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Broadband Deep UV Spectra of Interfacial Aqueous Iodide

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The behavior of ions at aqueous interfaces influences vital processes in many fields, but has long remained a subject of controversy. Over the past decade, counterintuitive surface concentration enhancement of several ions in aqueous solution has been demonstrated via nonlinear laser spectroscopy and mass spectrometry. While the evidence for significant ion enhancement at the air-water interface is convincing, the mechanism remains incompletely understood. Toward this end, we present the full charge-transfer-to-solvent (CTTS) spectrum of interfacial aqueous iodide measured in a single laser shot with a newly developed broadband deep UV-SFG technique, clearly revealing a ˜7 nm redshift and a significant linewidth narrowing relative to bulk solution spectra. KI and NaI solutions yield indistinguishable results. Additionally, we observe a dramatic change in the relative intensities of the J = 3/2 and J = 1/2 CTTS transitions. \Rizzuto, A.M., Irgen-Gioro, Shawn, Eftekhari-Bafrooei, A., Saykally, R. J. "Broadband Deep UV Spectra of Interfacial Aqueous Iodide" *J. Phys. Chem. Lett.*, **7**, 3882-3885 (2016).\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).