

## SPECTROSCOPIC MANIFESTATION OF VIBRATIONALLY-MEDIATED STRUCTURE CHANGE IN THE ISOLATED FORMATE MONOHYDRATE

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The breadth of the OH stretching manifold observed in the IR for bulk water is commonly attributed to the thermal population of excited states and the presence of many configurations within the water network. Here, I use carboxylate species as a rigid framework to isolate a single water molecule in the gas phase and cold ion vibrational pre-dissociation spectroscopy to explore excited state contributions to bandwidth. The spectrum of the carboxylate monohydrate exhibits a signature series of peaks in the OH stretching region of this system, providing an archetypal model to study vibrationally adiabatic mode separation. Previous analysis of this behavior accounts for the extensive progression in a Franck-Condon formalism involving displaced vibrationally adiabatic potentials<sup>a,b</sup>. In this talk I will challenge this prediction by using isotopic substitution to systematically change the level structure within these potentials. This picture quantitatively accounts for the diffuse spectrum of this complex at elevated temperature providing a convenient spectroscopic reporter for the temperature of ions in a trap.

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<sup>a</sup>E. M. Myshakin, K. D. Jordan, E. L. Sibert III, M. A. Johnson *J. Chem. Phys.* 119, 10138 (2003).

<sup>b</sup>W.H. Robertson, et al. *J. Phys Chem.* 107, 6527 (2003).