THE DESIGN OF AN ACCELERATOR FOR ADVANCED PULSE RADIOLYSIS EXPERIMENTS*

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Abstract

New accelerator techniques have made it possible to make shorter and shorter electron pulses. If appropriate detection techniques are available, these pulses make it possible to measure many important sub-picosecond chemical processes. We are proposing an accelerator system that can be used to measure important sub-picosecond chemical processes, such as solvation, vibrational relaxation, excited state relaxations and molecular fragmentation.

1 INTRODUCTION

It has long been known that radiation can induce highly complex reaction chemistry. At Argonne National Laboratory, one of the first pulse radiolysis experiments was done.[1] In pulse radiolysis a short pulse of ionizing radiation is used to create radicals and ions and the evolution of this chemistry is then observed.

In the more than 35 years since the first pulse radiolysis experiments, the time resolution of pulse radiolysis has increased from microseconds to under 5 ps.[2] With the advances in accelerator technology, it is now possible to push the time resolution to below a picosecond.

Pulse radiolysis and flash photolysis experiments are complementary. Pulse radiolysis excels in creating ions and in mimicking the chemistry that can occur in real-world systems such as waste storage tanks and biological systems after the impingement of ionizing radiation. In such systems, the concentration of reactants is very high and so the chemistry can occur at times less than a few picoseconds.

The important chemistry that needs study has prompted the Argonne Chemistry Division to propose a new pulse radiolysis facility. We envision a facility that will be used by the entire radiation chemical community to probe important chemical processes. In this paper we shall discuss

- The Chemical and Physical Processes that can occur.
- The design criteria for the facility.
- Some of the specific experiments that we plan to do

2 PHYSICAL AND CHEMICAL PROCESSES

Figure 1 displays a simplified picture of the chemical and physical processes that can occur after radiolysis. If there are high concentrations of reactants, they can easily compete with relaxation fragmentation and solvation.
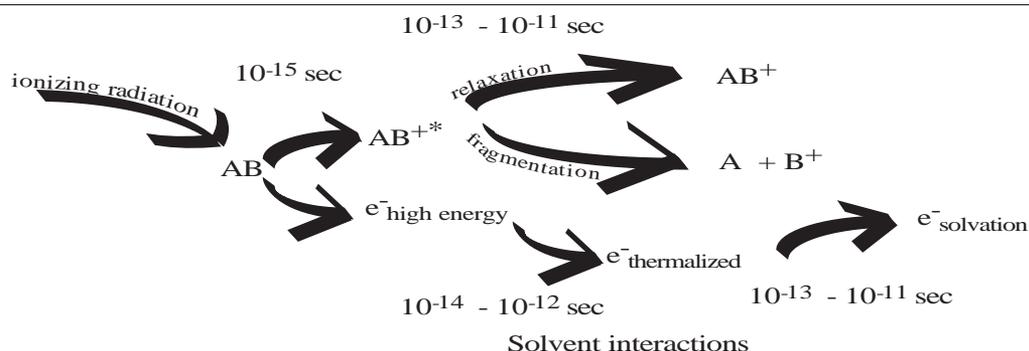

Figure 1: Schematic of the physical and processes occurring after radiolysis.

As one can see from looking at the figure, there are many processes that will occur at times where time resolution better than the 5-30 ps that are presently available in radiolysis experiments.

3 THE DESIGN CRITERIA FOR THE FACILITY

Recently there have been several reports of sub-picosecond pulses from linear accelerators.[3] However the goal of our project is to develop a sub-picosecond pulse radiolysis facility. This means that 1) there must be a sufficiently large concentration of species created and 2) there must be a detection technique that can make use of the short pulse and that will be of sufficient generality to

make meaningful measurements for a large variety of chemical systems. In addition, we had the desire to make a facility that would be usable for more general experiments and would not be limited to sub-picosecond experiments.

The initial design criterion was to create a system that could be used for optical absorption measurements. Optical absorption is applicable to a large variety of chemical systems. While single shot kinetics would be ideal, such measurements at short time scales are very difficult. Streak cameras are unsuited to such measurements. A typical experimental layout is shown in Figure 2.
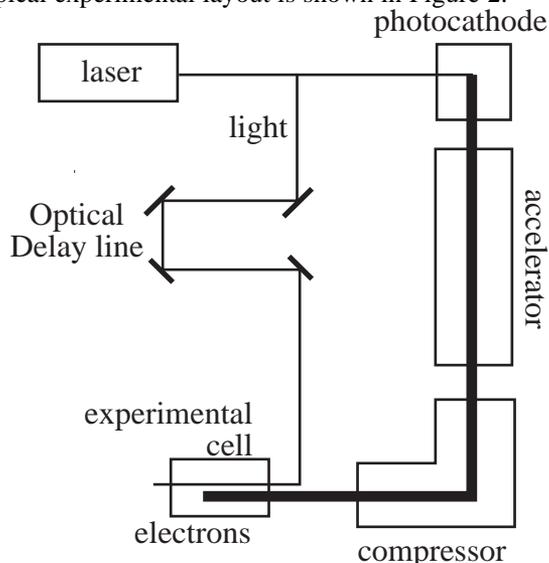

Figure 2: Pump probe measurement technique.

This figure shows a simple pump-probe detection technique. The time that the light strikes the cell can be altered by changing the length of the optical delay line. Thus time resolution depends only on the width of the electron pulse, the light pulse and the synchronism between them. Time resolution can then be reduced to a distance. For 1 ps, a distance of 0.3 mm is needed, easily measured and controlled. A similar technique could be used for fluorescence detection using upconversion or for 4-wave mixing techniques such as CARS (Coherent Anti-stokes Raman Scattering). These techniques make use of the availability of a synchronized laser.

3.1 General Requirements

To make use of the resolution available from the width of the accelerator pulse, it is necessary to
- Have the pulse width of the probe laser pulse to be less than the width of the electron pulse.
- Have the electron pulse and the accelerator pulse be synchronized as they pass through the sample cell
- Keep synchronization between the linac pulse and the laser pulse

The width of the laser will be narrower than the electron pulse. In fact, one of the problems will be stretching the laser pulse to a width that is appropriate for injecting electrons into the accelerator. Modern lasers will have a

pulse width of a few hundred femtoseconds, too short for injecting electrons into an accelerator.

The synchronization between the light and the electrons can be assured by keeping the length of the cell sufficiently short. If we assume a refractive index of 1.5 for the sample, then the difference in transit times for the electrons and the light will be less than 0.5 ps if the sample length is less than 0.3 mm long. There is no difficulty in creating a cell of that depth; the primary difficulty is that such a short cell will limit the amount of optical absorption.

The most difficult problem will be the synchronization between the light and the electrons. While the electrons and the light should be synchronized when the electrons are formed, they may not be synchronized at the exit of the accelerator. Because the compressor works by changing the transit time through the magnets as a function of electron energy, anything that changes the energy of the electron pulse will change the time at which the electrons strike the cell relative to the light pulse. These can include different amounts of energy in the accelerating waveguides and the synchronization of the laser pulse relative to the RF of the accelerator. For example calculations suggest that a shift of 1 ps in the timing between the RF and the laser can yield a shift of 0.5 ps in the transit time.

Table 1 shows the proposed pulse widths. The larger pulses will be very useful for experiments when second order reactions are studied or when weakly absorbing species are formed.

Table 1 – Pulse characteristics.

Pulse Width	Charge
0.6 ps	2 nC
1.0 ps	5 nC
3 ps	10 nC
8 ps	50 nC
45 ps	90 nC
30 ps	25 nC (present linac)

3.2 Detection Options

A large variety of optical detection techniques are available that will make use of the synchronized probe light source. Figure 2 shows the experimental layout for optical absorption. The diagram suggests that the laser that ejects the electron will be used as the detection light source. This is clearly an over simplification because techniques such as optical parametric oscillators can produce a wide variety of wavelengths that can be used as probe sources. With the high powers available, continuum generation can be used, which will provide a white light source that can be used as a probe light source.

Present picosecond experiments have used Cerenkov light as the probe light. Experiments using this probe source have been limited in signal-to-noise because of the shot-noise limit. With a laser available as a probe light source, the signal-to-noise should be much larger.

Fluorescence can be detected either using a streak camera or fluorescence upconversion. With fluorescence upconversion, one can impinge the fluorescence signal and the probe light on a crystal. The probe light source can act as an optical gate that will sample the fluorescence when the probe light is there.

With the availability of intense, synchronized probe laser pulses, all the sophisticated techniques available in laser spectroscopy may be used when appropriate. One well-known technique is CARS spectroscopy where the vibrational state of a molecule can be measured using visible spectroscopy.

4 SCIENTIFIC GOALS FOR A SUB-PICOSECOND PULSE RADIOLYSIS FACILITY

As stated in the introduction, pulse radiolysis and flash photolysis are complementary techniques. While the time resolution of flash photolysis has always been greater than pulse radiolysis, there are experiments that are best done using pulse radiolytic techniques. These include:

Studies of the primary processes in radiation chemistry can only be studied using these techniques. The kinetics of the geminate recombination reactions of the electron in water has been studied using lasers. It has been shown that the rates of these reactions depend on the photon energy producing the hydrated electron.[4] This means that the spatial distribution of the electron depends on the photon energy. Thus there will be no straight-forward correlation between the laser experiments and the radiation experiments. These recombination reactions depend on the distance distribution that is created in the ionization event and the distribution depends on the source of ionization.

Laser studies have been very effective in studying the solvation of excited states (dipole solvation). However until radiation chemical techniques were used to study solvation, ionic solvation was not measured. The unexpected differences between ion solvation and dipole (excited state) solvation were only discovered with pulse radiolytic techniques.

Ionization by lasers depends on the optical cross sections while ionization by ionizing particles depends on the number of electrons present. These differences will allow one to probe a wide variety of chemical processes.

4.1 Nonhomogeneous processes

Radiation deposits energy nonhomogeneously, which leads to many of the important characteristics of radiation-induced chemistry. These high local concentrations of radicals and ions will recombine very quickly. The competition between the fast recombination and reaction with other species in the system will determine the efficacy of the radiation-induced reactions. With the new radiolysis facility, we will probe these reactions on faster time scales.

4.2 Chemistry before Relaxation

Radiation will produce radicals, ions and highly excited states in fluids. In traditional chemical experiments, the concentration of additives is low so that the reactions with the additives will occur much more slowly than the relaxation of the excited states and highly excited vibrational states of the solvent. However, when the concentration of reactants is high, one will have reaction competing with the relaxation process. Without an explicit understanding of the relaxation processes, it then is not possible to predict the final chemistry.

We have tried to summarize a few of the experiments that will require the very fast time resolution of a new facility. In such a short space and in this forum further details are not appropriate.

5 SUMMARY

In this short discussion we have tried to summarize our design goals for a subpicosecond pulse radiolysis facility. We have tried to show that such a facility is more than a short pulse – detection techniques must be taken into account when designing the facility because the goal is to make chemically significant measurements. We have tried to highlight a few fields of study for the future.

Details on the machine design have been ignored in the present discussion. Information about the design process can be found in the paper by Hans Bluem and coworkers in this conference. Details about the laser design can be found in the paper by Robert Crowell and his coworkers.

6 ACKNOWLEDGMENTS

7 REFERENCES

[1] M. S. Matheson and L. M. Dorfman, Detection of short-lived transients in radiation chemistry. *J. Chem. Phys.* **32**, 1870-1 (1960).

[2] M. C. Sauer, Jr., Charles D. Jonah and C. A. Naleway "Study of Reactions of Geminate Ions in Irradiated Scintillator, Hydrocarbon Solutions Using Recombination Fluorescence and Stochastic Simulations" *J. Phys Chem.* **95**, 730-740 (1991).

[3] Kozawa, T.; Kobayashi, T.; Ueda, T.; Uesaka, M. "Generation of high-current (1 kA) subpicosecond electron single pulse". *Nucl. Instrum. Methods Phys. Res., Sect. A* **399** 180-184 (1997).

[4] Crowell, Robert A.; Bartels, David M. "Multiphoton Ionization of Liquid Water with 3.0-5.0 eV Photons". *J. Phys. Chem.* **100**, 17940-17949 (1996).