Radiation Chemistry and Photochemistry

One of the most common yet still poorly understood sources for chemical activation energy in the Universe is ionizing radiation. Radiation chemists study the rapid, energetic reactions that are initiated by the interaction of the ionizing radiation, such as high energy electrons, with matter. The rapid physical and chemical events that take place when ionizing radiation interacts with atoms and molecules occur on the picosecond and shorter time scales. Detailed knowledge of fundamental processes, such as thermalization, solvation, and the reactions of short-lived energetic species (excited states and ions), is critical in order to develop an understanding of the mechanism(s) for radiation damage. Understanding of these reactions impacts many fields including the design of nuclear reactors, radioactive waste management, radiation therapy, polymer processing, and planetary- and astro- physics. Studies of the fundamental processes of radiation induced reactions require an ultrafast source of ionizing radiation.

Researchers in the Chemistry Division have developed novel femtosecond (10^{-15} sec.) source of ionizing radiation, the Terawatt Ultrafast High Field Facility (TUHFF), that promises to unravel the mysterious events that cause radiation induced processes. TUHFF houses a 20 TW ($2x10^{13}$ W)Ti:sapphire laser system that generates 2.5 nC sub-picosecond pulses of multi-MeV electrons at 10 Hz using laser wakefield acceleration. The system has been specifically optimized for chemical measurements using pump-probe spectroscopy (see Figure 1). The TUHFF electron pulses were used to generate excess electrons in pulse radiolysis of liquid water and concentrated solutions of perchloric acid. The hydronium ions in the acidic solutions react with the hydrated electrons resulting in the rapid decay of the transient absorbance at 800 nm on the picosecond time scale (see Figure 2). Time resolution of a few picoseconds has been demonstrated. The current time resolution is determined primarily by the physical dimensions of the sample and the detection sensitivity. Subpicosecond time resolution can be achieved by using thinner samples, more sensitive detection techniques and improved electron beam quality.

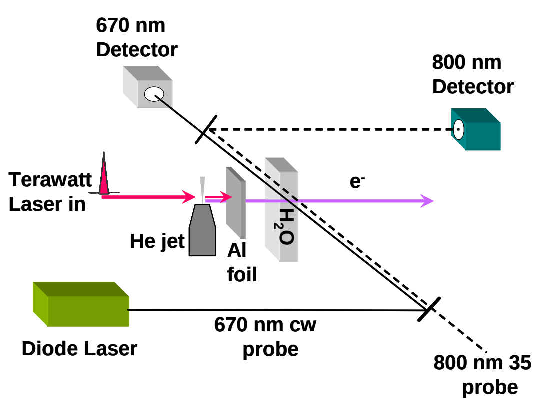

Figure 1. Experimental Set-up for ultrafast pulse radiolysis using a laser wakefield accelerator.

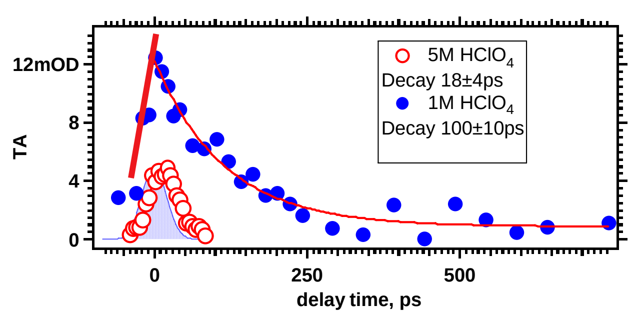

Figure 2. The decay kinetics of observed in pulse radiolysis of 1 and 5 mol dm^{-3} solutions of perchloric acid in water (filled squares and empty circles, respectively). The electron rapidly decays in a reaction with hydronium ion.