Chemistry in optical microcavities: Spectral fluctuations and energy transport

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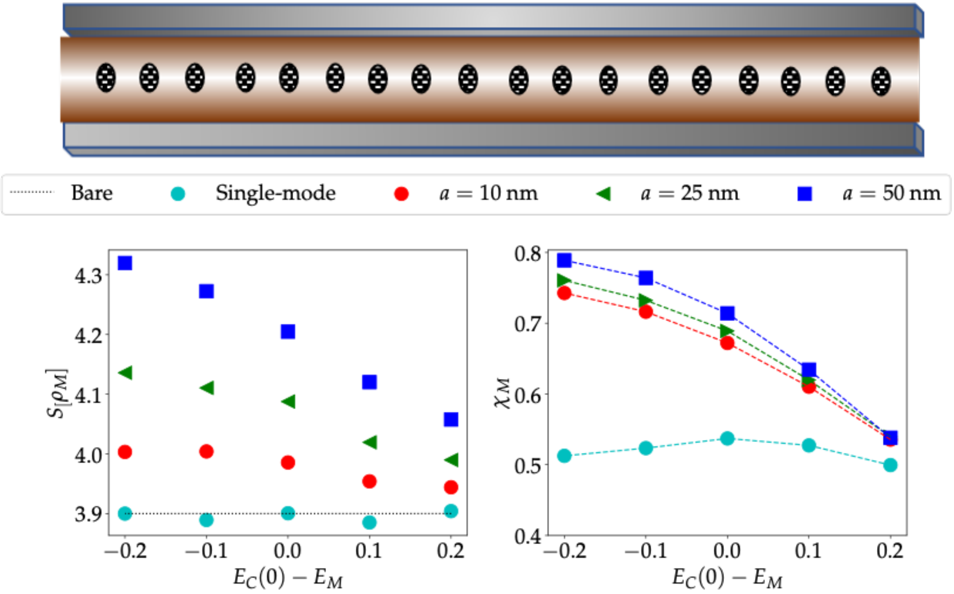


Vista Webinar
11.25.21

Ribeiro research group
@ Emory University

Postdoctoral positions available for work on molecular quantum electrodynamics and chemical dynamics on quantum materials

https://ribeiro.emorychem.science

$$\nabla \cdot \mathbf{E} = 4\pi\rho$$

$$\nabla \cdot \mathbf{B} = 0$$

$$\nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t}$$

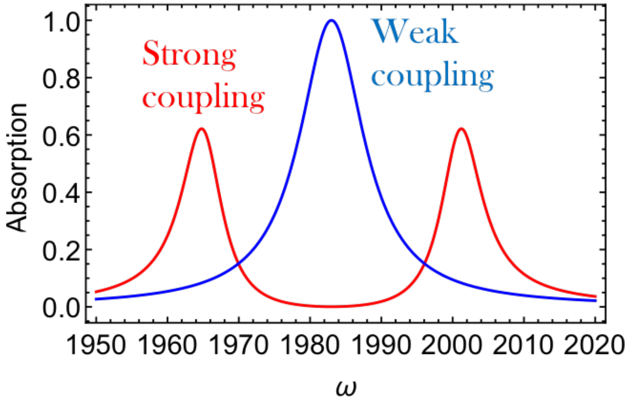
$$\nabla \times \mathbf{B} = \frac{4\pi}{c}\mathbf{j} + \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t}$$

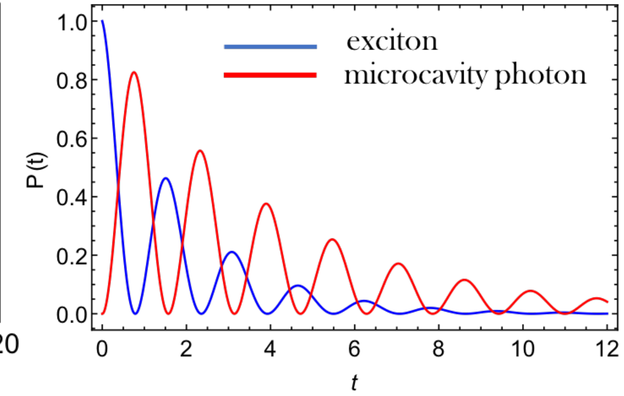
$$i\hbar\partial_t\psi(t) = \hat{H}\psi(t)$$

$$\hat{H}\psi(t) = E\psi(t)$$

$$i\hbar\partial_t\hat{\rho}(t) = [\hat{H}, \hat{\rho}(t)]$$

$$\omega_{\mathbf{q},m} = \omega_{\mathrm{exc}}$$

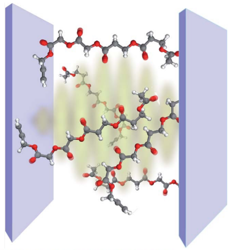


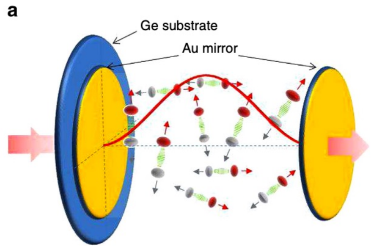


Outline

- Motivations for investigating molecular systems in optical cavities
- Basics of strong light-matter interactions and theory challenges
- Photonic wire model for polariton chemistry
- Cavity effects on local density of states and coherent transport

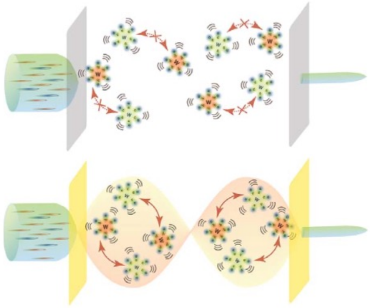
New chemistry in optical microcavities

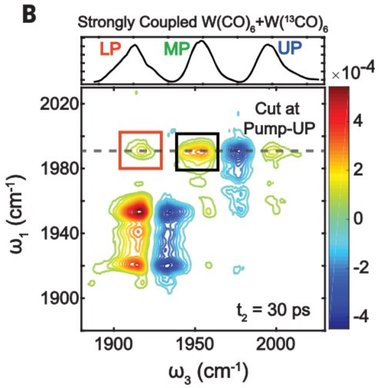




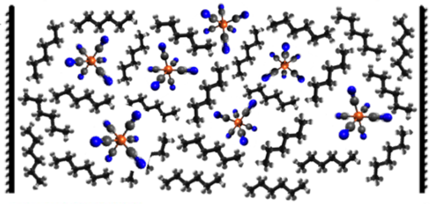
CHEMICAL PHYSICS

Intermolecular vibrational energy transfer enabled by microcavity strong light–matter coupling





Xiang, RFR et al., Science 368, 665 (2020)



CHEMISTRY

Tilting a ground-state reactivity landscape by vibrational strong coupling

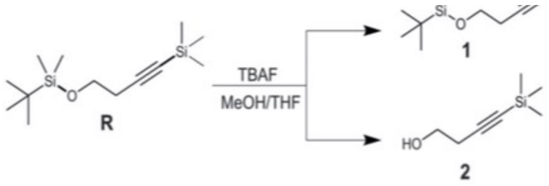


Table 1. Enthalpy and entropy of activation under strong coupling.

Products	Experiment	$\Delta H^‡$ (kJ mol^{-1})	$\Delta S^‡$ (J mol^{-1} K^{-1})
Product **1**	Outside cavity	34 ± 3	–173 ± 11
	On-resonance Si–C	60 ± 2	–95 ± 7
	On-resonance Si–O	57 ± 5	–106 ± 17
Product **2**	Outside cavity	23 ± 3	–214 ± 8
	On-resonance Si–C	85 ± 5	–6 ± 17
	On-resonance Si–O	76 ± 7	–39 ± 24

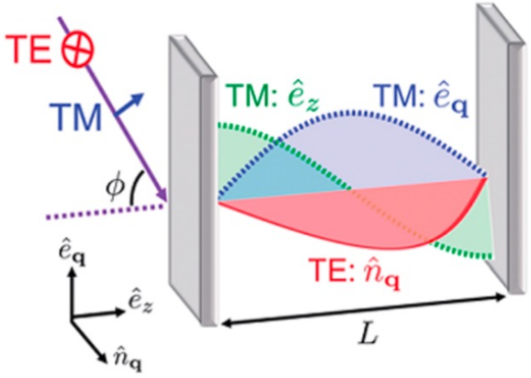
Thomas et al., Science 363, 615 (2019)

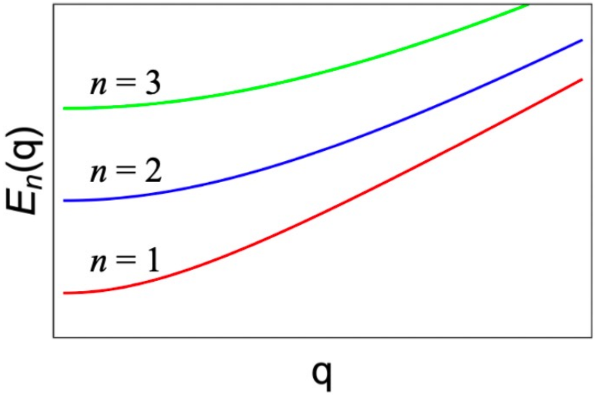
Exciting! But…

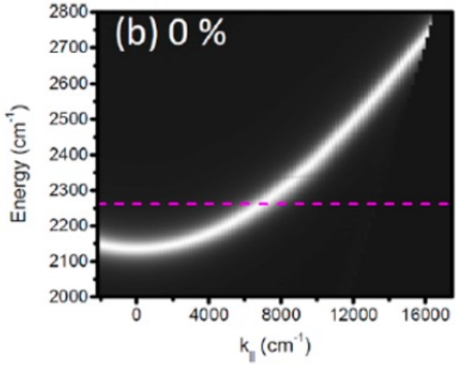
- What is the mechanism?
- What molecules are more or less susceptible to undergo changes in reaction, charge or energy transport dynamics?
- What optical cavities induce larger effects?

See recent reviews in Science by Garcia-Vidal, Ciuti and Ebbesen and in JACS by Nagrajan, Thomas and Ebbesen and in

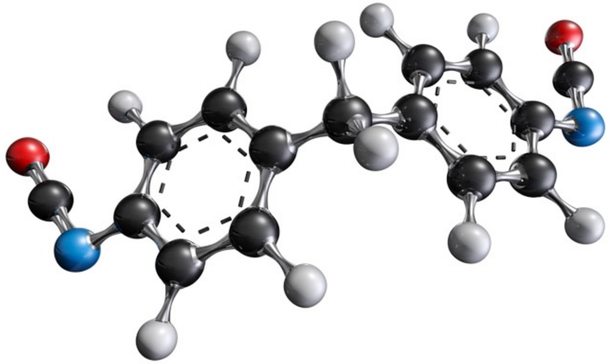
Phenomenology of strong light-matter interactions in optical microcavities



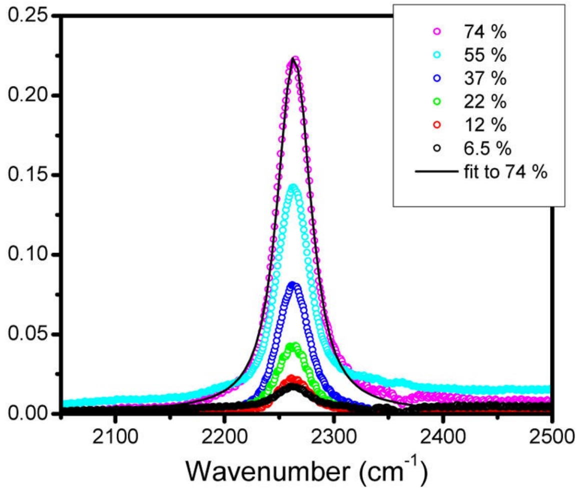


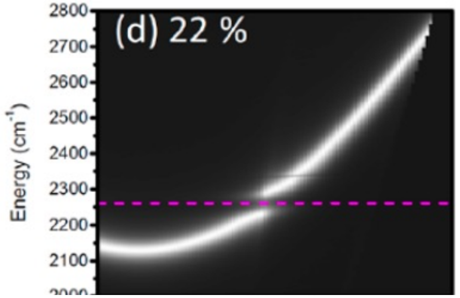


Transmission spectrum of optical cavity

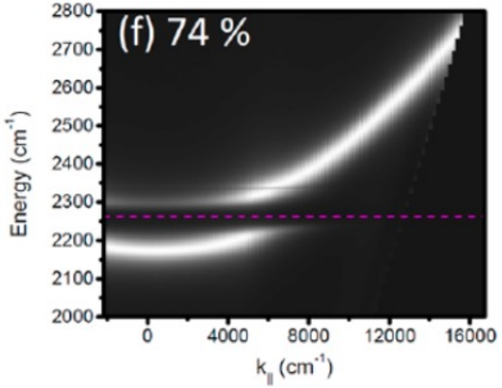


Absorption spectrum





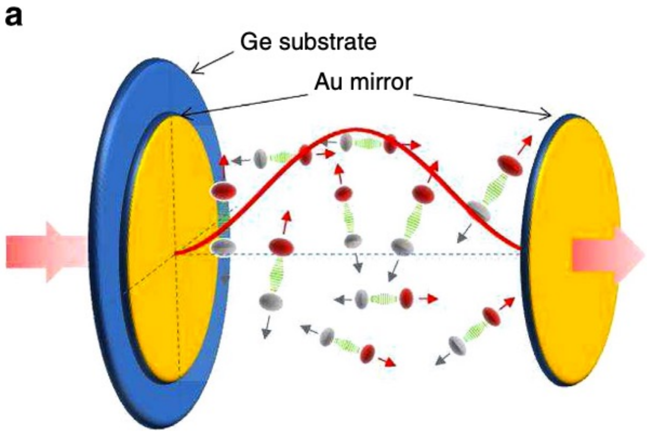
Weak coupling



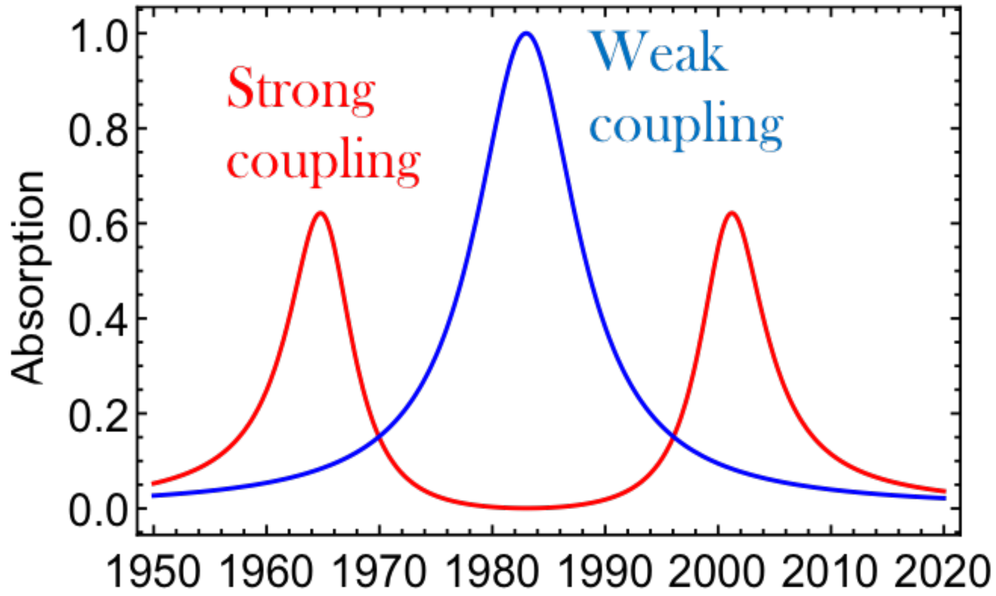
Strong coupling

Simpkins et al., ACS Photonics, 2, 1460 (2015)
RFR et al., Chem. Sci, 9, 6325 (2018)

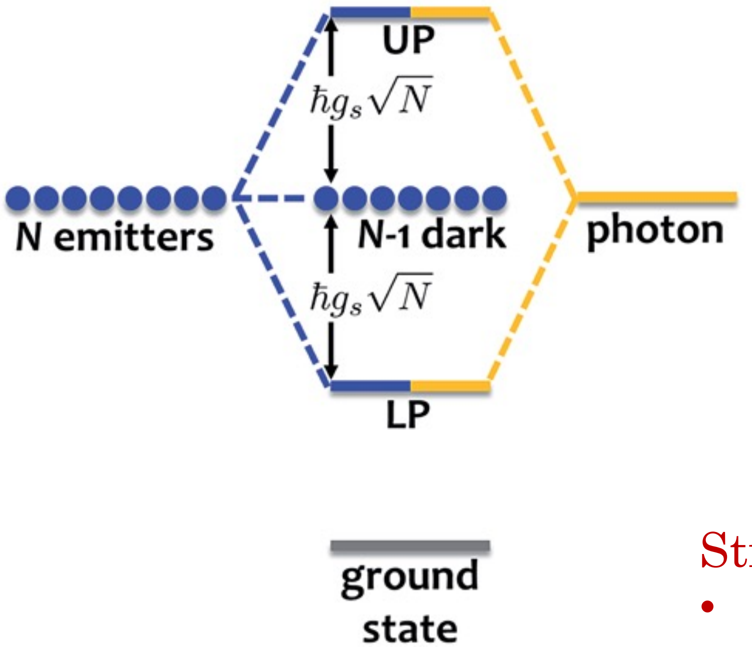
A minimal model for strong light-matter interactions



$$\omega_{\mathbf{q},m} = \omega_{\text{exc}}$$



Tavis-Cummings model



$$|1_0\rangle$$

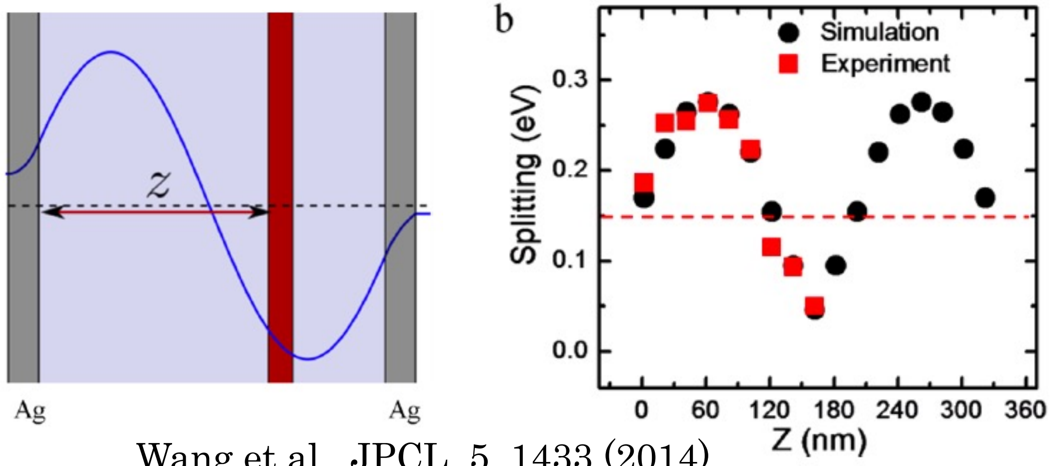
$$|1_m\rangle = \frac{1}{\sqrt{N}}\sum_{a=1}^{N}|1_a\rangle$$

$$H_1^{\mathrm{B}}(N) = \begin{pmatrix} \hbar\omega_c & \hbar g_s\sqrt{N} \\ \hbar g_s\sqrt{N} & \hbar\omega_0 \end{pmatrix}$$

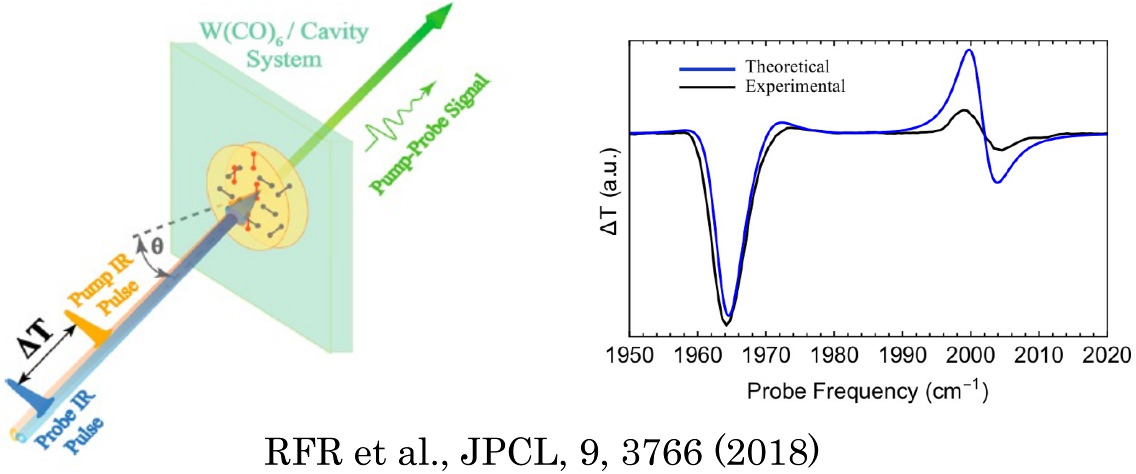
Strong assumptions

- Single-photon mode
- No energetic or structural disorder

Successes of minimal models



Wang et al., JPCL, 5, 1433 (2014)



RFR et al., JPCL, 9, 3766 (2018)

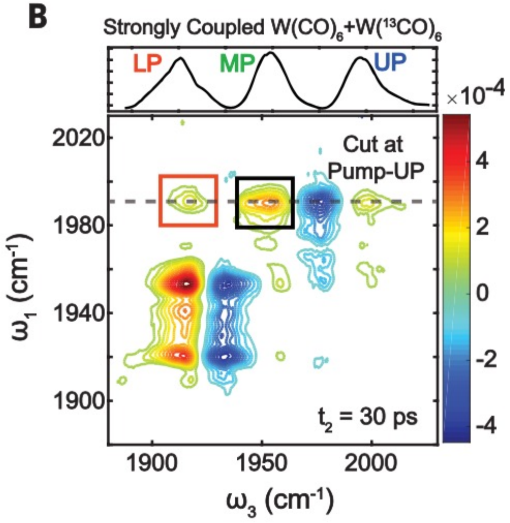
Failures of minimal models

RESEARCH

CHEMICAL PHYSICS

Intermolecular vibrational energy transfer enabled by microcavity strong light–matter coupling

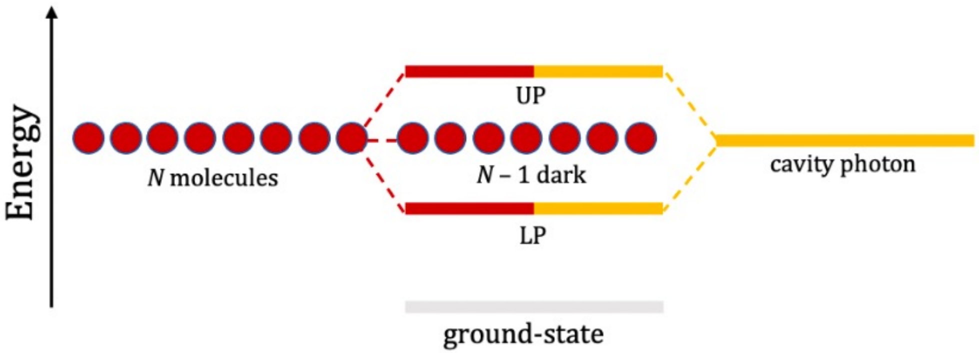
Bo Xiang[1], Raphael F. Ribeiro[2], Matthew Du[2], Liying Chen[2], Zimo Yang[1], Jiaxi Wang[2], Joel Yuen-Zhou[2]*, Wei Xiong[1,2]*



2D IR spectral assignment ✓

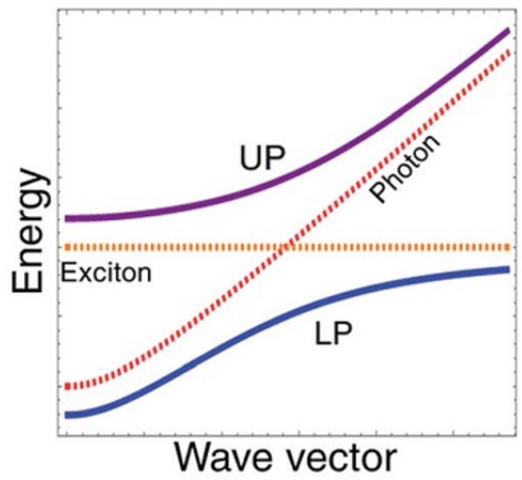
Energy transfer kinetics ✗

Incompleteness of minimal models

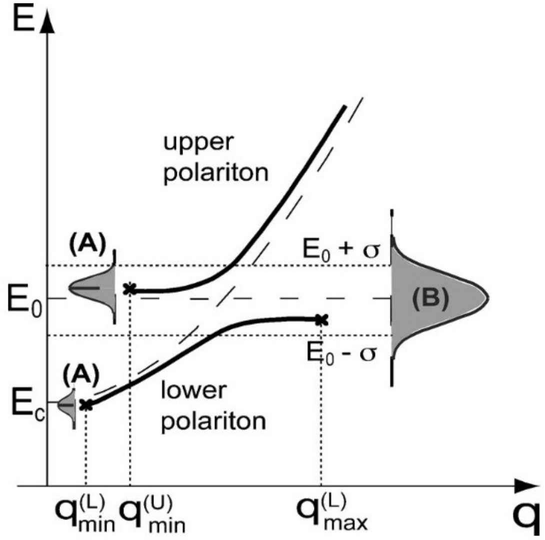


- Molecules are in highly **disordered** condensed-phase (e.g., liquid)
- Energetic and structural disorder strongly <u>suppress</u> polariton delocalization
- Polaritons are only well-defined on a small interval of wave-vector space
- Dark states are actually weakly-coupled to cavity
- Wave function localization and coherence lengths span $O(10^{-5} – 10^{-9}\ \mathrm{m})$

Ideal multimode



Disordered multimode



Agranovich, V.M. et al, PRB 67 (8) (2003): 085311.
Litinskaya, M., Reineker, P. PRB 74(16) (2006) 165320

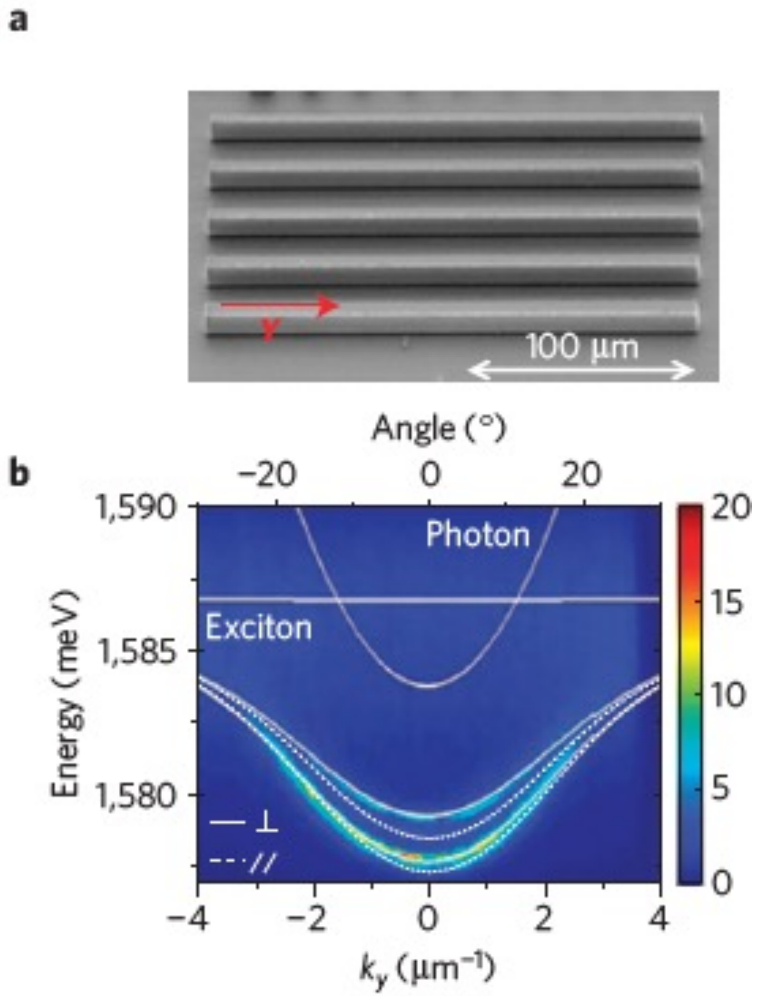
Photonic wire model for chemistry in optical cavities

Develop a real-space thermodynamic limit description of strongly coupled disordered molecular ensembles and photonic devices

Identify conditions for largest cavity effects on coherent energy transport and spectral properties of molecular systems

Compare to predictions of single-mode theories identifying their shortcomings

Ribeiro, R.F., “Strong light-matter interaction effects on molecular ensembles", preprint available at https://arxiv.org/abs/2107.07032



Nat. Phys., 6, 860 (2010)

Effective Hamiltonian

$$H = H_L + H_M + H_{LM}$$

$$H_{\mathrm{L}} = \sum_{|q|<q_{\max}} \hbar\omega_q a_q^\dagger a_q$$

$$H_M = \sum_{i=1}^{N_M} (E_M + \sigma_i) b_i^\dagger b_i$$

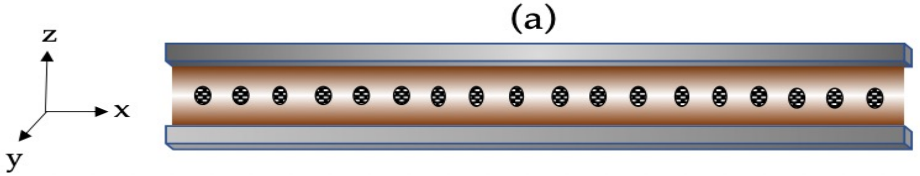
$$\langle \sigma_i \rangle = 0, \quad \langle \sigma_i \sigma_j \rangle = \delta_{ij}\sigma^2$$

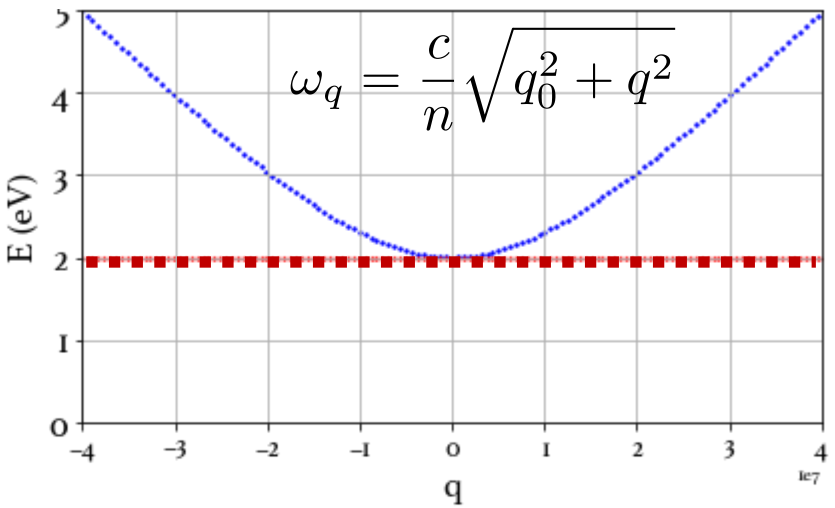
$$H_{\mathrm{LM}} = \sum_{j=1}^{N_M} \sum_q \frac{-i\Omega_R}{2} \sqrt{\frac{\omega_M}{N_M \omega_q}} \frac{\mu_j}{\mu_0} \left(e^{iqx_j} b_j^+ a_q - e^{-iqx_j} a_q^\dagger b_j^- \right)$$

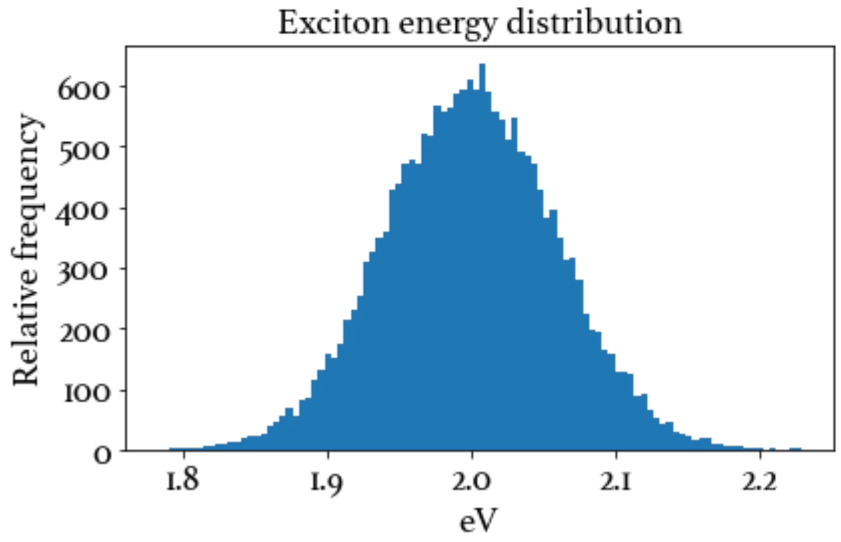
$$\langle \mu_i \rangle = \mu_0, \quad \langle \mu_i \mu_j \rangle = \delta_{ij}\sigma_\mu^2$$

$$x_j = ja + \Delta x_j$$

Ribeiro, R.F., “Strong light-matter interaction effects on molecular ensembles", preprint available at https://arxiv.org/abs/2107.07032







Observables I. LDOS

Local density of states of **molecular** excitations

$$\rho_n(E) = \langle n|\delta(\hat{H} - E)|n\rangle$$

$$\rho(E) = \frac{1}{N_M}\sum_{n=1}^{N_M}\langle n|\delta(\hat{H} - E)|n\rangle$$

Average probability that a molecule in its excited-state will be detected with energy E

Information entropy of **molecular** LDOS

$$S[\rho] = -\sum_E \rho(E)\ \ln\ [\rho(E)]$$

$$\Delta S = S[\rho] - S[\rho_0]$$

Quantifies fluctuations in molecular excited-state energies induced by strong light-matter interactions

$$\Delta S > 0$$

Observables II. Survival and escape probabilities

$$P_n(t) = |\langle n|e^{-iHt/\hbar}|n\rangle|^2$$

"n-th exciton survival probability at t"

$$\Pi_n = \lim_{t\to\infty} P_n(t)$$

$$\Pi = \frac{1}{N_M}\sum_{n=1}^{N_M}\Pi_n$$

mean "survival (return) probability"

$$\chi_M = 1 - \Pi$$

Escape probability

Tracks coherent energy diffusion at long times

Localized (Bare) limit

$$P_n(t) = 1, \quad \forall \;\; n \in [1, N_M]$$

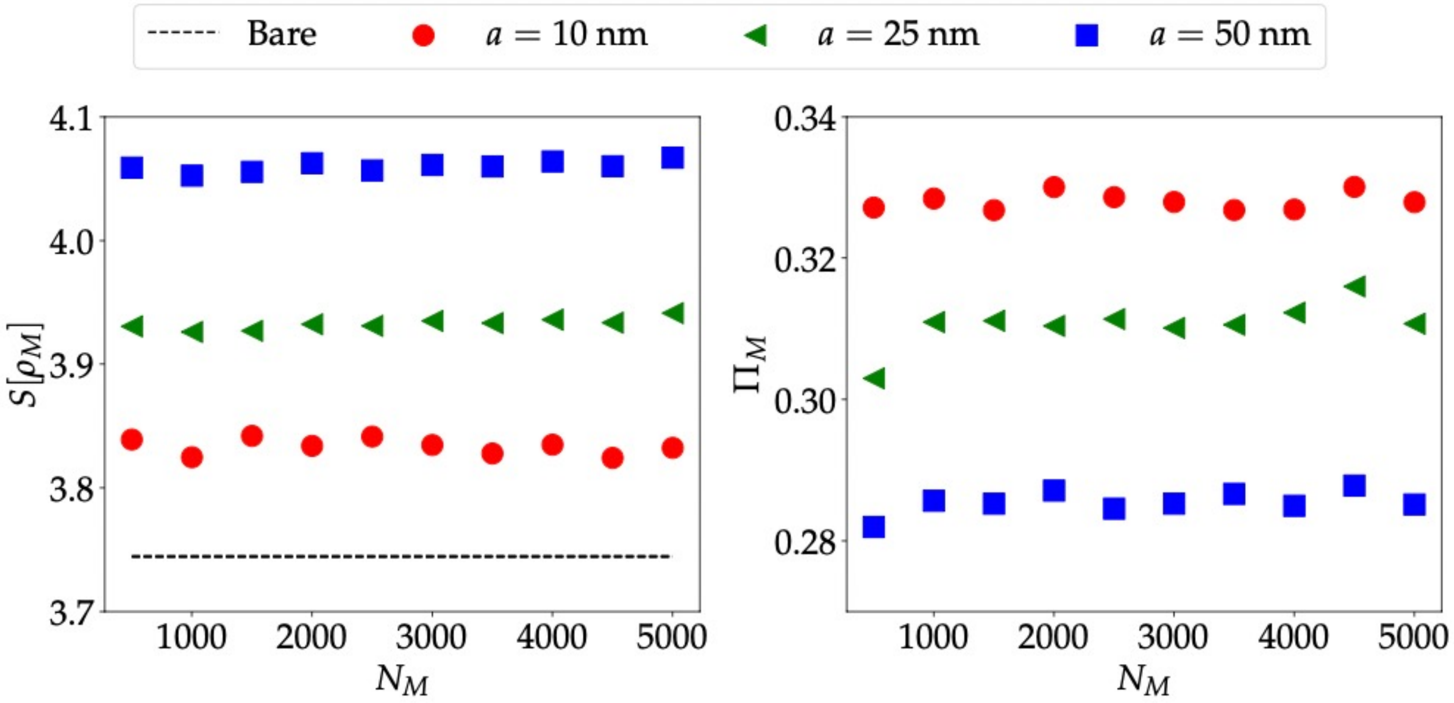
$$\Pi = 1, \quad \chi_M = 0$$

Delocalized limit

$$P_n(t) \overset{t\gg 0}{=} \frac{1}{N_M} \to 0, \quad N_M \to \infty$$

$$\Pi = 0, \quad \chi_M = 1$$

Thermodynamic Limit Convergence



$$\sigma/\Omega_R = 0.2$$

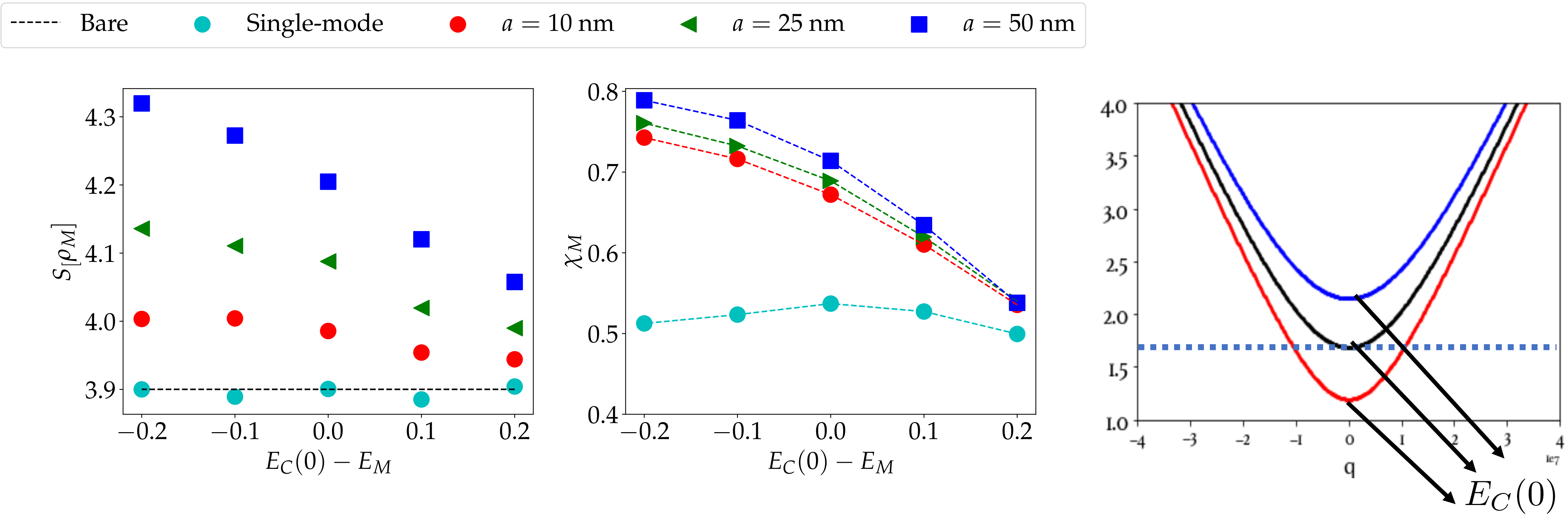
$N_{\text{sample}} = 10$

Size-independent S[E] (per particle)

Survival probabilities depend only on the density (1/*a*)

Ribeiro, R.F., "Strong light-matter interaction effects on molecular ensembles", preprint available at https://arxiv.org/abs/2107.07032

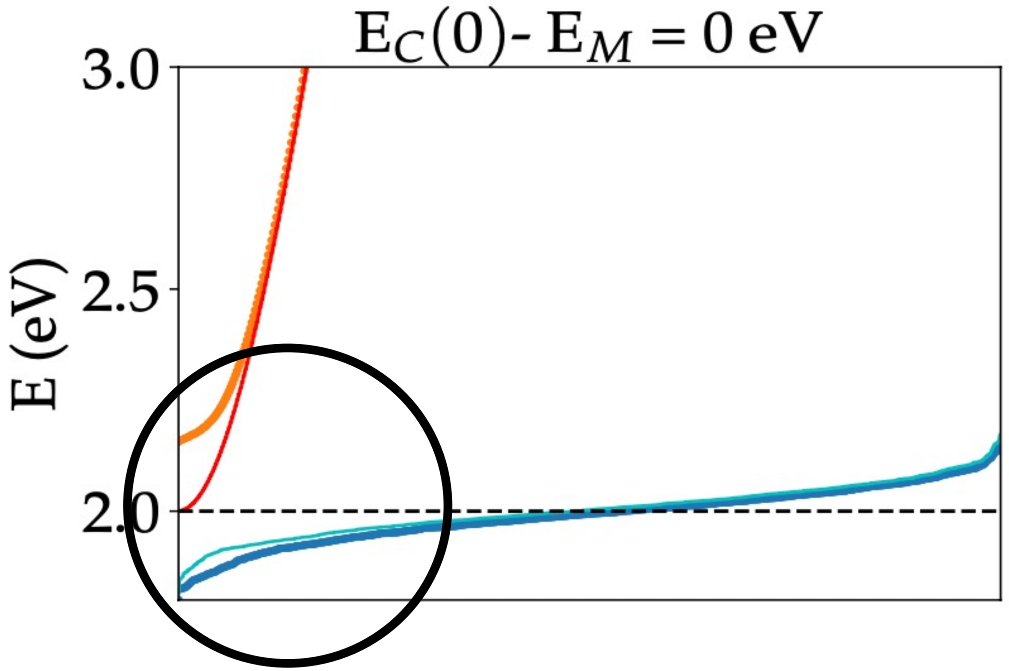
Results. Detuning effects

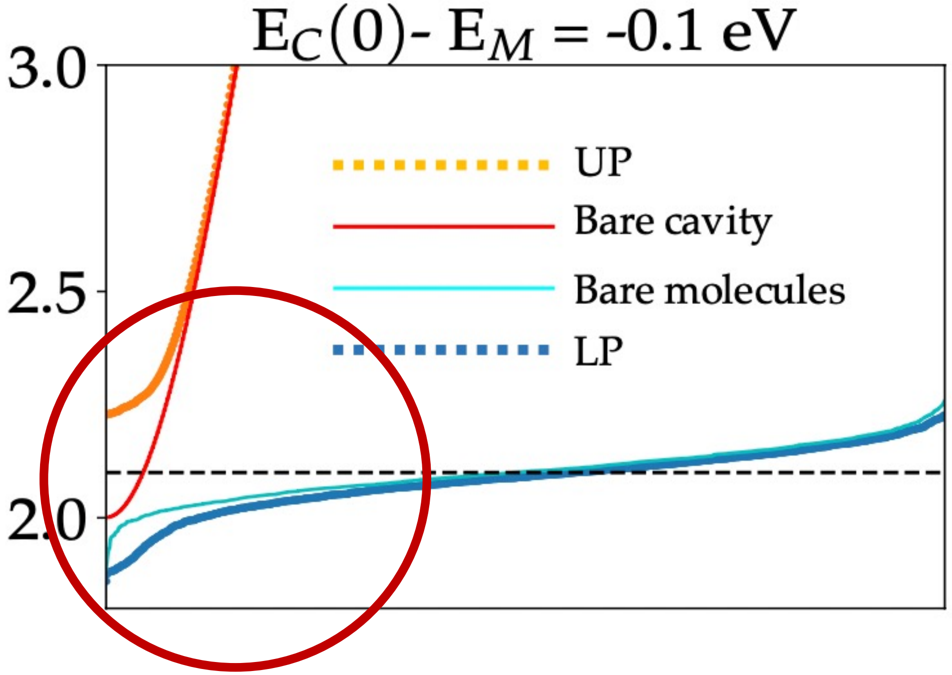


Energy transport and spectral fluctuations in single-excitation sector of Hilbert space will be maximally enhanced when cavity detuning is **negative** (redshifted cavity)

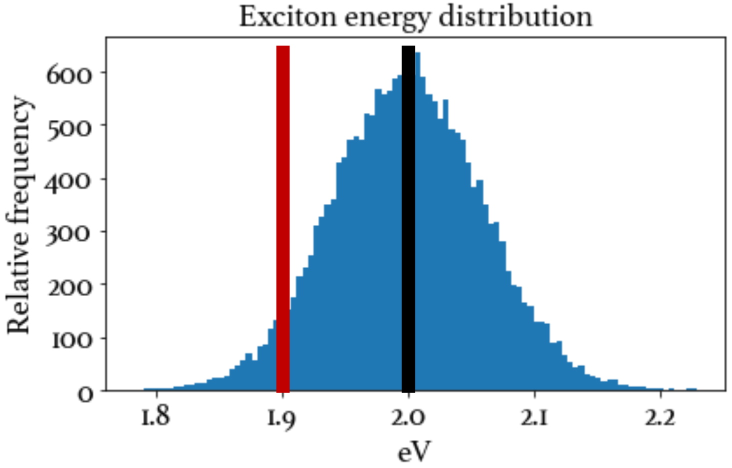
Ribeiro, R.F., "Strong light-matter interaction effects on molecular ensembles", preprint available at https://arxiv.org/abs/2107.07032

Enhanced excited-state delocalization with redshifted optical cavities





Enhanced spectral overlap

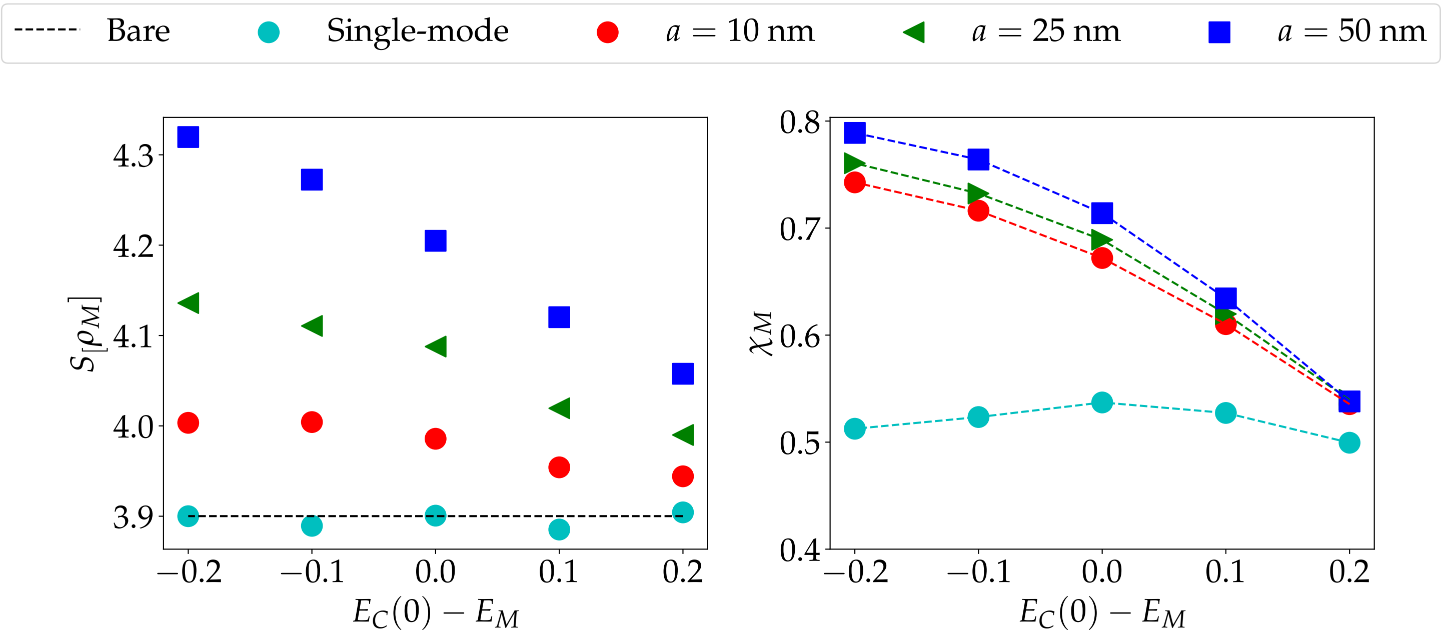


Greater coherence length of polariton excited-states due to

$$\delta q/q < 1$$

for a larger number of polariton states

Results. Density-dependence (with fixed Rabi)



For systems with equal *collective* light-matter interactions, cavity effects will be greatest for those with smaller density (greater *a*)

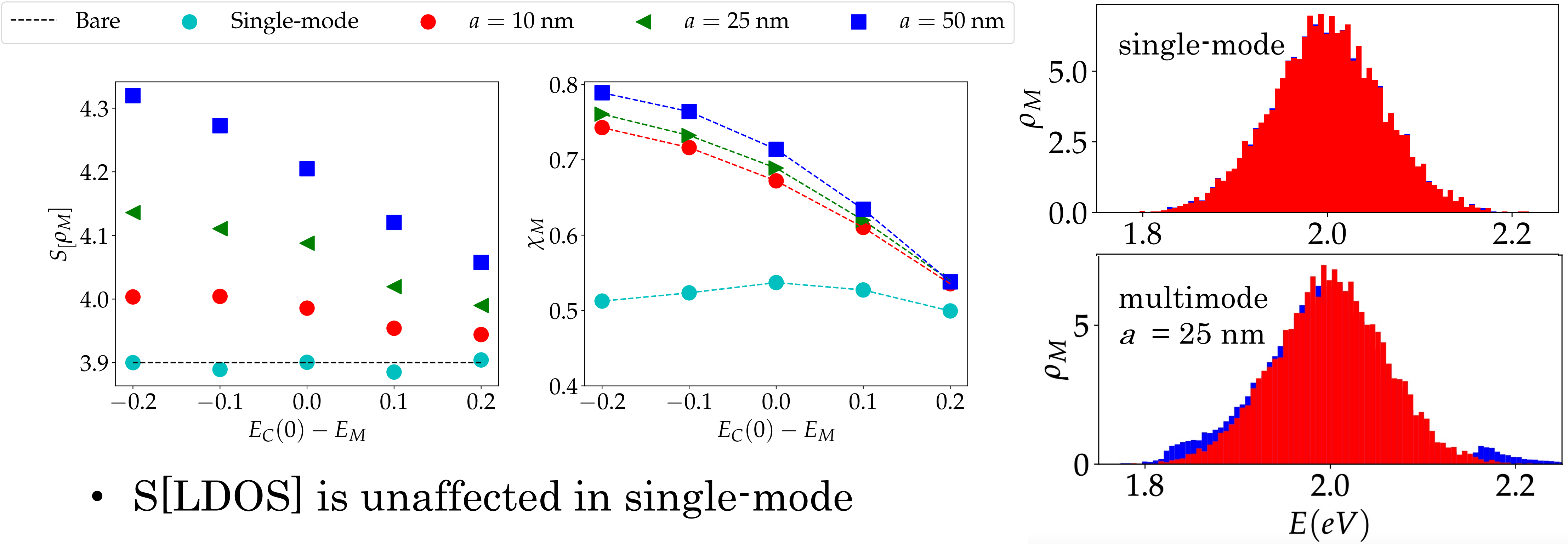
$$\Omega_R \propto \sqrt{\frac{\mu^2}{a}}$$

Single-molecule transition dipoles scale with $\sqrt{a}$

Cavity-induced intermolecular correlations increase with *a*

Ribeiro, R.F., “Strong light-matter interaction effects on molecular ensembles", preprint available at https://arxiv.org/abs/2107.07032

Comparison to single-mode theories



- S[LDOS] is unaffected in single-mode

- Spurious maximum in escape probability at zero detuning due to incorrect accounting for spectral overlap

- Single-mode theory fails to identify any density dependence

Summary

Redshifted optical cavities are likely to exert stronger influence on dynamical chemical processes

In systems with equal Rabi splitting, a lower density favors excited-state delocalization and stronger cavity-induced energy fluctuations

Single-mode theories may lead to incorrect qualitative trends

Trends are universal for 1D systems, but theoretical arguments apply also to 2D and 3D geometries

Ongoing related research: ultrastrong coupling, incoherent vs. ballistic transport, anomalous diffusion

Acknowledgments

Ribeiro group

https://ribeiro.emorychem.science

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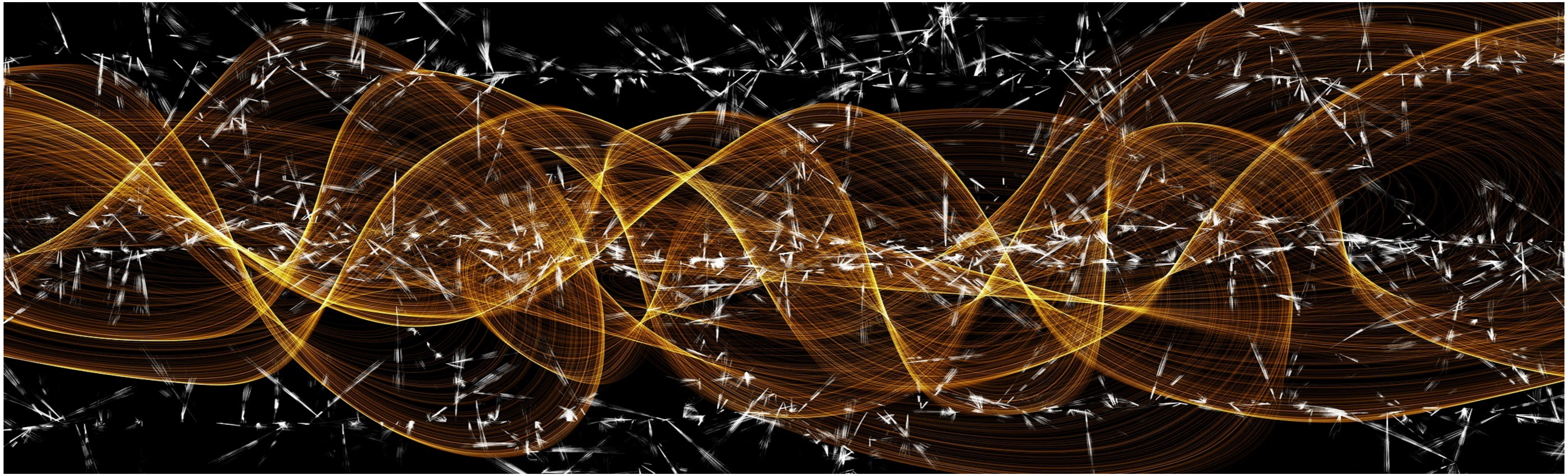

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