Determination of Thermodynamic Surface Properties of Carboxylic Acid Functionalized Silanes at Silica/Water Interfaces with Second Harmonic Generation

MICHAEL MUSORRAFITI, CHRISTOPHER KONEK, HIND AL-ALBADLEH, PAUL BERTIN, SONBINH NGUYEN, FRANZ GEIGER, Northwestern University — Using the $\chi^{(3)}$ method of second harmonic generation, we report surface pK$_a$ values for a monoprotic carboxylic acid functionalized silica/water interface. We observe two pK$_a$ values at 9(1) and 5.6(2). The acidic pK$_a$ is similar to pK$_a$ values of organic acids in solution. The more basic pK$_a$ is consistent with lateral hydrogen-bonding stabilization among the interfacial carboxylic acid groups. From the measured data, we obtained relative surface potentials and surface charge densities. Using these values in the Lippmann equation, we can tracked the changes in interfacial energy relative to the neutral reference state over seven orders of magnitude, from $10^{-7}$ mJ/m$^2$ to several mJ/m$^2$.