

## ICE AND WATER

**Allocation:** Blue Waters Professor/0.15 Mnh

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### EXECUTIVE SUMMARY:

Predictive condensed-phase simulations at an accurate first-principles (*ab initio*) theoretical level, treating all electrons quantum mechanically, has previously been unthinkable. We performed just such simulations for a whole range of structural, dynamical, thermodynamic, and response properties of ice and liquid water, undoubtedly the most important condensed-phase systems on Earth. An algorithmic breakthrough (the embedded fragmentation technique) combined with the massive computational power of Blue Waters made these simulations possible. The predominant solid phase of water (ice Ih) displays unusual behaviors such as negative thermal expansion at low temperatures and an anomalous volume isotope effect. Our *ab initio* calculation computationally reproduced both, while also hinting at a pressure-induced amorphization. For liquid water, structures, self-diffusion coefficients, infrared and Raman spectra, and the Raman non-coincidence effect were computationally explained. The calculations revealed an atomistic detail of the hydrogen-bond network dynamics in the liquid.

### INTRODUCTION

Chemistry of water in all three phases largely defines our planetary environment. Its influence is felt in subjects ranging from geology to climate, to biology and ecology, to geopolitics and history. Such a seemingly simple phenomenon—that the water volume collapses upon melting—has an immense impact on every structure and reaction found on the planetary surface and thus on every life form, but it derives from a subtle interplay of water's peculiar chemical bonding and dynamics. To this day, computationally determining some of the most delicate thermodynamic and response properties of ice and liquid water, such as melting temperature, from first principles (i.e.

with no reference to any experimental data) has not been possible.

In this work, we combined the massive computational power of Blue Waters with an algorithmic breakthrough (embedded fragmentation) that made *ab initio* quantum chemistry calculations vastly faster, scalable in parallel, and thus applicable to condensed-phase systems. With it, we addressed structural, dynamical, thermodynamic, and response properties of ice and liquid water. We used *ab initio* second-order many-body perturbation theory using a Gaussian-type basis set. The theory can account for all covalent, ionic, hydrogen-bond, and dispersion interactions from first principles.

For the dominant phase of ice on Earth (ice Ih), we aimed to computationally explain its unusual behavior: the negative thermal expansion at temperatures below 70 K and the anomalous volume isotope effect (which means that heavy water has a greater molar volume than normal water). We also monitored a possible pressure-induced phase transition from a crystalline, proton-disordered (ice Ih) phase to an amorphous phase. These rather strange behaviors may well be related to the negative thermal expansion and anomalous volume isotope effect also found in liquid water.

We calculated the structure (radial distribution function, coordinate number, dipole moment), dynamics (self-diffusion coefficient, fluctuation of coordination number and dipole moment), and response (infrared and Raman spectra) properties of liquid water. Some of these properties reflect the local hydrogen-bond environment and its dynamics, which is often difficult to probe experimentally.

### METHODS & RESULTS

We used the embedded fragmentation method [1]. This method first divides molecular crystal or liquid into overlapping molecular dimers embedded in the self-consistently determined electrostatic field of the crystal or liquid. Next, energies, atomic forces, force constants, dipole moments, infrared and Raman intensities, etc., are calculated for each dimer in parallel. These data are then combined to yield the corresponding properties of the bulk crystal or liquid at finite pressures and/or temperatures.

This method has been used successfully in the past, in conjunction with *ab initio* second-order many-body perturbation and/or coupled-cluster singles and doubles levels, to study the structure and spectra of ice Ih [2] and ice VIII [3] as well as the structure, spectra including pressure tuning of Fermi resonance [4], solid–solid phase transition [5], and thermal expansion [6] of dry ice (solid carbon dioxide phase I).

For ice Ih, our simulation reproduced the negative thermal expansion at low temperatures, which turned positive at higher temperatures. We found that this peculiar behavior was caused by the negative pressure dependence of the frequencies (Grüneisen parameters) of acoustic phonons, reflecting the sparse structure of the hydrogen-bond cage of ice. The anomalous volume isotope effect was reproduced correctly with only one choice of embedding field but not with another, suggesting that it is a result of a delicate balance between the competing pressure effects on vibrational and O–H stretching phonons. Furthermore, a pressure-induced volume collapse and corresponding softening of acoustic phonons were detected at a pressure similar to the one at which pressure-induced amorphization is observed experimentally. It is possible that we computationally observed a mechanical instability precursor to such a transition to the so-called high-density amorphous phase.

For liquid water, we performed probably the first molecular dynamics simulation using on-the-fly atomic forces evaluated by the *ab initio* electron-correlated molecular orbital method. The calculated radial distribution function and self-diffusion coefficient were in excellent agreement with the observed results. The simulated infrared and Raman spectra correctly predicted the shapes and widths of the O–H stretching bands, including the non-coincidence of the isotropic and anisotropic Raman components, which are known to reflect the local hydrogen-bond environment. The simulation also provided unique insights into the large fluctuation of the coordination number and the mechanism and time scale in which water molecules exchange their positions between first and second solvation shells, causing such large fluctuation. Our first-principles simulation, therefore, allowed us to study the electronic

details of the structure and dynamics of liquid water with unprecedented accuracy.

### WHY BLUE WATERS?

Condensed-phase applications of systematic *ab initio* electron-correlated molecular orbital theory, which goes beyond empirical force fields or even density-functional approximations, have long been unthinkable. Both algorithmic innovations and supercomputing resources at the scale of Blue Waters were essential for the project.