Using Sum Frequency Generation vibrational spectroscopy, SFG, the molecular orientation at the liquid-platinum electrode interface under potential control was determined for 1-butyl-3-methyl imidazolium cation, [BMIM]+, with [PF_6]- and [BF_4]- anions. Cyclic voltammetry was used to identify the electrochemical window which defined the potential range to be analyzed.

The SFG spectra were acquired in situ for each potential at the C-H stretch region from 2750 cm\(^{-1}\) to 3300 cm\(^{-1}\). Molecular orientation was determined by analysis of polarization-dependent SFG spectra for the ppp andssp polarization. Analysis was performed for potentials within the double layer region as determined on cyclic voltammetry.

Variations of the peaks intensities indicate that the cation changes orientation as a function of electrode potential. Different changes in orientations were observed between [BMIM][PF_6] and [BMIM][BF_4]. A model of the molecular orientation at the electrode surface is presented based on the SFG and electrochemical analysis.