# Supporting Information: Calorimetric Signature of Deuterated Ice II: Turning an Endotherm to an Exotherm

Violeta Fuentes-Landete,[†,‡] Soroush Rasti,[¶] Robert Schlögl,[‡] Jörg Meyer,[¶] and Thomas Loerting[*,†]

[†] *Institute of Physical Chemistry, University of Innsbruck, Innrain 52c, 6020 Innsbruck, Austria*

[‡] *Max Planck Institute for Chemical Energy Conversion, Stiftstr. 34-36, 45470 Mülheim an der Ruhr, Germany*

[¶] *Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands*

E-mail: thomas.loerting@uibk.ac.at

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# 1 Space-group-constrained Structure Optimizations

The calculations reported in the main text are based on structure optimizations that do not constrain the space group. We have repeated the structure optimizations for ice Ih using our in-house space-group constraint (SPGC) implemented in ASE and used in our previous work[S1]. Here we compare the results from these calculations to the corresponding ones in Tables 2 and 3.

Table S1: Lattice energies for ice Ih in kJ/mol as defined in Eqs. (3) and (4). Experimental values have been obtained by extrapolating experimental values for the vibrational frequencies back to 0 K and calculating the zero-point energy therefrom[S2,S3].

| | $E_{\mathrm{lat}}$ | $E_{\mathrm{lat}}^{\mathrm{ZPE}}$ | |
|---|---|---|---|
| | | $H_2O$ | $D_2O$ |
| ice Ih | | | |
| q-TIP4P/F | −59.782 | −47.216 | −49.885 |
| q-TIP4P/F (SPGC) | −59.645 | −46.911 | −49.600 |
| MB-pol | −59.464 | −46.756 | −49.552 |
| MB-pol (SPGC) | −59.390 | −46.817 | −49.609 |
| experiments | −58.82[a] | −47.341(15)[a,b] | −48.611(615)[b] |

[a] ref. S3; [b] ref. S2.

Table S2: Energy differences for the ice II → ice I transition in J/mol as defined by Eqs (3), (4), (6) and (7).

| | $\Delta E_{\mathrm{lat}}$ | $\Delta E_{\mathrm{lat}}^{\mathrm{ZPE}}$ | | $\Delta \tilde{H}(T = 150\,\mathrm{K})$ | | $\Delta H(T = 150\,\mathrm{K})$ | |
|---|---|---|---|---|---|---|---|
| | | $H_2O$ | $D_2O$ | $H_2O$ | $D_2O$ | $H_2O$ | $D_2O$ |
| q-TIP4P/F | −1466 | −595 | −732 | −627 | −762 | −121 | −256 |
| Isotope effect | | −137 | | −135 | | −135 | |
| q-TIP4P/F (SPGC) | −1379 | −290 | −477 | −662 | −809 | −156 | −303 |
| Isotope effect | | −187 | | −147 | | −147 | |
| MB-pol | −801 | −561 | −612 | −563 | −611 | −57 | −105 |
| Isotope effect | | −51 | | −48 | | −48 | |
| MB-pol (SPGC) | −875 | −622 | −669 | −673 | −715 | −167 | −209 |
| Isotope effect | | −47 | | −42 | | −42 | |

# 2 Calculated Thermal Expansion

Table S3: Thermal expansion at $T = 150\,\mathrm{K}$ relative to $T = 0\,\mathrm{K}$ in percent as calculated according to the quasi-harmonic approximation (QHA). See main text and[S1] for details.

| | $H_2O$ | $D_2O$ |
|---|---|---|
| ice Ih | | |
| q-TIP4P/F | 0.05 | 0.08 |
| MB-pol | 0.24 | 0.31 |
| ice II | | |
| q-TIP4P/F | 0.82 | 0.85 |
| MB-pol | 1.16 | 1.25 |

# References

(S1) Rasti, S.; Meyer, J. Importance of Zero-Point Energy for Crystalline Ice Phases: A Comparison of Force Fields and Density Functional Theory. *J. Chem. Phys.* **2019**, *150*, 234504, DOI: doi:10.1063/1.5097021.

(S2) Whalley, E. The Difference in the Intermolecular Forces of H2O and D2O. *Trans. Faraday Soc.* **1957**, *53*, 1578, DOI: doi:10.1039/tf9575301578.

(S3) Whalley, E. Energies of the Phases of Ice at Zero Temperature and Pressure. *J. Chem. Phys.* **1984**, *81*, 4087–4092, DOI: doi:10.1063/1.448153.