Supplementary materials -for-

Thermal decomposition mechanism of RDX/AP composites: *ab initio* neural network MD simulations

Kehui Pang [a], Mingjie Wen [a], Xiaoya Chang [a], Yabei Xu [a], Qingzhao Chu [a,*], Dongping Chen [a, *]

[a] *State Key Laboratory of Explosion Science and Safety Protection, Beijing Institute of Technology, Beijing 100081, P. R. China*

In the supplementary materials, we present:

1. Figure S1 shows the evolution of the total energy when the NNP model is used to conduct simulation of RDX system with NVE ensemble. The initial kinetic energy is 6000 K, and the simulation timesteps are 0.1 fs, 0.2 fs, 0.3 fs, 0.4 fs and 0.5 fs, respectively.
2. Figure S2 shows the evolution of total energy and CO_2 during the MD simulation of RDX crystals predicted using the NNP model in the 3000 K and NVE ensemble. The simulation timestep is 0.6-1.0 fs.
3. Figure S3 shows the average deviation in the number of CO_2 molecules predicted by the NNP model at 0.2-1.0 fs timesteps using the number of CO_2 molecules predicted at 0.1 fs timestep as a baseline.
4. Figure S4 shows the evolution of molecular number of RDR, $C_3H_3N_3$, NO_2 and CO_2 during RDX decomposition. The solid line indicates the average molecular number from three parallel simulations. The shading highlights the range within the maximum and minimum values.

* Corresponding authors, E-mail: chuqz@bit.edu.cn (Q. Chu); dc516@bit.edu.cn (D. Chen).

1. Numerical stability of NNP model at high temperature

To further verify the numerical stability of the NNP model at high temperatures, NVE-MD simulation of RDX is carried out using an initial kinetic energy as 6000 K, which is almost doubled compared to the case in Figure 4. The simulation timesteps are 0.1 fs, 0.2 fs, 0.3 fs, 0.4 fs and 0.5 fs, respectively. Figure S1 illustrates the evolution of the total energy and the CO_2 molecules number. Similarly, the total energy of all five timesteps are well conserved as we see in the case of lower kinetic energy (Figure 4). As the timestep increases from 0.1 fs to 0.5 fs, the fluctuation of predicted total energy amplifies. Overall, the NNP model exhibits a good numerical stability even considering a high temperature (i.e. high kinetic energy).

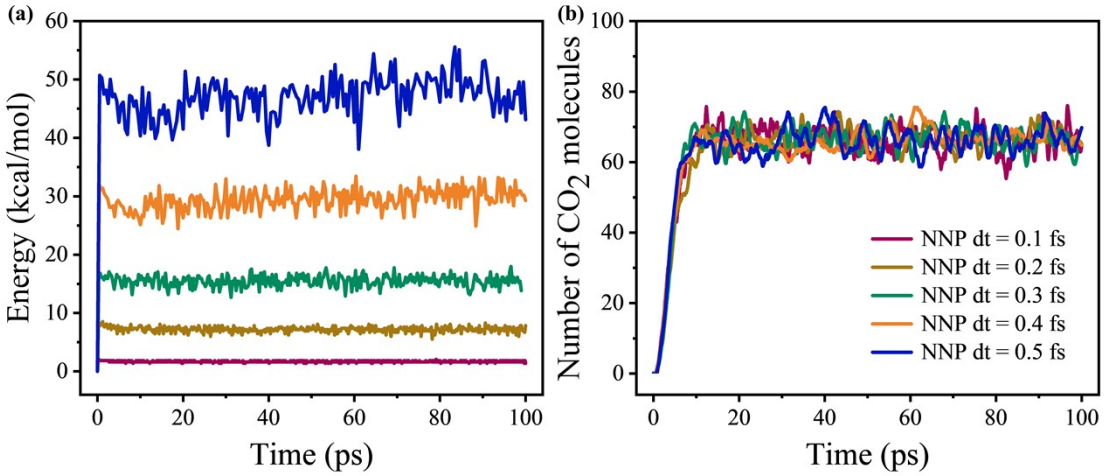

Figure S1 Total energy (a) and CO_2 molecules number (b) of the NNP model with five time steps.

2. Maximum simulation timestep allowed by the NNP model

To verify the maximum timestep allowed by NNP model, MD simulations of RDX decomposition with timesteps of 0.6-1.0 fs are carried out in the NVE ensemble. The initial kinetic energy corresponds to a temperature of 3000 K. Figure S2 shows the total energy of RDX crystals and the evolution of CO_2 predicted using the NNP model. In Figure S2a, the total energy shows reasonable stability if setting timestep as 0.6 fs. Further increasing the timestep, the NNP model exhibits significant energy drift. However, we do not identify significant deviation for large timestep in the evolution of CO_2.

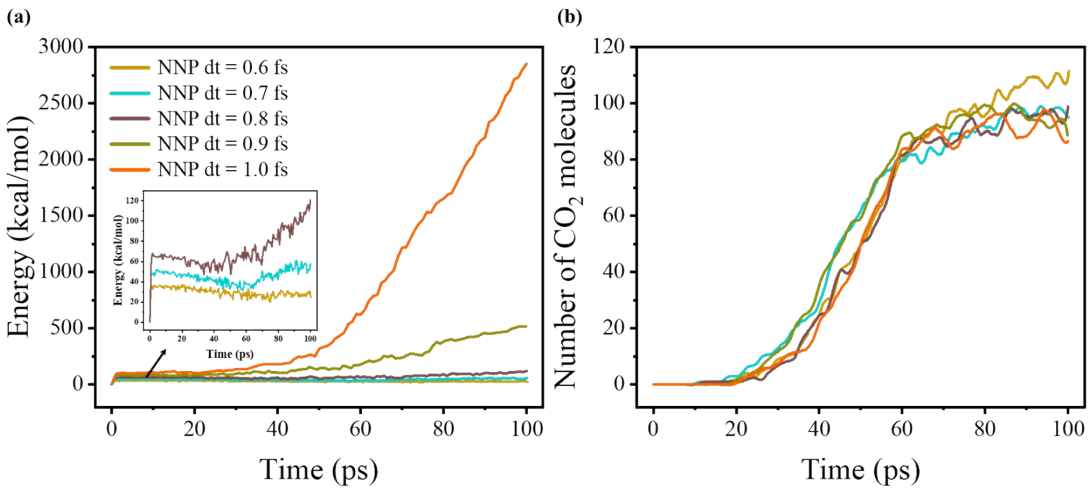

Figure S2 (a) Total energy of the NNP models. The inset shows the total energy of the NNP model with a timestep of 0.6-0.8 fs. (b) Number of CO_2 identified from the simulation of NNP models. The simulation timesteps for the NNP models are 0.6-1.0 fs.

To highlight the instability of species prediction, we compute the average deviation of different timestep with respect to the smallest one as 0.1 fs (Figure S3). The average deviation is defined as follows,

$$Average\ deviation = \frac{\sum |M_i - M_{0.1}|}{n},$$

where M_i is the number of CO_2 when the timestep corresponds to i fs, and n is the number of temporal snapshots in each case. i follows in the range of 0.2 to 1.0 fs. In Figure S3, the average deviation of cases using small timesteps (e.g. 0.2-0.4 fs) is almost kept the same as three CO_2 molecules, which is considered as acceptable. Further increasing the setting of timestep to 0.5 fs, the average deviation is doubled, and this is an indication that the predicted results have larger uncertainties. For even larger timestep (e.g. 0.6-1.0 fs), the uncertainties do not increase as expected. Combined with the findings in Figure S2a, we can conclude that the maximum timestep allowed by the NNP model is 0.4 fs in this work. However, we use 0.2 fs as the default timestep avoiding unexpected impacts on the reaction dynamics.

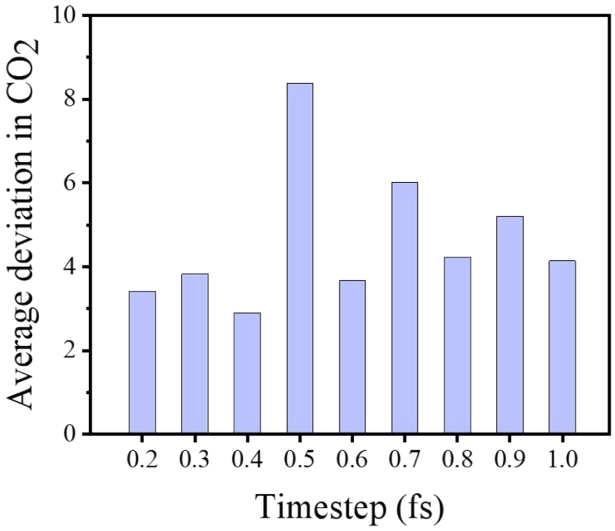

Figure S3 Average deviation in the predicted number of CO_2 molecules.

3. Molecular number of RDR and intermediate products during RDX decomposition.

Three parallel simulations of RDX/AP composites are carried out. In the process of temperature simulation, the evolution of the molecular number of RDR, $C_3H_3N_3$, NO_2 and CO_2 during RDX decomposition is shown in Figure S4. As the initial products of RDX decomposition, RDR and NO_2 appear 7 ps earlier in the composites than that in the pure system. At the same time, $C_3H_3N_3$ and CO_2 appeared 5 ps and 12 ps earlier in the composite material, respectively.

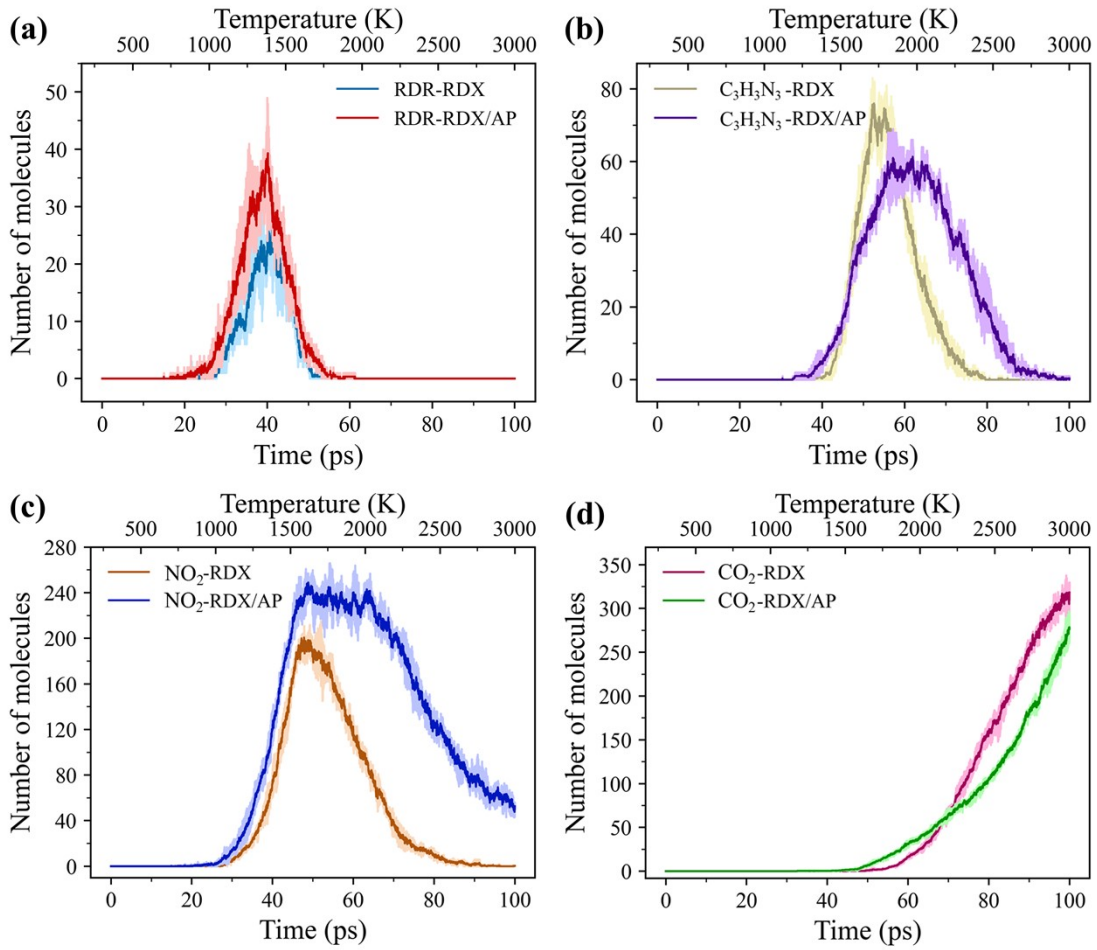

Figure S4 Number of RDR, $C_3H_3N_3$, NO_2 and CO_2 during RDX decomposition. The solid line indicates the average molecular number from three parallel simulations. The shading highlights the range within the maximum and minimum values.