Comparison between VUV light and gamma-rays irradiation for molecular hydrogen (H_2) and OH radical production

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Radiation Chemistry Symposium, 15-16 november 2011, Maison de la Chimie, Paris

Outline

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Context

Irradiation of water $H_2O + (h\nu \text{ or } \gamma) \rightarrow HO^\bullet, e_{aq}^-, H^\bullet$

$e_{aq}^- + e_{aq}^- \Rightarrow H_2 + 2\,OH^-$

$e_{aq}^- + H_3O^+ \Rightarrow H^\bullet + H_2O$ ⇨ $HO^\bullet + H_2 \Rightarrow H^\bullet + H_2O$

$H^\bullet + H^\bullet \Rightarrow H_2$

$HO^\bullet + HO^\bullet \Rightarrow H_2O_2$

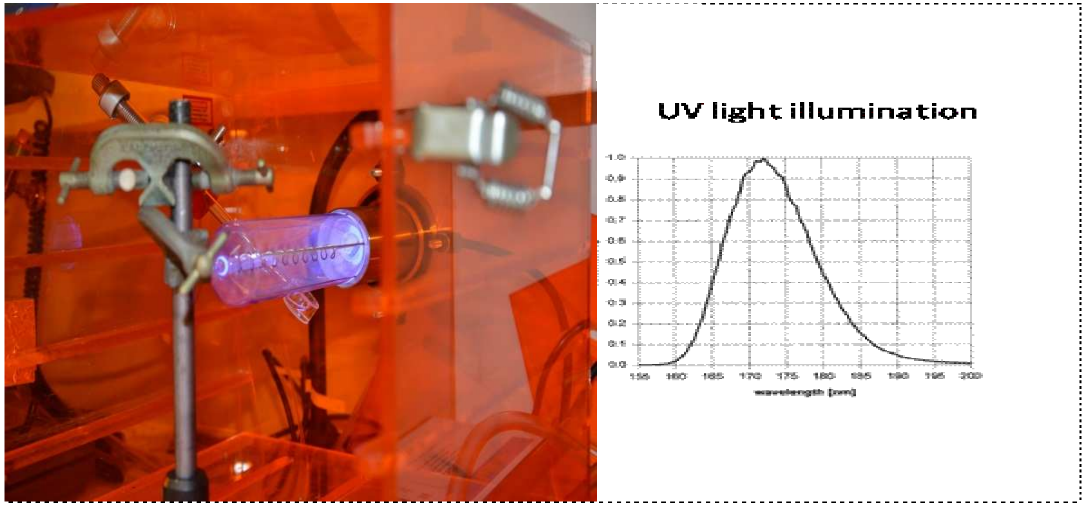
The radiolysis of pure water produces very low amount of molecular hydrogen and hydrogen peroxide.

Usually, scavengers such as halide (Br^-, Cl^-, etc) are used to promote the molecular hydrogen production by quenching process of OH radical.

Question: is it still true for UV light illumination ?

Experimental setup

Irradiation part



UV light

γ-rays

- UV light was generated by DBD discharge with Xenon as a gas.

- Maximum emission wavelengh was determined to be equal to 172 nm (7,2 eV)

- ^{137}Cs as gamma-rays source, with a dose rate of 5,5 Gy/mn by Fricke dosimeter method.

Experimental setup

Analysis part

Gas chromatography

For H_2 measurements

Samples

- All the chemicals were purchased from Sigma Aldrich and were higher purity available,
- NaCl concentration was varied from 10^{-3} to 1 M.

- Solutions were irradiated in deaerated conditions (with argon as the inert gas) in quartz and pyrex test tubes respectively for VUV and γ-rays irradiation.

Specific terms

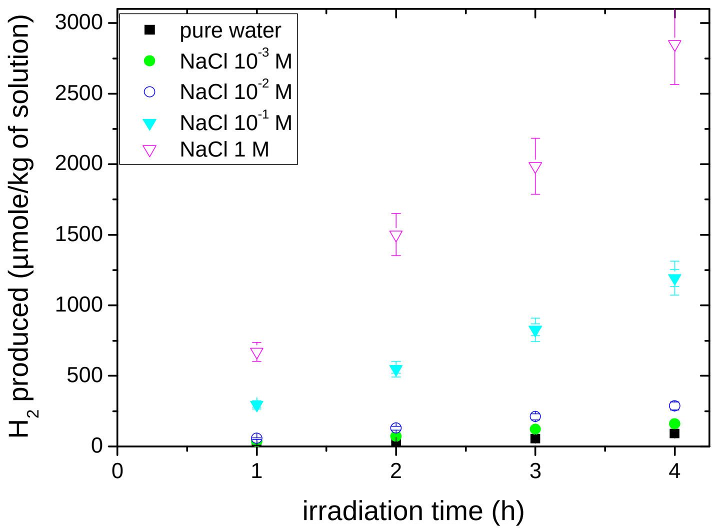
Production yield of (X) = number of mole of X per kilogram of solution and Gray (µmole/kg of solution/Gy or h)

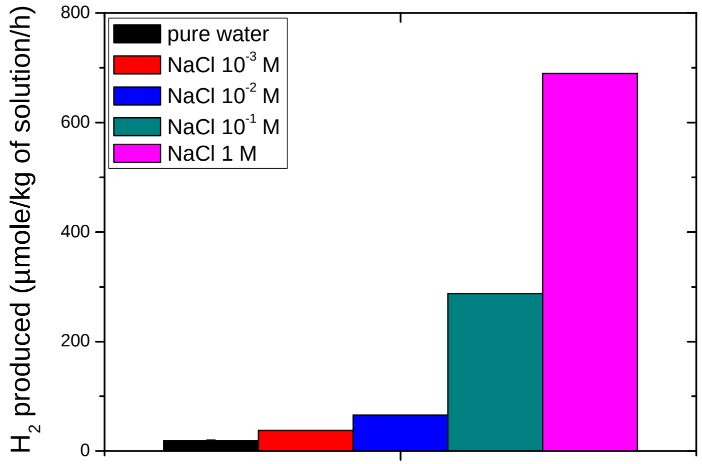
(X) stands for H_2

Results

UV light illumination

OH radical scavenged by Cl^-: production of H_2



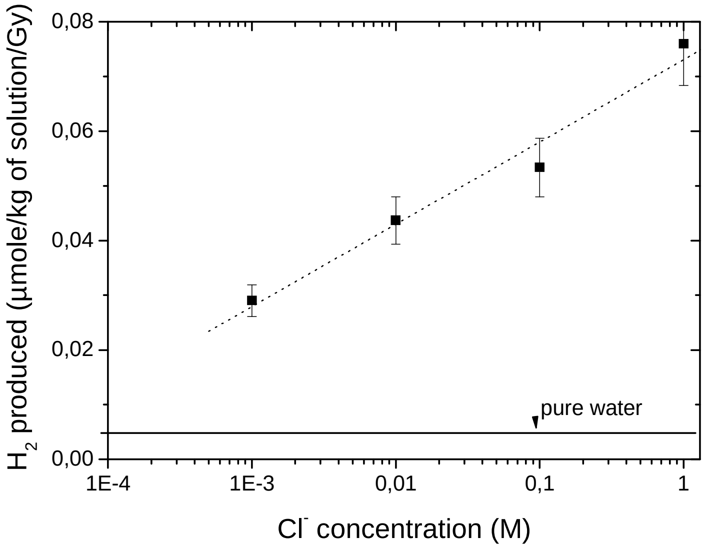


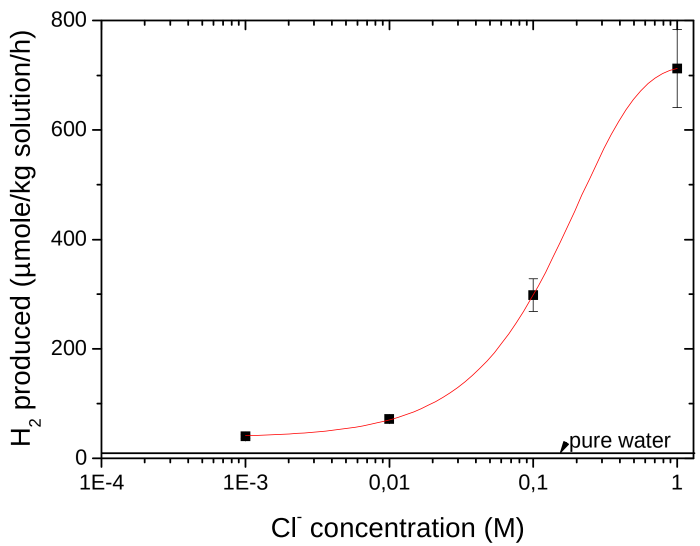
- H_2 production ↗ linearly as the time course ↗
- Production of H_2 ↗ with increasing Cl^- concentration

The production of H_2 is limited in VUV without HO scavenger, the question is: it's the same mechanism for that obtained in γ-rays ?

Results

Comparison between γ-rays and UV light



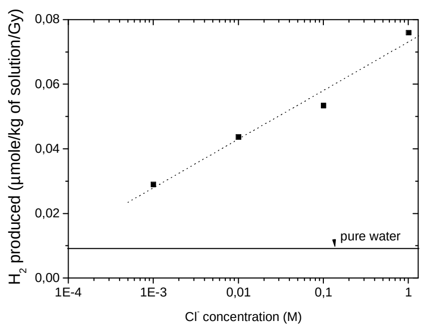


- In γ-rays production of H_2 ↗ smoothly with Cl^- concentration
- On the contrary, the production of H_2 in VUV exhibit an important ↗ at high $[Cl^-]$

Results

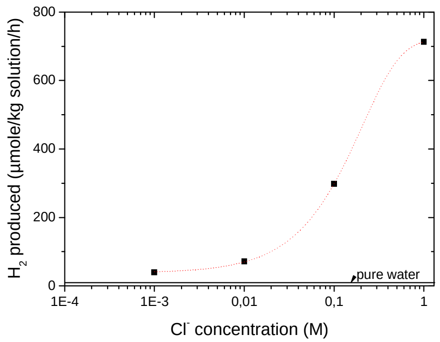
Comparison between γ-rays and VUV light

Gamma Irradiation



- $Cl^- + HO^\bullet \Rightarrow ClOH^{\bullet -}$ $4{,}3 \times 10^9\ M^{-1}.s^{-1}$
- $Cl^- \Rightarrow Cl^\bullet + e^-$? No direct effect observed in Littérature (Anna Balcerzyk et al, 2011; Ferradini)

VUV



- $H_2O + h\nu \Rightarrow HO^\bullet + H^\bullet$ VUV
- $Cl^- + h\nu \Rightarrow Cl^\bullet + e^-$ UV-VUV
- $Cl^- + H^\bullet \Rightarrow [HCl^{\bullet -}]$

Extensive H° production and Cl^- ionization can be expected in VUV

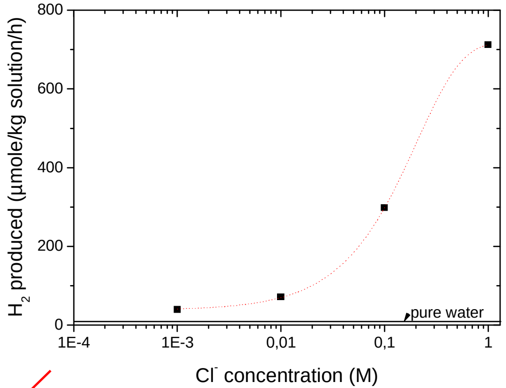
Hypothesis

$\Phi(H^{\bullet})$=0.45 (Braun)

Φ(chloride ionisation) =0.45 (Malcolm)

For VUV, all photons are absorbed by water ⇒ No a « dose effect »

« direct effect » can not increase H_2 production



$Cl^- + HO^{\bullet} \Rightarrow ClOH^{\bullet -}$ 4,3 x 10^9 M^{-1}

Scavenging of HO prior to recombination ?
But $Cl_2^{\bullet -}$ and $Cl^{\bullet}$ can also react with $H^{\bullet}$

- $H^{\bullet} + Cl^- \Rightarrow (HCl)^{\bullet -}$
- $(HCl)^{\bullet -} + H^+ \Rightarrow H_2 + Cl^{\bullet}$

This could be a possible way to double H_2 production

Conclusion

- For VUV, all photons are absorbed by water and by solute at high concentration

→ direct ionization

- Yield of H_2 increases with Cl^- concentration,
- Impact of a very early $HO^•$ scavenging, also present in γ-rays irradiation
- A specificity of VUV, a very high yield of $H^•$ in VUV $Ø(HO^•)≈Ø(H^•)$ (Get off, Braun) can be produced which leads to an increase of H_2 production,

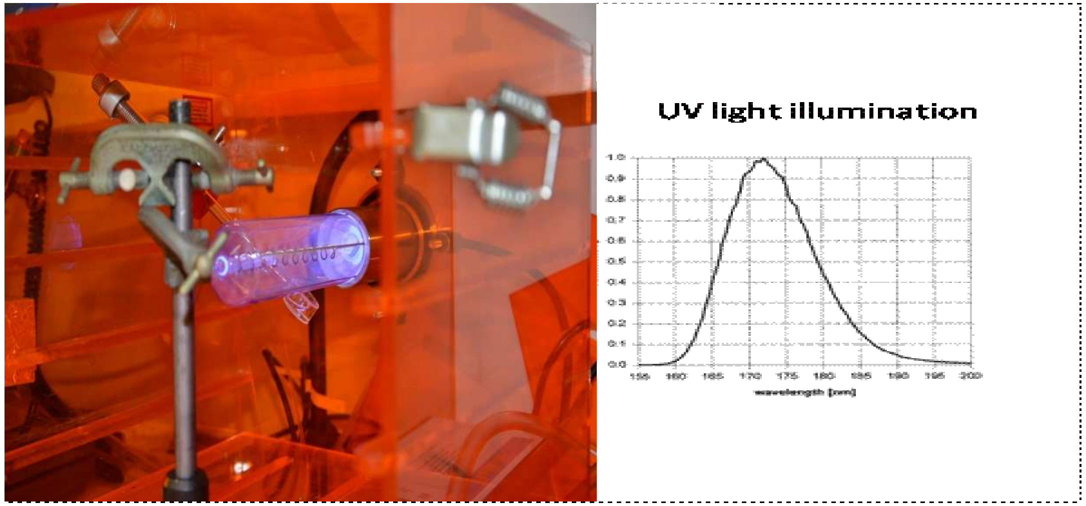
This increase in the production yield of H_2 in VUV is probably due to the direct ionization of the solute by the ionizing radiation. This assumption seems to be right for inorganic compound.

The question is, it is also true for organic compound ?

In other words, one would like to know if the quenching process of $Cl^•$+ e_{aq}^- is more or less efficient than recombination of $HO^•$+ $H^•$(excess energy in the electron or reaction with Cl^-).

Experimental setup

Irradiation part



UV light

γ-rays

- UV light was generated by DBD discharge with Xenon as a gas.

- Maximum emission wavelengh was determined to be equal to 172 nm (7,2 eV)

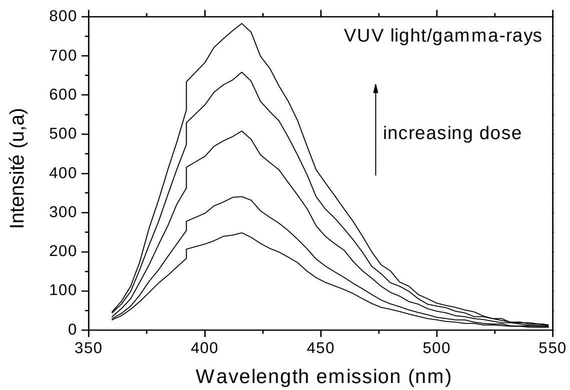
- ^{137}Cs as gamma-rays source, with a dose rate of 5,5 Gy/mn by Fricke dosimeter method.

- Dose was varied from 55 Gy up to 220 Gy

Experimental setup

Analysis part

Spectrofluorimeter
For fluorescence of 2-OHbenzoate



Samples

- Solutions were irradiated in aerated conditions in quartz tubes,
- Benzoate concentration was varied from 10^{-3} up to 0,1 M,
- Excitation and emission wavelengths were 290 and 416 nm respectively

$$HO^{\bullet} + \text{benzoate} \Rightarrow \text{2-OHbenzoate}$$

Less fluorescent   fluorescent

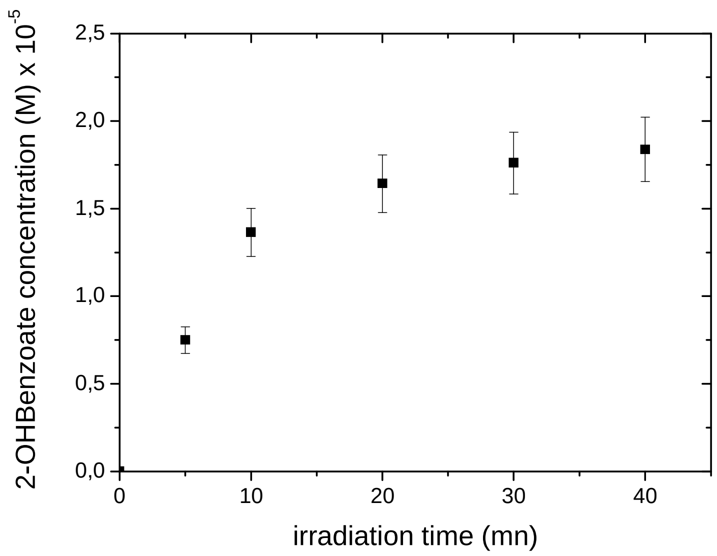
Production yield of (X) = number of mole of X per kilogram of solution and Gray (µmole/kg of solution/Gy or h)

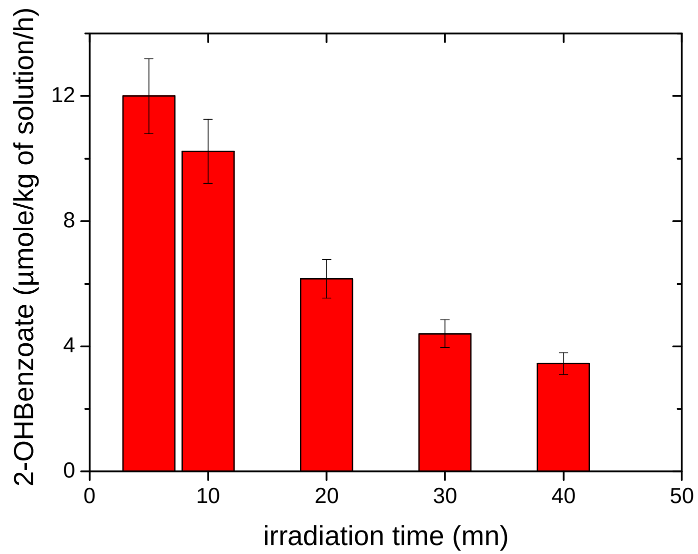
Time capture of ($HO^{\bullet}$) = 1/rate constant of reaction(HO + benzoate) x [benzoate] (s^{-1})

Results

UV light illumination

OH radical scavenged by benzoate: production of 2-OHbenzoate

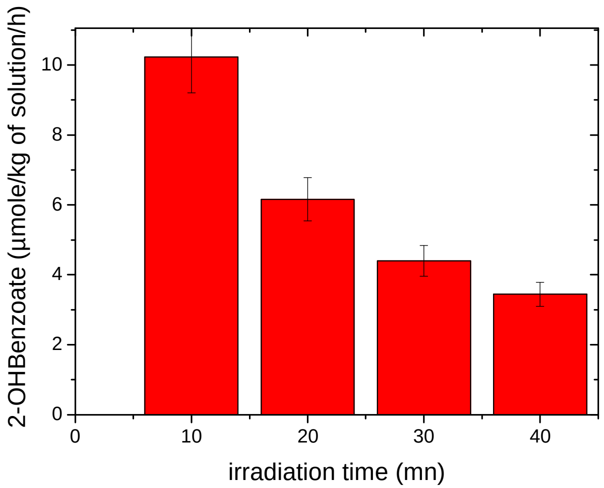




- 2-OHbenzoate production ↗ from 0 to 10 mn and above this time saturation occurs,
- Time dependencies on the production yield of 2-OHbenzoate
- Production yield of 2-OHbenzoate ↘ with increasing time illumination ⇨ degradation by direct ionization of Bz and (2-HOBz) ?

Results

UV light illumination



Benzoate ionisation does not lead to hydroxylation

Possible hydroxylation mechanisms

- $H_2O + h\nu \Rightarrow HO^\bullet + H^\bullet$
- $HO^\bullet + C_6H_5COO\text{-} \Rightarrow 2\text{-}HOC_6H_5COO^-$

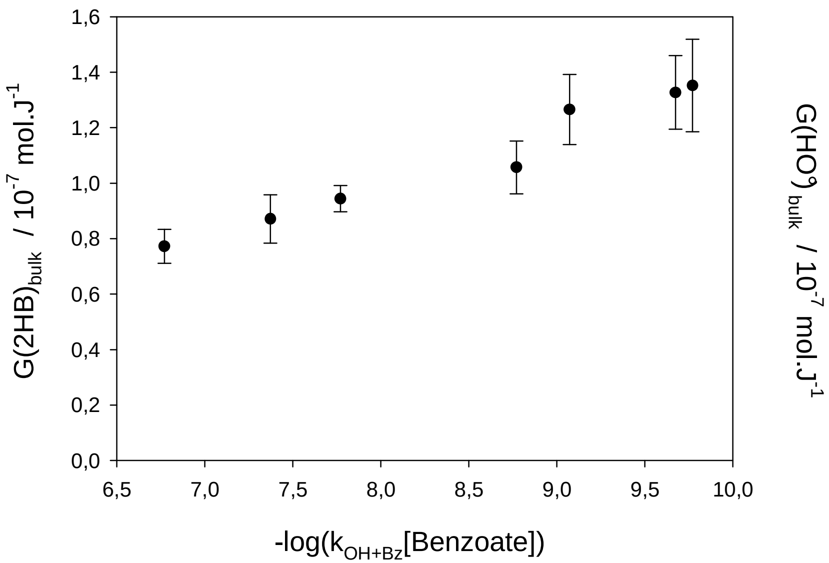
Possible degradation mechanism ?

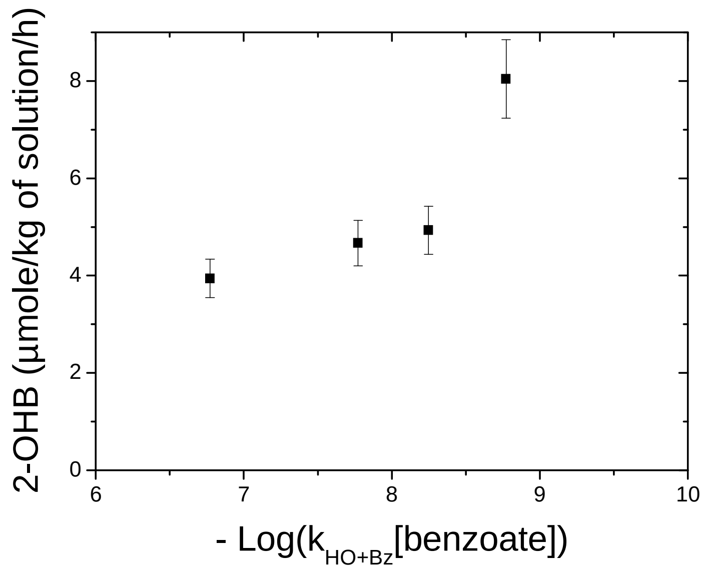
- $C_6H_5COO^- + h\nu \Rightarrow C_6H_5COO^\bullet + e^-$
- $C_6H_5COO^\bullet \Rightarrow {}^\bullet C_6H_5 + CO_2$
- ${}^\bullet C_6H_5 + HO^\bullet \Rightarrow C_6H_5HO$
- ...

Could we imagine the same mechanism in the case of γ-rays irradiation ?

Preliminary results

Comparison between γ-rays and UV light





- Both systems exhibit the same behavior, or trends
- The production yield of 2-OHbenzoate ↗ from 10^{-3} to 10^{-2} M, in VUV,
- Above 10^{-2} M, the yield of 2-OHbenzoate increases by a factor 2 up to short scavenging times, ns for γ, 10 ns for VUV

Hydroxylation of benzoate in gamma-rays, data obtained in a preliminary study done by Raluca. Musat, 2009

Conclusion

- In VUV, at low Cl^- concentration, there is no direct effect of the ionizing radiation on the solute,
- On the contrary, at high Cl^- concentration, direct ionization of solute occurs,
- The possible high H_2 production seems to be due to extensive production of $H^•$ and required suppression of the back reaction of $HO^• + H^• \rightarrow H_2O$
- Impact of a very early $HO^•$ scavenging, also present in γ-rays irradiation,

Futur works

⁄ Understand the mechanism involved during the high production of molecular hydrogen in VUV at high solute concentration. $H^• + Cl^- \rightarrow [HCl]^{•-} + H^+ \rightarrow H_2 + Cl$
In other words study the impact of this reaction on the H_2 production

⁄ Identifiy and quantify the by-products formed during the irradiation of benzoate by VUV light

⁄ Compare the efficiency of Cl^- and benzoate for $HO^•$ radical scavenging,

⁄ Explore the degradation of benzoate in both systems by ionizing radiation.

Acknowledgments

Financial support

DSM: Recherche Fondamentale pour l'énergie

All members of the Laboratoire de Radiolyse in particular

Stéphane Esnouff for GC Analysis
And Gerard Baldacchino

Thank you for your attention