Understanding the Energy Gap Law under Vibrational Strong Coupling

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(Dated: January 5, 2023)

The rate of non-radiative decay between two molecular electronic states is succinctly described by the energy gap law, which suggests an approximately-exponential dependence of the rate on the electronic energy gap. Here, we inquire whether this rate is modified under vibrational strong coupling, a regime whereby the molecular vibrations are strongly coupled to an infrared cavity. We show that, under most conditions, the collective light-matter coupling strength is not large enough to counter the entropic penalty involved with using the polariton modes, so the energy gap law remains unchanged. This effect (or the lack thereof) may be reversed with deep strong light-matter couplings or large detunings, both of which increase the upper polariton frequency. Finally, we demonstrate how vibrational polariton condensates mitigate the entropy problem by providing large occupation numbers in the polariton modes.

INTRODUCTION

When molecules are placed inside an optical cavity, they may interact strongly with the quantised radiation mode to form light-matter hybrid states called polaritons [1]. In particular, this phenomenon is most significant when energy cycles between the molecular transitions and the photon mode at a rate faster than the decay of each individual component. Molecular polaritons have different frequencies and potential energy surfaces than their pure-matter counterparts. As such, they offer an interesting avenue for controlling chemical properties of the system, potentially unachievable by strong coupling between the high-frequency vibrational modes of molecules and an infrared optical cavity that houses these molecules [2, 3]. This effect, also known as vibrational strong coupling (VSC), has been experimentally shown to modify reaction pathways and achieve chemoselectivity [7–11]. VSC is an ensemble effect: a large number of molecules, typically of the order of $10^{10}$, must collectively couple to a cavity mode to generate an appreciable collective light-matter coupling strength. The result is the formation of two polariton modes, which provide control over chemical properties and are desirable, alongside a large number of dark modes that behave effectively as uncoupled molecules in the absence of disorder [12] (with disorder, dark modes might behave differently from uncoupled molecular excitations, although the extent to which this occurs is still a subject of current exploration [13–15]). The latter is a source of concern; due to their sheer numbers, these non-photonic dark modes have dominant control over chemical properties of the system, potentially undoing any benefit created by the polariton modes. In principle, there exists a specific and reasonable parameter range that allows some unique properties of vibrational polariton modes to outweigh the entropic cost from using them [16]; yet, in practice, these molecular parameter requirements (such as ultralow reorganisation energies) have not been experimentally found. Meanwhile, more recently, polariton condensates have been theoretically shown as an alternative avenue for overcoming the entropic penalty associated with polariton modes [17, 19].

One chemical property that may benefit from VSC is the non-radiative decay rate between electronic states of an excited molecule (Fig. 1). The decay rate is concisely and elegantly described by the energy gap law [20, 21], which was first derived by Englman and Jortner in 1970 [20]. There, they applied Fermi’s golden rule to approximate the transfer rate between two displaced harmonic oscillators, representing the potential energy surfaces of two electronic states (|G⟩ and |E⟩), through a diabatic coupling term of amplitude |J_{GE}| that is treated perturbatively. More specifically, they considered the Hamiltonian

$$H_0 = \sum_m \hbar \omega_{vib,m} \hat{b}_{vib,m}^\dagger \hat{b}_{vib,m} |G⟩⟨G| + \sum_m \hbar \omega_{vib,m} \hat{b}_{vib,m}^\dagger \hat{b}_{vib,m} + \Delta E |E⟩⟨E|,$$

and a perturbative coupling term $V_{\text{trs}} = J_{GE} (|E⟩⟨G| + |G⟩⟨E|)$, where $\Delta E$ is the electronic energy gap, $\hat{b}_{vib,m}^\dagger$ (\hat{b}_{vib,m}) is the creation (annihilation) operator of the $m$-th vibrational mode in electronic state $|x⟩$ with frequency $\omega_{vib,m}$, and $b_{vib,m}^\dagger = b_{vib,M} - \sqrt{S_m}$, with $S_m$ being the Huang-Rhys factor representing the displacement of the two potential energy surfaces along mode $m$. In the low temperature limit, the non-radiative decay rate is approximately

$$W_{\text{bare}} \approx \left| J_{GE} \right|^2 \frac{2\pi}{\hbar \omega_{vib,M} \Delta E} \times e^{-\sum_m S_m} \exp \left( -\gamma \frac{\Delta E}{h \omega_{vib,M}} \right),$$

with $\gamma = \ln \left( \frac{\Delta E}{S_M \omega_{vib,M}} \right) - 1$. Here, $\omega_{vib,M}$ is the maximum vibrational frequency of the molecule, $S_M = \sum_{m \in \{M\}} S_m$ is the sum of the Huang-Rhys factors for
FIG. 1. Non-radiative decay of a molecule from a higher electronic state $|E\rangle$ to a lower electronic state $|G\rangle$. (a) This process may, in its simplest form, be modelled as a non-linear conversion of energy from electronic energy ($\Delta E$) in state $|E\rangle$ to vibrational quanta ($n\hbar\omega_{vib,M}$) in state $|E\rangle$ along the vibrational mode of maximum frequency $\omega_{vib,M}$. (b) Under collective VSC in an infrared cavity, the same electronic energy ($\Delta E$) may be redistributed among polariton quanta ($n_P\hbar\omega_P$, $P = LP, UP$) and dark mode quanta ($n_D\hbar\omega_D$), the former of which is useful because the UP mode has a higher frequency ($\omega_{UP}$) than the dark modes ($\omega_D = \omega_{vib,M}$) and can enhance the rate of non-radiative decay. However, under most circumstances, this advantage is not realised because the large number of dark modes makes it entropically unfavourable to decay through the polariton modes.

the set of vibrational modes $\{M\}$ with frequencies near $\omega_{vib,M}$, and the subscript “bare” indicates that the rate expression is computed for a molecule outside the cavity. There are theoretical foundations in grouping multiple vibrational modes into a single, effective vibrational mode with contributions from the highest frequency modes [20]. The inherent assumption in this expression is that the electronic energy is most likely lost through a number of high-frequency vibrations rather than many more low-frequency ones, valid when the total reorganisation energy $\sum_m S_m\hbar\omega_m$ of the high-frequency modes is much larger than that of the low-frequency modes [22]. An analytical generalisation of this model to account for low-frequency modes and finite temperatures has been provided by Jang [22]. In that work, Jang derives an improved rate expression that retains the same qualitative phenomena as Eq. (2) but with improved accuracy as compared to numerical results. Since Eq. (2) is often fitted into experimental data to obtain $J_{GE}$, one can potentially achieve more accurate estimates of $J_{GE}$ with Jang’s improved model. Going back to Eq. (2), in most cases, $\gamma$ may be regarded as a constant, giving an approximately-exponential dependence of the decay rate on the energy gap $\Delta E$ (hence the name). Overall, this model has found numerous applications in molecular spectroscopy [23–26] and optoelectronics [27–32], in particular for describing the quantum yields of radiative processes.

In this paper, we demonstrate how, under VSC, a large proportion of non-radiative decay occurs through the dark modes, which was expected due to their large numbers (Fig. 1b). At the same time, decay through the higher-frequency polariton channel, if significant, can reduce the effective energy gap for dark mode decay, thereby increasing the overall decay rate. These two effects work against each other and the polaritonic one dominates only under extreme conditions such as deep strong couplings and large detunings; otherwise, the rate of non-radiative decay, being dominated by the dark modes, takes a value similar to the bare one outside of the cavity. Finally, we investigate how this entropic problem may be mitigated by the use of polariton condensates.

RESULTS AND DISCUSSIONS

The model system

We consider a model system of $N$ identical molecules $i = 1, \cdots, N$, each with two electronic states ($|E_i\rangle$ and $|G_i\rangle$) and a set of molecular vibrational modes. The collective effects of these vibrational modes are represented by a single mode at the maximum frequency $\omega_{vib}$ with a collective Huang-Rhys factor $S$; this is consistent with the approach taken by Englman and Jortner [20].
Along this effective vibrational coordinate, the potential energy curves for both electronic states are modelled as a pair of displaced harmonic oscillators, each with the same frequency. Finally, all $N$ molecules are strongly coupled to a lossless cavity mode of frequency $\omega_{\text{ph}}$ that is in (or close to) resonance with the effective vibrational mode. To zeroth-order in the diabatic coupling $J_{\text{GE}}$, the Hamiltonian reads

$$H_0 = \hbar \omega_{\text{ph}} \hat{a}_{\text{ph}}^\dagger \hat{a}_{\text{ph}} + \sum_{i=1}^N \hbar \omega_{\text{vib}} \hat{b}_{\text{G},i}^\dagger \hat{b}_{\text{G},i} \langle G_i \rangle \langle G_i \rangle + \sum_{i=1}^N (\hbar \omega_{\text{vib}} \hat{b}_{\text{E},i}^\dagger \hat{b}_{\text{E},i} + \Delta E) \langle E_i \rangle \langle E_i \rangle + \sum_{i=1}^N g \hat{b}_{\text{G},i}^\dagger \hat{a}_{\text{ph}} + \hat{a}_{\text{ph}}^\dagger \hat{b}_{\text{G},i} \rangle \langle G_i \rangle \langle G_i \rangle + \sum_{i=1}^N g \hat{b}_{\text{E},i}^\dagger \hat{a}_{\text{ph}} + \hat{a}_{\text{ph}}^\dagger \hat{b}_{\text{E},i} \rangle \langle E_i \rangle \langle E_i \rangle,$$

where $\hat{a}_{\text{ph}}^\dagger (\hat{a}_{\text{ph}})$ is the creation (annihilation) operator of the photon mode, $\hat{b}_{\text{G},i}^\dagger (\hat{b}_{\text{G},i})$ is the creation (annihilation) operator of the $i$-th molecule’s vibrational mode ($x = G, E$) with $\hat{b}_{\text{G},i}^\dagger = \hat{b}_{\text{G},i} - \sqrt{S}$ for all $i$, $\Delta E$ is the energy gap between the two electronic states of each molecule and $g$ is the single-molecule light-matter coupling strength. Here, we have made the rotating wave approximation (RWA) and assumed that $g$ is the same for both electronic states. Also, zero-point energies of the vibrational states have been omitted since they only contribute constants to the final energies.

To model the non-radiative decay rate of a single molecule $c$ from the $|E_c\rangle$ electronic state to the $|G_c\rangle$ electronic state, we introduce a diabatic coupling term into the Hamiltonian,

$$\hat{V}_{\text{tr},c} = J_{\text{GE}} (|E_c\rangle \langle G_c | + |G_c\rangle \langle E_c |),$$

where $J_{\text{GE}}$ is the corresponding amplitude. Then, following the same procedure as Englman and Jortner [20], we may compute the non-radiative decay rate of molecule $c$ by Fermi’s golden rule, which assumes $\hat{V}_{\text{tr},c}$ to be a perturbation with respect to $H_0$. Despite the presence of light-matter couplings in $H_0$, this assumption remains valid since non-radiative decay effectively couples a single electronic excitation to a large number of vibrational excitations $\approx \Delta E/\hbar \omega_{\text{vib}} \gg 1$, all within the same molecule. As such, the nonlinearity of this process makes it slower than the molecule’s interactions with the cavity mode, which is linear. More quantitatively, non-radiative decay is characterised by the decay amplitude multiplied by the Franck-Condon overlap between the initial and final vibrational states of the decaying molecule; in the low-temperature limit, this takes the form of

$$J_{\text{GE}} \sqrt{e^{-\frac{\Delta E}{\hbar \omega_{\text{vib}}}}} \approx 10^{-9} \hbar \omega_{\text{vib}}$$

which is two orders of magnitude smaller than the decaying molecule’s light-matter coupling strength $g \approx 0.4 \hbar \omega_{\text{vib}}$, $g \sqrt{N} \approx 0.01 \omega_{\text{vib}}, S \approx 0.1, \Delta E \approx 10 \hbar \omega_{\text{vib}}$ and $N \approx 10^{10}$, conditions typical of $S_1 \rightarrow S_0$ transitions of aromatic hydrocarbons [23, 33] under collective VSC [11].

To find the initial and final eigenstates of $\hat{H}_0$, we may, without loss of generality, focus on the decay of molecule 1 from $|E\rangle$ to $|G\rangle$ while keeping the remaining $N - 1$ molecules in $|G\rangle$ (i.e. pick $c = 1$). Then, the initial and final electronic eigenstates of $\hat{H}_0$ may be written collectively as $|E, G, \ldots, G \rangle$ and $|G, G, \ldots, G \rangle$, where we have listed the electronic state of each molecule in increasing order of its index $i$. Each of the two electronic states above comprises $N$ vibrational modes coupled to a single cavity mode. Therefore, all that remains is finding the normal modes of $\hat{H}_0$ within these two electronic subspaces. Working first in the subspace of the initial electronic state, we transform the $N$ vibrational modes into a single bright (B) mode,

$$\hat{b}_B = \frac{1}{\sqrt{N}} (\hat{b}_{E,1} + \sum_{i=2}^N \hat{b}_{G,i}),$$

with the correct symmetry to interact with light and $N - 1$ dark (D) modes,

$$\hat{b}_{D,k} = C_{k,1} \hat{b}_{E,1} + \sum_{i=2}^N C_{k,i} \hat{b}_{G,i},$$

with $2 \leq k \leq N$, that do not couple to light. Note that the constants $\{C_{k,i}\}$ ($1 \leq i \leq N$) are chosen such that the dark modes are orthogonal to the bright mode, i.e. $\sum_{i=1}^N C_{k,i} = 0$, and to each other, i.e. $\sum_{i=1}^N C_{j,i} C_{k,i} = \delta_{jk}$. In this basis, the dark modes are already diagonal while the bright and photon modes mix to give the upper polariton (UP) $\hat{b}_{\text{UP}}$ and lower polariton (LP) $\hat{b}_{\text{LP}}$ modes,

$$\hat{b}_{\text{LP}} = -\sin (\theta) \hat{a}_{\text{ph}} + \cos (\theta) \hat{b}_B,$$

$$\hat{b}_{\text{UP}} = \cos (\theta) \hat{a}_{\text{ph}} + \sin (\theta) \hat{b}_B,$$

with a mixing angle of

$$\theta = \tan^{-1} \left( \frac{\Omega - \Delta}{2 \sqrt{N} g} \right),$$

where $\Omega = \sqrt{\Delta^2 + 4g^2 N}$ is the Rabi splitting, $\Delta = \omega_{\text{ph}} - \omega_{\text{vib}}$ is the detuning and $g \sqrt{N}$ is the collective light-matter coupling strength. Also, the mode frequencies are

$$\omega_{\text{LP}} = \omega_{\text{vib}} + \frac{\Delta - \Omega}{2},$$

$$\omega_{\text{UP}} = \omega_{\text{vib}} + \frac{\Delta + \Omega}{2},$$

$$\omega_{D,k} = \omega_{\text{vib}}$$

for all $k$. (10)

We may follow the same steps to define the bright, dark and polariton modes $\hat{b}_B$, $\{\hat{b}_{D,k}\}$, $\hat{b}_{\text{LP}}$ and $\hat{b}_{\text{UP}}$.
in the final electronic state subspace, where we shall therefore prime quantities belonging to the final state and unprime those for the initial state. Note that, since vibrational modes have the same light-matter coupling in both electronic states, the primed modes have the same frequencies as the unprimed ones, i.e. $\omega_{\text{LP}'} = \omega_{\text{LP}}$, $\omega_{\text{UP}'} = \omega_{\text{UP}}$ and $\omega_{\text{D}'} = \omega_{\text{D}}$. Notice also how, during the decay of molecule 1 from |E⟩ to |G⟩, all N + 1 modes change,

$$\text{LP} + \text{UP} + \sum_{k=1}^{N-1} D_k \rightarrow \text{LP}' + \text{UP}' + \sum_{k=1}^{N-1} D_k'. \quad (11)$$

However, by writing the dark modes in a highly localised basis [16, 37, 63], contributions from molecule 1 are completely localised onto one dark mode $D_{\text{loc}}$, such that we may reduce the number of reacting modes to three,

$$\text{LP} + \text{UP} + D_{\text{loc}} \rightarrow \text{LP}' + \text{UP}' + D_{\text{loc}}'. \quad (12)$$

Specifically, in this basis, the relevant dark mode operators are

$$\hat{b}_{D_{\text{loc}}} = \sqrt{\frac{N}{N-1}} \hat{b}_{\text{E,1}} - \sqrt{\frac{1}{N(N-1)}} \sum_{i=2}^{N} \hat{b}_{G,i}, \quad (13)$$

$$\hat{b}_{D_{\text{loc}}}' = \sqrt{\frac{N}{N-1}} \hat{b}_{\text{G,1}} - \sqrt{\frac{1}{N(N-1)}} \sum_{i=2}^{N} \hat{b}_{G,i}. \quad (14)$$

More details can be found in Supplementary Note 1.

### Evaluating the golden rule expression

Since the energy gap law is most widely applied in the low temperature limit, the same assumption is made here whereby all N molecules are in the ground vibrational state of their respective electronic states, given by $|0^{\text{LP}}, 0^{\text{UP}}, 0^{\text{D}}\rangle$. Here and hereafter, we will label eigenstates of the zeroth-order Hamiltonian $H_0$ within the electronic subspace by three numbers representing the occupancy numbers in the LP, UP and localised D modes respectively. By applying first-order time-dependent perturbation theory, we arrive at the expression

$$W_{\text{VSC}} \approx \frac{2\pi}{\hbar} \left| J_{\text{GE}} \right|^2 \sum_{n_{\text{LP}}, n_{\text{UP}}, n_{\text{D}}=0}^{\infty} \delta \left( \Delta E - n_{\text{LP}} \hbar \omega_{\text{LP}} - n_{\text{UP}} \hbar \omega_{\text{UP}} - n_{\text{D}} \hbar \omega_{\text{vib}} \right) \times \left| \langle n_{\text{LP}}^{(\text{LP}')}, n_{\text{UP}}^{(\text{UP}')}, n_{\text{D}}^{(\text{D}')}, 0^{(\text{LP})}, 0^{(\text{UP})}, 0^{(\text{D})} \rangle \right|^2, \quad (15)$$

where $W_{\text{VSC}}$ is the non-radiative decay rate under VSC and $\delta$ is the Dirac delta function. It may be shown that the potential energy surfaces of the initial and final electronic states along the LP, UP and D modes behave as displaced harmonic oscillators too, with effective Huang-Rhys factors of $S_{\text{LP}} = \frac{\tilde{S}}{2} \cos^2 \theta$, $S_{\text{UP}} = \frac{\tilde{S}}{2} \sin^2 \theta$ and $S_{\text{D}} = \tilde{S} (N - 1)$ respectively (see Supplementary Note 2). By expressing the Dirac delta function in its Fourier form and evaluating the Franck-Condon overlap of displaced harmonic oscillators, we get

$$W_{\text{VSC}} \approx \frac{|J_{\text{GE}}|^2}{\hbar (\hbar \omega_{\text{vib}})} e^{-S} \sum_{n_{\text{LP}}, n_{\text{UP}}, n_{\text{D}}=0}^{\infty} \int_{-\infty}^{\infty} dt \exp \left( i \frac{\Delta E}{\hbar \omega_{\text{vib}}} t - i n_{\text{LP}} \omega_{\text{LP}} t - i n_{\text{UP}} \omega_{\text{UP}} t - i n_{\text{D}} \omega_{\text{D}} t \right) \times \left( \frac{S_{\text{LP}}}{n_{\text{LP}}} \langle n_{\text{LP}}^{(\text{LP})} | (S_{\text{UP}}^{(\text{UP})} n_{\text{UP}}^{(\text{UP})} (S_{\text{D}}^{(\text{D})})^{n_{\text{D}}} \rangle \right), \quad (16)$$

where $\omega_{\text{P}} = \omega_{\text{F}} / \omega_{\text{vib}}$ is the frequency of the polariton modes $P = \text{LP}, \text{UP}$ relative to that of the dark mode (as well as the bare molecule) and t is dimensionless. Note that in the original work by Englnam and Jortner [20], the integral in Eq. [16] was evaluated via two approaches: (1) by performing a short time expansion, and (2) using the saddle point approximation. The first approach is valid when the vibronic couplings (characterised by the Huang-Rhys factors) are large, such that non-radiative relaxation occurs predominantly through a thermally activated pathway. Indeed, the resulting rate expression has an exponential dependence on the activation energy and has been used to describe electron transfer rates through the celebrated Marcus [33] and Marcus-Levich-Jortner [37, 39] theories. Applications of these theories to VSC have been explored by our group [16] and the Phuc and Ishizaki groups [40] and will not be discussed here. In contrast, the second approach is useful when the vibronic couplings are weak, such that nuclear tunneling is the main non-radiative decay pathway. This approach is more applicable to intersystem crossing and internal conversions – processes which are experimentally modelled by the energy gap law [23–32] and forms the focus of this paper. These differences have been detailed by Nitzan [11] and a useful guide on the saddle point method may be found in Morse and Feshbach [12]. More recently, an evaluation of such rate expressions through a path-integral approach [43] and the general case of VSC-mediated resonance energy transfer [44] have also been considered by the Cao group.

Returning to Eq. [16], one way to move forward is to bring all three summations into the integral and perform a single saddle point approximation (see Supplementary Note 3) to obtain

$$W_{\text{VSC}} \approx \frac{|J_{\text{GE}}|^2}{\hbar (\hbar \omega_{\text{vib}})} e^{-S} \int_{-\infty}^{\infty} dt \exp \left( -\frac{2\pi}{\hbar f'(\tau_0)} e^{-f(\tau_0)} \right), \quad (17)$$

where $f(\tau) = -\frac{\Delta E}{\hbar \omega_{\text{vib}}} \tau - S_{\text{LP}} e^{-\omega_{\text{LP}} \tau} - S_{\text{UP}} e^{-\omega_{\text{UP}} \tau} - S_{\text{D}} e^{-\omega_{\text{D}} \tau}$ and $\tau = \tau_0$ is the extremum of $\text{Re} f(\tau)$. This approach has the effect of taking the final vibrational states of all three modes to the continuum limit and is valid for $\frac{2\pi}{\hbar \omega_{\text{vib}}} \gg 1$. Finding $\tau_0$ is, however, challenging and involves solving a transcendental equation. Here, we seek an analytical solution for $W_{\text{VSC}}$ by setting the
detuning $\Delta$ to zero, expanding $\tau_0$ in powers of $\frac{g\sqrt{N}}{\omega_{\text{vib}}}$ and keeping the leading term to obtain

$$W_{\text{VSC}}^{\text{one}} \approx \frac{|J_{\text{GE}}|^2}{h} e^{-S} \sqrt{\frac{2\pi}{h\omega_{\text{vib}}\Delta E}} \exp \left[ -\Gamma \frac{\Delta E}{h\omega_{\text{vib}}} \right],$$

(18)

with

$$\Gamma = \gamma + \frac{g}{\omega_{\text{vib}}} \left[ \frac{1}{2} \left( \ln \frac{\Delta E}{S\hbar\omega_{\text{vib}}} \right)^2 \right] + O \left( \frac{g\sqrt{N}}{\omega_{\text{vib}}} \right)^4, \quad \phi = 1 + \frac{g}{\omega_{\text{vib}}} \left( \ln \frac{\Delta E}{S\hbar\omega_{\text{vib}}} + 1 \right) + O \left( \frac{g\sqrt{N}}{\omega_{\text{vib}}} \right)^4,$$

(19)

(20)

where $\gamma = \ln \frac{\Delta E}{S\hbar\omega_{\text{vib}}} - 1$. Comparing this result with Eq. [2], we notice that the first terms give the bare molecule rate while subsequent terms serve as corrections due to coupling to the cavity. Surprisingly, the first correction terms do not depend on $N$, a result that has been corroborated by Yang and Cao [43] and more recently by Kansanen [46]. Therefore, for some constant and small $g\sqrt{N}$ (relative to $\omega_{\text{vib}}$), we expect VSC to enhance the decay rate at small $N$, since this implies having a system with larger $g$. Physically, this implies that the cavity’s coupling to the single decaying molecule dominates the relaxation dynamics, and further interactions between the $N-1$ non-decaying molecules and the single decaying one, through the cavity, appear only as higher-order processes. This effect, which is further explained by Du and co-workers [47], is essentially the message from the polariton “large N problem” [48] (more to follow).

We now consider the case whereby, starting from Eq. (21), only the sum over final dark states is brought into the integral. Many saddle point approximations are now required, one for every $n_{\text{LP}}$ and $n_{\text{UP}}$ term, and we obtain

$$W_{\text{VSC}}^{\text{many}} \approx \frac{|J_{\text{GE}}|^2}{h} e^{-S} \sum_{n_{\text{LP}},n_{\text{UP}}=0}^{\infty} W_{\text{VSC}}^{\text{many}} (n_{\text{LP}}, n_{\text{UP}})$$

(21)

with

$$W_{\text{VSC}}^{\text{many}} (n_{\text{LP}}, n_{\text{UP}}) = (S_{\text{LP}})^{n_{\text{LP}}} (S_{\text{UP}})^{n_{\text{UP}}} \frac{n_{\text{LP}}!}{n_{\text{UP}}!} \times \sqrt{\frac{2\pi}{h\omega_{\text{vib}}\Delta E}} \exp \left( -\frac{\Delta E}{h\omega_{\text{vib}}} \right),$$

(22)

where $\gamma = \ln \frac{\Delta E}{S\hbar\omega_{\text{vib}}} - 1$ and $\Delta \tilde{E} = \Delta E - n_{\text{LP}} \hbar \omega_{\text{LP}} - n_{\text{UP}} \hbar \omega_{\text{UP}}$ is the effective energy gap for dark mode decay after subtracting any energy distributed through the LP and UP modes. This result is valid in the limit of $\frac{\Delta \tilde{E}}{\hbar \omega_{\text{vib}}} \gg 1$ for every $(n_{\text{LP}}, n_{\text{UP}})$ term (see Supplementary Note 4); effectively, this approach assumes a continuum of final dark states with discrete final polariton states or, equivalently, that most of the energy is being distributed through the dark mode. With this alternative, more intuitive approach, the polariton modes’ contribution to the decay rate may be separately identified. For instance, the $(n_{\text{LP}}, n_{\text{UP}}) = (0, 0)$ term in Eq. (21) reduces to the single molecule decay rate $W_{\text{bare}}$ in the large $N$ limit. This is the case whereby all of the energy is transferred through the dark mode. As such, terms of $n_{\text{LP}}, n_{\text{UP}} > 0$ signify the polaritons’ contributions to the decay rate and are generally small. For instance, $W_{\text{VSC}}^{\text{many}} (0, 1)$ is approximately

$$W_{\text{VSC}}^{\text{many}} (0, 1) \approx S_{\text{UP}} e^{-S_{\text{UP}}} W_{\text{VSC}}^{\text{many}} (0, 0).$$

(23)

where $\gamma = \ln \frac{\Delta E}{S\hbar\omega_{\text{vib}}} - 1$ and we have assumed $\omega_{\text{UP}} \approx \omega_{\text{vib}}$, which is true under typical conditions for VSC. Note that, near resonance, $S_{\text{UP}} \approx \frac{\pi}{2}$. Since $N$ is usually large, we expect $S_{\text{UP}}$ to be small and $W_{\text{VSC}}^{\text{many}} (0, 1) \ll W_{\text{VSC}}^{\text{many}} (0, 0)$. Similar arguments may be made for larger $n_{\text{LP}}$ terms and for $n_{\text{LP}}$, $n_{\text{UP}}$ terms (see Supplementary Note 5). Indeed, decay through the dark mode dominates the overall non-radiative decay rate. This is a manifestation of the “large $N$ problem” [49], while using the UP mode reduces the effective energy gap experienced by the dark modes, thereby increasing the non-radiative decay rate through the $\gamma^2$ factor in Eq. (23), this benefit is hampered by the entropic penalty from the polariton modes each containing only $\approx \frac{1}{N}$ part of a single molecule, where $N$ is typically large.

For VSC to be useful, we want the case of $W_{\text{VSC}}^{\text{many}} (0, 1) > W_{\text{VSC}}^{\text{many}} (0, 0)$, that is, when decay through the UP mode becomes significant. Near resonance, this condition simplifies to

$$N \lesssim \frac{1}{S_{\text{UP}}} \frac{\Delta E}{h\omega_{\text{vib}}},$$

(24)

With $W_{\text{VSC}}^{\text{one}}$, we concluded that, for some constant and small $g\sqrt{N}/\omega_{\text{vib}}$, rate enhancement under VSC may only be achieved at small $N$. Here, we specify the condition of small $N$ with Eq. (24). $N$ must be smaller than the electronic energy gap relative to the vibrational frequency. This condition arises because the system only sees the $\frac{\pi}{2N}$ entropic penalty and not the $g\sqrt{N}$ frequency increase in the UP mode; this again explains why $W_{\text{VSC}}^{\text{one}}$ had no $N$ dependence to leading order in $g\sqrt{N}$.

In practice, $\Delta E$ is usually around $7000 - 20000 \text{cm}^{-1}$ and $\omega_{\text{vib}}$ is usually chosen to be $3000 \text{cm}^{-1}$ (corresponding to the C–H stretch) [52, 53]. This gives $\frac{\Delta E}{\omega_{\text{vib}}} \approx 2 - 7$. Consequently, we must reach the $N \rightarrow 1$ limit, i.e., single molecule coupling limit, before we can observe rate enhancement under VSC. Such couplings may be achieved in nanophotonic cavities [50, 51]; however, under most circumstances, VSC should have minimal effects on the energy gap law.
The discussion above may be verified with some numerical simulations. We consider systems under resonance condition $\Delta = 0$ with $g\sqrt{N} = 0.01\omega_{\text{vib}}$ and $S = 0.1$ over a range of energy gaps $10 \leq \frac{\Delta E}{\hbar \omega_{\text{vib}}} \leq 50$ and number of molecules $10 \leq N \leq 10^4$. These energy gaps are larger than most chromophores and we expect an even smaller rate enhancement in usual chromophores; the remaining parameters are typical of non-radiative decays of aromatic hydrocarbons to the ground state [23, 33] under collective VSC [11]. Firstly, rates computed using $W_{\text{VSC}}^{\text{one}}$ and $W_{\text{VSC}}^{\text{many}}$ were within $\sim 0.1\%$ of each other, i.e. both ways of applying saddle point approximations give answers that are numerically similar (see Supplementary Note 4). Next, from Fig. 2 we verify that rate enhancement is only observed when $N \leq \frac{1}{5} \frac{\Delta E}{\hbar \omega_{\text{vib}}}$, a small parameter range that is difficult to achieve experimentally and, even so, gives little rate enhancements of $\sim 1\%$ higher rates than the bare molecule case. Finally, by observing the number of terms added before the sum in $W_{\text{VSC}}^{\text{many}}$ converges, we conclude that polaritons are indeed responsible for the observed rate enhancements. In fact, the largest decay rates in Fig. 2 are obtained from close-to-complete decay through the polariton modes.

In the next few sections, we will discuss how we may overcome the entropic penalty associated with polariton mode decay with (1) higher UP frequencies and (2) polariton condensates.

Overcoming the entropic penalty with larger UP frequencies

The UP mode offers a higher frequency decay channel that can potentially speed up non-radiative decay by reducing the effective energy gap $\Delta E$ for dark mode decay. However, under most experimental circumstances, this advantage cannot be exploited to its fullest. This is because the light-matter coupling strength $g\sqrt{N}$ is typically small at around $0.01 - 0.05\omega_{\text{vib}}$, so $\omega_{\text{UP}} \approx \omega_{\text{vib}}$. What if $\omega_{\text{UP}}$ is appreciably larger than $\omega_{\text{vib}}$? To answer this, we return to Eq. (23), but, this time, we do not set $\omega_{\text{UP}} \approx \omega_{\text{vib}}$. The expression becomes

$$w_{\text{VSC}}^{\text{many}}(0, 1) \approx S_{\text{UP}} e^{\gamma \omega_{\text{UP}}} w_{\text{VSC}}^{\text{many}}(0, 0),$$

where $\gamma = \ln \frac{\Delta E}{\hbar \omega_{\text{vib}}} - 1$. Then, decay through the UP mode becomes significant when $w_{\text{VSC}}^{\text{many}}(0, 1) > w_{\text{VSC}}^{\text{many}}(0, 0)$, which simplifies to

$$\frac{S_D}{S_{\text{UP}}} \leq \frac{\Delta E}{\hbar \omega_{\text{vib}}} e^{1 + \gamma (\omega_{\text{UP}} - 1)}.$$  

Near resonance, we have $S_{\text{UP}} \approx \frac{S}{N}$ and $\omega_{\text{UP}} \approx 1 + \frac{2\sqrt{N}}{\omega_{\text{vib}}}$, so the condition becomes

$$N \lesssim 1 \frac{\Delta E}{\hbar \omega_{\text{vib}}} e^{\gamma \left(\frac{\omega_{\text{UP}}}{\omega_{\text{vib}}} - 1\right)}.$$  

which suggests a competition between the UP mode frequency $\omega_{\text{UP}}$ improving decay rates and the entropic penalty $\frac{S}{N}$ reversing this effect. Here, we want the former to dominate over the latter.

For larger $\omega_{\text{UP}}$ values, the validity of rates computed using $W_{\text{VSC}}^{\text{one}}$ (Eq. (17)) cannot be easily verified. While there are techniques that may overcome this problem [43, 52, 54], for simplicity, we choose to rewrite the integral in Eq. (16) into another form so that we can continue to apply the saddle point approximation. This limitation and the alternative taken are detailed in Supplementary Note 6, and rates evaluated using this new approach will be labelled as $W_{\text{VSC}}^{\text{one}}$. 

![FIG. 2. Effect of collective VSC on single-molecule non-radiative decay rates over ranges of $N$, the number of molecules, and $\Delta E$, the relative electronic energy gap. Rates inside the cavity were calculated using many saddle point approximations ($W_{\text{VSC}}^{\text{many}}$, see Eq. (21)) and compared with that outside of the cavity ($W_{\text{bare}}$, see Eq. (24)) that needed to be summed before the subsequent term falls below $10^{-15}$. It increases with increasing rate changes, suggesting that the UP mode is responsible for the growing decay rates. Similar results were observed for the growing decay rates.](image-url)
Increasing the upper polariton frequency by deep strong light-matter couplings

One way to achieve higher $\omega_{\text{UP}}$ would be through stronger light-matter couplings such as those in the ultrastrong regime ($0.1\omega_{\text{ph}} \lesssim g\sqrt{N} < 1$) and deep strong regime ($\omega_{\text{ph}} \lesssim g\sqrt{N}$). In these regimes, the RWA is no longer valid and corrections to the polariton modes have to be made [55,58]. The approach closely follows the work by Hopfield [59] and has been detailed in Supplementary Note 7; here, we summarise the key results. For simplicity, we consider the zero detuning case ($\Delta = 0$), such that $\omega_{\text{ph}} = \omega_{\text{vib}}$ and we may categorise coupling regimes with $g\sqrt{N}$ as well. The corrected polariton modes have frequencies

$$\omega_{\text{LP}} = \omega_{\text{vib}}(\xi - \epsilon),$$

$$\omega_{\text{UP}} = \omega_{\text{vib}}(\xi + \epsilon),$$

with $\epsilon = g\sqrt{N}/\omega_{\text{vib}}$ and $\xi = \sqrt{1 + \epsilon^2}$, and Huang-Rhys factors

$$S_{\text{LP}} = \frac{S}{2N}\sigma_{\text{LP}},$$

$$S_{\text{UP}} = \frac{S}{2N}\sigma_{\text{UP}},$$

with $\sigma_{\text{LP}} = 2K^2(2\xi(\xi - \epsilon) - (\xi - \epsilon + 1)^2)$ and $\sigma_{\text{UP}} = 2K^2(2\xi(\xi + \epsilon) + (\xi + \epsilon + 1)^2) = 2\left[\pm \epsilon^3 + (1 + \epsilon)^2 + \epsilon^2(1 + 2\xi)\right]$. Substituting these into Eq. (26), we obtain the new condition for polariton-mediated rate enhancement

$$N \lesssim \frac{1}{5}\frac{\Delta E}{\hbar \omega_{\text{vib}}} e^{\gamma(\xi - 1)}\sigma_{\text{UP}},$$

(30)

with the last two terms being corrections from the counter-rotating and dipole self-energy terms. Note that $\xi - 1$ and $\sigma_{\text{UP}}$ are positive, monotonically increasing functions with respect to $\epsilon$. As such, the corrected UP mode will have higher frequencies and larger effective Huang-Rhys factors (than the RWA case) that, ultimately, make it easier to achieve rate enhancement. For instance, for a typical system ($\Delta = 0$, $S = 0.1$, $\Delta E = 15\hbar \omega_{\text{vib}}$) with reasonable $N$ of $10^{10}$, Eq. (30) simplifies to $\frac{g\sqrt{N}}{\omega_{\text{vib}}} \gtrsim 2.85$, as opposed to $\frac{g\sqrt{N}}{\omega_{\text{vib}}} \gtrsim 5.47$ from Eq. (27) (i.e. under the RWA). Regardless, decay through the UP is only significant in the deep strong coupling regime. Numerical simulations suggest that over two-fold rate enhancement may occur as early as $\frac{g\sqrt{N}}{\omega_{\text{vib}}} \gtrsim 2.5$ (Fig. 3) and the computed decay rate is accurate in this region. Systems of this regime, however, have not been realised experimentally.

Effects of positive detunings on the non-radiative decay rate

Perhaps a more practical way of achieving larger UP frequencies under typical coupling regimes is to introduce some positive detuning $\Delta > 0$. If we assume $g\sqrt{N}$ to be small such that $g\sqrt{N} \ll \frac{\Delta}{2}$, then the UP frequency is approximately $\omega_{\text{UP}} \approx \omega_{\text{vib}} + \Delta$ and can be increased with larger $\Delta$. This analysis is somewhat naive because larger detunings make the UP mode more photon-like and less matter-like, which in turn imposes a larger entropic penalty on UP mode decay. Again, we hope for the frequency increase to dominate over this greater entropy penalty. More specifically, we want

$$N \lesssim \frac{1}{5}\frac{\Delta E}{\hbar \omega_{\text{vib}}} e^{\gamma}\left(\frac{\omega_{\text{Vib}}}{2\sin^2 \theta}\right),$$

(31)

which is Eq. (26) after substituting $S_{\text{UP}} = \frac{S}{N}\sin^2 \theta$ and $\omega_{\text{UP}} \approx 1 + \frac{\Delta}{\omega_{\text{vib}}}$. This translates to $\Delta \gtrsim 8.7\omega_{\text{vib}}$ for a typical system ($g\sqrt{N} = 0.01\omega_{\text{vib}}$, $S = 0.1$, $\Delta E = 15\hbar \omega_{\text{vib}}$, $N = 10^{10}$).

Actually, this analysis is crude because the light-matter coupling strength $g$ changes with $\Delta$. From cavity QED, the collective light-matter coupling strength is [56]

$$g\sqrt{N} = \left(\frac{\omega_{\text{ph}}}{4\epsilon_0 V m \omega_{\text{vib}}} \mu_0^2 \right) \sqrt{N},$$

(32)

where $V$ is the effective quantisation volume of the cavity, $m$ is the reduced mass of the single-molecule vibrational mode, and $\mu_0^2 = \frac{\partial^2 \langle x \rangle}{\partial x^2} |_{x=0}$. $\epsilon$ is the linear change in the dipole moment $\mu$ along the single-molecule vibrational mode, projected onto the polarisation unit vector $\epsilon$ (see Supplementary Note 7 for more details). Also, for most experiments conducted in Fabry-Perot cavities, $\omega_{\text{ph}}$ is modified by changing the distance between the mirrors, so $V \propto \frac{1}{\omega_{\text{ph}}}$. Let us define the

![FIG. 3. Rate changes due to VSC over a range of collective light-matter coupling strengths $g\sqrt{N}/\omega_{\text{vib}}$. Rate enhancements relative to the bare-molecule rate remain small in the ultrastrong coupling regime (USC; characterised by $0.1\omega_{\text{vib}} \lesssim g\sqrt{N} < \omega_{\text{vib}}$) but become significant in the deep strong coupling regime (DSC; characterised by $g\sqrt{N} \gtrsim \omega_{\text{vib}}$). Note that the decay rates under VSC were computed with $W_{\text{One}}^{\text{USC}}$, which applies the saddle point approximation to a different integral form (see Supplementary Note 6). As such, these rates are accurate only along the green curve (see Supplementary Note 8). All plots were generated with the following parameters: detuning, $\Delta = 0$; bare-molecule Huang-Rhys factor, $S = 0.1$; relative electronic energy gap, $\Delta E = 15\hbar \omega_{\text{vib}}$; number of molecules, $N = 10^{10}$.](image_url)
zero-detuning collective light-matter coupling strength as \( \tilde{g} \sqrt{N} = \left( \frac{\omega_{\text{ph}}}{\omega_{\text{vib}}} \right) \sqrt{N} \), which is independent of \( \omega_{\text{ph}} \) and is known to be \( \approx 0.01 \omega_{\text{vib}} \). Then, under off-resonant conditions, the collective light-matter coupling strength becomes

\[
g \sqrt{N} = \frac{\omega_{\text{ph}}}{\omega_{\text{vib}}} \tilde{g} \sqrt{N} = \left( \frac{\Delta}{\omega_{\text{vib}}} + 1 \right) \tilde{g} \sqrt{N},
\]

which increases with detuning. Note that we need \( g \sqrt{N} < 0.1 \omega_{\text{ph}} \) or \( \tilde{g} \sqrt{N} < 0.1 \omega_{\text{vib}} \) for the RWA to remain valid \([55, 56]\). In other words, as we move towards positive detunings, the RWA remains valid as long as this was the case when the system was close to resonance.

Reformulating our numerical simulations with \( \tilde{g} \sqrt{N} = 0.01 \omega_{\text{vib}} \) and, as before, \( S = 0.1, \Delta E = 15 \hbar \omega_{\text{vib}} \) and \( N = 10^{10} \), we find more than 20-fold rate enhancements as early as \( \Delta \gtrsim 7 \omega_{\text{vib}} \) or \( \omega_{\text{ph}} \gtrsim 8 \omega_{\text{vib}} \) (Fig. 4). The computed decay rate is accurate in this region and agrees with our estimate of \( \Delta \gtrsim 8.7 \omega_{\text{vib}} \). Two comments are now in order:

- Firstly, at extremely large detunings of \( \Delta \approx 7 \omega_{\text{vib}} \), the UP mode is largely photonic. For instance, the Hopfield coefficient of the UP, given by \( \sin \theta \), is around 0.011. This means that rate enhancement is achieved by the creation of largely-photonic quasiparticles. Since optical cavities are imperfect with a certain degree of leakage, we wonder if these polaritons will result in photon emission from the cavity. Clearly this non-radiative process is no longer “non-radiative” under VSC, because, even though the diabatic coupling term \( J_{\text{GE}} \) belongs to the matter component, these processes may now emit quasiparticles that are primarily photons.

- Secondly, there are plausibly other off-resonant effects that will become crucial in this highly-detuned regime. For instance, a photon energy of \( 8.0 \hbar \omega_{\text{vib}} \) is more than half that of the electronic energy gap \( \Delta E = 15 \hbar \omega_{\text{vib}} \) and may fall into the electronic strong coupling regime \([60]\). Roughly-speaking, such systems have Hopfield coefficients of around 0.11 if we consider the lower exciton-polariton state in the single excitation manifold (assuming a typical collective electronic light-matter coupling strength \( \tilde{g} \sqrt{N} \) of 0.05 \( \Delta E \)). This is not trivial when compared to the Hopfield coefficient of 0.011 for the vibrational polariton mode; as such, our model is inaccurate under these circumstances since both electronic and vibrational strong couplings have to be considered.

\[
\text{FIG. 4. Rate changes due to VSC over a range of detunings } \Delta/\omega_{\text{vib}}. \text{ Significant rate enhancements are only observed at large positive detunings of } \Delta \gtrsim 7 \omega_{\text{vib}}. \text{ Note that the decay rates under VSC were computed with } \tilde{W}_{\text{VSC}}, \text{ which applies the saddle point approximation to a different integral form (see Supplementary Note 6). As such, these rates are accurate only along the green curve (see Supplementary Note 8). All plots were generated with the following parameters: zero-detuning collective light-matter coupling, } \tilde{g} \sqrt{N} = 0.01 \omega_{\text{vib}}; \text{ bare-molecule Huang-Rhys factor, } S = 0.1; \text{ relative electronic energy gap, } \Delta E = 15 \hbar \omega_{\text{vib}}; \text{ number of molecules, } N = 10^{10}.
\]

**Overcoming the entropic penalty with vibrational polariton condensates**

Polariton condensates provide a large number of initial excitations in the polariton modes \([61]\) and have been proposed as an avenue for improving chemical reactivities \([17, 19]\). In our case, a polariton condensate is expected to redistribute more of the vibrational energy into the polariton modes so that decay through these modes becomes more favourable. To illustrate this, we return to the golden rule expression, but, this time, we assume a lower polariton condensate with \( N_{\text{LP}} \) excitations in the initial state

\[
W_{\text{cond}} = \frac{2\pi}{\hbar} |J_{\text{GE}}|^2 \sum_{\Delta n_{\text{LP}}=-N_{\text{LP}}}^{\infty} \sum_{n_{\text{UP}},n_{\text{D}}=0}^{\infty} \delta (\Delta E - \Delta n_{\text{LP}} \hbar \omega_{\text{LP}} - n_{\text{UP}} \hbar \omega_{\text{UP}} - n_{\text{D}} \hbar \omega_{\text{vib}}) \times \langle n_{\text{LP}}', n_{\text{UP}}', n_{\text{D}}' | N_{\text{LP}} | 0_{\text{LP}}, 0_{\text{UP}}, 0_{\text{D}} \rangle^2,
\]

where \( W_{\text{cond}} \) is the non-radiative decay rate under VSC with a \( \text{LP} \) condensate and \( \Delta n_{\text{LP}} = n_{\text{LP}} - N_{\text{LP}} \) is an integer running from \( -N_{\text{LP}} \) to \( \infty \) and represents the change in number of LP quanta after non-radiative decay. By writing the Dirac delta function in its Fourier form, bringing only the sum over final dark states into the integral and performing many saddle point approximations, we obtain

\[
W_{\text{cond}} \approx \frac{2\pi}{\hbar} |J_{\text{GE}}|^2 e^{-S} \times \sum_{\Delta n_{\text{LP}}=-N_{\text{LP}}}^{\infty} \sum_{n_{\text{UP}}=0}^{\infty} W_{\text{cond}} (\Delta n_{\text{LP}}, n_{\text{UP}}),
\]

\( S \) being the entropy per molecule.
with

\[ w_{\text{cond}}(\Delta N_{LP}, n_{UP}) = e^{\frac{1}{2} S_{LP}(n_{LP}) |N_{LP}|^2} \left( \frac{S_{UP}}{n_{UP}} \right) \frac{2}{\sqrt{\hbar \omega_{\text{vib}} \Delta E_{\text{cond}}}} \times \exp \left[ -\left( \frac{\Delta E_{\text{cond}}}{\hbar \omega_{\text{vib}}} - 1 \right) \frac{\Delta E}{\hbar \omega_{\text{vib}}} \right], \]

where \( \Delta E_{\text{cond}} = \Delta E - \Delta N_{LP} \hbar \omega_{\text{LP}} - n_{UP} \hbar \omega_{\text{VSC}} \) is the new effective energy gap for dark mode decay. Again, the approximation is valid in the limit of \( \frac{\Delta E_{\text{cond}}}{\hbar \omega_{\text{vib}}} \gg 1 \). This result has the same physical interpretation as \( W_{\text{many VSC}} \).

By estimating the excited-state Franck-Condon overlap (see Supplementary Note 9), the \((\Delta N_{LP}, n_{UP}) = (0, 0)\) term in Eq. (35) reduces to the single molecule decay rate in the large \( N \) limit, signifying that terms of \( \Delta N_{LP}, n_{UP} \neq 0 \) represent the polariton contributions to the decay rate. The UP contribution may be represented by \( w_{\text{cond}}(0, 1) \approx S_{UP} \gamma_{\text{cond}}(0, 0) \), where \( \gamma = \ln \frac{\Delta E_{\text{cond}}}{\hbar \omega_{\text{vib}}} - 1 \). This equation takes the same form as Eq. (23) and may be reduced to Eq. (24): the small \( N \) condition for polariton-mediated rate enhancement. What is interesting, however, is the decay through the LP mode under the influence of a LP condensate. We compute

\[ w_{\text{cond}}(1, 0) \approx S_{LP}(N_{LP} + 1) e^{\frac{1}{2} w_{\text{cond}}(0, 0)}, \]

and find that the condensate effectively increases the LP Huang-Rhys factor from \( S_{LP} \) to \( S_{LP}(N_{LP} + 1) \). Finally, decay through the LP mode becomes significant when \( w_{\text{cond}}(1, 0) > w_{\text{cond}}(0, 0) \), or

\[ \frac{N_{LP}}{N} \geq 5.2 \frac{\hbar \omega_{\text{vib}}}{\Delta E}, \]

where we have noted that, near resonance, \( S_{LP} \approx \frac{S}{N} \). Physically, the LP condensate supplies energy to the LP mode, giving it more entropic “weight” during non-radiative decay. This effect is seen by an increase in the Huang-Rhys factor from \( S \) to \( \frac{S}{N} (N_{LP}) \), thereby providing a smaller “effective” \( N \) needed in the small \( N \) condition of Eq. (23). Running numerical simulations with the same conditions of \( \Delta = 0, g/\sqrt{N} = 0.01 \hbar \omega_{\text{vib}} \), \( S = 0.1 \) and a specific \( \Delta E = 15.2 \hbar \omega_{\text{vib}} \), we see in Fig. 2b that, with \( N_{LP} \geq 5.2 \frac{\hbar \omega_{\text{vib}}}{\Delta E} \approx 0.33 \), appreciable rate enhancements may be observed even at large \( N \) of \( 10^4 \). We may also verify in Fig. 3 and 4 that the LP is indeed responsible for this effect. Thus, large enhancement is now possible even for more realistic systems with smaller energy gaps; for instance, with \( \Delta E = 7 \hbar \omega_{\text{vib}} \approx 21000 \text{ cm}^{-1} \), we need a condensate ratio of \( \frac{N_{LP}}{N} \geq 0.7 \). Note that the condensate ratios considered by this work were estimated based on the fraction of excitations that can be achieved in a nonlinear optical spectroscopy experiment, which has been estimated by Ribeiro and co-workers to be \( \mathcal{O}(10^{-4}) \) [63]. As an aside, we have chosen \( \Delta N_{LP} = +1 \) and not \(-1\) to obtain Eq. (38) because the latter would increase the effective energy gap \( \Delta E_{\text{cond}} \) for dark mode decay and reduce the overall decay rate.

Similar arguments may be made for an upper polariton condensate with \( N_{UP} \) excitations in the initial state. By mapping LP \( \rightarrow \) UP, the condensate’s effects can be felt when \( \frac{N_{UP}}{N} \geq 5.2 \frac{\hbar \omega_{\text{vib}}}{\Delta E} \), which is verified by performing numerical simulations using the same set of parameters as before (Fig. 3b-f). Of course, the UP mode has a higher frequency than the LP mode, so the UP condensate gives faster decay rates than the LP condensate. Other than that, similar trends are observed for both types of condensates.

**CONCLUSIONS**

Collective VSC is an ensemble effect, that is, we need a macroscopic number of molecules \( N \) to couple to the cavity mode for the light-matter coupling to be appreciable. Where light-matter interactions are concerned, one reacting molecule is only a needle in a haystack: only \( \frac{1}{N} \) of the vibrational mode couples to the photon mode (through the polaritons) while the remaining \( \frac{N-1}{N} \) of it is distributed into the dark modes that are chemically identical to the bare molecule (at least in the absence of disorder and non-equilibrium effects [15]); this is the essence of the polariton “large \( N \) problem” [45]. As such, we do not expect VSC to modify the non-radiative decay rate unless the polariton modes possess some unique advantage over the dark modes. In this paper, we show how the higher UP frequency (relative to the dark mode) is this advantage, yet it cannot be appreciably exploited under most circumstances for VSC. Instead, we require conditions that are either not yet experimentally achievable (deep strong light-matter coupling) or associated with theoretical complications (highly off-resonant cavities). Vibrational polariton condensates, on the other hand, may provide an elegant solution to this entropy problem. By starting from a macroscopic occupation of a polariton mode, more of the vibrational energy may be redistributed through the polariton modes. Care must be taken in this regime though, since, under such extreme conditions, one may experience other effects, such as chemical reactions and other transfer processes, that have not been considered in this model. Regardless of the mechanism involved, once polaritons start affecting non-radiative decay rates, this process is no longer fully “non-radiative” since the quasiparticles produced have some light component in them. Moving forward, it would be interesting to investigate whether electronically excited molecules under VSC conditions may emit infrared photons out of the cavity via previously non-radiative pathways. This could potentially lead to new molecular optoelectronic applications.
FIG. 5. Effect of polariton condensates on non-radiative decay rate under VSC. (a) Rate changes due to VSC over ranges of number of molecules $N$ and LP condensate ratios $N_{LP}/N$. Larger values of $N_{LP}/N$ give higher rate changes that are no longer dependent on $N$ for sufficiently large $N$. (b,c) Contributions to the decay rate by the LP and UP modes. The value $\max (n)$ represents the number of $n$ terms ($n = \Delta n_{LP}, n_{UP}$) in Eq. (35) that needed to be summed before the subsequent term falls below $10^{-15}$. Changes in rate due to $N_{LP}/N$ may be attributed to changes in $\max (\Delta n_{LP})$, both of which remain constant over $N$ for sufficiently large $N$. Meanwhile, $\max (n_{UP})$ remains constant with increasing $N_{LP}/N$. All these indicate that a LP condensate speeds up non-radiative decay through the LP mode and not the UP mode. (d,e,f) Same plots as (a,b,c) but with an UP condensate. Both types of condensates follow similar trends, with the UP condensate giving higher decay rates due to the higher frequency associated with the UP mode. All plots were generated with the following parameters: detuning, $\Delta = 0$; collective light-matter coupling, $g\sqrt{N} = 0.01\hbar \omega_{vib}$; bare-molecule Huang-Rhys factor, $S = 0.1$; relative electronic energy gap, $\Delta E = 15\hbar \omega_{vib}$. Dotted lines represent $\frac{N_{LP}}{N} = 5\frac{\hbar \omega_{vib}}{\Delta E} \approx 0.33$, with $P = \text{LP, UP}$.

ACKNOWLEDGEMENTS

Y.R.P. was supported by the UCSD Graduate Student Growth and Excellent Initiative Model. S.P.-S. and J.Y-Z. were supported by the US Department of Energy, Office of Science, Basic Energy Sciences, CPIMS Program under Early Career Research Program Award DE-SC0019188. We also thank Jorge A. Campos-Gonzalez-Angulo for helpful discussions.

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