Supplementary Information — Disorder enhanced vibrational entanglement and dynamics in polaritonic chemistry

David Wellnitz,[1,2] Guido Pupillo,[2] and Johannes Schachenmayer[1,2,*]

[1] *IPCMS (UMR 7504), CNRS, 67000 Strasbourg, France*

[2] *Université de Strasbourg and CNRS, ISIS (UMR 7006) and icFRC, 67000 Strasbourg, France*

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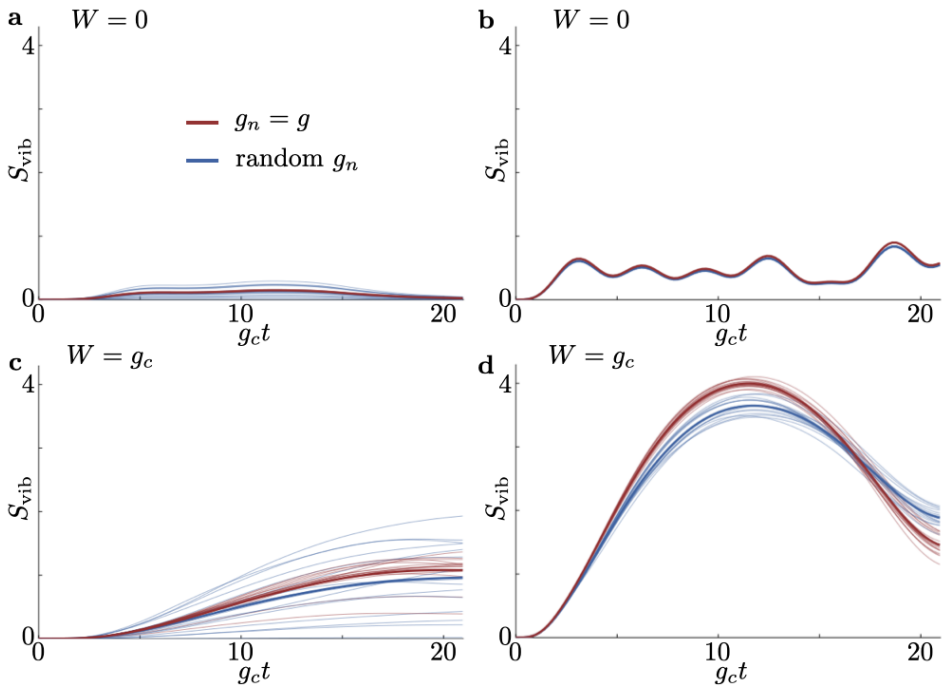
Supplementary Note 1. DISORDERED LIGHT-MATTER COUPLING STRENGTHS

In real experiments, due to the cavity mode profile and molecular orientations, typically the light-matter coupling strength differs for different molecules. In this case, Eq. (2) needs to be replaced by

$$\hat{H}_{\mathrm{TC}} = \sum_{n=1}^{N} \Delta \hat{\sigma}_n^+ \hat{\sigma}_n^- + \sum_{n=1}^{N} g_n \left(\hat{a} \hat{\sigma}_n^+ + \hat{a}^\dagger \hat{\sigma}_n^- \right). \tag{S1}$$

Supplementary Figure 1 shows the influence of such disordered coupling strengths on the results. While we find that uniform disorder in the local coupling strengths leads to minor modifications, most notably to increased variance, the general conclusion of entanglement enhanced by local energetic disorder remains true for both initial states.



Supplementary Figure 1. **Effect of local coupling strengths g_n.** The time evolution of the vibrational entanglement entropy S_{vib} is shown for constant $g_n = g$ (red), as considered in the main manuscript, and uniformly randomly distributed $g' \leq g_n \leq g$ (blue), while $g_{\mathrm{c}} = \sqrt{\sum_n g_n^2}$ (and thus the Rabi splitting) is kept constant. The thin, transparent lines represent individual disorder realizations (16 each), while the thick lines are the disorder average. The parameters are $N = 100$, $\lambda = 0.4$, $\nu = 0.3 g_{\mathrm{c}}$. The different panels show results for no energetic disorder $W = 0$ (a,b) and large energetic disorder $W = g_{\mathrm{c}}$ (c,d), each for the initial states $|\psi_0^{\mathrm{m}}\rangle$ (a,c) and $|\psi_0^{\mathrm{c}}\rangle$ (b,d).

* schachenmayer@unistra.fr

Supplementary Note 2. DARK STATE CONTRIBUTION TO $|\psi_0^{\mathrm{m}}\rangle$ WITHOUT DISORDER

The eigenstates of $\hat{H}_{\mathrm{TC}}$ are given by two polaritons $|\pm\rangle = \hat{a}^\dagger/\sqrt{2} \pm \sum_n \hat{\sigma}_n^+/\sqrt{2N}\,|0\rangle_{\mathrm{exc+ph}}$, and $N-1$ degenerate dark states, for which any orthonormal basis of $\mathcal{H}_{\mathrm{ph}} \otimes \mathcal{H}_{\mathrm{exc}}$ that does not contain the polaritons may be chosen. The most straightforward way to compute the dark state contribution of a state $|\psi\rangle$ is thus $\sum_d |\langle d|\psi\rangle|^2 = 1 - |\langle +|\psi\rangle|^2 - |\langle -|\psi\rangle|^2$. We find $\sum_d |\langle d|\psi_0^{\mathrm{m}}\rangle|^2 = 1 - 1/N$.

Supplementary Note 3. PERTURBATIVE PHOTO-CONTRIBUTION TO THE DARK STATES

In this section, we compute the photo-contribution to the dark states perturbatively in the regime $g_{\mathrm{c}} \gg W, \nu, \lambda\nu$. Starting from the analytically solvable Hamiltonian $\hat{H}_0 = \hat{H}_{\mathrm{TC}} + \hat{H}_{\mathrm{vib}}$ given by Eqs. (2) and (3) of the main text, we compute the perturbative corrections to the photo-contribution of the polaritons. The perturbative photo-contribution to the dark states can then be computed as $\sum_d |\langle d|1_{\mathrm{ph}}\rangle|^2 = 1 - |\langle +|1_{\mathrm{ph}}\rangle|^2 - |\langle -|1_{\mathrm{ph}}\rangle|^2$, analogous to the previous section.

The eigenstates of $\hat{H}_0$ are product states of the eigenstates of $\hat{H}_{\mathrm{TC}}$ and the eigenstates of $\hat{H}_{\mathrm{vib}}$, because the two sub-spaces remain uncoupled. The eigenstates of $\hat{H}_{\mathrm{TC}}$ are the two polaritons $|\pm\rangle$ and the $N-1$ degenerate dark states, for which we choose a momentum basis $|k\rangle = \left[\sum_{n=1}^N \exp(-2\pi \mathrm{i} kn/N)\hat{\sigma}_n^+/\sqrt{N}\right]|0\rangle_{\mathrm{exc+ph}}$. The eigenstates of $\hat{H}_{\mathrm{vib}}$ are Fock states $\left(\prod_n (\hat{b}_n^\dagger)^{i_n}/\sqrt{i_n!}\right)|0\rangle_{\mathrm{vib}}$ with i_n vibrational excitations on the n-th molecule.

Disorder

We first compute the perturbative corrections due to disorder $\hat{H}_{\mathrm{dis}}$, only. In this case, the vibrations are not entangled with the photo-electronic degrees of freedom, and we can restrict the perturbative analysis to the photo-electronic degrees of freedom, only. The second order corrections to the states $|\pm\rangle$ are given by [1]

$$|\pm\rangle = \left|\pm^{(0)}\right\rangle + \left|\pm^{(1)}\right\rangle + \left|\pm^{(2)}\right\rangle + \mathcal{O}(W^3/g_{\mathrm{c}}^3) \tag{S2}$$

$$\left\langle \psi^{(0)}\middle|\phi^{(1)}\right\rangle = \begin{cases} 0 & \text{for } \psi = \phi \\ \frac{\langle\psi^{(0)}|\hat{H}_{\mathrm{dis}}|\phi^{(0)}\rangle}{E_\phi^{(0)} - E_\psi^{(0)}} & \text{else} \end{cases} \tag{S3}$$

$$\left\langle \psi^{(0)}\middle|\phi^{(2)}\right\rangle = \begin{cases} -\frac{1}{2}\sum_{\eta\neq\phi} \frac{\langle\psi^{(0)}|\hat{H}_{\mathrm{dis}}|\eta^{(0)}\rangle\langle\eta^{(0)}|\hat{H}_{\mathrm{dis}}|\phi^{(0)}\rangle}{\left(E_\phi^{(0)} - E_\eta^{(0)}\right)^2} & \text{for } \psi = \phi \\ \sum_{\eta\neq\phi} \frac{\langle\psi^{(0)}|\hat{H}_{\mathrm{dis}}|\eta^{(0)}\rangle\langle\eta^{(0)}|\hat{H}_{\mathrm{dis}}|\phi^{(0)}\rangle}{\left(E_\phi^{(0)} - E_\eta^{(0)}\right)\left(E_\phi^{(0)} - E_\psi^{(0)}\right)} - \frac{\langle\psi^{(0)}|\hat{H}_{\mathrm{dis}}|\phi^{(0)}\rangle\langle\phi^{(0)}|\hat{H}_{\mathrm{dis}}|\phi^{(0)}\rangle}{\left(E_\phi^{(0)} - E_\psi^{(0)}\right)^2} & \text{else} \end{cases} \tag{S4}$$

with $\left|\psi^{(0)}\right\rangle$ and $E_\psi^{(0)}$ the eigenstates and eigenenergies for $W = 0$, and $\left|\psi^{(n)}\right\rangle$ the corrections to the eigenstates at order $(W/g_{\mathrm{c}})^n$. We find

$$\left\langle \mp^{(0)}\middle|\pm^{(1)}\right\rangle = \mp\frac{\tilde{\epsilon}_0}{4g_{\mathrm{c}}}, \tag{S5}$$

$$\left\langle k^{(0)}\middle|\pm^{(1)}\right\rangle = \pm\frac{\tilde{\epsilon}_k}{\sqrt{2}g_{\mathrm{c}}}, \tag{S6}$$

$$\left\langle \pm^{(0)}\middle|\pm^{(2)}\right\rangle = -\frac{|\tilde{\epsilon}_0|^2}{32g_{\mathrm{c}}^2} - \sum_{k=1}^{N-1}\frac{|\tilde{\epsilon}_k|^2}{4g_{\mathrm{c}}^2}, \tag{S7}$$

$$\left\langle \mp^{(0)}\middle|\pm^{(2)}\right\rangle = -\sum_{k=1}^{N-1}\frac{|\tilde{\epsilon}_k|^2}{4g_{\mathrm{c}}^2}, \tag{S8}$$

with $\tilde{\epsilon}_k = [\sum_{n=1}^N \exp(2\pi \mathrm{i} kn/N)\epsilon_n]/N$ the Fourier transform of the random energies. Using $|1_{\mathrm{ph}}\rangle = (\left|+^{(0)}\right\rangle + \left|-^{(0)}\right\rangle)/\sqrt{2}$, we find further

$$|\langle 1_{\mathrm{ph}}|\pm\rangle|^2 = \frac{1}{2} \mp \frac{\tilde{\epsilon}_0}{4g_{\mathrm{c}}} - \frac{1}{2}\sum_{k=1}^{N-1}\frac{|\tilde{\epsilon}_k|^2}{g_{\mathrm{c}}^2} + \mathcal{O}\left[(\tilde{\epsilon}/g_{\mathrm{c}})^3\right]. \tag{S9}$$

and finally for the photon weight of the dark states

$$\sum_d |\langle 1_{\rm ph}|d\rangle|^2 = \sum_{k=1}^{N-1} \frac{|\tilde{\epsilon}_k|^2}{g_{\rm c}^2}\,. \tag{S10}$$

Until here, the results are independent of the specific disorder model. We now assume that the energies ϵ_i are distributed according to a Gaussian with mean zero and standard deviation W. Then, we can further use that the discrete Fourier transform of a set of N Gaussian random variables is a set of N complex Gaussian random variables with real and imaginary part mean zero and standard deviation $W/\sqrt{2N}$, as can be straightforwardly shown by Fourier transforming the definition of $P(\tilde{\epsilon}_k)$. Taking the disorder average leaves us with

$$\overline{\sum_d |\langle 1_{\rm ph}|d\rangle|^2} = \frac{(N-1)W^2}{Ng_{\rm c}^2} + \mathcal{O}(W^3/g_{\rm c}^3) \xrightarrow{N\to\infty} \frac{W^2}{g_{\rm c}^2}\,. \tag{S11}$$

Vibronic coupling

We now proceed to compute the corrections due to vibronic coupling $\hat{H}_{\rm H}$ for $W = 0$. $\hat{H}_{\rm H}$ couples states with different numbers of vibrations, so that we need to take the vibrations into account explicitly. We write the states as $|\psi\rangle = |\psi_{\rm exc+ph}, n_{\rm vib}, v_1, \ldots, v_{n_{\rm vib}}\rangle \equiv \mathcal{N}\,|\psi_{\rm exc+ph}\rangle \prod_{i=1}^{n_{\rm vib}} \sum_n \exp(2\pi {\rm i} v_i n/N) \hat{b}_n^\dagger\,|0\rangle_{\rm vib}$, where $\psi_{\rm exc+ph} = \pm, k$ is the state in the electro-photonic sub-space, $n_{\rm vib}$ is the number of vibrations, and v_i is the Fourier mode of the vibration and $\mathcal{N}$ is a normalization factor. We are specifically interested in the contribution of the initial state $|\psi_0^{\rm c}\rangle = |1_{\rm ph}, 0\rangle$ to the dark states. Plugging $\hat{H}_{\rm H}$ instead of $\hat{H}_{\rm dis}$ into Eqs. (S2) to (S4), we find

$$\left\langle \pm^{(0)}, 1, 0 \middle| \pm^{(1)}, 0 \right\rangle = \frac{\lambda}{2\sqrt{N}}\,, \tag{S12}$$

$$\left\langle \mp^{(0)}, 1, 0 \middle| \pm^{(1)}, 0 \right\rangle = \frac{\pm\lambda\nu}{2\sqrt{N}(2g_{\rm c} \mp \nu)}\,, \tag{S13}$$

$$\left\langle k^{(0)}, 1, -k \middle| \pm^{(1)}, 0 \right\rangle = \frac{-\lambda\nu}{\sqrt{2N}(g_{\rm c} \mp \nu)}\,, \tag{S14}$$

$$\left\langle \pm^{(0)}, 0 \middle| \pm^{(2)}, 0 \right\rangle = -\frac{\lambda^2}{8N} - \frac{\lambda^2\nu^2}{8N(2g_{\rm c} \mp \nu)^2} - \frac{(N-1)\lambda^2\nu^2}{4N(g_{\rm c} \mp \nu)^2}\,, \tag{S15}$$

$$\left\langle \mp^{(0)}, 0 \middle| \pm^{(2)}, 0 \right\rangle = \pm\frac{\lambda^2\nu}{8Ng_{\rm c}} - \frac{\lambda^2\nu^2}{8Ng_{\rm c}(2g_{\rm c} \mp \nu)} - \frac{(N-1)\lambda^2\nu^2}{4N(g_{\rm c} \mp \nu)g_{\rm c}}\,, \tag{S16}$$

$$\left\langle \pm^{(0)}, 0 \middle| \pm^{(2)}, 2, 0, 0 \right\rangle = \frac{\sqrt{2}\lambda^2}{8N} \pm \frac{\sqrt{2}\lambda^2\nu}{8N(2g_{\rm c} \pm \nu)}\,, \tag{S17}$$

$$\left\langle \pm^{(0)}, 0 \middle| \pm^{(2)}, 2, k, -k \right\rangle = \pm\frac{\lambda^2\nu}{4N(g_{\rm c} \pm \nu)}\,, \tag{S18}$$

$$\left\langle \mp^{(0)}, 0 \middle| \pm^{(2)}, 2, 0, 0 \right\rangle = \mp\frac{\sqrt{2}\lambda^2\nu}{8N(g_{\rm c} \pm \nu)} - \frac{\sqrt{2}\lambda^2\nu^2}{8N(2g_{\rm c} \pm \nu)(g_{\rm c} \pm \nu)}\,, \tag{S19}$$

$$\left\langle \mp^{(0)}, 0 \middle| \pm^{(2)}, 2, k, -k \right\rangle = -\frac{\lambda^2\nu^2}{4N(g_{\rm c} \pm \nu)^2}\,, \tag{S20}$$

$$\left\langle \pm^{(0)}, 0 \middle| \pm^{(1)}, 1, 0 \right\rangle = -\frac{\lambda}{2\sqrt{N}}\,, \tag{S21}$$

$$\left\langle \mp^{(0)}, 0 \middle| \pm^{(1)}, 1, 0 \right\rangle = \pm\frac{\lambda\nu}{2\sqrt{N}(2g_{\rm c} \pm \nu)}\,. \tag{S22}$$

Analogous to above, we can compute the dark state amplitude of the state $|1_{\rm ph}, 0\rangle$ including an arbitrary number of vibrations as

$$\begin{aligned}\sum_d |\langle 1_{\rm ph}, 0|d\rangle|^2 = 1 &- |\langle 1_{\rm ph}, 0|+, 0\rangle|^2 - |\langle 1_{\rm ph}, 0|+, 1, 0\rangle|^2 - |\langle 1_{\rm ph}, 0|+, 2, 0, 0\rangle|^2 - \sum_k |\langle 1_{\rm ph}, 0|+, 2, k, -k\rangle|^2 \\ &- |\langle 1_{\rm ph}, 0|-, 0\rangle|^2 - |\langle 1_{\rm ph}, 0|-, 1, 0\rangle|^2 - |\langle 1_{\rm ph}, 0|-, 2, 0, 0\rangle|^2 - \sum_k |\langle 1_{\rm ph}, 0|-, 2, k, -k\rangle|^2\,.\end{aligned} \tag{S23}$$

Using $|1_{\rm ph},0\rangle = (|+^{(0)},0\rangle + |-^{(0)},0\rangle)/\sqrt{2}$, the only non-vanishing term for large N reads

$$|\langle 1_{\rm ph},0|\pm,0\rangle|^2 = \frac{1}{2} - \frac{\lambda^2\nu^2}{4(g_{\rm c}\mp\nu)^2} - \frac{\lambda^2\nu^2}{4(g_{\rm c}\mp\nu)g_{\rm c}} + \mathcal{O}\big[(\lambda\nu/g_{\rm c})^3\big]\,. \tag{S24}$$

As a result, the photo-contribution to the dark states is approximately

$$\sum_d |\langle 1_{\rm ph}|d\rangle|^2 \approx \frac{\lambda^2\nu^2}{4(g_{\rm c}\mp\nu)^2} + \frac{\lambda^2\nu^2}{4(g_{\rm c}\mp\nu)g_{\rm c}} \approx \frac{\lambda^2\nu^2}{2g_{\rm c}^2}\,, \tag{S25}$$

where we used $\nu \ll g_{\rm c}$ in the last step.

Supplementary Note 4. EXCITATION TRANSFER ESTIMATES

In the following, we derive analytical estimates for excitation transfer away from the initially excited molecule for the initial state $|\psi_0^{\rm m}\rangle = \hat\sigma_1^+|0\rangle$ (see main text). We consider disorder induced transfer only, i.e. we set $\lambda = 0$. We further restrict the analysis to the perturbative case by assuming $W \ll g_{\rm c}$.

$W = 0$

We start by analyzing the disorder-free scenario. For $W = \lambda = 0$, the electro-photonic state evolves with the Tavis-Cummings Hamiltonian $\hat H_{\rm TC}$, only. By diagonalizing $\hat H_{\rm TC} = (g_{\rm c}\,|+\rangle\langle+| - g_{\rm c}\,|-\rangle\langle-|)$, we compute the time-dependent excitation probability of the initially excited molecule

$$\begin{aligned}\langle\hat\sigma_1^+\hat\sigma_1^-\rangle(t) &= \langle 0|\,\hat\sigma_1^-\exp\Big(\mathrm{i}\hat H_{\rm TC}t\Big)\hat\sigma_1^+\hat\sigma_1^-\exp\Big(-\mathrm{i}\hat H_{\rm TC}t\Big)\hat\sigma_1^+|0\rangle \\ &= \frac{(N-1)^2}{N^2} + \frac{2(N-1)}{N^2}\cos(g_{\rm c}t) + \frac{1}{2N^2} + \frac{1}{2N^2}\cos(2g_{\rm c}t) \qquad \text{(S26)}\\ &= 1 + \frac{2}{N}[\cos(g_{\rm c}t) - 1] + \mathcal{O}\left(\frac{1}{N^2}\right). \qquad \text{(S27)}\end{aligned}$$

$W > 0$

In the following we compute the excitation probability of the initially excited molecule for finite disorder. Here, we choose a box disorder model, because the finite probability for a single molecule to have extreme energies (i.e. $\epsilon_i > +g_{\rm c}$ or $\epsilon_i < -g_{\rm c}$) adds significant complexity to the analytical treatment. In particular, we assume a uniform probability $P(\epsilon_i) = 1/(2W)$ for $-W < \epsilon_i < W$, and $P(\epsilon_i) = 0$ otherwise. We do not expect this choice for $P(\epsilon_i)$ to modify the overall scaling of our results with respect to the Gaussian choice in the rest of the paper.

In order to compute the time-dependent excitation probability of the first molecule, we treat the cavity coupling of the first molecule $g(\hat\sigma_1^+\hat a + \hat\sigma_1^-\hat a^\dagger)$ as a perturbation. The unperturbed Hamiltonian is given by $\hat H_0 = \hat H_{\rm TC} + \hat H_{\rm dis} - g(\hat\sigma_1^+\hat a + \hat\sigma_1^-\hat a^\dagger)$. In this case, the perturbation condition becomes that the single molecule coupling g is smaller than the energy differences between different states, which is on the order of $\sim W$ for most pairs of states. As $g = g_{\rm c}/\sqrt{N}$ becomes very small for large N, this condition is fulfilled for most energy levels. However, a few resonant energy levels do typically not fulfill this condition, with implications discussed below.

One eigenstate of $\hat H_0$ is the initial state $|1^{(0)}\rangle \equiv |\psi_0^{\rm m}\rangle$. For $W < g_{\rm c}$, the other eigenstates can be classified as polaritons and dark states. Although we cannot compute these states exactly, we can make sufficient statements about their statistics [2–4] to compute the time evolution of $\langle\hat\sigma_1^+\hat\sigma_1^-\rangle$. In particular, we can perturbatively compute their average photo contribution for $W < g_{\rm c}$ and large N as in the previous section. We find $|\langle 1_{\rm ph}|+\rangle| \approx 1/2 - W^2/(24g_{\rm c}^2)$ and $|\langle 1_{\rm ph}|d_i\rangle|^2 \sim W^2/(12Ng_{\rm c}^2)$, where the additional factor of 12 comes in due to the different disorder model. The

eigenstates of $\hat{H}_0$ are thus

$$\left|1^{(0)}\right\rangle = \hat{\sigma}_1^+ \left|0\right\rangle \,, \tag{S28}$$

$$\left|\pm^{(0)}\right\rangle = \left[\sqrt{\frac{1-W^2/(12g_\mathrm{c}^2)}{2}}\hat{a}^\dagger \pm \sum_{n=2}^{N} b_n^\pm \hat{\sigma}_n^+\right]\left|0\right\rangle \,, \tag{S29}$$

$$\left|d_i^{(0)}\right\rangle = \left[\frac{W}{\sqrt{12}Ng}\hat{a}^\dagger + \sum_{n=2}^{N} c_n^{(i)} \hat{\sigma}_n^+\right]\left|0\right\rangle \,, \tag{S30}$$

where we took the disorder-average of the photon-contribution on the state level. This approximation may be valid due to self-averaging for sufficiently large N, and it is validated by the agreement of the final results with the numerical simulations. The $b_n^\pm$ and $c_n^{(i)}$ are constants that determine the excitation probability of the specific molecules and are not needed in the following. The corresponding eigenenergies are

$$E_1^{(0)} = \epsilon_1 \,, \tag{S31}$$

$$E_\pm^{(0)} = \pm g_\mathrm{c} \,, \tag{S32}$$

$$E_{d,i}^{(0)} \equiv E_i \,, \tag{S33}$$

where the dark state energies E_i follow the same distribution as the random molecular excitation energies [2].

Importantly, all states $\left|\pm^{(0)}\right\rangle$ and $\left|d_i^{(0)}\right\rangle$ have no excitation probability for the first molecule. As a result, there are no corrections to the eigenenergies at first order. The perturbative corrections to the states are

$$\left|1^{(1)}\right\rangle = \frac{\sqrt{1-W^2/(12g_\mathrm{c}^2)}g}{\sqrt{2}(\epsilon_1 - g_\mathrm{c})}\left|+^{(0)}\right\rangle + \frac{\sqrt{1-W^2/(12g_\mathrm{c}^2)}g}{\sqrt{2}(\epsilon_1 + g_\mathrm{c})}\left|-^{(0)}\right\rangle + \sum_i \frac{W}{\sqrt{12}N(\epsilon_1 - E_i)}\left|d_i^{(0)}\right\rangle \,, \tag{S34}$$

$$\left|d_i^{(1)}\right\rangle = \frac{W}{\sqrt{12}N(E_i - \epsilon_1)}\left|1^{(0)}\right\rangle \,, \tag{S35}$$

$$\left|\pm^{(1)}\right\rangle = \frac{\sqrt{1-W^2/(12g_\mathrm{c}^2)}g}{\sqrt{2}(\pm g_\mathrm{c} - \epsilon_1)}\left|1^{(0)}\right\rangle \,, \tag{S36}$$

$$\left\langle 1^{(0)}\middle|1^{(2)}\right\rangle = -\frac{1}{2}\left\langle 1^{(1)}\middle|1^{(1)}\right\rangle \,. \tag{S37}$$

Here, unphysical divergences appear for the resonance condition $\epsilon_1 \to E_i$. These are related to the perturbation assumption $g \ll |\epsilon_1 - E_i|$. We will deal with these divergences below.

The time evolution is computed as

$$\begin{aligned}\langle\hat{\sigma}_1^+\hat{\sigma}_1^-\rangle(t) &= \langle\psi_0^m|\exp\left(\mathrm{i}\hat{H}t\right)\hat{\sigma}_1^+\hat{\sigma}_1^-\exp\left(-\mathrm{i}\hat{H}t\right)|\psi_0^\mathrm{m}\rangle \\ &= \left\langle 1^{(0)}\middle|\exp\left(\mathrm{i}\hat{H}t\right)\middle|1^{(0)}\right\rangle\left\langle 1^{(0)}\middle|\exp\left(-\mathrm{i}\hat{H}t\right)\middle|1^{(0)}\right\rangle \,.\end{aligned} \tag{S38}$$

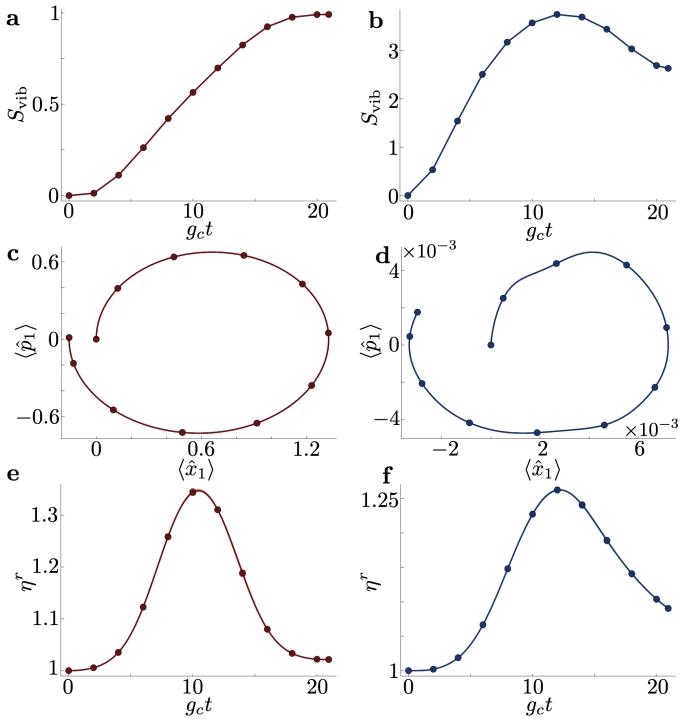
We expand $\exp(\mathrm{i}\hat{H}t) = \sum_\psi |\psi\rangle\langle\psi|\exp(\mathrm{i}E_\psi t)$ and keep terms only up to second order in W. We furthermore ignore second order corrections to the energies, which would lead to higher order corrections of the final result. We find

$$\left\langle 1^{(0)}\middle|1\right\rangle\exp(\mathrm{i}\epsilon_1 t)\left\langle 1\middle|1^{(0)}\right\rangle = \left[1 - \frac{g_\mathrm{c}^2 - W^2/12}{2N(\epsilon_1 - g_\mathrm{c})^2} - \frac{g_\mathrm{c}^2 - W^2/12}{2N(\epsilon_1 + g_\mathrm{c})^2} - \sum_i \frac{W^2}{12N^2(\epsilon_1 - E_i)^2}\right]\exp(\mathrm{i}\epsilon_1 t) \,, \tag{S39}$$

$$\left\langle 1^{(0)}\middle|\pm\right\rangle\exp(\pm\mathrm{i}g_\mathrm{c}t)\left\langle\pm\middle|1^{(0)}\right\rangle = \frac{g_\mathrm{c}^2 - W^2/12}{2N(\pm g_\mathrm{c} - \epsilon_1)^2}\exp(\pm\mathrm{i}g_\mathrm{c}t) \,, \tag{S40}$$

$$\left\langle 1^{(0)}\middle|d_i\right\rangle\exp(\mathrm{i}E_i t)\left\langle d_i\middle|1^{(0)}\right\rangle = \frac{W^2}{12N^2(\epsilon_1 - E_i)^2}\exp(\mathrm{i}E_i t) \,. \tag{S41}$$

These terms lead to oscillations of the energy between the initially excited molecule and the other states at frequencies $g_\mathrm{c} \pm \epsilon_1$ for the polaritons, and $E_i - \epsilon_1$ for the dark states, respectively. The combined effect of the slightly out-of-phase oscillations of the large number of dark states leads to an effective dephasing and a resulting unidirectional transfer of



Supplementary Figure 2. **Convergence with the maximum number of vibrations $n^{\mathrm{v}}_{\mathrm{max}}$.** **a**,**b** Time evolution of the vibrational entropy S_{vib} for an initial molecular (left, red) or cavity (right, blue) excitation. Darkness indicates $n^{\mathrm{v}}_{\mathrm{max}}$. ($n^{\mathrm{v}}_{\mathrm{max}} \in \{6, 8, 10, 12\}$). Overlapping of the trajectories indicates convergence for $n^{\mathrm{v}}_{\mathrm{max}} > 6$. In **a**,**b**, the lines are a guide to the eye, whereas in **c**-**f** the lines represent additional data points. **c**,**d** Phase-space evolution of a single molecule. Same color-code as in **a**,**b**. **e**,**f** Time evolution of the right tail weight η^{r} (see paper for definition). Same color-code as in **a**,**b**. Parameters for all plots: $N = 100$, $\lambda = 0.5$, $\nu = 0.3 g_{\mathrm{c}}$, $W = g_{\mathrm{c}}/2$, $\chi = 128$, $dt = 0.01$. Results for a single disorder realization.

energy away from the initially excited molecule on timescales analyzed in the paper. This behavior can be computed as

$$\sum_i \left\langle 1^{(0)} \middle| 1 \right\rangle \exp(\mathrm{i}\epsilon_1 t) \left\langle 1 \middle| 1^{(0)} \right\rangle \left\langle 1^{(0)} \middle| d_i \right\rangle \exp(\mathrm{i}E_i t) \left\langle d_i \middle| 1^{(0)} \right\rangle + \mathrm{h.c.} = \sum_i \frac{W^2}{6N^2 (E_i - \epsilon_1)^2} \cos[(E_i - \epsilon_1)t] \,. \tag{S42}$$

We finally take the disorder average $E_i \to \int dE/W$ to find:

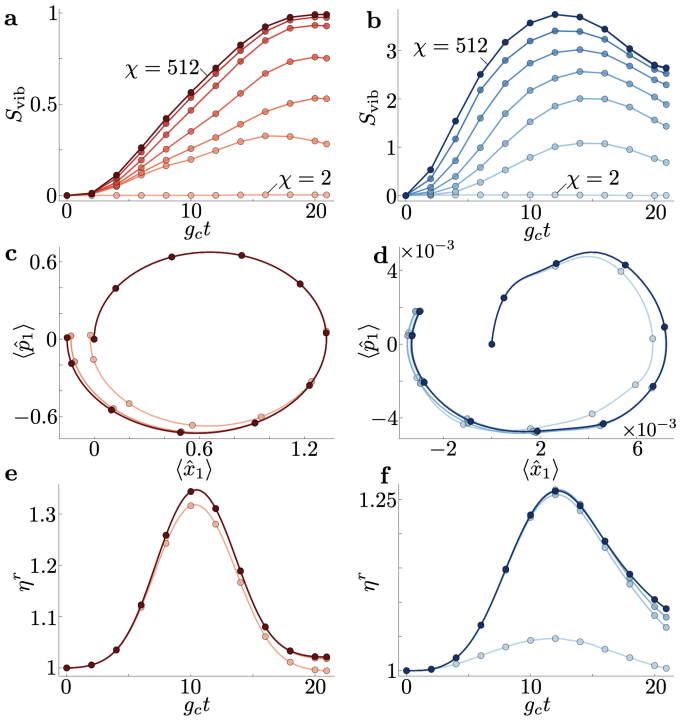
$$N \times \frac{W}{6N^2} \int_{-W/2}^{W/2} dE \frac{\cos[(E-\epsilon_1)t]}{(E-\epsilon_1)^2} \quad = \quad \frac{Wt}{6N} \int_{(-W/2-\epsilon_1)t}^{(W/2-\epsilon_1)t} d\Delta \frac{\cos(\Delta)}{\Delta^2} \,, \tag{S43}$$

where we substituted $(E - \epsilon_1)t \to \Delta$. Note that again an unphysical divergence arises due to the perturbation assumption $g^2 \ll (E_i - \epsilon_1)^2$, which we ignore here as we are only interested in the overall scaling behavior. As the integrand scales like $1/\Delta^2$, the integral becomes time independent for diverging boundaries, i.e. sufficiently large t. In this case, the population of the first state evolves like $1 - \langle \hat{\sigma}_1^+ \hat{\sigma}_1^- \rangle \sim Wt/N$ in addition to Rabi-oscillations. By straightforwardly evaluating all other terms we find that this term is indeed the largest contribution to the energy transfer. Botzung *et al.* [3] derived similar results in the long time limit for $N \to \infty$.

Supplementary Note 5. CONVERGENCE OF MPS SIMULATIONS

Supplementary Figure 2 shows the time evolution of S_{vib}, the phase space evolution, and η^{r} computed with different cutoffs for the number of vibrational excitations per molecule $n^{\mathrm{v}}_{\mathrm{max}}$ for a single disorder realization. We find again that all lines overlap, indicating convergence for $n^{\mathrm{v}}_{\mathrm{max}} > 6$.

Supplementary Figure 3 shows the time evolution of the same observables computed with increasing bond dimension χ. We find that the vibrational entanglement S_{vib} generally reaches larger values for larger $\chi < 128$, and for $\chi = 128, 256, 512$ the data points overlap perfectly. This indicates convergence for $\chi = 128$. For both the phase space



Supplementary Figure 3. **Convergence with the bond dimension χ.** **a**,**b** Time evolution of the vibrational entropy S_{vib} for an initial molecular (left, red) or cavity (right, blue) excitation. Darkness indicates χ on a log-scale ($\chi \in \{2, 4, 8, 16, 32, 64, 128, 256, 512\}$). Trajectories already fully overlap for for $\chi \geq 128$ indicating convergence. In **a**,**b**, the lines are a guide to the eye, whereas in **c**-**f** the lines represent additional data points. **c**,**d** Phase-space evolution of a single molecule. Same color-code as in **a**,**b**. **e**,**f** Time evolution of the right tail weight η^{r} (see paper for definition). Same color-code as in **a**,**b**. Parameters for all plots: $N = 100$, $\lambda = 0.5$, $\nu = 0.3 g_{\mathrm{c}}$, $W = g_{\mathrm{c}}/2$, $dt = 0.01$, $n^{\mathrm{v}}_{\mathrm{max}} = 10$. Results for a single disorder realization.

evolution and the right tail the trajectories overlap for $\chi > 16$ ($\chi > 8$ for a molecular excitation), indicating much faster convergence for these observables. We attribute the slow convergence of S_{vib} with χ to the large number of swap operations $\sim N^2$ and the unfavorable MPS structure when computing S_{vib}.

Supplementary Figure 4 shows the time evolution of the same observables computed using different time steps dt used in the second order sweep. All lines overlap, indicating that convergence is already reached for $dt = 0.2$. The small differences in the final data points are rounding errors $\sim dt$ for the choice of final time.

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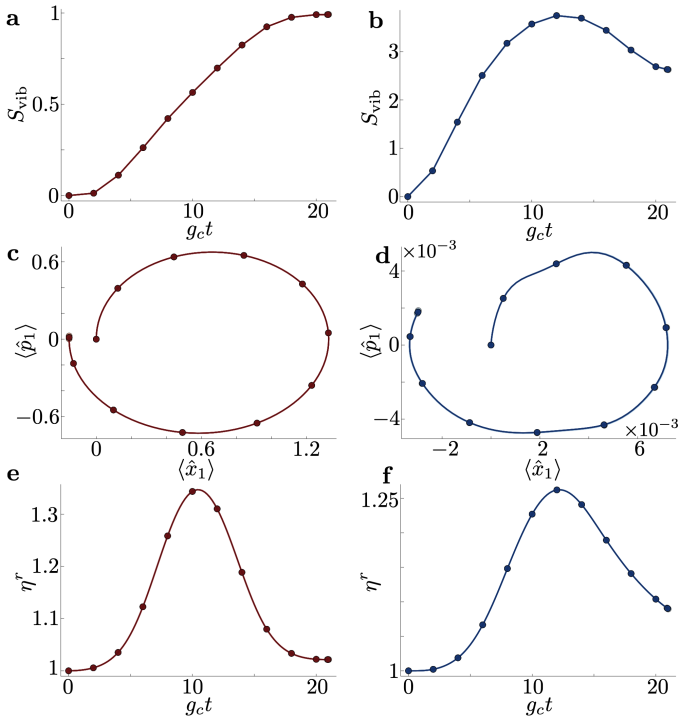

Supplementary Figure 4. **Convergence with the time step dt of the simulation.** **a**,**b** Time evolution of the vibrational entropy S_{vib} for an initial molecular (left, red) or cavity (right, blue) excitation. Darkness indicates dt on a log-scale ($dt \times g_{\mathrm{c}} \in \{0.2, 0.1, 0.04, 0.02, 0.01, 0.005, 0.0025\}$). Fully overlapping trajectories indicate convergence for $dt < 0.2$. In **a**,**b**, the lines are a guide to the eye, whereas in **c**-**f** the lines represent additional data points. **c**,**d** Phase-space evolution of a single molecule. Same color-code as in **a**,**b**. **e**,**f** Time evolution of the right tail weight η^{r} (see paper for definition). Same color-code as in **a**,**b**. Parameters for all plots: $N = 100$, $\lambda = 0.5$, $\nu = 0.3 g_{\mathrm{c}}$, $W = g_{\mathrm{c}}/2$, $\chi = 128$, $n^{\mathrm{v}}_{\mathrm{max}} = 10$. Results for a single disorder realization.