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Cryogenic absorption cells operating inside a Bruker IFS-125HR: First results for $^{13}CH_4$ at 7 μm

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ABSTRACT

New absorption cells designed specifically to achieve stable temperatures down to 66 K inside the sample compartment of an evacuated Bruker IFS-125HR Fourier transform spectrometer (FTS) were developed at Connecticut College and tested at the Jet Propulsion Laboratory (JPL). The temperature stabilized cryogenic cells with path lengths of 24.29 and 20.38 cm were constructed of oxygen free high conductivity (OFHC) copper and fitted with wedged ZnSe windows using vacuum tight indium seals. In operation, the temperature-controlled cooling by a closed-cycle helium refrigerator achieved stability of ±0.01 K. The unwanted absorption features arising from cryodeposits on the cell windows at low temperatures were eliminated by building an internal vacuum shroud box around the cell which significantly minimized the growth of cryodeposits. The effects of vibrations from the closed-cycle helium refrigerator on the FTS spectra were characterized. Using this set up, several high-resolution spectra of methane isotopologues broadened with nitrogen were recorded in the 1200–1800 cm^{-1} spectral region at various sample temperatures between 79.5 and 296 K. Such data are needed to characterize the temperature dependence of spectral line shapes at low temperatures for remote sensing of outer planets and their moons. Initial analysis of a limited number of spectra in the region of the R(2) manifold of the ν_4 fundamental band of $^{13}CH_4$ indicated that an empirical power law used for the temperature dependence of the N_2-broadened line widths would fail to fit the observed data in the entire temperature range from 80 to 296 K; instead, it follows a temperature-dependence similar to that reported by Mondelain et al. [17,18]. The initial test was very successful proving that a high precision Fourier transform spectrometer with a completely evacuated optical path can be configured for spectroscopic studies at low temperatures relevant to the planetary atmospheres.

1. Introduction

The spectrum of methane vapor, prevalent in the major outer planets [1–3] and some moons [4], is continually studied to obtain accurate spectral line parameters needed for radiative transfer calculations [5]. The temperature dependences of self- and foreign-gas broadening parameters are essential to model the atmospheres where temperatures can reach below 100 K.

Recording high-resolution spectra using gas samples at very low temperatures facilitates the interpretation of molecular dynamical processes. With the colder temperatures, complex molecules with low lying vibrational states give rise to greatly simplified spectroscopic patterns [6] and the variation of line intensities as a function of temperature can be measured to obtain empirical lower state energies of transitions [7]. In addition, the behavior of spectral line shapes can be monitored as a function of temperature to test and improve theoretical models [8]. Cooling can be achieved by placing an absorption cell directly inside a cold bath (e.g. [9]), by flowing LN_2 around the body of the chamber (e.g. [10–12]), and by placing it in thermal contact with a cold finger cooled by a closed-cycle refrigerator (e.g. [13]). Since the closed-cycle refrigerating system usually introduces significant vibrations [14], most cells are often mechanically isolated from spectrometers to avoid such vibrations adding noise to the spectra [15]. In the present study, we describe a temperature-controlled cell mounted on a closed-cycle helium-cooled cold finger designed to operate inside the evacuated sample compartment of a Bruker IFS-125HR spectrometer with no additional effort to isolate the interferometer from the refrigerator vibrations.

The primary motivation for this project is to support remote sensing of Titan's atmosphere [16]. As a demonstration of the new cell and FTS combined performance, we obtained the temperature

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dependence of the N_2-broadened line widths for the R(2) manifold in the ν_4 band of $^{13}CH_4$ in the 7.14 μm region using multiple spectra of N_2-broadened methane at different temperatures between 296 and 79.5 K. The combination of the new cold cell with the high resolution Fourier transform spectrometer is shown to be successful and reliable. It is demonstrated that the closed-cycle helium-cooled chamber works very well at low temperatures relevant to the planetary atmospheres, comparable to the results obtained from laser systems [17–19].

2. The closed-cycle cryogenic sample cells

Two cells (shown in Fig. 1, named Cell #1 and Cell #2) were specifically designed to operate inside the sample compartment of a Bruker IFS-125HR Fourier transform spectrometer (FTS). The cell bodies were made entirely from oxygen free high conductivity (OFHC) copper. Both cells had ZnSe windows of 2″ diameter with a 30 arc minute wedge to prevent optical fringing, and the windows were sealed to the copper body by compressed indium metal seals. For the gas input, a 6 mm diameter stainless steel tube with 0.102 mm wall thickness and length of 38 cm was silver soldered to each cell. Each cell was thermally connected to the cold head by suspending it from the cold tip of a CTI Cryogenics Model 22 Helium refrigerator. Since the heat conductivity of copper is the best among metals, 4.01–5.57 W/(cm K) at the temperatures between 80 and 300 K [20], no significant temperature gradient across the cell was observed in separate performance tests on each cell. Cell #2 is of nearly identical design to Cell #1, except for the shorter length to accommodate a vacuum shroud to isolate it from the residual gas adsorbed on surfaces inside the evacuated FTS, as well as a smaller mass. The configuration of the two cells is summarized in Table 1.

To maintain a constant temperature, the He-cooling of the cells was balanced by a $50\,\Omega$ heater capable of supplying up to 50 W power. The cell temperature was controlled with a Model 331 temperature controller supplied by Lakeshore Cryotronics Inc., and a silicon diode sensor (sensor A) mounted between the cold tip and the cell body for feedback in the temperature control loop; a second silicon diode sensor (sensor B) was placed on a lateral side in the middle of the cell to monitor cell temperature. The sensors were calibrated with an accuracy of 0.125 K at 77 and 0.105 K at 300 K. The parameters for a Proportional, Integrate and Differentiate (PID) temperature control loop were manually set up once for the system. The PID loop designed into the Lakeshore Model 331 temperature controller controlled the temperature of the cold finger with very high stability; the cell temperature varied typically less than 0.01 K for long periods in the presence of modest cryodeposits.

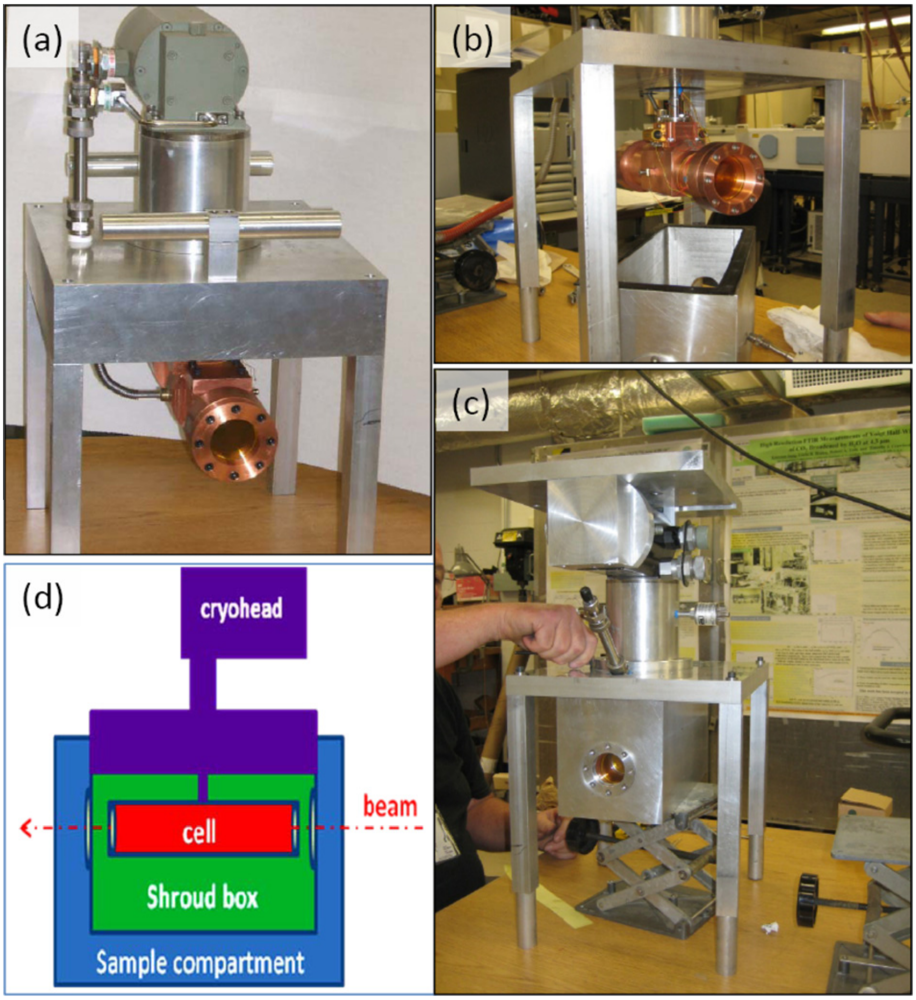

Fig. 1. Cryogenic sample cells. (a) The first generation coolable cell with no vacuum box. The cell base plate replaces the cover of the sample compartment of the Bruker IFS-125HR, (b) the redesigned coolable cell seen prior to mounting the vacuum shroud box (on the table) to the cell assembly, (c) the redesigned coolable cell with the vacuum shroud box mounted to the base plate. The supporting legs are removed when the system is placed into the sample compartment, (d) the schematic diagram of the cell and vacuum box inside the sample compartment.