

Giant-planet chemistry: Ammonium hydrosulfide (NH₄SH), its IR spectra and thermal and radiolytic stabilities



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ABSTRACT

Here we present our recent studies of proton-irradiated and unirradiated ammonium hydrosulfide, NH₄SH, a compound predicted to be an important tropospheric cloud component of Jupiter and other giant planets. We irradiated both crystalline and amorphous NH₄SH at 10–160 K and used IR spectroscopy to observe and identify reaction products in the ice, specifically NH₃ and long-chained sulfur-containing ions. Crystalline NH₄SH was amorphized during irradiation at all temperatures studied with the rate being the fastest at the lowest temperatures. Irradiation of amorphous NH₄SH at ~10–75 K showed that 60–80% of the NH₄⁺ remained when equilibrium was reached, and that NH₄SH destruction rates were relatively constant within this temperature range. Irradiations at higher temperatures produced different dose dependence and were accompanied by pressure outbursts that, in some cases, fractured the ice. The thermal stability of irradiated NH₄SH was found to be greater than that of unirradiated NH₄SH, suggesting that an irradiated giant-planet cloud precipitate can exist at temperatures and altitudes not previously considered.

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1. Introduction

1.1. Background

Theoretical models predict Jupiter's clouds to be mainly NH₃, H₂O, and NH₄SH condensates (Weidenschilling and Lewis, 1973), with NH₄SH believed to come from a thermal reaction between the NH₃ and H₂S that have been detected in the atmosphere (Atreya et al., 1997). Ammonium hydrosulfide (NH₄SH) is also predicted to be an important cloud component of the other giant planets (e.g., Atreya et al., 1999; Roman et al., 2013).

Adequate consideration of NH₃, H₂O, NH₄SH, and their reaction products as contributors to jovian clouds and aerosols and other giant-planet atmospheres requires laboratory studies on these compounds under relevant conditions. However, although ices made of H₂O, NH₃, and mixtures of the two have been studied extensively (e.g., Moore et al., 2007), far less work has been done with NH₄SH. The latter is not commercially available, being unstable to dissociation into NH₃ and H₂S at 298 K. It usually is synthesized through



at low temperatures, but the two reactants are toxic, odiferous, and somewhat detrimental to laboratory equipment, perhaps explaining the lack of attention paid to NH₄SH by experimentalists.

Vapor pressure measurements of NH₄SH were first reported by Isambert (1881), a melting point was published by Briner (1906), and crystallographic studies were done by West (1934). The first published infrared (IR) spectra of solid NH₄SH were from Bragin et al. (1977), who identified the strongest mid-IR absorptions as being near 3000, 1830, 1400, and 470 cm⁻¹ (~ 3.3, 5.5, 7.1, and 21 μm) for the crystalline solid near 100 K. A different NH₄SH ice was reported to have broad IR absorptions, and subsequent work by Ferraro et al. (1980) identified this solid as amorphous NH₄SH, with the amorphous-to-crystalline phase change being near 160 K. Nearly 30 years later the IR optical constants of NH₄SH were published by Howett et al. (2007). Work in other spectral regions is limited to the electronic spectra of Lebofsky and Fegley (1976), who reported that the ultraviolet–visible reflectance spectrum of NH₄SH is relatively featureless and flat, albeit with a slight rise from 300 to 1000 nm (slight red slope).

Ices made only of pure NH₃, H₂S, and NH₄SH lack strong absorptions in the visible region and cannot be the source of jovian colors. However, since Jupiter's atmosphere is subject to energetic particle bombardment and solar-UV photolysis, all cloud components will undergo chemical changes with possible alterations of color, and

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such changes lend themselves to laboratory experiments. Indeed, conference abstracts highlighting such work are available spanning 30 years (Bragin and Chang 1976; Huntress and Anicich, 1984; Delitsky and Baines 2007), but detailed studies of solid NH_4SH in the refereed literature are surprisingly scarce, and one still encounters publications calling for new investigations into the chemistry of NH_4SH (e.g., de Pater et al., 2001; Howett et al., 2007) and the $\text{NH}_3 + \text{H}_2\text{S}$ system (Wong et al., 2015).

The most-relevant laboratory work on NH_4SH chemistry is from Lebofsky and Fegley (1976), who photolyzed ices made of NH_3 , H_2O , H_2S , and NH_4SH at 77 K with a filtered xenon lamp, whose output at 220–300 nm served as an analog to the solar flux. Reflectance spectra from 300 to 1000 nm of NH_3 and H_2O hardly changed with photolysis, but a strong absorption was produced near 600 nm for H_2S and NH_4SH ices and was assigned to sulfur radicals. In addition, photolysis changed the nominally featureless reflection spectra of H_2S and NH_4SH to spectra that sloped downward from 700 to 300 nm, suggesting an absorber outside the range of wavelengths studied. No temperature variations or kinetic studies were reported.

In addition to the lack of relevant laboratory work, many of the relevant observational spectra are derived from the Hubble Space Telescope images that have a gap near the 600-nm absorption (Strycker et al., 2011), making comparisons to laboratory spectra even more difficult. At the least this all suggests that a much more detailed study of NH_4SH and its thermal, photochemical, and radiation chemical stabilities is warranted, keeping in mind that multiple components may be needed explain the color variations observed in Jupiter's atmosphere (Simon-Miller et al., 2001; Strycker et al., 2011).

1.2. Our approach

This paper describes our recent laboratory work focused on NH_4SH , particularly its IR spectra and reaction chemistry. A novelty of our approach is its use of radiation-chemical methods. Whitten et al. (2008) suggested that jovian clouds will be altered more by cosmic rays than solar photons since the latter will not penetrate deeply into the atmosphere. Therefore, to initiate reactions in NH_4SH we use ionizing radiation in the form of ~ 1 MeV protons (p^+), which are an analog to the low-energy, and more-abundant, cosmic rays. To first order the products of UV-photochemistry and radiation chemistry are the same (e.g., Hudson and Moore, 2001; Baratta et al., 2002), but our radiation-chemical approach permits the use of thicker samples than in conventional photochemistry, which in turn allows the detection of weaker IR features.

Some topics of specific interest here are the possible persistence of IR absorptions of NH_4SH after proton bombardment, the temperature dependence of any such spectral features, and whether assignments can be made to IR absorptions of chemical products. Here we present results on both of the reported phases of NH_4SH under vacuum from 10 to over 200 K. During the radiation experiments, each sample was monitored with IR spectroscopy and mass spectrometry to determine stability and chemical change as a function of temperature and radiation dose. The results of such measurements can serve as an important link between the IR region, which is sensitive to chemical composition and phase, and the ultraviolet-visible observations of Jupiter.

2. Experimental

Much of the experimental approach is as described in Loeffler et al. (2011), but a few points require additional comments.

2.1. Equipment and synthetic methods

Gases used (and purities) to prepare and study NH_4SH were NH_3 from Matheson (99.9992%), $^{15}\text{NH}_3$ from Cambridge Isotopes (98%+), and H_2S from Matheson (99.5%). All reagents were used as received. Indices of refraction (n) were needed to calculate thicknesses of samples made from these reagents. For NH_3 , we used $n = 1.48$ from Romanescu et al. (2010) and $n = 1.49$ for H_2S (liquid, Weast et al., 1984). Thicknesses of ice samples were 1.2 μm unless otherwise stated and were calculated from densities of 0.81 g cm^{-3} for NH_3 and 1.17 g cm^{-3} for H_2S and an assumption of uniform mixing.

Experiments were performed with a stainless steel high-vacuum chamber ($P < 1 \times 10^{-7}$ Torr) interfaced with a cryostat ($T_{\text{min}} \sim 10$ K) and gas-handling system. Ammonium hydrosulfide (NH_4SH) was synthesized *in situ* by co-deposition of H_2S and NH_3 gases from two separate lines onto a pre-cooled (10–90 K) substrate attached to the cryostat's cold-finger. The deposition rate of each gas was calibrated as in Loeffler et al. (2011) to ensure that the initial composition of each ice was known. Although a 1:1 stoichiometric ratio applies for the reaction $\text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g}) \rightarrow \text{NH}_4\text{SH}(\text{s})$, an initial ratio closer to 1.2:1 = $\text{NH}_3:\text{H}_2\text{S}$ was found to minimize the excess reactants for a mixture deposited at 50 K. Substrates made of unpolished aluminum, gold-coated unpolished aluminum, and gold-coated polished aluminum were used, with only the last one being considered optically flat. The spectra of Fig. 1 were recorded on the gold-coated polished aluminum substrate, but all others shown were with a gold-coated unpolished aluminum substrate. In general, the results in this paper were independent of the substrate employed.

After deposition of the reactant gases, the resulting solid-phase mixture was warmed to 120 K at 2 K min^{-1} to obtain amorphous NH_4SH and to 155 K to obtain a crystalline sample. Crystallization of NH_4SH began near 130 K, and sublimation into the vacuum occurred in a few minutes at 170 K. These temperatures were somewhat sensitive to the substrate's cleanliness, so after each radiation experiment the substrate was wiped with CS_2 to remove any sulfur residue that may have formed, followed by wiping with acetone. Material, if any, released from ices during irradiation was monitored with a Dycor DM300 mass spectrometer, with a dwell time of 120 ms on each peak selected. Samples prepared for irradiation were grown at 90 K to minimize the

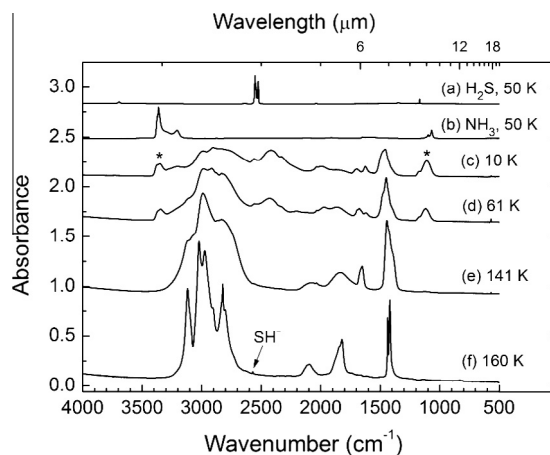


Fig. 1. Reference spectra of (a) H_2S and (b) NH_3 ices deposited at 50 K compared to spectra of a $\text{H}_2\text{S} + \text{NH}_3$ (1:1) mixture (c) deposited at 10 K and then (d)–(f) warmed to 160 K at 2 K min^{-1} . The spectra of the H_2S and NH_3 samples have been scaled by 0.25. The 141 K spectrum corresponds to amorphous NH_4SH and that at 160 K to crystalline NH_4SH . Asterisks (*) indicate features from NH_3 . Spectra in this and other figures have been offset for clarity.

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