The hydration structures of F^- and Cl^- investigated by *ab initio* QM/MM molecular dynamics simulations

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Combined *ab initio* quantum mechanical/molecular mechanical (QM/MM) molecular dynamics simulations have been performed to investigate the hydration shell properties of F^- and Cl^-. The chemically most relevant region, the hydration sphere of the anions, was treated by Born–Oppenheimer *ab initio* quantum mechanics using D95V+, 6-31+G and D95V++ basis sets for F^-, Cl^- and water, respectively, while the remaining part was described by classical pair potentials. The QM/MM simulations have predicted average coordination numbers of 4.6 ± 0.2 for F^- and 5.6 ± 0.1 for Cl^-, in contrast to the corresponding values of 5.8 ± 0.1 and 5.9 ± 0.1 resulting from classical pair potential simulations. Within the first hydration shell of F^-, the QM/MM results indicate more flexibility of the hydration complex in which the $F^- \cdots H$–O bond appears to be linear. For the case of Cl^-, a combination of linear and bridged forms, together with a competition between the solvation of the ion and hydrogen bonding among water molecules, are observed.