Stony Brook University
The Graduate School

Doctoral Defense Announcement

Abstract

Understanding the Dielectric Properties of Liquid Water

By

Daniel Christopher Elton

Water has many anomalous properties, several of which were of critical importance in the development of life on Earth. It is believed that these anomalies share a common origin in the structure and dynamics of water's hydrogen bond network. In this thesis we use molecular dynamics simulation to understand the dielectric spectra of water in terms of specific molecular processes. In the first part we compare three different types of forcefield that can be used in classical molecular dynamics – rigid, flexible, and polarizable. We show that polarizability is a necessary component for capturing the temperature dependence of the dielectric constant and dipole-dipole correlations of water. We quantify the range of dipole-dipole interactions in water using 1D and 2D correlation functions, finding that beyond separations of r=1.5 nm water behaves like a homogeneous dielectric continuum. We then calculate the nonlocal (*k*-dependent) dielectric function and observe dispersive optical-phonon like modes in the librational and OH stretching bands of liquid water. These modes exhibit longitudinal-transverse (LO-TO) splitting, suggesting the presence of long-range Coulombic interactions. The presence of LO-TO splitting provides a new window into water's structure and suggests that the dynamics of the liquid are more similar to ice than previously thought. The discovery of these modes leads to a reassignment of the peaks found in the librational band of Raman spectra, correcting a previously unrecognized discrepancy between peak assignments in Raman, dielectric, and IR spectra. In the final part of this thesis we turn to the problems of *ab-initio* simulation of water via density functional theory. A path integral molecular dynamics (PIMD) code was written to treat the nuclear quantum effects (NQEs) of hydrogen. A new PIMD technique is introduced which performs the PIMD calculation on a custom monomer potential energy surface. This technique promises to speed up calculation by roughly 30x while still accurately capturing the NQEs. We show why NQEs are important to include when testing density functionals and are necessary to understand many subtle effects due to isotopic substitution.

Date: October 28th , 2016
Time: 3pm
Place: Physics, B-131

Program: Physics
Dissertation Advisor: Marivi Fernández-Serra