Efficient Many-Body Non-Markovian Dynamics of Organic Polaritons

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We show how to simulate a model of many molecules with both strong coupling to many vibrational modes and collective coupling to a single photon mode. We do this by combining process tensor matrix product operator methods with a mean-field approximation which reduces the dimension of the problem. We analyze the steady state of the model under incoherent pumping to determine the dependence of the polariton lasing threshold on cavity detuning, light-matter coupling strength, and environmental temperature. Moreover, by measuring two-time correlations, we study quadratic fluctuations about the mean field to calculate the photoluminescence spectrum. Our method enables one to simulate many-body systems with strong coupling to multiple environments, and to extract both static and dynamical properties.

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The strong coupling between organic matter confined in a microcavity and light results in new collective modes—superpositions of molecular excitations and photons known as exciton polaritons [1]. Under sufficient pumping, these may condense into a coherent or lasing state, as has now been demonstrated in a diverse range of organic materials [2–7] (see Ref. [1] for a review). The rich photophysics of organic molecules allows for the possibility of room temperature lasing devices with ultralow thresholds, yet also makes the task of determining the optimal conditions for lasing a challenging one. In particular, one must consider the effect on the dynamics of the vibrational environment of each molecule [8], which is generally structured and beyond weak coupling or Markovian treatments [9–17]. To this end there have been studies of polariton condensation using simplified models with a few vibrational modes [8, 18–27], and also studies involving exact vibrational spectra for a small number of molecules [15, 16]. However, the real system has both a complex vibrational density of states and many, e.g., 10⁹, molecules. Therefore, what is needed is a method capable of handling large systems with non-Markovian effects. Here we provide such a method and show the consequences for the description of polariton lasing.

Process tensor matrix product operator (PT-MPO) methods are a class of numerical methods based upon the process tensor (PT) description of open quantum system dynamics [28–34]. The PT captures all possible effects of the environment on a system. The system Hamiltonian propagator, or any system operator, then forms a finite set of interventions that may be contracted with the PT and thus one can find any system observable or multitime correlation function. Crucially, the PT can be represented efficiently as a matrix product operator that only needs to be calculated once for a given system-bath interaction and set of bath conditions [31]. While this provides an efficient means to evolve a system with long memory times, such methods have so far been limited to systems of small Hilbert space dimension.

In this Letter we present a mean-field approach to reduce an N-body problem to one that can be handled by PT-MPO methods without further approximation. This approach does not require expressions for the system eigenstates and energies, and allows for genuine non-Markovian dynamics of many-body systems. As we will discuss, mean-field theory consists of the ansatz that there are no correlations between certain parts of the system. Here we employ this approach to accurately treat the vibrational environments of a many-molecule–cavity system. In particular, we develop a realistic model of an organic laser based on BODIPY-Br [Figs. 1(a) and 1(b)], an organic molecule which has shown polariton lasing [5, 7]. We find results that differ significantly from those obtained in the model where the vibrational environments cause simple dephasing—a model that cannot account for lasing in the presence of strong light-matter coupling. We determine how modifying the light-matter coupling and environmental temperature of our model changes the lasing threshold, and calculate the observed photoluminescence.

We model N identical molecules as a collection of two-level systems (Pauli matrices σα i) interacting with a single near-resonant cavity mode (bosonic operator a) according to the Dicke Hamiltonian under the rotating-wave approximation. Setting ħ = 1, the system Hamiltonian is

\[ H_S = \omega_c a^\dagger a + \sum_{i=1}^{N} \left( \frac{\omega_0}{2} \sigma_i^z + \frac{\Omega}{2\sqrt{N}} (a\sigma_i^+ + a^\dagger \sigma_i^-) \right) \]  (1)

where \( \omega_0 \) and \( \omega_c \) are the two-level system and cavity frequencies, and \( \sigma_i^+ (\sigma_i^-) \) the raising (lowering) operator for the ith spin. The collective coupling \( \Omega \) controls the light-matter interaction such that the bright eigenstates of \( H_S \), i.e. the polaritons, are split as \( \pm \Omega/2 \) at resonance.

The Hamiltonian Eq. (1) may be referred to as the Tavis-Cummings model. Its extension to include a single vibrational mode, the Holstein-Tavis-Cummings model, has frequently been used to describe cavity bound organic
emitters \([18, 19, 21–23, 25–27]\). We instead consider the interaction of each two-level system with a continuum of modes represented by the harmonic environment

\[
H_{E}^{(j)} = \sum_{j} \left[ \nu_{j} b_{j}^{\dagger} b_{j} + \frac{\xi_{j}}{2} (b_{j}^{\dagger} b_{j}) \sigma_{z}^{j} \right],
\]

where \(b_{j}\) is the annihilation operator for the \(j\)th mode of frequency \(\nu_{j}\). The system-environment coupling is characterized by a spectral density \(J(\nu) = \sum_{j} (\xi_{j}/2)^{2} \delta(\nu - \nu_{j})\), taken to be Ohmic in the form

\[
J(\nu) = 2\alpha \nu e^{-\nu/\nu_{c}}, \quad \nu > 0,
\]

where \(\alpha\) and \(\nu_{c}\) are chosen to reproduce the leading structure of the absorption spectrum of BODIPY-Br at \(T = 300\) K [Fig. 1(b)]. This effectively captures the low frequency modes arising from the host matrix of the molecule. The realistic picture of vibrational dephasing it affords is the most significant advancement of our work.

In the limit that the system-environment coupling is weak one might look to derive a Redfield theory \([35]\). However, as we discuss in the Supplemental Material \([36]\), this is difficult in the presence of strong light-matter coupling.

Finally we consider incoherent pump \(\Gamma_{\uparrow}\) and dissipation \(\Gamma_{\downarrow}\) of the two-level systems as well as field decay \(\kappa\). Since these are associated with baths at optical frequencies (e.g. \(10^{15}\) Hz) they may be well approximated \([35]\) by Markovian terms in the master equation for the total density operator \(\rho\),

\[
\partial_{t} \rho = -i \left[ H_{S} + \sum_{i=1}^{N} H_{E}^{(i)} + 2\kappa \mathcal{L}[a] \right] \rho + \sum_{i=1}^{N} (\Gamma_{\uparrow} \mathcal{L}[\sigma_{i}^{\dagger}] + \Gamma_{\downarrow} \mathcal{L}[\sigma_{i}^{-}] ),
\]

with \(\mathcal{L}[x] = x \rho x^{\dagger} - \{ x^{\dagger} x, \rho \}/2 \). If \(H_{E}^{(i)}\) is absent one recovers the Tavis-Cummings model with pumping and decay which, as we discuss below, requires inversion \(\Gamma_{\uparrow} > \Gamma_{\downarrow}\) to show lasing. Below we fix \(\Gamma_{\downarrow}\) and \(\kappa\) and observe the transition of the system from a normal state, where the expectation \(\langle a \rangle\) of the photon operator vanishes, to a lasing state, where \(\langle a \rangle\) is nonzero and time dependent, as \(\Gamma_{\uparrow}\) is increased from zero.

Simulating dynamics in the presence of strong coupling to a structured environment is a computationally intense task and as such PT-MPO methods cannot be used to solve for a large number of open systems simultaneously. Our strategy is to use mean-field theory to reduce the \(N\)-molecule–cavity system to a single molecule interacting with a coherent field [Figs. 1(c) and 1(d)].

According to mean-field theory, we assume a product state for the many-body density operator \(\rho\), i.e. a factorization between the photon and individual molecules, an ansatz known \([37, 38]\) to be exact as \(N \to \infty\). This reduces the problem to the coupled dynamics of the molecular mean-field Hamiltonian

\[
H_{MF} = \frac{\omega_{0}}{2} \sigma_{z}^{2} + \frac{\Omega}{\sqrt{N}} \left( \langle a \rangle \sigma^{+} + \langle a \rangle \sigma^{-} \right),
\]

combined with evolution of the field expectation

\[
\partial_{t} \langle a \rangle = -(i \omega_{c} + \kappa) \langle a \rangle - i \frac{\Omega}{\sqrt{N}} \langle a \rangle \langle \sigma^{-} \rangle.
\]

Here \(\langle \sigma^{-} \rangle\) (no subscript) is the average of any one of the identical spins. Thus, by propagating a single spin with \(H_{MF}\) and subject to the vibrational environment and individual losses described above, we can effectively simulate the \(N\)-molecule system using a PT-MPO method provided that at each time step we also evolve \(\langle a \rangle\) according to Eq. (6) [Fig. 1(d)]. In Ref. [36] we discuss the derivation of Eqs. (5) and (6) further as well as the role of “bright” and “dark” excitonic states \([8, 23, 24, 39–41]\) in mean-field theory.

To calculate the dynamics we use the PT-MPO provided by the time evolving MPO (TEMPO) method \([28, 31, 42, 43]\). Notable to our problem is that the system propagators depend on the field \(\langle a \rangle\), which depends self-consistently on the state of the system. A second-order Runge-Kutta method is used to integrate the field from
As the light-matter coupling increases, faster emission into the cavity mode sees the threshold reduce before eventually saturating. The threshold becomes less dependent on detuning as lasing is now dictated by whether the frequency of the lower polariton formed coincides with a region of gain in the spectrum, and this occurs for a larger range of cavity frequencies. Similar observations were made in models with sharp vibrational resonances [26]. In that work reentrance under $\Gamma_\uparrow$ was seen—behavior absent here because of the broader molecular spectrum we consider.

A key question in the study of organic polaritons is to what extent thermalization occurs, and thus how temperature affects the threshold [1, 46]. Motivated by this and the range of temperatures accessible in organic polariton experiments we examine the dependence of threshold on environmental temperature $T$ at fixed $\Omega = 200$ meV. Changing $T$ shifts, and increases the width of, the molecular spectrum. The result for the phase diagram, shown in Fig. 2(d), is a suppression of lasing with increasing $T$, most significantly for positive detunings where the lower polariton is more excitonic. This temperature dependence is one aspect of the phase diagram that cannot generally be captured by simplified models with a few vibrational modes, as we demonstrate in Ref. [36].

We next study quadratic fluctuations about the mean field, as described by two-time correlations and their Fourier transforms. Specifically we calculate the spectral weight and the photoluminescence (PL) spectrum, the latter of which is the actual measured observable in all polariton experiments [1]. Multitime correlations are naturally accessible within the PT-MPO framework, allowing us to calculate absorption and emission spectra without recourse to the quantum regression theorem.

We use that the retarded $D^R$ and Keldysh $D^K$ photon Green’s functions may be written in terms of the exciton self-energies [41, 48]

$$\Sigma^+(\omega) = \frac{i\Omega^2}{4} \int_0^\infty dt e^{i\omega t} \langle [\sigma^-(t), \sigma^+(0)] \rangle, \quad (7)$$

$$\Sigma^-(\omega) = \frac{i\Omega^2}{4} \int_{-\infty}^0 dt e^{i\omega t} \langle [\sigma^-(t), \sigma^+(0)] \rangle. \quad (8)$$

The photon Green’s functions then take the form

$$D^R(\omega) = \frac{1}{\omega - \omega_c + i\kappa + \Sigma^+(\omega)}; \quad (9)$$

$$D^K(\omega) = -\frac{\Sigma^-(\omega) + 2i\kappa}{|\omega - \omega_c + i\kappa + \Sigma^+(\omega)|^2}. \quad (10)$$

Hence, by calculating the correlators $\langle \sigma^-(t)\sigma^+(0) \rangle$ and $\langle \sigma^+(t)\sigma^-(0) \rangle$ using the PT-MPO approach, we can find the Green’s functions $D^R$ and $D^K$ which fully characterize the spectrum of the nonequilibrium system.
Thus far we have considered a model with a single photon mode for which mean-field theory is exact as $N \to \infty$. However, it is straightforward to extend our analysis to include multiple photon modes, where mean field can still provide a good approximation [36]. Hence we consider the model with cavity mode term $\sum_{k} \omega_{c,k} a_k^\dagger a_k$, where $\omega_{c,k} = \omega_c + k^2/2m_{ph}$ (recall $\hbar = 1$), and light-matter interaction $\sum_{k} \Omega_{d,k} a_k^\dagger \sigma_{-} + \text{H.c.}$. As discussed in Ref. [36], the mean field steady-state equations remain similar and one now has access to the photon Green’s functions $D_k^R(\omega)$, $D_k^F(\omega)$ of the multimode model.

We first consider the system without pumping ($\Gamma_\uparrow = 0$) and the spectral weight [49]

$$\varrho_k(\omega) = -2\text{Im}D_k^R(\omega).$$

(11)

As the system is in the normal state, $\langle \sigma^+(t)\sigma^-(0) \rangle \equiv 0$, while an exact expression for the other correlator may be found [46] as $\langle \sigma^-(t)\sigma^+(0) \rangle = e^{-i\omega_0 t}-\phi(t)-(\Gamma_\uparrow/2)t$ where

$$\phi(t) = \int_{-\infty}^{\infty} dw \frac{J(\omega)}{\omega^2} \left[ 2\coth \left( \frac{\omega}{2T} \right) \sin^2 \left( \frac{\omega t}{2} \right) + i \sin(\omega t) \right].$$

(12)

This provides a benchmark of our numerics: Figure 3(a) shows excellent agreement between the spectral weight derived from the analytical result Eq. (12) and that from measurement of the correlator using the PT-MPO method at $k = 0$. Figure 3(b) then illustrates the $k$ dependence of the spectrum for $\Omega = 200$ meV.

When the system is pumped, i.e. $\Gamma_\uparrow \neq 0$, no analytical results are available and it is necessary to determine both the spectrum and its occupation numerically. Here we calculate the photoluminescence [48],

$$L_k(\omega) = \frac{i}{2} \left( D_k^R(\omega) - D_k^F(\omega) + [D_k^R(\omega)]^* \right).$$

(13)

Figure 3(c) shows $L_k(\omega)$ at fixed detuning $\Delta = -20$ meV and $\Omega = 200$ meV for different pump strengths. At the weakest pump strength, $\Gamma_\uparrow = 0.1 \Gamma_\downarrow$, the system is below threshold yet $L_k(\omega)$ does not vanish since, in contrast to the mean-field calculation of the steady-state photon number, the photoluminescence contains an incoherent part. Plotting the $k$ dependence of the spectrum in this case [Fig. 3(d)] makes clear this arises from the lower polariton.

At higher pump strengths, $\Gamma_\uparrow = 0.3 \Gamma_\downarrow$ and $0.6 \Gamma_\downarrow$, the lasing frequency occurs noticeably to the right of the peak luminescence: the conditions to max-
imize $\mathcal{L}_k$, which depends on both the density of states and their populations, do not, in general, coincide with the point at which the lasing instability develops. We explore this further in Ref. [36] by examining the real and imaginary parts of the inverse Green’s functions as the transition is approached.

In conclusion, we have developed a technique for calculating the non-Markovian dynamics of a many-body open system using mean-field theory and PT-MPO methods. We applied this technique to model the polariton lasing of an organic dye in a microcavity including many molecules with realistic vibrational spectra. This provided the steady-state of the driven-dissipative system and, via the measurement of two-time correlations, its spectrum. We first determined the dependence of the threshold for lasing on cavity detuning under different light-matter coupling strengths and environmental temperatures. Second, we observed how the photoluminescence and lasing frequency of the model evolved with pump strength. For the case of a one-to-all interaction between the cavity and molecules, the mean-field treatment is exact as $N \rightarrow \infty$ [37, 38]. The same applies to all-to-all networks of open systems [36, 38]. More generally, there are situations where mean-field theory is not exact but offers a good approximation, including models of polariton condensation with multiple modes such as considered in Refs. [27, 36, 50].

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1. WEAK SYSTEM-ENVIRONMENT COUPLING

In the limit where the system-environment coupling is sufficiently weak, one might expect it would be possible to derive and use an accurate time-local (Markovian) description. In this section we discuss the challenges in doing this and explain why, even in this weak system-bath coupling limit, the PT-MPO approach may still be valuable.

When the system-environment coupling is weak, one can apply standard methods [35] to derive a Redfield theory describing the low frequency vibrational environment. In appropriate cases, one can further secularize this Redfield theory to give a density matrix equation of motion of the Gorini–Kossakowski–Sudarshan–Lindblad form [35]. For our model, considering system-bath coupling as written in Eq. (2), the contribution to the density matrix equation describing this bath takes the form:

$$\partial_t \rho_{\text{vib}} = \sum_{i,n} \left[ \Gamma(\lambda_n) \left( \xi_{i,n}^2 \rho \sigma_i^z - \sigma_i^z \xi_{i,n}^2 \rho \right) + \text{H.c.} \right].$$  \hspace{1cm} (S1)

Here $\Gamma(\lambda) = \int_0^\infty ds e^{i\lambda s} C(s)$ where $C(s)$ describes correlations of the bath operators which couple to the system, $x_j = b_j + b_j^\dagger$:

$$C(s) \equiv \sum_j \left( \frac{\xi_j}{2} \right)^2 \langle x_j(t) x_j(t-s) \rangle = \int d\nu J(\nu) \left[ \coth \left( \frac{\nu}{2T} \right) \cos(\nu s) - i \sin(\nu s) \right].$$ \hspace{1cm} (S2)

The operators $\xi_{i,n}$ are the eigen-operator decomposition of $\sigma_i^z$. They obey $[H_S, \xi_{i,n}^2] = -\lambda_n \xi_{i,n}^2$ where $H_S$ is the system Hamiltonian, and satisfy $\sum_n \xi_{i,n}^2 = \sigma_i^z$. Formally they can be found using the eigenstates of $H_S |n\rangle = \epsilon_n |n\rangle$, by writing a restricted sum over transitions with energy difference $\lambda_n$:

$$\xi_{i,n}^2 = \sum_{m,p} |m\rangle \langle m| \sigma_i^z |p\rangle \langle p| \delta_{\epsilon_m, \epsilon_p - \lambda_n}.$$ \hspace{1cm} (S3)

Evaluating this however presents a severe problem for the Tavis–Cummings model with strong light-matter coupling, as it requires expressions for the complete spectrum of eigenstates and energies. In general, for many-body problems, this is not available.

There do exist some special cases where one can give explicit forms of the dissipation. The simplest case—which recovers the phenomenological picture of vibrations causing dephasing—is to neglect light-matter coupling in deriving $\xi_{i,n}^2, \lambda_n$. In this case there is a single eigen-operator $\xi_{i,0}^2 = \sigma_i^z, \lambda_0 = 0$, and one finds a pure dephasing process. For the Ohmic spectrum $J(\nu)$ defined in the main text one finds $4\pi a T \sum \mathcal{L}|\sigma_i^z|$. The behavior of the driven-dissipative Tavis–Cummings model with dephasing has been extensively studied elsewhere (see e.g. Ref. [47]). In such a model lasing only occurs for $\Gamma_\uparrow > \Gamma_\downarrow$, and the threshold ratio $\Gamma_\uparrow/\Gamma_\downarrow$ is symmetric around cavity-molecule detuning $\Delta = 0$. Both these features are notably different to the results seen in Fig. 2. We may also note that the same statements apply when there is no effect of the vibrational bath at all. In that case our model becomes the Tavis–Cummings model with only pumping $\Gamma_\uparrow$, and decay $\Gamma_\downarrow, \kappa$ processes. As discussed extensively in previous work, e.g. [45, 55], this model also requires $\Gamma_\uparrow > \Gamma_\downarrow$ for lasing to occur. However, polariton splitting is suppressed at large pump strengths, so such models cannot provide a description of experiments [2–7] demonstrating polariton lasing in the strong light-matter coupling regime.

Another case where explicit results can be derived is at weak excitation, when the saturable two-level operators $\sigma_i^\pm$ can be replaced by bosonic operators $c_i^\dagger, c_i$. This yields a system Hamiltonian that is quadratic in bosonic operators, and can be solved exactly, see Refs. [56–58]. However, neglecting saturation of the two-level system is not valid when considering strong driving and lasing.

The fact that microscopic derivation of dissipation requires knowledge of the eigenspectrum of the system Hamiltonian in fact provides further motivation for methods such as the mean-field PT-MPO approach. That is, even when a weak coupling approach might be valid, it may not always be practical to evaluate the eigen-operators and values. Approaches based on the PT-MPO remove this requirement, enabling one to study the dynamics of many-body systems coupled to structured environments.

2. MEAN-FIELD EQUATIONS

In this section we derive the mean-field Hamiltonian Eq. (5) and equation of motion Eq. (6). As noted in the Letter, for models with many-to-one coupling, such as our emitter–cavity model, it can be shown [37, 38] that a mean-field ansatz is exact as $N \to \infty$.

In its most general form, mean-field theory can be understood as an assumption about the structure of the state of a many-body system [59–61]. Specifically, for our model, this means to consider the product state

$$\rho = \rho_0 \otimes \bigotimes_{i=1}^N \rho_i.$$ \hspace{1cm} (S4)

The reduced density matrix $\rho_0 = \text{Tr}_{\otimes i} \rho$ is obtained from
the partial trace taken over the Hilbert space of all two
level systems labelled \( i = 1, 2, \ldots, N \), and \( \rho_i = \text{Tr}_{\alpha \otimes \beta} \rho \)
from the partial trace over the photonic degree of freedom
and all but the \( i \)th two-level system.

In the calculations presented in the main text, we make
a further simplification by taking all molecules to be identi-
cal, so that only a single \( \rho \) needs to be calculated. We
note however that the mean-field method we describe
here does not require this. The mean-field treatment can
be applied to models where each molecular site has differ-
ent parameters, at the cost of requiring separate simula-
tions for each \( \rho_i \). We also note that even when all sites are
equivalent, the assumption of identical \( \rho_i \) is not the same
as restriction to the totally symmetric Hilbert space, par-
nicularly when incoherent processes are present. We dis-
cuss the consequences of this further below, in terms of
the role of “dark” exciton states within mean-field theory.

In our approach both the non-Markovian environment
and Markovian pumping and loss for each molecule are
handled by the PT-MPO method. As discussed below,
the PT-MPO can be derived starting from the dynamics
of the density matrix of an individual molecule \( \rho_i \). That
is, such dynamics could be considered as part of the evolu-
tion of \( \rho_i \), included within the system Hamiltonian, and
then handled through the PT-MPO approach. However,
explicitly including such dynamics in our discussion of
the mean-field approximation makes the derivation ap-
pear unnecessarily complicated. We therefore discuss the
mean-field decoupling approach to dynamics for a sim-
pler model (the Tavis–Cummings model), and then re-
introduce molecular dissipation terms in Sec. 4. As such
we start from the following master equation:

\[
\partial_t \rho = -i[H_S, \rho] + 2\kappa \mathcal{L}[\rho],
\]

(S5)

along with the system Hamiltonian from the Letter,
\[
H_S = \omega_c a^\dagger a + \sum_{i=1}^N \left[ \frac{\omega_0}{2} \sigma_i^+ + \frac{\Omega}{2\sqrt{N}} \left( a \sigma_i^+ + a^\dagger \sigma_i^- \right) \right].
\]

(1)

The equations of motion for the reduced density ma-
trices follow from

\[
\partial_t \rho_i = -i\text{Tr}_{\otimes 1}[H_S, \rho] + 2\kappa \text{Tr}_{\otimes 1} \mathcal{L}[\rho],
\]

(S6)

\[
\partial_t \rho_i = -i\text{Tr}_{\alpha \otimes \beta} [H_S, \rho] + 2\kappa \text{Tr}_{\alpha \otimes \beta} \mathcal{L}[\rho].
\]

(S7)

The partial traces can be performed by noting two
points. First, the separate reduced density matrices are
normalized to one. Second, the partial trace over sub-
system \( I \) of a commutator involving operators acting only
on subsystem \( I \) will vanish. Thus,

\[
-i\text{Tr}_{\otimes 1} [\omega_c a^\dagger a, \rho] = -i\omega_c [a^\dagger a, \rho],
\]

(S8)

\[
-i\text{Tr}_{\otimes 3} \sum_{i=1}^N \left[ \frac{\omega_0}{2} \sigma_i^+, \rho \right] = 0,
\]

(S9)

\[
2\kappa \text{Tr}_{\otimes 1} \mathcal{L}[\rho] = 2\kappa \mathcal{L}_a[\rho],
\]

(S10)

where \( \mathcal{L}_a[x] = x \rho_a x - \{ x^\dagger x, \rho_a \} / 2 \) is the Lindblad oper-
ator for the photon density matrix, and

\[
-i\text{Tr}_{\alpha \otimes 1} \left[ i^{\omega_0} a^\dagger a, \rho \right] = 0, \quad (S11)
\]

\[
-i\text{Tr}_{\alpha \otimes 3} \left[ \sum_{k=1}^N \frac{\omega_0}{2} \sigma_k^+, \rho \right] = -i \left[ \frac{\omega_0}{2} \sigma_i^+, \rho_i \right], \quad (S12)
\]

\[
2\kappa \text{Tr}_{\alpha \otimes 1} \mathcal{L}[\rho] = 0. \quad (S13)
\]

It remains to determine the terms arising from the
light-matter interaction in \( H_2 \). For the contribution to
the evolution of the photon degree of freedom Eq. (S6),
one has

\[
-i \sum_{i=1}^N \frac{\Omega}{2\sqrt{N}} \left( \text{Tr}_{\otimes 1} [a \sigma_i^+, \rho] + \text{H.c.} \right)
\]

(S14)

\[
= -i \frac{\Omega \sqrt{N}}{2} \left( \langle \sigma_+^a, \rho_a \rangle + \langle \sigma_-, a^\dagger \rangle \right).
\]

For the evolution of the matter degree of freedom
Eq. (S7), the contribution is instead

\[
-i \sum_{k=1}^N \frac{\Omega}{2\sqrt{N}} \left( \text{Tr}_{\alpha \otimes 1} [a \sigma_i^+, \rho] + \text{H.c.} \right)
\]

(S15)

\[
= -i \frac{\Omega \sqrt{N}}{2} \left( \langle a \sigma_+^i, \rho_i \rangle + \langle a^\dagger \sigma_-^i \rangle \right).
\]

From the above we find that the equation of motion for
each molecule \( \rho_i \) is

\[
\partial_t \rho_i = -i[H_i, \rho_i],
\]

(S16)

where

\[
H_i = \frac{\omega_0}{2} \sigma_i^+ + \frac{\Omega}{2\sqrt{N}} \left( \langle a \sigma_+^i \rangle + \langle a^\dagger \rangle \right).
\]

(S17)

is the mean-field Hamiltonian \( H_{\text{MF}} \), Eq. (5), for one of
the identical emitters. In the full dissipative model, \( H_i \)
would also include the bath terms for that molecule, and
could be used used to construct the system propagators
in the PT-MPO method described in Sec. 4. One may
note that in Eq. (S17), the only property of the photon
state \( \rho_a \) required is the expectation \( \langle a \rangle \). One may thus
take the equation of motion for \( \rho_a \),

\[
\partial_t \rho_a = -i[H_a, \rho_a] + 2\kappa \mathcal{L}_a[\rho],
\]

(S18)

with the Hamiltonian

\[
H_a = \omega_c a^\dagger a + \frac{\Omega \sqrt{N}}{2} \left( \langle a \langle a^\dagger \rangle + \langle a^\dagger \rangle \right).
\]

(S19)

and derive the equation of motion for \( \langle a \rangle \):

\[
\partial_t \langle a \rangle = \text{Tr}_a \left( a \partial_t \rho_a \right)
\]

\[
= -i\omega_c \text{Tr}_a \left( a \rho_a \right) - i \frac{\Omega \sqrt{N}}{2} \langle \sigma_- \rangle \text{Tr}_a \left( a \rho_a \right)
\]

\[
+ 2\kappa \text{Tr}_a \left( a a^\dagger \rho_a - a^\dagger a \rho_a / 2 - a^2 \rho_a / 2 \right)
\]

\[
= -(i\omega_c + \kappa) \langle a \rangle - i \frac{\Omega \sqrt{N}}{2} \langle \sigma_- \rangle.
\]

(S20)
Field rescaling

In the lasing phase $\langle a \rangle$ scales with $\sqrt{N}$ so it is convenient to work with the rescaled quantity $\langle \tilde{a} \rangle = \langle a \rangle / \sqrt{N}$ such that Eqs. (5) and (6) become

$$\partial_t \langle \tilde{a} \rangle = -(i\omega_c + \kappa)\langle \tilde{a} \rangle - i\frac{\Omega}{2} \langle \sigma^- \rangle$$  \hspace{1cm} (S21)$$

and

$$H_{MF} = \frac{i\hbar}{2} \sigma^z + \frac{\Omega}{2} \left( \langle \tilde{a} \rangle \sigma^+ + \langle \tilde{a} \rangle^* \sigma^- \right).$$  \hspace{1cm} (S22)$$

Hence only a single parameter $\Omega$ is used to specify the light-matter interaction. It is the rescaled photon number, $|\langle \tilde{a} \rangle|^2 \equiv n/N$, that is plotted in Figs. 2(a) and 2(b).

3. BRIGHT AND DARK EXCITON STATES IN MEAN-FIELD THEORY

In this section we discuss the role that bright and dark excitonic states play within a mean-field approach. As discussed elsewhere [39–41, 62], for a model of $N$ molecules coupled to a single photon mode, one can divide excitons into a single optically “bright” mode—the spatially uniform superposition which couples to the cavity mode, and $N - 1$ “dark” modes which are orthogonal to the bright mode. The bright modes hybridize with the cavity mode to form polaritons, while the dark modes remain at the bare exciton energy [63].

When the molecules are disordered (e.g. different on-site energies), this mixes the bright and dark states [39], leading to a non-vanishing spectral weight from the dark modes. Since our model has no disorder, one might expect the dark modes are absent. However, as we discuss here, one can directly show that within a mean field treatment, both bright and dark states are occupied. Furthermore, despite the absence of static disorder, the vibrational environment provides a form of dynamical disorder which makes the dark modes optically active [8, 23, 24, 41].

Exciton populations

We first show how one can extract exciton populations from the mean-field theory, and show that both the $k = 0$ “bright” states, as well as the $k \neq 0$ “dark” states are populated.

Firstly, the total exciton population is:

$$P_{tot.} = \sum_{i=1}^{N} \langle \sigma^+_i \sigma^-_i \rangle = \frac{N}{2} \left( 1 + \langle \sigma^z \rangle \right)$$  \hspace{1cm} (S23)$$

where we write $\langle \sigma^z \rangle$ for the expectation at any one of the $N$ identical sites. To find the bright and dark state populations, we can consider exciton modes with defined momenta corresponding to creation operators $\sum_i \sigma^+_i e^{-i{k} \cdot r_i} / \sqrt{N}$. Following this, the $k = 0$ exciton population is defined as

$$P_{k=0} = \frac{1}{N} \sum_{i,j=1}^{N} \langle \sigma^+_i \sigma^-_j \rangle.$$  \hspace{1cm} (S24)$$

Using the mean-field decoupling $\langle \sigma^+_i \sigma^-_j \rangle = \langle \sigma^+_i \sigma^-_j \rangle$ for distinct sites $i \neq j$ and the properties of Pauli operators for $i = j$, the $k = 0$ (bright) population is readily calculated as

$$P_{k=0} = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{1}{2} \left( 1 + \langle \sigma^z \rangle \right) + \frac{1}{N} \sum_{j \neq i} \langle \sigma^+_i \sigma^-_j \rangle \right) = \frac{1}{2} \left( 1 + \langle \sigma^z \rangle \right) + (N - 1) \left| \langle \sigma^+ \rangle \right|^2.$$  \hspace{1cm} (S26)$$

By completeness of any $k$-space representation, the total population of dark states can then be found as $P_{k \neq 0} = P_{tot.} - P_{k=0}$. Since $P_{k=0} \neq P_{tot.}$, one may clearly see that the mean-field approximation does not neglect the dark state population. The expressions for bright and dark mode populations simplify when we consider the limit of large $N$. In this case we may write:

$$P_{k=0} \approx N \left| \langle \sigma^+ \rangle \right|^2,$$  \hspace{1cm} (S25)$$

$$P_{k \neq 0} \approx \frac{N}{2} \left( 1 + \langle \sigma^z \rangle - 2 \left| \langle \sigma^+ \rangle \right|^2 \right).$$  \hspace{1cm} (S26)$$

In Fig. S1(a) we plot these steady-state populations as a function of pump strength, across the transition. When rescaled by $1/N$, the $k = 0$ has vanishing population in the normal state and becomes non-zero when macroscopic coherence arises in the lasing state.

Dark exciton spectral weight

An established signature of excitonic dark states in coupled light-matter systems is a residual peak in the absorption spectrum at the exciton energy [8, 23, 24, 39–41]. This occurs when either static [39, 40] or dynamic [8, 23, 24, 41] disorder can mix the bright and dark states. Mathematically, this arises due to the structure of the imaginary part of the molecular self-energy $\Sigma^{-}$, Eq. (7). One finds that the weight of any residual peak decreases as the light-matter coupling $\Omega$ increases—one may understand this by considering the imaginary part of Eq. (9) for which $|\Sigma^{-}|^2 \propto \Omega^2$ appears in the denominator. On the other hand, at small values of $\Omega$ the residual peak cannot be separated from the upper and lower polariton. The values of $\Omega$ shown in the Letter are in fact too small to separate the residual peak from the upper polariton. In Fig. S1(b) we show that by further increasing $\Omega$ this residual dark exciton peak may be clearly observed.
FIG. S1. (a) Exciton populations per site in the steady-state obtained using the PT-MPO method at \( \Omega = 200 \) meV. Below threshold the population per site of the \( k = 0 \) mode (or any single mode) vanishes as \( 1/N \). The \( k = 0 \) population becomes macroscopic above threshold. (b) Absorption spectrum, showing the existence of a residual excitonic peak at \( \Omega = 1000, 1600 \) meV. Both panels show the same data on different vertical scales. No residual peak is seen in the curve at \( \Omega = 400 \) meV, which is the largest light-matter coupling strength considered in the main text. This is due to the proximity of the upper polariton whose tail swamps the residual peak. Note the frequency structure of the vibrational environment means that this feature occurs at frequencies just above the zero-phonon line \( \omega = \omega_0 \). In this figure, the values of other parameters match those used in Fig. 2(a) of the Letter (\( \Delta = -20 \) meV, \( T = 300 \) K, \( \kappa = \Gamma_1 = 10 \) meV).

4. CALCULATING DYNAMICS WITH PT-TEMPO

In this section, for completeness, we discuss the TEMPO method introduced in Ref. [28], construction of the PT, and its combination with the mean-field dynamics. We also discuss the types of problems for which this method may be applied.

The TEMPO network is built around a discretized Feynman-Vernon influence functional [64–66], which captures the effect of the bath, including memory effects. Approaches based on the influence functional require summation over intermediate states. In TEMPO, this summation is formulated as the contraction of a tensor network. To derive the influence functional tensors and construct this tensor network, the coherent evolution of the system density operator \( \rho \) from time \( t_0 \) to \( t_M \), described by the total Liouvillian \( \mathcal{L}(t) = -i[H_S(t) + H_E(t)] \), is firstly divided into \( M \) short-time propagations,

\[
\rho(t_M) = T_\omega \exp\left(\int_{t_0}^{t_M} dt \mathcal{L}(t)\right) \rho(t_0) = T_\omega \prod_{m=0}^{M-1} \exp\left(\int_{t_m}^{t_{m+1}} dt \mathcal{L}(t)\right) \rho(t_0),
\]

where \( t_m = m\delta t \) and \( T_\omega \) time-orders these expressions, placing earlier times to the right. Next, the system and environment contributions at each time step are split up using a symmetrized Suzuki-Trotter expansion:

\[
\begin{align*}
\exp\left[-i \int_{t_m}^{t_{m+1}} dt \left( \mathcal{L}_S(t) + \mathcal{L}_E(t) \right) \right] &= \exp\left[-i \int_{t_m}^{t_{m+1}} dt \mathcal{L}_S(t) \right] \exp(-i\mathcal{L}_E\delta t) \\
&= \exp\left[-i \int_{t_m}^{t_{m+\delta t/2}} dt \mathcal{L}_S(t) \right] \exp\left[-i \int_{t_m+\delta t/2}^{t_{m+1}} dt \mathcal{L}_S(t) \right] \exp(-i\mathcal{L}_E\delta t) \\
&\times \exp\left[-i \int_{t_m+\delta t/2}^{t_{m+1}} dt \mathcal{L}_S(t) \right] + O(\delta t^3).
\end{align*}
\]

Note that \( \mathcal{L}_E = -i[H_E, \cdot] \) is time-independent, but \( \mathcal{L}_S(t) = -i[H_S(t), \cdot] \) depends on time in general. In our problem, \( \mathcal{L}_S \) depends implicitly on time via the time-dependent expectation value \( \langle a(t) \rangle \), \( \mathcal{L}_S = \mathcal{L}_S(\langle a(t) \rangle) \). The full time evolution is then written as a sum over system states by inserting a resolution of identity between successive short time propagators in Eq. (S27). To express this sum in tensor notation, it is convenient to vectorize system operators and matrices using a single index \( j = 1, \ldots, d^2 \), where \( d \) is the system Hilbert space dimension (\( d = 2 \) for the system we consider), and choose a basis for which the system-environment coupling is diagonal (\( \sigma^z \) in our model). In this basis the components of the system density matrix at \( t_M \) take the form [28]

\[
\rho_{j,j} (t_M) = \sum_{j_0, j_1, \ldots, j_M} \prod_{m=0}^{M-1} K_m'(j_{m+1}, j_m) \prod_{k=0}^{m-1} I_k(j_m, j_{m-k}) K_m(j_m, j_{m-1}) \rho_{j_0}(0),
\]

where \( K_m(j, j') = \left[T_\omega \exp\left(\int_{t_m}^{t_{m+\delta t/2}} dt \mathcal{L}_S(t)\right)\right]_{j,j'} \) is a two-index object i.e. a tensor such that contracting \( K_m(j, j') \) with \( \rho_{j'} \) enacts system-only evolution over the half-time step \( [t_m, t_m + \delta t/2] \), and similarly \( K_m'(j, j') = \left[T_\omega \exp\left(\int_{t_m}^{t_{m+\delta t/2}} dt \mathcal{L}_S(t)\right)\right]_{j,j'}. \) The index \( m \) on \( K_m \), \( K_m' \) indicates the fact that these tensors vary with time step, because of the time-dependent system Hamiltonian. The other objects \( I_k(j, j') \) are the bath influence functions that, taken together, capture all possible effects of the environment on the system. For these, the index \( k \) indicates the time difference over which the bath influence is evaluated. The bath influence function does not depend on the label \( m \) as the bath is time-independent. These influence functions depend both on the spectrum of the environment \( J(\nu) \) and the system operator coupling to the environment; see Ref. [28] for complete expressions. From these we define the bath tensors \( b_k \),

\[
[b_k]_{j,j',t,t'} = I_k(j, j')\delta_{j,t}\delta_{j',t'},
\]

such that at the \( M \)th time step, \( M \) bath tensors and two system propagators may be added to the network according to Eq. (S29), as seen in Fig. S2.
FIG. S2. Growth of the tensor network in the TEMPO method according to Eq. (S29). $M$ bath tensors (red) and two system propagators (orange) are added at the $M^{th}$ time step (here $M = 3$ in the blue dashed box). In practice, a finite memory approximation is made in which at most $K$ bath tensors are added in one step. The initial state—a vector with $d^2$ elements—is shown as a gray circle.

Process tensor MPO approach

So far we have discussed the tensor network which is common to both the TEMPO method as originally implemented [28] and the PT approach. In the PT approach, one uses the fact that the bath tensors at each time step may be contracted independently of the system propagators, as shown in Fig. S3(a). Contracting the tensor network makes use of standard tensor network techniques [67]. In particular, as the network is contracted, compression occurs by truncating the singular value decompositions that arise. After this compression, the storage requirement for the PT is a product of its length (i.e. number of time steps) and the average bond dimension. We discuss further below (Convergence of its length) how to ensure a small bond dimension and thus that the PT-MPO to be stored is of a manageable size.

Our PT-MPO runs at a fixed precision $\epsilon_{rel.}$ such that at each step in the construction of the PT singular values smaller than $\epsilon_{rel.}$ relative to the largest singular value are discarded. This is in contrast to other MPO methods where instead the bond dimension of the tensor is fixed and hence the precision varies. In addition, a finite memory approximation is made whereby all correlations are discarded after $K$ time steps.

The resulting object, the PT, may be stored and later combined with different sets of system propagators and initial states to obtain many time evolutions at relatively little cost. Additional operators may also be inserted between the system propagators at this stage for the purpose of calculating multitime correlation functions [29, 68].

Combining PT-TEMPO with mean-field theory

In the discussion so far, we described the PT-MPO method for a generic time-dependent system Hamiltonian $H_S(t)$. To combine this with mean-field theory, one then uses a molecular Hamiltonian $H_S(t) = H_t$ from Eq. (S17) which depends on $\langle a(t) \rangle$. To complete the mean-field PT-MPO, one needs to discretize the evolution of $\langle a \rangle$ consistently with the system evolution, and thus determine $K_m(j,j'), K'_m(j,j')$.

Suppose at time $t_M$ one has a field value $\langle a \rangle_M$ and a molecular state $\rho_M$ with corresponding spin expectation $\langle \sigma^- \rangle_M$. To construct the system propagators for the next time step, we use the linearization of the field

$$\langle a \rangle_M'(t) = \langle a \rangle_M + (t - t_M) \partial_t \langle a \rangle \big|_M, \quad t \in [t_M,t_{M+1}],$$

(S31)

where $\partial_t \langle a \rangle \big|_M$ is the equation of motion Eq. (6) at $t_M$:

$$\partial_t \langle a \rangle \big|_M \equiv \partial_t \langle a \rangle \big|_{\langle a \rangle_M,\langle \sigma^- \rangle_M} = - (i \omega_a + \kappa) \langle a \rangle_M - \frac{\Omega \sqrt{N}}{2} \langle \sigma^- \rangle_M.$$  

(S32)

Substituting $\langle a \rangle_M'(t)$ into $H_S$, the integrals in Eq. (S28) may then be performed without further approximation. Having applied the total propagator to $\rho_M$, the remainder of the PT (describing evolution under $H_E$ for $t > t_{M+1}$) may be traced over to yield the state $\rho_{M+1}$ and hence spin expectation $\langle \sigma^- \rangle_{M+1}$. This is used in conjunction with $\langle \sigma^- \rangle_M$ to evolve the field from $t_M$ to $t_{M+1}$ according to the second-order prescription

$$\langle a \rangle_{M+1} = \langle a \rangle_M + \frac{1}{2} \delta t (k_{M_1} + k_{M_2}),$$

(S33)

where

$$k_{M_1} = \partial_t \langle a \rangle \big|_{\langle a \rangle_M,\langle \sigma^- \rangle_M},$$

(S34)

$$k_{M_2} = \partial_t \langle a \rangle \big|_{\langle a \rangle_M,\delta t k_{M_1},\langle \sigma^- \rangle_{M+1}}.$$  

(S35)

Broader applicability of PT-TEMPO with mean-field theory

As noted in the Letter, there are two classes of problems for which the mean-field ansatz is exact as $N \rightarrow \infty$:
those with many-to-one coupling such as considered here, and those with all-to-all coupling [37, 38]. Systems with many-to-one coupling most typically arise in the context of cavity QED, including cold atoms in single-mode optical cavities, circuit QED, or molecules in optical cavities as discussed here. Systems with all-to-all coupling arise in the same contexts, when adiabatic elimination of the cavity mode is possible. More widely, as discussed below, such all-to-all coupling can become a good approximation in cases when each system couples to many others.

There are many physically relevant situations for which the mean-field theory is not exact but offers a good approximation, and so our method may be applied. The validity of mean-field approximations has been widely considered in equilibrium condensed matter physics [59]. In the equilibrium case it is known that for high enough dimensions (i.e. beyond the upper critical dimension, which depends on the problem), mean-field theory can be a good approximation to the problem. In particular, the effect of fluctuations beyond mean-field theory is controlled by the density of states for low energy modes. Similar questions have been explored in some open quantum systems. These include models of polariton condensation with multiple modes [27] (see Sec. 7 below for a discussion), non-equilibrium spin models (see e.g. [69–72] and refs. therein), or cold atoms in multimode cavities [73, 74].

As a general principle, the approach described in this work can be applied in any context where one has the following features: (1) One can consider many systems, each of which has its own non-Markovian environment. (2) These systems couple to each other in a way that can be reasonably approximated by mean-field theory. i.e., systems couple via collective modes, or couple to many of their neighbours, such that a mean-field approximation may become good.

### Convergence of dynamics

We next discuss the computational parameters relevant to the process tensor TEMPO algorithm (hereafter ‘PT-TEMPO’) and provide the values of these parameters used in the Letter, justified by convergence tests of the dynamics.

There are three computational parameters to consider: time step size $\delta t$, singular value cutoff $\epsilon_{\text{rel.}}$, and memory length $K$. Evidently $K \cdot \delta t$ should be chosen to be greater than physical correlation times of the system. In fact, we found that if the effective discontinuity introduced into the bath autocorrelation by truncating the PT after $K$ steps was significant on the scale set by $\epsilon_{\text{rel.}}$, then a large bond dimension resulted [Fig. S4]. That is, the cutoff effectively implies $C_{\text{eff}}(t) = C(t)\Theta(K\delta t - t)$, and the sharp step function leads to the existence of many singular values of order $C(K\delta t)$ in the process tensor. When

$$C(K\delta t) \gtrsim \epsilon_{\text{rel.}},$$

this significantly increases the bond dimension. At high precisions avoiding this issue required $K \cdot \delta t \gtrsim 80$ fs in excess of any correlation times in the system and hence the memory cutoff had no effect on the accuracy of our calculations [Fig. S5(a)].

Figs. S5(b) and S5(c) show, respectively, convergence tests under changes in $\delta t$ and $\epsilon_{\text{rel.}}$, where the value of the photon number $n/N$ was recorded (crosses) at $t = 0.66$ ps for one set of system parameters ($\Omega = 200$ meV, $\Delta = 20$ meV, $\Gamma^\uparrow = 0.4\Gamma^\downarrow$). In these panels the data corresponding to the computational parameters that were finally chosen, $\delta t = 0.4$ fs and $\epsilon_{\text{rel.}} = 5 \times 10^{-12}$, is indicated with a red circle. For comparison, we include results (filled circles) obtained using the original (non-PT) implementation [28] of the TEMPO method. Note that the accuracy of the two algorithms for a given set of computational parameters is not necessarily the same, because of the different ordering of tensor contractions in the two approaches. In particular, we noticed the error in the PT-TEMPO calculation become unstable below $\delta t = 0.4$ fs at $\epsilon_{\text{rel.}} = 5 \times 10^{-12}$ [Fig. S5(b)] whilst the non-PT results remained stable down to $\delta t = 0.1$ fs at this precision. This issue could not be resolved by further increases in precision, likely due to operations required to calculate singular values reaching the limits of machine (floating point) precision. Similarly in Fig. S5(c) at $\delta t = 0.4$ fs we found no benefit in reducing $\epsilon_{\text{rel.}}$ below $5 \times 10^{-12}$, instead
FIG. S5. Convergence tests for the computational parameters (a) \( K \), (b) \( \delta t \) and (c) \( \epsilon_{\text{rel.}} \). These panels show the \( t = 0.66 \) ps value of the scaled photon number \( n/N \) in simulations using the PT-TEMPO (crosses) and non-PT TEMPO (filled circles) methods at \( \Omega = 200 \text{ meV}, \Delta = 20 \text{ meV}, \Gamma_1 = 0.4\Gamma_1, \) and \( T = 300 \text{ K} \), with losses \( \kappa = \Gamma_1 = 10 \text{ meV} \) as in Fig. 2. In each panel, the horizontal axis is ordered so that convergence occurs on moving to the right. In addition, a red circle indicates data corresponding to the computational parameters used in the Letter (\( K = 250, \delta t = 0.4 \text{ fs}, \epsilon_{\text{rel.}} = 5 \times 10^{-12} \)). (a) The requirement on \( K \cdot \delta t \) to attain a manageable bond dimension \( \epsilon_{\text{rel.}} = 5 \times 10^{-12} \) is far beyond that at which any significant change in system dynamics is observed. (b) The PT-TEMPO result becomes unstable below \( \delta t = 0.4 \text{ fs} \) whilst the change in the non-PT result continues to decrease linearly with time step halvings. (c) The PT-TEMPO method appears to require a higher precision (smaller \( \epsilon_{\text{rel.}} \)) for comparable accuracy. This is a trade-off of the gain of computational efficiency: the PT-TEMPO data point at \( \epsilon_{\text{rel.}} = 5 \times 10^{-12} \) here took less than 5 minutes to obtain compared to 3.5 hours using the non-PT method. (d) Error in the PT-TEMPO value at \( \epsilon_{\text{rel.}} = 5 \times 10^{-12} \) for \( \Gamma_1/\Gamma_1 = 0.2, 0.4 \) and 0.6 relative to non-PT data with the smallest time step \( \delta t = 0.1 \text{ fs} \) at that precision.

observing fluctuations in the PT-TEMPO results about the non-PT value. The discrepancy between the two implementations did allow us to quantify the error in the PT-TEMPO calculation at \( \delta t = 0.4 \text{ fs}, \epsilon_{\text{rel.}} = 5 \times 10^{-12} \), taking the \( \delta t = 0.1 \text{ fs} \) non-PT result as an exact reference. This was done for three difference pump strengths at \( \Omega = 200 \text{ meV} \) to produce Fig. S5(d). By \( \delta t = 0.4 \text{ fs} \), the estimated error is well below 0.5\% in each case.

**Computational resources used**

For the spectral density Eq. (3) (\( \alpha = 0.25, \nu_e = 150 \text{ meV} \)) and temperature \( T = 300 \text{ K} \), and using the computational parameters described above, the PT took approximately 3-4 core hours to construct on a 2.1 GHz Intel® Xeon® processor. Calculations of similar length were required to construct PTs for the the other three temperatures \( T = 250 \text{ K}, T = 350 \text{ K} \) and \( T = 400 \text{ K} \) used in Fig. 2(d). Having precomputed a PT, subsequent contraction with the chosen initial state, system propagators and control operators took only minutes to complete (we found 10 minutes typical).

5. FITTING PROCEDURES FOR FIGS. 2 AND 3

In this section we detail the procedures used to extract the lasing threshold \( \Gamma_c \) plotted in Figs. 2(c) and 2(d). We also explain how we check that the steady-state has been reached before applying the operators that allow us to calculate the two-time correlators used to determine the spectrum in Fig. 3.

In order to obtain the steady-state scaled photon number \( n_s/N \) for each set of system parameters (\( \Omega, \Delta, \Gamma_1 \)) and environment temperature \( T \), the dynamics were firstly calculated to a final time \( t_f = 1.3 \) ps using a pre-computed PT for that temperature. An exponential \( a \exp(-b t) + c \) or constant \( (a = b = 0) \) fit was then made to the late time dynamics \( t \geq 1 \) ps. If the mean squared error of the fit, scaled by the magnitude of \( a \) (or \( c \) if \( a = 0 \)), was less than \( 10^{-2} \), the fit was accepted and \( c \) used as the value for \( n_s/N \) (e.g. filled circles in Fig. 2(b)). On the contrary, if the error exceeded this cutoff the fit was deemed poor and the data not used in the subsequent threshold calculation (open circles in Fig. 2(b)). Note in the case \( n(t_f)/N \) was less than \( 10^{-12} \) no fit was attempted and instead this final value was taken as the steady-state value.

Before extracting the threshold from the resulting plots of \( n_s/N \) against \( \Gamma_c \) such as those in Fig. 2(b), it was ensured that there were sufficient (> 5) values of \( \Gamma_c \) with valid fits in the lasing phase. A quadratic fit of the form \( \Theta(x - \Gamma_c) [a_1(x - \Gamma_c) + a_2(x - \Gamma_c)^2] \) was then made to the steady-state values at each light-matter coupling, detuning and temperature, yielding the threshold \( \Gamma_c \) at those parameters; a single point in Fig. 2(c) or Fig. 2(d).

To produce Figs. 3(a) to 3(d) the dynamics were calculated to \( t_f = 1.6 \) ps using the \( T = 300 \text{ K} \) PT (only 4/5ths of this tensor was used for Fig. 2). Firstly, to reach to steady-state (\( t_f = 1.3 \) ps) and, secondly, to measure either the \( \langle \sigma^+(t)\sigma^-(t_f) \rangle \) or \( \langle \sigma^-(t)\sigma^+(t_f) \rangle \) correlator \( (t_f \leq t \leq t_f^*) \). These measurements are performed by inserting a control operation \( \sigma^- \) (or \( \sigma^+ \)) in the tensor network at \( t = t_f \) and subsequently recording the expectation of \( \sigma^+ \) (or \( \sigma^- \)). To ensure the system had reached the steady-state by \( t_f = 1.3 \) ps, the exponential fitting described above was made up to \( t_f \); then only if the fit was valid and close (within 1\% or \( 10^{-5} \) in absolute value) to the observed value \( n(t_f)/N \) at this time was the state at \( t_f \) deemed suitable for determining the two-time correlations.
6. WEAK LIGHT-MATTER COUPLING THEORY

In Fig. 2(c) we included a weak light-matter coupling prediction for the phase boundary at $\Omega = 100 \text{ meV}$. Here we provide the supporting calculation and explain its failure to reproduce the observed boundary. This mismatch is a consequence of the conditions for lasing being outwith the weak light-matter coupling regime. Throughout this section “weak-coupling” should be interpreted as meaning weak light-matter coupling.

The weak-coupling limit of the model has been considered in Ref. [46]. In that paper the authors worked to second order in the light-matter coupling to derive a weak-coupling master equation of the form

$$ \partial_t \rho = -i [H_0, \rho] + 2\kappa \mathcal{L}[a] + \sum_{i=1}^{N} \left( \Gamma_1 \mathcal{L}[\sigma_i^+] + \Gamma_c \mathcal{L}[\sigma_i^-] \right) $$

$$ + \Gamma_{A,E}(\Delta) \mathcal{L}[a \sigma_i^+] + \Gamma_{E}(\Delta) \mathcal{L}[a^\dagger \sigma_i^-] \right), \quad (S36) $$

where the free Hamiltonian $H_0 = \Delta a^\dagger a$ ($\Delta = \omega_c - \omega_0$) and $\Gamma_{A,E}$ define rates of absorption and emission processes, given by

$$ \Gamma_{A,E}(\Delta) = \frac{\Omega^2}{4N} \int_{-\infty}^{\infty} dt e^{\pm i \Delta t} \langle \sigma^{-}(t) \sigma^{+}(0) \rangle_0. \quad (S37) $$

Here $\langle \sigma^{-}(t) \sigma^{+}(0) \rangle_0$ is the correlator for a free molecule i.e. measured in the absence of light-matter coupling. In Ref. [46], to calculate these quantities, it was assumed that the vibrational environment relaxes fast. This means that Eq. (S37) can be calculated starting from an equilibrium state of the molecules, an approximation known as Kasha’s rule [75]. For our parameters, this approximation does not necessarily hold (except for the special case of $\Gamma_\uparrow = 0$), so we use the PT-MPO method applied to an individual molecule to calculate $\Gamma_{A,E}$.

By making the mean-field factorization approximation, as discussed above, one can assume $\langle a^\dagger a \sigma^+ \sigma^- \rangle \approx \langle a^\dagger a \rangle \langle \sigma^+ \sigma^- \rangle$ between the photon number and spin operators. The resulting equation of motion for $n = \langle a^\dagger a \rangle$ is

$$ \partial_t n = -2\kappa n + N \left[ \Gamma_E(\Delta)(1 + n) \langle \sigma^+ \sigma^- \rangle - \Gamma_c(\Delta) (1 - \langle \sigma^+ \sigma^- \rangle) \right]. \quad (S38) $$

At threshold ($\Gamma_\uparrow = \Gamma_c$), the coefficient of $n$ on the right-hand side of this equation changes from negative to positive. Combining this with the steady-state population of excited molecules, $\langle \sigma^+ \sigma^- \rangle = \Gamma_\uparrow / (\Gamma_\uparrow + \Gamma_c)$, we have the critical condition

$$ -2\kappa + N \left[ \Gamma_E(\Delta) \frac{\Gamma_c}{\Gamma_\uparrow + \Gamma_c} - \Gamma_c(\Delta) \frac{\Gamma_\uparrow}{\Gamma_\uparrow + \Gamma_c} \right] = 0, \quad (S39) $$

from which

$$ \frac{\Gamma_c}{\Gamma_\uparrow} = \frac{2\kappa + N \Gamma_A(\Delta)}{N \Gamma_E(\Delta) - 2\kappa}. \quad (S40) $$

Since the rates $\Gamma_{A,E}$ themselves depend on $\Gamma_\uparrow$ through $\langle \sigma^{-}(t) \sigma^{+}(0) \rangle_0$, we solved Eq. (S40) iteratively for $\Gamma_\uparrow = \Gamma_c$, taking advantage of the efficiency with which many sets of system dynamics can be computed using a single PT. Setting $\Omega = 100 \text{ meV}$, at each step $\Gamma_\uparrow$ was incremented and $\Gamma_{A,E}(\Delta)$ evaluated on the range $\Delta \in [-100, -20] \text{ meV}$. The first time equality resulted between the two sides of Eq. (S40) for a particular $\Delta$ provided $\Gamma_c(\Delta)$ and hence a single point on the weak-coupling phase boundary in Fig. 2(c).

As is visible in Fig. 2(c), even at the smallest $\Omega$ used, the weak-coupling theory does not match the predictions of the full model. Reducing $\Omega$ much further leads to a regime where lasing never occurs—the collective cooperativity becomes too small [76]. As such, to verify that the full model does match the weak-coupling predictions, we must consider a different method of comparison. We choose to do this by comparing the photon absorption rates of unexcited molecules. This can be done by setting $\Gamma_\uparrow = 0$ and preparing an initial state with unexcited molecules and a small photon field. We then compare the rates at which this field decays.

---

**FIG. S6.** (a) Dependence of effective decay rate $\gamma$ (cyan) on light-matter coupling $\Omega$ for five different detunings when $\Gamma_\uparrow = 0$. The initial conditions and all other parameters were the same as used to produce Fig. 2(c) (in particular $\kappa = 20 \text{ meV}$= $\gamma(\Omega = 20)$). The weak-coupling prediction $\gamma_w$ for the rate, Eq. (S41), is indicated with a gray dashed line. (b) The difference $\gamma - \gamma_w$ at each detuning with a quartic fit (dashed) recorded in the table shown. Numerical error contributes a small constant and a small $\Omega^2$ term; it is the fourth-order term that describes behavior beyond the weak-coupling theory. Note the dependence on $\Omega$ is weaker for more negative detunings, providing an explanation for the varying error of the weak-coupling prediction for the phase boundary in Fig. 2(c).
7. COMPARISON TO EFFECTIVE HOLSTEIN–TAVIS–CUMMINGS MODEL

In this section we compare our results to a simplified model [18, 26] with a single vibrational mode and find that the simplified model cannot account for the temperature dependence of the phase boundary shown in Fig. 2(d).

We consider the Holstein–Tavis–Cummings (HTC) Hamiltonian,

\[
H = \omega_c a^\dagger a + \sum_{i=1}^N \left( \frac{\omega_0}{2} \sigma_i^+ + \frac{\Omega}{2\sqrt{N}} (a^\dagger \sigma_i^- + a \sigma_i^+) \right) \\
+ \sum_{i=1}^N \omega_\nu \left[ b_i^\dagger b_i + \sqrt{S} (b_i^\dagger + b_i) \sigma_i^\dagger \right],
\]

where \(b_i^\dagger\) creates vibrational excitations of frequency \(\omega_\nu\) on the \(i\)th molecule. These excitations couple to the electronic state of the molecule with strength \(\omega_c \sqrt{S}\). Note that in contrast to Ref. [26] we make the rotating wave approximation and so do not include a diamagnetic \(A^2\) term.

Incoherent processes are then included as Markovian terms in the master equation

\[
\frac{d}{dt} \rho = -i[H, \rho] + 2\kappa \mathcal{L}[a] + \sum_{i=1}^N \left( \Gamma^+ \mathcal{L}[\sigma_i^+] + \Gamma^- \mathcal{L}[\sigma_i^-] \right) \\
+ \Gamma_z \mathcal{L}[\sigma_z^\dagger] + \gamma_\nu \mathcal{L}[b_i + \sqrt{S} \sigma_i^\dagger] + \gamma_4 \mathcal{L}[b_i + \sqrt{S} \sigma_i^\dagger].
\]

In addition to the pump \(\Gamma^+\), dissipation \(\Gamma^-\) and field decay \(\kappa\) considered in the main text we have introduced dephasing of the electronic transition at rate \(\gamma_\nu\) and vibrational damping. The latter is due to relaxation of the vibrational mode to thermal equilibrium at temperature \(T\) with rates \(\gamma_\nu = \gamma_\nu n_B(T), \gamma_4 = \gamma_\nu (n_B(T) + 1)\) where \(n_B(T) = [\exp(\omega_\nu/T) - 1]^{-1}\). Together these additional processes approximately describe the effects of the remaining vibrational degrees of freedom.

Beyond those parameters that are in common with the model in the Letter there are then four extra parameters to determine: the vibrational frequency \(\omega_\nu\), the coupling \(S\), and the rates \(\Gamma_z\) and \(\gamma_\nu\). There are several different approaches one might take to decide these parameters. We choose to set \(\omega_\nu = 140\text{ meV}\) according to the shoulder of the absorption spectrum of BODIPY-Br [Fig. S7(a)] and proceed to choose \(S, \Gamma_z, \gamma_\nu\) so as to minimize the sum of squared deviations of the model’s spectrum from the experimental data [5]. This is consistent with the use of the molecular absorption data to determine values of the parameters \(\alpha\) and \(\nu_c\) for the spectral density Eq. (3) in the Letter.

In Fig. S7(c) we show the phase boundaries (overlapping dashed lines) for the HTC model at \(T = 300\text{ K}\).
and $T = 400$ K, calculated using code publicly available with Ref. [26]. Alongside we repeat the curves from Fig. 2(d) for the phase boundary of the full model at these temperatures. While the HTC model does allow for lasing without inversion, the boundary occurs at a noticeably higher pump strength over the majority of the region, and has a minimum controlled largely by the mode frequency $\omega_\nu = 140$ meV [26]. Most notably, the HTC model shows no dependence on temperature over the range we consider; this is in marked contrast to the results of the model described in the Letter. This occurs because the relaxation rates $\gamma_\uparrow, \gamma_\downarrow$ depend on temperature via the occupation $n_B = [\exp(\omega_\nu/T) - 1]^{-1}$ of the vibrational mode, but $\omega_\nu = 140$ meV far exceeds $T = 300\,K \sim 26\,m \text{eV}$ and $T = 400\,K \sim 35\,m \text{eV}$ hence $n_B(T) \sim 0$ for these and indeed all experimentally relevant temperatures. In contrast, the approach described in the main text involves a continuum of low-frequency vibrational modes; the population of those modes can vary significantly over the relevant temperature range.

8. MULTIMODE MODEL AND MOMENTUM-DEPENDENT SPECTRA

In this section we discuss the application of our method to an extended model containing multiple photon modes, and how this allows one to calculate the $k$-dependent optical spectra shown in Fig. 3.

When including multiple photon modes, the system Hamiltonian becomes

$$
H_S = \sum_k \omega_{c,k} \delta_k a_k^\dagger a_k + \sum_{i=1}^N \left[ \frac{\omega_0}{2} \sigma_i^z + \Omega \sum_k (a_k e^{-i k \cdot r_i} \sigma_i^+ + a_k^\dagger e^{i k \cdot r_i} \sigma_i^-) \right].
$$

The form of the mean-field equations in this multi-mode case remains similar to that presented in the main text. Indeed, if one assumes that only the $k = 0$ photon mode acquires a non-zero occupation, the mean-field equations are unchanged from those previously considered—the validity of this assumption is discussed further below.

For the optical spectra, derived from the two-time correlations, we must now consider momentum-dependent Green’s functions $D_{\mu}^{R,K}(\omega)$, which involve the photon energy $\omega_{c,k}$, and a $k$-dependent self energy. In a translation-invariant system, this self-energy is diagonal in momentum and takes the form:

$$
\Sigma_k^+(\omega) = \frac{i \Omega^2}{4N} \sum_{i,j=1}^N \int_0^\infty dt e^{i \omega t} \langle \{\sigma_i^-(t), \sigma_j^+(0)\} \rangle e^{i (r_i - r_j) \cdot k},
$$

(S45)

$$
\Sigma_k^-(\omega) = \frac{i \Omega^2}{4N} \sum_{i,j=1}^N \int_{-\infty}^\infty dt e^{i \omega t} \langle \{\sigma_i^-(t), \sigma_j^+(0)\} \rangle e^{i (r_i - r_j) \cdot k}.
$$

(S46)

Below threshold, where the expectations $\langle \sigma_i^-(t), \sigma_j^+(0) \rangle$ vanish, only terms with $i = j$ survive within our mean-field approximation. We then see the self-energies are independent of $k$ and reduce to those of the single mode model, Eqs. (7) and (8).

Above threshold, it is still true that the commutator in Eq. (S45) vanishes for $i \neq j$ within mean-field theory, giving a $k$-independent expression. For the anti-commutator in Eq. (S46) we must now note that the expectation $\langle \sigma_i^-(t) \rangle$ is non-zero. For the lasing state this term in fact oscillates at the lasing frequency, which we will denote $\mu$, i.e. $\langle \sigma_i^-(t) \rangle = \langle \sigma_i^-(0) \rangle e^{-i \omega t}$. When lasing occurs at $k = 0$, this expectation is identical on all sites, so the anti-commutator expectation takes the form:

$$
\langle \{\sigma_i^-(t), \sigma_j^+(0)\} \rangle = 2|\langle \sigma^- \rangle|^2 e^{-i \omega t} + A_c(t) \delta_{ij}
$$

(S47)

where $A_c(t) = \langle \{\sigma_i^-(t), \sigma_i^+(0)\} \rangle - 2|\langle \sigma^- \rangle|^2$ is the connected part of the expectation. Here we have used the fact that within mean-field theory, the connected part exists only for $i = j$. Using Eq. (S47) in Eq. (S46) we find:

$$
\Sigma_k^-(\omega) = \frac{i \Omega^2}{4} \left[ 2\pi \delta_{\mu,0} \delta(\omega - \mu) 2|\langle \sigma^- \rangle|^2 
\right.

+ \left. \int_{-\infty}^\infty dt e^{i \omega t} A_c(t) \right].
$$

(S48)

The first term here is the source of the delta-singularity seen in the photoluminescence spectrum in Fig. 2(c). This singularity exists only at the lasing wavevector, here taken to be $k = 0$.

We conclude this section by addressing the validity of a mean-field plus fluctuation treatment for the multimode model. As has been discussed extensively (see e.g. Ref. [1, 27]), such a treatment is valid provided the number of molecules is large compared to the number of relevant photon modes—those with energies sufficiently close the molecular transition energy.

To make this concrete, consider a finite system of area $A$. Denoting the areal density of molecules by $\rho$, the number of molecules is $\rho A$. To count photon modes, we use the mode spacing $k = 2\pi/\sqrt{A}$, and count the number of modes with energy less than $E$: $N_{ph} = m_{ph} AE/(2\pi)$ (recall $h = 1$). Hence the number of molecules per relevant photon mode is $N/N_{ph} = E_{\rho}/E$ where $E_{\rho} = 2\pi \rho/m_{ph}$. 


In this section we examine the inverse retarded and Keldysh Green’s functions below threshold which provide insight into the normal state excitation spectra and distributions. For reference we show in Fig. S8 the photoluminescence $\mathcal{L}_{k=0}(\omega)$, Eq. (13), at different pump strengths for light-matter couplings $\Omega = 100$ meV and $\Omega = 300$ meV, in addition to the panel at $\Omega = 200$ meV included in the Letter. To simplify the discussion, we work at $k = 0$ throughout this section.

Insight into the normal state excitation spectra and distributions is provided by studying the components of the inverse Green’s functions. We may define the components $A(\omega)$, $B(\omega)$, $C(\omega)$ via

$$[D^R(\omega)]^{-1} = A(\omega) + iB(\omega), \quad (S49)$$

$$[D^{-1}(\omega)]^K = iC(\omega), \quad (S50)$$

where $[D^{-1}]^K$ is such that $D^K = -D^R \left[D^{-1}\right] \, D^A$. The spectral weight (density of states) $\varrho(\omega) = -2\text{Im} \, D^R(\omega)$ and mode occupation function $2n(\omega) + 1 = iD^K(\omega)/\varrho(\omega)$ may then be written [78]

$$\varrho(\omega) = \frac{2B(\omega)}{A^2(\omega) + B^2(\omega)}, \quad (S51)$$

$$n(\omega) = \frac{1}{2} \left[ \frac{C(\omega)}{2B(\omega)} - 1 \right], \quad (S52)$$

and the photoluminescence

$$\mathcal{L}(\omega) = \frac{C(\omega) - 2B(\omega)}{2[A^2(\omega) + B^2(\omega)]} \equiv \varrho(\omega)n(\omega). \quad (S53)$$

The function $B(\omega)$ has the role of an effective linewidth for the normal modes whose position is determined by the zeros of $A(\omega)$. In the absence of light-matter coupling ($\Sigma^{-+} = \Sigma^{+-} = 0$), $B(\omega) = \kappa$ is a constant and $A(\omega) = \omega - \omega_c$. In general it is possible for the distribution to diverge as $n(\omega) \sim 1/(\omega - \omega^*)$, where $\omega^*$: $B(\omega^*) = 0$ defines an effective boson chemical potential, while the luminescence remains finite. Instead a condition for a divergence of $\mathcal{L}(\omega)$, i.e. a transition from the normal state to the lasing state, is a simultaneous zero of $A(\omega)$ and $B(\omega)$.

In the top row of Fig. S8 we show the components $A$, $B$ and $C$, as well as the derived $\varrho$, $n$ and $\mathcal{L}$ as a function of $\omega$ at $\Omega = 100$ meV for three pump strengths $\Gamma_\uparrow/\Gamma_\downarrow = 0.1$, 0.6 and 0.75 below threshold at $\Delta = -20$ meV ($\Gamma_\downarrow = 0.81\Gamma_\uparrow$ from Fig. 3(c)). As $\Gamma_\uparrow$ is increased we see the onset of a divergence in $n(\omega)$, which is established before the transition, as the graph of $B(\omega)$ (blue dotted line) moves downwards to develop two zeros (blue arrows), one of which is just left of the zero of $A(\omega)$ (red arrow).

At higher light-matter coupling strengths $\Omega = 200$ meV and 300 meV (bottom row of Fig. S8), the approach to the transition follows the same narrative albeit with more spectral weight—including additional zeros of $A(\omega)$ at $\Omega = 300$ meV—at the upper polariton $\sim (\omega - \omega_0)/\Omega = 0.5$.
FIG. S9. Real and imaginary parts of the inverse retarded and Keldysh Green’s functions (top axis in each panel) as defined in Eqs. (S49) and (S50) and the corresponding spectral weight, occupation and photoluminescence (bottom axis). Top row: $\Gamma_t/\Gamma_\downarrow = 0.1, 0.6, 0.75$ at $\Omega = 100$ meV ($\Delta = -20$ meV and $T = 300$ K). The first two pump strengths correspond to the red and blue curves in Fig. S8(a). The third, $\Gamma_t = 0.75\Gamma_\downarrow$, consists of separate data obtained using the non-PT TEMPO method (a longer time $t_f \sim 16$ ps was required to reach the steady-state at this $\Gamma_t$ and it was more efficient to perform a one-off calculation than compute an additional, longer PT). Red and blue arrows indicate, respectively, zeros of the real and imaginary parts $A(\omega)$ and $B(\omega)$ of $[D^R]^{-1}$. As the threshold $\Gamma_c = 0.81\Gamma_\downarrow$ (see Fig. 2(c)) is approached the imaginary part $B(\omega)$ decreases and develops two zeros (blue arrows). Of these, the rightmost is bound to reach the zero of $A(\omega)$ at $\Gamma_c$, at which point there is a real value $\omega^*$ such that $A(\omega^*) = B(\omega^*) = 0$, signaling instability of the normal state [48, 78]. Bottom row: $\Gamma_t/\Gamma_\downarrow = 0.1$ at $\Omega = 200$ meV and $\Omega = 300$ meV. Note $A(\omega)$ has two additional zeros at $\Omega = 300$ meV, a feature often taken to signal the strong coupling regime. Although the occupation function for this light-matter coupling is peaked on the right side of the first zero of $A(\omega)$ here, one expects this will move to the other side before the threshold (now at $\Gamma_c = 0.12\Gamma_\downarrow$) is reached.