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Water radiolysis with heavy-ion beams at GANIL. Back to 20 years of investigations.

G. Baldacchino¹

¹Physico-Chimie sous Rayonnement, IRAMIS, LIDYL, UMR 3299 CEA-CNRS
SIS2M, PC175, CEA Saclay, F-91191 Gif sur Yvette Cedex, France

E-mail: gerard.baldacchino@cea.fr

Abstract. This article reports a short history of the studies carried out in the domain of radiation chemistry with the swift heavy ions of GANIL (Grand Accélérateur National d'Ions Lourds) during the last 20 years. The originality of these studies lays on two main aspects which were never been investigated simultaneously before: 1/ the energy of the GANIL ions provides an energy deposition in small samples (few millimeters) that can be considered as almost constant; this allows studies on LET-effect on radiolytic yields, 2/ production of pulses as short as a few nanoseconds made available the access to pulse radiolysis method and the study of transient chemical species such as hydrated electron, hydroxyl radical and superoxide. Future is now focus on high temperature effects on water radiolysis for which, again, nothing exist but only simulations and speculations.

1. Context - A brief history of the heavy ion water radiolysis studies

As an introduction of the radiation chemistry investigations initiated at GANIL, we must depict the crucial issues in this domain. Actually the interaction of energetic heavy ion with the liquid water is found in many situations in nuclear industry (PWR, BWR reactors, nuclear waste storage and reprocessing), in hadrontherapy (carbon ions, protons), in cosmic rays involved in future space travel and interstellar chemistry [1]. This particular interaction is closely related to the Linear Energy Transfer (LET) value defined as: $LET = \left(\frac{dE}{dx}\right)_{elec}$ [2, 3]

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. For a long time, since the 60's, the physical-chemistry occurring in the ionisation tracks of heavy ions has been described in a general way [2, 4]. The current knowledge in radiation chemistry with high LET particles, and it was many times verified, is that radiolytic yields of the molecular products (H_2 and H_2O_2) increase with the LET whilst those for the radical species (e_{aq}^- , H^\bullet , OH^\bullet) decrease. This general tendency is a result of a more efficient recombination of the radical species to form molecular species in the tracks since the density of the ionisation events is greater with high LET particles. It can be considered as a local dose rate effect. These aspects have been deduced mainly from the studies involving the chemical scavenging method [5-8] which is based on concentration measurements of a 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 ionisation process because it needs very high concentrations of scavenger that can also suffer from the direct effect of the ionization.

¹ To whom any correspondence should be addressed.

Pulse radiolysis technique was sporadically used with energetic ions since it depends on the characteristics of accelerators almost essentially devoted to physics investigations. Since the 80's Burns et al. [9-11] have performed some experiments with particles having short ranges in sample and effects on yields of average values of LET were studied. Those were reference experiments for a long time because the nanosecond time resolution has been reached.

In 90's, new hopes in new machines delivered high energy particles. Then it was interesting to compare ions and other new chemical systems for various LET. Some experiments were performed with microsecond time resolution [12-14].

GANIL could provide high energy heavy ions ranging a few millimetres in liquid samples. Its beam control allowed the pulsing of the beam at high rate with a pulse selection. Considering that intrinsic pulse have duration of 1-2 ns, pulse radiolysis studies became evident. Figure 1 shows one of the first setup used at GANIL (IRABAT irradiation port). Many details of this experiments are collected in a recent short review on pulse radiolysis with heavy ions [15]. Actually it collects the technical aspects of the pulse radiolysis method and the specificities by using with heavy ions. Here one can give a short list of publications based on these experiments [16-25]. This method has also been applied to another installation with less energetic ions in Japan [26].

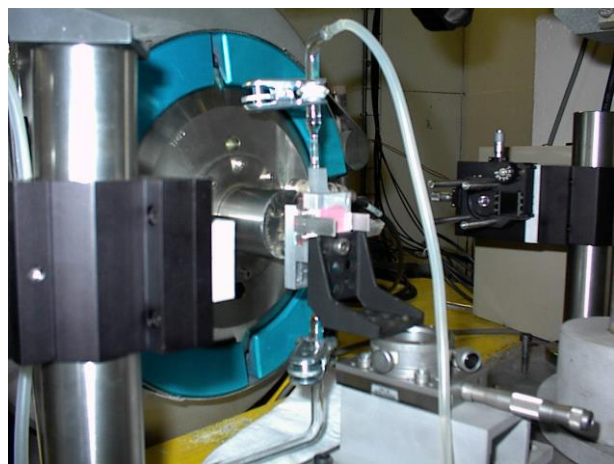


Figure 1. Setup for pulse radiolysis at GANIL (Experiment n°P492 on 19th of June 1999). Center of the picture: a vertical optical cell made of fused silica is irradiated with horizontal beam downstream the output “nose” of the machine made of a thin titanium foil.

Other water radiolysis studies have been carried out at GANIL without using the pulse structure of the beam [27, 28]. It concerned the production of stable products such as hydrogen peroxide (H₂O₂) or molecular hydrogen (H₂). In this short review we will focus essentially on the transient species studied by pulse radiolysis technique coupled to the high-energy ions at GANIL during the last 20 years.

2. Review of the main results by pulse radiolysis

2.1 Ion beam characteristics

The experiment setup used for pulse radiolysis with heavy ions is similar to those used in pulse radiolysis with electron beams or flash photolysis [29]. In principle the method consists of a pulsed source of high energy radiation coming from a particle accelerator and a synchronized acquisition of the transmitted signal. The detection used is commonly absorption spectroscopy, except for an experiment which has used chemiluminescence [20, 21], by using a spectral light of a sufficient intensity at a wavelength chosen to obtain a reasonable sensitivity. An absorbance limit of 10⁻⁴ has been reached to detect hydrated electron [17]. One special characteristic of the setup is the thickness of the irradiation window and the depth of the cell that 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 with SRIM program must be achieved to determine its thickness [30].

With GANIL cyclotron, carbon ions with energy of 95 MeV/nucleon (i.e. an energy of 1.1 GeV) 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 millimetre after the window has a LET value

of 30 ± 1 eV/nm [18]. The main other ions used in the pulse radiolysis experiments was $^{36}\text{Ar}^{18+}$ of 95 MeV/nucleon (i.e. 3 GeV) for a LET value of 280 eV/nm. Oxygen, Sulphur and Krypton ions were also used to vary LET.

The essential determinations were the radiolytic yield (G -value) as a function of time, typically in the ionization track and in the expansion period of time where the chemistry is strongly not classical since species are not homogeneously dispersed. We now present some important facts relevant to the implication of the main radicals in water radiolysis.

2.2 Hydrated electron

Hydrated electron (e_{aq}^-) has been extensively studied at low LET (mainly with electron beams) and its spectrum centred at 720 nm makes it easy to detect in visible-near IR domain [31]. Its high absorption coefficient allows its detection at very low concentration levels. This is an essential species in water radiolysis since it is the main precursor of H_2 . It is also a good candidate to probe the track structure at early time after the ion passage.

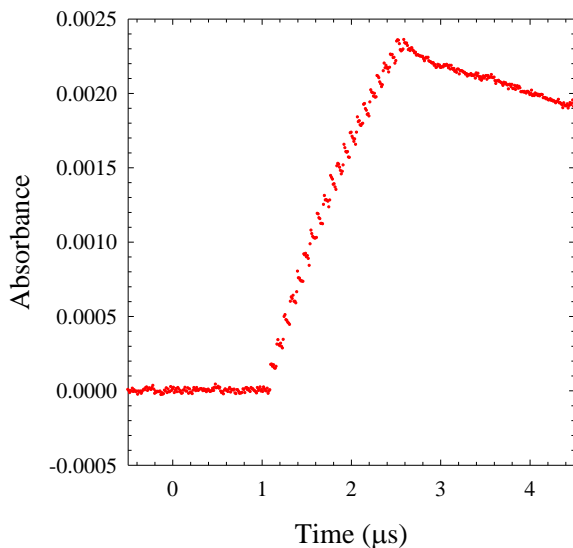


Figure 2. Real time formation of hydrated electron produced by a burst of 20 pulses $^{16}\text{O}^{8+}$ of 95MeV/nucleon having a LET of 50 keV/mm. Detection was performed at 670 nm in deaerated water at pH 12 in presence of formate at 0.01M. In these chemical conditions the hydrated electron has the longest life time because it cannot react with H^+ and OH^\bullet .

Figure 2 shows how the formation of hydrated electron was detected by using the time structure of GANIL beam. With enough intensity resolution and averaging of enough oscilloscope traces (about 1 million!) one can see the contribution of each ns pulse: the increasing absorbance is saw-teeth shaped. Since the recombination kinetics of hydrated electron is not fast enough due to the chemical conditions depicted in the figure legend, absorption signal is added to the previous one during a macro-pulse of almost $2 \mu\text{s}$ of duration. Single pulses are separated by a period of 70 ns which corresponds to the radiofrequency (14 MHz) of the cyclotron. Giving a G -value from only one single pulse of ions remained difficult because the absorption measurement was about 10^{-4} which was a real challenge. That means the concentrations were lower than 10^{-7}M . Moreover the dose must have been measured with a high accuracy. After the pulse, the concentration begins a slow decay. This evolution corresponding to the non-homogeneous chemistry is well depicted in the articles [17, 18]. Monte Carlo simulations [32, 33] reproduced the time dependence as far as the experimental G -value was suspected to be 10% too high at earliest times [34]. A better accuracy in the dosimetry was needed.

2.3 Hydroxyl radical

The hydroxyl radical is detectable only in deep UV (between 200 and 290 nm with a maximum around 220 nm) with a low absorption coefficient (about $600 \text{ M}^{-1}\text{cm}^{-1}$ at 210 nm). It is mainly detected by using scavengers. By using pulse radiolysis and the thiocyanate anion for which the reaction mechanism is now more controlled [35] OH^{\bullet} radicals can be specifically scavenged to give $(\text{SCN})_2^{\bullet-}$ radical which is more convenient to detect at the μs stage in the visible range with a relatively high extinction coefficient ($7600 \text{ M}^{-1}\text{cm}^{-1}$ at 475 nm). By this way one can observe absorption such as in Figure 3. This is not a direct detection of OH^{\bullet} but it gives reliable results if the concentration of thiocyanate is not too high ($<10^{-2}\text{M}$) [16] It was showed the scavenger molecule can be subject to multiple possible reactions in the track of heavy ions even by using other scavenger species like the bromide anion.

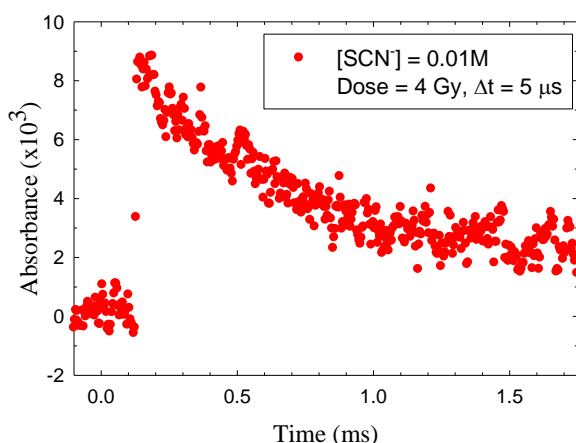


Figure 3. Formation and decrease of the absorption of $(\text{SCN})_2^{\bullet-}$ at 475 nm when using a $5 \mu\text{s}$ pulse of $^{12}\text{C}^{6+}$ of 1 GeV. This was a chemical condition of aerated solution containing 10^{-2} M of KSCN.

Another chemical system has been tested to detect hydroxyl radical (for very high LET value only) by using a light emitting chemical process. This was also a scavenging method which was associated to the pulsed heavy ion beam [19, 21]. In the chemical mechanism of luminol, the luminol molecule must react with hydroxyl and superoxide to form a molecule that emits fluorescence light at around 420 nm. At high LET value, the yield of OH^{\bullet} becomes lower than the yield of $\text{O}_2^{\bullet-}$. Therefore in this condition OH^{\bullet} yield is a limiting value. By this way, at a LET value of 280 eV/nm with Ar^{18+} ions, OH^{\bullet} yield was found to be $2.2 \times 10^{-8} \text{ mol/J}$ which was in good agreement with the literature. Due to the concentration of luminol (10^{-3}M), this yield is a primary yield, picture of an homogeneous solution in the time-range 300 ns-1 μs after the energy deposition stage[21]. That method has proved that one could detect very small concentrations of hydroxyl radical by using light emitting system that is known to be more sensitive than absorption spectroscopy[19].

2.4 Superoxide radical

The superoxide radical ($\text{HO}_2^{\bullet}/\text{O}_2^{\bullet-}$) is a special case in water radiolysis because its radiolytic yield increases with LET value. That is contrary to the recombination rule in dense ionization tracks. As stated before, the general tendency is the radical recombination increases the production of molecular species (H_2 and H_2O_2). The low reactivity of this radical in pure water essentially due to its dismutation (Reaction 1) allows it to escape the track and survives during the dense recombinations in the non-homogeneous stage.



Figure 4 gives a kinetic of formation and dismutation of superoxide under pulse heavy ion beam. To detect the superoxide radical one must know this species does not absorb too much. Its absorption coefficient at 245 nm does not exceed $2500 \text{ M}^{-1}\text{cm}^{-1}$. Associated to small concentrations, that makes this species difficult to detect. Moreover there is no scavenger available for this species. The only convenience is its lifetime, more than ms. Slow kinetics are of course more convenient to record on a large input impedance of an oscilloscope. By this way, its radiolytic yield has been determined with

ions such as Argon and Sulfur. The results have been unique and were simulated with Monte Carlo codes. Models including multiple-ionizations processes have shown they could reproduce the experimental values [36, 37].

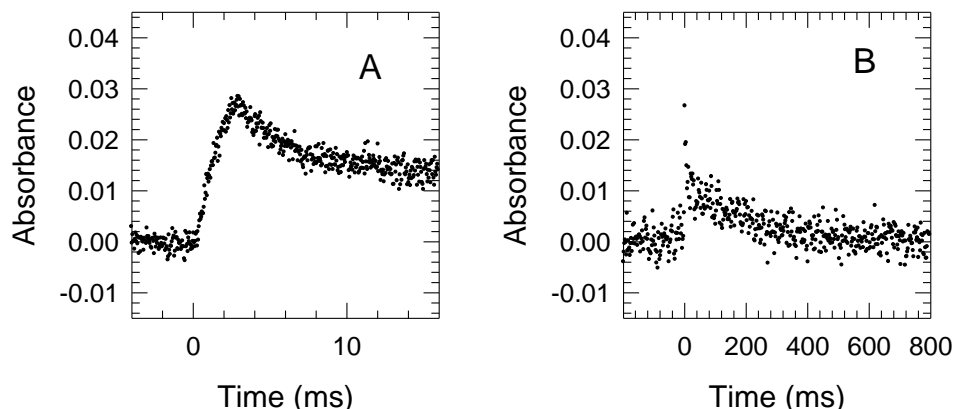


Figure 4. Formation and dismutation of superoxide after 2 ms pulse of Ar^{18+} of 3 GeV. Dose was 9.2×10^8 ions/s (500 Gy) and solution was deaerated water. The detection wavelength was 260 nm.

3. Future

3.1 Near future: extreme conditions of temperature at GANIL

Higher temperatures than ambient is now crucial for managing PWR water chemistry. Recent database focused on the lack of data for high LET particles and high temperature. These last years, our team has performed original experiment by using a special optical cell designed especially for heavy ions. The challenge is easy to conceive because heavy ions stop on a very short range and pressure due to temperature needs a strong optical cell, and therefore a sufficient thickness of material. This dilemma was overcome with a special designed window in Inconel 718 of 0.4 mm of thickness. Figure 5 shows the final optical cell containing 2 sapphire windows. Details were given in recent thesis report and article [38, 39].

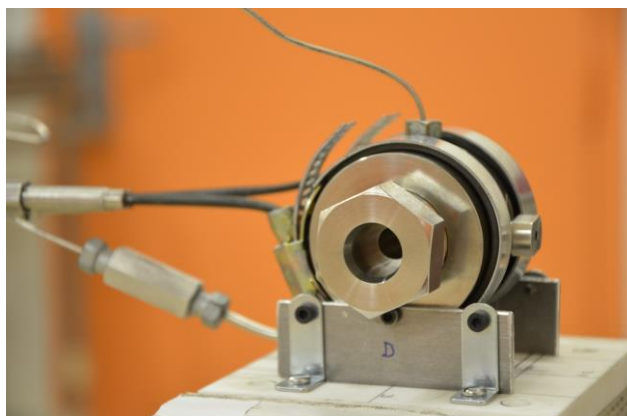


Figure 5. High temperature optical flow cell dedicated to Heavy ion irradiations. Imagine the ion beam come from the right side; ions enter in the hole of 3mm diameter to access the internal interaction chamber of 1.5mm of diameter. The main body is made of Inconel 718 in a 51 mm long and 51 mm diameter cylinder. Heaters (with their own thermocouples) and tubes are also going to the left. The picture does not include the main thermocouple and thermal protection made of silica wool.

We expect to deliver soon results concerning the radiolytic yields of HO^{\bullet} radicals as a function of temperature up to supercritical water conditions with a range of LET values from 30 to 250 eV/nm as it was already published for a limited range of temperature [39].

3.2 Future: Increasing time resolution

In the near future the ion-beam investigations will probably focus on earliest processes in the track of heavy ions. Accelerators must deliver shorter pulses than currently available and the detection must be more sensitive and highly time-resolved. The project of picosecond pulse radiolysis research with

heavy ions is possible because new designs of accelerators for proton and heavier ions swift by laser driven accelerator have already started [40-43].

Nevertheless orientations of GANIL with SPIRAL project may not concern at all radiation chemistry in the future in terms of shorter and shorter ion pulse durations[44]. Other installations based on high intensity femtosecond laser are much in phase with the radiation chemistry issues.

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