

Attosecond charge migration following Oxygen K-shell ionization of DNA bases and their base pairs: A Real-Time TDDFT study

Electronic Supplementary Information

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Time-dependent Bader hole charge

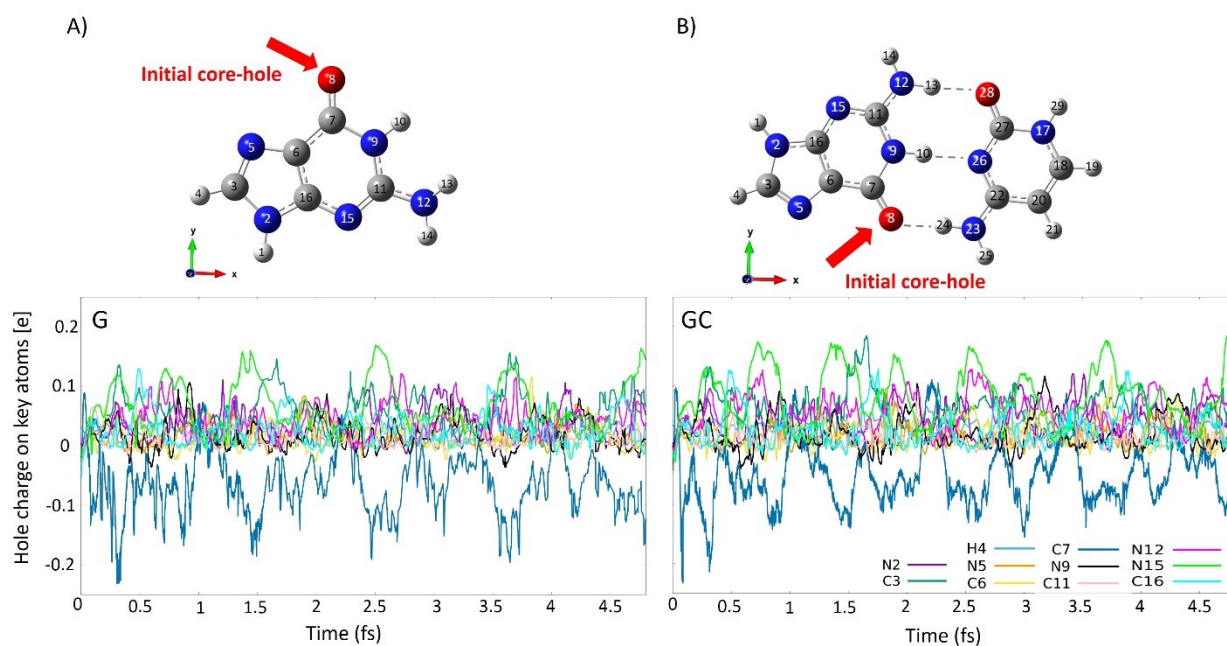


Fig S1. A, B) Time-dependent Bader hole charge on key atoms of G, GC cation after core ionization of oxygen at G site (O8).

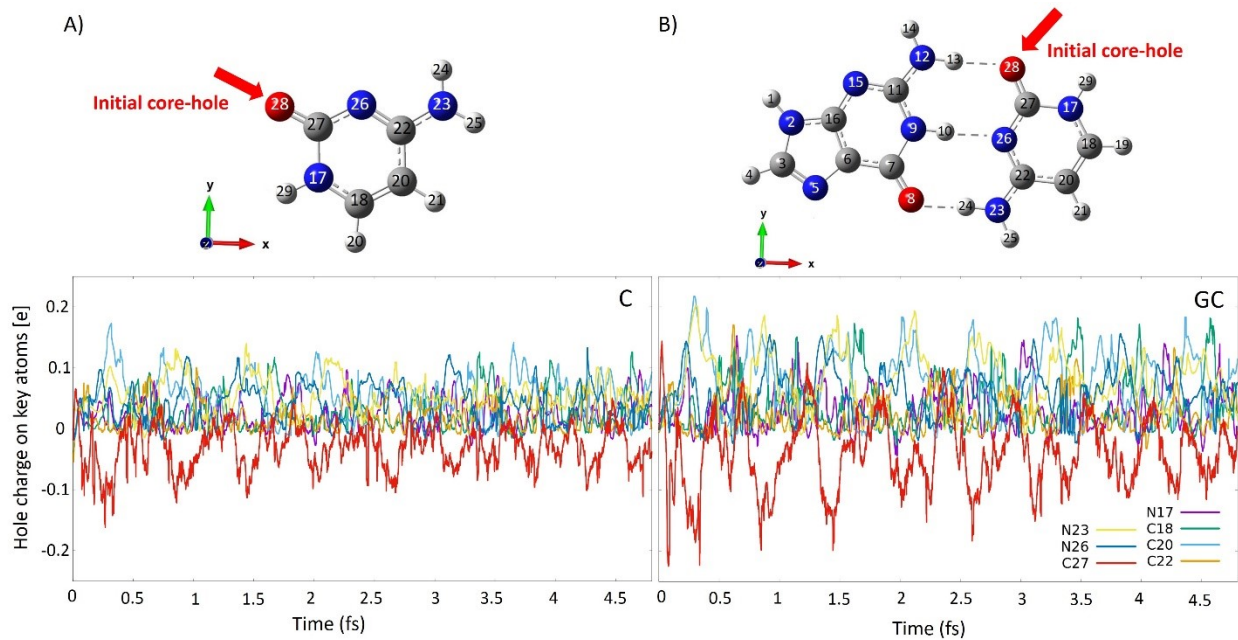


Fig S2. A, B) Time-dependent Bader hole charges on key atoms of C, GC cation after core ionization of oxygen at O28 site (O28).

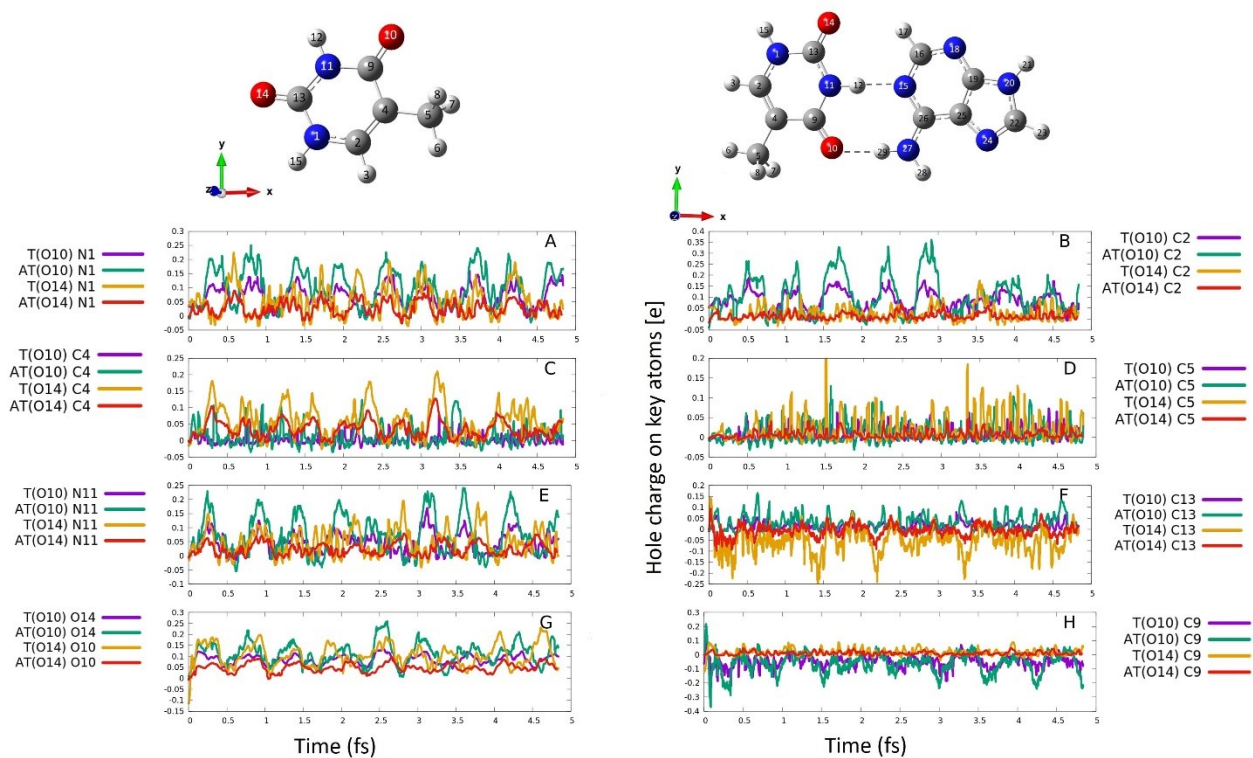


Fig S3. A-H) Time-dependent Bader hole charges on key atoms of T, and AT cation after core ionization of O10, and O14 at T site.

ACFs

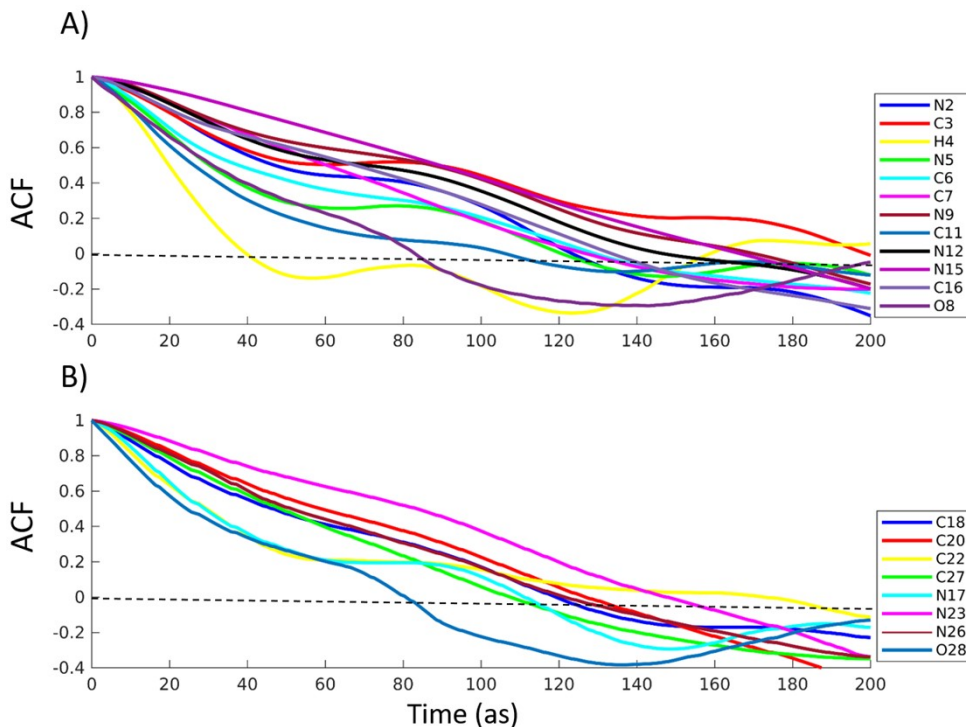


Fig. S4: A, B) ACFs of time-dependent Bader hole charges on key atoms of GC cation after core ionization of oxygen at G (O8), C (O28) site (according to the Fig. 3).

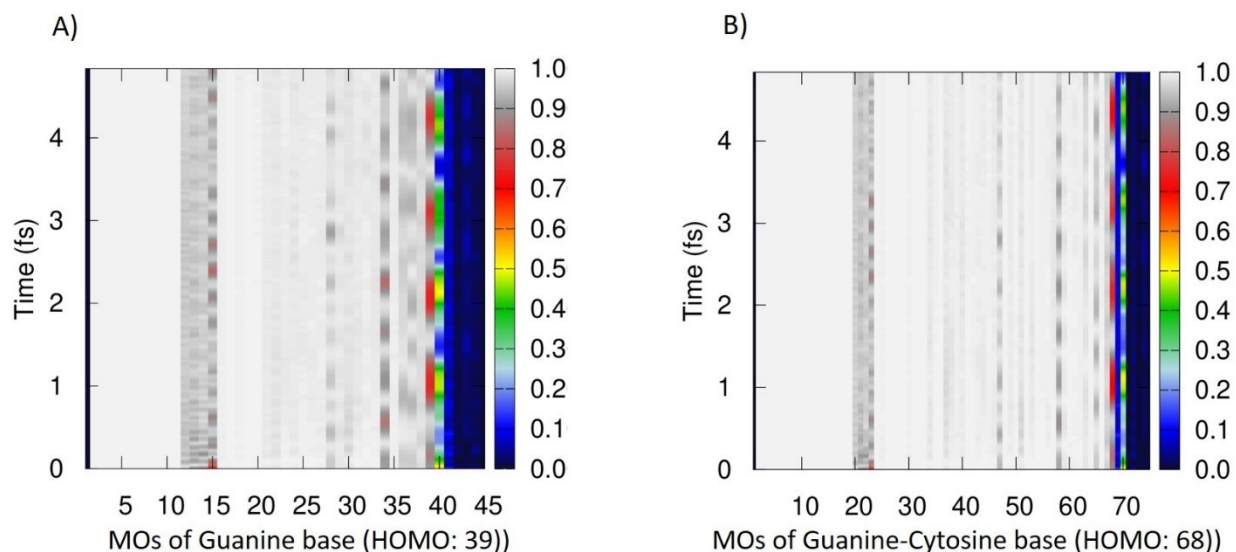
Molecular orbitals (MOs) occupation pattern

The time evolution and oscillations of all MOs occupation following sudden ionization at the oxygen K-edge for isolated DNA bases and their base pair are shown in panels (A) and (B) of Figure S5-S8. For a better comparison, the oscillation pattern of MOs with the largest variation of occupation numbers (the most contributed MOs) is represented at panel C, D for single base, and base pair, respectively.

The spectra of MOs occupation for G, and GC cations following an impulse core-electron ionization at the oxygen site of guanine are shown in Fig. S5. As seen at time=0 in both MOs occupation spectra, the initial hole is created in O1s orbital (MO=1). The respective occupation number stays unchanged at all times. With looking to the whole range of orbitals evolution in later times, it is clearly seen many valence orbitals are involved in the core dynamics. The occupation of MOs that contribute with more than 0.1e throughout the 5 fs hole dynamics are depicted separately in Fig. S5 (A), and (B) for G and GC structures. The dominant valence MOs involved in the case of single guanine are 15, 39 (the highest occupied molecular orbital (HOMO)), 34 (HOMO-5), and the lowest occupied molecular orbital (LOMO) 40. The

similar role is played in GC base pair by 23, 58, 68(HOMO), and 70 (LUMO+1) MOs. These orbitals have relatively similar energies. We may conclude that valence electrons migrate in the similar energy paths for single G and GC base pair triggered by the ionization of the same core orbitals. In panel C/D of Fig. S5, the oscillation patterns of 15/23, 34/58, 39/68, 40/70 MOs occupation for G/GC cations appear very similar. Among these valence orbitals, strong signature of hole oscillation is observed in 39,40 pair of G with 4.35 eV (0.95 fs) energy difference and 68,70 pair of GC with 5.20 eV (0.79 fs). In general, the core electron ionization at oxygen site of guanine is induced an attosecond charge migration at valence MOs. In the case of isolated G (GC base pair), significant hole density exchange happens between 39: HOMO (68: HOMO), and 40: LUMO (70: LUMO+2). However, the trend of CM dynamics pattern in individual G is similar to what we found for the GC base pair.

As one can see in the other spectrum, interestingly, the oscillation amplitude of the most contributed MOs increases from single C/T to the GC/AT pair at Fig. S6/S7, while the oscillation period remains nearly similar for both structures. It is nicely seen in Fig. S8 that the amplitude of oscillation decreases from single T to AT after ionization of upper oxygen (O10) of thymine which is not hydrogen bonded with Adenine.



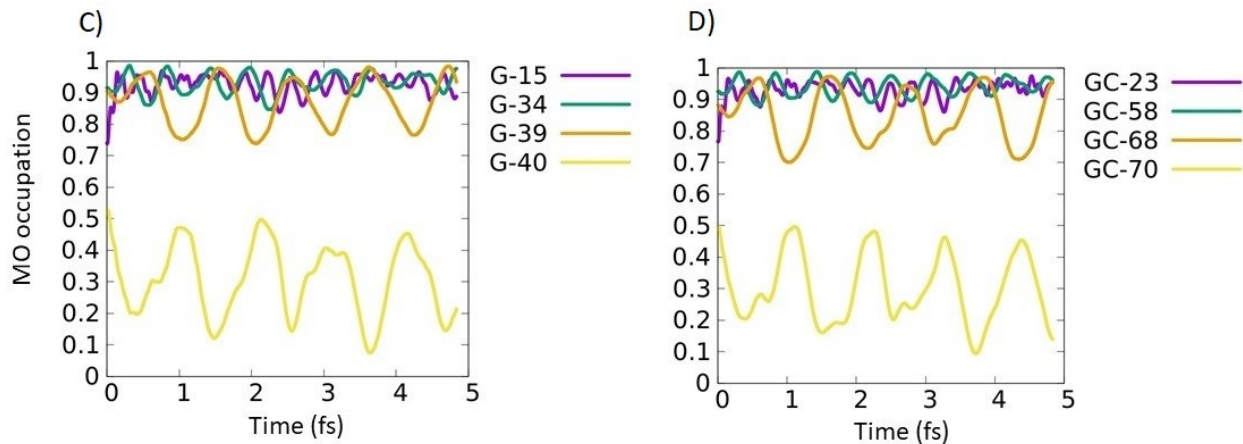


Fig S5. A, B) Time evolution of the molecular orbital occupation of G/GC structures in the cationic state; C, D) Time evolution of the selected most contributed MOs of G/GC after core ionization of O8.

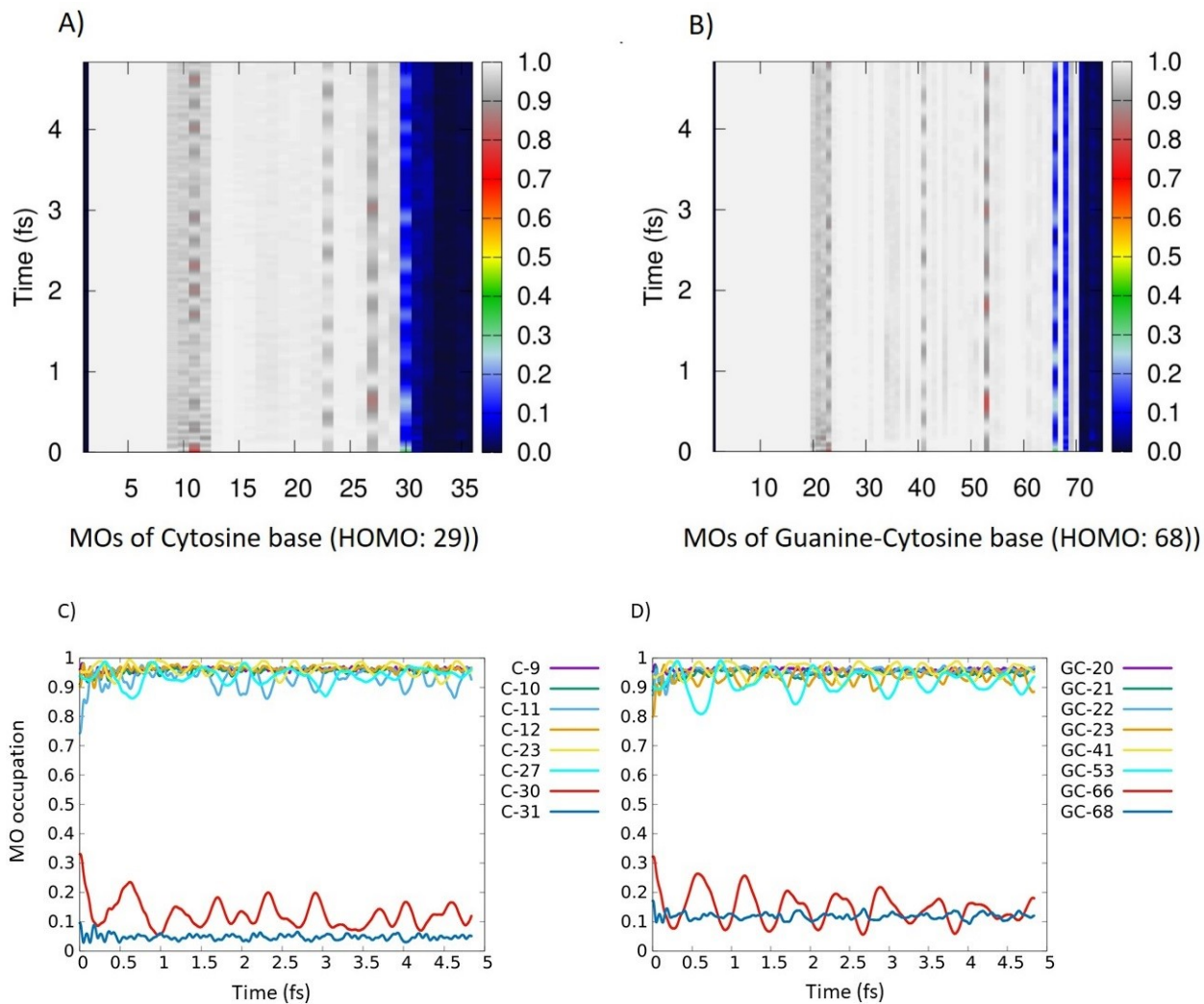


Fig S6. Same as Figure S5 but for C/GC after core ionization of O28.

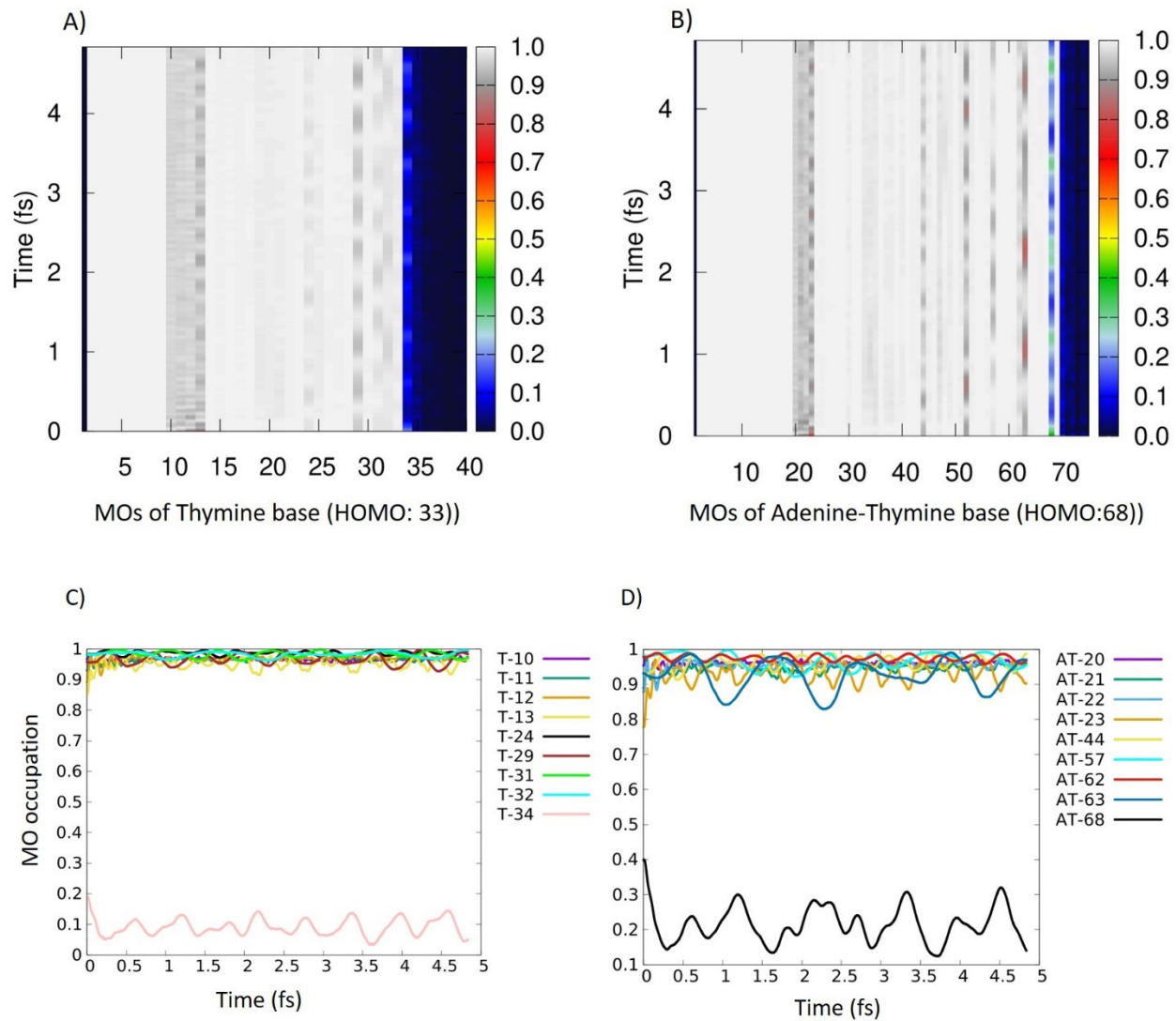


Fig S7. Same as Figure S5 but for T/AT after core ionization of O10.

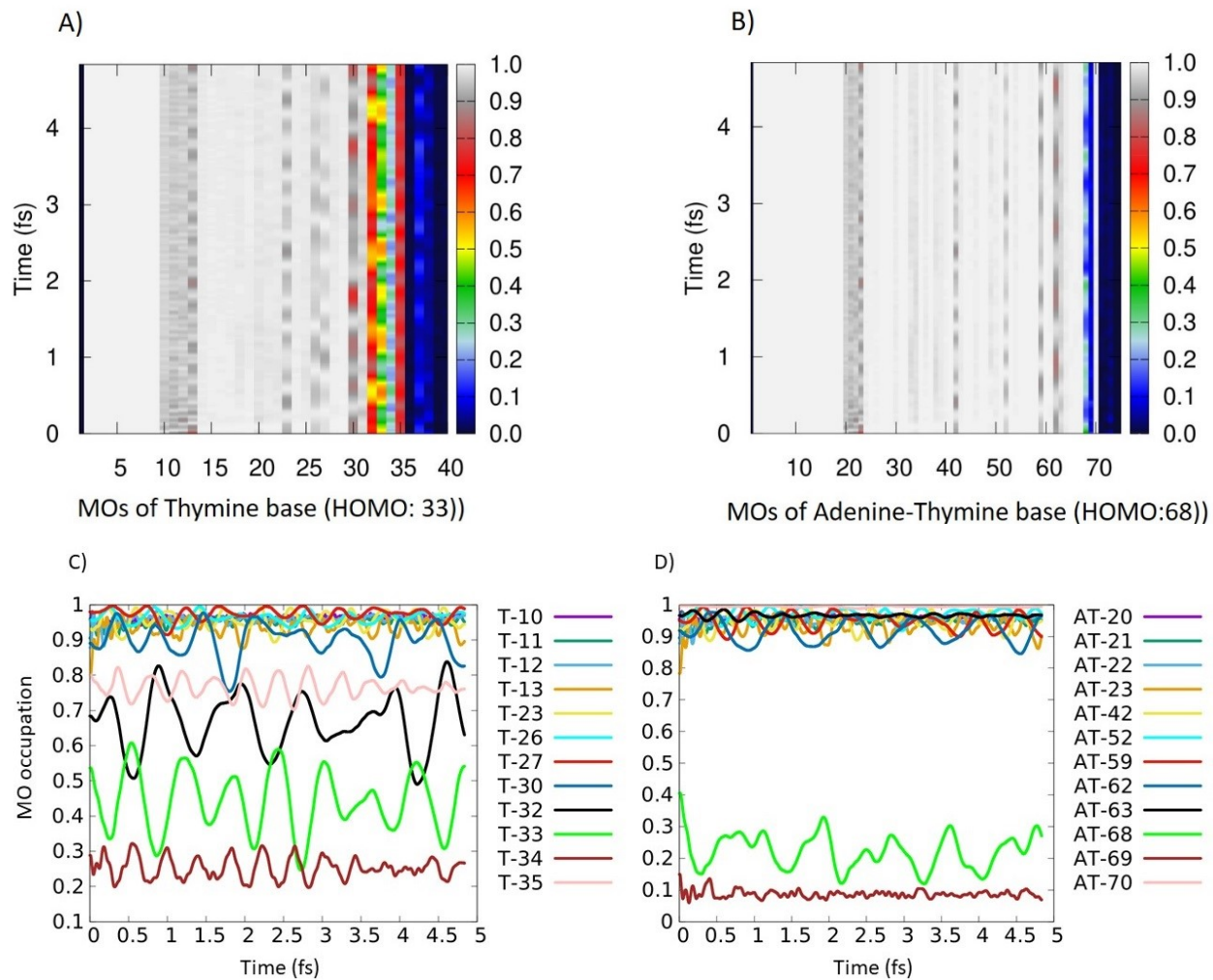


Fig S8. Same as Figure S5 but for T/AT after core ionization of O14.