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OZONE SYNTHESIS ON THE ICY SATELLITES

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ABSTRACT

Condensed O_2 and ozone on the surfaces of some icy satellites are thought to originate from the radiolytic decomposition of surface water ice by the impact of energetic magnetospheric ions, but decades of laboratory studies have produced no evidence for ozone from the radiolysis of pure water ice. Here we report for the first time the production of ozone in ice by 100 keV ions. Using a method that departs drastically from those used in all previous experiments, we have simulated more closely conditions on the icy satellites by performing ion irradiation while depositing water concurrently, which takes into account the effects of gravity and surface porosity. This codeposition causes the burial of a high concentration of radiolytic O_2 from which ozone is formed. Our results demonstrate that the enhanced trapping of oxygen in surface ices depends on temperature and should vary locally, depending on the rates of irradiation and recondensation. The burial of radiolytic products by redeposition will likely occur in many varied astronomical environments, besides icy satellites.

Subject headings: astrochemistry — atmospheric effects — methods: laboratory — molecular processes — planets and satellites: general — radiation mechanisms: general

Online material: color figures

1. INTRODUCTION

The *Hubble Space Telescope* and the *Cassini* spacecraft have shown tenuous oxygen atmospheres around the icy satellites Europa and Ganymede of Jupiter and Saturn's rings (Hall et al. 1998, 1995; Tokar et al. 2005). However, the detection of absorption bands corresponding to *solid* O_2 in the visible reflectance of Ganymede (Spencer et al. 1995), Europa, and Callisto (Spencer & Calvin 2002) was surprising, since the vapor pressure of solid oxygen exceeds the atmospheric pressures of these satellites (e.g., 10^{-3} to 10^{-8} mbar [Broadfoot et al. 1979; Carlson et al. 1973] at Ganymede and 10^{-8} mbar [Hall et al. 1995] at Europa) by several orders of magnitude at the reported surface temperatures. This discovery was augmented by the observation of ozone at Ganymede (Noll et al. 1996) and the Saturnian satellites Dione and Rhea (Noll et al. 1997), which was attributed to photolysis and/or radiolysis of solid O_2 (Baragiola et al. 1999; Johnson & Jesser 1997; Noll et al. 1996, 1997). The oxygen and ozone at Ganymede are more abundant on its trailing hemisphere, where the flux of impinging ions from Jupiter's magnetosphere is greatest, supporting the hypothesis that O_2 and O_3 form by radiolysis of the surface ice and are trapped in voids (Johnson & Jesser 1997; Spencer et al. 1995).

However, only miniscule amounts of O_2 molecules were produced and retained in ice by irradiation in a vacuum by 200 keV protons (Bahr et al. 2001) or by 87 eV and 5 keV electrons (Petrik et al. 2006; Zheng et al. 2006). The oxygen concentrations are insufficient to explain the O_2 absorption bands in Ganymede's visible spectrum or the production of detectable amounts of ozone, both of which require at least two neighboring O_2 molecules. Based on experiments using as-deposited O_2-H_2O ice mixtures, Vidal et al. (1997) and Baragiola & Bahr (1998) pointed out that a limiting factor in retention of O_2 in ice was the rapid out-diffusion of O_2 at temperatures typical of those measured at Ganymede. Thus, they advanced the alternative explanation for the observations of oxygen and ozone on the icy satellites that O_3 forms from solid O_2 condensed in cold surface patches. However, there is no evidence to confirm or deny this hypothesis.

2. TRAPPING THE OXYGEN: IRRADIATION AND CODEPOSITION

Our recent experiments (Teolis et al. 2005) suggest that the idea of O_2 trapping in irradiated water ice should be reconsidered. We observed that condensation of a fresh overlayer of water on irradiated ice suppresses sputtering of the radiolytic O_2 produced by 100 keV Ar^+, enhancing the amount of O_2 trapped in the ice. This contrasts with the observations using low-energy electrons, where a drop in O_2 emission by overlayers did not lead to significant trapped O_2 (Petrik & Kimmel 2006).

The enhancement of O_2 trapping by condensation of water overlayers, seen in the laboratory, will also occur at an icy satellite. In this case, the condensation will be due to water molecules returning due to gravity or coming from adjacent surfaces (Cassidy & Johnson 2005; Sieveka & Johnson 1982; Spencer 1987) after being ejected by sputtering, sublimation, cryovolcanism, or micrometeorite impact. The burial of oxygen by this process will depend on the competition of condensation and removal by sputtering or desorption, which should vary strongly with surface topography. In our previous experiments, the overlayers were removed by sputtering before significant O_2 could accumulate in the ice (Teolis et al. 2005). To replace the sputtered material, we have now performed ion irradiation during water condensation, and we found dramatic enhancements in the production of trapped O_2 and O_3.

We performed experiments in a cryopumped ultrahigh-vacuum chamber (base pressure of 10^{-10} torr) with ice films condensed by effusing pure water vapor onto a cooled, optically flat gold-coated quartz crystal microbalance. We measured the specular reflectance of the films in the ultraviolet (4° incidence angle) and infrared wavelengths (35° incidence angle) and used a quadrupole mass spectrometer to identify the molecules ejected during ion irradiation and desorbed during warming. We vapor deposited 8000 ML (monolayer) films (1 ML $= 10^{15}$ molecules cm^{-2}) and irradiated them with 100 keV Ar^+ ions (10^{12} cm^{-2} s^{-1}) while

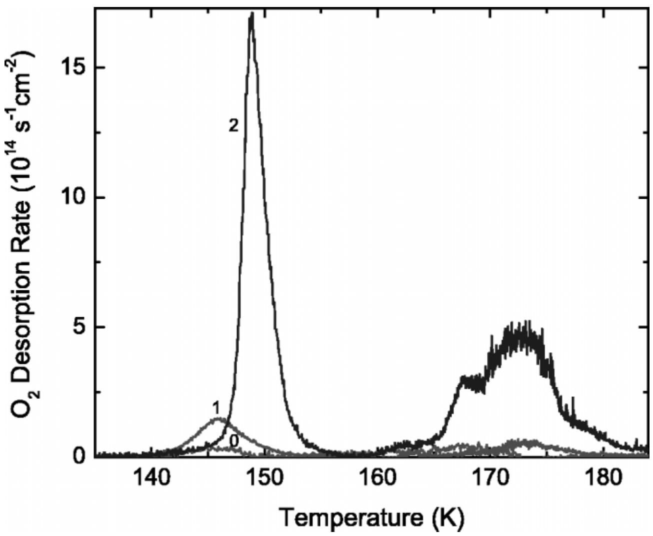

FIG. 1.—Thermal desorption spectra of O_2 during warming (0.6 K minute^{-1}) of ice films irradiated with 10^{16} Ar^+ cm^{-2} at 130 K. The number next to each curve is the parameter ρ, the ratio of mass condensation to mass removal by sputtering. For $\rho = 0$, a mass equivalent to ~1400 ML of water was removed by sputtering. At $\rho = 1$ there was no net mass change, and at $\rho = 2$ a mass equivalent to ~1300 ML of water was added. [*See the electronic edition of the Journal for a color version of this figure*.]

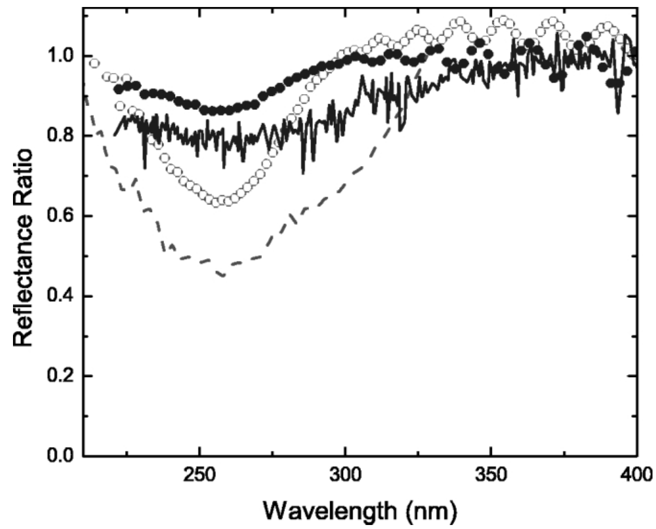

FIG. 2.—UV reflectance of ice at 130 K obtained by irradiation with 10^{16} Ar^+ cm^{-2} for $\rho \approx 1$ (blue solid circles) and $\rho \approx 2$ (red open circles). The reflectance is normalized to that of unirradiated ice. Oscillations above 300 nm are due to optical interference. Also included are the reflectance spectra of Ganymede's trailing hemisphere (Noll et al. 1996; *dashed line*) and Rhea's leading hemisphere (Noll et al. 1997; *solid line*). The Ganymede spectrum is normalized by dividing it by 0.45, and Rhea's spectrum was divided by the model continuum given in Noll et al. (1997). [*See the electronic edition of the Journal for a color version of this figure*.]

observing the ejection of H_2O and O_2 with the mass spectrometer. All samples were nonporous, since the irradiation fluences used were 1–2 orders of magnitude greater than that required to compact ice (Fama et al. 2001; Raut et al. 2004; Palumbo 2005). The Ar^+ ions were used to simulate the effect of heavy magnetospheric ions such as O and S. The O_2 sputtering rate dropped (e.g., by ~50% when the experiment was done at 130 K) when we admitted a background pressure of water in the range of 10^{-8} to 10^{-7} torr to deposit H_2O during irradiation. This drop indicates the blocking of O_2 escape by H_2O condensation and resulted in an enhancement of the concentration of trapped O_2. Figure 1 shows the O_2 desorption rate during warming of films first irradiated with 10^{16} Ar^+ cm^{-2} at 130 K during codeposition of water, compared to the case of irradiation without deposition. The O_2 desorption rate measured by the mass spectrometer was calibrated against the mass loss measured with the microbalance during warming between 140 and 155 K, a range in which water sublimation is minimal. The release of O_2 near 150 K is correlated with ice crystallization (Vidal et al. 1997), while that between 160 and 180 K occurs concurrently with water desorption. The time integral of the desorption rate gives the total amount of O_2 trapped in the ice. Remarkably, codeposition of water enhanced the column density of trapped O_2 by more than a factor of 2 from ~4×10^{16} to ~10^{17} cm^{-2} with $\rho \approx 1$, where ρ is the ratio of the mass uptake by condensation to the mass removal by

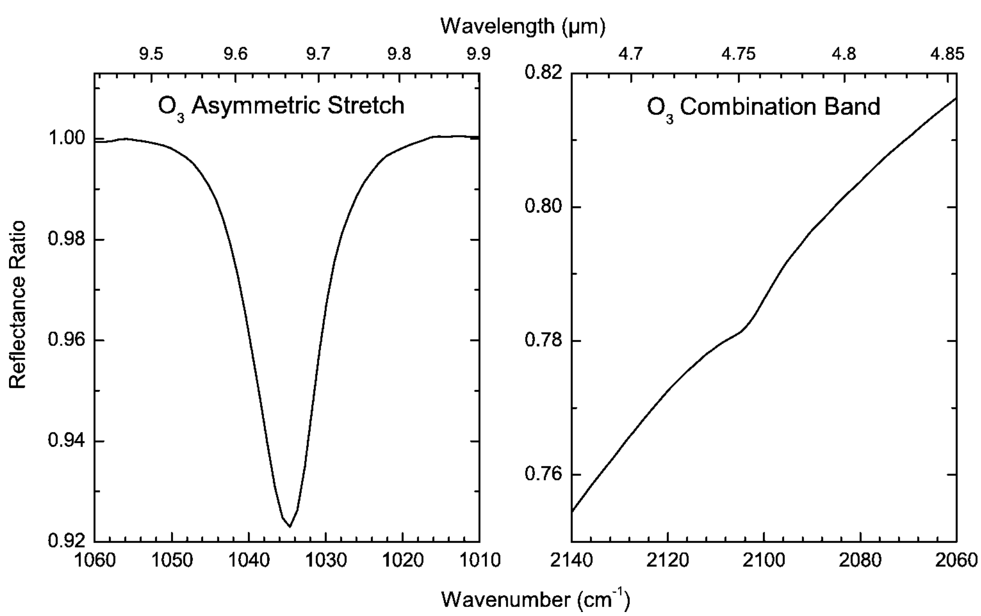

FIG. 3.—Infrared reflectance spectra obtained after irradiation of pure water ice with 6×10^{15} Ar^+ cm^{-2} for $\rho \approx 2$ showing the ν_3 asymmetric stretch absorption of ozone near 1035 cm^{-1} and the $\nu_1 + \nu_3$ combination mode absorption near 2104 cm^{-1}. The spectra have been normalized to that of the film prior to irradiation.

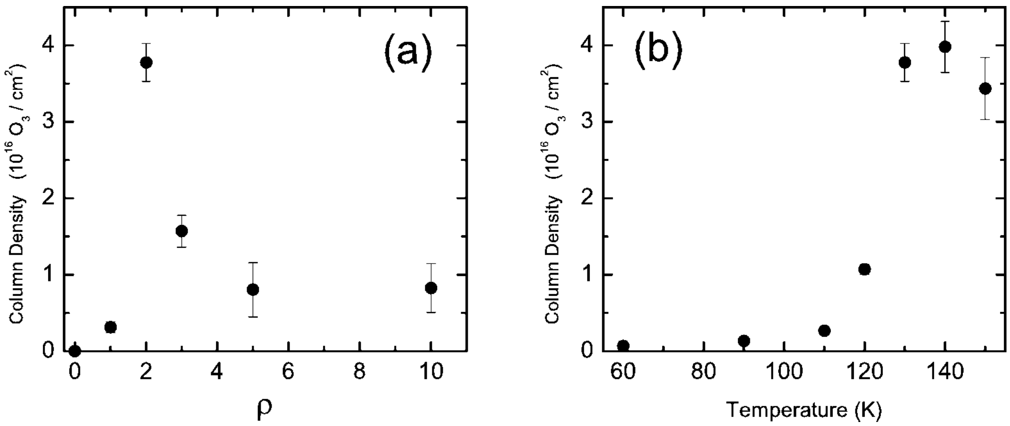

FIG. 4.—Column density of ozone in ice irradiated with 10^{16} Ar^+ cm^{-2} vs. (*a*) ρ at 130 K and (*b*) temperature at $\rho = 2$.

sputtering. The amount of O_2 increased further to ~5×10^{17} cm^{-2} for $\rho \approx 2$. We point out that the same O_2 enhancement also results when the experiment is performed in steps, alternating between periods of condensation and irradiation only. As in experiments without codeposition (Teolis et al. 2005), the trapped O_2 is not evenly produced, but concentrated in a subsurface layer. In an experiment at 130 K, we stopped irradiation and condensation ($\rho \approx 2$) and waited for 8 hr, during which we found that the O_2 loss was negligible (<0.1%), in contrast to the previous experiments using unirradiated O_2-H_2O mixtures (Baragiola & Bahr 1998; Vidal et al. 1997). This is likely due to radiation-induced defects that trap diffusing O_2 (Teolis et al. 2005; Loeffler et al. 2006).

3. OZONE SYNTHESIS

The O_2 concentration in our codeposition experiments is high enough that detectable amounts of ozone are also produced by the ions, unlike the case for $\rho = 0$. This is evident in the reflectance spectra for ice irradiated at 130 K with 10^{16} Ar^+ cm^{-2} during codeposition with $\rho \approx 1$ and $\rho \approx 2$ (Fig. 2). The spectra, which have been normalized to that of the film prior to irradiation, show a broad absorption feature corresponding to the Hartley band of ozone. In both cases there is good agreement with the ozone band observed on Ganymede and Rhea (Fig. 2). The broadening of Ganymede's ozone band compared to our spectra may be due to other absorbing species in Ganymede's ice (Noll et al. 1996). In addition to the Hartley band, we observed infrared absorption bands characteristic of condensed ozone (Chaabouni et al. 2000) at 1035 (ν_3) and 2104 cm^{-1} ($\nu_1 + \nu_3$), as shown in Figure 3. Experiments with 100 keV protons were also tried with and without water condensation, but O_3 was not detected. This is attributed to the lower density of energy deposition by protons than by heavy ions, which is known to result in less O_2 production (Bahr et al. 2001).

The amount of ozone produced in our experiments depends strongly on ρ, as shown in Figure 4*a*, where we plot the O_3 column density calculated from the depth of the Hartley band for ice irradiated at 130 K with 10^{16} Ar^+ cm^{-2} at different ρ. The column density initially rises with increasing ρ as more O_2 is prevented from escaping the ice. At high values of ρ the dilution of the trapped O_2 results in less O_3 production. The O_3 column density is also sensitive to temperature, as shown in Figure 4*b* for irradiation of ice by 10^{16} Ar^+ cm^{-2} using $\rho \approx 2$. The rise in O_3 production between 60 and 130 K agrees with the increase in the concentration of trapped O_2 previously reported (Teolis et al. 2005), which is due to the increase of O_2 production with temperature, first seen by Brown et al. (1982). The small decrease in ozone production above 130 K could be related to crystallization of the ice, which was shown to reduce O_2 production by low-energy electrons (Sieger et al. 1998). We note that the O_3 column density saturates at a fluence of 10^{16} Ar^+ cm^{-2} for $\rho \leq 1$ but continues increasing with irradiation fluence (and thickness) for $\rho > 1$.

4. SCENARIOS FOR THE ICY SATELLITES

The results presented here provide the first reported experimental evidence for the production of ozone directly from water by radiolysis and suggest three conditions for O_3 production on icy satellites: (1) surface temperatures greater than ~60 K (Fig. 4*b*), (2) irradiation of the surface by heavy ions, and (3) recondensation of water onto the surface. The temperature and irradiation conditions (Cooper et al. 2001; Krimigis et al. 2005; Young et al. 2005) can be satisfied on the Galilean and Saturnian satellites. The role of highly energetic magnetospheric electrons discussed by Cooper et al. (2001) is uncertain, but judging by the lack of ozone production by protons found in this work, we anticipate that the contribution of such weakly ionizing particles will likely be secondary.

Regarding the recondensation condition, the parameter ρ will have a distribution of values at different locations depending on the ion flux and on the fraction of sputtered or sublimed H_2O that impacts the surface due to the effect of gravity and the surface topography. At Ganymede, daytime temperatures are sufficiently high that water sublimation is also important, causing water transport from warmer to cooler surfaces over distances of tens of kilometers (Sieveka & Johnson 1982; Spencer 1987). As the direction of solar illumination changes throughout the day, previously shaded regions are illuminated, and vice versa, causing variations in surface temperature and water condensation rates with time and location. In contrast with Ganymede, sublimation is negligible at Dione and Rhea because of the low surface temperatures. Still, the porous icy regolith produced by meteorite bombardment (Veverka et al. 1986) will trap ~70% of the molecules sputtered by neighboring grains (Cassidy & Johnson 2005), and in addition, ~10%–20% of the remaining fraction will return by gravity (Johnson 1990). Therefore, the average rates of sputtering and redeposition should be nearly equal on these satellites ($\rho \sim 1$), leading to ozone buildup.

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