Polariton relaxation under vibrational strong coupling: Comparing cavity molecular dynamics simulations against Fermi’s golden rule rate

Cite as: J. Chem. Phys. 156, 134106 (2022); https://doi.org/10.1063/5.0079784
Submitted: 24 November 2021 • Accepted: 11 March 2022 • Published Online: 04 April 2022

Tao E. Li, Abraham Nitzan and Joseph E. Subotnik
Polariton relaxation under vibrational strong coupling: Comparing cavity molecular dynamics simulations against Fermi’s golden rule rate

Tao E. Li,1,a) Abraham Nitzan,1,2,b) and Joseph E. Subotnik1,c)

AFFILIATIONS
1 Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA
2 School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel

a) Author to whom correspondence should be addressed: taoli@sas.upenn.edu
b) Electronic mail: anitzan@sas.upenn.edu
c) Electronic mail: subotnik@sas.upenn.edu

ABSTRACT
Under vibrational strong coupling (VSC), the formation of molecular polaritons may significantly modify the photo-induced or thermal properties of molecules. In an effort to understand these intriguing modifications, both experimental and theoretical studies have focused on the ultrafast dynamics of vibrational polaritons. Here, following our recent work [Li et al., J. Chem. Phys. 154, 094124 (2021)], we systematically study the mechanism of polariton relaxation for liquid CO2 under a weak external pumping. Classical cavity molecular dynamics (CavMD) simulations confirm that polariton relaxation results from the combined effects of (i) cavity loss through the photonic component and (ii) dephasing of the bright-mode component to vibrational dark modes as mediated by intermolecular interactions. The latter polaritonic dephasing rate is proportional to the product of the weight of the bright mode in the polariton wave function and the spectral overlap between the polariton and dark modes. Both these factors are sensitive to parameters such as the Rabi splitting and cavity mode detuning. Compared to a Fermi’s golden rule calculation based on a tight-binding harmonic model, CavMD yields a similar parameter dependence for the upper polariton relaxation lifetime but sometimes a modest disagreement for the lower polariton. We suggest that this disagreement results from polariton-enhanced molecular nonlinear absorption due to molecular anharmonicity, which is not included in our analytical model. We also summarize recent progress on probing nonreactive VSC dynamics with CavMD.

Published under an exclusive license by AIP Publishing. https://doi.org/10.1063/5.0079784

I. INTRODUCTION

Strong light–matter interactions provide a novel approach toward modifying molecular properties by forming hybrid light–matter states—known as polaritons.1–4 In the past decade, vibrational strong coupling (VSC) was experimentally observed when a large number of molecules in the condensed phase were placed in a Fabry–Pérot microcavity and a vibrational mode of molecules formed strong coupling with a cavity mode.5 Under VSC, one of the most intriguing experimental observations is the possibility of modifying thermally activated ground-state chemical reactions through such a Fabry–Pérot microcavity and without a direct external pumping.1 Inspired by this seminal observation1 from the Ebbesen group, intensive experimental and theoretical attempts have now been made to understand VSC-related chemistry. From an experimental point of view, there has been an extensive exploration of VSC catalytic effects in different types of chemical reactions,14–20 and the use of VSC to alter other molecular properties in the absence of an external laser pumping21 has also been investigated; at the same time, spectroscopists have also focused on the ultrafast dynamics of vibrational polaritons by pump–probe22–24 and two-dimensional infrared (IR)25–30 spectroscopies. From a theoretical point of view, while the detailed mechanism of “VSC catalysis” is still not well understood,31–39 the current models of ultrafast polariton dynamics appear to be largely consistent with observations.
As far as the ultrafast dynamics of vibrational polaritons are concerned, recent experiments have emphasized the complicated interaction between polaritons and vibrational dark modes after the polariton pumping with an external laser field; see Ref. 7 for a recent review. Two of the most nontrivial observations include (i) polariton mediated intermolecular vibrational energy transfer between two molecular species after the upper polariton (UP) pumping and (ii) polariton-enhanced molecular nonlinear absorption after the lower polariton (LP) pumping. While there have been a few theory papers on polariton relaxation based on analytic models and realistic modeling, a systematic study of vibrational polariton relaxation when realistic molecules are considered is still unavailable, which will be the focus of this paper.

Our approach for studying polariton relaxation is classical cavity molecular dynamics (CavMD) simulations, in which both the cavity modes and molecular vibrations are treated classically and move along an electronic ground-state surface. Compared with standard theories for strong light–matter interactions, CavMD has two advantages: the ability to (i) describe realistic molecules and (ii) treat a very large number of molecules coupled to the cavity with an affordable computational cost. These advantages allow CavMD to identify nontrivial VSC effects beyond, e.g., the Tavis–Cummings Hamiltonian or the coupled oscillator model. The latter is necessary because, to date, most VSC experiments were performed with Fabry–Pérot cavities, in which the cavity volume is \( \lambda^3 \) (where \( \lambda \) denotes the wavelength of the cavity mode) and the corresponding molecular number is very large (say, \( N \sim 10^{10} \)).

We note that recent considerations of the role of VSC played by symmetry and selection rules can, in principle, be studied by CavMD. However, we do not address these issues here. We also emphasize that CavMD is a classical approximation, so this approach may fail if any quantum effect (from either the nuclei or cavity photons) dominates the VSC effect (which is largely unexplored). In order to understand the applicability of CavMD, it is necessary to benchmark the performance of CavMD under various situations against experiments or analytic models; see the next paragraph and also Fig. 1 for a summary. Following the method in Ref. 46, here we will focus on using CavMD to describe polariton relaxation when the polariton is weakly pumped by an external laser field. In the weak pumping limit (which is also the condition for most ultrafast experiments), we will compare the CavMD results with a quantum model where the polariton relaxation lifetime can be calculated by a Fermi’s golden rule (FGR) rate. Together with an extensive parameter dependence study of polariton relaxation, this comparison will not only serve as an important performance benchmark of CavMD but also facilitate a mechanistic understanding of vibrational polariton relaxation.

Before focusing on the details of vibrational polariton relaxation, as shown in Fig. 1, let us summarize some of the most important observations by CavMD from a series of recent publications (including this work) and the connection to different experiments and theories.

(a) Asymmetric Rabi splitting from equilibrium CavMD simulations. We have included the self-dipole term in CavMD, a direct consequence of which is a renormalized vibrational frequency inside the cavity and the asymmetry of the Rabi splitting even when the cavity mode
is at resonance with the bare vibrational mode outside the
cavity. For the linear IR spectrum of liquid water under VSC,
CavMD not only yields similar results as the coupled oscil-
lator model but also shows that the polaritonic line shape
is much smaller than the inhomogeneous broadening of the
water O–H peak. This result—which cannot be obtained
from the coupled oscillator model—agrees with an early the-
orical prediction\textsuperscript{13} and experimental observations for liquid
water VSC.\textsuperscript{14} This simulation also suggests that individual
molecular properties are not meaningfully modified under
VSC when thermal equilibrium is considered, suggesting a
nonequilibrium or quantum origin of “VSC catalysis.”

(b) Mechanism of vibrational polariton relaxation (this work).
Here, we will demonstrate that, for the UP, CavMD predicts
a similar parameter dependence for the UP lifetime as does
a FGR rate calculation based on a tight-binding harmonic
model. We also highlight the significance of the dephasing
process from the polariton to the dark modes due to the
spectral overlap between the polariton and dark modes; this
overlap can be controlled by the Rabi splitting and cavity
mode detuning. The results here validate the ability of the
CavMD simulation approach as far as the capacity to match
more conventional quantum optics approaches in polariton
physics.

(c) Polariton-enhanced molecular nonlinear absorption.\textsuperscript{46}
When twice the LP roughly matches the vibrational 0 \rightarrow 2
transition (due to molecular anharmonicity), CavMD shows
that strongly exciting the LP can directly transfer energy to
the second (2D) or higher excited states of vibrational dark
modes; at later times, this excess energy gradually transfers
to the first excited state of vibrational dark modes (1D)).
The delayed excitation of 1D states after the LP pumping
has been experimentally reported previously\textsuperscript{47} and a direct
observation of the initial pumping of 2D states has also
been shown recently. These experimental observations,
together with a quantum model study,\textsuperscript{48} appear to validate
our simulation results.

(d) Selectively exciting solute molecules via solvent polariton
pumping.\textsuperscript{3} Given the validity of the polariton-enhanced
molecular nonlinear absorption mechanism, CavMD shows
that, if the LP of the solvent molecules can support the
nonlinear transition of the solute (not the solvent) molecules
only (i.e., twice the solvent LP roughly matches the solute
0 \rightarrow 2 vibrational transition), pumping the solvent LP may
highly excite the solute molecules, leaving the solvent
molecules barely excited. This finding deserves experimental
exploration in the near future.

(e) Nonequilibrium dark-mode dynamics.\textsuperscript{53} For a small fraction
of hot CO\textsubscript{2} molecules immersed inside a CO\textsubscript{2} thermal bath,
in the absence of external pumping, the LP can be transiently
excited even when the molecular system size is large. The
transiently excited LP can accelerate vibrational relaxation of
the hot molecules and promote energy transfer to the ther-
mal molecules. For small-volume cavities ($N < 10^3$), the VSC
effect on the relaxation rate per molecule resonantly depends
on the cavity mode frequency; for cavities with larger vol-
umes, the VSC effect per molecule vanishes, despite the fact
that the transiently excited LP prefers to transfer energy to
the molecules at the tail of the energy distribution (which
may connect to a VSC+ catalytic effect). The fact that all VSC
effects on dark mode relaxation becomes vanishingly small
(per molecule) for large a cavity volume is consistent with a
recent experiment with Fabry–Pérot cavities.\textsuperscript{57}

We now turn to (b) above and in the rest of this paper focus
on investigating the mechanism of vibrational polariton relaxation.
This paper is organized as follows. In Sec. II, we introduce the FGR
calculation and CavMD simulations that we will employ in order
to describe the polariton relaxation lifetime. In Sec. III, we present
results. We conclude in Sec. IV.

II. METHODS

A. Model system and the FGR rate

The standard theory for describing strong light–matter inter-
actions in the collective regime is the Tavis–Cummings (TC)
Hamiltonian\textsuperscript{57,58}. In this model, a single cavity mode with frequen-
cy $\omega_0$, is coupled to $N$ identical two-level systems with transition
frequency $\omega_0$,

$$\hat{H} = \hbar \omega_0 \hat{a}^\dagger \hat{a} + \hbar \omega_0 \sum_{n=1}^{N} \sigma_+^{(n)} \sigma_-^{(n)} + \hbar g_0 \sum_{n=1}^{N} \left( \hat{a}^\dagger \sigma_+^{(n)} + \hat{a} \sigma_-^{(n)} \right).$$ \hspace{1cm} (1)

Here, $\hat{a}^\dagger$ and $\hat{a}$ denote the creation and annihilation operators for
the cavity photon; $\sigma_+^{(n)} \equiv |n\rangle\langle n+1|$ and $\sigma_-^{(n)} \equiv |n+1\rangle\langle n|$, where $|n\rangle$ and $|n+1\rangle$ denote the ground and excited state for the $n$th two-level
system; $g_0$ denotes the coupling constant between the cavity pho-
ton and each two-level system. In the light–matter coupling term
(the last term above), both the long-wave approximation and the
rotating-wave approximation have been taken.

For VSC, since high-frequency molecular vibrations can be
approximated as harmonic oscillators at and below room tem-
perature, we replace the two-level systems in Eq. (1) by quantum
harmonic oscillators (with the creation and annihilation operators
denoted by $b_n^\dagger$ and $b_n$) and obtain the following Hamiltonian:

$$\hat{H} = \hbar \omega_c \hat{a}^\dagger \hat{a} + \hbar \omega_0 \sum_{n=1}^{N} \hat{b}_n^\dagger \hat{b}_n + \hbar g_0 \sum_{n=1}^{N} (\hat{a}^\dagger \hat{b}_n + \hat{a} \hat{b}_n^\dagger).$$ \hspace{1cm} (2)

This model Hamiltonian serves as the starting point of our
derivation.

In the light–matter coupling term of Eq. (2), since the cavity
photon interacts with a symmetric combination of the molecular
operators only, one can introduce the bright-mode creation
and annihilation operators as follows:

$$\hat{B} = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} \hat{b}_n, \hspace{1cm} \hat{B}^\dagger = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} \hat{b}_n^\dagger.$$ \hspace{1cm} (3)

These operators correspond to a single collective mode of
motion for the entire molecular system, which is the bright
mode of the system (if all the harmonic oscillators are in their
ground states). The cavity Hamiltonian can be rewritten in ter-

J. Chem. Phys. 156, 134106 (2022); doi: 10.1063/5.0079784
Published under an exclusive license by AIP Publishing
All the other $N - 1$ linear combinations of the molecular operators are decoupled from the cavity mode and are called the dark modes,

$$\hat{D}_{\mu} = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{2\pi i n / N} \hat{b}_{\mu n},$$

$$\hat{D}_{\mu}' = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{2\pi i n / N} \hat{b}_{\mu n}'$$

Here, $\mu = 1, 2, \ldots, N - 1$ indexes the dark modes.

With the separation of bright and dark modes, the Hamiltonian in Eq. (2) becomes

$$\hat{H} = \hbar \omega_c \hat{a}^\dagger \hat{a} + \hbar \omega_0 \hat{B}^\dagger \hat{B} + \frac{1}{2} \hbar \Omega_N \left( \hat{a}^\dagger \hat{B} + \hat{a} \hat{B}^\dagger \right) + \hat{H}_D,$$  

where $\Omega_N \equiv 2 \sqrt{N} \delta_i$ and $\hat{H}_D$ is the Hamiltonian for the dark modes: $\hat{H}_D = \hbar \omega_0 \sum_{n=1}^{N} \hat{D}_{\mu n} \hat{D}_{\mu}^\dagger$. Equation (5) can be further diagonalized, which leads to the following Hamiltonian:

$$\hat{H} = \hbar \omega_c \hat{P}_B + \hbar \omega_0 \hat{P}_B^\dagger + \hbar \Omega_N \left( \hat{a}^\dagger \hat{B} + \hat{a} \hat{B}^\dagger \right) + \hat{H}_D.$$  

Here, the frequencies of the eigenstates are given as

$$\omega = \frac{1}{2} \left[ \omega_0 + \omega_c \pm \sqrt{\Omega_N^2 + (\omega_0 - \omega_c)^2} \right].$$

When the cavity photon and the bright mode are at resonance ($\omega_c = \omega_0$), the frequency difference between the two eigenstates is $\omega_0 - \omega_c$. Once $\Omega_N$ exceeds the linewidth of the bright mode (which can be measured from the linear spectrum of molecules outside the cavity) and the loss rate of the cavity (due to the imperfections in the cavity mirrors), a peak splitting can be measured from the linear spectrum of the coupled cavity molecular system. The peak splitting, which is called the collective Rabi splitting, is equal to $\Omega_N = 2 \sqrt{N} \delta_i$.

In Eq. (6), the creation and annihilation operators for the eigenstates ($\hat{P}_B$ and $\hat{P}_{B\dagger}$) are defined as linear combinations of the cavity photon and bright-mode operators,

$$\hat{P}_B = \hat{X}_B^{(n)} \hat{B} + \hat{X}_C^{(n)} \hat{a},$$

$$\hat{P}_{B\dagger} = \hat{X}_B^{(n)} \hat{B}^\dagger + \hat{X}_C^{(n)} \hat{a}^\dagger,$$  

where the coefficients are $\hat{X}_B^{(n)} = - \hat{X}_C^{(n)} = - \sin(\theta)$ and $\hat{X}_B^{(n)} = \hat{X}_C^{(n)} = \cos(\theta)$ and the mixing angle $\theta$ is $\theta = \frac{\pi}{4} \tan^{-1} \left( \frac{\Omega_N}{\omega_0 - \omega_c} \right)$. When a Rabi splitting is observed, the two eigenstates ($-\rho$ and $+\rho$) are called the lower polariton (LP) or upper (UP) polariton, respectively.

### 1. Calculating the polariton lifetime

In the absence of intermolecular interactions, as shown in Eq. (6), the polaritons are completely decoupled from the dark modes, so once the LP or UP is excited to the first excited state, the polaritonic decay rate $(1/\tau)$ should be simply a linear combination of the relaxation rates of the photonic and the molecular parts,

$$\frac{1}{\tau} = |X_B^{(n)}|^2 k_c + |X_B^{(n)}|^2 k_B.$$  

Here, $k_c$ denotes the cavity loss rate and $k_B$ denotes the relaxation rate of the bright state from the first excited to the ground state outside a cavity, which could be approximated as the linewidth of the vibrational peak from molecular linear IR spectroscopy outside the cavity (if the molecular system has no inhomogeneous broadening). Note that the bright-mode relaxation rate $k_B$ reflects both the radiative and non-radiative relaxation pathways, and the radiative relaxation contribution can be superradiant (meaning a $N$ dependence). For molecular vibrations, since the radiative relaxation rates (with a typical lifetime of seconds) are usually much slower than the non-radiative rates (with a typical lifetime from ns to ps), we will disregard the radiative relaxation contribution of $k_B.$

The rate equation in Eq. (9) has widely been known by the polariton community. For realistic molecular systems in the condensed phase, however, we need to consider another decay pathway of the polaritons. Since molecules do interact with each other, polaritons (which are partially composed of the molecular degrees of freedom) can interact with the dark modes through intermolecular interactions. Naturally, the interaction between polaritons and dark modes may introduce an additional dephasing pathway for the decay of polaritons.

In order to account for this additional dephasing process, on top of the standard polaritonic Hamiltonian in Eq. (6), we add a simple tight-binding intermolecular interaction between neighboring molecules,

$$\hat{V} = \frac{\hbar}{\sqrt{N}} \sum_{n=1}^{N} \sum_{\lambda=1}^{M_n} \left( \hat{b}_{\lambda n}^\dagger \hat{b}_{\lambda n} + \hat{b}_{\lambda n} \hat{b}_{\lambda n}^\dagger \right).$$

where $M_n$ denotes all the possible nearest neighbors (with a total number of $N_{nn}$) of molecule $n$ and $\Delta_n$ denotes the coupling strength between the nearest neighboring molecules. For different $n$, $\{\Delta_n\}$ are uncorrelated but should have similar magnitude. In Eq. (10), since the operators of each molecule can be expressed as linear combinations of the bright and dark modes, the interaction between bright (which contributes to the polaritons) and dark modes has been included. In order to better illustrate this point, if we consider only the bright-mode contribution of $\hat{b}_{\lambda n}$, i.e., $\hat{b}_{\lambda n} \sim \hat{B}/\sqrt{N} + \cdots$, we can approximate Eq. (10) as

$$\hat{V} = \frac{\hbar N_{nn}}{\sqrt{N}} \sum_{n=1}^{N} \Delta_n \left( \hat{b}_{\lambda n}^\dagger \hat{B} + \hat{b}_{\lambda n} \hat{B}^\dagger \right) + \cdots,$$  

where $\cdots$ represents the interaction between individual molecules (indexed by $n$) and the dark modes. For large $N$, since $\hat{b}_{\lambda n}$ ($\hat{b}_{\lambda n}^\dagger$) is predominately composed of the dark modes, Eq. (11) can be used to calculate the polaritonic dephasing rate to the dark modes.

We now calculate the dephasing rate from polaritons to vibrational dark modes with a FGR calculation,

$$\gamma = \sum \frac{2 \pi}{N} |V_{fi}|^2 \delta(\omega - \omega_f).$$  

Here, $i$ and $f$ denote the initial (polaritonic) and final (dark) states; $\delta(\omega - \omega_f)$ denotes the density of states (DOS) for state $f$; and $V_{fi} = (\langle f | V | i \rangle)$ denotes the transition matrix element, where we have defined $V$ in (11). By substituting $|i\rangle = \hat{P}_B |0\rangle$ (exciting a polariton)
and the definition of $\hat{p}_l^k$ in Eq. (8), we obtain the transition matrix element as
\[ V_{fi} = \langle f | \hat{V} | i \rangle = \frac{\hbar n_m \Delta \epsilon}{\sqrt{N}} X_k^{(B)}. \] (13)
Hence, the polaritonic dephasing rate becomes
\[ \gamma_s = \sum_{f=1}^{N} \frac{2}{N} \left( \frac{\hbar n_m \Delta \epsilon}{\sqrt{N}} X_k^{(B)} \right)^2 \delta(\omega - \omega_f) \]
\[ = 2\pi \Delta^2 |X_k^{(B)}|^2 f \rho_0(\omega). \] (14)
Here, we have defined $\Delta^2 \equiv \sum_{j=1}^{N} \hbar n_m \Delta \epsilon^2 \delta(\omega - \omega_f)/\sum_{j=1}^{N} \delta(\omega - \omega_f)$ to denote the average intermolecular coupling strength; $\rho_0(\omega) \equiv \frac{1}{\sqrt{2}} \sum_{j=1}^{N} \delta(\omega - \omega_f)$ denotes the DOS for the dark-mode manifold per molecule. Note that here we have assumed that polariton states are orthogonal to the individual molecular basis ({$\{b_n\}$}), which is valid in the limit of large $N$.

In the presence of disorder, the polariton is not an eigenstate of the Hamiltonian and has a finite experimental linewidth. In our calculation, we introduce a phenomenological DOS for the polariton to account for this width [$\rho_s(\omega)$, where $\int_0^{\infty} d\omega \rho_s(\omega) = 1$], so the polaritonic dephasing rate is further smeared out,
\[ \gamma_s = 2\pi \Delta^2 |X_k^{(B)}|^2 f, \] (15a)
where $f_s$ denotes the spectral overlap between the polariton and the dark modes,
\[ f_s \equiv \int_0^{\infty} d\omega \rho_s(\omega) \rho(\omega). \] (15b)
Equation (15) shows that the polaritonic dephasing rate is determined by three factors: the magnitude of intermolecular interactions ($\Delta^2$), the molecular weight of polaritons ($|X_k^{(B)}|^2$), and the spectral overlap between the polariton and dark modes ($f_s$). This equation is reminiscent of the Förster resonance energy transfer rate. Note that the linear relationship between the polaritonic dephasing rate and the spectral overlap has been numerically demonstrated for exciton-polaritons. Similar analytic results as in Eq. (15) have also been obtained previously.

Finally, given Eqs. (9) and (15), the observed polariton lifetime becomes
\[ \tau_s = \frac{1}{\gamma_s} = |X_k^{(B)}|^2 k_s + |X_k^{(B)}|^2 k_b + \gamma_s(k_s,k_b). \] (16)
Here, we write $\gamma_s(k_s,k_b)$ (instead of $\gamma_s$) to emphasize the fact that the polaritonic dephasing rate $\gamma_s$ depends on $k_s$ and $k_b$, whose values can modify $f_s$ by altering the polaritonic line shape [see Eq. (15b)]. In this sense, the difference between Eqs. (9) and (16) not only comes from the introduction of the polaritonic dephasing rate $\gamma_s$ (which arises from intermolecular interactions) but also stems from the more complicated parameter dependence on $k_s$ and $k_b$, e.g., $\partial(1/\tau_s)/\partial k_s = |X_k^{(B)}|^2 + \partial \gamma_s/\partial k_s = |X_k^{(B)}|^2$. See Appendix B for a detailed discussion.

For Eq. (16), let us consider the limit when the cavity and the bright modes are decoupled. In this limit, Eq. (16) is expected to recover the lifetimes of the cavity and the bright mode, respectively. For example, in the limit of a highly red-detuned cavity mode ($\omega_c \ll \omega_0$), the “LP” is mostly composed of the cavity mode ($|X_k^{(C)}|^2 \to 1$ and $|X_k^{(B)}|^2 \to 0$) and the “UP” is mostly composed of the bright mode ($|X_k^{(B)}|^2 \to 0$ and $|X_k^{(C)}|^2 \to 1$). The lifetimes of the two “polaritons” become
\[ \frac{1}{\tau_s} \to k_s, \] (17a)
\[ \frac{1}{\tau_s} \to k_b + 2\pi \Delta^2 \int_0^{\infty} d\omega \rho_s(\omega) \rho(\omega). \] (17b)
In this limit, the “LP” lifetime is the inverse of the cavity loss rate ($k_s$), and the “UP” lifetime becomes the inverse of the bright-mode relaxation ($k_b$) plus the dephasing rates ($2\pi \Delta^2 \int_0^{\infty} d\omega \rho_s(\omega) \rho(\omega)$) outside a cavity. This expected result shows the self-consistency of Eq. (16).

B. CavMD simulations of polariton lifetime

Apart from the above analytic approach, the recently developed CavMD simulations can also be used to determine the polariton lifetime under VSC. Within the framework of CavMD, the coupled photon-nuclear dynamics are propagated on an electronic ground-state surface. The light–matter Hamiltonian for CavMD is defined as follows:
\[ H_{\text{QED}}^{\text{CavMD}} = H_{\text{SM}}^{\text{CavMD}} + H_{\text{VF}}^{\text{CavMD}}, \] (18a)
where $H_{\text{QED}}$ is the conventional molecular (kinetic + potential) Hamiltonian on an electronic ground-state surface outside a cavity and $H_{\text{VF}}^{\text{CavMD}}$ denotes the field-related Hamiltonian,
\[ H_{\text{VF}}^{\text{CavMD}} = \sum_{k,l} \hat{\tilde{p}}_{kl} + \frac{1}{2} m_{kl} \omega_{kl} \hat{q}_{kl} + \frac{\omega_{kl}}{m_{kl} \omega_{kl}} \sum_{k,l} \hat{d}_{kl}. \] (18b)
Here, $\hat{\tilde{p}}_{kl}$, $\hat{q}_{kl}$, $\omega_{kl}$, and $m_{kl}$ denote the momentum operator, position operator, frequency, and auxiliary mass for the cavity photon mode defined by a wave vector $k$ and polarization direction $\xi$. The auxiliary mass $m_{kl}$ introduced here is solely for the convenience of molecular dynamics simulations, and the value of $m_{kl}$ does not change the VSC dynamics. $\hat{d}_{kl}$ denotes the electronic ground-state dipole operator for molecule $n$ projected along the direction of $\xi$. The quantity $\omega_{kl} \equiv \sqrt{m_{kl} \omega_{kl}^2 / \Omega}$ characterizes the coupling strength between each cavity photon and individual molecule, where $\Omega$ denotes the cavity mode volume and $\epsilon_0$ denotes the vacuum permittivity.

In order to reduce the computational cost, we (i) map all quantum operators in Eq. (18) to classical variables and also (ii) apply periodic boundary conditions for the molecular degrees of freedom, i.e., in Eq. (18b), we assume $\sum_{k,l} \hat{d}_{kl} = N_{\text{cell}} \sum_{l} \hat{d}_{l}$, where $N_{\text{cell}}$ denotes the number of the periodic cells and $N_{\text{sub}} = N / N_{\text{cell}}$ is the number of molecules in a single simulation cell. By also denoting $\hat{q}_{l} = \hat{q}_{ll} / \sqrt{N_{\text{cell}}}$ and an effective light–matter coupling strength...
we obtain classical equations of motion for the coupled photon-nuclear system that are suitable for practical simulations,

\[ M_q \ddot{\mathbf{r}}_q = \sum_{i,j} F_{ij}^{n} \mathbf{e}_{ij} \left( \mathbf{r}_{ij} \right) + \sum_{i,j} \mathbf{E}_{ij} \mathbf{e}_{ij} \left( \mathbf{r}_{ij} \right) \]

\[ m_q \ddot{\mathbf{r}}_q = -m_q \omega_q^2 \mathbf{q}_q - \ddot{\mathbf{c}}_{1,2} \sum_{i,j} d_{n,j} \cdot \mathbf{d}_{n,j} \cdot \mathbf{r}_{ij} \]

Here, the subscript \( nj \) denotes the \( j \)th atom in molecule \( n \), and \( F_{nj}^{(s)} \) denotes the force on each nucleus outside a cavity,

\[ F_{nj}^{(s)} = \sum_{i,j} \left( \ddot{\mathbf{c}}_{1,2} \mathbf{q}_{1,2} + \frac{\ddot{\mathbf{c}}_{1,2}^2}{m_q \omega_q^2} \sum_{i,j} d_{n,j} \cdot \mathbf{d}_{n,j} \cdot \mathbf{r}_{ij} \right) \frac{\partial \mathbf{d}_{n,j} \cdot \mathbf{r}_{ij}}{\partial \mathbf{r}_{ij}} \]

denotes the cavity force on each nucleus. \( \mathbf{E}_{ext}(t) = Q_{nj} \mathbf{E}_{ext}(t) \) denotes the external force on each nucleus [with partial charge \( Q_{nj} \) (due to the bare nuclear charge plus the shielding effect due to the surrounding electrons)] that arises from the time-dependent electric field \( \mathbf{E}_{ext}(t) \). Note that, since our goal is to excite the polariton (which is a hybrid light–matter state), it is equivalent to either pump the cavity mode or pump the molecules, given the fast energy exchange between these two subsystems (which is characterized by the Rabi splitting). In Eq. (20), we have chosen to excite the molecular subsystem just for simplicity [to avoid the introduction of a new phenomenological term when pumping the cavity mode is considered (namely, the effective transition dipole moment of the cavity mode)]

1. Calculating polariton lifetime

The numerical scheme in Eq. (20) allows us to calculate the polariton lifetime by performing a nonequilibrium CavMD simulation after an IR pulse excitation. Following the method and simulation details in Ref. 46, we capture the polariton lifetime as follows. We consider a liquid CO\(_2\) system (where \( N_{sub} = 216 \)) in a cubic simulation cell with a cell length of 24.292 Å (which corresponds to a molecular density of 1.101 g/cm\(^3\)). This molecular system is coupled to a cavity mode with two polarization directions (along x and y); see the cartoon in Fig. 1 for the simulation setup. At \( t = 0 \), the coupled cavity molecular system has been thermally equilibrated under an NVT (constant molecular number, volume, and temperature) ensemble with an Langevin thermostat applied to all particles (nuclei + photons). If we assume no cavity loss, when \( t > 0 \), the equilibrated system is propagated under an NVE (constant molecular number, volume, and energy) ensemble, and the polariton is pumped by sending an external \( x \)-polarized pulse

\[ \mathbf{E}_{ext}(t) = E_0 \cos(\omega t + \phi) \mathbf{e}_x \]

during a time interval \( t_{start} < t < t_{end} \) ps, where the pulse frequency \( \omega = \omega_x \) excites either the LP or UP and \( \phi \) denotes a random phase. For parameters, we set \( t_{start} = 0.1 \) ps, \( t_{end} = 0.6 \) ps, and \( E_0 = 3.084 \times 10^6 \) V/m \((6 \times 10^{-17} \) a.u.), so the input pulse fluence is \( F = \frac{1}{2} \epsilon_{exc} \epsilon_0 \) \((t_{end} - t_{start}) = 6.32 \text{ ml/cm}^2\). Such a pulse fluence is taken strong enough so that the polariton relaxation signal overcomes thermal and computational noise. At the same time, this fluence is weak enough so that the system is not significantly excited (e.g., the magnitude of cavity excitation in Fig. 2 is around one quantum) and the possible nonlinear absorption channel due to molecular anharmonicity is also small (see Fig. 6 in Ref. 46 for the nonlinear signal vs pulse fluence), so it is possible to compare CavMD results with the FGR rate derived from a harmonic model. We note that previous research\(^{24}\) has suggested that one might find a contraction of the Rabi splitting at this fluence. This contraction arises from depletion of the ground-state population; such a contraction should be observable with a two-level (quantum) molecular model and, to a lesser extent, with an anharmonic (quantum) oscillator model. In the latter case, a classical analog of depleting the ground-state population obviously exists but will not be observed in our linear response calculation [Fig. 4(a)].\(^{46}\)

Immediately after the polariton pumping, we monitor the time-resolved dynamics of the cavity photon energy \( E_{ph} = \sum_{\omega} \frac{\epsilon^2}{2m_e} \)

\[ + \frac{1}{2} m_e \omega_0^2 \frac{\epsilon^2}{2m_e} \]

where we have set the auxiliary phononic mass \( m_e = 1 \) a.u. for simplicity. By fitting the cavity photon energy

![FIG. 2. The polariton lifetime for liquid CO\(_2\) under VSC as a function of cavity loss \((k_c = 1/\tau_c)\). Time-resolved cavity photon energy dynamics after a weak (a) UP or (b) LP excitation. Lines with different colors denote different cavity lifetimes (from black to yellow). (c) The corresponding fitted polaritonic decay rate \((1/\tau)\) vs cavity loss rate \((k_c = 1/\tau_c)\) for the UP (magenta circles) and the LP (cyan stars). The slopes of the linear fits (dashed lines) are labeled accordingly. See Sec. II B 1 for other simulation details.](https://doi.org/10.1063/5.0079784)
dynamics (which is averaged by 40 trajectories) with an exponential function, we obtain the polaron lifetime. See Ref. 46 for all necessary simulation details. Note that during the above NVE simulation, although the cavity loss has been ignored, bright-mode relaxation and dephasing processes have been included explicitly due to an explicit propagation of all molecular degrees of freedom.

In order to further include the effect of cavity loss, during the nonequilibrium simulation, we attach a Langevin thermostat to the explicit propagation of all molecular degrees of freedom. The procedure for nonequilibrium simulation, we attach a Langevin thermostat to the simulation details. Note that during the above NVE simulation, we obtain the polariton lifetime. See Ref. 46 for all necessary simulation details. Note that during the above NVE simulation, we obtain the polariton lifetime. See Ref. 46 for all necessary simulation details.

C. Connecting the FGR rate to CavMD simulations

We have introduced two (analytic + numerical) approaches to obtain the polaron lifetime. Both approaches have advantages and disadvantages. On the one hand, while the FGR rate in Eqs. (15) and (16) is very straightforward, this rate relies on many parameters, including the cavity loss rate, bright-mode relaxation rate, the Rabi splitting and cavity mode detuning (to determine \(X^2\) and \(X^2\)), the DOS of dark modes, and the polaritons and intermolecular coupling \(\Delta\) (to determine the dephasing rate). In short, the FGR rate relies heavily on the input.

On the other hand, despite the practical simplicity of CavMD, the polaron lifetime obtained from nonequilibrium CavMD relies heavily on the accuracy of molecular force fields. While state-of-art molecular dynamics techniques allow for an accurate description of both molecular DOS and the relaxation rate,\(^{27,29}\) an experimentally accurate simulation can be very nontrivial.

With this background in mind, we will compare CavMD and the FGR rate as follows. With the anharmonic CO\(_2\) force field\(^{28}\) (which largely resembles the CO\(_2\) force field in Ref. 76 except for the use of an anharmonic C = O bond potential), we will directly obtain the polaron decay rate from nonequilibrium CavMD simulations after sending a pulse to excite the polaron; we will also obtain the polaron and molecular DOS from equilibrium CavMD simulations. Thereafter, we will calculate the FGR rate and check for internal consistency.

Let us now introduce how to estimate the FGR rate from equilibrium CavMD results, in practice.

1. Practical way to calculate \(|X^{(0)}|^2 J_a\) from equilibrium CavMD simulations

For the FGR rate, among all parameters in Eqs. (15) and (16), the most nontrivial property related to the strong coupling is the molecule-weighted spectral overlap integral \(\langle|X^{(0)}|^2\rangle J_a\) in Eq. (15). Here, we will demonstrate how to calculate this property practically.

Since the equilibrium IR absorption spectrum can be accurately obtained from both experiments and equilibrium CavMD simulations, in the expression for \(J_a\), we approximate the DOS of the dark modes \(|\rho_{\text{dark}}(\omega)|\) as the normalized molecular linear IR absorption line shape outside the cavity of \(\rho_{\text{IR,incav}}(\omega)/N_0\), where \(N_0 = \int_{\omega_{\text{mid}}}^{\omega_{\text{max}}} \rho_{\text{IR,incav}}(\omega) d\omega\) denotes the normalization factor and \(\omega_{\text{mid}}\) and \(\omega_{\text{max}}\) denote the lower and upper limits of the vibrational line shape. Similarly, we approximate the DOS of the LP or UP \(|\rho_{\text{LP,incav}}(\omega)|\) as the normalized linear molecular IR absorption line shape for the polaron, respectively. Note that, because the LP and UP line shapes appear together in the molecular IR spectrum inside the cavity \(|\rho_{\text{LP,incav}}(\omega)|\), here we simply assign a dividing frequency \(\omega_{\text{mid}} \equiv (\omega_{\text{up}} + \omega_{\text{down}})/2\) to separate the LP and UP and obtain the line shapes for them, respectively. Quantitatively, we can calculate \(|X^{(0)}|^2 J_a\) as follows:

\[
\begin{align*}
|X^{(0)}|_c^2 J_c &= \frac{1}{N_0 N_{\text{LP}}} \int_{\omega_{\text{mid}}}^{\omega_{\text{max}}} \rho_{\text{IR,incav}}(\omega) \rho_{\text{IR,incav}}(\omega), \\
|X^{(0)}|_u^2 J_u &= \frac{1}{N_0 N_{\text{UP}}} \int_{\omega_{\text{mid}}}^{\omega_{\text{max}}} \rho_{\text{IR,incav}}(\omega) \rho_{\text{IR,incav}}(\omega).
\end{align*}
\]

The integral in Eq. (22a) spans from \(\omega_{\text{mid}}\) to \(\omega_{\text{max}}\), which accounts for the spectral overlap between the LP and the dark modes; similarly, the integral in Eq. (22b) spans from \(\omega_{\text{mid}}\) to \(\omega_{\text{max}}\), which accounts for the spectral overlap between the UP and the dark modes. The denominators above ensure the normalization of the corresponding line shapes:

\[
\begin{align*}
N_c &= \int_{\omega_{\text{mid}}}^{\omega_{\text{max}}} \rho_{\text{IR,incav}}(\omega), \\
N_{\text{LP}} &= \int_{\omega_{\text{mid}}}^{\omega_{\text{max}}} \rho_{\text{IR,incav}}(\omega), \\
N_{\text{UP}} &= \int_{\omega_{\text{mid}}}^{\omega_{\text{max}}} \rho_{\text{IR,incav}}(\omega).
\end{align*}
\]

Note that, from our previous study,\(^{28}\) we have learned that the integrated peak area of the LP (or UP) is proportional to the molecular weight \(\langle|X^{(0)}|^2\rangle\) times a correction factor (which transforms a classical dipole autocorrelation function to an experimentally comparable IR spectrum), i.e., \(\int_{\omega_{\text{mid}}}^{\omega_{\text{max}}} \rho_{\text{IR,incav}}(\omega) \rho_{\text{IR,incav}}(\omega) \sim |X^{(0)}|_a^2\) and \(\int_{\omega_{\text{mid}}}^{\omega_{\text{max}}} \rho_{\text{IR,incav}}(\omega) \rho_{\text{IR,incav}}(\omega) \sim |X^{(0)}|_a^2\) (where we have assumed that the correction factor can be largely eliminated between the numerator and denominator). Hence, we may rewrite Eq. (22) in a simpler form,

\[
\begin{align*}
|X^{(0)}|^2 J_c &\approx \frac{1}{N_0} \int_{\omega_{\text{mid}}}^{\omega_{\text{max}}} \rho_{\text{IR,incav}}(\omega) \rho_{\text{IR,incav}}(\omega), \\
|X^{(0)}|^2 J_u &\approx \frac{1}{N_0} \int_{\omega_{\text{mid}}}^{\omega_{\text{max}}} \rho_{\text{IR,incav}}(\omega) \rho_{\text{IR,incav}}(\omega),
\end{align*}
\]

where

\[
N_c = \int_{\omega_{\text{mid}}}^{\omega_{\text{max}}} \rho_{\text{IR,incav}}(\omega) \int_{\omega_{\text{mid}}}^{\omega_{\text{max}}} \rho_{\text{IR,incav}}(\omega).
\]

This expression avoids directly evaluating \(|X^{(0)}|^2\) and appears easier to handle compared with Eq. (22). Note that it is preferable to avoid evaluating \(|X^{(0)}|^2\) explicitly since, in CavMD, the inclusion of the self-dipole term in the Hamiltonian (18) leads to a slightly different expression for \(|X^{(0)}|^2\) relative to the quantum model (where the self-dipole term is excluded—although when the Rabi splitting is small, such a difference is always negligible\(^{28}\)).

By comparing the polaron lifetime fitted from nonequilibrium CavMD simulations and \(|X^{(0)}|^2 J_a\) in Eq. (23), we can evaluate the
inherent consistency and validity of CavMD as far as describing the polariton relaxation process.

D. Evaluating IR spectroscopy

For the sake of completeness, the equation we use to numerically evaluate the molecular IR spectrum outside the cavity is given as follows:77–80

\[
n(\omega)\alpha(\omega) = \frac{\pi\beta\omega^2}{2V_c} \int_{-\infty}^{+\infty} dt \ e^{-i\omega t} \left( \mathbf{p}_s(0) \cdot \mathbf{p}_s(t) \right).
\]

Here, \(\alpha(\omega)\) denotes the absorption coefficient, \(n(\omega)\) denotes the refractive index, \(V\) is the volume of the system (i.e., the simulation cell), \(c\) denotes the speed of light, \(\beta = k_bT\) and \(\mathbf{p}_s(t)\) denotes the total dipole moment of the molecules at time \(t\). Similarly, inside the cavity, we evaluate the IR spectrum as follows:

\[
n(\omega)\alpha(\omega) = \frac{\pi\beta\omega^2}{2V_c} \int_{-\infty}^{+\infty} dt \ e^{-i\omega t} \left( \sum_{i=1}^{n_v} \mathbf{E}_i(\omega) \cdot \mathbf{e}_i \right) (\mathbf{p}_s(0) \cdot \mathbf{e}_i).
\]

where \(\mathbf{e}_i\) denotes the unit vector along direction \(i = x, y, z\). Different from Eq. (25), inside the cavity, since the supposedly \(z\)-oriented cavity (see the cartoon in Fig. 1) is coupled to the molecular dipole moment along the \(x\) and \(y\) directions, only these two components of the molecular dipole moment are included when we calculate the IR spectrum of the polaritons.

III. RESULTS AND DISCUSSION

According to the analytic expression in Eq. (16), the polariton lifetime is determined by three factors: (i) the vibrational relaxation rate of the bright mode (to the ground state) outside the cavity \(k_b\), (ii) the cavity loss rate \(k_c\), and (iii) the polariton dephasing rate to the dark modes \(\gamma_d\). As far as \(k_b\) is considered, since the bright and the dark modes are degenerate outside the cavity, the vibrational relaxation rates of the bright and dark modes should also be the same, equal to the vibrational relaxation rates of individual molecules. For the liquid CO\(_2\) system we simulate, since the vibrational relaxation rate outside the cavity is the smallest (∼0.03 ps\(^{-1}\)), while the other two factors usually take a rate of ∼ps\(^{-1}\), below, we will neglect the contribution of \(k_b\) to the polariton lifetime and focus only on the contributions of \(k_c\) and \(\gamma_d\).

A. Role of cavity loss

1. Liquid CO\(_2\)

Let us first investigate the polariton lifetime dependence on the cavity loss rate \(k_c\) when a liquid CO\(_2\) system (with a molecular density of 1.101 g/cm\(^3\)) forms VSC. The inset of Fig. 2(a) plots the equilibrium IR spectrum outside a cavity [black line; see Eq. (24) for the definition]. Here, the C = O asymmetric stretch of CO\(_2\) peaks at 2327 cm\(^{-1}\), in good agreement with experimental values.41

When a cavity mode (with two polarization directions) at 2320 cm\(^{-1}\) [denoted as the vertical blue line in the inset of Fig. 2(a)] is coupled to the molecular subsystem with an effective coupling strength \(\Gamma = 2 \times 10^{-4}\) a.u., a pair of UP (peaked at \(\omega_s = 2428\) cm\(^{-1}\)) and LP (peaked at \(\omega_s = 2241\) cm\(^{-1}\)) is observed in the molecular IR spectrum [red line; see Eq. (25) for the definition].

Under VSC conditions, Fig. 2(a) plots the photon energy dynamics when the UP is resonantly pumped by a relatively weak external E-field \(E_{\text{ext}}(t) = E_0 \cos(\omega t + \phi)\) with a fluence of 6.32 ml/cm\(^2\) and a 0.5 ps duration, which is labeled as a yellow shadow; see Sec. II B 1 for details on the IR excitation. When the cavity lifetime \(\tau_c = 1/k_c\) is tuned from ∞ (orange line) to 0.3 ps (black line), the photonic energy decays faster. In Fig. 2(a), the fast oscillations (with a period of ∼0.2 ps) during the photonic energy decay are in agreement with the Rabi splitting (187 cm\(^{-1}\) = 0.18 ps\(^{-1}\)), indicating a fast coherent energy exchange between cavity photons and the C = O asymmetric stretch. Note that for Fabry–Pérot VSC, the experimental cavity lifetime usually takes 1−10 ps.\(^7\)

Since cavity photons contribute to the polaritons, we can extract the polariton lifetime \((1/\tau_p)\) by fitting the photonic energy dynamics with an exponential function after the IR excitation (when \(t > 0.6\) ps). Figure 2(c) plots the fitted UP lifetime \((1/\tau_p)\) vs the cavity loss rate (magenta circles). A linear fit of the UP lifetime data yields a slope of 0.58, meaning that roughly half of the cavity loss rate contributes to the polariton decay.

After investigating the UP lifetime, we study the LP lifetime dependence on the cavity loss rate. Similarly, Fig. 2(b) plots the photonic energy dynamics when the LP is resonantly excited by the external E-field with the same fluence (6.32 ml/cm\(^2\)) as the UP excitation. Figure 2(c) plots the fitted LP decay rate vs the cavity loss rate (cyan stars), where the slope of the LP data is 1.09 after a linear fit.

At this moment, we cannot make an immediate connection between the CavMD results with the analytic rate in Eq. (16). As emphasized in Eq. (16) (see also Appendix B), since changing the value of \(k_c\) not only directly modifies \(|X^{(c)}_s|^2\) but also indirectly alters the polaritonic dephasing rate \(\gamma_d\) through the polaritonic line shape, the slope obtained by fitting \(1/\tau_p\) vs \(k_c\) [as in Fig. 2(c)] does not necessarily recover \(|X^{(c)}_s|^2\) — it is \(|X^{(c)}_s|^2 + \partial \gamma_d / \partial k_c\) instead. Therefore, only when \(\gamma_d\) is not very sensitive to \(k_c\) \((\partial \gamma_d / \partial k_c \ll |X^{(c)}_s|^2\)) we expect to obtain the agreement between the fitted slope and \(|X^{(c)}_s|^2\). In our case, the cavity mode and the C = O asymmetric stretch are near resonance, so the cavity weight of the polariton \((|X^{(c)}_s|^2)\) is roughly a half. In Fig. 2(c), we have observed that the fitted slope for the UP (not the LP) agrees well with \(|X^{(c)}_s|^2\). Because the value of \(\partial \gamma_d / \partial k_c\) is unknown, however, the agreement between the UP fitted slope and \(|X^{(c)}_s|^2\) cannot fully verify any consistency between CavMD and the analytic rate, not to mention the LP data.

2. A diluted CO\(_2\) ensemble

In order to better compare the CavMD results with the analytic expression in Eq. (16), we need to exclude the influence of polaritonic dephasing in the CavMD results (note that \(k_b\) is always negligibly small for our simulations). This can be achieved, since \(\gamma_d \propto \Delta^2\) [Eq. (15)], by reducing intermolecular interactions (\(\Delta\)) or equivalently decreasing the CO\(_2\) molecular density. Hence, we further repeat our simulation in Fig. 2 with a diluted CO\(_2\) ensemble (with a density of 0.073 g/cm\(^3\)). The molecular density is reduced by increasing the simulation cell length to 60.0 Å while fixing \(N_{\text{sub}}\), the molecular number in the cell, so the Rabi splitting remains the same [see the inset of Fig. 3(a)]. One can imagine that such a process
FIG. 3. The same plot as Fig. 2 when the CO$_2$ molecular density is decreased from 1.101 to 0.073 g/cm$^3$ and all other simulation details are kept the same. In the inset of (a), the black dashed lines represent the corresponding spectra in Fig. 2 and the solid lines represent the spectra when the density is reduced. As shown in the inset, the Rabi splitting is largely unchanged when the molecular density changes.

Figs. 2 and 3, the LP results for liquid CO$_2$ (see Fig. 2) no longer show this dependence on the cavity loss. The deviation for the LP is an example for the complicated interplay between cavity loss and polaritonic dephasing under liquid-phase VSC, which might prevent the LP from forming a more coherent and long-lived state than the cavity photon mode.

B. Role of polariton dephasing to the dark modes

Next, let us focus on the effect of polariton dephasing on the polariton lifetime. For the results below, we set the cavity loss rate to be zero. Since the bright-mode relaxation rate $k_B$ is much smaller than the dephasing rate, below, the fitted polariton decay rate from CavMD simulations should largely equal the polaritonic dephasing rate.

1. Rabi splitting dependence

Figure 4(a) plots the equilibrium IR spectrum calculated from CavMD simulations. Here, the cavity mode frequency is $\omega_c = 2320$ cm$^{-1}$, and the effective light–matter coupling strength is set from $\tilde{\varepsilon} = 2 \times 10^{-4}$ a.u. (red lines from bottom to top;
α dephasing rate from CavMD simulations, we multiply a prefactor in Fig. 4(a). Here, in order to directly compare with the polariton dephasing rate with the FGR calculation, Fig. 4(b) also plots the fitted polaritonic dephasing rate (magenta squares) decay rates are plotted as a function of the polaritonic peak frequency [see Eq. (23)]. As mentioned above, because the bright-mode relaxation rate $k_0$ is intrinsically small and we have also set the cavity loss rate to zero, the fitted polariton lifetime from nonequilibrium CavMD simulations should capture the polariton dephasing rate.

In order to explicitly compare the simulated polaritonic dephasing rate with the FGR calculation, Fig. 4(b) also plots the molecule-weighted spectral overlap $\langle |X^{(B)}_k|^2/\tau \rangle$ for the polaritons by numerically evaluating Eq. (23), given the line shapes in Fig. 4(a). Here, in order to directly compare with the polariton dephasing rate from CavMD simulations, we multiply a prefactor $\alpha = 1200 \text{ ps}^{-1}/\text{cm}$ on top of $|X^{(B)}_k|^2/\tau$, where the prefactor $\alpha$ is chosen to best fit the CavMD dephasing rates. In Fig. 4(b), the $\alpha|X^{(B)}_k|^2/\tau$ values and the fitted rates generally agree with each other (especially for the UP). Both the UP and LP results show a maximum when the polariton frequency is closer to the C-O asymmetric stretch outside the cavity ($\omega_0 = 2327 \text{ cm}^{-1}$). However, the agreement disappears for the LP regime near 2241 cm$^{-1}$, where the CavMD rates are larger than the $\alpha|X^{(B)}_k|^2/\tau$ values. Such a disagreement can be explained by the polariton-enhanced molecular nonlinear absorption mechanism when the LP frequency is close to 2241 cm$^{-1}$ and twice the LP is near resonance with $0 \rightarrow 2$ vibrational transition of the dark modes, an additional nonlinear mechanism occurs for the LP and causes a faster LP dephasing rate than that from a harmonic model $\langle |X^{(B)}_k|^2/\tau \rangle$. Because the pulse fluence we use here is not very strong, the nonlinear effect does not dominate the polariton dephasing, and only a modest disagreement between the fitted rates and $|X^{(B)}_k|^2/\tau$ appears for the LP regime. Note that in Fig. 6 of Ref. 46, we have shown that, when the LP frequency is 2241 cm$^{-1}$, after the LP excitation, the high excited state population of the dark modes amplifies nonlinearly when the pulse fluence increases, affirming our suggestion of a nonlinear effect.

As a side note, let us mention that the rotating-wave approximation used in our quantum model is expected to fail in the ultrastrong coupling limit, i.e., when $\Omega_N/2\omega_0 > 0.1$ (which corresponds to a Rabi splitting of $\Omega_N \approx 400 \text{ cm}^{-1}$ for our case). In Fig. 4, only a single data point falls in this regime ($\overline{\tau} = 5 \times 10^{-4} \text{ a.u}$.) and we believe that the results here should be valid.

2. Detuning dependence

After studying how vibrational relaxation and polariton dephasing depends on the Rabi splitting, we will now address how these observables depend on the cavity mode frequency detuning. When we set the effective coupling strength to $\overline{\tau} = 2 \times 10^{-4} \text{ a.u.}$ and tune the cavity mode frequency from 2150 to 2500 cm$^{-1}$, Fig. 4(c) plots the fitted polaritonic dephasing rate (magenta squares for the UP and cyan circles for the LP) vs the cavity mode detuning from nonequilibrium CavMD simulations after a weak, resonant pumping of the corresponding polaritons. Similar to Fig. 4(b), here we also compare the fitted rate to $\alpha|X^{(B)}_k|^2/\tau$ [where $\alpha = 1200 \text{ ps}^{-1}/\text{cm}$ is set the same as in Fig. 4(b)], which is calculated from the linear IR spectra inside vs outside the cavity [see Eq. (23)]. Note that the IR spectra for a detuned cavity mode have been plotted in Ref. 46 and are not given here.

As shown in Fig. 4(c), the two results agree well for the UP (magenta squares). For the LP, there is a modest understereestimation of $\alpha|X^{(B)}_k|^2/\tau$ compared with the fitted dephasing rate (cyan circles) when the cavity mode detuning is near zero, which corresponds to the LP frequency ($\sim 2241 \text{ cm}^{-1}$) where polariton-enhanced molecular nonlinear absorption occurs. Interestingly, when the cavity mode is very positively detuned, the fitted dephasing rate becomes slightly smaller than $\alpha|X^{(B)}_k|^2/\tau$, where we expect that the two results agree with each other (since the nonlinear absorption mechanism should vanish when the LP frequency becomes closer to the fundamental vibrational frequency). For the moment, there is no obvious explanation for this disagreement. Because the fitted dephasing rate is very large when the cavity mode is very positively detuned, an error in numerical fitting cannot be entirely ruled out.

3. Molecular density dependence

The Rabi splitting and cavity mode detuning studies have shown that the fitted polaritonic dephasing rate agrees with $|X^{(B)}_k|^2/\tau$ very well if polariton-enhanced molecular nonlinear mechanism does not play an important role. In order to fully validate the agreement between CavMD and the FGR rate in Eq. (16), we further examine the correlation between intermolecular interactions ($\Delta$) and the polaritonic dephasing rate. Figures 2 and 3 show such an example: by decreasing intermolecular interactions (via reducing the molecular density), both the UP and LP lifetimes become longer.

Figure 5 shows more comprehensive data examining how the polariton decay rate $1/\tau_\alpha$ depends on molecular density (under a fixed Rabi splitting). When the cavity mode frequency is $\omega_\alpha = 2320 \text{ cm}^{-1}$ and the effective light–matter coupling is $\overline{\tau} = 2 \times 10^{-4} \text{ a.u.}$, Fig. 5(a) shows that both the fitted UP and LP dephasing rates increase when the molecular density increases. Moreover, this dependence appears to be linear. Note that as shown in the inset of Fig. 3(a), since changing the molecular density can slightly modify the line shapes (while keeping the Rabi splitting constant), the spectral overlap $\tau_\alpha$ is also a function of the molecular density. In order to exclude the influence of $\tau_\alpha$, in Fig. 5(b), we plot the corresponding $1/(\tau_\alpha J_\alpha)$ vs the molecular density. Again, $1/(\tau_\alpha J_\alpha)$ increases when the molecular density increases. This dependence highlights the fact that it is intermolecular interactions that control the polariton dephasing rate under a weak external excitation; this conclusion is consistent with the premise of the FGR rate in Eq. (16), although the linear dependence on the density no longer holds for the UP.

4. Molecular system size dependence

There is a piece of hidden information in Eq. (16): the polaritonic dephasing rate should be independent of the molecular number—provided the Rabi splitting, cavity mode frequency, and molecular density are the same. In Ref. 46 (see Fig. 7 therein), we have reported that the CavMD polariton dephasing rate shows this independence for both the LP and the UP.
Future, we emphasize the advantages and limitations of using classical CavMD simulations on describing VSC-related phenomena. As summarized in Fig. 1 and the surrounding text, CavMD is an affordable tool, which can recover many nonreactive VSC dynamics when realistic molecules are considered. Hence, from a practical point of view, for an arbitrary VSC-related problem, due to the low cost of CavMD, it is always beneficial to run a simulation and check if an experimental finding can be roughly obtained from this approach. However, we must keep in mind that as a classical simulation, CavMD is expected to provide only a qualitative description of VSC dynamics and some experimental results cannot be quantitatively described by CavMD. For example, for pump–probe and 2D-IR experiments of VSC, the exact frequency-resolved nonlinear spectra cannot be recovered from a direct nonequilibrium classical CavMD simulation and one must do some quantum or semiclassical treatments to recover the frequency-resolved information in the nonlinear regime. Looking forward, there are many research opportunities within the framework of CavMD, including improving the performance on frequency-resolved nonlinear spectra and extending this approach to simulate quantum effects and chemical reactions.

ACKNOWLEDGMENTS

This work was supported by the U.S. National Science Foundation under Grant No. CHE1953701 (A.N.) and the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division, under Award No. DE-SC0019397 (J.E.S.).

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study (including source code, input and post-processing scripts, and the corresponding tutorials) are openly available in Github at https://github.com/TaoELi/cavity-md-ipi.

APPENDIX A: THE PULSE PROFILE

Figure 6 plots the profile of the pulse [Eq. (21)] in both time and frequency domains.
increasing the cavity loss rate $k_c$ can broaden the polaritonic line shape and alter the spectral overlap between the polaritons and dark modes, leading to modified $\gamma_{a}^*$. Similarly, changing $k_c$ can simultaneously alter the polaritonic and dark-mode line shapes, which can also influence $\gamma_{a}^*$. In Fig. 2(c), we have shown that $\partial(1/\tau_c)/\partial k_c = |X^{(2)}_b|^2$ for liquid CO$_2$ under VSC.

REFERENCES

1. 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).
2. R. F. Ribiero, L. A. Martínez-Martínez, M. Du, J. Campos-Gonzalez-Angulo, and J. Yuen-Zhou, “Polariton chemistry: Controlling molecular dynamics with optical cavities,” Chem. Sci. 9, 6325–6339 (2018).
3. J. Flick, N. Rivera, and P. Narang, “Strong light-matter coupling in quantum chemistry and quantum photonics,” Nanophotonics 7, 1479–1501 (2018).
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 vibropolariton chemistry,” ChemPlusChem 85, 1981–1988 (2020).
6. C. Climent, F. J. Garcia-Vidal, and J. Feist, “Chapter 10: Cavity-modified chemistry: Towards vacuum-field catalysis,” in Effects of Electric Fields on Structure and Reactivity: New Horizons in Chemistry (Royal Society of Chemistry, 2021), pp. 343–393.
7. B. Xiang and W. Xiong, “Molecular vibrational polariton: Its dynamics and potentials in novel chemistry and quantum technology,” J. Chem. Phys. 155, 050901 (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. A. Shalabney, J. George, H. Hiura, J. A. Hutchison, C. Genet, P. Hellwig, and T. W. Ebbesen, “Enhanced Raman scattering from vibro-polariton hybrid states,” Nanophotonics 4, 808–8086 (2015).
10. P. Long and B. S. Simpkins, “Coherent coupling between a molecular vibration and Fabry–Perot optical cavity to give hybridized states in the strong coupling limit,” ACS Photonics 2, 130–136 (2015).
11. B. S. Simpkins, K. P. Fears, W. J. Dressick, B. T. Spann, A. D. Dunkelberger, and J. C. Owrutsky, “Spanning strong to weak normal mode coupling between vibrational and Fabry–Perot cavity modes through tuning of vibrational absorption strengths,” ACS Photonics 2, 1460–1467 (2015).
12. J. George, A. Shalabney, J. A. Hutchison, C. Genet, and T. W. Ebbesen, “Liquid-phase vibrational strong coupling,” J. Phys. Chem. Lett. 6, 1027–1031 (2015).
13. A. Thomas, J. George, A. Shalabney, M. Dryzhakov, S. J. Varma, J. Moran, T. Cheryv, 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,” Angew. Chem., Int. Ed. 55, 11462–11466 (2016).
14. R. M. A. Vergauwe, A. Thomas, K. Nagarajan, A. Shalabney, J. George, T. Cheryv, M. Seidel, E. Devaux, V. Torbee, and T. W. Ebbesen, “Modification of enzyme activity by vibrational strong coupling of water,” Angew. Chem., Int. Ed. 58, 15324–15328 (2019).
15. A. Thomas, A. Jayachandran, L. Lethuillier-Karl, R. M. A. Vergauwe, K. Nagarajan, E. Devaux, C. Genet, J. Moran, and T. W. Ebbesen, “Ground state chemistry under vibrational strong coupling: Dependence of thermodynamic parameters on the Rabi splitting energy,” Nanophotonics 9, 249–255 (2020).
16. A. Thomas, L. Lethuillier-Karl, K. Nagarajan, R. M. A. Vergauwe, J. George, T. Cheryv, A. Shalabney, E. Devaux, C. Genet, J. Moran, and T. W. Ebbesen, “Tilting a ground-state reactivity landscape by vibrational strong coupling,” Science 363, 615–619 (2019).
17. J. Lather, P. Bhatt, A. Thomas, T. W. Ebbesen, and J. George, “Cavity catalysis by cooperative vibrational strong coupling of reactant and solvent molecules,” Angew. Chem., Int. Ed. 58, 10635–10638 (2019).
18. Y. Pang, A. Thomas, K. Nagarajan, R. M. A. Vergauwe, K. Joseph, B. Patrahau, K. Wang, C. Genet, and T. W. Ebbesen, “On the role of symmetry in vibrational strong coupling: The case of charge-transfer complexation,” Angew. Chem., Int. Ed. 59, 10436–10440 (2020).

APPENDIX B: NONADDITIVE EFFECTS IN POLARITONIC DECAY RATES

Polaritons are hybrid light–matter states, so one might naively think that a polaritonic property is a linear combination of the photonetic contribution (with a weight $|X^{(1)}_a|^2$) plus the molecular bright-mode contribution (with a weight $|X^{(1)}_b|^2$). For example, for the polaritonic decay rate under VSC, if one applies Eq. (9), one can simply obtain

$$\frac{\partial (1/\tau_c)}{\partial k_c} = |X^{(1)}_a|^2,$$
$$\frac{\partial (1/\tau_c)}{\partial k_b} = |X^{(1)}_b|^2.$$  

In this work, we have found the importance of the polaritonic dephasing rate $\gamma_{a}^*$ on the polaritonic decay rate. According to Eqs. (15) and (16), since $\gamma_{a}^*$ is a complicated function of $k_c$, $k_b$, and the Rabi splitting, we find that

$$\frac{\partial (1/\tau_c)}{\partial k_c} = |X^{(2)}_a|^2 + \frac{\partial \gamma_{a}^*}{\partial k_c} |X^{(1)}_a|^2,$$
$$\frac{\partial (1/\tau_c)}{\partial k_b} = |X^{(2)}_b|^2 + \frac{\partial \gamma_{a}^*}{\partial k_b} |X^{(1)}_b|^2.$$  

This equation implies that the simple additive feature no longer holds when the polaritonic dephasing rate is large. For example, extending the spectrum in the inset of Fig. 2(a).
chemical reactions with vibrational polaritons, Phys. Rev. B 105, 064205 (2022).

30. R. F. Ribeiro, J. A. Campos-Gonzalez-Angulo, N. C. Giebink, W. Xiong, and J. Yuen-Zhou, “Enhanced optical nonlinearities under collective strong light-matter coupling,” Phys. Rev. A 103, 063111 (2021).

31. T. E. Li, A. Nitzan, and J. E. Subotnik, “Cavity molecular dynamics simulations of vibrational polarization-enhanced molecular nonlinear absorption,” J. Chem. Phys. 154, 094124 (2021).

32. R. Sáez-Blázquez, J. Feist, A. I. Fernández-Dominguez, and F. J. García-Vidal, “Organic polaritons enable local vibrations to drive long-range energy transfer,” Phys. Rev. B 97, 241407 (2018).

33. C. Sommer, M. Reitz, F. Mimeo, and C. Genes, “Molecular polaritons in dense mesoscopic disordered ensembles,” Phys. Rev. Res. 3, 033141 (2021).

34. G. Engelhardt and J. Cao, “Unusual dynamical properties of disordered polaritons in microcavities,” Phys. Rev. B 105, 064205 (2022).

35. 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).

36. D. Xiong, C. Climent, J. Feist, D. Morozov, and J. J. Toppari, “Tracking polariton relaxation with multiscale molecular dynamics simulations,” J. Phys. Chem. Lett. 10, 5476–5483 (2019).

37. R. H. Tichauer, J. Feist, and G. Groenhof, “Multi-scale dynamics simulations of molecular polaritons: The effect of multiple cavity modes on polariton relaxation,” J. Chem. Phys. 152, 234111 (2020).

38. 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).

39. T. E. Li, A. Nitzan, and J. E. Subotnik, “Collective vibrational strong coupling effects on molecular vibrational relaxation and energy transfer: Numerical insights via cavity molecular dynamics simulations,” Angew. Chem., Int. Ed. 60, 15533–15540 (2021).

40. T. E. Li, A. Nitzan, and J. E. Subotnik, “Energy-efficient pathway for selectively exciting solute molecules to high vibrational states via solvent vibration-polariton pumping,” arXiv:2104.15121 (2021).

41. M. Tavis and W. F. Cummings, “Exact solution for an N-molecule–radiation-field Hamiltonian,” Phys. Rev. 170, 379–384 (1968).

42. M. Tavis and W. F. Cummings, “Approximate solutions for an N-molecule–radiation-field Hamiltonian,” Phys. Rev. 188, 692–695 (1969).

43. S. Rudin and T. L. Reinecke, “Oscillator model for vacuum Rabi splitting in microcavities,” Phys. Rev. B 59, 10227–10233 (1999).

44. A. Jungherr, F. Wackenhut, A. Stuhl, F. Blendinger, M. Brecht, and A. J. Meixner, “Tunable strong coupling of two adjacent optical λ/2 Fabry-Pérot microresonators,” Opt. Express 28, 485 (2020).

45. Note that there is a debate on the proper gauge-invariant quantum-electrodynamical Hamiltonian for strong coupling. See p. 159.

46. E. Cortese and S. De Liberato, “Exact solution of polaritonic systems with arbitrary light and matter frequency-dependent losses,” J. Chem. Phys. 156, 084106 (2022).

47. B. Houdré, R. P. Stanley, and M. Ilegems, “Vacuum-field Rabi splitting in the presence of inhomogeneous broadening: Resolution of a homogeneous linewidth in an inhomogeneously broadened system,” Phys. Rev. A 53, 2711–2715 (1996).

48. H. Deng, H. Haug, and Y. Yamamoto, “Exciton-polariton Bose-Einstein condensation,” Rev. Mod. Phys. 82, 1489–1537 (2010).
Note that this expression is valid only when Rabi splitting is larger than the linewidth of either the photonic or molecular peak.

When considering the radiative relaxation of $k_{\text{R}}$, we also disregard the possibility that collective radiative emission can be faster than single molecule emission and also the Purcell effect.

T. Förster, “Zwischenmolekulare energiewanderung und fluoreszenz,” Ann. Phys. 437, 55–75 (1948).

Of course, $\gamma_3$ is also a function of the Rabi splitting.

It is, in principle, possible to perform such a check with classical CavMD, but doing so would require a more involved calculation with two incoming pulses (pump and probe beams), and resolving such a signal would require additional efforts. Quantum simulations of a Tavis–Cummings type model with anharmonic oscillators may be examined for comparison. Future work is necessary to explore these possibilities.

V. Kapil, M. Rossi, O. Marsalek, R. Petraglia, Y. Litman, T. Spura, B. Cheng, A. Cuzzocrea, R. H. Meißner, D. M. Wilkins, B. A. Helfrech, P. Juda, S. P. Bienvenue, W. Fang, J. Kessler, L. Poltavsky, S. Vandenbrande, J. Wieme, C. Corminboeuf, T. D. Kühne, T. E. Markland, J. O. Richardson, A. Tkatchenko, G. A. Tribello, V. Van Speybroeck, and M. Ceriotti, “i-PI 2.0: A universal force engine for advanced molecular simulations,” Comput. Phys. Commun. 236, 214–223 (2019).

S. Plimpton, “Fast parallel algorithms for short-range molecular dynamics,” J. Comput. Phys. 117, 1–19 (1995).

G. R. Medders and F. Paesani, “Infrared and Raman spectroscopy of liquid water through ‘first-principles’ many-body molecular dynamics,” J. Chem. Theory Comput. 11, 1145–1154 (2015).

C. Heidelbach, I. I. Fedchinenko, D. Schwarzer, and J. Schroeder, “Molecular-dynamics simulation of collisional energy transfer from vibrationally highly excited azulene in compressed CO$_2$,” J. Chem. Phys. 108, 10152–10161 (1998).

V. N. Kabadi and B. M. Rice, “Molecular dynamics simulations of normal mode vibrational energy transfer in liquid nitromethane,” J. Phys. Chem. A 108, 532–540 (2004).

A. Kandratsenkova, J. Schroeder, D. Schwarzer, and V. S. Vîrchenko, “Nonequilibrium molecular dynamics simulations of vibrational energy relaxation of HOD in D$_2$O,” J. Chem. Phys. 130, 174507 (2009).

R. T. Cygan, V. N. Romanov, and E. M. Myshakin, “Molecular simulation of carbon dioxide capture by montmorillonite using an accurate and flexible force field,” J. Phys. Chem. C 116, 13079–13091 (2012).

D. A. McQuarrie, Statistical Mechanics (Harper-Collins Publishers, New York, 1976).

M.-P. Gaigeot and M. Sprik, “Ab initio molecular dynamics computation of the infrared spectrum of aqueous uracil,” J. Phys. Chem. B 107, 10344–10358 (2003).

S. Habershon, D. E. Manolopoulos, T. E. Markland, and T. F. Miller, “Ring-polymer molecular dynamics: Quantum effects in chemical dynamics from classical trajectories in an extended phase space,” Annu. Rev. Phys. Chem. 64, 387–413 (2013).

A. Nitzan, Chemical Dynamics in Condensed Phases: Relaxation, Transfer and Reactions in Condensed Molecular Systems (Oxford University Press, New York, 2006).

T. Seki, J.-D. Grunwaldt, and A. Baiker, “In situ attenuated total reflection infrared spectroscopy of imidazolium-based room-temperature liquid ionic liquids under ‘supercritical’ CO$_2,”$ J. Phys. Chem. B 113, 114–122 (2009).

A. Frisk Kockum, A. Miranowicz, S. De Liberato, S. Savasta, and F. Nori, “Ultrastrong coupling between light and matter,” Nat. Rev. Phys. 1, 19–40 (2019).

A. E. Krasnosk, A. P. Slobuzhnyuk, C. R. Simovski, S. A. Tretyakov, A. N. Poddubny, A. E. Miroshnichenko, Y. S. Kivshar, and P. A. Belov, “An antenna model for the Purcell effect,” Sci. Rep. 5, 12596 (2015).

J. D. Jackson, Classical Electrodynamics, 3rd ed. (John Wiley & Sons, New York, 1999).

W. H. Miller, “A classical/semiclassical theory for the interaction of infrared radiation with molecular systems,” J. Chem. Phys. 69, 2188–2195 (1978).

T. E. Li, Cavity molecular dynamics simulations tool sets, https://github.com/TaoELI/cavity-md-mpi, 2020.

O. Di Stefano, A. Settineri, V. Macri, L. Garziano, R. Stassi, S. Savasta, and F. Nori, “Resolution of gauge ambiguities in ultrastrong-coupling cavity quantum electrodynamics,” Nat. Phys. 15, 803–808 (2019).

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).

M. A. D. Taylor, A. Mandal, W. Zhou, and P. Huo, “Resolution of gauge ambiguities in molecular cavity quantum electrodynamics,” Phys. Rev. Lett. 125, 236302 (2020).

D. L. Andrews, G. A. Jones, A. Salam, and R. G. Woolley, “Perspective: Quantum Hamiltonians for optical interactions,” J. Chem. Phys. 148, 040901 (2018); arXiv:1801.07735.

J. Feist, A. I. Fernández-Domínguez, and F. J. García-Vidal, “Macroscopic QED for quantum nanophotonics: Emitter-centered modes as a minimal basis for multimitter problems,” Nanophotonics 10, 477–489 (2020); arXiv:2008.02106.