Isothermal Decomposition of Hydrogen Peroxide Dihydrate

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ABSTRACT: We present a new method of growing pure solid hydrogen peroxide in an ultra high vacuum environment and apply it to determine thermal stability of the dihydrate compound that forms when water and hydrogen peroxide are mixed at low temperatures. Using infrared spectroscopy and thermogravimetric analysis, we quantified the isothermal decomposition of the metastable dihydrate at 151.6 K. This decomposition occurs by fractional distillation through the preferential sublimation of water, which leads to the formation of pure hydrogen peroxide. The results imply that in an astronomical environment where condensed mixtures of H_2O_2 and H_2O are shielded from radiolytic decomposition and warmed to temperatures where sublimation is significant, highly concentrated or even pure hydrogen peroxide may form.
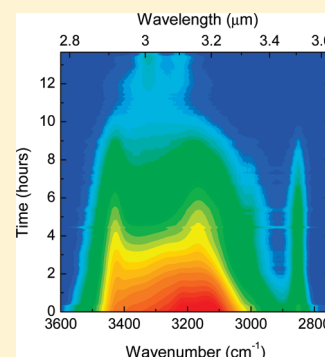
INTRODUCTION

Solid hydrogen peroxide is interesting as one of the simplest molecular solids, and for its role in cold astrophysical environments and in the upper atmosphere of the Earth.[1] H_2O_2 diluted in water ice has been discovered on the surface of one of Jupiter's icy moons, Europa.[2] It was proposed to exist also on Enceladus,[3] but later laboratory experiments did not confirm the interpretation of the infrared absorption band used for the assignment.[4] In addition, H_2O_2 has also been detected in the atmosphere of Mars[5] and is predicted to exist in the interstellar medium,[6] though it has not been observed yet.

Because the primary mechanism for hydrogen peroxide formation in space is radiolysis of water,[7] it is important to know the properties of solid $H_2O_2-H_2O$ solutions. Early X-ray diffraction measurements[8] showed that an intermediate compound phase exists in crystalline mixtures, the dihydrate $H_2O_2 \cdot 2H_2O$. This compound was also identified in the determination of the equilibrium phase diagram of water—hydrogen peroxide,[9] indicating that when solutions approach equilibrium, there is a competition between the formation of three phases: water ice, H_2O_2, and the dihydrate. This dihydrate phase can be identified using infrared spectroscopy.[10] In our previous experiments,[10b,11] the temperatures at which the dihydrate formed (140—200 K) were similar to those on the warmer icy satellites of Jupiter. This prompted us to study more quantitatively how the dihydrate forms and decomposes in vacuum and to advance understanding of the underlying physicochemical processes.

The scarcity of studies on either pure solid H_2O_2 or solid aqueous solutions in a vacuum environment is due partly to the difficulty in containing this reactive molecule and partly because high concentrations of H_2O_2 are no longer commercially available. Thus, to obtain pure H_2O_2 or even high concentrations of H_2O_2, the sample has to be prepared from the more dilute solutions or from the decomposition of urea hydrogen peroxide in a vacuum.[12] In addition to this obstacle, another problem arises from the need to study hydrogen peroxide in ultra high vacuum (UHV) conditions. The hydrogen peroxide molecule efficiently decomposes when it contacts any surface of the stainless steel vacuum chamber and of the gas-handling manifold. To avoid this problem in our studies of pure solid hydrogen peroxide in UHV, we have used two different methods to distill hydrogen peroxide from a dilute aqueous solution. Both techniques rely on the lower vapor pressures of H_2O_2 than of H_2O: either we evaporate the water after the sample is deposited from a gas mixture,[10b] or we pump the water out of the liquid $H_2O_2-H_2O$ solution before it is deposited, while it is in an ampule that is connected to the gas manifold.[4,13] The latter method only works if the manifold is made of a nonreactive material such as glass, while the former can work with any type of gas manifold.

In this research reported here, we utilized the latter technique to place precise amounts of hydrogen peroxide in a mixture of water, which allowed us to monitor compositional changes in our sample using infrared spectroscopy and microbalance gravimetry during isothermal sublimation. We show how the sublimation rates depend on the interaction of water and hydrogen peroxide and determine whether the dihydrate compound, which has its own crystal structure and IR signature, evaporates congruently.
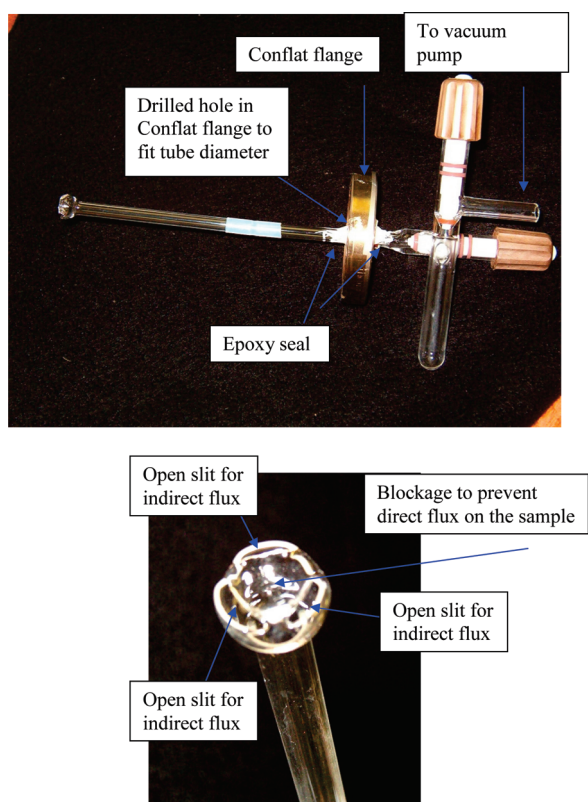
Figure 1. Top: glass manifold attached to conflat flange. Bottom: close-up view of the tip of the doser.

■ EXPERIMENTAL SETUP

All experiments were performed with a radiation-shielded cryostat within a stainless steel vacuum chamber.[10b] The base pressure of the chamber was ~10^{-10} Torr and 1−2 orders of magnitude lower inside the shield. Films were grown by vapor deposition on an optically flat gold mirror electrode of a 6 MHz quartz-crystal microbalance (QCM). The areal mass Q (mass/unit area) of the films was determined 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,[14] corresponding to 0.04 monlayers (ML) for water ice, where 1 ML = 10^{15} molecules/cm^2. The measured Q can be converted to film column density η (molecules/cm^2) if the film composition is known and converted to thickness if the mass density is known.[14]

Previously, to obtain pure H_2O_2, we would grow a mixture of water and hydrogen peroxide at high temperatures and then distill out the water.[10b] While the method was effective in producing films of purity >97%, it did not give us the ability to mix known quantities of H_2O_2 with water, because we purified our sample after it had been deposited. To obtain pure H_2O_2 *before* we deposited the sample, we designed a glass doser that could be attached to our chamber (Figure 1). It was made of glass to minimize the catalytic decomposition of H_2O_2 that occurs readily on metal surfaces. In an attempt to remove any residual impurities in the surface glass, we bathed the glass components in a 1:1 mixture of water and nitric acid for 24 h and rinsed in a water bath for another 24 h before we attached the doser to the vacuum system. The doser was attached to the chamber through a hole in a blank 2.75 in. Conflat flange and sealed with Torr Seal, an epoxy suitable for ultrahigh vacuum. The valves of the glass ampule are
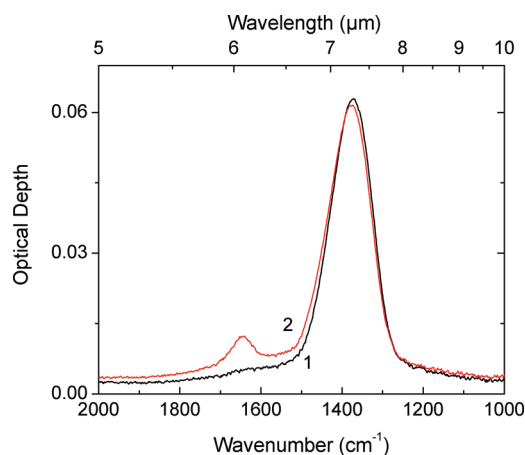

Figure 2. Infrared reflectance spectra of 49 μg/cm^2 of H_2O_2 grown at 110 K with the glass doser: (1) "pure" hydrogen peroxide film and (2) a film with 10% water contamination.

made of Teflon, while the seals were made of Viton O-rings, which we coated with 25-S halocarbon vacuum grease that is stable against strong oxidizers, such as H_2O_2 or O_3. In addition, to eliminate the possibility of deposition of clusters that may be present in the incident vapor flux, the tip of the doser (Figure 1 bottom) had an obstruction to ensure the vapor collided with the doser walls before entering the chamber.

To prepare a solid sample of H_2O_2, we distilled an H_2O_2−H_2O aqueous solution of 50 wt % H_2O_2 (Fischer Scientific) in the glass ampule with a dry pump for 1−2 h; the actual time depended on the amount of liquid placed in the manifold. We determined the purity of our H_2O_2 samples by comparing the band area of the 1650 cm^{-1} H_2O absorption band in our purest samples with those of another sample (grown to the same thickness) that had a known column density of water (10% by number) added in from a separate gas doser (Figure 2). From this measurement we found that the highest purity (99%) hydrogen peroxide can be obtained by pumping the solution until most of the liquid is gone; on average the purity was greater than 97%. We note that if H_2O_2 is left in the manifold for a few days, then it will decompose into water and oxygen gas, but generally leaving it for ~12 h caused little decomposition (~5% that could easily be pumped away).

We deposited water−peroxide mixtures in known concentrations by supplying each molecule through its own dedicated doser. We began by depositing water at a constant rate measured with the microbalance. Next, while continuing to monitor the deposition rate, we leaked in H_2O_2. At the end of growth, we closed the leak valve of H_2O_2 and verified that the water deposition rate had not changed. By subtracting out the amount of water deposited during deposition of the mixture, we were able to precisely determine the amount of H_2O_2 in our sample, which is a distinct advantage over our previous work.[10b]

Solid films of water and hydrogen peroxide−water mixtures were grown at 151.6 K to a total areal mass of 31 μg/cm.^{2} For the pure water sample, this is equivalent to 1040 ML. To grow the mixture, we codeposited H_2O (0.6 ML/s) and H_2O_2 (0.05 ML/s) to obtain a mixed ice that contained the equivalent of 920 ML of H_2O and 61 ML of H_2O_2. The relatively high deposition temperature not only allows us to explore distillation kinetics but also minimizes the chance that impurities, formed when scattered H_2O_2 reacts with the chamber walls, would not stick on the

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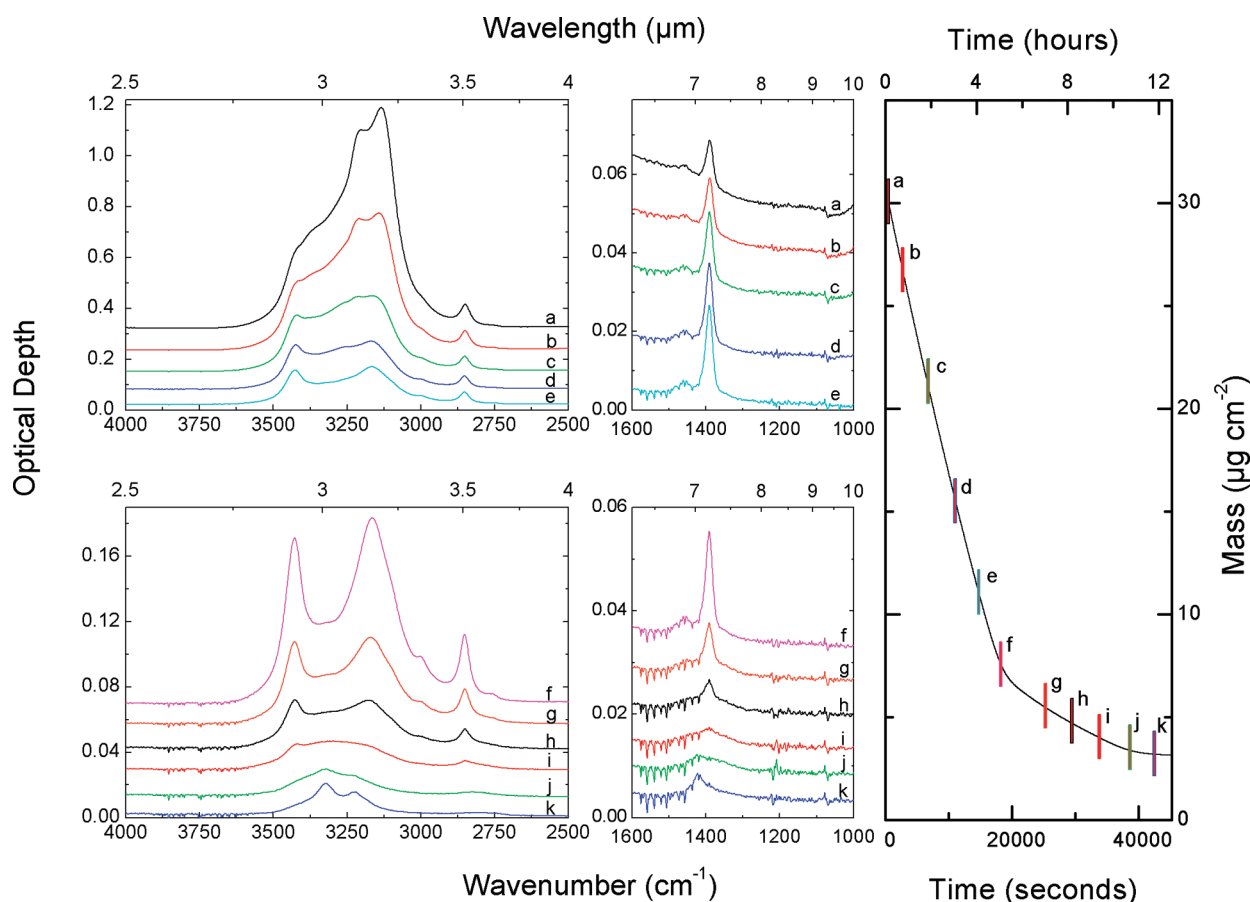dx.doi.org/10.1021/jp200188b |*J. Phys. Chem. A* 2011, 115, 5324–5328

Figure 3. Infrared spectra between 4000 and 2500 cm^{-1} (top and bottom left) and between 1600 and 1000 cm^{-1} (top and bottom middle) of a water−hydrogen peroxide mixture taken as a function of time. In all four panels, letters correspond to (a) 0, (b) 0.78, (c) 1.85, (d) 3.02, (e) 4.10, (f) 5.07, (g) 7.02, (h) 8.19, (i) 9.37, (j) 10.73, and (k) 11.81 h. Right panel: corresponding sample areal mass as a function of time. The vertical lines correspond to times at which infrared spectra were taken.

substrate. For infrared active molecules, such as CO_2, we were able to verify this easily by checking the infrared spectrum of the deposit. However, another likely impurity, O_2, is very difficult to detect in small amounts using IR spectroscopy, but we suspect its presence is also negligible, as after we finished depositing our sample, the mass spectrometer signal for 32 amu drops below the noise level.

The specular 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. The spectra were divided by that from the gold mirror substrate taken before film deposition. The ratios $R(\lambda)$ were then converted to optical depth units, $-\ln R(\lambda)$. Absorption band areas were derived after subtraction of base lines that matched the continuum under the bands.

■ RESULTS AND DISCUSSION

Identification of the Compound. To monitor the phase evolution of the mixture of H_2O (920 ML) and H_2O_2 (61 ML) during distillation at 151.6 K, we monitored the change in appearance and position of the sample's infrared absorption features (Figures 3 and 4) in the OH stretching region ($\sim$3300 cm^{-1}) as well as the mass loss measured on our microbalance (Figure 3 right panel and Figure 5). The infrared spectra show that initially,
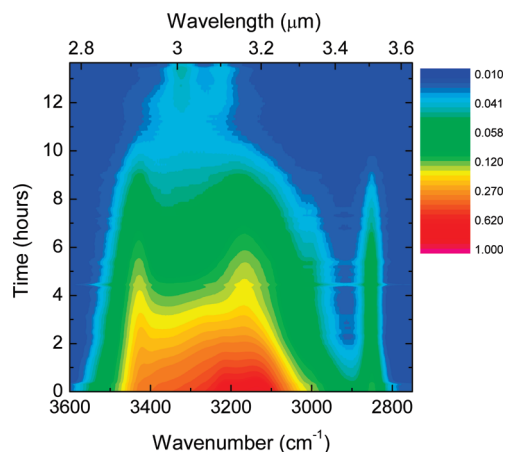

Figure 4. Compilation of all the spectra in the OH stretch region plotted as a function of time. The scale on the right correlates the color to the absorption peak height in optical depth units.

the main absorption feature in our reflectance spectrum is the OH stretching mode of crystalline water ice (centered at $\sim$3200 cm^{-1}). As sublimation progresses, the band for crystalline water ice is attenuated, a new feature appears on the edge of the water ice band at 3425 cm^{-1} (spectrum c of Figure 3), and
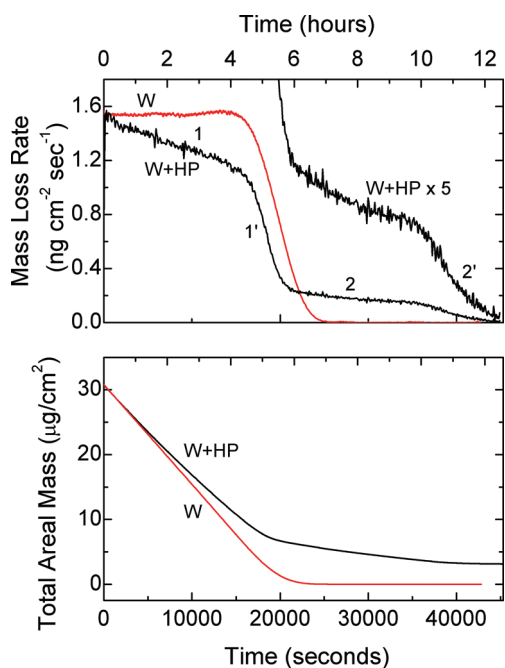
Figure 5. Bottom: evolution of the mass of a pure 1040 ML pure water sample (W) and the mass of a film composed of 920 ML water and 62 ML hydrogen peroxide (W + HP) during isothermal sublimation at 151.6 K. Top: derivative plot, giving the sublimation rates.

the areal mass continues to decrease, although with a slope decreased by ~10% (Figure 5 top). Further distillation (spectrum e and f of Figure 3) shows complete attenuation of the crystalline water ice band, leaving the very distinct bands at 3425 and 3167 cm^{-1}, which we previously attributed to crystalline $H_2O_2 \cdot 2H_2O$.[10b] Interestingly, between the time the spectra f and g in Figure 3 were taken, the sublimation rate slowed by a factor of 6, which is significantly more than the earlier slow rate decrease. Previously, we had suggested that this transition observed in the microbalance indicated that all of the H_2O bound to other H_2O molecules had sublimated from the sample and only water bound in the $H_2O_2 \cdot 2H_2O$ phase remained on our substrate.[10b] Now because we have been able to measure the initial sample composition in these experiments, we confirm that in the region where the sublimation drops by a factor of 6 ($t = 18000-20000$ s), the amount of water left in the sample makes a stoichiometric sample of $H_2O_2 \cdot 2H_2O$.

As sublimation progresses, we observe that although the sublimation rate has slowed, the dihydrate compound is not thermally stable but decomposes as the water bound to the hydrogen peroxide compound sublimates. This change appears in both the decrease in areal mass of our sample (due to water bound to hydrogen peroxide) and more directly in the loss of the infrared signature of the dihydrate, which is replaced by a broad feature (3302 cm^{-1}) due to the OH stretching vibration of amorphous H_2O_2 (spectrum i of Figure 3). At longer times, this feature eventually transitions to that shown in spectrum k of Figure 3, with two distinct absorption bands (3321, 3224 cm^{-1}) due to crystalline hydrogen peroxide. By the time we have pure hydrogen peroxide on the substrate, the sublimation rate has slowed to ~0.007 ng cm^{-2} s^{-1}, which is more than 200 times slower than the initial sublimation rate of our sample and 58 ± 2 ML of crystalline H_2O_2 is left on the substrate. The difference

(3 ± 2 ML) between the amount of H_2O_2 deposited (61 ML) and that remaining in the film is from the slow sublimation of H_2O_2 during distillation.

Model of Sublimation. *Sublimation of Pure H_2O.* We were interested in investigating potential mechanisms that drive the shape in the sublimation rate for water and water–hydrogen peroxide mixtures shown in Figure 5. For simplicity, let us consider the water ice film shown in Figure 5. Initially, the sublimation rate is constant, then it increases slightly by ~2%, and when there is ~270 ML of water left on the substrate the rate begins to decrease to zero over a 3 h period. Figure 6 is a schematic to explain this behavior. Initially, there is no change in the physical characteristics of the sample as the sublimation rate is constant with time. The slight increase in sublimation rate may indicate that there is some increase in surface roughness, which would likely be an indicator of a transition from the multilayer film to more granular one. The sublimation rate ultimately decreases, because as the grains are exposed they are also sublimating and shrinking, which decreases the net surface area by exposing the gold substrate. This picture is similar to that proposed by Lofgren et al.[15] to explain the decrease in the sublimation rate with remaining thickness of crystalline ice films grown on some substrates.

Sublimation of a Mixture of H_2O_2 and H_2O. Before we compare our water result to our mixture experiments, we remind the reader that at 151.6 K, the sublimation measured in Figure 5 is almost entirely due to water and not to hydrogen peroxide. In this figure we see two regions where the sublimation rate has a small slope (0–4 h [region 1] and 6–10 h [region 2]) and two regions where the slope is relatively large (regions 1′ and 2′). Figure 7 is a qualitative schematic drawing to explain this behavior. Initially, the sublimation rate of this mixture is the same as it is for pure water ice, indicating that all the water sublimating from the surface belongs to water bound to water (Figure 7 panel 1). However, immediately the sublimation rate slowly decreases (region 1), indicating that some of the dihydrate compound is replacing pure crystalline water at the surface (Figure 7 panels 2–3), which effectively lowers the exposed surface area of pure water and slows the sublimation rate. This decrease continues
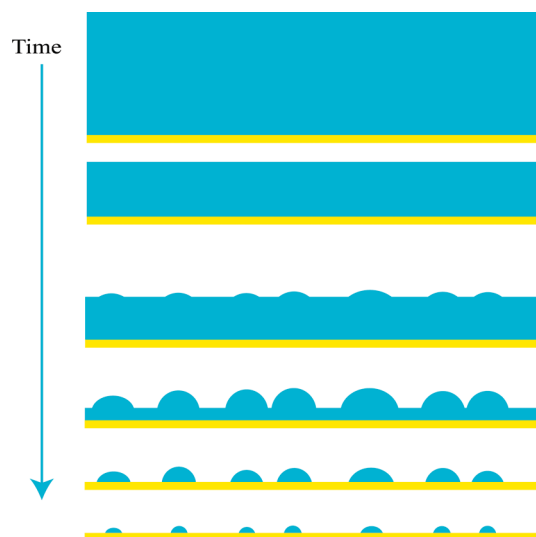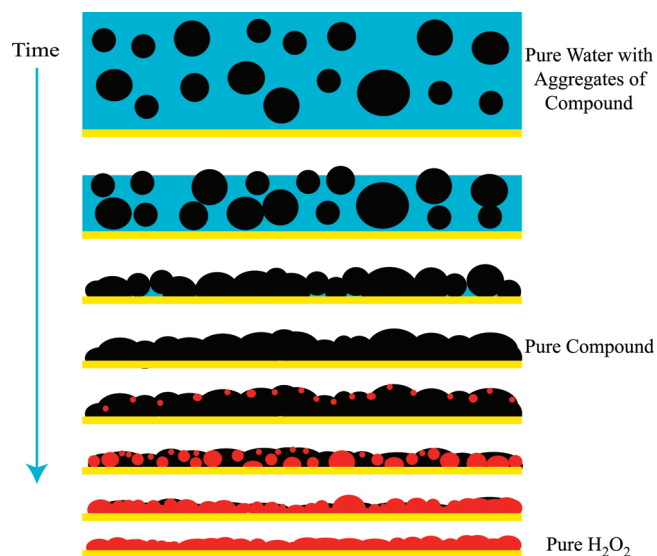

Figure 6. Schematic of the evolution of a pure water sample during sublimation (see text). The yellow is the gold substrate, and blue is water.

Figure 7. Schematic of the evolution of a water—hydrogen peroxide mixture during sublimation (see text). The yellow is the gold substrate, blue is water, black is the dihydrate compound, and red is hydrogen peroxide.

until the pure water precipitates fully sublimate and the first transition region (region $1'$) is reached (Figure 7 panel 4). At the end of this transition region, the sublimation rate does not go to zero as it did for the case of pure water ice; it begins to follow sublimation of water bound to hydrogen peroxide. As this occurs, pure hydrogen peroxide begins to replace water bound to hydrogen peroxide at the surface (Figure 7 panel 5—7), again effectively lowering the surface area of the desorbing water, which causes the sublimation rate to slowly decrease. The final transition region occurs after the water bound in the dihydrate sublimates and hydrogen peroxide has replaced water at the surface (Figure 7 panel 8).

Astrophysical Implications. Any icy object subject to energetic ion or photon irradiation, such as icy satellites or ice-coated planetary or interstellar grains, is expected to contain hydrogen peroxide as a result of radiolysis. At low temperatures, where diffusion is not significant, H_2O and H_2O_2 will be randomly mixed. As the temperatures of the icy object increase above $\sim$110 K, the species will interdiffuse and, eventually, a crystalline mixture of water and the dihydrate compound will form. When the sublimation of water becomes significant, pure aggregates of H_2O_2 will form, which could be detected by infrared spectroscopy. However, if the radiation environment persists, such as for icy satellites immersed in planetary magnetospheres, the process will be suppressed by the quick decomposition of pure H_2O_2 back to water and oxygen.[13b]

CONCLUSIONS

The method for growing pure hydrogen peroxide in a vacuum environment, detailed here, has allowed us to precisely deposit known amounts of water and hydrogen peroxide. We found that the hydrogen peroxide dihydrate is only stable at temperatures where the sublimation rate of water is very small. At higher temperatures the dihydrate is metastable, decomposing by simple sublimation, leaving the hydrogen peroxide behind. This implies that it is possible that, in an astronomical environment where the production and heating of H_2O_2 are decoupled,

preferential evaporation of water may result in highly concentrated and even possibly pure hydrogen peroxide.

REFERENCES

(1) Jackson, A. V.; Hewitt, C. N. *Crit. Rev. Environ. Sci. Technol.* **1999**, *29*, 175–228.

(2) Carlson, R. W.; Anderson, M. S.; Johnson, R. E.; Smythe, W. D.; Hendrix, A. R.; Barth, C. A.; Soderblom, L. A.; Hansen, G. B.; McCord, T. B.; Dalton, J. B.; Clark, R. N.; Shirley, J. H.; Ocampo, A. C.; Matson, D. L. *Science* **1999**, *283*, 2062–2064.

(3) Newman, S. F.; Buratti, B. J.; Jaumann, R.; Bauer, J. M.; Momary, T. W. *Astrophys. J.* **2007**, *670*, L143–L146.

(4) Loeffler, M. J.; Baragiola, R. A. *Astrophys. J.* **2009**, *694*, L92–L94.

(5) Encrenaz, T.; Greathouse, T. K.; Bézard, B.; Atreya, S. K.; Wong, A. S.; Richter, M. J.; Lacy, J. H. *Astron. Astrophys.* **2002**, *396*, 1037–1044.

(6) (a) Hasegawa, T. I.; Herbst, E. *MNRAS* **1993**, *263*, 589. (b) Tielens, A. G. G. M.; Hagen, W. *Astron. Astrophys.* **1982**, *114*, 245–260.

(7) (a) Gomis, O.; Satorre, M. A.; Strazzulla, G.; Leto, G. *Planet. Space Sci.* **2004**, *52*, 371–8. (b) Loeffler, M. J.; Raut, U.; Vidal, R. A.; Baragiola, R. A.; Carlson, R. W. *Icarus* **2006**, *180*, 265–273. (c) Moore, M. H.; Hudson, R. L. *Icarus* **2000**, *145*, 282–8.

(8) Natta, G.; Rigamonti, R. *Gazz. Chim. Ital.* **1936**, *66*, 762.

(9) Foley, W.; Giguere, P. A. *Can. J. Chem.* **1951**, *29*, 123–132.

(10) (a) Giguere, P. A.; Harvey, K. B. *J. Mol. Spectrosc.* **1959**, *3*, 36–45. (b) Loeffler, M. J.; Teolis, B. D.; Baragiola, R. A. *J. Phys. Chem. B* **2006**, *110*, 6911–6915.

(11) Loeffler, M. J.; Baragiola, R. A. *Geophys. Res. Lett.* **2005**, *32*, 17202.

(12) (a) Cooper, P. D.; Moore, M. H.; Hudson, R. L. *J. Phys. Chem. A* **2006**, *110*, 7985–7988. (b) Pettersson, M.; Tuominen, S.; Markku, R. *J. Phys. Chem. A* **1997**, *101*, 1166–1171.

(13) (a) Loeffler, M. J. Space weathering of planetary regoliths. *Ph. D. Dissertation*; University of Virginia: Charlottesville, VA, 2007. (b) Loeffler, M. J.; Teolis, B. D.; Baragiola, R. A. *J. Chem. Phys.* **2006**, *124*, 104702. (c) Loeffler, M. J.; Teolis, B. D.; Baragiola, R. A. *Astrophys. J.* **2006**, *639*, L103–L106.

(14) Sack, N. J.; Baragiola, R. A. *Phys. Rev. B* **1993**, *48*, 9973–8.

(15) Lödfgren, P.; Ahlström, P.; Lausma, J.; Kasemo, B.; Chakarov, D. *Langmuir* **2003**, *19*, 265–274.