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

of

PAUL COVERT

MSc (Oregon State University, 2001)
BA (Reed College, 1995)

“Examination of Aqueous Interfaces with Mineral and Polymer Surfaces by Conventional and Phase-sensitive Sum-frequency Generation Spectroscopy”

Department of Chemistry

Wednesday April 22, 2015
10:00 A.M.
Engineering and Computer Science Building
Room 130

Supervisory Committee:
Dr. Dennis Hore, Department of Chemistry, University of Victoria (Supervisor)
Dr. David Harrington, Department of Chemistry, UVic (Member)
Dr. Alex Brolo, Department of Chemistry, UVic (Member)
Dr. Robie Macdonald, Institute of Ocean Sciences, Fisheries and Oceans Canada (Outside Member)

External Examiner:
Dr. James Donaldson, Department of Chemistry, University of Toronto

Chair of Oral Examination:
Dr. Stephen Neville, Department of Electrical and Computer Engineering, UVic

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

The molecular structure of solvent and adsorbates at naturally occurring solid-liquid interfaces is a feature that defines much of the chemistry of the natural environment. Because of its importance, this chemistry has been studied for many decades. More recently, nonlinear optical techniques have emerged as a valuable tool for non-invasive investigation of environmental interfaces, in part because of their inherent surface specificity. Solid-aqueous interfaces are complex regions in which chemical and electrostatic forces combine to drive adsorption processes. Second-harmonic generation and sum-frequency generation (SFG) spectroscopies have been employed by many groups to investigate water structure at these interfaces over a range of pH and ionic strength environments. In this thesis, I report results of further investigation of water structure adjacent silica, fluorite, polystyrene, and poly (methyl methacrylate) surfaces in the presence of varying concentrations of Na+ and Cl-. A model is developed to describe the SFG response from the fused silica-solution interface as ionic strength is increased. This model reveals both details of interfacial water structure and the interplay between second- and third-order optical responses present at charged interfaces. In context of this model, water structure at the three other interfaces is discussed.

Knowledge of the phase of the SFG response provides additional surface structural information that can be related to the polar orientation of a molecule or functional group, for example, a ip in the orientation of water at an interface. Methods to capture the phase information at exposed interfaces are well established, but buried interface phase measurement remains a challenge. Therefore, I focused on development a systematic method for buried interface phase measurement. In this thesis, I demonstrate improvements in the precision and accuracy of two phase-sensitive SFG techniques for measurement of exposed interfaces. Results from efforts to extend the theory to the buried interface are presented, along with an examination of the challenges encountered along the way.