COMMENTARY

Polariton chemistry: Thinking inside the (photon) box

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The study of single quantum objects embedded in confined electromagnetic environments is the main focus of the field of cavity quantum electrodynamics (CQED). According to a recent historical account by the 2012 Nobel laureate Sergei Haroche (1), the origins of this field can be traced back to the early days of quantum mechanics, with the famous debate between Albert Einstein and Niels Bohr concerning a gedankenexperiment about a photon in a box. While Einstein invoked the photon in a box as a theoretical construct, he might not have imagined that such a concept would reincarnate decades later into one of the favorite experimental playgrounds for scientists to test, explore, and control quantum mechanics. In fact, atoms in optical cavities have become one of the quintessential building blocks of contemporary quantum technologies, giving rise to high-fidelity sources of single photons, platforms to recreate effective photon–photon interactions, or even quantum simulators of many-particle systems. In recent years, an interdisciplinary outlook at the crossroads of CQED and chemistry termed "polariton chemistry" (2, 3) has emerged, which is centered around the question: Can materials change their chemical properties merely by being immersed in an optical cavity? Far-reaching consequences could follow if the answer to this question is positive, as one could potentially bypass time-consuming synthetic modifications of materials by harnessing CQED effects as an alternative. Indeed, much experimental (4–6) and theoretical evidence (7–9) points toward the fact that under certain circumstances, modifications to photochemical and ground-state kinetics, energy transfer, and charge transport are possible with the use of optical cavities. In PNAS, Schäfer et al. (10) present compelling theoretical and computational evidence in support of these statements. Schäfer et al. perform a study of a minimalistic quantum mechanical model which demonstrates that molecular excitation energy and charge-transfer processes can be nontrivially modified upon strong coupling of a molecular dimer with an optical-cavity mode.

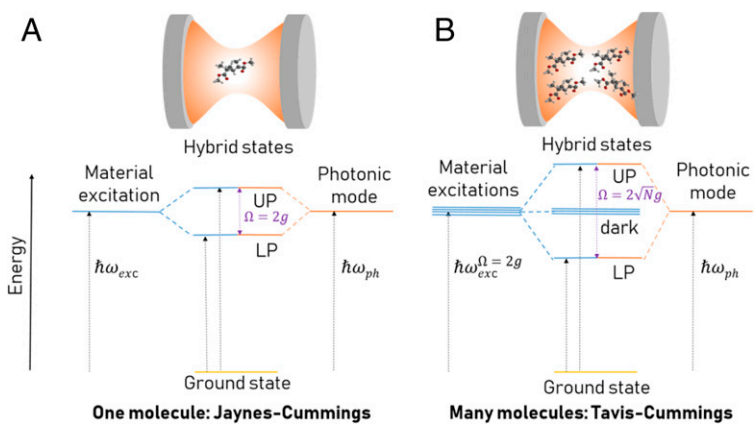

Fig. 1. (*A* and *B*) The various flavors of molecular strong coupling with a single molecule (*A*) and with $N > 1$ molecules (*B*). The energy spectrum is given by the JC model (*A*) and the TC model (*B*). At light–matter resonance ($\hbar\omega_{ph} = \hbar\omega_{exc}$), the UP and LP are half-light–half-matter states separated by a Rabi splitting Ω, which is twice the single-molecule light–matter coupling g for *A*, and twice the collective coupling $\sqrt{N}g$ for *B*. The superradiant enhancement of the coupling in *B* comes at the price of having $N-1$ dark states parked at the material excitation energy. $N > 10^7$ is a macroscopic number in typical experiments and serves as a very efficient relaxation trap for both UP and LP.

When the coupling between photon $|ph\rangle$ and a material (two-level system) excitation $|exc\rangle$ is stronger than the individual decay rates ($g \gg \Gamma, \kappa$, where Γ and κ are material and cavity linewidths), a proper description of the composite light–matter system relies on the Jaynes–Cummings (JC) model, which predicts that the eigenstates of the coupled system are polaritons, coherent superpositions of light and matter states. Fig. 1*A* shows that the lowest-energy eigenstates of the JC model at light–matter resonance (the excitation frequencies are equal, $\omega_{ph} = \omega_{exc}$) are the lower polariton (LP) and upper polariton (UP) $|\mp\rangle = \frac{1}{\sqrt{2}}(|exc\rangle \pm |ph\rangle)$, which are symmetric and antisymmetric combinations of the individual excitations and have eigenfrequencies of $\hbar\omega_{\mp} = \hbar\omega_{exc} \mp g$, where $g = -\sqrt{\frac{\hbar\omega_{ph}}{2\epsilon_0 V}}\mu$ is given by the projection of the single-photon electric field ($\hbar$ is the reduced Planck's constant, ϵ_0 is the permittivity of

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vacuum, and V is the cavity mode volume) on the transition dipole μ of the material; the energy difference $\Omega = 2g$ between UP and LP is known as the Rabi splitting. The symmetries of these polaritons are reminiscent to those of the bonding and antibonding orbitals for the hydrogen molecule.

At first glance, the marriage of CQED with chemistry seems at odds with the precepts of quantum optics, which emphasize pristine and highly controllable physical systems. However, if we are willing to harness the toolkit of optical cavities while embracing the complexity of chemical systems, we might open doors to a new generation of molecular materials whose catalytic or optoelectronic properties could be switched on demand for synthesis, spectroscopy, and sensing applications. Specifically in the context of strong light–matter coupling, the hybridization between light and matter allows one to exploit the best of both worlds to alter physicochemical properties of the molecular systems. Given the infancy of polariton chemistry, it is fundamental to develop simple and tractable theoretical models that provide intuition and guidance into understanding experimental phenomenology, as well as to develop fruitful experimental strategies. Schäfer et al. (10) explore one of the simplest ab initio quantum-chemical models that can be constructed for polariton chemistry: a one-dimensional electronic Hamiltonian comprising two-electrons that interact via soft Coulomb potentials between themselves and with two clamped nuclei and, at the same time, couple to a single photon mode. This model serves as a minimal description of a donor–acceptor chromophore pair which, upon photoexcitation of the donor, transfers energy to the acceptor via a virtual longitudinal photon (Förster mechanism) or an electron (Dexter mechanism) exchange; the effects of strong light–matter coupling (measured in terms of g/ω_{ph}) on these chemical processes are analyzed by characterizing the eigenstates of the Hamiltonian as well as the corresponding time-dependent dynamics. These excitation energy transfer (EET) mechanisms are at the heart of many processes in light-harvesting and photochemistry in biological and artificial antennae. On the one hand, Förster EET efficiencies typically scale as R^{-6} (R being the interchromophoric distance), given that dipole–dipole interactions mediate them; this fact allows for Förster EET to serve as a molecular ruler in biophysical applications. On the other hand, the efficiency of Dexter EET processes decays exponentially with R due to fast decay of wavefunction overlap between chromophores. In their study, Schäfer et al. (10) demonstrate that the spatial delocalization of the photon mode (see refs. 11–13 for similar findings) and its simultaneous interaction with the electrons renders both Dexter and Förster transfer processes significantly enhanced in terms of their typical spatial ranges of operation. This is a remarkable finding, especially given that Dexter processes are typically operative within intermolecular contact distances only. A unique value of this real-space model is the ability to accurately compute metrics of quantum entanglement for electrons or photons induced by light–matter coupling. From our knowledge of quantum chemistry, it is no mystery that longitudinal photons, which are at the heart of Coulomb interactions, can induce significant electronic correlations; however, the authors find that this is remarkably true also for transversal photons, albeit to a lesser extent than their longitudinal counterparts. Lastly, the authors find that the photons develop anharmonicities due to their strong interaction with the electrons. This is again expected from our understanding of nonlinear optics, whereby effective interactions between photons can be recreated by an anharmonic material medium. The beauty of the result from Schäfer et al. (10), however, is that it arises naturally from ab initio nonrelativistic quantum mechanics of the interacting electrons and the photons altogether.

The highlighted study thus serves as a great incentive for experimentalists to design systems that exhibit strong light–matter coupling at the single- or few-molecule level. Broad molecular linewidths often overwhelm single-molecule coupling, $\Gamma \gg g$, rendering this regime difficult to achieve with typical Fabry–Perot microcavities. Importantly, recent *tour de force* experiments have demonstrated the possibility of entering the single-molecule strong-coupling regime using extreme electromagnetic mode confinement in plasmonic junctions, albeit at the price of enhanced electromagnetic losses due to the metal (14). However, through careful design of cavity structures, whereby loss and mode volume are optimized, more streamlined realizations of the single-molecule strong-coupling regime should be achievable.

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On the other hand, a wealth of intriguing room-temperature experiments (2) in the last decade have demonstrated a variety of polariton chemistry effects due to strong light–matter coupling between ensembles of $N > 10^7$ molecular dipoles and a cavity mode, a scenario that can be described by the so-called Tavis–Cummings (TC) model (Fig. 1*B*). These realizations have demonstrated substantial changes in rates and mechanisms of chemical processes (4–6, 15) upon onset of strong coupling. In these architectures, the burden of achieving strong coupling at the single-molecule level is circumvented by demanding a less stringent condition, $\Omega = \sqrt{N}g \gg \Gamma, \kappa$, namely, that the collective light–matter interaction, which is superradiantly enhanced by $\sqrt{N}$, is larger than the independent excitation linewidths. In fact, giant Rabi splittings $2\sqrt{N}g$ of ~ 1 *eV* for electronic transitions in organic chromophores (16) or ~ 60 meV for vibrational excitations in organometallic compounds (17) have been recently demonstrated, corresponding to the so-called ultrastrong-coupling regime, where the Rabi splitting is a sizable fraction of the material optical gap (18). However, this superradiant enhancement of light–matter coupling comes at an important cost: The optical mode chooses a totally symmetric (superradiant) linear combination of dipoles with which to mix and leaves a macroscopic number ($N-1$) of dark (subradiant) combinations parked at the same energy as the bare molecular excitations (3). Fig. 1*B* shows these lowest-energy excitations of the TC model. Again, an analogy with molecular orbital theory comes in handy: While the symmetries of the polariton states resemble those of bonding and antibonding orbitals, the dark states correspond to the nonbonding orbitals that do not have the right symmetry to undergo chemical bond formation.

Although there are obvious commonalities between single-molecule and ensemble strong coupling, the presence of a macroscopic dark-state reservoir in the latter can result in distinct phenomena. To start with, the JC model features strong few-photon nonlinearities due to the ready saturation of a single molecule, whereas these effects are diluted in the TC model. More related to the discussed work, previous experimental demonstrations of polariton-assisted remote energy transfer in the ensemble regime have shown an almost distance-independent rate of energy transfer between ensembles of donor and acceptor

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chromophores, both of them strongly coupled to a cavity (5, 15), a conclusion that was also obtained in the work of Schäfer et al. (10). The distance independence in both single-molecule and ensemble cases stems from the long-range coherence of the photonic component that makes up the polariton. However, the kinetics of the ensemble system is markedly distinct from the single-molecule scenario due to the role played by the dark states in mediating EET between polaritons via vibrational relaxation (11, 12), in a mechanism that closely resembles the Redfield regime of EET. An ab initio quantum-mechanical treatment of the ensemble strong-coupling regime is computationally too complex. Thus, a synergistic combination of CQED density functional (19) and mean-field theories (20), together with (appropriately!) coarse-grained low-energy models, is expected to yield an informative characterization of these complex systems.

To summarize, we hope to have convinced the reader that polariton chemistry, being a nascent field of research aimed at developing CQED for chemistry and materials science, offers attractive prospects for fundamental and applied science. Some technical challenges from both theory and experiment standpoints have been highlighted, for which we anticipate creative solutions to be reported in the near future. By invoking concepts of CQED into chemistry and materials science, one can go beyond traditional synthesis-based approaches and engineer matter by coherently combining material excitations with light. We therefore expect that polariton chemistry will deliver a new generation of quantum technologies that will go beyond standard applications of quantum computation and simulation in pristine platforms and, instead, offer creative ways to control complex chemical systems. After all, maybe it will pay off to think creatively "inside the (photon) box."

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