



Line shape study of acetylene transitions in the $\nu_1 + \nu_2 + \nu_4 + \nu_5$ band over a range of temperatures

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ABSTRACT

In this study we have retrieved the line intensities, self broadened widths, pressure-induced shifts and selected line mixing coefficients for 20 R-branch transitions in the $\nu_1 + \nu_2 + \nu_4 + \nu_5$ band of acetylene. The spectra were recorded using our 3-channels diode laser spectrometer, a temperature controlled cell of fixed length and a second, room temperature cell. The Voigt and speed-dependent Voigt profiles with inclusion of line mixing effects were used to retrieve the line parameters. We determined the temperature dependencies for line broadening, shift and line mixing coefficients.

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1. Introduction

In the past decade numerous acetylene transitions have been used as frequency standards for fiber optic communications [1 and references therein]. Most of the spectroscopic studies are dedicated to the astrophysical and planetary applications of acetylene's line parameters. For example, spectra of Titan's atmosphere recorded by the Cassini instrument reported that acetylene is one of the most abundant trace constituents after methane [2].

The first study on record focused on measuring self- and H₂-broadened line parameters in acetylene is by Varanasi and Bangaru [3]. Laser spectroscopy was used by Wong [4] to measure the self-broadening coefficients for acetylene for transitions in the range of his dye laser. The self-broadening parameters of acetylene in the ν_5 band for 27 R and P-branch transitions were first studied by Lambot et al. [5] using a diode laser spectrometer. Pine [6] used a difference frequency laser system to measure the self-, N₂- and Ar-broadening coefficients for acetylene transitions in the $\nu_1 + \nu_5$ band. A follow-up study of Ref. [5] reports on the low temperature spectrum [7] of 21 transitions in the same band. Lucchesini et al. [8] used diode laser spectroscopy to measure self-broadening and shifting for several weak acetylene transitions belonging to overtone bands located in the 12 700 to 11 800 cm⁻¹ spectral range. Laser

spectroscopy was also used by Georges et al. [9] to measure Ar- and self-broadening in one transition of the $5\nu_3$ band of acetylene.

Biswas et al. [10] have studied self- and nitrogen-broadening for transitions in the $\nu_1 + 3\nu_3$ band using spectra recorded with a diode laser spectrometer working nearby 782 cm⁻¹. Transitions in the same band were studied by Herregodts et al. [11] using a Ti:Sa autoscan laser spectrometer. Diode laser spectroscopy was used by Yelleswarapu and Sharma [12] to measure the self-broadening and pressure-induced self- shifts for several transitions in the $\nu_1 + 3\nu_3$ band. The spectra were modeled using the Voigt profile.

Minutolo et al. [13] measured self-, N₂-, O₂- and CO₂-broadening and pressure shifts for transitions of C₂H₂ and H¹³C¹²CH in four combination bands located in the 1.54 μm range. Twenty acetylene transitions belonging to the $\nu_1 + 3\nu_3$ band have been studied in detail by Valipour and Zimmerman [14] with numerous broadeners: acetylene, N₂, O₂, air, He, Ne, Ar, Kr, Xe. An extensive study of cold bands located in the 5 μm range was performed by Jacquemart et al. [15].

Thirty absorption lines in the $\nu_4 + \nu_5$ band of acetylene were recorded and studied by Lepere et al. [16].

Jacquemart et al. [17] measured line parameters for 550 lines belonging to 13 acetylene bands located between 1.7 and 1.9 μm. Self-broadening coefficients have also been measured for 10 P branch transitions located nearby 1.533 μm. Ten self-broadened P-branch transitions in the $\nu_1 + \nu_3$ band of acetylene have been studied by Li et al. [18] using diode laser spectroscopy.

In this study, using the 3-channels tunable diode laser spectrometer described in the following sections we have measured

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20 lines in the $\nu_1 + \nu_2 + \nu_4 + \nu_5$ band of acetylene specifically examining the effects due to temperature and pressure changes. A selection of six pressures has been chosen and for each pressure seven temperatures were used ranging from 213 K to 350 K.

2. Experimental details

2.1. Background information on temperature controlled cells

We have developed a 3-channels tunable diode laser spectrometer that can be used to complete temperature and pressure controlled line shape studies on atmospheric gases. This research apparatus may be used for the spectroscopic characterization of molecules found within planetary atmospheres, by high-resolution laboratory studies.

For atmospheric research, long path lengths are required for absorption cells at various temperatures [19] and pressures. White type cells typically meet the prerequisite for path length due to their multi-pass configurations [20]. Ref. [21] reports on a long path cell (16–96 m) that operates between 215 and 470 K at gas pressures ranging from vacuum to 10 atm. A temperature controlled White type long path cell was built by McKellar [22,23] to enable studies of weakly bound complexes at low temperatures. The cell has a base of 5 m and allows the users to achieve up to 100 m pathlength. Another example of a variable temperature absorption cell (White design) that can accommodate path lengths up to 512 m and pressures up to 5 atm was built for laboratory spectroscopic studies of gases found in terrestrial and planetary atmospheres [24–28]. A large fraction of the published results are restricted to temperatures near room temperature. Ref. [29] provides a good example at the other end of the temperature range using the concept of collisional cooling within their cell. The minimum temperature that can be maintained in the cell is 10–12 K.

Over the last few decades many variable temperature cells have been published, but a key concern commonly examined within them is the temperature variability and instability of the cell. Short term stability is necessary for the efficient use of any cell as it reduces the time for experimental procedures within the laboratory. In 2004, Valentin et al. [30] reported on a stabilized low temperature infrared absorption cell cooled by an open cycle refrigerator, which can run with liquid nitrogen from 250 to 80 K or with liquid helium from 80 K to a few K. The authors have reported temperature stability better than 0.1 K within 4 h for a 300 to 4.5 K temperature spread. Other absorption cells reported within the literature deviate little from this range of temperatures and stability values.

Thermal gradients are often impossible to completely alleviate from the design of absorption cells but improvements have been made within this area. Multiple temperatures sensors are often used to monitor the temperature variability of the cells over their base length. Smith and colleagues [31] mounted six thermocouples in contact with their coolant along the length of their cell and have measured an agreement of ± 2 K between them. Eight thermocouples are distributed evenly along another cell built by Cann [32] and three were employed within Schaeffer et al.'s [33] multi-pass high temperature cell achieving accuracy of ± 1 K. Gradients less than 0.1 K/m have also been shown within Ref. [21]. The behavior of these thermal gradients is obvious and is highly dependent upon the base length of the cell. Accordingly, a compromise between a desired optical path length and thermal congruence is often necessary.

A 147.5 cm long variable-temperature absorption gas cell was designed [34] and built for spectroscopic measurements of gases of atmospheric interest using a Bomem DA8.3 Fourier transform

spectrometer. The heating/cooling system enveloping the cell allows spectroscopic studies of gas samples at temperatures ranging from 205 to 350 K and at pressures up to atmospheric pressure. The temperature gradients inside the cell are within ± 0.31 K, highlighting the very good performance of this system.

A short coolable gas cell designed for lineshape studies was presented by Lambot et al. [7]. The temperature can be stabilized to within 2 K for temperatures between 120 K and room temperature and accommodates any absorption pathlength between 0 and 3 cm. An experimental setup that integrates a low-temperature optical cell UV-visible (UV-Vis) with a liquid X-ray absorption spectroscopy (XAS) cell is reported in Ref. [35]. The proposed gas cell is suitable for the measurement of gases at variable temperatures from room temperature to 195 K.

2.2. Mechanical and optical design of the variable temperature cell

The overall design of the system is presented in Fig. 1. The first channel contains the temperature and pressure controlled cell. The second channel contains a room temperature reference cell of similar path length. The third channel records the background of the laser system. By measuring all three channels simultaneously we are able to perform accurate line shape analysis including pressure-induced line shift measurements.

The pathlength of the variable temperature cell presented here is 1.54 m. The 3-D layout of the temperature controlled cell is presented in Fig. 2. We have employed two main design features: (i) the absorption cell which is centered inside a vacuum jacket to minimize the thermal conductive/convective coupling to the outside cell and (ii) heating/cooling will be supplied by temperature-controlled fluid in direct contact with almost the complete cell body ensuring that the temperature gradients are minimized. The mechanical and optical components have been selected while paying attention to the type of gases (both stable and flammable) that will be studied.

The inner chamber is a single-pass cell and is made up of a nominal 4" schedule 40 stainless steel pipe that is 5' long. Both ends have a welded custom designed stainless steel flange which has four ports each where both flanges have the same diameter as the pipe. One of the flanges has two temperature ports, one pressure port, and a gas inlet port. The other flange has three temperature ports and one gas outlet port. Platinum resistor thermometers are mounted on rods and attached to the cell flanges by 1/8" diameter fittings. The 6", 18", and 30" long rods are mounted as shown in Fig. 2 to ensure that we are able to monitor the temperature at various depths of the cell with an additional sensor being mounted within the vacuum jacket.

The gas pressure inside the inner cell is measured using a MKS pressure module (0–1000 Torr) with a Model 670 signal conditioner which is monitored via LabVIEW software. The center counter-bore in the end flanges house crystal windows that can be interchanged for the desired spectral range. At the moment the cell is provided with anti-reflection coated CaF_2 windows. To suppress channel spectra caused by multiple reflections of the sample beam between the surfaces of the windows, the windows are also wedged. Fluoro-silicone O-rings are used on the inner sides of the crystal to seal the CaF_2 windows to the inner test chamber. The chamber is completely sealed from the outside. A stainless steel compression ring is applied to the outside side of each window to hold the window and o-ring assembly together.

The coolant fluid is supplied through a second chamber of 6" diameter shown in Fig. 2. This chamber is configured with six fins that allow the fluid to flow uniformly across the length of the cell. The heating/cooling of the gas inside the temperature controlled cell is provided by a Neslab ULT-80 thermal bath using ethanol or methanol as the coolant. The Neslab Chiller ULT-80 is needed

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