Unoccupied electronic states at the interface of alkanethiol SAMs on Au(111) MATTHIAS MUNTWILER, CHAD LINDSTROM, XIAOYANG ZHU, University of Minnesota, Minneapolis — Alkanethiol self-assembled monolayers (SAMs) on Au(111) are model systems for metal-molecule contacts in molecular electronics. Using time-resolved two-photon photoemission (TR- 2PPE) we probe the unoccupied electronic structure of the alkanethiolate/Au interface. Two distinct peaks appear in the spectra: The first, non-dispersive peak is attributed to the antibonding $\sigma^*$ orbital of the Au-S chemisorption bond, and the second, dispersive peak to a laterally delocalized interfacial resonance induced by the image potential at the metal surface. Both peaks show lifetimes shorter than 30 fs. For the $\sigma^*$ resonance such a short lifetime is expected due to the wavefunction overlap with the metal, whereas for the second resonance it is an effect of scattering at S atoms inside the molecular layer. In fact, the insensitivity of the energy level, dispersion, and lifetime to layer thickness suggests that the electron wavefunction is concentrated inside the dielectric layer close to the metal-molecule interface — in contrast to physisorbed alkanes where it is pushed out of the layer.