Variations in the electron detachment spectra of $F^-\cdots H_2O$ Anion induced by proton motion

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For the understanding of the solvation structure of ions in the aqueous phase, one has to define observables that change with solvation structure. In the condensed phase due to complex thermal fluctuation, the definition of the structure becomes very unambiguous. Therefore, the researchers in the gas phase community have studied size selected gas phase charged clusters to help decode the complexity. Through the comparison with theoretical simulations, vibrational spectra of anion clusters have given information toward the geometrical structure of these clusters. On the other hand, photodetachment and X-ray absorption spectra are used to probe the electronic structure of anions in the aqueous phase. In most previous studies on the photodetachment spectra, the simulation of the spectra was performed by calculating the vertical detachment energies at equilibrium geometries, at cluster cut out from classical trajectories or at zero-point vibration distributions. Here, we aim to provide new insight from the simulation of vibrational state dependent photodetachment spectra for $X^-\cdots(H_2O)_n$ anion, where X= F, Cl, Br. Utilizing the reflection principle, we simulated the photodetachment spectra from different vibrational excited states for F^-H_2O, Cl^-H_2O and Br^-H_2O.[1] From these spectra, we can observe changes in the electron distribution between the anion and neutral $X\cdots H_2O$ system that are induced by vibrational excitation. Notably, for F^-H_2O, the excitation of the ionic hydrogen bonded (IHB) OH stretching vibration causes a large tail on the low energy side of the photodetachment spectra compared to the detachment from the zero-point vibration state. This low tail shows that IHB OH stretching vibration of F^-H_2O causes charge delocalization from F^- to the oxygen atom in H_2O and the photodetachment from $FH\cdots OH^-$ occurs at lower energies.