# Control of plasmon-molecule energy flow as probed by ultrafast SERS

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Plasmonic nanomaterials show promise for highly selective and controlled chemistry, due to the creation of localized enhanced electromagnetic fields, hot carriers, and heating that can occur following photoexcitation. However, the efficiency of chemical reactions driven by plasmonic materials is typically low, and a lack of mechanistic understanding of how energy transfers from plasmon to molecule hinders reaction optimization for use on large scales. To decode the complex chemical and physical processes involved in plasmon-driven photocatalytic reactions, we use surface-enhanced Raman spectroscopy (SERS). We detail SERS techniques that we have used and are developing to study molecular transformations, charge transfer, and plasmonic heating in dynamic plasmon-molecule systems on timescales ranging from seconds to femtoseconds. SERS is an ideal analytical tool for understanding plasmon-molecule interactions, as it gives highly specific information about molecular vibrations with high sensitivity, down to the single-molecule level. Importantly, SERS allows for simultaneous pumping of a plasmonic resonance and probing of enhanced Raman signal from nearby molecules. We have used ultrafast SERS to quantify charge transfer from plasmonic nanomaterials to proximal adsorbates, and to quantify the degree of heating experienced by reactants. We also demonstrate nanoscale spatial specificity in some chemical reactions, in which the nanomaterial can be tailored to provide patterned reactivity. Finally, we demonstrate a unique "plasmon refrigeration" scheme, in which plasmonic materials can be used to cool molecules, akin to laser cooling methods but for much more complicated systems. Our continued development of these SERS-based techniques shows promise in answering questions regarding direct charge transfer, resonance energy transfer, and excitation conditions on plasmon-mediated chemistries.

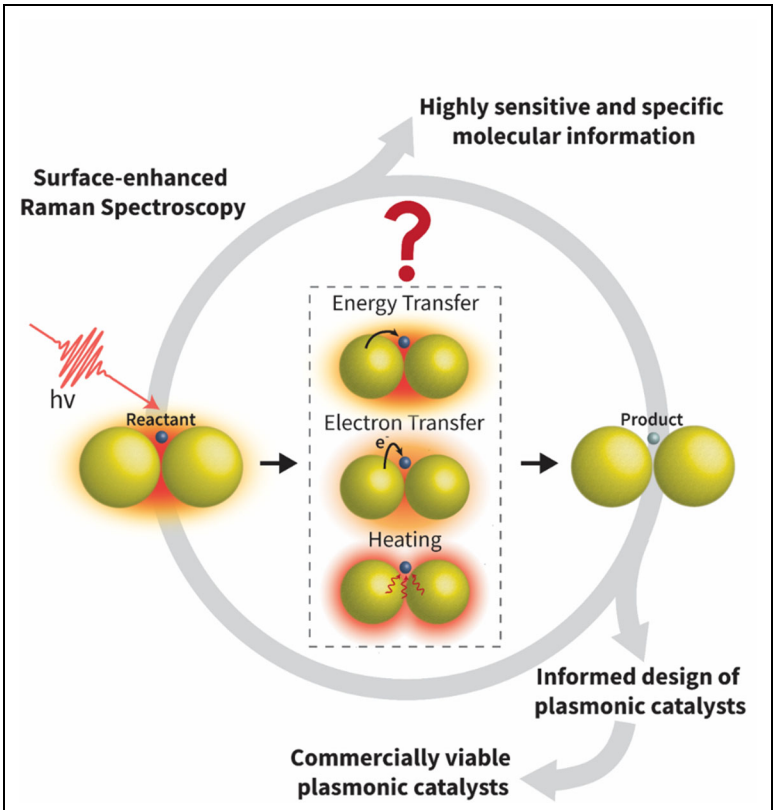


Figure 1. Ultrafast Surface-Enhanced Raman Spectroscopy (SERS) is used to provide quantitative understanding of the mechanism of plasmon-driven chemical processes.