

CHEMISTRY



How many water molecules does it take to ionise HCl?

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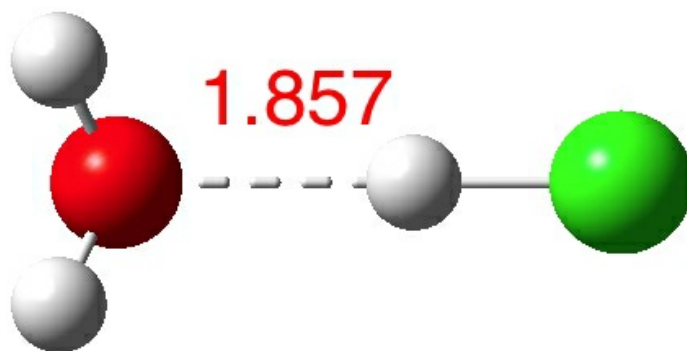
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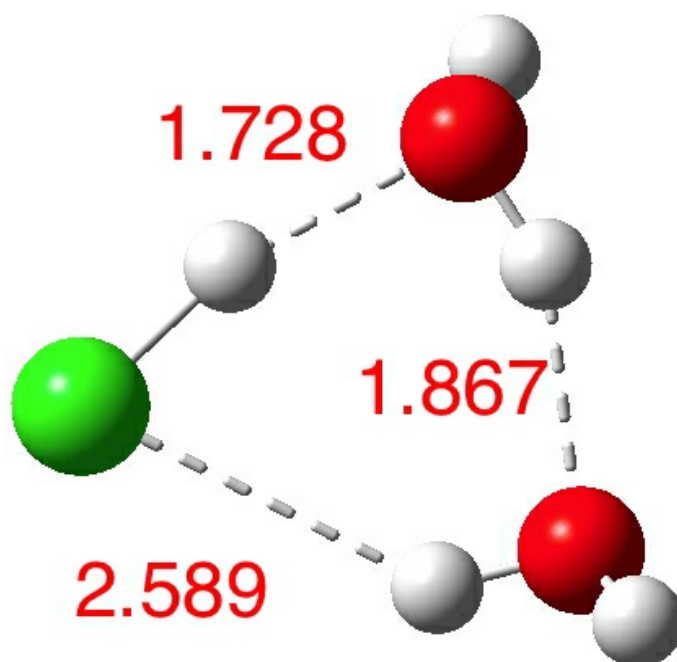
According to Guggemos, Slavicek and Kresin, about 5-6^[1]. This is one of those simple ideas, which is probably quite tough to do experimentally. It involved blasting water vapour through a pinhole, adding HCl and measuring the dipole-moment induced deflection by an electric field. They found “*evidence for a noticeable rise in the dipole moment occurring at $n \approx 5-6$* ”.

Modelling the structures takes little time. So here are some ω B97XD/6-311++G(2d,2p) gas phase models. I state at the outset that these are not dynamic-stochastic models, averaged over many conformations, but a static picture of individual poses. As usual, click on individual images to obtain an interactive 3D model (Java required).‡

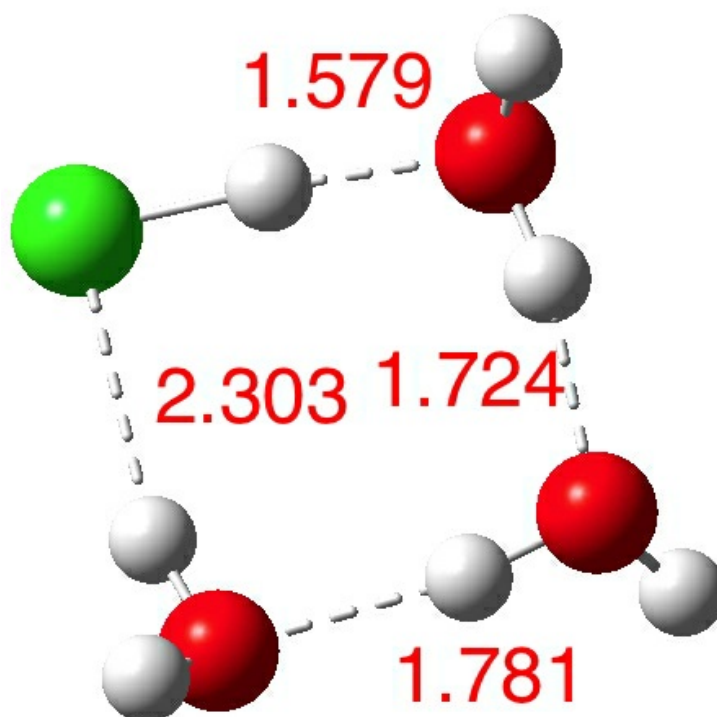
$n=1$.^[2] Dipole moment 3.7D



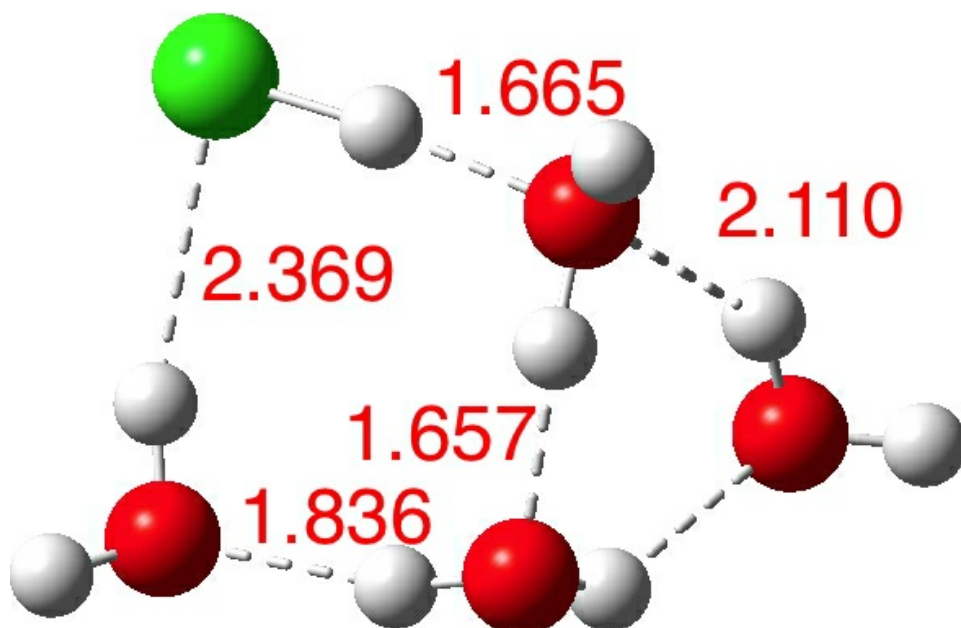
$n=2$.^[3] Dipole moment 2.4D. Note how the O...H bond becomes shorter.



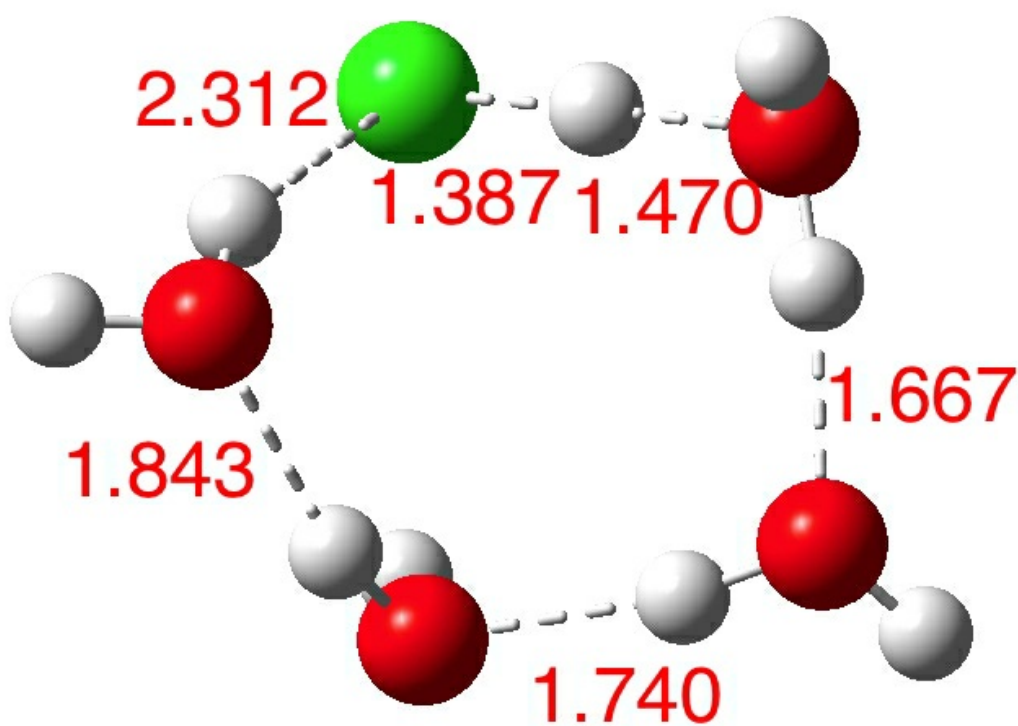
n=3.[4] Dipole moment 2.5D. Note how the key O..H bond is contracting rapidly, as are the other H-bond interactions. This is the cyclic polarisation effect, where each bond influences the others. We are starting to approach the formation of H_3O^+ and Cl^- !



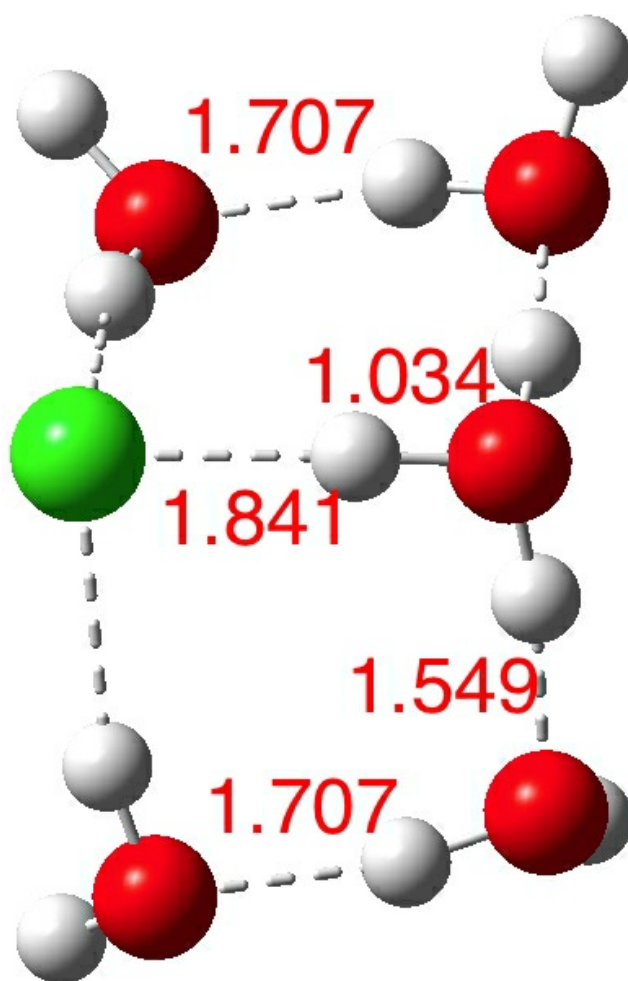
n=4.[5] Dipole moment 2.3 D, We have two ways to add the next water molecule, firstly to try to stabilise the H_3O^+ . Nope.



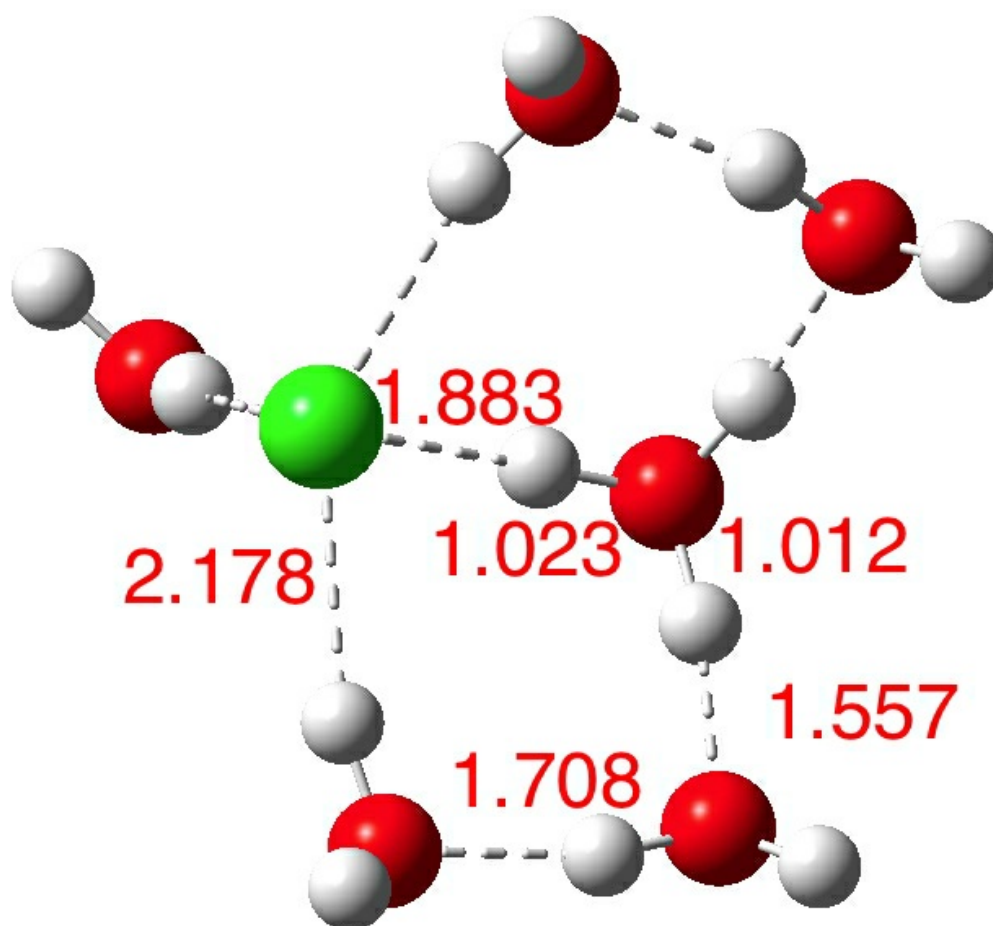
n=4,[5] Dipole moment 1.1 D. Better by solvating the Cl-! The proton originally attached to the Cl is now starting its transfer to the water to form that hydronium cation, but the dipole moment is not yet large.



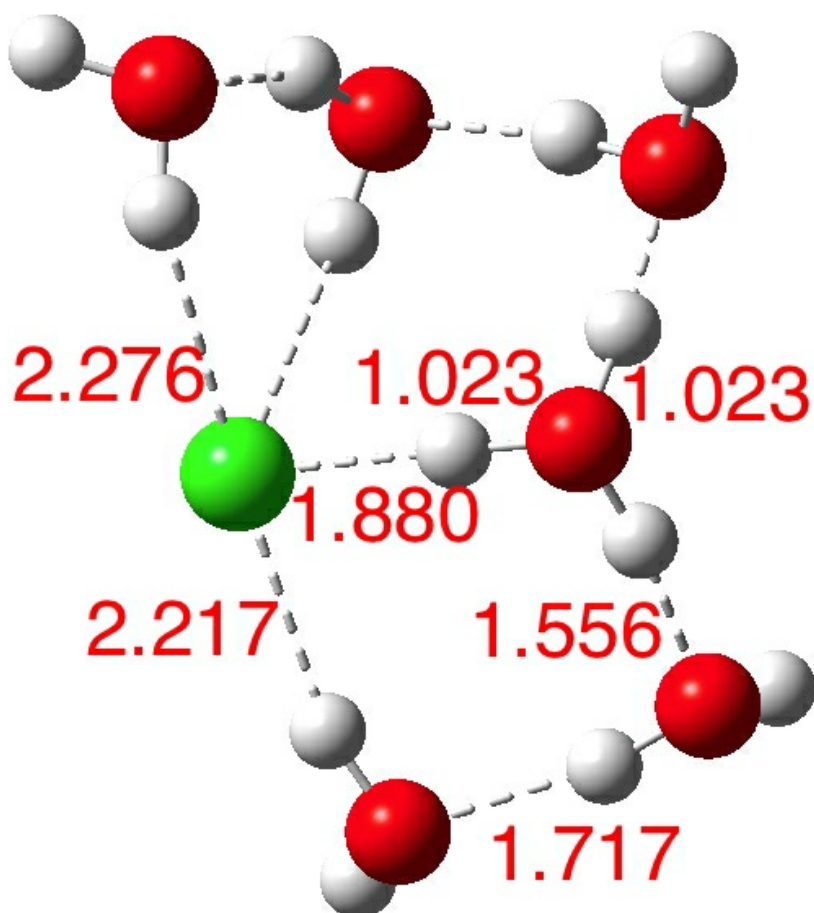
n=5,[6] Dipole moment 4.7D. The ionisation is almost complete and the dipole moment is on the increase.



$n=6$.^[7] The dipole moment is up to 8.2D and the three H-O bonds of the hydronium cation are almost all equal in length.



A cautionary observation though. The isomer below for $n=6$ is lower in energy by ΔG -1.2 kcal/mol, and its dipole moment is only 2.5D! The charges (summed onto heavy atoms) show the chloride to have -0.88 and the hydronium cation +0.88, so it is a true ion-pair, despite its dipole moment.



So these calculations do indeed appear to confirm that 5-6 water molecules are required to ionise HCl. But it does raise the interesting issue that even for $n=6$, there are poses for the assembly which have low dipole moments. Clearly of course the observed dipole moment is a dynamic average over many conformations of similar energy but the prediction that some of these may have low dipole moments should be noted.

‡ If you right-click in the 3D model area, you can bring down a list of vibrational modes for each complex from the first item of the pop-up menu that appears (labelled model). You might wish to e.g. explore how the H-Cl stretch vibration changes as the ionisation increases.

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