

Line profile study by diode laser spectroscopy in the $^{12}\text{CH}_4$ $\nu_2 + \nu_4$ band

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Abstract

We present a complete study on four methane lines for two atmospheric micro-windows (in the $\nu_2 + \nu_4$ absorption band) used for the determination of atmospheric methane concentrations with ground-based Fourier transform spectrometers. Thanks to our tunable diode laser (TDL) spectrometer with active wavenumber control and step-by-step recording mode we have improved the accuracy on intensity, broadening, narrowing, and pressure shift parameters. To make our results directly useable in atmospheric models which usually assume a Voigt line shape, we have parameterised an effective-broadening parameter $\gamma_{\text{Voigt}}(P)$ for each line and each gas mixture ($\text{CH}_4\text{-N}_2$ and $\text{CH}_4\text{-O}_2$). When this parameterisation is used to fit a “true” line profile, the same concentration as with more sophisticated models is retrieved using a consistent set of spectroscopic parameters in both approaches.

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1. Introduction

Atmospheric sounding by infrared spectroscopy requires the selection of appropriate spectral micro-windows covering isolated spectral features of atmospheric trace species with sufficient absorption for accurate quantitative measurements. In the UFTIR project (Time series of Upper Free Troposphere observations from a European ground-based FTIR network <http://www.nilo.no/uftir>), a micro-window near 2921 cm^{-1} has been selected to extract the tropospheric concentration of CH_4 using an absorption line of the $\nu_2 + \nu_4$ band. To compete with the accuracy of other methods (chemical analyses, gas chromatography, etc.), it is of first importance to improve the accuracy of infrared spectroscopic

parameters to reduce one of the major source of systematic error in the trace species abundances derived from quantitative spectroscopy, especially for low concentrations.

Atmospheric NO_2 absorption lines belonging to the $\nu_1 + \nu_3$ band near 2900 cm^{-1} and recorded using ground-based high resolution Fourier transform spectrometers are used since several years to extract vertical column densities [1]. More precisely, the region centred at 2914.6 cm^{-1} has been selected as an atmospheric micro-window suitable to quantify the NO_2 column (see the Spectroscopic Atlas of Meier et al. [2]). But an important drawback of this window is the interference with the CH_4 absorption especially because the spectroscopic parameters of the $\nu_2 + \nu_4$ band are not accurately known.

Despite the fact that several bands of methane have been extensively studied as the ν_3 band by Benner

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Table 1
Identification of the $\nu_2 + \nu_4$ transitions of $^{12}\text{CH}_4$ considered in this work

Identification (JCN)' \leftarrow (JCN)''	$[J = 5, F_2, 14 \leftarrow J = 4, F_1, 1]$	$[J = 8, F_1, 17 \leftarrow J = 7, F_2, 2]$	$[J = 8, F_1, 17 \leftarrow J = 7, F_2, 1]$	$[J = 8, F_2, 20 \leftarrow J = 7, F_2, 2]$
Wavenumber (cm^{-1})	2914.49860	2914.88110	2914.91950	2921.33185

The assigned quantum numbers J, C, N represent the angular momentum, the rovibrational symmetry, and a running number according to increasing energies within the polyads [20]. The prime and second exponents represent, respectively, the upper and the lower states. The wavenumber values are extracted from the HITRAN 2001 database.

et al. [3] and Pine and Gabard [4] (using a tunable difference-frequency laser spectrometer), few experimental studies concern the $\nu_2 + \nu_4$ band [5–8] and none was performed using high resolution laser spectroscopy.

The present paper reports an investigation of $\nu_2 + \nu_4$ lines in two micro-windows around 2914 and 2921 cm^{-1} (Table 1) using a tunable diode laser (TDL) spectrometer to achieve the best accuracy. The measured spectroscopic parameters are the intensity, the self-broadening, narrowing, and pressure shifting coefficients as well as the N_2 and O_2 broadening, narrowing, and pressure shifting coefficients (only the n temperature dependence parameter is not measured).

2. Experimental details

The analysed spectra were recorded at high resolution using the diode laser spectrometer of LPMAA described elsewhere [9] operating with a lead salt diode laser from Laser Components cooled at liquid nitrogen (LN_2) temperature. Using a Michelson interferometer to control actively the diode laser emission, the residual wavenumber fluctuations (phase noise) of the diode are reduced to less than $4 \times 10^{-5} \text{ cm}^{-1}$. An absorption line is scanned step-by-step with a sampling step equal to $0.28 \times 10^{-3} \text{ cm}^{-1}$ at 2900 cm^{-1} . The TDL beam used for absorption measurements is divided into three light paths; one beam is used as a background signal I_0 , another one goes through the sample cell and is providing a transmitted signal I_t . A third part of the beam goes through a cell of 30 cm path length filled with a low pressure of pure OCS (2.14 Torr for 2914 cm^{-1} region and 0.52 Torr for 2921 cm^{-1} region) providing a reference signal I_{ref} , used to check the spectral linearity and the instrument line shape. At each step the beam intensities I_0 , I_t , and I_{ref} are measured simultaneously, and the ratios I_t/I_0 and I_{ref}/I_0 are determined with a relative precision of 5×10^{-4} .

The pure gas or the gas mixtures were contained in a multipass White-type cell [10] (sample cell) with an adjustable optical path allowing optimisation of the peak absorption close to 50%. The pressure for pure CH_4 was measured with an Edwards Barocel (model 655) with 10 Torr full scale. The pressure for gas mixtures was measured with a MKS Baratron manometer

(model 127) with 100 Torr full scale. Manometers have, respectively, a five digit and a four digit display with a stated accuracy of 0.15% on the reading. The methane ($\text{N}35$ quality) with a stated purity of 99.95% was supplied by Air Liquide and used without further purification. The isotopic abundance is close to the natural abundance, so that no correction is necessary to compare our measurements to HITRAN [11]. All measurements were achieved at room temperature with a temperature varying less than 0.1 K during a spectrum acquisition. These small temperature fluctuations lead to negligible errors on line parameters (i.e., maximum error of 0.04% on intensity). For a given couple of pressure and path length, three spectra were recorded to reduce systematic errors.

The observed spectrum $I_t(\tilde{\nu})/I_0(\tilde{\nu})$ is the convolution product of the theoretical spectrum $\exp[-lk(\tilde{\nu}, P)]$ with the TDL emission shape $A_L(\tilde{\nu})$

$$I_t(\tilde{\nu})/I_0(\tilde{\nu}) = A_L(\tilde{\nu}) \otimes \exp[-Lk(\tilde{\nu}, P, T)] + \text{offset}.$$

In this equation L is the path length (in cm), $k(\tilde{\nu}, P, T)$ the absorption coefficient (in cm^{-1}) which defines the absorption line profile (at total pressure P and temperature T). The line intensity $S(T)$, the line-broadening $\gamma(T)$, and other spectroscopic parameters are involved in the expression of k . The spectroscopic parameters S and γ are the most critical ones for accurate trace species measurements (using infrared Fourier transform spectroscopy like UFTIR) in the troposphere, where pressure-broadening effects are contributing most. The *offset* represents the part of the laser radiation emitted by the TDL outside the main laser mode, and this contribution is assumed constant over the spectral range covered by the absorption line. We have checked this using different nearby OCS lines. As described in [12], the *offset* is determined by recording the same spectral range under strong absorption conditions (saturated line). To achieve precise intensity measurements, the TDL emission shape and the offset were determined using saturated and non-saturated OCS spectra. Different instrument line shapes were tried (Gaussian, Lorentzian, Voigt). The best residuals were obtained with a pure Lorentz function with a half width at half maximum (HWHM) of $2 \times 10^{-4} \text{ cm}^{-1}$ and an *offset* equal to, respectively, 1.6% around 2914 cm^{-1} and 0.5% around 2921 cm^{-1} . This offset contribution is small

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