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Pulse radiolysis in water with heavy-ion beams. A short review

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ABSTRACT

This article presents a short review of the studies in radiation chemistry of liquid water with heavy ions, which have used pulse radiolysis methods during the last 20 years. The interests and the difficulties of developing this kind of experiment are depicted. The linear energy transfer (LET) effect is the main topic of these studies. The earliest effects close to the structure of the deposited energy can be observed directly by transient absorption spectroscopy by following the hydrated electron, the superoxide radical produced in the absence of molecular oxygen and the hydroxyl radical, which still requires the use of scavenger. Finally, the results can be compared to the heterogeneous chemical processes in the time range of 1 ns to 1 μs described by Monte Carlo simulations. The absolute values of the radiolytic yields are still uncertain because of the dosimetry accuracy. The future aspects of the method are discussed in terms of new types of particle accelerators giving better time resolutions.

1. Introduction

The interaction of energetic heavy ion with the liquid water is found in many kinds of situations like the nuclear industry (alpha rays, neutrons, recoil ions), the hadrontherapy (carbon ions, protons), the ions of the cosmic rays involved in future space travel. This particular interaction is closely linked to the linear energy transfer (LET) value defined as $\mathrm{LET} = (\mathrm{d}E/\mathrm{d}X)_{\mathrm{elec}}$ (Spinks and Woods, 1990). To depict the effects of LET on the radiolysis of liquid water the use of heavy-ion beams of various energies, charges and types are necessary to determine the spatial distribution of the deposited energy, the fate of the deposited energy (excitation, ionization, multi-ionization, etc.) and the time-dependence of the diffusion and reaction processes. These determinations must be experimental and theoretical (e.g. simulation). Actually, for many years the physical chemistry occurring in the ionization tracks of heavy ions has been described in a general way (Allen, 1961; Magee and Chatterjee, 1987). What is commonly accepted is that radiolytic yields for the molecular products (H_2 and H_2O_2) increase with the LET whilst those for the radical species ($e_{aq}^{-\bullet}$,$H^{\bullet}$, $OH^{\bullet}$) decrease. This trend is a result of a more efficient recombining of the radical species to form molecular species in the tracks since the density of the ionization events is greater with high LET particles. These aspects have been deduced mainly from the studies involving the chemical scavenging method (LaVerne and Schuler, 1983; LaVerne, 1989a, b, 2000, 2004), which is based on concentration measurements of the final stable product of reactions. In this method the time dependence of the radiolytic yields is determined from the concentration and the rate constant of the reaction between the scavenger and the radical species. This method becomes less accurate at early time after the ionization process because it needs very high concentrations of scavenger that can also suffer from the direct effect of the ionization. Actually the direct effects can explain the radiolytic-yield values obtained by using the thiocyanate OH-scavenger under heavy-ion irradiation (Baldacchino et al., 2006; Chitose et al., 1997).

Pulse radiolysis studies with high-energy heavy ions are few and especially on the liquid water radiolysis. A short list of publications can be done easily (Baldacchino et al., 1998a, b, 1999, 2001, 2003, 2004, 2006; Burns et al., 1977, 1981; Chitose et al., 1997, 1999a, b, 2001, Rice et al., 1982, Sauer et al., 1977, 1978, 1983, Wasselin-Trupin et al., 2000). There is one main reason why research is not developed in this field: the available ion beams in the world are concentrated in the biggest cyclotrons delivering intense beams of high energy. A pulse controller is required in order to offer the possibility of extracting a bunch of ions as short as possible, from ps to ms. This kind of accelerator is not a common laboratory tool such as an electron accelerator. Therefore access is difficult and performing systematic experiments remains impossible even within one year. Nevertheless, because of recent interests, new developments (Umstadter, 2001; Malka, 2002; Noda et al, 2005) and opportunities, the studies with the pulse radiolysis method with heavy ions are hopeful.

The first aim of this short review is to show what was already studied by the pulse radiolysis technique coupled to the high-energy ions during the last 20 years. This should allow explaining the advantage of using pulse radiolysis to obtain the

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time-resolved dependence of the radical species in the ionization track. This paper is structured by the radical species that are more specifically studied because they are involved very early in the physical processes of the energy deposit.

2. Experimental

To study the reactivity in the ion track most of the authors have used the so-called scavenging method, which is an indirect method to convert the transient radical into a stable chemical species, which is more conveniently analyzed after the irradiation. To be approved, this method must be compared to the pulse radiolysis studies as it was done between the pulsed electron beam and gamma rays continuous irradiation within some specific conditions and adjustments (Pimblott et al., 1996). A simple extrapolation of the low-LET behavior to the strongly heterogeneous energy deposition, which is the main characteristic of the high-LET particles, should be simply wrong especially at the earliest steps shorter than 10 ns. Actually the high local density of ionizations can undoubtedly affect the integrity of the scavenging molecule under the direct effect of the ion beam and the high-energy secondary electrons.

2.1. Setup

The experiment setup used for pulse radiolysis with heavy ions is similar to those used in pulse radiolysis with electron beams or flash photolysis (Tabata, 1991). In principle the method consists of a pulsed source of high-energy radiation (accelerator) and a synchronized acquisition of the detection signal. When the detection used is absorption spectroscopy a spectral light is necessary with a sufficient intensity at the considered wavelength in order to obtain a reasonable sensitivity. A limit of 10^{-4} can be reached with a continuous stable light within the linearity limit of the detector and by using a preamplifier (Baldacchino et al., 2004). A few experiments have used a pulsed laser (Argon laser) (Sauer et al., 1983), others used continuous laser beams (a HeNe, a CW Argon laser or a laser diode) and also Xenon arc lamps for detecting mainly the superoxide radical around 250 nm and thiocyanate radical at its maximum absorption band at 480 nm. In this latter case a monochromator is necessary to select the wavelength. For emission spectroscopy there is no need of incident light, and the emitted light is collected through an optical system and transferred to a detector by using optical fibers. The detection is carried out by using a photomultiplier (e.g. Hamamatsu photomultiplier R928) or a silicon photodiode with an adapted rise time in case of using a laser beam.

The main critical part of the setup is the interaction cell where the solution is flushed, irradiated and analyzed. For the absorption spectroscopy the cell needs two optical windows. These windows must be protected from the irradiation by which they are subject to generate additional transient absorptions. This appears especially in silica. Sometimes it is convenient to use plastic for the cell-body (Wasselin et al., 2000). The thickness of the irradiation window and the depth of the cell are dependent on the ion energy used for the experiment and whether the experimentalist wants to analyze a track segment or a mean effect along the total penetration of the ion in water. Calculations must be achieved to determine these thicknesses. The data base included in the SRIM program is conveniently used for many common materials (Ziegler et al., 1985).

2.2. Ion beams

Most of experiments with ion beams have been performed with mean LET value where the ion is slowing down in the sample and eventually stopping and depositing its whole energy in the Bragg peak. This was the case of the proton beam of 3-MeV used by Burns et al. These authors had the difficulty to design the irradiation cell with ions that stop in 0.15 mm and the way to control the water jet and the collinear optical system for absorption spectroscopy (Burns et al., 1977, 1981, Rice et al., 1982).

In the case of analyzing the effect for a track segment corresponding to a small domain of LET values, high-energy ions are necessary in order to keep unchanged the LET value in the sample as far as possible. Unfortunately the choice of the ion energy often depends on the cyclotron used. Then the adaptation of the cell size and material becomes critical. As an example, Fig. 1 presents a recent setup installed at GANIL (Grand Accélérateur National d'Ions Lourd, Caen, France). With this cyclotron, carbon ions with energy of 95 MeV/nucleon can be delivered with an intensity of a few μA. With a cell having a thickness of 0.5 mm of the entrance window, the track segment directly analyzed in the first millimeter after the window has a LET value of 30 eV/nm (Baldacchino et al., 2003).

2.3. Data analysis

In pulse radiolysis experiment, the detector current is analyzed by using a fast oscilloscope through impedance, which is chosen by considering the time resolution (50 Ω for ns and 1 kΩ for about 1 μs). In the recent years the characteristics of 1-GHz bandwidth oscilloscopes changed drastically by the implementation of higher and higher sampling rates (e.g. 10 GS/s) and memory sizes (e.g. 10^6 samples instead of 500 can depict multi-order of magnitude of time in the kinetics, from ns to ms) and faster acquisition modes allowing a faster and greater averaging (e.g. Digital Phosphore Oscilloscope, DPO in recent Tektronix oscilloscope). Transient absorption spectroscopy can obviously take advantages of these new characteristics in order to increase the signal-to-noise ratio of the signals.

3. Review of the results

3.1. Hydrated electron

Hydrated electron ($e^{-}_{aq}{}^{\bullet}$) has been extensively studied at low LET (electron beam or gamma rays) and its spectrum makes it easy to detect in visible-near IR domain (Spinks and Woods, 1990). Its high absorptivity allows its detection at very low concentration levels. This is an essential species also to provide information on the ionization track structure. It is a good candidate to be a probe of the track at early time after its formation.

The hydrated electron is commonly detected by pulse radiolysis with electron beams. In the case of highly structured track, this very reducing species reacts easily with oxidant like $OH^{\bullet}$ radical in its vicinity at earliest time after the ionization track is formed. That is the reason why it is a real challenge to detect this species with heavy-ion irradiation. In other terms, the time resolution must be sufficient in order to increase the signal level corresponding to the hydrated electron. Giving a G-value remains difficult because the concentrations are lower than 10^{-7} M and the dose must be measured with a high accuracy. As it is shown in Fig. 2, the time dependence of the hydrated electron is typical of a track structure in space and time: in the first 100 ns the concentration of initial hydrated electron is at least decayed