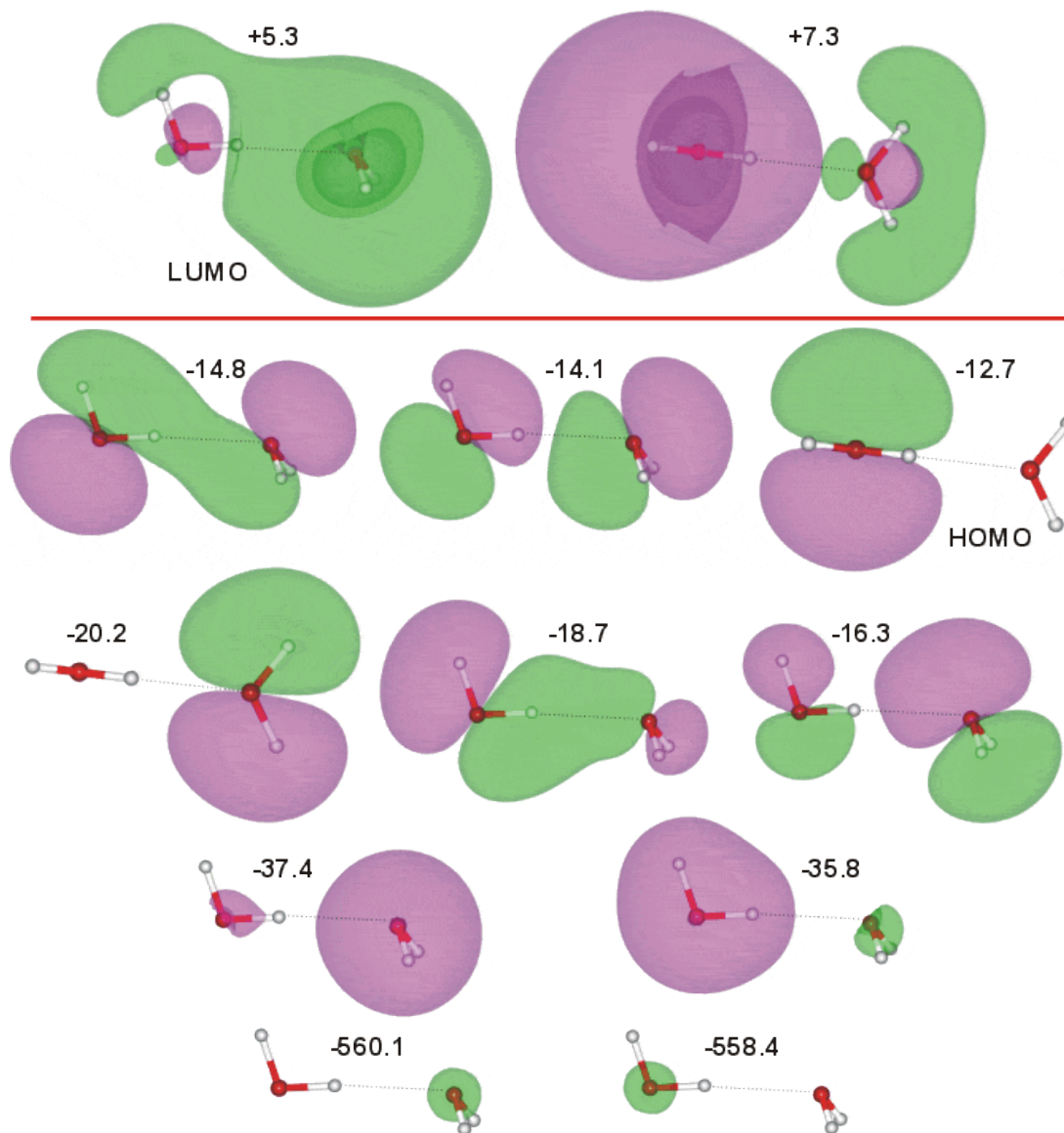
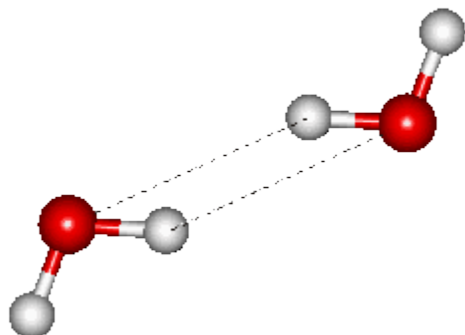


Molecular Orbitals for the Water Dimer (H₂O-H₂O)



The water (gas-phase) dimer has C_s symmetry molecular geometry. The occupied molecular orbitals were calculated using the Restricted Hartree-Fock wave function (RHF) using the 6-31G** basis set. The calculated energies are -560.1 eV (O-atom 1s proton acceptor), -558.4 eV (O-atom 1s proton donor), -37.4 eV ($2a_1$ proton acceptor), -35.8 eV ($2a_1$ proton donor), -20.2 eV ($1b_2$ proton acceptor; $0/b_2$ -19.48 eV [1450]), -18.7 eV (major $1b_2$ proton donor, minor $3a_1$ proton acceptor; b_2/a_1 -17.98 eV [1450]), -16.3 eV (major $3a_1$ proton acceptor, minor $1b_2$ proton donor; $(b_2/a_1)^*$ -15.41 eV [1450]), -14.8 eV ($3a_1$ proton donor, $1b_1$ proton acceptor; a_1/b_1 -13.66 eV [1450]), -14.1 eV ($3a_1$ proton donor, $1b_1$ proton acceptor; $(a_1/b_1)^*$ -12.91 eV [1450]) and -12.7 eV ($1b_1$ proton donor; $b_1/0$ -11.41 eV [1450]), the HOMO. Two of the orbitals show overlap across the hydrogen bond. The two lowest unoccupied orbitals, including the LUMO, are also shown (contributed by the $4a_1$ atomic

orbitals). The molecular orbitals of the two forms (C_S and C_1) proton-transferred dimers $H_3O^+ \cdots OH^-$ have also been calculated [1450].



At short distances ($<2.66 \text{ \AA}$), the doubly-hydrogen bonded C_i dimer (opposite) has been found to be more stable than the above C_S dimer [1029]. This dimer is normally about 3 kJ mol^{-1} less stable than the C_S dimer and is the transition structure for the interchange between the molecules being the hydrogen donor or acceptor [1462].

Interactive structures with orbitals are available (COW [Plug-in, ActiveX] only).

Source:<http://www1.lsbu.ac.uk/water/h4o2orb.html>