



Millennium Institute
for Research in Optics

MiRO



Vibronic and Vibrational Polaritons Spectroscopy and Chemistry

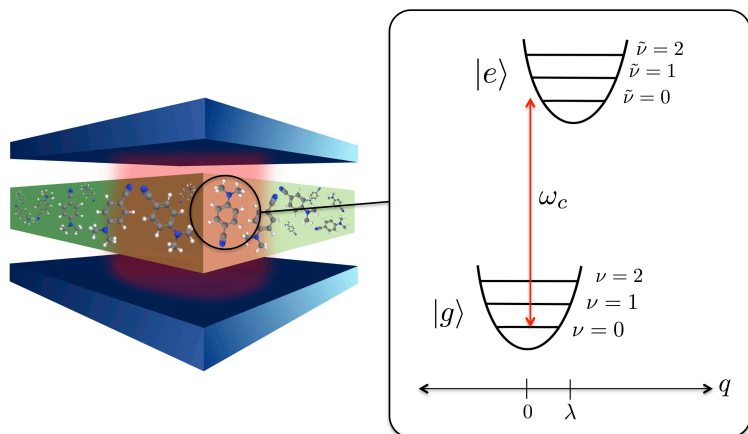
Felipe Herrera

Department of Physics, Universidad de Santiago de Chile USACH
<http://fherreralab.com>

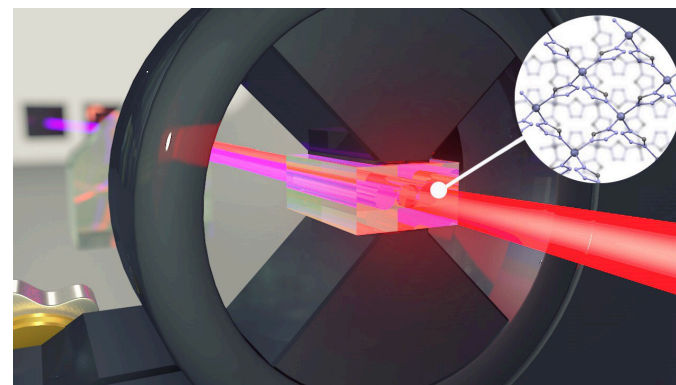


Workshop on Molecular Polaritonics, July 8th, 2019

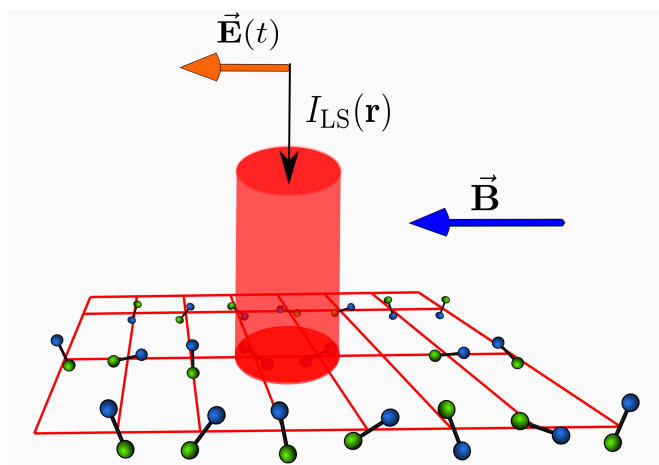
Molecular Quantum Technology Group



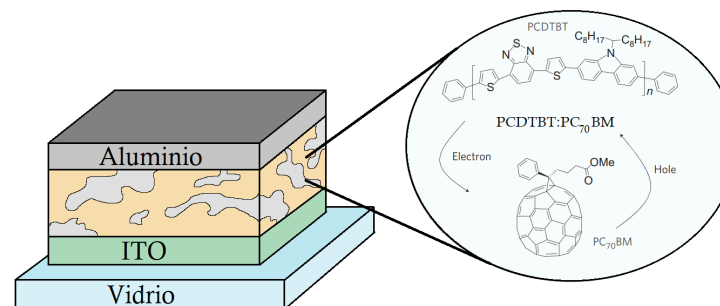
Organic Cavity QED



Materials Design for QKD



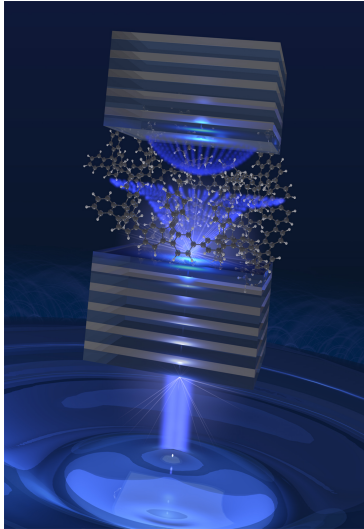
Ultracold Molecules



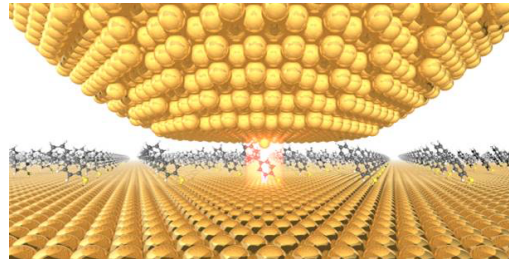
Organic Photovoltaics

Cavity QED with Molecules

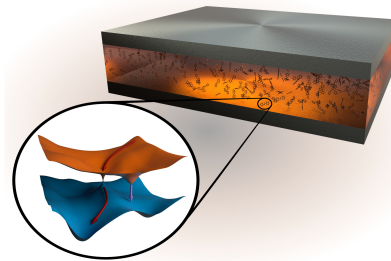
Dielectric microcavity



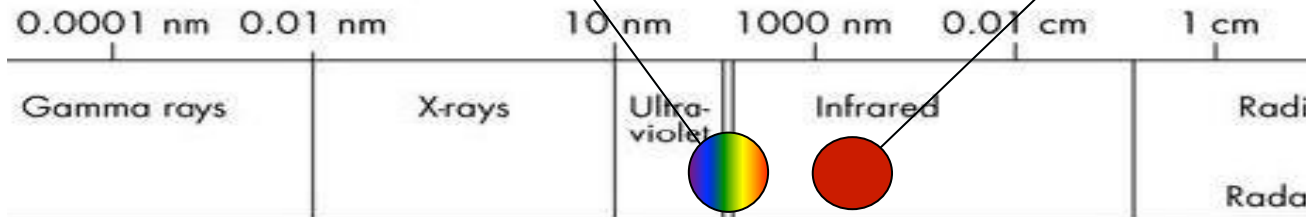
Plasmonic nanocavity



Metal microcavity



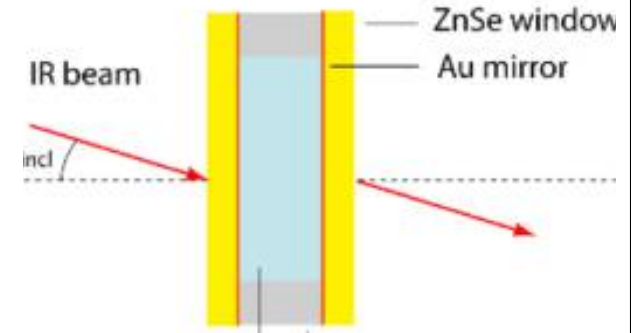
@Kena-Cohen;@Lidzey;@Ebbesen;@Baumberg;@Shegai;@Bellessa,...



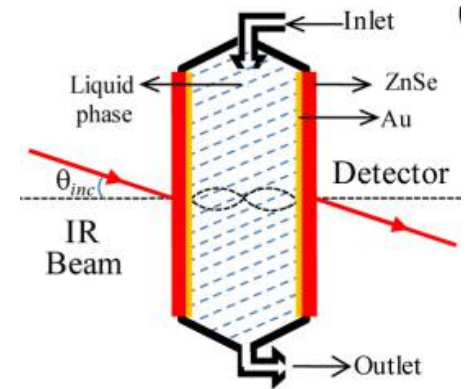
Visible light



IR Fabry-Perot

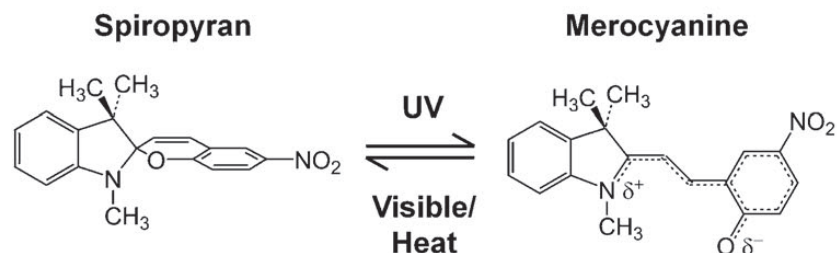


Microfluidic IR Fabry-Perot



@Ebbesen;@Simpkins,...

Cavity-controlled chemistry: Early evidence



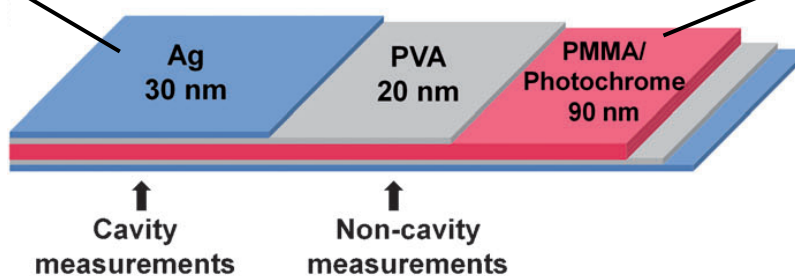
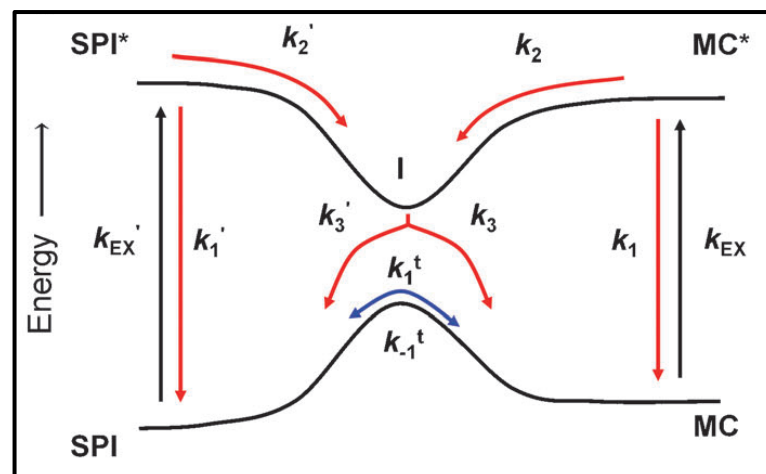
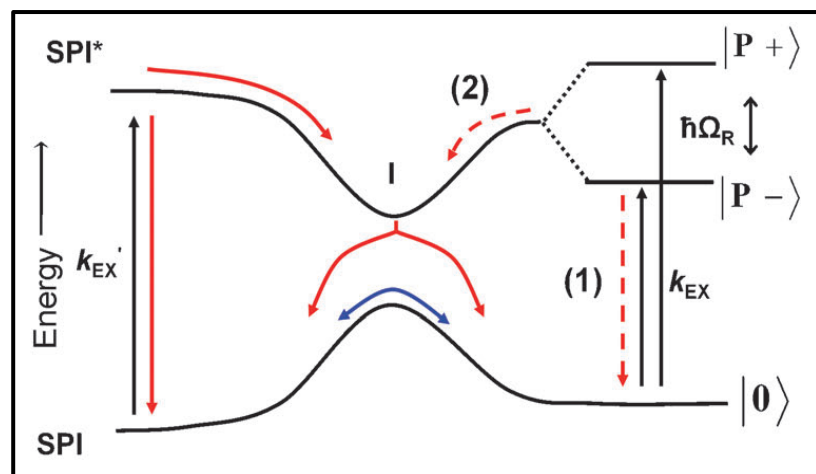
Angewandte
Communications

Quantum Electrodynamics

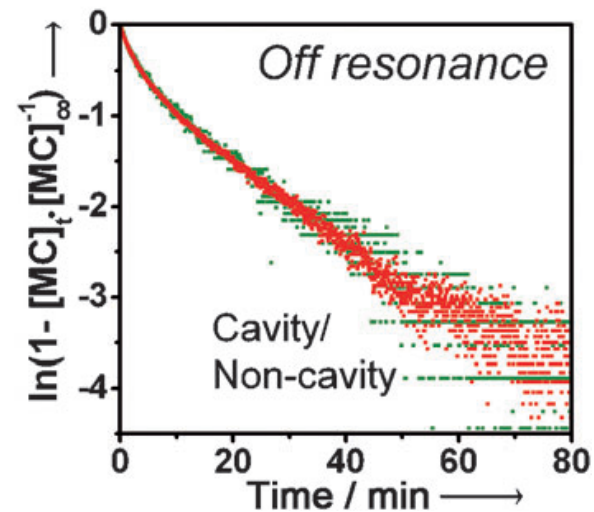
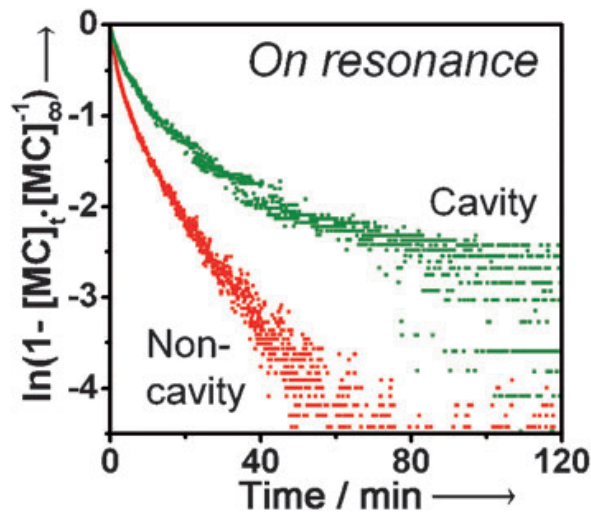
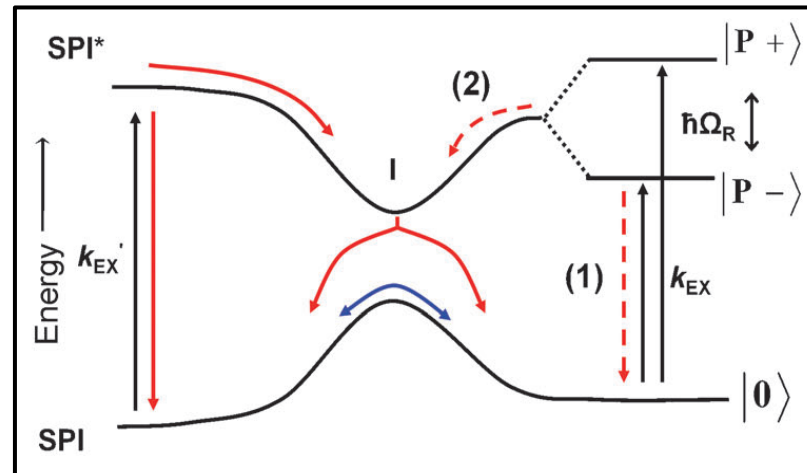
Angew. Chem. Int. Ed. 51, 1592, 2012

Modifying Chemical Landscapes by Coupling to Vacuum Fields**

James A. Hutchison, Tal Schwartz, Cyriaque Genet, Eloïse Devaux, and [Thomas W. Ebbesen*](#)



SPI to MC rate suppression

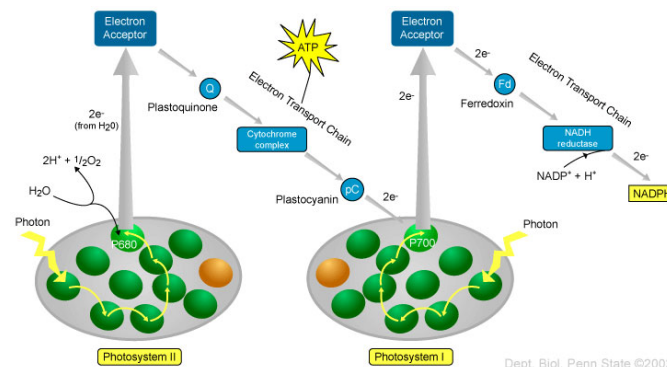
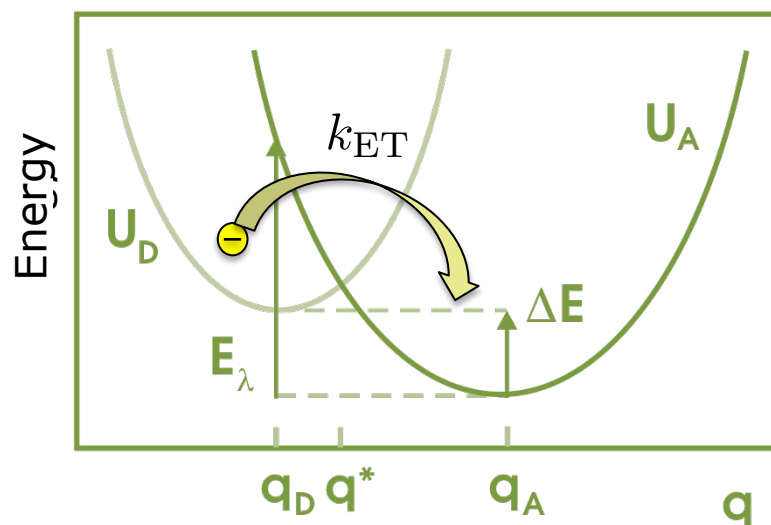


General trend confirmed by independent experiments (S. Kena-Cohen,...)

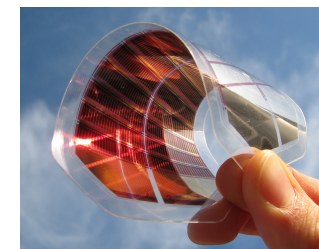
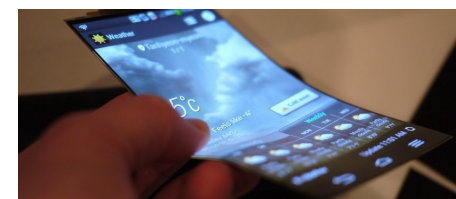
What is the mechanism?

Electron transfer in chemistry & biology

- **Marcus Theory:** Electron transfer rate controlled by relative energetics of donor (D) and acceptor (A) potential energy surfaces.



Dept. Biol. Penn State ©2002



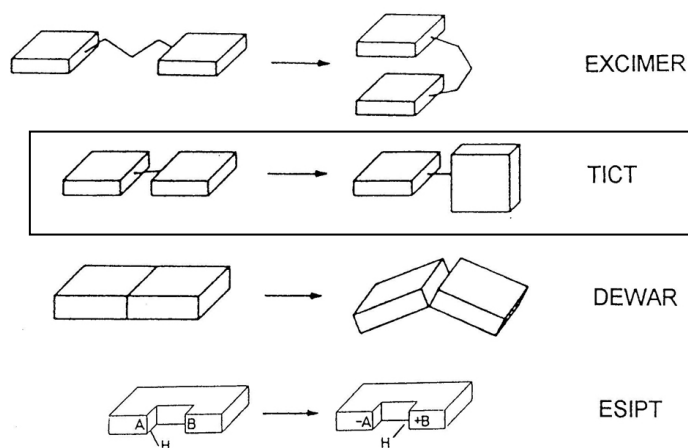
$$k_{ET} = |V_{DA}|^2 \sqrt{\frac{\pi}{\hbar^2 k_B T E_\lambda}} \exp \left\{ -\frac{(\Delta E - E_\lambda)^2}{4 E_\lambda k_B T} \right\}$$

- Reorganization energy E_λ is crucial parameter for control [solvents, E-fields,...]

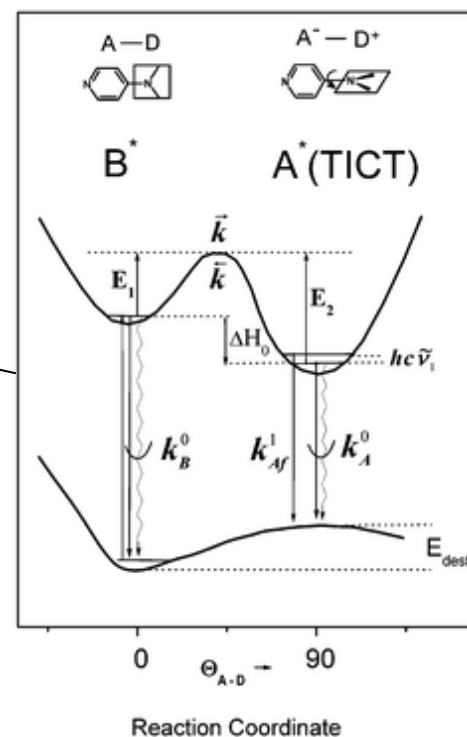
Test Case: Donor-to-charge-transfer states

- Charge Transfer (CT) states are the precursors of charge separation in organic photovoltaics.
- Photoinduced ET reactions involving Twisted-Intramolecular Charge Transfer (TICT) states, where reducing S_0 - S_1 reorganization energy can have significant effects on reaction rate.

Electron Donor-Acceptor Complexes with Intramolecular Configuration Changes

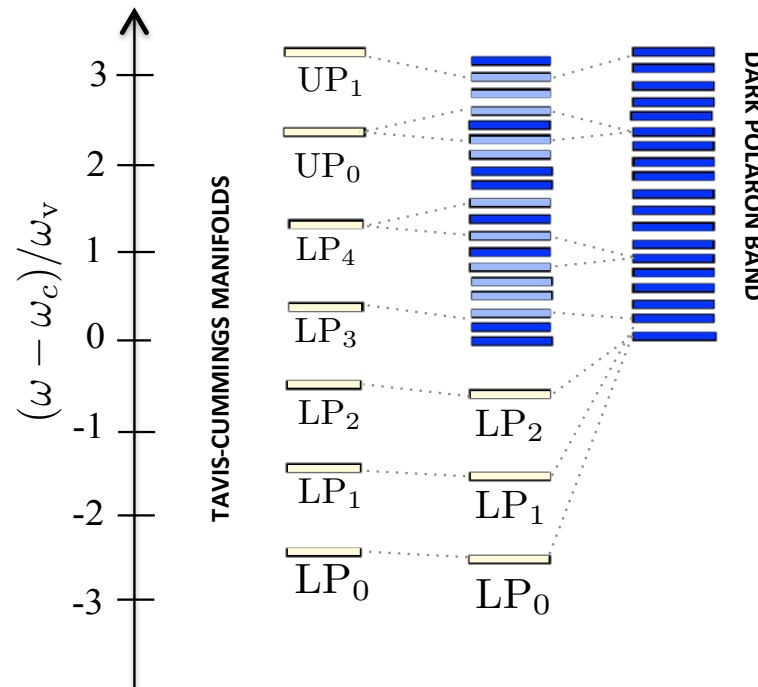


PES for Photoinduced ET reaction



Polaron decoupling limit

- For Rabi couplings, the polariton spectrum simplifies and vibrations become separable from electron-photon degrees of freedom in the lower polariton manifold.
- Inner-shell reorganization energy is collectively eliminated in an ensemble



$$\sqrt{N}\Omega \gg \lambda^2\omega_v$$

LOWER POLARITON STATE

$$|\text{LP}_0\rangle \approx \frac{1}{\sqrt{2}} \left[\frac{1}{\sqrt{N}} \sum_{n=1}^N |g_1, \dots, e_n, \dots, g_N\rangle |0_c\rangle - |g_1, g_2, \dots, g_N\rangle |1_c\rangle \right] \otimes |\nu_1 = 0, \nu_2 = 0, \dots, \nu_N = 0\rangle$$

Cavity-enhanced electron transfer

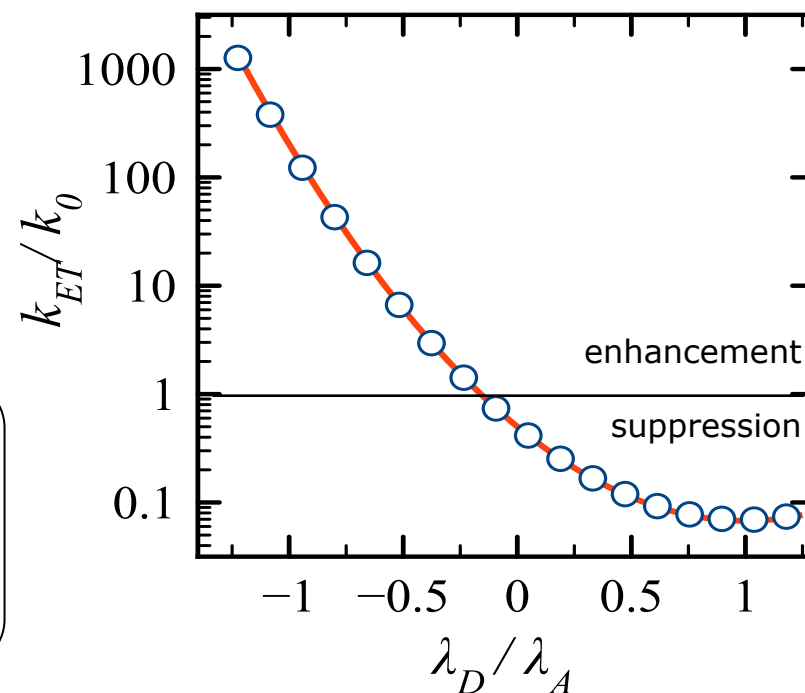
- In the polaron-decoupling regime, the reorganization energy of a cavity-dressed donor manifold is eliminated relative to the ground potential, enhancing donor-to-acceptor tunneling along reaction coordinate.

$$k_{ET} = \sum_{n=1}^N \frac{|V_{DA}|^2}{2N} \sum_{\nu_{nA}} \sum_{\nu_D} \rho_{\nu_D} |\langle \nu_D | \nu_{nA} \rangle|^2 D(\omega_{\nu_D} - \omega_{\nu_A})$$

Collective suppression of D-A Reorganization Energy

$$\lambda_{DA} = (\lambda_D / 2\sqrt{N} - \lambda_G) - (\lambda_A - \lambda_G)$$

$$\langle \nu_D = 0 | \nu_{nA} \rangle = \frac{(\lambda_{DA})^{2\nu_{nA}}}{(\nu_{nA})!} e^{-\lambda_{DA}^2}$$

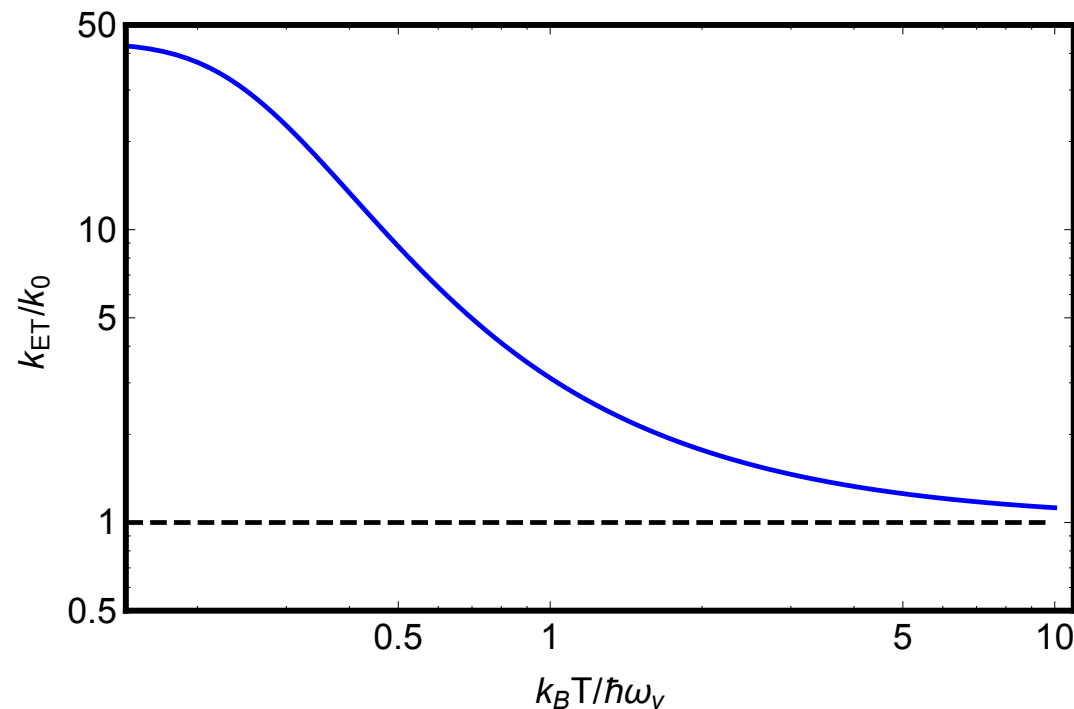


$$N \rightarrow \infty \quad \longrightarrow \quad e^{-\lambda_{DA}^2} \rightarrow e^{-\lambda_A^2}$$

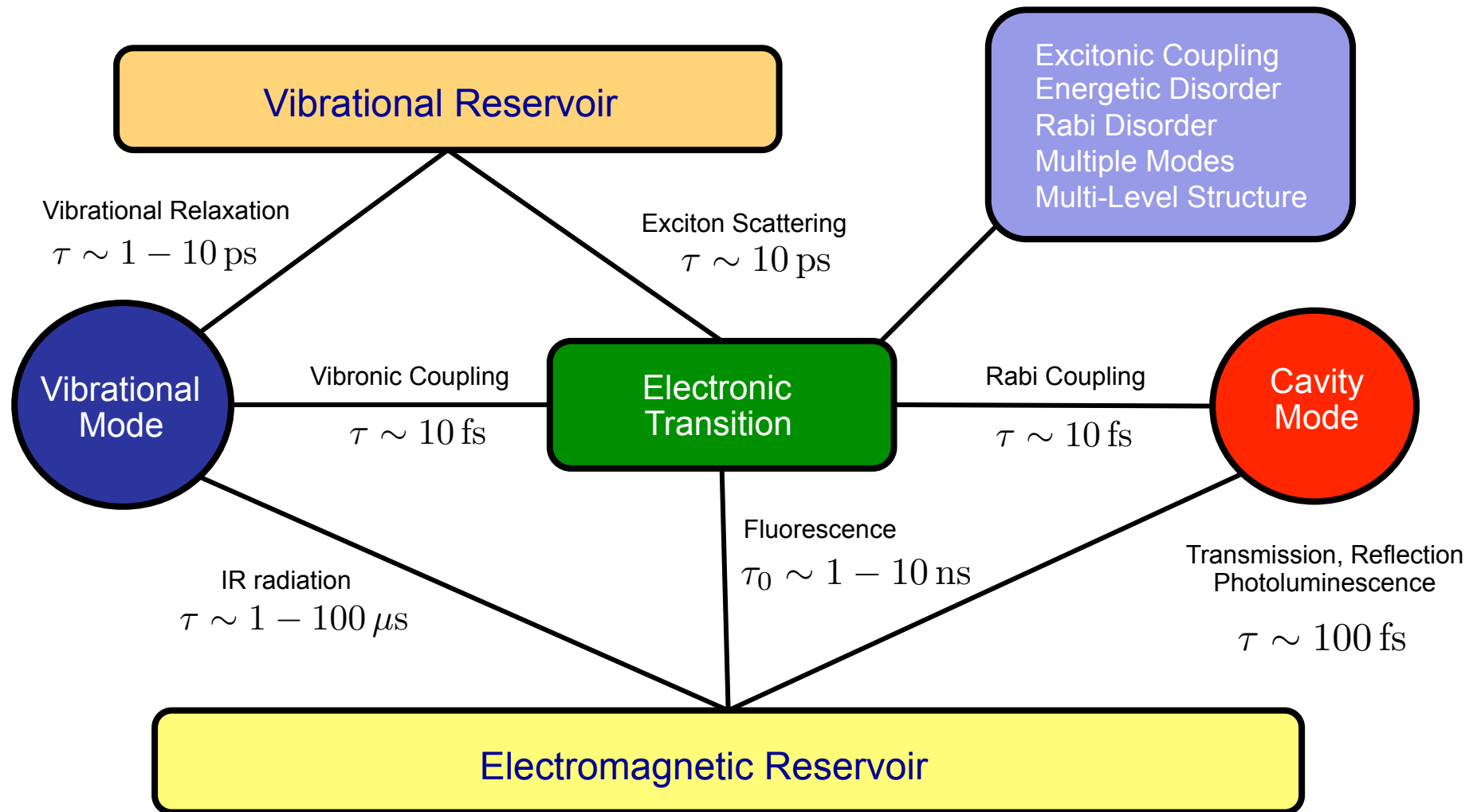
Exponential ET rate enhancement

Where is the ET rate enhancement?

- Orders-of-magnitude rate enhancements for electron transfer have yet to be measured.
- Rate enhancement due to polaron decoupling is only moderate for higher thermal energies.



A modeling challenge



Complementary approaches

Full *ab-initio*:

- Field quantization consistent with Maxwell equations in dispersive and absorptive media[Barnett, Welch, Drummond...]
- Atomistic treatment of large number of material degrees of freedom [QM/MM, HEQM,...].



ab-initio Materials
+
ab-initio Quantum Optics

Semi *ab-initio*



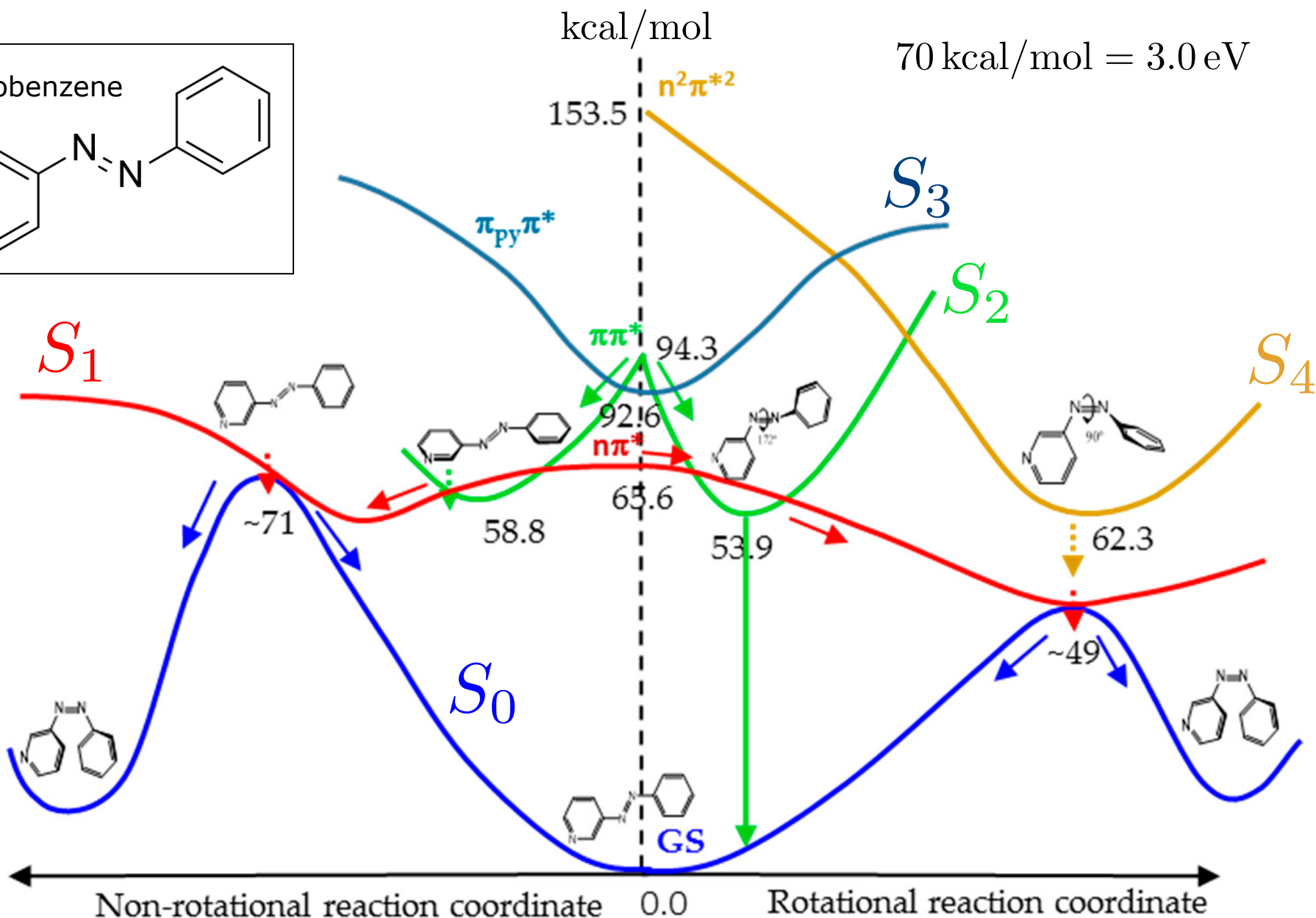
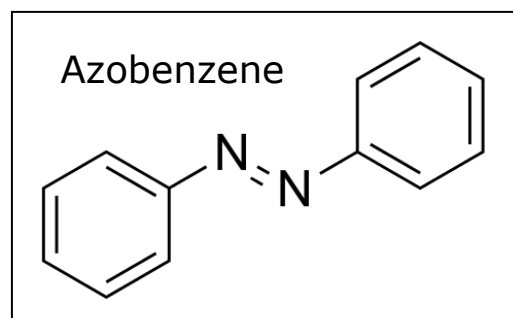
ab-initio Materials
+
Model Quantum Optics

Full phenomenological



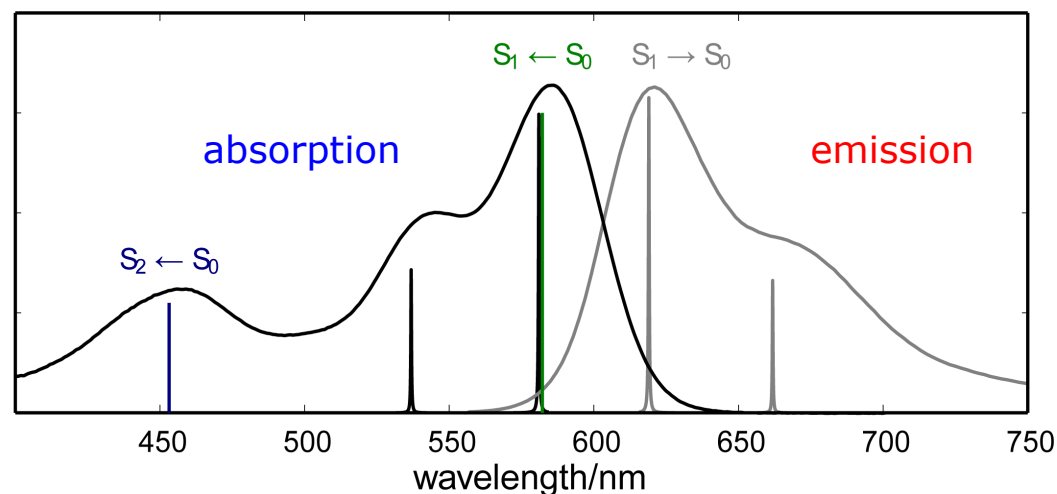
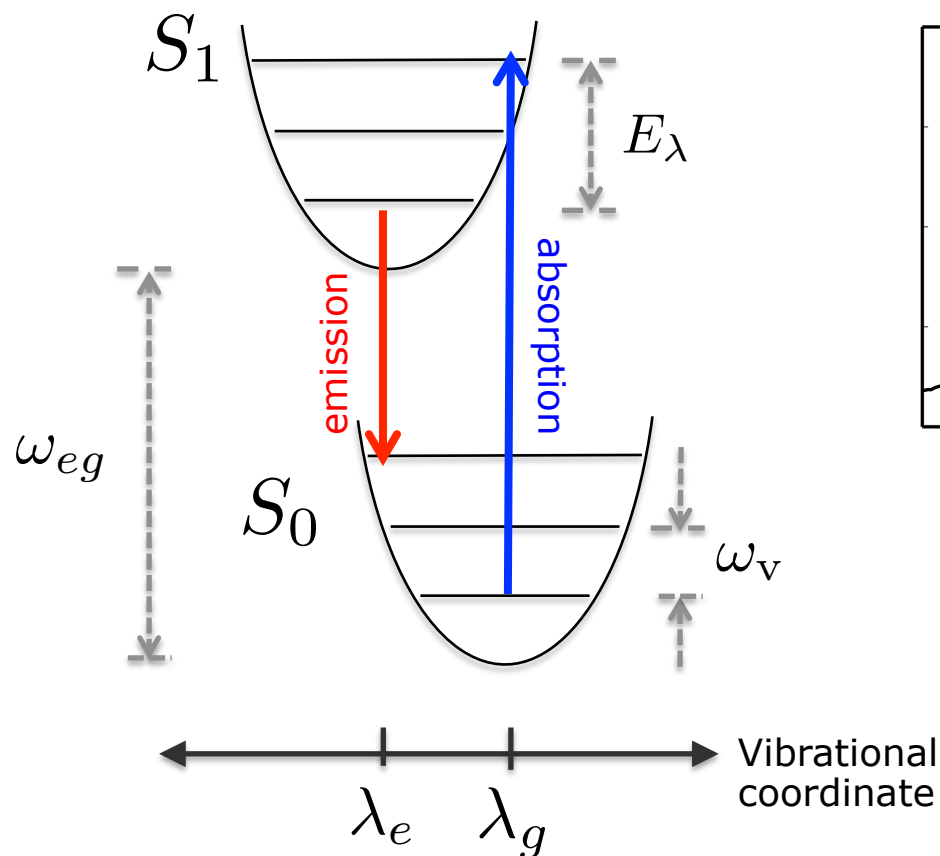
Model Materials
+
Model Quantum Optics

ab-initio spectroscopy



Model spectroscopy

- **Displaced Oscillator Model** accounts for coupling of a single *high-frequency* intramolecular vibration (~ 180 - 200 meV) with lowest singlet transition.
- Widely used model in physical chemistry to describe absorption lineshapes of a large family of organic chromophores



O. Kuhn, arXiv:1108.4834

$$E_\lambda = \frac{\omega_v}{2} (\lambda_e - \lambda_g)^2$$

Inner-shell reorganization energy

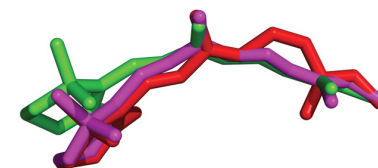
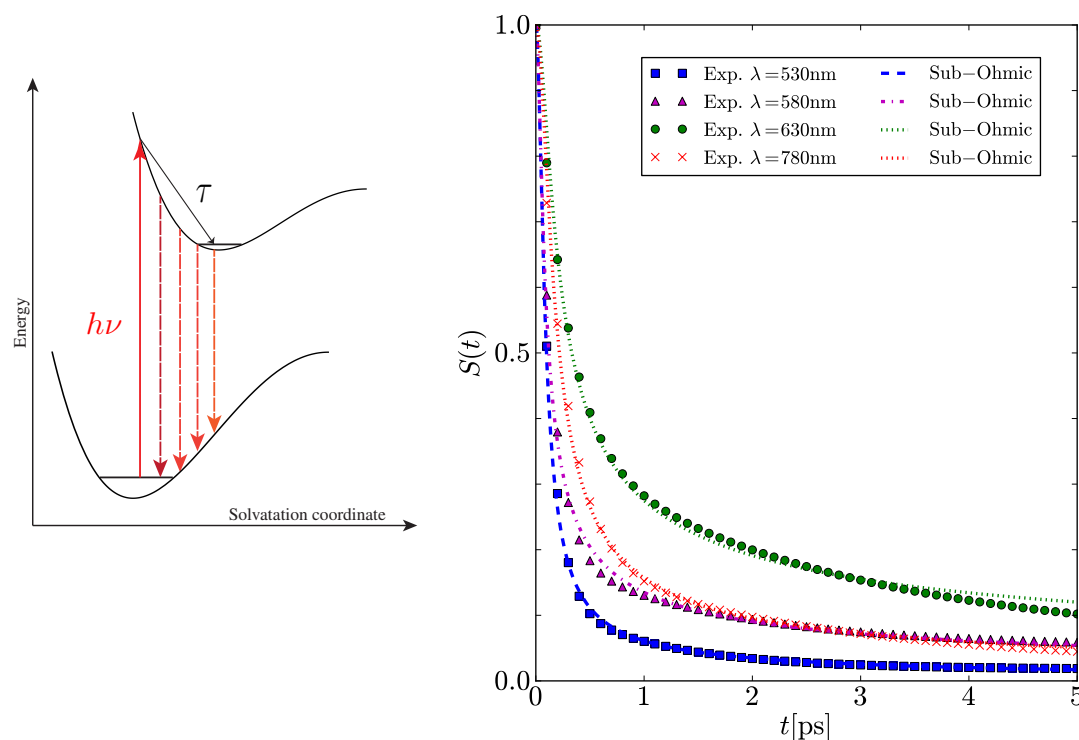
Low frequency vibrations

- Weak coupling of electronic transitions with low-frequency modes with spectral density $J(\omega)$ modulate the dynamics of fluorescence Stokes shift $S(t)$

$$S(t) = \frac{\Delta E(t) - \Delta E(\infty)}{\Delta E(0) - \Delta E(\infty)} \longrightarrow J(\omega) = \frac{1}{\pi} \frac{\lambda}{h\omega} \hbar \int_0^\infty dt S(t) \cos \omega t$$

Reservoir Spectral Density

Example: Bovine Rhodopsin & Sub-Ohmic SD



Rhodopsin: 11-cis-retinylidene
Batho: all-trans-retinylidene
Lumi: all-trans-retinylidene

The HTC model



with **Frank Spano**

Temple University

Holstein-Tavis-Cummings model

- The HTC model describes an ensemble of electronic transitions simultaneously coupled with a high-frequency vibration and a quantized electromagnetic field.

$$\hat{\mathcal{H}} = \omega_c \hat{a}^\dagger \hat{a} + \omega_v \sum_{n=1}^N \hat{b}_n^\dagger \hat{b}_n + \sum_{n=1}^N \left[\omega_e + \omega_v \lambda (\hat{b}_n + \hat{b}_n^\dagger) \right] |e_n\rangle \langle e_n| + \frac{\Omega}{2} \sum_{n=1}^N (|g_n\rangle \langle e_n| \hat{a}^\dagger + |e_n\rangle \langle g_n| \hat{a})$$

First used in: Cwik, Keeling *et al.* Eur. Phys. Lett. 105, 47009, **2014**
F. C. Spano, J. Chem. Phys 142, 184707, **2015**

Main Model Features

- Consistent with previous quasi-particle theories (Agranovich, La Rocca, Litinskaya,...).
- Novel photonic states dressed by intramolecular vibrations can also exchange energy with excited electronic states.
- Coupling to a continuum of low-frequency vibrations is straightforward to implement.

Symmetries of the HTC Model

- For $N = 1$, HTC Hamiltonian commutes with the generalized parity operator S .
- For $N > 1$, HTC eigenstates have a well-defined permutation quantum number.

Generalized Parity Transformation

$$\hat{S} = \hat{\sigma}_x \hat{Q}_a \hat{D}_g^\dagger(\lambda) \hat{D}_e^\dagger(-\lambda) \hat{\Pi}_g \hat{\Pi}_e$$

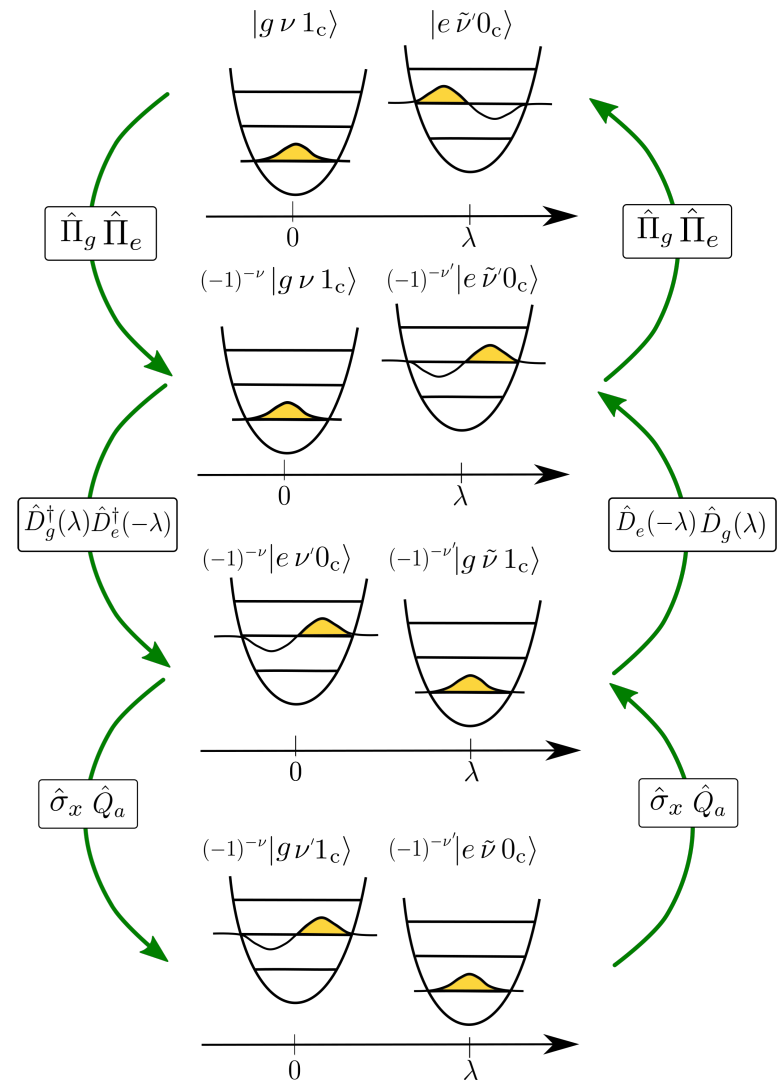
$\hat{\mathcal{H}}/\omega_v =$

$$\begin{pmatrix} \bar{\Omega}_{00} & \bar{\Omega}_{0\bar{1}} & \bar{\Omega}_{0\bar{2}} & 0 & 0 & 0 \\ \bar{\Omega}_{0\bar{1}} & 1 - \bar{\Omega}_{1\bar{1}} & \bar{\Omega}_{1\bar{2}} & 0 & 0 & 0 \\ \bar{\Omega}_{0\bar{2}} & \bar{\Omega}_{1\bar{2}} & 2 + \bar{\Omega}_{2\bar{2}} & 0 & 0 & 0 \\ 0 & 0 & 0 & -\bar{\Omega}_{00} & \bar{\Omega}_{0\bar{1}} & \bar{\Omega}_{0\bar{2}} \\ 0 & 0 & 0 & \bar{\Omega}_{0\bar{1}} & 1 + \bar{\Omega}_{1\bar{1}} & \bar{\Omega}_{1\bar{2}} \\ 0 & 0 & 0 & \bar{\Omega}_{0\bar{2}} & \bar{\Omega}_{1\bar{2}} & 2 - \bar{\Omega}_{2\bar{2}} \end{pmatrix}$$

Permutation-Symmetric Generalized Parity

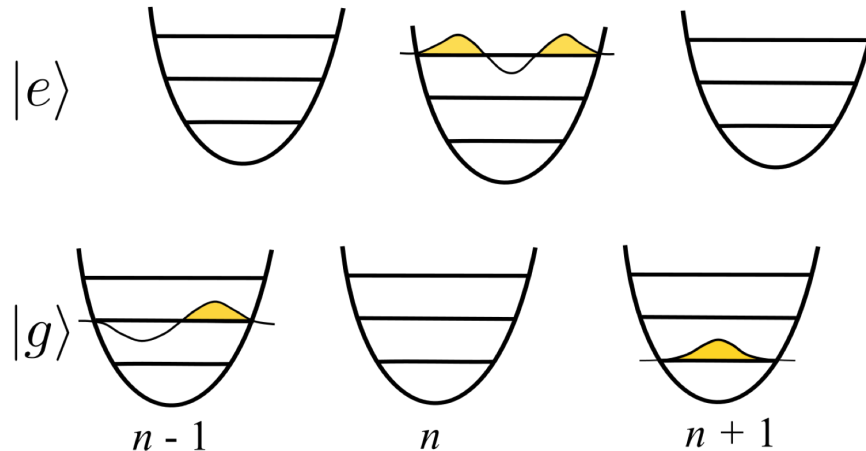
$$\hat{S}_\alpha = \sum_{n=1}^N c_{\alpha n} \hat{S}_n \quad N \geq 2$$

Permutation symmetry generalizes translational invariance



Two-particle Material States

- Excited electronic states coexist with one or more purely vibrational excitations in a molecular ensemble.



$$|\alpha_0\beta, \tilde{\nu}'\nu, 0_c\rangle = \sum_{n \neq m} \sum_m \frac{c_{\beta m}}{\sqrt{N-1}} |g_1 0_1, \dots, e_n \tilde{\nu}'_n, \dots, g_m \nu_m, \dots, g_N 0_N, 0_c\rangle$$

Permutation quantum number β determines the symmetry of collective vibrational excitation

Diabatic Two-particle Polaritons

- HTC Hamiltonian couples two-particle material states with collective vibration-photon states. Coupling can lead to the formation of **two-particle polaritons**.

Collective Vibration-Photon State

$$|\beta, \nu, 1_c\rangle = \sum_{n=1}^N c_{\beta n} |g_1 0_1 \dots, g_n \nu_n, \dots, g_N 0_N, 1_c\rangle$$

$$\langle \beta', \nu, 1_c | \hat{H}_{\text{LM}} | \alpha_0 \beta, \tilde{\nu}' \nu, 0_c \rangle = \sqrt{N-1} \left(\frac{\Omega}{2} \right) \langle 0 | \tilde{\nu}' \rangle \delta_{\beta \beta'}$$

Light-matter coupling conserves the vibrational permutation quantum number

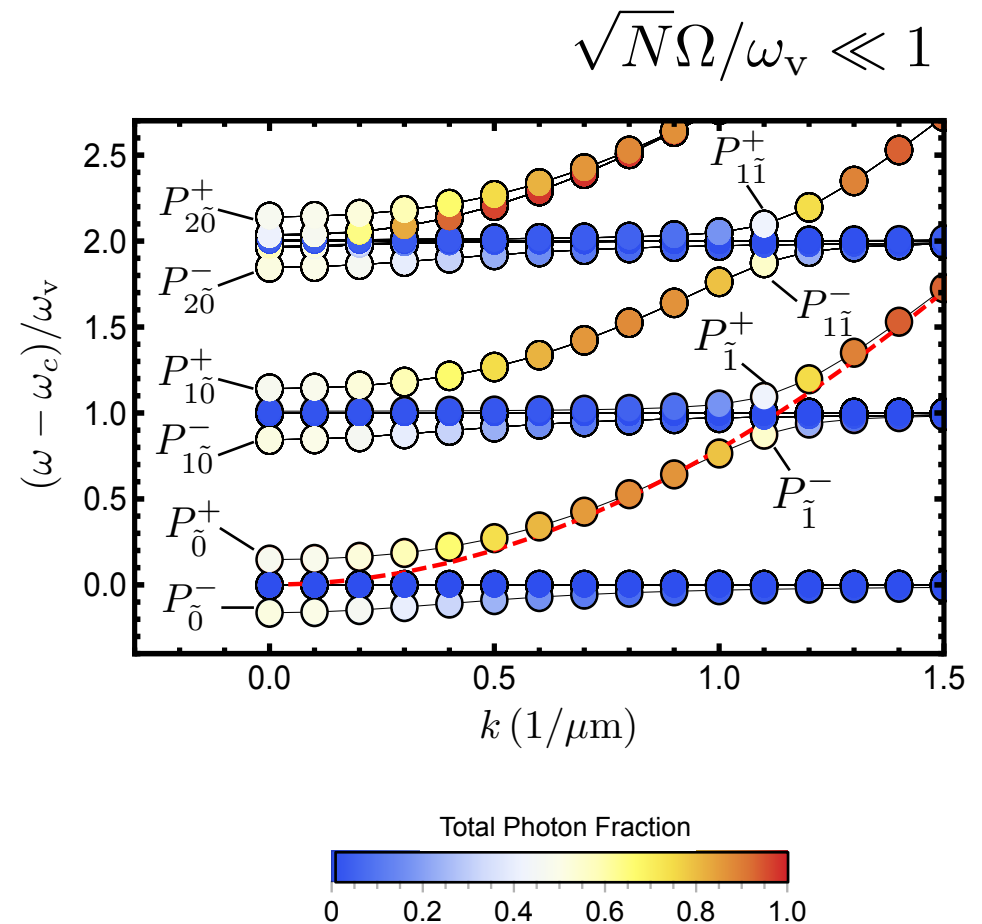
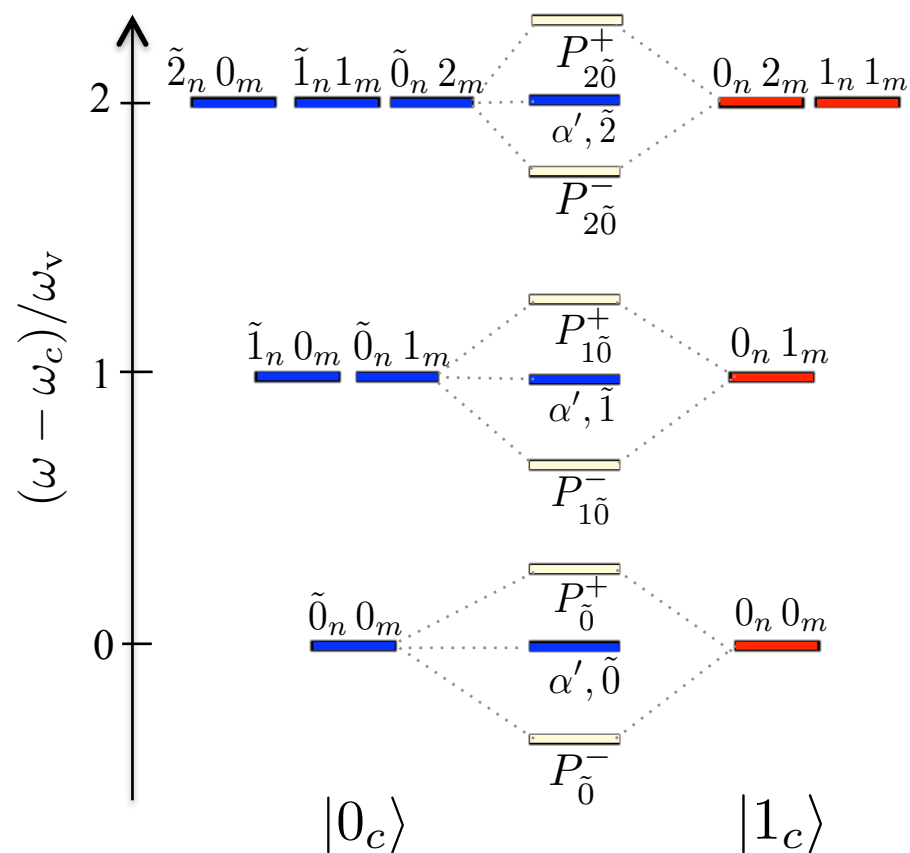
Two-Particle Diabatic Polariton State

$$|P_{\nu \tilde{\nu}'}^{\pm}, \beta\rangle = \frac{1}{\sqrt{2}} (|\alpha_0 \beta, \tilde{\nu}' \nu, 0_c\rangle \pm |\beta, \nu, 1_c\rangle)$$

Novel two-particle polaritons

- HTC excited states include conventional vibronic polaritons (e.g. Mazza, La Rocca, Michetti), and *also* novel two-particle vibronic polaritons.

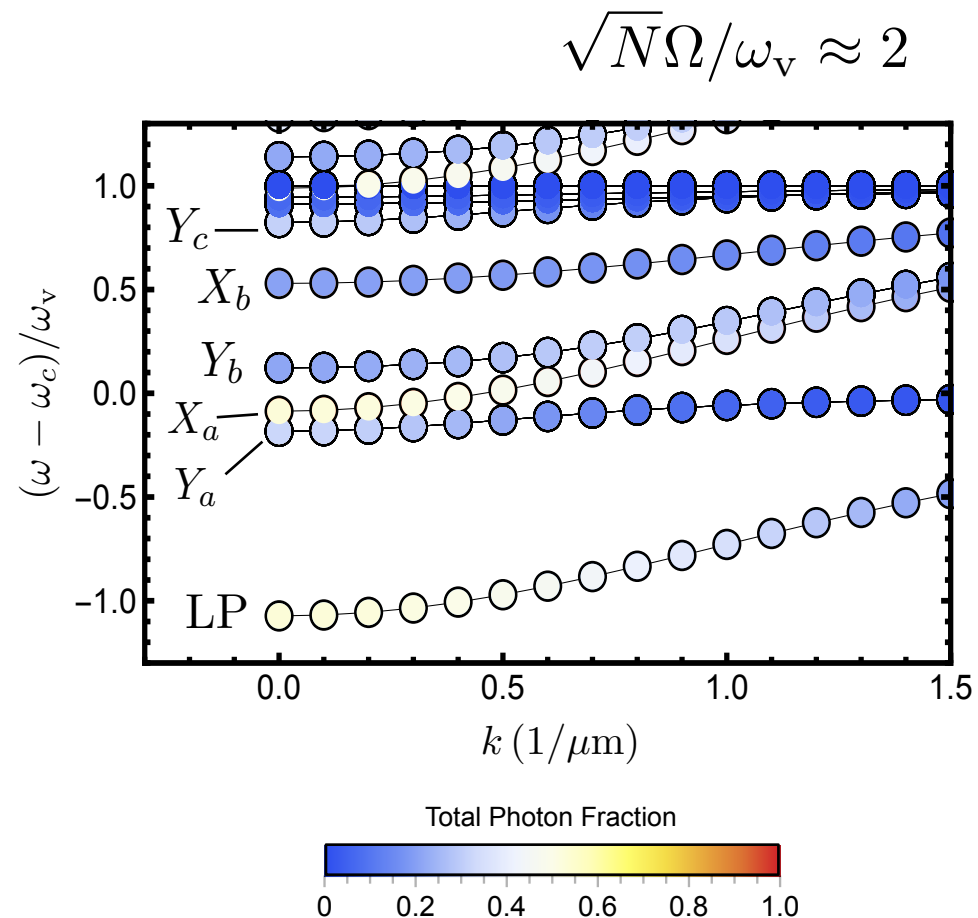
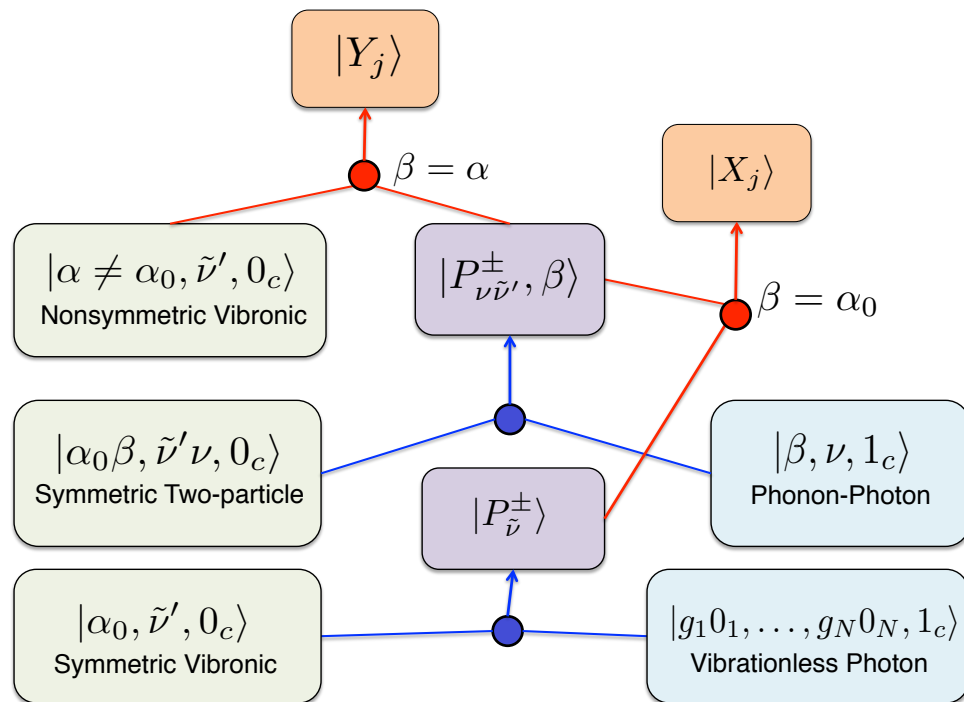
HTC Excitation Spectrum in Small Rabi Regime



Dark states with photon character

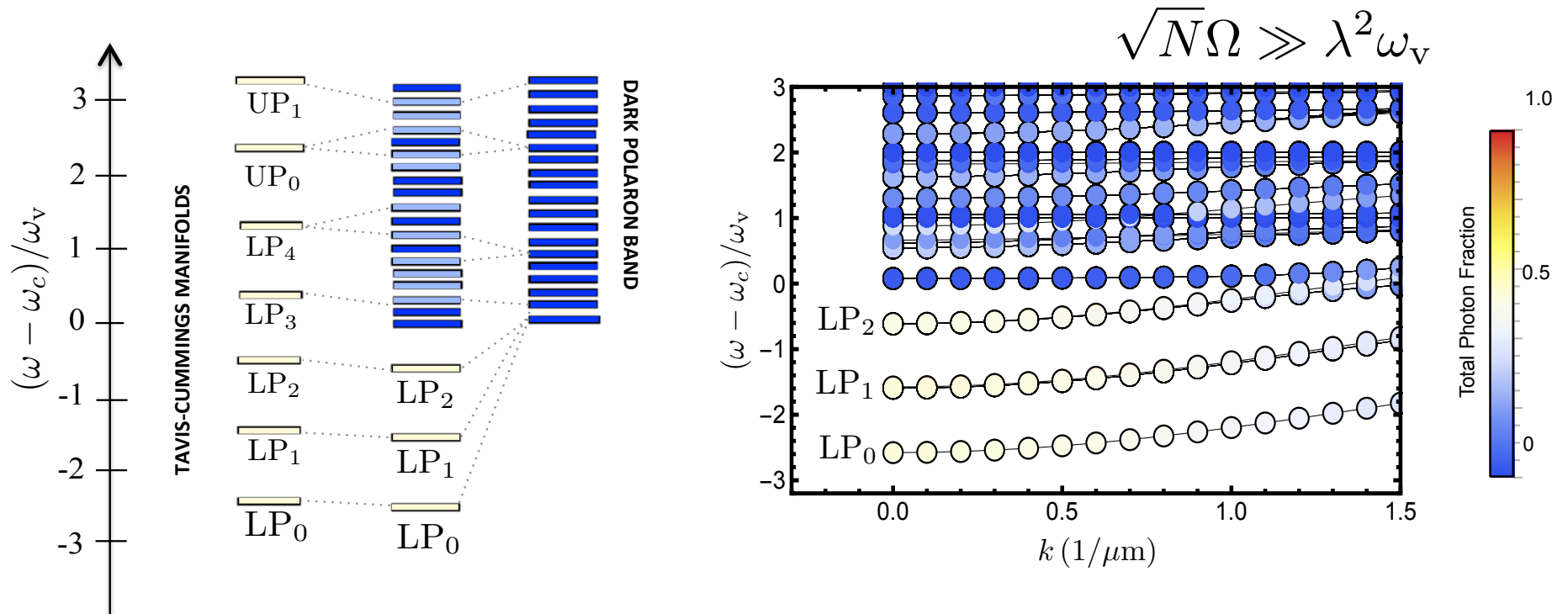
- For intermediate Rabi frequencies, the so-called *dark exciton reservoir* can have a **significant photon character** by admixing with diabatic two-particle polaritons.
- Depending on total permutation symmetry, we classify the resulting eigenstates as *X-type* or *Y-type* dark vibronic polaritons.

HTC Coupling Hierarchy



Polaron decoupling limit

- For larger Rabi couplings, the HTC spectrum simplifies and vibrations separable from electron-photon degrees of freedom in the lower polariton manifold.



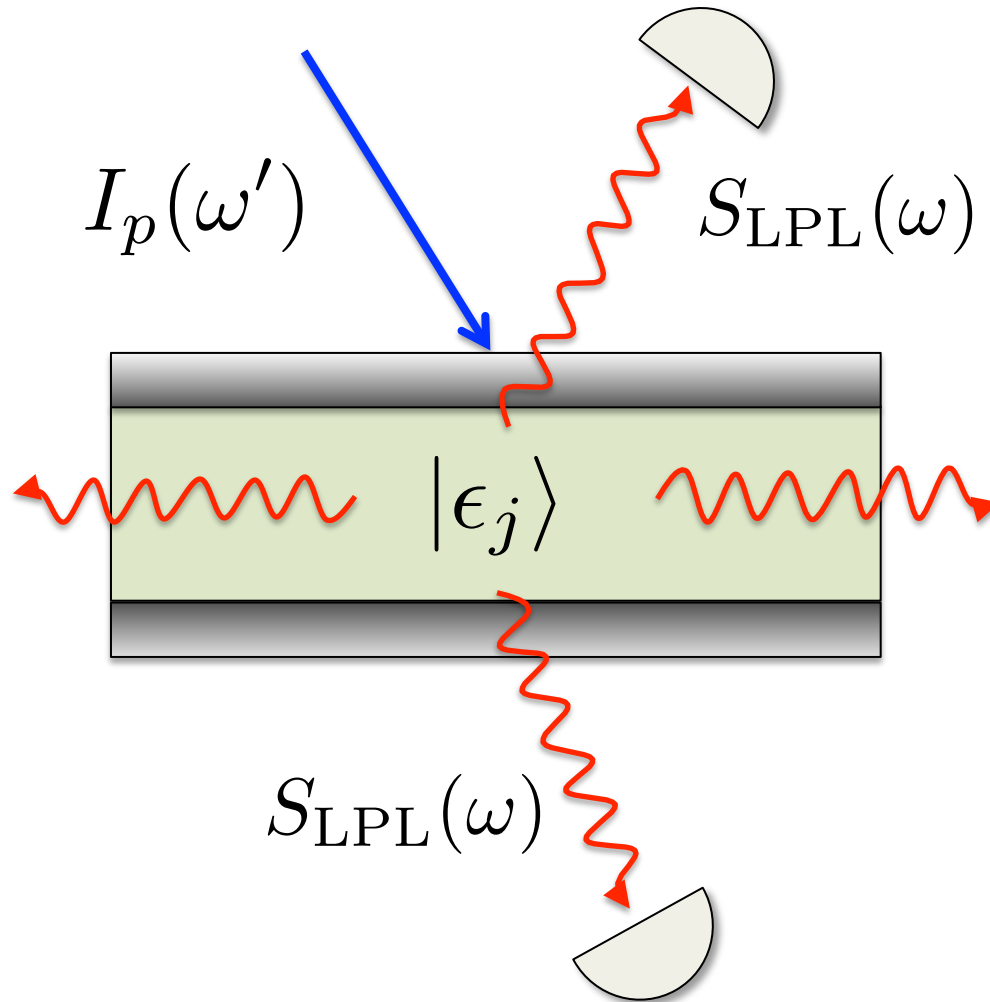
LOWER POLARITON STATE

$$|\text{LP}_0\rangle \approx \frac{1}{\sqrt{2}} \left[\frac{1}{\sqrt{N}} \sum_{n=1}^N |g_1, \dots, e_n, \dots, g_N\rangle |0_c\rangle - |g_1, g_2, \dots, g_N\rangle |1_c\rangle \right] \otimes |\nu_1 = 0, \nu_2 = 0, \dots, \nu_N = 0\rangle$$

- Inner-shell reorganization energy is collectively eliminated in an ensemble

Does the HTC model work?

Photoluminescence of HTC polaritons



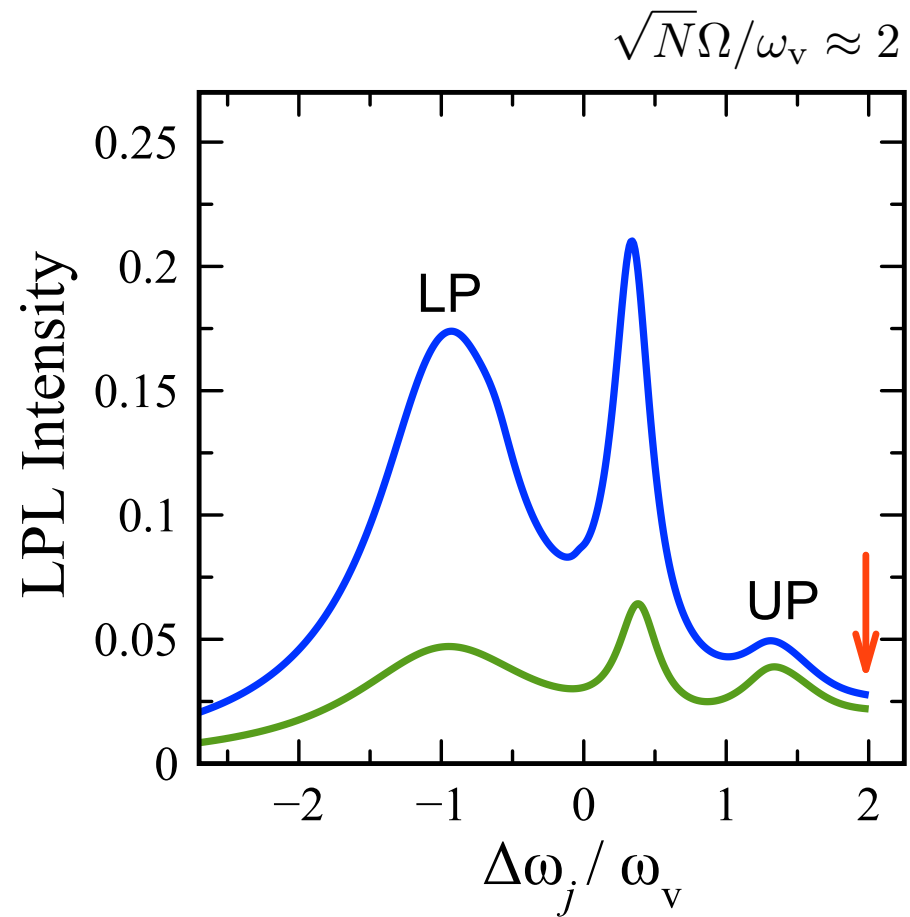
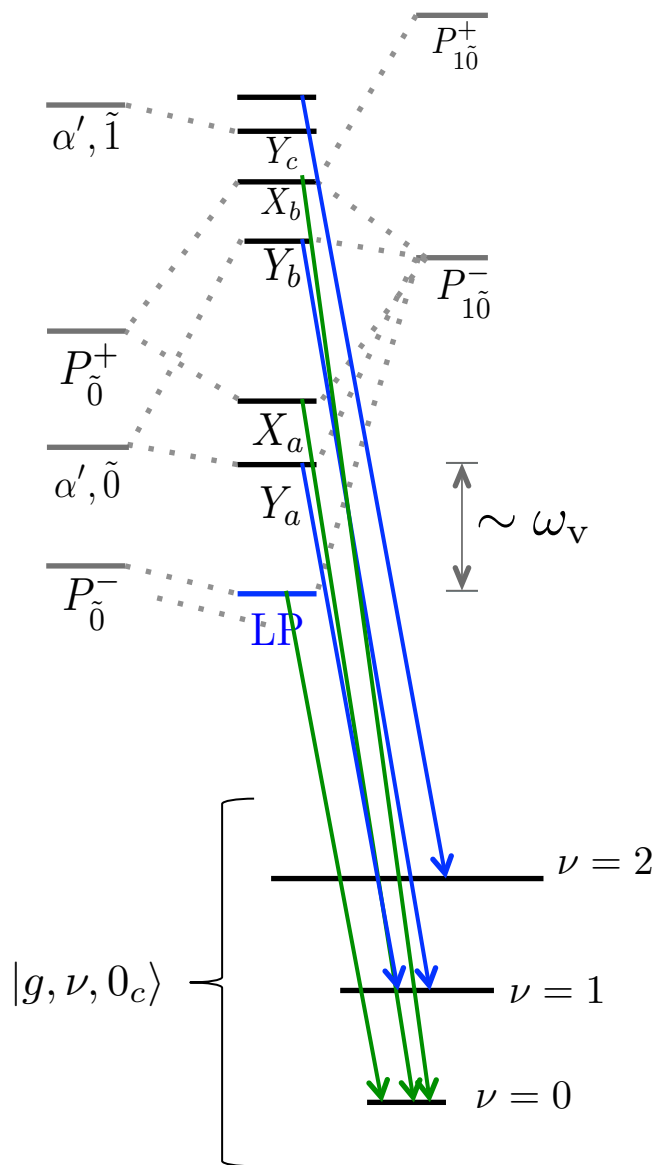
PL is a quantum jump

$$\hat{a} |\epsilon_j\rangle \rightarrow |g, \nu, 0_c\rangle + \hbar\omega$$

$$\omega = \omega_j - \nu \omega_v$$

Photoluminescence of HTC polaritons

- Depending on the final vibrational system of the system after photon loss, we distinguish two types of photoluminescence: *direct* PL vs *indirect* PL.

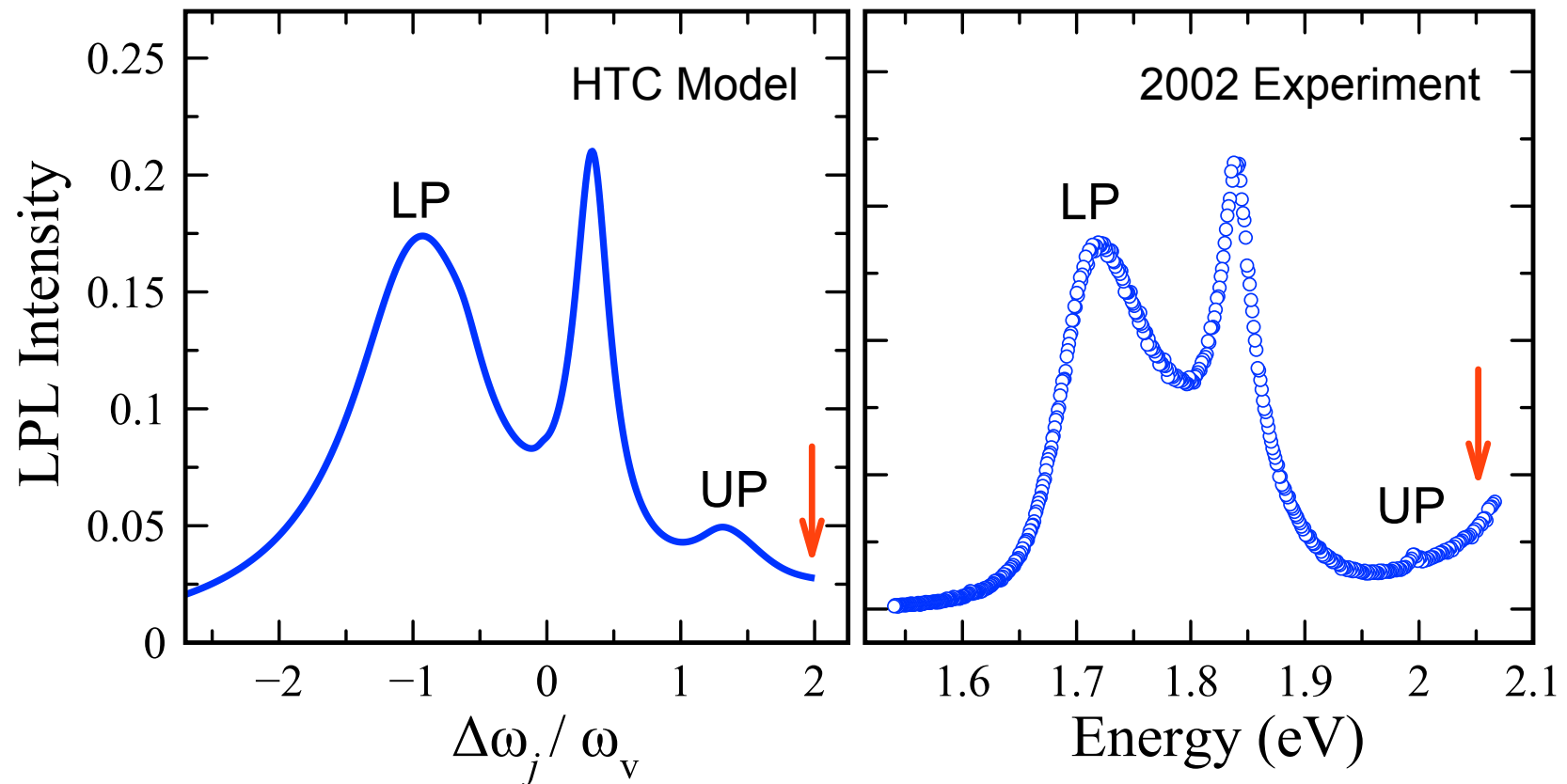


Direct PL
 $\nu_{\text{final}} = 0$

Indirect PL
 $\nu_{\text{final}} \geq 1$

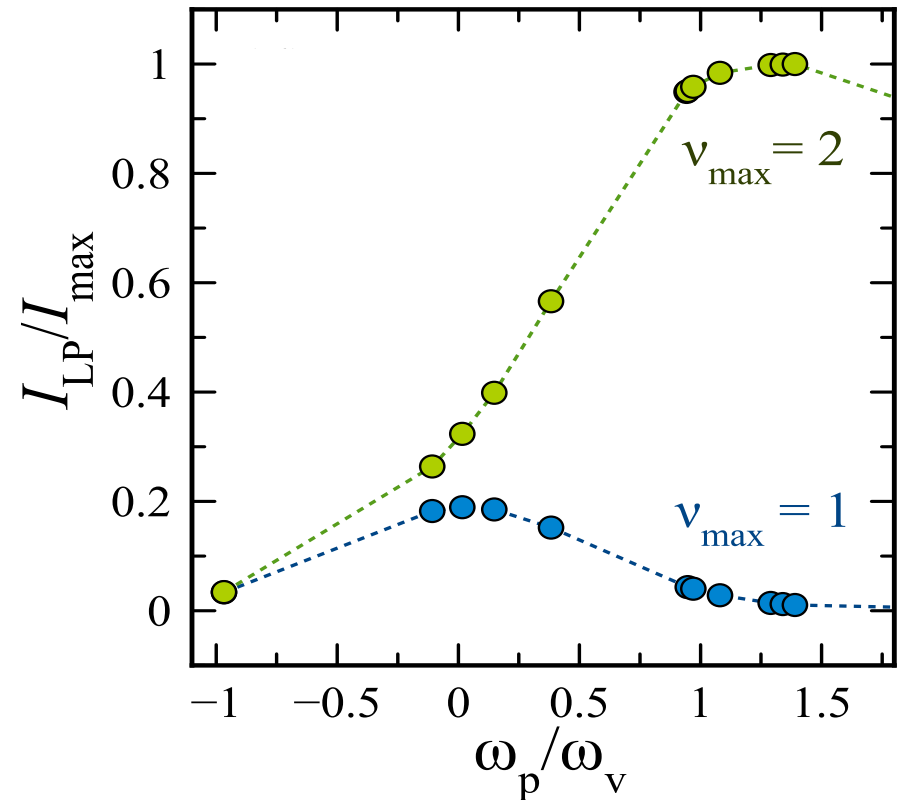
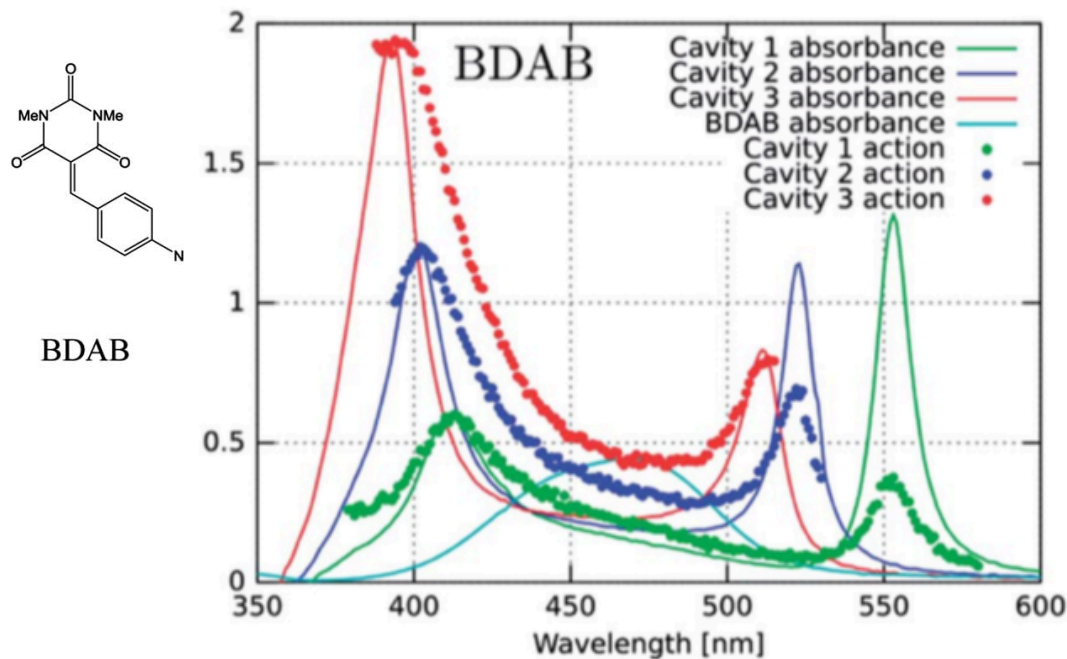
Comparison with experiments

- HTC model with Lindblad optical dissipation and quantum regression theorem agrees *qualitatively* with PL spectra measured by group of Bill Barnes in 2002.



Comparison with experiments

- The HTC model also qualitatively agrees with measured stationary excitation spectrum (action spectrum).





Phenomenological models give us a great initial vision of complex quantum systems

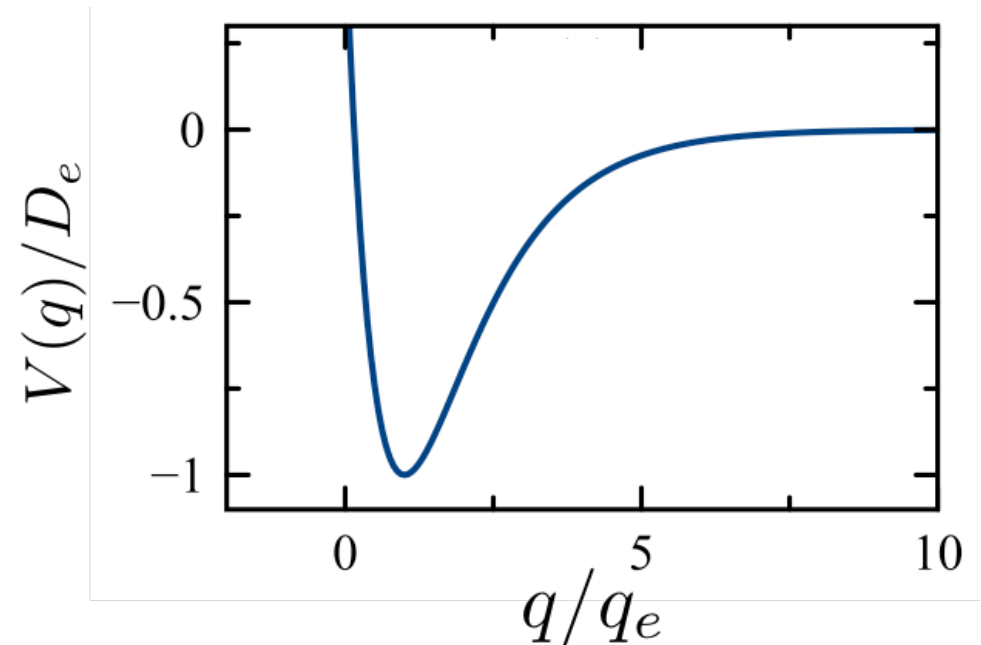
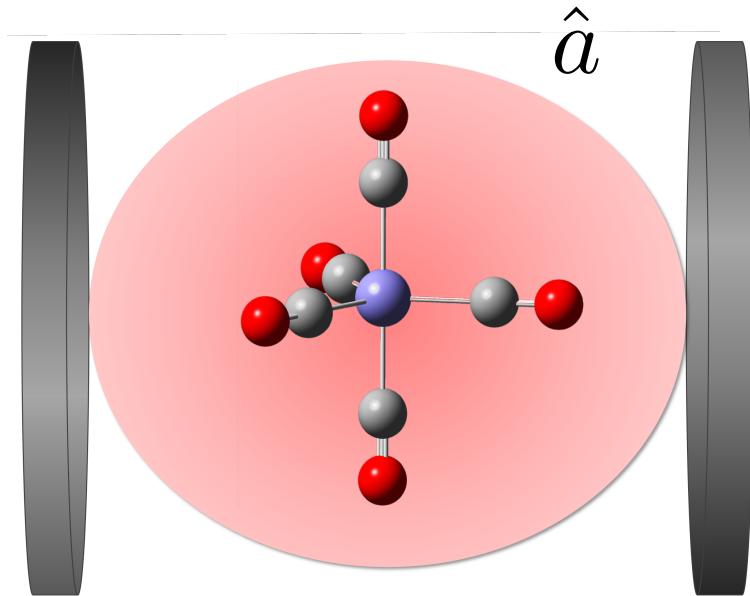
Vibrational Polaritons in USC

arXiv:1906.04374, **2019**

POSTER #12 by Federico Hernandez

Single Morse oscillator in an IR cavity

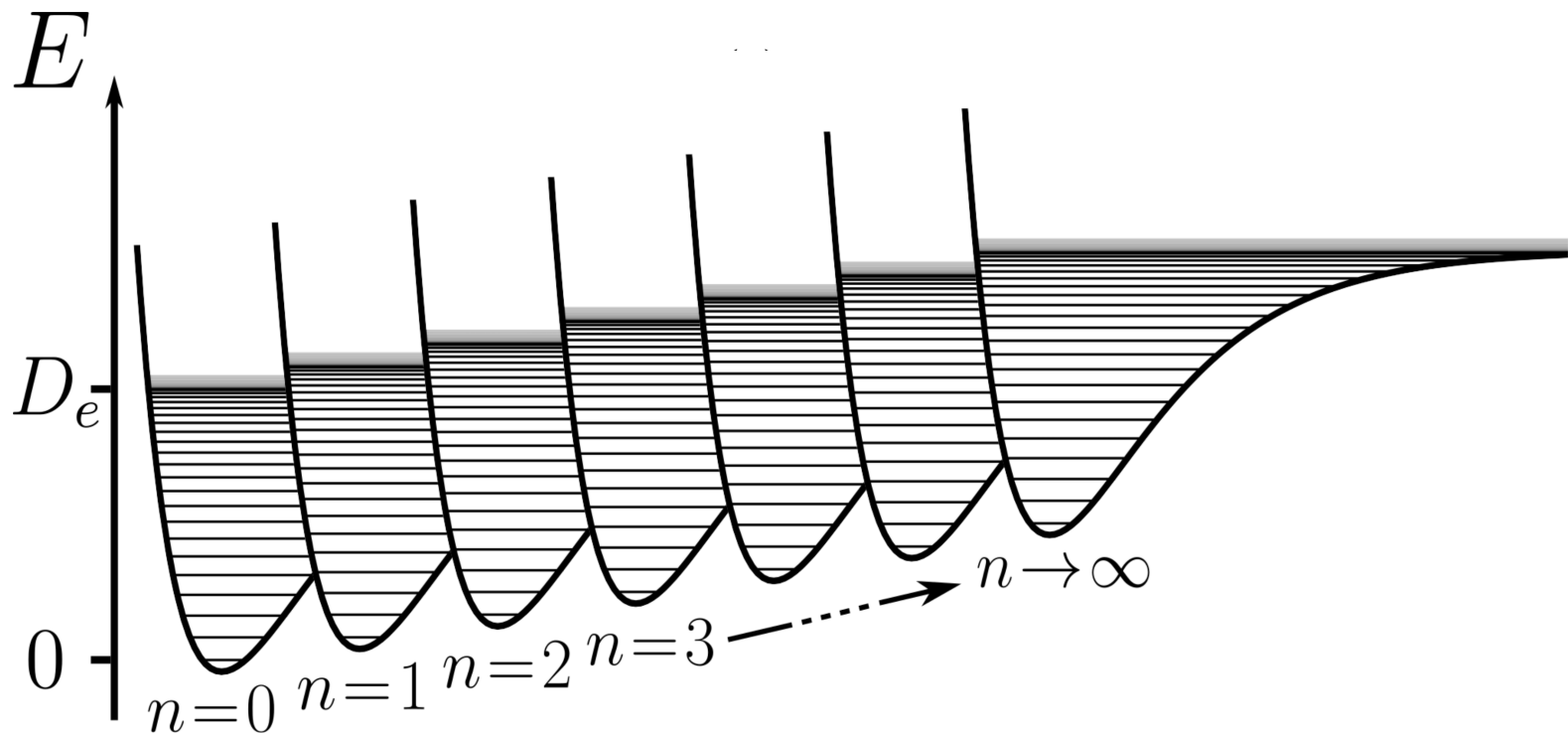
- Morse potential gives qualitatively correct bond dissociation dynamics.



$$V(q) = D_e \left(1 - e^{-\alpha(q-q_e)} \right)^2$$

Coupling scheme

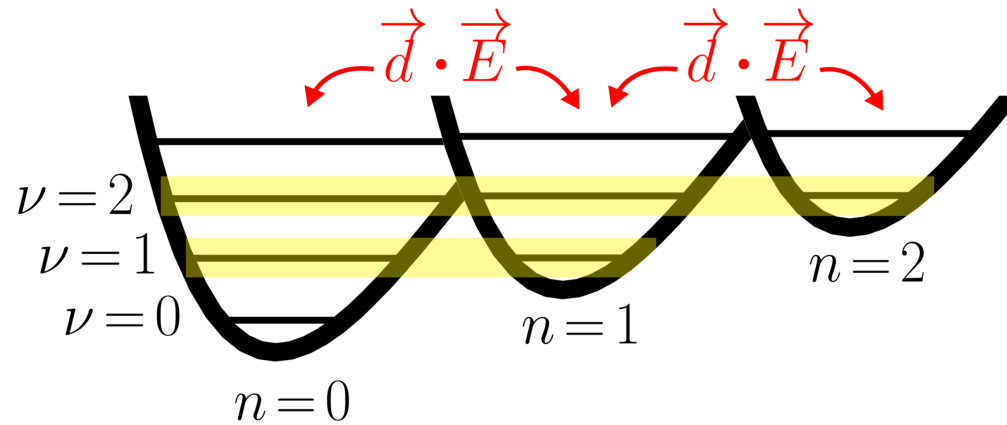
- An infinite number of Morse potentials can be defined, one for each cavity Fock state
- [Corolary](#): Dissociation threshold depends on quantum state of the cavity field



Coupling scheme

- Light-matter coupling in dipole approximation admixes anharmonic vibrational manifolds. **Morse potential breaks total parity.**

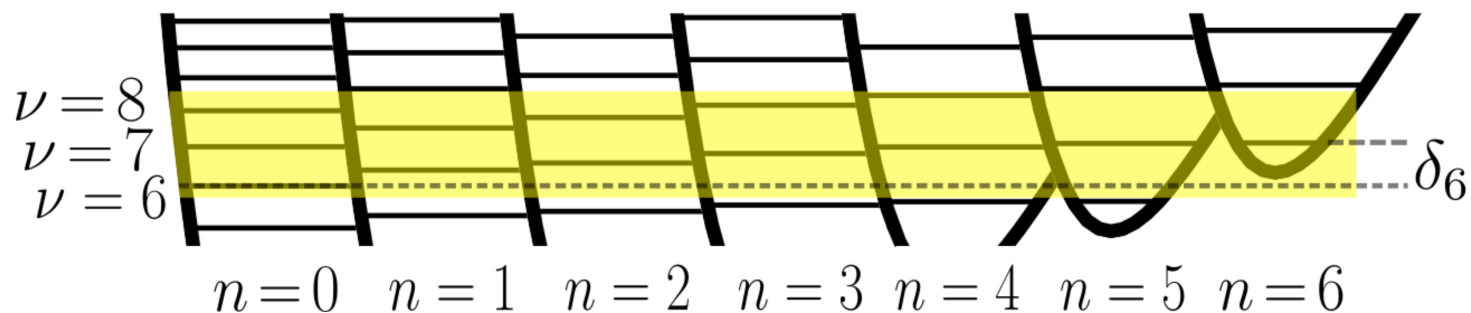
low - ν



PHOTONIC PARITY

$$\Delta n = \pm 1$$

high - ν



Multi-level Quantum Rabi Model

- Transform classical field theory in minimal-coupling to a multipolar form using PZW transformation:

$$U_{\text{PZW}} = e^{i \int d\mathbf{x} \mathbf{P}(\mathbf{x}) \cdot \mathbf{A}(\mathbf{x})}$$

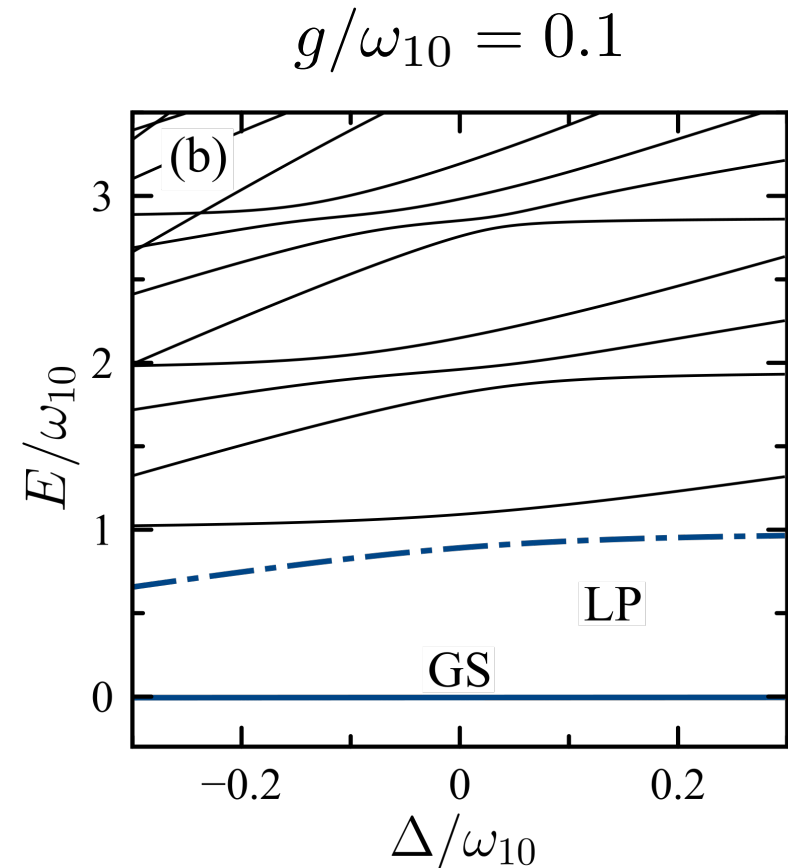
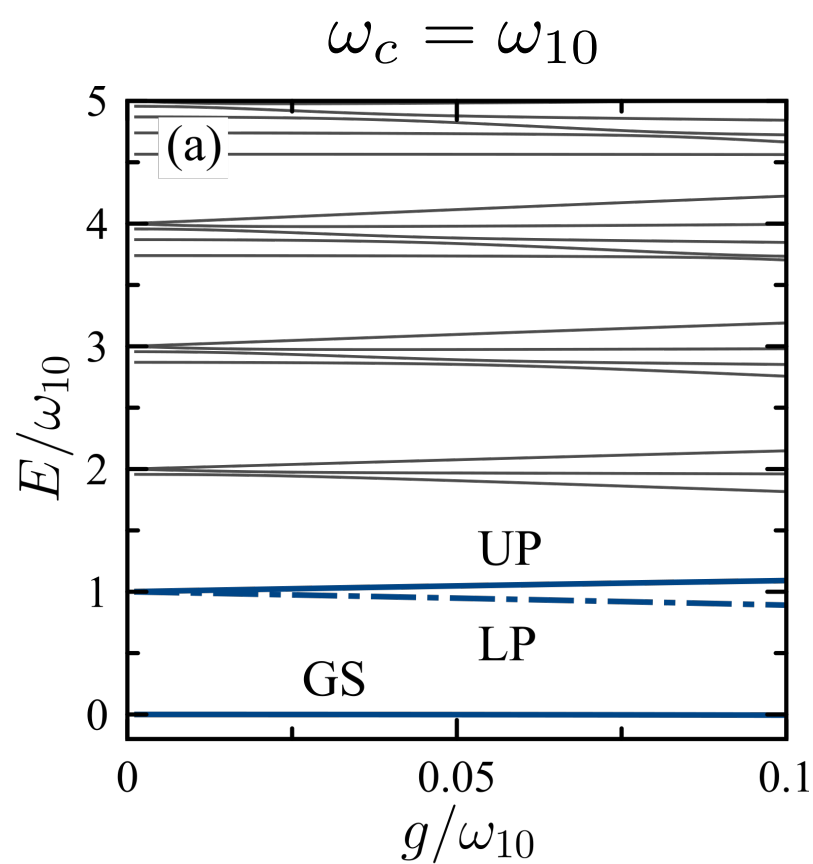
- Ansatz*: Impose single-mode quantization of dielectric displacement for a point-dipole medium [*yet to be proven correct*].
- Up to a vacuum-field-independent polarization self-energy, the resulting PZW Hamiltonian is a generalized quantum Rabi model

$$\hat{\mathcal{H}} = \omega_c \hat{a}^\dagger \hat{a} + \sum_{\nu} \omega_{\nu} |\nu\rangle \langle \nu| + \sum_{\nu} \sum_{\nu' > \nu} g_{\nu\nu'} (|\nu'\rangle \langle \nu| + |\nu\rangle \langle \nu'|) (\hat{a} + \hat{a}^\dagger)$$

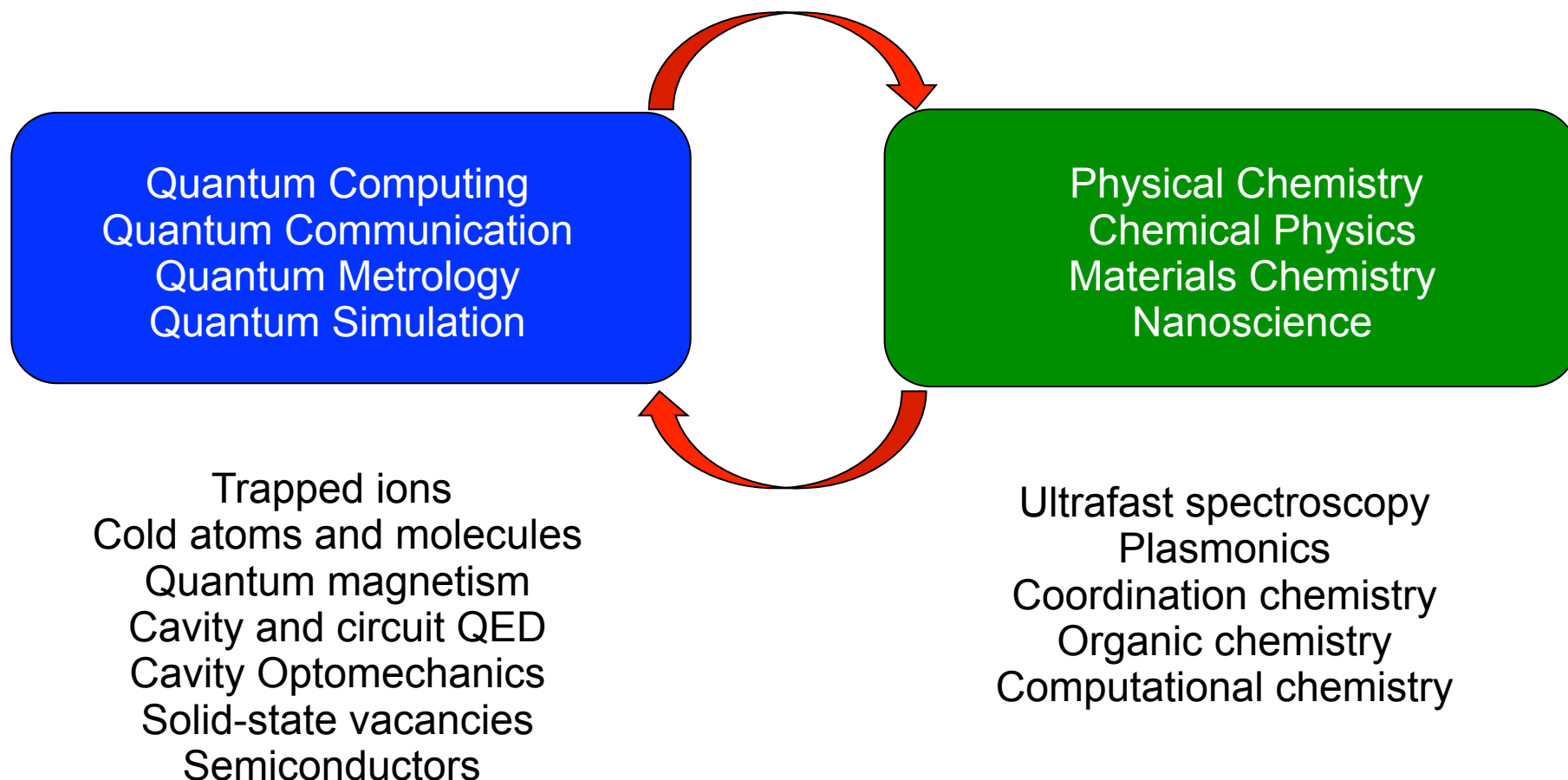
$$g_{\nu\nu'} = \langle \nu | d_{\text{el}}(q) | \nu' \rangle \mathcal{E}_0$$

Vibrational polariton spectrum beyond RWA

- We focus on IR-active anharmonic modes without permanent dipole at equilibrium



Molecular Quantum Technology



MQT Theory group



Collaborators

Frank Spano @Temple

Marina Litinskaya @UBC

Jianshu Cao @MIT

Timur Shegai @Chalmers

Blake Simpkins @NRL

S. Kena-Cohen @Poly. Montreal

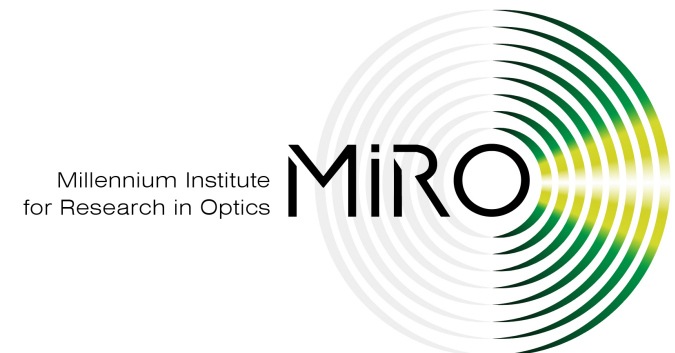
Dinesh Singh @USACH

Gustavo Lima @UdeC

Esteban Sepúlveda @UdeC

Aldo Delgado @UdeC

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