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MW $\text{H}_6\text{O}_3$ **Water trimer**  
(weakly bound complex) $\text{C}_3$   
(effective symmetry class)  
(large-amplitude motion)  
 $(\text{H}_2\text{O})_3$ 

As Fig.1 shows, the equilibrium structure of the water trimer is a near-oblate symmetric top. Torsion of the free hydrogen atoms approximately about the hydrogen bonds is the dominant low-frequency motion of this trimer.

This low barrier rearrangement process involves the motion of a free hydrogen atom from one side of the O–O–O plane to the other (“flipping”) and is predicted to have a  $90\text{ cm}^{-1}$  barrier. As a result each free hydrogen atom spends an equal amount of time above and below the O–O–O plane, thus vibrationally averaging the asymmetric ( $\text{C}_1$ ) equilibrium structure to that of an oblate symmetric top in the ground state. The O–O bond distance has been determined as  $2.84\text{ \AA}$  through a simple model calculation based on

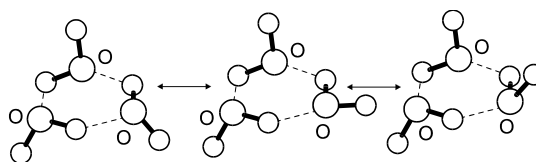


Fig.1

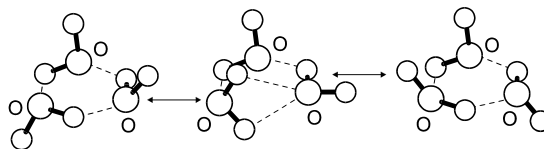


Fig.2

the spectroscopic data. On the other hand, Fig.2 shows a higher barrier rearrangement process, which is bifurcation tunneling, where the roles of the free and bound hydrogen atoms of a water molecule in the cluster are switched. The pathway for this process is predicted to traverse a bifurcated transition state. This arrangement gives rise to the quartet tunneling splitting observed for each torsional band of the complex. Note that an adjacent water molecule flips as part of the tunneling pathway.

Brown, M.G., Viant, M.R., McLaughlin, R.P., Keoshian, C.J., Michael, E., Cruzan, J.D., Saykally, R.J., van der Avoird, A.: J. Chem. Phys. **111** (1999) 7789.

See also: Viant, M.R., Brown, M.G., Cruzan, J.D., Saykally, R.J., Geleijns, M., van der Avoird, A.: J. Chem. Phys. **110** (1999) 4369.

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