Supporting Information for
Temperature and Nuclear Quantum Effects on the Stretching Modes of the Water Hexamer

Nagaprasad Reddy Samala, Noam Agmon
The Fritz Haber Research Center, Institute of Chemistry, The Hebrew University of Jerusalem 91904, Israel.

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Table S1. Comparison with experiment of the book-isomer OH-stretch spectrum calculated on various MB-PESs (no scaling factors apply here). The correlation between theoretically calculated and experimentally determined frequencies used for the error estimates in HBed-OH frequencies is explained in the footnotes.

| mode  | Exper.\(^{a}\) | WHBB\(^{b}\) | E3B2\(^{c}\) | shifted E3B2\(^{d}\) | MB-pol/LM\(^{e}\) | shifted MB-pol/VACF\(^{f}\) |
|-------|----------------|-------------|-------------|---------------------|-----------------|-----------------------------|
| 1-4\(^{g}\) | 3711 | 3712 | 3746 | 3720 | 3707 |
| 5 |  | 3716 | 3713 | 3693 |
| 6 | 3572 | 3551 | 3560 | 3620 | 3572 | 3584 |
| 7 | 3464 | 3436 | 3421 | 3481 | 3434.5 | 3467 |
| 8 |  | 3380 | 3440 | 3431.7 | 3452 |
| 9 | 3423 | 3397 | 3309 | 3369 | 3416.2 | 3410 |
| 10 | 3327 | 3336 | 3276 | 3336 | 3285.1 | 3327 |
| 11 | 3287 | 3313 | 3170 | 3230 | 3268 | 3278 |
| 12 | 3201 | 3276 | 3105 | 3165 | 3246.4 | 3218 |
| bend**2 | 3169 | 3170 | | | 3147 |
| meanD\(^{b}\) | 0 | 5 | –60 | 35 | –6.1 | 0.5 |
| MAD\(^{b}\) | 0 | 27 | 70 | 35 | 22 | 9.2 |
| maxD\(^{b}\) | 0 | 75 | 117 | 57 | 45 | 17 |

\(^{a}\)Gas-phase, Table 1 of Diken et al.\(^{13}\) Band 5 merges with 1-4, bands 7-8 merge into a single band.

\(^{b}\)Digitized from Figure 1 of Wang and Bowman.\(^{27}\) Bands 5 and 8 not seen here (see above).

\(^{c}\)From Figure 7 of Kananenka et al.\(^{24}\) No bend overtone (bend**2) seen in classical MD.

\(^{d}\)E3B2 HBed OH frequencies shifted by \(\text{meanD} = 60 \text{ cm}^{-1}\), to best fit experiment.

\(^{e}\)MB-pol with the Local Monomer (LM) approximation. From Table S4 of Brown et al.\(^{29}\) Bend overtones and combinations were not assigned there, so we cite here the average of the two strongest bands below 3200 cm\(^{-1}\) as the bend overtone. A weak band at 3251.8 cm\(^{-1}\) is not assigned.

\(^{f}\)Our results, shifted by 208 cm\(^{-1}\). No bend overtone seen in classical MD.

\(^{g}\)Bands 1-4 are averaged together.

\(^{h}\)Errors with respect to experiment for modes 6,7, 9-12 (i.e., all available HBed-OH stretching modes). Whenever modes 7 and 8 are resolved, they are averaged together for this comparison.
Table S2. Comparison with experiment of the book-isomer OH-stretch spectrum calculated by scaled-harmonic quantum chemistry methods.

| mode | Exper.\(^a\) | MP2\(^b\) 6-311+G** | MP2\(^c\) aug-cc-pVDZ | VPT2\(^d\) |
|------|---------------|----------------------|-----------------------|------------|
| 1-4\(^e\) | 3711 | 3711 | 3763 | 3693 |
| 5 | -- | 3696 | 3755 | 3686 |
| 6 | 3572 | 3594 | 3617 | 3546 |
| 7 | 3464 | 3472 | 3473 | 3415 |
| 8 | | 3450 | 3458 | 3398 |
| 9 | 3423 | 3406 | 3405 | 3356 |
| 10 | 3327 | 3324 | 3307 | 3265 |
| 11 | 3287 | 3274 | 3256 | 3170 |
| 12 | 3201 | 3211 | 3182 | 3068 |
| meanD\(^f,g\) | 0 | -0.6 | 1.5 | -1.4 |
| MAD\(^g\) | 0 | 9.8 | 26 | 68 |
| maxD\(^g\) | 0 | 22 | 45 | 133 |

\(^a\)Gas-phase, Table 1 of Diken et al.\(^{13}\)
\(^b\)Table V of Kim & Kim, scaled by 0.938.\(^{17}\)
\(^c\)Table S7 of Temelso et al., harmonic, scaled by 0.9685.\(^{19}\)
\(^d\)Table S7 of Temelso et al. (anharmonic).\(^{19}\) Unscaled (i.e., scaled by 1.0).
\(^e\)Bands 1-4 are averaged together.
\(^f\)Mean deviation (calculated minus experiment).
\(^g\)Calculated with respect to experiment for modes 6,7, 9-12 (i.e., all available HBed-OH stretching modes). Whenever modes 7 and 8 are resolved, they are averaged for making this comparison.
**Table S3.** Comparison with experiment of the MB-pol book-isomer OH-stretch spectrum when the shift is determined to generate best agreement with the optimally-scaled quantum chemistry methods of Table S2.

| mode | Exper. | MB-pol/MP2<sup>b</sup> 6-311+G** | MB-pol/MP2<sup>c</sup> aug-cc-pVDZ | MB-pol/VPT2<sup>d</sup> |
|------|--------|-------------------------------|---------------------------------|------------------|
| 1-4<sup>e</sup> | 3711 | 3707 | 3709 | 3706 |
| 5     |       | 3693 | 3695 | 3695 |
| 6     | 3572  | 3584 | 3586 | 3583 |
| 7     | 3464  | 3460 | 3462 | 3459 |
| 8     |       | 3452 | 3454 | 3451 |
| 9     | 3423  | 3410 | 3412 | 3409 |
| 10    | 3327  | 3327 | 3329 | 3326 |
| 11    | 3287  | 3278 | 3280 | 3277 |
| 12    | 3201  | 3218 | 3220 | 3217 |
|      | MAD<sup>f</sup> | 8.4 | 8.1 | 8.9 |
|      | maxD<sup>f</sup> | 0  | 17  | 19  |

<sup>a</sup>Gas-phase, Table 1 of Diken et al.<sup>13</sup>
<sup>b</sup>MB-pol shifted by 208 cm<sup>-1</sup>, to obtain best agreement with Table V of Kim & Kim.<sup>17</sup> scaled by 0.938.
<sup>c</sup>MB-pol shifted by 206 cm<sup>-1</sup>, to obtain best agreement with Table S7 of Temelso et al., harmonic frequencies, scaled by 0.9685.<sup>19</sup>
<sup>d</sup>MB-pol shifted by 209 cm<sup>-1</sup>, to obtain best agreement with Table S7 of Temelso et al. (anharmonic),<sup>19</sup> scaled by 1.02.
<sup>e</sup>Bands 1-4 are averaged together.
<sup>f</sup>MAD and maxD with respect to experiment for modes 6, 7, 9-12 (i.e., all available HBed-OH stretching modes). Whenever modes 7 and 8 are resolved, they are averaged for making this comparison.
Figure S1: VACF vibrational spectrum of the cage isomer at 10K and a 10 ns length of trajectory, (a) All H-atom VACF and (b) Partial VACF for the OH distances color coded in panel (a). The LMA of the HBed OH stretches can be read from this figure as follows (low to high) O6H6 (DAA), O4H4 (DAA), O2H2 (DA), O5H5 (DA), O1H1 (DDA), O3H3 (DDA), O1H1’ (DDA), O3H3’ (DDA).
Figure S2: Same as Figure S1 at 30K.
Figure S3: Same as Figure S1 at 50K.
Figure S4: Same as Figure S1 at 70K.
Figure S5: VACF vibrational spectrum of the ring isomer at 10K and a 10 ns length of trajectory, (a) All H-atom VACF and (b) Partial VACF for the OH distances color coded in panel (a).
Figure S6: VACF vibrational spectrum of the prism isomer at 10K and a 10 ns length of trajectory, (a) All H-atom VACF and (b) Partial VACF for the OH distances color coded in panel (a). The LMA of the HBed OH stretches can be read from this figure as follows (low to high) O5H5 (DAA), O2H2 (DAA), O6H6 (DDA), O4H4 (DAA), O1H1’ (DDA), O3H3’ (DDA), O6H6’ (DDA), O1H1 (DDA), O3H3 (DDA).