

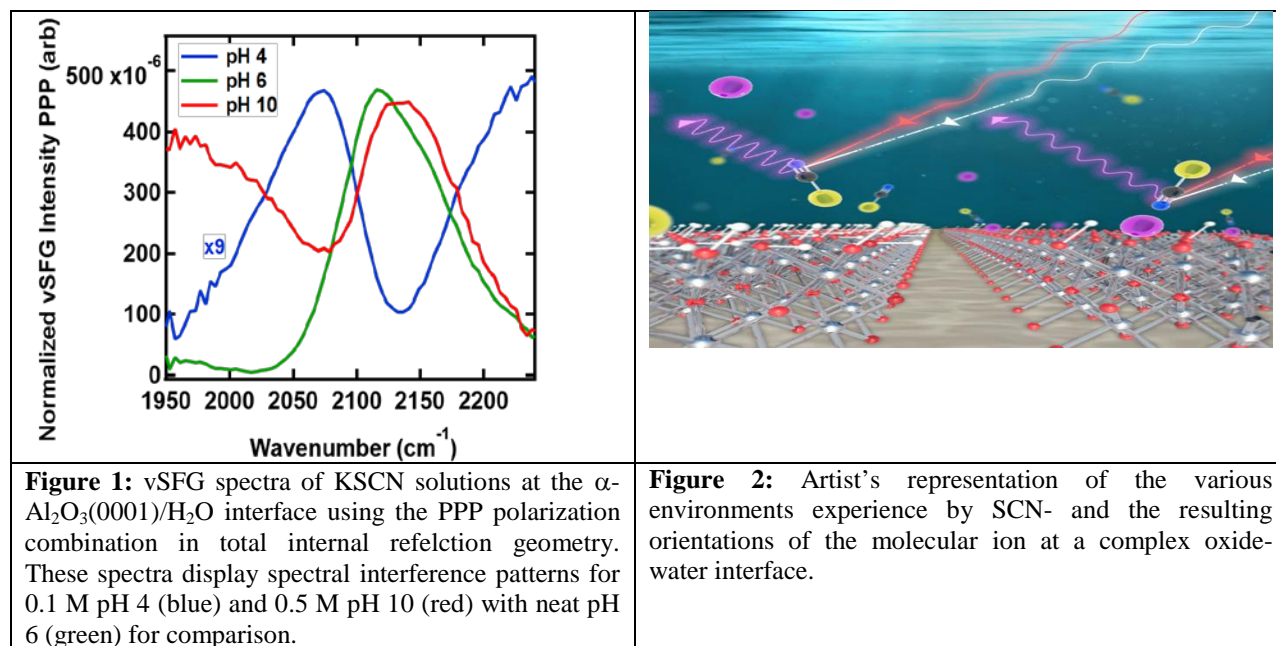
Sept 1, 2019 – Aug 31, 2019

1. PRF#: 58559-ND5

2. Project Title: "Investigating Complex Solid-Liquid Interfaces Using the Vibrational Spectroscopy and Dynamics of Molecular Ions"

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Unlike metal or semiconductor electrodes, the surface charge resulting from the protonation or deprotonation of insulating mineral oxides is highly localized and heterogeneous in nature. To understand such complex environments, we deployed the Stark active $C \equiv N$ stretch of potassium thiocyanate as a molecular probe of the heterogeneity of the interfacial electrostatic potential at the $\alpha\text{-Al}_2\text{O}_3(0001)/\text{H}_2\text{O}$ interface. Changes in the electrostatic potential were then tracked *via* Stark shifts of the vibrational frequency of the thiocyanate stretch. Our vSFG measurements showed that we can simultaneously measure the vSFG response of SCN^- ions experiencing different environments such as charged and neutral surface sites. We assign a local potential of +308 mV, 0 mV and -154 mV to positively, neutral and negatively charged aluminol groups that are present at pH = 4 and pH = 10, respectively. Thiocyanate anions at positively charged surface sites, negatively charged surface sites, and participating in contact ion pairing adopt similar orientations, and are oppositely oriented relative to thiocyanate ions near neutral surface sites. All four species followed Langmuir adsorption isotherms. MD-DFT simulations of SCN^- near the neutral $\alpha\text{-Al}_2\text{O}_3(0001)/\text{H}_2\text{O}$ interface showed that the vSFG response in the $C \equiv N$ stretch region originates from a SCN-H-O-Al complex, supporting the surface site specificity of these experiments. Vibrational sum frequency generation (vSFG) measurements performed in the OH stretching region suggest that thiocyanate species organize interfacial water similarly to halide ions.



To our knowledge this is the first spectroscopic measurement of local potentials associated with a heterogeneously charged surface. The traditional method of determining the surface potential, the zeta potential technique, yields a surface averaged result and ignores the possible heterogeneity of the surface potential. This work uses vibrational Sum Frequency Generation spectroscopy to correlate the response of SCN^- ions to measure the local potential *in situ* of an alumina/water interface. The spectra reveal the heterogeneous nature of charge distributions at a mineral oxide-aqueous interface caused by the protonation and deprotonation of surface hydroxyl sites. The ability to probe the evolution of local charges *in situ* could provide vital insight into many industrial, electrochemical, and geochemically relevant interfaces.

The results of this PRF supported for research have been submitted for publication (Probing Heterogeneous Charge Distributions at the $\alpha\text{-Al}_2\text{O}_3(0001)/\text{H}_2\text{O}$ Interface, Stefan M. Piontek, Mark DelloStritto, Bijoya Mandal, Tim Marshall, Michael L. Klein²⁻³, and Eric Borguet) and are currently under review.

This grant has opened up a new avenue of research for this PI and his students. The graduate student, Stefan Piontek, who led the work successfully defended his doctoral dissertation and was recruited to be a post-doctoral fellow in Germany as part of a multi-institution effort to investigate solvation phenomena.