Hydrogen peroxide production by ion irradiation of thin water ice films

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Abstract. In this paper we present the results of new experiments on ion irradiation of water ice performed on thin films to study the synthesis of the hydrogen peroxide molecule and discuss the possibility of detecting it in icy mantles on interstellar grains. The used experimental technique has been in situ infrared spectroscopy. We have irradiated thin films (i.e. the ice thickness was smaller than the penetration depth of the used ion) with three different ions, namely 200 keV of H^+ and He^+ and 400 keV of Ar^{++} . The experiments were carried out at temperatures of 16 and 77 K. We have found that hydrogen peroxide is produced by all of the different ions at both temperatures. The detection of such a molecule has been possible from the study of its infrared feature centered at about 2850 cm^{-1} ($3.5\text{ }\mu\text{m}$). The obtained results also show that the produced $H_2O_2/H_2O(\%)$ ratio is greater for the heaviest ion ($\sim 6\%$ for the case of Ar^{++}) and that H^+ is the ion that produces the smallest quantity ($\sim 1\%$). These upper limits in the production of hydrogen peroxide constrain the quantity of H_2O_2 that can be formed after bombardment by cosmic particles on icy mantles of grains in the interstellar medium.

Key words. astrochemistry – methods: laboratory – techniques: spectroscopic – ISM: molecules – ISM: dust, extinction – molecular processes

1. Introduction

Water is the dominant ice present in the Universe. It can be found in the Solar System as a constituent of the surfaces of some planets or satellites, of the trans-Neptunian objects, of some planetary rings (e.g., Saturn's rings), and also as part of the nucleus of the comets (see e.g., Schmitt et al. 1998). For a long time frozen water has been identified as the dominant component of ice mantles of dust grains in the interstellar medium (ISM) (Willner et al. 1982; Smith et al. 1989).

In dense interstellar and circumstellar environments absorption features attributed to other molecules in solid state have also been found by ground-based, air-borne and space observations (Ehrenfreund & Schutte 2000). These ices are embedded in polar (H_2O -rich) matrices and in non-polar (CO -rich) matrices depending on the local H/H_2 ratio present in the particular scenario (Pendleton & Chiar 1997; Sandford et al. 1997; Whittet & Tielens 1997; Ehrenfreund & Fraser 2003). Among the solid state species that have been reported are CO , CO_2 , OCS , H_2CO , $HCOOH$, CH_4 , CH_3OH , NH_3 , OCN^- , and NH_4^+ (Boogert & Ehrenfreund 2004).

However, the number of securely identified molecules is much lower than that predicted by theoretical models. In fact, chemical models that consider ion-molecule gas phase reactions and/or grain-surface reactions predict the existence of a

number of species in the solid state much greater than those detected up to now (Tielens & Hagen 1982; d'Hendecourt et al. 1985; Hasegawa et al. 1992; Hasegawa & Herbst 1993; Shalabiea & Greenberg 1994). As an example, the hydrogen peroxide molecule (H_2O_2) has been predicted to be produced on grain surfaces by hydrogenation of molecular oxygen (Tielens & Hagen 1982; Hasegawa et al. 1992; Hasegawa & Herbst 1993). The calculations made by those authors predict H_2O_2 abundances not greater than 5% with respect to H_2O .

Solid molecules in the interstellar and circumstellar medium can also undergo chemical reactions driven by energy released from energetic charged particle irradiation and/or UV photolysis. When an energetic ion or a UV photon collides with the ice, part of the deposited energy destroys molecular bonds in the target, producing radicals that can then react to synthesize new molecules. To study some of the effects induced by the radiation, and to identify part of the newly produced molecules, laboratory experiments on ice irradiation are carried out under physical conditions as close as possible to the astrophysical ones (e.g. Johnson 1998; Strazzulla 1998; Moore et al. 2001; Baragiola et al. 2003).

In a recent paper, Gomis et al. (2004) presented results on ion implantation in water ice (i.e. with a film thickness greater than the penetration depth of the used ion) to study the formation of the hydrogen peroxide molecule. The experiments were carried out using five different ions, namely H^+ , C^+ , N^+ , O^+

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and Ar^+ at two different temperatures, 16 and 77 K. They have shown that hydrogen peroxide has been produced by all of the ions at both temperatures. It also has been shown that the quantity of H_2O_2 produced is much greater for the heaviest ions. In particular, the maximum quantity of hydrogen peroxide formed has been about 4% for O^+ at 77 K. The obtained results have been applied to the Galilean satellite Europa in which hydrogen peroxide has been observed (Carlson et al. 1999).

Another recent work on irradiation of water ice to study and characterize the hydrogen peroxide molecule produced by radiolysis is that accomplished by Moore & Hudson (2000). They have carried out experiments on irradiation (with 800 keV H^+) of thin water ice and mixtures (film thickness $\sim 5 \mu\text{m}$), at temperatures of 16 and 80 K. Their results show that H_2O_2 is produced after irradiation of water at 16 K, and the presence of oxidants such as O_2 and CO_2 in the icy mixture enhances the production of H_2O_2 by radiolysis.

In this paper we present new experiments on ion irradiation of water ice that complement those carried out by Gomis et al. (2004). In this case we have irradiated thin films of water ice (i.e. with a film thickness smaller than the penetration depth of the used ion) at temperatures of 16 and 77 K. The used ions have been 200 keV of H^+ and He^+ , and 400 keV of Ar^{++} . The experimental results are discussed in view of their relevance to the icy mantles present on grains in the interstellar and/or circumstellar medium. We have obtained an upper limit for the quantity of icy hydrogen peroxide that can be found on the icy grain mantles. This paper is structured as follows. In Sect. 2 we describe the experimental equipment. Our results are presented in Sect. 3 and the discussion in Sect. 4. We conclude with the astrophysical applications which are discussed in Sect. 5.

2. Experimental apparatus

The infrared spectra here shown have been obtained by infrared absorption spectroscopy performed in a high-vacuum chamber ($P < 10^{-7}$ mbar) faced, through IR-transparent windows, to a FTIR spectrophotometer (Bruker Equinox 55). Pre-prepared gases (or mixtures) are admitted into the chamber by a needle valve and subsequently are accreted as ices on a silicon crystal substrate. The substrate is put in thermal contact with a closed-cycle helium cryostat whose temperature can be varied between 10 and 300 K. The vacuum chamber is interfaced to an ion implanter (200 kV; Danfysik 1080–200) from which ions with energy up to 200 keV (400 keV for double ionization) can be obtained. The ion beam produces a spot greater than the area probed by the infrared beam. To avoid macroscopic heating of the target the current density is maintained in the range of 100 nA cm^{-2} to a few $\mu\text{A cm}^{-2}$. The integrated ion flux (fluence in ions cm^{-2}) is directly related to the ion current measured during irradiation. The substrate plane is placed at an angle of 45 degrees with the IR beam and the ion beam so that spectra can be easily taken in situ, even during irradiation, without tilting the sample. Spectra can also be taken after warm up at selected temperatures in the range 10–300 K. All the spectra shown in the following have been taken with a resolution of 1 cm^{-1} and a sampling of 0.25 cm^{-1} . In our experiments we have used films with a thickness of $\sim 0.5 \mu\text{m}$. More details

Fig. 1. Column density ($\times 10^{17} \text{ molecules cm}^{-2}$) of the water ice stretching band as a function of the ion fluence for 200 keV He^+ and 400 keV Ar^{++} at temperatures of 16 and 77 K.

on the experimental setup have been recently given (Strazzulla et al. 2001).

To calculate the column density of a given species N (molecules cm^{-2}) the following equation is used:

$$N = \frac{\int \tau_\nu d\nu}{A}, \quad (1)$$

where $\int \tau_\nu d\nu \text{ (cm}^{-1}\text{)}$ is the integrated area measured on the optical depth scale and A is the integrated band absorbance (cm molecule^{-1}). The integrated area has been calculated by removing the underlying continuum using only two fixed points.

Water ice films have been obtained depositing H_2O vapour onto a silicon substrate at a rate of about $2 \text{ \AA s}^{-1}$. Deposition times have varied between 30 and 60 min approximately. In this way we have obtained a film thickness that ranges between 3600 and 7200 $\text{\AA}$.

3. Results

3.1. H_2O destruction

Figure 1 shows the water ice column density (molecules cm^{-2}), measured from the integrated intensity of the 3275 cm^{-1} ($3.053 \mu\text{m}$) band, as a function of ion (200 keV He^+ , 400 keV Ar^{++}) fluence at temperatures of 16 and 77 K. An integrated absorbance $A(\text{H}_2\text{O}) = 2.0 \times 10^{-16} \text{ cm molecule}^{-1}$ (Allamandola et al. 1988) has been used to evaluate the column density. All data sets plotted in Fig. 1 exhibit no initial H_2O loss at low irradiation fluences (less than $1 \times 10^{14} \text{ ions cm}^{-2}$). This apparent increase in the amount of water ice is due to the variation of the band strength induced by ion irradiation. Leto & Baratta (2003) have recently shown that the band strength of water ice undergoes a 10% increase already at low ion fluences. This behavior at low fluences is probably due to the competition between the increase of the band strength and the destruction process of the water ice layer. However, in this work we prefer to use the integrated absorbance of an unirradiated ice because the new value has not been measured at 77 K. In addition, even at 10 K an increase of only about 10% has been observed but a new value has not been evaluated.

Fig. 2. IR transmission spectra of H₂O ice as deposited (solid line) and after irradiation with 200 keV H⁺ at 77 K with fluences of 0.4×10^{14} and 2.4×10^{14} ions cm⁻² (dashed and dotted lines respectively). The appearance of an absorption band centered at 2852 cm⁻¹ testifies to the formation of hydrogen peroxide molecules. The spectra after irradiation are shifted downwards for clarity.

From Fig. 1 the H₂O destruction yield (molecules ion⁻¹) can be obtained by means of a linear fit. We have been able to calculate this quantity only for He⁺ at 16 K and for Ar⁺⁺ at 77 K obtaining values of 26 ± 8 and 370 ± 10 molecules ion⁻¹ respectively. The case of 200 keV H⁺ is not shown since for this ion we have obtained a slight increase in the H₂O column density attributed to the increase in the band strength. We must stress that the destruction yields given here are not equivalent to the sputtering yields. The latter represent the number of molecules lost from the target. The destruction yields shown here include both the molecules sputtered away from the target and the molecules which are transformed into some new species. As a result, destruction yields shown above should be greater than the corresponding sputtering yields. In a recent paper, Baragiola et al. (2003) presented a review on sputtering of water ice. Looking, as an example, at their Fig. 3 it can be seen that the sputtering yield for 200 keV He⁺, in the range 20–77 K, is lower than 20 molecules ion⁻¹. In addition, from their Fig. 5 one expects a value of the sputtering yield for 400 keV Ar⁺⁺ lower than 300 molecules ion⁻¹. Thus, the results here reported are in agreement with the values obtained by those authors.

3.2. H₂O₂ band

Figure 2 shows the IR transmission spectra, in the 3060–2500 cm⁻¹ range, of water ice deposited at 77 K and after irradiation with 200 keV of H⁺ at two different fluences (0.4 and 2.4×10^{14} ions cm⁻² respectively). In this particular case the water ice sample is about $0.6 \mu\text{m}$ thick. The appearance of an absorption feature near the long wavelength wing of the $3 \mu\text{m}$ H₂O band testifies to the formation of a new species. This new band, produced after irradiation, is attributed to the $(\nu_2 + \nu_6)/2\nu_6$ OH bending feature of the hydrogen peroxide molecule (Giguere & Harvey 1959; Miller & Horning 1961). The spectra show that the feature is centered at about

Table 1. Hydrogen peroxide destruction and formation cross-sections calculated by using Eqs. (3) and (4) and maximum H₂O₂/H₂O(%) ratio obtained from Figs. 4 and 5.

Ion	Temp. (K)	Cross-sections		Maximum H ₂ O ₂ /H ₂ O(%)
		destruction (σ_d) $\times 10^{-15}$ cm ²	formation (σ_f) $\times 10^{-15}$ cm ²	
H ⁺	16	9.0 ± 1.2	0.099 ± 0.017	1.2
H ⁺	77	16 ± 5	0.056 ± 0.021	0.4
He ⁺	16	13.0 ± 1.0	0.29 ± 0.02	2.4
He ⁺	77	30 ± 5	0.38 ± 0.05	1.3
Ar ⁺⁺	16	3.8 ± 0.4	0.115 ± 0.008	6
Ar ⁺⁺	77	9.5 ± 2.0	0.26 ± 0.05	3.0

2850 cm⁻¹ ($3.5 \mu\text{m}$) which is in agreement with previously published work (Moore & Hudson 2000).

3.3. H₂O₂ production

In Fig. 3 the percentage abundance of hydrogen peroxide is reported as a function of the ion fluence at two different temperatures, i.e., 16 and 77 K, for the case of H⁺, He⁺ and Ar⁺⁺. This H₂O₂/H₂O ratio, calculated in percentage and by number of molecules, has been obtained using Eq. (1). To obtain the column density for the H₂O₂ ice, we have used a value of the integrated band absorbance taken from the literature. The used value has been $A(\text{H}_2\text{O}_2) = 2.7 \times 10^{-17}$ cm molecule⁻¹ (Moore & Hudson 2000).

The quantity of hydrogen peroxide produced is greater at 16 K than at 77 K for H⁺ and He⁺ ions, and for Ar⁺⁺ it is the same at both temperatures. This result is in agreement with the work by Moore & Hudson (2000) who irradiated water ice films with 800 keV of H⁺. They found lower H₂O₂ yields at 80 K compared to 16 K. They suggested that the lower yield at the higher temperature could be traced to a change in the balance between H₂O₂ formation and destruction, which our Table 1 confirms and quantifies. They also proposed several reaction mechanisms to give a reason for this unexpected observation (see Moore & Hudson 2000; Hudson & Moore 2001, for further details).

In Figs. 4 and 5 we plotted the H₂O₂/H₂O(%) ratio, by number of molecules, as a function of the deposited energy (dose). This quantity is given in eV per small molecule (16 amu). In this case we use dose (eV/16 amu) instead of ion fluence (ions cm⁻²) because the former is a better way to compare the results obtained with different ions and by different authors. The doses have been calculated using SRIM2003 (Ziegler et al. 1985), which is a program that simulates the interaction of ions with matter and calculates the energy released to the sample.

Figures 4 and 5 demonstrate that the maximum amount of H₂O₂ produced at 16 and 77 K increases as the atomic number of the incoming ion increases. Thus Ar⁺⁺ is the ion that produces the greatest, and H⁺ the ion that produces the smallest quantity. This result is in agreement with the previous work of Gomis et al. (2004) with thick film experiments, i.e., implantation of ions in samples having a thickness larger than

Fig. 3. Percentage of $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ in number of molecules for each of the used ions at temperatures of 16 and 77 K. The ratio is plotted as a function of the ion fluence (ions cm^{-2}).

Fig. 4. $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (%) production (in number of molecules) after irradiation of thin films of water ice at a temperature of 16 K. The used ions are 200 keV of H^+ and He^+ , and 400 of Ar^{++} . The $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (%) ratio has been plotted as a function of the energy deposited in the target measured in eV/16 amu.

Fig. 5. $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (%) production (in number of molecules) after irradiation of thin films of water ice at a temperature of 77 K. The used ions are 200 keV of H^+ and He^+ , and 400 of Ar^{++} . The $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (%) ratio has been plotted as a function of the energy deposited in the target measured in eV/16 amu.

the penetration depth of used ions. Their results showed that H_2O_2 was produced by all the ions used both at 16 and 77 K. Moreover, they found that the quantity of H_2O_2 produced is

greater for 30 keV C^+ , N^+ , O^+ , and Ar^+ than for 30 keV H^+ . As the heaviest ions have stopping powers much larger than H^+ , their conclusion was that the energy released into the sample

by elastic collisions with target nuclei plays an important role in the process of formation of the hydrogen peroxide molecule. The results obtained in this work reinforce this argument and show that the heaviest ions also form more H_2O_2 in thin films.

From Figs. 3–5 it is clear that the H_2O_2 percentage increases quickly as the ion fluence increases. Furthermore, it is observed that the $\text{H}_2\text{O}_2/\text{H}_2\text{O}(\%)$ ratio remains constant or starts to decrease as the fluence keeps growing. The decrease is due to the fact that as the ion fluence increases the water ice column density decreases (water molecules are destroyed and produce radicals that react to form new molecules or are lost as a consequence of sputtering) and therefore there is less available water to form hydrogen peroxide. Moreover, H_2O_2 itself is also destroyed by further irradiation.

4. Discussion

The number of H_2O_2 molecules present in our sample as a function of time is given by the balance between formation and destruction mechanisms (Gomis et al. 2004):

$$\frac{dn_h}{dt} = \sigma_f \phi n - \sigma_d \phi n_h, \quad (2)$$

where n_h is the hydrogen peroxide column density; n the H_2O column density; σ_f the H_2O_2 formation cross-section; σ_d the H_2O_2 destruction cross-section and ϕ the ion flux.

When the H_2O column density remains constant a solution for Eq. (2) is the following:

$$n_h(t) = n_\infty (1 - e^{-\sigma_d \phi t}), \quad (3)$$

where $x = \phi t$ is the ion fluence and n_∞ the asymptotic value for the H_2O_2 column density as the ion fluence goes to infinity.

If the H_2O column density n decreases linearly with ion fluence, a solution for Eq. (2) can be written as follows:

$$n_h(t) = \frac{n_0 \sigma_f \sigma_d + \sigma_f \sigma_{dw}}{(\sigma_d)^2} (1 - e^{-\sigma_d x}) - \frac{\sigma_f \sigma_{dw}}{\sigma_d} x, \quad (4)$$

where n_0 is the initial H_2O column density and σ_{dw} is H_2O destruction yield (measured in molecules ion⁻¹).

We have fitted the H_2O_2 column densities as a function of ion fluence using Eqs. (3) and (4). The parameters to be determined by the fit are σ_d and n_∞ in the case of Eq. (3) and σ_d and σ_f in the case of Eq. (4). Table 1 shows the values obtained for the hydrogen peroxide destruction and formation cross-sections for each of the used ions at both temperatures.

For the case of He^+ and Ar^{++} irradiation, σ_d and σ_f are obtained directly from the nonlinear fit (Eq. (4)). The required values for the initial H_2O column density n_0 and the H_2O destruction yield σ_{dw} are obtained from a linear fit of the points shown in Fig. 1. For those two ions we have used the same values of the water destruction yield for the temperatures of 16 and 77 K.

In contrast, for the case of H^+ , the H_2O destruction yield is lower and a constant value for the amount of water ice can be assumed. In this case, the value for σ_d has been obtained directly from Eq. (3). The value for σ_f has been evaluated from the asymptotic value for the H_2O_2 column density n_∞ taking into account that $\sigma_f/\sigma_d = n_\infty/n$ in which n is

the H_2O column density. The corresponding values for n_∞ obtained after fitting the data points with Eq. (3) are 2.1×10^{16} and 0.88×10^{16} molecules cm^{-2} at 16 and 77 K respectively (see Gomis et al. 2004, for further details).

5. Astrophysical considerations

Simple molecules are found in the form of ices on silicate or carbonaceous grain mantles in the circumstellar and interstellar medium. In the formation and evolution of those ices a number of different processes play a role. Actually, those solid molecules can be directly frozen from the gas phase or synthesized on grains via surface reactions or by more energetic processes such as UV photolysis, cosmic ray irradiation and thermal annealing.

To study the role played by each of the latter processes in the evolution of the ice, laboratory experiments which simulate the astrophysical conditions are carried out by different groups. In this way, surface chemistry experiments (Collings et al. 2003; Watanabe & Kouchi 2002a; Watanabe et al. 2003), UV photolysis (Gerakines et al. 1996; Watanabe & Kouchi 2002b) and ion irradiation (radiolysis, e.g., Hudson & Moore 1999, 2000; Palumbo & Strazzulla 1993; Palumbo et al. 2000; Baragiola et al. 2003) give us information about the basic processes of ice mantle formation, adsorption, diffusion, desorption and reaction pathways.

In the present work we have simulated the low energy cosmic ray radiation expected for ice mantles in the dense ISM. As reported by Greenberg (1982), the time spent by a grain in the interstellar medium is 3×10^7 – 5×10^8 yr. At the densities of dense molecular clouds (10^3 – 10^5 H atoms cm^{-3}), the timescale for the condensation of molecules on the dust particles is small ($\sim 10^5$ yr; e.g., Tielens & Allamandola 1987). Thus icy grain mantles suffer irradiation for 10^5 – 5×10^8 yr.

The flux of low energy cosmic rays irradiating grains in the interstellar medium is not well known. A reasonable estimation is a proton flux $J(E = 1 \text{ MeV}) = 10 \text{ cm}^{-2} \text{ s}^{-1}$ (Strazzulla & Johnson 1991). Palumbo & Strazzulla (1993) estimated a dose released to interstellar ices via cosmic ray bombardment between 0.05 and 50 eV/molecule while Moore (1999) gives values between 3 and 300 eV/molecule assuming a cloud lifetime of 10^7 and 10^9 yr respectively.

Figure 4 and Table 1 show the maximum value of the $\text{H}_2\text{O}_2/\text{H}_2\text{O}(\%)$ ratio produced after irradiation of thin films of water ice with H^+ , He^+ and Ar^{++} ions at the given energies at 16 K, a temperature that well mimics that of the grains in interstellar dense clouds. We can see that protons produce a maximum ratio of $\sim 1\%$, He^+ of $\sim 2.5\%$ and for Ar^{++} we measure a value of $\sim 6\%$. These limits in the production of hydrogen peroxide by ion irradiation put a constraint on the quantity of H_2O_2 that can be synthesized on grain mantles in dense molecular clouds. As can be seen from Fig. 4, the levels of deposited energy obtained experimentally cover the range of radiation exposure expected for the ices during the dense cloud lifetimes. Furthermore, the dominant contribution of cosmic rays comes mainly from low energy protons in the MeV range (Moore 1999), which are comparable to those used in our experiments.

This justifies the extrapolation of our results to the ISM astrophysical scenario.

To conclude, we wish to stress that our results exclude the possibility that hydrogen peroxide abundances are greater than a few percent of water in interstellar ices. This puts severe limits on the possibility of detecting hydrogen peroxide in interstellar ice mantles. Boudin et al. (1998) derived an upper limit of 6.1% for the H_2O_2 abundance by comparing results obtained from IR spectroscopy experiments on water/hydrogen peroxide mixtures and astronomical observations of the high-mass protostar NGC 7538: IRS 9. Moreover, Smith et al. (2003) have carried out additional laboratory experiments on water/hydrogen peroxide mixtures with subsequent comparison with the spectrum of a low-mass protostar provided by ISO. Smith et al. (2003) stressed the difficulty in unambiguously identifying interstellar hydrogen peroxide ice, although they have not excluded its presence in grain mantles. Further searches for solid H_2O_2 require observations with more sensitive instruments.

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