Ultrafast SERS probing of molecular heating and hot carrier transfer in plasmonic photocatalysis

Emily L. Keller, James L. Brooks, and Renee R. Frontiera
Department of Chemistry, University of Minnesota, Minneapolis, MN 55104

Plasmonic nanomaterials are promising candidates for solar-driven catalytic devices, as they interact strongly with light and are known to be capable of driving energetically unfavorable chemical reactions. Their ability to concentrate light to subwavelength volumes leads to the formation of hot spots and hot electrons, which can drive energy flow, modify potential energy surfaces, and enable new photochemical and photophysical processes. However, significant questions remain as to the mechanism of action of a plasmonic photocatalytic system, in part because of difficulties in characterizing the rapid photo-induced dynamics and interactions between the nanoparticle surfaces and proximal molecular species. In particular, the contribution of thermal effects on increases in the rate and yield of plasmonic photocatalysis is unclear, as measurements designed to look at transfer of energy in the form of heat from plasmonic materials to molecules on the ultrafast timescale of chemical reactivity are lacking.

Here we use ultrafast surface-enhanced Raman spectroscopy, a pump-probe technique designed to follow the molecular response of molecules adsorbed on plasmonic nanomaterials, to investigate the response of the coupled molecule-plasmon system to light (Figure 1). By tracking the transient Raman frequency evolution on the Stokes and anti-Stokes sides, we can determine the role of heating in plasmonic catalysis. We probe the effective temperature, equivalent to the mode-specific increase of vibrational kinetic energy on the picosecond timescale of molecular motion. We find that plasmon excitation increases the effective temperature of the system by less than 100 K, even at peak fluences 10^8 stronger than focused sunlight. This modest energy transfer of the most active plasmonic regions proves that thermal contributions to plasmonic catalysis are surprisingly small. This material is based on work supported by the Air Force Office of Scientific Research under AFOSR Award No. FA9550-15-1-0022.