Supplementary Information

The first application of an adaptive quantum mechanics/molecular mechanics method to the infrared spectrum of water: Incorporation of the quantum effect between solute and solvent

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QM Water spectrum in vacuo

In order to evaluate anharmonic effect on infrared spectrum of vapor water by DFTB, we conducted both FTTCF and NMA analyses on an isolated water molecule. Water is well known to have three distinctive band peaks, a symmetric stretch v_1, an angle bending v_2, and an asymmetric stretch v_3. As shown in Figure 1, the two approaches are generally in agreement with respect to position of the three peaks with shift smaller than 1% in agreement with a previous study by Kaminski et al[1]. As shown in Table 1 harmonic approximation causes $10 \sim 20$ cm^{-1} lower-frequency shift on v_1 and v_3 both in DFTB2 and 3, while the effect on v_2 is smaller and no consensus in the shift direction between DFTB2 & 3. It is contrast to MM water models that show systematic higher-frequency shift with regard to v_2.

When compared to the experiment[2], DFTB2 reproduces v_2 shifted to lower-frequency side by 70 cm^{-1}, whereas it shows considerably higher-frequency shifted v_1 and v_3. On the other hand, DFTB3 improves these two stretching modes, in particular v_1 in good agreement with the experiment, whereas it gives rise to further deviation of v_2. These errors presumably arise from the different equilibrated structures. DFTB3 improves the OH bond length as shown in Table 3, although it yields larger deviation about the bending angle than DFTB2 instead. We found the angle is fairly subject to a damping parameter ζ newly introduced in DFTB3[3] to account peculiarity of hydrogen (data is not shown). Note that DFTB parameter sets have been determined to reproduce several physicochemical properties of diverse molecule set with minimal errors. In general, DFTB3 with 3ob parameter gives better results than DFTB2 with mio parameter for diverse molecules[4], although it can trade off improvement of specific molecular properties, as is now the case for the bending angle of the water. However, the fact that DFTB2 leads to better reproduction of the angle implies room for further improvement of parameterization in DFTB3, because of the common theoretical framework

Supplementary Table 1. Peak positions (cm^{-1}) of the infrared spectra of water in the gas phase. In FTTCF analyses, the peak positions were estimated with Lorentzian fitting.

| Method		ν_1	ν_2	ν_3
TIP3P-Fs	NMA	3603	1362	3656
	FTTCF	3621	1386	3675
SPC-Fw	NMA	3587	1371	3671
	FTTCF	3606	1378	3691
DFTB2	NMA	3720	1523	3983
	FTTCF	3729	1524	4005
DFTB3	NMA	3651	1379	3919
	FTTCF	3668	1373	3940
Experiment		3657 [a]	1595 [a]	3756 [a,b]

[a] Shimanouchi et al., 1972[5],

[b] Huber et al., 1979 [6]

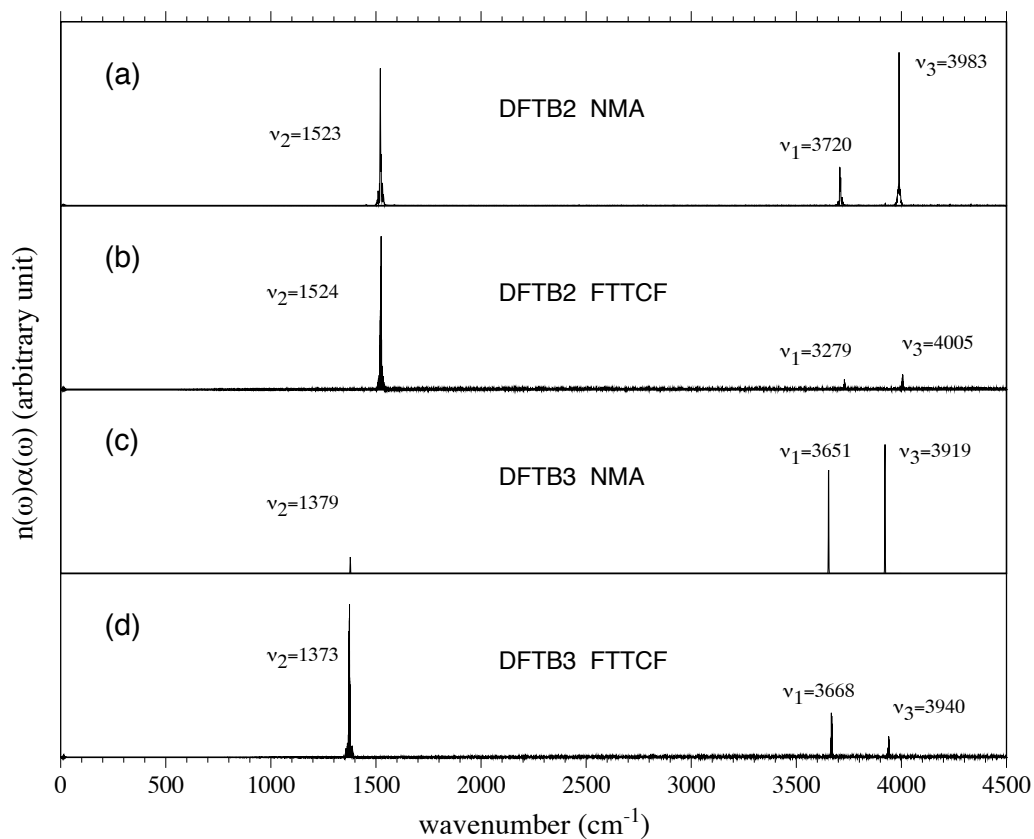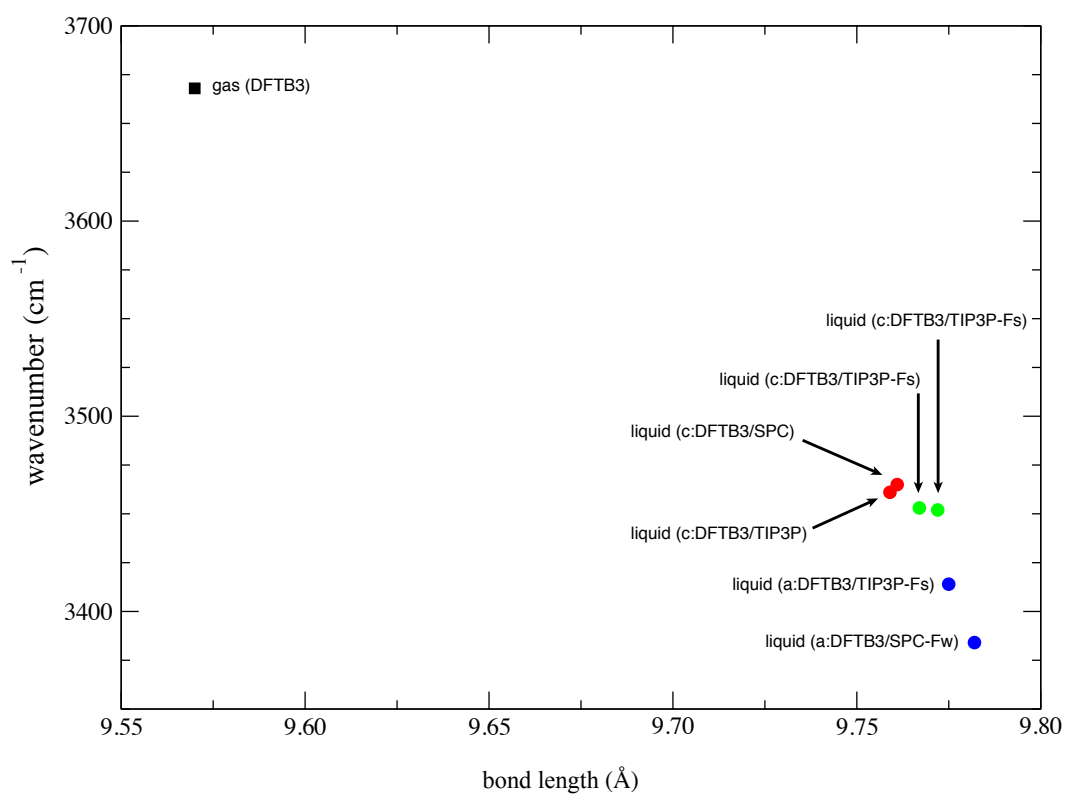**Figures**
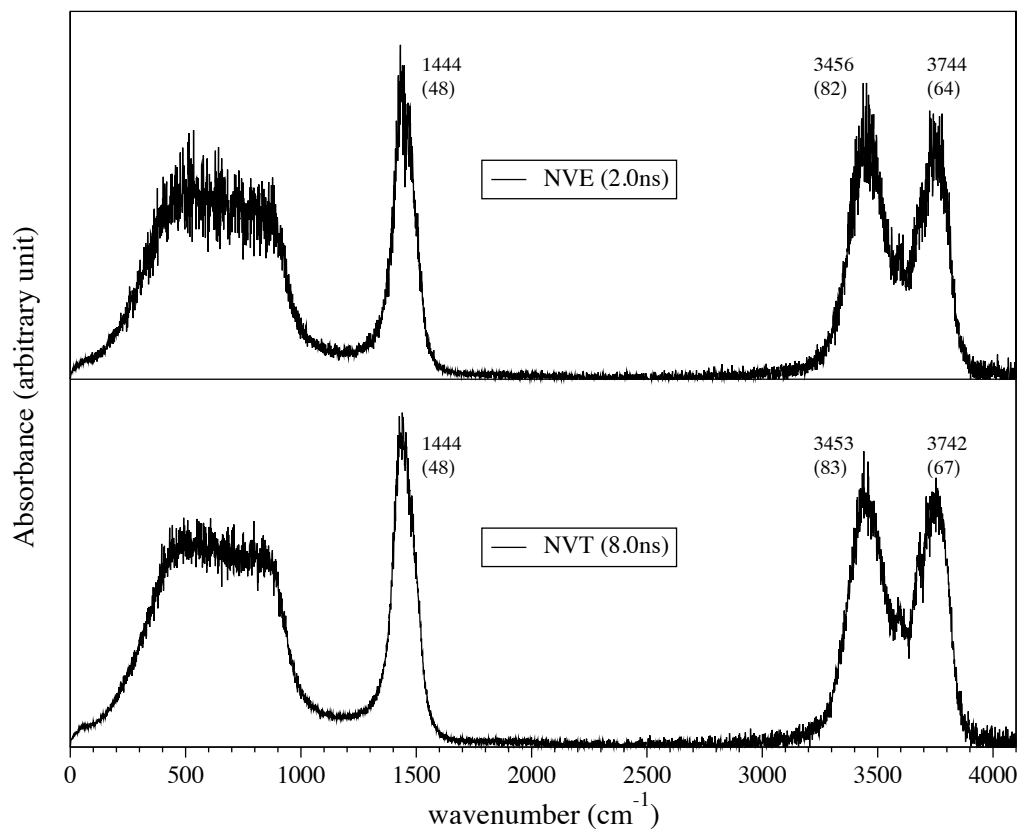
Supplementary Figure 1. Comparison of liquid water spectra of c:DFTB3/SPC-Fw system between NVE (top) and NVT simulations (bottom). The average temperature of the NVE simulation was found to be 302.5 K. For the NVT simulation at 300K, the Nosé-Hoover thermostat was adopted at time constant of 500 fs.
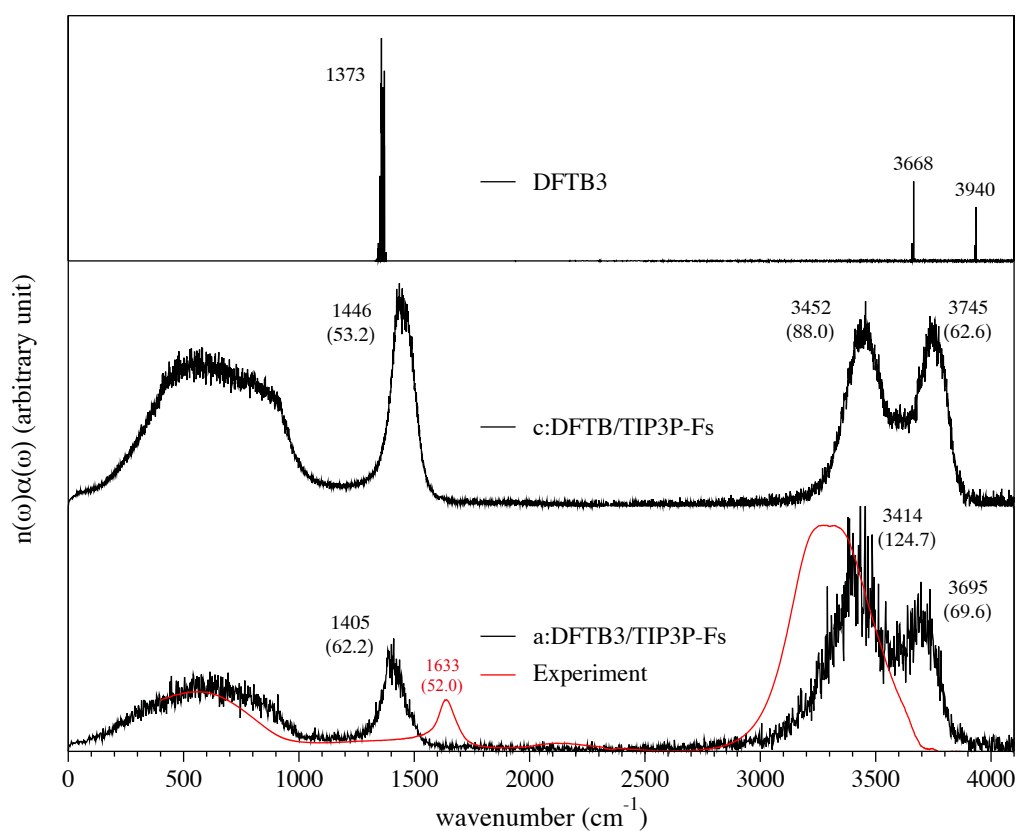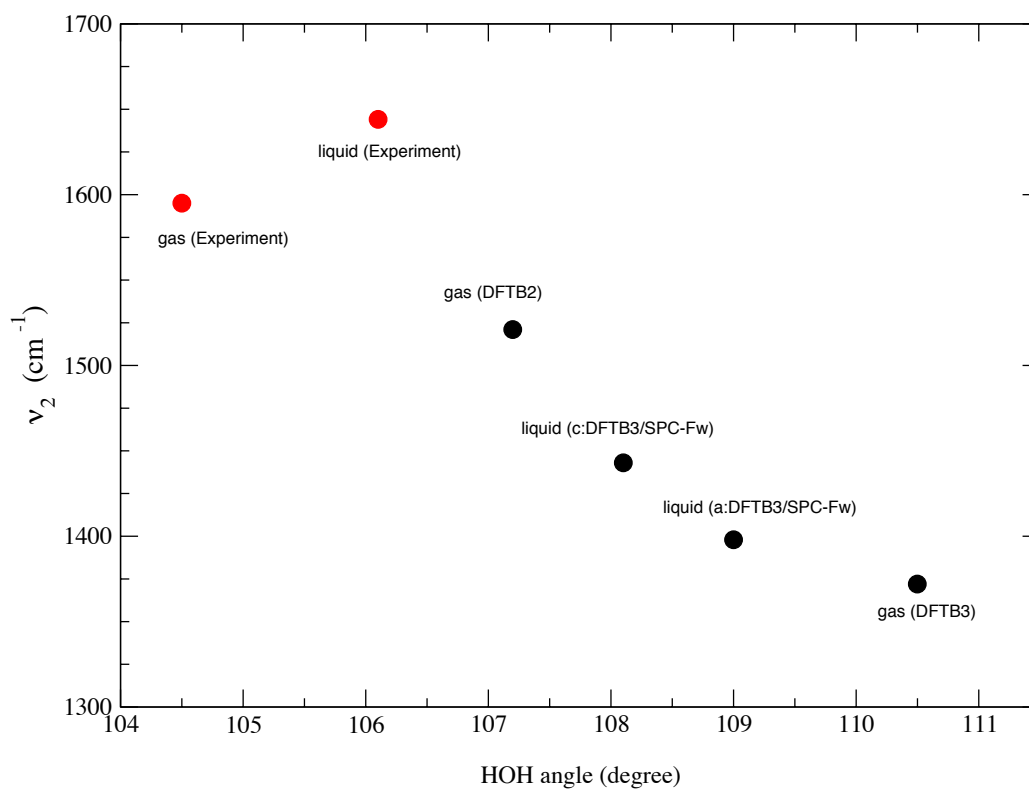
Supplementary Figure 2. Comparison between (top) gaseous water spectrum with DFTB3, and liquid water spectra of c:DFTB3/TIP3P-Fs (middle), and a:DFTB3/TIP3P-Fs system (bottom). Experimental spectrum of liquid water is represented by red line as a reference. The band peak positions are presented in the figures accompanied by the HWFM values in parentheses. The spectra are represented with resolution of 2 cm^{-1}.

Supplementary Figure 3. Comparison of gaseous water spectra between NMA and FTTCF approaches. DFTB2 water spectra with (a) NMA and FTTCF approaches, (c) DFTB3 water spectra with (a) NMA and FTTCF approaches. The band peak positions are presented in the figures accompanied by HWFM values in parentheses.
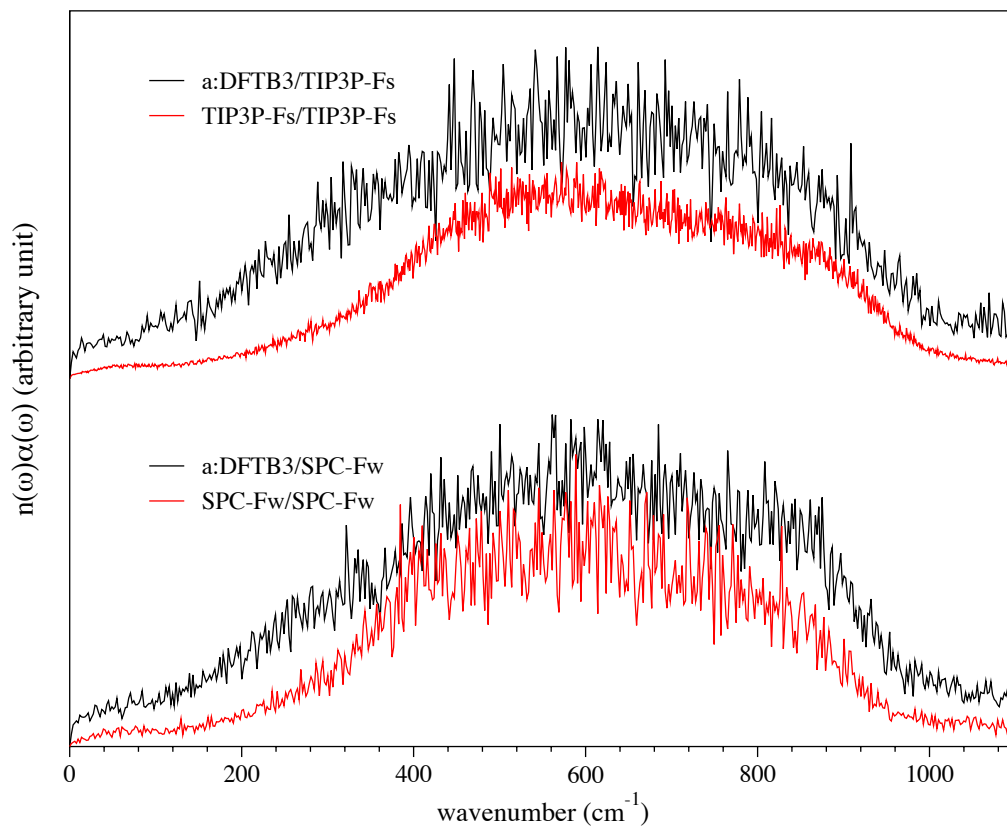
Supplementary Figure 4. Relation between OH bond length and the ν_1 and ν_3 positions.

Supplementary Figure 5. Relation between HOH bending angles and ν_2. Black and red circles stand for simulation and experimental values, respectively.

Supplementary Figure 6. Comparison of the far infrared spectra of liquid water spectra. (a) The a:DFTB3/TIP3P-Fs (black) and TIP3P-Fs/TIP3P-Fs (red) spectra. (b) The a:DFTB3/SPC-Fw (black) and SPC-Fw/SPC-Fw (red) spectra.

References

1.   Kaminski, S.; Gaus, M.; Elstner, M. J Phys Chem A 2012, 116(48), 11927-11937.

2.   Barker, E. F.; Sleator, W. W. J Chem Phys 1935, 3(11), 660-663.

3.   Gaus, M.; Cui, Q. A.; Elstner, M. J Chem Theory Comput 2011, 7(4), 931-948.

4.   Gaus, M.; Goez, A.; Elstner, M. J Chem Theory Comput 2013, 9(1), 338-354.

5.   Shimanouchi, T.; DTIC Document, 1972.

6.   Huber, K. P.; Herzberg, G. Molecular Spectra and Molecular Structure. IV. Constants Of Diatomic Molecules; Van Nostrand Reinhold Inc., 1979.