Shining Light on Molecules

From Ultrafast X-Ray Spectroscopy to Photochemistry in Nano Resonators

Markus Kowalewski

Department of Physics
Chemical Physics
Stockholm University

April 23, 2025

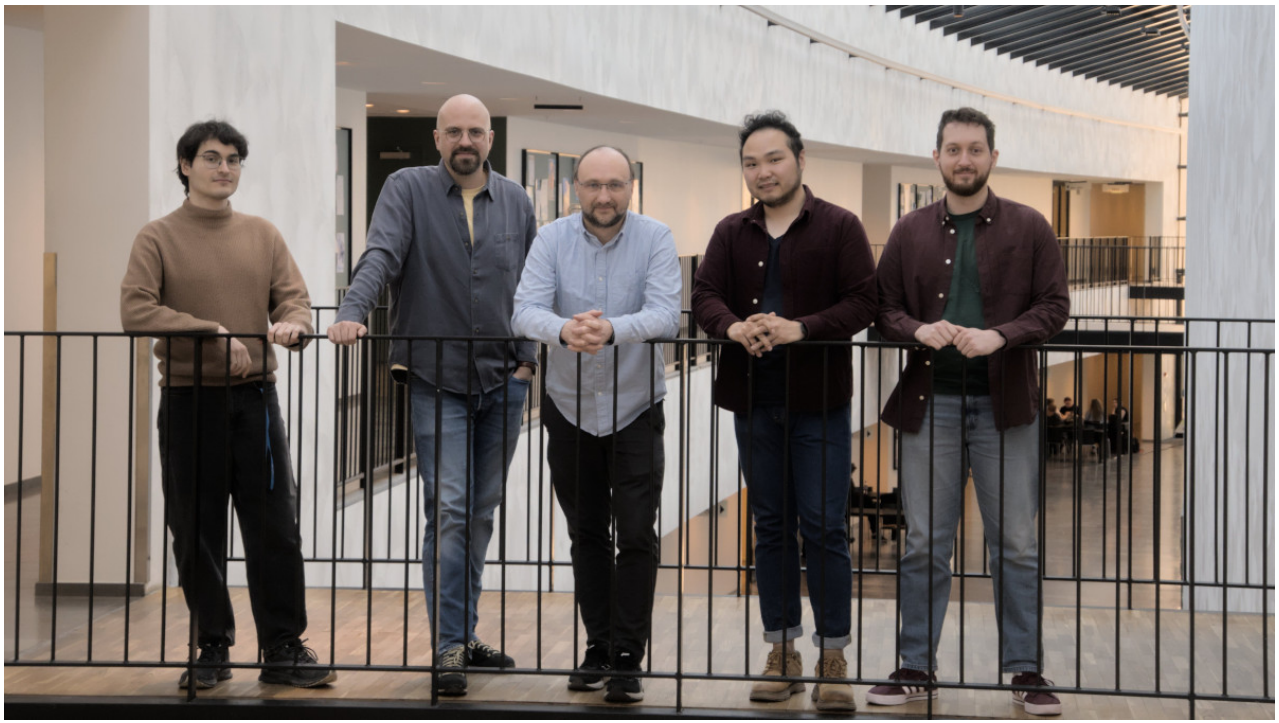
Stockholm University

Our Group

Bluesky: @tqdspec.bsky.social, homepage: https://tqdspecweb.fysik.su.se/

Molecular Quantum Optics, Dynamics, and Spectroscopy

The group:
Thomas Schnappinger, Lucas Borges, Lorenzo Restaino, Jiahao Fan (visitor)

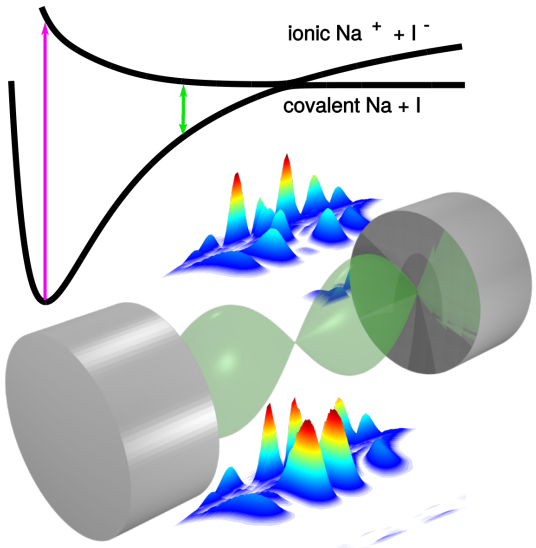


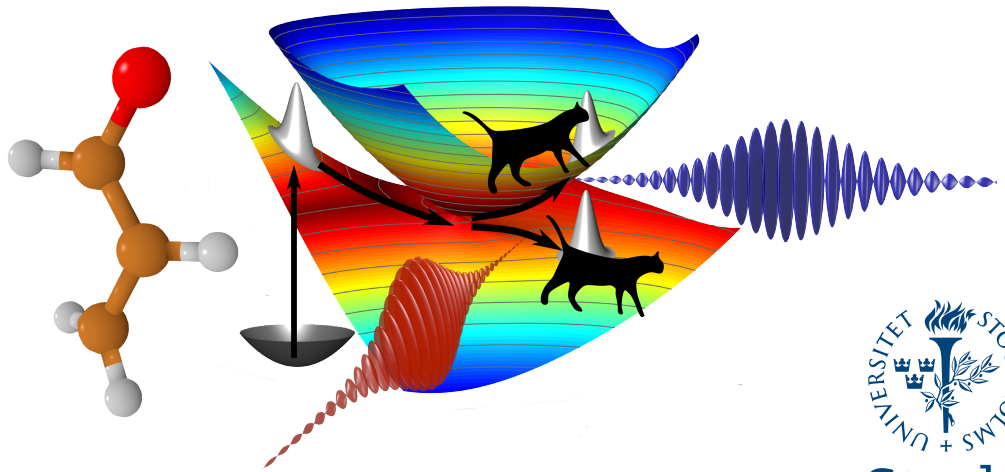
Stockholm University

Overview

Our Theory Activities: Molecular Quantum Optics, Dynamics, Spectroscopy

1. Non-adiabatic quantum dynamics in molecules:
   Simulating X-ray spectroscopy, disentangling dynamics
2. Using confined light fields to control chemistry
   Modifying chemical reactions with nano-resonators



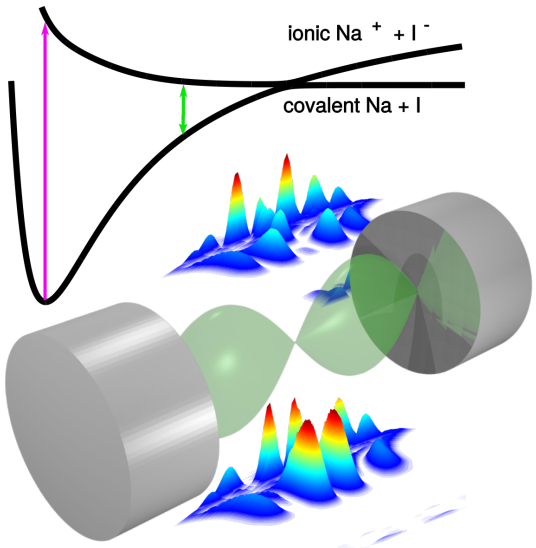


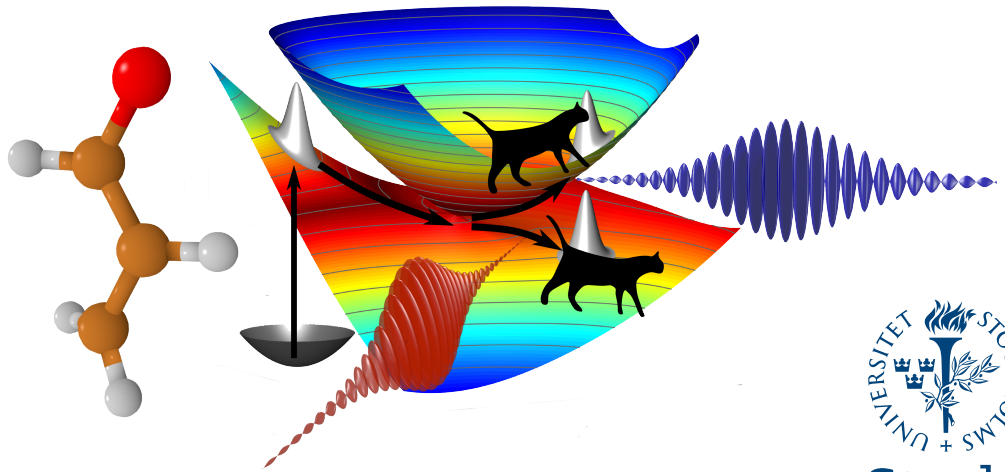
Stockholm University

Overview

Our Theory Activities: Molecular Quantum Optics, Dynamics, Spectroscopy

1. **Non-adiabatic quantum dynamics in molecules: Simulating X-ray spectroscopy, disentangling dynamics**
2. Using confined light fields to control chemistry
   Modifying chemical reactions with nano-resonators

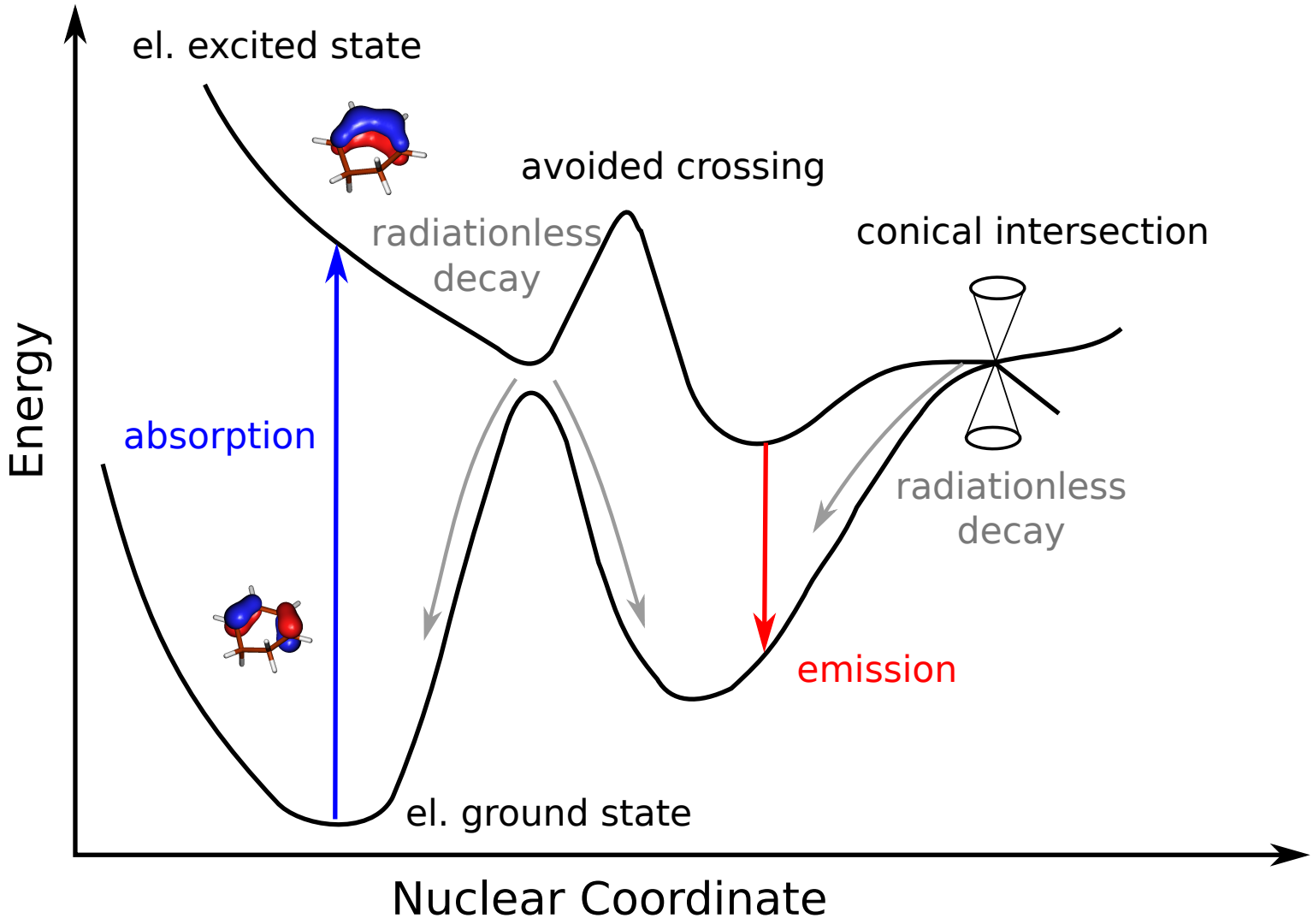




Stockholm University

Overview – Non-adiabatic Dynamics in Molecules

What Happens When a Molecule Absorbs a Photon?



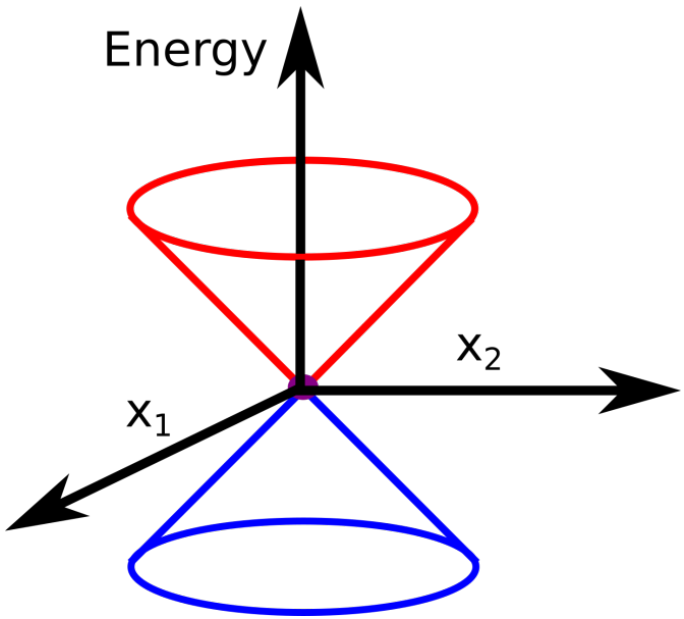
Stockholm University

What is a Conical Intersection?

Breakdown of the Born-Oppenheimer Approximation

Born-Oppenheimer Approximation:
e^- and nuclei have different mass.
$\Rightarrow$ Separate equation of motion.

- More than 3 atoms
- At least 2 dimensions
- $\Rightarrow$ Degenerate electronic states
- e^- and nuclear motion coupled!

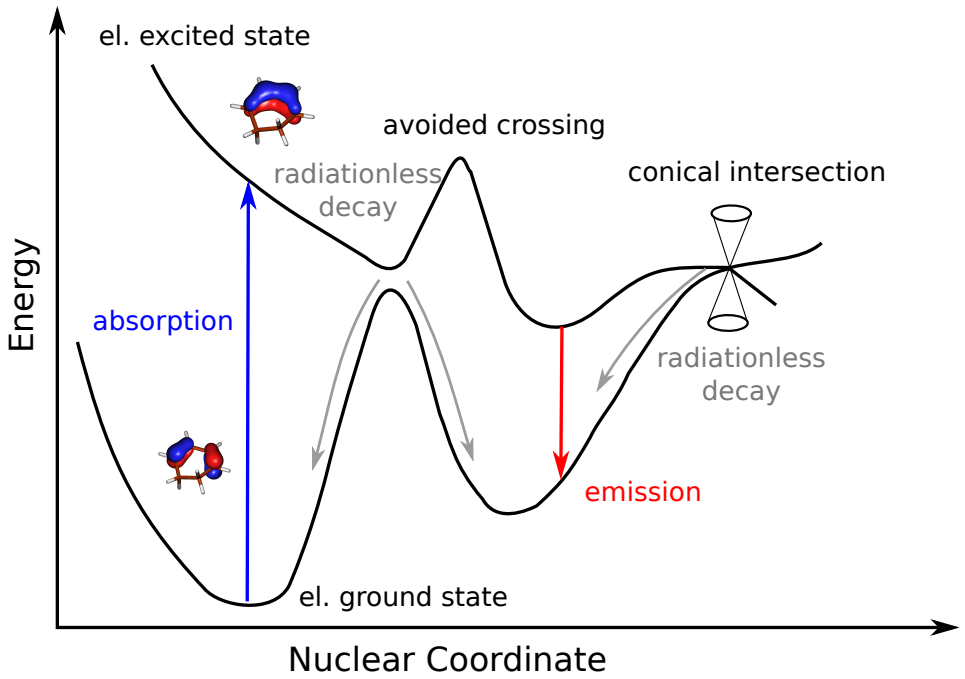


Stockholm University

Conical Intersection in Molecules

Abundant and Yet Elusive Funnels

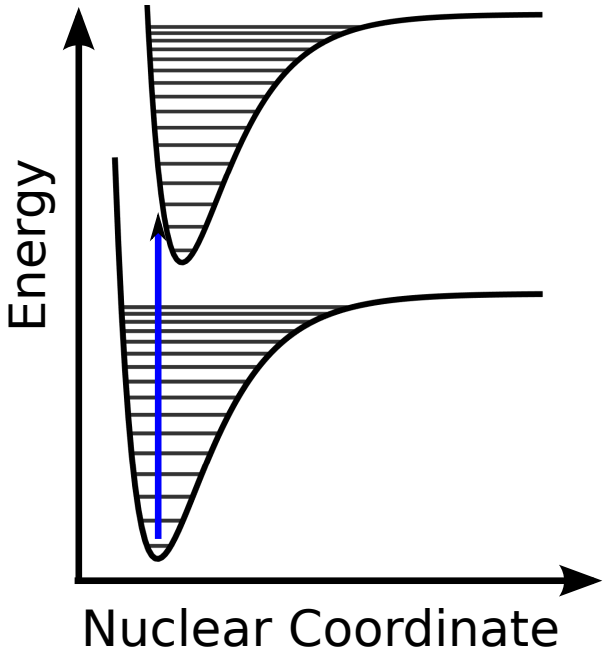
- Conical Intersections common in poly-atomic molecules
- Ultrafast processes ($< 100\,\mathrm{fs}$).
- Important in bio-molecules, i.e. process of vision.
- Ultraviolet DNA damage and repair (?)
- Relevant in sunscreen active ingredients.

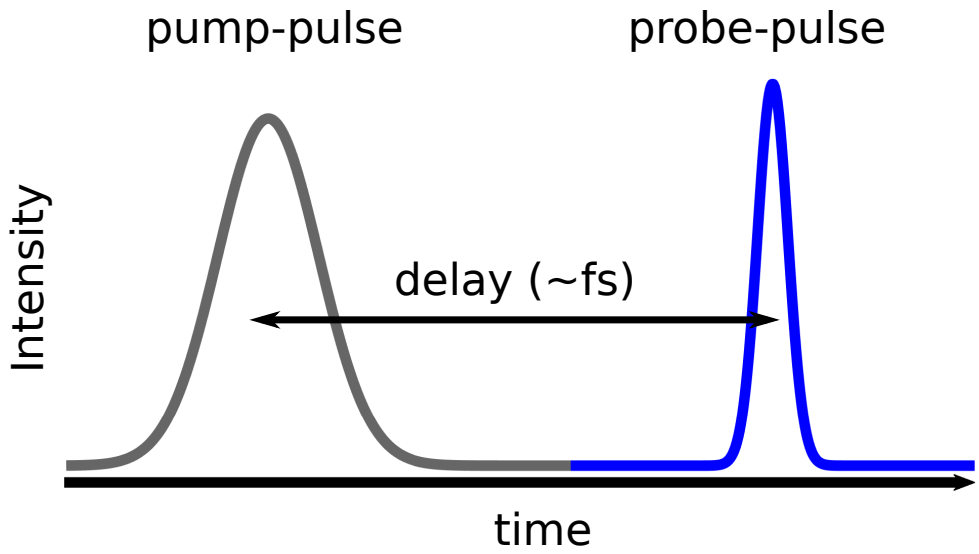


Stockholm University

Time-Resolved Spectroscopy

Pump-Probe Spectroscopy





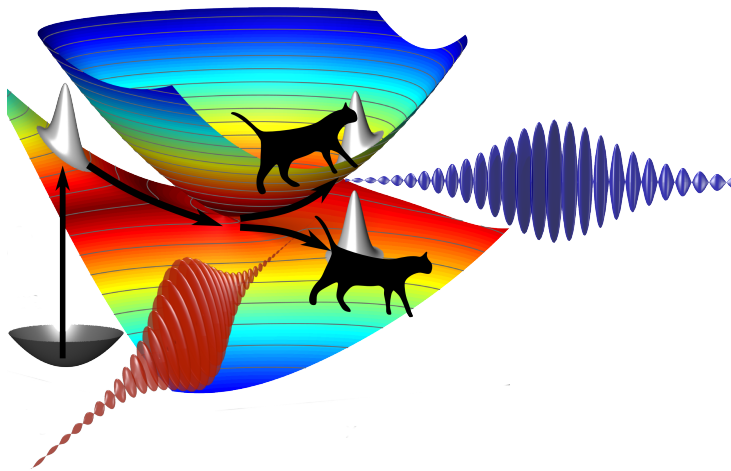
- $\approx$ femtosecond duration (record to date 35 attoseconds)
- large intensity (kW-GW)
- short pulse $\rightarrow$ large bandwidth: $\Delta\omega\Delta t \leq 2\pi$

Stockholm University

Spectroscopic Signatures of CoIns

Modern Ultra-fast Light Sources

- Methods are based on pop. dynamics
- Transient absorption
- Infrared/Optical pulses
- Challenge: rapidly decreasing energy gap
  $\rightarrow$ huge bandwidth needed
- Solution: X-ray/attosecond pulses
  Free electron lasers
  high-harmonic generation
- Detection via electronic coherences



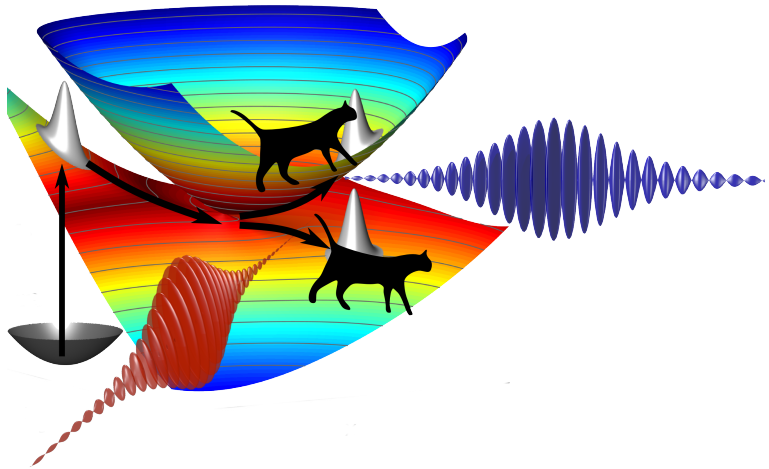
M. Kowalewski et al., "Simulating Coherent Multidimensional Spectroscopy of Non-adiabatic Molecular Processes: From the Infrared to the X-Ray Regime", Chem. Rev., **117**, 12165 (2017).

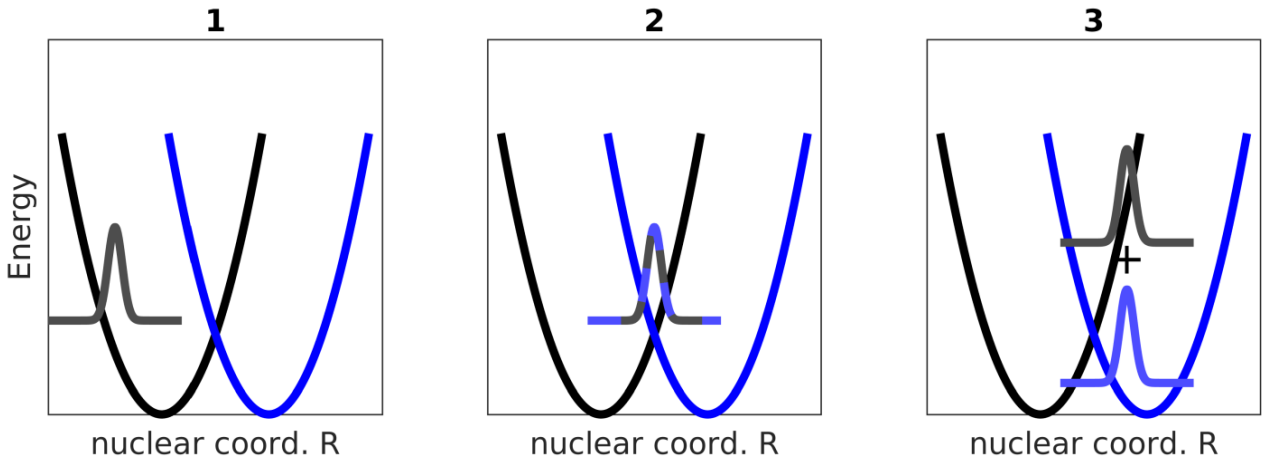
Stockholm University

Detecting Electronic Coherences

The finger print of conical intersections

- Pump creates a wave packet
- Wave packet splits at intersection
- Electronic super position
- $\rho_{ge} = \int dR \Psi_g^*(R) \Psi_e(R)$

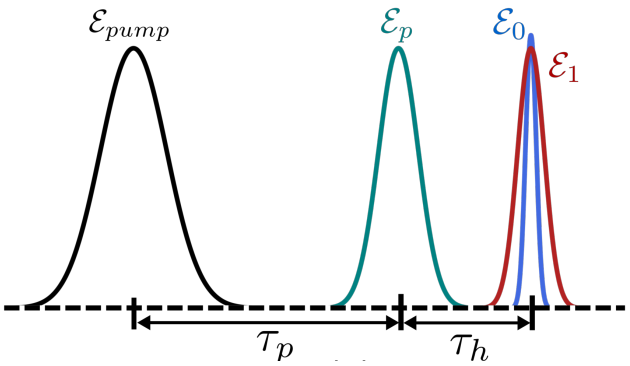


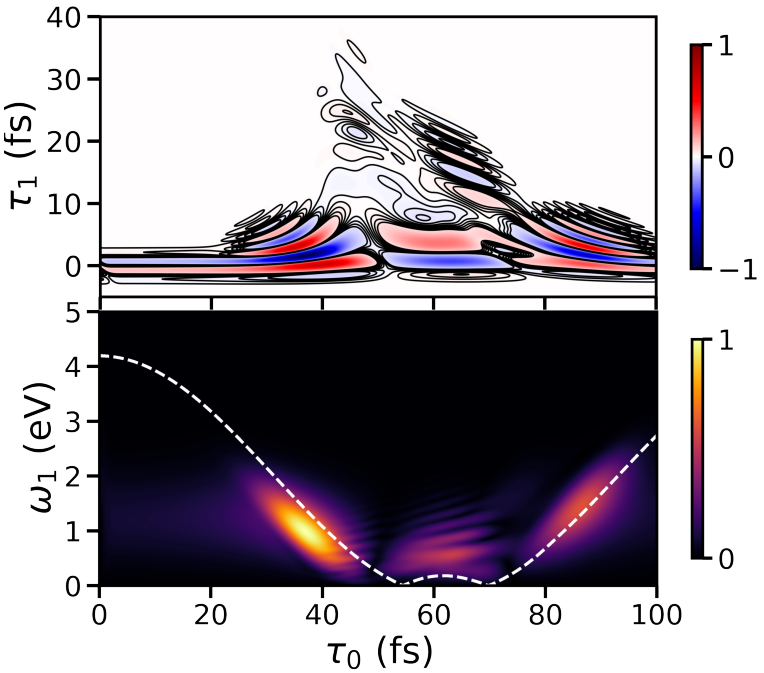


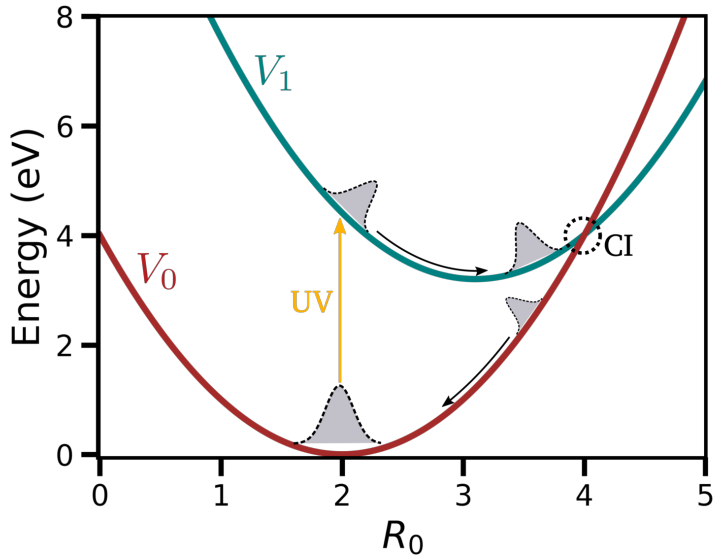
Stockholm University

Simulating Ultrafast X-ray Spectroscopy

Map Out Conical Intersections (in Theory)







- "Visualize" intersections
- Ultrashort pulses
- Large bandwidth
  $\rightarrow$ XUV/X-ray

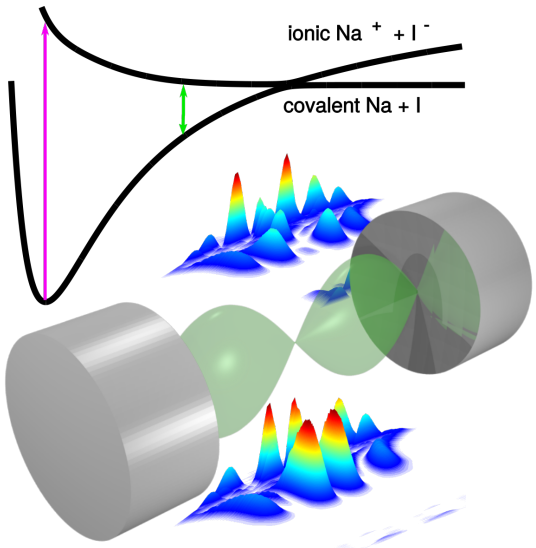
D. Jadoun, M. Kowalewski, Ultrafast Sci., 2022, 0003 (2022).

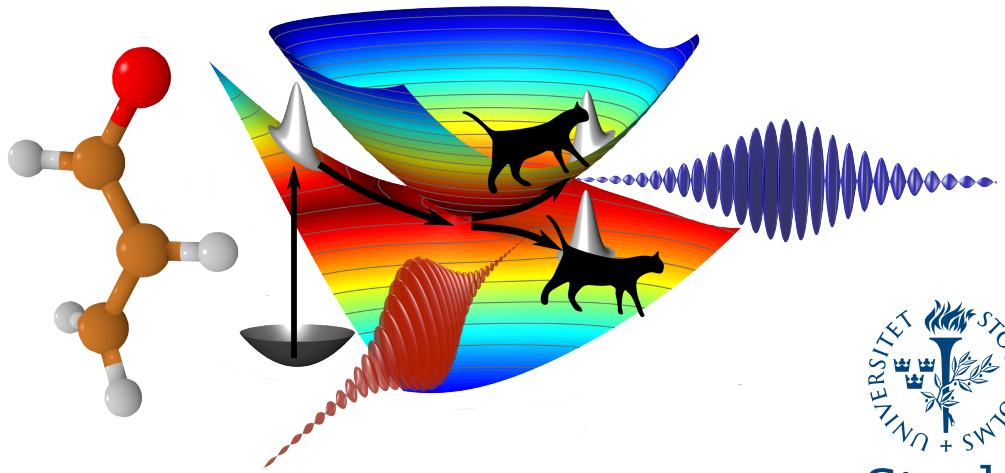
Stockholm University

Overview

Our Theory Activities

1. Non-adiabatics quantum dynamics in molecules: Using X-ray spectroscopy to gain more insight
2. **Using confined light fields to modify chemistry Controlling chemistry with nano-resonators**

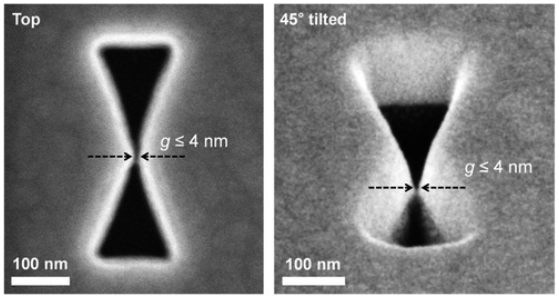


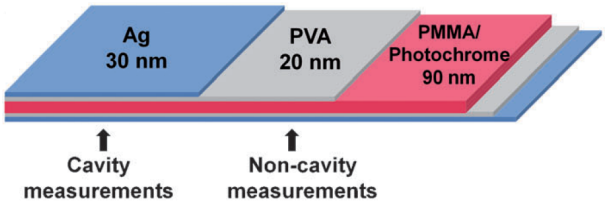


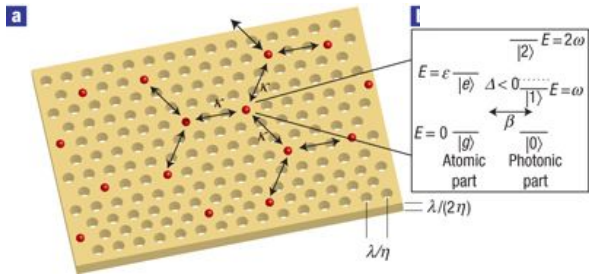
Stockholm University

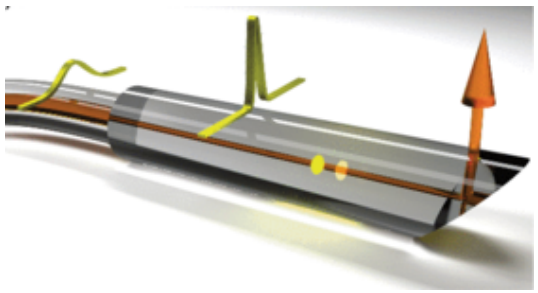
Molecules In Optical Cavities

Quantum Optics Meets Chemical Physics









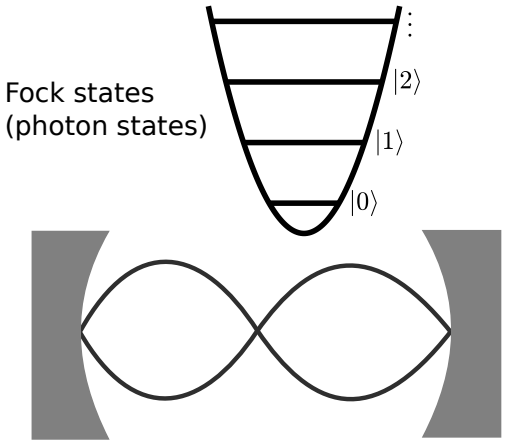
- Confined light modes
- Experiments:
  Modified reactions rates!
- Strong light-matter coupling
- Modification of molecular potential energy surfaces
- Applications in photo chemistry

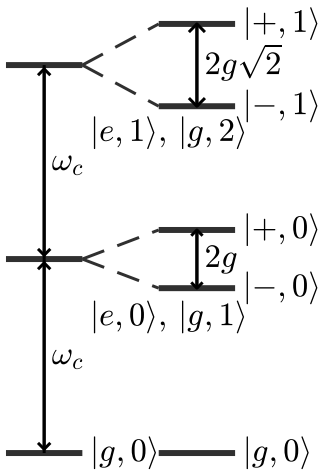
S. Faez et al., PRL, **113**, 21601 (2014)
J. F. Triana, et al. JPC A, **122**, 2266 (2018)
J. A Hutchison et al., Angew. Chem. Int. Ed., **51**, 1592 (2012)

Stockholm University

Underlying Idea – Molecular Jaynes-Cummings Model

Coherent Control with Confined Light Modes

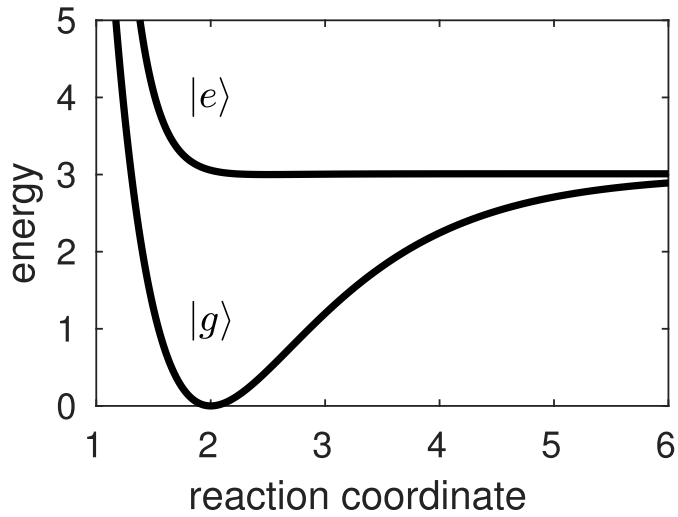


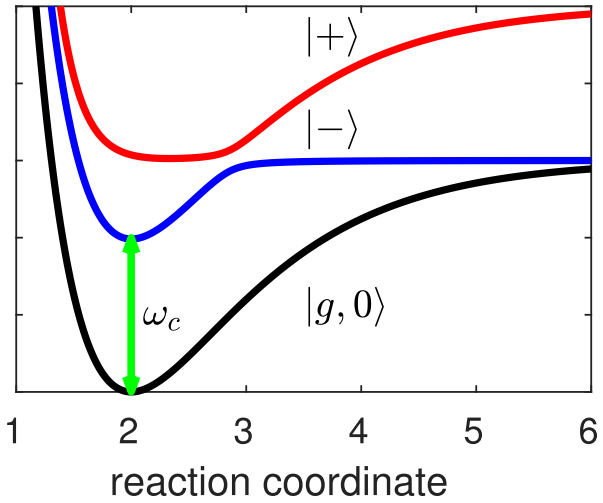


Simple idea:

- Hybrid light-matter states (dressed states)
- Modify potential energy surfaces
- Modify photo chemistry Photonic Catalysts!

M. Kowalewski and S. Mukamel, PNAS, **114**, 3278 (2017)
M. Kowalewski et al., JCP, **144**, 054309 (2016)



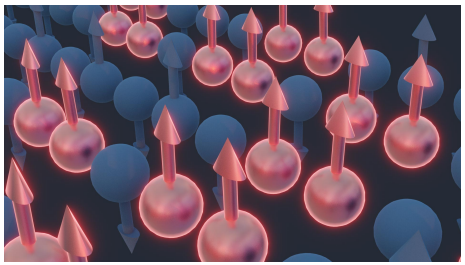


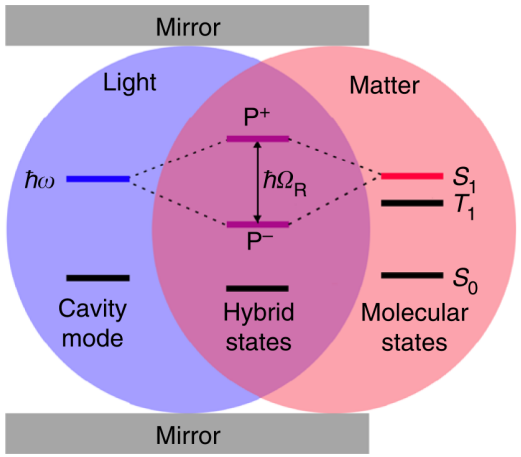
Stockholm University

Open Questions

Mismatch between Theory and Experiment

- No comprehensive theory available to explain experiments
- Collective effects important: Molecules "talk to each other" through light field
- Regular chemistry in cavities? Vibrational modes vs. electronic
- What is the limit of controllability? What can we do with it?





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

https://scitechdaily.com/quantum-materials-unconventional-spin-behavior-proves-theoretical-predictions/

Stockholm University

Open Questions

Mismatch between Theory and Experiment

- No comprehensive theory available to explain experiments
- Collective effects important: Molecules "talk to each other" through light field
- Regular chemistry in cavities? Vibrational modes vs. electronic
- What is the limit of controllability? What can we do with it?

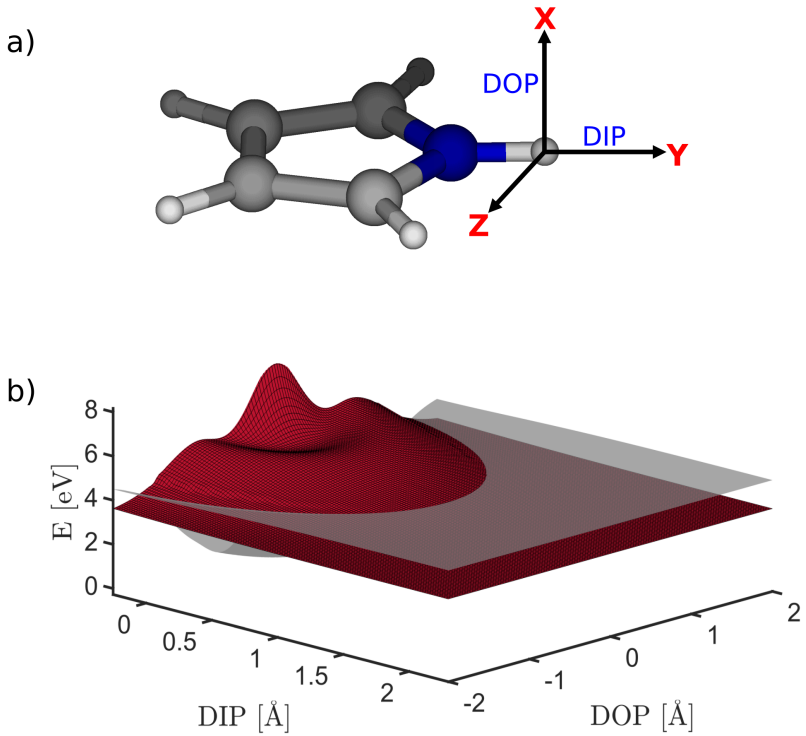
K. Stranius, et al., Nat. Comm., **9**, 2273 (2018);

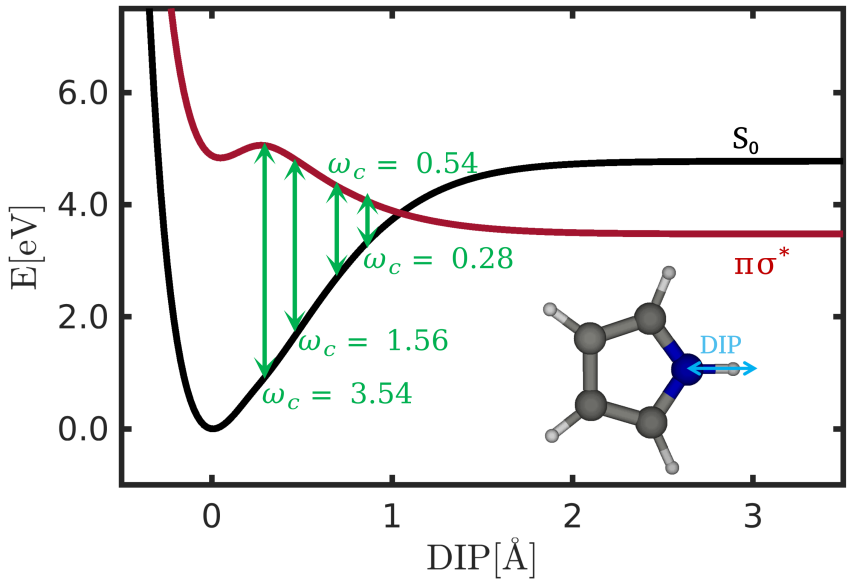
https://scitechdaily.com/quantum-materials-unconventional-spin-behavior-proves-theoretical-predictions/

Stockholm University

Control the Conical Intersection in Pyrole

2D Model System + Cavity



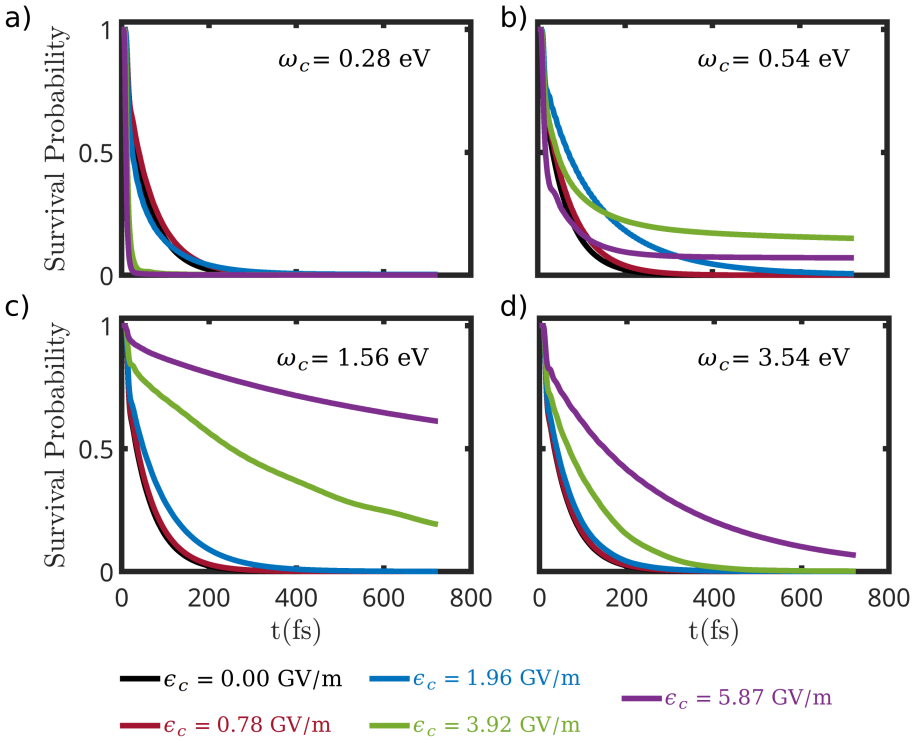


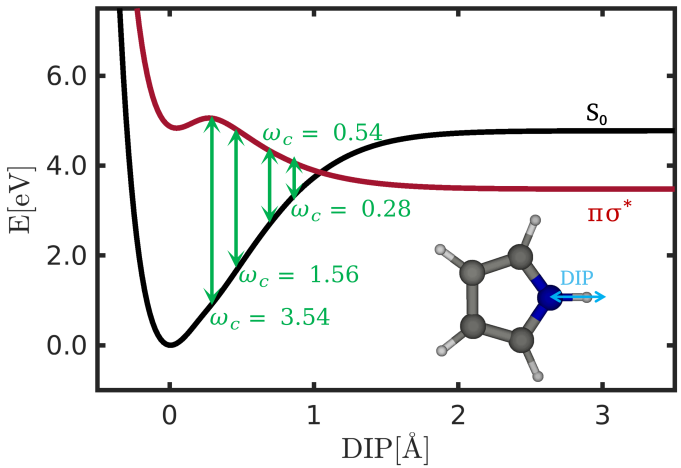
- Population transfer at CoIn.
- Dissociation can be controlled.

Stockholm University

Simulation of Dynamics in the Cavity?

Different Resonances, Different Field Strengths





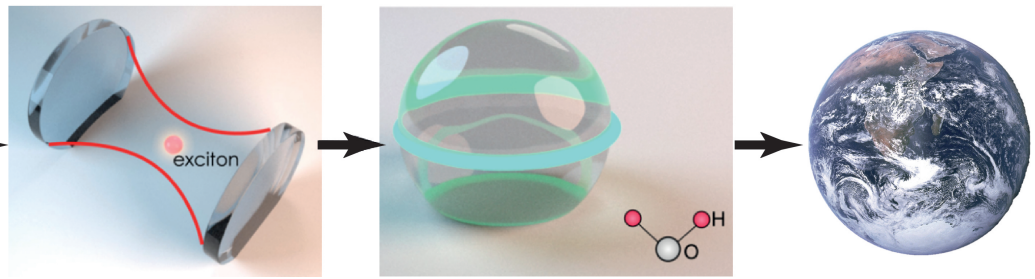
$\Rightarrow$ Suppress or accelerate dissociation!

Stockholm University

Outlook

- Modern X-ray spectroscopy
  - → Improve simulations; bring new techniques to life.
  - → Entangled photons and non-classical light.
  - → How do sunscreen molecules really work?
- Controlling chemical reactions with cavities
  - → Develop models and techniques.
  - → Self hybridization in natural systems?
  - → Water droplets can act as nano-resonators!

$$H = \begin{bmatrix} E_c & \cdots & \hbar\Omega/2 \\ \vdots & \ddots & \vdots \\ \hbar\Omega/2 & \cdots & E_{ex} \end{bmatrix}$$



Stockholm University

Thank you for your attention!

Interested in doing a master thesis with us?

Stockholm University