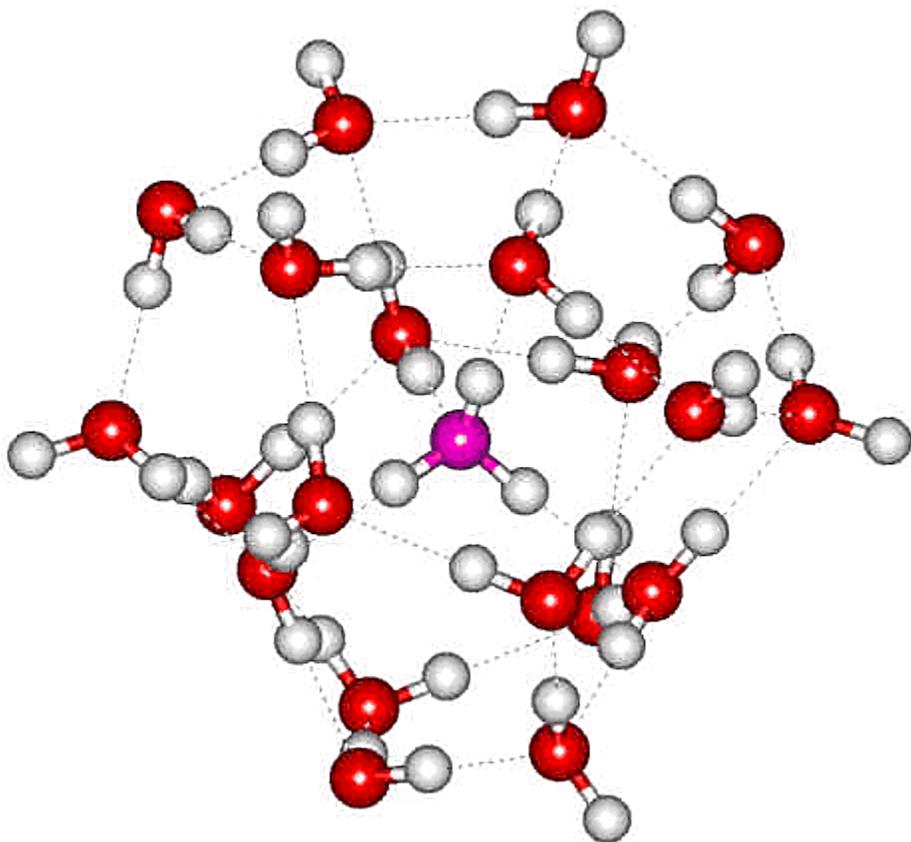# Magic Number Water Clusters



A oxonium (H_3O^+) or ammonium (NH_4^+) ion may sit in the tetrahedral cavity of a collapsed water dodecahedron so forming the magic number cluster $H_3O^+(H_2O)_{20}$ m/z 379 (as opposite with the oxonium oxygen colored magenta,[a] or $NH_4^+(H_2O)_{20}$ m/z 378) as found by electrospray mass spectrometry [113]. Infrared studies confirm the dodecahedral clustering by showing that all the dangling OH groups arise from similarly situated water molecules [113c]. It should be noted that the extra proton does not need to be associated with the central water molecule in the above structure. It could hop to any of the other 20 water molecules, and this would be expected in an isolated cluster where the poor H-bond donation to H_3O^+ is avoided. Such a surface protonated structure has been recently confirmed, and found to be retained at higher temperatures when two-coordinated water occurs [774]. Such magic number ions are followed by a reduced mass peak at the next H_2O addition, an antimagic number [1918]. due to a weak appendaging of an extra H_2O to the magic number ion.

$H_3O^+(H_2O)_{20}$ cluster ions have calculated dipole moments of about 10 D (cf. H_2O dipole 1.86 D) and may contribute to the intense terahertz emission of water vapor under optical excitation [1868]. Anti-magic number clusters, where the cluster is particularly unstable, have been found where the water cluster has one more water molecule than the magic number ion [1995]. This is due to the single extra water molecule being tagged on to the outside of the stable cluster and so being easily removed from it.

Interactive Jmol structures are given.

This symmetric structure was not as found in an *ab initio* search [114], but might be expected to be more stable than the one found there as the bond distortion is less and it has one fewer non-hydrogen bonding hydrogen atom.[b] The symmetric clathrate structure, containing a single water molecule, is found as the $(H_2O)_{21}$ global minimum energy structure using the TIP5P model [857]. In contrast the $(H_2O)_{21}$ global minimum found using the TIP4P model [115] is very different and mostly consists of 4-membered rings. Although such low-energy structures (*e.g.* the structure formed by four fused cubes) are sometimes found as global minima, they have weaker hydrogen bonds and far fewer positions are available for further hydrogen bonding (*e.g.* the fused cube structure only has 8 such positions compared with 30 on the dodecahedral cluster). Such clusters are therefore thought (by this author) unlikely to be found in real situations. The collapsed clathrate structure (similar to $H_3O^+(H_2O)_{20}$ above) for $(H_2O)_{21}$ (with ring structure $(20,1)_8$) is preferred over the convex cluster (with ring structure $(20,1)_{10}$) in contrast to the preferred convex clathrate structure of $H_2S.(H_2O)_{20}$, rationalizing the formation of solid H_2S but not H_2O clathrates [1114].
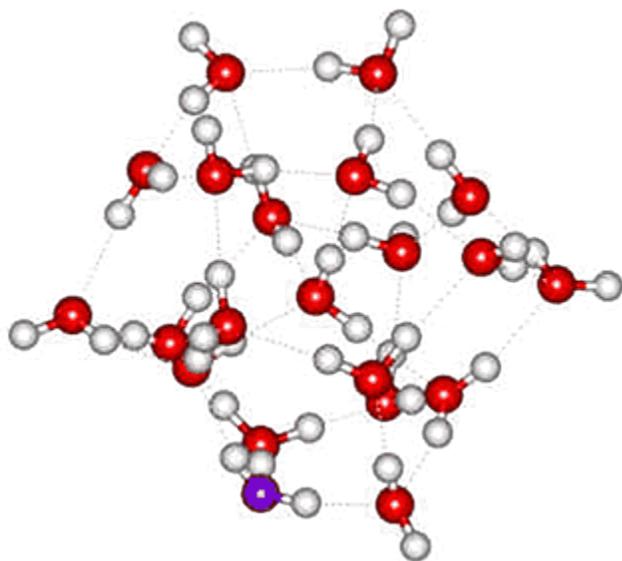
The clathrate structure has also been found as a global minimum for H3O+(H2O)20 using a polarizable model potential [72], where the oxonium ion preferred to sit away from the center; see opposite (the oxonium ion is towards the bottom left and colored magenta with the slightly hydrophobic lone pair pointing outwards). Similar results have been obtained using an ab initio approach where surfaceZundel ions (H5O2+) were also found [854].

Although there is a preference for the oxonium ion to occupy a cluster surface position in an isolated cluster this is not likely to be the case in bulk water; a factor that, if not ignored in such gas-phase and theoretical studies concerning ionic clusters, is often understated when results are extrapolated, directly or by inference, to the bulk water scenario.

The low energy hydroxide cluster ion cluster $OH^-(H_2O)_{20}$ behaves differently with the OH^- ion centrally placed, accepting four hydrogen bonds and donating one hydrogen bond [1828].

In $NH_4^+(H_2O)_{20}$, the NH_4^+ ion sits centrally in the water dodecahedron with all the hydrogen bonds from the central ammonium ion equivalent, so helping to explain the apparent increased structural stability of this ion relative to $H_3O^+(H_2O)_{20}$. In agreement with this, an *ab initio* molecular dynamics simulation found NH_4^+ to form four relatively long-lived hydrogen bonds[c] to tetrahedrally arranged water molecules [136] and such a structure is found to be much more stable than a cluster with a NH_3 in the center and a H_3O^+ on the surface [194]. Exchange of hydrogen bond partners by the central NH_4^+ may explain its faster than expected rotation [855].

Other hydrogen bonding molecules can substitute for water in these clusters (for example, methanol, with its methyl group pointing away from the cluster, $H^+(H_2O)_{21-n}.(CH_3OH)_n$, n =1, 2, 3...) or add to the outside of the cluster (*e.g.* acetonitrile, $H^+(H_2O)_{21}.(CH_3CN)_n$, n =1, 2, 3...) [587].

The energy of $H_2O(H_2O)_{20}$ clusters with H_2O inside a $(H_2O)_{20}$ dodecahedral clathrate cage have been determined [1114]. It was found that the puckered cluster (similar to the top structure of the $H_3O^+(H_2O)_{20}$ magic ion) was 38 kJ mol^{-1} more stable compared with the convex clathrate containing the H_2O molecule [1114]. As the puckered structure is more able to undergo rapidly rearrangement, this offers explanation for the reason why no crystalline aqueous clathrate structures contain water molecules in their cavities.

Footnotes

[a]   There are many possible hydrogen-bonding arrangements. The one shown has been chosen for comparison to the modeled minimum-energy structure [72]. [Back]

[b]   In the top structure above, a hydrogen bond is shown donating to the oxonium ion (H_3O^+). This is expected to be ordinarily very weak (or nonexistent) but strengthened in the structure shown due to the possibility of the nuclear delocalization from proton hopping. [Back]

[c]   Note that a single H_2O hydrogen-bonded NH_4^+ forms one of the strongest hydrogen bonds known at 92.5 kJ mol^{-1}[447]. [Back]

Source:http://www1.lsbu.ac.uk/water/magic.html