# 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

Vibrational energy relaxation can prove the time evolution of the environment near vibrational excitation.
[1]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.

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## ❖ 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. [2]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.

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## ❖ Instantaneous KESD

The atomic velocities generated from MD simulation

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

FT form are given as

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

Power spectrum of velocities

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

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

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

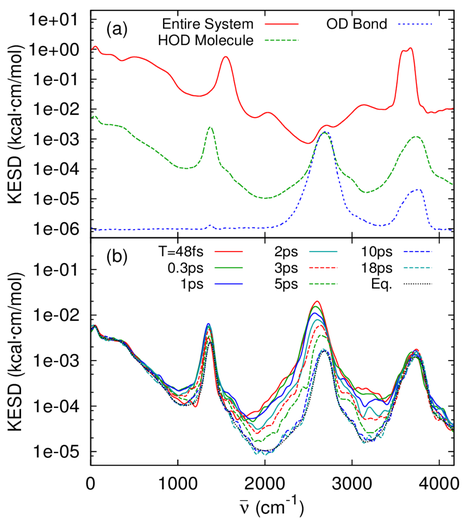
$$\int_{-\infty}^{\infty}d\omega\rho_i^{\mathrm{P}}(\omega;T,t_0)=\frac{m_i}{2}\left|\mathbf{v}_i(T)\right|^2$$

➡ **Integral value of KESD = kinetic energy**

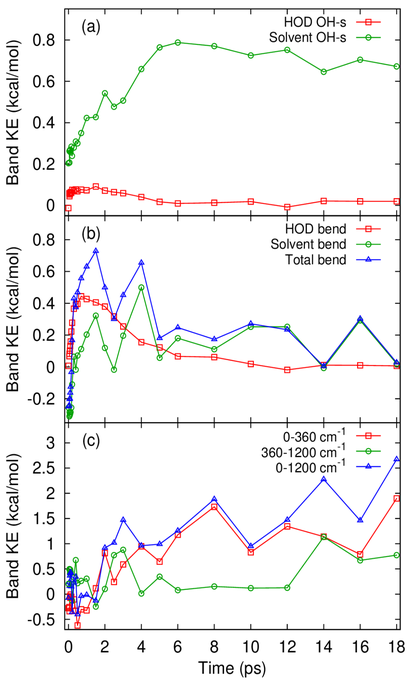
### Simulation details

- Single QM HOD + 281 MM $D_2O$ 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

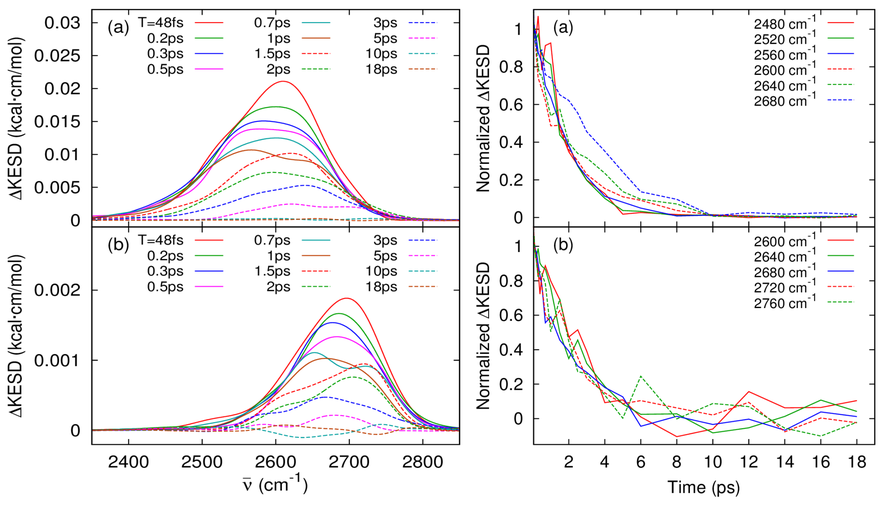
## ❖ Previous study : OD bond energy relaxation in $H_2O$



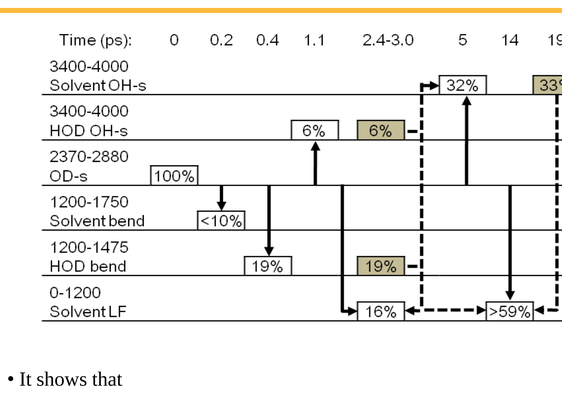

- The figure captures the gradual decrease of the OD stretch band after its excitation at time zero and also the intramolecular vibrational energy redistribution (IVR) processes of smaller magnitude taking place mainly in the bands of the HOD bending and OH stretch motions.




- From (a), the OH vibrations of the solvent $H_2O$ molecules take up more than 0.4 kcal/mol of KE (11% of the OD bond KE at T = 48 fs, 3.654 kcal/mol). This kind of uphill energy transfer is likely to be overestimated in this study due to the classical description of vibration employed. In contrast, the KE of the HOD bending band in (b) shows a rapid initial increase up to 0.7 ps then slowly decays to zero. The HOH bending band from the solvent also plays a significant role in the VER process, with transient absorption of more than 0.5 kcal/mol (14% of the initial OD bond KE) at 4 ps. Finally, the intermolecular bands below 1200 $cm^{-1}$ from the solvent in (c) begin to absorb KE after ~1.5 ps and eventually take up ~2.5 kcal/mol (68% of the initial OD bond KE). We can see from this figure that more energy is transferred to the low frequency band below 360 $cm^{-1}$ than to the libration band in the 360−1200 $cm^{-1}$ region.



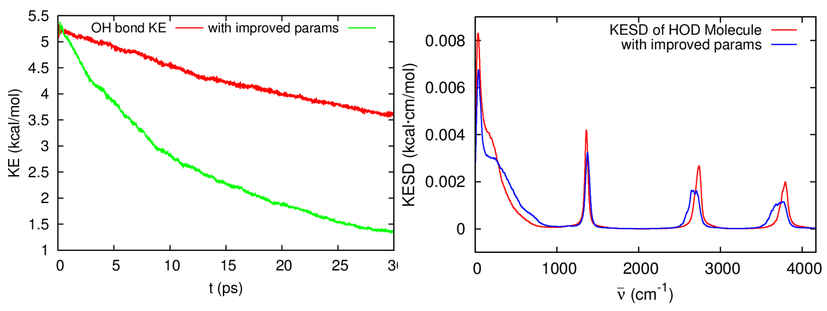

- Relaxation of the OD bond fKESD after bond excitation by 7.660 kcal/mol and (b) 0.592 kcal/mol (thermal energy).
The decay up to 0.5ps proceeds slightly faster on the blue side of the band. Between 1.0 and 1.5 ps, however, a kind of transition in mechanism takes place, and the amplitude in the red side begins to decrease faster than in the blue side, resulting in the crossing of the curves at 1.0 and 1.5 ps. Comparing the initial fKESD at 48 fs and the later ones between 1.5 and 5 ps, we can clearly identify a blue shift of the band. In the small perturbation case shown in (b), the early decay pattern is analogous to the large perturbation case, and we can find the same doublet feature at 0.7 ps as in Figure 5a at 1.0 ps. However, the later part of the decay does not show pronounced red shift as was found in the large perturbation case. We can attribute this red shift of decay to the anharmonicity of the OD stretch mode described by the scc- DFTB potential.



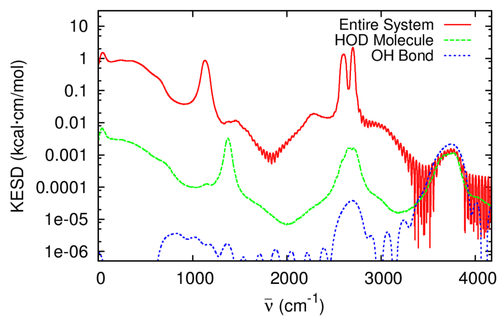

- It shows that
(i) ~20% of the excess KE of the OD bond is initially transferred to the HOD bending mode within 1 ps.
(ii) the intramolecular modes of the solvent H2O (OH stertch and HOH bending modes) transiently take up more than one-quarter of the energy either directly from the OD bond or from the HOD bending mode over the 0−5 ps range.
(iii) eventually more than 75% of the excess KE is stored in the low frequency solvent intermolecular modes.

## ❖ Simulation results

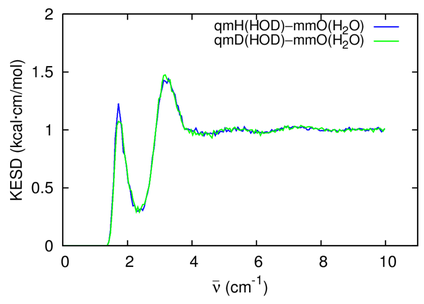
### LJ radius dependence

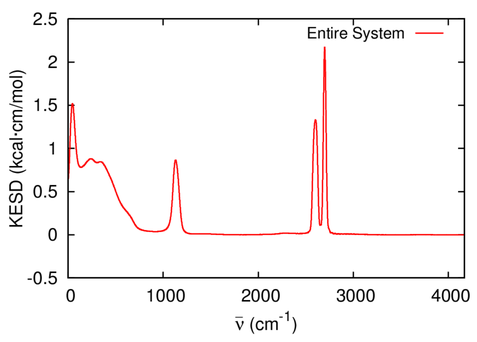


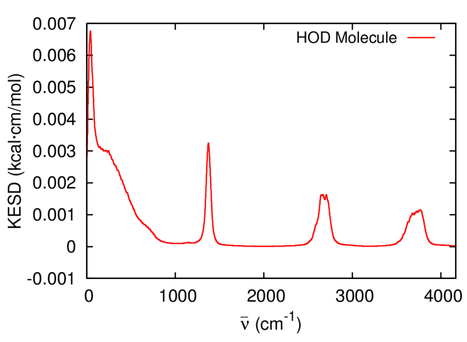

- scc-DFTB potential : underestimates the HOD bending mode frequencies
overestimates the OD and OH stretch frequencies
- HOD with QM potential/ MM potential : showed different HOD bending mode frequency (~70 $cm^{-1}$) → Increase the bending force constant of SPC/Fw model by 13%
- For strength QM-MM interaction, 6% smaller Lennard-Jones radius for QM oxygen used
- As changing LJ radius of QM O and bending force constant of MM $D_2O$, OH bond energy decay much faster and peak position of KESD spectrum was changed a bit → QM-MM interaction improved

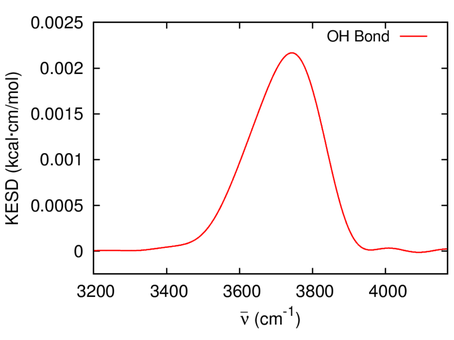



- The KESD for the HOD molecule in the same figure shows three major peaks and also a broad band below 1200 $cm^{-1}$ arising from the hindered translation and rotation of the HOD molecule as a whole. The OH bond KESD shows a single dominant peak at ~3800 $cm^{-1}$ arising from the OH stretch degree of freedom. We can also identify two peaks at 2650 and 1380 $cm^{-1}$ in HOD molecule KESD, corresponding to OD stretch and HOD bending motions.




- By using KESD spectrum, we can get each mode's kinetic informations separately. And we can also estimates vibrational frequency and kinetic energy of each mode. As intergrating KESD spectrum, we can get kinetic energy of each mode easily.

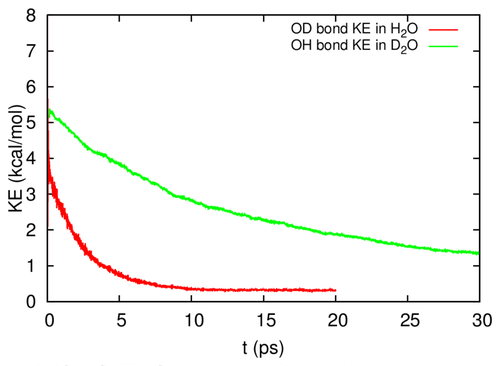
## ❖ Future works

### 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

### Solutions

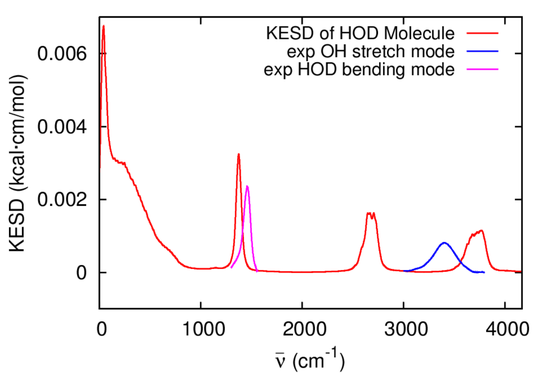
- As changing LJ radius and MM bending force constant, difference between KESD and experimental value might be decreased
- Changing QM force field (ab initio, DFT, HF )
- We also think using CP2K method




OD bond KE relaxation time (Dr. jeon) : 2.4 ps
(exp value : 1.794 ps)

OH bond KE relaxation time : 11.77 ps
(exp value : 0.5~1 ps )

- Kinetic energy relaxation of OH bond is too slow when compare it to experimental result and OD bond KE relaxation time in Dr. Jeon's paper.




OH stretch ($cm^{-1}$)
- 3640(+240 than exp value)

HOD bending ($cm^{-1}$)
- 1385 (-72 than exp value)

- From KESD,
bending overtone mode : 2770 $cm^{-1}$
difference between bending overtone and OH stretch mode : 870 $cm^{-1}$
- From experimental value,
bending overtone mode : 2914 $cm^{-1}$
difference between bending overtone and OH stretch mode : 486 $cm^{-1}$