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Ultrafast Deep-Ultraviolet Spectroscopy of Ionised liquid Water

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Abstract

The ionisation of liquid water is a phenomenon that accompanies high-energy radiation with biological systems and aqueous solutions. The study of this process is of fundamental importance to radiation biology and radiation chemistry.^[1-3] Upon photoionisation, a water radical cation, $\text{H}_2\text{O}^{\bullet+}$, is produced upon an ejection of an electron which subsequently relaxes into the localized hydrated electron, e_{hyd}^- . The $\text{H}_2\text{O}^{\bullet+}$ radical cation undergoes a proton transfer reaction to yield a hydroxyl radical, $\bullet\text{OH}$ and a hydronium ion, H_3O^+ . Previous studies have measured the timescale of decay of the $\text{H}_2\text{O}^{\bullet+}$ radical cation to be 46 fs.^[4] To build on that discovery, this study focuses on detecting the formation time of the proton transfer product, the $\bullet\text{OH}$ radical, by monitoring its deep-ultraviolet (DUV) absorption. Herein, this study presents the successful generation of ultrashort DUV pulses, and the ultrafast pump-probe spectroscopic measurements of the absorption of the $\bullet\text{OH}$ radical. An upper bound of 100 fs for the time constant of the formation of the $\bullet\text{OH}$ radical was obtained (Fig. 1). With evidence of the formation of the $\bullet\text{OH}$ radical and the limitations identified, this study lays the foundation for investigating the formation and vibrational relaxation dynamics of the $\bullet\text{OH}$ radical, produced from the proton transfer reaction of $\text{H}_2\text{O}^{\bullet+}$.

Fig. 1: Time trace fitting with biexponential growth equation of upper bound of $\bullet\text{OH}$ radical formation dynamics

Keywords: ionised water, spectroscopy, deep-ultraviolet, ultrafast, hydroxyl radical, photoionisation.

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