DEVELOPMENT OF A FEMTOSECOND PULSE RADIOLYSIS FOR REACTION ANALYSIS IN NANO-SPACE

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Abstract

Pulse radiolysis based on linear accelerator is studied in Osaka University for the observation of radiation-induced ultrafast physical and chemical reactions. A subpicosecond pulse radiolysis was developed by using a subpicosecond electron pulse from L-band linear accelerator and a femtosecond laser pulse. The geminate ion recombination in n-dodecane was investigated by using the subpicosecond pulse radiolysis. The geminate decay of cation radical after 50 ps can be explained by the diffusion theory. However, the difference between the experimental result and the theory was observed within 50 ps. In order to explain the difference, a new femtosecond pulse radiolysis based on a photocathode RF gun linac is developed. A time resolution of <100 fs is expected in the pulse radiolysis system for the analysis of ultrafast physical and chemical reactions in nano-space.

INTRODUCTION

The geminate ion recombination[1-3] has been studied as an important reaction in the primary process of radiation chemistry. The initial distributions and geminate decay were observed by using picosecond pulse radiolysis, and the recombination process was analyzed by the Smoluchowski equation base on the diffusion theory. However, only tail part of the geminate decay could be observed in the picosecond pulse radiolysis, because its time-scale is several picoseconds.

Picosecond pulse radiolysis is one of the promising methods to measure such a fast reaction and has been developed all over the world. Previously, the measurement of reactions that occur within 30 ps had been difficult because of a low time resolution for a few decades. Recently, a new picosecond pulse radiolysis system, in which a femtosecond laser was used, was proposed. The synchronization of the femtosecond laser with the subpicosecond electron single pulse was succeeded at the Institute of Scientific and Industrial Research, Osaka University [4-5]. Very recently, the new system[6] was improved to the higher resolution pulse radiolysis system by using a subpicosecond electron pulse and a jitter compensation system. We reexamined the geminate process in subpicosecond time region.

In order to investigate the reactions and the processes in femtosecond time region, a new femtosecond pulse radiolysis is developed by using a femtosecond electron pulse produced with a photocathode RF gun linac. An oblique incidence of the probe light is considered in the system to reduce the degradation of velocity difference between the electron and the laser light in samples.

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SUBPICOSECOND PULSE RADIOLYSIS

Experimental Setup

Figure 1 shows the subpicosecond pulse radiolysis system. The system consists of a subpicosecond electron linac as an irradiation source, a femtosecond laser as an analyzing light, and a jitter compensation system. A sample was irradiated by a subpicosecond electron single pulse. The subpicosecond electron single pulse was obtained by compressing a 30 ps electron single pulse from the ISIR L-band linac with a magnetic pulse compressor. This system can compress the width of electron pulse to approximately 125 fs (rms)[6]. The time-resolved optical absorption was detected with a femtosecond laser. A modelocked ultra fast Ti:Sapphire laser (Tsunami, Spectra-Physics Lasers, Inc.) was synchronized to the ISIR L-band Linac using a commercially available phase lock loop. The width of the laser pulse was 60 fs (FWHM). The intensity of the laser pulse was measured by a Si photodiode. The timing between the electron pulse and the laser pulse was controlled by radio frequency (RF) system.

The jitter between the laser pulse and the electron pulse was estimated from the measurement using a femtosecond streak camera, because the jitter is one of important factors which decide the time resolution of the pulse radiolysis. The jitter was several picoseconds. In order to avoid effects of the jitter on the time resolution, a jitter compensation system was designed. The time interval between the electron pulse (Cherenkov light) and the laser pulse was measured by the streak camera at every shot. The Cherenkov radiation was emitted by the electron pulse in air at the end of the beam line. The laser pulse was separated from the analyzing light by a half mirror. The precious time interval could be obtained by the analysis of the streak image. All equipment described above was controlled by a personal computer. The acquisition time was 1 second per one shot.

The difficulty of the system was the stability of the laser pulse. If there is no fluctuation of laser intensity, we will get a good s/n ratio. Actually, the envelope of laser pulses changes in a relatively long time range (typically from several minutes to a few tens of minutes) due to the change of environmental factors such as room temperature, and coolant temperature. There is also an intensity jitter caused by factors such as the mechanical vibration of mirrors and the timing jitter of electronics. Furthermore, in our system, the laser system is located about 10 m from the beam port in order to prevent

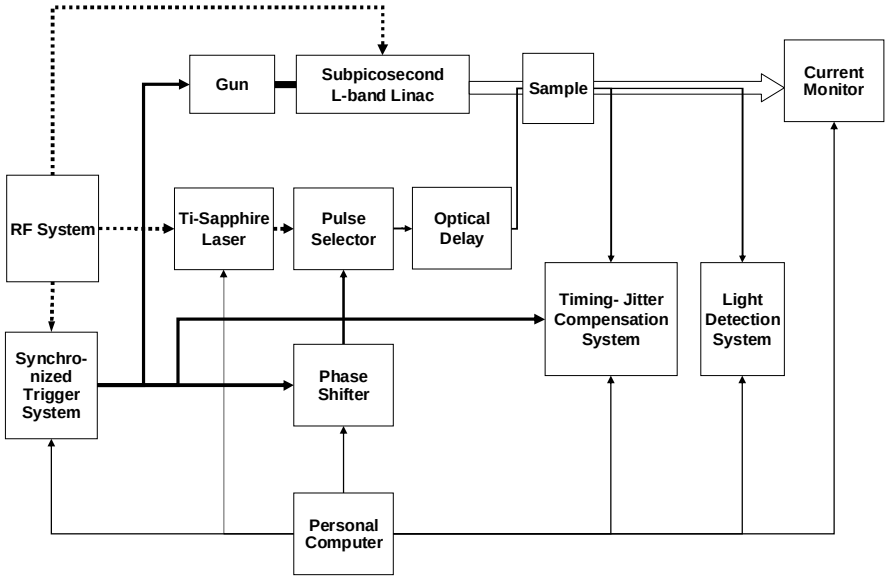

Figure 1: Block diagram of subpicosecond pulse radiolysis system.

radiation damage to the laser system. Therefore, it is predicted that a slight tilt of a mirror placed upstream will cause a displacement of the laser pulse at the downstream position.

We devised a new method to measure the intensity of the analyzing laser pulse with a good S/N ratio. We named it the "double pulse method". Two analyzing laser pulses were produced. Since the frequency of the Ti:sapphire laser is 81 MHz, the time interval of two laser pulses is 12.3 ns. The electron beam was irradiated between the two pulses. The first analyzing laser pulse was used as reference light. The second laser pulse was used as the probe of the absorption.

The two laser pulses are expected not to suffer from the vibration of optical elements because it is thought that the frequency of mechanical vibration mainly caused by the vibration of coolant and ventilator systems is lower than the MHz order. The fluctuation of 5.34% is reduced to 0.80% using the newly developed method.

Geminate Ion Recombination in n-dodecane

A thermalized electron and a parent positive ion (geminate ion pair) in irradiated non-polar liquid diffuse under the Coulomb attracting potential. Most of the geminate ion pairs recombine inhomogeneously in the picosecond order. Theoretically, the geminate ion recombination can be described by the Smoluchowski equation, as follows,

$$\frac{\partial w}{\partial t} = D\nabla\left(\nabla w + \frac{w}{kT}\nabla V\right) \qquad (1)$$

where w, D, k and V are the probability density function of the geminate ion, the sum of the diffusion coefficient of the ions, Boltzman constant and the Coulomb potential, respectively.

Figure 2 shows the time-dependent behaviour of radical cation obtained in the subpicosecond pulse radiolysis of n-dodecane monitored at 790 nm. The solid line shows the theoretical decay based on the Smoluchowski equation. Sum of the diffusion coefficient of 6 x 10^{-4} cm^2/s and the experimental distribution with the initial separation of 6.6 nm were used[6]. The geminate decay of cation radical after 50 ps can be explained by the diffusion theory. However, the difference between the experimental result and the theory was observed within 50 ps.

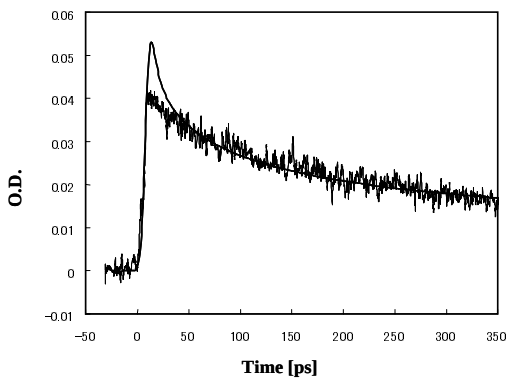

Figure 2: Time-dependent behaviour of radical cation obtained in the subpicosecond pulse radiolysis of n-dodecane monitored at 790 nm.

Thinking the reason of the difference in the short time region we should consider the following points.

1) Overlap of the optical absorption by another short-lived species
2) Effect of the multi ion spur
3) High mobile precursor of the radical cation
4) Diffusion theory

The absorption peaks of radical cation, the electron and the excited state in n-dodecane are 850 nm, 1300 nm and 650 nm, respectively. The band of the excited state is not so broad, the contribution of the excited states is not so large. Furthermore, since the excited state forms from the geminate ion recombination, its contribution to the initial yield is thought to be negligible. The contribution of the electron is also negligible, because the time-dependent behaviour should be the same as the radical cation.

The Smoluchowski equation is based on the single ion spur model, where the one geminate pair exits in the spur. In the case of the multi ion spur model, where several geminate pairs exists in the spur, the geminate decay should be rapid in the short-time region, because the cross recombination occurs.

A preliminary calculation including a contribution of high mobile precursor was carried out and showed correspondence with the experimental data with a parameter set regarding a precursor such as life time of 10 ps, mobility of 50 times larger than the one of normal radical cation. However, other sets of parameters are thought to show the correspondence as well. In addition, the ratio of absorption coefficients at monitored wavelength should be considered when a complete assignment is needed. Namely, there are several uncertain parameters when a precursor of radical cation is introduced.

Finally, we should consider the limitation of the diffusion theory in the short time region. The boundary condition of the recombination should be taken account. The similar study on the scavenging experiment of the cation radical was reported [5].

FEMTOSECOND PULSE RADIOLYSIS

In order to investigate the reactions in spur, a new pulse radiolysis based an S-band photocathode femtosecond linac is shown in Fig.3. In the new system, a 1.6-cell S-band (2856MHz) RF gun was used to produce a picosecond electron pulse. A 2m-long linear accelerator was used to accelerate the electron beam up to 35 MeV with energy modulation. Finally, the picosecond electron pulse was compressed into femtosecond by a magnetic pulse compressor.

The compressed femtosecond electron pulse was used as an irradiation source, while a mode-locked Ti:Sapphire femtosecond laser was used as a probe light source. The Ti:Sapphire laser oscillator output was phase-locked with the 79.3 MHz RF (the 36th sub-harmonic of the 2856MHz accelerating RF). The femtosecond oscillator light was stretched to 200ps by a pulse stretcher, and amplified the pulse energy up to about 1 mJ in a regenerative amplifier with a Pockels cell. The repetition rate of the regenerative amplifier is 1 KHz. An optical parametric amplifier (OPA) was located at exit of the regenerative amplifier. The probe light wavelength from 300nm to 1200nm can be selected by changing BBO crystals for applications.

The measurement system was similar with that in the subpicosecond pulse radiolysis. The jitter compensation technique and the double pulse method were used for the measurement. The degradation of the time resolution, caused by the time jitter between the electron pulse and the analysis femtosecond laser, can be improved, because the electron pulse produced in the photocathode RF gun is synchronized with the injection laser pulse.

Finally, in the femtosecond pulse radiolysis system, the time resolution is limited by the velocity difference between the electron and the laser light in samples. The use of a thin sample leads to a higher time-resolution, but the S/N ratio would be decreased in the measurement. An oblique incidence of the probe light was considered in the system.

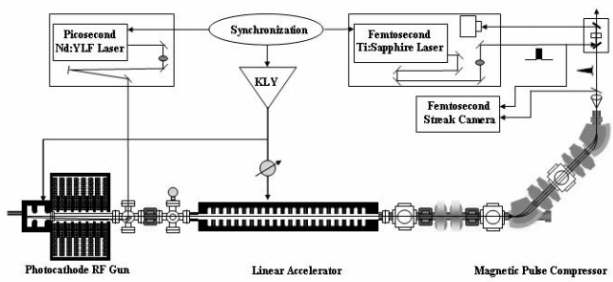

Figure 3: A new femtosecond femtosecond pulse radiolysis system

CONCLUSION

A subpicosecond pulse radiolysis based on an L-band linear accelerator and a femtosecond laser was developed for the study of the ultrafast radiation-induced reactions. The geminate ion recombination in n-dodecane was investigated. The geminate decay of cation radical was measured in the subpicosecond time resolution and compared with the diffusion theory.

A new femtosecond pulse radiolysis based on a photocathode RF gun linac was presented. A time resolution of <100 fs is expected in the pulse radiolysis system for the analysis of ultrafast physical and chemical reactions in nano-space.

REFERENCES

[1] Y. Yoshida, et al., Radit. Phys. Chem., **60**, (2001) 313-318.

[2] K. Kozawa, et al., Nucl. Instrum. Meth. **A440**, (2000) 251-254.

[3] K. Kozawa, et al., Jpn. J. Appl. Phys. Pt. 1, **41,** (2002) 4208-4212.

[4] A. Saeki, et al., Radiat. Phys. Chem., **62,** (2001) 319-322.

[5] A. Saeki, et al., J. Phys. Chem., **A108,** (2003) 1475-1481.

[6] Y. Yoshida, et al., Nucl. Instrum. Meth. **A327**, (1993) 41-43.

[7] J. Yang, et al., in the proceedings.