How many water molecules does it take to ionise HF and HBr?

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No doubt answers to the question posed in the previous post are already being obtained by experiment. Just in case that does not emerge in the next day or so, I offer a prediction here.

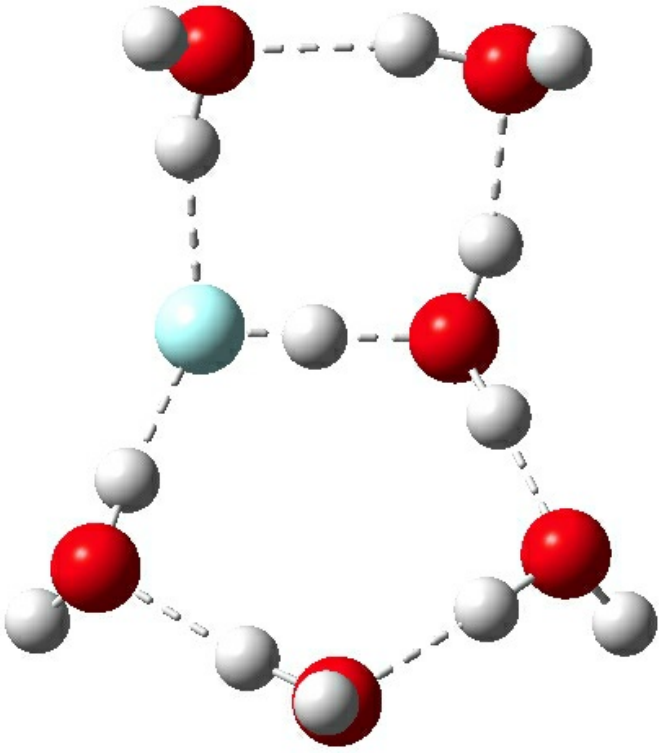
The methodology is the same as before, and I have not tried to look for new isomeric forms compared with the structures found with HCl. The method as before is DFT-based: ωB97XD/6-311++G(2d,2p). In the table below, I am recording the halogen-H distance and the distance from the same H to oxygen. You might also observe a more general principle here; first calibrate the method you intend to use with a system where there is an experimental answer. If the two match, use the same method to predict (extrapolate) to systems as yet unmeasured.

F	Cl	Br	n	F-H, Å	H-O	Cl-H	H-O	Br-H	H-O
1	0.937	1.702[1]		1.300	1.857	1.438	1.912[2]		
2	0.951	1.631[3]		1.322	1.728	1.463	1.754[4]		
3	0.967	1.532[5]		1.351	1.579	1.506	1.554[6]		
4	0.972	1.504[7]		1.387	1.470	2.032	**1.028**[8]		
5	1.043	1.329[9]		1.841	**1.034**	2.039	1.021[10]		
6	1.067	1.283[11]		1.880	1.023	2.073	1.013[12]		

From the bond distances, one notices that “ionisation” is an abrupt discontinuous event, happening for four molecules with HBr, five molecules with HCl and more than six molecules with HF. This nicely parallels the pka values: HBr (pKa = -9.0) < HCl (pKa = -6.0) << HF (pKa = +3.1).

It is good to see that such a process modelled on the nanoscale using just a few discrete molecules can map onto the macroscopic scale of solutions.

Postscript: If you check on the structures of these systems (click on the pictures in the previous post) you will see that the discontinuous ionisation event occurs in a bicyclic system, with the water forming two separate rings. Evidence that this really is the structure of microsolvated species has recently been put forward[13].



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