Enhanced optical nonlinearities under collective strong light-matter coupling

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Optical microcavities and metallic nanostructures have been shown to significantly modulate the dynamics and spectroscopic response of molecular systems. We present a study of the nonlinear optics of a model consisting of N anharmonic multilevel systems (e.g., Morse oscillators) undergoing collective strong coupling with a resonant infrared microcavity. We find that, under experimentally accessible conditions, molecular systems in microcavities may have nonlinear phenomena significantly intensified due to the high quality of polariton resonances and the enhanced microcavity electromagnetic energy density relative to free space. Particularly large enhancement of multiphoton absorption happens when multipolariton states are resonant with bare molecule multiphoton transitions. In particular, our model predicts two-photon absorption cross section enhancements by several orders of magnitude relative to free space when the Rabi splitting Ω_R is approximately equal to the molecular anharmonic shift 2Δ. Our results provide rough upper bounds to resonant nonlinear response enhancement factors as relaxation to dark states is treated phenomenologically. Notably, ensembles of two-level systems undergoing strong coupling with a cavity (described by the Tavis-Cummings model) show no such optical nonlinearity enhancements, highlighting the rich phenomenology afforded by multilevel anharmonic systems. Similar conclusions are expected to hold for excitonic systems that share features with our model (e.g., collections of molecular dyes with accessible $S_0 \to S_1 \to S_2$ transitions) and strongly interact with a UV-visible cavity.

1. INTRODUCTION

Light-induced nonequilibrium phenomena is a topic of great contemporary interest due to its relevance to the energy, biochemical, and material sciences. Nonlinear spectroscopy provides tools for probing and controlling nonequilibrium quantum dynamics [1, 2] driven by external radiation. Applications of nonlinear optics to chemistry include investigations of the dynamics of energy and charge transport in light-harvesting complexes [3, 4], organic electronics [5], and other excitonic systems [6]. Nonlinear optical processes are also basic to various developing technologies including all-optical devices [7, 8], quantum information processors [9, 10], and enhanced sensors [11].

Unfortunately, the nonlinearities of molecular systems are generally weak [12]. Recently, hybrid materials consisting of a molecular ensemble hosted by a photonic (or plasmonic) device (e.g., optical microcavities and metallic nanostructures) have been explored as potential sources of magnified nonlinear optical response [13–15]. Under accessible experimental conditions (e.g.,room temperature and atmospheric pressure) the light-matter interaction in photonic materials can become strong enough that excited states corresponding to superposition of (collective) material polarization and cavity excitations emerge [16–18]. The corresponding hybrid quasiparticles (modes) are commonly denoted by *(cavity)-polaritons*[19]. They show controllable coherence and relaxation dynamics that allow modulation of various physical and chemical properties. Molecular phenomena significantly influenced by strong light-matter interactions include: energy transfer[20–22], charge and exciton transport [23–25], and chemical kinetics [26–28].

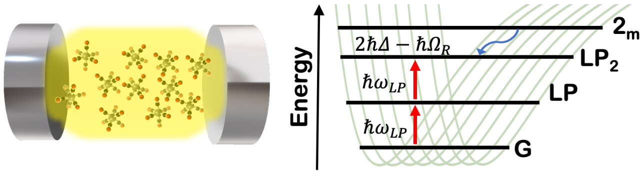

FIG. 1. Left: Planar microcavity consisting of two highly reflective mirrors filled with a molecular ensemble (e.g., $W(CO)_6$ in solution) with sufficiently large collective oscillator strength that hybrid polaritonic states are formed. Right: Mechanism for enhancement of two-photon absorption by a molecular system under strong coupling with an optical cavity. An external field resonant with the lower-polariton (LP) drives the hybrid cavity and excites two-LP states which can be tuned to be near-resonant with the anharmonically shifted doubly-excited molecular states. This polariton-mediated absorption channel allows enhancement of several orders of magnitude of the molecular two-photon absorption cross-section.

Recent experiments [29–32] have surveyed the nonlinear optics of polaritonic systems to gain further insight into the relaxation kinetics and optical response of strongly coupled devices. In Refs. [30–33], the transient response and relaxation to equilibrium of vibrational polaritons (polaritons arising from the strong coupling of molecular infrared polarization with a resonant microcavity) were investigated with pump-probe and two-dimensional infrared spectroscopy. These studies demonstrated how vibrational anharmonicity is manifested in the pump-probe polariton response [34]. However, the observed time-resolved spectra were sensitive to various system-dependent effects arising from the small Rabi splittings of the studied materials, and significant static and dynamical disorder which induces ultrafast polariton decay into the weakly-coupled (dark) molecular modes.

In this work, we focus on universal (system-independent) features of molecular polariton nonlinear optics. Our aim is to provide qualitative and quantitative insight on the potential to achieve giant optical nonlinearities with molecular polaritons in the *collective* regime (which is the case in most experiments) with a large number of molecules in a microcavity (nonlinear optical effects of *single-molecule* polaritonic systems have been studied within a non-adiabatic model of the dynamical Casimir effect in Ref. [35], as well as in vibrational polariton spectra in Ref. [36]).

In Sec. 2, we describe our model, provide an analytical expression for the nonlinear optical susceptibility of an ideal molecular ensemble under strong interaction with a microcavity (the full derivation is in the SI Sec. 2), and discuss its main features. In Sec. 3, we compare the free space and the polariton-mediated two-photon absorption (TPA) rates, and show that, especially when overtone polariton transitions are resonant with multiphoton molecular transitions, nonlinearity enhancements of several orders of magnitude may be achieved with currently available optical cavities (Fig. 1) as a result of three main effects: increased electromagnetic energy density in the optical microcavity relative to free space [13, 37], creation of new optical resonances, and strong coupling induced suppression of lineshape broadening [38]. A discussion of our main results and conclusions are given in 4. Our article is accompanied by Supporting Information (SI) containing detailed derivations of the molecular nonlinear susceptibility, and rate of nonlinear absorption in free space and under strong coupling with an optical microcavity.

2. MOLECULAR NONLINEAR RESPONSE

2.1. Effective Hamiltonian

The physical system investigated in this article consists of a molecular ensemble containing N molecules uniformly distributed in a region enclosed by two highly-reflective planar mirrors separated by a distance L_c of the order of the wavelength of a specific material infrared excitation (L_c is usually between 0.1 and 20 μm) [39–41]. This setup corresponds to a Fabry-Perot (FP) microcavity [13, 37] filled with a homogeneous molecular system. Our description of the molecular subsystem will include explicitly only the modes which are nearly-resonant with the optical cavity. All other molecular degrees of freedom will be ignored. Their effects will be treated phenomenologically by introduction of damping to the molecular polarization (see below).

We suppose that the interaction between the cavity field and the molecular polarization $\sum_{i=1}^{N} \langle 1_i|p_i|0_i\rangle$ (where p_i is the effective dipole operator of the ith molecule and 0_i and 1_i denotes states where the ith molecule is in the ground and first excited-state, respectively, whereas all other molecules are in the ground-state) is significantly stronger than the coupling of either subsystem to external (bath) degrees of freedom, but still only a tenth or less of the bare vibrational and cavity frequencies (so considerations exclusive to ultrastrong coupling can be ignored [42, 43]).

The total Hamiltonian of the composite material is given by $H(t) = H_{\mathrm{L}}(t) + H_{\mathrm{M}} + H_{\mathrm{LM}}$, where $H_{\mathrm{L}}(t)$ and H_{M} are the bare cavity (driven by an external time-dependent field) and molecular Hamiltonians and H_{LM} contains the interaction between the cavity EM field and matter. The cavity Hamiltonian is given by:

$$
\begin{aligned}
H_{\mathrm{L}}(t) = &\sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}} b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}} \\
&+ i\hbar\sqrt{\frac{\kappa}{2}} \sum_{\mathbf{k}} \left\{ \left[b^{\mathrm{L}}_{\mathbf{k}\mathrm{in}}(t)\right]^{\dagger} b_{\mathbf{k}} - b_{\mathbf{k}}^{\dagger} b^{\mathrm{L}}_{\mathbf{k}\mathrm{in}}(t) \right\}, \qquad (1)
\end{aligned}
$$

where we used input-output theory [44, 45] to describe the external driving of the optical cavity, with left input and right output flux operators $b^{\mathrm{L}}_{\mathbf{k}\mathrm{in}}(t)$ and $b^{\mathrm{R}}_{\mathbf{k}\mathrm{out}}(t)$, respectively (SI, Sec. I), and include only a single cavity band and EM field polarization (as the cavity band gaps are much larger than the cavity and molecular linewidths, due to the smallness of the cavity's longitudinal length L_c), and electric field polarization conversion gives a tiny perturbation [46] on the results presented here, especially as we consider isotropic molecular ensembles. The frequency of the mode with (in-plane) wave-vector $\mathbf{k} = (k_x, k_y)$ is $\omega_{\mathbf{k}} = c\sqrt{\mathbf{k}^2 + m^2\pi^2/L_c^2}/n$ ($m \in \mathbb{Z}$ is the index of the cavity band; n is the index of refraction of the cavity interior; from now on we take $n = 1$), and $b_{\mathbf{k}}$ is its annihilation operator. The cavity leakage (decay) rate is given by κ in the relevant frequency-region near the molecular resonance. The Heisenberg equations of motion generated by Eq. 1 are turned into the Heisenberg-Langevin equations when the replacement $\omega_{\mathbf{k}} \to \tilde{\omega}_{\mathbf{k}} \equiv \omega_{\mathbf{k}} - i\kappa/2$ is performed (SI Sec. 1).

The bare vibrational dynamics is generated by the Hamiltonian H_M given by

$$
H_{\mathrm{M}} = \sum_{i=1}^{N} \hbar\omega_0 a_i^{\dagger} a_i - \hbar\Delta \sum_{i=1}^{N} a_i^{\dagger} a_i^{\dagger} a_i a_i, \qquad (2)
$$

where the vibrational creation and annihilation operators of the ith molecule are $a_i^{\dagger}$ and a_i, respectively. The fundamental frequency of each molecule is ω_0, and the anharmonic coupling is $\Delta > 0$. We neglect intermolecular interactions as they are too weak relative to light-matter coupling (the situation could be different in other situations, e.g., molecular crystals and liquid-solid interfaces [19, 47]). We treat the relaxation of the molecular subsystem phenomenologically by converting the Heisenberg equations of motion (EOMs) of molecular operators into Heisenberg-Langevin EOMs via the substitution

$\omega_0 \to \tilde{\omega}_0 = \omega_0 - i\gamma_m/2$, where γ_m is the bare molecule fundamental transition (homogeneous) linewidth.

The light-matter interaction is treated with the multipolar gauge [48] in the long-wavelength limit within the rotating wave approximation[45] (see next paragraph for a discussion of these and other approximations):

$$H_{\mathrm{LM}} = -\sum_{\mathbf{k}}\sum_{i=1}^{N}\left(g_{i\mathbf{k}}a_i^\dagger b_{\mathbf{k}} + \bar{g}_{i\mathbf{k}}a_i b_{\mathbf{k}}^\dagger\right) + H_{\mathrm{P}^2}, \qquad (3)$$

where $g_{j\mathbf{k}} = \mu_j \cdot E^c_{j\mathbf{k}}$ is the coupling constant for the interaction between the jth molecular vibration (with effective transition dipole moment μ_j) and the cavity mode $\mathbf{k}$, with mode profile evaluated at the position $\mathbf{r}_j$ of the jth molecule, i.e., $E^c_{j\mathbf{k}} = i\sqrt{\hbar\omega_{\mathbf{k}}/(2\epsilon_0 V_c)}e^{i\mathbf{k}\cdot\mathbf{r}_j}\sin(m\pi z_j/L_z)$ (ϵ_0 is the electrical permittivity of free space, V_c is the cavity quantization volume and z_j is the position of the molecule along the cavity longitudinal axis), $\bar{f}$ denotes the complex conjugate of f, and H_{P^2} is the molecular self-polarization energy [48]. Although this term ensures the existence of a ground-state for the composite system [49] and it becomes essential for an appropriate treatment of a system with total light-matter interaction energy approaching or surpassing the bare cavity and molecular frequencies [50], H_{P^2} can be neglected under the strong coupling conditions assumed here. Therefore, we will disregard this term onward.

The length scale over which the cavity mode profile varies substantially (of order 0.1-20 μm) is much larger than typical molecular diameters (of order $0.5 - 5$nm). Thus, under strong coupling, the $\mathbf{k} \approx 0$ cavity modes interact coherently with material polarization consisting of a macroscopic number of molecules. This notion forms the basis for neglecting spatial, orientational and energetic dispersion of the molecular excitations, since fluctuations of these quantities are necessarily weak effects compared to the collective light-matter interactions from which polaritons emerge.

Fluctuations about the mean values of the molecular transition frequency and dipole moment can lead to dephasing-induced polariton decay [51], weak-coupling of light to states which are dark according to Eq. 3, as well as polariton [52, 53] and dark-state localization [52, 54]. For instance, inhomogeneous broadening (or static disorder) of the molecular or photonic subsystem is known to localize, or reduce the coherence length of polariton modes at $\mathbf{k} \approx 0$. These modes are, thus, better described as superpositions of 2D plane-waves, or wavepackets (see Ref. [53] for an illustrative numerical computation of generic behavior in 1D). However, these effects are expected to be inessential here, since we are not concerned with transport phenomena. Similarly, we neglect dynamical fluctuations (disorder) of molecular transition frequencies, as we are interested in obtaining a general understanding of polaritonic nonlinear optical response under the most ideal conditions. These approximations become better at relatively short times in comparison to polariton lifetimes (for a numerical study of dynamical disorder effects on the polariton nonlinear response, see Ref. [55]). In Eq. 3, we also assumed validity of the so-called rotating-wave-approximation: only light-matter interactions preserving the total number of cavity and molecular excitations are retained. This approximation is justified by the fact that $\sqrt{\sum_{i=1}^N |g_{i\mathbf{k}}|^2} \ll \omega_0, \quad \forall \quad \mathbf{k}$. Finally, we reiterate that while our treatment does not include disorder-induced phenomena, our model accounts for polariton dissipation via cavity leakage *and* molecular homogeneous dephasing. These decays follow naturally from an input-output treatment of the dynamics of each degree of freedom [34, 44, 45, 56]). We return to a discussion of disorder effects on our model in Sec. 4.

In what follows, we investigate the nonlinear response of the hybrid system to an input radiation field with $\mathbf{k} \in \mathbb{R}^2$ centered at $\mathbf{k}_0 \approx 0$, with a small width $\delta\mathbf{k}$. The frequency $\omega_{\mathbf{k}_0}$ is nearly resonant with the bare molecule fundamental frequency ω_0. Therefore, from now on, we also retain only a single cavity-mode corresponding to $\mathbf{k}_0 \approx 0$. This assumes there is no variation in the polariton nonlinear response with respect to changes of magnitude $|\delta\mathbf{k}|$ in the incident wave-vector $\mathbf{k}_0$.

In light of the prior considerations, from now on, we employ the following effective Hamiltonian for the hybrid cavity-matter system

$$\begin{aligned} H_T =& \hbar\omega_c b^\dagger b + \sum_{i=1}^N \hbar\omega_0 a_i^\dagger a_i - \hbar\Delta\sum_{i=1}^N a_i^\dagger a_i^\dagger a_i a_i \\ & - \sum_{i=1}^N \mu\left(E_0^c a_i^\dagger b + \bar{E}_0^c b^\dagger a_i\right) \\ & - i\hbar\sqrt{\frac{\kappa}{2}}\left\{\left[b_{\mathrm{in}}^{\mathrm{L}}(t)\right]^\dagger b - b^\dagger b_{\mathrm{in}}^{\mathrm{L}}(t)\right\}, \end{aligned} \qquad (4)$$

where $\omega_c \equiv \omega_{\mathbf{k}_0}$, $b = b_{\mathbf{k}_0}$, $b^{\mathrm{L}}_{\mathbf{k}_0\mathrm{in}} = b^{\mathrm{L}}_{\mathrm{in}}$, and $\mu E_0^c \equiv g_{j\mathbf{k}_0} = i\mu\sqrt{\hbar\omega_c/(2\epsilon_0 V_c)}$.

2.2. Nonlinear molecular polarization under strong light-matter coupling

The optical response of a hybrid microcavity can be investigated by measuring the transmission, reflection or absorption spectrum of light input into the system. For instance, transmission and reflection spectra can be obtained by applying the input-output relations to the steady-state cavity field $b(t) = \sum_{\omega>0} b(\omega)e^{-i\omega t}$. Because the cavity is weakly-coupled to the external fields, the expectation value $\langle b(t)\rangle$ admits an expansion in powers of the input amplitude $\langle b(t)\rangle = \sum_{p=1}^{\infty}\langle b(t)\rangle^{(2p-1)}$, where $\langle b(t)\rangle^{(2p-1)} = O\left[|b_{\mathrm{in}}^{\mathrm{L}}|^{2p-1}\right]$ (only odd powers of the input field appear in the cavity response because the material is assumed to be homogeneous and symmetric with respect to spatial inversion [1, 12]). The material polarization $P(t) = \mu\sum_{i=1}^N a_i(t)$ is strongly coupled to the optical cavity. Therefore, molecular observables also admit a perturbative series expansion in terms of the input field amplitudes. Note that the empty cavity is a linear system, and thus, the source of the nonlinear part of $\langle b(t)\rangle$ is the molecular subsystem. Specifically, the source of $\langle b(t)\rangle^{(3)}$ is $\langle P(t)\rangle^{(3)} = \sum_{i=1}^{N}\mu\,\langle a_i(t)\rangle^{(3)}$ (see SI Sec. 2). Therefore, $\langle P(t)\rangle^{(3)}$ directly determines the amplitude of the nonlinear optical response of a strongly coupled system as measured by the output transmitted and reflected light.

We will neglect quantum fluctuations of the input field throughout. In this case, $b_{\mathrm{in}}(t)$ is a complex number that we express as:

$$b_{\mathrm{in}}(t) = i\sum_{\omega>0}\sqrt{\frac{\mathcal{P}(\omega)}{\hbar\omega}}e^{i\theta_{\mathrm{in}}(\omega)}e^{-i\omega t}, \tag{5}$$

where $\mathcal{P}(\omega)$ is the power of the free space mode driving the hybrid cavity with frequency ω, and $\theta_{\mathrm{in}}(\omega)$ is its phase (see SI Sec. 1 for additional details).

As shown explicitly in the SI Sec. 2, it follows that the third-order polarization in the frequency domain $\langle P\rangle^{(3)}(\omega_s)$ can be written in terms of the input electric fields as follows

$$\langle P\rangle^{(3)}(\omega_s) = \sum_{\omega_u,\omega_v,\omega_w}\chi^{(3)}(-\omega_s;\omega_v,-\omega_w,\omega_u)E^{(+)}_{\mathrm{in}}(\omega_v)\times E^{(-)}_{\mathrm{in}}(\omega_w)E^{(+)}_{\mathrm{in}}(\omega_u) + \mathrm{h.c.}, \tag{6}$$

where $\omega_s > 0$ is the signal frequency, the brackets denote expectation values, the driving frequencies $\omega_u, \omega_v, \omega_w$ are all positive, the input fields $E^{(+)}_{\mathrm{in}}(\omega_u)$ are directly proportional to the $b_{\mathrm{in}}(\omega_u)$ (see SI Sec. 1), and $\chi^{(3)}$ is the nonlinear molecular susceptibility (as we shall see below, $\chi^{(3)}$ is symmetric with respect to an interchange of ω_u and ω_v) under strong light-matter interaction conditions. The ratio between $\chi^{(3)}$ and the bare molecular system nonlinear susceptibility $\chi^{(3)}_0$ provides an external-field independent measure of strong light-matter coupling effects on the optical nonlinearities of an arbitrary molecular system.

To obtain $\chi^{(3)}$ for the system described by Eq. 4, we solve perturbatively the Heisenberg-Langevin equations of motion (EOM) for the molecular polarization to third-order in the driving field $b^{\mathrm{L}}_{\mathrm{in}}$. The EOMs for the cavity and material polarization expectation values are solved perturbatively in a straightforward way since the time-evolution of our system ensures that it remains in a *pure state* at all times. The complete derivation of the molecular nonlinear susceptibility is given in the SI Sec. 2. Here, we focus on the main properties of the nonlinear susceptibility, which can be written as:

$$\begin{aligned}\chi^{(3)}(-\omega_s;\omega_v,-\omega_w,\omega_u) =& 2\hbar\Delta N\mu G_{mm}(\omega_s)\bar{G}_{mm}(\omega_w)\Gamma_{mm,mm}(\omega_u+\omega_v)G_{mm}(\omega_u)G_{mm}(\omega_v)\times\\ &\left[\mu\sqrt{\frac{2\mathcal{F}}{\pi}}G^{(0)}_{pp}(\omega_v)\frac{\hbar\kappa}{2}\right]\left[\mu\sqrt{\frac{2\mathcal{F}}{\pi}}\frac{\hbar\kappa}{2}\bar{G}^{(0)}_{pp}(\omega_w)\right]\left[\mu\frac{\hbar\kappa}{2}\sqrt{\frac{2\mathcal{F}}{\pi}}G^{(0)}_{pp}(\omega_u)\right]\delta_{\omega_s,\omega_v-\omega_w+\omega_u},\end{aligned} \tag{7}$$

where $\mathcal{F}$ is the cavity finesse (the electromagnetic field intensity in a resonant cavity is stronger than in free space by the factor $2\mathcal{F}/\pi$, or alternatively, $\mathcal{F} = Q/m$, where m is the aforementioned band index, and $Q = \omega_c/\kappa$ is the quality factor; see SI Sec. I and Ref. [37]), and $G_{mm}(\omega)$ is the Fourier transform (FT) of the retarded single-molecule propagator

$$G_{mm}(\omega) = \frac{1}{\hbar\omega - \hbar\omega_0 + i\hbar\gamma_m/2 - \frac{|\mu E_0|^2 N}{\hbar\omega - \hbar\omega_c + i\kappa/2}}. \tag{8}$$

Note the real part of the poles of $G_{pp}(\omega)$ are the fundamental polariton resonance frequencies

$$\omega_{\mathrm{LP}} = \frac{\omega_c+\omega_0}{2} - \frac{\sqrt{(\omega_c-\omega_0)^2+\Omega_R^2}}{2}, \tag{9}$$

$$\omega_{\mathrm{UP}} = \frac{\omega_c+\omega_0}{2} + \frac{\sqrt{(\omega_c-\omega_0)^2+\Omega_R^2}}{2}. \tag{10}$$

where $\Omega_R = 2|\mu E^c_0|\sqrt{N}/\hbar$ is the Rabi frequency (splitting). The corresponding imaginary parts of the polariton poles in $G_{mm}(\omega)$ correspond to their (linear) absorption linewidths. Under weak-coupling conditions, we can neglect the cavity-induced self-energy $\frac{|\mu E_0|^2 N}{\hbar\omega - \hbar\omega_c + i\kappa/2}$ to obtain the bare molecule propagator $G^{(0)}_{mm}(\omega) = 1/(\hbar\omega - \hbar\omega_0 + i\hbar\gamma_m/2)$. Similarly, the photon-photon correlator $G_{pp}(\omega)$ has resonances at the polariton frequencies, as is clear from its explicit form:

$$G_{pp}(\omega) = \frac{1}{\hbar\omega - \hbar\omega_c + i\hbar\kappa/2 - \frac{|\mu E^c_0|^2 N}{\hbar\omega - \hbar\omega_0 + i\hbar\gamma_m/2}}. \tag{11}$$

In the weak-coupling limit, $G_{pp}(\omega)$ approaches the empty cavity frequency-domain propagator $G^{(0)}_{pp}(\omega) = 1/(\hbar\omega - \hbar\omega_c + i\hbar\kappa/2)$.

The function $\Gamma_{mm,mm}(\omega_u+\omega_v)$ is the two-particle elastic scattering matrix element given by:

$$\Gamma_{mm,mm}(\omega) = \frac{(\hbar\omega - 2\hbar\tilde{\omega}_0)(\hbar\omega - \hbar\tilde{\omega}_0 - \hbar\tilde{\omega}_c)\left[(\hbar\omega - 2\hbar\tilde{\omega}_0)(\hbar\omega - 2\hbar\tilde{\omega}_c) - 4g^2 N\right]}{D(\omega)}, \tag{12}$$

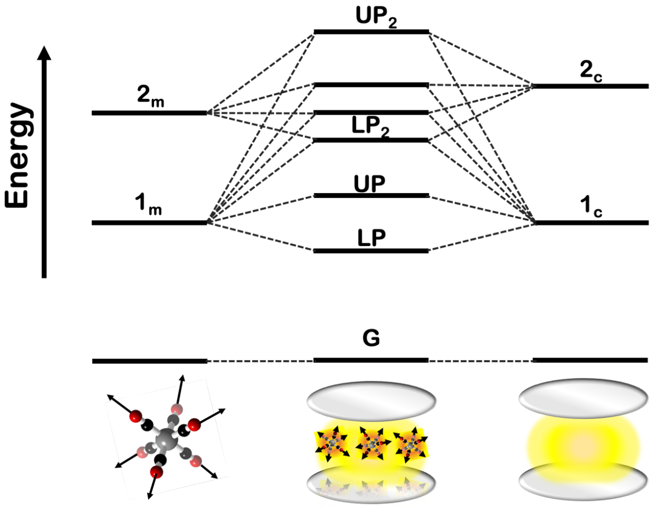

FIG. 2. Energy level diagram for a model system (Rabi splitting $\Omega_R >$ anharmonicity 2Δ) including only bright excitations of the first and doubly-excited manifolds in the zero-detuning case ($\omega_c = \omega_0$).

where $D(\omega)$ is a 4th order polynomial of ω given by:

$$\begin{aligned} D(\omega) =& D^{(0)}(\omega) - 2g^2 N(\hbar\omega - 2\hbar\tilde{\omega}_0)(\hbar\omega - 2\hbar\tilde{\omega}_0 + 2\hbar\Delta) \\ &- 2g^2(N-1)(\hbar\omega - 2\hbar\tilde{\omega}_0 + 2\hbar\Delta)(\hbar\omega - 2\hbar\tilde{\omega}_c) \\ &- 2g^2(\hbar\omega - 2\hbar\tilde{\omega}_c)(\hbar\omega - 2\hbar\tilde{\omega}_0), \end{aligned} \tag{13}$$

where $g = |\mu E_0^c|$ and $D^{(0)}(\omega) = (\hbar\omega - \hbar\tilde{\omega}_c - \hbar\tilde{\omega}_0)(\hbar\omega - 2\hbar\tilde{\omega}_0 + 2\hbar\Delta)\times$ $(\hbar\omega - 2\hbar\tilde{\omega}_c)(\hbar\omega - 2\hbar\tilde{\omega}_0)$. The roots of $D(\omega)$ correspond to the *bright* two-particle resonances of the hybrid system, as can be verified by comparison to the eigenvalues of the doubly-excited block of the Hamiltonian in Eq. 4 with $b^{\mathrm{L}}_{\mathrm{in}} = 0$ (see SI Sec. 7 for a discussion and analytical results for the $\omega_c = \omega_0$ case). In the large N limit appropriate to almost all experimental studies of infrared strong coupling, the real parts of the two-particle resonances in the zero-detuning case are given by $\omega_{2\mathrm{UP}} = 2\omega_{\mathrm{UP}} + O(g/\sqrt{N})$, $\omega_{\mathrm{LU}} = \omega_c + \omega_0$, $\omega_{2_m} = 2\omega_0 - 2\Delta + O(\Delta/N)$, and $\omega_{2\mathrm{LP}} = 2\omega_{\mathrm{LP}} + O(g/\sqrt{N})$, where the subscripts label the dominant character of each state, e.g., the highest-frequency resonance is dominated by the component with a doubly-excited UP mode while the resonance with frequency ω_{LU} corresponds to that containing an LP,UP pair (see Fig. 2 for a summary).

Physically, $\Gamma_{mm}(\omega_u + \omega_v) \propto G_{mm,mm}(\omega_u, \omega_v)$ (see SI Sec. 2), where $G_{mm,mm}(\omega)$ is the frequency-domain single-molecule two-excitation propagator, i.e., it is the FT of the probability amplitude that a molecule initially in its doubly excited-state remains in the same state after time t.

An essential feature of Eq. 12 is that when $N \to \infty$, it follows that

$$\Gamma_{mm,mm}(\omega) \approx \Gamma^{(0)}_{mm,mm}(\omega) \equiv \frac{\omega - 2\tilde{\omega}_0}{\omega - 2\tilde{\omega}_0 + 2\Delta},\ N \to \infty, \tag{14}$$

where $\Gamma^{(0)}(\omega)$ is the bare single-molecule two-particle (elastic) scattering matrix (see next subsection and SI Sec. 4). This result is not too unexpected, since $\Gamma_{mm,mm}(t)$ describes the time-dependent propagation of single-molecule doubly excited-states under interaction with the optical cavity, and as we show in the SI Sec. 7, the totally-symmetric doubly-excited molecular state $|2_m\rangle = \frac{1}{\sqrt{N}}\sum_{i=1}^{N}|2_i\rangle$ (where $|2_i\rangle$ is the state where the ith molecule is in the 2nd excited-state while the cavity and all other molecules are in the ground-state) is only *weakly-coupled* to two-polariton states via an interaction that is proportional to the single-molecule light-matter coupling μE_0^c. Therefore, while polaritons play an essential role as intermediate states for TPA by the molecular subsystem, Eq. 14 indicates the dynamics of molecular doubly excited-states is almost insensitive to their coupling to the cavity electromagnetic field in the ensemble strong coupling limit.

To gain further insight into the molecular nonlinear polarization in the strong light-matter coupling regime, we now compare Eq. 7 to the nonlinear susceptibility of the bare molecules in free space given by

$$\chi_0^{(3)}(-\omega_s; \omega_v, -\omega_w, \omega_u) = 2\hbar\Delta N\mu^4 G^{(0)}_{mm}(\omega_s)\bar{G}^{(0)}_{mm}(\omega_w)\Gamma^{(0)}_{mm,mm}(\omega_u + \omega_v)G^{(0)}_{mm}(\omega_v)G^{(0)}_{mm}(\omega_u)\delta_{\omega_s,\omega_v-\omega_w+\omega_u}. \tag{15}$$

By contrasting Eqs. 15 and 7, we find that the nonlinear optical response of a molecular system (e.g., solution, polymer, etc) in an optical microcavity is significantly distinct from that in free space mainly because of: (i) near-resonant intracavity field intensity enhancement [which renormalizes the induced molecular transition dipole moments $\mu \to \mu\sqrt{2\mathcal{F}/\pi}i\hbar\sqrt{\kappa/2}G_{pp}^{(0)}(\omega)$], and (ii) the appearance of new (polariton) resonances corresponding to hybrid superpositions of molecular polarization and cavity modes. In other words, the molecular nonlinear response under strong coupling can be written entirely in terms of *cavity-renormalized* single-particle and two-particle molecular response functions which are non-perturbatively dressed by the interaction with the cavity field, as well as (ii) molecular transition dipoles μ which are renormalized by factors that depend on the cavity finesse $\mathcal{F}$ and the bare photon propagator. The renormalization of the induced molecular dipoles is a result of the well-known enhancement of the intracavity electric field relative to free space [37, 57]. As expected, when the interaction between the cavity and the material system is weak, the molecular nonlinear susceptibility in a microcavity (Eq. 7) is simply related to that of the bare system (Eq. 15). Specifically, under weak light-matter coupling conditions, one recovers a Purcell-type result, $\chi^{(3)} \to \chi_0^{(3)} \times$ intracavity field enhancement factors [58].

As discussed in the next section, by virtue of the cavity-matter strong coupling, the nonlinear polarization contribution to the energy absorbed by the molecular subsystem is *not* directly proportional to the imaginary part of $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$. Therefore, we focus below on the nonlinear absorption of the strongly coupled material, and leave a detailed comparison of the real and imaginary parts of Eqs. 7 and 15 as a function of cavity detuning and Rabi splitting to the SI (Sec. 6).

3. POLARITON-ENHANCED TWO-PHOTON ABSORPTION

The steady-state rate of excitation of a molecular system driven by the electromagnetic field can be written as (see SI, Sections 3 and 5)

$$W_T(\omega) \equiv \frac{2}{\hbar}\left[\mathrm{Im}\left\langle [E(\omega)]^\dagger P(\omega)\right\rangle\right], \tag{16}$$

where $E(\omega)$ is the frequency-domain representation of the free space or cavity Heisenberg electric field operator. For a molecular system in free space interacting weakly with a classical monochromatic EM field with (positive-frequency) amplitude $E_{\text{in}}^{(+)}(\omega)$, it follows that the photon absorption rate (in the rotating-wave approximation) is given by [1]

$$\begin{aligned} W_0(\omega) \equiv& \frac{2}{\hbar}\mathrm{Im}\left[\chi_0^{(1)}(-\omega;\omega)\right]|E_{\text{in}}^{(+)}(\omega)|^2 \\ &+ \frac{2}{\hbar}\mathrm{Im}\left[\chi_0^{(3)}(-\omega;\omega,-\omega,\omega)\right]|E_{\text{in}}^{(+)}(\omega)|^4 + ... \end{aligned} \tag{17}$$

This expression is clearly invalid when the molecular ensemble interacts strongly with a cavity, since in this instance, the cavity field and the material electrical polarization are correlated, and therefore $\langle E(\omega)P(\omega)\rangle$ cannot (in general) be factorized into $\langle E\rangle(\omega)\langle P\rangle(\omega)$ (where E refers to the cavity EM field). Nevertheless, the external input field interacts weakly with the cavity, and the rate of absorption by the strongly coupled molecular system admits the following perturbative expansion in of powers of the input field amplitude

$$W(\omega) = \frac{2}{\hbar}\mathrm{Im}\left[\left\langle [E_c(\omega)]^\dagger P(\omega)\right\rangle^{(2)} + \left\langle [E_c(\omega)]^\dagger P(\omega)\right\rangle^{(4)}\right] + ..., \tag{18}$$

where $E_c(\omega) = E_0^c b(\omega)$. The contribution to the absorption spectrum dependent on the nonlinear response of the molecular subsystem is given by $W^{\text{NL}}(\omega) = \frac{2}{\hbar}\mathrm{Im}\left[\langle E_c^\dagger(\omega)P(\omega)\rangle^{(4)}\right]$. In the SI Sec. 3, we obtain $W^{\text{NL}}(\omega)$ by employing the Heisenberg-Langevin EOMs following the same approach taken to derive Eq. 7.

For the sake of simplicity, below we restrict our analysis of the nonlinear absorption spectrum to the zero-detuning case where $\omega_c = \omega_0$. We also simplify $W^{\text{NL}}(\omega)$ by using the following conditions necessarily valid at strong coupling: $\Omega_R \gg \hbar\eta_s \equiv \hbar(\kappa+\gamma_m)$, and $\Omega_R \gg \hbar\eta \equiv \hbar\kappa\gamma_m/(\kappa+\gamma_m)$. Under these assumptions, the nonlinear component of molecular absorption under strong coupling with a cavity can be expressed as $W^{\text{NL}}(\omega) = \sum_{\alpha=1}^{5} W^{\text{NL}_\alpha}(\omega)\left|E_{\text{in}}^{(+)}(\omega)\right|^4$, where

$$W^{\text{NL}_1}(\omega) \approx \frac{-2\eta\hbar^{-1}\kappa}{4(\omega-\omega_0)^2+\kappa^2}\mathrm{Re}\left[\sqrt{\frac{2\mathcal{F}}{\pi}}\chi^{(3)}(\omega)\right], \tag{19}$$

$$W^{\text{NL}_2}(\omega) \approx \frac{4\eta\hbar^{-1}(\omega-\omega_0)}{4(\omega-\omega_0)^2+\kappa^2}\mathrm{Im}\left[\sqrt{\frac{2\mathcal{F}}{\pi}}\chi^{(3)}(\omega)\right], \tag{20}$$

$$W^{\text{NL}_3}(\omega) \approx \frac{-2\eta\hbar^{-1}\kappa}{(\Omega_R/\hbar)^2}\mathrm{Re}\left[\sqrt{\frac{2\mathcal{F}}{\pi}}\chi^{(3)}(\omega)\right], \tag{21}$$

$$W^{\text{NL}_4}(\omega) \approx \eta\frac{4\Delta^2 N}{(\omega-\omega_0)^2+\gamma_m^2/4}\frac{\left|\langle a_i a_i\rangle^{(2)}(2\omega)\right|^2}{|E_{\text{in}}^{(+)}(\omega)|^4}, \tag{22}$$

$$W^{\text{NL}_5}(\omega) \approx -\eta\frac{(2\omega-\omega_{20})2\Delta N}{(\Omega_R/2\hbar)^2}\frac{\left|\langle a_i a_i\rangle^{(2)}(2\omega)\right|^2}{|E_{\text{in}}^{(+)}(\omega)|^4}, \tag{23}$$

where $\chi^{(3)}(\omega) \equiv \chi^{(3)}(-\omega;\omega,-\omega,\omega)$, $\omega_{20} \equiv 2\omega_0 - 2\Delta$, and

$$\begin{aligned} \langle a_i a_i\rangle^{(2)}(2\omega) = &-\Gamma_{mm,mm}(2\omega)G_{mm}(\omega)G_{mm}(\omega) \\ &\times\left[\mu\sqrt{\frac{2\mathcal{F}}{\pi}}G_{pp}^{(0)}(\omega)\frac{\hbar\kappa}{2}E_{\text{in}}^{(+)}(\omega)\right]^2. \end{aligned} \tag{24}$$

Note that some of Clearly, the rate of nonlinear absorption by the molecular system under strong coupling with a cavity is substantially complicated relative to the bare system given by $W_0^{\text{NL}}(\omega)|E_{\text{in}}^{(+)}(\omega)|^4 = \frac{2}{\hbar}\mathrm{Im}\left[\chi_0^{(3)}(-\omega;\omega,-\omega,\omega)\right]|E_{\text{in}}^{(+)}(\omega)|^4$. This additional

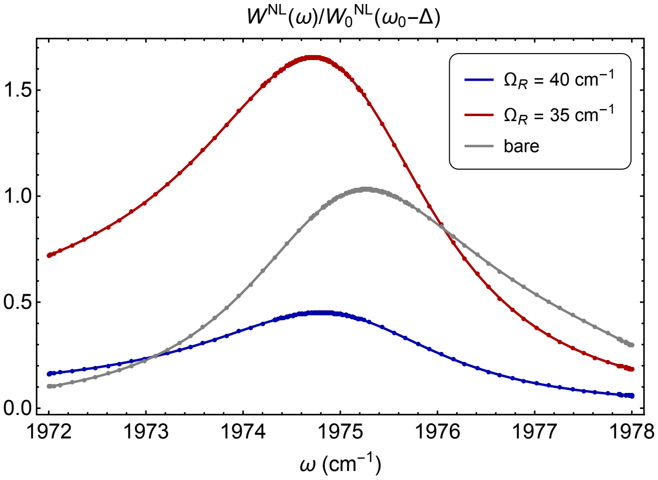

FIG. 3. Ratio of two-photon absorption rate of strongly coupled ($\omega_0 = \omega_c = 1983$ cm^{-1}, $\gamma_m = \kappa = 3$ cm^{-1}, $\Delta = 8$ cm^{-1}, and $\Omega_R = 40$ cm^{-1} or $\Omega_R = 35$ cm^{-1}) system to that of the molecular system in free space normalized by the maximum value of the latter.

complexity is expected, since while the external field acting on the bare system drives transitions between three molecular states (ground, first and second excited-state), at least seven energy levels (Fig. 2) may play a role in the nonlinear response of a material strongly coupled to an optical cavity. Nevertheless, the main features of $W^{\mathrm{NL}}(\omega)$ can be obtained from Eqs. 19−23. Specifically,

1. The nonlinear absorption intensity will be largest when the input field is nearly-resonant with either the LP or UP, since this maximizes $|G_{mm}(\omega)|^4$ which appears in all of Eqs. 19−23. Physically, the polariton resonance condition for maximal photon absorption is a consequence of the optical filtering performed by a microcavity (off-resonant external fields are suppressed).

2. $W^{\mathrm{NL}_4}(\omega)$ is the only component of $W^{\mathrm{NL}}(\omega)$ which is positive for all values of the input frequency. Therefore, it necessarily gives molecular excited-state absorption contributions to $W^{\mathrm{NL}}(\omega)$. Further evidence is given by the fact that $W^{\mathrm{NL}_4}(\omega)$ is proportional to the steady-state population of molecules in the doubly-excited state $P^{\mathrm{T}}_{2_m}(2\omega) = \sum_{i=1}^{N} P_{2_i}(2\omega) \equiv \sum_{i=1}^{N} |\langle a_i a_i\rangle^{(2)}(2\omega)|^2/2$, and thus,

$$W^{\mathrm{NL}_4}(\omega) \approx \frac{2\eta(2\hbar\Delta)^2}{(\hbar\omega-\hbar\omega_0)^2+\hbar^2\gamma_m^2/4}\,\frac{P^{\mathrm{T}}_{2_m}(2\omega)}{\left|E^{(+)}_{\mathrm{in}}(\omega)\right|^4}. \tag{25}$$

   All other contributions to the nonlinear absorption can be either positive or negative depending on ω.

3. Based on items 1 and 2, we expect the TPA rate will be largely enhanced relative to free space when the doubly-excited molecular states are approximately resonant with either one of the available two-polariton transitions (see Fig. 1), i.e.,

$$\begin{aligned} 2\omega_0 - 2\Delta &= 2\omega_{\mathrm{LP}}, \quad \Delta > 0, \text{ or} \\ 2\omega_0 - 2\Delta &= 2\omega_{\mathrm{UP}}, \quad \Delta < 0, \end{aligned} \tag{26}$$

   since in this case, all response functions $G_{mm}(\omega)$, and the scattering amplitude $\Gamma_{mm,mm}(2\omega)$ have resonances at $\omega = \omega_{\mathrm{LP}}$ (if $\Delta > 0$) or $\omega = \omega_{\mathrm{UP}}$ (if $\Delta < 0$). Physically, the polaritons provide the resonant optical window to efficiently drive the transitions of interest. In the studied case of zero cavity detuning, the conditions described in Eq. 26 can be summarized as the Rabi splitting being approximately equal to the anharmonic shift, that is, $\Omega_R = \pm 2\Delta$.

   When the criteria in Eq. 26 are satisfied, we expect strong enhancement of nonlinear absorption based on the following argument: if the input field consists of photons with $\omega = \omega_0 - \Delta$ and Eq. 26 is satisfied, polaritons will be efficiently pumped, and a fraction of those will subsequently decay by populating molecular doubly-excited states. In other words, when the two-polariton resonance condition is satisfied, the molecular doubly excited-states provides an efficient sink for the energy stored in two-polariton modes. This effect was indeed reported in a recent experiment [33], where evidence was given that (for systems with weak system-bath interactions and slow molecular polarization dephasing) the second excited vibrational state was preferentially populated over the first when the pump (input) field was resonant with LP.

4. Conversely, in the limit where two-polariton states are highly off-resonant with the molecular TPA ($|2\Delta - \Omega_R| \gg 0$, Fig. 3), the nonlinear response substantially weakens. In this limit, the studied model approaches the Tavis-Cummings [59], where a collection of two-level systems interact strongly with a single-mode cavity. The nonlinear response given by this system is known to become negligible in the large N limit [60] (e.g., as we show in the SI Sec. 7, in the Tavis-Cummings model, the two-level system nonlinearity produces a large N limit anharmonic shift proportional to $|\mu E_0^c|/\sqrt{N}$).

   It follows, therefore, that the condition given in Eq. 26 allows the harnessing of the enhanced electromagnetic field of optical cavities to enhance TPA.

Points 3 and 4 are the main conclusions of our work. We will now quantitatively illustrate that under experimentally accessible conditions, it is possible to employ cavity-strong coupling to substantially enhance the TPA cross section of a resonant molecular system. In Fig. 3, we present the TPA of the molecular system in free space ($\omega_0 = 1983$ cm^{-1}, $\Delta = 8$ cm^{-1}, $\gamma = 3$ cm^{-1}), and under strong coupling with a microcavity ($\omega_c = \omega_0, \kappa = \gamma$) for

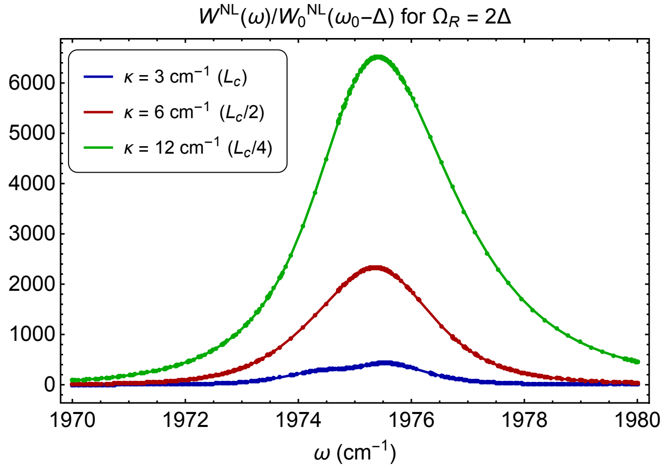

FIG. 4. Enhancement of TPA rate of strongly coupled system when $\Omega_R = 2\Delta$, with $\omega_0 = \omega_c, \gamma = 3$ cm$^{-1}, \Delta = 8$ cm^{-1} for optical microcavities with different cavity lengths ($L_c, L_c/2, L_c/4$) and corresponding decay rates.

$\Omega_R = 40$ cm^{-1} and $\Omega_R = 35$ cm^{-1}. The curves are normalized by the maximum of the bare system TPA. Figure 3 shows the strong dependence of the TPA cross-section on the light-matter interaction: when $\Omega_R = 40$ cm^{-1} ($\Omega_R - 2\Delta = 24$ cm^{-1}), the nonlinear absorption is suppressed relative to that given by the bare system. However, a slight decrease of Ω_R to 35 cm^{-1} leads to enhanced TPA due to a stronger spectral overlap between the LP$_2$ mode and the molecular doubly excited-state transition from the ground-state.

In Fig. 4, we explore the great potential for obtaining polariton-enhanced TPA with optical microcavities of varying longitudinal lengths $L_c, L_c/2$ and $L_c/4$ (with $L_c = 10$ μm, and cavity-mode indices $m = 4, m = 2$ and $m = 1$, respectively, which would require cavity mirrors with transmissivity $|t|^2 \approx 0.01\%$) and equal reflectivity. We assume the cavities are resonant with the molecular fundamental transition, and that the TPA condition $\Omega_R = 2\Delta = 16$ cm^{-1} is valid (the remaining bare molecule parameters are the same as in Fig. 3). The two main conclusions that Fig. 4 provide are that: (a) the polariton-mediated TPA cross section predicted by our model can be larger than the bare one by close to 4 orders of magnitude for accessible parameters, and (b) a decrease in cavity length leads to stronger nonlinear signals, so that the cavity-mediated TPA will be maximally efficient when the strongly coupled cavity mode has the lowest possible longitudinal quantum number and mirrors with highest available reflectivity.

The increase in nonlinear response signals with decreasing molecular concentration (Rabi splitting) (Fig. 3 or cavity longitudinal length (Fig. 4), were observed and qualitatively analyzed in a different context in Ref. [61].

4. DISCUSSION AND CONCLUSIONS

The computed enhanced polariton-mediated TPA provides an upper bound estimate to future measurements of TPA under strong coupling conditions. Experiments performed on analogous systems could give reduced enhancements relative to those here presented for at least two reasons: (a) the intracavity enhancement factor (represented by the cavity finesse) varies spatially according to the cavity mode profile ($\sin(\pi z/L)$ in the simplest case), whereas we assumed that all molecules are within a small region around an antinode of the cavity field (so that the cavity field enhancement factor is maximal), and (b) inhomogeneous broadening of the molecular subsystem allows photonic intensity borrowing from polaritons into reservoir (dark) modes, which reduces the efficiency of polariton pumping, and also leads to potentially fast polariton relaxation to the reservoir mode. Although we recognize the importance of these approximations, we disregard them in our explorations, since the inhomogeneity of the cavity mode profile is expected to change the nonlinear response properties by factors of order 1 (alternatively, spacers may be introduced between the molecular system and the optical cavity so that the molecules occupy only a small region around the antinode of the cavity mode profile), while (lower) polariton decay can be slowed down by increasing the Rabi splitting and (or) lowering the temperature. Moreover, polariton transitions are well-known to be homogeneously broadened within their lifetimes [38], and therefore, for molecular systems with significant inhomogeneously broadened transitions, we expect polariton lineshapes to be significantly narrower than that of the bare system (given the polariton “hole-burning” effect [62]). In this instance, the mechanism for polariton-mediated TPA presented in our article would become even more efficient than in the model considered here.

While our study focused on infrared polaritonics, we note that the phenomenology observed in molecular vibrational and electronic strong coupling can be very similar depending on the system. For instance, ultrafast pump-probe transmission recorded for a microcavity strongly coupled to an organic semiconductor in Ref. [63] showed qualitative features identical to the first reported vibrational polariton pump-probe data [30]. In fact, whenever electronic transitions are only weakly coupled to high-frequency vibrational modes, and the electronic $S_1 \rightarrow S_2$ (first to second excited-state) transition is dipole-allowed and slightly red-shifted from the $S_0 \rightarrow S_1$ (ground to first excited-state), we expect electronic TPA rates to have similarly appealing potential for enhancement in optical cavities under the strong coupling regime as discussed in Sec. 3.

In summary, we have derived and analyzed the nonlinear optical susceptibility and TPA rates for a molecular system under strong coupling with an infrared microcavity. By contrasting the polaritonic response with that of bare molecules in free space, we found that enhanced nonlinearities in the strong coupling regime may emerge due to intracavity field enhancement, creation of suitable optical resonances, and subnatural polaritonic linewidths. Our results suggest an increase of several orders of magnitude can potentially be achieved for the polaritonic nonlinear optical response, especially, when a multipolariton transition is resonant with a multiphonon absorption of the molecular system. Our work suggests new application of molecular polaritonics in two-photon imaging [64], and efficient generation of hot molecular excited-state distributions via (polariton) ladder climbing [65, 66], possibly bypassing deleterious intramolecular vibrational relaxation.

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