Supporting Information

Imaging intramolecular hydrogen migration with time- and momentum-resolved photoelectron diffraction

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Fig. S.1 represents the statistics extracted for the hydrogen migration times in the molecular dynamics simulations. The calculations were performed with internal excitation energy $E_{exc} = 10 \text{ eV}$ and we have analyzed the time required for single- and double-hydrogen migration (SHM and DHM respectively). We considered that one hydrogen atom has migrated when the distance O – H reaches 1 Å for the first time in the corresponding trajectory. In the case of H_3^+ formation, three H atoms are involved and different dynamical processes as roaming and scrambling are observed in the trajectories. Furthermore, the H_3^+ that has been formed is rotationally and vibrationally excited. Thus, the criteria for hydrogen migration times in this case is ambiguous and have not been analyzed. Typically a few tens of femtoseconds is enough for the production of H_3^+ .

We have schematically represented in Fig. S.2 the most relevant energetic aspects of the potential energy surface in the different dynamical processes studied in this work. The ionization energy required to produce doubly- and quadruply-charged ethanol has been computed keeping the geometry of the neutral molecule, i.e., assuming a Franck-Condon transition. Among all the pathways through which doubly-ionized ethanol can evolve, we have computed the relative energies for four possible exit channels: (i) no hydrogen migration $C_2H_5O^+ + H^+$, (ii) single-hydrogen migration $C_2H_4^+ + H_2O^+$, (iii) double-hydrogen migration $C_2H_3^+ + H_3O^+$, and (iv) H_3^+ formation $C_2H_3O^+ + H_3^+$. In each channel, further double ionization of the fragment containing oxygen leads to several dissociation possibilities, all of them dominated by Coulomb repulsion of the produced charged species. Snapshots of PA-MFPADs for one representative trajectory of SHM and DMH, and two representative trajectories of H₃⁺ formation are shown in Figs. S.3, S.4, S.5 and S.6, respectively. For H₃⁺, we show a trajectory for the dominant reaction channel in which the hydrogen migrates from $C_2H_2^+$ (~88 % trajectories) and the less important, but still not negligible channel in which hydrogen migrates from OH (~12 % trajectories). We have considered in these figures photoelectron energies of 100 eV and 2.5 keV. The complete movies for the SHM and DHM results shown in Figs. 2 and 3 of the main text are provided in four separate files. The conventions used in these movies are the same as in those figures (see the corresponding captions).



Figure S.1: Hydrogen migration time statistics in molecular dynamics simulations performed for ethanol²⁺ with excitation energy $E_{exc} = 10$ eV. We consider that one H atom has migrated when the O-H distance is smaller than 1 Å for the first time in the trajectory. Left panel: time for the single-hydrogen migration (SHM) in red, and for the first hydrogen migration in double-hydrogen migration (DHM - 1st H) in blue and the sum of both in black bars; we integrated the number of events every 5 fs. Right panel: time for the second hydrogen migration in the double-hydrogen migraton (DHM - 2nd H) in blue bars; we integrated the number of events every 20 fs.



Figure S.2: Critical points in the potential energy surface of ionized ethanol computed at the CCSD(T)/aug-cc-pVTZ level of theory over the geometry optimized with B3LYP/6-31++G(d,p). Vertical ionization potentials from the optimized neutral molecule leading to the doubly and quadruply-charged ethanol are given. Relative energy values are referred to the neutral molecule and corrected using the DFT zero-point-energy.



Figure S.3: Snapshots of PA-MFPADs of one representative trajectory of SHM at photoelectron energies (a) 100 eV and (b) 2.5 keV. The blue arrows indicate the position of the peak associated with hydrogen migration in each time frame. Notice that panel (b) is identical to Fig. 1c of the main text.



Figure S.4: Snapshots of PA-MFPADs of one representative trajectory of DHM at photoelectron energies (a) 100 eV and (b) 2.5 keV. The blue arrows indicate the position of the peak associated with hydrogen migration in each time frame.



Figure S.5: Snapshots of PA-MFPADs for one representative trajectory of H_3^+ for the major reaction channel (~88 % trajectories) with the reaction plane defined by the momentum correlations between H_{mig}^+ , $C_2H_2^+$ (or the sum of CH_m^+ and CH_n^+ with m + n = 2) at photoelectron energies (a) 100 eV and (b) 2.5 keV. The blue arrows indicate the position of the peak associated with hydrogen migration in each time frame.



Figure S.6: Snapshots of PA-MFPADs of one representative trajectory of H_3^+ for the minor reaction channel (~12 % trajectories) with the reaction plane defined by the momentum correlations between H_{mig}^+ , $C_2H_3^+$ (or the sum of CH_m^+ and CH_n^+ with m + n = 3) at photoelectron energies (a) 100 eV and (b) 2.5 keV. The blue arrows indicate the position of the peak associated with hydrogen migration in each time frame.