

## Supplementary Information

# $\text{H}_2\text{O}^+$ and $\text{OH}^+$ Reactivity versus Furan: Experimental Low Energy Absolute Cross Sections for Modeling Radiation Damage

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## 1. Calculation of charge transfer cross sections

In the IOS model, and applying the Franck-Condon approximation, the scattering wave function  $\Psi$  depends on the electronic coordinates,  $\mathbf{r}$  and the distance  $R$  between the center of mass of the reactants. The scattering wave function is expanded on a set of electronic wave functions,  $\chi_j(\mathbf{r}; R)$  (seven in the present calculation) of the (H<sub>2</sub>O-furan)<sup>•+</sup> supermolecule; they are approximate eigenfunctions of the clamped-nuclei Born-Oppenheimer Hamiltonian for the orientation considered.

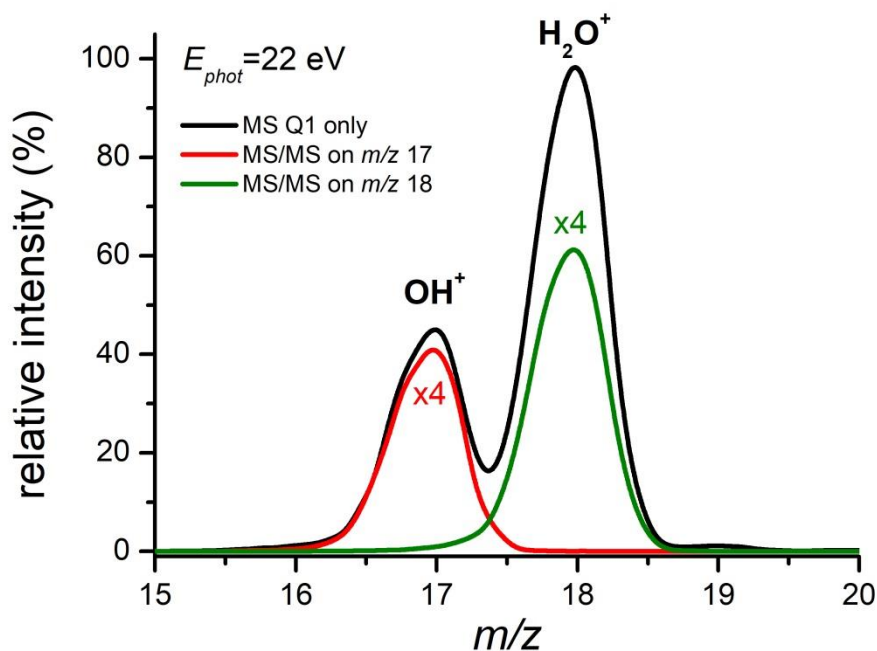
$$\Psi^L(\mathbf{r}, \rho) = \sum_j F_j^L(\rho) \chi_j(\mathbf{r}; R = \rho), \quad (1)$$

where  $\rho$  is a common reaction coordinate that ensures that the expansion fulfills the boundary conditions.  $L$  is the angular momentum quantum number that is introduced in the partial wave expansion of the scattering function. The nuclear wave functions  $F_j^L$  are obtained by substituting the expansion (1) into the stationary Schrödinger equation, which leads to a system of second order differential equations. The number of partial waves depends on the energy of the collisions, reaching in the present case the number of 4700. The total cross section for transition from the initial electronic state  $i$  to the state  $j$  is, for each orientation:

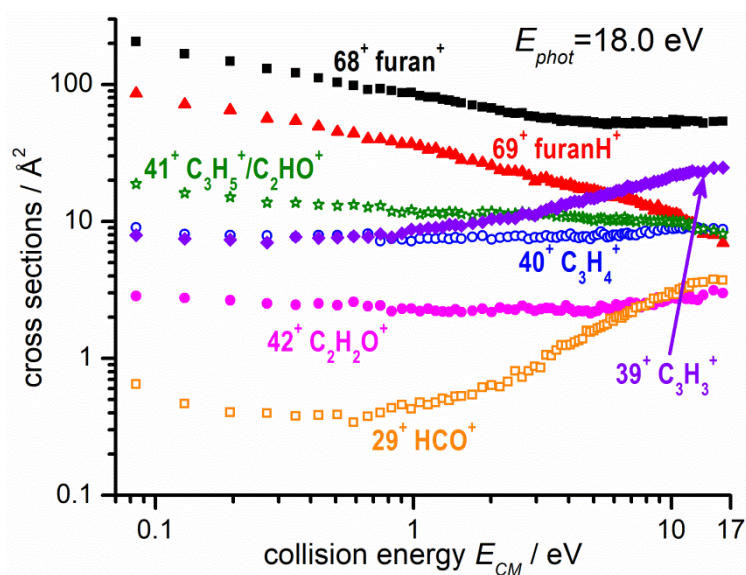
$$\sigma_{ij}(E) = \frac{\pi}{k_i^2} \sum_L (2L + 1) |S_{ij}^L|^2, \quad (2)$$

where  $S$  is the scattering matrix, calculated from the nuclear functions  $F_j^L$ , and  $k_i$  is the initial momentum. The total CT cross section is then obtained by adding the cross sections for transitions to the channels where the functions  $\chi_j(\mathbf{r}; R)$  dissociate into furan<sup>+</sup> + H<sub>2</sub>O.

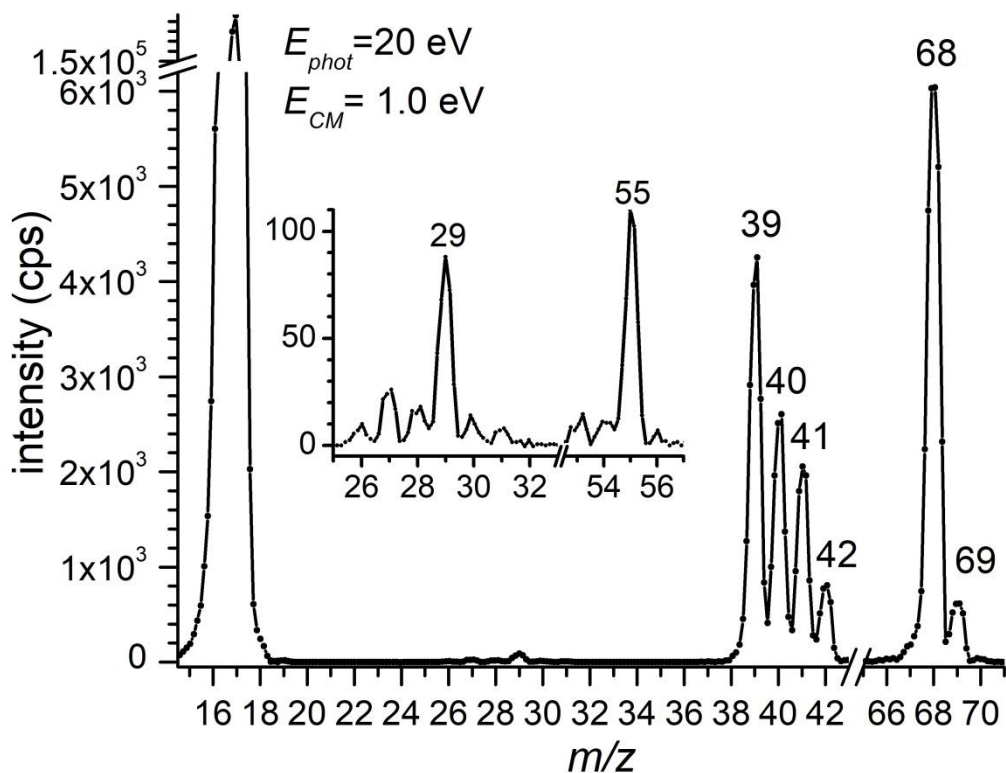
## 2. Supplementary figures.



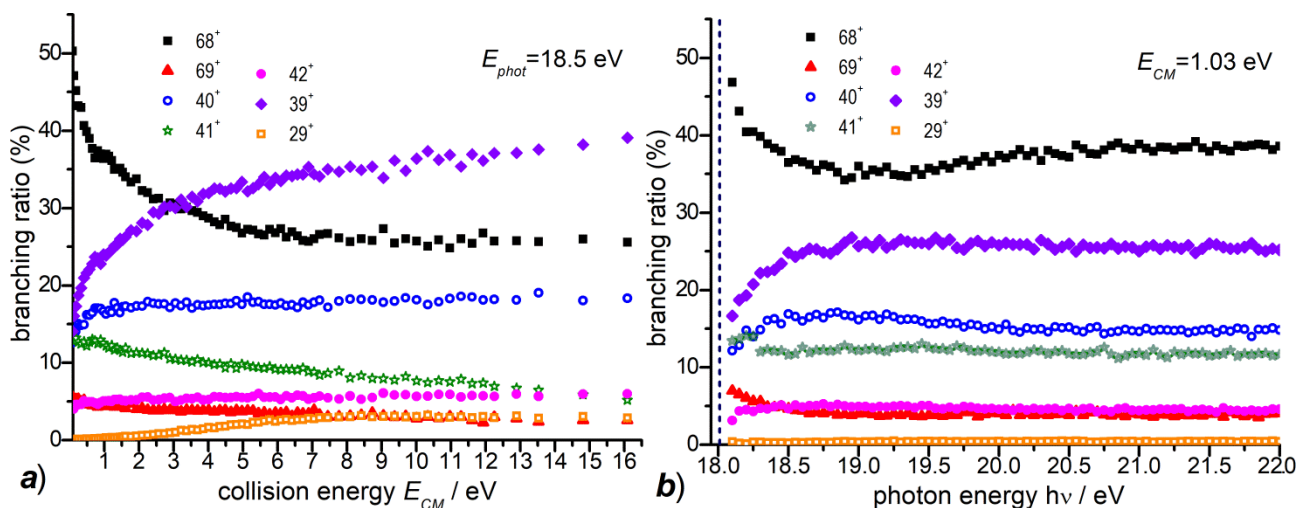
**Figure S1.** Mass spectra of the nascent ions (measured with Q1 in total transmission and Q2 is in mass selection, black line), of the mass selected parent ions  $\text{OH}^+$  at  $m/z$  17 (MS/MS, Q1 on  $m/z$  17, red line) and of the mass selected parent ions  $\text{H}_2\text{O}^+$  at  $m/z$  18 (MS/MS, Q1 on  $m/z$  18, green line). The mass spectra were recorded at the photon energy  $E_{phot}=22 \text{ eV}$  to ensure both ionization and dissociative ionization of  $\text{H}_2\text{O}$ . Relative intensities are normalized to the most intense peak ( $m/z$  18). For clarity reasons red and green lines have been plotted using a multiplication factor of 4.



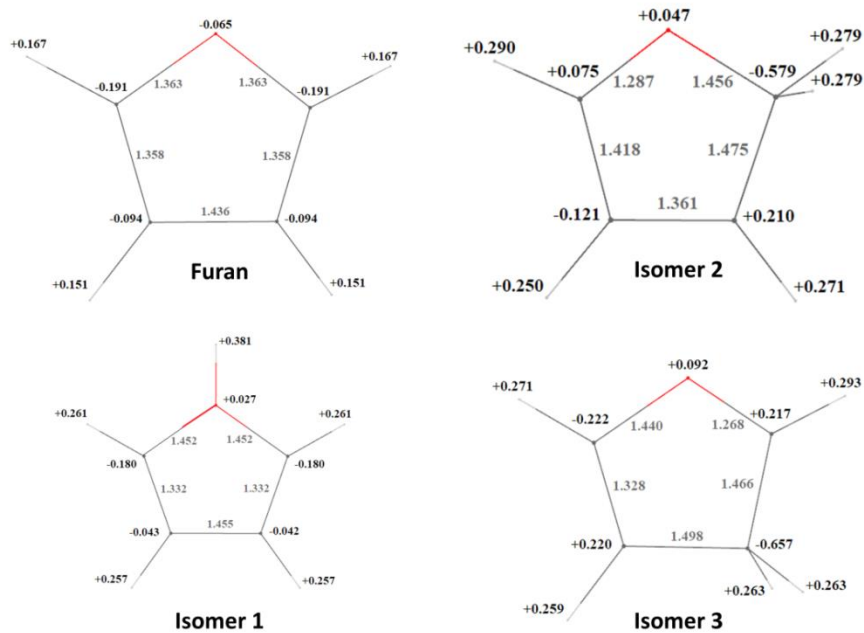
**Figure S2.** Reactive cross sections in log scale for products ( $m/z=69$ ,  $68$ ,  $42$ ,  $41$ ,  $40$ ,  $39$  and  $29$ ) measured as a function of the collision energy ( $E_{CM}$ ) from ion-molecule collision of  $\text{H}_2\text{O}^{++}$  with furan when  $\text{H}_2\text{O}^{++}$  is produced at the photon energy of  $18.0 \text{ eV}$ .



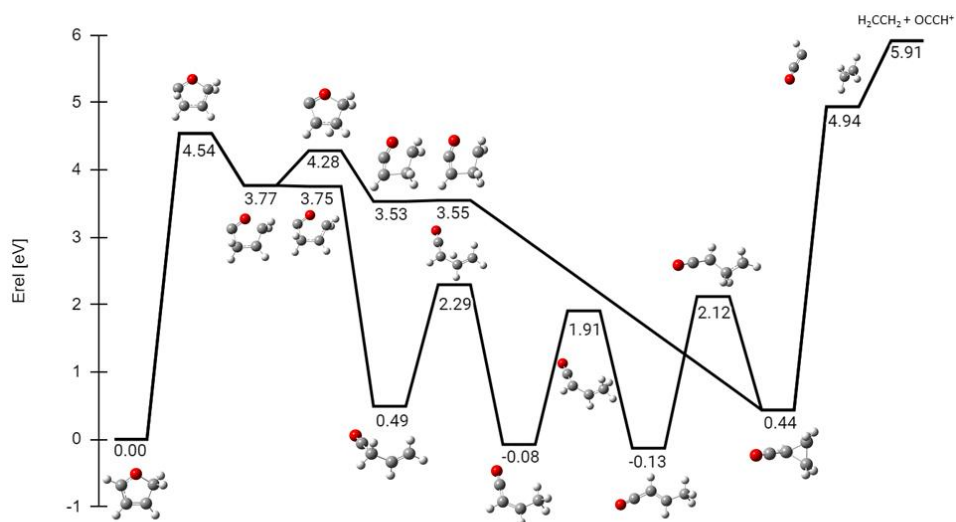
**Figure S3.** Mass spectrum of the products of the reaction between  $\text{OH}^+$  and furan ( $P=5\times 10^{-5}$  mbar) acquired at collision energy  $E_{CM}=1.0$  eV and photon energy 20.0 eV. The inset shows a zoom-in of the  $m/z$  regions 25-33 and 53-57. Intensities are in counts/sec (cps).



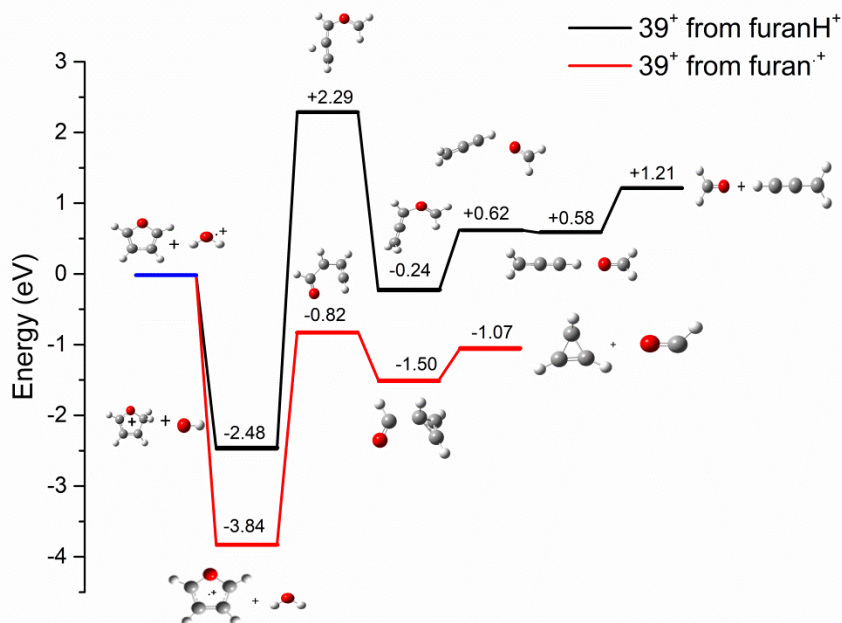
**Figure S4. a)** BRs for the products  $68^+$ ,  $69^+$ ,  $39^+$ ,  $40^+$ ,  $41^+$ ,  $42^+$  and  $29^+$  (see the legend) from the reaction of  $\text{OH}^+$  with furan, measured as a function of the collision energy ( $E_{CM}$ ), at a fixed photon energy of 18.5 eV; **b)** BRs for the same products as in panel **a)** as a function of the photon energy at the fixed  $E_{CM}=1.03$  eV. In all panels, the estimated uncertain of about 20% are not displayed, for sake of clarity.



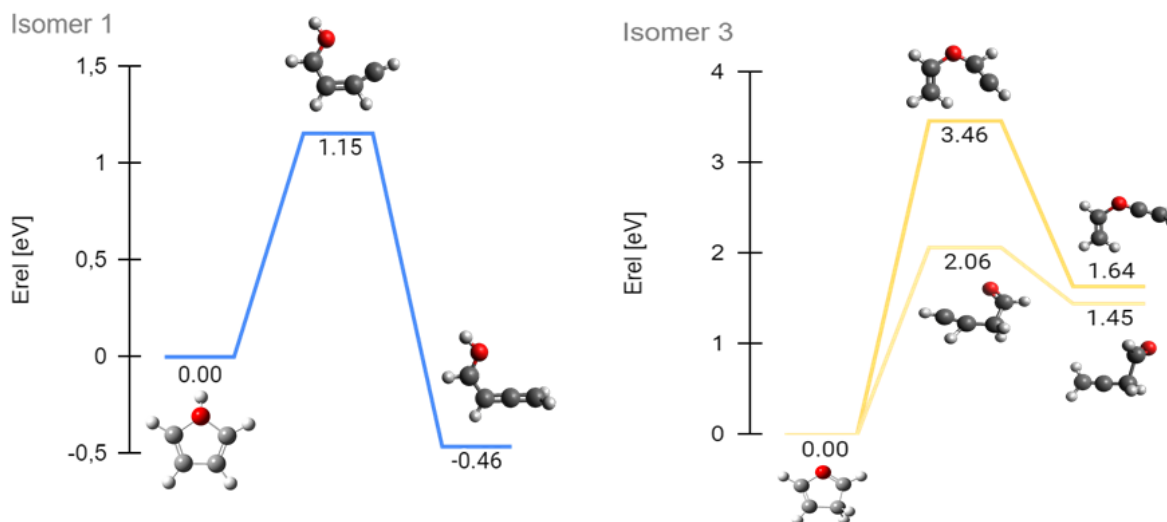
**Figure S5.** Structures of furan and furanH<sup>+</sup> (isomer 1, 2 and 3) optimized at the B3LYP/6-311++G(d,p) level of theory together with bond lengths (in grey) and Mulliken charges (in black).



**Figure S6.** ZPV-corrected relative energy diagram corresponding to the C<sub>2</sub>H<sub>4</sub> loss channels from protonated isomer 2 of furan. Relative energies with respect to isomer 2 (eV) obtained at the B3LYP/6-311++G(d,p) level of theory and with ZPE corrections are indicated for each structure and TS.



**Figure S7.** Comparison of the ZPV-corrected relative energy diagram (eV) for the formation of the fragment ion  $39^+$  from furanH $^+$  and furan $^+$  formed by the ion-molecule reaction of H $_2$ O $^+$  with furan. See Table 1 and reference 40 of the manuscript.



**Figure S8.** ZPV-corrected relative energy diagram of the ring opening from furanH $^+$  isomers **1** and **3**. The relative energies (eV) to isomer **1** and **3** are evaluated at the B3LYP/6-311++G(d,p) level of theory and with ZPE corrections.