Molecular Dynamics Simulations of the Polariton Transport

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Acknowledgements

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CSC

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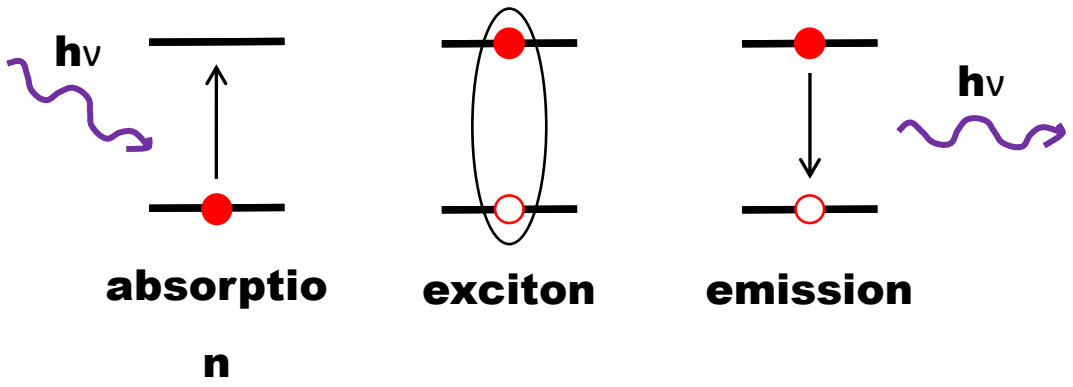
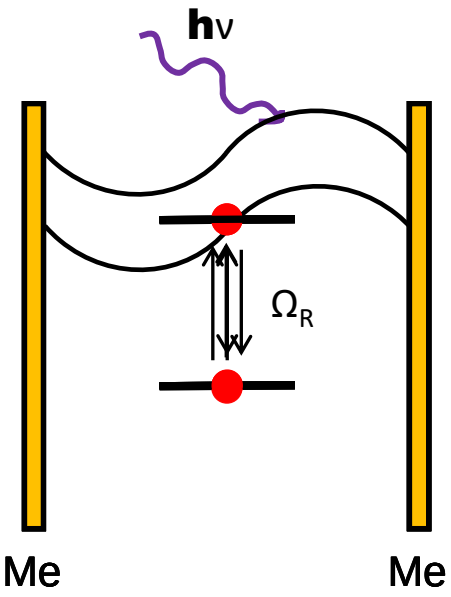
Interactions between a molecule and a photon

in free space



weak coupling

in a cavity



excitation **cavity leakage**

decay

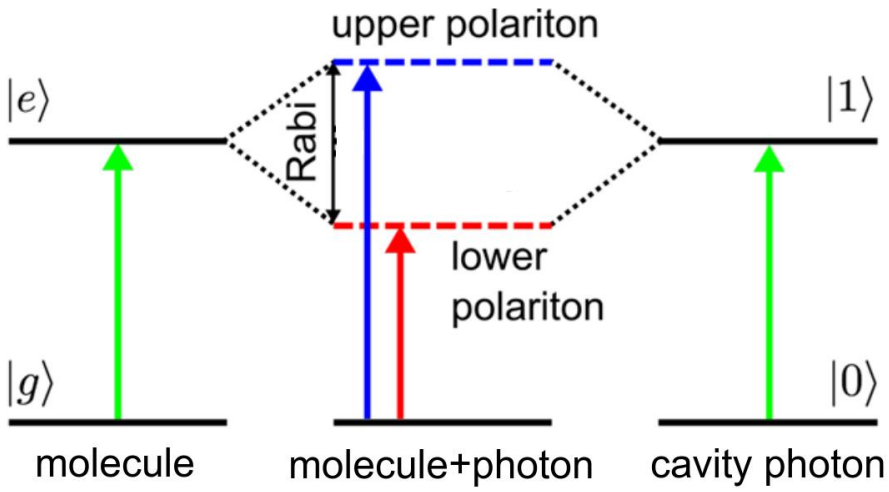
$$\Omega_R > \frac{\gamma_{mol} + \gamma_{cav}}{2}$$

strong coupling

Strong coupling phenomenon

At the strong coupling, two hybrid states (polaritons) inheriting properties of both the exciton and the cavity photon emerge.

N_{mol} = 1, n_{mode} = 1:



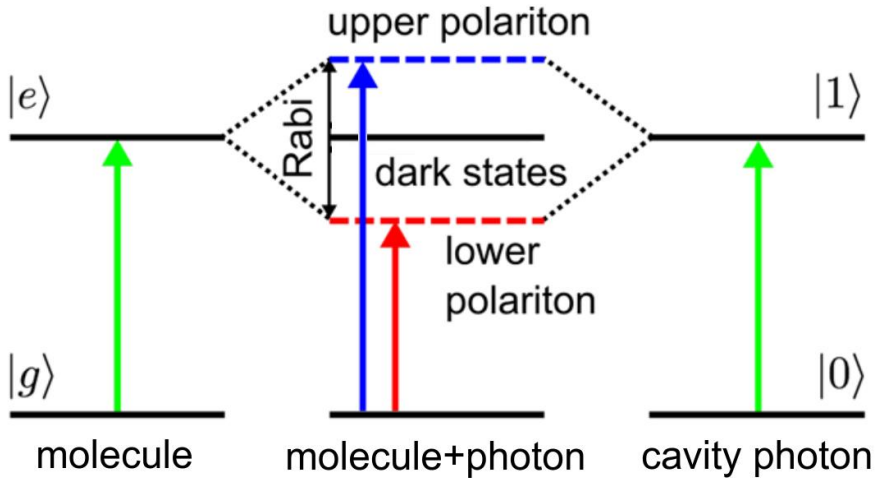
G. Groenhof et al., H, *J. Phys. Chem. Lett.*, **2019**, 10, 18, 5476–5483.

$$|LP\rangle = \frac{1}{\sqrt{2}}\left(|e,0\rangle - |g,1\rangle\right)$$

$$|UP\rangle = \frac{1}{\sqrt{2}}\left(|e,0\rangle + |g,1\rangle\right)$$

When N_{mol} > 1, the dark states appear

$N_{DS} = N_{mol} - n_{mode}$



$$\hbar\Omega_R = \boldsymbol{\mu}_{tr}\boldsymbol{u}_{EM}\sqrt{\frac{\hbar\omega_{EM}}{2\varepsilon_0 V}\cdot N_{mol}}$$

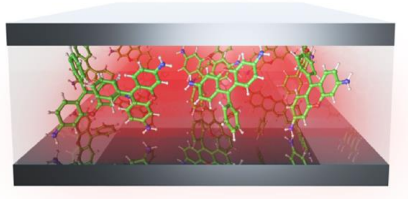
Strong coupling phenomenon

Theory

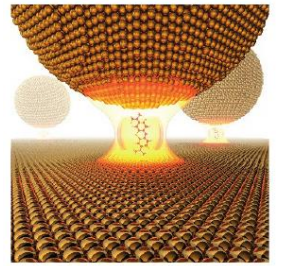
- describes chemistry for a single (or several) molecule
- N > ~1000 — too expensive
- usually a single cavity mode is treated

Experiments

- deal with huge molecular ensembles
- $N \leq$ ~1000 — difficult to achieve



J. Phys. Chem. Lett., **2019**, 10, 5476−5483

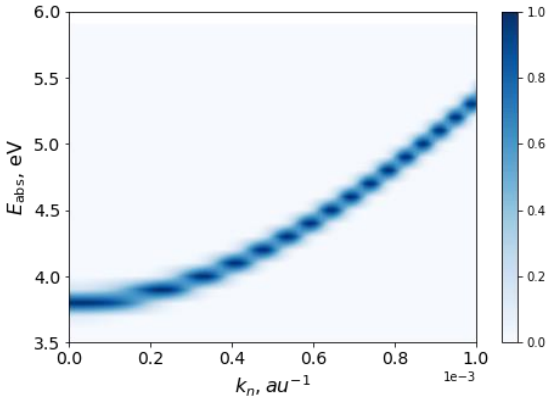


Nature, **2016**, 535, 127–130

Theoretical studies ⟷ Computer simulations ⟷ Experiments

<u>Requirements</u>:

- treat as many molecules as possible
- multiple cavity modes (dispersion)
- to choose an appropriate method

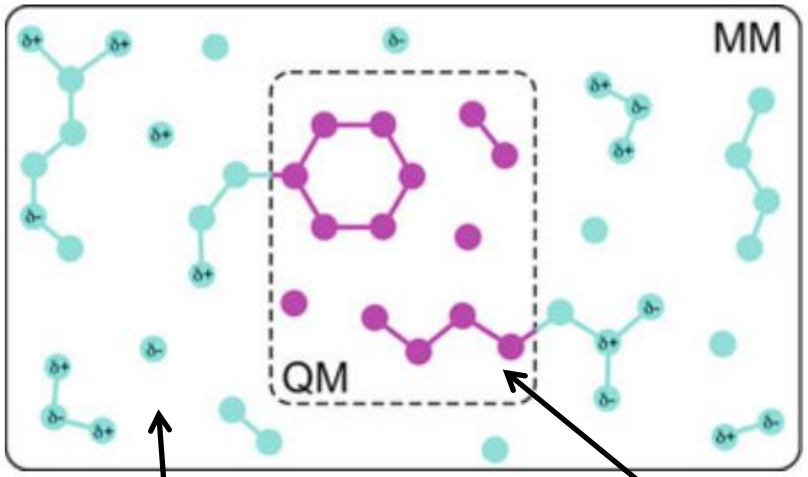


Quantum mechanics/Molecular mechanics (QM/MM)

A system in study is separated in two parts:

- **Quantum mechanical (QM) part** → ab inito methods

- Molecular mechanical (MM) part → mechanical force fields



Methods Mol Biol., **2013**, 924, 43-66.

atoms not (directly) involved in a chemical

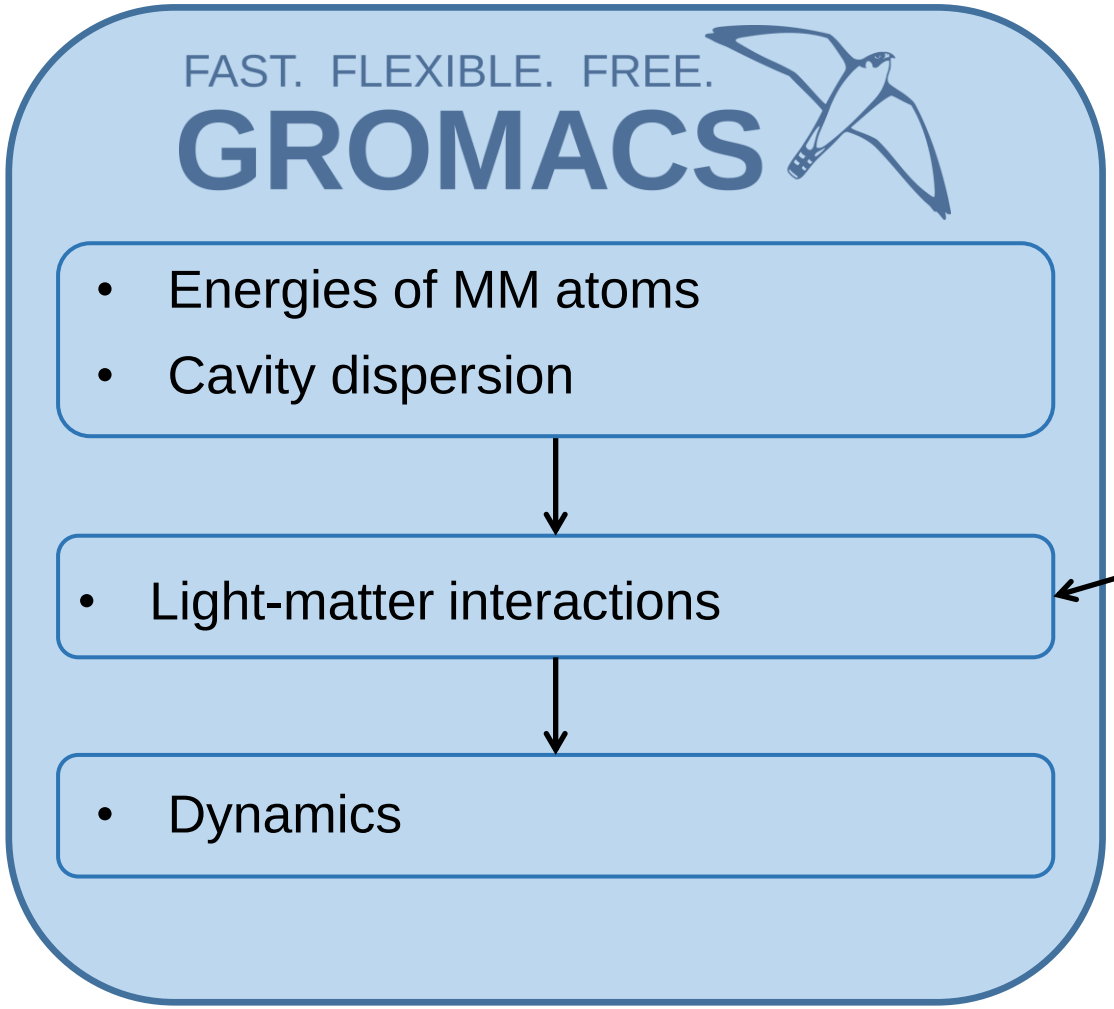
atoms involved in a chemical process

$$V_{\mathrm{MM}} = \sum_i V_i^{\mathrm{bonds}} + \sum_j V_j^{\mathrm{angles}} + \sum_k V_k^{\mathrm{torsions}} + \sum_{ij} V_{ij}^{\mathrm{Coulomb}} + \sum_{ij} V_{ij}^{\mathrm{VDW}}$$

Connection between QM and MM parts:

$$V_{\mathrm{QM/MM}} = V_{\mathrm{QM}} + V_{\mathrm{MM}} + V_{\mathrm{QM-MM}}$$

Quantum mechanics/Molecular mechanics (QM/MM)



QM atoms:

- ground excited state energies
- first excited state energies
- transition dipole moments

Gaussian, Inc.

Modified Gromacs code

(https://github.com/rhti/gromacs_qed)

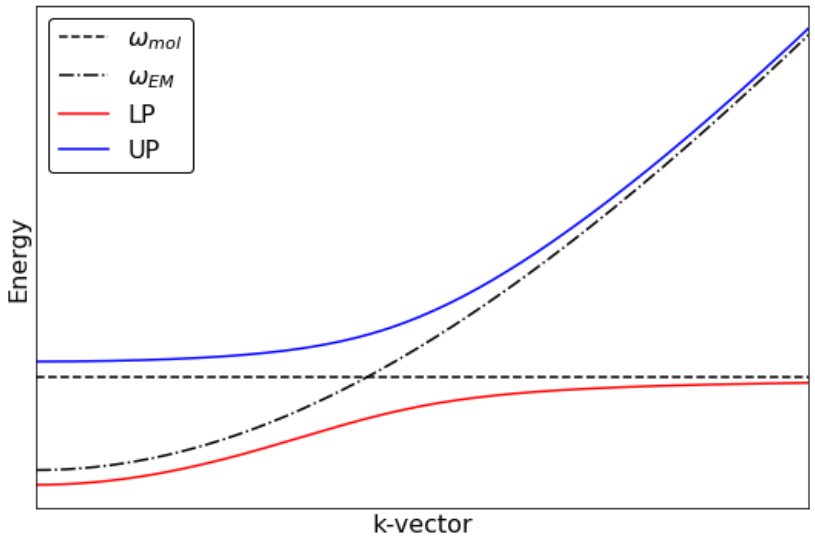
Motivation to study polariton transport

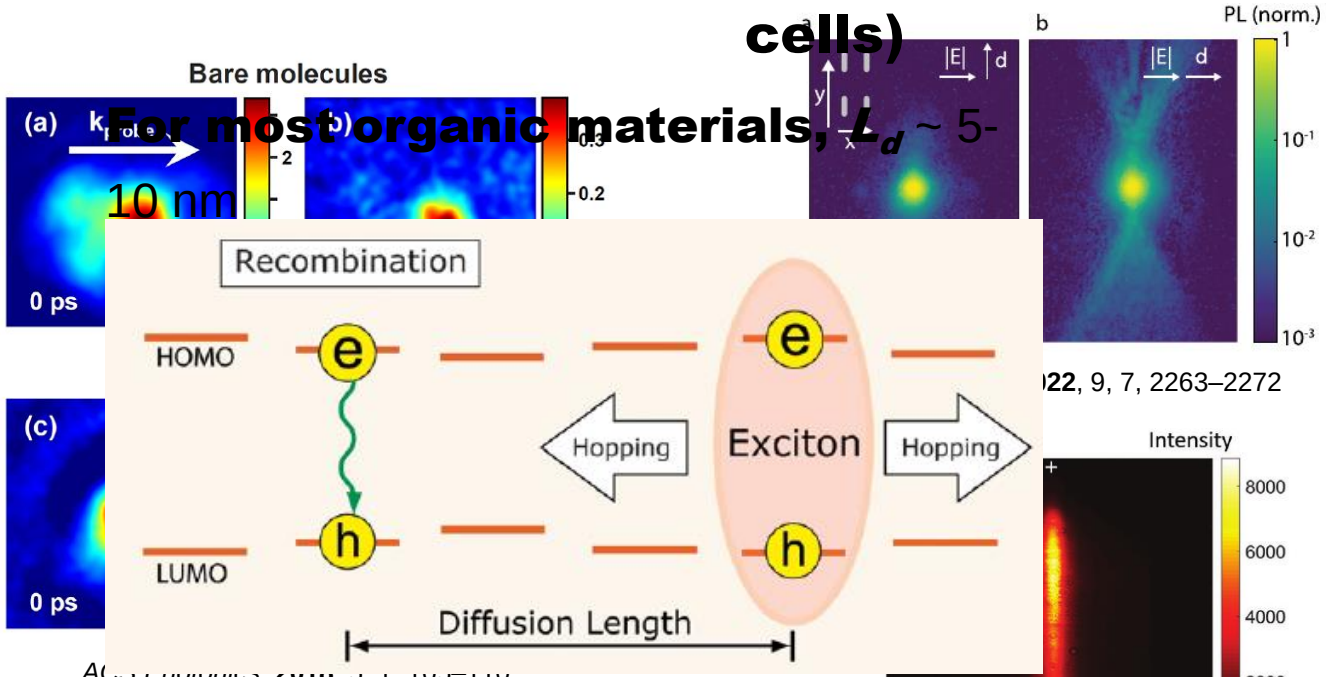
$N_{mol} \gg 1$, $n_{mode} > 1$

Since cavities have dispersion, polaritons possess a group velocity: $v_{gr} = \frac{1}{\hbar}\frac{d\omega}{dk}$

v_{gr} **can reach units—tens % of the speed of light → enhanced transport (for organic solar cells)**

For most organic materials, L_d ~ 5-





ACS Photonics, **2018**, 5, 1, 105−110.

Energy Environ. Sci., **2015**, 8, 1867.

22, 9, 7, 2263–2272

Adv. Mater., **2020**, 32, 28, 2002127

Simulations of polariton transport

$$H = \sum_{j}^{N} V_{S1}^{\mathrm{mol}}(\boldsymbol{R}_j) + \sum_{i}^{N} V_{S_0}(\boldsymbol{R}_i) + \sum_{k_z}^{n_{\mathrm{mode}}} \hbar\omega_{\mathrm{cav}}(k_z) + \sum_{j}\sum_{k_z} \boldsymbol{\mu}_j(\boldsymbol{R}_j)\boldsymbol{u}_{\mathrm{cav}} \sqrt{\frac{\hbar\omega_{\mathrm{cav}}(k_z)}{2\varepsilon_0 V_{\mathrm{cav}}}}\, e^{ik_z z_j}$$

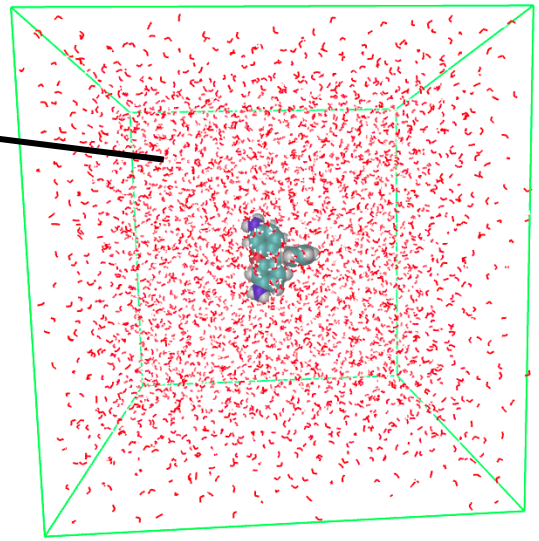
molecular part | ground state | cavity part | light-matter interactions

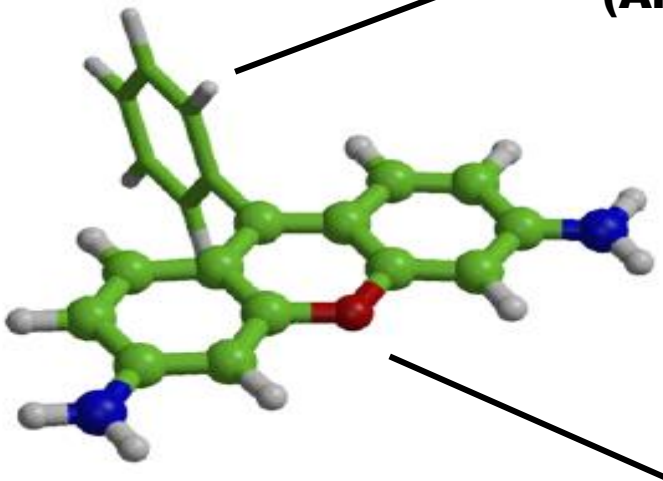
$$H = \begin{bmatrix} H^{\mathrm{mol}} & H^{\mathrm{int}} \\ (H^{\mathrm{int}})^{\dagger} & H^{cav} \end{bmatrix}$$

Rhodamine molecules in water solution

Classical subsystem

(Amber03-ff)





Quantum mechanical subsystem

(S_0 - RHF/3-21G, S1 - CIS/3-21G)

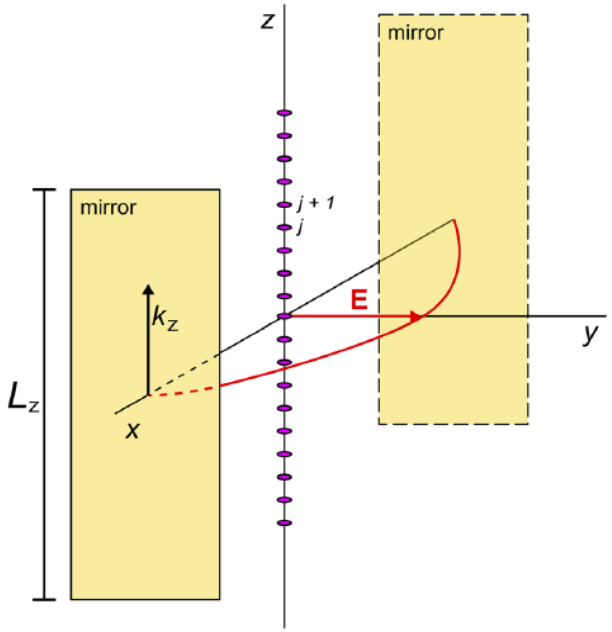
Gaussian, Inc.

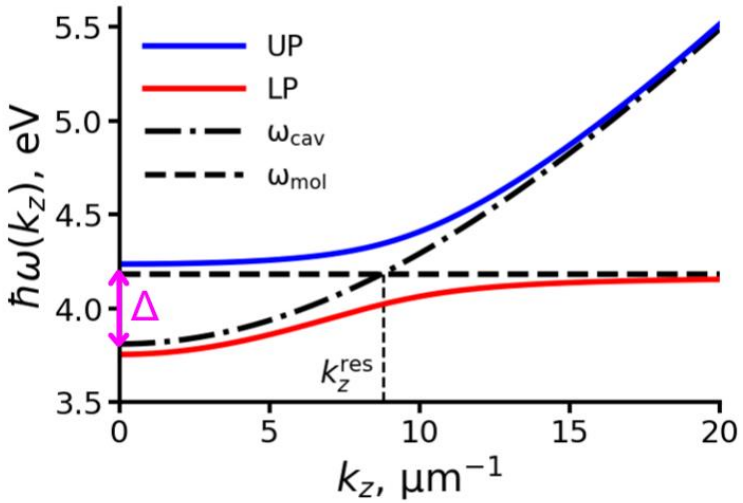
Simulations of polariton transport

$$H = \sum_{j}^{N} V_{S1}^{\mathrm{mol}}(R_j) + \sum_{i}^{N} V_{S_0}(R_i) + \sum_{k_z}^{n_{\mathrm{mode}}} \hbar\omega_{\mathrm{cav}}(k_z) + \sum_{j}\sum_{k_z} \boldsymbol{\mu}_j(R_j) u_{\mathrm{cav}} \sqrt{\frac{\hbar\omega_{\mathrm{cav}}(k_z)}{2\varepsilon_0 V_{\mathrm{cav}}}}\, e^{ik_z z_j}$$

molecular part | ground state | **cavity part** | light-matter interactions

$$H = \begin{bmatrix} H^{\mathrm{mol}} & H^{\mathrm{int}} \\ (H^{\mathrm{int}})^{\dagger} & H^{cav} \end{bmatrix}$$





$$\omega_{\mathrm{c}}(k_{\mathrm{z}}) = \frac{c}{n_r}\sqrt{\left(\frac{\pi}{L_{\mathrm{x}}}\right)^2 + \left(\frac{2\pi n}{L_z}\right)^2},\ n \in \mathbb{Z}$$

Main parameters:

L_z = 50 μm - cavity length

N_{mol} = 1024 - number of molecules

n_{modes} = 160 ($0 \leqslant n \leqslant 159$) - number of modes

E_c^{max} ~ 5.5 eV - cavity energy cut-off

$h\nu$ = 4.18 eV - excitation energy of Rhodamine

Δ = 370 meV - cavity detuning

$\hbar\Omega_R$ = 325 meV - Rabi splitting

γ_{cav} = 66.7 ps^{-1} - cavity decay rate

$$\rho_m(t+\Delta t) = \rho_m(t)\exp\left[-\gamma_{\mathrm{cav}}\sum|\alpha_n^m(t)|^2\Delta t\right.$$

Simulations of polariton transport

$$H = \sum_{j}^{N} V_{S1}^{\mathrm{mol}}(\boldsymbol{R}_j) + \sum_{i}^{N} V_{S_0}(\boldsymbol{R}_i) + \sum_{k_z}^{n_{\mathrm{mode}}} \hbar\omega_{\mathrm{cav}}(k_z) + \sum_{j}\sum_{k_z} \boldsymbol{\mu}_j(\boldsymbol{R}_j)\boldsymbol{u}_{\mathbf{cav}} \sqrt{\frac{\hbar\omega_{\mathrm{cav}}(k_z)}{2\varepsilon_0 V_{\mathrm{cav}}}}\, e^{ik_z z_j}$$

molecular part

ground state

cavity part

light-matter interactions

$$H = \begin{bmatrix} H^{\mathrm{mol}} & H^{\mathrm{int}} \\ \left(H^{\mathrm{int}}\right)^{\dagger} & H^{cav} \end{bmatrix}$$

Simulations of polariton transport

- **diagonalise hamiltonian** → eigenfunc $|\psi^m\rangle = \left(\sum_j^N \beta_j^m \hat{\sigma}_j^+ + \sum_n^{n_{\mathrm{mode}}} \alpha_n^m \hat{a}_n^\dagger\right) |\mathrm{S}_0^1 \mathrm{S}_0^2 .. \mathrm{S}_0^{N-1} \mathrm{S}_0^N\rangle |0\rangle$
- total wave function is expanded in the basis of the polaritonic states: $|\Psi(t)\rangle = \sum_m c_m(t) |\psi^m\rangle$

Expanstion coefficients $c_m(t)$ are integrated in a (stable) *local diabatic basis :**

$\mathbf{c}(t+\Delta t) = \mathbf{T}^\dagger \exp[-i\mathbf{Z}\Delta t]\mathbf{c}(t)$ with

$\mathbf{T} = \mathbf{S}\left(\mathbf{S}^{\mathrm{T}}\mathbf{S}\right)^{-1/2}$, where $S_{ml} = \langle \psi^m(t) | \psi^l(t+\Delta t)\rangle$

$\mathbf{Z} = \frac{1}{2}\left[\mathbf{V}(t) + \boldsymbol{H}^{\mathrm{ldb}}(t+\Delta t)\right]$

eigenvalues of H

$\mathbf{T}\mathbf{V}(t+\Delta t)\mathbf{T}^\dagger$

*) J. CHem. Phys. 114 (2001) 10608

Simulations of polariton transport

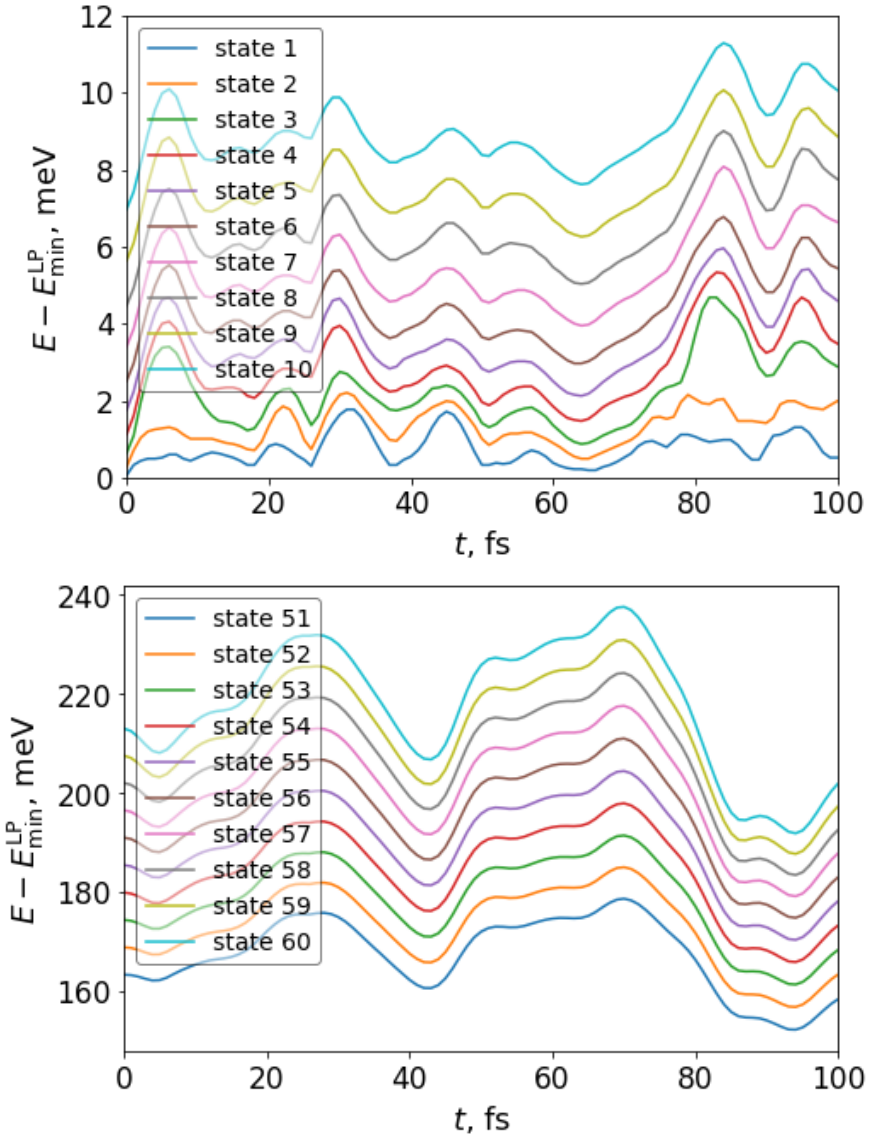
- Ehrenfest dynamics

  Hellmann–Feynman theorem:

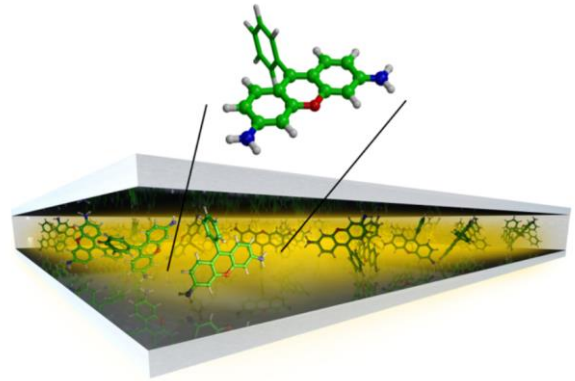
$$\boldsymbol{F}_a = -\langle \Psi(t) | \nabla_a H_{TC} | \Psi(t) \rangle$$

- non-adiabatic couplings are calculated:

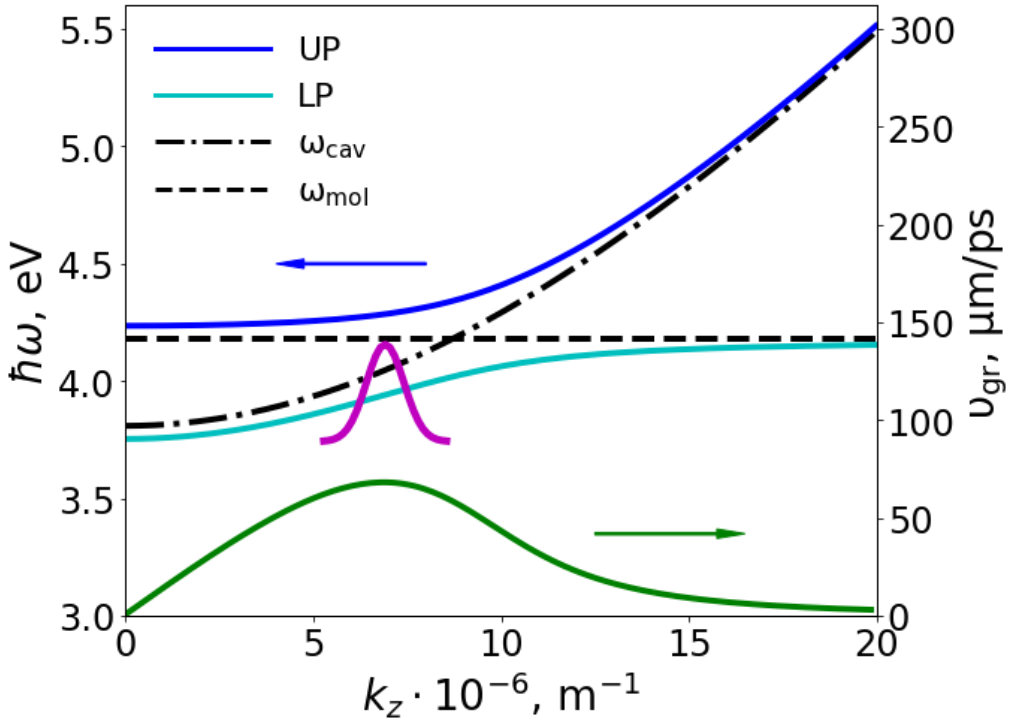
$$\boldsymbol{d}_{n,m} = \frac{\langle \psi^m | \nabla_a H_{TC} | \psi^n \rangle}{E_n - E_m}$$



Results

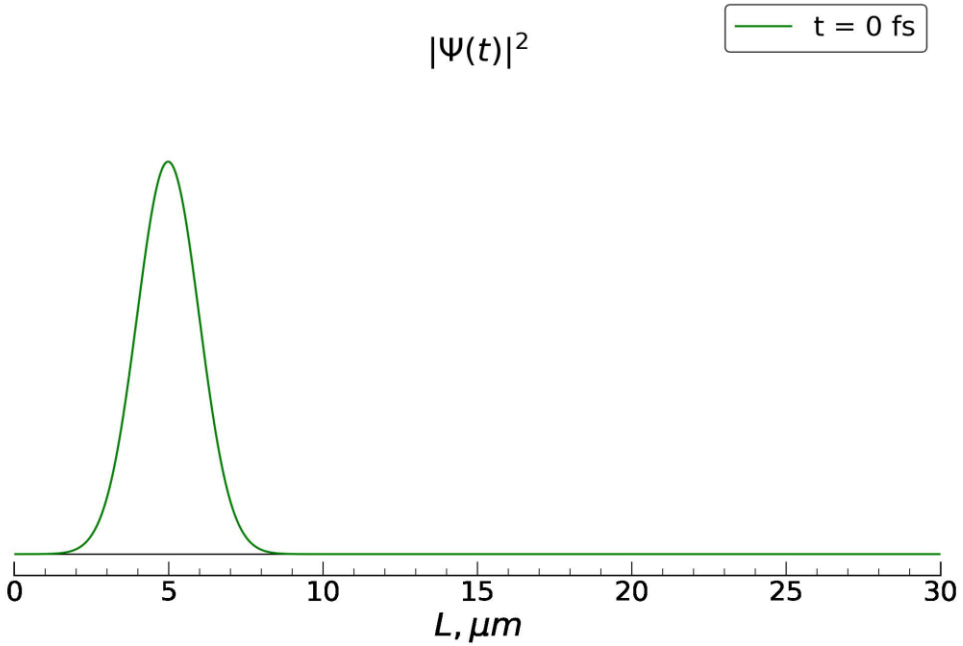


1) Resonant (direct) excitation of polaritons



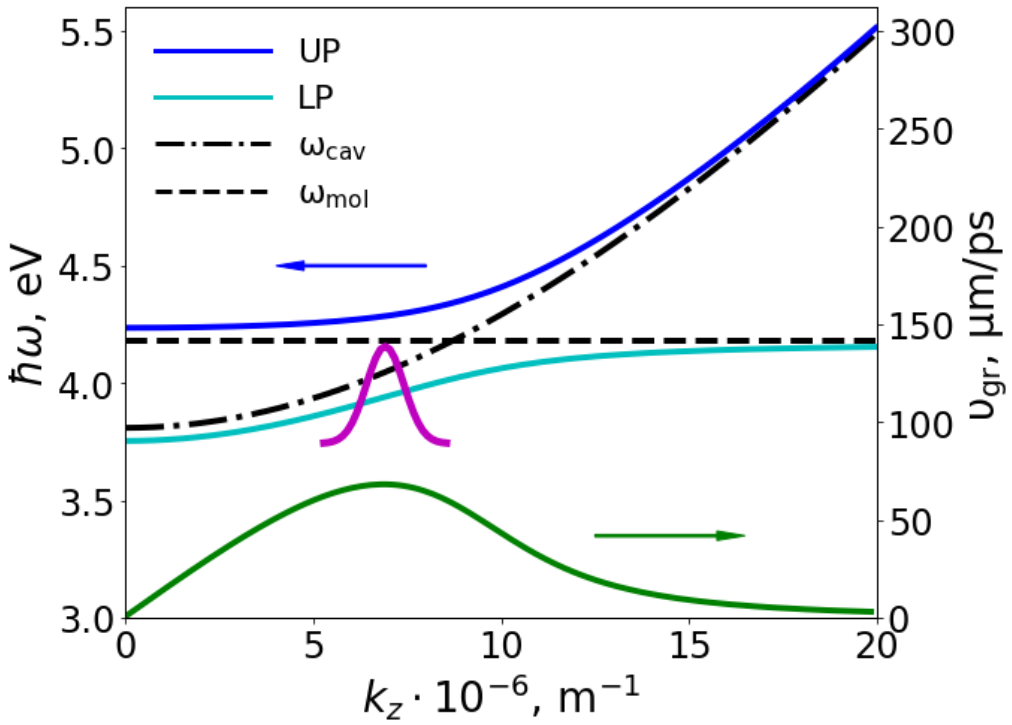
$$|\Psi(t)\rangle = \sum_m c_m e^{iE_m t/\hbar} |\psi^m\rangle$$

$$c_m(0) \sim e^{-\beta(k_m - k_0)}$$



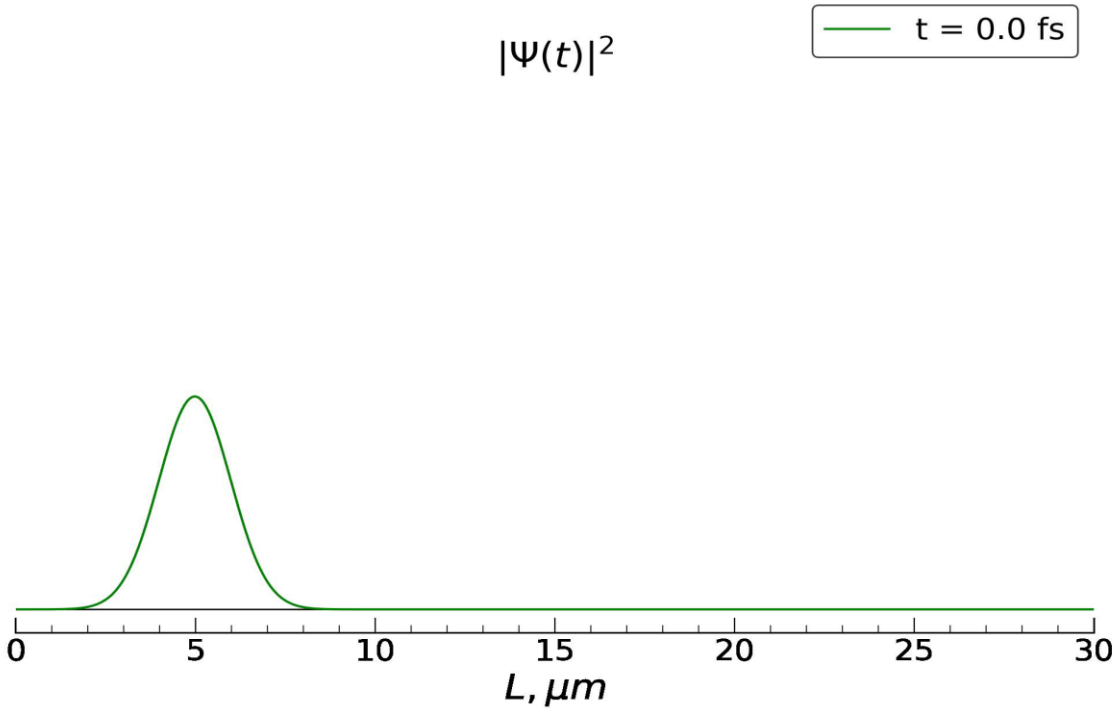
Results

1) Resonant (direct) excitation of polaritons



$$c_m(0) \sim e^{-\beta(k_m - k_0)}$$

QM/MM simulations:

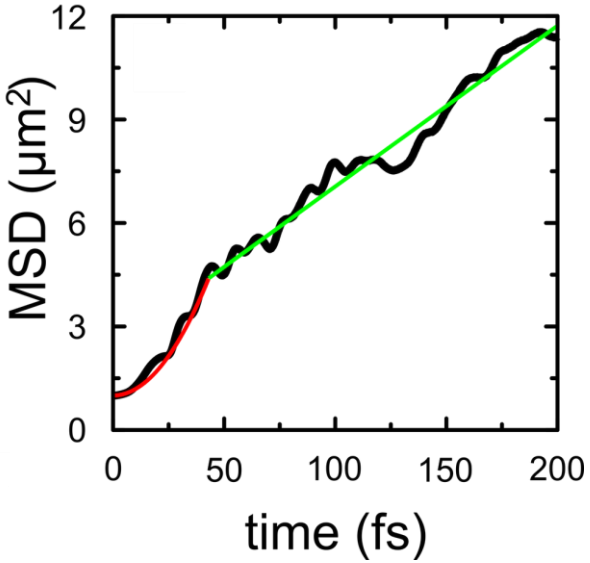


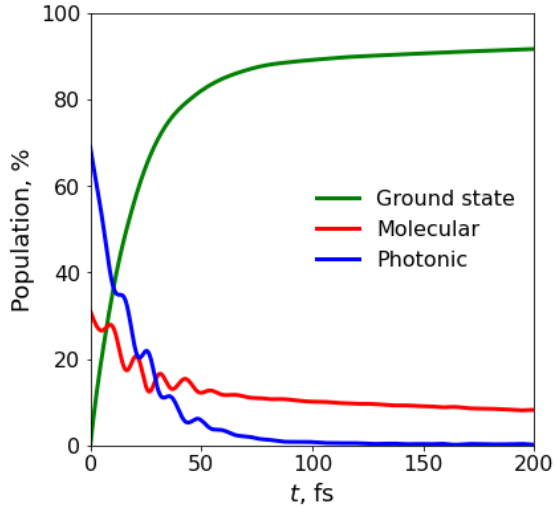
- **μm-scale propagation**
- **influence of vibronic transitions and**

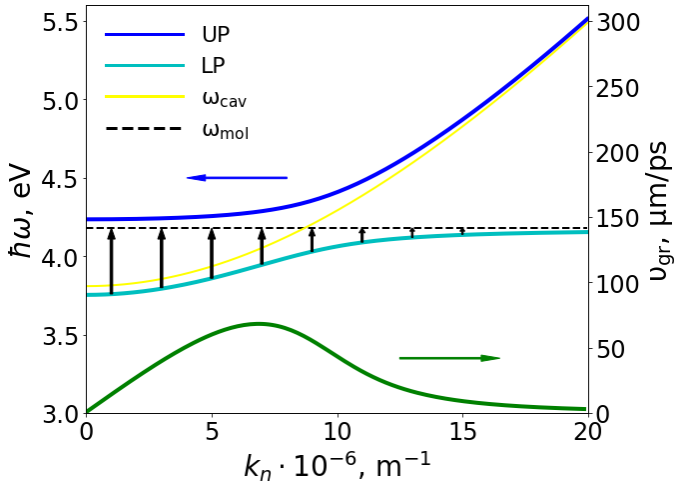
Results

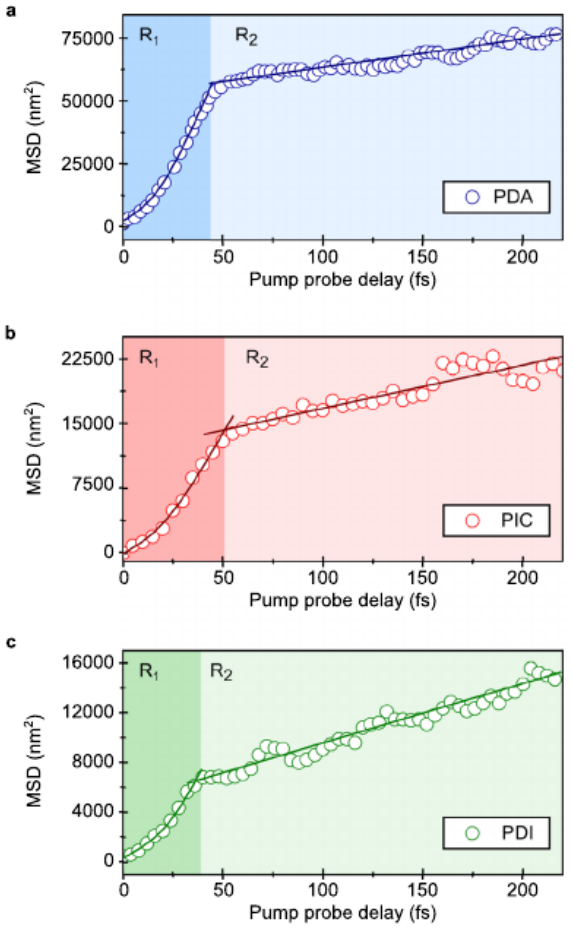
2) Resonant excitation

$$\mathrm{MSD} = \langle |z(t) - z(0)|^2 \rangle$$







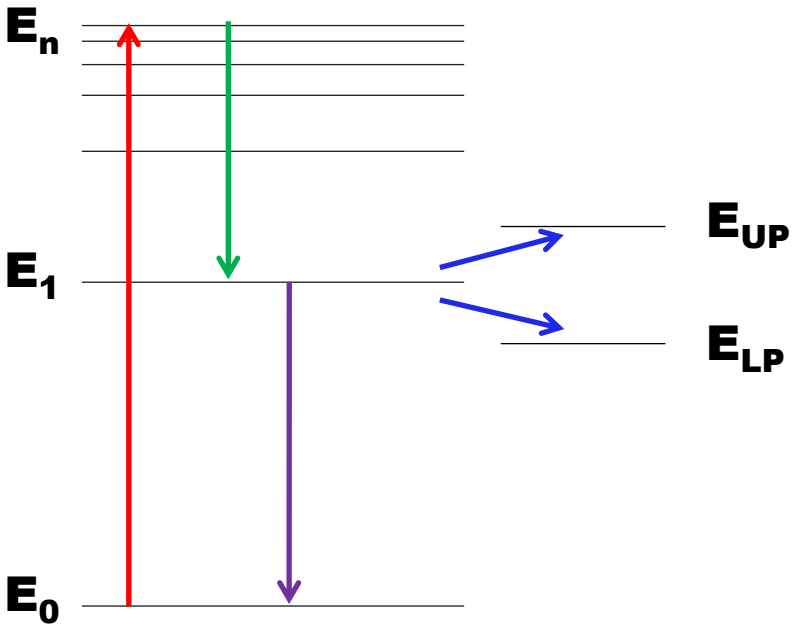


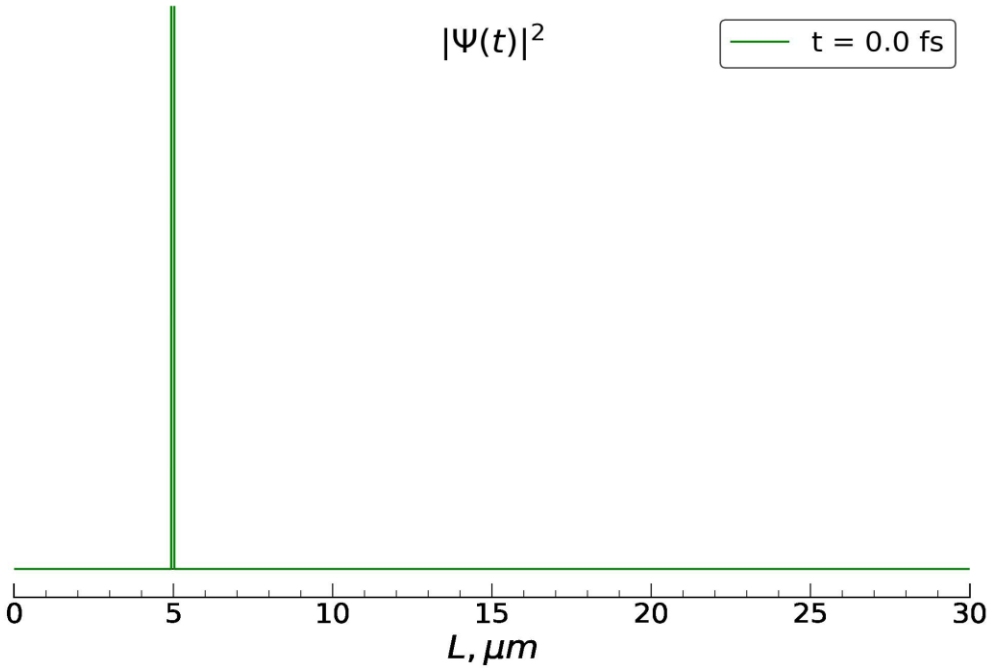
- **ballistic transport of the initial wave packet**
- transition to ballistic motion at *t* ~ 40 fs

Nat. Commun., **2021**, 12, 6519

Results

2) Off-resonant (indirect) excitation





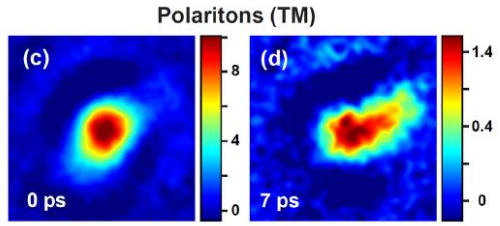
1. excitation

2. fast relaxation to E_1

3. relaxation to the ground state

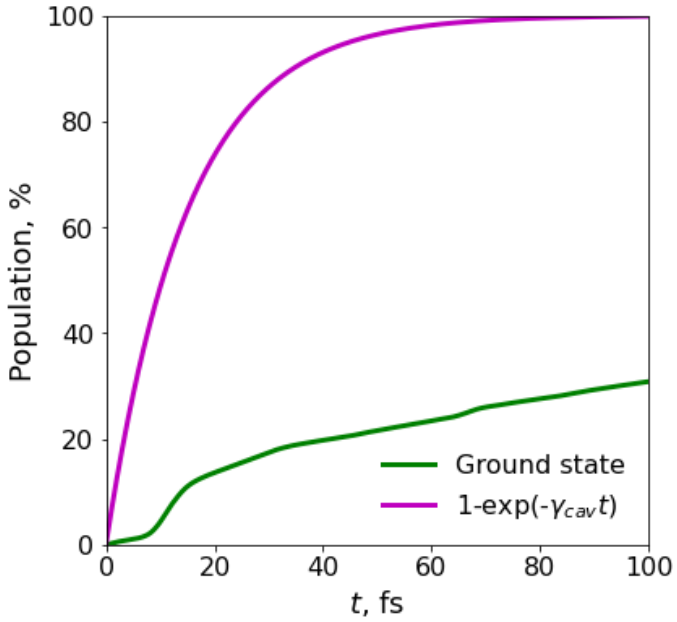
4. feeding upper and lower polaritons

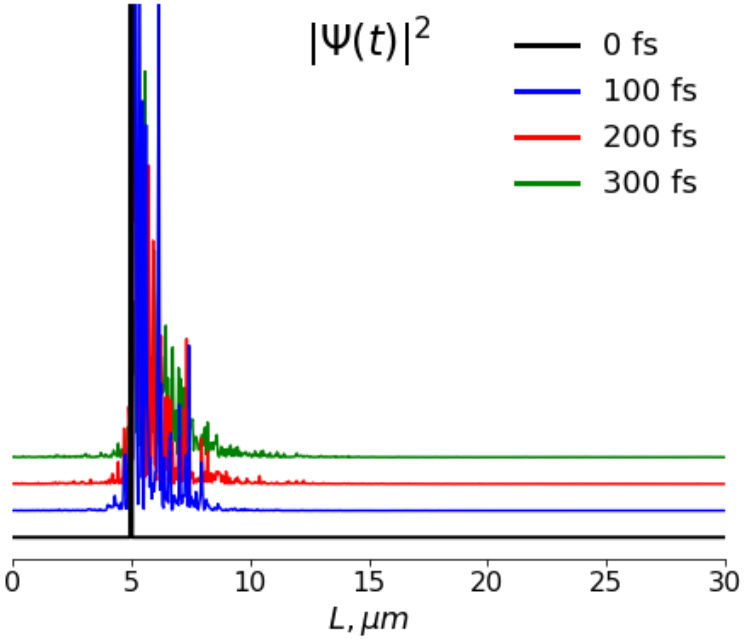
Results

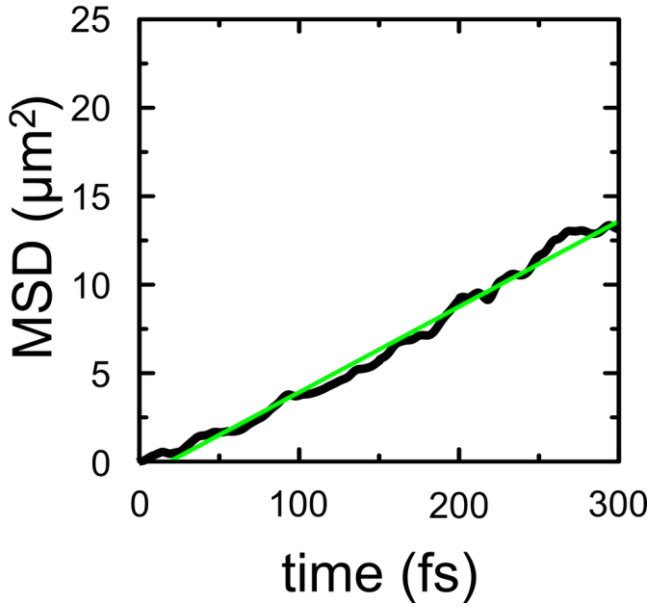


2) Off-resonant excitation

Cavity decay:







- **propagation is of the μm-scale**
- polaritons survive for much longer than ascribed by the cavity lifetime (τ_{cav} **= 15 fs)**

Summary

- **Polariton propagation was studied by means of QM/MM simulations**
- **The transport is of** μm-range, which is 2−3 orders of magnitude higher than the diffusion length of typical organic materials
- **Polaritons can survive much longer than the cavity lifetime due to the dark states**
- **We believe that these findings will help rationally design of molecule-cavity systems for achieving coherent long-range energy transport**

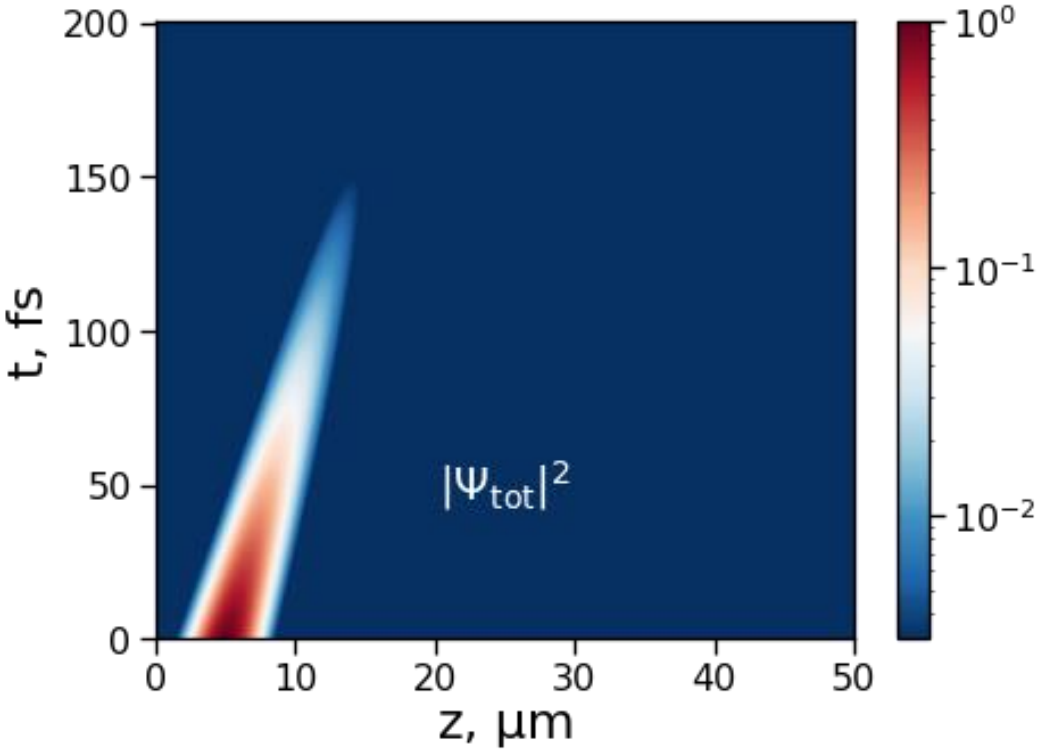
References

- **IRENA 2016: https://www.irena.org/publications/2016/Jun/End-of-life-management-Solar-Photovoltaic-Panel**
- **IEA 2022: https://iea-pvps.org/wp-content/uploads/2022/09/PVPS_Trend_Report_2022.pdf**
- **NREL chart: https://www.nrel.gov/pv/cell-efficiency.html**

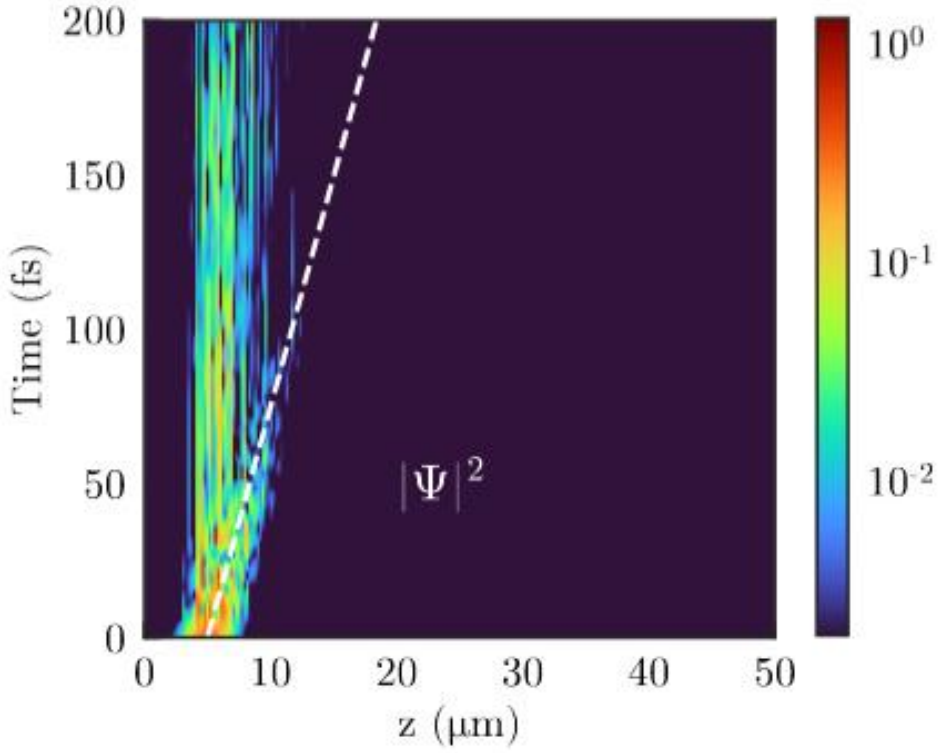
Results

1) Resonant excitation

$$|\Psi(t)\rangle = \sum_m c_m e^{iE_m t/\hbar} |\psi^m\rangle$$



analytical solution with disorder
(σ = 0.05 eV, average of 50 runs)



full MD