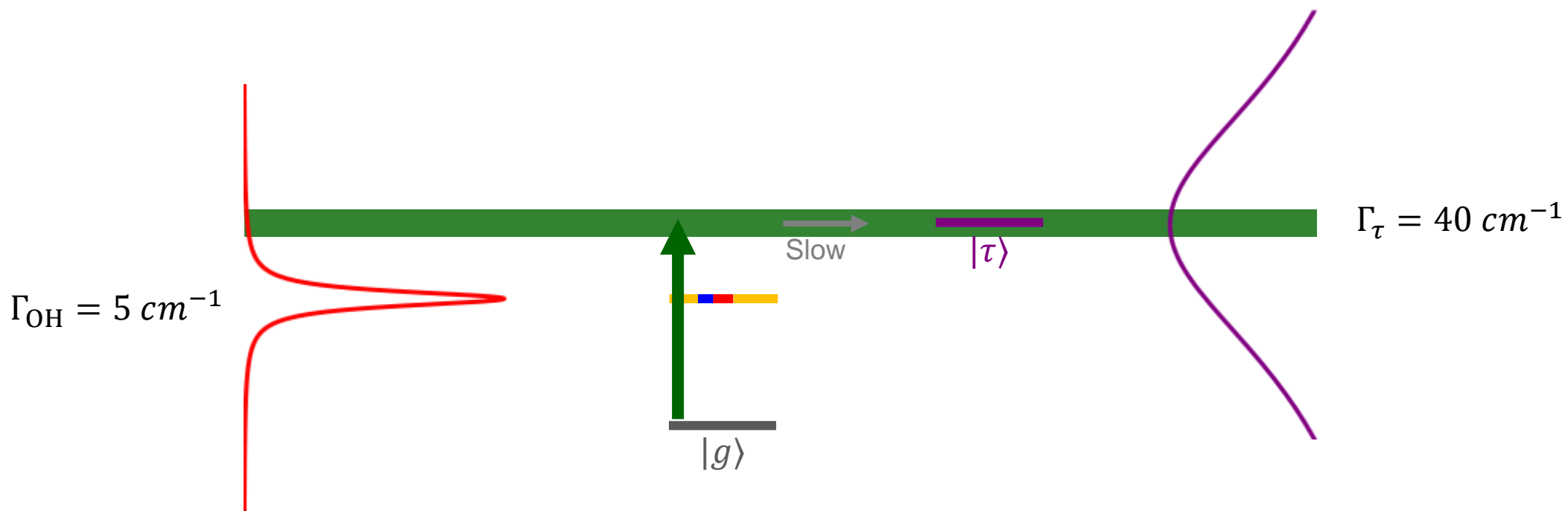
B. Xiang, R. F. Ribeiro, A. D. Dunkelberger, J. C. Owrutsky, B. S. Simpkins, J. Yuen-Zhou, and W. Xiong, PNAS 115, 19 (2018).

R.F. Ribeiro, R. F. Ribeiro, A. D. Dunkelberger, J. C. Owrutsky, B. S. Simpkins, W. Xiong, J. Yuen-Zhou, J. Phys. Chem. Lett. 9, 13 (2018).

Ultrafast remote-control chemistry

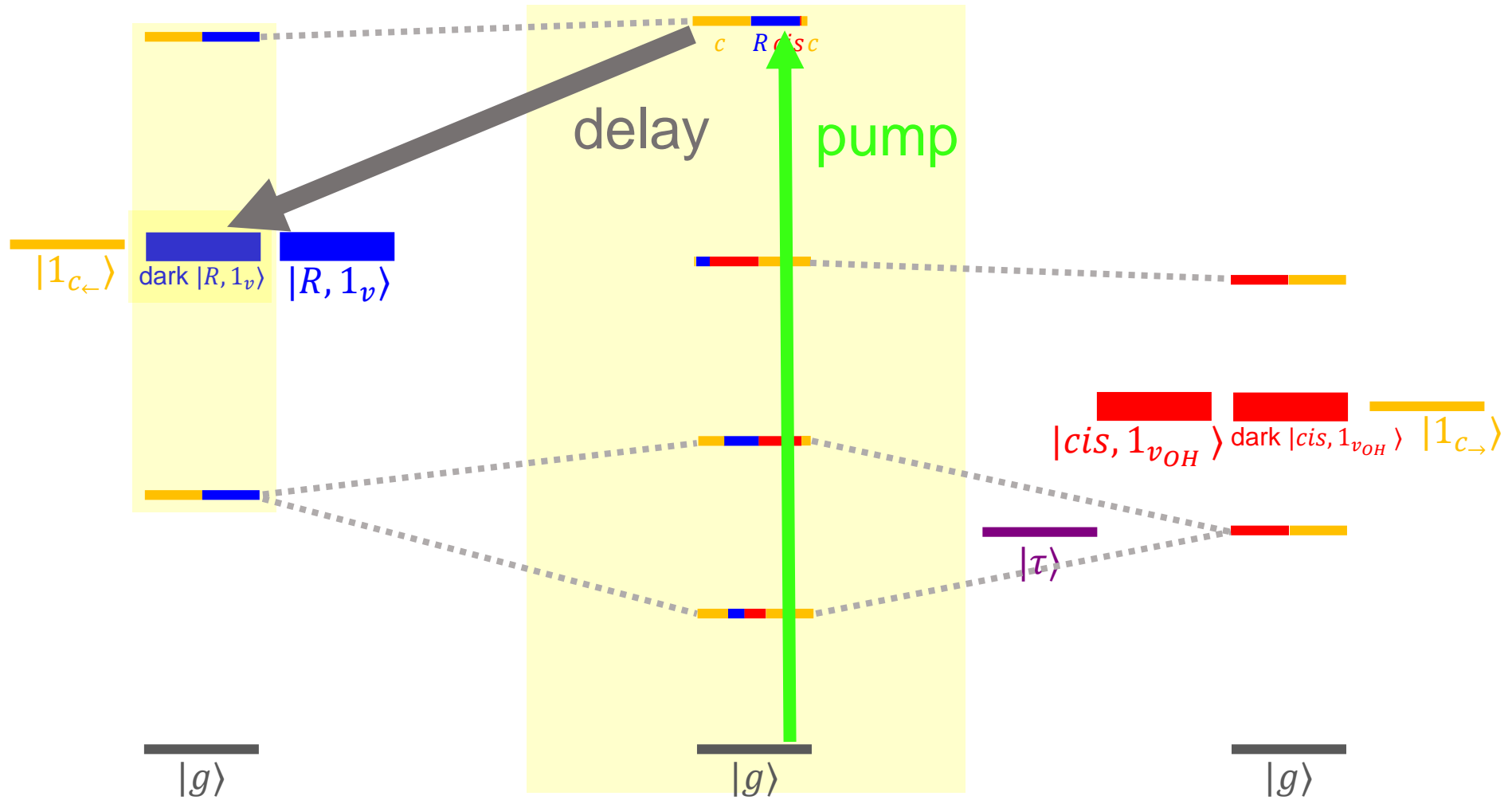


Ultrafast remote-control chemistry

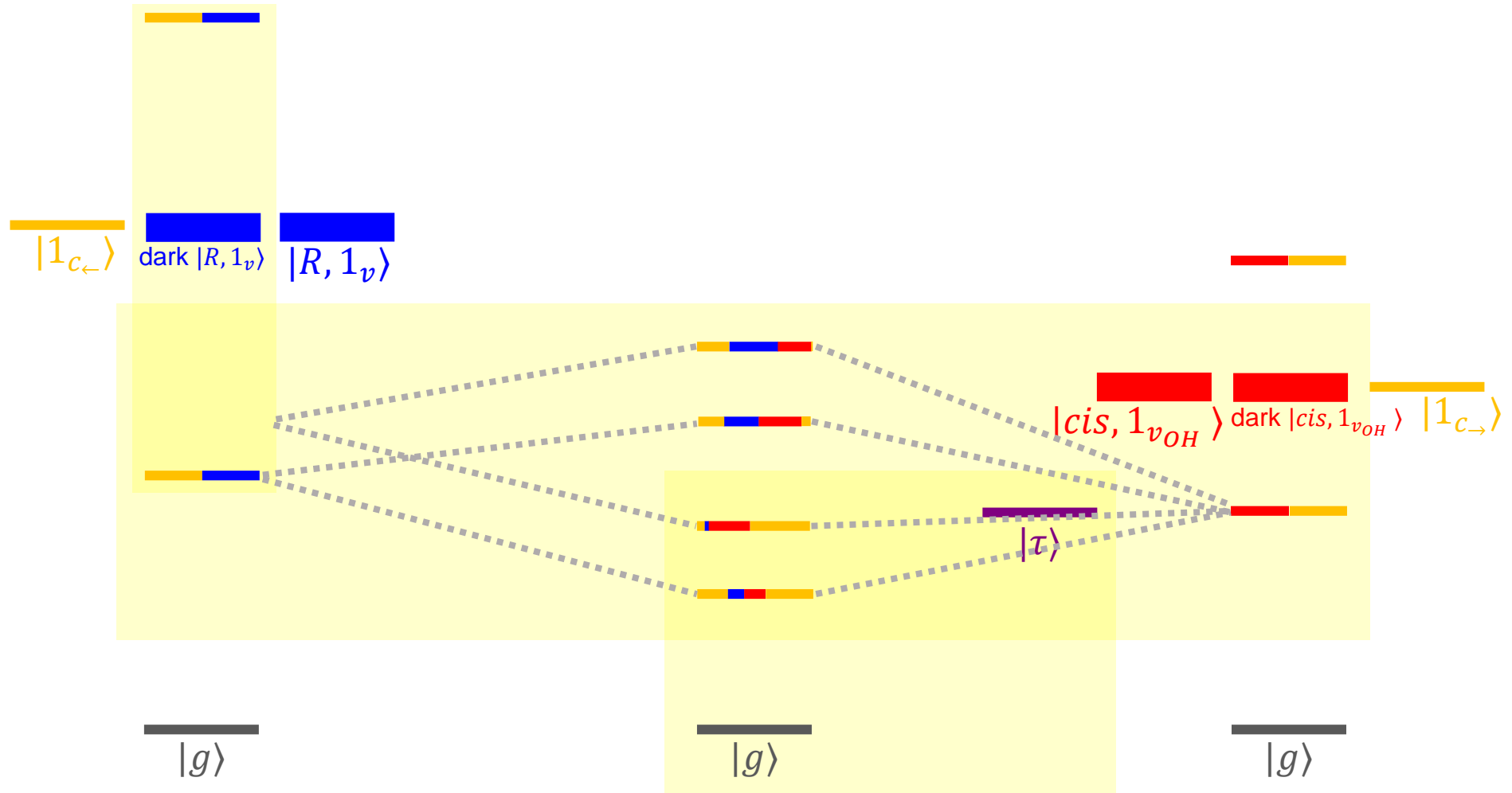


M. Du, R. F. Ribeiro, J. Yuen-Zhou, Chem 5, 5, 1167 (2019)

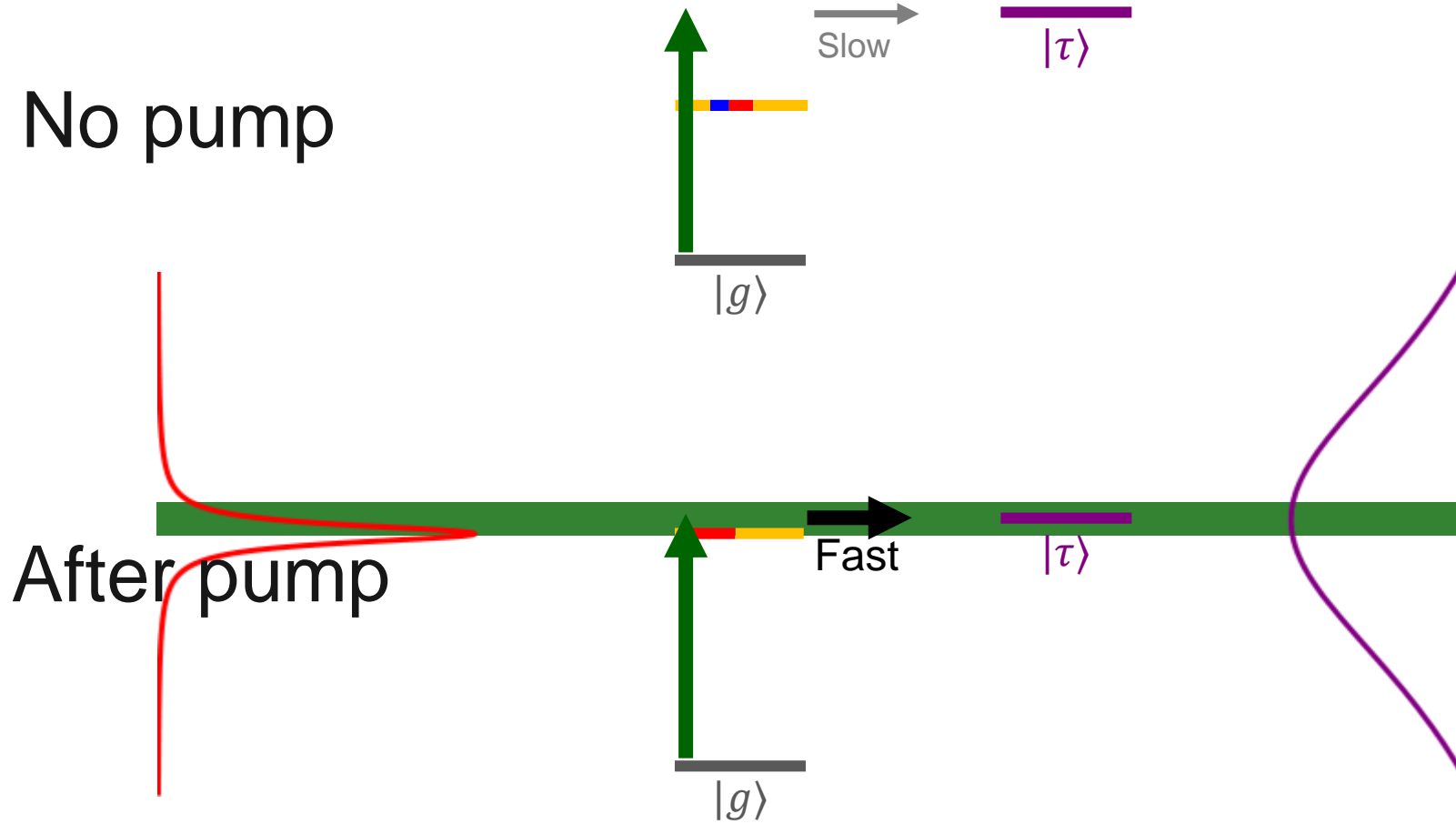
Ultrafast remote-control chemistry



Ultrafast remote-control chemistry

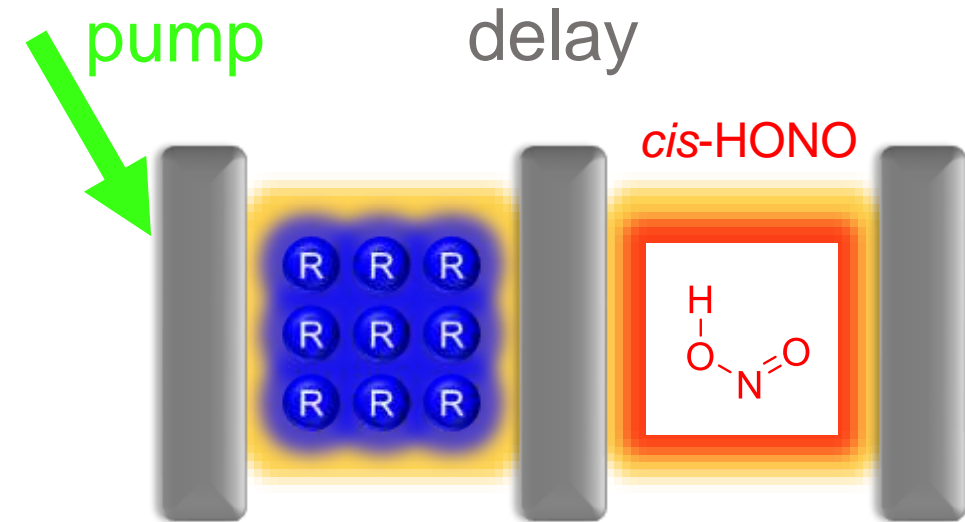


Ultrafast remote-control chemistry

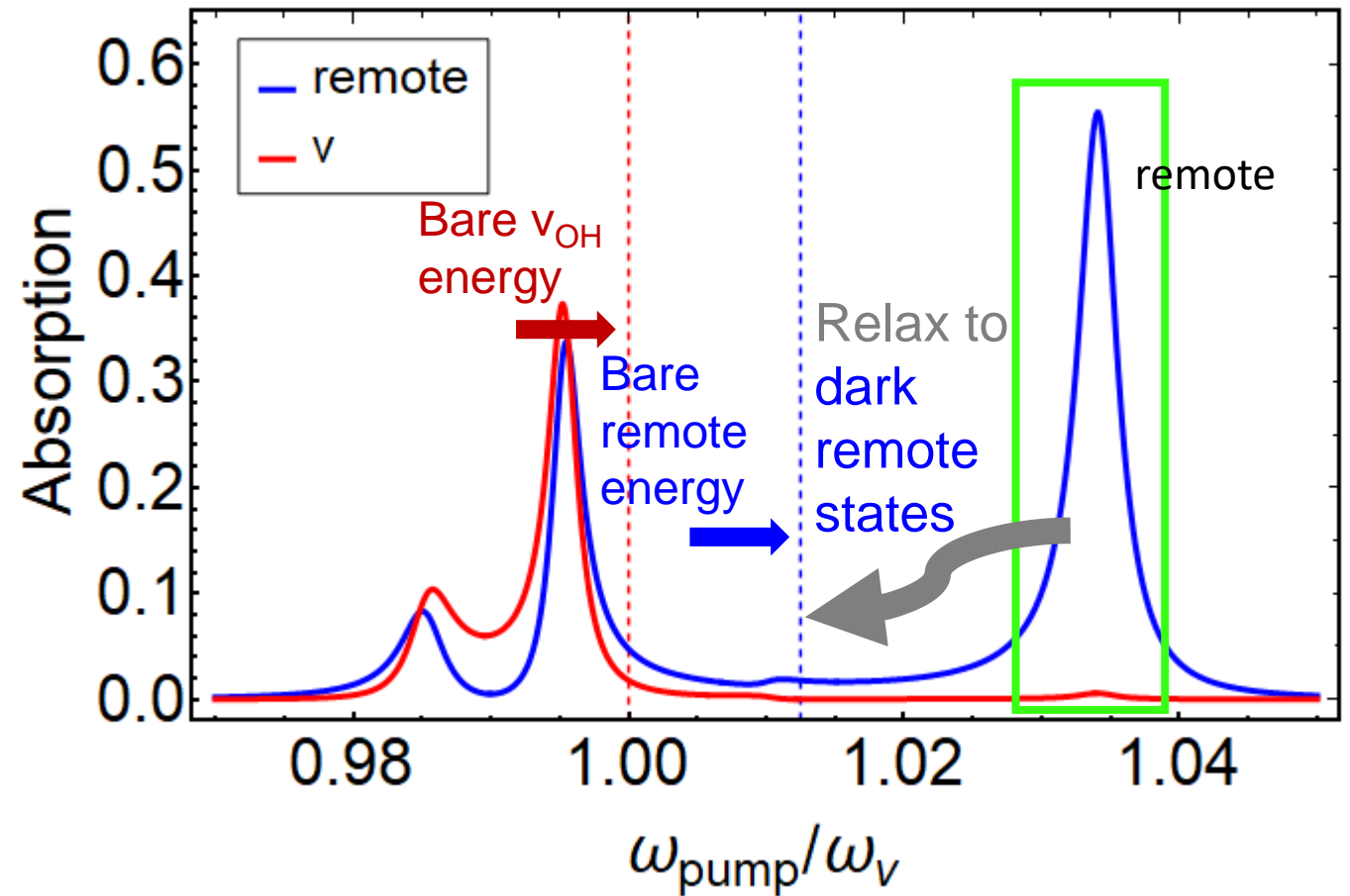


M. Du, R. F. Ribeiro, J. Yuen-Zhou, Chem 5, 5, 1167 (2019)

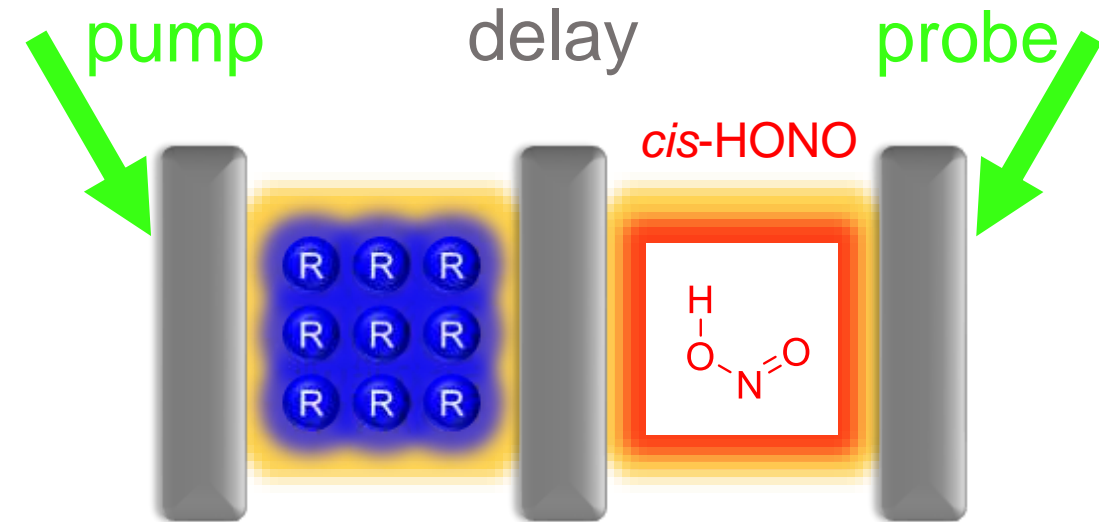
Pump tunes polariton energies on ultrafast timescale



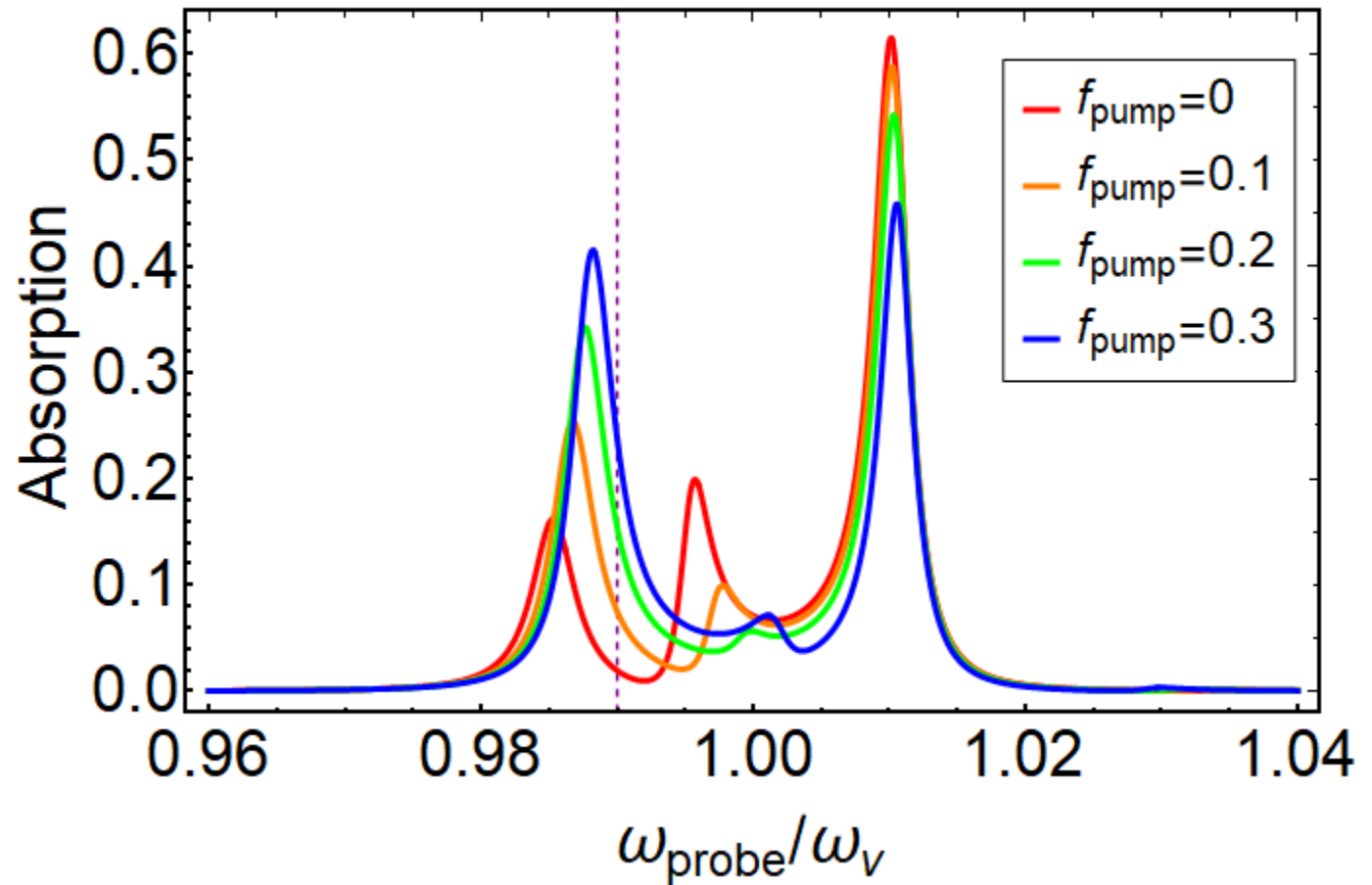
Linear absorption of pump



Pump tunes polariton energies on ultrafast timescale

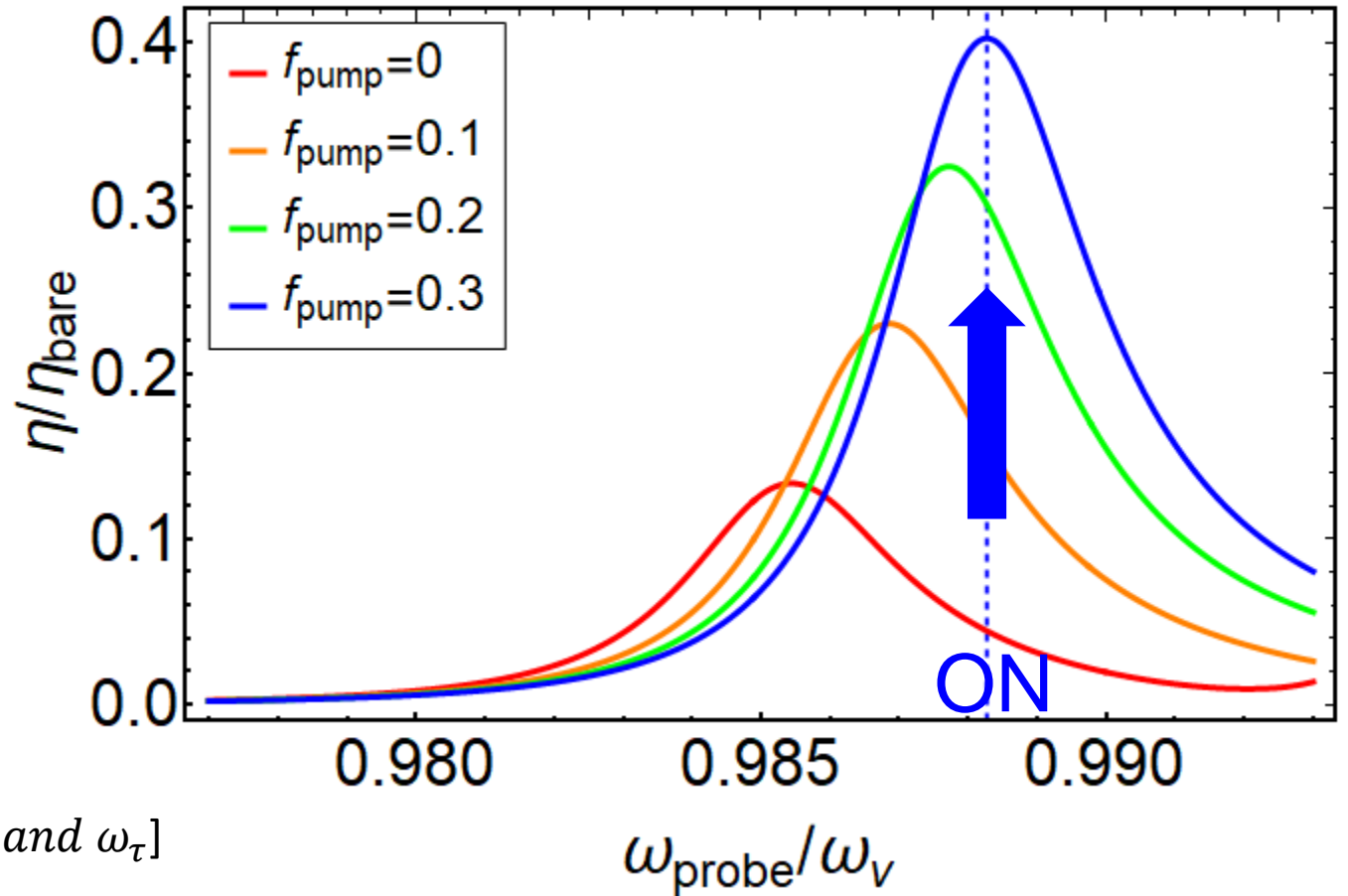
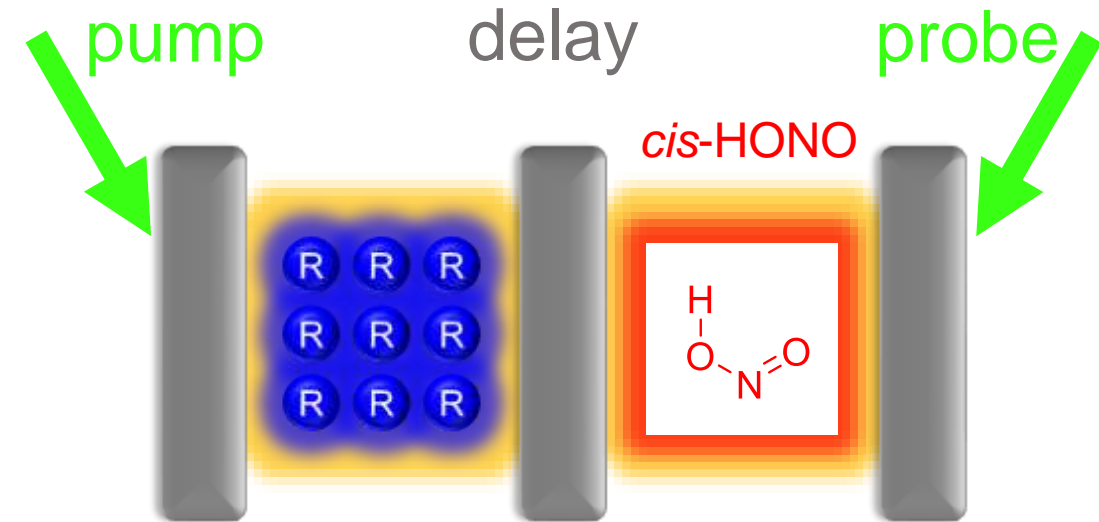


Nonlinear absorption of probe



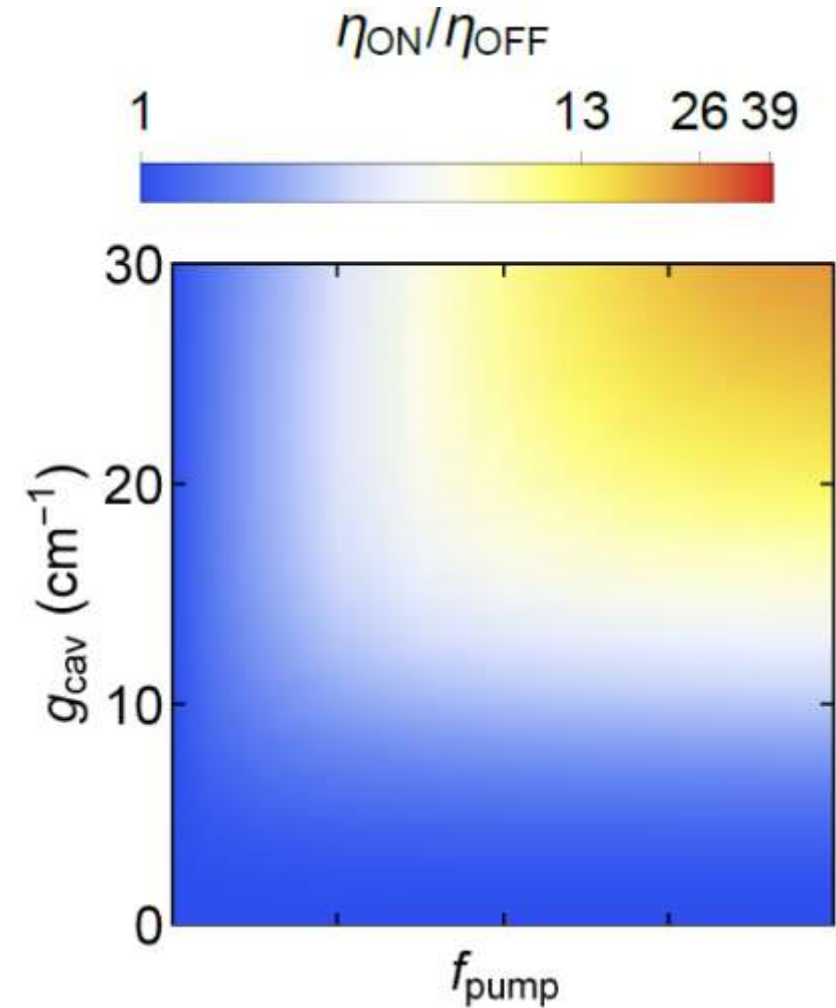
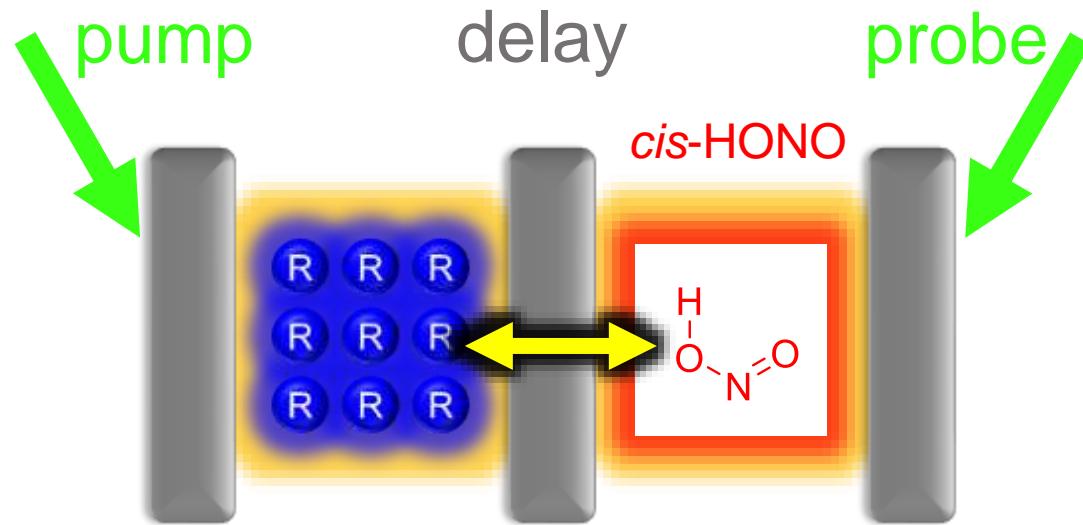
Pump turns ON reaction on ultrafast timescale

Nonlinear absorption of probe

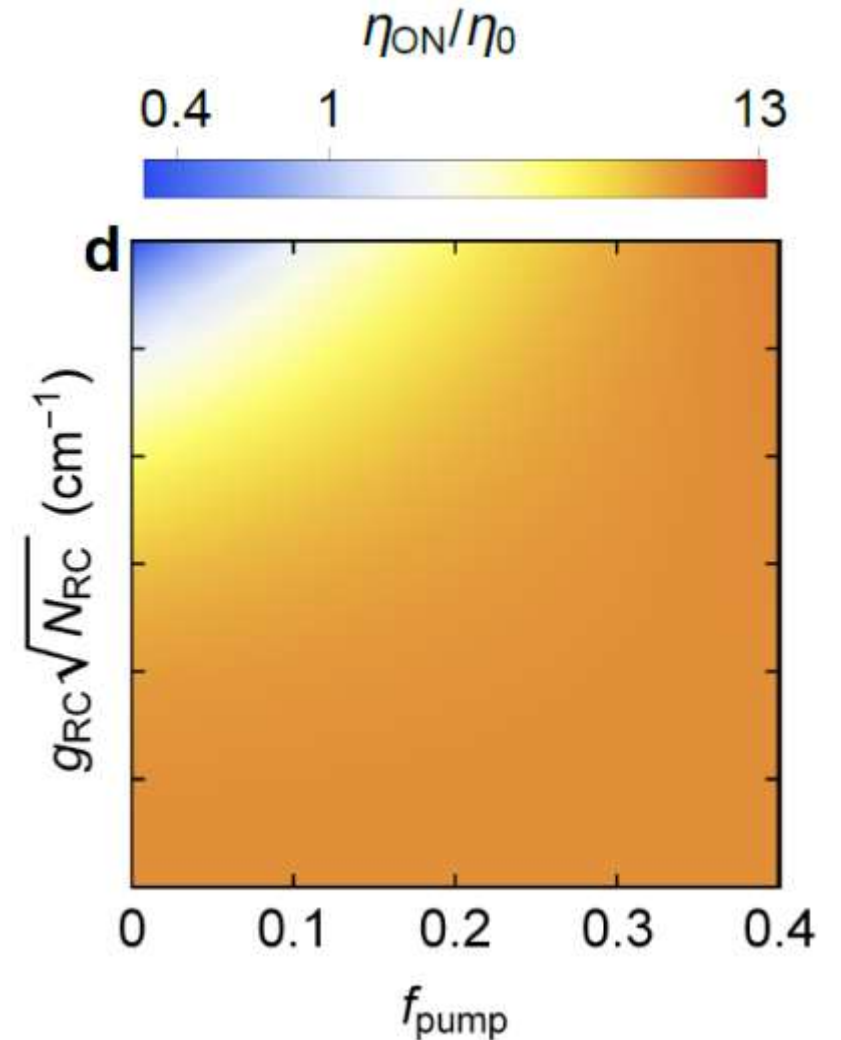
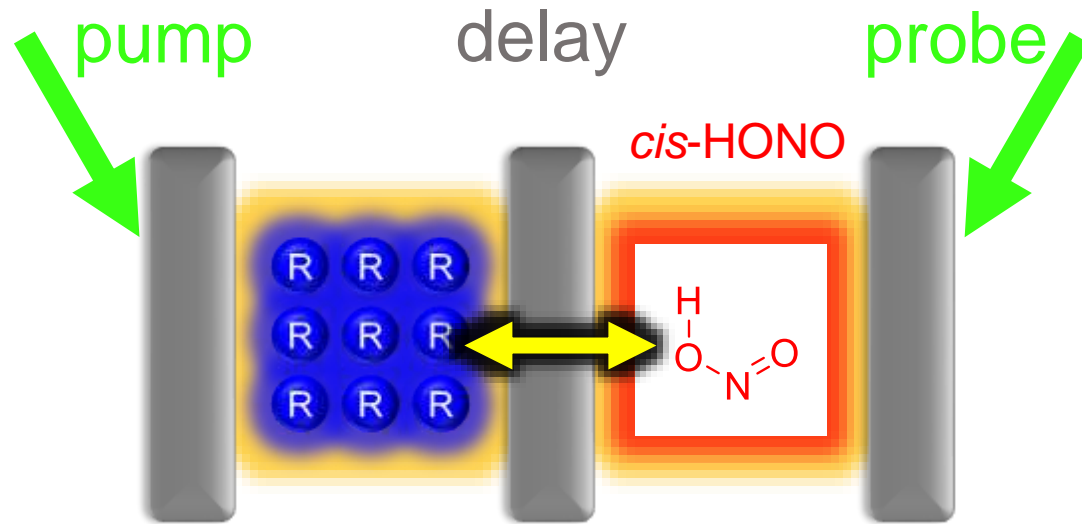


$$\begin{aligned}\eta(\omega) &= \text{Abs}_{\text{polariton}}(\omega) \times QY(\omega) \\ &= \text{Abs}_{\text{polariton}}(\omega) \times [\text{Overlap between } \omega \text{ and } \omega_{\tau}]\end{aligned}$$

Cavity-cavity coupling g_c increases REACTION ENHANCEMENT of pump



Cavity-cavity coupling g_c increases REACTION ENHANCEMENT of pump



From PARET to remote control of chemistry



Theory suggesting a catalyst never needs to touch its reactant breaks textbook principle

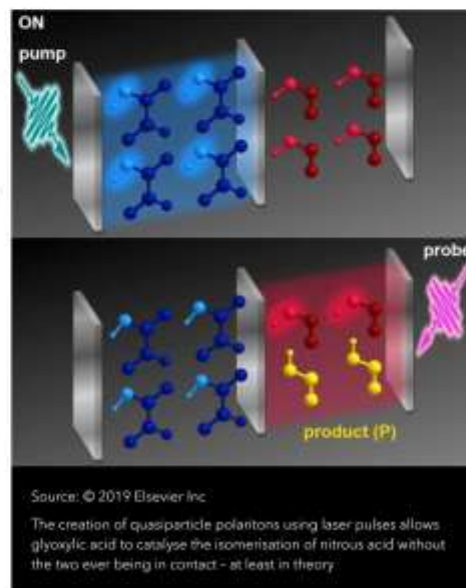


BY KATRINA KRÄMER | 1 APRIL 2019



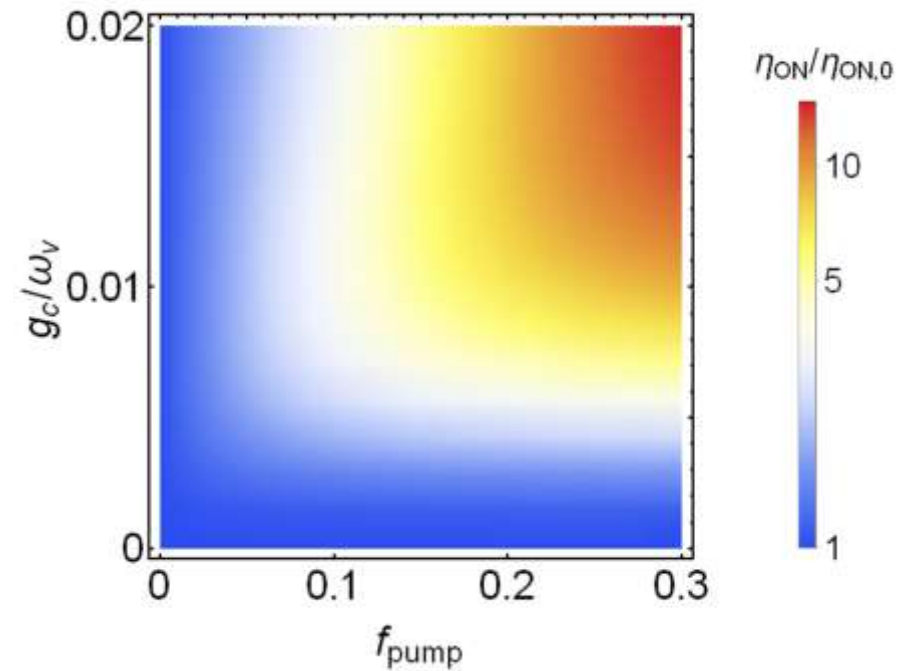
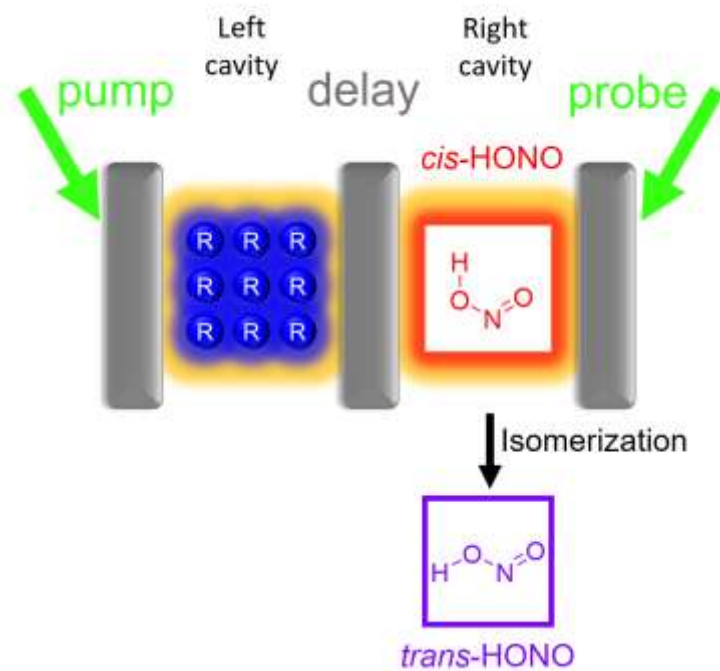
'We want to challenge the textbook paradigm that reactants and catalyst need to bind to each other to induce some chemical reactivity,' says Joel Yuen-Zhou from the University of California, San Diego, US. Yuen-Zhou's team has shown, at least in theory, that a catalyst trapped between two mirrors can control a reagent stack between two adjacent mirrors – without the two ever touching. The concept could allow chemists to break bonds that they can't access through other means.

What allows this to happen are optical microcavities. Mirrors set



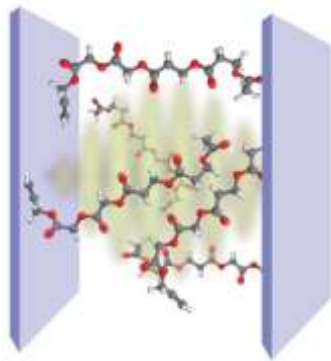
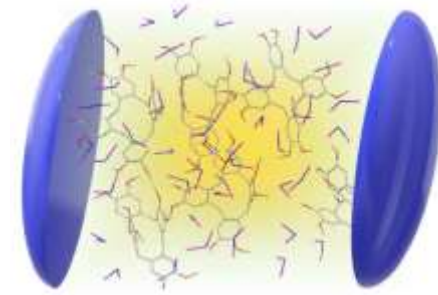
Summary #2

- ❖ Nonlinear ultrafast switching of polaritons should allow for remote control of a chemical reaction.
- ❖ Large tunability of efficiencies is expected for a simple IVR isomerization.



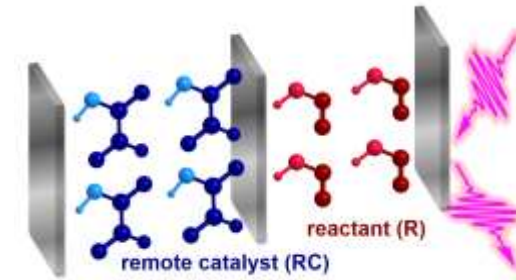
Outline of talk

Ground-state
reactivity



Vibrational
polaritons

Remote control



An outlook

Polariton chemistry: Thinking inside the (photon) box

Joel Yuen-Zhou^{a,1} and Vinod M. Menon^{b,1}

The study of single quantum objects embedded in confined electromagnetic environments is the main focus of the field of cavity quantum electrodynamics (CQED). According to a recent historical account by the 2012 Nobel laureate Sergei Haroche (1), the origins of this field can be traced back to the early days of quantum mechanics, with the famous debate between Albert Einstein and Niels Bohr concerning a gedankenexperiment about a photon in a box. While Einstein invoked the photon in a box as a theoretical construct, he might not have imagined that such a concept would reincarnate decades later into one of the favorite experimental playgrounds for scientists to test, explore, and control quantum mechanics. In fact, atoms in optical cavities have become one of the quintessential building blocks of contemporary quantum technologies, giving rise to high-fidelity sources of single photons, platforms to recreate effective photon–photon interactions, or even quantum simulators of many-particle systems. In recent years, an interdisciplinary outlook at the crossroads of CQED and chemistry termed “polariton chemistry” (2, 3) has emerged, which is centered around

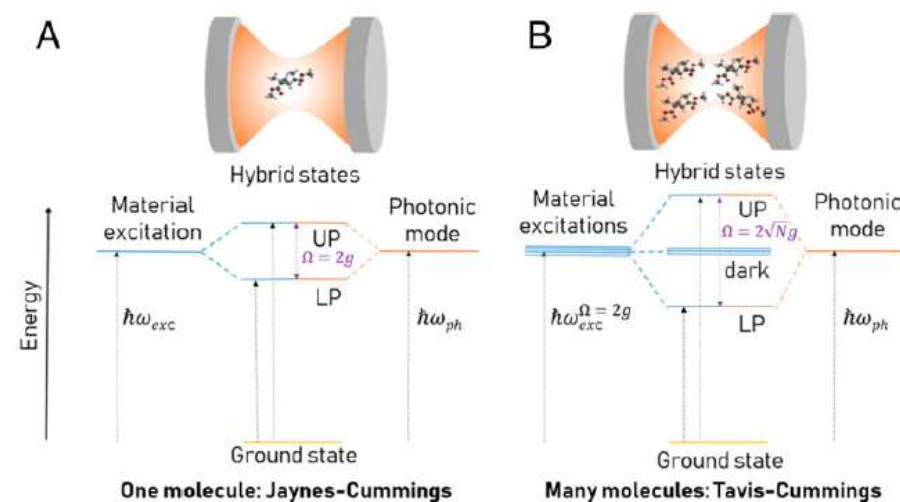
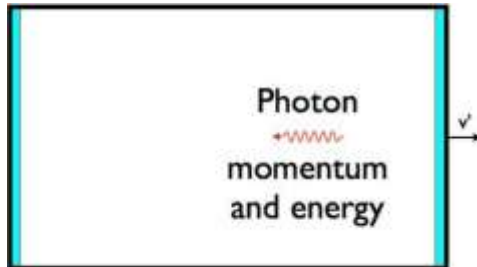


Fig. 1. (A and B) The various flavors of molecular strong coupling with a single molecule (A) and with $N > 1$ molecules (B). The energy spectrum is given by the JC model (A) and the TC model (B). At light–matter resonance ($\hbar\omega_{ph} = \hbar\omega_{exc}$), the UP and LP are half-light–half-matter states separated by a Rabi splitting Ω , which is twice the single-molecule light–matter coupling g for A, and twice the collective coupling $\sqrt{N}g$ for B. The superradiant enhancement of the coupling in B comes at the price of having $N - 1$ dark states parked at the material excitation energy. $N > 10^7$ is a macroscopic number in typical experiments and serves as a very efficient relaxation trap for both UP and LP.

Is cavity QED ready for chemistry?

Einstein-Bohr debates



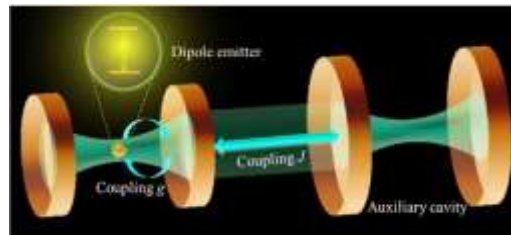
1920s

Cavity QED



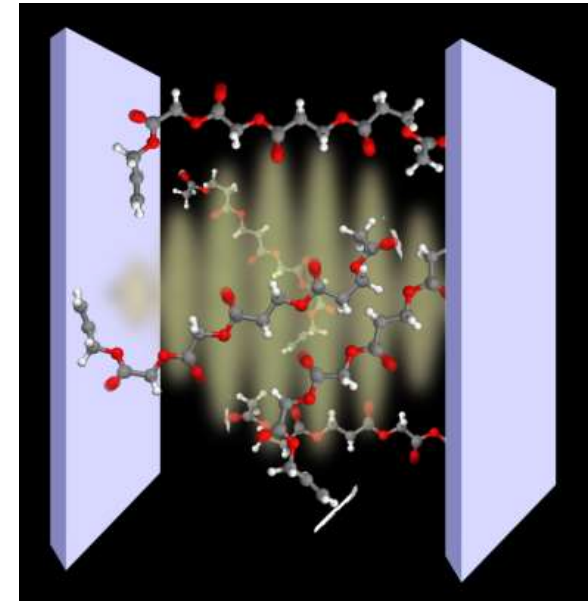
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1960s

Polariton chemistry

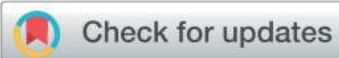


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Polariton chemistry: controlling molecular dynamics with optical cavities

Raphael F. Ribeiro,  Luis A. Martínez-Martínez,  Matthew Du, Jorge Campos-Gonzalez-Angulo  and Joel Yuen-Zhou*

Molecular polaritons are the optical excitations which emerge when molecular transitions interact strongly with confined electromagnetic fields. Increasing interest in the hybrid molecular-photonic materials that host these excitations stems from recent observations of their novel and tunable chemistry. Some of the remarkable functionalities exhibited by polaritons include the ability to induce long-range excitation energy transfer, enhance charge conductivity, and inhibit or accelerate chemical reactions. In this review, we explain the effective theories of molecular polaritons which form a basis for the interpretation and guidance of experiments at the strong coupling limit. The theoretical discussion is illustrated with the analysis of innovative applications of strongly coupled molecular-photonic systems to chemical phenomena of fundamental importance to future technologies.

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