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Mechanism of Selective Adsorption of Ions to Aqueous Interfaces: Graphene/Water vs. Air/Water RICHARD SAYKALLY, University of California-Berkeley — The behavior of ions at aqueous interfaces has been a subject of much controversy for over a century. By exploiting the strong charge-transfer-to-solvent (CTTS) resonances of selected anions in aqueous electrolytes, their adsorption properties have measured by deep UV-SHG spectroscopy methods for both air/water and graphene/water interfaces. Temperature and concentration dependences determined by both experiment and computer simulations for the air/water case reveal that the strong interfacial adsorption observed for weakly hydrated ions is enthalpically driven by hydration forces and impeded by a novel entropy effect(capillary wave suppression). Extension of this approach to the water-graphene interface reveals a surprising similarity to the air-water case, albiet with different mechanistic details. Our recent development of a broadband deep UV SFG spectroscopy technique has produced detailed CTTS spectra of interfacial ions, for which comparisons with bulk CTTS spectra provide additional new insights.

D.E. Otten, P. Shaffer, P. Geissler, R.J. Saykally, *Elucidating the Mechanism of Selective Ion Adsorption to the Liquid Water Surface*, PNAS **109**, 701(2012).

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