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When do molecular polaritons behave like optical filters?

Kai Schwennicke,[a] Arghadip Koner,[a] Juan B. Pérez-Sánchez,[a] Wei Xiong,[a] Noel C. Giebink,[b] Marissa L. Weichman,[c] and Joel Yuen-Zhou*[a]

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S1 Estimating the number of molecules per cavity mode in the strong coupling regime

For a one dimensional cavity of length L_z, the dispersion for the $m-$th transversal mode is:

$$\omega = \frac{c}{\sqrt{\varepsilon}}\sqrt{|\vec{k}_{\|}|^2 + \left(\frac{m\pi}{L_z}\right)^2}, \tag{S1}$$

where $\vec{k}_{\|}$ is the component of the wave vector parallel to the plane of the cavity mirrors, c is the speed of light, and ε is the background permittivity. Assuming periodic boundary conditions parallel to the mirrors, the wave vector values are discrete points in a reciprocal lattice with grid spacings $\Delta_{k_{x,y}} = \frac{2\pi}{L_{x,y}}$, where L_x and L_y refer to the height and width of the cavity mirrors. The protocol is to define an area in this reciprocal lattice and then divide by the area unit of the grid $(\Delta_{k_x}\Delta_{k_y})$ to calculate the number of cavity modes N_{modes} within this area of interest. Next the total number of molecules N_{mol} within the cavity is calculated, and finally the number of molecules per cavity modes is estimated as $N = N_{mol}/N_{modes}$.

S1.1 Electronic strong coupling

Here we estimate N for electronic strong coupling following the protocol of ref. 1. The authors consider a square in reciprocal space of length $|\vec{k}_{max}| = \frac{2\pi}{\lambda}$, where λ is a characteristic wavelength associated with UV-visible organic exciton-polaritons (~ 500 nm). Assuming a one dimensional cavity, the total number of cavity modes is:

$$\begin{aligned} N_{modes} &= 2 \times \frac{|\vec{k}_{max}|^2}{\Delta_{k_x}\Delta_{k_y}} \\ &= L_x L_y \frac{2}{\lambda^2} \end{aligned} \tag{S2}$$

where the factor of two accounts for the fact that for each k there are two polarizations. The number of molecules in the cavity is given by

$$N_{mol} = \rho L_x L_y L_z, \tag{S3}$$

where ρ is the molecule number density. Then the number of molecules per mode is:

$$N = \frac{N_{mol}}{N_{modes}} = \frac{\rho L_z \lambda^2}{2}. \tag{S4}$$

Taking $\rho = 10^9\ \mu\text{m}^{-3}$ and $L_z = 100$ nm from ref. 1, we estimate the number of molecules per mode for electronic strong coupling to be $N \sim 1.25 \times 10^7$ as reported in the main text.

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[a] Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093, USA.
[b] Department of Electrical Engineering and Computer Science, and Physics, University of Michigan, Ann Arbor, MI 48109, USA.
[c] Department of Chemistry, Princeton University, Princeton, NJ 08544, USA.

S1.2 Vibrational strong coupling

Here we estimate N following the protocol of ref. 2. From Eq. S1, the magnitude of the parallel wave vector component for $m = 1$ is:

$$|\vec{k}_{\parallel}| = \sqrt{\frac{\varepsilon\omega^2}{c^2} - \left(\frac{\pi}{L_z}\right)^2}. \tag{S5}$$

Considering a circle in reciprocal space of radius $|\vec{k}_{max}|$, the number of photon cavity modes is

$$\begin{aligned} N_{modes} &= \frac{\pi |k_{\parallel,max}|^2}{\Delta_{k_x}\Delta_{k_y}} \\ &= \frac{\pi\left[\frac{\varepsilon\omega_{max}^2}{c^2} - \left(\frac{\pi}{L_z}\right)^2\right]}{\Delta_{k_x}\Delta_{k_y}} \\ &= \frac{L_x L_y}{4\pi}\left[\frac{\varepsilon\omega_{max}^2}{c^2} - \left(\frac{\pi}{L_z}\right)^2\right] \end{aligned} \tag{S6}$$

The number of molecules in the cavity is given by

$$N_{mol} = \rho L_x L_y L_z \tag{S7}$$

where ρ is the molecule number density. Then the number of molecules per mode is:

$$N = \frac{N_{mol}}{N_{modes}} = \frac{4\pi\rho L_z}{\left[\frac{\varepsilon\omega_{max}^2}{c^2} - \left(\frac{\pi}{L_z}\right)^2\right]}. \tag{S8}$$

From ref. 2, we take $\varepsilon = (1.41)^2$, $\omega_{max} = 0.3581 \times 10^{15}$ s^{-1} (which is characteristic for vibrational strong coupling), $L_z = 2$ μm, and $\rho = 8 \times 10^9$ μm^{-3}, resulting in $N \sim 10^{12}$ as reported in the main text.

Notes and references

1 K. S. Daskalakis, S. A. Maier and S. Kéna-Cohen, *Quantum Plasmonics*, 2017, 151–163.

2 J. del Pino, J. Feist and F. J. Garcia-Vidal, *New J. Phys.*, 2015, **17**, 053040.