Electronic Supporting Information for

"Confined Water Radiolysis in Aluminosilicate Nanotubes:

The Importance of Charge Separation Effects"

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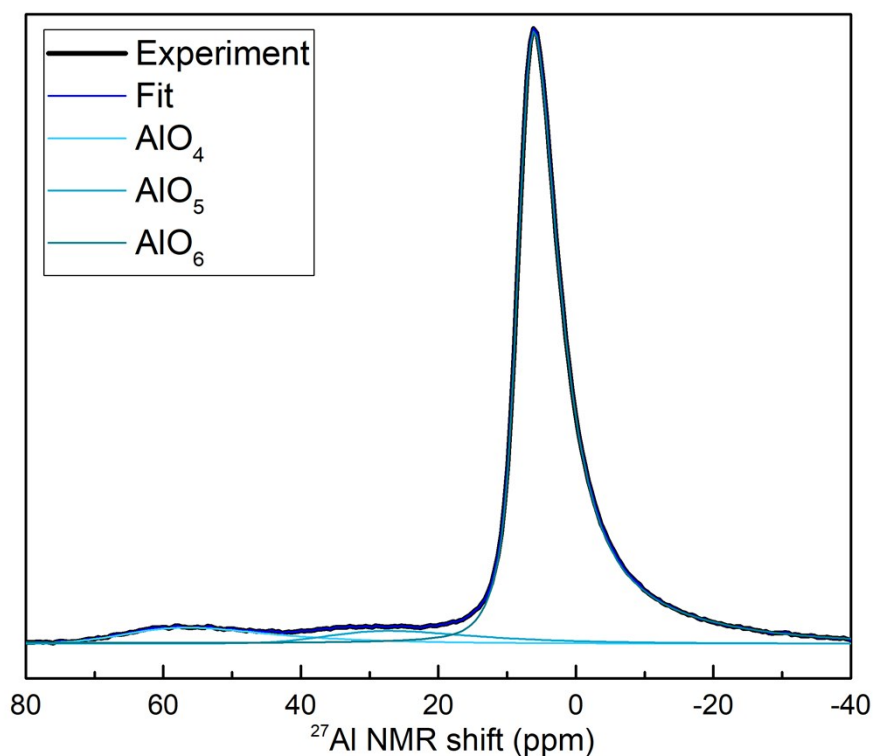
NMR experiments

Figure S1. *^{27}Al MAS spectra for imogolite (IMO-OH) equilibrated at 43% relative humidity (in black) and the corresponding simulation together with the different components of aluminum (in blue).*

Quantitative analysis of the ^{27}Al MAS NMR spectra, as shown in Figure S1 for IMO-OH equilibrated at 43% relative humidity (RH), gave the following proportions: 88% of octahedral aluminum (AlO_6), 5% of pentahedral aluminum (AlO_5) and 7% of tetrahedral aluminum (AlO_4). For more details on the simulation methods, please see reference [1].
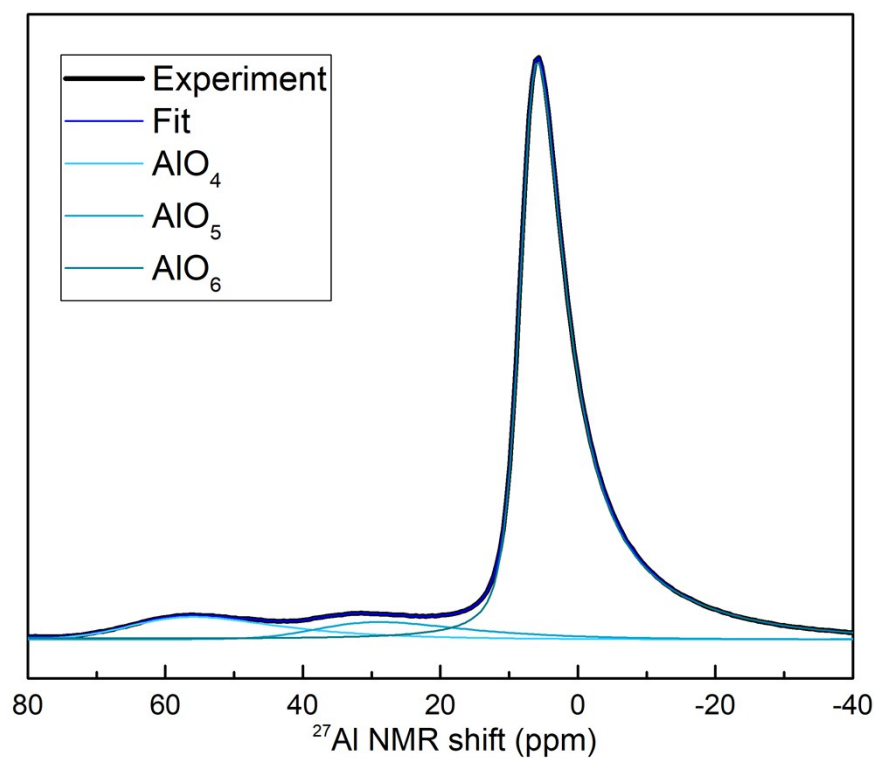
Figure S2. *^{27}Al MAS spectra of imogolite (IMO-OH) equilibrated at 43% relative humidity after irradiation at a dose of 520 kGy (in black) and the corresponding simulation together with the different components of aluminum (in blue).*

Similarly, simulations performed on the ^{27}Al MAS NMR spectra of the same compound, but after irradiation at a dose of 520 kGy gave the following proportions: 85% of octahedral aluminum (AlO_6), 7% of pentahedral aluminum (AlO_5) and 8% of tetrahedral aluminum (AlO_4).
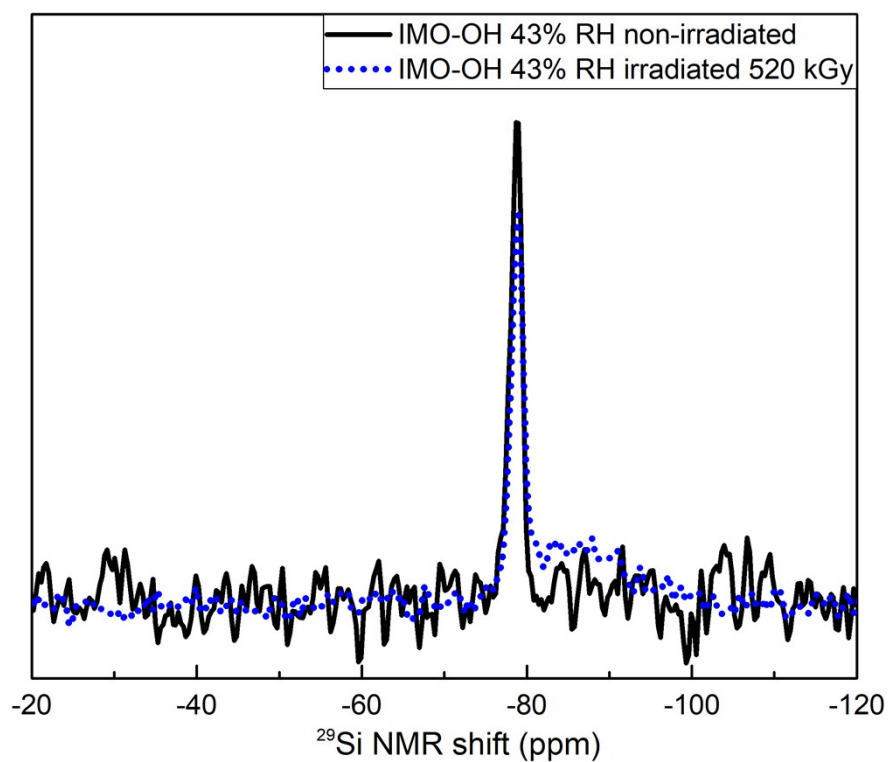
Figure S3. *^{29}Si MAS spectra of imogolite (IMO-OH) equilibrated at 43% relative humidity before and after irradiation at a dose of 520 kGy, normalized to the same area and sample weight.*

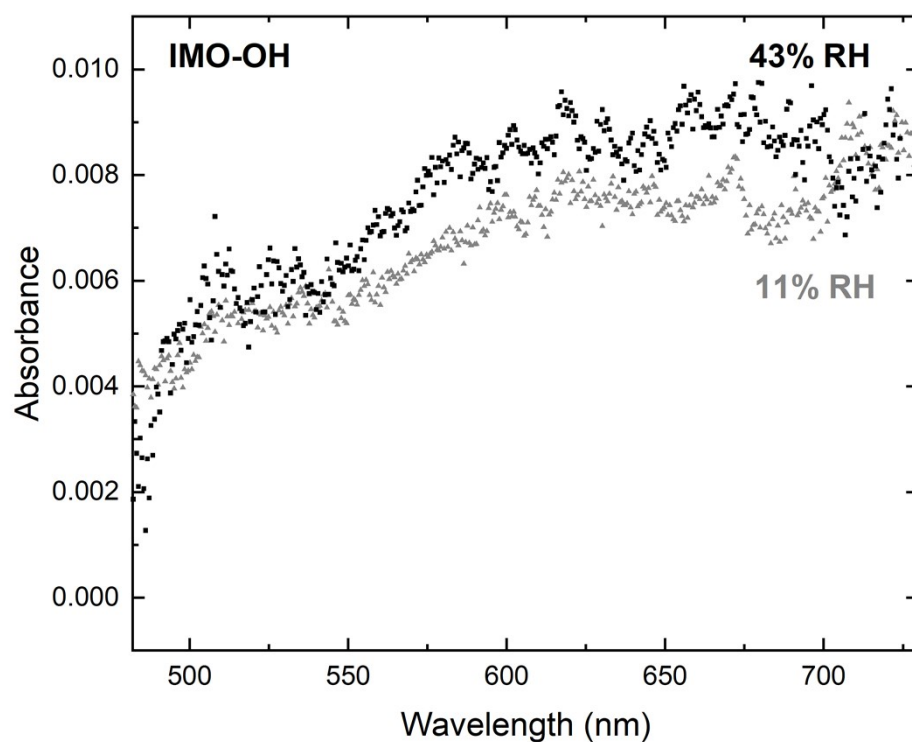**Picosecond pulse radiolysis experiments**

Figure S4. *Spectra (symbols) measured in imogolite (IMO-OH), at two different RH values: 11 and 43%. The spectra correspond to an average performed between 7 ps and 4 ns, but were scaled to the value measured 7 ps after the electron pulse for the sake of clarity. The irradiation dose was 115 Gy.*
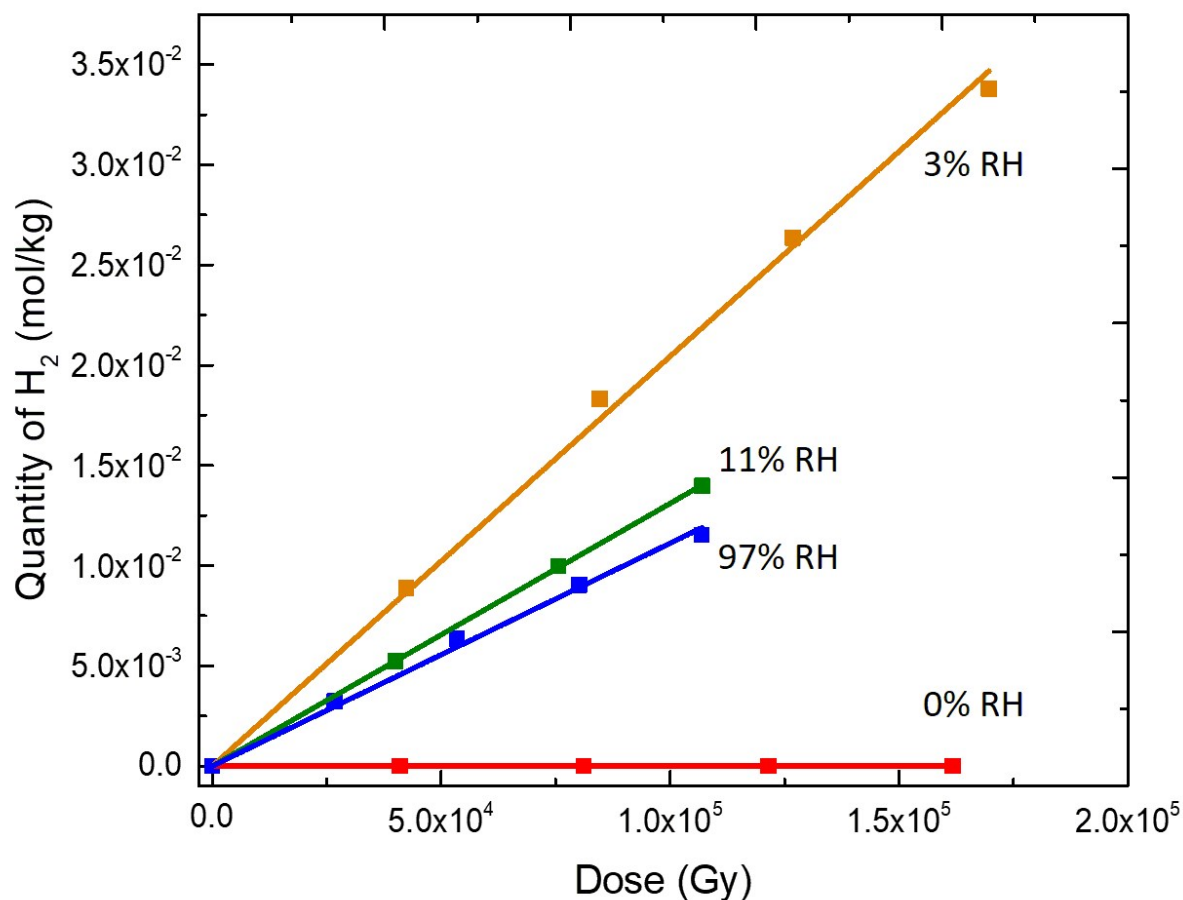
Gas produced upon irradiation

Figure S5. *Change in H₂ production as a function of irradiation dose in imogolite (IMO-OH) equilibrated at some different relative humidity (RH) values. The trend is linear. The H₂ radiolytic yields were obtained from the slopes of the lines and are as follows: <0.01 µmol.J⁻¹ in dry IMO-OH, 0.23 µmol.J⁻¹ at 3% RH, 0.13 µmol.J⁻¹ at 11% RH and 0.11 µmol.J⁻¹ at 97% RH.*
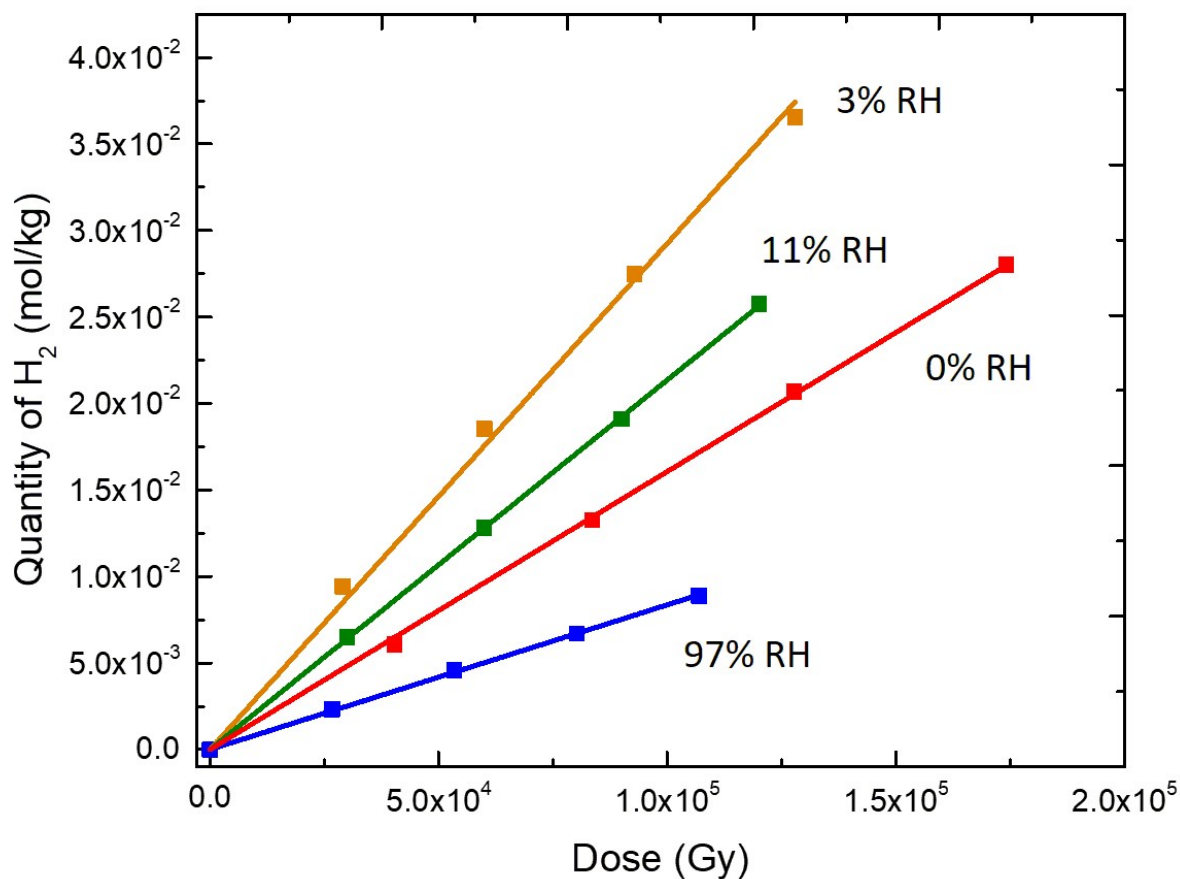
Figure S6. *Change in H₂ production as a function of irradiation dose in hybrid imogolite (IMO-CH₃) equilibrated at some different relative humidity (RH) values. The trend is linear. The H₂ radiolytic yields were obtained from the slopes of the lines and are as follows: 0.13 μmol.J⁻¹ in dry IMO-CH₃, 0.29 μmol.J⁻¹ at 3% RH, 0.20 μmol.J⁻¹ at 11% RH and 0.084 μmol.J⁻¹ at 97% RH.*
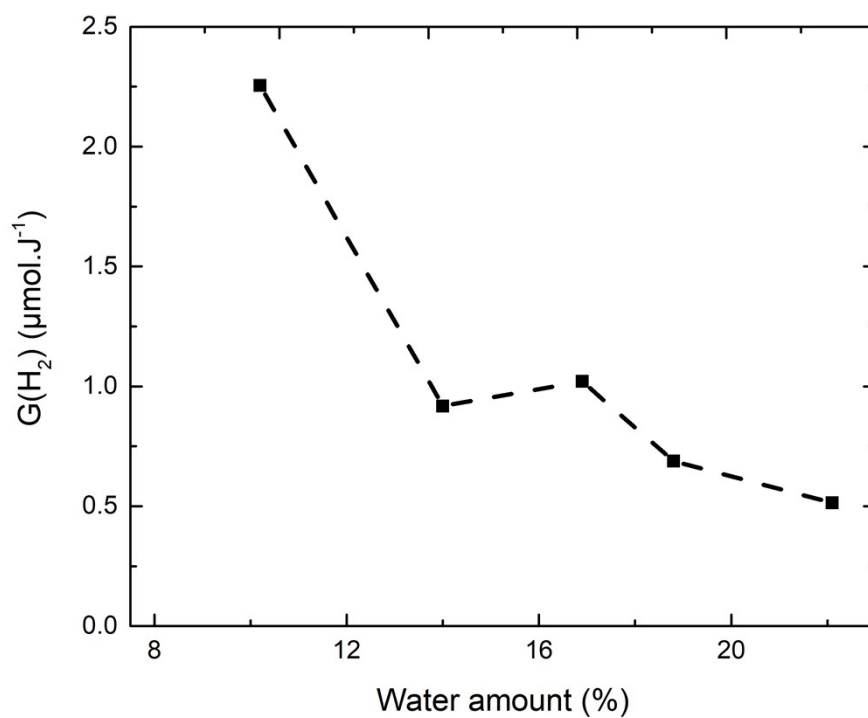
Figure S7. *H₂ radiolytic yield (in μmol.J⁻¹) calculated from energy absorbed by water (internal and external) only as a function of the percentage of water in the IMO-OH sample. The dashed line is shown for clarity.*
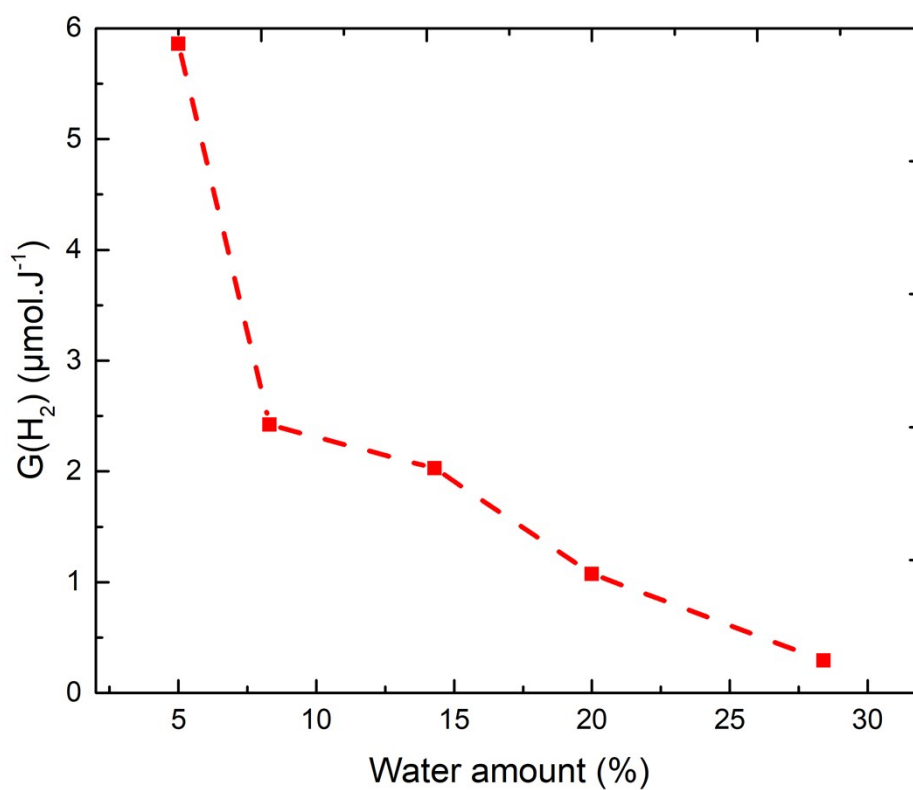
Figure S8. *H_2 radiolytic yield (in µmol.J^{-1}) calculated from energy absorbed by water only as a function of the percentage of water in the hybrid imogolite (IMO-CH$_3$) sample. The dashed line is shown for clarity.*

Energy partitioning between imogolite and water

For a mixture under irradiation, the fraction of the total absorbed energy transferred to each component of the mixture is proportional to the weight fraction of the component and to the mean mass collision stopping power of the component for the ionizing particles of various energies present in the medium.[2] One simple approximation to estimate this latter contribution consists in assuming that it is proportional to the Z/A ratio, with Z and A the atomic and mass number, respectively, of the component.[2]

For water, $Z_{water}/A_{water} = 10/18 = 0.56$

For IMO-OH (and almost the same for IMO-CH$_3$), $Z_{IMO-OH}/A_{IMO-OH} = 100/198 = 0.51$. These two values are almost equal within 10%, and are considered to be similar.

The H$_2$ radiolytic yield can be expressed as the sum of two terms:

$G(H_2) = f_{H2O}*G(H_2)_{water} + f_{Imo}*G(H_2)_{Imo}$

with • f_{H2O} (resp. f_{Imo}) the fraction of energy received by water and imogolite, respectively. The fraction of energy absorbed in each phase is assumed to be equal to the mass fraction of each phase (see above, within 10%).

• $G(H_2)_{water}$ is the dihydrogen radiolytic yield in water and is assumed to be equal to the value measured in the bulk phase (i.e., 0.047 µmol.J^{-1}).

• $G(H_2)_{Imo}$ is the dihydrogen radiolytic yield due to the energy transfer from imogolite to water.

If we consider a case with a significant amount of water, for instance IMO-OH at 74% RH value, water represents 19% of the total mass of the sample (Table 1). Hence, $f_{H2O} = 0.19$ and $f_{Imo} = 0.81$. Knowing that $G(H_2) = 0.13$ µmol.J^{-1} (Table 2), then $f_{H2O}*G(H_2)_{water}$ is equal to 0.01 µmol.J^{-1}. Therefore, direct water radiolysis can be considered as minor.

Even for IMO-OH equilibrated at RH = 97%, $f_{H2O} = 0.22$ and $f_{Imo} = 0.78$ (Table 1). Knowing that $G(H_2) = 0.11$ µmol.J^{-1} (Table 2), then $f_{H2O}*G(H_2)_{water}$ is equal to 0.01 µmol.J^{-1}. Therefore, direct water radiolysis can still be considered as minor.

References

1   T. Lange, T. Charpentier, F. Gobeaux, S. Charton, F. Testard and A. Thill, *Langmuir*, 2019, **35**, 4068-4076.

2   J. W. T. Spinks and R. J. Woods, *An Introduction to Radiation Chemistry*, 3rd ed.; Wiley-Interscience Publication: New York, USA, 1990.