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# Descent without Modification? The Thermal Chemistry of $H_2O_2$ on Europa and Other Icy Worlds

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## Abstract

The strong oxidant $H_2O_2$ is known to exist in solid form on Europa and is suspected to exist on several other Solar System worlds at temperatures below 200 K. However, little is known of the thermal chemistry that $H_2O_2$ might induce under these conditions. Here, we report new laboratory results on the reactivity of solid $H_2O_2$ with eight different compounds in $H_2O$-rich ices. Using infrared spectroscopy, we monitored compositional changes in ice mixtures during warming. The compounds $CH_4$ (methane), $C_3H_4$ (propyne), $CH_3OH$ (methanol), and $CH_3CN$ (acetonitrile) were unaltered by the presence of $H_2O_2$ in ices, showing that exposure to either solid $H_2O_2$ or frozen $H_2O + H_2O_2$ at cryogenic temperatures will not oxidize these organics, much less convert them to $CO_2$. This contrasts strongly with the much greater reactivity of organics with $H_2O_2$ at higher temperatures, and particularly in the liquid and gas phases. Of the four inorganic compounds studied, CO, $H_2S$, $NH_3$, and $SO_2$, only the last two reacted in ices containing $H_2O_2$, $NH_3$ making $NH_4^+$ and $SO_2$ making $SO_4^{2-}$ by $H^+$ and $e^-$ transfer, respectively. An important astrobiological conclusion is that formation of surface $H_2O_2$ on Europa and that molecule's downward movement with $H_2O$-ice do not necessarily mean that all organics encountered in icy subsurface regions will be destroyed by $H_2O_2$ oxidation. Key Words: Europa—Laboratory investigations—Icy moons—Infrared spectroscopy—$H_2O_2$ resistance. Astrobiology 15, 453–461.

## 1. Introduction

The possibility of life within and below the surface ices of Europa has been the subject of numerous studies following reports from NASA's Galileo mission, suggesting that liquid water may exist below the surface ice (Carr *et al.*, 1998). Life beneath the ice shell was treated by Gaidos *et al.* (1999), while life within the ice itself, perhaps aided by rising subsurface thermal plumes, was examined by Ruiz *et al.* (2007). Aside from harboring living organisms, it has been speculated that Europa's ices also could contain evidence for subsurface biology in the form of molecular by-products or organic material (Marion *et al.*, 2003) brought upward by convection (Pappalardo *et al.*, 1998). Hand *et al.* (2009) summarized and extended much of the earlier work on Europa astrobiology and described possible scenarios for biogeochemical cycles and the putative subsurface ocean's chemistry.

The persistence and detection of any material within or beneath Europa's ice shell depend strongly on such material's response to the local environment of high-energy radiation, strong oxidants, and low temperatures. In general, one can divide the solid-phase chemistry that is expected to occur on Europa and other icy moons of the Solar System into that which is driven by UV photons ($E \sim 10\,\mathrm{eV}$), by kiloelectronvolt and megaelectronvolt external particle radiation, and by thermal processes at about 30–130 K. The chemistry induced by UV photons is largely confined to surface depths of less than a centimeter, whereas ionizing radiation can alter the chemistry for several meters below the surface (Barnett *et al.*, 2012). Thermal chemistry, which does not rely on an external energy source, will be active at all depths below the surface but may be more important at increasing depths as temperatures rise.

To date, telescopic and spectroscopic observations of Europa have probed its surface composition to depths of at best a few centimeters, with deeper subsurface chemistry remaining hidden. We and others have examined Europa's ice chemistry through extensive photo- and radiation-chemical laboratory experiments on icy materials (Hudson and Moore, 2001; Baratta *et al.*, 2002; Hand and Carlson, 2011; Johnson *et al.*, 2012). However, low-temperature thermal processes relevant to Europa have been studied much less frequently. In a recent paper, we described a thermally driven chemical reaction that can occur at europan temperatures even in the absence of external photons and ionizing radiation (Loeffler and Hudson, 2010). Amorphous ices consisting of $H_2O$ and $SO_2$ showed changes in their IR

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spectra on warming from 50 to 100 K, demonstrating that $H_2O$ and $SO_2$ combined to form $H_3O^+$ and $HSO_3^-$ (bisulfite):

$$2H_2O + SO_2 \rightarrow H_3O^+ + HSO_3^- \tag{1}$$

That this reaction took place in the absence of far-UV photons and ionizing radiation means that it also can occur beneath Europa's surface. Thus, the results we reported can be regarded as ''hidden chemistry'' in that they are changes that will occur at depths greater than those which current instrumentation can probe.

Moore *et al.* (2007b) showed that the irradiation of $H_2O + SO_2$ ice mixtures at 86–132 K with 0.8 MeV protons resulted in oxidation of $SO_2$ into $SO_4^{2-}$ (sulfate). The suspected overall reaction was

$$4H_2O + SO_2 \rightarrow 2H_3O^+ + SO_4^{2-} + H_2 \tag{2}$$

This radiation-driven process is a plausible source of the $SO_4^{2-}$ that was identified on Europa's surface by way of observations from the Galileo spacecraft's Near Infrared Mapping Spectrometer (NIMS) instrument (Carlson *et al.*, 1999b). Since the ion irradiation of $H_2O$-ice already has been reported (Moore and Hudson, 2000) to produce hydrogen peroxide ($H_2O_2$), we suspected that $H_2O_2$ acts as an oxidizing agent for Reaction 2. This, in turn, led to our most recent study (Loeffler and Hudson, 2013), in which we examined whether adding $H_2O_2$ to solids rich in $H_2O$-ice could promote oxidation-reduction chemistry solely by thermal means. In those studies, we found that warming a $H_2O + H_2O_2 + SO_2$ ice from 50 to 130 K initiated the formation of $HSO_3^-$ and $SO_4^{2-}$ through the following reactions:

$$2H_2O + SO_2 \rightarrow H_3O^+ + HSO_3^- \tag{3}$$

$$H_2O_2 + HSO_3^- \rightarrow H_3O^+ + SO_4^{2-} \tag{4}$$

Having shown that $H_2O_2$ can produce sulfate through Reaction 3 followed by Reaction 4, we now consider whether thermally induced $H_2O_2$ reactions also are important in other systems. The ability of frozen $H_2O_2$ to oxidize other molecules is of considerable interest to astrobiologists for several reasons. Greenberg (2010) summarized the case for downward transport of surface ices on Europa. Such movement would transfer surface material toward subsurface liquid and higher temperatures, carrying with it Europa's radiolytically generated $H_2O_2$ (Carlson *et al.*, 1999a). If the $H_2O_2$ reaches the subsurface liquid, then it could significantly alter the chemistry occurring there, as the liquid would become more acidic (Pasek and Greenberg, 2012). Were subsurface oxidation by frozen $H_2O_2$ possible, then it could weaken the argument that organics (*e.g.*, $CH_4$), originating from endogenic or exogenic sources (Zolotov and Kargel, 2009), trapped in ices could be available as nutrients for subsurface life. Conversely, any $SO_2$ that is oxidized by $H_2O_2$ could provide a potential nutrient for subsurface sulfate-reducing bacteria or their extraterrestrial analogues. There also is a connection to planetary protection in our interest in low-temperature $H_2O_2$ reactions. Such reaction chemistry can be used to understand the fate of molecules deposited by accident on icy Solar System surfaces and in subsurface regions that are shielded from direct exposure to UV light or ionizing radiation but which still may contain $H_2O_2$.

In the present study, we examined how $H_2O_2$ in $H_2O$-ice might promote chemical changes in the absence of ionizing radiation and far-UV photons. Our goal was to determine whether relatively simple molecules, specifically those listed in Table 1, can react in the solid state with $H_2O_2$. We point out that for this study we chose a relatively simple reaction system to compare the propensity of hydrogen peroxide to react with a variety of astrobiologically relevant molecules. Including more reactants or adding a known room-temperature catalyst (*e.g.*, metal ions) might have affected our results. Although $H_2O_2$ is a potent room-temperature oxidant, to our knowledge the present study and our previous one (Loeffler and Hudson, 2013) are the first to investigate its oxidizing abilities in ices at temperatures relevant to the outer Solar System. Here, we first briefly review our earlier $SO_2$ work and then extend it and move on to other new results obtained by *in situ* measurements with IR spectroscopy.

## 2. Experimental Methods

Experiments were performed with a cryostat ($T_{min} \sim 10$ K) operating in a stainless steel high-vacuum chamber

TABLE 1. COMPOUNDS COMBINED WITH $H_2O_2$ IN ICES

| *Molecule* | *Seen in the interstellar medium?*[a] | *Seen in cometary comae?*[b] | *Seen on Solar System moons?*[c] | *Which objects in the Solar System?* |
|---|---|---|---|---|
| Inorganic | | | | |
| $SO_2$ | Yes | Yes | Yes | Galilean satellites[d,e] |
| $H_2S$ | Yes | Yes | Yes? | Suspected on Galilean satellites[e] |
| $NH_3$ | Yes | Yes | Yes | Charon[f] and possibly Miranda[g] |
| CO | Yes | Yes | Yes | Triton[h] and Pluto[i] |
| Organic | | | | |
| $CH_4$ | Yes | Yes | Yes | Triton[j] and Pluto[k] |
| $C_3H_4$ | No | No | Yes | Titan's atmosphere[l] |
| $CH_3OH$ | Yes | Yes | No | Centaur object Pholus[m] |
| $CH_3CN$ | Yes | Yes | Yes | Titan's atmosphere[n] |

[a]See Tielens (2013). [b]See Mumma and Charnley (2011). [c]See, for example, Dalton *et al.* (2010), [d]Lane *et al.* (1981), [e]McCord *et al.* (1998), [f]Brown and Calvin (2000), [g]Bauer *et al.* (2002), [h]Cruikshank *et al.* (1993), [i]Owen *et al.* (1993), [j]Cruikshank *et al.* (1976), [k]Cruikshank and Silvaggio (1979), [l]Maguire *et al.*, (1981). [m]Based on modeling of spectra (Merlin *et al.*, 2012) and [n]Marten *et al.* (2002).

($P \sim 1 \times 10^{-7}$ torr) interfaced to an IR spectrometer. Ices were prepared by co-deposition of $H_2O$, $H_2O_2$, and an organic or inorganic molecule, chosen from those listed in Table 1, onto a pre-cooled (10–50 K) gold-coated aluminum mirror (area $\approx 5\,cm^2$) by using three separate pre-calibrated gas lines. Mixtures that contained CO and $CH_4$ were deposited at 10 K, but all other samples were prepared at 50 K. Pure $H_2O_2$ was prepared in a glass manifold as previously described (Loeffler and Baragiola, 2011). During deposition, the increase in the sample's thickness was monitored by interferometry with a diode laser (670 nm), and the deposition was halted when a thickness of about 1.5 $\mu$m was reached.

After deposition of a sample, its IR spectrum was recorded before, during, and after warming at 1 K $min^{-1}$. A closed-cycle helium cryostat and a resistive heater served to maintain ices at the desired temperature within the 10–200 K range studied. Higher temperatures could be reached but were avoided, as they were accompanied by sample loss by sublimation, which complicated the interpretation of our experiments.

Spectra were measured from 7000 to 400 $cm^{-1}$ with a Bruker Vector 22 Fourier transform infrared spectrometer at 2 $cm^{-1}$ resolution and with 200-scan accumulations. To obtain a spectrum, the IR reflectance ($R$) from the ice-coated substrate was divided by the reflectance of the bare metal substrate ($R_0$), taken before ice formation, and then converted to an absorbance-type scale, $-\log(R/R_0)$, for the figures we show in this paper. See the work of Loeffler and Hudson (2010, 2012) for additional experimental details.

Each compound studied was examined in the solid phase mixed with frozen $H_2O_2$, both in the presence and absence of $H_2O$-ice. During experiments, ices were held as long as 20 h at the higher temperatures (*e.g.*, 100–170 K) to check for thermal changes. At the end of each experiment, the sample was warmed to room temperature, but no residual material was observed either visually or through IR spectroscopy.

The sensitivity of our spectrometer to detect the products of a thermally induced reaction under the conditions employed was checked with appropriate background and calibration experiments. For example, when working with CO we sometimes observed a weak $CO_2$ feature before warming with $H_2O_2$ (or $^{13}CO_2$ when $^{13}CO$ was being studied). Blank experiments without $H_2O_2$ present traced this initial $CO_2$ in our samples to low-level $CO_2$ contamination, on the order of 0.002%, in our CO source and a small background contamination in our vacuum system. Possible products, such as $H_2CO$, $CH_3OH$, or $SO_2$, from other reactants have weaker IR absorptions than $CO_2$ but were still strong enough to be easily identified if present. We estimate that these possible products were detectable down to $\sim 1 \times 10^{15}$ molecules $cm^{-2}$ or better, corresponding to a number ratio of $\sim 2 \times 10^{-3}$ ($\sim$0.2%) when compared to the initial reactants. Thus, any nondetection we reported corresponds to an upper limit of these values.

It should be emphasized that the design of our experiments allowed all data to be collected *in situ* at the temperatures of choice. This avoided the need to raise samples to room temperature for chemical analyses. Also, the co-condensation method used to prepare our ices avoided the uncertainties in freezing room-temperature solutions, which will crystallize to give regions of varying $H_2O_2$ concentration in the sample. In short, the value of our results is enhanced both by the way the samples were prepared and by our method of analysis. For recent amino acid work in which similar experimental methods were used, see a study by Gerakines and Hudson (2013).

The reagents and suppliers used were $H_2O_2$ (Sigma-Aldrich, 50% by weight), $SO_2$ (Matheson, 99.98%), $H_2S$ (Matheson, 99.5%), $^{12}CO$ (Matheson, 99.998%), $^{13}CO$ (Sigma-Aldrich, 99% $^{13}C$), $NH_3$ (Matheson, 99.9992%), $CH_4$ (Matheson, 99.999%), $C_3H_4$ (Sigma-Aldrich, 98%), $CH_3OH$ (Sigma-Aldrich, >99.8%), and $CH_3CN$ (Sigma-Aldrich, 99.93%). The water used was triply distilled with a resistivity greater than $10^7\ \Omega$ cm.

Finally, we point out that our use of the terms *oxidation* and *reduction* refers to the loss and gain of electrons as deduced by both formal charges and oxidation states. The meaning and method for assigning oxidation states continues to be debated and discussed (Gupta *et al.*, 2014; Karen *et al.*, 2014), but for now we still employ the IUPAC-recommended convention (McNaught and Wilkinson, 1997). For a careful review of redox (oxidation-reduction) chemistry in a planetary setting other than Europa, see the work of Nixon *et al.* (2012).

## 3. Results

### 3.1. Inorganic compounds

Table 1 lists the four inorganic compounds we studied. Sulfur dioxide ($SO_2$) was selected since we already have data for it under other conditions (Loeffler and Hudson, 2010, 2013), and hydrogen sulfide ($H_2S$) was chosen as a possible precursor to $SO_2$. Carbon monoxide (CO) and ammonia ($NH_3$) were studied as they are among the simplest of carbon- and nitrogen-containing compounds, respectively. Moreover, each of these molecules is known to be extraterrestrial, with $SO_2$ having been reported for Europa and the other molecules suspected to be present either from cometary or meteoritic delivery or as primordial material.

Figure 1 shows the IR features of a $H_2O + SO_2$ ice on warming from 50 K. The most obvious change seen is the

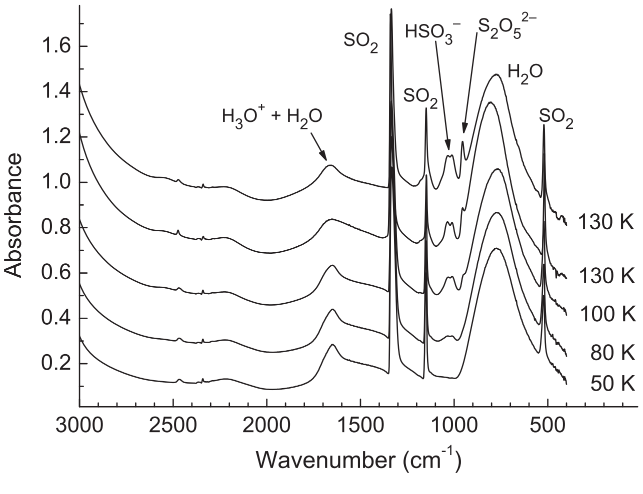

**FIG. 1.** Infrared spectra of an $H_2O + SO_2$ (6:1) ice mixture made at 50 K and then warmed at 1 K $min^{-1}$ to 130 K. The top spectrum was recorded after the sample had been at 130 K for 40 min. Spectra have been offset for clarity.

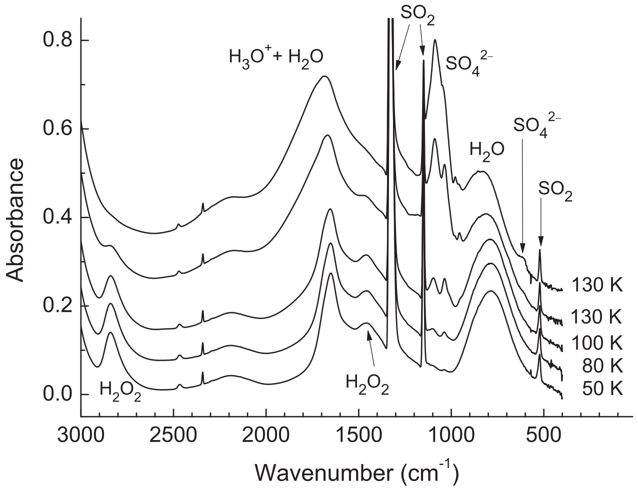

**FIG. 2.** Infrared spectra of an $H_2O + SO_2 + H_2O_2$ (80:14:6) mixture deposited at 50 K and then warmed at 1 K min$^{-1}$ to 130 K. The top spectrum was recorded after the sample had been at 130 K for 40 min. All spectra have been offset for clarity.

appearance of vibrational bands near 1050 cm$^{-1}$ due to the formation of $HSO_3^-$. Figure 2 shows a similar experiment but where $H_2O_2$ has been added to the ice; the strongest unobscured $H_2O_2$ absorptions are at 2840 and 1454 cm$^{-1}$. As the sample was heated, the $H_2O_2$ and $SO_2$ bands decreased, and absorptions of sulfur oxyanions appeared. Figure 3 quantifies these changes in a plot of IR band areas over time for $H_2O_2$ (2840 cm$^{-1}$), $SO_2$ (1150 cm$^{-1}$), and the sulfur oxyanions (1170–940 cm$^{-1}$), whose main component is $SO_4^{2-}$ (1068 cm$^{-1}$). It is seen that the $H_2O_2$ feature in the sample began to decrease by ~70 K, dropped by a factor of two by ~125 K, and was at the noise level about 10 min after reaching 130 K. We note that on warming anhydrous $H_2O_2 + SO_2$ ices, binary mixtures, we found no evidence for oxidation to make $SO_4^{2-}$. This agrees with, and confirms, an earlier computational study that found that the $HSO_3^- \rightarrow SO_4^{2-}$ conversion requires $H_2O$, $H_2O_2$, and $SO_2$ (Vincent *et al.*, 1997).

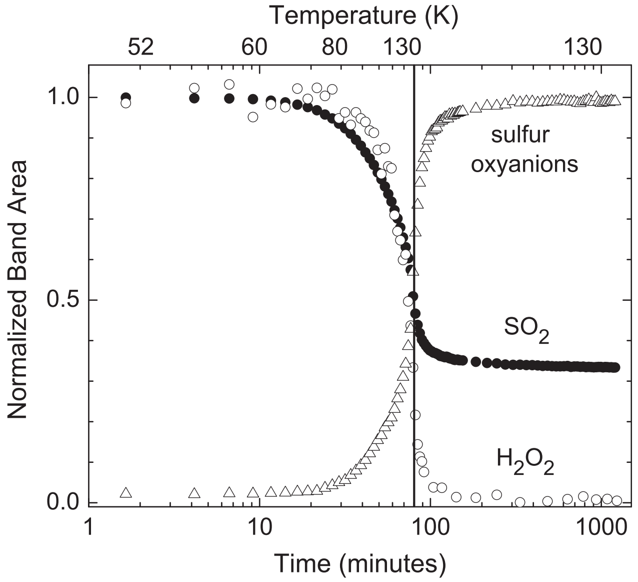

**FIG. 3.** Normalized areas for IR bands of $H_2O_2$ (2840 cm$^{-1}$), $SO_2$ (1150 cm$^{-1}$), and sulfur oxyanions (940–1170 cm$^{-1}$) in a $H_2O + SO_2 + H_2O_2$ (80:14:6) mixture deposited at 50 K and warmed at 1 K min$^{-1}$ to 130 K. A temperature of 50 K corresponds to time = 0, and the vertical line corresponds to 130 K. The sulfur oxyanions feature has contributions from $S_2O_5^{2-}$, $HSO_3^-$, $SO_4^{2-}$, and $HSO_4^-$.

Previously, we showed that ion irradiation of $H_2O + H_2S$ ices near 100 K results in the formation of $SO_2$ at the expense of $H_2S$ (Moore *et al.*, 2007a). A straightforward explanation is that reactions such as (5) and (6) convert $H_2S$ first into elemental sulfur (S) and then into $SO_2$, with both processes requiring $H_2O_2$ and perhaps involving numerous mechanistic steps (*e.g.*, Hoffmann, 1977).

$$H_2O_2 + H_2S \rightarrow 2H_2O + S \tag{5}$$

$$2H_2O_2 + S \rightarrow 2H_2O + SO_2 \tag{6}$$

To examine the ability of $H_2O_2$ to effect the $H_2S \rightarrow SO_2$ conversion in *unirradiated* ices, we prepared frozen $H_2O_2 + H_2S$ and $H_2O + H_2O_2 + H_2S$ mixtures at 50 K and slowly warmed them to sublimation. We saw no evidence for $H_2S$ decomposition and $SO_2$ formation, and the $H_2O_2$ bands remained relatively constant as the temperature increased. We conclude that no thermally induced redox reactions occurred between $H_2O_2$ and $H_2S$ at even the highest temperature studied (~200 K), or at least there was no formation of detectable products.

Turning to ammonia ($NH_3$), we can envision two types of reactions with $H_2O_2$. Our previous work (Moore *et al.*, 2007a) showed that no reactions are seen on warming $H_2O + NH_3$ ices, which we verified in the present study (see Fig. 4). For the present experiments, an oxidation sequence for $NH_3$ such as

$$NH_3 \rightarrow NH_2OH \rightarrow NO_2^- \rightarrow NO_3^- \tag{7}$$

can be envisioned, giving both $NO_2^-$ (nitrite) and $NO_3^-$ (nitrate) ions. However, we also recognized that $H_2O_2$ is on

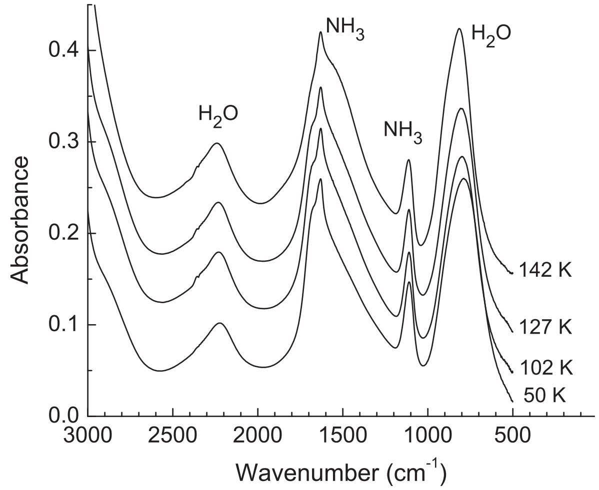

**FIG. 4.** Infrared spectra of an $H_2O + NH_3$ (10:1) mixture deposited at 50 K and then warmed at 1 K min$^{-1}$. Spectra have been offset for clarity.

the order of ten thousand times more acidic than $H_2O$ (Evans and Uri, 1949), so an acid-base reaction of the type

$$H_2O_2 + NH_3 \rightarrow NH_4^+ + O_2H^- \qquad (8)$$

might be possible. To test these ideas, we conducted warming experiments with and without $H_2O$-ice present. Figure 5 shows the IR spectrum of an anhydrous $H_2O_2 + NH_3$ mixture deposited at 50 K and then warmed to sublimation. The deposited sample possessed absorptions that do not belong to either $H_2O_2$ or $NH_3$, indicating that a reaction occurred. The strong, sharp IR feature of $NH_2OH$ near $1190\,cm^{-1}$ (Nightingale and Wagner, 1954) is not seen, arguing for this molecule's absence. However, there are multiple absorptions (see Discussion) that can be assigned to $NH_4^+$ ($1467\,cm^{-1}$) and $NH_4O_2H$ (2650, 1099, and $832\,cm^{-1}$).

All these observations can be interpreted to mean that Reaction 8 took place. Interestingly, a subsequent warming of this same sample had little effect on its spectrum until ~180 K, where the sample appeared to crystallize. In addition, lowering the deposition temperature to ~10 K did little to alter the initial spectrum, suggesting that the energy released on deposition was enough to cause Reaction 8 to occur. No IR features were found for the oxidized nitrogen-containing species of (7).

From this anhydrous binary system, we then examined a more complex, three-component sample. Figure 6 shows IR spectra of a three-component $H_2O + H_2O_2 + NH_3$ ice (10:1:1) after deposition at 50 K and warming to sublimation. Initially, the only IR absorptions seen were for those of the three reactants. However, on heating the sample, the $H_2O_2$ bands began to decrease at ~100 K and reached the noise level by 130 K. Accompanying this decrease, we observed an increase in the $NH_4^+$ feature near $1467\,cm^{-1}$. To highlight the differences in Figs. 5 and 6, in Fig. 7 we show spectra of ices containing $H_2O_2$ and $NH_3$ with $H_2O$ present and absent, along with reference spectra of $H_2O + NH_3$ and $H_2O + H_2O_2$ ices.

The fourth inorganic molecule we examined was CO. Ices made of $H_2O_2 + CO$ and $H_2O + H_2O_2 + CO$ were warmed from 10 to sublimation at $1\,K\,min^{-1}$ with an eye toward $CO_2$ formation. However, Fig. 8 shows that no $CO_2$ formation was observed above the estimated background level in our experiments, with the only major spectral changes corresponding to $H_2O_2$ crystallization near 160 K. We observed that much of the CO initially present sublimed from the ice as the temperature increased. We suspect that any residual CO present above ~100 K was likely too small to produce a detectable amount of $CO_2$, with the large intrinsic strength of the latter's IR features aiding their detection.

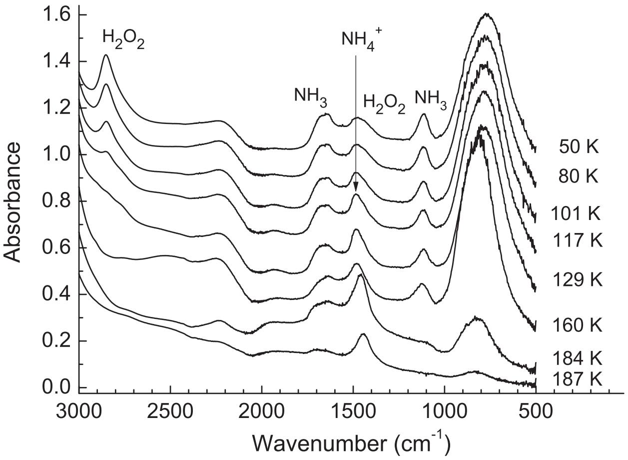

**FIG. 6.** Infrared spectra of an $H_2O + H_2O_2 + NH_3$ (10:1:1) mixture deposited at 50 K and warmed at $1\,K\,min^{-1}$. Spectra have been offset for clarity.

### 3.2. Organic compounds

Each of the four inorganic molecules we combined with $H_2O_2$ presented a particular appeal, but the present work initially was motivated by the possibility of observing thermal reactions of organics below 200 K. Table 1 lists the four organic compounds we studied. Methane ($CH_4$) was selected for its simplicity, its presence in a variety of

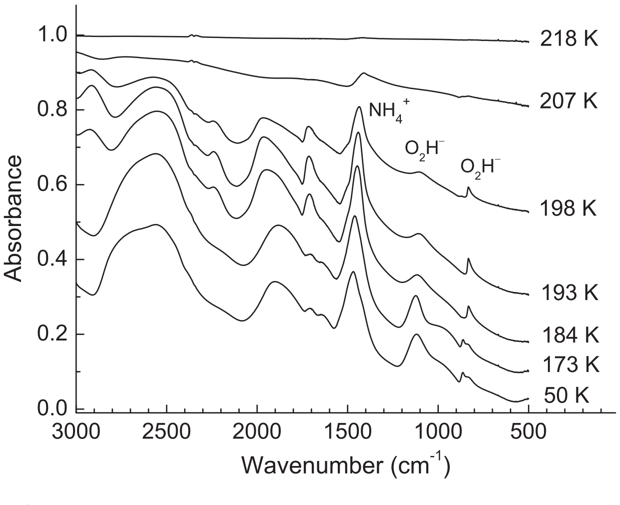

**FIG. 5.** Infrared spectra of an $H_2O_2 + NH_3$ (1:1) mixture deposited at 50 K and then warmed at $1\,K\,min^{-1}$. Spectra have been offset for clarity.

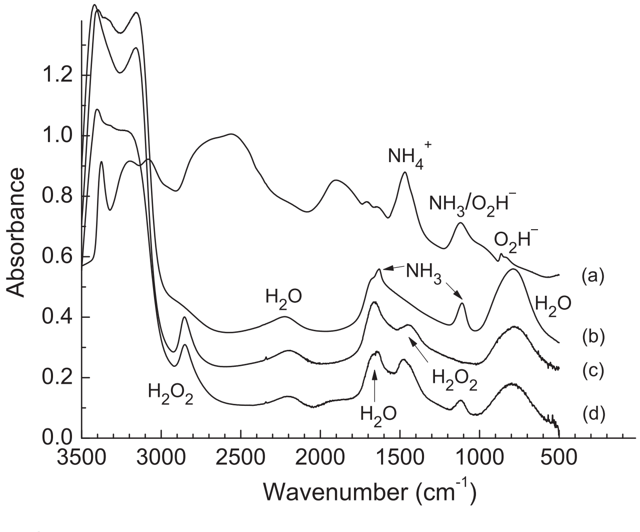

**FIG. 7.** Infrared spectra of four ice mixtures each at 50 K: (**a**) $H_2O_2 + NH_3$ (1:1), (**b**) $H_2O + NH_3$ (10:1), (**c**) $H_2O + H_2O_2$ (10:1), and (**d**) $H_2O + H_2O_2 + NH_3$ (10:1:1).

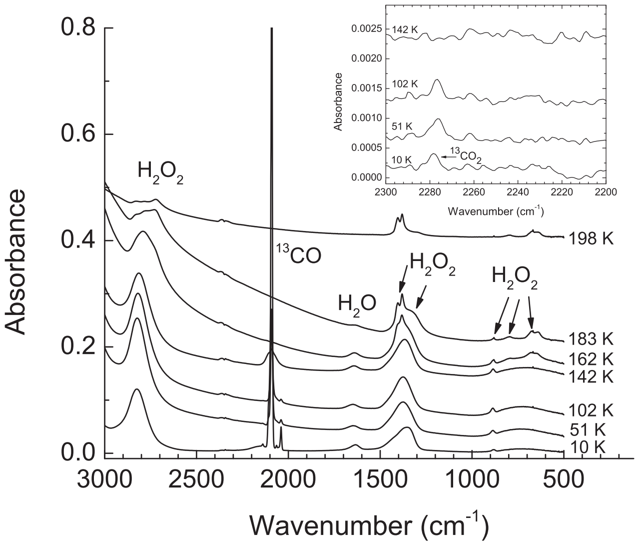

**FIG. 8.** Infrared spectra of a $H_2O_2 + {}^{13}CO$ (1:1) mixture deposited at 10 K and warmed at 1 K min$^{-1}$. Spectra have been offset for clarity. The inset uses an expanded scale to illustrate the detection limits in our measurements. The $^{13}CO_2$ band shown at 10 K is an impurity on the level of 0.002% in our $^{13}CO$ source.

astronomical environments, and its potential presence in many astrobiological settings, both as a possible metabolic product and as a nutrient. Propyne ($C_3H_4$) was chosen as a typical unsaturated molecule and as one that is potentially more reactive than $CH_4$. Methanol ($CH_3OH$) and acetonitrile ($CH_3CN$) were taken as simple representatives of the alcohols and nitriles, respectively. Oxidation products can be written easily for each of these organic molecules, with those of $C_3H_4$ perhaps being the most varied. Suffice it to say, however, that no oxidation products were seen within the detection limits in any of our experiments with $H_2O + H_2O_2 + X$ ices ($X = CH_4$, $C_3H_4$, $CH_3OH$, and $CH_3CN$) or in the simpler $H_2O_2 + X$ ices. This suggests that these four molecules are not easily destroyed by thermal reactions with $H_2O_2$ in either $H_2O$-rich ices at 50–170 K or the simpler two-component anhydrous mixtures with frozen $H_2O_2$.

## 4. Discussion

### 4.1. $H_2O_2$ oxidation of $SO_2$ in ices

Thermal reactions between $SO_2$ and $H_2O_2$ have been investigated extensively within the atmospheric science community due to their importance in removing $SO_2$ from Earth's atmosphere (*e.g.*, Clegg and Abbatt, 2001). Based on those studies, (3) and (4) are believed to be the primary reactions between $H_2O_2$ and $SO_2$ in the presence of $H_2O$. Although Earth's clouds are generally much warmer than surfaces of icy satellites, the $SO_4{}^{2-}$ we have seen in our experiments is likely from similar processes. Critical tests of our analysis of the chemistry are shown in Fig. 3. As required by our interpretation, the decrease in the IR features of the limiting reagents $SO_2$ and $H_2O_2$, near 60 K in our experiments, is accompanied by a simultaneous increase in the IR absorbance of sulfur oxyanions, primarily $SO_4^{2-}$. More significantly, and as expected, the locations of the inflection points for the deceases in reactants and the increase in products are essentially the same ($\sim$130 K).

The subsurface depth on Europa to which these $H_2O_2$ observations, and others in this paper, apply will depend on the thickness and other properties of that satellite's ice shell. Numerous studies have addressed the ice shell's thickness and have yielded values between about 1 and 40 km (Billings and Kattenhorn, 2005). Taking 100 K as the temperature of surface ices and 270 K for the bottom of the ice shell, as is typically done (*e.g.*, Bray *et al.*, 2014), and making a simple assumption of linearity, we estimate a temperature gradient of 17 K km$^{-1}$ for an intermediate shell thickness of 10 km. Thus, the highest temperature reported in this paper ($\sim$190 K) corresponds to a depth of about 5 km below Europa's surface.

### 4.2. $H_2O_2$ reactions with $NH_3$

Besides $SO_2$, the only other molecule in Table 1 that reacted with $H_2O_2$ was $NH_3$. However, unlike $SO_2$, where we observed that $H_2O$-ice was needed to initiate the reaction, $NH_3$ combined with $H_2O_2$ in the absence of $H_2O$. The first study to show that $NH_3$ and $H_2O_2$ react to form a stable compound was published nearly 100 years ago by Maass and Hatcher (1922). The white crystalline powder that formed in their experiments melted near 25°C, leading Knop and Giguere (1959) to propose that the bonding in the reaction product might be ionic and not the weaker bonding found in hydrates of $NH_3$ and $H_2O_2$. Knop and Giguere's spectroscopic work, along with a previous study (Simon and Kriegsmann, 1955), suggested that the new ionic species was ammonium hydroperoxide ($NH_4O_2H$), consisting of $NH_4^+$ and $O_2H^-$ ions, a suggestion later confirmed by X-ray diffraction measurements (Tegenfel and Olovsson, 1966; Churakov *et al.*, 2010). That $NH_4^+$ is present in our $H_2O_2 + NH_3$ ices is indicated clearly by an IR feature near 1467 cm$^{-1}$, suggesting that the protonation reaction (8) occurs more readily than the redox reaction (7). The likely counter-ion is $O_2H^-$, to which broad IR absorptions at 1100 and 836 cm$^{-1}$ have been assigned (Knop and Giguere, 1959). While only the lower wavenumber band is unobstructed at 50 K, Fig. 6 clearly shows both absorptions ($\sim$1099, $\sim$832 cm$^{-1}$) after the sample was warmed and allowed to crystallize. Interestingly, the strong IR band seen near 2560 cm$^{-1}$ in Fig. 7a appears to be outside the spectral range of either of the two previous studies of $H_2O_2 + NH_3$ ices. It is reasonable to assign at least part of this broad IR feature to an O-H or N-H stretching vibration in $NH_4O_2H$ (*e.g.*, Churakov *et al.*, 2010).

A comparison of Figs. 5 and 6 shows that the addition of excess $H_2O$-ice to the $H_2O_2 + NH_3$ system significantly changed the IR spectra and the associated chemistry. Warming the 50 K sample produced $NH_4^+$ at the expense of $H_2O_2$ as shown by the significant sharpening near 1467 cm$^{-1}$ and the dramatic decrease at 2850 cm$^{-1}$, respectively, with both changes being seen even at the highest temperature studied. One interpretation is that solvent-assisted protonation gave the compound $(NH_4)_2O_2$ or one of its hydrates in our ices. Although our spectra do not allow a firm assignment to be made, hydrate formation agrees with the report of $(NH_4)_2O_2 \cdot 2H_2O$ in the $H_2O + H_2O_2 + NH_3$ ice system, based on thermal analyses (Giguere and Chin, 1959), and is consistent with observations that $NH_4O_2H$ readily decomposes in the presence of $H_2O$ (Maass and Hatcher, 1922; Knop and Giguere, 1959), perhaps to give $OH^-$ at the expense of $O_2H^-$. In any case, the formation and persistence of $NH_4^+$ is readily seen in Fig. 6 for an $H_2O + H_2O_2 + NH_3$ ice.

### 4.3. $H_2O_2$ reactions and astrobiology

Redox reactions with liquid- and gas-phase $H_2O_2$ readily occur at room temperature and above but not necessarily at temperatures expected in the outer Solar System. In the present work, we were particularly interested in determining how the eight molecules we examined (Table 1), which included several with biological connections, might respond to frozen $H_2O_2$ at low temperatures. The concentrations of $H_2O_2$ used in our experiments are much higher than what has been detected (Carlson *et al.*, 1999a) and are expected in extraterrestrial environments, so negative results in our work (*i.e.*, no reaction seen) suggest no reaction under less-harsh, more-realistic conditions.

For our experiments with solid $H_2O_2$, we selected as reactants the four organic and four inorganic compounds of Table 1. Of the inorganics, no thermally induced reactions were observed between $H_2O_2$ and either CO or $H_2S$. Reaction of the former could have made $CO_2$, while the latter could have produced $SO_2$, as given in (5) and (6). No such thermal conversion was seen. Extraterrestrial thermal oxidation of $H_2S$ at low temperatures appears to require a more complex set of conditions than those we employed, perhaps even biological conditions akin to those relevant to sulfur-oxidizing bacteria. In contrast to the reluctance of solid $H_2S$ to react with $H_2O_2$, here and elsewhere we have documented the relative ease of the $SO_2 \rightarrow SO_4^{2-}$ conversion (Loeffler and Hudson, 2013). The activation energy derived from an Arrhenius plot in our earlier work led to half-life predictions for $SO_2$ of about 1 year at 100 K and about 0.3 h at 120 K. The reported subsurface ocean of Europa is presumably at temperatures higher than those of the surface ($\sim$86–130 K), so any subsurface $H_2O_2$ present, such as from downward transport from the surface itself (Greenberg, 2010), will readily convert $SO_2$ into $SO_4^{2-}$, a potential energy source for certain extremophiles such as sulfur-reducing bacteria.

Ammonia ($NH_3$) was the fourth inorganic compound we examined. Our initial thoughts were of a possible thermal nitrification of $NH_3$ in $H_2O_2$-containing ices to make the oxyanions $NO_2^-$ and $NO_3^-$, as in (7). Chemical reactions indeed were observed on warming ices that contained $H_2O_2$ and $NH_3$, but neither $NO_2^-$ nor $NO_3^-$ was seen. The best that can be said is that under the conditions of our experiments, $NH_3$ was consumed in $H_2O_2$-containing ices at $\sim$100 K and higher. Although the observed reaction products differed in the presence and in the absence of $H_2O$ (see Figs. 5 and 6), $NH_4^+$ was formed in all cases and so would be available as a nutrient for any extraterrestrial counterparts of terrestrial nitrifying bacteria.

Turning to the organic compounds we examined, solid methane ($CH_4$) and solid methanol ($CH_3OH$) conceivably could have undergone multiple thermal oxidations in the presence of $H_2O_2$, such as through the sequence

$$CH_4 \rightarrow CH_3OH \rightarrow H_2CO \rightarrow CO \rightarrow CO_2 \qquad (9)$$

to make $CO_2$, but we observed no $CO_2$ on warming ice mixtures containing either $CH_4$ and $H_2O_2$ or $CH_3OH$ and $H_2O_2$. Each product molecule in (9) has at least one fairly strong IR spectral feature that would easily have been detected, but none were seen in the 10–150 K region examined. At room temperature and above, propyne ($C_3H_4$) can undergo oxidative cleavage to make $CO_2$ and $CH_3COOH$ (acetic acid), but no evidence for either was found in our low-temperature experiments, and both $CO_2$ and $CH_3COOH$ would have been relatively easy to detect with our IR methods. Finally, from earlier work we already knew that low-temperature radiation-induced oxidation of acetonitrile ($CH_3CN$) first makes $OCN^-$ and then $CO_2$ (Hudson and Moore, 2004), but neither of these products was seen in our warmed, unirradiated $CH_3CN$-containing ices.

This leads to perhaps the most significant astrobiological implication of our experiments with organics, namely, the stability of these four typical, relatively simple organic molecules in the presence of solid $H_2O_2$. One can envision a situation in which, for example, vertical transport of material on Europa brings surface oxidants, such as $H_2O_2$, down to subsurface regions and into contact with organics trapped in ice (Greenberg, 2010). Our experiments showed that such encounters do not necessarily destroy those same organic compounds. In the particular case of $CH_4$, whether it is primordial, endogenous, or exogenous, it would remain available for methanotrophs.

Finally, this study emphasizes that understanding and predicting Europa's low-temperature solid-phase chemistry, and its contribution to astrobiology, will require substantial laboratory efforts. For example, with standard tables of $E^{\theta}$ values (reduction potentials) for half-cell reactions, one can predict that all of the eight compounds we combined with $H_2O_2$ should be oxidized by that molecule, which does not agree with our observations. However, such reference data are nearly always for a standard set of conditions near 25°C, 1 bar, and 1 molar concentration, conditions markedly different from those of Europa ices. Furthermore, extrapolating from calculations on systems with liquid phases to those, like ours, that are entirely formed from solids is not straightforward. Since the influence and interplay of both thermodynamic and kinetic contributions to ice chemistry cannot yet be predicted *a priori*, we anticipate a significant role for experimental work for the foreseeable future.

## 5. Summary and Conclusions

Laboratory results have been presented here on the reactivity of $H_2O_2$ with selected organic and inorganic molecules in ice mixtures at temperatures of the outer Solar System. Using IR spectroscopy, we observed that two of the inorganic compounds studied, $SO_2$ and $NH_3$, were consumed in $H_2O_2$-containing ices by thermally induced reactions, yielding $NH_4^+$ and $SO_4^{2-}$, respectively. These ions are predicted to exist in both surface and subsurface europan ices, although in the latter case they will be hidden from remote observations.

In contrast, at the timescales of our experiments we found that none of the four organic compounds examined underwent low-temperature thermally induced reactions with solid $H_2O_2$ in either the presence or absence of $H_2O$-ice. We believe that these observations of a *nonreaction* speak positively for future attempts to find organics on Europa. On a frozen world where $H_2O_2$ could move downward to meet trapped subsurface organics, it could descend without modification by them, leaving those organics unaltered, so we can anticipate their discovery through future explorations. Put another way, the formation of surface radiolytically generated $H_2O_2$ on Europa, and that molecule's downward movement with $H_2O$-ice, does not necessarily mean that all organics encountered in icy subsurface regions will be destroyed by $H_2O_2$ oxidation.

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## Author Disclosure Statement

No competing financial interests exist.

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