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Laboratory study of the IR spectra of methane ices in the polar environment

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Abstract. We grew the pure methane ice and mixed binary ices of methane with polar molecules: water, carbon dioxide, methanol and ammonia under ultrahigh vacuum cryogenic conditions similar to those in cold prestellar clouds. The composition of ices was chosen to reflect current astrochemical notions. The following interstellar ice analogues were obtained: $H_2O : CH_4 = 10 : 1$, $CO_2 : CH_4 = 5 : 1$, $CH_3OH : CH_4 = 2 : 1$, $NH_3 : CH_4 = 1 : 1$, that are new to the literature and infrared spectra ice analogues databases. We report the significance of deposition temperature for the internal structure of ices, which gets revealed on infrared spectra during the warm up for ices deposited at 6.7 K and 10 K. We link the observed differences to solid methane being in amorphous phase ($T < 9.3$ K) and low-temperature crystalline ($9.3 \text{ K} < T < 20$ K) phases. We also note that the direct comparison between laboratory and observational spectra is possible since the deformation mode line shape doesn't depend on the grain size or shape near 7.7 μm, only on the temperature and molecular environment. Solid methane is a fairly abundant molecule in prestellar objects. With the James Webb Space Telescope (JWST) launch the quality of spectra has risen significantly and we hope that this work will be an asset to assigning the methane component in star-forming regions.

Keywords: ISM: molecules, clouds, lines and bands; infrared: ISM; methods: laboratory: solid state; astrochemistry

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1 Introduction

Dark cold clouds include matter in gaseous and solid phases. The solid phase includes silicate or carbon dust particles with a frozen component in the form of an ice mantle. The composition of the condensed phase on the surface of dust particles is considered to be partially determined. The main component of ice mantles is water, followed by carbon monoxide, carbon dioxide, methanol, ammonia, methane, etc (Boogert et al. 2015; McClure et al. 2023).

The object of our study is the deformation mode region of methane, which has an absorption band of 1300 cm^{-1} (7.7 μm) in the mid-IR range. For a qualitative description of this region, spectra of mixtures with methane were obtained for the first time at deposition temperatures below 10 K, which corresponds to the phase of amorphous methane. The importance of using the previously little-studied amorphous phase of methane to identify it on observational data is also demonstrated, since only the crystalline phases of methane and band strengths are currently used in the literature. We also found differences in the shape of methane bands in mixtures with water, carbon dioxide, methanol and ammonia.

2 Experiment

Experiments are performed using Ice Spectroscopy Experimental Aggregate (ISEAge). This installation is used to grow analogues of interstellar ice. In the main chamber, the Ge window mounted on a cryogenic holder can be cooled to a temperature as low as 6.7 K and the ultra-high vacuum (up to 2×10^{-10} mbar) is maintained. To check the purity of the studied substances and to control their quantitative content in the main chamber, the ISEAge setup is equipped with a quadrupole mass spectrometer SRS RGA 200. Transmittance IR spectra are acquired using the Thermo Scientific Nicolet iS50 FTIR spectrometer in the range between 4000 cm^{-1} and 630 cm^{-1} (2.5 μm and 15.9 μm) with 1 cm^{-1} resolution.

We obtained the reference laboratory spectra of methane in various polar molecular environments to describe the observational region near 7.7 μm. Methane was codeposited for 120 minutes with polar molecules: water, carbon dioxide, methanol and ammonia.

Methane has three phases: high-temperature (above 20 K), amorphous (below 10 K) and low-temperature (10–20 K) (Gerakines & Hudson 2015). Therefore, the mixtures were obtained at temperatures corresponding to the amorphous and low-temperature phases of methane, 6.7 K and 10 K respectively. The rate of methane deposition was 5.9×10^{12} cm^{-2} s^{-1}, which corresponds to a column density on the line of sight of 4.25×10^{16} cm^{-2} in all experiments. Methane was supplied from the same leak valve across all experiments, that valve was opened first, then the valve with the second component, a polar molecule, was opened. As a result, two ice components were deposited together on the substrate. The obtained profiles of the absorption band of methane deformation mode in the case of pure matter and in mixtures are shown in Fig. 1. The obtained spectra are an average of 45 seconds (an average of 32 scans).

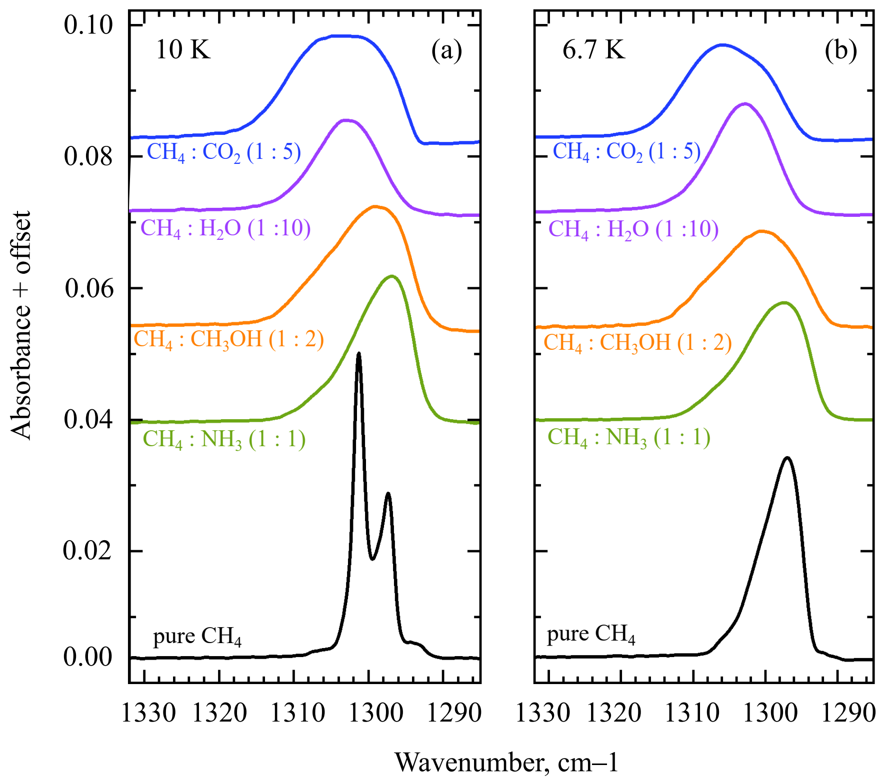

Fig. 1. Laboratory specta of solid pure methane and methane mixed with polar molecules. Panel (a): 10 K and panel (b): 6.7 K.

3 Summary

In this study, we present the reference laboratory spectra in the 7.7 μm region that is commonly assigned to methane deformation mode in different environments. The main results are summarised as follows.

1. For the first time we carried out the experiments in which the IR spectra of methane in mixed ices at temperatures below 10 K were obtained.
2. We report significant differences in line shape and peak position of 1300 cm^{-1} methane band in mixtures with polar molecules.
3. The obtained IR data can be used directly for comparison with the IR data of JWST.

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