ICE AND WATER

Allocation: Blue Waters Professor/200 Knh
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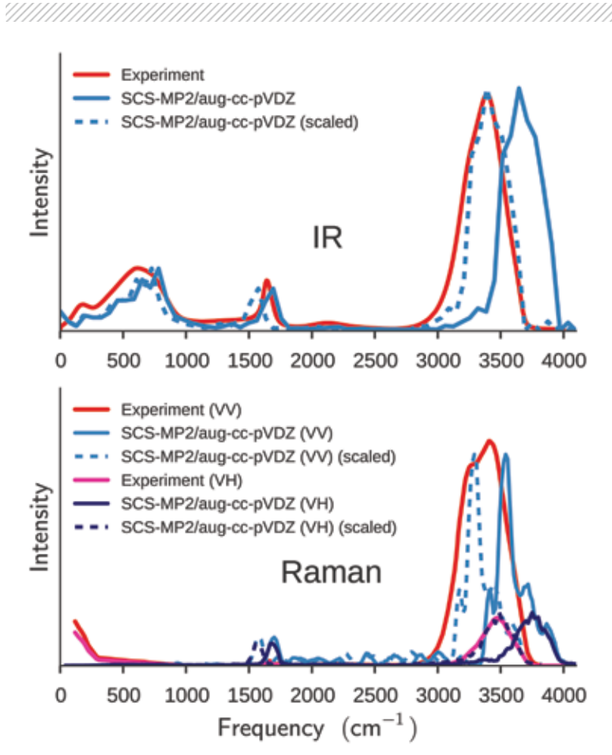
EXECUTIVE SUMMARY

Systematic *ab initio* many-body approximations to electronic Schrödinger equations have transformed molecular sciences. Thanks to Blue Waters, they are now routinely applicable to a certain class of condensed matter: molecular crystals, amorphous solids, and liquids, enabling predictive simulations at such theoretical levels as *ab initio* many-body perturbation and coupled-cluster theories for a wide range of their structural, thermodynamic, and spectroscopic properties. This class of matter includes nature's most important and abundant solids and liquids: ice and liquid water. Here, we performed *ab initio* second-order many-body perturbation (MP2) calculation of liquid water to predict its structural, thermodynamic, response, and spectral properties. We also computationally reproduced the thermal contraction of ice-Ih (the hexagonal crystal form of ordinary ice) at low temperatures followed by expansion at higher temperatures, anomalous volume isotope effect, and pressure-induced amorphization to glass-like high-density amorphous phase.

FIGURE 1: The infrared and Raman spectra of liquid water. Reproduced from [1].



INTRODUCTION

As described more fully in [1], the properties of ice and liquid water have the most decisive influence on everything from climate to geology to biology on Earth. What may be surprising is that there are some unsolved mysteries and unsettled controversies surrounding these properties. For instance, unlike most other solids, ice-Ih contracts thermally at low temperatures before it expands at higher temperatures. Ice-Ih expands upon heavy-isotope (deuterium) substitution, which is the opposite behavior from normal solids and is said to have the anomalous volume isotope effect (VIE). Furthermore, ice-Ih undergoes a pressure-induced amorphization to become high-density amorphous (HDA) ice, which is distinct from low-density amorphous (LDA) ice. There seems perennial disagreement among researchers about the average number of hydrogen bonds per molecule and the mean dipole moment in liquid water.

Using Blue Waters, we performed direct applications of systematic *ab initio* many-body electronic structure theories, which go far beyond empirical force fields or density-functional theories that have dominated condensed-phase thermodynamic simulations, for a variety of properties of ice and liquid water. They mark the **beginning of a new era** of condensed-matter simulations with a systematic path to exactness.

METHODS & RESULTS

Our *ab initio* simulation of liquid water [2] is based on molecular dynamics (MD) using on-the-fly atomic forces calculated fully quantum mechanically in each MD step by highly scalable embedded-fragment MP2 method.

Our simulation accurately predicts the oxygen-oxygen radial distribution function of liquid water, i.e., its average structure, and shows that the distribution of the hydrogen-bond number is strongly peaked at four, confirming "the standard picture" of liquid water with an average hydrogen-bond number of 3.8, while disagreeing with "the string theory" of liquid water that asserts that each water molecule has an average of only two hydrogen bonds in a chain or a ring. It also reproduces the general intensity profiles of the observed infrared and parallel- and perpendicular-polarized Raman spectra extremely well (Fig. 1), including the Raman noncoincidence effect.

Ice-Ih, unlike other solids, contracts upon heating at low temperatures (< 70° K), and then expands at higher temperatures (solid curves in Fig. 2). Upon deuterium substitution for hydrogens, it expands by 0.09% at 0° K (the anomalous VIE; solid curves in Fig. 2). These are quantum effects of lattice vibrations in anharmonic potentials, which require high-power methods to explain computationally. Our study [3] reproduces the thermal contraction at low temperatures quantitatively and the thermal expansion at higher temperatures qualitatively (dots in Fig. 2). The study confirms the origin of the thermal contraction as the volume-collapsing effect of hydrogen-bond bending modes, whereas the subsequent thermal expansion is caused primarily by the hydrogen bond-stretching modes.

The same MP2 calculation gives qualitatively varied predictions about the anomalous VIE, depending on calculation details, although the one shown in figure 2 reproduces it quantitatively. The extreme sensitivity to VIE is traced to the fact that net VIE at 0° K is the result of delicate cancellation of competing (i.e., volume-expanding and contracting) effects of *all* fundamental phonons that exist in the zero-point state.

Compression of ice-Ih at slightly below 0° C results in a phase transition to liquid water because the latter is denser than the former; the thermodynamic phase boundary then has a negative slope. In 1984, Mishima et al. [4] extrapolated the negative-slope melting curve to lower temperatures, predicting and then observing a pressure-induced transition from ice-Ih to glass-like disordered HDA phase at 1.0 GPa and 77° K.

With increasing pressure, MP2 geometry optimization of ice-Ih, starting from an initial crystalline structure, becomes more difficult at pressures greater than 2.35 GPa. By 3 GPa, the optimized crystalline structure never converges to a minimum-energy crystalline structure, but instead, leads to a loss of symmetry and long-range order with a 15% reduction in volume relative to the ambient-pressure value. Figure 3 contrasts the optimized crystalline structure at 0 GPa and a nonconverged, semi-amorphous structure at 3 GPa. Concomitant with the difficulty in optimizing the geometry, we observe pressure-induced red-shifting of acoustic phonons, starting at around 2 GPa. Our calculated thermodynamic transition pressure between the two phases is 1.6 GPa at 0° K, which is consistent with experimental values. These constitute the first *ab initio* computational detection of the pressure-induced amorphization of ice-Ih.

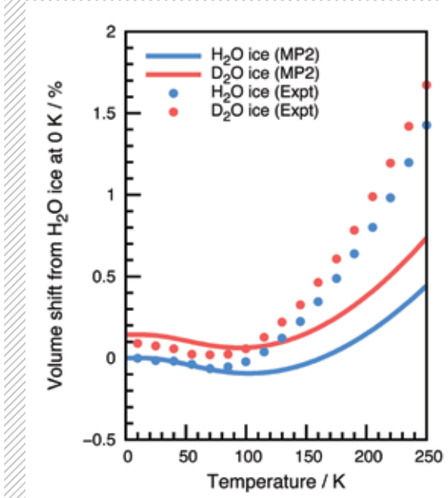


FIGURE 2: Temperature-dependence of the volume of H2O and D2O ice-ih. Reprinted [3].

WHY BLUE WATERS

A first-principles quantum-mechanical calculation of an infinitely extended solid, not to mention liquid, was previously unthinkable. Blue Waters has now **made these calculations a reality** using a combination of computing power and the algorithmic breakthrough (embedded-fragmentation) that exposes scalability with both system and computer sizes.

NEXT GENERATION WORK

We will fully develop a software system that will allow routine applications of predictive *ab initio* all-electron quantum-mechanical methods to a whole range of properties of any molecular solids and molecular liquids on supercomputers. Thanks to Blue Waters, it will no longer be necessary to rely on empirical potentials or density-functional approximations.

PUBLICATIONS AND DATA SETS

Hirata, K. et al., *Ab initio* ice, dry ice, and liquid water. *Fragmentation: Toward Accurate Calculations on Complex Molecular Systems*, Ed by Mark S. Gordon, in review.

Salim, M.A., S. Y. Willow, and S. Hirata, Ice Ih anomalies: Thermal contraction, anomalous volume isotope effect, and pressure-induced amorphization. *J. Chem. Phys.*, 144, (2016), doi: 10.1063/1.4951687

Willow, S.Y., M. A. Salim, K. S. Kim, and S. Hirata, *Ab initio* molecular dynamics of liquid water using embedded-fragment second-order many-body perturbation theory towards its accurate property prediction. *Scientific Reports*, 5 (2015), doi:10.1038/srep14358

Willow, S.Y., et al., Why is MP2-water "cooler" and "denser" than DFT-water? *J. Phys. Chem. Lett.* 7 (2016), p. 680-684, doi: 10.1021/acs.jpclett.5b02430

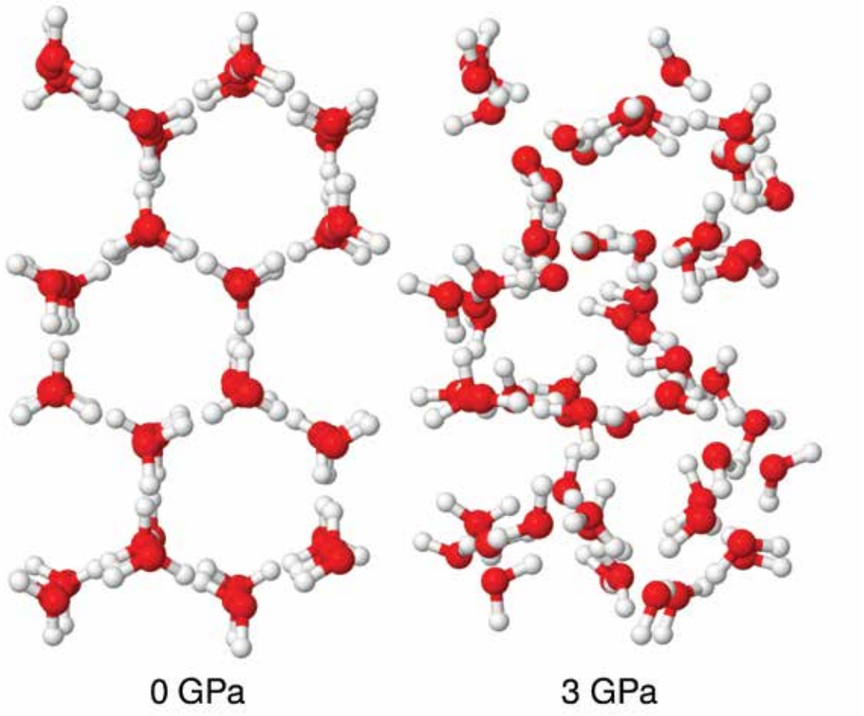
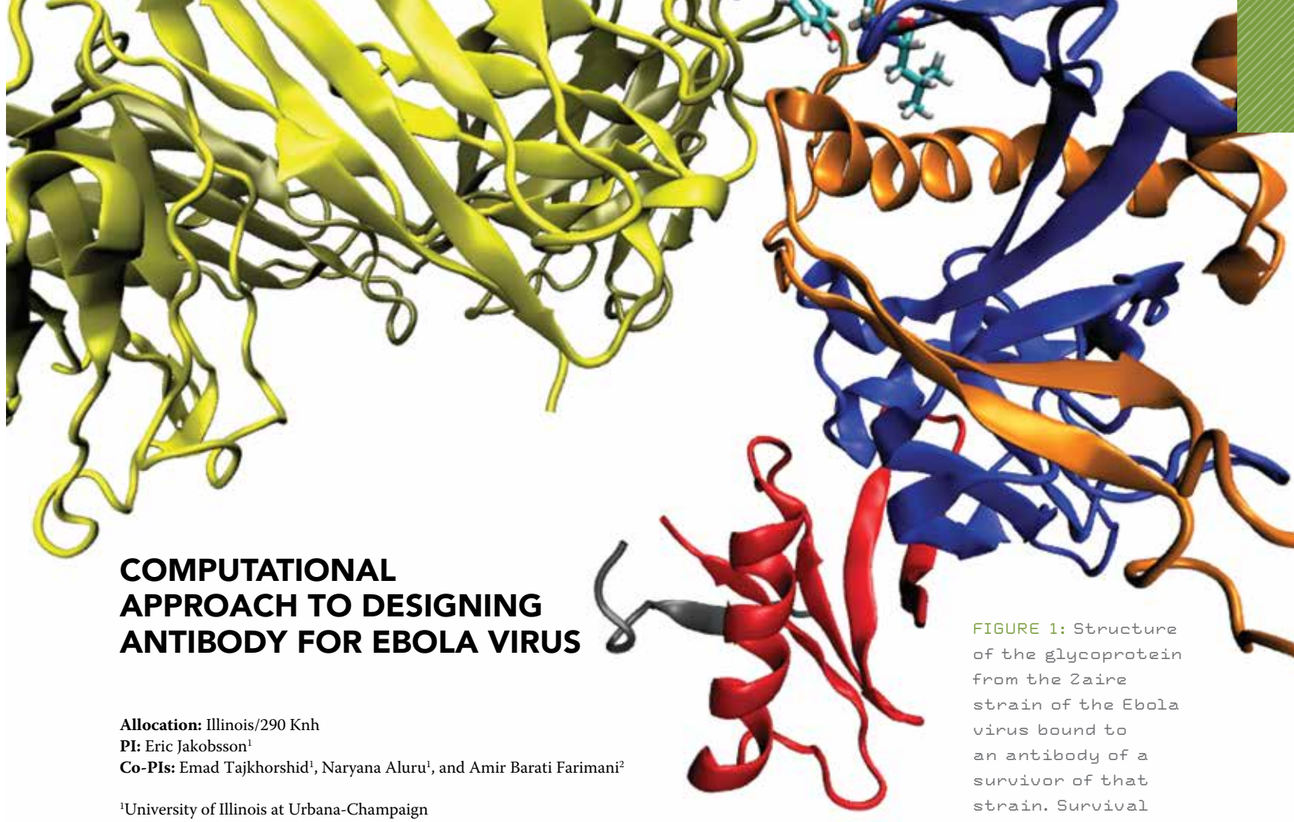


FIGURE 3: Optimized (left) and partially optimized (right) structures of ice-Ih and ice-HDA. Reprinted from [3].



COMPUTATIONAL APPROACH TO DESIGNING ANTIBODY FOR EBOLA VIRUS

FIGURE 1: Structure of the glycoprotein from the Zaire strain of the Ebola virus bound to an antibody of a survivor of that strain. Survival was because of the effective binding of the glycoprotein to the virus pictured. The glycoprotein is essential to the virus' ability to enter the host cell.

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EXECUTIVE SUMMARY

Our work on Blue Waters successfully demonstrated the feasibility of computational design of synthetic antibodies against evolving Ebola infections. We simulated multiple cycles of viral mutation and redesign of a synthetic antibody to counter the mutations successfully and restore high-affinity binding of the antibody to the virus. Viral mutations were selected by random walk theory biased according to the statistical propensity for amino acid substitution. Trial substitutions for redesign were selected according to the statistical propensity for forming favorable interfaces. The success of the redesign was evaluated by using molecular dynamics (MD) to compute viral protein-antibody binding energy. Blue Waters provided the essential computational power to do the many simulations to test the ability to redesign successfully, and we feel this approach should be extendable to other viruses. In combination with experimental sequencing and structure determination, our approach should enable rapid design and redesign of synthetic antibody therapy in response to rapidly evolving viral challenges.

INTRODUCTION

The ability to produce antibodies specific to predefined biomolecular targets was a landmark development in biological research and potential therapy [1]. At the core of this work was engineering at the cellular level, in particular induced cell fusion to produce hybrid cells. A fundamental advance was to extend the engineering to the molecular level, including the engineering of chimaeric antibodies [2]. It should be possible to engineer antibodies against viruses, specifically, the coat glycoprotein that is an essential component of the entry mechanism for Ebola and many viruses into the host cell [3]. Nature has afforded us with a proof-of-concept for such engineering, by providing us with definable sequences and structures for Ebola glycoprotein bound to antibodies that enabled the host to survive the disease [4]. On the other hand, nature makes our task harder by enabling the virus to evolve in such a way as to neutralize the effect of the antibody [5]. Sequences and structures provide an outline of how the evolutionary arms race proceeds between Ebola virus glycoprotein vs. antibodies from the host immune system for multiple glycoprotein-