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## ABSTRACT

This is a tutorial-style introduction to the field of molecular polaritons. We describe the basic physical principles and consequences of strong light–matter coupling common to molecular ensembles embedded in UV–visible or infrared cavities. Using a microscopic quantum electrodynamics formulation, we discuss the competition between the collective cooperative dipolar response of a molecular ensemble and local dynamical processes that molecules typically undergo, including chemical reactions. We highlight some of the observable consequences of this competition between local and collective effects in linear transmission spectroscopy, including the formal equivalence between quantum mechanical theory and the classical transfer matrix method, under specific conditions of molecular density and indistinguishability. We also overview recent experimental and theoretical developments on strong and ultrastrong coupling with electronic and vibrational transitions, with a special focus on cavity-modified chemistry and infrared spectroscopy under vibrational strong coupling. We finally suggest several opportunities for further studies that may lead to novel applications in chemical and electromagnetic sensing, energy conversion, optoelectronics, quantum control, and quantum technology.

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## I. INTRODUCTION

Quantum optics traditionally concerns the preparation of light having non-classical statistical properties,<sup>1</sup> which is essentially a quantum control task. In cavity quantum electrodynamics (QED<sup>2</sup>), this goal can be achieved through the energy exchange between quantum emitters and a confined electromagnetic vacuum.<sup>3</sup> In chemistry, quantum control of molecular and material processes using external fields has been a long-standing goal for decades.<sup>4,5</sup> In contrast with quantum optics, where control schemes often involve temporal manipulation of a small number of variables,<sup>6</sup> coherent control of molecular processes typically requires a targeted exploration of a multi-dimensional landscape of control parameters,<sup>7,8</sup> even for systems in isolation from their environments. Excitation dynamics in biological systems is a particularly complex problem for quantum control, given the large number of strongly interacting electronic and nuclear degrees of freedom involved.<sup>9</sup> Despite the complexity, quantum optimal control schemes<sup>10,11</sup>

can still be designed to steer the system dynamics toward a desired objective.<sup>12,13</sup>

Coherent control protocols in molecular systems often rely on perturbative linear or nonlinear light–matter interactions.<sup>4</sup> In order for the control lasers to imprint their amplitude and phase information onto a material wavefunction, it is best for the matter and field degrees of freedom to evolve independently. Although perturbative coherent control schemes are often simpler to understand and design, strong field schemes for coherent control of population transfer<sup>14–16</sup> are known to be more robust to protocol imperfections<sup>17</sup> and have enabled several results such as the formation of ultracold molecules,<sup>18</sup> light-induced chemical dynamics,<sup>19</sup> single-photon transistors,<sup>20</sup> deterministic single-photon sources,<sup>21</sup> and noise-resilient quantum gates.<sup>22–26</sup>

Despite their conceptual differences, the fields involved in weak field and strong field quantum control protocols are largely classical and have large mean photon numbers. Therefore, the field amplitudes can be safely regarded as scalar parameters that drive the

evolution of a target material system. In this semiclassical regime, the quantum state of light does not undergo evolution, apart from trivial propagation effects. On the other hand, in quantum optics, the photon number statistics of an incoming control field could, in principle, change due to free evolution of the coupled light–matter system, an effect that is not possible in the semiclassical picture of light–matter interaction so often used in molecular spectroscopy.<sup>27</sup> Altering the quantum state of light would correspond to a type of *quantum back-action* on the control field that researchers can take into account when designing novel optimal control strategies with quantum light. The increased complexity and potential scope of such non-perturbative quantum optical control schemes could open novel prospects for manipulating chemical reactions and material properties.

In recent years, several experimental groups have used a diverse set of photonic structures to establish the possibility of manipulating intrinsic properties of molecules and molecular materials under conditions of strong and ultrastrong light–matter coupling with a confined electromagnetic vacuum in the optical<sup>28–37</sup> and infrared<sup>38–56</sup> regimes. This growing body of experimental results have positioned molecular cavity systems as novel implementations of cavity QED that complement other physical platforms with atomic gases,<sup>57</sup> quantum dots,<sup>58</sup> quantum wells,<sup>59</sup> or superconducting circuits.<sup>60</sup> Molecular cavities under strong and ultrastrong coupling lead to the dynamical formation of *molecular polaritons*: hybrid energy eigenstates composed of entangled photonic, electronic, and vibrational degrees of freedom.

The formation of molecular polaritons in optical and infrared cavities can offer viable routes for pursuing coherent control of molecular processes in condensed phase and room temperature, possibly without involving external laser fields but only vacuum effects. Moreover, these novel cavity systems may enable advances in the development of integrated photonic quantum technology.<sup>61</sup> Further opportunities for technological applications are expected to emerge from the study of light–matter interaction in exotic coupling regimes.<sup>62,63</sup>

The growing literature on molecular polaritons has already been reviewed extensively. We refer the reader to previous reviews for a thorough description of previous literature. Most of the early experimental work on strong coupling with J-aggregates is reviewed in Refs. 64 and 65. Recent demonstrations of cavity-modified chemistry and molecular properties are reviewed in Refs. 31, 66, and 67. Strong light–matter coupling of molecular transitions near plasmonic nanoparticles is reviewed in Refs. 68–71. For a description of the early work on organic polariton spectroscopy, we refer the reader to Refs. 72–74. Recent molecular polariton theory is reviewed in Refs. 75–79.

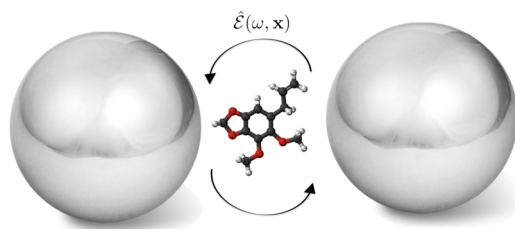
This perspective is intended to serve as a tutorial-style introduction to the field of molecular polaritons. We first provide a brief account of pioneering experimental results and then discuss with relative detail the basic physical principles of intracavity light–matter coupling that are common to both optical and infrared cavities. We focus on the interplay between local and collective effects from a microscopic quantum description, an important topic that is a largely ignored in the literature. We finally discuss recent theoretical and experimental progress in the field, highlighting future challenges and opportunities for further research.

## II. EARLY EXPERIMENTS

The low-energy excitations of a material that strongly interacts with a quantized electromagnetic field are traditionally described as polaritons. From one point of view, a *polariton* can be considered as an excitation of hybrid light–matter energy eigenstates of the strongly coupled system, just like a single *photon* is an excitation of an electromagnetic field eigenstate. In crystalline solids, polaritons are considered quasi-particles with well-defined energy and momentum,<sup>80</sup> although polaritons not only form in crystals. Exciton–polariton quasiparticles were introduced independently by Agranovich and Hopfield in the early 1960s to describe the microscopic origin of the dielectric constant of materials.<sup>81,82</sup> In 1982, Pockrand *et al.* observed the spectroscopic signatures of strong coupling between organic excitons with the near field of a plasmonic nanostructure, intuitively discussing their observations in terms of system excitations with hybrid light–matter character,<sup>83</sup> without further theoretical analysis on the nature of such hybrid states. Due to the maturity of semiconductor fabrication techniques, exciton–polaritons have been widely studied in inorganic semiconductor microstructures,<sup>84,85</sup> mostly at cryogenic temperatures. In 1997, Agranovich introduced the idea of using Frenkel excitons in organic semiconductors to enhance the emission properties of polaritons in dielectric microcavities.<sup>86</sup> It was soon demonstrated by Lidzey that an anthracene crystal could reach the strong coupling regime with the vacuum field of a dielectric microcavity at room temperature.<sup>87</sup> This was a key innovation in comparison with inorganic semiconductors, as Wannier excitons are likely to undergo charge separation at room temperature because of their lower binding energies.<sup>80</sup> Wannier excitons form in crystalline inorganic semiconductors<sup>85</sup> and Frenkel excitons in organic materials.<sup>80</sup> Among other fundamental studies and applications, strong light–matter coupling with dense films of organic chromophores and molecular aggregates in optical microcavities was initially explored as a route to enhance the emission properties of organic light-emitting devices<sup>34,88,89</sup> and lower the threshold for organic lasing.<sup>35</sup>

In the search for novel metal-based organic microcavities, it was later shown that room-temperature strong coupling between organic excitons and surface plasmon resonances could also be achieved.<sup>90,91</sup> This extended the range of possible applications of plasmonic nanoparticles beyond enhanced sensing and spectroscopy.<sup>92–95</sup> Recently, quantum optical effects with a single organic chromophore under strong electronic coupling in the near field have also been demonstrated using plasmonic<sup>96–98</sup> and dielectric<sup>99</sup> nanocavities. In Fig. 1, we illustrate a single-molecule cavity composed of metal nanoparticles.

After the pioneering demonstration by the group of Ebbesen<sup>28</sup> of modified photoisomerization of merocyanine derivatives inside optical microcavities under electronic strong coupling (ESC), the field of molecular polaritons experienced a renewal of interest from a diverse group of experimental and theoretical researchers in chemistry, physics, and materials science. In a few years, the field has evolved into a challenging and fertile area in which researchers with complementary expertise must combine efforts in order to properly address open questions. It can be expected that relevant advances in quantum nanophotonics,<sup>100</sup> microfluidics and nanofluidics,<sup>101</sup> electron microscopy,<sup>102</sup> spectroscopy with quantum light,<sup>103,104</sup> and



**FIG. 1.** Schematic nanoscale optical cavity made with two spherical nanoparticles with an individual organic chromophore located in the near field hotspot (gap). In the strong coupling regime, electronic or vibrational excitations of the molecule can coherently exchange energy with the dispersive and spatially inhomogeneous quantized near field  $\hat{E}(\omega, \mathbf{x})$ .

quantum control theory<sup>11</sup> open exciting possibilities for the development of integrated quantum devices able to manipulate chemical systems by exploiting light–matter hybridization effects intrinsic to molecular polaritons.

### III. MOLECULAR POLARITON BASICS

Experiments have shown that any meaningful analysis of the spectroscopy and dynamics of molecular polaritons in the optical and infrared regimes must take into account several specific features of the molecular species and the photonic structures involved. These details include—but are not limited to—an accurate knowledge of the electronic and vibrational structure of the material system, the geometry and dielectric functions of the materials that compose the cavity structure, knowledge of the predominant material and electromagnetic dissipation channels, and the presence or absence of external coherent (laser) and incoherent (thermal) energy sources. On the other hand, it has also been observed that while the rate of some molecular processes can be significantly affected upon resonant interaction with cavity fields,<sup>31,66</sup> the dynamics of other material processes occurs at rates that are basically indistinguishable from a cavity-free scenario.<sup>105</sup>

By combining recent developments in quantum optics theory<sup>106</sup> with state-of-the-art electronic structure methods, it should be possible to construct a fully *ab initio* quantum theory of molecular polaritons that can simultaneously make precise testable predictions about the optical and chemical response of molecular ensembles in confined electromagnetic fields. However, even if such a theoretical framework is eventually developed, researchers are still likely to continue interpreting their experimental data using the classical and semiclassical modeling tools that have proven useful for providing a good qualitative picture of optical and the infrared cavities under strong coupling.

The more widely used modeling tools to rationalize experiments are the *transfer matrix* method (TMM)<sup>107</sup> and a simplified approach to model light–matter coupling that we can call the *fitting matrix* (FM) method. The former is a classical electrodynamics approach based on Maxwell's equations in continuous media, and the latter is a semiclassical model that closely resembles the treatment of coherent light–matter coupling in multi-level atomic gases.<sup>108</sup>

In the rest of this section, we briefly describe the main ideas behind the transfer matrix and fitting matrix methods for modeling molecular polaritons in the optical and infrared regimes, highlighting their strengths and limitations. We then provide a tutorial-style discussion of a more complete microscopic cavity QED approach to describe molecular polaritons, explicitly showing the conditions under which the microscopic model would provide the same level of information about the coupled cavity system as the transfer and fitting matrix approaches. We discuss the interplay between collective and local effects in molecular ensembles, and how this interplay determines the properties of what are commonly known as the *dark states* of a coupled cavity.

The discussion in this section suggests that QED methods are more appropriate to understand experiments that probe the non-radiative dynamics of a molecular system inside a cavity, including chemical reactions. The transfer matrix and fitting matrix methods are suitable for analyzing linear cavity transmission and reflection experiments.

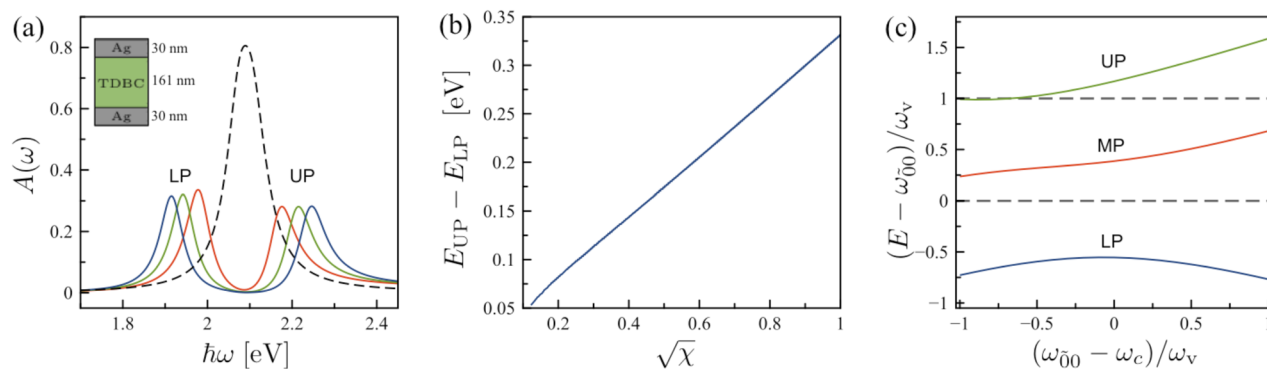
#### A. Classical transfer matrix method

Consider the planar silver microcavity filled with a layer of TDBC molecular aggregates, as first used in Ref. 89 (Fig. 2(a) inset). The empty silver cavity is a Fabry–Pérot resonator<sup>107,111</sup> with a resonant transmission peak near the absorption maximum of a bare TDBC film. Starting from Maxwell's equations with linear dielectric constitutive relations, together with the boundary conditions imposed by the multi-layer geometry, it is straightforward to derive relations between the incoming and outgoing electric and magnetic fields at each interface of this cavity nanostructure.<sup>107</sup> These input–output relations can be written in matrix form as

$$\mathbf{X}_b = \mathbf{M}(\omega)\mathbf{X}_a, \quad (1)$$

where  $\mathbf{X}_a$  and  $\mathbf{X}_b$  are two-component vectors that contain information about the electric and magnetic fields at two opposite silver–air cavity interfaces (*a* and *b*), and  $\mathbf{M}(\omega)$  is the so-called *transfer matrix* of the entire structure, which connects the incoming and outgoing fields at these border locations.<sup>107</sup> The frequency dependence of transfer matrix elements encodes the dispersive and absorptive properties of all the materials involved. In the linear regime, the optical response of materials is given by their dielectric function  $\epsilon(\omega)$ .<sup>112,113</sup> The dielectric functions of each layer in the cavity are commonly parametrized using specific models (e.g., Drude–Lorentz<sup>114</sup>), with model parameters obtained by fitting spectroscopic observables. Once the dielectric functions and thicknesses of each layer are known, the transfer matrix  $\mathbf{M}(\omega)$  can be used to compute the transmission (*T*), reflection (*R*), and absorption coefficients ( $A \equiv 1 - R - T$ ). Further adjustments of the dielectric function parameters for the active material may be needed to improve the fitting with cavity measurements.<sup>31</sup>

In this classical optics approach, information about resonant light–matter coupling is obtained indirectly from splittings between peaks in a linear optical signal (transmission, reflection, and absorption). No microscopic knowledge of the material system is needed to successfully interpret an experimental spectrum. In order to illustrate this point, consider the absorption spectrum shown in Fig. 2(a). The dielectric constant of the TDBC layer is fitted to a Lorentz oscillator model,<sup>112,113</sup>



**FIG. 2.** (a) Absorption spectrum of a planar silver microcavity with TDBC J-aggregates (inset). The lower polariton (LP) and upper polariton (UP) peaks are shown for three values of the oscillator strength  $\chi f_0$ , with  $\chi = 1/3$  (red line),  $\chi = 2/3$  (green line), and  $\chi = 1$  (blue line).  $f_0$  is the oscillator strength of a pure J-aggregate film with an absorption spectrum (dashed line). Dielectric function parameters are taken from Ref. 109 for silver and Ref. 110 for TDBC aggregates. (b) Scaling of the UP–LP energy splitting as a function of  $\sqrt{\chi}$ . (c) Eigenvalues of a semiclassical fitting matrix model for an organic chromophore with two vibronic resonances, as a function of detuning of the field frequency  $\omega_c$  from the zero-phonon absorption peak. The resulting lower, middle, and upper polariton (dressed) levels are shown.  $\omega_v$  is the vibrational frequency of the chromophore in the excited electronic state.

$$\epsilon(\omega) = \epsilon_\infty + \frac{f_0 \omega_0^2}{\omega_0^2 - \omega^2 - i\gamma_0 \omega}, \quad (2)$$

where  $\epsilon_\infty$  is the dielectric background contribution,  $\omega_0$  is the frequency of the zero-phonon (0-0) absorption peak of a bare TDBC sample,  $\gamma_0$  is the associated resonance linewidth, and  $f_0$  is the oscillator strength of the transition. The values of these parameters are obtained from experiments.<sup>110</sup> The oscillator strength  $f_0$  is, in general, another fitting parameter; although for a system of  $N$  oscillating transition dipoles that are *independent* (i.e., not correlated),  $f_0$  can be shown to scale linearly with the number of dipoles using perturbation theory.<sup>112</sup>

Maxwell equations are such that the near resonant coupling of a cavity resonance with a single Lorentz absorption peak [dashed line in Fig. 2(a)] gives rise to two new normal modes [lower polariton (LP) and upper polariton (UP)] that increasingly split from each other as the value of  $f_0$  grows. Let us rescale the oscillator strength in Eq. (2) as  $f_0 \rightarrow \chi f_0$ , with  $0 \leq \chi \leq 1$  being a free scaling parameter. Figure 2(b) shows that the splitting between LP and UP peaks then scales as  $\chi^{1/2}$ .

In experiments, the energy splitting between LP and UP peaks (Rabi splitting) is associated with the strength of light–matter coupling. If we *assume* that the free parameter  $\chi$  is proportional to the number of emitters in the cavity, we then have a  $\sqrt{N}$  scaling commonly associated with collective light–matter interaction. However, we emphasize that *no quantum theory* was necessary to obtain the square-root scaling in Fig. 2(b). We later show that the square-root scaling, in general, does not hold for every molecular cavity system but emerges from a microscopic quantum model for molecular transition dipoles in an ensemble that are indistinguishable.

The transfer matrix method is directly applicable to planar multi-layer structures<sup>107</sup> and therefore has been widely used to analyze strong and ultrastrong coupling in optical microcavities and also infrared Fabry–Pérot resonators.<sup>115</sup> In order to model light–matter coupling in plasmonic nanostructures using

classical electrodynamics, a direct numerical or analytical solution of Maxwell equations is preferred.<sup>68</sup> Numerical solvers such as the Finite-Difference Time Domain method (FDTD<sup>114</sup>) can be used to compute near fields and also simulate far field signals of an active organic medium with the known dielectric function that is in the near field of a plasmonic nanostructure with essentially arbitrary geometry and material composition. Accurate analytical solutions for nanostructures without a well-defined symmetry have also been developed.<sup>116,117</sup> They provide valuable insight into the relative contributions of the different plasmon modes to light–matter interaction processes in experimentally relevant nanocavities.

## B. Semiclassical fitting matrix method

The fitting matrix ( $F$ -matrix) method is another approach that has been used to interpret spectral signals of molecular polaritons in the UV–visible.<sup>65</sup> It involves fitting the eigenvalues of a low-rank matrix to the frequencies of selected peaks obtained in cavity transmission, reflection, or absorption. From a theoretical point of view,  $F$ -matrices can be derived from a Hopfield model of coupled quantum harmonic oscillators,<sup>81</sup> truncated to the first excitation manifold.<sup>65</sup> In the Appendix, we show that  $F$ -matrices can equivalently be derived under the assumption that the material has quantized energy levels, but the field is entirely classical. The fact that the same model can be obtained using a quantum or a semiclassical approach for light–matter interaction shows that the quantized nature of the electromagnetic field is not necessarily relevant to understand the linear response of a strongly coupled cavity. For example, anti-crossings in the transmission and reflection spectra of strongly coupled cavities can already be captured using the classical transfer matrix method.<sup>65</sup> This equivalence, however, is purely formal, as it is not necessary (nor feasible) to introduce external laser fields to achieve the Rabi splittings on the order of 0.1–1 eV observed in experiments. Polariton level splittings occur already in the dark due to the vacuum field. We observe (not produce) split levels in

transmission and reflection experiments by driving transitions into polaritonic states.

The details of the derivation of the  $F$ -matrix method from a semiclassical model are given in the Appendix. The corresponding Hamiltonian can be written as<sup>1</sup>

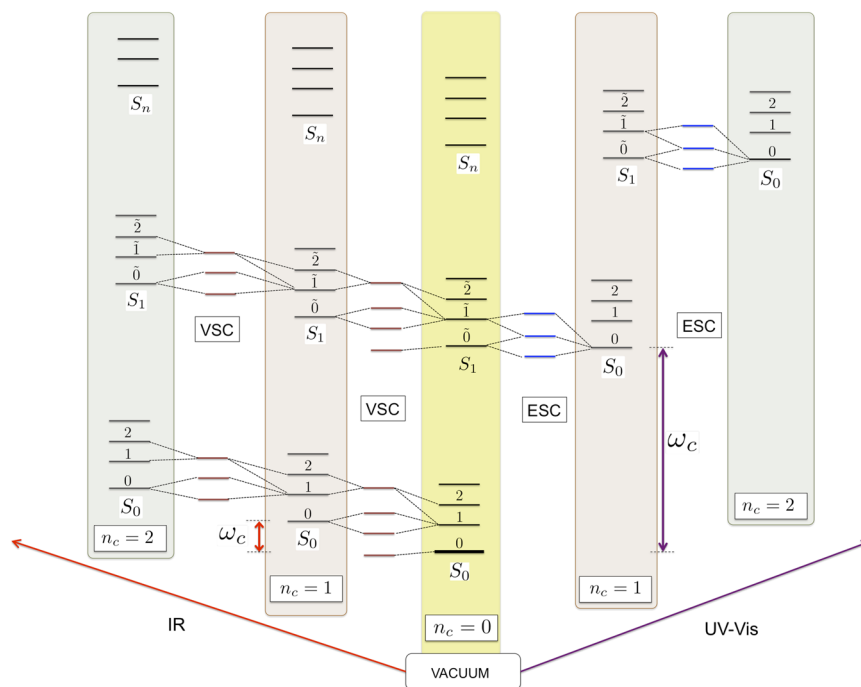
$$\hat{H}(t) = \sum_k \omega_k |E_k\rangle \langle E_k| + \sum_{k,k' \neq k} d_{kk'} \mathcal{E}(t) |E_{k'}\rangle \langle E_k|, \quad (3)$$

where  $|E_k\rangle$  describes the set of discrete energy eigenstates of the relevant molecular degrees of freedom (e.g., vibrational and vibronic) with eigenvalues  $\hbar\omega_k$ . Dipole transitions between molecular eigenstates are determined by the dipole matrix elements,  $d_{kk'}$ , in the presence of a classical monochromatic electromagnetic field  $\mathcal{E}_0(t) = \mathcal{E}_0 \cos(\omega_c t)$  with amplitude  $\mathcal{E}_0$  and frequency  $\omega_c$ . Equation (3) can be written in a rotating frame with respect to the external field,<sup>118</sup> which eliminates the explicit time dependence of the light–matter coupling term. Several fundamental effects in coherent optics, including electromagnetically induced transparency,<sup>108</sup> are determined by the eigenvalues and eigenstates of multi-level interaction Hamiltonians such as the one in Eq. (3). Semiclassical light–matter interaction eigenstates are known as *dressed states*.<sup>1</sup> Manipulating the dynamics of dressed states has

proven essential to develop several coherent population transfer techniques.<sup>17</sup>

In order to illustrate the relation between the semiclassical model in Eq. (3) and the fitting matrix method, consider the following example: one molecule embedded in an optical microcavity with cavity frequency  $\omega_c$  in the UV–visible, as illustrated in Fig. 3 (right-hand side). We can describe vibronic transitions in the molecule using a displaced oscillator model.<sup>119,120</sup> The state  $|E_0\rangle$  in Eq. (3) then corresponds to the lowest vibrational level ( $\nu = 0$ ) in the ground electronic state  $S_0$ . States  $|E_{\bar{0}}\rangle$  and  $|E_{\bar{1}}\rangle$  correspond to the lowest ( $\bar{\nu} = 0$ ) and first excited ( $\bar{\nu} = 1$ ) vibrational levels in the excited electronic state  $S_1$ , respectively. In free space (i.e., no cavity), the electric-dipole transitions  $0 \rightarrow \bar{0}$  and  $0 \rightarrow \bar{1}$  give rise to a vibronic progression in absorption from the absolute ground state  $|E_0\rangle$  with transition frequencies  $\omega_{\bar{\nu}\nu} = \omega_{\bar{0}0} + \bar{\nu}\omega_v$ , where  $\omega_{\bar{0}0}$  is the zero-phonon transition frequency and  $\omega_v$  is the vibrational frequency in  $S_1$ . For this system, we can write Eq. (3) in a frame rotating at the *fixed* classical frequency,  $\omega_c$ , as a matrix given by

$$\mathbf{F}(\omega_c) = \frac{1}{2} \begin{pmatrix} -\Delta_{\bar{0}0} & 2g_{\bar{0}0} & 2g_{\bar{1}0} \\ 2g_{\bar{0}0} & \Delta_{\bar{0}0} & 0 \\ 2g_{\bar{1}0} & 0 & \Delta_{\bar{0}0} + \omega_v \end{pmatrix}, \quad (4)$$



**FIG. 3.** Coupling scheme between diabatic molecule–photon states in the single-molecule regime. The center vacuum energy level diagram corresponds to the bare electronic and vibrational energy level structure in vacuum ( $n_c = 0$ ). This includes vibrational manifolds in the two lowest electronic states ( $S_0$ ,  $S_1$ ) and multiple excited electronic manifolds  $S_n$ . To the right-hand side of the vacuum diagram, we illustrate electronic strong coupling (ESC) with a single-mode cavity field at frequency  $\omega_c$  in the UV–visible. For each cavity photon number  $n_c \geq 1$ , a diabatic replica of the entire electronic and vibrational spectrum can be defined, only shifted from the absolute ground level ( $S_0$ ,  $\nu = 0$ ,  $n_c = 0$ ) by the energy  $n_c\omega_c$ . In the UV–visible, ESC between diabatic states with different photon numbers ( $|\Delta n_c| = 1$ ) leads to *vibronic polaritons* (blue energy levels). To the left-hand side of the vacuum diagram, we illustrate vibrational strong coupling (VSC) for a cavity field frequency  $\omega_c$  in the infrared. Coupling between diabatic states with different photon numbers ( $|\Delta n_c| = 1$ ) leads to the formation of *vibrational polaritons* (magenta energy levels) involving fundamentals and higher excited states (overtones) within the same electronic potential. Higher excited polariton splittings can be detected by driving a transition from a lower energy vibrational polariton that is initially populated.

where  $\Delta_{00} = \omega_{00} - \omega_c$  is the detuning of the external field from the  $0 \rightarrow \tilde{0}$  transition frequency. The off-diagonal state-dependent Rabi frequencies are defined as  $g_{\tilde{\nu}\nu} \equiv d_{\tilde{\nu}\nu} \mathcal{E}_0 / 2$ . We show in the Appendix that the semiclassical matrix  $\mathbf{F}(\omega_c)$  is formally equivalent to a truncated quantum model for a single-mode cavity field, which demonstrates that field quantization is *irrelevant* to describe linear transmission signals in strongly coupled cavities.

In Fig. 2(c), we plot the eigenvalues of the  $F$ -matrix in Eq. (4) as a function of the detuning  $\Delta_{00}$ . For concreteness, we set  $g_{00} = \omega_\nu$  and  $g_{10} = 0.8 g_{00}$ . The  $F$ -matrix gives rise to lower, middle, and upper dressed levels that exhibit anti-crossing behavior near exact resonance ( $\Delta_{00} = 0$ ). If we set  $g_{10} = 0$  in Eq. (4), the middle level disappears. The scaling of the energy difference between the resulting lower and upper dressed levels can be shown to scale linearly with  $g_{00}$  at exact resonance (not shown), which is the same behavior in Fig. 2(b) for a single Lorentz resonance ( $0 \rightarrow \tilde{0}$ ) in the transfer matrix method, which again illustrates the fact that the  $F$ -matrix and the transfer matrix provide an equivalent level of physical information about a strongly coupled cavity system.

In experiments, the values of the couplings  $g_{\tilde{\nu}\nu}$  are not necessarily known from microscopic considerations. These coupling constants are usually inferred from a *fitting* procedure that compares the eigenvalues of the  $F$ -matrix at fixed  $\omega_c$  with the positions of relevant peaks in cavity transmission, reflection, or absorption measurements. The couplings could also be estimated using transfer matrix theory.<sup>42</sup> The dispersive character of optical and infrared cavities can be taken into account in the fitting process by diagonalizing  $\mathbf{F}(\omega_c)$  for different values of  $\omega_c$  along the empty cavity dispersion curve.

### C. Microscopic cavity QED approach

Molecular polaritons are energy eigenstates of a light-matter interaction Hamiltonian that describes a cavity system in the optical or infrared regimes, with the electromagnetic field being a quantum mechanical operator. In other words, polaritons are the quantum analogs of the semiclassical dressed states discussed in Sec. III B. Unlike their semiclassical analogs, polariton eigenstates can be used to describe the full quantum statistics of electromagnetic field observables<sup>121</sup> as well as the dependence of the field observables on the internal degrees of freedom of the molecular system.<sup>122</sup> This type of microscopic understanding of molecular polaritons is *not* available in the transfer matrix or fitting matrix methods. In this section, we discuss polariton systems from a microscopic quantum mechanical point of view.

Consider a general cavity system composed of  $N$  inhomogeneously broadened molecular dipoles embedded in an optical or infrared cavity. We start from an inhomogeneous ensemble first and then discuss the conditions under which the commonly used homogeneous results emerge. We describe light-matter coupling in the point-dipole approximation within a multipolar framework<sup>123</sup> to give the Hamiltonian

$$\hat{H} = \hat{H}_c + \sum_{i=1}^N (\hat{H}_m(i) + \mathbf{d}_i \cdot \hat{\mathbf{D}}(\mathbf{x}_i)). \quad (5)$$

The first term describes an empty cavity (no molecules). This term is, in general, defined by the electromagnetic energy density over the

optical structure and takes into account the dispersive and absorptive character of the cavity materials.<sup>123</sup> The term  $\hat{H}_m(\mathbf{x}_i)$  describes the electronic, vibrational, and rotational degrees of freedom of the  $i$ th molecule in the ensemble, located at position  $\mathbf{x}_i$ . We ignore direct electrostatic or retarded interaction between molecules.  $\mathbf{d}_i$  is the electric dipole operator of molecule  $i$ , including electronic and nuclear charges, and  $\hat{\mathbf{D}}(\mathbf{x}_i)$  is the dielectric displacement field operator evaluated at the location of each molecular emitter. The light-matter coupling model in Eq. (5) can, in principle, be used to interpret any experiment for which electric dipole coupling is relevant, provided that we accurately know each of the operators involved. This is currently unfeasible, in general, for molecular ensembles ( $N \gg 1$ ), but we show below that under a minimal set of assumptions, the general expression in Eq. (5) can be rewritten in a way that can be directly used to interpret experiments and give a microscopic justification to the transfer matrix and fitting matrix approaches.

#### 1. Light-matter coupling in the homogeneous limit

The system Hamiltonian in Eq. (5) is strictly local in the assumed point-dipole approximation. Light-matter coupling can thus be considered as the quantized version of the semiclassical Autler-Townes effect.<sup>108</sup> In condensed phase, this local electric dipole interaction competes with other electrostatic shifts induced locally by molecules in the environment. For a molecular ensemble embedded in an optical or infrared cavity, a simple estimate shows that the light-matter interaction strength must be locally very weak for typical values of the polariton splittings observed in experiments. This raises an interesting question as follows: If light-matter coupling is locally weak, *where do the strong coupling effects observed in experiments come from?*

Intuitively, macroscopic cooperative behavior of molecular dipoles should emerge when the molecules in an ensemble become indistinguishable. Indistinguishability leads to the delocalization of molecular dipoles into a giant collective dipole that strongly interacts with light. Therefore, any physical or chemical process that is intrinsically local would tend to destroy the strong collective coupling of molecular dipoles with the electromagnetic field. We can thus expect that *every* molecular polariton signal obtained in experiments results from the competition between these two opposing effects: the cooperative exchange of energy between molecular transitions with the cavity field, which leads to polariton formation, and local coherent and dissipative processes that occur at the level of individual molecules. *The specific details of this competition between local and collective effects are what ultimately determine the observed chemical, transport, and optical properties of molecular polaritons in the optical and infrared regimes.*

In order to formalize this intuition, let us relax the locality constraints in Eq. (5). First, we neglect all the spatial derivatives of the dielectric displacement field, i.e.,  $\hat{\mathbf{D}}(\mathbf{x}) \approx \hat{\mathbf{D}}$ . Next, assume that all dipole vectors in the ensemble  $\mathbf{d}_i$  are either equally oriented or uniformly distributed with respect to the spatial orientation of the dielectric displacement field (both situations are equivalent<sup>124</sup>). Finally, we ignore local shifts of the molecular energy levels (inhomogeneous broadening) and other coherent local effects in the bare molecular system. This allows us to make the replacement

$\hat{H}_m(i) \rightarrow \hat{H}_m$ . Under these conditions, Eq. (5) can be rewritten in the simpler form

$$\hat{H} = \hat{H}_c + \hat{H}_N + \frac{\sqrt{N}\Omega}{2} \hat{a}_N \hat{D}, \quad (6)$$

where  $\hat{H}_N = \sum_i \hat{H}_m$ ,  $\hat{a}_N = \sum_i \hat{a}_i / \sqrt{N}$ , and  $\hat{D}$  is the dielectric field operator. The single-particle Rabi frequency  $\Omega$  is proportional to the magnitude of  $\mathbf{d} \cdot \hat{\mathbf{D}}$  for each molecular dipole, assumed identical for all molecules in the ensemble. Given the indistinguishability of molecular emitters that our conditions impose, the energy eigenstates of the many-body *homogeneous* Hamiltonian in Eq. (6) are delocalized and have a well-defined permutation symmetry under particle exchange.

Consider a truncated state space defined by a ground state  $|g\rangle$  and an excited state  $|e\rangle$ , which may equally well represent the two lowest electronic singlet states ( $S_0, S_1$ ) in a molecule or the two lowest vibrational levels  $v = 0$  and  $v = 1$  in the lowest singlet potential ( $S_0$ ). For an ensemble of  $N$  molecules, we can define the totally symmetric collective excited state

$$|\alpha_0\rangle = \frac{1}{\sqrt{N}} \sum_i^N |g_1, \dots, e_i, \dots, g_N\rangle, \quad (7)$$

with  $\hat{H}_N |\alpha_0\rangle = \omega_e |\alpha_0\rangle$ , where  $\omega_e$  is the relevant UV-visible or infrared transition frequency of a bare molecule. We also define the collective ground state  $|G\rangle = |g_1, g_2, \dots, g_N\rangle$  with  $\hat{H}_N |G\rangle = \omega_g |G\rangle$ , where  $\omega_g$  is the energy reference. In the collective basis  $\{|G\rangle, |\alpha_0\rangle\}$ , we can thus write Eq. (6) as

$$\hat{H} = \hat{H}_c + \begin{pmatrix} \omega_g & \sqrt{N}\Omega_{eg} \hat{D}/2 \\ \sqrt{N}\Omega_{eg} \hat{D}/2 & \omega_e \end{pmatrix} + \sum_{k \geq 2} \hat{H}_N^{(k)}, \quad (8)$$

where  $\Omega_{eg} \equiv \langle e | \hat{d} | g \rangle \Omega$ , where  $\hat{d}$  is a dimensionless dipole operator with no diagonal elements in the  $\{|g\rangle, |e\rangle\}$  basis, as is typical for material states with well-defined parity. The terms  $\hat{H}_N^{(k)}$  with  $k = \{2, 3, \dots, N\}$  in Eq. (8) describe the contributions of states with two or more molecular excitations in the ensemble.

Molecular cavity experiments are typically either carried out in the dark or involve weak laser or electrical pumping. In this so-called linear regime, the nonlinear contributions to the Hamiltonian ( $k \geq 2$ ) are irrelevant and can be safely ignored. One can also consider that at most one cavity photon is present in the system within a cavity lifetime and that the electromagnetic field can be reduced to a single cavity mode with discrete frequency  $\omega_c$ . Under these conditions, Eq. (8) with  $\omega_g \equiv 0$  can be written in matrix form as

$$\mathbf{H} = \begin{pmatrix} \omega_c & \sqrt{N}\Omega_{eg}/2 \\ \sqrt{N}\Omega_{eg}/2 & \omega_e \end{pmatrix} - i \begin{pmatrix} \kappa/2 & 0 \\ 0 & \gamma/2 \end{pmatrix}, \quad (9)$$

with eigenvalues given by

$$E_{\pm} = \frac{\omega_e + \omega_c}{2} - i \frac{\kappa + \gamma}{4} \pm \frac{1}{2} \sqrt{N\Omega_{eg}^2 - \left(\frac{\kappa - \gamma}{2} - i\Delta_c\right)^2}, \quad (10)$$

where  $\Delta_c = \omega_e - \omega_c$  is the detuning of the single cavity mode from the molecular transition frequency. The real parts of  $E_-$  and  $E_+$  are the energies of lower and upper polariton eigenstates, respectively.

The Hermitian contribution in Eq. (9) is formally equivalent to a two-level version of the semiclassical  $F$ -matrix up to a trivial global energy shift (see the derivation in the Appendix). Introducing a non-Hermitian contribution in Eq. (9) is an effective way to take dissipation into account.<sup>125</sup> The cavity photon is lost into the far field at rate  $\kappa$ , and the coherence of the symmetric collective state decays at the rate  $\gamma$  via radiative relaxation, non-radiative relaxation, and pure dephasing. Under the condition that the molecular ensemble is spatially distributed over a region shorter than an optical wavelength (Dicke regime), radiative decay would be superradiant relative to the bare molecular rate  $\gamma_0$ , i.e.,  $\gamma = N\gamma_0$ ,<sup>126</sup> due to the permutation symmetry of  $|\alpha_0\rangle$ . Therefore, the imaginary parts of  $E_{\pm}$  correspond to the homogeneous linewidths of the polariton peaks, as would be measured in a linear absorption experiment starting from the ground state  $|G, 0_c\rangle$ . Non-Hermitian Hamiltonians are used to describe dissipation of quantum systems in an approximate way. The approximation ignores the conditional evolution induced by quantum jumps on the system wavefunction.<sup>121</sup>

The polariton energies in Eq. (10) exhibit an important feature that is often ignored. Even for a single-mode cavity that is on resonance with a molecular transition frequency, i.e.,  $\Delta_c = 0$ , the lower and upper polariton splitting, in general, cannot be expected to scale as  $\sqrt{N}$  with the molecule density. First, the Rabi splitting  $\Delta E = \text{Re}[E_+ - E_-]$  on resonance is a maximum when the material and cavity linewidths are equal ( $\kappa = \gamma$ ). If they are not identical, but nevertheless are of comparable magnitude, the splitting can be rewritten as

$$\Delta E \approx \sqrt{N}\Omega_{eg} \left[ 1 - \frac{x(N)}{2} \right], \quad (11)$$

where  $x(N) = (\gamma - \kappa)^2 / N\Omega_{eg}^2$ . The condition  $x \ll 1$  for  $\gamma \neq \kappa$  also implies that the so-called collective cooperativity parameter  $C_N = N\Omega_{eg}^2 / \kappa\gamma$ <sup>111,121</sup> is greater than unity. In other words, strong coupling emerges in the regime of large collective cooperativity.

We have thus shown that a microscopic many-particle Hamiltonian with local-only molecular contributions [Eq. (5)] can support a collective basis under specific assumptions in which the light-matter interaction Hamiltonian acquires a simple low-rank form [Eq. (9)]. This corresponds to the homogeneous regime of light-matter interaction, where the cavity field cannot distinguish between molecules in the ensemble. In this homogeneous limit, the microscopic theory, truncated to the single-excitation manifold, is formally equivalent to the semiclassical  $F$ -matrix method described previously. We also showed that taking into account the homogeneous linewidths of the material and cavity excitations ( $\gamma, \kappa$ ) gives a polariton spectrum that coincides with the results of the  $F$ -matrix or transfer matrix methods in the large cooperativity limit  $C_N \gg 1$ .

To further illustrate the equivalence between classical and quantum results of linear optical signals in the high cooperativity regime, compare Eq. (11) with the transfer matrix expression for the splitting in transmission for quantum well excitons in semiconductor microcavities in the low-reflectivity limit,<sup>127</sup>

$$\Delta E = 2\sqrt{\sqrt{V^4 + 2V^2\gamma(\gamma + \kappa)} - \gamma^2}, \quad (12)$$



where  $V = (2c\Gamma_0/(n_{\text{cav}})L_{\text{eff}})^{1/2}$  is the element of the transfer matrix that couples the exciton and cavity resonances (i.e., the classical analog of  $\Omega_{eg}$ ),  $\gamma$  is the homogeneous exciton linewidth,  $\Gamma_0$  is the exciton radiative width,  $\kappa = c(1 - R)/(2n_{\text{cav}}L_{\text{eff}})$  is bare cavity linewidth,  $R$  is the cavity reflectivity,  $L_{\text{eff}}$  is the effective cavity length,  $n_{\text{cav}}$  is the intracavity refractive index, and  $c$  is the speed of light. For large enough  $V$ , the transmission splitting in Eq. (12) becomes  $\Delta E \propto \sqrt{\alpha_0\gamma/n_{\text{cav}}}$ , where  $\alpha_0$  is the absorptivity of the medium. This relation has been used to accurately estimate the molecular concentration needed to observe a splitting in the transmission spectrum of liquid-phase infrared cavities,<sup>42</sup> i.e., the concentration required to reach the high cooperativity regime.

## 2. The role of inhomogeneities

Now consider a more realistic scenario in which local shifts of molecular levels cannot be ignored. This is the usual case in solid and liquid-phase cavities, where vibrational and electronic absorption linewidths are dominated by inhomogeneous broadening.<sup>119,128,129</sup> In this case, the molecular transition frequency of the  $i$ th molecular emitter can be written as

$$\omega_e(i) = \langle \omega_e \rangle + \Delta\omega_i, \quad (13)$$

where  $\langle \omega_e \rangle$  would correspond to the center of an absorption band and  $\Delta\omega_i$  is a static local frequency fluctuation (energy disorder), commonly assumed to be Gaussian with a standard deviation  $\sigma_E \ll \langle \omega_e \rangle$ .<sup>119</sup>

In a cavity, another type of static disorder corresponds to the unknown and possibly random location of emitters within the cavity field profile. The local Rabi frequency can thus be written as

$$\Omega_i = \langle \Omega \rangle + \Delta\Omega_i, \quad (14)$$

where  $\Delta\Omega_i$  is a local static fluctuation, which we refer to as *Rabi disorder*. The distribution of  $\Delta\Omega_i$  is not well understood experimentally, as it depends on the cavity fabrication method. However, it has been shown that Rabi disorder does not qualitatively change the nature of polaritonic states in comparison with the case  $\Delta\Omega_i = 0$  as long as  $|\Delta\Omega_i|/\sqrt{N}\langle \Omega \rangle \ll 1$  over the distribution.<sup>129,130</sup> Efforts can be made to fill the cavity volume homogeneously with molecular dipoles such that  $\Omega_i$  roughly matches the electric field profile of the cavity.<sup>69</sup> We ignore *orientational disorder* arising from the random orientation of molecular dipoles, as it has been shown that the linear response of a random but uniformly oriented dipole does not qualitatively differ from a situation where all dipoles are equally oriented.<sup>124</sup> This conclusion also holds for some coherent nonlinear optical signals.<sup>131</sup>

Not all local effects in the material system are statically random. Molecules have multiple sources of coherent and incoherent internal couplings between electronic, vibrational, rotational, and spin degrees of freedom. These local couplings tend to destroy indistinguishability of molecules in an intracavity ensemble, since at any given time the internal state configuration of a specific molecule is, in principle, unknown and different from the rest.

Consider, for example, vibronic coupling in organic chromophores. Intramolecular vibrations with frequencies  $\omega_\xi$  can couple with an electronic transition  $|g_i\rangle \leftrightarrow |e_i\rangle$  by dynamically modulating

the electronic energy of the excited state.<sup>125</sup> To lowest order in the mode displacements from equilibrium, this interaction leads to a local term of the form

$$\hat{V}_i = \sum_{\xi} \lambda_{\xi i} \omega_{\xi} (\hat{b}_{\xi i}^{\dagger} + \hat{b}_{\xi i}) \otimes |e_i\rangle\langle e_i|, \quad (15)$$

where  $\hat{b}_{\xi i}$  is the mode operator for the  $\xi$ th vibrational mode in the  $i$ th molecule, and the dimensionless parameter  $\lambda_{\xi i}$  quantifies the local electron-photon coupling strength via the spectral density  $J_i(\omega) = \sum_{\xi} \lambda_{\xi i}^2 \delta(\omega - \omega_{\xi})$ .<sup>125</sup> Due to vibronic coupling and the Condon principle, different molecules in an ensemble would have different probabilities of exchanging energy with a cavity vacuum, according to their instantaneous local vibrational configuration.

Current experiments often only probe the global properties of a coupled molecular cavity system, although single-molecule local state addressing and manipulation may be possible in open cavities using nanotips. Consequently, any measured optical or chemical polariton signal must simultaneously carry information about collective homogeneous effects as well as local inhomogeneities. Therefore, the interpretation of observables based on homogeneous-only approaches such as the  $F$ -matrix method or its quantum analog should necessarily be incomplete.

Ignoring inhomogeneities in a polariton model is equivalent to neglecting the role of collective material states that are not fully symmetric with respect to permutations of molecular emitters. These non-symmetric collective states are commonly known as *dark states* of the cavity, akin to states without oscillator strength that emerge in molecular aggregates and molecular crystals.<sup>119,132,133</sup>

## 3. How dark are dark states inside a cavity?

To answer this question, begin by considering a translationally invariant linear array of  $N$  molecules in free space with lattice constant  $a$ . For array excitations involving individual  $S_0 \rightarrow S_1$  transition dipoles, dark exciton states can be defined as<sup>119,125</sup>

$$|k \neq 0\rangle = \frac{1}{\sqrt{N}} \sum_{i=1}^N e^{ikx_i} |g_1, \dots, e_i, \dots, g_N\rangle, \quad (16)$$

where  $x_i$  is the position of the  $i$ th molecule in the array and  $k$  is the exciton wavevector. In general, the exciton wavevector can take  $N$  allowed values in the range  $\{-\pi/a, -\pi/a + 1, \dots, 0, \dots, \pi/a\}$ . For dark excitons, we must have  $k \neq 0$ , as only for the *bright* exciton we have  $k = 0$ . In free space, the bright exciton is the only state that can formally couple with a resonant photon of wavelength  $\lambda \gg a$  satisfying momentum conservation, leaving  $N - 1$  quasi-degenerate exciton states with  $k \neq 0$  essentially uncoupled from the light-matter interaction process to first order due to momentum mismatch.<sup>125</sup> The number of dark excitons grows linearly with  $N$ ; therefore, their density of states can easily exceed the bright exciton density in molecular aggregates and crystals.

Despite they are formally uncoupled from light, dark exciton states ( $k' \neq 0$ ) can still borrow oscillator strength from the bright exciton ( $k = 0$ ) due to vibronic coupling and static energy disorder<sup>119</sup> via higher-order processes and thus contribute to the aggregate absorption and emission spectra. In other words, dark exciton states are not fully dark in realistic molecular aggregates,

precisely because of local terms in the system Hamiltonian. Note that more general photon mode dispersions (other than free space) could enable the direct coupling of light modes with dark exciton states.

Consider now an ensemble of  $N$  molecules inside an optical or infrared cavity. We assume that their individual Rabi frequencies are identical (i.e., no Rabi disorder), despite that molecules may reside in unknown locations within the mode volume. We can describe single material excitations in a collective basis of the form

$$|\alpha\rangle = \frac{1}{\sqrt{N}} \sum_{i=1}^N c_{\alpha i} |g_1, \dots, e_i, \dots, g_N\rangle, \quad (17)$$

where the vector  $[c_{\alpha 1}, c_{\alpha 2}, \dots, c_{\alpha N}]^T$  physically encodes the relative phases for all molecular dipoles in the ensemble. The totally symmetric state in Eq. (7) thus corresponds to the case where  $c_{\alpha i} = 1$  for  $i = \{1, 2, \dots, N\}$ . Spontaneous emission of a collective state  $|\alpha\rangle$  occurs at a rate  $\gamma_\alpha = |\sum_i c_{\alpha i} \gamma_e|^2$ , where  $\gamma_e$  is the spontaneous emission rate of an individual molecule. Radiative decay of the collective state  $|\alpha\rangle$  would thus be superradiant only for the totally symmetric state, and there would be no radiative decay ( $\gamma_\alpha = 0$ ) for the remaining  $N - 1$  sets of  $c_{\alpha i}$  coefficients that are not symmetric with respect to particle permutation. In other words, non-symmetric collective states are formally dark, despite the associated material excitations being *fully delocalized* over the mode volume.

The classification of collective material eigenstates into a bright manifold  $\mathcal{P} = \{|G\rangle, |\alpha_0\rangle\}$  and a dark manifold  $\mathcal{Q} = \{|\alpha_1\rangle, |\alpha_2\rangle, \dots, |\alpha_{N-1}\rangle\}$  is a trivial consequence of orthogonality of the  $N$  vectors  $[c_{\alpha 1}, c_{\alpha 2}, \dots, c_{\alpha N}]^T$  and has nothing to do with momentum conservation, as it is the case in molecular aggregates and molecular crystals. Comparison of Eqs. (17) and (16) therefore suggests that a Frenkel exciton  $|k\rangle$  in a translationally invariant system is only a special type of collective state  $|\alpha\rangle$ .

Litinskaya, Reineker, and Agranovich<sup>124,134</sup> first proposed that in a strongly coupled cavity, bright polariton states, in which material excitations are delocalized over the entire cavity volume, could coexist and interact with a large density of incoherent dark excitons over a common spectral range. For the set of intracavity dark excitations, the term *dark state reservoir* was coined. It is a reservoir in the sense that for large  $N$ , the number of dark states is overwhelmingly large in comparison with the number of bright polariton states. In the single-excitation manifold, the latter can be written on resonance as

$$|\Psi_\pm\rangle = \frac{1}{\sqrt{2}} (|\alpha_0\rangle|0_c\rangle \pm |G\rangle|1_c\rangle), \quad (18)$$

where  $|0_c\rangle$  and  $|1_c\rangle$  represent the cavity vacuum and one-photon states, respectively. Just as in molecular aggregates, it is possible for dark excitons  $|k' \neq 0\rangle$  to borrow oscillator strength from a bright exciton  $|k = 0\rangle$  due to the presence of local inhomogeneities, and *intracavity* dark states  $|\alpha \neq \alpha_0\rangle$  can also borrow photonic character from a bright polariton state  $|\Psi_\pm\rangle$  in the single excitation manifold or beyond the one-excitation regime.<sup>120</sup>

This type of *cavity photon borrowing* can occur due to *coherent* local effects in the polariton dynamics. For instance, inhomogeneities such as energy disorder, Rabi disorder, and intramolecular vibronic coupling can give rise to couplings between the

totally symmetric polariton states and non-symmetric material excitations.<sup>130,135,136</sup> It is also known in quantum optics that local *dissipative* processes, such as the presence of local non-radiative relaxation and dephasing, can also drive population away from a totally symmetric polariton manifold into a dark state reservoir.<sup>137</sup> Moreover, in molecular ensembles with strong vibronic coupling (e.g., rubrene), local effects can lead to the emergence of novel types of vibronic polaritons that have large photonic character but give emission signals in regions of the spectrum that are seemingly dark in cavity absorption.<sup>120,138</sup>

## IV. CURRENT STATUS AND CHALLENGES

Research on molecular polaritons is thriving in terms of both experimental and theoretical developments. Even though experiments have been the driving force in the field, a fruitful interaction between theory and experiments is paving the way toward envisioned applications in quantum technology and quantum control. In this section, we briefly overview selected recent theoretical and experimental results.

### A. Recent experimental progress

The field of molecular polaritons has been primarily driven by experimental breakthroughs. Several pioneering results have advanced the field in directions that may eventually lead to the development of room-temperature integrated quantum technology. Among these achievements, we highlight the demonstration of strong coupling of organic molecules with optical microcavities<sup>87</sup> and surface plasmons,<sup>83,94</sup> ultrastrong coupling with organic photoswitches,<sup>29</sup> and the demonstration of vibrational strong and ultrastrong coupling in solid phase<sup>38,49</sup> and liquid phase Fabry–Pérot cavities.<sup>46,47,51</sup> Many experimental and theoretical works directly build on these results. In Table I, we list some of the experimental problems explored so far. For reviews of earlier experiments, we refer the reader to Refs. 64, 65, and 68.

The demonstration by Hutchison *et al.*<sup>28</sup> of a modified photoisomerization reaction rate under conditions of strong coupling with a cavity vacuum for one of the involved isomers may be regarded as the origin of a new research field in physical chemistry.<sup>66,67,76,77</sup> There are several widely used technologies that ultimately base their efficiency on the rates of chemical reactions or electron transfer processes that occur in excited electronic states [e.g., sunscreens, polymers, catalysis, solar cells, and organic light emitting diodes (OLEDs)]. Therefore, the ability to manipulate the rates and branching ratios of these fundamental chemical processes in a reversible manner using light–matter interaction with a vacuum field suggests a promising route for targeted control of excited state reactivity, without exposing fragile molecular species or materials to the damaging effects of intense laser fields.

Promising results in this direction are the demonstrations of cavity-modified intramolecular electron transfer between different electronic manifolds (singlet fission), under conditions of strong coupling of singlet states inside an optical microcavity.<sup>105,145,147</sup> The proposed mechanism for this process involves the manipulation of the relative energy levels between electron donor and acceptor

**TABLE I.** Recent experimental developments on vibrational strong coupling (VSC), vibrational ultrastrong coupling (VUSC), electronic strong coupling (ESC), and electronic ultrastrong coupling (EUSC).

Regime	Description	References
ESC	Cavity-enhanced energy transfer and conductivity in organic media	30 and 139–141
ESC/VSC	Strong coupling with biological light-harvesting systems	44 and 142–144
ESC	Cavity-modified photoisomerization and intersystem crossing	28, 105, and 145–147
ESC	Strong coupling with an individual molecule in a plasmonic nanocavity	96, 97, 99, and 148
ESC	Polariton-enhanced organic light emitting devices	32, 35, 149, and 150
EUSC	Ultrastrong light–matter interaction with molecular ensembles	29, 36, 93, 149, and 151–153
VSC/VUSC	Vibrational polaritons in solid phase and liquid phase Fabry–Pérot cavities	38–40, 45–47, 49–54, and 154
VSC	Manipulation of chemical reactivity in the ground electronic state	43, 55, and 155

manifolds via polariton formation.<sup>136,158</sup> The reversible control of singlet-to-triplet conversion may serve to improve the external quantum efficiency of organic optoelectronic devices. Electronic strong coupling in plasmonic systems has also been observed to suppress bimolecular photoreactions.<sup>192</sup>

While experiments on strong coupling with electronic transitions date back decades,<sup>87</sup> similar studies for vibrational strong coupling (VSC) are more recent. Current experimental focus is on the manipulation of chemical reactions in the ground electronic state inside Fabry–Pérot cavities<sup>43,55,155</sup> and also cavity-controlled steady-state<sup>38–40,42,44,46,47,49,53,154,193</sup> and ultrafast<sup>51,52,54,56,194,195</sup> vibrational spectroscopy. Chemical reactivity experiments under VSC are typically carried out in the dark, i.e., the cavity is not driven by external laser light, and thus, the role of dark states may be different and potentially more important than the bright states, but the connection between dark states and dark experiments is still not well understood. For example, modified reaction rates have been ascribed to dramatic changes (near 1 eV) of free energy,<sup>55</sup> which are difficult to reconcile with the relatively small Rabi splittings on the order of 10 meV realized in infrared transmission.

Infrared spectroscopy studies of VSC systems may shed light on the mechanism of cavity-modified chemistry. Initial spectroscopic studies on VSC were carried out on first-order Fabry–Pérot cavities that were several micrometers long, involving carbonyl absorption bands of polyvinyl acetate<sup>49</sup> and polymethylmethacrylate.<sup>38,40</sup> VSC was quickly extended to several neat liquids (diphenyl phosphoramide and benzonitrile) and to longer cavities.<sup>46</sup> It was important to achieve strong coupling in longer cavities to conveniently incorporate a wider range of chemically relevant materials, including species dissolved in solution as demonstrated for W(CO)<sub>6</sub> in hexane.<sup>42</sup> In this sense, it is advantageous that the Rabi splitting scales with the concentration and not the cavity length (provided the concentration is preserved) so that longer cavities can be used without sacrificing coupling strength. Vibrational ultrastrong coupling (VUSC), in which the splitting is a substantial fraction of the vibrational frequency  $\Omega/\omega_0 > 0.1$ , was achieved with neat liquids of strong absorbers including CS<sub>2</sub>.<sup>47</sup> Steady-state spectroscopy has also been used to show simultaneous coupling between a cavity mode and multiple vibrational absorptions in complex molecules and mixtures.<sup>40,193</sup>

Understanding the dynamics of vibrational polaritons will likely be key to understanding reactivity, especially for

photo-initiated processes. To that end, time resolved, IR pump–probe, and 2DIR studies of cavity-coupled W(CO)<sub>6</sub> in hexane have been used to identify transient effects in strongly coupled molecular ensembles. Initial pump–probe results showed two predominant features after excitation that transferred population from the ground vibrational state to excited states: polariton contraction resulting from depletion of the ground state and a large contribution from dark excited state absorption. The dark state transient population was found to decay at the same rate as the excited vibration in free space, consistent with these dark states behaving much like free uncoupled molecules. In addition, features that relax more rapidly were tentatively attributed to polariton population changes.<sup>51</sup>

Subsequent studies with 2DIR have further elucidated the dynamics of vibrational polaritons in W(CO)<sub>6</sub>.<sup>52</sup> Because 2DIR studies give excitation–frequency resolution, they conclusively show that the polariton modes, and the dark reservoir, can be readily excited by incident light. Multidimensional spectroscopy also gives facile experimental access to excitation pathways that revealed coherent exchange between the upper and lower vibrational polaritons.<sup>194</sup> The coherence led to strongly modulated transmission across the polariton spectrum, with potential implications for VSC-based photonic devices. Extending 2DIR studies to W(CO)<sub>6</sub> in a series of organic solvents has recently shown that the homogeneous linewidth of the vibrational absorber has a strong impact on the observed dynamics.<sup>195</sup>

Additional ultrafast studies with W(CO)<sub>6</sub> have explored the boundary between vibrational weak and strong coupling.<sup>54,56</sup> Reducing the Rabi splitting in this material system reduces the overlap between the lower polariton and higher-lying states of the uncoupled vibration and simplifies the experimental spectra. More importantly, it was reported that these intermediate-coupling samples are excellent candidates for photonic devices. The transmission, reflection, and absorption spectra are highly dependent on the incident power because the material absorption is easily saturated. As the absorption saturates, the Rabi splitting decreases. At sufficiently high excitation fluences, the spectrum can collapse to a single transmission peak at the empty-cavity mode frequency reversibly over sub-nanosecond timescales.

The time-resolved studies described above have, thus far, been limited to an ideal absorber and are not easily connected to the promising results reported for VSC-modified reactions. Under

conditions of vibrational strong coupling in liquid phase, ground state chemical reactions can proceed through novel pathways that have yet to be fully characterized from a mechanistic perspective. For some molecular species, reactions are inhibited, and for other systems, they are catalyzed. For instance, strong coupling of a Si–C bond in a substituted acetylene molecule with an infrared cavity vacuum led to a decreased rate of the Si–C bond breakage by a moderate factor in comparison with a control.<sup>43</sup> It has also been shown that the solvolysis of *para*-nitrophenyl acetate (reactant) in ethyl acetate (solvent) proceeds up to an order of magnitude faster when the C=O bonds of both the reactant and solvent are resonant with a cavity mode, but only the solvent is strongly coupled.<sup>155</sup> In other words, by strongly coupling a molecular species in excess (solvent), it is possible to modify the chemical reactivity of a dilute component in solution, for which light–matter coupling is weak. Despite recent theoretical efforts,<sup>122,184,196</sup> the underlying microscopic mechanism for these remarkable observations is not well understood.

## B. Recent theoretical progress

In Table II, we list some of the recent theoretical research directions explored to date. The initial condensed-matter approach to organic polaritons<sup>72–74,134,166,197</sup> has been gradually replaced in recent years by what can be called a “quantum optics” approach. The traditional atomic cavity QED theory<sup>2</sup> is here extended to take into account the relevant physics and chemistry of molecular degrees of freedom. This quantum optics approach was initially used by Cwik *et al.*<sup>172</sup> to describe polariton condensation in microcavities and by Herrera *et al.*<sup>174</sup> to describe light-by-light switching with molecular aggregates in microcavities. The works listed in Table II predominantly use a quantum optics approach to predict or interpret experimental observables. Among these results, the development of the Holstein–Tavis–Cummings (HTC) model of vibronic polaritons<sup>75,136</sup> has been particularly useful, as it has been successfully used to explain features in the optical signals of organic microcavities that were notoriously confusing, such as the apparent breakdown of reciprocity in the oscillator strengths in absorption and emission strengths over specific frequencies.<sup>89,198</sup> Further predictions of the HTC model regarding the nature of the lower polariton manifold

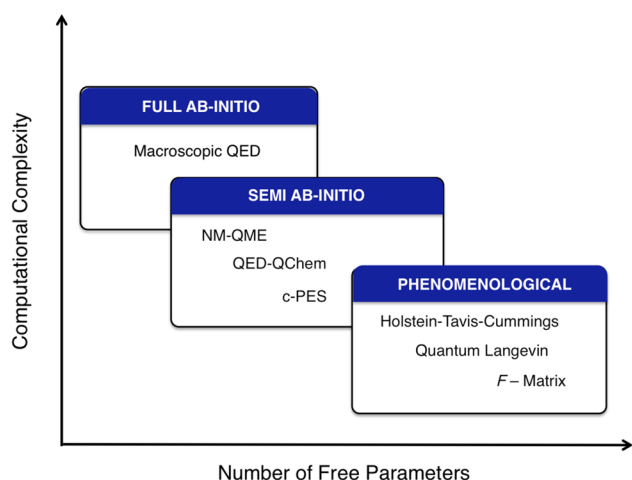
were later confirmed using variational techniques<sup>199,200</sup> and applied in subsequent work on singlet fission<sup>201</sup> and long-range energy transfer.<sup>160</sup> Recent experiments with rubrene microcavities<sup>145</sup> confirm the validity of the HTC model to describe the optical response and chemical reactivity of molecular polaritons in the optical regime, thus consolidating the quantum optics approach to describe these systems.

Another promising trend in the field is the development of (semi-) *ab initio* methods for non-adiabatic molecular polariton dynamics, as first proposed by Galego *et al.*<sup>177</sup> This integrative approach has been further developed by several groups.<sup>175,176,178,180,183,185,186,202,203</sup> The main strength of this methodology is its compatibility with conventional electronic structure and molecular dynamics techniques. In this approach, a single-mode cavity field is essentially treated as another *effective* nuclear degree of freedom to which electrons can strongly couple. In this coordinate-only formalism, polaritonic energy surfaces and reaction coordinates can be defined.<sup>175</sup> This methodology has been primarily focused on strong light–matter coupling with individual molecules, but extensions to molecular ensembles are possible either via a coordinate-only approach<sup>182,204,205</sup> or using a Tavis–Cummings model for electron–photon interaction, with the two-level energy gaps parameterized by nuclear coordinates.<sup>177,184</sup> Predictions made with this methodology, however, have yet to be confirmed in experiments.

For classification purposes, we propose in Fig. 4 a complexity hierarchy for theory methods in the field. At the lower-right end of the complexity scale, we have the simple phenomenological models, such as the semiclassical fitting matrix method (*F*-matrix), which involve a relatively large number of fitting parameters. At the upper-left end of the complexity scale, we have a hypothetical theory of molecular polaritons where the electron and nuclear dynamics of molecules in an ensemble are treated using *ab initio* methods with quantum chemical accuracy, and *also* the electromagnetic field is treated using macroscopic quantum electrodynamics,<sup>106,206,207</sup> which generalizes empty-space quantum optics to treat dispersive and absorptive media. This superior fully *ab initio* theory would have essentially no fitting parameters and has yet to be developed. All other methods used to date, including the HTC model,<sup>136</sup> cavity potential energy surfaces (c-PES<sup>177</sup>), QED quantum chemistry (QED-QChem<sup>203</sup>), non-Markovian quantum master equation

**TABLE II.** Recent theoretical developments on vibrational strong coupling (VSC), vibrational ultrastrong coupling (VUSC), and electronic strong coupling (ESC).

Regime	Description	References
ESC	Cavity-controlled intramolecular electron transfer in molecular ensembles	136 and 156–159
VSC/ESC	Controlled chemical reactivity with spatially separated donor and acceptor molecules	160 and 161
ESC	Cavity-enhanced energy and charge transport with molecular ensembles	162–165
ESC	Absorption and photoluminescence of vibronic polaritons in molecular ensembles	74, 120, 134, 166, and 167
VSC	Linear and nonlinear spectroscopy of vibrational polaritons in molecular ensembles	168–171
ESC	Polariton condensation and lasing with vibronic transitions in molecular ensembles	172 and 173
ESC	Few-photon nonlinear quantum optics with molecular ensembles	131 and 174
VUSC	Ultrastrong light–matter interaction with molecular vibrations	122 and 175
ESC	Non-adiabatic electron–photon–nuclear dynamics using <i>ab initio</i> and semiclassical methods	175–188
ESC	Driven-dissipative polariton dynamics using open quantum system methods	189–191



**FIG. 4.** Diagram of quantum mechanical methods for molecular polaritons in terms of the number of free parameters and computational complexity. Fully phenomenological models describe both material and field degrees of freedom using semi-empirical Hamiltonians with parameters obtained from experiments. Semi-*ab initio* methods treat the material degrees of freedom using quantum chemical methods, but the cavity field and the light-matter coupling parameters are obtained from experiments. Full *ab initio* methods would also involve a description of the dispersive and absorptive properties of the cavity field using macroscopic quantum electrodynamics, which essentially has no fitting parameters. Classical transfer matrix theory cannot provide more information than phenomenological quantum methods.

(NM-QME<sup>189</sup>), and Langevin equations,<sup>191</sup> would fit somewhere in between these two complexity extremes.

## V. CONCLUSION AND OUTLOOK

Experimental efforts in the field of molecular polaritons have significantly evolved in the last two decades since the first demonstration of strong light-matter coupling with molecular crystals.<sup>87</sup> Over the first decade, the main focus was the development of novel organic solid-state light emitting devices with polariton-enhanced efficiencies.<sup>64</sup> Although this continues to be an important research direction that may lead to novel applications in quantum technology,<sup>35</sup> the idea of building infrared and optical cavity structures for controlling chemical reactions has gained significant traction in recent years.<sup>31</sup> Understanding the microscopic mechanisms that determine the rate of reactive processes in solid and liquid phases, for example, may stimulate the development of novel coherent control techniques that exploit the quantization of the electromagnetic field to achieve a target reaction branching ratio. Moreover, the micrometer-sized cavities in the infrared regime enable an integration with conventional microfluidics technology, which would allow the study and control of intracavity chemical processes in solution. The use of mirror materials that are semi-transparent in the UV-visible could also enable the *in situ* ultrafast optical monitoring of reaction intermediates. Applications in polariton-assisted chemical and electromagnetic sensing can also be envisioned.

New research directions can emerge from a more focused theoretical and experimental study of coherent and dissipative dynamical effects that have been observed in molecular cavity systems. For example, our understanding of polariton lifetimes in optical microcavities is still far from complete,<sup>198</sup> possibly due to the difficulty of spectroscopically resolving the pathways for population transfer between molecular polaritons and the collective dark state manifold. Moreover, the interaction of molecular polaritons with their thermal reservoir under electronic strong coupling has only recently attracted experimental and theoretical interest.<sup>159,208</sup>

The development of technology based on the dynamics of molecular polaritons would thus benefit from a more active interplay between theoretical and experimental research. The recent experimental verification of the Holstein-Tavis-Cummings<sup>136</sup> using rubrene microcavities<sup>145</sup> is a promising step in this direction. Experiments can also motivate the development of theoretical tools and protocols for cavity-controlled chemistry. For example, a recent proposal for tuning the rate of energy transfer between spatially separated donor and acceptor molecular species<sup>161</sup> builds on the experimental demonstration of ultrafast manipulation of the light-matter interaction strength in UV-visible<sup>139-141</sup> and infrared<sup>54</sup> cavities. This proposal for “remote control chemistry”<sup>161</sup> may, in turn, stimulate the fabrication of unconventional infrared cavity structures and the development of novel detection schemes. In the optical regime, detailed electronic structure calculations including polariton formation have recently predicted that the hydrolysis of *tert*-butyl chloride can be “self-catalyzed” at the single-molecule level in the near field of plasmonic nanoparticles without external stimuli.<sup>209</sup> Testing whether this predicted effect is indeed due to strong coupling would require the use of advanced single-molecule detection techniques, possibly in integration with nanofluidics.<sup>210</sup>

Another problem where a collaboration between theory and experiments can be fruitful is strong coupling in the gas phase. Detailed theoretical predictions about spontaneous generation of infrared light with diatomic molecules under conditions of electronic strong coupling<sup>186,187</sup> represent a challenge for experimental verification, as achieving the strong coupling regime with gas-phase cavities is comparably difficult, although, in principle, possible. This should present new challenges and opportunities, given the additional degrees of freedom involved and prospects for state-to-state chemical studies, in particular, at ultracold temperatures.<sup>211</sup> Gas-phase strong coupling has already been implemented with atomic gases in photonic crystal cavities.<sup>212</sup>

Strong coupling to vibrational transitions in gas-phase molecules in infrared cavities should also be considered. Even though the number density of species is much lower in gases than in condensed phase, the linewidths are considerably narrower. Rotationally resolved vibrational transitions of small diatomic or polyatomic molecules are attractive for strong coupling since they afford the opportunity to explore whether state to state processes including energy transfer and reactions can be modified and perhaps offer better opportunities to understand mechanistic details. Assessing the feasibility of this would require a careful analysis of broadening processes in various pressure regimes. At low pressure (and higher frequency), rovibrational lines tend to be inhomogeneously Doppler broadened. On the other hand, at higher pressures,

spectral lines are homogeneously pressure broadened. For a pure gas, the peak absorption intensity remains constant and the line broadens as the pressure increases. Simple estimates suggest that in the pressure broadened regime, the condition for strong coupling reduces to the absorption cross section being larger than the pressure broadening coefficient. In addition, since increasing the pressure of the absorbing gas increases the Rabi frequency at the same rate as the linewidth, a cavity width that is matched to the absorption linewidth of the gas medium would still lead to strong coupling. It might also be possible to reduce Doppler broadening in a jet or a trap configuration so that strong coupling could be achieved at very low number densities.

Further research opportunities can arise from the integration of molecular polariton systems with traditional photonic and chemical technologies. For example, by using a nematic liquid crystal embedded in an infrared cavity with conductive mirrors,<sup>48</sup> researchers were able to manipulate the light–matter interaction strength by applying an external voltage. The voltage was used to induce a macroscopic rotation of the medium polarization relative to the cavity field orientation. Further explorations in this direction may lead to the development of novel screen displays. Moreover, upon integration of liquid crystal cavities with microfluidics and nanofluidics,<sup>101</sup> novel polariton-enhanced chemical sensors can be envisioned. Topological photonics based on polaritonic systems is another interesting approach for unconventional light emission.<sup>213,214</sup>

There should also be interesting and informative polarization effects for strongly coupled molecules in cavities. Polarization dependent transient absorption is a popular way to measure anisotropy decay and characterize solvation of species in visible absorption and emission studies as well as Raman and infrared spectroscopy.<sup>215–218</sup> Longer anisotropy decays result from stronger solvent friction that scales with the solute–solvent interaction strength and can be correlated with other properties such as energy relaxation, energy and charge transfer, and isomerization. For an ensemble of strongly coupled molecules inside a cavity, excitations are expected to be delocalized throughout the ensemble due to coherent light–matter coupling, as has been already demonstrated by the observation of long range intracavity energy transfer.<sup>140,219</sup> In some respects, the delocalization of a dipole excitation in a cavity resembles a transition in a degenerate vibrational mode of a free-space molecule because it provides a way to rapidly reorient the transition dipole moment. Anisotropy decay for nondegenerate modes outside a cavity requires the physical rotation of a molecule. Degenerate modes can reorient the direction of an excitation without the molecule having to undergo overall rotation. The initial anisotropy is also more rapidly relaxed, as first shown for  $W(CO)_6$ .<sup>220</sup> Therefore, strongly coupled molecules in a cavity may exhibit faster anisotropy decay due to rapid dipole reorientation among the coupled ensemble than cavity-free molecular species and also exhibit a lower initial anisotropy. Further theory and precise ultrafast cavity measurements would be required to verify this intuition.

Optical resonators are already widely used for enhanced sensing in cavity ring-down spectroscopy.<sup>221</sup> Here, the concentration of a gas-phase absorber is usually small, and the goal of the technique is to achieve as low a minimum detectable concentration as possible (ppb or lower). Strong coupling studies would represent the opposite extreme in which a high concentration of strong absorbers is loaded

into the cavity to identify coherently coupled and quantum optical effects on the spectroscopy, photophysics, and molecular reaction dynamics.

Coupling electronic or vibrational bands to surface plasmon polariton resonances (SPRs) is a popular approach to enhanced sensing with surface-enhanced Raman spectroscopy (SERS<sup>222</sup>) and surface-enhanced infrared spectroscopy (SEIRA<sup>223</sup>). SERS is a mature field in which many orders of magnitude of enhancement can be achieved for otherwise weak signals. SEIRA is also well established with plasmonic resonances of localized particles or meshes<sup>224–226</sup> even though the enhancements tend to be much smaller than in SERS. In a recent related study, enhanced interactions of molecular vibrations with relatively narrow surface phonon polariton resonances (SPhPs) of hexagonal boron nitride (hBN) demonstrated not just enhanced absorption but also strong coupling as a result of the similar widths for the vibration and SPhPs.<sup>227</sup>

Several open questions in the field relate to potential consequences of reaching the strong coupling regime for other degrees of freedom that are not directly involved in light–matter interaction. Consider energy transfer between vibrational polaritons in an infrared cavity and a thermal source or sink that is not coupled to light. The coherent energy exchange between cavity photons and the vibrational motion of molecules in an ensemble may modify the rates of thermal energy flux between the system and a reservoir. Additionally, thermal conductivity under electronic strong coupling has yet to be explored. Novel types of coherent control schemes with fewer requirements and constraints on the systems that can be explored, in comparison with gas phase systems, may also be investigated. The potential for inducing polariton-assisted pathways for enhancing the light-harvesting efficiency of biologically inspired devices is another interesting possibility.<sup>44,142</sup> Fundamental questions regarding the effect of strong vibrational coupling in the diffusive transport of dilute molecules in solutions, the macroscopic fluid properties of neat liquids, and the dynamics of non-equilibrium and possibly non-statistical chemical reactions should also be explored.

We would finally like to highlight how in two decades the field of molecular polaritons has reached a stage of maturity where emerging research directions can potentially lead to novel room-temperature devices with enhanced transport, optical, and chemical properties, partly due to the formation of molecular polaritons in the optical or infrared regimes. We believe that in order to materialize this promise, it will be necessary for theoretical and experimental researchers to interact closely and focus on the many open research questions in the field. Addressing these challenges would require the successful integration of concepts and techniques from physical chemistry, quantum optics, quantum control, computational physics, and materials science.

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## APPENDIX: HOMOGENEOUS QUANTUM MODEL FROM SEMICLASSICAL THEORY

Consider an individual molecule with three relevant energy eigenstates denoted  $|E_0\rangle$ ,  $|E_1\rangle$ , and  $|E_2\rangle$ . Transitions between these molecular states couple to a quantized single-mode electromagnetic field with annihilation operator  $\hat{a}$  and frequency  $\omega_c$  according to the Hamiltonian (units of  $\hbar = 1$ )

$$\hat{H}_Q = \omega_c \hat{a}^\dagger \hat{a} + \sum_n \omega_n |E_n\rangle \langle E_n| + (\Omega_{01} |E_0\rangle \langle E_1| + \Omega_{02} |E_0\rangle \langle E_2|) \otimes (\hat{a}^\dagger + \hat{a}) + \text{H. c.}, \quad (\text{A1})$$

where  $\omega_m$  are the state energies, and  $\Omega_{nm} = \Omega_{mn}$  are the state-dependent Rabi frequencies associated with the cavity-induced transitions  $E_n \leftrightarrow E_m$  ( $n \neq m$ ). Counter-rotating terms are kept, but permanent dipole moments are ignored. In Hamiltonian  $\hat{H}_Q$ , both light and matter degrees of freedom are quantized. Upon truncating the photon number to the vacuum state ( $n_c = 0$ ) and the single photon Fock state ( $n_c = 1$ ), Eq. (A1) can be written in matrix form as

$$\hat{H}_Q = \begin{pmatrix} \omega_0 & 0 & 0 & 0 & \Omega_{01} & \Omega_{02} \\ 0 & \omega_1 & 0 & \Omega_{01} & 0 & 0 \\ 0 & 0 & \omega_2 & \Omega_{02} & 0 & 0 \\ 0 & \Omega_{01} & \Omega_{02} & \omega_0 + \omega_c & 0 & 0 \\ \Omega_{01} & 0 & 0 & 0 & \omega_1 + \omega_c & 0 \\ \Omega_{02} & 0 & 0 & 0 & 0 & \omega_2 + \omega_c \end{pmatrix}. \quad (\text{A2})$$

The upper-right sub-block and its Hermitian conjugate lead to counter-rotating modifications of the ground state  $|E_0, n_c = 0\rangle$ , which can be ignored when  $\Omega_{01} \ll (\omega_{10} + \omega_c)$  and  $\Omega_{02} \ll (\omega_{20} + \omega_c)$  with transition frequencies  $\omega_{mn} \equiv \omega_m - \omega_n$ . These conditions impose the rotating-wave approximation (RWA). The first excited polaritons are thus given by the eigenstates of the center sub-block. Upon subtraction of the ground state energy  $\omega_0$  along the diagonal and using  $\omega_{20} = \omega_{10} + \delta_{21}$ , the rotating-wave sub-block reads

$$\hat{H}_Q^{\text{RWA}} = \begin{pmatrix} \omega_{10} & 0 & \Omega_{01} \\ 0 & \omega_{10} + \delta_{12} & \Omega_{02} \\ \Omega_{01} & \Omega_{02} & \omega_c \end{pmatrix}. \quad (\text{A3})$$

The two-level version of Eq. (A3) is obtained by setting  $\Omega_{02} = 0$ . Alternatively, it can be derived from a truncated Hopfield model of coupled quantum harmonic oscillators, the Jaynes–Cummings model, or the Tavis–Cummings model in the bosonic (Holstein–Primakoff) approximation.

Now consider a *semiclassical* version of the light–matter Hamiltonian [Eq. (A1)] in which the single cavity mode at frequency  $\omega_c$  is treated as the time-dependent field amplitude  $\mathcal{E}_c(t) = \mathcal{E}_0 \cos \omega_c t$ . We can rewrite the bare molecular frequencies to give the semiclassical Hamiltonian

$$\hat{H}_{\text{SC}}(t) = \frac{(\omega_0 + \omega_1)}{2} \hat{1}_{3 \times 3} - \frac{\omega_{10}}{2} |E_0\rangle \langle E_0| + \frac{\omega_{10}}{2} |E_1\rangle \langle E_1| + \left( \frac{\omega_{10}}{2} + \delta_{21} \right) |E_2\rangle \langle E_2| + (d_{01} |E_0\rangle \langle E_1| + d_{02} |E_0\rangle \langle E_2|) \mathcal{E}_0 \cos \omega_c t + \text{H.c.}, \quad (\text{A4})$$

where  $d_{nm} = d_{mn}$  are the relevant transition dipole moments ( $n \neq m$ ). The first term is a state-independent matrix that only contributes with a global phase to the system eigenstates and can thus be ignored. The explicit time dependence in  $\hat{H}_{\text{SC}}(t)$  can be removed with a unitary (rotating frame) transformation of the form

$$\hat{U}(t) = e^{i\lambda_0 t} |E_0\rangle \langle E_0| + e^{i\lambda_1 t} |E_1\rangle \langle E_1| + e^{i\lambda_2 t} |E_2\rangle \langle E_2| \quad (\text{A5})$$

with frequency parameters  $\lambda_n$  that up to this point can be left undetermined. We define a transformed rotating-frame Hamiltonian in the usual form as  $\tilde{H}_{\text{SC}} = \hat{U} \hat{H}_{\text{SC}} \hat{U}^\dagger + i \left[ \frac{d}{dt} \hat{U} \right] \hat{U}^\dagger$ , which explicitly reads

$$\tilde{H}_{\text{SC}}(t) = \left( -\frac{\omega_{10}}{2} - \lambda_0 \right) |E_0\rangle \langle E_0| + \left( \frac{\omega_{10}}{2} - \lambda_1 \right) |E_1\rangle \langle E_1| + \left( \frac{\omega_{10}}{2} + \delta_{21} - \lambda_2 \right) |E_2\rangle \langle E_2| + (g_{01} |E_0\rangle \langle E_1| e^{i(\lambda_0 - \lambda_1)t} + g_{02} |E_0\rangle \langle E_2| e^{i(\lambda_0 - \lambda_2)t}) (e^{i\omega_c t} + e^{-i\omega_c t}) + (g_{01} |E_1\rangle \langle E_0| e^{-i(\lambda_0 - \lambda_1)t} + g_{02} |E_2\rangle \langle E_0| e^{-i(\lambda_0 - \lambda_2)t}) \times (e^{i\omega_c t} + e^{-i\omega_c t}), \quad (\text{A6})$$

where we have defined Rabi frequencies  $g_{nm} \equiv d_{nm} \mathcal{E}_0 / 2$ . We now constrain two of the parameters in  $U(t)$  by setting  $\lambda_1 = \lambda_2$  and  $\lambda_1 - \lambda_0 = \omega_c$ , with  $\lambda_0$  free, to give

$$\tilde{H}_{\text{SC}}(t) = \left( -\frac{\omega_{10}}{2} - \lambda_0 \right) |E_0\rangle \langle E_0| + \left( \frac{\omega_{10}}{2} - \lambda_1 \right) |E_1\rangle \langle E_1| + \left( \frac{\omega_{10}}{2} + \delta_{21} - \lambda_1 \right) |E_2\rangle \langle E_2| + g_{01} (|E_0\rangle \langle E_1| + |E_1\rangle \langle E_0|) + g_{02} (|E_0\rangle \langle E_2| + |E_2\rangle \langle E_0|) + \hat{V}(t), \quad (\text{A7})$$

where  $\hat{V}(t)$  contains residual terms oscillating at frequencies on the order of  $\omega_c + \omega_{10}$  ( $|\delta_{21}| \ll \omega_{10}$ ), which can be ignored in a rotating-wave approximation. We can now fix the remaining phase by setting  $\lambda_0 = -\omega_c / 2$  to arrive at a time-independent Hamiltonian  $\tilde{H}_{\text{SC}}^{\text{RWA}} \equiv \tilde{H}_{\text{SC}}(t) - \hat{V}(t)$ , given in matrix form by

$$\tilde{H}_{\text{SC}}^{\text{RWA}} = \frac{1}{2} \begin{pmatrix} \omega_{10} - \omega_c & 0 & 2g_{01} \\ 0 & \omega_{10} - \omega_c + 2\delta_{21} & 2g_{02} \\ 2g_{01} & 2g_{02} & -\omega_{10} + \omega_c \end{pmatrix}. \quad (\text{A8})$$

This matrix is equivalent to the semiclassical fitting matrix  $\mathbf{F}(\omega_c)$  in Eq. (4) of the main text, after making the identifications:  $|E_1\rangle = |E_0^{\dagger}\rangle$ ,  $|E_2\rangle = |E_1^{\dagger}\rangle$ , and  $\delta_{21} = \omega_v$ . The equivalence of  $\tilde{H}_{\text{SC}}^{\text{RWA}}$  with the *quantum* Hamiltonian  $\hat{H}_Q^{\text{RWA}}$  in Eq. (A3) is established by making the replacement  $g_{mn} \rightarrow \Omega_{nm}$  and adding the overall shift  $(\omega_{10} + \omega_c) / 2$  to the diagonal elements in Eq. (A8), which again only introduces an irrelevant global phase to the system evolution.

This simple derivation proves that the quantized nature of a cavity field is *irrelevant* to describe the dynamics of the

lowest excited polariton eigenstates in the rotating-wave approximation, and therefore, most cavity spectroscopy experiments in the linear regime, i.e., a classical field, give the same predictions. This conclusion holds for both the Jaynes–Cummings (single molecule) and the homogeneous Tavis–Cummings model (ensemble), upon truncation to the single-excitation manifold.

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