Vibrational polariton chemistry

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Department of Chemistry and Biochemistry

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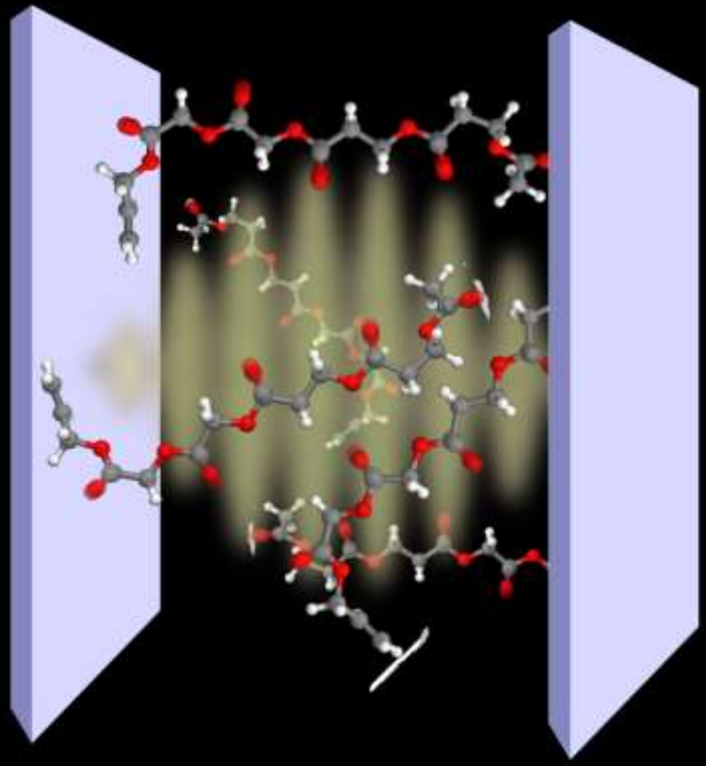
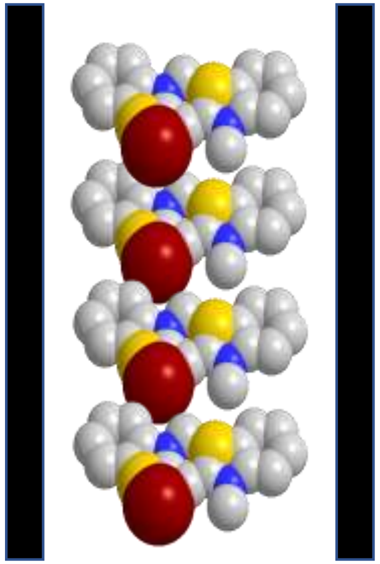
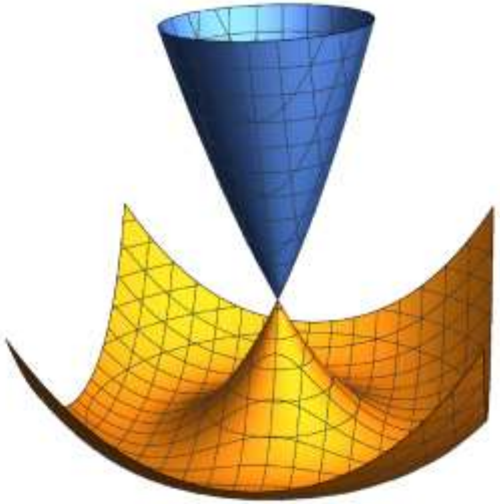


Molecular polaritonics, Madrid, July 2019

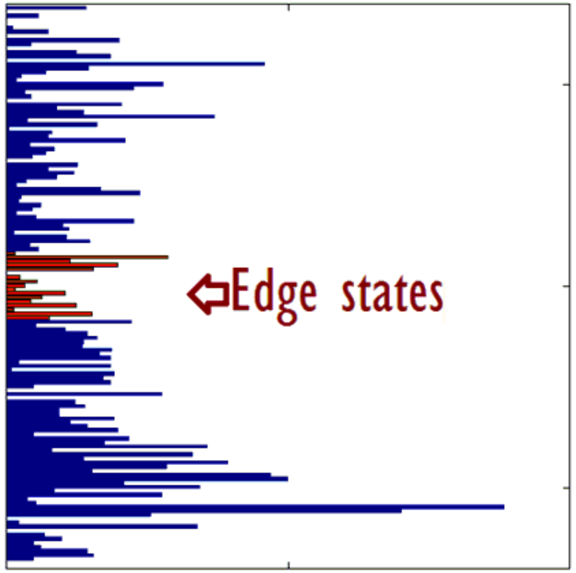
Research on theoretical molecular photonics



Quantum optics



Physical/theoretical chemistry



Condensed matter

The group and the campus

December 2018

UC San Diego

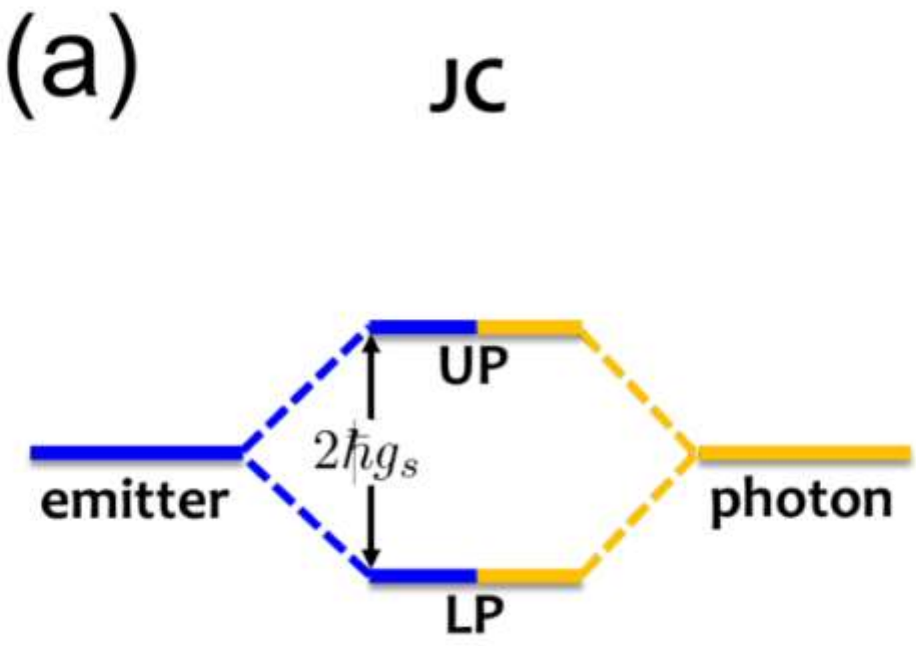
The group

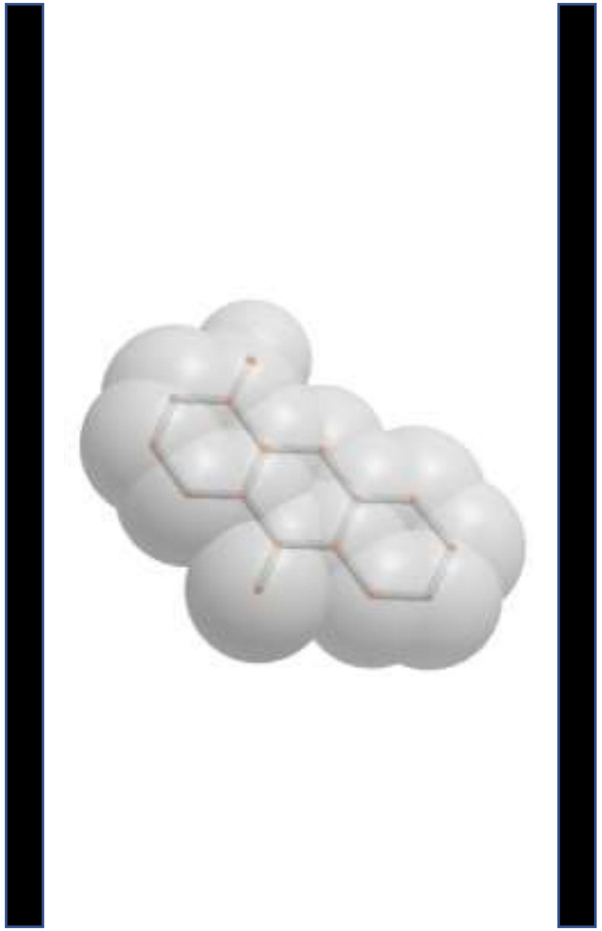
Group photo, UCSD December 2018

Jorge and Matt,
COMICON July 2018

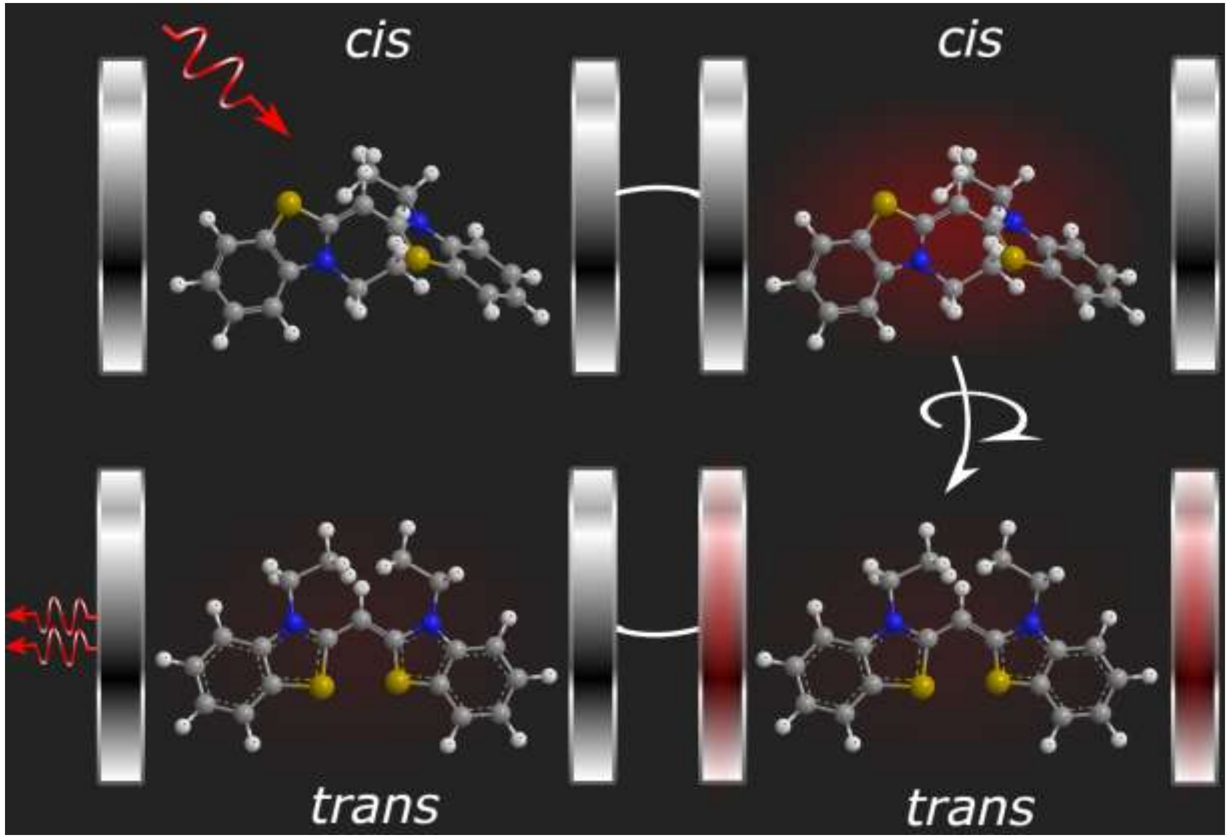
Introduction

One molecule in a cavity: Jaynes-Cummings

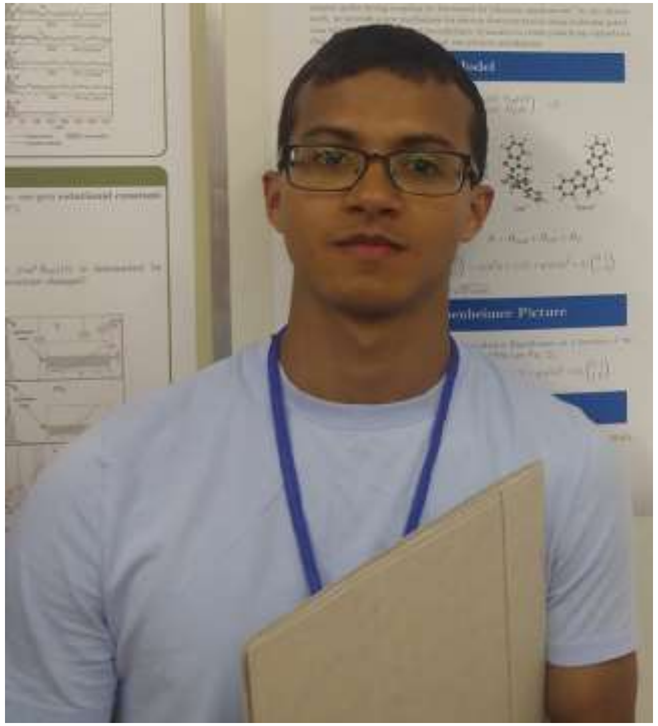




One molecule in a cavity: Jaynes-Cummings

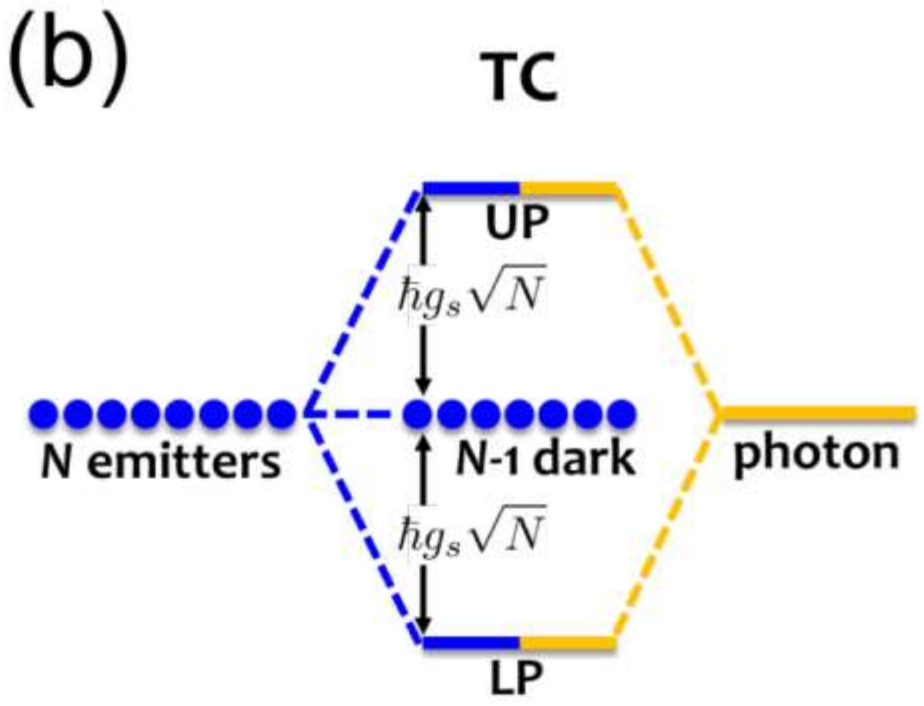


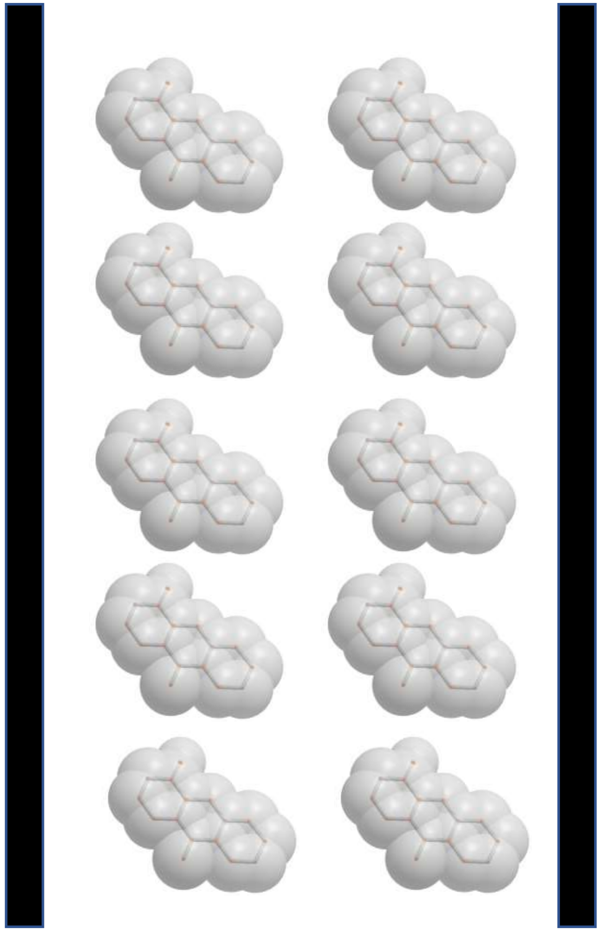
POSTER: Polariton-assisted photon downconversion



Juan Bernardo Pérez-Sánchez

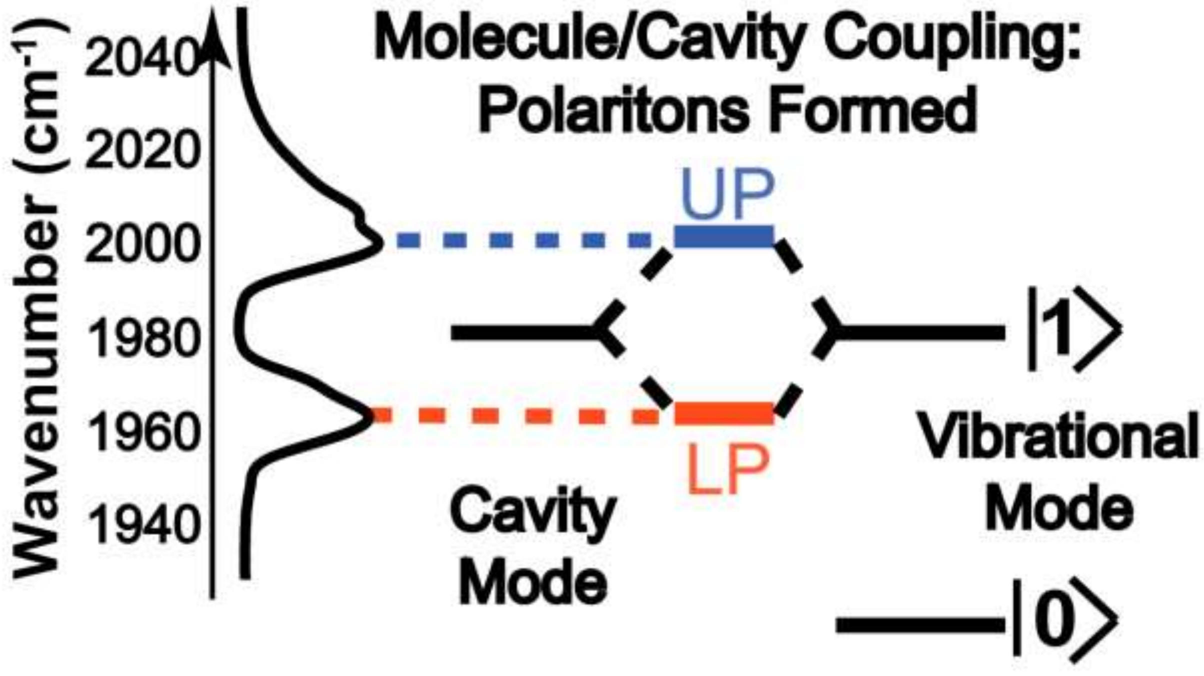
Many molecules in a cavity: Tavis-Cummings

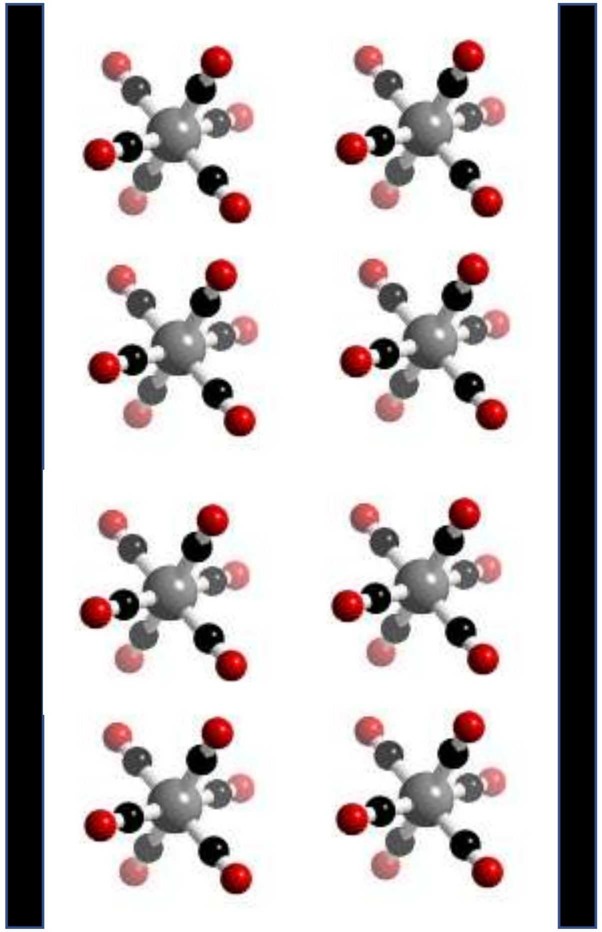




Rabi splitting $\Omega = 2\sqrt{N}\hbar g_s$ where $N = 10^6 - 10^{10}$

Many molecules in a cavity: Tavis-Cummings



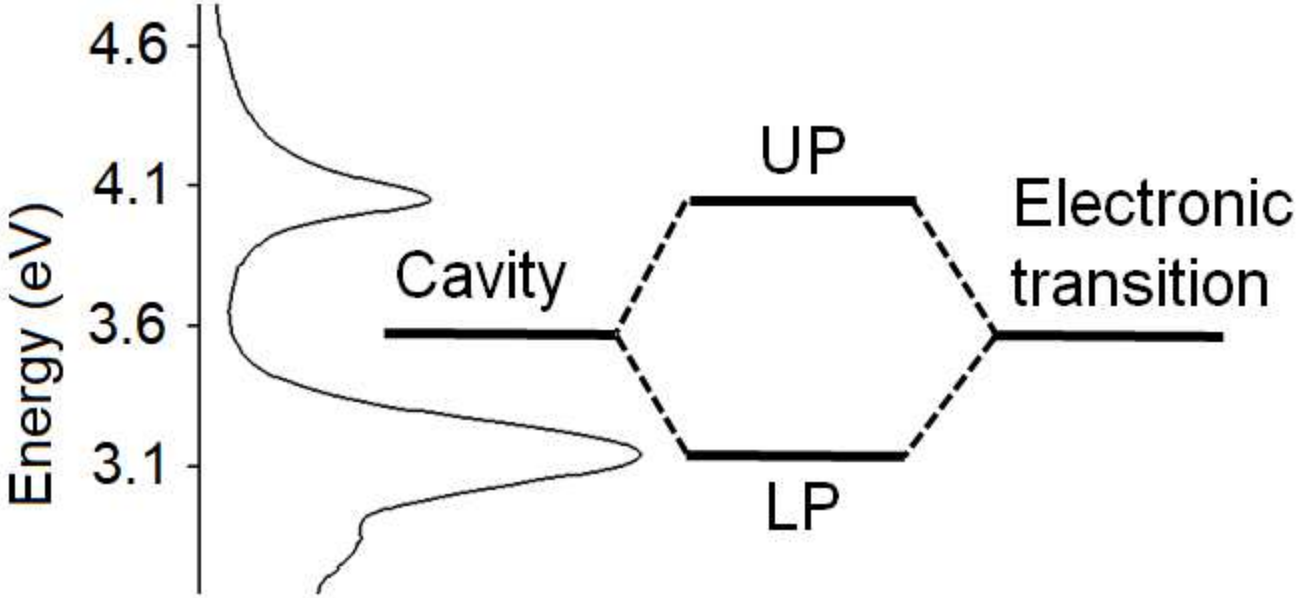


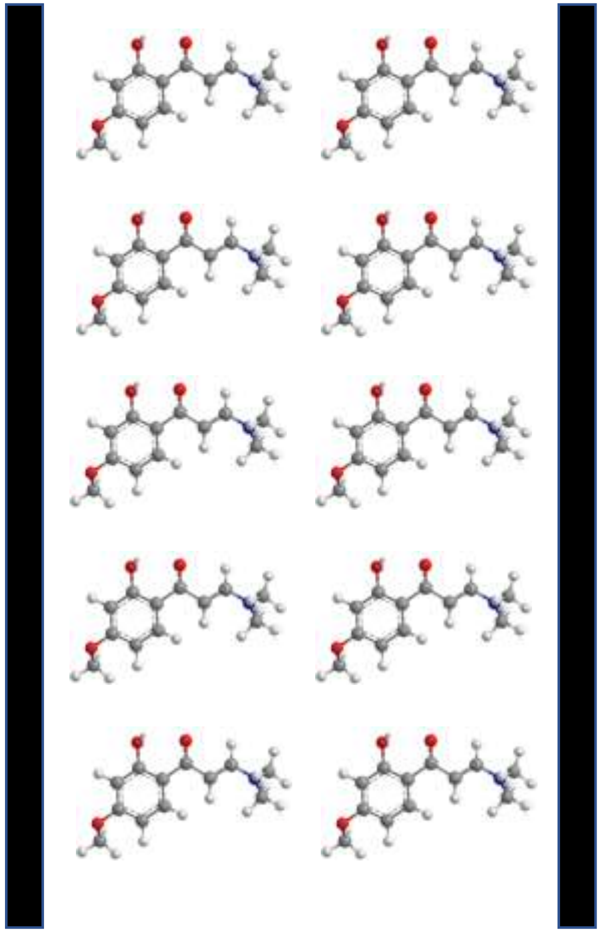
B. Xiang, R. F. Ribeiro, A. D. Dunkelberger, J. C. Owrutsky, B. S. Simpkins, J. Yuen-Zhou, and W. Xiong, PNAS 115, 19 (2018).

$W(CO)_6$

$\omega_{10} = 1983\ cm^{-1}$

Many molecules in a cavity: Tavis-Cummings



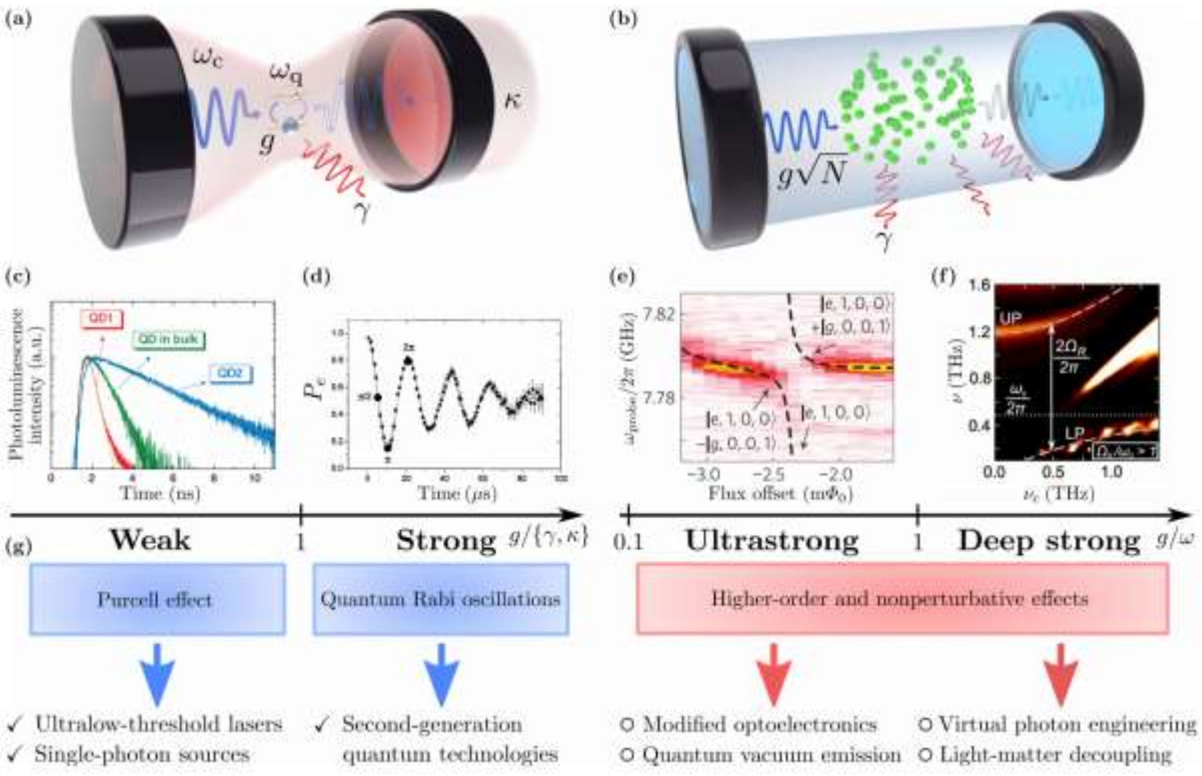


HMPP

$\omega_{10} = 3.6\ eV$

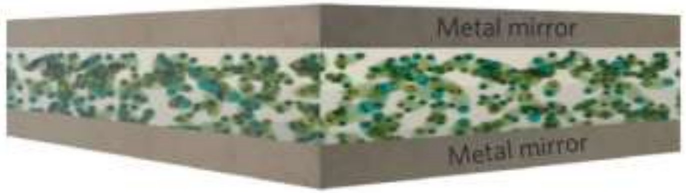
D.P. Kizhmuri, R. Desmukh, L. Martínez, J. Yuen-Zhou, E. Hohenstein, G. John, V. Menon, *in preparation.*

The various regimes of light-matter coupling



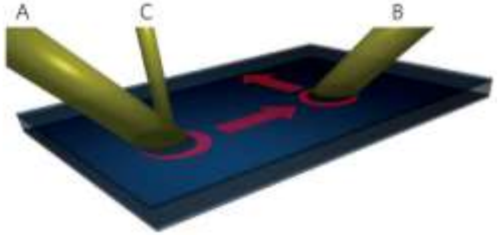
Kockum, Anton Frisk, et al. "Ultrastrong coupling between light and matter." *Nature Reviews Physics* 1.1 (2019): 19.

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.
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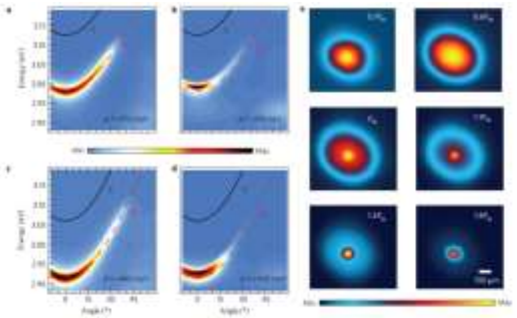

Polariton chemistry

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T.W. Ebbesen, Acc. Chem. Res. 49(11):2403-12;
D.M. Coles, Nat. Mater. 13.7 (2014): 712;
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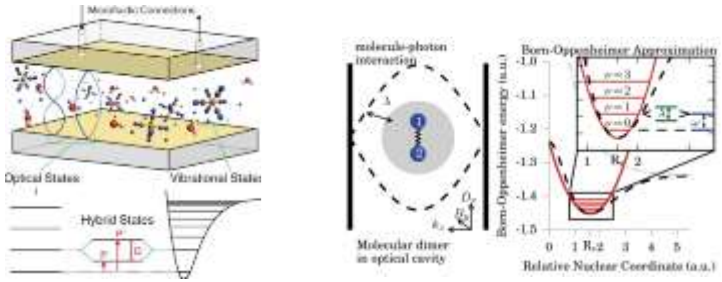
J. Galego, et al, PRX 5.4 (2015) 041022;
F. Herrera and F. Spano, PRL 116 23 (2016).
M. Kowalewski, K. Bennett, and S. Mukamel, J. Phys. Chem. Lett. 7 11 (2016) 2050-2054.



Chem. Sci., 9, 6325-6339 (2018)

Chemical Science

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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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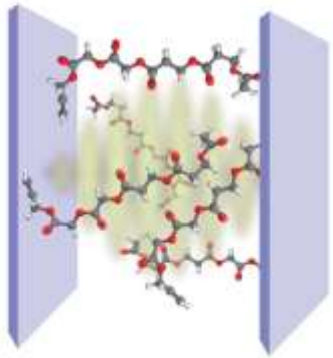
DOI: 10.1039/c8sc01043a

rsc.li/chemical-science

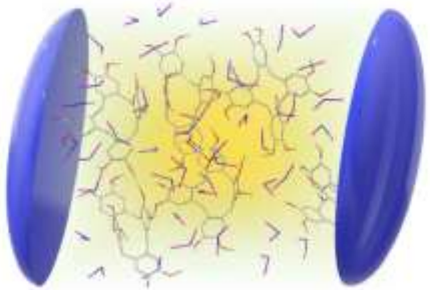
See also reviews by Ebbesen, Feist, Shegai, Narang

Outline of talk

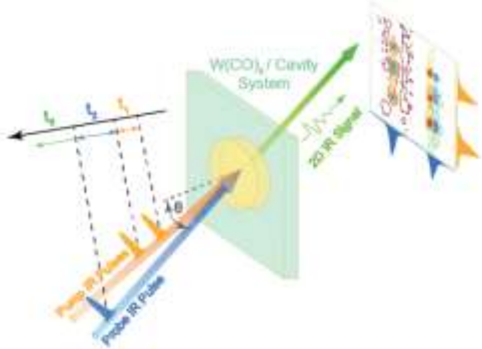


Vibrational polaritons

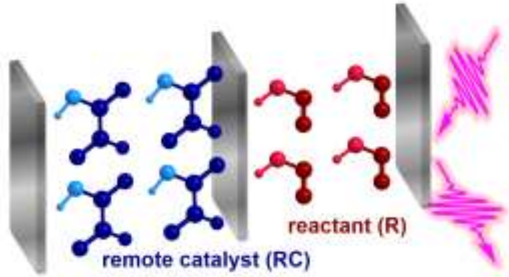
Ground-state reactivity



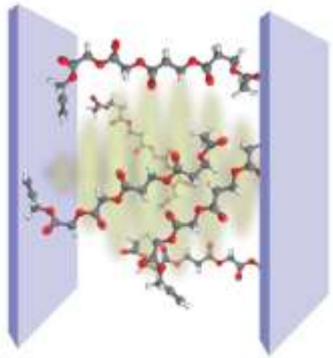
Nonlinearities



Remote control

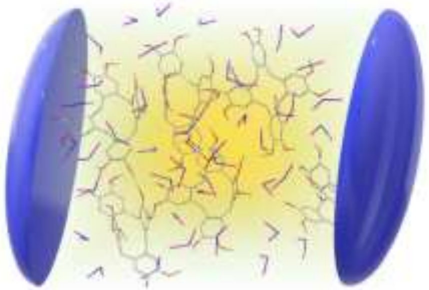


Outline of talk

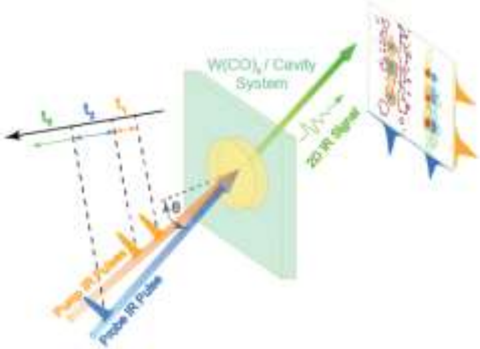


Vibrational polaritons

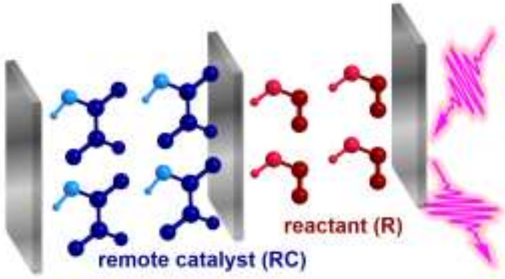
Ground-state reactivity



Nonlinearities



Remote control



Polariton chemistry in the dark?

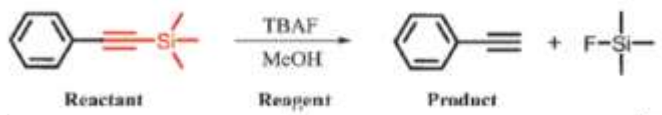
GDCh Communications Angewandte Chemie International Edition

Kinetics Hot Paper

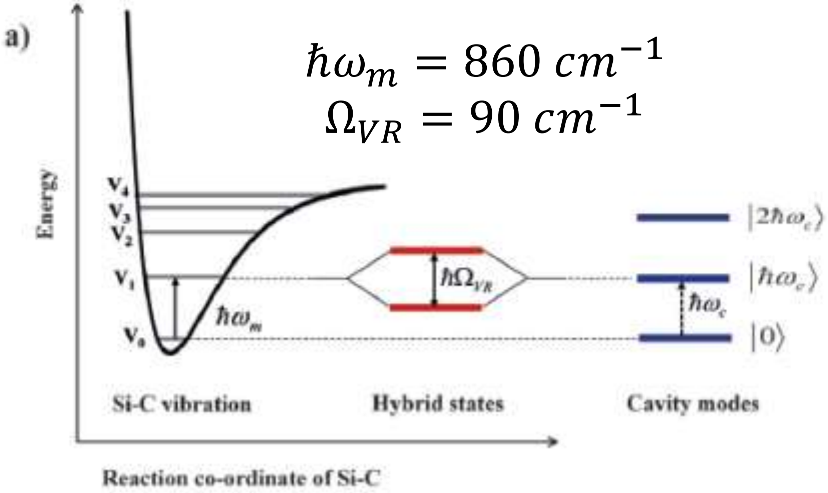
International Edition: DOI: 10.1002/anie.201605504
German Edition: DOI: 10.1002/ange.201605504

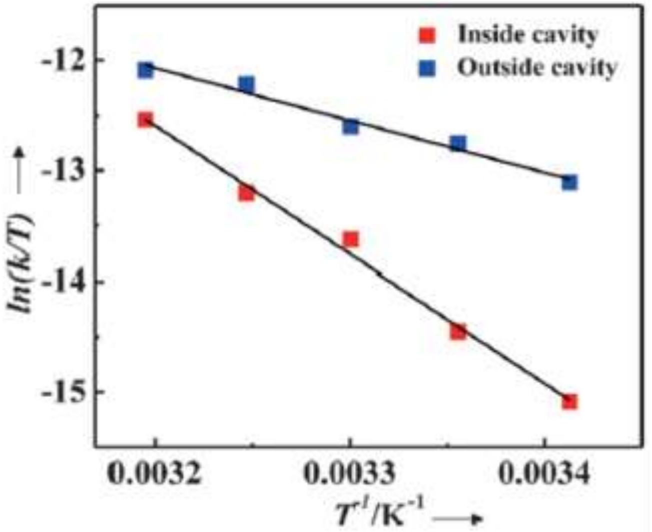
Ground-State Chemical Reactivity under Vibrational Coupling to the Vacuum Electromagnetic Field

*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**

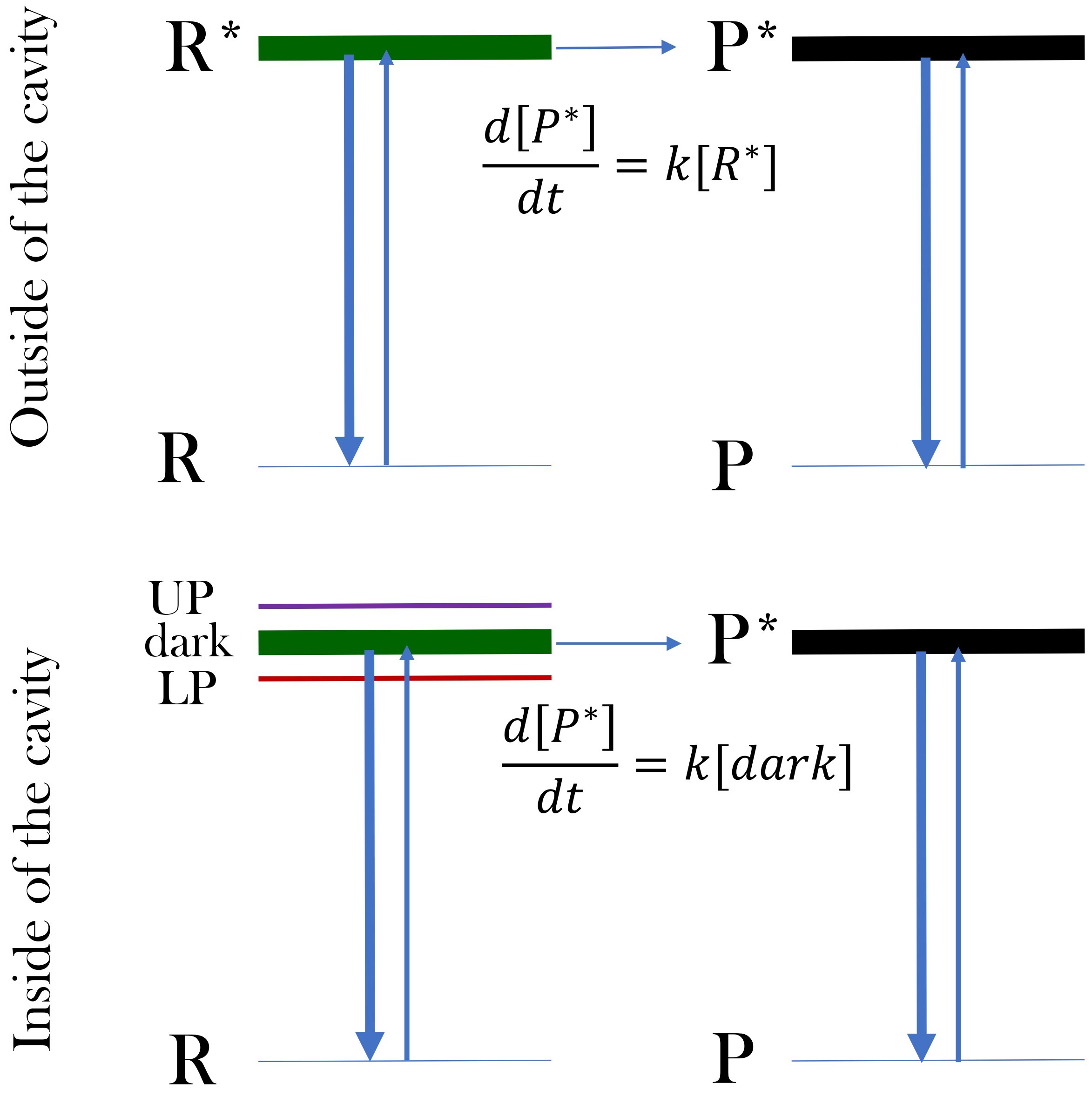


$$\hbar\omega_m = 860\ cm^{-1}$$
$$\Omega_{VR} = 90\ cm^{-1}$$





Polariton chemistry in the dark? Our thoughts a year ago



(Koreatown - LA, February 2018)

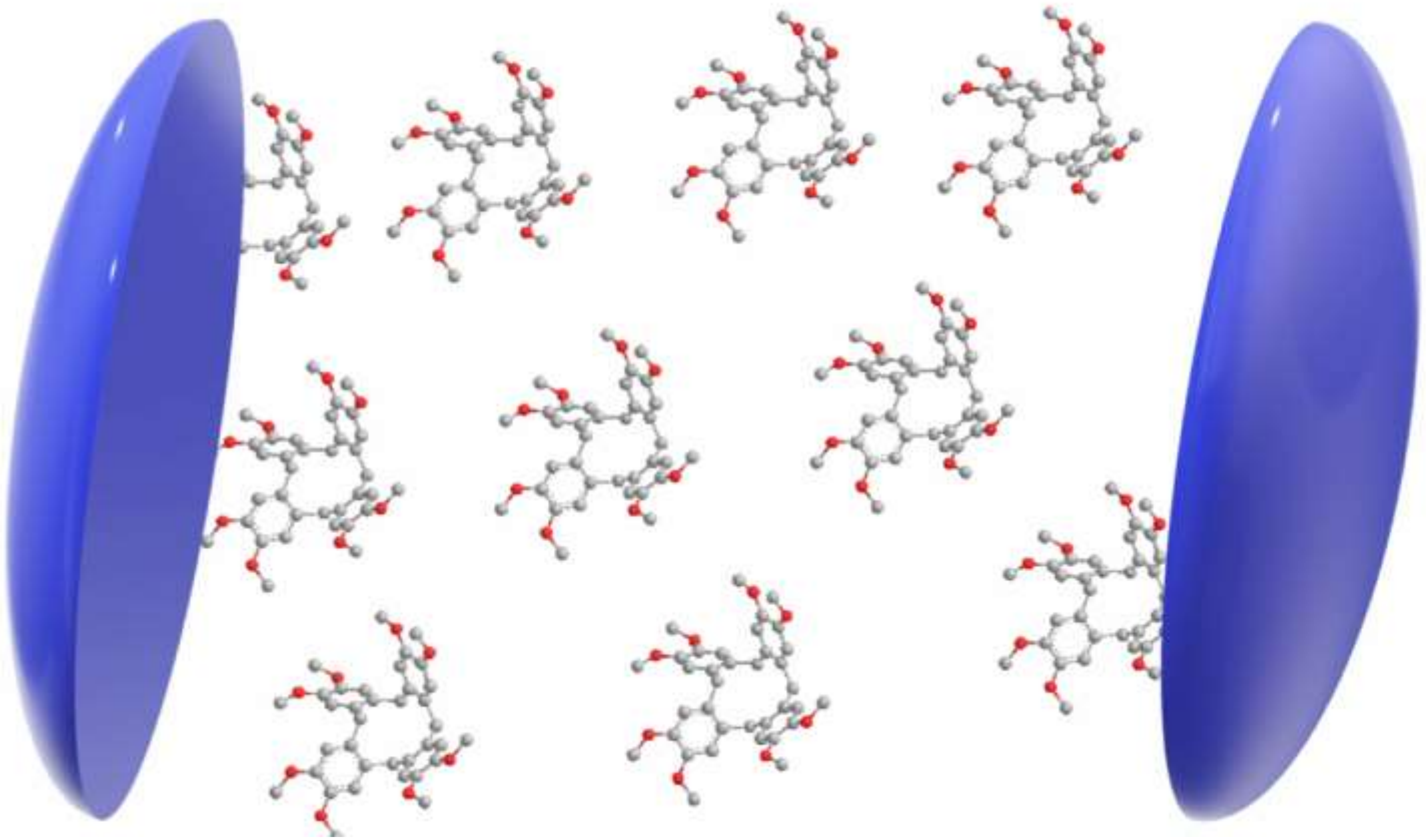
$\frac{[dark]}{[LP]} = 10^{10}$ at 298 K $\Rightarrow [R^*] \approx [dark]$.

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.



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

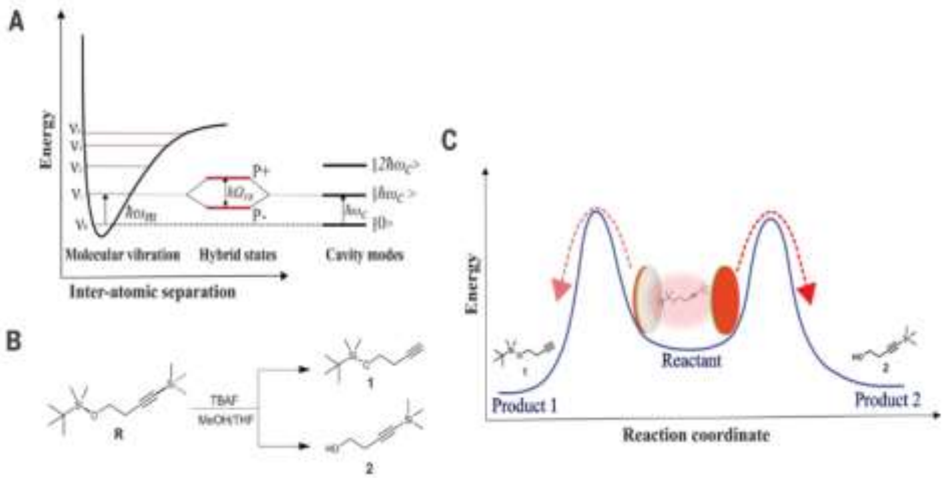
Polariton chemistry in the dark? Our present thoughts

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. Nagarajan[1], R. M. A. Vergauwe[1], J. George[1†], T. Chervy[1‡], A. Shalabney[2], E. Devaux[1], C. Genet[1], J. Moran[1§], T. W. Ebbesen[1§]



ACS central science FIRST REACTIONS

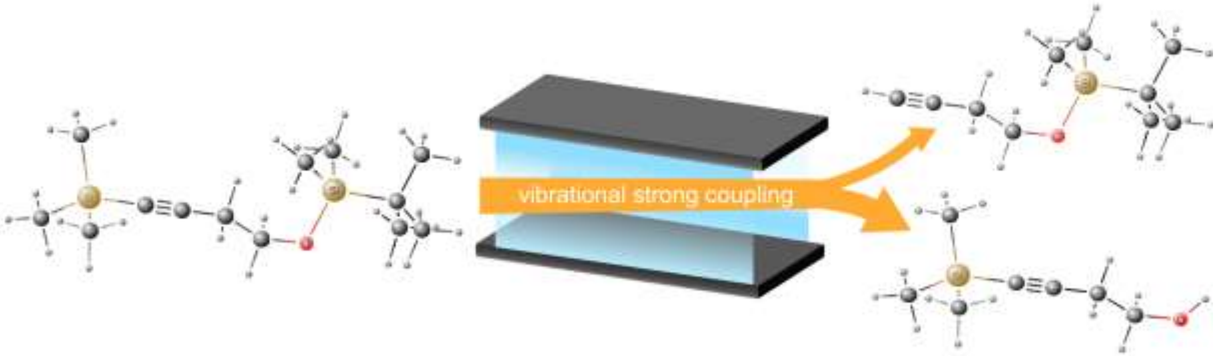
Polariton Chemistry: Action in the Dark

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

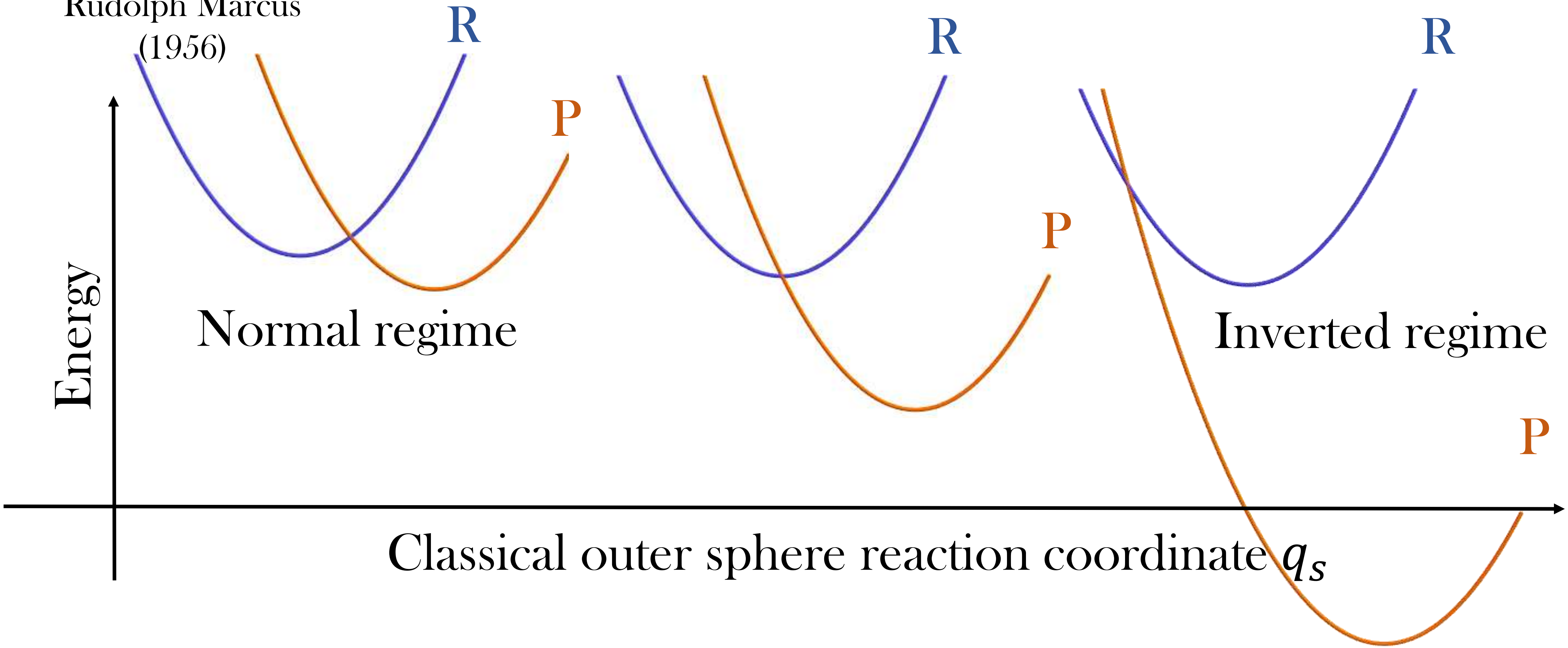
The findings of Ebbesen, Moran, and co-workers could revive the mode-selective chemistry program within the contemporary context of molecules in optical cavities or "polariton chemistry".



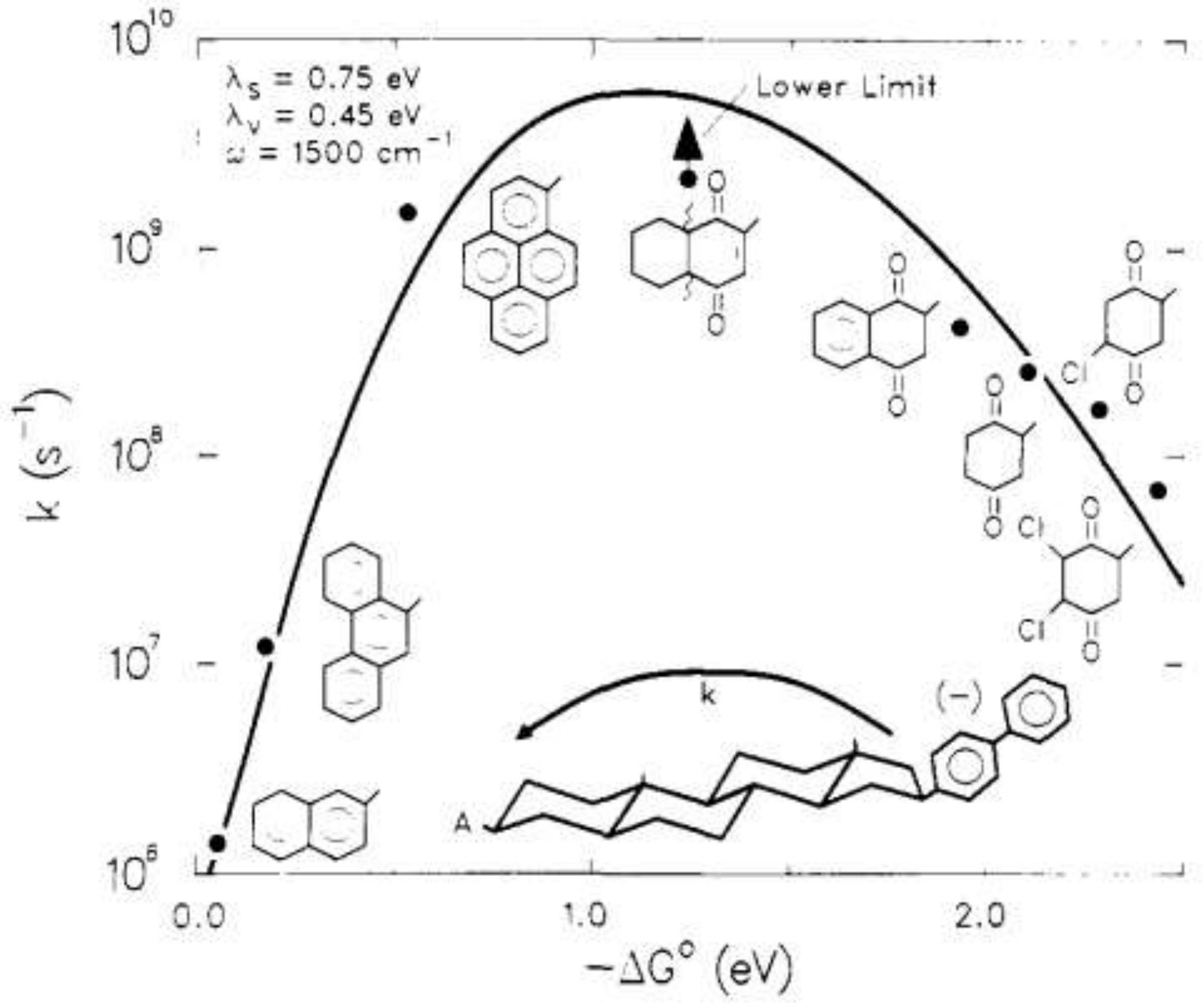
Background: Marcus theory

Rudolph Marcus (1956)

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



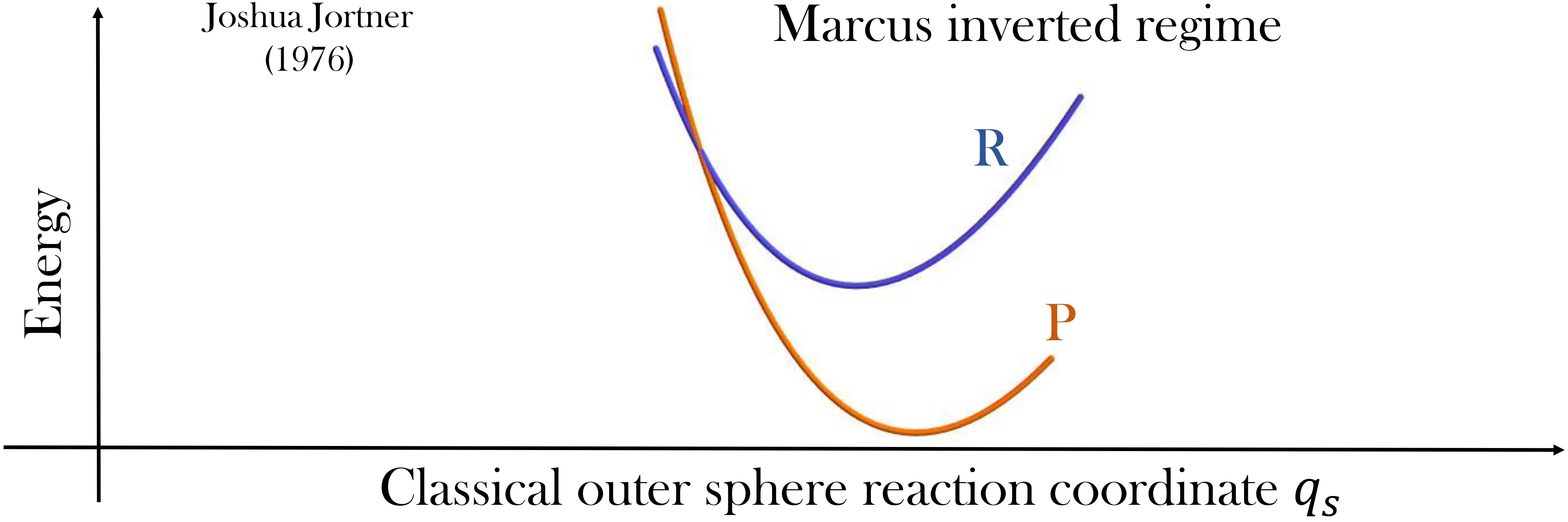
Background: Marcus theory



Gerhard Closs
(1984)

Background: Marcus theory - a caveat due to Jortner

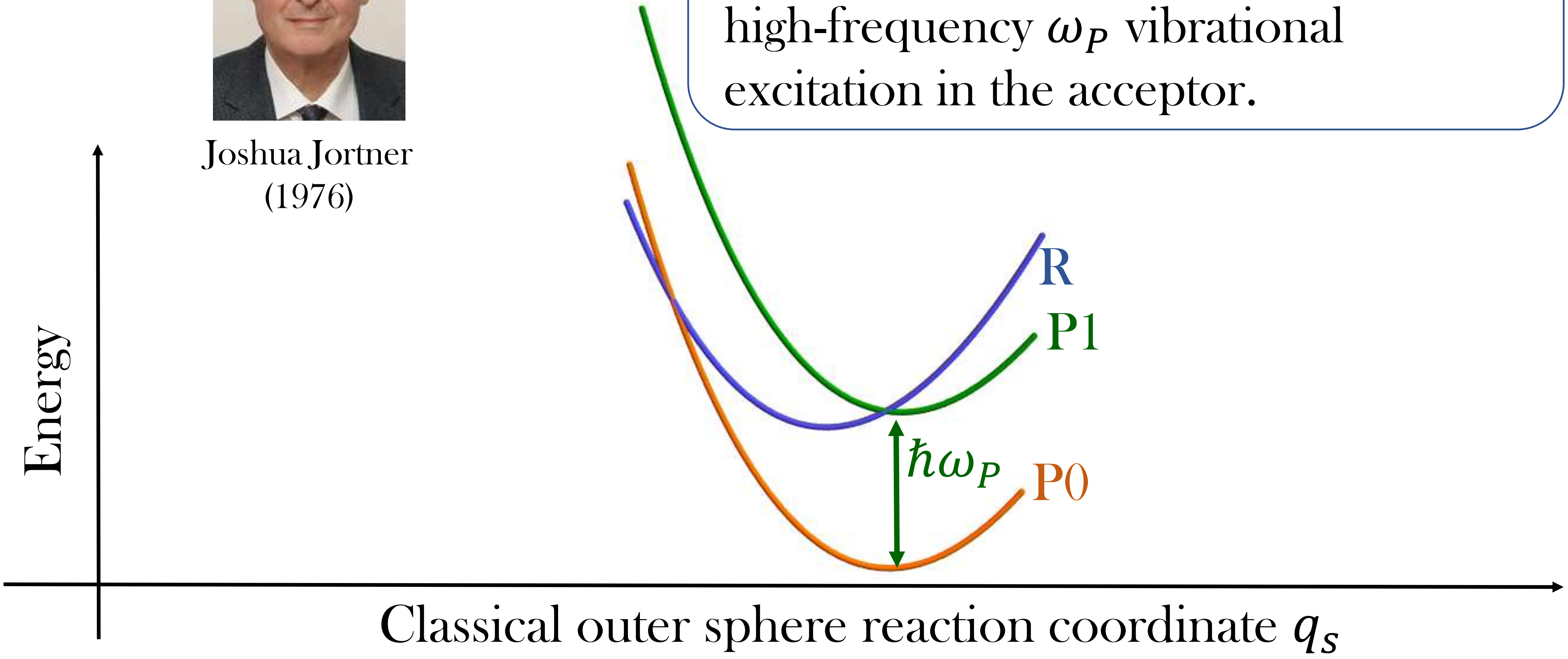
Joshua Jortner
(1976)



Background: Marcus theory - a caveat due to Jortner

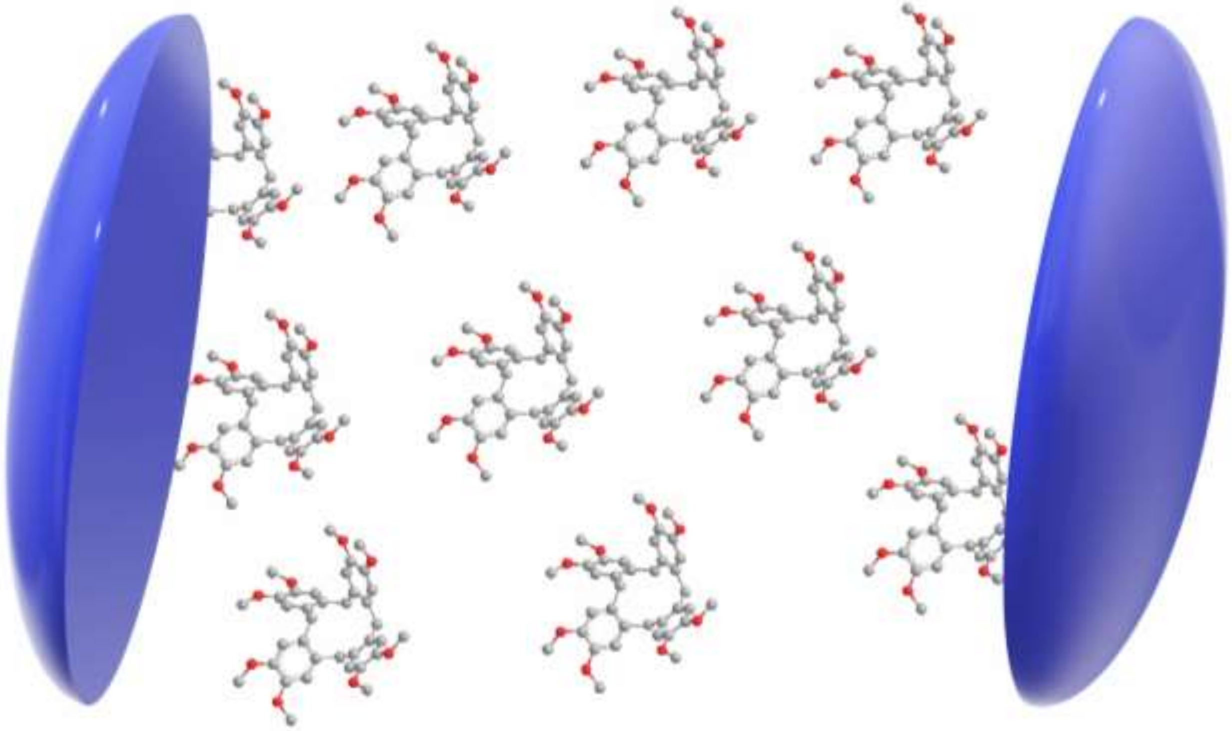
Joshua Jortner
(1976)

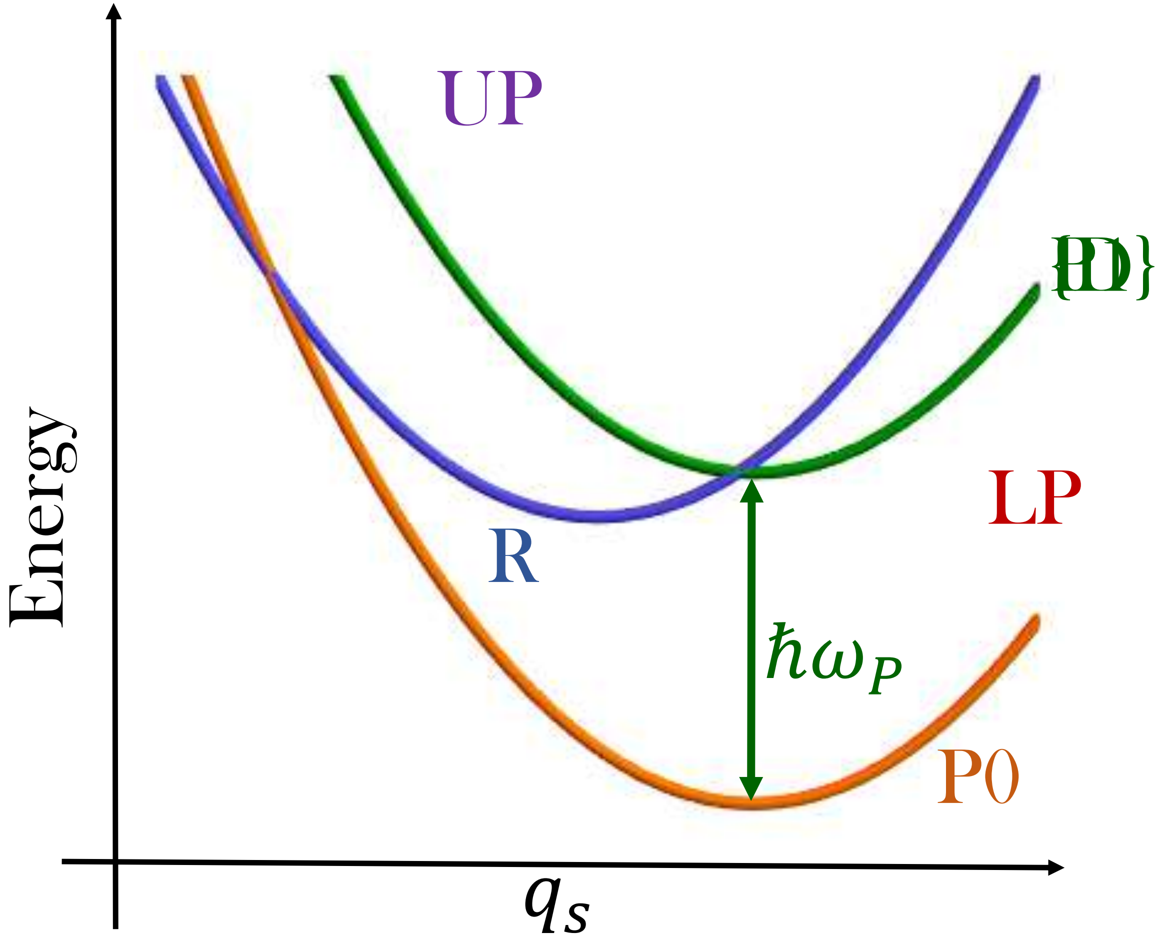
A slow rate in the Marcus inverted regime can be accelerated by creating a high-frequency ω_P vibrational excitation in the acceptor.



Catalysis of Marcus-Jortner ET with an IR cavity

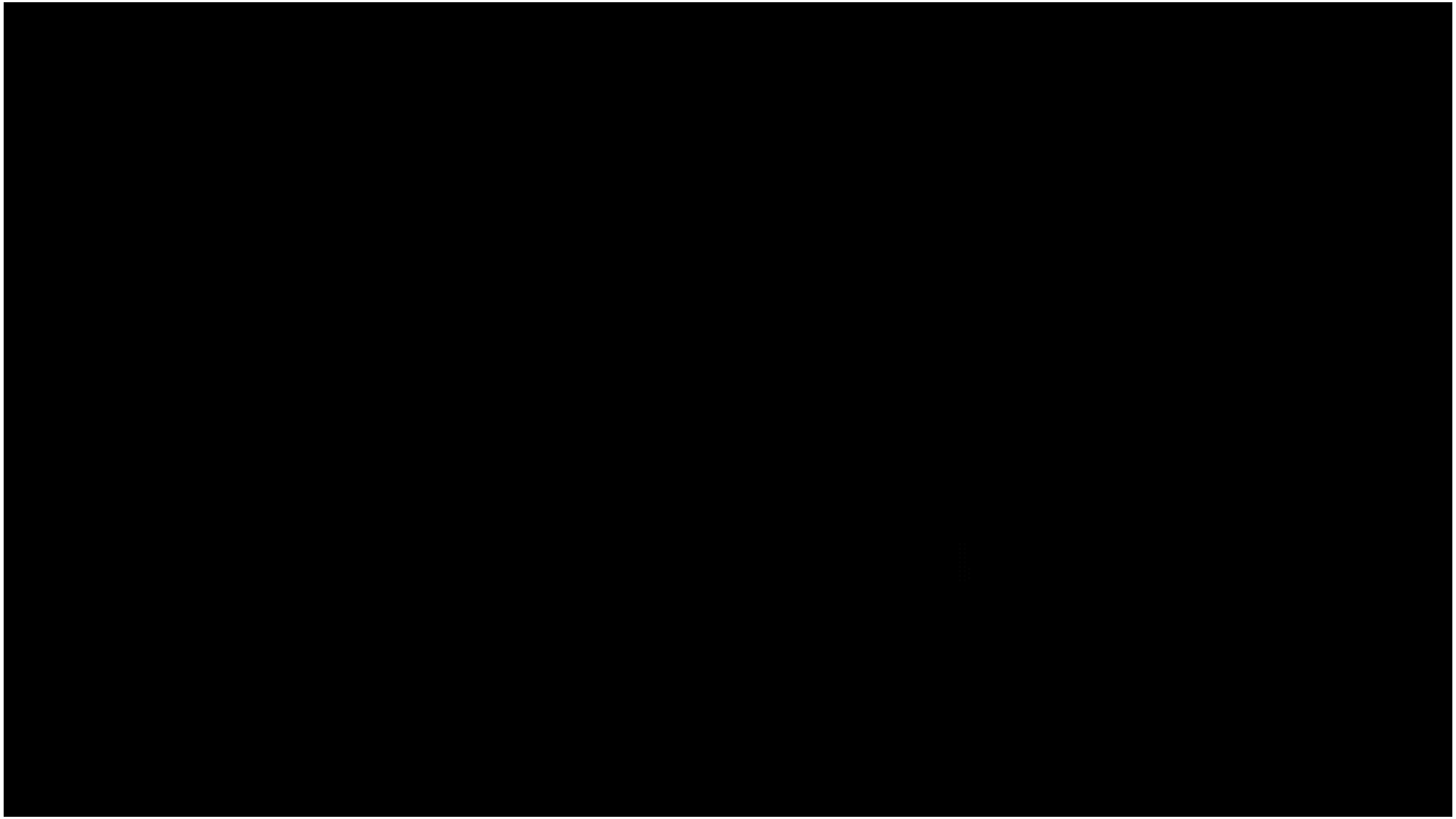
Let cavity couple to the high-frequency modes of molecules undergoing ET. Place $M = 10^{10}$ reactants in cavity. As rxn proceeds from R to P, coupling to light becomes stronger!





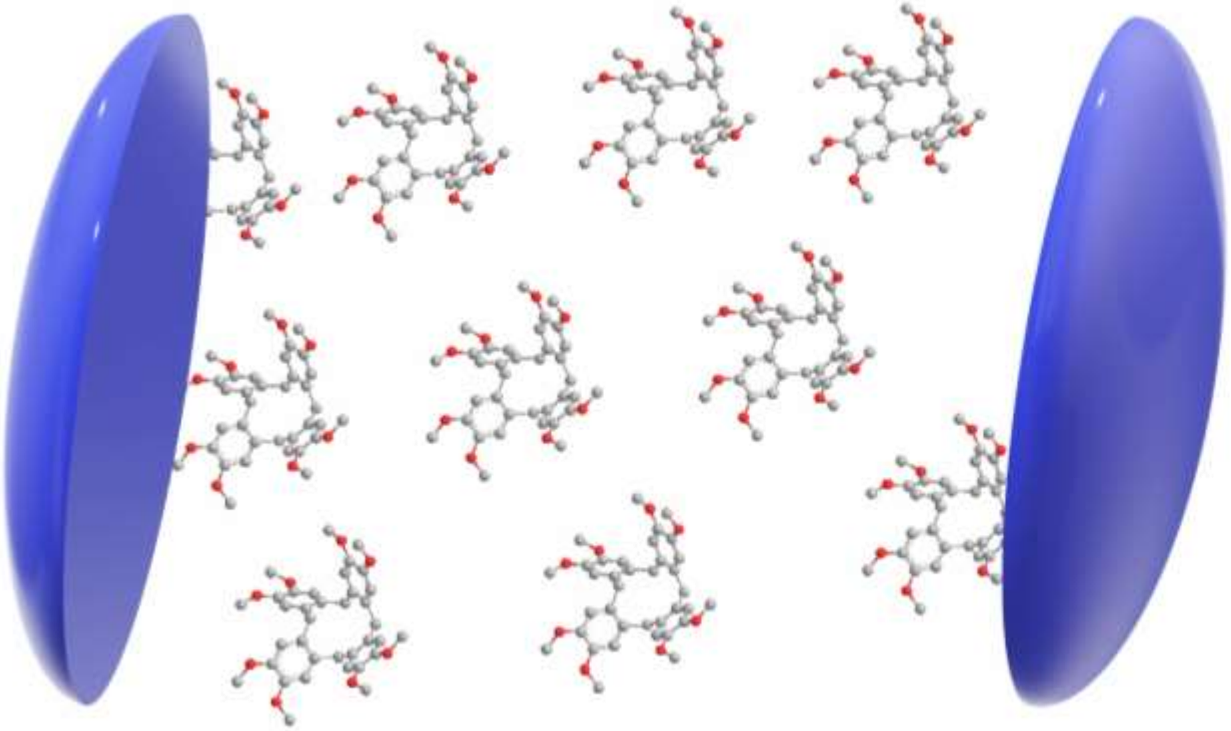
J. Campos-González-Angulo, R.F. Ribeiro, J. Yuen-Zhou, arXiV:1902.10264.

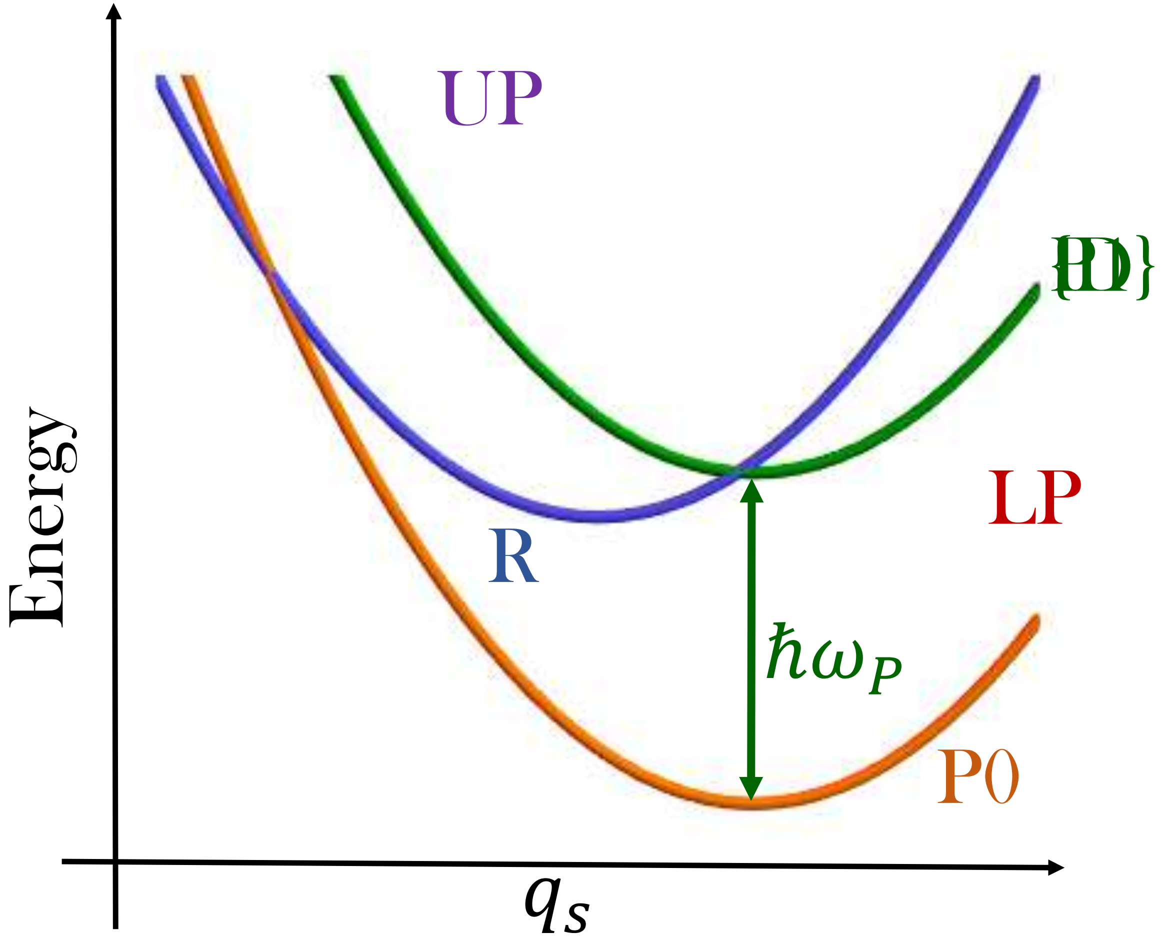
Anomalous kinetics a.k.a. leadership



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!





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

Catalysis of Marcus-Jortner ET with an IR cavity

N = # P molecules formed.

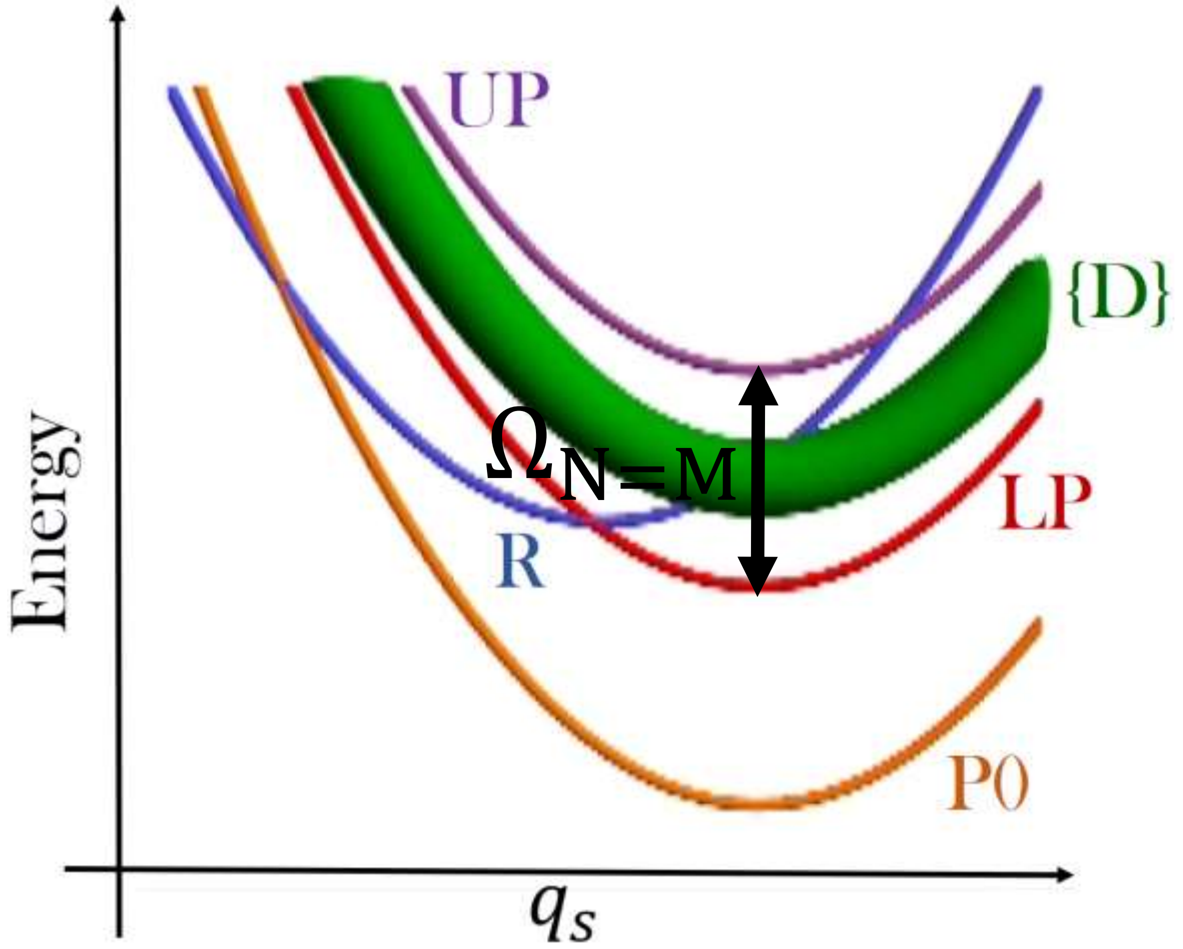
$N \leq M = 10^{10}$ total # molecules.

If we want:

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

We need:

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

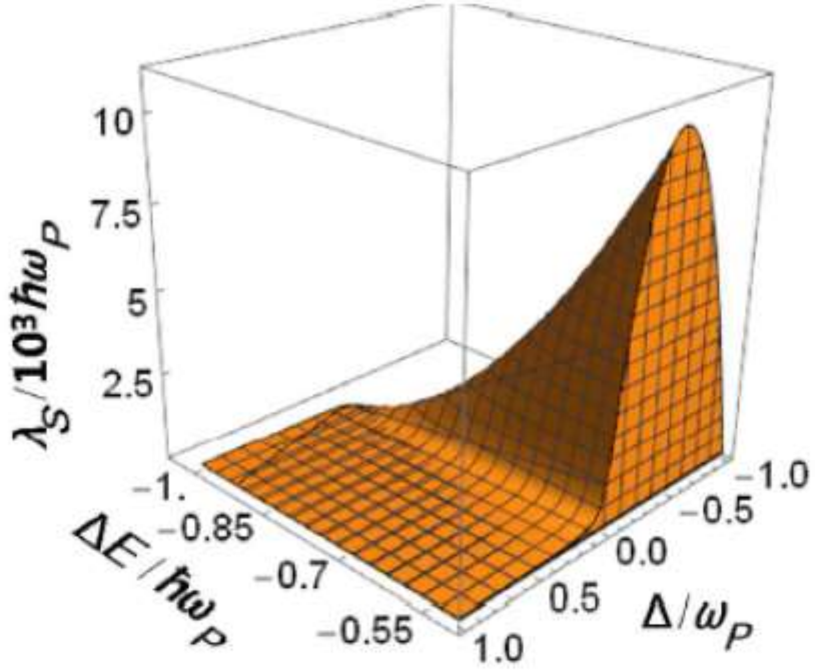


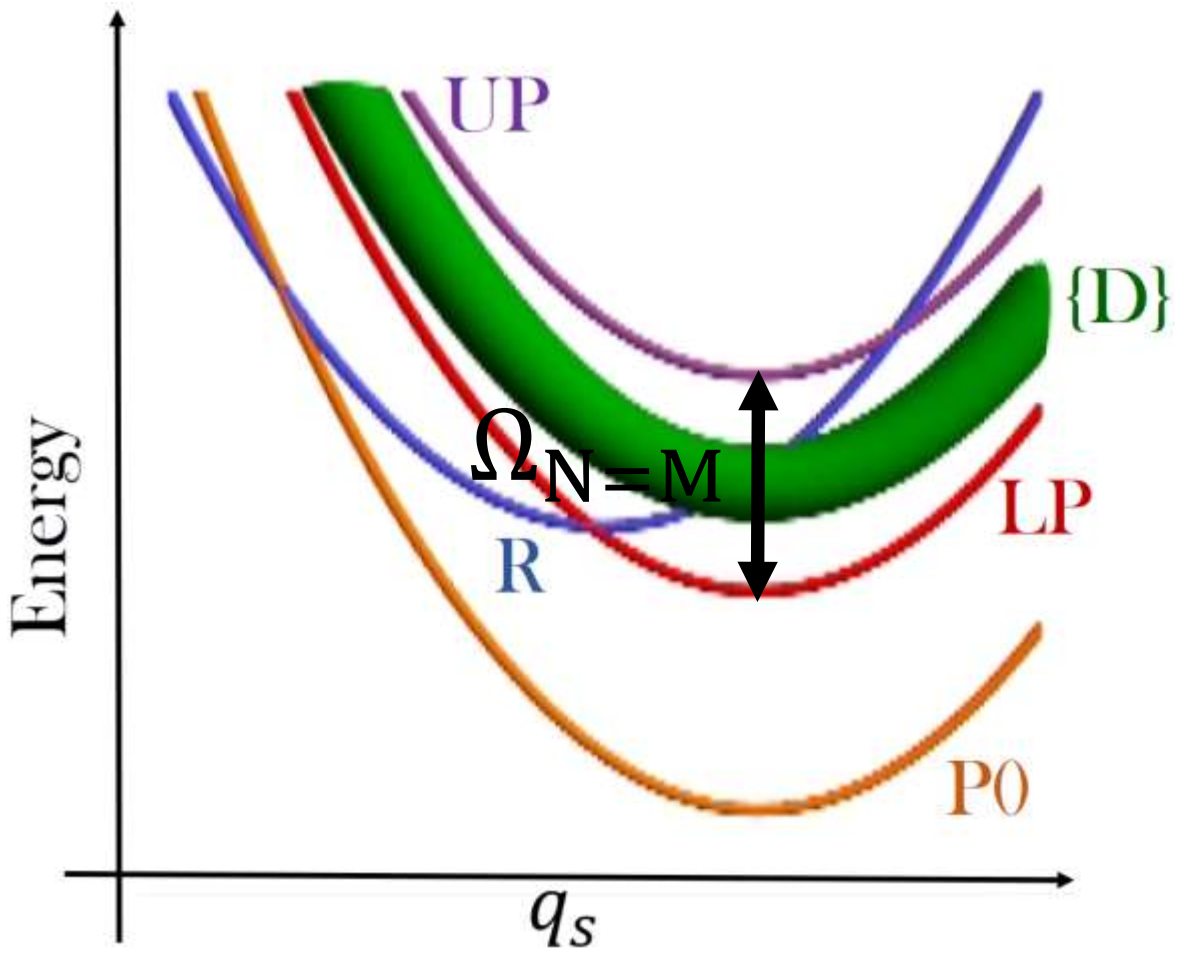
Activation energy reduction due to LP can outcompete large activation entropy of {D}!!!

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

Catalysis of Marcus-Jortner ET with an IR cavity

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





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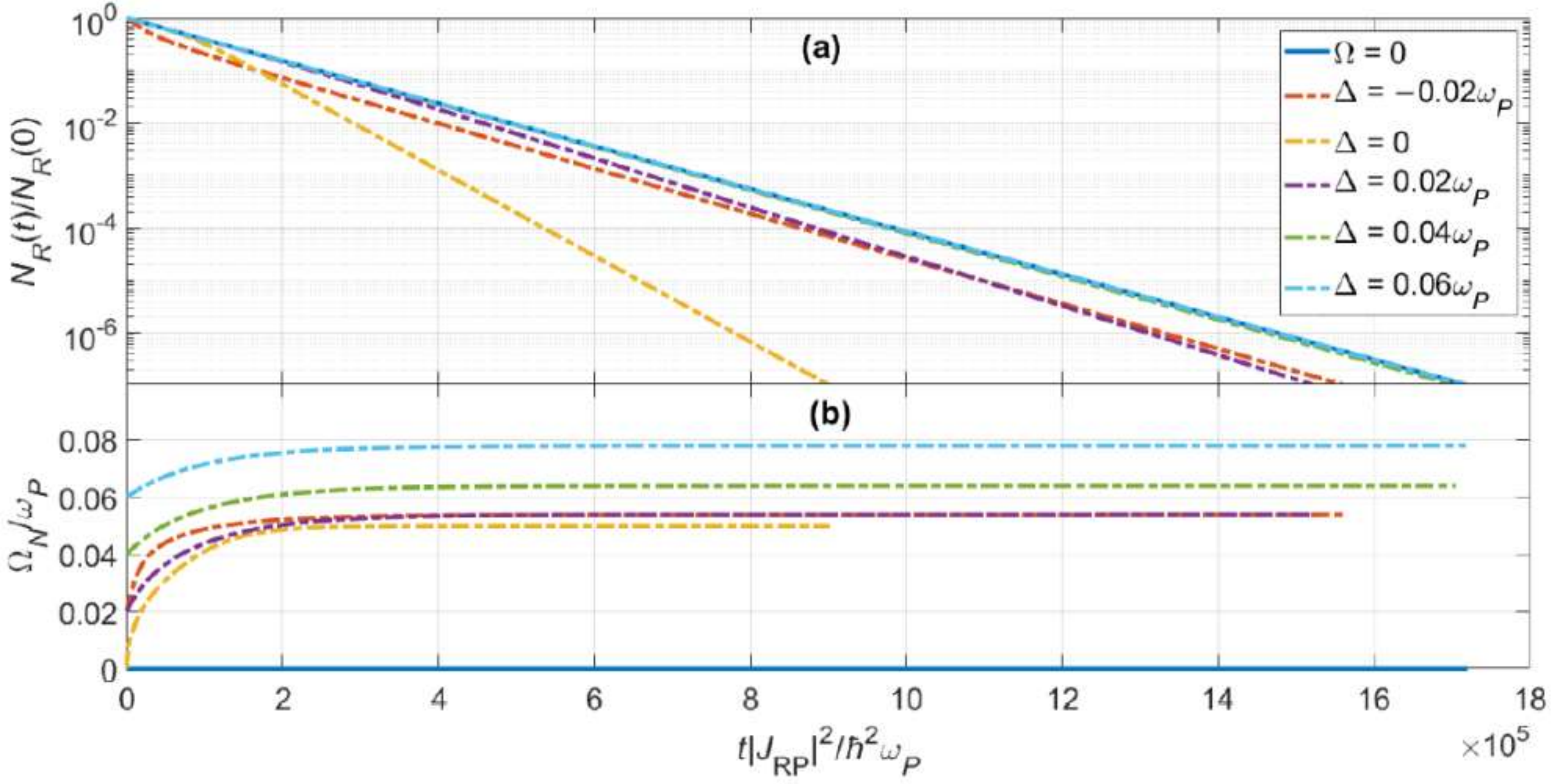
Catalysis of Marcus-Jortner ET with an IR cavity



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

Catalysis of Marcus-Jortner ET with an IR cavity

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

$$R + UP_{N-1} + LP_{N-1} + \sum_{k=1}^{N-2} D_{N-1}^{(k)} \longrightarrow UP_N + LP_N + \sum_{k=1}^{N-1} D_N^{(k)}$$

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

$$R + UP_{N-1} + LP_{N-1} \longrightarrow UP_N + LP_N + D_{N-1}^{(N-1)}$$

See also: A. Strashko, A. & J. Keeling, (2016), *Physical Review A*, *94*(2), 023843.

Catalysis of Marcus-Jortner ET with an IR cavity

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

Jorge Campos

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

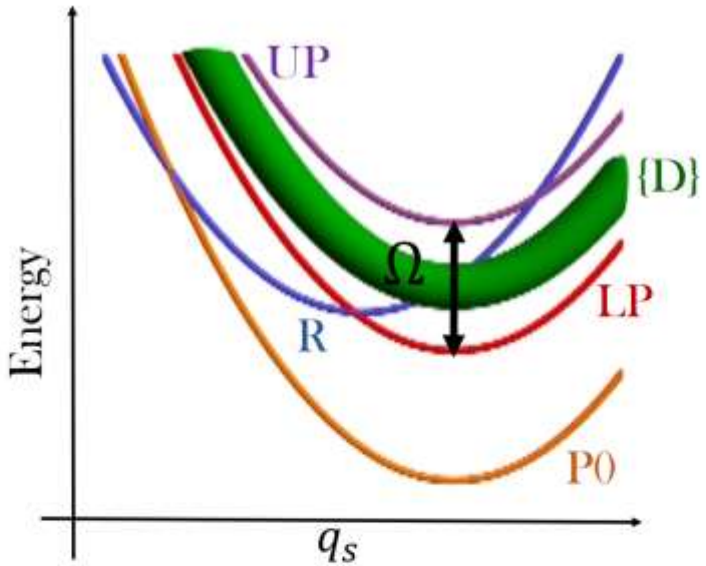
$$W_{v_+,v_-,v_D} = |F_{v_+,v_-,v_D}|^2 \exp\left(-\frac{E^{\ddagger}_{v_+,v_-,v_D}}{k_B T}\right)$$

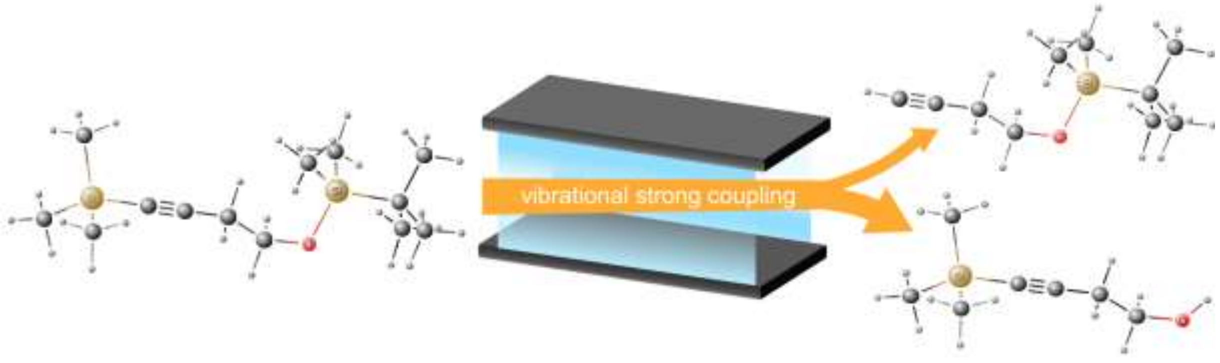
$$\begin{aligned} |F_{v_+,v_-,v_D}|^2 &= |\langle 0_{+(N-1)} 0_{-(N-1)} 0_R | v_+ v_- v_D \rangle|^2 \\ &= \left(\frac{\sin^2\theta_N}{N}\right)^{v_+} \left(\frac{\cos^2\theta_N}{N}\right)^{v_-} \left(\frac{N-1}{N}\right)^{v_D} \\ &\times \binom{v_+ + v_- + v_D}{v_+, v_-, v_D} |\langle 0' | v_+ + v_-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

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

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?

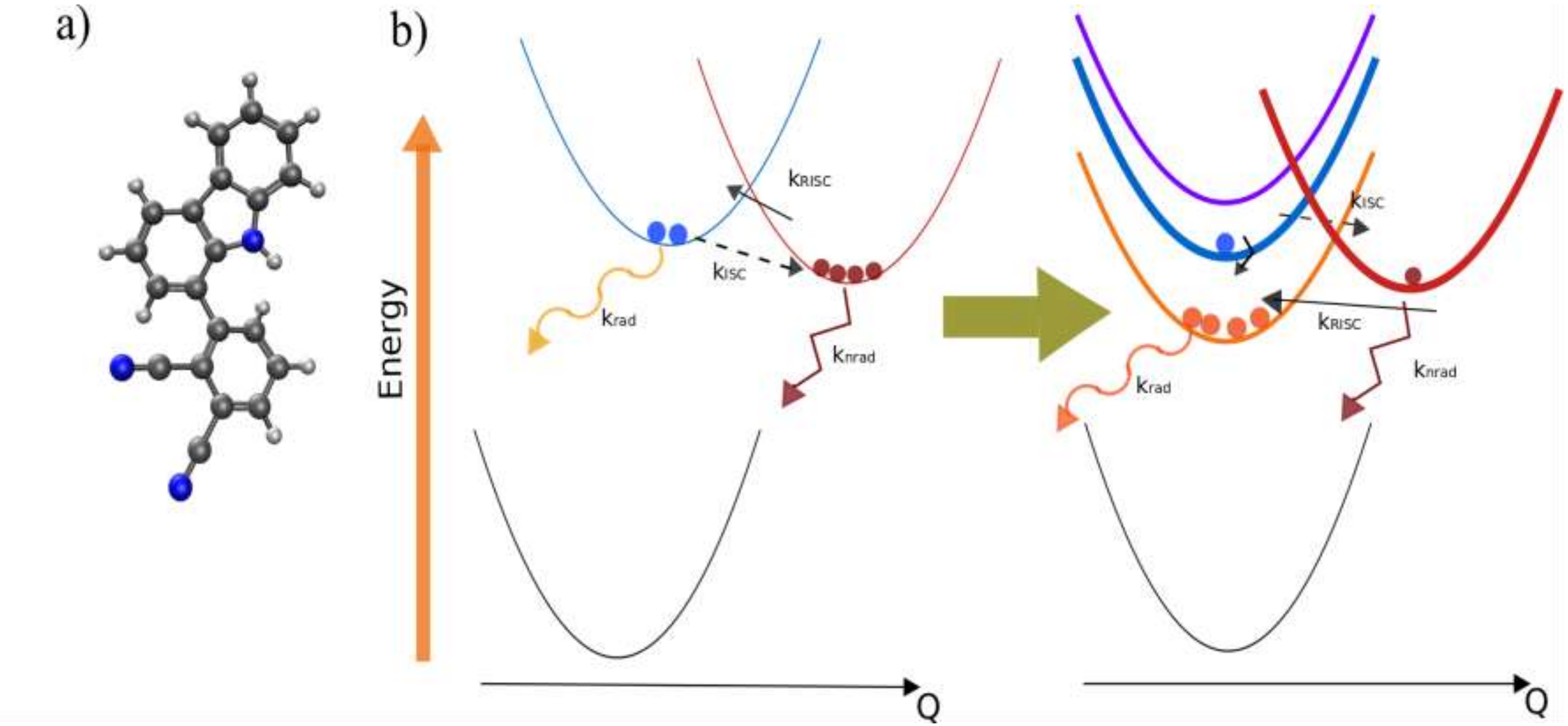




S. Kena-Cohen and J. Yuen-Zhou, ACS Cent. Sci., First reactions, 2019.
J. Campos-González-Angulo, R.F. Ribeiro, J. Yuen-Zhou, arXiV:1902.10264.

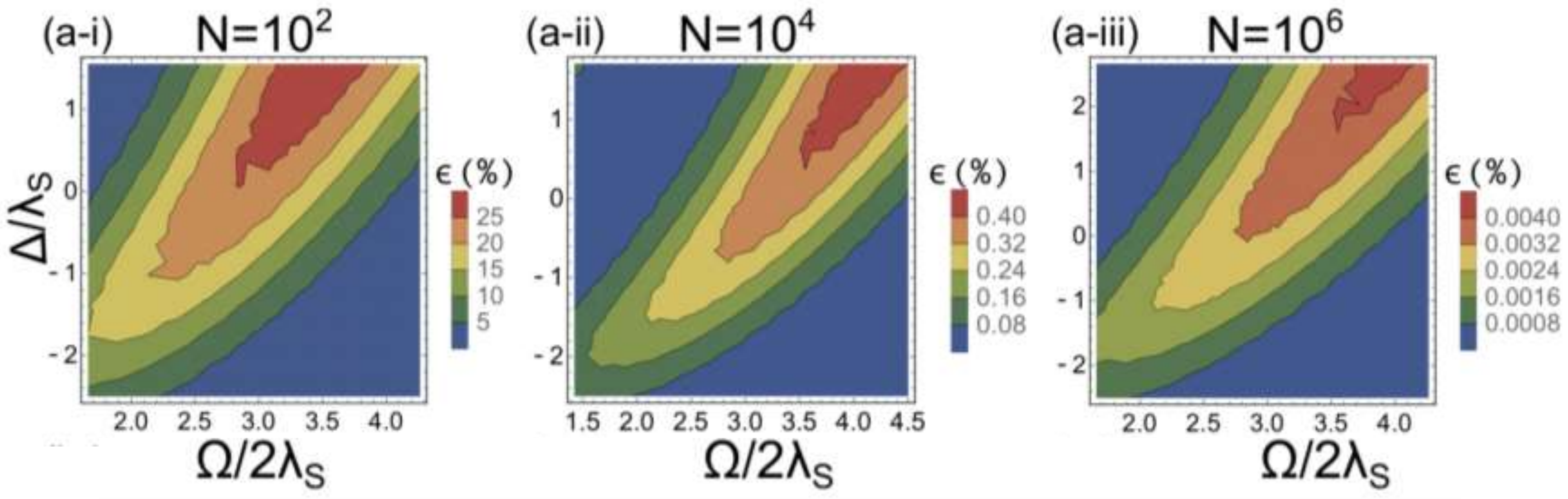
SIMILAR PROBLEM: Harvesting of triplets: the idea

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



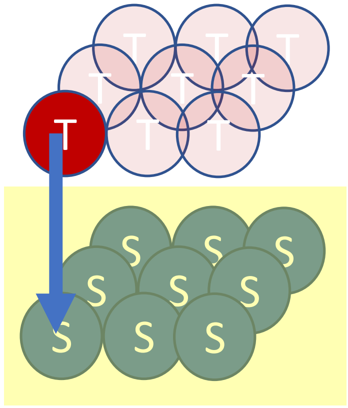
L.A. Martínez-Martínez, E. Eizner, S. Kena-Cohen, J. Yuen-Zhou, J. Chem. Phys., in press
E. Eizner, L.A. Martínez-Martínez, J. Yuen-Zhou, S. Kena-Cohen, arXiV:1903.09251

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

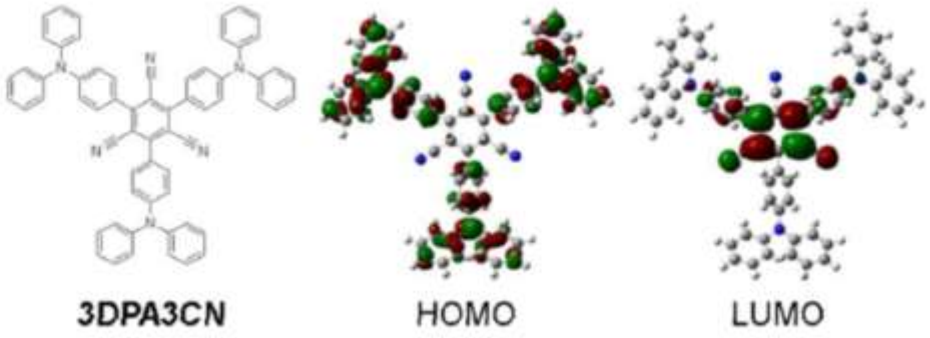


As the number of molecules N in the cavity becomes larger, the fluorescence efficiency decreases. The maximum rate is bounded at

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

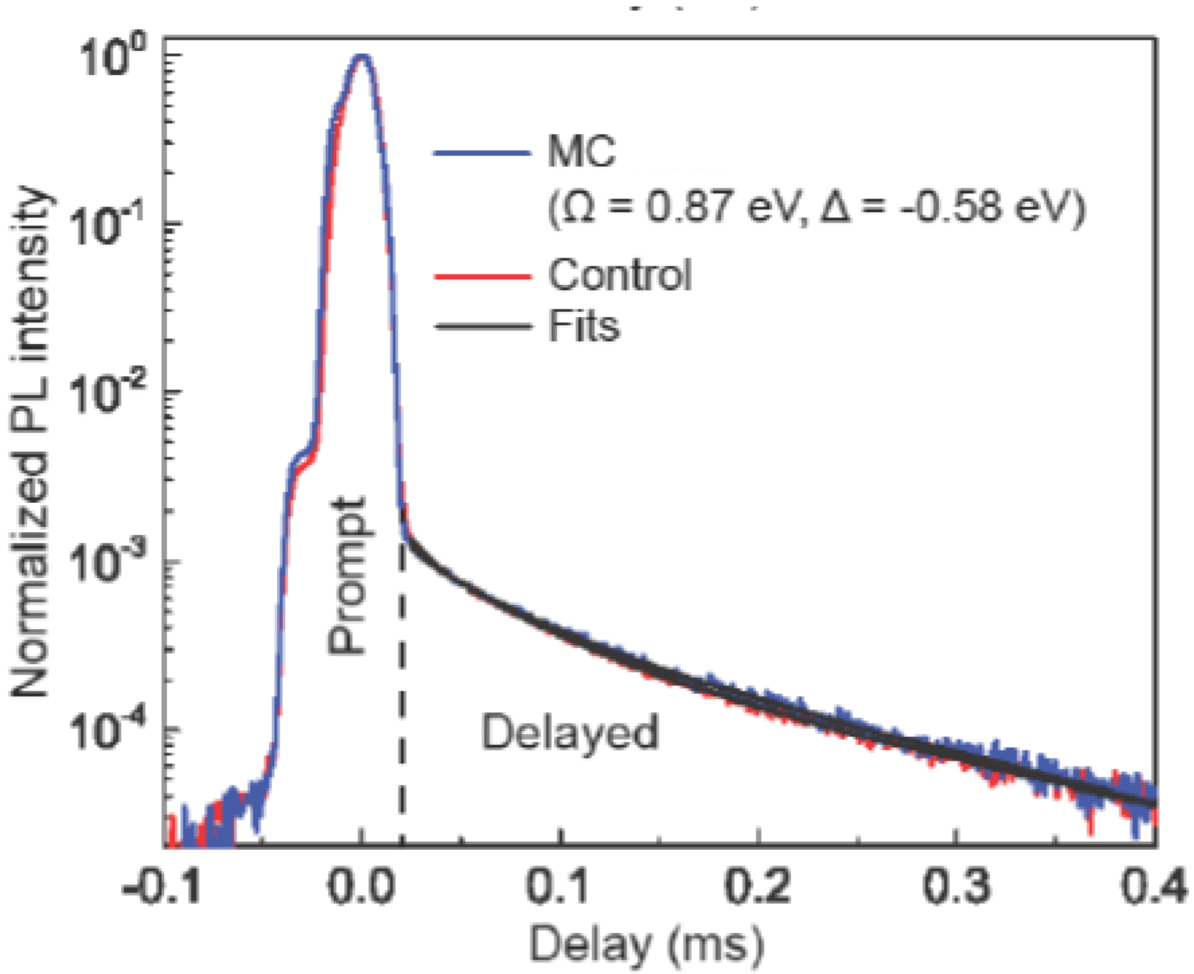


Harvesting of triplets: the experiment



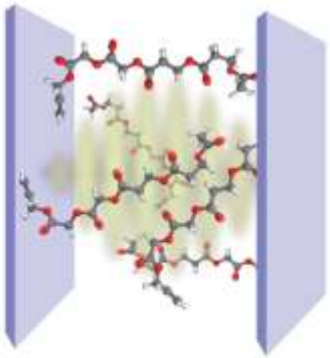
Goushi, K., Yoshida, K., Sato, K. & Adachi, C., Nat. Photonics 6, 253–258 (2012)

No changes in triplet lifetime was observed in experiment with 3DPA3CN when put in a microcavity!



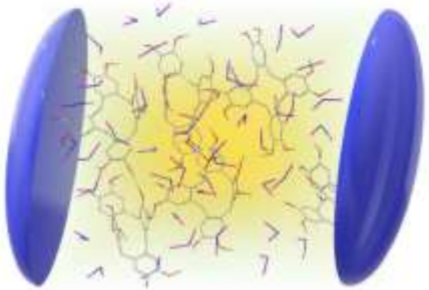
E. Eizner, L.A. Martínez-Martínez, J. Yuen-Zhou, S. Kena-Cohen, arXiV:1903.09251

Outline of talk

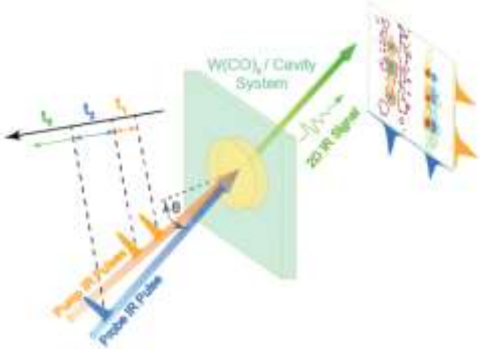


Vibrational polaritons

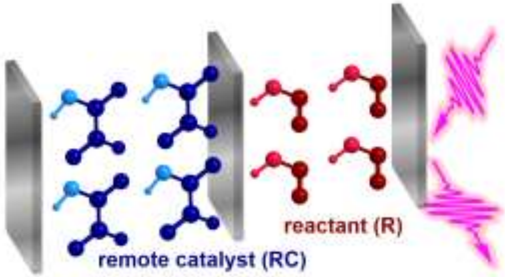
Ground-state reactivity



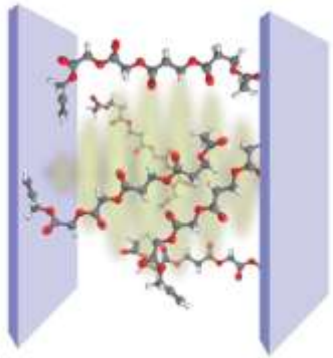
Nonlinearities



Remote control

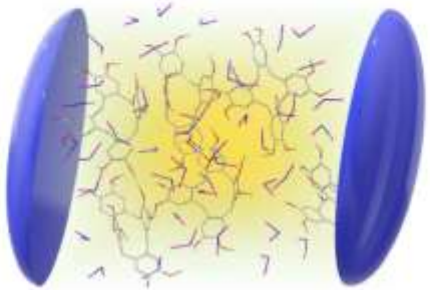


Outline of talk

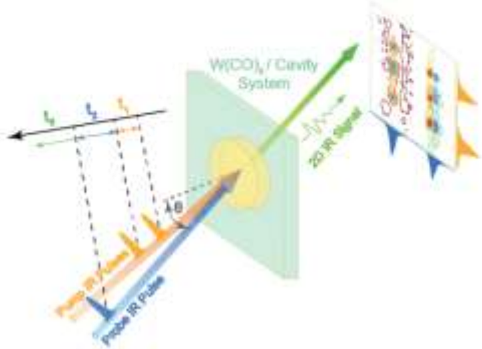


Vibrational polaritons

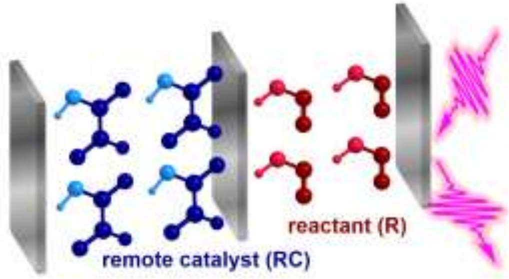
Ground-state reactivity



Nonlinearities



Remote control



Acknowledgements

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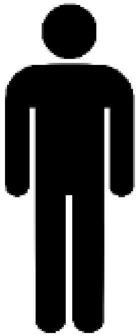
Naval Research Laboratory

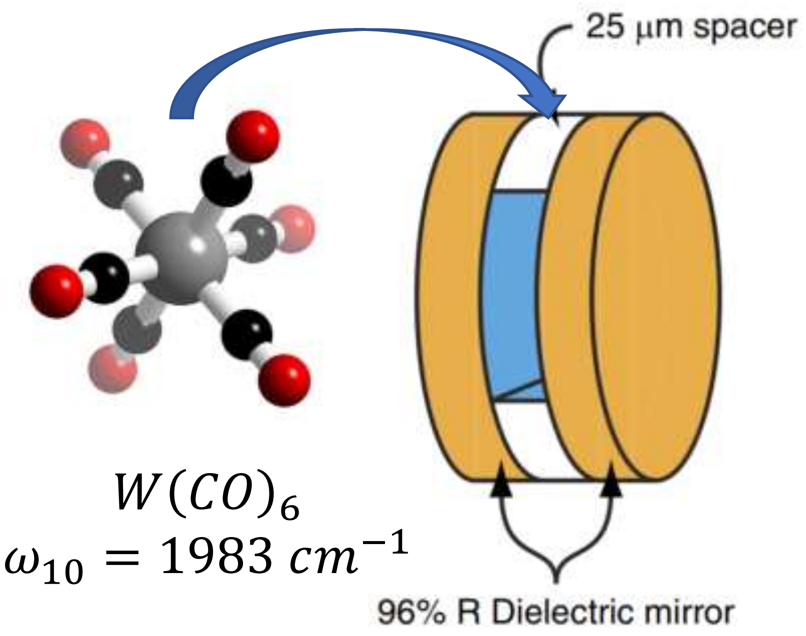
Adam Dunkelberger

Jeff Owrutsky



Blake Simpkins

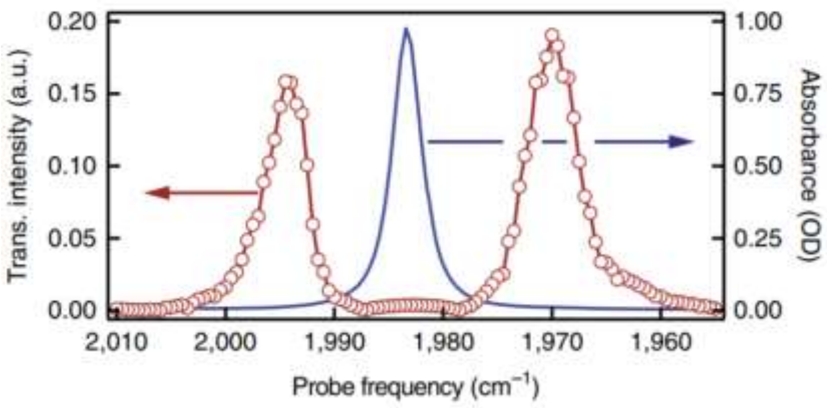
The experiment #1



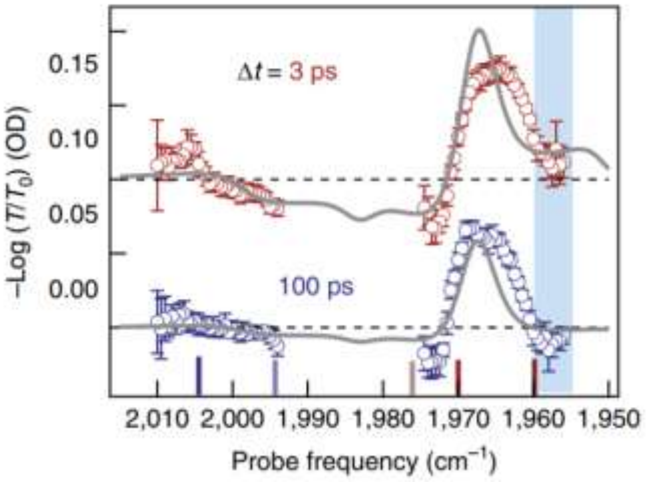
$W(CO)_6$

$\omega_{10} = 1983\ cm^{-1}$

Dunkelberger et al. Nat. Comm. 7, 13504, 2016



Linear absorption

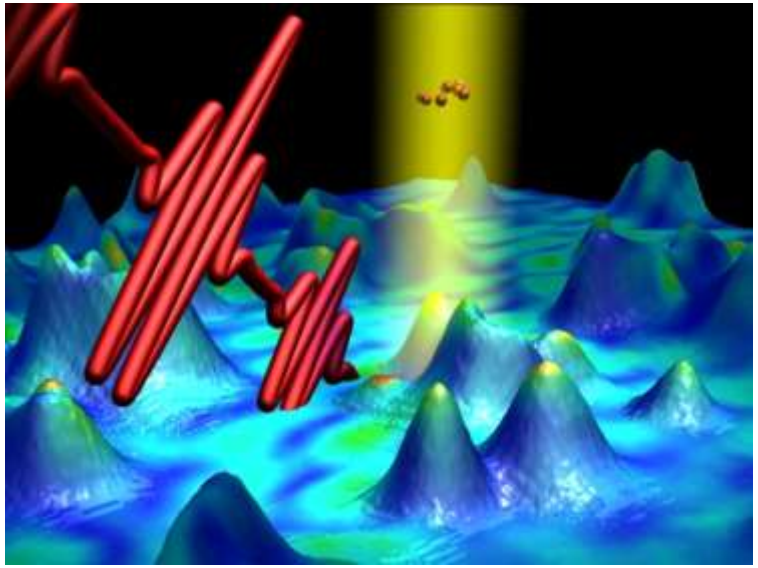


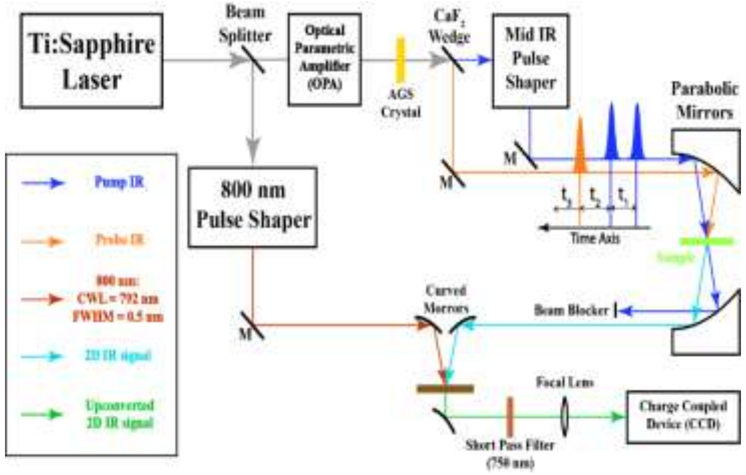
Transient absorption

The experiment #2

Wei Xiong

Bo Xiang

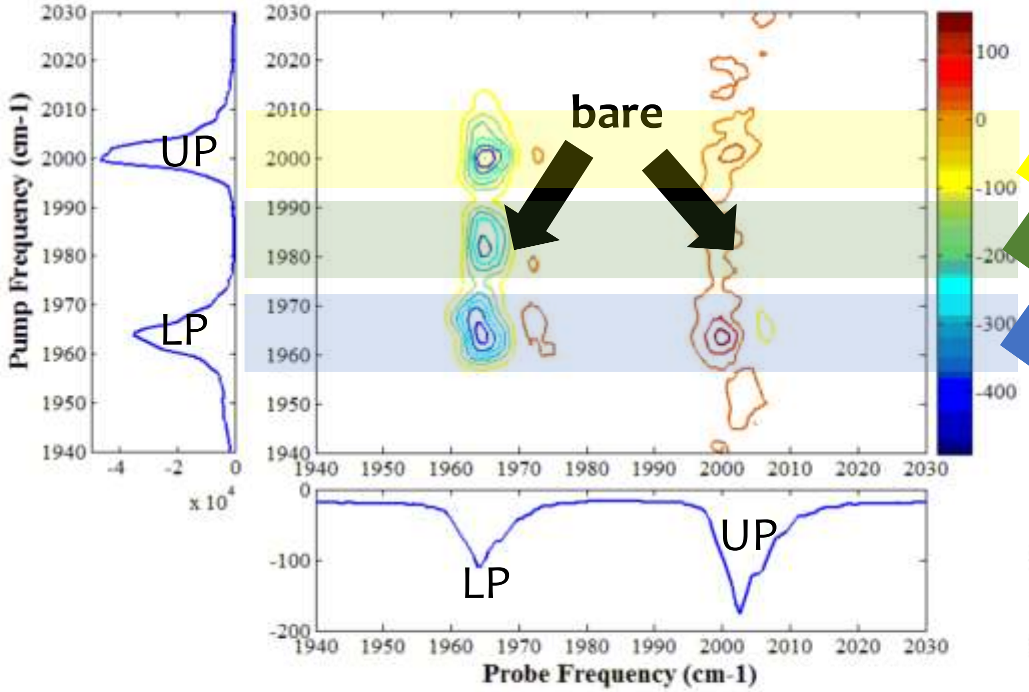




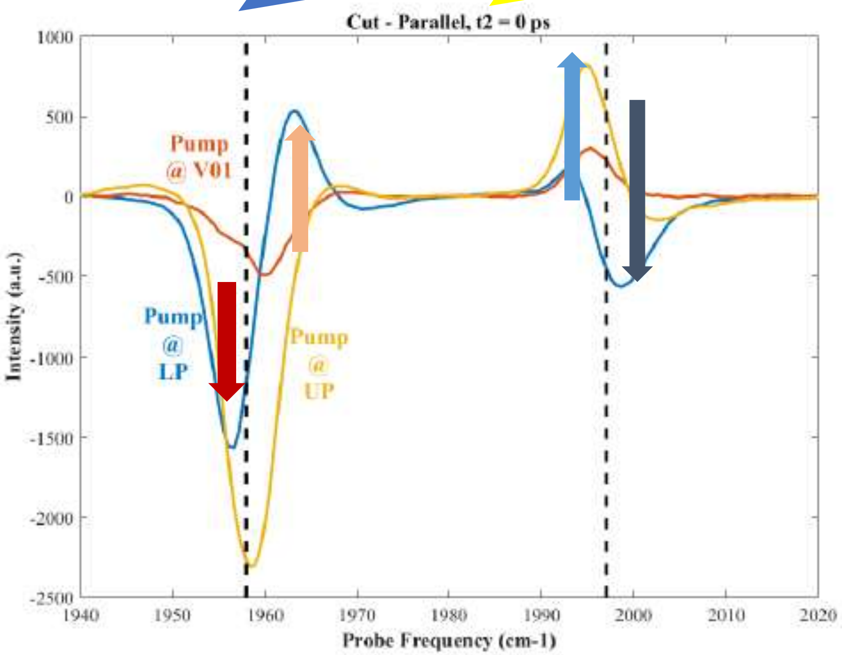
B. Xiang, R. F. Ribeiro, A. D. Dunkelberger, J. C. Owrutsky, B. S. Simpkins, J. Yuen-Zhou, and W. Xiong, PNAS 115, 19 (2018).
R.F. Ribeiro, R. F. Ribeiro, A. D. Dunkelberger, J. C. Owrutsky, B. S. Simpkins, W. Xiong, J. Yuen-Zhou, J. Phys. Chem. Lett. 9, 13 (2018).

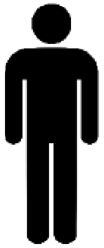
Nonlinear spectroscopy provides a variety of spectral projections of the many-body response.

The experiment #2



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





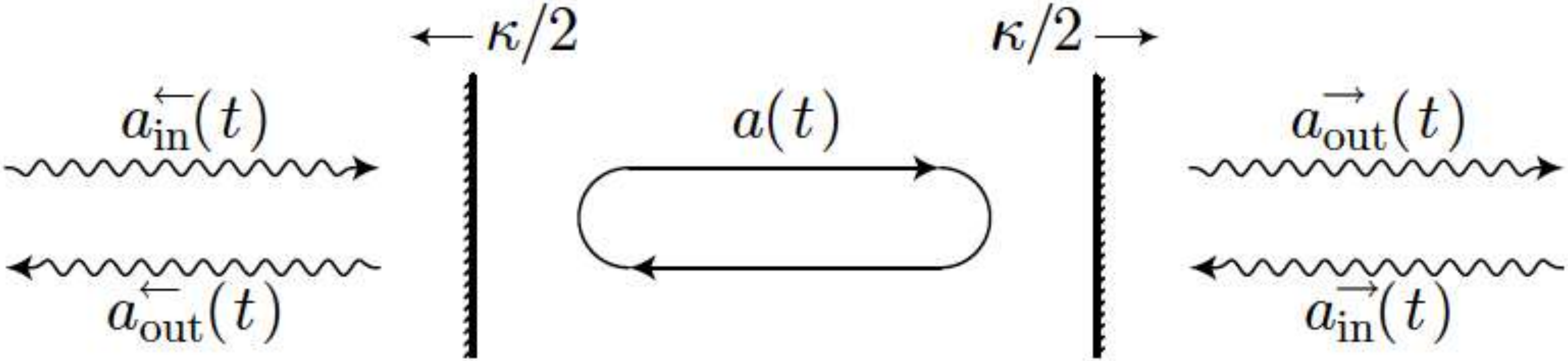
What are those derivative lineshapes?

Blake Simpkins

Theory: QOptics + QChem

Input-output theory

J. Collett and C. W. Gardiner, *PRA* **30**, 1386 (1984)
C. W. Gardiner and M. J. Collett, *PRA* **31**, 3761 (1985)



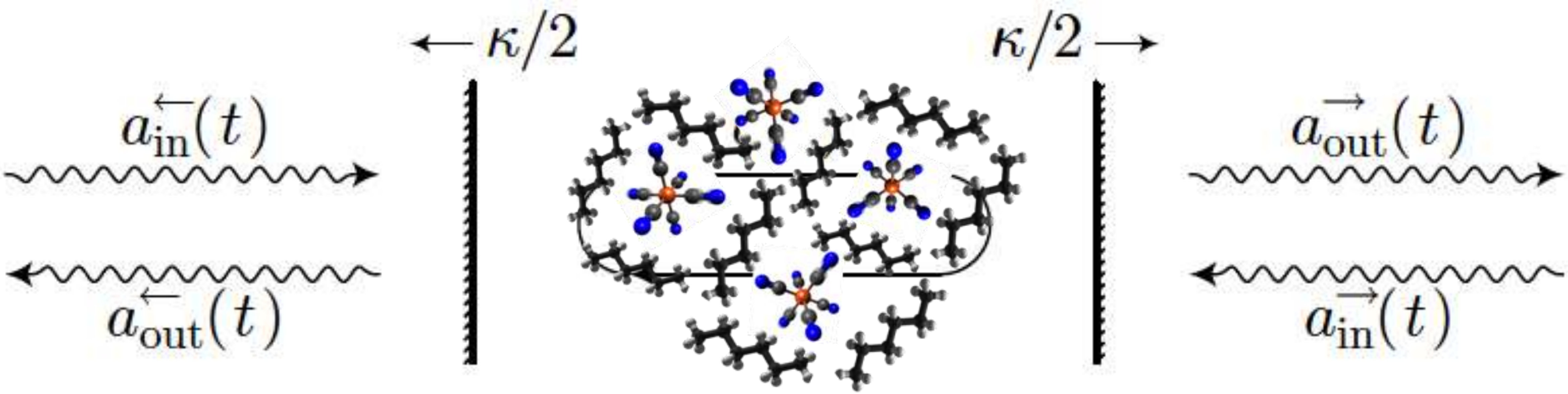
Theory: QOptics + QChem

Input-output theory

J. Collett and C. W. Gardiner, *PRA* **30**, 1386 (1984)
C. W. Gardiner and M. J. Collett, *PRA* **31**, 3761 (1985)

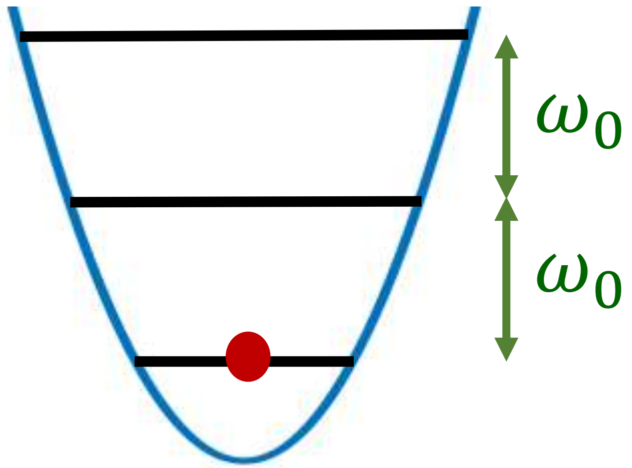
Anharmonic vibrations in condensed phase

M. Khalil, N. Demirdöven, and A. Tokmakoff, *J. Phys. Chem. A,* 107.27 (2003): 5258-5279.

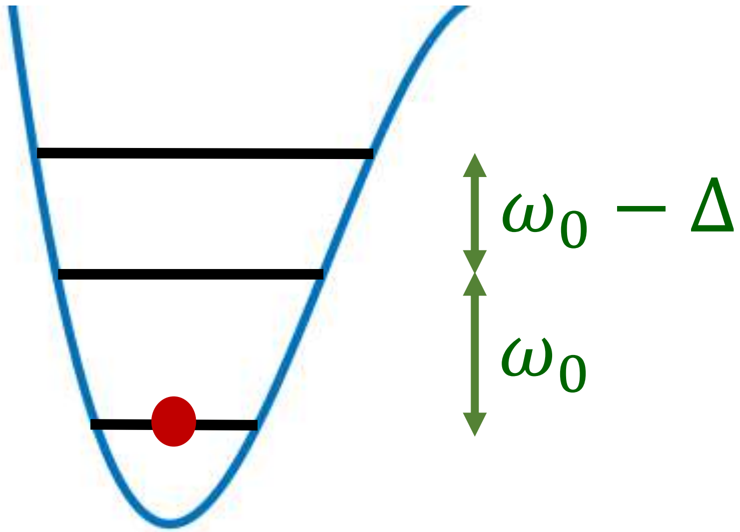


B. Xiang, R. F. Ribeiro, A. D. Dunkelberger, J. C. Owrutsky, B. S. Simpkins, J. Yuen-Zhou, and W. Xiong, PNAS 115, 19 (2018).
R.F. Ribeiro, R. F. Ribeiro, A. D. Dunkelberger, J. C. Owrutsky, B. S. Simpkins, W. Xiong, J. Yuen-Zhou, J. Phys. Chem. Lett. 9, 13 (2018).

Refresher on nonlinear optics

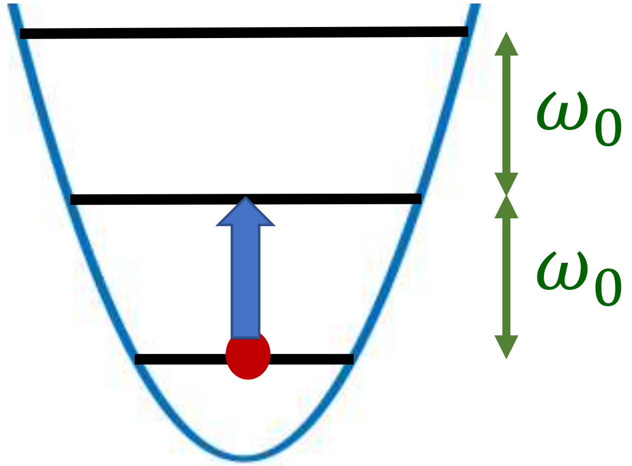


Harmonic oscillator

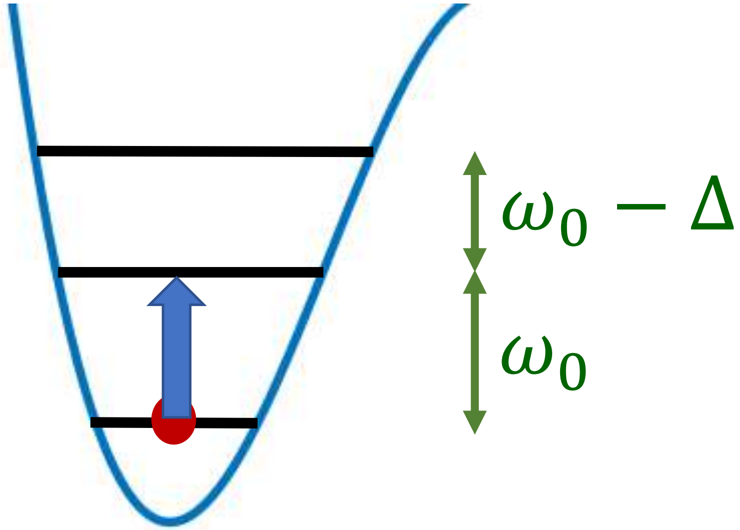


Anharmonic oscillator

Refresher on nonlinear optics

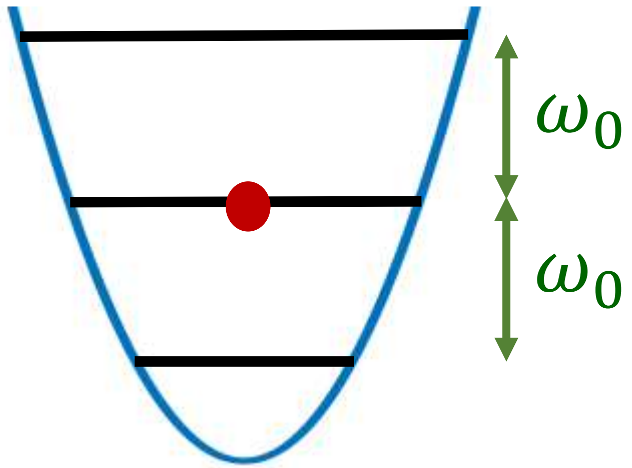


Harmonic oscillator

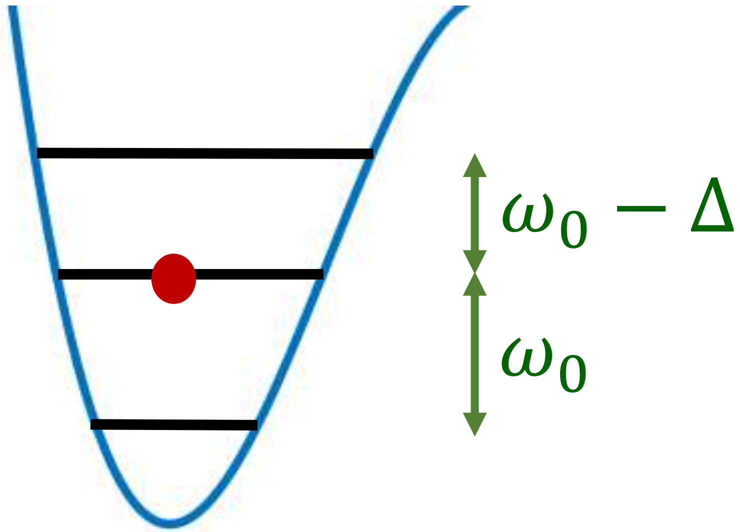


Anharmonic oscillator

Refresher on nonlinear optics

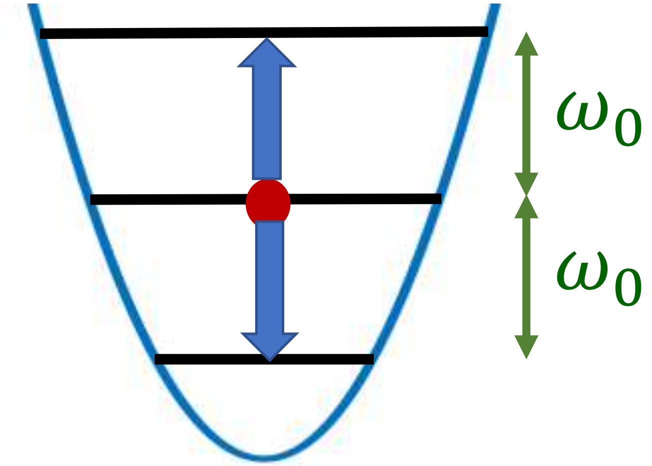


Harmonic oscillator

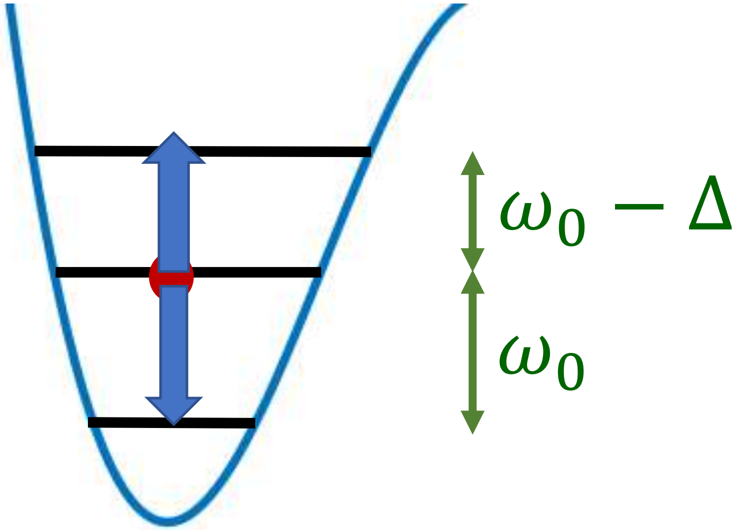


Anharmonic oscillator

Refresher on nonlinear optics

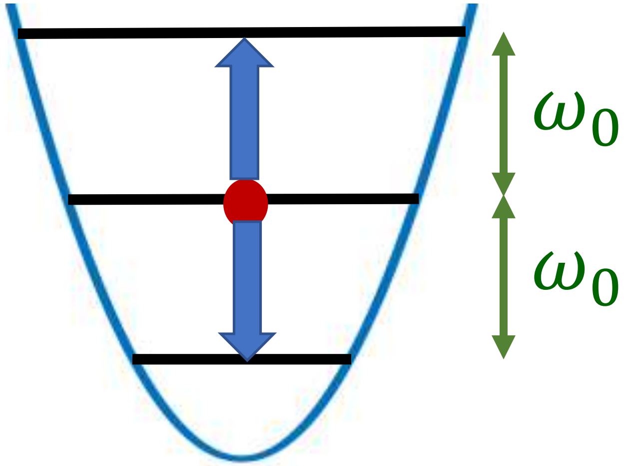


Harmonic oscillator

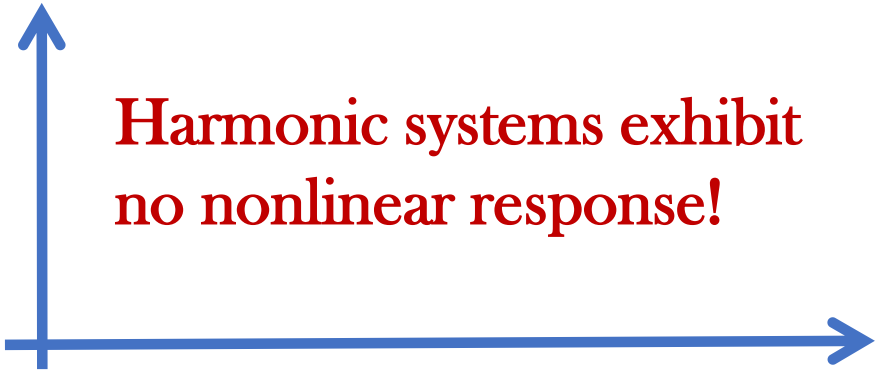


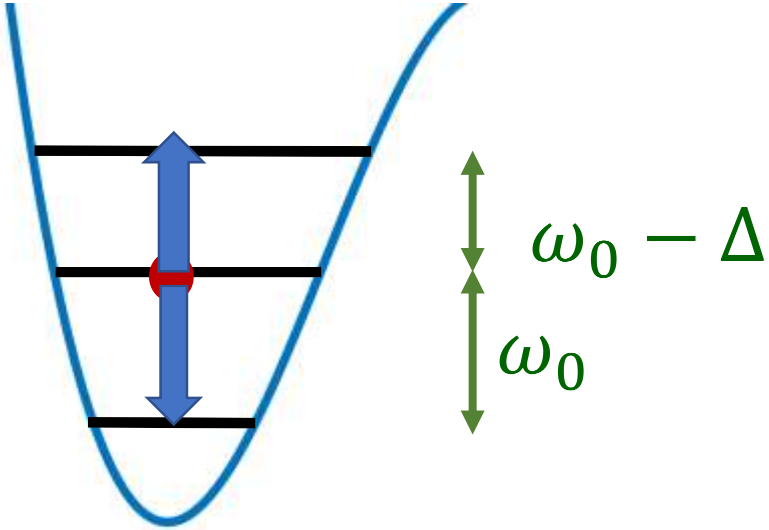
Anharmonic oscillator

Refresher on nonlinear optics

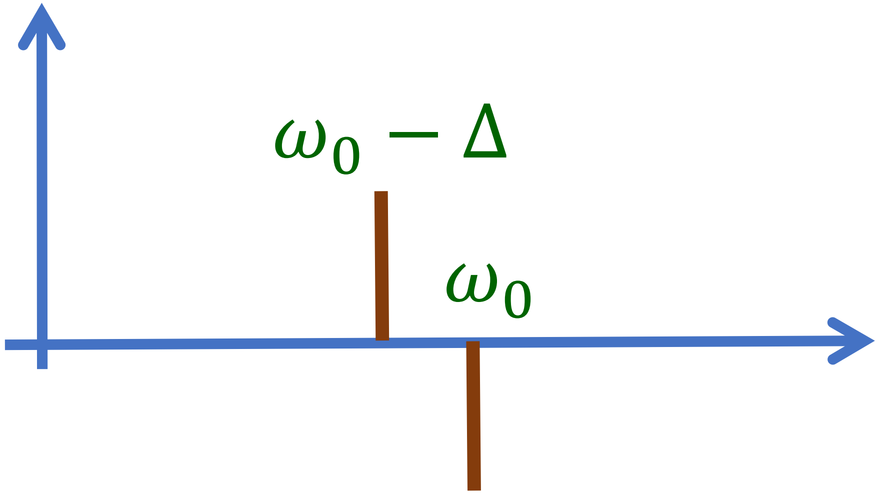


Harmonic oscillator





Anharmonic oscillator



Theory: QOptics + QChem

$$\hat{H} = \hat{H}_{\mathrm{mol}} + \hat{H}_{\mathrm{ph}} + \hat{H}_{\mathrm{lm}} + \hat{H}_{\mathrm{SB}}$$

$$\hat{H}_{\mathrm{ph}} = \omega_c b^\dagger b$$

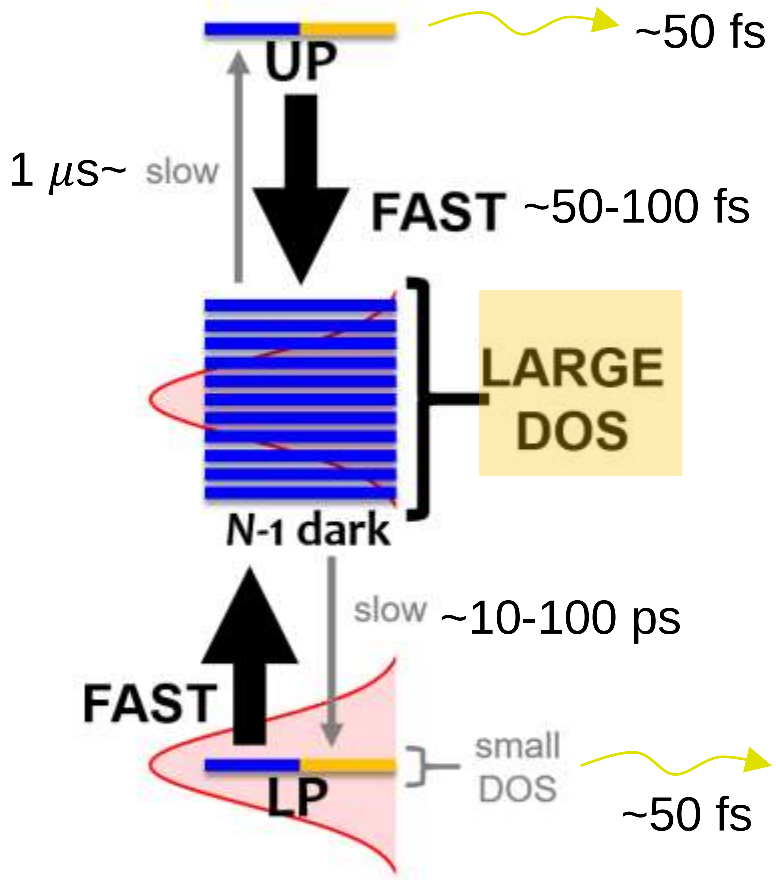
$$\hat{H}_{\mathrm{mol}} = \omega_0 \sum_{i=1}^{N} a_i^\dagger a_i - \Delta \sum_{i=1}^{N} a_i^\dagger a_i^\dagger a_i a_i$$

$$\hat{H}_{\mathrm{lm}} = -g \sum_{i=1}^{N} \left[b^\dagger \left(1 + \delta a_i^\dagger a_i\right) a_i + a_i^\dagger \left(1 + \delta a_i^\dagger a_i\right) b \right]$$

Some timescales to keep in mind

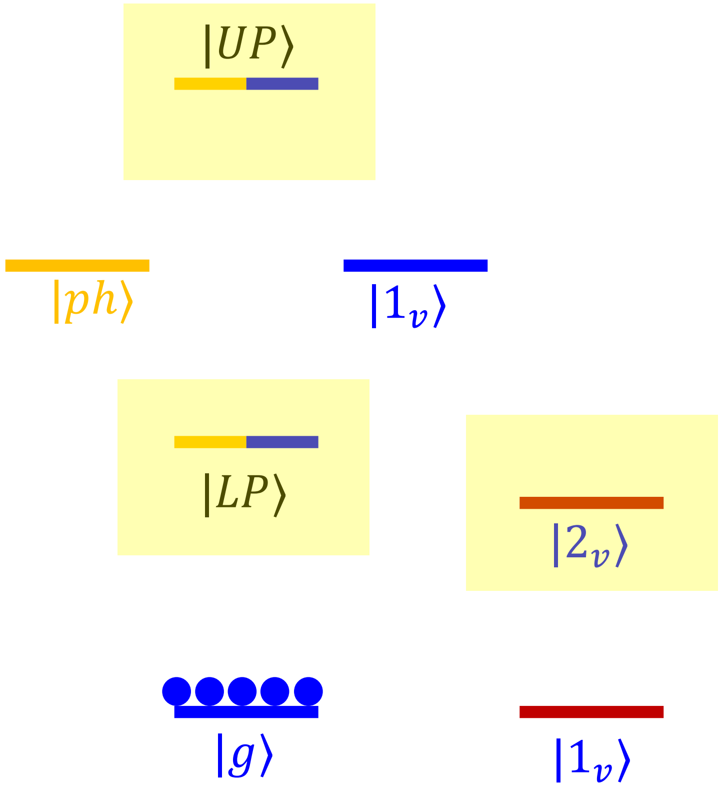
In condensed phases, vibrational couplings V lead to relaxation mechanisms.

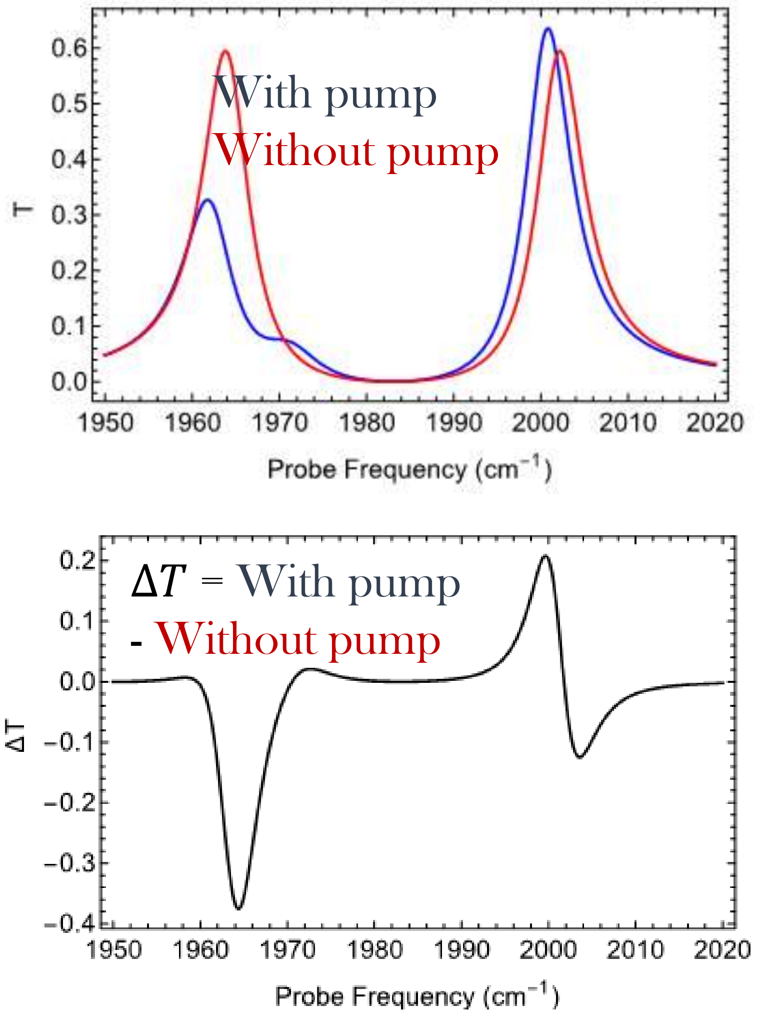
$$\gamma_{F\leftarrow I} = \frac{2\pi}{\hbar}\sum_f \sum_i p_i |\langle f|V|i\rangle|^2 \rho(\hbar\omega_{f,i})$$



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).

(a) Ultrafast switching of polaritons: saturation effects (t_2>20 ps)





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).

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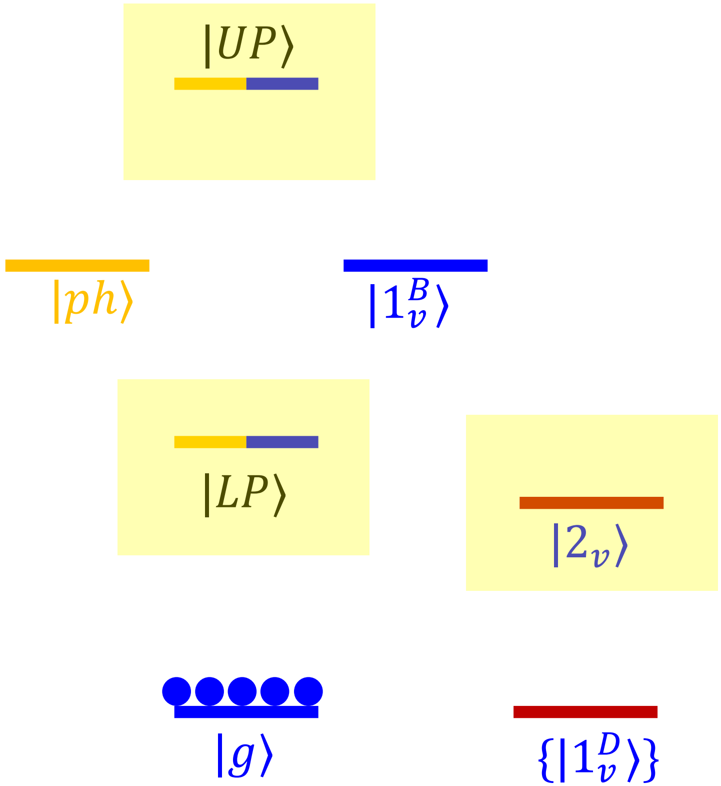
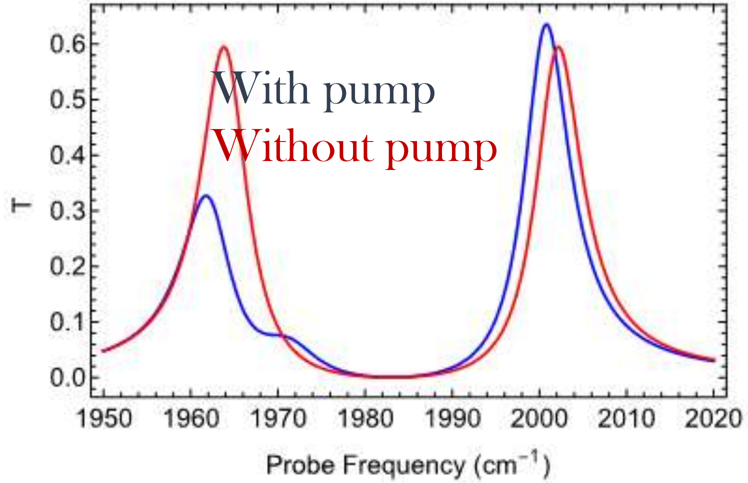
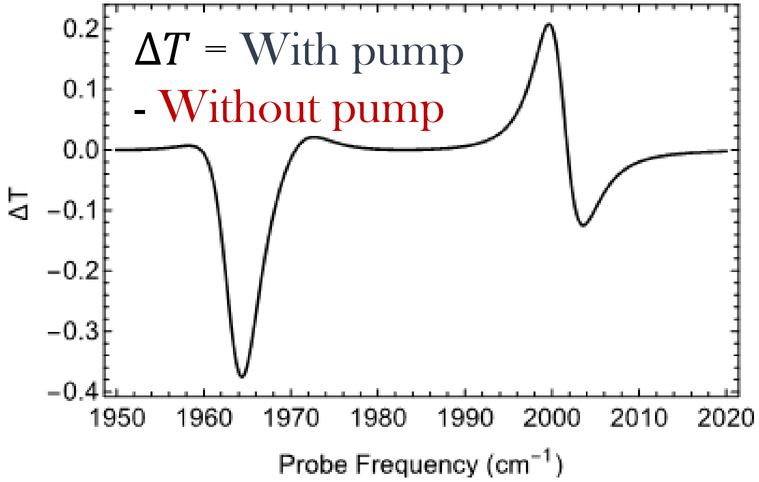


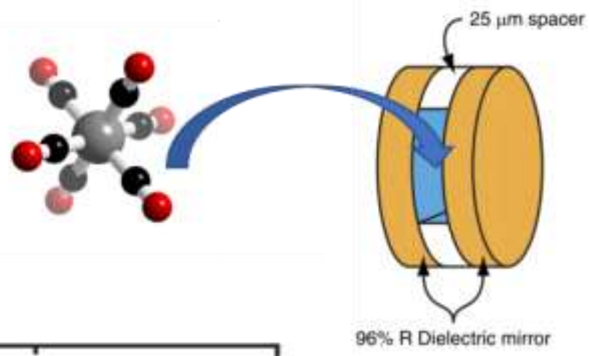


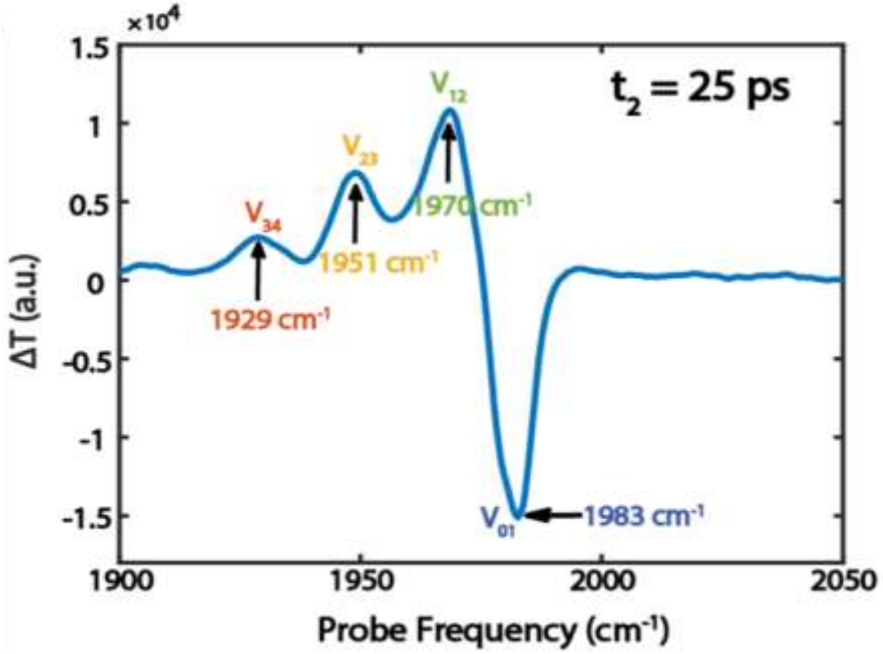


B. Xiang, R. F. Ribeiro, A. D. Dunkelberger, J. C. Owrutsky, B. S. Simpkins, J. Yuen-Zhou, and W. Xiong, PNAS 115, 19 (2018).
R.F. Ribeiro, R. F. Ribeiro, A. D. Dunkelberger, J. C. Owrutsky, B. S. Simpkins, W. Xiong, J. Yuen-Zhou, J. Phys. Chem. Lett. 9, 13 (2018).

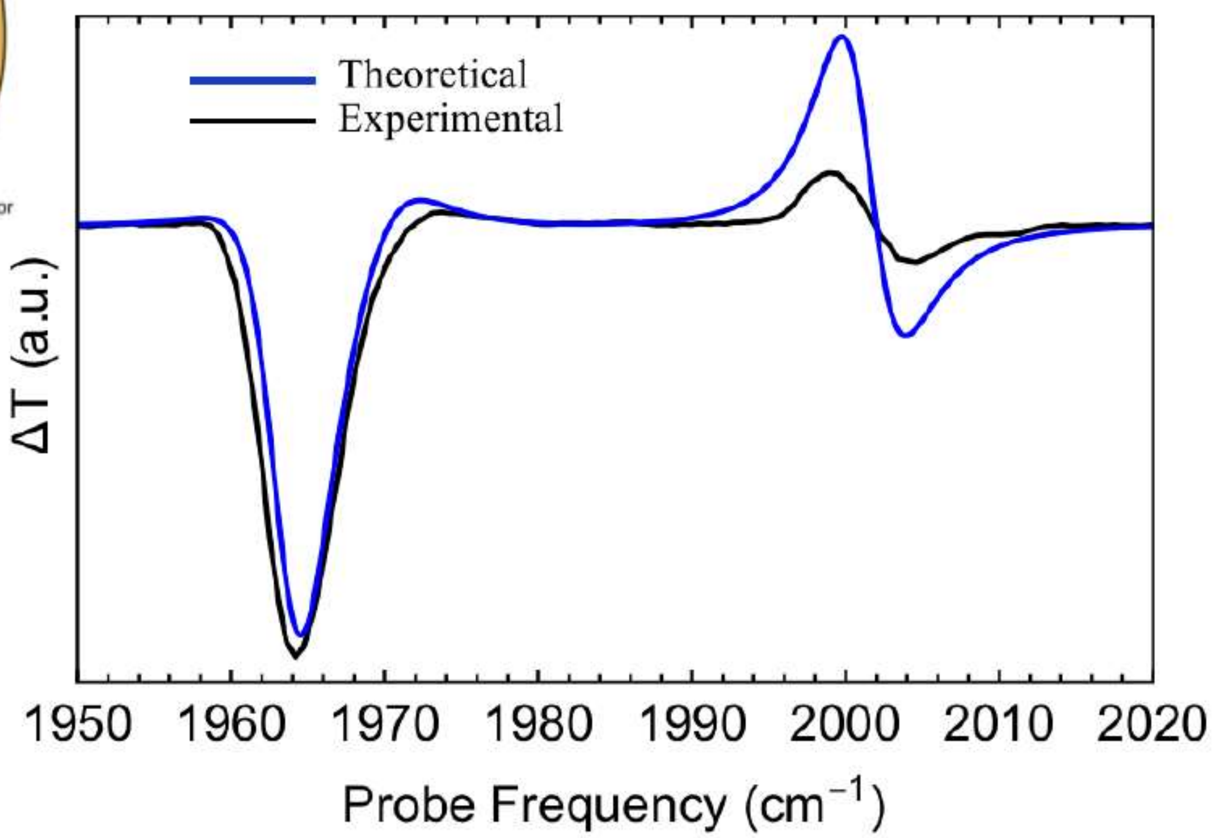
(a) Ultrafast switching of polaritons: saturation effects (t_2>20 ps)

40mM $W(CO)_6$ in n-hexane solution





$$\omega_c = \omega_0$$

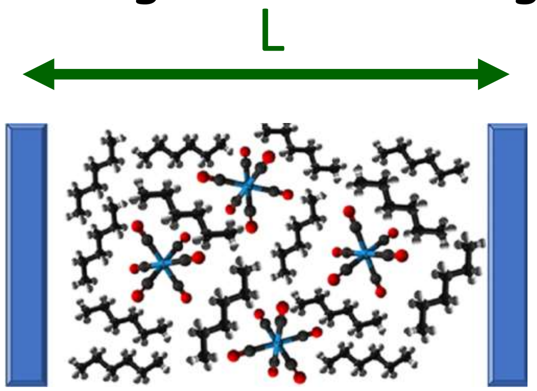


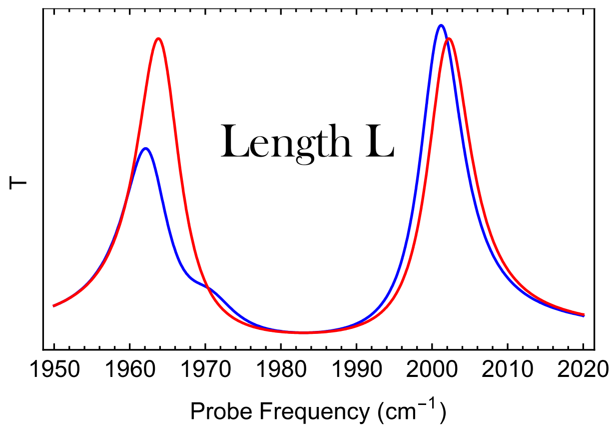
B. Xiang, R. F. Ribeiro, A. D. Dunkelberger, J. C. Owrutsky, B. S. Simpkins, J. Yuen-Zhou, and W. Xiong, PNAS 115, 19 (2018).
R.F. Ribeiro, R. F. Ribeiro, A. D. Dunkelberger, J. C. Owrutsky, B. S. Simpkins, W. Xiong, J. Yuen-Zhou, J. Phys. Chem. Lett. 9, 13 (2018).

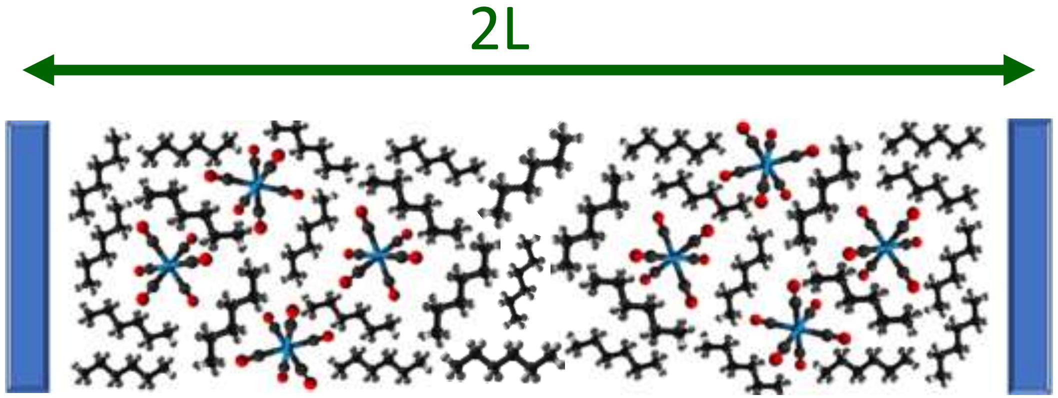
(a) “Clicker” question

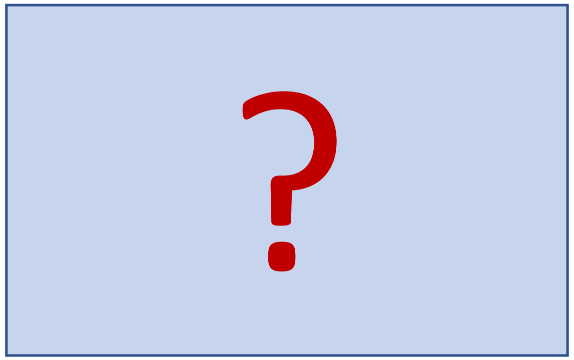
Prof. Wei Xiong and his student Bo Xiang changed the cavity length from L to 2L while keeping concentration (Rabi splitting) fixed. They saw:

a. Same nonlinear signal.
b. Weaker nonlinear signal.
c. Stronger nonlinear signal.

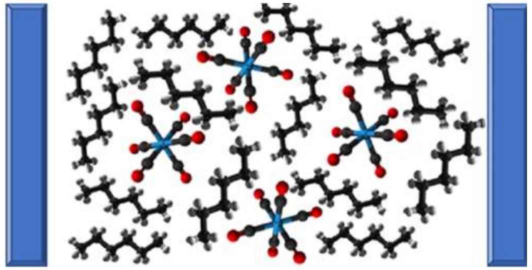


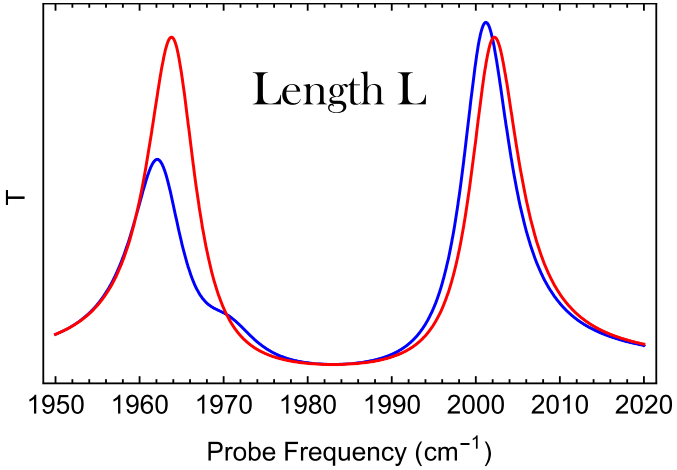




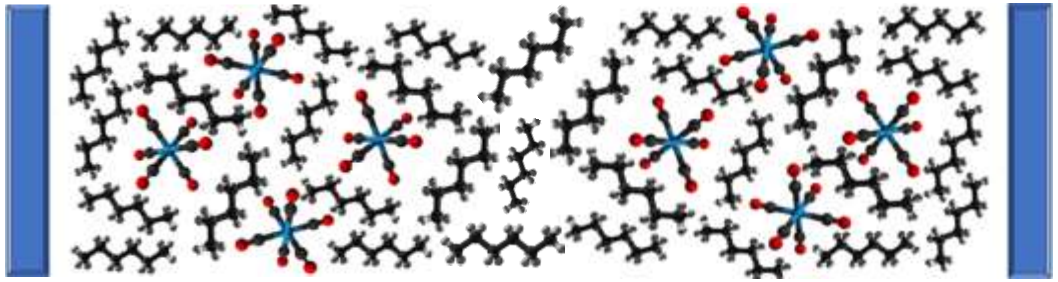


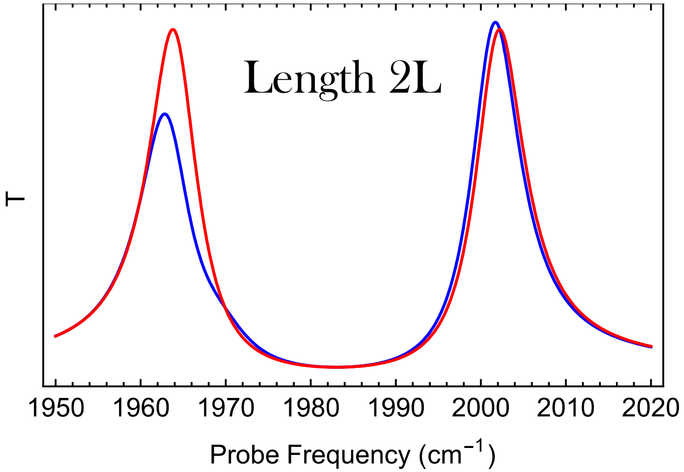
(a) Ultrafast switching of polaritons: saturation effects (t_2>20 ps)





Weaker nonlinearities for larger samples of same concentration!

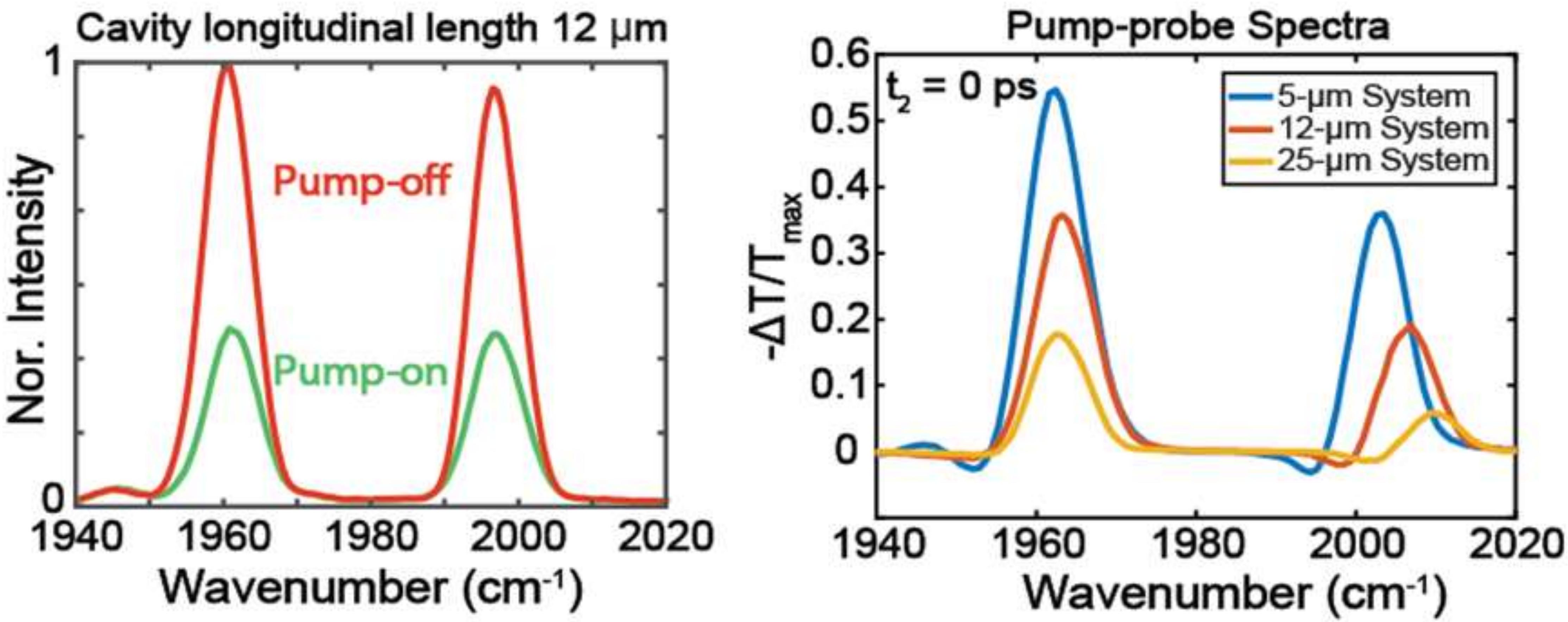




Anharmonicity is *local*, but polariton is spread out across the cavity!

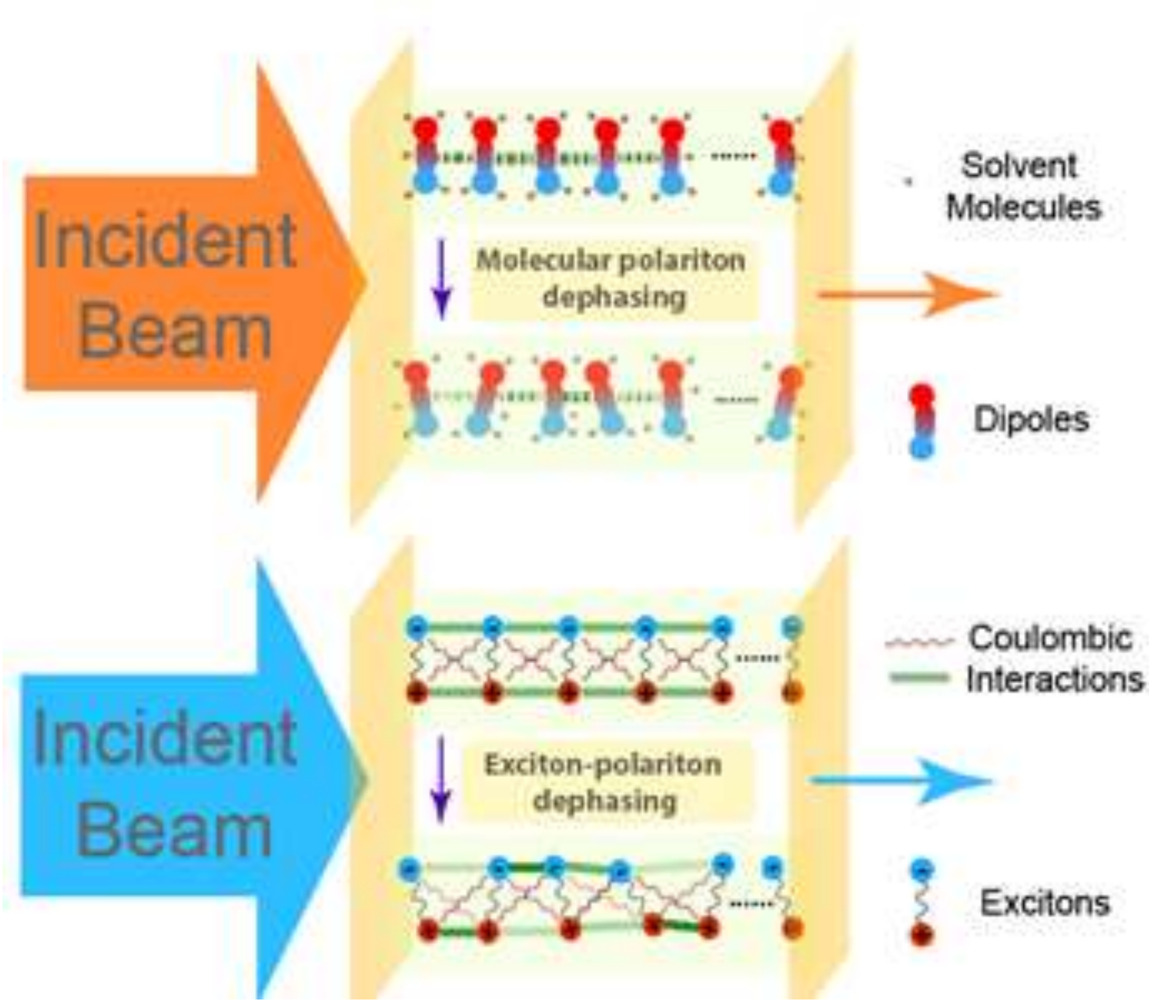
B. Xiang, R. F. Ribeiro, Y. Li, A. D. Dunkelberger, B. B. Simpkins, J. Yuen-Zhou, W. Xiong, arXiV: 1901.05526

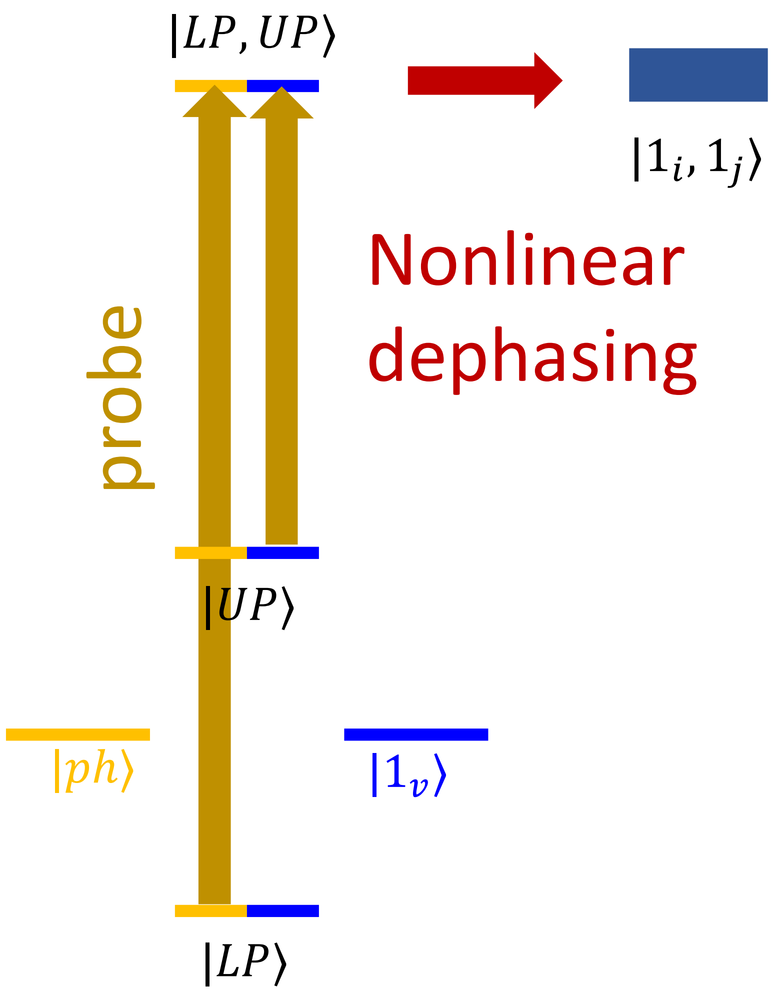
(b) Ultrafast switching of polaritons: coherent effects (T<20 ps)



B. Xiang, R. F. Ribeiro, Y. Li, A. D. Dunkelberger, B. B. Simpkins, J. Yuen-Zhou, W. Xiong, arXiV: 1901.05526

(b) Ultrafast switching of polaritons: coherent effects (T<20 ps)

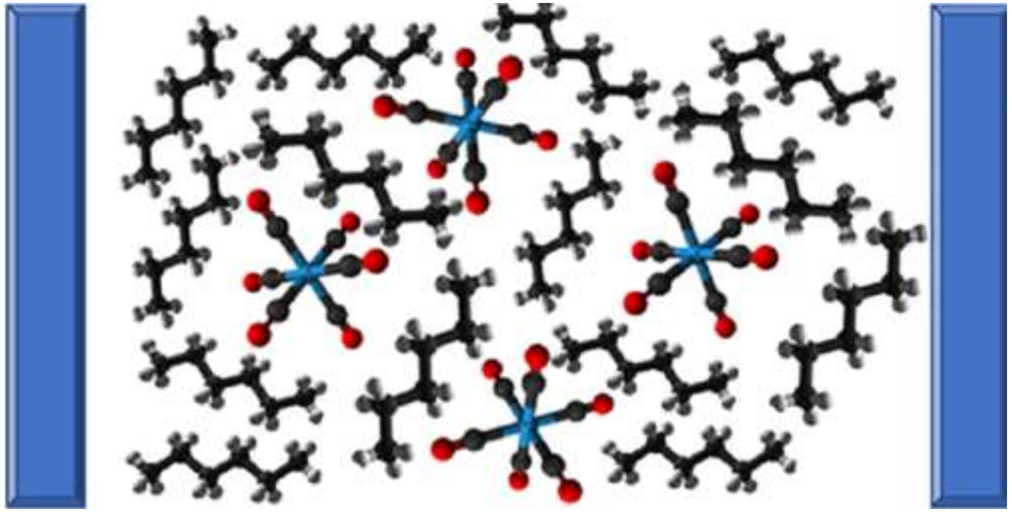


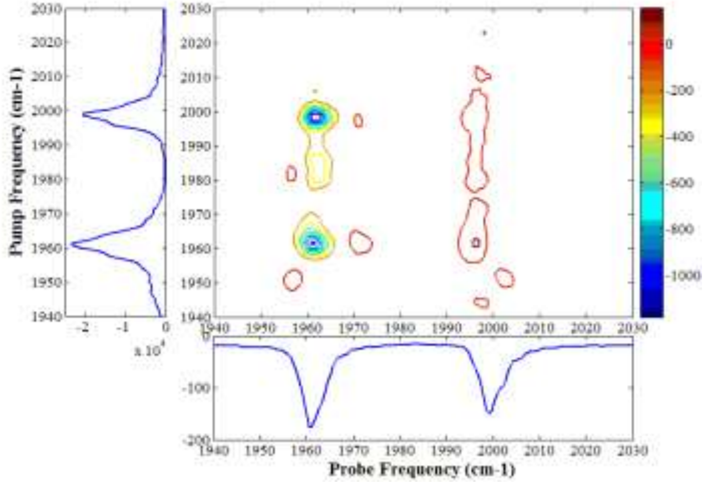


B. Xiang, R. F. Ribeiro, Y. Li, A. D. Dunkelberger, B. B. Simpkins, J. Yuen-Zhou, W. Xiong, arXiV: 1901.05526

Summary #2

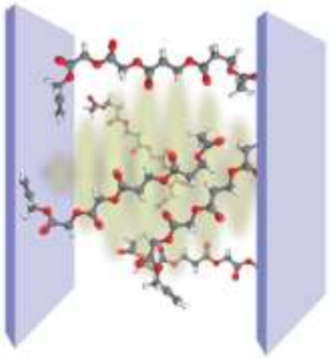
- Obtained and explained first vibrational polariton 2D spectra.
- Larger polariton samples have weaker nonlinearities.
- Coherent nonlinear optical "polariton bleach" effect (nonlinear dephasing) at short times.





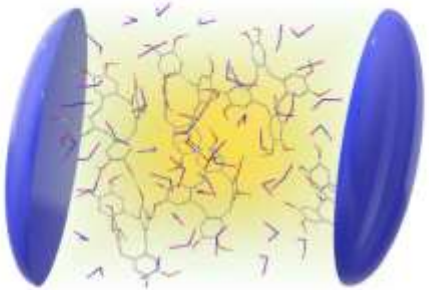
B. Xiang, R. F. Ribeiro, A. D. Dunkelberger, J. C. Owrutsky, B. S. Simpkins, J. Yuen-Zhou, and W. Xiong, PNAS 115, 19 (2018).
R.F. Ribeiro, R. F. Ribeiro, A. D. Dunkelberger, J. C. Owrutsky, B. S. Simpkins, W. Xiong, J. Yuen-Zhou, J. Phys. Chem. Lett. 9, 13 (2018).
B. Xiang, R. F. Ribeiro, Y. Li, A. D. Dunkelberger, B. B. Simpkins, J. Yuen-Zhou, W. Xiong, arXiV: 1901.05526

Outline of talk

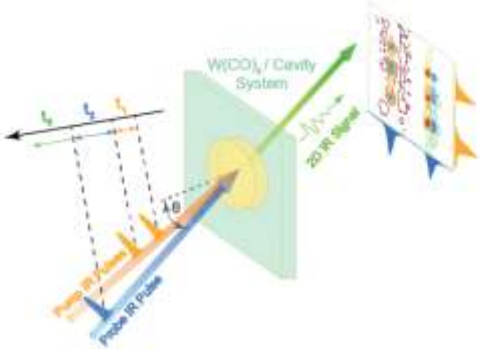


Vibrational polaritons

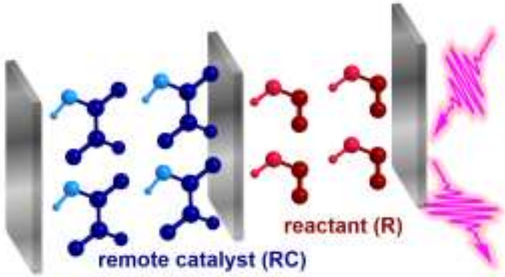
Ground-state reactivity



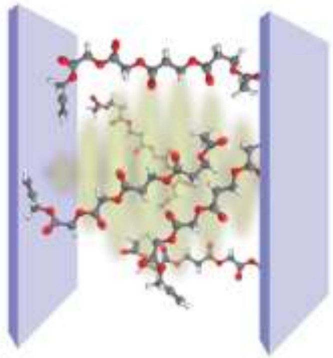
Nonlinearities



Remote control

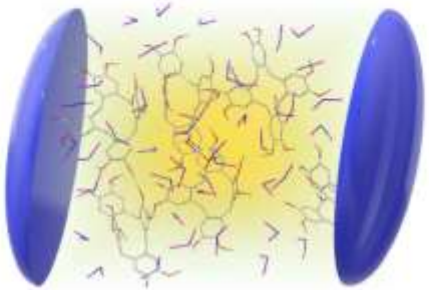


Outline of talk

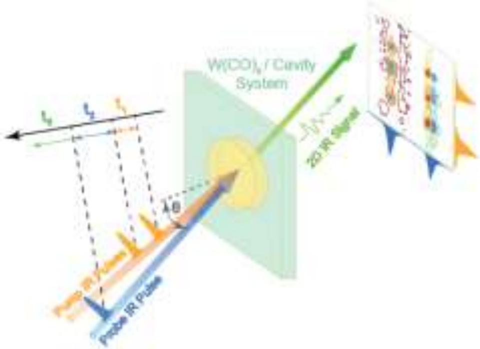


Vibrational polaritons

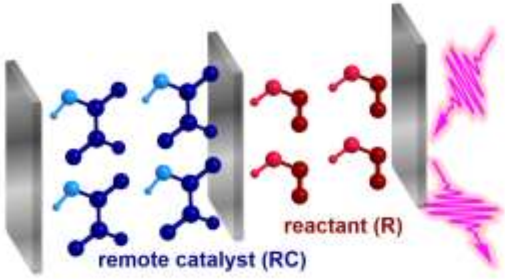
Ground-state reactivity



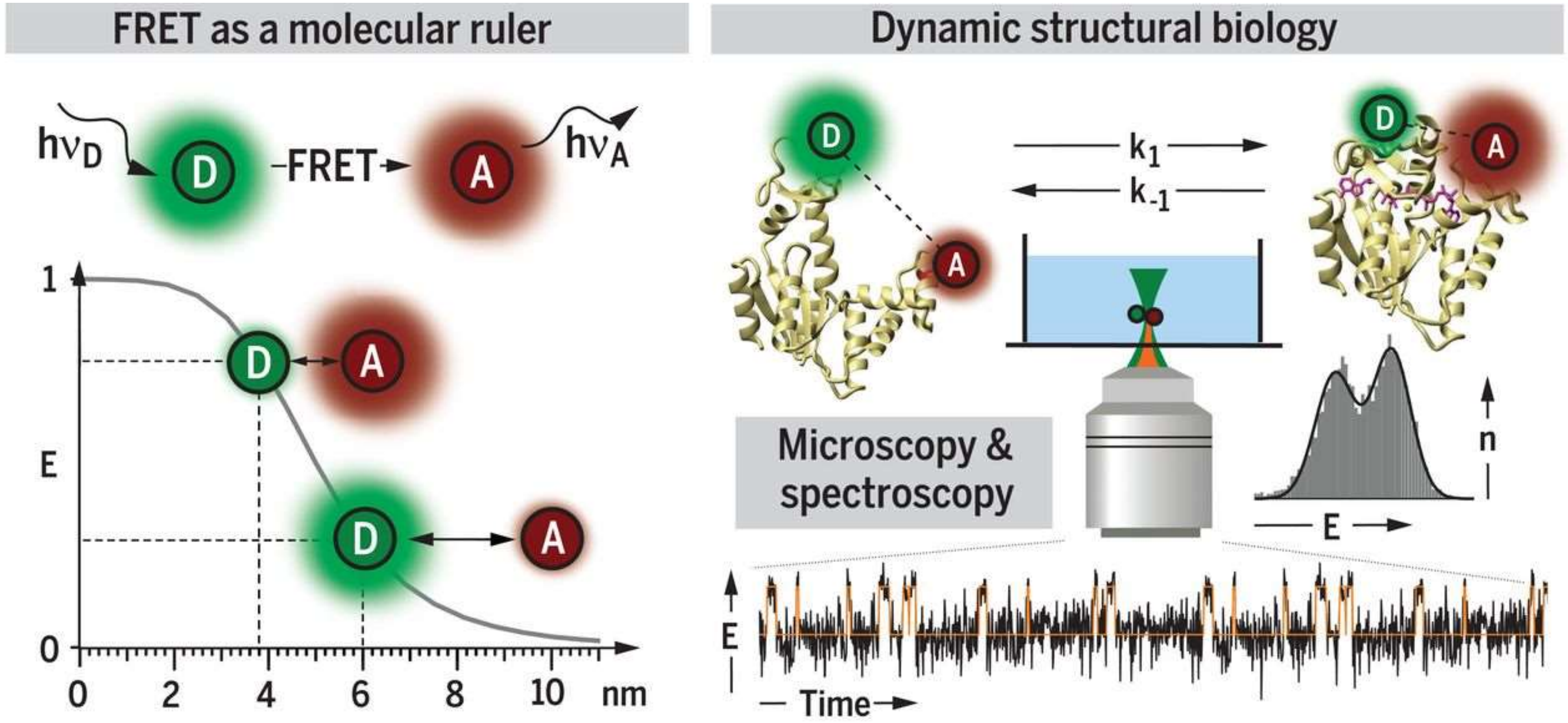
Nonlinearities



Remote control



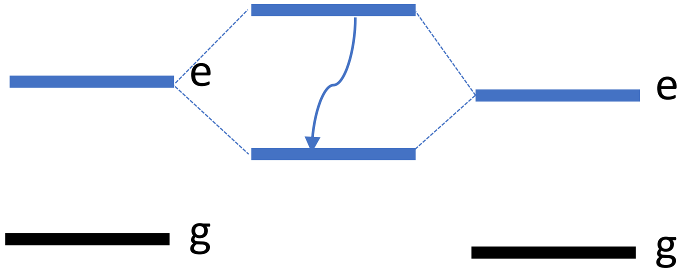
Forster Resonance Energy Transfer (FRET)



Energy transfer across ~10 nm.

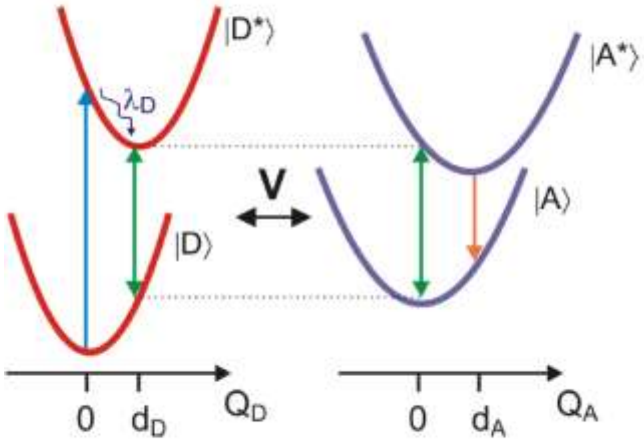
Excitation energy transfer: two cases

Davydov (1948)/Redfield (1965)



V>>coupling to phonons

Forster (1948)

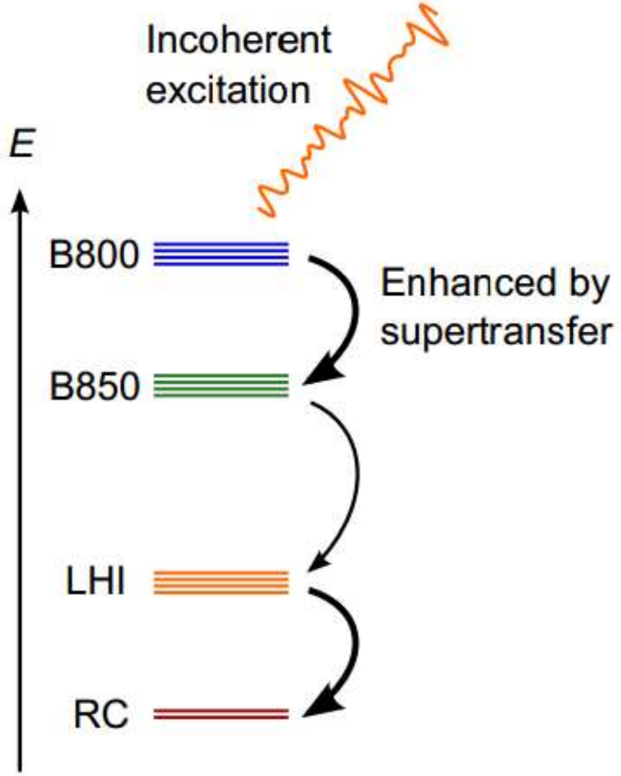


A. Tokmakoff (UChicago, online notes)

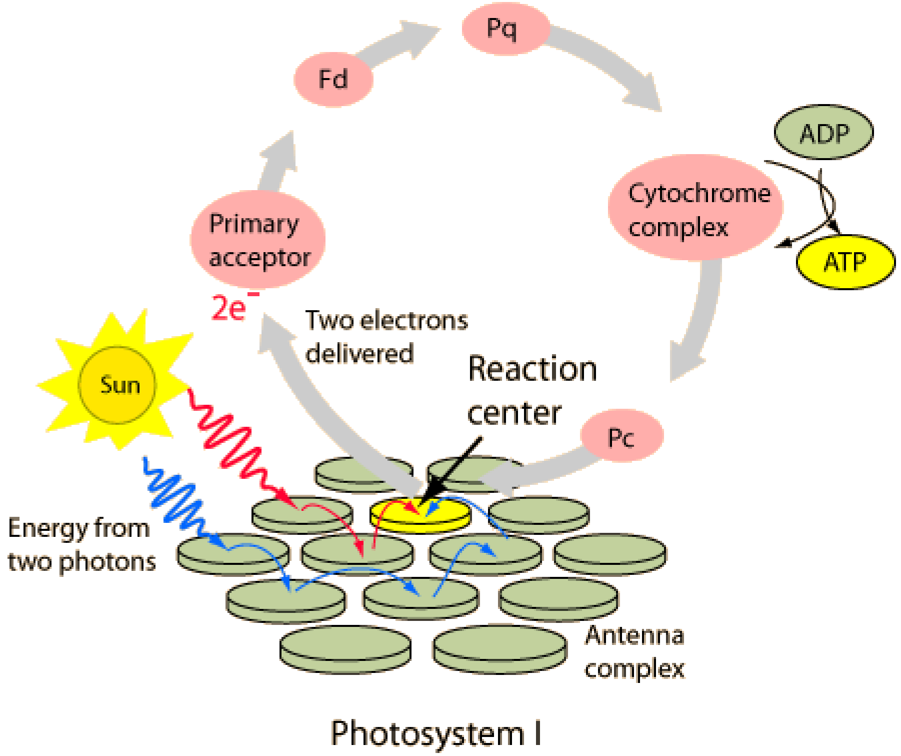
V<<coupling to phonons

Excitation energy transfer: two cases

Davydov (1948)/Redfield (1965)



Forster (1948)



V>>coupling to phonons

V<<coupling to phonons

Polariton assisted remote energy transfer (PARET)

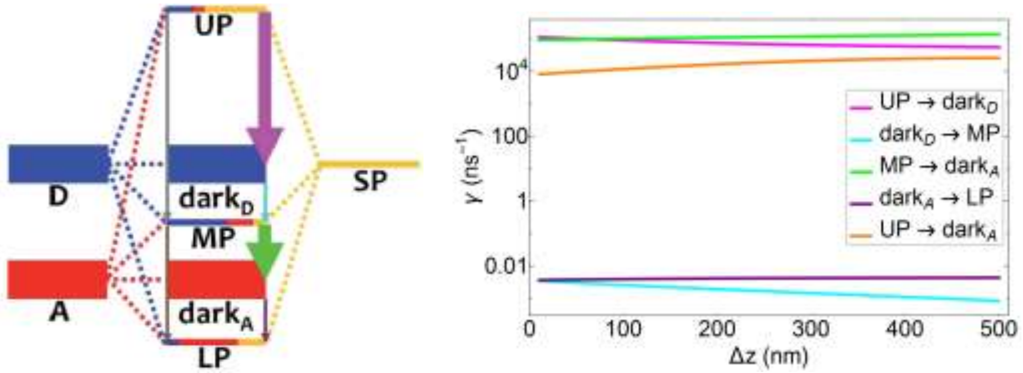
ARTICLES
PUBLISHED ONLINE: 4 MAY 2014 | DOI: 10.1038/NMAT3950
nature materials

Polariton-mediated energy transfer between organic dyes in a strongly coupled optical microcavity

David M. Coles[1†], Niccolo Somaschi[2,3], Paolo Michetti[4], Caspar Clark[5], Pavlos G. Lagoudakis[2], Pavlos G. Savvidis[6,7] and David G. Lidzey[1*]

Theory for polariton-assisted remote energy transfer†

Matthew Du,[a] Luis A. Martínez-Martínez,[a] Raphael F. Ribeiro,[a], Zixuan Hu,[bc] Vinod M. Menon,[de] and Joel Yuen-Zhou*[a]

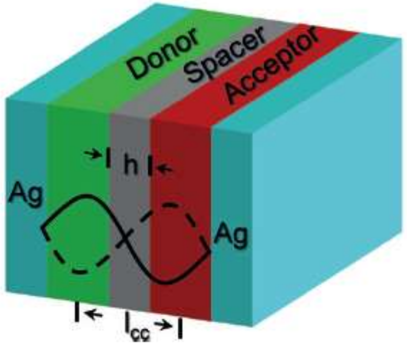


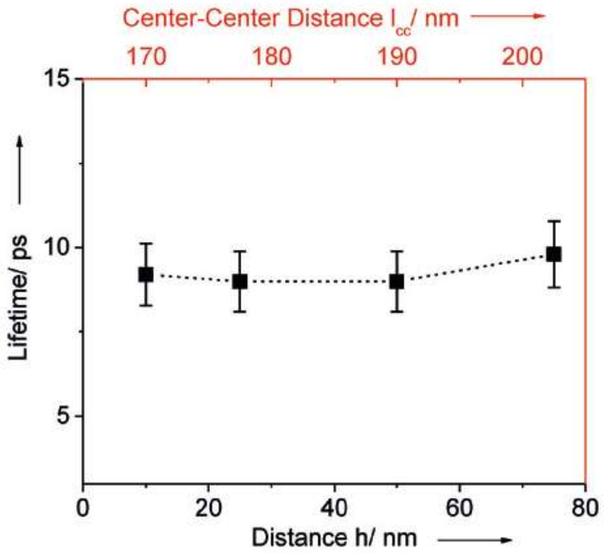
M. Du, L.A. Martinez-Martinez, R.F. Ribeiro, V.M. Menon, J. Yuen-Zhou, *Chem. Sci.* 9, 6659-6669 (2018).

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**

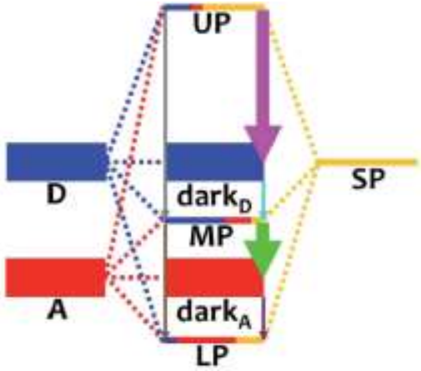


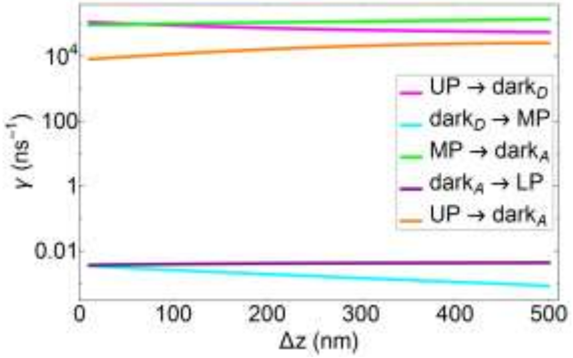


Zhong et al., Angew. Chem., Int. Ed., 2017, 56, 9034–9038.

Theory for polariton-assisted remote energy transfer†

Matthew Du,[a] Luis A. Martínez-Martínez,[a] Raphael F. Ribeiro,[a], Zixuan Hu,[bc] Vinod M. Menon,[de] and Joel Yuen-Zhou*[a]





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

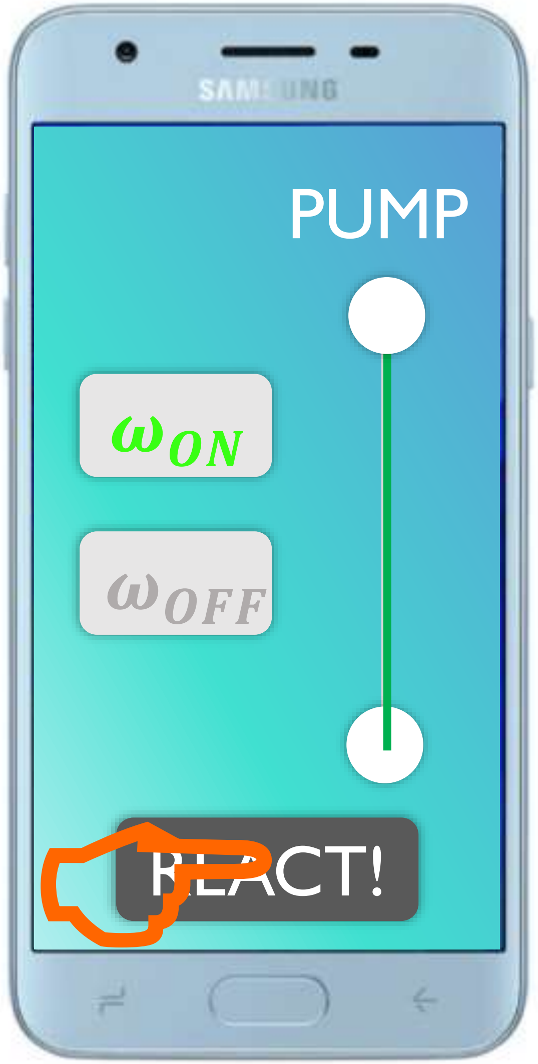
Acknowledgements

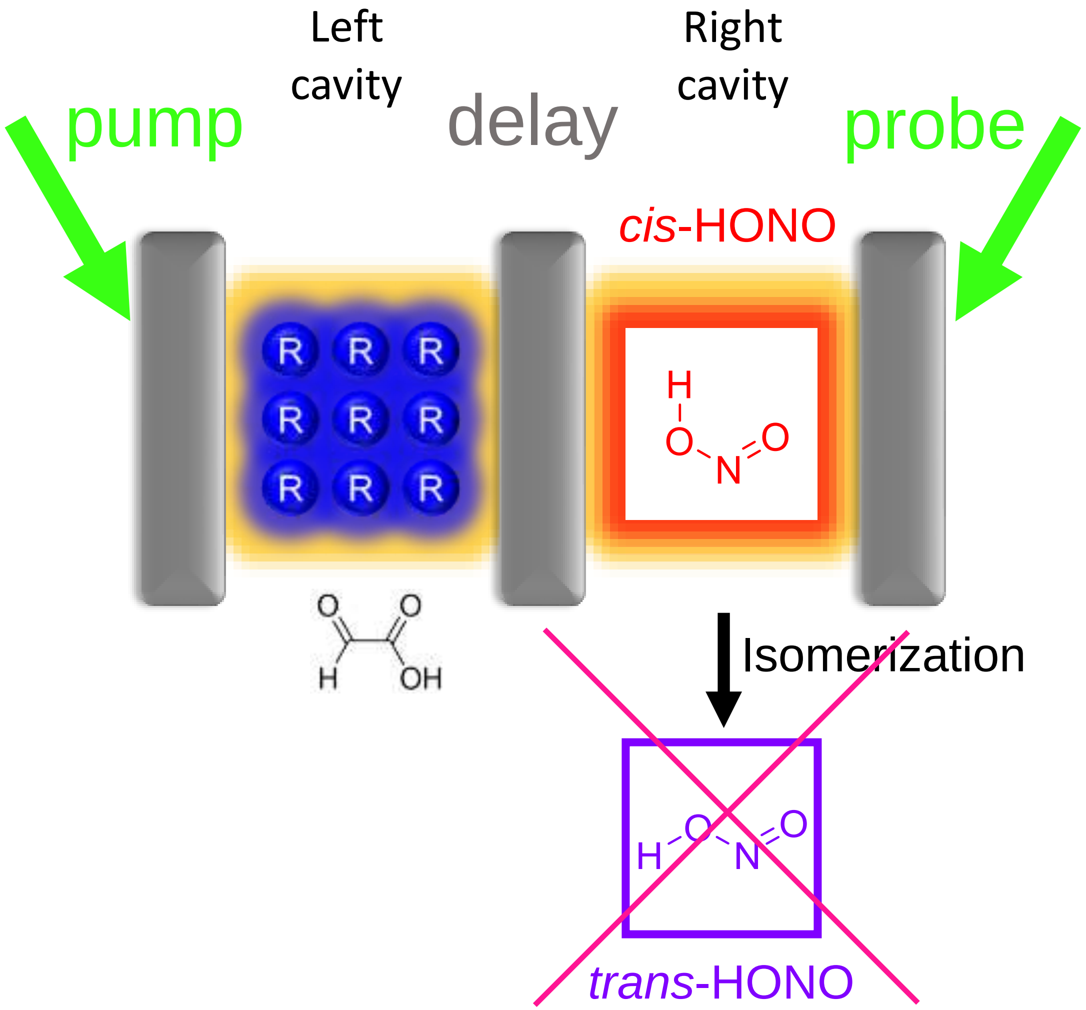
Matthew Du

Raphael Ribeiro

Is remote control of chemistry possible?

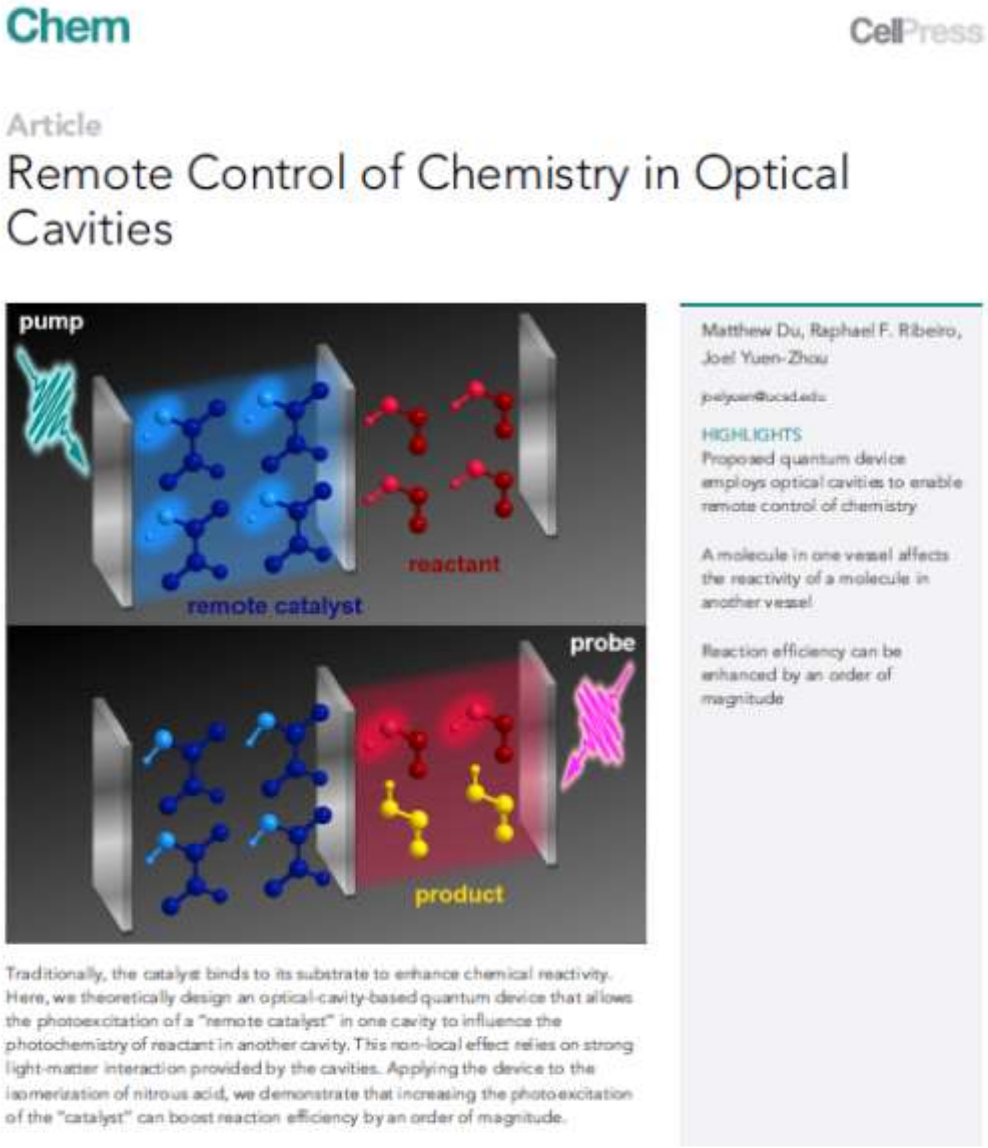
From PARET to remote control of chemistry





M. Du, R. F. Ribeiro, J. Yuen-Zhou, *Chem.* 5, 1167-1181 (2019)

From PARET to remote control of chemistry



Chem

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Article

Remote Control of Chemistry in Optical Cavities

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

joelyuen@ucsd.edu

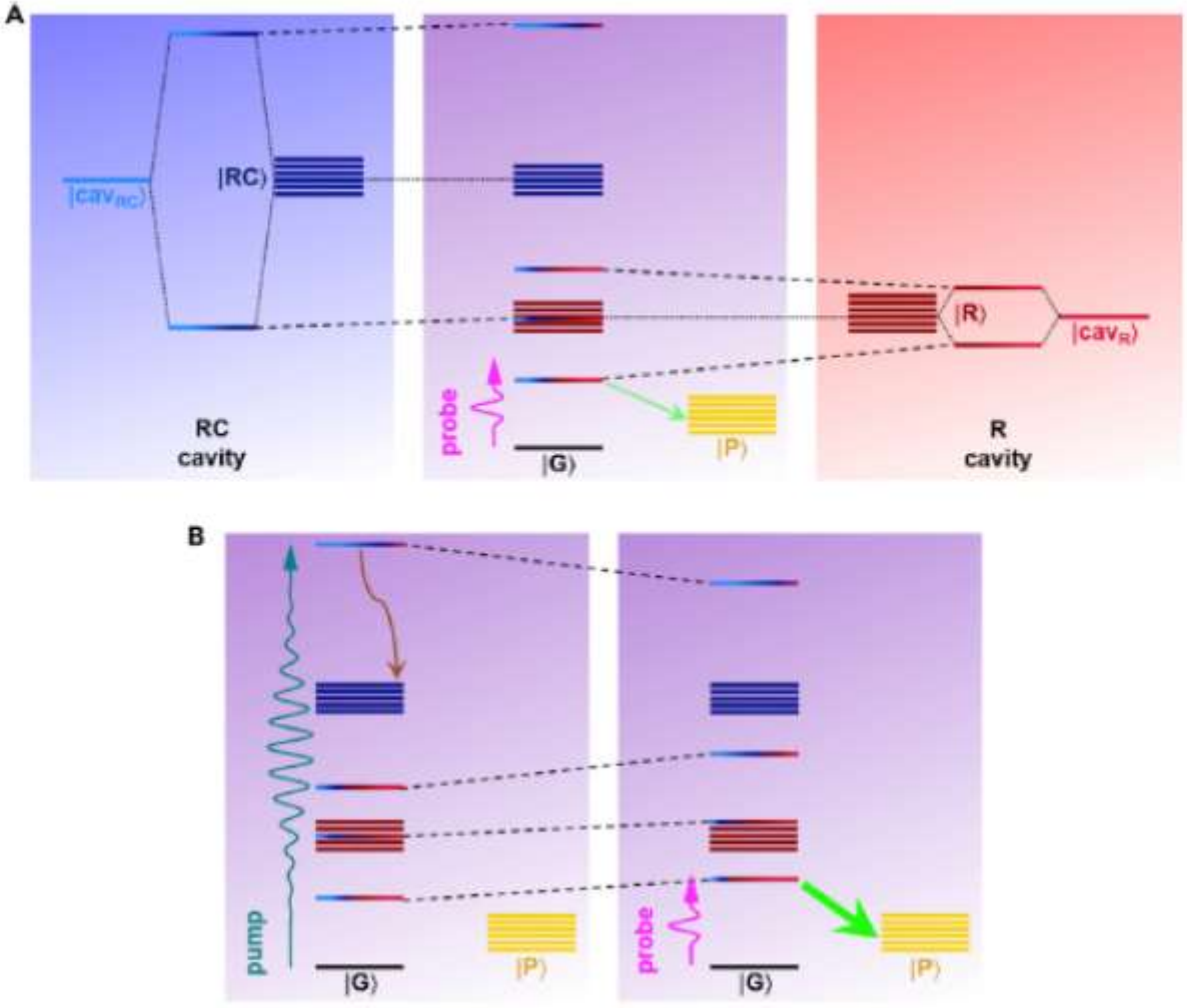
HIGHLIGHTS

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

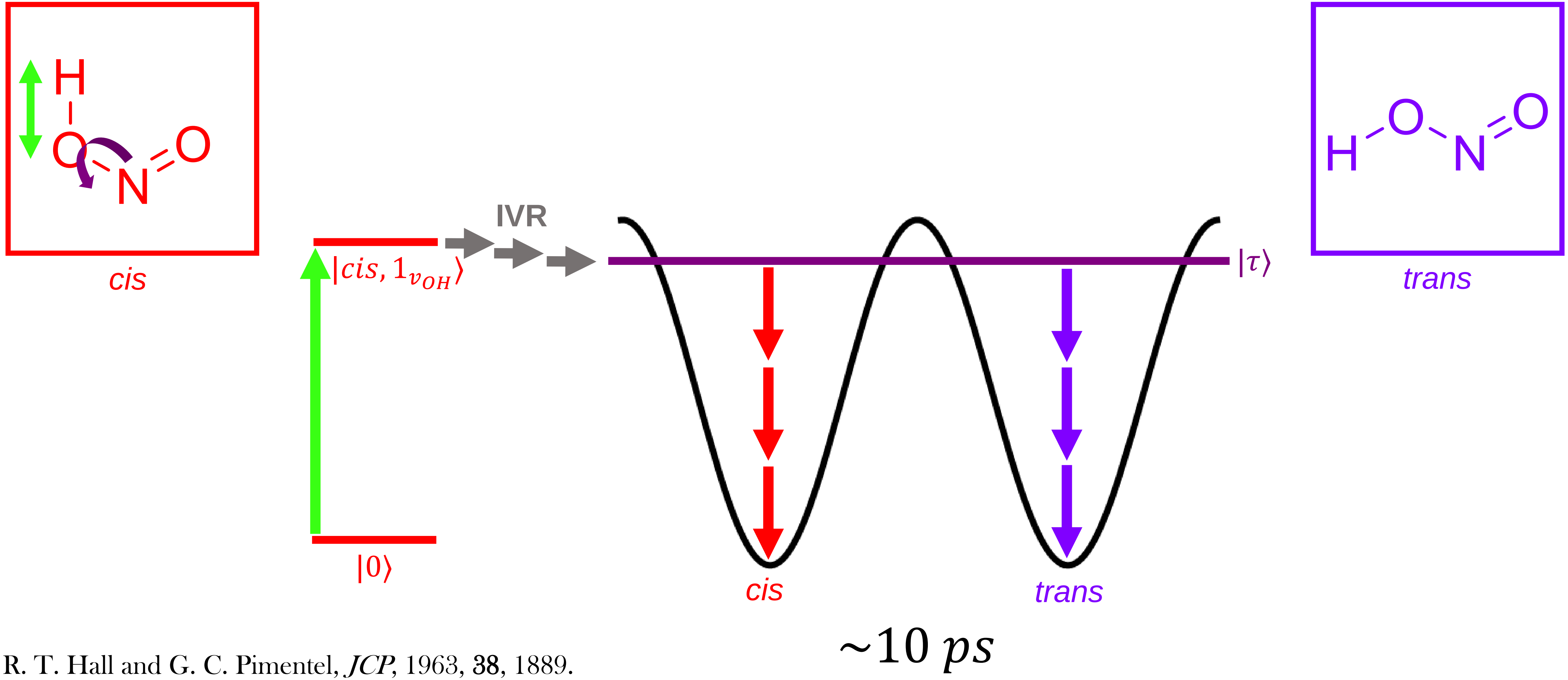
Reaction efficiency can be enhanced by an order of magnitude

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.



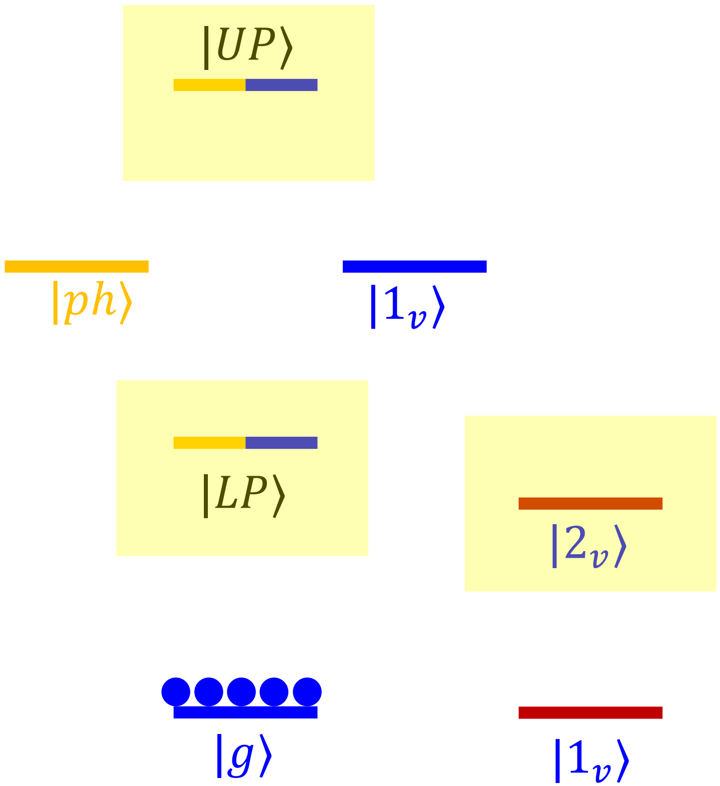
M. Du, R. F. Ribeiro, J. Yuen-Zhou, *Chem.* 5, 1167-1181 (2019)

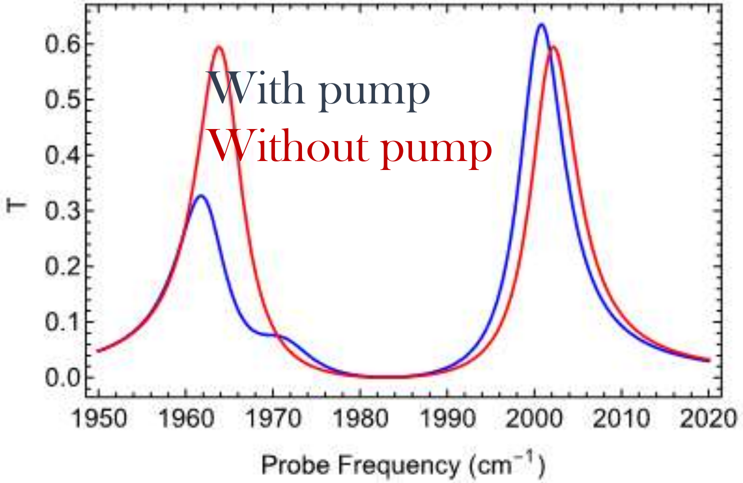
IR-induced, vibrationally-selective chemistry: *cis*→*trans* isomerization of HONO

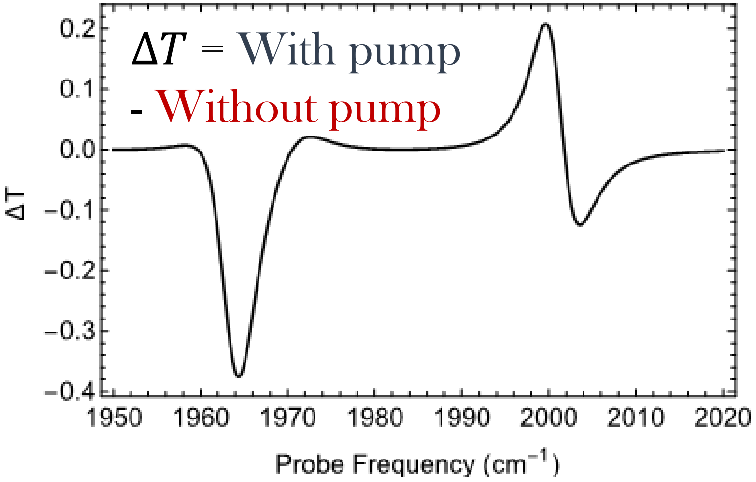


R. T. Hall and G. C. Pimentel, *JCP*, 1963, **38**, 1889.
R. Schanz, V. Botan, and P. Hamm, *JCP*, 2005, **122**, 044509.

Ultrafast switching of polaritons



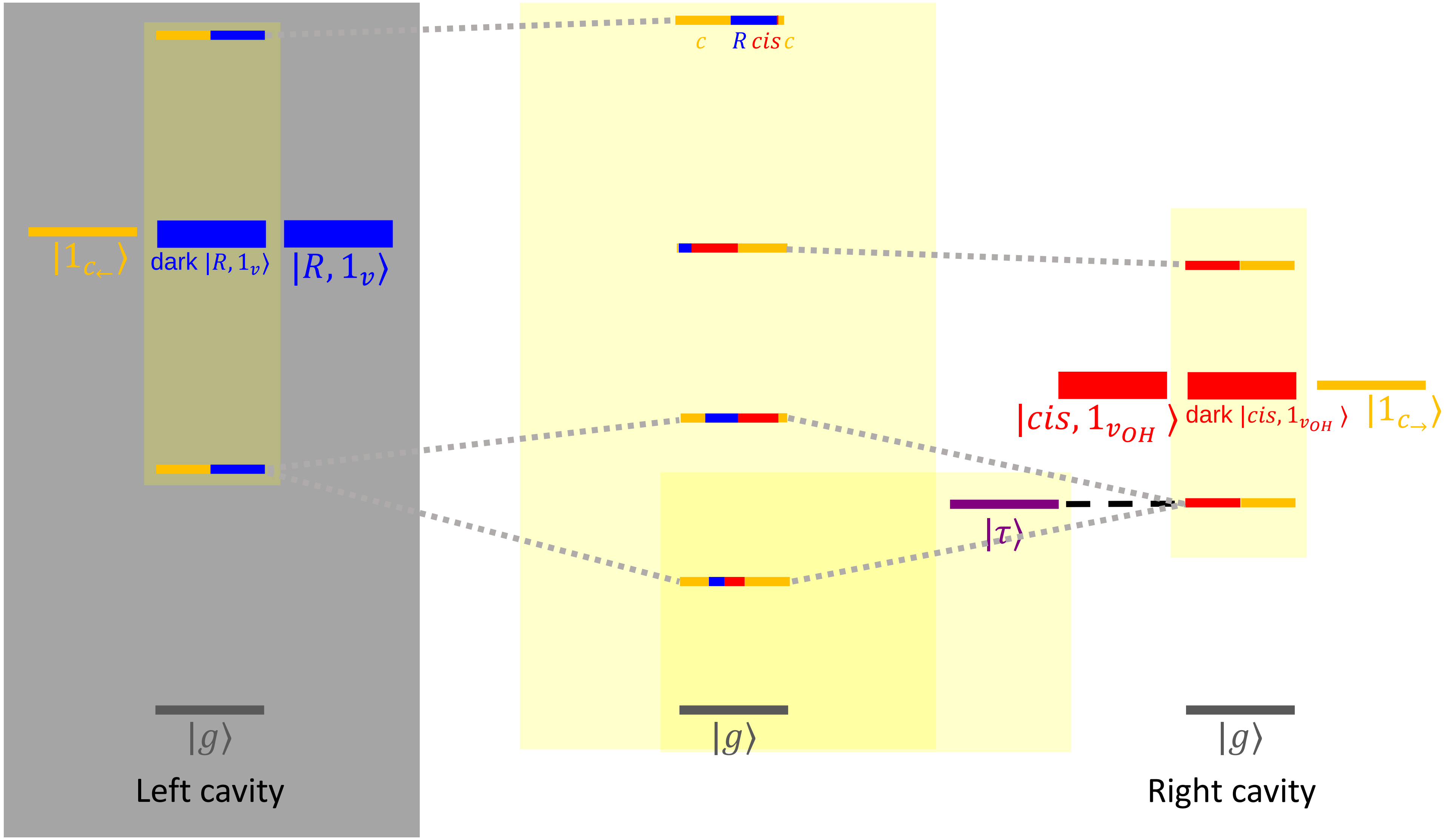




B. Xiang, R. F. Ribeiro, A. D. Dunkelberger, J. C. Owrutsky, B. S. Simpkins, J. Yuen-Zhou, and W. Xiong, PNAS 115, 19 (2018).

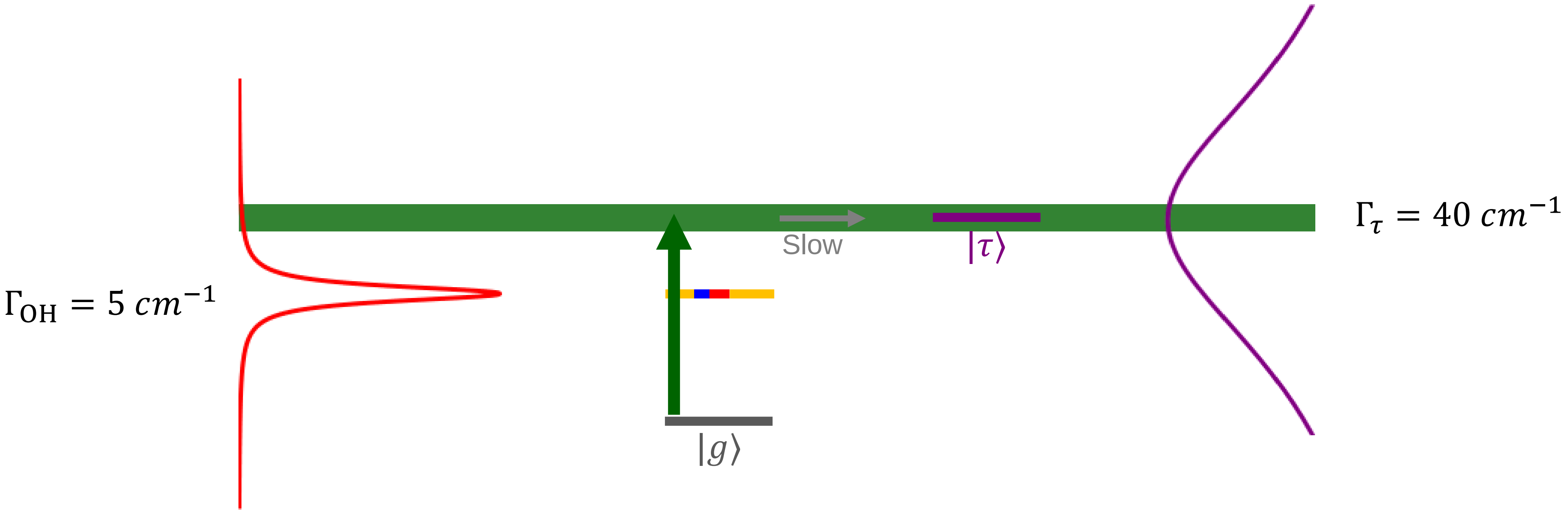
R.F. Ribeiro, R. F. Ribeiro, A. D. Dunkelberger, J. C. Owrutsky, B. S. Simpkins, W. Xiong, J. Yuen-Zhou, J. Phys. Chem. Lett. 9, 13 (2018).

Ultrafast remote-control chemistry



M. Du, R. F. Ribeiro, J. Yuen-Zhou, *Chem.* 5, 1167-1181 (2019)

Ultrafast remote-control chemistry



M. Du, R. F. Ribeiro, J. Yuen-Zhou, *Chem.* 5, 1167-1181 (2019)

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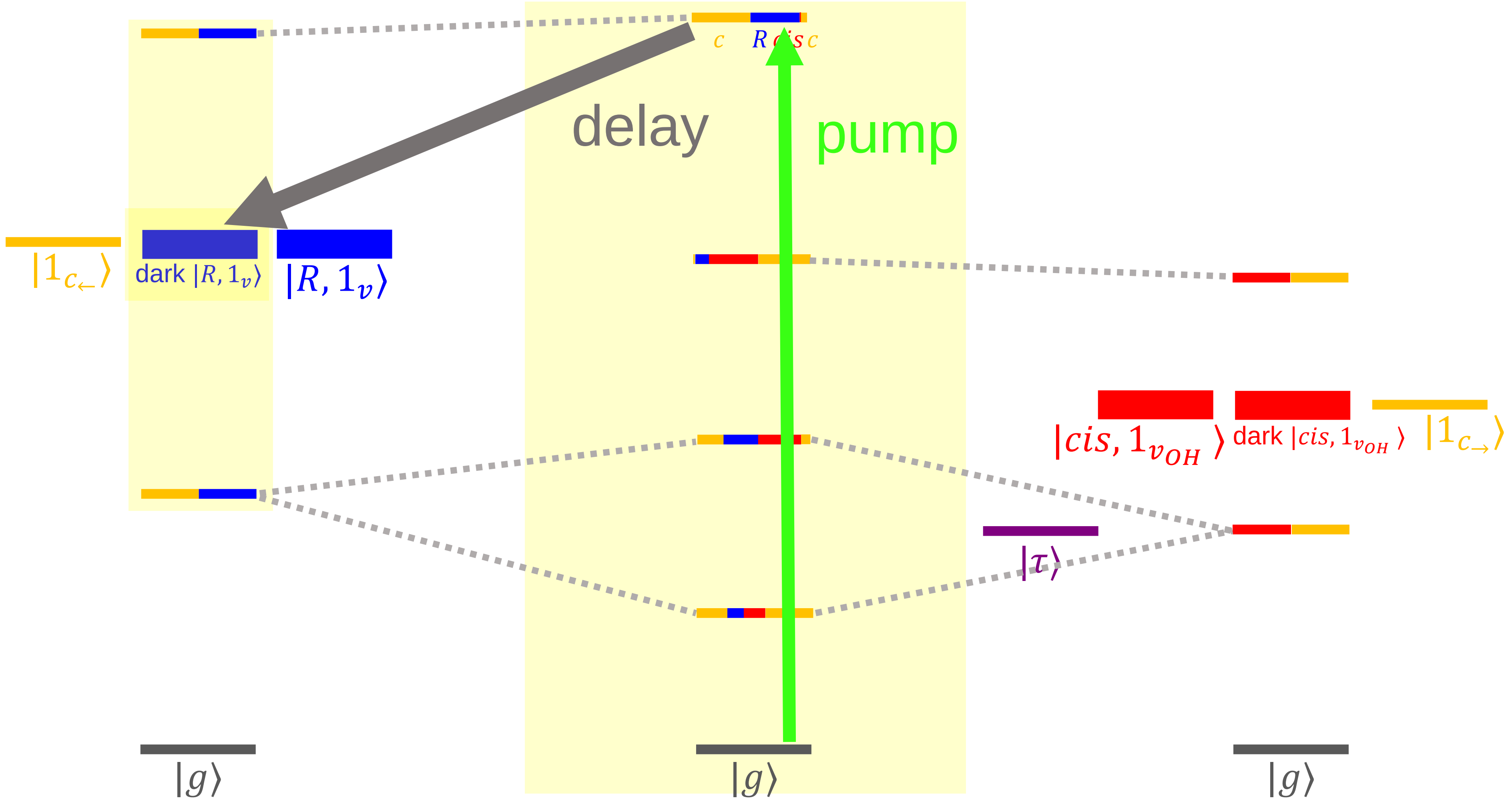

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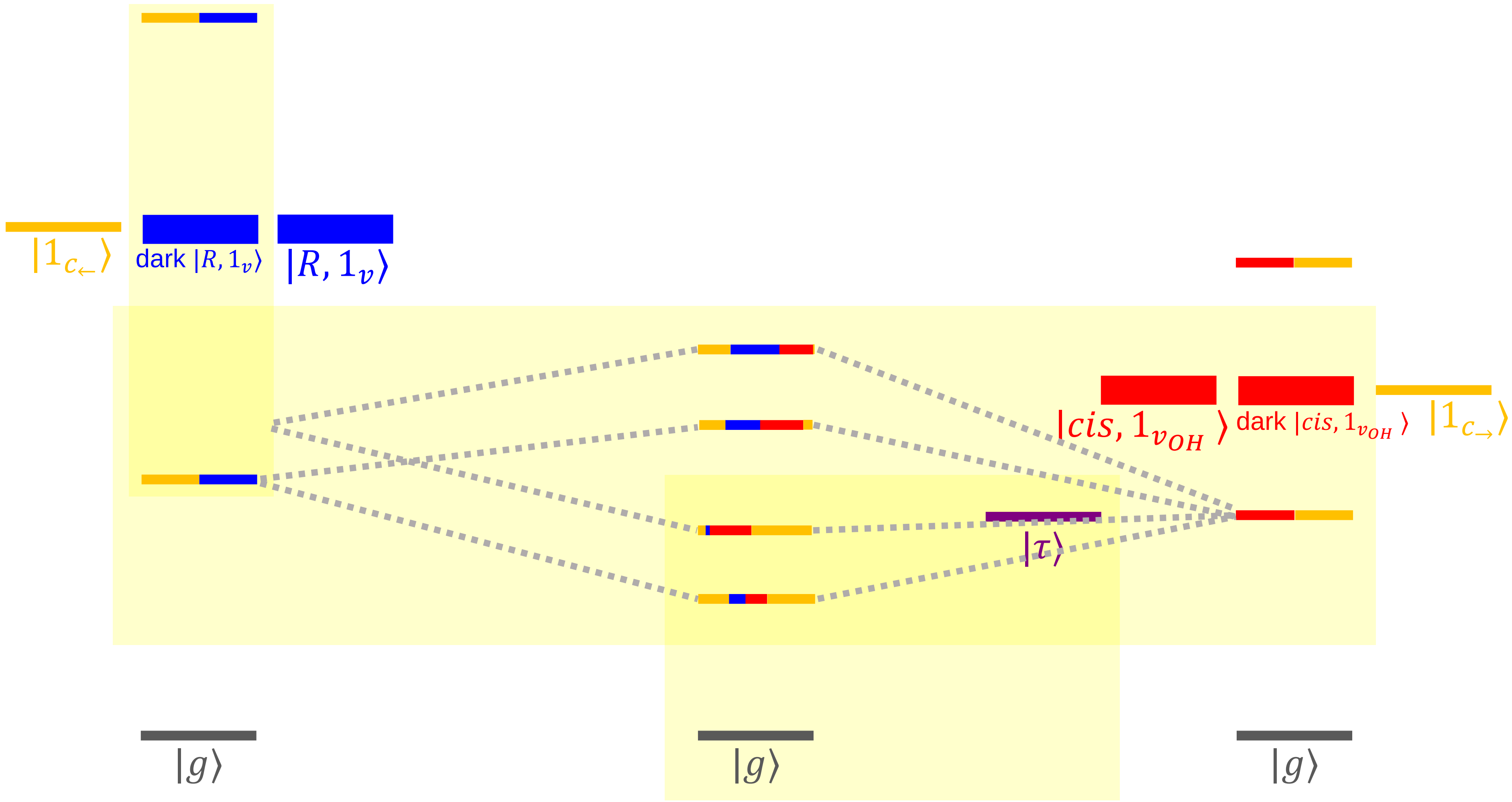
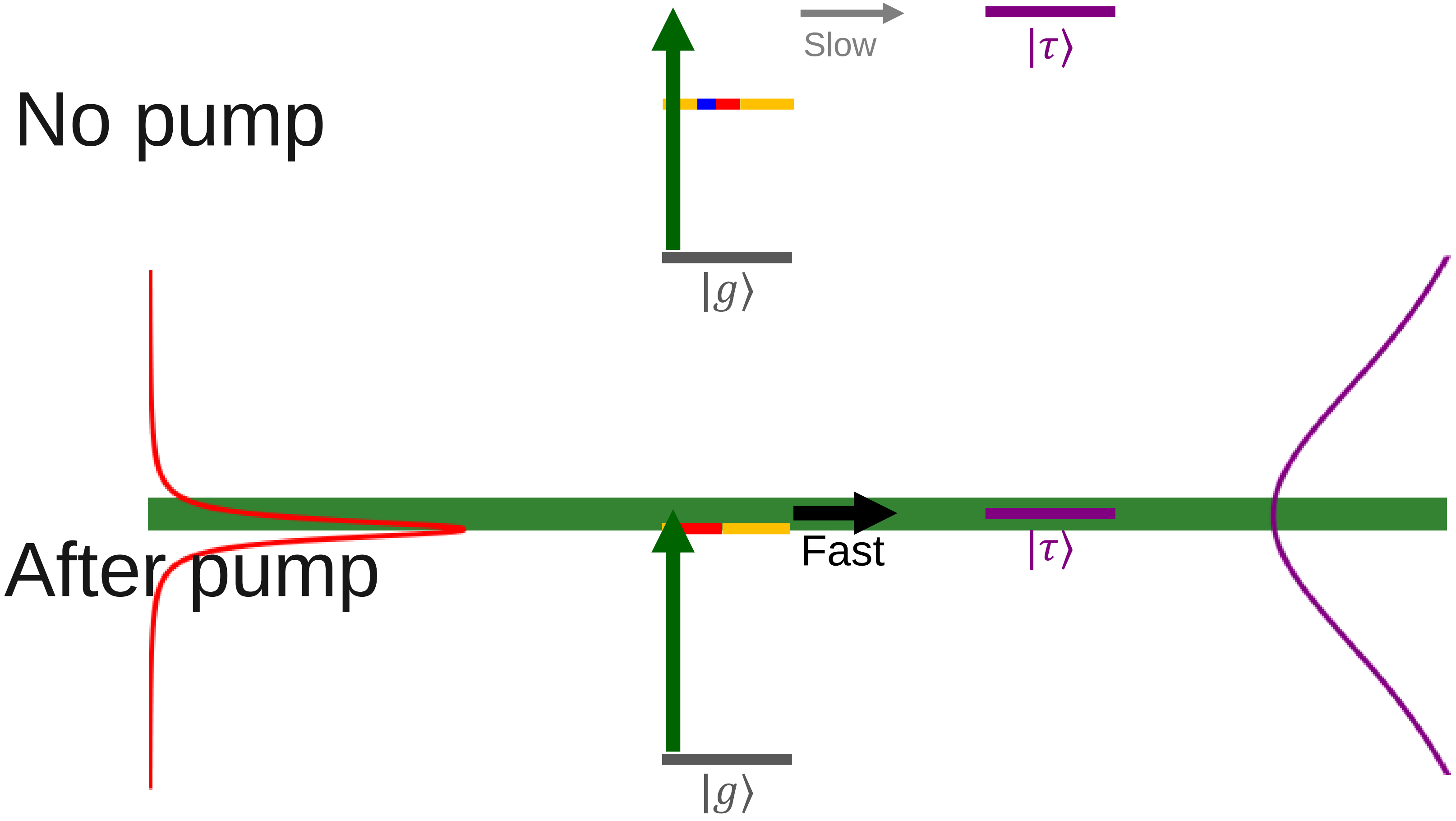
Ultrafast remote-control chemistry



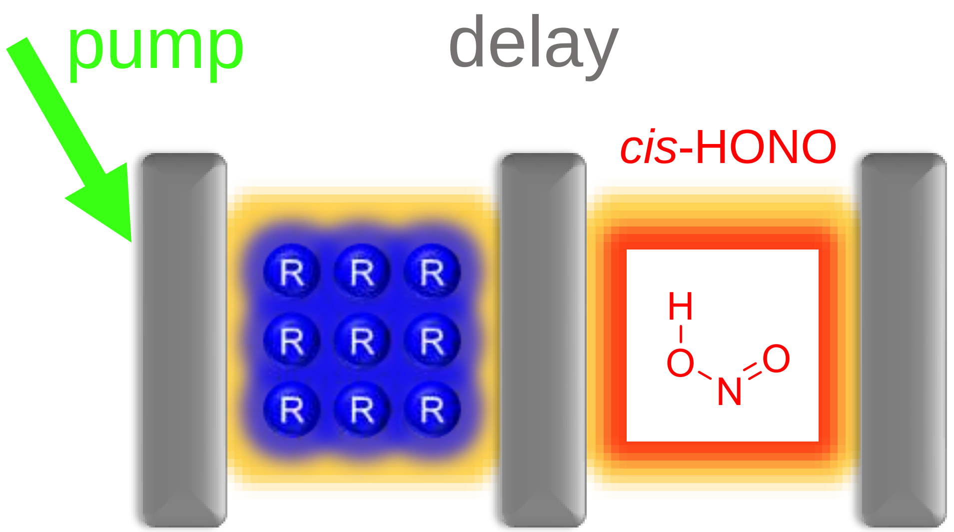
M. Du, R. F. Ribeiro, J. Yuen-Zhou, *Chem.* 5, 1167-1181 (2019)

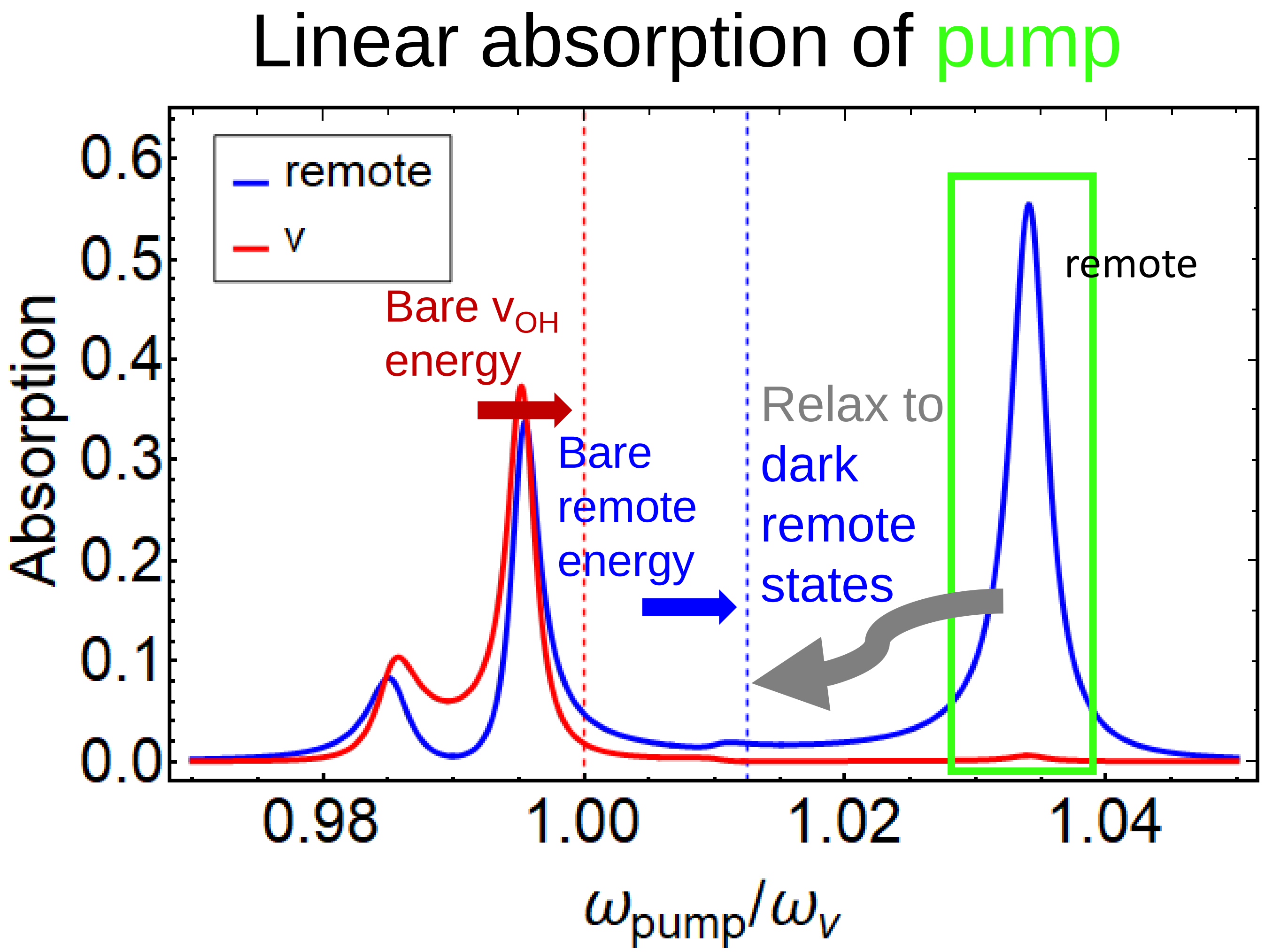
Ultrafast remote-control chemistry



M. Du, R. F. Ribeiro, J. Yuen-Zhou, *Chem.* 5, 1167-1181 (2019)

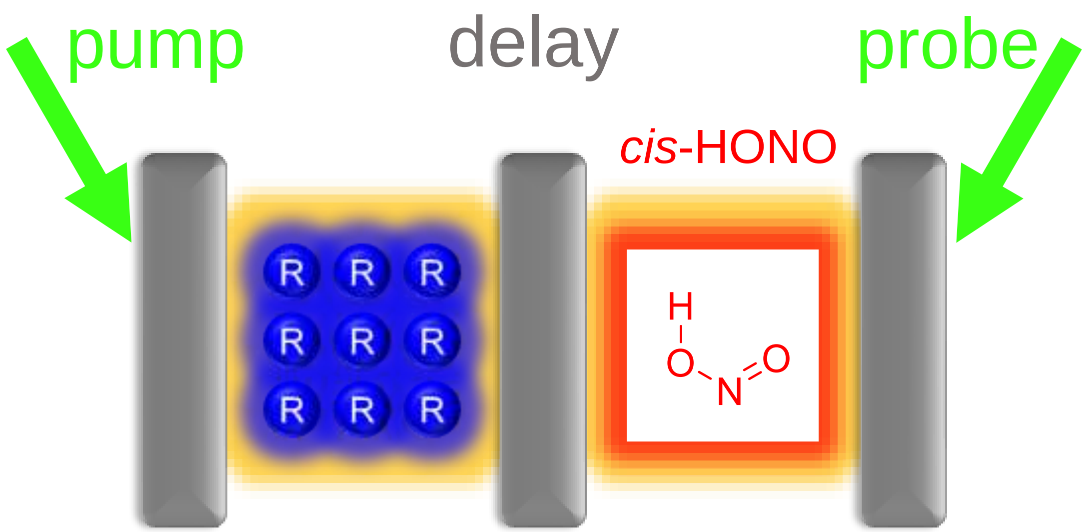
Pump tunes polariton energies on ultrafast timescale

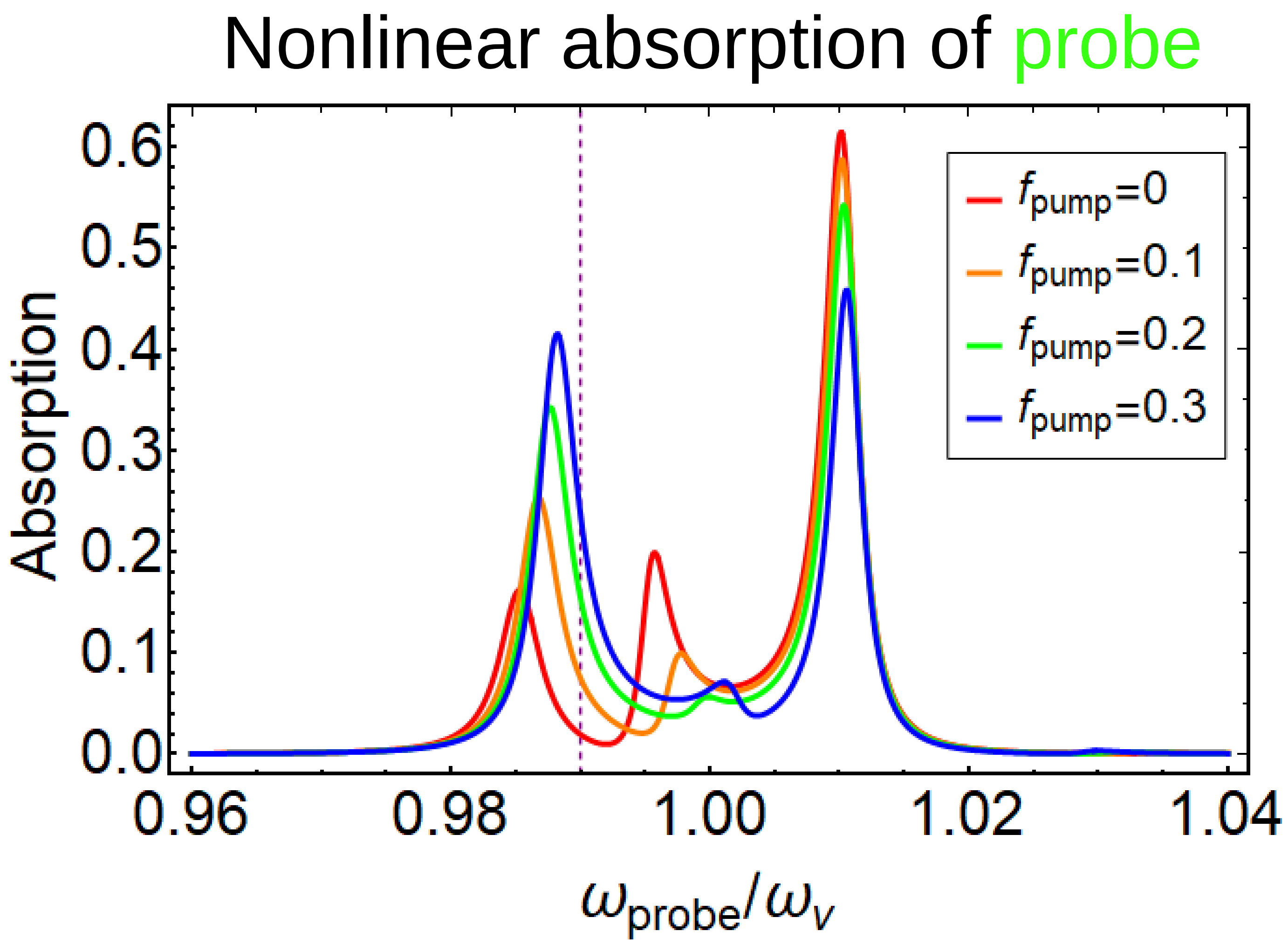




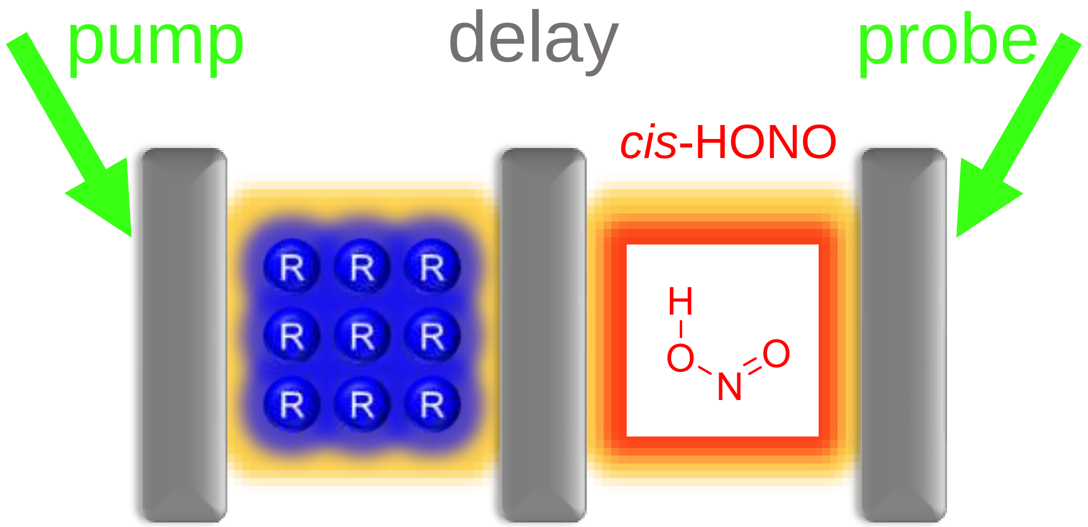
M. Du, R. F. Ribeiro, J. Yuen-Zhou, *Chem.* 5, 1167-1181 (2019)

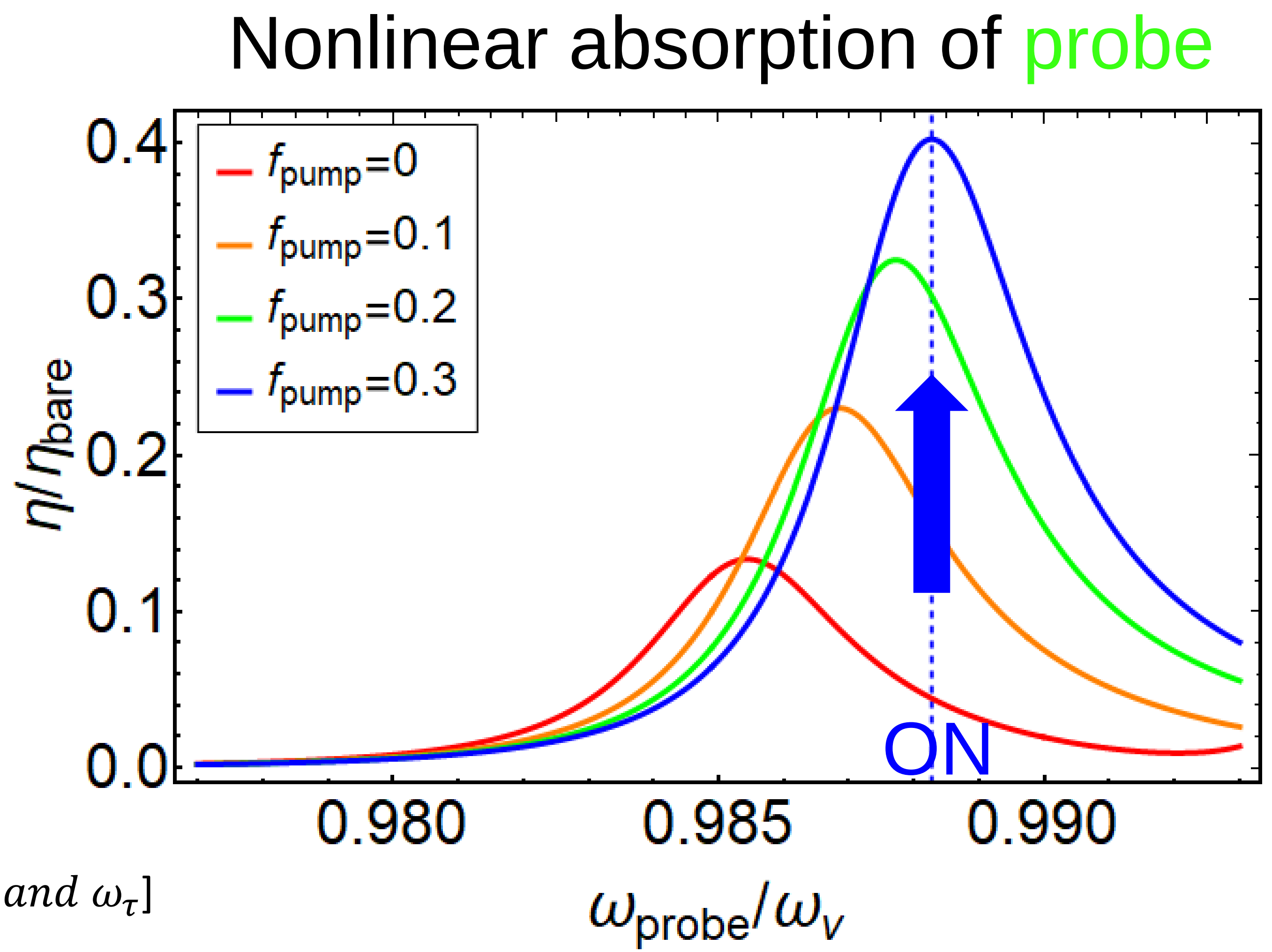
Pump tunes polariton energies on ultrafast timescale





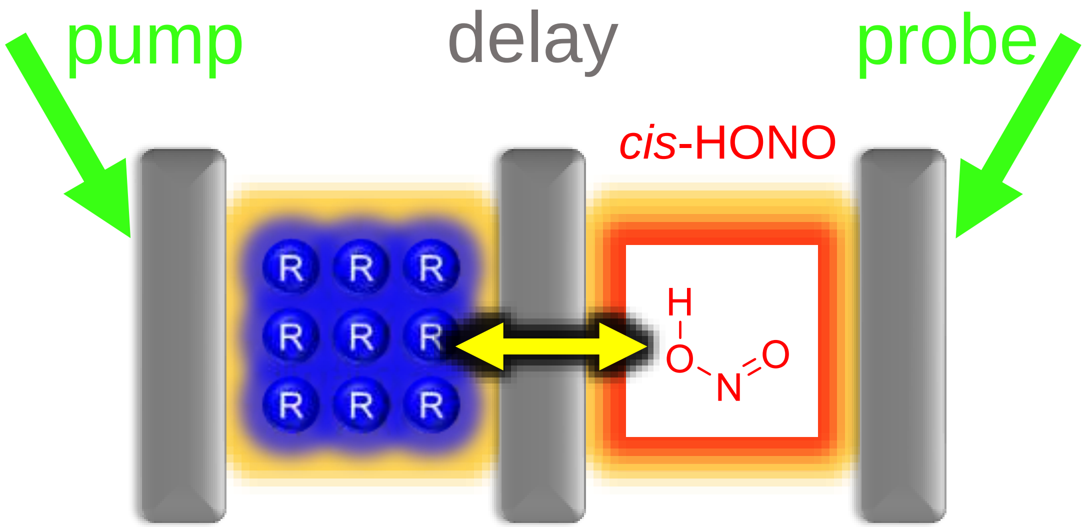
Pump turns ON reaction on ultrafast timescale

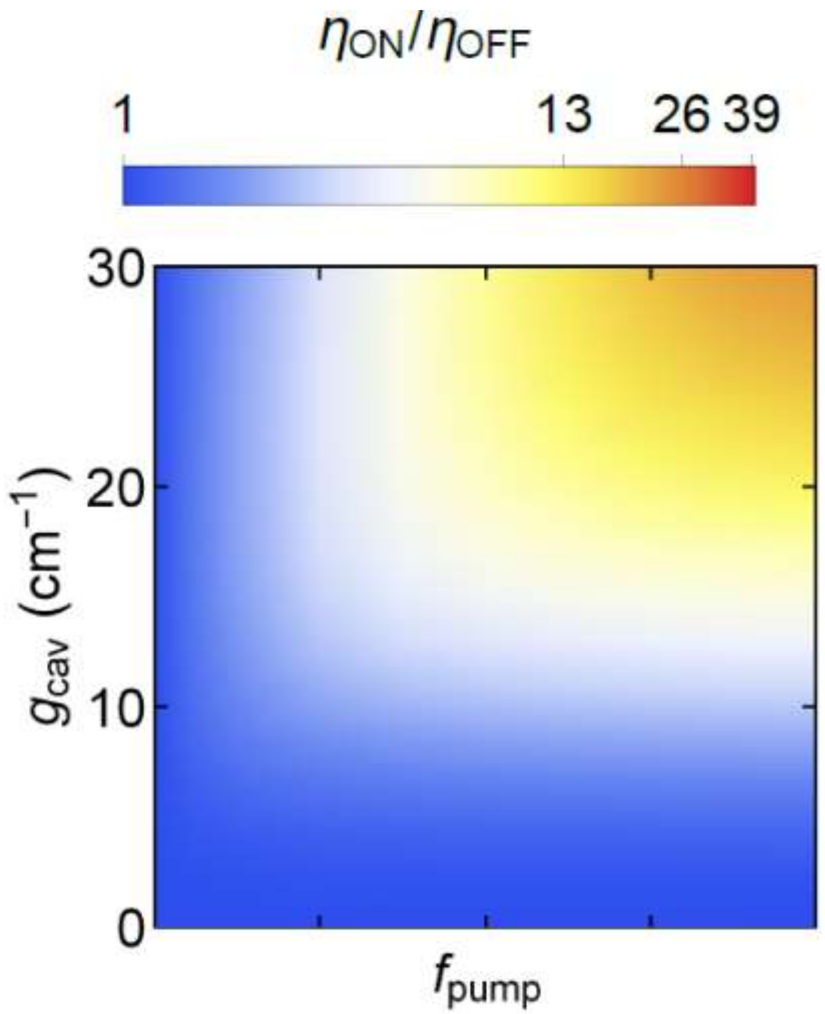




$$\eta(\omega) = Abs_{polariton}(\omega) \times QY(\omega)$$
$$= Abs_{polariton}(\omega) \times [Overlap\ between\ \omega\ and\ \omega_\tau]$$

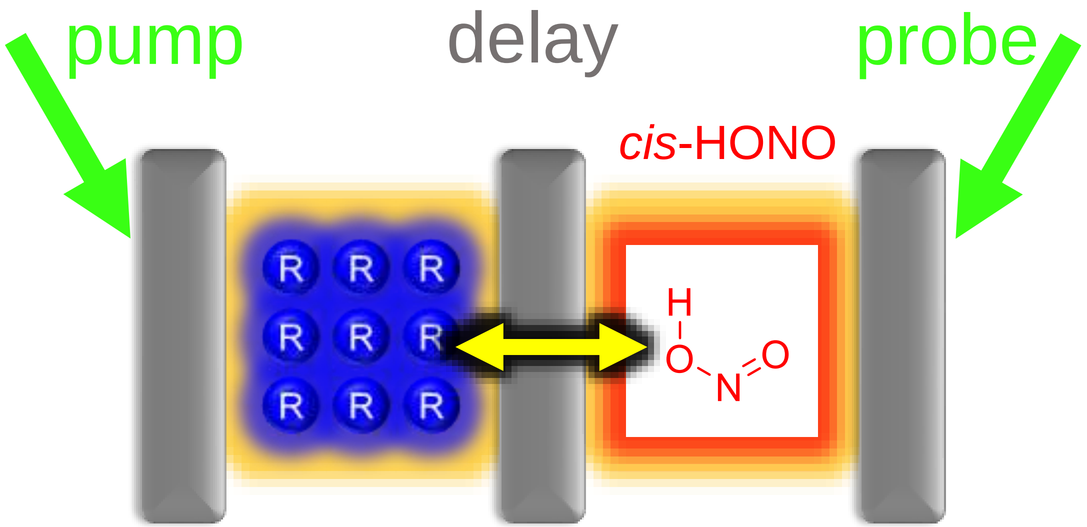
Cavity-cavity coupling g_c increases REACTION ENHANCEMENT of pump

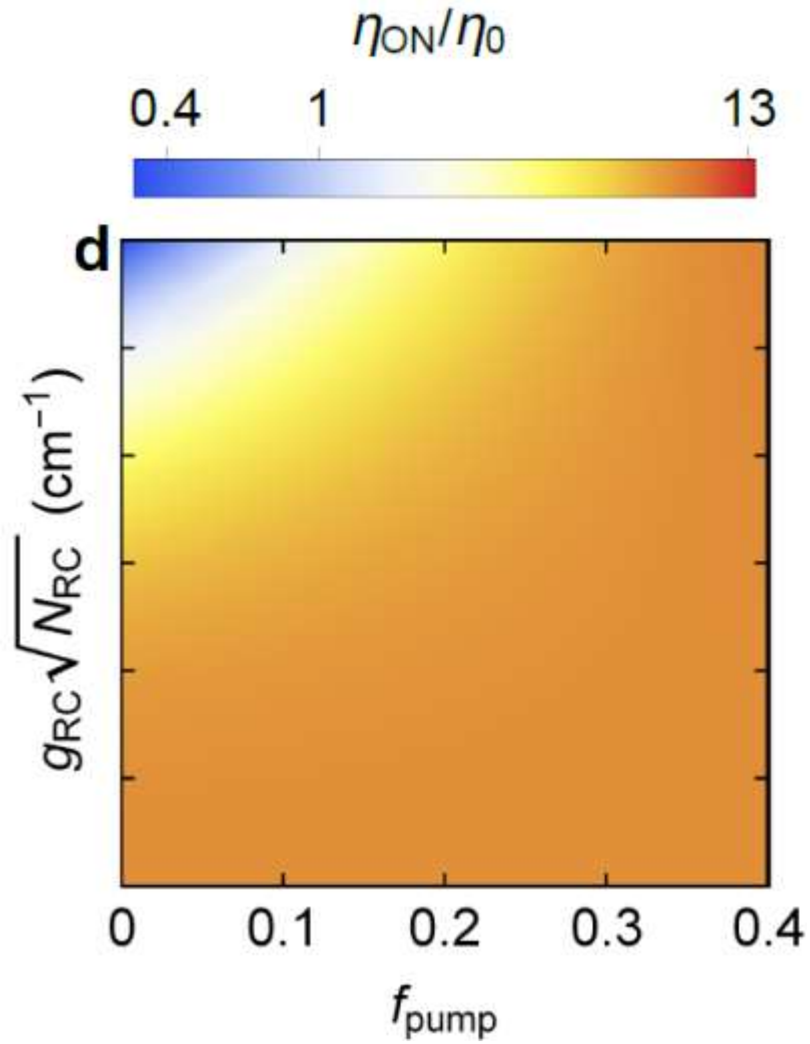




M. Du, R. F. Ribeiro, J. Yuen-Zhou, *Chem.* 5, 1167-1181 (2019)

Cavity-cavity coupling g_c increases REACTION ENHANCEMENT of pump

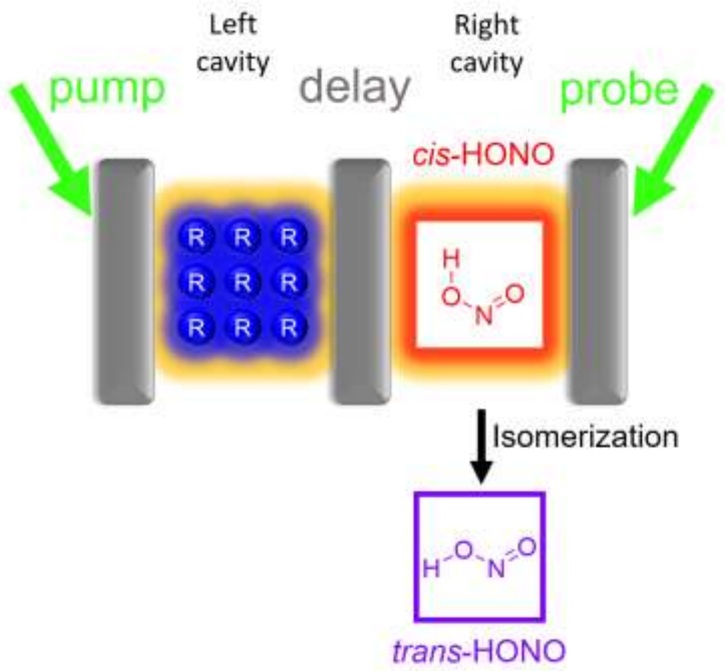


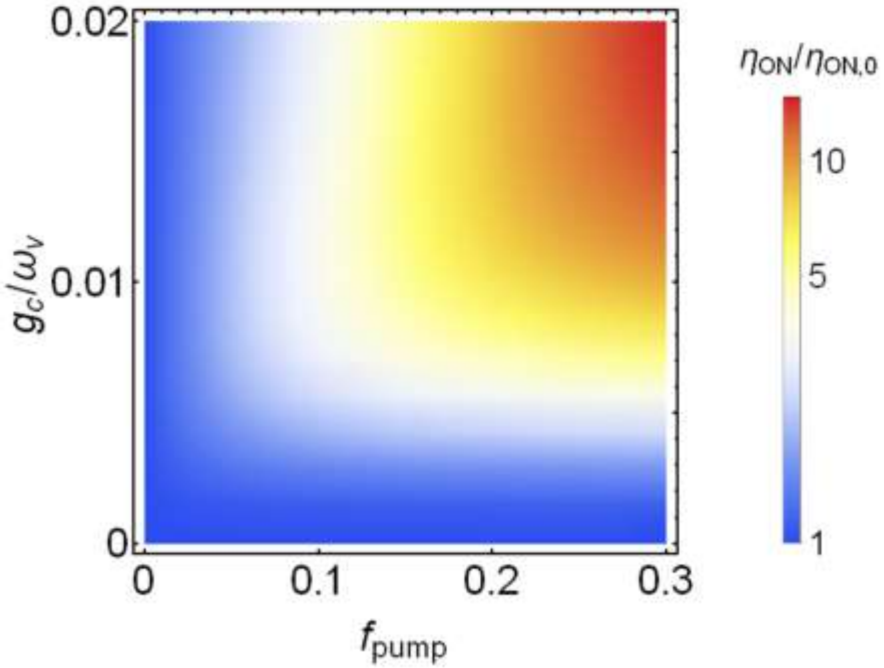


M. Du, R. F. Ribeiro, J. Yuen-Zhou, *Chem.* 5, 1167-1181 (2019)

Summary #3

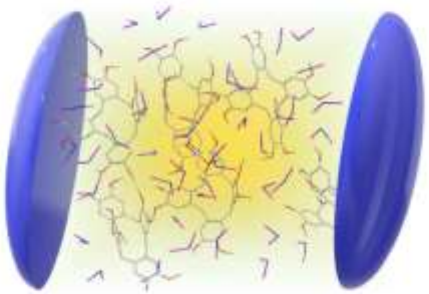
- Nonlinear ultrafast switching of polaritons should allow for remote control of a chemical reaction.
- Large tunability of efficiencies is expected for an IR-photoinduced isomerization.



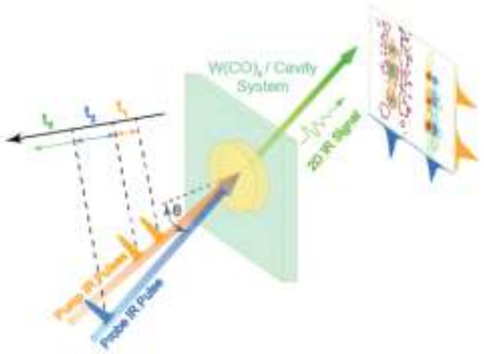


Outline of talk

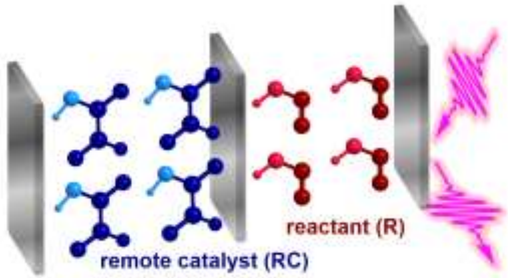
Ground-state reactivity

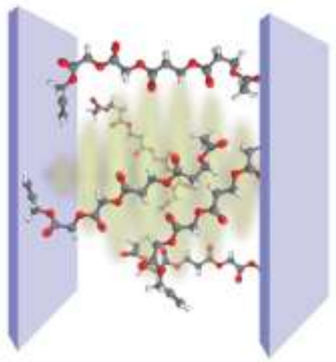


Nonlinearities



Remote control





Vibrational polaritons

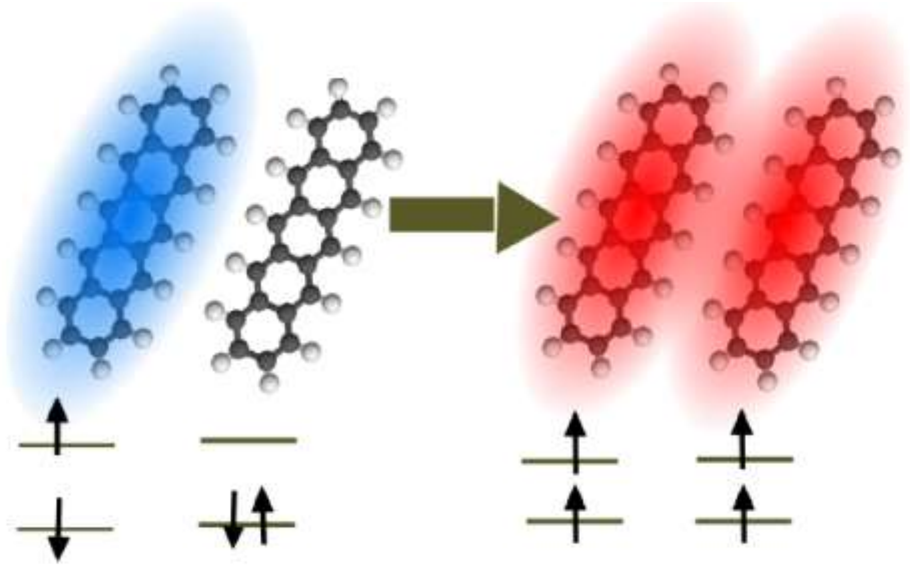
Other works: Photophysics

The Journal of Physical Chemistry Letters
Letter
Cite This: J. Phys. Chem. Lett. 2018, 9, 1951−1957
pubs.acs.org/JPCL

Polariton-Assisted Singlet Fission in Acene Aggregates

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

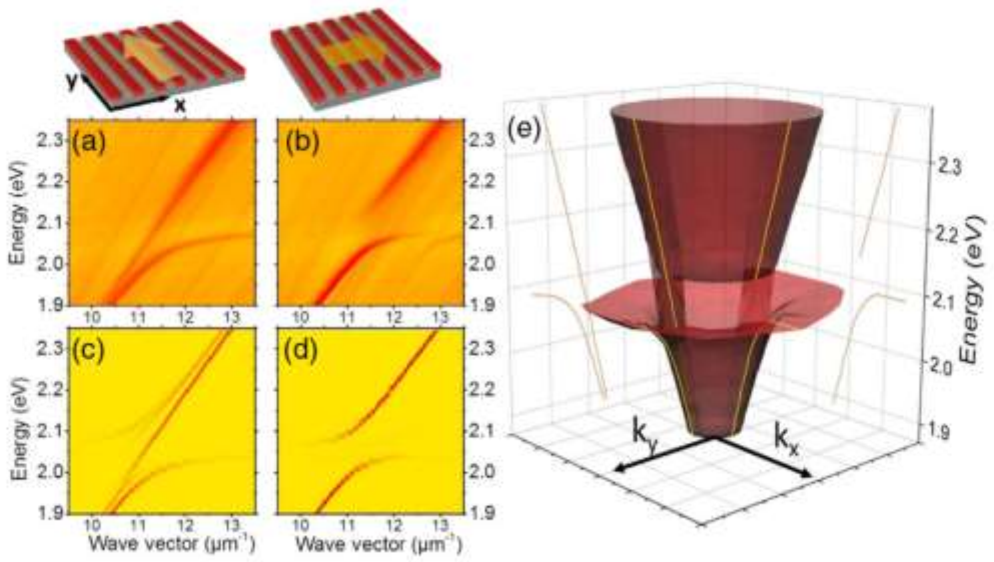
[†]Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, California 92093, United States
[‡]Department of Engineering Physics, École Polytechnique de Montréal, Montréal H3C 3A7, Quebec, Canada



PHYSICAL REVIEW LETTERS 122, 173902 (2019)

Anisotropy and Controllable Band Structure in Suprawavelength Polaritonic Metasurfaces

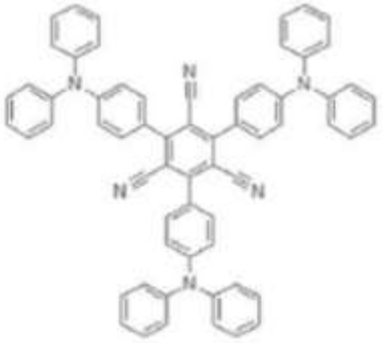
K. Chevrier,[1] J. M. Benoit,[1] C. Symonds,[1] S. K. Saikin,[2,3] J. Yuen-Zhou,[4] and J. Bellessa[1,*]
[1]Université Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622, Lyon, France
[2]Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, USA
[3]Institute of Physics, Kazan Federal University, Kazan 420008, Russian Federation
[4]Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, California 92093, USA



Other works: Photophysics

Inverting Singlet and Triplet Excited States using Strong Light-Matter Coupling

Elad Eizner[1,], Luis A. Martínez-Martínez[2], Joel Yuen-Zhou[2], Stéphane Kéna-Cohen[1,*]*



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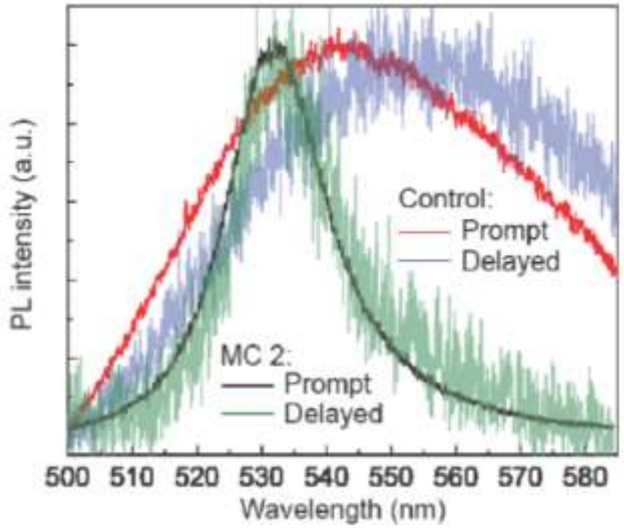

Triplet harvesting in the polaritonic regime: a variational polaron approach

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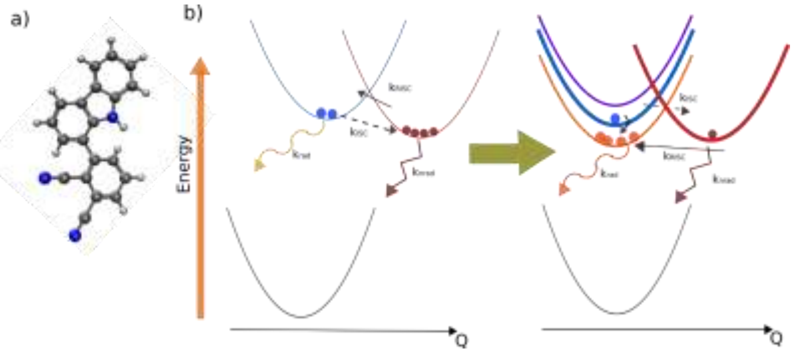

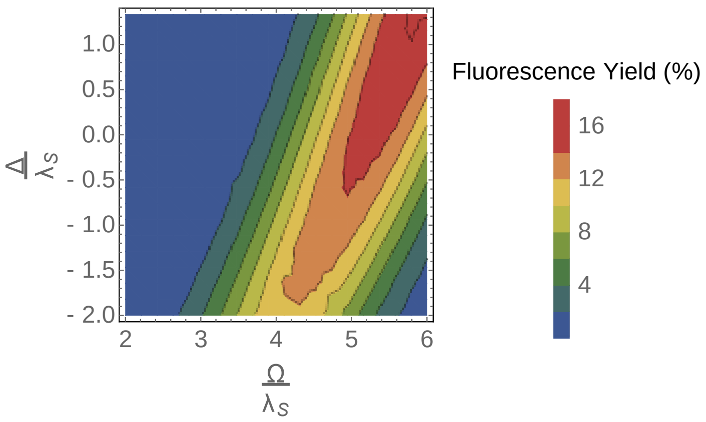

Other works: Ultrastrong coupling, Drexhage problem revisited

ACS Photonics
Article
Cite This: ACS Photonics XXXX, XXX, XXX−XXX
pubs.acs.org/journal/apchd5

Can Ultrastrong Coupling Change Ground-State Chemical Reactions?

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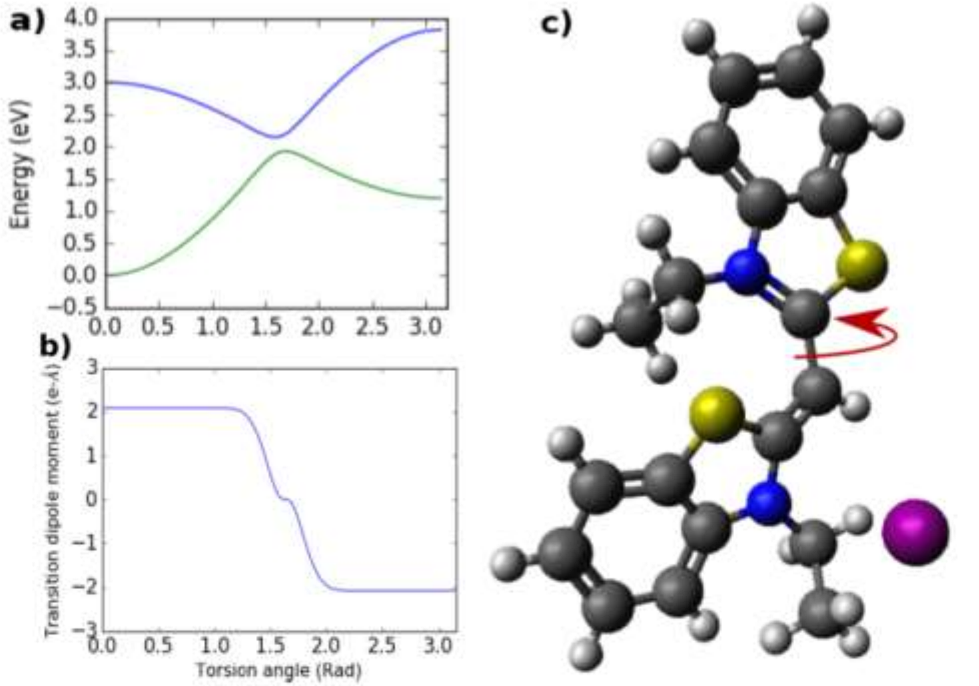

The Journal of Physical Chemistry Letters
Letter
Cite This: J. Phys. Chem. Lett. 2018, 9, 6511−6516
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Molecular Emission near Metal Interfaces: The Polaritonic Regime

Joel Yuen-Zhou,*[†] Semion K. Saikin,[‡,§] and Vinod M. Menon[∥]

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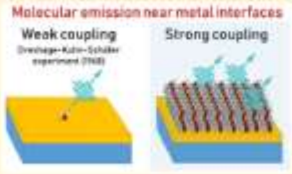
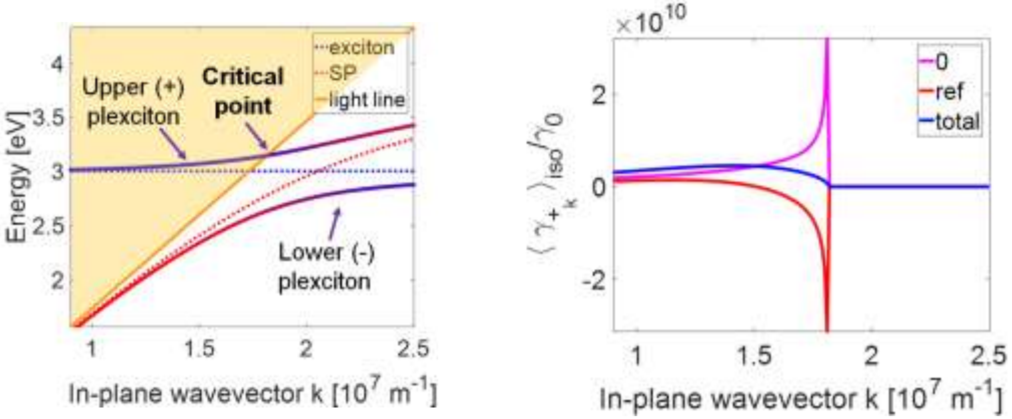
Supporting Information

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.



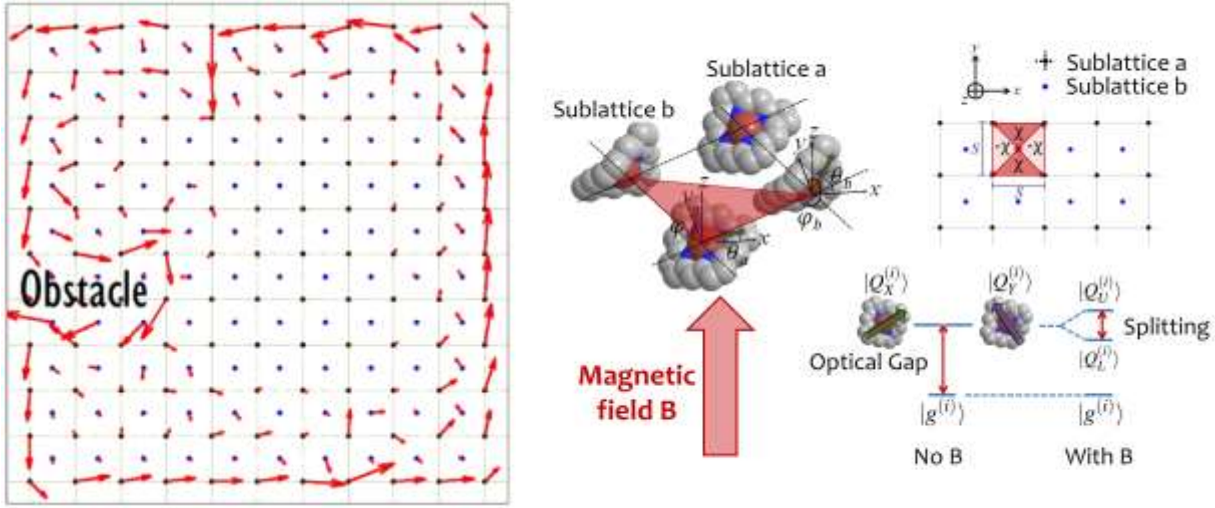


Other works: How about DIRECTIONALITY of energy transfer?

nature materials
ARTICLES
PUBLISHED ONLINE: 21 SEPTEMBER 2014 | DOI: 10.1038/NMAT4073

Topologically protected excitons in porphyrin thin films

Joel Yuen-Zhou[1]*, Semion K. Saikin[1,2], Norman Y. Yao[3] and Alán Aspuru-Guzik[1,2]



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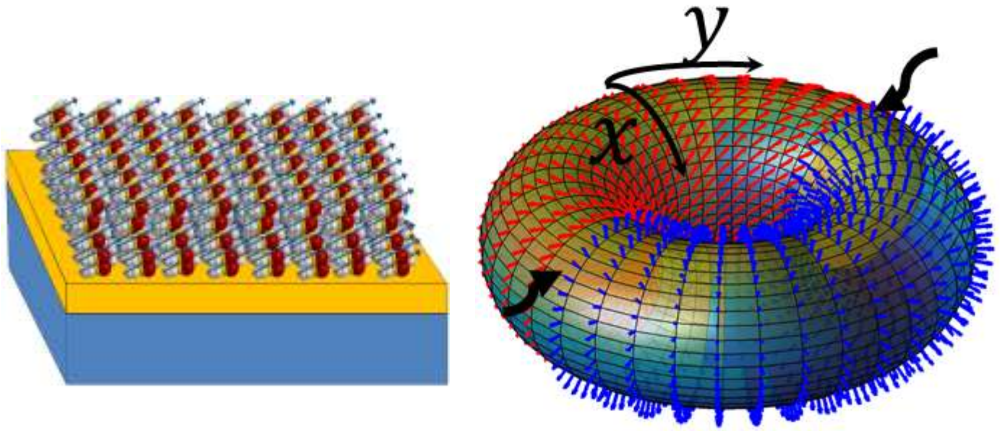
OPEN

Plexciton Dirac points and topological modes

Joel Yuen-Zhou[1], Semion K. Saikin[2,3], Tony Zhu[4,5], Mehmet C. Onbasli[6], Caroline A. Ross[6], Vladimir Bulovic[5,7] & Marc A. Baldo[5,7]



Other works: Topological effects in Born-Oppenheimer dynamics

THE JOURNAL OF PHYSICAL CHEMISTRY Letters
Letter
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Vibronic Ground-State Degeneracies and the Berry Phase: A Continuous Symmetry Perspective

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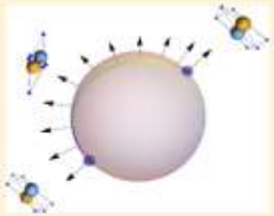
ABSTRACT: We develop a geometric construction to prove the inevitability of the electronic ground-state (adiabatic) Berry phase for a class of Jahn–Teller (JT) models with maximal continuous symmetries and $N > 2$ intersecting electronic states. Given that vibronic ground-state degeneracy in JT models 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.



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Journal of Physics: Condensed Matter
J. Phys.: Condens. Matter 30 (2018) 333001 (20pp)
https://doi.org/10.1088/1361-648X/aac89e

Topical Review

Continuous vibronic symmetries in Jahn–Teller models

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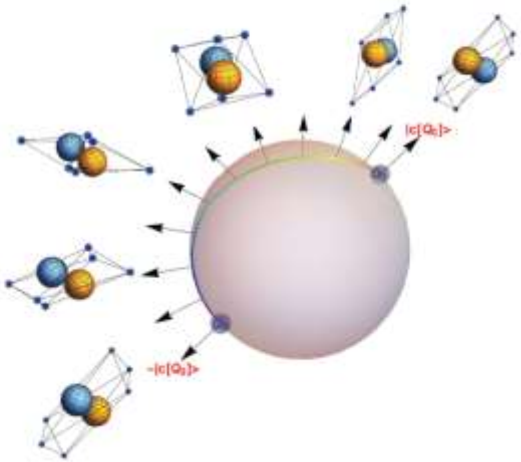
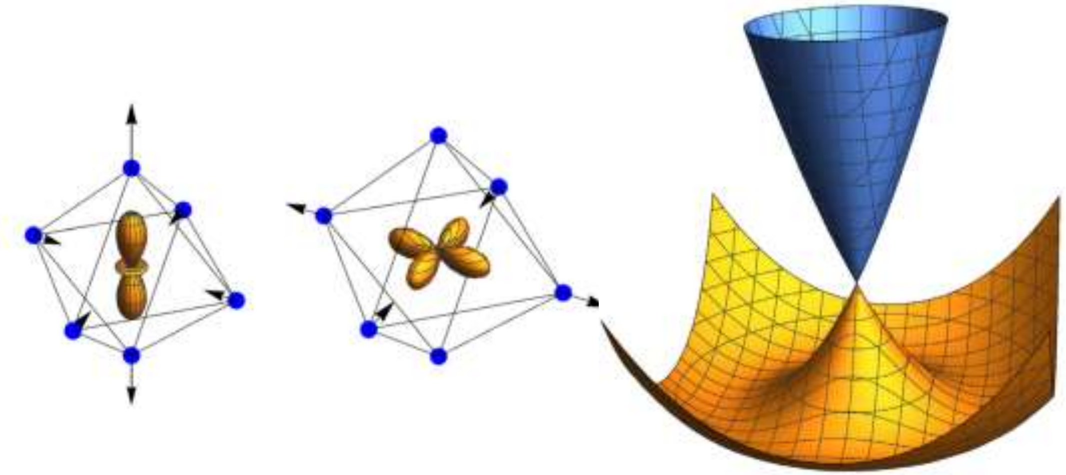




An outlook

PNAS

COMMENTARY

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

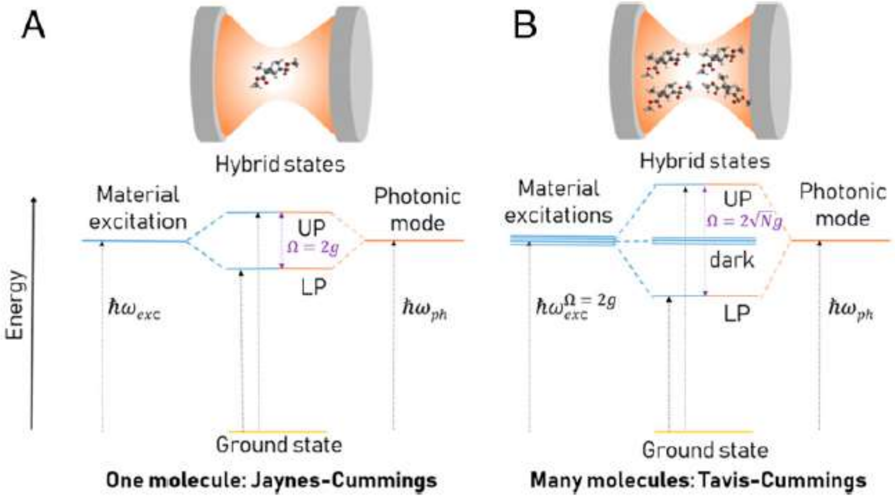
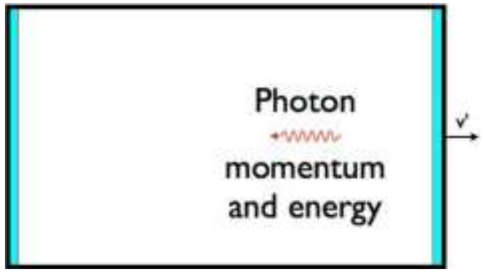


Fig. 1. (*A* and *B*) The various flavors of molecular strong coupling with a single molecule (*A*) and with $N > 1$ molecules (*B*). The energy spectrum is given by the JC model (*A*) and the TC model (*B*). At light–matter resonance ($\hbar\omega_{ph} = \hbar\omega_{exc}$), the UP and LP are half-light–half-matter 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.

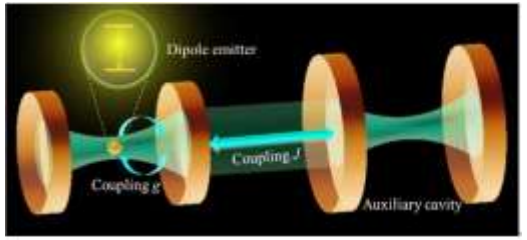
Is cavity QED ready for chemistry?

Einstein-Bohr debates



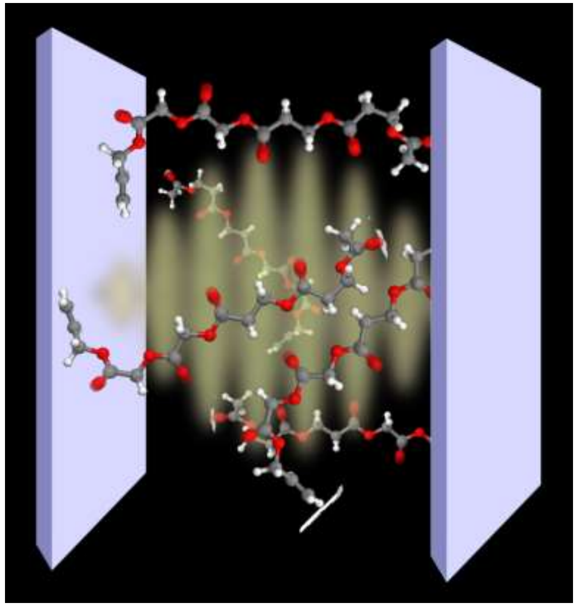
1920s

Cavity QED



1960s

Polariton chemistry



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Chem. Sci., 9, 6325-6339 (2018)

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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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