

# Theoretical Studies on Condensed Phase Dynamics

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Liquids and biological systems show complicated dynamics because of their structural flexibility and dynamical hierarchy. Understanding these complicated dynamics is indispensable to elucidate chemical reactions and relaxation in solutions and functions of proteins. In this year, we investigated ultrafast proton transfer in solution<sup>1)</sup> and dynamics of liquid and supercooled states.<sup>2-5)</sup> In particular, we examined complicated dynamics in terms of nonlinear response functions and multi-time correlation functions.

## 1. Direct Simulation of Excited-State Intramolecular Proton Transfer and Vibrational Coherence of 10-Hydroxybenzo[*h*]quinoline in Solution<sup>1)</sup>

We investigate an ultrafast excited-state intramolecular proton transfer (ESIPT) reaction and the subsequent coherent vibrational motion of 10-hydroxybenzo-*[h]*quinoline in cyclohexane by the electronically embedded multiconfiguration Shepard interpolation method, which enables us to generate the potential energy surface of the reaction effectively and thus carry out a direct excited-state dynamics simulation with low computational costs. The calculated time scale of the ESIPT and the frequencies and lifetimes of coherent motions are in good agreement with the experimental results. The present study reveals that the coherent motions are caused by not only the proton transfer itself but also the backbone displacement induced by the ESIPT. We also discuss the effects of the solvent on the dynamics of the coherent vibrational modes.

## 2. Insights in Quantum Dynamical Effects in the Infrared Spectroscopy of Liquid Water from a Semiclassical Study with an *Ab Initio*-Based Flexible and Polarizable Force Field<sup>2)</sup>

The dynamical properties of liquid water play an important role in many processes in Nature. In this paper we focus on the infrared (IR) absorption spectrum of liquid water based on the linearized semiclassical initial value representation (LSC-IVR) with the local Gaussian approximation (LGA) [Liu and Miller, *J. Chem. Phys.* **131**, 074113 (2009)] and an *ab initio* based, flexible, polarizable Thole-type model (TTM3-F) [Fanourgakis and Xantheas, *J. Chem. Phys.* **128**, 074506 (2008)]. Although the LSC-IVR (LGA) gives the exact result for the isolated 3-dimensional shifted harmonic stretching model, it yields a blue-shifted peak position for the more realistic anharmonic stretching potential. By using the short time information of the LSCIVR correlation function, however, it is shown how one can obtain more accurate results for the position of the stretching peak. Due to the physical decay in the condensed phase system, the LSC-IVR (LGA) is a good and practical approximate quantum approach for the IR spectrum of liquid water. The present results offer valuable insight into future attempts to improve the accuracy of the TTM3-F potential or other *ab initio*-based models in reproducing the IR spectrum of liquid water.

### 3. Energy Relaxation of Intermolecular Motions in Supercooled Water and Ice: A Molecular Dynamics Study<sup>3)</sup>

We investigate the energy relaxation of intermolecular motions in liquid water at temperatures ranging from 220 K to 300 K and in ice at 220 K using molecular dynamics simulations. We employ the recently developed frequency resolved transient kinetic energy analysis, which provides detailed information on energy relaxation in condensed phases like two-color pump-probe spectroscopy. It is shown that the energy cascading in liquid water is characterized by four processes. The temperature dependences of the earlier three processes, the rotational–rotational, rotational–translational, and translational–translational energy transfers, are explained in terms of the density of states of the intermolecular motions. The last process is the slow energy transfer arising from the transitions between potential energy basins caused by the excitation of the low frequency translational motion. This process is absent in ice because the hydrogen bond network rearrangement, which accompanies the interbasin transitions in liquid water, cannot take place in the solid phase. We find that the last process in supercooled water is well approximated by a stretched exponential function. The stretching parameter,  $\beta$ , decreases from 1 to 0.72 with decreasing temperature. This result indicates that the dynamics of liquid water becomes heterogeneous at lower temperatures.

### 4. Fluctuations and Dynamics of Liquid Water Revealed by Nonlinear Spectroscopy<sup>4)</sup>

Many efforts have been devoted to elucidate the intra- and intermolecular dynamics in liquid water because of its important roles in many fields of science and engineering. Multi-dimensional nonlinear spectroscopy is a powerful tool to investigate the dynamics. Since nonlinear response functions are described by more than one time variable, it is possible to analyze static and dynamic mode couplings. Here, we review the intra- and intermolecular dynamics of liquid water revealed by recent nonlinear spectroscopic experiments and computer simulations. In particular, we discuss the anharmonic coupling, population relaxation, anisotropy decay, and spectral diffusion of intra- and intermolecular motions of water and their temperature dependence, which play important role in ultrafast dynamics and relaxations in water.

### 5. Anomalous Temperature Dependence of Isobaric Heat Capacity of Water below 0 °C<sup>5)</sup>

When pure liquid water is cooled below its freezing/melting temperature, it exhibits a number of striking anomalies. Most remarkable among these anomalies is the temperature dependence of the isobaric heat capacity,  $C_P$ , that exhibits first a rise, and then a fall, on lowering temperature substantially below 0 °C.<sup>1–4)</sup> In contrast, the isochoric heat capacity,  $C_V$ , remains weakly temperature dependent and displays no such anomaly. The reason for this surprisingly large difference is not well understood. To understand this and other anomalies of low temperature water, we examine both *wave number and frequency dependent temperature fluctuation* by long molecular dynamics simulations. Significant differences between constant pressure and constant volume conditions appear below 240 K in the spatio-temporal correlation of temperature fluctuation. Shell-wise decomposition of relative contribution to the temperature fluctuation reveals an increase in contribution from the distant regions, extending even up to the *fifth hydration shell, at low temperatures*, more significant under isobaric than under isochoric conditions. While the temperature fluctuation time correlation function (TFCF) exhibits the expected slow-down with lowering temperature, it shows a rather surprisingly sharp crossover from a markedly fragile to a weakly fragile liquid around 220 K. We establish that this crossover of TFCF (and the related anomalies) arises from a percolation transition in the population of clusters made of liquid-like molecules, defined by coordination number (and consistent with local volumes obtained from Voronoi polyhedra). The disappearance of large liquid-like clusters below 220 K display characteristic features consistent with theory<sup>5)</sup> of percolation. As temperature is further lowered, TFCF exhibits a power law decay and the relaxation time, when fitted to Vogel-Fulcher-Tammann law, reveal a dynamic transition around 160–170 K. Our computed two-dimensional IR and Raman spectra both also signal a dynamical transition around 170 K and additionally carry signatures of the percolation transition at 220 K that could be measured experimentally.

#### References

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