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非平衡第一原理分子動力学シミュレーションによる

水の超高速振動ダイナミクス

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**Ultrafast vibrational dynamics of water disentangled by reverse non-equilibrium *ab initio* molecular dynamics simulations**

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Liquid water provides a unique environment for chemical reactions occurring in biological systems and many technological applications, in that water has the distinguishing ability to transfer and dissipate vibrational energy on exceptionally short timescales. The experiments have shown that water's ultrafast vibrational dynamics are intimately connected to its hydrogen bond dynamics. The ultrafast vibrational dynamics of water is significantly connected to its hydrogen-bond dynamics and in fact the spectral diffusion of OH stretch mode in pure H<sub>2</sub>O [1] is significantly faster than that of D<sub>2</sub>O, presumably because of the intermolecular/intramolecular couplings [2]. However, the mechanism of the acceleration remained unclear.

Recently, we developed an *ab initio* non-equilibrium molecular dynamics (AINEMD) algorithm (Figure 1a) that allows generating non-equilibrium vibrationally excited states at targeted vibrational frequencies. Our AINEMD simulation predicts the spectral diffusion timescale of 140 fs in pure H<sub>2</sub>O (Figure 1b), which is in good agreement with the experimental data (180 fs) [1]. The results illustrate that intermolecular energy transfer and the delocalization of the O-H stretch mode are remarkably contributed to the acceleration of the spectral diffusion in H<sub>2</sub>O.

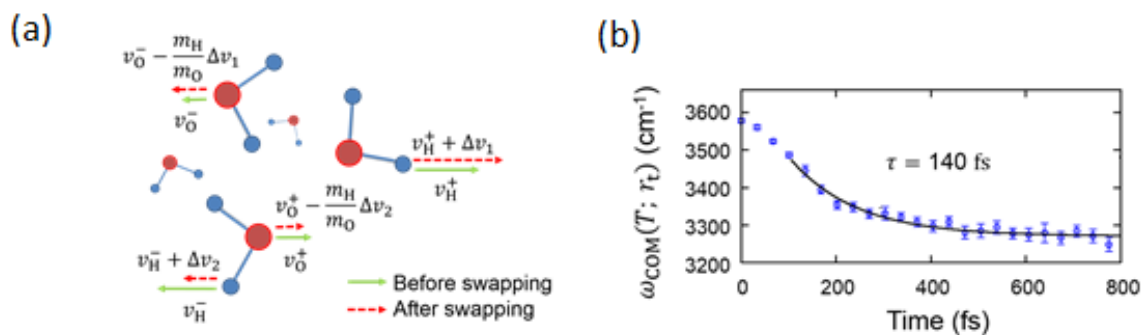


Figure 1: (a) Schematic picture of our NEMD method. (b) Time trace of center of mass frequency of OH stretching mode.

#### References

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- [2] C. P. Lawrence and J. L. Skinner, J. Chem. Phys. **118**, 264 (2003).
- [3] Y. Nagata, S. Yoshimune, C. -S. Hsieh, J. Hunger and M. Bonn, *submitted*.