**ICE AND WATER**

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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 been impossible to probe computationally. With the advent of Blue Waters, we were able to correctly predict the shapes and widths of 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 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.

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.

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**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.

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