Journal of Quantitative Spectroscopy & Radiative Transfer 112 (2011) 28–40

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

First assignment of the $5\nu_4$ and $\nu_2+4\nu_4$ band systems of $^{12}CH_4$ in the 6287–6550 cm^{-1} region

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ARTICLE INFO

Article history:
Received 8 June 2010
Received in revised form
4 August 2010
Accepted 6 August 2010

Keywords:
Methane
Spectra
Assignment
Transparency window
Icosad
Titan
CRDS
Long-path FTS

ABSTRACT

This paper reports the first assignment of rovibrational transitions of the $5\nu_4$ and $\nu_2+4\nu_4$ band systems of $^{12}CH_4$ in the 6287–6550 cm^{-1} region, which is usually referred to as part of the 1.58 μm methane transparency window. The analysis was based on two line lists previously obtained in Grenoble by cavity ring down spectroscopy at $T=297$ and 79 K completed by three long-path Fourier transform spectra recorded in Reims (at 290 K, $L=1603$ m, $P=1$–34 mbar). In order to determine the dipole transition moment parameters and quantify the intensity borrowing due to the resonance interactions, we had to include in the fit of the effective Hamiltonian model some lines of the stronger $\nu_1+3\nu_4$ and $\nu_2+4\nu_4$ bands. For this purpose, intensities of 179 additional lines were retrieved from FTS spectra above 6550 cm^{-1} though the analysis of these higher bands is not complete. About 1955 experimental line positions and 1462 line intensities were fitted with RMS standard deviations of 0.003 cm^{-1} and 13.1%, respectively. A line list of 8029 calculated and observed transitions which are considered as dominant was constructed for $^{12}CH_4$ in the 6287–6550 cm^{-1} region. This is the first high-resolution analysis and modelling of 5-quanta band systems of $^{12}CH_4$.

1. Introduction

The precise knowledge of the methane absorption in the study of planetary systems, and especially of Titan (Saturn's largest satellite whose atmosphere is mainly composed of nitrogen and methane at temperatures ranging between 70 and 200 K), is of great importance because it gives access to the determination of the physical properties of these objects [1–5]. The full interpretation of the Titan data returned by the ground-based and space observations is severely limited by the lack of precise knowledge of the methane absorption, which dominates the spectrum in the near infrared.

Despite many years of experimental and theoretical studies [6–28], the infrared methane spectrum is still insufficiently understood. In particular, the line-by-line analyses based on the expansion of an effective Hamiltonian and dipole moment, were able to provide precise data reductions only up to 4800 cm^{-1} [15–17]. This is because the number of strongly interacting near-degenerate vibration levels increases very rapidly with energy due to the high symmetry of the methane molecule. On the other hand direct variational predictions of methane ro-vibrational lines using *ab initio* potential energy and dipole moment surfaces [25–28] are not at present sufficiently accurate for the assignment of experimental spectra and a calculation of high-*J* rotational transitions is not yet possible.

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doi:10.1016/j.jqsrt.2010.08.006

Considering the weakness of the absorption of $^{12}CH_4$ and $^{13}CH_4$, the 6287–6550 cm^{-1} region studied in this work can be used to detect other planetary species such as CH_3D and CO. A description of the methane absorbance in transparency windows presents a particular difficulty for the theoretical approach because it requires an extrapolation to high-J transitions and because intensities of these weak transitions are extremely sensitive to numerous resonance interactions, which are still poorly defined. As already presented in [20], the CH_3D isotopologue contributes significant absorption in the region, complicating any analysis of laboratory spectra using natural methane samples.

Theoretically speaking, in terms of the resonance polyad structure of methane vibration states, the considered spectral range corresponds to the lowest frequency bands of the icosad which are very weak bands in interaction. The complexity of the vibrational structure is illustrated in Fig. 1. This scheme shows the vibrational levels $5\nu_4$, ν_2+$4\nu_4$, ν_1+$3\nu_4$ splitted into 26 vibrational sublevels. The $5\nu_4$ vibrational system has eight sublevels of A_1, E, $3F_1$, $3F_2$ symmetry types, the ν_2+$4\nu_4$ system has 14 sublevels ($2A_1$, $2A_2$, 4E, $3F_1$, $3F_2$) and the ν_1+$3\nu_4$ system has 4 sublevels (A_1, F_1, $2F_2$). The symmetry notations correspond to irreducible representations of the T_d point group [9,10]. The $n\nu_4$ bending overtone levels are the lowest energy levels of the different vibrational polyads of methane and separate progressively from the remaining part of the polyad due to the high anharmonicity in the ν_4 mode.

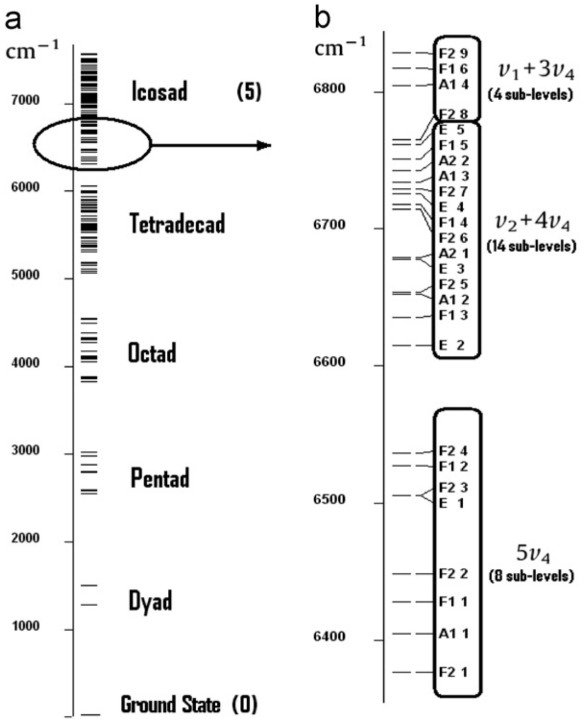

Fig. 1. Scheme of vibrational level patterns of methane polyads (a), and of vibration sublevels of the lower icosad edge (b) corresponding to rovibrational bands analyzed in this work. At the right hand side panel, the principal vibration quantum numbers, symmetry types (T_d irreps) of vibration sublevels and vibrational ranking numbers within the icosad are given.

Rovibrational transitions from the vibration ground state (GS) to icosad sub-levels form the corresponding absorption band systems. An accurate characterization of these weak absorption features and of their dependence with the temperature is mandatory for the interpretation of various optical measurements at large optical paths. As already stressed, this is particularly important for a remote sounding of the Titan surface [1–5].

Until recently, the only line list available in the literature for the considered transparency window was constructed by Brown [7] from spectra recorded at room temperature by Fourier transform spectroscopy (FTS) with path lengths up to 97 m. In absence of theoretical modelling, this FTS list, adopted in the HITRAN 2008 database [23], was limited to empirical line positions and intensities at room temperature without rovibrational assignments. Another limitation was the lack of sensitivity resulting in relatively high intensity cut off (about 4×10^{-26} cm/molecule).

A considerable improvement has been recently achieved by some of us using two spectra recorded by cavity ring down spectroscopy (CRDS) at room temperature and at 79 K [19,20]. For the 6289–6526 cm^{-1} region, two lists of 6868 and 4555 transitions with intensities as weak as 1×10^{-29} cm/molecule were constructed from the recordings at 297 and 79 K, respectively. The empirical lower state energy and lower state J'' values were derived from the variation of their line intensities at 297 and 79 K. Although a complete assignment was not provided, the low-J quantum numbers from Ref. [20] provide the temperature dependence of the line intensities and a considerable help in the line identification. In order to complete the review of the previous observations in our region of interest, the results obtained by Deng et al. [29] in the 6607–6625 cm^{-1} section should be mentioned. These authors used direct absorption with a tunable diode laser and a White cell with a 973 m path length to detect 288 lines with intensities down to 1.4×10^{-27} cm/molecule.

The forthcoming analysis is based on the CRDS line lists of Ref. [20] completed with new long-path FTS spectra recorded at 290 K in Reims with a 1603 m path length and pressures of 1, 7 and 34 mbar. The paper is structured as follows. In Sections 2 and 3 the experimental setup and recordings of long-path FTS and CRDS spectra are outlined. Section 4 is devoted to the assignment, line position and intensity modelling of the $5\nu_4$ and ν_2+$4\nu_4$ band systems. We argue about the necessity to consider the coupling with the ν_1+$3\nu_4$ band to correctly reproduce the measured intensities. Section 5 presents the construction of a synthetic $^{12}CH_4$ line list that combines both experimental data and predicted lines. The advantages and shortcomings of the calculated line list as well as possible applications of new data are discussed in the concluding Section 6.

2. Long-path FTS spectra and calibration

Several long path spectra of methane at "natural" abundance were recorded in Reims in the 3800–8100 cm^{-1}