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Theory for the response of hybrid light-matter modes in the presence of vibrations

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P(E) theory for molecular vibrations

A molecular excitation coupled to a vibration mode

$$H_{v+m,j} = \omega_m \sigma_j^\dagger \sigma_j + \frac{\omega_v}{2}\left(x_j^2 + p_j^2\right) + \omega_v \sqrt{S} \sigma_j^\dagger \sigma_j x_j$$

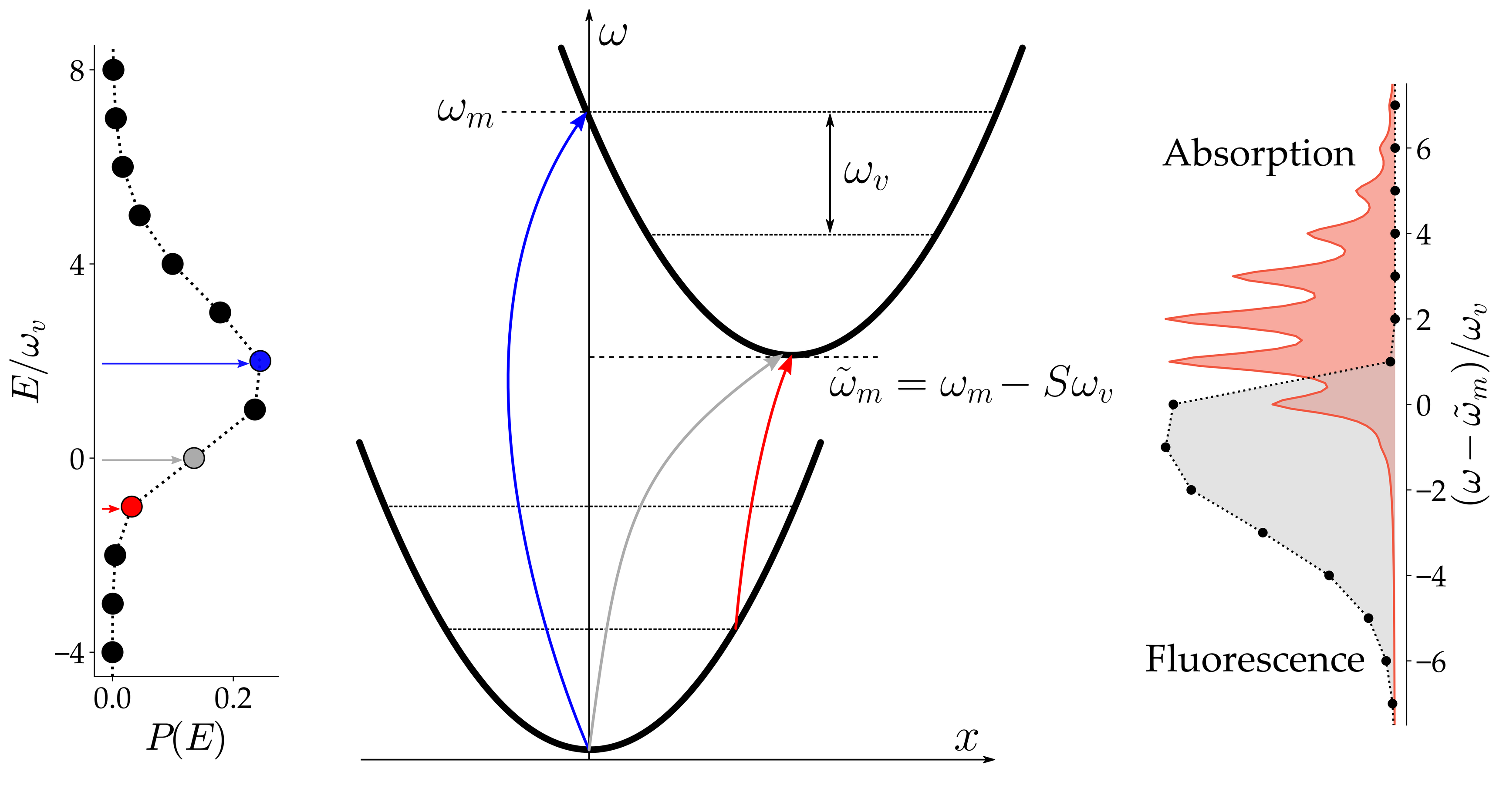

FIG. 1: *P(E)* function and its relation to the Franck-Condon picture.

Vibrational transitions described by

$$P(E) = \frac{1}{2\pi}\int \mathrm{d}t\, e^{iEt}\left\langle e^{i\sqrt{S}p_j(t)} e^{-i\sqrt{S}p_j(0)}\right\rangle$$

$P(E)$ is determined by $\langle p(t)p(0)\rangle$, assuming Gaussian fluctuations, which we solve from the Caldeira-Leggett model without dissipation (which we hope to include in the future)

Absorption and fluorescence of a molecule is determined by

$$A(\Delta) = \int \mathrm{d}E\, P(E)\chi(\Delta - E)$$

$$F = \int \mathrm{d}\omega_1\, \mathrm{d}\omega_2\, L(\omega_1, \omega_d - \omega - \omega_1, \omega_2)\chi(\omega_1 - \Delta)\chi(\omega_2 + \Delta)$$

where

$$\Delta = \omega_d - \tilde{\omega}_m$$

$$\chi(\omega) = \left(i\omega - \frac{\kappa_m}{2}\right)^{-1}$$

$$L(t_1, t_2, t_3) = \left\langle e^{i\sqrt{S}p(t_1)} e^{-i\sqrt{S}p(t_2)} e^{i\sqrt{S}p(0)} e^{-i\sqrt{S}p(t_3)}\right\rangle$$

Related to $P(E)$

Strong coupling between surface plasmon polariton and molecules

We take into account

- N identical and non-interacting molecules
- Their positions $\vec{r}_j$ and dipole moments $\hat{n}_j$
- Polarization of plasmon

$$H_{sc,j} = g_j \sigma_j^\dagger c + g_j^* c^\dagger \sigma_j$$

$$g_j = g e^{i\vec{k}\cdot\vec{r}_j}(\hat{n}_j \cdot \hat{u}_{pl})$$

$$\eta_{j,s/p}^{T/R} = \sqrt{\kappa_m^{T/R}}(\hat{n}_j \cdot \hat{u}_{s/p})$$

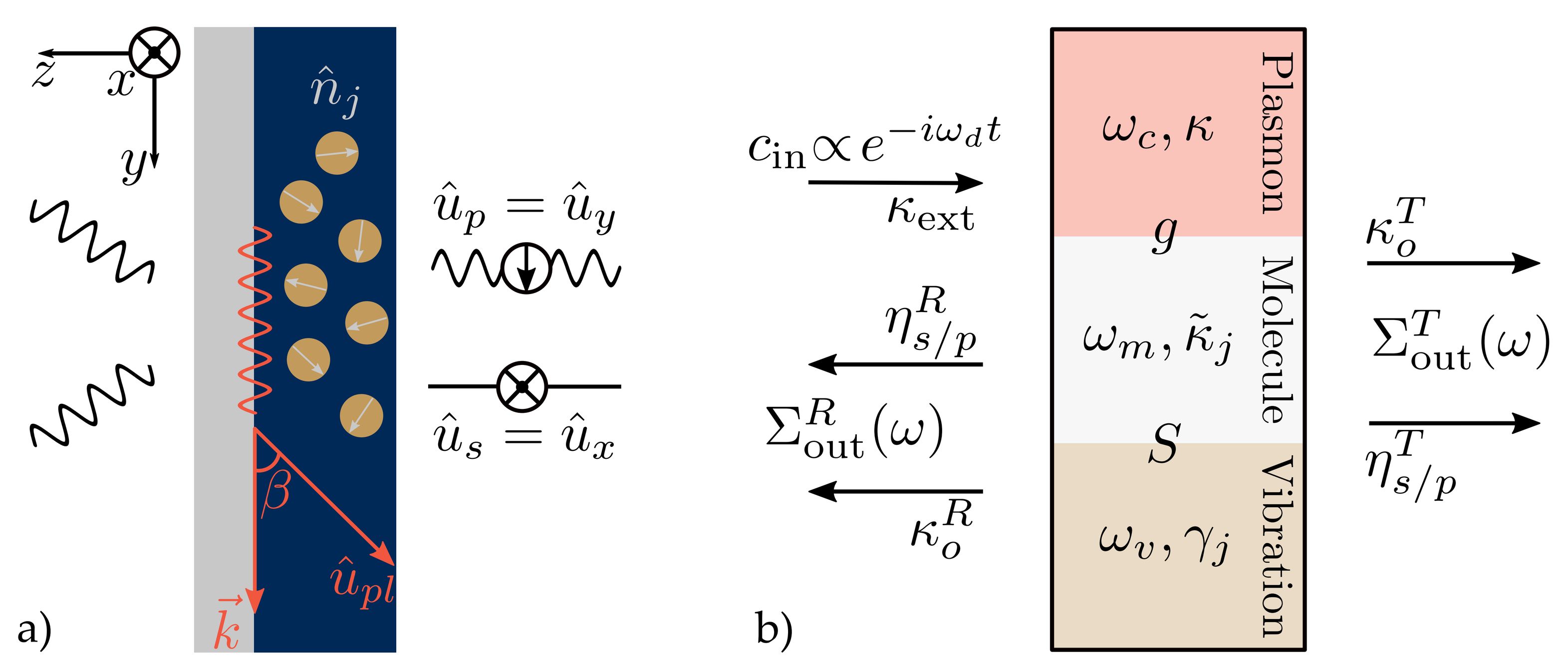

FIG. 2: a) Measurement setup. b) Schematic input-output picture.

Theoretical description from **input-output formalism**

Approximations: low driving power ($\rightarrow \sigma_j^\dagger \sigma_j \approx 0$), low temperature compared to ω_c, ω_m and ω_v.

The polaron operator $\sigma_j^S = e^{-i\sqrt{S}p_j}\sigma_j$ simplifies the dynamics

$$\dot{c} = -i\omega_c c - i\sum_j g_j^* \sigma_j^S e^{i\sqrt{S}p_j} - \frac{\kappa}{2}c - \sqrt{\kappa_{\mathrm{ext}}}c_{\mathrm{in}}$$

$$\dot{\sigma}_j^S = -i\tilde{\omega}_m \sigma_j^S - i g_j e^{-i\sqrt{S}p_j} c - \frac{\kappa_m}{2}\sigma_j^S - \sqrt{\kappa_m^{\mathrm{ext}}} e^{-i\sqrt{S}p_j}\sigma_{\mathrm{in},j}$$

Observable: the power spectral density of reflected and transmitted fields

$$\Sigma_{\mathrm{out},s/p}^{T/R} = \left(\delta_R^{T/R} c_{\mathrm{in}} + \sqrt{\kappa_o^{T/R}}c\right)\delta_p^{s/p} + \sum_j \eta_{j,s/p}^{T/R}\sigma_j$$

$$S_{s/p}^{T/R}(\omega;\omega_d) = \frac{1}{2\pi}\int \mathrm{d}t\, e^{i\omega t}\left\langle \Sigma_{\mathrm{out},s/p}^{T/R\dagger}(0)\Sigma_{\mathrm{out},s/p}^{T/R}(t)\right\rangle$$

Polaritonic response function and polarized emission spectra

$$r(\omega_d) = \sqrt{\kappa_{\mathrm{ext}}}\left[i(\omega_d - \omega_c) - \frac{\kappa}{2} + \sum_j |g_j|^2 A(\Delta)\right]^{-1}$$

Plasmon response

Molecular response, asymmetry in absorbance w.r.t. zero-phonon line causes asymmetry between upper and lower polariton

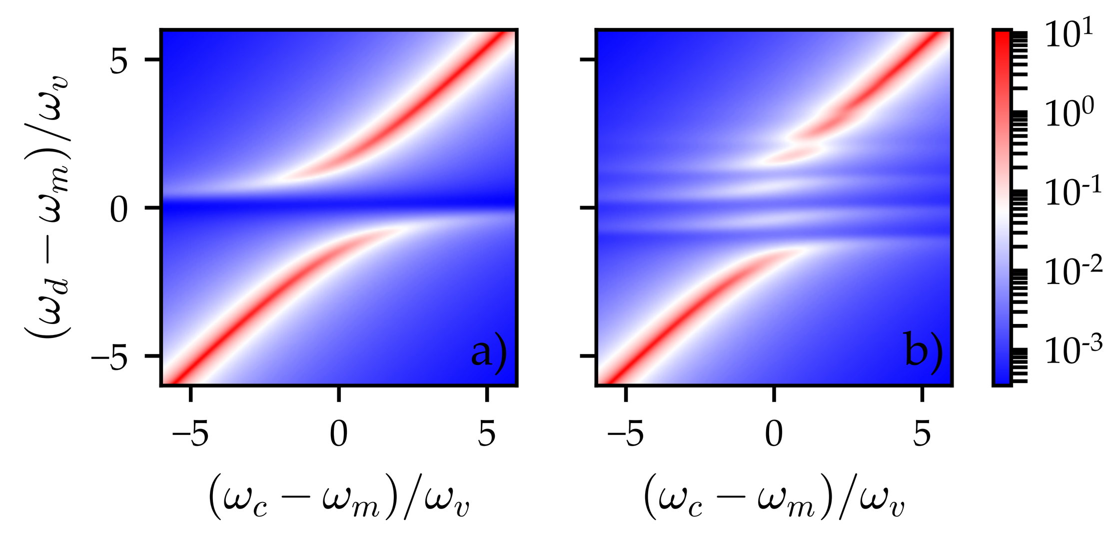

FIG. 3: Response function $|r(\omega_d)|^2/\omega_v$ for one molecule when a) $S = 0$ and b) $S = 1$.

Incoherent emission spectra, uniformly random positions

$$S_s^T(\omega;\omega_d) = |\alpha r(\omega_d)|^2 C_s F$$

$$S_p^T(\omega;\omega_d) = |\alpha r(\omega_d)|^2\left[\kappa_o^T \delta(\omega - \omega_d) + C_p F\right]$$

Coherent emission $e^{i\vec{k}\cdot\vec{r}_j} = \mathrm{constant}$, superradiance and vanishing s-polarized emission without vibrations

$$S_s^T(\omega;\omega_d) = |\alpha r(\omega_d)|^2 C_s\left[F - |A(\Delta)|^2\delta(\omega - \omega_d)\right]$$

$$S_p^T(\omega;\omega_d) = |\alpha r(\omega_d)|^2 \kappa_o^T\left|1 + i\frac{\sqrt{N}\tilde{C}_p}{\sqrt{\kappa_o^T}}A(\Delta)\right|^2\delta(\omega - \omega_d) + |\alpha r(\omega_d)|^2 C_p\left[F - |A(\Delta)|^2\delta(\omega - \omega_d)\right]$$

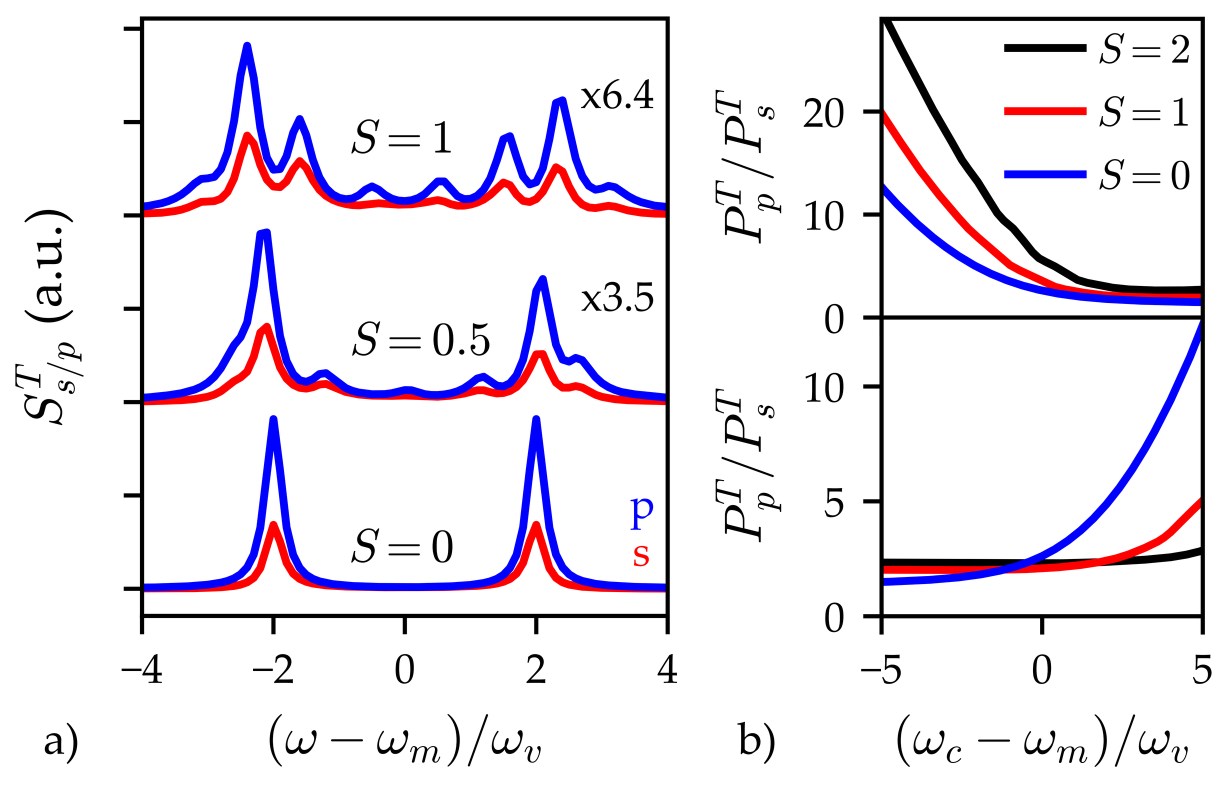

FIG. 4: a) Elastic emission spectra for s- and p-polarization when $\omega_c = \omega_m$. b) The ratio between elastically emitted p- and s-polarized power $P_{s/p}^T$ integrated over the lower ($\omega < \omega_m$) and upper ($\omega > \omega_m$) polariton branches (upper and lower panels, respectively).