

## Quantum Acid-Water

*Zero-point effects and electric dipole moments of acid-doped water clusters*

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**Recommended with a commentary by Marivi Fernandez-Serra,  
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It is not uncommon to hear the question, is water really that special or are there other light molecules that have a similar range of “anomalous behavior”? Considering only the complicated phase diagram of its solid phase, with over 12 different polymorphs of ice, or the large number of anomalies of the liquid phase, (which could most of them be explained by the existence of a second critical point in the metastable supercooled liquid phase and which would make ambient water a supercritical liquid), the straightforward answer should be yes, water is really a special molecule. Interestingly, in principle there is no need to account for quantum fluctuations of the hydrogen to explain most of the anomalies of water. However, zero point effects add to the list of the anomalies of water. For example, it was recently shown that in hexagonal ice and water, there is an anomalous isotope effect, where the number density decreases when hydrogen is replaced by deuterium, as opposed to the expected volume expansion effect. What is even more surprising is that, this effect, rather than going away with increasing temperature, i.e. approaching the classical limit, becomes more pronounced and dominant and is even larger in liquid water than it is in ice.

$H_2O$  is a textbook example of a molecule with a permanent electric dipole moment. In the gas phase, this dipole moment can be measured using the rotational Stark effect with a very high precision, the result is 1.8546(6) Debyes. The changes of the dipole moment in the different condensed phases of water is mostly due to changes in the molecular polarizability upon formation of hydrogen bonds (Hbonds). Understanding the evolution of the dipole moment of water clusters upon increasing the number of water molecules is a perfect example of a problem that appears simple but which is certainly not. It is also a perfect platform to combine both experimental and theoretical observations in a symbiotic way. Not only theory helps understanding the experiments, but also experiments help improving the theory. Indeed simple problems like this have largely been used by the quantum chemists to validate and evaluate electronic structure calculations at different levels of theory, all the way from density functional theory to high level wave function methods like coupled cluster and fully correlated configuration iteration methods.

While water molecules are polar, small water clusters, up to 10 molecules, do not necessarily need to be polar, if their structures are highly symmetrical. A measurement of the dipole moment of these clusters therefore can provide a direct connection to the structure of these clusters, and serve to validate or challenge the absolute energy minima structures predicted by different theoretical methods.

The vibration-rotational-tunneling Stark effect can also be used to measure the dipole moment of water clusters. However, an alternative method, the beam reflection method, has proven to be a much more powerful and accurate tool to measure both dipole moments and polarizabilities of water clusters. The method is relatively simple. A cluster will interact with an static external electric field if it posses an electric dipole moment. The clusters are produced in a laser vaporization source forming a supersonic molecular beam. When this

beam passes an inhomogeneous electric field it will be deflected due to the force induced on the cluster (as long as it has a net electric dipole moment). A movable slit and a UV laser are used to detect the molecular beam deflection and ionize the clusters, and a time-of-flight mass spectrometer is used to identify the number of molecules in the cluster. A quantitative analysis of the field induced beam deflection allows to obtain both the dipole moment and polarizabilities of the clusters.

In a preceding paper [PRL 97,123401 (2006)], using the previously described technique, the same research group reported values for both the dipole moments and polarizabilities of  $(H_2O)_n$  and  $(D_2O)_n$  clusters with  $n$  ranging from 3-18. They showed that a sudden increase of the dipole moment per molecule in the clusters occurred somewhere within the  $n=3-8$  region. The polarizability per molecule of water clusters also shows a large increase with respect to that of the isolated molecule. The softer the normal modes of the molecules or clusters, the larger is the effective polarizability. With light atoms like H, zero point fluctuations will also contribute to make this effective polarizability larger. The presence of Hbonds increases the fluctuations of H along the Hbond direction, increasing the effective polarizability of the molecule, and shortening the Hbond length. However, whether these fluctuations also increase the effective polarizability of the clusters depends on what the dominant quantum effects are. As shown by Pamuk and collaborators [PRL 108, 193003 (2012)], the net effect of these quantum fluctuations in ice is to decrease the compressibility and increase the density of  $H_2O$  hexagonal ice Ih as compared to the heavy ice lattice  $D_2O$ , an anomalous result. A simple way of looking at it, is to think that the Hbonds in  $H_2O$  ice are stiffer (and shorter) than those in  $D_2O$  ice. Interestingly in [PRL 97,123401 (2006)], the research group also reported that the effective polarizability of  $(D_2O)_n$  clusters is in average 13% larger than that of  $(H_2O)_n$  clusters, indicating that the same anomalous behavior observed in ice might occur in these small clusters.

In their recent contribution [PRL 114, 043401, (2015)], Nicholas Guggemos and co-authors have shown a different, although not completely unrelated aspect of how zero point fluctuations of protons in small water clusters can be the cause of large effects on their dipole moments and polarizabilities and can induce dissociation of the acid molecule hydrogen chloride (HCl, although in this research paper experiments are performed with the deuterated version of the molecule, DCl) at cluster sizes as small as 5-6 water molecules in size. They observe that adding just one single acid molecule, the dipole moment of  $(H_2O)_n$  clusters are largely enhanced. They also observe an anomalous increase of both the cluster dipole moments and polarizabilities, which they narrow to the  $n \approx 5-6$  molecules in size. What is really interesting is that this increase occurs for the same cluster size in acid-doped clusters, but it is much larger in magnitude. Performing ab initio path integral molecular dynamics simulations the authors conclude that the origin of this enhancement is the onset of molecular dissociation of the acid into  $H_3O^+$  and  $Cl^-$ . This is surprisingly a small size for the cluster, but indicates that dynamical effects are critical on the onset of the dissociation. These results provide great insight into the role that nuclear quantum effects play in the dissociation and solvation of ions. The observations can have important implications in our understanding of the electrochemical interface, and the electrochemical double layer formed at the water/electrolyte interface. This is currently a very active field of research, and this research paper hints that nuclear quantum effects might be much more important than previously assumed in order to understand and simulate aqueous electrolytes.

It will be very interesting to see how similar experiments for  $(D_2O)_n$  clusters compare. In particular, if the increase of polarizability on heavy water doped clusters is the same or larger than that for  $(H_2O)_n$  clusters will provide additional information on how ions affect

the stability of the Hbond network from the point of view of nuclear quantum effects.