Exploring Proton Hydration in the Gas Phase Through Infrared Spectroscopy

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The physics of proton hydration is investigated based on experimental vibrational spectra of cryogenically cooled gas-phase water clusters containing an excess proton. We compare the OH stretch modes of the hydronium ion to those of the Eigen ion and the distorted clathrate structure $H^+(H_2O)_{21}$. Scanning the potential energy of the hydronium ion's OH bond as a function of hydration shows that the effects of hydration are localized to the first two hydration shells. Decomposition of the interaction energy of the hydronium ion with its hydration shells suggests that electrostatics and induction are the dominant components leading to a field-effect regime. Reduced-dimensional second-order vibrational perturbation theory shows a sequential growth in the cubic coupling between the three OH stretch modes of the hydronium ion as the first two hydration shells are added. We conclude that the large experimentally observed red-shifts in the hydronium ion's OH stretch modes due to hydration arise from a field-effect, one consequence of which is the departure of the OH bond potential from the quasi-harmonic nature observed in the bare hydronium ion. Finally, we briefly mention our current work exploring the Grotthuss proton relay mechanism in water using the same approach.