



## Thermal regeneration of sulfuric acid hydrates after irradiation

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### ABSTRACT

In an attempt to more completely understand the surface chemistry of the jovian icy satellites, we have investigated the effect of heating on two irradiated crystalline sulfuric acid hydrates,  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ . At temperatures relevant to Europa and the warmer jovian satellites, post-irradiation heating recrystallized the amorphized samples and increased the intensities of the remaining hydrate's infrared absorptions. This thermal regeneration of the original hydrates was nearly 100% efficient, indicating that over geological times, thermally-induced phase transitions enhanced by temperature fluctuations will reform a large fraction of crystalline hydrated sulfuric acid that is destroyed by radiation processing. The work described is the first demonstration of the competition between radiation-induced amorphization and thermally-induced recrystallization in icy ionic solids relevant to the outer Solar System.

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### 1. Introduction

Remote sensing of Jupiter's icy satellites has revealed that even though their surfaces are composed mostly of water ice (Kuiper, 1957; Johnson and McCord, 1971), other molecules also are present, many of which are a consequence of the radiation chemistry induced by the high radiation (Hudson and Moore, 2001; Johnson et al., 2004). For instance,  $\text{H}_2\text{O}_2$  on Europa's surface (Carlson et al., 1999a),  $\text{O}_2$  on Europa, Callisto, and Ganymede (Spencer and Klesman, 2001; Spencer and Calvin, 2002), and  $\text{O}_3$  on the surface of Ganymede (Noll et al., 1996) are all believed to be direct results of the radiolysis of water–ice and its products. In addition, it has been suggested that other detections, such as those of  $\text{SO}_2$ ,  $\text{SO}_4^{2-}$ , or  $\text{CO}_2$ , also could indicate radiolysis. Specifically,  $\text{SO}_2$  (Lane et al., 1981) and/or  $\text{SO}_4^{2-}$  (Strazzulla et al., 2007) can form by implantation of iogenic sulfur and subsequent reactions, while  $\text{CO}_2$  can form via irradiation of water–ice on the surface of carbonaceous material (Hibbitts et al., 2000; Gomis and Strazzulla, 2005).

While radiolysis can produce many of the molecules detected on the surface of the icy satellites, it is not the only way these molecules could have originated. Micrometeorite and cometary impacts could have delivered exogenic material, such as  $\text{CO}_2$  (Hibbitts et al., 2000). A subsurface ocean, proposed to exist not only on Europa (Cassen et al., 1979) but also on Ganymede (McCord et al., 2001) and Callisto (Khurana et al., 1998), may be a source for some of the species detected. Material, possibly organ-

ic, salty, or acidic, could be transported to a surface by a variety of mechanisms (Kargel et al., 2000; Greenburg, 2010). Primordial subsurface  $\text{SO}_2$  (Noll et al., 1995) and  $\text{CO}_2$  (Moore et al., 1999) could also be carried upward by geological processes.

In the absence of sampling missions, laboratory investigations are the surest way to address the chemical details of such issues. However, the continual evolution of icy-satellite surfaces makes their study by laboratory experiments difficult. Temperature is one factor contributing to this difficulty, as it usually varies over latitudinally- and compositionally-dependent diurnal and seasonal time scales. Laboratory studies of radiation processing typically address this complication by determining if the observed radiation-induced chemistry varies over the relevant temperature range (e.g., Moore et al., 2007b). There is also the possibility that some reaction products may only be metastable, and that an increase in temperature could cause them to react or to sublime. This is often recognized and checked by heating an irradiated sample and monitoring any changes that may occur (Moore and Hudson, 2000; Loeffler et al., 2006). It is important to note that since thermally-induced changes depend on both time and temperature, one way to mimic slow processes is to raise a sample to slightly higher temperatures than may seem immediately relevant to the objects under study.

We presently are involved in laboratory investigations to identify and quantify thermal and radiolytic changes involving sulfur-containing molecules and ions at Europa-like temperatures. Our first paper covered radiation–chemical reactions of  $\text{H}_2\text{O} + \text{SO}_2$  ices at 80–132 K, showing the formation of hydronium ( $\text{H}_3\text{O}^+$ ) and sulfate ( $\text{SO}_4^{2-}$ ) ions (Moore et al., 2007b). Warming such irradiated

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ices produced sulfuric acid ( $\text{H}_2\text{SO}_4$ ) or one of its crystalline hydrates, depending on the starting material. In a second study we again examined  $\text{H}_2\text{O} + \text{SO}_2$  ices, but focused on thermally-induced reactions to form  $\text{H}_3\text{O}^+$  and bisulfite ( $\text{HSO}_3^-$ ) ions (Loeffler and Hudson, 2010) in unirradiated ices. Our third investigation of solid  $\text{H}_2\text{O} + \text{SO}_2$  mixtures involved the radiation stability of  $\text{H}_2\text{SO}_4$  and two of its crystalline hydrates,  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ , to quantify their stability on Europa's surface (Loeffler et al., 2011). Lifetimes for each material were determined at various temperatures.

In all such work it is important to distinguish between what is studied in the laboratory and the spectroscopic observations of Europa and their interpretation. Carlson et al. (1999b, 2005) interpreted the positions, shapes, and intensities of  $\text{H}_2\text{O}$ –ice near-IR features in terms of a sulfuric acid hydrate, based on spectral matches with laboratory samples prepared by freezing liquid mixtures. However, this presents something of a paradox since the optical constants used were for crystalline hydrates, yet Jupiter's intense radiation field should amorphize Europa's surface ices. Interestingly, Carlson et al. (2005) most recently noted that the near-IR spectrum of the crystalline sulfuric acid octahydrate ( $\text{H}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$ ) was similar to that of its liquid solution (amorphous analog), suggesting that the sulfuric acid on Europa's surface is likely a combination of both amorphous and crystalline phases. The most straightforward explanation for the possible persistence of crystalline material arises from the heating of the irradiated ices. This agrees with our earlier work in which  $\text{H}_3\text{O}^+$  and  $\text{SO}_4^{2-}$  were produced in  $\text{H}_2\text{O} + \text{SO}_2$  solids that were amorphous before and after ion irradiation, but which crystallized into sulfuric acid hydrates on subsequent warming.

In this paper we take our work a step further. We already have shown that warming irradiated amorphous  $\text{H}_2\text{O} + \text{SO}_2$  solids can form sulfuric acid and crystalline sulfuric acid hydrates, but what of the subsequent fate of such hydrates? Radiolysis will reduce the hydrates infrared absorption bands and in some cases completely destroy them. As mentioned previously (Loeffler et al., 2011), these spectral changes may be due to either radiation-induced amorphization of the sample or destruction of the sulfur species in the samples. Our goal now is to show that subsequent warming of these same irradiated sulfuric acid hydrates will reform much of the hydrate. Using infrared (IR) spectroscopy, we investigate the extent to which radiation-induced amorphization and destruction of solid  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  can be reversed by heating.

In describing our results we employ the term “hydrate” in the strict sense usually employed by chemists, namely to refer to a crystalline material with  $\text{H}_2\text{O}$  molecules making up part of a lattice cell (Xueref and Domine, 2003). Amorphous solids with the same stoichiometry or composition as a crystalline material are not traditionally designated as hydrates, and so we avoid doing so here. We note that “hydrate” has sometimes been used for non-crystalline, amorphous materials for which “wet” might be a better description (Ahlqvist and Taylor, 2002). At other times “hydrate” has been employed for amorphous solids with the same composition as a known crystalline material or from which the later can be formed (Delzeit et al., 1993). The related term “hydrated” also can lead to confusion, as molecules and ions can be “hydrated” yet not be part of a hydrated solid, such as with either common sugar (sucrose) or salt (sodium chloride) dissolved in liquid water. Freezing of such liquid mixtures does not result in pure crystalline single-phase solids with water molecules occupying specific sites within a unit cell. To avoid ambiguity in the present paper, we sometimes use the somewhat redundant “crystalline hydrate”, and follow the practice of Barone et al. (1999) in avoiding “hydrate” when referring to amorphous films.

The formulae used for sulfuric acid hydrates also can lead to confusion. Although we and others use expressions such as  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ , in the presence of  $\text{H}_2\text{O}$  molecules  $\text{H}_2\text{SO}_4$  is a strong acid, readily dissociating into ions. In other words, the crystalline hydrates denoted  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  are not two molecular solids. Crystallographic studies have shown that the monohydrate is actually  $(\text{H}_3\text{O}^+)(\text{HSO}_4^-)$  and  $(\text{H}_5\text{O}_2^+)_2(\text{SO}_4^{2-})$  is the tetrahydrate's composition (Taesler and Olovsson, 1968; Kjallman and Olovsson, 1972). In other words, the monohydrate ice is made of  $\text{H}_3\text{O}^+$  and  $\text{HSO}_4^-$  ions and the tetrahydrate is composed of  $\text{H}_5\text{O}_2^+$  and  $\text{SO}_4^{2-}$  ions. This lends a novelty to the results we now report as essentially all related laboratory studies in the astrochemical literature have been conducted on polar molecular solids, such as frozen  $\text{NH}_3$  (Moore et al., 2007a) or crystalline  $\text{CH}_3\text{OH}$  (Hudson and Moore, 1995), and with most experiments being done on  $\text{H}_2\text{O}$  ice (Baragiola, 2003). What is left open for study are crystalline ionic solids, such as the sulfuric acid hydrates thought to be on Europa's surface, and which are the subject of this paper.

## 2. Experimental methods

All experiments were performed on a thermal-radiation shielded cryostat ( $T_{\text{min}} \sim 10$  K) inside a stainless steel high-vacuum chamber with a base pressure below  $1 \times 10^{-7}$  Torr. Ice samples made of  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  (thickness  $\sim 1$   $\mu\text{m}$ ) were irradiated with 0.8 MeV protons on a gold-coated aluminum substrate to a maximum fluence of  $1.8 \times 10^{15}$   $\text{H}^+/\text{cm}^2$  (or  $\sim 12$  eV/16-amu molecule) at temperatures between 10 and 180 K. Irradiated samples then were warmed at 1–2 K/min to 160–180 (tetrahydrate) and 195 K (monohydrate) while hydrate reformation was monitored from 7000 to 400  $\text{cm}^{-1}$  with a Bruker Vector Fourier Transform infrared spectrometer at 2- $\text{cm}^{-1}$  resolution with 100-scan accumulations. In each case, the intensity ( $I$ ) of the IR beam after passing through the ice and reflecting from the underlying substrate was divided by the intensity of the reflectance ( $I_0$ ) of the substrate alone, measured before the original ice sample was made. The resulting ratio then was converted to absorbance units as  $-\log_{10}(I/I_0)$ . For more details on sample preparation and irradiation see (Loeffler et al., 2011) and references therein.

To quantify the hydrate recovered on heating an irradiated sample, we measured the growth of IR absorptions at 1063  $\text{cm}^{-1}$  (tetrahydrate) and 887  $\text{cm}^{-1}$  (monohydrate). Each band was integrated after subtraction of baselines that best matched the surrounding continuum (Loeffler et al., 2011). Similar to the technique we used earlier, for  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  we simplified the continuum by subtracting the spectrum of the unirradiated sample, which left a baseline that could accurately be removed with a straight line. Likewise, for  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  we fitted the continuum with a non-linear baseline. For each such warming experiment, the fraction of hydrate reformed was calculated by dividing the relevant band area of the hydrate (see earlier) at each temperature by the initial band area obtained from the spectrum of an unirradiated sample either at 160 K (tetrahydrate) or 195 K. We note that the 1063  $\text{cm}^{-1}$  sulfate band remained, albeit weakened, in the tetrahydrate ices irradiated at higher temperatures, and thus the regenerated fraction reported here includes this residual amount.

Finally, we recognize that ices of different thicknesses might have similar compositions yet display different relative IR band areas due to optical interference effects (Maeda and Schatz, 1961; Pacansky and England, 1986; Teolis et al., 2007). For our experiments we estimate that this leads to an uncertainty of 10–15% in the final numerical results. This estimate is based on the shapes of the continuum (overriding interference pattern) and the alteration of other absorption bands in the sample (i.e., the OH stretching features).

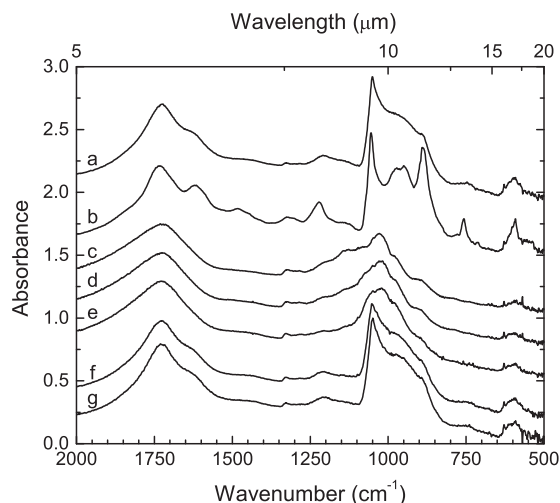
### 3. Results

#### 3.1. Warming of $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$ irradiated at 10 K

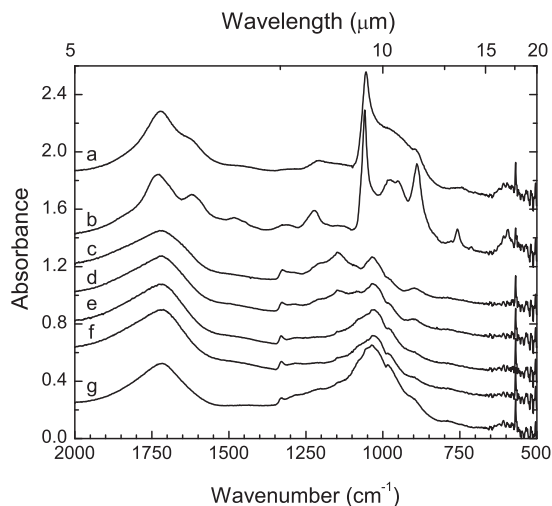
Covalently-bonded molecules exposed to ionizing radiation undergo chemical change. If a collection of such molecules forms either a single crystal or a polycrystalline solid then amorphization also can occur. For relatively simple molecular systems, such as crystalline  $\text{H}_2\text{O}$ -ice, radiation-induced amorphization does not actually produce *pure* amorphous  $\text{H}_2\text{O}$ -ice, but rather a non-crystalline mixture dominated by  $\text{H}_2\text{O}$  molecules and also containing reaction products such as  $\text{H}_2\text{O}_2$  and  $\text{O}_2$ . Similar comments will apply to other crystalline molecular solids, such as  $\text{CH}_3\text{OH}$  and  $\text{NH}_3$ . Radiation-chemical products may or may not be observed, depending on the choice of the analytical technique employed and the reaction conditions, such as temperature and radiation dose.

To illustrate these points, Fig. 1 shows the result of irradiating crystalline  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$  at 10 K. Keeping in mind that  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$  is actually  $(\text{H}_5\text{O}_2^+)_2(\text{SO}_4^{2-})$ , in spectrum (a) the broad feature near  $1724\text{ cm}^{-1}$  is assigned to  $\text{H}_5\text{O}_2^+$ , with a possible contribution from  $\text{H}_2\text{O}$ , and the sharp peak near  $1063\text{ cm}^{-1}$  is assigned to  $\text{SO}_4^{2-}$ , with smaller  $\text{SO}_4^{2-}$  features at  $1216$  and  $600\text{ cm}^{-1}$  (Moore et al., 2007b). Going from spectrum (a) to spectrum (b) corresponds to cooling the unirradiated ice sample from 160 K to 10 K, which results in significant sharpening of the peaks. Spectrum (c) shows that irradiation to a dose of  $1.5 \times 10^{14}\text{ H}^+/\text{cm}^2$  both broadens and reduces these same IR features, an indication of amorphization (e.g., Hudson and Moore, 1995). The ice of spectrum (c) then was warmed at 1 K/min to 160 K, during which spectra (d–g) were recorded. As (a and g) are essentially identical in appearance we conclude that the sample has undergone recrystallization. To our knowledge this is the first demonstration of the recovery of crystallinity in an irradiated ionic solid of this type.

A close inspection of spectrum (c) in Fig. 1 shows that irradiation of the sample produced a few small IR features at  $1400$ – $1000\text{ cm}^{-1}$ . These can, for the most part, be assigned to  $\text{SO}_2$  and  $\text{HSO}_4^-$  (bisulfate) by reference to earlier work (Moore et al., 2007b). These same features are more readily seen in Fig. 2 where spectrum (a) is again  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$  at 160 K and (b) is after cooling to 10 K, but (c) is after a radiation exposure of  $1.8 \times 10^{15}\text{ H}^+/\text{cm}^2$ , ten times larger than in the previous experiment. An absorbance



**Fig. 1.** Infrared spectra of  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$  (a) at 160 K, (b) after cooling to 10 K, (c) after irradiation with  $1.8 \times 10^{14}\text{ H}^+/\text{cm}^2$  at 10 K, and during warming to 160 K at 1 K/min: (d) 99 K, (e) 149 K, (f) 160 K, 0 h and (g) 160 K, 16.6 h. Spectra were translated vertically for clarity.

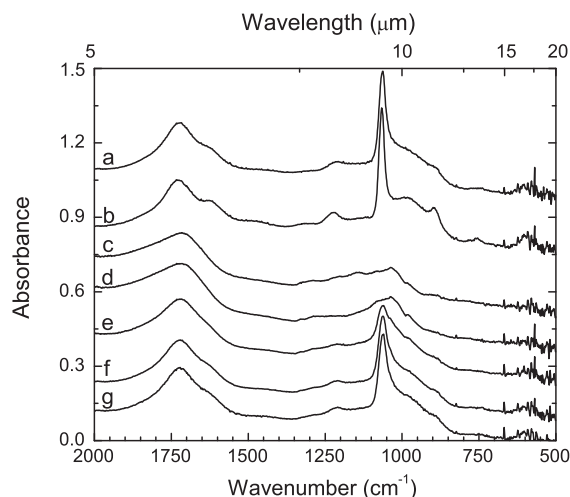


**Fig. 2.** Infrared spectra of  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$  (a) at 160 K, (b) after cooling to 10 K, (c) after irradiation with  $1.8 \times 10^{15}\text{ H}^+/\text{cm}^2$  at 10 K, and during warming to 160 K at 1 K/min: (d) 99 K, (e) 149 K, (f) 160 K, 0 h, and (g) 160 K, 11.6 h. Spectra were translated vertically for clarity.

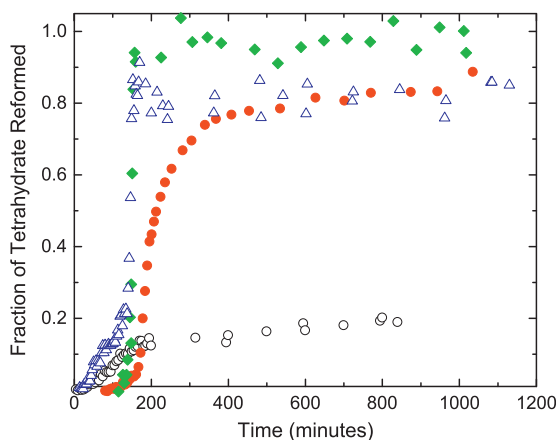
appearing at  $1327\text{ cm}^{-1}$  is assigned to  $\text{SO}_2$ , while the peak near  $1145\text{ cm}^{-1}$  is assigned to  $\text{HSO}_4^-$ , and one around  $783\text{ cm}^{-1}$  is assigned to  $(\text{S}_2\text{O}_3)_x$ . Other  $\text{HSO}_4^-$  bands are difficult to distinguish from the overlapping  $\text{SO}_4^{2-}$  absorption features that remain in the spectrum. Unlike in the previous experiments, no crystallization was seen after warming this more-heavily irradiated ice to 160 K (spectra (d–g)). Clearly the greater dose in this experiment, along with the material lost and the products formed, blocked the tetrahydrate's recovery.

#### 3.2. Warming of $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$ irradiated at 86 K

The two 10-K experiments just described illustrate the interplay of temperature and radiation dose on the amorphization of  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$  at 10 K and the solid's eventual recovery and recrystallization. More important for jovian icy satellites are the irradiations we did at 86 K. Fig. 3a once more shows  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$  at 160 K, but now (b) is after cooling to only 86 K, a temperature found at



**Fig. 3.** Infrared spectra of  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$  (a) at 160 K, (b) after cooling to 86 K, (c) after irradiation with  $1.8 \times 10^{15}\text{ H}^+/\text{cm}^2$  at 86 K, and after warming to 160 K at 1 K/min: (d) 160 K, 0 min, (e) 160 K, 40 min, (f) 160 K, 3.5 h, and (g) 160 K, 14 h. Spectra were translated vertically for clarity.



**Fig. 4.** Reformation of  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$  during warming to 160 K at 1 K/min. Symbols represent the sample after irradiation to  $1.8 \times 10^{15} \text{ H}^+/\text{cm}^2$  at 10 K ( $\circ$ ), 86 K ( $\bullet$ ), 120 K ( $\blacklozenge$ ), and after irradiation to  $1.8 \times 10^{14} \text{ H}^+/\text{cm}^2$  at 10 K ( $\triangle$ ). Curves for higher irradiation temperatures have been shifted so that all samples reach 160 K at  $t = 150$  min, where after the samples remained at 160 K. Note the final data point for the 86 K curve (1034.6 min) is after warming to 180 K; further waiting gave sublimation of  $\text{H}_2\text{O}$ , decreasing the tetrahydrate's abundance.

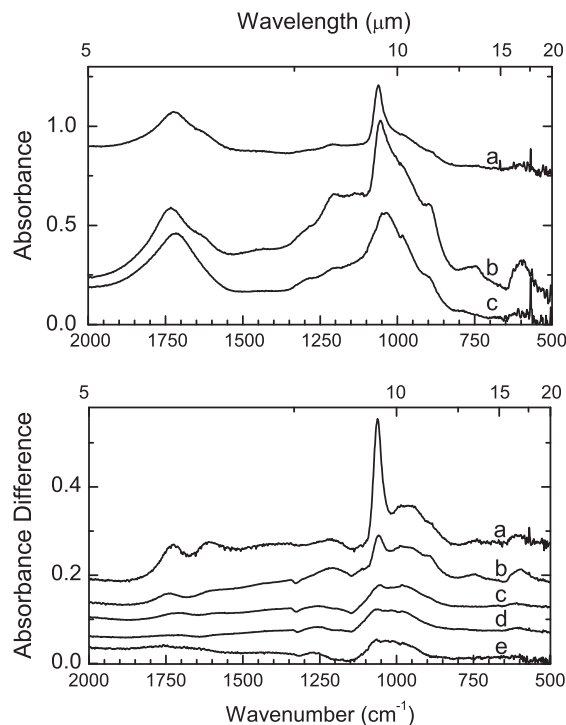
Europa. Ion irradiation of the sample to  $1.8 \times 10^{15} \text{ H}^+/\text{cm}^2$  gave spectrum (c), once more showing that amorphization occurred. Lower doses gave a similar result. A new observation, illustrated in spectra (d–g), is that unlike the 10-K experiments of Fig. 2 in this one at 86 K the crystalline ionic starting material was recovered on rewarming to 160 K. Spectra (a and g) are nearly indistinguishable, both being dominated by the sharp  $\text{SO}_4^{2-}$  peak near  $1063 \text{ cm}^{-1}$  and the broad  $\text{H}_3\text{O}_2^+$  feature near  $1724 \text{ cm}^{-1}$ . The recovery of  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$  on warming was nearly complete for this 86-K irradiation as well as for those done with lower doses at this same temperature (spectra not shown).

Fig. 4 quantifies these experiments and others by showing the recovery of  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$  following irradiations at several temperatures, and for two different doses at 10 K. It is seen that the higher the irradiation temperature, the greater was the final recovery of the crystalline solid. For the two 10-K experiments, the larger the radiation dose, the smaller was the fraction of  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$  recovered on warming. In all of these experiments, the recovery of crystalline material was measured by integration of the sulfate band at  $1063 \text{ cm}^{-1}$ .

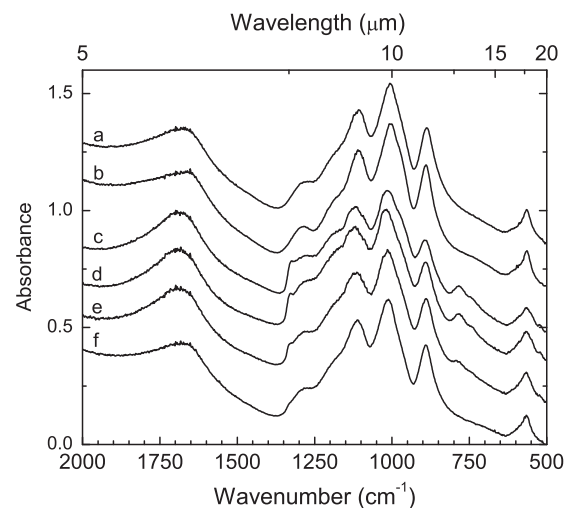
Fig. 5 represents a different experiment from those already presented. Since ion irradiation of  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$  to  $1.8 \times 10^{15} \text{ H}^+/\text{cm}^2$  at 10 K destroyed some of the original material present, including  $\text{H}_2\text{O}$  and related ions, and post-irradiation warming failed to regenerate the original crystalline acid hydrate (Fig. 2), we suspected that adding new  $\text{H}_2\text{O}$ –ice to the irradiated sample might assist in hydrate recovery (recrystallization). Fig. 5 shows that this indeed occurred. Depositing  $\text{H}_2\text{O}$  ( $\sim 1.8 \mu\text{m}$ )<sup>1</sup> on an  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$  ice irradiated at 10 K caused the tetrahydrate absorption's area at  $1063 \text{ cm}^{-1}$  to increase during warming by a factor of  $\sim 2.5$  (Fig. 5b) with respect to Fig. 2 (or Fig. 5c).

### 3.3. Warming of irradiated $\text{H}_2\text{SO}_4\cdot \text{H}_2\text{O}$

The majority of the experiments described in this paper are for the tetrahydrate of sulfuric acid, but a few were done with sulfuric acid monohydrate. Fig. 6, spectrum (a), shows the IR spectrum of  $\text{H}_2\text{SO}_4\cdot \text{H}_2\text{O}$  at 195 K and (b) shows the effect of cooling to 86 K. An absorption near  $1665 \text{ cm}^{-1}$ , which is a combination of the



**Fig. 5.** Top: Infrared spectra of  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$  (a) after irradiation at 86 K and warming to 180 K, (b) after irradiation at 10 K, warming to 70 K and depositing  $1.8 \mu\text{m}$  of water ice, and warming to 180 K, and (c) after irradiation at 10 K and warming to 180 K. Bottom: absorbance difference spectra (absorbance spectra minus absorbance spectrum after irradiating sample to  $1.8 \times 10^{15} \text{ H}^+/\text{cm}^2$ ): (a, b, and c) are the same spectra as in the top panel, while (d and e) are the samples shown in (a and c) right after they reached 160 K. We note that in the bottom panel, (b, c, and d) were also divided by 5 so that all spectra could be easily compared. Spectra were translated vertically for clarity.



**Fig. 6.** Infrared spectra of  $\text{H}_2\text{SO}_4\cdot \text{H}_2\text{O}$  (a) at 195 K before irradiation, (b) after cooling to 86 K, (c) after irradiation with  $1.8 \times 10^{15} \text{ H}^+/\text{cm}^2$ , and after warming to 195 K at 2 K/min: (d) 195 K, 0 min, (e) 195 K, 10 min, and (f) 195 K, 120 min. Spectra were translated vertically for clarity.

bending modes of  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{O}$ , and features at  $1295$ ,  $1108$ ,  $887$ , and  $566 \text{ cm}^{-1}$  from  $\text{HSO}_4^-$  (bisulfate) are observed. The main changes seen after irradiation were a decrease in the bisulfate features, an increase in the  $1665 \text{ cm}^{-1}$  band, and the appearance of  $\text{SO}_2$  ( $1327 \text{ cm}^{-1}$ ) and a broad absorption at  $785 \text{ cm}^{-1}$ , likely from  $(\text{S}_2\text{O}_3)_x$  (Hopkins et al., 1973). The remaining spectra show the result of warming this same irradiated sample from 86 to 195 K.

<sup>1</sup> We deposited water at 70 K, because this thickness deposited at 10 K typically caused our ices to crack, which significantly diminished their optical quality.

Interestingly, the new IR features produced by the irradiation disappeared and the  $\text{HSO}_4^-$  bands increased, such that the heated sample's spectrum closely resembled that of the original unirradiated ice, as shown by a comparison of spectra (a and f) in Fig. 6. Measurements of the  $887\text{-cm}^{-1}$  band's area showed that the monohydrate's abundance rose from 0.5 to 0.85 during heating (compare spectra (c and f)). We note that for irradiations above 86 K the amount of monohydrate regenerated was similar to what was observed at 86 K, but for irradiations at 10 K the amount regenerated was slightly lower (going from 0.4 to 0.7).

#### 4. Discussion

In judging the extent to which our results apply to icy satellites, it is important to document the conditions for the thermal recovery of sulfuric-acid hydrates, particularly how the extent of recovery depends on the irradiation temperature. For this we will focus on our results from  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$  as the majority of the temperature dependence observed in the  $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$  experiments was within the range of our experimental uncertainty (see Section 3).

Figs. 1c and 3c are spectra of  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$  ices proton irradiated at 10 K and 86 K, respectively, and then warmed to 160 K. These traces show that heating gave nearly identical growth in the broad  $\text{SO}_4^{2-}$  absorption near  $1063\text{ cm}^{-1}$ . This indicates that at least some of the destroyed crystalline sulfuric acid tetrahydrate reformed in each case. However, Fig. 2 shows that warming tetrahydrates ices irradiated at 10 K to a higher dose than in Fig. 1, but the same as Fig. 3, failed to produce crystallization. Thus, post-irradiation warming caused  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$  to reform in all of our samples except some of those irradiated at 10 K, a temperature far below those found on Europa.

The lack of recrystallization we observed in some of our irradiated 10-K ices is reminiscent of our earlier work on irradiated crystalline methanol,  $\text{CH}_3\text{OH}$  (Hudson and Moore, 1995). There we described how the build-up of radiation products, such as ethylene glycol, would prevent crystallization from occurring among the remaining  $\text{CH}_3\text{OH}$  molecules, through disruption of the requisite crystalline lattice. A related study of irradiated ammonia,  $\text{NH}_3$ , showed a delay of crystallization, again caused by product formation (Zheng et al., 2008). Comparing the  $1400\text{--}1000\text{ cm}^{-1}$  regions of Figs. 1c and 2c, both 10-K experiments, one finds different product yields, and that the greater product yield of Fig. 2c was for the ice that never recrystallized on warming.

Somewhat more difficult to explain are the differences due solely to temperature, such as the experiments of Fig. 2 (10 K) and Fig. 3 (86 K) where the two ices received the same radiation dose. Figs. 2c and 3c clearly show that the latter, at 86 K, possessed the smaller abundance of reaction products, and thus that ice's recrystallization was expected. However, specific thermodynamic or kinetic reasons for lower product yields are unknown. The radiation products may simply be more likely to revert back to the starting material ( $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$ ) at the higher temperature

due to the great ease of surmounting the relevant activation barrier. Alternatively, the products at 86 K may be rapidly converted to chemical species that undergo sublimation or segregation within the ice at that same temperature, so that crystallization would be essentially unaltered. Such would also explain why amorphization was slower at the higher temperatures, a result seen previously by us (Moore and Hudson, 1992) and others (Strazzulla et al., 1992; Mastrapa and Brown, 2006).

For Fig. 2 we note that the lack of tetrahydrate recovery after prolonged 10-K irradiations might also have been seen at 86 K had a higher radiation dose been used there. We also suspect that this same lack of recrystallization to produce  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$  after a 10-K irradiation (Fig. 2) was related to the fact that samples held at the higher temperatures lost water by sublimation before crystallization could occur. Water loss is important as it would prevent the recovery of the sample's original 1:4 stoichiometry for pure  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$ , and likely lead to a mixture of  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ , composed of  $\text{H}_5\text{O}_2^+$ ,  $\text{H}_3\text{O}^+$ ,  $\text{HSO}_4^-$ , and  $\text{SO}_4^{2-}$ . This hypothesis is supported by our experiment showing that  $\text{H}_2\text{O}$  deposited on a sample after a 10-K irradiation increased the tetrahydrate band at  $1063\text{ cm}^{-1}$  by a factor of 2.5 (compare Fig. 5b and c). It is possible that even more of the tetrahydrate could have been recovered if after depositing  $\text{H}_2\text{O}$  we had warmed the sample more slowly or kept the sample at a lower temperature (e.g., 140–150 K), where excess  $\text{H}_2\text{O}$  would sublimate more slowly.

To summarize, our laboratory work shows that irradiated  $\text{SO}_2$  on Europa's  $\text{H}_2\text{O}$ -rich surface will be oxidized to  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$ , and then undergo crystallization on warming, forming a sulfuric acid hydrate. Subsequent irradiation will certainly amorphize the hydrate, but additional heating will recrystallize it. Thus, we suspect that Europa's surface will likely consist of hydrated sulfuric acid in both amorphous and crystalline phases, in agreement with Carlson et al. (2005). Although we have focused our discussion here on  $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$ , we expect that similar comments will apply to other hydrates of sulfuric acid, such as the hemihydrate ( $\text{H}_2\text{SO}_4\cdot 6.5\text{H}_2\text{O}$ ) and octahydrate ( $\text{H}_2\text{SO}_4\cdot 8\text{H}_2\text{O}$ ), both of which are believed to be present on Europa's surface (Carlson et al., 1999b, 2005).

Fig. 7 represents the chemical changes in the  $\text{H}_2\text{O} + \text{SO}_2$  ices we have studied to date. The two arrows on the far right, and adjacent to one another, are for the two transformations described in this paper. Warming an amorphous irradiated  $\text{H}_2\text{O} + \text{SO}_2$  mixture (central rectangle) produces hydrated sulfuric acid or pure sulfuric acid, depending mainly on the amount of water present. With additional irradiation the resulting solid will amorphize and decompose into molecules ( $\text{SO}_2$ ,  $(\text{S}_2\text{O}_3)_x$ ) and ions ( $\text{H}_3\text{O}^+$ ,  $\text{HSO}_3^-$ ,  $\text{HSO}_4^-$ ,  $\text{SO}_4^{2-}$ ), with a composition that depends on the irradiation temperature (Loeffler et al., 2011). Warming these amorphous irradiated samples, as evidenced by the present work, will cause the hydrate(s) to reform in nearly the same abundance as originally present. The net result will be their persistence over geological times.

Finally, although many of the main chemical and physical changes occurring in  $\text{H}_2\text{O} + \text{SO}_2$  ices are now known, their connec-

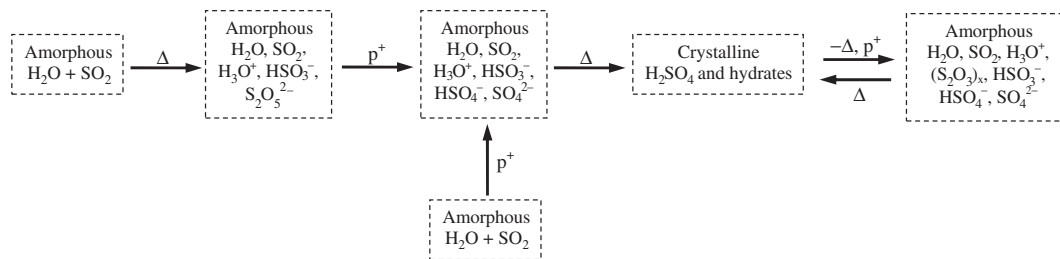


Fig. 7. Sulfur species observed from thermal and radiolytic chemistry in  $\text{H}_2\text{O} + \text{SO}_2$  ices.

tions to specific geological processes require further study. The effects observed in this study and in our previous work on forming the crystalline hydrates occur at higher temperature than the temperatures reported for Europa. However, crystallization should also take place after long periods at lower temperatures, such as 130 K, or by local warming (Rathbun et al., 2010). Alternatively, amorphized Europa surface material could move downward toward a warmer sub-surface ocean, recrystallize, and then be transported upwards again. Details of such geological processes remain to be determined.

## 5. Conclusions

We have presented new results on the reformation of crystalline  $\text{H}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4\cdot \text{H}_2\text{O}$  hydrates irradiated with 0.8 MeV protons. In all cases, post-irradiation heating caused an increase in intensity in the IR features of the hydrates, by an amount that depended on the irradiation temperature and dose. At the lower irradiation temperatures (10 K), the lower recovery can be explained by the crystallization process occurring more slowly than the sublimation of  $\text{H}_2\text{O}$ -ice. At the warmer irradiation temperatures ( $T \geq 86$  K), relevant to Europa and the warmer jovian satellites, the thermal regeneration of the hydrate absorption features was nearly 100% efficient, which suggests that over geological times thermally-induced phase transitions enhanced by temperature variations will regenerate a large fraction of the crystalline sulfuric-acid hydrates destroyed by on-going radiation processes.

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