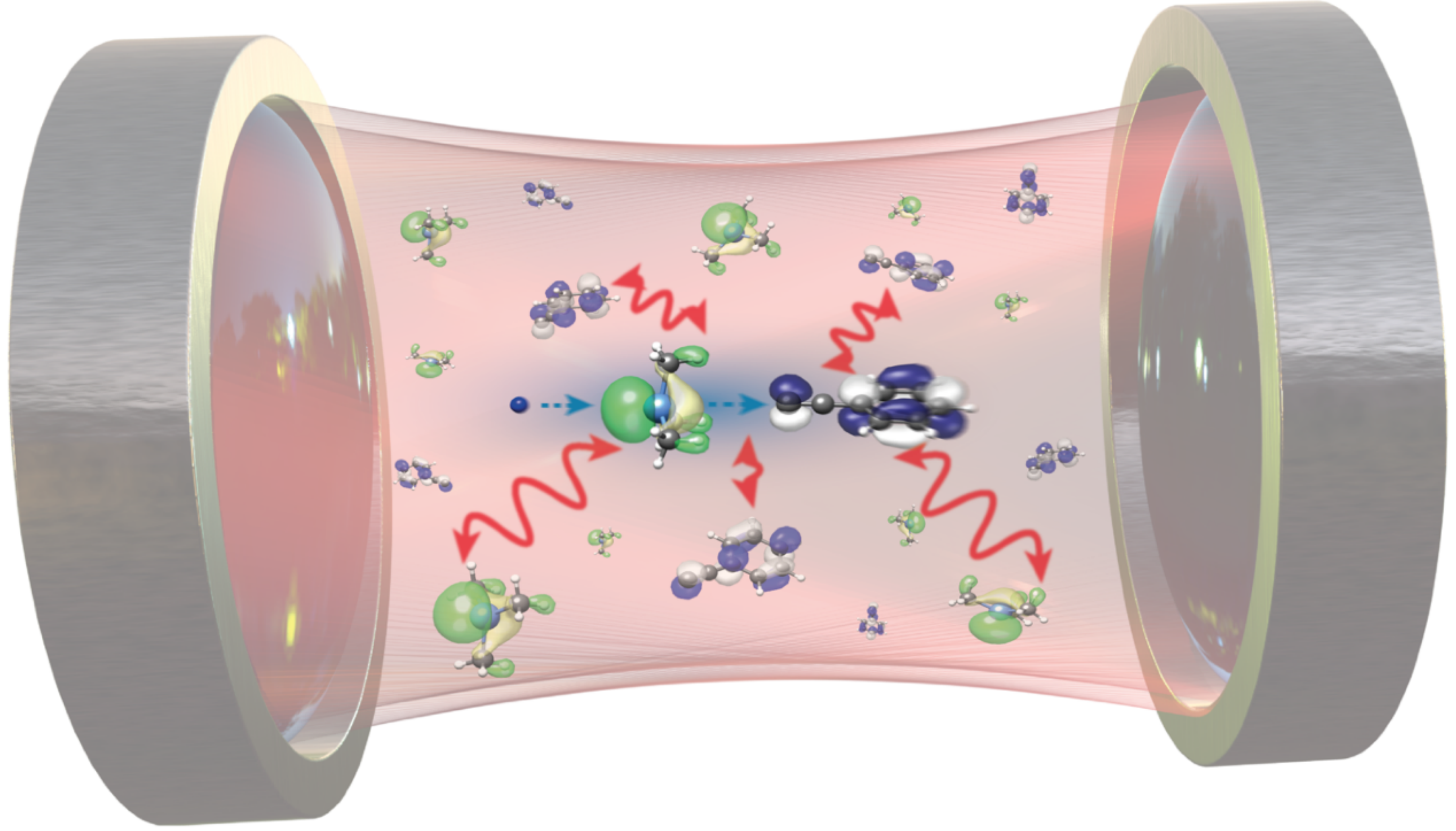
Dominik Sidler, January 2025

Polaritonic / QED Chemistry

Lecture 1: Introduction



mpsd
Max-Planck-Institut für Struktur und Dynamik der Materie

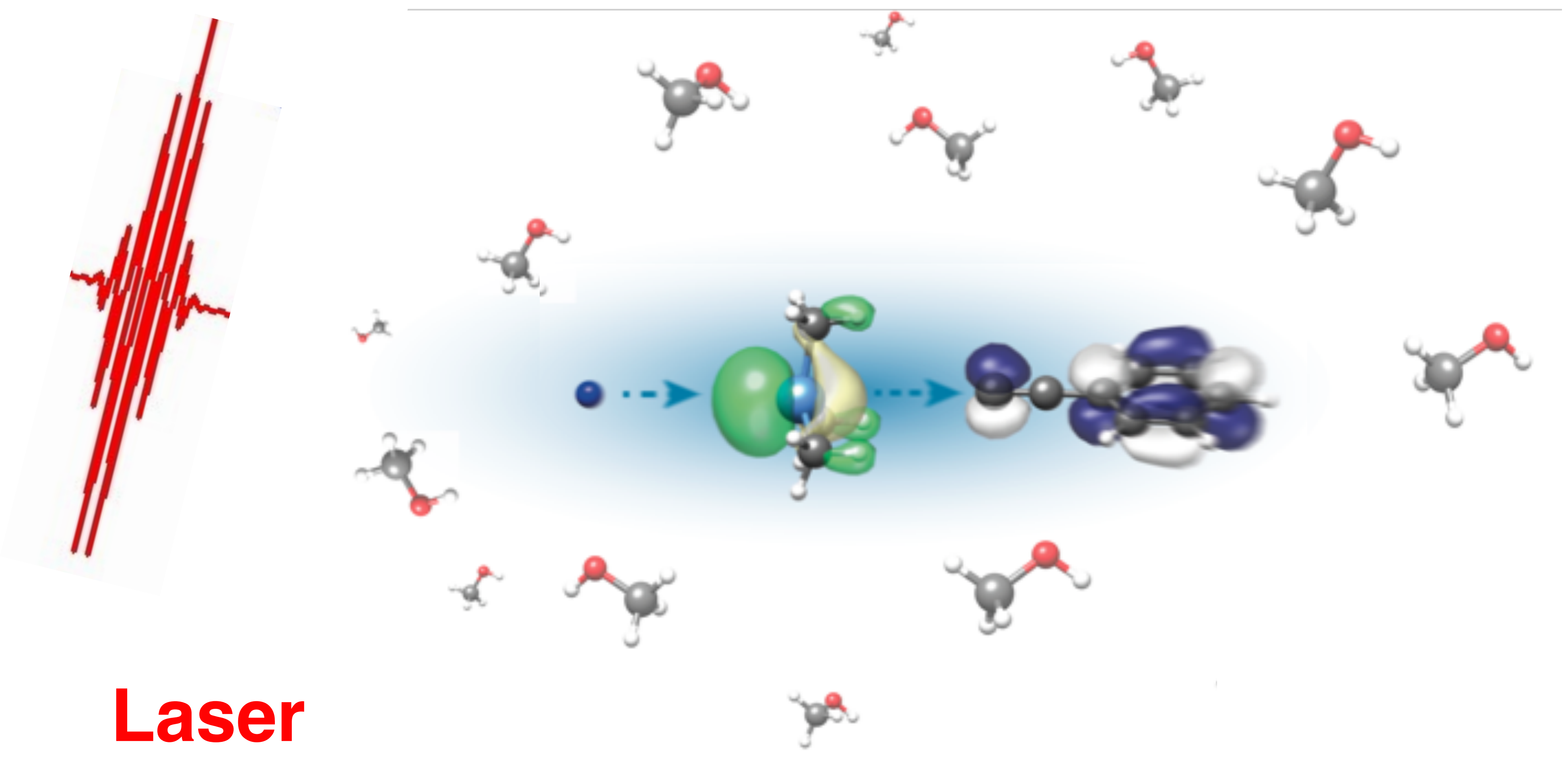
PSI

University of Zurich[UZH]

Polaritonic Chemistry

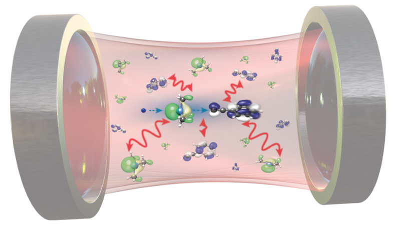
Coupling Light and Matter

Frequency (bond / site) selective control of chemistry?



Laser driving with undesired heating

Control chemistry by temperature, pressure, solvent, catalyst,…

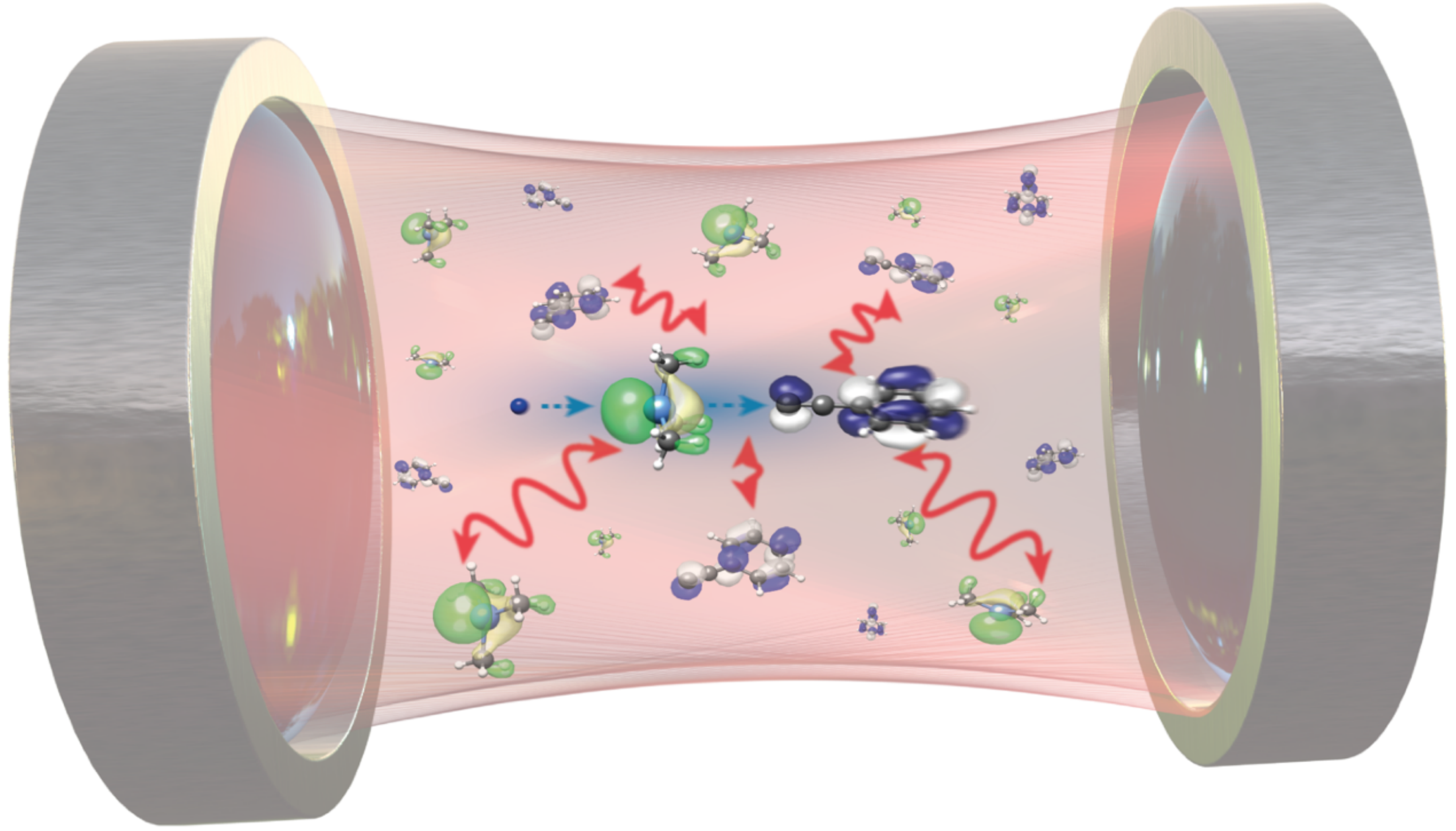


Polaritonic Chemistry

Coupling Light and Matter Strongly

Frequency (bond / site) selective control of chemistry?

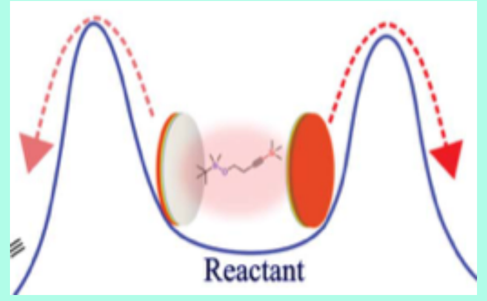
Optical cavity



Restructuring vacuum modes

Hybridisation of quantum light and matter

Experimental success



Engineer equilibrium properties

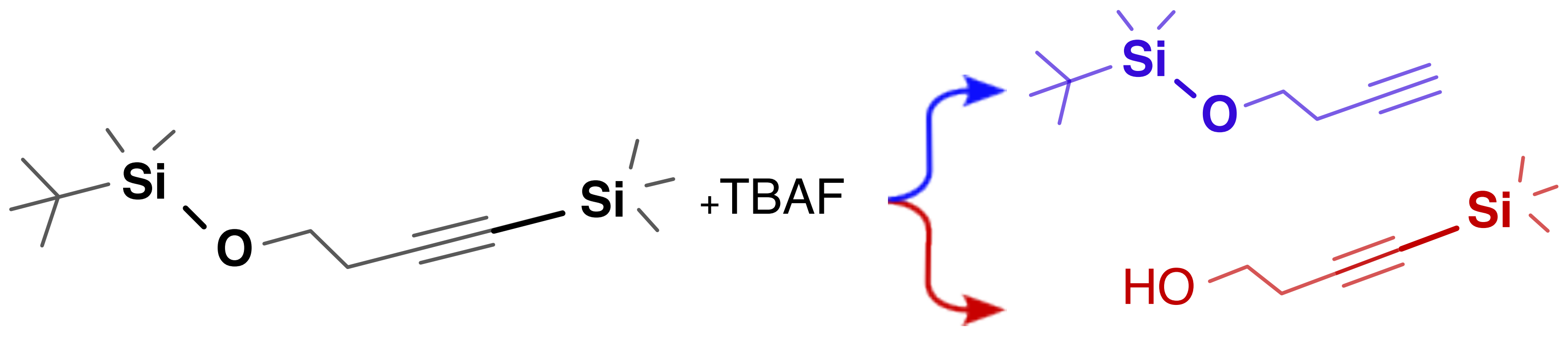
Novel chemical effects

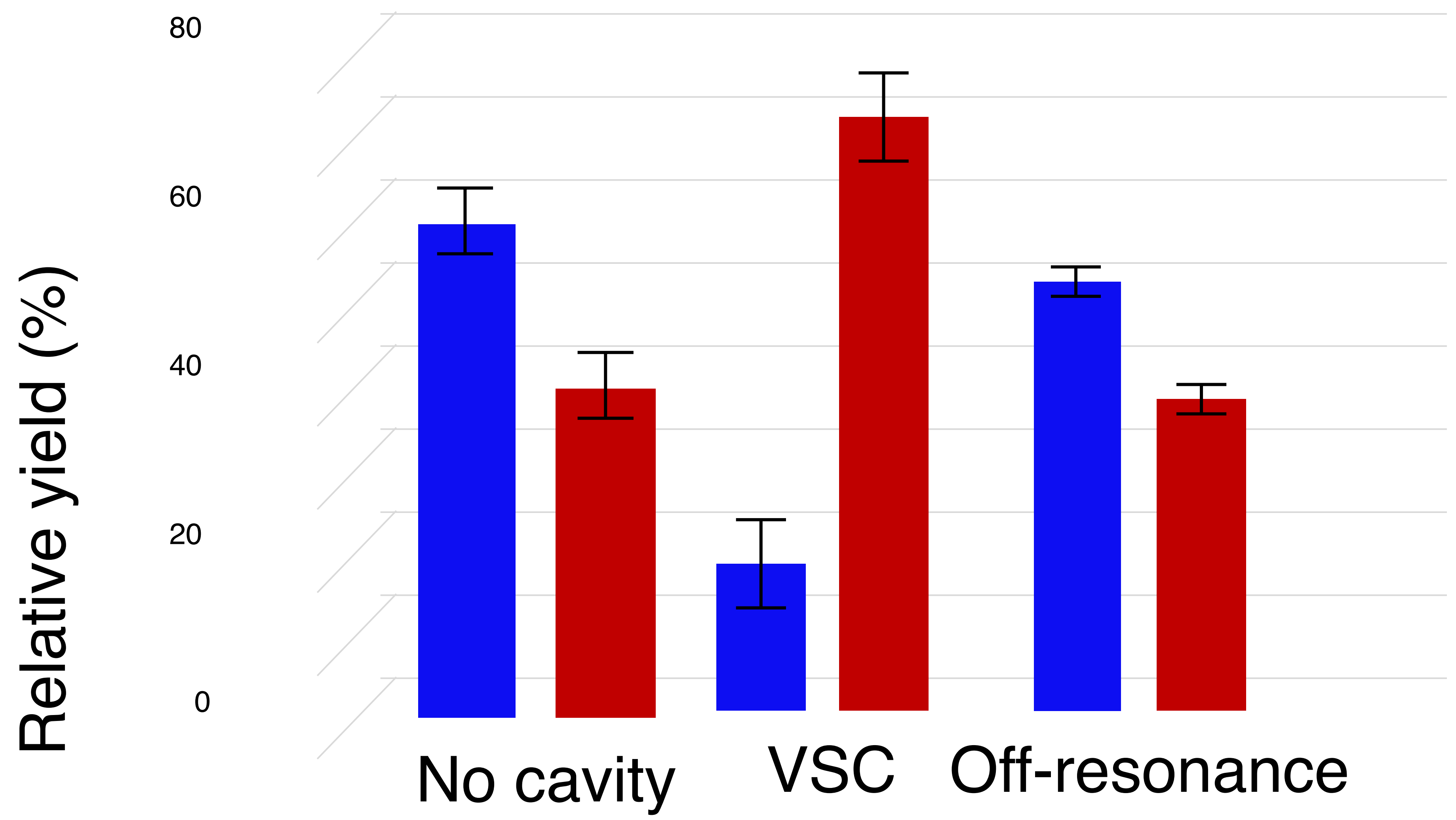
Industrial relevance

Seminal Experiments

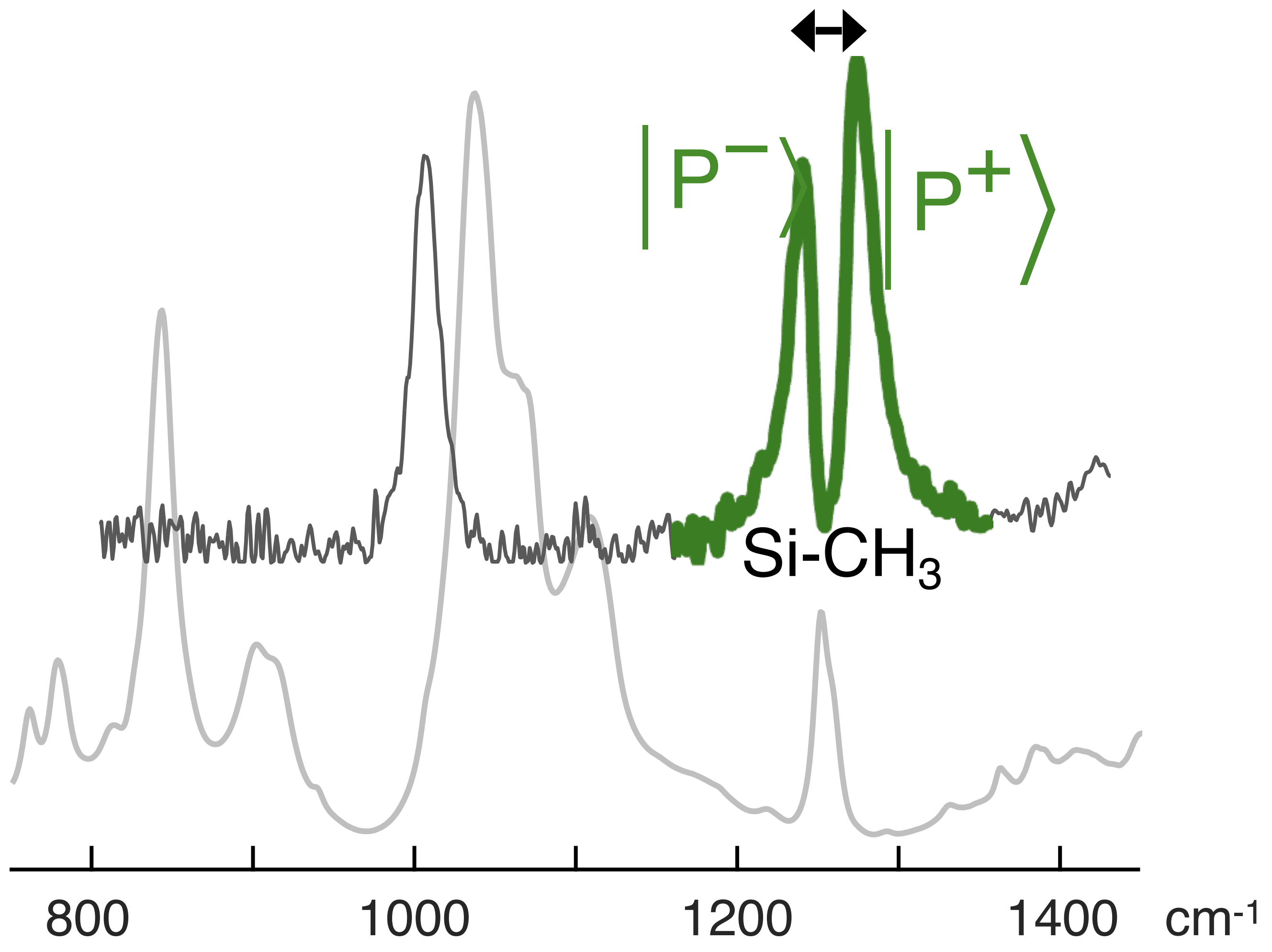
Vibrational Strong Coupling (VSC): A Novel Tool for Tailoring Reactivity

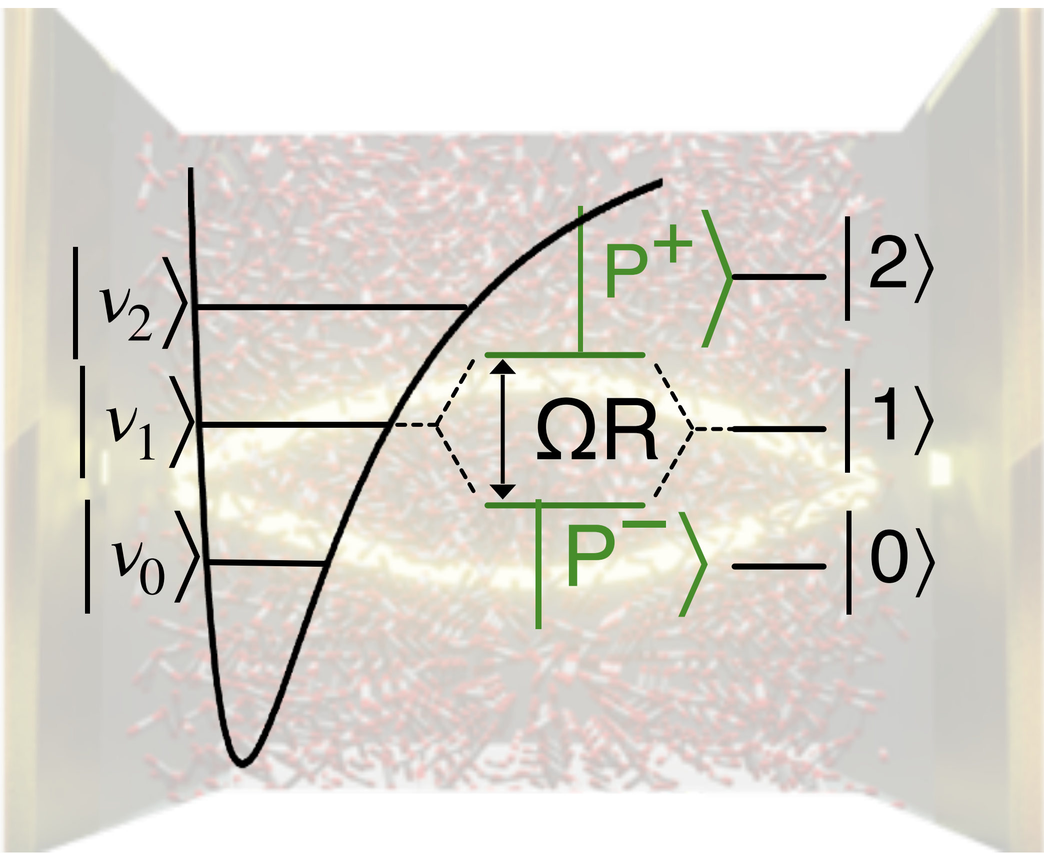
Example: Site-selective silyl bond cleavage





Rabi splitting Ω_R



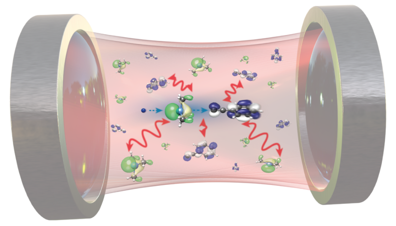


A “different” molecule with modified properties

∗∗∗ In the “dark”

∗∗∗ At room temperature

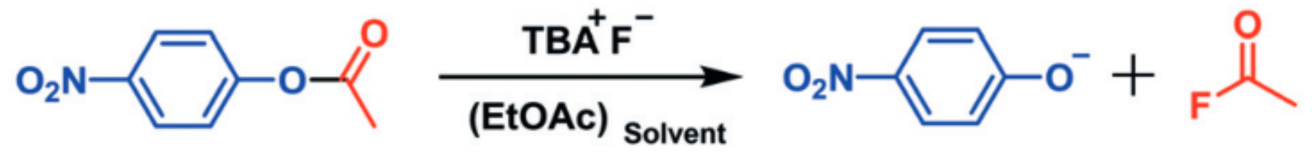
A. Thomas et. al. Science (2019), DOI: 10.1126/science.aau7742



Seminal Experiments

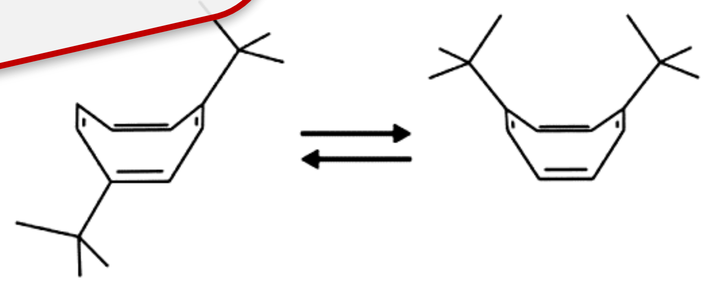
VSC: A Novel Tool for Tailoring Reactivity

Hydrolysis reaction
Lather et al., *Angew. Chem.* 2019



Ionic conductivity of water
Fukushima et al., *JACS* 2022

Isomerization reaction
Patrahau et al.,
Angew. Chem. 2024



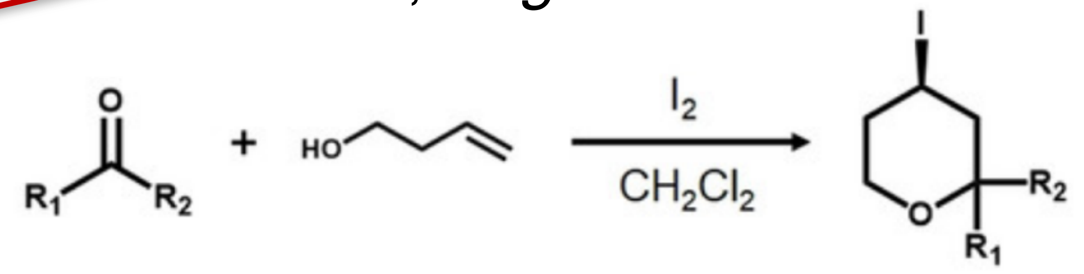
Synergy Grants

erc
European Research Council
Established by the European Commission

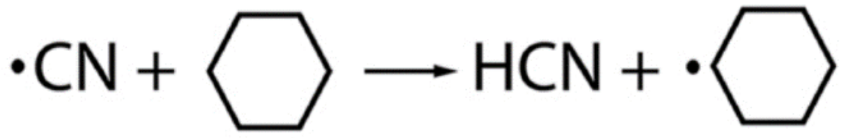
Underlying mechanism(s) still unknown!

Deprotection reaction
Thomas et al.,
Angew. Chem. 2016

Prins Cyclization
Hirai et al., *Angew. Chem.* 2020

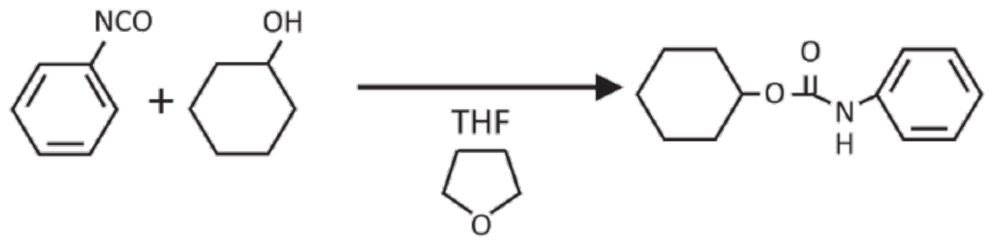


No effect: H-abstraction
Chen et al., *Nanophotonics* 2024



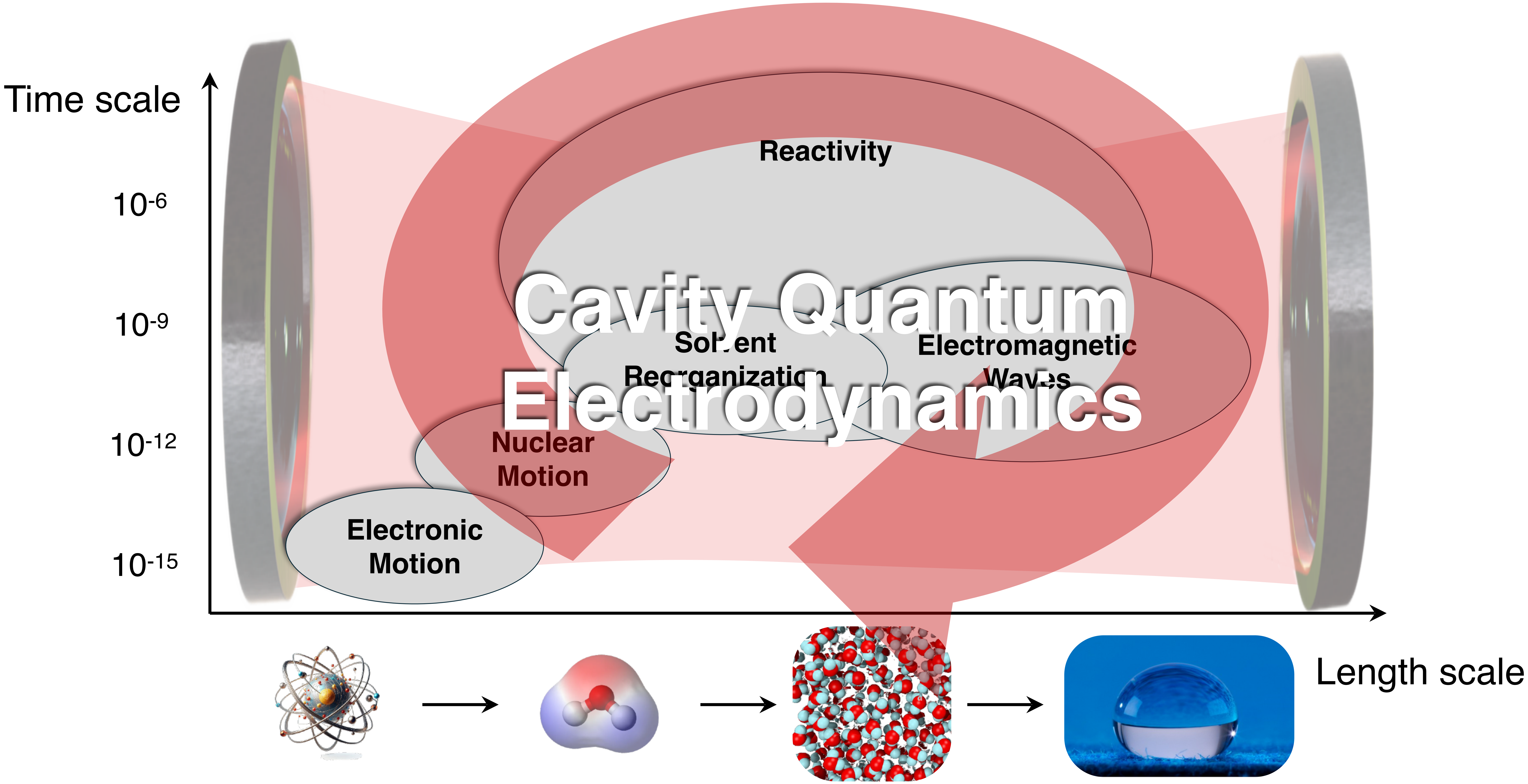
(+ Unpublished results)

Addition reaction
Ahn et al., *Science* 2023



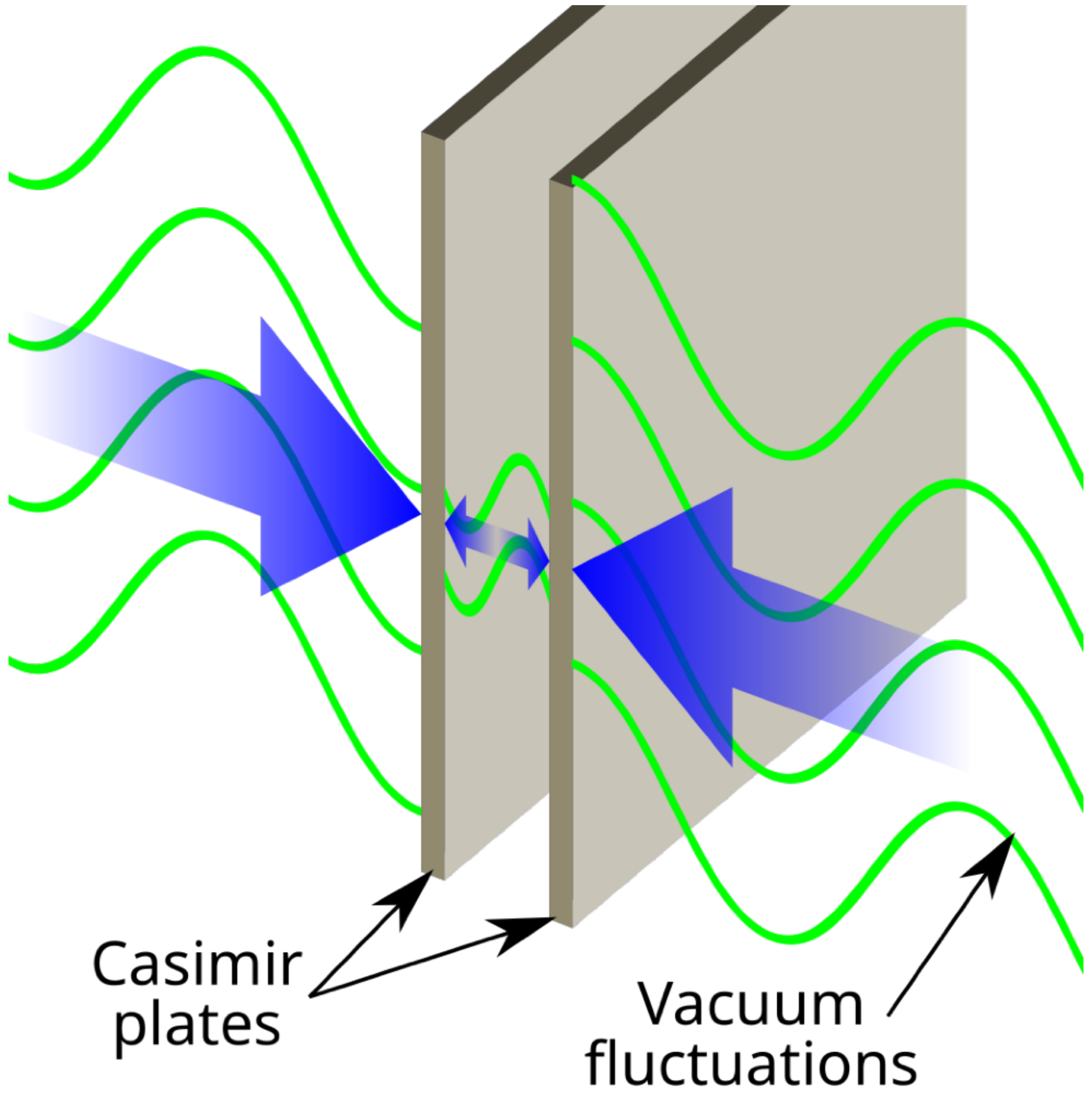
Polaritonic Chemistry

A Multiscale Challenge



Why Quantum Light?

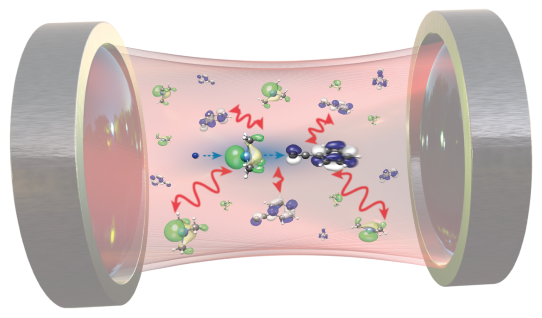
Famous Example: Casimir Forces



- Metal plates (cavity) **impose boundary conditions** (BC) on electromagnetic field.
- Only **discrete number of field modes** are allowed in cavity.
- **Breaks isotropy of space** / vacuum field is restructured that introduces **attractive force on metal plates.**

 For example: S. Scheel and S. Y. Buhmann, „Macroscopic quantum electrodynamics - concepts and applications“, arXiv:0902.3586, (2009)

Lecture: Aims and Concept



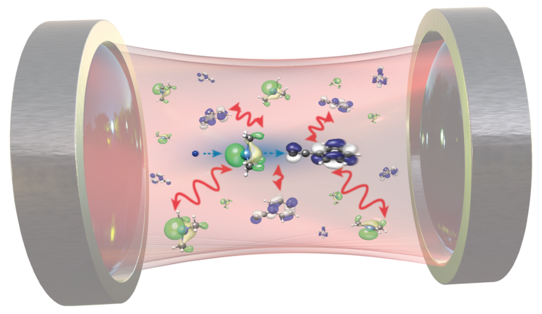
Polaritonic chemistry is a young and active research discipline and no general consensus about the relevant theoretical mechanism has been achieved!

1. Introduce fundamental theoretical concepts.
2. Focus on ab-initio methods, complementary with standard quantum / computational chemistry.
3. Standard numerical solution strategies adjusted for optical cavities.
4. Illustrate several open theoretical questions.
5. Equip students to contribute their expertise to the highly interdisciplinary theoretical developments in the field.
6. Practical python exercises to familiarize with some key features.
7. Short presentations

Open PhD and postdoc positions at MPSD!

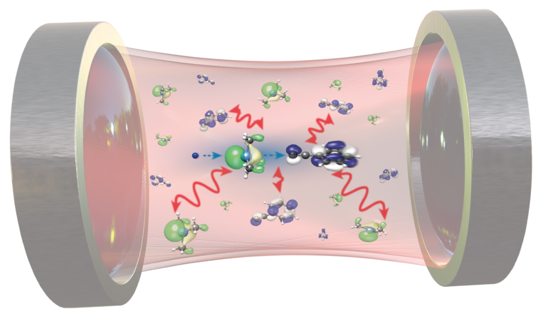
Be critical! Polaritonic chemistry is not established knowledge!
There are a lot of research opportunities awaiting for you!

Who are you?



Background, expectations, interests, …?

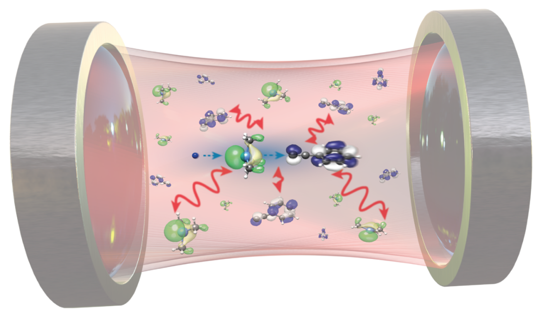
Outline



Course overview

Dates	Topic
24.02.2025	1) Introduction
03.03.2025	2) Macroscopic cavities / Maxwell’s equations
10.03.2025	3) Quantum optics
24.03.2025	4) Pauli-Fierz theory
31.03.2025	5) Electronic strong coupling: Hartree Fock
07.04.2025	6) Vibration strong coupling: Cavity Born-Oppenheimer molecular dynamics
14.04.2025	No lecture (programming task)
21.04.2025	No lecture (Easter Monday)
28.04.2025	No lecture (Sechseläuten)
05.05.2025	7) Fundamental open questions: Local vs. collective and thermodynamics
12.05.2025	8) Advanced topic: Electron correlation and connection to a spin glass
19.05.2025	9) Advanced topic: TBD (e.g. polaritonic reaction rates, or advanced electronic structure methods)
26.05.2025	Presentations / literature seminar / ongoing research

Course Informations

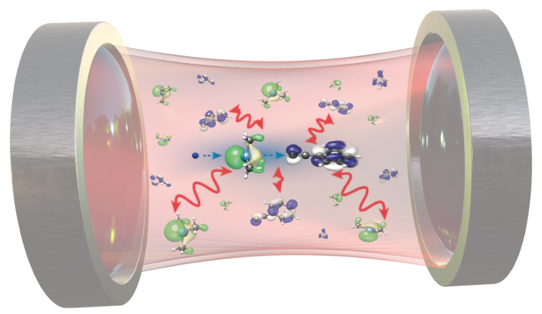


This course is based on the 2024 CECAM school: „Ab initio quantum electrodynamics for quantum materials engineering“. (https://memento.epfl.ch/event/cecam-school-ab-initio-quantum-electrodynamics-for/)

Lecturer: Dr. Dominik Sidler (dominik.sidler@psi.ch)
Scientist at PSI and Groupleader at MPSD (Prof. A. Rubio)

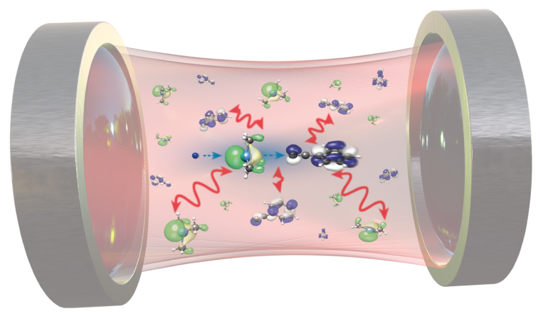
Python exercises and lecture notes:
Git access: git clone https://github.com/sidu85/polaritonic_chemistry_lecture_public.git
Run exercises with *jupyter notebook* on your personal notebook.
Recommended to install python with anaconda: https://docs.anaconda.com/anaconda/install/
Programming exercises start during lecture 2. Be prepared!

Notebook 1



Test jupyter, git access etc. Please run at home…

Theoretical Complexity



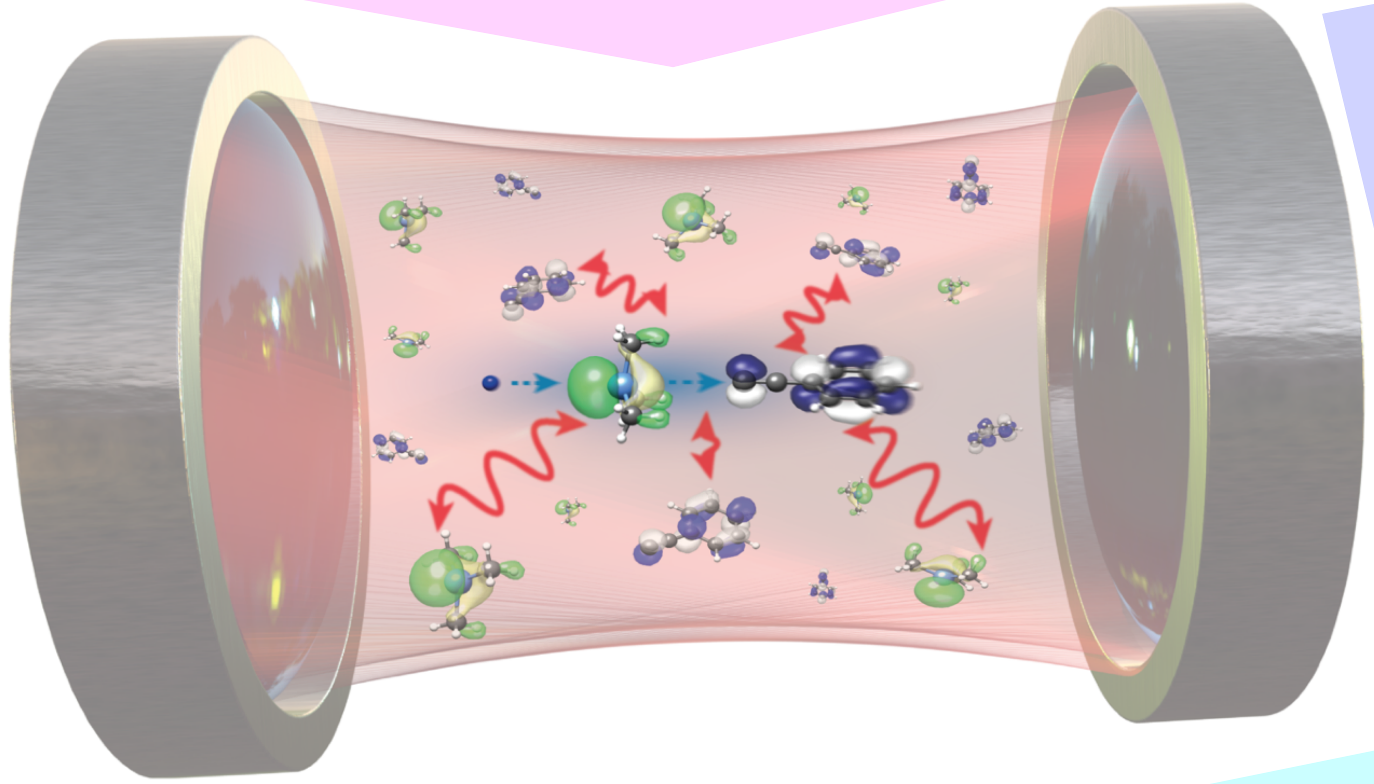
The beauty and the beast

correlations
quantum vs. classical
stochastic resonances
resonance effects

modified response
mirror material
mirror shape
losses
engineer cavity / mode structure

partitioning of wave-function
photochemical proceses
electronic vs. vibrational coupling
nucelar dynamics

real space vs. k-space
gauge choice
solid, liquid, gaseous phase



minimal statistical entity
Boson vs. Fermion
thermodynamics
free energy and entropy
frustration

matter vs. light
symmetry breaking
degeneracy

external driving
electric / magnetic pumping
time-resolved

experimental observables
IR
Raman
NMR
Optical Activity

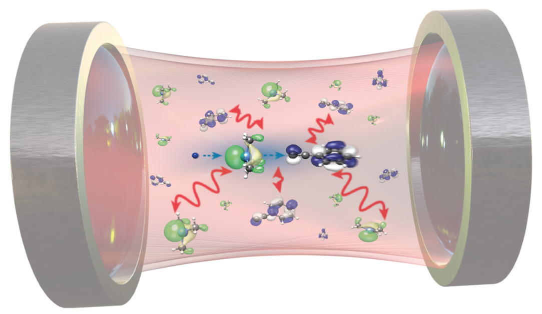
collective vs. local
spin glass
thermodynamic limit
Tavis-Cummings model

numerics
QEDFT
cavity CC
cavity HF
multi reference
MD

reactions
kinetics vs. PES

No-one possess expertise in all relevant fields, but cavity connects them!

Fabry-Pérot Cavity



Prototypical Cavity Setup

Assume normal incident light

speed of light $c = c_0/n$

refractive index n

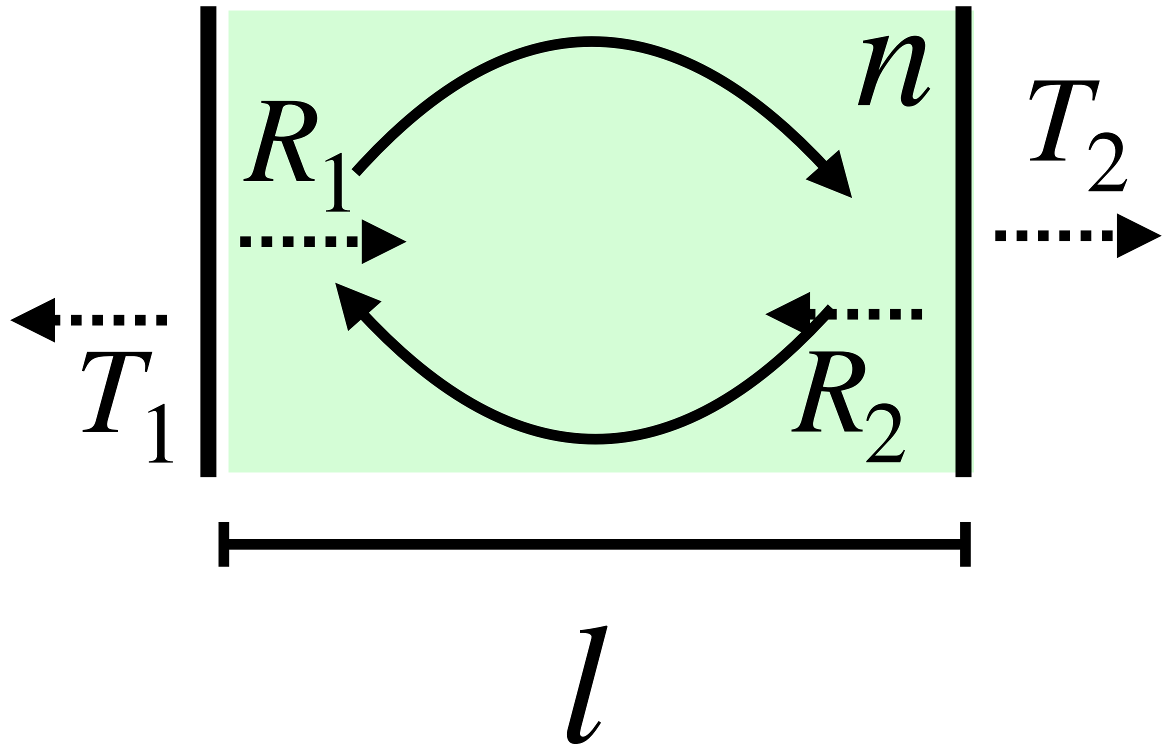
round-trip time $t_{RT} = \frac{2l}{c}$

electric-field r_i^2 or intensity reflectivity R_i

transmitted intensity T_i

losses at mirror τ_i

$$R_i = 1 - T_i = e^{-\frac{t_{RT}}{\tau_i}}$$



photon decay time of resonator $\frac{1}{\tau_c} = \sum_i \frac{1}{\tau_i}$

number of photons decay as $\varphi(t) = \varphi(0)e^{-t/\tau_c}$

single-pass phase shift $\phi(\nu)$ at frequency ν

resonance condition for constructive interference

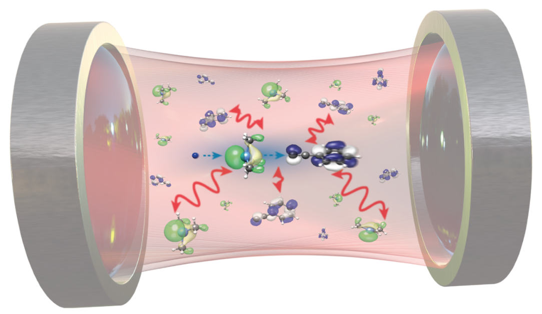
$$2\phi = 2\phi\nu_{\mathrm{FSR}}t_{RT} \stackrel{!}{=} 2\pi$$

free spectra range ν_{FSR}

resonator modes $\nu_q = q\nu_{\mathrm{FSR}},\ q \in \mathbb{Z}$

N. Ismail et al., Opt. Express 24, 15, 16366, (2016)

Fabry-Pérot Cavity



Lorentzian Finesse

Can we resolve different resonator modes?

Use Taylor criterion: Two spectral lines resolved if the individual lines cross at half intensity.

Assume electric field at frequency ν_q represented by damped harmonic oscillator of the following form: $E_q(t) = Ee^{i2\pi\nu_q t}e^{-t/(2\tau_c)}$

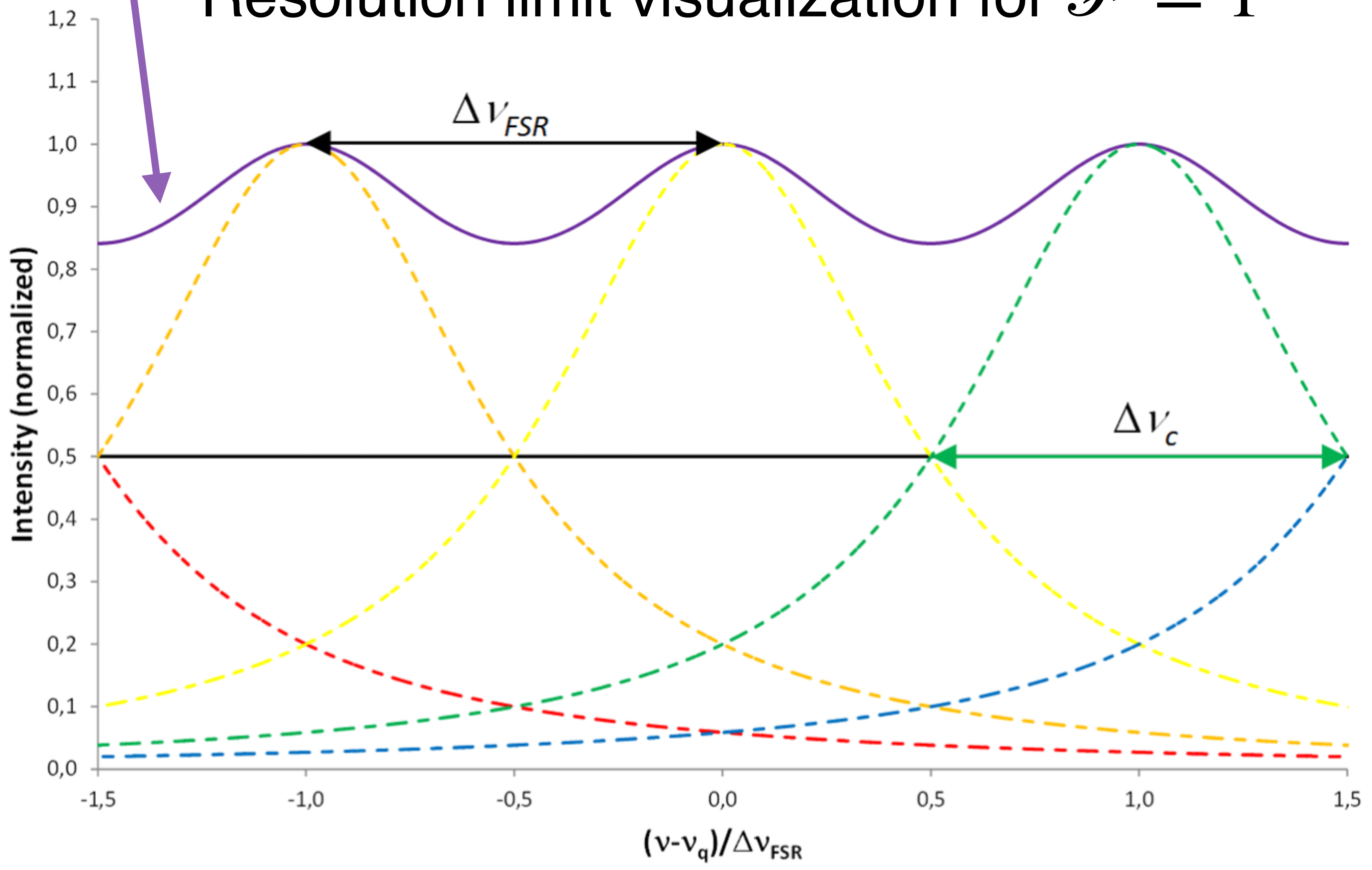
Normalized spectral line shape per mode (Lorentzian):

$$\gamma_q(\nu) = \frac{1}{\tau_c}\left|\frac{FT\{E_q(t)\}}{E}\right|^2 = \frac{1}{\pi}\frac{\Delta\nu_c/2}{(\Delta\nu_c/2)^2 + (\nu-\nu_q)^2}$$

Lorentzian finesse $\mathscr{F} = \dfrac{\Delta\nu_{\mathrm{FSR}}}{\Delta\nu_c}$ Single modes resolved if $\mathscr{F} \geq 1$

Airy distribution (from superposition of modes)

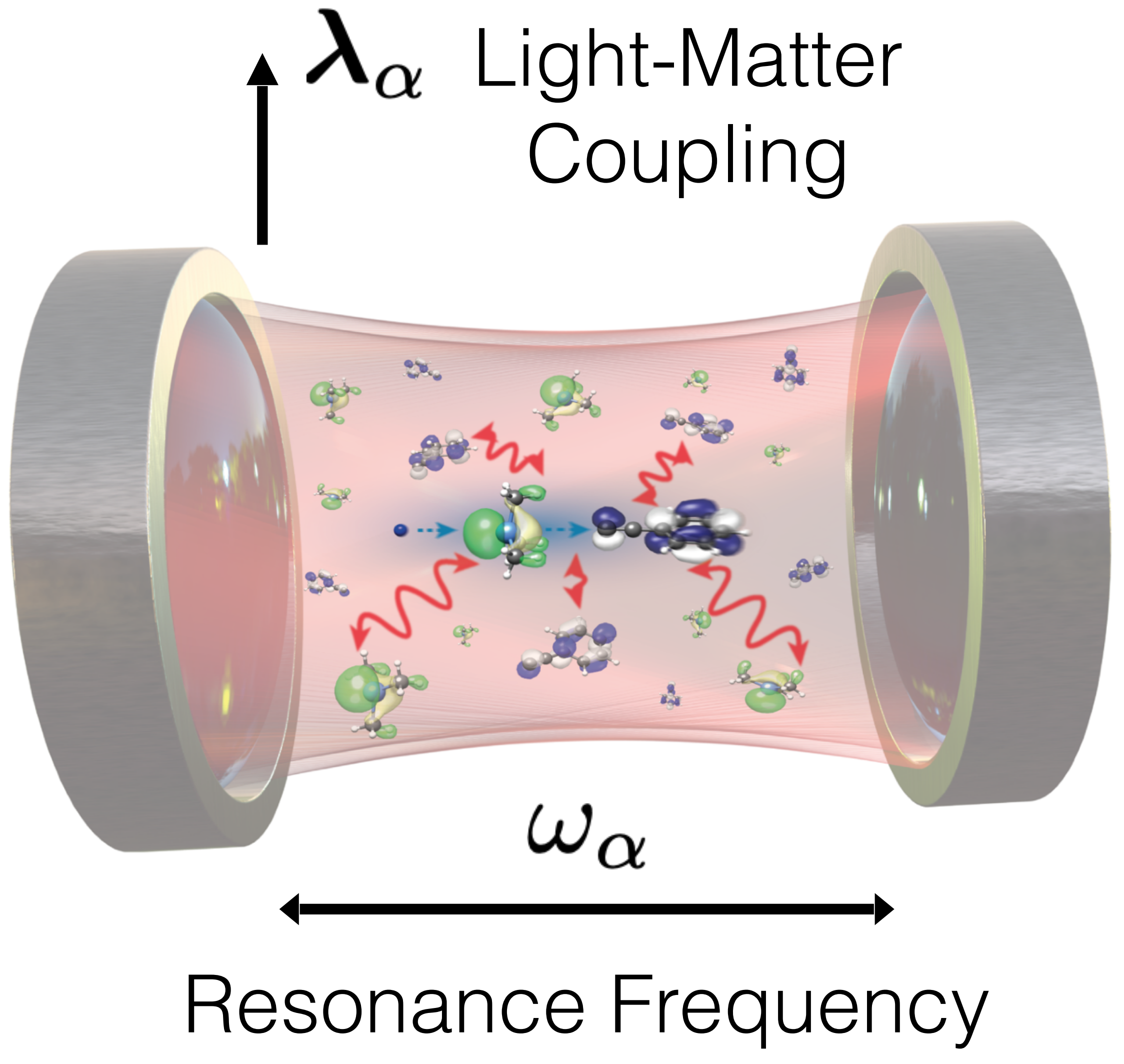
Resolution limit visualization for $\mathscr{F} = 1$



N. Ismail et al., Opt. Express 24, 15, 16366, (2016)

Ab-initio Quantum Theory

Pauli-Fierz Hamiltonian (in Dipole Approximation)



$$\hat{H} = \underbrace{\sum_i^n \frac{\hat{\mathbf{p}}_i^2}{2m} + \sum_i^N \frac{\hat{\mathbf{P}}_i^2}{2M_i} + \sum_{i<j}^n \frac{e^2}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} + \sum_{i<j}^N \frac{e^2 Z_i Z_j}{|\hat{\mathbf{R}}_i - \hat{\mathbf{R}}_j|} - \sum_{i,j}^{n,N} \frac{e^2 Z_j}{|\hat{\mathbf{r}}_i - \hat{\mathbf{R}}_j|}}_{\text{Quantized Matter}} + \sum_\alpha^M \frac{1}{2}\left[\underbrace{\hat{p}_\alpha^2}_{\text{Quantized Light}} + \underbrace{\omega_\alpha^2\left(\hat{q}_\alpha - \frac{\boldsymbol{\lambda}_\alpha}{\omega_\alpha}\cdot\hat{\mathbf{X}}\right)^2}_{\text{Light-Matter Interaction}}\right]$$

$$\hat{X}_\alpha := \sum_{n=1}^{N} \sum_{i_n=1}^{N_n} Z_{i_n} \boldsymbol{\lambda}_\alpha \cdot \hat{\boldsymbol{R}}_{i_n} \qquad \hat{x}_\alpha := -\sum_{n=1}^{N} \sum_{i_n=1}^{N_e} \boldsymbol{\lambda}_\alpha \cdot \hat{\boldsymbol{r}}_{i_n}$$

- Non-relativistic limit of quantum electrodynamics
- Schrödinger-type equation
- Possesses ground-state (variational principle applicable)

M. Ruggenthaler, D. Sidler and A. Rubio, Chem. Rev. 123, 19, 11191, (2023)

Repetition of Quantum Mechanics

Quantum Harmonic Oscillator, Perturbation Theory, Polarizability

Blackboard

Summary Quantum Harmonic Osc.

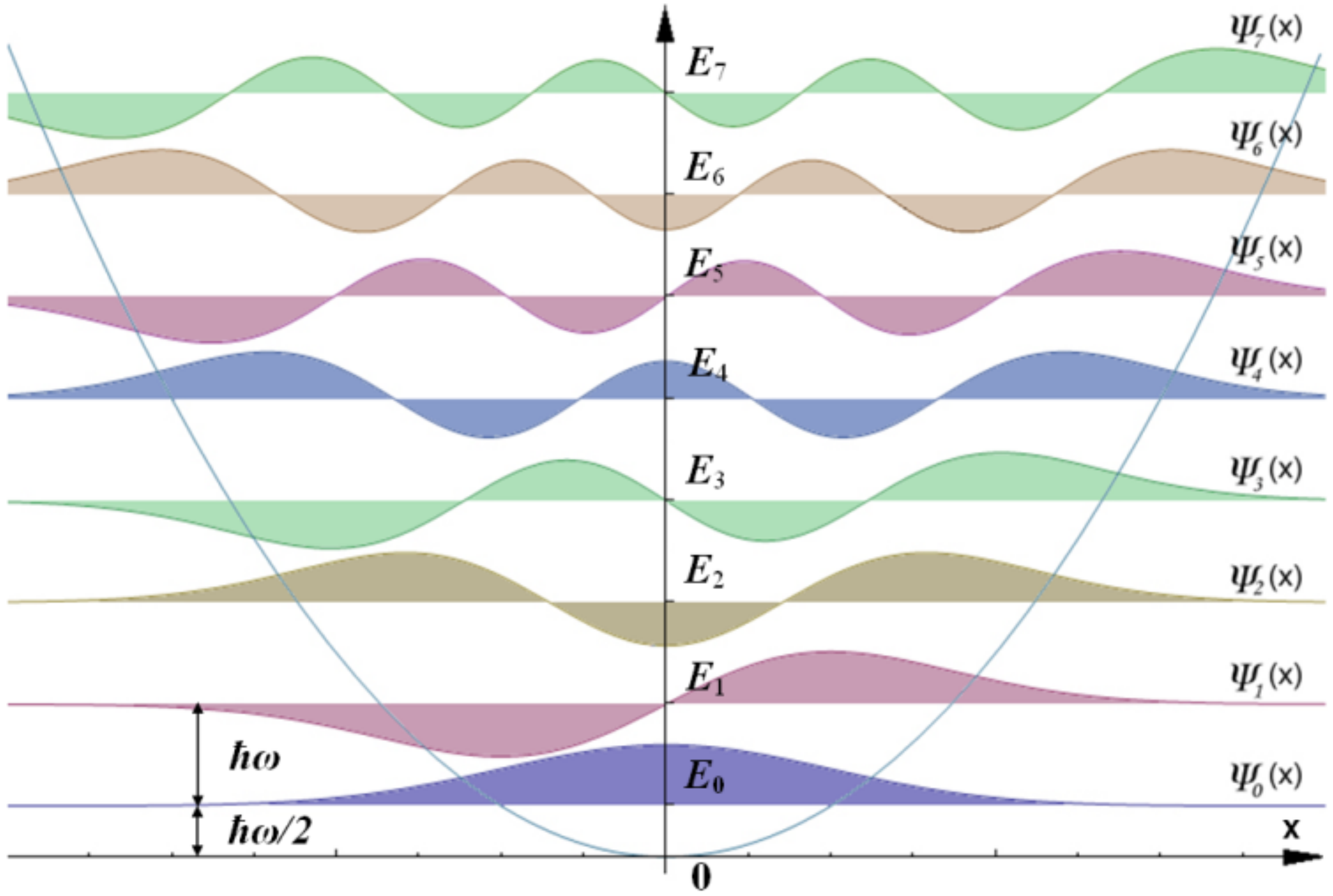
$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{k}{2}\hat{x}^2 = \hbar\omega\left(\hat{N} + \frac{1}{2}\right) = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right) \qquad \omega = \sqrt{k/m}$$

Ladder operator method $\hat{p} = i\sqrt{\frac{\hbar m\omega}{2}}(a^\dagger - a) \qquad \hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(a^\dagger + a)$

Creation Op. $a^\dagger|n> = \sqrt{n+1}\,|n+1> \qquad <n|m> = \delta_{nm}$

Annihilation Op. $a|n> = \sqrt{n}\,|n-1> \qquad a|0> = 0 \quad [a^\dagger, a] = 1$

Energy eigenvalues $E_n = <n|\hat{H}|n> = \hbar\omega(n + \frac{1}{2})$



Position representation: $\Psi_\nu(x) \propto H_\nu(\beta x)e^{-\beta x^2/2}$

Apply static external electric field ϵ

$$\hat{H}(\epsilon) = \frac{\hat{p}^2}{2m} + \frac{k}{2}\hat{x}^2 + \epsilon e\hat{x}$$

Polarizability $\alpha = \frac{d}{d\epsilon} <0|e\hat{x}|0>$

Using Hellmann-Feynman theorem $<0|e\hat{x}|0> = \frac{d}{d\epsilon}<0|\hat{H}(\epsilon)|0>$

Examples of Hermite Polynomials

0	1
1	$2z$
2	$4z^2 - 2$
3	$8z^3 - 12z$
4	$16z^4 - 48z^2 + 12$

~~Assume $\epsilon \approx 0$, use 2nd order perturbation theory~~

$$E_n(\epsilon) = E_n + \epsilon <n|e\hat{x}|n> + \epsilon^2 \sum_{k\neq n} \frac{|<k|e\hat{x}|n>|^2}{E_n - E_k} + O(\epsilon^3)$$

$$\cancel{\Rightarrow \alpha = \frac{e^2}{k}}$$

Outlook: Perturbation theory can break down under strong light-matter coupling in optical cavities even for $\epsilon \approx 0$.

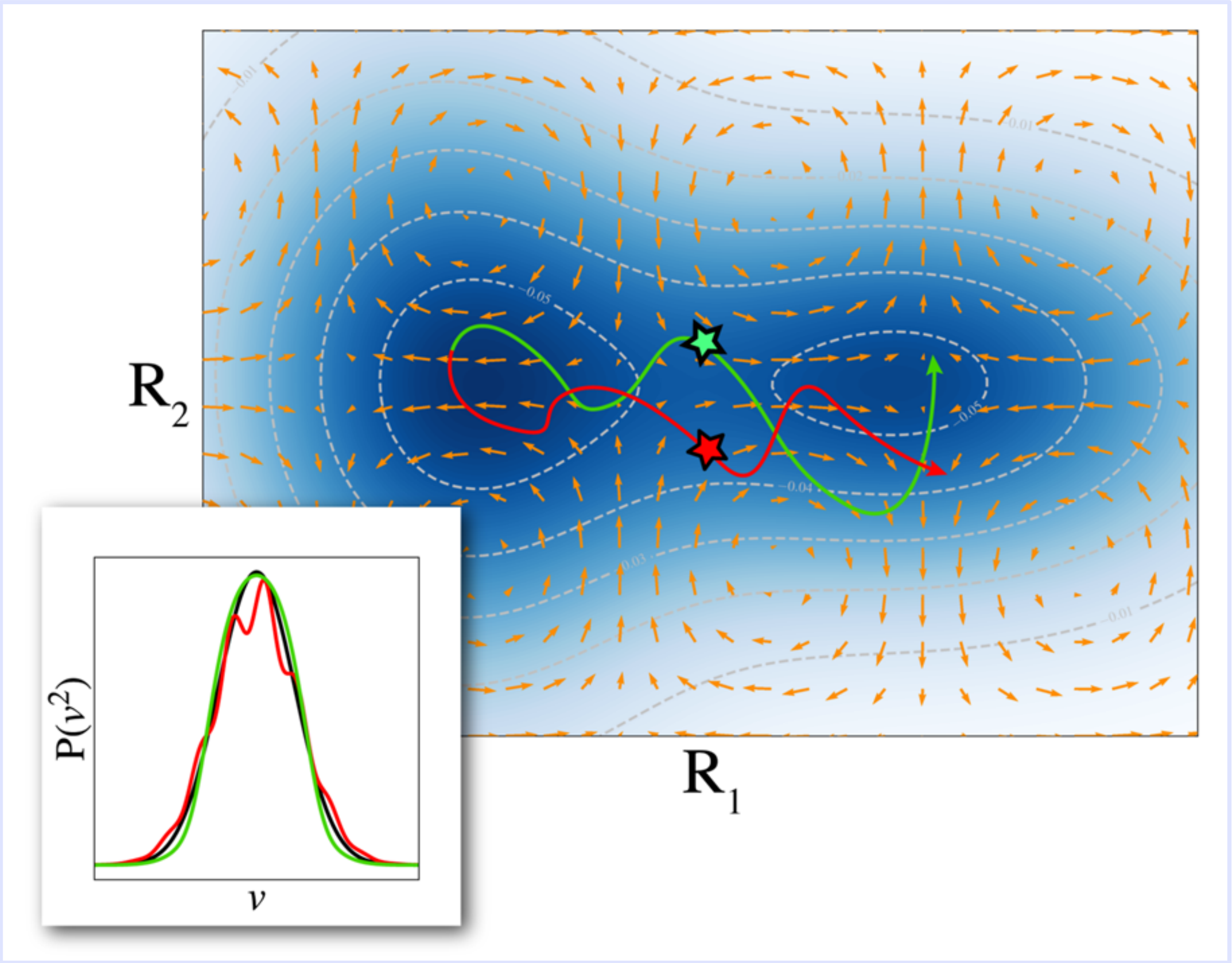
P. W. Atkins and R. Friedman „Molecular quantum mechanics", Oxford Univ. Press, 2011 and wikipedia

Outlook: What About the Nuclei?

Electronic structure problem will be complex

Classical Cavity Born-Oppenheimer Molecular Dynamics

$$H^{\mathrm{npt}} := H_{\mathrm{m}}^{\mathrm{n}} + \sum_{\alpha=1}^{M}\left(\frac{p_\alpha^2}{2} + \frac{\omega_\alpha^2}{2}\left(q_\alpha - \frac{X_\alpha}{\omega_\alpha}\right)^2 + \boxed{\langle\psi_0|\hat{H}_e(\underline{\mathbf{R}},\underline{q})|\psi_0\rangle}\right)$$

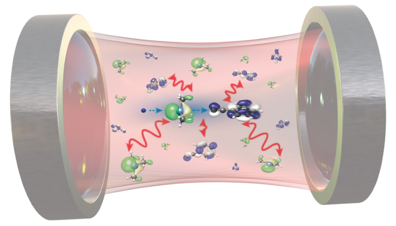


Electronic problem:
Spin glass correlations and aging effects introduce explicit **time-dependent electronic forces**

Add (nuclear) temperature:
Classical Langevin equations of motion.

Non-conservative forces imply non-canonical (!) dynamics and possibly stochastic resonances.

D. Sidler et al., J. Chem. Phys. 156, 230901 (2022), D. Sidler et al., J. Chem. Theory Comput. 19, 23, 8801 (2023)

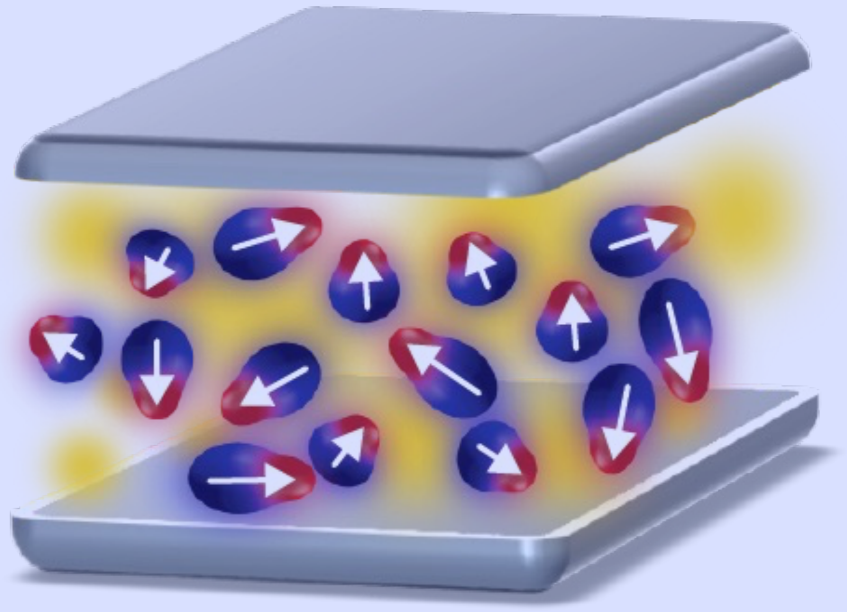


Outlook

Non-trivial Feedback in VSC

Electronic Structure

$$\langle\Psi|\sum_{i}^{N_e}\left\{\frac{\hat{\boldsymbol{p}}_i^2}{2}-\frac{1}{2}\sum_{l}^{N_N}\frac{Z_n}{|\hat{\boldsymbol{r}}_i-\boldsymbol{R}_l|}+\frac{1}{2}\sum_{j}^{N_e}\frac{1}{|\hat{\boldsymbol{r}}_i-\hat{\boldsymbol{r}}_j|}\right\}$$
$$+\left(\frac{1}{2}\hat{x}^2+\hat{x}X-\omega_\beta\hat{x}q_\beta\right)|\Psi\rangle$$



Seed of VSC:
Collectively induced polarization instability.
Replica symmetry breaking & (dynamic) frustration.

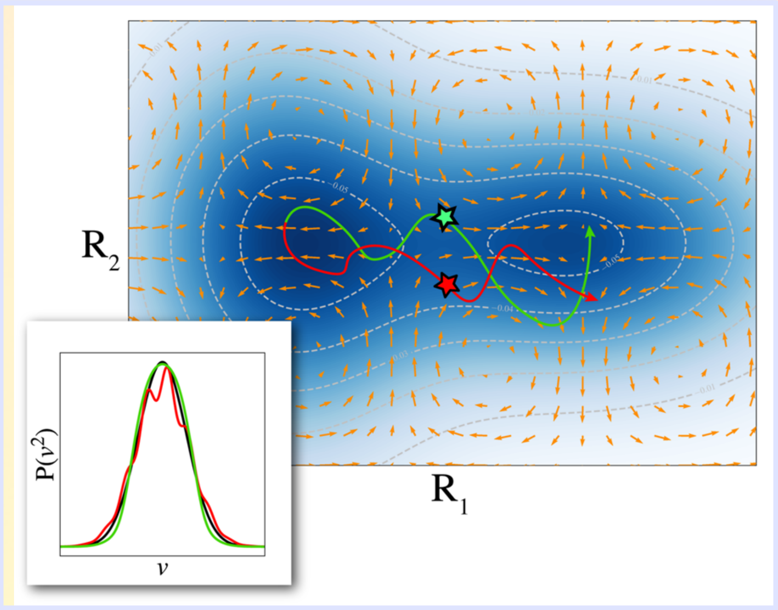
?

European Research Council
Established by the European Commission

Synergy Grants

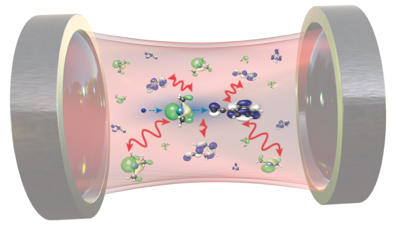
Nuclei

$$H^{\mathrm{npt}} := H^{\mathrm{n}}_{\mathrm{m}}+\sum_{\alpha=1}^{M}\left(\frac{p_\alpha^2}{2}+\frac{\omega_\alpha^2}{2}\left(q_\alpha-\frac{X_\alpha}{\omega_\alpha}\right)^2+\langle\psi_0|\hat{H}_e(\underline{\mathbf{R}},\underline{q})|\psi_0\rangle\right)$$



Stochastic Resonances:
non-equilibrium thermodynamics

Displacement Field



Summary and Conclusion

1. Feedback between spatiotemporal scales makes polaritonic chemistry theoretically hard.
2. Quantized light-matter interaction starting point.
3. Brief repetition of quantum mechanics and perturbation theory.
4. Quantum harmonic oscillator will play a crucial role to describe photons.
5. Many fundamentally open questions make polaritonic chemistry a highly active field of research.

Feedback?

Should I provide more basic introductions to QM, electrodynamics, programming etc. or stay more advanced?

Did you like the blackboard calculations?