Supplemental Material for:

“Hydrogen Bond Network Rearrangement Dynamics in Water Clusters: Effects of Intermolecular Vibrational Excitation on Tunneling Rates”

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Supplemental Material Outline

I. Water dimer minima
II. Water Trimer minima
III. Water Pentamer Tunneling Hamiltonian
   a. Water Pentamer Minima

I. Water Dimer Minima

The minima for the water dimer are given in Figure S1. The hydrogens are labeled 1-4 and the oxygens are labeled a and b. The labels |1> - |8> are given above the structure in additional to the group element for the G_{16} CNPI group needed to arrive at the given structure. By comparison to the Hamiltonian given in Figure 2A of the main text, one can find the acceptor switching tunneling corresponds to structure |1> permuting to structure |4>. Likewise the bifurcation mechanism take structure |1> to |2>, the geared interchange pathway takes |1> to structure |5> or |6>, and the antigeared interchange pathway takes |1> to |7> or |8>.

![Figure S1](image-url): Structures for the 8 degenerate minima of the water dimer.
II. Water Trimer Minima

The 8 degenerate minima of the water trimer are given in Figure S2. The notation for the structures is as follows: the structure is represented as (xyz) where x, y, and z represents each of the monomers, and can have values of 1 or 0 to represent which hydrogen of the monomer is participating in the hydrogen bond. Thus we can represent the bifurcation tunneling motion as flipping the value of x, y, or z (i.e. (010) → (000)). We can neglect considering the orientation of the free hydrogen with respect to the oxygen plane due to the low barrier of the flipping motion in contrast to the bifurcation motion as discussed in the text.

Figure S2: Diagram representing how the 8 degenerate minima of the water trimer are connected by bifurcation. Red lines show bifurcation of the first monomer, blue lines represent bifurcation of the second monomer, and black lines represent bifurcation of the third monomer. The first, second, and third monomers refer to the x, y, and z monomer respectively.

For clarity we reproduce the trimer Hamiltonian form Figure 2A of this manuscript with the minima labeled as shown above.
### Figure S3: Tunneling Hamiltonian matrix for the water trimer with minima labels

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<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
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<tr>
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<td>&lt;1</td>
<td>O</td>
<td>A</td>
<td>A</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
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<td>&lt;2</td>
<td>A</td>
<td>O</td>
<td>B</td>
<td>B</td>
<td>A</td>
<td>A</td>
<td>C</td>
</tr>
<tr>
<td>(010)</td>
<td>&lt;3</td>
<td>A</td>
<td>B</td>
<td>O</td>
<td>B</td>
<td>A</td>
<td>C</td>
<td>A</td>
</tr>
<tr>
<td>(001)</td>
<td>&lt;4</td>
<td>A</td>
<td>B</td>
<td>B</td>
<td>O</td>
<td>C</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>(110)</td>
<td>&lt;5</td>
<td>B</td>
<td>A</td>
<td>A</td>
<td>C</td>
<td>O</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>(011)</td>
<td>&lt;6</td>
<td>B</td>
<td>A</td>
<td>C</td>
<td>A</td>
<td>B</td>
<td>O</td>
<td>B</td>
</tr>
<tr>
<td>(101)</td>
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<td>C</td>
<td>A</td>
<td>A</td>
<td>B</td>
<td>B</td>
<td>O</td>
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<tr>
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<td>B</td>
<td>B</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
</tbody>
</table>

### III. Water Pentamer

#### a. Tunneling Hamiltonian

The tunneling Hamiltonian for the water pentamer is given in Figure S3. Analogous to the trimer’s tunneling Hamiltonian, the elements represent consecutive bifurcation events with A representing single bifurcation, B representing two consecutive bifurcation events, and so forth. We neglect the flipping motion as discussed in the main text. In keeping with experimental results we set all elements representing multiple bifurcations to zero (B=C=D=E=0). The tunneling Hamiltonian is constructed in the basis of the 32 degenerate minima described below in Figure S4.
**Figure S4:** Tunneling Hamiltonian of the water pentamer
b. Minima

The 32 degenerate minima of the water pentamer are given in Figure S4. The notation for the structures is as follows: the structure is represented as (xyzmn) where x, y, z, m, and n represents each of the monomers, and can have values of 1 or 0 to represent which hydrogen of the monomer is participating in the hydrogen bond. Thus we can represent the bifurcation tunneling motion as flipping the value of x, y, z, m, or n (i.e. (01000) \(\rightarrow\) (00000)). We can neglect considering the orientation of the free hydrogen with respect to the oxygen plane due to the low barrier of the flipping motion in contrast to the bifurcation motion as discussed in the text.
**Figure S5**: Diagram representing how the 32 degenerate minima of the water pentamer are connected by bifurcation. Red lines show bifurcation of the first monomer, blue lines represent bifurcation of the second monomer, green shows bifurcation of the third monomer, orange shows bifurcation of the fourth monomer, and black lines represent bifurcation of the fifth monomer. The first, second, and third monomers refer to the x, y, z, m, and n monomer respectively.
Figure S6: Tunneling Hamiltonians used with zeroed out elements which are bolded to aid comparison to the full tunneling Hamiltonians. The dimer Hamiltonian has the AS element set to zero. The trimer Hamiltonian has elements B=C=0. The pentamer Hamiltonian has elements B=C=D=E=0.

A) Dimer Hamiltonian

\[
\begin{array}{cccccccc}
\hat{1} & \hat{2} & \hat{3} & \hat{4} & \hat{5} & \hat{6} & \hat{7} & \hat{8} \\
<1| & O & B & 0 & 0 & G & G & I & I \\
<2| & B & O & 0 & 0 & G & G & I & I \\
<3| & 0 & 0 & O & B & I & I & G & G \\
<4| & 0 & 0 & B & O & I & I & G & G \\
<5| & G & G & I & I & O & B & 0 & 0 \\
<6| & G & G & I & I & B & O & 0 & 0 \\
<7| & I & I & G & G & 0 & 0 & O & B \\
<8| & I & I & G & G & 0 & 0 & B & O \\
\end{array}
\]

B) Trimer Hamiltonian

\[
\begin{array}{cccccccc}
\hat{1} & \hat{2} & \hat{3} & \hat{4} & \hat{5} & \hat{6} & \hat{7} & \hat{8} \\
(000) & <1| & O & A & A & A & 0 & 0 & 0 & 0 \\
(100) & <2| & A & O & 0 & 0 & A & A & 0 & 0 \\
(010) & <3| & A & 0 & O & 0 & A & 0 & A & 0 \\
(001) & <4| & A & 0 & 0 & O & 0 & A & A & 0 \\
(110) & <5| & 0 & A & A & 0 & O & 0 & 0 & A \\
(011) & <6| & 0 & A & 0 & A & 0 & O & 0 & A \\
(101) & <7| & 0 & 0 & A & A & 0 & 0 & O & A \\
(111) & <8| & 0 & 0 & 0 & 0 & A & A & A & O \\
\end{array}
\]

C) Pentamer Hamiltonian