

Vibrational energy relaxation of HOD in D₂O

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❖ Vibrational energy relaxation

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.

❖ Spectral density of kinetic energy (KESD)

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 information of hydrogen bonding system.

Y. Zhang et al. *Curr. Opin. Chem. Biol.* 2006, 10, 658-663

❖ Instantaneous KESD

The atomic velocities generated from MD simulation

$$\mathbf{u}_i(t; t_0, T) = \begin{cases} \mathbf{v}_i(t) & t_0 \leq t \leq T \\ 0 & \text{otherwise} \end{cases}$$

FT form are given as

$$\begin{aligned} \bar{\mathbf{u}}_i(\omega; t_0, T) &= \int_{-\infty}^{\infty} dt \mathbf{u}_i(t; t_0, T) e^{i\omega t} \\ &= \int_{t_0}^T dt \mathbf{v}_i(t) e^{i\omega t} \end{aligned}$$

Power spectrum of velocities

$$\begin{aligned} P_i(\omega; t_0, T) &= \frac{1}{2\pi} |\bar{\mathbf{u}}_i(\omega; t_0, T)|^2 \\ &= \frac{1}{2\pi} \int_{t_0}^T dt_1 \mathbf{v}_i(t_1) \cdot \int_{t_1-T}^{t_1-t_0} d\tau \mathbf{v}_i(t_1 - \tau) e^{i\omega\tau} \end{aligned}$$

The instantaneous KESD at time T is given by time derivative of $P_i(\omega; t_0, T)$

$$\begin{aligned} \rho_i^p(\omega; T, t_0) &= \frac{m_i}{2} \frac{\partial}{\partial T} P_i(\omega; t_0, T) \\ &= \frac{m_i}{2\pi} \int_0^{T-t_0} d\tau \mathbf{v}_i(T) \cdot \mathbf{v}_i(T - \tau) \cos \omega\tau \\ &= \frac{m_i}{2\pi} \int_{-\infty}^{\infty} d\tau \mathbf{u}_i(T; t_0, T) \cdot \mathbf{u}_i(T - \tau; t_0, T) \cos \omega\tau \end{aligned}$$

$$\int_{-\infty}^{\infty} d\omega \rho_i^p(\omega; T, t_0) = \frac{m_i}{2} |\mathbf{v}_i(T)|^2$$

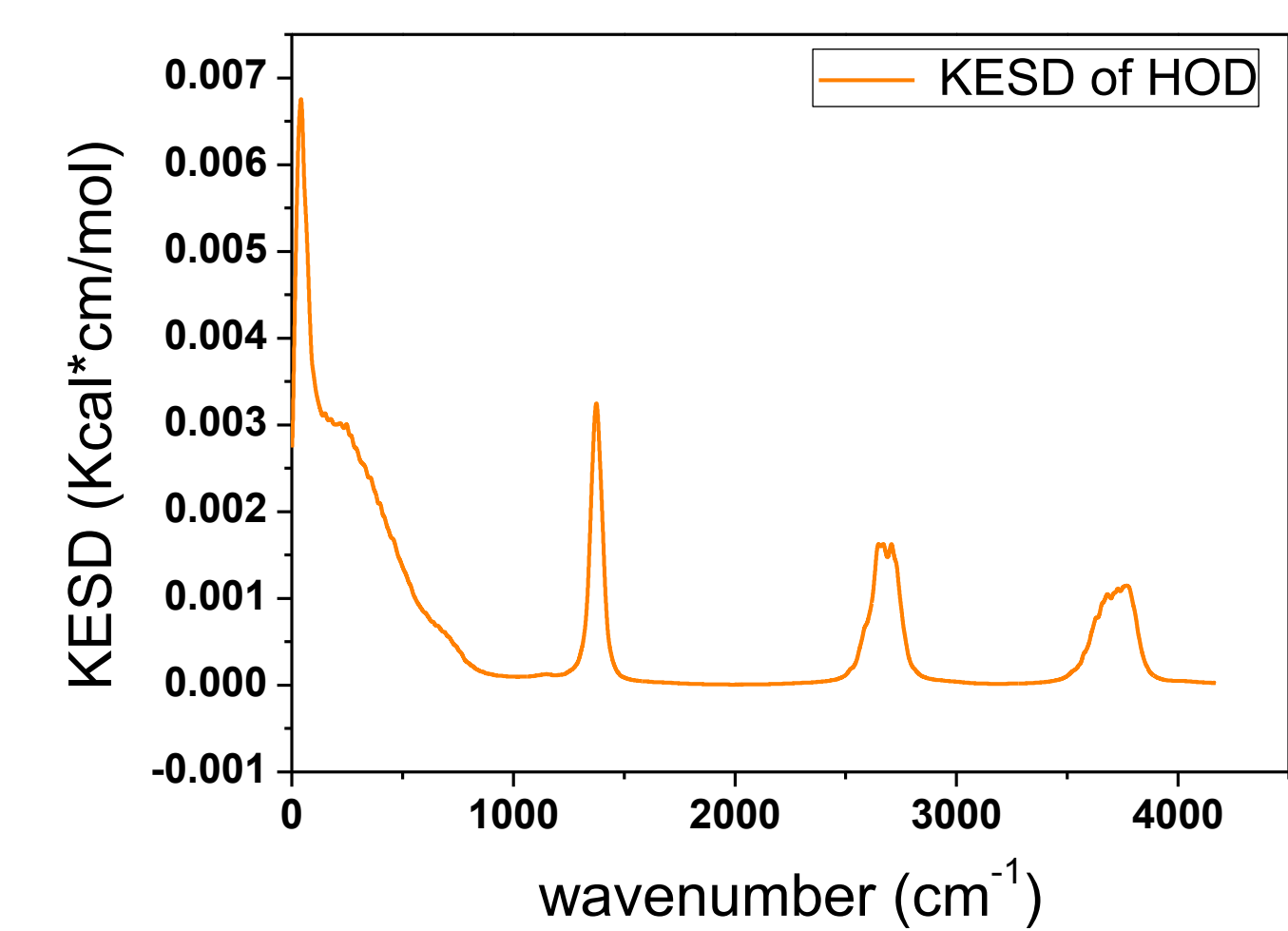
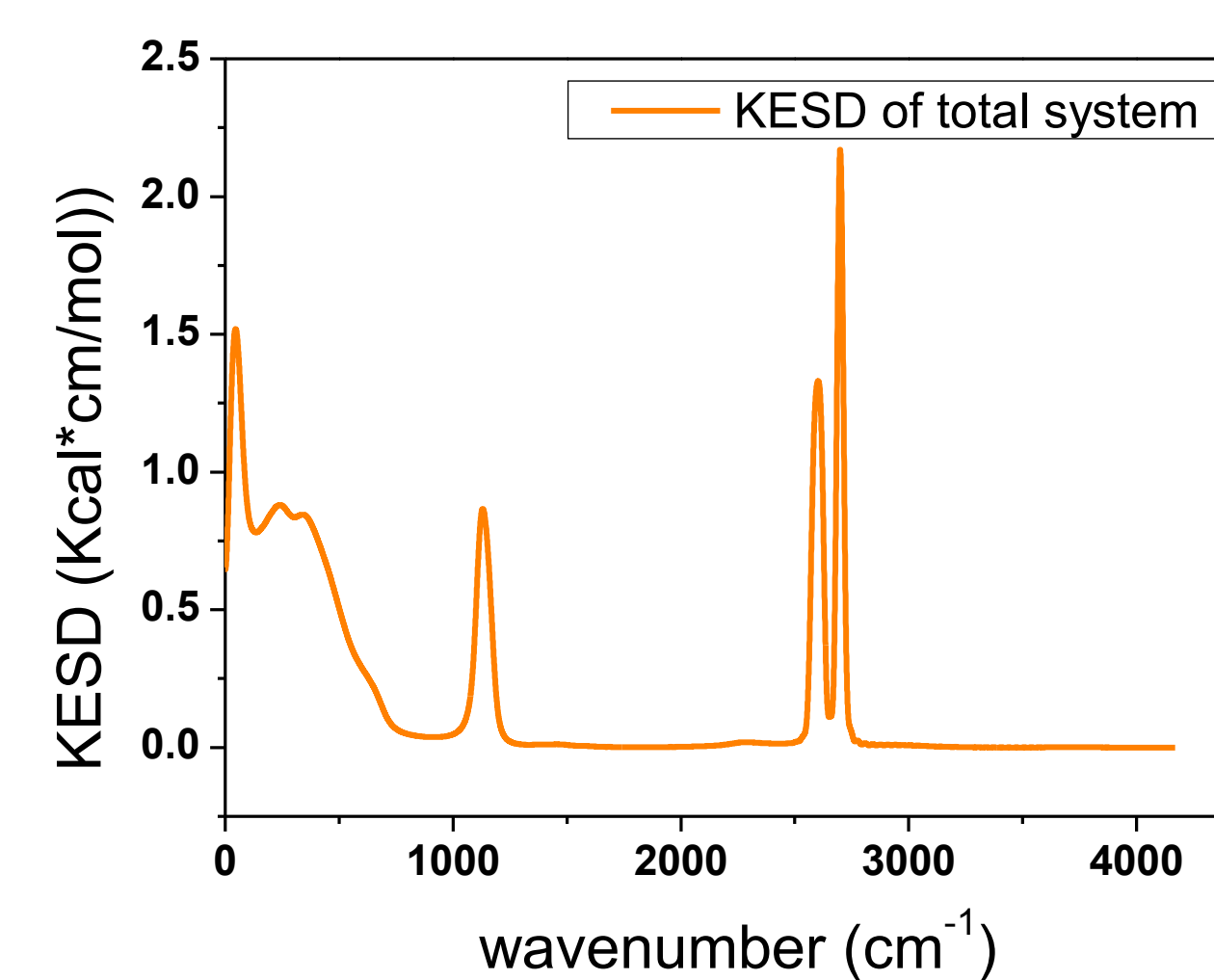
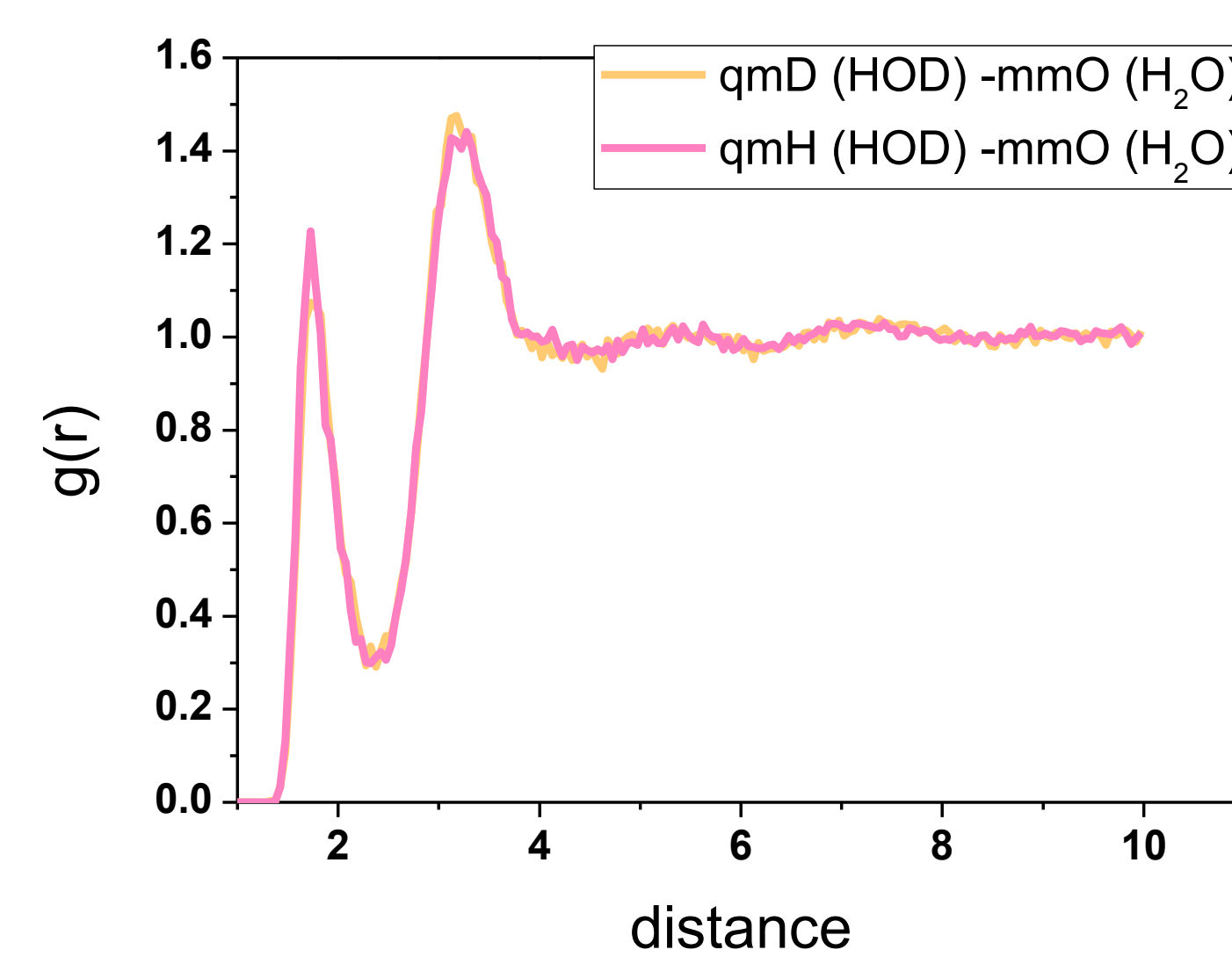
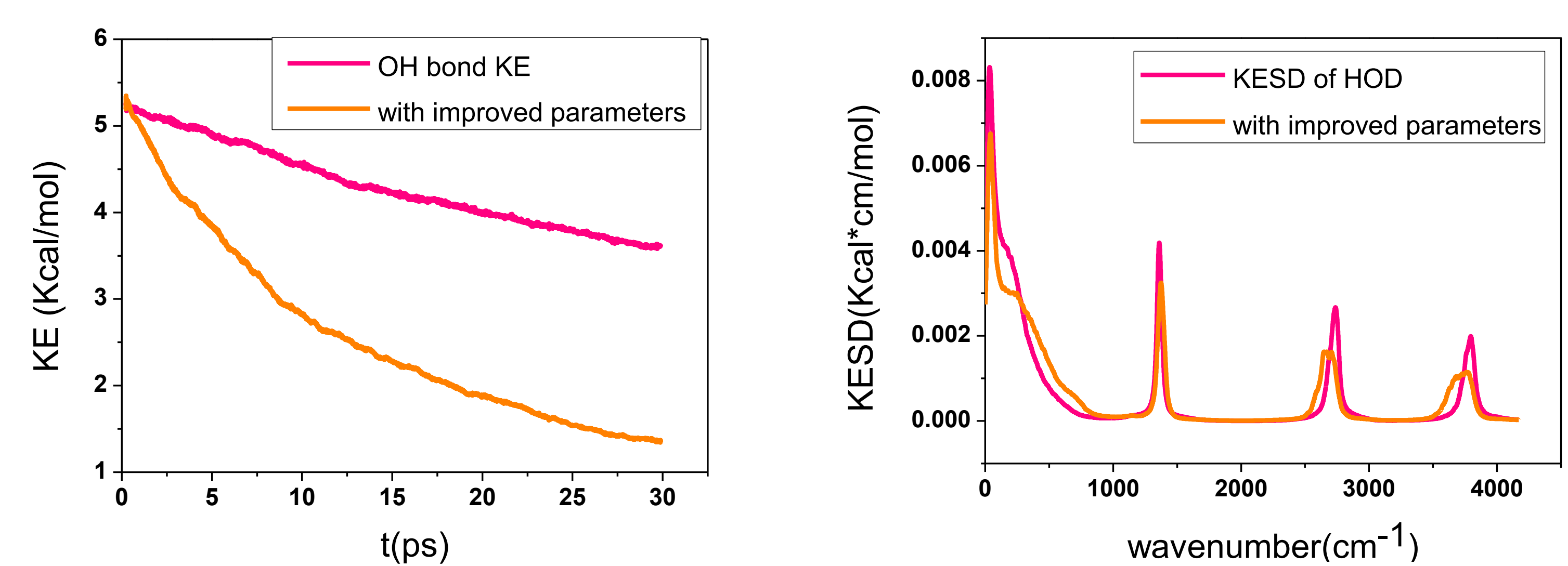
➡ Integral value of KESD = kinetic energy

Simulation details

- Single QM HOD + 281 MM D₂O in a cubic periodic box
- scc-DFTB QM potential for HOD, flexible SPC/Fw MM potential for D₂O
- Nonequilibrium MD simulation with 1000 samples generated from equilibrated canonical ensemble
- HOD with QM potential/ MM potential : showed different HOD bending mode frequency (~70 cm⁻¹)
→ Increase the bending force constant of SPC/Fw model by 13%
- For strength QM-MM interaction, 6% smaller Lennard-Jones(LJ) radius for QM oxygen used

❖ Simulation results

LJ radius dependence



❖ Future works

Current problems

- Too slow kinetic energy relaxation of OH bond
- Different peak frequencies between KESD and experimental value
- scc-DFTB's multidimensional potential energy surface cannot reproduce real system properly