Cavity molecular dynamics simulations of vibrational polariton enhanced molecular nonlinear absorption

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Recent experiments have observed that the chemical and photophysical properties of molecules can be modified inside an optical Fabry–Pérot cavity under collective vibrational strong coupling (VSC) conditions, and such modification is currently not well understood by theory. In an effort to understand the origin of such cavity induced phenomena, some recent studies have focused on the effect of the cavity environment on the nonlinear optical response of the molecular subsystem. Here, we use a recently proposed protocol for classical cavity molecular dynamics (CavMD) simulations to numerically investigate the linear and nonlinear response of liquid carbon dioxide under such VSC conditions following an optical pulse excitation. We find that applying a strong pulse of excitation to the lower hybrid light-matter state, i.e., the lower polariton (LP), can lead to molecular nonlinear absorption which is enhanced by up to two orders of magnitude relative to the excitation outside the cavity. The underlying mechanism is polariton-enhanced multiphoton absorption which leads to an ultrashort LP lifetime (0.2 ps) under strong illumination. Because the mechanism of the observed phenomenon is generic in nature, we expect these numerical predictions to be experimentally observed in different molecular systems.

I. INTRODUCTION

Molecular polaritons, the hybrid quasi-particles stemming from strong light-matter interactions, open a new avenue to control molecular properties. Particular attention has recently focused on the vibrational strong coupling (VSC) regime, where the interaction between a molecular ensemble and a cavity mode of a micron-size Fabry–Pérot cavity results in an observed Rabi splitting of order ~ 100 cm−1. Vibrational polaritons have been implicated in the observed modification of various molecular properties in the electronic ground state, including (i) changes in ground-state chemical reaction rates, reaction pathways selectivities, and even chemical equilibria without external pumping; (ii) modification of optical nonlinearities and (iii) enhanced intermolecular vibrational energy transfer (VET) rates. Significantly, these modifications appear to be collective phenomena, originating from the interaction of cavity mode(s) with a large number of molecules.

From a theoretical perspective, collective optical response is easily understandable. In particular, vibrational Rabi splitting is easily modeled by mapping molecular vibrations and cavity modes onto harmonic oscillators. By contrast, cavity induced chemical phenomena must involve a nuanced balance of collective and individual effects, and many questions remain as to the exact origin of the observed cavity-induced chemical effects. Indeed, so named "chemical catalysis" under VSC cannot be explained by a simple transition-state theory of chemical reactions because the potential of mean force along a reaction pathway is unchanged inside the cavity. Currently, descriptions of polariton relaxation, polariton-enhanced optical nonlinearity, and intermolecular VET rates under VSC are largely limited to either phenomenological master equations (which rely on the parameter fitting from experiments) or single-molecule analytical models that cannot address the collective aspects of the observed phenomena.

For a different perspective, we have recently proposed a numerical scheme to study cavity effects — cavity molecular dynamics simulations (CavMD) in which classical dynamics is used to propagate coupled photon-nuclei dynamics for realistic molecular models. Compared with recently proposed theoretical methods in polariton chemistry which mainly focus on electronic structure calculations for a large ensemble of realistic molecules with full atomic resolution. Our approach serves as an affordable classical tool for describing VSC for a large ensemble of realistic molecules with full atomic resolution. Our approach captures the asymmetric Rabi splitting under VSC and even vibrational ultrastrong coupling when the O–H stretch mode of liquid water is strongly coupled to a cavity mode.

An important result from CavMD simulations of liquid water is that the static equilibrium properties of H2O are completely unchanged inside versus outside the cavity, and dynamic response functions (evaluated in the linear response regime) of individual molecules also show very little or no effect. Thus, one must conclude that any significant VSC modification, e.g., VSC "catalysis" and (or) the acceleration of an intermolecular VET rate, cannot be explained from an equilibrium or linear-response point of view. This conclusion suggests that cavity effects that apply to individual molecules may reflect cavity modification of the nonequilibrium dynamics of the molecular subsystem.

In this paper we will present the results of such
Here, \( \hat{H}_M^G \) denotes the conventional ground-state molecular Hamiltonian:

\[
\hat{H}_M^G = \sum_{n=1}^{N} \left( \sum_{j \in n} \frac{\hat{P}_{nj}^2}{2M_{nj}} + \hat{V}_g^{(n)}(\{\hat{\mathbf{R}}_{nj}\}) \right) + \sum_{n=1}^{N} \sum_{l > n} \hat{V}_{\text{inter}}^{(nl)} \tag{1b}
\]

where \( \hat{P}_{nj}, \hat{\mathbf{R}}_{nj}, \) and \( M_{nj} \) denote the momentum operator, position operator, and mass for the \( j \)-th nucleus in molecule \( n \), \( \hat{V}_g^{(n)} \) denotes the intramolecular potential for molecule \( n \), and \( \hat{V}_{\text{inter}}^{(nl)} \) denotes the intermolecular interactions between molecule \( n \) and \( l \). \( \hat{H}_F^G \) denotes the field-related Hamiltonian:

\[
\hat{H}_F^G = \sum_{k,\lambda} \frac{\tilde{p}_{k,\lambda}^2}{2m_{k,\lambda}} + \frac{1}{2} m_{k,\lambda}\omega_{k,\lambda}^2 \left( \tilde{q}_{k,\lambda} + \sum_{n=1}^{N} \frac{d_{ng,\lambda}}{\Omega \omega_{k,\lambda} \sqrt{\Omega_0 m_{k,\lambda}}} \right)^2 \tag{1c}
\]

where \( \tilde{p}_{k,\lambda}, \tilde{q}_{k,\lambda}, \) and \( m_{k,\lambda} \) denote the momentum operator, position operator, frequency, and the auxiliary mass for each cavity photon mode with wave vector \( k \) and polarization direction \( \lambda \). Note that the use of the auxiliary mass does not alter any dynamics and is necessary only because most MD packages require such mass. \( \Omega \) denotes the volume for the microcavity, \( \epsilon_0 \) denotes the vacuum permittivity, and \( d_{ng,\lambda} \) denotes the electronic ground-state dipole operator for molecule \( n \) projected along the direction of \( \xi_\lambda \). Note that Eq. (1c) assumes the long-wave approximation, i.e., the molecular ensemble is assumed to be much smaller than the wavelength of the cavity mode. Eq. (1c) is exact when the cavity volume is large, e.g., in a microcavity where collective VSC is studied, otherwise an additional self-dipole fluctuation term will also emerge due to the quantum nature of electron.

After reducing all of the operators in Eq. (1) to classical observables and also applying periodic boundary conditions for the molecules, we arrive at equations of motion for the coupled photon-nuclei system:

\[
M_{nj} \ddot{\mathbf{R}}_{nj} = F_{nj}^{(0)} + F_{nj}^{\text{cav}} + F_{nj}^{\text{ext}}(t) \tag{2a}
\]

\[
m_{k,\lambda} \ddot{q}_{k,\lambda} = -m_{k,\lambda}\omega_{k,\lambda}^2 \ddot{q}_{k,\lambda} - \tilde{\varepsilon}_{k,\lambda} \sum_{n=1}^{N_{\text{sub}}} d_{ng,\lambda} \tag{2b}
\]

Here, the subscript \( nj \) denotes the \( j \)-th atom in molecule \( n \); \( F_{nj}^{(0)} = -\partial V_g^{(n)} / \partial \mathbf{R}_{nj} - \sum_{\lambda} \partial V_{\text{inter}}^{(nl)} / \partial \mathbf{R}_{nj} \) denotes the molecular part of the force on each nuclei; \( F_{nj}^{\text{cav}} = -\sum_{k,\lambda} (\tilde{\varepsilon}_{k,\lambda} q_{k,\lambda} + \frac{\tilde{p}_{k,\lambda}^2}{m_{k,\lambda}}) \sum_{l=1}^{N_{\text{sub}}} d_{n+l,\lambda} \sqrt{\frac{\Omega_0 m_{k,\lambda}}{\Omega \omega_{k,\lambda}}} \) denotes the cavity force on each nuclei; \( F_{nj}^{\text{ext}}(t) = -Q_{nj} E_{\text{ext}}(t) \) denotes an external driving force acting on each nuclei with partial charge \( Q_{nj} \) under the pumping of a time-dependent electric field \( E_{\text{ext}}(t) \). Note that this \( F_{nj}^{\text{ext}}(t) \) was not introduced in Ref. and is included here to represent the optical pulse excitation that leads to the molecular nonequilibrium response. Under periodic boundary conditions, we have defined \( \tilde{q}_{k,\lambda} = \hat{q}_{k,\lambda} / \sqrt{N_{\text{cell}}} \) and an
effective coupling strength \( \tilde{\varepsilon}_{k, \lambda} = \sqrt{N_{\text{cell}} m_{k, \lambda} \omega^2_{k, \lambda} / \Omega_0} \), where \( N_{\text{cell}} \) denotes the number of the periodic simulation cells for molecules. With the number of molecules in a single simulation cell as \( N_{\text{sub}} \), the total number of molecules is \( N = N_{\text{sub}} N_{\text{cell}} \). Note that when CavMD is used to reproduce experimental observations such as polariton relaxation, given the value of \( N_{\text{sub}} \), \( \tilde{\varepsilon}_{k, \lambda} \propto \sqrt{N_{\text{cell}}} \) can be taken to fit the experimentally observed Rabi splitting since \( \tilde{\varepsilon}_{k, \lambda} \) and Rabi splitting are linearly related; see Fig. 2.

A. Molecular spectroscopy

Below we will calculate two different spectroscopic response functions: the global infrared (IR) absorption spectrum and its "local" correspondence which is the spectrum obtained if the molecules respond to light individually. The former is calculated by Fourier transforming the dipole auto-correlation function.\(^{20,23}\)

\[
n(\omega)\alpha(\omega) = \frac{\pi \beta \omega^2}{2 \varepsilon_0 V c} \int_{-\infty}^{+\infty} dt \ e^{-i \omega t} \sum_{i=x,y} \left\langle \mu_S(0) \cdot e_i \right\rangle \left( \mu_S(t) \cdot e_i \right) \tag{3}
\]

while the latter is defined by

\[
n(\omega)\alpha_{\text{local}}(\omega) = \frac{\pi \beta \omega^2}{2 \varepsilon_0 V c} \int_{-\infty}^{+\infty} dt \ e^{-i \omega t} \sum_{n=1}^{N_{\text{sub}}} \frac{1}{N_{\text{sub}}} \langle \mu_n(0) \cdot \mu_n(t) \rangle \tag{4}
\]

In Eqs. (3) and (4), \( \alpha(\omega) \) or \( \alpha_{\text{local}}(\omega) \) denotes the absorption coefficient, \( n(\omega) \) denotes the refractive index, \( V \) is the volume of the system (i.e., the simulation cell), \( e_i \) denotes the unit vector along direction \( i = x, y \), and \( \mu_S(t) \) denotes the total dipole moment of the molecules at time \( t \), where \( \mu_S(t) = \sum_{nj} Q_{nj} R_{nj}(t) \). Note that in our force field calculations, the partial charges \( Q_{nj} \) of molecules are fixed. \( \mu_n(t) = \sum_{nj} Q_{nj} R_{nj}(t) \) denotes the nuclear dipole moment for molecule \( n \). In Eq. (3), the summation over \( x \) and \( y \) is a summation over the two possible polarizations of the relevant cavity mode of the \( z \)-oriented cavity (see Fig. 1 for the simulation setup).

It is important to note that \( \alpha(\omega) \) of Eq. (3) represents the molecular IR absorption (for a molecular sample much smaller than the wavelength of light). Its local correspondence, \( \alpha_{\text{local}}(\omega) \) of Eq. (4), corresponds to the absorption of a fictitious molecular system in which each molecule responds to the field individually. Thus, Eq. (3) describes the collective behavior of the molecular dipole system, while Eq. (4) provides information about the dynamics of individual molecules. The individual response can be expressed as a linear combination of the collective modes, the bright and all dark modes of the molecular ensemble, but is predominately dominated by the dark modes.

III. SIMULATION DETAILS

A sketch of the cavity structure used in our simulation is plotted in Fig. 1. The cavity is placed along the \( z \)-axis. In addition to the (assumed perfect) mirrors that define the Fabry–Pérot cavity, we assume that additional parallel inert layers (e.g., SiO\(_2\), which has been used in references\(^{20,23}\)) confine the molecular system in a region small enough to guarantee the validity of the long wave approximation and also far enough from the mirrors so that image charge effects can be disregarded. Both assumptions are made in writing the model Hamiltonian (1). Only one cavity mode with frequency near the \( \ddot{\text{C}=\text{O}} \) asymmetric stretch is considered. This cavity mode contains two polarization directions along the \( x \) and \( y \) directions. We set the auxiliary mass for the cavity mode as \( m_{k, \lambda} = 1 \) a.u. (atomic units) though, as mentioned above, this mass does not affect any dynamics. Under periodic boundary conditions, we simulate 216 \( \text{CO}_2 \) molecules in a cubic cell with cell length 24.292 Å (45.905 a.u.); the density of the liquid \( \text{CO}_2 \) is 1.101 g/cm\(^3\). Unless stated otherwise, by default, we set the cavity mode frequency as 2320 cm\(^{-1}\) with an effective coupling strength \( \tilde{\varepsilon} = 2 \times 10^{-4} \) a.u.. Compared with VSC experiments for which usually \( N = 10^9 \sim 10^{11} \) molecules are involved, our choice of the effective coupling strength \( \tilde{\varepsilon} \propto \sqrt{N_{\text{cell}}} \) should correspond to the involvement of \( N_{\text{cell}} = 10^7 \sim 10^8 \) periodic simulation cells.

When calculating equilibrium properties, we perform simulations as follows. At 300 K, we first run the simulation for 150 ps to guarantee thermal equilibrium under a NVT ensemble where a Langevin thermostat with a lifetime (i.e., inverse friction) of 100 fs is applied to the momenta of all particles (nuclei + photon). The resulting equilibrium configurations are used as starting points for 40 consecutive NVE trajectories of length 20 ps. At the beginning of each trajectory the velocities are resampled by a Maxwell-Boltzman distribution under 300 K. The intermolecular Coulombic interactions are calculated by an Ewald summation. The simulation step is set as 0.5 fs and we store the snapshots of trajectories every 2 fs.

When performing nonequilibrium simulations under an external pulse, we start each simulation with an equilibrium geometry, which is chosen from the starting configurations of the above 40 NVE trajectories. Each nonequilibrium trajectory is run for 100 ps under a NVE ensemble and the physical properties are calculated by averaging over these 40 nonequilibrium trajectories. Note that the use of NVE trajectories when calculating equilibrium or nonequilibrium physical properties implies the assumption that cavity losses are small on the timescale of simulations and can be ignored.

The form of the external pulse is taken as follows:

\[
E_{\text{ext}}(t) = E_0 \cos (\omega t + \phi) e_x \tag{5}
\]

where the phase \( \phi \in [0, 2\pi] \) is set as random. This pulse is turned on at \( t_{\text{start}} = 0.1 \) ps and is turned off at \( t_{\text{end}} = 0.6 \) ps. Below we will show results obtained after weak pumping, i.e., \( E_0 = 3.084 \times 10^6 \) V/m (6 × 10\(^{-4}\))
a.u.) and the input pulse fluence \( F = \frac{1}{2} \varepsilon_0 c E_0^2 (t_{\text{end}} - t_{\text{start}}) \) = 6.32 mJ/cm\(^2\), and also after strong pumping, i.e., \( E_0 = 3.084 \times 10^7 \text{ V/m} \) (6 \times 10\(^{-3}\) a.u.) and \( F = 632 \text{ mJ/cm}^2\). The choice of an \( x \)-polarized pumping pulse implies that molecules with dipole component in the \( x \) direction can be excited, and because the cavity sits along the \( z \)-direction, the \( x \)-polarized pulse (in Eq. (5)) can excite the polariton associated with the cavity mode polarized along the same \( x \)-direction. Throughout this manuscript, we will refer to exciting the polaritons as exciting the molecular ensemble with such a \( x \)-polarized pulse. Similarly, polaritons can also be excited with a \( y \)-polarized pulse.

For the force field of CO\(_2\), we largely follow Ref.\(^ {13}\). The only difference is that while Ref.\(^ {13}\) uses a harmonic potential for the C=O bond, we change this harmonic potential to the following anharmonic form:

\[
V_{\text{CO}}(r) = D_r \left[ \alpha_r^2 \Delta \Delta r^2 - \alpha_r^3 \Delta r^3 + \frac{7}{12} \alpha_r^4 \Delta r^4 \right] \tag{6}
\]

where \( \Delta r = r - r_{\text{eq}} \). Eq. (6) is a fourth-order Taylor expansion of a Morse potential \( V_{\text{M}}(r) = D_r [1 - \exp(-\alpha_r r)]^2 \). The parameters are taken as follows: \( r_{\text{eq}} = 1.162 \text{ Å} \) (2.196 a.u.), \( D_r = 127.13 \text{ kcal mol}^{-1} \) (0.026 a.u.), and \( \alpha_r = 2.819 \text{ Å}^{-1} \) (1.492 a.u.) are chosen to fit the harmonic potential used in Ref.\(^ {13}\) in the harmonic limit and the value of \( D_r \) takes the bond dissociation energy of O=CO at room temperature\(^ {35}\). A comparison of Eq. (6), the Morse potential, and the harmonic limit is plotted in Appendix Fig. \( S1 \). When the C=O bond energy is smaller than \( 0.05 \text{ a.u.} \) (10\(^4\) cm\(^{-1}\)), Eq. (6) agrees with the Morse potential very well. However, the Morse potential is not present for the present simulation as we wish to avoid any potential molecular dissociation.

As far as the technical details are concerned, the initial configuration is prepared with PACKMOL\(^ {36}\), the CavMD scheme is implemented by modifying the I-PI package\(^ {37}\) and the nuclear forces are evaluated by calling LAMMPS\(^ {38}\). A toolkit including source code, input and post-processing scripts, and the corresponding tutorials is available on Github\(^ {39}\).

IV. RESULTS AND DISCUSSION

A. Rabi splitting and avoided crossing

In Fig. 2, we plot the IR spectrum obtained from Eq. (3) for different values of the effective coupling strength \( \varepsilon \); the value of \( \varepsilon \) (in a.u.) are labeled on each lineshape and the case of molecular system outside the cavity corresponds to \( \varepsilon = 0 \). The Rabi splitting seen in Fig. 2 confirms the existence of a strong coupling between the C=O asymmetric stretch and the cavity mode at frequency 2320 cm\(^{-1}\). Note that with the periodic boundary conditions applied during CavMD simulations, the effective coupling strength \( \varepsilon \) scales as \( \varepsilon \propto \sqrt{N} \) with the total number of molecules \( N \); see Sec. \( II \) for details. Therefore, increasing \( \varepsilon \) provides a simple way to study the Rabi splitting as a function of the total number of molecules \( N \). As shown in Fig. 2a, the lineshape outside a cavity (bottom), inside a cavity a pair of UP and LP is formed under VSC and the Rabi splitting increases with \( \varepsilon \). The inset plots the Rabi frequency, or the frequency difference between the UP and LP peaks, as a function of \( \varepsilon \) \( \propto \sqrt{N} \). Here, a linear relationship is observed, which agrees with both analytical models of coupled harmonic oscillators and many experiments. Note that the asymmetry in the positions and amplitudes of the UP and LP seen in Fig. 2a is discussed in detail in Ref.\(^ {22}\).

Fig. 2b, plots Rabi splitting as a function of the cavity mode frequency for the condition \( \varepsilon = 2 \times 10^{-4} \text{ a.u.} \). When the cavity mode frequency is highly negatively detuned — i.e., when the cavity frequency is much smaller than the bare C=O asymmetric stretch at 2327 cm\(^{-1}\) (white dashed line) — the UP is close to the bare C=O asymmetric stretch and its character is dominated by this molecular vibrational mode, while the LP is close to the cavity mode frequency (green dashed line) and is dominated by this cavity mode. By contrast, when the cavity mode frequency is highly positively detuned, the LP (UP) is mostly contributed by the molecular vibration (cavity mode). The avoided crossing seen between these limits expresses the Rabi splitting that measures the collective coupling strength.

B. Polariton relaxation and ultrashort LP lifetime

Next we use nonequilibrium CavMD simulations to explore the polariton relaxation following pulse excitation of the UP or the LP (see Eq. (5)). Because polaritons are hybrid light-matter quasi-particles, their relaxation can be captured by monitoring either the photonic or matter side. The photonic energy \( (\sum_{\lambda=x,y} m_{k,\lambda} \omega_{k,\lambda} \hat{p}_{k,\lambda}^2/2 + \hat{p}_{k,\lambda}^2/2m_{k,\lambda}) \) is simpler to calculate and is used in this calculation\(^ {10}\).

Fig. 3 shows the time-resolved photonic energy, in a system where the cavity mode frequency is set to 3230 cm\(^{-1}\) and effective coupling strength \( \varepsilon = 2 \times 10^{-4} \text{ a.u.} \), after resonantly exciting the UP (magenta; peaked at 2428 cm\(^{-1}\)) or LP (cyan; peaked at 2241 cm\(^{-1}\)) with a weak incoming pulse \( E(t) = E_0 \cos(\omega t + \phi) \varepsilon_x \) (with fluence \( F = 6.32 \text{ mJ/cm}^2\)), where the yellow-shaded region denotes the 0.5 ps time window during which the pulse is applied. By fitting the energy decay observed after the pulse to an exponential function, the polariton lifetime can be captured: the UP lifetime is \( \tau_{\text{UP}} = 2.5 \text{ ps} \) and the LP lifetime is \( \tau_{\text{LP}} = 1.0 \text{ ps} \). By contrast, under a strong incoming pulse \( (F = 632 \text{ mJ/cm}^2) \), the same plot in Fig. 3 shows that while the UP lifetime is largely unchanged \( (\tau_{\text{UP}} = 3.5 \text{ ps}) \), the LP shows an ultrashort decay with lifetime greatly reduced to \( \tau_{\text{LP}} = 0.2 \text{ ps} \). Note that this residual decay follows the 0.5 ps pumping pulse, implying that much of the LP relaxation has already taken place during the pumping stage. Also
note that because we have assumed no cavity loss, the polariton relaxation observed here must reflect energy transfer to the molecular degrees of freedom. Therefore, the fact that the LP relaxation is faster than that of the UP implies either a stronger interaction between the LP and individual molecular motions, or the existence of a decay channel for the LP that is not open for the UP. Below we provide evidence in support of the latter scenario. A more detailed study of vibrational polariton relaxation combined with analytical theory and CavMD simulations will be given elsewhere.

C. Polariton-enhanced nonlinear absorption

In order to investigate the origin of the ultrashort LP lifetime, we next study the molecular response to the pulse excitation as expressed by its transient IR spectrum. Here, the transient IR spectrum about time $T_i$ is calculated by evaluating Eq. (3) in a time window $[T_i, T_i + \Delta T]$, where $\Delta T = 5$ ps. Note that in this classical calculation the spectrum in Eq. (3) yields information about the molecular frequency distribution, and the corresponding transient spectrum corresponds to this distribution in the excited molecular ensemble.
FIG. 4. Time-resolved spectra after exciting the LP with a strong pulse ($F = 632$ mJ/cm$^2$). Three cases are compared: Figs. a,d: exciting the LP (2241 cm$^{-1}$) inside a 2320 cm$^{-1}$ cavity; Figs. b,e: exciting LP (2167 cm$^{-1}$) inside a 2200 cm$^{-1}$ cavity; Figs. c,f: off-resonant excitation at 2241 cm$^{-1}$ outside the cavity. The corresponding incident exciting frequency is also labeled as a red arrow in each subplot, and Figs. c,f have been multiplied by a factor of four for better visualization. Here, the IR spectra (top panel, evaluated with Eq. (3)) reflects information about the molecular collective bright state, while the local IR spectra (bottom panel, evaluated with Eq. (4)) reflects mostly information about the molecular dark modes. At every time snapshot $T_i$, the IR or local IR spectrum is calculated by averaging over the time period $[T_i, T_i + \Delta T]$ with Eq. (3) or (4), where $\Delta T = 5$ ps. See Sec. III for other simulation details. To better distinguish between the linear and nonlinear absorption, the region of the linear absorption is labeled within blue horizontal lines (i.e., from 2220 to 2360 cm$^{-1}$) and the region of the nonlinear absorption is labeled within cyan horizontal lines (i.e., from 2150 to 2220 cm$^{-1}$). Note that inside the cavity, when exciting the LP, the nonlinear absorption can be greatly enhanced than that outside the cavity; see Figs. b,e for comparison. After the pulse, the system temperature is increased from 300 K to 505 K, 366 K, 331 K (from left to right), respectively.

1. **Cavity mode at 2320 cm$^{-1}$**

For the same parameters as in Fig. 3b, Fig. 4b shows the time-resolved IR spectra after exciting the LP at 2241 cm$^{-1}$ (the red arrow) with a strong pulse ($F = 632$ mJ/cm$^{-2}$). Two observations can be made: (a) There is an ultrafast relaxation of the LP signal which disappears almost immediately after the exciting pulse, and (b) a distribution of lower frequencies, peaked at $\sim 2170$ cm$^{-1}$, emerges. The existence of such lower frequencies indicates the appearance of molecules with higher vibrational energies (see Appendix S-II where we establish an explicit semiclassical relationship between the vibrational frequency and vibrational quanta for our anharmonic CO$_2$ force field). In particular, for the anharmonic potential that we use to simulate CO$_2$ dynamics, the frequency $\sim 2200$ cm$^{-1}$ roughly corresponds to a vibrational energy of two quanta. This suggests that the additional peak $\sim 2170$ cm$^{-1}$ is a signal of nonlinear multiphoton absorption.

For the same transient state that yields Fig. 4b, Fig. 4h plots the corresponding time-resolved local IR spectra obtained from Eq. (4) which reflects information about the individual molecular modes rather than a collective bright state. During and after excitation of the LP at 2241 cm$^{-1}$ (red arrow), a large fraction of the energy is transferred to the higher vibrational excited states of C=O asymmetric stretch, leading to a broad distribution of frequencies showing a peak at $\sim 2170$ cm$^{-1}$ (see the frequency region in the cyan rectangle) in addition to a peak about 2327 cm$^{-1}$ (see the frequency region in the blue rectangle) that corresponds to the asymmetric C=O stretch absorption of individual thermally relaxed molecules. As time increases, the excess energy in the higher excited states gradually relaxes to the thermal distribution of vibrational states.

To understand the nature of the vibrational states distribution that is manifested in the spectra shown in Fig. 4, we should keep in mind that these simulations are classical. For a single anharmonic oscillator driven by an external field, true quantum dynamics is expected to show broadened peaks that reflect the discrete nature of the molecular vibrational states. By contrast, a classical simulation predicts only a single broadened vibrational peak for a system under external field excitation. When the external field is amplified, the classical peak frequency red shifts, which corresponds semiclassically to an increase of multiphoton absorption contribution. One interesting feature of the anharmonic potential in Eq. (4) is that when the vibrational energy exceeds a threshold $3\hbar\omega_0$ (where $\omega_0$ denotes the frequency near ground state), the frequency will change very slowly above $\sim 2150$ cm$^{-1}$ (see Fig. 52). In our CavMD simulations where hundreds of CO$_2$ molecules are simulated explicitly, because each
O bond potential energy

O bond potential energy is vibrational energy

(a) excite LP in 2320 cm$^{-1}$ cavity

(b) excite LP in 2200 cm$^{-1}$ cavity

(c) excite 2241 cm$^{-1}$ outside cavity

C=O bond potential energy in CO$_2$ [ℏω$_0$]

FIG. 5. The corresponding density distribution of C=O bond potential energy per molecule at time $T_i = 1$ ps for Fig. 4. Three cases are compared: exciting the LP inside a (a) 2320 cm$^{-1}$ or (b) 2200 cm$^{-1}$ cavity, and (c) exciting 2241 cm$^{-1}$ (the LP frequency for Fig. a) outside the cavity. All parameters are the same as Fig. 4. The C=O bond potential energy is calculated according to Eq. (6) and is shown in units of ℏω$_0$ ($ω_0 = 2327$ cm$^{-1}$). Note that exciting LP in a 2320 cm$^{-1}$ cavity induces a meaningful fraction of vibrationally highly excited molecules, which corresponds to the nonlinear local IR peak $\sim 2170$ cm$^{-1}$ in Fig. 4.

CO$_2$ molecule can respond to the external field differently due to variations in the local environment, molecules with energy content (in the asymmetric C=O vibration under discussion) higher than the threshold (3ℏω$_0$) will contribute to an accumulated density of frequencies at the lower frequency regime of the local IR spectrum, which corresponds to the multiphoton nonlinear absorption peak near 2170 cm$^{-1}$, while the dynamics of the remaining weakly excited molecules are incorporated by the peak near 2327 cm$^{-1}$. This give rise to the two-peak feature in Fig. 4.

This picture can be verified by directly studying the probability density for the C=O bond potential energy of individual molecules. Fig. 5a plots this probability distributions (in logarithmic scale) at early time of absorption ($T_i = 1$ ps) under the same condition as Fig. 4. Fig. 5a clearly shows that the C=O vibrational energy probability distribution has not only a strong peak in the low (thermal) energy regime, but also a large shoulder for states above 2ℏω$_0$ ($ω_0 = 2327$ cm$^{-1}$) — which agrees with the two-peak feature in Fig. 4.

2. Excitation outside the cavity

The data above suggest that exciting the system at the LP frequency can facilitate large nonlinear absorption of energy. For this to happen, the LP frequency needs to be close to frequency needed to excite the C=O mode above the lowest excited state so that the LP provides a resonance pathway to multiphoton absorption by the molecules. To confirm this finding, in Figs. 3f we plot the corresponding IR and local IR spectra when the molecules are excited outside the cavity with the same strong pulse (centered at 2241 cm$^{-1}$) as in Figs. 1a,d. A very weak nonlinear absorption peaked $\sim 2200$ cm$^{-1}$ can be detected. As mentioned above, this $\sim 2200$ cm$^{-1}$ weak peak may correspond to a small number of molecules with two or more quanta of vibrational energy. Note that this interpretation agrees with the corresponding C=O bond potential energy distribution in Fig. 5c, where we find a very small fraction of molecules have C=O bond potential energies near 2ℏω$_0$, and the large population of highly excited molecules seen in Fig. 4c is not reproduced here. This finding leads to the conclusion that the LP can greatly enhance the multiphoton nonlinear absorption of molecules, but, significantly, this signal is much weaker than inside the cavity (Figs. 1a,d).

Note that polariton-enhanced multiphoton absorption under strong illumination has been shown experimentally for various setups, such as organic excitons in a Fabry–Pérot cavity and quantum dots near surface plasmons, while its possibility under collective VSC has not been extensively studied, especially under strong illumination.

3. Cavity mode at 2200 cm$^{-1}$

Next, consider the case when the cavity mode frequency is slightly off resonance with respect to the molecular ground-state frequency. Figs. 4e show results of similar simulations for a system with cavity mode frequency 2200 cm$^{-1}$. Now, when the LP (peaked at 2167 cm$^{-1}$) is resonantly excited with a strong pulse ($F = 632$ mJ/cm$^{-2}$), as shown in Figs. 4e, the large nonlinear absorption at initial times does not appear; see also Fig. 5c for the corresponding C=O bond potential energy distribution. In the present case, the LP frequency does not match the frequency needed to move the molecule above its first excited state, so the LP cannot function as a resonant gateway for nonlinear molecular absorption. Consequently, the LP lifetime becomes much longer: An exponential fit of the LP intensity in the time-resolved IR spectra (Fig. 4b) gives $\tau_{LP} = 8.5$ ps, while a consistent result of $\tau_{LP} = 7.5$ ps can be obtained by an exponential fit of the photonic energy (which is calculated in the same way as in Fig. 3). In this relatively slow relaxation process, energy is transferred from the LP to the lower excited states of individual molecules.
4. Pulse intensity dependence of nonlinear absorption

The cavity effect in enhancing nonlinear absorption can be further seen by studying the nonlinear dependence on the pulse fluence in and outside the cavity. Fig. 6 shows the local IR spectrum from Fig. 4i, integrated over the frequency region that corresponds to the nonlinear absorption inside a 2320 cm\(^{-1}\) cavity (the same as Figs. 4a,d) and outside a cavity, as a function of the pulse fluence. In order to make a quantitative analysis, we define the relevant integration region as the area colored cyan in Fig. 6i and evaluate this integral at the early time \(T_i = 1\) ps. All other parameters are the same as in Figs. 3a,b. Note that compared with the nonlinear absorption outside the cavity (black squares) under the same pulse, the nonlinear signal inside the cavity (blue circles) can be enhanced by up to two orders of magnitude by polariton-enhanced multiphoton absorption.

V. EFFECT OF PERIODIC BOUNDARY CONDITIONS

Before ending our manuscript, we emphasize that there is a huge numerical gap between realistic VSC experiments and our CavMD simulations. In experiments a macroscopic number of molecules forms VSC in Fabry–Pérot cavities and the coupling to a cavity mode for each molecule (\(\varepsilon\)) is very small. By contrast, in CavMD simulations hundreds of molecules are explicitly simulated and the light-matter interaction per molecule \(\tilde{\varepsilon} = \sqrt{N_{cell}}\varepsilon\) is artificially amplified proportionally to the number of periodic simulation cells (\(N_{cell}\)) due to the invoking of periodic boundary conditions (see Ref. [22] for details). In order to validate the intriguing simulation results above, we have performed additional simulations to investigate the effect of the imposed periodic boundary conditions on the simulation results. When macroscopic observables (such as Rabi splitting and molecular density) are kept the same, we increase the number of molecules in the simulation cell (\(N_{sub}\)) and study the polariton lifetime dependence on \(N_{sub}\). Note that fixing Rabi splitting while increasing \(N_{sub}\) will lead to a decrease of \(\tilde{\varepsilon}\) and therefore the reduction of any artifacts due to the use of periodic boundary conditions.

Fig. 7 shows that the polariton lifetimes are unchanged against \(1/N_{sub}\) under the same conditions as in Fig. 3: the left panel plots the LP lifetime under the weak (Fig. 7a; \(F = 6.32\) mJ/cm\(^2\)) or strong (Fig. 7b; \(F = 632\) mJ/cm\(^2\)) pulse as in Fig. 3, the right panel plots the UP lifetime accordingly. For all situations (including the ultrashort LP lifetime in Fig. 7c), the results show no dependence on \(1/N_{sub}\), suggesting that the reported simulation results are not sensitive to renormalization applied to the light-matter interaction (\(\tilde{\varepsilon}\)) and implying that these predictions may hold in realistic situations including Fabry–Pérot cavities which are usually applied in VSC experiments.
VI. CONCLUSION

To summarize our observations, by studying how molecules respond both individually and collectively after a polariton has been weakly excited, we have found that polariton relaxation to molecular dark modes usually occurs on a timescale of several ps, in agreement with previous experiments. However, when a strong pulse is applied to the LP in a suitable cavity and the LP energy can support transitions to higher molecular states, the LP lifetime can become ultrashort (0.2 ps) and one can find individual molecules in very highly excited vibrational states. This so-called multiphoton nonlinear molecular absorption of light can be as large as two orders of magnitude relative to the excitation outside the cavity and arises only in concert with the LP (not the UP) because, for a realistic vibration, the $0 \rightarrow 1$ transition always has a larger frequency than the $1 \rightarrow 2$ transition so that the $0 \rightarrow 2$ transition can approximately match twice the LP frequency. Given that this LP relaxation behavior is robust within our simulation, and especially to the choice against of periodic boundary conditions used in our CavMD simulations, we have every reason to believe that our microscopic simulations presented here will have real macroscopic experimental consequences, and we expect such intriguing ultrashort LP lifetime and LP-enhanced molecular nonlinear absorption will soon be experimentally verified in usual VSC setups such as Fabry–Pérot cavities (where a macroscopic number of molecules form VSC). Looking forward, the open question remains as to if and how the present CavMD simulations to study the key outstanding and unexplained VSC phenomenon: chemical catalysis.

Appendix S-I  POTENTIAL OF C=O BOND

FIG. S1. C=O bond potential in our force field. The fourth-order anharmonic potential in Eq. 4 (red solid) is compared with the corresponding Morse potential (black dash-dot) and the harmonic approximation (green dashed).

The potential of the C=O bond in our force field is plotted in Fig. S1.

FIG. S2. C=O asymmetric peak frequency as a function of the potential energy of a single CO$_2$ molecule in gas phase. The potential energy is plotted in units of $\hbar \omega_0$, where $\omega_0 = 2342$ cm$^{-1}$ denotes the peak frequency in thermal equilibrium at 300 K. See text around for simulation details.

Appendix S-II  CORRESPONDENCE BETWEEN VIBRATIONAL FREQUENCY AND ENERGY

In simulations we have found the emergence of the low-frequency absorption after exciting the LP, UP, or individual molecular vibrations. In order to quantify the vibrational state for the corresponding frequencies, we perform a simple simulation for a bare CO$_2$ in gas phase after an external pulse peaked at 2327 cm$^{-1}$ with duration 0.1 ps; see Eq. 4. The simulation is performed for 20 ps in a NVE ensemble and the initial configuration of the molecule is set at the global minimum of potential energy surface with no initial velocity. Under different pulse amplitudes, the C=O asymmetric stretch can oscillate with different vibrational energies.

Fig. S2 plots the corresponding C=O asymmetric peak frequency by evaluating the dipole auto-correlation function in Eq. 3 as a function of the vibrational energy of the molecule, which is predominately contributed by the vibrational energy of the C=O asymmetric stretch mode. While at thermal equilibrium the C=O asymmetric stretch peaks at $\omega_0 = 2342$ cm$^{-1}$, Fig. S2 shows that the peak frequency exhibits a negative relationship with the vibrational potential energy. For example, the frequency near 2200 cm$^{-1}$ corresponds to roughly two vibrational quanta. According to the correspondence between frequency and vibrational energy, we attribute the frequency range $[2220, 2360]$ cm$^{-1}$ as lower excited states (or linear absorption; see the blue region) and the frequency range $[2150, 2220]$ cm$^{-1}$ as higher excited states, (or nonlinear absorption; the cyan region).

VII. ACKNOWLEDGEMENTS

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VIII. DATA AVAILABILITY STATEMENT

The data that support the findings of this study (including source code, input and post-processing scripts, and the corresponding tutorials) are openly available on Github at https://github.com/TaoELi/cavity-md-ipi[39].

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