Supplementary Information for Refining Potential Energy Surface through Dynamical Properties via Differentiable Molecular Simulation

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Supplementary Methods

Fitting IR spectrum of liquid water using q-SPC/Fw model

The q-SPC/Fw model was used to fit the spectrum from truncated TCF and the experimental spectrum separately.

As for the spectrum from truncated TCF, the force field parameters we perturbed includes the hydrogen charge q, the oxygen σ, the OH bond force constant k_b, and the HOH angle force constant k_a. The fitting traget is the spectrum of Fouier transformed truncated (0.2 ps) TCF from original q-SPC/Fw model, which is shown in Supplementary Fig. 2 (panel a and b). After fitting, as shown in Supplementary Fig. 5 and Supplementary Table. 1, we run a converged spectrum (2 ps TCF) and compare with the original spectrum. This fitting use short time dynamics to refine PES, and use such PES to imply long-time dynamics. Physically, such strategy can work as long as we believe that both short- and long-time dynamics are determined by the same underlying PES, so the improvement of the PES is beneficial for both limits.

As for the experimental spectrum, the force field parameters we perturbed includes the oxygen charge q, the oxygen σ and ϵ, the OH bond force constant k_b and length, and the HOH angle force constant k_a and angle. We use point charge to construct the dipole surface, so the O charge is in principle related to the dipole surface. Therefore, we optimize not only the PES, but also the dipole surface. The fitting traget is the experimental spectrum. As shown in Supplementary Fig. 2 (panel c and d), the experimental IR spectrum is smooth thus can be converged relatively quickly, 0.2 ps TCF already gives a very accurate spectrum. However, due to the inherently insufficient capability of the classical force field (i.e., harmonic bonding terms), the low wavenumber region can be fitted accurately, and the positions of other peaks are also correct, but the shape of the high-frequency peak is wrong (shown in Supplementary Fig. 6, panel a). Moreover, as the panel b shows, the err of self-diffusion coefficient increase in the optimization, we also test other properties such as O-O and O-H RDF (panel c and d) and dielectric constant (42 versus 97) using the refined q-SPC/Fw model, the O-O RDF and the dielectric constant also get worse.

Supplementary Figures

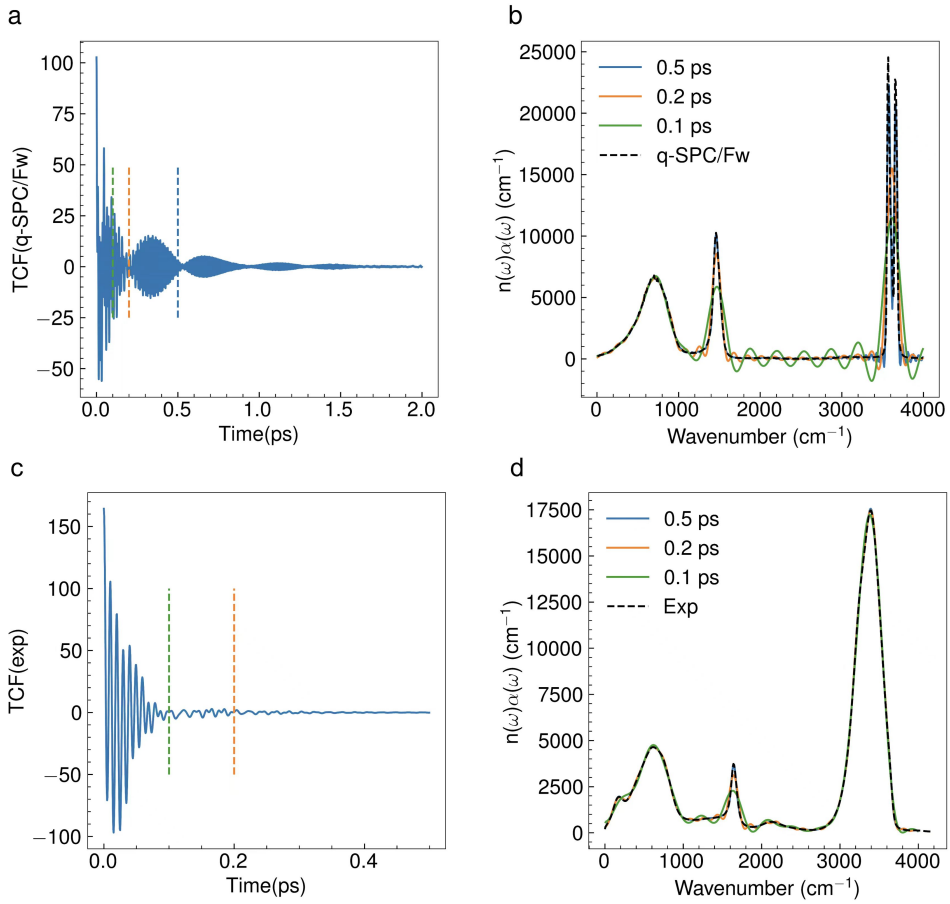

Figure 1: Truncations on the time correlation function (TCF) from q-SPC/Fw force field[1] for liquid water. (**a**) The TCF curve, different truncation times (0.5 ps, 0.2 ps and 0.1 ps) are marked using dashed line. (**b**) IR spectrum after truncation, the q-SPC/Fw model (dashed line) use the 2 ps long TCF as in the left figure. (**c**) The TCF curve after inverse Fourier transform of the experimental infrared (IR) spectrum. (**d**) IR spectrum after truncation on TCF of the inverse Fouier transformed experimental IR spectrum

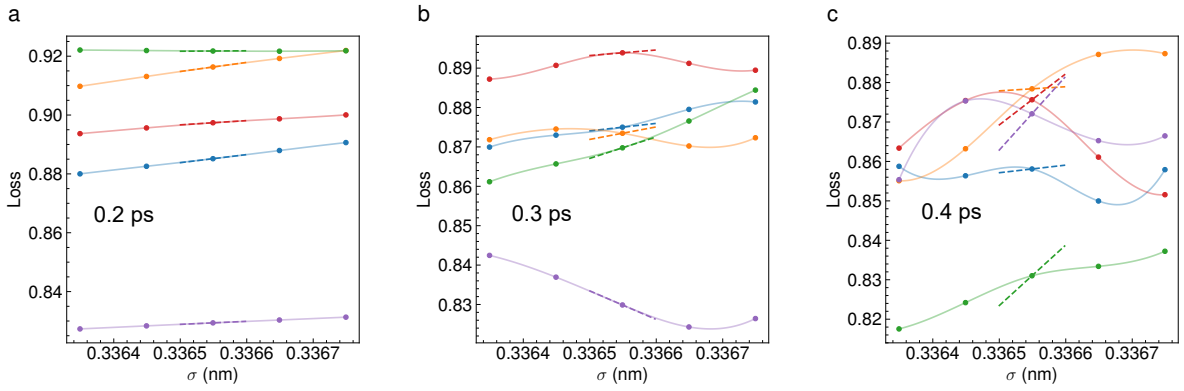

Figure 2: Verifying the effectiveness of the gradients from the time correlation function curves at (**a**) 0.2 ps, (**b**) 0.3 ps, and (**c**) 0.4 ps on the loss surfaces derived from the infrared (IR) spectrum: solid line is the loss surface by interpolation, the slope of the dashed line is the gradient calculated, 5 experiments are made to show that long time simulation gives rough loss surface and invalid gradient

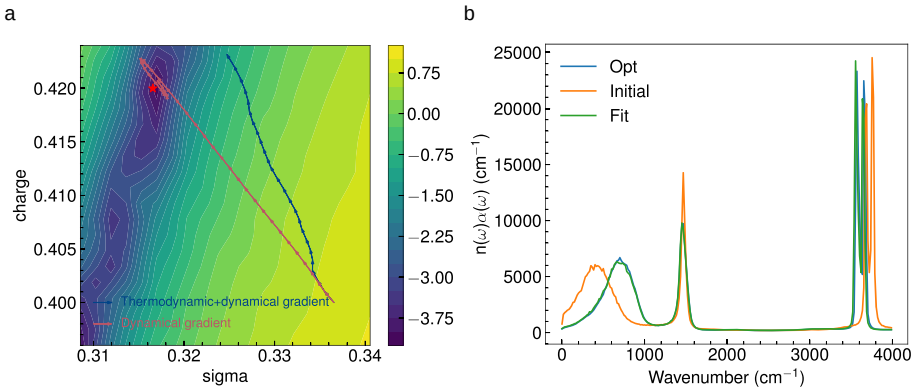

Figure 3: Fitting the infrared (IR) spectrum to revert the parameters to original values using q-SPC/Fw force field. (**a**) Optimizing only charge ($q(e)$) and sigma (σ(nm)) to fit the IR spectrum of liquid water, only using dynamical gradient is more effective. (**b**) Converged IR spectrum from refined q-SPC/Fw model (optimizing q, σ, k_b, and k_a)

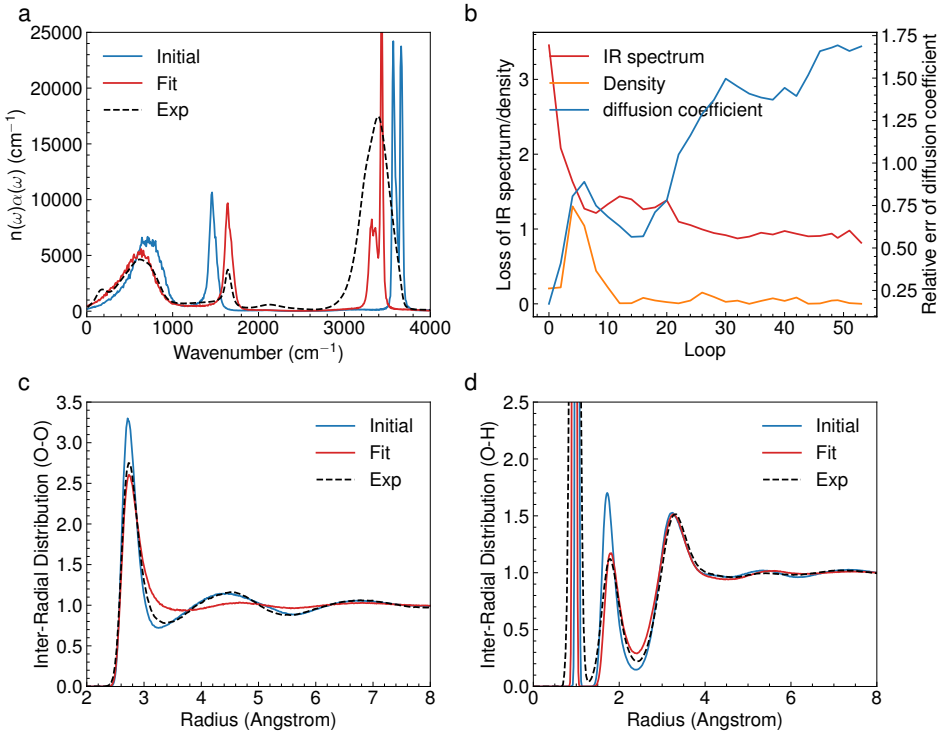

Figure 4: Fitting both density and experimental infrared (IR) spectrum using q-SPC/Fw force field. (**a**) IR spectrum before and after optimization, comparing with experimental results (Exp) [2] (**b**) Optimization process using both IR spectrum and density targets. The change of diffusion coefficient error is also plotted along the side of density and IR spectrum errors. (**c**) O-O and (**d**) O-H radial distribution functions (RDFs) comparing with experimental data

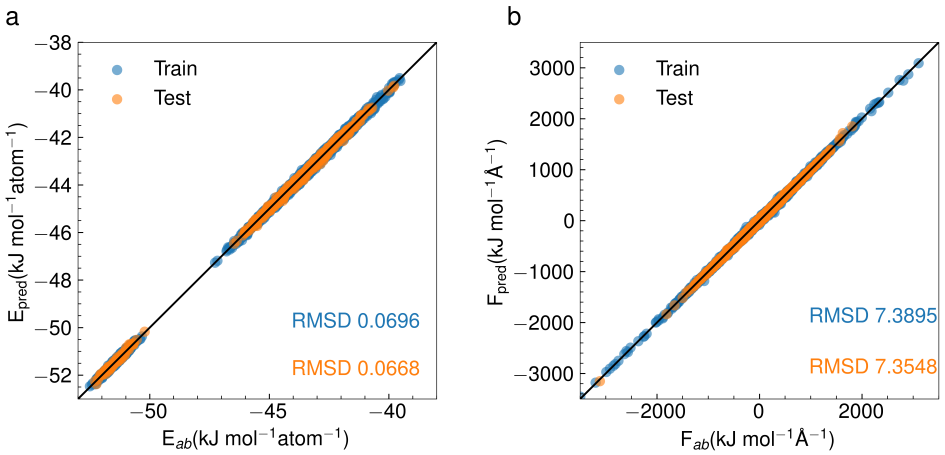

Figure 5: The root mean squared deviations (RMSD) of (**a**) energy and (**b**) force from EANN model after training

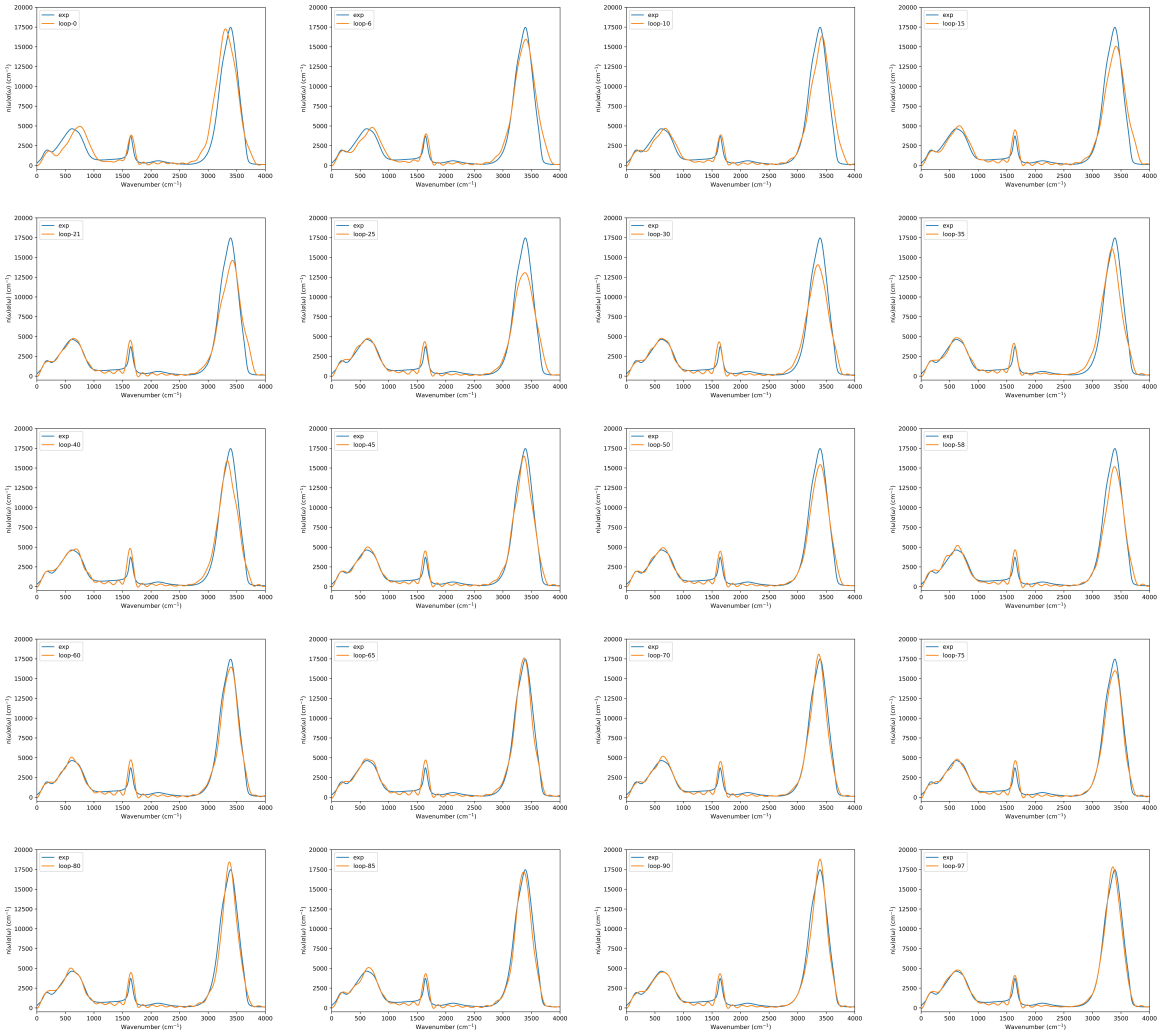

Figure 6: The evolution of the infrared (IR) spectrum versus the experimental reference once every 5 loops, blue line is the experimental result[2], yellow line is the calculated spectrum

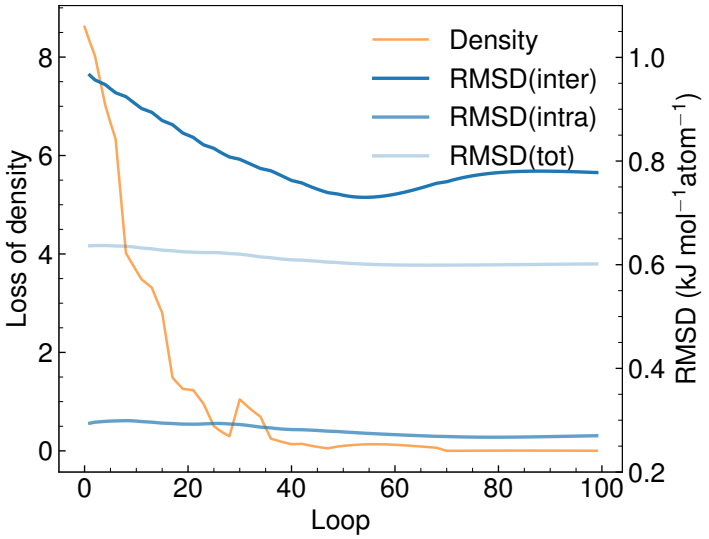

Figure 7: The root mean squared deviations (RMSD) changes of intermolecular, intramolecular and total energy in the optimization for only density

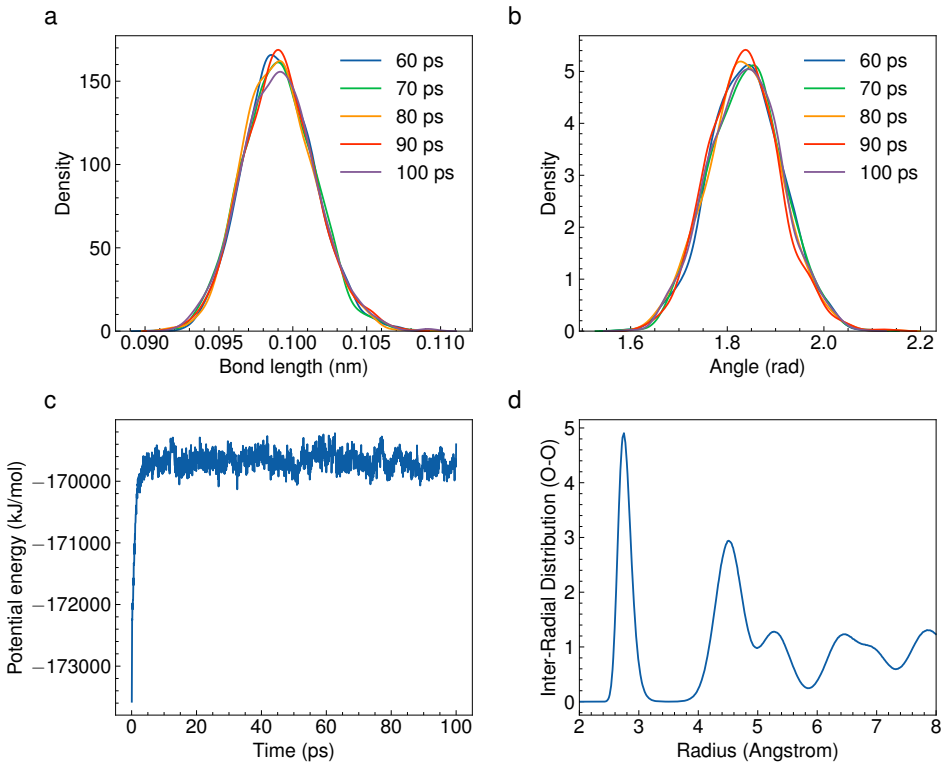

Figure 8: Testing the refined potential energy surface on ice Ih phase, a 100 ps NVT simulation on a density of 0.92 g/cm^3 at 241.65 K is conducted. (**a**) Bond length and (**b**) angle distribution at different time points. (**c**) Potential energy at equilibrium. (**d**) O-O radial distribution function (RDF) at equilibrium

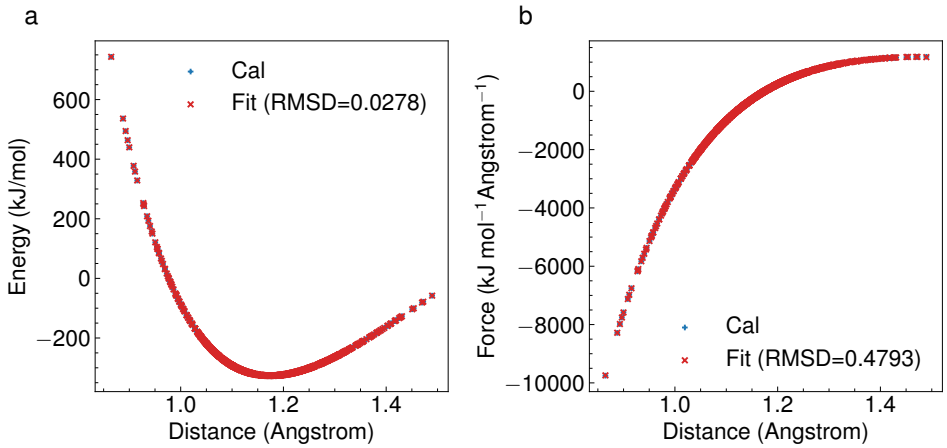

Figure 9: The root mean squared deviations (RMSD) of (**a**) energy and (**b**) force from N-C EANN potential model after training

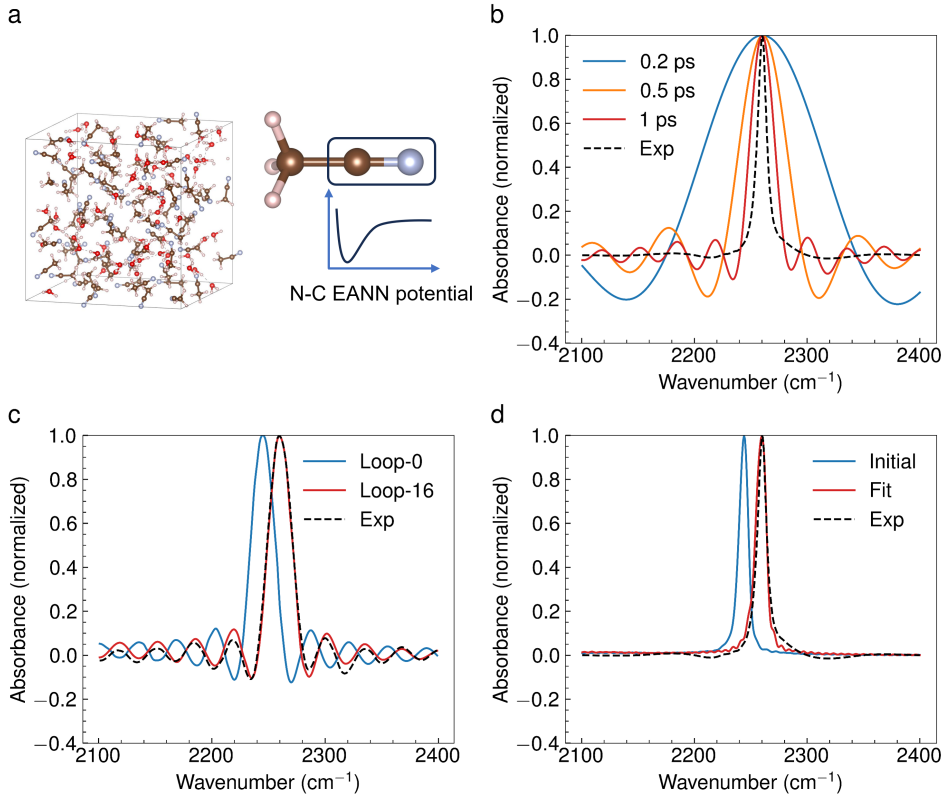

Figure 10: Fitting the C-N vibrational peak in acetonitrile-water mixture. (**a**) Simulation system. (**b**) C-N vibrational peak after truncation (**c**) Fitting quality of the truncated C-N vibrational peak. (**d**) Fully converged C-N vibrational peak compared with experimental result[3]

Supplementary Tables

Table 1: Comparison between the initial parameters, the fitted parameters and the optimal parameters (original parameters) for q-SPC/Fw force field

	Initial	Fit	Opt
σ (nm)	0.3365492	0.3188048	0.3165492
q (e)	0.40	0.4248	0.42
k_b (kJ mol^{-1}nm^{-2})	463153.3808	439379.7187	443153.3808
k_a (kJ mol^{-1}rad^{-2})	337.5656	317.8841	317.5656

Table 2: Comparison between the initial parameters, the fitted parameters for q-SPC/Fw force field

	Initial	Fit
σ (nm)	0.3165492	0.3103229
ϵ (kJ mol^{-1})	0.6502990368	0.6456576536
k_b (kJ mol^{-1}nm^{-2})	443153.3808	385342.1689
length	0.1	0.0941
k_a (kJ mol^{-1}rad^{-2})	317.5656	371.9439
angle (rad)	1.9547687622336491	2.0709569372027614
$q(e)$	-0.84	-0.8160

References

[1] Paesani, F., Zhang, W., Case, D. A., Cheatham, T. E. & Voth, G. A. An accurate and simple quantum model for liquid water. *The Journal of Chemical Physics* **125**, 184507 (2006).

[2] Bertie, J. E. & Lan, Z. Infrared intensities of liquids xx: The intensity of the oh stretching band of liquid water revisited, and the best current values of the optical constants of h 2 o (l) at 25 c between 15,000 and 1 cm-1. *Applied Spectroscopy* **50**, 1047–1057 (1996).

[3] Oh, K.-I. *et al.* Nitrile and thiocyanate ir probes: Molecular dynamics simulation studies. *The Journal of chemical physics* **128** (2008).