Computational-chemistry studies of water clusters and ice

Lars Ojamäe

Department of Chemistry, IFM, Linköping University, 581 83 Linköping, Sweden,
lars@ifm.liu.se,
WWW home page: http://ww.ifm.liu.se/compchem

Abstract. Computer modelling of chemical systems such as ice crystals, water clusters and surfaces has been performed, and it is demonstrated how a combination of quantum-chemical computations and statistical simulations can be used to study and predict thermodynamic properties and phase transitions. For example, the most stable form of hexagonal ice as well as its H-bond order-disorder temperature can be derived, and the calculations provide insight regarding the structure and dynamics in water clusters and in liquid water.

1 Introduction

When studying chemical thermodynamical processes using computer simulations at the molecular level, one is faced with the problem of both representing the intermolecular forces in a realistic fashion and at the same time enabling a proper statistical sampling of the many-molecule system. The molecular interactions can be obtained from quantum-chemical calculations and the statistics provided through molecular dynamics (MD) or Monte Carlo (MC) simulations, but to use the two methods in combination is computationally very demanding. Still, in order to obtain a correct picture of chemical phenomena such a route can be necessary, which we here exemplify by considering properties and phase transitions of water in the solid, liquid and gaseous states and at surfaces.

2 Computations

The ice phase present in nature on earth, ice Ih, has a structure where the oxygens are ordered on a hexagonal lattice, whereas the protons are disordered, i.e. the hydrogen bond arrangement between neighbouring water molecules is almost a random quantity. Pauling showed in 1935 that for N water molecules there are about $(3/2)^N$ ways to realize such a network, and from this relation it is possible to estimate the configurational entropy. This type of relation is valid only for a completely random network, a "proton glas", where all different H-bond arrangements possess equal lattice energies. Ever since Pauling's proposition there have been vivid discussions whether the network is truly random, and

whether there exists a phase transition to a proton-ordered ice phase when the temperature is lowered.

In our studies of ice Ih [1, 2], we generated representative H-bond topologies, for which extensive quantum-chemical DFT calculations were performed. Using these data, structural characteristics of the H-bond topology that were important for stabilizing the lattice energy were identified, and thereby structure-topology relations could be derived. These relationships provided a basis for the computation of the thermodynamic properties of ice. By applying the the topology-energy relationships in Monte Carlo simulations it was possible to predict the proton-ordering phase transition temperature, to reproduce the experimental configurational entropies, and furthermore to firmly establish the structure of the proton-ordered ice phase, ice XI.

It was found that above the disorder temperature (just below 100K) the H-bond is not entirely random, not even close to the melting point, as evidenced by the computed entropy. The ice XI phase was confirmed to be an orthorombic ferroelectric crystal.

The thermodynamics of water clusters is also intriguing [3]. In mass spectra certain cluster sizes appear particularly abundant: they constitute "magic numbers". Also here topology considerations joined with thermodynamic simulations provided valuable insight that may be of relevance for the liquid [4] as well as for the structures and equilibria of water clusters and surfaces [5, 6]. Cage-shaped clusters were found to be energetically at disadvantage compared to more dense structures, but the former could be favoured by entropy.

References

1. Hirsch, T. K., Ojamäe, L.: Quantum-chemical and force-field investigations of Ice Ih: computation of proton-ordered structures and prediction of their lattice energies. J. Phys. Chem. B **108** (2004) 15856–15864
2. Singer, S. J., Kuo, J-.L., Hirsch, T. K., Knight, C., Ojamäe, L., and Klein, M. L.: Hydrogen-bond topology and the ice VII/VIII and ice Ih/XI proton-ordering phase transitions. Phys. Rev. Letters **94** (2005) 135701
3. Öhrwall, G., Fink, R. F., Tchaplyguine, M., Ojamäe, L., Lundwall, M., Marinbo, R. R. T., Naves de Brito, A., Sorensen, S. L., Gisselbrecht, M., Feifel, R., Rander, T., Lindblad, A., Schulz, J., Borve, K. J., Sæthre, L. J., Mårtensson, N., Svensson, S., and Björneholm, O.: The electronic structure of free water clusters probed by Auger electron spectroscopy. J. Chem. Phys. **123** (2005) 054310
4. Wernet, Ph., Nordlund, D., Bergmann, U., Cavalleri, M., Odelius, M., Ogasawara, H., Näslund, L. Å., Hirsch, T. K., Ojamäe, L., Glatzel, P., Pettersson, L. G. M., and Nilsson, A.: The structure of the first coordination shell in liquid water. Science **304** (2004) 995–999
5. Lenz, A., Ojamäe, L.: A theoretical study of water clusters: the relation between hydrogen-bond topology and interaction energy from quantum-chemical computations for clusters with up to 22 molecules. Phys. Chem. Chem. Phys. **7** (2005) 1905
6. Lenz, A., Ojamäe, L.: On the stability of dense versus cage-shaped water clusters: quantum-chemical investigations of zero-point energies, free energies, basis-set effects and IR spectra of $(H_2O)_{12}$ and $(H_2O)_{20}$. Chem. Phys. Letters **418** (2006) 361–367