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Dark Vibronic Polaritons and the Spectroscopy of Organic Microcavities

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Organic microcavities are photonic nanostructures that strongly confine the electromagnetic field, allowing exotic quantum regimes of light-matter interaction with disordered organic semiconductors. The unambiguous interpretation of the spectra of organic microcavities has been a long-standing challenge due to several competing effects involving electrons, vibrations, and cavity photons. Here we present a theoretical framework that is able to describe the main spectroscopic features of organic microcavities consistently. We introduce a class of light-matter excitations called dark vibronic polaritons, which strongly emit but only weakly absorb light in the same frequency region of the bare electronic transition. A successful comparison with experimental data demonstrates the applicability of our theory. The proposed microscopic understanding of organic microcavities paves the way for the development of optoelectronic devices enhanced by quantum optics.

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Optical microcavities containing organic semiconductor materials can confine the electromagnetic field within tens of nanometers at room temperature. Such small field volumes allow current experiments to reach the regimes of strong [1–3] and ultrastrong [4–6] coupling of cavity quantum electrodynamics (QED) with organic matter. The quantum optical properties of these organic microcavities can be analogous to atomic cavities [7] or superconducting resonators [8], but molecular systems are unique, because they can undergo a variety of chemical processes involving electronic and vibrational degrees of freedom while simultaneously interacting with a confined electromagnetic vacuum. This versatility has stimulated the development of nanoscale molecular devices whose electronic transport properties [9] or chemical reactivity [10,11] can be manipulated using quantum optics.

The photophysics and transport properties of organic materials are largely determined by vibronic coupling [12,13]. In microcavities, the vibronic coupling strength can be comparable with the vacuum Rabi frequency, which quantifies the strength of the light-matter interaction. The resulting interplay between electrons, vibrations, and cavity photons has for years obscured the interpretation of absorption and emission data. Several experiments [14–18] have showed the emergence of strong emission lines but negligible absorption in the frequency region near the bare molecular resonance, which is unexpected, because reciprocity dictates that a strong emitter should also be a good absorber [19]. These unusual observations have been made on systems where the Rabi splitting is roughly twice the frequency of the vinyl stretching mode characteristic of conjugated organic molecules [12]. Our goal is to understand the polariton structure in this intermediate coupling regime, with a focus on the spectral region in the middle of the conventional lower and upper polariton doublet, where quasiparticle theories predict the existence of an incoherent exciton reservoir [20–25].

In order to achieve this goal, we develop a theoretical framework that is able to account for several unexplained features of the optical spectra of organic microcavities consistently. Our theory is based on the Holstein-Tavis-Cummings (HTC) model [11,26–29] and a Lindblad approach for the dissipative dynamics of organic polaritons. We provide a microscopic interpretation of organic microcavity spectroscopy in terms of *dark vibronic polaritons*, collective light-matter states that weakly absorb but strongly emit radiation. Dark vibronic polaritons can emerge by two possible mechanisms: (a) the destructive interference between diabatic polariton states associated with different vibronic transitions and (b) the admixture of diabatic two-particle states [12] with dark excitonic material states.

We describe an ensemble of N organic emitters inside an optical cavity by the HTC model [11,26–29], given by $\hat{\mathcal{H}} = \hat{H}_C + \hat{H}_M + \hat{V}_a$. $\hat{H}_C = \omega_c \hat{a}^\dagger \hat{a}$ is the free cavity Hamiltonian; the molecular degrees of freedom are described by the Holstein model [12,30]

$$\hat{H}_M = \omega_v \sum_{n=1}^{N} \hat{b}_n^\dagger \hat{b}_n + \sum_{n=1}^{N} [\omega_e + \omega_v \lambda(\hat{b}_n + \hat{b}_n^\dagger)] |e_n\rangle\langle e_n| \tag{1}$$

and the cavity-matter coupling by a Tavis-Cummings [31] term

$$\hat{V}_a = (\Omega/2) \sum_{n=1}^{N} (|g_n\rangle\langle e_n| \hat{a}^\dagger + |e_n\rangle\langle g_n| \hat{a}). \tag{2}$$

The transition frequency is $\omega_e = \omega_{00} + \omega_v \lambda^2$, where ω_{00} is the frequency of the zero-phonon (0-0) transition, $\omega_v \approx 0.15$–0.18 eV is the intramolecular vibrational frequency, and $\lambda^2 \sim 0.1$–1.2 is the Huang-Rhys factor. Operator $\hat{b}_n$ annihilates an intramolecular vibration on the nth chomophore, $\hat{a}$ annihilates a cavity photon, and Ω is the single-particle Rabi frequency. Throughout this work, we assume zero detuning $\Delta \equiv \omega_{00} - \omega_c = 0$ at normal incidence.

The HTC model describes organic samples composed of individual chromophores, molecular aggregates, or molecular crystals in polycrystalline samples, for cavity modes having negligible dispersion within the photon linewidth. We have previously studied systems with energetic disorder [11] and excitonic coupling [27], but here we focus on homogeneous ensembles. Since the high-frequency vibrational mode included in the Hamiltonian is not thermally populated, temperature enters in the model as a parameter that determines the phonon-assisted relaxation rate of polariton eigenstates [32].

We are interested in the eigenstates of the HTC Hamiltonian $\hat{\mathcal{H}}$ whose energy equals the bare molecular transition, since an unexpectedly strong cavity emission is observed in this frequency region [14–17]. In the rotating frame of the resonant cavity mode, a polariton state at the bare molecular frequency satisfies $\hat{\mathcal{H}}|X\rangle = 0$. It is straightforward to show that a vanishing eigenvalue implies that the transition dipole moment $\mu_{XG} \equiv \langle G|\hat{\mu}|X\rangle$ also vanishes, for $|G\rangle$ being the absolute ground state of the cavity (no vibronic, vibrational, or cavity excitations) and $\hat{\mu}$ the dipole operator [32]. In general, we refer to any HTC eigenstate $|\epsilon_j\rangle$ with a vanishing transition dipole with the absolute ground state ($\mu_{jG} = 0$) as a *dark vibronic polariton*, since it is effectively invisible in room temperature absorption experiments that probe material dipole transitions directly, as in Refs. [3,33].

The vanishing dipole strength of the zero-energy dark vibronic polariton $|X\rangle$ can be understood as a destructive interference effect. For $N = 1$, we introduce the diabatic polariton states

$$|\nu_\pm\rangle = \frac{1}{\sqrt{2}}(|e, \tilde{\nu}, 0_c\rangle \pm |g, \nu, 1_c\rangle), \tag{3}$$

where $|g, \nu, 1_c\rangle$ represents a molecule in its ground state $|g\rangle$ and vibrational eigenstate $|\nu\rangle$ with one cavity photon and $|e, \tilde{\nu}, 0_c\rangle$ represents a molecule in the excited state $|e\rangle$ and vibrational eigenstate $|\tilde{\nu}\rangle$ in the cavity vacuum. $\tilde{\nu}$ is the number of vibrational quanta in the excited state nuclear potential, which is shifted relative to the ground potential by λ along a dimensionless vibrational coordinate [12,19].

The light-matter coupling term of the HTC model admixes vibronic polariton states with different numbers of vibrational quanta. In particular, the $|X\rangle$ state can be expanded as $|X\rangle \approx c_0|0_+\rangle - c_1|1_-\rangle - c_2|2_+\rangle$, giving $\mu_{XG} \approx \mu(c_0\langle 0|\tilde{0}\rangle - c_1\langle 0|\tilde{1}\rangle - c_2\langle 0|\tilde{2}\rangle)$, where μ is the molecular transition dipole moment, $c_\nu > c_{\nu+1} > 0$, and $\lambda > 0$. In other words, the destructive interference between the Franck-Condon factors of bare vibronic transitions leads to a vanishing transition dipole. For a single molecule, the zero-energy dark vibronic polariton $|X\rangle$ forms at the critical coupling $\Omega = 1.7\omega_v$.

For large ensembles, the HTC model can support multiple vibronic polariton eigenstates in the vicinity of the bare molecular frequency with a small or vanishing transition dipole to the absolute ground state ($\mu_{jG} \approx 0$), mainly due to destructive interference effects like the one discussed above. Such states are nondegenerate, and we refer to them as dark vibronic polaritons of the X type. For $N \geq 2$, we find that, for $\lambda^2 \sim 0.1-1.0$, the critical Rabi coupling for the formation of a zero-energy X state is in the range $\sqrt{N}\Omega/\omega_v \approx 1.8$–$2.5$ [32]. In this work, we focus on this intermediate coupling regime, where the electron and cavity degrees of freedom remain entangled with the nuclear degrees of freedom [11,28]. Several experimental realizations belong to this coupling regime [14–18].

For intermediate Rabi couplings, two-particle material states become important to describe the spectra of organic cavities [27]. Such states are represented by $|e_n, \tilde{\nu}_n, g_m, \nu_m, 0_c\rangle$, where n labels the location of a vibronic excitation with $\tilde{\nu}$ displaced vibrational quanta, while molecule m is in a vibrational eigenstate with $\nu \geq 1$ vibrational quanta [32]. Two-particle *material* states give rise, on resonance ($\omega_c = \omega_{00}$), to the two-particle diabatic *polariton* states [27,32]

$$|P^\pm_{\nu\tilde{\nu}'}\beta\rangle = \frac{1}{\sqrt{2}}(|\alpha_0\beta, \tilde{\nu}'\nu, 0_c\rangle \pm |\beta, \nu, 1_c\rangle), \tag{4}$$

where the material component is an N-fold degenerate permutation-symmetric state given by

$$|\alpha_0\beta, \tilde{\nu}'\nu, 0_c\rangle = \sum_{m=1}^{N}\sum_{n\neq m}^{N} \frac{c_{\beta,m}}{\sqrt{N-1}} |e_n, \tilde{\nu}'_n, g_m, \nu_m, 0_c\rangle, \tag{5}$$

and $|\beta, \nu, 1_c\rangle = \sum_{m=1}^{N} c_{\beta m}|g_m, \nu_m, 1_c\rangle$, is a single-photon state dressed by a collective vibrational excitation. The quantum number β in Eq. (4) quantifies the symmetry under a particle permutation of the material states. We associate the value $\beta = \alpha_0$ to the totally symmetric superposition, i.e., $c_{\alpha_0,m} = 1/\sqrt{N}$, for all m. In the language of molecular aggregates [12], this would correspond to a state with zero momentum. For $\omega_c = \omega_{00}$, polaritons in Eq. (4) have the N-fold degenerate diabatic energies $E^\pm_{\tilde{\nu},\nu} = (\tilde{\nu} + \nu)\omega_v \pm \sqrt{N-1}|\langle 0|\tilde{\nu}\rangle|\Omega/2$, which form a polariton doublet for small Rabi couplings $\sqrt{N}\Omega/\omega_v \ll 1$ [32]. For such small couplings, two-particle polaritons coexist with conventional diabatic polaritons of the form

$$|P^{\pm}_{\tilde{\nu}}\rangle = \frac{1}{\sqrt{2}}(|\alpha_0, \tilde{\nu}, 0_c\rangle \pm |g_1 0_1, g_2 0_2, \ldots, g_N 0_N, 1_c\rangle), \qquad (6)$$

where $|\alpha_0, \tilde{\nu}, 0_c\rangle = \sum_n |e_n \tilde{\nu}_n, 0_c\rangle/\sqrt{N}$ for $\tilde{\nu} \geq 0$. These polariton states have energies $E^{\pm}_{\tilde{\nu}} = \tilde{\nu}\omega_v \pm \sqrt{N}|\langle 0|\tilde{\nu}\rangle|\Omega/2$.

For intermediate Rabi couplings, two-particle diabatic polaritons given by Eq. (4) that are permutation symmetric ($\beta = \alpha_0$) can admix with the single-particle polariton states given in Eq. (6) [11,32] to form a set of *nondegenerate* states that we designate as the dark vibronic polaritons of the X type. Such polaritons have a vanishing or negligible transition dipole moment with the absolute ground state of the system $|G\rangle$ but nevertheless contribute to the photoluminescence spectra.

The HTC model also allows the admixture of single- and two-particle states that are not totally symmetric ($\beta \neq \alpha_0$). We refer to the resulting eigenstates as dark vibronic polaritons of the Y type. As a specific example of this mixing between nonsymmetric states, we consider the material states $|\beta \neq \alpha_0, \tilde{0}, 0_c\rangle$, commonly known as dark exciton states [11,34], which admix with the nonsymmetric two-particle diabatic polariton state $|P^{-}_{1\tilde{0}}, \beta \neq \alpha_0\rangle$. Such mixing is allowed by nonvanishing Franck-Condon factors between oscillator states in the ground and excited manifolds, effectively giving a photonic character to the otherwise uncoupled dark excitons [32].

For intermediate Rabi couplings, the states involved in the mixture mentioned above are nearby in energy and generate two manifolds of $N - 1$ dark vibronic polariton states of the Y type near the bare molecular resonance ($\omega_j/\omega_v \sim 0.1$), which can be approximately written as

$$|Y_j\rangle \approx a_j|\beta, \tilde{0}, 0_c\rangle + b_j|P^{-}_{1\tilde{0}}, \beta\rangle, \qquad (7)$$

independent of $\beta \neq \alpha_0$. Such Y-type vibronic polaritons carry a photonic component with one quantum of vibration. Light emitted by state $|Y_j\rangle$ through photon leakage therefore has frequency $\omega = \omega_j - \omega_v$, which is near the lower polariton frequency for the Rabi frequencies considered. In addition to the states given by Eq. (7), there are also multiple dark vibronic polaritons of the Y type near the conventional upper polariton frequency ($\omega_j \approx \omega_v$), having photonic components with one or more vibrational excitations. Such states can emit light near the bare molecular resonance frequency ($\omega \approx 0$) upon photon leakage. As we show below, the structure of dark vibronic polaritons of the Y type greatly influences the photoluminescence spectra of organic cavities.

In order to understand specific spectral features of dark vibronic polaritons of the X and Y types, we focus on the two most commonly measured signals: absorption $A(\omega)$ and leakage photoluminescence $S_{\mathrm{LPL}}(\omega)$. These are illustrated in Fig. 1. In general, there are two types of absorption experiments, depending on whether a resonant laser pump drives the cavity through the mirrors [18], as in Fig. 1, or by directly driving the organic material orthogonal to the cavity confinement axis [33]. We refer to the latter as bound absorption. Bound mode absorption is directly proportional to the dipole oscillator strength of the polariton states in the molecular ensemble [32]. Once a polariton is populated, it can lose its energy by photon leakage through the mirrors, generating the leakage photoluminescence (LPL) signal, or by fluoresce into bound modes [3,27]. The latter process is responsible for resonant pump attenuation and thus determines the conventional absorption spectra by the relation $A = 1 - R - T$.

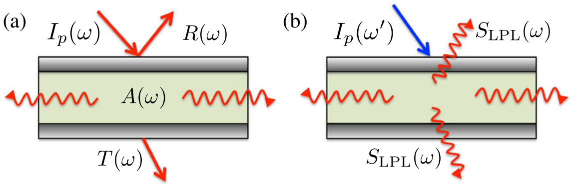

FIG. 1. Spectral signals. (a) Reflection R, transmission T, and absorption $A = 1 - R - T$ of an external pump $I_p(\omega)$. Absorption is due to spontaneous emission into bound modes of the microcavity. (b) Leakage photoluminescence $S_{\mathrm{LPL}}(\omega)$ following weak laser pumping at frequency $\omega' > \omega$. Bound photoluminescence [27] is shown as horizontal wavy arrows.

We derive expressions for the conventional absorption and leakage PL spectra in organic microcavities, using a standard cavity QED approach [32]. The resulting expressions depend on the generalized spectrum of fluctuations $S(\omega) = \sum_j \rho_j S^{(j)}_{\hat{O}}(\omega)$, where

$$S^{(j)}_{\hat{O}}(\omega) = \sum_i |\langle \epsilon_i|\hat{O}|\epsilon_j\rangle|^2 \frac{\kappa_j}{(\omega - \omega_{ji})^2 + \kappa_j^2} \qquad (8)$$

is a state-dependent line shape function and $\kappa_j \approx \Gamma_j/2$ is the decay rate of the polariton coherence. States $|\epsilon_j\rangle$ and $|\epsilon_i\rangle$ are eigenstates of the Holstein-Tavis-Cummings model in the one-polariton and ground state manifolds, respectively. ρ_j is the stationary population of the jth polariton eigenstate, $\omega_{ji} > 0$ is the frequency of the transition $|\epsilon_j\rangle \leftrightarrow |\epsilon_i\rangle$, and $\Gamma_j = \kappa \sum_i |\langle \epsilon_i|\hat{a}|\epsilon_j\rangle|^2 + N\gamma_e \sum_i |\langle \epsilon_i|\hat{J}_-|\epsilon_j\rangle|^2$ is the polariton decay rate. κ is the empty-cavity photon decay rate, and $N\gamma_e$ is a size-enhanced fluorescence rate. $\hat{J}_-$ is related to the dipole operator by $\hat{\mu} = \sqrt{N}(\hat{J}_- + \hat{J}_+)$, with $\hat{J}_+ = [\hat{J}_-]^\dagger$.

LPL is defined as $S_{\mathrm{LPL}}(\omega) = \sum_j \rho_j S^{(j)}_{\hat{a}}(\omega)$, where $S^{(j)}_{\hat{a}}(\omega)$ is given by Eq. (8) with $\hat{O} = \hat{a}$. In our simulations, we assume that polariton energy levels are evenly populated, independent of degeneracy. Leakage photoluminescence involves dissipative transitions in which the material is projected onto a state $|\epsilon_i\rangle$ in the ground manifold after the cavity photon in a polariton state $|\epsilon_j\rangle$ decays through the mirrors. We can represent such a process by the mapping $\hat{a}|\epsilon_j\rangle \to |\epsilon_i\rangle + \hbar\omega$, where $\omega = \omega_j - \nu\omega_v$ is the emitted light frequency and ν is the number of vibrational quanta in state $|\epsilon_i\rangle$. For $\nu \geq 1$, the emitted photon has an energy lower than its parent polariton, a fact that is ignored in previous theories of organic microcavities [20–25]. We show below that photon leakage transitions into states with up to $\nu = 2$ vibrational quanta are important to interpret experiments.

The conventional absorption spectra $A(\omega)$ is obtained by introducing a laser-driving term of the form $\hat{V}_p(t) = \Omega_p(\hat{a}^\dagger e^{-i\omega t} + \hat{a}e^{i\omega t})$ to the Holstein-Tavis-Cummings model, Ω_p being a weak pumping strength and ω the driving frequency. Solving for the polariton population ρ_j to second order in Ω_p for a system initially in the absolute ground state $|G\rangle$, setting $\hat{O} = \sqrt{N}\hat{J}_-$ in Eq. (8), and integrating over all dipole emission frequencies gives the expression [32]

$$A(\omega_p) = \pi|\Omega_p|^2 \sum_j \frac{|\langle G|\hat{a}|\epsilon_j\rangle|^2(\kappa_{Gj}/\Gamma_j)}{(\omega_p - \omega_{jG})^2 + \kappa_{Gj}^2} F_j, \qquad (9)$$

where κ_{Gj} is the decay rate for the coherence $\rho_{Gj} \equiv \langle G|\hat{\rho}|\epsilon_j\rangle$, which we can allow to account for nonradiative relaxation processes [32], and $F_j = N\sum_i |\langle\epsilon_i|\hat{J}_-|\epsilon_j\rangle|^2$ is the total dipole emission strength of the jth polariton. This expression shows that, if $F_j = 0$ for a polariton eigenstate $|\epsilon_j\rangle$, there is no resonant absorption at that polariton frequency either. In other words, polaritons that fluoresce poorly into bound modes of the nanostructure cannot attenuate the reflected and transmitted fields efficiently.

In order to illustrate our theory, we show in Fig. 2 the simulated absorption and LPL spectra for a system with $N = 20$ emitters, a size representative of the thermodynamic limit [28]. We set $\sqrt{N}\Omega/\omega_v = 2.4$, which is the critical coupling for the formation of a dark vibronic polariton $|X\rangle$ with zero energy $\omega_X = 0$ for $\lambda^2 = 1$. Figure 2(a) shows that conventional absorption (dashed line) of the $|X\rangle$ state is negligible due to its small photonic component $\langle G|\hat{a}|X\rangle$, while bound absorption (solid line) of this state is exactly zero because $\mu_X = 0$ [32]. The system also supports a second nondegenerate vibronic polariton $|Xb\rangle$ at frequency $\omega_j \approx 0.4\omega_v$, which has a weak transition dipole moment. Such a state is weakly bright in both types of absorption measurement. On the contrary, there is no absorption from any of the multiple Y-type dark vibronic polaritons $|Y_j\rangle$ that exist in the frequency region between the lower and upper polariton peaks. This happens because for polaritons of the Y type we have $\langle G|\hat{a}|Y_j\rangle = \langle G|\hat{\mu}|Y_j\rangle = 0$.

In Fig. 2(b), we show the computed LPL spectra. Our results qualitatively reproduce the experimental photoluminescence spectra obtained by Hobson *et al.* [14], shown in Fig. 2(c), and are also consistent with more recent measurements [17]. In order to obtain a good qualitative agreement with the experimental spectra, it is important to take into account the emission from the dark vibronic polariton states labeled X, Xb, Ya, and Yb in Fig. 2(a) (inset) that leave the system with one quantum of vibration ($\nu = 1$) in the ground manifold. Such an emission enhances to the photoluminescence intensity near the lower polariton frequency and blueshifts the peak maximum in that frequency region relative to the absorption peak. For the parameters in Fig. 2, we obtain a blueshift of $\delta_{\mathrm{LP}} \approx 20$ meV for $\omega_v = 180$ meV (vinyl stretch [12]), which is consistent with recent measurements [17].

In order to quantify the importance of emission from dark vibronic polaritons of the Y type, we show in Fig. 2(d) the PL intensity I_{LP} collected at the frequency of the lower polariton state ω_{LP}, as a function of the center frequency ω_p of a

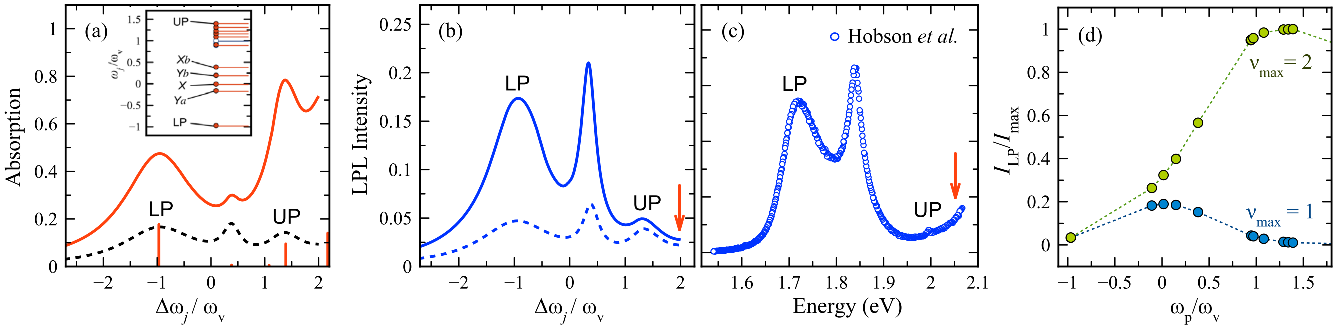

FIG. 2. Model microcavity spectra for $N = 20$ emitters. (a) Absorption spectra $A = 1 - R - T$ (dashed line) and bound mode absorption (solid line), indicating the lower (LP) and upper polariton (UP) peaks. Vertical bars indicate the peak position and dipole oscillator strength. (b) LPL spectra including transitions that project the material onto the absolute ground state (dashed line) or onto states in the ground manifold with up to one quantum of vibration (solid line). The red arrow indicates the highest energy polariton considered. (c) Experimental LPL spectra for an ensemble of cyanine dye J-aggregates in a microcavity, adapted from data provided by Bill Barnes for Fig. 3 in Ref. [14]. The red arrow indicates the laser pump energy. (d) Relative emission intensity at the lower polariton frequency I_{LP}, for a Gaussian polariton population centered at ω_p with standard deviation $\sigma_p/\omega_v = 0.5$. Transitions to the ground state with up to ν_{max} vibrational quanta are included. We use $\lambda^2 = 1$, $\sqrt{N}\Omega/\omega_v = 2.4$, $\kappa/\omega_v = 0.9$, and $N\gamma_e/\omega_v = 3.0$, where ω_v is the vibrational frequency.

Gaussian polariton population distribution with standard deviation $\sigma_p = 0.5\omega_v$. Such polariton distributions can be produced by a laser pulse [17]. Our results show that emission at $\omega_{\rm LP}$ can also result directly from polaritons with higher energy decaying to the environment by photon leakage through the partially reflecting mirrors. Such decay projects the organic material onto a state with one or more vibrational excitations in the ground electronic manifold. It is thus not necessary to invoke nonradiative relaxation by phonon scattering in order to explain the measured enhancements of PL emission [35], as is done in quasiparticle theories [20–22,24,25]. For metallic cavities with photon decay times $1/\kappa \sim 10$ fs [14–18], subpicosecond photon leakage emission from Y-type dark vibronic polaritons can already explain the observed emission enhancements.

In summary, we have developed a theoretical framework based on the Holstein-Tavis-Cummings model [11,26,27] to describe the spectroscopy of organic microcavities. The model provides a consistent microscopic interpretation for several observed features in the absorption and emission spectra of these systems for the first time. We do this by introducing dark vibronic polaritons, a class of light-matter excitations that, in general, involve an admixture of multiple material vibronic transitions with single photon states of the cavity that are dressed by purely vibrational material excitations. For model parameters consistent with available experimental data, we show that emission from dark vibronic polaritons can appear in the vicinity of the bare molecular absorption frequency. Our theory does not exclude the possibility of residual emission from bare molecular states that are not strongly coupled to the cavity. However, we expect the signals from weakly coupled emitters to behave differently from those of dark vibronic polaritons [32].

Our developed theory can be further extended to treat microcavities in the ultrastrong coupling regime [4–6] that have arbitrary mode dispersion, as well as materials with excitonic couplings, strong disorder, or non-Markovian reservoirs. Understanding the ultrafast dynamics of organic microcavities may lead to the development of novel nonlinear optical devices [36,37], chemical reactors [10,11], and optoelectronic devices [9,38–40] that are enhanced by quantum optics.

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