

Supporting Information for:

Density-Functional Tight-Binding Molecular Dynamics Simulations of  
Excess Proton Diffusion in Ice I<sub>h</sub>, Ice I<sub>c</sub>, Ice III, and Melted Ice VI  
Phases

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## Details of Pre-Equilibrated Ice Structures

**Table S1.** Unit cell sizes and densities of ice I<sub>h</sub> obtained with TIP4P/ice<sup>S1</sup> force field<sup>a</sup>

| <i>T</i> [K] | Unit cell size [Å <sup>3</sup> ] | Density [g/cm <sup>3</sup> ] |
|--------------|----------------------------------|------------------------------|
| 50           | 22.530×23.334×21.875             | 0.936                        |
| 70           | 22.586×23.393×21.930             | 0.929                        |
| 120          | 22.627×23.435×21.970             | 0.924                        |
| 230          | 22.739×23.551×22.078             | 0.910                        |
| 250          | 22.752×23.565×22.091             | 0.909                        |
| 270          | 22.778×23.592×22.117             | 0.906                        |

<sup>a</sup>Number of water molecules is 360 and target pressure is 0.101325 MPa.

**Table S2.** Unit cell sizes and densities of ice I<sub>c</sub> obtained with TIP4P/ice<sup>S1</sup> force field<sup>a</sup>

| <i>T</i> [K] | Unit cell size [Å <sup>3</sup> ] | Density [g/cm <sup>3</sup> ] |
|--------------|----------------------------------|------------------------------|
| 50           | 20.107×18.526×18.550             | 0.935                        |
| 70           | 20.117×18.535×18.559             | 0.933                        |
| 120          | 20.138×18.554×18.578             | 0.930                        |
| 230          | 20.222×18.632×18.656             | 0.919                        |
| 250          | 20.241×18.649×18.673             | 0.916                        |
| 270          | 20.249×18.667×18.681             | 0.914                        |

<sup>a</sup>Number of water molecules is 216 and target pressure is 0.101325 MPa.

**Table S3.** Unit cell sizes and densities of ice III obtained with TIP4P/2005<sup>S2</sup> force field<sup>a</sup>

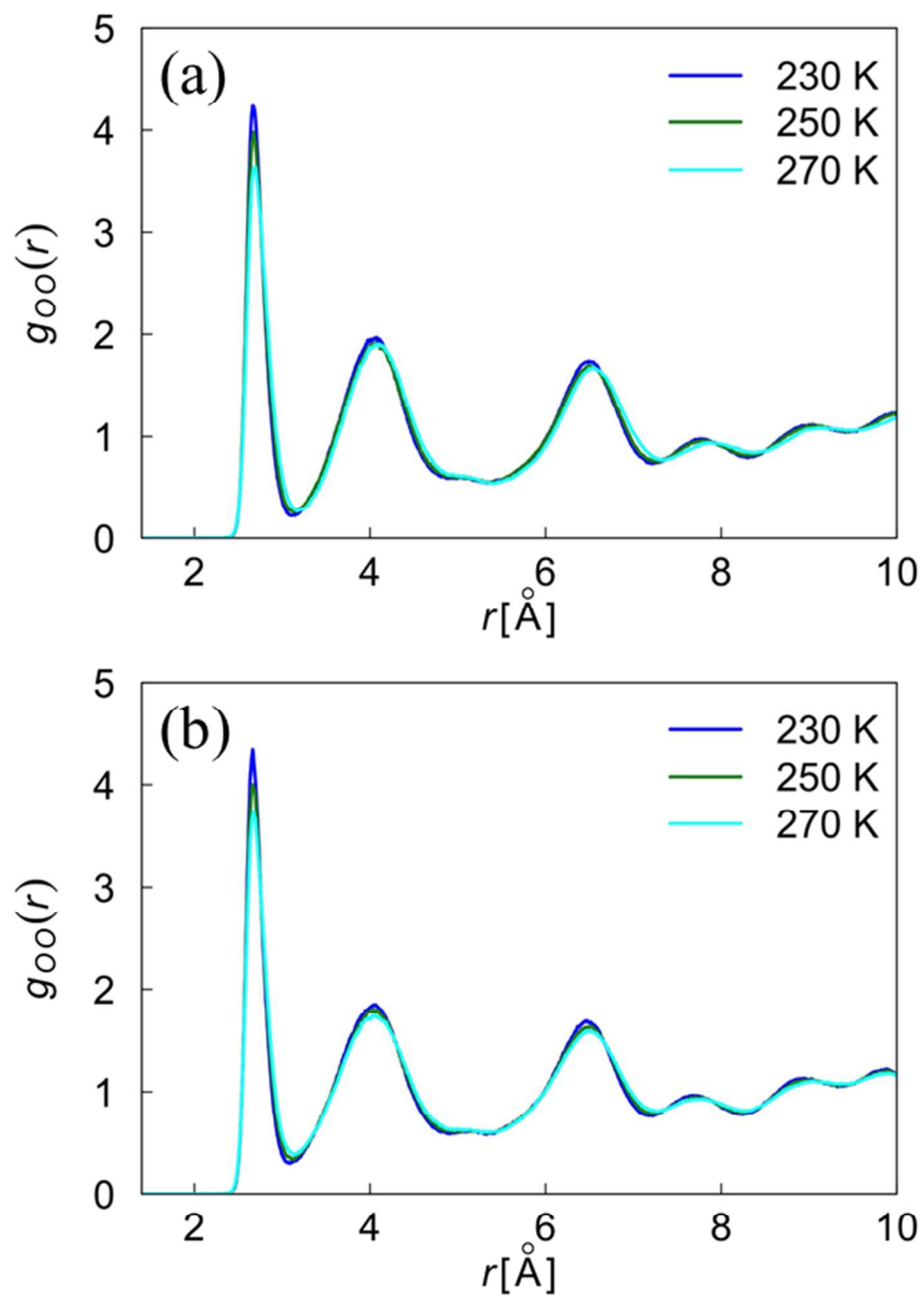
| <i>P</i> [MPa] | <i>T</i> [K] | Unit cell size [Å <sup>3</sup> ] | Density [g/cm <sup>3</sup> ] |
|----------------|--------------|----------------------------------|------------------------------|
| 280            | 230          | 19.673×20.082×21.024             | 1.166                        |
|                | 250          | 19.685×20.095×21.037             | 1.164                        |
|                | 270          | 19.710×20.119×21.063             | 1.160                        |
| 290            | 230          | 19.446×19.851×20.782             | 1.207                        |
|                | 250          | 19.489×19.895×20.828             | 1.200                        |
|                | 270          | 19.532×19.938×20.873             | 1.192                        |
| 300            | 230          | 19.277×19.677×20.600             | 1.240                        |
|                | 250          | 19.323×19.725×20.650             | 1.231                        |
|                | 270          | 19.393×19.797×20.725             | 1.217                        |

<sup>a</sup>Number of water molecules is 324.**Table S4.** Unit cell sizes and densities of melted ice VI obtained with TIP4P/2005<sup>S2</sup> force field<sup>a</sup>

| <i>T</i> [K] | Unit cell size [Å <sup>3</sup> ] | Density [g/cm <sup>3</sup> ] |
|--------------|----------------------------------|------------------------------|
| 230          | 18.141×19.216×16.878             | 1.372                        |
| 250          | 18.155×19.231×16.891             | 1.368                        |
| 270          | 18.170×19.247×16.904             | 1.365                        |

<sup>a</sup>Number of water molecules is 270 and target pressure is 1100 MPa.

### Radial Distribution Functions of Ice III



**Figure S1.** Temperature dependence of the O–O pair RDF for ice III pre-equilibrated at (a) 290 and (b) 300 MPa.

### Statistics of Bond Order Parameter Calculations for Ice

**Table S5.** Mean of averaged form of cubic ( $\langle q_4(i) \rangle$ ) and hexagonal ( $\langle q_6(i) \rangle$ ) bond order parameters and its standard deviation for ice I<sub>h</sub>

| <i>T</i> [K] | Mean                     |                          | Standard deviation       |                          |
|--------------|--------------------------|--------------------------|--------------------------|--------------------------|
|              | $\langle q_4(i) \rangle$ | $\langle q_6(i) \rangle$ | $\langle q_4(i) \rangle$ | $\langle q_6(i) \rangle$ |
| 50           | 0.3650                   | 0.5428                   | 0.0143                   | 0.0150                   |
| 70           | 0.3641                   | 0.5379                   | 0.0148                   | 0.0164                   |
| 120          | 0.3621                   | 0.5252                   | 0.0152                   | 0.0166                   |
| 230          | 0.3528                   | 0.4822                   | 0.0219                   | 0.0282                   |
| 250          | 0.3526                   | 0.4821                   | 0.0219                   | 0.0282                   |
| 270          | 0.3479                   | 0.4497                   | 0.0348                   | 0.0400                   |

**Table S6.** Mean of averaged form of cubic ( $\langle q_4(i) \rangle$ ) and hexagonal ( $\langle q_6(i) \rangle$ ) bond order parameters and its standard deviation for ice I<sub>c</sub>

| <i>T</i> [K] | Mean                     |                          | Standard deviation       |                          |
|--------------|--------------------------|--------------------------|--------------------------|--------------------------|
|              | $\langle q_4(i) \rangle$ | $\langle q_6(i) \rangle$ | $\langle q_4(i) \rangle$ | $\langle q_6(i) \rangle$ |
| 50           | 0.4914                   | 0.5921                   | 0.0325                   | 0.0346                   |
| 70           | 0.4942                   | 0.5868                   | 0.0072                   | 0.0153                   |
| 120          | 0.4875                   | 0.5718                   | 0.0234                   | 0.0361                   |
| 230          | 0.4500                   | 0.4876                   | 0.0402                   | 0.0533                   |
| 250          | 0.4404                   | 0.4765                   | 0.0402                   | 0.0601                   |
| 270          | 0.4021                   | 0.3962                   | 0.0587                   | 0.0679                   |

**Table S7.** Mean of averaged form of cubic ( $\langle q_4(i) \rangle$ ) and hexagonal ( $\langle q_6(i) \rangle$ ) bond order parameters and its standard deviation for ice III

| $P$ [MPa] | $T$ [K] | Mean                     |                          | Standard deviation       |                          |
|-----------|---------|--------------------------|--------------------------|--------------------------|--------------------------|
|           |         | $\langle q_4(i) \rangle$ | $\langle q_6(i) \rangle$ | $\langle q_4(i) \rangle$ | $\langle q_6(i) \rangle$ |
| 280       | 230     | 0.3298                   | 0.1926                   | 0.0339                   | 0.0383                   |
|           | 250     | 0.3217                   | 0.1917                   | 0.0397                   | 0.0369                   |
|           | 270     | 0.3207                   | 0.1945                   | 0.0385                   | 0.0354                   |
| 290       | 230     | 0.3271                   | 0.2012                   | 0.0353                   | 0.0361                   |
|           | 250     | 0.3249                   | 0.1933                   | 0.0324                   | 0.0350                   |
|           | 270     | 0.3311                   | 0.1941                   | 0.0347                   | 0.0365                   |
| 300       | 230     | 0.3070                   | 0.1898                   | 0.0414                   | 0.0375                   |
|           | 250     | 0.3049                   | 0.1937                   | 0.0412                   | 0.0326                   |
|           | 270     | 0.2968                   | 0.2024                   | 0.0374                   | 0.0392                   |

**Table S8.** Mean of averaged form of cubic ( $\langle q_4(i) \rangle$ ) and hexagonal ( $\langle q_6(i) \rangle$ ) bond order parameters and its standard deviation for melted ice VI

| $T$ [K] | Mean                     |                          | Standard deviation       |                          |
|---------|--------------------------|--------------------------|--------------------------|--------------------------|
|         | $\langle q_4(i) \rangle$ | $\langle q_6(i) \rangle$ | $\langle q_4(i) \rangle$ | $\langle q_6(i) \rangle$ |
| 230     | 0.1386                   | 0.1739                   | 0.0408                   | 0.0337                   |
| 250     | 0.1186                   | 0.1717                   | 0.0332                   | 0.0342                   |
| 270     | 0.1222                   | 0.1752                   | 0.0356                   | 0.0372                   |

## References

- (S1) Abascal, J. L. F.; Sanz, E.; García Fernández, R.; Vega, C. A Potential Model for the Study of Ices and Amorphous Water: TIP4P/Ice. *J. Chem. Phys.* **2005**, *122*, 234511.
- (S2) Abascal, J. L. F.; Vega, C. A General Purpose Model for the Condensed Phases of Water: TIP4P/2005. *J. Chem. Phys.* **2005**, *123*, 234505.