FORMATION OF CYCLIC WATER COMPLEXES BY SEQUENTIAL RING INSERTION

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Recent work[a] has shown that previously unobserved water cluster isomers may be formed in the unique He nanodroplet environment. The formation of water clusters in He nanodroplets proceeds as in the gas phase for the addition of up to five water molecules, forming the cyclic isomers. Theory predicts these cyclic structures to be the global minima on the potential energy surfaces. However with the addition of the sixth water molecule the "caged" isomer becomes the global minimum stabilized by approximately 2 Kcal/mol over the cyclic ring. In accordance with this, gas phase studies on the water hexamer have exclusively probed the "caged" isomer. However due to the relatively fast cooling in the He nanodroplet, the cyclic hexamer is not only formed, but formed preferentially to the "caged" hexamer. The sequential growth of the water clusters in He nanodroplets, where each subsequent ring structure is built by the addition of a single water molecule to the smaller ring (in equilibrium with the 0.37 K droplet), implies that the ring insertion process has a very low or non-existent barrier. Theoretical work using the TTM2-F flexible, polarizable water potential, confirms the low barrier to ring insertion and qualitatively reproduces the branching ratio for the formation of the ring and caged hexamers.

[a] Nauta K.; Miller, R. E., *Science*, **2000**, 293.