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

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Calorimetric studies on ice II reveal a surprising H2O/D2O isotope effect. While the ice II to ice Ic transition is endothermic for H2O, it is exothermic for D2O samples. The transition enthalpies are +40 and −140 J/mol, respectively, where such a sign change upon isotope substitution is unprecedented in ice research. To understand the observations we employ force field calculations using two water models known to perform well for H2O ice phases and their vibrational properties. These simulations reveal that the isotope effect can be traced back to zero-point energy. q-TIP4P/F fares better and is able to account for approximately three-fourths of the isotope effect, while MB-pol only catches approximately one-third. Phonon and configurational entropy contributions are necessary to predict reasonable transition enthalpies, but they do not have an impact on the isotope effect. We suggest using these calorimetric isotope data as a benchmark for water models.