The Dynamics and Spectroscopic Fingerprint of Hydroxyl Radical Generation through Water Dimer Ionization: *ab initio* Molecular Dynamic Simulation Study

Supplementary Information

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The 200 fs waiting time is meant to confirm if there is any correlation problem between the successive cationic events for the first 20 trajectories. An analysis on the dynamics of the norm vector of water molecule in respect to r_{OO} axis is carried out. The rotation (or *flipping*) period is estimated at about 147 fs (based upon red curve in Figure S2: 34 maxima are counted with the *flipping* amplitude large than 20 degree in respect to the prior minimum within time step = 1000-6000 fs of the neutral water dimer simulation) and the average *flipping* amplitude of 37 degree. This suggests the 50 fs interval per cation sampling should have about 12 degree slipping difference for one water in respect to r_{OO} axis without taking account the geometrical change of other degrees of freedom, e.g. HOH bending, OH vibration, intermolecular OO vibration, and dihedral angle of $C_{2v}^{W1} - r_{OO} - C_{2v}^{W2}$. The similarity of the dynamics of r_{OO}, e.g. the ionized events of 1700-1950 fs shown in

Figure S4, is attributed by: (1) simplified one dimensional presentation of using r_{OO}; (2) size of the finite degree of freedom for water dimer. For instance, similarity of r_{OO} can still be found for the ionization events of 4600-5000 where 200 fs (>> 147 fs, the average *flipping* period) interval was used.

Table S1. Cartesian coordinates for the dimeric derivatives optimized at CCSD/aug-cc-pVDZ where *hm*-($HO^{\bullet}$)•(OH_2) is taken from Reference 10

($HO^{\bullet}$)•H_3O^+

O	-1.34780	-0.07697	0.09033
H	0.14047	0.06511	-0.00821
H	-1.96298	0.61532	-0.24027
O	1.17927	0.03481	-0.10614
H	1.63545	0.72216	0.41459
H	1.54571	-0.84322	0.11260

trans-($HO^{\bullet}$)•H_2O

H	-0.97672	1.41444	0.00000
O	-0.00898	1.56230	0.00000
O	-0.00898	-1.42113	0.00000
H	0.36901	-0.53111	0.00000
H	0.75141	-2.01269	0.00000

hm-(H_2O^+)•(OH_2)

O	-1.01387	-0.03058	0.12193
H	-1.14302	-0.62347	-0.64994
H	-1.24492	0.86809	-0.19772
O	1.01389	-0.03058	-0.12194
H	1.24483	0.86812	0.19772
H	1.14297	-0.62346	0.64995

H_2O•($HO^{\bullet}$)

H	0.05969	0.65732	0.00000
O	0.03645	1.63903	0.00000
O	0.03645	-1.28360	0.00000
H	-0.32143	-1.75039	0.76419
H	-0.32143	-1.75039	-0.76419

trans-(H_2O)$_2$

O	-1.53175	0.00142	-0.12209
H	-0.57696	-0.00119	0.04643
H	-1.93073	-0.00883	0.75479
O	1.40351	-0.00119	0.11082
H	1.76769	-0.75848	-0.36344
H	1.76595	0.76663	-0.34763

hm-($HO^{\bullet}$)•(OH_2)

H	0.00000	0.00000	0.00000
O	0.00000	0.00000	0.97330
O	2.58224	0.00000	0.25233
H	2.31219	0.75871	0.77778
H	2.31219	-0.75871	0.77778

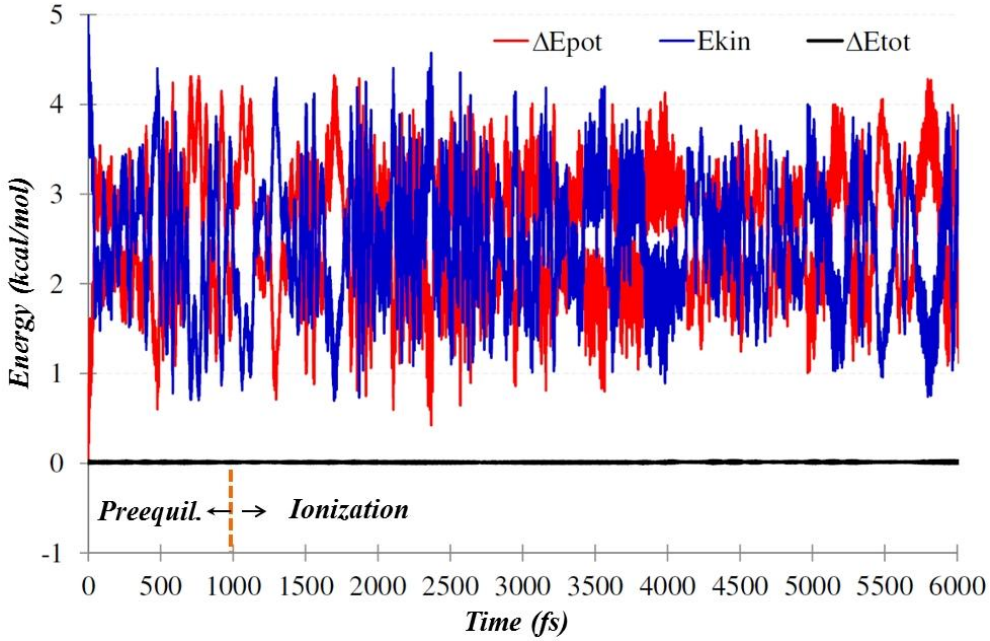

Figure S1. Dynamics of ΔEpot (red), Ekin (blue), and ΔEtot fs for $(H_2O)_2$ simulation where Δ is calculated in respect to time step = 0 fs. The vertical orange dashed line shows the collection of the first ionization events.

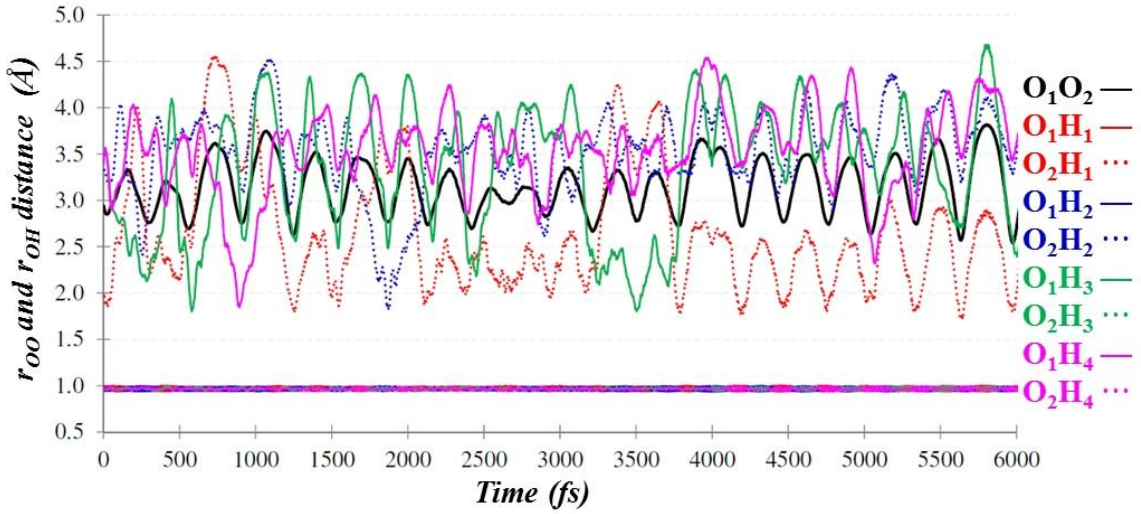

Figure S2. Dynamics of OO and OH distances in Å for $(H_2O)_2$ simulation. Each solid and dotted lines of the same color correspond to the distance of the particular hydrogen to either oxygen atoms.

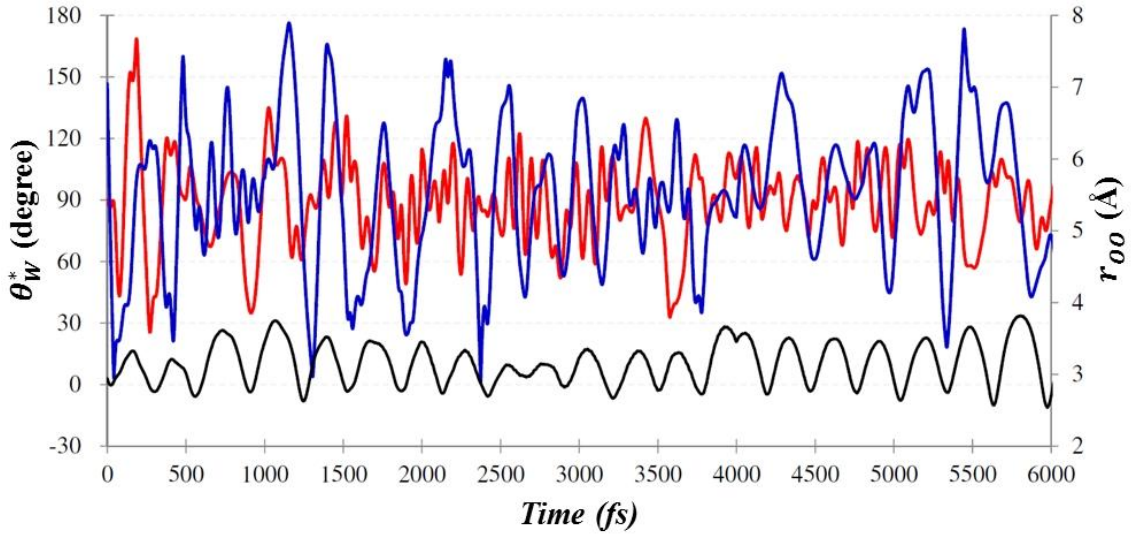

Figure S3. Dynamics of water molecule rotation for $(H_2O)_2$ simulation, in which the angles (θ_W^*) between the norm vector of each water (v_{W1}^n/v_{W2}^n) and r_{OO} are plotted in red and blue, respectively, and the distance of r_{OO} is shown by the right axis in Å.

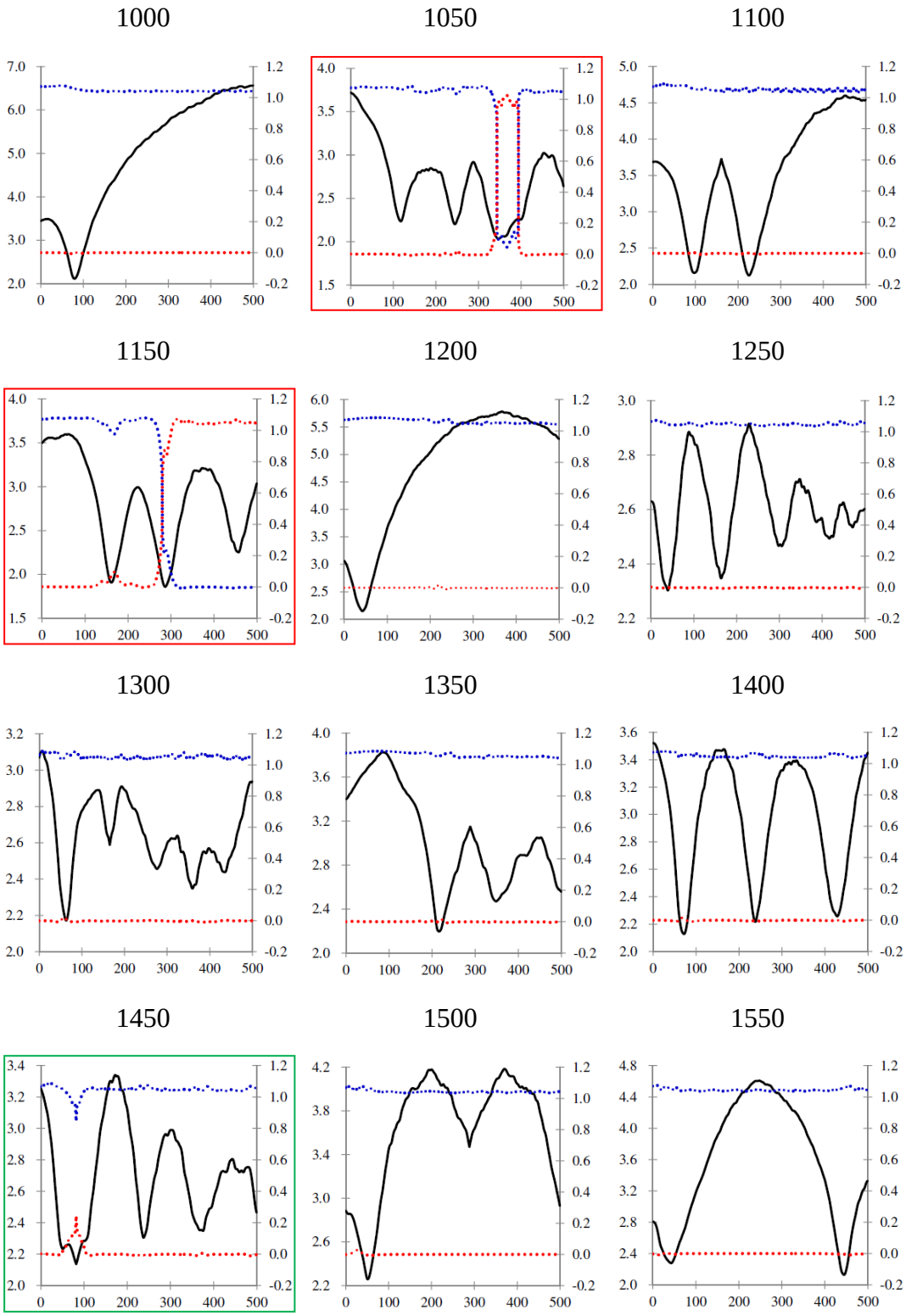

Figure S4. Dynamics of r_{OO} in Å (black line by left axis) and the spin density of each water molecule (red/blue dots by right axis) for the 500 fs $(H_2O)_2^+$ simulations. The number above each plot denotes the time step of ionization in fs. The red/green boxes represent the event of successful/unsuccessful electron transfer, respectively.

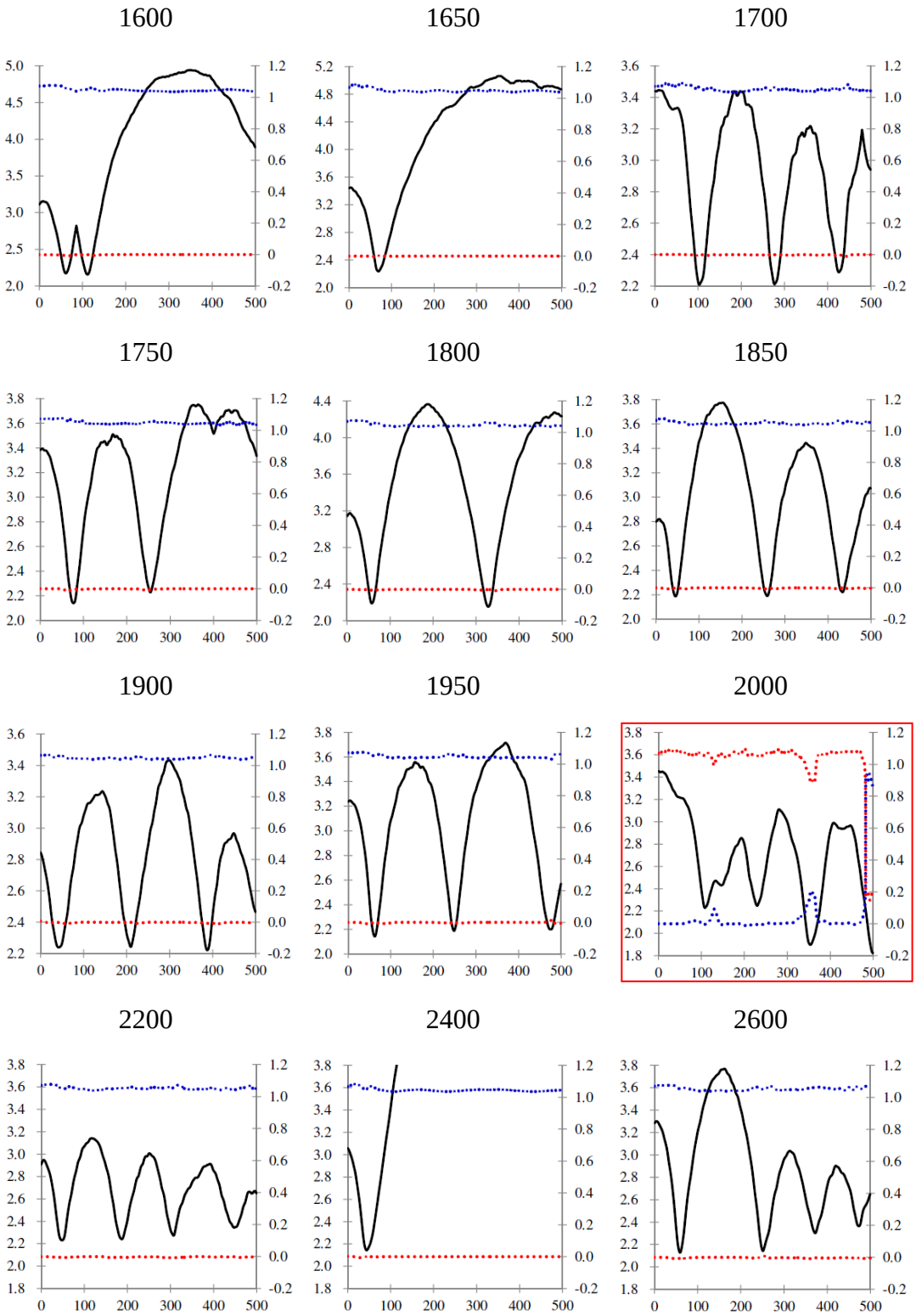

Figure S5. Dynamics of r_{OO} in Å (black line by left axis) and the spin density of each water molecule (red/blue dots by right axis) for the 500 fs $(H_2O)_2^+$ simulations. The number above each plot denotes the time step of ionization in fs. The red boxes represent the event of successful electron transfer.

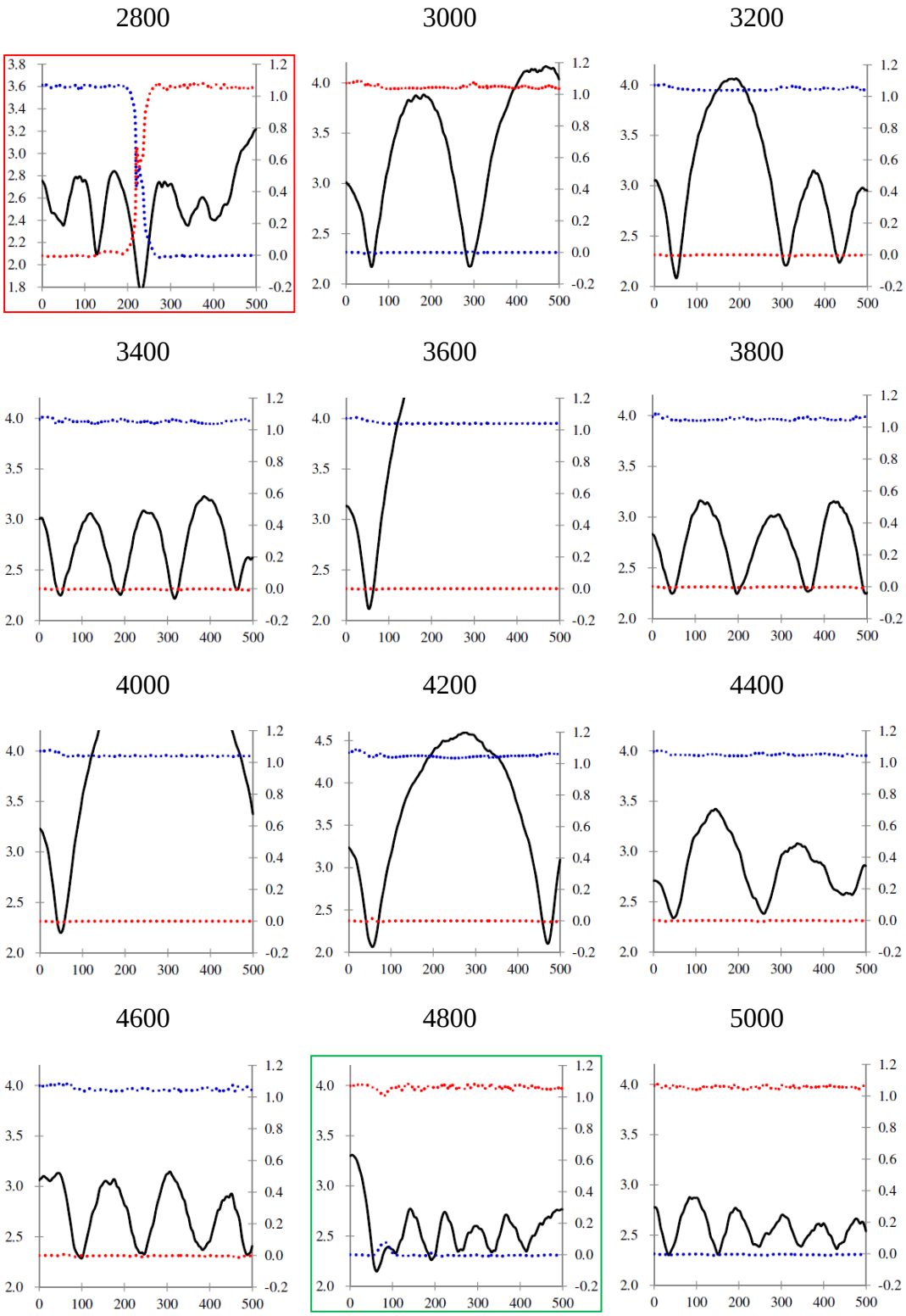

Figure S6. Dynamics of r_{OO} in Å (black line by left axis) and the spin density of each water molecule (red/blue dots by right axis) for the 500 fs $(H_2O)_2^+$ simulations. The number above each plot denotes the time step of ionization in fs. The red/green boxes represent the event of successful/unsuccessful electron transfer, respectively.

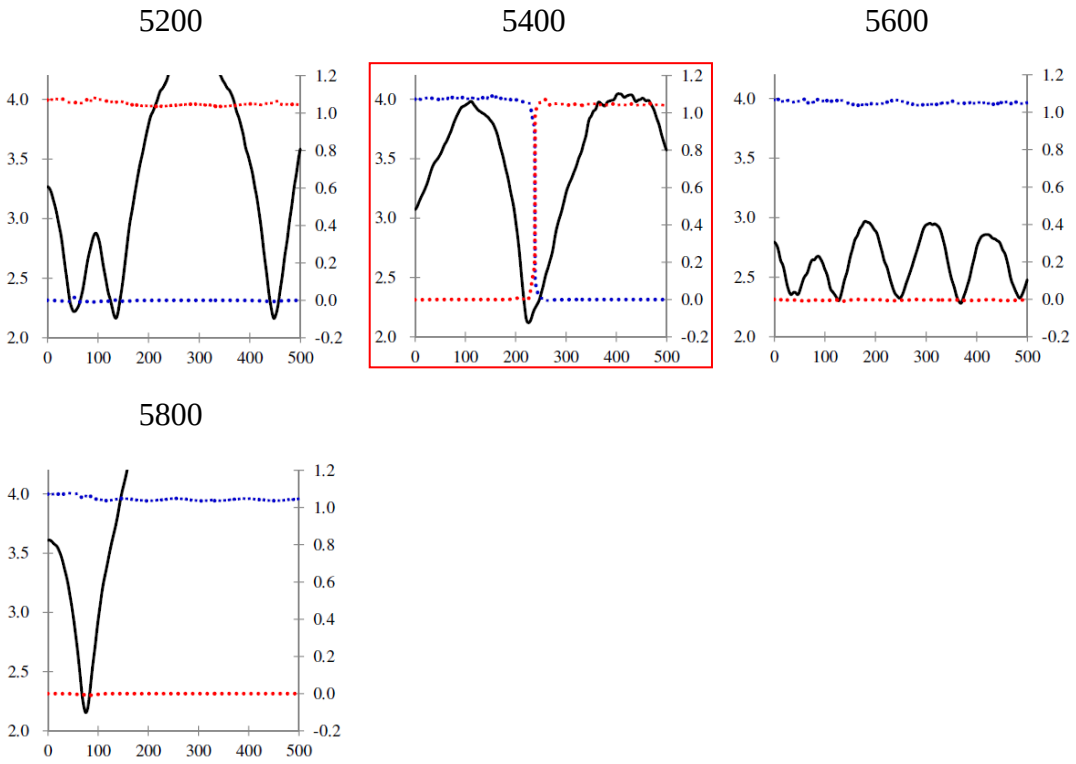

Figure S7. Dynamics of r_{OO} in Å (black line by left axis) and the spin density of each water molecule (red/blue dots by right axis) for the 500 fs $(H_2O)_2^+$ simulations. The number above each plot denotes the time step of ionization in fs. The red boxes represent the event of successful electron transfer, respectively.

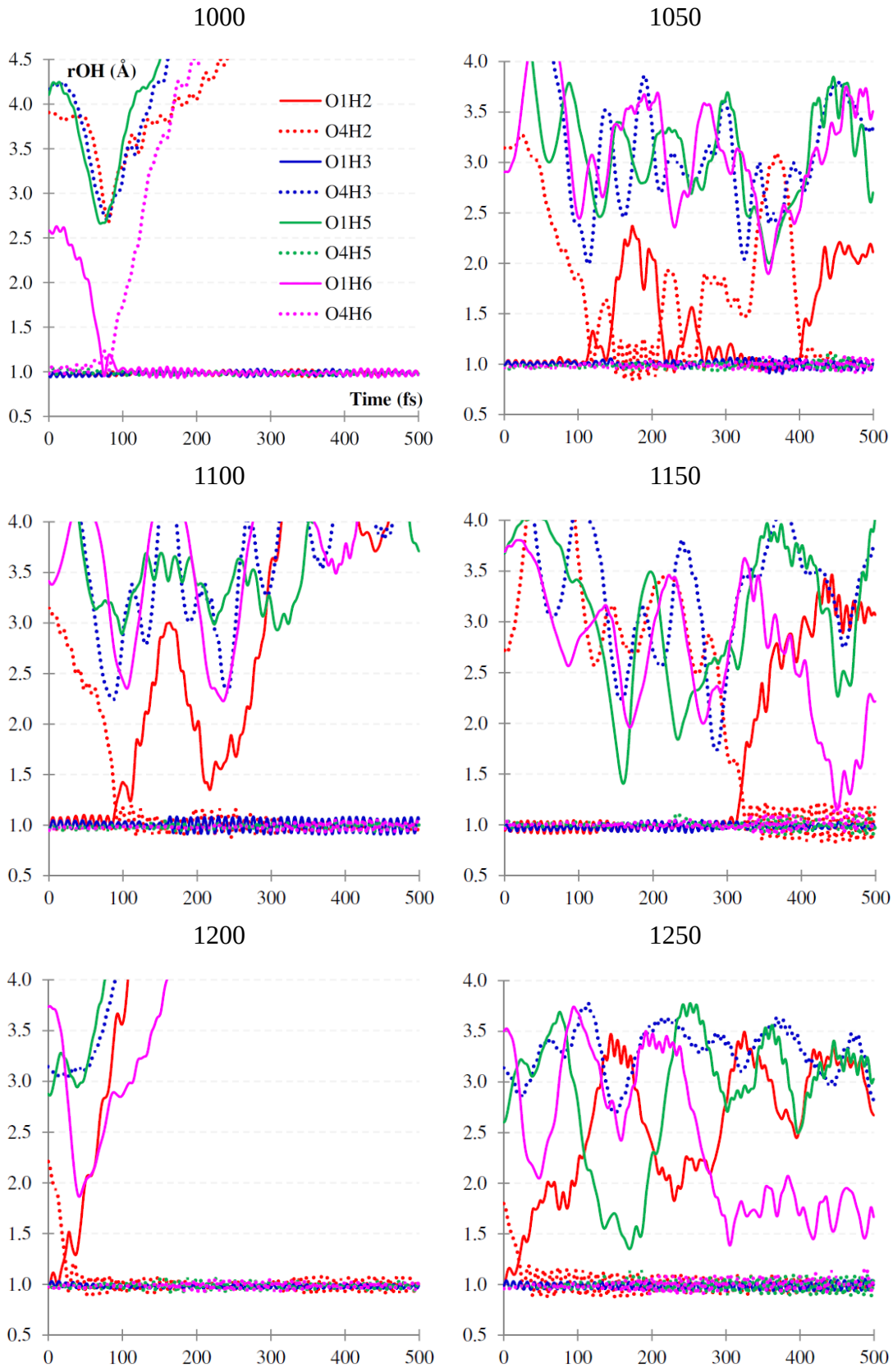

Figure S8. Dynamics of r_{OH} in Å for the 500 fs $(H_2O)_2^+$ simulations. The number above each plot denotes the time step of ionization in fs. Legend and axis label are listed in upper left.

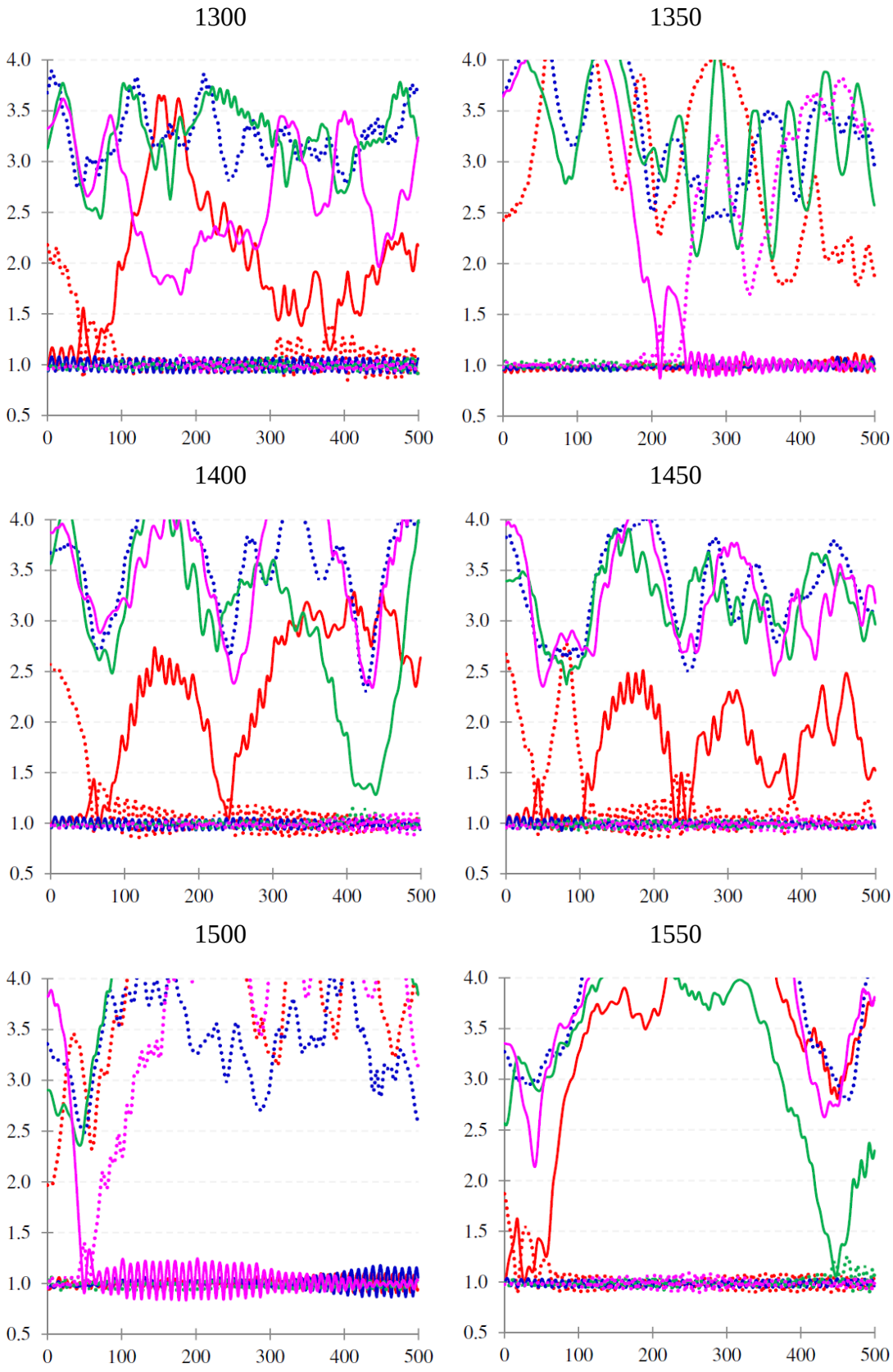

Figure S9 Dynamics of r_{OH} in Å for the 500 fs $(H_2O)_2^+$ simulations. The number above each plot denotes the time step of ionization in fs. Legend and axis label are the same as that in upper left of Figure S8.

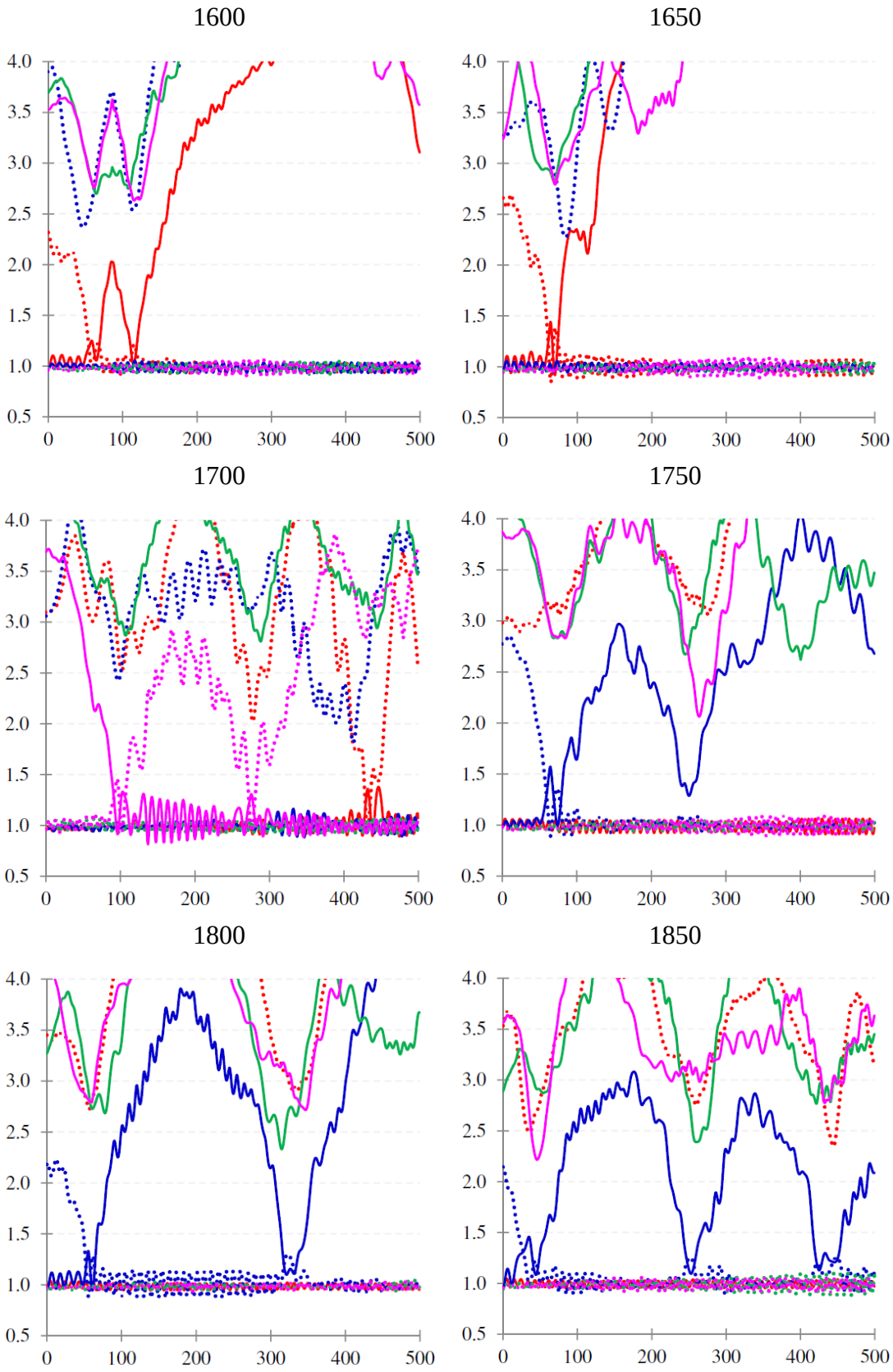

Figure S10 Dynamics of r_{OH} in Å for the 500 fs $(H_2O)_2^+$ simulations. The number above each plot denotes the time step of ionization in fs. Legend and axis label are the same as that in upper left of Figure S8.

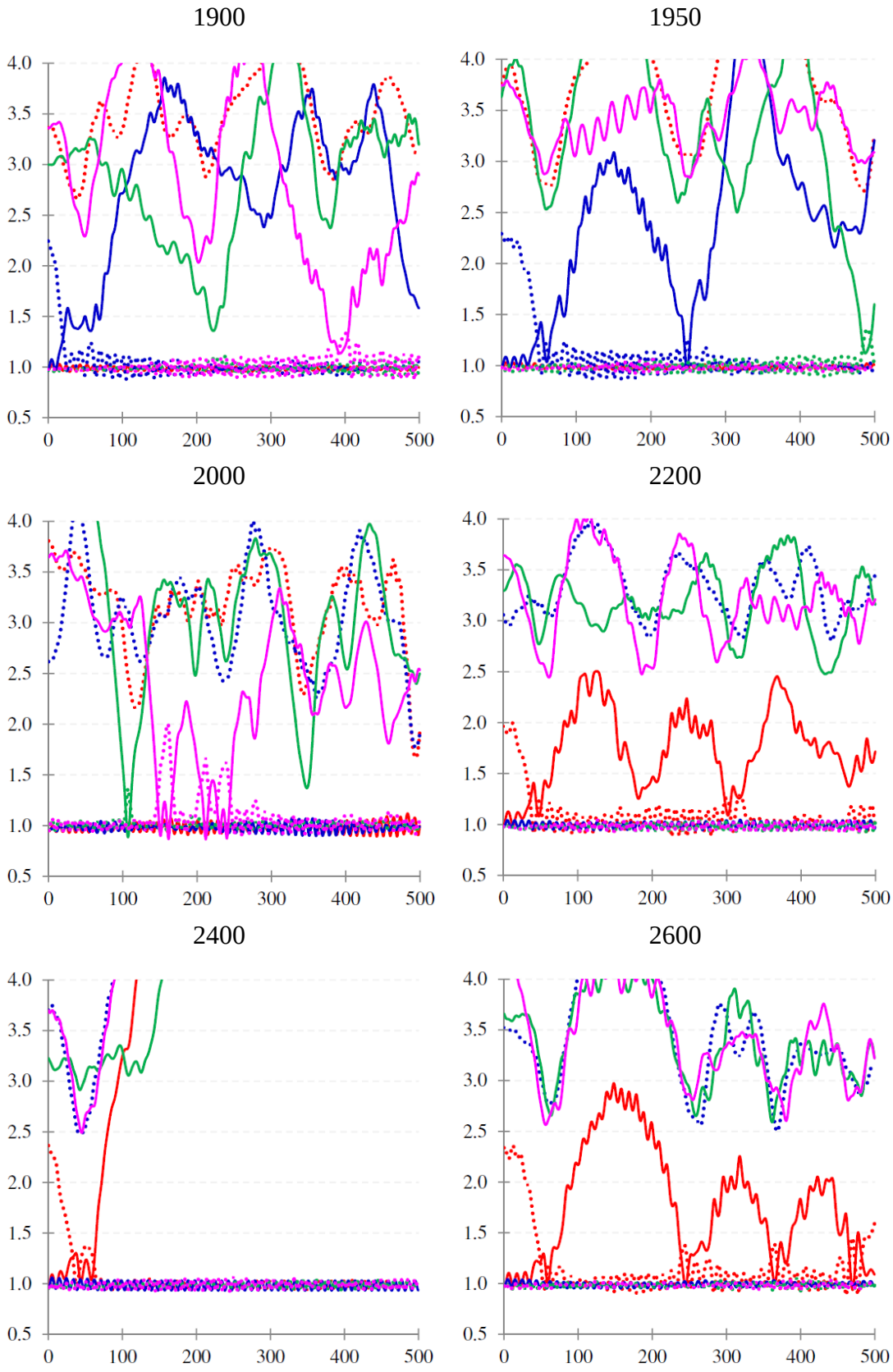

Figure S11 Dynamics of r_{OH} in Å for the 500 fs $(H_2O)_2^+$ simulations. The number above each plot denotes the time step of ionization in fs. Legend and axis label are the same as that in upper left of Figure S8.

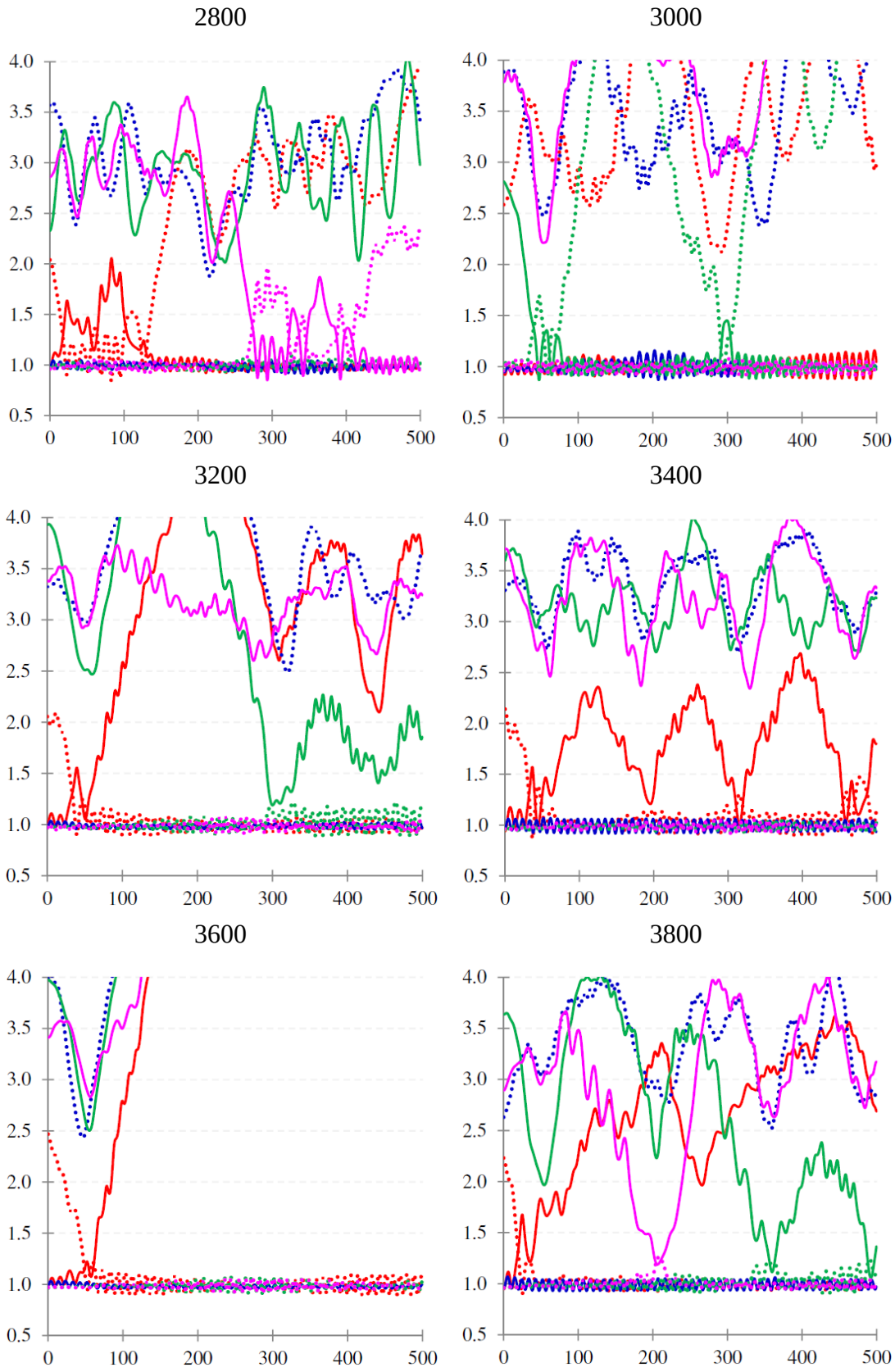

Figure S12 Dynamics of r_{OH} in Å for the 500 fs $(H_2O)_2^+$ simulations. The number above each plot denotes the time step of ionization in fs. Legend and axis label are the same as that in upper left of Figure S8.

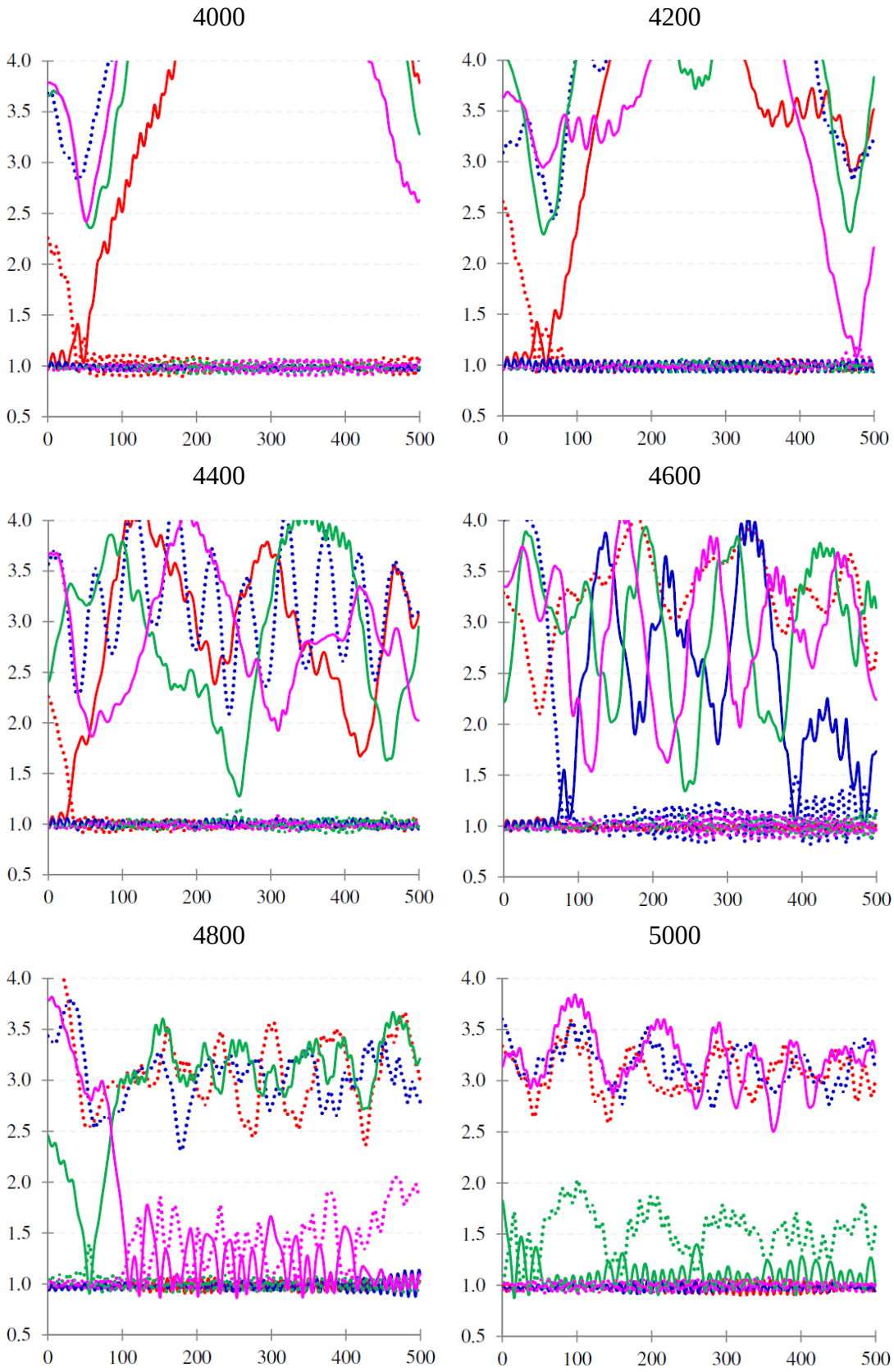

Figure S13 Dynamics of r_{OH} in Å for the 500 fs $(H_2O)_2^+$ simulations. The number above each plot denotes the time step of ionization in fs. Legend and axis label are the same as that in upper left of Figure S8.

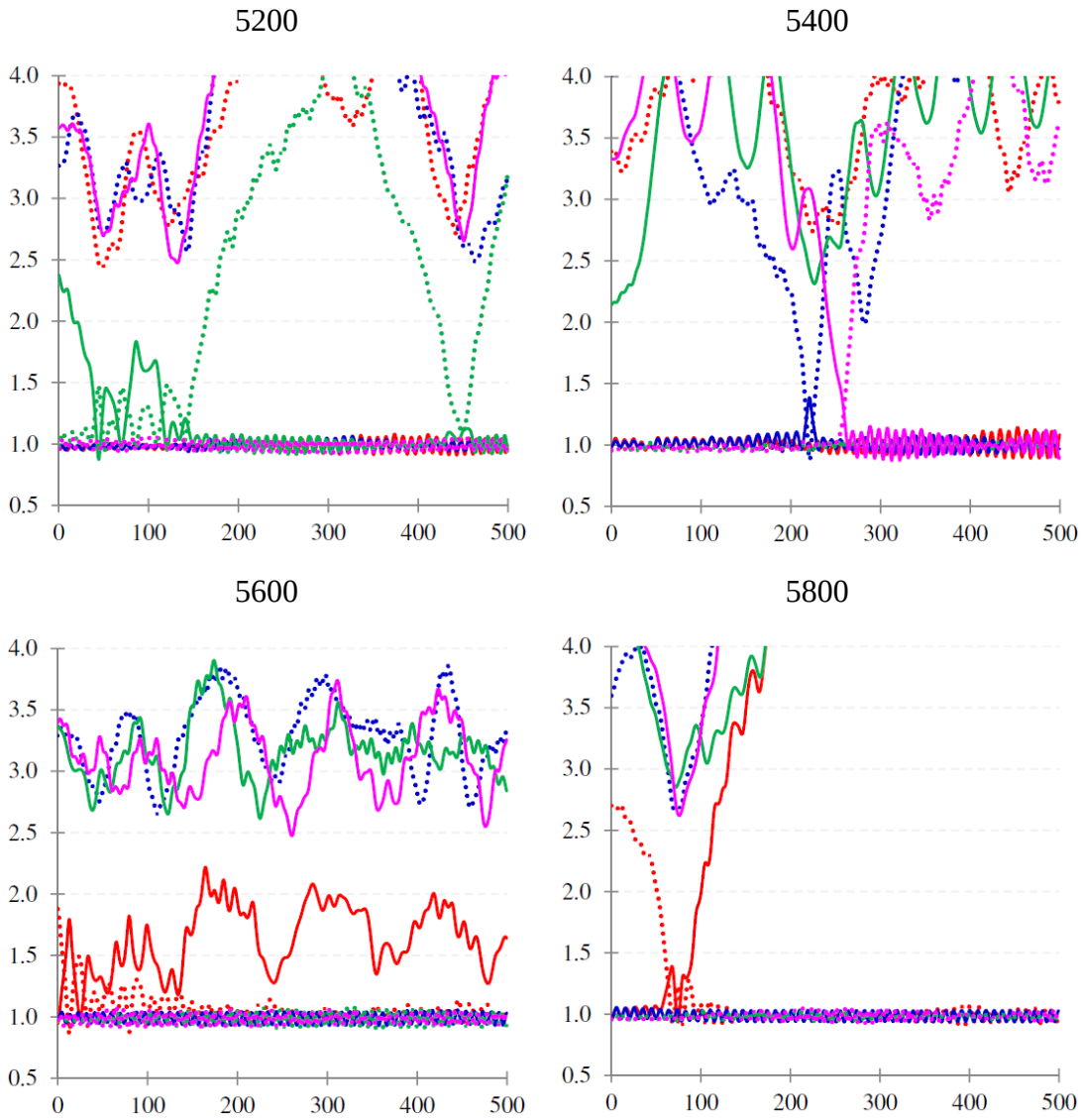

Figure S14 Dynamics of r_{OH} in Å for the 500 fs $(H_2O)_2^+$ simulations. The number above each plot denotes the time step of ionization in fs. Legend and axis label are the same as that in upper left of Figure S8.

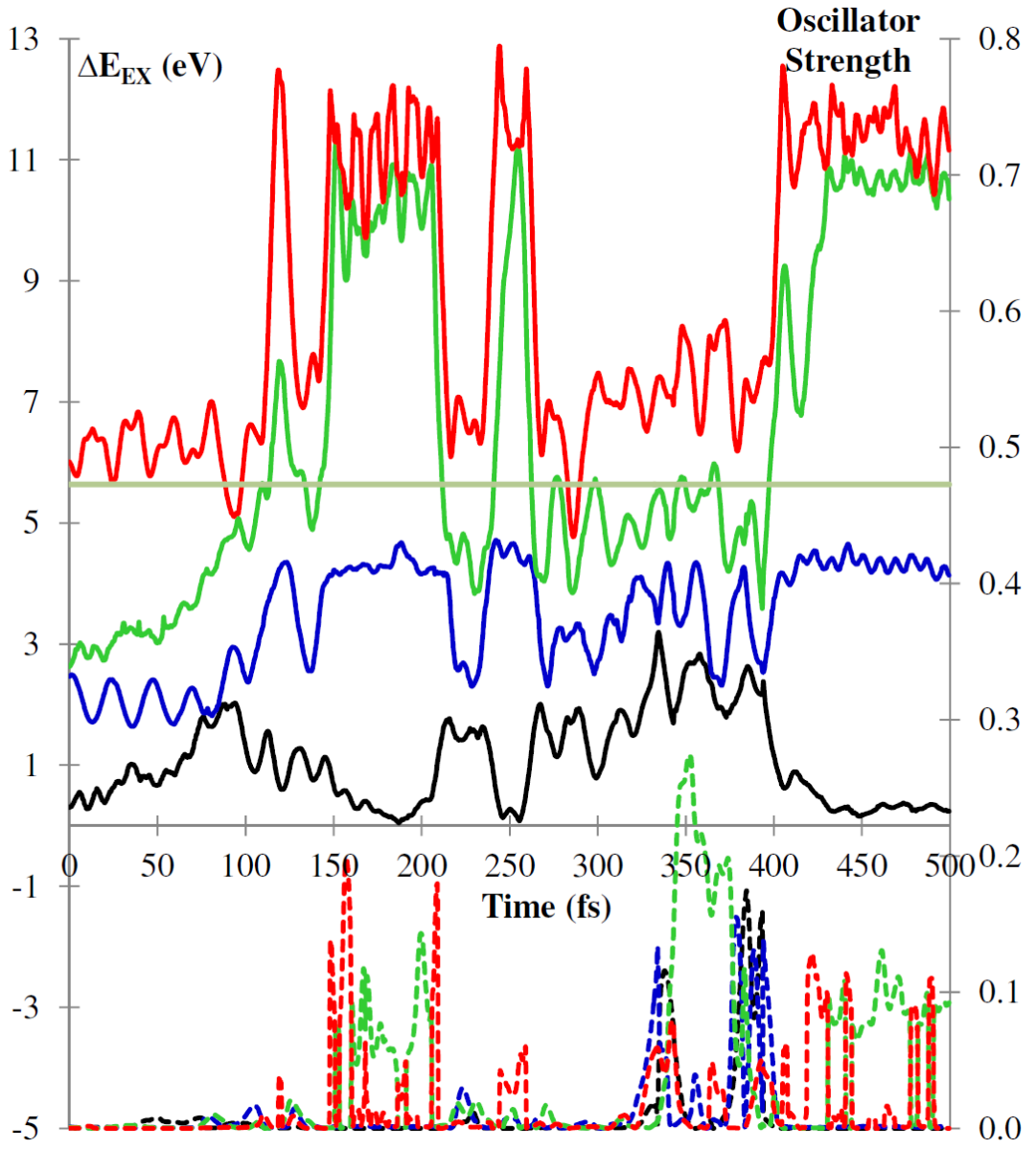

Figure 15. 500 fs excited state analysis along the trajectory of the time step = 1050 fs ionization event. The first four excitation energies (solid color lines) are plotted in eV by the left axis, and the corresponding color-coded calculated oscillator strengths (dashed lines) are shown by the right axis.

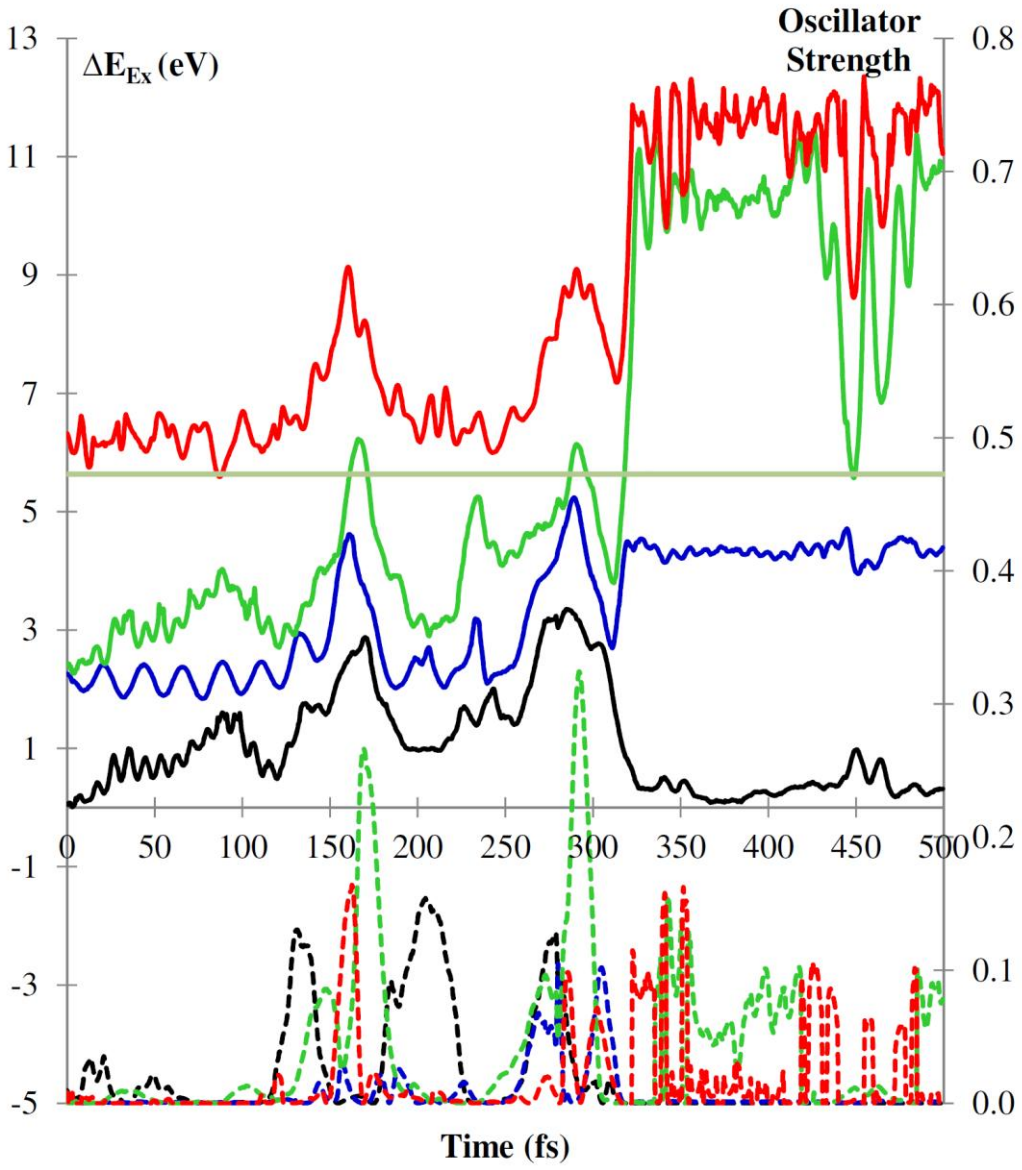

Figure S16. 500 fs excited state analysis along the trajectory of the time step = 1150 fs ionization event. The first four excitation energies (solid color lines) are plotted in eV by the left axis, and the corresponding color-coded calculated oscillator strengths (dashed lines) are shown by the right axis.

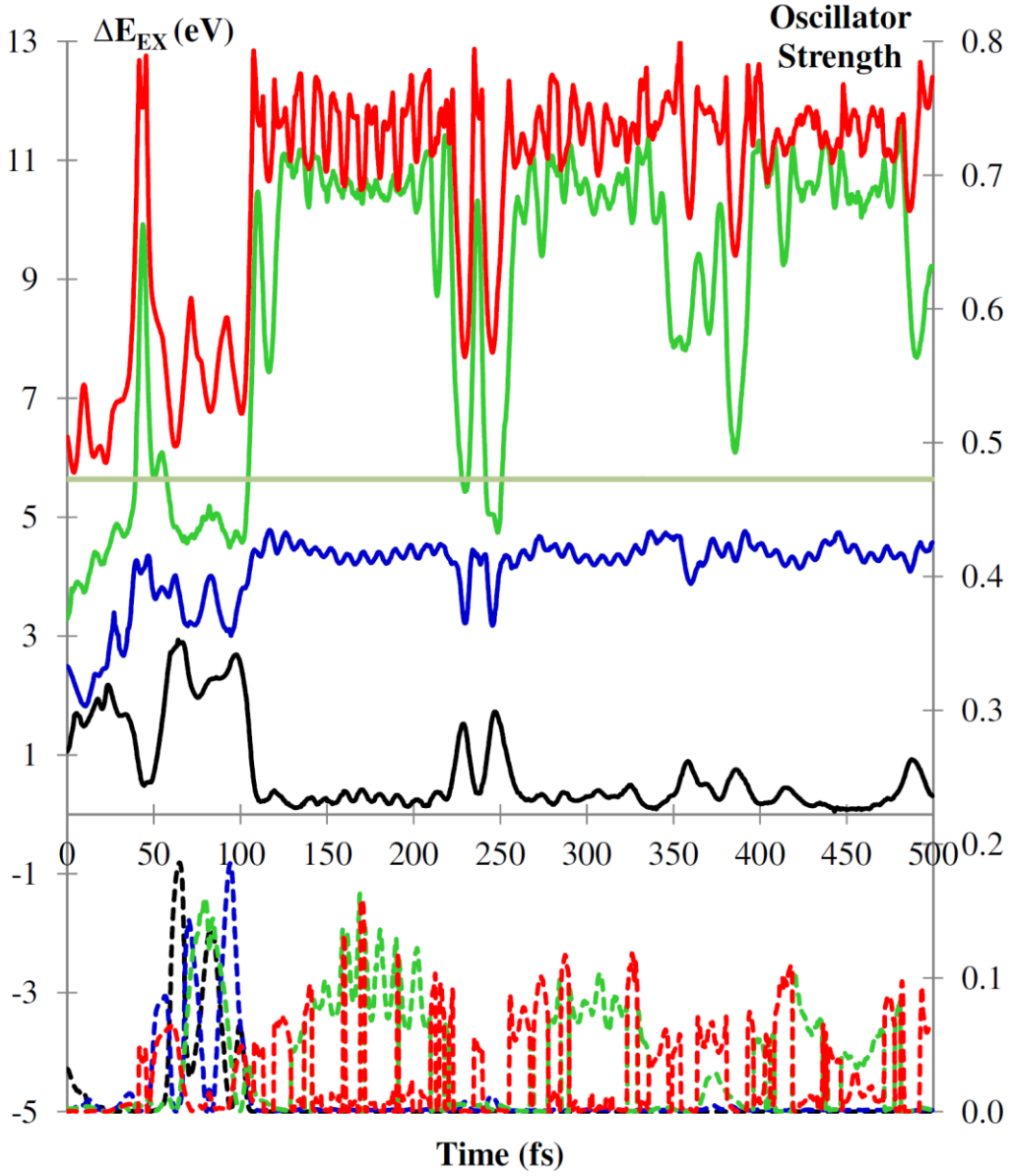

Figure S17. 500 fs excited state analysis along the trajectory of the time step = 1450 fs ionization event. The first four excitation energies (solid color lines) are plotted in eV by the left axis, and the corresponding color-coded calculated oscillator strengths (dashed lines) are shown by the right axis.

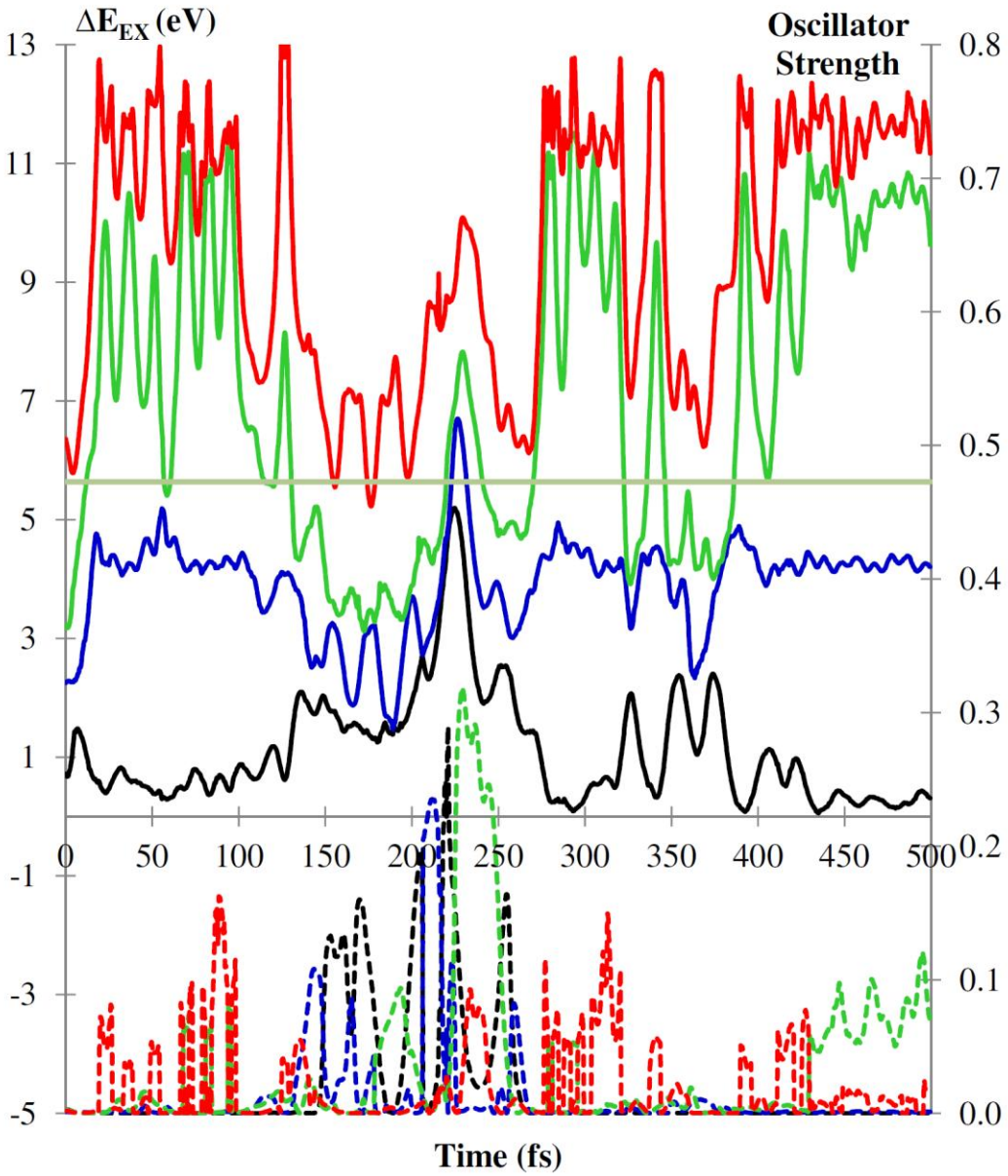

Figure S18. 500 fs excited state analysis along the trajectory of the time step = 2800 fs ionization event. The first four excitation energies (solid color lines) are plotted in eV by the left axis, and the corresponding color-coded calculated oscillator strengths (dashed lines) are shown by the right axis.

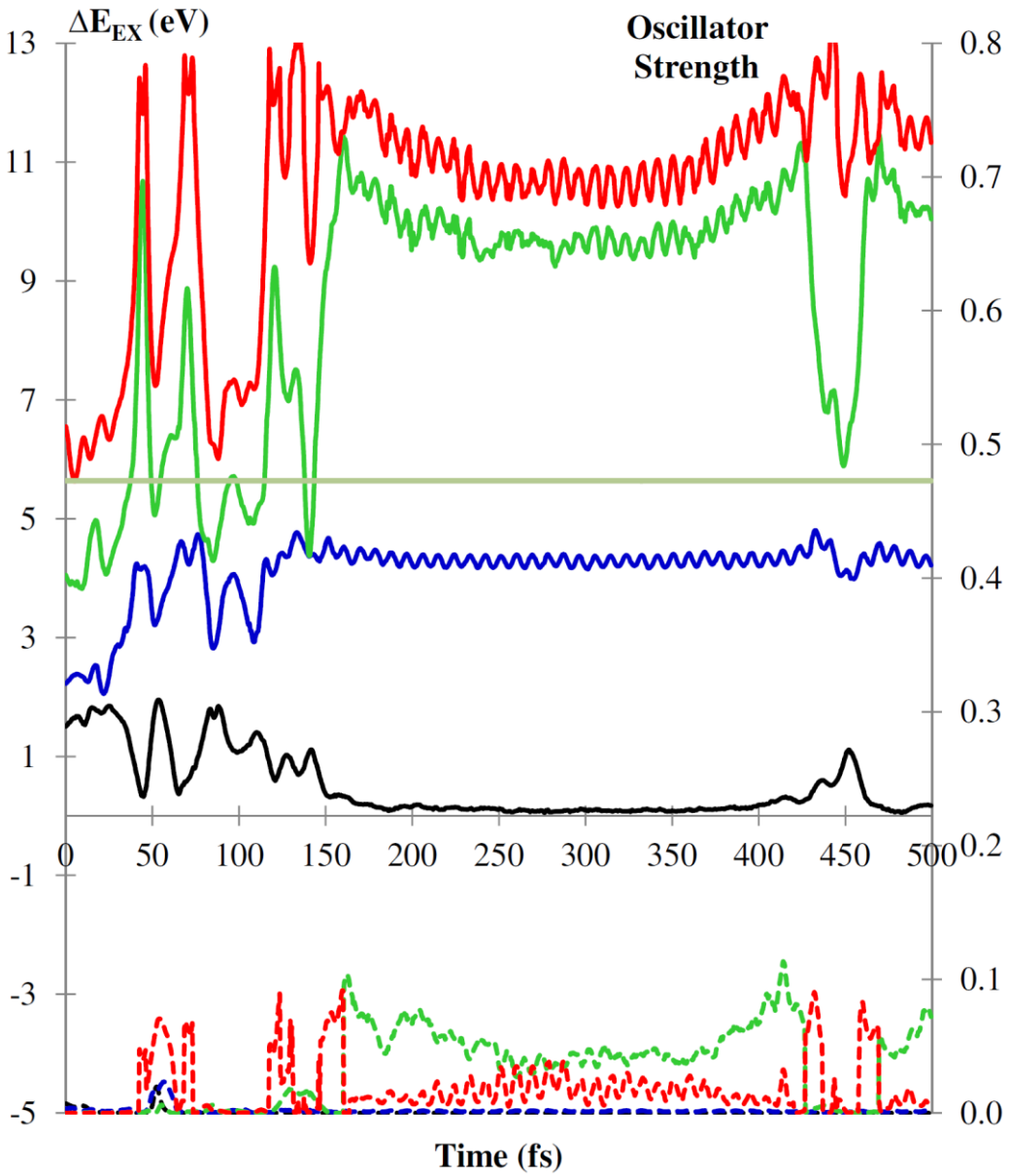

Figure S19. 500 fs excited state analysis along the trajectory of the time step = 5200 fs ionization event. The first four excitation energies (solid color lines) are plotted in eV by the left axis, and the corresponding color-coded calculated oscillator strengths (dashed lines) are shown by the right axis.

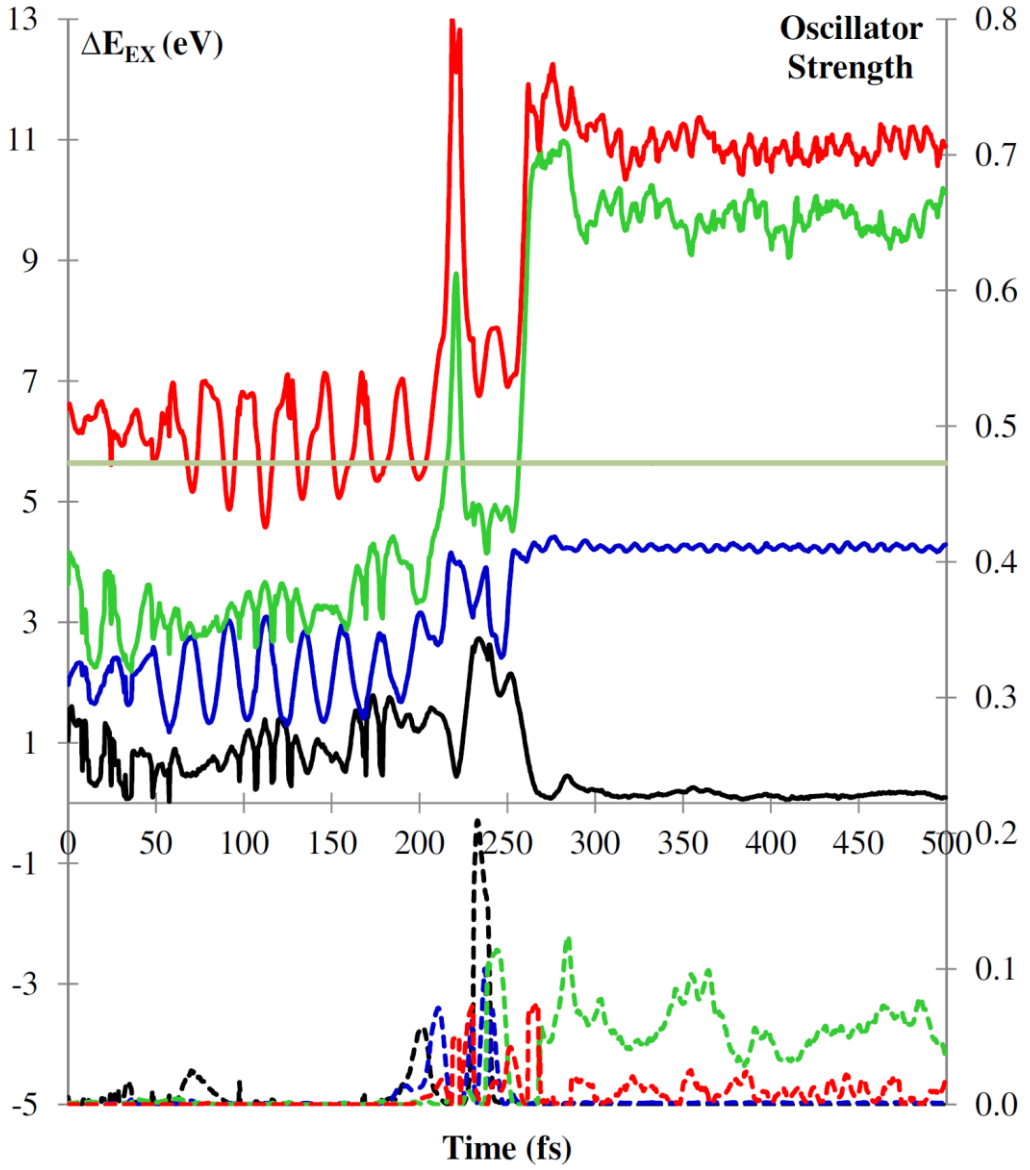

Figure S20. 500 fs excited state analysis along the trajectory of the time step = 5400 fs ionization event. The first four excitation energies (solid color lines) are plotted in eV by the left axis, and the corresponding color-coded calculated oscillator strengths (dashed lines) are shown by the right axis.