Unlocking Delocalization: How Much Coupling Strength can Overcome Energy Disorder in Molecular Polaritons?

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Abstract

We investigated the criteria to ensure delocalization exists in molecular polaritons – quasiparticles formed from the collective strong coupling of light and matter that have shown capabilities to modify chemical reactions. Importantly, delocalization, i.e., polaritons possess delocalized wavefunctions, is one of the hallmarks of polaritons which enables energy transport and chemical dynamics. Delocalization in polariton systems has been long assumed to be robust against energy disorder that is ubiquitous in real molecular systems. However, this study reveals that disorder destroys delocalization in polaritons. In order to mitigate the impact of disorder, a collective coupling strength exceeding 3 times the inhomogeneous linewidth is necessary. When the coupling strength is smaller, the delocalization properties of polaritons are significantly compromised both in a static picture and from a dynamic point of view. This observation indicates a more stringent criterion for preserving the unique characteristics of polaritons compared to the conventionally adopted standard (collective coupling strengths larger than photonic and molecular spectral linewidths). This work sheds lights on previous works to explain why the onset of modified dynamics is larger than the strong coupling criteria, and also serves as an important consideration for existing and future polariton studies involving high levels of energy disorder.

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Polaritons,[1-5] hybrid quasiparticles between photons and matters, have recently shown their potential in modifying chemical reactions.[4, 6-14] Polaritons are formed under the so-called collective strong light-matter coupling conditions – when N quantum emitters, such as molecular transitions, and a cavity mode coherently exchange energy at a rate faster than their dissipation rates. Such a hybridization renders polaritons to mix both light and matter properties via delocalized wavefunctions. Delocalization – the polariton wavefunctions are shared among many individual molecular wavefunctions – has been viewed as a key property that leads to considerable enhancements of energy transmission,[9-10, 12, 15-17] and subsequently influences reactions. Recently, the investigation of the critical role of delocalization is further extended to dark states.[18-20]

The delocalized nature of polaritons is concluded from an ideal system where all molecular modes emit at the same frequency (homogeneous limit),[21] however, in most polaritonic systems demonstrated in chemistry, energy disorder (inhomogeneous limit) exists, i.e. molecular transitions occur at slightly different frequencies influenced by local environments. For example, the strong coupling of water stretching modes can be achieved and is reported to modify reactions or ion transportations, despite of their large inhomogeneous linewidths.[22-25]

Although it has been shown that energy disorder could influence polariton properties, including altering excitation lifetimes[26] and accelerating decoherence,[27-28] a premise – delocalization is robust against disorder – has been held. This premise was supported by a seminal paper in 1995,[29] in which Houdré et al. showed that peak separations (Rabi splitting, Ω) and linewidths (e.g. full-width-of-half-maximum, fwhm) of polariton states are generally immune to inhomogeneity, as long as $\Omega >$ fwhm. The disorder only disrupts the symmetry of dark modes, resulting in slightly optically bright dark states.[11] In a lossless cavity with an inhomogeneous distribution of molecular transitions, this criterion can be translated to $g\sqrt{N} > 1.17\sigma$, or $\sigma/(g\sqrt{N}) < 0.85$ [30] where g is the single molecule coupling strength, N is the number of molecules, and the inhomogeneity is described by a normal distribution as $P(\omega) = 1/(\sigma\sqrt{2\pi})\exp(-(\omega-\omega_0)^2/(2\sigma^2))$. This criterion will be referenced constantly hereafter.

However, recent spectroscopic studies involving high disorder reported that the transient signals of polaritons highly resemble those originating from the corresponding filtered molecular absorption spectra by polariton transmission.[31-35] These results hinted that under high disorder, polaritons may behave similar to localized molecules. Currently, a critical question – at the inhomogeneous limit, how delocalized are polaritons – remains little explored. In this work, we investigated this question by solving the disordered Tavis-Cummings model,[36] and found a critical threshold ratio between the inhomogeneous standard deviation and the collective coupling strength, $\sigma/(g\sqrt{N}) \approx 0.25$, above which delocalized polaritons become localized molecular states. Notably, this ratio means that a ca. 3-folder larger Rabi splitting than

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the widely adopted strong coupling criterion is required to preserve delocalization in polaritonic systems with energy inhomogeneity.

We conducted our analyses by examining the Hopfield coefficients (Section S1 of the Supporting Information), and resorted to the normalized inverse participation ratio (nIPR)[32, 37] to characterize delocalization, as defined in Equation 1:

$$\text{nIPR(m)} = \frac{1}{N} \frac{1}{\sum_i^N \left| c_i^{'(m)} \right|^4} \qquad \text{Equation 1}$$

The $c_i^{'(m)}$ is a modified linear combination coefficient representing the contribution from the i-th molecular transition to the m-th hybridized state, where the eigenvector is renormalized to 1 after excluding its photonic entry. Furthermore, the nIPR is normalized by the number of molecules, such that its value ranges between $1/N$ and 1, denoting completely localized and delocalized wavefunctions, respectively.
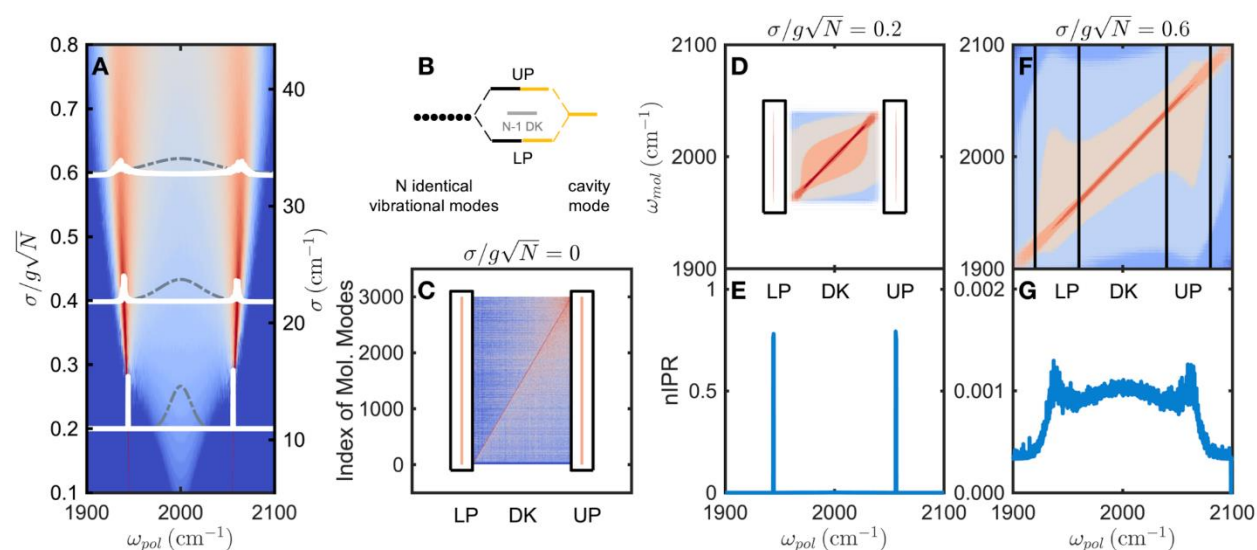

Figure 1. Evolution of polaritons as a function of energy disorder. (A) Spectra for light-matter coupled systems involving different disorders (σ). The gray dashed lines represent selected energy distributions, and the white solid lines show the corresponding polariton spectra. (B) and (C) demonstrate an ideal case with no inhomogeneity, where (B) is a schematic picture, and (C) shows the contribution from each molecular mode (y-axis, indexed 1 to 3000) to hybridized states. Note, because each molecule is identical in frequency, they are artificially differentiated by indices. (D) and (F) demonstrate the contribution from each molecular transition (y-axis, binned by energy) to hybridized states, at $\sigma/(g\sqrt{N}) = 0.2$ and 0.6, respectively, and (E) and (G) show the corresponding nIPRs. The polariton regions are circled by boxes. Note in (D) and (F), molecules can be differentiated by energies because of the inhomogeneous distribution, thus there is no need to use indices as (B). Intensities in the 2D plots are on logarithmic-scale, and red indicates a higher intensity than blue. Parameters: $\omega_{mol,0} = \omega_{cav} = 2000$ cm^{-1}, g = 1 cm^{-1} and N = 3000.

We first reconfirmed the conclusion of Houdré's work: In the strong coupling regime, polariton spectra remain qualitatively similar (Figure 1A). A higher disorder (σ) leads to a slightly increased splitting, decreased optical brightness, and linewidth broadening of polaritonic states, as a result of coupling between

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the cavity mode and detuned molecules, aligning well with previous theory and experiments.[28, 38-41] However, it is worth noting that in a recent work by Zeb, he pointed out that at $\sigma/(g\sqrt{N}) \geqslant 0.5$, the polariton spectra transition to Fano resonances, and simply correspond to strongly absorbing emitter states.[41]

Despite the modest spectral evolution, the underlying composition of polaritons change drastically with increasing disorder. To provide a comparison, we first show an ideal strong coupling case without disorder (Figure 1B-C). Two bright polaritonic states emerge, evenly shifted from the resonance energy by $g\sqrt{N}$, whereas the energy levels of the remaining N-1 dark modes remain unaltered. Figure 1C illustrates the composition of the polaritonic wavefunctions (ω_{pol}) from individual molecular wavefunctions. The matter component of polaritons involves all coupled molecular transitions uniformly (delocalized), as evident by the vertical red lines at the polariton regions of $\omega_{pol} = 1944$ and 2056 cm^{-1}, respectively. In contrast, dark modes at 2000 cm^{-1} are degenerate, and the red line lying along the diagonal area indicates complete localization, with one-to-one correspondence with bare molecular transitions.

With a small disorder of $\sigma/(g\sqrt{N}) = 0.2$ (Figure 1D), the distribution of polariton wavefunctions is still delocalized as manifested by vertical red shadings (highlighted by rectangular boxes); similarly, the dark modes are localized to limited molecules, indicated by the diagonal distribution. The nIPRs of polaritons are calculated to be ca. 0.8 (Figure 1E), agreeing with their delocalized nature depicted in Figure 1D, while the nIPRs of dark modes are negligible, characteristic of localized states. However, with a large disorder of $\sigma/(g\sqrt{N}) = 0.6$ (Figure 1F), localized polaritons are revealed by their diagonal matter distribution. Moreover, Figure 1G shows nIPRs of ca. 0.001 through the spectrum. Both signify that polaritons become analogous to dark modes, which are composed of molecular modes of close-by energies. Noticeably, both scenarios (Figure 1D-F) fall into the strong coupling regime according to the conventional standard ($\sigma/g\sqrt{N} < 0.85$). Therefore, it is noteworthy that, even under strong coupling conditions, polaritons may lose delocalization due to high disorder.

By exploring how nIPRs change with disorders at various coupling strengths, we found a threshold when polaritons transition from delocalized to localized. For example, Figure 2A shows a representative nIPR curve as a function of σ with a collective coupling strength ($g\sqrt{N}$) of ~55 cm^{-1}. For σ below 10 cm^{-1}, the nIPRs of polaritons gradually decrease from 1 to ca. 0.8 when σ increases due to hampered delocalization. A subsequent rapid decline occurs when σ reaches ca. 13 cm^{-1}, marking a sharp transition to localization. With σ greater than 18 cm^{-1}, the nIPRs are constantly around 0, thus polaritons are fully localized states. Therefore, a transition value of $\sigma_{tran} = 13$ cm^{-1} is identified, where the decline of the nIPR is the fastest (Figure 2B).

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In fact, we identified a linear relationship between σ_{tran} and $g\sqrt{N}$. Alternatively speaking, the transition threshold is constant in terms of $\sigma/(g\sqrt{N})$. Shown in Figure 2C, the delocalization boundary is approximately $\sigma = 0.25(g\sqrt{N})$; below it, the nIPRs of polaritons remain close to 1 and delocalized; above it, the localization occurs. The threshold ratio $\sigma/(g\sqrt{N}) = 0.25$ suggests that the collective coupling strength needs to be 4 times of the standard deviation to reach delocalization for inhomogeneous molecular systems – more strenuous than the criteria of strong coupling. Three regions are concluded: (I) satisfies strong coupling and delocalization, (II) is within the strong coupling regime but polaritons become localized, and (III) is the weak coupling regime. These results are tested against the simulation size and various detuning conditions (Section S2).
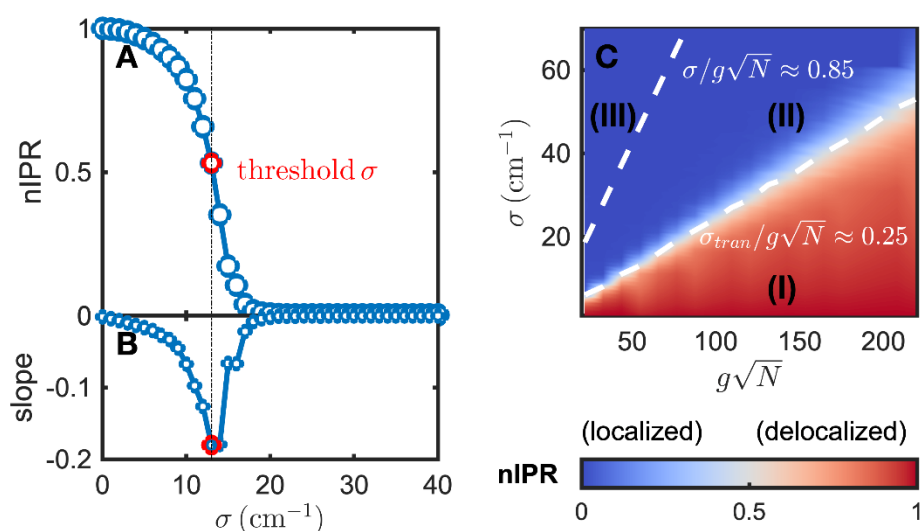

Figure 2. Delocalization threshold. (A) The nIPR of polaritons for coupled systems (g = 1 cm^{-1}) with different disorders (σ). The transition threshold in red corresponds to the point in (B), $\sigma_{tran} = 13$ cm^{-1}. (C) shows the nIPR of polaritons as a function of both σ and $g\sqrt{N}$. The blue and red shadings correspond to localized and delocalized polariton wavefunctions, respectively. The dashed line between (I) and (II) indicates the delocalization threshold (σ_{tran}), and the one between (II) and (III) indicates the conventional strong coupling threshold. Parameters: N = 3000, and $\omega_{mol,0} = \omega_{cav} = 2000$ cm^{-1}.

Interestingly, we found such a threshold ratio also applies when considering the dynamical impact of energy disorder on the delocalization of the system. Here, we initialized a wavefunction in the photonic mode to mimic broadband coherent excitation of polaritons – a common scenario of ultrafast measurements.[1, 10-13, 33-34] Then, we calculated the photonic population and the delocalization of the entire system as a function of time. The photonic population show a smooth decrease in its lifetime as the disorder increase from $\sigma/(g\sqrt{N}) = 0.1$ to 0.5 (Figure 3A-C). The limited polariton lifetime is a consequence of the loss of coherent return of energy from excited molecules to the photonic mode, when different oscillation frequencies destructively interfere.

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However, the delocalization exhibits less robustness towards energy disorder than its photonic counterparts. As shown in Figure 3D, at $\sigma/(g\sqrt{N}) = 0.1$, when the energy periodically transfers back from the photonic mode to molecular modes, nearly all molecules are excited, and their distribution resembles the initial distribution of energy (white solid line). This scenario represents the strong-coupling phenomenon – the entire molecular ensemble is collectively and coherently populated when the system is excited. However, at $\sigma/(g\sqrt{N}) = 0.3$ and 0.5, such delocalization is lost (Figure 3E-F). In both cases, the initial broadband excitation quickly funnels the energy to molecular modes whose frequencies match those of polaritons. These excited molecules only account for a small fraction of molecules, whose absorption frequencies coincide with the polariton transmission window (black solid line), implying a filter effect by the polariton spectrum. This is dramatically different from the delocalized case at $\sigma/(g\sqrt{N}) = 0.1$. We surveyed other $\sigma/(g\sqrt{N})$ values and confirmed the validity of this observation (Figure 3G). Interestingly, $\sigma/(g\sqrt{N}) \sim 0.25$ (white dashed line) can still serve as an empirical boundary for maintaining delocalization in the time domain.
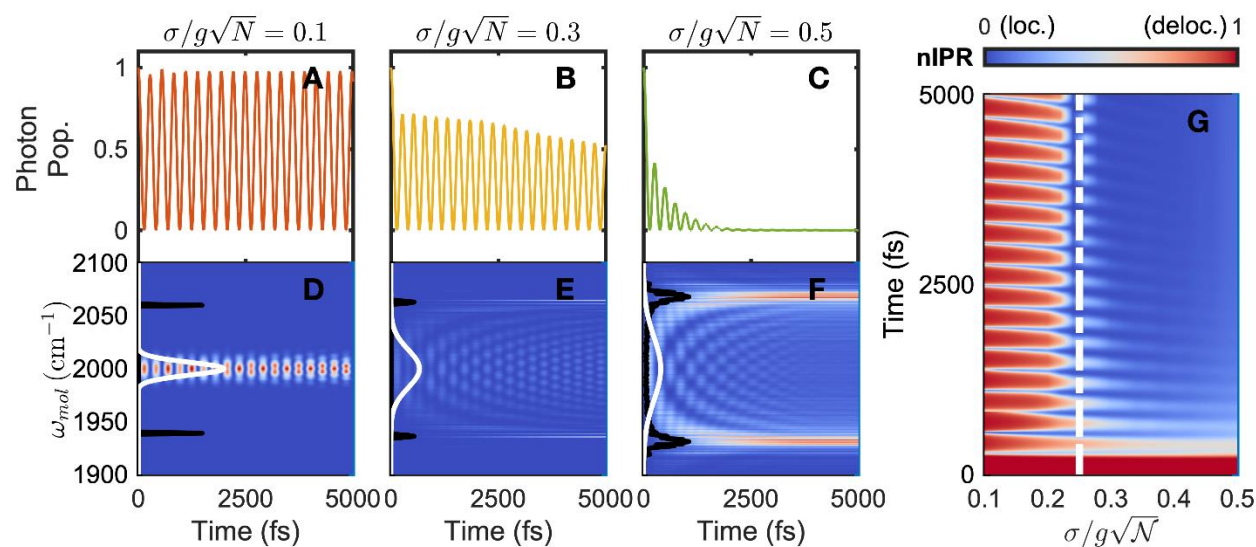

Figure 3. Effects of the energy disorder on the temporal evolution of optical and molecular properties of polaritons. (A-C) Time-dependent population of the photonic state with $\sigma/(g\sqrt{N}) = 0.1, 0.3, 0.5$, respectively (D-F) time-dependent population of molecular vibrational excited states with $\sigma/(g\sqrt{N}) = 0.1, 0.3, 0.5$, respectively. (G) The time evolution of the nIPR of the system calculated for different disorders, where the dot-dashed line indicates $\sigma/(g\sqrt{N}) = 0.25$. Parameters: g = 0.6 cm⁻¹ and N = 10000.

In summary, even if under strong coupling conditions, polaritons may not possess delocalized wavefunctions if the energy disorder exceeds a threshold of $\sigma/(g\sqrt{N}) \sim 0.25$. This threshold remains valid for both static polariton wavefunctions, and the dynamic behavior of the entire systems. In fact, the delocalization of polaritons is more vulnerable to disorder compared to spectral features and the photonic lifetime. Importantly, in many reported vibrational strong-coupled systems involving inhomogeneously

broadened vibrational modes, e.g. water stretching modes,[22-25] it is questionable whether delocalization is preserved. Relatedly, our group previously reported strong-coupling modified ultrafast molecular dynamics, e.g., energy transfer, and we found that the coupling strength needs to be larger than the onset of strong coupling.[10, 42] This observation may be corroborated by that delocalization is required to modify molecular dynamics, yet achieving strong coupling alone may not ensure delocalization. The conclusion here may shed insight to recent null effects, too.[43-46] Thus, for systems with inhomogeneous broadening, larger Rabi splittings are essential to secure delocalization, especially when investigating the relationship between coupling strength and changes in chemical reactivity.
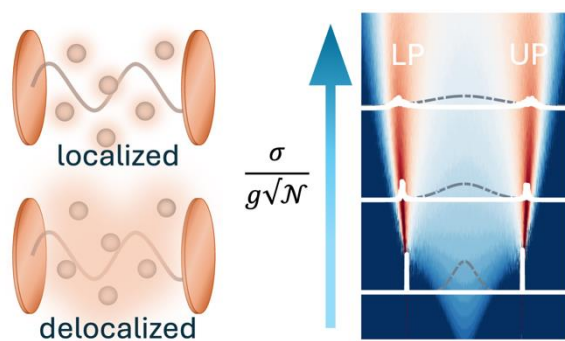
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Supporting Information

The simulation details, calculation results of the threshold ratio identified under different simulation size and detuning conditions, and impact on population relaxation and decoherence can be found in the Supporting Information.

Acknowledgements

TOC figure

$$\frac{\sigma}{g\sqrt{\mathcal{N}}}$$

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