Electronic Supplementary Information

Ultrafast Fragmentation of Highly-Excited Doubly-Ionized Deoxyribose: Role of the Liquid Water Environment

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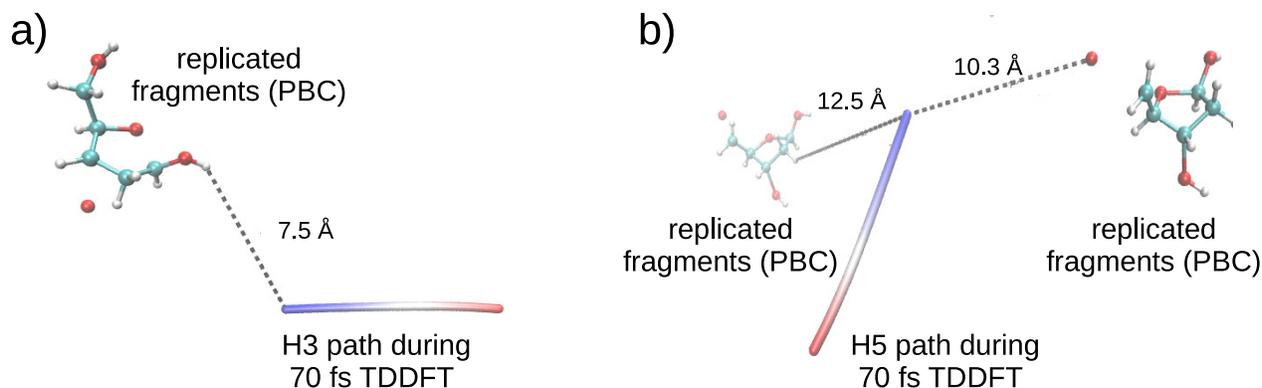
Fig. S1 Emitted H atoms trajectories during a 70 fs TD-DFT MD initiated by removing two electrons from a) MO2 and b) MO3 of isolated DR. The replicated fragments closest to the H atoms at the end of its path are also shown.

Prolongating Ehrenfest molecular dynamics by switching to Born Oppenheimer molecular dynamics

In pure liquid water, H_2O^{2+} molecules were shown to explode into three atomic fragments in less than 4 fs, whatever the ionized orbital [1]. In the case of uracil (U) [2, 3] or deoxyribose (DR), fragmentation was found to span over tens to hundreds of femtoseconds. The time dependent Density Functional Theory (TD-DFT) method is however limited to tens of femtoseconds, so we then switch to ground-state Born-Oppenheimer (BO) molecular dynamics (MD). When switching from TD-DFT to BO MD, the geometry (atomic positions and velocities) is kept unchanged, while the electronic structure is optimized to reach the BO surface, leading to a slight redistribution of the electronic cloud.

In the case of isolated DR^{2+}, following the protocol developed for isolated U^{2+} [2], Ehrenfest molecular dynamics were propagated long enough to ensure that the fragmentation pattern remained unchanged during the ensuing BOMD.[1] In the case of aqueous DR^{2+}, the double charge was initially localized on one of the DR oxygen atoms, which is ejected in less than 10 fs. The change in the electron density at the end of the 62 fs TD-DFT MD and when the system is set in its fundamental electronic state, is thus partly localized in the liquid water environment, as shown in Fig. S2.

Regarding indirect effects, Ehrenfest molecular dynamics were propagated for 10 to 20 fs. This enables modeling the Coulomb explosion of H_2O^{2+} and the first interactions of its atomic fragments. Sugar damage however often begins after tens of femtosecond, as it is initiated either by collisions with the hydrogen atoms or through hydrogen abstraction by the oxygen atoms (see Tables S4 and S5). It was therefore investigated in the framework of BO MD, in which the system wave function is set in its fundamental state. It is however worth noticing that the dissociation of a CO bond by hydrogen atom impact was here modeled using TD-DFT MD (molecules D4). Also, hydrogen abstraction by an oxygen atom was shown to occur both along Ehrenfest and BO dynamics (molecule A1), despite the difference in the oxygen atom's electronic state [4].

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[1]It was neither possible for orbital MO3, because H5 exited the box at $t \simeq 70$ fs (see Fig. S1), nor for orbital MO1, because of a late intramolecular hydrogen transfer (see Table S1).
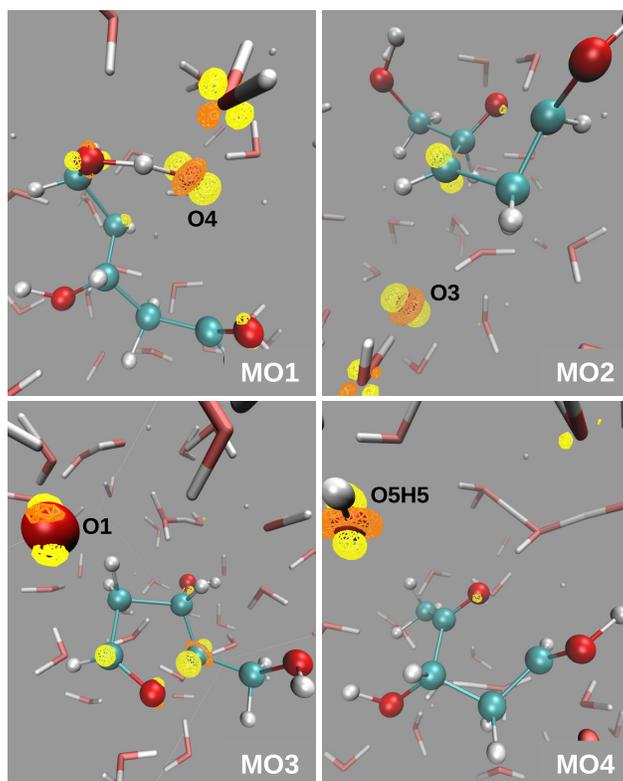
Fig. S2 Trajectories initiated from an electronic configuration, where two electrons were removed from one of the four deepest MO of a desoxyribose molecule embedded in liquid water (MO1 to MO4). Difference between the electronic density of the fundamental state wave function and that of the TD-DFT wave function at t = 62 fs. Positive (orange contour) and negative (yellow contour) isovalues of 0.03.

References

[1] I. Tavernelli, M.-P. Gaigeot, R. Vuilleumier, C. Stia, M.-A. Hervé du Penhoat, and M.-F. Politis. Time-dependent density functional theory molecular dynamics simulations of liquid water radiolysis. *ChemPhysChem*, 9(14):2099 – 2103, 2008.

[2] P. López-Tarifa, M.-A. Hervé du Penhoat, R. Vuilleumier, M.-P. Gaigeot, I. Tavernelli, A. Le Padellec, J.-P. Champeaux, M. Alcamí, P. Moretto-Capelle, F. Martín, and M.-F. Politis. Ultrafast nonadiabatic fragmentation dynamics of doubly charged uracil in a gas phase. *Physical Review Letters*, 107(2):023202 – 023205, 2011.

[3] Pablo López-Tarifa, Marie-Pierre Gaigeot, Rodolphe Vuilleumier, Ivano Tavernelli, Manuel Alcamí, Fernando Martín, Marie-Anne Hervé du Penhoat, and Marie-Françoise Politis. Ultrafast damage following radiation-induced oxidation of uracil in aqueous solution. *Angewandte Chemie International Edition*, 52(11):3160–3163, 2013.

[4] Marie-Anne Hervé du Penhoat, Nely Rodríguez Moraga, Marie-Pierre Gaigeot, Rodolphe Vuilleumier, Ivano Tavernelli, and Marie-Françoise Politis. Proton collision on deoxyribose originating from doubly ionized water molecule dissociation. *The Journal of Physical Chemistry A*, 122(24):5311–5320, 2018. PMID: 29846073.

Table S1 Isolated DR fragmentation after removing two electrons from selected molecular orbitals. Left: Molecular orbitals and time of the switch from TD-DFT to BO MD. Middle: Fragmentation steps and species formed at the end of the BO MD. The text in gray corresponds to events occurring during the BO MD. Right: Geometry at the end of the TD-DFT MD propagation.

MO removed (switch time)	Time (fs)	Events	Fragments at end of the TDDFT MD
MO1 (135 fs)	10.5	(1) C1 – O1 bond dissociation	$CH_2OH-CH^{+0.87} + CHOH-CH_2-CHO^{+1.01} + OH^{+0.12}$
	15.3	(2) C4 – O4 bond dissociation	
	65.1	(3) C3 – C4 bond dissociation	
	195	(4) H5'' transfer from C5 to C4	
		Fragments after 121 fs BOMD :	
		$CHOH-CH_2^{+0.78} + CHOH-CH_2-CHO^{+1.00} + OH^{+0.22}$	
MO2 (70 fs)	2.5	(1) O3 – H3 bond dissociation	$CH_2OH^{+0.48} + CHO-CH-CH_2-CHOH^{+1.23} + O^{+0.05} + H^{+0.24}$
	7.6	(2) C3 – O3 bond dissociation	
	30.6	(3) C1 – O4 bond dissociation	
	58.7	(4) C4 – C5 bond dissociation	
		Fragments after 145 fs BOMD (without H3) :	
		$CH_2OH^{+0.85} + CHO-CH-CH_2-CHOH^{+1.06} + O^{+0.08}$	
MO3 (70 fs)	2.4	(1) O5 – H5 bond dissociation	$CH_2-CH-CH-CH_2-CHOOH^{+1.70} + OH^{+0.08} + O^{+0.12} + H^{+0.10}$
	7.2	(2) C5 – O5 bond dissociation	
	40.9	(3) C3 – O3 bond dissociation	
	43.0	(4) C4 – O4 bond dissociation	
	116	(5) C1 – O1 bond dissociation	
		Fragments after 121 fs BOMD (without H5) :	
		$CH_2-CH-CH-CH_2-CHO^{+1.24} + OH^{+0.19} + OH^{+0.35} + O^{+0.22}$	
MO4 (113 fs)	10.3	(1) C4 – O4 bond dissociation	$CH_2OH-CH-CHOH^{+1.16} + CH_2-CO^{+0.65} + H_2O^{+0.19}$
	33.3	(2) C2 – C3 bond dissociation	
	65.7	(3) C1 – O1 bond dissociation	
	93.6	(4) H1'' abstraction from C1 by OH	
		Fragments after 121 fs BOMD :	
		$CH_2OH-CH-CHOH^{+1.11} + CH_2 - CO^{+0.68} + H_2O^{+0.21}$	
MO5 (139 fs)	28.2	(1) C1 – O4 bond dissociation	$CH_2OH^{+0.59} + CHO-CHOH^{+0.87} + CH_2-CHOH^{+0.55}$
	62.6	(2) C4 – C5 bond dissociation	
	67.7	(3) C2 – C3 bond dissociation	
		Fragments after 121 fs BOMD :	
		$CH_2OH^{+0.81} + CHO-CHOH^{+0.74} + CH_2-CHOH^{+0.45}$	
MO16 (70 fs)	109	(1) C4 – C5 bond dissociation	
	147	(2) C1 – O4 bond dissociation	
		Fragments after 145 fs BOMD :	
		$CH_2OH^{+0.97} + CHO-CHOH-CH_2-CHOH^{+1.03}$	
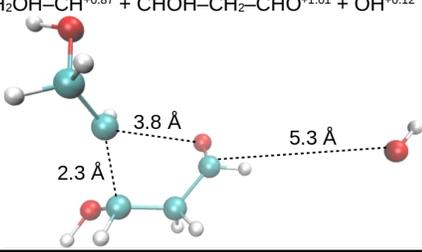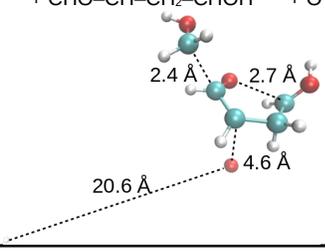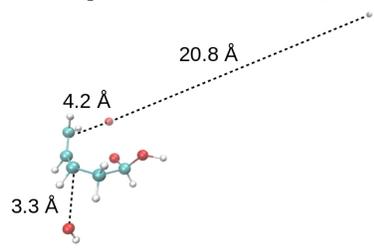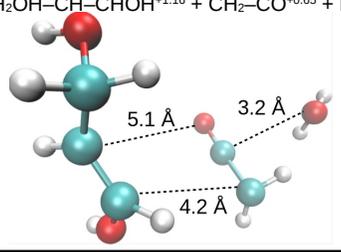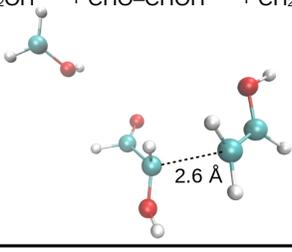
Table S2 Hydrated DR fragmentation after removing two electrons from selected molecular orbitals. Left: Molecular orbitals and time of the switch from TD-DFT to BO MD. Middle: Fragmentation steps. The text in gray corresponds to transient events. Right: Geometry at the end of the 1 ps BO MD propagation.

MO removed (switch time)	Time (fs)	Events	Products at the end of the BO MD
MO1 (61.7 fs)	9.0	(1) C1 – O4 bond dissociation	**Sugar :** $CH_2O + CHO – CHOH – CH_2 – CHO$ $(CH_2O + C_4H_6O_3)$ **Water :** $2 H_3O^+$
	9.5 – 84	(*) C4 – O4 transient bond dissociation	
	29.3	(2) O1 – H1 bond dissociation	
	60 – 329	(**) O4 – H5 transient bond formation	
	66.1	(3) O5 – H5 bond dissociation	
	110	(4) C4 – C5 bond dissociation	
MO2 (61.7 fs)	2.6	(1) O3 – H3 bond dissociation	**Sugar :** $CH_2OH – CO – CH_2 – CH_2 – CHO$ $(C_5H_8O_3)$ **Water :** $H_2O_2 + 2 H_5O_2^+$
	7.0	(2) C3 – O3 bond dissociation	
	51.8	(3) C1 – O4 bond dissociation	
	65.5	(4) O1 – H1 bond dissociation	
	82 – 84	(5) H4'' intramolecular transfer from C4 to C3	
MO3 (61.7 fs)	2.3	(1) O1 – H1 bond dissociation	**Sugar :** Loss of O1H1 $(C_5H_9O_3^+)$ **Water :** $H_2O_2 + H_3O^+$
	7.5	(2) C1 – O1 bond dissociation	
	50 – 664	(*) C4 – O4 transient bond dissociation	
MO4 (61.7 fs)	2.4 – 40.2	(*) O5 – H5 transient bond dissociation	**Sugar :** $CH_3 – CO – CO – CH_2 – CHO$ $(C_5H_6O_3)$ **Water :** $2 H_3O^+$
	8.6	(1) C5 – O5 bond dissociation	
	41 – 43	(2) H4'' intramolecular transfer from C4 to C5	
	48.6	(3) C1 – O4 bond dissociation	
	90.5	(4) O1 – H1 bond dissociation	
	236.2	(5) C3 – H3' bond dissociation	
	259	(6) O3 – H3 bond dissociation	
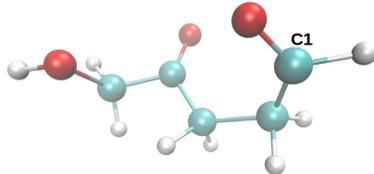
Table S3 Parameters of the hydrogen bonds between DR and water molecules: Distance between the hydrogen atom and the oxygen atom accepting the hydrogen bond (O_A). Angle at the oxygen atom donating the hydrogen (O_D).

H_2O^{2+}	DR group	$H \cdots O_A$ distance (Å)	$\widehat{O_A O_D}H$ Angle (°)
HB acceptor from DR group			
A1	O5H5	1.56	7.84
A2	O1H1	1.67	19.54
A3	O3H3	1.83	13.98
HB donor to DR group			
D1	O3	1.99	23.72
D2	O1	2.17	24.48
D3	O4	1.79	3.85
D4	O5	1.77	14.60
D5	O5	2.22	31.62
D6	O3	2.03	13.51

Table S4 Hydrated DR damage after removing two electrons from the 2A1 MO of water molecules donating an HB to the sugar. Left: Water molecules and time of the switch from TD-DFT to BO MD. Middle: Fragmentation steps. The atoms labeled in red initially belonged to the doubly-ionized water molecule, those in blue belong to other water molecules. Right: Geometry at the end of the 1 ps BO MD propagation.

Water molecule (switch time)	Time (fs)	Events involving DR	Products at the end of the BO MD
D1 (9.92 fs)	230 299 444	(1) H4'' abstraction by **O** (2) C1 – O4 bond dissociation (3) O1 – H1 bond dissociation	**Sugar :** $CH_2OH – CO – CHOH – CH_2 – CHO$ ($C_5H_8O_4$) **Water :** $2\ H_3O^+$
D2 (10.45 fs)	38.7 157 – 160 170 429 619 659	(1) H2'' abstraction by **H** (2) H3' intramolecular transfer from C3 to C2 (3) O3 – H3 bond dissociation (4) **H** addition to O4 (5) C1 – O4 bond dissociation (6) O1 – H1 bond dissociation	**Sugar :** $CH_2OH – CHO$**H**$ – CO – CH_2 – CHO$ ($C_5H_8O_4$) **Water :** $H_2O_2 + H_2 + 2\ H_3O^+$
D3 (9.24 fs)	33.4 116 127 165	(1) O1 – H1 bond dissociation (2) C3 – C4 bond dissociation (3) O3 – H3 bond dissociation (4) C1 – O4 bond dissociation	**Sugar :** $CH_2OH – CHO + CHO – CH_2 – CHO$ ($C_2H_4O_2 + C_3H_4O_2$) **Water :** $2\ H_3O^+$
D4 (19.59 fs)	12.6 45.9 – 46.1 68.2 150	(1) C5 – O5 bond dissociation after **H collision** (2) H4'' intramolecular transfer from C4 to C5 (3) C1 – O4 bond dissociation (4) O1 – H1 bond dissociation	**Sugar :** $CH_3 – CO – CHOH – CH_2 – CHO$ ($C_5H_8O_3$) **Water :** $H_2O_2 + 2\ H_3O^+$
D6 (20.08 fs)	105 305	(1) O3 – H3 bond dissociation (2) **H** addition to O3	**Sugar :** intact **Water :** $H_2O_2 + 2\ H_3O^+$
D5 (9.92 fs)			**Sugar :** intact **Water :** $H_2O_2 + 2\ H_3O^+$
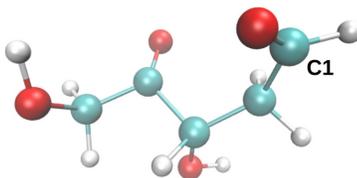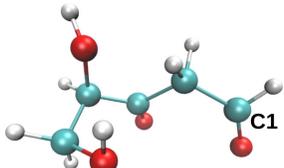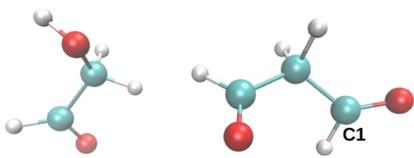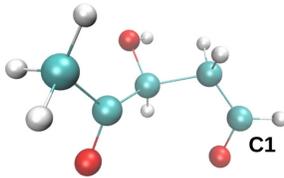
Table S5 Hydrated DR damage after removing two electrons from the 2A1 MO of water molecules accepting an HB from the sugar. Left: Water molecules and time of the switch from TD-DFT to BO MD. Middle: Fragmentation steps. The atoms labeled in red initially belonged to the doubly-ionized water molecule, those in blue belong to other water molecules. Right: Geometry at the end of the 1 ps BO MD propagation.
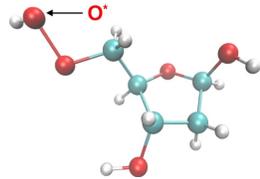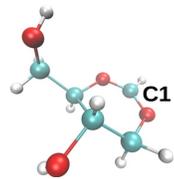
Water	Time (fs)	Events involving DR	Products at the end of the BO MD
A1 (9.92 fs)	11.3 69.3	(1) H5 abstraction by **O** (2) O5 – **O** bond formation	**Sugar :** Hydroperoxide group on C5 ($C_5H_{10}O_5$) **Water :** 2 H_3O^+
A2 (9.92 fs)	63.6 115 168	(1) H1 abstraction by **O** (2) C1 – C2 bond dissociation (3) C2 – O1 bond formation	**Sugar :** ($C_5H_9O_4^+$) **Water :** H_3O^+
A3 (9.92 fs)			**Sugar :** intact **Water :** H_2O_2 + 2 H_3O^+