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Title:	Cavity Catalysis: Controlling Chemical Reactions Through Cooperative Vibrational Strong Coupling
Authors:	Jyoti
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Abstract:	Selective vibrational excitation using lasers has introduced coherent, site-selective and mode-selective chemistry. Here, the conversion efficiency is poor due to the availability of internal vibrational relaxation pathways within the molecule. Selective and collective vibrational excitation is possible by coupling a fundamental vibrational transition to a confined electromagnetic field of a cavity. This phenomenon occurs in the absence of external photons (external stimuli) at room temperature. It offers a unique way to activate or deactivate a chemical bond in a ground state chemical reaction. This new research area that studies chemical reactivity under strong light-matter coupling is known as polaritonic chemistry. Strong coupling is typically achieved by placing molecules in an infrared micro-cavity resonator which couples the vibrational transition to the cavity mode. Collective coupling of Avogadro number of vibrational resonators results in large Rabi splitting energy that can affect the potential energy landscape of the reacting molecules. According to quantum electrodynamics, a molecular state is dressed by the confined electromagnetic field resulting in vacuum Rabi splitting. The notion of zero-point energy is invoked here. VSC has been shown to accelerate or retard the chemical reactivity of various organic and biomolecular reactions. Furthermore, VSC is not only a tool to control chemical reactions but also gives insight into which vibrations are involved in a reaction. In the current thesis, we focus on the influence of vibrational strong coupling (VSC) that can control chemical reactivity by site-selective/band-selective coupling of vibrational states. In the chapter I, for the first time, we discussed the idea of cooperative VSC between the solvent and reactant molecules that can catalyze a chemical reaction (aka-cavity catalysis). Solvolysis of para-nitrophenyl acetate enhances reaction rate by resonant coupling to 12 C=O stretching mode of ethyl acetate molecules. The thermodynamics suggest that solute-solvent interaction is modified under VSC due to the reshuffling of activation parameters. In chapter II, the same concept is applied to study the structure-reactivity behavior under cooperative VSC conditions. Interestingly, resonant coupling shows a non-linear behavior in the Hammett plot suggesting a drastic electron density variation at the C=O active site. Various control experiments, both in cavity and non-cavity, show the role of solvent vibrational overlap has a major influence on chemical reactivity. Further studies suggest that the mechanism of the reaction remains the same under strong coupling conditions. In chapter III, we look into the behavior of biomolecular reactions under VSC. Here, the role of water molecules in an enzymatic reaction I
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