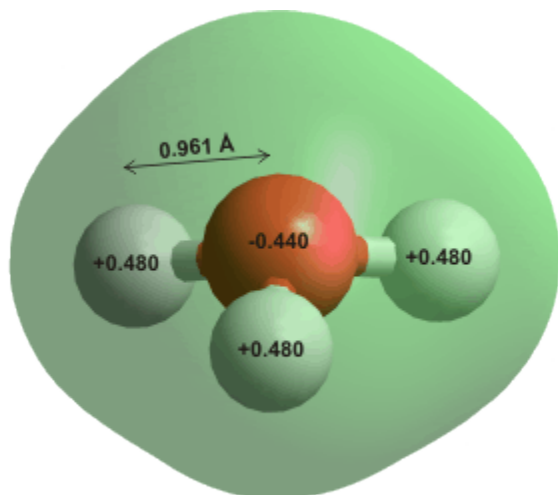


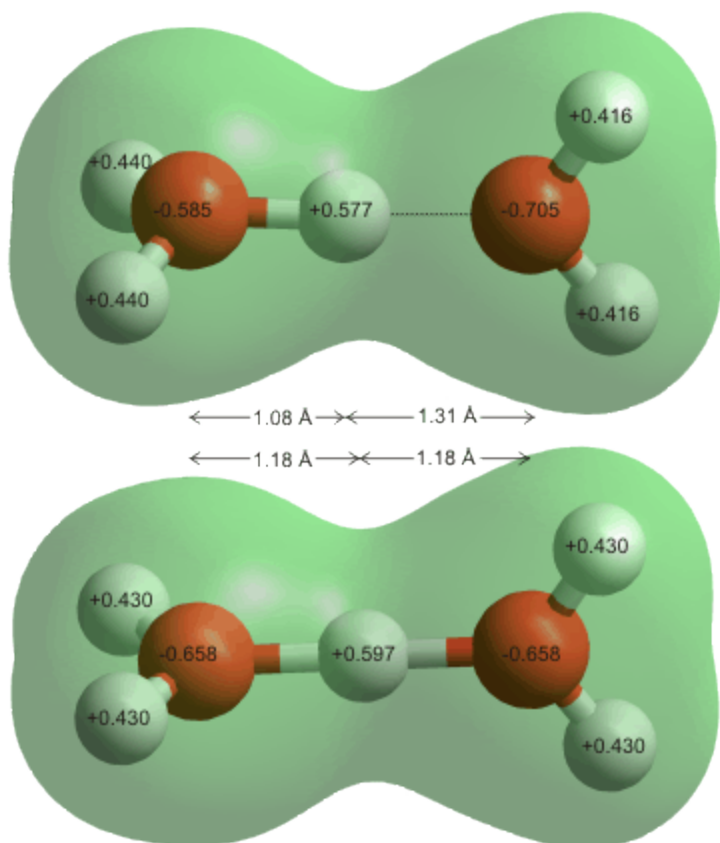
# Hydrogen ions

- ◀ The ionic product,  $K_w$
- ◀ pH
- ◀ Hydroxide ions
- ◀ Grotthuss mechanism



The bare hydrogen ion (a proton) readily hydrates<sup>f</sup> and cannot exist freely in solution. Initial hydration forms the oxonium ion ( $\text{H}_3\text{O}^+$ ) (sometimes called the hydrogen ion).<sup>d</sup> This has a flattened trigonal pyramidal structure (calculated gas phase values O-H bond length 0.961 Å, H-O-H angle 114.7°;<sup>e</sup> compare with the significantly different calculated liquid values of O-H bond length 1.002 Å, H-O-H angle 106.7° [709]) with  $C_{3v}$  symmetry and equivalent protons.  $\text{H}_3\text{O}^+$  has an effective ionic radius of 0.100 nm [1946], somewhat less than that of the  $\text{H}_2\text{O}$  molecular radius (0.138 nm). Its molar volume is  $-5.4 \text{ cm}^3 \text{ mol}^{-1}$  due to electrostriction [1946]. It forms the core of the 'Eigen' cation,<sup>a</sup> described later. The structure can invert (like a wind-blown umbrella) with an activation energy less than that of a hydrogen bond and this may occur as an alternative, or even preferred, pathway to rotation within a dynamic hydrogen bonded clusters.  $\text{H}_3\text{O}^+$  is also found in the monohydrates of HCl,  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$ , for example,  $[\text{H}_3\text{O}^+]_2[\text{SO}_4^{2-}]$ .<sup>b</sup> All the occupied molecular orbitals of  $\text{H}_3\text{O}^+$  are on another page.

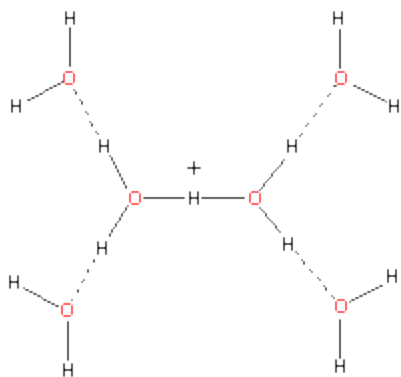
It has been shown that  $\text{H}_3\text{O}^+$  can donate three hydrogen bonds (but accepts almost none); the strength of these donated hydrogen bonds being over twice as strong as those between  $\text{H}_2\text{O}$  molecules in bulk water [1198]. This effectively means that the  $\text{H}_3\text{O}^+$  cation can be considered as  $\text{H}_9\text{O}_4^+$  in solution. The polarization causes these first shell water molecules to also each donate two further hydrogen bonds (but also accept little) with strengths still somewhat higher than bulk water [1198]. Second shell water molecules also donate two hydrogen bonds (but also accept only one with a rather weak hydrogen bond) with strengths still fractionally higher than bulk water [1198]. The bias towards donated hydrogen bonds, within the two-shell  $\text{H}_{21}\text{O}_{10}^+$  ion cluster, requires that it must be surrounded by a zone of broken hydrogen bonds. This is confirmed by infrared spectra that show that the presence of an  $\text{H}_3\text{O}^+$  ion extends to affect the hydrogen bonding of at least 100 surrounding water molecules [1246].



The oxonium ion binds strongly to another water molecule in two possible manners. Opposite are shown the two  $\text{H}_5\text{O}_2^+$  dihydronium ions with closely matched energies, where the proton is asymmetrically (top) or symmetrically (bottom) centered between the O-atoms.<sup>e</sup> The asymmetric structure (top) of  $\text{H}_5\text{O}_2^+$  is found to be more stable using the 6-31G\*\* basis set. However, other more thorough *ab initio* treatments have found the symmetric hydrogen-bonded structure (bottom), with a slightly shorter hydrogen bond, to be the global minimum of by about  $0.6 \text{ kJ mol}^{-1}$  [118].

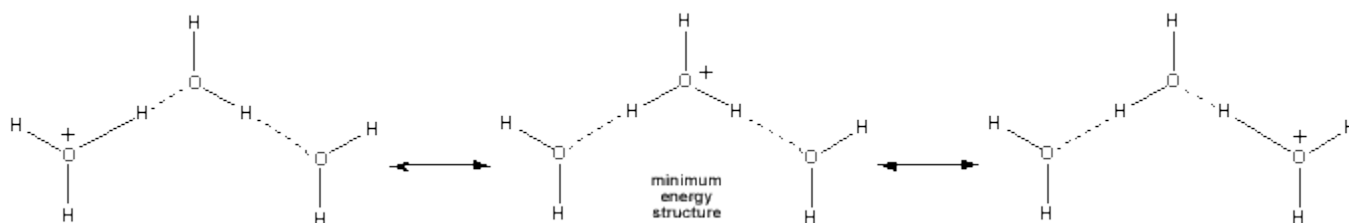
In this symmetric form (the 'Zundel' cation, shown bottom opposite), all O-H bonds are the same length ( $0.95 \text{ \AA}$ ) except the two involved in the hydrogen bond, which are covalent and equally-spaced ( $1.18 \text{ \AA}$ ; similar to that in ice-ten, and as found by neutron diffraction in some crystals midway between the oxygen atoms [118a], such as the dihydrates of HCl and  $\text{HClO}_4$ , for example,  $[\text{H}_5\text{O}_2^+][\text{ClO}_4^-]$ ). There is localized but low electron density around the central hydrogen atom. The vibrational spectrum of  $\text{H}_5\text{O}_2^+$  shows a strong sharp peak (at  $1090 \text{ cm}^{-1}$ ) for its shared proton, similar to  $\text{H}_3\text{O}_2^-$ . As expected, these spectra are much broadened, shifted and poorly resolved in bulk liquid water.

All the occupied molecular orbitals, found using the 6-31G\*\* basis set, of  $\text{H}_5\text{O}_2^+$  are on another page.

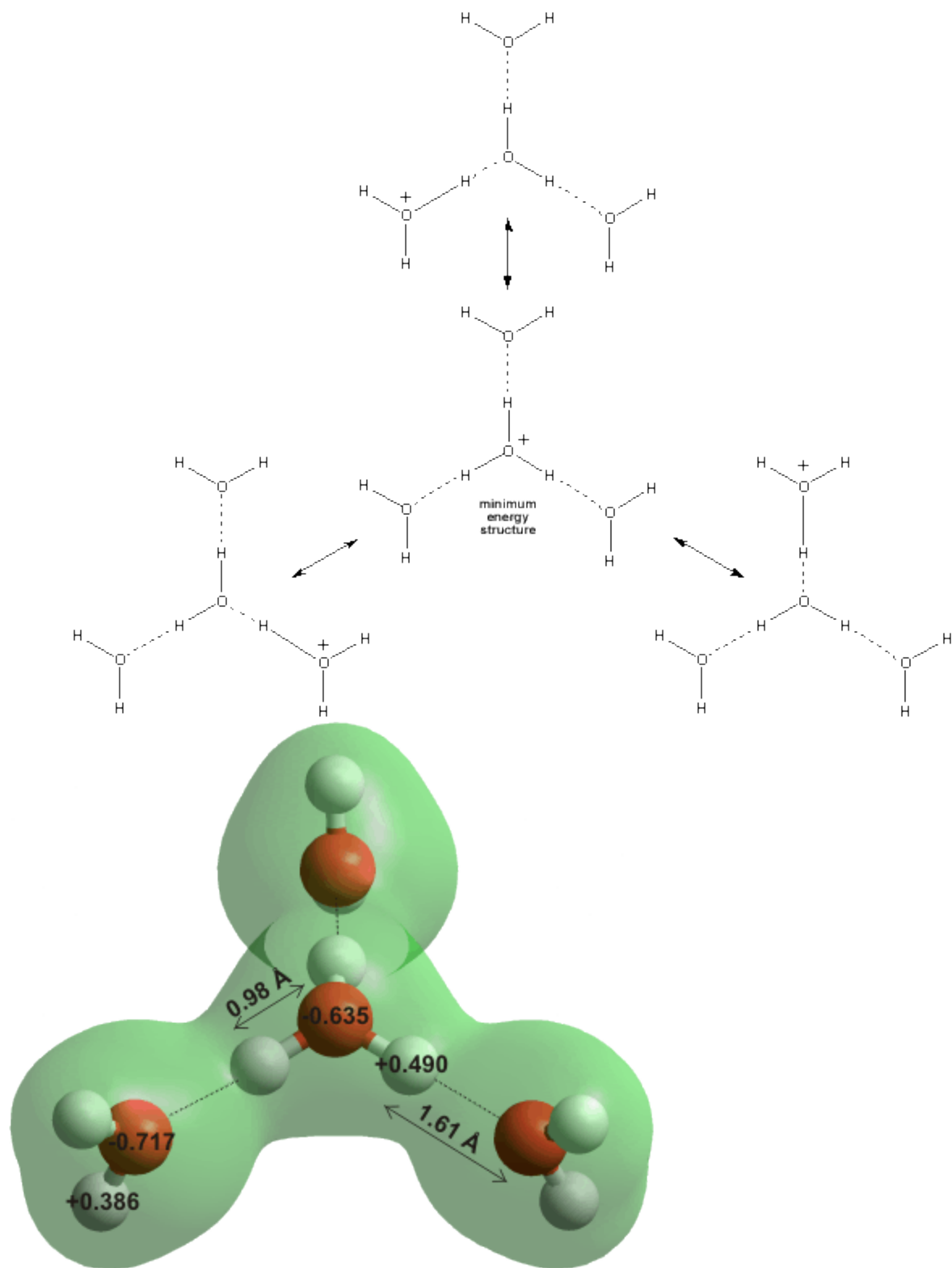


$\text{H}_5\text{O}_2^+$  may be fully hydrated, also with an equally spaced central hydrogen bond, with one water molecule hydrogen bonded to the four free hydrogen atoms as  $\text{H}_{13}\text{O}_6^+$ . The presence of these three similar energy minima for the proton lying so close between the two oxygen atoms is surely the major reason for the ease of transfer of protons between water molecules; the proton moving very quickly ( $< 100$  fs, [1032]) between the extremes of triply-hydrogen bonded  $\text{H}_3\text{O}^+$  ( $\text{H}_9\text{O}_4^+$ , 'Eigen cation') ions through symmetrical  $\text{H}_5\text{O}_2^+$  ions ('Zundel cation')<sup>a</sup> [161], with the low potential energy barriers washed out by the zero-point motion of the proton [1032]. Note that the small movement of the proton gives rise to a much greater movement of the center of positive charge. Preference for the Zundel cation structure occurs when its outer hydrogen bonding is approximately symmetrical as in  $\text{H}_{13}\text{O}_6^+$  (right) [815], although the  $\text{O}\cdots\text{O}$  separation may be greater than expected for the lone  $\text{H}_5\text{O}_2^+$  Zundel ion [1633].

When the extra proton is shared equally between more than one water molecule the approximate structure can be deduced from a consideration of the resonance structures; for example, the two shared protons in  $\text{H}_7\text{O}_3^+$  give rise to bond lengths half way between those in  $(\text{H}_2\text{O})_2$  and  $\text{H}_5\text{O}_2^+$  (the calculated minimum energy structure is shown [815]),



and the three shared protons in  $\text{H}_9\text{O}_4^+$  giving rise to bond lengths a third of the way between those in  $(\text{H}_2\text{O})_2$  and  $\text{H}_5\text{O}_2^+$  (below; the calculated minimum energy structure is shown [815]). Once correctly oriented, the potential energy barrier to proton transfer is believed to be very small [161].



However, the hydrated oxonium ion (opposite; the 'Eigen' cation)<sup>e</sup> may be the most stable hydrated proton species in liquid water, being slightly more stable than the symmetrical dihydronium ion, due

to electronic delocalization over several water molecules being preferred over the nuclear delocalization.

In acid<sup>c</sup> solutions, there will be many contributing structures giving rise to particularly broad stretching vibrations associated with the excess protons (for example, magic number ions). It has been determined from studies of freezing point depression that  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_6$  (that is,  $\text{H}_{15}\text{O}_7^+$ ) is the mean structural ion in cold water [250].  $\text{H}_7\text{O}_3^+$  and  $\text{H}_9\text{O}_4^+$  are both also found in  $\text{HBr}\cdot 4\text{H}_2\text{O}$ , i.e.  $[\text{H}_9\text{O}_4^+][\text{H}_7\text{O}_3^+][\text{Br}^-]_2\cdot\text{H}_2\text{O}$ .

The central (positively charged) hydrated proton interacts very much more strongly with the oxygen of neighboring water molecules rather than any weakly forming hydrogen bonds;  $\text{H}_2\text{O}\cdots\text{OH}_3^+(\text{H}_2\text{O})_3$  being a much stronger link than the hydrogen bond  $\text{HO}-\text{H}\cdots\text{OH}_3^+(\text{H}_2\text{O})_3$  [1956]. This causes rotations in the neighboring water molecules as a hydrogen ion moves through the solution so disrupting the hydrogen bonded network. This  $\text{O}\cdots\text{O}$  attraction even exists between  $\text{H}_3\text{O}^+$  species as in more concentrated acid solutions ( $\sim 0.5 - \sim 3$  M) with the hydrated protons appearing to form contact ion pairs, with the oxonium lone-pair sides pointing toward one another and the oxygen atoms only about 0.34 nm apart.. This unusual "amphiphilic" behavior minimises the disruption to the water's hydrogen bond network caused by the strong hydration of the protons [1837, 2042]. A similar effect may occur at the surface of concentrated acid solutions, causing the lone pairs to point towards the (hydrophobic) gas phase.

As hydrogen ions can be readily stripped from aqueous surfaces [1883], by themselves, as constituents of small clusters or as aerosol, there may be a build -up of positive charge within clouds and negative charge on Earth that leads to thunder and lightning.

[[Back to Top](#) ▲]

---

## Footnotes

<sup>a</sup> The hydration of 'Eigen' ( $\text{H}_9\text{O}_4^+$ ) and 'Zundel' ( $\text{H}_5\text{O}_2^+$ ) ions has been investigated [1372]. [[Back](#)]

<sup>b</sup>  $\text{H}_2\text{O}$  accepts protons from stronger acids to form  $\text{H}_3\text{O}^+$  and  $\text{H}_3\text{O}^+$  donates protons to the bases of weaker acids. The acidity constant ( $K_a$ ) of  $\text{H}_3\text{O}^+$  is defined (as other acids) by the equation  $\text{H}_3\text{O}^+(\text{H}_2\text{O}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{H}_2\text{O}$ . Therefore  $K_a = [\text{H}^+][\text{H}_2\text{O}]/[\text{H}_3\text{O}^+]$  and as  $[\text{H}^+]$  is the same as  $[\text{H}_3\text{O}^+]$ ,  $K_a = [\text{H}_2\text{O}] = 55.345$  M (at 25 °C), and  $\text{p}K_a = -1.743$  (at 25 °C). There is a difficulty that has been ignored in this definition as the  $K_a$  should be expressed in terms of activities rather than concentrations [1188] and the activity of pure  $\text{H}_2\text{O}$  is defined as unity whereas that of solutes is defined relative to their standard state (1 mol  $\text{kg}^{-1}$ ). [[Back](#)]

<sup>c</sup> Note that acid-base neutrality only occurs when the concentration of hydrogen ions equals the concentration of hydroxyl ions (whatever the pH). Neutrality is at pH 7 only in pure water when at 25 °C. A solution is acidic when the hydrogen ion concentration is greater than the hydroxide ion concentration, whatever the pH. [[Back](#)]

<sup>d</sup> The term 'oxonium ion' should be reserved for the  $\text{H}_3\text{O}^+$  ion with the term 'hydronium ion' now obsolete. The term 'hydrogen ion' may refer to any of the group of protonated water clusters including  $\text{H}_3\text{O}^+$ . [[Back](#)]

<sup>e</sup> The oxonium ion and small hydrated hydrogen ion clusters shown on this page were drawn using *ab initio* calculations using the 6-31G\*\* basis set. Where not otherwise referenced, bond distances, angles and atomic charges are derived from these calculations. [[Back](#), 2, 3]

$\text{H}^+ + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+$  ( $\Delta G^\circ = -651.4 \text{ kJ mol}^{-1}$ ), this is followed by  $\text{H}_3\text{O}^+ + \text{aq} \longrightarrow \text{H}_3\text{O}^+(\text{aq})$  ( $\Delta G^\circ = 461.1 \text{ kJ mol}^{-1}$ ;  $\sim 260 \text{ nm}$ ) giving an overall  $\text{H}^+ + \text{aq} \longrightarrow \text{H}_3\text{O}^+(\text{aq})$  ( $\Delta G^\circ = -1112.5 \text{ kJ mol}^{-1}$ ). These calculations assume that the standard state of the solvent water is taken as 1.0 M. [1067]. [Back]

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