Strong light-matter interaction effects on molecular ensembles

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Despite the potential paradigm breaking capability of microcavities to control chemical processes, the extent to which photonic devices change properties of molecular materials is still unclear, in part due to challenges in modeling hybrid light-matter excitations delocalized over many length scales. We overcome these challenges for a photonic wire under strong coupling with a molecular ensemble. Our simulations provide a detailed picture of the effect of photonic wires on spectral and transport properties of a disordered molecular material. We find stronger changes to the probed molecular observables when the cavity is redshifted relative to the molecules and energetic disorder is weak. These trends are expected to hold also in higher-dimensional cavities, but are not captured with theories that only include a single cavity-mode. Therefore, our results raise important issues for future experiments and model building focused on unraveling new ways to manipulate chemistry with optical cavities.

Strong light-matter interactions hosted by nanostructures and optical microcavities can induce significant and qualitative changes to chemical processes [15] including photoconductivity [4, 5], energy transport [6–8], and optical nonlinearities [9–11]. Much of the observed phenomenology stems from the hybridization of the collective material polarization and the resonances of an optical cavity, which leads to the formation of delocalized polariton modes when the energy exchange between the collective molecular excitations and the photonic structure is faster than the dissipative processes acting on each subsystem [12–14]. Polaritonic states are always accompanied by molecular states weakly coupled to light [15]. The latter are also sometimes called “dark states”, since the optical response of strongly coupled molecular ensembles is dominated by polaritonic excitations. The weakly coupled states form a reservoir containing the vast majority of the states of the system with significant molecular character [15–17], and therefore, they play an essential role in equilibrium and non-equilibrium molecular phenomena in optical cavities [18–21].

Polaritons dominate the optical response of a strongly coupled device, but the reservoir states are much more numerous [15–17]. Therefore, it is puzzling that significant changes in thermal reaction rates and branching ratios of some organic systems [22–27] were observed under conditions of infrared collective strong coupling. The dominance of molecular reservoir modes over the polaritonic [17] [28–29] suggests there is no simple explanation of the cavity effect on thermal reactions based on transition-state theory. [30–32]. This notion has motivated the hypothesis that cavity-induced changes to chemical reactions originate from dynamical effects of the electromagnetic environment on intramolecular dynamics [33–35] (see also [36–39], for theoretical treatments of strong light-matter interaction effects on chemical reaction dynamics when a single molecule is strongly coupled to a cavity photon mode and dark states are absent).

Given the complexity of polaritonic systems with states delocalized over length scales of the order of the optical wavelength, much of what is known about collective strong coupling relies on quantum mechanical simulations of effective models [30–32] where the cavity is modeled as a single bosonic mode and the molecular system has permutational symmetry, i.e., it consists of an ensemble of identical $N_M \gg 1$ two-level systems with equal transition energy and dipole moment $|13\rangle$ and $|14\rangle$. In these models, hybrid light-matter excitations (lower and upper polaritons, LP and UP, respectively) extending over the entire system emerge from the interaction of the homogeneous cavity field with the molecular bright mode corresponding to the totally symmetric combination of molecular states where a single molecule is excited. The other $N_M - 1$ molecular modes are degenerate and correspond to the dark reservoir discussed above. Permutationally invariant models deviating from this Tavis-Cummings (TC) picture via introduction of exciton-phonon interactions [17] [42–44] have also been thoroughly investigated.

The effects of material imperfections on polaritonic and dark states were probed in early work by Houdre et al. [15] who showed that the presence of energetic and structural disorder lead to weak photonic intensity borrowing by the reservoir states, but only minor changes to the TC picture when the collective light-matter interaction $\Omega/2$ (Rabi splitting) is much greater than the mean fluctuation $\sigma$ of the material transition energies. Recently, Scholes revisited the polariton coherence protection in single-mode (0D) cavities [35], whereas Botzung et al. [46] provided quantitative localization properties of the reservoir states of an energetically disordered emitter ensemble under strong coupling to a single spatially homogeneous cavity mode. Both studies showed in agreement with Ref. [15] that polariton coherence is largely unaffected by energetic disorder weaker than the collective light-matter coupling, but also noted that dark modes inherit spatial delocalization (see also Refs. [18–21]).

However, the majority of photonic materials employed in polariton chemistry research are multimode Fabry-
Perot (FP) or plasmonic cavities with a continuous spectrum. For example, in a FP cavity, each electromagnetic mode is characterized by its polarization (TE or TM), cavity order \( m = 1, 2, 3, \ldots \) (equivalent to the longitudinal wave-vector \( k_z \)), and the essentially continuous in-plane wave-vector \( q = (q_x, q_y) \). In systems such as FP cavities, disorder is known to severely restrict polariton space-time coherence \([55, 56]\) and may lead to weak or strong Anderson localization as well as diffusive and ballistic transport depending on the initial wave-packet, disorder strength, cavity geometric parameters, and magnitude of light-matter interactions \([57]\). Numerical simulations have shown that polariton wave functions can be localized over different length scales depending on their mean wave-vector \([58, 59]\) (see \([55]\) for a recent study of multimode cavity effects on polariton relaxation).

Despite their prominence, much less attention has been paid to multimode strong coupling effects on the reservoir states of structurally and energetically disordered molecular ensembles. These states form the majority of the excitations with significant molecular character, and therefore, they largely determine the equilibrium and transport properties of a molecular subsystem under collective strong coupling with an optical cavity.

Here, we employ numerical simulations of the microscopic states of a multimode photonic wire under strong coupling with a disordered molecular ensemble to investigate the influence of the cavity on the local molecular density of states and the exciton return probability. These quantities essentially reflect properties of the reservoir modes (since they are much more numerous than the polaritonic) and allow us to quantitatively probe the effects of multimode optical cavities on the molecular ensemble.

Our results have significant implications for future model-building in polariton chemistry since they provide detailed illustrations of qualitative shortcomings of single-mode representations of multimode devices. We also suggest practical principles to enhance cavity effects on molecular properties likely holding for generic systems, e.g., we find that for systems with equal collective light-matter interaction, polariton effects on the molecular ensemble are largest when the cavity is red-shifted, the distance between molecules is largest and energetic disorder is weak. Wave function localization theory \([48, 49, 54]\) and simple spectral overlap arguments explain these facts which provide another piece to the puzzle \([55]\) of the optical cavity effect on chemical reactions since some experimental observations suggest that the influence of photonic materials on chemical reactions is greater when the cavity-matter detuning vanishes \([59]\).

**Results and Discussion**

**Microscopic model.** We model an optical microcavity with \( O(\mu m) \) longitudinal and lateral confinement lengths \( L_x \) and \( L_y \) along the \( z \) and \( y \) axes, respectively \([57]\). The length of the long axis is \( L \gg L_x, L_y \). The molecules are distributed homogeneously along \( x \) and have equal \( y, z \) coordinates (see Fig. 1). Ideal reflective surfaces confine the EM field along \( z \) and \( y \), whereas periodic boundary conditions are assumed along \( x \). We include a single polarization of the EM field parallel to the direction of each molecule’s transition dipole moment. The bare cavity modes have frequency \( \omega = (c/\sqrt{\epsilon}) k \), where \( c \) is the speed of light, \( \epsilon \) is the static dielectric constant of the intracavity medium and \( k \) is the magnitude of the three-dimensional wave-vector \( \mathbf{k} = (2\pi m_x/L, n_y\pi/L_y, n_z\pi/L_z) \), where \( m_x \in \mathbb{Z} \) and \( n_y \) and \( n_z \) are positive integers. The parameters \( L, L_y, L_z \) and \( \epsilon \) are chosen such that the vast majority of the molecules are only resonant with cavity modes in its lowest energy band \((n_z = n_y = 1)\). Therefore, we ignore all other bands, and only include photons with \( \mathbf{k} = (2\pi m/L, \pi/L_y, \pi/L_z) \), \( m \in \mathbb{Z} \). From now on, we label the cavity modes by \( q \equiv k_z \), omit any reference to

![FIG. 1: (a) Section of photonic wire model employed in this work. Molecules (ovals) extend homogeneously (in average) along a single long cavity axis (x) with constant z and y. The distance between each of the \( N_M \) molecule is in average \( a \). (b) Subset of the energy spectrum \( E_i \) (obtained from exact diagonalization of a single realization of the Hamiltonian of a system with 1001 molecules and cavity modes, \( \Omega_R = 0.3 \text{ eV} \), \( \sigma/\Omega_R = 0.2 \), and other parameters as listed in the Sec. Thermodynamic limit convergence) of bare cavity, LP and UP as a function of integer eigenstate index \( i = 1, 2, \ldots, 1001 \), such that \( E_1 < E_2 < \ldots \) for cavities with \( q = 0 \) (top left) and \( q > 0 \) (top right) modes on-resonance with the (mean excitation energy) disordered molecular ensemble. The LP band includes the molecular reservoir modes only weakly coupled to the electromagnetic field (“dark states’’). The bottom left and bottom right, figures show the corresponding (single-realization) bare molecule DOS, and rescaled (for the sake of clarity, as the exact number is too small compared to the molecular even with \( N_M = N_C = 1001 \)) discretized photonic DOS for zero and red-detuned cavities (in the \( N_C \to \infty \) limit, this curve becomes continuous and a singularity arises at \( E_C(0) \)). Note that in the zero-detuning case, the subset of molecules with lowest energies is off-resonant with any cavity mode and therefore the effects of the confined field on such molecules is smaller. This point is further corroborated by Figs. 6 and 7.](image-url)
employ the Coulomb gauge \[58\] in the rotating-wave
approximation since we take \(\Omega_R/2 < 0.1E_M\) \[59\]. It follows that,
\[
H_{LM} = \sum_{j=1}^{N_M} \sum_q \frac{-i\Omega_R}{2\sqrt{\Omega_M^2 \mu_j}} \left( e^{iqx_j} a_q^\dagger a_q - e^{-iqx_j} a_q^\dagger a_q^\dagger \right)
\]

where \(\Omega_R = \mu_0 \sqrt{\hbar \omega_0 2\pi}, \rho = N_M / L S\), and \(S = L_y L_z\). We ignored the diamagnetic contribution (A^2 term) to \(H_{LM}\) since its effects are negligible under the studied conditions \[60\].

For a given \(\Omega_R\) and \(a = 1/\rho\), the number of molecules \(N_M\) and photon modes \(N_C\) are free parameters. A choice of \(N_M\) and \(N_C\) is equivalent to imposing low and high-energy cutoffs to the EM field. Specifically, \(L = N_M a\) defines the resolution of the cavity in reciprocal space, \(\Delta q = 2\pi/L\), and \(N_C\) defines the maximal cavity mode energy \(E_{max}\). Simulation results are independent of these cutoffs as long as \(L\) is larger than the longest coherence length of the system and \(E_{max}\) is greater than any relevant energy scale. Alternatively, thermodynamic limit \((N_M, L \to \infty \text{ with fixed } \rho\) independence of molecular observables to the number of included degrees of freedom can be imposed to obtain a minimal number of molecular and cavity modes. Such computationally optimal number of modes can be strongly dependent on the molecular observable of interest and may also vary significantly with \(\Omega_R\) and \(\sigma\).

We employ \(N_C = N_M\) in our simulations below, since in this case, the thermodynamic limit is reached with a small number of disorder realizations for the observables and range of parameters probed in our studies. A significant fraction of cavity modes is highly off-resonant with the molecular system in every case studied \((N_M \geq 1001)\), and we checked that a smaller number of cavity modes \(N_C^0\) would suffice to obtain thermodynamic limit predictions. However, as mentioned above, \(N_C^0\) depends on various parameters and we leave for future work a detailed analysis of optimal multimode cavity representations \[61\] for the study of the effects of photonic devices on molecules.

**Observables.** Let the eigenstates and eigenvalues of \(H\) be denoted by \(\psi\) and \(E_\psi\), respectively. The ensemble averaged molecular local density of states (LDOS) gives the conditional probability that an excited molecule will be detected with energy \(E\):

\[
\rho_M(E) = \frac{1}{N_M} \sum_{n=1}^{N_M} \langle 1_n | \delta(H - E) | 1_n \rangle
= \sum_\psi \langle P_{n\psi} \rangle \delta(E_\psi - E),
\]

where \(P_{n\psi} = | \langle 1_n | \psi \rangle |^2\) and \(\langle P_{n\psi} \rangle = \sum_{n=1}^{N_M} | \langle 1_n | \psi \rangle |^2 / N_M\) is the average probability to find a specific molecule excited when the system is in the eigenstate \(| \psi \rangle \). In the absence of light-matter interactions, the molecular LDOS \(\rho_M^{(0)}(E)\) is a Gaussian distribution centered at \(E_M\) and width \(\sigma\). Notably, We quantify the photonic effect on \(\rho_M(E)\) by
evaluating the cavity-induced change in its Shannon entropy
\[ \Delta S = S[\rho_M] - S[\rho_M^{(0)}], \quad (6) \]
\[ S[\rho_M] = - \int_0^\infty dE \rho_M(E) \ln[\rho_M(E)]. \quad (7) \]

\( \Delta S[\rho_M] \) allows us to quantify the cavity effect on the molecular ensemble energy fluctuations. Roughly speaking, \( \Delta S[\rho_M] \) provides a measure of molecular excited-state delocalization in energy space. Therefore, we expect \( \Delta S[\rho_M] \) to be a nondecreasing function of \( \Omega_R \) that is greater than or equal to zero, since polaritons have energies separated from the bare molecule excited-states by approximately \( \pm \Omega_R/2 \) (Fig. 1). However, the reduced bare photonic DOS relative to the molecular at energies where the molecular DOS is maximal suggests weakly coupled reservoir states dominate the molecular LDOS and the cavity-driven change in \( S[\rho_M] \) is expected to be small.

The mean probability that an initially excited molecule at time \( t = 0 \) will be detected in the same state at \( t > 0 \) is the time-dependent exciton survival (return) probability
\[ P_M(t) = \frac{\sum_{j=1}^{N_M} P_j(t)}{N_M}, \]
where
\[ P_j(t) = |\langle 1_n|e^{-iHt/\hbar}|1_n \rangle|^2. \quad (8) \]

The exciton return probability \( \Pi_M \) is the \( t \to \infty \) limit of \( P_M(t) \):
\[ \Pi_M \equiv \lim_{t \to \infty} P_M(t) = \frac{1}{N_M} \sum_{n=1}^{N_M} \sum_{\psi} P_{n\psi}^2 \]
\[ = \sum_{\psi} \langle p_{n\psi}^2 \rangle. \quad (9) \]

The exciton escape probability \( \chi_M \) is simply related to \( \Pi_M \) via:
\[ \chi_M = 1 - \Pi_M. \quad (10) \]

This quantity provides the ensemble-averaged probability that energy initially stored as a localized molecular exciton migrates to a distinct molecule or is converted into a cavity photon after an infinite amount of time.

\( \Pi_M \) provides a measure of excited-state delocalization in real-space and coherent energy diffusion efficiency: in systems where all Hamiltonian eigenstates are delocalized \( P_{n\psi} \propto 1/N_M \) for all \( \psi \) and \( n \), and therefore, \( \Pi_M \) vanishes in the thermodynamic limit, whereas in noninteracting systems with maximally localized excited-states, each molecule corresponds to a Hamiltonian eigenstate, and therefore \( P_{n\epsilon}(t) = \delta_{n\epsilon} \) and \( \pi_M = 1 \). In our model, the case where \( \pi_M = 1 \) corresponds to the molecules outside of the cavity (since we assume direct intermolecular interactions are insignificant), while we find \( \pi_M \to 0 \) when energetic disorder vanishes (see Fig. 1). Dark states are expected to have much large contribution to \( \Pi_M \) than polaritons since the latter inherit greater delocalization from their strong mixing with cavity modes.

Note that for a disordered multimode system there is no unambiguous definition of polariton and dark states since there is no energy gap between the LP band and the reservoir modes which are weakly coupled to the cavity. However, given a definition of polariton and weakly coupled modes, it is possible to decompose \( \Pi_M \) and \( \chi_M \) into a sum of contributions from polariton and reservoir modes and gauge the sensitivity of polariton and dark state delocalization to increasing disorder. To analyze our numerical simulations, we choose polaritons to consist of all states where the total photonic content is greater than 15%, but less than 85%, whereas dark states are all eigenstates with total molecular content greater than 85%. We briefly discuss this choice in the section Density and energetic disorder dependence.

**Thermodynamic limit convergence.** Before presenting a detailed quantitative study of the photonic effects on the mentioned molecular observables, we first show that with a relatively small number of molecules and modes we obtain robust predictions for cavity-induced changes in molecular properties. We set \( L_y = 400 \text{ nm}, \ L_z = 200 \text{ nm}, \) and dielectric constant \( \epsilon = 3. \) This gives a lowest energy cavity mode with \( E_C(0) \equiv \hbar \omega_0 = 2.0 \text{ eV} \). The highest energy wave-vector is \( q_{\text{max}} \approx \pi/a \) with \( a = 10.25, \) and 50 nm. To probe the thermodynamic limit of \( \rho_M(E) \) and \( \Pi_M \), we take \( \Omega_R = 0.3 \text{ eV}, \ E_M = 2.0 \text{ eV}, \ \sigma = 0.2 \Omega_R, \ \sigma_{\mu} = 0.05 \mu_0, \) and \( f = 0.1 \) in both cases. Other parameters are listed in the text (See Thermodynamic limit convergence).

![Fig. 2: Local molecular density of states obtained from five realizations of a molecular system in free space (red) and under strong coupling (blue) to a photonic wire (\( N_C = N_M \)) with \( E_M - E_C(0) = 0 \) (zero detuning), \( N_M = 1001 \) and 5001, \( \Omega_R = 0.3 \text{ eV}, \ \sigma/\Omega_R = 0.2, \ \sigma_{\mu} = 0.05 \mu_0, \) and \( f = 0.1 \) in both cases. Other parameters are listed in the text (See Thermodynamic limit convergence).](image-url)
1/a. This feature ensures that we have reached the thermodynamic limit for these observables, and justifies our utilization of $N_M = N_C = 1001$ in subsequent sections of this article.

**Microscopic states.** Our computations reveal quasi-extended and localized low energy polariton states in qualitative agreement with earlier work focused on disorder effects on 1D polaritonic states [50, 52] (although, we note that the Hamiltonians used in these studies break time-reversal symmetry and therefore lead to quantitatively distinct properties relative to our work since coherent localization is generally weakened when time-reversal symmetry is absent). These qualitative features of polariton localization in photonic wires have been thoroughly investigated so we provide no detailed discussion, except to mention that there is a clear analogy between the polariton states obtained in photonic wires and the local exciton ground-states and the quasi-extended exciton states of polymers [62, 63]. This analogy is a consequence of Anderson localization universality according to which, in general, there are no extended states over a 1D system in the thermodynamic limit. Instead, any small amount of disorder leads to a breakdown of long-range order.

In photonic wires strongly coupled to a resonant material, wave function localization and more generally, the expected distance-dependent decay of intermolecular correlations (mediated by the optical cavity) emerge only when both disorder and multiple electromagnetic field modes are included in the light-matter Hamiltonian.

**Density and energetic disorder dependence.** In Fig. 4, we report the changes induced by strong light-matter interactions in the molecular LDOS entropy (Eq. 6) and the molecular excited-state escape probability $\chi_M$ (Eq. 10) as a function of energetic disorder for various mean intermolecular distances at zero detuning and $\Omega_R = 0.3$ eV. Both $\Delta S[\rho_M]$ and $\chi_M$ show a generic decay with increasing disorder (except when $a = 10$ nm and $\sigma/\Omega_R < 0.4$ where $\chi_M$ has a shallow local minimum). This behavior is not surprising: when the molecular system is perfectly ordered, all excitations are maximally delocalized across the entire system (including the weakly coupled molecular states with negligible photonic content) and both $\Delta S[\rho_M]$ and $\chi_M$ take their largest possible value. For even small values of $\sigma/\Omega_R < 0.1$, scattering induced by energetic disorder induces weak and strong localization of polaritonic and reservoir modes, respectively. This notion is corroborated by Fig. 5 where the left and right plots show the polariton and dark state contributions to the exciton survival probability, respectively (according to the criterion that polaritons are hybrid states where the photonic content is greater than 15%, but less than 85%, and reservoir modes have greater than 85% molecular composition – while quantitative results depend on these choices, qualitative features are robust). According to our results, reservoir modes are highly sensitive to disorder, undergoing strong localization even when $\sigma/\Omega_R \leq 0.1$. Conversely, the polaritonic contribution to the survival probability is minimal at small values of $\sigma/\Omega_R$, but becomes significant when the energetic disorder is sufficiently large, further confirming that both weakly and strongly coupled excitations become localized over distances smaller than the size of the system. These trends agree with general ideas of wave function localization theory, namely that exciton localization becomes more prominent, in general, as $\sigma$ increases.

The consistent increase of $\Delta S[\rho_M]$ and $\chi_M$ with the intermolecular distance is more intriguing, since in the thermodynamic limit polariton scattering induced by energetic fluctuations is expected to be independent of $a$ when $q$ is nearly conserved [45]. Moreover, while elastic scattering induced by structural fluctuations is expected to be stronger as $a$ approaches 1/q, we show numerically in the SI Sec. 1 that unless $\sigma$ vanishes, energetic disorder provides the dominant contribution to polariton and reservoir localization.

The origin of the enhancement of photonic wire effects on the molecular ensemble with $a$ for fixed $\Omega_R$ may be understood by noting that if the cavity modes are integrated out in a path integral representation of the partition function of the system [65, 66], the effective action for the molecular system acquires retarded two-body intermolecular interactions mediated by the cavity with coupling constant proportional to the product of the mean transition dipole moment and $\chi_M$, with their largest possible value. For even small values of $\sigma/\Omega_R < 1$, the mean transition dipole moment is proportional to $1/\sqrt{\rho}$, (since $\Omega_R \propto \sqrt{\rho a^2}$ and $\rho \propto 1/a$). Therefore, when $\Omega_R$ and $N_M$ are fixed, the cavity influence on each molecule becomes stronger with decreasing value of $a$. Evidence for this feature can be obtained from the dark-state contribution to $\Pi_M$ in Fig. 5 (right). This shows the reservoir modes become significantly more delocalized when $a$ is increased from 10 to 50 nm. Note that, while the polaritonic contribution to $\Pi_M$ in Fig. 5...
also increases with $a$, the gain in escape probability is dominated by the reservoir modes since their contribution to $\Pi_M$ is nearly one order of magnitude larger than the polaritonic.

Cavity detuning effects. In several chemical reactions where strong influence by optical cavities has been reported, the obtained data suggests that the photonic material maximizes its effect on the reactive system when a specific transition of the reactant is on-resonance with the $q = 0$ mode of the optical cavity $[22][21][27]$. This feature motivates our study of $S[\rho_M]$ and $\chi_M$ as a function of cavity detuning. In Fig. 6 we present the results given by our multimode theory. The same figure also includes the predictions of theories including a single cavity mode, but a discussion of these results is left to the next section.

As shown by Fig. 6 under strong coupling with a photonic wire, the local molecular DOS entropy and the exciton escape probability are maximally affected by the optical cavity when the lowest-energy photon mode is redshifted relative to the molecular system. In our disordered multimode model, the photonic material is least effective at modifying low-energy properties of the molecular ensemble when the photons are all blue-shifted relative to the excitons. This trend is robust with respect to changes in the molecular density, and the observed dependence of $\chi_M$ and $S[\rho_M]$ on the density follows the pattern discussed in the previous subsection.

The maximization of the effects of multimode photonic devices on low-energy observable properties (i.e., depending only on the ground and first excited-states of the excitonic subsystem) of the molecular system when $E_C(0) < E_M$ can be understood as follows. First, when the mean molecular excited-state energy is smaller than or equal to all allowed cavity photon energies ($E_C(0) - E_M \geq 0$), a significant fraction of the molecular excitons will be off-resonant with all cavity modes (especially if $\sigma/\Omega_R$ is small) and the spectral overlap of photonic and molecular modes will be weaker (See bottom of Fig. 1b) for a comparison of the case where $E_C(0) = E_M$ and $E_C(0) < E_M$ showing that a large number of molecules will be off-resonant with all cavity modes when $E_C(0) = E_M$). This notion is confirmed in Fig. 2 (bottom left and right), where we show that the number of polaritons $N_P$ becomes largest at negative detuning, whereas the number

FIG. 4: Left: Entropy gained by the molecular LDOS upon strong coupling with a photonic wire as a function of $\sigma/\Omega_R$ for varying intermolecular distances (molecular density) with fixed $\Omega_R$ and vanishing detuning $E_C - E_M = 0$. In all computations, $N_M = N_C$, $\sigma_p/\mu_0 = 0.05$ and $f = 0.1$. Other parameters are given in the text (see Thermodynamic limit convergence). Right: Molecular excited-state escape probabilities for the same systems. Each point corresponds to an average obtained over 20 disorder realizations.

FIG. 5: Polariton and dark-state delocalization dependence on energetic disorder and density for fixed $\Omega_R$. Left: Total contribution of polariton states (with photonic content greater than 15% but less than 85%) to the molecular excited-state survival probability vs. energetic disorder (with zero detuning and $\Omega_R = 0.3$ eV). Right: Total contribution of dark states (with molecular content greater than 85%) to the molecular survival probability. Excited-state localization leads to an increase in the molecular excited-state survival probability and therefore, we can infer both polaritons and reservoir modes become more localized with increasing $\sigma$, although the effect is much stronger on the latter, especially at small values of $\sigma/\Omega_R$.

FIG. 6: Left: Entropy of molecular local density of states as a function of cavity detuning for systems with varying particle densities (but equal number of molecules $N_M = 1001$) and $\sigma/\Omega_R = 0.2$ (other parameters are as in prior figures). The dashed line corresponds to entropy of the bare LDOS. Right: Escape probability ($\chi_M = 1 - \Pi_M$) for molecular excitons as a function of cavity detuning for the same model systems. Note, for the bare molecules, the escape probability vanishes. Each point corresponds an average over 10 disorder realizations (error bars indicate standard deviation).
Comparison to single-mode theories. Before concluding we want to contrast the main results of this article with the behavior predicted by optical cavity models that include only a single mode.

Detuning: In systems with equal $\Omega_R$, $\sigma$ and detuning, Fig. 5 shows that single-mode (0D) cavities act on strongly coupled molecular systems in qualitatively distinct fashion relative to a multimode photonic device. This is unsurprising, since the photonic modes of 0D microwires are isolated. Therefore, the spectral overlap between the cavity and the molecular subsystem is maximized when they are resonant. This leads to a maximal cavity-mediated exciton escape probability at zero detuning (Fig. 5), since if the retained mode were off-resonant with the molecular system, the spectral overlap of the material and the cavity would be weaker. This behavior is exclusive to 0D systems with isolated modes and does not apply to cavities with a continuous spectrum, such as those employed in almost all polariton chemistry experiments. In Fabry-Perot cavities or photonic wires, neg-
tive cavity detuning gives enhanced light-matter spectral overlap, and a larger number of propagating (delocalized) polariton modes relative to a cavity with zero detuning. Hence, low-energy properties of molecular ensembles are expected to be more affected by a photonic material when it is redshifted relative to the molecules. A related conclusion was reached in Ref. [29] upon analysis of the viability of a hypothetical mechanism for cavity effects on charge transfer rates [19].

Density: Additional examples of qualitative disagreements between single- and multimode-cavity theories are displayed in Fig. 8 where we compare the cavity-modified $\rho_M(E)$ (red) and bare $\rho_M^0(E)$ (blue) at zero (left panel) and negative (right panel) detuning with equal $\Omega_R$ and $N_M$. The top panel (Figs. 8a and 8b) contains the results obtained assuming a single electromagnetic mode interacts with the molecular system, whereas the middle (Figs. 8c and 8d) and bottom (Figs. 8e and 8f) panels show the predicted $\rho_M(E)$ for multimode cavities where the intermolecular distances are in average equal to 10 nm and 25 nm, respectively.

Figures 8a and 8b show that the molecular LDOS is essentially unaffected by a single-mode optical cavity, and $\rho_M(E)$ is indistinguishable from $\rho_M^0(E)$. On the other hand, Figs. 8c-f show the effect of a multimode photonic wire on the molecular LDOS is finite and particularly prominent at the tails of $\rho_M(E)$. This feature leads to finite $\Delta S[\rho_M]$ for a multimode cavity (in contrast to a single-mode theory, for which $\Delta S[\rho_M] = 0$). In addition, the single-mode cavity is completely insensitive to the intermolecular distance, whereas our multimode photonic wire captures the stronger effects of the electromagnetic field on molecular ensembles with greater dipole moment per molecule required to preserve the Rabi splitting when the molecular density is smaller (see discussion under Density and energetic disorder dependence).

Energetic disorder: Contrary to the predictions of single-mode theories [46], we find that, except for a narrow interval of values of $\sigma/\Omega_R$ where the escape probability does not change too much (Fig. 4), energetic disorder tends to localize both dark and polaritonic excitations, thus resulting in a reduced escape probability for molecular excited-states.

Conclusions

We investigated spectral and transport properties of disordered molecular excitons under collective strong coupling with a photonic wire. Our results suggest that low-energy effects of polaritons on bulk properties of the molecular ensemble are largest when the single-molecule transition dipole moment is large, inhomogeneous disorder is small, and when the cavity is redshifted (negatively detuned) relative to the molecular system. In negatively detuned devices, there exists enhanced spectral overlap between the cavity and the molecular system. In addition, polariton modes with significant molecular content have mean wave-vector far from zero, and delocalization is protected from the small fluctuations induced by structural and energetic disorder.

The detuning dependence of cavity effects on molecular properties is particularly relevant when viewed in the context of recent research on polariton effects on thermal chemical reactions [22][25]. Several of the reported experiments imply that photonic materials are more effective at changing reaction rates when the molecular system is resonant with the lowest energy mode of a cavity band (zero detuning). Our results suggest otherwise, but do not contradict experiments, since we only assess low-energy properties of the molecular system, whereas the studied slow chemical reactions are complex events often involving higher excited states than those included in our model.

Increasing the number of molecules, cavity photon modes, dimensionality, and introducing dynamical disorder and cavity leakage are unlikely to qualitatively change any of the trends reported in this work. We expect the behavior with cavity detuning, energetic disorder, and density (for a fixed $\Omega_R$), of molecular properties under strong coupling to photonic devices to be generic for low-energy polariton models. For example, while wave function delocalization is significantly more favored in 2D and 3D [70] relative to the case studied in this paper, it remains true that the spectral overlap between excitons and the optical cavity will be weaker at zero or positive detuning when compared to negative. Dynamical disorder (time-dependent fluctuations of the exciton frequency, position and dipole magnitude/orientation) in-

![Fig. 8: Local molecular density of states for 10 realizations of a molecular system in free space (red) and under strong coupling (blue) to a photonic wire. $N_M = 1001$, $\Omega_R = 0.3$ eV, $\sigma/\Omega_R = 0.2$, $\sigma_M = 0.05\sigma_0$, and $f = 0.1$ in all of the studied scenarios. In panels, where only $a$ is specified, $N_C = N_M$. Note that larger single-molecule transition dipole moments are required to preserve $\Omega_R$ when $a$ is increased. This explains the stronger cavity effects on the molecular density of states when $a = 25$ nm.)](image-url)
roduces further exciton localization and ultrafast coherence decay [71] further reducing the efficiency of intermolecular exciton transport reported here, but is unlikely to affect any of the qualitative trends reported.

To conclude, we reiterate that although 0D single-mode cavity theories are insightful and predictive of many features of polaritonic optical response, these models give incorrect qualitative predictions for the cavity effects on molecular ensembles analyzed in this work. Specifically, single-mode models fail to capture the detuning, density, and disorder strength dependence of the exciton escape probability and molecular LDOS entropy gain upon collective strong coupling with a photonic device. These shortcomings must be recognized in future model building aimed at predicting novel ways to control chemistry with optical microcavities.

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[1] T. W. Ebbesen, Hybrid Light–Matter States in a Molecular and Material Science Perspective, Accounts of Chemical Research 49, 2403 (2016)
[2] K. Hirai, J. A. Hutchison, and H. Uji-i, Recent progress in vibropolaritonic chemistry, ChemPlusChem 85, 1981 (2020).
[3] F. J. Garcia-Vidal, C. Ciuti, and T. W. Ebbesen, Manipulating matter by strong coupling to vacuum fields, Science 373 (2021).
[4] E. Orgiu, J. George, J. A. Hutchison, E. Devaux, J. F. Dayen, B. Doudin, F. Stellacci, C. Genet, J. Schachenmayer, C. Genes, G. Pupillo, P. Samori, and T. W. Ebbesen, Conductivity in organic semiconductors hybridized with the vacuum field, Nature Materials 14, 1123 (2015).
[5] N. Krainova, A. J. Grede, D. Tsokkou, N. Banerji, and N. C. Giebink, Polaron Photoconductivity in the Weak and Strong Light–Matter Coupling Regime, Physical Review Letters 124, 177401 (2020).
[6] D. M. Coles, N. Somaschi, P. Michetti, C. Clark, P. G. Lagoudakis, P. G. Suvvidis, and D. G. Lidzey, Polariton-mediated energy transfer between organic dyes in a strongly coupled optical microcavity, Nature Materials 13, 712 (2014).
[7] X. Zhong, T. Chervy, L. Zhang, A. Thomas, J. George, C. Genet, J. A. Hutchison, and T. W. Ebbesen, Energy Transfer between Spatially Separated Entangled Molecules, Angewandte Chemie International Edition 56, 9034 (2017).
[8] B. Xiang, R. F. Ribeiro, M. Du, L. Chen, Z. Yang, J. Wang, J. Yuen-Zhou, and W. Xiong, Intermolecular vibrational energy transfer enabled by microwaveness using vacuum couplings, Science 368, 665 (2020).
[9] D. Sauvatto and S. Kéna-Cohen, The road towards polaritonic devices, Nature Materials 15, 1061 (2016).
[10] A. D. Dunkelberger, R. B. Davidson, W. Ahn, B. S. Simpkins, and J. C. Owrtuky, Ultrafast Transmission Modulation and Recovery via Vibrational Strong Coupling, The Journal of Physical Chemistry A 122, 965 (2018).
[11] B. Xiang, R. F. Ribeiro, Y. Li, A. D. Dunkelberger, B. B. Simpkins, J. Yuen-Zhou, and W. Xiong, Manipulating optical nonlinearity of molecular polaritons by delocalization, Science Advances 5, eaau5196 (2019).
[12] J. Feist, J. Galego, and F. J. Garcia-Vidal, Polaritonic Chemistry with Organic Molecules, ACS Photonics (2017).
[13] R. F. Ribeiro, L. A. Martínez-Martínez, M. Du, J. Campos-Gonzalez-Angulo, and J. Yuen-Zhou, Polariton chemistry: Controlling molecular dynamics with optical cavities, Chemical Science 9, 6325 (2018).
[14] F. Herrera and J. Owrutsky, Molecular polaritons for controlling chemistry with quantum optics, The Journal of Chemical Physics 152, 100902 (2020).
[15] V. M. Agranovich, M. Litinskaya, and D. G. Lidzey, Cavity polaritons in microcavities containing disordered organic semiconductors, Physical Review B 67, 085311 (2003).
[16] R. Houdré, R. P. Stanley, and M. Ilegems, Vacuum-field Rabi splitting in the presence of inhomogeneous broadening: Resolution of a homogeneous linewidth in an inhomogeneously broadened system, Physical Review A 53, 2711 (1996).
[17] J. del Pino, J. Feist, and F. J. Garcia-Vidal, Quantum theory of collective strong coupling of molecular vibrations with a microcavity mode, New Journal of Physics 17, 053040 (2015).
[18] J. Schachenmayer, C. Genes, E. Tignone, and G. Pupillo, Cavity-Enhanced Transport of Excitons, Physical Review Letters 114, 196403 (2015).
[19] J. Feist and F. J. Garcia-Vidal, Extraordinary Exciton Conductance Induced by Strong Coupling, Physical Review Letters 114, 196402 (2015).
[20] C. Gonzalez-Ballestero, J. Feist, E. Gonzalo Badía, E. Moreno, and F. J. Garcia-Vidal, Uncoupled Dark States Can Inherit Polaritonic Properties, Physical Review Letters 117, 156402 (2016).
[21] B. Xiang, R. F. Ribeiro, L. Chen, J. Wang, M. Du, J. Yuen-Zhou, and W. Xiong, State-Selective Polariton to Dark State Relaxation Dynamics, The Journal of Physical Chemistry A 123, 5918 (2019).
[22] A. Thomas, J. George, A. Shalabney, M. Dryzhakov, S. J. Varma, J. Moran, T. Chervy, X. Zhong, E. Devaux, C. Genet, J. A. Hutchison, and T. W. Ebbesen, Ground-State Chemical Reactivity under Vibrational Coupling to the Vacuum Electromagnetic Field, Angewandte Chemie International Edition 55, 11462 (2016).
[23] J. Lather, P. Bhatt, A. Thomas, T. W. Ebbesen, and J. George, Cavity Catalysis by Cooperative Vibrational Strong Coupling of Reactant and Solvent Molecules, Angewandte Chemie International Edition 58, 10635 (2019).
[24] A. Thomas, L. Lethuillier-Karl, K. Nagarajan, R. M. A.
[25] R. M. A. Vergauwe, A. Thomas, K. Nagarajan, A. Shalabney, J. George, T. Chervy, M. Seidel, E. Devaux, V. Torbeev, and T. W. Ebbesen, Modification of Enzyme Activity by Vibrational Strong Coupling of Water, Angewandte Chemie International Edition 0, 10.1002/anie.201908876

[26] H. Hiura, A. Shalabney, and J. George, Vacuum-Field Catalysis: Accelerated Reactions by Vibrational Ultra Strong Coupling 10.26434/chemrxiv.7234721.v4 (2019).

[27] K. Hirai, R. Takeda, J. A. Hutchison, and H. Uji-i, Modulation of Prins Cyclization by Vibrational Strong Coupling, Angewandte Chemie International Edition 59, 5332 (2020).

[28] K. S. Daskalakis, A. S. Maier, and S. Kéna-Cohen, Polariton Condensation in Organic Semiconductors, in Quantum Plasmonics, edited by S. I. Bozhevolnyi, L. Martin-Moreno, and F. García-Vidal (Springer International Publishing, Cham, 2017) pp. 151–163.

[29] I. Vurgaftman, B. S. Simpkins, A. D. Dunkelberger, and J. C. Owtrutsky, Negligible effect of vibrational polaritons on chemical reaction rates via the density of states pathway, The journal of physical chemistry letters 11, 3557 (2020).

[30] J. Galego, C. Climent, F. J. Garcia-Vidal, and J. Feist, Cavity Casimir-Polder Forces and Their Effects in Ground-State Chemical Reactivity, Physical Review X 9, 021057 (2019).

[31] T. E. Li, A. Nitzan, and J. E. Subotnik, On the origin of ground-state vacuum-field catalysis: Equilibrium consideration, The Journal of Chemical Physics 152, 234107 (2020).

[32] J. A. Campos-Gonzalez-Angulo and J. Yuen-Zhou, Polariton normal modes in transition state theory, The Journal of Chemical Physics 152, 161101 (2020).

[33] M. Du, J. A. Campos-Gonzalez-Angulo, and J. Yuen-Zhou, Nonequilibrium effects of cavity leakage and vibrational dissipation in thermally activated polariton chemistry, The Journal of Chemical Physics 154, 084108 (2021).

[34] M. Du and J. Yuen-Zhou, Can Dark States Explain Vihropolaritonic Chemistry?, arXiv:2104.07214 [quant-ph] (2021), arXiv:2104.07214 [quant-ph].

[35] A. Mandal, X. Li, and P. Huo, Theory of vibrational polariton chemistry in the collective coupling regime, arXiv preprint arXiv:2107.04156 (2021).

[36] J. Triana and F. Herrera, Self-dissociation of polar molecules in a confined infrared vacuum, (2020).

[37] C. Schäfer, J. Flick, E. Ronca, P. Narang, and A. Rubio, Shining light on the microscopic resonant mechanism responsible for cavity-mediated chemical reactivity, (2021), arXiv:2104.12429 [quant-ph].

[38] X. Li, A. Mandal, and P. Huo, Theory of mode-selective chemistry through polaritonic vibrational strong coupling, The Journal of Physical Chemistry Letters 12, 6974 (2021).

[39] D. S. Wang, T. Neuman, S. F. Yelin, and J. Flick, Cavity-modified unimolecular dissociation reactions via intramolecular vibrational energy redistribution, arXiv preprint arXiv:2109.06631 (2021).

[40] M. Tavis and F. W. Cummings, Exact Solution for an N-Molecule-Radiation-Field Hamiltonian, Physical Review 170, 379 (1968).

[41] M. Tavis and F. W. Cummings, Approximate Solutions for an N-Molecule-Radiation-Field Hamiltonian, Physical Review 188, 692 (1969).

[42] J. A. Cwik, S. Reja, P. B. Littlewood, and J. Keeling, Polariton condensation with saturable molecules dressed by vibrational modes, EPL (Europhysics Letters) 105, 47009 (2014).

[43] N. Wu, J. Feist, and F. J. Garcia-Vidal, When polarons meet polaritons: Exciton-Vibration interactions in organic molecules strongly coupled to confined light fields, Physical Review B 94, 195409 (2016).

[44] F. Herrera and F. C. Spano, Cavity-Controlled Chemistry in Molecular Ensembles, Physical Review Letters 116, 238301 (2016).

[45] G. D. Scholes, Polaritons and excitons: Hamiltonian design for enhanced coherence, Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences 476, 20200278 (2020).

[46] T. Botzung, D. Hagenmüller, S. Schütz, J. Dubail, G. Pupillo, and J. Schachenmayer, Dark state semilocalization of quantum emitters in a cavity, Physical Review B 102, 144202 (2020).

[47] C. Gonzalez-Ballestero, J. Feist, E. Gonzalo Badía, E. Moreno, and F. J. Garcia-Vidal, Uncoupled Dark States Can Inherit Polaritonic Properties, Physical Review Letters 117, 156402 (2016).

[48] M. Litinskaya and P. Reineker, Loss of coherence of exciton polaritons in inhomogeneous organic microcavities, Physical Review B 74, 165320 (2006).

[49] M. Litinskaya, Propagation and localization of polaritons in disordered organic microcavities, Physics Letters A 372, 3898 (2008).

[50] P. Michetti and G. C. La Rocca, Polariton states in disordered organic microcavities, Physical Review B 71, 115320 (2005).

[51] P. Michetti and G. C. La Rocca, Polariton dynamics in disordered microcavities, Physica E: Low-dimensional Systems and Nanostructures 40, 1926 (2008).

[52] V. M. Agranovich and Y. N. Gartstein, Nature and dynamics of low-energy exciton polaritons in semiconductor microcavities, Physical Review B 75, 075302 (2007).

[53] R. H. Tichauer, J. Feist, and G. Groenewol, Multi-scale dynamics simulations of molecular polaritons: The effect of multiple cavity modes on polariton relaxation, The Journal of Chemical Physics 154, 104112 (2021).

[54] F. Domínguez-Adame and V. A. Malyshev, A simple approach to Anderson localization in one-dimensional disordered lattices, American Journal of Physics 72, 226 (2004).

[55] M. V. Imperatore, J. B. Asbury, and N. C. Giebink, Reproducibility of cavity-enhanced chemical reaction rates in the vibrational strong coupling regime, The Journal of Chemical Physics 154, 191103 (2021).

[56] .

[57] A. Kuther, M. Bayer, T. Gutbroad, A. Forchel, P. A. Knipp, T. L. Reinecke, and R. Werner, Confined optical modes in photonic wires, Physical Review B 58, 15744 (1998).

[58] D. Craig and T. Thirumamachandran, Molecular Quantum Electrodynamics: An Introduction to Radiation-Molecule Interactions, Dover Books on Chemistry Series
A. Frisk Kockum, A. Miranowicz, S. De Liberato, S. Savasta, and F. Nori, Ultrastrong coupling between light and matter, Nature Reviews Physics 1, 19 (2019).

S. De Liberato, Light-Matter Decoupling in the Deep Strong Coupling Regime: The Breakdown of the Purcell Effect, Physical Review Letters 112, 016401 (2014).

A. Stokes and A. Nazir, Implications of gauge-freedom for nonrelativistic quantum electrodynamics, arXiv preprint arXiv:2009.10662 (2020).

A. V. Malyshev and V. A. Malyshev, Statistics of low energy levels of a one-dimensional weakly localized Frenkel exciton: A numerical study, Physical Review B 63, 195111 (2001).

W. Barford and D. Trembath, Exciton localization in polymers with static disorder, Physical Review B 80, 165418 (2009).

P. W. Anderson, Absence of diffusion in certain random lattices, Physical review 109, 1492 (1958).

H. Kleinert, Path Integrals in Quantum Mechanics, Statistics, Polymer Physics, and Financial Markets (World scientific, 2009).

A. Altland and B. D. Simons, Condensed Matter Field Theory (Cambridge University Press, 2010).

V. Chernyak and S. Mukamel, Path integral formulation of retardation effects in nonlinear optics, The Journal of Chemical Physics 100, 2953 (1994).

B. S. Simpkins, K. P. Fears, W. J. Dressick, B. T. Spann, A. D. Dunkelberger, and J. C. Owrutsky, Spanning Strong to Weak Normal Mode Coupling between Vibrational and Fabry–Pérot Cavity Modes through Tuning of Vibrational Absorption Strength, ACS Photonics 2, 1460 (2015).

J. A. Campos-Gonzalez-Angulo, R. F. Ribeiro, and J. Yuen-Zhou, Resonant catalysis of thermally activated chemical reactions with vibrational polaritons, Nature communications 10, 1 (2019).

P. A. Lee and T. V. Ramakrishnan, Disordered electronic systems, Reviews of Modern Physics 57, 287 (1985).

Z. Zhang, K. Wang, Z. Yi, M. S. Zubairy, M. O. Scully, and S. Mukamel, Polariton-Assisted Cooperativity of Molecules in Microcavities Monitored by Two-Dimensional Infrared Spectroscopy, The Journal of Physical Chemistry Letters 10.1021/acs.jpclett.9b00979 (2019).