Reply to “Comment on: ‘Isolating Vibrational Polariton 2D-IR Transmission Spectra’”

Rong Duan(1,§), Joseph N. Mastron(1,2,¶), Yin Song(2,#), Kevin J. Kubarych(1)*

[1] Department of Chemistry, University of Michigan, 930 N. University Ave, Ann Arbor, MI 48109
[2] Department of Physics, University of Michigan, 430 Church Ave, Ann Arbor, MI 48109
[#] Present address: Beijing Institute of Technology, 5 South Zhong Guan Cun St., Beijing, China
[§] Present address: Cutera, Inc., 3240 Bayshore Blvd. Brisbane, CA 94005
[¶] Present address: TOPTICA Photonics, Inc., 1120 Pittsford, NY 14534

Abstract

In a comment on our recent Letter, the authors take issue with our method of refining 2D-IR transmission spectra to remove a background contribution that arises from non-polaritonic molecules that are uncoupled to the cavity. In our response to their comment, we describe how our approach was motivated by the previous work of the authors, and we present a spatially dependent molecule-cavity Tavis-Cummings model that explains why there are significant numbers of uncoupled molecules with non-zero oscillator strengths. The telltale signature of the uncoupled response is the spectral diffusion dynamics of the bare $W(CO)_6$ molecules in the polar butyl acetate solvent. Inhomogeneous broadening is absent from polaritonic states due to the extreme degree of exchange narrowing in coupling very large numbers of molecules to a cavity mode.

In their Comment on our recent Letter,[1] the authors have taken issue with some of the conclusions and potentially some of the assignments we have made using two-dimensional infrared (2D-IR) spectroscopy to study vibrational polaritons formed by coupling $W(CO)_6$ to a resonant cavity in butyl acetate solution. As we discuss in detail below, we feel that we agree on much more than the comment suggests, and we welcome the opportunity to attempt to clarify some issues in the application of nonlinear spectroscopy to vibrational strong coupling.

The principal objection is that we attempt to remove a background 2D-IR response by computing and subtracting the background obtained from 2D-IR spectra of the bare molecules filtered by the polariton transmission. We were motivated to take this approach by previous work of some of the Comment’s authors,[2] though we use a slightly different strategy that takes into account the spectral shaping that arises from spectral diffusion of the background molecules. The inspiration to pursue the background subtraction arose out of our observations of spectral diffusion in the cavity response, made possible by our separation of the rephasing and non-rephasing 2D-IR spectra using phase cycling.[3] It is well-known and discussed below that even when there is energetic disorder in the molecular transitions, the polaritons do not inherit any of that disorder in the form of spectral inhomogeneity,[4] and the disorder is transferred to the dark states. Therefore, the observation of a large spectral diffusion contribution is a signature of the presence of either the dark or uncoupled response, or both, adding to the polaritonic spectrum. In this response, we describe in detail a model of the uncoupled molecules by explicitly including the spatially non-uniform field amplitude within the cavity in a Tavis-Cummings Hamiltonian. The model illustrates how the uncoupled molecules can contribute to the measured cavity response.

One issue that the Comment authors discuss is the so-called Rabi contraction, which has been argued to be the main source of nonlinearity in vibrational polaritonic systems.[5] Rabi contraction presumes that the molecule-cavity coupling is altered by exciting molecules out of the ground state, reducing the effective number of oscillators coupled to the cavity. Because the coupling scales as the square-root of N,[6] the Rabi splitting should be smaller after excitation.

Rabi contraction would lead to a red shift of the upper polariton and a blue shift of the lower polariton states. Most 2D-IR spectra of vibrational polaritons indeed show the red-shifted UP, but due to spectral overlap between the dark reservoir 1-2 absorption and the LP detection, the blue shifted LP signal is obscured.[2, 5, 7] For this reason, we find it difficult to confirm the Rabi contraction unambiguously from the 2D-IR spectra, and after performing the background subtraction approach, we see some evidence for a red-shifted LP response, which would be consistent with an anharmonic polariton ladder.[8] In our Letter, we estimated the excited state energies using this polariton ladder perspective.

The authors present their own analysis of 2D-IR spectra of a cavity containing $W(CO)_6$ in hexane, making the case that the background contribution is small. Due to the relatively small broadening caused by the nonpolar solvent, we are not surprised that the background contribution is small because it has less spectral overlap with the polariton transitions. We do note, however, the shoulder on the high-frequency side of the LP (Fig. 3B from the Comment), which we would attribute to the 1-2 transition leaking through the polariton filter. The spectral overlap of the bare molecule and the cavity response is shown explicitly in our Letter in Fig. 2B, and we advocate that in cases where a background response cannot be removed, its presence should be acknowledged.

Background Subtraction. Our background subtraction method was inspired by recent work by some of the Comment's authors studying sodium nitroprusside coupled to a cavity.[2] We modified their procedure by subtracting the experimentally measured bare-molecule response (spectrally filtered by the polaritonic transmission) rather than the constructed response obtained by multiplying two slices of the long waiting time delay 2D spectrum. It is clear in 2D-IR spectra of cavities where the molecules are dissolved in polar solvents that the spectral features detected near the LP transition are tilted at early waiting times and become parallel to the excitation axis at later times. We recognized this tilt to arise from the usual frequency correlation observed in inhomogeneously broadened 2D spectra. Based on how well our simple model of a pure polaritonic ladder response added to a filtered bare molecule background reproduced the features of our spectra as well as those of the sodium nitroprusside results (**Fig. 1**), we decided to attempt to remove the background as described in our Letter. We do not see any problem in subtracting different contributions when using spectroscopy that records the signal field (rather than its intensity). The net response is a linear sum of all the contributions and our heterodyne detected measurement makes that possible (pump-probe is a form of heterodyne detection using the probe as a local oscillator).

Polaritonic Ladder. Interpreting the spectral features using a polaritonic ladder was not an original idea of ours; we followed the same approach as Ref. 2, which was developed by Herrera et al.[8] Our simulated spectrum uses standard 2D-IR response functions[9] for the polariton states as well as the inhomogeneously broadened SNP response.[10] The simulation agrees very well with the cavity 2D-IR data. We did not attempt to fit the data, but merely to show an early time spectrum before spectral diffusion has occurred appreciably. At late times, the simulated spectra also agree with the experimental data (Fig. 1).

Polariton Lifetime. Regarding the lifetime of the polaritons. We obtained a ~3 ps lifetime that is consistent with other published reports, and is to be expected because we used mirrors made by the same vendor (Universal Thin Film Lab Corp.).[11] The main difference is that our solvent is butyl acetate rather than water, and hence the reflectivity may differ due to the difference in the index of refraction at the interface and any solvent permeating into the mirror itself. We adopted

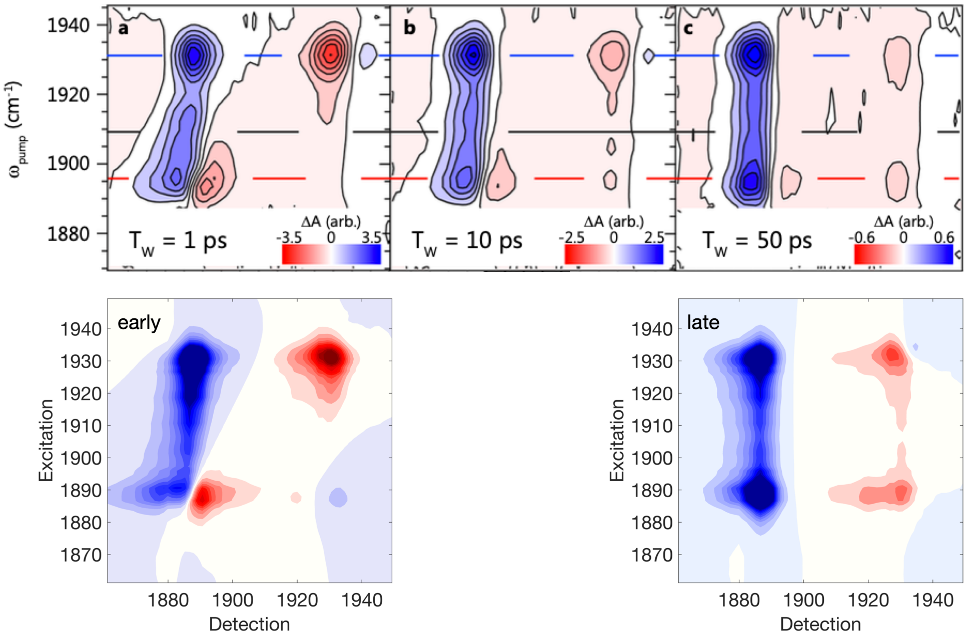

Fig. 1. 2DIR spectra from Paper 1 shown in comparison with a model response consisting of a sum of a ladder polariton response and a filtered background 2DIR spectrum. The filter is taken from Ref. 2 and the background response is an estimate from previous work by Khalil et al.[3] using standard line shape methods.[2] We note that the features of our own data (both in the published paper and several other unpublished results) are also consistent with this general construction. We use the terms "early" and "late" to indicate the time delay relative to the correlation time in the response function. The experimental data are adapted from Ref. 2.

the explanation given previously for the long-time appearance of the polariton excited state transitions. They arise from "incoherently" populated UP (and LP).[2, 5, 7] We chose to adopt a more traditional chemistry language indicating an equilibrium of population between the reservoir and the polaritons. We feel this picture was also used to explain results in the Xiong group.[5, 7]

Uncoupled Response. Regarding the relative magnitude of the background response, we have come to realize that a simple extension of the Tavis-Cummings Hamiltonian to the case of spatially varying coupling reveals the nature of polariton and non-polaritonic states in the cavity.[4, 12] In many simplified discussions of vibrational polaritons, the field-dependent coupling is not included explicitly in the Hamiltonian. We now show how to build the model and interpret the resulting eigenvectors.

$$H = \begin{pmatrix} E_{cav} & J(z_1) & J(z_2) & J(z_3) & \cdots \\ J(z_1) & E_{mol} + \delta_1 & \square & \square & \square \\ J(z_2) & \square & E_{mol} + \delta_2 & \square & \square \\ J(z_3) & \square & \square & E_{mol} + \delta_3 & \square \\ \vdots & \square & \square & \square & \ddots \end{pmatrix}$$

Here we have a single cavity mode with energy E_{cav}, and a large number of molecules each with a transition at E_{mol}. We can add energetic disorder to the molecular energies through the δ_i's; these may be Gaussian distributed or assigned using some other distribution. The coupling is

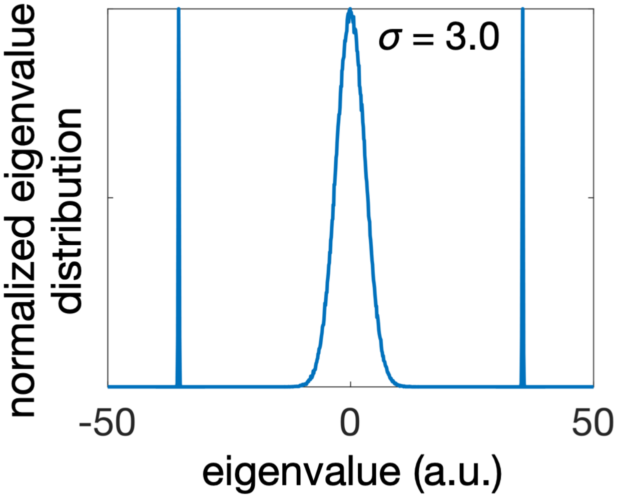

Fig. 2. Eigenvalue distribution for 1000 repetitions of the T-C Hamiltonian with Gaussian site disorder and spatially dependent coupling corresponding to a cavity mode index of 3. Note the inhomogeneous broadening in the dark states that is absent in the two polaritons.

dependent on the molecule's position in the cavity (z_i). We simply scale the single molecule coupling by the field amplitude. We collect statistics on the eigenvalues of this Hamiltonian by evaluating it many times (here we chose 1000 replications). Despite both the energetic disorder and the spatially dependent coupling, the polaritons remain immune to inhomogeneous broadening (**Fig. 2**). For these calculations, $N = 401$, and we set $E_{cav} = E_{mol} = 0$, couplings were chosen to yield a vacuum Rabi splitting of 70 cm^{-1}, and the Gaussian random noise has a standard deviation of 3.0 cm^{-1}.

Turning off the energy disorder, we can inspect the eigenvectors (**Fig. 3**). The disorder can be left on, but then each realization will be different, though the variations do not qualitatively alter the observations. The polariton eigenvectors can be plotted in a spatial representation because each molecular vector element is located at a specific distance along the cavity. The polaritons are found to track the intensity of light in the field mode. Molecules located in the regions of low amplitude do not participate in the polariton eigenvector.

The question of whether there are "dark modes" or "uncoupled molecules" is somewhat more subtle, but can be analyzed using the well-established techniques applied to molecular aggregates. The most important metric is the inverse participation ratio (IPR),[13-14] which gives the eigenvector's delocalization in terms

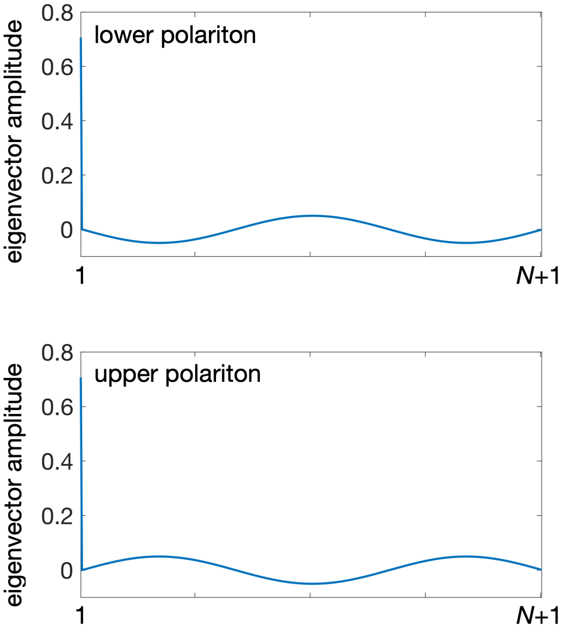

Fig. 3. Polariton eigenvectors show a large photonic contribution in the first entry (our basis is shown in the T-C Hamiltonian), with an oscillatory amplitude as a function of location in the cavity. The mode index is 3, hence there are two nodes in the field.

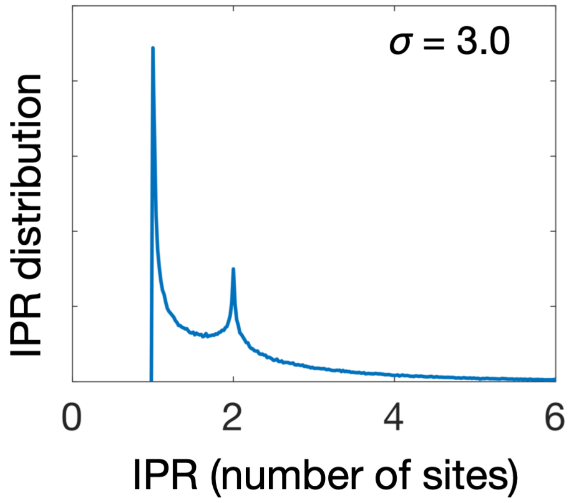

Fig. 4. IPR distribution showing two peaks at ~1 and ~2. These are identified below as arising from the uncoupled molecules and dark states, respectively.

of the number of local basis sites that participate in the eigenvector. For the *n*th eigenvector, expressed in the basis of local molecule sites (labeled by *j*), the IPR is given by:

$$IPR_n = \left[\sum_j \left|v_j^{(n)}\right|^4\right]^{-1}$$

where the $v_j^{(n)}$ are the eigenvector components. Because we are interested in the molecular contribution to the polaritonic eigenvectors (with *N*+1 elements), we renormalize the eigenvectors such that the *N* molecular components are themselves normalized. This renormalization is accomplished by deleting the cavity entry in the eigenvector and then rescaling the remaining elements such that the vector is normalized. Another way to view is this is that we are taking the scalar product with the relevant field mode, and analyzing the non-photonic part of the eigenfunction. In fact, for the non-polaritonic states, the photonic character vanishes (the first element is practically zero), so it is not even necessary to renormalize those states. Using the molecular renormalized eigenvectors, we find that the IPR of the polariton states is 2*N*/3, regardless of the cavity mode index. Since the identification of this factor of 2/3 comes from numerical evaluations, we do not currently have a simple analytical origin of the factor, but there is likely one to be found. Therefore, the inhomogeneous cavity coupling, which arises from the inherently spatially non-uniform cavity mode field distribution, results in a 1/3 reduction in the IPR relative to the uniform case, where the IPR is equal to *N* (i.e. the polariton is delocalized evenly over all the molecules) in the case lacking disorder. Disorder reduces the IPR somewhat but not dramatically. With fewer molecules participating in the polariton states (and dark states as we show below), there are indeed many molecules available to provide a background 2D-IR response.

Regarding the dark states, we have a bit of a difficulty due to the degeneracy. The IPR is not uniquely defined for eigenvectors corresponding to the same eigenvalue because any linear combination of degenerate eigenvectors is also an eigenvector with the same eigenvalue (but possibly different IPR). Nevertheless, we do not expect any physical system to lack disorder, and even the slightest degree of disorder will lift the degeneracy. For the IPR distributions of the non-polaritonic states, we can add a small amount of disorder. Here we collect all of the IPR values for a large number of evaluations of the Hamiltonian and analyze the IPR distribution (**Fig. 4**). There is a large peak at IPR ≈ 1 and a smaller peak at IPR ≈ 2. An IPR value of 2 is what is expected for a single dark state: it is the anti-symmetric combination of two molecule excitations. This anti-symmetry is responsible for the "dark" classification because for aligned molecules, the net transition dipole moment (TDM) of the dark state is exactly zero. When they are not aligned, the TDM is smaller than the individual molecule TDM on average.

The peak at IPR ≈ 1 corresponds to molecules that are indistinguishable from ordinary molecules in the sample cell. They do not even have the anti-symmetric property of dark states, and they do not occur when the field is taken to be spatially uniform (**Fig. 5**). Their TDMs do not cancel because they are identical to the ordinary molecules.

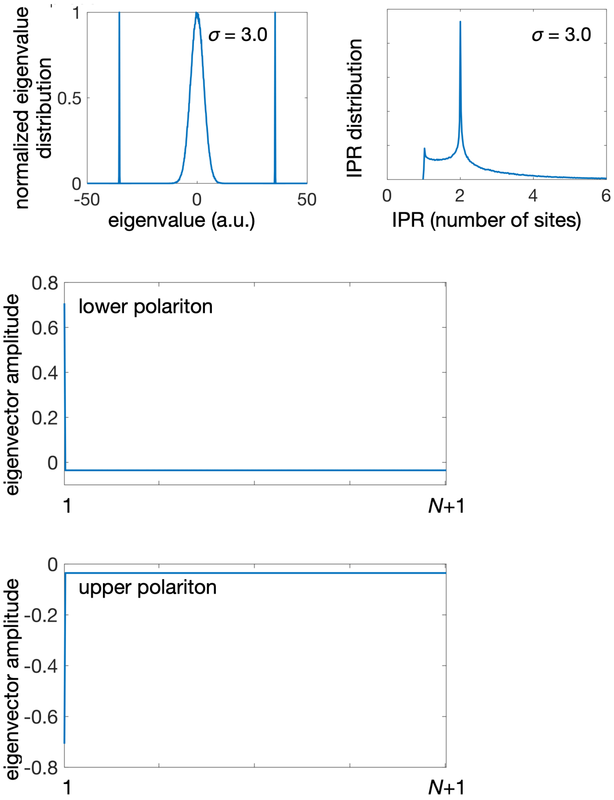

Fig. 5. Eigenvalue distribution, IPR distribution, and polariton eigenvectors for the hypothetical case with no longitudinal coupling dependence. Besides the uniform probability density of the polaritons, there is only a very small IPR feature at ~1, indicating that there are very few uncoupled molecules.

We can further analyze this distribution by identifying which molecules are responsible for the various features in the IPR distribution. Sorting the eigenvectors according to IPR, we sum the spatial probability distributions subject to having IPR values in a given range. Collecting these distributions on many evaluations of the Hamiltonian, we can quantify where in the cavity there is a likelihood of finding molecules that participate in eigenvectors of given degrees of IPR. The results are represented in two ways (**Fig. 6**): first, as the IPR bin conditional probability, and, second, as a map. The dark states, with IPR values near 2, appear in regions of high field intensity, whereas the IPR values of around 1 are in the low-field regions. Hence, it is reasonable to view the fully localized molecules as being "uncoupled" in the sense that they really are distinct from both the polaritons and the dark states. We note that the first low-field region encountered by the optical fields used in spectroscopy is at the entrance mirror, and given the very high concentrations used to establish strong coupling, sufficient signal can be produced in the sample near that entry point to lead to a background 2D-IR signal. We also note that the dark states and the polaritons are co-localized, which is a necessary condition for there to be efficient energy equilibration among them. The basic outlines of the findings described in the preceding section were shown in a cartoon in the Supporting Information (Figure S1) of our Letter.[1]

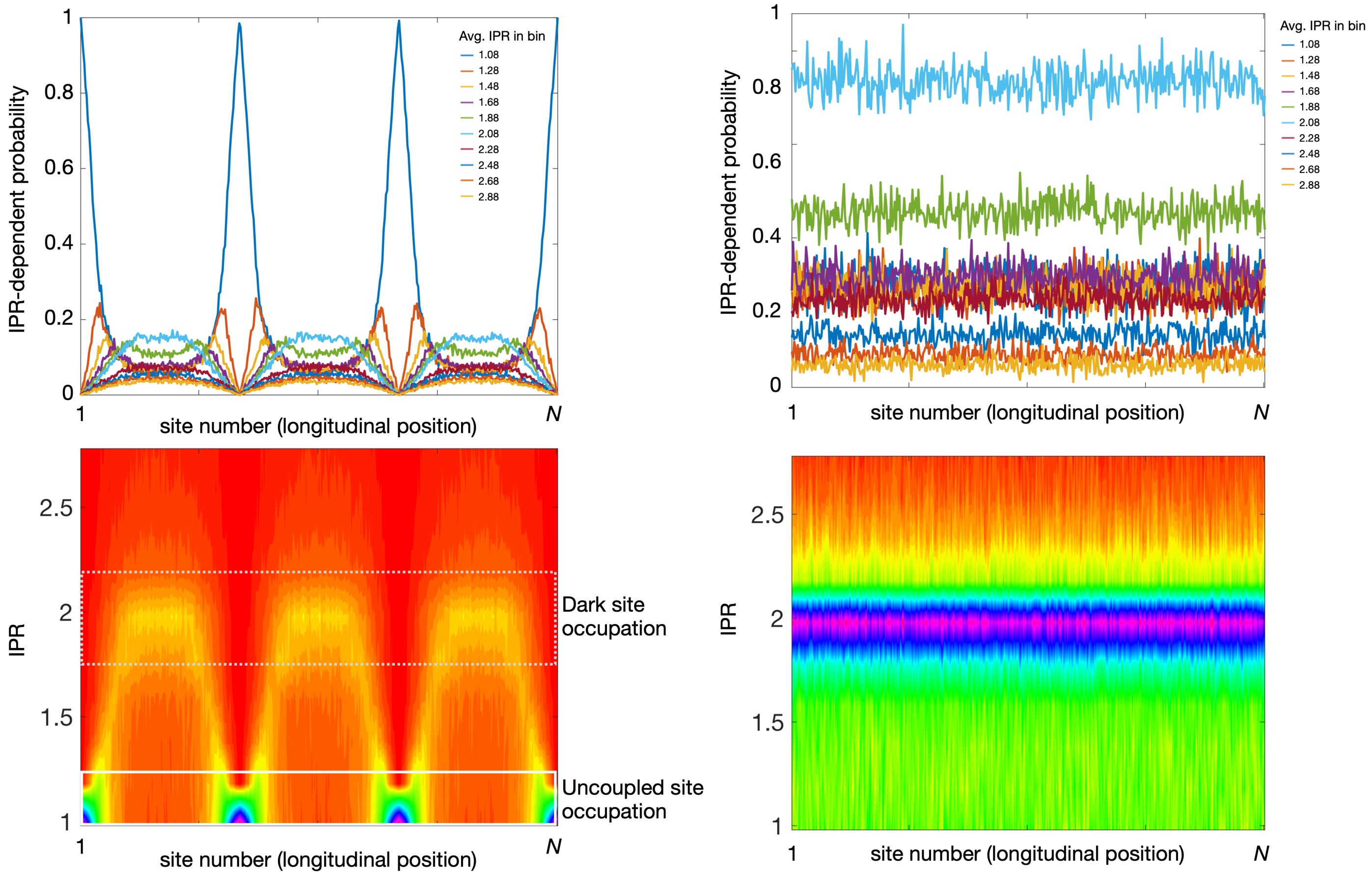

Fig. 6. IPR conditioned probability densities of the non-polaritonic states for the case of spatially varying field-matter coupling (left), and for uniform field-matter coupling (right). The IPR distribution shown in Fig. 4 can be spatially assigned using this approach. The states with IPR near a value of 1 are localized at the low-field regions of the cavity mode, whereas the states with IPR near 2 are in the high-field regions. The spatial overlap between the dark states and the polaritonic states is a requirement for efficient polariton-to-dark energy equilibration. In the absence of spatial coupling dependence, none of these features are observed (right); the dark states are uniformly distributed in the cavity and have IPR values that peak sharply at 2.

Regarding the Use of Effective Linear Responses. The authors use an effective linear response that is changed by pumping the system and altering the populations. Results of this model seem to resemble many features in the experimental pump probe spectrum. Our model using a polaritonic response added to a background filtered 2D spectrum produces spectra that resemble our and other 2D spectra of cavities. The background contribution is reduced when the spectral overlap is small, as in the case shown by the authors. However, one of the principal motivations for the development of multidimensional optical spectroscopy is the difficulty of disentangling contributions to a 1D line shape, particularly transient absorption. Unfortunately, the effective linear response approach is not capable of producing a 2D spectrum, especially at short times when the interesting polariton dynamics are apparent. Our model reproduces nearly all the features of experimental cavity 2D-IR spectra, including the changes in line shape that are observed in our spectra and those of others.[2, 7] It is unfortunate that the background signal appears similarly to how a polariton contraction would manifest, so it is unlikely that an effective 1D response will be able to be definitive in specifying the relative contributions of Rabi contraction, a polariton ladder, and any background response. Clearly, there are more experimental measurements needed to characterize the nature of the nonlinearities in molecular vibrational polaritons. One promising route forward will be to employ nonlinear spectroscopy approaches that avoid population states by making use of fully coherent pathways. For example, double-quantum coherence 2D spectroscopy has been demonstrated by Cundiff et al. to be capable of elucidating the polaritonic ladder in semiconductor quantum wells coupled to a resonant cavity.[15]

AUTHOR INFORMATION

Corresponding Author

Kevin J. Kubarych – Department of Chemistry, University of Michigan, 930 N. University Ave, Ann Arbor, MI 48109, USA; orcid.org/0000-0003-1152-4734; Email: kubarych@umich.edu

AUTHORS

Rong Duan – Department of Chemistry, University of Michigan, 930 N. University Ave, Ann Arbor, MI 48109, USA; orcid.org/000-0003-1077-8134; Email: drong@umich.edu. Present address: Cutera, Inc., 3240 Bayshore Blvd. Brisbane, CA 94005

Joseph N. Mastron – Department of Chemistry, University of Michigan, 930 N. University Ave, Ann Arbor, MI 48109, USA; Department of Physics, University of Michigan, 450 Church St., Ann Arbor, MI 48109, USA; orcid.org/0000-0003-0681-2627; Email: mastron@umich.edu. Present address: TOPTICA Photonics, Inc., 1120 Pittsford, NY 14534

Yin Song – Department of Physics, University of Michigan, 450 Church St., Ann Arbor, MI 48109, USA; orcid.org/0000-0001-8978-2958; Email: songyi@umich.edu. Present address: Beijing Institute of Technology, 5 South Zhong Guan Cun St., Beijing, China

NOTES

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation (CHE-1836529 and CHE-1955026).

REFERENCES

1. Duan, R.; Mastron, J. N.; Song, Y.; Kubarych, K. J., Isolating Polaritonic 2D-IR Transmission Spectra. *J. Phys. Chem. Lett.* **2021,** *12*, 11406-11414.
2. Grafton, A. B.; Dunkelberger, A. D.; Simpkins, B. S.; Triana, J. F.; Hernandez, F. J.; Herrera, F.; Owrutsky, J. C., Excited-state vibration-polariton transitions and dynamics in nitroprusside. *Nat. Commun.* **2021,** *12*, 214.
3. Duan, R.; Mastron, J. N.; Song, Y.; Kubarych, K. J., Direct comparison of amplitude and geometric measures of spectral inhomogeneity using phase-cycled 2D-IR spectroscopy. *J. Chem. Phys.* **2021,** *154*, 174202.

4. Houdre, R.; Stanley, R. P.; Ilegems, M., Vacuum-field Rabi splitting in the presence of inhomogeneous broadening: Resolution of a homogeneous linewidth in an inhomogeneously broadened system. *Phys. Rev. A* **1996,** *53*, 2711-2715.
5. Xiang, B.; Ribeiro, R. F.; Dunkelberger, A. D.; Wang, J. X.; Li, Y. M.; Simpkins, B. S.; Owrutsky, J. C.; Yuen-Zhou, J.; Xiong, W., Two-dimensional infrared spectroscopy of vibrational polaritons. *Proc. Natl. Acad. Sci. U. S. A.* **2018,** *115*, 4845-4850.
6. Norris, T., Strong Coupling in Semiconductor Microcavities. In *Confined Electrons and Photons: New Physics and Appliations*, Burstein, E.; Weisbauch, C., Eds. Springer: 1995; pp 503-522.
7. Xiang, B.; Ribeiro, R. F.; Chen, L. Y.; Wang, J. X.; Du, M.; Yuen, O. E. Z.; Xiong, W., State-Selective Polariton to Dark State Relaxation Dynamics. *J. Phys. Chem. A* **2019,** *123*, 5918-5927.
8. Hernandez, F.; Herrera, F., Multi-level quantum Rabi model for anharmonic vibrational polaritons. *J. Chem. Phys.* **2019,** *151*, 144116.
9. Hamm, P.; Zanni, M. T., *Concepts and Methods of 2D Infrared Spectroscopy*. Cambridge University Press: New York, 2011.
10. Brookes, J. F.; Slenkamp, K. M.; Lynch, M. S.; Khalil, M., Effect of Solvent Polarity on the Vibrational Dephasing Dynamics of the Nitrosyl Stretch in an Fe-II Complex Revealed by 2D IR Spectroscopy. *J. Phys. Chem. A* **2013,** *117*, 6234-6243.
11. Dunkelberger, A. D.; Spann, B. T.; Fears, K. P.; Simpkins, B. S.; Owrutsky, J. C., Modified relaxation dynamics and coherent energy exchange in coupled vibration-cavity polaritons. *Nat. Commun.* **2016,** *7*, 13504.
12. Tavis, M.; Cummings, F. W., Approximate Solutions for an N-Molecule-Radiation-Field Hamiltonian. *Phys. Rev.* **1969,** *188*, 692-695.
13. Bell, R. J.; Dean, P., Atomic VIbrations in Vitreous Silica. *Discussions of the Faraday Society* **1970**, 55-61.
14. Thouless, D. J., Electrons in Disordered Systems and the Theory of Localization. *Physics Reports* **1974,** *13*, 93-142.
15. Autry, T. M.; Nardin, G.; Smallwood, C. L.; Silverman, K.; Bajoni, D.; Lemaitre, A.; Bouchoule, S.; Bloch, J.; Cundiff, S., Excitation Ladder of Cavity Polaritons. *Phys. Rev. Lett.* **2020,** *125*.