

VIBRATIONAL SIGNATURES OF LARGE AMPLITUDE MOTIONS FOR THE SHACKLED HYDRONIUM ION NESTED IN 18-CROWN-6 ETHER USING D<sub>2</sub> TAGGING

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The diffuse spectra arising from the excess proton in dilute acids suggests that its behavior is highly dependent on the local environment surrounding it. In this work, we report how the spectra of the H<sub>3</sub>O<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, and CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> ions respond when docked to the rigid, tri-coordinated binding pocket of the 18-crown-6 ether using cryogenic ion vibrational predissociation (CIVP) spectroscopy with D<sub>2</sub> tagging at 10 K. The H<sub>3</sub>O<sup>+</sup>•18-crown-6 ether complex displays a broad (350 cm<sup>-1</sup> FWHM) unstructured band arising from the OH stretching fundamentals, which is significantly broader than the corresponding band (125 cm<sup>-1</sup> FWHM) in the Eigen cation (H<sub>9</sub>O<sub>4</sub><sup>+</sup>) spectrum. Perdeuterated isotopologue studies for both systems yield sharper bands with clear multiplet structures, indicating that the broadening arises from nuclear quantum effects. The key displacements underlying this coupling were explored using the vibrationally adiabatic scheme introduced by McCoy in the context of similar broadening in the Ca<sub>2</sub><sup>+</sup>OH<sup>-</sup>(H<sub>2</sub>O)<sub>n</sub> system.<sup>a</sup>

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<sup>a</sup>Christopher J. Johnson, Laura C. Dzigan, Arron B. Wolk, Christopher M. Leavitt, Joseph A. Fournier, Anne B. McCoy, Mark A. Johnson, *J. Phys. Chem. A* **118**, 2014.