Supplementary Information

Vibrational Mode Frequency Correction of Liquid Water in Density Functional Theory Molecular Dynamics Simulations with van der Waals Correction

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Contents:

1. Convergence check for VDOS spectra

We calculated the VDOS spectra with the revPBE-D3(0) level of theory with split trajectories into two equal parts. (Figure S1). The data show that the intensities for these spectra are slightly different, while the center mass of frequencies for the O-D stretch and D-O-D bending modes are completely the same (2530 cm^{-1} and 1204 cm^{-1}, respectively). This indicates that the results are rather independent on the initial configurations and each sub-trajectory has sampled sufficient water configurations.

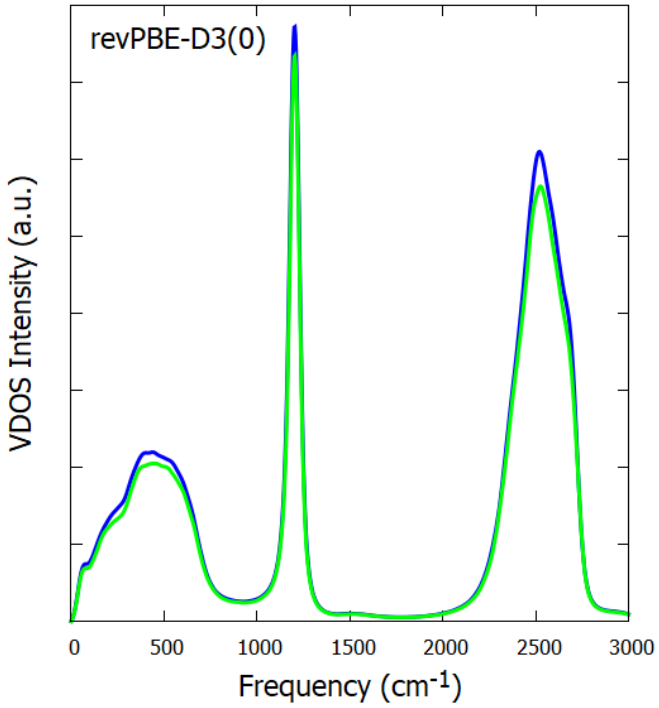

Figure S1. The VDOS spectra calculated with the half of trajectories with the revPBE-D3(0) level of theory. The blue and green lines are obtained by the first and second half trajectories, respectively.

2. Decomposition of the O-D stretch spectra

Decomposed VDOS spectra obtained from the rest of the DFT methods are shown in Figure S2.

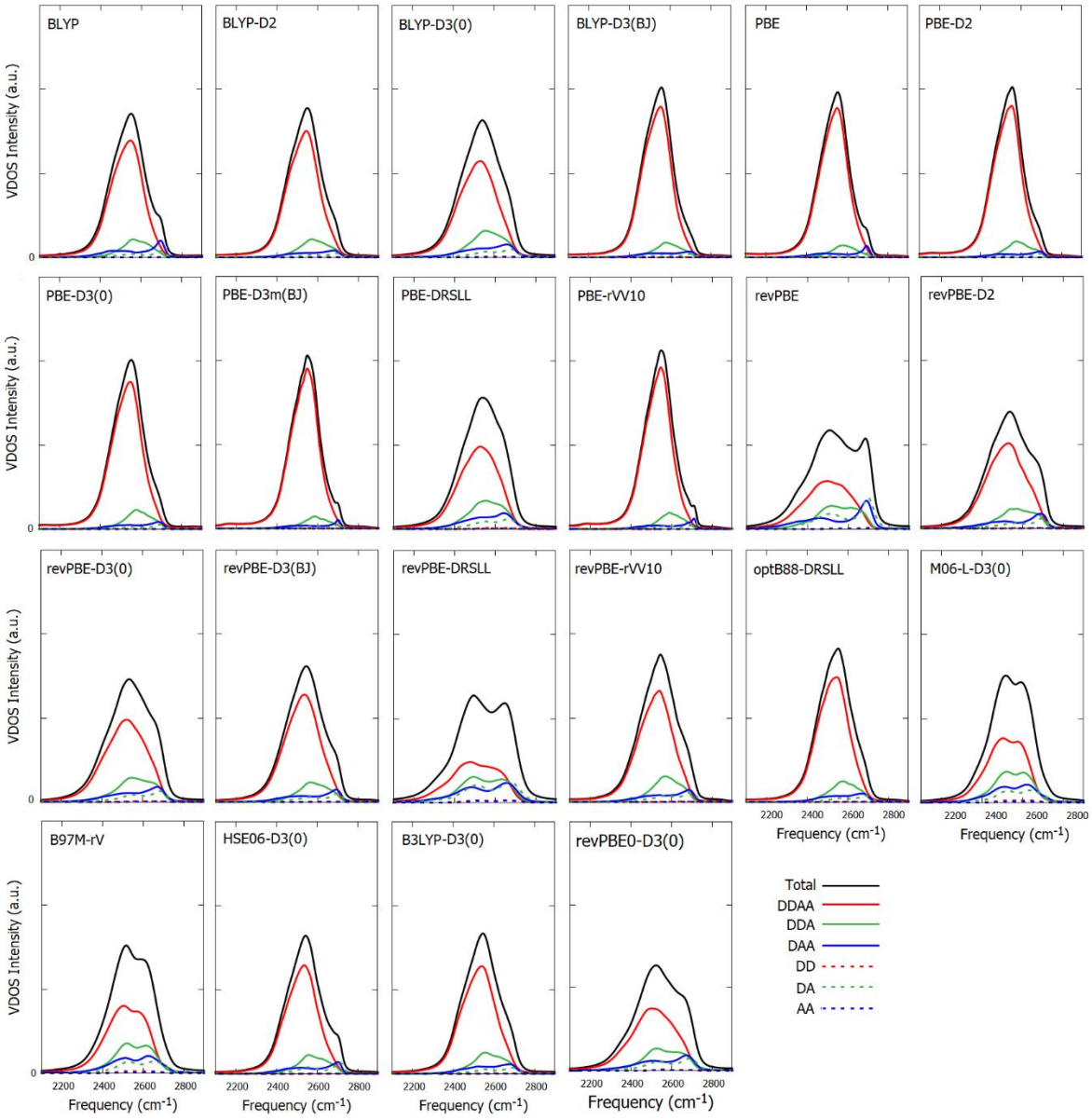

Figure S2. Decomposed VDOS spectra for the O-D stretch mode of D_2O calculated with various DFT methods.

3. Simulated IR spectra for D_2O

The simulated IR spectra for D_2O are shown in Figure S3. The simulated IR spectra for D_2O with revPBE0-D3(0) functional is obtained from Ref. 1 with scaling H_2O spectrum by the factor of 0.735,[2] and the simulated IR spectra for D_2O with SCAN functional is obtained from Ref. 3. The simulated IR spectra for D_2O with POLI2VS model is obtained from Ref. 4 with scaling H_2O spectrum by the factor of 0.735.[2] The POLI2VS model does not account for nuclear quantum effects.[4] Thus, we scaled the frequency axis with a factor of 0.96 for both the O-D stretch and the D-O-D bending modes.[5]

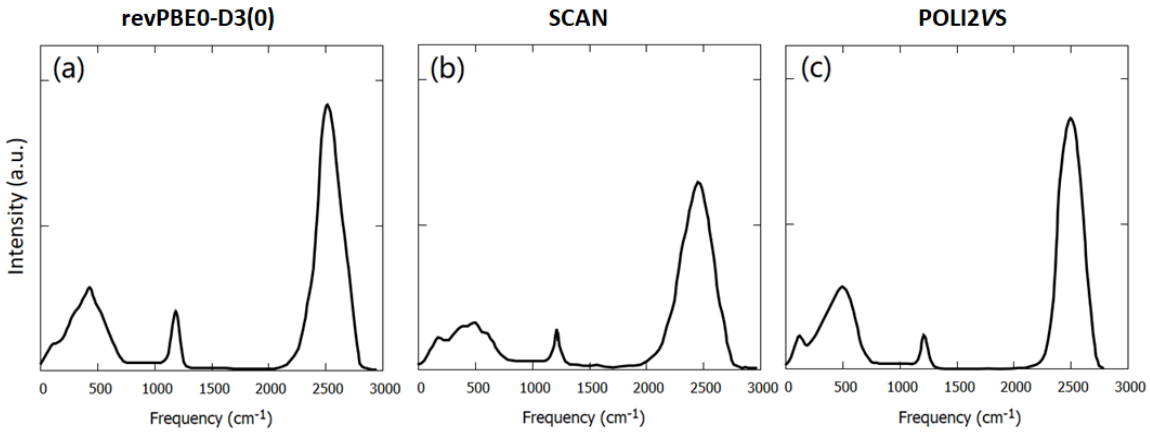

Figure S3. IR spectra for D_2O (a) at the revPBE0-D3(0) level of theory[1] (b) at the SCAN level of theory[3] (c) with the POLI2VS model of D_2O.[4]

4. Validity of the frequency scale for stretch and bending modes between H_2O and D_2O

The vibrational frequency is drastically changed upon isotope dilution. The correspondence of the O-H stretch mode of H_2O and O-D stretch mode of D_2O has been checked and it turned out that the scale factor of 0.735 provides the best frequency match between O-H and O-D stretch mode.[6,7]

For the H-O-H bending mode, we measured the IR spectra of H_2O and D_2O. The H_2O data has a peak centered at 1650 cm^{-1}. By scaling the frequency axis of the H_2O data, we

compared it with the D_2O data. As shown in Figure S4, the spectrum of the H-O-H bending mode shows large overlap with that of the D-O-D bending mode after scaling the frequency axis with the factor of 0.735. This demonstrates that the scale factor can be used for transferring the information on the D-O-D bending mode to the H-O-H bending mode.

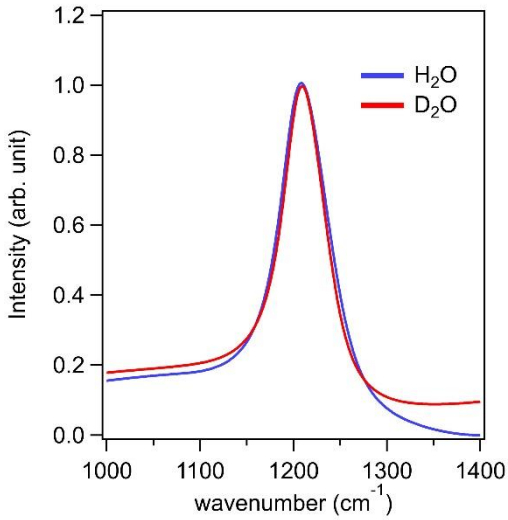

Figure S4. The FTIR spectra of H_2O and D_2O. Both of the spectra were normalized at the peak maximum. The frequency axis of the H_2O spectrum is scaling with the factor of 0.735.

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