

## Accessing New Catalyst Chemistries via Light–Matter Strong Coupling

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### Overview

Catalysts are a central component of the majority of processes used in the conversion of petroleum based feedstocks to upstream petrochemicals. Organometallic species, an important class of catalysts, are strongly influenced by the arrangement and identity of the ligands around the metal center which, when chosen appropriately, allow all the individual reactions in a catalytic cycle to occur at an economically practical rate. Key challenges in catalyst design remain and novel approaches are necessary for new generations of catalysts to provide greater specificity, yield, and efficiency. Existing design techniques follow a familiar tenet of chemistry where the physical and chemical properties of molecules are controlled by changing the constituent atoms and/or the way in which those atoms are bonded together.

This work aims to investigate vibrational strong coupling (VSC) as an alternative paradigm to this “chemical” approach to tuning catalyst properties, where, instead, molecular properties are altered without changing the constituent atoms, bonds, or geometry in a formal sense. An infrared photon emitted from a molecular vibrational mode inside of an optical cavity, tuned to the same frequency, has an increased probability of being reabsorbed. If the probability of this exchange process is greater than that of the photon escaping the cavity and molecular non–resonant decay, then energy can oscillate between the cavity and the molecular bond. Under these conditions, two new light–matter superposition eigenstates, known as polaritons, are formed, shifted from the original frequency by half the Rabi splitting frequency,  $\Omega_R$ . Vibrational polariton formation may provide a novel way to tune the overall physical and chemical characteristics of catalyst molecules.

### Progress

The Rabi splitting energy,  $\hbar\Omega$ , is known to increase with a near square root dependence on concentration. This poses a challenge for modifying the properties of catalysts, which are typically at a fixed, low concentration. Therefore, the first goal of this project was to study how a co–resonator molecule could influence the coupling of a different molecule at a low concentration. Solutions of three organometallic ions,  $\text{Fe}(\text{CN})_5\text{NO}^{2-}$ ,  $\text{Fe}(\text{CN})_6^{4-}$ , and  $\text{Fe}(\text{CN})_6^{3-}$ , were used to control the number, energy, and intensity of molecular resonances in a  $200\text{ cm}^{-1}$  window, allowing for a systematic investigation of the formation of three, four, and five polaritons. A schematic of the overall experiment is shown in Figure 1, where the three ions are colocalized with a quantized optical state of a microcavity. The resulting transmission spectrum is shown in Figure 2, where the simultaneous coupling of four vibrations between three distinct, solute molecules results in the formation of upper, midupper, middle, midlower, and lower polaritons.

A more detailed analysis and discussion can be found in our recently published paper.<sup>1</sup> Overall, the presence of additional molecules simultaneously coupled to an optical mode did not significantly affect the Rabi splitting energy of a given molecular resonance, but did substantially alter the light/matter composition (Hopfield mixing coefficients) of the resulting polaritons. Importantly, co–resonator molecules were found to assist in distributing the photonic/molecular character across the polaritons. The introduction of a co–resonator is thus an alternative means for the modification of polaritons made from species at a fixed, low concentration, such as chemical catalysts, via strong

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<sup>1</sup><https://pubs.acs.org/doi/10.1021/acsphotonics.9b01040>

coupling. However, the concentration of the species of interest must be above the critical concentration determined by the collective transition dipole moment.

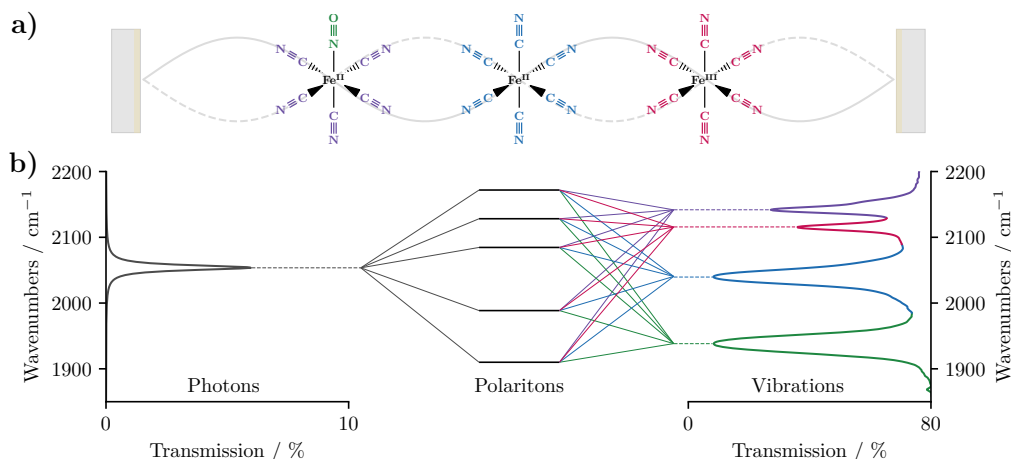


Figure 1: a) Colocalization of up to four molecular vibrations and an optical resonance was achieved by placing a solution of the ions within an optical cavity made from two Au coated CaF<sub>2</sub> windows. b) The excitations of the optical cavity (left) and the molecular resonances (color coded, right) are hybridized via VSC to result in the formation of five polaritons with four Rabi splitting energies ( $\hbar\Omega_{R_i}$ ).

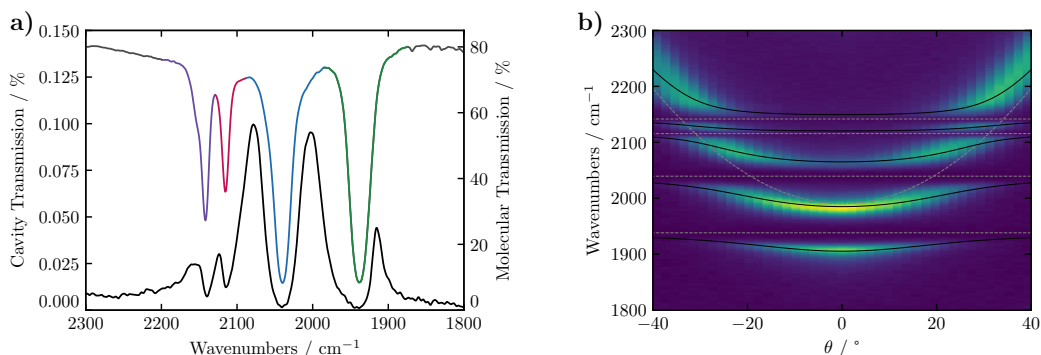


Figure 2: a) Transmission spectrum (black, left axis) of the optical cavity with a 0.9 M Fe(CN)<sub>5</sub>NO<sub>2</sub><sup>-</sup>, 0.3 M Fe(CN)<sub>6</sub><sup>4-</sup>, and 0.4 M Fe(CN)<sub>6</sub><sup>3-</sup> solution with the energy of the optical mode tuned to the midpoint of the two Fe(CN)<sub>5</sub>NO<sub>2</sub><sup>-</sup> vibrations (2050 cm<sup>-1</sup>). The spectrum of the uncoupled molecular resonances is shown on the right axis for reference. b) Experimental dispersion of the polariton branches (colormap) along with uncoupled molecular and optical resonances for reference as horizontal and curved dashed lines, respectively. The results of fitting to a coupled oscillator Hamiltonian are overlaid as solid lines.

## Impact

The support of the Petroleum Research Fund has been very influential in the development of my research program. The grant has funded three undergraduate research students over the past year during both the academic semester and the summer. The students have gained invaluable experience in designing experiments, reading literature, and writing code for data analysis and instrument control. The funding provided a spin coater and other supplies that have allowed for much more precise optical cavity fabrication compared to earlier methods. This has accelerated the progress of the project and led to a publication in ACS Photonics. The students have also given local poster presentations and seminars and will present at the upcoming ACS national meeting.