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Complete List of Authors:	Hudson, Reggie; NASA Goddard Space Flight Center, Astrochemistry Laboratory Loeffler, Mark; NASA Goddard Space Flight Center, Astrochemistry Laboratory
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Descent without Modification? The Thermal Chemistry of H_2O_2 on Europa and Other Icy Worlds

Mark J. Loeffler and Reggie L. Hudson

Astrochemistry Laboratory, Code 691,

NASA Goddard Space Flight Center, Greenbelt, MD 20771

Person to whom correspondence should be directed:

Reggie L. Hudson
Astrochemistry Laboratory, Code 691
NASA Goddard Space Flight Center
Greenbelt, MD 20771
phone: 301-286-6961
fax: 301-286-0440
reggie.hudson@nasa.gov

Running title: Thermal Chemistry of H_2O_2 in Icy Environments

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, does not necessarily mean that all organics encountered in icy sub-surface regions will be destroyed by H_2O_2 oxidation.

Keywords:

Europa, laboratory investigations, icy moons, infrared spectroscopy, H_2O_2 resistance

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 has been treated by Gaidos *et al.* (1999), while life within the ice itself, perhaps aided by rising sub-surface thermal plumes, has been examined by Ruiz *et al.* (2007). Aside from harboring living organisms, it has been speculated that Europa's ices also could contain evidence for sub-surface biology in the form of molecular by-products or organic material (Marion *et al.*, 2003) brought upwards by convection (Pappalardo *et al.*, 1998). Hand *et al.* (2009) have summarized and extended much of the earlier work on Europa astrobiology, and have described possible scenarios for biogeochemical cycles and the putative sub-surface ocean's chemistry.

The persistence and detection of any material within or beneath Europa's ice shell depends 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 ~ 10 eV), by keV and MeV 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, not relying 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 Europa 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 spectra on warming from 50 to 100 K demonstrating that H_2O and SO_2 combined to form H_3O^+ and HSO_3^- (bisulfite):

$$2\,H_2O \;+\; SO_2 \;\rightarrow\; H_3O^+ \;+\; HSO_3^- \qquad (1)$$

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.

In another paper (Moore *et al.*, 2007b) we 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

$$4\,H_2O + SO_2 \rightarrow 2\,H_3O^+ + SO_4^{2-} + H_2 \qquad (2)$$

This radiation-driven process is a plausible source of the SO_4^{2-} identified on Europa’s surface using observations from the Galileo spacecraft’s 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), which 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 K to 130 K initiated the formation HSO_3^- and SO_4^{2-} through the following reactions:

$$2\,H_2O + SO_2 \rightarrow H_3O^+ + HSO_3^- \qquad (3)$$

$$H_2O_2 \quad + \quad HSO_3^{-} \rightarrow \quad H_3O^{+} \quad + \quad SO_4^{2-} \qquad (4)$$

Having shown that H_2O_2 can produce sulfate through reaction (3) followed by (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) recently has summarized the case for downward transport of surface ices on Europa. Such movement would transfer surface material toward sub-surface 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 sub-surface liquid then it could significantly alter the chemistry occurring there as the liquid would become more acidic (Pasek and Greenberg 2012). Were sub-surface 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 sub-surface life. Conversely, any SO_2 that is oxidized by H_2O_2 could provide a potential nutrient for sub-surface sulfate-reducing bacteria, or their extraterrestrial analogs. 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 sub-surface regions that are shielded from direct exposure to UV light or ionizing radiation, but still which may contain H_2O_2.

In this paper we examine how H_2O_2 in H_2O-ice might promote chemical changes in the absence of ionizing radiation and far-UV photons. Our goal is 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 have chosen 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 affect our results. Although H_2O_2 is a potent room-temperature oxidant, to our knowledge the present paper 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 using infrared (IR) spectroscopy.

2. Experimental Methods

Experiments were performed with a cryostat (T_{min} ~ 10 K) operating in a stainless steel high-vacuum chamber ($P \sim 1 \times 10^{-7}$ 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 I, onto a pre-cooled (10 - 50 K) gold-coated aluminum mirror (area ≈ 5 cm^2) 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 with interferometry using a diode laser (670 nm), and the deposition was halted when a thickness of about 1.5 μm 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 FTIR 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 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 hours 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 $\sim 2 \times 10^{-3}$ (~0.2%) when compared to the initial reactants.

Thus, any non-detection 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. See Gerakines and Hudson (2013) for recent amino-acid work using similar experimental methods.

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 Ω 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 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; Loeffler and Hudson, 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 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, had dropped by a factor of two by ~125 K, and was at the noise level about 10 minutes 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).

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).

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

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

To examine the ability of H_2O_2 to effect the $H_2S \rightarrow SO_2$ conversion in *un*irradiated ices, we prepared a frozen H_2O_2 + H_2S and H_2O + H_2O_2 + H_2S mixtures at 50 K and slowly warmed them to 195 K. 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

$$NH_3 \rightarrow NH_2OH \rightarrow NO_2^- \rightarrow NO_3^- \qquad (7)$$

can be envisioned, giving both NO_2^- (nitrite) and NO_3^- (nitrate) ions. However, we also recognized that H_2O_2 is on the order of ten thousand times more acidic than H_2O (Evans and Uri, 1949) and 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 of 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 195 K. Initially, the only infrared 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 K to 195 K 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.

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, for its presence in a variety of astronomical environments, and for 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 (~130 K).

The sub-surface 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 (~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 showing 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 (7) occurs more readily than the redox reaction (8). 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 (~1099, ~832 cm^{-1}) after the sample was warmed and allowed to crystallize. Interestingly, the strong IR band seen near 2560 cm^{-1} in Fig. 7(a) 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 (187 K). 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 $(NH_4)_2O_2 \bullet 2H_2O$ 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 that are expected in extraterrestrial environments, and so negative results in our work (*i.e.*, no reaction seen) suggests 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 yr at 100 K and about 0.3 hr at 120 K. The reported sub-surface ocean of Europa is presumably at temperatures higher than those of the surface (~86 - 130 K) and 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 (8). 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 ~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 sub-surface regions and into contact with organics trapped in ice (Greenberg, 2010). Our experiments show 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^{θ} 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 is nearly always for a standard set of conditions near 25 °C, 1 bar, and 1 molar concentrations, 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 infrared 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 sub-surface Europa ices, although in the latter case they will be hidden from remote observations.

In contrast, 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. As with the curious incident of the dog who did not bark at night (Doyle, 1892), we believe that these observations of a *non*-reaction speak loudly for future attempts to find organics on Europa. On a frozen world where H_2O_2 could move downward to meet trapped sub-surface organics, it will descend without modification by them, leaving those organics unaltered, and 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 sub-surface 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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Tables

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?
Inorganics				
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]
Organics				
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 (1976), [k] Cruikshank and Silvaggio (1979), [l] Maguire *et al.*, (1981), [m] Based on modeling of spectra (Merlin *et al.*, 2002), and [n] Marten *et al.* (2002).

Figure Legends

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 minutes. 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 minutes. All spectra have been offset for clarity.

FIG. 3. Normalized areas for infrared 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^-.

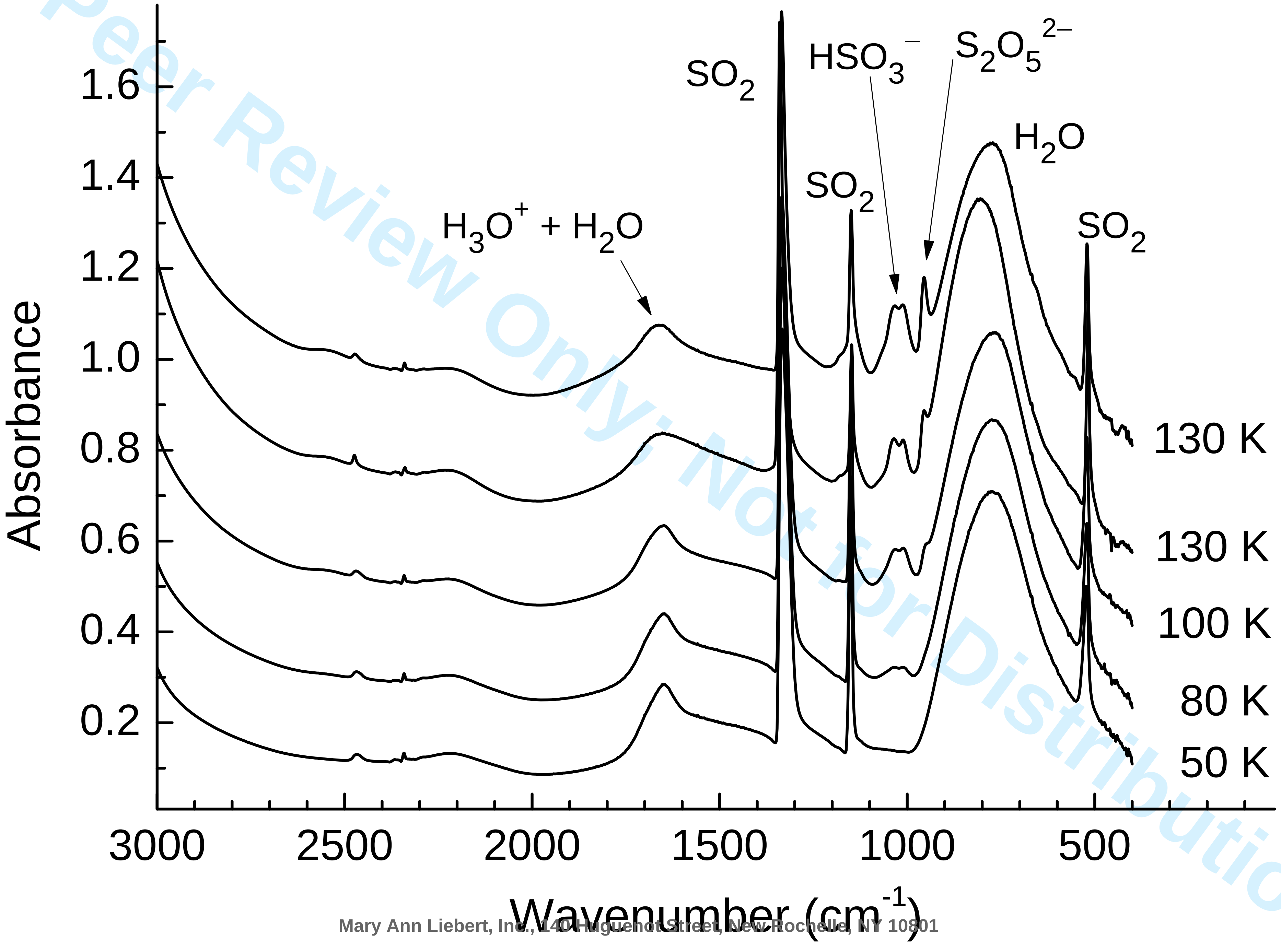
FIG. 4. Infrared spectra of an H_2O + NH_3 (10:1) mixture deposited at 50 K and then warmed at 1 K min^{-1} to 142 K. Spectra have been offset for clarity.

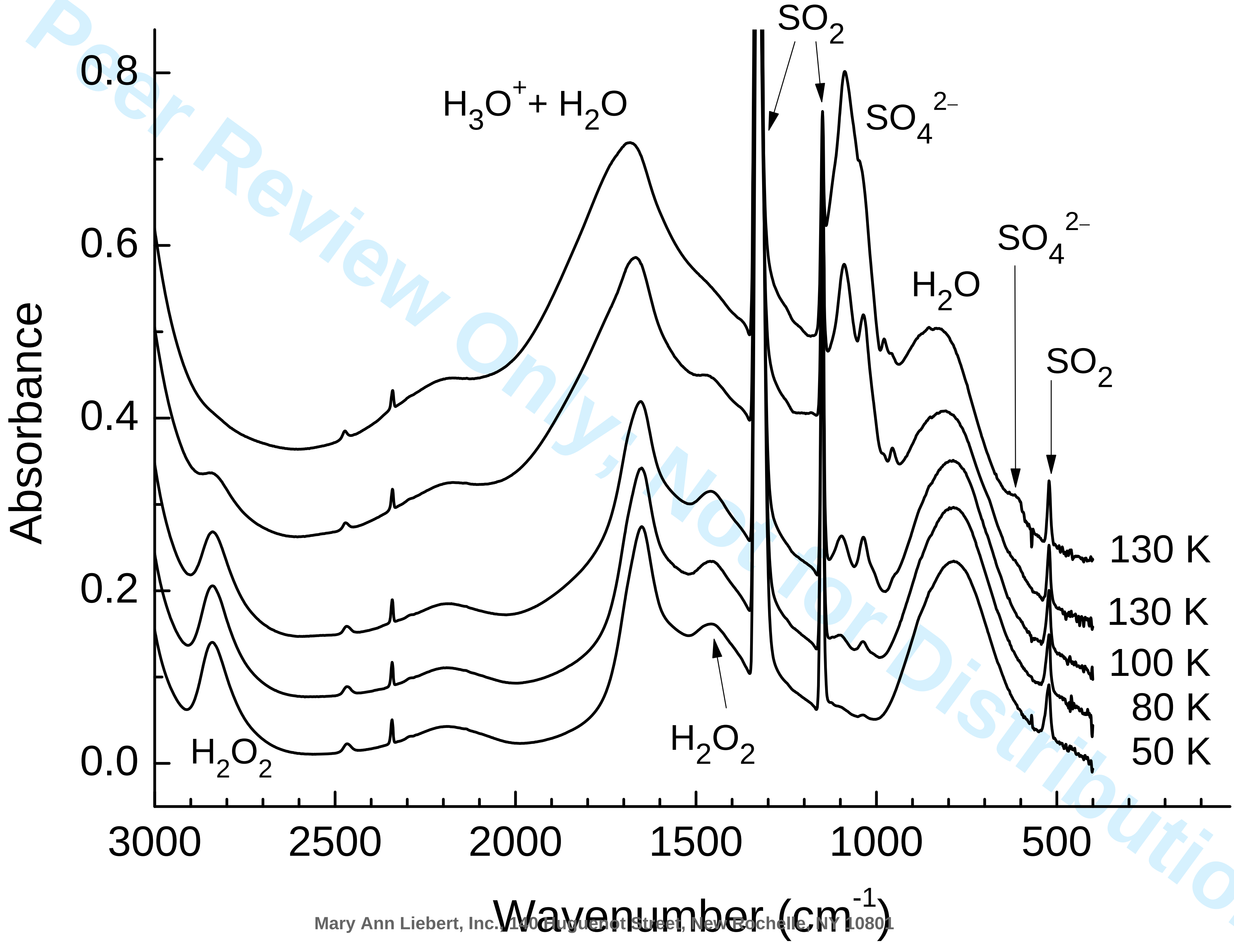
FIG. 5. IR spectra of an H_2O_2 + NH_3 (1:1) mixture deposited at 50 K and then warmed at 1 K min^{-1} to 218 K. Spectra have been offset for clarity.

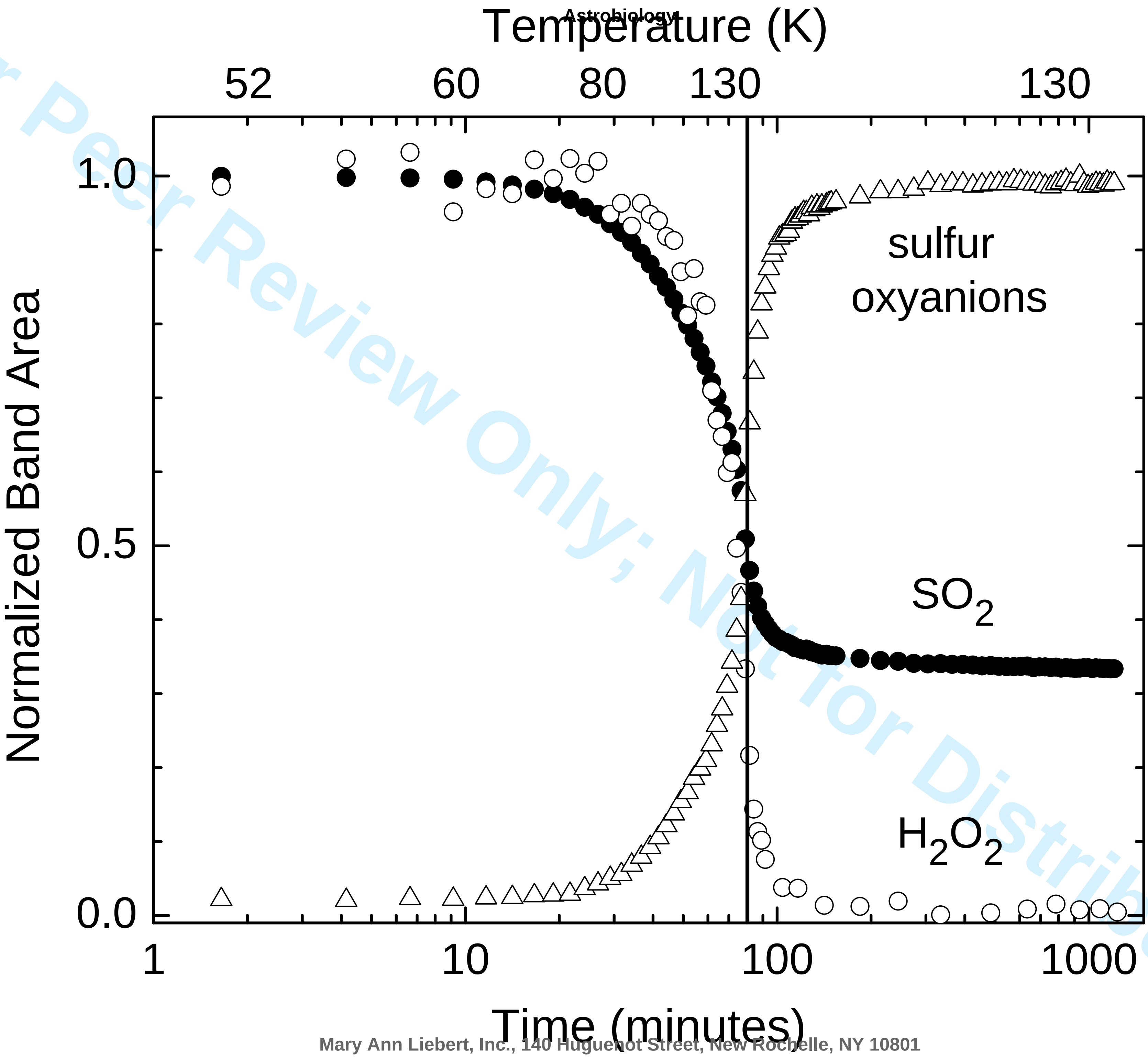
FIG. 6. IR spectra of an H_2O + H_2O_2 + NH_3 (10:1:1) mixture deposited at 50 K and warmed at 1 K min^{-1} to 187 K. Spectra have been offset for clarity.

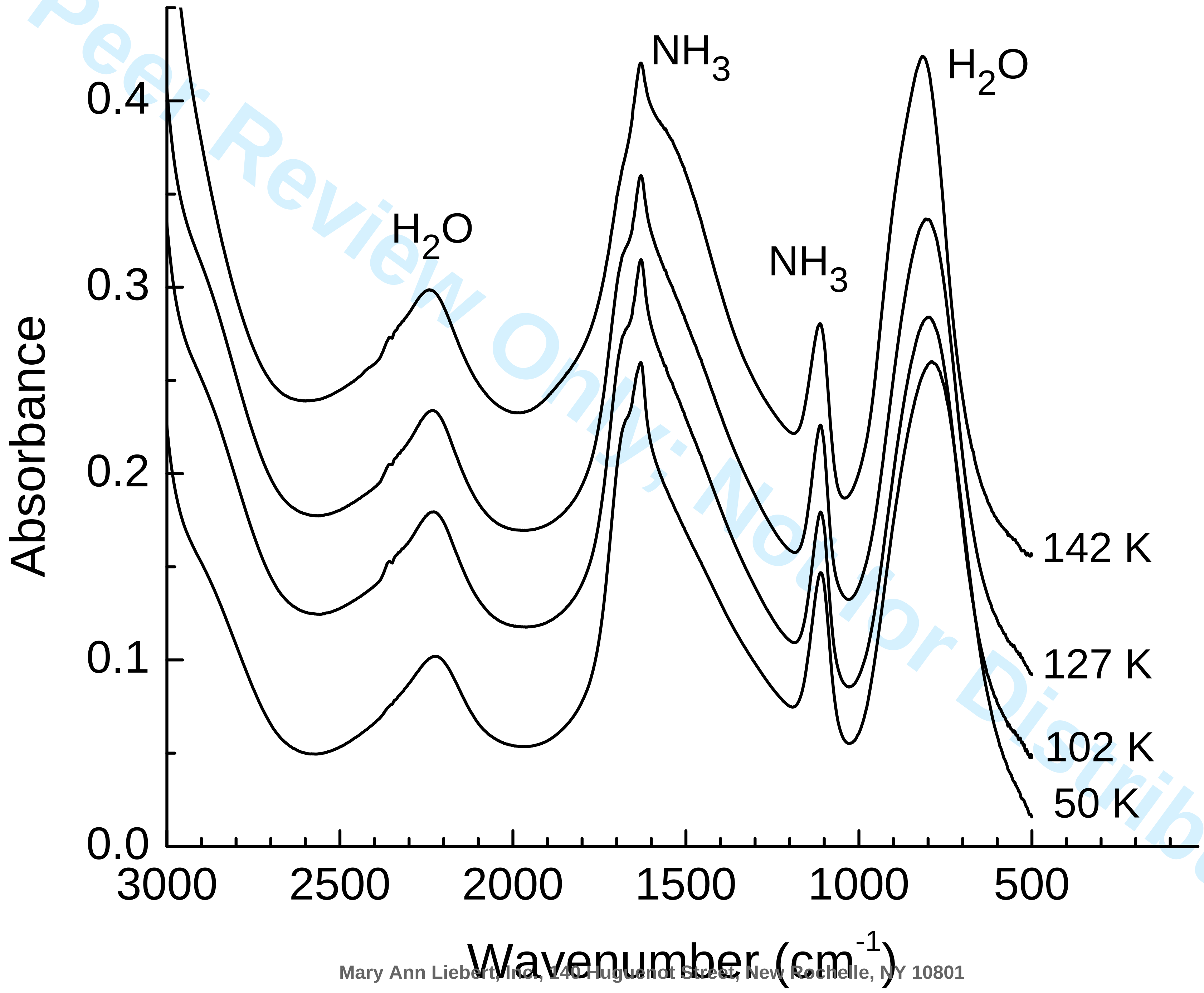
FIG. 7. IR spectra of four ice mixtures each at 50 K: (a) H_2O_2 + NH_3 (1:1), (b) H_2O + NH_3 (10:1), (c) H_2O + H_2O_2 (10:1), and (d) H_2O + H_2O_2 + NH_3 (10:1:1).

FIG. 8. IR spectra of a H_2O_2 + ^{13}CO (1:1) mixture deposited at 10 K and warmed at 1 K min^{-1} to 198 K. 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.

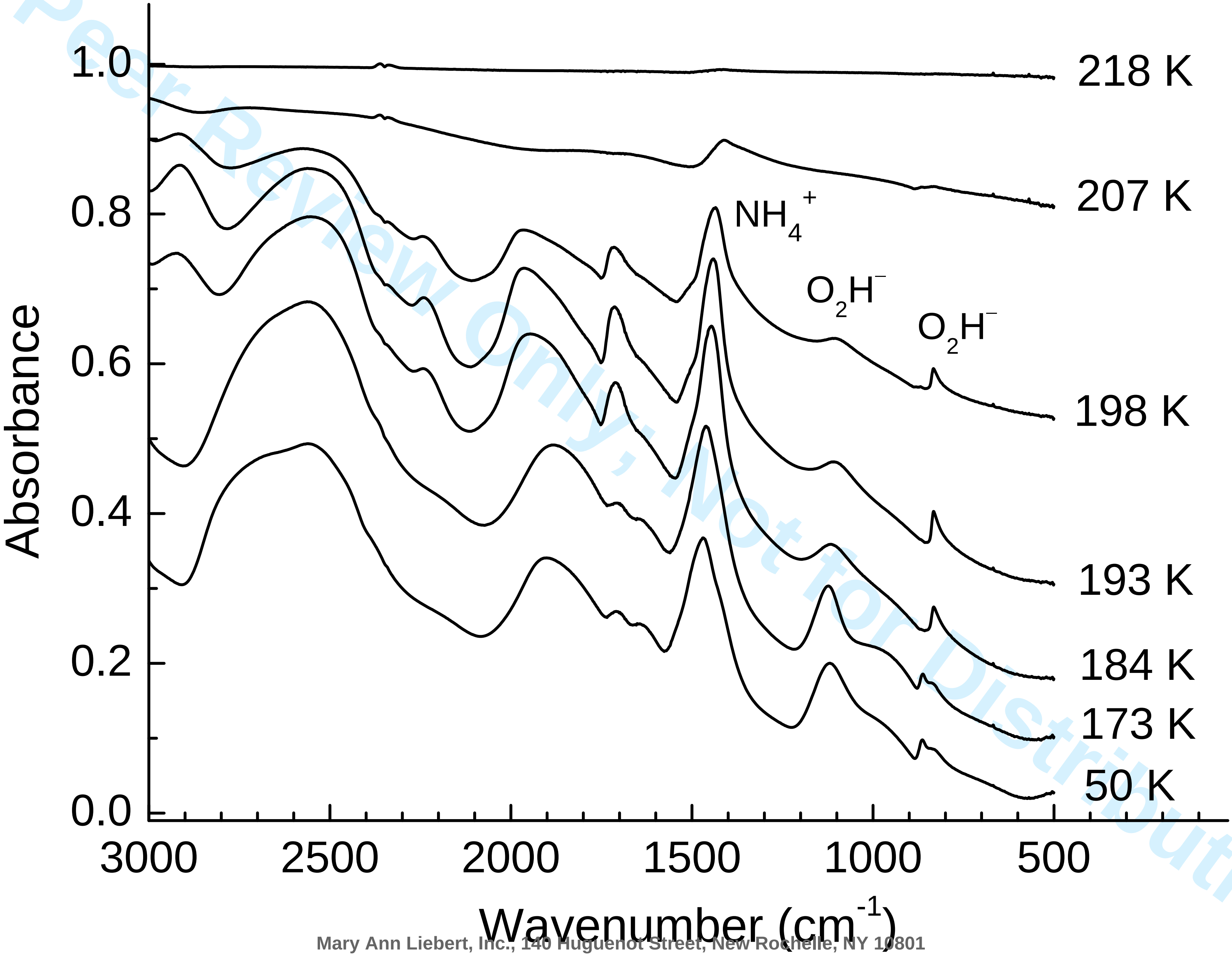

Absorbance
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})
$H_3O^+ + H_2O$
SO_2
HSO_3^-
$S_2O_5^{2-}$
SO_2
H_2O
SO_2
130 K
130 K
100 K
80 K
50 K

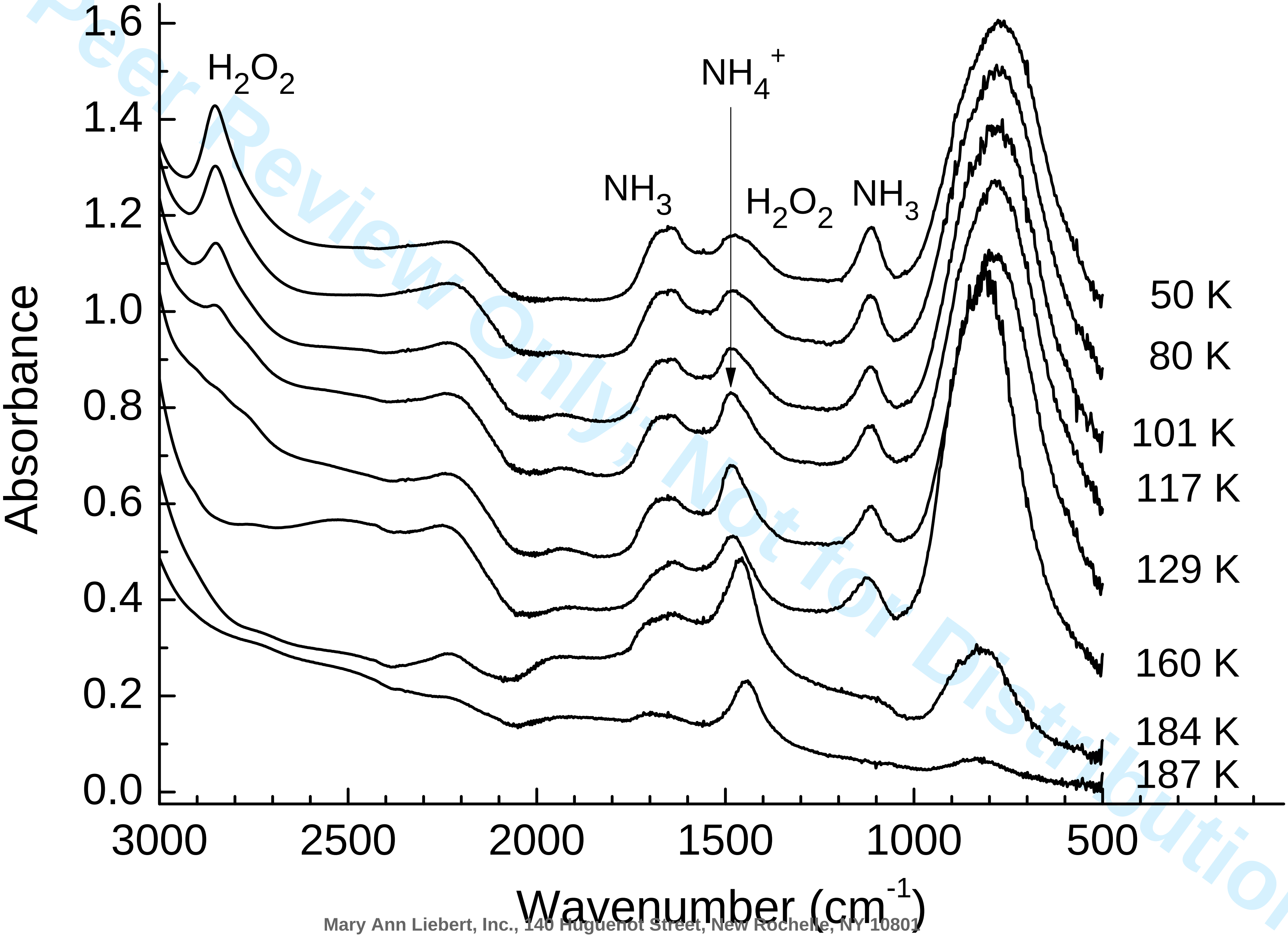

Absorbance
0.8
0.6
0.4
0.2
0.0
Wavenumber (cm^{-1})
3000
2500
2000
1500
1000
500
$H_3O^+ + H_2O$
SO_2
SO_4^{2-}
SO_4^{2-}
H_2O
SO_2
H_2O_2
H_2O_2
130 K
130 K
100 K
80 K
50 K

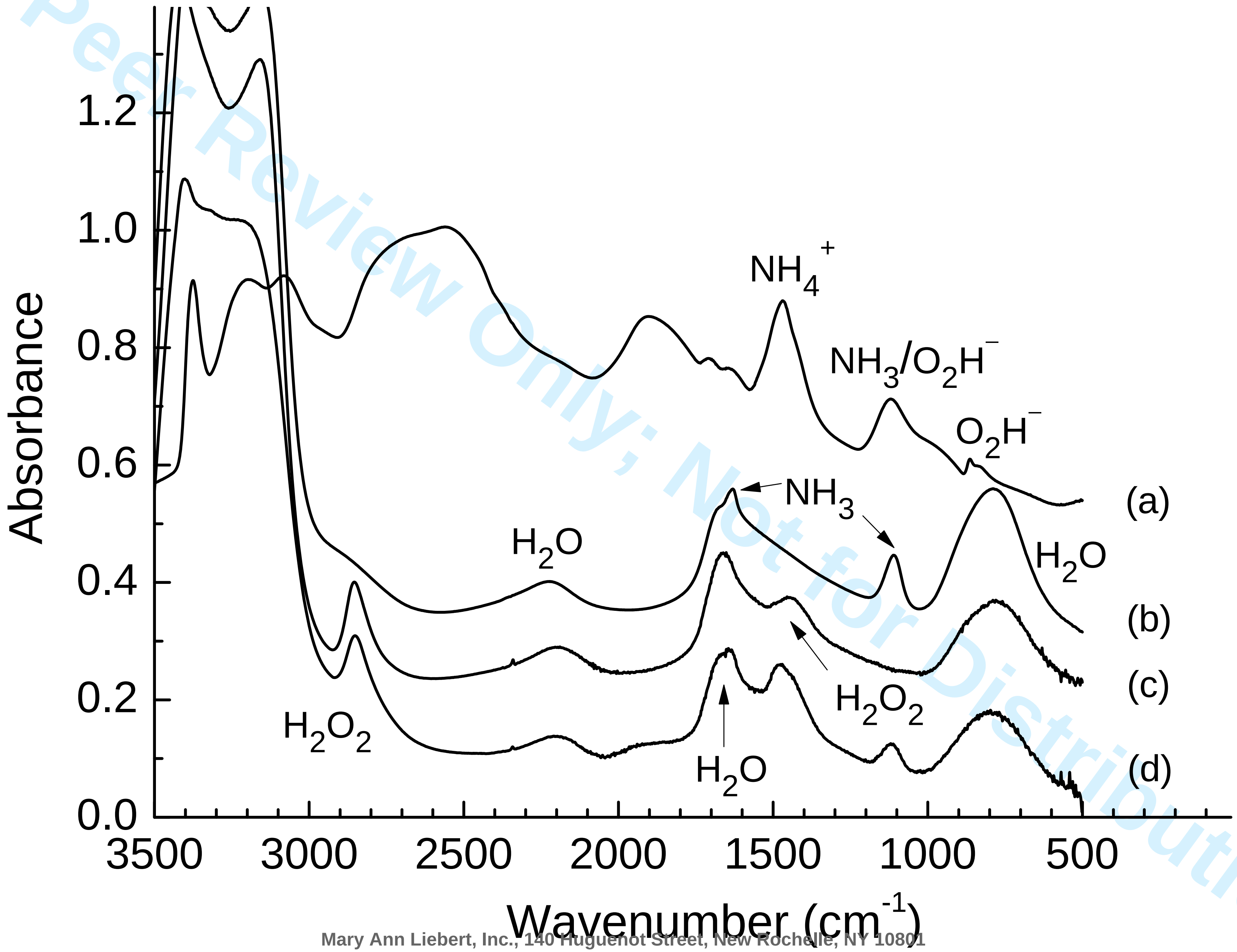

Temperature (K)
52
60
80
130
130
Normalized Band Area
1.0
0.5
0.0
sulfur oxyanions
SO2
H2O2
1
10
100
1000
Time (minutes)



Absorbance
0.4
0.3
0.2
0.1
0.0
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
H_2O
NH_3
NH_3
H_2O
142 K
127 K
102 K
50 K


218 K
207 K
198 K
193 K
184 K
173 K
50 K
NH_4^+
O_2H^-
O_2H^-
Absorbance
1.0
0.8
0.6
0.4
0.2
0.0
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})


Absorbance
Wavenumber (cm^{-1})
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
3000
2500
2000
1500
1000
500
H_2O_2
NH_4^+
NH_3
H_2O_2
NH_3
50 K
80 K
101 K
117 K
129 K
160 K
184 K
187 K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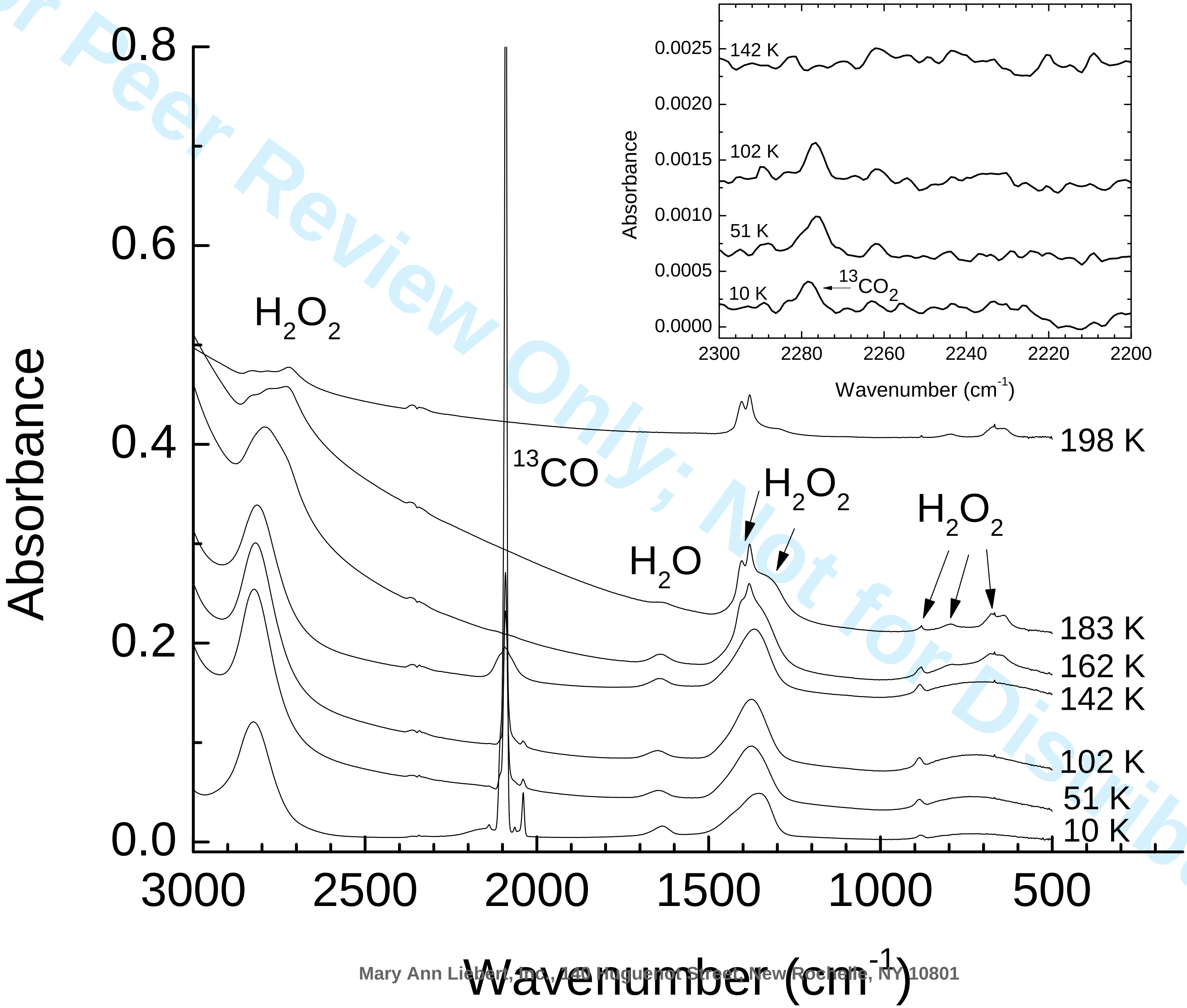
0.4
0.6
0.8
1.0
1.2
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})
NH_4^+
NH_3/O_2H^-
O_2H^-
NH_3
H_2O
H_2O
H_2O_2
H_2O_2
H_2O
(a)
(b)
(c)
(d)


0.8
0.6
0.4
0.2
0.0
Absorbance
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})
H_2O_2
^{13}CO
H_2O
H_2O_2
H_2O_2
198 K
183 K
162 K
142 K
102 K
51 K
10 K
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
Absorbance
142 K
102 K
51 K
10 K
$^{13}CO_2$
2300
2280
2260
2240
2220
2200
Wavenumber (cm^{-1})