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Measurements and modeling of long-path $^{12}CH_4$ spectra in the 5300–5550 cm^{-1} region

A.V. Nikitin[a,*], X. Thomas[b], L. Daumont[b], M. Rey[b], K. Sung[c], G.C. Toon[c], M.A.H. Smith[d], A.W. Mantz[e], S.A. Tashkun[a,f], Vl.G. Tyuterev[b]

[a] Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, Russian Academy of Sciences, 1, Akademichesky Avenue, 634055 Tomsk, Russian Federation
[b] Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 6089, Université de Reims, U.F.R. Sciences, B.P. 1039, 51687 Reims Cedex 2, France
[c] Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA
[d] Science Directorate, NASA Langley Research Center, Hampton, VA 23681, USA
[e] Department of Physics, Astronomy and Geophysics, Connecticut College, New London, CT, USA
[f] QUAMER, Tomsk State University, 36 Lenin Avenue, 634050 Tomsk, Russian Federation

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ABSTRACT

A new study of $^{12}CH_4$ line positions and intensities was performed for part of the Tetradecad region between 5300 and 5550 cm^{-1} using four long path (202 m, 602 m, 1604 m and 1804 m) spectra of normal samples of CH_4 at different pressures recorded with a Fourier transform spectrometer in Reims, France. Line positions and intensities were retrieved by least square curve-fitting procedures and analyzed using the effective Hamiltonian and the effective dipole moment expressed in terms of irreducible tensor operators adapted to spherical top molecules. An 80 K spectrum from JPL of enriched $^{12}CH_4$ was used for low-J line positions. One other 80 K spectrum from JPL of enriched $^{13}CH_4$ was used to discern the isotopic lines. A new measured linelist contains positions and intensities for 5934 features. Quantum assignments were made for 2847 transitions, which represent ~90% of the integrated line intensity observed in this region. All assigned line positions and 2227 selected line intensities were fitted with RMS standard deviations of 0.0025 cm^{-1} and 8.6%, respectively. The sum of observed intensities between 5300 and 5550 cm^{-1} fell within 2% of the predicted value from *ab initio* variational calculations.

1. Introduction

Precise knowledge of methane absorption is crucial in the study of planetary systems because its spectral features are used to determine the physical properties of their atmospheres [1–3]. This is especially true for Titan (Saturn's largest satellite) whose atmosphere is composed of 98.6% nitrogen and 1.4% methane at temperatures ranging between 70 K and 200 K. Improving the methane spectroscopic parameters is essential for full interpretation of near infrared observations returned by the ground-based and orbiting observatories [4–8]. Missing or insufficiently accurate lines in available analyses of laboratory measurements and in the corresponding methane compilations is also a major hindrance for such outer planet studies [9–11].

It is well-known that the four normal mode frequencies of methane exhibit an approximate relation between stretching and bending frequencies with $\omega_1 \cong \omega_3 \cong 2\omega_2 \cong 2\omega_4$ resulting in vibrational levels grouped into polyads (Dyad, Pentad, Octad, Tetradecad, Icosad, etc.) involving levels of nearby energies [12]. The scheme of $^{12}CH_4$ vibrational states is given in Fig. 1, where the blown-up scale at the right-hand side represents sub-band centers with their symmetry types related to the present study.

The aim of the present work is to improve the analysis and extend the assignments of the $^{12}CH_4$ transitions in the 5300–5550 cm^{-1} region of the Tetradecad [13]. The lower portion of the Tetradecad (mostly $4\nu_4$) was first studied by Robert et al. [14,15] who modeled 193 line positions and 160 measured intensities between 4909–5271 cm^{-1} (obtained from eight Kitt Peak spectra) with standard deviations of 0.107 cm^{-1} and 18.5%, respectively [14]. Some rare transitions of $\nu_1 + 2\nu_4$ were also given. The assignments were included in the empirical linelist [16] given to the public databases: HITRAN [17,18] and GEISA [19]. Global fitting of all assigned lines of $^{12}CH_4$ in the 0–6200 cm^{-1} region was performed [13] where the number of assigned $4\nu_4$ features increased to 457 line positions and 314 line intensities. Recently a new linelist including 13,045 calculated positions and intensities

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[*] Corresponding author.
E-mail address: avn@iao.ru (A.V. Nikitin).

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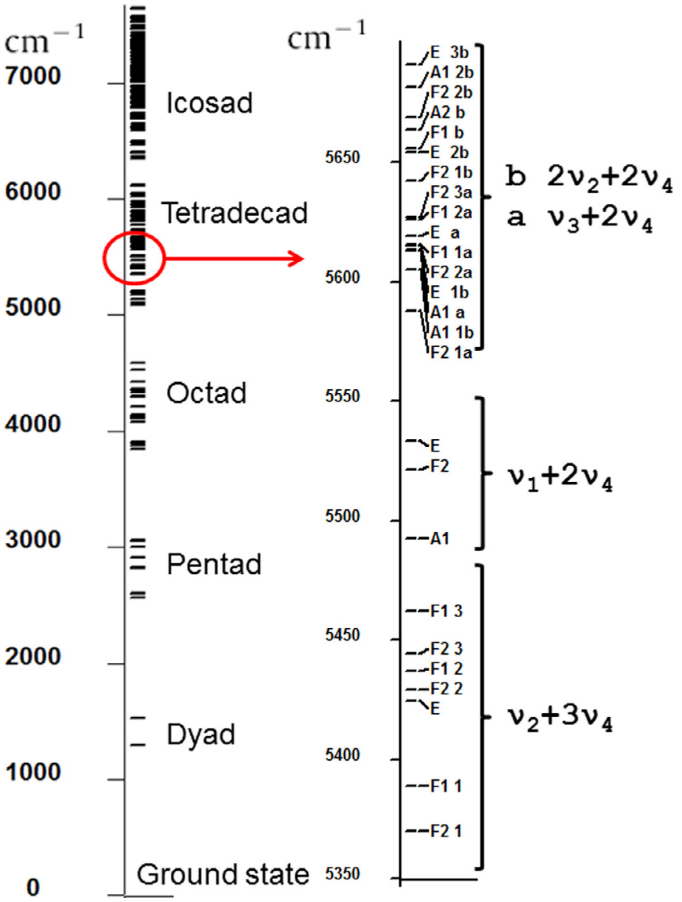

Fig. 1. Scheme of the vibrational level patterns of the $^{12}CH_4$ polyads (left side), with the vibration sublevels of the part of Tetradecad (right side) corresponding to rovibrational bands analyzed in this work. At the right hand side panel, the principal vibration quantum numbers (combinations of $\nu_1\nu_2\nu_3\nu_4$), symmetry types corresponding to the T_d irreducible representations of vibration sublevels and vibrational ranking numbers with the Tetradecad are shown. The symmetry notations correspond to irreducible representations of the T_d point group [12,35].

has been obtained in the range 4800–5300 cm^{-1} [20], in which 2725 experimental line positions and 1764 selected line intensities have been fitted with RMS standard deviations of 0.004 cm^{-1} and 7.3%, respectively. The most complete set of rovibrational assignments available in the literature above 5550 cm^{-1} was obtained in the frame of a GOSAT project from spectra recorded by Fourier Transform Spectroscopy [21]. The GOSAT empirical list includes about 5200 lines and provides about 2000 rovibrational assignments. Recently part of WKLMC experimental line lists [22] (see also [11,23]) at 296 K have been assigned [24] in the range 5855–6250 cm^{-1}. This range is part of whole WKLMC [22] lists at 296 K and 80 K measured in Grenoble in the region 5855–7912 cm^{-1} by Differential Absorption Spectroscopy (DAS) in the strong absorption regions (the $2\nu_3$ region of the Tetradecad [11,23] and in the Icosad [25–28]) and high sensitivity CW-Cavity Ring Down Spectroscopy (CRDS) in the 1.58 µm and 1.28 µm transparency windows [31]. All known IR transitions from three lower polyads [32], from Tetradecad [20,24,33] including 2846 experimental line positions from this work and from lower part of Icosad [25,34] were involved in effective Hamiltonian parameters adjustment of this work.

The paper is structured as follows. Experimental spectra recorded in GSMA Reims and JPL NASA are described in Sections 2.1 and 2.2. Section 3 is devoted to the determination of line parameters and Section 4 to spectra analysis and assignments where recent *ab initio* calculations are also briefly reviewed. Section 5 gives the information on the new assigned line lists provided in the Supplementary Materials.

2. Experiment

2.1. Reims FTS spectra

The experimental spectra from Reims were obtained in 2011 with the Connes type Fourier Transform Spectrometer designed at the Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA) fitted to the 50 m base-length White type cell as already described in [20,32]. A first series of spectra with 1.6 km absorption path-length dealing with the transparency windows of methane was already explored [25] for the Titan atmospheric spectra analysis [11]. Later on we registered three new series of spectra of methane gas in natural isotopic constitution. The natural abundance sample and path length conditions enable to capture many transitions originating from $^{13}CH_4$, $^{12}CH_3D$ simultaneously. Series of spectra with 202, 602, 1604, and 1804 m were recorded in 2011 by filling the cell with 1, 5 and 25 Torr as detailed in Table 1 (spectra A–L, see also Figs. 2a and 2b). The maximal optical path difference (MOPD) was chosen to achieve a spectral resolution to be the mean value of the half width for unsaturated lines, which was found to be in the Doppler regime. In the 1804 m path long spectra the center of the absorbing bands were saturated, so only the transparency windows were studied. In the present study we thus focus on the 202 m and 602 m spectra where most of the lines are not saturated. The spectra M to O were used in the previous paper [20] to study the 2 µm transparency window.

The wavenumber calibration was obtained using CO_2 sample filled in the 8.5 m vacuum tank containing the optical elements between the cell and the spectrometer. It leads to CO_2 absorption bands easily seen in spectra *A*, *D*, *M* and *N*. The wavelength correction is based on the work of Miller et al. [36]. The CO_2 lines contribution had to be taken into account when overlapping exist with CH_4 lines.

Most of the measured lines in this work come from spectra *M* and *N*. Spectrum *O* was not used in the end as too many lines are saturated and have overlapping wings.

2.2. JPL experimental details for $^{12}CH_4$ spectrum in the tetradecad

We obtained a pair of high-resolution spectra at the Jet Propulsion Laboratory; one for a ^{12}C-enriched methane sample, $^{12}CH_4$ (99.95%) and the other for a corresponding background (*i.e.*, empty cell) under the same optics and instrument conditions, for instance, the same spectral resolution of 0.0044 cm^{-1}(unapodized), the same temperature, 79.7(1) K, and the same path length, 20.941 m. The $^{12}CH_4$ spectrum was acquired with a sample pressure of 5.164(1) Torr. For this, we employed a high resolution Bruker 125HR Fourier transform spectrometer, and a temperature-controlled cryogenic Herriott cell vacuum-coupled to the spectrometer. The temperature stability of the Herriott cell was observed to be excellent, for instance, holding any set temperature between 50 and 250 K within 0.1 K drift for a few days. Further details on the optics configuration and the performance of the Herriott cell can be found in [37]. The frequency of the spectrum has been calibrated to the precision of 0.0006 cm^{-1} by using a frequency scaling factor derived from the observed water features in the $\nu_2 + \nu_3$ band compared to those in the HITRAN 2012 database [18]. Further information regarding the instrument set-up and other experimental conditions has been detailed in a companion article [38] dedicated to $^{13}CH_4$ spectra.

For the analysis, a ratioed spectrum of the $^{12}CH_4$ sample, *i.e.*, normalized to the corresponding background spectrum, was used, in which the residual water features were cancelled out. However,