Icarus 215 (2011) 226–233

Contents lists available at ScienceDirect

Icarus

journal homepage: www.elsevier.com/locate/icarus

H_2O_2 production by high-energy electrons on icy satellites as a function of surface temperature and electron flux

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ARTICLE INFO

Article history:
Received 30 January 2011
Revised 17 June 2011
Accepted 21 June 2011
Available online 8 July 2011

Keywords:
Ices
Europa
Enceladus
Experimental techniques
Satellites, Composition
Ices, IR Spectroscopy

ABSTRACT

Chemistry on the icy surface of Europa is heavily influenced by the incident energetic particle flux from the jovian magnetosphere. The majority (>75%) of this energy is in the form of high energy electrons (extending to >10 MeV). We have simulated the electron irradiation environment of Europa with a vacuum system containing a high-energy electron gun for irradiation of ice samples formed on a gold mirror cooled with a cryostat. Pure water films of ~2.6 μm thickness were grown at 100 K and then either cooled (to 80 K), warmed (to 120 K) or left at 100 K and subsequently irradiated with 10 keV electrons. The production of hydrogen peroxide (H_2O_2) was monitored by observation of the 2850 cm^{-1} (3.5 μm) band. Equilibrium concentrations of H_2O_2, in units of percent by number H_2O_2 relative to water, were found to be 0.043% (80 K), 0.029% (100 K), and 0.0063% (120 K). These values are 33%, 22%, and 5%, respectively, that of the reported surface concentration on the leading hemisphere of Europa (Carlson, R.W., Anderson, M.S., Johnson, R.E., Smythe, W.D., Hendrix, A.R., Barth, C.A., et al. [1999]. Science 283(5410), 2062–2064) and less than the equilibrium concentrations formed by ion irradiation. In addition to the ice film temperature, the current of electrons was varied between different experiments to determine the production and destruction of H_2O_2 as a function of both electron flux and ice temperature. Variation in current was found to have little effect on the results other than accelerating arrival at radiolytic equilibrium.

1. Introduction

Understanding the production of H_2O_2 on icy satellites is important for two primary reasons: (1) spacecraft observations, *e.g.* the Near Infrared Mapping Spectrometer on board the *Galileo* spacecraft, have revealed the presence of H_2O_2 as an important surface constituent (Carlson et al., 1999) and (2) the production of other surface materials, specifically O_2 and perhaps CO_2 and SO_2, may depend in part on H_2O_2 as a necessary precursor in the pathway toward production. Fig. 1 shows possible pathways toward O_2 as determined by Cooper et al. (2003), all of which have H_2O_2 as a key intermediary. In addition, from an astrobiological perspective, H_2O_2 and oxidants derived from H_2O_2 may play a critical role in maintaining biologically useful redox gradients in the subsurface ocean, if mechanisms for delivering the surface material to the subsurface are identified (Chyba and Phillips, 2001; Hand et al., 2007).

Laboratory simulation and production of H_2O_2 has been shown with protons, ions, and UV (Gerakines et al., 1996; Moore and Hudson, 2000; Gomis et al., 2004b,a; Loeffler et al., 2006) and with low-energy electrons (Sieger et al., 1998; Pan et al., 2004). Some high-energy electron work has been performed (Zheng et al., 2006), but the low temperatures used during irradiation (12 K) make it hard to justify as a system comparable to the surfaces of icy satellites (50–150 K).

Here we employ 10 keV electrons and temperatures relevant to Europa and the warmer regions of Enceladus (80–120 K). High-energy electrons dominate the surface irradiation flux (Cooper et al., 2001) and they penetrate deeper into the surface than ions. Furthermore, after impact, much of the energy from protons and ions is dissipated as energetic electrons (though the majority of these secondary electrons are at energies lower than a few eV) (Johnson, 1990; Mozumder, 1999). For these reasons, understanding the role of energetic electrons in H_2O_2 production is critical for a comprehensive understanding of the surface and near surface chemistry.

2. Experiment details

We have constructed a high-vacuum stainless steel chamber capable of replicating the temperatures and pressures of planetary and astrophysical ices. Mounted onto the chamber is a He-cryostat with a temperature range down to a few Kelvin. A Varian 300 l/s turbo-pump, backed by an oil-free Alcatel fore-pump, produces pressures of $\sim 5 \times 10^{-9}$ Torr. Ice films of diameter ~0.8 cm and a few microns in thickness are grown by vapor-deposition on a gold

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doi:10.1016/j.icarus.2011.06.031

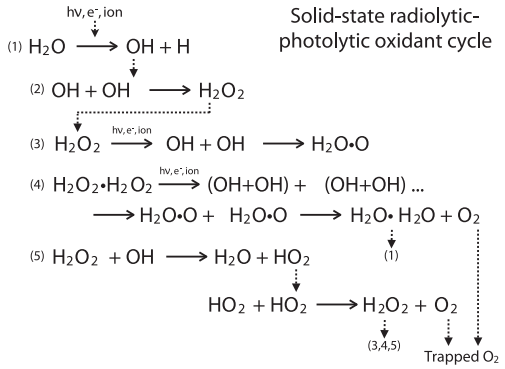

Fig. 1. Chemical pathways in the radiolytic production of H_2O_2 and O_2 from water. This diagram is based on Cooper et al. (2003) and illustrates the importance of H_2O_2 production as a precursor for O_2.

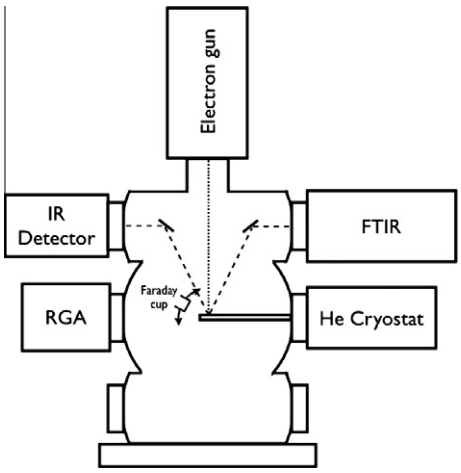

Fig. 2. Diagram of the laboratory set-up. Ice films are vapor deposited and grown on the end of the cryostat cold-finger and then irradiated with high-energy electrons from the electron gun. In situ spectral analysis is accomplished in transmission with the Fourier-transform infrared spectrometer (FTIR) and a mass-spectrometer capable of detecting volatile species of 1–300 a.m.u. (RGA). The Faraday cup allows for measurement of the electron beam current throughout the experiment.

mirror mounted on the cryostat's cold finger. An external manifold allows for mixing of volatiles prior to deposition. For the results presented here all ices were neat H_2O. To ensure purity of our ices, nanopore de-ionized water was heated and quenched at least three times to remove dissolved gases before mounting onto the manifold in preparation for deposition.

A 100-keV electron gun mounted on the chamber, perpendicular to the plane of the ice film, provides for high-energy electron irradiation of the ice sample. A Faraday cup on a rotation stage within the chamber allows for monitoring of the electron beam current directly above the ice sample. Here we present results from experiments using 10 keV electrons and beam currents of 10–1000s of nA.

A Fourier-transform infrared spectrometer (FTIR) was used for analysis of the sample before, during, and after irradiation. The ice-coated mirror was illuminated by the FTIR at 22° angle of incidence. Light passes through the ice and is reflected by the gold surface, giving a double pass through the ice film. Spectra with 4 cm^{-1} resolution and 1024 coadded spectra were collected continuously, with a ~9-min integration period for each spectrum. For all experiments three spectra were collected prior to ice deposition and prior to irradiation. The average of the either the pre-deposition or pre-irradiation spectra were then used for calculating absorbance, A_ν,

$$A_\nu = -\log(I_{Sample}/I_{Baseline}), \tag{1}$$

where I_{Sample} and $I_{Baseline}$ are the spectral intensities of the sample and reference baseline. In all results presented here the average of the pre-irradiation spectra was used for the absorbance baseline. Using the pre-irradiation average allowed removal of the broad H_2O peak at ~3200 cm^{-1} that dominates the region near the H_2O_2 2850 cm^{-1} band. The optical depth of the film is,

$$\tau = \frac{\ln(10)}{2} \cdot A_\nu \cdot \cos(\phi), \tag{2}$$

where ϕ is the angle of refraction in the film (ϕ = 16°). More accurately, τ is the opacity that would be observed in transmission at normal incidence for an ice sample of equivalent thickness (as opposed to our case of reflection at 22°). Fig. 2 provides a diagram of the experimental set-up.

For each ice film grown and irradiated as part of this work, the ice film thickness in each case was monitored and measured using two complimentary techniques. First, during deposition the average film thickness was determined by monitoring the absorbance at 3500 cm^{-1} to calculate τ, as in Eq. (2). The absorbance at 3500 cm^{-1} measured relative to the pre-deposition spectra yields the film thickness via the relation,

$$d = \frac{\tau}{(4\pi k/\lambda)}, \tag{3}$$

where the quantity in the denominator is the absorption coefficient and k is the temperature-dependent imaginary component of the index of refraction at wavelength λ (Hudgins et al., 1993). The film thickness acquired from this technique represents an average over the ~0.8 cm diameter of the infrared beam on the ice. Thus, while channel fringes may complicate the measurement of the thickness using one measurement at one small spot on the film (Hirschfeld and Mantz, 1976), the variations in thickness across the film surface serve to mitigate against large errors due to channel fringing.

The second technique employed for measuring the ice film thickness utilized a laser to interrogate a small spot through the film, thus serving to compliment the average value gained from the first technique. Monitoring of interference fringes from 6328-Å laser radiation transmitted through the ice films was used to measure film thickness as per Sill et al. (1980). Each fringe of the interference sinusoid corresponds to a half wavelength thickness, or ~0.3 μm, and by counting fringes during deposition we gauged our film thickness.

In all of our experiments the above two techniques were used to grow ice films to a thickness comparable to, but greater than, the projected range of the energetic electron. Johnson (1990) provides an approximation for the range, $R(E)$, as a function of electron energy, E, in keV,

$$R(E) \approx R_\rho E^\alpha. \tag{4}$$

The exponent α was empirically determined to be 1.76 and for unit density material (*e.g.* ice, $\rho \sim 1$ g cm^{-3}), $R_\rho = R_1 = 0.046$ μm. Irradiating films slightly thicker than $R(E)$ ensures that all of the energy from the electron beam is deposited into the ice film.

For our experiments on the temperature dependence of H_2O_2 production all films were deposited at 100 K. This temperature is the broad average surface temperature for low latitude regions on Europa, but high latitude regions and diurnal variations lead to temperatures in the range of ~70–130 K (Spencer et al., 1999). After deposition, films were then either cooled to 80 K, warmed to 120 K, or kept at 100 K. In all case the vapor deposited ice was initially amorphous and stayed amorphous throughout the experiments as determined by the spectral profile of the 3-μm H_2O absorption band which is different for amorphous and crystalline