

X-ray absorption spectroscopy of HBr aqueous solutions.

*D. Saffré¹, E. Atinault¹, G. Vigneron¹, S. Pin¹, O. Proux², D. Testemale², J.-L. Hazemann²,
G. Baldacchino¹*

¹CEA, DSM, IRAMIS, SIS2M, Laboratoire de Radiolyse, 91191 Gif-sur-Yvette, France

²Institut Néel, CNRS, Grenoble, France

ESRF (European Synchrotron Radiation Facility) in Grenoble provides an intense beam of wide range X-rays wavelengths. This is commonly used as analyzing beam light for diffraction, diffusion or X-ray spectroscopy. The characteristics of the beam allow the study of radiolytic species in various conditions. We aim at using pulse radiolysis thanks to this source.

The first main objectives were to carry out a beamline dosimetry, to check if pulse radiolysis could be settled and to use the high temperature and high pressure irradiation cell designed by the laboratory of Jean-Louis Hazemann.

I) Pulse radiolysis of HBr aqueous solutions with X-rays beams at the Br-edge.

Aims of the experiment and scientific background

Water under X-ray irradiation is subject to be ionized since the ionization potential of water is around 10 eV. The ionization process is mainly due to the photoelectric process and the production of electrons in excess in the bulk of water is the starting point of the production of the water radicals: the hydrated electron, the hydroxyl radical, the hydrogen atom. These radicals recombine and give molecular species: H₂ and H₂O₂ [1-2]. Knowing the first steps of the ionization dynamics, solvation and heterogeneous recombination in the ionization spurs during the first μ s is a great challenge and is very useful to control the long term production of molecular species.

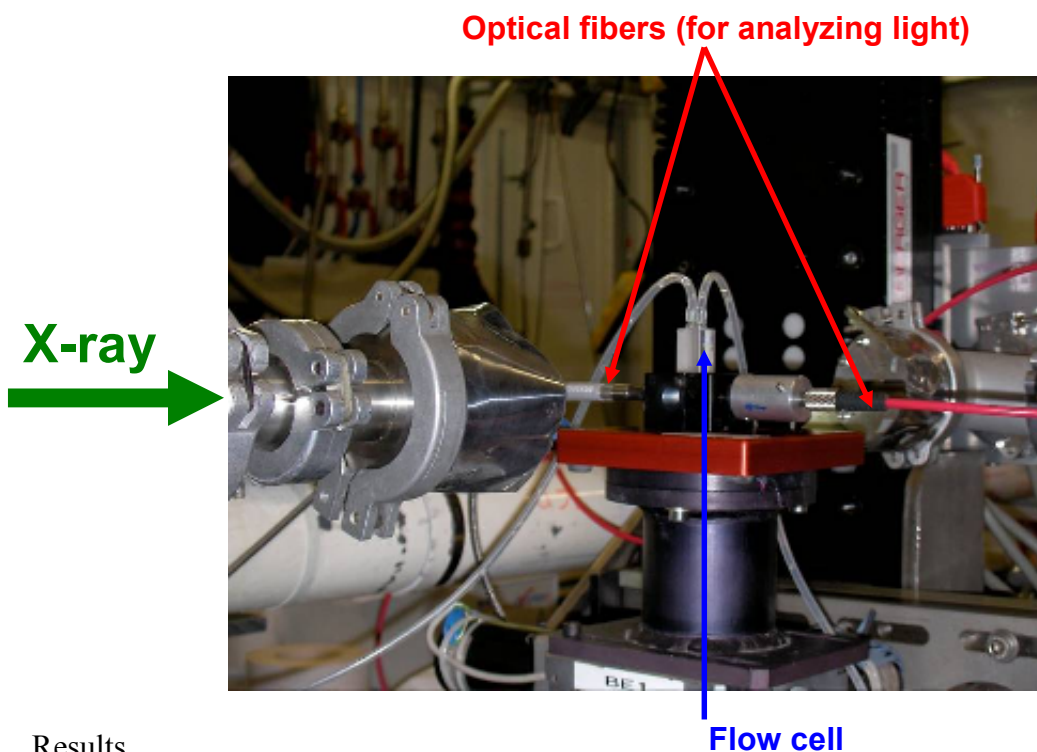
Many experiments have been performed with gamma rays, high energy electron beams and heavy ions by using continuous or pulse mode in order to depict the kinetics of the chemical mechanism from the ps to ms [3, 4, 5, 6]. Some recent pioneer articles are now talking about the formation of hydrated electrons in the ps regime produced under the effect of high energy X-rays on liquid water [4].

The ultimate aim of the collaboration is to link the structure of water radicals (solvation, charge transfer, short distance order, structure...) with their formation and reaction. By using X-ray beam, the approach is ideal because the same particle is used for ionization and structural detection (XANES, EXAFS...). A recent paper has shown the feasibility of the coupling with X-ray detection methods could be applied [5]. We have also recently performed some tests to know if this kind of investigation is realistic. Now we can propose a setup to obtain a signal from hydrated electron in pure water and in water containing Br⁻ ions. These ions can be ionized with the X-beam and the generated excess of hydrated electrons could be seen by pulse radiolysis too.

Experimental method

The time resolved spectroscopy is used for the direct detection in visible-near IR (600-800 nm) of the hydrated electron. The method consists in a pump-probe configuration where the pump is the X-ray beam and the probe is a laser [3]. The first experiment will use a CW

laser such as a laser diode at 680 nm, or a pulse laser at 266 nm synchronized with the X-ray bunch.



Results

We have checked the synchronization with the RF structure of ESRF in 4 bunches configuration. The detection was achieved by using a photodiode and a fast oscilloscope. The time resolution is given by the pulse duration of the X-ray pulse and the laser pulse (for pulsed 266 nm) or the oscilloscope (for CW 680 nm). The 4 bunches configuration allows one pulse delivery of 45 ps of duration every 700 ns (we measured it with a good accuracy). In this simple configuration, we have not obtained any transient signal from hydrated electron. The reason is the very low dose delivered by one pulse (a few mGy measured by Fricke dosimeter) and the short optical path length in the optical analysis (perpendicularly to the X-ray axis) : 300 μ m.

In the future, we expect to obtain a signal by using a collinear detection (X beam and laser beam are collinear along a 2 cm optical pathway). This will be achieved with special triangular optical flow cell. This cell has very thin Al-coated windows for a better X rays penetration and enabling a double path analysis. The alignment of this optical system remains a challenge and the setup must be performed in our laboratory in Saclay before mounting in line on BM30. We expect to gain a factor 100 on the signal compared to the perpendicular detection made previously.

The expected kinetics could be compared with the recent results obtained by using high intensity laser which can generate X-ray bunches^[4].

In the case of high concentration of Br⁻ aqueous solutions, electrons could be ejected from Br⁻ and form an excess of hydrated electrons. That depends on the X-rays energy used, that surely happened over the energy of 13.47 keV which is the ionization edge of Br atoms. An excess of hydrated electron coming from this ionization is expected. The detection of hydrated electron will be done at 680 nm.

On the other hand, an irradiated molar Br⁻ solution can produce a non negligible concentration of stable Br₃⁻ (see the second part of this report). Its formation can be probed at 266 nm. In paper^[5], the laser at 266 nm also allowed to produce Br⁰, Br₂⁻ (at low concentration). We

expect that in a high concentration configuration, Br_3^- can be analyzed by XANES and EXAFS.

II) X-rays radiolysis of HBr aqueous solutions.

Aims of the experiment and scientific background

The great challenge of the future is to examine the radiation chemistry in supercritical conditions (for water : $T > 374^\circ\text{C}$, $P > 22\text{ MPa}$) in relation with the Gen 4 project of future nuclear reactors and especially the one using supercritical water (SCWR).

The preliminary results obtained in experiment in BM30 hutch during 2009, about the Fricke-dosimetry and HBr solutions give us the opportunity to work in a supercritical medium. Moreover, changing the conditions of temperature and pressure gives the access to the dynamics of water radicals in supercritical fluids as obtained recently with electron pulses [7].

Experimental method

The aqueous solutions were prepared using ultra pure water from a Millipore system. The chemicals were used as received without further purification: HBr (purity $> 62\%$) from Sigma-Aldrich. The pH of the HBr aqueous solutions was either the natural one (between 0 and 2). The solutions were saturated with dinitrogen, or nitrous oxide by bubbling 20–30 min before irradiation. All solutions were irradiated at room temperature (about 22°C) with X-rays from a synchrotron source (ESRF, Grenoble) providing dose rates between 36 and $120\text{ kGy}\cdot\text{h}^{-1}$. The X-ray beam went through an optical cell (fused silica 10 mm cell with an efficient optical path length of $300\ \mu\text{m}$ due to the X-beam size, HELLMA) for spectrophotometric measurements under the saturation gas atmosphere. The steady-state absorption spectra were recorded with a single beam diode array UV–visible spectrophotometer (AVANTES) operated at a resolution of 2 nm and connected with multimode optical fibers ($400\ \mu\text{m}$). The light of a deuterium-lamp is analyzed and recorded in the UV domain (220–380 nm).

The dose rates used in the experiments were precisely determined by means of the Fricke method.

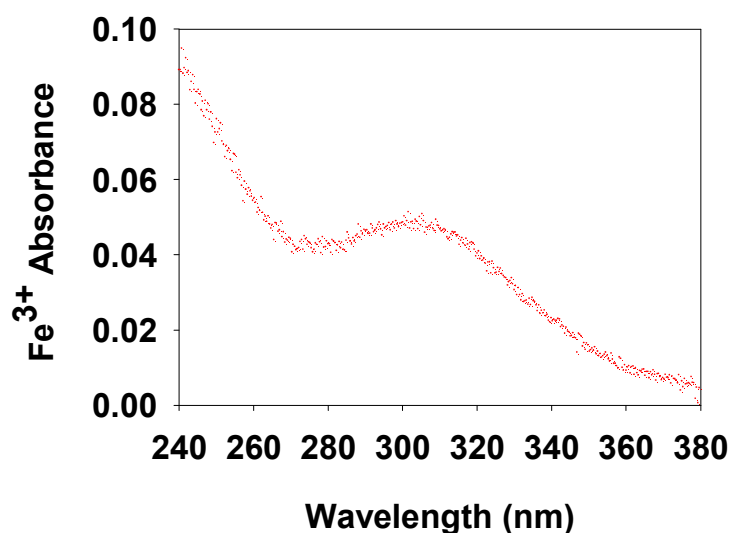


Figure : Fricke dosimeter spectrum during irradiation at 18 keV after 20 s.

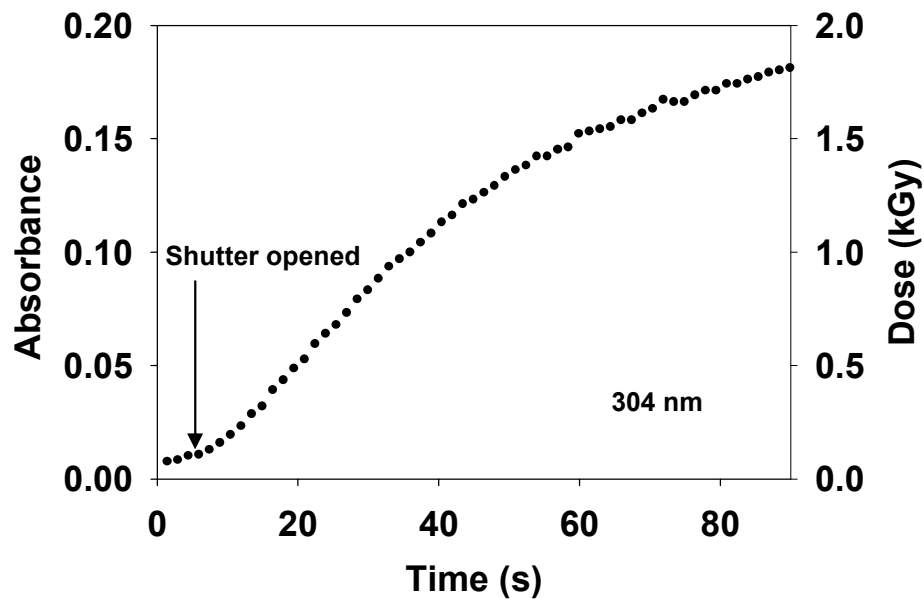
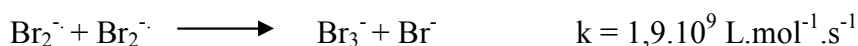


Figure : Absorbance of the Fricke dosimeter solution with the dose during 18 keV X-ray irradiation at 304 nm.

From the slope of the line, we deduced a dose rate of 120 kGy.h⁻¹.

Then we aimed at analyzing the *in situ* formation of tribromine ion, Br₃⁻. The oxidation of bromide ions leads to this species which remains stable under supercritical conditions. The oxidation of bromide ions, Br⁻, in aqueous solution under irradiation represents a **complex mechanism** and involves many reactions^[12,13]. Moreover, there is an equilibrium^[14] between Br₃⁻ and Br₂ (K = 16,1 dm³.mol⁻¹). It was also found that the absorption band maximum of Br₃⁻ is located at **266 nm** (ε(Br₃⁻) = 40900 ± 400 M⁻¹.cm⁻¹ ^[15]).

Here is a simplified mechanism which leads to the formation of Br₃⁻ :



Different HBr aqueous solutions were irradiated at room temperature and atmospheric pressure with an X-ray beam whose energy was between 13 and 18 keV (below and above the ionization edge of Br atom). The irradiation of these solutions aims at studying the effect of the initial concentration of Br⁻ on the oxidation mechanism of Br⁻. Then, it was possible to determine the value of the radiolytic yield of the formed tribromine ion and thus the value of the hydroxyl radical OH[·]. These solutions were also irradiated at different energies and under different saturation gas (N₂, N₂O)^[16] in order to understand better the processes which control the oxidation. We have determined the formation yield of the tribromine ion by using pulse or steady-state^[17] radiolysis and by analyzing the temporal evolution of the absorption spectrum during short time (a few seconds) irradiations.

1) At low initial Br⁻ concentration

HBr aqueous solutions at different concentrations were irradiated at different dose rates and different saturation gaz.

[Br ⁻] (mol.L ⁻¹)	pH	Energy (keV)	Saturation gaz
$8,9 \cdot 10^{-3}$	2.1	14-18	N ₂ , N ₂ O
$4,5 \cdot 10^{-2}$	1.3	14-18	N ₂ , N ₂ O
$8,9 \cdot 10^{-2}$	1.1	14-18	N ₂ , N ₂ O
$3,1 \cdot 10^{-1}$	0.5	14-18	N ₂ , N ₂ O

Table : Characteristics of the studied bromide aqueous solutions

Taking into account the extinction coefficient of the tribromine ion and considering that absorption due to Br₂⁻ is negligible, the tribromine ion formation yield can be determined for each sample. Before irradiation, the absorption spectra of all the solutions did not present any absorbance above 250 nm. After X-ray irradiation, for all the solutions at acidic pH, an absorption band around 266 nm was present.

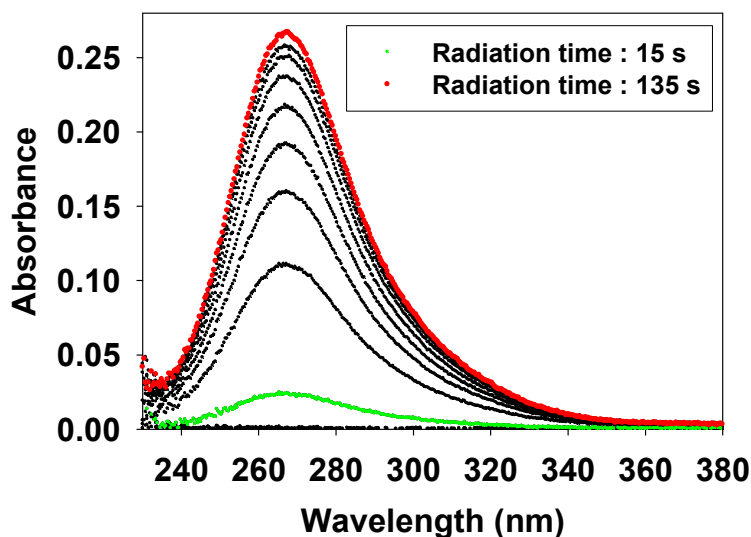


Figure : Evolution of the absorption spectrum of Br₃⁻ during a short period of irradiation at 18 keV (aerated solution, 0.31 M Br⁻).

We present the absorbance at 266 nm as a function of the irradiation time for the studied solutions.

For the aerated solutions, by increasing the irradiation dose, the intensity of the absorption band at 266 nm increases without any change in the shape. That means one stable species is produced under irradiation, with a specific radiolytic yield. The intensity of the absorption band depends on the conditions, the highest intensity being obtained for the solution containing 0,31 M Br⁻. The increase in the absorbance at 266 nm versus irradiation time is linear for a delimited range of dose. The product formed by X-irradiation in aerated solutions is stable as the shape and the intensity of the absorption spectrum remains the same after irradiation. Knowing that the absorption of Br₂ is negligible in that spectral domain ($\epsilon_{266\text{nm}}(\text{Br}_2) = 47 \text{ M}^{-1} \cdot \text{cm}^{-1}$) (Beckwith et al., 1996), the absorption band observed around 266 nm corresponds to that of Br₃⁻. Nevertheless, after irradiation, both species Br₃⁻ and Br₂ are present in solution. Given the equilibrium constant, $K = 16.1 \pm 0.3 \text{ M}^{-1}$ (Wang et al., 1994), for

0,31 M Br⁻ solutions, Br₃⁻ represents around 83.3% of the oxidized Br⁻ and Br₂ 16.7%, while for 8,9.10⁻³ M Br⁻ solutions, the Br₃⁻ percentage is reduced to 12.5%.

[Br ⁻] (mol.L ⁻¹)	% Br ₃ ⁻	% Br ₂
8,9.10 ⁻³	12.5	87.5
4,5.10 ⁻²	42	58
8,9.10 ⁻²	58.9	41.1
3,1.10 ⁻¹	83.3	16.7

Table : Evolution of the predominance of the tribromine ion with the initial Br⁻ concentration.

If we assume that, for a given irradiation dose, taking $\epsilon_{266\text{nm}}(\text{Br}_3^-) = 40900 \text{ M}^{-1} \text{ cm}^{-1}$, we should have observed that for lower initial concentrations than 0.31 M, the observed values for absorbance are lower than the expected ones. That indicates that the Br⁻ oxidation yield depends on the concentration of bromide.

The behaviour of the N₂-saturated solutions at acidic pH during and after X-irradiation is the same as that previously described for the aerated solutions, except that, for a given dose, the intensity of the 266 nm absorption band is much lower. In N₂-saturated solution at high pH, the hydrated electron is not scavenged and reacts with HO[•] and mainly with Br₂⁻ as soon as it is formed in the spurs. Following a similar reasoning as previously, we may roughly estimate that the radiolytic yield of Br₂⁻ is that of HO[•] at short time : $G(\text{Br}_2^-) \simeq G_{4\text{ns}}(\text{HO}^\bullet) = 3,6.10^{-7} \text{ mol.J}^{-1}$. Then the radiolytic yield of Br₃⁻ would correspond to half the yield of Br₂⁻ Diminished by the radiolytic yield of the hydrated electron for the homogeneous step : $G(\text{Br}_3^-) \simeq (G(\text{Br}_2^-) - G(e_{\text{aq}}^-))/2 = 0,45.10^{-7} \text{ mol.J}^{-1}$. This deduced value for G(Br₃⁻) is in good agreement with the experimental value of 4,4.10⁻⁸ mol.J⁻¹(obtained at 18 keV).

To sum up, for solutions with low concentrations in bromide, as expected, the radiolytic yield of Br₃⁻ is reduced. Two main reasons account for that decrease. First, by reducing the concentration of Br⁻, the HO[•] scavenging power is diminished and the time constant for the formation of Br₂⁻ gets longer. So, the reaction between HO[•] and e_{aq}⁻ is favored and the oxidation yield of Br⁻ is decreased. Second, owing to the equilibrium, by lowering the concentration of Br⁻, the ratio between Br₃⁻ and Br₂⁻ is diminished and the absorbance at 266 nm due to Br₃⁻ is lower.

Thanks to the figure 1, we have noticed that, at acidic pH, Br₃⁻ is still formed under irradiation since the absorbance at 266 nm rises with the irradiation dose, but the variation is no more linear, the formation yield of Br₃⁻ decreasing with the dose. Initial radiolytic yield of Br₃⁻ are found to be slightly lower than the yield determined for bromide solutions at natural pH. At pH 1, the hydrated electron is not scavenged by N₂O, but reacts with H₃O⁺ and is converted to H[•] atom. Thus, the hydrated electron does not contribute to the oxidation of Br⁻. In addition, the generated H[•] may react with Br₂⁻ in the spurs and then, with Br₃⁻, reducing the radiolytic yield of Br₃⁻. It is worth noticing that, at acidic pH, Br₂⁻ is formed from HO[•] much rapidly than at neutral pH, as already observed in the analog case of Cl₂⁻ (Atinault et al., 2008). By increasing the irradiation dose, the concentration of Br₃⁻ increases and some reactions become more favored, hence a decrease in the formation yield with the dose.

In the presence of dioxygen (10⁻⁴ M in pure water), H[•] atom is partially scavenged by O₂ to form HO₂[•]. Then, HO₂[•] takes part in the oxidation mechanism and contributes to increase the radiolytic yield of Br₃⁻. However, when the concentration in tribromine is high enough (> 10⁻⁴ M), there is a competition between the scavenging of H[•] atom by O₂ and the scavenging of the H[•] atom by Br₃⁻. The second reaction leads to a decrease in the radiolytic yield of Br₃⁻ similar to that obtained in the absence of O₂.

Br_3^- is still produced under X-ray irradiation in an aqueous solution containing 0.3 M HBr at acidic pH but purged by N_2 gas. In that case the radiolytic yield is quite low and decreases with the dose.

$[\text{Br}^-]$ (mol.L ⁻¹)	G (mol.J ⁻¹)
$8,9 \cdot 10^{-3}$	$2,1 \cdot 10^{-9}$
$4,5 \cdot 10^{-2}$	$5,1 \cdot 10^{-9}$
$8,9 \cdot 10^{-2}$	$6,9 \cdot 10^{-9}$
$3,1 \cdot 10^{-1}$	$4,9 \cdot 10^{-8}$

Table : Evolution of G(Br_3^-) at low initial Br^- concentrations.

2) At high initial Br^- concentration

A) Influence of the initial Br^- concentration on the formation yield of Br_3^-

1) At 13 keV

Br ⁻ concentration (M)	Scavenging time of HO [·] by Br ⁻	G (10 ⁷ mol.J ⁻¹)		
		Air	N ₂	N ₂ O
0.1	~ 900 ps	0.6-1.3	0.9-1.8	1.0-2.1
0.3	~ 300 ps	1.6-3.4	1.1-2.3	1.4-3.1
0.6	~ 150 ps	2.4-5.2	1.9-4.2	1.9-4.0

Table : evolution of G(Br_3^-) with the initial Br^- concentration.

Those radiolytic yields are obtained from the slope of the line $A = f(t)$.

For aerated bromide solutions, HO₂[·] is present and plays its role of oxidizing species but this phenomenon is not visible because of the fast disappearance of Br_3^- which hides this theoretical increase of G(Br_3^-).

For the N₂-saturated solutions, the radical HO₂[·] can not be formed and can not take part in the oxidation mechanism. For a same initial concentration in Br⁻ (above 0.3 M), we have noticed that the radiolytic yield of the tribromine ion for N₂-saturated solutions is lower than for the aerated solutions. Under N₂ atmosphere, hydrogen atoms are not scavenged and are free to react with Br_3^- : the radiolytic yield of Br_3^- decreases.

The presence of N₂ for lower concentrations has no effect on the oxidation. The mechanism must be changing with the initial concentration of bromide. Some reactions may become predominant. Moreover, the equilibrium between Br₂ and Br_3^- is shifted to the formation of Br₂.

With the presence of nitrous oxide, the medium is oxidizing. All hydrogen atoms are transformed into radicals OH[·]. H atom can not react anymore with the formed tribromine ions. The oxidation of bromide ions should be more important. But it is not visible if we compare G(Br_3^-) obtained in aerated solutions and in N₂O-saturated solutions at high concentrations. We must also bear in mind that the X-ray beam energy is quite low and it could be a reason to explain this limited oxidation. The transmission of the X-ray beam through the silica input window of the optical cell may not be sufficient enough to irradiate any molecule included in the analyzed volume.

2) At 17keV

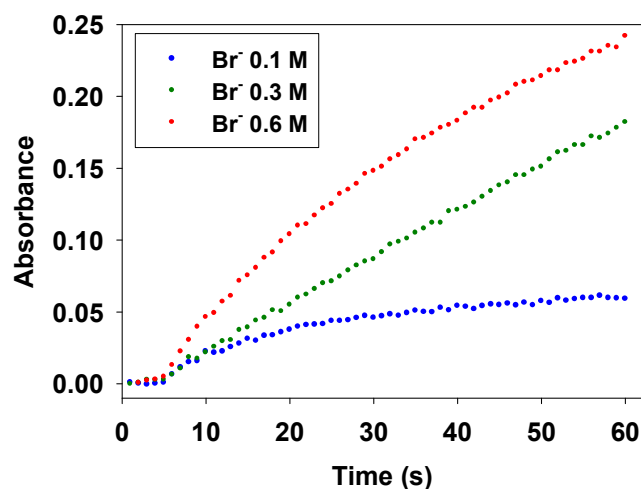


Figure : Absorption kinetics of different aerated solutions of Br⁻ at 17 keV.

Br ⁻ concentration (M)	Scavenging time of HO [·] by Br ⁻	ρG (10 ⁷ mol.J ⁻¹)		
		air	N ₂	N ₂ O
0.1	~ 900 ps	1.0-1.2	1.1-1.3	1.6-1.8
0.3	~ 300 ps	1.3-1.4	1.4-1.6	1.3-1.4
0.6	~ 150 ps	2.4-2.7	1.2-1.4	3.8-4.3
0.9	~ 100 ps	4.6-5.2		

Table : Evolution of G(Br₃⁻) with the initial Br⁻ concentration.

We find higher G(Br₃⁻) values when the X-ray beam energy increases. The penetration inside the optical cell is better at 17 keV than at 13 keV. More bromide ions are irradiated in the analyzed volume.

We can compare the result obtained for the 0.9M HBr aerated solution with the result obtained for 2 M NaBr aerated solutions at natural pH (Mirdamadi-Esfahani, 2009). It was found that G(Br₃⁻) = 5.10⁻⁷ mol.J⁻¹ for 2 M HBr aerated solutions. Our experimental value is in good agreement with the value obtained at 2M NaBr.

As, in 0.9 M Br⁻ solution, almost all the oxidized Br⁻ are under the form of Br₃⁻ and as producing one tribromine ion requires oxidation of two bromide ions, we deduce that, in these conditions, the Br⁻ oxidation yield is about 9,8 ± 0,6.10⁻⁷ mol.J⁻¹.

For lower concentrations in bromide (0.1M), the presence of N₂ has no effect for the same reasons as previously.

The N₂O effect is more visible at this energy. G values of N₂O-saturated solutions are found to be higher than G values of aerated solutions. The oxidation is more important at any concentration in bromide ion.

In N₂O-saturated (2.5.10⁻² mol.dm⁻³ at atmospheric pressure) aqueous solution, the scavenging power of hydrated electron by N₂O is 2,3.10⁸ s⁻¹ and the hydrated electron is converted into HO[·] radical. In the presence of 0.6 M Br⁻, the scavenging power of HO[·] radical by Br⁻ is 6,6.10⁹ s⁻¹. HO[·] radicals produce BrOH[·] with a time constant of 150 ps, and so, the competition with HO[·] radical combination (k = 4,2.10⁹ dm³.mol⁻¹.s⁻¹), is avoided. Then, Br₂⁻

is formed from BrOH^- mostly with a time constant of 8.8 ns. As the hydrated electron is converted to OH^- with a time constant of 4.3 ns, it may partially react with Br_2^- in the spurs. Moreover in these conditions, the H^\cdot atom is not scavenged by either N_2O or Br^- and may also react with Br_2^- in the spurs. These reactions may contribute to slightly reduce the oxidation yield of Br^- . But, as suggested by Sutton et al. (1965) if we consider that, in the spurs, despite conversion into Br_2^- , the radiolytic yields of hydrated electron and oxidizing species do not change drastically, we can assume that, in our conditions, the formation yield of Br_2^- is $G(\text{Br}_2^-) = G_{4\text{ns}}(e_{\text{aq}}^-) + G_{4\text{ns}}(\text{HO}^\cdot) = (3.5 + 3,6) \cdot 10^{-7} \text{ mol} \cdot \text{J}^{-1} = 7,1 \cdot 10^{-7} \text{ mol} \cdot \text{J}^{-1}$ (Draganic and Draganic, 1973, LaVerne and Pimblott, 1993). Then, Br_2^- disappears, leading to Br_3^- , and also reacts partially with H^\cdot atom. H^\cdot atom may also react with the formed Br_3^- , still reducing the formation yield of Br_3^- . This reaction is not negligible at high concentration of Br_3^- ($>10^{-4} \text{ M}$) due to the competition reactions between H^\cdot and N_2O or Br^- , respectively. It is to be noted that the reaction between e_{aq}^- and Br_3^- does not occur as the hydrated electron has already totally disappeared when Br_3^- is formed, which is not the case for H^\cdot atom. Hence, the formation yield of Br_3^- should be slightly lower than half the formation yield of Br_2^- , i.e. $G(\text{Br}_3^-) \simeq G(\text{Br}_2^-)/2 \simeq 3,5 \cdot 10^{-7} \text{ mol} \cdot \text{J}^{-1}$. Our experimental value is found to be $4,0 \pm 0,2 \cdot 10^{-7} \text{ mol} \cdot \text{J}^{-1}$ and is clearly similar to the expected value.

B) Influence of the X-beam energy on the formation yield of Br_3^-

1) At 0.1 M

Energy (keV)	G ($10^7 \text{ mol} \cdot \text{J}^{-1}$)		
	air	N_2	N_2O
13	0.7-1.6	0.9-1.8	1.0-2.0
15	0.6-1.0	1.0-1.6	1.3-2.0
17	1.0-1.2	1.1-1.3	1.5-1.8

Table : Evolution of $G(\text{Br}_3^-)$ with the X-beam energy.

At low concentrations in bromide ions, there is no significant energy influence. G values are quite similar under air and any gas saturation. The diffusion seems to be the phenomenon which controls the oxidation mechanism. Kinetics is limited by the diffusion. It can explain the low G values.

The presence of N_2 has no effect on the oxidation process. G values for N_2 -saturated solutions are higher than G values for aerated solutions. It's true for low and high concentrations in HBr .

The presence of N_2O is responsible for a slight increase in G values at low and high concentrations in Br^- .

2) At 0.6 M

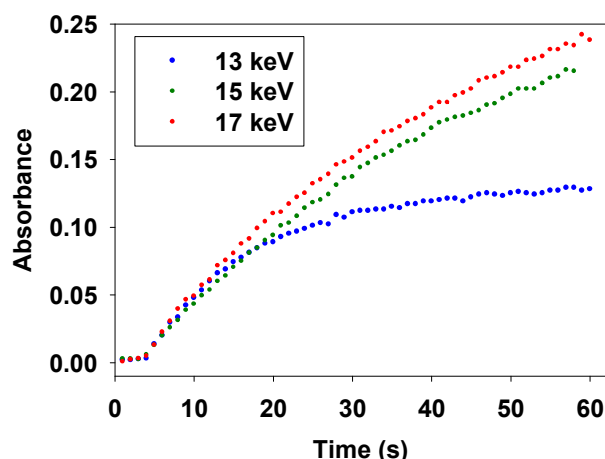


Figure : Absorption kinetics of an aerated solution of 0.6 M Br⁻ at different energies.

Energy (keV)	G (10 ⁷ mol.J ⁻¹)		
	air	N ₂	N ₂ O
13	2.5-5.3	1.9-4.0	1.8-3.8
15	1.9-2.9	1.4-2.3	2.1-3.3
17	2.4-2.7	1.2-1.3	3.8-4.3

Table : Evolution of G(Br₃⁻) with the X-beam energy.

We notice that radiolytic yields are higher when initial concentration in Br⁻ increases.

There is a significant N₂ effect. G values are lower than at aerated solutions.

N₂O effect is visible when the energy is superior to 15 keV (above the ionization edge of Br atom). The X-beam energy is above the ionization edge of Br atom. There are direct and indirect ionizations.

Below the ionization edge of Br atom, indirect ionizations happen. Products from the water radiolysis (water radicals) react with bromide ions. Above the ionization edge of Br atom, there are direct and indirect ionizations. If the beam energy is high enough, it can lead directly to the creation of Br[·]. This Br[·] atom reacts with a bromide ion to lead to the formation of Br₂⁻.

In the future...

This collaboration takes the benefit of the main competences and background in the water radiolysis analysis method and the X-ray spectroscopy.

The expected results are from the comparisons of various concentrations in bromide, various X-ray beam energies and various saturation gas on the X-rays spectra. This should give much fundamental information about the dynamic structure of the water radicals in those conditions.

The different experiments with the synchrotron source let us first carry out a dosimetry of the beamline and study the feasibility of the X-pulse radiolysis. It was also possible to learn more about the oxidation mechanism of the bromide ion and to prepare some experiments using X-pulse radiolysis under aqueous supercritical conditions. Our laboratory has designed a special cell for pulse radiolysis with electrons or heavy ions beam of greater energy (> MeV). Nevertheless showing the feasibility of the experiment by using the HT/HP X-ray cell

developed by Jean-Louis Hazemann and Denis Testemale at the Institut Néel in Grenoble^[11] should be useful to continue the experiment by changing the conditions of T and P for supercritical conditions of water^[8-11].

References

- [1] Spinks J.W.T., Wood R.J. (1990) Introduction to Radiation Chemistry, 3rd Edition, A Wiley-Interscience Publication, John Wiley & Sons, Inc., New-York, USA.
- [2] Tabata Y. (1991) Pulse Radiolysis, CRC Press, Boca Raton, Florida, USA.
- [3] A nanosecond pulse radiolysis study of the hydrated electron with high energy ions with a narrow velocity distribution, G. Baldacchino et al., Chem. Phys. Lett. **385**, 66-71 (2004).
- [4] Ultrafast processes in radiation chemistry, Crowell RA, Gosztola DJ, Shkrob IA, Oulianov DA, Jonah CD, Rajh T, Radiation Physics and Chemistry **70** (4-5): 501-509, (2004).
- [5] Transient x-ray absorption spectroscopy of hydrated halogen atom, C.G. Elles, I.A. Shkrob, R.A. Crowell, D.A. Arms, E.C. Landahl, J. Chem. Phys. **128**, 061102 (2008).
- [6] Radiation induced synthesis of silver nanoshells formed onto organic micelles, Remita S, Fontaine P, Rochas C, et al., European Physical Journal D **34** (1-3): 231-233, (2005).
- [7] Hydrated electron decay measurements with picosecond pulse radiolysis at elevated temperatures up to 350°C, Baldacchino et al., Chemical Physics Letters (2006).
- [8] Testemale D., “Structures locales en solution aqueuse supercritique”, Thèse de l’Université Joseph Fourier de Grenoble spécialité Physique (2003).
- [9] Testemale D. *et al.* “Small Angle X-Ray Scattering of a supercritical electrolyte aqueous solution: the effect of ions on local density inhomogeneities”, J. Chem. Phys., **122**, 194505 (2005).
- [10] Ph. Wernet, D. Testemale, J.-L. Hazemann, R. Argoud, P. Glatzel, L. G. M. Pettersson, A. Nilsson, and U. Bergmann “Spectroscopic characterization of microscopic hydrogen-bonding disparities in supercritical water”, J. Chem. Phys. **123**, 154503 (2005).
- [11] Testemale D., R. Argoud, O. Geaymond, J.-L. Hazemann, “A high pressure / high temperature cell for X-ray absorption and scattering techniques”, Review of Scientific Instruments **76** (2005) 043905.
- [12] Mamou, A., Rabani, J., Behar, D., 1977. On the oxidation of aqueous Br⁻ by OH radicals, studied by pulse radiolysis. J. Phys. Chem. **81**, 1447–1448.
- [13] Zehavi, D., Rabani, J., 1972. The oxidation of aqueous bromide ions by hydroxyl radicals. A pulse radiolytic investigation. J. Phys. Chem. **76**, 312–319.
- [14] Beckwith, R.C., Wang, T.X., Margerum, D.W., 1996. Equilibrium and kinetics of bromine hydrolysis. Inorg. Chem. **35**, 995–1000.
- [15] Wang, T.X., Kelley, M.D., Cooper, J.N., Beckwith, R.C., Margerum, D.W., 1994. Equilibrium, kinetic, and UV-spectral characteristics of aqueous bromine chloride, bromine, and chlorine species. Inorg. Chem. **33**, 5872–5878.

[16] Matheson, M.S., Mulac, W.A., Weeks, J.L., Rabani, J., 1966. The pulse radiolysis of deaerated aqueous bromide solutions. *J. Phys. Chem.* 70, 2092–2099.

[17] Mirdamadi-Esfahani, M., Lampre, I., Marignier, J.L., DeWaele, V., Mostafavi, M., 2009. Radiolytic formation of tribromine ion Br_3^- in aqueous solutions, a system for steady-state dosimetry. *Rad. Phys. Chem.* 78, 106–111.