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# Annual Review of Physical Chemistry Vibration-Cavity Polariton Chemistry and Dynamics

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#### **Keywords**

light-matter interactions, vibration-cavity polaritons, polariton chemistry, strong coupling, vibrational dynamics, quantum optical chemistry

#### Abstract

Molecular polaritons result from light-matter coupling between optical resonances and molecular electronic or vibrational transitions. When the coupling is strong enough, new hybridized states with mixed photon-material character are observed spectroscopically, with resonances shifted above and below the uncoupled frequency. These new modes have unique optical properties and can be exploited to promote or inhibit physical and chemical processes. One remarkable result is that vibrational strong coupling to cavities can alter reaction rates and product branching ratios with no optical excitation whatsoever. In this work we review the ability of vibration-cavity polaritons to modify chemical and physical processes including chemical reactivity, as well as steady-state and transient spectroscopy. We discuss the larger context of these works and highlight their most important contributions and implications. Our goal is to provide insight for systematically manipulating molecular polaritons in photonic and chemical applications.

#### **INTRODUCTION**

Since the invention of the laser about 60 years ago, chemists have dreamed of optical alchemy that is, on-demand methods to control chemistry with light (1, 2). The initial idea was to use narrow-frequency, high-power lasers to excite a specific bond, causing it to break preferentially, regardless of the relative strength of this bond. This process would achieve mode-specific control, unattainable with simple heating. Although there are select examples of this mission being accomplished (3, 4), the idea has been undermined primarily by inherently rapid deactivation of the excited bond through intramolecular vibrational relaxation (IVR) or intermolecular energy transfer (IET) to the surrounding bath. This rapid loss of excitation to the surroundings in condensed phases remains difficult to overcome, resulting in extensive studies of those relaxation processes (5, 6). In the past few years, a new technique has emerged that appears to circumvent these complications: strong coupling to optical modes. Interest in this field among chemists has increased dramatically following reports of using strong coupling not only to modify photophysics and photochemistry (7–9) but also to alter electronic ground-state reaction rates and product branching ratios simply by placing molecules between two properly spaced mirrors (10–12).

This breakthrough relies on achieving strong coupling between an optical resonance and an optically active material transition to realize hybridized light-matter states. These polariton states are spectrally shifted from the uncoupled transitions and have hybrid characteristics stemming from their light and matter constituents, as well as novel spectroscopic features concomitant with changes in physical and chemical behavior (13, 14). The nascent field of polaritonic chemistry combines well-established strong coupling concepts from quantum electrodynamics (QED) and semiconductor physics (14, 15) with the physical chemistry of molecular systems. The initial discoveries of modified photochemistry under electronic strong coupling (ESC) (7-9, 16) were, in some respects, explicable because they involved excitation into a polariton state to initiate the reaction. Despite the great interest, there is considerably less understanding of ground-state reactions modified under vibrational strong coupling (VSC) (17, 18). This approach is more broadly applicable to important chemical reactions because it occurs in the dark, does not require photochemical pathways, and has the potential for specific reaction site targeting. However, the role of the polariton states in VSC is not easily identified. Strong coupling to an ensemble of molecules is inherently a collective phenomenon (19, 20), but most chemical reactions are thought to take place locally on individual reacting molecules. A large majority of the states, typically called dark states, exhibit many of the characteristics of uncoupled molecules, apart from a limited degree of delocalization and mediation of relaxation processes in exciton-polaritons (21, 22). The role these dark states might play in VSC remains unclear, nor is there any agreement on what aspects of the better-understood ESC-modified behavior are transferable to VSC.

In this review we begin with a brief discussion of the history and background of strong coupling and its extension to molecular vibrations. We then review cavity-modified chemistry, including our perspective on potential explanations. Although perhaps the greatest excitement of the past few years centers on how polaritons can modify chemistry, VSC also leads to unique and exciting nonlinear and transient optical phenomena, which we will review. Finally, we conclude with a discussion of potential future directions for the field.

## BACKGROUND AND STEADY-STATE VIBRATIONAL STRONG COUPLING

Optical modes, such as Fabry–Pérot cavity modes or propagating plasmon polaritons, can couple to optically active transitions of a nearby material when the modes are resonant with one another and have similar decay rates. If the coupling rate (i.e., the energy exchange rate) is faster than



#### Figure 1

Strong coupling between a cavity optical mode and a vibrational transition results in hybridized light-matter states above and below the uncoupled transitions separated by the Rabi splitting,  $\Omega$ . Figure adapted from Reference 78 (CC BY 4.0).

the losses of either mode—put differently, if the splitting between the newly created polaritons is greater than the linewidth of either participant mode-the system is in the strong coupling regime. Spectroscopic observations indicate the formation of two polariton modes separated by the so-called vacuum Rabi splitting,  $\Omega \equiv 2g\sqrt{N}$ , where g is the single particle coupling parameter and N is the number of absorbers. The single particle coupling parameter can be expressed as  $\hbar g = \mu \times \sqrt{\hbar \omega_c/2 \varepsilon V_c}$ , where  $\mu$  is the transition dipole moment of the transition of the material,  $\omega_{\epsilon}$  is the cavity resonance frequency,  $\varepsilon$  is the dielectric constant of the material in the cavity, and  $V_{c}$  is the mode volume of the optical mode (17). These hybridized states, the upper polaritons (UP) and lower polaritons (LP) shown in Figure 1, have partial character of the optical mode and material excitation and provide an opportunity to modify a wide range of physical and chemical properties of the component material or optical modes (13, 23, 24). For planar microcavities, the UP and LP states indicated in Figure 1 in fact belong to two separate polariton branches with continuous dispersion as a function of in-plane wavevector. For strong coupling to an ensemble, there also exists a large reservoir of dark states, as mentioned above, comprising modes that are mostly similar to those of uncoupled molecules (21, 22, 25-29). This strong coupling behavior established and exploited in atomic physics and exciton-polariton systems is now being extended to modify chemical and physical processes in molecules. Many of the effects observed using steadystate and transient spectroscopy in exciton polaritons have served as a guide for what to expect under similar circumstances for VSC.

There have been numerous reviews of strong coupling in cavities and plasmonic structures (24, 30–36). Following initial studies of cold atoms (37, 38) and inorganic Wannier–Mott exciton-polaritons in cavities (39), it was realized that Frenkel excitons (see the sidebar titled Excitonic Strong Coupling) in organic materials have the advantages of larger transition strengths and

#### **EXCITONIC STRONG COUPLING**

Excitonic strong coupling has bridged the physics and chemistry communities in that it has been demonstrated for Wannier–Mott excitons, which usually comprise an electron and a hole bound to one another in a semiconducting material, and Frankel excitons, which usually comprise an electron bound to a positively charged molecule. Although the physics of the two classes of excitons differ in important ways, with Frankel excitons tending to be much smaller and more strongly bound, strong coupling has been achieved with both. Coupling to an optical field can even mix two excitons of different classes.

higher binding energies, which allow for Bose-Einstein condensation at room temperature (40, 41). Initial reports of organic exciton-polaritons were reflection studies of cavity-coupled porphyrins followed by observation of emission for J-aggregates under strong coupling (42, 43). Photoluminescence, ultrafast studies, and simulations of these types of systems have shown fast decay of the UP to the dark-state reservoir with slower population of the LP from the reservoir (44, 45). Observations of LP lifetimes longer than that of the photonic mode have triggered debate about the mechanisms of population transfer from dark states to the LP (29, 34, 46-48), which likely varies with their spectral overlap (49, 50). Furthermore, vibrational transitions play a role in facilitating relaxation from dark states to polaritons and can influence other excitonic processes as well (51-53). Numerous physical and molecular properties have been modified or predicted to be altered with strong coupling, including the work function (54), electron-phonon coupling and superconductivity (55, 56), singlet fission (57-60), novel phases such as Bose-Einstein condensates (BECs) (40, 41, 61-63), lower threshold lasing (64, 65), superfluidity (66, 67), enhanced conductivity (68–70), and long-range energy transfer (71–74). Most of these dramatic results occurred under coupling to electronic transitions, which has inspired the move toward coupling to vibrational transitions in search of similar novel phenomena and opportunities.

VSC was first observed in several instances of coupling phonon modes to the plasmonic resonances of metamaterials (75–77). More recent studies on steady-state VSC, especially as a prelude to modified ground-state chemistry, have been carried out in Fabry–Pérot cavities. The earliest of these studies, by Shalabney et al. (78) and Long & Simpkins (79), demonstrated strong coupling to carbonyl bands of polymers in first-order ( $\lambda/2$ ) cavities. Similar results for coupling to a polymer carbonyl were also reported by Muallem et al. (80). These initial demonstrations showed that coherent coupling of a high-concentration ensemble of vibrational modes provides the requisite interaction strength to achieve strong coupling at room temperature. Shalabney et al. (78) clearly recognized the opportunity to translate the ESC-modified photochemistry their group had previously discovered (7) to a different regime. Another important achievement was to extend VSC from polymer devices to neat liquids (81) in microfluidic flow cells. These experiments included coupling to carbon-carbon, cyanide, carbonyl, and azide vibrational bands of small organic liquids with splittings exceeding 100 cm<sup>-1</sup>.

These developments were critical for extending VSC to platforms compatible with exploring chemical reactions, where solution phase and flow capability are highly desirable. Our group then extended VSC from neat liquids to dissolved species by showing that solutions of  $W(CO)_6$  in hexane could achieve strong coupling (82), which eventually became the primary system to investigate transient behavior of vibration-cavity polaritons. That work also reinforced the expected squareroot scaling of the coupling with concentration (43, 83), independent of cavity length, for cavities completely filled with molecular ensembles, as previously demonstrated for ESC systems. Similar results were reported for coupling to ferrocyanide bands (84). When  $\Omega > 0.1\omega_0$ , where  $\Omega$  is the Rabi splitting and  $\omega_0$  is the uncoupled transition frequency, the system is in the ultrastrong coupling (USC) regime (85). George et al. (86) demonstrated vibrational USC in microcavities using the neat, strongly absorbing species  $Fe(CO)_5$  and  $CS_2$ , where the splitting exceeded 25% of the transition frequency and extended across several cavity modes, demonstrating very narrow resonances that possessed a strong vibrational character. Biological systems are also attractive targets for VSC, and in analogy to the ESC demonstrated for light-harvesting complexes and carotene (87, 88), VSC was reported for amide and carbonate bands of proteins and water absorption bands in enzyme-containing solutions; the latter yielded USC, modified the enzymatic activity (89, 90), and was recently investigated theoretically (91).

The collective, coherent nature of strong coupling has led to unique demonstrations of VSC to different resonances within the same molecule (78, 81), cooperative coupling to resonances supported on distinct species, and several absorption bands simultaneously resulting in the formation of multiple polariton bands (92–95). Examples include coupling to two carbonyl bands, one from dimethyl formamide trapped in polymethyl methacrylate (PMMA) and one from the polymer itself, producing three distinct polariton branches (95); using two metals in hexacyanides to couple two nearby bands (84); and, in a more complicated example, producing five vibration-cavity polaritons by coupling three aqueous organometallic complexes (92). Menghrajani et al. (94) reported strong coupling to both cavities and plasmonic gratings in which CH<sub>2</sub>, CH<sub>3</sub>, and CO bands of PMMA are all coupled to one another.

Simultaneous ESC to multiple material resonances had been previously reported for different exciton types (inorganic and organic) and spatially separated species, where the coherent coupling includes all the near-resonant species in the cavity and thereby induces interactions among all of them (74, 96–98). This delocalization leads to enhanced conductivity; opens the prospects of nonlocal, extended-range energy transfer; and has led to predictions for remote chemistry, that is, for controlling reactivity in one spatial region of a sample by modifying the optical coupling of a separate, spatially distinct region (99, 100). Measurements reinforcing the coherent nature of the coupling were carried out in our group by examining how the Rabi splitting varied for individual thin layers of absorbing material placed in different positions within a cavity (101). This method correlated the observed Rabi splitting with the first- and second-order cavity mode field profiles, and by placing several spatially separated layers of absorbing material within a cavity, it verified the delocalized nature of ensemble coupling by showing the cumulative coupling effect.

The broader understanding of how coupling depends on absorber transition strength, concentration, and spatial distribution has led to schemes for its modulation. In addition to the works above describing static systems and their spectroscopy, there have also been examples of using voltage to modulate VSC. Hertzog et al. (102) showed that external voltage could be used to mediate the orientation of the liquid crystal 5CB in a cavity to alter the coupling strength with its C-N stretching band by nearly a factor of two. Electrochemical conversion of the benzoquinone/dihydroquinone redox couple yielded nearly complete removal of the Rabi splitting through reduction of the carbonyls to hydroxyls (103). The body of work on the design, control, and spectroscopy of VSC reviewed above constitutes the foundation for VSC-modified chemical reactivity, which we review in the following section.

#### VIBRATIONAL STRONG COUPLING-MODIFIED CHEMISTRY

Exerting control over chemical processes by means of VSC is an exciting and unique opportunity, which has been described in previous reviews (12, 31, 34, 55, 104, 105). Because VSC can potentially alter the energetics or dynamics of a specific mode within a larger molecule, it may be possible not only to influence reaction rates, but also to direct bond-specific chemistry with this new tool. As described above, ESC can modify photoreactivity by providing new excitation and relaxation channels in the form of the polariton modes (7–9). Under VSC, on the other hand, modified chemistry is achieved without direct excitation. VSC has been shown to alter reaction rates (10) and to enable some degree of bond specificity in its modification of reaction processes (11). However, the operative mechanisms are not currently well understood. Here we review the most important demonstrations of VSC-modified chemistry and, in the section that follows, describe several ideas put forward to explain the experimental observations (26, 106, 107).

The most prolific group contributing to the literature on VSC-modified chemistry is led by Thomas Ebbesen at the University of Strasbourg. Their 2016 article, published in *Angewandte*  *Chemie*, represented the first demonstration of a chemical reaction rate modified under strong cavity coupling to a vibrational mode (10). In addition to being the first demonstration of VSCmodified chemistry (a ground-state deprotection of an alkynyl-silane), this work (a) presented cavity fringe tracking as a convenient method for monitoring reaction progress within a Fabry-Pérot cavity and (b) measured substantial cavity-induced modification of the enthalpy and entropy of activation based on fits to the Eyring equation. This work was followed by a more thorough examination revealing a nonlinear dependence of these parameters on coupling strength (108). We note that the changes in the extracted enthalpy of activation sometimes greatly exceed the Rabi splitting itself, but the meaning of the fits is unclear outside of the transition-state-theory framework, which may not be appropriate for the VSC environment (25, 109-111). Nevertheless, these studies represent an important attempt to understand VSC processes. Shortly thereafter, the same group published perhaps the most significant work in this field to date, which contributed additional important pieces to this puzzle (11). In the examined system, bond cleavage occurs at one of two sites, either Si-C or Si-O, with Si-C cleavage weakly favored in the absence of VSC. By cavity coupling to vibrational modes associated with either of these bonds (Si-C or Si-O), the product branching ratio was inverted and the overall reaction rate was reduced. Although there has been subsequent debate regarding the correct identification of the vibrational modes coupled (i.e., the mode at  $\sim$ 1,100 cm<sup>-1</sup> was identified as Si-O in Reference 11 but was calculated to be purely C-O in Reference 112), this was an initial demonstration of reaction site selectivity, which, when more fully developed, will become an invaluable tool in molecular design and synthesis. Secondly, a relatively complete action spectrum was created showing the dependence of reaction rate and branching ratio on the identity of the coupled mode, including spectator modes (i.e., those not directly associated with the bonds involved in the reaction). This result showed that we are not limited to coupling to modes associated with bonds being broken, and it should guide us away from simplistic descriptions invoking bond-specific hardening or softening under VSC.

These first studies stimulated the development of experimental approaches aimed at understanding when, why, and by how much VSC affects chemistry. Moving to molecules with simpler structural symmetry (mesitylene) allowed for the targeting of vibrational modes of different symmetries (113), producing the potentially revealing result that the equilibrium constant of chargetransfer complexation between mesitylene and  $I_2$  could be increased or decreased depending on whether one strongly couples to a mode with E' symmetries (i.e., doubly degenerate and symmetric with respect to reflection in a horizontal plane) or with A' symmetries (i.e., symmetric with respect to the principal axis and with respect to reflection in a horizontal plane), respectively. The absorption strength of the complex was also modified in a way that depended on the symmetry of the vibration undergoing VSC; it increased more for coupling to A' than for coupling to E' states. Subsequent examination of the role of vibrational mode symmetry revealed the preferential generation of symmetry-forbidden trans-trans butadiene products when applying VSC to C-H bending modes of cyclobutane derivatives (114). These results might provide clues to account for the large changes in reaction rates (and the correspondingly large enthalpy and entropy changes determined from transition-state analyses), even though the energetic changes associated with the Rabi splittings are relatively small (55).

This brings us to another important class of cavity-modified reactions: those that rely on strong coupling to water molecule vibrations (90). This class is distinct from the studies discussed above in that (*a*) coupling to such a common solvent mode opens up a broad variety of aqueous chemistries; (*b*) coupling to the solvent relaxes the requirement for the high reactant concentrations needed to attain strong coupling; and (*c*) water's OH stretch is tremendously inhomogeneously broadened, which positions it as a unique case for strong coupling and USC. The inhomogeneity of the hydrogen bonding environment gives the band an  $\approx$ 400 cm<sup>-1</sup> linewidth, such that the width exceeds

 $0.1\omega_0$ , where  $\omega_0$  is the transition frequency. The confusion this generates is that the system can simultaneously be in the USC regime and have a splitting that is smaller than the inhomogeneous linewidth. Perhaps it is more relevant to discuss the ratio of splitting to linewidth rather than the ratio of splitting to transition frequency in such cases. It has long been recognized that for sufficiently strong coupling, the homogeneous absorption line rather than the entire width contributes to the polariton width, which resembles a hole-burning effect for strong coupling (115). The homogeneous contribution to the linewidth of the OH stretch in water is also rather large compared to most vibrational bands (116), suggesting that careful attention should be paid to coupling conditions for this solvent. Nevertheless, strong coupling to water's OH stretch decelerates peptide hydrolysis and can influence crystallization processes, as highlighted below (90, 117). However, at this time, an entirely consistent picture has not been formed regarding the effects of strong coupling to water bands for modifying reactions rates (118, 119).

Recent demonstrations of cavity-modified kinetic behavior include fundamental synthetic operations, cooperative coupling with reactant and solvent modes, and crystallization (117, 120-122). We highlight these results for their unique contributions. The modification of Prins cyclization may represent the first step toward a cavity-enabled synthesis of small molecule building blocks, currently plagued by very low yield (120), and site-selective synthesis of otherwise inaccessible species is one of the most exciting areas of impact for VSC. The approach of cocoupling a reactant mode and a solvent mode yielded the first demonstration of an increased reaction rate and has two important general implications (121). First, as in the case of coupling to water modes, it provides a practical benefit by relaxing the requirement of high reactant concentrations to achieve strong coupling. Second, it causes us to rethink chemical kinetics and energetics, because one is able to modify the chemical activity of species A (reactant) by altering the concentration of species B (solvent) even though they may have no chemical interactions whatsoever. One might even imagine altering chemical activity in real-time by modulating cavity or system parameters (e.g., concentration or excitation level of cocoupled, but noninteracting, species B). In addition, the use of a nonoptical means of monitoring a chemical process [e.g., scanning electron microscopy (SEM) identification of the crystallization phase] inspires researchers to seek alternative means of monitoring chemical systems (117). This is particularly important given that optical interrogation can be susceptible to artifacts (119), and alternative characterization techniques should give access to new or complementary information. We summarize the published demonstrations of VSC-modified chemistry in Table 1, and we further note that the field continues to identify new examples of VSC-modified chemistry that we expect will lead to a better framework for explaining the underlying mechanisms. We now turn to a discussion of the theoretical questions and explanations proposed in the literature for the effects discussed above.

#### **OUTSTANDING ISSUES AND POSSIBLE EXPLANATIONS**

In spite of the significant progress made in the demonstration of VSC in a wide range of molecular materials and the apparent success in modifying the reaction rates in multiple instances of chemical reactions, as discussed above, the underlying mechanisms behind the modified chemical reactivity under VSC remain poorly understood (91, 109–111, 123, 124). Nevertheless, progress toward viable explanations has been made [see also the review in this volume by Li et al. (125)]. To start with, it seems intuitive that VSC would exert its effect via the light-matter polariton states. However, the molecular concentrations c required for realizing VSC in a planar microcavity correspond to an intermolecular spacing of  $\propto \sqrt[3]{c} \approx 10$  nm, which is nearly three orders of magnitude less than the wavelength of the cavity photons. Therefore, we expect  $N = 10^8 - 10^9$  molecules to be present for each cavity mode, so that, as mentioned above, the number of hybridized

#### Table 1 Summary of published VSC-modified chemistry

Scheme	Reaction	VSC-induced modification	Proposed mechanism	Reference
$ \begin{array}{c} \hline \\ \hline \\$	Deprotection of 1-phenyl-2- trimethyl- silylacetylene	5.5× rate reduction under VSC to C-Si mode	Mechanistic shift from associative to dissociated process	10
Si O TBAF MeOH/THF OH Si OH	Cleavage of tert-butyldimethyl {[4-(trimethylsilyl) but-3-yn-1-yl]oxy} silane	6× rate reduction and inversion of product ratio under VSC to Si-C, Si-O, Si-CH <sub>3</sub>	Shifting of transition state and suppression of associative mechanisms	11
H 0H H H ASP <sup>32</sup> ASP <sup>32</sup> ASP <sup>215</sup>	In-house synthesized peptide digested by pepsin	4.5× rate reduction under VSC to water's OH mode	Altered nucleophilic attachment of water to active site or changes in conformation due to solvent binding	90
$O_2N \longrightarrow O \longrightarrow O_2N \longrightarrow O^-$ SER <sup>195</sup> HIS <sup>57</sup> ASP <sup>102</sup>	Enzymatic ester hydrolysis by α-chymotrypsin	7× rate increase under cooperative VSC to water's OH and enzyme's OH and NH modes	VSC either controls charge relay processes or stabilizes the transition state	121
	Charge transfer complexation of mesitylene with iodine	4× reduction under VSC to (A') C-H stretch, bend; 2.5× increase under VSC to (E') aromatic CH stretch, ring C=C stretch	Since symmetries of reactants, transition states, and products influence kinetics, VSC must be modifying symmetries of correlation diagram	113
$H \xrightarrow{CO_2M} H \xrightarrow{CO_2M} H \xrightarrow{CO_2M} H \xrightarrow{CO_2M} H \xrightarrow{CO_2M} H \xrightarrow{H} H \xrightarrow{H} H \xrightarrow{H} H \xrightarrow{H} H \xrightarrow{H} H \xrightarrow{CO_2M} H \xrightarrow{CO_2Me} H \xrightarrow{CO_2Me}$	Modified stereo- selectivity of cyclo-butane derivative ring opening	2.5× reduction of trans-trans product under VSC to C-O; 2× enhancement under VSC to C-H; rate reduced 30%	Dipolar interactions between molecule and cavity field; variation for coaligned or misaligned configurations	114
$\begin{array}{c} \begin{array}{c} \begin{array}{c} \\ R_1 \end{array} + \\ R_2 \end{array} + \\ \begin{array}{c} \\ \\ \\ \end{array} + \\ \begin{array}{c} \\ \\ \\ \\ \\ \\ \end{array} + \\ \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{array} + \\ \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{array} + \\ \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	Prins cyclization of MeCHO propion-aldehyde, acetone, cyclo-hexanone	Reduced rate by factors of 4, 4.4, 3.5, and 5.3 under VSC to C-O groups	Increased activation energy of reaction possibly related to modified polarity of functional groups	120
$O_2 N \xrightarrow{O} O_2 V O_$	Para-nitrophenyl acetate hydrolysis	12.5× increased rate under cooperative VSC to solvent and reactant C=O	Enhanced stabilization of the transition state	121

Abbreviations: ASP, aspartic acid; EtOAc, ethyl acetate; HIS, histidine; MeOH, methanol; SER, serine; TBAF, tetra-n-butylammonium fluoride; THF, tetrahydrofuran; VSC, vibrational strong coupling.

(polariton) modes is negligible compared to the number of molecules with relevant vibrational modes in all practical cases studied to date (126). The practical consequence is that almost all vibrational modes remain essentially uncoupled (dark) and clustered at the bare transition energy, while a limited set of polariton modes shift to energies determined by molecular concentrations and transition dipole moments with typical (spectroscopically observed) Rabi splitting of up to several hundreds of wavenumbers ( $\hbar\Omega = 1-100$  meV).

Considering that the largest Rabi splitting for VSC is at best comparable to  $k_BT$  at room temperature (~200 cm<sup>-1</sup>), whereas the ratio between the number of uncoupled dark states and polaritons is very large (ln  $N \sim 20$ ), simple entropic considerations show that the static effect on the activation of chemical reactions should be negligible. That is to say, the huge disparity between the density of dark states and that of polariton states suggests the dark states dominate the system when it is at equilibrium (127). Another way of describing this conceptual mismatch is that the strong coupling is a collective phenomenon requiring contributions from all of the *N* oscillators, but chemical reactions typically concern a single reactant or set of reactants. Understanding how to connect the collective nature of the polariton modes to the localized nature of a reaction event will be critical for describing how VSC modifies reactivity.

A similar line of reasoning suggests that the LP and UP excitations should exhibit relatively quick decay to the dark states at room temperature in place of the relaxation to the bottom of the LP branch observed in some ESC scenarios, which is mostly consistent with experimental observations. Finally, note that  $\frac{\hbar\omega}{k_BT} \sim 10$  combined with  $N = 10^8 - 10^9$  implies that a large number of excitations per mode are present in the dark at room temperature (103, 104), in sharp contrast with strong coupling in most excitonic systems. Therefore, the ensemble VSC system cannot be rigorously treated using the first few excitation subspaces of the fully quantum Hamiltonian, as is often done in the literature.

In light of these considerations, how can we understand the observed modification of chemical reactivity under VSC? Although the full answer currently remains elusive, several interesting hypotheses have been put forward. First, it has been proposed that the modified reactivity has little to do with the spectroscopically observed vibrational transitions. Instead, the cavity introduces an additional potential that leads to dynamical caging of the reaction coordinates and multiple crossings and recrossings of the potential energy surface (107). In this case, the desired resonance, to the extent that it exists, is with the negative curvature near the top of the reaction barrier. Contrary to the available experimental data, this model predicts very broad spectral features and only suppression (no enhancement) of reactivity. The lack of a resonant effect also implies that any attempt to tune the cavity to target a vibrational mode of interest is doomed to failure. Very recently (128), it was reported that ab initio quantum dynamics simulations can capture the resonant effect reported in Thomas et al. (10, 11). This work, together with the considerable literature that preceded it in developing an appropriate ab initio framework for VSC (128-131), has come closest to explaining some of the most intriguing results. We note, as do Thomas and colleagues, that the validity of this explanation relies on connecting the collective nature of ensemble VSC to a strong modification of one reactant molecule.

Another ingenious line of thinking is that in some electron-transfer reactions (namely, nonadiabatic reactions in the Marcus inverted regime), the change in the activation energy can be quite large even when the energy difference between the states in question is small (123). In particular, differences in the activation energy  $E_a = (\Delta E + \hbar \omega_p + \lambda_s)^2 / \lambda_s$  for states with different  $\Delta E$ become very large for small values of the classical reorganization energy  $\lambda_s$  and can overcome the large entropy of dark states in some circumstances. A related explanation focuses on the possibility that in some reactions, the product may not fully thermalize before it undergoes the reverse transition to the reactant. Therefore, the observed reaction rate, which is typically many orders of magnitude larger, is determined largely by the ratio between the back reaction and thermalization rates (106). Then, if the excitations are transferred to polaritons (e.g., LP), the relaxation rate can be enhanced by cavity losses, thus stabilizing the product and enhancing the observed reaction rates. Note that if this effect is present, it should be observable by varying the cavity Q, with the largest impact on reactivity occurring at the edge of strong coupling. In other work (132), classical cavity molecular dynamical simulations indicate that intermolecular vibrational energy transfer can be enhanced for a few hundred molecules strongly coupled to a single cavity mode via transient excitation of polaritons. However, it is not yet clear whether an observable effect survives for  $N = 10^8 - 10^9$ , even granting that only a tiny fraction of molecules takes part in chemical reactions on the timescales involved.

Another, somewhat counterintuitive, proposal is that the light-matter interaction affects not only the polariton states but also the dark states of the system (25, 26). The dark states of inhomogeneously broadened molecular ensembles interacting with light can encompass two to three molecules, a situation termed semilocalization (133, 134). As a result, the reverse reaction rate can be suppressed by the excitation's effective spreading over multiple molecules, most of which cannot undergo the back electron transfer in the initial stages of the reaction.

The scope of these potential explanations can be made clearer by considering the following points. First of all, inhomogeneous broadening of molecular ensembles under VSC is quite common, the extreme case discussed above being the  $\approx$ 400 cm<sup>-1</sup> linewidth of the OH stretch in water (90, 91). Owing to the large ratio between the wavelength and intermolecular spacing in VSC systems, it is in fact nontrivial to ensure that the polariton density of states dominates the dark state density even at the polariton energies. To do so, the full width at half maximum of the ensemble must be approximately an order of magnitude smaller than the Rabi splitting, which is a much more stringent condition than the one for strong coupling itself. This limits the applicability of the first two mechanisms discussed above, because, should dark states dominate at the polariton energies, the polariton states themselves would be less likely to participate in the reaction pathways (126).

A second, crucial consideration is that the light-matter interaction is not an exclusive property of conventional optical cavities but is present in virtually any optical configuration (e.g., bulk, slabs, wires, droplets, etc.; 135, 136) (see the sidebar titled Bulk and Cavity Polaritons). In fact, for a sufficiently strong interaction, coinciding with the VSC regime, the properties of the optical cavity itself are unimportant, so that the Rabi splitting depends only on molecular concentration

#### **BULK AND CAVITY POLARITONS**

Cavity polaritons are formed as a result of the interaction between Fabry–Pérot modes of optical cavities and a material resonance, with no modes present below a frequency corresponding to zero in-plane wavevector. Bulk polaritons are formed as a result of the interaction between unconfined, free-space electromagnetic waves and molecular transitions, with no cutoff for the optical waves. In other words, even in a homogeneous bulk material with unconstrained optical modes, a photon with sufficiently high momentum can couple to a transition in that medium. For slab modes, formed from waveguide modes in a thin slab of a medium, the lowest  $TE_0$  mode has no cutoff, but all higher transverse electric (TE) modes and all transverse magnetic (TM) modes are cut off at some frequency. In a sense, the presence of a cavity, slab, or any optical resonator can lead to a dispersion regime where strong coupling is easier to observe, but polaritons can and do exist even in bulk media. In terms of available states, the significant difference between cavity and bulk/slab polaritons is that a cavity mode resonating at normal incidence displays an enhanced polaritonic DOS near the LP and UP.

and transition dipole moment. This suggests that the mechanism of altered reaction dynamics must involve, in some shape or form, the characteristics of the cavity-for example, a dependence of the reaction rate on cavity Q or a specific kind of cavity resonance-rather than simply those of the light-matter coupling. In our opinion, a viable theoretical explanation of cavity-modified reactivity should demonstrate qualitative or quantitative differences between the properties of cavity polaritons and those of bulk polaritons. For example, a key difference between bulk and cavity polaritons, for cavities tuned to the molecular resonance at zero in-plane wavevector ( $k_{\parallel} = 0$ ), is that bulk polaritons do not exhibit a pronounced gap in their integrated densities of states (DOS) between the vibrational resonance and UP (typical experimental values of Rabi splitting) or peaks in their DOS near the LP and UP frequencies. This behavior of bulk polaritons is exactly paralleled by cavity polaritons resonant with vibrational transitions at  $k_{\parallel} > 0$ , which perhaps hints at the reason that modified reactivity has not been observed under detuned conditions. Therefore, any explanation that relies on delocalization of dark states under VSC in optical cavities should also consider whether the same phenomenon would occur in bulk or slabs of the same molecular material. Put differently, the effects associated with dark state delocalization may well be present (25), but they may occur both in and out of the cavity and hence fail to account for the differences between the two systems. In fact, we suggest it is good practice to start any potential explanation with bulk polaritons as the baseline scenario for out-of-cavity reactivity (depending on the experimental conditions) and then consider the differential effect of the cavity.

Whereas modification of chemical reactions is by far the most exciting application of VSC, it can be useful in other contexts as well. In particular, as discussed in the next section, nonlinear absorption characteristics, which can be modulated on ultrafast timescales, may have applications in optical limiting (137, 138). In addition, the multipass nature of the cavity, often used for enhanced sensing of low-concentration species, promotes enhanced excited-state absorption and up-pumping, which have been explored experimentally (139) and theoretically (140, 141). In the following section, we review the body of literature on transient and nonlinear spectroscopy of VSC systems.

#### TIME-RESOLVED STUDIES OF VIBRATIONAL STRONG COUPLING

One route to understanding the mechanisms by which VSC modifies chemistry is to elucidate the excited-state dynamics of the vibration-polaritons, which necessitates an exploration of the ultrafast nonlinear optical behavior of VSC systems. In this section, we describe the progress toward understanding VSC dynamics and nonlinear optical processes; although the connection between these experiments and VSC-modified chemistry is thus far tenuous, there have been several key discoveries of important and useful optical phenomena.

We begin by noting that with regard to time-resolved measurements, the key difference between VSC and ESC is that photoluminescence (PL) is practically nonexistent for vibrational modes in the condensed phase, and so transient absorption and other nonlinear spectroscopies that do not rely on emission are required. The lack of PL belies a fundamental difference between the timescales involved in ESC and in VSC. Electronic transitions are typically broad, spanning hundreds to thousands of wavenumbers, with contributions to the width coming from numerous processes including vibronic transitions and electronic dephasing, whereas molecular vibrations and phonons are typically much narrower, with widths of a few wavenumbers (with some important exceptions in either direction) dominated by dephasing and nonradiative energy transfer. Considering these disparate lifetimes, one immediately recognizes that optical cavity modes with linewidths matched to vibrational modes are narrower than those with linewidths matched to excitons, and so they have lifetimes on the order of a few picoseconds compared to tens of femtoseconds seen for many ESC systems. The longer lifetime of the cavity mode leads to rich physics because, for nearly all systems, the coherent and incoherent dynamics of the vibrational mode or phonon occur on this same timescale of a few to hundreds of picoseconds. This is in stark contrast to ESC, where many systems (and perhaps the vast majority of useful ones) have excited-state population lifetimes that are orders of magnitude longer than the cavity lifetime (30, 49).

To elucidate the VSC dynamics, we and Xiong and coworkers have employed time-resolved infrared spectroscopy (TRIR) and two-dimensional infrared spectroscopy (2DIR) (142, 143). In TRIR, the simpler technique, an ultrafast infrared pump pulse, whose spectrum generally spans the UP, the LP, and the dark state reservoir absorption bands, excites the system. A second probe pulse arrives at a fixed time delay later. By comparing the transmissions of that probe pulse with and without the presence of the pump pulse, we can then determine a transient spectrum.

The vast majority of ultrafast experiments with VSC have studied  $W(CO)_6$ , an exceptionally strong absorber that has been a prototype for many ultrafast measurements in the infrared. In organic solution, the triply degenerate asymmetric stretching band appears between 1,970 and 1,985 cm<sup>-1</sup>, with a center position and width that depend on the solvent (144, 145). The transient spectroscopy of  $W(CO)_6$  in free space serves as the foundation from which we can understand the VSC dynamics. Immediately after excitation, a negative feature induced by stimulated emission and ground-state bleaching appears at the fundamental frequency. At lower frequencies, anharmonically shifted excited-state absorptions appear. After excitation, the excited states relax with solvent-dependent lifetimes ranging from tens of picoseconds to nearly one nanosecond.

The first report of TRIR of vibration-polaritons was published by our group in 2016 with a system comprising  $W(CO)_6$  in hexane in a Fabry–Pérot cavity with a high-order mode of a 25- $\mu$ m cavity resonant with the C-O stretching band (142). With this strong absorber, one can readily achieve Rabi splittings of up to 40 cm<sup>-1</sup>, well within the strong coupling regime. Early results revealed that exciting the UP, LP, and dark states simultaneously yields complex transient spectra. It is most straightforward to discuss the late-time (>100 ps delay) excited-state spectra of the polaritonic system before moving to earlier delays. **Figure 2** shows the transient spectrum of 20 mM  $W(CO)_6$  in hexane with a Rabi splitting of 34 cm<sup>-1</sup> at a series of pump-probe delay times. The



#### Figure 2

Transient absorption observed for W(CO)<sub>6</sub> in hexane in a cavity with a 25 mm spacer. The derivative-like feature in the upper polariton region (~1,995 cm<sup>-1</sup>) is due to the polariton contraction that results from reduced ground-state population. The strong positive feature at the lower polariton (~1,968 cm<sup>-1</sup>) is due to the reservoir excited-state transition ( $v = 1 \rightarrow 2$ ). Data collected under similar conditions as those described in Reference 142.

content of the spectra is identical to those we reported in 2016, but the data fidelity is higher due to multiplexed detection. Our key insight in this initial report was to understand that the multiple spectral features seen in late-time spectra can be completely described by reduced ground-state population and excitation into the dark state reservoir. When population is promoted from v =0 to v = 1, the probe pulse interrogates this nonequilibrium distribution and finds a reduced concentration of ground-state absorbers so that the polariton positions are contracted. This contraction gives rise to the derivative-like lineshape in the UP spectral region. In the LP region, the spectrum is dominated by a positive signal associated with the first excited-state absorption band ( $v = 1 \rightarrow 2$ ) in free space. We used an analytical expression for transmission through a cavity to show that this band can be reproduced with an absorber at the excited-state absorption frequency, and we further found that this response decayed with a lifetime indistinguishable from the freespace lifetime of 140 ps. We also found, to our initial surprise, that only a very small excitation fraction accounts for the signals observed. Indeed, the vast majority of the light that reaches the cavity-coupled sample is reflected from the sample.

At early times, the spectral features become more difficult to assign and there remains ambiguity about the specific processes involved in cavity-coupled W(CO)<sub>6</sub> excitation and decay. We identified a shoulder on the low-frequency side of the  $v = 1 \rightarrow 2$  band center (between 1,950 cm<sup>-1</sup> and 1,960 cm<sup>-1</sup> in **Figure 2**) and assigned it to polaritonic absorption because its lifetime appeared to depend on the detuning between the cavity and molecular modes. As we noted, however, this absorption inconveniently overlaps with the higher excited-state absorption ( $v = 2 \rightarrow 3$ ), and we now suspect that our initial assignment may have been, at least partially, incorrect. Alternate assignments will be discussed as we review the subsequent literature below. Finally, in the first few picoseconds after excitation, we directly observed Rabi oscillations—that is, coherent exchange between the UP and LP—analogous to those observed previously in excitonic strong coupling (146).

After developing a rudimentary understanding of the spectral features and their origins, we turned to evaluating saturable absorption on ultrafast timescales in cavity-coupled  $W(CO)_6$  (137, 138). For samples where the splitting is near the weak-to-strong coupling transition, absorption is strong and enough oscillators can be promoted into the excited state to completely collapse the polariton modes (i.e., entirely eliminate the Rabi splitting), resulting in a dramatic modulation of the transmission. Again, the dark state population relaxation and reorientation dynamics were indistinguishable from those of the free molecules. Furthermore, we noticed a peculiar effect: The Rabi splitting measured by the pump pulse itself was measurably reduced. We immediately realized that the intense pump pulse could saturate the molecular absorbers. Under the lowest concentrations (i.e., weakest coupling conditions), the saturation fluence of the system was identical to that measured in free space. At higher concentrations (i.e., stronger coupling), however, the saturation fluence increased to a much larger degree than we could account for with classical calculations. This demonstrated that cavity coupling provides a unique handle to tune the saturation fluence, a typically intrinsic property of an absorber. It is clear that cavity-coupled absorbers may provide a platform for the design of tunable ultrafast optical modulators, but further work is needed to fully understand how the saturation fluence depends on system characteristics and the limits to which the fluence can be controlled.

Yuen-Zhou, Xiong, and coworkers collaborated with us to conduct the first 2DIR experiments on a VSC system (143). Instead of a single excitation pulse, the sample was excited with two excitation pulses separated by a variable time delay. These two pulses generated coherences and populations in the sample that were then interrogated by a third probe pulse. As the first and second pump pulses generated and then modulated coherences via multiple excitation pathways, the probe spectrum oscillated with respect to the delay between the pump pulses. Performing a Fourier transform on the time-dependent probe signal produced a two-dimensional spectrum



#### Figure 3

Two-dimensional infrared spectrum of W(CO)<sub>6</sub>/cavity-polariton system with a 25 ps delay (waiting time) between the pair of pump pulses and the probe pulse. Each region is individually intensity scaled, and spectra of the pump ( $\omega_1$ ) and probe ( $\omega_3$ ) pulses are shown on their respective axes. Red is positive and blue is negative. An important result is evident in panels *b* and *e*, which show that there is excitation of the reservoir at the uncoupled, bare frequency transition in addition to via the polaritons. Abbreviations: LP, lower polariton; UP, upper polariton. Figure adapted from Reference 143.

that dispersed the probe response along a pump frequency axis. The 2DIR spectrum is, in effect, a map of which excitation frequencies produce which responses in the sample.

Again we turn to  $W(CO)_6$  in hexane placed in a Fabry–Pérot cavity. **Figure 3** reproduces one of the first 2DIR spectra of said system, where we observed a complex spectrum replete with both diagonal and off-diagonal features. Strong coupling makes the conventional distinction between diagonal and cross peaks less informative in VSC systems (147). As expected, strong features appeared when either the LP or UP was excited. Cuts along the probe axis at either the UP or LP largely agreed with the pump-probe spectra we reported in 2016 (142). What we did not expect was the similar response that appeared when the excitation frequency was between the two polaritons, where the cavity does not transmit. The cavity does not transmit at the uncoupled absorber frequency, but neither does it perfectly reflect. There was appreciable absorption at the uncoupled frequency for the Rabi splitting employed in this experiment. To our disappointment, the low-frequency feature that we assigned to UP excited-state absorption in 2016 appeared when the LP rather than the UP was excited, further confusing the issue of its assignment. Aside from this feature, the vast majority of the response after the first few picoseconds is adequately described both by the analytical method used in our first report and by a quantum-mechanical model employed by Yuen-Zhou and coworkers in the first 2DIR work (148).

The next reports on cavity-coupled  $W(CO)_6$  focused on untangling which parts of the complex responses are truly a consequence of strong coupling and how parameters of system design influence those responses. In another collaborative effort led by Xiang et al. (149), we reported a detailed study of the Rabi oscillations at early time delays. A careful analysis revealed a polariton bleach, that is, a strong reduction in the overall cavity transmission that oscillates at the Rabi frequency. We demonstrated that the intensity of this effect increases with shorter cavities and weaker coupling [i.e., lower concentration of  $W(CO)_6$ ]. Using spectrally filtered excitation, Xiong and coworkers later showed convincingly that the oscillatory polariton bleach requires excitation pathways that include both UP and LP photons and the generation of a UP-LP coherence (150). This strong, tailorable nonlinear effect decays with the dephasing rate of the coupled system.

Despite the recognized importance of molecular linewidth, which influences excitation, determines strong coupling conditions, and defines molecular dephasing, this parameter has been the main subject of relatively few works. One such study examined how the solvent's effect on the lineshape of the CO absorption band of  $W(CO)_6$  influenced the cavity-coupled dynamics (139). It was found that, in solvents with a broader absorption band, the shorter-lived low-energy feature, which had thus far evaded reliable assignment, did not appear. In solvents with a narrow absorption (i.e., hexane and pentane), Xiang et al. (139) demonstrated convincingly that at least a large part of that response is due to the higher-lying excited-state absorption of the reservoir. The decay rate of this feature, however, appeared to be significantly faster than the v = 2 relaxation in free space, which was attributed to the presence of an accepting mode unique to the cavitycoupled system. We note here that the enhanced absorption into higher-lying excited states has recently been attributed to excitation through the lower polariton by a few important theoretical works (140, 141). In this way, the cavity coupling may offer a route to selective excitation of highly vibrationally excited molecules.

Our most recent work has sought to better assign the early-time transient features apparent in polaritonic systems by moving to a new molecular system, nitroprusside [Fe(CN)<sub>5</sub>NO<sup>2-</sup>] in methanol (147). Nitroprusside is, in many ways, similar to  $W(CO)_6$ . It has an octahedral geometry with six ligands, but five ligands are cyano groups and the sixth is a nitrosyl, which is the band that is strongly coupled in Grafton et al.'s (147) work. We used both 2DIR (Figure 4) and pump-probe studies with filtered pulses to definitively identify the polaritonic spectral features. The approach involved subtracting the response due only to the ground-state population changes and the reservoir excited-state absorption from the pump-probe spectra in order to isolate the polariton excited-state feature. In collaboration with Hernández & Herrera (151), we were able to assign these transitions to rungs in the polaritonic ladder-for example, a spectrally isolated UP-to-2UP transition-based on their multilevel quantum model. However, differences between single-molecule and ensemble predictions in this case deserve further study. We found that these polaritonic transitions persisted for far longer ( $\sim 8$  ps) than the  $\sim 2$  ps dephasing time of the system, representing incoherent population in the polariton modes. We plan to further investigate the differences between hexacarbonyl and nitroprusside that precluded our observation of these features in the former.

We end this section with the two most exciting works in VSC dynamics, both demonstrating nonlocal energy transfer in cavity-coupled systems. In the first report, Xiong and coworkers synthesized <sup>13</sup>C-substituted W(CO)<sub>6</sub>, whose absorption frequency is redshifted by about 40 cm<sup>-1</sup>, and coupled a mixture of the <sup>13</sup>C and <sup>12</sup>C isotopologues to the same Fabry–Pérot cavity mode (152). They found that exciting the UP, which is primarily <sup>12</sup>C in character, leads to efficient population of the <sup>13</sup>C reservoir in a matter of picoseconds. This is a clear demonstration that the polaritons are delocalized among many molecules and that this delocalization is not restricted to ensembles of the same species. In the second report, the same group fabricated a multimode cavity



#### Figure 4

Two-dimensional infrared spectra of the NO stretching band of nitroprusside in methanol strongly coupled to a 25- $\mu$ m-long Fabry– Pérot cavity measured at (*a*) 1 ps, (*b*) 10 ps, and (*c*) 50 ps waiting times. Pump frequency slices in the 2DIR spectra (*a*-*c*) are shown for the UP (blue), reservoir (black), and LP (red) frequencies in panels *d*-*f*. The signal at long time (50 ps; see panel *f*) is the same for all the slices and represents the response due only to the polariton contraction and uncoupled excited-state absorption. Abbreviations: 2DIR, two-dimensional infrared spectroscopy; LP, lower polaritor; UP, upper polariton. Figure adapted from Reference 147 (CC BY 4.0).

with two main resonances separated both in frequency and spatially. By coupling both modes to the same ensemble of  $W(CO)_6$  absorbers, the researchers again demonstrated delocalization, this time between the two disparate cavity modes (153). This delocalization has significant potential for applications, like optical interconnects, made possible by the cooperation of molecular absorbers and optical modes.

In our view, the existing literature on the time-resolved spectroscopy of VSC leads to two main conclusions. First, the transient spectroscopy of cavity-coupled systems is complex but there exist clear signatures of polaritonic excited states and coherences to be extracted with the proper framework for analysis. The field has not yet reached a consensus on the identity of these transitions, but we hope that further studies, especially collaborations between theoretical and experimental efforts, will help to show how the presence of the manifold of polariton states modifies chemical reactivity. Second, Xiong and coworkers have clearly shown that, just as in ESC, strong coupling creates unprecedented delocalization among ensembles of vibrational absorbers (152). It remains to be established if and how this delocalization affects VSC-modified chemistry.

#### **CONCLUDING REMARKS**

We have reviewed the existing literature on VSC, broadly dividing the work in the past decade into steady-state spectroscopy, VSC-modified chemistry with its proposed explanations, and nonlinear and time-resolved spectroscopy. In our view, the results from this new field are incredibly exciting, and we expect they will lead to significant changes in how we, as chemists and physicists, understand and control molecular properties and reactivity. The field is ripe with new opportunities for VSC research. These avenues include coupling to gas-phase species, which offers the opportunity to investigate polariton effects on energy transfer and reactivity with a state specificity that is typically impossible in the condensed phase. Gas-phase VSC also exhibits the unique property that the strong coupling criterion becomes an intrinsic property of the molecule, demanding only that the extinction coefficient (peak intensity) exceed the pressure broadening rate (104). Vibration-polariton condensates are another exciting direction that might offer unique potential for realizing infrared lasing or might provide an altogether new platform for chemistry (154). We and others have just begun to explore the nonlinear optical response of VSC systems, and we may now be ready to employ them in ultrafast modulators or to utilize their tailored optical response to renew the pursuit of mode-specific chemistry by improving the selective yield of higher excited-state populations through nonlinear up-pumping. Lastly, the properties of vibrational bands (infrared regime operation, long radiative lifetimes, and narrow linewidths at room temperature) might make vibration-polaritons good candidates for quantum science and quantum sensing applications.

#### **DISCLOSURE STATEMENT**

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