HIGH RESOLUTION SPECTROSCOPY IN A 5K CRYOGENIC ION TRAP: REVISITNG THE OH STRETCHING BANDS OF THE H_20 AND HDO ISOTOPOLOGUES OF THE BINARY COMPLEXES WITH IODIDE

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We report fully rotationally resolved spectra of the $I^-(H_2O)$ and I^-(HDO) ion-molecule complexes measured by predissociation spectroscopy in a 3D cryogenic ion trap. The spectra were obtained by excitation with a single-frequency, cw infrared laser (TOPAS by Toptica Corp.) directly into the trap. The formation of bare iodide photoproducts was observed by first ejecting the bare ion from the trap by excitation at the secular frequency, followed by formation of I^- photoproducts on the timescale of 40 ms. The product ions were then detected by injecting the contents of the trap into a time-of-flight mass spectrometer. The spectra reveal a plethora of very sharp transitions associated with overlapping rotational band structures arising from at least three vibrational transitions. Despite the fact that this excitation occurs about 300 cm^{-1}above the dissociation threshold, the lines are very narrow, revealing very long lived (ca. 2 ns) rovibrational levels. Analysis of these patterns quantifies the anharmonic behavior of this system arising from tunneling as well as intramolecular mode coupling involving soft modes and the bending overtone.