On-the-Fly Cavity–Molecular Dynamics of Vibrational Polaritons

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Computational parameters

Table 1: DFTB+ input parameters used in this work.

Parameter	**Value**
SCF Tolerance	`Hamiltonian_SCCTolerance = 1e-5`
Maximum SCC Iterations	`Hamiltonian_MaxSCCIterations = 400`
Mixer	`Hamiltonian_Mixer = Anderson{ MixingParameter = 0.026 }`
Convergent SCC Only	`Hamiltonian_ConvergentSccOnly = Yes`
k-point Grid	`(3, 3, 3)`

Table 2: Cavity mode frequencies and coupling prefactors used in this work.

Cavity Frequency ω_c (eV)	η_0 **(a.u.)**
0.16	0.00009
0.19	0.00010
0.22	0.00012
0.43	0.00034

The light–matter coupling parameter η in the Eq. 5 of the main text, constructed as multiplication of η_0

Convergence

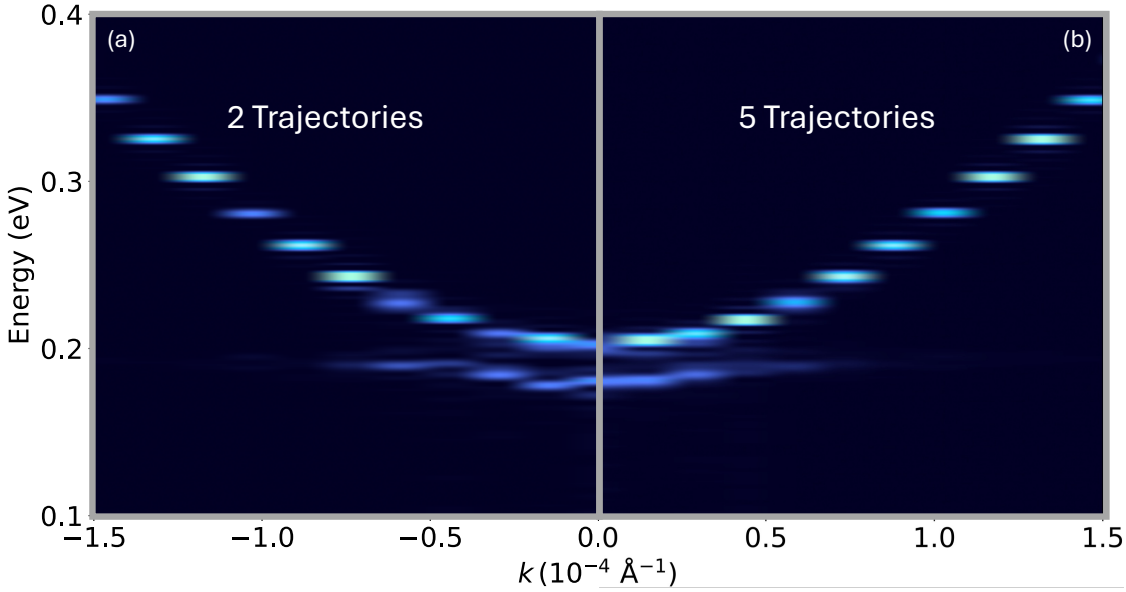

Figure 1: Angle-resolved spectra obtained with (a) 2 and (b) 5 trajectories. As seen here, due to the large number of particles (> 8000) leads to a rapid convergence; even 2 trajectories are sufficient to obtain a reasonable angle-resolved spectrum.

To assess the accuracy of the approximation $\sqrt{\omega_k}(g_0.\mu_n) \approx \sqrt{\omega_0}(g_0.\mu_n)$ used in the main text, we consider the following two band model, written as ($\hbar = 1$)

$$\hat{H} = \begin{bmatrix} E_0 & g_k \\ g_k & \omega_k \end{bmatrix} \tag{1}$$

where $E_0 = 1564.71$ cm^{-1} is the molecular normal mode frequency and $g_k = g_0\sqrt{\omega_k/\omega_0}$ is the light-matter coupling and the polariton band are obtained by diagonalizing $\hat{H}$. In Fig. 2, we compare the results obtained by diagonalizing $\hat{H}$ with the approximation $g_k = g_0\sqrt{\omega_k/\omega_0} \approx g_0\sqrt{\omega_0/\omega_0} = g_0$ (we obtain g_0 by fitting our on-the-fly spectra). The results confirm that this approximation does not alter the polaritonic angle resolved spectra, validating the approximation we made.

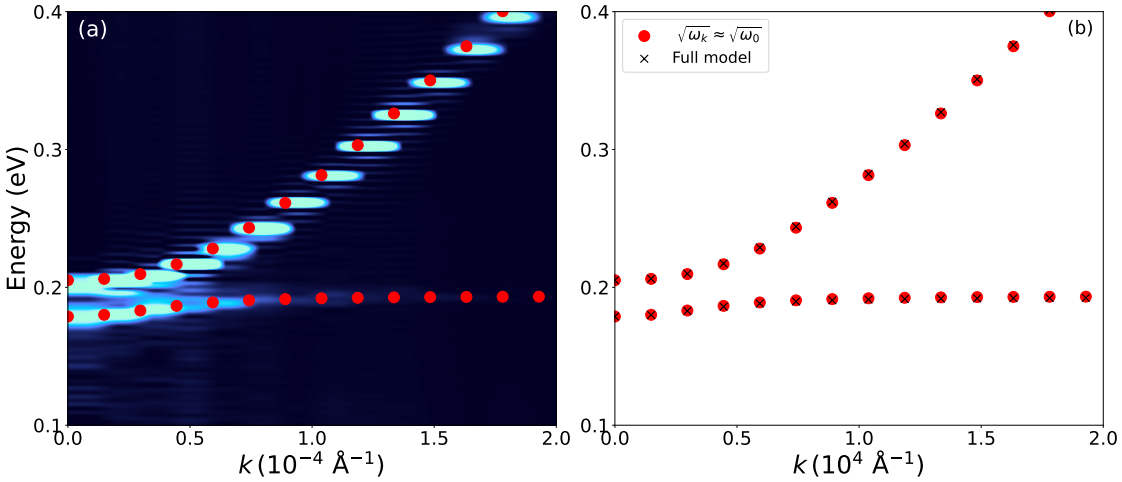

Figure 2: (a) Angle-resolved spectra obtained from cavity molecular dynamics simulations, overlaid with corresponding energy dispersion obtained from effective model Hamiltonian with $\sqrt{\omega_k} \approx \sqrt{\omega_0}$ approximation in the coupling. (b) Comparison between the approximate model and the model retaining the full $\sqrt{\omega_k}$ dependence of the light–matter coupling.