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## Solid-state ozone synthesis by energetic ions

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### Abstract

We have synthesized ozone by irradiating thin solid films of oxygen and oxygen–water mixtures with 100 keV protons, motivated by recent reports of condensed O<sub>3</sub> on icy satellites in the outer Solar system. We measured the depth of the Hartley absorption band in the ultraviolet by reflectance spectroscopy and used it to quantify the column density of ozone. We analyzed the results using a three-component (O, O<sub>2</sub> and O<sub>3</sub>) model that successfully explains the fluence dependence of ozone production. © 1999 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

Surfaces of airless bodies in space are subject to irradiation by energetic ions from stellar sources and magnetospheric plasmas. Among the most relevant surfaces in astronomical environments are those of minerals and ices, both insulators; unfortunately this class of materials has been the least studied in the laboratory. Ion irradiation of ices is particularly important on icy satellites, planetary rings, and comets in the outer solar system. The information of irradiation effects comes mainly from reflectance spectroscopy, the measurement of the fraction of sunlight reflected by the body as a function of wavelength. Decreases

in reflectance at particular wavelengths, referred to as absorption bands, are often useful indicators for the presence of particular chemical species. These species can be an intrinsic component of the surface material or can be the product of irradiation. For instance, absorption bands in the infrared have allowed the identification of water ice as a primary surface component on the Jovian satellites Europa, Ganymede and Callisto, several Saturnian satellites and in Saturn's rings. Absorption bands in the visible have been used to identify condensed O<sub>2</sub> on Ganymede's surface [1,2]; the origin [3–6] of this surface material and its location [3,7,8] are still controversial.

From the existence of condensed O<sub>2</sub> on Ganymede, it is reasonable to infer that a broad absorption feature in the ultraviolet (UV) reflectance spectrum of this satellite [9] is the Hartley band of ozone. However, Ganymede's UV absorption feature is not satisfactorily fitted by the Hartley band, raising questions on the existence of other

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species and on the environment of  $O_3$ . Other questions are: what is the relative importance of UV photolysis and irradiation by energetic magnetospheric ions in producing  $O_3$ ? What information about surface properties and irradiation history can be obtained from the band position, depth, and shape? Our research was aimed at answering those questions. Below, we report first experiments on the synthesis of condensed  $O_3$  in molecular gases by irradiation with 100 keV protons, typical of Ganymede's environment.

## 2. Experiments

The experiments were made in a cryopumped UHV chamber attached to a 300 kV ion accelerator. Different aspects of the experimental setup and procedures for ion irradiation and reflectance measurements were described previously [7,8,10–14]. The substrate was an optically flat gold mirror attached to a liquid-He cryostat. A uniform stream of gases was produced by a microcapillary array doser and directed onto the cold substrate, where ices grew at a rate of about 10 nm/s. The gases were either pure oxygen or 1:1  $O_2:H_2O$  mixtures. We used mixed ices to retain oxygen up to relatively high temperatures relevant to the icy satellites; in these films, oxygen precipitates in relatively large inclusions, as judged from optical spectroscopy [7,8]. Bi-directional reflectance was measured using a Xe-discharge lamp in the geometry shown in Fig. 1. The reflected light was analyzed at 2-nm resolution by a grating spectrometer equipped with a CCD detector. The wavelength scale was calibrated to  $\pm 0.1$  nm using a Hg reference lamp. To remove the shape of the Xe-lamp spectrum and spectrometer efficiency function the spectrum of the reflected light was normalized to that obtained before irradiation.

Fig. 1 shows normalized reflectance spectra for a mixed ice irradiated at 5 K with 100 keV protons at  $45^\circ$  incidence that shows the Hartley band, broader than that seen in the gas phase [15]. Data for other temperatures or pure oxygen are qualitatively similar but shifted in wavelength. The reflectance obtained at 50 K, closer to the temperature of Ganymede's polar region, show

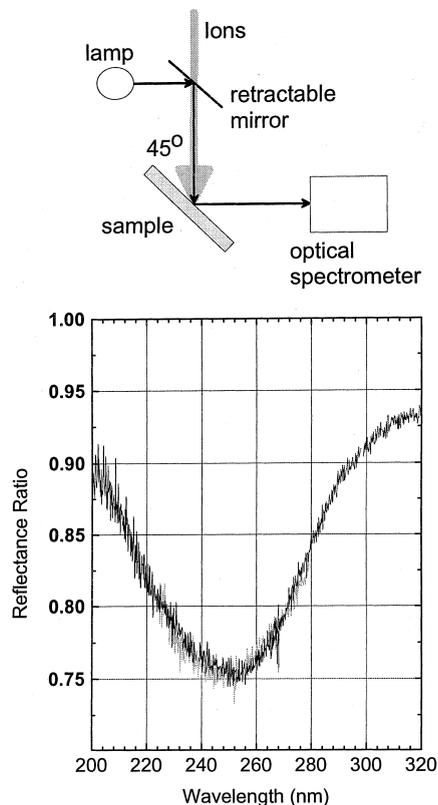


Fig. 1. Top: schematic diagram of the experiment. Bottom: Ozone Hartley band in the ratio of light reflectance spectrum for an irradiated,  $10\ \mu\text{m}$  thick 1:1  $O_2:H_2O$  mixed-ice film, to the reflectance spectrum prior to irradiation. The ice film was grown and maintained at 5 K, and irradiated by  $3.8 \times 10^{12}$   $H^+$ / $\text{cm}^2$  at 100 keV.

that the band position and width can account for most of the absorption structure seen on this satellite [9]. However, differences at long wavelengths suggest the existence of other chemical species. The astronomical implications will be discussed in a separate paper, due to space constraints. Here we focus the discussion on elucidation of atomic collisions aspects from the analysis of the depth of the Hartley band as a function of irradiation fluence. The relative drop in reflectance is given by  $\exp(-\sigma\eta)$ , Beer's law, where  $\sigma$  is the photo-absorption coefficient ( $10^{-17}$   $\text{cm}^2$  at the band minimum [16,17]) and  $\eta$  the column density ( $O_3/\text{cm}^2$ ). We studied the fluence dependence of the absorbance  $\sigma\eta$ , which we show in Fig. 2. We found no

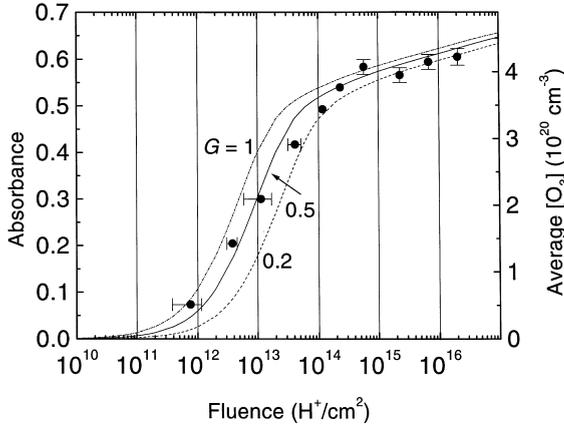


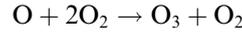
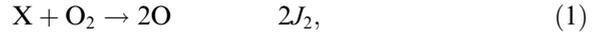
Fig. 2. Proton fluence dependence of the column density of  $O_3$  seen by the reflectance experiment on 1:1  $O_2:H_2O$  mixed-ice films. The lines are results of the model described in the text.  $G$  is the number of geminate O atoms produced per 100 eV of electronically deposited energy.

flux dependence of the observed band depths within experimental error for fluxes between  $10^{11}$  and  $10^{12}$   $H^+/cm^2$  s.

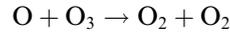
### 3. Model and discussion

The chemical reactions leading to the formation of ozone have been extensively studied in the case of the higher atmosphere of Earth, where the relevant energizing radiation is ultraviolet photons from the sun [15]. The main photochemical reactions, the Chapman reactions, involve the following species: ground state  $O^3P$ , excited  $O^1D$ ,  $O_3$ , ground state  $O_2^3\Sigma$ , electronically excited  $O_2^1\Delta$ , and vibrationally excited  $O_2$ . The situation is more complicated in the case of ionizing radiation, where ionic species like  $O_2^+$ ,  $O^+$ ,  $O_3^+$ ,  $O_2^-$ ,  $O^-$ , and electrons are also important [18]. An attempt to describe radiolysis based on all these species is not feasible at present, since most production and reaction rates are unknown. To achieve insight on the most important processes, one must simplify the description, retaining only the most important species and reactions. We start the description after the electron–ion recombination stage is over, when we assume we are left with species:  $O^3P$ ,  $O^1D$ ,  $O_3$ , and  $O_2$ . Vibrationally excited molecules,

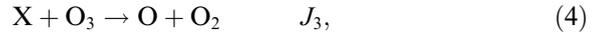
which are important in gas-phase chemistry, are not considered since vibrations should be quickly quenched in the condensed state [16,17]. We denote the density of O,  $O_2$  and  $O_3$  (molecules/ $cm^3$ ) as  $[O]$ ,  $[O_2]$  and  $[O_3]$ . The following are the important reactions with their gas-phase rates  $k$  [15]:



$$k_{12} = 6.2 \times 10^{-34} (300/T)^2 \text{cm}^6/\text{s}, \quad (2)$$



$$k_{13} = 8 \times 10^{-12} \exp(2060/T) \text{cm}^3/\text{s}, \quad (3)$$



where  $X$  signifies the radiation source,  $J_i$  the dissociation rates ( $s^{-1}$ ) of species  $O_i$ , and  $T$  the temperature in Kelvin. In reaction (1) the factor 2 takes into account that two O atoms are produced in a dissociation collision. Reaction (2) is assumed to be important only for  $O^3P$  whereas reaction (4) is assumed to be important only for  $O^1D$  [16,17]. The reaction:  $2O + O_2 \rightarrow 2O_2$ , which occurs at a rate  $4 \times 10^{-8} [O]^2 \text{cm}^3/\text{s}$  at 30 K in the gas-phase will be neglected in comparison with reactions (2) or (3), the main ones limiting the O concentration. We can safely assume that the sample remains mostly  $O_2$  during irradiation, since experiments show that the concentration of  $O_3$  is small, and since O atoms react very fast with  $O_2$  and  $O_3$ . The observation that the ozone concentration during ion irradiation is much smaller than that of the  $O_2$  matrix allows taking  $[O_2]$  as constant. The relevant rate equations are then:

$$d[O]/dt = 2J_2[O_2] + J_3[O_3] - k_{13}[O][O_3] - r_{12}[O], \quad (6)$$

$$d[O_3]/dt = r_{12}[O] - k_{13}[O][O_3] - J_3[O_3], \quad (7)$$

where the rates  $k_{13}$  and  $r_{12} = k_{12} [O_2]^2$  should be considered average values for a mixture of singlet and triplet O states. These equations are similar to the Chapman equations used to describe processes in the Earth's upper atmosphere. For the  $O_2:H_2O$  ices the description is analogous inside the  $O_2$  inclusions which, being large [7,8], will not be affected much by reactions involving  $H_2O$  at the

boundaries, that may lead to hydrogen peroxide [16,17].

We now consider the rate constants. For non-ionizing photons,  $J_{2,3} = \sigma_{2,3}\phi$ , where  $\sigma_2$  and  $\sigma_3$  are the cross sections for dissociating  $O_2$  and  $O_3$ , respectively, and where  $\phi$  is the radiation flux. For energetic ions, the cross sections should be interpreted as effective values, which include not only direct processes but also collisions involving secondary electrons. A well-known relation in radiation chemistry is that the number of primary (geminate) radiation products equals the electronically deposited energy times a constant factor  $G$  [18]. Thus, the effective cross sections are  $\sigma_i = S_e G_i$ , where  $S_e$  is the electronic stopping cross section and  $G_i$  the number of geminate species  $i$  produced per unit of electronic energy deposited.

Reactions rates have been well studied in the gas phase. In the solid, an electronic excitation to a repulsive state does not necessarily lead to dissociation due to the cage effect, where recombination of the fragment O may occur fast inside the cage (geminate recombination). This cage effect decreases with the kinetic energy of the fragment O and with temperature. Reaction rate data also exist for temperatures much higher than those used in this work. Extrapolating the rate for conversion of O atoms to ozone to 5 K gives  $r_{12} = 1.5 \times 10^{15}/s$ , clearly unphysical since it implies a transition time much shorter than what an atom needs to move to an adjacent lattice site. The lifetime of oxygen atoms in the solid should still be expected to be extremely short, but limited to a time of the order of a vibration period, i.e.  $r_{12} \approx 10^{13}/s$ . Extrapolating the rate  $k_{13}$  for destruction of ozone by O, leads to extremely small values at low temperatures. However, in the dense tracks of fast ions there is sufficient kinetic and vibrational energy supplied that the low background temperature should not be a limitation to the rates. In addition to the uncertainty of using gas-phase reaction rates for the solid, we note that, in the case of films much thinner than those used in our experiments, one would also need to consider the out-diffusion of O, and less likely  $O_3$  during irradiation. We look first at the equilibrium values, ( $d[O]/dt = d[O_3]/dt = 0$ ):

$$[O]_{\infty} = \frac{J_2[O_2]}{k_{13}[O_3]}, \quad (8)$$

$$[O_3]_{\infty} = \frac{r_{12}[O]_{\infty}}{J_3 + k_{13}[O]_{\infty}} = \frac{r_{12}}{k_{13}} \frac{1 + J_2[O_3]_{\infty}}{J_2[O_2]}, \quad (9)$$

$$\frac{J_3[O_3]_{\infty}^2}{J_2[O_2]} + [O_3]_{\infty} - \frac{r_{12}}{k_{13}} = 0. \quad (10)$$

Calling  $J_3/J_2 = R$  and  $g = r_{12}/k_{13} [O_2]$ , and using concentrations relative to  $[O_2]$ ,  $C_i = [O_i]/[O_2]$ :

$$C_{3\infty} = \frac{J_2}{2J_3} \left( \sqrt{1 + 4gR} - 1 \right). \quad (11)$$

Since  $C_{3\infty}$  depends on the ratio  $J_3/J_2$ , the equilibrium concentration of ozone is independent of the particle flux, in agreement with experiment. This means we can safely simulate conditions at Ganymede, where energy fluxes are about three orders of magnitude lower than used in this work [19]. If we assume that  $R$ , the ratio of  $O_3$  to  $O_2$  destruction is inversely proportional to the dissociation energies,  $R \sim 5.1 \text{ eV}/1.05 \text{ eV} \sim 5$ . To obtain  $O_3$  concentrations we use measured absorbances and consider that the ozone is only produced at depths where ionization is important ( $\approx 1 \mu\text{m}$  for 100 keV  $H^+$  at  $45^\circ$  incidence). This corresponds to an optical path length of  $\approx 3 \mu\text{m}$  since the light goes twice through the affected region. From Fig. 2 we thus obtain a maximum column density of  $6 \times 10^{16} O_3/\text{cm}^2$ , giving  $[O_3] = 2.1 \times 10^{20} O_3/\text{cm}^3$  or  $C_{3\infty} = 0.016$ , where we have considered that only half of the film consists of oxygen. The small  $C_{3\infty}$  implies, from Eq. (11),

$$4gR \ll 1. \quad (12)$$

Therefore, we can approximate Eq. (11) further as:

$$C_{3\infty} \approx \frac{r_{12}}{k_{13}[O_2]} = g, \quad (13)$$

$$C_{1\infty} \approx \frac{J_2}{r_{12}}. \quad (14)$$

To discuss the time evolution, we introduce the following dimensionless variables:  $f_1 = C_{1\infty}/C_1$ ,  $f_3 = C_{3\infty}/C_3$ ,  $\tau = r_{12} t$ ,  $j_2 = J_2/r_{12}$  and  $j_3 = J_3/r_{12}$ . We note that  $C_{1\infty} = j_2$ . Eqs. (6) and (7) then transform into:

$$df_1/d\tau = 2 + j_3 f_3 C_{3\infty}/C_{1\infty} - f_1 f_3 - f_1, \quad (15)$$

$$df_3/d\tau = f_1 C_{1\infty}/C_{3\infty} - f_1 f_3 C_{1\infty}/C_{3\infty} - j_3 f_3. \quad (16)$$

But Eq. (12) implies  $j_3 C_{3\infty}/C_{1\infty} \ll 1$ . Thus, Eqs. (15) and (16) simplify to:

$$df_1/d\tau = 2 - f_1(1 + f_3), \quad (17)$$

$$df_3/d\tau = f_1(1 - f_3)C_{1\infty}/C_{3\infty}. \quad (18)$$

No analytical solution to these equations has been found. We notice, however, that the time constant for [O] equilibration,  $1/r_{12}$ , is extremely short compared to that for [O<sub>3</sub>],  $C_{3\infty}/(f_1 J_2)$ . The solution for experimentally relevant time scales,  $\tau \gg 1$ , is:

$$2\ln(1 - f_3) + f_3 = -2F\sigma_2/C_{3\infty}, \quad (19)$$

where  $F = \phi t$  is the irradiation fluence. We can distinguish two limiting cases. The initial growth of the ozone concentration ( $f_3 \ll 1$ ) is  $f_3 \approx 2F\sigma_2/C_{3\infty}$ , or  $C_3 \approx 2J_2 t$ , the solution that can also be obtained immediately from Eqs. (6) and (12). Near saturation,  $C_{3\infty} \approx 1 - \exp(-2F\sigma_2/C_{3\infty})$ . We can define a characteristic fluence  $F_{\frac{1}{2}}$  as that at which  $f_3 = 0.5$ . Using Eq. (15),  $F_{\frac{1}{2}} = 0.44 C_{3\infty}/\sigma_2$ . Since the stopping cross section (and effective  $\sigma_2$ ) decreases as the ions penetrate the solid, the surface region, with larger  $\sigma_2$ , will saturate first, whereas at the end of the range, where  $\sigma_2$  should be small, the O<sub>3</sub> concentration will saturate last. We thus integrate the concentration  $C_3$  from Eq. (19) over depth in the solid for different values of the oxygen yield  $G_O$ . At each depth, we take  $\sigma_2$  to equal  $G_O$  times the electronic energy deposited per unit depth calculated by TRIM [20]. The integral is normalized so that  $C_{3\infty} = 0.016$  (see above). The results are shown in Fig. 2 for different values of  $G_O$ . We find a very good agreement in the shape of the fluence dependence. The value of  $G_O$  that gives the best fit,  $G_O \approx 0.5$  O/100 eV is reasonable for primary radiation yields [18], as is the effective dissociation cross section for 100 keV H<sup>+</sup> near the surface,  $\sigma_2 = S_e G_O = 2.3 \times 10^{-16}$  cm<sup>2</sup>/molecule.

In summary, we have shown that energetic protons can produce ozone efficiently from solid oxygen. The Hartley absorption band for mixed oxygen:water ices is similar to that observed on icy

satellites. We have explained the fluence dependence with a model for the relevant reactions. It shows a very fast equilibration of the O-atom concentration and a slow build-up of ozone up to a maximum concentration. The depth distribution of electronic energy deposited is important in determining the fluence distribution of the O<sub>3</sub> column density. Our results imply that, at the ion energy fluxes present at Ganymede,  $2 \times 10^{13}$  eV/cm<sup>2</sup>/s [19], the observed band depths will be achieved in about a day.

### Acknowledgements

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