

Supporting Information for “Decelerated Liquid Dynamics Induced by Component-Dependent Supercooling in Hydrogen and Deuterium Quantum Mixtures”

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Mixing Ratio	Average Temperature		
0% D ₂	30.0	25.1	18.1
25% D ₂	30.0	25.0	17.9
50% D ₂	30.1	25.0	17.9
75% D ₂	30.1	24.9	18.0
100% D ₂	30.0	24.9	18.1

Table S1: Average temperatures obtained by the the NVE (microcanonical) simulations.

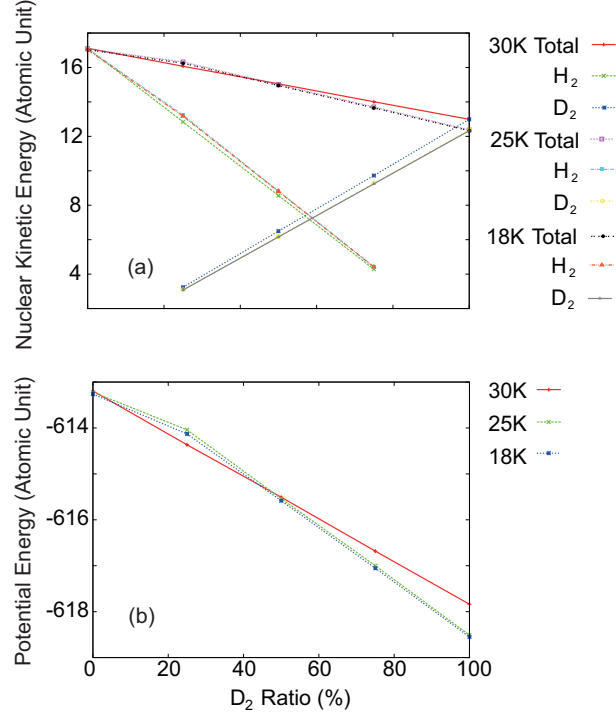
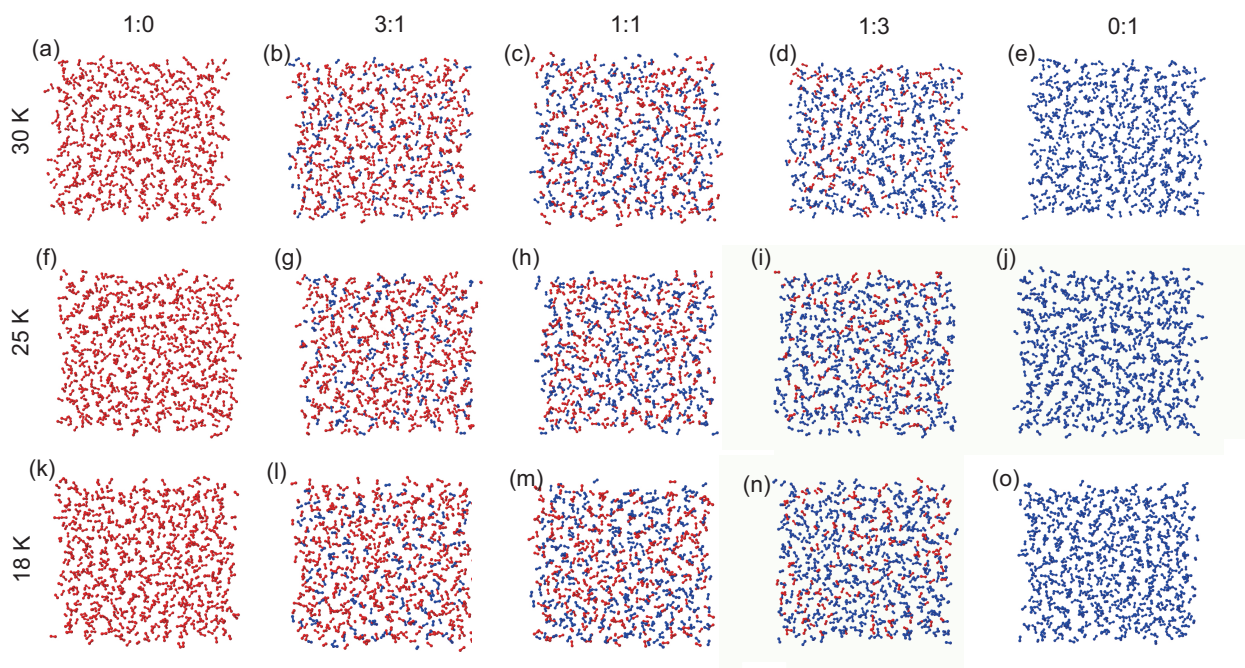


Figure S1: (a) Nuclear kinetic energies and (b) remaining potential energies. The nuclear kinetic energies, which originate from the kinetic energy operator, can be decomposed into the H₂ and D₂ contributions. The total nuclear kinetic energies almost monotonically decrease with increasing the D₂ mixing ratio because of the larger mass of D₂ molecules compared to H₂ molecules. The nuclear kinetic energies decomposed into each isotope essentially reflect the component ratio H₂:D₂; the nuclear kinetic energies of H₂ decreases while the nuclear kinetic energies of D₂ increases with increasing the D₂ mixing ratio. The potential energies including the internuclear interaction between H and D exhibit the similar dependence on the D₂ mixing ratio and temperature to the total nuclear kinetic energies. The lower potential energies with the higher D₂ mixing ratio imply that the current liquid states whose molar volume is close to the vapor-pressure molar volume of D₂ are more stable when more D₂ molecules are included especially at the lower temperatures.



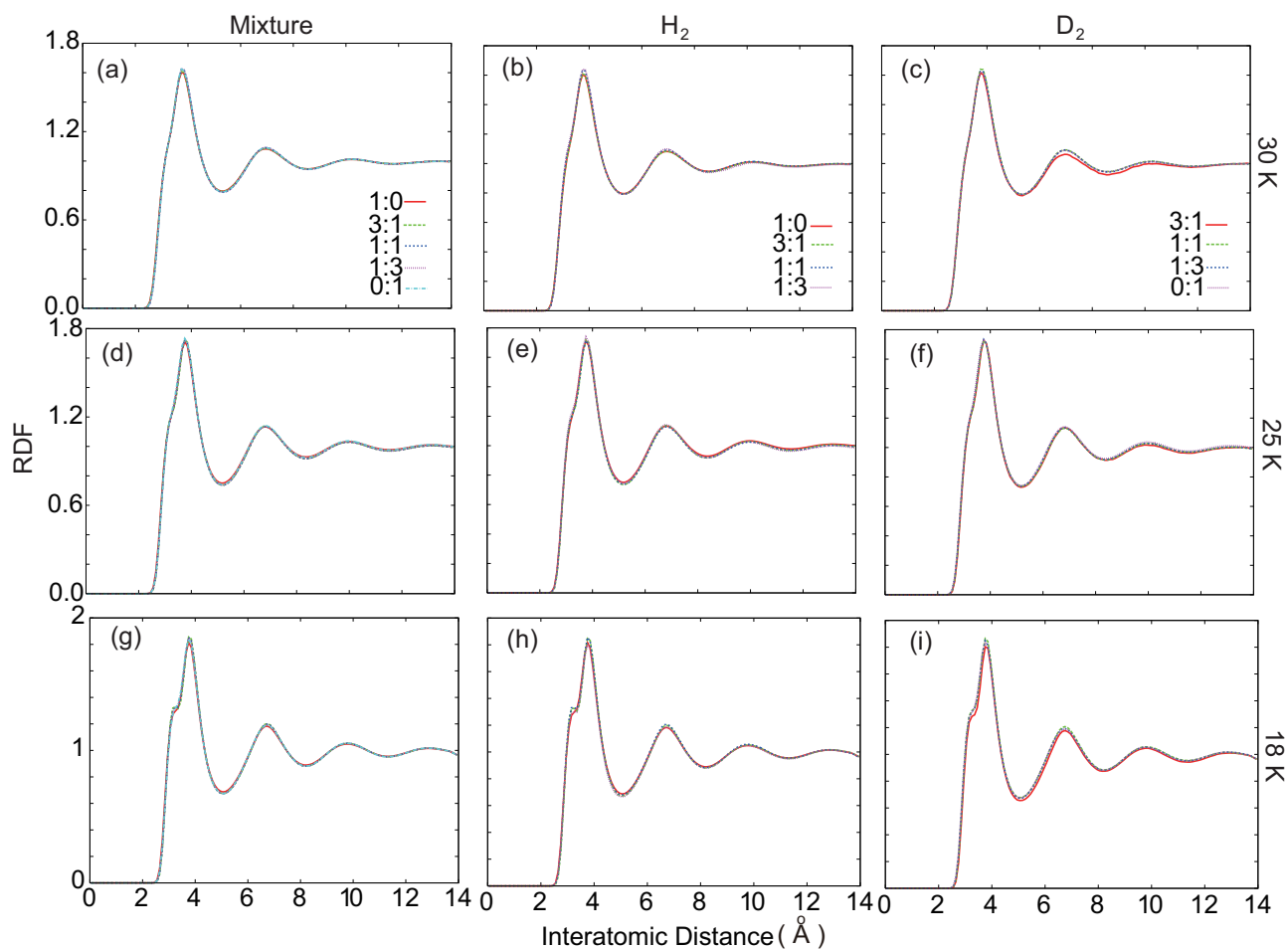


Figure S3: Radial distribution functions(RDFs) at (a)-(c) 30 K, (d)-(f) 25 K and (g)-(i) 18 K. The left panels show the whole shapes of the RDFs for the mixture including both of H_2 and D_2 while the center and right panels display the RDFs of only one component, H_2 and D_2 , respectively. The shoulders in the left part of the first RDF peaks, which become apparent at the low temperature regardless of the D_2 ratio, reflect a diatomic structure of H_2 and D_2 in a first solvation shell. The most stable solvation structure of a pair of H_2 and D_2 is a T-shape configuration, and its nearest atoms appear as the shoulder especially at the low temperature due to smaller thermal modulations of molecules in a first solvation cage.^{1,2}

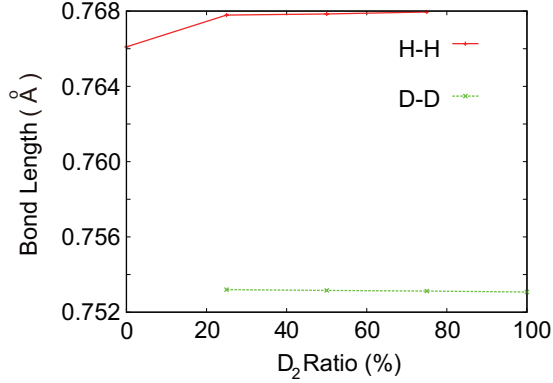


Figure S4: Average H-H and D-D bond length in the mixtures at 18 K. The H-H bond length becomes larger when D₂ molecules are mixed by 25 % because it is hard for light H₂ molecules to escape from the first solvation shell including heavy D₂ molecules; especially the present H₂ molecules are supercooled at 18 K and their mobility for escaping is suppressed. Further, mixing of D₂ molecules which have the shorter bond length and the smaller nuclear wave packet than H₂ molecules provides freer space for the H-H bond to stretch more compared to the pure H₂ liquid case. The D-D bond length slightly becomes longer with decreasing the D₂ ratio, *i.e.*, with increasing the H₂ ratio. As more light H₂ molecules surround a D₂ molecule in a solvation cage, it becomes easier for a D₂ molecule to push surrounding light H₂ molecules and stretch. The average bond length of isolated H₂ and D₂ molecules, which is purely determined by the intramolecular interaction including the isotope-dependent nuclear quantum effects, was calculated by the nuclear and electron wave packet molecular dynamics (NEWPMD) method as 0.76429 Å and 0.75163 Å, respectively.^{1,2} Since the experimental bond length in a gas phase was measured as 0.7510 Å for H₂ and 0.7482 Å for D₂, the difference between the computed and experimentally observed bond length is only 1.8% for H₂ and 0.5% for D₂, which is surprising taking into account that the NEWPMD method does not include any empirical parameter or model potential.

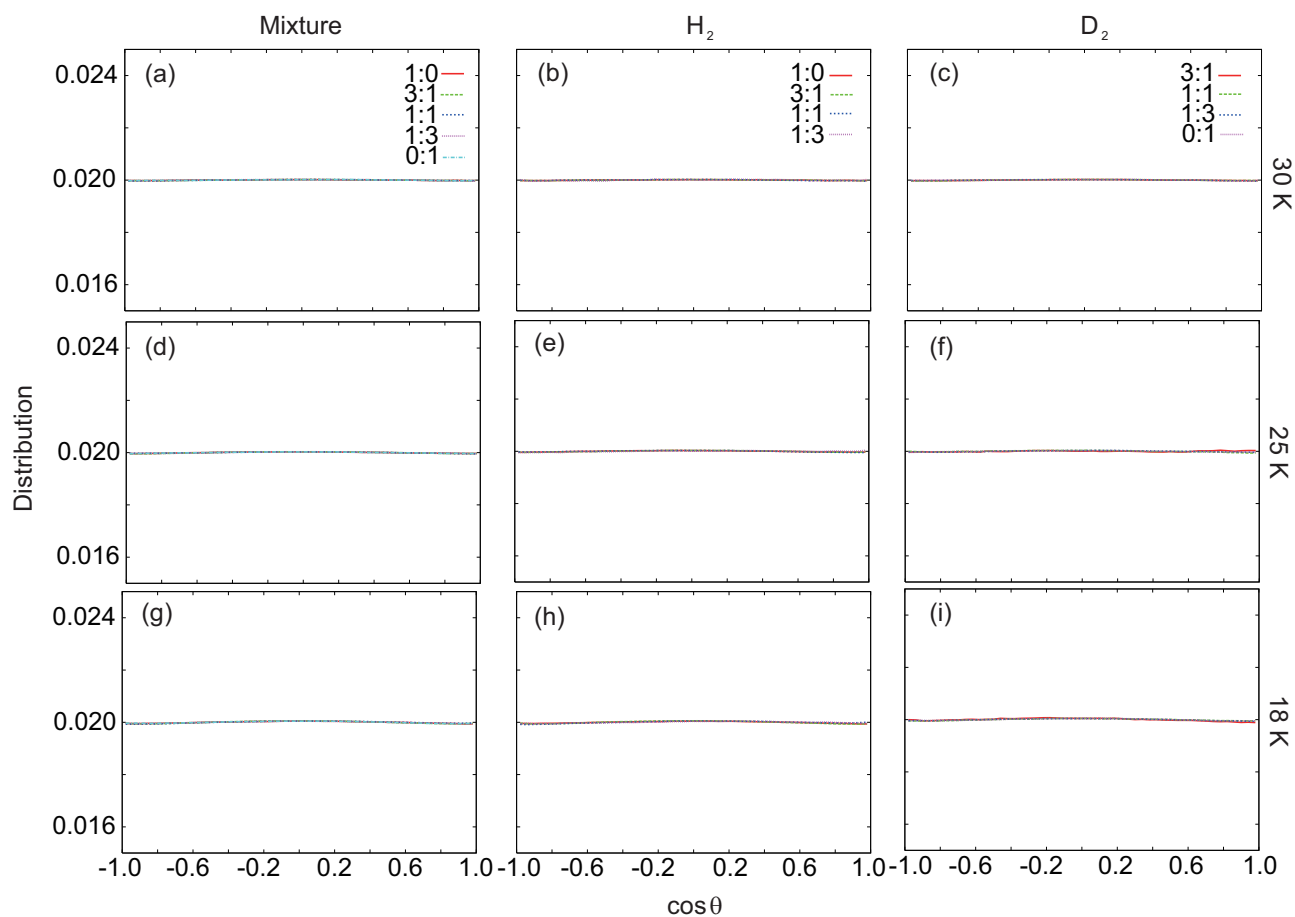


Figure S5: Distributions of the intermolecular angle θ , defined by a relative angle formed by a pair of molar vectors of two molecules, at (a)-(c) 30 K, (d)-(f) 25 K and (g)-(i) 18 K. The left panels show θ of the mixture including both of H_2 and D_2 , while the center and right panels correspond to θ -distributions of only one component, H_2 and D_2 , respectively.

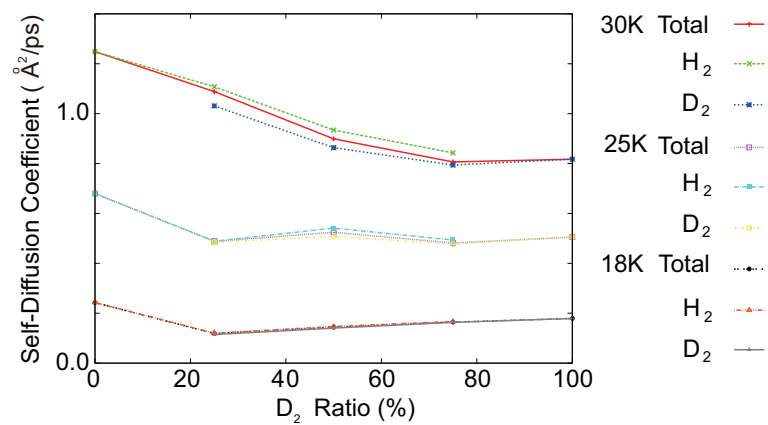


Figure S6: Self-diffusion coefficients of each isotope at the different temperatures as a function of the D₂ ratio.

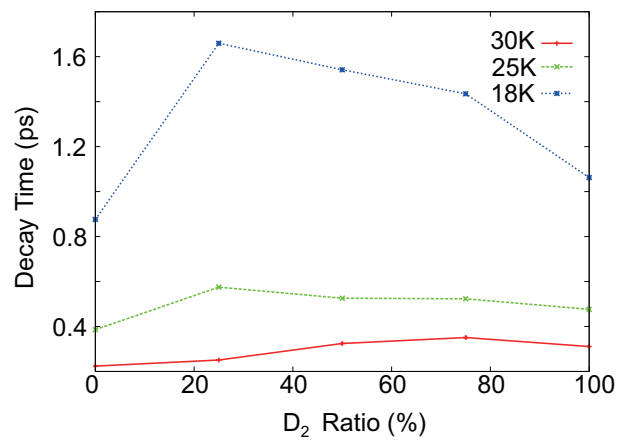


Figure S7: Decay timescales estimated by fitting the long-time time correlation functions(TCFs) of $\theta(t)$ shown in Fig.3(a)-3(c) with an exponential function.

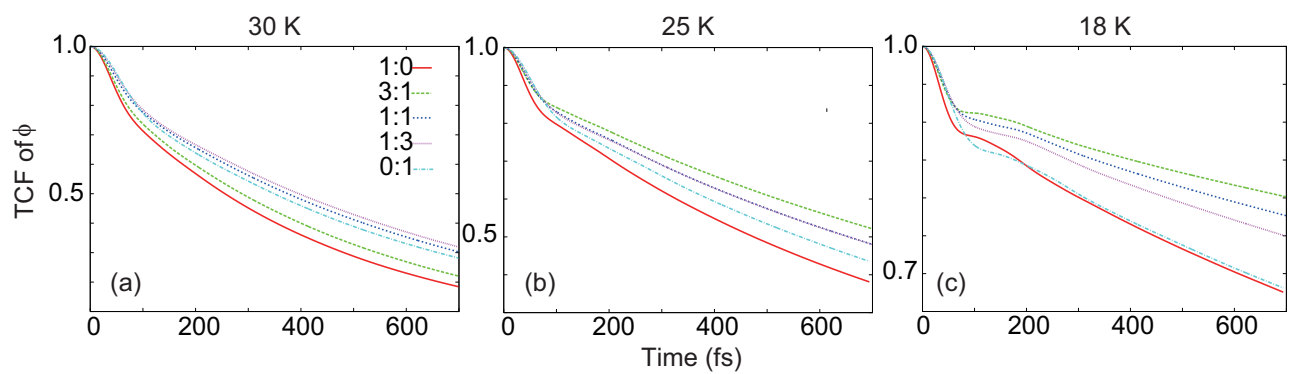


Figure S8: TCFs of the self-orientation of a molecule $\phi(t)$, which is defined as a molecular angle projected on the xy -plane, at (a) 30 K, (b) 25 K and (c) 18 K.

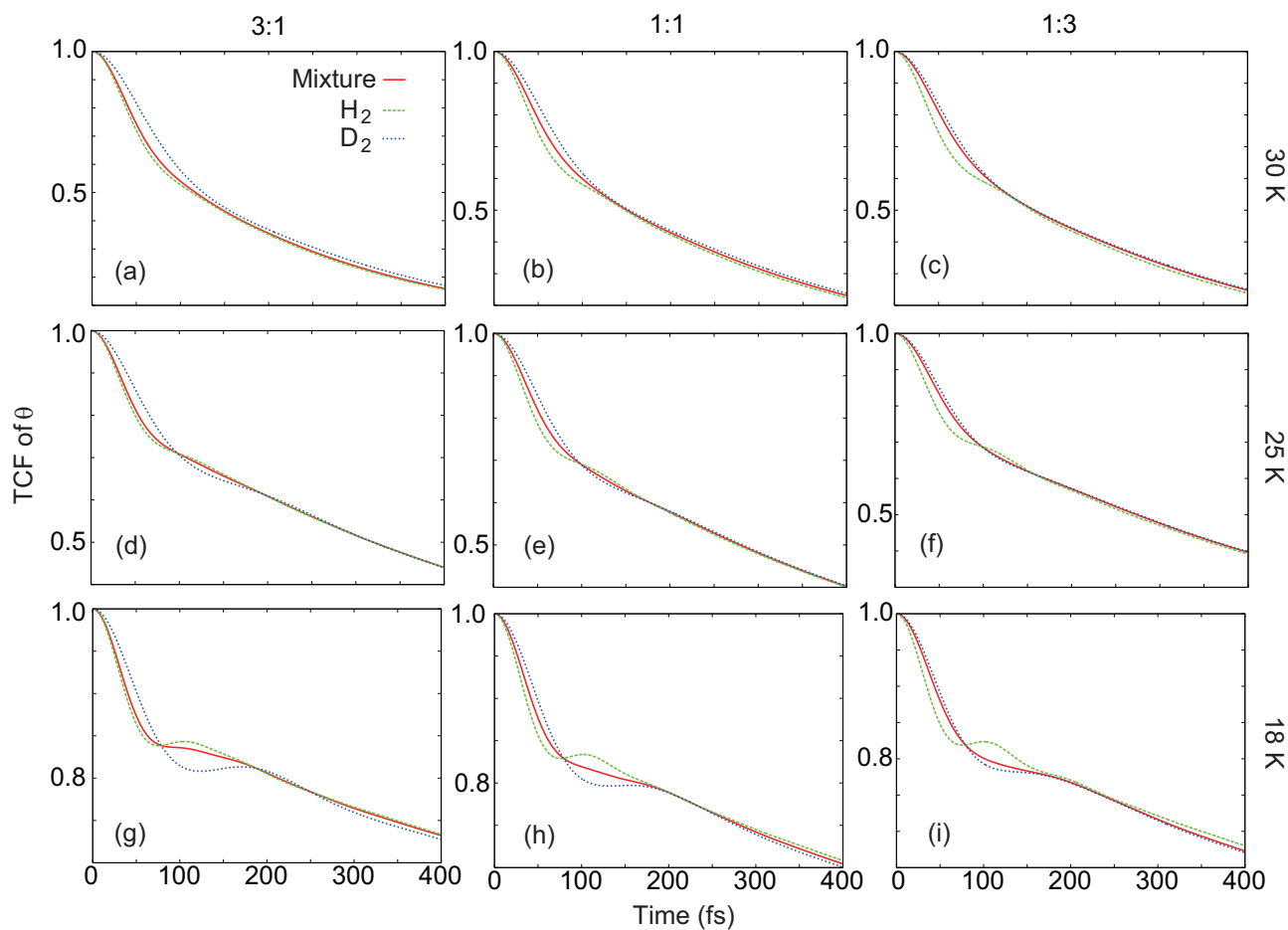


Figure S9: θ -TCFs for the 3:1, 1:1 and 1:3 mixtures at (a)-(c) 30 K, (d)-(f) 25 K and (g)-(i) 18 K. Contributions from the total mixture, H_2 and D_2 are plotted by the red, green and blue lines, respectively.

References

- (1) Hyeon-Deuk, K.; Ando, K. Correlations of Intra- and Intermolecular Dynamics and Structure in Liquid Para-Hydrogen. *Phys. Rev. B* **2014**, *90*, 165132.
- (2) Abe, K.; Yamaoka, S.; Hyeon-Deuk, K. Isotopic Effects on Intermolecular and Intramolecular Structure and Dynamics in Hydrogen, Deuterium and Tritium Liquids: Normal Liquid and Weakly and Strongly Cooled Liquids. *J. Phys. Chem. B* **2018**, *122*, 8233–8242.