Electronic Supplementary Information for

Proton Transport in Liquid Phosphoric Acid: The Role of Nuclear Quantum Effects Revealed by Neural Network Potential

Pei Liu, Wei Li*, and Shuhua Li*

Key Laboratory of Mesoscopic Chemistry of Ministry of Education, New Cornerstone Science Laboratory, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210023, People's Republic of China

* Corresponding author, E-mail: Shuhua Li: shuhua@nju.edu.cn, Wei Li: wli@nju.edu.cn

S1. DFT Calibration

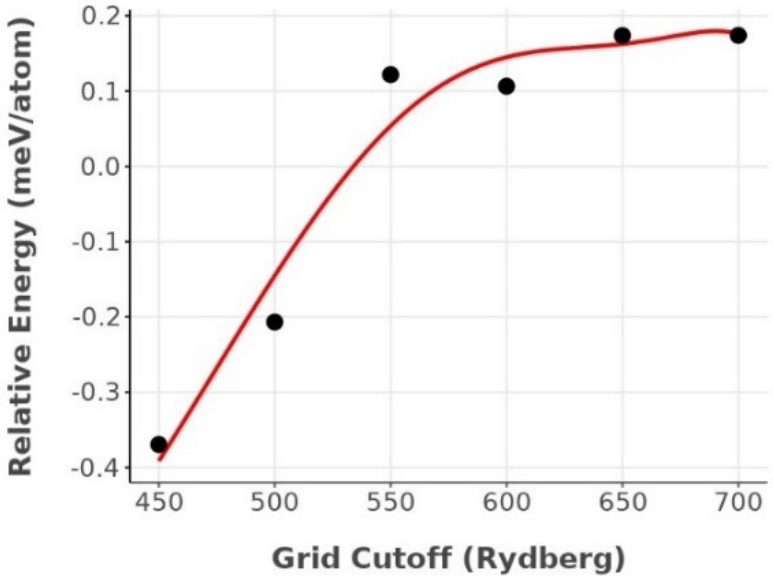

Figure S1. Convergence test for grid spacing in CP2K density functional theory (DFT) calculations. The y-axis represents the relative single-point energy, calculated as the difference between the single-point energy and the average single-point energy across various grid spacings.

Table S1. Convergence test of grid cutoff in CP2K DFT calculations. The cutoff values are presented in Rydberg (Ry), and the energies are given in atomic units (a.u.).

Cutoff	450	500	550	600	650	700
Energy	-2759.2962	-2759.2944	-2759.2907	-2759.2909	-2759.2901	-2759.2901

In performing density functional theory (DFT) calculations using CP2K, products of Gaussian functions are mapped onto real-space grids. The plane-wave cutoff parameter determines the grid resolution: higher cutoff values enhance accuracy but reduce computational efficiency. To find an optimal balance between accuracy and efficiency, we conducted a convergence test on the plane-wave cutoff. Our results show that at a cutoff of 550 Ry, the energies converge to within 0.1 meV/atom. Consequently, all CP2K calculations in this study were performed using a cutoff of 550 Ry.

S2. Dataset Statistics and MLP Performance Calibration

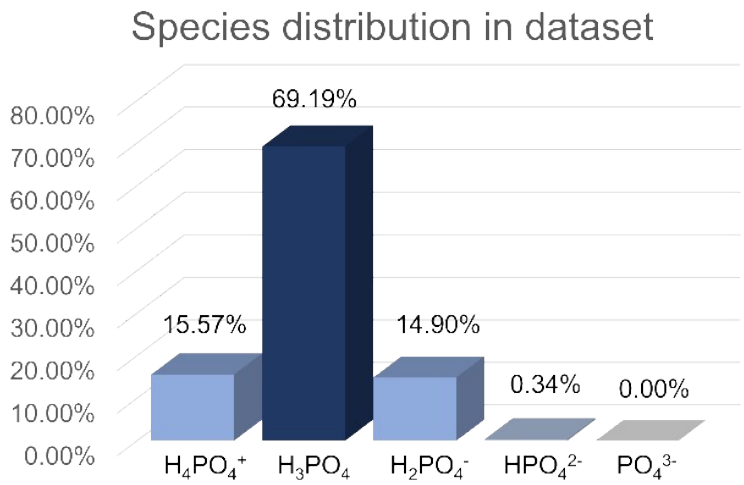

Figure S2. Distribution of phosphoric acid molecules and ions in the liquid phosphoric acid dataset.

Figure S2 compares the proportions of five different species within the complete dataset. It is evident that neutral H_3PO_4 molecules dominate the samples generated by active learning, comprising 69.19% of the dataset. The proportions of $H_2PO_4^-$ and $H_4PO_4^+$ are nearly equal, at 15.57% and 14.90%, respectively. This distribution aligns with the characteristic electrical neutrality of liquid phosphoric acid, suggesting that only the first ionization has taken place in the simulated environment. In contrast, the presence of HPO_4^{2-} is minimal, constituting just 0.34% of the dataset, which implies that the second ionization reaction is limited. Furthermore, PO_4^{3-} is virtually absent, indicating that the third ionization reaction occurs at an extremely low frequency throughout the active learning simulation.

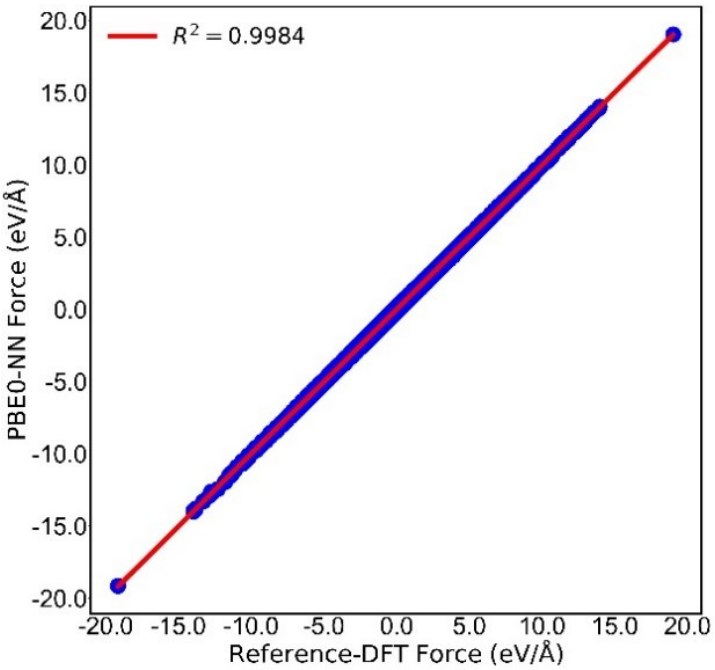

Figure S3. Linear regression plot comparing atomic forces predicted by PBE0-NN to reference data from the test set. Blue points represent the distribution of predicted versus reference values, while the red solid line indicates the linear regression fit of the data.

Table S2. Mean Absolute Error (MAE) values for total energy (meV/atom), atomic forces (meV/Å), and atomic charges (e), along with the coefficient of determination (R^2) for atomic forces.

Datasets	MAE			R^2 of Force
	Energy	Force	Charge	
Training	0.205	35.25	0.003	0.998
Validation	0.196	35.21	0.003	0.998
Test	0.238	35.13	0.003	0.998

The linear regression results comparing predicted and reference atomic forces for liquid phosphoric acid structures in the test set, as calculated using the PBE0-NN model, are shown in Figure S3. The coefficient of determination (R^2) for predicted atomic forces exceeds 0.998, indicating a high level of accuracy. Detailed mean absolute error (MAE) values for these predictions are provided in Table S2.

S3. Computational Resources

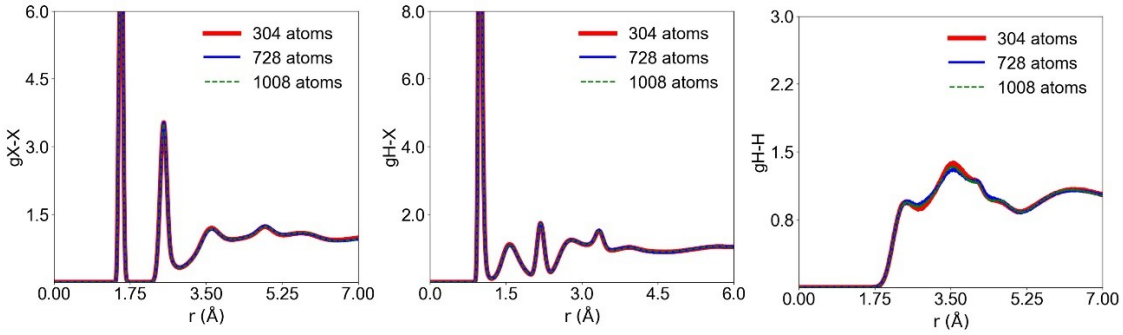

Figure S4. Comparison of radial distribution function (RDF) plots from PBE0-NN MD simulations of liquid phosphoric acid in cubic boxes of various sizes.

Table S4. Computational time (in seconds) for PBE0-NN-based MD and RPMD simulations on CPU and GPU, compared to DFT calculations.

Method[a]	304 atoms	728 atoms	1008 atoms
DFT MD	1345.9	3556.3	5756.3
NN MD[b]	0.54 / 0.09	1.28 / 0.14	1.70 / 0.17
NN RPMD[b]	6.86 / 1.02	18.88 / 1.77	24.69 / 2.29

[a]All CPU-based simulations and DFT calculations were performed on an AMD EPYC 7443P 24-Core Processor, while all GPU-based simulations were conducted using a Tesla V100-SXM2-16GB.

[b] The time values before and after the slash correspond to CPU and GPU, respectively.

MD and RPMD simulations were performed using the PBE0-NN model on three cubic simulation boxes of varying sizes at 333.15 K to evaluate the average computational time. The MD simulations were conducted for 100 ps, while the RPMD simulations were carried out for 500 steps. For the periodic structure with 304 atoms, the PBE0-NN model demonstrated a speedup of approximately 2,400 times compared to DFT calculations on the same hardware, and for the 1008-atom structure, the speedup was about 3,400 times. The simulation time per step for RPMD is slightly greater than the MD time multiplied by the number of beads (12).

To provide a reference for future work, we estimated the time required to construct the dataset and train the ML models. The dataset consists of 4,947 liquid phosphoric acid structures. On average, DFT calculations for individual structures take 0.51 hours of wall time on an Intel Xeon Gold 6126 CPU (2.60 GHz, 24 cores). Nine rounds of active learning were performed, and 40 PBE0-NN models were trained. Each model took approximately 14.4 hours to train on a Tesla V100-SXM2-16GB. The training time for the Qeq-NN model was very short, as it converged quickly during the active learning iterations.