Plasmonic materials are highly promising as catalysts for driving energetically unfavorable chemical reactions with light, due to their unique optical focusing and hot carrier generation properties. However, a complete mechanistic understanding of plasmonic photocatalysis is lacking, in part due to the rapid timescales of plasmonic processes and chemical bond-making and -breaking processes, which occur on the femtosecond and picosecond timescales. Plasmons can concentrate electromagnetic fields, can generate highly energetic electrons and holes, and can heat up local environments. An understanding of the energy partitioning into each of these processes is crucial to the design of plasmonic photocatalysts which are optimized for chemical selectivity. Here I’ll discuss our development of ultrafast surface-enhanced Raman spectroscopy (SERS) to probe the behavior of molecules in plasmonic hot spots. By probing on the relevant timescales, we are able to uncover how and when the plasmon energy is converted into hot carriers, molecular heating, or resonant energy transfer. We use a new form of ultrafast Raman thermometry to probe energy transferred into adsorbed molecules as heat, showing that the plasmon-induced heating contribution to catalysis is negligible. Additionally, we probe hot carrier transfer events and use SERS substrates with tunable electromagnetic field enhancements to examine the effects of local fields on chemical reactivity. These results quantitatively determine the energy partitioning of plasmon decay, and highlight the unique ability of these plasmonic materials to drive energetically unfavorable chemical reactions.