Origin of coverage dependence in photoreactivity of carboxylate on TiO$_2$(110) surface. IGOR LYUBINETSKY, Oregon State University, ZHI- TAO WANG, MICHAEL HENDERSON, Pacific Northwest National Lab — Employing scanning tunneling microscopy (STM) and ultraviolet photoelectron spectroscopy (UPS), we have observed a strong nonlinear decay of the reaction rate constant with coverage for the photolysis of trimethyl acetate on TiO$_2$(110). This effect was not linked to intermolecular interactions of TMA but to the accumulation of the coadsorbed bridging hydroxyls (HO$_b$) deposited during (thermal) dissociative adsorption of the parent, trimethylacetic acid (TMAA). Confirmation of the hindering influence of HO$_b$ groups was obtained by the observation that HO$_b$ species originated from H$_2$O dissociation at O-vacancy sites have a similar hindering effect on TMA photochemistry. Though HO$_b$'s are photoinactive on TiO$_2$(110) under ultrahigh vacuum conditions, UPS results show that these sites trap photoexcited electrons, which in turn likely (electrostatically) attract and neutralize photoexcited holes, thus suppressing the hole-mediated photoreactivity of TMA. This negative influence of surface hydroxyls on hole-mediated photochemistry is likely a major factor in other anaerobic photochemical processes on reducible oxide surfaces.