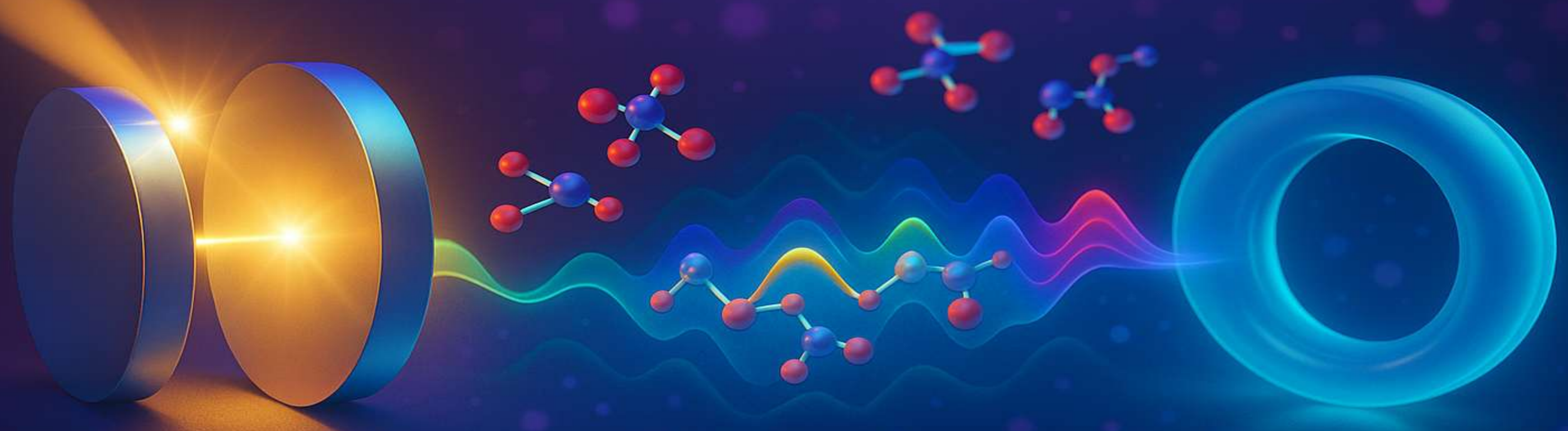
# State of development of molecular polaritonics

JOEL YUEN-ZHOU

CAMOS, Irvine 2025



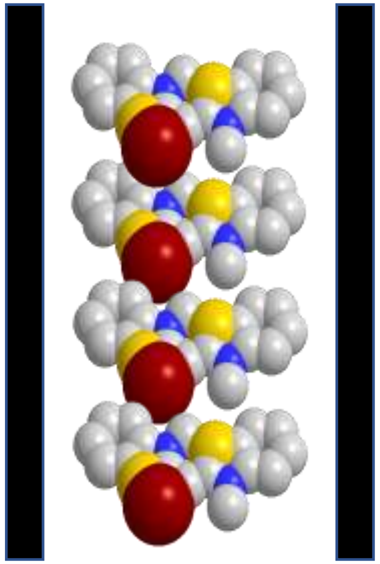
@ucsd_yuen

UC San Diego

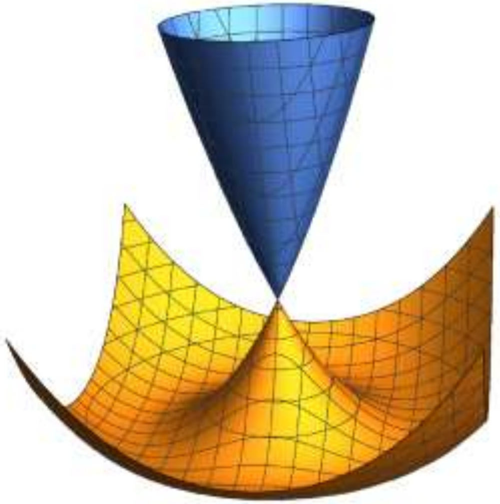
# Our group

July 2024

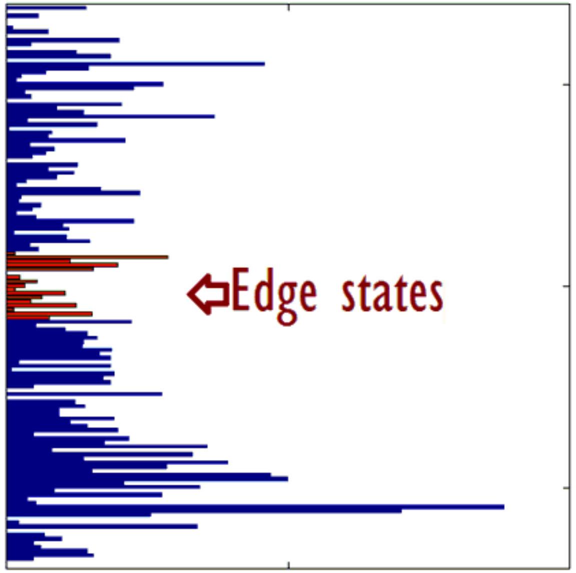
# Our group



Quantum optics

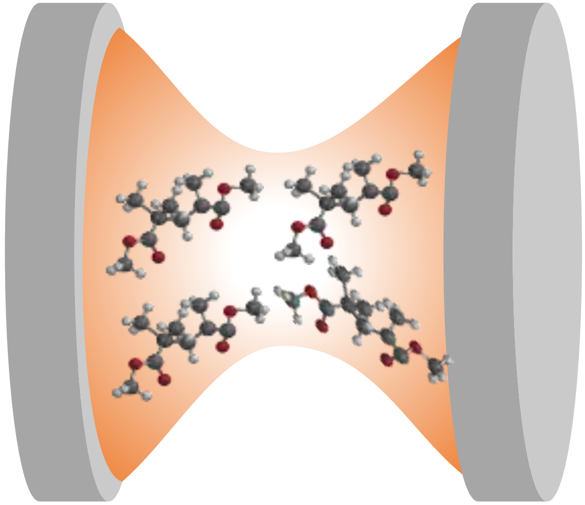


Physical/theoretical chemistry

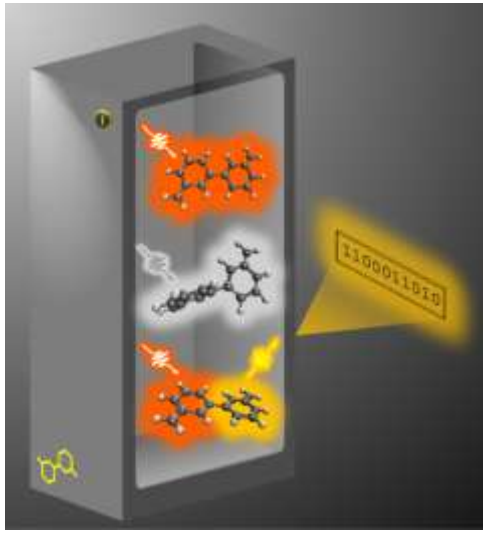



Condensed matter

# Research vision



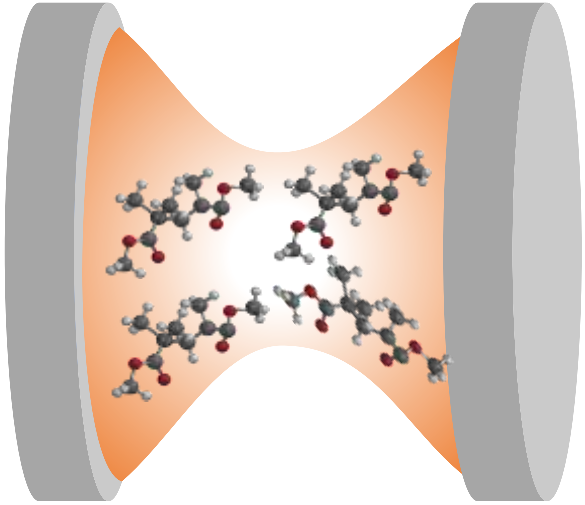
**Molecular polaritonics**



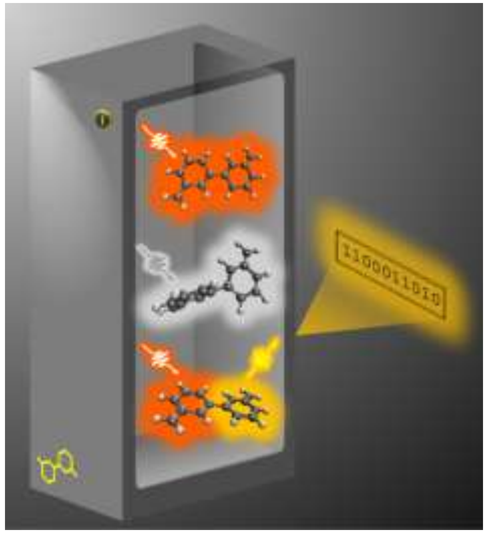
**Molecular spins**

**Control and detection of molecular processes with novel forms of light-matter interfaces**

# Research vision



**Molecular polaritonics**



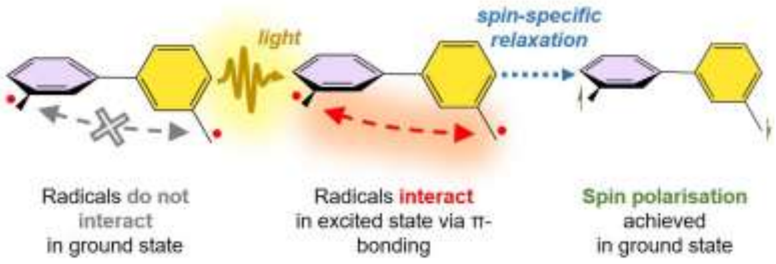
**Molecular spins**

**Control and detection of molecular processes with novel forms of light-matter interfaces**

# Research on molecular spins

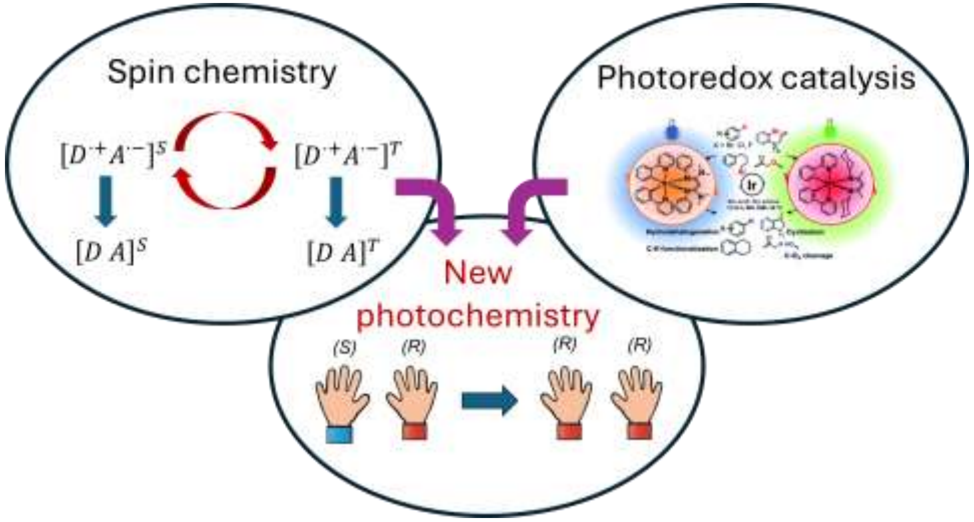
Chemistry

Spin photophysics



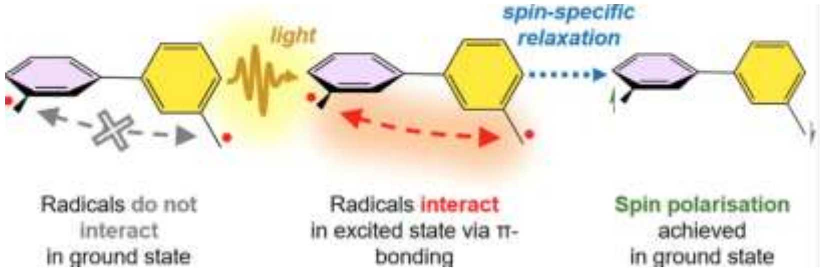

Spin photophysics

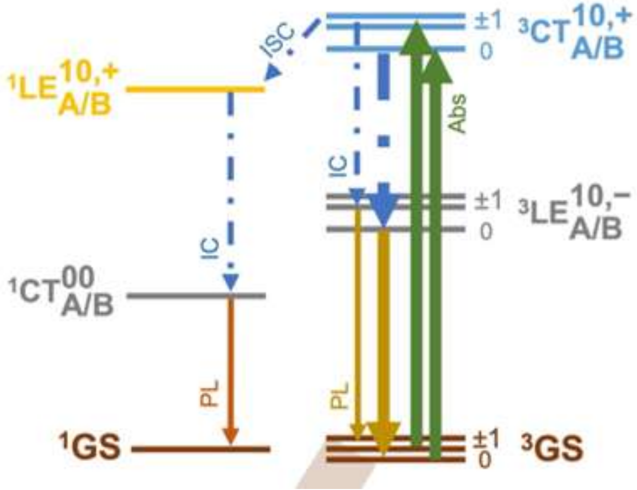
Chemistry



# Organic molecules as NV surrogates

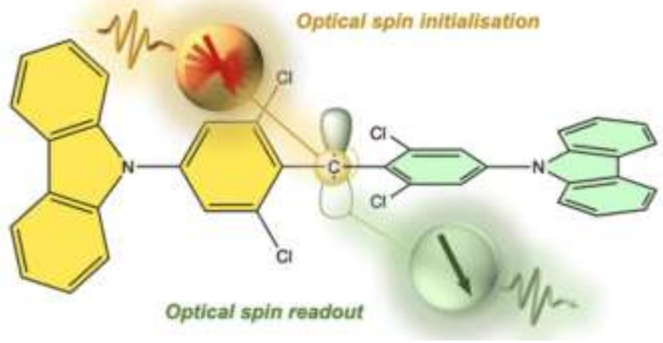
**Luminescent diradicals: First class of organic molecules showing ground-state optically-detected magnetic resonance (ODMR)**

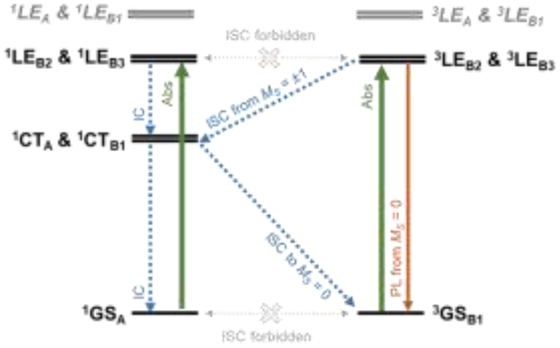



JACS 147, 26, 22529–22541 (2025) (theory)
JACS 146, 40, 27935 (2024) (experiment + theory)
ACS Cent. Sci. 11, 1, 116–126 (2025) (theory)
JACS 147, 26, 22951–22960 (2025) (experiment+ theory)
(collaboration with Wasielewski in Northwestern)

**Luminescent triplet carbenes: New organic molecules showing enhanced ground-state ODMR**

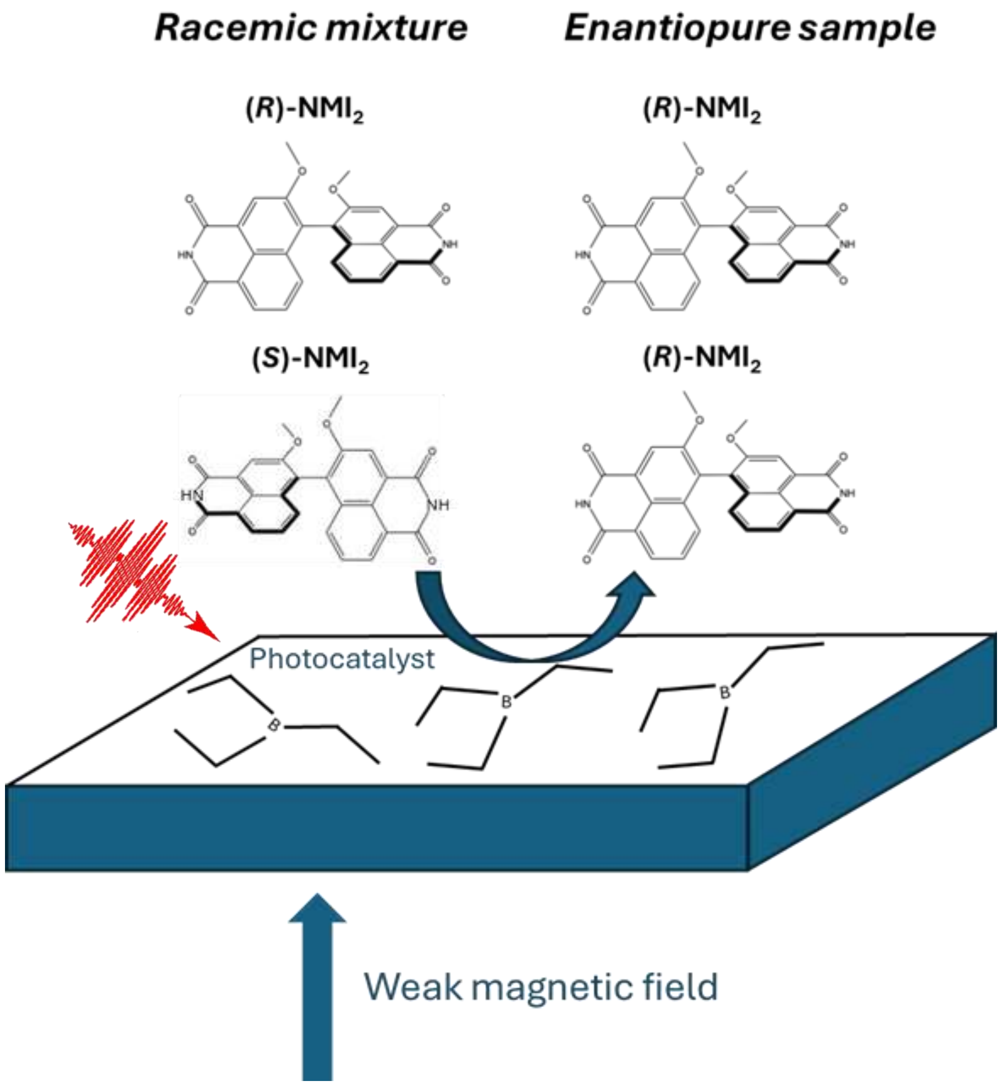


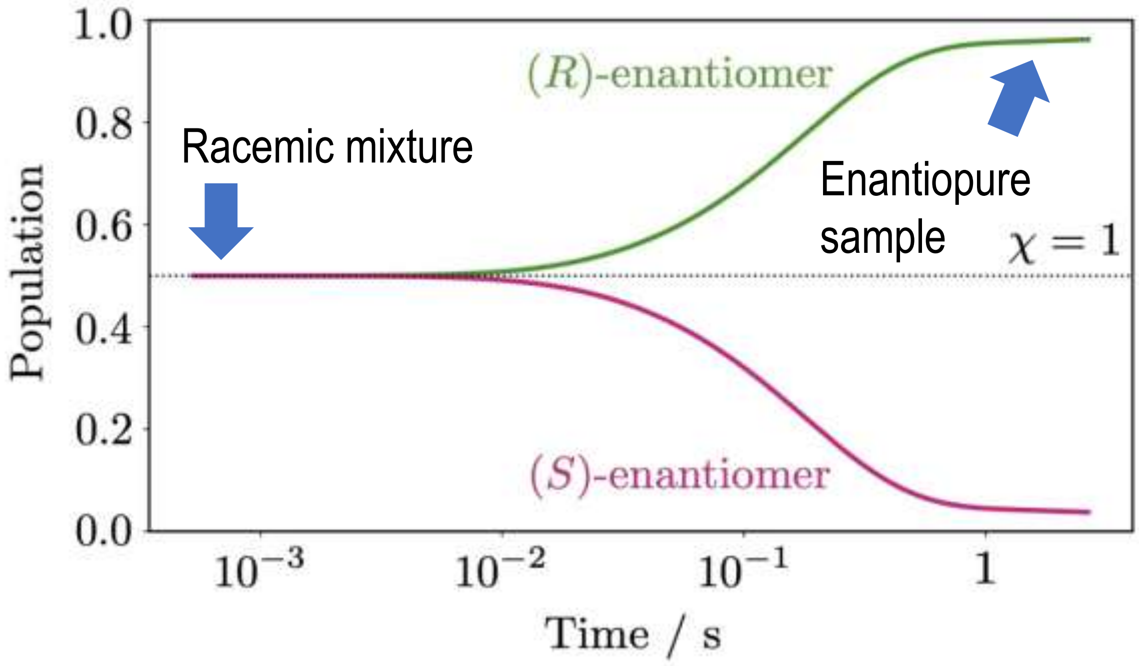

JACS 147, 26, 22529–22541 (2025) (theory)

See also: JACS 147, 40, 36383–36392 (2025)
(experiment + theory, Schaub & Schwartz groups)

# Spin chemistry for chiral resolution



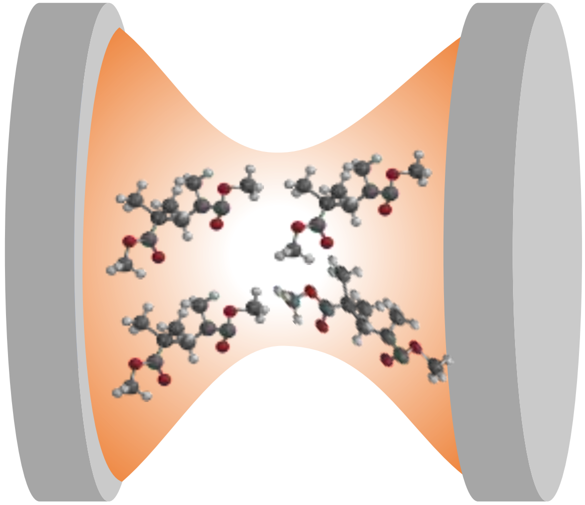

Can we repurpose spin chemistry for enantioselective photoredox catalysis?



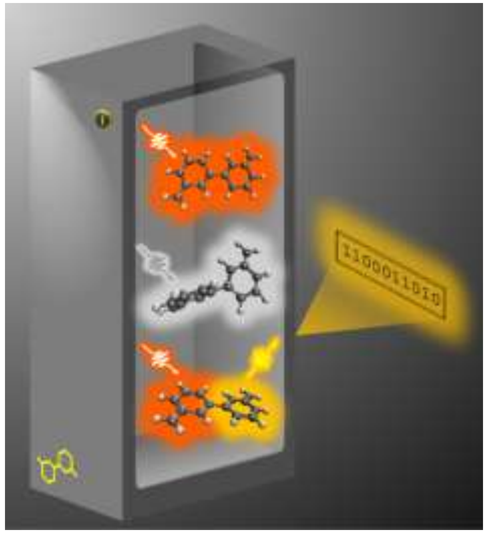

$B \sim 0.12\ T$, $\mathrm{P} \sim 40\ mW$ laser

Y. R. Poh, A. Koner, M. Reitz, J. Yuen-Zhou, Photoredox catalysis with spin magnetic fields, JACS 147, 40, 36579–36588 (2025).

# Research vision



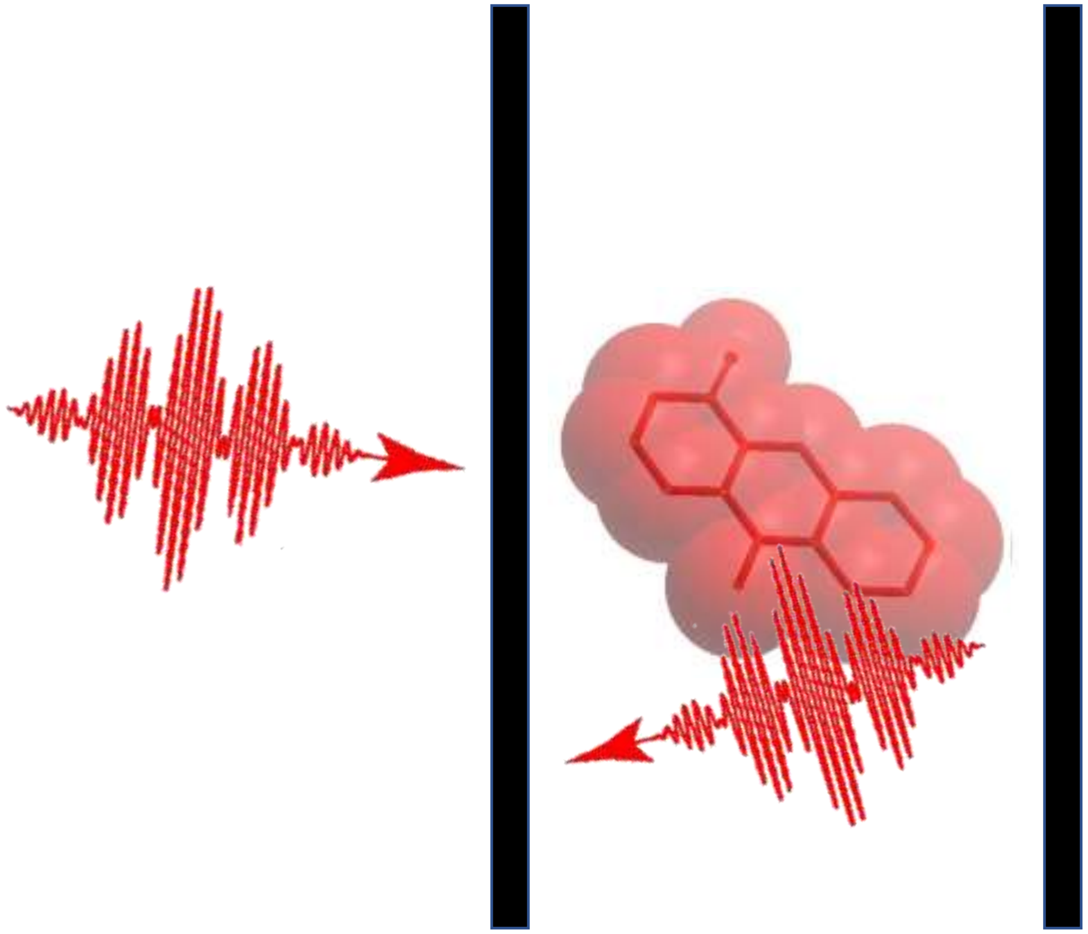
**Molecular polaritonics**



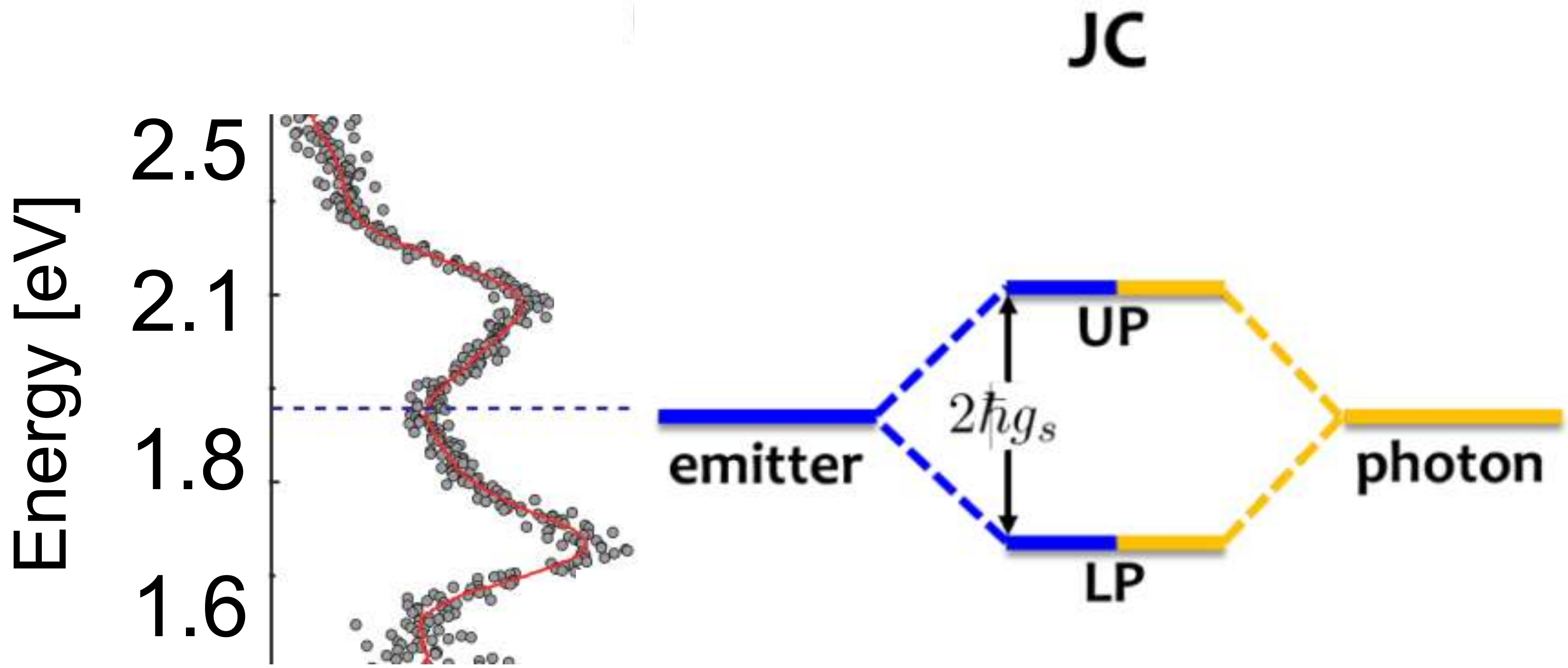
**Molecular spins**

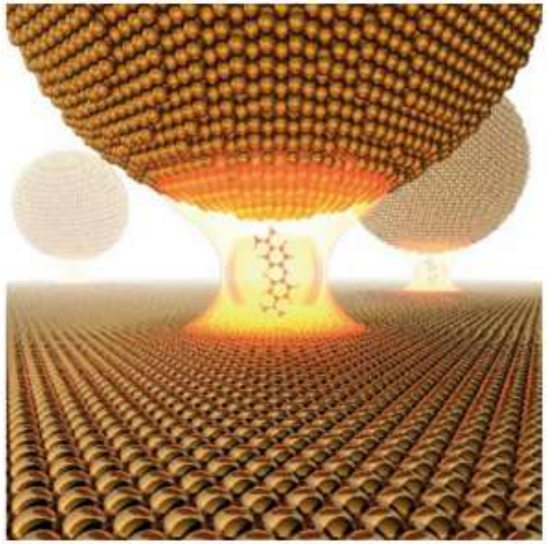
**Control and detection of molecular processes with novel forms of light-matter interfaces**

# One molecule in a cavity: Jaynes-Cummings model



# One molecule in a cavity: Jaynes-Cummings model

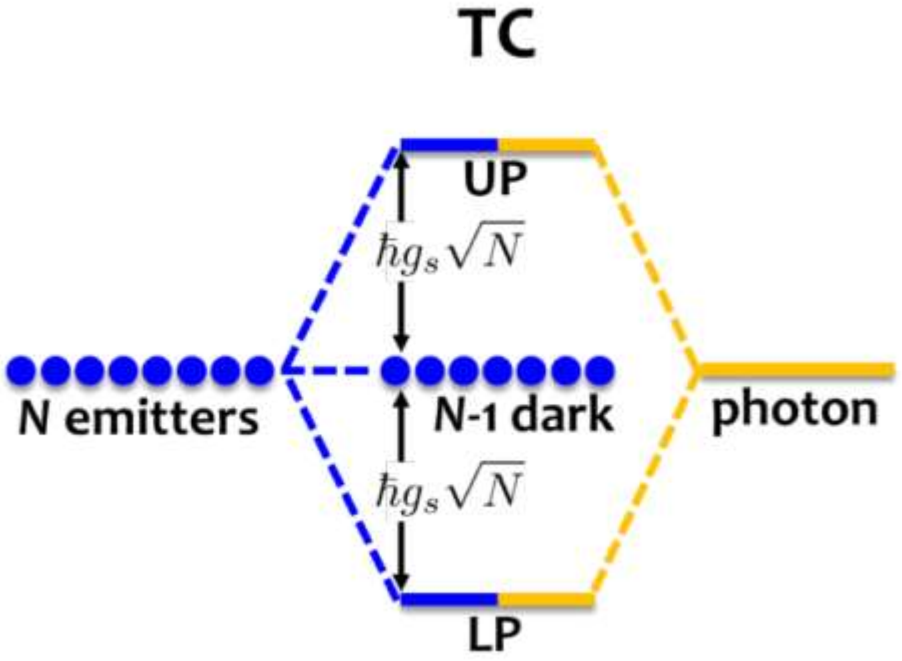


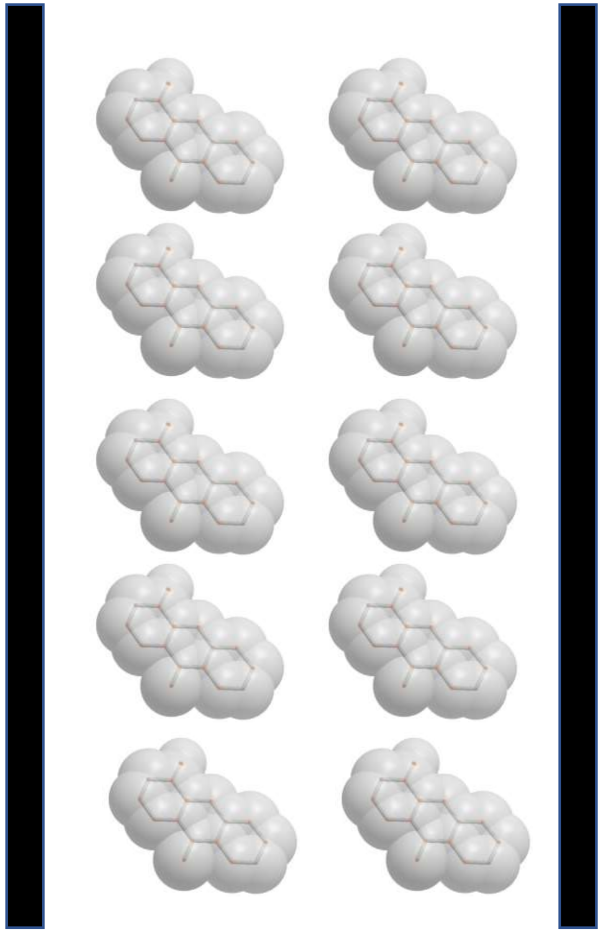



R. Chikkaraddy, …, J. J. Baumberg, *Nature* 535, 7610, 127-130 (2016)

See also: Santhosh, K., Bitton, O., Chuntonov, L., & Haran, G., *Nature communications*, *7*(1), 11823 (2016).
Leng, H., …, & Pelton, M., *Nature communications*, *9*(1), 4012 (2018).

# Many molecules in a cavity: Tavis-Cummings model

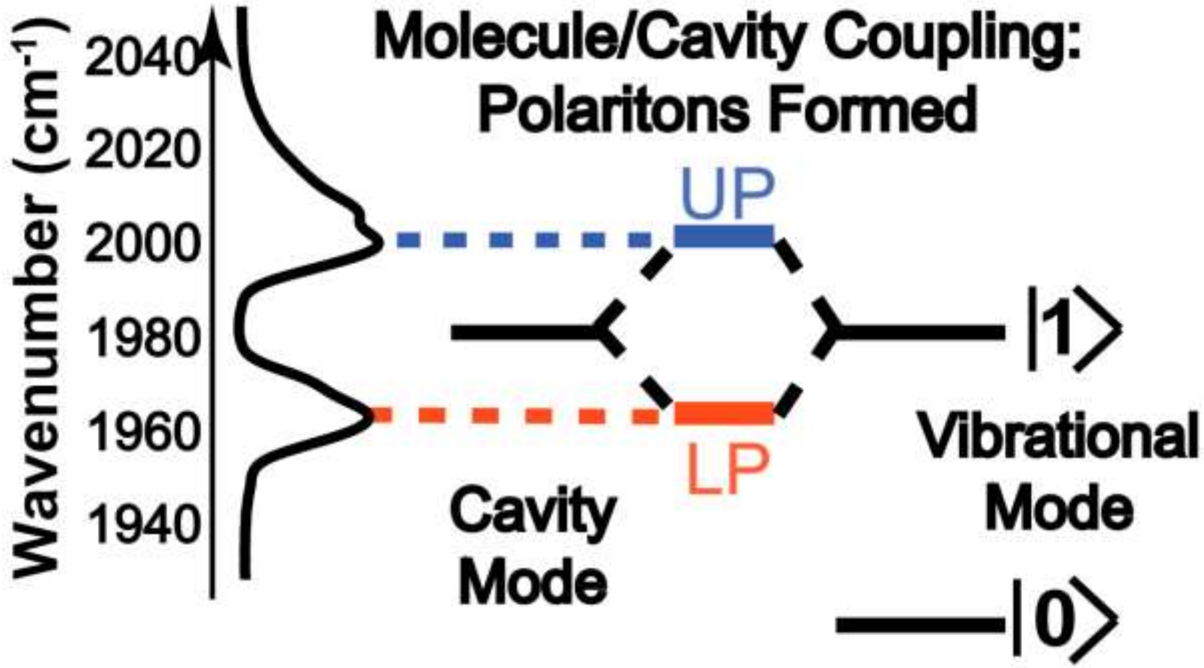


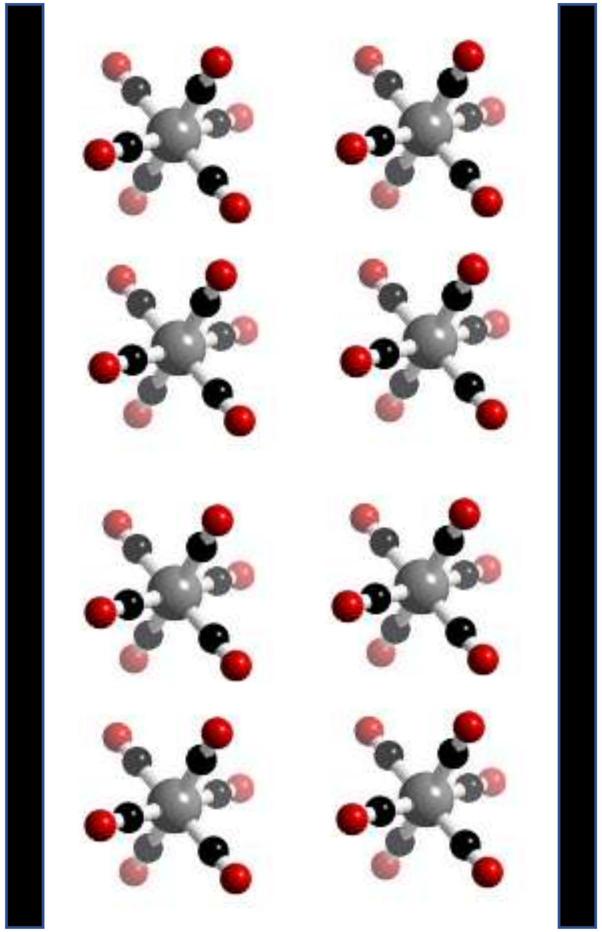
Rabi splitting $\Omega = 2\sqrt{N}\hbar g_s$ where $N = 10^3 - 10^{12}$

# Many molecules in a cavity: Tavis-Cummings model

Vibrational strong coupling (VSC)



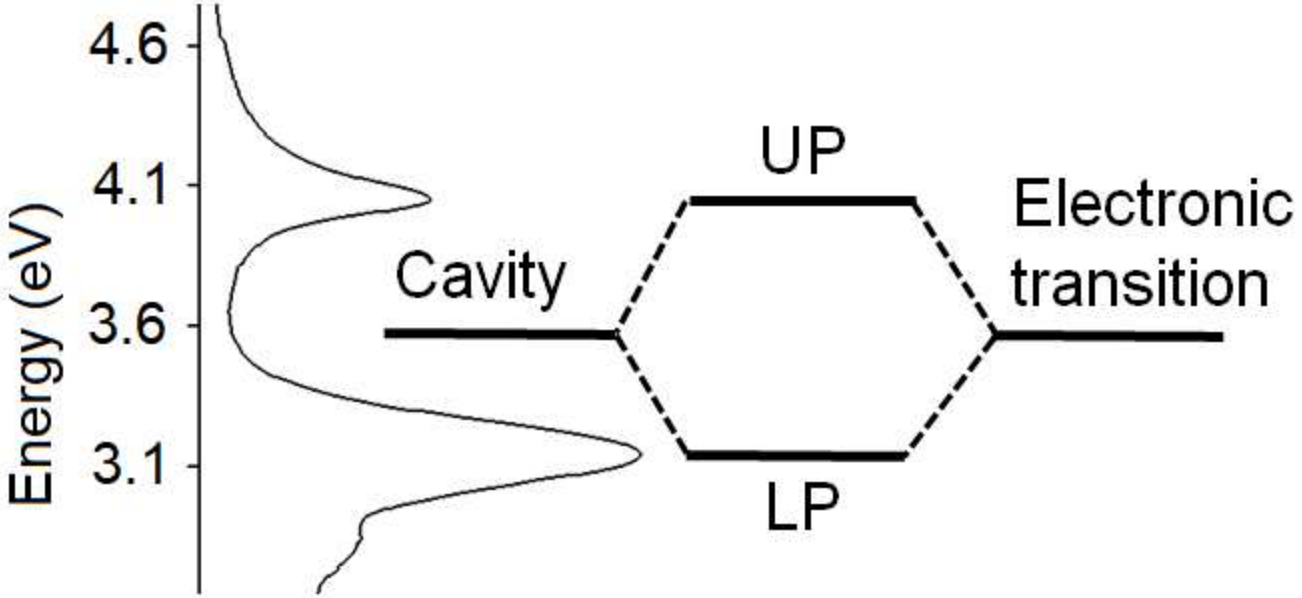

B. Xiang, R. F. Ribeiro, A. D. Dunkelberger, J. C. Owrutsky, B. S. Simpkins, J. Yuen-Zhou, and W. Xiong, PNAS 115, 19 (2018).



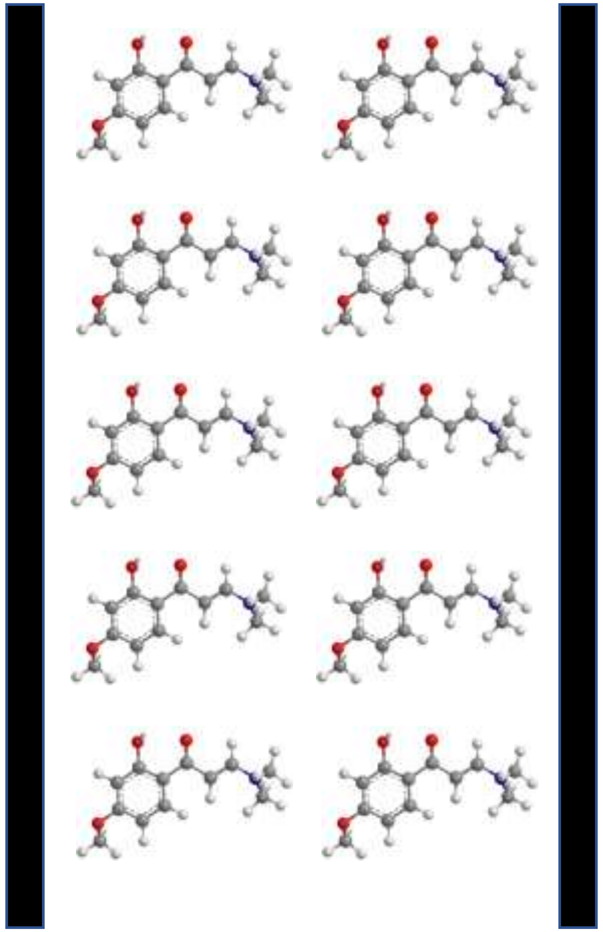
$W(CO)_6$ solution
$\omega_{10} = 1983\ cm^{-1}$

# Many molecules in a cavity: Tavis-Cummings

## Electronic ultrastrong coupling (USC)




D.P. Kizhmuri, R. Desmukh, L. Martínez, J. Yuen-Zhou, E. Hohenstein, G. John, V. Menon, *in preparation*.



HMPP film

$\omega_{10} = 3.6\ eV$

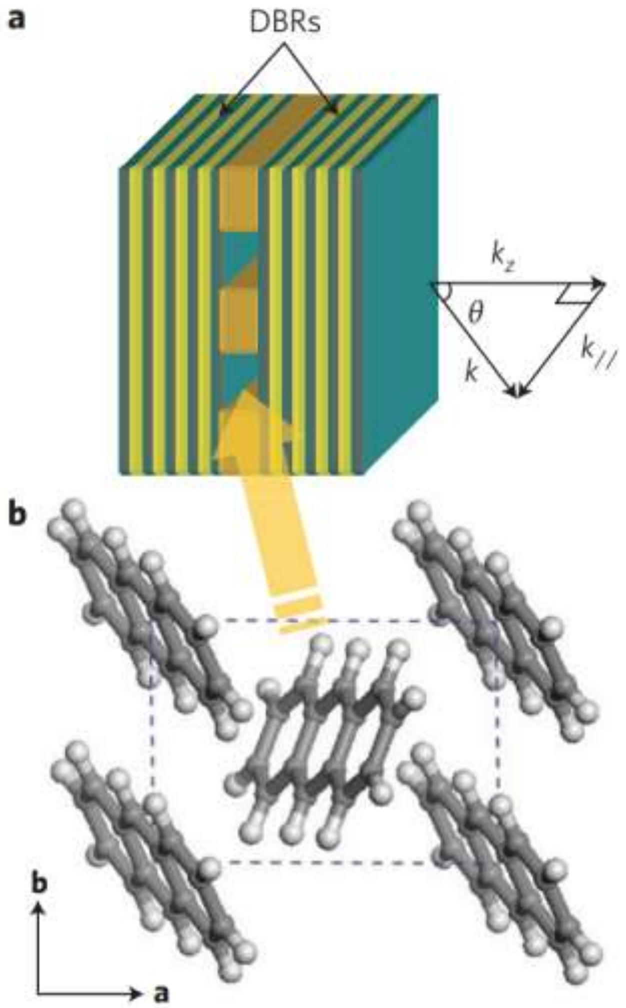
# Molecular polaritonics timeline

- ❑ K. Tolpygo (1950), K. Huang (1951): Phonons in solids mix with confined EM modes to form polaritons.
- ❑ V. M. Agranovich (1957), J. J. Hopfield (1958): Excitons in solids mix with confined EM modes to form polaritons.

- ❑ C. Weisbuch (1992): GaAs quantum well polaritons in microcavities.
- ❑ D. Lidzey (1998): Organic (tetraphenyl 4TBPP-Zn) in microcavities.

- ❑ H. Deng (2002): GaAs quantum well polariton condensation at 4K.
- ❑ S. Kena-Cohen (2010): Anthracene polariton condensation at 298 K.

- ❑ T. Ebbesen (2012-): Changes in thermally-activated reactions and photoinduced reactions and processes due to polariton formation.



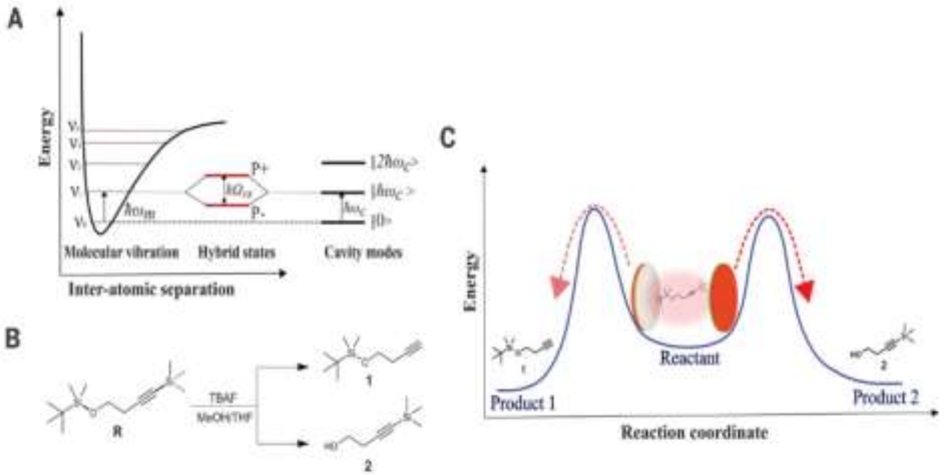
# Polariton chemistry (2012-)

RESEARCH Science 363, 615–619 (2019)

CHEMISTRY

## 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]§




**(a) Thermal polariton chemistry aka vibropolaritonic chemistry (without lasers)**

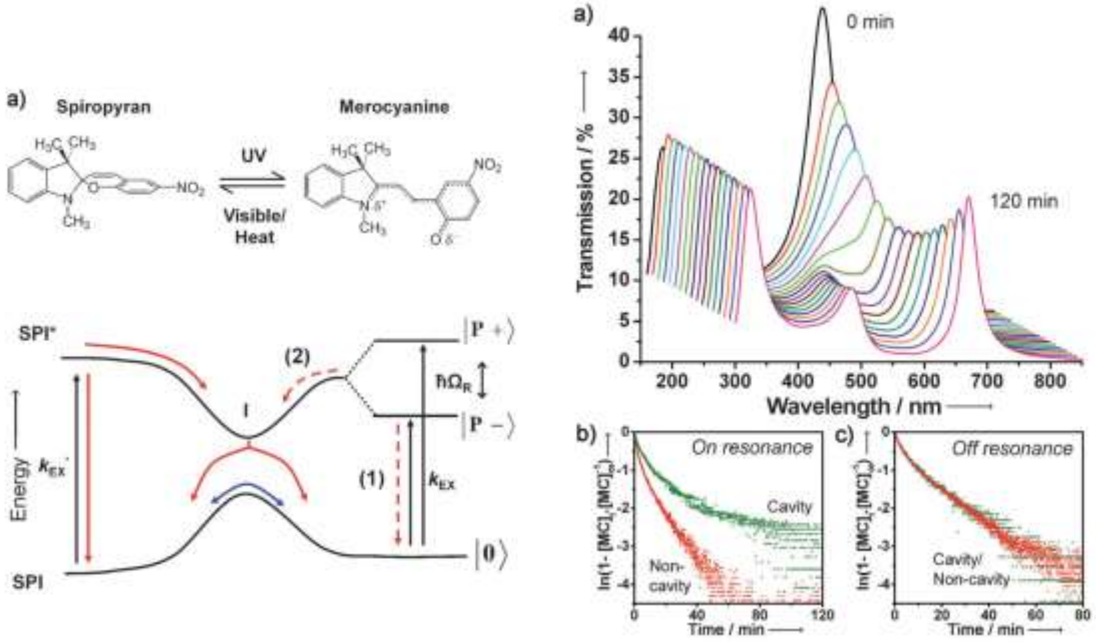
Angewandte Communications

Quantum Electrodynamics

DOI: 10.1002/anie.201107033

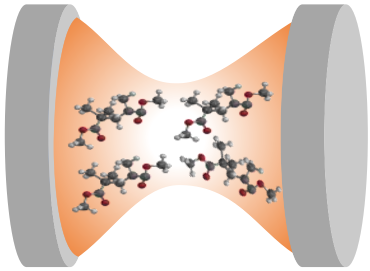
## Modifying Chemical Landscapes by Coupling to Vacuum Fields**

*James A. Hutchison, Tal Schwartz, Cyriaque Genet, Eloïse Devaux, and Thomas W. Ebbesen**




**(b) Photoinduced polariton chemistry (with lasers)**

POLARITON CHEMISTRY



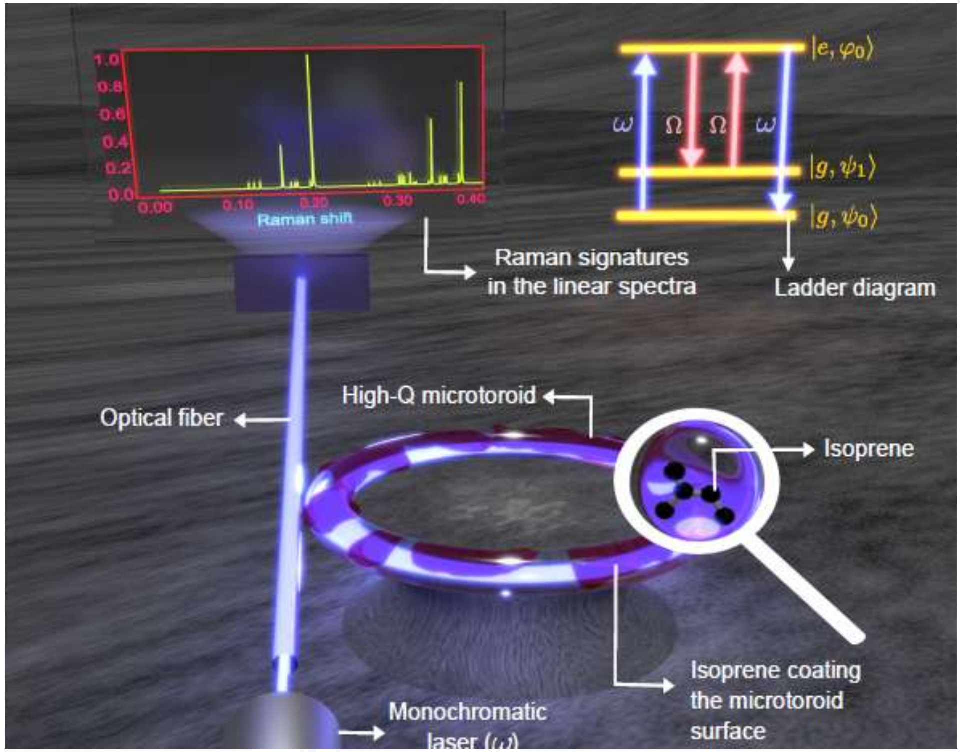
- Thermal
  - IR (vibropolaritonic chemistry)
- Photoinduced
  - UV/vis
  - IR

# SCOM23

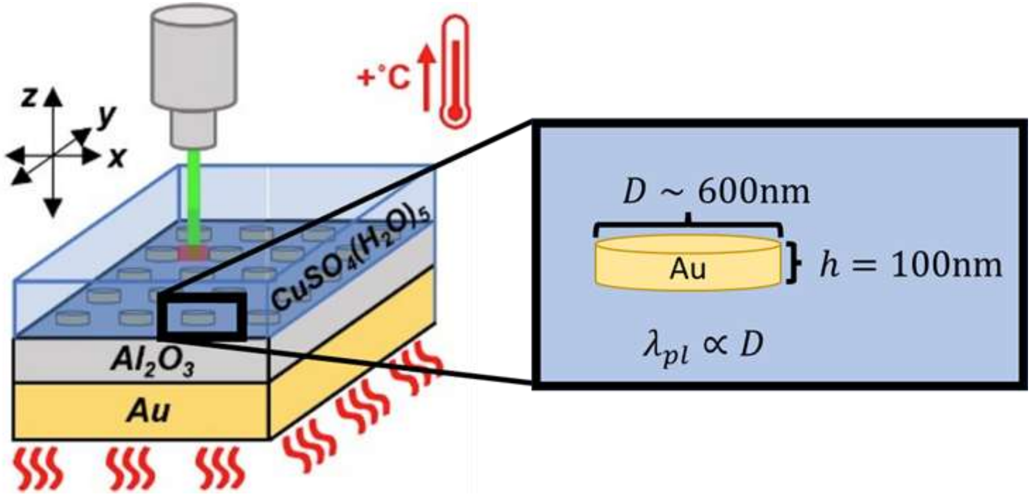

During SCOM23, there was a consensus as a community to try to distinguish standard cavity phenomena (classical field enhancement, lasing, Purcell effect, etc.) from "nontrivial" strong coupling phenomena.

MAIN QUESTION OF THE FIELD: Which polaritonic effects are *truly cavity induced* and cannot be obtained outside the cavity and which ones are not?

# Molecular polaritonics

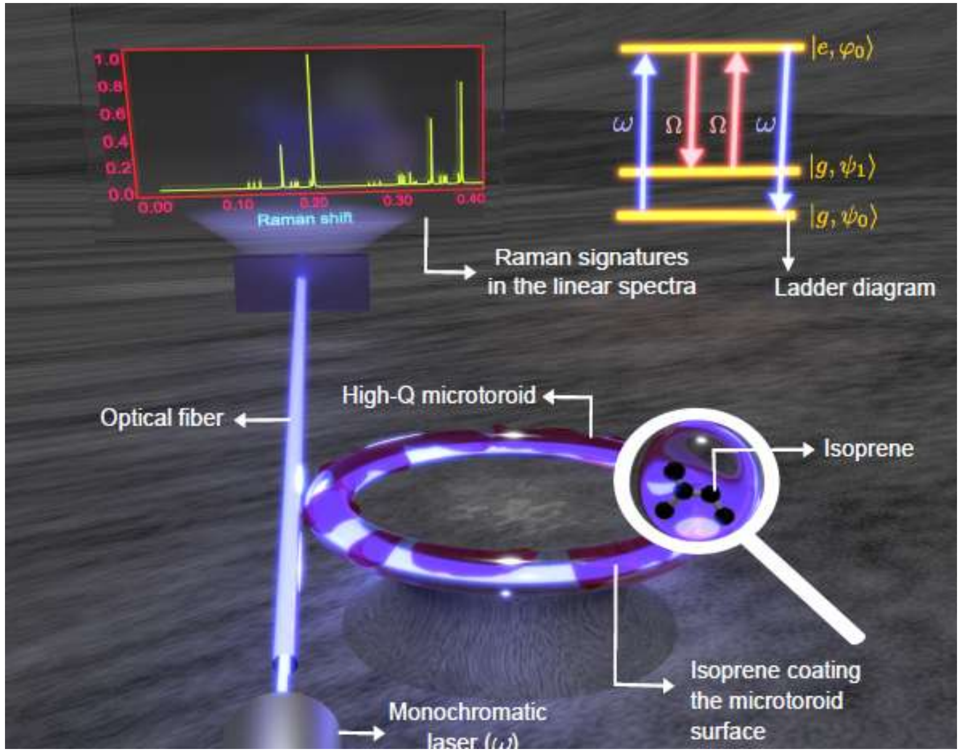



**(a) Photoinduced processes**

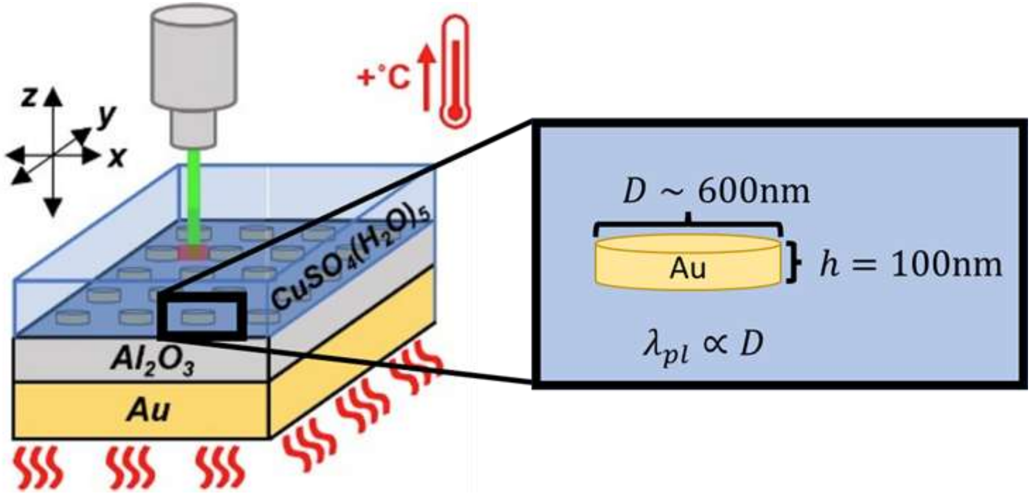



**(b) Thermal processes**

# Molecular polaritonics

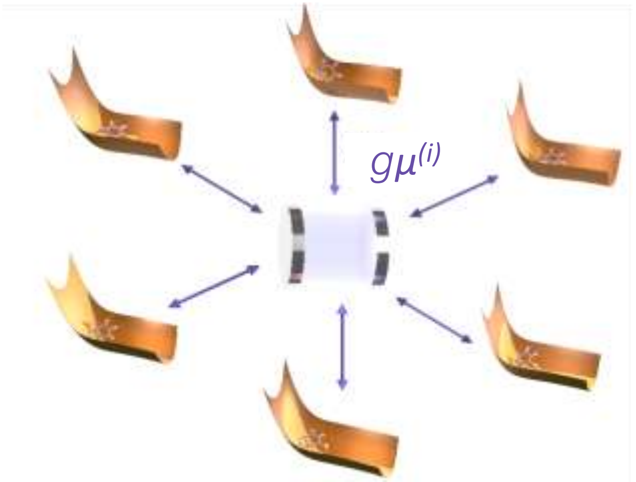


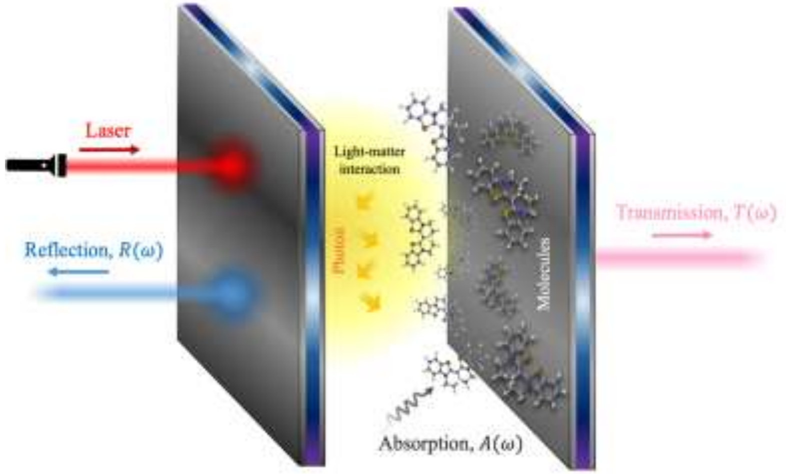

**(a) Photoinduced processes**




**(b) Thermal processes**

# The theory-experiment conundrum in molecular polaritonics



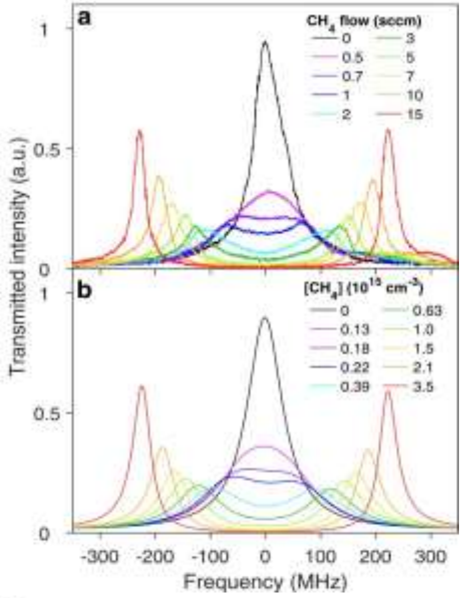

THEORY:
Quantum, ab initio

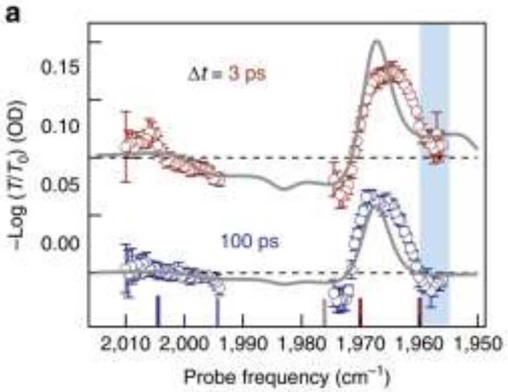
A large number ($N$=$10^6$ - $10^{10}$) of molecules with complex lineshapes, coupled to a cavity: **intractable computational simulations?**

Multiple exchanges of excitation between the light and the matter: **nontrivial changes in optical response?**

EXPERIMENTS:
(Semi)-classical optics

Experimentalists use classical linear optical methods like transfer matrix method to **successfully fit** linear and even some nonlinear polaritonic spectra





1.Wright, A. D., J. C. Nelson, and M. L. Weichman, Journal of the American Chemical Society 145, 10 (2023): 5982-5987.

2.Dunkelberger, A. D., et al. "Modified relaxation dynamics and coherent energy exchange in coupled vibration-cavity polaritons." Nature Communications 7.1 (2016): 13504.

3. Thomas, P. A.; Tan, W. J.; Kravets, V. G.; Grigorenko, A. N.; Barnes, W. L. Non Polaritonic Effects in Cavity-Modified Photochemistry. Adv. Mater. 2023, 2309393.

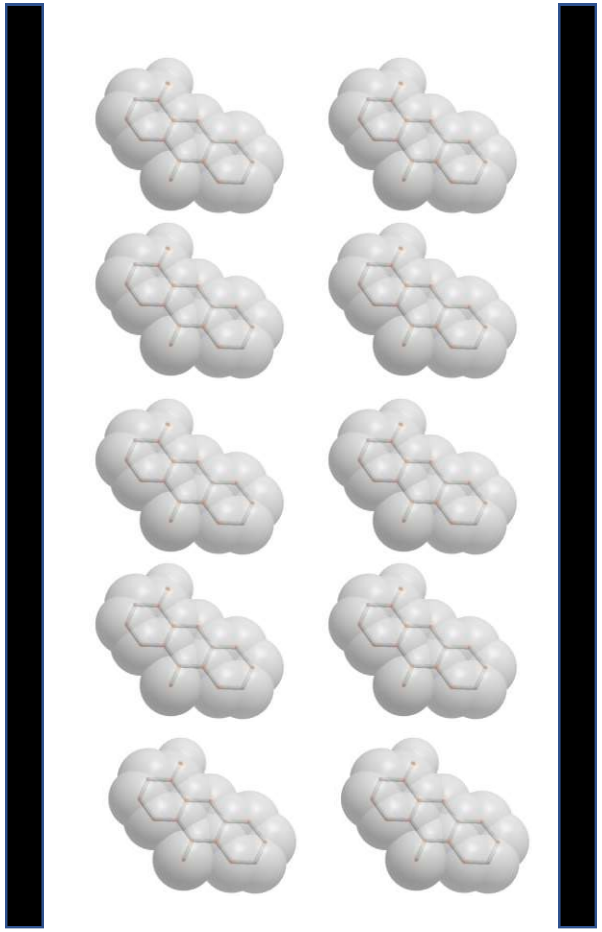
# Molecular polaritons as quantum impurity problems

Hamiltonian for N molecules + cavity:

$$\hat{H} = \sum_{i}^{N} \left( \hat{H}_m^{(i)} + \hat{H}_I^{(i)} \right) + \hat{H}_{cav}$$

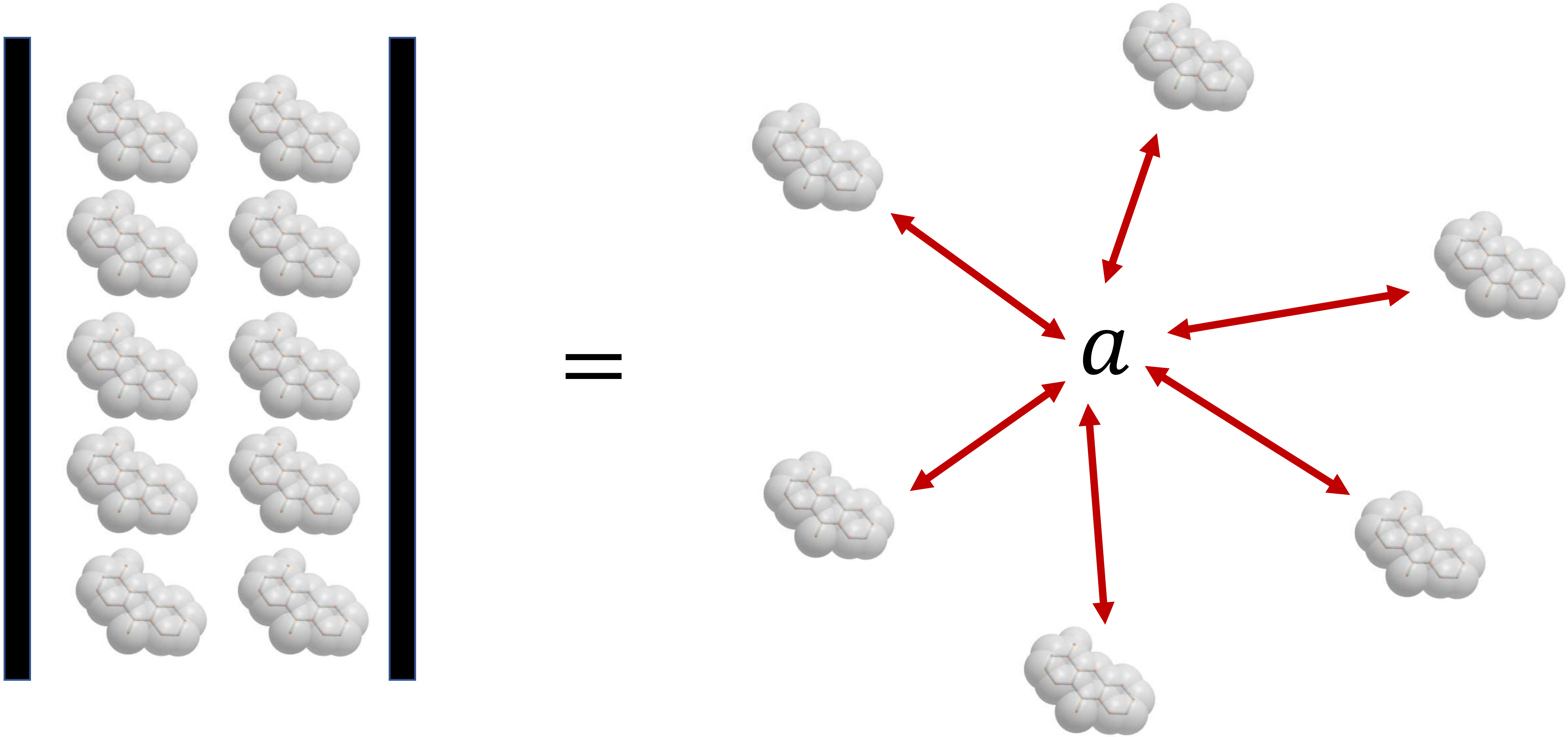
$$\hat{H}_m^{(i)} = -\frac{1}{2m}\frac{\partial^2}{\partial q_i^2} + V_g(q_i)|g_i\rangle\langle g_i| + V_e(q_i)|e_i\rangle\langle e_i|,$$

$$\hat{H}_{cav} = \omega_c \hat{a}^\dagger \hat{a}, \qquad \hat{H}_I^{(i)} = g\left(|e_i\rangle\langle g_i|\hat{a} + |g_i\rangle\langle e_i|\hat{a}^\dagger\right)$$



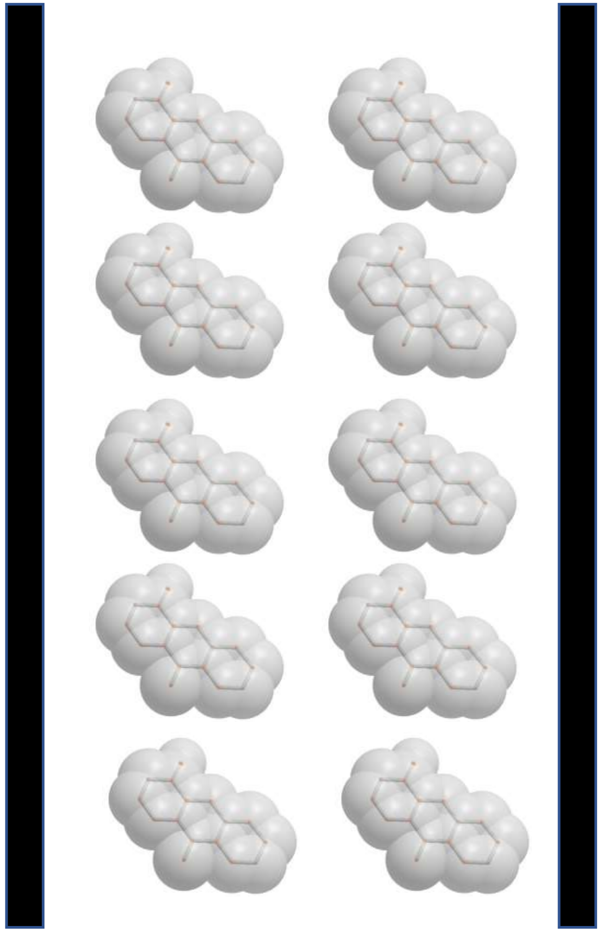
J. Pérez-Sánchez, A. Koner, N.P. Stern, J. Yuen-Zhou, PNAS. 120 (15) e2219223120, 2023.

# Molecular polaritons as quantum impurity problems

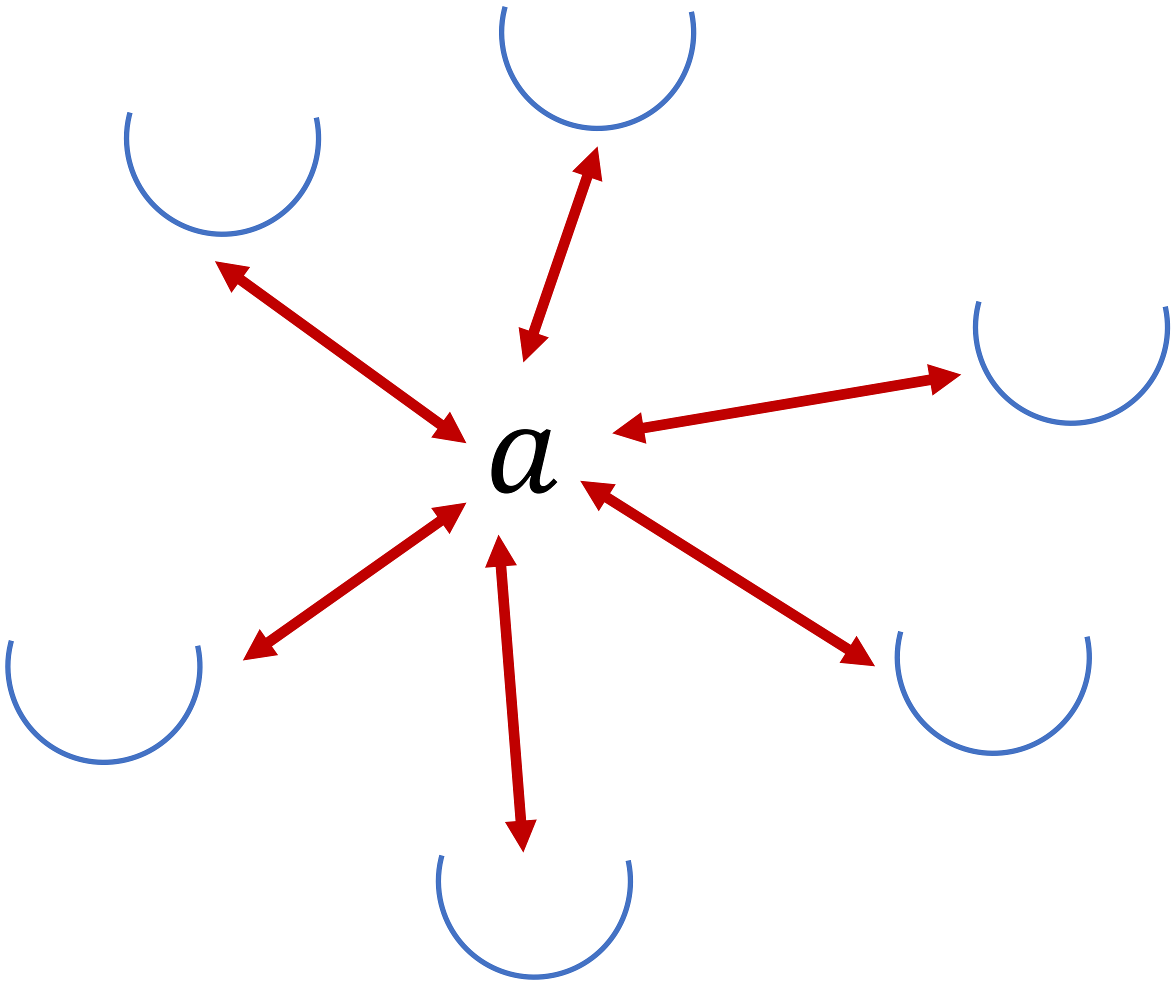



Gull, Emanuel, Andrew J. Millis, Alexander I. Lichtenstein, Alexey N. Rubtsov, Matthias Troyer, and Philipp Werner. "Continuous-time Monte Carlo methods for quantum impurity models." *Reviews of Modern Physics* 83, no. 2 (2011): 349.

# Normally, $N$ is large $\sim 10^6 - 10^{12}$



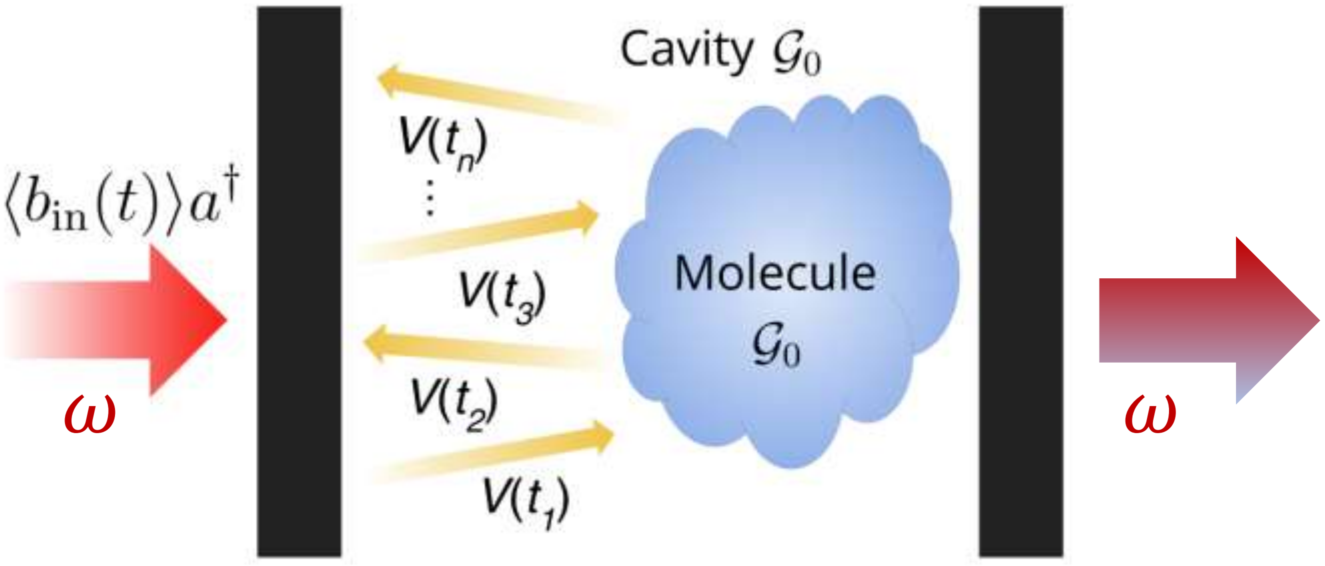
$\approx$




Makri, Nancy. "The linear response approximation and its lowest order corrections: An influence functional approach." *The Journal of Physical Chemistry B* 103.15 (1999): 2823-2829.

# Linear response of molecular polaritons

$$T(\omega) = \kappa_L \kappa_R |D^R(\omega)|^2,$$
$$R(\omega) = 1 + 2\kappa_L \Im D^R(\omega) + \kappa_L^2 |D^R(\omega)|^2,$$
$$A(\omega) = -\kappa_L [\kappa |D^R(\omega)|^2 + 2\Im D^R(\omega)].$$




$$\mathcal{G} = \mathcal{G}_0 + \mathcal{G}_0 \mathcal{V} \mathcal{G}_0 + \mathcal{G}_0 \mathcal{V} \mathcal{G}_0 \mathcal{V} \mathcal{G}_0 + \mathcal{G}_0 \mathcal{V} \mathcal{G}_0 \mathcal{V} \mathcal{G}_0 \mathcal{V} \mathcal{G}_0$$

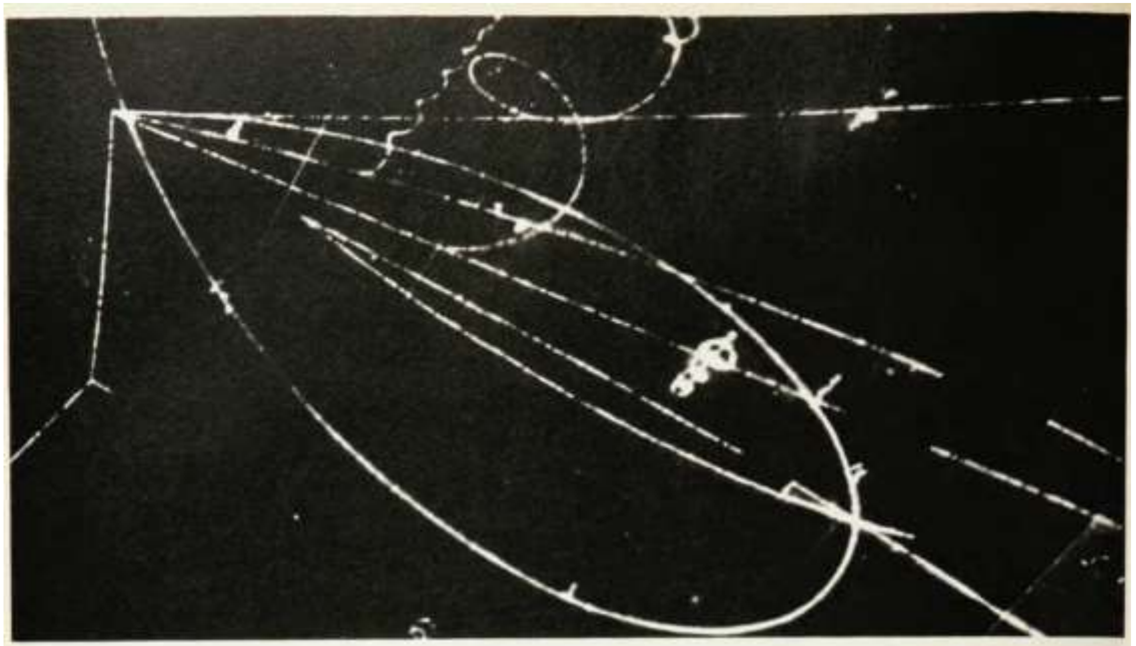
*Photon Green's function*

STRATEGY: Carry a 1/N expansion of $D^R(\omega)$ keeping $\Omega = \sqrt{N}g$ fixed.

$$\begin{aligned} D^R(\omega) &= -i \int_{-\infty}^{\infty} dt e^{i\omega t} \Theta(t) \langle [a(t), a^\dagger] \rangle \\ &= -i \int_{-\infty}^{\infty} dt e^{i\omega t} \Theta(t) \langle \mathscr{A}(t) a^\dagger \rangle \\ &= -i \int_{-\infty}^{\infty} dt e^{i\omega t} \Theta(t) \langle e^{i\mathscr{L}' t/\hbar} \mathscr{A} e^{-i\mathscr{L}' t/\hbar} a^\dagger \rangle \\ &= \langle \mathscr{A} \mathscr{G}(\omega) a^\dagger \rangle \end{aligned}$$


J. Yuen-Zhou, A. Koner, *Linear response of molecular polaritons*, *J. Chem. Phys.* 160, 154107 (2024).

# 1/N expansion



## Quarks, atoms, and the 1/N expansion

Problems in quantum chromodynamics that are currently impossible to solve may have useful approximate solutions when one assumes that quarks can have a large number, N, of "colors" instead of three.

Edward Witten

## Dimensional interpolation for two-electron atoms

D. R. Herschbach[a)]
*Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138 and Corporate Research Science Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801*

(Received 9 September, 1985; accepted 7 October 1985)

On expanding the effective mass in terms of $1/D$, this becomes

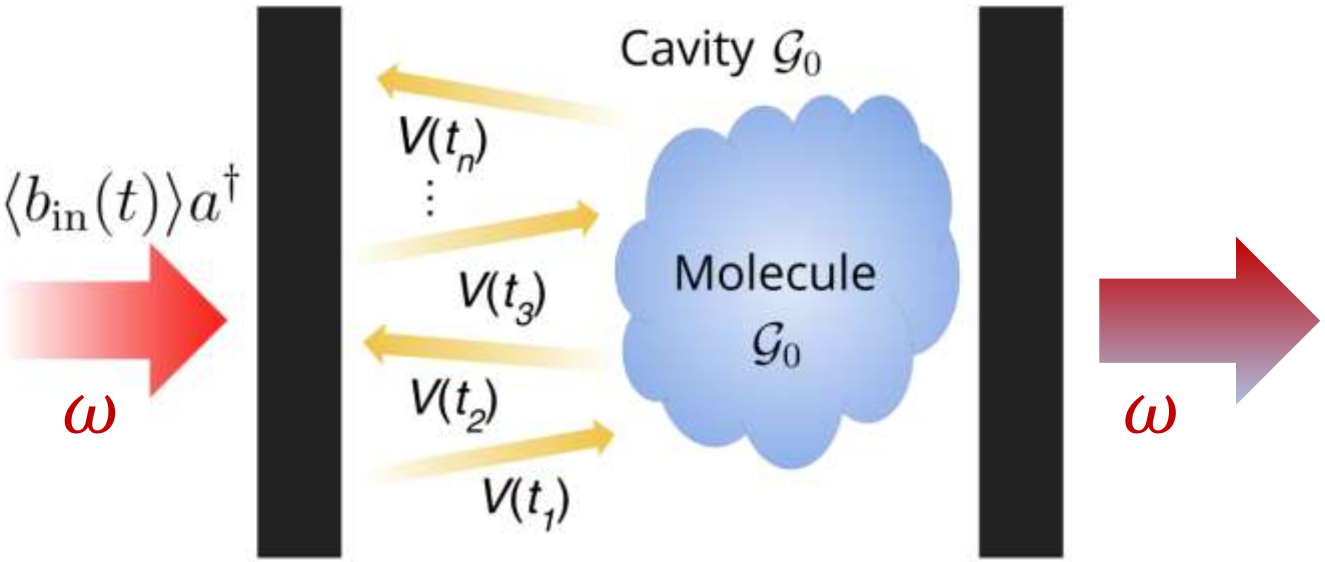
$$E_{0,D} = -\frac{1}{2}(2Z/D)^2\left(1 + \frac{2}{D} + \frac{3}{D^2} + \cdots\right). \quad (16)$$

TABLE I. Expectation values for ground state hydrogenic atom.

| | |
|---|---|
| $\langle R\rangle = \left(\frac{D-1}{2Z}\right)\left(\frac{D}{2}\right)$ | |
| $\langle R\rangle = \left(\frac{D-1}{2Z}\right)^2\left(\frac{D}{2}\right)\left(\frac{D+1}{2}\right)$ | |
| $\langle R^n\rangle = \langle R\rangle^n \frac{(D+n-1)!}{D^{n-1}D!}$ | |
| $\langle R^{-1}\rangle = \left(\frac{2}{D-1}\right)^2 Z$ | for $D>1$ |
| $\langle R^{-2}\rangle = \left(\frac{2}{D-1}\right)^3\left(\frac{2}{D-2}\right)Z^2$ | for $D>2$ |
| $\langle R^{-n}\rangle = \langle R^{-1}\rangle^n \frac{(D-1)^{n-1}(D-n-1)!}{(D-2)!}$ | for $D>n$ |

# Linear response of molecular polaritons ($N \to \infty$)

$$T(\omega) = \kappa_L \kappa_R |D^R(\omega)|^2,$$
$$R(\omega) = 1 + 2\kappa_L \Im D^R(\omega) + \kappa_L^2 |D^R(\omega)|^2,$$
$$A(\omega) = -\kappa_L[\kappa |D^R(\omega)|^2 + 2\Im D^R(\omega)].$$



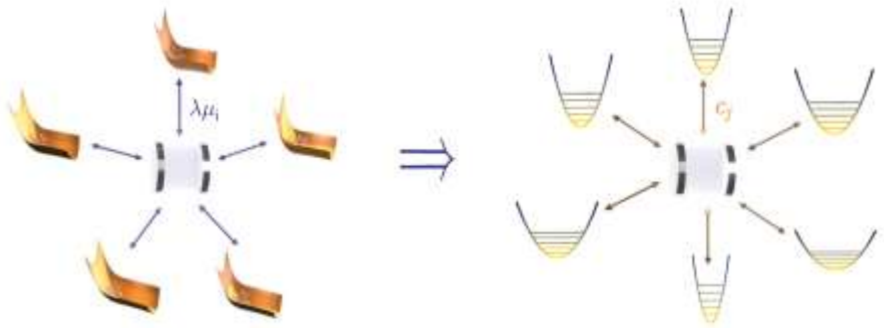

$$\mathcal{G} = \mathcal{G}_0 + \mathcal{G}_0 \mathcal{V} \mathcal{G}_0 + \mathcal{G}_0 \mathcal{V} \mathcal{G}_0 \mathcal{V} \mathcal{G}_0 + \mathcal{G}_0 \mathcal{V} \mathcal{G}_0 \mathcal{V} \mathcal{G}_0 \mathcal{V} \mathcal{G}_0$$

Photon Green's function

$$\begin{aligned} D^R(\omega) &= -i \int_{-\infty}^{\infty} dt e^{i\omega t} \Theta(t) \langle [a(t), a^\dagger] \rangle \\ &= -i \int_{-\infty}^{\infty} dt e^{i\omega t} \Theta(t) \langle \mathscr{A}(t) a^\dagger \rangle \\ &= -i \int_{-\infty}^{\infty} dt e^{i\omega t} \Theta(t) \langle e^{i\mathscr{L}' t/\hbar} \mathscr{A} e^{-i\mathscr{L}' t/\hbar} a^\dagger \rangle \\ &= \langle \mathscr{A} \mathscr{G}(\omega) a^\dagger \rangle \\ &\overset{N \to \infty}{=} \frac{1}{\omega - \omega_{ph} + i\frac{\kappa}{2} + \chi^{(1)}(\omega)} \end{aligned}$$

J. Yuen-Zhou, A. Koner, *Linear response of molecular polaritons*, *J. Chem. Phys.* 160, 154107 (2024).

# Linear response of molecular polaritons ($N \to \infty$)



$$T(\omega) = \frac{\kappa_L \kappa_R}{\left|\omega - \omega_{ph} + i\frac{\kappa}{2} + \frac{\omega_c}{2}\chi^{(1)}(\omega)\right|^2}$$

$$A(\omega) = \frac{\kappa_L \omega_{ph} \, \Im\chi^{(1)}(\omega)}{\left|\omega - \omega_{ph} + i\frac{\kappa}{2} + \frac{\omega_c}{2}\chi^{(1)}(\omega)\right|^2}$$

$$= \frac{\omega_{ph}}{\kappa_R} \mathrm{Im}[\chi^{(1)}(\omega)] T(\omega)$$

$$R(\omega) = 1 - T(\omega) - A(\omega)$$

When $N \to \infty$ and $\rho(0) = \rho_{cav} \otimes \rho_{mol}$,

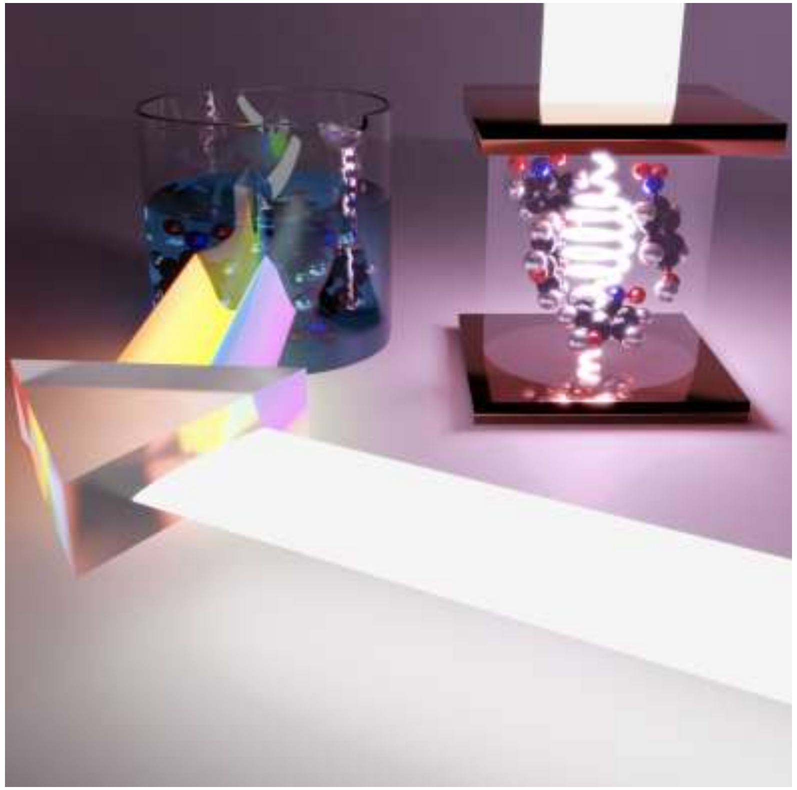
- ❖ Molecular polariton problem becomes harmonic.
- ❖ Linear response depends only on linear susceptibility $\chi(\omega)$ of the ensemble!
- ❖ Works for disorder, finite $T$, any lineshape…
- ❖ Recover classical optics!

J. Yuen-Zhou, A. Koner, *Linear response of molecular polaritons*, *J. Chem. Phys.* 160, 154107 (2024).
See also: J. A. Ćwik, …, J. Keeling. "Excitonic spectral features in strongly coupled organic polaritons." *Physical Review A* 93.3 (2016): 033840.
M. Ahsan Zeb, P. G. Kirton, and J. Keeling, "Exact states and spectra of vibrationally dressed polaritons." *ACS Photonics* 5.1 (2018): 249-257.

# Under very general assumptions, when $N \to \infty$, polaritons are just optical filters

In the thermodynamic limit, the linear response of polaritons is just optical filtering of the material response through polariton transmission windows:

$$A(\omega) = \frac{\omega_{ph}}{\kappa_R} \mathrm{Im}[\chi^{(1)}(\omega)]T(\omega)$$

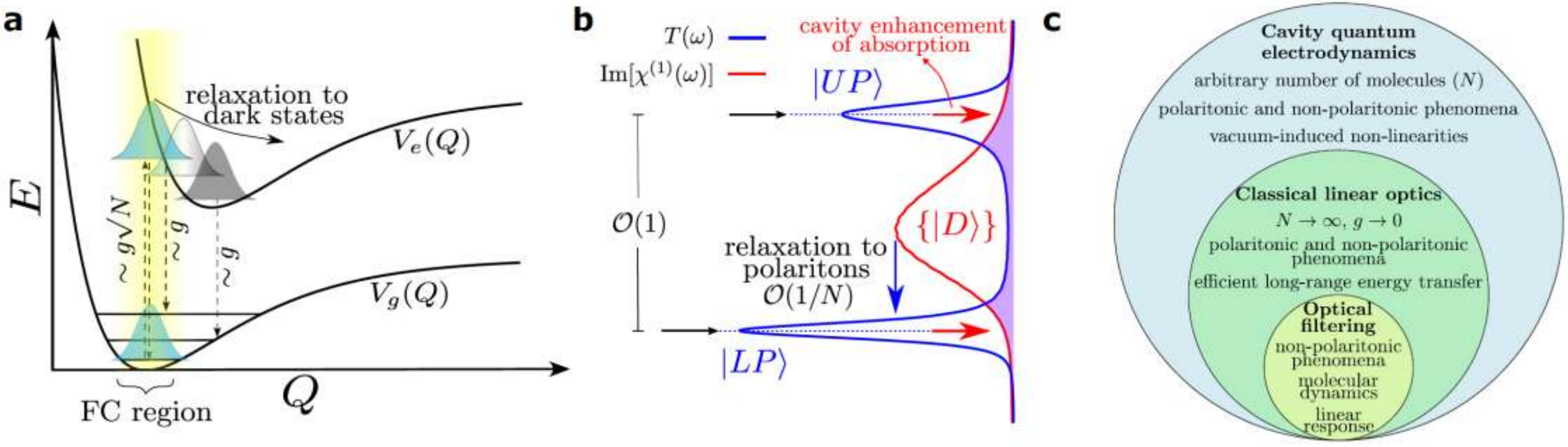


Kai Schwennicke

Kai Schwennicke, Arghadip Koner, Juan B. Pérez-Sánchez, Wei Xiong, Noel C. Giebink, Marissa L. Weichman, Joel Yuen-Zhou, Chem. Soc. Rev. **54**, 6482-6504, 2025

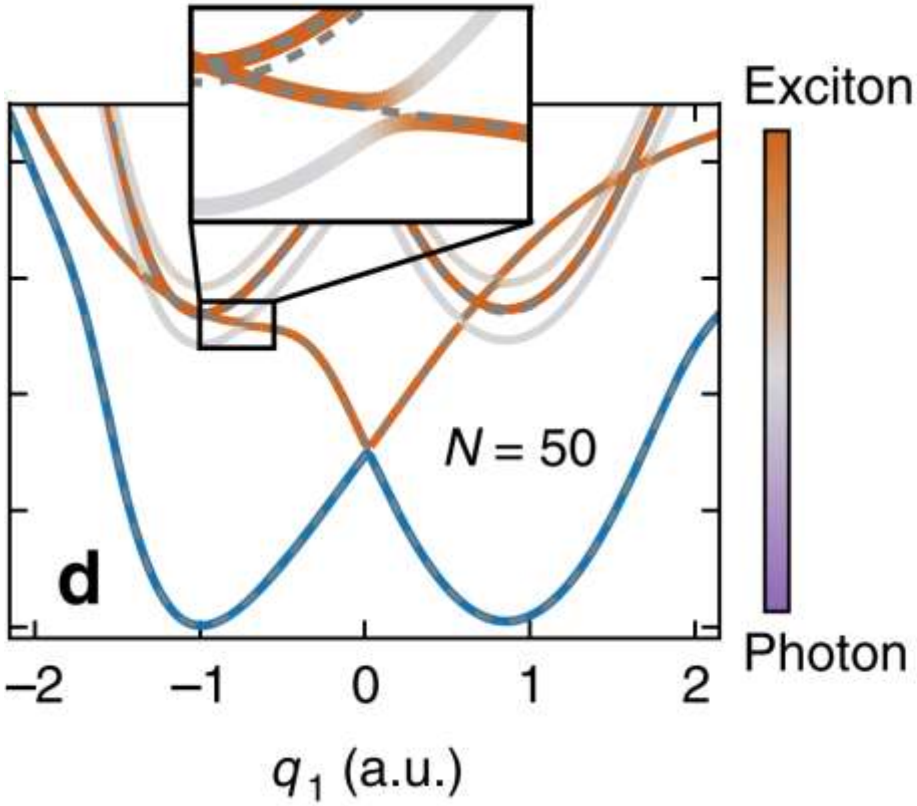
# Under very general assumptions, when $N \to \infty$, polaritons are just optical filters

IMPORTANT: Not just the linear absorption, but also the ultrafast polariton dynamics in the first-excitation manifold can be completely replicated using a shaped pulse outside of the cavity.




Kai Schwennicke, Arghadip Koner, Juan B. Pérez-Sánchez, Wei Xiong, Noel C. Giebink, Marissa L. Weichman, Joel Yuen-Zhou, Chem. Soc. Rev. **54**, 6482-6504, 2025

# Consistency with previous studies




Galego, Javier, Francisco J. Garcia-Vidal, and Johannes Feist, Nature Communications 7.1 (2016): 1-6

*CLAIM: Polaritonic potential energy surface doesn't show vibronic coupling for large enough Rabi splitting (polaron decoupling)*

Phenomenon: For sufficiently large Rabi splitting, polaritons don't even show homogeneous broadening from molecules.

Explanation 1: Polaritonic potential energy surfaces show "polaron decoupling" (Herrera, Felipe, and Frank C. Spano, Physical Review Letters 116.23 (2016): 238301; Galego, Javier, Francisco J. Garcia-Vidal, and Johannes Feist, Nature Communications 7.1 (2016): 1-6).

Explanation 2: (frequency domain) Optical filtering (K. Schwennicke, et. al., Chem. Soc. Rev. Chem. Soc. Rev. **54**, 6482-6504, 2025).

# SCOM23

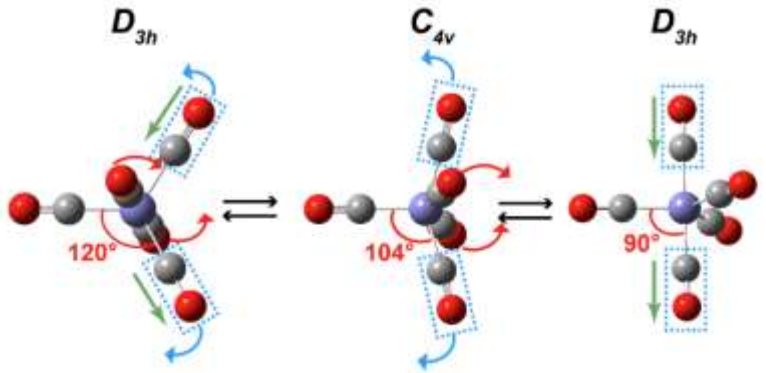

During SCOM23, there was a consensus as a community to try to distinguish standard cavity phenomena (classical field enhancement, lasing, Purcell effect, etc.) from "nontrivial" strong coupling phenomena.

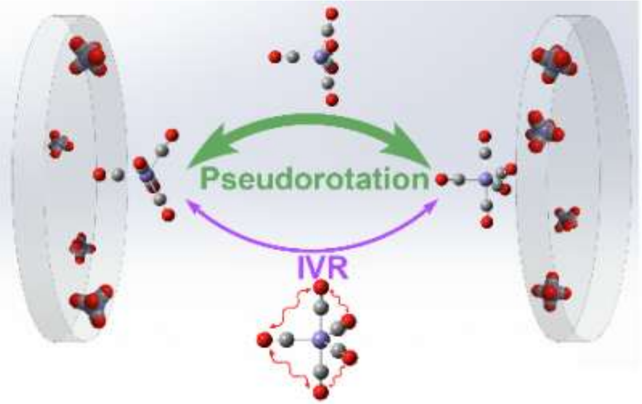
MAIN QUESTION OF THE FIELD: Which polaritonic effects are *truly cavity induced* and cannot be obtained outside the cavity and which ones are not?

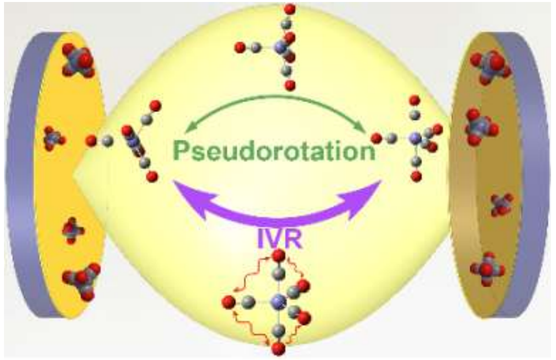
## So why do experimentalists still report experiments beyond this optical filtering paradigm?

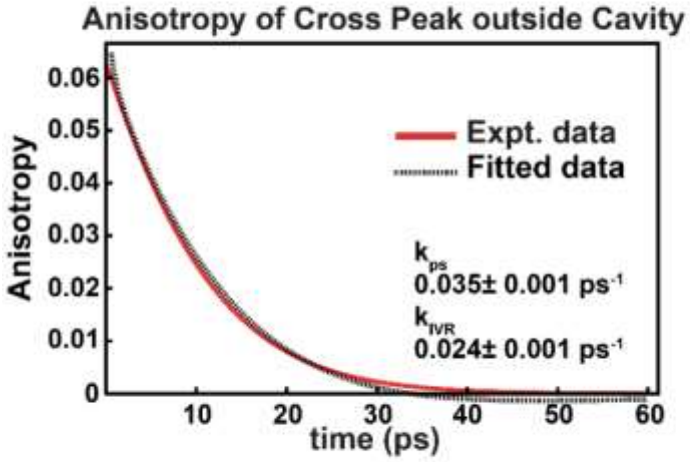
IVR < Pseudorotation: Out of cavity
IVR > Pseudorotation: In cavity

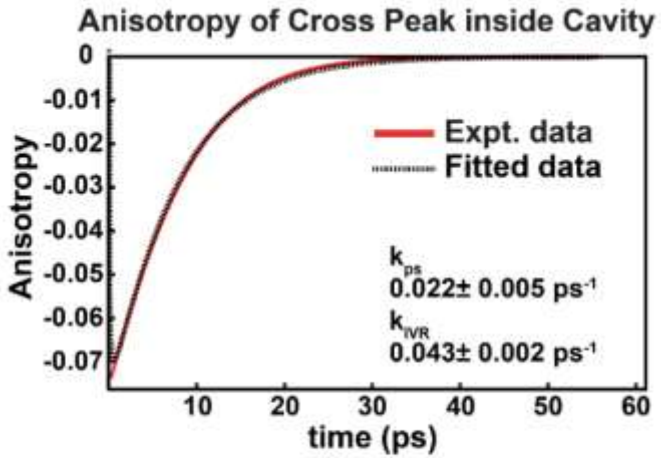
$Fe(CO)_5$: Pseudorotation vs IVR



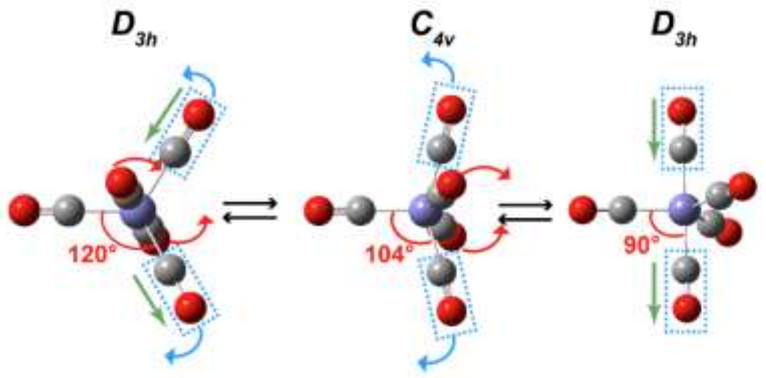



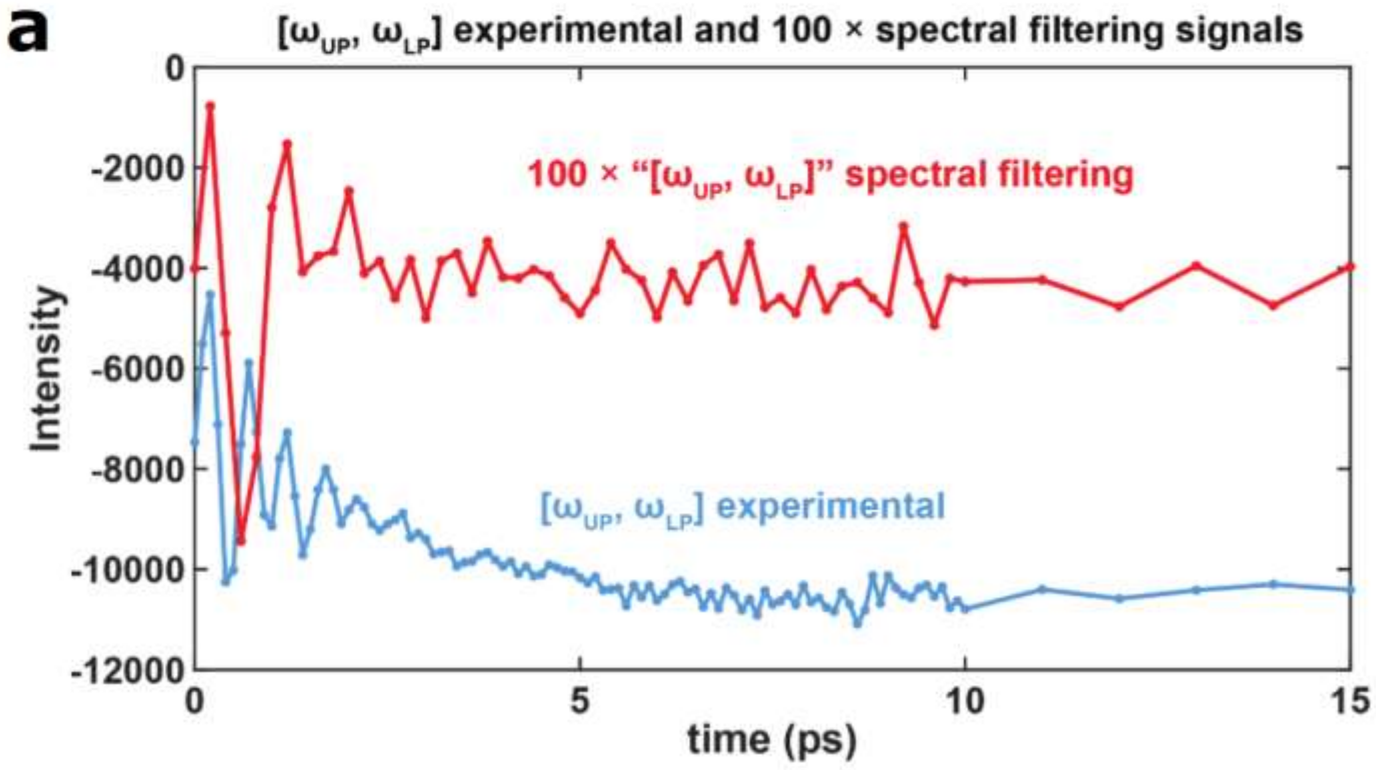

T.T. Chen, M. Du, Z. Yang, J. Yuen-Zhou, and W. Xiong, Cavity-Enabled Enhancement of Ultrafast Intramolecular Vibrational Redistribution over Pseudorotation, Science 378, 6621, 790-794 (2022).

# So why do experimentalists still report experiments beyond this optical filtering paradigm?

We still don't understand any of these experiments: Why are there any ultrafast (<10 ps) dynamics different from out-of-cavity excitation?

$Fe(CO)_5$: Pseudorotation vs IVR




T.T. Chen, M. Du, Z. Yang, J. Yuen-Zhou, and W. Xiong, Cavity-Enabled Enhancement of Ultrafast Intramolecular Vibrational Redistribution over Pseudorotation, Science 378, 6621, 790-794 (2022).

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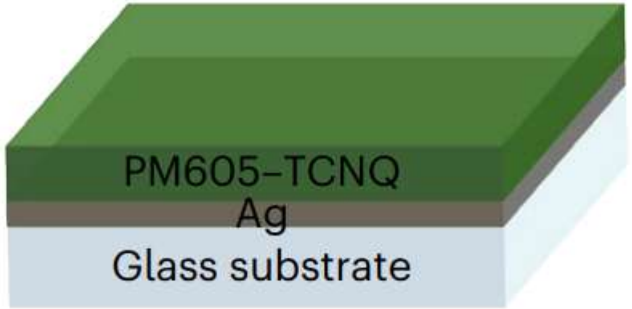
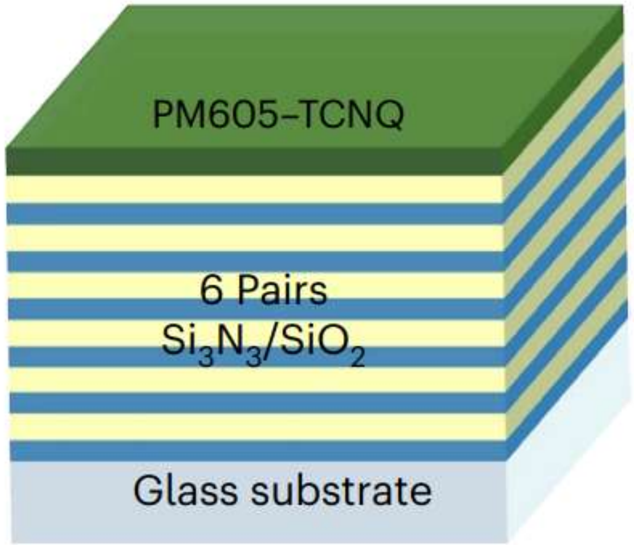
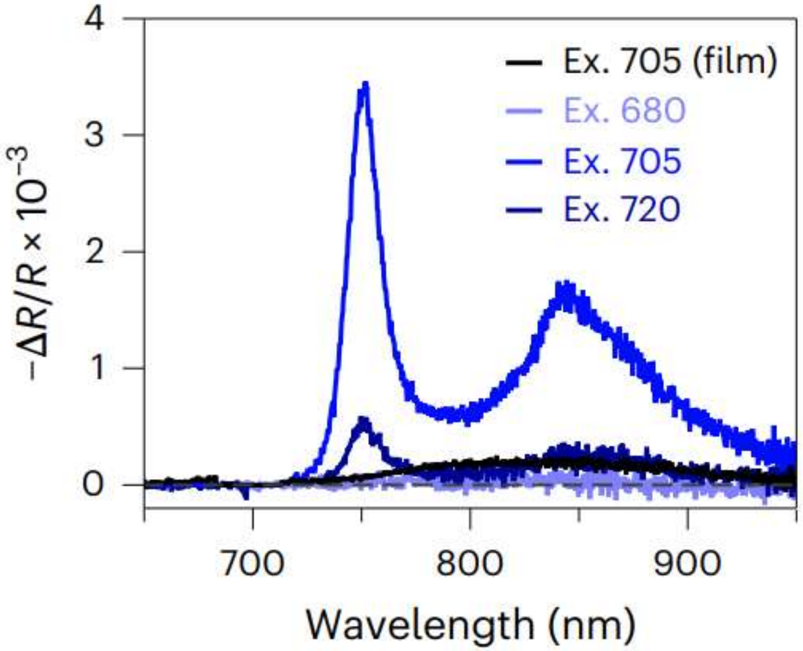


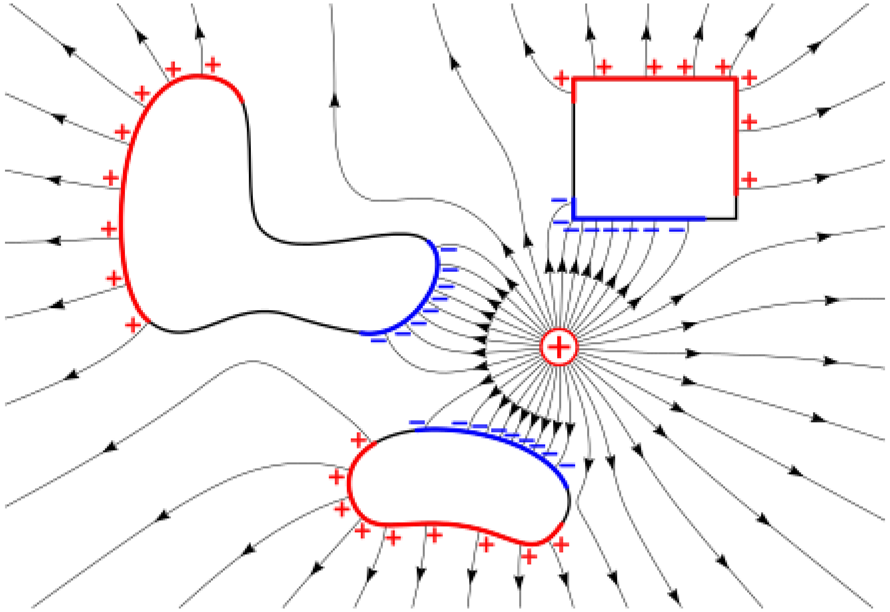




K. Rashidi, E. Michail, B. Salcido-Santacruz, B., Y. Paudel, V. M. Menon, and M. Y. Sfeir, Efficient and tunable photochemical charge transfer via long-lived bloch surface wave polaritons. *Nature Nanotechnology*, 1-7 (2025).

# Summary a1: Polaritons as optical filters

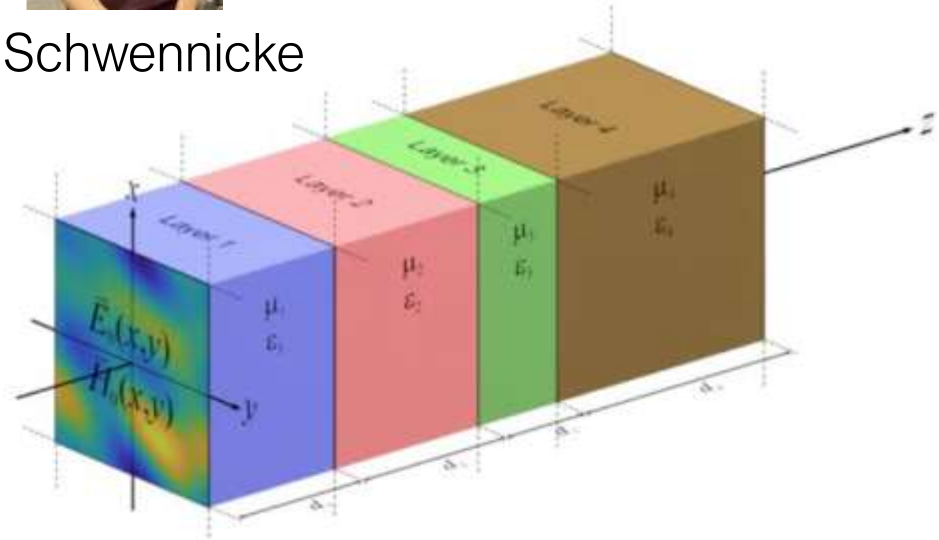
Atoms and molecules
in $D \to \infty$ dimensions



Quantum mechanics
⇒ Classical electrostatics

Kai Schwennicke

Molecular polaritons
when $N \to \infty$



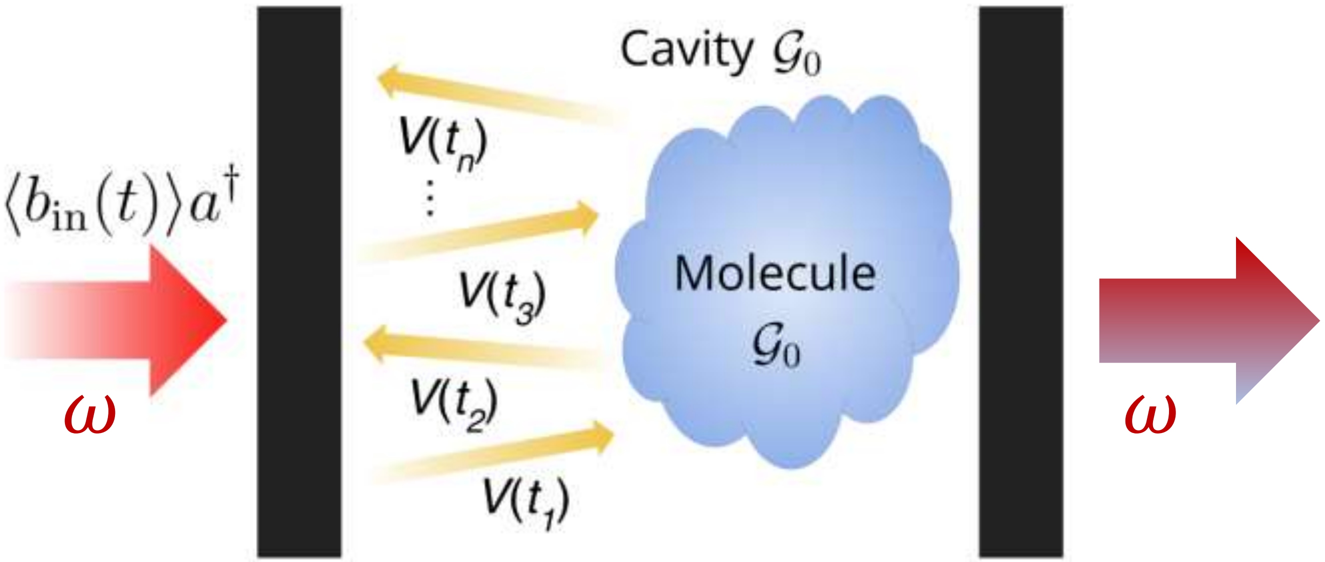
Quantum optics
⇒ Classical optics
(consequence of CUT-E $0^{th}$ order)

Kai Schwennicke, Arghadip Koner, Juan B. Pérez-Sánchez, Wei Xiong, Noel C. Giebink, Marissa L. Weichman, Joel Yuen-Zhou, Chem. Soc. Rev. **54**, 6482-6504, 2025

# For finite $N$, there are hidden optical nonlinearities even in cavity linear spectra!

$$T(\omega) = \kappa_L \kappa_R |D^R(\omega)|^2,$$
$$R(\omega) = 1 + 2\kappa_L \Im D^R(\omega) + \kappa_L^2 |D^R(\omega)|^2,$$
$$A(\omega) = -\kappa_L[\kappa |D^R(\omega)|^2 + 2\Im D^R(\omega)].$$

Light bounces back and forth between the molecules and the photon. Hence, there are in principle multiple pump-dump processes already buried in linear optical spectra!




$$\begin{aligned} D^R(\omega) &= -i\int_{-\infty}^{\infty} dt e^{i\omega t}\Theta(t)\langle[a(t), a^\dagger]\rangle \\ &= -i\int_{-\infty}^{\infty} dt e^{i\omega t}\Theta(t)\langle \mathscr{A}(t) a^\dagger\rangle \\ &= -i\int_{-\infty}^{\infty} dt e^{i\omega t}\Theta(t)\langle e^{i\mathscr{L}'t/\hbar}\mathscr{A} e^{-i\mathscr{L}'t/\hbar} a^\dagger\rangle \\ &= \langle \mathscr{A}\mathscr{G}(\omega) a^\dagger\rangle \end{aligned}$$

$$\mathscr{G} = \mathscr{G}_0 + \mathscr{G}_0\mathscr{V}\mathscr{G}_0 + \mathscr{G}_0\mathscr{V}\mathscr{G}_0\mathscr{V}\mathscr{G}_0 + \mathscr{G}_0\mathscr{V}\mathscr{G}_0\mathscr{V}\mathscr{G}_0\mathscr{V}\mathscr{G}_0$$

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Light bounces back and forth between the molecules and the photon. Hence, there are in principle multiple pump-dump processes already buried in linear optical spectra!

For arbitrary $N$, there are hidden optical nonlinearities in polariton spectra,

$$D^R(\omega) = \frac{1}{\omega - \omega_{ph} + i\frac{\kappa}{2} + \sum_{l=0}^{\infty}\left(\frac{\omega_c}{2}\right)^l \chi_N^{(2l+1)}(\omega, [-\omega_{ph}, \omega_{ph}]^l)^2}$$

These go away when $N \to \infty$,

$$D^R(\omega) \overset{N \to \infty}{=} \frac{1}{\omega - \omega_{ph} + i\frac{\kappa}{2} + \chi^{(1)}(\omega)}$$

Arghadip Koner

A. Koner and J. Yuen-Zhou, *Hidden nonlinear optical susceptibilities in linear polaritonic spectra*, Optica 12 (10), 1625-1631 (2025).
S. Raghavan-chitra, J. Yuen-Zhou, and A. Koner, *High Q microcavities unveil quantum rare events*, submitted, 2025.

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In very different language, similar results:


M. Ahsan Zeb, P. G. Kirton, and J. Keeling. Exact states and spectra of vibrationally dressed polaritons. *ACS Photonics* 5.1 (2018): 249-257.

H. P. Ojeda Collado, M. H. Michael, J. Skulte, A. Rubio, and L. Mathey. Equilibrium parametric amplification in Raman-cavity hybrids. *Physical Review Letters* 133.11 (2024): 116901.

J. Román-Roche and D. Zueco. Effective theory for matter in non-perturbative cavity QED. *SciPost Physics Lecture Notes* (2022): 050.

J. Román-Roche, A. Gómez-León, F. Luis, D. Zueco, Linear response theory for cavity QED materials at arbitrary light-matter coupling strengths. Physical Review B. 2025 Jan 15;111(3):035156.

D. Barberena, Generalized Holstein-Primakoff mapping and 1/N expansion of collective spin systems undergoing single particle dissipation. *arXiv preprint arXiv:2508.05751* (2025).

# For finite $N$, there are hidden optical nonlinearities even in cavity linear spectra!

Need 3D photon confinement + high Q cavity: If photon is trapped long enough, it will experience rare events mediated by vacuum.

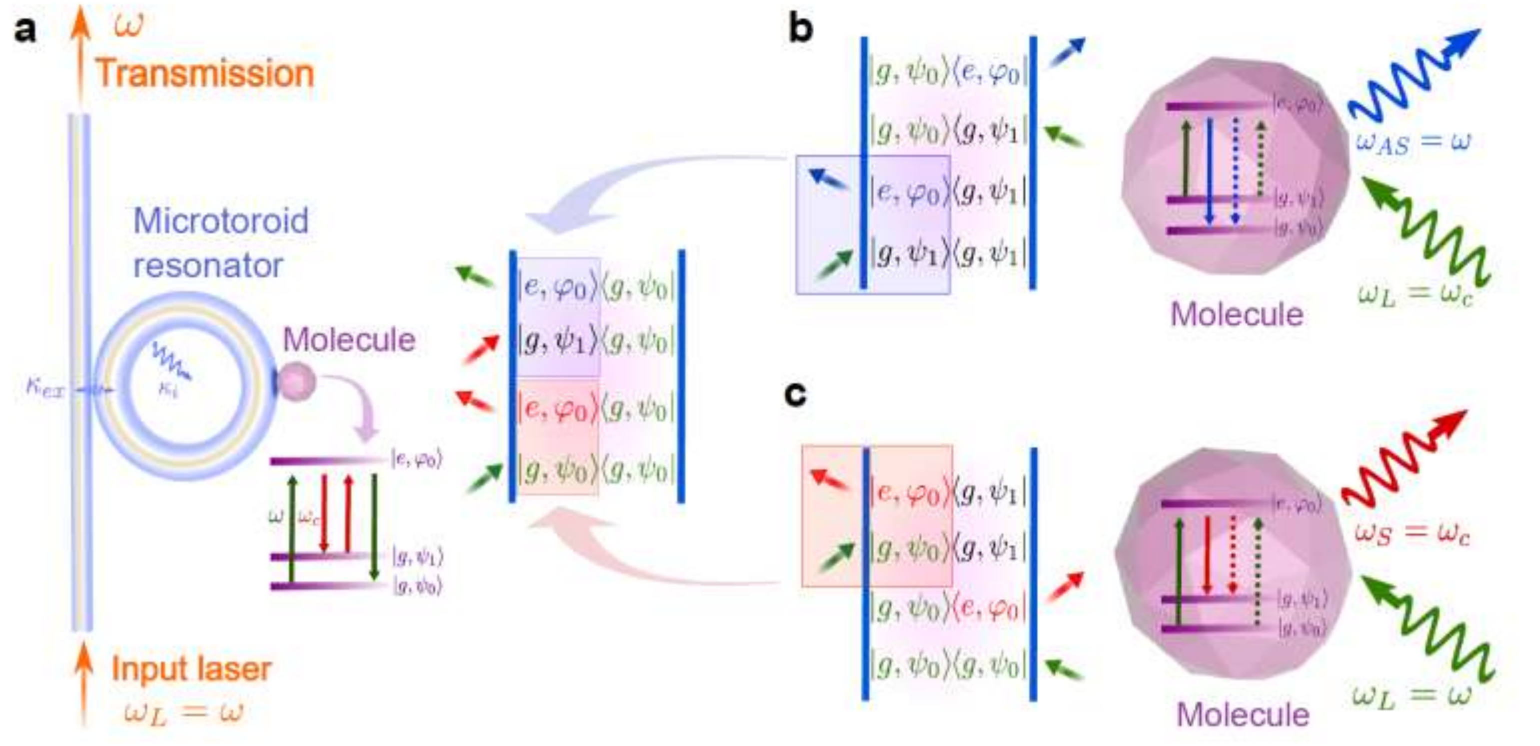


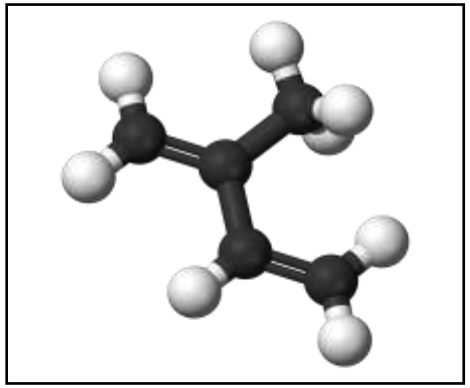

FIG. 1. **Schematic illustration of vacuum-mediated Raman processes in the linear optics of a microresonator system, highlighting the Stokes and anti-Stokes components. a,** A high-$Q$ microtoroid

Sricharan Raghavan-chitra

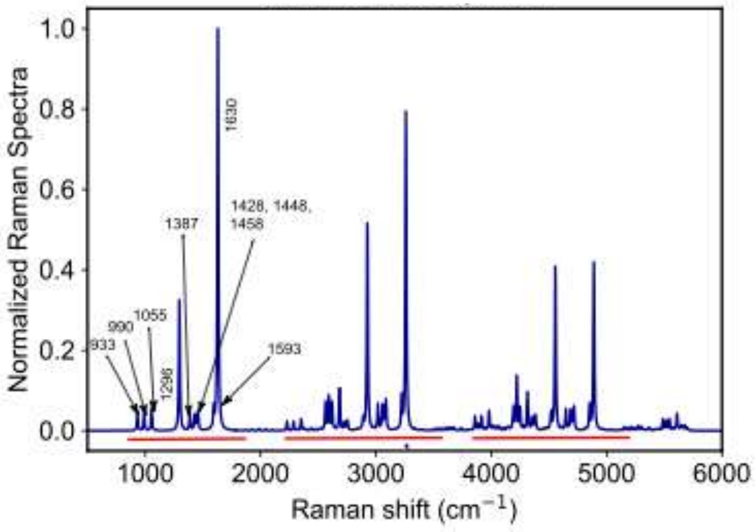
A. Koner and J. Yuen-Zhou, *Hidden nonlinear optical susceptibilities in linear polaritonic spectra*, Optica 12 (10), 1625-1631 (2025).
S. Raghavan-chitra, J. Yuen-Zhou, and A. Koner, *High Q microcavities unveil quantum rare events*, submitted, 2025.

# For finite $N$, there are hidden optical nonlinearities even in cavity linear spectra!

## *Isoprene*



Bare Raman spectrum




**Parameters:**

$\kappa^{-1} = 555$ ps

$\omega_c = \omega_{00}$

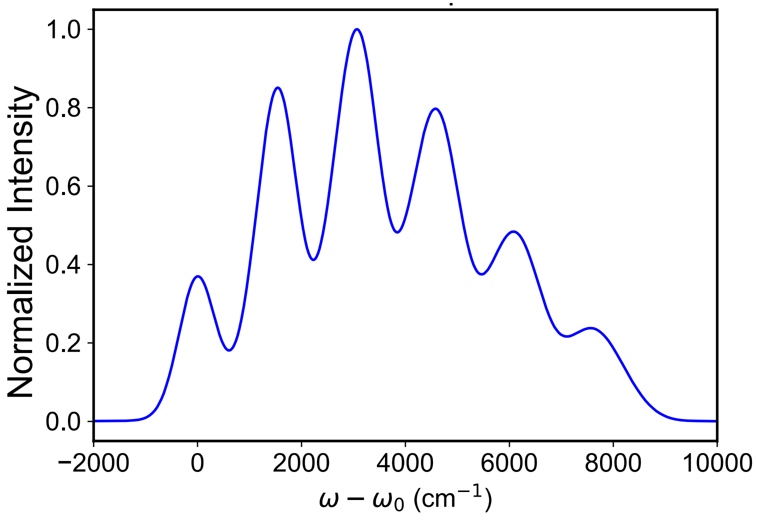
$\omega_{00} \approx 4.5$ eV

$g\sqrt{N} = 1$ eV

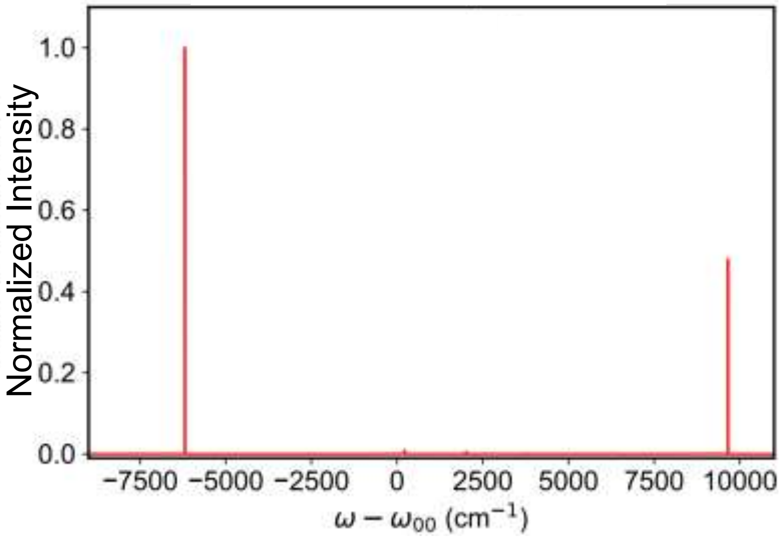
$N = 10^6$

Cavity $Q \approx 10^5$

Bare linear absorption




Polariton absorption



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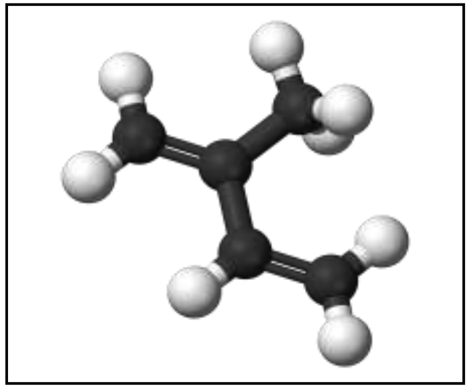
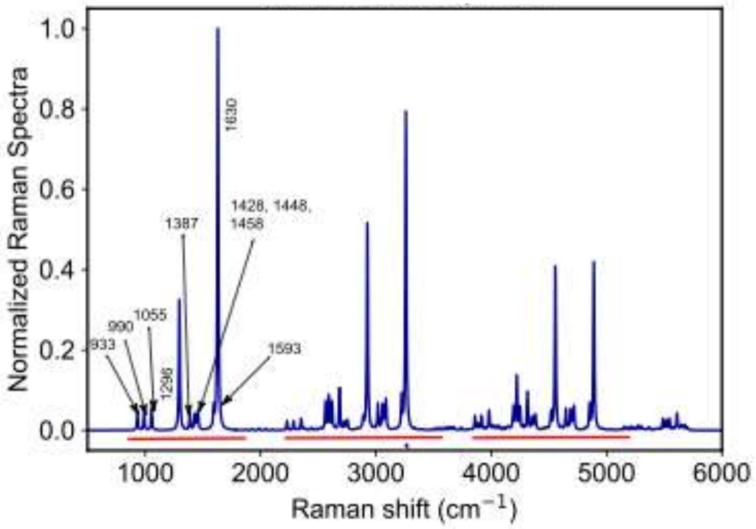


Bare Raman spectrum

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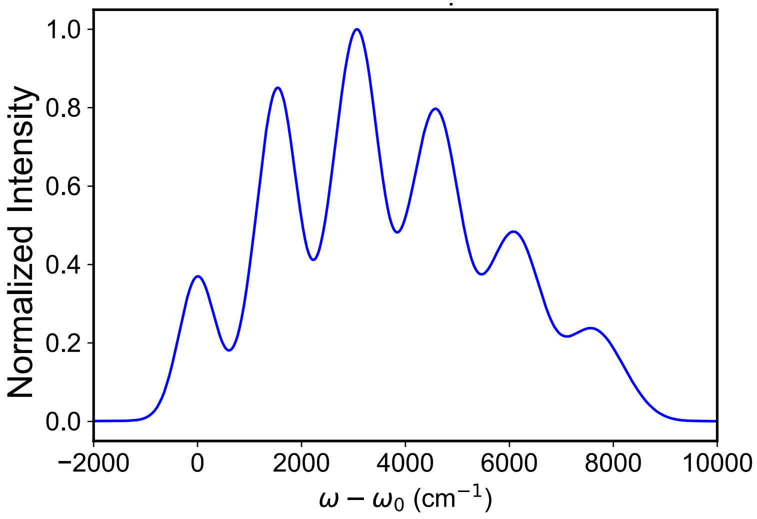
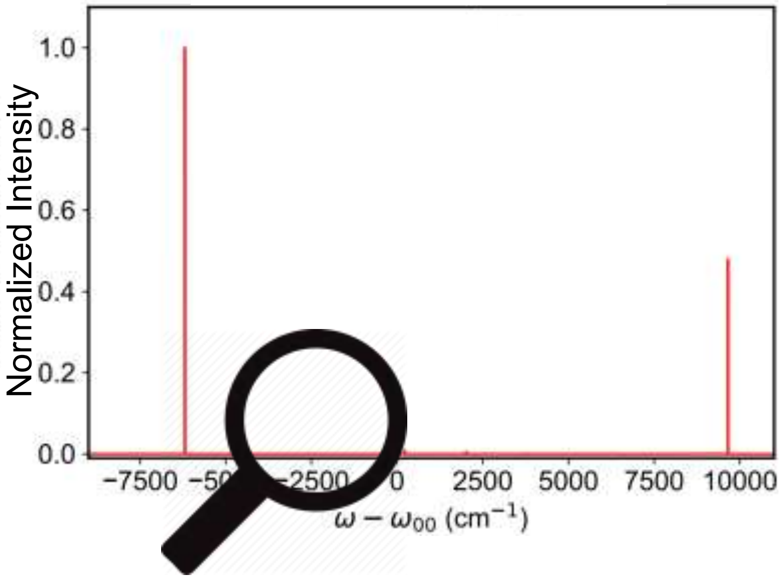
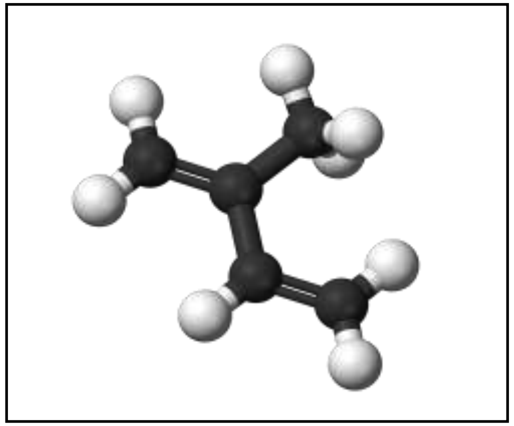


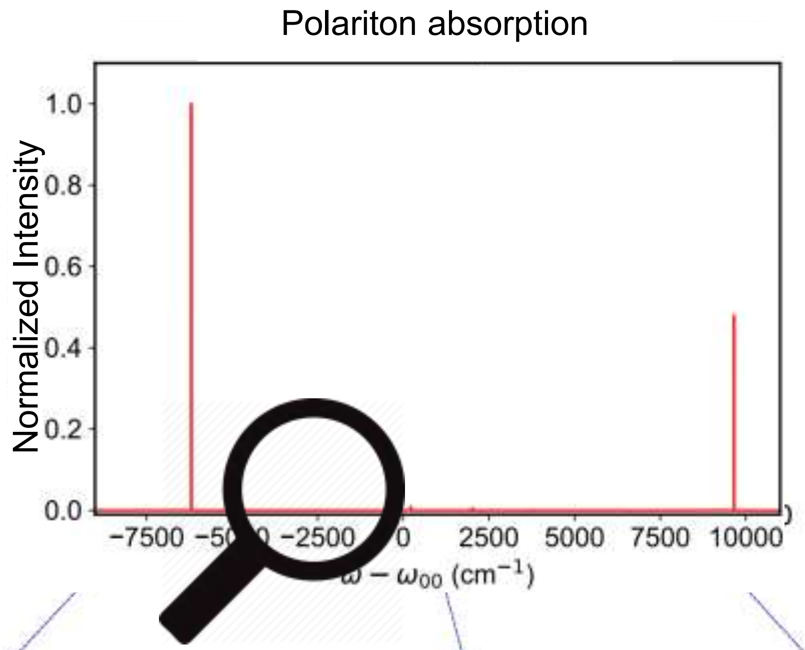

Polariton absorption



# For finite $N$, there are hidden optical nonlinearities even in cavity linear spectra!

*Isoprene*



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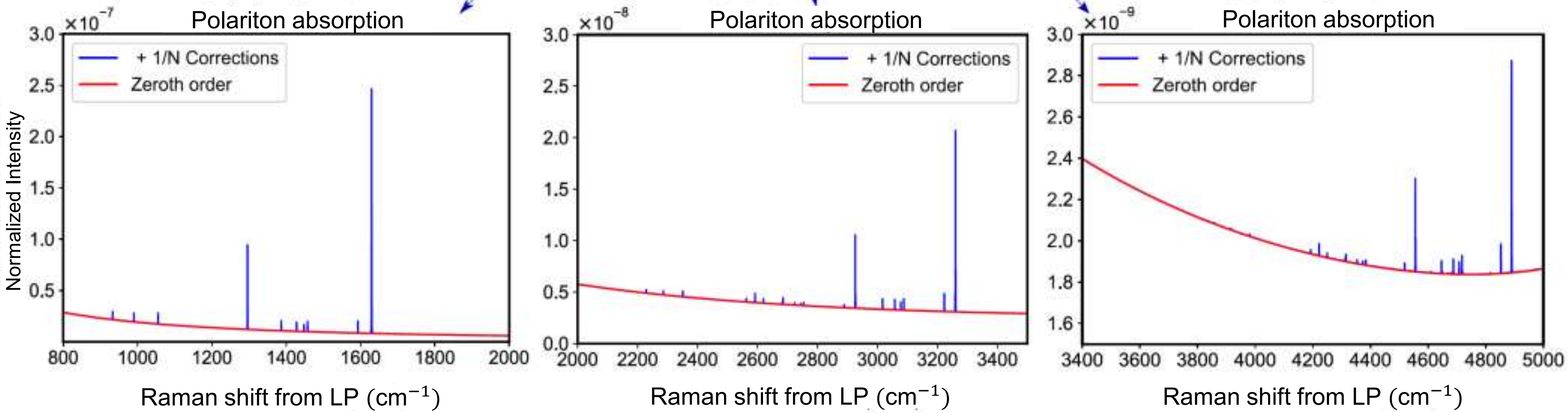

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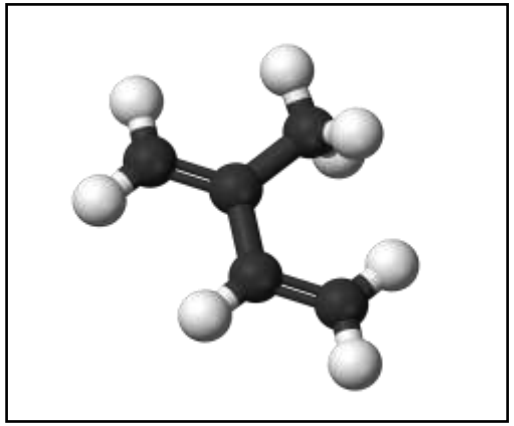

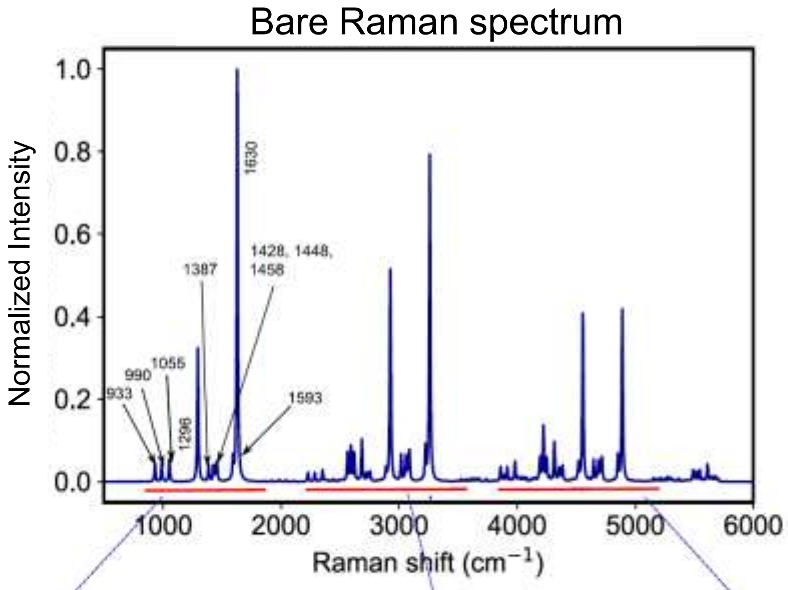


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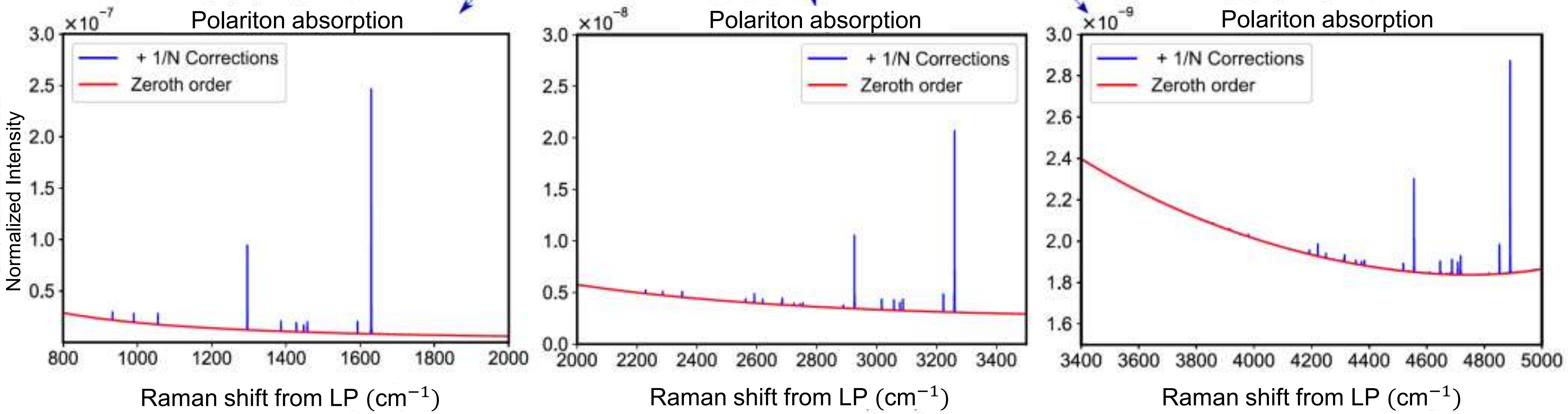
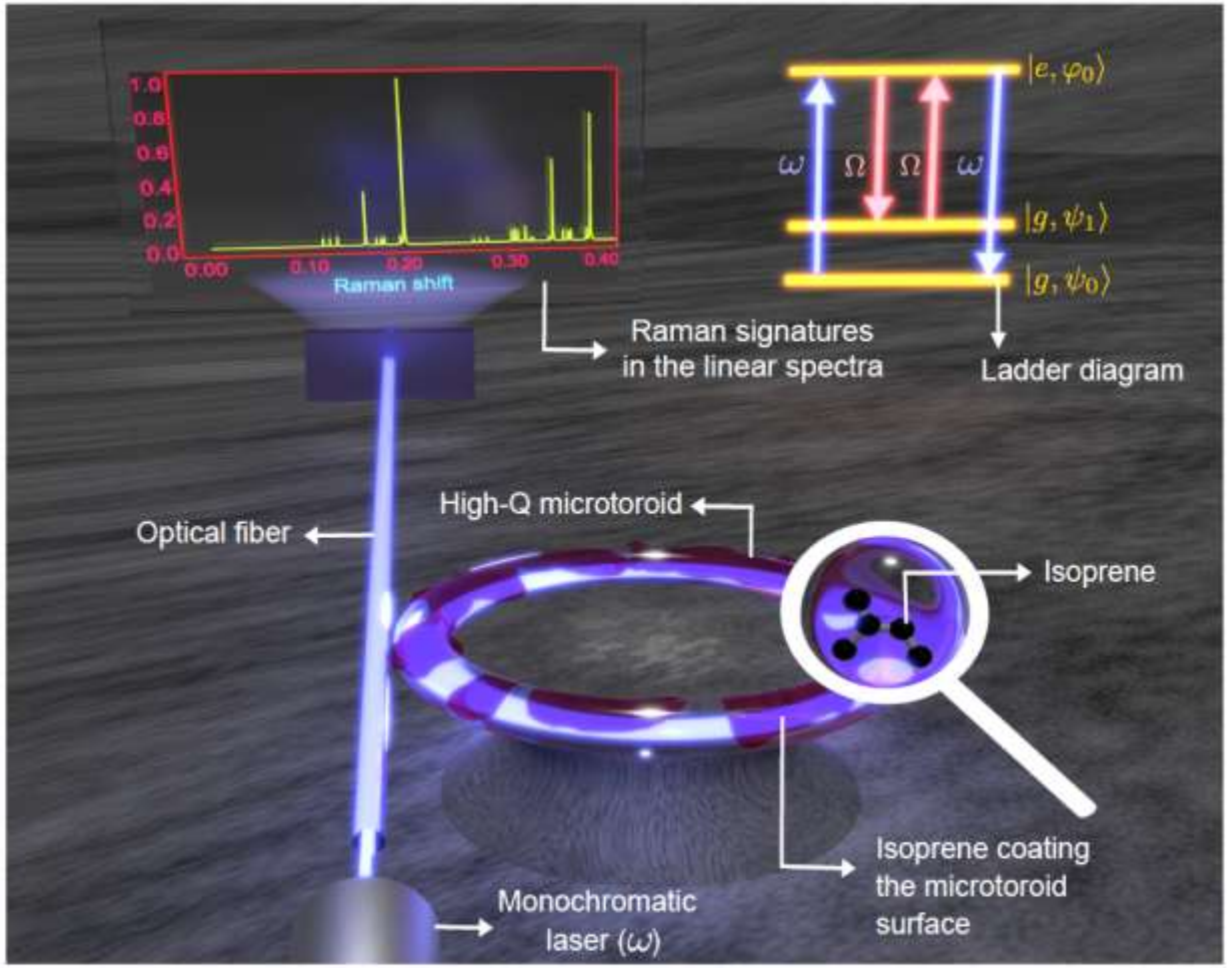
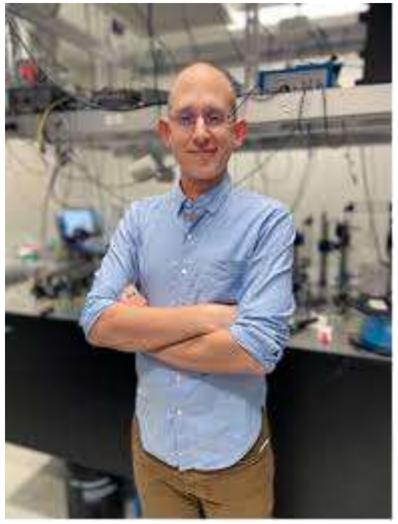


# New frontier of molecular polaritonics: high Q cavities




Carlos Saavedra

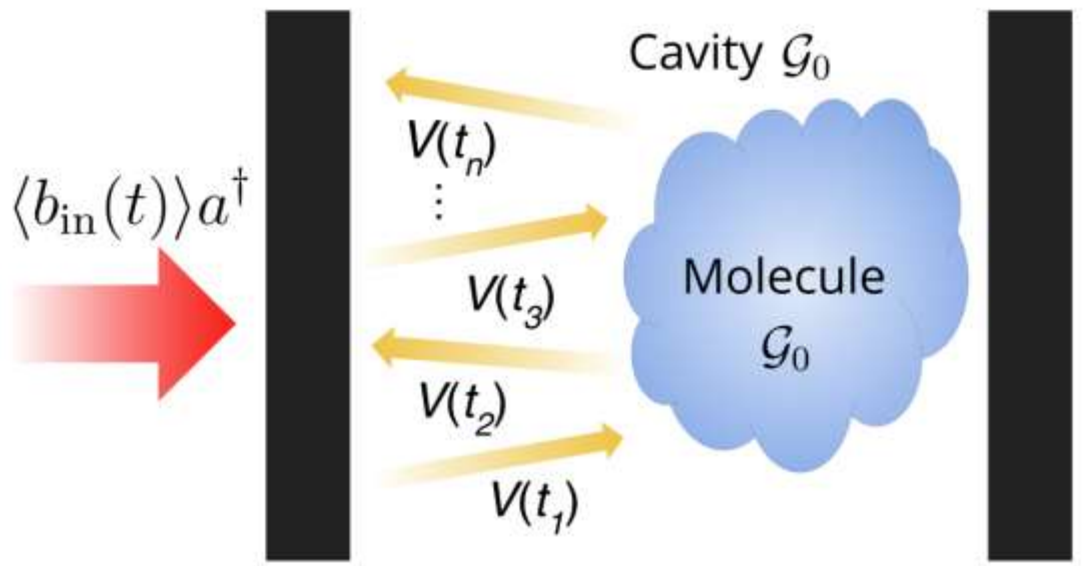


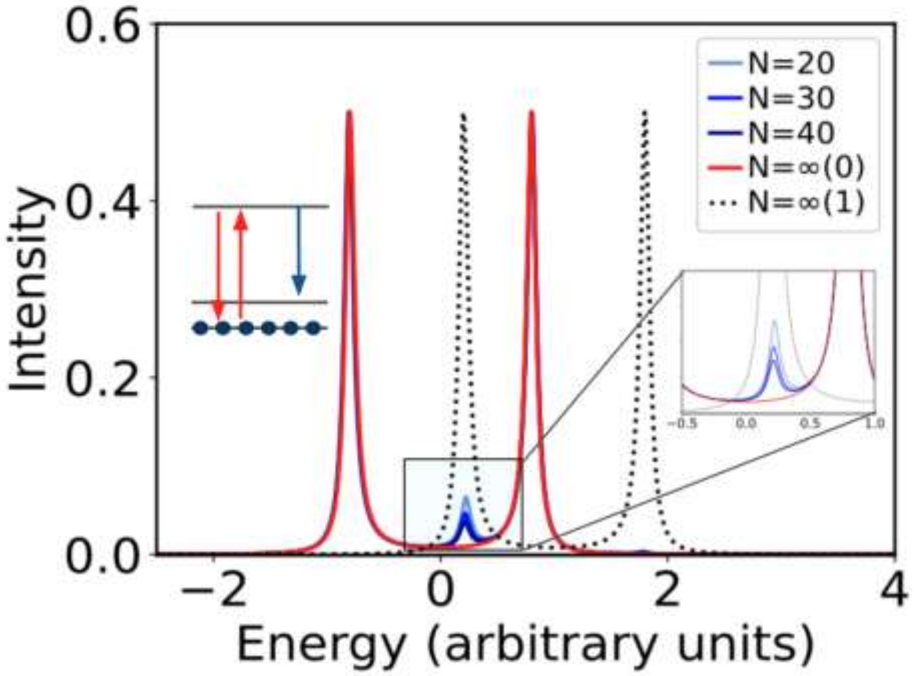
Randall Goldsmith

*UW Madison*

# SUMMARY a2: Vacuum corrections to linear optics

- High Q cavities harvest rare events (Vacuum induced Raman dressing). These are signatures of light-matter entanglement (Welman, Millan F., Tao E. Li, and Sharon Hammes-Schiffer, JCTC, 21.17 (2025): 8291-8307).
- Matter is anharmonic, cavity is harmonic. Given enough time, transmission of light will inform about material anharmonicities.
- Need $Q{\sim}10^5$ and $g{\sim}\kappa{\sim}\mu eV$ and discrete photon mode structure (3D photon confinement).




A. Koner and J. Yuen-Zhou, *Hidden nonlinear optical susceptibilities in linear polaritonic spectra*, Optica 12 (10), 1625-1631 (2025).
S. Raghavan-chitra, J. Yuen-Zhou, and A. Koner, *High Q microcavities reveal quantum rare events*, submitted, 2025.

# The big picture

## Optics

### Linear optics (Signal ∝ $I_{input}$)

#### Classical

- Absorption
- Refraction
- Diffraction
- Dispersion

#### Quantum

- Fluorescence and Purcell effect
- Fine structure of hydrogen
- Single photon interference
- **Vacuum-Induced Raman dressing**

### Nonlinear optics (Signal ∝ $I^{k>1}_{input}$)

#### Semi-Classical

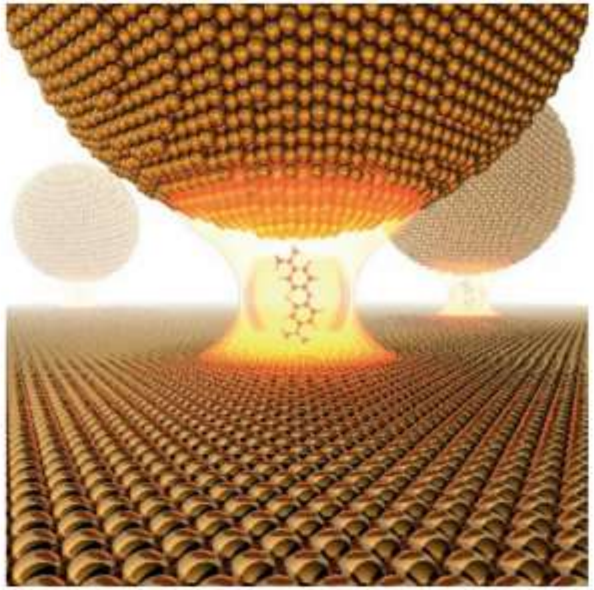
- Sum frequency generation,
- Stimulated emission
- Kerr effect, …

#### Quantum

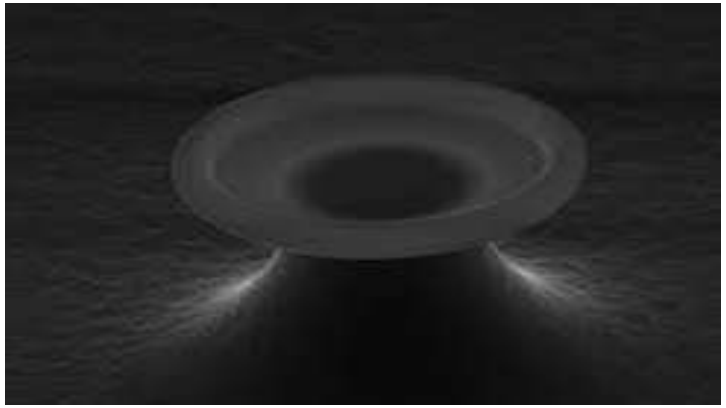
- Generation of squeezed light
- Superradiance
- SPDC
- SFWM, …

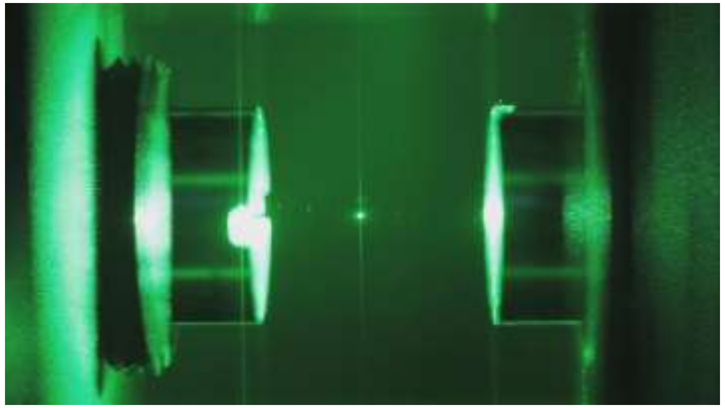
# When does classical linear optics break down? When $g \sim \kappa$

$$D^R(\omega) = \frac{1}{\omega - \omega_{ph} + i\frac{\kappa}{2} + \sum_{l=0}^{\infty} \left(\frac{\omega_c}{2}\right)^l \chi_N^{(2l+1)}(\omega, [-\omega_{ph}, \omega_{ph}]^l)^2}$$



Nanophotonics
$\kappa$ is large but $g$ is too
(small $N$)

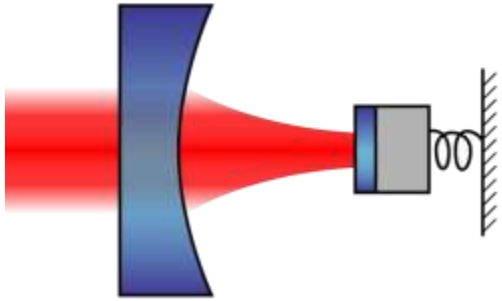




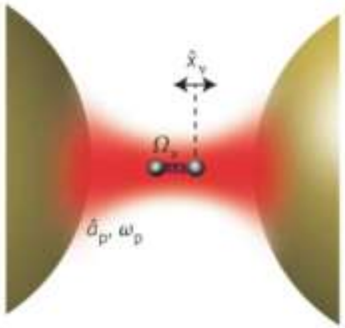
High Q dielectric cavities
$g$ is tiny but $\kappa$ is tiny too
(small or large $N$)

# Is vibrational strong coupling possible with $N$ =1, 2 molecules?

Cavity optomechanics



Molecular Cavity optomechanics



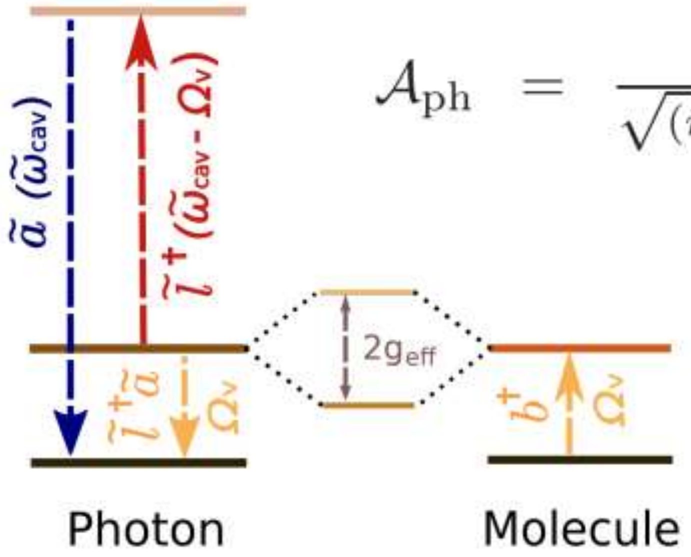
M. Aspelmeyer, T. J. Kippenberg, and F. Marquardt, Rev. Mod. Phys. 86, 1391 (2014). P. Roelli, C. Galland, N. Piro, and T. J. Kippenberg, Nature Nanotechnology 11, 164 (2016).

The cavity optomechanical Hamiltonian reads, ($b$ is vibrational mode, $a$ is the UV-vis cavity)

$$H_{\text{C-M}} = \hbar[\omega_{\text{cav}} + g_0(b^\dagger + b)]a^\dagger a + \hbar\Omega_{\text{v}} b^\dagger b$$

Pumping the cavity with a Raman pump laser $l$ such that $\omega_L = \omega_{cav} - \Delta \approx \omega_{cav} - \Omega_v$ gives rise to

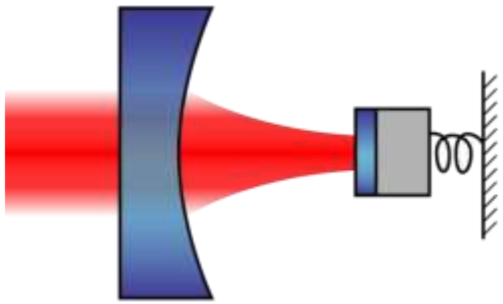
$$H_{C-M,\text{eff}} = \hbar\Delta \mathcal{A}_{ph}^\dagger \mathcal{A}_{ph} + \hbar g_0\left(\frac{J}{\Delta}\right)\sqrt{n_L}(\mathcal{A}_{ph}^\dagger b + \mathcal{A}_{ph} b^\dagger) + \hbar\Omega_{\text{v}} b^\dagger b$$



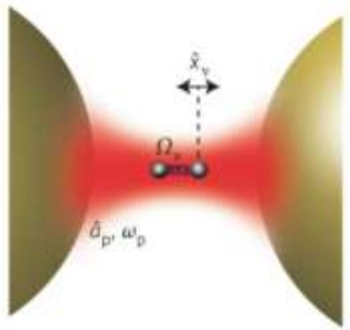

$$\mathcal{A}_{\text{ph}} = \frac{\tilde{l}^\dagger \tilde{a}}{\sqrt{(\tilde{n}_{\text{L}} - \tilde{n}_a)}}$$

# Is vibrational strong coupling possible with $N$ =1, 2 molecules?

## Cavity optomechanics



## Molecular Cavity optomechanics



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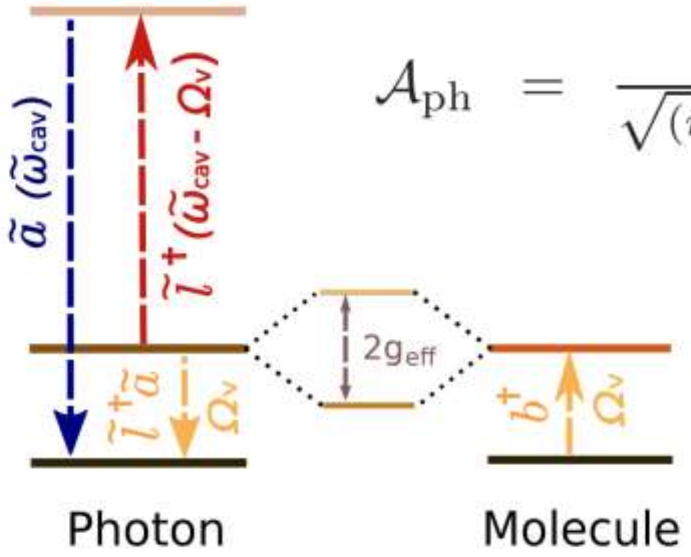
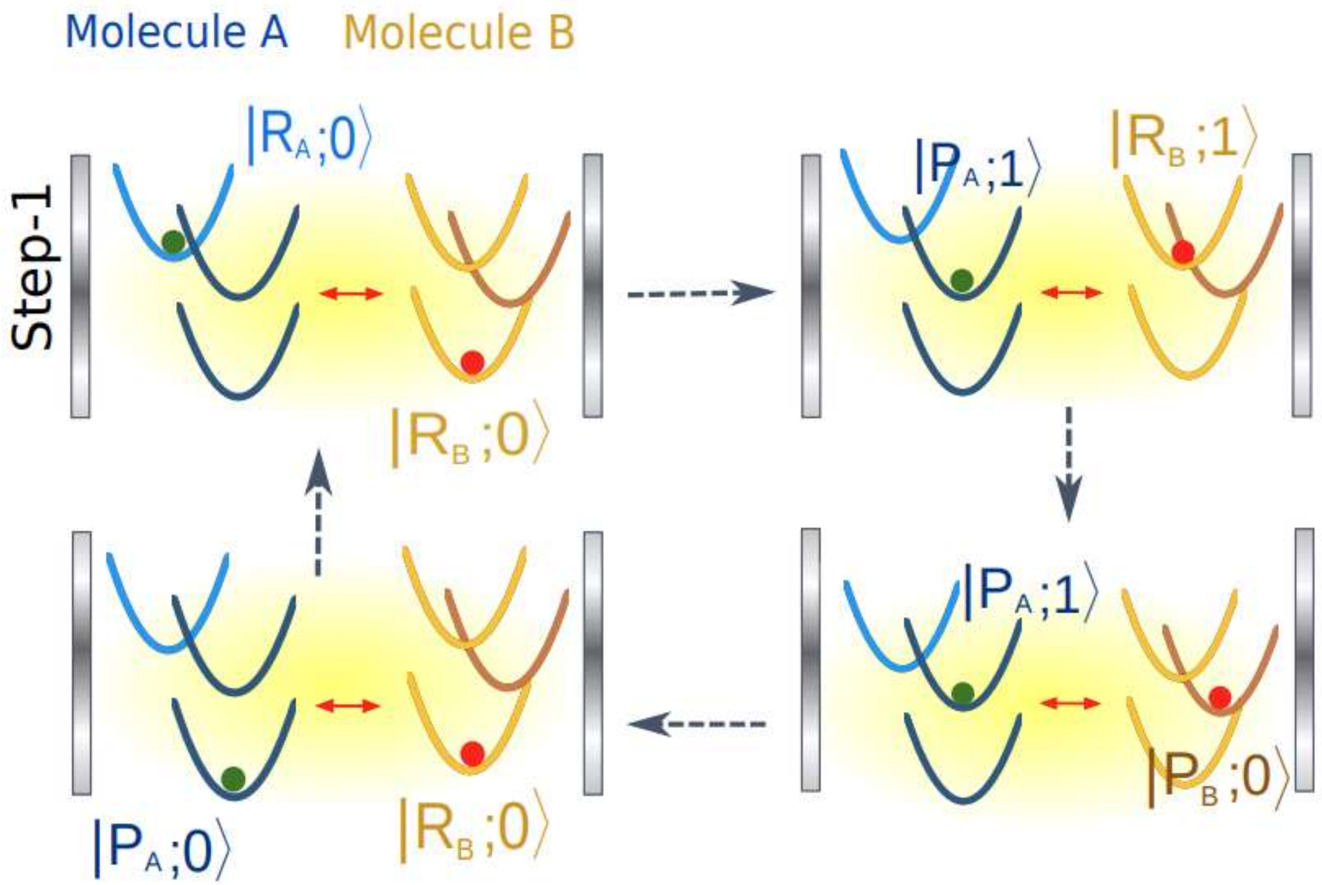
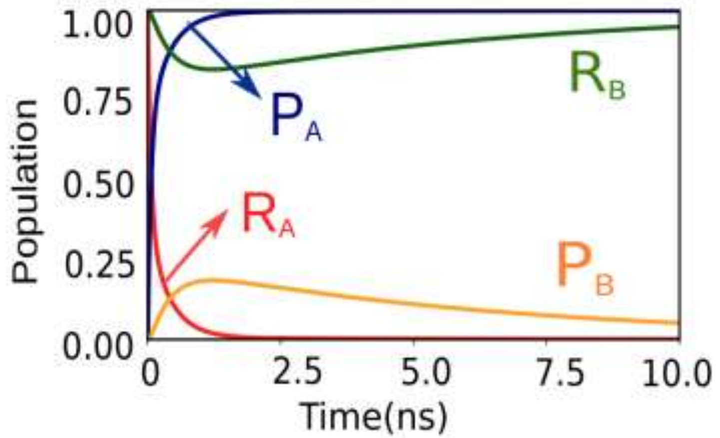
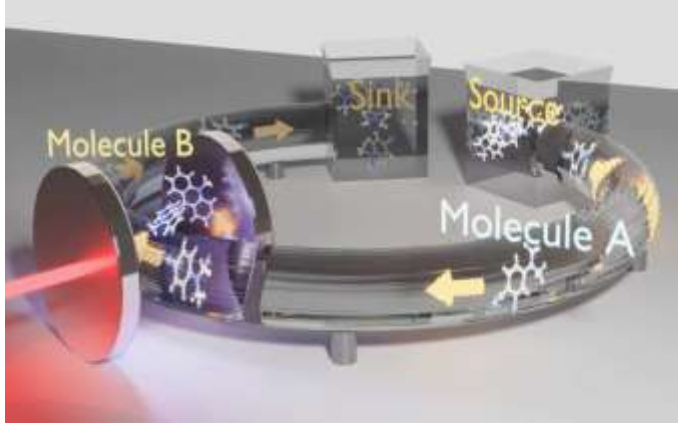



$$\mathcal{A}_{\text{ph}} = \frac{\tilde{l}^\dagger\tilde{a}}{\sqrt{(\tilde{n}_{\text{L}} - \tilde{n}_a)}}$$

# Is vibrational strong coupling possible with $N$ =1, 2 molecules?




A. Koner, M. Du, S. Pannir-Sivajothi, R. H. Goldsmith, and J. Yuen-Zhou, A path towards single molecule vibrational strong coupling in a Fabry–Pérot microcavity. *Chemical Science*, *14*(28), pp.7753-7761 (2023).
See also: A. Bourzutschky, B. L. Lev, and J. Keeling. "Raman-phonon-polariton condensation in a transversely pumped cavity." *npj Quantum Materials* 9.1 (2024): 81.

# When does classical linear optics break down? When $g \sim \kappa$

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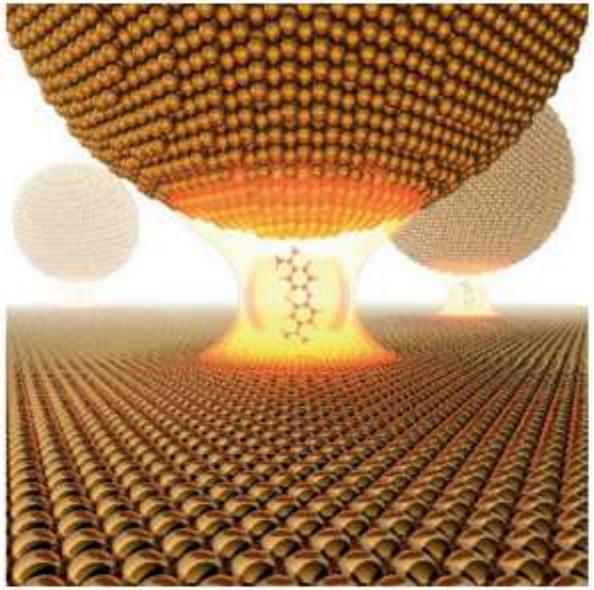

Nanophotonics
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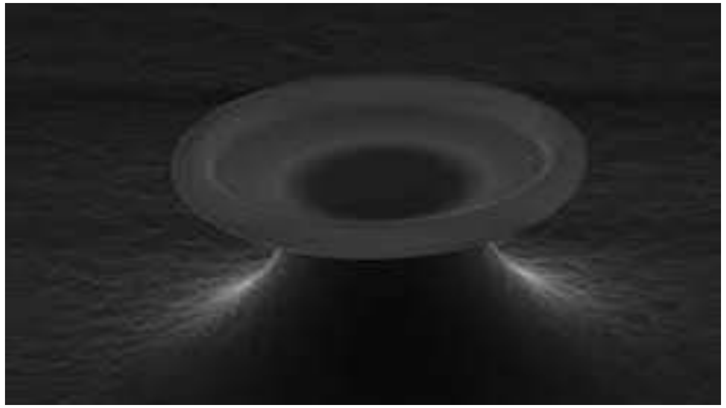

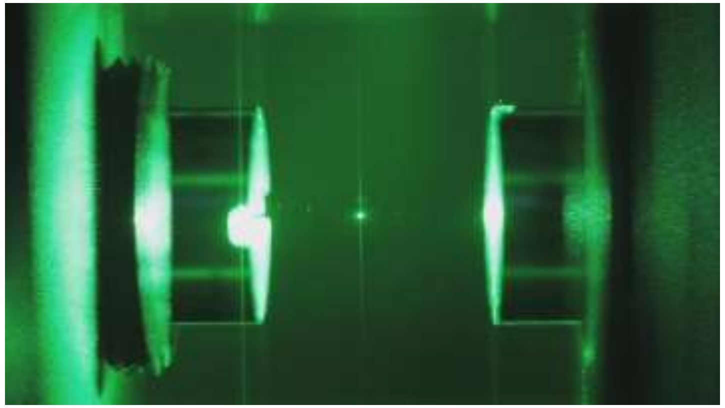

High Q dielectric cavities
$g$ is tiny but $\kappa$ is tiny too
(small or large $N$)

# More conventional use of cavities: Chemical use of Purcell effect

NANO LETTERS

Letter

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## Giant Suppression of Photobleaching for Single Molecule Detection via the Purcell Effect

Hu Cang,[†,‡] Yongmin Liu,[†,§,∥] Yuan Wang,[†] Xiaobo Yin,[†,⊥] and Xiang Zhang*[,†,⊥]

[†]NSF Nanoscale Science and Engineering Center (NSEC), 3112 Etcheverry Hall, University of California, Berkeley, California 94720, United States

[‡]Waitt Advanced Biophotonics Center, Salk Institute for Biological Studies, 10010 North Torrey Pines Road, San Diego, California 92037, United States

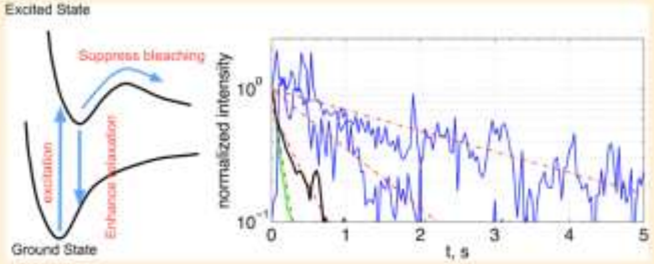
[§]Department of Mechanical and Industrial Engineering, Northeastern University, 360 Huntington Avenue, Boston, Massachusetts 02115, United States

[∥]Department of Electrical and Computer Engineering, Northeastern University, 360 Huntington Avenue, Boston, Massachusetts 02115, United States

[⊥]Materials Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, United States

*Supporting Information*

**ABSTRACT:** We report giant suppression of photobleaching and a prolonged lifespan of single fluorescent molecules via the Purcell effect in plasmonic nanostructures. The plasmonic structures enhance the spontaneous emission of excited fluorescent molecules, reduce the probability of activating photochemical reactions that destroy the molecules, and hence suppress the bleaching. Experimentally, we observe up to a 1000-fold increase in the total number of photons that we can harvest from a single fluorescent molecule before it bleaches. This approach demonstrates the potential of using the Purcell effect to manipulate photochemical reactions at the subwavelength scale.




**KEYWORDS:** *Nano-optics, single-molecule fluorescence spectroscopy, plasmonics*

$$\frac{d}{dt}e = -(k_f + k_{iNR} + \Gamma) + k_A g$$

$$\frac{d}{dt}g = (k_f + k_{iNR})e - k_A g$$

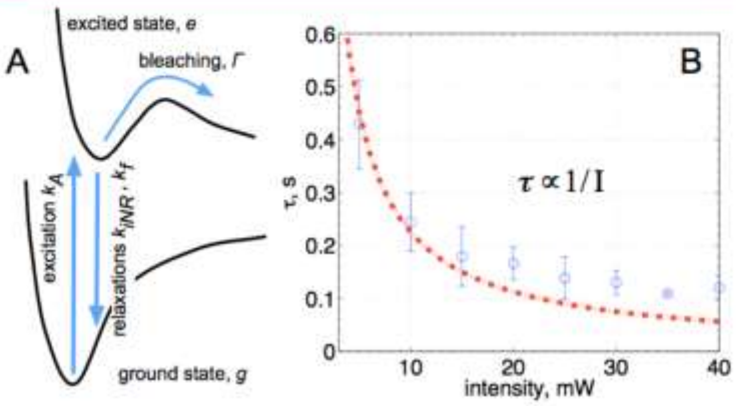



**Figure 1.** (a) After adsorbing a photon, the molecule reaches an excited state *e* from the ground state *g*. The excited molecule will most likely relax back to the ground state, but with a small probability, it suffers permanent damages as a result of a photochemical reaction—bleaching. (b) A control experiment measures the lifespan $\tau$ of chromeo-642 dyes on glass slide as a function of the excitation power *I*. An inverse relation (red dash−dot curve), $1/I$, can be seen in the figure. The discrepancy at higher excitation power is due to the limited time resolution of the experiments, which is 50 ms.

# More conventional use of cavities: Chemical use of Purcell effect

**ORIGINAL PAPER**

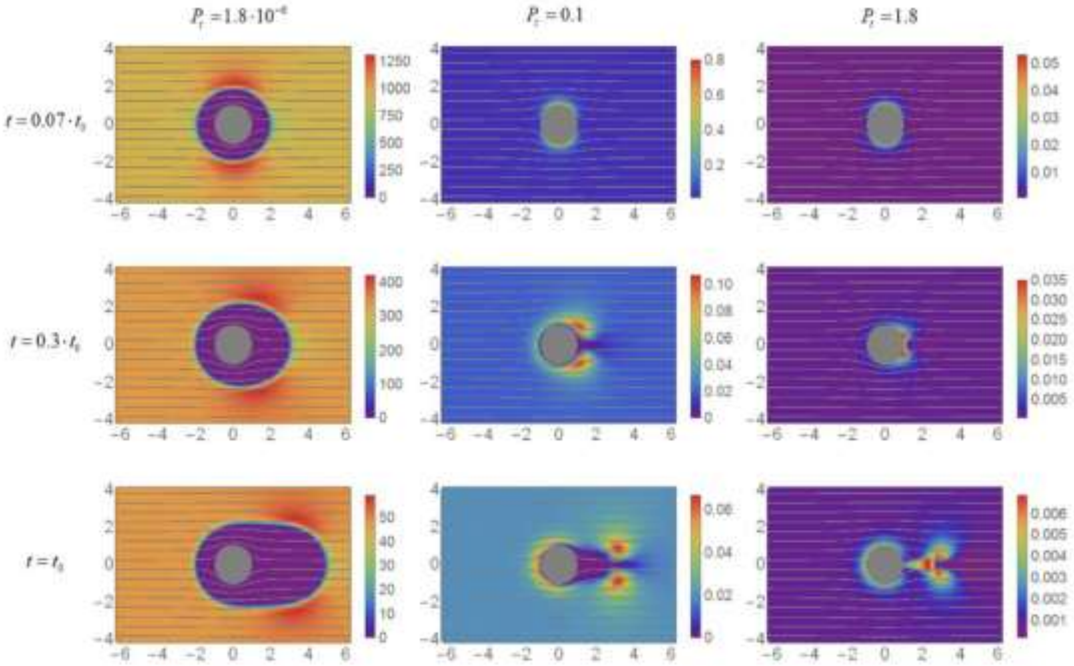
Quantum Sensing

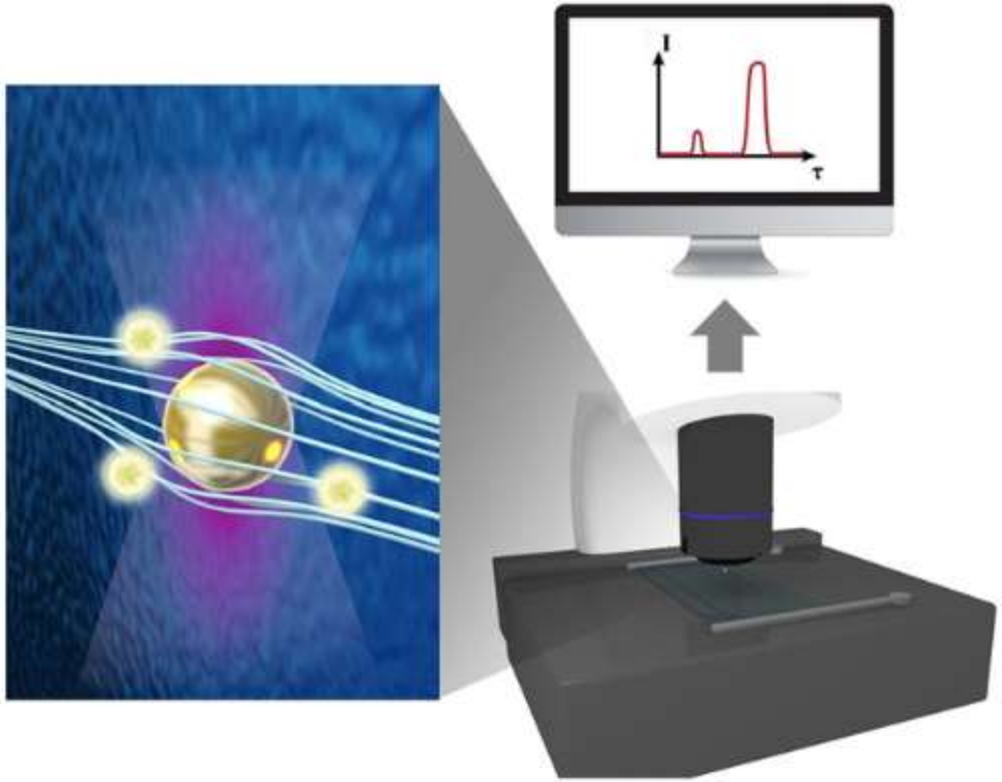
LASER & PHOTONICS REVIEWS

www.lpr-journal.org

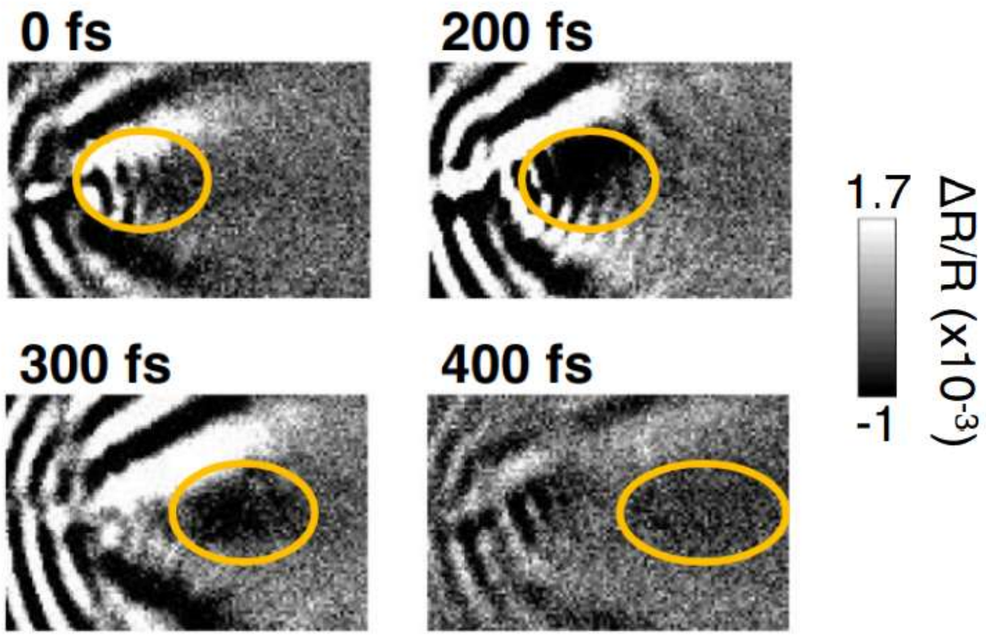
## Quantum Sensing of Motion in Colloids via Time-Dependent Purcell Effect

*Alexey S. Kadochkin,* Ivan I. Shishkin, Alexander S. Shalin, and Pavel Ginzburg*

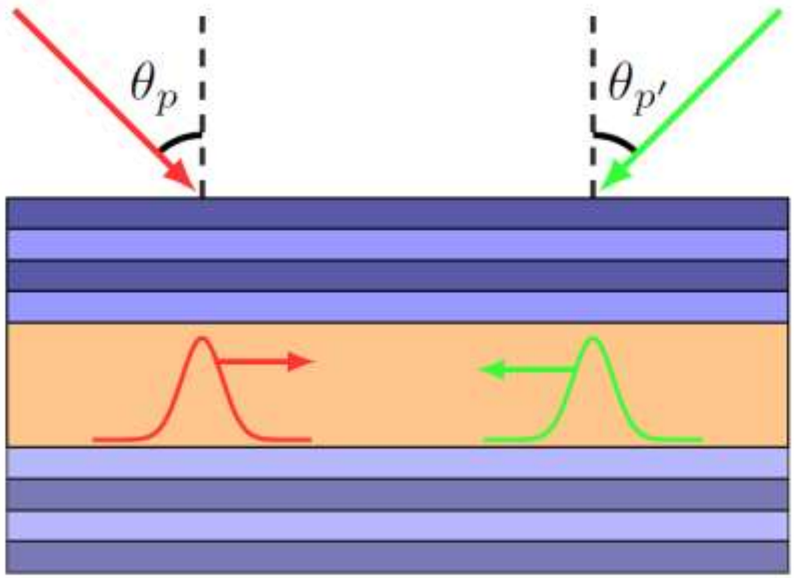


# More conventional use of cavities: Polariton transport




D. Xu, A. Mandal, J. M. Baxter, S.-W. Cheng, I. Lee, H. Su, S. Liu, D. R. Reichman, and M. Delor, *Nat. Commun.* 14, no. 1 (2023): 3881.

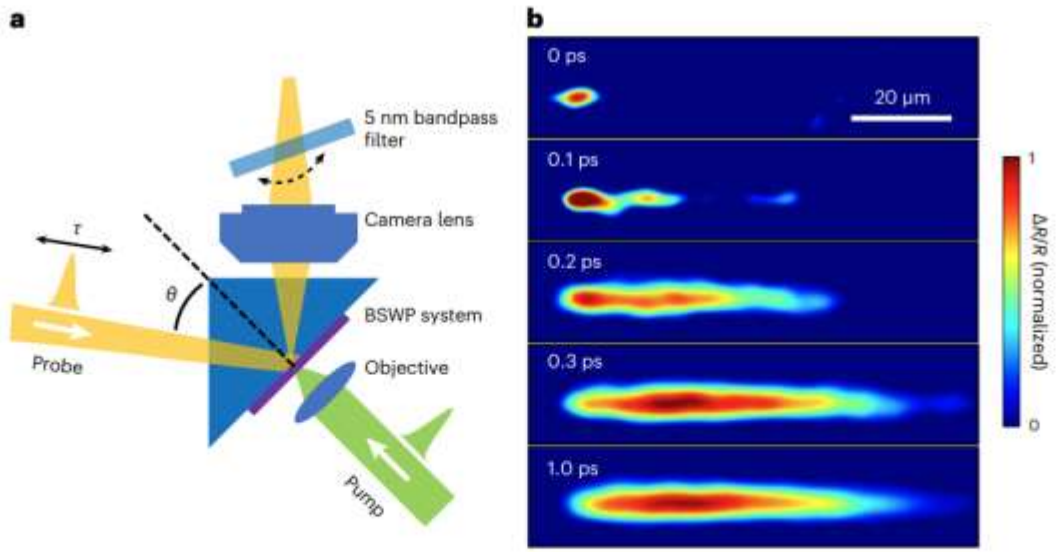



- probe delay $\Delta\tau$
- differential transmission $\Delta T_n(\omega) = T_n^{\text{on}}(\omega) - T_n^{\text{off}}(\omega)$

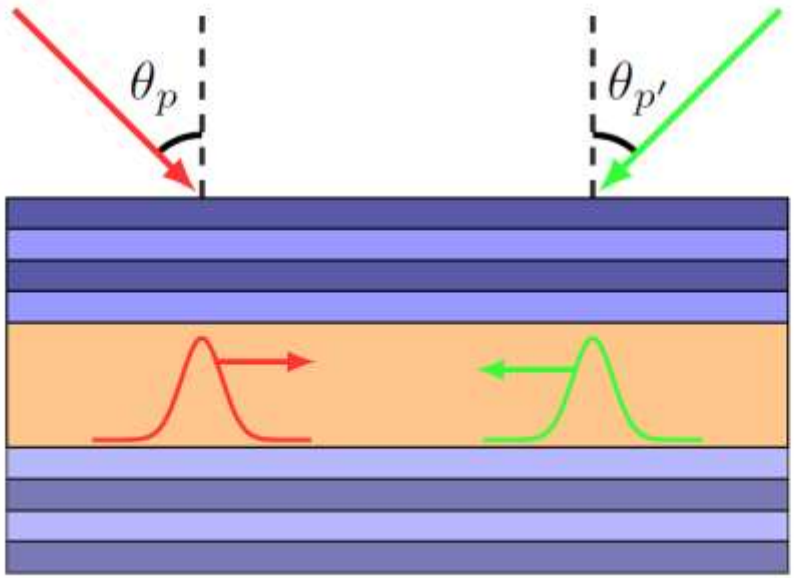
$$\Delta T_n(\omega) \sim 2\kappa^2 \text{Re}\left[\alpha_n^{(0,1)}(\omega)\overline{\alpha}_n^{(2,1)}(\omega)\right]$$

M. Reitz, A. Koner, J. Yuen-Zhou, Nonlinear semiclassical spectroscopy of molecular polaritons, Phys. Rev. Lett. 134, 193803 (2025).
P. Fowler-Wright, M. Reitz, J. Yuen-Zhou, Nonlinear microscopy of polaritons, arXiV:2504.15501.

# More conventional use of cavities: Polariton transport




M. Balasubrahmaniyam, A. Simkhovich, A. Golombek, G. Sandik, G. Ankonina, and T. Schwartz, *Nat. Mater.* 22, no. 3 (2023): 338-344.

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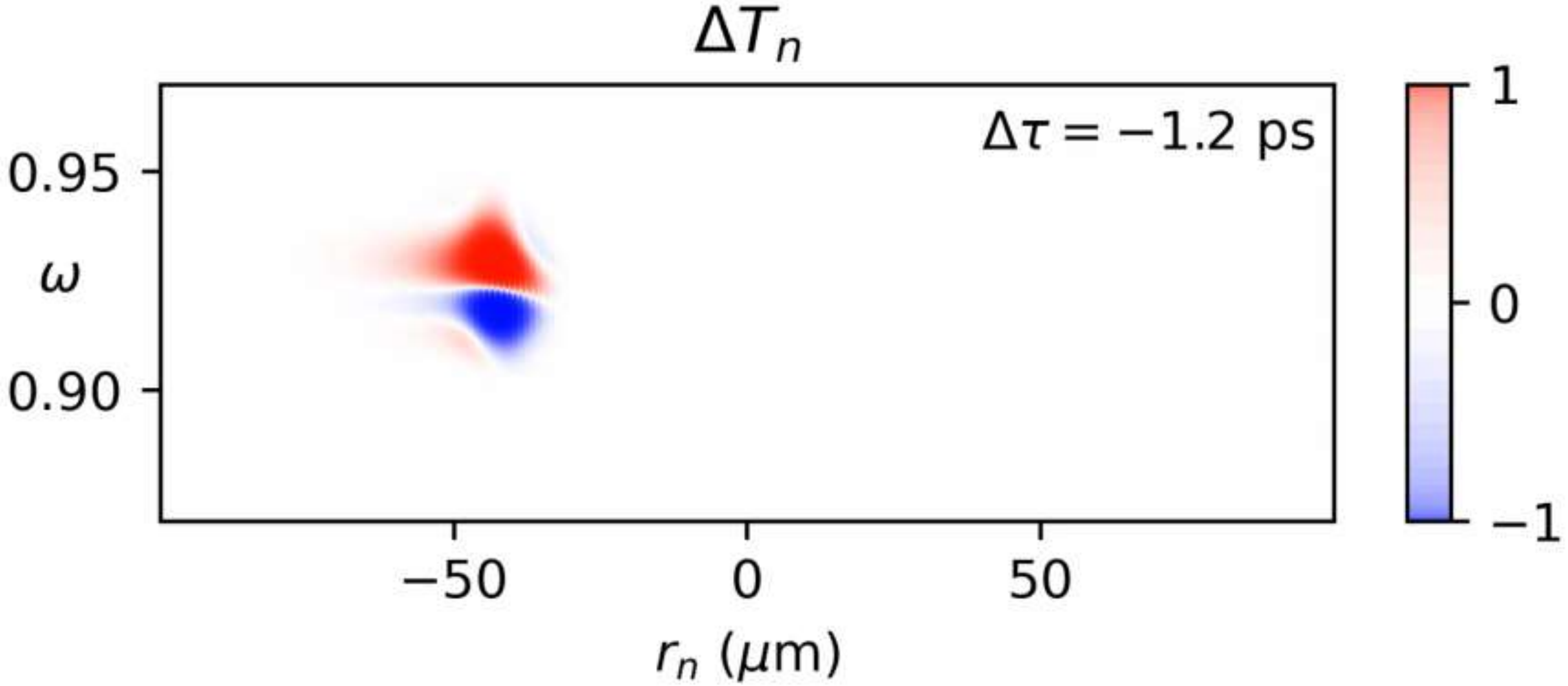
# Better understood phenomena: Polariton nonlinear microscopy

Piper Fowler-Wright

Michael Reitz

Coupled-wave mean-field simulations:

$$\rho(t) = \rho_{light}(t) \otimes \rho_{matter}(t)$$



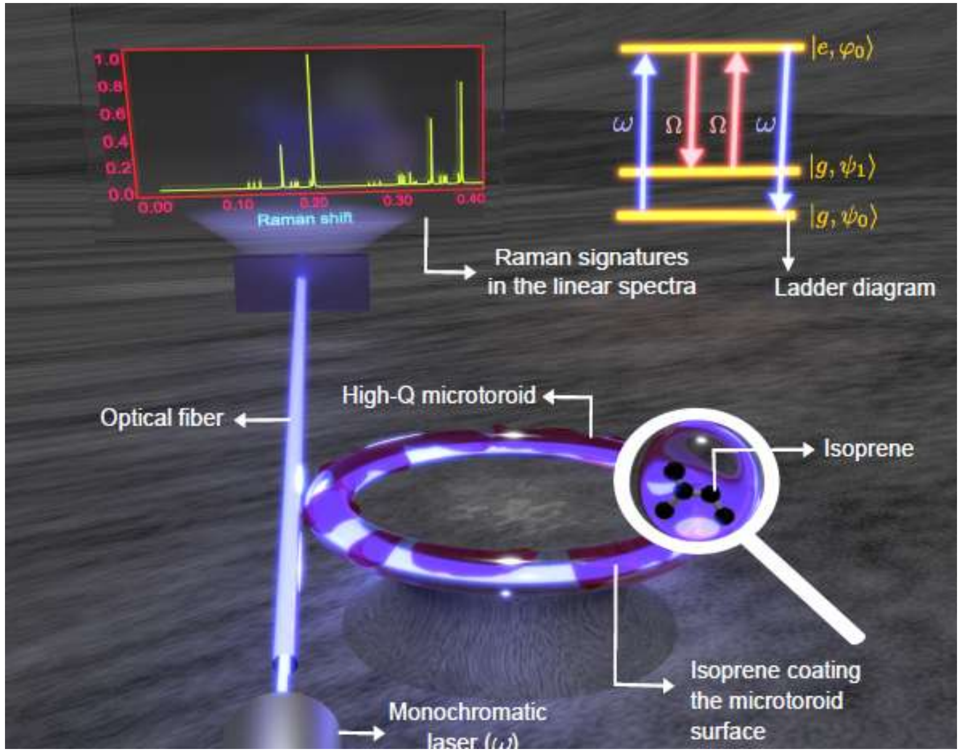

P. Fowler-Wright, M. Reitz, J. Yuen-Zhou, Nonlinear microscopy of polaritons, arXiV:2504.15501.

# SCOM23


During SCOM23, there was a consensus as a community to try to distinguish standard cavity phenomena (classical field enhancement, lasing, Purcell effect, etc.) from "nontrivial" strong coupling phenomena.

MAIN QUESTION OF THE FIELD: Which polaritonic effects are *truly cavity induced* and cannot be obtained outside the cavity and which ones are not?

# Molecular polaritonics




**(a) Photoinduced processes**

- ❑ Non-interacting molecules, thermodynamic limit ($N \to \infty$)

$$\rho(t) = \rho_{light}(t) \otimes \rho_{matter}(t)$$

- Linear regime: Classical optics: Optical filtering

No change in optical response or molecular dynamics of molecules

- Nonlinear regime: (Semi)-classical nonlinear optics, coupled-wave equations, condensation/lasing, optical engineering, transport

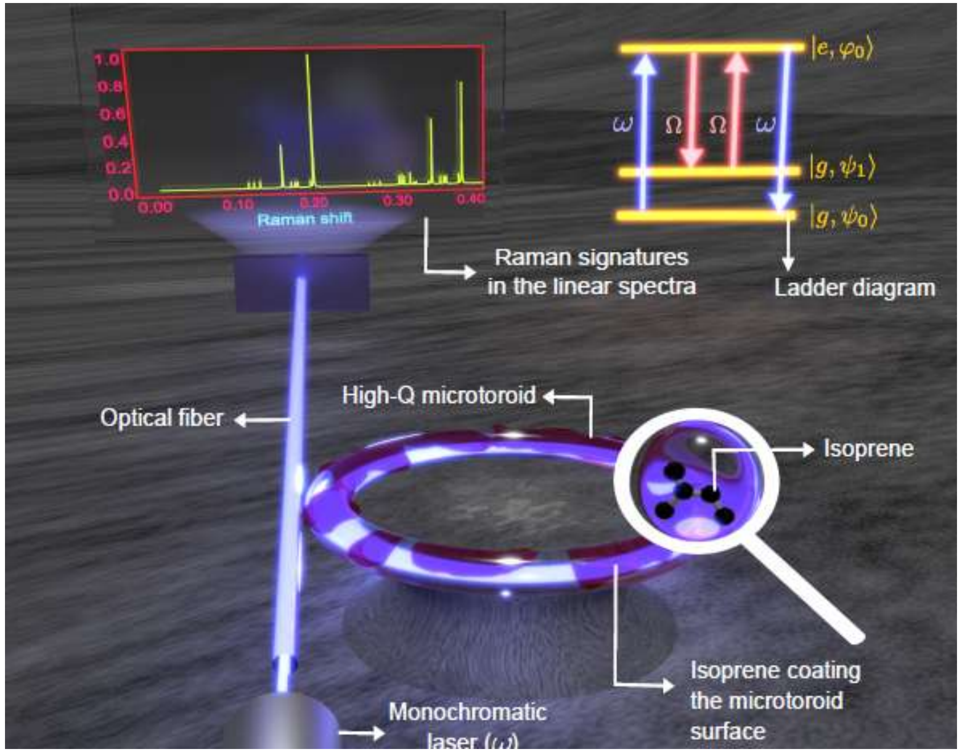
- ❑ Non-interacting molecules, finite $N$

$$\rho(t) \neq \rho_{light}(t) \otimes \rho_{matter}(t)$$

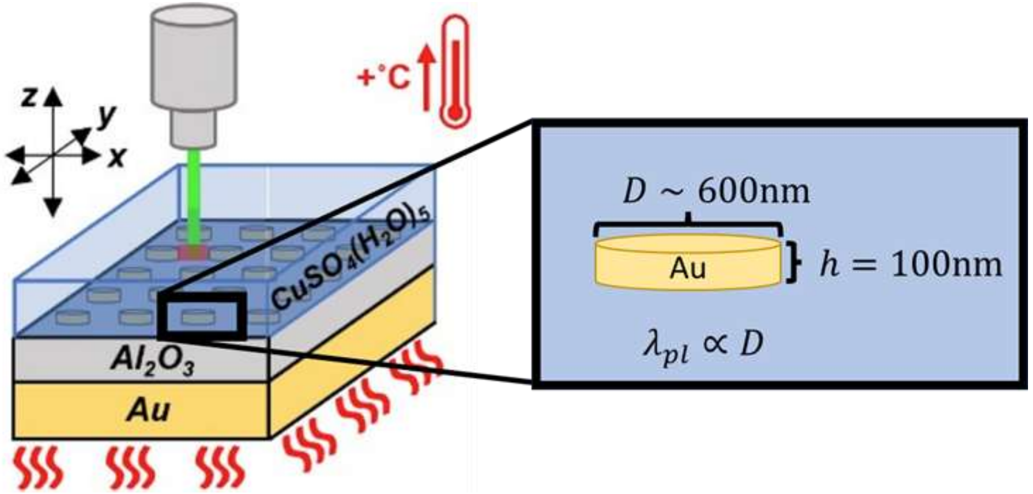
- Purcell effect, cavity induced reabsorption, polariton relaxation, exciton thermalization, …
- Vacuum induced Raman dressing (new QED effect) with high Q cavities.

- ❑ Still theory behind experiments. Why do experiments show phenomena beyond optical filtering in the linear regime?

# Molecular polaritonics




**(a) Photoinduced processes**




**(b) Thermal processes**

# Thermal polariton chemistry: still a mystery

AFOSR

The Journal of Chemical Physics PERSPECTIVE scitation.org/journal/jcp

## Swinging between shine and shadow: Theoretical advances on thermally activated vibropolaritonic chemistry

TABLE I. Theories of vibropolaritonic chemistry.

| Mechanism | $k_{VSC}/k_{bare}$ | Adiabatic | Collective effects | Frequency condition for maximum effect | Effect on rate | Notes |
|---|---|---|---|---|---|---|
| Permanent dipole-induced changes in activation energy[101,102,106,107] | eq. (21) | ✓ | With anistropic alignment | ✗ | ↕ | Neglects self-interaction |
| Dynamical photon caging[105,111,132] | eq. (22) | ✓ | With solvent | $\omega_0 \approx \lvert\omega_{\ddagger}\rvert$ | ↓ | |
| Zero-point energy[69] | eq. (23) | ✓ | ✗ | ✓ | ↕ | Restricted to low temperatures<br>Resonance condition not inherent |
| Cavity-induced friction[113,115] | eq. (25) | ✓ | ✗ | $\omega_0 = \omega_{RS}$ | ↑ | Requires low friction |
| Charge transfer (polaritons)[68,133] | eq. (28) | ✗ | ✓ | $\omega_0 \approx \omega_{PS}$ | ↑ | Vanishes with broadening |
| Counter-rotating effects on groundstate[134] | eq. (30) | ✗ | ✗ | $\omega_0 = \omega_{RS}$ | ↓ | Both RS and PS must couple |
| Charge transfer (dark modes)[135,136] | eq. (32) | ✗ | ✓ | ✓ | ↕ | |
| IMER[112,124,125,127,128] | N/A | ✓ | With anisotropic alignment (?) | $\omega_0 = \omega_{RS}$ | ↕ | Nonequilibrium initial conditions<br>Collective effects seen in ref. 127 but not in ref. 124 |

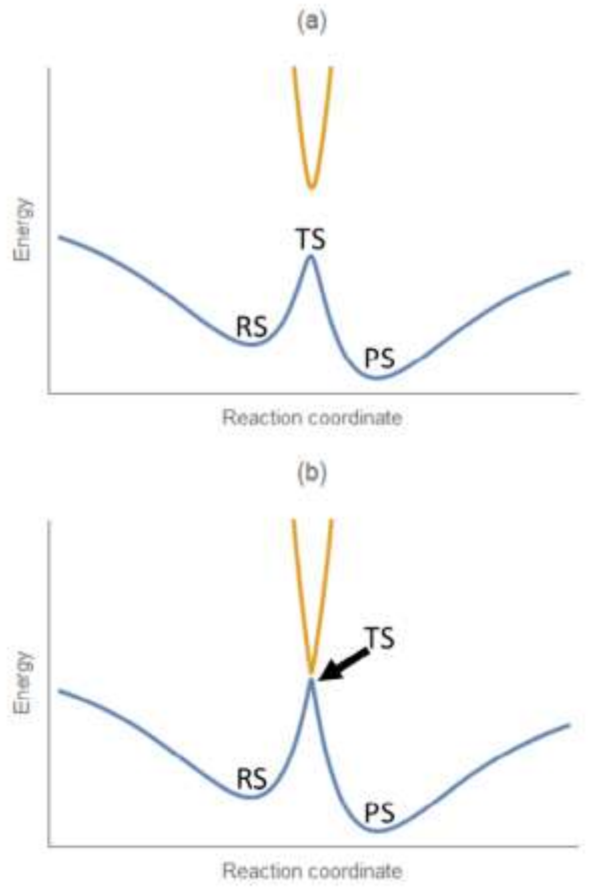



FIG. 2. Ground and first-excited electronic PESs along the reaction coordinate of (a) an adiabatic reaction and (b) a non-adiabatic reaction.

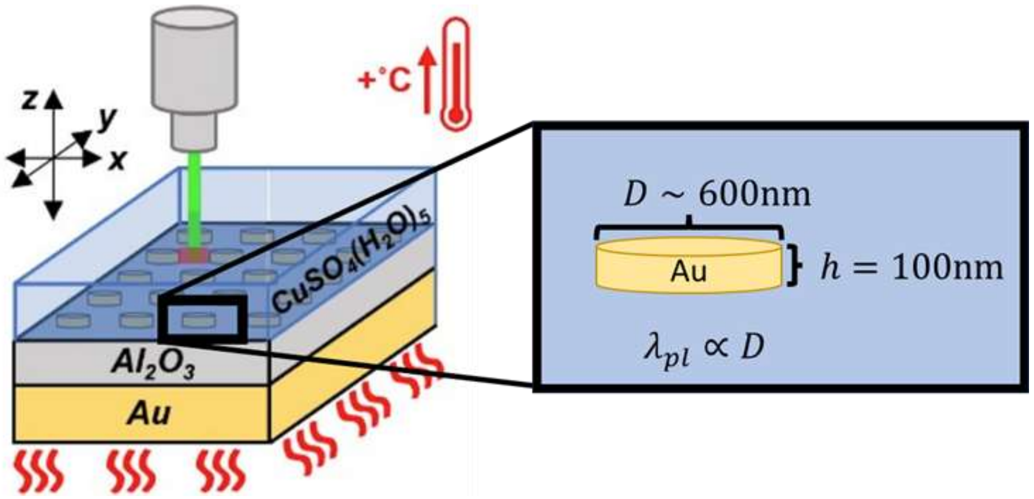
J. A. Campos-Gonzalez-Angulo, Y. R. Poh, M. Du, and J. Yuen-Zhou, J. Chem. Phys. 158, 230901 (2023).
See: T. E. Li, A. Nitzan, and J. E. Subotnik. J. Chem. Phys. 152.23 (2020).

# Vibrational polaritons can facilitate heat transport

nature chemistry

Article https://doi.org/10.1038/s41557-024-01723-6

**Vibrational weak and strong coupling modify a chemical reaction via cavity-mediated radiative energy transfer**




EXPERIMENTAL OBSERVATIONS:

- The dehydration reaction
  $CuSO_4 \cdot 5H_2O(s)$
  $\rightarrow CuSO_4 \cdot 3H_2O(s) + 2H_2O(g)$

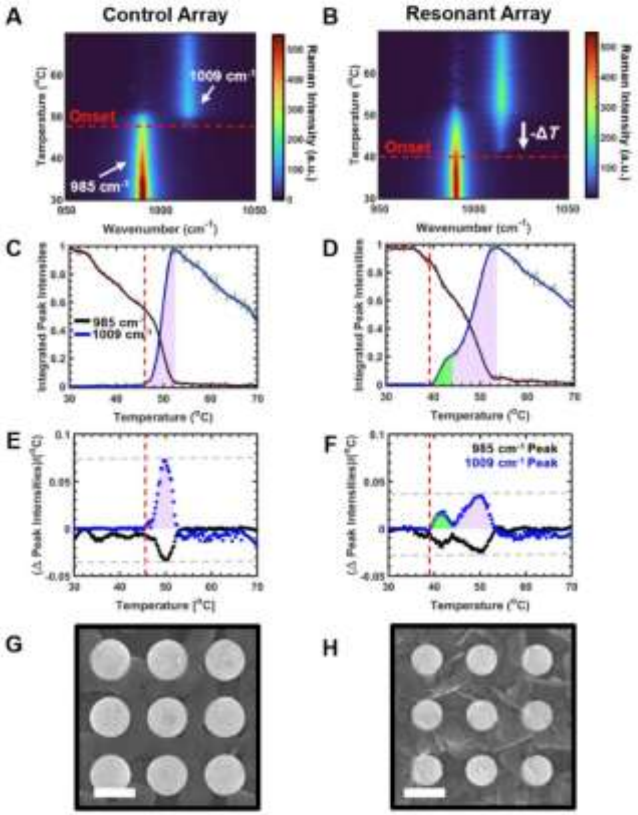
typically occurs at the heating stage temperature $T = 47\ C$.

- Under vibrational strong coupling (VSC) to the OH stretch of reactant, the heating stage temperature decreases to $\mathrm{T} = 39.5\ C$.

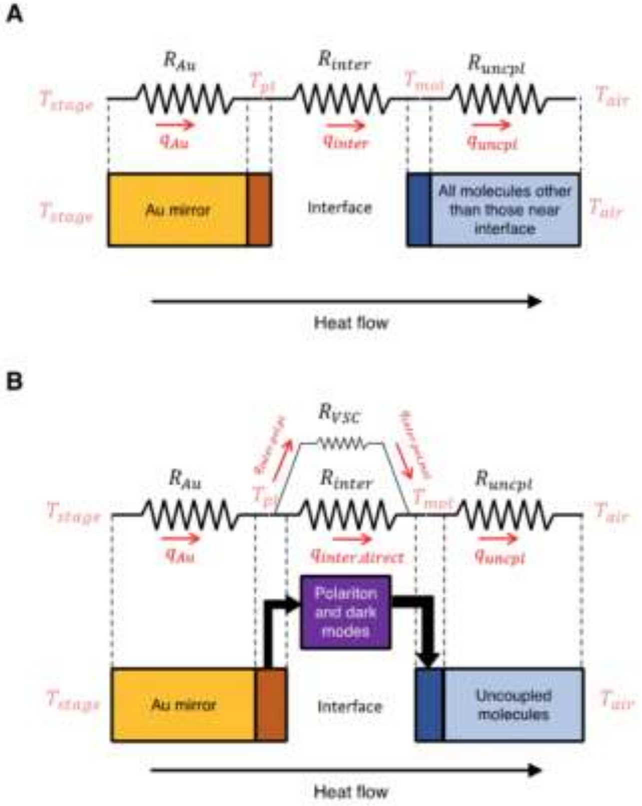
Z. Brawley*, S. Pannir-Sivajothi*, J. E. Yim, Y. Rui Poh, J. Yuen-Zhou, M. Sheldon, Nat. Chem. 17, 439–447 (2025).

# Vibrational polaritons can facilitate heat transport

Raman microscopy of sulfate bonds in reactant and product




Polaritons provide extra radiative heat transport channels that reduce thermal gradients




Sindhana Pannir-sivajothi

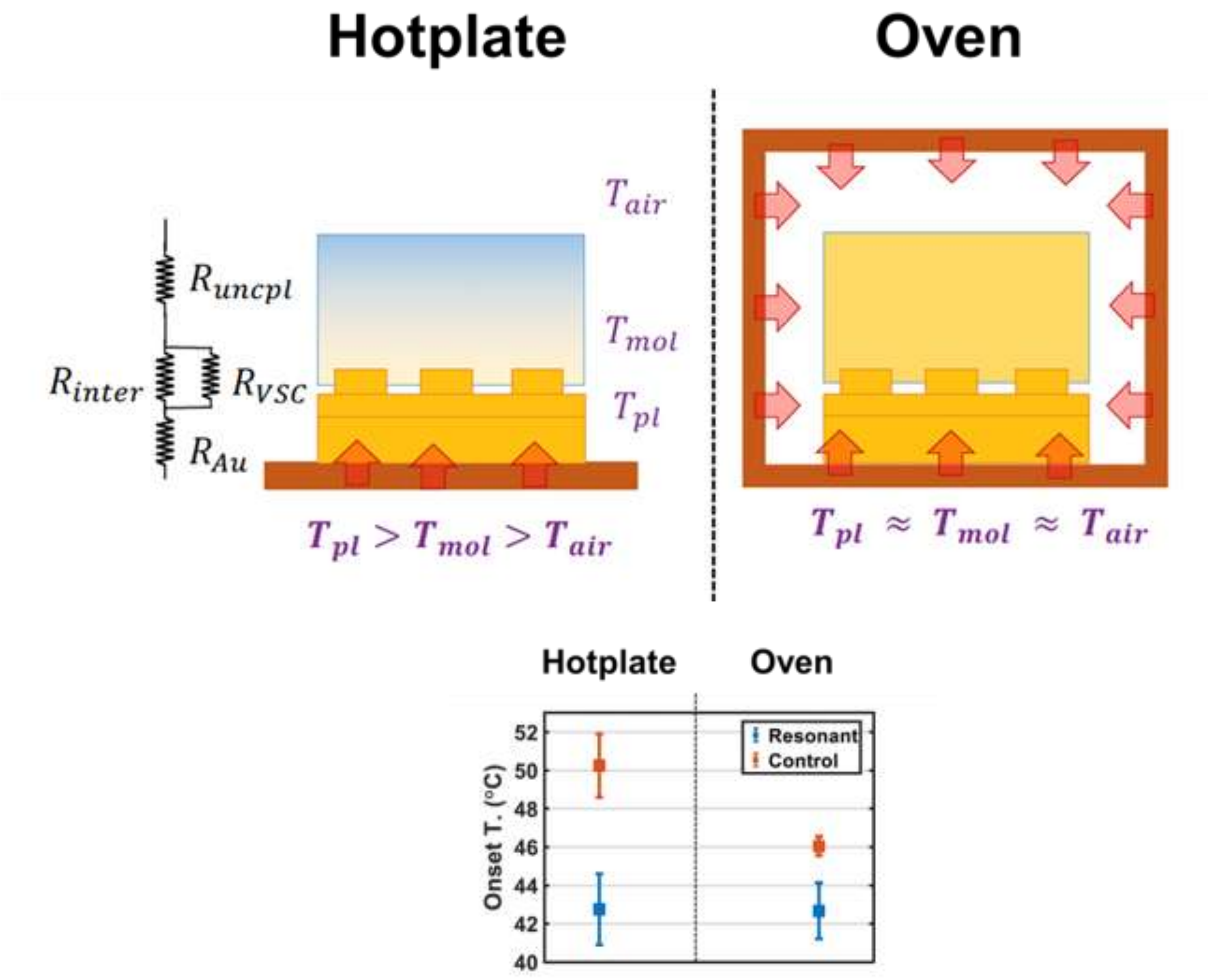
Yong Rui Poh

## HYPOTHESIS

- There is a thermal gradient between the heat stage and the $CuSO_4$ crystals.
- Vibrational polaritons ameliorate such gradient.
- $T_{trans}$ not changing!
- Under strong coupling, heating state needs to be at lower temperature to reach the same $T_{trans}$.

Z. Brawley*, S. Pannir-Sivajothi*, J. E. Yim, Y. Rui Poh, J. Yuen-Zhou, M. Sheldon, Nat. Chem. 17, 439–447 (2025).

# Vibrational polaritons can facilitate heat transport




EXPERIMENTAL VALIDATION OF HYPOTHESIS:

In oven, effect goes away because thermalization happens because thermal gradients disappear.

*OUTLOOK:*

Near-field radiative heat transfer can be used in chemistry across poorly conductive interfaces. See:

S. Pannir-Sivajothi, and Joel Yuen-Zhou, "Blackbody radiation and thermal effects on chemical reactions and phase transitions in cavities," ACS Nano, 19, 10, 9896–9905 (2025).

Z. Brawley*, S. Pannir-Sivajothi*, J. E. Yim, Y. Rui Poh, J. Yuen-Zhou, M. Sheldon, Nat. Chem. 17, 439–447 (2025).

# A timeline of thermal polariton chemistry

**Positive results:**

2016 — Reaction rate change VSC

Thomas[+], George[+], …, Ebbesen

2019 — Reaction yield change VSC

Thomas, …, Ebbesen

2023 — Reaction rate change VSC

Ahn …, Simpkins*

**Negative results:**

2021

Wiesehan, …, Xiong

No change in reaction rate VSC

2021

Imperatore, …, Giebink

No change in reaction rate VSC

2023

Fidler, …, Weichman

No change in reaction rate VSC

Change in radiative energy transfer rate under VSC

Brawley*, **Pannir-Sivajothi***, Yim*, *et al.*

No change in transition temperature under VSC

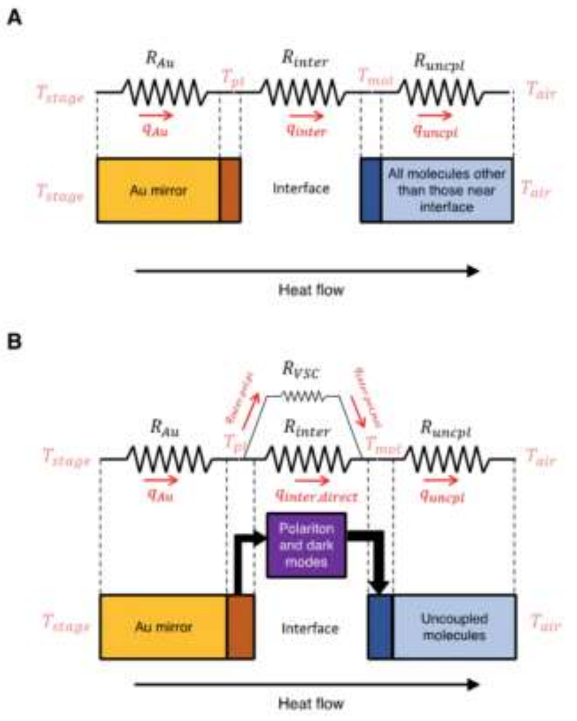
* W. Ahn, J. F. Triana, F. Recabal, F. Herrera, and B. Simpkins (2023), *Science*, *380*(6650), 1165-1168.

# SUMMARY b: Thermal polariton chemistry

- ❖ Many thermally activated experiments show changes in chemical kinetics upon polariton formation.
- ❖ Cannot be easily explained through equilibrium theories.

- ❖ For at least one experiment, VSC does not change $T_{trans}$ but simply homogeneizes temperature with additional near-field radiative heat transfer.
- ❖ What are the conditions under which radiative heat transfer bypasses conductive heat transfer?

See: A. C. Jones, C. Andrew, B. T. O'Callahan, H. U. Yang, and M. B. Raschke. "The thermal near-field: Coherence, spectroscopy, heat-transfer, and optical forces." *Progress in Surface Science* 88, no. 4 (2013): 349-392.




J. A. Campos-Gonzalez-Angulo, Y. R. Poh, M. Du, and J. Yuen-Zhou, Swinging between shine and shadow: Theoretical advances on thermally activated vibropolaritonic chemistry, J. Chem. Phys. 158, 230901 (2023).
Z. Brawley*, S. Pannir-Sivajothi*, J. E. Yim, Y. Rui Poh, J. Yuen-Zhou, M. Sheldon, Sub-wavelength chemical imaging of a modified reaction due to vibrational strong coupling, Nat. Chem. 17, 439–447 (2025).
S. Pannir-Sivajothi, and Joel Yuen-Zhou, "Blackbody radiation and thermal effects on chemical reactions and phase transitions in cavities," ACS Nano, 19, 10, 9896–9905 (2025).

# SUMMARY b: Thermal polariton chemistry

For heat transport controlled by polaritons:
See: G. Jarc, … & D. Fausti, D. (2023). Cavity-mediated thermal control of metal-to-insulator transition in 1T-TaS2. *Nature*, *622*(7983), 487-492.
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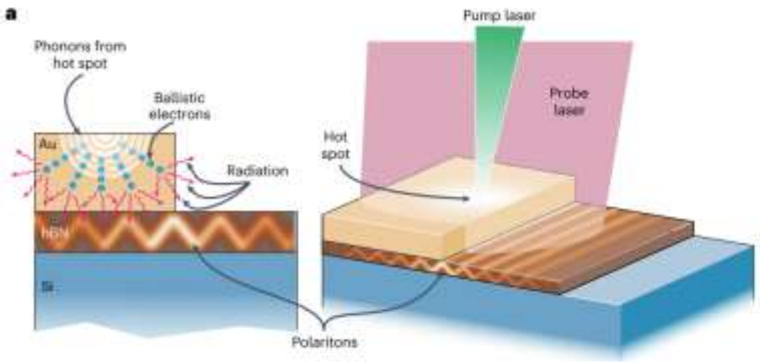
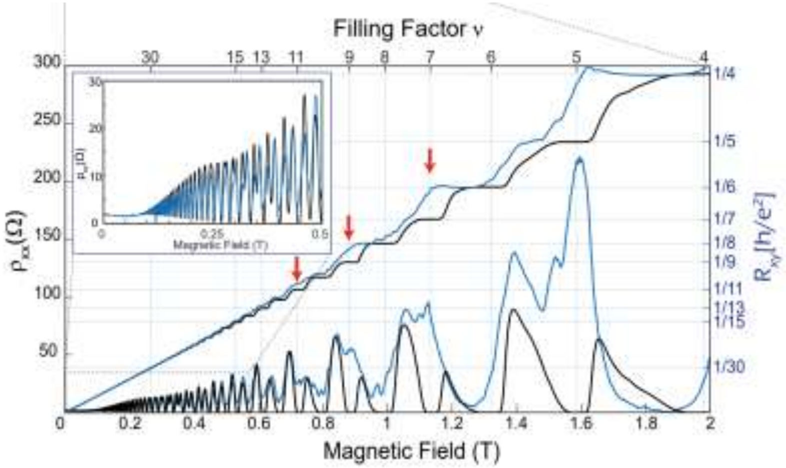


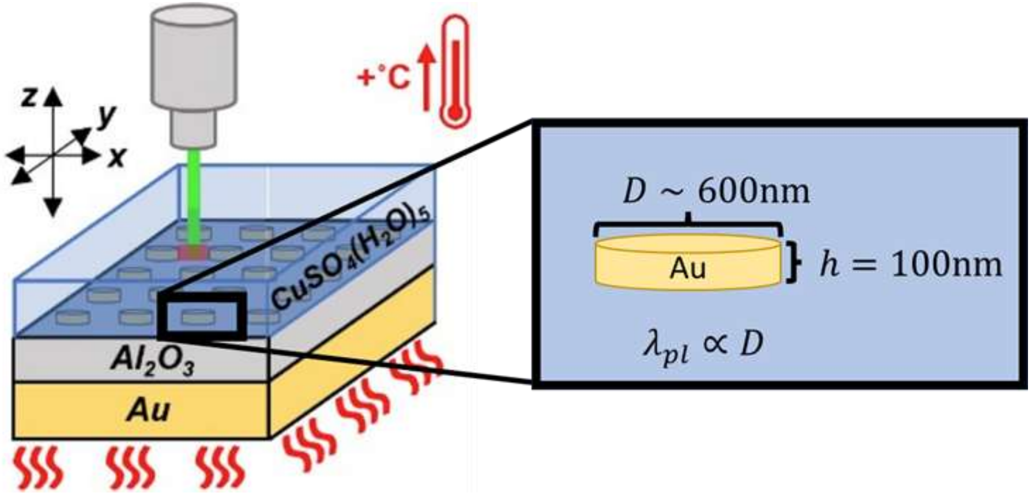

See also QHE studies with cavities:
- F. Appugliese, …, J. Faist, Breakdown of topological protection by cavity vacuum fields in the integer quantum Hall effect, *Science* 375.6584 (2022): 1030-1034
- J. Enkner, …, J. Faist, Tunable vacuum-field control of fractional and integer quantum Hall phases. *Nature (2025)*, 1-6.



# Molecular polaritonics

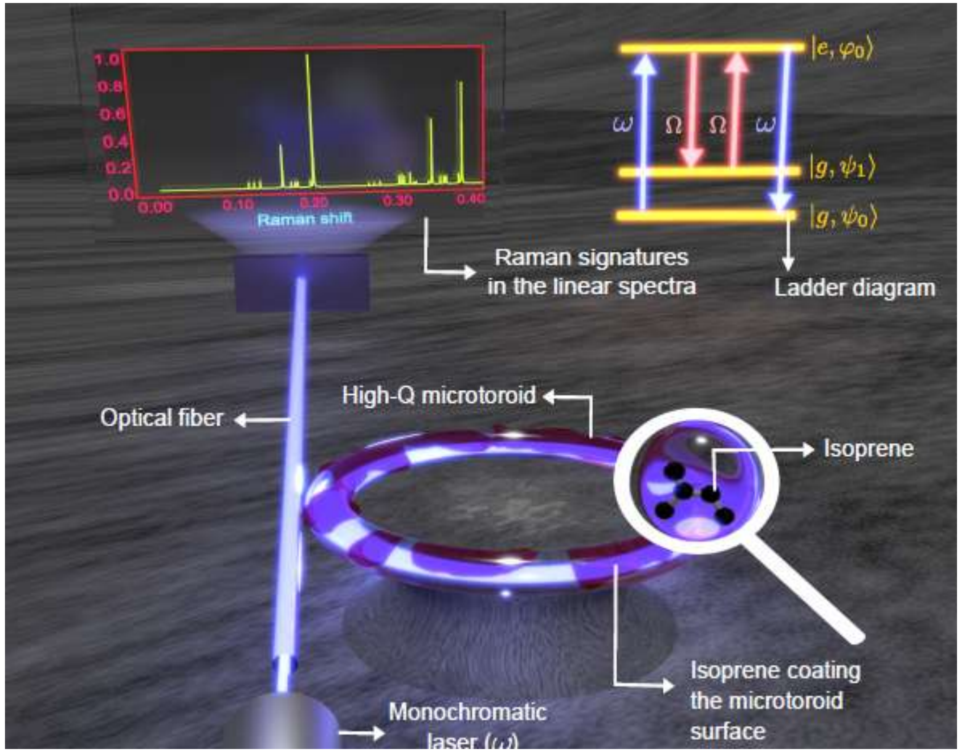
❑ Ground state reactivity
No obvious reason why cavities affect ground-state chemical reactions under equilibrium conditions.

❑ Nanoscale radiative heat transport
A clearer mechanism (thermal near field) where polaritons play a role.
Blackbody effects not obvious in all experiments (S. Pannir-Sivajothi, and J. Yuen-Zhou, ACS Nano, 19, 10, 9896–9905 (2025)).
Can it modify intramolecular dynamics?

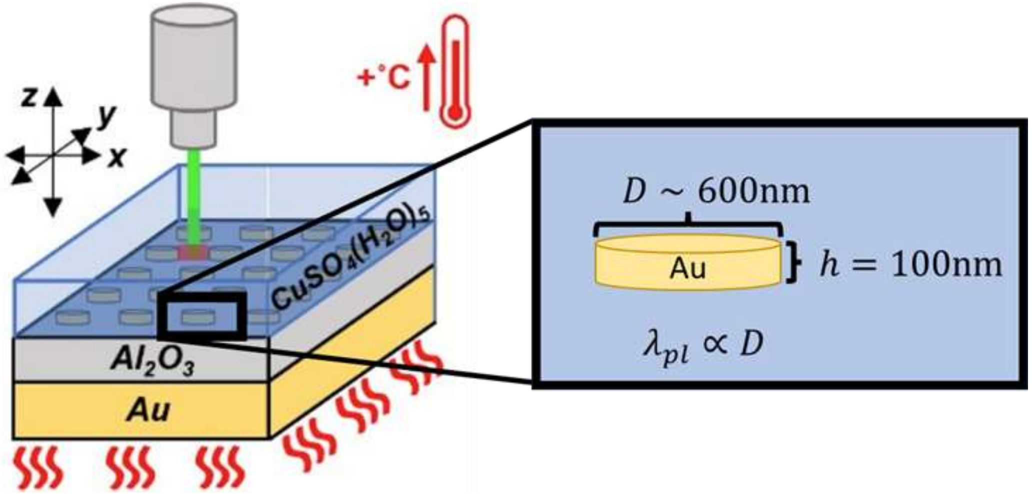



**(b) Thermal processes**

# Molecular polaritonics




**(a) Photoinduced processes**




**(b) Thermal processes**

# Still debating about blackbody effects in reactions!

# Still debating about blackbody effects in reactions!

*DISCUSSION ON "THE RADIATION THEORY OF CHEMICAL ACTION".*

**Professor J. Perrin** (*reply, partly communicated*): (1) Professor Lowry reminds us that the necessity of the intervention of a catalyst has been demonstrated for a great number of reactions which were in the first instance regarded as unimolecular. But this holds also for multimolecular reactions.

(3) I entirely agree with Professor Langmuir that all the chemical phenomena are "quantum phenomena," in which the same universal constant *h* intervenes. I attempted to make that clear in my contribution (Section 13) and in my previous researches.[1] The radiochemical theory has, first of all theories, extended the quantum notion to chemical reactions, and I think that this extension, which is not merely qualitative, but quantitative (Section 13), constitutes one of the achievements of the theory.

**Jean Baptiste Perrin**
(1870–1942)

*Transactions of the Faraday Society* 17 (1922): 598-606.

# Still debating about blackbody effects in reactions!

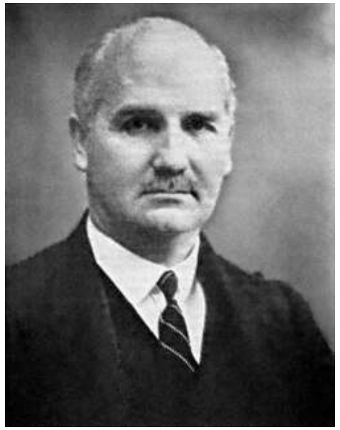
*DISCUSSION ON "THE RADIATION THEORY OF CHEMICAL ACTION".*

**Professor F. A. Lindemann:** In view of the short time at my disposal I will confine my remarks to the criticism of the radiation theory of chemical reaction velocity, which I myself have published.

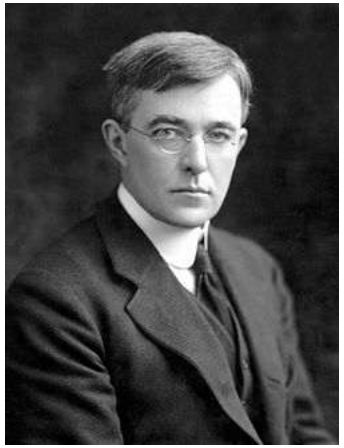
**Dr. Irving Langmuir:** I think that Professor Perrin, by bringing forward again this radiation hypothesis in such clear form has done us a great service. His original paper of two or three years ago on this subject, and particularly his pointing out the impossibility of assuming that collisions have anything to do with unimolecular reactions, have more than anything else stimulated our discussion of this aspect of the mechanism of chemical action.

When we think over the matter, however, we find that we have no direct evidence in confirmation of the radiation hypothesis. It is all sur-

*Transactions of the Faraday Society* 17 (1922): 598-606.



**Frederick A. Lindemann**
(1886 – 1957)



**Irving Langmuir**
(1881–1957)

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