Supporting Information

Ultrafast Proton and Electron Dynamics in Core-Ionized Hydrated Hydrogen Peroxide: Photoemission Measurements with Isotopically Substituted Hydrogen Peroxide

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**Figure SI-1:** Schematic of the two autoionization channels of the transient proton-transferred anionic structure, \([\text{HO}^* \cdots \text{H}^+ \cdots \text{H}_2\text{O}]_{\text{aq}}\), formed upon core-level ionization of neat water (1, top left). The asterisk denotes the highly excited anionic state. Route 3 depicts the ICD process, and route 2 refers to the Auger process with subsequent proton hop. Analogous transients and reactive species will be occurring upon oxygen 1s ionization of hydrogen-peroxide aqueous solution. The figure has been adapted from ref 1.

**SI 2: The role of initial conditions**

The core-excited state is fast decaying (with the estimated core-hole lifetime around 4 fs) and the potential energy surface around the Franck-Condon point is rather flat. As a result, the dynamics of the proton transfer is not dominated by the slope of the potential energy surface but it rather reflects the dispersion of the initial wavepacket. This is demonstrated in Figure SI-2. We compare the simulations with initial velocities set to zero (dispersion of the wavepacket is initially blocked) with the simulation where the initial velocities are properly sampled. It is clearly seen that the proton transfer is much less pronounced when the wavepacket dispersion is disabled. The figure also shows how the proton transfer is controlled by the O···O distance.
Figure SI-2: Comparison of hydrogen atom distributions along the O-H distance indicating the proton transfer from H$_2$O$_2$ to H$_2$O in the asymmetric H$_2$O$_2$(H$_2$O)$_2$ complex. The distribution at time $t = 0$ fs is shown as full black line while the distributions after 4 fs long dynamics are shown as dashed lines. The black dashed line is the distribution resulting from the Wigner sampling of initial velocities. The green line is the distribution from the simulations with initial velocities set to zero. The blue line represents the simulations with Wigner initial velocities and with water molecules closer to hydrogen peroxide by 0.15 Å.

SI 3: Proton transfer between water and hydrogen peroxide

Water can act both as the hydrogen bond acceptor and hydrogen bond donor. The proton transfer between the two moieties is possible in both cases. In the main text, we focused on the proton transfer between hydrogen peroxide (as donor) and water. The barrierless potential energy surface for initially ionized hydrogen peroxide is shown in Figure SI-2B. Figure SI-2A shows that also the proton transfer from water to hydrogen peroxide is possible with only a small barrier.
Figure SI-3: Potential energy surfaces of all core ionized states along the respective O-H coordinate in H$_2$O$_2$(H$_2$O)$_2$ asymmetric complex. The water molecules were shifted with respect to the equilibrium geometry by 0.15 Å closer to hydrogen peroxide to better represent the structures find in solution. Panel A shows proton transfer from the donor water molecule to hydrogen peroxide while panel B shows proton transfer from the hydrogen peroxide to acceptor water molecule. Black lines correspond to the core ionized state with charge localized at the acceptor water molecule, red lines corresponds to the charge localized on the donor water molecule and green and blue lines correspond to charge localized on the hydrogen peroxide.