Visible and near infrared reflectivity of solid and liquid methane: application to hydrocarbon lakes on Titan.

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Introduction: Methane is abundant on icy bodies in the solar system including Pluto [1,2] and Triton [3,4,5] as identified in observational spectra from characteristic absorption bands at around 1.7 and 2.3 µm. The physical state of CH_4 and other hydrocarbons in the solar system, however, cannot be interpreted from the positions of absorption bands alone. Recent discoveries of lakes on Titan from the *Cassini* mission come from interpreting a compelling combination of low-lying and flat surfaces measured by Radar [6,7] and corresponding dark features observed by infrared (IR) reflectivity [8]. Interpretation of recent and forthcoming mission observations of planetary bodies requires laboratory-based reflectance spectroscopy of planetary ices and liquids at relevant temperatures, especially to distinguish states of surface phases.

Low-temperature IR-absorption measurements of methane-ice have been made for CH_4-I from 30-90K, CH_4-II at 20K, and liquid methane at 93 K between 0.7 and 5 µm [9]. Because the nitrogen-rich atmosphere of Titan contains 1-4 mol% of CH_4 [10,11], even surface observations of IR-reflectivity within the critical 1.6, 2.0, and 5 µm transparency windows of Titan's atmosphere [8] prevent using the positions of characteristic absorption bands of methane or other hydrocarbons to identify the states of material. Motivated by the dark regions in the northern and southern latitudes of Titan corresponding to low-lying and flat Radar features suggesting lakes, we have undertaken laboratory reflectivity measurements of solid and liquid states of methane at relevant temperatures for Titan's surface.

Methods: In the current experiments, we used a diamond-anvil cell as an optical sample holder to contain the methane sample. Prior to loading methane in the cell, a small ruby was placed in the sample chamber to act as a pressure marker during the experiments using laser-excited ruby fluorescence [12].

The methane-filled DAC was loaded into a helium-cooled cryostat on the U2A beamline of the NSLS, Brookhaven National Laboratory. IR-reflectivity measurements were made at 5-10 K temperature increments between 100 and 50 K, with two measurements for methane in the liquid phase, and seven spectra in the solid phase (Figure 1).

Reflectiviy Measurements: The optical experiments performed at NSLS were made on a Bruker IFS 66v/S Fourier transform infrared (FTIR) spectrometer using a mid-band MCT IR-detector and a custom-built, confocal microscope with all-reflecting optics. IR measurements were acquired between 0.91 and 3.84 µm. Visible reflectance was obtained using a tungsten lamp source, Princeton Instruments spectrograph and N_2-cooled visible CCD detector, between 0.4 and 1.09 µm.

For the visible and IR-measurements at each temperature, and before focusing the light onto the sample, the intensity from the air-diamond interface (I_d) was measured. Intensities from the sample diamond interface (I_{sd}) were normalized to I_d to correct for the decaying storage-ring current between electron injections of the VUV ring at NSLS. The reflectivity of the sample-diamond interface (R_{sd}) was further treated for optical properties of the cell following previous procedures [13] with:

$$R_{sd}(\lambda) = \frac{I_{sd}}{I_e}\frac{I_d}{I_0} \qquad (1)$$

Where I_{sd} is the intensity reflected from the sample-diamond interface, I_e is the intensity reflected from the culet of an empty cell, I_d is the intensity reflected from the air-diamond interface, and I_0 is the source intensity, approximated by the measured power reflected from a gold foil. The ratio I_d/I_0 is the reflectivity of the diamond anvil window, and found to be approximately 0.18 ($\pm$0.01) over the wavelength range of 0.5-2.5 µm from many individual measurements on the U2A beamline at NSLS. The ratio I_e/I_d gives the power reflected from the diamond culet as $I_e = 0.65I_d$, and was found to be constant over the current wavelength range of 1-2.5 µm. Substituting $I_e = 0.65I_d$ into equation (1), gives:

$$R_{sd} = \frac{I_{sd}}{0.65I_d} \cdot 0.18 \qquad (2)$$

where I_{sd} and I_d were measured at every temperature and as a function of wavelength in the visible through near-IR. Whereas we cannot obtain the reflectivity of the methane sample against air in this experimental setup, equation (2) provides an adequate way of determining the relative change in reflectivity of solid versus liquid methane at temperatures relevant to the surface of Titan.

Results: Near-IR reflectivity of solid and liquid methane from 50-100 K are shown in Figure 1. Consistent with previous absorption measurements [9] we observe three sharp absorption bands at 1.6-1.8 µm and three sharp absorption bands at 2.2-2.4 µm. The positions of these absorption bands do not vary systematically with state (solid versus liquid) or tempera-
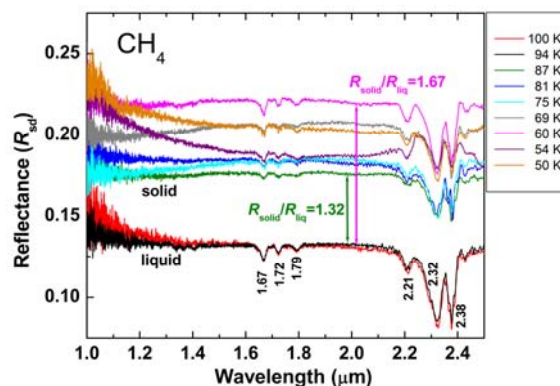
ture. However, between 87 and 94 K, the reflectivity of methane dramatically decreases upon transition from the solid to the liquid state. At 2 μm, $R_{sd} = 0.175$ for solid methane at 87 K (green spectrum in Figure 1), decreasing to $R_{sd} = 0.132$ for liquid methane at 94 K (black spectrum in Figure 1). The ratio, $R_{solid}/R_{liquid} = 1.32$ at these temperatures represents the minimum contrast between liquid and solid CH_4 at 2 μm. Although the broad reflectivity values of liquid methane between 1.6 and 2.5 μm do not vary systematically with temperature, the maximum contrast was observed between the spectrum of liquid CH_4 at 94 K and solid CH_4 at 60 K, with $R_{sd} = 0.22$ (pink spectrum in Figure 1). The contrast between liquid methane at 94 K and solid methane at 60 K is $R_{solid}/R_{liquid} = 1.67$.

The visible reflectance of solid and liquid methane is shown in Figure 2. In the visible region, interference fringes resulting from reflections within the diamond-anvil cell were observed for the liquid state, but are minimal upon transition to solid methane between 87 and 94 K, perhaps by scattering from the grain boundaries observed. For the purpose of estimating R_{solid}/R_{liquid} at visible wavelengths, we fitted polynomial curves through the data to approximate the value of R_{sd} (solid curves in Figure 2). Similar to the near-IR results, we observe a decrease in the sample reflectance at the diamond interface (R_{sd}) in going from solid to liquid. The visible reflectance at 87 K for solid methane is 0.232, and decreases to 0.183 for liquid methane at 94 K. The contrast at 87-94 K between solid and liquid methane is $R_{solid}/R_{liquid} = 1.27$, similar to the near-IR results.

Discussion: Our measured values of liquid methane reflectance at 94 K and linear brightness profiles through VIMS images of Titan's northern lake agree to within a few percent. We therefore conclude that observed solid/liquid reflectance ratios of CH_4 at Titan's surface temperatures are consistent with the hydrocarbon lake observations from VIMS. Because the dominant compound in Titan's lakes is likely ethane with minor amounts of methane [8] , similar experiments on ethane and ethane-methane mixtures are underway.

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Figure 1: Near-IR reflectance of methane at the sample-diamond interface (R_{sd}) as a function of temperature. Spectra obtained at 100 and 94 K are from the liquid phase and at 87 K and below the sample was single-crystal CH_4. The ratio of reflectance of the solid phase to the liquid phase was 1.32-1.57 indicating a significant darkening of liquid methane at 2 μm.
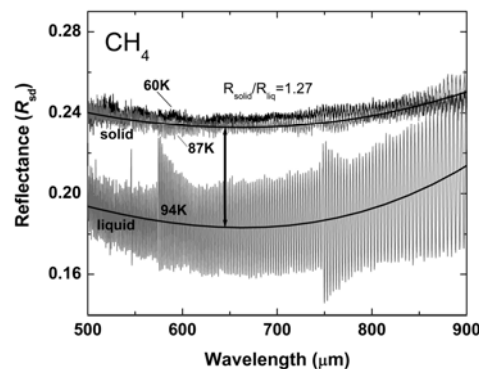
Figure 2: Visible reflectance of methane at the sample-diamond interface (R_{sd}) as a function of temperature. The solid curves show a polynomial fit to the data, from which we infer a ratio of R_{solid}/R_{liquid} of about 1.27 at 0.65 μm between 94 and 87 K.