

Sum Frequency Generation Spectroscopy of the Aqueous Interface: Ionic and Soluble Molecular Solutions

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The liquid interface of aqueous solutions is of central importance to numerous phenomena from cloud processing of combustion generated oxides to corrosion degradation of structural materials to transport across cell membranes. Despite the importance of this interface, little molecular-level information was known about it prior to the last decade-and-a-half. Molecular level information is important not only for a fundamental understanding of processes at interfaces, but also for predicting methods for diminishing deleterious effects. Recently, the nonlinear spectroscopic method, sum frequency generation (SFG), has been applied to the investigation of the structure of the liquid interface. This review focuses on the liquid-air interface of aqueous solutions containing soluble, ionic species - H_2SO_4 , HNO_3 , HCl , alkali sulphates and bisulphates, NaCl , and NaNO_3 - as well as soluble molecular species - glycerol, sulphuric acid, and ammonia. Ionic materials influence the structure of water at the interface through an electric double layer which arises from the differential distribution of anions and cations near the interface. Due to the extreme size of the proton, the strongest field is generated by acidic materials. As the concentration of these ionic materials increases, ion pairs form diminishing the strength of the double layer. This enables the ion-pair complex to penetrate to the interface and either displace water or bind it into hydrated complexes. Soluble materials of lower surface tension partition to the interface and either displace water from the interface or bind water into hydrated complexes. In particular, the ammonia-water complex on aqueous solutions is observed and it is determined to tilt $34 - 38^\circ$ from the normal.