

**Stony Brook University  
The Graduate School**

Doctoral Defense Announcement

**Abstract**

Nuclear Quantum Effects in Ice Phases and Water From First Principles Calculations

By

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Despite the simplicity of the molecule, condensed phases of water show many physical anomalies, some of which are still unexplained to date. This thesis focuses on one striking anomaly that has been largely neglected and never explained. When hydrogen ( $^1\text{H}$ ) is replaced by deuterium ( $^2\text{D}$ ), zero point fluctuations of the heavy isotope causes ice to expand, whereas in normal isotope effect, heavy isotope causes volume contraction. Furthermore, in a normal isotope effect, the shift in volume should decrease with increasing temperature, while, in ice, the volume shift increases with increasing temperature and persists up to the melting temperature and also exists in liquid water.

In this dissertation, nuclear quantum effects on structural and cohesive properties of different ice polymorphs are investigated. We show that the anomalous isotope effect is well described by first principles density functional theory with van der Waals (vdW-DF) functionals within the quasi-harmonic approximation. Our theoretical modeling explains how the competition between the intra- and inter-molecular bonding of ice leads to an anomalous isotope effect in the volume and bulk modulus of ice. In addition, we predict a normal isotope effect when  $^{16}\text{O}$  is replaced by  $^{18}\text{O}$ , which is experimentally confirmed. Furthermore, the transition from proton disordered hexagonal phase, ice Ih to proton ordered hexagonal phase, ice XI occurs with a temperature difference between  $^1\text{H}$  and  $^2\text{D}$  of 6K, in good agreement with experimental value of 4K. We explain for first time that this temperature difference is entirely due to the zero point energy.

In the second half of this thesis, we expand our study to the other ice phases: ice Ic, ice IX, ice II, ice VIII, clathrate hydrates, and low and high density amorphous ices. We employ the methodology that we have developed to investigate the isotope effect in structures with different configurations. We show that there is a transition from anomalous isotope effect to normal isotope effect in these structures as the density increases. We analyze the bonding mechanism of these structures and make links to the most important anomalies of liquid water.

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