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Theoretical Chemistry

A new water force field was obtained recently from high-quality *ab initio* calculations of the binding energy of the water dimer in more than 2500 conformations and of the three-body interactions in the water trimer for three times as many conformations. The results of these calculations were fitted to an analytical function that can be used in simulations, while ensuring through additional calculations that this function has the correct long-range behavior. Accurate quantum computations of the vibration-rotation-tunneling levels of the water dimer and trimer from this force field gave very good agreement with the measured high-resolution spectra. The force field, including the many-body polarization and exchange interactions, was also used in molecular dynamics (MD) simulations of liquid water and reproduces a number of measured properties. It was found that the pair interactions alone cannot produce the structure of the dynamical hydrogen-bonded network in liquid water, see Figure 1. Especially the three-body interactions are essential to obtain the correct surroundings of the water molecules in the liquid, see Figure 2. None of the many existing empirical and *ab initio* force fields could simultaneously reproduce the properties of small water clusters and of the bulk liquid, so this development represents a breakthrough¹.

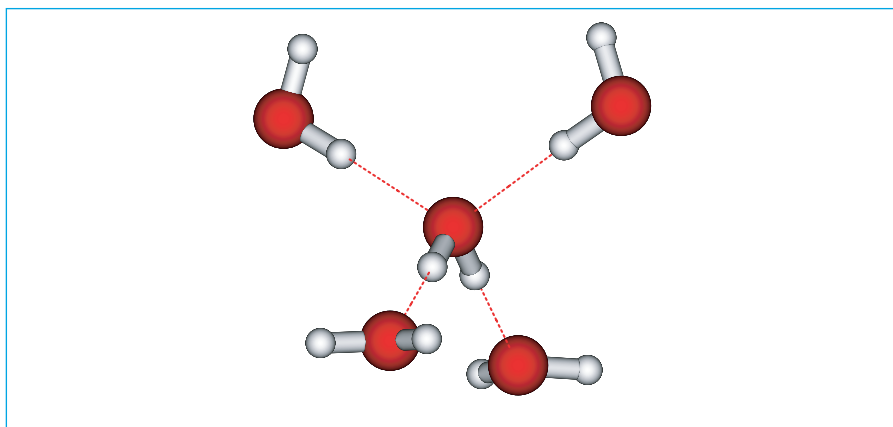


Figure 1 Surrounding of a water molecule by four hydrogen-bonded neighbors. Ice consists of a network of such tetrahedrons. Also in liquid water one finds such networks, but they are continuously being broken and reconstructed by the thermal motions.

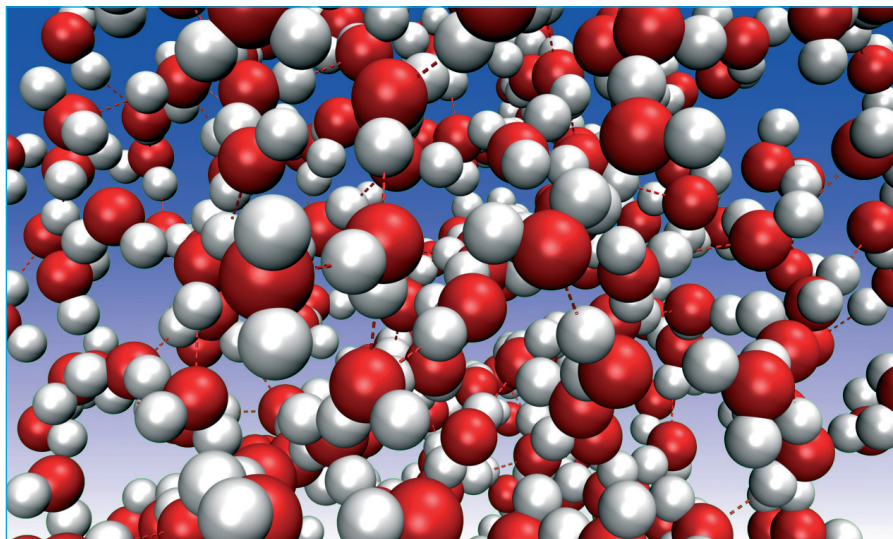


Figure 2 Snapshot of an MD simulation of water at room temperature with the new force field. The dashed lines indicate hydrogen bonds.