Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Revealing the thermal decomposition mechanism of RDX crystal by a neural network potential

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In the supplementary material, we present:

- Fig. S1 the potential energy surface of N-N homolysis in bulk RDX crystal.
- Fig. S2 Equation of state curve for RDX unit cell and 2x2x2 supercell predicted by NNP and DFT methods.
- Fig. S3 Evolution of the major species (RDX, NO_2, NO and H_2O) during the initial decomposition process predicted by AIMD, NNP, and ReaxFF models.
- Table S1 Detailed values of potential energy surface of N-N homolysis in bulk RDX crystal.

To test the accuracy of NNP, the PES of N-N homolysis in bulk RDX crystal is calculated by the DFT and NNP methods. The PES is calculated by changing the bond length of N-NO2 from 0 to 1 while keep other atoms freeze, as shown in Fig. S1a. The DFT calculation is performed by CP2k at PBE/DZVP-MOLOPT level of theory. The PES results are shown in Fig. S1b, where the NNP shows a good agreement with the DFT method. Detailed values of potential energy surface are listed in Table S1.

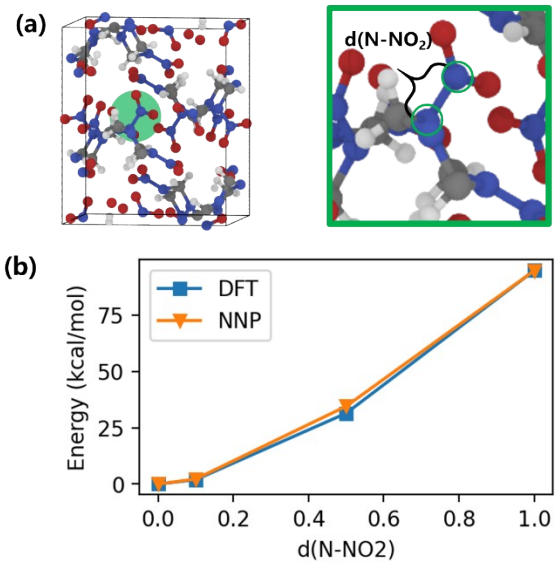

Fig. S1 (a) Illustration of N-N homolysis in bulk RDX crystal, (b) the potential energy surface of N-N homolysis in bulk RDX crystal predicted by DFT (PBE/DZVP-MOLOPT) and NNP.

Table S1 Detailed values of potential energy surface of N-N homolysis in bulk RDX crystal.

d(N-NO2)	E_{DFT} (kcal/mol) [1]	E_{NNP} (kcal/mol)
0	0.00	0.00
0.1	1.92	2.21
0.5	31.42	34.52
1	94.76	94.71

[1] The DFT calculation is performed by CP2k at PBE/DZVP-MOLOPT level of theory.

We have tested the size effects of the NNPs on the calculation of RDX equation of states (EOS). As shown in Fig. S2, the NNP predictions of EOS curve on RDX unit cell and 2x2x2 supercell are evaluated. The results shown that the NNP trained on the RDX unit cell datasets could describe the EOS of larger structures.

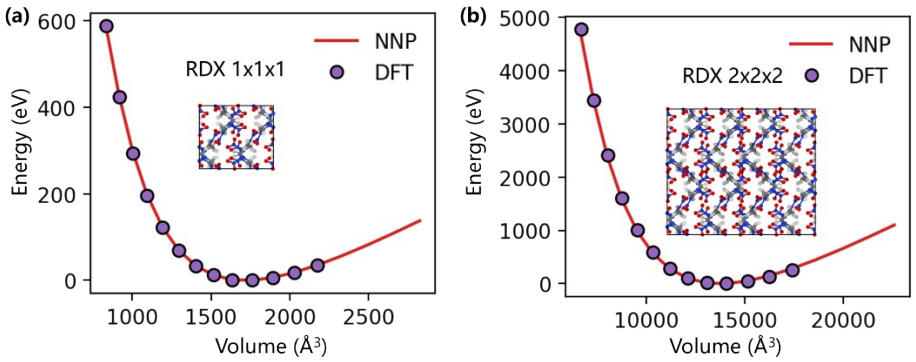

Fig. S2 Equation of state curve for (a) RDX unit cell and (b) 2x2x2 supercell predicted by NNP and DFT methods. The NNP is trained on the RDX unit cell datasets.

To validate the accuracy of the NNP model in species evolution, the evolution of NO_2, NO, and H_2O are also compared in Fig. S3. For RDX, NO_2, and NO molecules, the species evolution of our NNP model is almost the same as the AIMD by CP2K packages except for the prediction of H_2O. In contrast, the ReaxFF simulations exhibits significant deviations. For H_2O molecules, the NNP model captures the initial production of H_2O, but overestimating the molecule number after the first 1 ps.

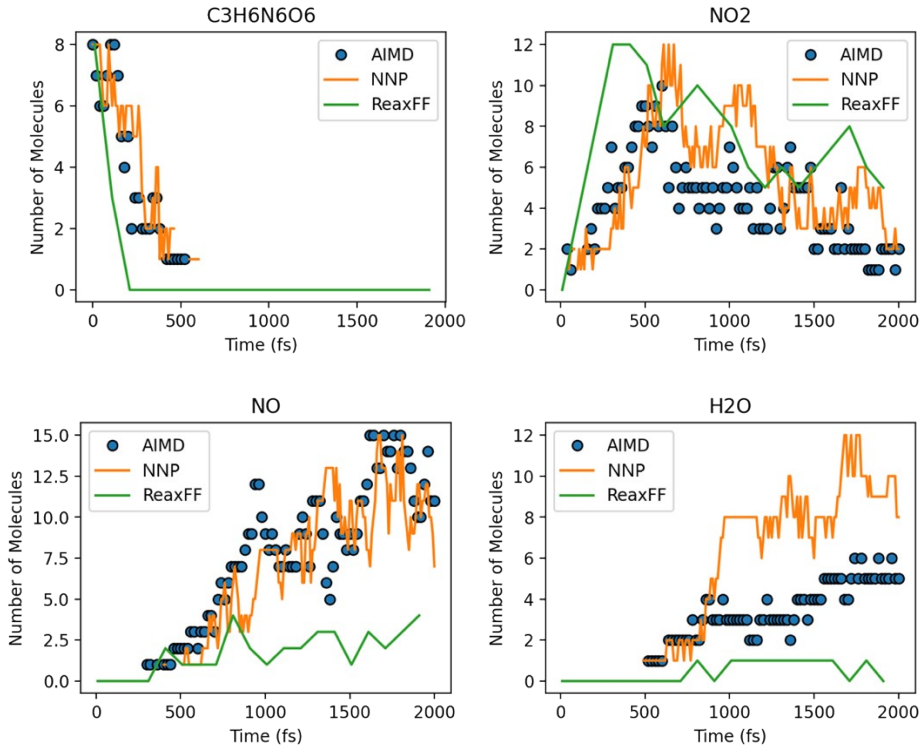

Fig. S3 Evolution of the major species (RDX, NO_2, NO and H_2O) during the initial decomposition process predicted by AIMD, NNP, and ReaxFF models.