

Introduction: Polaritonic Chemistry

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In the early 1990s it was reported¹ that a single atom in a precisely designed Fabry–Perot cavity could be directly seen to produce a fascinating kind of excited state. The excited state of the atom couples strongly to a quantized mode of the electromagnetic field to produce hybrid light–matter states.² Studies of these polaritonic states have broadened over the years.³ The demonstration in 2012 that chemical reactivity could be modified in the presence of these states spurred the emergence of a new field, now known as polaritonic chemistry—the subject of this virtual issue.⁴ The potential of the field was further enhanced when it was subsequently shown that simply coupling vibrational transitions could lead to large changes in the ground state reactions.⁵ One of the surprising findings that is impacting the field from a chemical perspective is that molecules in high concentration within a Fabry–Perot cavity couple collectively—and surprisingly robustly—to an effective mode of the electromagnetic field.⁶

A remarkably large splitting of these collective molecular light–matter hybrid states is observed in spectroscopic measurements because the structure of the coupling matrix means that the lowest and highest eigenvalues correspond to emergent hybrid light–matter states. That is, those eigenvalues scale with the number of molecules collectively coupled, specifically the square root of that number in this case. Thus, the more molecules that are coupled, the more the polaritonic states split away from the frequency of absorption bands of the excited molecules uncoupled to the cavity. Either the electronic excitations or vibrational states of chemical systems can couple to the electromagnetic field, to produce electronic or vibrational polaritons, respectively. Researchers have been inspired to ask, among other things, how this prominent collective phenomenon might influence chemical reactions or photophysical dynamics⁷ or quantum materials properties.⁸ Theoretical attempts to determine how the coupling of the cavity to the ensemble of molecules can modify the chemistry of individual molecules in the thermodynamic limit have so far been unsuccessful. While there have been theoretical suggestions that collective strong coupling can lead to local changes once impurities or (thermally induced) disorder are introduced in an ensemble,⁹ the existence and nature of such effects for a large ensemble of molecules is an active field of research.

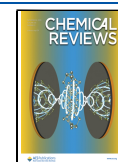
The field of polariton chemistry is yielding many exciting new results and ideas. This [virtual thematic issue](#) of *Chemical Reviews* gives an overview of current research. Specifically, there are detailed reviews of Control, Modulation, and Analytical Descriptions of Vibrational Strong Coupling,

Molecular Energy Transfer under the Strong Light–Matter Interaction Regime, Molecular Chemistry in Cavity Strong Coupling, Understanding Polaritonic Chemistry from Ab Initio Quantum Electrodynamics, Theoretical Advances in Polariton Chemistry and Molecular Cavity Quantum Electrodynamics, and The Rise and Current Status of Polaritonic Photochemistry and Photophysics.

The field of polaritonic chemistry is still developing and growing. Accompanying the new developments and insights, there are many interesting questions. Why are ground state properties only modified when the material transition is coupled with an optical mode at zero parallel wave-vector? What are the roles of coherence and the collective nature of the coupling? How do individual molecules experience cavity-induced modifications under collective strong coupling? For instance, the collective nature of the light–matter coupling is spectacular, with likely much more than 10^5 molecules typically coupling to an effective mode of the radiation field. What this means is that, while two states carry the oscillator strength (the upper and lower polariton states), there is an associated manifold of 99,999 “dark states”. What roles do these dark states play in photophysical dynamics?⁸ What is the role of other states in the cavity population, associated with localized, or “uncoupled”, molecules? How can we predict the dynamical interplay and relaxation kinetics of population among such a vast manifold of states?

Other questions concern how chemistry is modified by the collective coupling.⁹ Why does symmetry appear to play a key role in the outcome? Why does the relatively small collective Rabi splitting in vibrational strong coupling lead to such large changes in reactive landscapes—all the more so because the large collective effect seen in spectroscopy can obscure the “back action” on individual molecules?¹⁰ Even though the vector potential in a Fabry–Perot cavity is enhanced relative to vacuum, it is insufficient to perturb potential energy landscapes. Nevertheless, experiments reveal tantalizing and surprisingly strong effects and the precise mechanisms underpinning polaritonic chemistry are yet to be completely elucidated.

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We hope that the articles in this thematic issue inspire advances in the field of polaritonic chemistry. There remains much to discover and resolve.

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Notes

Views expressed in this editorial are those of the authors and not necessarily the views of the ACS.

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