Cluster Evolution during the Early Stages of Heating Explosives and its Relationship to Sensitivity: A Comparative Study of TATB, β-HMX and PETN by Molecular Reactive Force Field Simulations

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Electronic Supplementary Information

Table of Contents

S1. The detailed information of the supercells

Table s1. The detailed information of the supercells

supercells	TATB			HMX			PETN		
enlargement times from unit cells	6×6×6			8×5×5			4×3×7		
Lattice Parameters	a	b	c	a	b	c	a	b	c
	54.06 Å	54.17 Å	40.87 Å	52.32 Å	55.25 Å	43.50 Å	53.16 Å	40.47 Å	47.81 Å
	α	β	γ	α	β	γ	α	β	γ
	108.58°	119.97 °	91.82°	90.00°	90.00°	90.00°	90.00°	90.00°	90.00°
Amounts of molecules	432			400			336		
Amounts of atoms	10368			11200			9744		

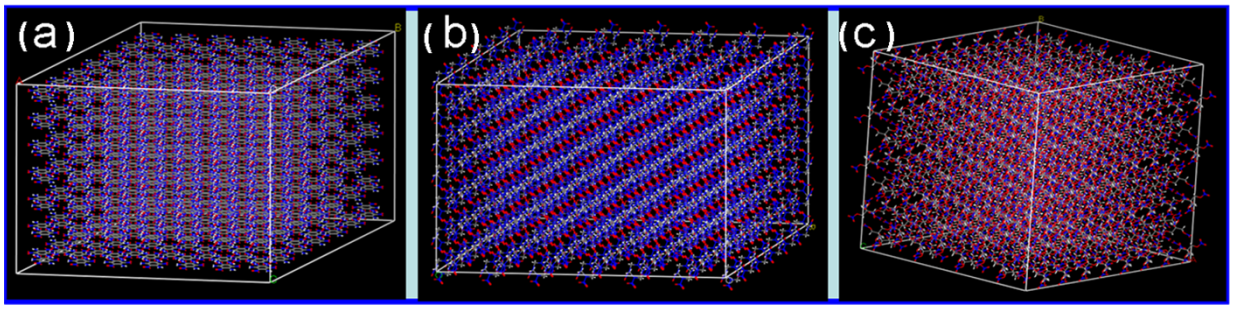

Fig. s1. Supercells of TATB, β-HMX and PETN. The carbon, hydrogen, oxygen and nitrogen atoms are indicated in grey, white, red and blue, respectively.

S2. Validation of ReaxFF_lg to this work

The validity of ReaxFF_lg to the three representatives has also been reexamined in this work from two aspects: **(1) cell geometries and packing densities.** 10ps NPT simulations at 273K and atmospheric pressure using ReaxFF_lg were implemented to obtain the initial configurations of TATB, HMX and PETN; and **(2) reaction product kinds.** Upon the initial configurations of three representatives, a 50 ps NVT (3000K) heating simulation was conducted for each. As results, the NPT simulations showed that the lattice parameters of TATB, HMX and PETN reduce about -1.6%, -1.2 %, and -1.1% on average, namely, there are only a 4.76%, 3.5 %, and 3.2% density errors compared with the experimental values, respectively (Table s2). Table s3 also, indicating that ReaxFF_lg can appropriately describe the physical processes of TATB, HMX and PETN. The initial chemical species of our thermal simulations also confirmed that ReaxFF_lg can appropriately describe the chemical behaviors of TATB, HMX and PETN under high temperatures ().

Table s2. The results of NPT simulations (T=273K and P=1atom)

explosives	Lattice parameters of supercells	Expt.	ReaxFF_lg	a,b and c error	density error
TATB	a	54.06	53.19	-1.61%	4.76%
	b	54.17	53.31	-1.59%	
	c	40.87	40.22	-1.60%	
HMX	a	52.32	51.69	-1.2%	3.5%
	b	55.25	54.59	-1.2%	
	c	43.50	42.98	-1.2%	
PETN	a	53.16	52.58	-1.1%	3.2%
	b	40.47	39.98436	-1.2%	
	c	47.81	47.28409	-1.1%	

Table s3.The initial chemical species of our thermal simulations

	TATB		HMX		PETN	
chemical species	[a] DFT Calculation	ReaxFF_lg Calculation	[b] Expt.	ReaxFF_lg	[c] Expt.	ReaxFF_lg
CO_2	√	√	√	√	√	√
CO		exists	√	√	√	√
C(s)	exists	exists	√	exists		
H_2O	√	√	√	√	√	√
N_2	√	√	√	√	√	√
H_2	exists	√	√	√	√	√
CH_4		exists	√	exists	exists	exists
HCN			exists	exists		
Other (very tiny)	NCO, NCO_2, CN_2	NO,NO_2,HONO, HON,NH_3,OH,H	Not detected	NO,NO_2,HONO, HON,NH_3,OH,H, CON,CH_2O	NH3	NO,NO_2,HONO, HON,NH_3,OH, C_2O_3,CH_2O

√-main products

[a] Calculated by Manaa et al.[1]

[b] Observed by Donald L. Ornellas.[2]

[c] Observed by Donald L. Ornellas.[3]

S3. List of bond order minimum values used to determine molecules

Table s4. List of bond order minimum values used to determine molecules.

Atom type	Atom type	Bond order
C	N	0.3
C	C	0.55
C	O	0.65
C	H	0.4
O	O	0.65
N	O	0.4
O	H	0.4
H	H	0.55
H	N	0.55
N	N	0.55

S4. The products in different temperatures of TATB, HMX and PETN

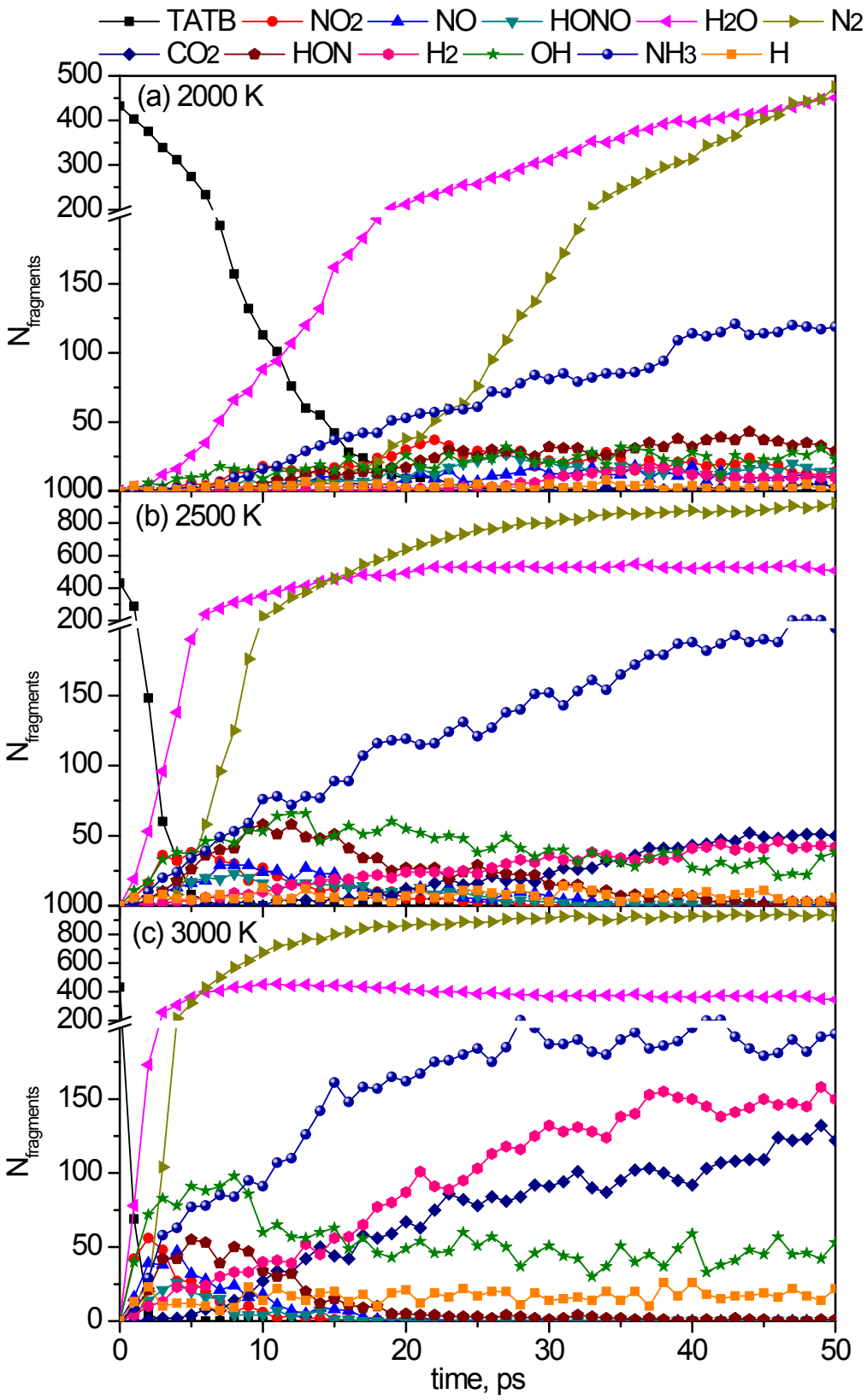

Fig. s2. The products in different temperatures of TATB

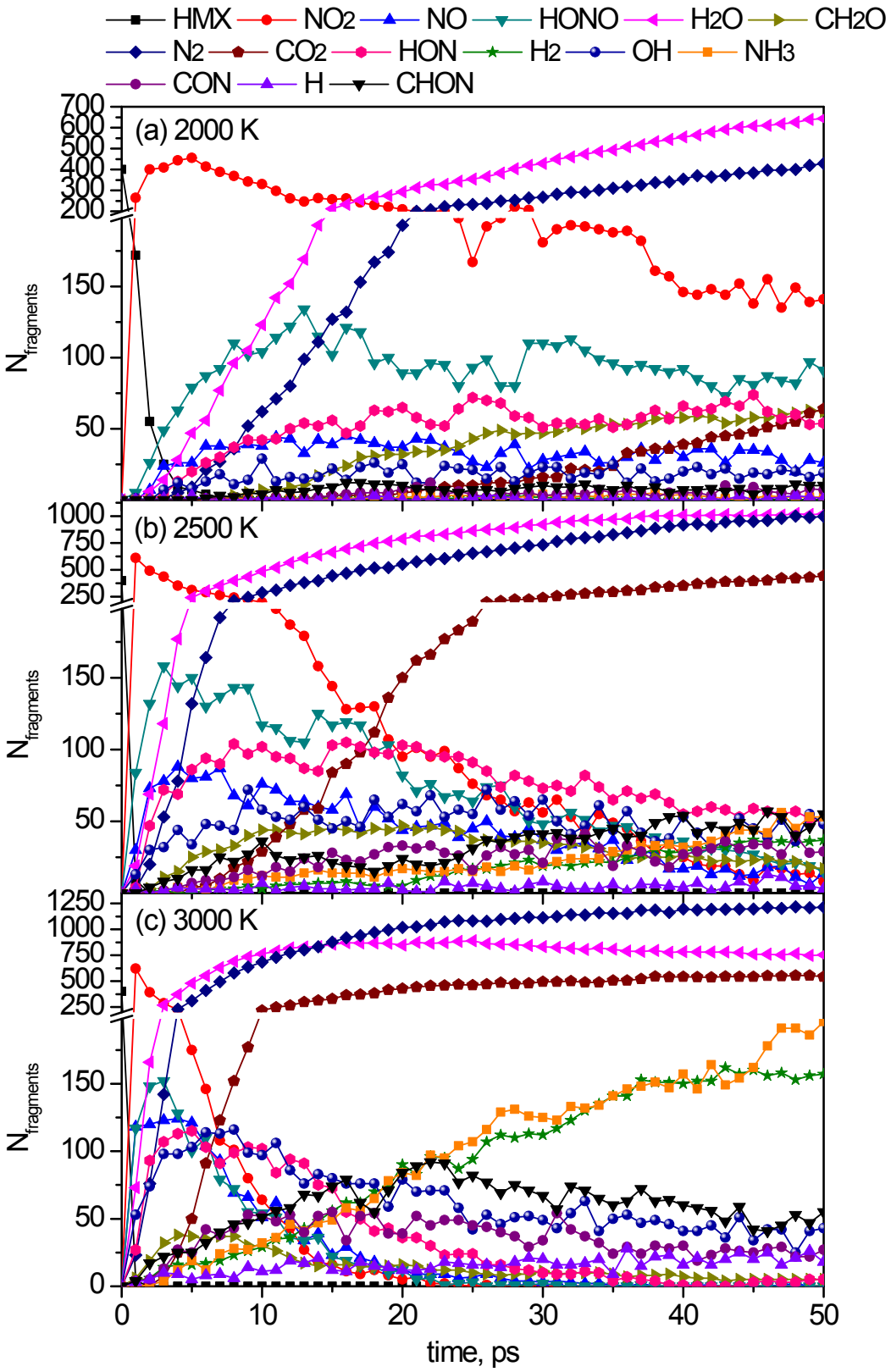

Fig. s3. The products in different temperatures of HMX.

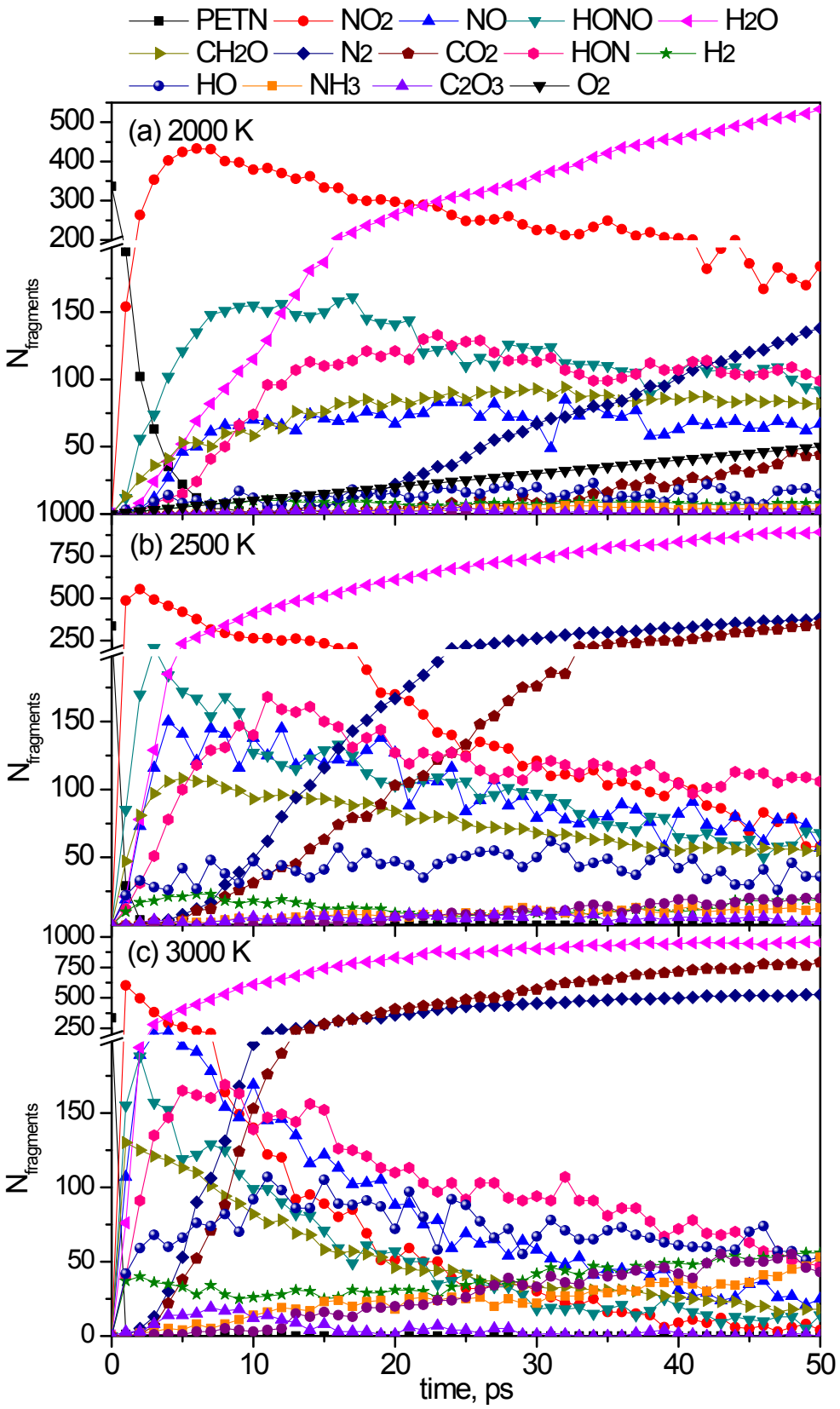

Fig. s4. The products in different temperatures of PETN

S5. The evolutions of atom-atom pair correlation functions of TATB, HMX, and PETN heated at 2500 K

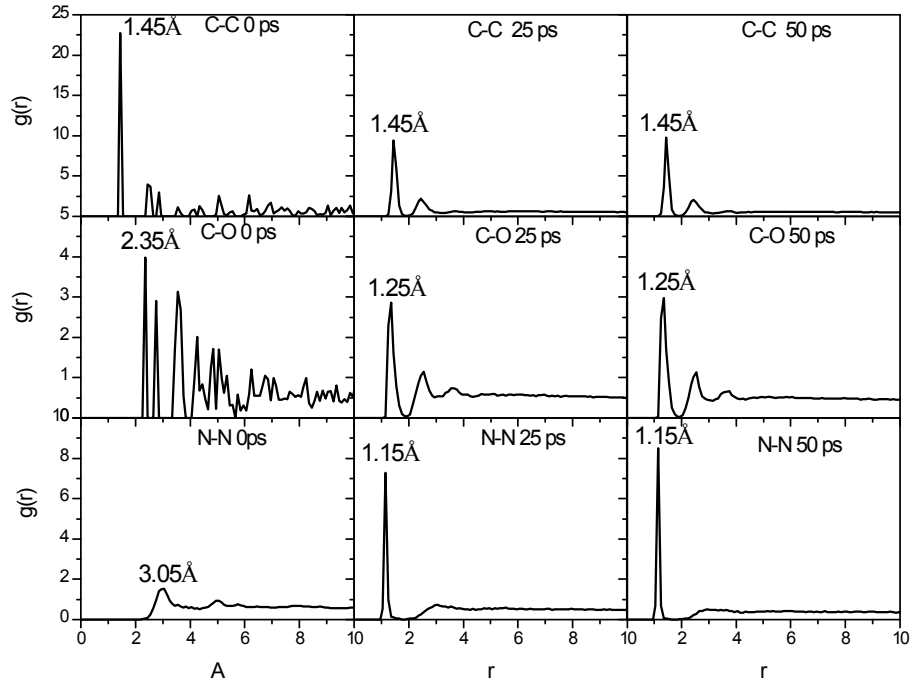

Fig. s5. Evolution of atom-atom pair correlation functions of TATB heated at 2500 K.

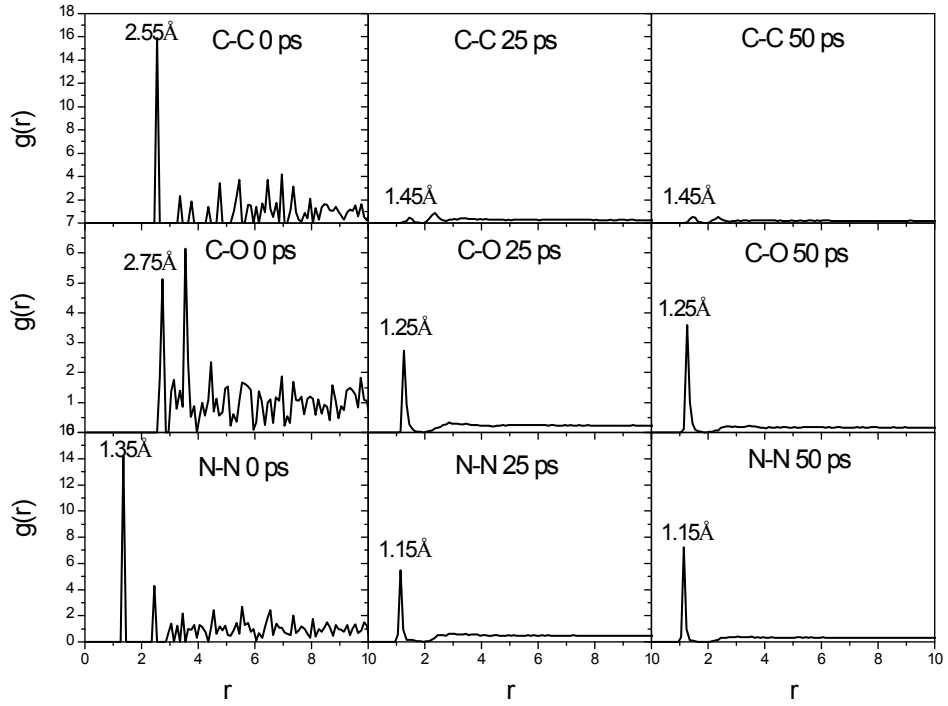

Fig. s6. Evolution of atom-atom pair correlation functions of HMX heated at 2500 K.

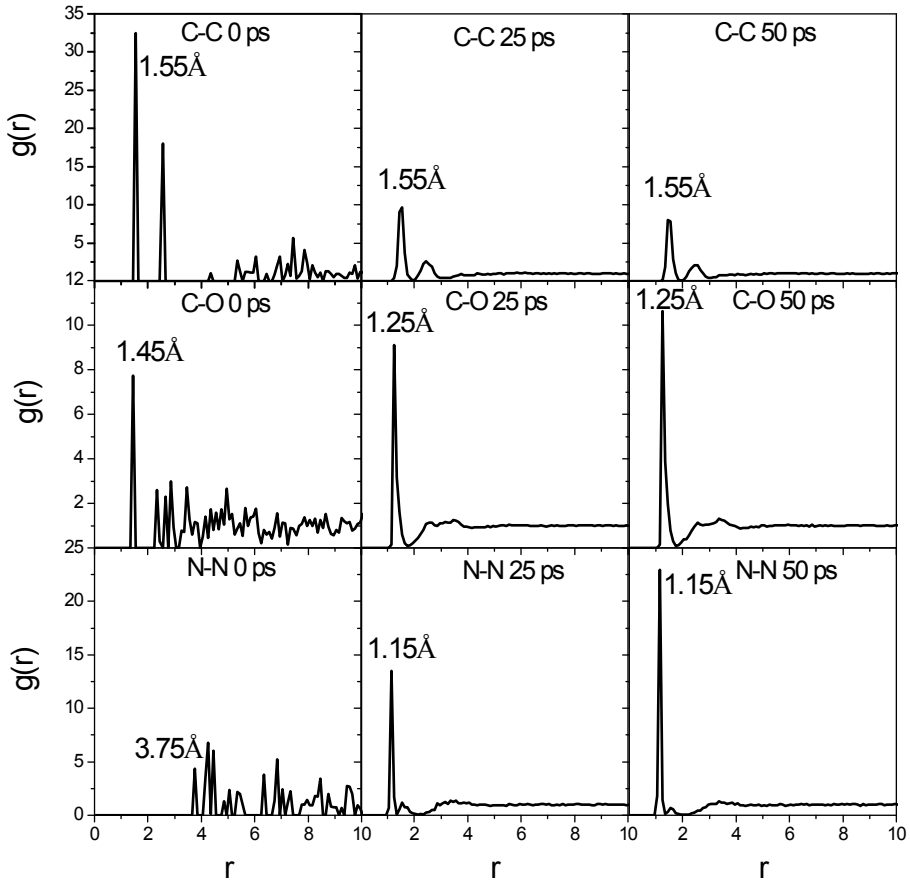

Fig. s7. Evolution of atom-atom pair correlation functions of PETN heated at 2500 K.

We used atom-atom pair correlation functions or radius distribution functions (RDFs, g(r)) shown by Figs. s5-s7 to describe the evolution of heated TATB, HMX and PETN at 2500 K.

For TATB (Fig. s5), the largest g(r) of C-C is always located at r=1.45 Å with different intensity, suggesting the benzene structures retain during the heating. The largest g(r) of C-O is transferred from 2.35 to 1.25 Å, denoting the CO and CO_2 formation. Similarly, g(r) of N-N of 1.15 Å suggests the formation of N_2. Also, g(r) can used to analyze the reactions in heated HMX and PETN.

S6. References

(1) M. R. Manaa, E. J. Reed, L. E. Fried, and N. Goldman, *J. Am. Chem. Soc.* **2009,** 131, 5483.

(2) Donald L. Ornellas, *The Journal of Physical Chemistry* **1968,** 72, 2390.

(3) Donald L. Ornellas, John H. Carpenter and Stuart R. Gunn, *The Review of Scientific Insturments* **1966,** **3**7, 907.