ZWITTERIONS AND CAGES: NEW RESULTS FOR NEUTRAL AND PROTONATED WATER CLUSTERS

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Commonly held wisdom stipulates that hydrogen bonds between water molecules stabilize a structure by $\sim 5\frac{kcal}{mol}$ apiece. Therefore aqueous clusters that differ only by the direction of hydrogen bonds, but otherwise have the same number of H-bonds and placement of oxygen atoms should have roughly the same energy, and spread of energies should be far less than $\sim 5\frac{kcal}{mol}$ per water molecule. This belief lies behind calulations performed to date for the $(\mathrm{H_2O})_{20}$ dodecahedron, and the associated $\mathrm{H^+(H_2O)_{21}}$ formed by adding a hydronium ion, in which only one, or a handful of arbitrarily chosen hydrogen bond arrangements were selected for study. Presumably the H-bond arrangement in the dodecahedral cage has minor effect on the chemistry of this cluster. In this work we show that H-bond topology strongly affects the structure and energy of $(\mathrm{H_2O})_{20}$. This was implicated in our previous studies of $(\mathrm{H_2O})_{20}$ [a] [b] using empirical and semi-empirical models, and is now confirmed by *ab initio* electronic structure calculations. Furthermore, we find that the H-bond arrangement strongly affects not just the structure and energy of $(\mathrm{H_2O})_{20}$, but also its *chemistry*. In fact, a seeming innocuous rearrangement of the H-bonds in $(\mathrm{H_2O})_{20}$ leads to spontaneous autoionization of this structure, producing spatially separated hydrogen and hydroxide ions in the cluster. Thermal behavior and zwitterion formation in smaller aqueous clusters is also considered.

[a] Shannon McDonald, Lars Ojamäe and Sherwin J. Singer, J. Phys. Chem. A **102**, 2824 (1998)

[b] Jer-Lai Kuo, James V. Coe, Sherwin J. Singer, Yehuda B. Band, and Lars Ojamäe, J. Chem. Phys. **114**, 2527 (2001)