NEXAFS : a unique tool to follow the photochemistry of small organic molecules in condensed water

Ph Parent¹, C Laffon¹, F Bournel¹, J Lasne¹ and S Lacombe²
¹Laboratoire de Chimie–Physique, Matière et Rayonnement, Université Pierre et Marie Curie (UPMC–Univ Paris 06) and CNRS (UMR 7614), 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France - ²Institut des Sciences Moléculaires d’Orsay, ISMO (FRE 3363), 91405 Orsay Cedex, France and Université Paris Sud 11, CNRS-Bât 351, 91405 Orsay Cedex, France.
E-mail: philippe.parent@upmc.fr

Abstract. Soft X–ray induced chemistry of simple organic molecules as carbon monoxide (CO), methanol (CH₃OH) and glycine (NH₂CH₂COOH) in water and nitric acid hydrate has been investigated with NEXAFS spectroscopy. In the pure species, extremely high survival rates are observed, a consequence of the back reactions allowed in the condensed phase. When mixed with water, the survival rates are considerably reduced by reaction with the hydroxyl radical (OH). The formation of CO₂ is also enhanced at the expense of CO, the main byproduct in the photolysis of the pure species. Finally, it is shown that water plays no role in the destruction of the amino acid.

1. Introduction
Radiation damages of organic molecules in water are of fundamental importance in radiobiology. They are caused by the direct interaction with the radiation and by chemical attack of the target molecule by the reactive oxygenated species (ROS) released by water, especially OH [1,2]. We have recently used the X–ray absorption spectroscopy (NEXAFS) for studying these processes at a molecular scale, starting with pure water ice [3], water doped with O₂ [4], and ammonia ice [5]. The advantage of NEXAFS is to display all the byproducts created after irradiation, regardless of their chemical form (i.e., atoms, molecules, radicals), with spectral intensities only related to their concentrations, which allows identifying the dominant reaction channels. In the present work, we study further simple (CO) and more complex molecules condensed in water (and nitric acid hydrate), like methanol (CH₃OH) and glycine (NH₂CH₂COOH), the simplest amino acid. The comparisons between the irradiation of the pure species and the mixes with H₂O reveal the interplay between direct photolysis and indirect chemistry induced by the ROS in H₂O.

2. Experimental
The experiments on methanol were performed at MAX–Lab (MAXII, Lund, Sweden) on the I311 undulator beamline equipped with a SX–700 monochromator. The experiments on CO:H₂O mixtures were performed at LURE (SuperACO, Orsay, France) on the SA22 bending magnet beamline equipped with a plane grating spherical mirror monochromator. The experiments on glycine were recorded at the Synchrotron SOLEIL (Saint Aubin, France) on the TEMPO beamline equipped with a plane grating spherical mirror monochromator. The C and O K edges were recalibrated after the
experiments in order to match the $\pi^*$ absorption features of CO at 287.3 eV for the C K edge and 534.1 eV for the O K edge. The sample preparation and the NEXAFS measurements have been performed in a similar manner in the three experiments, except the irradiations. They were done at LURE using the unmonochromatized white beam delivered at the zero–order of the monochromator (the bandwidth is then 1–1000 eV), and with 150 and 530 eV at MAX–II and SOLEIL, respectively. The absorbed doses were estimated from the photocurrent measured on the sample (LURE) and from a calibrated photodiode (MAX–II, SOLEIL). All the experiments were achieved under ultrahigh vacuum (base pressure 1x10$^{-10}$ mbar) by condensing pure or mixed vapors on a metallic substrate cooled by a liquid helium cryostat. For CH$_3$OH and H$_2$O, the gases were introduced from the vapor pressure of the liquids (after purification by several freeze–pump–thaw cycles) using separated circuitries in case of mixed ices. Ultrapure CO (99.997 %) gas was provided by Air Liquide. The nitric acid hydrate ice film was obtained by directly dosing the vapor from the azeotrope mixture of 68 wt % HNO$_3$ in H$_2$O (about HNO$_3$.1.65H$_2$O of molar composition). The partial pressures were calibrated both in the primary dosing circuitry with Pirani gauges and by mass spectrometry into the UHV vessel. The sticking coefficient being 1 for all the compounds at the deposition temperatures, these pressures directly provide the composition of the films. Depending on the case, the film thickness was typically 120 and 200 monolayers (ML), controlled by the exposure times. This is thick enough to ensure that the probed depth (typically 50–100 Å) is not perturbed by the substrate. The glycine/H$_2$O mixtures were prepared from the vapor pressure of the pure components and/or by mixing the appropriated gas phase, adjusting the water vapor pressure to obtain the desired glycine dilution, followed by the co–deposition on a cold substrate maintained at 30 K. Vaporization of glycine was achieved using a Knudsen cell held at 413 K under UHV. The deposition rates were monitored to deposit about 600 ML.

3. Results and discussion

3.1. CO/H$_2$O

Figure 1a presents the normalized C K–edge NEXAFS spectra of three CO:H$_2$O mixtures: 100:0 (pure CO), 66:34 and 24:76, deposited and irradiated at 20 K. The peak at 287.3 eV is the C1s $\rightarrow$ $\pi^*(CO)$ transition [6]. It decreases after irradiation as a result of the CO destruction. One main feature appears at 290.7 eV, which is the C1s $\rightarrow$ $\pi^*$ transition of CO$_2$ [6]. This indicates that CO is mainly converted into CO$_2$ [7]. On the 66:34 and 24:76 films, the $\pi^*(CO)$ is smaller and the $\pi^*(CO_2)$ larger. Thus, mixing CO with water amplifies the destruction and enhances the formation of CO$_2$. In figure 1b are displayed the remaining parts of the initial $\pi^*(CO)$ intensity as a function of the absorbed dose, which rates the survival of CO at the various dilutions. The survival rates are modelled accounting for the balance between the destruction reaction (1) and the back reactions (2):

$$\text{CO} + (h\nu, e^-) \rightarrow C + O$$ \hspace{1cm} (1)

$$C + O \rightarrow \text{CO}$$ \hspace{1cm} (2)

where (h\nu, e^-) indicates that the CO may decompose either through direct absorption of the incident photons or by interaction with secondary electrons emitted on the track of the photons. The CO concentration can be written:

$$\frac{dc}{dt} = \left[-\sigma_d c + \sigma_f (1-c)\right] \Phi$$ \hspace{1cm} (3)

where $c$=[CO], $\sigma_d$ and $\sigma_f$ are the reaction yields of reactions 1 and 2, respectively; $c_0$ is the initial CO concentration, $\Phi$ the photon flux and $t$ the exposure time ($\Phi$,$t$ is proportional to the absorbed dose). By integration of equation 3 we get:

$$c = c_0 \left\{(\sigma_f/(\sigma_d-\sigma_f))(1-(1-(\sigma_f/(\sigma_d-\sigma_f))\exp(-(\sigma_d-\sigma_f)\Phi t))\right\}$$ \hspace{1cm} (4)
Equation 4 is used to fit the survival rate presented in figure 1b; it is in excellent agreement with the experiments. Concerning the production of CO$_2$ in pure CO, it can be formed after reaction 1 by addition of O to a neighboring CO molecule [8]:

$$\text{CO} + \text{O}^* \rightarrow \text{CO}_2$$  \hspace{1cm} (5)

And also by the Boudouard reaction [7–10]:

$$\text{CO} + (h\nu, e^-) \rightarrow \text{CO}^*$$  \hspace{1cm} (6)
$$\text{CO} + \text{CO}^* \rightarrow \text{CO}_2 + \text{C}$$  \hspace{1cm} (7)

When mixed with water, CO$_2$ can also be formed by the addition of OH to CO [8]:

$$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$$  \hspace{1cm} (8)

This reaction strongly reduces the CO concentration and hence, lowers its survival rate. It also increases the CO$_2$ concentration. Figure 1c presents the ratio of the $\pi^*(\text{CO}_2)$ over the $\pi^*(\text{CO})$ areas, a quantity proportional to the CO$_2$/CO ratio. In the 24:76 film, the formation of CO$_2$ is 8 times more efficient than in pure CO.

3.2. CH$_3$OH/H$_2$O and HNO$_3$.

Figure 2a presents the C K-edge NEXAFS spectra of pure methanol (100:0), methanol in water (50:50, 16:84), and 34% of methanol into 66% of HNO$_3$.1.65H$_2$O (34:66 NitHyd). The films have been deposited at 60 K and irradiated at 20 K with a photon energy of 150 eV. Methanol before irradiation (dotted lines) shows two peaks labeled $\sigma^*$ at 288.5 eV and $\pi^*$ at 289.7 eV. They decrease as methanol is destroyed. Two main peaks appear then at 287.3 eV and 290.7 eV, which are the $\pi^*$ transition in CO and CO$_2$, respectively. This shows that methanol is mainly converted into CO and
CO$_2$. As observed previously for CO, the $\pi^*$ transition becomes smaller and the $\pi^*(\text{CO}_2)$ larger as the water concentration increases. The most probable photolysis reaction is [11]:

$$\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O} + \text{H}$$  \hspace{1cm} (9)

Then, methanol can recombine:

$$\text{CH}_3\text{O} + \text{H} \rightarrow \text{CH}_3\text{OH}$$  \hspace{1cm} (10)

This back reaction easily occurs, since it is barrierless [12]. The survival rates of methanol in the various mixes have been calculated by the relative decrease of the spectral intensity at 288.5 eV, where only methanol contributes. They are plotted on figure 2b as function of the absorbed dose. These data are also fitted with equation 4 (with $c=[\text{CH}_3\text{OH}]$), accounting for a balance between reactions 9 and 10. In pure methanol, about 50% of the initial methanol concentration has survived to the irradiation. This rate drops when mixed with water (30% in the 16:84 film), and strongly decreases to 5% of survival in presence of HNO$_3$.

In pure methanol, the fact that CO is the main byproduct indicates that irradiation essentially causes dehydrogenation, through a reaction scheme that has been investigated in detail by Bennett et al. [12], schematically condensed in reaction 11:

$$\text{CH}_3\text{OH} + 4(h\nu, e^-) \rightarrow \text{CO} + 4\text{H}$$  \hspace{1cm} (11)

In this reaction, low energy electrons are very efficient [13]. CO formed by reaction 11 is then transformed in CO$_2$, as discussed in the previous section (reactions 5–7).

In water, the methanol photolysis has been reviewed in ref. [14]. In brief, most of the reactions occur with the OH radical to form intermediate dehydrogenated methanol species $\text{H}_4\text{CO}$ and end in CO. This is schematically condensed in reaction 12:

**Figure 2.** C K-edge NEXAFS spectra of pure methanol (100:0), methanol in water (50:50, 16:84), and 34% of methanol into 66% of HNO$_3$.1.65H$_2$O (34:66 NitHyd). The films have been deposited at 60 K and irradiated at 20 K and 150 eV. (b) Survival rates of methanol in the four samples, as function of the absorbed dose; experimental data and fit using Eq. (4). (c) CO$_2$/CO ratios as function of the methanol concentration, calculated from the intensity ratios of the $\pi^*$ transition of the two species.
CH$_3$OH + 4OH$\rightarrow$ CO + 4H$_2$O  \hspace{1cm} (12)

At the end of reaction 12, CO will further react with OH (reaction 8), as observed for CO in ice, which explains the enhanced formation of CO$_2$ in water compared to pure methanol. This is illustrated in figure 2c, which presents the CO$_2$/CO ratio for the various films. We see that for methanol diluted in water at 16%, the formation of CO$_2$ is 6 times more efficient than in pure methanol.

In the nitric acid hydrate sample, the solvated NO$_3^-$ ion is readily photo–decomposed into NO$_2^-$+O and NO$_2^-$+OH [15,16], which further increases the OH and the O concentrations, then the destruction of methanol by reaction (12) (and a similar dehydrogenation reaction with O). It ends in CO, which, again, will react with O and OH to form CO$_2$, increasing the CO$_2$/CO ratio to 4.2 for the 34:66 methanol/nitric acid hydrate mixture, a ratio obtained for methanol in pure water ice at higher dilution (16:84) (figure 2c).

3.3. Glycine/H$_2$O

Soft X-ray irradiation of glycine has been already studied using NEXAFS spectroscopy, but not at low temperature in ice [17,18,19]. Figure 3a presents the O K–edge NEXAFS spectra of pure glycine (top) and of 15% of glycine in H$_2$O ice (15:85, bottom) before and after irradiation at 530 eV at 20 K. The fingerprint of glycine is the narrow peak at 532.5 eV, labeled Gly COO$^-$, which is the O1s$\rightarrow$$\pi^*(COO^-)$ excitation in the zwitterionic glycine [20]. In water, the broad band centered at 540 eV is the conduction band of ice, and the shoulder at 535 eV is the O1s$\rightarrow$$\sigma^*(O-H)$ (3a$_1$) excitation in H$_2$O [21].

![Figure 3](image_url)

**Figure 3.** (a) O K-edge NEXAFS spectra at the of pure glycine: 15% glycine in water ice (b), before and at the end of the irradiation. (b) Amount of glycine remaining in the samples (pure glycine, 50% and 15% glycine in water ice) as a function of the photon exposure.
Under irradiation, the $\pi^{*}(\text{COO}^-)$ intensity decreases in the two samples, resulting from the glycine destruction. At the same time, two main peaks grow at 534.3 eV and 535.4 eV, characteristic of CO and CO$_2$, respectively, a result of the removal of the carbonyl group [19]. The CO$_2$/CO peak intensities ratio is 3 times higher for glycine in ice than in pure glycine (not presented), an indication that, again, water favors the formation of CO$_2$ at the expense of CO (reaction (8)). The rate of destruction of glycine can be derived from the decrease of the $\pi^{*}(\text{COO}^-)$ intensity (figure 3b). This time, the survival rate of glycine is fairly the same in pure glycine and in glycine in ice. In all the cases, it tends to a limit of about 30% of the initial glycine concentration. Quantum calculations have shown that the reaction of isolated glycine with OH is possible, under the restricted conditions that the OH radical approaches with a specific reaction coordinate that facilitate the reaction [22]. Our results show that for glycine in ice, such reaction geometry is unlikely. Thus, contrary to what is observed for CO and methanol in H$_2$O, water plays no role in the destruction of glycine.

4. Conclusion
This study shows that the condensed phase allows back–reactions that enhance the survival rates, a strong limit to the photolysis efficiency. In the pure CO film, CO is transformed mainly into CO$_2$ by CO+O. In presence of water, the CO+OH reaction enhances the CO destruction and increases the CO$_2$/CO ratio. CH$_3$OH is also mainly transformed into CO by successive dehydrogenations, and then into CO$_2$ by CO+O. In presence of water, methanol is further transformed into CO by an additional sequence of dehydrogenations reactions with OH (and O in nitrate hydrate), ending into CO$_2$ by reaction with OH (and O). The nitrate photolysis strongly increases the methanol destruction through the release of O (a factor of 10 at the studied concentration). This show how important can be the effect of the reactive oxygenated species. However, this cannot be generalized: glycine is an example where the OH radical plays no role. Finally, as shown above, NEXAFS in condensed films is a synchrotron based technique, which allows the study of the chemical reaction steps involved in the photochemistry of biologically relevant molecules. The role of the chemical environment (water and oxygen in particular) can be investigated.

Acknowledgments
The authors thank K. Shulte, J. N. Andersen, F. Sirotti and M. Silly for their assistance during the experiments.

References
[1] Fujii K, Shikazono N and Yokoya A 2009 J. Phys. Chem. B 113 16007.
[2] Lacombe S and Le Sech C 2009 Surf. Sci. 603 1953.
[3] Laffon C, Lacombe S, Bournel F and Parent Ph 2006 J. Chem. Phys. 125 204714.
[4] Lacombe S, Bournel F, Laffon C and Parent Ph 2006 Angw. Chem. Int. Ed. 45 4159.
[5] Parent Ph, Bournel F, Lasne J, Lacombe S, Strazzula G, Gardonio S, Lizzit S, Kappler J-P, Joly L, Laffon C and Carniato S 2009 J. Chem. Phys. 131 154308.
[6] McLaren R, Clark S A C, Ishii I, Hitchcock A P 1987 Phys. Rev. A 36 1683.
[7] Jamieson C S, Mebel A M, Kaiser R I 2006 Astrophys. J. Suppl. Ser. 163 184.
[8] Watanabe N, Kouchi A 2002 Astrophys. J. 567 651.
[9] Luiti G, Dondes S, Herteck P 1966 J. Chem. Phys. 44 405.
[10] Gerakines P A, Schute W A, Ehrenfreund P 1996 Astron. Astrophys. 312 289.
[11] Porter R P, Noyes W A 1958 J. Am. Chem. Soc. 88 2310.
[12] Bennett C J, Chen S-H, Sun B-J, Chang H H A, Kaiser R I 2007 Astrophys. J. 660 1588.
[13] Lepage M, Michaud M and Sanche L 1997 J. Chem. Phys. 107 3478.
[14] Krim L, Lasne J, Laffon C and Parent Ph 2009 J. Phys. Chem. A 113 8979.
[15] Fisher M and Warneck P J 1996 Phys. Chem. 100 18745.
[16] Bock J and Jacobi H-W 2010 J. Phys. Chem. A 114 1790.
[17] Zubavichus Y, Fuch O, Weinhart L, Heske C, Umbach E, Denlinger JD, Grunze M 2004 
Radiat. Res. 161 346.

[18] Kaneko F, Tanaka M, Narita S, Kitada T, Matsui T, Nakagawa K, Agui A, Fujii K and 
Yokoya A 2005 J. Electron Spectrosc. Relat. Phenom. 144 291.

[19] Wilks R G, MacNaughton J B, Kraatz H –B, Regier T, Blyth R I R and Moewes A 2009 J. 
Phys. Chem. A 133 5360.

[20] Gordon M L, Cooper G, Morin C, Araki T, Turci C C, Kaznatcheev K and Hitchcock A P 
2003 Phys Chem A 107 6144.

[21] Parent Ph, Laffon C, Mangeney C, Bournel F and Tronc M 2002 J. Chem. Phys. 117 10842.

[22] Galano A, Alvarez-Idaboy J R, Montero L A and Vivier-Bunge A 2001 J. Comput. Chem. 22 
1138.