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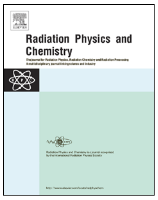

Short Communication

Quick measurement of continuous absorption spectrum in ion beam pulse radiolysis: Application of optical multi-channel detector into transient species observation

Kazuhiro Iwamatsu [a,b,1], Yusa Muroya [c], Shinichi Yamashita [d], Atsushi Kimura [b], Mitsumasa Taguchi [b,*], Yosuke Katsumura [a,d,2]

[a] *Department of Nuclear Engineering and Management, School of Engineering, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113-8656, Japan*
[b] *Quantum Beam Science Center, Japan Atomic Energy Agency, Watanuki-machi 1233, Takasaki, Gunma 370-1292, Japan*
[c] *Department of Beam Materials Science, Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan*
[d] *Nuclear Professional School, School of Engineering, The University of Tokyo, 2-22 Shirakata-shirane, Tokai-mura, Naka-gun, Ibaraki 319-1188, Japan*

HIGHLIGHTS

- A quick measurement system of a continuous absorption spectrum was constructed and applied in ion beam pulse radiolysis.
- Transient absorption spectra during and after pulsed ion beam irradiation could be obtained within a few minutes.
- High sensitivity of 0.001–0.003 in absorbance was attained in the range from 260 to 660 nm.
- Transient species, $(SCN)_2^{\bullet-}$, was observed in KSCN aqueous solution.
- Transient species having different absorption bands, $Br_2^{\bullet-}$ at 360 nm and Br_3^- at 260 nm, were observed simultaneously in NaBr aqueous solutions.

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ABSTRACT

A quick measurement system of a continuous absorption spectrum covering a wide range from 200 to 950 nm was constructed by employing an optical multi-channel detector. Ion beam pulse radiolysis with 12.5 MeV/u He, 18.3 MeV/u C and 17.5 MeV/u Ne ions were performed with the measurement system. Transient absorption spectrum of $(SCN)_2^{\bullet-}$ was clearly observed in KSCN aqueous solutions within a few minutes in spite of their very small absorbance, demonstrating high sensitivity of 0.001–0.003 in absorbance in the range from 260 to 660 nm as well as short measurement time of a few minutes. Two different absorption peaks attributed to $Br_2^{\bullet-}$ and Br_3^- were observed simultaneously in NaBr aqueous solutions, showing powerfulness of the measurement system in overviewing chemical kinetics under ion beam irradiation especially in not well investigated chemical systems.

1. Introduction

High Linear Energy Transfer (LET) radiations, such as ion beam, deposit their energies densely and non-homogeneously along their trajectories. Yields and behaviors of chemical species generated by high LET radiations are much different from those by low LET radiations such as γ-rays and electron beam because of difference in microscopic radical distributions near radiation trajectories (LaVerne, 2004; Baldacchino and Katsumura, 2010; Meesungnoen and Jay-Gerin, 2010; Yamashita et al., 2010). Pulse radiolysis method with very short pulse of electron beam has been well developed and is a powerful tool to observe time dependent behaviors of radical species. Ion beam pulse radiolysis has also been carried out at several facilities (Burns et al., 1977; Sauer et al., 1983; Chitose et al., 1997; Baldacchino et al., 2006; Taguchi et al., 2009; Iwamatsu et al., 2011). They essentially used laser diodes as light source to improve signal to noise ratio (S/N) because absorption signal for ion beam irradiation is normally very weak due to small current and limitations of penetrated and irradiated areas. It is difficult to clarify the whole reaction mechanism only based

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[*] Corresponding author. Fax: +81 27 346 9386x9694.
E-mail address: taguchi.mitsumasa@jaea.go.jp (M. Taguchi).
[1] Present address: Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556, USA.
[2] Present address: Japan Radioisotope Association (JRIA), Honkomagome 2-28-45, Bunkyo-ku, Tokyo 113-8941, Japan.

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on sole-wavelength observation with a laser diode. Transient absorption spectrum observation associated with electron beam pulse radiolysis is without any doubt a powerful tool to clarify time dependent behaviors of radical species and to seek unknown reactions (Mostafavi and Lampre, 2010). Its extension to ion beam pulse radiolysis would provide us a tool for investigation of distinctive radiation chemistry in high LET radiolysis.

There are few reports on transient absorption spectrum observation in ion beam pulse radiolysis (Chitose et al., 1997; Taguchi et al., 2009). They needed several hours to obtain one spectrum because of repetitions of kinetics measurement at each wavelength one by one. Transient absorption measurement with a multi-channel detector is expected less time-consuming than the abovementioned classical method. Briefly speaking, utilization of a multi-channel detector would reduce time for measurement of a transient absorption spectrum from hours to minutes. As is often the case with ion beam accelerator facilities, machine time for one group is not much and it is typically several tens hours per year in the case of TIARA, JAEA in Japan. In addition, inhibition of accumulation of radiolysis products in samples is critical in such measurements to avoid change of chemical systems during the measurement. Thus, construction of a new system for quick observation of transient absorption would push forward understanding of ion beam radiation chemistry.

In the present study, we describe a new ion beam pulse radiolysis system using an optical multi-channel detector and white probing light from a Xe flash lamp. The measurement system is highly sensitive and effective for quick spectroscopy of transient absorption. Within a few minutes, time dependent continuous absorption spectra of transient species produced by pulsed ion beam can be observed at a one-time measurement. Here the system is briefly introduced together with the preliminary experimental data using KSCN and NaBr aqueous solutions.

2. Experimental

Ion beam pulse radiolysis experiments were carried out using 12.5 MeV/u He, 18.3 MeV/u C and 17.5 MeV/u Ne ions from AVF cyclotron in TIARA facility in JAEA, Takasaki. The ion beams were focused to about 1 cm in diameter. The shape of the beams was not a precise circular but an ellipse so that the beam spot overlaps as much as possible with the spot of focused probing light. We used a custom-made optical measurement cell ($20 \times 20 \times 2\ \text{mm}^3$) consisting of quartz windows at the top and bottom surfaces, spaced by stainless frame of 2-mm thickness. The sample cell was horizontally set at vertical irradiation port in TIARA facility. Probing light, injected from the window at the top surface of the cell and reflected on the mirror set under the cell, passes through the cell twice. Details of the cell structure, optical system, and signal control including pulse formation of ion beam are described elsewhere (Taguchi et al., 2009; Iwamatsu et al., 2011). Optical path length was almost twofold of the sample thickness (i.e. 4 mm). Ion beam range was shorter than the thickness, so effective optical path excluding non-irradiated volume can be briefly estimated as twofold of the range. The range varies depending on the energy and charge of the projectile ions of the beam. Note that observed data is track average absorption spectrum in this measurement because all ions used in the present study completely stop in the sample cell. TRIM code (Ziegler et al., 1985) was used to estimate ion energies and ranges considering thickness of titanium beam extract window (30 μm), distance from the beam extract window to sample cell (10 cm) and thickness of quartz window of sample cell (50 μm). The incident energies of the ions were estimated to be 11.4, 15.8, and 12.8 MeV/u for He, C, and Ne ions, respectively. The ranges in sample solutions were estimated to be 1.58, 0.93 and 0.41 mm for He, C, and Ne ions, respectively. Note that, strictly speaking, the effective optical path length would be a little bit longer than twofold of the range because the axis of the probing light is slightly inclined to that of the ion beam.

Potassium thiocyanate (KSCN, >99.5%) and sodium bromide (NaBr, >99.9%) were purchased from Wako Pure Chemical Industries, Ltd. and used as received. They were dissolved in ultrapure water (>18.3 MΩ cm) from Water Purification System (Direct-Q 3 UV, Millipore). The aqueous solutions were saturated with N_2O gas. The hydrated electron was converted to $^{\bullet}OH$ by N_2O as follows:

$$e^-_{aq} + N_2O \rightarrow O^{\bullet -} + N_2 \quad 9.1 \times 10^9\,M^{-1}\,s^{-1}$$ (Buxton et al., 1988)

$$O^{\bullet -} + H_2O \rightarrow {}^{\bullet}OH + OH^- \quad 9.3 \times 10^7\,M^{-1}\,s^{-1}$$ (Buxton, 1970)

Since N_2O can be dissolved up to 25 mM in pure water, time scale of the first step of this conversion is about 4.4 ns.

3. Results and discussion

3.1. Development of the system

Signals in ion beam pulse radiolysis is expected very small (i.e. typically in the range of 0.001–0.01 in absorbance), so measurement system requires intense probing light to attain sufficient sensitivity. A Xe flash lamp (L7684: Hamamatsu Photonics), which has high stability (±3%) and high intensity (1 J/flash), was used as probing light source. An optical multi-channel detector (PMA: Hamamatsu Photonics), 1024 channels of which corresponds to wavelength from 200 to 950 nm, was used to acquire continuous spectrum of the probing light. Wavelength resolution of the PMA detector is 0.70 nm. Such high resolution is usually not necessary in pulse radiolysis, thus, light intensities detected by four neighboring channels were averaged, leading to better S/N as well as slightly lower wavelength resolution (i.e. 2.8 nm), which is still sufficient compared with reported data. Note that wavelength of the PMA detector was preliminarily certified using a mercury argon calibration source (HG-1: Ocean Optics).

A schematic of the whole measurement system is shown in Fig. 1. PMA was installed behind 1-m wall of concrete with sufficient distance from the irradiation port in order to suppress the noise due to irradiation, which would be effects of neutrons and γ-rays. Probing light was transmitted to the analyzing spot of the irradiation port and then was brought to the PMA detector by using several aluminum mirrors (TFAN series: Sigma Koki Co., Ltd.), reflectivity of which in near ultraviolet and near-infrared

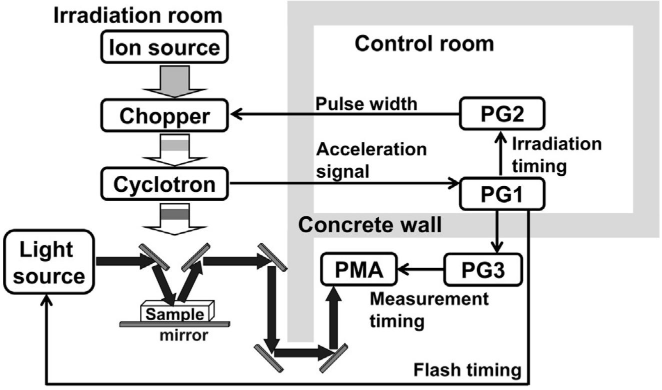

Fig. 1. A schematic of the whole measurement system (optical detection, pulse formation, signal control, and so on). PG1-3: pulse generators, PMA: photonic multi-channel analyzer.