ELSEVIER

Journal of Molecular Liquids 110 (2004) 105–122

journal of MOLECULAR LIQUIDS

www.elsevier.com/locate/molliq

Structure and dynamics of hydrated ions—new insights through quantum mechanical simulations

Bernd M. Rode[a,*], Christian F. Schwenk[a], Anan Tongraar[b]

[a]*Department of Theoretical Chemistry, Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria*

[b]*School of Chemistry, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand*

Abstract

For more than three decades, classical statistical mechanics simulations have been employed in the study of pure liquids and solutions, often revealing valuable details of the composition and structure of these systems. The question whether the basic assumptions underlying the classical simulations, in particular the neglect of higher *n*-body effects, are justified and do not have any adverse effect on the results could only be answered after the progress in soft- and hardware enabled the performance of extended quantum-mechanics-based simulations. In the past few years, on the basis of a systematic investigation of ion solvation by means of this new technique, the importance of the 'quantum effects' has been identified and their inclusion has been clearly recognised as an often crucial condition to obtain accurate structural data and a reliable description of the solvation dynamics of ions. By now, quantum-mechanics-based simulations have justified their high computational demands by giving access to a large set of otherwise hardly accessible data such as the detailed molecular structure of microspecies formed in solution and ligand exchange processes at the picosecond time scale. From such simulations, and with the help of appropriate evaluation and visualisation tools, new insights have been obtained into the molecular pathways of reactions in solution for a series of main group and transition metal ions as well as for some anions, forming a new theoretical basis for the interpretation of experimental data in terms of reactivity and mechanisms.