ELECTRON IRRADIATION OF METHANE AND METHANE/WATER ICES AT 20 K THROUGH 100 K.

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Introduction: Active geological processes on the seafloors of ocean worlds are expected to produce methane gas which can then become entrained in materials during the ascent and eruption at the icy surface [e.g., 1]. Exposure to particle irradiation at the surface will chemically alter these materials and can produce more complex molecules [2–4]. Understanding the reaction pathways of materials irradiated at the surfaces of these worlds is important for the interpretation of the geological evolution of these bodies and the availability of reactants for chemical evolution of surface materials.

CH_4 is an alteration product released during the serpentinization reaction and may be produced at the seafloor of ocean worlds such as Enceladus or Europa [5]. It may also be retained from initial formation [5] or produced from biological sources [6]. To investigate the possibility of methane ice undergoing irradiation and chemical alteration at the surface of icy ocean worlds, we performed environmental chamber experiments focused on $^{12}CH_4$ and $^{13}CH_4$ at a variety of temperatures and studied the molecules produced after irradiation by a 10 keV electron source.

Methods: Measurements were performed using the Minos ultra-high vacuum experiment chamber in the Ocean Worlds Laboratory at the Jet Propulsion Laboratory. This chamber has been described in detail previously [3]. A closed-cycle He cryostat cooling system controls the temperature of a coldfinger that supports a gold mirror substrate at its end. The sample gases were vapor-deposited onto this substrate which was held at cryogenic temperatures. The chamber was operated nominally at an ultra-high vacuum of 10^{-8} torr. A Fourier transform infrared spectrometer measured the samples from 2.6 μm to 15 μm. A beam current of 500 nA was used to irradiate the samples.

Results: Our experiments of irradiation of $^{12}CH_4$ generated chemical products including ethane, ethylene, and propane, matching previous experiments [2,7]. Irradiation of pure $^{13}CH_4$ produced similar products, but with the spectral position of the peaks shifted as a result of the heavier carbon atoms. Representative absorbance spectra of these two phases are presented in **Figure 1**. The slow warming of these methane ices leads to a complete loss of spectral features by 50 to 60 K.

Preliminary results from the investigation of methane retention at elevated temperatures under water ice generates absorbance spectra that appear to retain very weak, but present, methane absorption features up to 100 K. Products resulting from the irradiation of the methane at 100 K are much reduced in variety and intensity from the irradiation at colder temperatures. At 100 K, the products largely consist of $^{13}CO_2$ and an additional species bearing a carbon pi bond. A spectral feature indicative of radiation-formed $^{13}CO_2$ is presented in **Figure 2**.

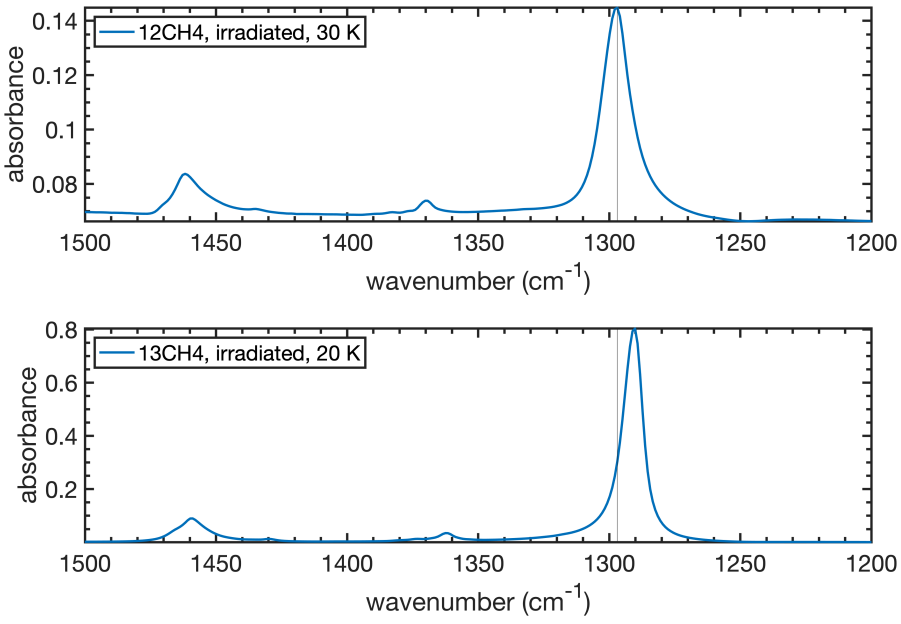

Figure 1: Mid-infrared absorbance spectra of (top) $^{12}CH_4$ and (bottom) $^{13}CH_4$ at 30 and 20 K, respectively, after 2 hours of irradiation by 10 keV electrons at 500 nA. Note the shifting absorption peaks as exemplified by the shifting ν_4 fundamental near 1300 cm^{-1}.

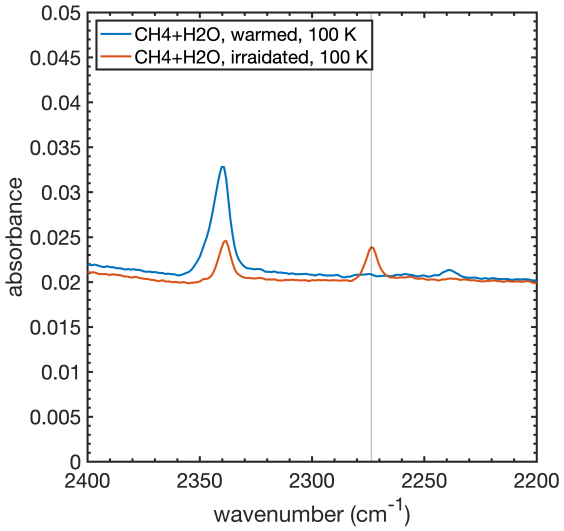

Figure 2: Mid-infrared absorbance spectra of a layer of $^{13}CH_4$ with a layer of H_2O deposited on top at 20 K. The sample was subsequently warmed to 100 K and irradiated by 10 keV electrons at 500 nA. An absorbance spectral feature of $^{13}CO_2$ appears at 2273 cm^{-1} following the application of the radiation field.

Future Work: Experiments are ongoing in this investigation of methane-bearing ices at temperatures elevated above the stability field of methane ice. These results demonstrate that simply because a specific surface may not have the temperature or pressure conditions favorable for particular molecules, processes may have occurred or be occurring throughout a body's structure or history that entrench exotic molecules or phases in materials that are comparatively more stable. These processes may lead to molecules of astrobiological interest being present on the surfaces of oceans worlds throughout the Solar System.

References: [1] Waite J. H. et al. (2017) Science, 356, 155–159. [2] Bennett C. J. et al. (2006) ApJ, 653, 792. [3] Hand K. P. and Carlson R. W. (2011) Icarus, 215, 226–233. [4] Hand K. P. and Carlson R. W. (2012) JGR: Planets, 117. [5] Mousis O. et al. (2009) ApJ, 701, L39. [6] Taubner R. S. et al. (2018) Nat. Commun., 9, 1–11. [7] Gerakines P. A. et al. (1996) Astron. Astrophys., 312, 289–305.