

LABORATORY STUDIES OF THE FORMATION AND STABILITY OF HYDRATES RELEVANT TO ICY SURFACES. R. L. Hudson^{1,2} and M. H. Moore^{2,3}, ¹Department of Chemistry, Eckerd College, St. Petersburg, FL 33733, USA (hudsonrl@eckerd.edu), ²Goddard Center for Astrobiology, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA, ³Code 691, Astrochemistry Branch, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA (Marla.H.Moore@nasa.gov).

Introduction: Ices on planetary satellites of the outer Solar System are characterized by a variety of compositions, temperatures, and radiation environments. However, the dominance of H₂O in many ices suggests that this molecule strongly influences the chemistry and the spectroscopy of all other observed materials. It further suggests that the formation of hydrates and hydrated ions may be common.

Two molecules to which these ideas might apply are SO₂ and NH₃, both of which are observed in the outer Solar System. For SO₂, the application is to Europa, where the intense jovian magnetospheric radiation can convert SO₂, in the presence of H₂O-ice, into a variety of sulfur-containing ions. The overall amorphous structure for such a mixture will slowly convert, on warming, into that of a crystalline hydrate, with a yield that is balanced by the radiolytic destruction of the hydrates themselves as part of a sulfur cycle. Beyond Jupiter, NH₃ is thought to exist on Miranda, Charon, and Quaoar, a possible source being cryomagma brought up to cold surfaces where it is quenched. For these latter three objects, the radiation environments are less intense and the temperatures lower than near Jupiter, but hydrates might still form and undergo radiation-induced chemical changes. In all cases, thermal processing might still promote dehydration of SO₂- and NH₃-hydrates on surfaces. Unfortunately, significant gaps exist in our knowledge of hydrate formation, stability, and chemistry for the

relevant physical conditions.

Results: To study all of these processes, we have prepared H₂O-rich mixtures of both SO₂ and NH₃ in order to investigate their thermal and chemical stability and evolution in high-radiation environments, such as icy moons of the outer Solar System [1], [2]. For Europa applications, we have recorded the mid-infrared spectra of 0.8 MeV proton-irradiated SO₂ and H₂O + SO₂ ices in order to measure the radiolytic half-life of SO₂ itself, as well as to identify radiation products. Formation of several sulfur-containing ions has been documented and, on warming the irradiated ices, hydrated sulfuric acid was observed. The thermal evolution of the hydrate in a vacuum is one of slow H₂O loss to yield pure sulfuric acid. As an example, Figure 1(a) is the IR spectrum of H₂O + SO₂ (3:1) after irradiation to a dose of 15 eV molec⁻¹ at 86 K. Spectrum (a) evolves with warming, as shown. Reference spectrum (d) is for crystalline H₂SO₄ monohydrate, H₂SO₄ • H₂O, at 210 K [3]. These spectra have different scaling factors, as indicated, and are stacked for clarity. By 260 K, the monohydrate has evolved into sulfuric acid, with the spectrum of trace (f).

We also have completed low-temperature IR spectroscopic studies (1 to 20 μm) of H₂O + NH₃ mixtures, with an emphasis on features in the near-IR region, which is accessible to ground-based observers. Conditions for the formation and thermal stability of the

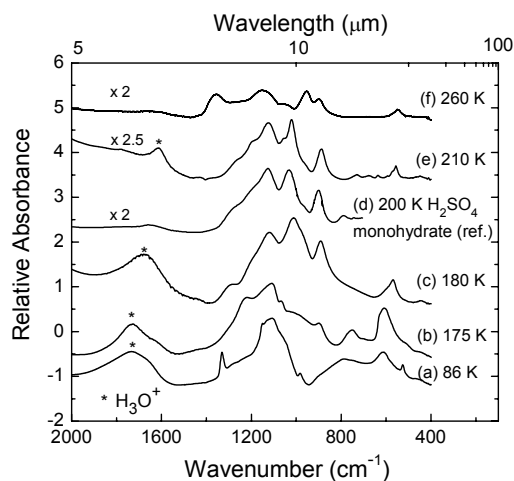


Figure 1

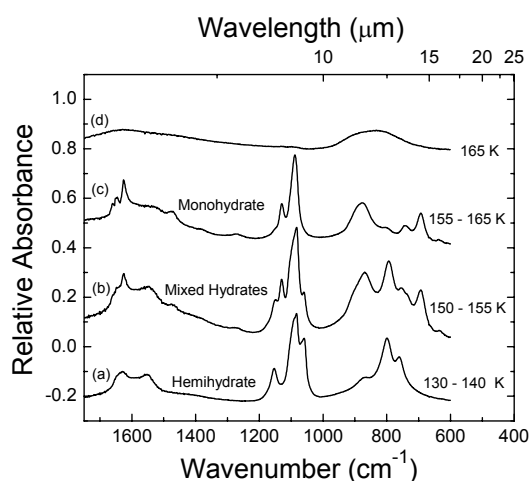


Figure 2

ammonia hemihydrate ($2\text{NH}_3\cdot\text{H}_2\text{O}$) and the ammonia monohydrate ($\text{NH}_3\cdot\text{H}_2\text{O}$) have been examined. The former undergoes a slow loss of NH_3 in a vacuum environment, to give the monohydrate. Figure 2 shows this thermal evolution of $2\text{NH}_3\cdot\text{H}_2\text{O}$ from trace (a) to a mixture of $2\text{NH}_3\cdot\text{H}_2\text{O}$ and $\text{NH}_3\cdot\text{H}_2\text{O}$ hydrates in (b), and then to (c) after a complete the conversion to $\text{NH}_3\cdot\text{H}_2\text{O}$. Additional warming removes the remaining NH_3 to give spectrum (d), which is characteristic of H_2O -ice. Again, spectra are stacked for clarity.

IR band positions of both SO_2 and NH_3 in different H_2O -ices have been tabulated at 86 K and higher, and compared to the positions for SO_2 and NH_3 hydrates. We report spectral shifts that depend on both concentration and temperature. The radiation-induced amorphization of hydrates was observed and the radiolytic destruction of SO_2 and NH_3 in H_2O -ices was measured. We also have tabulated IR spectral positions of sulfur- and nitrogen-containing ions. Implications of these results for the formation, stability, and detection of SO_2 and NH_3 on outer satellite surfaces will be discussed.

References: [1] Moore, M. H., Hudson R. L., Carlson, R. W., 2007. The radiolysis of SO_2 and H_2S in water ice: Implications for the icy jovian satellites. *Icarus* (in press). [2] Moore, M. H., Ferrante, R. F., Hudson R. L., Stone, J. N., 2007. Ammonia-water ice laboratory studies relevant to outer Solar System surfaces. *Icarus* (in press). [3] Couling, S. B., Nash, K. L., Fletcher, J., Henderson, A., Vickerman, J. C., Horn, A. B., 2003. Identification of surface molecular hydrates on solid sulfuric acid films. *J. Amer. Chem. Soc.* 125, 13038-13039.