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I. INTRODUCTION

When ensembles of chromophores are embedded in sufficiently confined photonic environments, the electromagnetic modes strongly couple with delocalized superpositions of molecular transitions, giving rise to hybrid light–matter states known as (upper and lower) polaritons[1] (UP, LP; see Fig. 1) as well as (in many cases, a large number of) dark modes. Polaritons can alter the bare molecular energy landscapes and are therefore expected to influence physicochemical properties as well as a class of thermal or photo-initiated molecular processes including chemical reactions. In the last few years, efforts to understand these phenomena have created much momentum in the emergent field of "Polariton Chemistry," where the hopes are that strong light–matter coupling (hereafter, referred to simply as "strong coupling") will provide a simple and robust alternative to costly synthetic modifications for altering material properties and processes. We are honored to serve as guest editors in this special issue devoted to this fascinating topic.

The hybridization of light and material excitations in crystalline solids outside of cavities is not new and, in fact, has been long known since the seminal works of Tolpygo[2] and Huang[3] on phonon-polaritons and Agranovich[4] and Hopfield[5] on exciton-polaritons in the 1950s. It was, however, until 1992, when Weisbuch *et al.*[6] demonstrated that these strong coupling phenomena in inorganic semiconductors could be significantly enhanced with optical microcavities. A few years later, Lidzey *et al.*[7] reported the same feat with excitons in disordered organic films. Much attention in the polaritonics community initially focused on condensation of polaritons;[8,9] but, in the last decade, an effort spearheaded as the Ebbesen group in Strasbourg has demonstrated that polariton formation may lead to modified chemical kinetics and thermodynamics.[10] Ebbesen and others have reported polariton-induced changes in photoisomerization yields,[11] selectivity of thermal organic reactions,[12–14] and optoelectronic properties of molecular films[15] and solutions.[16,17] These promising results have prompted a large number of theoretical and experimental research groups to understand the mechanisms and strategies of polariton chemistry, with a sizable sample of them showcased in the present issue. This special issue aims to catalyze discussions on the underlying mechanisms of polariton chemistry and to explore new frontiers for enhancing chemical modification through strong coupling.

One of the appeals of polariton chemistry is that it provides a versatile microscopic control knob that could substitute for more costly synthetic modifications.[18] Furthermore, it resuscitates dreams of mode-selective chemistry[19] but with a resonant cavity instead of with intense laser pulses. This special issue reflects the breath and excitement of this emergent Chemical Physics research topic at the crossroads of photonics and materials science.

II. BACKGROUND

Figure 1 shows a simplified picture that captures the essential physics of molecular polariton formation. An optical cavity mode interacts dipolarly with N molecular transitions, with coupling amplitude g per transition. At light–matter resonance, two polariton modes are formed (upper and lower polaritons, UP and LP, respectively) separated in energy by a Rabi splitting $\Omega = 2\sqrt{N}g$, with $N-1$ dark modes remaining parked at the same energy as the original molecular transitions and devoid of the photonic component. When g is large compared to the molecular and photonic linewidths, as in plasmonic nano- and picocavities, N can be on the order of a dozen or even a single-molecule.[20–23] However, the much more ubiquitous case is when g is a negligible quantity compared to the aforementioned linewidths, as in UV–visible and infrared optical

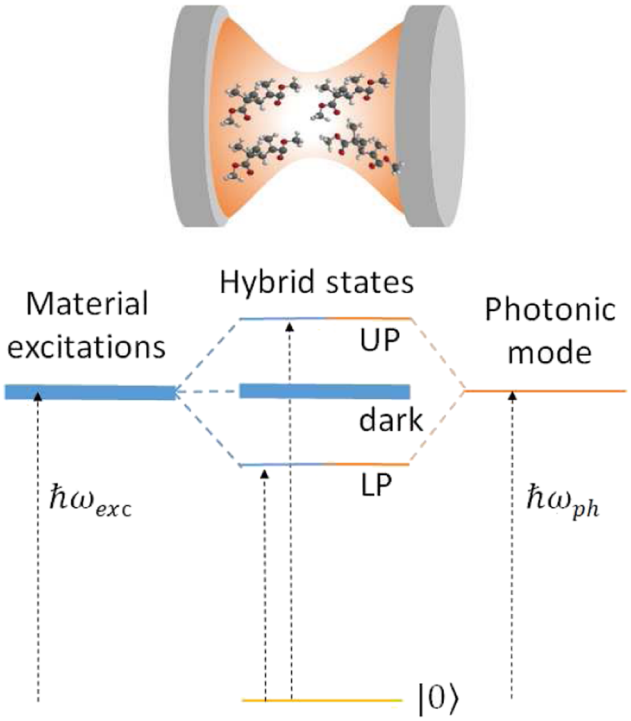

FIG. 1. The strong coupling between resonant molecular transitions and photonic modes in a microcavity gives rise to hybrid light–matter states called upper and lower polaritons (UP, LP), with chemical dynamics distinct from those of their uncoupled molecular counterparts. Adapted from Ref. 1.

microcavities, in which case, the strong coupling is *collective*, involving a large number $N \approx 10^6 - 10^{12}$ of molecules, and, thus, also a large number of dark modes.[24,25]

Given that dark modes do not show up in linear spectroscopy, one might assume they have a perfunctory role in polariton chemistry and, thus, conclude that single-molecule coupling and collective strong coupling are essentially the same phenomenon. However, in the condensed phase, dissipative processes connecting polariton and dark states make them essential to properly understand the chemical dynamics afforded by these systems.[26] For instance, an elementary Boltzmann statistics calculation indicates that if we want most of the population to be in LP rather than the dark modes, then the temperature T must be lower than a critical temperature, $T < T_c = \frac{\Omega}{2k_B \ln(N-1)}$, where k_B is Boltzmann's constant. Taking a typical UV–visible Rabi splitting of $\Omega = 0.1$ eV and $N = 10^6$, we find that $T_c = 42$ K, a temperature that is even lower than the gas–liquid nitrogen transition. Thus, upon excited-state population thermalization, the majority of the population is allocated in the dark modes under collective strong coupling conditions, a situation that drastically differs for the single-molecule case.

III. SUMMARY OF AREAS COVERED

As a steppingstone into studies of the strong-coupling regime, this special issue features a number of important studies in the much better understood weak light–matter coupling regime, but placing much attention to modification of molecular structure and properties. Kumar *et al.*[27] report a plasmonic Purcell effect on the photoluminescence of a germanium defect in diamond, a topic that is relevant to the on-demand generation of single photons using solid-state architectures. Haugland *et al.*[28] inquire whether intermolecular forces can be affected by an optical cavity; they provide theoretical evidence that this can indeed be the case and that the effects can be understood as stemming from off-resonant electron–photon correlations. Furthermore, Fiedler *et al.*[29] provide a formalism for the simplified calculation of van der Waals interactions C_6 coefficients in the presence of a realistic off-resonant dielectric environment.

Yet most of the research addressed in the present volume concerns single-molecule and collective-strong coupling. Historically, quantum chemistry and dynamics *ab initio* calculations are carried out considering one molecule at a time, so it is understandable that much progress of the theoretical activity has been carried out in the single-molecule realm. Yet contrary to theory, most molecular strong-coupling experiments are carried out in the collective regime owing to the much simpler procedures involved in microfabrication rather than nanofabrication. In particular, the aforementioned experiments reporting changes in ground-state chemical reactivity upon strong coupling are carried out in the collective regime (vibropolaritonic chemistry),[12–14] and they still remain a puzzle from a theoretical standpoint: While simulation results based on a single-molecule strong coupling regime routinely demonstrate that polaritons can modify chemistry in evident ways, standard theories in the collective regime are incapable yet of explaining these modifications,[30–33] and more advanced theoretical investigations are currently being pursued along this front. Thus, one of the greatest challenges in this new field of research is to converge theory and experiment along the single-molecule and collective regimes.

In Subsections III A and III B, we summarize the content of this special issue in terms of the two types of strong coupling. For the single-molecule strong-coupling regime, we showcase one scanning tunneling microscope (STM) experiment and a large number of theoretical studies concerning cavity-modified nonadiabatic dynamics and electronic structure as well as a theoretical proposal of strong-coupling mediated quantum information processing architectures. For the collective strong-coupling regime, we feature a more balanced experimental and theoretical focus and we showcase an article reporting on the fabrication of a polariton mediated photodiode, a series of classical electromagnetic (EM) and EM-quantum mechanics (EM-QM) studies modeling polaritonic systems, theoretical and experimental works concerning the nonadiabatic dynamics in the regime (pertaining the role of dark modes), our current understanding of vibropolaritonic chemistry, and the spectroscopy, ultrafast dynamics, and new photonic structures to realize vibrational polaritons.

A. Single (and few)-molecule regime

1. STM experiments

Reflecting the inherent difficulty of realizing single-molecule strong-coupling experiments, our issue contains only one experimental report in this regime, an STM induced luminescence experiment, where Luo *et al.*[34] demonstrate that the evolution of the Fano lineshapes due to the coupling of a molecular transition to the

plasmonic modes of the STM can be a sensitive probe of the isomerization dynamics of the nanoenvironment at the vicinity. More experiments in the single-molecule regime are certainly welcome in the future to realize the predictions from the theoretical studies discussed in the next paragraph.

2. Nonadiabatic dynamics

As opposed to its experimental counterpart, our issue contains a wealth of theoretical studies in this regime, most of them describing how consideration of photonic degrees of freedom on top of the electronic and nuclear ones enriches the zoo of nonadiabatic phenomena in many ways. A number of articles are concerned with the characterization of light-induced conical intersections (LICIs) due to strong coupling. For instance, Szidarovszky *et al.*[35] explore the novel nonadiabatic phenomena involving two identical or isotopomer molecules of HCl molecules interacting with a single IR cavity mode, taking into account that the high-frequency vibrational modes are coupled to lower frequency rotational transitions. Fabri *et al.*[36] carry out the first full-dimensional simulation of the photoinduced dynamics of formaldehyde with its six vibrational modes in the presence of an optical cavity and concludes that previous reduced-dimensionality studies are not able to capture most of its rich physics, prompting caution about reduced dimensional studies. Triana and Sanz-Vicario[37] study the dynamics afforded by electronic strong coupling of polar diatomic molecules to an optical cavity and discuss the conditions under which the photoinduced dynamics is comparable to the case outside on an optical cavity; they thoroughly examine the importance of Hamiltonian terms that are often neglected in the theoretical description of these systems, namely, the permanent dipole moment and self-energy. Reitz and Genes[38] provide a toy model studying the Floquet driving of molecular vibrations and its effect on electronic transitions, demonstrating how Purcell enhancement of vibrational emission can lead to exquisite control of vibrational relaxation dynamics and concomitant changes in electronic dynamics.

Other works extend powerful quantum dynamics methodologies to account for strong coupling. As an example, Martínez *et al.*[39] revisit the formalism of time-dependent potential energy surfaces within the context of polaritonic systems to examine the intricate correlations appearing in the proton-coupled electron-transfer (PCET) dynamics of coupled electrons, nuclei, and UV–visible photons. Chowdury *et al.*[40] extend the capabilities of nonadiabatic ring-polymer molecular dynamics (RPMD) to account for photons as additional degrees of freedom to the molecular ones.

Yet another group of theoretical articles are concerned with a more accurate description of single-molecule strong coupling phenomena involving the important effects of photon or plasmon losses. Wang *et al.*[41] extend the formalism of quantum electrodynamics density-functional theory (QED-DFT) to account for dissipative processes such as cavity leakage. Torres-Sánchez and Feist[42] harness the inherent loss of plasmonic nanoparticles to induce new avenues for energy management that lead to ultrafast photodissociation of molecules, thus highlighting the virtue (rather than the burden) of plasmonic dissipation. Similarly, Davidsson and Kowalewski[43] study the effects of plasmonic dissipation of molecular dynamics and conclude that the optimal conditions to suppress a photodissociation occur at coupling strengths that are barely in the strong coupling regime, thus implying an important interplay between strong coupling and cavity cooling.

3. Electronic structure

While all the highlighted work in this section concerns nuclear dynamics, DePrince[44] explores the extent to which a cavity affects the electronic structure alone; he does so by developing a QED coupled cluster theory to compute ionization potentials and electron affinities of molecules in cavities and concludes that the latter can be substantially modified, while the former is modified to a lesser extent.

4. Quantum information processing

Finally, we also mention the interesting work of Zheng *et al.*,[45] which designs a coherent control scheme to induce Landau–Zener transitions in a robust quantum-information processing architecture consisting of coupled qubits in optical resonators.

B. Collective strong coupling

In this regime, we note a more balanced experimental–theoretical emphasis in the featured works.

1. Device applications

From an optoelectronic device viewpoint, Mischok *et al.*[46] experimentally demonstrate the fabrication of spectrally tunable photodiodes based on strong coupling of single-walled carbon nanotubes and optical microcavities. Strong coupling creates lower polariton states that are in the near-infrared beyond the band edge of silicon; absorption into the lower polariton band generates substantial photocurrent across the P3HT-PC70BM interface of the diode.

2. Classical electromagnetics

A number of articles in this special issue concern classical electromagnetic simulations or semiclassical couple-mode theories that aim to connect with experiment. Georgiou *et al.*[47] experimentally and computationally demonstrate the tunability of multimode microcavity photon-mode coupling/decoupling via J-aggregate transitions. Such tunability is obtained by varying the oscillator strengths of the dyes in the aggregate. The authors show that at a high concentration of the dyes, photon-mode decoupling occurs—adjacent cavity modes do not couple to the same set of dye molecules; instead, each mode couples to different dye subsets. Tan *et al.*[48] use transfer-matrix simulations to study the strong coupling of surface plasmons and molecular excitons and show that for low exciton oscillator strengths, regular anticrossing ensues, but for large enough ones, additional resonances emerge involving exciton surface modes, consistent with experiments. Bai *et al.*[49] deploy an evolutionary optimization algorithm to design the structure of a surface lattice plasmon array that can couple to poly(3-hexylthiophene-2,5-diyl) (P3HT) transitions with a large Rabi splitting; they successfully realize their experimental design.

From a theoretical standpoint, Canales *et al.*[50] demonstrate that polariton formation occurs naturally in a variety of bulk or droplet materials that exhibit properly confined optical modes which strongly mix with their own material excitations, obviating the need of an optical microcavity; this work places the mentioned seminal 1950s works (before use of optical cavities) in a broader context,

demonstrating that polaritons occur in a wider range of materials than previously expected. Using coupled oscillator models, Hu *et al.*[51] provide a unified approach to model scattering, absorption, and luminescence spectra of strongly coupled molecule–plasmon systems; they calculate the coupling parameters required to obtain the maximum photoluminescence, which requires a balance of strong brightness and short lifetime.

3. Classical electromagnetics and quantum mechanical modeling

Yet another set of theoretical works provide a powerful formalism that simultaneously accounts for an accurate description of strong coupling of complex and dissipative electromagnetic media (such as plasmonic nanoparticles and arrays) with quantum mechanical degrees of freedom of molecules. In this regard, Fojt *et al.*[52] present a computational method to efficiently model the optical spectra of nanoparticle–molecule assemblies and show that a judicious choice of subsystems affords a subsequent coupling between them that only requires accounting of the dipolar interactions alone. Varguet *et al.*[53] develop a macroscopic QED approach to accurately model strongly coupled plasmon–exciton systems and demonstrate that, due to the inhomogeneity of the plasmonic fields, the collective coupling afforded by these systems can drastically differ from the homogeneous limit of $\sqrt{N}g$, where g is the single-molecule coupling and N is the number of emitters. Their quantum formalism also provides a proper way to compute collective Lamb shifts. In terms of new phenomenology, Sukharev *et al.*[54] present strategies to enhance second-harmonic generation by creating gain in a collection of emitters that are coupled to a resonant square lattice of silver nanopillars.

4. Nonadiabatic dynamics

Generalizing the single-molecule strong-coupling studies, several works explore the effects of vibronic coupling under collective strong coupling conditions, where dark mode populations play a central role. In a joint experiment–theory collaboration, Hulkko *et al.*[55] examine the mechanisms of photoluminescence of molecular polaritons. Upon excitation of polaritons, an ultrafast decay to dark modes ensues. If the excitonic transitions have a significant Stokes shift (such as Rhodamine 6G), the emission transition becomes out of resonance with the cavity, but enters resonance with the lower polariton, upon photoluminescence ensues (radiative pumping). If the excitonic transitions do not have a significant Stokes shift (such as J-aggregates), vibrational relaxation promotes population from dark states to the lower polariton (vibrational assisted scattering). In a related study, Tichauer *et al.*[56] study the effects of a multimode cavity dispersion in the ultrafast dynamics of polaritons. They use atomistic simulations to demonstrate ultrafast relaxation from polaritons into dark modes, but much slower relaxation from the latter back into polaritons upon which photoluminescence ensues, in agreement with experiments. Using zinc–porphyrin microcavities, Avramenko and Rury[57] experimentally demonstrate that the ultrafast dynamics of polaritons in the electronic regime defy the simple characterization that simplified theories provide. Specifically, they show that interpolaritonic exchange of population occurs in an ultrafast timescale and that the internal conversion between electronic states that are not coupled to the cavity is affected by it. Kansanen *et al.*[58] develop a theory to study the linear optical response of a molecular polariton system in the presence of Brownian dissipation which represents the condensed phase environment. Ulusoy *et al.*[59] carry out computational simulations of ensembles of molecules in a cavity to study the role of nuclear dynamics in the preservation of superradiant emission. They demonstrate that this superradiance can expectedly deteriorate with system size, but may also surprisingly revive after passage through conical intersections. Wellnitz *et al.*[60] develop an open-quantum systems approach to theoretically study photoinduced electron transfer in optical cavities in the presence of material and photonic dissipation, and demonstrate that, contrary to previous expectations, the strongest effects occur under weak light–matter coupling.

5. Vibropolaritonic chemistry

In vibropolaritonic chemistry, collective vibrational strong-coupling of infrared cavities to high-frequency molecular vibrations leads to modifications of ground-state chemical kinetics in the absence of optical pumping;[12–14] this phenomenon is still poorly understood. In a benchmark experimental study, Imperatore *et al.*[61] caution that strong coupling of OH modes of water to an infrared cavity does not provide any substantial catalysis on cyanate ion hydrolysis, contrary to previous claims in the literature.[62] Using a Marcus–Levich–Jortner mode, Du *et al.*[63] demonstrate that cavity leakage and vibrational dissipation can indeed affect reactions under vibrational strong coupling, but these effects only remain for a small number of molecules per photon mode, becoming irrelevant in the collective strong-coupling regime.

6. Spectroscopy, ultrafast dynamics, and new photonic structures of vibrational polaritons

Xiang and Xiong[64] present a broad overview of vibrational polaritonics, namely, the strong coupling of infrared optical microcavities with ensembles of localized high-frequency vibrational modes in molecules. They summarize their experimental findings which include the observation of ultrafast dynamics involving polariton and dark modes as well as the demonstration of intermolecular energy transfer which do not exist in the absence of a cavity, thus opening doors for new avenues to control vibrational energy in the condensed phase. Brawley *et al.*[65] provide a new photonic architecture to realize vibrational strong coupling using plasmonic substrates that feature smaller mode volumes than Fabry–Pérot resonators. They demonstrate this for strong coupling with CO vibrations in thin films of PMMA as well as with asymmetric vibrational modes in copper sulfate monohydrate. Finally, carrying out classical molecular dynamics simulations in liquid CO_2, Li *et al.*[66] demonstrate that polariton resonances can provide efficient new channels for multiphoton absorption (vibrational ladder climbing) which can circumvent the ultrafast decay to first-excitation-manifold dark modes, consistent with other experimental[67] and theoretical works in the literature.[68]

IV. CONCLUSIONS

The works presented in this special issue demonstrate the vitality of current research in polariton chemistry. Strong coupling of confined electromagnetic modes to molecular degrees of freedom promises a new paradigm to control physicochemical properties and processes in room-temperature condensed-phase molecular systems

that, if understood properly, could supersede certain procedures in chemical synthesis. However, the field is at its infancy, with many puzzles that remain to be solved. Strong coupling leads to rich phenomenology that requires novel experimental and theoretical tools centered in Chemical Physics, but liberally borrowed also from the fields of photonics and materials science. Common themes of the works presented in this issue include the study of novel correlations involving electronic, nuclear, and photonic degrees of freedom; the accurate characterization of complex electromagnetic environments and quantum mechanical degrees of freedom; the essential role of photonic (and plasmonic) and molecular dissipation; the drastic differences of single vs collective strong coupling regimes; and the challenges to connect experimental results in the field with tractable theoretical tools. We hope that this issue provides the reader with a broad perspective of a field that still has much to offer from a fundamental and practical standpoint.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors declare no conflict of interest in this article.

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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