Quantum Tunneling in the Low-Lying Water Hexamer Isomers

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Studying water clusters is of great importance because the behavioral essence of intermolecular forces between the water molecules mimics that of the bulk. The water hexamer is a particularly interesting water cluster to investigate both experimentally and theoretically because it is the smallest one with a 3D structure, often called the smallest water droplet. The energetically lowest structural isomers detected experimentally are prism, cage, and book [1].

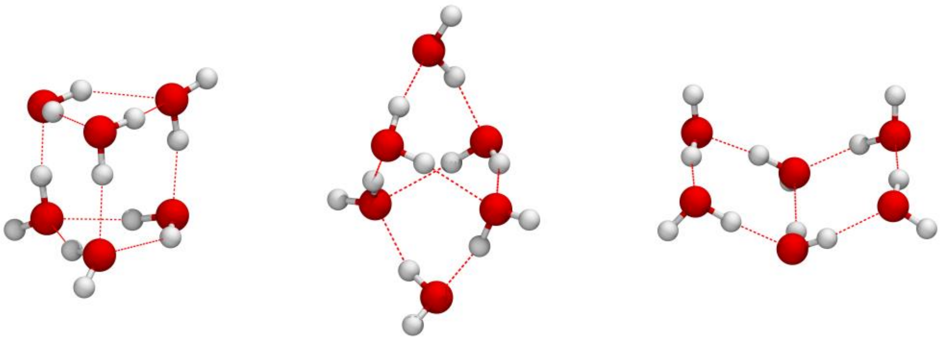

Figure 1. The lowest-energy structural isomers of the water hexamer: prism (left), cage (middle) and book (right).

Tunneling splittings (TSs) of these isomers are calculated using the modified WKB (Wentzel–Kramers–Brillouin), a semiclassical method based on instanton theory [2]. The method starts with finding the minimum action path, along which the semiclassical wavefunction is constructed and inserted into the Herring formula, yielding tunneling matrix elements. Finally, splittings are obtained by diagonalizing the tunneling matrix. TSs in the water hexamer prism are determined for a number of excited low-frequency vibrational modes. Internal rotation of a double-donor water monomer is identified as the mechanism that potentially plays a role in the appearance of the TS pattern in vibrationally excited states in addition to the mechanisms that shape the TS pattern in the ground state. The ground-state TSs of the water hexamer cage were found to form a doublet of doublets. The finer splitting is two orders of magnitude smaller due to a significant difference in the barrier heights for bifurcations of the water monomers at the two opposite vertices of the cage. First estimates of the ground-state TSs in the water hexamer book structure are also calculated. The TS pattern is again a doublet of doublets, caused by the monomer motions on one side of the book isomer. The wider doublet is of similar size to that in the cage and the narrower doublets an order of magnitude larger than that in the cage.

References:

[1] C. Pérez, M. T. Muckle, D. P. Zaleski, N. A. Seifert, B, Temelso, G. C. Shields, Z. Kisiel, B. H. Pate, *Science* **336** (2012) 897–901.

[2] M. Eraković, M. T. Cvitaš, *J. Chem. Phys.* **153** (2020) 134106.