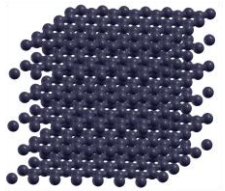
SIMONS CENTER FOR COMPUTATIONAL PHYSICAL CHEMISTRY

NYU

Exploring the Complexity of Polaritonics:

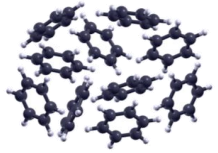
From Single-Molecule Strong Coupling to Twin Polaritons

Norah M. Hoffmann – *Department of Chemistry & Department of Physics –* ***New York University****, New York*

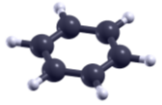


Solid

Cluster



Molecules



Molecule

Energy Levels

Complexity of matter

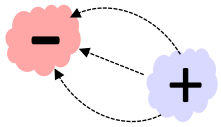
Chemistry in electric fields

?

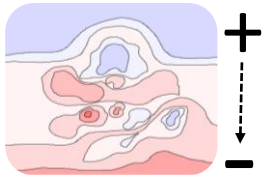
Polaritonics

Quantum Information

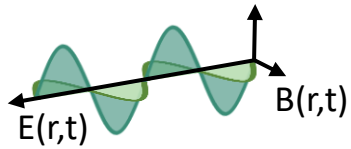
Complexity of light



Static E-Field



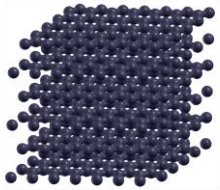
Inhomogeneous static E-Field



Dynamical E-Field

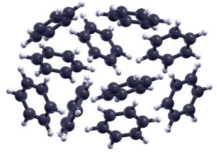
Classical modes

Quantum

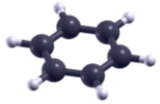


Solid

Cluster



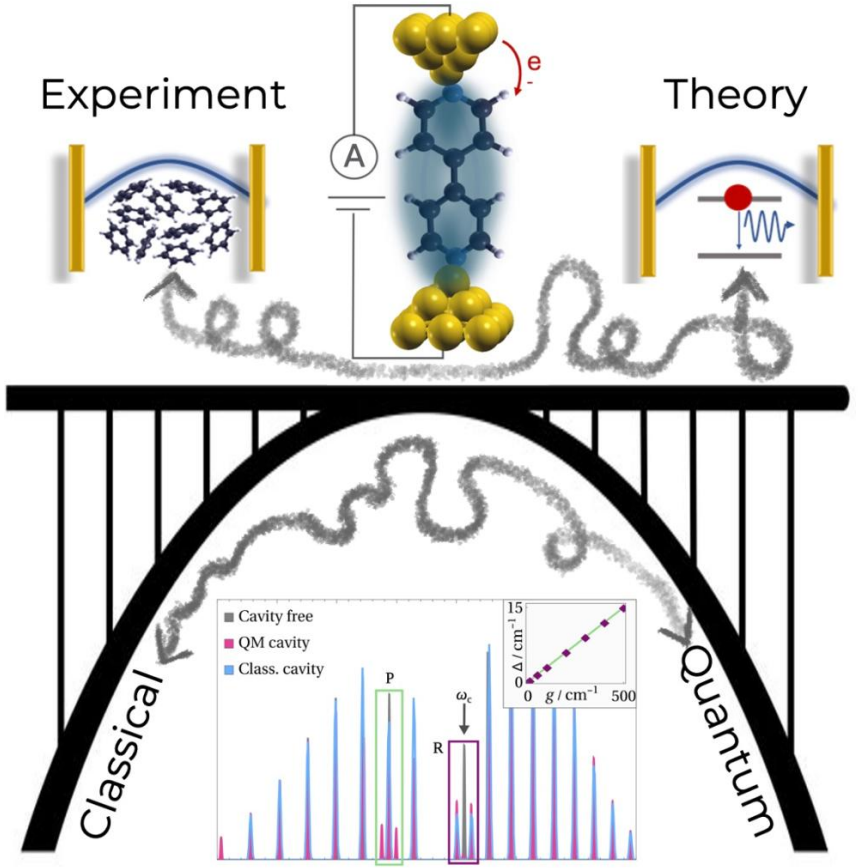
Molecules



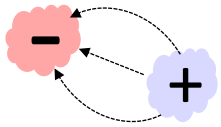
Molecule

Energy Levels

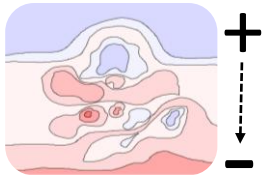
Complexity of matter



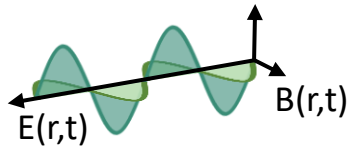
Complexity of light



Static
E-Field



Inhomogeneous
static E-Field



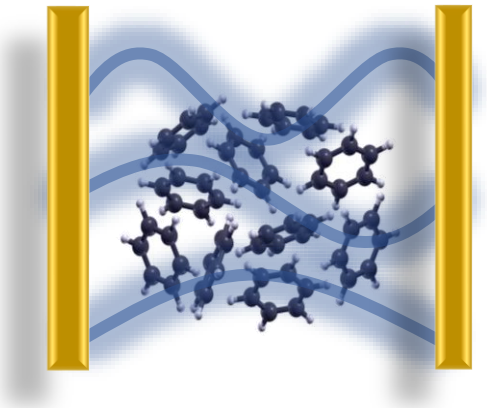
Dynamical
E-Field

Classical
modes

Quantum

Polaritonic Chemistry

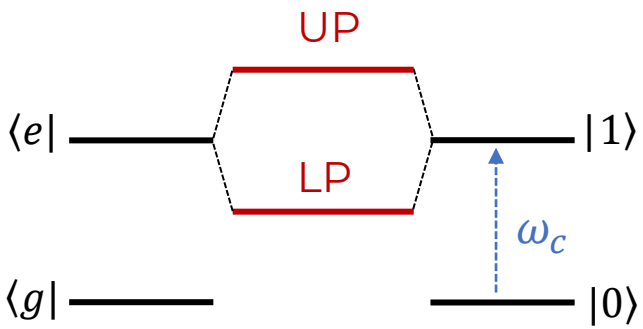
Idea: Change chemical reactivity with polaritons

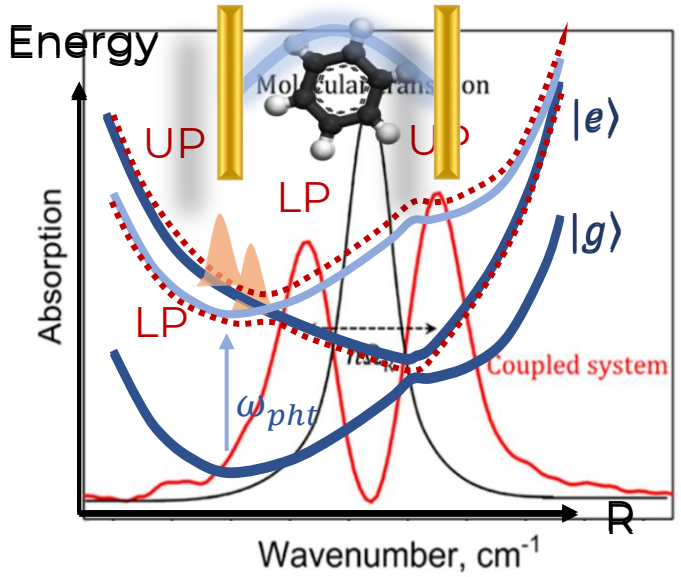


Hybrid light-matter states

-

Polaritons





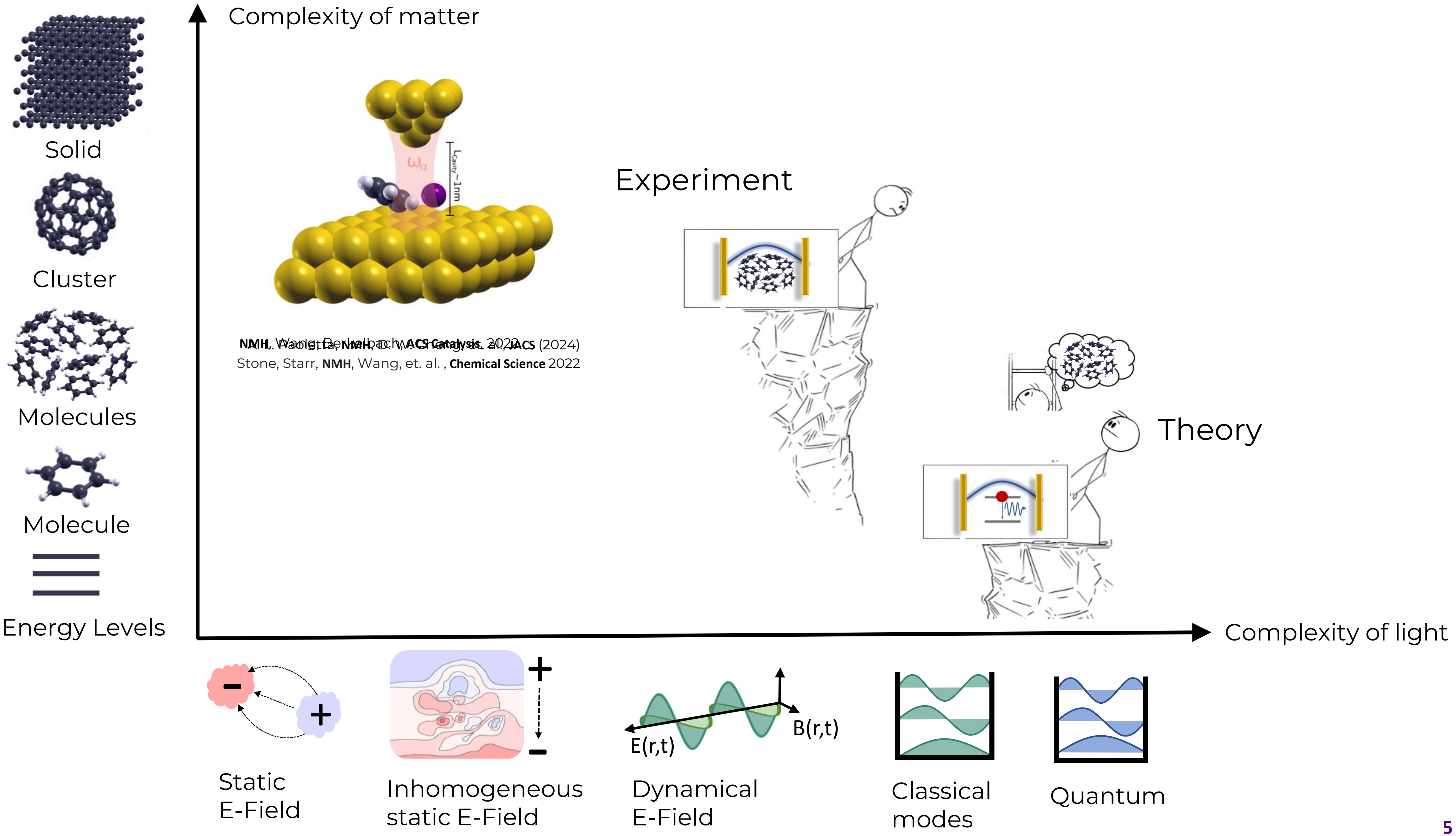
Changing something macroscopically (mirrors) changes something microscopically (molecular properties)

CHEMISTRY Science

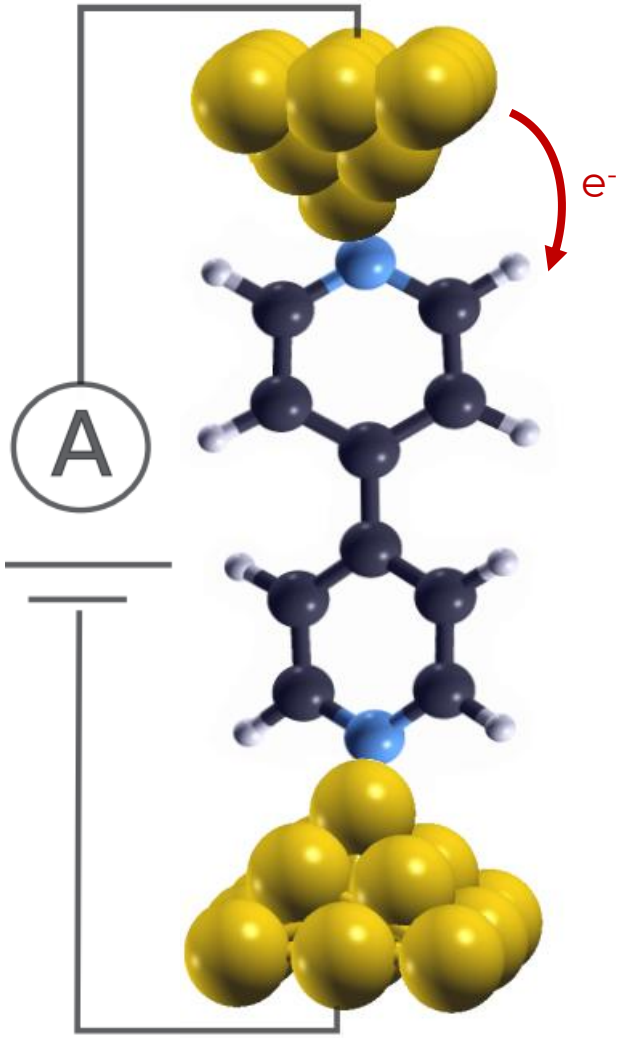
Tilting a ground-state reactivity landscape by vibrational strong coupling

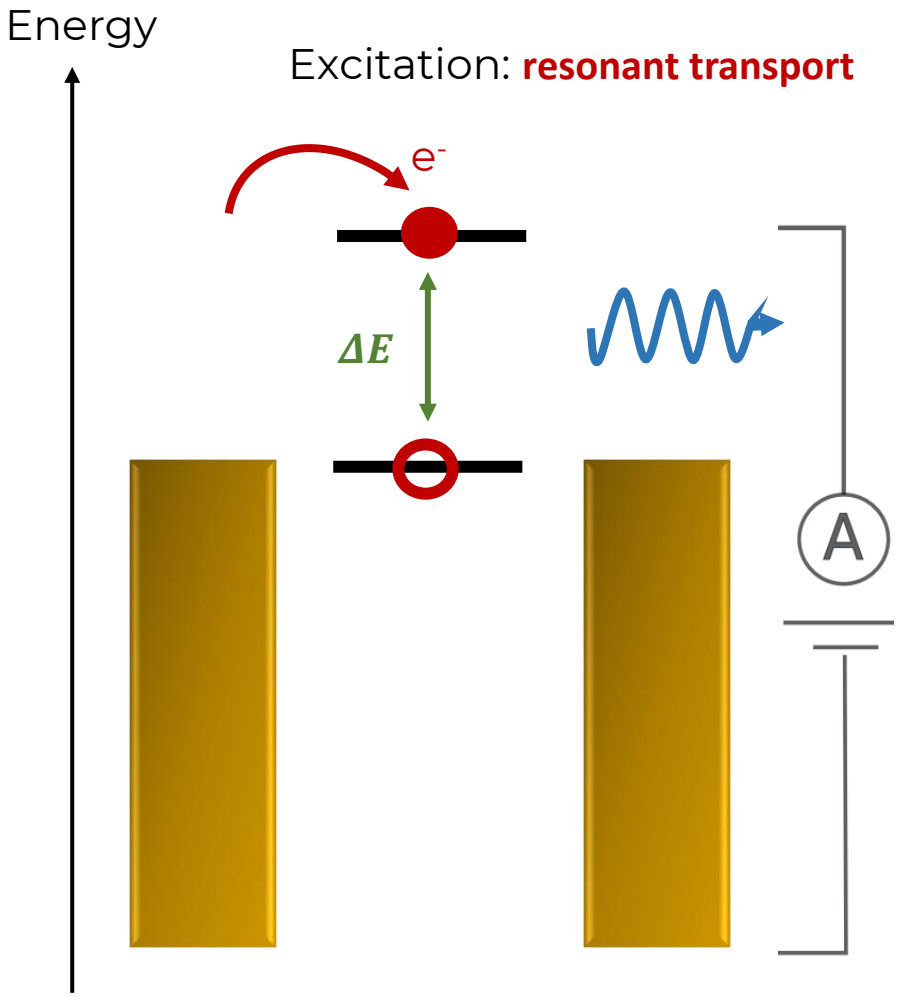
A. Thomas[1*], L. Lethuillier-Karl[1*], K. Nagarajan[1], R. M. A. Vergauwe[1], J. George[1†], T. Chervy[1‡], A. Shalabney[2], E. Devaux[1], C. Genet[1], J. Moran[1§], T. W. Ebbesen[1§]

Vacuum-field catalysis?


Complexity of matter
Solid
Cluster
Molecules
Molecule
Energy Levels
ω_α
L_{Cavity}~1nm
NMH, Wang, Berkelbach, ACS Catalysis, 2022
A. L. Paoletta, NMH, D. W. Cheng, et. al., JACS (2024)
Stone, Starr, NMH, Wang, et. al. , Chemical Science 2022
Experiment
Theory
Complexity of light
E(r,t)
B(r,t)
Static
E-Field
Inhomogeneous
static E-Field
Dynamical
E-Field
Classical
modes
Quantum

STM-BJ as Plasmonic Cavities



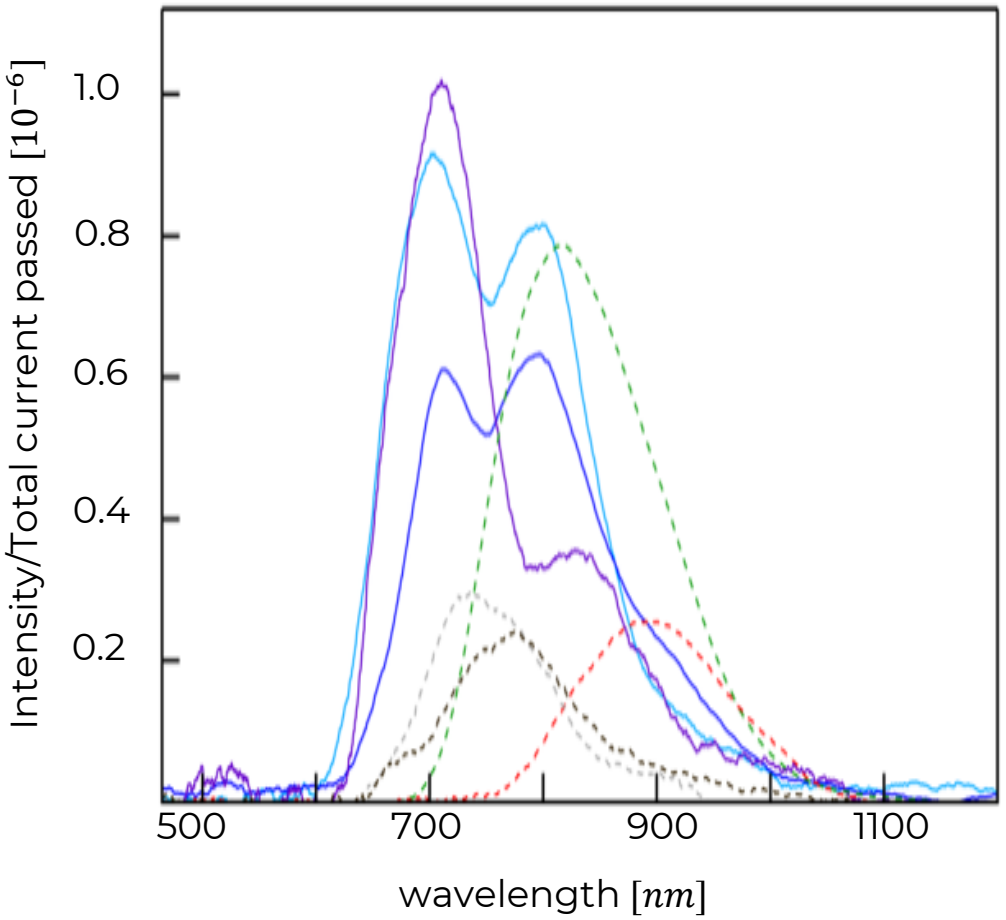


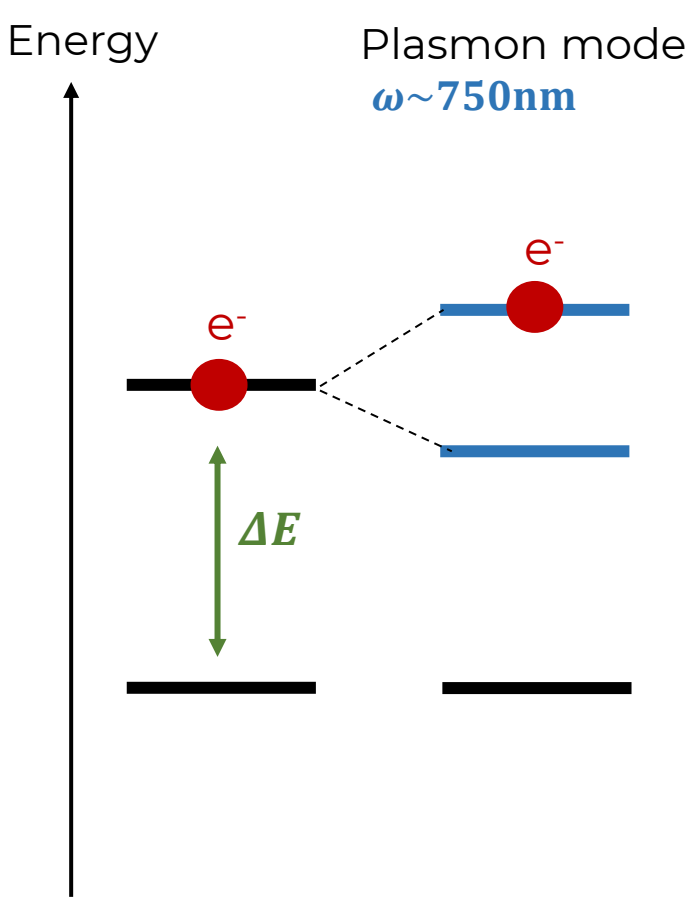
Electroluminescence spectra

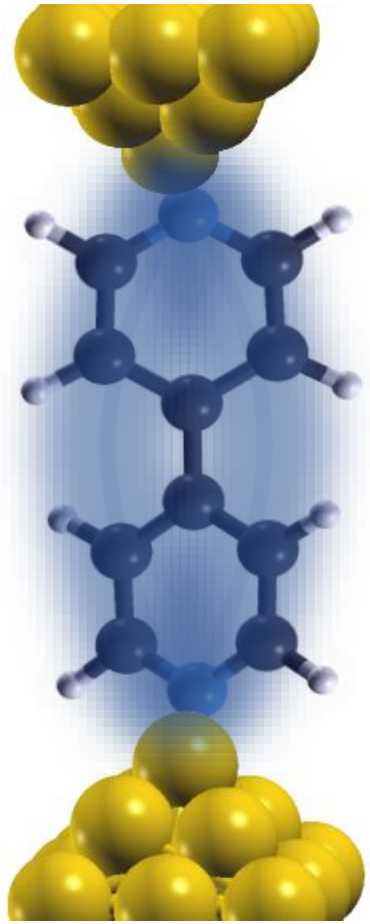
A. L. Paoletta, **NMH**, D. W. Cheng, et. al., **JACS** (2024)

STM-BJ as Plasmonic Cavities

Resonant transport: 1.9V (solid)
Off resonant: 1.4V, 1.6V, 2.25V, 2.4V (dashed)



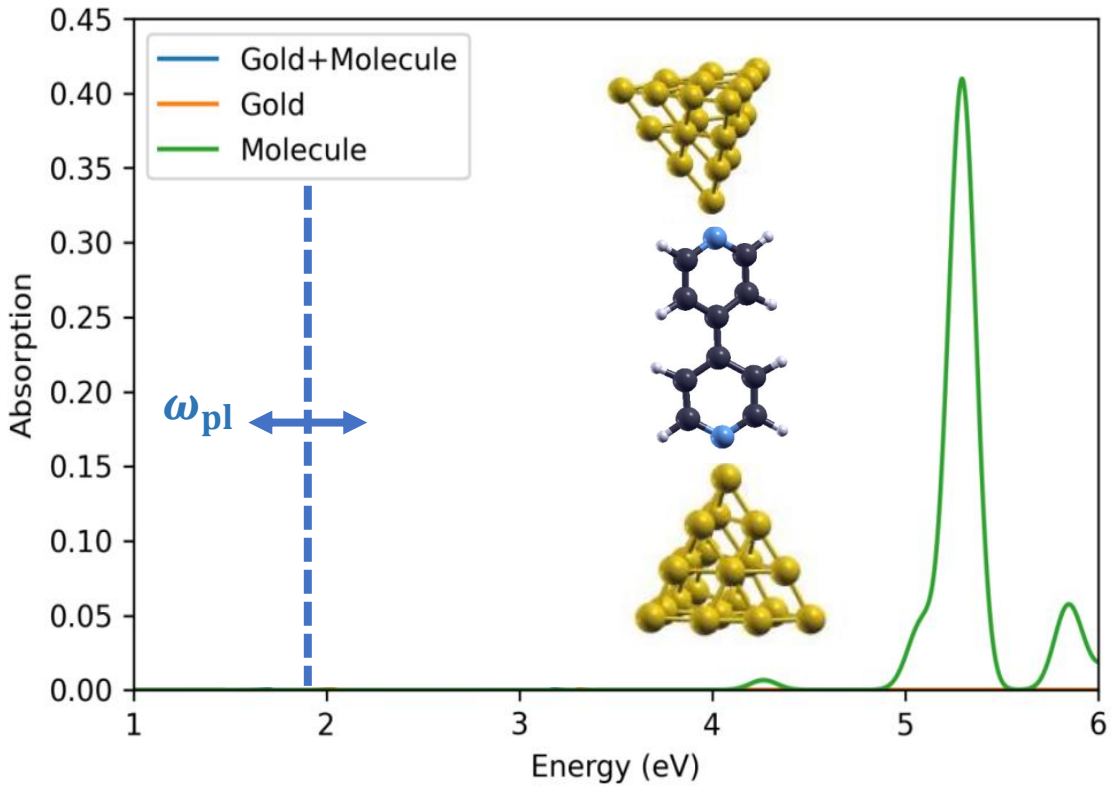




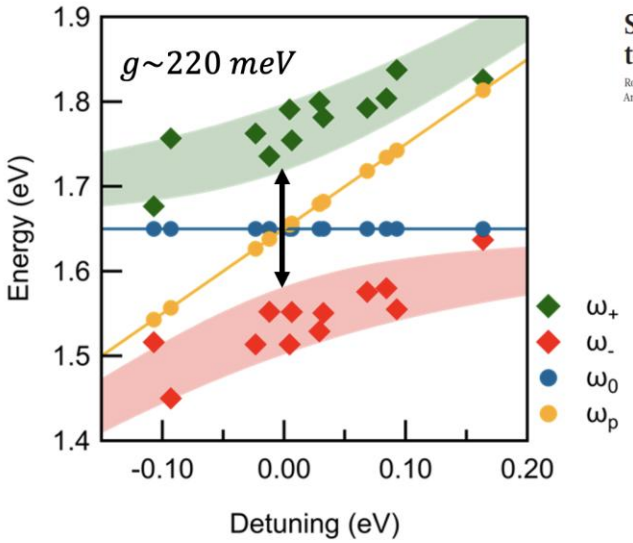
The Open Questions

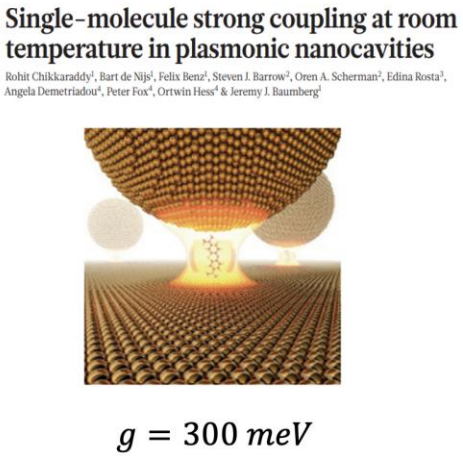
Plasmon mode vs Bipyridine → Interfacial Exciton ✓

Theory: TDDFT Linear Response (Orca)



Strong coupling regime ✓





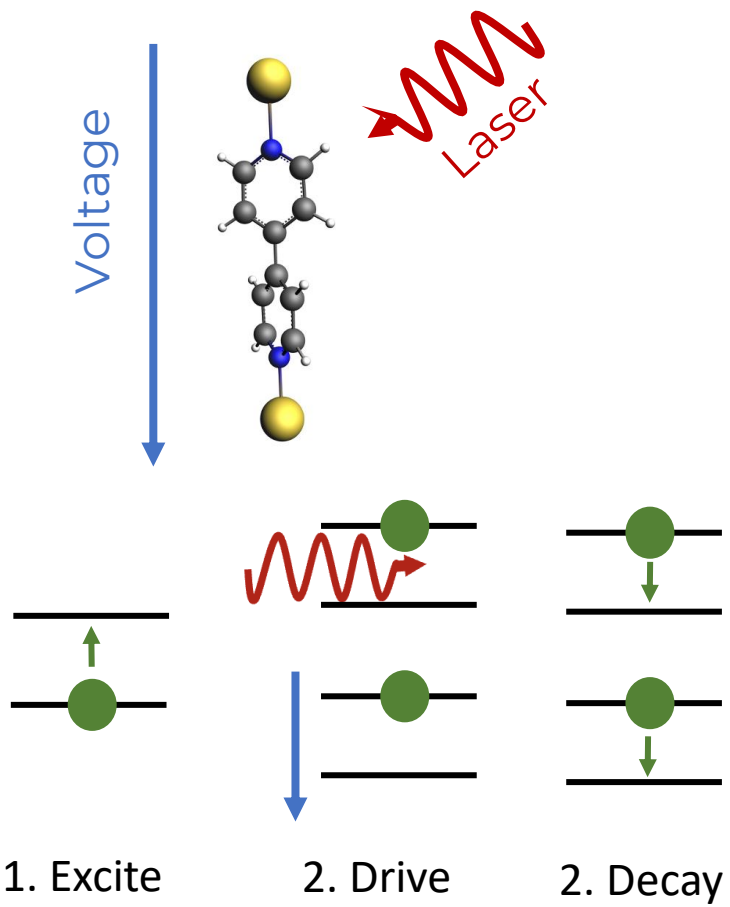
A. L. Paoletta, **NMH**, D. W. Cheng, et. al., **JACS** (2024)

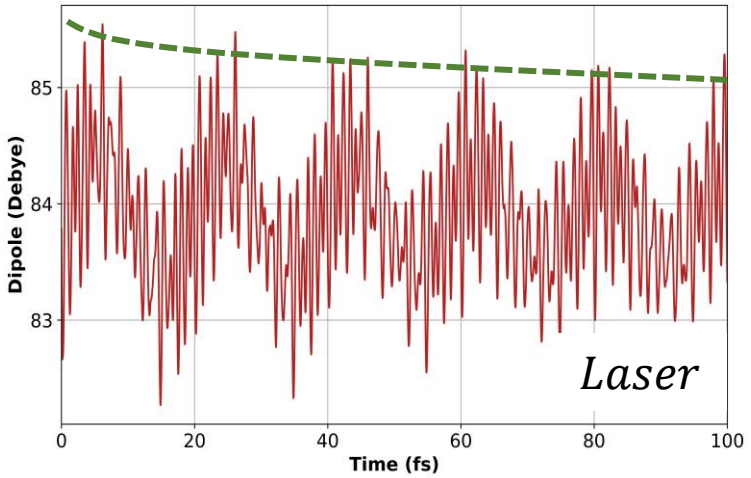
The Open Questions

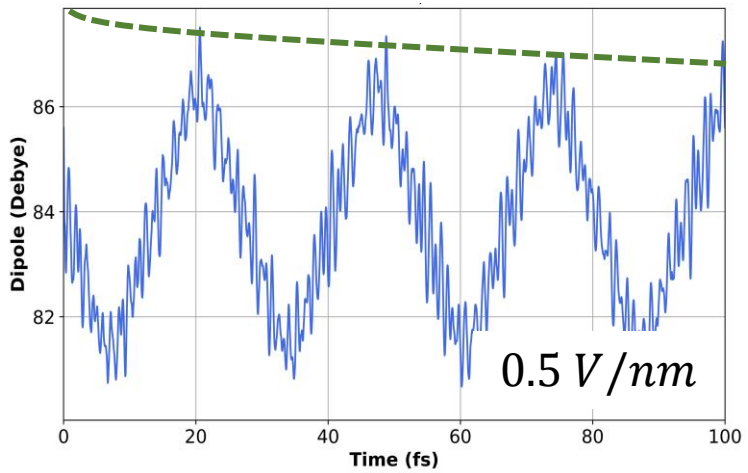
Yuchen Wang

- Why do we have such long Exciton lifetime
- What is the difference to laser driven systems

Real-time TDDFT

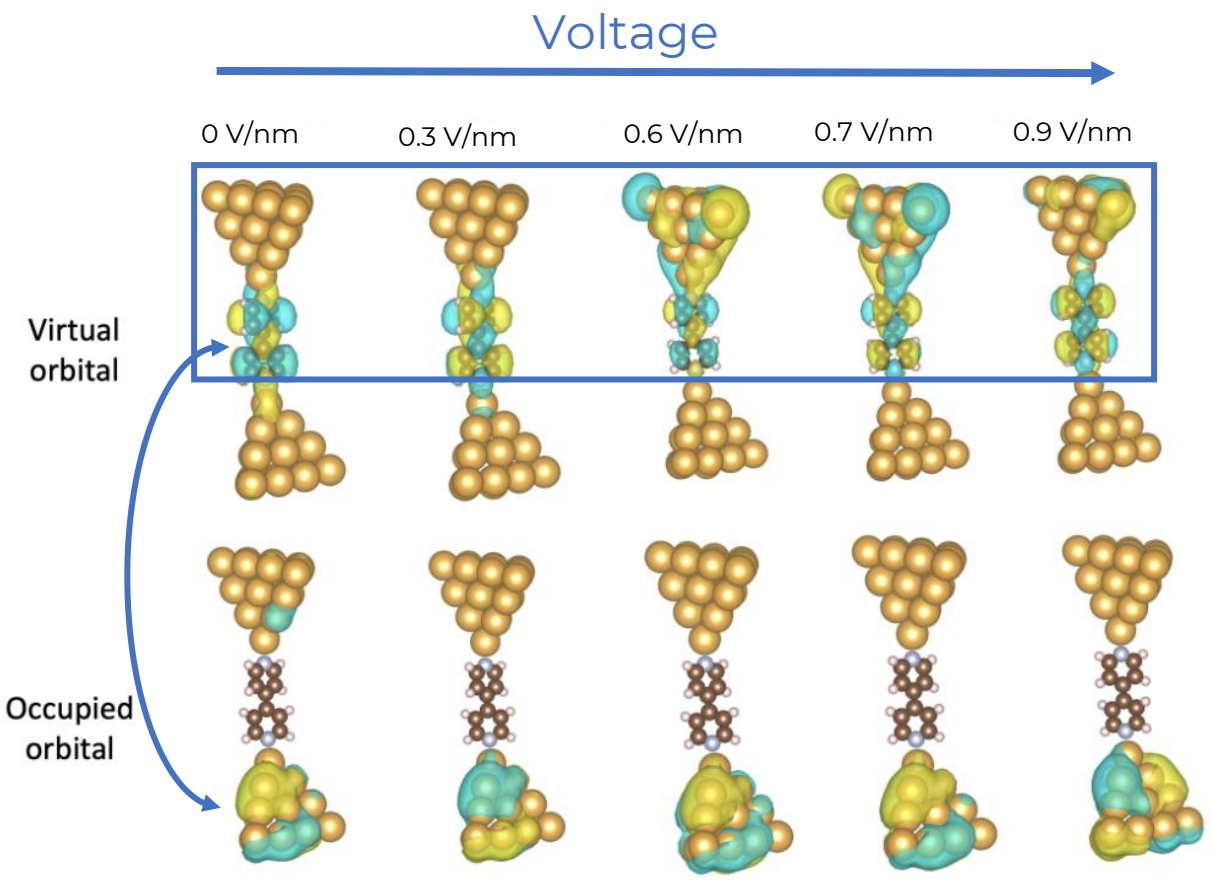


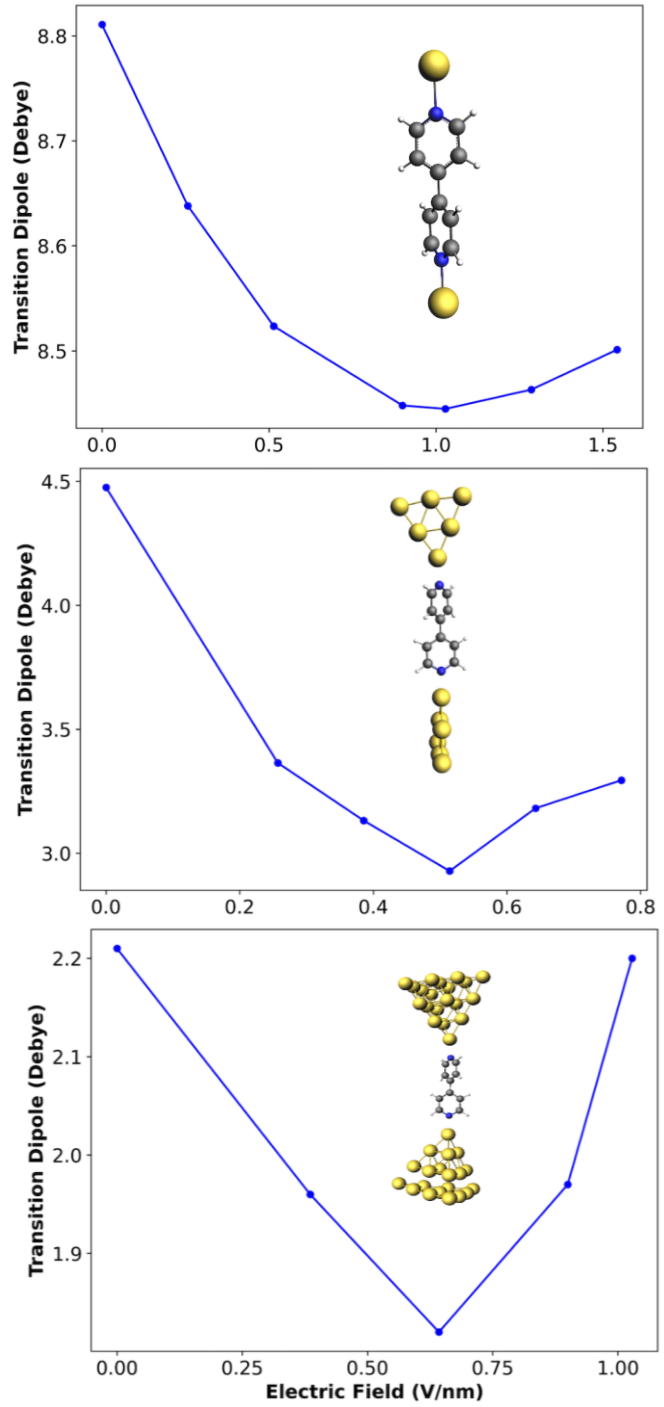




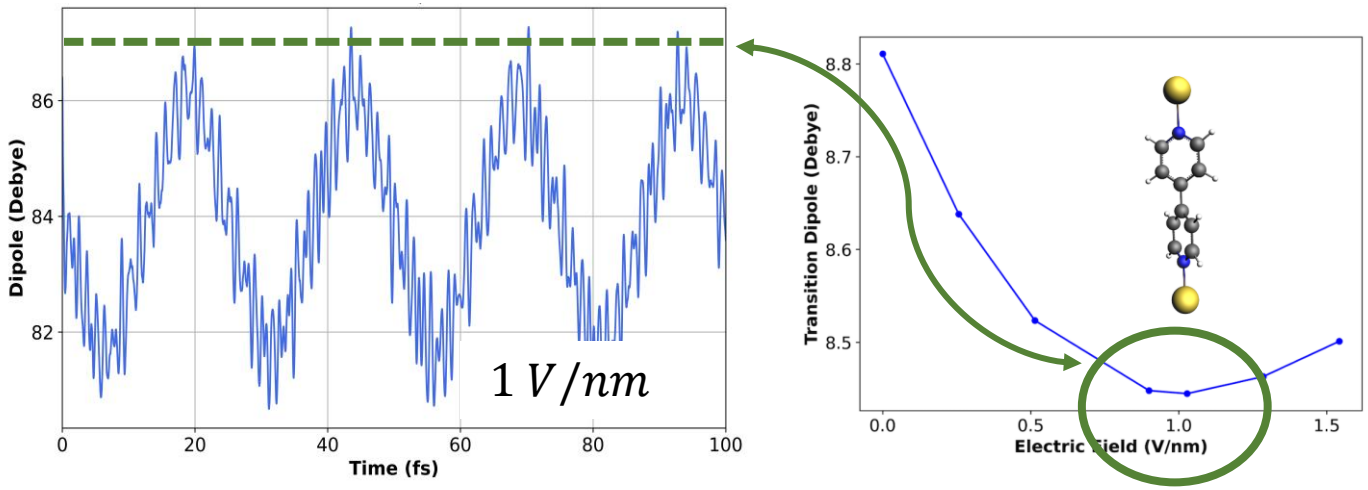
Lifetimes of Interfacial Excitons in STM-BJs

Densities in electric fields (Linear Response TDDFT)

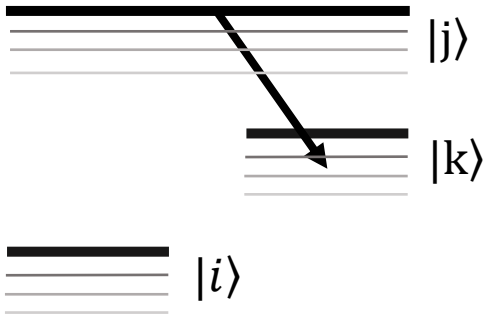




Lifetimes of Interfacial Excitons in STM-BJs

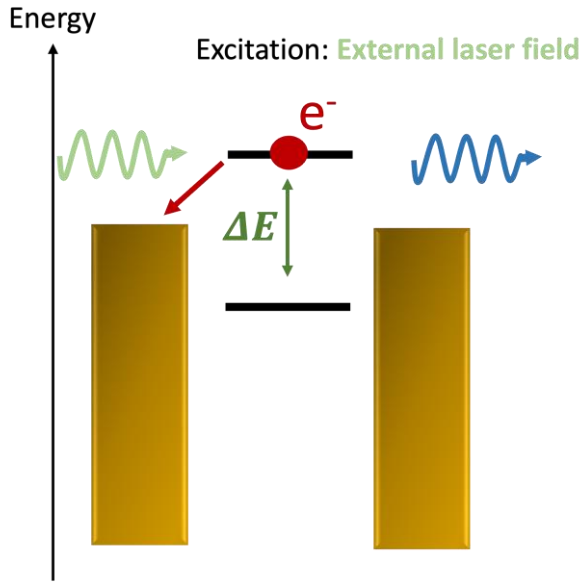


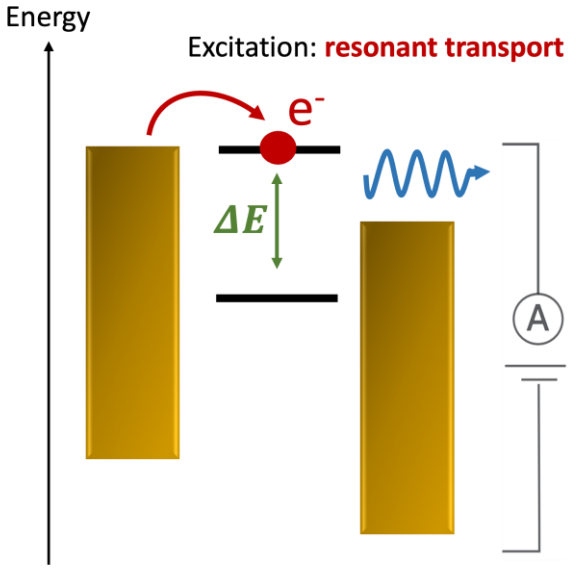
News-Anderson model



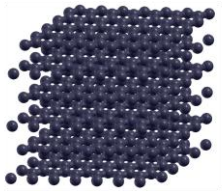
$$|\langle j|\Psi(t)\rangle|^2 = e^{-2\pi\mu^2\left(\frac{1}{\Delta E}\right)t}$$

$$\tau \sim \frac{1}{\mu^2}$$



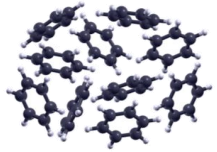


Yuchen Wang, Oliver Tan, **NMH**, in preparation

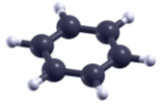


Solid

Cluster



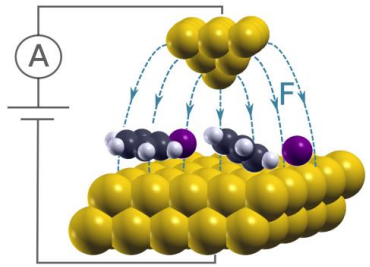
Molecules

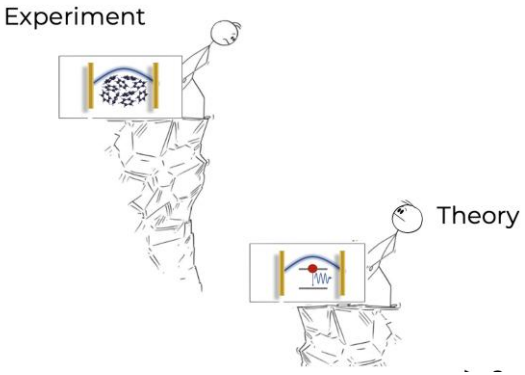


Molecule

Energy Levels

Complexity of matter



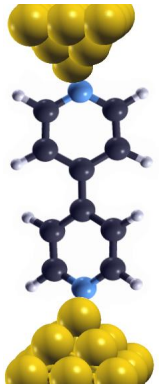


- STM-BJ are used to monitor reaction

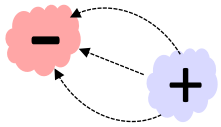
  (But Exciton polaritons)

- Strong coupling at single molecular level

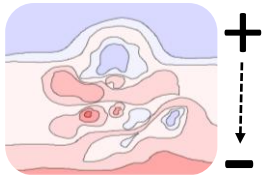
- Long exciton lifetimes through voltage



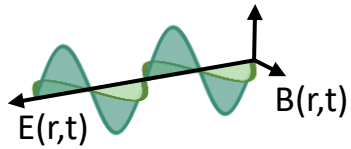
Complexity of light



Static
E-Field



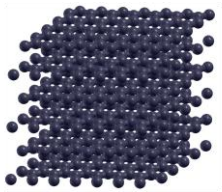
Inhomogeneous
static E-Field



Dynamical
E-Field

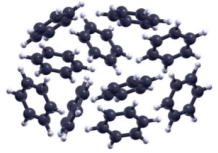
Classical
modes

Quantum

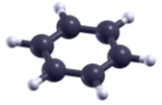


Solid

Cluster



Molecules

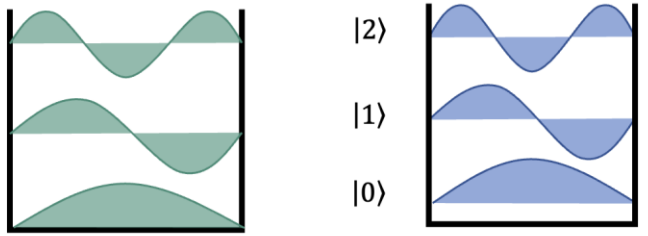


Molecule

Energy Levels

Complexity of matter

Particle in a box - Photons



Maxwell's Equation (classical)

Schördinger equation (quantum)

Quantized ≠ Quantum

$$\hat{H} = \hat{H}_{\mathrm{mol}} + \omega_c \hat{a}^\dagger \hat{a} + g(\hat{a}^\dagger + \hat{a})(\hat{\boldsymbol{\mu}} \cdot \boldsymbol{\xi}) + \frac{g^2}{\omega_c}(\hat{\boldsymbol{\mu}} \cdot \boldsymbol{\xi})^2$$

+ Diagonalization

$$\hat{H} = \hat{H}_{\mathrm{mol}} + \hat{H}_{\mathrm{ph}} + g\sqrt{2\omega_c} q(\hat{\boldsymbol{\mu}} \cdot \boldsymbol{\xi}) + \frac{g^2}{\omega_c}(\hat{\boldsymbol{\mu}} \cdot \boldsymbol{\xi})^2$$

$$|\dot{\Psi}(t)\rangle = -i\left(\hat{H}_{\mathrm{mol}} + g\sqrt{2\omega_c} q(t)(\hat{\boldsymbol{\mu}} \cdot \boldsymbol{\xi}) + \frac{g^2}{\omega_c}(\hat{\boldsymbol{\mu}} \cdot \boldsymbol{\xi})^2\right)|\Psi(t)\rangle$$

$$\dot{p}(t) = -\omega_c^2 q(t) - g\sqrt{2\omega_c}\,\langle\Psi(t)|\hat{\boldsymbol{\mu}} \cdot \boldsymbol{\xi}|\Psi(t)\rangle$$

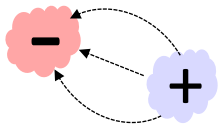
Classical:

- No vacuum field fluctuation
- No Fock state representation
- No Entanglement

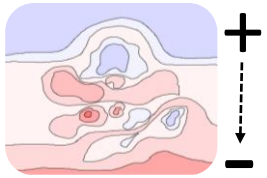
Polaritonics

Irén Simkó

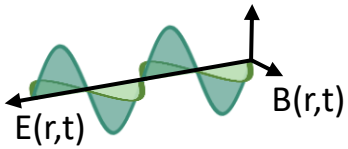
Complexity of light



Static E-Field



Inhomogeneous static E-Field

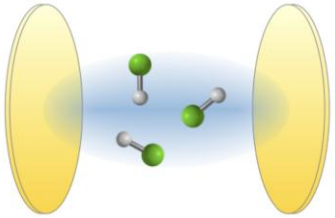


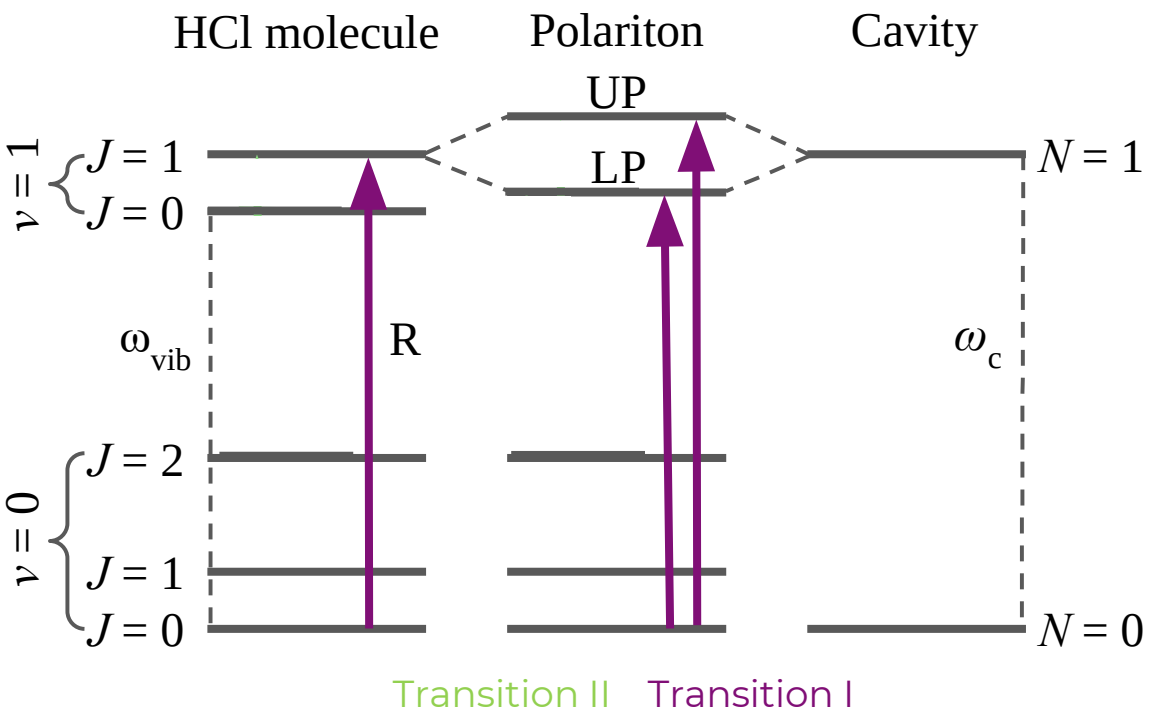
Dynamical E-Field

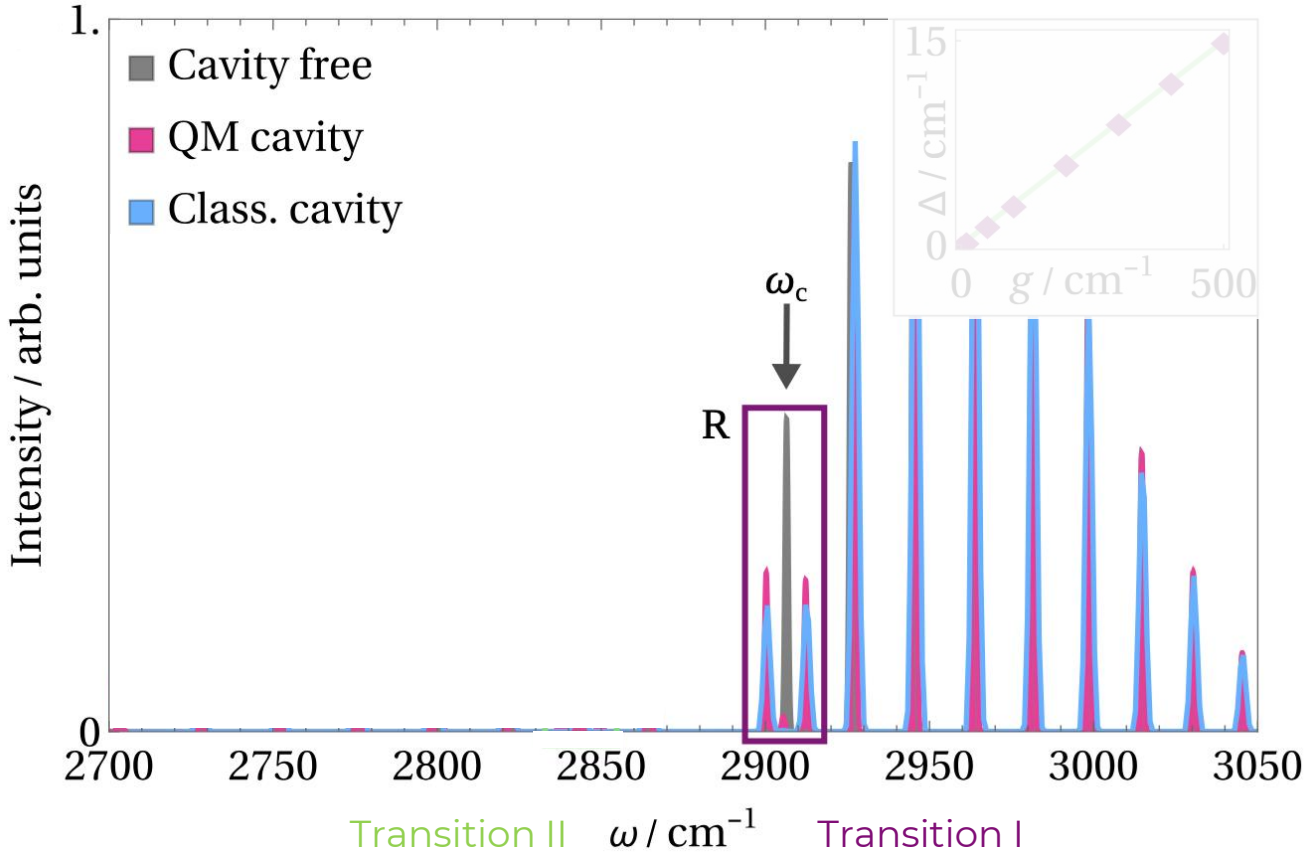
Classical modes

Quantum

Classical vs Quantum Light Effects in Polaritonic Spectra





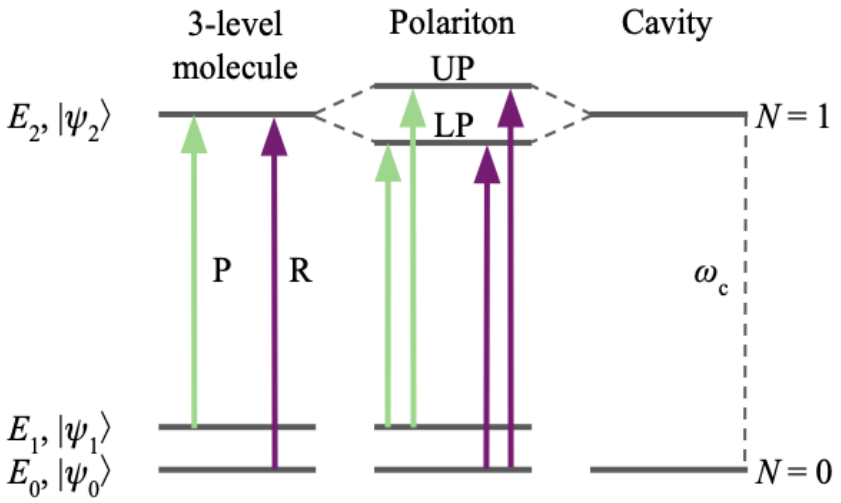


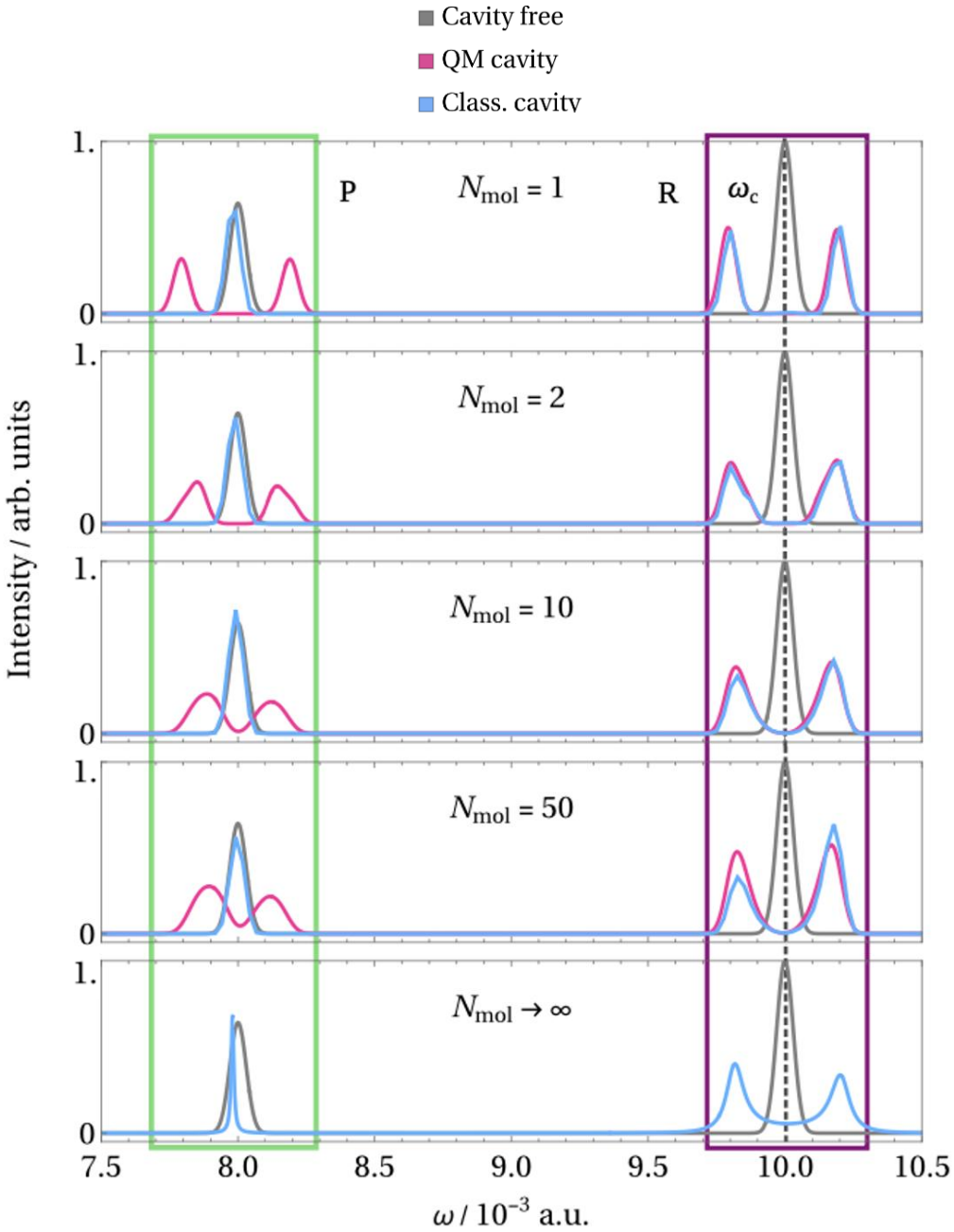
Is this effect really **quantum** and does it persist for **many molecules**?

Schwennicke, Kai, et al., **arXiv** preprint arXiv:2408.05036 (2024).

Wright, Adam D., Jane C. Nelson, and Marissa L. Weichman., ***JACS*** 145.10 (2023): 5982-5987.

Twin-Polaritons: Many Molecule Case





- Feature persist for many molecules
- Not a residual from a semi-classical approximation (thermodynamic limit)

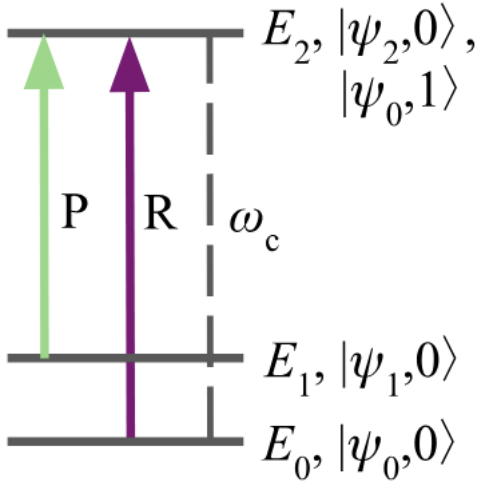
J. Yuen-Zhou, et al., **JCP** 160.15 (2024).

Twin-Polaritons: Source of Quantumness

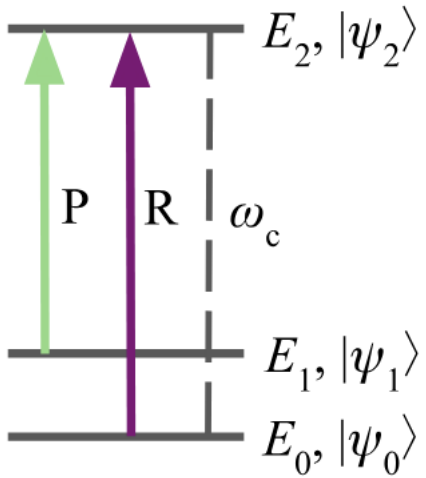
What's the origin of the *quantumness*:

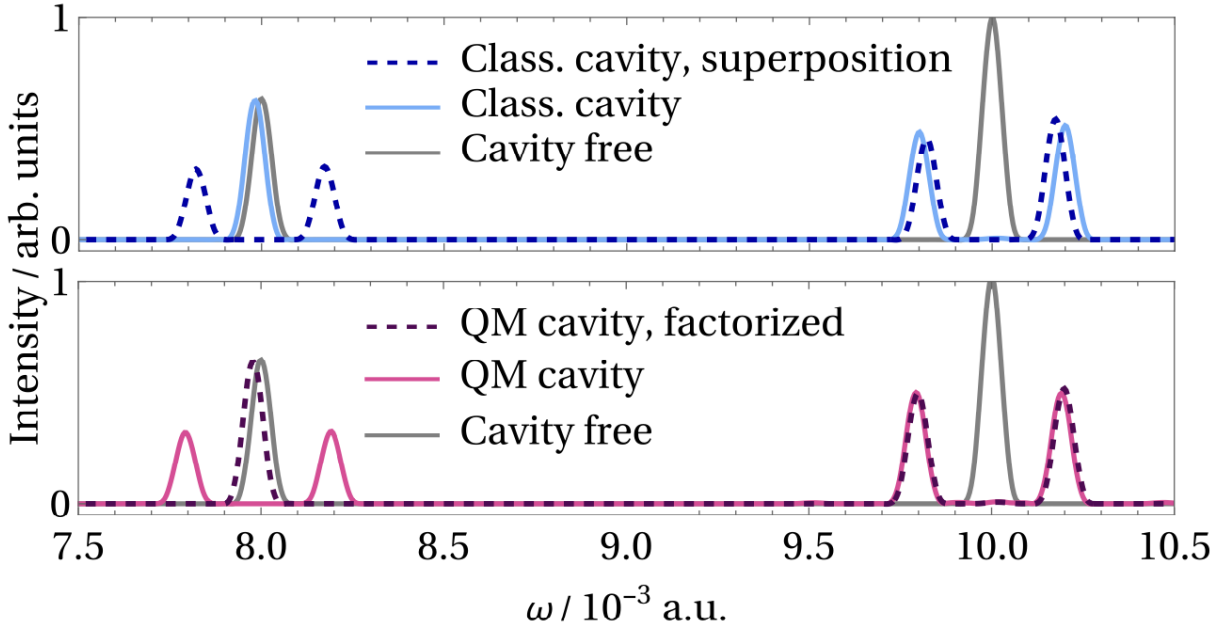
(i) Vacuum field fluctuation (ii) Fock-state (iii) Entanglement (No factorization)

Quantum



Classical





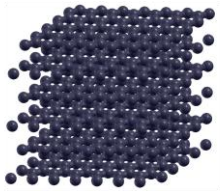
Break the quantum:

$$|\Psi(t)\rangle = \left(\sum_i a_i |\psi_i\rangle\right)\left(\sum_N b_N |N\rangle\right)$$

Fix the classical:

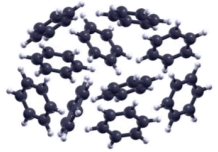
$$|\Psi(0)\rangle = |\psi_{1,q}\rangle + |\psi_{2,q}\rangle$$

Iren Simko, **NMH**, in preparation

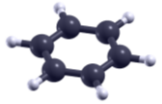


Solid

Cluster



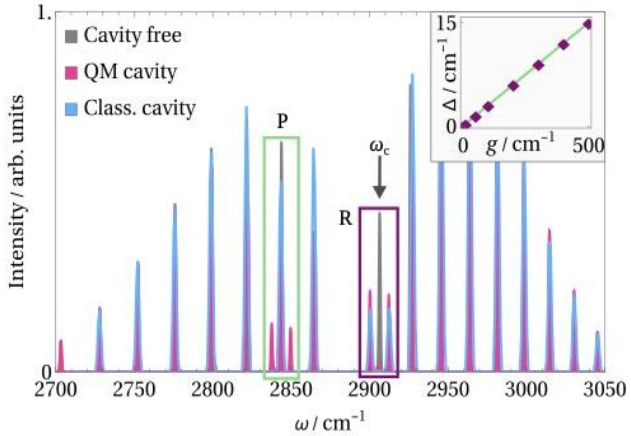
Molecules

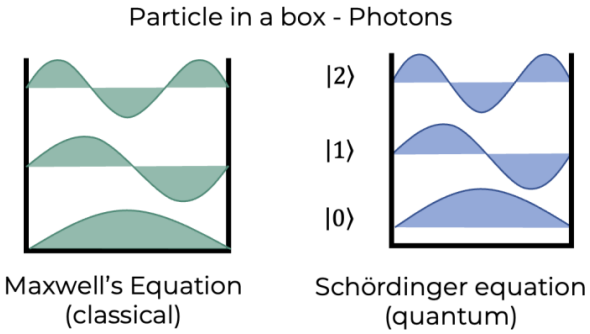


Molecule

Energy Levels

Complexity of matter





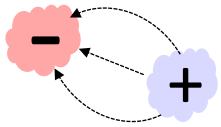
Quantized ≠ Quantum

Twin Polaritons:

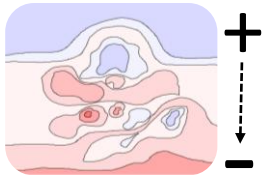
- New quantum features
- Inherently quantum
- Persist for many molecule case
- Tuning a quantum feature with a classical one

Polaritonics

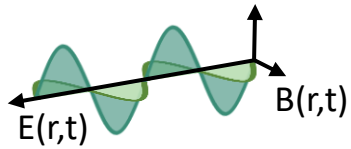
Complexity of light



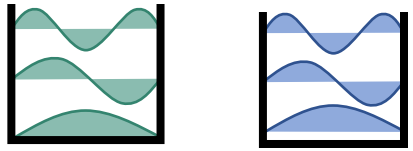
Static E-Field



Inhomogeneous static E-Field

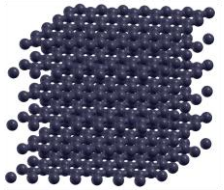


Dynamical E-Field



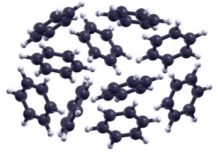
Classical modes

Quantum

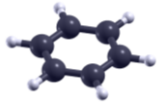


Solid

Cluster



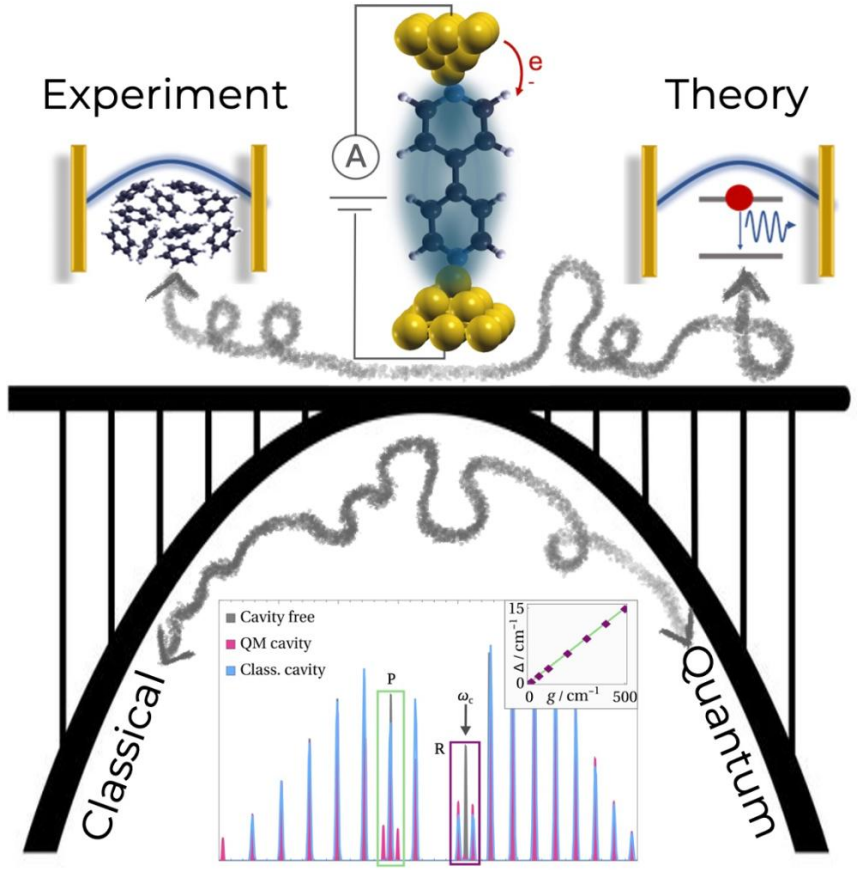
Molecules



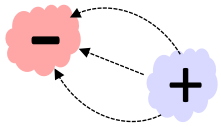
Molecule

Energy Levels

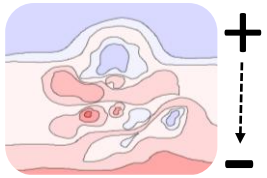
Complexity of matter



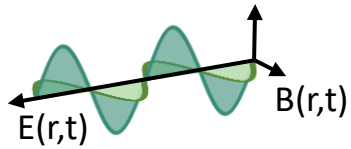
Complexity of light



Static
E-Field



Inhomogeneous
static E-Field



Dynamical
E-Field

Classical
modes

Quantum

Acknowledgements

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Thank you!