Kinematically complete photolysis studies of $\text{H}_2\text{O}^+$ and $\text{H}_3\text{O}^+$ through di-cationic states using FLASH


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Molecular hydrides and their ions are important species in astrophysical models of interstellar plasmas since hydrides are among the first molecules to form in a gas dominated by hydrogen. In particular, the molecular hydrides ions enter as key players in chemical networks to form large molecules [1-2]. Recent results from the Herschel Space Observatory have highlighted this importance of hydrides in the interstellar medium though the direct observations of both oxygen [3] and nitrogen hydrides [4]. Using the TIFF (Trapped Ion Fragmentation with a FEL) setup at the PG2 (Plane Grating monochromator) beam line at FLASH we have recently studied the photolysis of the two fundamental oxygen hydrides $\text{H}_2\text{O}^+$ [5] and $\text{H}_3\text{O}^+$ [6] under ionizing radiation in the form of XUV photons.

With the TIFF experiment, pulses of fast moving ions (keV energies) and photon pulses from FLASH are brought to interact in a crossed beams geometry, and all types of emerging photofragments, i.e. electrons, ions, and neutrals are detected in coincidence for isolated ions. A schematic drawing of the TIFF interaction zone is displayed in Fig. 1. Moreover, the applied detectors (eDET 1-2 and DET 1-3) are time and position resolving which, combined with the crossed beams geometry, allows for the analysis of the momenta of individual fragments. Hence the kinetic energy released for particular fragmentation routes as well as the angular correlations in the fragmentation process can be determined.

For the $\text{H}_2\text{O}^+$ radical ion [5], XUV photoionization into di-cationic states ($\text{H}_2\text{O}^{2+}$) was thus demonstrated to yield mainly the dissociation channels $\text{OH}^+ + \text{H}^+$ and $\text{O}^0 + 2\text{H}^+$, while a smaller contribution was identified from $\text{O}^+ + \text{H}_2$. At the photon energies of 35 eV and 57 eV applied in this experiment, kinematically complete analyses of dissociative photoionization events revealed for instance that the OH$^-$-fragments from the OH$^+ + \text{H}^+$ channel most often emerges in...
electronically excited states. For the $\text{H}_3\text{O}^+$ [6], the major fragmentation channels were found to be $\text{H}_2\text{O}^+ + \text{H}^+$, $\text{OH}^0 + 2\text{H}^+$, and $\text{OH}^- + \text{H}^+ + \text{H}^0$. Interestingly, also for the $\text{H}_3\text{O}^+$ ion, the detailed kinematical analysis showed the emerging water radicals ($\text{H}_2\text{O}^+$) to be produced in electronically excited states.

In previous [7] and ongoing [8] studies we have addressed the XUV photofragmentation of the proton-bridged dimer $\text{H}_2\text{O}-\text{H}^+-\text{OH}_2$ using the TIFF setup at FLASH. A central finding from these studies has been that a major fragmentation channel after valence ionization is two-body break-up into the channel $\text{H}_2\text{O}^+ + \text{H}_3\text{O}^+$. This result has been rationalized theoretically [9] as resulting from a fast dissociation process dominated by correlated proton-hole dynamics in combination with strong non-adiabatic couplings among the lowest potential energy surfaces of the di-cationic $\text{H}_5\text{O}_2^{2+}$ system. With the present detailed study of the photolysis of both products (i.e. $\text{H}_2\text{O}^+$ and $\text{H}_3\text{O}^+$) of this dissociation, the possibility to perform time resolved studies, i.e. XUV-pump-XUV-probe experiments, for instance exploiting the split-delay system [10] installed at the PG2 beam line, becomes realistically in the future.

References