Supplementary Information

Phase transition of titanium dioxide based on quantum dynamics

Zhang Bing[1,2,3], Chen Shengbin[3], Yang Yang[3], Luo Rui[3], Xia Yuangu[3], Wang Xiaogang[3], Lu Qiang[1,2,3] and Hu Bin [*1,2,3]

1 National Engineering Research Center of New Energy Power Generation, North China Electric Power University, Beijing 102206, People's Republic of China

2 State Key Laboratory of Alternate Electrical Power System With Renewable Energy Sources, North China Electric Power University, Beijing 102206, People's Republic of China

3 School of New Energy, North China Electric Power University, Beijing 102206, People's Republic of China

*Email: binhu@ncepu.edu.cn

1. Results of the high-temperature quenching experiments

The root mean square deviation (RMSD) curves of atomic motions in different temperature quenching experiments are shown in Fig. S1. For the 2000 K quenching experiment, the quenching time of molten TiO_2 exceeds 300 ps. The rising trend of the curve indicates that the Ti and O atoms still move violently in space, and the system structure is difficult to stabilize.

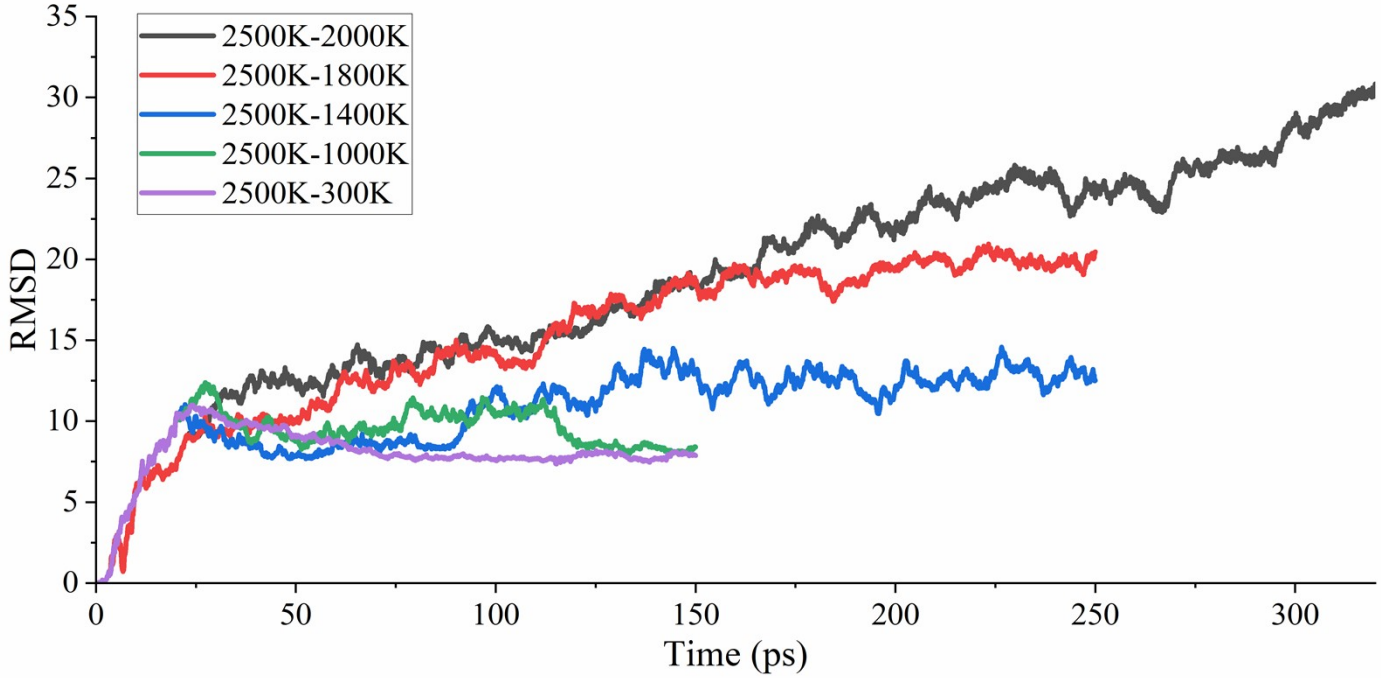


Fig. S1 The RMSD curve of atomic motions in the 2000 K quenching experiment.

In the four groups of quenching experiments at 1800 K, 1400 K, 1000 K and 300 K, the structure of TiO_2 finally stabilizes. The structural parameters and diagrams of stable states at different quenching temperatures are shown in Table S1 and Fig. S2 respectively.

Table S1 Stable state structure parameters of the quenching experiments.

Quenching temperature (K)	Ti coordination number	$[TiO_4]$	$[TiO_5]$	$[TiO_6]$	$[TiO_7]$	Vertex/edge-sharing ratio
1800	6	0	0	100 %	0	4
1400	5.81	6.25 %	6.25 %	87.5 %	0	2.68
1000	5.81	0	25 %	68.75 %	6.25 %	2.09
300	5.69	0	31.25 %	68.75 %	0	3

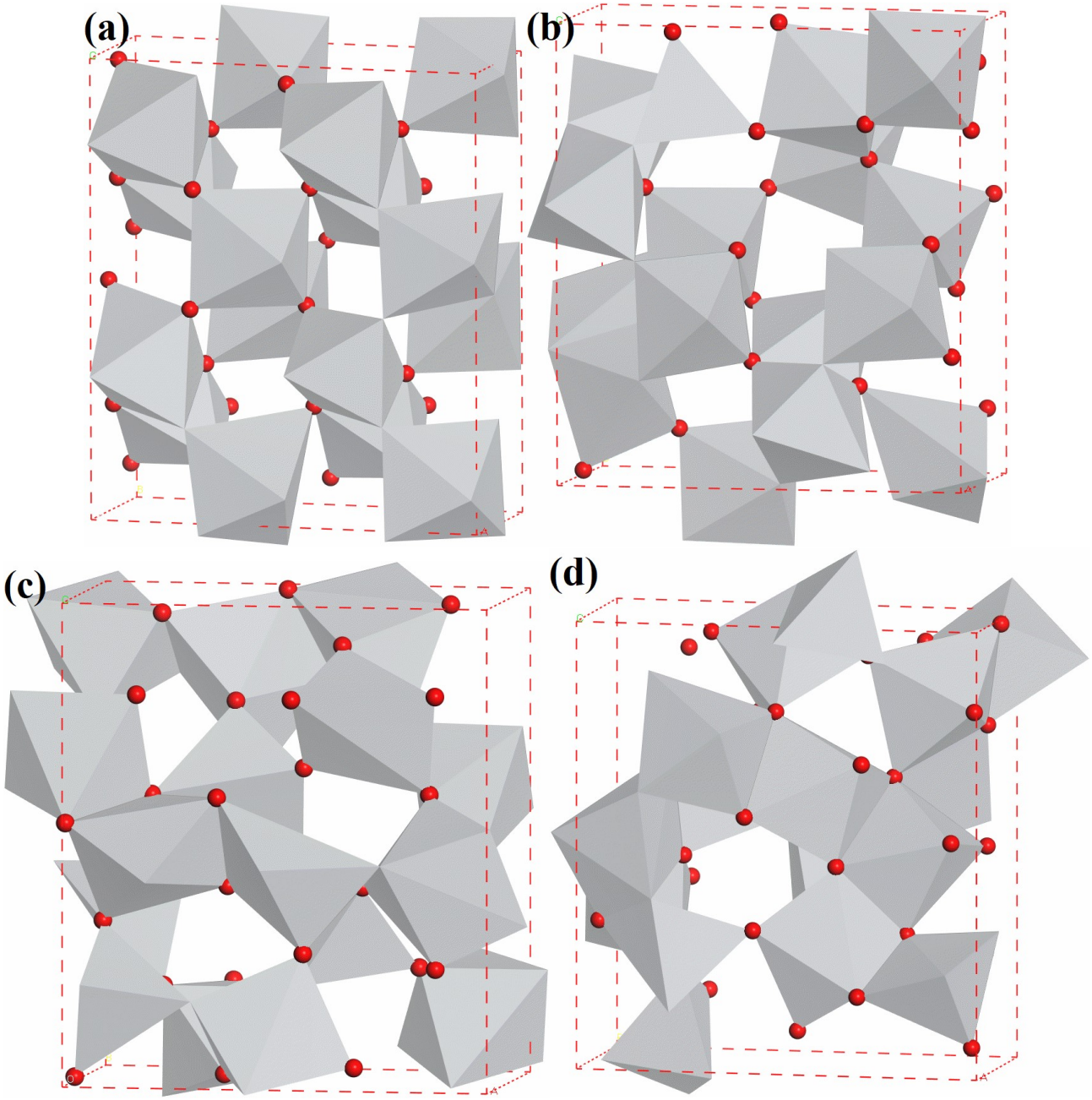


Fig. S2 Structural diagrams of stable states in the (a) 1800 K, (b) 1400 K, (c) 1000 K and (d) 300 K quenching experiments.

After quenching at 1800 K, the stable structure of TiO_2 is shown in Fig. S2(a). The Ti atoms in the crystal

structure only have [TiO_6] octahedron as coordination environment, and the vertex/edge-sharing ratio of [TiO_6] octahedra is 4. Moreover, the [TiO_6] octahedral chains with common edge connection are zig-zag chains instead of straight chains and both chains are connected in a manner consistent with vertex-sharing. Therefore, it can be preliminarily judged that the crystal structure of molten TiO_2 transforms from amorphous to columbite at 1800 K.

After quenching at 1400 K, the stable structure of TiO_2 is shown in Fig. S2(b). The average coordination number of Ti atoms is 5.81, and the proportions of Ti atoms with coordination environment of [TiO_4], [TiO_5] and [TiO_6] are 6.25%, 6.25% and 87.5% respectively. The vertex/edge-sharing ratio of [TiO_x] polyhedrons is 2.68, and the material structure remains in the amorphous phase at last.

After quenching at 1000 K, the stable structure of TiO_2 is shown in Fig. S2(c). The average coordination number of Ti atoms in the stable structure is also 5.81, and the proportions of Ti atoms with coordination environment of [TiO_5], [TiO_6] and [TiO_7] are 25%, 68.75% and 6.25% respectively. The vertex/edge-sharing ratio of [TiO_x] polyhedrons is 2.09, and the final structure of TiO_2 material is also amorphous.

After quenching at 300 K, the stable structure of TiO_2 is shown in Fig. S2(d). The average coordination number of Ti atoms in the stable structure is 5.69, and Ti atoms have only two polyhedral units of [TiO_5] and [TiO_6]. The vertex/edge-sharing ratio of [TiO_x] polyhedrons is 3, which is different from the known crystalline phase. Therefore, it can be judged that after quenching at 300 K, the TiO_2 material is still amorphous at last.

2. XRD analysis of phase transition process

The XRD spectrum of the starting structure is compared with that of the brookite phase from the Inorganic Crystal Structure Database (ICSD). The high similarities between the calculations and the ICSD data verify the reliability of the XRD simulations. The XRD results are shown in Fig. S3.

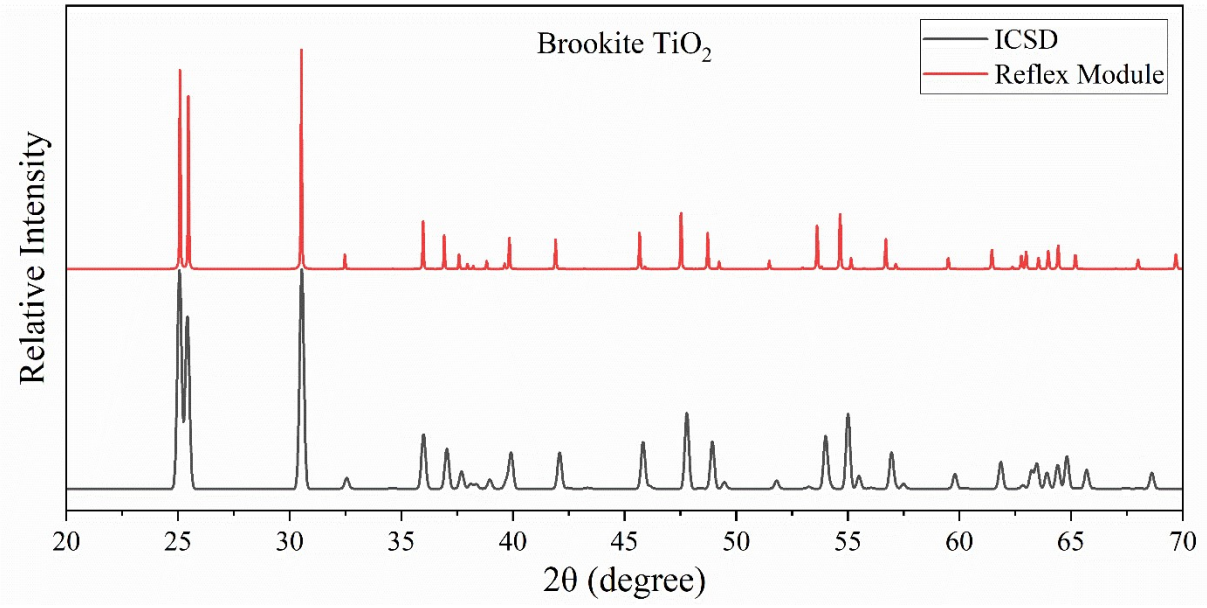
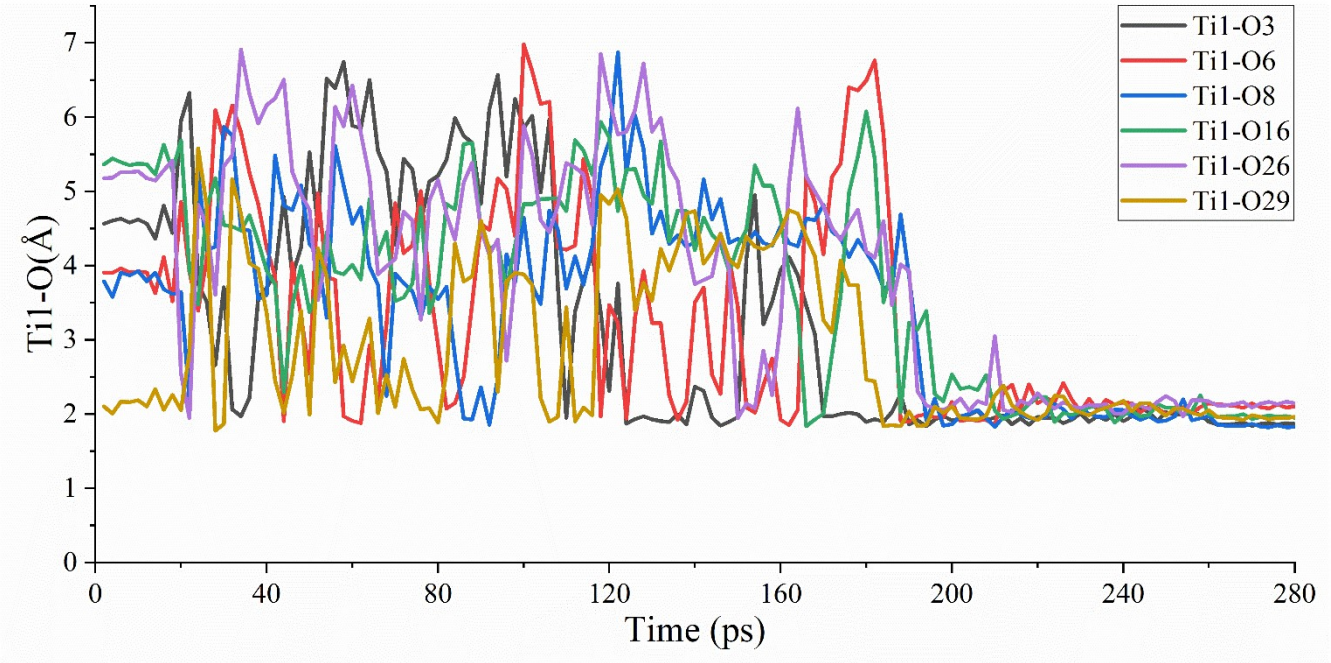
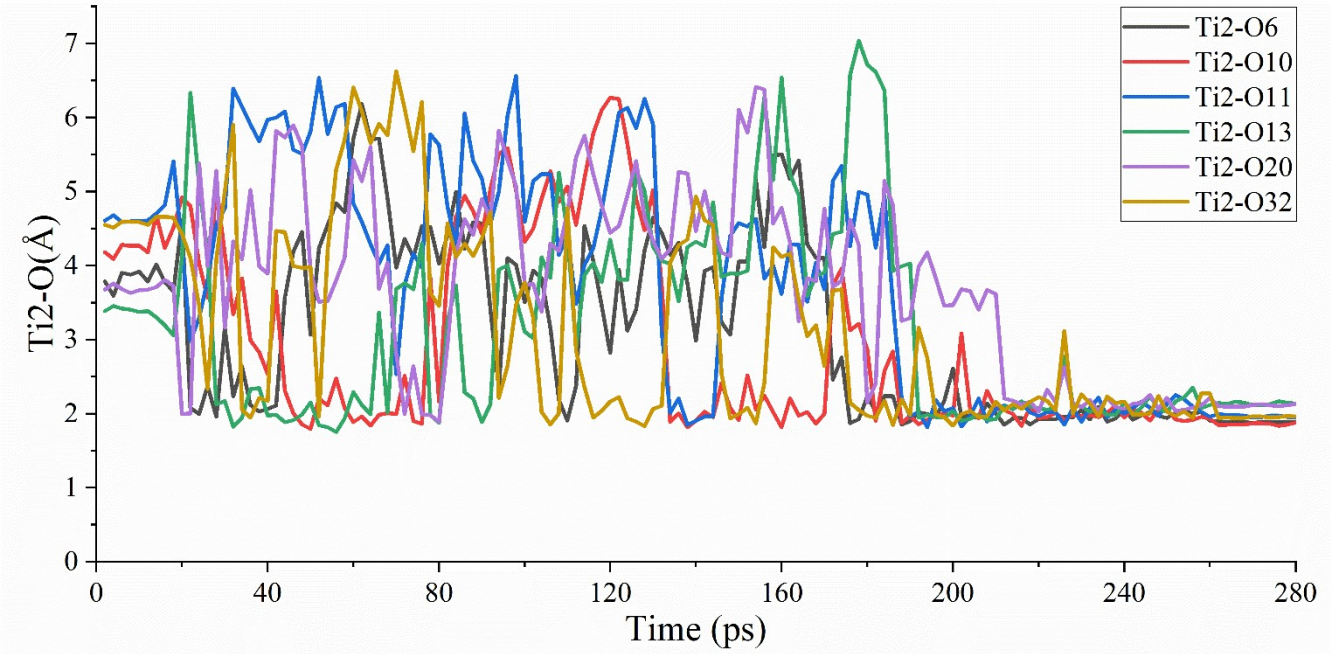


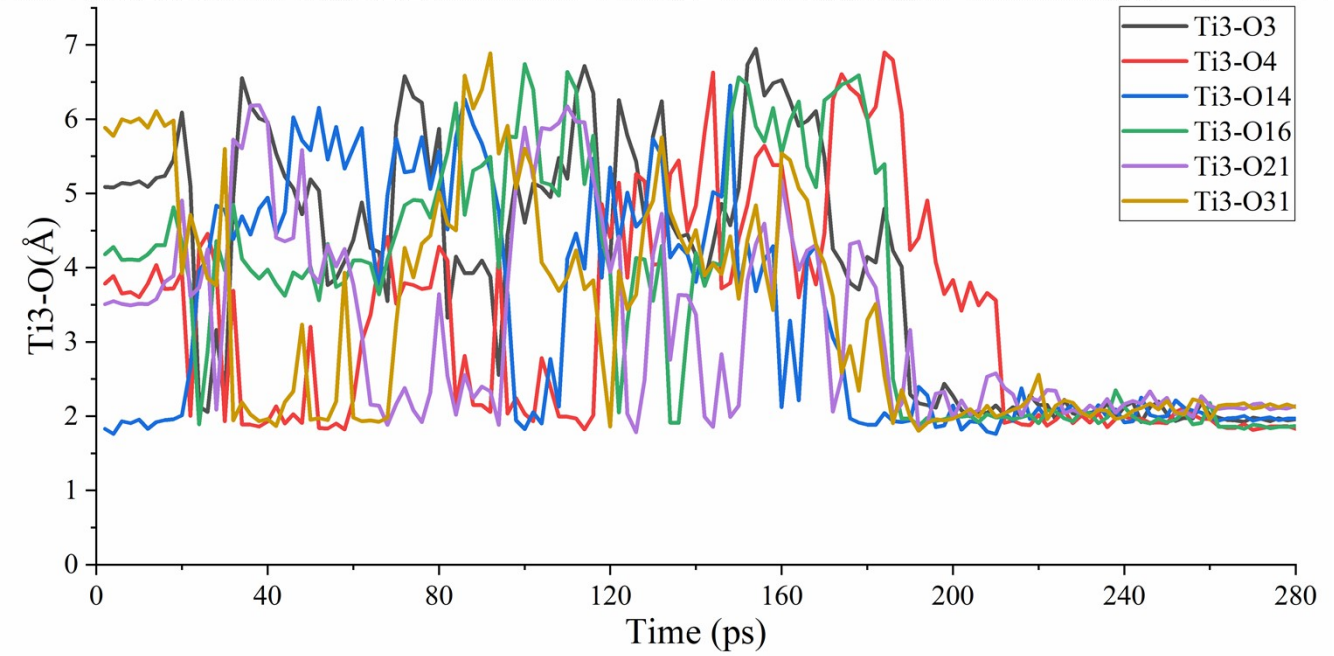
Fig. S3 XRD spectra of brookite TiO_2 simulated by Reflex module and from ICSD.

3. Ti-O bond length in phase transition process

The Ti-O distance curves in the [TiO_6] octahedron where each Ti atom in the columbite phase is located are shown in Fig. S4. The changes of Ti-O bond lengths indicate that when the temperature rises sharply from 300 K to 2500 K, the Ti and O atoms in the system move violently, the disorder of crystal structure increases sharply, and the structure changes directly from brookite to molten amorphous phase. This active state continues for a period of time after quenching, until about 160 ps after quenching, the movement of Ti and O atoms gradually slows down, and the system gradually forms new [TiO_6] octahedral units and stabilizes. The formation time of new [TiO_6] octahedra is different, and the formation process lasts from 190 to 211 ps, which corresponds to the dynamic process of the system energy and volume decrease. In addition, it can be found that the O atoms of [TiO_6] octahedra in the columbite phase are not all the original O atoms around the Ti atom. Most of them come from other different TiO_2 molecules. This phenomenon is consistent with the characteristics of the reconstructive phase transition.




Ti2-O6
Ti2-O10
Ti2-O11
Ti2-O13
Ti2-O20
Ti2-O32
Ti2-O(Å)
Time (ps)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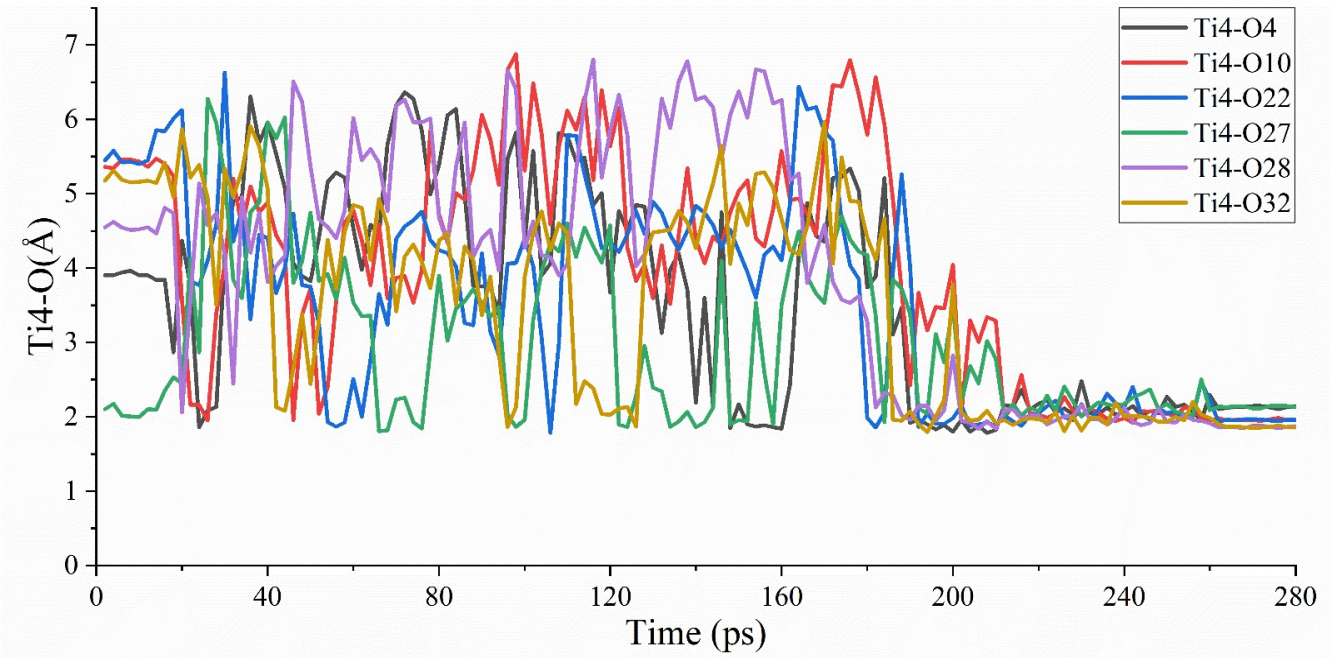
Ti3-O4
Ti3-O14
Ti3-O16
Ti3-O21
Ti3-O31
Ti3-O(Å)
Time (ps)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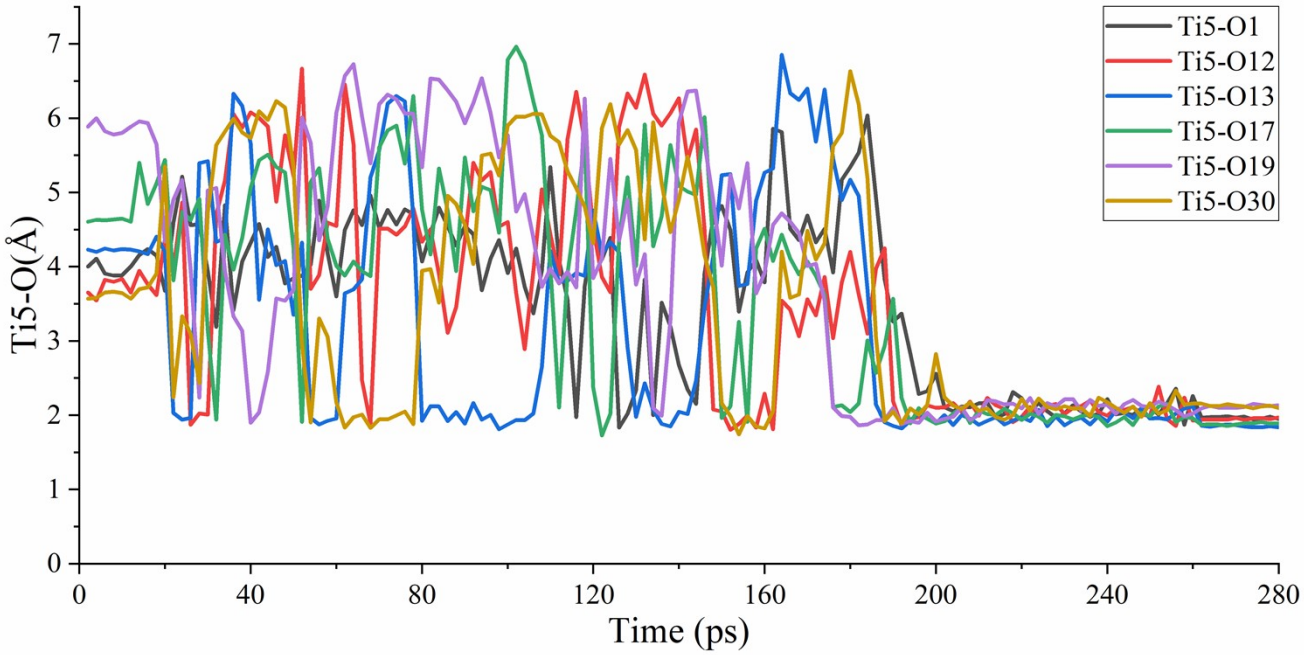
Ti4-O10
Ti4-O22
Ti4-O27
Ti4-O28
Ti4-O32
Ti4-O(Å)
Time (ps)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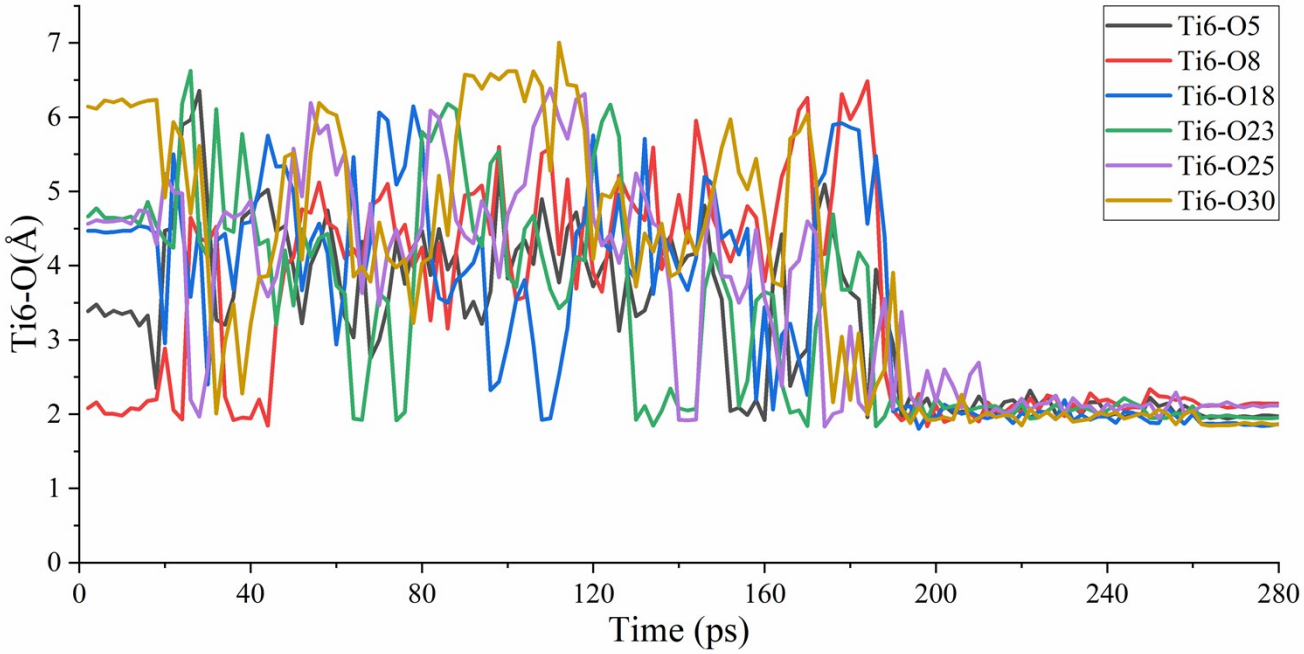
Ti5-O12
Ti5-O13
Ti5-O17
Ti5-O19
Ti5-O30
Ti5-O(Å)
Time (ps)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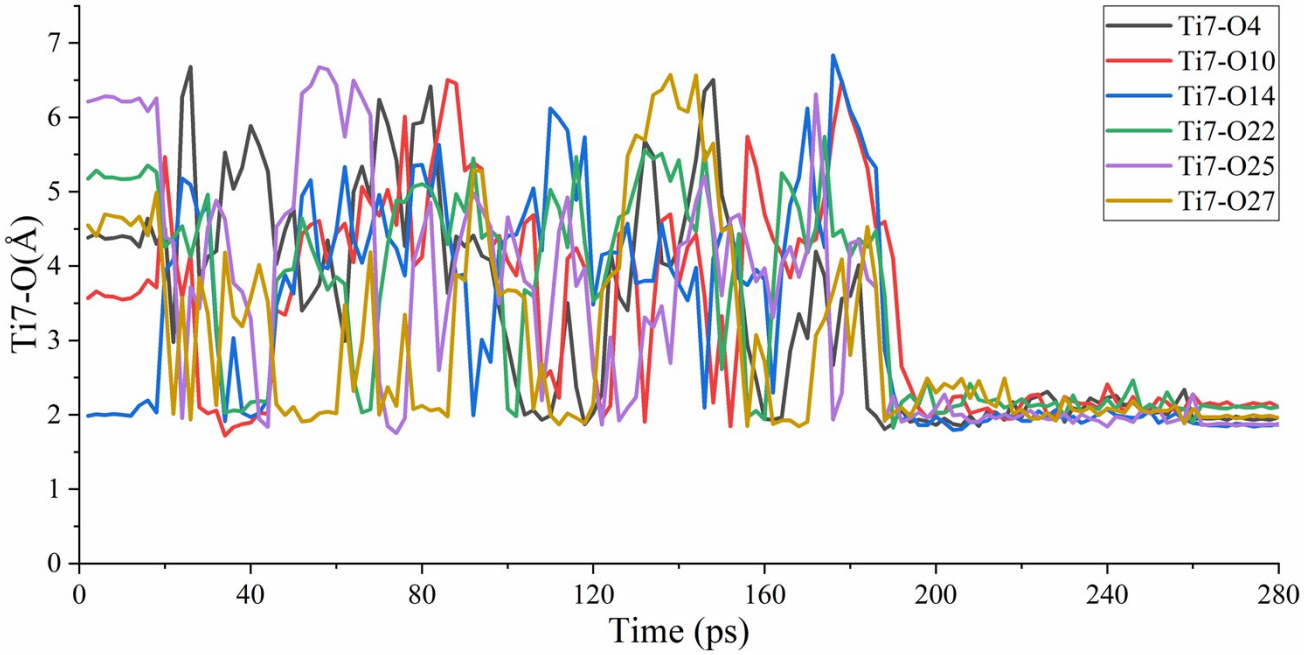
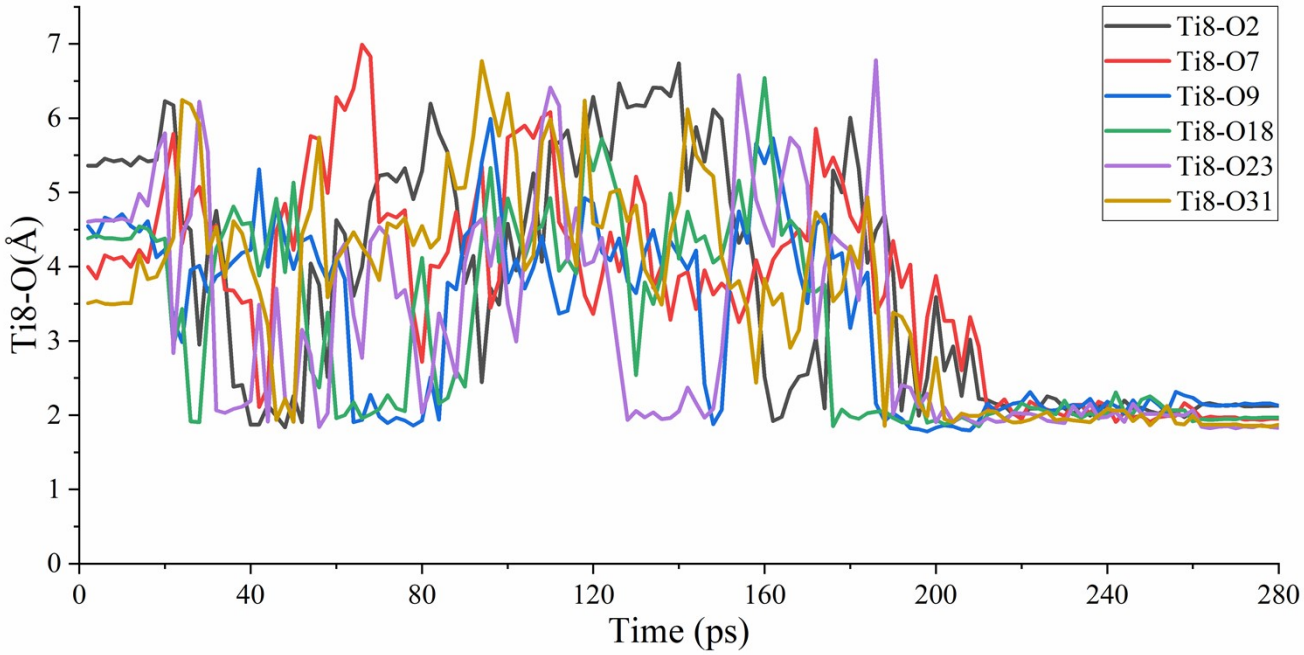
Ti6-O8
Ti6-O18
Ti6-O23
Ti6-O25
Ti6-O30
Ti6-O(Å)
Time (ps)


Ti7-O4
Ti7-O10
Ti7-O14
Ti7-O22
Ti7-O25
Ti7-O27
Ti7-O(Å)
Time (ps)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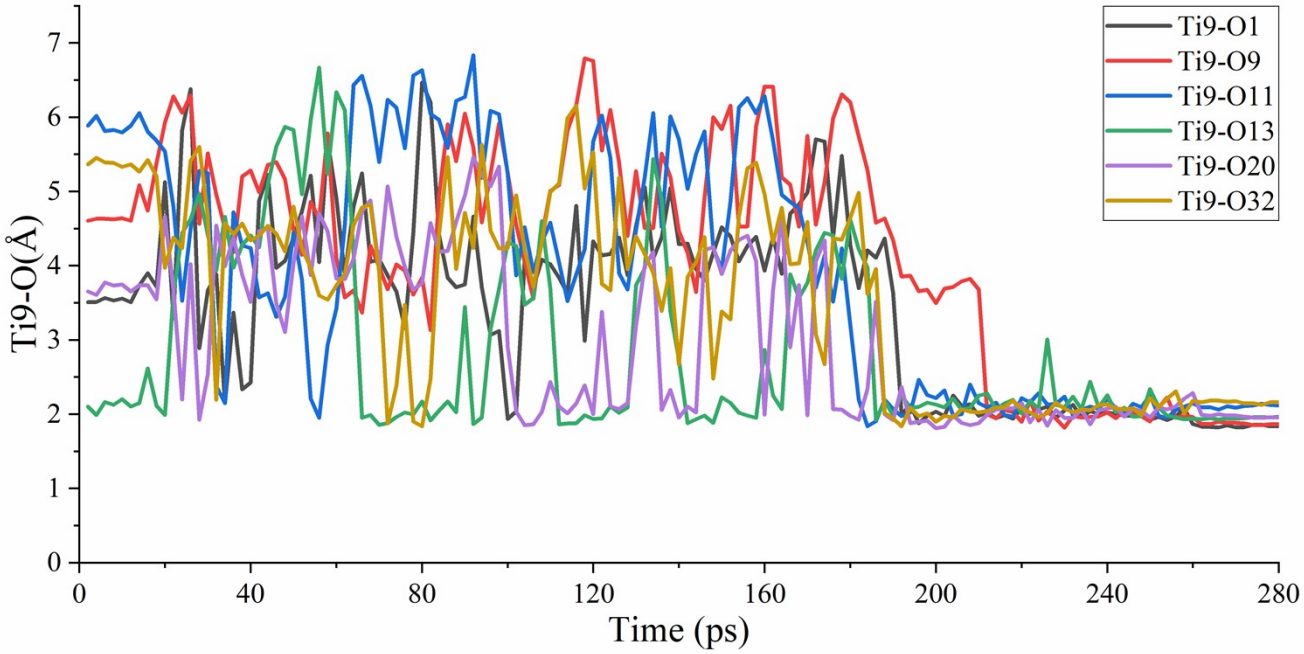
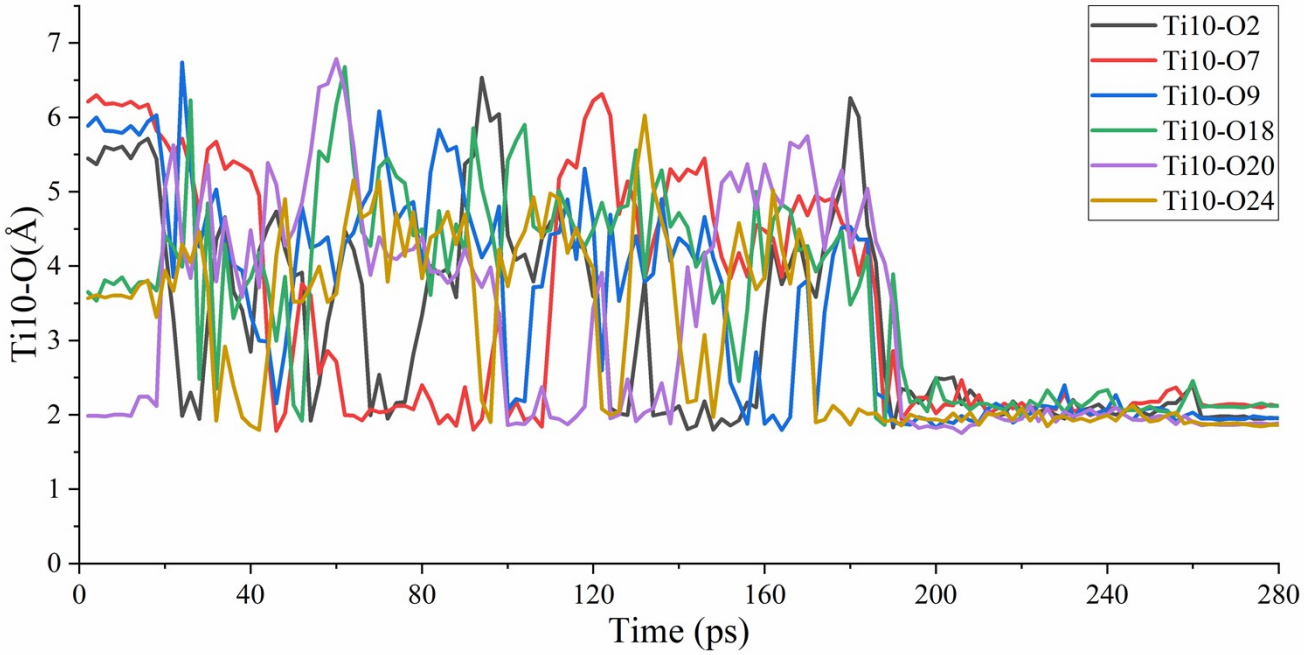
Ti8-O7
Ti8-O9
Ti8-O18
Ti8-O23
Ti8-O31
Ti8-O(Å)
Time (ps)


Ti9-O1
Ti9-O9
Ti9-O11
Ti9-O13
Ti9-O20
Ti9-O32
Ti9-O(Å)
Time (ps)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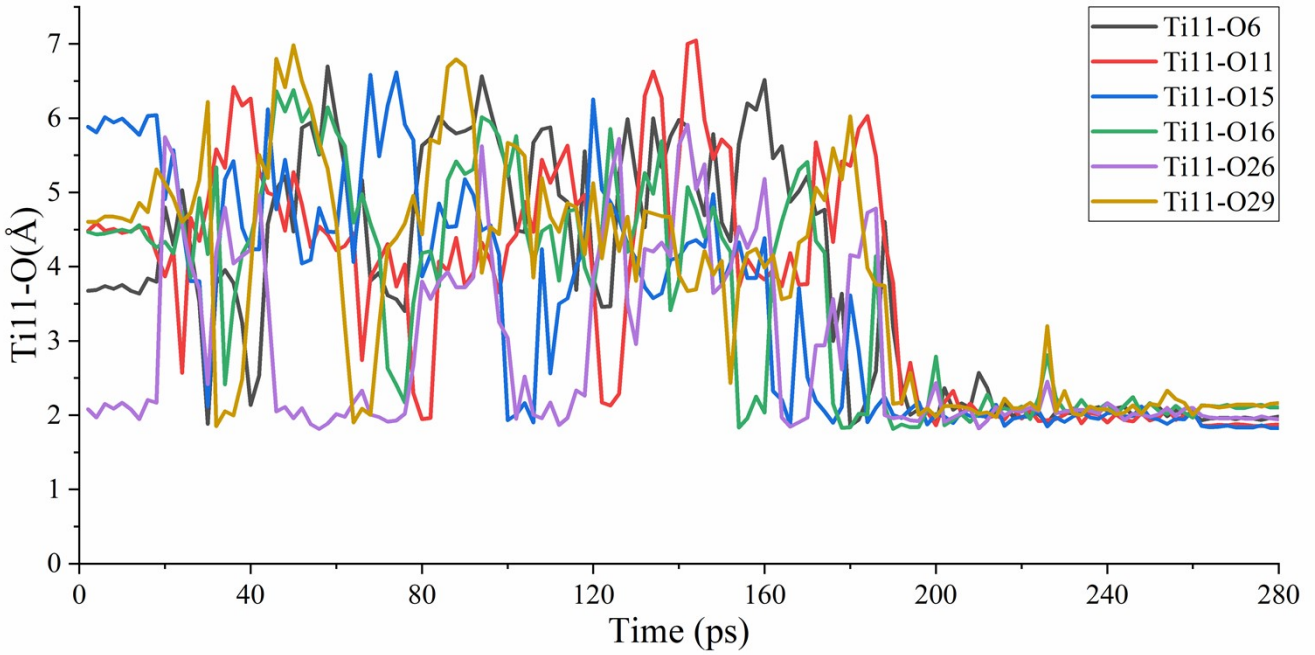
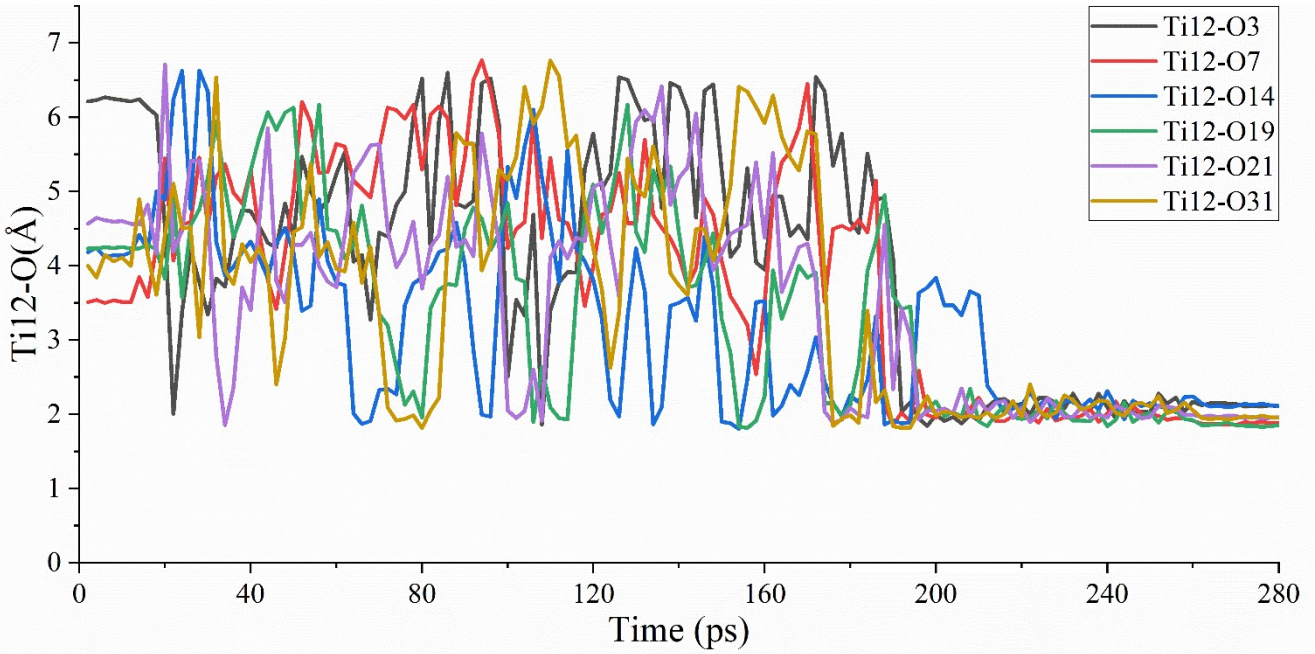
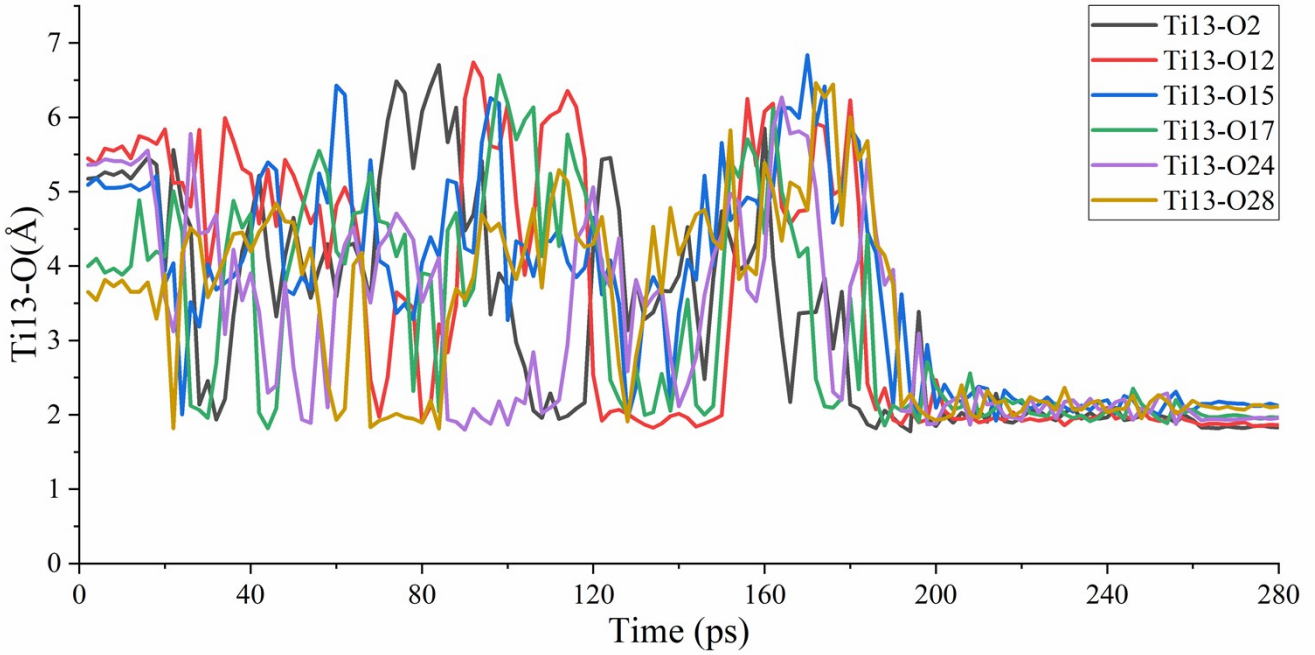
Ti10-O7
Ti10-O9
Ti10-O18
Ti10-O20
Ti10-O24
Ti10-O(Å)
Time (ps)


Ti11-O6
Ti11-O11
Ti11-O15
Ti11-O16
Ti11-O26
Ti11-O29
Ti11-O(Å)
Time (ps)
0
40
80
120
160
200
240
280
1
2
3
4
5
6
7


Ti12-O3
Ti12-O7
Ti12-O14
Ti12-O19
Ti12-O21
Ti12-O31
Ti12-O(Å)
Time (ps)
0
40
80
120
160
200
240
280
1
2
3
4
5
6
7


Ti13-O2
Ti13-O12
Ti13-O15
Ti13-O17
Ti13-O24
Ti13-O28
Ti13-O(Å)
Time (ps)
0
40
80
120
160
200
240
280
1
2
3
4
5
6
7

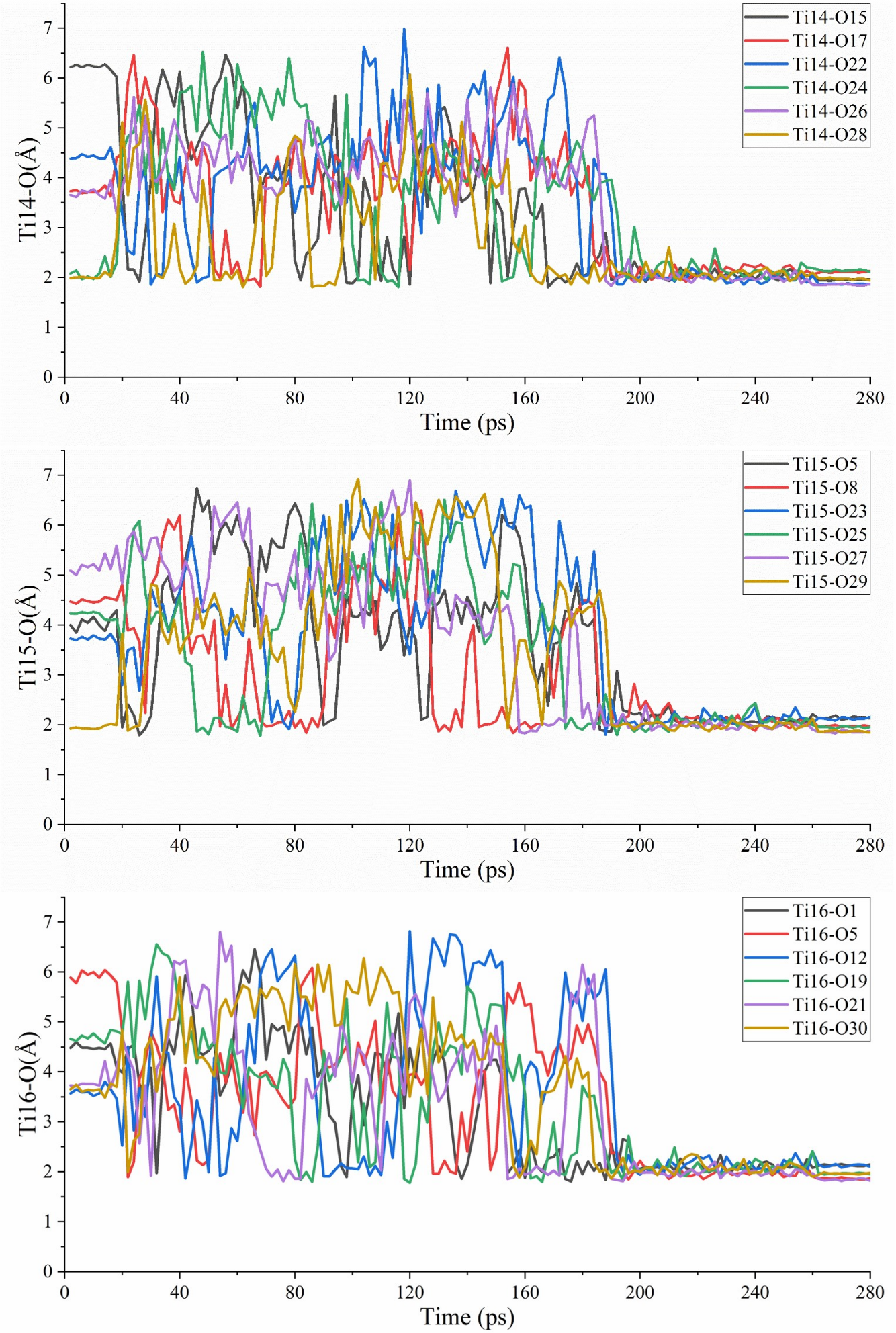
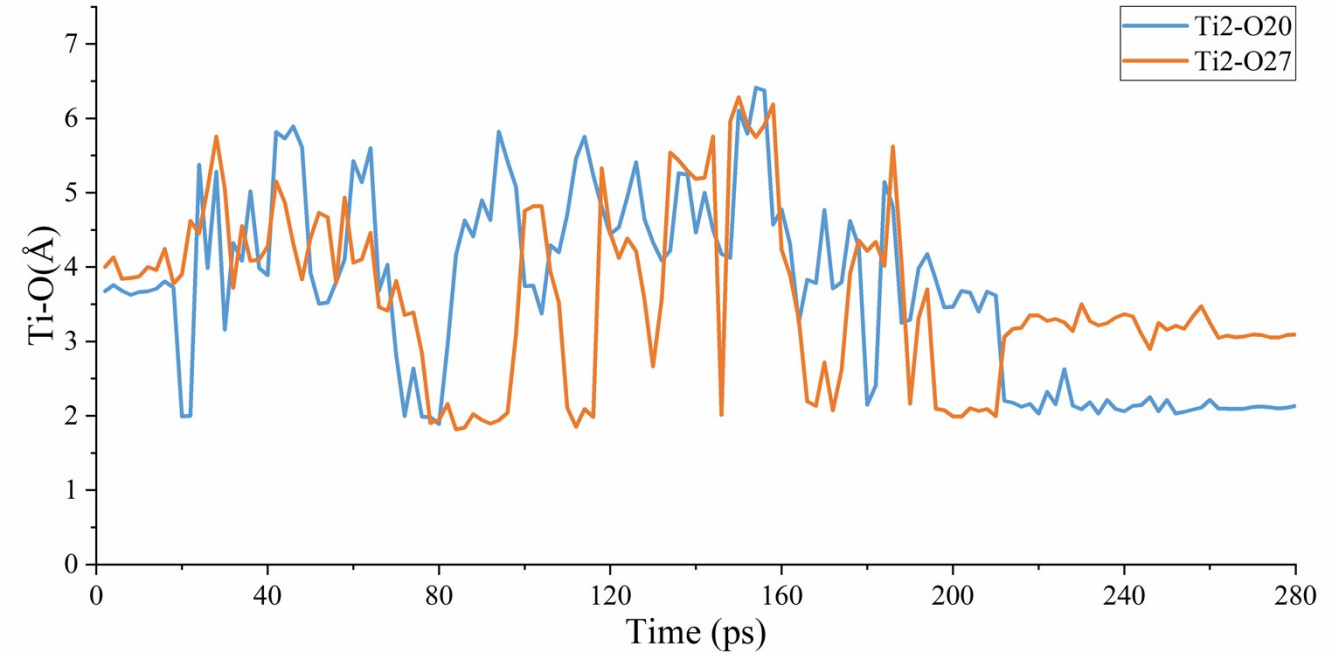
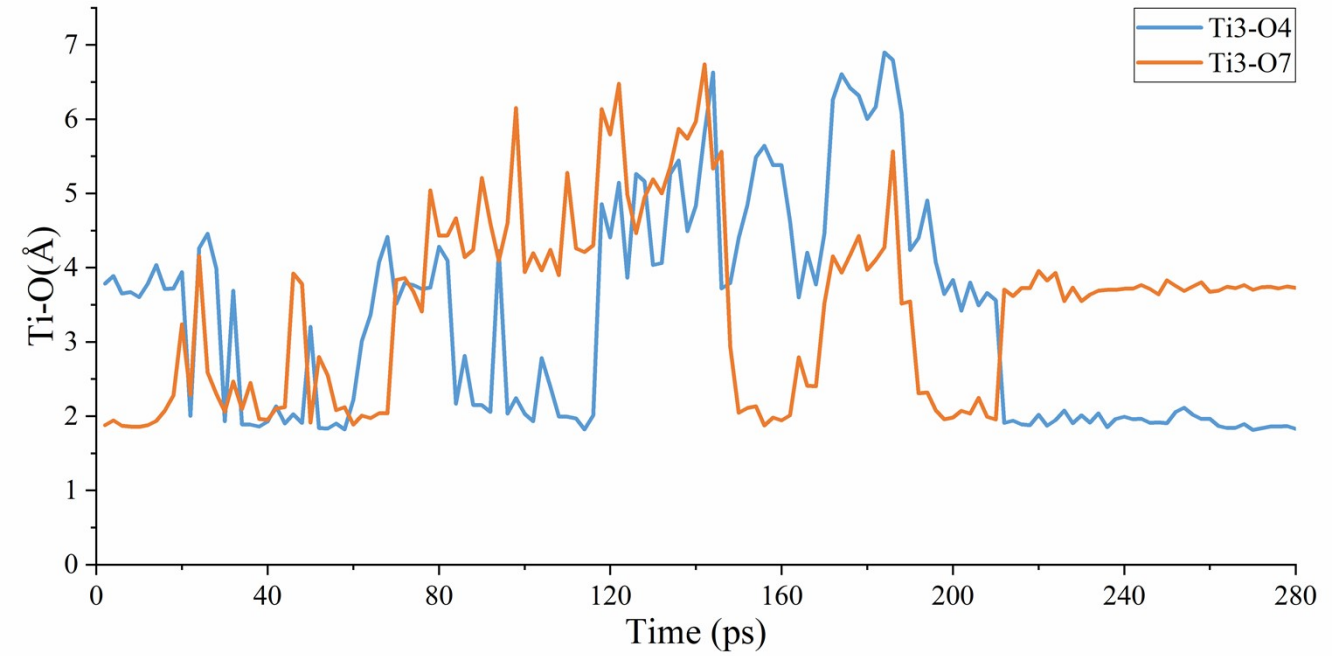


Fig. S4 Changes of all Ti-O bond lengths during the phase transition.

As shown in Fig. S5, Ti2, Ti3, Ti9 and Ti12 are connected with O27, O7, O10 and O14 respectively to form [TiO_6] octahedra in the metastable structure before the formation of the columbite phase. At about 211 ps, with the breakage of the old Ti-O bonds, Ti2, Ti3, Ti9 and Ti12 move in space, close to O20, O4, O9 and O2 respectively, and form new Ti-O bonds and octahedral units. The motion of these Ti atoms finally transforms the metastable structure into columbite.





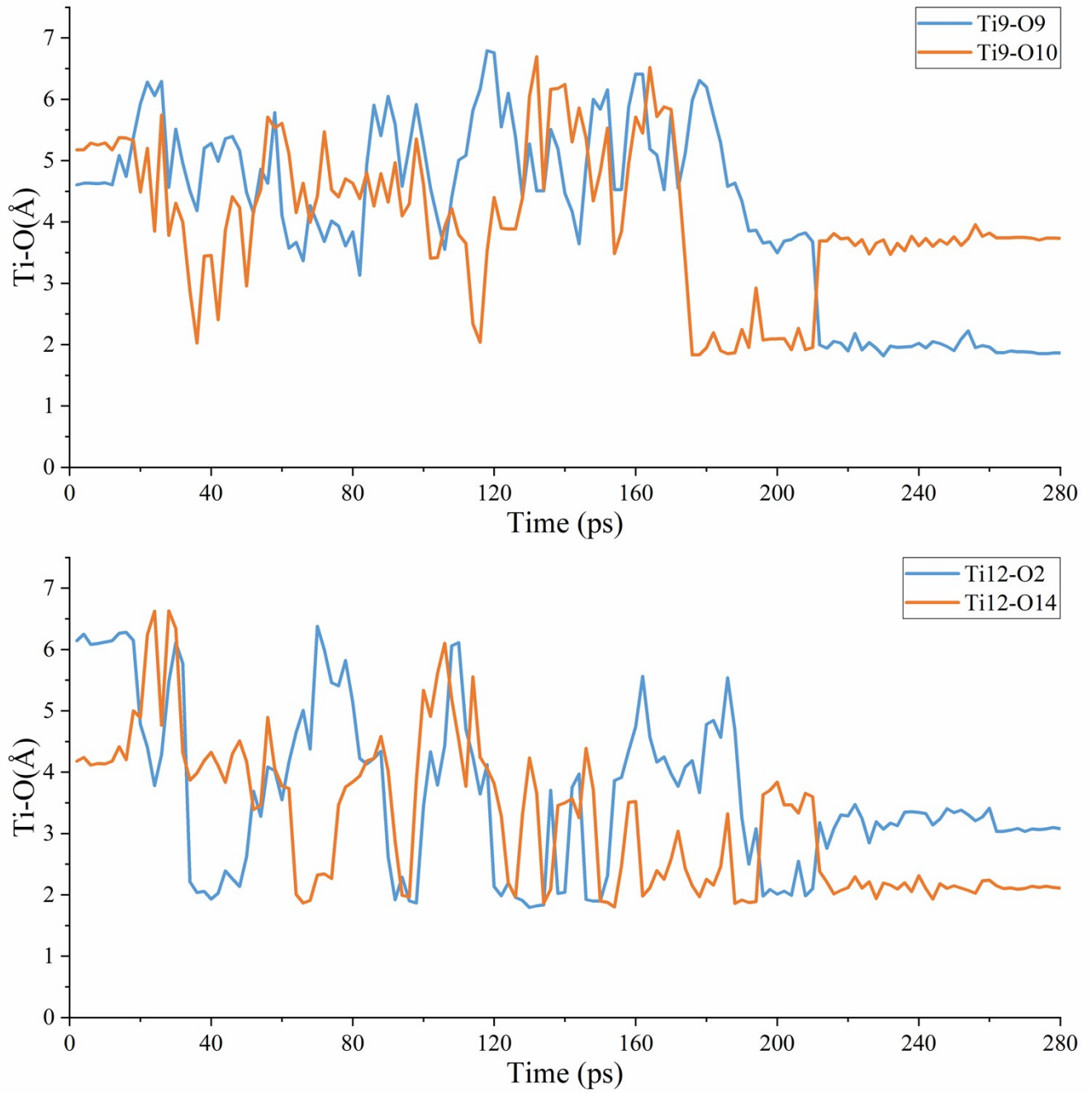


Fig. S5 Changes of distances between Ti2, Ti3, Ti9, Ti12 and special O atoms