How many water molecules does it take to ionise HI?

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Why is this post orphaned from the previous? In order to have the opportunity of noting that treating iodine computationally can be a little different from the procedures used for F, Cl and Br.

As the nuclear charge increases proceeding down the periodic table, the inner electron shells start becoming relativistic. Iodine is the first halogen where this might really start to matter.* There are two ways in which one can compute molecules with I; the first adopts the same procedure as for the earlier halogens, whereby all the electrons are described by basis functions (called an all-electron basis). This effect does not really include the effects of relativistic contractions on the inner (1s) shell unless special relativistic Hamiltonians are also used. The second replaces these inner cores with a pseudopotential, and this does incorporate some of the relativistic effects. To find out how much this might matter, I have included both types:

I n	I-H	H-O
1	1.637†/1.623‡	2.032/2.060[1]
2	1.657/1.641	1.863/1.889[2]
3	1.696/1.675	1.641/1.670[3]
4	2.316/2.304	1.014/1.015[4]

†Non-relativistic calculation with an all-electron 6-311G(d,p) basis on I, 6-311++G(2d,2p) on O and H.
‡Def2-TZVPPD basis, with pseudopotential just on I.

As with bromine, iodine shows a precipitous ionisation when the 4th water molecule is added. In the previous post, I compared this with pKa values, and a comment posted there reminded us that a pKa is measured for macroscopic bulk water and that all sorts of new effects due to free energy/entropy, continuum solvation and much else will take hold. But qualitatively at least, the ionisation of HI in a gas-phase cluster of water molecules seems to match the bulk properties. Relativistic effects do not appear to play a major role here.

*Whilst such effects can be prominent for I, arguably they actually start at Cl *via* an effect called spin-orbit (SO) coupling. This manifests in the calculation of chemical magnetic shieldings. If one uses standard GIAO NMR theories, one can calculate shieldings for e.g. C pretty accurately. But with Cl, the shieldings may be SO-perturbed by about 3ppm, with Br it's about 12 ppm and with I it reaches 50 ppm![5]

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