Coherence as a probe of ultrafast dynamics, entropy as a resource

Gregory D. Scholes, Princeton University

Coherence is considered to be a potentially valuable resource for chemical dynamics. As an example, I will discuss ultrafast electron transfer as well as proton transfer reactions. Electron transfer is fundamentally important for a variety of chemical reactions. It is desirable to learn more ways to control this fundamental reaction. In this regard, our understanding of the intramolecular reaction coordinate is less well explored. I will report experiments that illustrate how vibrational wavepackets can serve as a molecular-scale probe to give insight into the reaction coordinate of electron transfer reactions [1]. Valuable insights into electron transfer reactions have been established using Marcus theory. However, a complementary theoretical model explaining how vibrational wavepackets evolve during electron transfer reactions has not yet been established. I will describe a "quantum quench" model to address this gap [2].

The second part of the talk is relevant to collective states produced by strong light-matter coupling. In particular, a focus of the presentation will be to discuss the delocalization of molecular polaritons and consequences for solar photochemistry. The main result is that the incredibly long-range phase coherence of the polariton states formed by strong coupling between a photon mode in a cavity and an ensemble of molecules leads to exceptionally low entropy of the upper and lower polariton states, starkly contrasting with the dark states [3]. That result means that spectroscopy does not correctly order the free energy of the excited states because there is a significant entropic contribution to the free energy. The entropic contribution adds to the polariton electronic gap, rendering states surprisingly more reactive that anticipated from the input excitation energy. This apparently 'additional' reactivity, evident from the thermodynamics, suggests how the low entropy of highly coherent states can be exploited as a resource.

[1] Shahnawaz Rafiq, Bo Fu, Bryan Kudisch, and Gregory D. Scholes: Nature Chem. 13, 70–76 (2021). Interplay of Vibrational Wavepackets During an Ultrafast Electron Transfer Reaction
[2] Yuanheng Wang, Alfy Benny, Brieuc Le Dé, Alex W. Chin, and Gregory D. Scholes, A Numerically Exact Description of Ultrafast Vibrational Decoherence in Vibration-coupled Electron Transfer: Proc. Natl. Acad. Sci. (USA) 122, e2416542122 (2025).
[3] Gregory D. Scholes, C. A. DelPo, and B. Kudisch: Entropy Reorders Polariton States. J. Phys. Chem. Lett. 11, 6389−6395 (2020).

What can strong coupling do for organic chemists?

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Reaction outcomes are defined by their potential energy landscape. Classically, synthetic chemists have manipulated this landscape to accelerate reactions and achieve selectivity through the introduction of catalysts. In recent years, photochemistry has transformed the field of organic synthesis by adding non-thermal energy to reactions and accessing new products through excited-state manifolds. Will the next frontier in organic chemistry rest on delocalized hybrid light-matter states? While physical chemists have demonstrated its influence on processes such as lasing, energy and charge transfer, intersystem crossing, and triplet-triplet annihilation, only a handful of bond-forming and -breaking reactions have been studied under electronic strong coupling. In most cases, strong coupling to a substrate decelerates reactions. We have shown that in a Fabry-Perot cavity, photoreaction of a strongly coupled closed fulgide photoswitch to its open, uncoupled state is accelerated. The implications of this result, subsequent studies by others in the field, and future opportunities of interest to synthetic chemists will be discussed.

Tamm modes for the development of laser sources

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Optical Tamm states are surface modes formed at the interface between a dielectric distributed Bragg reflector and a metal film. The metallic part of the structure provides a simple way to achieve optical confinement while also enabling electrical injection, making Tamm modes a versatile approach to engineer light emission in semiconductor structures.
In this talk, I will review our work on the development of Tamm lasers, from optically pumped structures to electrically injected devices. I will first present the demonstration of lasing in confined Tamm structures, and show how this confinement can be exploited to reduce the threshold or control the polarization. I will then discus the development of a fabrication process for electrical injection and the demonstration of Tamm laser diodes.

Ab Initio Advances in Polaritonic Chemistry: Chemical Control through a QEDFT Framework

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Polaritonic chemistry has gained significant attention due to experimental breakthroughs demonstrating site- and bond-selective reactivity under strong collective coupling in optical cavities. However, the underlying theoretical mechanisms remain elusive. A major challenge is developing accurate and efficient theories for non-equilibrium, light-driven phenomena and emerging states of matter. Building on Time-Dependent Density Functional Theory (TDDFT), Quantum Electrodynamics Density Functional Theory (QEDFT) provides a first-principles framework for predicting and manipulating ordered phases in strongly coupled light-matter hybrids (polaritons). In this talk, we present the foundations of nonrelativistic QEDFT, which ensures a stable ground state while seamlessly integrating light-matter coupling with electronic properties. QEDFT offers critical insights into photon-induced chemical modifications, cavity-modified reactivity, and quantum phase transitions driven by vacuum fluctuations. This burgeoning field, Cavity Materials Engineering, leverages strong electron-photon coupling to design novel states of matter. Recent theoretical advances reveal that ground-state quantum phase transitions can occur in this "dark" regime, underscoring the fundamental role of vacuum fluctuations. A key breakthrough links polaritonic chemistry to spin glasses by mapping the dressed electronic structure under collective vibrational strong coupling to the Sherrington-Kirkpatrick model. This reveals a collectively induced instability—spontaneous symmetry breaking—that could drive local chemical modifications. This connection introduces concepts such as frustration and stochastic resonances into polaritonic chemistry while extending spin glass theory beyond condensed matter physics. These advancements pave the way for a predictive understanding of polaritonic chemistry, enabling quantum material design through strong light-matter interactions and shaping future research directions