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Absorption coefficients of the methane–nitrogen binary ice system: Implications for Pluto

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ABSTRACT

The methane–nitrogen phase diagram of Prokhvatilov and Yantsevich (1983. Sov. J. Low Temp. Phys. 9, 94–98) indicates that at temperatures relevant to the surfaces of icy dwarf planets like Pluto, two phases contribute to the methane absorptions: nitrogen saturated with methane $\overline{N_2}$:CH_4 and methane saturated with nitrogen $\overline{CH_4}$:N_2. No optical constants are available so far for the latter component limiting construction of a proper model, in compliance with thermodynamic equilibrium considerations. New optical constants for solid solutions of methane diluted in nitrogen (N_2:CH_4) and nitrogen diluted in methane (CH_4:N_2) are presented at temperatures between 40 and 90 K, in the wavelength range 1.1–2.7 μm at different mixing ratios. These optical constants are derived from transmission measurements of crystals grown from the liquid phase in closed cells. A systematic study of the changes of methane and nitrogen solid mixtures spectral behavior with mixing ratio and temperature is presented.

1. Introduction

Pluto, Eris, and Makemake, unlike most trans-Neptunian objects (TNOs) with water–ice rich or featureless surfaces (Barucci et al., 2008), display infrared spectra dominated by methane ice (Brown, 2008). These three TNOs are often compared with Neptune's large satellite Triton, since its spectrum is dominated by methane ice and it is thought to have formed similarly to Pluto, Eris, and Makemake, prior to its capture into a retrograde orbit around Neptune. In addition to methane ice, nitrogen ice has been directly detected on Pluto and Triton via the 2.148-μm absorption band (Cruikshank et al., 1984; Owen et al., 1993). Additional evidence for nitrogen ice on Pluto and Triton comes from shifts of their methane absorption bands to shorter wavelengths, which occurs, as described by Quirico and Schmitt (1997), when methane is dissolved at low concentrations in a matrix of solid nitrogen. Moderately high signal-to-noise spectra of Makemake and Eris show no evidence for the presence of the 2.148-μm nitrogen absorption feature. Their methane bands do present subtle shifts, albeit smaller than the shifts measured in spectra of Pluto and Triton. A laboratory study by Brunetto et al. (2008) showed that smaller shifts correspond to higher methane abundances. The lack of the 2.15-μm nitrogen absorption band and the smaller methane wavelength shifts led several authors (Brown et al., 2007; Alvarez-Candal et al., 2011; Merlin et al., 2009) to the conclusion that Eris and Makemake are not nitrogen dominated, contrary to Pluto and Triton.

Thermodynamic equilibrium dictates that if methane and nitrogen ices are both present, for most of the range of possible nitrogen/methane relative abundances, two distinct phases must coexist at temperatures relevant to the surfaces of these icy dwarf planets (Prokhvatilov and Yantsevich, 1983; Lunine and Stevenson, 1985): methane ice saturated with nitrogen and nitrogen ice saturated with methane.

Tegler et al. (2010) demonstrated that the depth of the methane and nitrogen absorption bands and the wavelength shift of the observed methane absorption features should not be used as proxy for the methane–nitrogen mixing ratio. The phase composition as dictated by thermodynamic equilibrium must be taken into account. In particular, Tegler et al. (2010) model each of the observed methane absorption bands with a binary mixture of methane ice saturated with nitrogen and nitrogen ice saturated with methane, according to the methane–nitrogen phase diagram of Prokhvatilov and Yantsevich (1983). This technique, applied so far to the cases of Eris and Pluto only, results in the finding that the bulk volatile composition of Eris is similar to that of Pluto, with both objects being dominated by nitrogen ice. A correct modeling

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of the methane absorption bands has strong implications not only on the methane–nitrogen mixing ratio, but also enables exploration of stratification properties as well as heterogeneity of these targets (Tegler et al., 2010, 2012). Because of the lack of absorption coefficients for methane saturated in nitrogen and for nitrogen saturated in methane at the appropriate temperatures in the visible wavelength ranges, Tegler et al. (2010) approximate the methane-dominated phase by using pure methane absorption coefficients and the highly diluted phase by shifting pure methane coefficients by amounts seen for highly diluted samples (Quirico and Schmitt, 1997).

In this paper we provide optical constants in the wavelength range 1.1–2.7 μm of solid solutions of methane diluted in nitrogen, N_2:CH_4, and nitrogen diluted in methane, CH_4:N_2, at temperatures between 40 and 90 K and at different mixing ratios (http://www2.lowell.edu/users/grundy/abstracts/2015.CH4+N2.html), allowing a proper model to be constructed for any TNO where the methane/nitrogen ratio falls between the two solubility limits such that both saturated phases are present. Gaining more detailed knowledge of the methane/nitrogen mixing ratio and phase state of Pluto, Triton, Eris, and Makemake will enable a better understanding of the processes responsible for volatile loss and retention on TNOs (Schaller and Brown, 2007). It will also help constrain the seasonal behaviors of their atmospheres, supported by vapor pressure equilibrium with surface ices. It will also shed light on the photolytic and radiolytic chemistry that can occur within the surface ices, since radicals produced by energetic radiation will encounter and react with different molecules within a nitrogen-dominated or a methane-dominated solid phase.

2. Laboratory experiments

The experiments reported here were conducted in a new laboratory ice facility located in the Department of Physics and Astronomy of Northern Arizona University. A detailed description of this facility is given by Tegler et al. (2010, 2012) and Grundy et al. (2011). We used the closed cell technique for the ice sample preparation. This technique consists in the growth of crystals from the liquid phase in a closed cryogenic cell. Crystals are grown as follows. The sample is prepared in gas form in a 2 liter mixing volume. Here we report experiments obtained mixing methane (CH_4) and nitrogen (N_2). The purities of the gases used are 99.999% for CH_4 and 99.9% for N_2, as reported by the vendors. The gas is set to flow into an empty cell, which is at a temperature slightly higher than the melting point of the ice sample. In the case of mixtures, the melting point depends on the mixing ratio of the gases and we use, as reference, the CH_4–N_2 phase diagram of Prokhvatilov and Yantsevich (1983). The gas, once in the cell, condenses immediately to liquid. The liquid is frozen by reducing the temperature in the cell at a rate of 0.1 K min^{-1}. A thermal gradient is maintained within the cell with the top and bottom heaters such that the crystal grows from the bottom to the top. Once the sample is frozen, the vertical thermal gradient is minimized. After the initial ice spectrum is recorded, the temperature is ramped down at 0.1 K min^{-1}. We recorded spectra at temperatures between 40 and 90 K.

A 5 mm cell, with sapphire (Al_2O_3) windows, was used (Fig. 1). Thinner samples, needed in the case of mixtures with high CH_4 content, were prepared by use of a transparent potassium bromide (KBr) or calcium fluoride (CaF_2) spacer between the windows. These KBr and CaF_2 spacers occupied only part of the cell, enabling the choice of the full or reduced thickness, simply by moving the sample relative to the spectrometer beam. The thickness of the sample in absence of spacer is equal to the cell depth, $d = d'$, which is known. On the other side of the cell, due to the uncertainties on the depth of the KBr and CaF_2 spacers, the sample has an unknown thickness, $d = d''$. This is computed with a liquid CH_4 experiment. Two transmission spectra are recorded, T' and T'', by positioning the spectrometer beam away and in correspondence of the spacer, respectively. From the two transmission spectra, we compute the imaginary part of the refractive index, k' and k'', which will be function of d' and the unknown d'', respectively. Because the imaginary part of the refractive index, k, is a property intrinsic to the material, we compute d'' by setting $k' = k''$ (see Section 3).

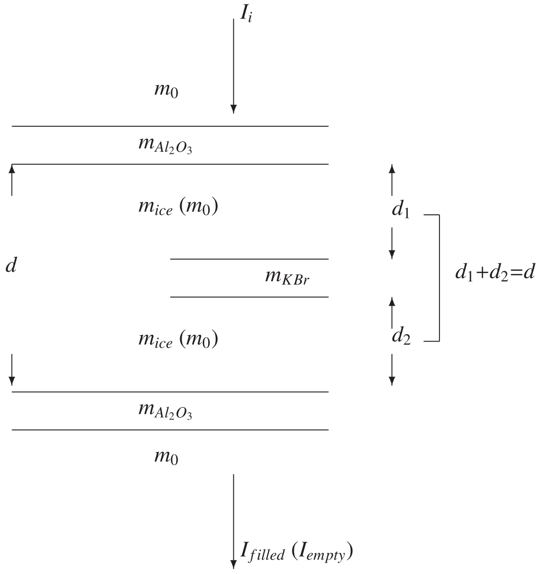

Fig. 1. Schematic view of the cell interior. See text for details. The incident radiation I_i is transmitted through media of different refractive index m. I_{empty} and I_{filled} represent the transmitted radiation when the cell is empty (the vacuum m_0 is between the sapphire windows $m_{Al_2O_3}$, and the potassium bromide spacer m_{KBr}) and filled by the sample (m_{ice}), respectively.

Spectra were recorded with a Nicolet Nexus 670 Fourier transform infrared (FTIR) spectrometer, covering the range 2799.9–12000.1 cm^{-1} at a sampling interval of 0.24 cm^{-1}, resulting in a spectral resolution of 0.6 cm^{-1} (FWHM of unresolved lines). We averaged over 100 spectral scans to improve the signal-to-noise ratio.

3. Data analysis

3.1. Calculation of n and k

The purpose of our measurements is to compute optical constants of methane–nitrogen ice mixtures, CH_4–N_2. The optical constants of a material are the real and imaginary part of the complex refractive index $m(\nu) = n(\nu) + ik(\nu)$, and are both functions of the frequency ν. Let $T(\nu)$ be the transmission spectrum of an ice sample within a cell of thickness d (Fig. 1), we compute the imaginary part of the refractive index, k, via the Beer–Lambert absorption law:

$$k(\nu) = -\frac{1}{4\pi\nu d}\ln T(\nu). \tag{1}$$

In order to remove the flux distribution of the illumination source, the transmission function of the spectrometer and the cell, the detector spectral sensitivity function, and the water vapor contamination (Grundy and Schmitt, 1998; Tegler et al., 2012), we compute the transmission spectrum $T(\nu)$ as:

$$T(\nu) = \frac{T_{filled}(\nu)}{T_{empty}(\nu)}, \tag{2}$$