Spectral analysis of kinetic energies in non-equilibrium system by spectral density of kinetic energy (KESD) approach: HOD in D2O

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Vibrational energy relaxation can prove the time evolution of the environment near vibrational excitation. Especially, in HOD in D2O system, OH stretching vibrations are localized on their bonds whereas vibrations of water are localized over the molecules, which can show more clear information of water H-bonding structure.

We used equilibrium and non-equilibrium QM/MM MD simulation to study vibrational energy relaxation of OH stretch mode in D2O solvent. And we also show system's H-bonding dynamics by using spectral density of kinetic energy (KESD)

Key words **:** Vibrational energy relaxation, H-bonding structure, MD simulation

Kinetic energy (KE) is a fundamental dynamic observable that can be calculated at any point in time from classical molecular dynamics simulation. While the potential energy is often difficult to analyze because it involves many-body interactions and cannot be easily decomposed for subsets of the system, the KE can be decomposed to atomic components and can be defined precisely for arbitrary subsets of the system. In addition, the KE is more closely associated with the dynamics of the system. In these reasons, by using spectral density of kinetic energy (KESD), we can obtain

many informations of hydrogen bonding system.

We tried to show overall picture of spectrum through equilibrium system's KESD, and time evolution of various spectral components of a molecular system and analyze the energy exchange process among those components through non-equilibrium KESD. We employ a hybrid quantum mechanical/molecular mechanical potential to describe the HOD and solvent water molecules. The QM description of the HOD molecule, implemented with the semiempirical scc-DFTB potential, and solvent water molecules are described by the flexible SPC/Fw MM potential. Since the scc-DFTB potential tends to underestimates the HOD bending mode frequency and overestimates the OD and OH stretch frequencies, we have used a new Lennard-Jones (LJ) radius for the QM oxygen (6% smaller than the standard value of the SPC/Fw model). Furthermore, another system with an HOD described by MM potential showed that the HOD bending frequencies differ by ~70 cm^{-1}. Therefore, we have increased the bending force constant of the SPC/Fw model by 13%.

However, even though we used these improved values for MD simulation, OH bond kinetic energy relaxation was too slow to compare with OD bond KE relaxation. Furthermore, KESD couldn't reproduce experimental peak frequencies well. We thought that scc-DFTB's multidimensional potential energy surface cannot reproduce real system properly, and it makes hard to energy flow from OH stretch mode to HOD bending mode. To solve this problem, we are trying to find new QM force field (and basis set) which makes possible for MD simulation and give reasonable peak frequencies.