arXiv:2306.06004v2 [quant-ph] 22 Jun 2023

Unraveling a cavity induced molecular polarization mechanism from collective vibrational strong coupling

Dominik Sidler,[1,2] Thomas Schnappinger,[3] Anatoly Obzhirov,[1,2] Michael Ruggenthaler,[1,2] Markus Kowalewski,[3] and Angel Rubio[1,2,4,5]

[1)]*Max Planck Institute for the Structure and Dynamics of Matter and Center for Free-Electron Laser Science, Luruper Chaussee 149, 22761 Hamburg, Germany*

[2)]*The Hamburg Center for Ultrafast Imaging, Luruper Chaussee 149, 22761 Hamburg, Germany*

[3)]*Department of Physics, Stockholm University, AlbaNova University Center, SE-106 91 Stockholm, Sweden*

[4)]*Center for Computational Quantum Physics, Flatiron Institute, 162 5th Avenue, New York, NY 10010, USA*

[5)]*Nano-Bio Spectroscopy Group, University of the Basque Country (UPV/EHU), 20018 San Sebastián, Spain*

(*Electronic mail: angel.rubio@mpsd.mpg.de)

(*Electronic mail: markus.kowalewski@fysik.su.se)

(*Electronic mail: michael.ruggenthaler@mpsd.mpg.de)

(*Electronic mail: anatoly.obzhirov@mpsd.mpg.de)

(*Electronic mail: thomas.schnappinger@fysik.su.se)

(*Electronic mail: dsidler@mpsd.mpg.de)

(Dated: 23 June 2023)

We demonstrate that collective vibrational strong coupling of molecules in thermal equilibrium can give rise to significant local electronic polarization effects in the thermodynamic limit. We do so by first showing that the full non-relativistic Pauli-Fierz problem of an ensemble of strongly-coupled molecules in the dilute-gas limit reduces in the cavity Born-Oppenheimer approximation to a cavity-Hartree equation. Consequently, each molecule experiences a self-consistent coupling to the dipoles of all other molecules. In the thermodynamic limit, the sum of all molecular dipoles constitutes the macroscopic polarization field and the self-consistency then accounts for the delicate back-action on its heterogeneous microscopic constituents. The here derived cavity-Hartree equations allow for a computationally efficient implementation in an ab-initio molecular dynamics setting. For a randomly oriented ensemble of slowly rotating model molecules, we observe a red shift of the cavity resonance due to the polarization field, which is in agreement with experiments. We then demonstrate that the back-action on the *local* polarization takes a non-negligible value in the thermodynamic limit and hence the collective vibrational strong coupling can modify individual molecular properties *locally*. This is not the case, however, for atomic ensembles, where room temperature does not induce any disorder and local polarization effects are absent in the dilute limit. Our findings suggest that the thorough understanding of polaritonic chemistry, such as the modification of chemical reactions, requires self-consistent treatment of the cavity induced polarization and the usually applied restrictions to the displacement field effects may be insufficient.

Polaritonic chemistry and materials science is a rapidly growing research field evidenced by a large number of recent review articles.[1–11] The strong coupling of matter and light within optical cavities offers a novel way not only to alter and design matter properties, but also to shape the (quantum) properties of light in various ways. For example, magnetic[12] or metal-to-insulator[13] phase transitions can be altered. Furthermore, cavities can also cause the breakdown of topological protection as reported for the integer quantum Hall effect.[14] In chemistry, the electronic strong coupling, the quantum yield of emissions[15] or inter-system crossings[16] can be modified, and photo-chemical reactions can be influenced[17–21]. For vibrational strong coupling even ground-state (thermally-driven) chemical reactions can be affected[22–25] However, despite a plethora of suggested applications and observed novel effects, we still lack a fundamental understanding of all the relevant underlying microscopic/macroscopic physical mechanisms, specifically in the context of vibrational strong coupling effects.[6,26,27] One of the main reason for this deficiency is the complexity of the full description, which *a priori* requires a holistic approach combining the expertise from different fields of physics and chemistry such as quantum optics, electronic-structure theory, (quantum) statistical mechanics, quantum electrodynamics, molecular and solid state physics.[11] Besides questions concerning the observed resonance conditions[28–30], currently one of the most pressing, unresolved issue in the field is how individual molecules can experience cavity-induced modifications under collective strong coupling. [6,11,26,27] Theoretical attempts to determine how the coupling of the cavity to the ensemble of molecules can modify the chemistry of individual molecules in the thermodynamic limit have so far only been able to describe certain aspects.[31–34] While there have been theoretical suggestions that collective strong coupling can lead to local changes once impurities or (thermally-induced) disorder are introduced in an ensemble[35,36] the existence and nature of such effects for a large ensemble of molecules remained elusive. In this letter we close this important gap by demonstrating numerically that the cavity can indeed induce local polarization effects akin to those observed for small molecular ensembles[36] for collective coupling in the thermodynamic limit, when treating the many-molecule problem self-consistently within the cavity Born-Oppenheimer approximation of the full Pauli-Fierz theory.

We consider a dilute gas-phase ensemble of N molecules coupled to a photonic environment with confined modes α. Each molecule consists of N_e electrons and N_n nuclei/ions such that in the long-wavelength limit the Pauli-Fierz Hamiltonian becomes[37–39]

$$\hat{H} \;=\; \hat{H}_{\rm m} + \frac{1}{2}\sum_{\alpha=1}^{M}\left[\hat{p}_\alpha^2 + \omega_\alpha^2\left(\hat{q}_\alpha - \frac{\hat{X}_\alpha + \hat{x}_\alpha}{\omega_\alpha}\right)^2\right] \tag{1}$$

with $\hat{H}_{\rm m}$ the usual cavity-free/bare matter Hamiltonian consisting of N molecules. The coupled polarization operators are defined as $\hat{X}_\alpha := \sum_{n=1}^{N}\sum_{i_n=1}^{N_n} Z_{i_n}\boldsymbol{\lambda}_\alpha\cdot\hat{\boldsymbol{R}}_{i_n}$ and $\hat{x}_\alpha := -\sum_{n=1}^{N}\sum_{i_n=1}^{N_e}\boldsymbol{\lambda}_\alpha\cdot\hat{\boldsymbol{r}}_{i_n}$, where Z_{i_n} is the nuclear charge and $\hat{\boldsymbol{R}}_{i_n}$ is the coordinate of the i-th nucleus/ion of the n-th molecule and accordingly for the electrons $\hat{\mathbf{r}}_{i_n}$. The coupling strength and polarization to the canonical displacement field operators $\hat{q}_\alpha, \hat{p}_\alpha$ with mode frequency ω_α is defined by $\boldsymbol{\lambda}_\alpha$ and can be obtained from, e.g., macroscopic quantum electrodynamics.[40,41]

In the next step we perform the cavity Born-Oppenheimer approximation (cBOA),[42–44] i.e., we treat the electrons of the ensemble as a conditional many-body wave function of all the nuclear degrees of freedom $\underline{\mathbf{R}}$ and all the displacement field coordinates $\underline{q}$.[12] We subsequently assume the dilute-gas limit and thus the overlaps of *local* many-electron ground-state wave functions $|\chi_n\rangle$ of different molecules is considered negligible, and thus a mean-field ansatz for the *ensemble* electronic wave function

$$|\Psi\rangle = |\chi_1\rangle\otimes\cdots\otimes|\chi_N\rangle \tag{2}$$

becomes accurate (see Supporting Information). We note that this ansatz leads to the same set of equations as a Slater determinant of *all* electrons, where we assume that the individual electronic wave functions of different molecules do not overlap. This leads to a set of coupled equations, where the *local* electronic structure of the n-th molecule depends self-consistently on all the $N-1$ other molecules. Disregarding bare molecular interaction in the dilute limit, we then have to find the lowest electronic energy state for the following cavity-Hartree equations

$$\left(\hat{H}_n(\underline{\mathbf{R}}_n) + \sum_{\alpha=1}^{M}\left[\frac{p_\alpha^2}{2} + \frac{\omega_\alpha^2}{2}\left(q_\alpha - \frac{X_\alpha}{\omega_\alpha}\right)^2 + \left(X_\alpha - q_\alpha\omega_\alpha + \sum_{m\neq n}^{N}\langle\chi_m|\hat{x}_{m,\alpha}|\chi_m\rangle\right)\hat{x}_{n,\alpha} + \frac{\hat{x}_{n,\alpha}^2}{2}\right]\right)\chi_n(\mathbf{z}_1,\ldots,\mathbf{z}_{N_e}) = \varepsilon_n\chi_n(\mathbf{z}_1,\ldots,\mathbf{z}_{N_e}) \tag{3}$$

for all N molecules simultaneously, i.e., by a self-consistent solution. The bare matter Hamiltonian of a single molecule is defined as $\hat{H}_n$ from $\hat{H}_{\rm m}(\underline{\mathbf{R}}) = \sum_{n=1}^{N}\hat{H}_n(\underline{\mathbf{R}}_n)$ within the dilute-limit approximation and $\hat{x}_{n,\alpha} = -\sum_{i_n=1}^{N_e}\boldsymbol{\lambda}_\alpha\cdot\hat{\boldsymbol{r}}_{i_n}$ is the electronic polarization operator of the n-th molecule

and $\mathbf{z} = \mathbf{r}\sigma$ the space-spin variable of an individual electron. Consequently, the cavity induces an inter-molecular dipole-dipole energy term

$$V_{\mathrm{dd}} = \sum_{\alpha=1}^{M} \sum_{n=1}^{N} \langle \chi_n | \hat{x}_{n,\alpha} | \chi_n \rangle \sum_{m \neq n}^{N} \langle \chi_m | \hat{x}_{m,\alpha} | \chi_m \rangle \tag{4}$$

that scales with $N(N-1)$ over the entire ensemble size. This macroscopic scaling is crucial for molecular ensembles, since it counteracts the usual $1/\sqrt{N}$ scaling law of the coupling terms $\boldsymbol{\lambda}_\alpha$ for a fixed Rabi splitting, as we show subsequently. Indeed, the inter-molecular dipole-dipole interaction V_{dd} is physically straightforward to understand. Because we work in the length gauge, the electric field operator is

$$\hat{\boldsymbol{E}} = \hat{\boldsymbol{D}} - \hat{\boldsymbol{P}}. \tag{5}$$

Notice that the effect of the macroscopic polarization $\hat{\boldsymbol{P}}$ on the microscopic constituents is captured by the dipole self-interaction and scales as $\boldsymbol{\lambda}_\alpha^2$. That these self-interaction terms are important to properly describe the optical response of a material system has been pointed out earlier.[45] In addition, it is also established that disregarding this term (as often done in model calculations) and only keeping the cavity-mediated displacement field $\hat{\boldsymbol{D}}$ introduces severe theoretical inconsistencies for *ab-initio* simulations.[46,47] In the following, we will investigate the chemical relevance of treating $\hat{\boldsymbol{P}}$ self-consistently on macroscopic and microscopic scale.

From the self-consistent solution of Eq. (3) for all N molecules, we obtain the classical forces for the nuclei/ions and the displacement-field coordinates. In more detail, we can perform an ab-initio molecular dynamics simulation on the polarization-dressed ground-state potential energy surface. To account for classical canonical equilibrium conditions at temperature T, which are relevant for many ground-state chemical processes, the classical Langevin equations of motion are propagated, i.e.,[6,48]

$$\begin{aligned} M_{i_n} \ddot{\boldsymbol{R}}_{i_n} &= -\partial_{\boldsymbol{R}_{i_n}} H_n^{\mathrm{n}} - \langle \partial_{\boldsymbol{R}_{i_n}} \hat{H}_n^{\mathrm{e}} \rangle_0 + \sum_{\alpha=1}^{M} Z_{i_n} \boldsymbol{\lambda}_\alpha \Big(\omega_\alpha q_\alpha - X_\alpha - \langle \hat{x}_\alpha \rangle_0 \Big) \\ &\quad - \gamma M_{i_n} \dot{\boldsymbol{R}}_{i_n} + \sqrt{2 M_{i_n} \gamma k_B T}\, \boldsymbol{S}_{i_n} \qquad (6) \\ \ddot{q}_\alpha &= -\omega_\alpha^2 q_\alpha + \omega_\alpha X_\alpha + \omega_\alpha \langle \hat{x}_\alpha \rangle_0 - \gamma \dot{q}_\alpha + \sqrt{2\gamma k_B T} S_\alpha. \qquad (7) \end{aligned}$$

These equations implicitly assume that the Hellmann-Feynman theorem applies, i.e., that the cavity Hartree equations are not only globally but also locally solved using a variational method. The bare matter Hamiltonian $\hat{H}_n$ is separated into a classical part, describing nuclear interactions

H_n^{n}, and the quantized electronic part $\hat{H}_n^{\mathrm{e}}$ that parametrically depends on the nuclear positions. Furthermore, we have introduced nuclear masses M_{i_n}, friction constant γ and component-wise delta-correlated Gaussian noise terms, i.e., $\langle S(t)\rangle = 0$, $\langle S(t)S(t')\rangle = \delta(t-t')$. Each degree of freedom possesses its individual independent stochastic noise term indexed by i_n and α respectively. We note here that treating the displacement coordinates classically with thermal noise means that we consider photonic excitations due to free charges to be in a classical thermal state[47].

In the first step, the collective Rabi splitting is calculated for a model system consisting of $N = 900$ randomly-oriented and slowly rotating Shin-Metiu molecules[49] strongly coupled to a single cavity mode ω_α at $T = 158$ K, yielding a clear lower and upper polaritonic resonance, as depicted by the dotted line in Fig. 1a (see SI for further details). Taking into account the self-consistent treatment of the cavity-induced molecular polarization $\hat{\boldsymbol{P}}$ leads to a detuning of the cavity towards lower frequencies, which manifests itself in the asymmetric splitting with respect to the bare cavity mode ω_α, indicated by the black vertical line. Simulations of a few less polarizable hydrogen fluoride (HF) dimers show the same tendency as demonstrated in Fig. 1b and Fig. S3, but of significantly smaller magnitude. Qualitatively similar results can also be found for perfectly aligned Shin-Metiu molecules (see Fig. S1 in the SI). The observed cavity induced de-tuning resembles the dipole-dipole interaction induced Lorentz redshift within dense atomic ensembles (in absence of a cavity), which depends strongly on the microscopic polarizability of the media, similar to our result.[50,51] Notice that when tuning the cavity to much lower frequencies (e.g. ro-vibrational regime), the presence (back-action) of permanent molecular dipoles is expected to significantly contribute to the red-shift alongside with the molecular polarizability. This dynamic re-orientation contribution is neglected in our simulations. The observed collectively induced redshift of a filled cavity with respect to a bare one has also been seen in experiments[52] and may in principle be simply approximated by a suitably chosen refractive index of the ensemble.[6] We note, however, that we get the redshift now directly from the simulation, where we calculate the self-consistent polarization of the ensemble of molecules. That is, we calculate implicitly the ensemble polarizability and its back-action on the cavity mode. In the case of free-space modes, this is the standard way to determine the refractive index of a material.[45,53,54] Now the question arises whether the accurate self-consistent and microscopic treatment of the polarization can additionally induce local field effects that cannot be disregarded in the thermodynamic limit ($N \gg 1$)? Earlier evidence for collective electronic strong coupling for a few molecules indeed indicates that there might be such an effect,[36] yet the existence of similar local polarization effects for a

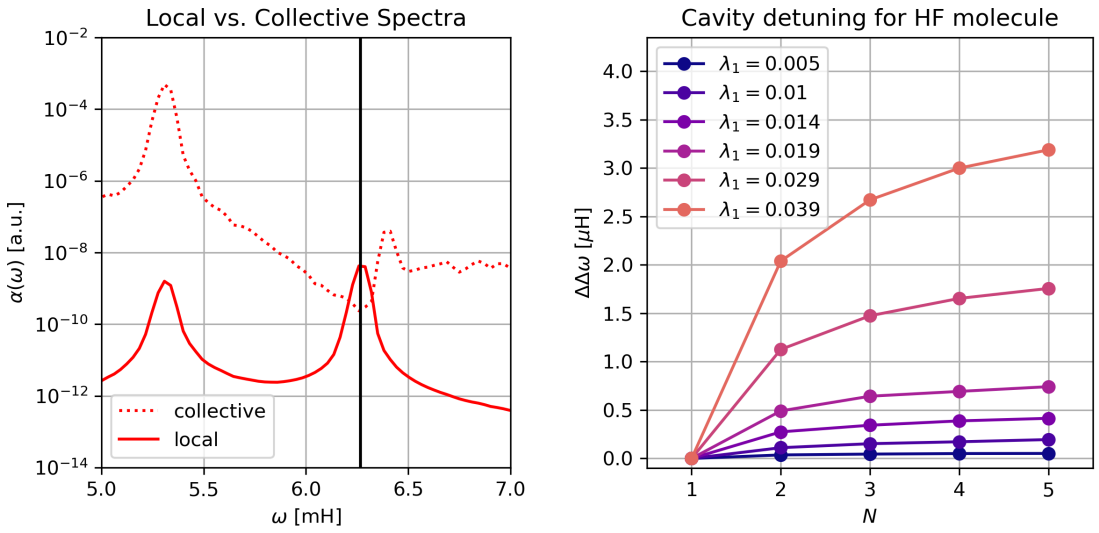
thermal ensemble under vibrational strong coupling in the large-N limit remained unclear. As the first local observable, we analyze the local molecular dipole vibrations for individual Shin-Metiu molecules, which reveals a (locally) populated lower polariton (solid line in Fig. 1a) and a strongly populated dark state at $\omega = \omega_\alpha$. A local upper polariton could not be identified, i.e., may be too weakly populated to overcome the thermal broadening for the given system. Simulations show that the usual $\sqrt{N}$-collective Rabi split scaling law of the Tavis-Cumming model remains preserved collectively as well as locally, when including local polarization effects self-consistently (see Fig. S1 of the Supporting Information). As the second local observable, we propagate the system self-consistently and measure at every time step, i.e., for every realized classical configuration $(\underline{R}, q_\alpha)$, the difference between the exact solution of Eq. (3) and the electronic bare matter problem by monitoring $\Delta r_n(t) = \langle \hat{r}_n \rangle_\lambda - \langle \hat{r}_n \rangle_{\lambda=0}$ in the electronic ground-state. This allows to measure cavity-induced local polarization effects in thermal equilibrium, since the full electronic problem reduces to the bare local matter problem in the thermodynamic limit only if the displacement field is considered. Our simulation results in Fig. 2 reveal a nonvanishing cavity-induced local ensemble polarization, i.e., $\langle |\Delta r_n| \rangle \neq 0$, that persist even in the large-N limit. At the same time, the total electronic polarization of the ensemble remains zero, i.e., $\langle \Delta r_n \rangle = 0$, as expected from the symmetry of Eq. (1). This merely guarantees the simple fact that thermally no net polarization is expected. Consequently, our numerical results show that the chemical properties of individual molecules can be locally modified by a strong collective vibrational coupling to the cavity. Analogous results hold also for perfectly aligned ones, as shown in Fig. S2 of the Supporting Information. Physically, the appearance of local strong-coupling effects can be understood by interpreting the local polarization in a dipole picture, as previously done for electronic strong coupling of a few nitrogen dimers[36]. While the total (macroscopic) polarization is zero, non-trivial local dipole modifications are possible for heterogeneous systems that can still cancel each other, i.e., as seen from the sum $m \neq n$ in Eq. (3). This local polarization induces a mirror dipole in the rest of the ensemble. At this point, we would like to highlight the relevance of disorder in the ensemble (temperature and/or different molecular orientations and polarizabilities), which enables a heterogeneous structure of modified local polarizations that can cancel collectively. For atoms, which do not have a static dipole moment, no local effect is expected, as can be confirmed by simulating a small ensemble of up to five neon atoms (see Fig S4 in the Supporting Information). In other words, having spherically symmetric systems without (different) internal nuclear degrees of freedom, all local dipole contributions will be equivalent and thus the local polarization needs to

be zero, in order to have a zero macroscopic polarization. Consequently, our results do not contradict well-established knowledge from quantum-optical models for *atomic* systems. However, they show that for molecular ensembles, the formalism becomes more involved, and the self-consistent (!) treatment of the local polarization may become decisive in capturing all relevant aspects of polaritonic chemistry. We also note that the free-space mode structure of the electromagnetic field, which is homogeneous and isotropic, is not able to test for disorder in the same way as cavity modes by having preferred polarization directions and frequencies. This breaking of symmetry explains why similar effects are not expected for coupling to free-space modes.

To conclude, we have reformulated the computationally inaccessible many-molecule Pauli-Fierz problem of polaritonic chemistry in terms of an efficient cavity-Hartree many-molecule problem, within the dilute-gas limit and the cBOA. Simulating the corresponding Langevin equations of motion under vibrational strong coupling in thermal equilibrium reveals that solving the cavity-Hartree equations self-consistently, and thus including dipole-dipole interactions between molecules, can be decisive to capture all relevant aspects of polaritonic chemistry. The reason is that non-trivial local (on the individual-molecule level) polarizations can arise, which can persist in the thermodynamic limit. Furthermore, accounting for ensemble polarization effects lead to a detuning of the cavity towards lower frequencies, which is in line with experimental evidence[52] and shows that the dipole self-interaction term is a necessary ingredient to capture the basic effect of a changed refractive index.

The present result may have far-reaching consequences for the theoretical description of polaritonic chemistry and materials science, since they provide a so far overlooked, yet simple and intuitive physical mechanism that can induce local molecular changes in the thermodynamic limit. This local mechanism may be the missing piece to settle current discrepancies between existing simplified models for a macroscopic ensemble of molecules and experiments. Furthermore, our cavity-Hartree equations are well suited to be included in existing computational methods,[38,43,55–60] which will enable the efficient exploration of the large chemical space with a multitude of observables. Particularly, large ensemble sizes under self-consistent vibrational strong coupling should become accessible by established ab-initio molecular dynamics codes[56–58,61] and potentially with the help of self-consistent embedding schemes[62]. Last but not least, the existence of a macroscopically induced microscopic polarization mechanism opens many interesting fundamental physical questions. For instance, can we efficiently control microscopic (quantum) properties of individual molecules via a thermal macroscopic field, or are the experimentally observed

modifications of chemical reactions purely due to change in the statistics? On the more theoretical side, can our results be generalized to the liquid or even solid phase under collective strong coupling conditions? All these aspects open many interesting questions that lie at the boundaries between different fields of physics and need the combination of various different viewpoints and methods[2].



(a) (b)

FIG. 1: (a) Vibrational absorption spectra $\alpha(\omega)$ for 900 randomly oriented Shin-Metiu molecules under collective vibrational strong coupling in canonical equilibrium at $k_BT = 0.5$ [mH]. The cavity is tuned to the first vibrational mode of the uncoupled molecule at $\omega_\alpha = 6.27$ [mH] (black vertical line) with $\lambda_\alpha = 0.0085$. The collective Rabi splitting (dotted line) is calculated from the fluctuations of the total ensemble dipole moment (see SI) and shows an asymmetric splitting (red-shifted cavity). In addition, local molecular vibrations (bold line) are monitored in a similar way (see SI), which reveals a significant fraction of individual molecules that are locally strongly coupled, i.e. that vibrate at the frequency of the lower polariton. Furthermore, the local spectrum also indicates that the dark states at $\omega = \omega_\alpha$ are strongly populated. In contrast, no local populations of the upper polaritonic states could be detected at the given temperature. (b) Relative red-shifted cavity frequencies $\Delta\Delta\omega = |\Delta\omega(N) - \Delta\omega(1)|$ with respect to the single molecule shift $\Delta\omega(1)$ for a few perfectly parallelly aligned HF molecules. The collective Rabi splitting was kept constant with respect to N for each chosen λ_1 by re-scaling $\lambda = \lambda_1/\sqrt{N}$ throughout the computations. The cavity is tuned to the first vibrational mode of the uncoupled HF at $\omega_\alpha = 20.35$ [mH] (see SI for further details). Notice the de-tuning is about two orders of magnitude smaller for the HF molecule than for the Shin-Metiu molecule. However, the results agree qualitatively, since they suggests a similar finite collective detuning in the large N limit. The overall very small shift is a consequence of the very low polarizability 0.8 [Å^3] of the HF molecules.[63]

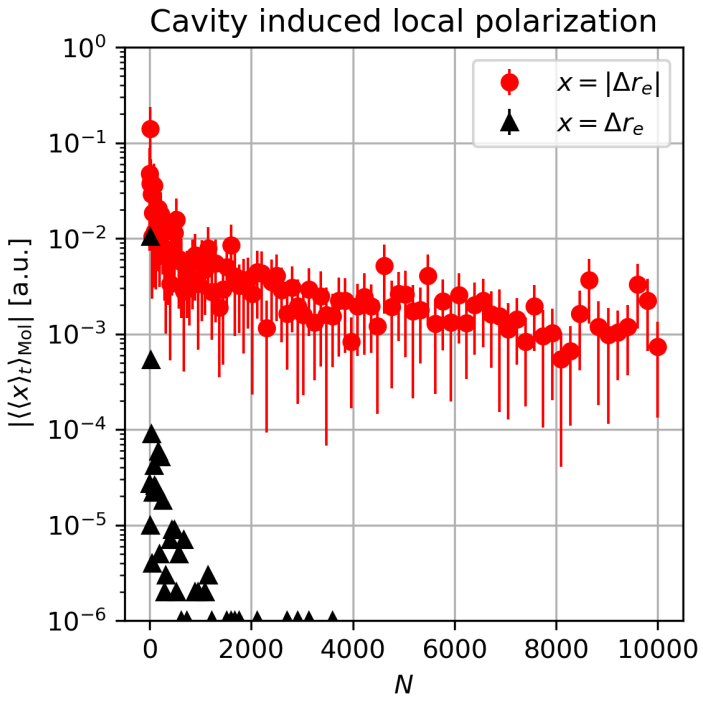


FIG. 2: Statistical evaluation of cavity-induced local electronic changes $\Delta r_n(t) = \langle \hat{r}_n \rangle_\lambda - \langle \hat{r}_n \rangle_{\lambda=0}$ of the n-th molecule with respect to the bare Shin-Metiu molecule in canonical equilibrium at $k_B T = 0.5$ [mH] for randomly-oriented molecules (see Supporting Information for details). The Rabi-splitting was kept constant when increasing the number of molecules by choosing a re-scaled $\lambda_\alpha(N) = 0.256/\sqrt{N}$. By monitoring $|\Delta r_n|$ (red dots), we observe a non-zero saturation of the cavity induced local polarizations in the large-N limit, where the standard deviations with respect to different molecules are indicated by vertical red lines. At the same time, the total polarization of the ensemble, which is related to Δr_n (black triangles), quickly approaches zero, since the cavity cannot induce a non-zero polarization of the ensemble. Consequently, our simulations suggest that cavity-induced local strong coupling effects persist in the thermodynamic limit $(N \gg 1)$ of a molecular ensemble under collective vibrational strong coupling. In other words, the self-consistent treatment of Eq. (3) is decisive to describe ground-state polaritonic chemistry accurately for realistic molecular ensembles.

ACKNOWLEDGMENTS

We thank I-Te Lu, Simone Latini, Abraham Nitzan and Gerrit Groenhof for inspiring discussions and helpful comments. This work was made possible through the support of the RouTe

Project (13N14839), financed by the Federal Ministry of Education and Research (Bundesministerium für Bildung und Forschung (BMBF)) and supported by the European Research Council (ERC-2015-AdG694097), the Cluster of Excellence "CUI: Advanced Imaging of Matter" of the Deutsche Forschungsgemeinschaft (DFG), EXC 2056, project ID 390715994 and the Grupos Consolidados (IT1249-19). The Flatiron Institute is a division of the Simons Foundation. M.K. acknowledges funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (grant agreement no. 852286).

REFERENCES

[1]T. W. Ebbesen, "Hybrid light–matter states in a molecular and material science perspective," Acc. Chem. Res. **49**, 2403–2412 (2016).

[2]M. Ruggenthaler, N. Tancogne-Dejean, J. Flick, H. Appel, and A. Rubio, "From a quantum-electrodynamical light–matter description to novel spectroscopies," Nat. Rev. Chem. **2**, 1–16 (2018).

[3]J. Gargiulo, R. Berte, Y. Li, S. A. Maier, and E. Cortes, "From optical to chemical hot spots in plasmonics," Acc. Chem. Res. **52**, 2525–2535 (2019).

[4]F. Herrera and J. Owrutsky, "Molecular polaritons for controlling chemistry with quantum optics," J. Chem. Phys. **152**, 100902 (2020).

[5]K. Hirai, J. A. Hutchison, and H. Uji-i, "Recent progress in vibropolaritonic chemistry," ChemPlusChem **85**, 1981–1988 (2020).

[6]D. Sidler, M. Ruggenthaler, C. Schaefer, E. Ronca, and A. Rubio, "A perspective on ab initio modeling of polaritonic chemistry: The role of non-equilibrium effects and quantum collectivity," J. Chem. Phys. **156** (2022), 10.1063/5.0094956, 230901.

[7]K. Nagarajan, A. Thomas, and T. W. Ebbesen, "Chemistry under vibrational strong coupling," J. Am. Chem. Soc. **143**, 16877–16889 (2021).

[8]F. J. Garcia-Vidal, C. Ciuti, and T. W. Ebbesen, "Manipulating matter by strong coupling to vacuum fields," Science **373**, eabd0336 (2021).

[9]T. E. Li, B. Cui, J. E. Subotnik, and A. Nitzan, "Molecular polaritonics: chemical dynamics under strong light–matter coupling," Annu. Rev. Phys. Chem. **73**, 43–71 (2022), https://doi.org/10.1146/annurev-physchem-090519-042621.

[10]J. Fregoni, F. J. Garcia-Vidal, and J. Feist, "Theoretical challenges in polaritonic chemistry,"

ACS photonics **9**, 1096–1107 (2022).

[11]M. Ruggenthaler, D. Sidler, and A. Rubio, "Understanding polaritonic chemistry from ab initio quantum electrodynamics," arXiv preprint arXiv:2211.04241 (2022).

[12]S. Latini, D. Shin, S. A. Sato, C. Schäfer, U. De Giovannini, H. Hübener, and A. Rubio, "The ferroelectric photo ground state of srtio3: Cavity materials engineering," Proc. Natl. Acad. Sci. U.S.A. **118** (2021), 10.1073/pnas.2105618118.

[13]G. Jarc, S. Y. Mathengattil, A. Montanaro, F. Giusti, E. M. Rigoni, F. Fassioli, S. Winnerl, S. D. Zilio, D. Mihailovic, P. Prelovšek, M. Eckstein, and D. Fausti, "Cavity control of the metal-to-insulator transition in 1t-tas$_2$," arXiv preprint arXiv:2210.02346 (2022).

[14]F. Appugliese, J. Enkner, G. L. Paravicini-Bagliani, M. Beck, C. Reichl, W. Wegscheider, G. Scalari, C. Ciuti, and J. Faist, "Breakdown of topological protection by cavity vacuum fields in the integer quantum hall effect," Science **375**, 1030–1034 (2022).

[15]S. Wang, T. Chervy, J. George, J. A. Hutchison, C. Genet, and T. W. Ebbesen, "Quantum yield of polariton emission from hybrid light-matter states," The Journal of Physical Chemistry Letters **5**, 1433–1439 (2014), pMID: 26269990.

[16]E. Eizner, L. A. Martínez-Martínez, J. Yuen-Zhou, and S. Kéna-Cohen, "Inverting singlet and triplet excited states using strong light-matter coupling," Science Advances **5**, eaax4482 (2019).

[17]T. Schwartz, J. A. Hutchison, C. Genet, and T. W. Ebbesen, "Reversible switching of ultrastrong light-molecule coupling," Phys. Rev. Lett. **106**, 196405 (2011).

[18]S. Felicetti, J. Fregoni, T. Schnappinger, S. Reiter, R. de Vivie-Riedle, and J. Feist, "Photoprotecting uracil by coupling with lossy nanocavities," J. Phys. Chem. Lett. **11**, 8810–8818 (2020).

[19]M. Gudem and M. Kowalewski, "Controlling the photostability of pyrrole with optical nanocavities," J. Phys. Chem. A **125**, 1142–1151 (2021).

[20]M. Gudem and M. Kowalewski, "Triplet-triplet annihilation dynamics of naphthalene," Chemistry **28**, e202200781 (2022).

[21]R. C. Couto and M. Kowalewski, "Suppressing non-radiative decay of photochromic organic molecular systems in the strong coupling regime," Phys. Chem. Chem. Phys. **24**, 19199–19208 (2022).

[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**, 11462–11466 (2016).

[23]K. Hirai, R. Takeda, J. A. Hutchison, and H. Uji-i, "Modulation of prins cyclization by vibrational strong coupling," Angewandte Chemie **132**, 5370–5373 (2020).

[24]K. Hirai, J. A. Hutchison, and H. Uji-i, "Recent progress in vibropolaritonic chemistry," ChemPlusChem **85**, 1981–1988 (2020).

[25]W. Ahn, J. F. Triana, F. Recabal, F. Herrera, and B. S. Simpkins, "Modification of ground-state chemical reactivity via light–matter coherence in infrared cavities," Science **380**, 1165–1168 (2023).

[26]B. S. Simpkins, A. D. Dunkelberger, and I. Vurgaftman, "Control, modulation, and analytical descriptions of vibrational strong coupling," Chemical Reviews **123**, 5020–5048 (2023), pMID: 37018158, https://doi.org/10.1021/acs.chemrev.2c00774.

[27]J. A. Campos-Gonzalez-Angulo, Y. R. Poh, M. Du, and J. Yuen-Zhou, "Swinging between shine and shadow: Theoretical advances on thermally-activated vibropolaritonic chemistry (a perspective)," arXiv preprint arXiv:2212.04017 (2022).

[28]X. Li, A. Mandal, and P. Huo, "Cavity frequency-dependent theory for vibrational polariton chemistry," Nat. Commun. **12**, 1315 (2021).

[29]C. Schäfer, J. Flick, E. Ronca, P. Narang, and A. Rubio, "Shining light on the microscopic resonant mechanism responsible for cavity-mediated chemical reactivity," Nature Communications **13**, 7817 (2022).

[30]L. P. Lindoy, A. Mandal, and D. R. Reichman, "Quantum dynamical effects of vibrational strong coupling in chemical reactivity," Nature Communications **14**, 2733 (2023).

[31]T. E. Li, A. Nitzan, and J. E. Subotnik, "On the origin of ground-state vacuum-field catalysis: Equilibrium consideration," J. Chem. Phys. **152**, 234107 (2020).

[32]T. E. Li, J. E. Subotnik, and A. Nitzan, "Cavity molecular dynamics simulations of liquid water under vibrational ultrastrong coupling," Proc. Natl. Acad. Sci. U.S.A. **117**, 18324–18331 (2020).

[33]J. Sun and O. Vendrell, "Suppression and enhancement of thermal chemical rates in a cavity," The Journal of Physical Chemistry Letters **13**, 4441–4446 (2022), pMID: 35549344, https://doi.org/10.1021/acs.jpclett.2c00974.

[34]E. Davidsson and M. Kowalewski, "The role of dephasing for dark state coupling in a molecular tavis-cummings model," arXiv preprint arXiv:2304.09583 (2023).

[35]S. Schütz, J. Schachenmayer, D. Hagenmüller, G. K. Brennen, T. Volz, V. Sandoghdar, T. W. Ebbesen, C. Genes, and G. Pupillo, "Ensemble-induced strong light-matter coupling of a single quantum emitter," Phys. Rev. Lett. **124**, 113602 (2020).

[36]D. Sidler, C. Schaefer, M. Ruggenthaler, and A. Rubio, "Polaritonic chemistry: Collective strong coupling implies strong local modification of chemical properties," J. Phys. Chem. Lett. **12**, 508–516 (2021).

[37]H. Spohn, *Dynamics of charged particles and their radiation field* (Cambridge university press, 2004).

[38]R. Jestädt, M. Ruggenthaler, M. J. Oliveira, A. Rubio, and H. Appel, "Light-matter interactions within the ehrenfest–maxwell–pauli–kohn–sham framework: fundamentals, implementation, and nano-optical applications," Adv. Phys. **68**, 225–333 (2019).

[39]I. V. Tokatly, "Time-dependent density functional theory for many-electron systems interacting with cavity photons," Phys. Rev. Lett. **110**, 233001 (2013).

[40]S. Y. Buhmann, *Dispersion Forces I: Macroscopic quantum electrodynamics and ground-state Casimir, Casimir–Polder and van der Waals forces*, Vol. 247 (Springer, 2013).

[41]M. K. Svendsen, K. S. Thygesen, A. Rubio, and J. Flick, "Molecules in real cavities with quantum electroynamical density functional theory," arXiv preprint arXiv:2305.02391 (2023).

[42]J. Flick, M. Ruggenthaler, H. Appel, and A. Rubio, "Atoms and molecules in cavities, from weak to strong coupling in quantum-electrodynamics (qed) chemistry," Proc. Natl. Acad. Sci. U.S.A. **114**, 3026–3034 (2017).

[43]J. Flick, H. Appel, M. Ruggenthaler, and A. Rubio, "Cavity born–oppenheimer approximation for correlated electron–nuclear-photon systems," J. Chem. Theory Comput. **13**, 1616–1625 (2017).

[44]J. Flick and P. Narang, "Cavity-correlated electron-nuclear dynamics from first principles," Phys. Rev. Lett. **121**, 113002 (2018).

[45]S. Mukamel, *Principles of nonlinear optical spectroscopy*, 6 (Oxford University Press, USA, 1995).

[46]V. Rokaj, D. M. Welakuh, M. Ruggenthaler, and A. Rubio, "Light–matter interaction in the long-wavelength limit: no ground-state without dipole self-energy," Journal of Physics B: Atomic, Molecular and Optical Physics **51**, 034005 (2018).

[47]C. Schäfer, M. Ruggenthaler, V. Rokaj, and A. Rubio, "Relevance of the quadratic diamagnetic and self-polarization terms in cavity quantum electrodynamics," ACS Photonics **7**, 975–990 (2020).

[48]J. Hutter, "Car–parrinello molecular dynamics," Wiley Interdiscip. Rev. Comput. Mol. Sci. **2**, 604–612 (2012).

[49]S. Shin and H. Metiu, "Nonadiabatic effects on the charge transfer rate constant: A numerical study of a simple model system," J. Chem. Phys. **102**, 9285–9295 (1995).

[50]J. J. Maki, M. S. Malcuit, J. E. Sipe, and R. W. Boyd, "Linear and nonlinear optical measurements of the lorentz local field," Phys. Rev. Lett. **67**, 972–975 (1991).

[51]J. Javanainen, J. Ruostekoski, Y. Li, and S.-M. Yoo, "Shifts of a resonance line in a dense atomic sample," Phys. Rev. Lett. **112**, 113603 (2014).

[52]A. Thomas, J. George, A. Shalabney, M. Dryzhakov, S. J. Varma, J. Moran, T. Chervy, X. Zhong, E. Devaux, C. Genet, *et al.*, "Ground-state chemical reactivity under vibrational coupling to the vacuum electromagnetic field," Angew. Chem. **128**, 11634–11638 (2016).

[53]C. A. Ullrich, "Time-dependent density-functional theory: concepts and applications," (2011).

[54]M. A. Marques, N. T. Maitra, F. M. Nogueira, E. K. Gross, and A. Rubio, *Fundamentals of time-dependent density functional theory*, Vol. 837 (Springer, 2012).

[55]M. Ruggenthaler, J. Flick, C. Pellegrini, H. Appel, I. V. Tokatly, and A. Rubio, "Quantum-electrodynamical density-functional theory: Bridging quantum optics and electronic-structure theory," Phys. Rev. A **90**, 012508 (2014).

[56]H. L. Luk, J. Feist, J. J. Toppari, and G. Groenhof, "Multiscale molecular dynamics simulations of polaritonic chemistry," J. Chem. Theory Comput. **13**, 4324–4335 (2017).

[57]H.-T. Chen, T. E. Li, M. Sukharev, A. Nitzan, and J. E. Subotnik, "Ehrenfest+r dynamics. i. a mixed quantum–classical electrodynamics simulation of spontaneous emission," J. Chem. Phys. **150**, 044102 (2019), https://doi.org/10.1063/1.5057365.

[58]H.-T. Chen, T. E. Li, M. Sukharev, A. Nitzan, and J. E. Subotnik, "Ehrenfest+r dynamics. ii. a semiclassical qed framework for raman scattering," J. Chem. Phys. **150**, 044103 (2019), https://doi.org/10.1063/1.5057366.

[59]D. Sidler, M. Ruggenthaler, H. Appel, and A. Rubio, "Chemistry in quantum cavities: Exact results, the impact of thermal velocities, and modified dissociation," J. Phys. Chem. Lett. **11**, 7525–7530 (2020).

[60]T. S. Haugland, E. Ronca, E. F. Kjønstad, A. Rubio, and H. Koch, "Coupled cluster theory for molecular polaritons: Changing ground and excited states," Phys. Rev. X **10**, 041043 (2020).

[61]T. Schnappinger and M. Kowalewski, "Nonadiabatic wave packet dynamics with ab initio cavity-born-oppenheimer potential energy surfaces," J. Chem. Theory Comput. **19**, 460–471 (2023).

[62]C. Schäfer, "Polaritonic chemistry from first principles via embedding radiation reaction," J. Phys. Chem. Lett. **13**, 6905–6911 (2022).

[63]M. Gussoni, M. Rui, and G. Zerbi, "Electronic and relaxation contribution to linear molecular polarizability. an analysis of the experimental values," Journal of Molecular Structure **447**, 163–215 (1998).

arXiv:2306.06004v2 [quant-ph] 22 Jun 2023

SUPPORTING INFORMATION: Unraveling a cavity induced molecular polarization mechanism from collective vibrational strong coupling

Dominik Sidler,[1,2] Thomas Schnappinger,[3] Anatoly Obzhirov,[1,2] Michael Ruggenthaler,[1,2] Markus Kowalewski,[3] and Angel Rubio[1,2,4,5]

[1)]*Max Planck Institute for the Structure and Dynamics of Matter and Center for Free-Electron Laser Science, Luruper Chaussee 149, 22761 Hamburg, Germany*

[2)]*The Hamburg Center for Ultrafast Imaging, Luruper Chaussee 149, 22761 Hamburg, Germany*

[3)]*Department of Physics, Stockholm University, AlbaNova University Center, SE-106 91 Stockholm, Sweden*

[4)]*Center for Computational Quantum Physics, Flatiron Institute, 162 5th Avenue, New York, NY 10010, USA*

[5)]*Nano-Bio Spectroscopy Group, University of the Basque Country (UPV/EHU), 20018 San Sebastián, Spain*

(*Electronic mail: angel.rubio@mpsd.mpg.de)

(*Electronic mail: markus.kowalewski@fysik.su.se)

(*Electronic mail: michael.ruggenthaler@mpsd.mpg.de)

(*Electronic mail: anatoly.obzhirov@mpsd.mpg.de)

(*Electronic mail: thomas.schnappinger@fysik.su.se)

(*Electronic mail: dsidler@mpsd.mpg.de)

(Dated: 23 June 2023)

I. CAVITY HARTREE EQUATIONS

In order to derive the cavity Hartree Eq. (3) in the letter, we start from the fully quantize Pauli-Fierz Hamiltonian given in Eq. (1) and apply a Born-Huang expansion to the total wave function following Ref. 1. In more detail, we separate the electronic degrees of freedom from the nuclear-photonic degrees of freedom yielding $\Psi_i = \sum_{j=1}^{\infty} \gamma_{ij}(\mathbf{R},q)\psi_j(\mathbf{r},\mathbf{R},q)$ that solves $\hat{H}\Psi_i = E_i\Psi_i$. Afterwards, we employ the cavity Born-Oppenheimer approximation in its simplest form, which assumes a classical treatment of the nuclear and photonic degrees of freedom.[1] This approximation accurately describes cavity mediated ground-state chemistry, i.e. when the cavity is tuned on the vibrational degrees of freedom and the electronic excitations are sufficiently separated energetically such that non-adiabatic couplings (e.g. conical intersections) are negligible.[1–5] Consequently, the system separates into an electronic subsystem $\hat{H}^{\mathrm{e}}$, which parametrically depends on the modes $\underline{q}$ and the nuclear position vector $\underline{\boldsymbol{R}}$, and into a nuclear-photonic part $\hat{H}^{\mathrm{npt}}$. Following the notation of the letter, the resulting electronic Hamiltonian operator becomes

$$\hat{H}^{\mathrm{e}} \;:=\; \hat{H}^{\mathrm{e}}_{\mathrm{m}} + \sum_{\alpha=1}^{M}\left(\frac{1}{2}\hat{x}_\alpha^2 + \hat{x}_\alpha X_\alpha - \omega_\alpha \hat{x}_\alpha q_\alpha\right), \tag{S1}$$

which depends parametrically on $\mathbf{R}, q_\alpha$. The corresponding groundstate Hamiltonian of the coupled nuclear-photon degrees of freedom is given by,

$$H^{\mathrm{npt}} \;:=\; H^{\mathrm{n}}_{\mathrm{m}} + \sum_{\alpha=1}^{M}\left(\frac{p_\alpha^2}{2} + \frac{\omega_\alpha^2}{2}\left(q_\alpha - \frac{X_\alpha}{\omega_\alpha}\right)^2 + \langle\psi_0|\hat{H}_e(\underline{\mathbf{R}},\underline{q})\,|\psi_0\rangle\right). \tag{S2}$$

In a next step, we demonstrate that the groundstate many-electron eigenvalue problem imposed by $\hat{H}^{\mathrm{e}}$ can be solved exactly in the dilute limit by a simple Hartree product ansatz. To show this, we start from a Hartree-Fock mean-field Ansatz given in Eq. (2) of the letter to solve for $\varepsilon_0 = \min E_{HF} = \min\langle\psi_{HF}|\hat{H}^{\mathrm{e}}|\psi_{HF}\rangle$. The resulting Hartree-Fock energy can then simply be written as,

$$\begin{aligned} E_{HF} \;=\; & \sum_{n=1}^{N}\langle\chi_n|\hat{H}^{\mathrm{e}}_n + \sum_{\alpha=1}^{M}\left[\frac{1}{2}\hat{x}_{n,\alpha}^2 + \hat{x}_{n,\alpha}X_\alpha - \omega_\alpha\hat{x}_{n,\alpha}q_\alpha\right]|\chi_n\rangle \\ & + \frac{1}{2}\sum_{n,m}^{N}\sum_{\alpha=1}^{M}\langle\chi_n|\hat{x}_{n,\alpha}|\chi_n\rangle\langle\chi_m|\hat{x}_{m,\alpha}|\chi_m\rangle - \cancel{\frac{1}{2}\sum_{n,m}^{N}\sum_{\alpha=1}^{M}\langle\chi_n|\hat{x}_{n,\alpha}|\chi_m\rangle\langle\chi_m|\hat{x}_{m,\alpha}|\chi_n\rangle}, \end{aligned} \tag{S3}$$

where the cavity-induced electron-electron exchange cancel in the last terms, except for $n = m$, due to the dilute limit assumption, i.e, the electronic structure of different molecules must not overlap. Notice that for non-overlapping electronic structures the inter-molecular exchange and correlation energies are zero, and if the molecules are far apart also the Coulomb Hartree energy

goes to zero. Therefore we have $\hat{H}^{\mathrm{e}}_{\mathrm{m}}$ simplifies to $\hat{H}^{\mathrm{e}}_{\mathrm{m}} = \sum_{n=1}^{N} \hat{H}^{\mathrm{e}}_{n}$ in Eq. (S3). Consequently, our mean-field ansatz becomes exact in the dilute limit. However, the exact solution of the local bare matter problem, i.e., finding accurate eigenfunctions of $\hat{H}^{\mathrm{e}}_{n}$, may itself be a highly non-trivial problem that requires to consider the intra-molecular correlations with computationally expensive post Hartree-Fock methods. From Eq. (S3) we find the resulting Hartree equations for the n-th orbital upon variation of the orbitals χ as presented in Eq. (3) of the letter. Orthogonality conditions $\langle \chi_n | \chi_m \rangle = \delta_{nm}$ are automatically obeyed, i.e., our orbitals are automatically canonical, since we assume non overlapping orbitals. Eventually, we are ready to perform an ab-initio molecular dynamics simulation on the exactly dressed ground-state potential energy surface in classical canonical equilibrium by time-propagation of the standard Langevin equations of motion as given in Eqs. (6) and (7) of the letter. For the force calculation, we use that the Hellmann-Feynman theorem applies for the variational cavity Hartree eigenvalue problem, provided that the local eigenvalue problem of the n-th molcecule can be solved with a variational method (as we do for the Shin-Metiu molecule by exact diagonalization below).

II. CAVITY AB-INITIO MOLECULAR DYNAMICS FOR RANDOM ORIENTED SHIN-METIU MOLECULES

To mimic the impact of rotational molecular disorder on collective vibrational strong couplig, we simulated rotational molecular motion at finite temperature by an overdamped rotational Langevin equation, i.b. by rotational Brownian motion. This can efficiently be done for 1D Shin-Metiu molecules by introducing a time-dependent coupling constant

$$\lambda_{\alpha,n}(t) = \boldsymbol{\lambda}_{\alpha} \cdot \mathbf{n}_n(t), \tag{S4}$$

for each individual molecule n. We have assumed a cavity polarization along the z-axis, i.e., $\boldsymbol{\lambda}_{\alpha} = \lambda_{\alpha} \mathbf{e}_z$ and that the 1D molecule should be aligned in 3D along the $\mathbf{n}_n(t)$-direction. Notice that there is no feedback from the molecular and/or cavity state onto the normalized orientation $\mathbf{n}_n(t)$. In other words, we assume in the following that the rotational motion is solely determined by the rotational Debey relaxation time $\tau_R = 2\pi/\omega_R$, which we will choose considerably smaller than the timescale of the nuclear vibrations (off-resonant with respect to the tuning of the cavity). However, the slowly changing random molecular orientation, will certainly influence the collective strong coupling effects between the molecules and the cavity. To mimic random rotational motion

by $\mathbf{n}_n(t)$ the rotational Langevin equation in the overdamped limit can be used, i.e., as,[6,7]

$$\frac{d\boldsymbol{n}_n(t)}{dt} = \sqrt{\tau_R}\boldsymbol{S}_n(t) \times \boldsymbol{n}_n(t) \tag{S5}$$

with Debye relaxation time $\tau_R = 2k_BT/\eta_R$ and unbiased, delta-correlated Gaussian noise sources $\boldsymbol{S}(t)$. The rotational friction coefficient is labeled by η_R. This first order stochastic PDE is propagated numerically using forward Euler method in a similar spirit to Ref. 8, for which we yield

$$\boldsymbol{n}_{n,t+\Delta t} = \frac{\boldsymbol{n}_{n,t}}{|\boldsymbol{n}_{n,t}|} + \sqrt{\Delta t\,\tau_R}\boldsymbol{S}_{n,t} \times \frac{\boldsymbol{n}_{n,t}}{|\boldsymbol{n}_{n,t}|}. \tag{S6}$$

and exact normalisation is imposed at every time-step. Eqs. (S4) and (S6) then allow the simple simulation of vibrational strong coupling for a randomly oriented molecular ensemble within our self-consistent cBOA approach.

III. SIMULATION SETUP

A. Shin-Metiu molecular dynamics simulation

The Hamiltonian operator $\hat{H}_{\mathrm{SM}}$ of the n-th Shin-Metiu molecule is given by,[9,10]

$$\begin{aligned}\hat{H}_n \;=\; & \frac{\hat{P}^2}{2M} + \frac{\hat{p}^2}{2} + \frac{1}{|L/2-\hat{R}|} + \frac{1}{|L/2+\hat{R}|} \\ & - \frac{\mathrm{erf}(|\hat{R}-\hat{r}|/R_f)}{|\hat{R}-\hat{r}|} - \frac{\mathrm{erf}(|\hat{r}-L/2|/R_r)}{|\hat{r}-L/2|} - \frac{\mathrm{erf}(|\hat{r}+L/2|/R_l)}{|\hat{r}+L/2|}.\end{aligned} \tag{S7}$$

We have used atomic units throughout our calculations with $R_f = R_l = R_r = 1.511$ and $L = 9.45$. We chose the proton mass $M = 1836$ for the moving nuclei with positive unit charge and $m = 1$ for the electron with negative unit charge. For the 1D electron, we chose a converged grid basis set representation with 41 equidistant grid points and a grid spacing of 0.8. Notice that having a large enough basis set for the electrons is pivotal to resolve local polarization effects.[11] The cavity Hartree equations were minimized self-consistently until converging the total electronic ensemble energy up to $\Delta E < 1 \times 10^{-7}$. The classical Langevin equations of motion were propagated numerically using the scheme of Ref. 12 with a time step $\delta t = 50$. Trajectories were simulated over 2000 time-steps to evaluate the local polarization effects and for 50000 time-steps for the spectra calculations. Nuclei were initialized randomly distributed in the vicinity of the ground-state. Thermostating parameters were set to $k_BT = 0.5 \times 10^{-3}$ with low friction coefficient $\gamma = 0.3 \times 10^{-5}$ (underdamped regime). In case of randomly oriented molecules, the Debye relaxation time was

set to $\tau_R = 0.5 \times 10^{-5}$. Notice that the parametrization of the Shin-Metiu molecule and the temperature was chosen such that non-adiabatic coupling effects should not play a role, i.e., the ground-state cBOA approximation is valid. Furthermore, the temperature was chosen small enough that the thermal broadening does not interfere with our spectral interpretation. In addition, no chemical reaction occurs at such low temperatures on the chosen time-scale (no proton transfer between the two energy minima of the Shin-Metiu molecule). The impact of local polarization effects on chemical reaction rates will be the focus of future work instead.

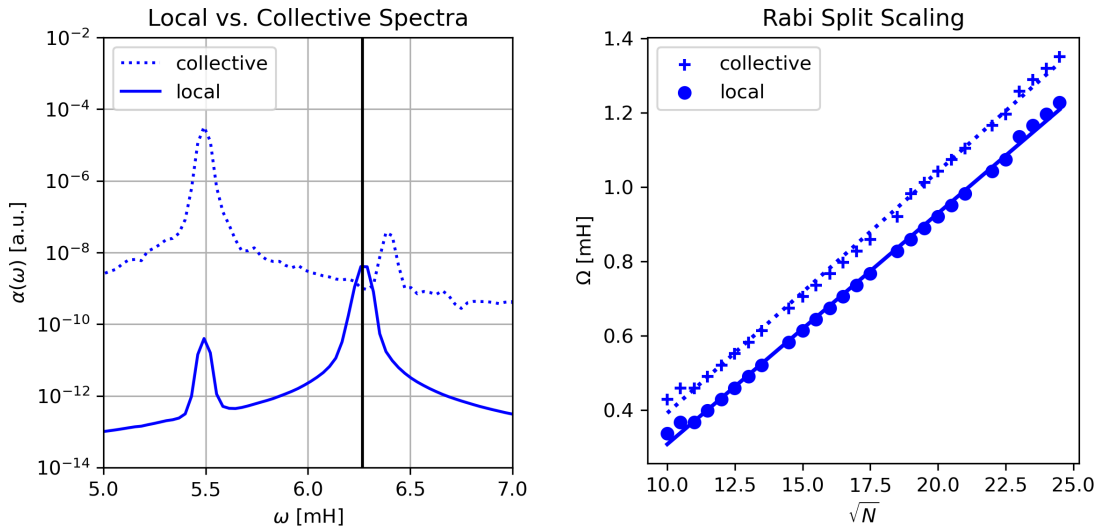
The vibrational absorption spectra was calculated using the power spectra method in Ref. 13 with a Blackman filter window[14] averaged over 33 overlapping trajectory windows containing 4096 time steps, each of them shifted by $1/3$ of the window size. While for the global absorption spectrum the total dipole (electronic + nuclear contribution) were post-processed accordingly (doted lines), we did the same for each individual molecular dipole in case of the local spectra calculation instead. Afterwards, the summation over all local spectra was taken yielding the bold lines in the spectral figures.

Supplementary simulation results for aligned Shin-Metiu molecules (spectra, Rabi-split scaling and local polarizations) are shown in Figs. S1 and S2.

B. Ensembles of HF molecules and Ne atoms

The cBOA Hartree-Fock method and corresponding analytic nuclear gradients were implemented in the Psi4NumPy environment[15], which is an extension of the PSI4[16] electronic structure package. All calculations were performed using the aug-cc-pVDZ basis set[17] and the geometry of the isolated single HF molecule is optimized at the Hartree-Fock level of theory. Note that we have not reoptimized the geometries of the molecular systems in the cavity; as such, our calculations do not account for any geometric relaxation effects stemming from the presence of the cavity. In all cavity Hartree-Fock calculations performed in this work, we consider a single-mode and non-lossy cavity. The fundamental cavity frequency ω_α is tuned to the first vibrational mode of the uncoupled HF at 20.35 [mH].

For the molecular ensembles studied, the optimized structure of a single HF molecule is replicated N times. All these replicas are separated by 800 Å and placed inside a cavity. All individual molecular dipole moments are aligned with the cavity polarization axes, and the zero transversal electric field condition is satisfied for the whole ensemble. The same distance of 800 Å is used



(a) (b)

FIG. S1: (a) Vibrational absorption spectra $\alpha(\omega)$ for 900 aligned Shin-Metiu molecules under collective vibrational strong coupling similar to the random oriented molecules shown in the letter. The cavity is again tuned on the first vibrational mode of the uncoupled molecule at $\omega_\alpha = 6.27$ [mH] (black vertical line). However, the coupling is reduce to $\lambda_\alpha = 0.00425$ in order to achieve a Rabi splitting of similar magnitude. We find qualitative identical results for the aligned molecules as for the random oriented setup, i.e. a de-tuning of the cavity to lower frequencies in combination with a locally populated lower polaritonic state.
(b) The collective $\sqrt{N}$-scaling law of the Rabi splitting remains preserved, when solving the self-consistently the coupled electronic problem for the molecules under vibrational strong coupling. Similarly, the observed local splitting follows the same $\sqrt{N}$-scaling law, where we defined the splitting between (local) lower polariton and the dark states located at ω_α. This suggests that local strong coupling can be increased by collectively enhancement of the coupling. Small discrete patterns in the data emerge from finite spectral resolution of the discrete Fourier transformation applied to dipole trajectories of finite length.

for the small ensembles of neon atoms. The vibrational spectra for the cavity-coupled ensembles are calculated in the harmonic approximation using numerical second derivatives of the cavity Hartree-Fock energy. All calculations were performed in a reproducible environment using the Nix package manager (nixpkgs, 22.11, commit 594ef126) in combination with NixOS-QChem (commit f5dad404).[18]

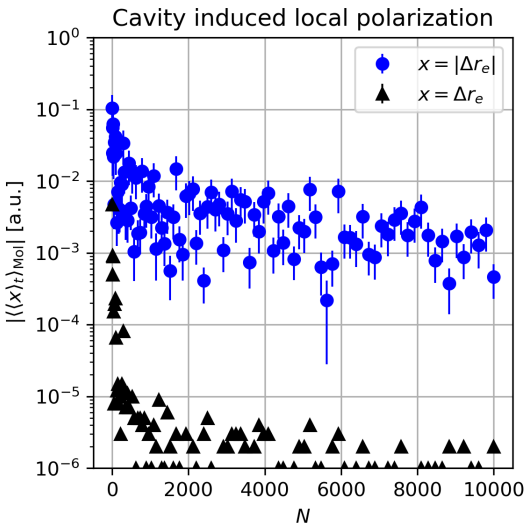


FIG. S2: Statistical evaluation of the electronic polarization $\Delta r_n(t) = \langle \hat{r}_n \rangle_\lambda - \langle \hat{r}_n \rangle_{\lambda=0}$ of the n-th molecule with respect to the bare molecule Shin-Metiu molecule in canonical equilibrium at $k_B T = 0.5$ [mH] for aligned molecules. The Rabi-splitting was kept constant when increasing the number of molecules by choosing a re-scaled $\lambda_\alpha(N) = 0.256/\sqrt{2N}$. By monitoring $|\Delta r_n|$ (blue dots), we observe qualitatively similar results comparing with the random oriented molecules. The simulations suggest a non-zero saturation of the cavity induced local polarizations in the large N limit, where the standard deviations with respect to different molecules are displayed by vertical blue lines. At the same time, the total polarization of the ensemble, which is related to Δr_n (black triangle), quickly approaches zero (exactly zero when averaging over longer time-scales), since the cavity cannot induce a non-zero ensemble polarization in thermal equilibrium. Consequently, our simulations suggest that cavity induced local strong coupling effects persist in the thermodynamic limit $(N \to \infty)$ of a molecular ensemble under collective vibrational strong coupling. In other words, the self-consistent treatment is decisive to describe ground-state polaritonic chemistry accurately for collectively coupled molecular ensembles.

Supplementary simulation results for the vibrational absorption spectra of the molecular ensembles are shown in Fig. S3.

Local energy modifications for the ensembles of neon atoms are shown in Fig. S4. Since atoms do not have a permanent dipole moment, the energy contribution of the cavity-induced photon displacement $\hat{\boldsymbol{D}}$ and the dipole-dipole interaction term V_{dd} are exactly zero, see Fig. S4 b) and d). Only the local cavity-induced polarization, see (Fig. S4 c), give rise to a non-zero contribution to

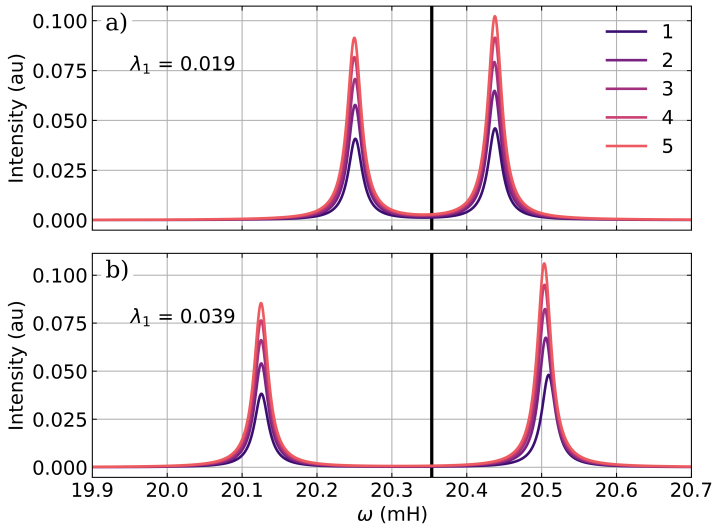


FIG. S3: Vibrational absorption spectra in the harmonic approximation for a few perfectly parallel aligned HF molecules under collective vibrational strong coupling. The number of molecules is color coded. The cavity is tuned to the first vibrational mode of the uncoupled HF molecule at $\omega_\alpha = 20.35$ [mH] (black vertical line) with unscaled coupling strength of a) $\lambda_1 = 0.019$ and b) $\lambda_1 = 0.039$.

the locale energy (see Fig. S4 a)) for the investigated ensemble sizes. However, this contribution decays with $\frac{1}{N}$ and is negligible in the large-N limit.

REFERENCES

[1]J. Flick, H. Appel, M. Ruggenthaler, and A. Rubio, "Cavity born–oppenheimer approximation for correlated electron–nuclear-photon systems," J. Chem. Theory Comput. **13**, 1616–1625 (2017).

[2]D. Sidler, M. Ruggenthaler, C. Schaefer, E. Ronca, and A. Rubio, "A perspective on ab initio modeling of polaritonic chemistry: The role of non-equilibrium effects and quantum collectivity," J. Chem. Phys. **156** (2022), 10.1063/5.0094956, 230901.

[3]M. Ruggenthaler, D. Sidler, and A. Rubio, "Understanding polaritonic chemistry from ab initio quantum electrodynamics," arXiv preprint arXiv:2211.04241 (2022).

[4]T. Schnappinger and M. Kowalewski, "Nonadiabatic wave packet dynamics with ab initio cavity-born-oppenheimer potential energy surfaces," J. Chem. Theory Comput. **19**, 460–471 (2023).

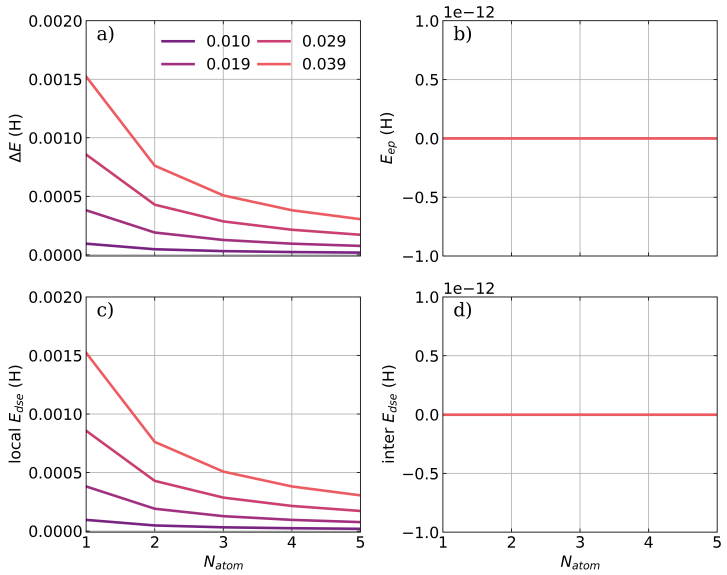


FIG. S4: Influence of the cavity interaction on an individual neon atom in ensembles of different size. a) The total energy change with respect to the cavity free situation, b) the local contribution of the cavity-induced photon displacement E_{ep}, c) the local cavity induced polarization contribution E_{dse} and d) the dipole-dipole interaction term V_{dd} as a function of N_{atom}. A cavity frequency ω_α of 20.35 [mH] is used. The value of the unscaled coupling strength λ_1 is increased from 0.010 to 0.039 (color coded).

[5]E. W. Fischer and P. Saalfrank, "Vibro-Polaritonic chemistry beyond the cavity Born-Oppenheimer approximation and the role of Electron-Photon correlation," (2023), arXiv:2305.11153 [physics.chem-ph].

[6]R. M. Mazo, *Brownian motion: fluctuations, dynamics, and applications*, Vol. 112 (OUP Oxford, 2008).

[7]R. Marino, R. Eichhorn, and E. Aurell, "Entropy production of a brownian ellipsoid in the overdamped limit," Physical Review E **93**, 012132 (2016).

[8]G. Volpe and G. Volpe, "Simulation of a brownian particle in an optical trap," American Journal of Physics **81**, 224–230 (2013).

[9]S. Shin and H. Metiu, "Nonadiabatic effects on the charge transfer rate constant: A numerical study of a simple model system," J. Chem. Phys. **102**, 9285–9295 (1995).

[10]G. Albareda, H. Appel, I. Franco, A. Abedi, and A. Rubio, "Correlated electron-nuclear dynamics with conditional wave functions," Phys. Rev. Lett. **113**, 083003 (2014).

[11]J. Yang, Q. Ou, Z. Pei, H. Wang, B. Weng, Z. Shuai, K. Mullen, and Y. Shao, "Quantum-electrodynamical time-dependent density functional theory within gaussian atomic basis," The Journal of Chemical Physics **155**, 064107 (2021).

[12]G. Bussi and M. Parrinello, "Accurate sampling using langevin dynamics," Physical Review E **75**, 056707 (2007).

[13]P. H. Berens and K. R. Wilson, "Molecular dynamics and spectra. I. Diatomic rotation and vibration," J. Chem. Phys. **74**, 4872–4882 (1981).

[14]R. B. Blackman and J. W. Tukey, "The measurement of power spectra from the point of view of communications engineering—part i," Bell System Technical Journal **37**, 185–282 (1958).

[15]D. G. Smith, L. A. Burns, D. A. Sirianni, D. R. Nascimento, A. Kumar, A. M. James, J. B. Schriber, T. Zhang, B. Zhang, A. S. Abbott, *et al.*, "Psi4numpy: An interactive quantum chemistry programming environment for reference implementations and rapid development," Journal of chemical theory and computation **14**, 3504–3511 (2018).

[16]D. G. Smith, L. A. Burns, A. C. Simmonett, R. M. Parrish, M. C. Schieber, R. Galvelis, P. Kraus, H. Kruse, R. Di Remigio, A. Alenaizan, *et al.*, "Psi4 1.4: Open-source software for high-throughput quantum chemistry," The Journal of chemical physics **152** (2020).

[17]R. A. Kendall, T. H. Dunning, and R. J. Harrison, "Electron affinities of the first-row atoms revisited. systematic basis sets and wave functions," The Journal of chemical physics **96**, 6796–6806 (1992).

[18]M. Kowalewski and P. Seeber, "Sustainable packaging of quantum chemistry software with the nix package manager," Int. J. Quant. Chem. **122**, e26872 (2022).