

## DECIPHERING THE EXCITED-STATE VIBRATIONAL SIGNATURES OF THE WATER-IODIDE BINARY COMPLEX THROUGH QUANTUM SIMULATIONS.

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The water-iodide monomer ( $I^-H_2O$ ), nominally the simplest of the halide-water complexes, challenges our current understanding of ion hydration. Most notably, this seemingly simple complex displays multiple resonant vibrational transitions, a low tunneling barrier, and a strong transition dipole moment along the bound OH-I coordinate. These effects combine to yield spectroscopic signatures that deviate strongly from traditional harmonic analyses and are even difficult to qualitatively reproduce with anharmonic methodologies. Among these signatures is a quartet of peaks in the 3300 – 3500  $cm^{-1}$  range that is unexplained using traditional single-photon spectroscopy. Challenging both experiment and theory alike, this situation required the interpretation of newly developed IR-IR 2-color photodissociation spectroscopy that probes well below the dissociation threshold. In this work, we use both exact eigensolver techniques and a newly developed vibrationally adiabatic model, along with a new potential energy surface<sup>a</sup> to computationally explore the excited-state spectra. The resulting analyses identify the source of the strength of the resonant transitions, directly assign the vibrational and rotational spectroscopic signatures, and discern the electronic origin of these surprising effects in this fundamental model of ion hydration.

<sup>a</sup>Bajaj, P. Gotz, A.W., Paesani, F. *Journal of Chemical Theory and Computation*, 2016, 12 (6), 2698-2705.