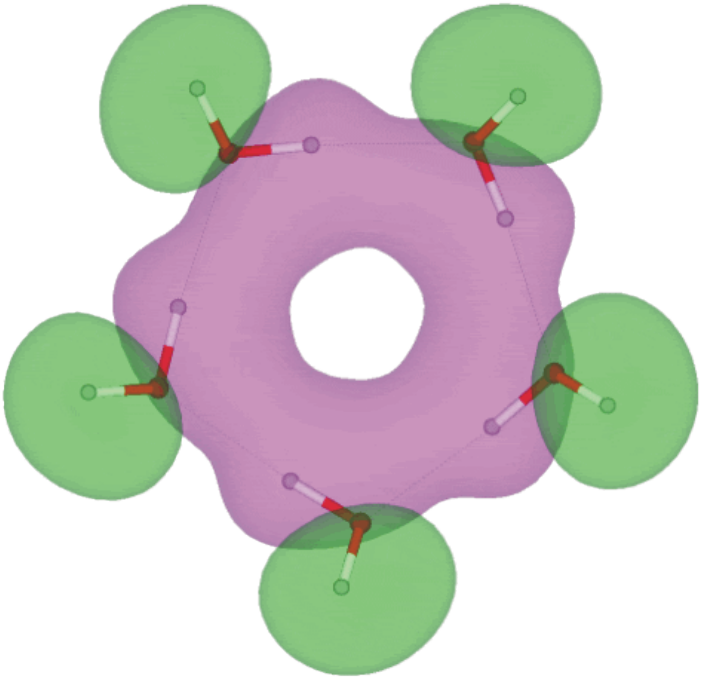
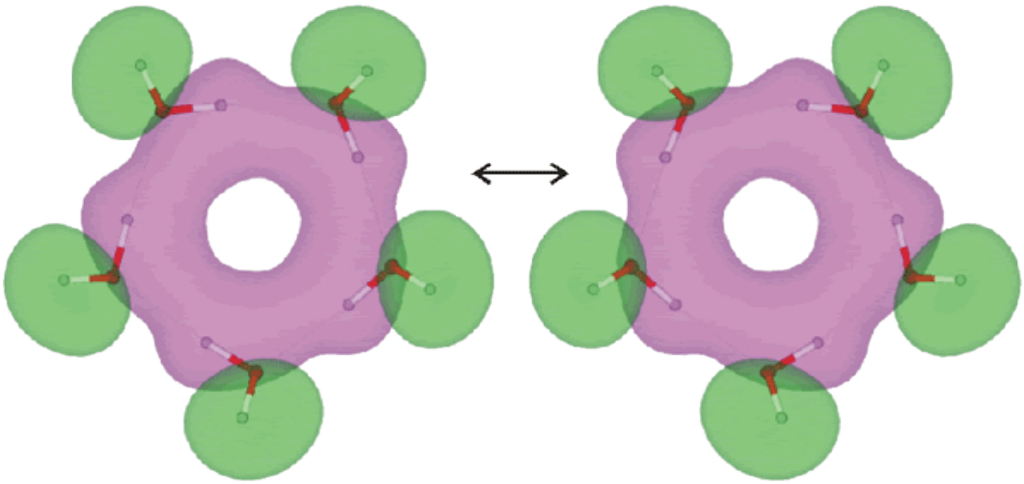
Molecular Orbitals for the Water Pentamer, $(H_2O)_5$



A water pentamer $(H_2O)_5$ structure. This is molecular orbital eleven out of twenty-five showing the electron overlap possible for extended hydrogen bonding; an interactive structure with orbitals is available (COW [Plug-in, ActiveX] only), also without orbitals (Jmol). The $(H_2O)_5$ structure is a local minimum-energy structure but not a global minimum for a pentamer[a] or even for a cyclic pentamer as all the non-hydrogen-bonded hydrogen atoms are *cis;* the global minimum for a water pentamer has a chiral mostly *trans* cyclic structure (Jmol) but also possesses a similar molecular orbital eleven (COW [Plug-in, ActiveX] only). The occupied molecular orbitals were calculated using the Restricted Hartree-Fock wave function (RHF) using the 6-31G** basis set. The presence of extensive molecular orbitals allows the possibility that this planar pentameric structure may be responsible for the absorption at about 270 nm noticed in water under certain circumstances where it is thought not due to impurities [1328]. For comparison, chains of water molecules give a calculated absorption at about 288 nm, but this should shift to shorter wavelengths when surrounded by further water molecules [2083].

For both of these cyclic pentamers, the bond energies indicate that cooperation of two hydrogen bonds increase the average bond strength by 22%, cooperation of three hydrogen bonds increase the average bond strength by 40-41% and cooperation of all five hydrogen bonds increase the average bond strength by 52-53%. Water pentameric clusters can be produced by bubbling inert gas through the liquid water followed by adiabatic expansion into a vacuum [837]. The vibrationally-averaged structure involving pseudorotation of the ring pucker is a flattened planar structure with C_{5h}symmetry.

The large orbitals indicated by semiempirical and density-functional computations [165] are supported by this *ab initio* method. Such orbitals, indicated in isolated clusters (that is, *in vacuo*), should be taken as indicative only of the type of orbitals that exist in liquid water clusters.



Synchronous oscillations of protons (as above) have been shown to be coupled to vibrations of the oxygen skeleton of the molecular ring, and the typical frequencies of the complex vibrations lie in the range of 230-330 cm^{-1} [2053].

Footnotes

[a] There are 161 topologically distinct hydrogen-bonded pentamer (that is, consisting of five molecules) arrangements of water possible [517]. A recent computational study gives this ring (as the global minimum) a puckered conformation with one free hydrogen bond approximately at right-angles to the plane of the ring [1713]. [Back]