Notice of the Final Oral Examination
for the Degree of Doctor of Philosophy

of

SANDRA ROY

MSc (University of Victoria, 2012)
BSc (Université Laval, 2010)

“Distinguishing and Correlating Surface and Bulk Behaviour Using Linear and Nonlinear Vibrational Spectroscopy”

Department of Chemistry

Monday, December 18, 2017
3:00 P.M.
Elliott Building
Room 305

Supervisory Committee:
Dr. Dennis Hore, Department of Chemistry, University of Victoria (Supervisor)
Dr. Fraser Hof, Department of Chemistry, UVic (Member)
Dr. Irina Paci, Department of Chemistry, Uvic (Member)
Dr. Stephanie Willerth, Department of Mechanical Engineering, UVic (Outside Member)

External Examiner:
Dr. Zhan Chen, Department of Chemistry, University of Michigan

Chair of Oral Examination:
Dr. Rogerio de Sousa, Department of Physics, UVic

Dr. David Capson, Dean, Faculty of Graduate Studies
Abstract

Infrared absorption, Raman scattering and sum frequency generation were used as vibrational probes of different features of interfacial systems including the ability to measure surface and bulk effects. Two-dimension correlation analysis was used to study the relationship between the spectral response of the different techniques. Attenuated total reflection absorption, bulk Raman scattering and sum frequency generation were used to study the adsorption of ethanol–water mixture on fused silica. With the use of two dimension correlation analysis, interesting results were observed concerning the behavior of the surface in respect to the bulk. Surface concentration of ethanol were concluded to be higher than in the bulk indicative of competitive adsorption. Furthermore, at low concentration ethanol was shown to adsorb to the surface in dimers, to then form a bilayer of strongly oriented ethanol molecules at higher concentration. At highest concentration, this bilayer is disturbed, leaving only one layer at the surface of oriented ethanol molecules. The same spectroscopic techniques were applied to pressure sensitive adhesives of different composition while drying on a sapphire surface. The presence or absence of acrylic acid in the material was shown to alter the reorientation at the surface while drying. In the case where no acrylic acid is present, the orientation of the polymer at the surface was driven by the packing of the molecules at the surface. When acrylic acid was present in the pressure sensitive adhesive, reorientation occurred much faster and was caused by strong hydrogen bonding with the surface of the sapphire. An increase in acrylic acid composition, increased the rate of reorientation. An experimental set up was constructed to specifically study interfaces with a nonuniform distribution within the plane of the surface. This allows for concomitant measurement of polarized total internal reflection Raman scattering and sum frequency generation spectroscopy along with bright field imaging and cross polarized imaging. This set up was used to study the L-histidine crystal in situ adsorbed on fused silica. The polarized experiments along with calculations allowed for a more in-depth analysis of the crystal orientation effect on the birefringence, the Raman and the sum frequency generation.