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Radical Photochemistry in Oxygen-Loaded Ices

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The photochemistry of molecular oxygen and water films is a fundamental and growing field of investigation for which the main interest is a full understanding of the "far-out" chemistry[1–6] relevant to the new field of astrobiology.[7–9] Another field of interest concerns the study of oxygen and water radiation chemistry relevant to the medical applications of radiobiology.[10] Indeed, oxygen-derived radicals are known to play an important role in the biochemistry of living cells exposed to ionizing radiation. Therefore, a better understanding of the basic physicochemical processes involved in the transformation of oxygen and aqueous media exposed to ionizing radiation is of fundamental interest.

The last decade has seen a proliferation of studies concerning the chemical reactivity of condensed molecular films submitted to different types of ionizing radiation. The reactivity of molecular oxygen and ozone films induced by electronic,[11] ionic,[12] and UV/IR[13] irradiation as well as the reactivity of water ice[14–18] has been extensively studied. In most of these studies, ozone (O_3) and hydrogen peroxide (H_2O_2) molecules, transient species such as the hydroperoxy ($HO_2^{\bullet}$) and the hydroxyl ($OH^{\bullet}$) radicals, and atomic oxygen are often mentioned as possible intermediate products. To the best of our knowledge there are two direct techniques that have been used to characterize the chemical composition of films in situ. IR spectroscopy led to the observation of O_3 in a molecular-oxygen film irradiated by UV light.[14] The same technique allowed the observation of H_2O_2 and $OH^{\bullet}$ in water ice irradiated by high energy ions[19] and by UV light.[17,20] In these studies the chemical analysis was not complete—in particular, the atomic oxygen and the $HO_2^{\bullet}$ radicals were not detected. In earlier studies Taub and Eiben[21] used electron spin resonance spectroscopy to follow the production of $OH^{\bullet}$ and $HO_2^{\bullet}$ as radiolytic products from crystalline ice irradiated with high energy electrons. However the radicals were observed at temperatures up to 0 °C, which is in contradiction with many recent studies, and requires reconsideration of their identification. The ESR technique has more recently been successfully applied as a direct technique for the observation of radicals in water ice irradiated by γ rays, with

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$OH^•$ and $HO_2^•$ being detected simultaneously.[18] However, in this case the film characterization remained incomplete since the other radiolysis products such as the $O^•$ radicals, H_2O_2, and O_2 were absent.

Here we show a complete in situ measurement of all the oxygen-derived radiolysis products. We can thus clearly analyze the final chemical composition of an irradiated matrix as a function of the irradiation dose and the initial composition of the film. In the case of oxygen-loaded films we observe the presence of atomic oxygen as well as ozone, whereas ozone does not appear in the irradiated pure water ice. In the condensed films containing water, the irradiation induces the production of radicals, for example, $OH^•$, $O^•$, and $HO_2^•$, as well as H_2O_2. These results indicate the advantage of low-temperature near-edge X-ray absorption fine structure (NEXAFS) spectroscopy as a direct and powerful probe technique which allows the simultaneous detection of the products (molecules or radicals) in situ. It opens up exciting new perspectives in the advances of chemical analysis, dose-dependence analysis, and the kinetic study of irradiated condensed media.

The oxygen k-edge absorption spectra of a pure O_2 film measured before and after irradiation are presented in Figure 1. The results have been background-subtracted and normalized at 552 eV. Spectrum a corresponds to the typical NEXAFS spectrum of non-irradiated condensed oxygen.[23] Spectra b–d were measured after three successive irradiations of the film.

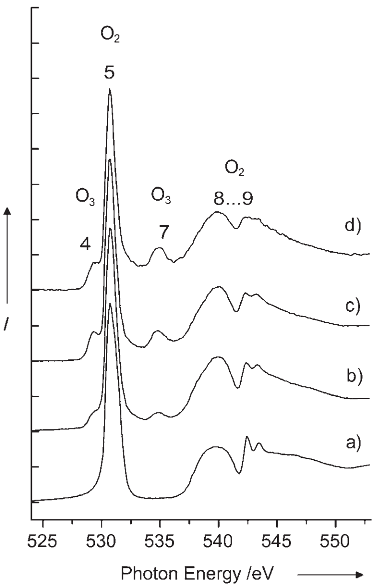

Figure 1. O K-edge photoabsorption spectrum of a molecular O_2 film, before irradiation (a) and after increasing irradiation (b: 1/3×1.6, c: 2/3×1.6, d: 1.6 eV mol^{-1}). The background has been subtracted from the spectra and they have been vertically shifted for clarity. The assignment of the peaks is given in Table 1.

The peaks 5, 8, and 9 are characteristic of the electronic transitions of molecular oxygen $O1s\rightarrow\pi^*$, $O1s\rightarrow\sigma^*$ ($^2\Sigma$ state), and $O1s\rightarrow\sigma^*$ ($^4\Sigma$ state), respectively.[23] Peak 5 is found at 530.7 eV as previously reported[23,24] and is used here as the energy reference for the other measurements. In addition to the structures arising from O_2 molecules (peaks 5, 8, and 9) we observe two new features (peaks 4 and 7) after irradiation. According to previous measurements[24] these two structures correspond to the NEXAFS signature of O_3 in the condensed phase. Peak 4 corresponds to the $O_{terminal}1s\rightarrow\pi^*(2b_1)$ transition in O_3. Peak 7 is asymmetric, as in the gas phase, and consists of two (not resolved) contributions: $O_{central}1s\rightarrow\pi^*(2b_1)$ and $O_{terminal}1s\rightarrow\sigma^*(7a_1)$. This structure is shifted to slightly lower energy relative to that in the gas phase (0.6 eV). Since peak 4 remains at the same position, the corresponding orbitals (π^* and $O_{terminal}1s$) are not perturbed by the condensed phase environment. The $O_{central}1s$ orbital, which is an inner orbital, should not be perturbed either. Therefore, we explain this low energy shift of peak 7 by the perturbation of the external molecular orbital σ^* of ozone, which sees its bonding character modified as a result of the solvation in the condensed matrix.[23] Finally our results show chemical changes in the irradiated O_2 film, in particular the synthesis of O_3, which agrees with previous measurements.[11]

The simplest mechanism for the synthesis of O_3 consists of the following two-step reaction:

1) O_2 dissociates by photoexcitation[25,26] or dissociative electron attachment:[27] $O_2 + h\nu$ (or e^-)$\rightarrow O(^1D)$ or $O(^3P)$ or $O^-(^2P)$, and associated products;
2) O_3 is synthesized in the presence of atomic and molecular oxygen by the exothermic reaction: $O_2 + O \rightarrow O_3$.[28] There is no atomic oxygen released in the film (no peak at 527.2 eV). The reaction of O^- with O_2, which presents an energy threshold, is not considered as a favorite pathway for the formation of O_3.

O_3 may further dissociate by photolysis, by electron-stimulated dissociation,[25,29] or by collision.[16] The maximum intensity of the O_3 peak corresponds to the maximum concentration of O_3 when an equilibrium between the production/destruction of the product is achieved. The spectra presented in Figure 1 have been measured under the same experimental conditions. The peak intensities are thus indicative of the chemical composition of the film. According to the absorption cross-sections of Gejo et al.,[24] the estimated proportion of O_3 produced in pure O_2 is on the order of 8 % at saturation.

The role of the environment on the chemical reactivity of the film was investigated by performing measurements with different heterogeneous films: O_2 in an inert matrix (argon) and O_2 in a reactive matrix (H_2O). The NEXAFS spectra obtained after irradiation of the pure O_2 layer at saturation and of the film composed of O_2/Ar (50 %:50 %) are presented in Figure 2. Irradiation of the heterogeneous film leads to the production of O_3 (peaks 4 and 7) as observed in the pure O_2 medium. The intensity of O_3 relative to O_2 decreases from approximately 8 % in the pure O_2 film, as mentioned previously, to 4 % in the O_2/Ar mixture. The decrease in the rate of O_3 synthesis by a factor of two in Ar corresponds to the dilution factor of O_2 in Ar. Under these conditions the irradiation of O_2 leads to the formation of atomic oxygen but half of it interacts with the surrounding oxygen molecules to produce O_3, while the second half migrates to be trapped in

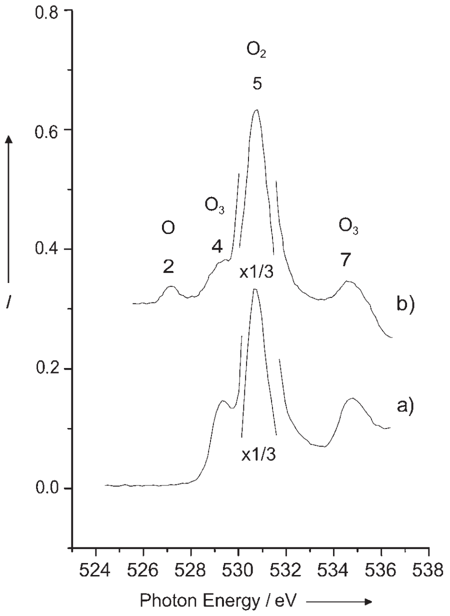

Figure 2. O K-edge absorption spectra obtained after irradiation of a) pure O_2 and b) 50:50 O_2/Ar films. The results have been background-subtracted and normalized to peak 5. The spectra have been vertically shifted for clarity. The identification of the peaks is given in Table 1.

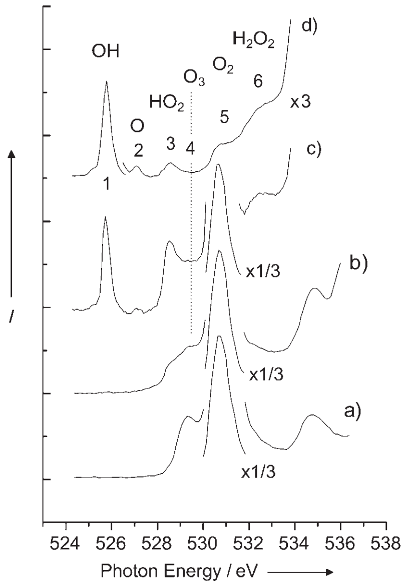

Figure 3. O K-edge absorption spectra obtained after irradiation of pure and heterogeneous films a) pure O_2, b) 50:50 O_2/H_2O, c) 10:90 O_2/H_2O, and d) pure water ice. The results have been background-subtracted. Spectra a–c have been normalized against peak 5. Spectrum d has been normalized against peak 1 of spectrum 2 c. The spectra have been vertically shifted for clarity. The identification of the peaks is given in Table 1.

the Ar matrix. This proposal is supported by the observation of peak 2 at 527.2 eV which corresponds to atomic oxygen[30] (Table 1). The spectra measured with 10 % and 50 % O_2 in the water ice, as well as the spectra obtained with pure O_2 and pure H_2O condensed films are shown in Figure 3.

Table 1: Energy position of the different features observed in the successive NEXAFS measurements.

Peak	Energy [eV] (±0.1 eV)	Electronic transition
1	525.8	$OH^{\bullet}$ ($O1s \rightarrow 2p_O$)[30,31] (1π)
2	527.2	$O^{\bullet}$ ($O1s \rightarrow 2p_O$)[30,31] (2p)
3	528.6	$HO_2^{\bullet}$ ($O1s \rightarrow \pi^*_{O\text{-}O}$) (2A″)
4	529.3	O_3 ($O1s_{terminal} \rightarrow \pi^*_{O\text{-}O\text{-}O}$)[24] ($2B_1$)
5	530.7	O_2 ($O1s \rightarrow \pi^*_{O\text{-}O}$)[23,24] ($1\pi_g$)
6	532.6	H_2O_2 ($O1s \rightarrow \sigma^*_{O\text{-}O}$)[33] ($3B_u$)
7	534.8	O_3 ($O1s_{central} \rightarrow \pi^*_{O\text{-}O}$)[24] ($2B_1$) O_3 ($O1s_{terminal} \rightarrow \sigma^*_{O\text{-}O}$)[24] ($4B_2$) and/or H_2O ($O\ 1s \rightarrow \sigma^*_{O\text{-}H}$)[22] ($4a_1$)
8⋯9	540⋯	O_2($O1s \rightarrow \sigma^*_{O\text{-}O}$)[23] ($2\sigma_u$) ($^2\Sigma$, $^4\Sigma$)

Before irradiation O_2 does not react chemically with H_2O at 25 K. After irradiation the spectra indicate the presence of new products. The very low temperature means that transient species are stabilized in the condensed media and can be characterized by absorption spectroscopy. We were thus able to identify three different radicals. Peaks 1 and 2 are characteristic of the hydroxyl radical ($OH^{\bullet}$) and of atomic oxygen ($O^{\bullet}$), respectively.[30,31] Atomic oxygen in particular has already been mentioned as coexisting with water ice through formation of the complex $H_2O{\cdot}O$.[32] The structure observed at 532.6 eV (peak 6) corresponds to hydrogen peroxide (H_2O_2).[33] To the best of our knowledge, the species giving rise to peak 3 at 528.5 eV has not been characterized yet. The intensity of this peak varies differently with the composition of the film from those of $OH^{\bullet}$, $O^{\bullet}$, O_2, O_3, and H_2O_2, thus showing that peak 3 is related to another chemical species. The fact that peak 3 increases in intensity in 10:90 O_2/H_2O indicates that the concentration of the product is enhanced by reactions that mix the O_2 and H_2O photoproducts or/and O_2 and H_2O reactant molecules. Such reactions lead to $H^{\bullet}$, H_2 (which are not detected), $OH^{\bullet}$, $O^{\bullet}$, O_3, O_2, H_2O_2, and $HO_2^{\bullet}$. Among these six oxygen compounds, five have been already identified ($OH^{\bullet}$, $O^{\bullet}$, O_2, O_3, and H_2O_2), but not the $HO_2^{\bullet}$ radical. We therefore assign peak 3 to $HO_2^{\bullet}$. $HO_2^{\bullet}$, an expected product from the radiolysis of pure water ice,[15,16,19,21] is also observed in Figure 3 trace d. Peak 3 is less intense in the 50:50 O_2/H_2O mixture than in the 10:90 O_2/H_2O mixture; this observation is explained by the decrease in H and $OH^{\bullet}$ availability as the water content decreases, as discussed below. Similar to the $OH^{\bullet}$ transition, peak 3 corresponds to the less energetic excitation, for example, from the inner shell (O1s) to the low-lying orbital (that is, the half-occupied π orbital). Peak 3 is the first identification of the hydroperoxyl radical ($HO_2^{\bullet}$) by NEXAFS spectroscopy.

We have shown that this experimental method consists of a direct chemical analysis of the medium, which allows the simultaneous observation of the different products, such as neutral molecules and radicals, synthesized at the early stage of irradiation. In particular, these results show how strongly the presence of molecular oxygen influences the reactivity of the ice under irradiation. This procedure gives an insight into the processes involved in the chemistry of the film. The reactions (1)–(5) are exothermic in the condensed phase and give rise to the production of the hydroperoxyl radical and hydrogen peroxide:[16]

$$O_2 + H^{\cdot} \rightarrow HO_2^{\cdot} \quad \Delta H = -2.00\,\text{eV} \qquad (1)$$

$$O^{\cdot} + OH^{\cdot} \rightarrow HO_2^{\cdot} \quad \Delta H = -2.73\,\text{eV} \qquad (2)$$

$$OH^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \quad \Delta H = -1.28\,\text{eV} \qquad (3)$$

$$H^{\cdot} + HO_2^{\cdot} \rightarrow 2\,OH^{\cdot} \quad \Delta H = -1.67\,\text{eV} \qquad (4)$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \quad \Delta H = -2.17\,\text{eV} \qquad (5)$$

The production of H_2O_2, which is thermodynamically allowed in the condensed phase, consists of the interaction of two hydroxyl radicals (reaction 5). Recently it has been shown that the dissociation of O_2 by electron attachment and production of negative ions, leads to the formation of H_2O_2 by an exothermic reaction between O^- and H_2O.[34,38] This process would explain the increase in H_2O_2 relative to $OH^{\cdot}$ in the presence of 10% O_2 in ice. Other reactions which are exothermic in aqueous solutions ($HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2$)[35] or in the gas phase ($O(1D) + H_2O \rightarrow H_2O_2$),[36] have been proposed to explain the synthesis of H_2O_2.[34,37] However, the transposition of these results to the condensed phase is not apparent. It has also been proposed that H_2O_2 can be produced by dissociation of a complex such as $H{-}OH{\cdots}O_3 \rightarrow 2\,H_2O_2$, which is not compatible with our findings since O_3 is not observed in the irradiated water ice.[20] The synthesis of $HO_2^{\cdot}$ takes place through the three reactions (1)–(3). The bimolecular reaction (1), which involves a molecule of the matrix (O_2) and a dissociation product ($H^{\cdot}$), must be more efficient than reactions (2) and (3), which involve two dissociation products. The increase in the intensity of peak 3 relative to that of peaks 1, 2, and 6 when water is loaded with 10% oxygen (Figure 3c) is consistent with a higher yield of reaction (1) in the presence of O_2. When the proportion of O_2 reaches 50% in the film (Figure 3b), peaks 1, 3, and 6 should decrease with the amount of water in the mixture (by a factor of approximately 2). Peak 1 ($OH^{\cdot}$) however disappears totally. This observation shows that reaction (2) becomes more efficient when atomic oxygen is present in the film (because of O_2 dissociation). Peak 3 ($HO_2^{\cdot}$), however, does not increase since the rates of reactions (1)–(3) also decrease with the water proportion. Finally, peak 2 (O) disappears as a consequence of reaction (2) occurring, as well as through the competitive synthesis of ozone ($O_2 + O \rightarrow O_3$).

In conclusion, the radiation chemistry of condensed molecular films has been investigated by NEXAFS spectroscopy. Experiments performed at low temperature with different heterogeneous films of O_2 mixed with inert (Ar) and reactive (H_2O) media have underlined the crucial role of the environment. We present here, in particular, the first simultaneous observation of all the transients (molecules and radicals) produced in an irradiated molecular film. This method is thus directly applicable to astrochemistry: the simultaneous analysis of the transient species produced in ices submitted to irradiation would give a more complete picture of the photochemistry in interstellar and stratospheric ice particles. This technique also has applications in an another field of the radiation chemistry; in particular it is promising for the study of the properties of complex molecules of medical interest, such as radiosensitizers. Such molecules are known to enhance the lethal effect of ionizing radiation in living cells, which is commonly attributed to the production of $OH^{\cdot}$ radicals in the medium.[10] NEXAFS spectroscopy would therefore be a valuable tool for studying the radiation chemistry of radiosensitizing molecules trapped in water ice and would thus greatly advance the understanding of their function at a molecular level.

Experimental Section

The NEXAFS experiments were performed on the SACEMOR UHV experimental setup on the high-energy SM-PGM monochromator ($E/\Delta E = 5000$) of the SuperACO SA2 bending magnet beamline (LURE—Orsay, France).[22] The data presented here were recorded in the total electron yield (TEY) mode. The films were deposited at 25 K by background exposure of a clean Pt(111) surface to the desired proportions of oxygen (99.99%, Air Liquide), argon (99.99%, Messer), and/or ultrapure water at a rate of 0.1 Langmuir (1 Langmuir $= 1 \times 10^{-6}$ Torr s). The film compositions were deduced from the mass spectra of the gas mixtures recorded during the dosing (assuming a sticking coefficient of unity for O_2, H_2O, and Ar at 25 K). The films were typically 100 monolayers thick. The synchrotron beam was used for irradiation. The accumulated dose for a saturation concentration of the photoproducts (see below) is on the order of 1.6 eV mol^{-1}. The measurements resulting from the irradiation of the sample either with monochromatic beams of 530.7 eV (resonant excitation to the electronic state of the oxygen), 520 eV, or 540 eV (out of the oxygen resonance) or with a white beam (continuous light from 3 to 900 eV) did not show any significant difference. We can deduce that the energy of the primary photon excitation (in the 500 eV range) does not play a key role: the photoprocess is thus dominated by interactions of the material with the low-energy secondary electrons produced by the primary photon interaction, regardless of whether the photon interaction is resonant on an electronic state (monochromatic beam) or not (white beam).[14] The white beam, whose photon flux is 200 times higher than the monochromatic beam, was used to reduce the time of irradiation. The NEXAFS spectra were recorded under low-intensity monochromatic conditions, so the irradiation damage to the films during the acquisition was negligible.

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