Photolysis of H_2O–H_2O_2 mixtures: The destruction of H_2O_2

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ABSTRACT

We present laboratory results on the loss of H_2O_2 in solid $H_2O + H_2O_2$ mixtures at temperatures between 21 and 145 K initiated by UV photolysis (193 nm). Using infrared spectroscopy and microbalance gravimetry, we measured the decrease of the 3.5 μm infrared absorption band during UV irradiation and obtained a photodestruction cross section that varies with temperature, being lowest at 70 K. We use our results, along with our previously measured H_2O_2 production rates via ionizing radiation and ion energy fluxes from the spacecraft to compare H_2O_2 creation and destruction at icy satellites by ions from their planetary magnetosphere and from solar UV photons. We conclude that, in many cases, H_2O_2 is not observed on icy satellite surfaces because the H_2O_2 photodestruction rate is much higher than the production rate via energetic particles, effectively keeping the H_2O_2 infrared signature at or below the noise level.

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1. Introduction

Surfaces of most icy bodies in the outer Solar System and interstellar space are constantly bombarded with energetic particles and photons. Radiolytic products from these impacts can be detected from Earth and spacecraft by comparison of features in their reflectance spectra with those obtained in the laboratory. Some of our more recent laboratory studies using radiolysis to simulate the space environment (Loeffler et al., 2006a,b; Raut et al., 2012) have been motivated by the detection of H_2O_2 on Europa (Carlson et al., 1999), the lack of or lower than expected abundance of NH_3 detected on the surface of many saturnian icy satellites, such as Enceladus (Brown et al., 2006; Verbiscer et al., 2006), and the higher than expected CO_2:CO ratio found in the interstellar medium (Whittet et al., 1998).

In the work we report here, we have investigated the stability of H_2O_2 mixed in H_2O–ice when it is photolyzed with longer wavelength UV photons (>180 nm), which are weakly absorbed by H_2O. Our previous work on H_2O_2 was initially motivated by the detection of the 3.5 μm absorption band on the surface of Europa by the Galileo Near-Infrared Mapping Spectrometer (NIMS) (Carlson et al., 1999; Hansen and McCord, 2008). More recent ground-based studies have confirmed the NIMS results and have shown that there is nearly an order of magnitude more H_2O_2 in Europa's leading hemisphere than in its trailing hemisphere (Hand and Brown, 2013). The presence of H_2O_2 on Europa's surface, predicted by Johnson and Quickenden (1997), is not too surprising given that this satellite is subject to a high radiation flux (Cooper et al., 2001) and is mostly composed of water ice, a combination of which has long ago been shown to lead to H_2O_2 production (Ghormley and Stewart, 1956). Soon after the discovery of H_2O_2 on Europa, multiple laboratories verified that under relevant experimental conditions H_2O_2 could indeed be formed via radiolysis of water ice (Moore and Hudson, 2000; Gomis et al., 2004; Loeffler et al., 2006b; Zheng et al., 2006; Hand and Carlson, 2011). Unlike former studies, these radiolysis measurements were made in situ at the irradiation temperature studied, ensuring that the H_2O_2 detected was from irradiation and not from thermal reactions that may occur during warming. Although the amount estimated on Europa and in the laboratory was <1% with respect to H_2O, the strength and location of the absorption band made it seem likely that the NIMS detection on Europa would be the first of many on solid icy surfaces. However, new detections of condensed H_2O_2 on other surfaces have not been forthcoming, as the only other possible detection of H_2O_2 (Newman et al., 2007) on the icy satellite Enceladus has been disputed (Hodyss et al., 2009; Loeffler and Baragiola, 2009). Interestingly, Ganymede and Callisto, two other jovian satellites similar in composition and surface temperature to Europa but with lower radiation flux, have shown a slope in their ultraviolet reflectance spectra that is suggestive of H_2O_2 (Hendrix et al., 1999) yet no infrared absorption feature near 3.5 μm absorption region has been detected.

It is important to note that while Europa's surface is the only one in outer space where condensed H_2O_2 has been unequivocally

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detected, there have been a few gas phase detections of H_2O_2. For instance, H_2O_2 has been detected in Mars' atmosphere using both submillimeter (Clancy et al., 2004) and infrared spectroscopy (Encrenaz et al., 2004). Interestingly, the abundance of H_2O_2 in the martian atmosphere appears to have a time dependence, as these values were three to six times higher than previous upper limits provided estimated infrared spectroscopy (Encrenaz et al., 2002). This temporal dependence is also supported by more recent measurements by the Herschel telescope, which has not been able to observe H_2O_2 up to the previous detected levels (Hartogh et al., 2010). Most recently, using submillimeter spectroscopy gas phase H_2O_2 has been detected in the interstellar medium (Bergman et al., 2011), where solid H_2O_2 has been predicted to exist (Tielens and Hagen, 1982) but has yet to be detected.

The paucity of definitive H_2O_2 detections in outer space, especially in the solid phase, contrasted with its relative ease to produce and detect in the laboratory has led us to begin investigating possible mechanisms that could preferentially destroy H_2O_2 throughout the detection depth of the icy satellite surfaces (ten's of microns for the 3.5 μm band). Recent laboratory studies show that one possibility for the absence of H_2O_2 on Ganymede, Callisto and the trailing hemisphere of Europa is that this molecule may be consumed by thermally-induced reactions with contaminants in the ice, such as SO_2 (Loeffler and Hudson, 2013). Another likely mechanism, which is likely active in both pure and contaminated ice, is that the hydrogen peroxide may be efficiently destroyed by longer wavelength UV photons (>180 nm), which are weakly absorbed by water (>2 cm absorption length, Warren and Brandt, 2008) and can thus penetrate deeply into the surface ice. To test this possibility, we have photolyzed low concentrations of H_2O_2 in solid H_2O mixtures with UV photons (193 nm) at temperatures between 21 and 145 K. During photolysis, we have measured the photodestruction of H_2O_2 by monitoring the decrease of the 3.5 μm band with infrared spectroscopy and the photodesorption of the sample by monitoring the mass loss of our sample with our quartz crystal microbalance. Finally, we have extrapolated our photodestruction results to estimate the timescale on which this mechanism would be active on multiple surfaces in outer space.

2. Experimental details

All experiments were performed inside a cryopumped stainless-steel vacuum chamber on a radiation-shielded cryostat (see Loeffler et al., 2006c). The base pressure of the chamber was $\sim 3 \times 10^{-10}$ Torr and 1–2 orders of magnitude lower inside the shield. Solid hydrogen peroxide–water films were vapor deposited at 110 K onto an optically flat gold mirror electrode of a 6-MHz quartz-crystal microbalance (QCM). The areal mass (mass/area) of the films was determined (153 μg/cm²–2 μm) by the change in the resonance frequency of the crystal, which was measured with an Inficon IC/5 controller to a resolution of 0.1 Hz (Sack and Baragiola, 1993). The measured areal mass can be converted to film column density η (molecules/cm²) if the film composition is known, and converted to thickness if the mass density is known (Sack and Baragiola, 1993).

The H_2O–H_2O_2 mixtures were grown from a liquid solution of hydrogen peroxide and water using a glass doser (Loeffler and Baragiola, 2011). Each film contained between 0.5% and 2% H_2O_2, which was calculated from the band area of the infrared H_2O_2 absorption band at 3.5 μm, using previously calibrated band strengths at the same thickness (Loeffler et al., 2006b). After growth, samples were annealed to 135 K to allow diffusion to form the thermodynamically stable dihydrate diluted in water instead of clusters of hydrogen peroxide (Loeffler and Baragiola, 2005). After warming to 135 K, the samples were subsequently taken to the temperature where they were irradiated: 21–145 K.
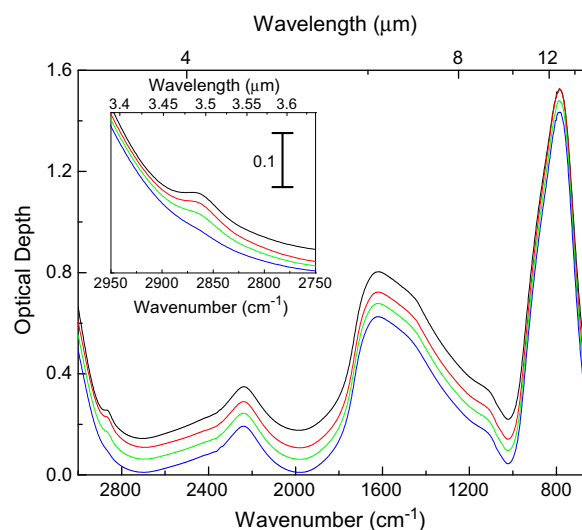

Fig. 1. Infrared spectrum of an $H_2O + H_2O_2$ mixture photolyzed at 100 K with 193 nm photons. Spectra from top to bottom at 2850 cm⁻¹ is after 0, 1.6, 6.3, and 50×10^{19} photons/cm². The spectra have been offset vertically for clarity. The caption focuses in on the 3.5 μm absorption band of H_2O_2.

Irradiation was performed at normal incidence using a GAM ArF excimer laser (193 nm; 10 ns pulse width). The laser beam was defocused using a MgF₂ lens ($f = 50$ cm) to cover a rectangular spot ~ 25 mm × 75 mm at the target, larger than the active diameter of the microbalance (6 mm) to avoid multi-photon excitations or heating during each laser pulse. To measure the photon fluence reaching the target, we replaced the QCM with an Ophir power meter, which measured constant beam intensity across the area of the QCM. In these experiments, we measured that the laser delivered pulses of 1.2×10^{15} photons/cm²/pulse uniformly across the films at a rate that we varied from 2 to 16 Hz during the experiment. The values of fluence are calculated taking into account the $\sim 20\%$ light reflected by the gold substrate (Canfield et al., 1964).

In addition to microbalance gravimetry, *in situ* characterization of our films was performed using infrared spectroscopy. The infrared specular reflectance between 1.5 and 15 μm was measured at an incident angle of 35° using a Thermo-Nicolet Nexus 670 Fourier Transform infrared spectrometer at 2-cm⁻¹ resolution. The spectra were divided by the reflectance of the gold mirror substrate taken before film deposition and converted into absorption by taking the natural logarithm.

To quantify the column density of hydrogen peroxide present in the sample, we have typically calculated the band area of the infrared absorption feature at 3.5 μm by subtracting a non-linear continuum from the spectrum in optical depth units (Loeffler et al., 2006b). However, as is seen in Fig. 1, the H_2O_2 absorption band is very weak at high fluences, and thus here we analyze the derivative of the optical depth ($-\ln$ reflectance) spectrum. Fig. 2 shows that the absorption feature is more pronounced in the derivative, making quantification of small values (high fluences) more accurate. As the H_2O_2 absorption band does not change shape as it attenuates during photolysis, analysis using the band area or the derivative peak height yielded the same results within 5% over the region where a band area could be accurately calculated. Thus, data shown here will be given as the normalized peak-to-peak height of the derivative, which is obtained after subtracting the continuum baseline.

3. Results

Fig. 1 shows the infrared spectrum of our $H_2O + H_2O_2$ mixture before, during and after UV photolysis at 100 K between 3000 and