The state of hydrogen peroxide on Europa

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[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 H₂O₂•2H₂O. If the temperature on an icy body containing H₂O₂ approaches 150 K, as on Ganymede, the trimers aggregate into precipitates of crystalline dihydrate H₂O₂•2H₂O. 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 H₂O₂ 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 H₂O₂ exists in crystalline inclusions, with potential consequences for O₂ 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 surfaced 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 5–10 × 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 H₂O₂ 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 H₂O₂ by vacuum distillation of a 50% commercial grade H₂O₂ 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 ML = 10¹⁵ 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 H₂O₂ in Different Environments

[5] Figure 1 shows spectra for H₂O₂ 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 H₂O₂ 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 H₂O₂ isolated in water we grew films at 110 K with simultaneous deposition rates of 0.037 ML/s for H₂O₂ and 0.65 ML/s for H₂O to a total of 69 ML of H₂O₂ cm⁻² and 10³ ML of H₂O (Figure 1, c). To simulate pure H₂O₂ precipitates or inclusions we grew a film with highly concentrated regions of H₂O₂ at 110 K by depositing ~100 ML of pure water alternated with 10 ML layers of...
H$_2$O$_2$ to a total of 100 ML of H$_2$O and 1300 ML of water (Figure 1, d). Finally, we grew a crystalline mixture at 158 K, composed of 6.5% H$_2$O$_2$ dispersed in water ice grown at 110 K; d, layered film with alternate 100 ML of water and 10 ML layers of H$_2$O$_2$ at 110 K, total concentration 7% H$_2$O$_2$; e, crystalline mixture of 3% H$_2$O$_2$ in water ice at 110 K; f, 2.5% H$_2$O$_2$ dispersed in ice grown at 80 K; g, 0.14% H$_2$O$_2$ produced by ion irradiation of pure amorphous water ice at 80 K. The dotted line is a baseline subtracted spectrum of the 3.5 $\mu$m band observed by Carlson et al. [1999] on Europa. See color version of this figure in the HTML.

Table 1 gives band positions and widths for the 3.5 $\mu$m band resulting from these different experiments.

In addition to the measurements discussed above, we have also measured the 3.5 $\mu$m absorption feature of H$_2$O$_2$ 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$_2$O$_2$ 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

![Figure 1](image1.png)

Figure 1. Laboratory measurements of the 3.5 $\mu$m infrared absorption band of H$_2$O$_2$ in different environments: a, pure (>97%) amorphous at 110 K; b, pure (>97%) crystalline at 110 K; c, 6.5% H$_2$O$_2$ dispersed in water ice grown at 110 K; d, layered film with alternate 100 ML of water and 10 ML layers of H$_2$O$_2$ at 110 K, total concentration 7% H$_2$O$_2$; e, crystalline mixture of 3% H$_2$O$_2$ in water ice at 110 K; f, 2.5% H$_2$O$_2$ dispersed in ice grown at 80 K; g, 0.14% H$_2$O$_2$ produced by ion irradiation of pure amorphous water ice at 80 K. The dotted line is a baseline subtracted spectrum of the 3.5 $\mu$m band observed by Carlson et al. [1999] on Europa. See color version of this figure in the HTML.

![Table 1](image2.png)

Table 1. Band Positions of H$_2$O$_2$ in Different Environments

<table>
<thead>
<tr>
<th>Type of Film</th>
<th>T, K</th>
<th>Band Position cm$^{-1}$</th>
<th>FWHM, $\mu$m</th>
<th>FWHM, cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td>110</td>
<td>2807.5(4)</td>
<td>3.562(5)</td>
<td>124</td>
</tr>
<tr>
<td>Crystalline</td>
<td>110</td>
<td>2730(4)</td>
<td>3.663(5)</td>
<td>122</td>
</tr>
<tr>
<td>Crystalline mixture (3% H$_2$O$_2$)</td>
<td>110</td>
<td>2855.6(2)</td>
<td>3.502(2.5)</td>
<td>33</td>
</tr>
<tr>
<td>Disperse (6.5% H$_2$O$_2$)</td>
<td>16</td>
<td>2853.2(2)</td>
<td>3.505(2.5)</td>
<td>74</td>
</tr>
<tr>
<td>Disperse (2.5% H$_2$O$_2$)</td>
<td>80</td>
<td>2853.0(2)</td>
<td>3.505(2.5)</td>
<td>71</td>
</tr>
<tr>
<td>Disperse (6.5% H$_2$O$_2$)</td>
<td>110</td>
<td>2852.5(2)</td>
<td>3.506(2.5)</td>
<td>75</td>
</tr>
<tr>
<td>In 10 ML layers (7% H$_2$O$_2$)</td>
<td>110</td>
<td>2832.1(2)</td>
<td>3.531(2.5)</td>
<td>106</td>
</tr>
<tr>
<td>In 10 ML layers annealed 14 h at 128 K</td>
<td>110</td>
<td>2841.2(2)</td>
<td>3.520(2.5)</td>
<td>89</td>
</tr>
<tr>
<td>From radiolysis of amorphous water ice (0.14% H$_2$O$_2$)</td>
<td>80</td>
<td>2862(1.5)</td>
<td>3.494(2)</td>
<td>70</td>
</tr>
<tr>
<td>On Europa</td>
<td>85–130</td>
<td>2857(12)</td>
<td>3.500(15)</td>
<td>72*</td>
</tr>
</tbody>
</table>

*From 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](image3.png)

Figure 2. A comparison of infrared spectra of dispersed H$_2$O$_2$ and layered films: a, grown disperse at 110 K with 6.5% H$_2$O$_2$ (same as Figure 1, c); b, layered film with alternate 100 ML of water and 10 ML layers of H$_2$O$_2$ at 110 K, total concentration 7% H$_2$O$_2$ (same as Figure 1, d); c, film b, held for 14 hours at 128 K. See color version of this figure in the HTML.
and 1, f) and radiolyzed H\textsubscript{2}O\textsubscript{2} (Figure 1, g) are close between the formation of three phases: water ice, H\textsubscript{2}O\textsubscript{2}, and H\textsubscript{2}O\textsubscript{2} dihydrate compound. A high concentration of water ice yields H\textsubscript{2}O and H\textsubscript{2}O\textsubscript{2}•2H\textsubscript{2}O, while high concentrations of hydrogen peroxide result in pure H\textsubscript{2}O\textsubscript{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\textsubscript{2}O and H\textsubscript{2}O\textsubscript{2} mixtures and to infrared spectroscopy results [Giguere and Harvey, 1959] indicates that the precipitated phases are instead water and H\textsubscript{2}O\textsubscript{2}•2H\textsubscript{2}O.

4.2. Application to Europa

[9] Infrared spectroscopy shows that most of the different states of H\textsubscript{2}O\textsubscript{2} in H\textsubscript{2}O can be distinguished by the shape and position of their 3.5 \(\mu\)m absorption (Figure 1). The spectra shows that layered films of H\textsubscript{2}O\textsubscript{2} and H\textsubscript{2}O 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 H\textsubscript{2}O\textsubscript{2}:H\textsubscript{2}O ratios smaller than 1:2, diffusion will allow H\textsubscript{2}O\textsubscript{2} molecules to aggregate with pairs of H\textsubscript{2}O, forming the dihydrate H\textsubscript{2}O\textsubscript{2}•2H\textsubscript{2}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 H\textsubscript{2}O•H\textsubscript{2}O\textsubscript{2}•H\textsubscript{2}O from H\textsubscript{2}O\textsubscript{2} isolated in amorphous water ice. These trimers are the nuclei at higher temperatures coalesce into the stoichiometric H\textsubscript{2}O\textsubscript{2}•2H\textsubscript{2}O phase. An interesting question is whether such nucleation occurs at Europa 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\textsubscript{2}O\textsubscript{2} in H\textsubscript{2}O 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\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{2} concentration is too low. Furthermore, precipitation of the H\textsubscript{2}O\textsubscript{2}•2H\textsubscript{2}O trimer is unlikely, because the temperature is too low for diffusion and H\textsubscript{2}O\textsubscript{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 H\textsubscript{2}O\textsubscript{2}•2H\textsubscript{2}O trimers. If H\textsubscript{2}O\textsubscript{2} were produced on bodies which can reach
higher temperatures than Europa, say \(\sim 150 \text{ K}\), 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 \(\text{H}_2\text{O}_2\) 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 \(\text{H}_2\text{O}_2\) band on Europa after background subtraction improved over that published by Carlson et al. [1999].

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