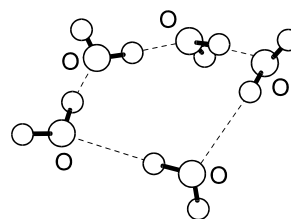


279	H_{10}O_5	Water pentamer (weakly bound complex)	C_{5h} or G_{10} (effective symmetry class) (large-amplitude motion) $(\text{H}_2\text{O})_5$
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The vibrationally averaged rotational constants correspond rigorously to those of a quasiplanar (C_{5h}) oblate top whereas the equilibrium cyclic structure is predicted to be slightly asymmetric due to puckering of the oxygen framework and uneven distribution of the free O–D bonds above and below the ring. The vibrational averaging which underlies the symmetric top behavior, the absence of a first-order Stark effect, as well as the origin of the observed intermolecular vibration, is consequently rationalized using a five-dimensional model of the pseudorotation, analogous to that established for the water trimer. Pseudorotation is induced by the nearly barrierless “flipping” of the monomers about their donor hydrogen bonds and by accompanying hydrogen bond network puckering motions. The experimentally deduced inter-oxygen separations for water clusters up to the pentamer (for which the vibrationally averaged result is $\text{O}\cdots\text{O} = 2.76 \text{ \AA}$) as a function of the cluster size exhibit exponential contraction toward the corresponding distance in ice I_h .

In the asymmetric equilibrium structure of the cyclic water pentamer, shown in the figure, the $\text{O}\cdots\text{O}$ distances are 2.729, 2.726, 2.726, 2.724 and 2.731 \AA from O_A to O_E . The respective hydrogen bond angles $\text{O}–\text{H}\cdots\text{O}$ are 176.2° , 176.0° , 175.8° , 173.3° and 177.1° . The out-of-plane flipping angles of the free hydrogen atoms attached to the oxygen atoms from O_A to O_E can be expressed as the dihedral angle between the individual monomer plane and the plane formed by the monomer oxygen and its two adjacent oxygen atoms, since the oxygen ring is puckered; these are 53.0° , 55.3° , 52.2° , 58.9° and 36.4° , respectively. The degree of puckering can be seen from the dihedral angles between the oxygen planes, which are 20.4° between the $\text{O}_A\cdots\text{O}_B\cdots\text{O}_D$ and $\text{O}_B\cdots\text{O}_C\cdots\text{O}_D$ planes and 2.1° between $\text{O}_A\cdots\text{O}_B\cdots\text{O}_D$ and $\text{O}_A\cdots\text{O}_E\cdots\text{O}_D$.



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