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Development of pulse radiolysis system by using femtosecond white light continuum

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Abstract

In order to research the primary processes of the radiation chemistry, a pulse radiolysis system using a femtosecond laser has been developed at the Institute of Scientific and Industrial Research (ISIR), Osaka University. One of the merits to use the laser is to be able to extend the measurable wavelength region. The system using the fundamental light has already worked. For the use of the white light continuum, we have improved the trigger system and the optical system. As a result, the data with a good S/N ratio has been obtained.

1. Introduction

The pulse radiolysis is a powerful method to investigate the time dependent behavior of the short lived intermediates such as an electron and radical species produced by a pulsed radiation. To detect so fast reaction, a so-called stroboscopic method is used in the picosecond pulse radiolysis. The time-resolution of this method depends only on the pulse width of an irradiation source, pulse width of an analyzing light, the time jitter between these pulses, and the sample cell length, and doesn't depend on the time-resolution of the measurement apparatuses. The laser synchronized pulse radiolysis system[1] have some advantages as follows:

1) Able to improve the time-resolution of the system due to the very short pulse width,
2) By using a white light continuum and nonlinear optical effects such as SHG, THG and OPO, the available wavelength region is extended from 250 nm to 2000 nm,

and so on. The effectiveness of the femtosecond white light continuum using the preliminary system was demonstrated, as reported in previous paper[2]. However, the stability of the system wasn't good. After consideration, the reason was found to be attributed to the issue of the trigger system and the phase shifters which changed the RF phase to change the time difference between the electron pulse and the laser pulse. Therefore, we have improved the trigger system and the optical system.

2. The outline of the new improved system

Fig. 1 shows the improved laser synchronized pulse radiolysis system by using the femtosecond white light continuum. The electron pulse from ISIR L-band linac (28 MeV, 20 ps) and the white light continuum (400 nm to 1000 nm, 100 fs) have been used as an irradiation source and an analyzing light, respectively.

The Ti:Sapphire is synchronized with the electron pulse by means of the reference RF of 81 MHz from the master oscillator[2]. The Ti:Sapphire laser and the Nd:YAG laser penetrate into the Ti:Sapphire rod in the Regen. Amp. as a seed laser and a pump laser, respectively. The Regen. Amp. has two Q-switches (the Pockels cell) in the cavity. One controls the single pulse operation (12 Hz, 1.5 mJ) of the Regen. Amp., and the other controls the pick-up timing of the amplified laser. The output laser pulse is focused into water and generates the white light continuum.

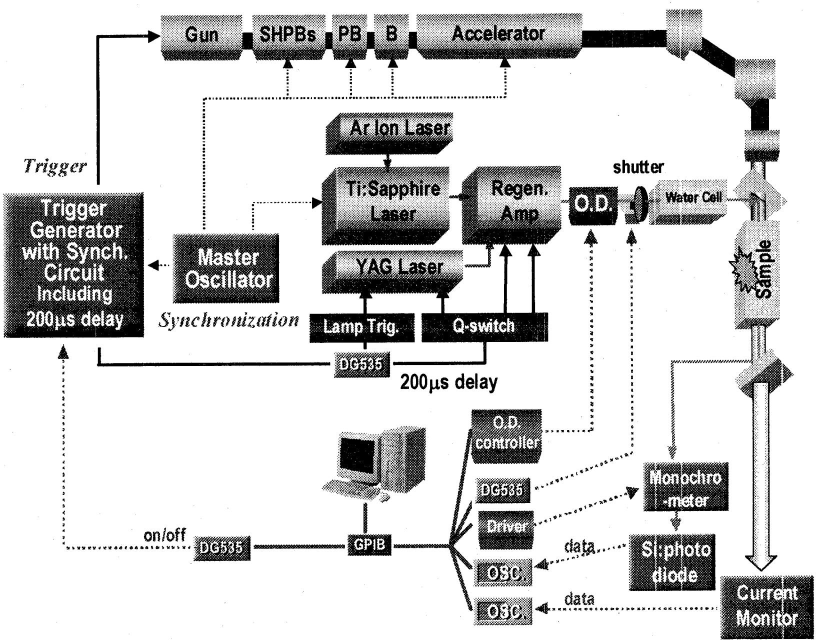


Fig.1 The improved laser synchronized pulse radiolysis system by using the femtosecond white light continuum.

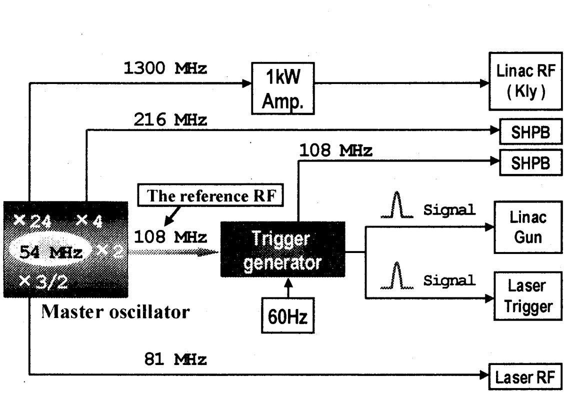


Fig.2 The master oscillator and the RF system.

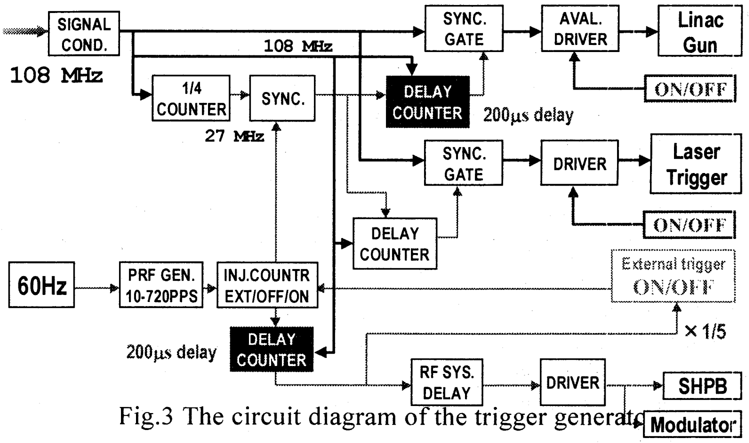


Fig.3 The circuit diagram of the trigger generator

The laser pulse through the sample cell is reflected and led to the monochrometer by the mirrors. After passed through the monochrometer, the intensity of the laser pulse is measured by the Si:photodiode. The current of the electron beam is also measured by the current monitor so as to compensate the dispersion of the signal intensity caused by the of the current dispersion. The signals from the Si:photodiode and the current monitor are took by the oscilloscopes and sent to the computer. The on/off switches of the laser pulse and the electron pulse are performed by the shutter and the enable circuit, respectively. The shutter, the enable circuit and the optical delay are driven by the signals from the computer.

As a result of the investigation on the reason why the former system was so unstable, it was found that the precision of the lamp trigger to the Nd:YAG laser and the disturbance due to the use of the RF phase shifter during the measurements had a bad influence on the laser system. The improvement of the trigger system described in the next section and the installation of the optical delay were carried out. In the system using the fundamental light, the time difference between the electron pulse and the laser pulse has been changed by the two phase shifters, because the phase shifter can easily change the time difference without changing the light pass. The stability of the Ti:Sapphire laser doesn't suffer from the phase shifter. However, the Regen. Amp. and the Nd:YAG laser are unstable. Therefore, we have installed the optical delay instead of the phase shifters.

With the improvement of the system, the measurement program, which can control the whole system, have been made. The measurement of a time profile takes about one hour and is carried out automatically by the measurement program.

3. The trigger generator for the white light continuum

Fig.2 shows the master oscillator and the RF system. The crystal oscillator (VCXO) oscillates at the frequency of 54 MHz and the stability of the frequency is 0.0001 %. The 27MHz RF (54 MHz divided by two) has been used as the standard frequency. In the master oscillator, the 27 MHz RF is multiplied by 3, 4, 8 and 48 and then sent to the laser reference, the 108MHz SHPBs, the 216MHz SHPB and the klystrons, respectively. The RF of 108 MHz is supplied to the trigger generator.

Fig. 3 shows the circuit diagram of the trigger generator. The trigger generator is composed of the ECL. The electron pulse and the laser pulse are synchronized precisely by means of the RF system, and the trigger generator must be also synchronized with the linac and the laser. Thus, for the synchronization, the standard RF of 108 MHz is divided by 4 and delayed every 37 ns (27 MHz) in the 1/4 counter. The electron pulse and laser pulse are controlled by the computer via the enable circuits added to the driver circuits.

The Nd:YAG laser, which is a pump laser of the Regen. Amp., has the lamp trigger to the Xe flash lamp and the Q-switch for single pulse operation. The most important thing is that the Nd:YAG laser needs 200 μs to oscillate after the irradiation of the Xe flash lamp. Therefore, in the former trigger system, the trigger to the lamp trigger was provided by one fifth of the 60 Hz signal which drives the klystron modulator and so on. However, the output laser pulse from the Regen. Amp. was unstable due to the jitter of the trigger. So, at the first time, we improved the trigger system using the 27 MHz RF as the reference RF in order to delay the whole trigger system without the trigger to the Nd:YAG laser. The 200 μs delays have been installed in the trigger generator shown in Fig. 1 and 3. However, the output was unstable, because the jitter was still large. Therefore, we have changed the reference RF for the delay circuit from 27 MHz to 108 MHz. As a result, the stable outputs from both the linac and the Regen. Amp. have been obtained.

4. Experiments and results

Fig. 4 shows the typical time dependent behavior of the n-dodecane cation radical obtained by the picosecond pulse radiolysis system. The dots and the solid line are the experimental data and the theoretical ones, respectively. The data of Fig. 4 (a) and (b) are obtained by using the fundamental light and the white light continuum, respectively.

When the electron pulse goes through the liquid, radical cations and electrons are produced by the ionization. In the nonpolar liquid, the produced electrons are thermalized immediately (< 1 ps) and most of them recombined with the radical cations in the picosecond time scale. That is called the geminate ion recombination [3] and an important process in the primary process of the radiation chemistry.

$$\begin{aligned} &\mathrm{RH} \rightsquigarrow \mathrm{RH}^{\dot{+}} + e^- \\ &\mathrm{RH}^{\dot{+}} + e^- \longrightarrow \mathrm{RH}^* \end{aligned} \qquad (1)$$

To observe the formation process and the electron thermalization process is impossible, because these processes occur within the time-resolution of the system, but the recombination process is clearly observed by the system. The decay in Fig. 4 indicates the geminate decay of the radical cations.

The theoretical analysis is based on the following Smoluchowski equation[4]:

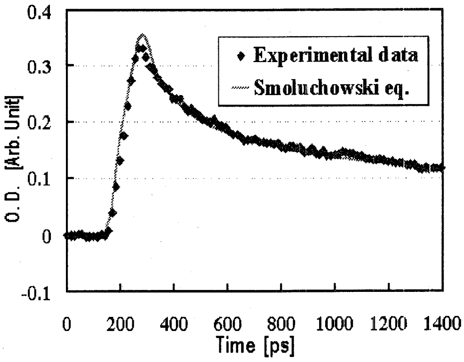
$$\frac{\partial w}{\partial t} = D\nabla\left(\nabla w + w\frac{1}{kT}\nabla V\right) \qquad (2)$$

w : probability density
D : sum of diffusion coefficients
V : Coulomb potential

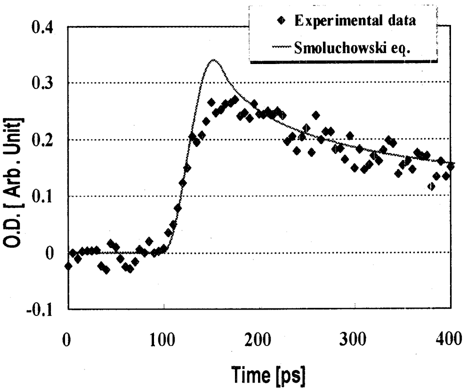
In the analysis, the sum of the diffusion coefficients as 6.4 x 10^{-4} $\mathrm{cm^2/s}$, the initial distribution of electrons as the exponential function, and the initial distribution distance between cations and electrons as 6.6 nm were used. These parameters agree with the reported values[5,6], and the experimental data is in good agreement with the theoretical data. In addition, as the n-dodecane cation radical has the broad absorption spectrum at the center of 850 nm, both of the data in Fig.4 (a) (monitored at 820 nm) and the data in Fig.4 (b) (monitored at 850 nm) are attributed to the time profile of the n-dodecane cation radical. And, since these data correspond with each other, the validity of the new system using the white light continuum was proved.

5. Conclusion

We have improved the trigger system for the precise synchronization between the linac and the laser system and installed the optical delay for the stabilization of the laser system. With the improvement of the system, the measurement program, which can control the whole system and take the data automatically, have been made. The data obtained by the improved pulse radiolysis system using the white light continuum was in good agreement with the theoretical data and the data obtained by the system using fundamental light. Thus, the validity of the new system was proved. The next work is to apply the white light continuum to the ISIR subpicosecond pulse radiolysis system.



(a) Obtained by the fundamental light at 820 nm



(b) Obtained by the white light continuum (monitored at 850 nm)

Fig.4 The time dependent behavior of the n-dodecane cation radical (dots: the experimental data, solid line: the theoretical data).

References

[1] Y.Yoshida et al., Proc. Femtosecond Technol '95, 63 (1995)

[2] Y.Mizutani et al., Proc. Accel. Science and Tech. '97, 148 (1997)

[3] Y.Yoshida, S.Tagawa and Y.Tabata, Pulse Radiolysis, (Edited by Y.Tabata), CRC Press, 343 (1991)

[4] A.Hummel, Adv. Radiat. Chem., 4, 1 (1974)

[5] Y. Yoshida, T.Ueda, T.Kobayashi, H.Shibata and S.Tagawa, Nucl. Instr. Meth. A327, 41 (1993)

[6] Y.Yoshida and S.Tagawa, Dynamics and Mechanisms of Photoinduced Electron Transfer and Related Phenomena, (Edited by N.Mataga, T.Okasa and H.Masuhara, Elsevier Sci. Pub., 435 (1992)