

## Water Spectroscopy at Solid/Liquid Interfaces: Hydrogen Bonding and Local Structure

Diedrich Schmidt,<sup>a</sup> Michio Niwano,<sup>b</sup> Kazushi Miki<sup>c</sup>

<sup>a</sup>International Center for Young Scientists, National Institute for Materials Science, Tsukuba, 305-0044, Japan

<sup>b</sup>Research Institute of Electrical Communication, Tohoku University, Sendai, 980-8577, Japan

<sup>c</sup>National Institute for Materials Science, Tsukuba, 305-0044, Japan

Molecular interactions in water are extremely important and responsible for a wide-range of behavior seen in many phenomena including ion distributions at liquid-liquid interfaces,<sup>1</sup> molecular structuring within liquid water,<sup>2-4</sup> and long-range hydrophobic interactions that affect the mediation of various phenomena such as adhesion, protein folding, and colloidal stability.<sup>5</sup>

Classically, water has been treated as either continuum or mixture models. Recently, a generally accepted model of liquid water has been to consider it as a mixed-state of assorted cluster geometries. Common techniques used to investigate the structural properties of water and aqueous solutions include neutron diffraction, X-ray diffraction (XRD), and spectroscopic methods. Raman and infrared absorption spectroscopies are particularly well-suited for studying the local structuring of water molecules under standard temperature and pressure conditions.

This work focuses on examining the vibrational spectra of liquid water at solid/liquid interfaces in an effort to understand how such interfaces affect the clustering properties and geometries of water. Changes in the vibrational modes of water as a function of distance from a sample are probed using Raman spectroscopy. However, to obtain surface sensitive information about possible structural changes of water under various conditions such as ionic species, concentration, and voltage dependence, we use multiple internal reflection infrared absorption spectroscopy (MIR-IRAS).

Raman and MIR-IRAS spectra are deconvoluted and assigned according to the Hydrogen-bonding description method developed by Ohno *et al.* Results are discussed with an emphasis on changes in the Hydrogen-bonding, i.e. local structuring, of water clusters at solid/liquid interfaces. Recent results of a water/Nafion® interface are in agreement with previous experiments on polyvinyl alcohol gels that exhibited exclusion zones and were explained by the possibility of structured water at the gel/liquid interface.<sup>6</sup> Additional MIR-IRAS experiments comparing the spectral analysis of KCl and NaCl water solutions indicate that K<sup>+</sup> ions have a more disruptive effect at the solid/liquid interface than Na<sup>+</sup> ions, consistent with the hydrated K<sup>+</sup> ion behaving as a hydrophobic molecule and causing collapse of structured water, leading to increased local water mobility,<sup>7</sup> and thus altering the surface reflection properties of the MIR prism.

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