CONNECTING POLARITONIC CHEMISTRY AND SPIN GLASS PHYSICS: AN AB INITIO PERSPECTIVE ON QUANTUM COLLECTIVITY AND NON-CANONICAL EQUILIBRIUM EFFECTS

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1. Present State of Research on Chemistry in Confined Spaces: a personal view

Polaritonic chemistry explores how embedding molecules within optical cavities and coupling them to the quantized electromagnetic vacuum can modify chemical reactivity and material response in ways not achievable under free-space conditions [1]. Under vibrational strong coupling (VSC), hybridization between molecular vibrations and confined cavity modes—occurring even in the absence of illumination—has been shown to alter reaction rates, energy transfer pathways, dielectric properties, and vibrational relaxation dynamics [1-4]. These phenomena are fundamentally modification of the ground state, pointing to a reshaping of the electronic ground-state energy landscape mediated by light–matter interactions.

Pioneering experimental studies [2–4] have demonstrated that tuning the resonance between specific molecular vibrations and cavity modes can either accelerate or suppress chemical reactions, modify selectivity, and influence solvent polarity. These effects involve collective coupling of large ensembles—on the order of 10^4–10^{12} molecules—to a shared electromagnetic mode, suggesting that cooperative mechanisms dominate over single-molecule perturbative responses. Despite considerable theoretical and computational progress [5–10], a complete mechanistic framework reconciling the local molecular nature of chemical change with the global, collective character of strong coupling remains elusive (see Fig. 1). Perturbative treatments often predict effects that vanish in the thermodynamic limit, in stark contrast to experimental reality. As highlighted in two recent review papers [11,12], understanding how global quantum fields induce persistent, local modifications of polarizabilities, barrier heights, and charge distributions remains one of the central open problems in the field.

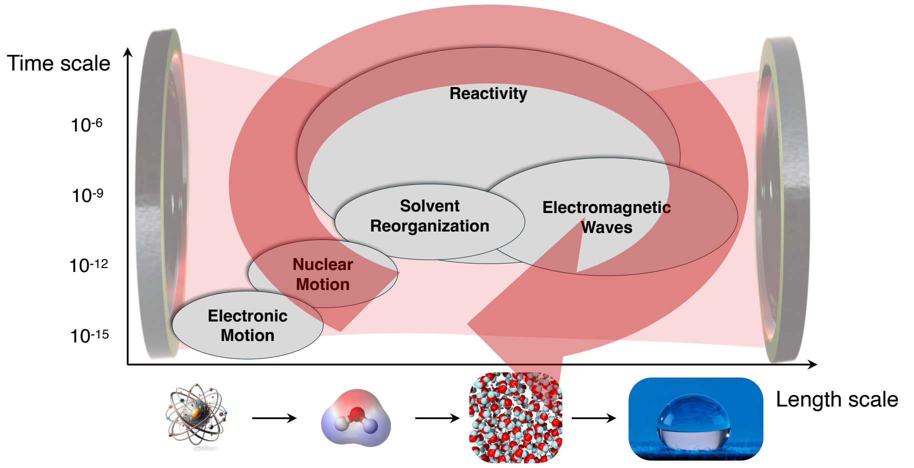


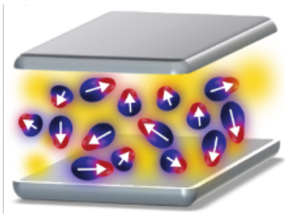
Fig. 1 | Spatiotemporal Challenge: Collective strong coupling induces non-perturbative feedback effects across different spatiotemporal scales. This makes polaritonic chemistry extremely challenging from a theoretical and computational perspective.

2. Our Recent Contributions to Chemistry in Confined Spaces

To address the fundamental question of how collective coupling to the electromagnetic vacuum field produces measurable local chemical modifications, we have developed a microscopic, *ab initio* theoretical framework that uncovers the many-body mechanisms underlying cavity-induced reactivity changes. Using quantum electrodynamical density functional theory (QEDFT) [13] and cavity Born–Oppenheimer approaches [14] applied to the full Pauli–Fierz Hamiltonian, we demonstrate that placing molecular ensembles inside an optical cavity generates not only local self-polarization but also long-range, frustrated dipole–dipole interactions mediated by the quantized cavity field [15].

In disordered ensembles, this frustration prevents the system from achieving a globally optimal polarization configuration, leading to glassy polarization landscapes with multiple metastable minima. The resulting physics is directly analogous to that of disordered magnetic systems and enables a formal mapping of the cavity-coupled molecular ensemble onto the spherical Sherrington–Kirkpatrick model (see Fig. 2), a canonical spin-glass framework in statistical mechanics [12]. This mapping predicts the existence of polarization-glass phases and cavity-induced phase transitions driven by the competition between thermal disorder and long-range cavity-mediated dipolar coupling.

Detailed numerical simulations corroborate these predictions, showing that under vibrational strong coupling, reactivity, vibrational frequencies, and dipole fluctuations are systematically shifted in quantitative agreement with experimental observations—but only when the collective nature of the coupling is properly incorporated. Single-molecule models, even with artificially strong per-molecule coupling, often fail to reproduce these effects, underscoring that polaritonic chemistry is intrinsically a many-body phenomenon. Furthermore, our simulations reveal that the cavity-modified energy landscape supports long-lived temporal correlations and hysteresis, signaling a departure from ergodic dynamics. These non-Markovian effects, often neglected, are particularly relevant under strong light–matter coupling for processes such as solvent reorganization, energy redistribution, and charge transport.



$$E_{\mathrm{corr}} \mapsto -\sum_{i<j}^{N} J_{ij} s_i s_j$$

Fig. 2 | **Mapping collective electron correlations to a spin glass [12]:** Experimental evidence shows that the cavity modifies inter-molecular electron correlations (i.e., London dispersion forces) collectively [16]. Surprisingly, the corresponding transverse electron correlation problem can be mapped onto the analytically solvable *spherical Sherrington-Kirkpatrick* (SSK) model, known from continuous spin glass physics. Comparing predictions from the mapped SSK solution with experimental evidence reveals qualitative agreement across different chemical observables [12]

To further strengthen the theoretical foundation, we developed a non-perturbative analytic model for an ensemble of harmonic molecules under VSC. By applying the cavity Born–Oppenheimer partitioning in the dilute limit, we solved the system self-consistently and analytically, revealing that molecular polarizabilities are modified even in the limit of vanishingly small single-molecule coupling—and that these modifications persist in the large-N limit [14,17]. This behavior stands in stark contrast to perturbative treatments, which erroneously predict vanishing effects as the ensemble size increases. Our model also shows that certain properties such as exact polarizabilities can be extracted from single-molecule strong coupling simulations, providing both conceptual clarity and computational efficiency for exploring collective coupling effects in realistic systems.

Together, these results establish a predictive and quantitative theory linking microscopic observables to macroscopic cavity-induced correlations, introducing concepts from disordered statistical physics—such as frustration, glassy phases, and broken ergodicity—into the molecular QED framework. These advances form the theoretical foundation of our ERC Synergy project Unraveling the Mysteries of Vibrational Strong Coupling (UnMyst, https://cordis.europa.eu/project/id/101167294), which seeks to unify the understanding of how collective electromagnetic coupling shapes local chemical function, how non-canonical equilibrium processes are modulated by cavity environments, and how symmetry principles can be leveraged to engineer chemical reactivity.

3. Outlook to Future Developments on Chemistry in Confined Spaces

Our recent findings show that polaritonic chemistry cannot be described by traditional models that treat molecules as independent entities subject only to local perturbations. When a large number of molecules couple collectively to a common electromagnetic mode within an optical cavity, the system enters a qualitatively different regime in which non-local correlations reshape the ground-state energy landscape. This collective behavior gives rise to phenomena closely analogous to those in disordered condensed matter systems—most notably spin glasses—where frustration, metastability, and memory effects dominate both dynamics and thermodynamics.

Within this framework, local chemical observables such as bond lengths, polarizabilities, and reactivity become encoded in the global polarization configuration of the molecular ensemble, itself constrained by the cavity field. The incompatibility between global electromagnetic coherence and local energetic disorder introduces frustration, producing a glassy energy landscape with multiple metastable states and broken ergodicity. By mapping the cavity-coupled ensemble onto a spin-glass-model, we have provided a predictive, physically grounded explanation for longstanding experimental puzzles, including reactivity shifts in the absence of illumination, strong system-to-system variability, and hysteresis in cavity-modified reactions.

Recognizing that chemical function can emerge from collective electromagnetic correlations enables a new paradigm: reaction engineering by collective design. Here, reactivity is tuned not solely through molecular functionalization but also by controlling the ensemble-scale environment—its disorder distribution, density, and dipolar alignment—and by engineering cavity structures to impose or break symmetries that determine the frustration and correlation length. This shifts the focus from single-molecule photophysics to the deliberate design of emergent phases in molecular materials under strong light–matter coupling.

Several theoretical and experimental challenges must be addressed to establish this approach as a predictive science. On the theoretical side, finite-temperature field theories are needed to capture the interplay between disorder, long-range interactions, and temporal correlations in strongly coupled ensembles, providing a basis for understanding phase transitions, susceptibility spectra, and fluctuation–dissipation behavior under vibrational strong coupling. Computationally, *ab initio* QED methods must be extended to large, heterogeneous systems and to non-canonical equilibrium regimes, enabling realistic modeling of charge transfer, barrier crossing, and solvent reorganization in cavity-coupled settings. Experimentally, new cavity architectures—multimode, plasmonic, open, or quasi-periodic—offer routes to tailor the degree and nature of frustration and correlation [18].

The persistence of long-lived correlations and delayed relaxation seen in simulations and experiments further calls for a quantum thermodynamic framework that incorporates non-conservative forces, non-canonical equilibrium steady states, and memory-retaining dynamics.[19] Taken together, these directions converge toward a coherent vision: a collective form of chemical engineering grounded in quantum electrodynamics, statistical physics, and molecular design. The UnMySt project is uniquely positioned to realize this vision through tightly integrated theory and experiment, building a general framework for cavity-controlled chemistry that explains past observations and enables new strategies for reactivity control, materials engineering, and quantum-informed functional design. In this light, polaritonic chemistry becomes not a niche curiosity, but a blueprint for manipulating matter through its collective electromagnetic environment.

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