Concerted hydrogen-bond breaking by quantum tunnelling

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The study of gas-phase water clusters provides a direct experimental probe of the intermolecular forces which also exist in the liquid phase. Hydrogen-bond network rearrangements occurring via quantum tunnelling manifest themselves in the splitting patterns observed by spectroscopy. At low temperature, these tunnelling rearrangements follow pathways which can differ considerably from the minimum-energy pathway. The tunnelling pathways can however be computed using quantum dynamical approaches such as is provided by the ring-polymer instanton method [1].

A recent joint experimental and theoretical study of the water hexamer prism [2] has discovered unexpectedly complex tunnelling pathways showing cooperative behaviour of the water molecules. One of these leads to the simultaneous breaking of two hydrogen bonds (Figure 1). Similar pathways may also exist in the rearrangement of water clusters adsorbed on surfaces, or water in confined or interfacial environments such as at the surface of ice.

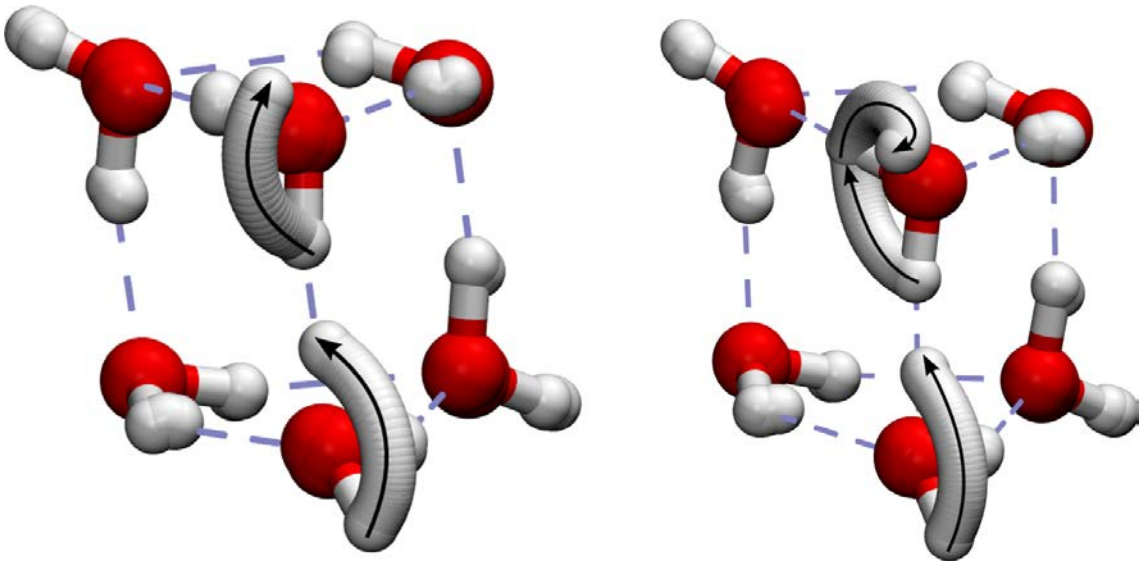

Figure 1: The two feasible tunnelling pathways in the water hexamer prism involving cooperative motion of the water molecules. The first rearrangement breaks only one hydrogen bond whereas the second is able to break two simultaneously.

References

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[2] J. O. Richardson, C. Pérez, S. Lobsiger, A. A. Reid, B. Temelso, G. C. Shields, Z. Kisiel, D. J. Wales, B. H. Pate, S. C. Althorpe, Science 2016, 351, 1310–1313.