nature portfolio

Peer Review File

Disorder enhanced vibrational entanglement and dynamics in polaritonic chemistry

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

This is a wonderful work that explored the role of disorder in polariton chemistry via the Holstein-Tavis-Cummings model. By employing a time-dependent matrix product state approach, the exact dynamics of 100 molecules are simulated. Nost importantly this paper report that the quantum entanglement between nuclear and hybrid electro-photonic parts could have a direct impact on the reaction coordinates. Such findings are very interesting and stimulate more investigations along this direction. But there is a critical issue that should be addressed before publication:

1) this paper only considers the on-site disorder. However, the disorders affect the photon-electron interaction as well via the (transition) dipole. A justification for neglecting disorder in the light-matter coupling is desired.

Reviewer #2 (Remarks to the Author):

The article "Disorder enhanced vibrational entanglement and dynamics in polaritonic chemistry" discusses the dynamics of a collection of model molecules coupled to a cavity mode in the presence of disorder. The authors use a state-of-the-art method based on matrix product states to solve the full quantum dynamics of the system (within the approximations performed in deriving the model). They find significant vibrational entanglement due to energetic disorder and present several models to analyze their results in detail. The full quantum calculations allow insight into aspects of the dynamics that are not well-represented by the methods that have been used in the field up to now (in particular, semiclassical schemes where nuclear motion is treated classically), while at the same time finding broad overall agreement with well-known properties of such systems. In my opinion, the results will be interesting to researchers in the area and could motivate new research directions. While the results are necessarily obtained using quite severe approximations (single vibrational mode per molecule, harmonic potentials, single lossless cavity mode), the authors discuss most of the approximations and their expected influence in some detail. I recommend publication in Communications Physics.

Reviewer #3 (Remarks to the Author):

See attached.

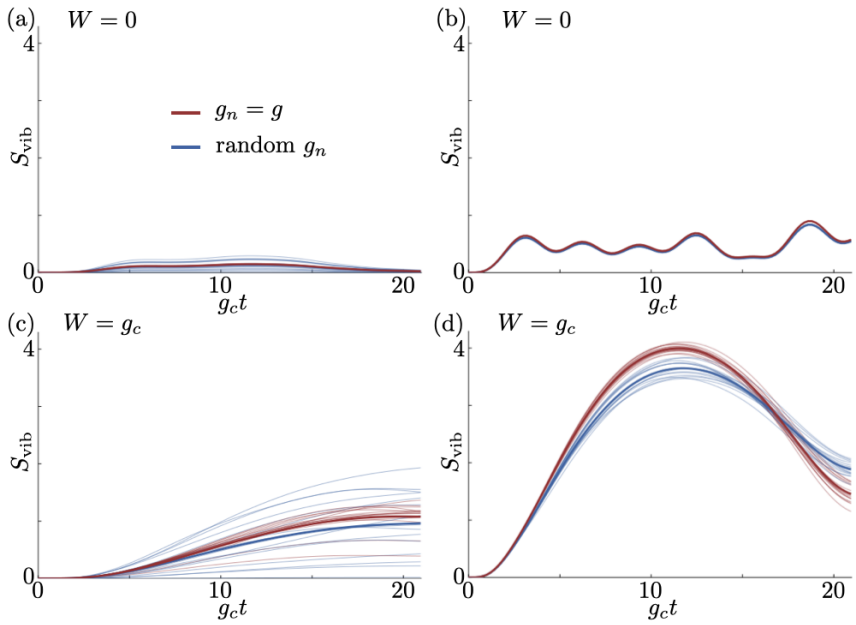
1. Detailed response to Reviewer #1

- This is a wonderful work that explored the role of disorder in polariton chemistry via the Holstein-Tavis-Cummings model. By employing a time-dependent matrix product state approach, the exact dynamics of 100 molecules are simulated. Nost importantly this paper report that the quantum entanglement between nuclear and hybrid electro-photonic parts could have a direct impact on the reaction coordinates. Such findings are very interesting and stimulate more investigations along this direction. But there is a critical issue that should be addressed before publication:

  1) this paper only considers the on-site disorder. However, the disorders affect the photon-electron interaction as well via the (transition) dipole. A justification for neglecting disorder in the light-matter coupling is desired.

We thank the Reviewer for his/her very positive remarks on our work and the general suggestion for publication after addressing point 1).

We do agree with the Reviewer that disorder in the cavity-coupling constants is another important imperfection in realistic experimental setups, either due to the cavity mode profile or due to disorder in the dipole orientations. Therefore, considering also such disorder has been an important part of our research agenda, and we have already performed some simulations. The following figure shows the influence of local random coupling constants g_n on the entanglement growth behavior



Here, as an example, the two scenarios with constant $g_n = g$ (red) and with uniformly randomly distributed $-g' \leq g_n \leq g'$ (blue) are compared, while $g_c = \sqrt{\sum_n g_n^2}$ is kept constant. The further parameters are $N = 100$, $\lambda = 0.4$, $\nu = 0.3 g_c$, $W = 0$ (a,b) or $W = g_c$ (c,d), and the initial states are $|\psi_0^m\rangle$ (a,c) and $|\psi_0^c\rangle$ (b,d). The thin, transparent lines in each panel are individual disorder realizations (16 per panel per color), while the thick lines represent the disorder-average. Although the disorder model is simplified, we see that

disorder in the cavity coupling g_n only leads to minor modifications, and does not affect the general conclusion of entanglement enhanced by energetic disorder.

While these modifications are interesting, we believe that a detailed discussion of this additional disorder would go beyond the current scope of the paper, which is focused on the fundamental modification of vibrational dynamics and entanglement due to energetic disorder in the HTC model. We leave discussion of disorder in the cavity-couplings to future works.

To improve the presentation in our work, we now more clearly justify our choice of a single type of disorder in the main text (page 3 lines 231-239). In addition, we added the topic of disorder in the cavity-coupling as interesting aspect to the outlook. We also added a section including the figure in the Supplemental Material.

2. Detailed response to Reviewer #2

- The article "Disorder enhanced vibrational entanglement and dynamics in polaritonic chemistry" discusses the dynamics of a collection of model molecules coupled to a cavity mode in the presence of disorder. The authors use a state-of-the-art method based on matrix product states to solve the full quantum dynamics of the system (within the approximations performed in deriving the model). They find significant vibrational entanglement due to energetic disorder and present several models to analyze their results in detail. The full quantum calculations allow insight into aspects of the dynamics that are not well-represented by the methods that have been used in the field up to now (in particular, semiclassical schemes where nuclear motion is treated classically), while at the same time finding broad overall agreement with well-known properties of such systems. In my opinion, the results will be interesting to researchers in the area and could motivate new research directions. While the results are necessarily obtained using quite severe approximations (single vibrational mode per molecule, harmonic potentials, single lossless cavity mode), the authors discuss most of the approximations and their expected influence in some detail. I recommend publication in Communications Physics.

We thank the Reviewer for the very positive evaluation of our work and appreciate the suggestion for publication.

3. Detailed response to Reviewer #3

- In this work, Wellnitz et al. theoretically study the excited-state vibrational dynamics of a inhomogeneously disordered molecular ensemble coupled to an optical cavity mode. Unlike previous works, the authors focus on a regime that they call "intermediate light-matter coupling", where the light-matter coupling is large (relative to the molecular transition energy) and the disorder is similarly large. The cavity-molecule system is modeled using the Holstein-Tavis-Cummings (HTC) Hamiltonian. The dynamics are simulated using a tensor network method, which enables numerically exact results for a system with as many as 100 molecules. When the cavity is initially excited, the excitation is converted to molecular vibrational excitations with much higher efficiency than compared to the case of no inhomogeneous disorder. In particular, vibrations of different molecules become significantly entangled, another effect absent in the disorder-free case. The authors show that neglecting this entanglement can lead to incorrect dynamics of the tails of the nuclear probability distribution, where the tails can play a notable

role in chemical reaction dynamics. As a result, the authors conclude that accounting for the entanglement is potentially important for understanding chemical reactions in the intermediate coupling regime. The reported phenomena are quite intriguing and should inspire researchers to better understand how polariton chemistry is affected by disorder, a feature that is ubiquitous in molecular systems but often neglected in models. However, there are several details of the paper that are possibly incorrect, misleading, or confusing. Thus, I recommend publication if these concerns (see below) are addressed.

We thank the Reviewer for his/her very positive assessment of our work and the general recommendation for publication. We thank the Reviewer for the constructive criticism and address all comments on misleading details in the following:

- Throughout the work, "reaction coordinate" is used to refer to the vibrational coordinate of each molecule. However, the nomenclature is misleading, since no chemical reaction is studied here. I suggest changing "reaction coordinate" to "vibrational coordinate" or "nuclear coordinate".

  We followed the suggestion of the Reviewer and replaced all occurrences of "reaction coordinate" at misleading places throughout the text.

- (p. 2, lines 115-117) The authors write that the HTC model "includes the main ingredients for microscopically understanding physical mechanisms in polariton chemistry". When reading this, some may incorrectly assume that the HTC model explains key features of chemical reactions under strong light-matter coupling. In reality, however, important experiments in polariton chemistry cannot be explained by simple models such as HTC (for example, see a recent review by Sidler et al.: https://arxiv.org/abs/2108.12244). Nevertheless, the HTC model has been able to qualitatively explain relaxation dynamics of organic exciton-polaritons. I therefore suggest changing "polariton chemistry" to something like "organic exciton-polaritons".

  We agree with the Reviewer that the HTC model can only describe cavity-modified vibrational dynamics and not key features of chemical reactions. We now changed the terminology to "..., which despite its simplicity includes the main ingredients for microscopically understanding modifications of vibrational dynamics in cavity-coupled molecular ensembles, in particular in organic systems". We also added the new review article that the Reviewer suggested as citation.

- It would be insightful if the authors could comment on how their approach to dynamics goes beyond what other methods do, say, a variational polaron transformation approach, which has been applied to the problem of polariton chemistry (see Martínez-Martínez, et al, J. Chem. Phys. 151(5), 054106 (2019)).

  We thank the Reviewer for bringing up the variational polaron transformation approach as additional alternative technique. We now comment on this and related ideas in the introduction, citing J. Chem. Phys. 151(5), 054106 (2019), Phys. Rev. Lett. 122, 203602 (2019), Phys. Rev. Lett. 116, 238301 (2016), Phys. Rev. B 103, 165412 (2021), and ACS Photonics 5, 249 (2018).

- (p. 4, lines 272-277) May the authors comment on why they choose a light-matter coupling strength in the ultrastrong coupling regime? This choice seems in contradiction to the fact that the authors want their work to be (as written on lines 276-277) "relevant for strong coupling experiments".

  All our parameters, except the cavity-dependent Rabi splitting, were inspired by typical values in the literature for Rhodamine 800 (Christensson *et al.*, Vibrational Spectroscopy

53, 2 (2010), Ref. [62] of the manuscript). However, our calculations were not meant to be exclusively for this molecule. Very large Rabi splittings of 700meV had been reported in some of the very first polaritonic chemistry experiments (Hutchison *et al.*, Angew. Chem. Int. Ed. 51, 1592 (2012), Ref. [10] of the manuscript). We chose this value for historic reasons. Only for Rhodamine 800 it corresponds to a cavity coupling of $\sim 18\%$ of the level spacing, just beyond the on-set of ultra-strong coupling (more than 10%). However, we did not want to complicate the effects with counter-rotating terms. We note that simply increasing the level spacing, e.g. beyond 2eV does not change any of the dynamics of our system, and the results can therefore be in a strong-coupling regime for other molecular ensembles than Rhodamine 800. Our simulations should be considered as a good cavity scenario (just at the edge of ultra-strong coupling for the case of Rhodamine 800). In the case of relatively smaller cavity-coupling strengths, i.e. for increased $\lambda\nu/g_c$, relatively more entanglement with vibrations would also be induced directly due to the Holstein coupling. Our choice therefore has the advantage of clearly demonstrating the disorder-induced part of entanglement with the vibrational Hilbert space. To not confuse the reader, we justify our choice now more clearly in the respective paragraph on page 4.

- (p. 5-6, the paragraph titled "Excitation transfer dynamics") The authors describe the calculations of Fig. 3. However, it is not clear, from this paragraph or Fig. 3 caption, what simulation time is used for Fig. 3a/c. Also, on line 464, should "$t = 2\pi/\nu$" actually read "$t > 2\pi/\nu$"?

  We thank the Reviewer for pointing out this mistake, we now added time-range, which is always, $0 \leq t \leq 2\pi/\nu$, to the caption of Fig. 3. In the main text it should really read "until $t = 2\pi/\nu$" which is always the maximum time we consider.

- (p. 5, line 394) It is written that, under inhomogeneous disorder, excitations are transferred from the cavity to molecules on timescale $\sim 1/g_c$ where g_c is the collective light-matter coupling. Since this is also the timescale of Rabi oscillations, are the authors referring to transfer of excitations from polaritons to dark states? If so, I believe the transfer should happen on W is the disorder width, since the transfer from polaritons to dark states should have rate $= 0$ if $W = 0$.

  Thanks to the Reviewer's comment, we now understand that in the previous manuscript it was unclear whether we referred to transfer from polaritons to dark states or to transfer from photons to molecular excitations. We are in fact considering transfer from photons to molecular excitations, which is (for strong coupling) governed by Rabi oscillations and thus occurs at a time scale $1/g_c$. We now point this out more clearly in the text.

- (p. 5, line 455) I suggest changing "homogeneous disorder-less case with $W = 0$" to just "disorder-less case", since the phrase is alluding to inhomogeneous disorder, not homogeneous broadening.

  We thank the Reviewer for pointing out this ambiguity. We now removed "homogeneous".

- (p. 7, lines 594-597) The authors say that the time-integrated left tail weight, η^l_{avg}, "increases significantly compared to the no-cavity case". However, this statement is inconsistent with Figs. 4a/b, which shows that the mentioned increase corresponds to $< 1\%$ relative change (i.e., $\approx 1.005 \times 20$ vs $\approx 1 \times 20$)

  We agree with the Reviewer that in particular for the integrated left tail weight, "significant change" may be an exaggeration. We therefore removed it.

4. List of Changes

- We now justify in more detail our choice of diagonal energetic disorder (page 3 lines 231-239), and added a discussion of disorder in the light-matter coupling to the Outlook section (page 8 lines 744-747).
- We added a section "Disordered light-matter coupling strengths" to the Supplemental Material.
- We now avoid the terminology of "reaction coordinate" and replaced it with "nuclear coordinate" at misleading places throughout the text.
- We more precisely clarify the scope of the HTC model for describing "cavity-modified vibrational dynamics (instead of "chemistry"), and specifically refer to organic exciton-polaritons (page 2 lines 123-125).
- We also added polaron transformation approaches to our comparison with other methods (page 1 lines 72-78) .
- We clarified a previously confusing discussion on ultra-strong vs. strong coupling regime (page 4 lines 288-298).
- We clarified the excitation transfer time scale (page 5 lines 415-424).
- We now specify the simulation time in the caption of Fig. 3.
- We removed the word "homogeneous" on page 5 line 482.
- We removed the notion of a "significant change" for the integrated left tail weight (page 7 line 622).
- We added the following citations:
  Martìnez-Martìnez, *et al.*, J. Chem. Phys. 151(5), 054106 (2019)
  S. Sidler *et al.*, arXiv:2108.12244
  Reitz *et al.*, Phys. Rev. Lett. 122, 203602 (2019)
  Mauro *et al.*, Phys. Rev. B 103, 165412 (2021)
  Garcia-Vidal *et al.*, Science 373, eabd0336 (2021)
- We updated the citation:
  Sommer *et al.*, Phys. Rev. Res. 3, 033141 (2021)
- We added some funding sources to the acknowledgements.
- We added a Data Availability statement.

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

The authors addressed all the concerns carefully and properly. Now the manuscript is publishable as is.

Reviewer #3 (Remarks to the Author):

The authors have addressed my comments quite precisely and I endorse the publication of their work in Comm Phys.