

The state of hydrogen peroxide on Europa

M. J. Loeffler and R. A. Baragiola

Laboratory for Atomic and Surface Physics, University of Virginia, Charlottesville, Virginia, USA

Received 19 May 2005; revised 1 July 2005; accepted 3 August 2005; published 10 September 2005.

[1] We report infrared reflectance studies in the laboratory that reveal the state of hydrogen peroxide on Europa. Detailed analysis of the 3.5 μm infrared absorption band for hydrogen peroxide grown in a number of water ice environments shows that, for temperatures and concentrations relevant to Europa (80–130 K), hydrogen peroxide molecules exist in isolated trimers $\text{H}_2\text{O}_2 \bullet 2\text{H}_2\text{O}$. If the temperature on an icy body containing H_2O_2 approaches 150 K, as on Ganymede, the trimers aggregate into precipitates of crystalline dihydrate $\text{H}_2\text{O}_2 \bullet 2\text{H}_2\text{O}$. **Citation:** Loeffler, M. J., and R. A. Baragiola (2005), The state of hydrogen peroxide on Europa, *Geophys. Res. Lett.*, 32, L17202, doi:10.1029/2005GL023569.

1. Introduction

[2] Hydrogen peroxide has been unequivocally detected in the leading hemisphere of Europa at equatorial and mid latitudes [Carlson *et al.*, 1999] from its 3.5 μm infrared absorption band and inferred from its ultraviolet reflectance spectra [Hendrix *et al.*, 1999]. Laboratory studies have established that this molecule can be formed by radiolysis of surface water ice induced by energetic ions from Jupiter's magnetosphere [Moore and Hudson, 2000; Gomis *et al.*, 2004a, 2004b; Baragiola *et al.*, 2005; Loeffler *et al.*, 2005]. In particular, Loeffler *et al.* [2005] has shown that the band shape of the 3.5 μm H_2O_2 absorption band on Europa and that produced by ion irradiation are in very good agreement, indicating that they are likely in the same state. However, the nature of this state has not yet been determined. Carlson *et al.* [1999] noted that the absorption band position was outside the range of the pure amorphous and of crystalline phases whereas Cooper *et al.* [2003] proposed that H_2O_2 exists in crystalline inclusions, with potential consequences for O_2 production and retention in ice. The high reactivity of hydrogen peroxide, which depends on its state (pure aggregates or diluted in water), could imply that the surface of Europa is more a hostile than a supporting environment to organic molecules surfacing from a hypothetical underground ocean harboring life [Chyba and Hand, 2001].

[3] To shed light on the question of the state of hydrogen peroxide molecules on Europa, we have measured its 3.5 μm absorption band under a variety of laboratory conditions, including its production in water ice by ion irradiation, and its dependence on temperature variations that might be expected to occur in the environment of different icy satellites.

2. Experimental Details

[4] All experiments were performed in a stainless steel ultra high vacuum (UHV) chamber on a radiation-shielded cryostat [Loeffler *et al.*, 2005]. The base pressure of the chamber was $5\text{--}10 \times 10^{-10}$ Torr and 1–2 orders of magnitude lower inside the shield. Mixtures of hydrogen peroxide and water were grown by vapor deposition on the mirror gold electrode of a quartz-crystal microbalance (QCM) that measures accurately the mass deposited per unit area, which can be converted to film column density (molecules cm^{-2} or thickness if the density is known) [Sack and Baragiola, 1993]. For most of these experiments, we used two separate gas dosers to control the deposition flux of each molecule; water was deposited at 47.5° from the surface normal, while H_2O_2 was deposited at 2.5° from the surface normal. Films were grown between 16 and 160 K depending on the desired phase of the film. The doser and manifold where hydrogen peroxide was produced were made of glass to prevent significant decomposition of this reactive molecule, which allowed us to obtain a purity (mole fraction) >0.97 M H_2O_2 by vacuum distillation of a 50% commercial grade H_2O_2 solution (M. J. Loeffler *et al.*, manuscript in preparation, 2005). Since the microbalance gives the total mass deposited per unit area rather than film thickness (which depends on density), we report the column densities in the films and use as a unit the monolayer, defined here as $1 \text{ ML} = 10^{15}$ molecules cm^{-2} . The specular infrared reflectance of the films on the gold mirror was measured at an incident angle of 35° with a Thermo-Nicolet Nexus 670 Fourier Transform infrared spectrometer at 2-cm^{-1} resolution. All other methods for quantification of our infrared spectra are detailed by Loeffler *et al.* [2005].

3. Results

3.1. A Comparison of H_2O_2 in Different Environments

[5] Figure 1 shows spectra for H_2O_2 in a variety of environments. Initially, we grew 870 ML of hydrogen peroxide by vapor deposition at a rate of 0.4 ML/s at 110 K (Figure 1, a). At this temperature, molecular mobility is negligibly low, and the structure of the film is amorphous [Giguere and Harvey, 1959]. To create crystalline H_2O_2 the amorphous film was taken to 140 K and held there for 10–15 minutes; it was then cooled back to 110 K (Figure 1, b) to compare to the amorphous spectrum at the same temperature. To produce H_2O_2 isolated in water we grew films at 110 K with simultaneous deposition rates of 0.037 ML/s for H_2O_2 and 0.65 ML/s for H_2O to a total of 69 ML of H_2O_2 cm^{-2} and 10^3 ML of H_2O (Figure 1, c). To simulate pure H_2O_2 precipitates or inclusions we grew a film with highly concentrated regions of H_2O_2 at 110 K by depositing ~ 100 ML of pure water alternated with 10 ML layers of

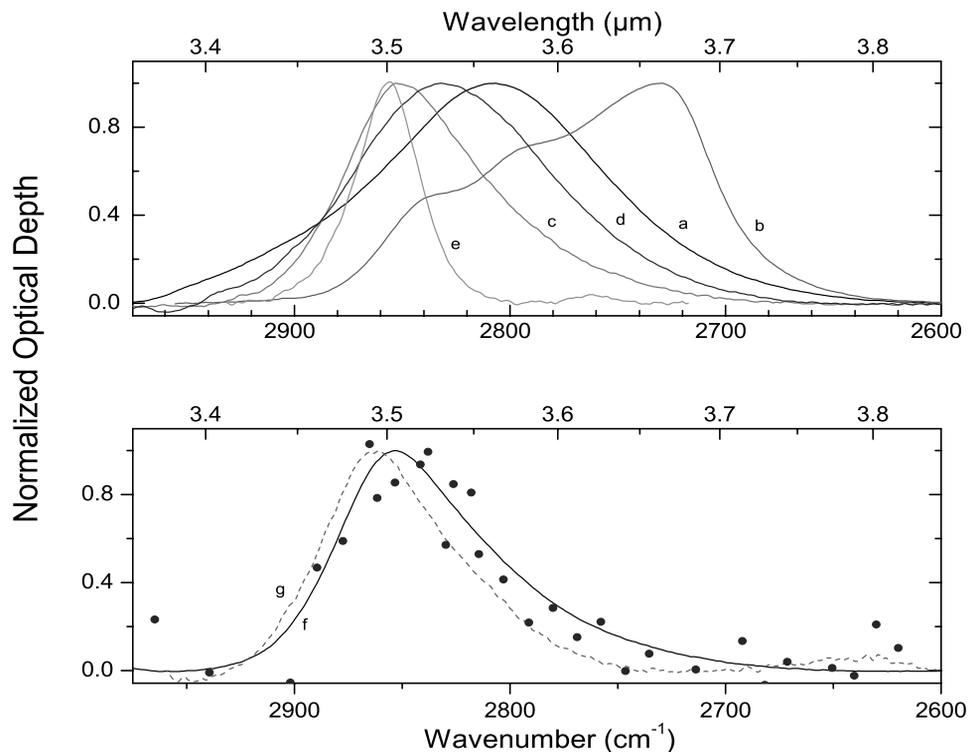


Figure 1. Laboratory measurements of the 3.5 μm infrared absorption band of H_2O_2 in different environments: a, pure (>97%) amorphous at 110 K; b, pure (>97%) crystalline at 110 K; c, 6.5% H_2O_2 dispersed in water ice grown at 110 K; d, layered film with alternate 100 ML of water and 10 ML layers of H_2O_2 at 110 K, total concentration 7% H_2O_2 ; e, crystalline mixture of 3% H_2O_2 in water ice at 110 K; f, 2.5% H_2O_2 disperse in ice grown at 80 K; g, 0.14 % H_2O_2 produced by ion irradiation of pure amorphous water ice at 80 K. The dotted line is a baseline subtracted spectrum of the 3.5 μm band observed by *Carlson et al.* [1999] on Europa. See color version of this figure in the HTML.

H_2O_2 to a total of 100 ML of H_2O_2 and 1300 ML of water (Figure 1, d). Finally, we grew a crystalline mixture at 158 K, composed of ~ 600 ML of H_2O and ~ 20 ML of H_2O_2 , and cooled it to 110 K for comparison (Figure 1, e). Table 1 gives band positions and widths for the 3.5 μm band resulting from these different experiments.

[6] In addition to the measurements discussed above, we have also measured the 3.5 μm absorption feature of H_2O_2 isolated in water at 80 K (Figure 1, f), finding that its shape

and position is essentially the same as it is at 110 K (see Table 1). We also find that the absorption band of H_2O_2 molecules isolated in water (Figure 1, c and 1, f) agree, within experimental uncertainties, with the band of hydrogen peroxide produced by 100 keV H^+ irradiation of water

Table 1. Band Positions of H_2O_2 in Different Environments

Type of Film	T, K	Band Position		FWHM, cm^{-1}
		cm^{-1}	μm	
Amorphous	110	2807.5(4)	3.562(5)	124
Crystalline	110	2730(4)	3.663(5)	122
		2789(10)	3.58(1)	
		2833(10)	3.53(1)	
Crystalline mixture (3% H_2O_2)	110	2855.6(2)	3.502(2.5)	33
Disperse (6.5% H_2O_2)	16	2853.2(2)	3.505(2.5)	74
Disperse (2.5% H_2O_2)	80	2853.0(2)	3.505(2.5)	71
Disperse (6.5% H_2O_2)	110	2852.5(2)	3.506(2.5)	75
In 10 ML layers (7% H_2O_2)	110	2832.1(2)	3.531(2.5)	106
In 10 ML layers annealed 14 h at 128 K	110	2841.2(2)	3.520(2.5)	89
From radiolysis of amorphous water ice (0.14% H_2O_2)	80	2862(1.5)	3.494(2)	70
On Europa	85–130	2857(12)	3.500(15)	72 ^a

^aFrom an improved fit to the data published by *Carlson et al.* [1999], provided by R.W. Carlson. The numbers in parentheses are the uncertainties in the least-significant digits.

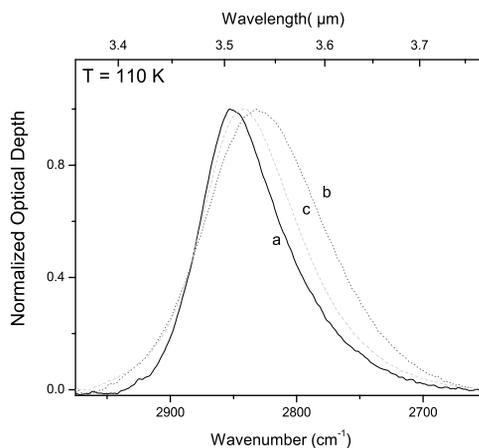


Figure 2. A comparison of infrared spectra of dispersed H_2O_2 and layered films: a, grown disperse at 110 K with 6.5% H_2O_2 (same as Figure 1, c); b, layered film with alternate 100 ML of water and 10 ML layers of H_2O_2 at 110 K, total concentration 7% H_2O_2 (same as Figure 1, d); c, film b, held for 14 hours at 128 K. See color version of this figure in the HTML.

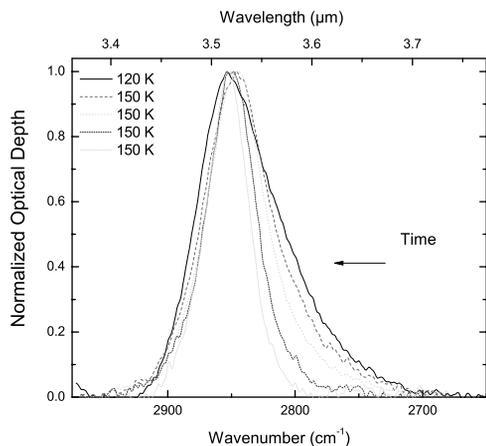


Figure 3. Evolution of the 3.5 μm band for a 6.5% $\text{H}_2\text{O}_2\text{:H}_2\text{O}$ film grown at 16 K, annealed to 150 K, and held at that temperature. See color version of this figure in the HTML.

(Figure 1, g) measured by *Loeffler et al.* [2005] and with that observed on Europa.

3.2. Annealing to Temperatures Relevant to Europa

[7] Even though the spectra of both isolated (Figure 1, c and 1, f) and radiolyzed H_2O_2 (Figure 1, g) are close matches to 3.5 μm absorption band on Europa, one or both of these states may change into a more energetically favorable one due to diffusion that may be activated at the higher temperatures that can be reached on the icy satellite. To investigate this possibility, we measured the evolution of the infrared spectra of films of H_2O_2 in water ice as we warmed them to temperatures (125–128 K) close to the highest measured on Europa, and held the temperature constant for 14 hours. For the layered film (Figure 1, d and 2, b) the absorption maximum of the 3.5 μm band shifted towards the position of the isolated mixture (Figures 1, c, 1, f, and 2, a), increased in intensity, and became slightly more asymmetric (as shown in Figure 2, c), indicating that the aggregated H_2O_2 diffuses into H_2O at these temperatures. In the end, the annealed layered film (Figure 2, c) had an absorption band that was quite close to that of the water film containing isolated H_2O_2 , and continued to shift up in frequency at a slow rate.

4. Discussion and Astronomical Implications

4.1. Previous Experiments on Mixtures

[8] Previous experimental studies on ice mixtures of water and hydrogen peroxide [*Giguere and Harvey*, 1959; *Gurman et al.*, 1967] support the equilibrium phase diagrams for mixtures determined previously [*Foley and Giguere*, 1951]. Such diagrams can be very useful for understanding the lowest energy states of mixtures, however, they should be used with caution at the low temperatures of Europa, because equilibrium may not be achieved due to the lack of significant diffusion. The phase diagrams indicate that when mixtures are warmed up and can approach equilibrium, there is a competition between the formation of three phases: water ice, H_2O_2 , and the $\text{H}_2\text{O}_2\bullet 2\text{H}_2\text{O}$ dihydrate compound. A high con-

centration of water ice yields H_2O and $\text{H}_2\text{O}_2\bullet 2\text{H}_2\text{O}$, while high concentrations of hydrogen peroxide result in pure H_2O_2 and dihydrate phases. The precipitation of phases upon warming an amorphous mixture to ~ 194 K (where it crystallized) was observed by *Gurman et al.* [1967] through photolysis experiments. Although these authors concluded that such phases are pure water and pure hydrogen peroxide, a comparison of their experiment to the phase diagram for H_2O and H_2O_2 mixtures and to infrared spectroscopy results [*Giguere and Harvey*, 1959] indicates that the precipitated phases are instead water and $\text{H}_2\text{O}_2\bullet 2\text{H}_2\text{O}$.

4.2. Application to Europa

[9] Infrared spectroscopy shows that most of the different states of H_2O_2 in H_2O can be distinguished by the shape and position of their 3.5 μm absorption (Figure 1). The spectra shows that layered films of H_2O_2 and H_2O tend to mix at temperatures relevant to Europa ~ 125 K (Figure 2), as expected from the onset of molecular diffusion in ice. This result is consistent with the expectations based on the phase diagram, which states that for mixtures with $\text{H}_2\text{O}_2\text{:H}_2\text{O}$ ratios smaller than 1:2, diffusion will allow H_2O_2 molecules to aggregate with pairs of H_2O , forming the dihydrate $\text{H}_2\text{O}_2\bullet 2\text{H}_2\text{O}$, rather than forming pure hydrogen peroxide precipitates.

[10] At lower temperatures, where diffusion is not significant, molecular reorientation could still be possible and allow the formation of trimers $\text{H}_2\text{O}-\text{H}_2\text{O}_2-\text{H}_2\text{O}$ from H_2O_2 isolated in amorphous water ice. These trimers are the nuclei that at higher temperatures coalesce into the stoichiometric $\text{H}_2\text{O}_2\bullet 2\text{H}_2\text{O}$ phase. An interesting question is whether such nucleation occurs at European temperatures; the answer from our measurements is that, either the trimer does not precipitate efficiently at 128 K or that its infrared signature does not differ from that of the precipitate. Now, *Gurman et al.* [1967] noticed that the photochemical rates of dilute mixtures of H_2O_2 in H_2O are very different for amorphous and for crystalline mixtures, which they attributed to the formation of precipitates in the crystalline mixture. This could imply that high temperatures, where crystallization can occur, are needed to grow precipitates efficiently. In our experiments we found that holding dilute mixtures at 128 K for 14 hours produced no signs of crystallization, noting that these laboratory time scales here are pertinent to Europa, where H_2O_2 molecules have a lifetime of less than 20 days (*Loeffler et al.*, submitted manuscript, 2005). On the other hand, crystallization occurred in less than 1 hour (Figure 3) at 150 K.

[11] In light of both the previous and new laboratory measurements presented here, it appears that precipitation of hydrogen peroxide, proposed by *Cooper et al.* [2003], will not occur on Europa, because the H_2O_2 concentration is too low. Furthermore, precipitation of the $\text{H}_2\text{O}_2\bullet 2\text{H}_2\text{O}$ trimer is unlikely, because the temperature is too low for diffusion and H_2O_2 is destroyed on relatively short time scales.

[12] In conclusion, the hydrogen peroxide on Europa (and potentially on colder icy satellites such as those around Saturn and beyond) is in the form of dispersed $\text{H}_2\text{O}_2\bullet 2\text{H}_2\text{O}$ trimers. If H_2O_2 were produced on bodies which can reach

higher temperatures than Europa, say ~ 150 K, such as Ganymede and Callisto, then hydrogen peroxide would quickly precipitate and crystallize into the dihydrate. This phase has a different infrared signature, but unfortunately although the existence of H_2O_2 on these satellites is suggested by the ultraviolet reflectance [Hendrix *et al.*, 1999], the $3.5 \mu\text{m}$ infrared signature has yet to be identified on Ganymede or Callisto.

[13] **Acknowledgments.** We acknowledge support for the NASA Cosmochemistry Program and from the Virginia Space Grant Consortium. We thank W. H. Shoup for constructing the glass manifold used in these experiments, A. Volkov for his help in translating the Gurman *et al.* [1967] article, W. A. Jesser for useful discussions, U. Raut and B. D. Teolis for their assistance in the laboratory, and R. W. Carlson for his useful comments and for providing us with the H_2O_2 band on Europa after background subtraction improved over that published by Carlson *et al.* [1999].

References

- Baragiola, R. A., M. J. Loeffler, U. Raut, R. A. Vidal, and C. D. Wilson (2005), Laboratory studies of radiation effects in water ice in the outer solar system, *Radiat. Phys. Chem.*, *72*, 187–191.
- Carlson, R. W., et al. (1999), Hydrogen peroxide on the surface of Europa, *Science*, *283*, 2062–2064.
- Chyba, C. F., and K. P. Hand (2001), Planetary science: Enhanced: Life without photosynthesis, *Science*, *292*, 2026–2027.
- Cooper, P. D., R. E. Johnson, and T. I. Quickenden (2003), Hydrogen peroxide dimers and the production of O_2 in icy satellite surfaces, *Icarus*, *166*, 444–446.
- Foley, W. T., and P. A. Giguere (1951), Hydrogen peroxide and its analogues, II. Phase equilibrium in the system hydrogen peroxide–water, *Can. J. Chem.*, *29*, 123–132.
- Giguere, P. A., and K. B. Harvey (1959), An infrared study of hydrogen bonding in solid H_2O_2 and H_2O - H_2O_2 mixtures, *J. Mol. Spectrosc.*, *3*, 36–45.
- Gomis, O., G. Leto, and G. Strazzulla (2004a), Hydrogen peroxide production by ion irradiation of thin water ice films, *Astron. Astrophys.*, *420*, 405–410.
- Gomis, O., M. A. Satorre, G. Strazzulla, and G. Leto (2004b), Hydrogen peroxide formation by ion implantation in water ice and its relevance to the Galilean satellites, *Planet. Space Sci.*, *52*, 371–378.
- Gurman, V. S., V. A. Batyuk, and G. B. Sergeev (1967), Photolysis of frozen dilute solution of hydrogen peroxide in water (in Russian), *Kinet. Katal.*, *8*, 527–531.
- Hendrix, A. R., C. A. Barth, A. I. F. Stewart, C. W. Hord, and A. L. Lane (1999), Hydrogen peroxide on the icy Galilean satellites, *Proc. Lunar Planet. Sci. Conf.*, *30th*, 2043.
- Loeffler, M. J., U. Raut, R. A. Vidal, R. A. Baragiola, and R. W. Carlson (2005), Synthesis of hydrogen peroxide in water ice by ion irradiation, *Icarus*, in press.
- Moore, M. H., and R. L. Hudson (2000), IR detection of H_2O_2 at 80 K in ion-irradiated laboratory ices relevant to Europa, *Icarus*, *145*, 282–288.
- Sack, N. J., and R. A. Baragiola (1993), Sublimation of vapor-deposited water ice below 170 K, and its dependence on growth conditions, *Phys. Rev. B*, *48*, 9973–9978.

R. A. Baragiola and M. J. Loeffler, Laboratory for Atomic and Surface Physics, University of Virginia, Thornton Hall, Charlottesville, VA 22904–4238, USA. (mjl8r@virginia.edu)