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Abstract

The goal of the proposed research is to utilize fundamental light-matter interactions of strong coupling and confinement to alter molecular potential energy surfaces (PESs) to control chemical reaction dynamics. This research proposal explores three interrelated topics.

Topic 1: Strong coupling of plasmonic-dielectric metamaterials. We will control Rabi splitting in optical devices through the use of hybrid plasmonic waveguides (HPWGs). We will (1) create static two-level splitting in J-aggregated doped HPWGs; (2) design the first excited state transient Rabi splitting optical device; and (3) investigate the timescales of Rabi splitting using dopant molecules with different excited state lifetimes.

Topic 2: Confinement effects on PESs. Stimulated Raman scattering (SRS) has been proposed as an explanation for the observation of new chemical phenomena in strongly confined optical cavities. We propose a detailed investigation of SRS in the strong confinement regime for: (1) understanding the influence of optomechanical cavity effects on tip-enhanced Raman scattering (TERS); (2) observing coherent Raman scattering (CRS) effects in the light-matter interactions within the tip-sample junction in TERS; and (3) use the effects of confinement with SRS in TERS to study elementary reactions of small non-resonant molecules.

Topic 3: Polaritonic molecular states by strong confinement and coupling. To understand polaritonic molecular states that arise from strong coupling and confinement by cavity modes, we will: (1) use the sensitivity of CRS to probe strong coupling in molecular-optical cavity polaritonic states of small molecules and (2) perform spectroelectrochemistry in coupled molecular-electrochemical cavities to examine vibrational polaritonic effects.

Outcomes. The proposed research program will transform our ability to control and even re-program chemical reaction pathways and dynamics on the nanometer length scale. Consequently we anticipate that it will have a major impact on the fields of chemistry, materials science, and photonics.