Far Ultraviolet Spectroscopy and Photochemistry of Sulfur Dioxide/ Water Ice Mixtures. Robert Hodyss, Paul V. Johnson, and Stephen M. Meckler, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA. (Robert.P.Hodyss@jpl.nasa.gov)

Introduction: Sulfur dioxide's presence on the trailing hemisphere of the Europan surface is well established, and both its presence and its chemistry are thought to be driven by sulfur ion implantation [1]. Traditionally, particle irradiation is considered the significant radiolysis source, for the mean ultraviolet (UV) solar flux at wavelengths applicable to water chemistry is orders of magnitude lower than the magnetospheric flux [2]. However, longer wavelength solar radiation provides a very large flux across Europa's surface, around 4.0×10^{15} eV cm^{-2} s^{-1} between 100 and 280 nm (Fig. 1), compared to a global average of 8×10^{13} eV cm^{-2} s^{-1} from particle irradiation [3]. The photochemistry at longer wavelengths is less well studied. These wavelengths, here modeled as 147 nm, 206 nm, and 254 nm, represent a significant radiation flux with the potential for interesting sulfur/water chemistry.

Sulfur dioxide possesses a strong UV absorption at 280 nm, leading to the possibility for electronic excitation from this UV absorption to result in significant photochemistry.

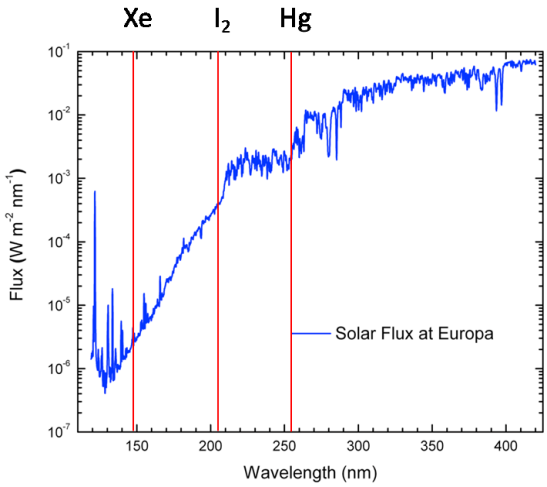

Figure 1. Solar photon flux at Europa as a function of wavelength, with the wavelength of the photolysis lamps superimposed.

In this work we sought to spectrally characterize chemical changes in thin, cryogenic films of SO_2 and SO_2/H_2O at temperatures relevant to Europa's surface when subjected to temperature changes and UV fluxes at 147 nm, 206 nm, 254 nm and 280 nm. Spectra were collected in both the mid IR range, suitable for measuring chemical changes, and the UV range, which elucidates electronic transitions that are less diagnostic but more applicable to reflectance spectra of solar system bodies.

Experimental: Ice films are cooled on a CaF_2 window cooled by a closed cycle He refrigerator (ARS 202B). The temperature of the window is monitored with a Si diode thermometer affixed to the window frame. The thickness of the ice film is monitored during growth by laser interferometry and was approximately 0.3 μm. The deposition rate was ~0.3 μm/h. Where appropriate, the samples were left to equilibrate for 5 minutes at the temperature of interest before spectra were taken. H_2O and SO_2 were premixed manometrically into 1 L glass bulbs prior to deposition

IR spectra were recorded in transmission with a Nicolet 6700 FTIR spectrometer, at a resolution of 2 cm^{-1}. Each spectrum is the result of 2000 co-added single scan spectra. UV spectra were recorded with a Ocean Optics fiber spectrometer, with scan times of 0.4 to 1.2 seconds. Each UV spectrum is the result of 25 to 35 co-added single scan spectra.

UV irradiation of the ice samples was performed with a xenon, iodine, or mercury lamp connected to an Opthos microwave generator. Figure 2 compares these wavelengths to the absorption spectra of SO_2. 280 nm radiation was generated with a filtered Xe arc lamp.

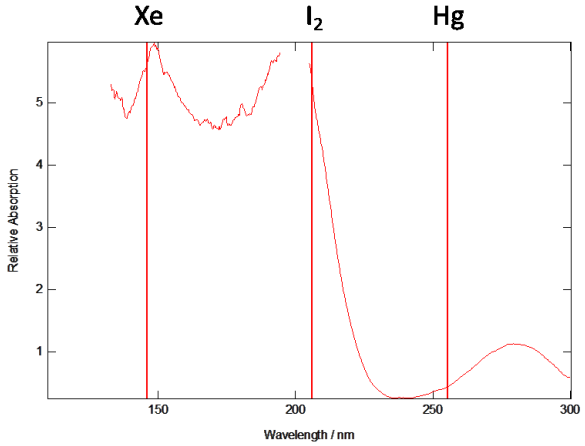

Figure 2. VUV absorption spectrum of a solid SO_2 ice film, with the wavelengths of the photolysis lamps superimposed.

Results and Discussion. Figure 3 shows the ultraviolet absorption spectrum of a 5% SO_2/H_2O ice at 12K and 125 K. The peak of the absorption wavelength is strongly affected by temperature. Figure 4 plots the peak absorption wavelength as a function of temperature for an ice which has been warmed to 100

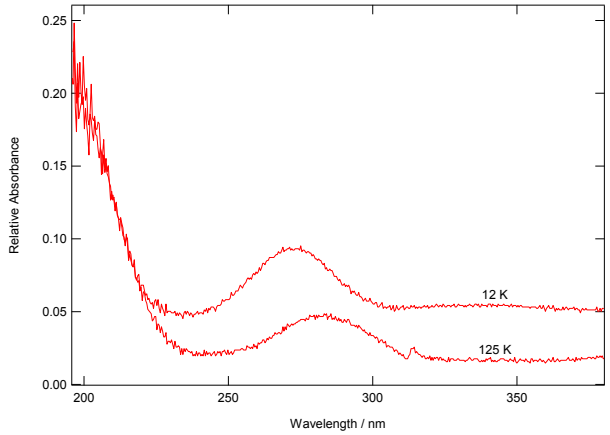

Figure 3. UV absorption spectrum of a 5% SO_2/H_2O ice film at 12 K and 125 K. The peak absorption wavelength shifts significantly as function of temperature.

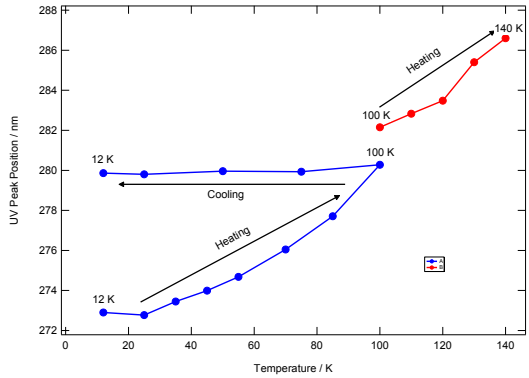

Figure 4. Peak position of the 280 nm absorption band in 5% SO_2/H_2O ice as a function of wavelength for two thermal paths. Peak position is linear with temperature above ~30 K, and is irreversible on later cooling.

K from 12 K, and then cooled back to 12 K. The change in peak absorption wavelength is irreversible. This change may be a result of cryistallization of the ice film at higher temperature, or due to the formation of sulfur oxyanions through reaction of sulfur dioxide with water at higher temperatures [4].

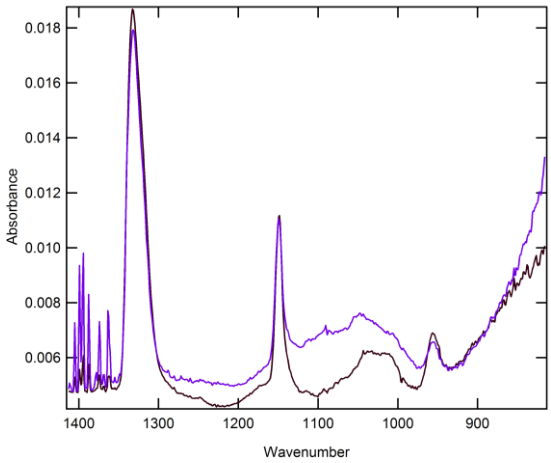

Figure 5. IR absorption spectra of a 5% SO_2/ H_2O ice film at 100K, showing the formation of photochemical products after irradiation with 280 nm photons.

Figure 5 compares the mid-infrared spectrum of a 5% SO_2 ice film at 100 K (black) to the same film after irradiation at 280 nm (purple). The decrease in the strength of the SO_2 bands and growth of absorbance at 1100 cm^{-1} indicates the formation of photochemical products.

Conclusions:

1. Irradiation at 147, 206, 254 and 280 nm all produce similar photochemical products.
2. When coupled with significant solar flux at longer wavelengths, substantial photochemical reaction on laboratory timescales at 206 and 280 nm suggests that ultraviolet photolysis at these wavelengths is a major, and possibly dominant, driver of SO_2 chemistry on Europa.
3. The position of the 280 nm SO_2 absorption is irreversibly temperature dependent, and may useful as a thermometer on Europa's surface.

Acknowledgement: Financial support through NASA's Outer Planets Research Program is gratefully acknowldeged.

References: [1] Lane et al. *Nature*, Vol. 292, pp. 38-39. [2] Pappalardo et al. *Europa*, The University of Arizona Press, Tucson, 2009, pp. 287 [3] Madey et al. *Surface Science* 500, 838-858. [4] Loeffler et al., GRL 37, L19201.