



Thermal regeneration of sulfuric acid hydrates after irradiation

Mark J. Loeffler*, Reggie L. Hudson

Astrochemistry Laboratory, NASA Goddard Space Flight Center, Mail Code 691, Greenbelt, MD 20771, United States

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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, H_2O_2 on Europa's surface (Carlson et al., 1999a), O_2 on Europa, Callisto, and Ganymede (Spencer and Klesman, 2001; Spencer and Calvin, 2002), and 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 SO_2 , SO_4^{2-} , or CO_2 , also could indicate radiolysis. Specifically, SO_2 (Lane et al., 1981) and/or SO_4^{2-} (Strazzulla et al., 2007) can form by implantation of iogenic sulfur and subsequent reactions, while 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 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 SO_2 (Noll et al., 1995) and 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 (H_3O^+) and sulfate (SO_4^{2-}) ions (Moore et al., 2007b). Warming such irradiated

* Corresponding author. Fax: +1 301 286 0440.

E-mail address: mark.loeffler@nasa.gov (M.J. Loeffler).

ices produced sulfuric acid (H_2SO_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 H_3O^+ and bisulfite (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 H_2SO_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 H_2O –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 H_3O^+ and 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 H_2O 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 H_2O molecules H_2SO_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 H_3O^+ and HSO_4^- ions and the tetrahydrate is composed of H_5O_2^+ and 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 NH_3 (Moore et al., 2007a) or crystalline CH_3OH (Hudson and Moore, 1995), and with most experiments being done on H_2O 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 1×10^{-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 ~ 1 μm) were irradiated with 0.8 MeV protons on a gold-coated aluminum substrate to a maximum fluence of 1.8×10^{15} H^+/cm^2 (or ~ 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 cm^{-1} with a Bruker Vector Fourier Transform infrared spectrometer at 2- 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 cm^{-1} (tetrahydrate) and 887 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 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).

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