UNDERSTANDING COMPLEX SPECTRAL SIGNATURES OF EMBEDDED EXCESS PROTONS IN MOLECULAR SCAFFOLDS WITH THIRD ORDER CORRECTIONS TO THE HARMONIC POTENTIAL SURFACE

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Overtones and combination bands observed in vibrational predissociation spectra of cold ions can often be anticipated by expanding the potential energy surface to third order. This is achieved by relating the third derivatives to the matrix elements that couple the allowed and forbidden states in the harmonic basis. Such a strategy has been successful in predicting Fermi resonances in formic acid clusters and some charged H-bonded complexes. Furthermore, third order couplings have been used to develop a vibrational adiabatic model in which excitation of a bright state is distributed over a Franck-Condon envelop of a lower energy mode, such as a water rocking against triatomic domains of molecular anions. Previous applications include the analysis of long vibrational progressions of soft modes in the OH stretching region of the actetate-water binary complex. Here we explore to extent to which this order of correction captures the irregular patterns associated with intramolecular proton bonds.