MOLECULAR POLARITONICS 2019: Theoretical and Numerical Approaches

Miraflores de la Sierra, Madrid, July 7-11, 2019

Organizers: Claudiu Genes and Johannes Feist

Introduction / overview / perspective of the field

UAM Universidad Autónoma de Madrid

IfiMAC Condensed Matter Physics Center

MAX PLANCK INSTITUTE for the science of light

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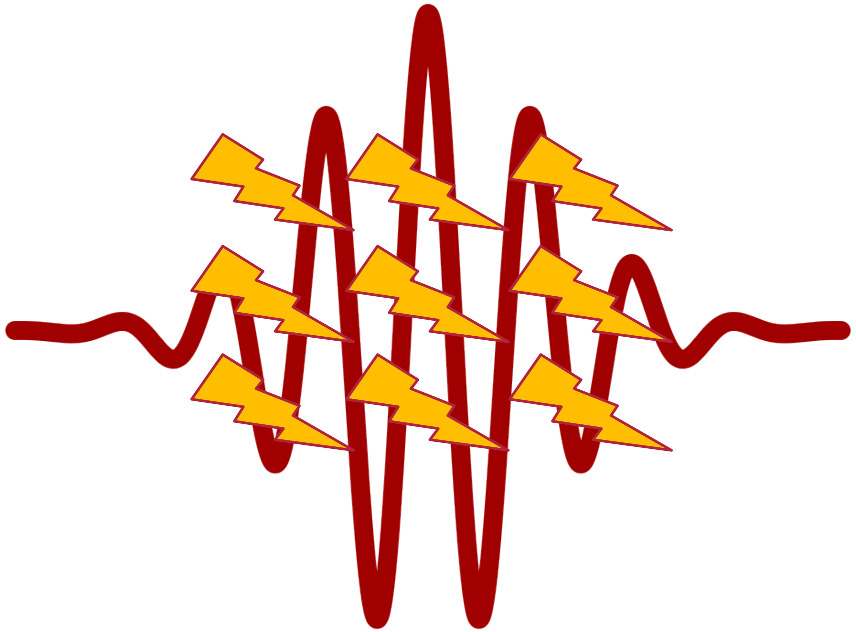
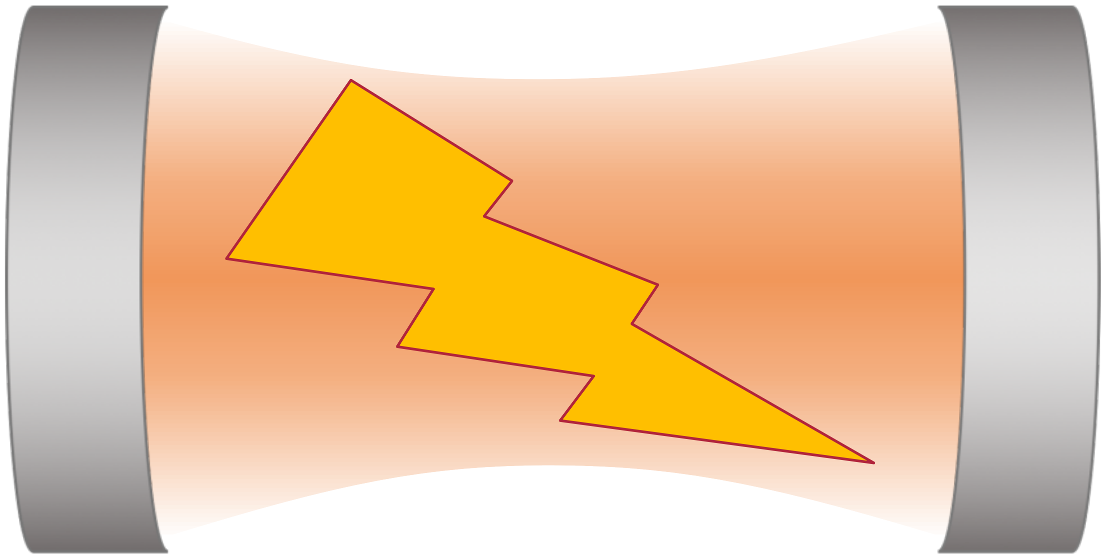
Molecular Polaritonics: Introduction

Laser:
Many coherent photons



Alternative:
Make single photon "strong" by confining it in space



Cavity-modified material properties

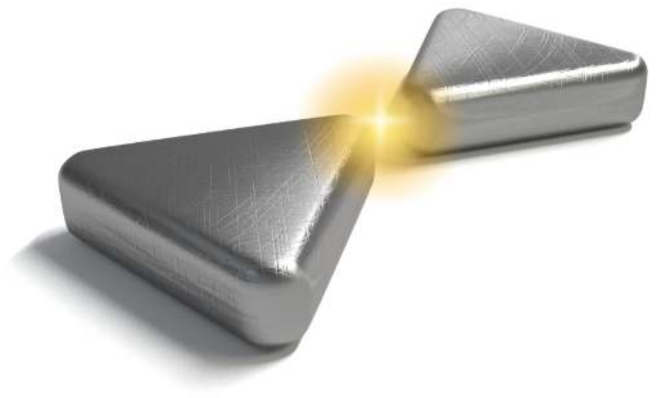
Use light (*vacuum field*) to modify material properties?

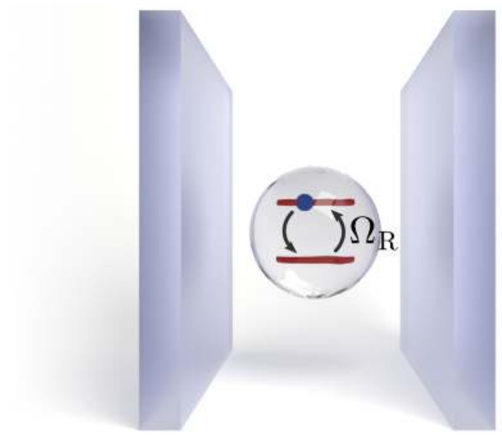
Confine light in space to get strong **few-photon** interaction with **interesting materials**

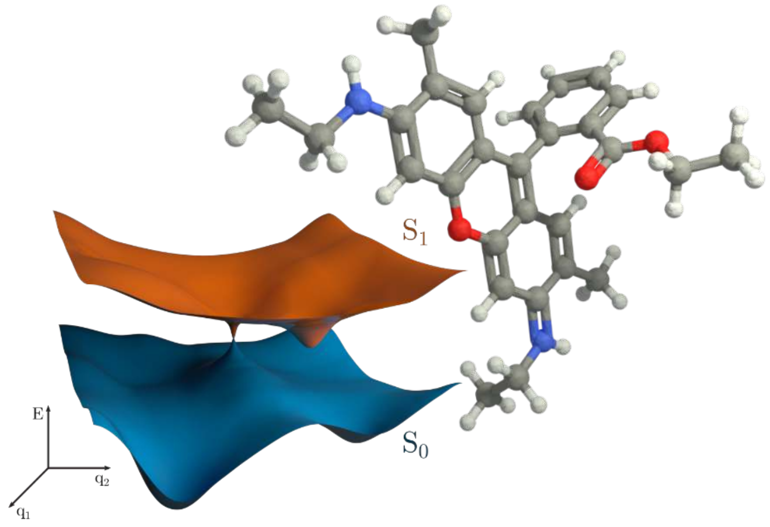
Nanophotonics
Plasmonics

Cavity QED
Quantum Optics

Materials Science
Chemistry

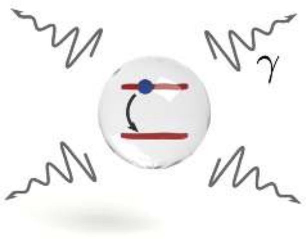




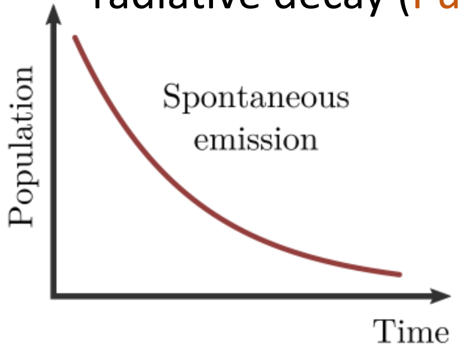


Strong light–matter coupling

Weak coupling



- Absorption and emission
- EM environment → modify radiative decay (Purcell effect)



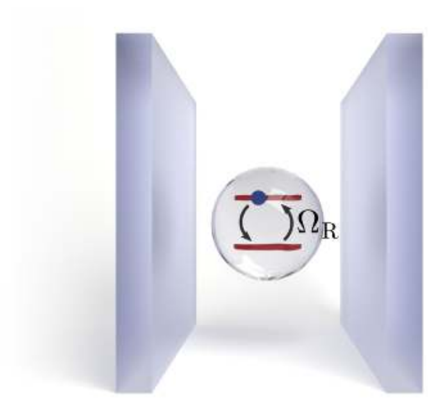
Simple model

$$H = \begin{pmatrix} \omega_0 - i\frac{\gamma}{2} & g \\ g & \omega_0 - i\frac{\kappa}{2} \end{pmatrix}$$

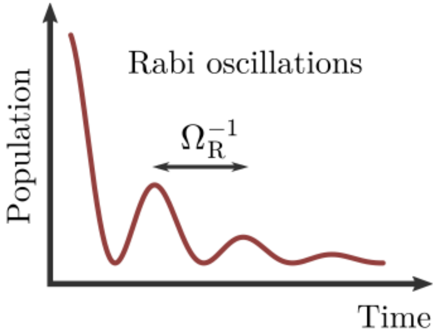
excited emitter · coupling · photon

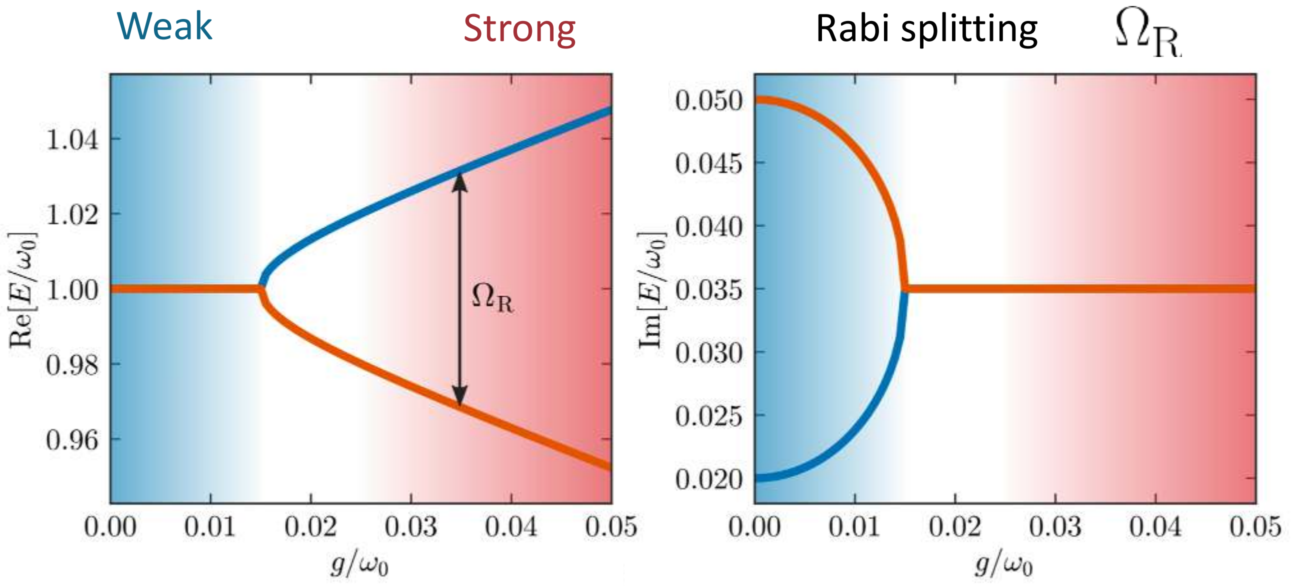
$$g = \boldsymbol{\mu} \cdot \mathbf{E}_{1\mathrm{ph}} \qquad \mathbf{E}_{1\mathrm{ph}} \propto \frac{1}{\sqrt{V}}$$

Strong coupling



- Vacuum Rabi oscillations (coherent energy exchange)
- Interaction faster than decay
- Hybrid light-matter states (polaritons / dressed states)



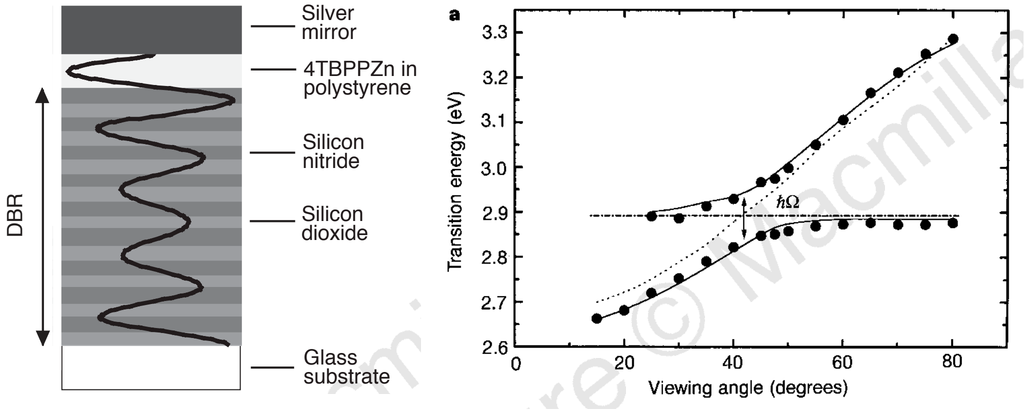


Strong coupling with organic molecules

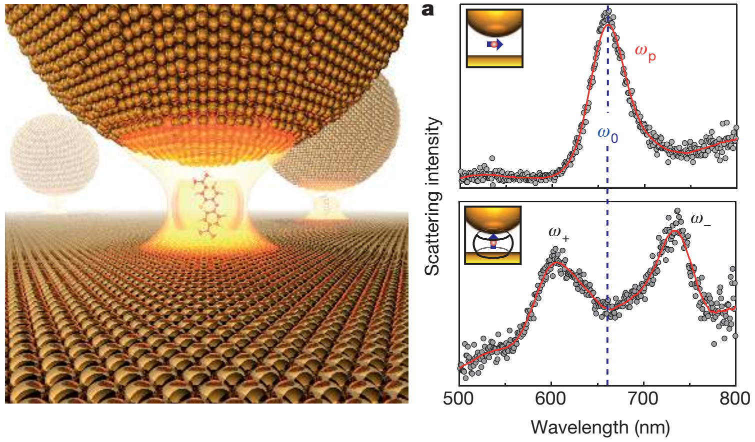
Organic molecules:

- Large dipole moments
- High densities $\Omega_R \propto \sqrt{\rho}\mu$
- **Rabi splitting can be >1 eV** (large fraction of transition energy)
- **Room temperature!**

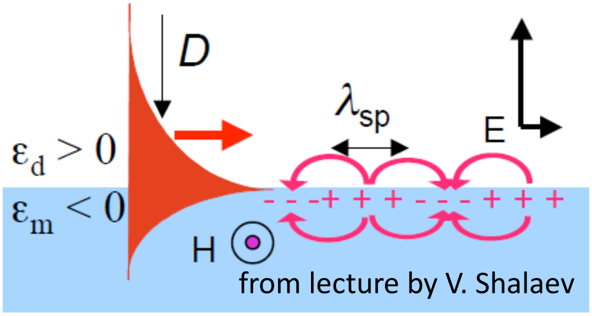
Microcavity: D. G. Lidzey et al., Nature **395**, 53 (1998)

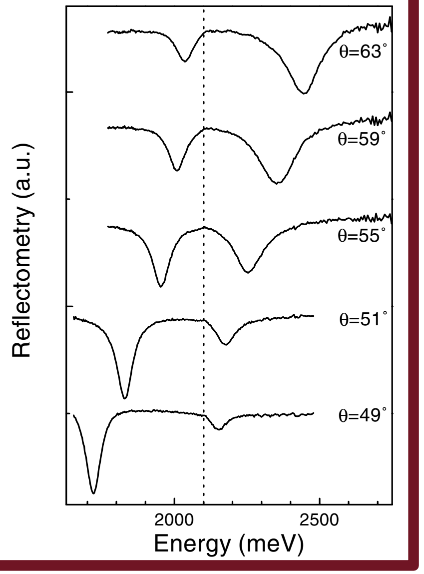


Few molecules with gap plasmon: Chikkaraddy et al., Nature **535**, 127 (2016)



Surface plasmons: J. Bellessa et al., Phys. Rev. Lett. **93**, 036404 (2004)





Many vs single organic molecules

Room temperature:

Many molecules / macroscopic

Promises
- ”Easy” to reach strong coupling
- Modifications of electronic properties
- Tunable chemistry
- Could integrate in devices

Problems
- Many effects “classical” (Maxwell’s eqs)
- No few-photon nonlinearity
- Small polariton density of states compared to “dark” states
- delocalized → single-molecule effects small

Single (or few) molecules

Promises
- Single molecule!
- ~all states/properties affected
- Quantum nature (more) evident
- Generates non-linearities (photon blockade)

Problems
- Experimentally very challenging
- Extremely strong field confinement necessary (mode volume ~50 nm^3) → large losses
- “Messy” system (molecules close to metal: quenching, chemical modification, etc.)

Many vs single organic molecules

Cryogenic single molecule

Promises

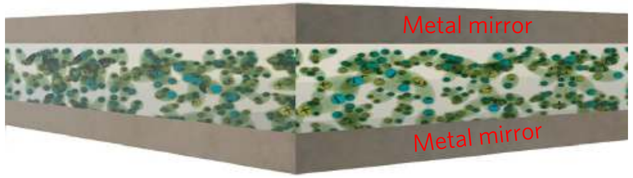
- Coherent control of quantum states
- Coherent quantum light-matter interface
- Generates **non-linearities** (photon blockade)
- Integrated into quantum networks

Problems

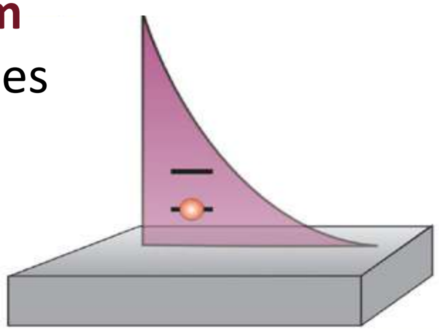
- Requires good cavities while minimizing the mode volume
- Requires **cryogenic** conditions
- Reactivity is bad for experiments

What is a cavity?

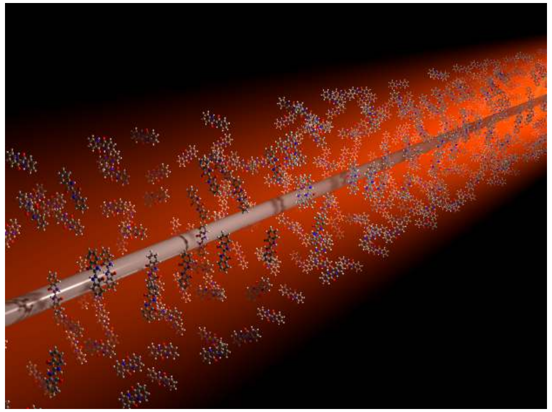
"Cavity" in this context: **any material system**
… that confines or enhances light / EM modes



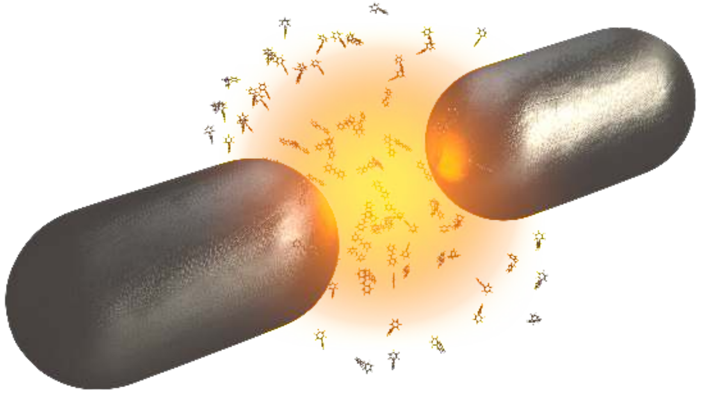
Fabry-Perot / planar cavities
Sanvitto & Kéna-Cohen,
Nat. Mater. **15**, 1061 (2016)



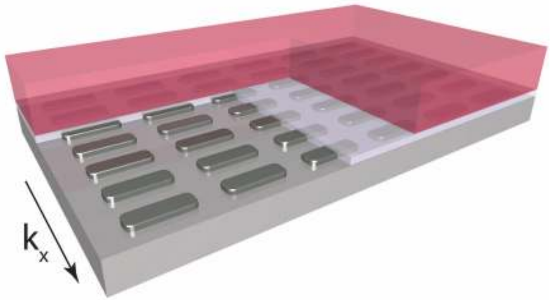
Surface plasmon polaritons
Törmä & Barnes,
Rep. Prog. Phys. **78**, 13901 (2015)



Nanowires



Localized surface plasmon resonances
Galego et al., Nature Commun. **7**, 13841 (2016)



Plasmonic nanoparticle array
Ramezani et al., Optica **4**, 31 (2017)

Photonic Crystal
Galego, PhD thesis (2019)

Almost never a single cavity mode!

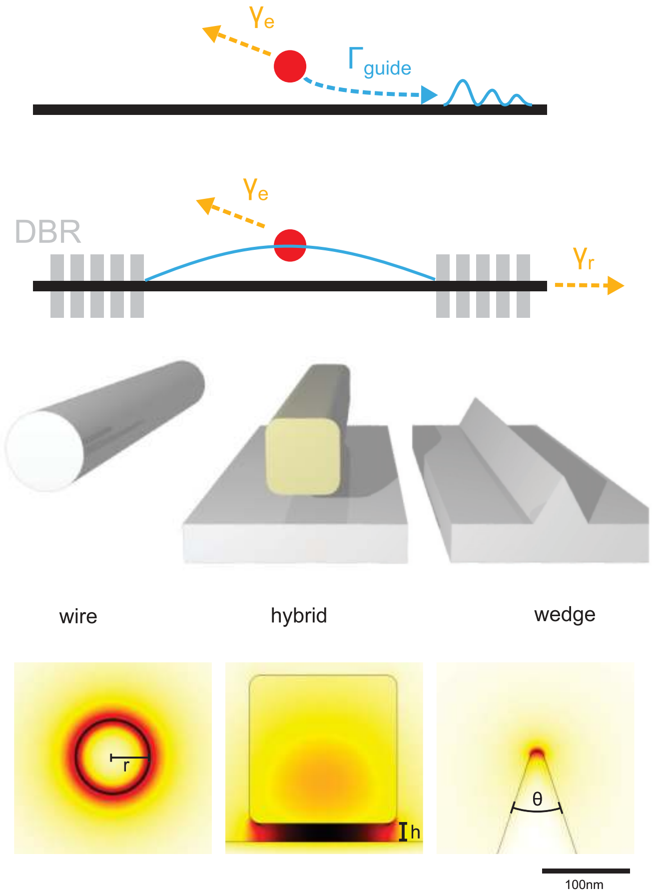
Proper quantized description?

Macroscopic QED?

Quantized approaches to plasmonic “cavities”

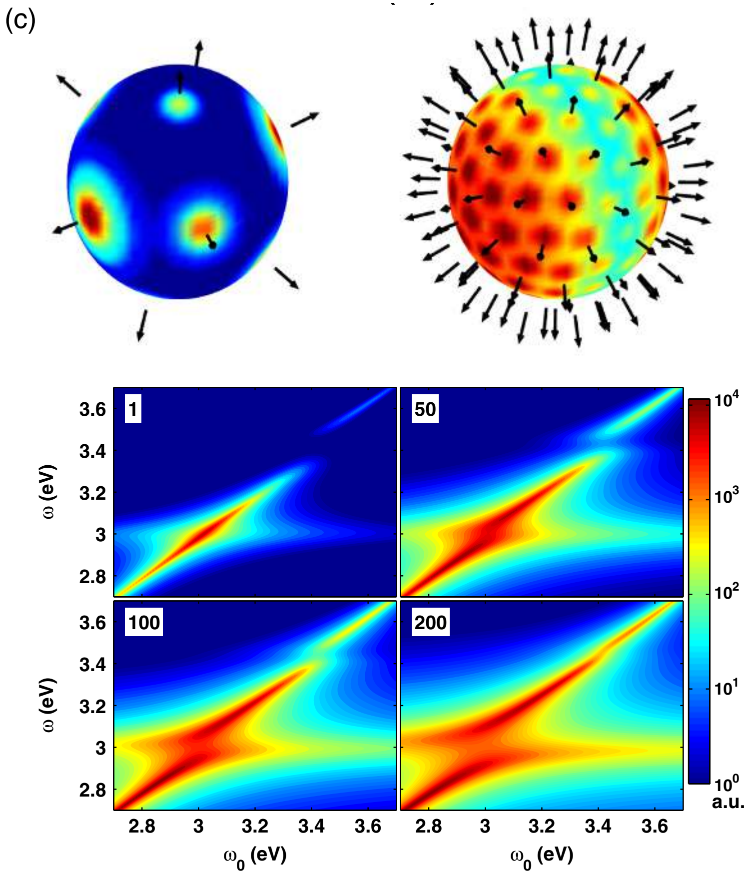
Weak and strong coupling regimes in plasmonic QED

T. Hümmer et al., Phys. Rev. B **87**, 115419 (2013)



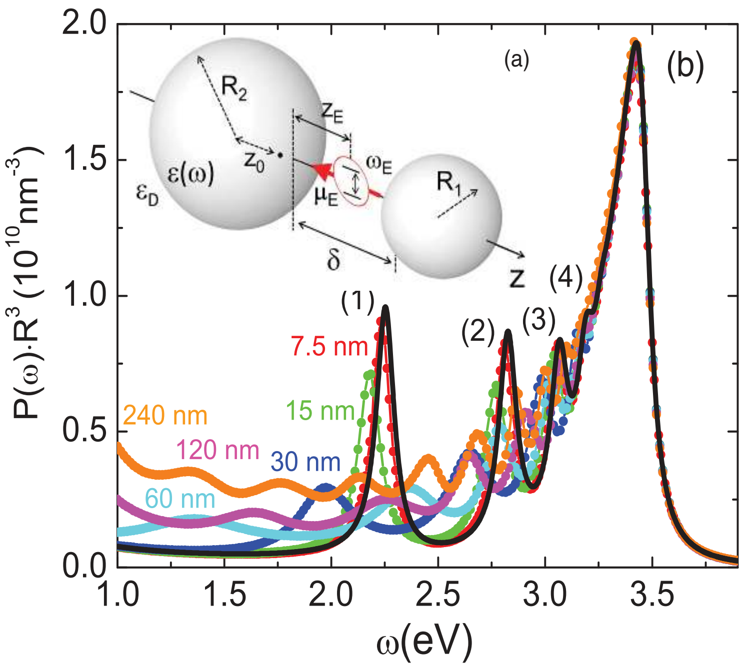
Quantum Emitters Near a Metal Nanoparticle: Strong Coupling and Quenching

A. Delga et al, Phys. Rev. Lett. **112**, 253601 (2014)



Transformation Optics Approach to Plasmon-Exciton Strong Coupling in Nanocavities

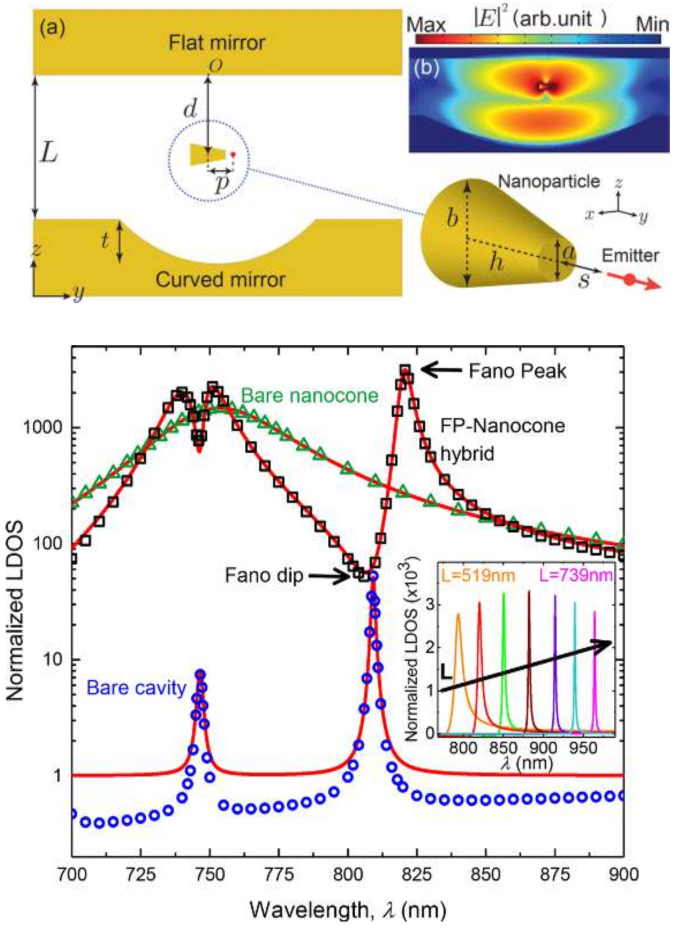
R.-Q. Li et al., Phys. Rev. Lett. **117**, 107401 (2016)



Hybrid cavities

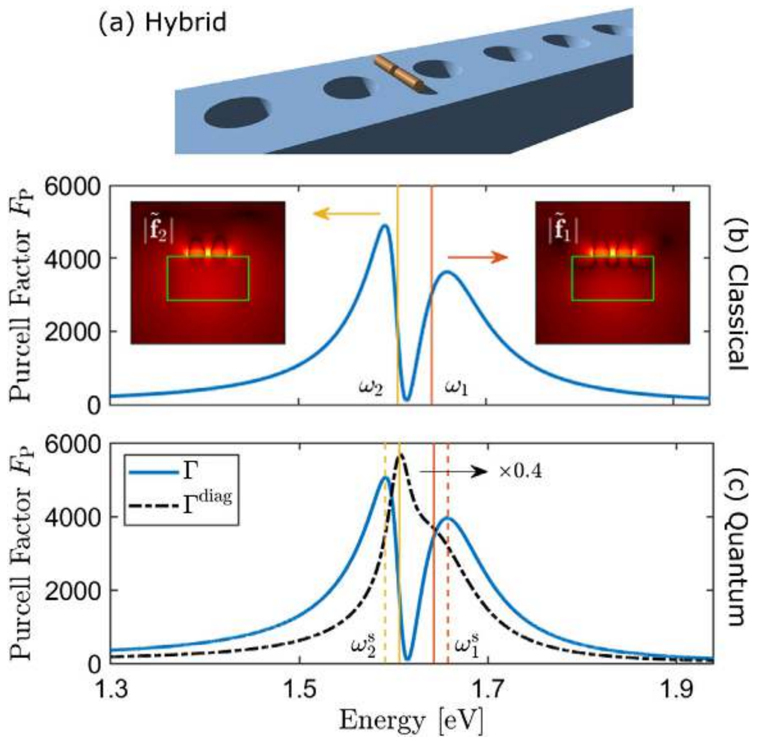
Hybrid cavities to manipulate quenching and strong coupling

B. Gurlek et al., ACS Phot. **5**, 456 (2018)



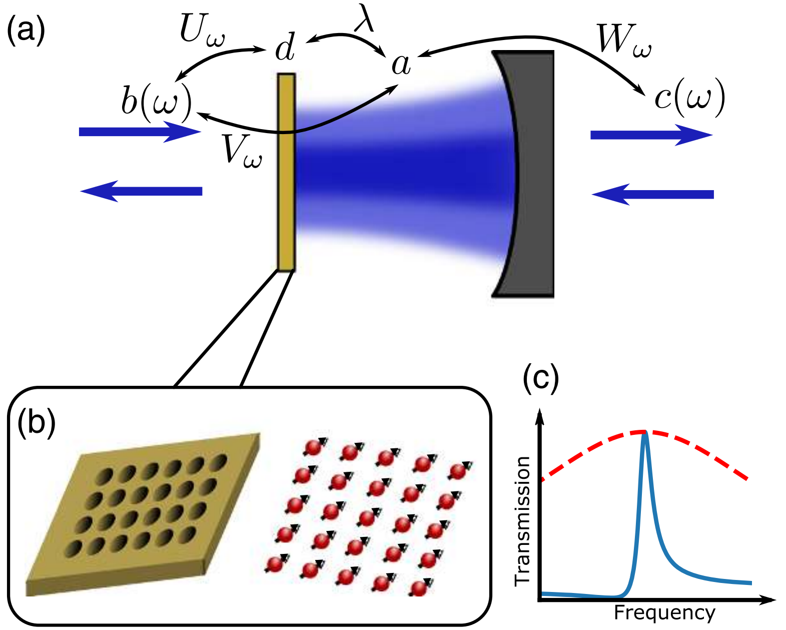
Explicit quantization of quasinormal modes

S. Franke et al., Phys. Rev. Lett. **122**, 213901 (2019)



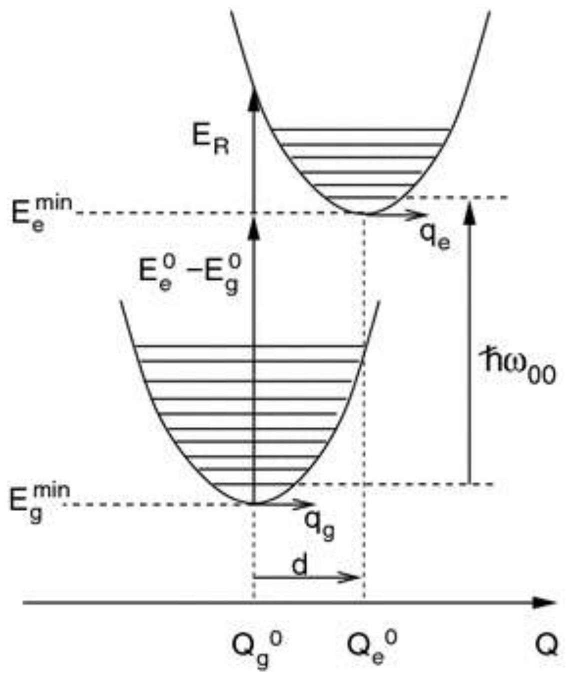
Cavity Quantum Electrodynamics with Frequency-Dependent Reflectors

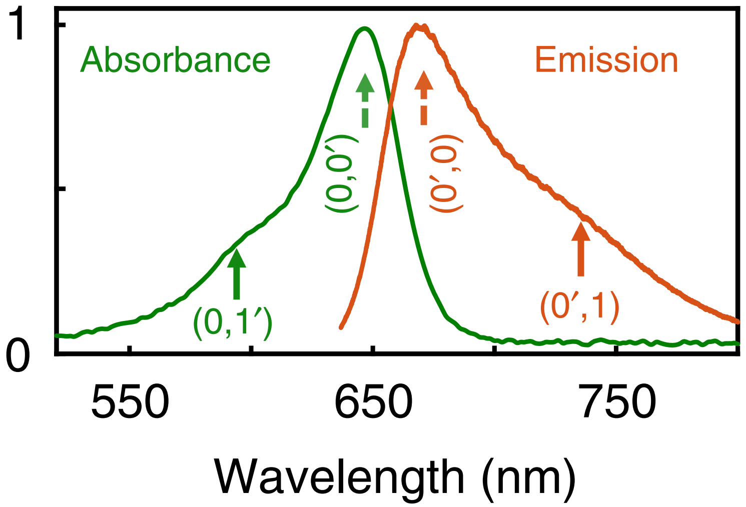
O. Černotík et al., Phys. Rev. Lett. **122**, 243601 (2019)

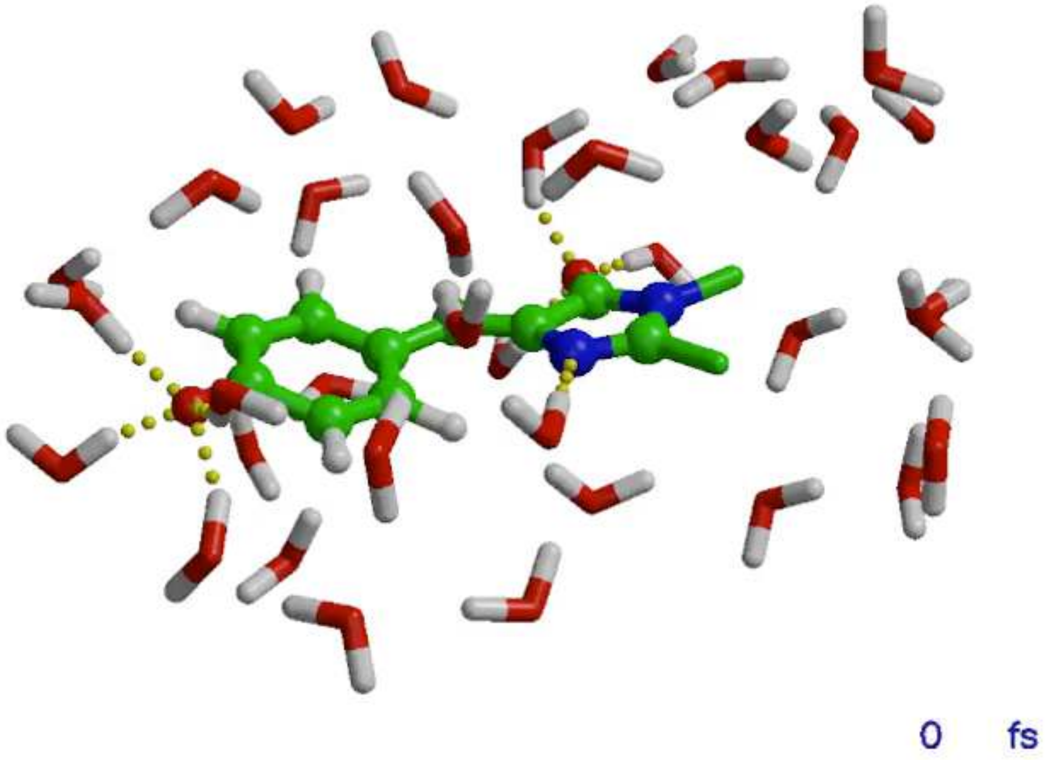


Two-level emitters?

This is not a molecule!



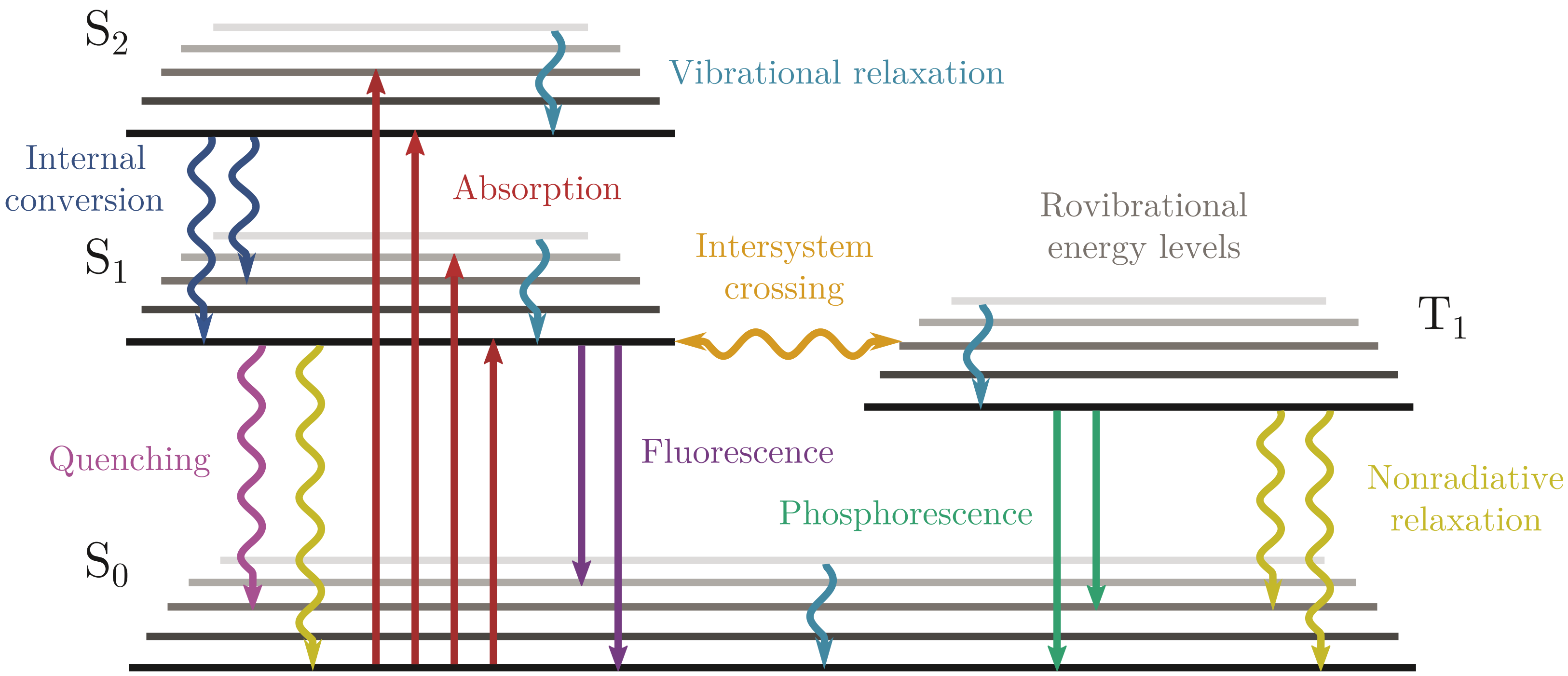




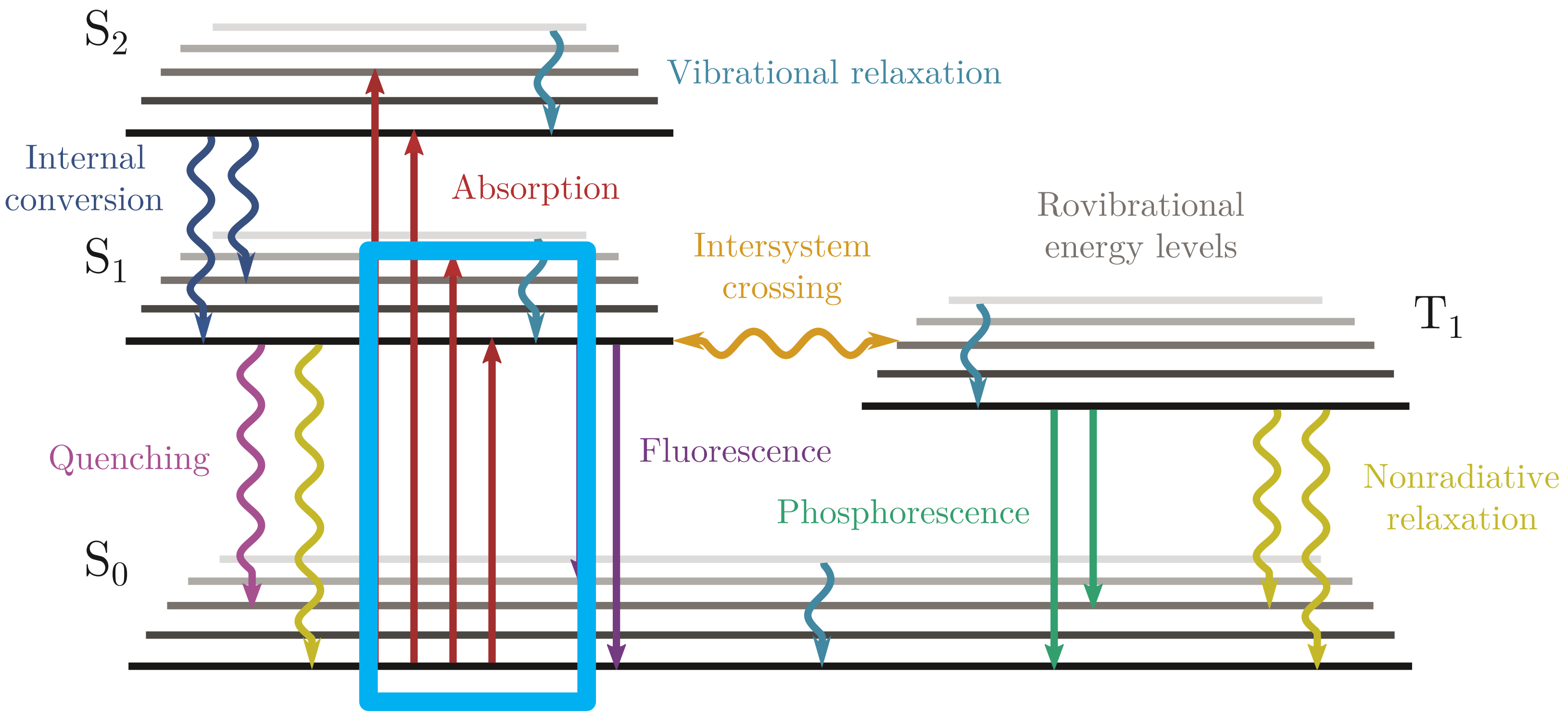
Real molecules:

- Many nuclear (vibrational) DOFs
- Large exciton-phonon coupling
- Fast nuclear dynamics

The complex nature of molecules



Coupling to electronic transitions



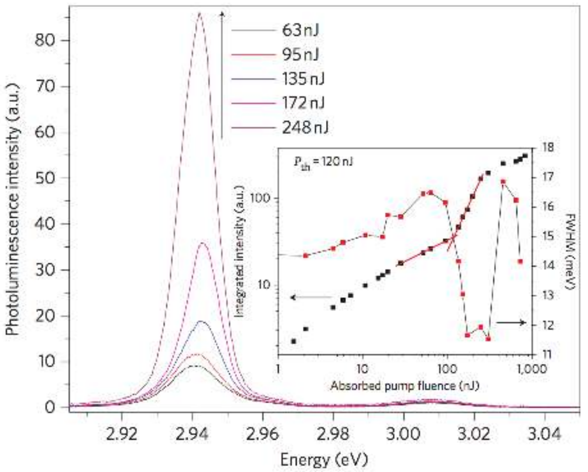
Coupling at optical frequencies

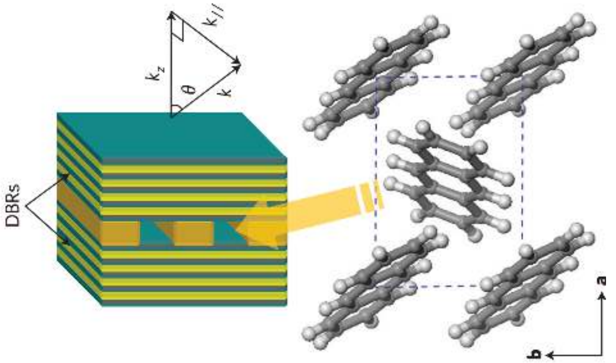
- Experimentally: chemistry, charge/exciton transport, polariton condensation, etc.
- Theory: **role of vibrations**, Tavis-Cummings-Holstein model, polaritonic potential energy surfaces, polariton cross-talk, etc...

Coupling to electronic transitions - experiments

Polariton lasing

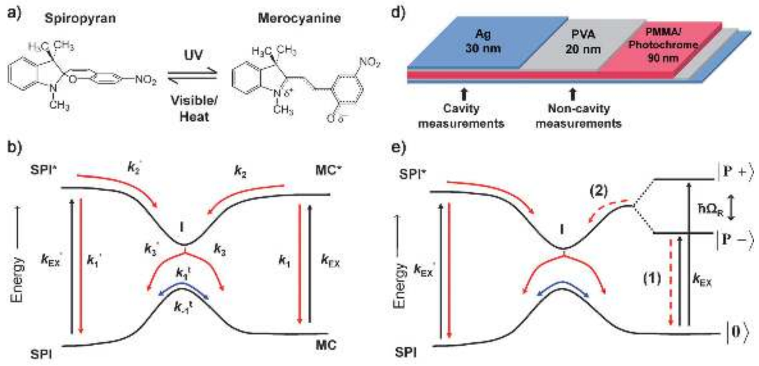
S. Kéna-Cohen and S. Forrest, Nat. Phot. **4**, 402 (2010)

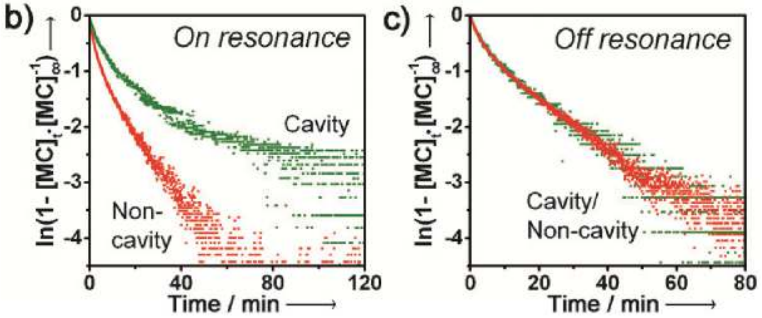




Modify photochemical reaction rates

J. A. Hutchison *et al.*, Angew. Chemie **124**, 1624 (2012)



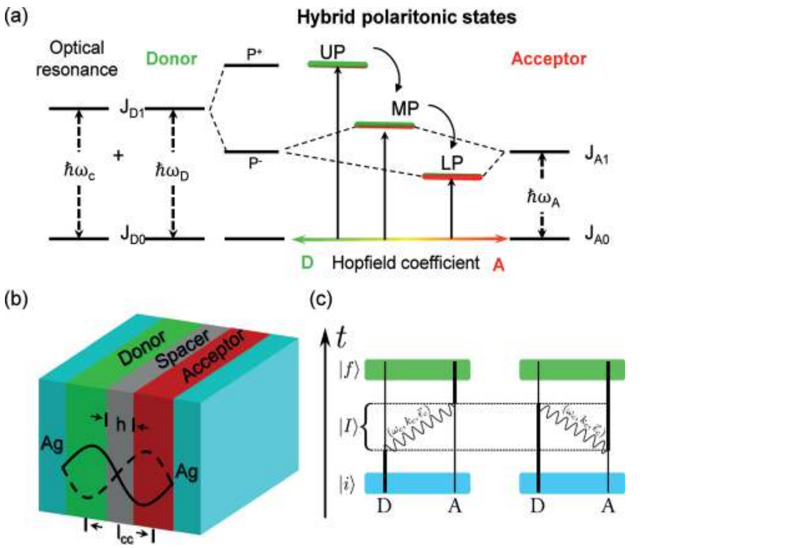


Polariton-mediated energy transfer

D. M. Coles *et al.*, Nat. Mater. **13**, 712 (2014)

Spatially separated donor and acceptor

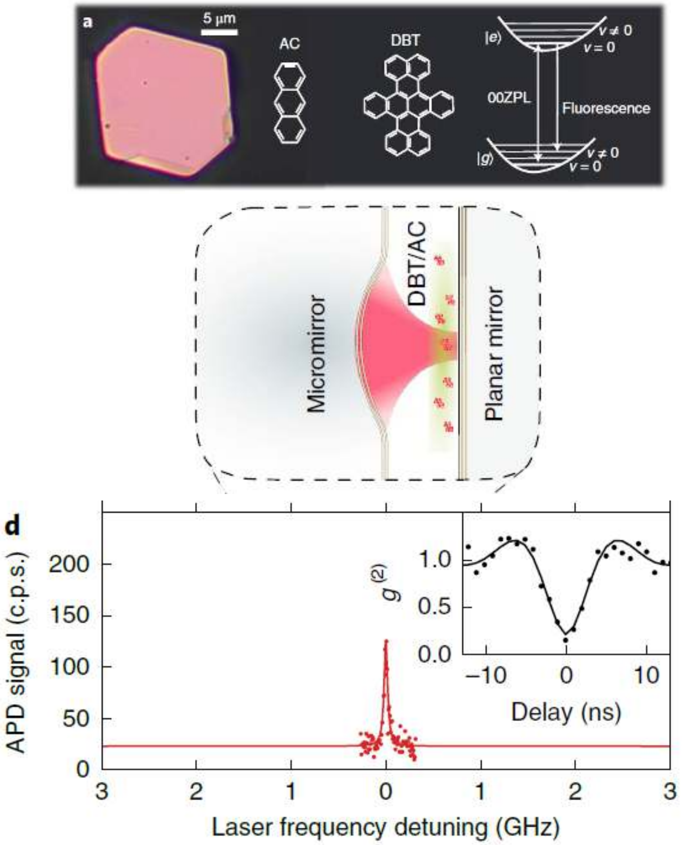
X. Zhong et al., Angew. Chem. Int.Ed. **56**, 9034 (2017)



Coupling to electronic transitions - experiments

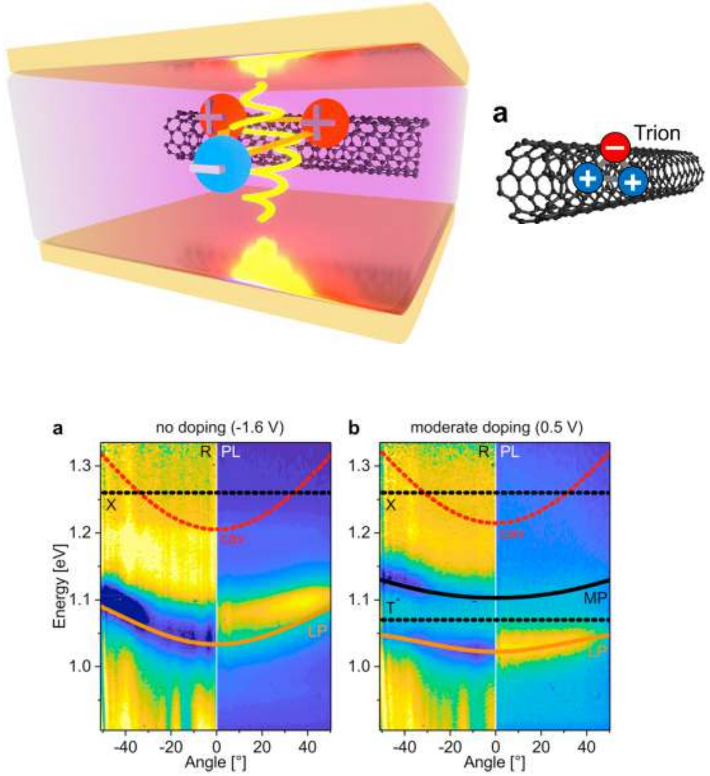
Turning a molecule into a coherent two-level quantum system

D. Wang et al, Nat. Phys. **15**, 483 (2019)



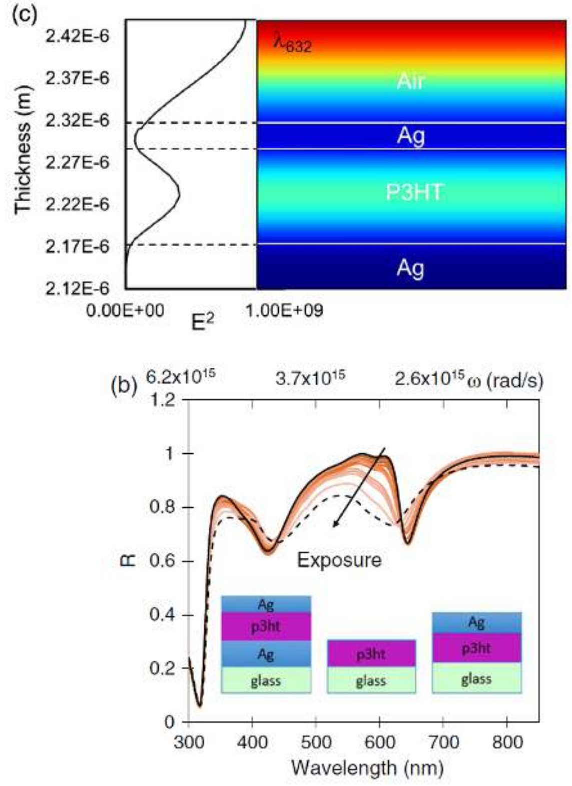
Trion-Polariton Formation in Single-Walled Carbon Nanotube Microcavities

C. Möhl et al, ACS Phot., **5**, 2074 (2018)



Effect of strong coupling on photo-degradation of the semiconducting polymer P3HT

V. N. Peters et al, Optica, **6**, 318 (2019)



Ultrafast dynamics of everything

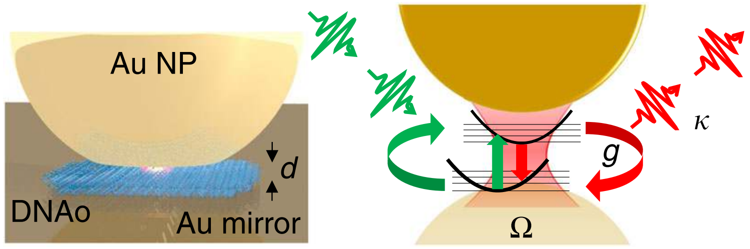
nature COMMUNICATIONS

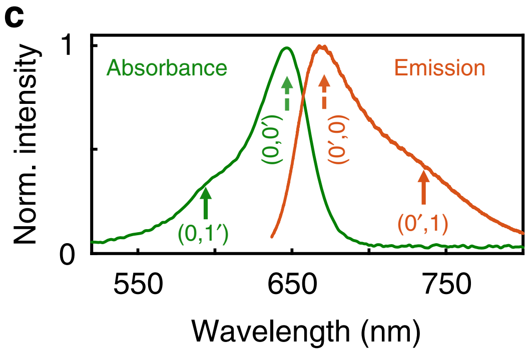
ARTICLE

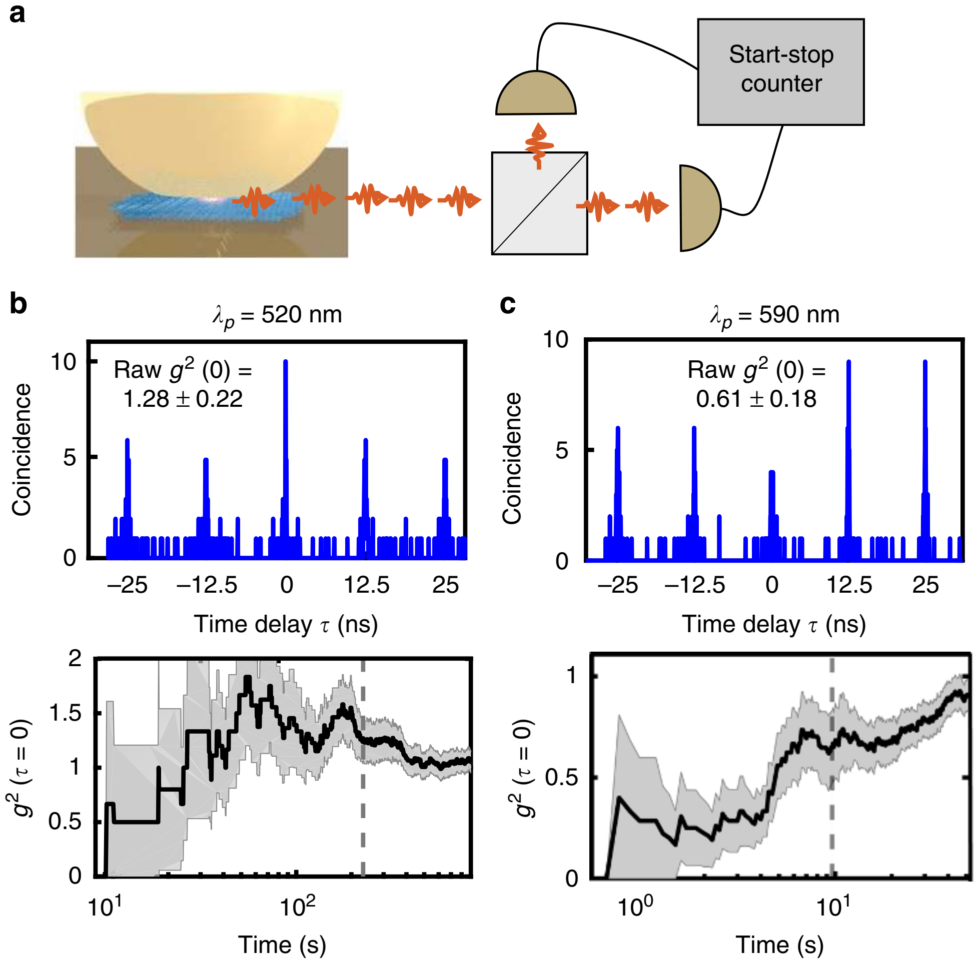
https://doi.org/10.1038/s41467-019-08611-5 OPEN

Quantum electrodynamics at room temperature coupling a single vibrating molecule with a plasmonic nanocavity

Oluwafemi S. Ojambati[1], Rohit Chikkaraddy[1], William D. Deacon[1], Matthew Horton[1], Dean Kos[1], Vladimir A. Turek[1], Ulrich F. Keyser[1] & Jeremy J. Baumberg[1]



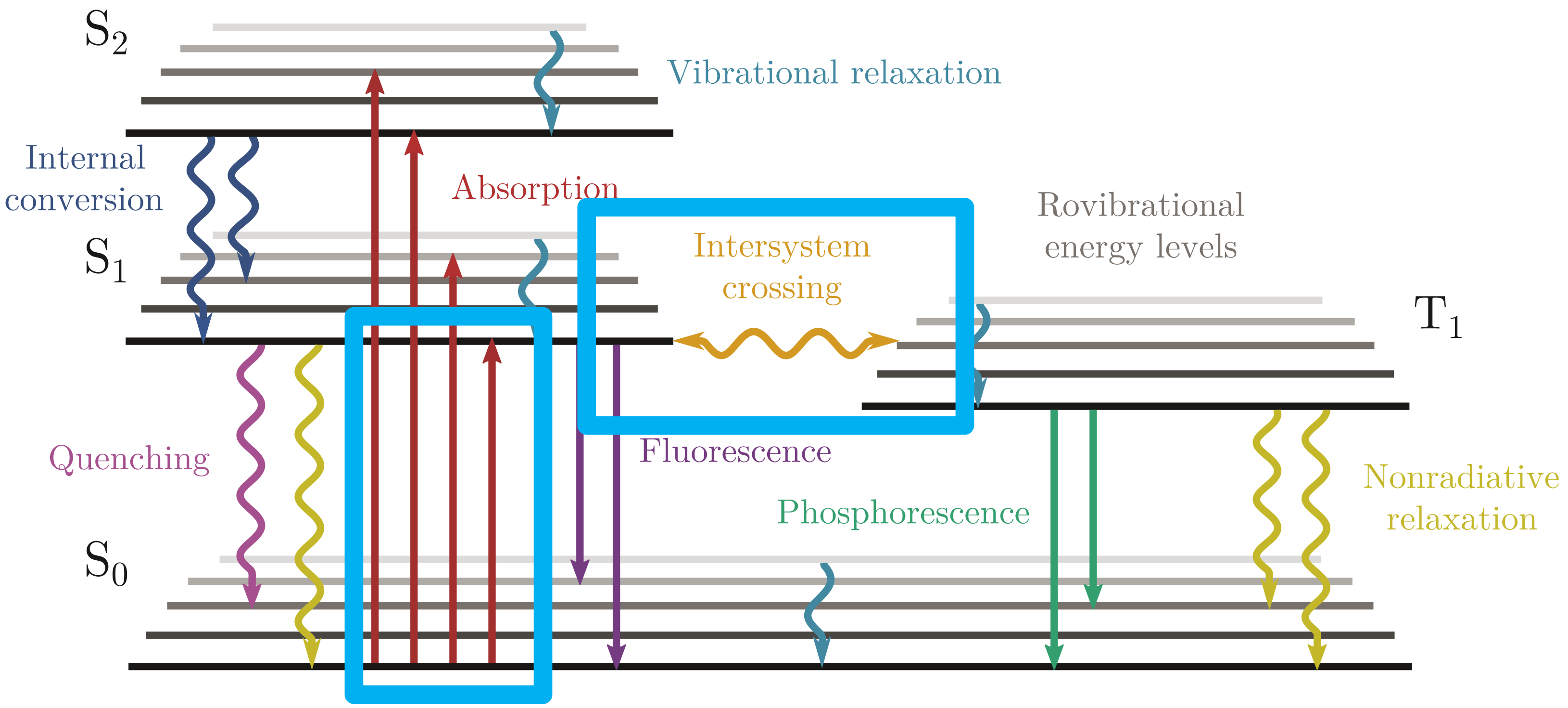




- **Short-pulse driving**
- **short plasmon lifetime**
- **$\Omega_R \approx \omega_v$**

Ultrafast electronic, photonic & phononic dynamics!
Both in system and in absorption and emission.

Coupling to electronic transitions – intersystem crossing



Coupling at optical frequencies

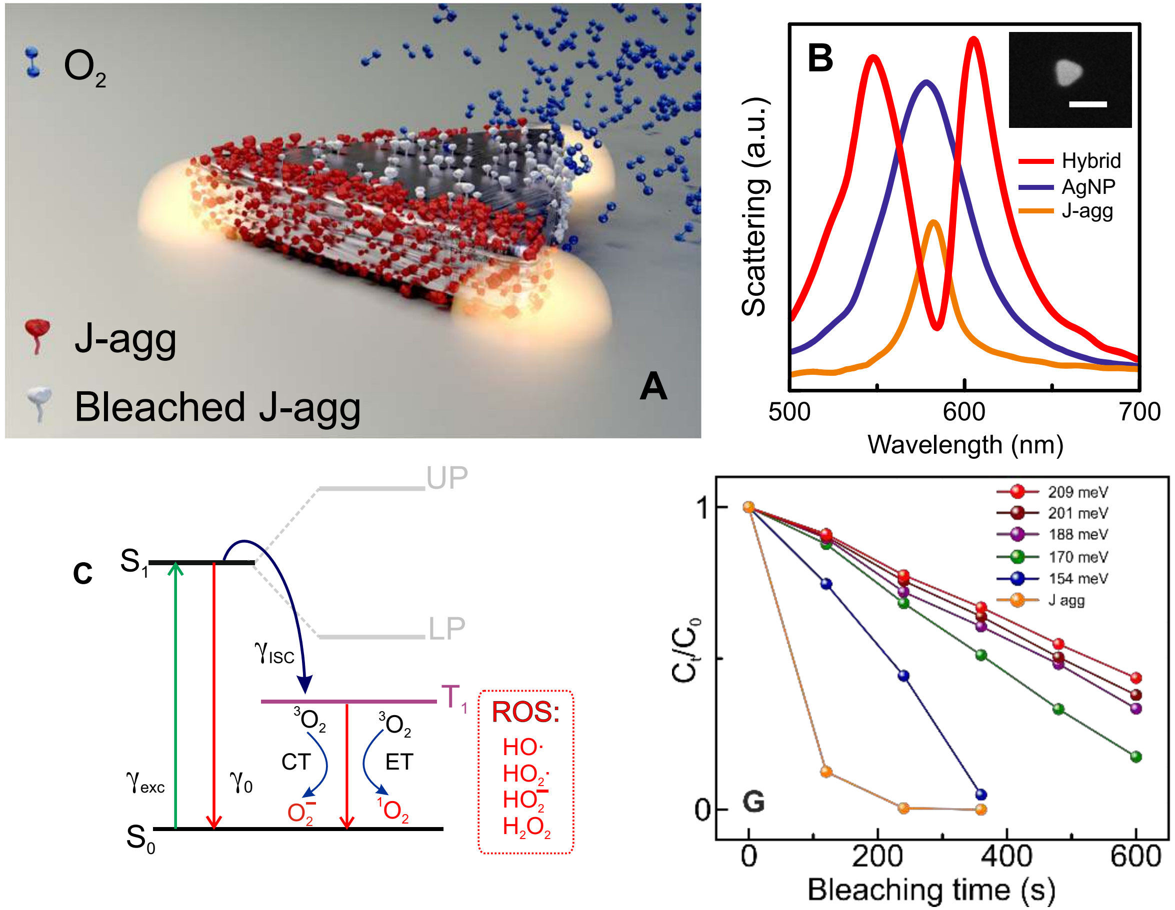
- Modifications of the intersystem crossing dynamics

Intersystem crossing – experimental progress

Suppression of photo-oxidation of organic chromophores

Significantly increased lifetime against photobleaching under strong coupling

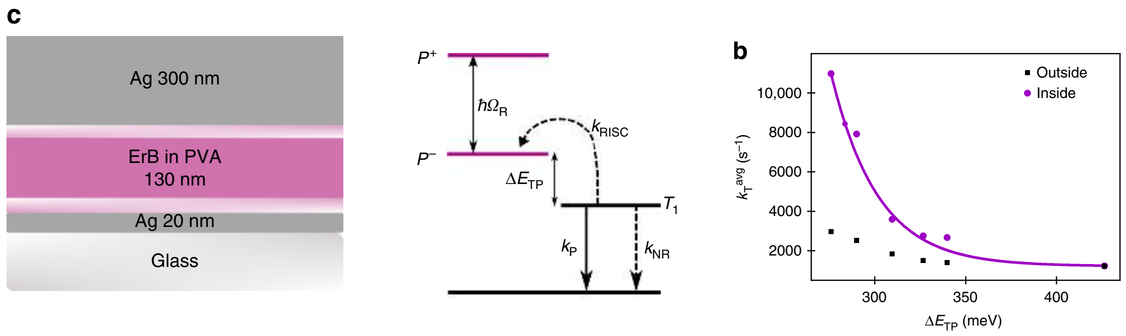
B. Munkhbat et al., Science Advances **4**, eaas9552 (2018).



Increased reverse intersystem crossing

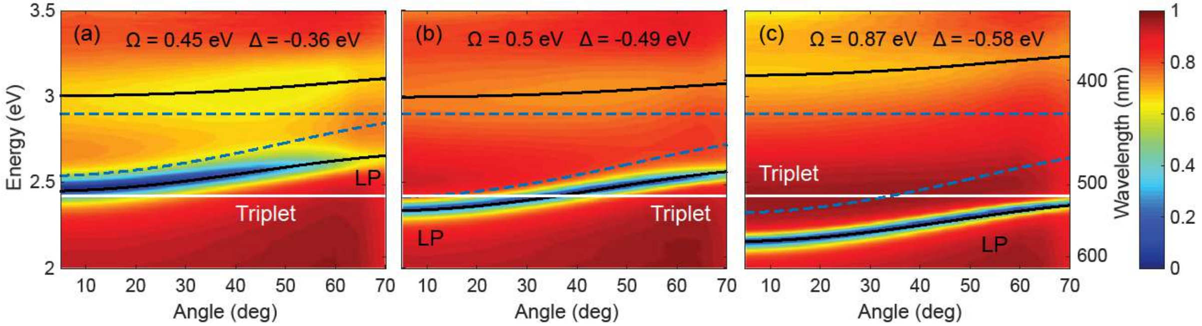
Crossing from triplet to singlet increased by reducing gap

K. Stranius et al., Nat. Commun. **9**, 2273 (2018)



Inverting singlet and triplet

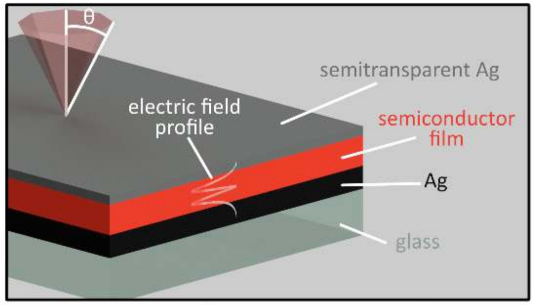
E. Eizner et al., arXiv:1903.09251 (2019)

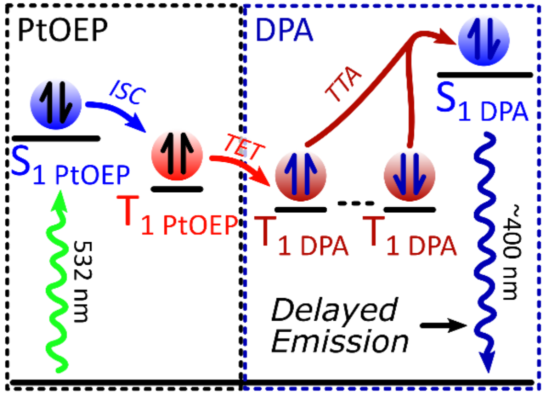


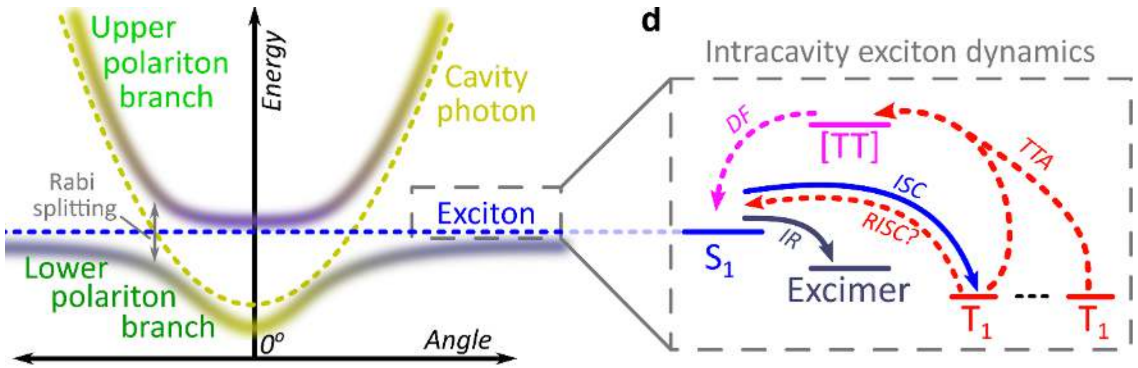
Intersystem crossing – experimental progress

Manipulating matter with strong coupling: harvesting triplet excitons in organic exciton microcavities

D. Polak et al., arXiv:1806.09990 (2018).





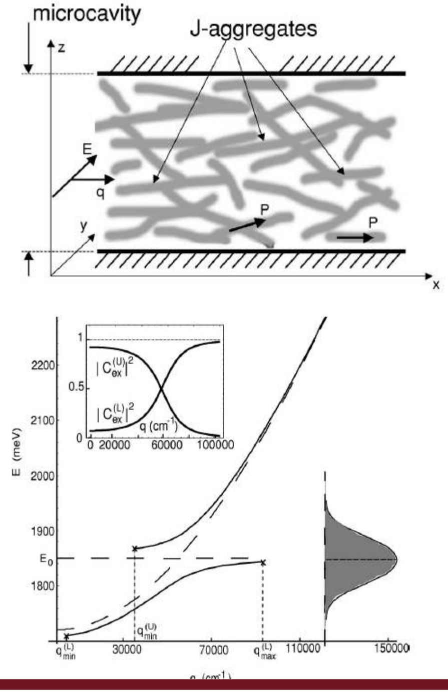


Coupling to electronic transitions – theoretical approaches

Quantum optics/condensed matter approaches

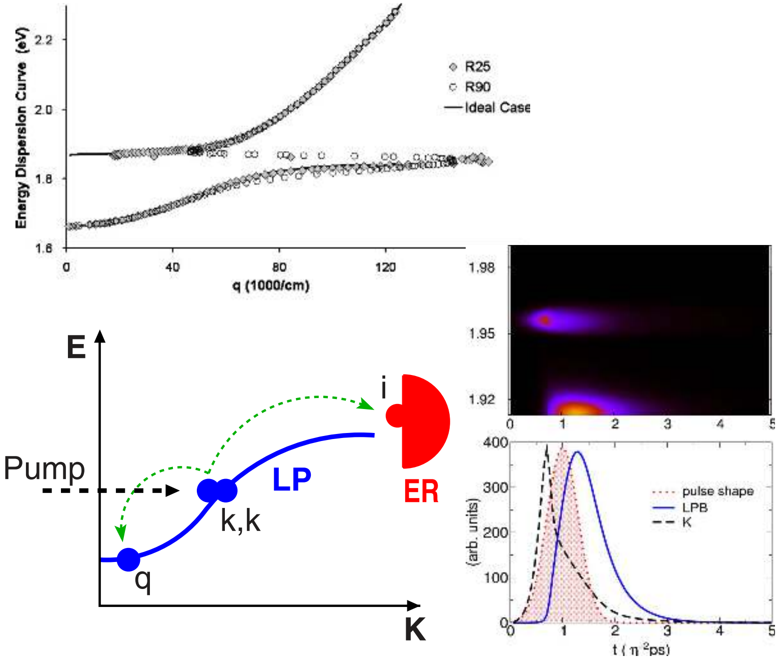
Cavity polaritons in microcavities containing disordered organic semiconductors

V. M. Agranovich, M. Litinskaya and D. G. Lidzey, Phys. Rev. B **67**, 085311 (2003)



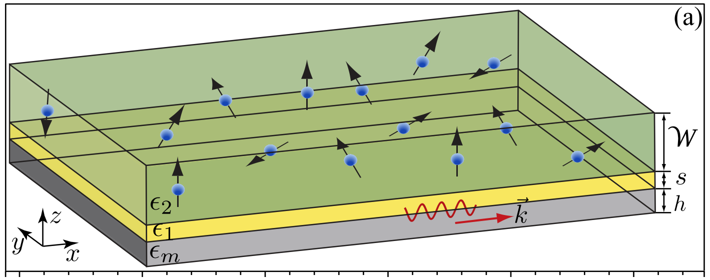
Polariton states & polariton-polariton scattering in disordered organic microcavities

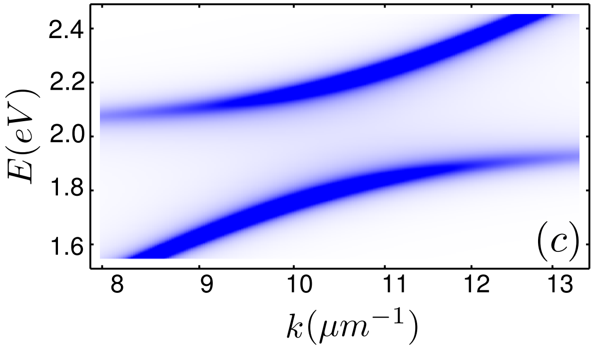
P. Michetti and G. C. La Rocca, Phys. Rev. B **71**, 115320 (2005); Phys. Rev. B **82**, 115327 (2010)



Theory of Strong Coupling between Quantum Emitters and Propagating Surface Plasmons

A. González-Tudela et al, Phys. Rev. Lett. **110**, 126801 (2013).





Coupling to electronic transitions – theoretical approaches

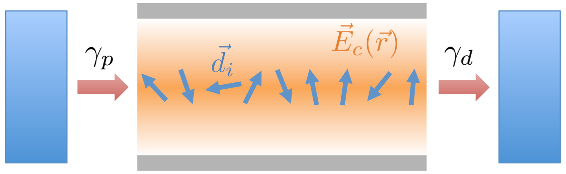
Quantum optics/condensed matter approaches

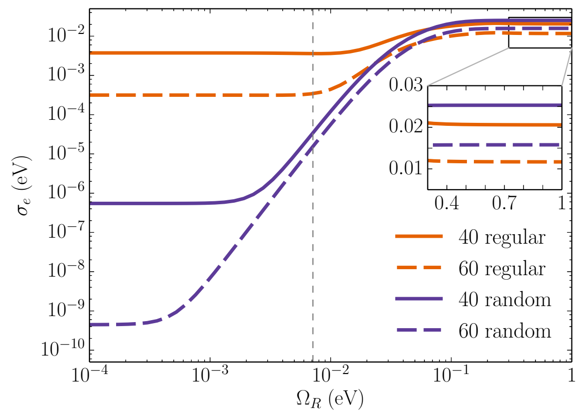
Extraordinary exciton conductance

J. Feist, F. J. Garcia-Vidal, Phys. Rev. Lett. **114**, 196402 (2015)

Cavity enhanced transport of excitons

J. Schachenmayer, C. Genes, E. Tignone and G. Pupillo , Phys. Rev. Lett. **114**, 196403 (2015)



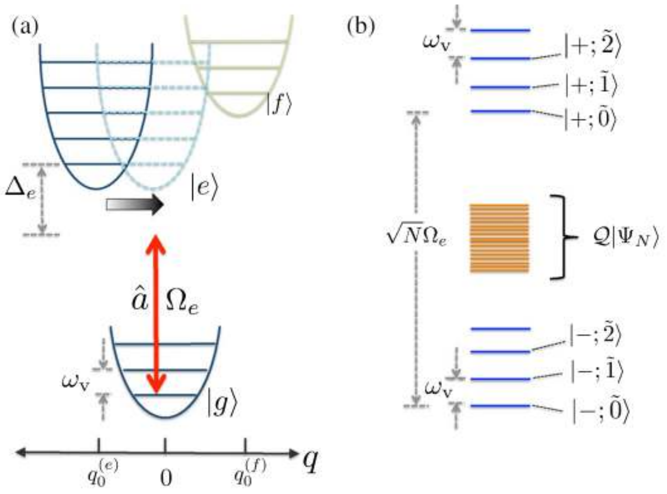


Cavity-controlled chemistry in molecular ensembles

F. Herrera and F. C. Spano, Phys. Rev. Lett **116**, 238301 (2016)

Dark vibronic polaritons and the spectroscopy of organic microcavities

F. Herrera and F. C. Spano, Phys. Rev. Lett **118**, 223601 (2017)

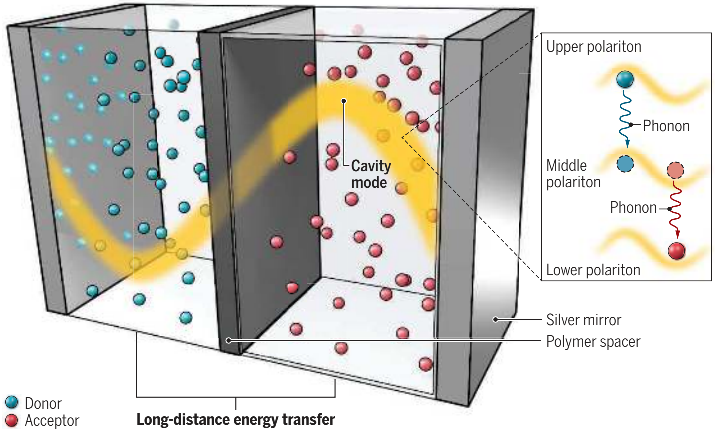


Coupling to electronic transitions – theoretical approaches

Quantum optics/condensed matter approaches

Long-distance operator for energy transfer

F. J. Garcia-Vidal, J. Feist, Science **357**, 1357 (2017) (perspective on Zhong, Angew. Chem. **56**, 9034)

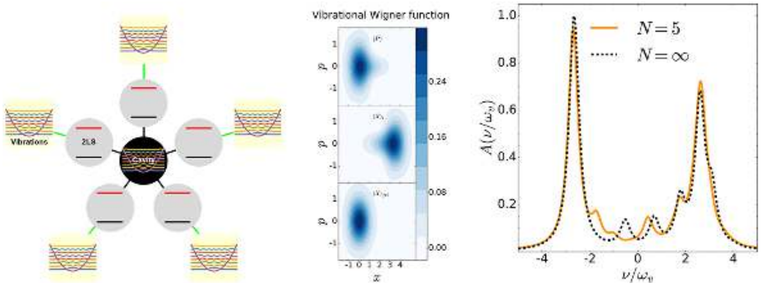


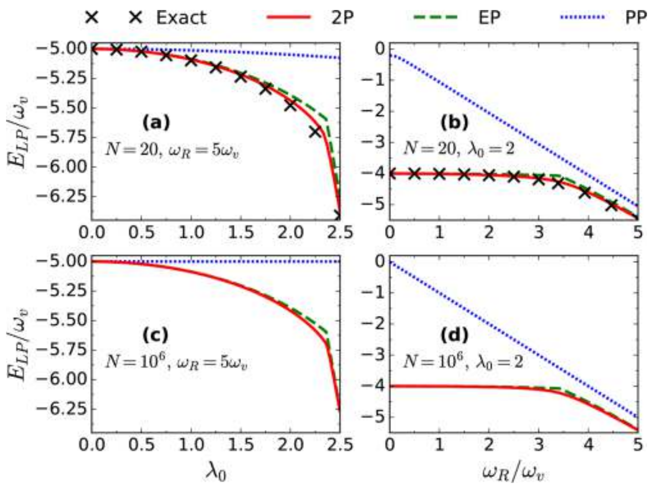
Quantitative explanation:

R. Sáez-Blázquez, J. Feist, A.I. Fernández-Domínguez, F.J. García-Vidal, Phys. Rev. B **97**, 241407(R) (2018)

Vibrational dressing of polaritons

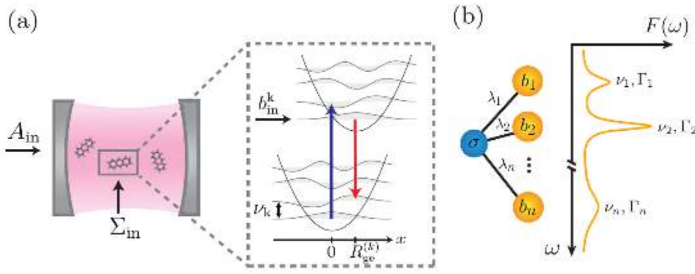
M. A. Zeb et al., ACS Photonics **5**, 249 (2018).

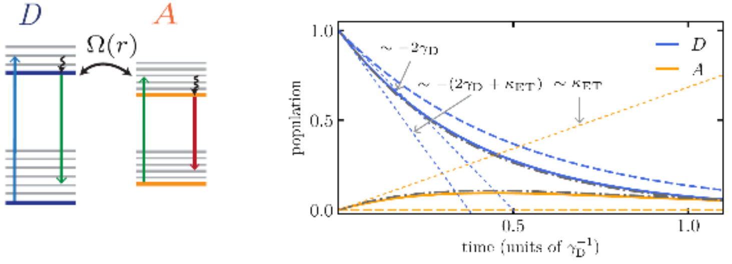




Quantum Langevin approach to quantum optics with molecules

M. Reitz, C. Sommer and C. Genes, Phys. Rev. Lett **122**, 203602 (2019)



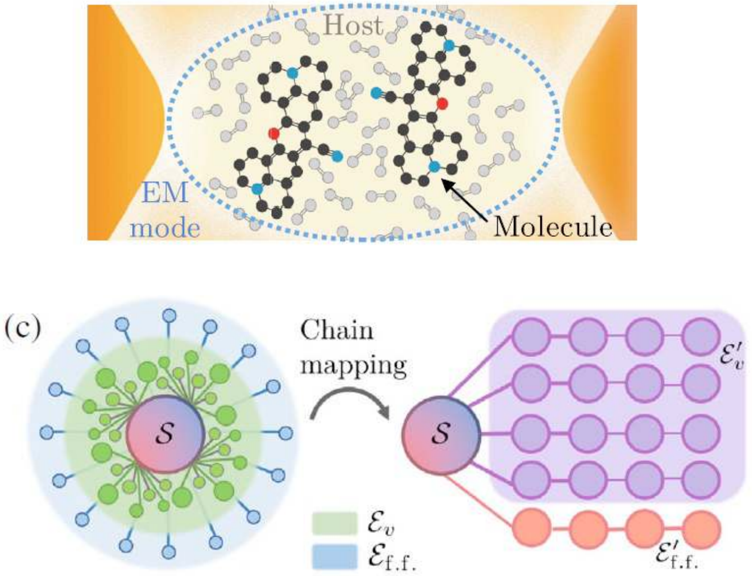


Coupling to electronic transitions – theoretical approaches

Quantum optics approaches – numerical tensor matrix simulations

Tensor network simulations of non-markovian dynamics in organic polaritons

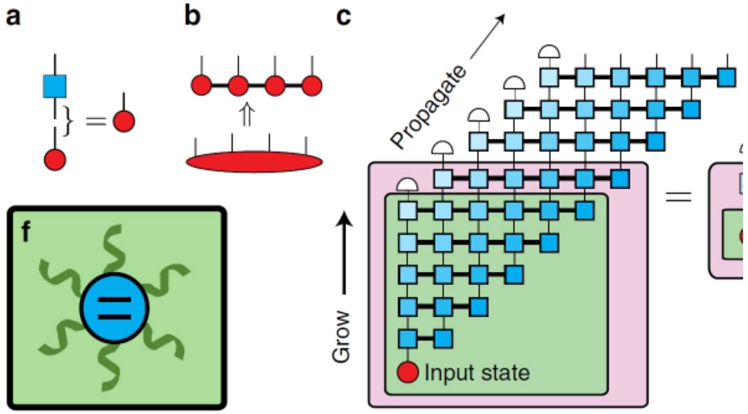
J. Del Pino et al, Phys. Rev Lett. **121**, 227401 (2018)



Efficient non-markovian quantum dynamics using time-evolving matrix product operators

A. Strathearn et al, Nat. Comms. **9**, 3322 (2018)

Quantum optics approaches

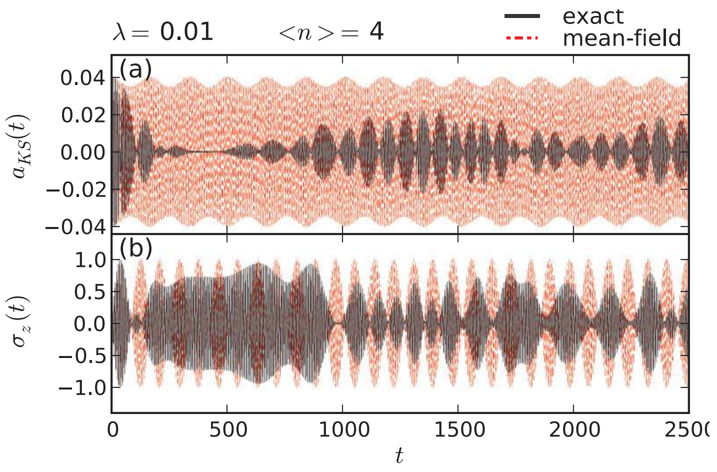


Coupling to electronic transitions – theoretical approaches

Ab initio / electronic-structure-based approaches

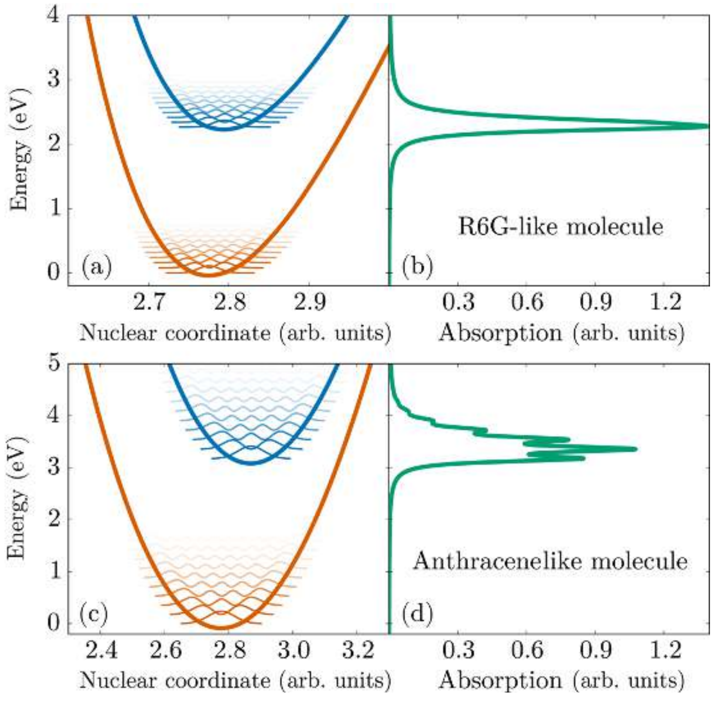
Quantum-electrodynamical DFT

I. V. Tokatly, Phys. Rev. Lett. **110**, 233001 (2013)
M. Ruggenthaler et al., Phys. Rev. A **90**, 012508 (2014)



Polaritonic potential energy surfaces

J. Galego et al., Phys. Rev. X **5**, 041022 (2015)

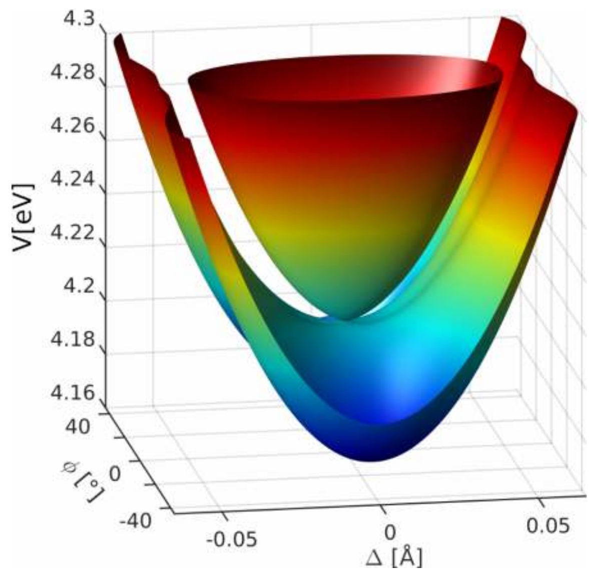


Nonadiabatic dynamics in cavities

M. Kowalewski et al, J. Chem. Phys. **144**, 054309 (2016).

Quantum light-induced conical intersections

A. Csehi et al., arXiv:1902.03640



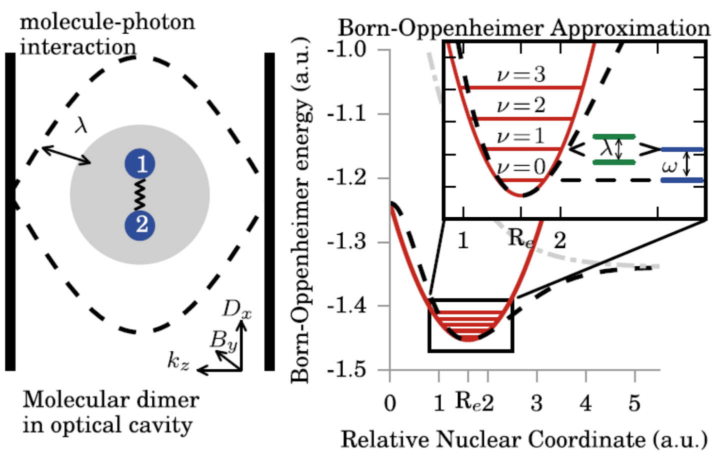
Coupling to electronic transitions – theoretical approaches

Ab initio / electronic-structure-based approaches

Cavity Born-Oppenheimer approximation

J. Flick et al., PNAS **114**, 3026 (2017)

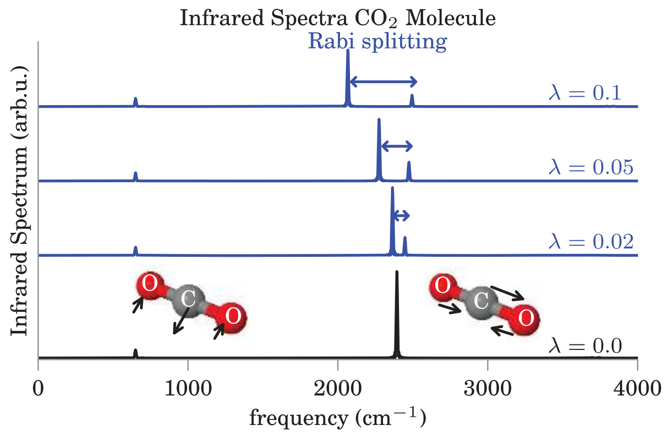
J. Flick et al.; JCTC **13**, 1616 (2017)

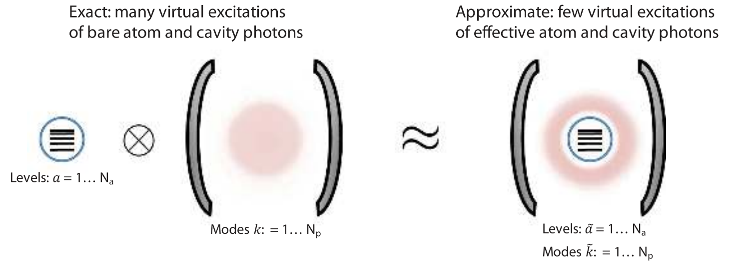


Cavity-Correlated Electron-Nuclear Dynamics & Variational Theory

J. Flick and P. Narang, Phys. Rev. Lett. **121**, 113002 (2018).

N. Rivera et al., Phys. Rev. Lett. **122**, 193603 (2019).

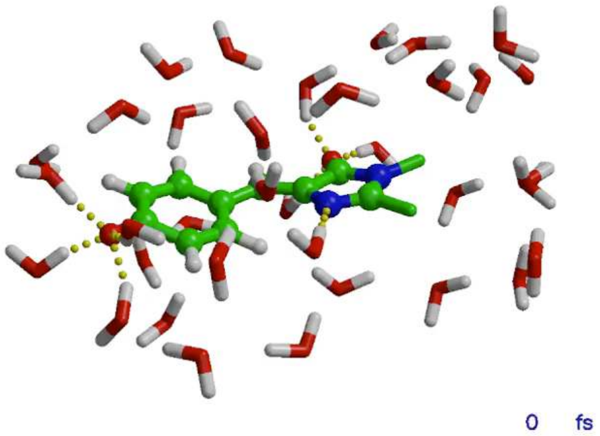




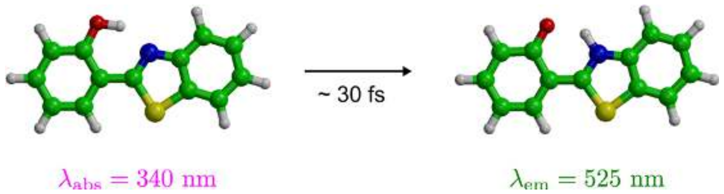
Coupling to electronic transitions – theoretical approaches

Molecular dynamics / quantum chemistry etc

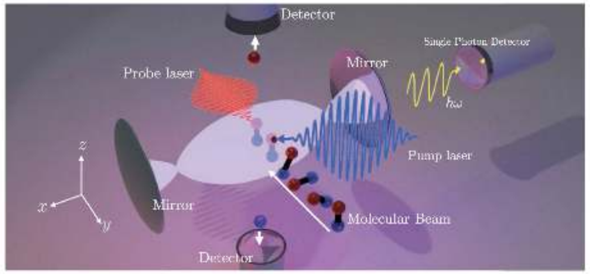
Multiscale QM/MM molecular dynamics
H. L. Luk et al., JCTC **13**, 4324 (2017)

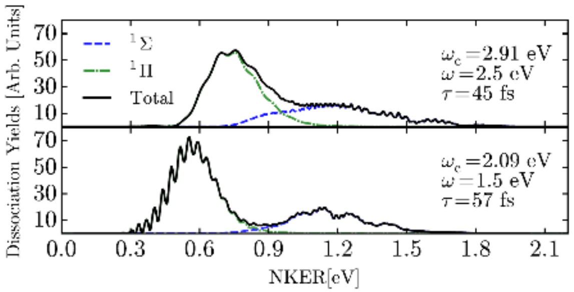


Coherent Light Harvesting
G. Groenhof, J. J. Toppari, J. Phys. Chem. Lett. **9**, 4848 (2018)

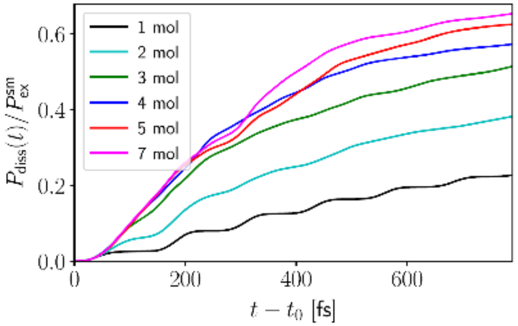


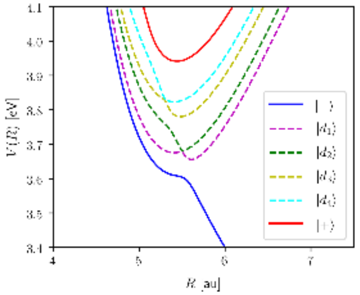
Revealing the Presence of Potential Crossings in Diatomics Induced by Quantum Cavity Radiation
J. F. Triana and J. L. Sanz-Vicario, Phys. Rev. Lett. **122**, 063603 (2019)



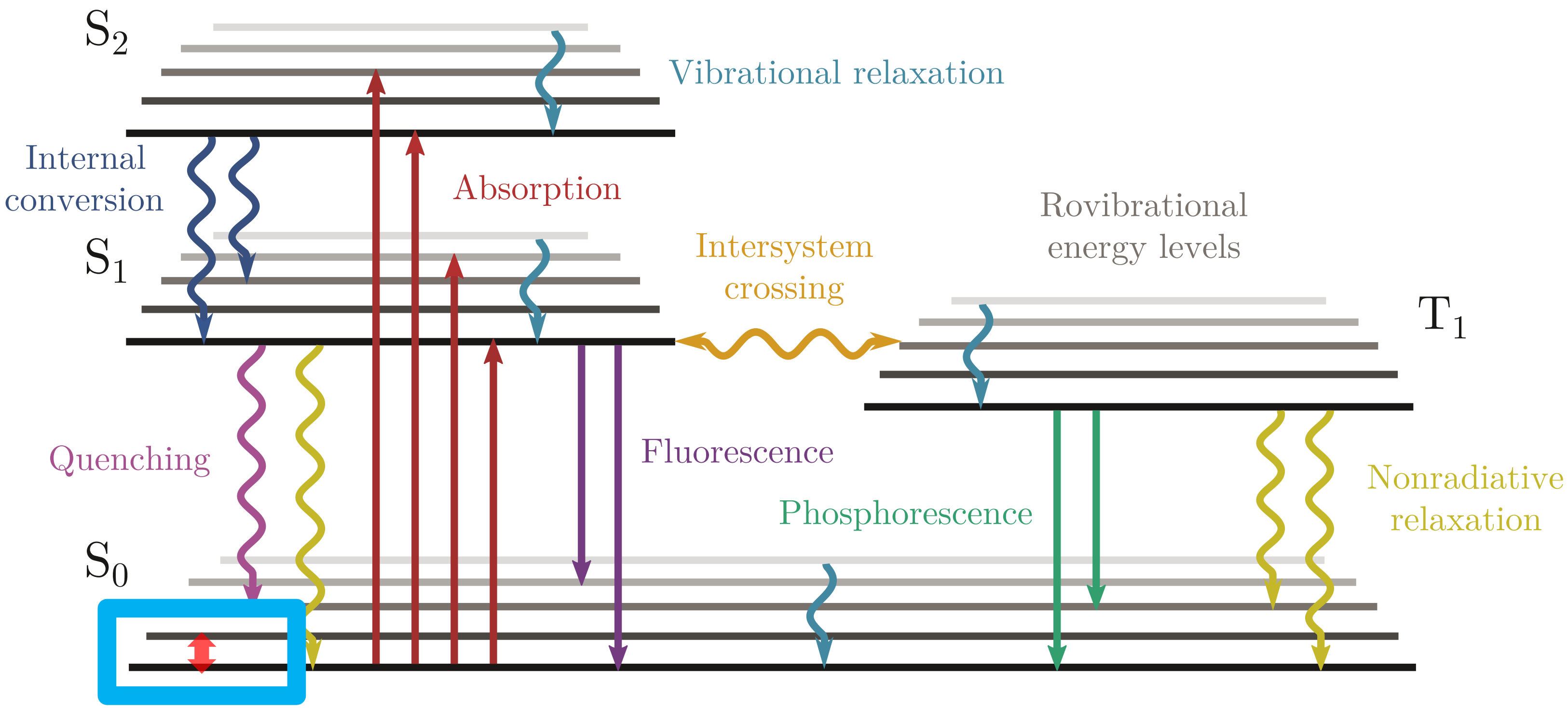


Collective Jahn-Teller Interactions through Light-Matter Coupling in a Cavity (MCTDH)
O. Vendrell, Phys. Rev. Lett. **121**, 253001 (2018)





The complex nature of molecules



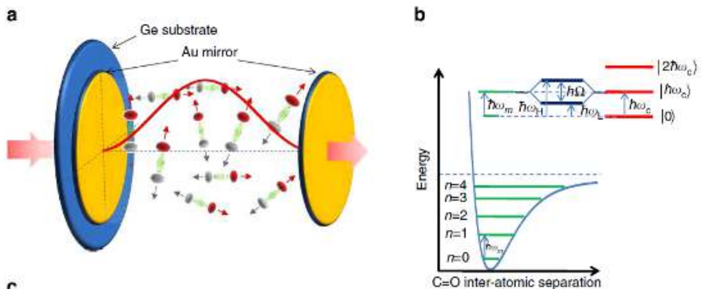
Coupling at infrared frequencies

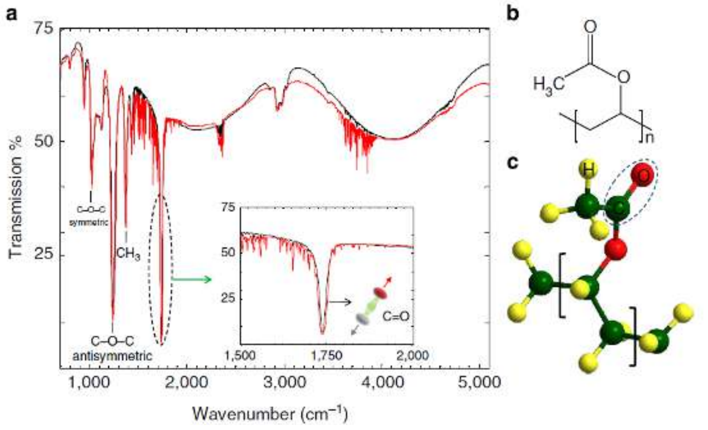
- All within electronic ground state – thermally driven effects
- “Optomechanical” (nuclear motion coupled to light)
- Modification of ground-state chemical reactions

Strong coupling to vibrations – experimental progress

Coherent coupling of molecular resonators with a microcavity mode

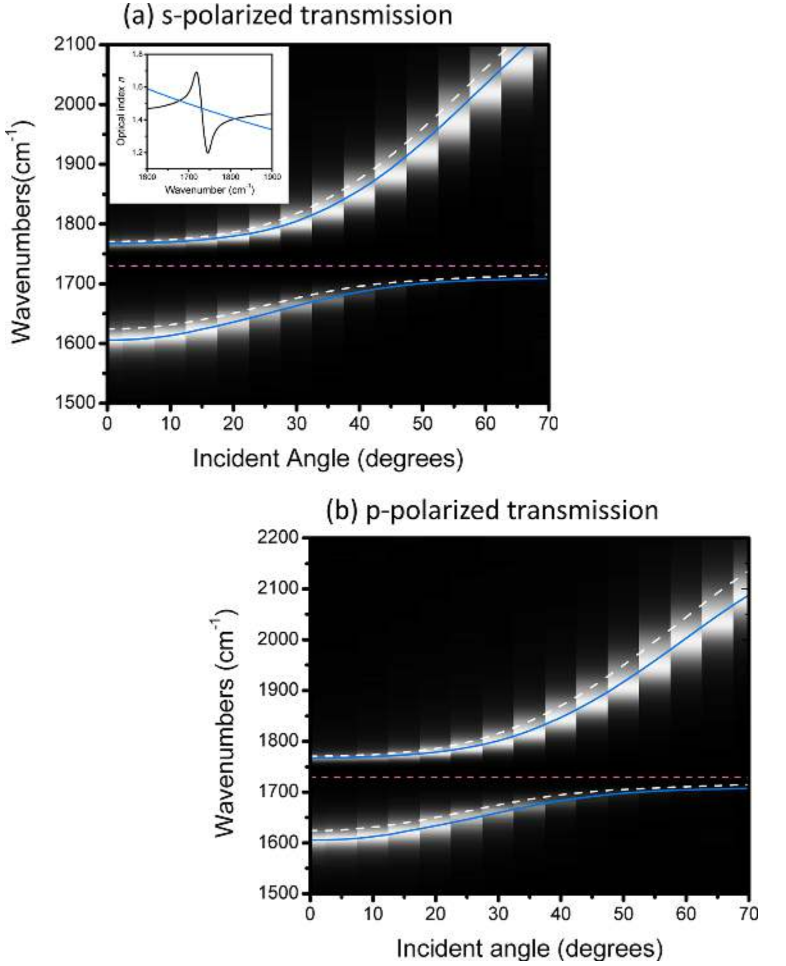
A. Shalabney et al, Nat Comms. **6**, 6981 (2015)





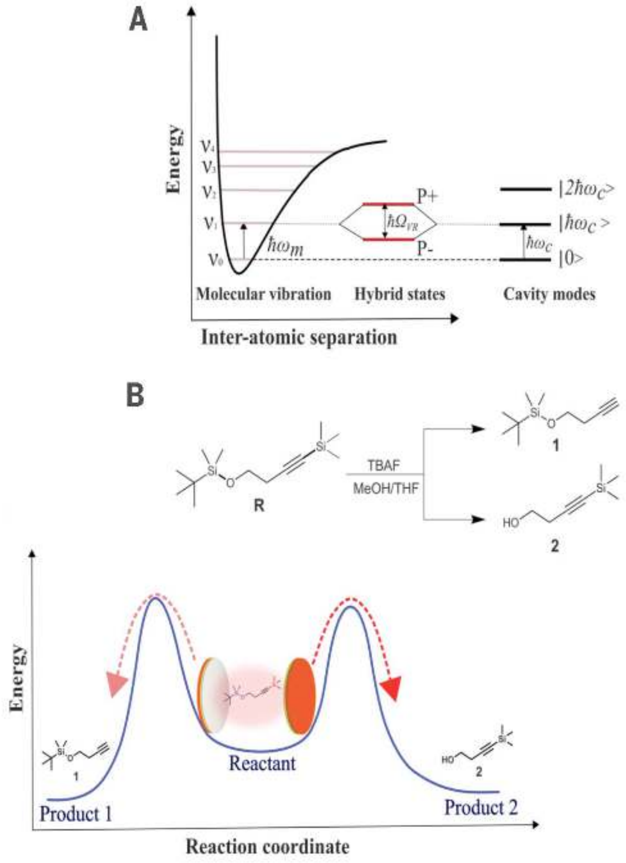
Vibrational strong coupling

J. P. Long and B. S. Simpkins, ACS Phot. **2**, 130 (2015)



Changing ground-state chemistry

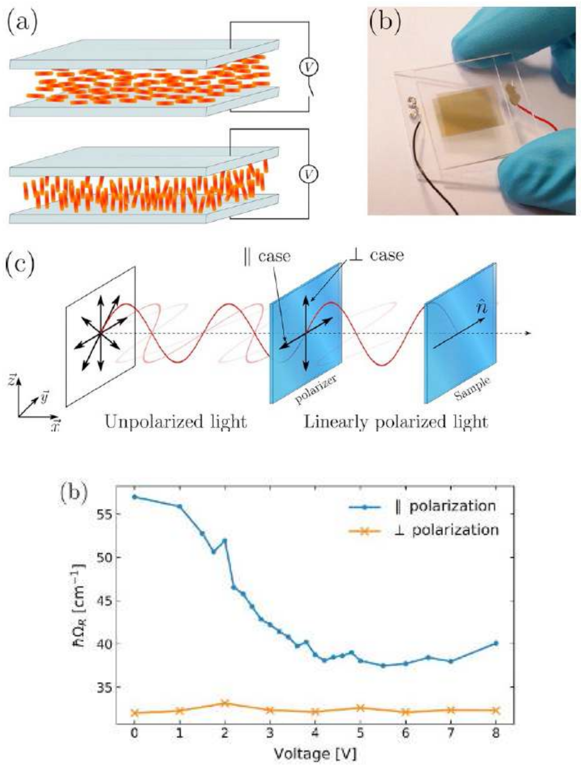
A. Thomas et al., Angew. Chem. Int. Ed. **55**, 6202 (2016);
Science, **363**, 6427 (2019)



Strong coupling to vibrations – experimental progress

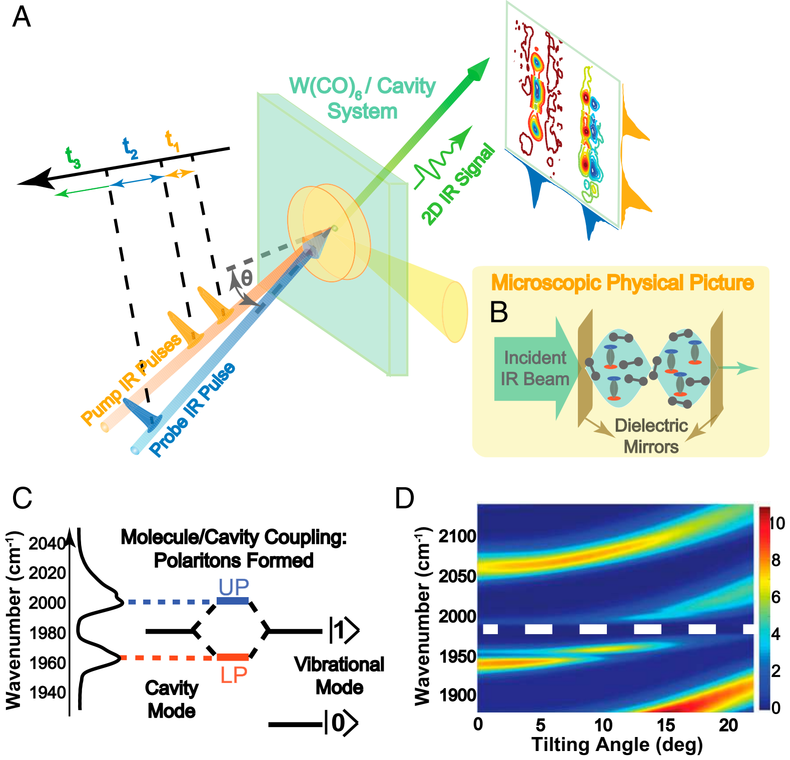
Voltage-controlled switching of strong light–matter interactions using liquid crystals

M. Hertzog et al, Chem. Eur. J., **23,** 18166 (2017)



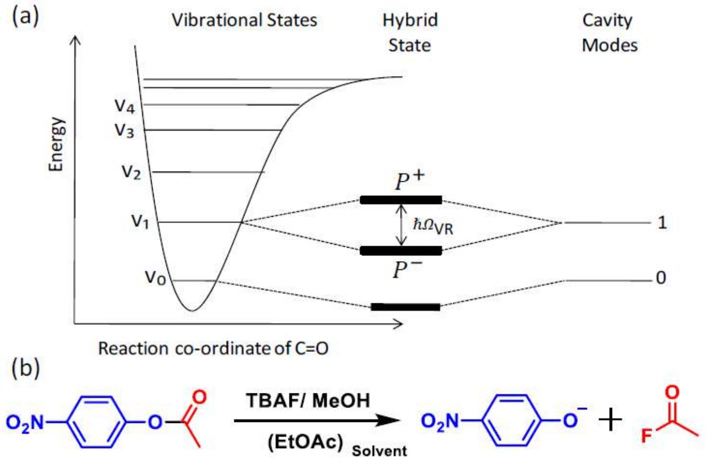
Nonlinear Spectroscopy of Vibrational Polaritons

B. Xiang et al., PNAS **115**, 4845 (2018)



Cavity catalysis by cooperative vibrational strong coupling of reactant and solvent molecules

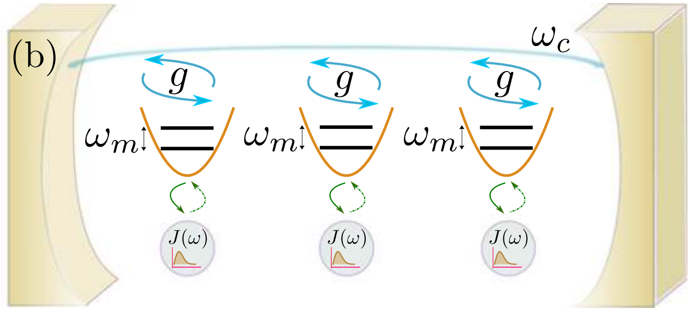
J. Lather et al, Ang. Chemie (2019)

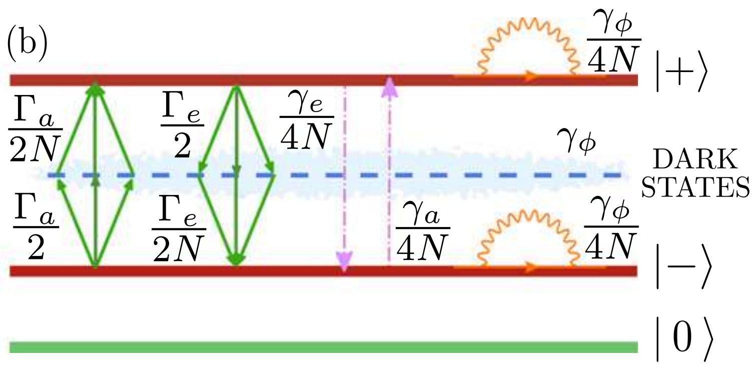


Strong coupling to vibrations – theory

Quantum theory of collective strong coupling of molecular vibrations with a microcavity mode

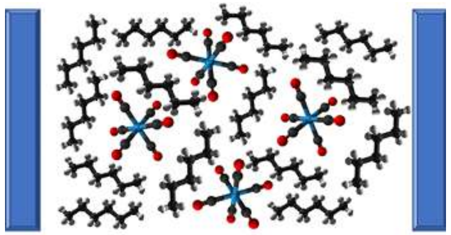
J. del Pino et al., New J. Phys. **17**, 053040 (2015)

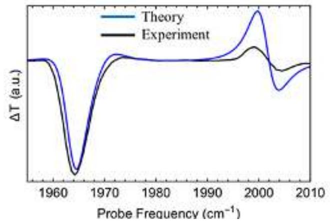


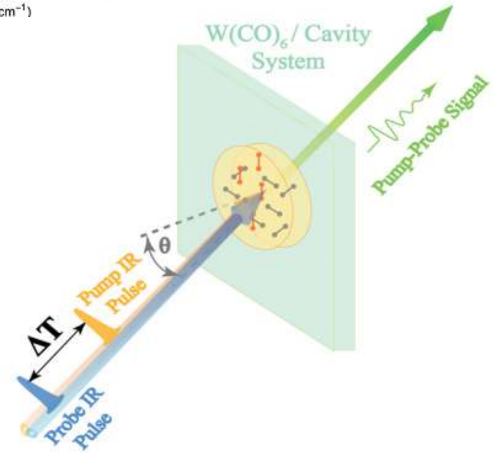


Theory for Nonlinear Spectroscopy of Vibrational Polaritons

R. F. Ribeiro et al, J. Phys. Chem. Lett. **9** 3766, (2019)



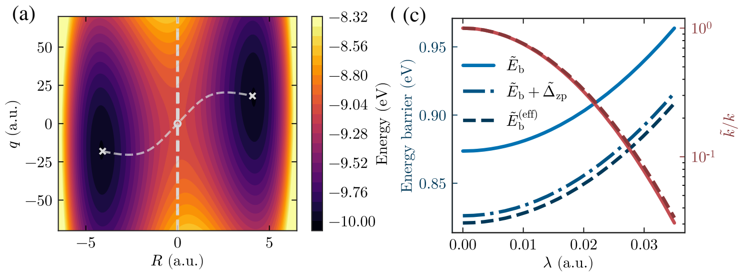


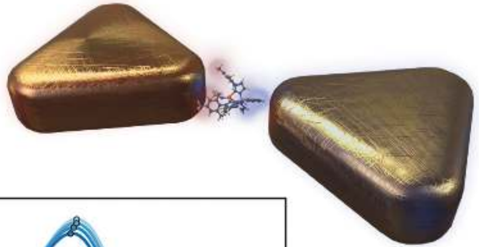


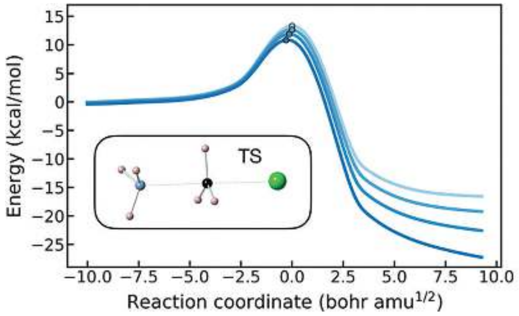
Cavity Casimir-Polder forces & self-induced electrostatic catalysis

J. Galego et al., Phys. Rev. X **9**, 021057 (2019)

C. Climent et al., Angew. Chem. Int. Ed. **58**, 8698 (2019).







Theoretical challenges ahead…

Proper modelling of light-matter interaction in non-trivial cavities (plasmonic structures, hybrid cavities, frequency dependent mirrors etc)

Efficient/reliable simulations for many particles (including many vibrations, dissipative coupling to bulks or solvent etc)

Huge playing field!

- Identify interesting effects that can be controlled/manipulated/enhanced via strong coupling
- Which chemical reactions can be affected, and how? (ground state, solvent effects…)
- Room-temperature quantum optics?
- Connection to ultrafast laser physics?