

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/229311596>

A nanosecond pulse radiolysis study of the hydrated electron with high energy carbon ions

ARTICLE *in* NUCLEAR INSTRUMENTS AND METHODS IN PHYSICS RESEARCH SECTION B BEAM INTERACTIONS WITH MATERIALS AND ATOMS · AUGUST 2003

Impact Factor: 1.12 · DOI: 10.1016/S0168-583X(02)02019-0

CITATIONS

17

READS

25

12 AUTHORS, INCLUDING:



Gerard Baldacchino

Atomic Energy and Alternative Energie...

75 PUBLICATIONS 670 CITATIONS

SEE PROFILE



Sammy Remita

Conservatoire National des Arts et Mét...

53 PUBLICATIONS 645 CITATIONS

SEE PROFILE



Emmanuel Balanzat

French National Centre for Scientific R...

167 PUBLICATIONS 2,725 CITATIONS

SEE PROFILE



Serge Bouffard

Centre de Recherche sur les Ions, les M...

161 PUBLICATIONS 2,820 CITATIONS

SEE PROFILE



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Nuclear Instruments and Methods in Physics Research B 209 (2003) 219–223

NIM B
Beam Interactions
with Materials & Atomswww.elsevier.com/locate/nimb

A nanosecond pulse radiolysis study of the hydrated electron with high energy carbon ions

G. Baldacchino ^{a,*}, G. Vigneron ^a, J.-P. Renault ^a, S. Pin ^a,
S. Rémita ^b, Z. Abedinzadeh ^b, S. Deycard ^c, E. Balanzat ^d,
S. Bouffard ^d, M. Gardès-Albert ^b, B. Hickel ^a, J.-C. Mialocq ^a

^a DSM/DRECAM/SCM URA331 CNRS, Laboratoire de Radiolyse, Bât. 546, CEA Saclay, 91191 Gif sur Yvette Cedex, France

^b Laboratoire de Chimie-Physique, UMR8601, Université René Descartes – Paris V, rue des Saints Pères, 75000 Paris, France

^c Université de Caen, UFR Pharmacie, rue H. Bequerel, 14000 Caen, France

^d CIRIL, CEA-CNRS, rue C. Bloch, 14000 Caen, France

Abstract

The radiolysis yields in pure water were determined using nanosecond pulse radiolysis using high linear energy transfer (LET) particles (1 ns pulses of high energy 1 GeV carbon ion beam). The main characteristics of this experiment were the nanosecond time resolution with heavy ion beam and the single value of LET along the ion track: 27 eV/nm. The kHz repetition rate of the pulsed beam used to reach a good signal-to-noise ratio in these experiments required the development of an acquisition method and a mathematical treatment of a DPO screen. The measured radiolytic yield for the hydrated electron at the nanosecond scale is quite high at 4.5×10^{-7} mol/J. A comparison of the experimental results obtained with a Monte Carlo simulation shows a rather good agreement at this LET value. To a certain extent this will allow a better adjustment of the Monte Carlo code.

© 2002 Elsevier B.V. All rights reserved.

PACS: 82.40.Js; 82.40.Mw; 82.50.Gw; 87.50.Ln

Keywords: LET effect; Heavy ions; Pulse radiolysis; Water radiolysis; Hydrated electron; Monte Carlo simulation

1. Introduction

The effect of linear energy transfer ($\text{LET} = (dE/dx)_{\text{elec}}$) on the radiolysis of liquid water has been understood in a general way for some time. Studies in this field remain interest in order to

depict the detailed physical-chemistry occurring in the tracks [1,2]. The LET-dependence on the radiolytic yields for the radical species generated by swift heavy particles is known as a general trend: the yields for the molecular products (H_2 and H_2O_2) increase whilst those for the radical species (e_{aq}^- , H^\cdot , OH^\cdot) decrease (except for HO_2^\cdot which does not exist as a primary species for low LET particles irradiation). This trend is understood to be a result of a more efficient recombining of the radical species to form molecular species in the tracks since the density of the ionisation events is greater

* Corresponding author. Tel.: +33-1-6908-5702; fax: +33-1-6908-3466.

E-mail address: baldacchino@drecam.cea.fr (G. Baldacchino).

with high LET particles. It is essential to know how the various species react in the track and earlier in the track in order to validate models. The hydrated electron (e_{aq}^-) is often considered as a probe for the track geometry since it has been extensively studied at low LET and its spectrum and absorptivity make it relatively easy to detect. Two methods exist which allow the reactivity of the species early in the track to be determined: the chemical scavenging method [3–8] is based on measurements of the final stable products of reactions, however the deduced time dependence of the radiolytic yields remains difficult and often involves high concentrations of scavenger species when earlier information is required. The second method is pulse radiolysis which has been used by a few groups with swift ions often restricted to light particles (protons, deuterons, helium ions) [9–12] and which has provided some recent results in absorption [13–16] and luminescence spectroscopy [17] with heavier pulsed ion beams.

This article presents a new advance in the determination of time-resolved radiolytic yields obtained for the hydrated electron in pure deaerated water at the nanosecond time scale. The ion beam used was $^{12}C^{6+}$ with an LET in water of 27 eV/nm. After the description of the experimental setup, the formation and decay of the hydrated electron will be presented and compared to that for a Monte Carlo simulation.

2. Setup and acquisition method

The experimental setup used in the nanosecond absorption spectroscopy has previously been described elsewhere [15]. It can be briefly reported here. The experiments were performed at the Grand Accélérateur National d'Ions Lourds (GANIL – France) cyclotron. The irradiation cell was a flow-through cell made of Suprasil quartz. In order to have a value of LET inside the thickness of the sample that varies within less than 1 eV/nm, the input window thickness of the cell was 0.5 mm. The absorption analysis is performed along a 2.5 cm optical pathway using a continuous laser diode at 670 nm collimated with two 0.1 mm pinholes. The transmitted light of the laser was

then focused into a 50 m length multimode optical fibre in order to perform the detection in a room far from the irradiation site. A beam of 1.14 GeV (95 MeV/A) C^{6+} is used giving an energy of 1.12 GeV in the water sample. The LET value under these conditions is 27 eV/nm. One pulse of 1 ns is extracted from the radio-frequency structure of the beam every 1 ms. The dose delivered to the sample is then determined by the LET value and the intensity of beam measured with a secondary electron detector located into the beam [15]. The dose for all measurements presented in this article was approximately 6 mGy/pulse.

Due to the very weak transient signals expected, two improvements were made in order to obtain a better accuracy in the determination of the radiolytic yields at the nanosecond time scale. A Faraday cup collects the ions that cross the sample cell. A calibration of this device was achieved by placing the Faraday cup in the beam prior to the actual experiment. Secondly the photodiode current was amplified by a factor of 10 (BX-31A wide band preamplifier, NF Electronic Instruments). This was then numerised by a 1 GHz, TDS 784D, Tektronix oscilloscope configured in DPO (Digital Phosphor Oscilloscope) mode. This choice of mode allows us to record millions of sweeps in a wide memory and with a high repetition rate up to 100 kHz. As a result of an improved renewal of the water sample in front of the ion beam, the repetition rate was limited to 1 kHz. Using a flow rate of 1 cm³/s, the number of acquisitions was 1–2 millions. After the scope memory was recorded in a file and translated in ASCII format in *xyz* file where *x*, *y* and *z* are time, voltage (with a 8-bit resolution) and weight (with a 16-bit resolution) respectively. To obtain a time versus voltage record it is necessary to process *x*, *y* and *z* columns by applying the following simple mathematical treatment:

$$Y(x) = V_{\text{off}} + \frac{\sum_{i=1}^{255} y_i(x) z_i(x)}{\sum_{i=1}^{255} z_i(x)},$$

where V_{off} is the offset voltage added to capture the signal on the screen of the scope and $Y(x)$ is the plot needed in order to determine the time dependence of the absorption signal $A(x) = \log(Y_0/Y(x))$. Y_0 is the voltage level without any transient

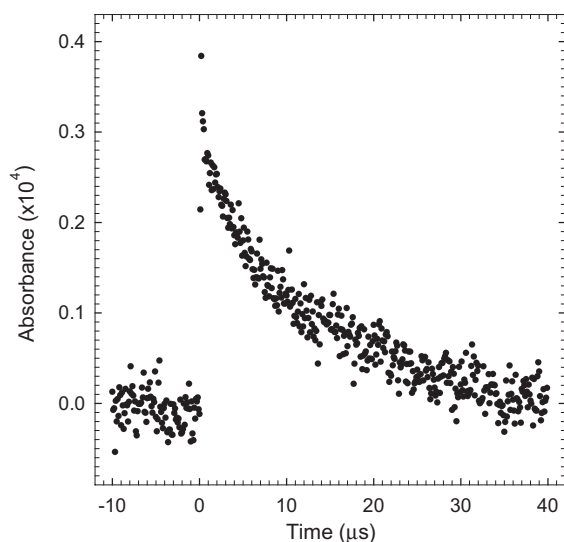


Fig. 1. Absorption kinetic in the time range of 50 μs for the hydrated electron at 670 nm in pure deaerated water after a 1 ns pulse of $^{12}\text{C}^{6+}$.

absorption. An example of an $A(x)$ curve is presented in Fig. 1. To convert the absorbance $A(x)$ into concentration using the Beer–Lambert law the extinction coefficient of $17020 \text{ M}^{-1} \text{ cm}^{-1}$ at 670 nm for hydrated electron was used [18].

The pure water was prepared using a Millipore Alpha-Q device giving a water resistivity of $18.2 \text{ M}\Omega \text{ cm}$ and a low total organic carbon less than 10 ppb. The solutions were deaerated by bubbling with high purity argon (99.9995%).

3. Results and discussion

Fig. 1 shows the transient absorption of the hydrated electron at 670 nm generated using an irradiation pulse of 1 ns of C^{6+} . The dose delivered to the sample at each pulse was 5.6 mGy calculated from the LET value of 27 eV/nm and the irradiated volume ($25 \times 3 \times 2.5 \text{ mm}^3$). The formation of hydrated electron takes place during the irradiation pulse and is not numerised within this time scale. The absorbance maximum corresponds to a concentration of e_{aq}^- of about 10^{-9} mol/dm^3 . The decay during the following 40 μs is well fitted with a nice signal-to-noise ratio, by pseudo-first order

kinetics corresponding to the reaction of e_{aq}^- with a small concentration of diluted oxygen (a concentration of $5 \times 10^{-6} \text{ mol/dm}^3$ can be calculated from the rate constant $1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [19]). This result is coherent with a previous result [15] and depends only on the way the solution is deaerated. In this experiment, a volume of 5 dm^3 was deaerated during more than 1 h.

A better time resolution allows a more precise determination of the formation and decay of the hydrated electron (Fig. 2). Fig. 2 shows how the formation of the hydrated electron follows the duration of the pulse attaining a maximum absorbance of 1.2×10^{-4} which corresponds to a concentration of $2.8 \times 10^{-9} \text{ mol/dm}^3$. Considering the delivered dose of 6.2 mGy/pulse, the radiolytic yield of hydrated electron at the nanosecond time scale is thus $4.5 \times 10^{-7} \text{ mol/J}$ (4.3 molecule/100 eV). This value is greater than those obtained by other authors with the same order of magnitude of LET but using helium ions of 35 eV/nm with the scavenging method with $\text{S}_2\text{O}_8^{2-}$ as the scavenger species [6]. The yield obtained by LaVerne and Yoshida [4] also with helium ions and with the glycylglycine scavenger species is similar to our

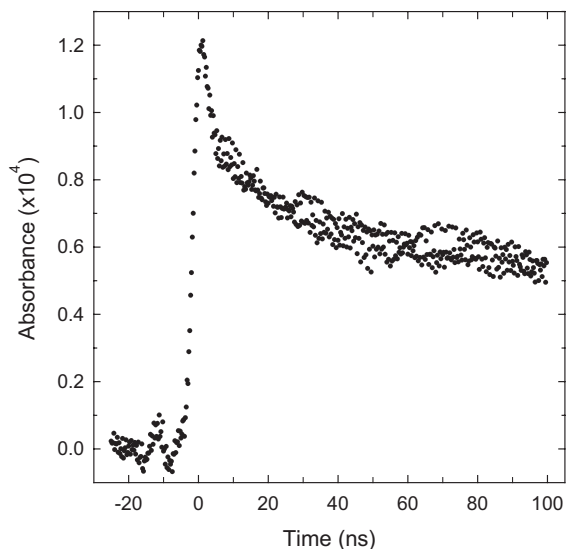


Fig. 2. Absorption kinetic in the time range of 100 ns for the hydrated electron at 670 nm in pure deaerated water after a 1 ns pulse of $^{12}\text{C}^{6+}$.

value at 10^{-8} s (these authors found $g(e_{aq}^-) = 2.5$ mol/J). In all case this value is now close to the low LET radiolytic yields of hydrated electron. The only nanosecond time-resolved measurement of radiolytic yields of the hydrated electron approaching this experiment was performed using a 3-MeV proton beam of 1 ns with a mean LET of 29 eV/nm [11,12]. These authors found a yield of 3.2 molecules/100 eV in pure water which is again less than it is found with our experiment. One reason for these differences is the values of LET considered. A mean value of LET including the Bragg peak energy deposition can enhance the high values of LET in a thin sample (0.15 mm in [11,12]).

The kinetic decay illustrated in Fig. 2 shows a very rapid decay within the first 5 ns after the end of the pulse and results in the concentration of the hydrated electron being 2/3 of the maximum. After this time range, the other surviving electrons can diffuse and react in another time range (Fig. 2 limits the observation to 100 ns) although this still does not correspond to the homogeneous chemistry (reaction with oxygen or impurities) which commonly starts in the microsecond time domain [1,2]. These results have to be compared with a diffusion kinetic model.

4. Monte Carlo simulation

A comparison of the experimental results with a Monte Carlo simulation is presented in Fig. 3. The experimental results are a collection of 3 various time-resolutions acquisitions in order to cover the whole range 200 ps to 40 μ s. The solid line is the simulation result obtained using a Monte Carlo program using a diffusion kinetic model [20–22] which is based on the accumulation of the results of 10 independent tracks 4 μ m in length. The initial parameters for the simulation was given to fit with those of our experimental conditions ($^{12}\text{C}^{6+}$ of 1.1 GeV, pure water). The kinetics for the decay of e_{aq}^- obtained for the experiment correspond well with that obtained using the Monte Carlo simulation but the experimental yield is about 30% higher than simulation. The small agreement between these two approaches can be explained. This

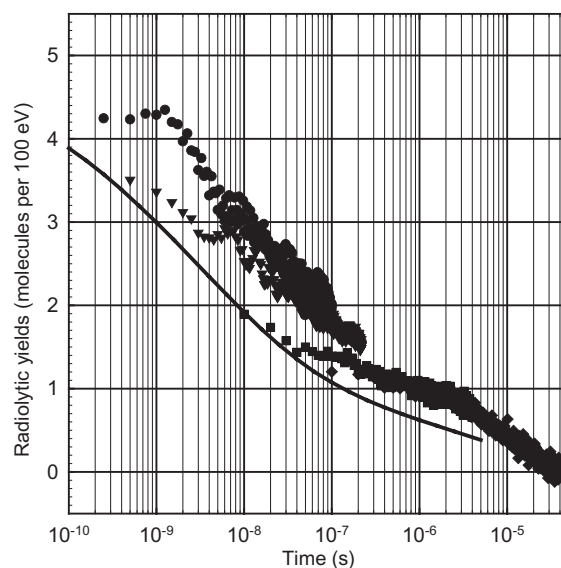


Fig. 3. A comparison of (—) Monte Carlo simulation result obtained for an average of 10 single tracks of $^{12}\text{C}^{6+}$ of 1.1 GeV and (●, ■, ▼, ◆) experimental results obtained with 3 different time-resolutions for a 1 ns pulse irradiation of $^{12}\text{C}^{6+}$ of 1.1 GeV.

Monte Carlo code is adjusted (cross-sections mainly) on the basis of a few experimental results [20] particularly with protons, resulting in the drawbacks seen before. Nevertheless, it is clear that the experimental determination of the radiolytic yields is very sensitive to the accuracy of the concentrations and dose measurements. Further works is required to improve the signal-to-noise ratio and the dosimetry for further determinations.

Acknowledgements

These studies were performed at the GANIL. The authors thank Dr. S. Foley for the corrections of this manuscript.

References

- [1] A.O. Allen, Radiat. Res. 1 (1954) 85.
- [2] J.A. LaVerne, Radiat. Res. 153 (2001) 487.
- [3] A. Appleby, H.A. Schwartz, J. Phys. Chem. 73 (1969) 1937.
- [4] J.A. LaVerne, J. Yoshida, J. Phys. Chem. 97 (1993) 10720.
- [5] N. Chitose, Y. Katsumura, Z. Zuo, M. Domae, K. Ishigure, T. Murakami, J. Chem. Soc., Faraday Trans. 93 (1997) 3939.

- [6] N. Chitose, Y. Katsumura, M. Domae, Z. Zuo, T. Murakami, *Radiat. Phys. Chem.* 54 (1999) 385.
- [7] N. Chitose, Y. Katsumura, M. Domae, Z. Cai, T. Murakami, J.A. LaVerne, *J. Phys. Chem. A* 103 (1999) 4769.
- [8] N. Chitose, Y. Katsumura, M. Domae, Z. Cai, Y. Muroya, T. Murakami, J.A. LaVerne, *J. Phys. Chem. A* 105 (2001) 4902.
- [9] M.C. Sauer, K.H. Schmidt, E.J. Hart, C.A. Naleway, C.D. Jonah, *Radiat. Res.* 70 (1977) 91.
- [10] M.C. Sauer, K.H. Schmidt, C.D. Jonah, C.A. Naleway, E.J. Hart, *Radiat. Res.* 75 (1978) 519.
- [11] W.G. Burns, R. May, G.V. Buxton, G.S. Tough, *Faraday Discuss. Chem. Soc.* 63 (1977) 47.
- [12] W.G. Burns, R. May, G.V. Buxton, G.S. Wilkinson-Tough, *J. Chem. Soc., Faraday Trans.* 1543 (1981) 77.
- [13] G. Baldacchino, S. Bouffard, E. Balanzat, V. Mouton, M. Gardès-Albert, Z. Abedinzadeh, D. Jore, S. Deycard, D. Le Parc, B. Hickel, *J. Chim. Phys.* 94 (1997) 200.
- [14] G. Baldacchino, V. Wasselin-Trupin, S. Bouffard, E. Balanzat, M. Gardès-Albert, Z. Abedinzadeh, D. Jore, S. Deycard, B. Hickel, *J. Chim. Phys.* 96 (1999) 50.
- [15] G. Baldacchino, S. Bouffard, E. Balanzat, M. Gardès-Albert, Z. Abedinzadeh, D. Jore, S. Deycard, B. Hickel, *Nucl. Instr. and Meth. B* 146 (1998) 528.
- [16] G. Baldacchino, D. Le Parc, B. Hickel, M. Gardès-Albert, Z. Abedinzadeh, D. Jore, S. Deycard, S. Bouffard, V. Mouton, E. Balanzat, *Radiat. Res.* 149 (1998) 128.
- [17] V. Wasselin-Trupin, G. Baldacchino, S. Bouffard, E. Balanzat, M. Gardès-Albert, Z. Abedinzadeh, D. Jore, S. Deycard, B. Hickel, *J. Phys. Chem. A* 104 (2000) 8709.
- [18] B.D. Michael, E.J. Hart, K.H. Schmidt, *J. Phys. Chem.* 75 (1971) 2798.
- [19] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, *J. Phys. Chem. Ref. Data* 17 (1988) 513.
- [20] Y. Frongillo, M.J. Fraser, V. Cobut, T. Goulet, J.P. Jay-Gérin, J.P. Patau, *J. Chim. Phys.* 93 (1996) 93.
- [21] V. Cobut, Y. Frongillo, J.P. Patau, T. Goulet, M.J. Fraser, J.P. Jay-Gérin, *Radiat. Phys. Chem.* 51 (1998) 229.
- [22] Y. Frongillo, T. Goulet, M.J. Fraser, V. Cobut, J.P. Patau, J.P. Jay-Gérin, *Radiat. Phys. Chem.* 51 (1998) 245.