

# Capturing Transient Species in Ionized Liquid Water and Aqueous Solutions

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## Abstract

The ionization of liquid water serves as the principal trigger for a myriad of phenomena that are relevant to radiation chemistry and radiation biology. The earliest events that follow the ionization of water, however, remain relatively unknown. By employing few-cycle pulses in the visible to near-infrared (500 – 900 nm) and the short-wave infrared (0.9 – 1.7  $\mu\text{m}$ ), we have performed a comprehensive probe of the fate of the electron that is initially injected into the conduction band by ionization. The results suggest that the relaxation of the conduction band electron to the hydrated electron proceeds via an intermediate state, whose lifetime is found to be  $77 \pm 6$  fs ( $118 \pm 7$  fs) in  $\text{H}_2\text{O}$  ( $\text{D}_2\text{O}$ ). In complementary experiments, femtosecond soft X-ray free-electron laser probing at the oxygen K edge is employed to track the primary proton transfer reaction of ionized liquid water [1]. The experimental results suggest that  $\text{H}_2\text{O}^+$  first undergoes proton transfer to yield vibrationally excited OH on the timescale of  $46 \pm 10$  fs. Subsequent vibrational relaxation of OH occurs with a time constant of  $0.18 \pm 0.02$  ps. Our studies of ionized liquid water have also been extended to anion photodetachment in aqueous solution. For example, in the case of phenoxide, which serves as a model for the redox-active amino acid tyrosine, photodetachment launches vibrational wave packet motion along multiple vibrational modes of the phenoxyl radical product [2]. Analysis of the vibrational wave packet dynamics reveals the normal modes that drive structural reorganization upon photodetachment. Our results shed light on the elementary ultrafast dynamics that accompany the interaction of ionizing radiation with molecules of biological relevance.

**Keywords:** hydrated electron, proton transfer, vibrational wave packets, ultrafast spectroscopy, X-ray absorption, radiation chemistry

## References:

- [1] Z.-H. Loh, G. Doumy, C. Arnold, L. Kjellsson, S. H. Southworth, A. Al Haddad, Y. Kumagai, M.-F. Tu, P. J. Ho, A. M. March, R. D. Schaller, M. S. Bin Mohd Yusof, T. Debnath, M. Simon, R. Welsch, L. Inhester, K. Khalili, K. Nanda, A. I. Krylov, S. Moeller, G. Coslovich, J. Koralek, M. P. Minitti, W. F. Schlotter, J.-E. Rubensson, R. Santra, and L. Young, "Observation of the Fastest Chemical Processes in the Radiolysis of Water," *Science*, **367**, 179-182 (2020).
- [2] T. Debnath, M. S. Bin Mohd Yusof, P. J. Low, and Z.-H. Loh, "Ultrafast Structural Rearrangement Dynamics Induced by the Photodetachment of Phenoxide in Aqueous Solution," *Nat. Commun.*, **10**, 2944 (2019).