Computational Verification of Heating Mechanisms at Radio and Microwave Frequencies Using Density Functional Theory

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Introduction

Matsuo and Seki succeeded of heating a cyclohexanol solution under irradiance of radio frequency wave, at 0.81 and 10.1 MHz, stating that radio frequency heating results from dielectric loss factor[1]. As for effective microwave (MW) heating of water, dielectric loss of water between 0 to 100°C is shown in the wavelength range 0.01-10 cm, equivalent to respective 3 THz - 0.3 GHz (the microwave 2.45-GHz frequency corresponds to a 12.2-cm wavelength). In order to find out what is molecularly taking place in cyclohexanol and water under respective radio and microwave irradiances, molecular alignment of their liquid state are modeled at the molecular level on the basis of density-functional theory (DFT) using the B3LYP exchange-correlation functional and the 6–31G(d) basis set with Spartan 16 (Wavefunction, Inc. Irvine, CA). It is worth noting that DFT-based molecular modeling (DFT/MM) calculates not only the infrared (IR, 4000-500 $\mathrm{cm^{-1}}$) but also far infrared (FIR, >500 $\mathrm{cm^{-1}}$) spectra and below. In addition, as absorption peaks in IR can recognize bond vibration, absorption peaks in FIR also recognize intermolecular vibration of aggregated molecules. On the basis of an intermolecular vibration analysis in FIR region, we propose in this study that the radio and MW frequency heating may be explained as due to *thermo-upconversion.*

Results and Discussion

Verification of radio frequency heating of cyclo-hexanol solution

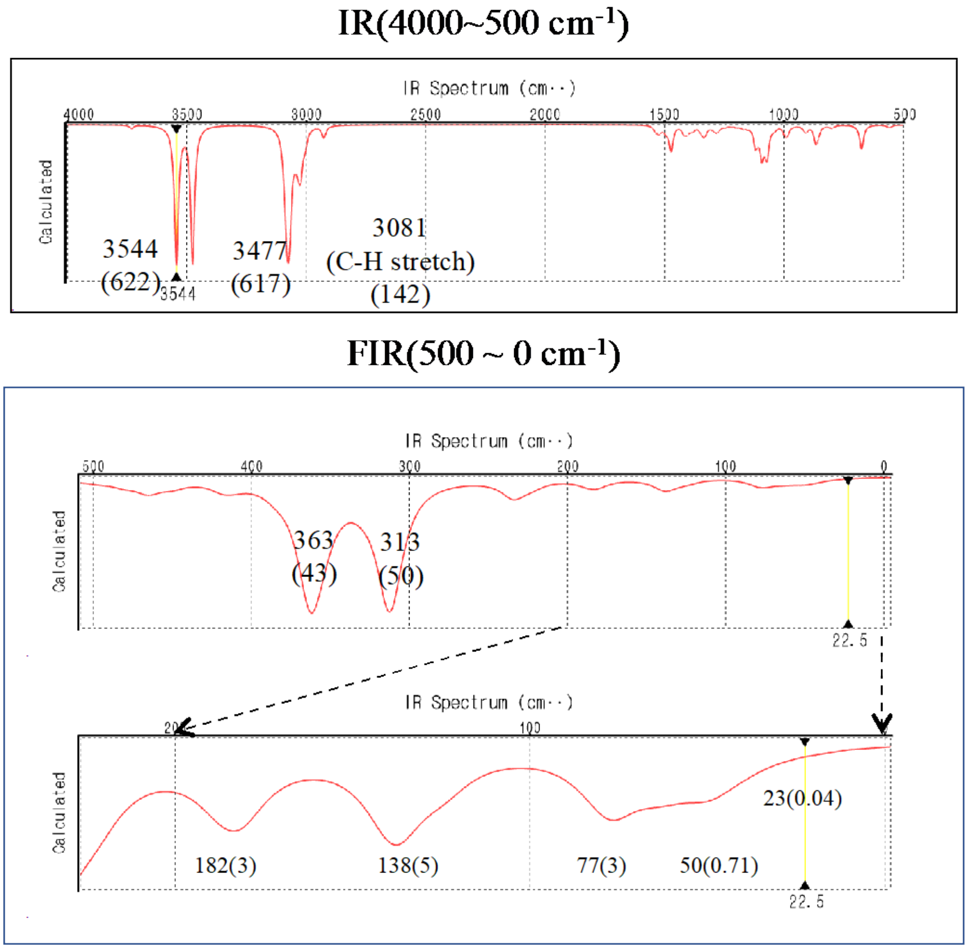
Supposing that cyclohexanol solution consists of a cyclohexanol monomer, and its hydrogen-bonded dimer and trimer, they are molecular-modeled, respectively, using the B3LYP exchange-correlation functional, and the 6–31G(d) basis set in the *Spartan-16* PC-installed software (Wavefunction, Inc. Irvine, CA). In this analysis we obtain the formation energy (ΔE), the energy levels of the lowest-unoccupied and the highest-occupied molecular orbitals (ELUMO and EHOMO, respectively), the electron transfer gap (ΔE_t, calculated from ELUMO and EHOMO), the infrared (IR) absorption with high intensity, and a series of far infrared (FIR) peak absorptions, as listed in Table 1. The intense IR absorptions are assigned to O-H stretching. Interestingly, the lower peak absorptions in FIR (0-200 $\mathrm{cm^{-1}}$) are assigned to a concerted cyclo-hexane ring vibration and the other upper peaks to O-H and C-H concerted bending of cyclohexanol.

Table 1: DFT-based calculations for IR/FIR spectra of liquid-state cyclohexanol

Name	Energy (au)	ΔE (kcal/mol)	ELUMO (eV)	EHOMO (eV)	ΔEt (eV)	Dipole (debye)	IR O-H stretching $\mathrm{cm^{-1}}$(intensity)	FIR Cyclohexane concerted ring vibration $\mathrm{cm^{-1}}$(intensity)
$C_6H_{11}OH$	-311.090472	-	2,18	-6.91	9.09	1.73	3724(6.28) (C-H stretching) 3073(62.5) 3089(63.4)	361(30.0) (O-H and C-H concerted bending), 163(1.9), 223(16.9), 264(70.8), 464(1.57)
$(C_6H_{11}OH)_2$	-622.193893	-8.12	1.68	-6.35	8.03	2.75	3577(453) (C-H stretching) 3068(67.7) 3077(58.2)	19(0.31), 58(1.08), 63(2.14) 130(2.62), 187(4.21), 268(1.87) 330(28.1), 401(66.5), (O-H and C-H concerted bending), 715(94.0)
$(C_6H_{11}OH)_3$	-933.301076	-18.6	1,54	-6.39	7.93	3.12	3477(617), 3544(622) (C-H stretching) 3081(142)	23(0.04), 39(0.43), 77(2.92), 138(4.53), 182(2.84), 234(6.64), (O-H and C-H concerted bending), 313(49.7), 363(43), 466(3.58)

Formation of cyclohexanol trimer is the most exothermic (ΔE=-18.6 kcal/mol), giving the highest dipole moment of 3.12 debye. In addition, intense two absorption peaks in IR are assigned to O-H stretching, and interestingly, some peak absorption in broad FIR absorption calculated in the region, 0-234 cm^{-1} can be assigned to a concerted cyclohexane ring vibration of all cyclohexanol rings, as shown in Fig. 1. The trimer undergoes concurrent absorption and emission of radio and MW frequency, i.e., FIR/IR energy, giving heat by final thermal emission of the thermo-upconverted O-H stretching energy. Then, such intermolecular concerted vibration predicts that the radio-frequency-induced heating phenomenon could be explained as due to thermo-upconversion rather than molecular friction and/or dielectric loss.

Figure 2 shows the three dimensional (3D) and electron density structures of cyclohexanol trimer. The trimer has the least electron transfer gap (ΔE), and the electrostatic potential indicates that the trimer locates in the potential between 2.44 and –2.02 eV. The trimer is very easily energized by the low energy of the radio frequency energy. The energized trimer emits and absorbs higher radio frequency, undergoing successive thermo-upconversion to the O-H stretching energy.


IR(4000~500 cm^{-1})

FIR(500 ~ 0 cm^{-1})

Figure 1: DFT-based IR/FIR spectra of hydrogen-bonded trimer of cyclohexanol

Verification of microwave heating of water solution

Conceivable water aggregates $(H_2O)_n$(n=1-6) and ice model of piled-$[(H_2O)_6]_2$ [3,4] are divided into three water aggregates, i.e., at high-temperature liquid state, at liquid state, and at low-temperature state (Fig. 3), which is on the basis of O-H stretching wavenumber in DFT/MM-based IR data in Table 2.

In general, the wavenumber above 3600 cm^{-1} is assigned to free O-H bond observable at high-temperature liquid water state, and the wavenumber below 3000 cm^{-1} to hydrogen-bonded OH that are observable at low-temperature liquid or crystal water states. All water aggregates at liquid state will be heated up by thermo-upconversion under MW irradiation as suggested by intense absorption of OH-stretching and effective and sequential absorption in FIR region.

It is reported that dielectric loss of pure water depends on wavenumber of IR/FIR and temperature, and of the temperature increases, the absorption wavenumber increases with decreased intensity[2]. In Fig. 4, IR/FIR spectra of ts-$(H_2O)_3$ and piled-[ts-$(H_2O)_3]_2$ are shown as a water model of low temperature and of high temperature, respectively.

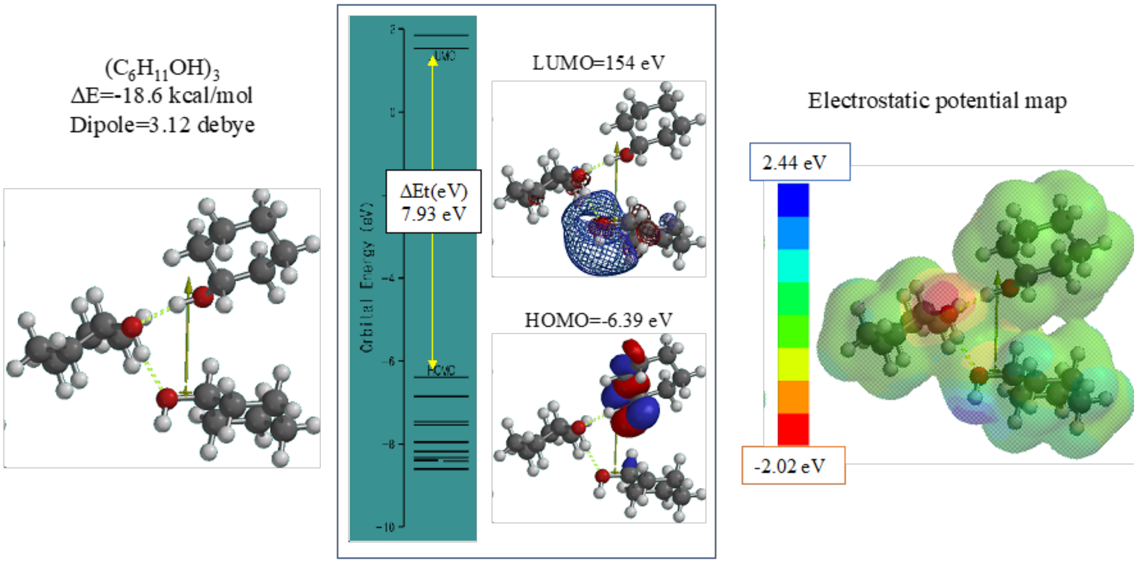
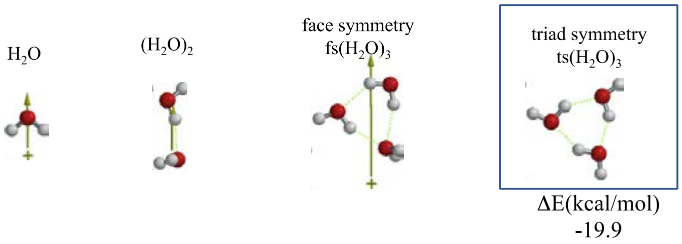
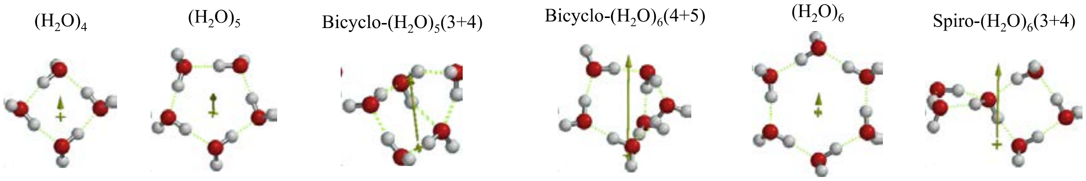


Figure 2: Hydrogen-bonded structure and electron density structure of cyclohexanol trimer $(C_6H_{11}OH)_3$

H_2O aggregates at high-temperature liquid state (~100℃)



H_2O aggregates at liquid state



H_2O aggregates at low-temperature liquid state

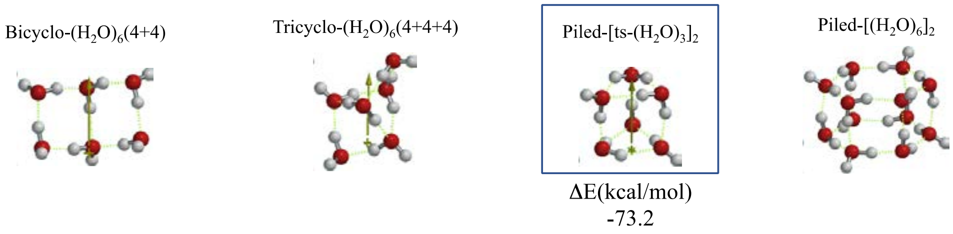


Figure 3: Hydrogen-bonded H_2O aggregates $(H_2O)_n$ for n=1-6.

Table 2: DFT-based IR/FIR spectra analysis of hydrogen-bonding H2O alignments

Name	Energy (au)	ΔE (kcal/mol)	Dipole (debye)	ΔEt (eV)	IR OH stretching cm^{-1}(intensity) Wavenumber max	FIR Ring hydrogen bond vibration cm^{-1}(intensity) Initial onset peak, three representative peaks
H_2O	-76.4089462		2.1	9.62	3850(19.3)	-
$(H_2O)_2$	-152.830154	-7.69	1.71	8.31	3625(251)	37(31), 147(223), 183(197), 241(222), 692(122)
fs$(H_2O)_3$	-229.249859	-14.4	5.3	7.18	3693(119)	100(6.4), 135(182), 178(141), 400(173), 591(377)
ts$(H_2O)_3$	-229.258482	-19.9	0	9.33	3623(434), 3624(433)	209(14.2), 210(13.6), 407(248), 418(249), 593(268),
$(H_2O)_4$	-305.703511	-42.5	0.02	9.49	3317(1588), 3318(1585)	63(0), 298(73), 299(70), 315(263), 317(266),
$(H_2O)_5$	-382.130909	-54.1	1.3	9.34	3267(2426), 3272(2324)	11(5.4), 236(21.6), 239(36.9), 279(34.4), 284(291)
Bicycl-$(H_2O)_5$(3+4)	-382.131557	-54.5	2.97	8.95	3232(1910)	33(1.0), 256(57), 288(95), 315(125), 361(1 14)
Bicycl-$(H_2O)_6$(4+5)	-458.556075	-64.3	3.98	8.36	3204(2369)	41(0.18), 56(13), 218(26.6), 231(123), 245(37),
$(H_2O)_6$	-458.558453	-65.7	0.01	9.46	3255(3076), 3256(3081)	26(0.75), 103(6.6), 230(22), 248(41), 249(35),
Spiro-$(H_2O)_6$(3+4)	-458.558529	-65.8	2.92	9.25	3312(1681), 3325(1573)	19(1.39), 45(7.9), 228(25), 257(83), 273(52)
Bicycl-$(H_2O)_6$(4+4)	-458.564511	-69.5	2.68	8.72	3157((2464)	27(1.1), 107(5.2), 218(5.0), 240(32), 93), 148(93)
Tricycl-$(H_2O)_6$(4+4+4)	-458.568281	-71.9	2.46	8.75	2947(869), 3406(925)	41(2.8), 65(6.8), 256(20), 260(17), 277(19),
Piled-$(H_2O)_3]_2$	-458.570384	-73.2	2.96	8.54	2929(1019), 3250(93)	79(2.9), 189(4.0), 224(19), 228(21), 260(7.31)
Piled-$[(H_2O)_6]_2$	-917.183023	-173	0	8.87	2997(4088)	53(0), 56(2.6), 83(3.6), 104(8.9), 287(125)

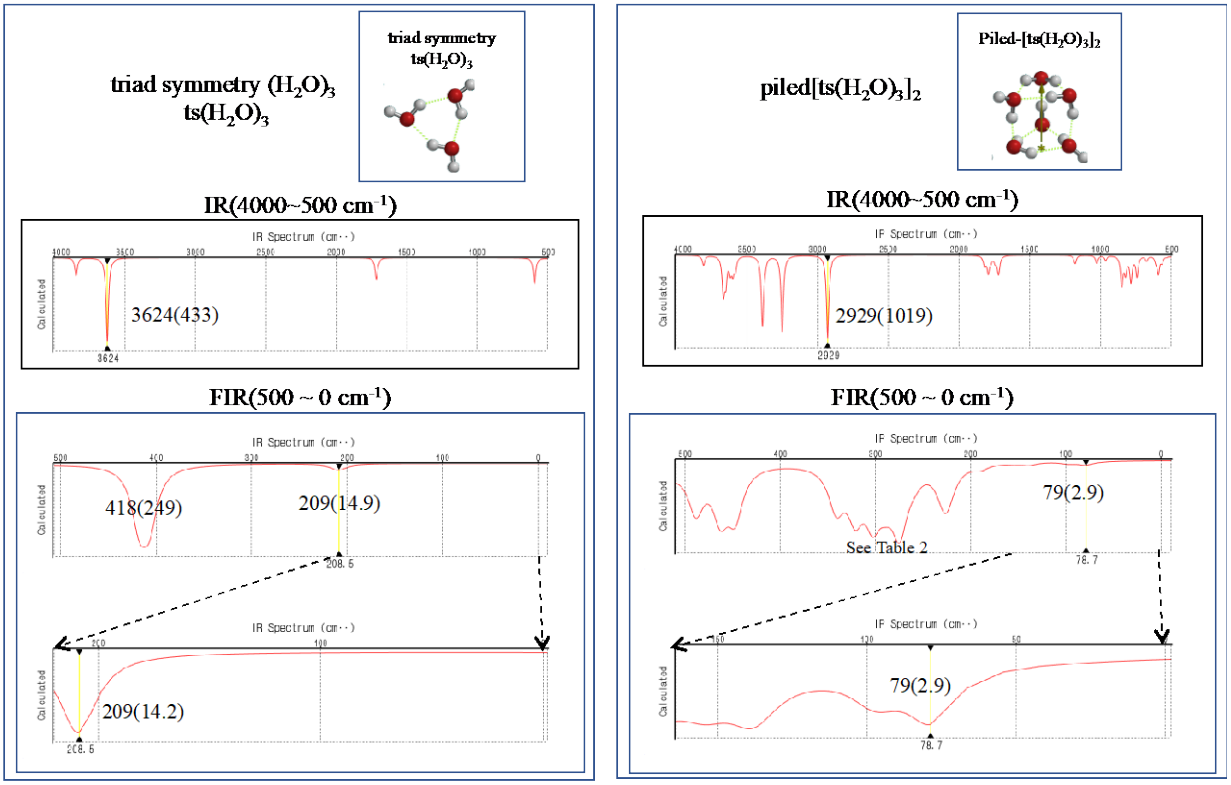


Figure 4: DFT-based IR/FIR spectra of triad symmetry H2O, ts(H2O)3 as a high-temperature water model, and piled [ts(H2O)3]2 as a low-temperature water model.

The ts$(H_2O)_3$ model starts to absorb at longer wavenumber of FIR and the emission from the OH-stretching is not strong. As for the electron density structure (Fig. 5), the large ΔEt (eV) 9.33 eV and the electrostatic potential gap of 7.75 eV rationalize that FIR starts at longer wavenumber when compared with other water aggregates.

On the other hand, DFT-based IR/FIR spectrum of the piled-$[(H_2O)_3]_2$ verifies effective heating under MW irradiance as a result of thermo-upconversion. The electron density analysis supports the effective heating by smaller ΔEt (eV), 8.36 eV and smaller electrostatic potential gap of 4.72 eV (Fig. 6). We further state that the piled-$[(H_2O)_3]_2$ may contribute to the high density of water around 4 degree.

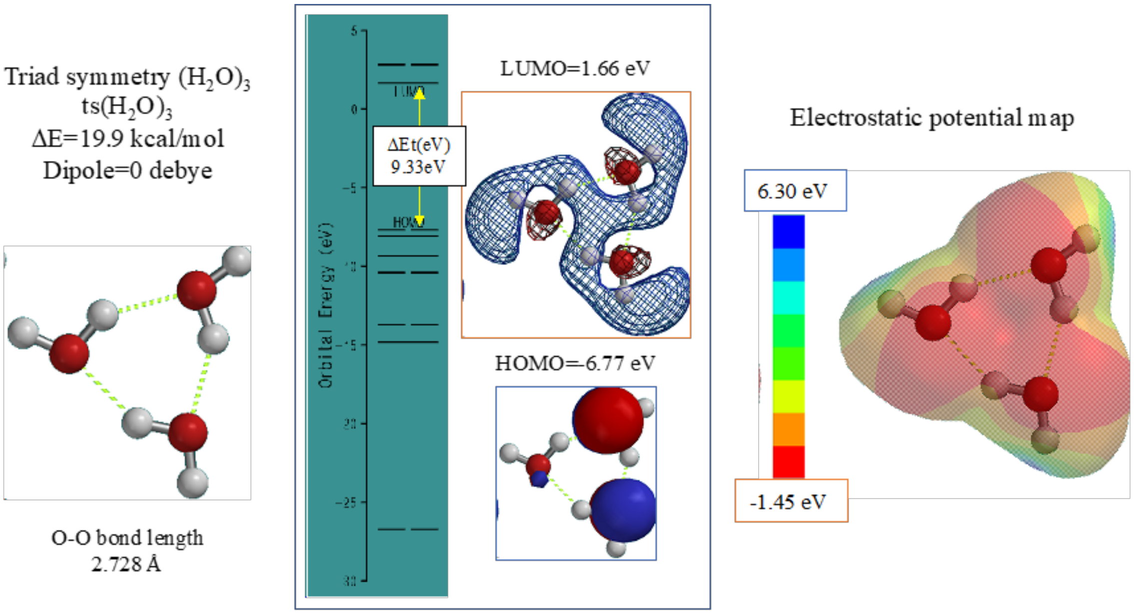


Figure 5: Hydrogen-bonded structure and electron density structure of triad symmetry (H_2O), ts$(H_2O)_3$.

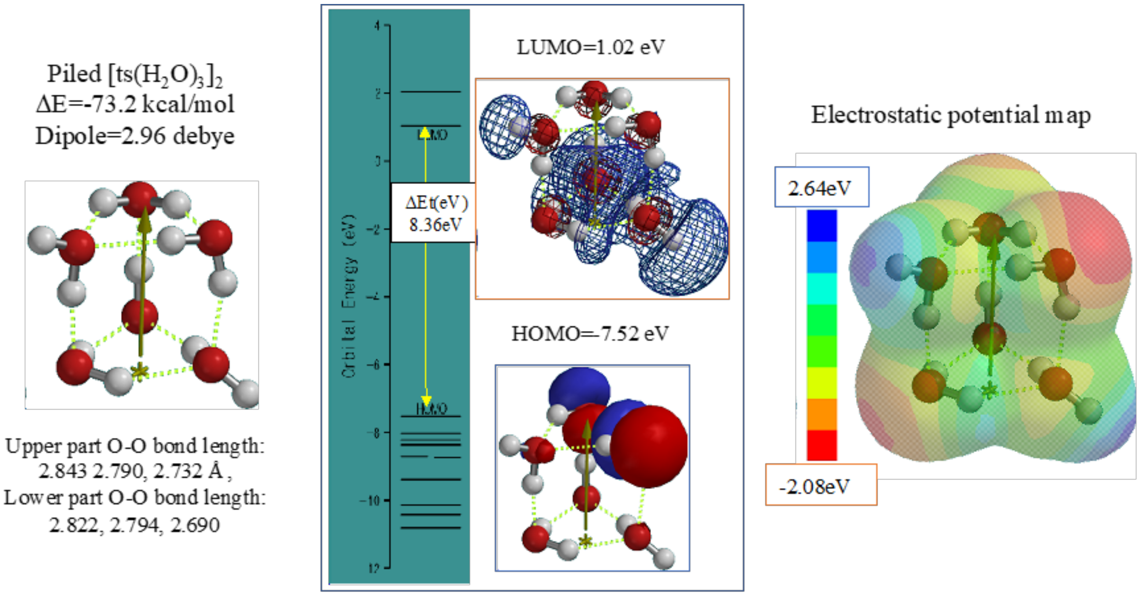


Figure 6: Hydrogen-bonded structure and electron density structure of piled $[ts(H_2O)_3]$.

Conclusions

Liquid-state molecules interact with each other via van der Waals and Coulomb interactions, giving various alignments of their aggregates, which may be called amorphous states of liquid. DFT-based molecular modeling (DFT/MM) can characterize each aggregate in amorphous state as one non-covalent bonding molecule, giving an electron density energy structure for each aggregate. In addition, DFT/MM of molecular aggregates verifies and predicts electromagnetic absorption spectra such as IR/FIR and UV/Vis.[5, 6)] The proposed thermo-upconversion mechanism for radio and MW frequency heating is a DFT-predicted mechanism. We conclude that MW-assisted quick and clean organic synthesis will be called "MW thermo-catalytic synthesis", because reactants aggregate each other via van der Waals and Coulomb interactions, being heated up instantly by thermo-upconversion of the aggregated reactants under MW irradiance.

For further reading:

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Acknowledgments

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