PROBING THIN FILMS AND MONOLAYERS ON GOLD WITH LARGE AMPLITUDE TEMPERATURE JUMPS

YUXIAO SUN, CHRISTOPHER M BERG, DANA DLOTT, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA*.

A methodology to probe localized vibrational transitions of self-assembled monolayers (SAMs) adsorbed on gold films using vibrational sum-frequency generation (SFG) is described. The gold film is subjected to heating from a 400nm pump laser, exposing the adsorbed molecules to a temperature jump in the 30-175 ° K range, calibrated using ultrafast reflectance measurements of the gold compared to steady state oven heating . SAMs of alkyl thiols as well as nitro functionalized aryl thiols were deposited and temperature jumped while be observed with SFG, monitoring the symmetric and asymmetric methyl vibrations as well as nitro vibrations.

The amplitude, center, and width of the transitions were measured and provide information about delay and orientation of the molecules, as well as providing an indicator of the overall monolayer state. All transitions probed exhibited overshoot decay plateau patterns, attributed to a fast hot electron process directly exciting the probed transitions, followed by a slower bulk heating process causing monolayer disordering. This leads to a shift in the average angle of the terminal methyl, manifesting itself as a change in the amplitude of the vibration.

These techniques will be applied to thin films of energetic materials to study reactions to temperature jumps. HMX is known to have a peak in sensitivity as δ-HMX transitions to β-HMX at high temperatures, but fairly little information about the reason for this is known. This technique should be able to probe that process and provide data that can be used with computational models to gain some understanding of the process.