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Determination of the low energy values of $^{13}CH_4$ transitions in the $2\nu_3$ region near 1.66 μm from absorption spectra at 296 and 81 K

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ABSTRACT

The high resolution absorption spectra of $^{13}CH_4$ were recorded at 81 K by differential absorption spectroscopy using a cryogenic cell and a series of distributed feed back (DFB) diode lasers and at room temperature by Fourier transform spectroscopy. The investigated spectral region corresponds to the high energy part of the $^{13}CH_4$ tetradecad dominated by the $2\nu_3$ overtone near 5988 cm^{-1}. Empirical line lists were constructed containing, respectively, 1629 $^{13}CH_4$ transitions detected at 81 K (5852–6124 cm^{-1}) and 3481 features (including 85 lines of $^{12}CH_4$) measured at room temperature (5850–6150 cm^{-1}); the smallest measured intensities are about 3×10^{-26} and 4×10^{-25} cm/molecule at 81 and 296 K, respectively. The lower state energy values were derived for 1196 $^{13}CH_4$ transitions from the variation of the line intensities between 81 and 296 K. These transitions represent 99.2% and 84.6% of the total absorbance in the region, at 81 and 296 K, respectively. Over 400 additional weak features were measured at 81 K and could not be matched to lines observed at room temperature. The quality of the resulting empirical low energy values is demonstrated by the excellent agreement with the already-assigned transitions and the clear propensity of the empirical low *J* values to be close to integers. The two line lists at 81 and at 296 K provided as Supplementary material will enable future theoretical analyses of the upper $^{13}CH_4$ tetradecad.

1. Introduction

At room temperature, the near infrared spectrum of methane is particularly congested as a result of the complex structure of the rovibrational levels affected by numerous interactions. This is mainly due to the high symmetry of this tetrahedral molecule which leads to many degeneracies and an intricate vibrational structure. In fact, the $3 \times 5-6 = 9$ normal vibrational modes correspond to only four fundamental vibration frequencies (three of them being degenerate). In addition, they obey a simple approximate relation $\nu_1 \approx \nu_3 \approx 2\nu_2 \approx 2\nu_4$ between the stretching and bending harmonic frequencies leading to a polyad structure. As a result, the vibrational levels corresponding to the same number, $P = 2V_s + V_b = 2(V_1 + V_3) + (V_2 + V_4)$ have close energy values and constitute a polyad of levels in strong interaction. The number of vibrational levels in a given polyad increases rapidly with the energy, considerably complicating the analysis. Thus, despite important experimental and theoretical efforts, a satisfactory interpretation of near infrared methane still remains elusive. For the main isotopologue, $^{12}CH_4$, systematic identification is only available up through the octad region at 2.3 μm ($P = 3$ with 8 levels and 24 sublevels) [1] and significant progress has been achieved [2] only very recently in the tetradecad region ($P = 4$ with 14 levels, 60 sublevels) which extends between 4900 and 6200 cm^{-1}. For the $^{13}CH_4$ species, only the lower polyads up to 3200 cm^{-1} are satisfactorily understood [3] to the extent that observed positions and intensities can be reproduced at or close to experimental uncertainties. As a result, the representation of $^{13}CH_4$ absorptions at 1.67 μm in the public databases [4,5] has been marginal for 25 years. Some 93 positions first introduced in 1986 [6] assumed calculated line intensities of the main isotopologue scaled by the values from Fox et al. [7,8]. Later measurements of Margolis [9,10] replaced some of the assigned $^{13}CH_4$ lines of $2\nu_3$ if intensities were greater than 4×10^{-24} cm/molecule at room temperature.

The present contribution is devoted to the analysis of the $^{13}CH_4$ absorption spectrum in the high energy part of the tetradecad dominated by the $2\nu_3$ band centered at 5988 cm^{-1}. Being the strongest band in the region and located at the "edge" of the tetradecad, $2\nu_3$ is less subject to perturbations and has the regular *P*, *Q* and *R* branch structure seen in the ν_3 fundamental near 3018 cm^{-1}. Thirty years ago, Fox et al. [7,8] assigned the F2 component of $2\nu_3$ up to $J = 8$ and determined the spectroscopic constants using absorption spectrum recorded with a grating spectrometer and a 4.28 m optical

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path. The prevalent assumption that isotopic substitution of the central carbon atom would not significantly affect the intensities of the transitions in $^{12}CH_4$ and $^{13}CH_4$ was challenged by their $2\nu_3$ intensity measurements [8]. From their experiment dedicated to the measurements of the relative intensities of the Q_1, R_0 and R_1 in $^{12}CH_4$ and $^{13}CH_4$, Fox et al. concluded that the $^{12}CH_4$ line strengths were stronger by more than 30%. This "anomalous" line strength ratio was confirmed by Varanasi [11] from a series of spectra recorded at low temperatures down to 100 K.

The tetradecad, with 14 bands with a total of 60 sub-vibrational states, gives rise to the strong $2\nu_3$ band and numerous weaker transitions between 4800 and 6200 cm^{-1}. It should be noted that half of the 60 sub-states are not nominally infrared active and must borrow intensity to be observed in absorption. Very recently, Nikitin et al. performed a very enlightening comparative study of this polyad for both $^{12}CH_4$ and $^{13}CH_4$ [12]. It revealed a one-to-one correspondence between the lines of the strong bands of the two isotopologues, the $^{13}CH_4$ bands being shifted by a constant value varying between 6 and 30 cm^{-1} according to the vibrational band. These authors used the isotopic shifts to establish the identification of 339 stronger transitions between 5553 and 6114 cm^{-1} in both $^{12}CH_4$ and $^{13}CH_4$ with new identifications of $\nu_2 + \nu_3 + \nu_4$ near 5830 cm^{-1}, $2\nu_2 + \nu_3$ near 6060 cm^{-1} and the E component of $2\nu_3$ near 6030 cm^{-1}. Furthermore, the isotopic shifts between the $^{12}CH_4$ and $^{13}CH_4$ vibrational levels were computed from an *ab initio* potential energy surface with accuracies of nearly 1 cm^{-1}, making the isotopic shifts between$^{12}CH_4$ and $^{13}CH_4$ a reliable criterion to locate new bands. Thus, the $^{13}CH_4$ spectrum provided highly valuable information to substantiate tentative vibrational assignments of $^{12}CH_4$, and in turn, the advanced understanding of the $^{12}CH_4$ spectrum was applied to the $^{13}CH_4$ spectrum. This advantage is particularly important because an effective Hamiltonian in the $^{13}CH_4$ tetradecad cannot be successfully implemented without a prior reliable modeling of the $^{13}CH_4$ octad (3600–4800 cm^{-1}) [1].

Lacking guidance from theoretical models, a complementary and independent insight of the $^{13}CH_4$ tetradecad structure can be obtained by determining empirical lower state energies using the temperature dependence of the measured line intensities. Independent of any theoretical interpretation, the lower state energy value, $E'' \approx B_0 J''(J''+1)$, and thus the value of the angular momentum J'', can be deduced from the intensity values of a given transition, $S_{\nu_0}(T)$ and $S_{\nu_0}(T_0)$, observed at two temperatures, T and T_0. This approach (hereafter called *the two temperature method*) has been successfully applied to methane in natural abundance in a number of studies, including the Margolis studies [9,10] and our recent studies of the $^{12}CH_4$ tetradecad [13,14] and the icosad near 1.3 µm [15,16]. For example, cold temperature intensities of the $^{12}CH_4$ tetradecad [14] were combined with the intensity values at room temperature (RT) from a preliminary version of the line list [2] constructed in relation with the "Greenhouse Gases Observing Satellite" (GOSAT) project. The advantage of the GOSAT line list is that it has a two orders of magnitude smaller intensity cut off compared to HITRAN and GEISA [4,5] line list in the 5500–6184 cm^{-1} region. A perquisite of the application of the same method to the $^{13}CH_4$ isotopologue is the construction of two extensive line lists with accurate intensities at two temperatures. In the present contribution, intensity measurements were performed at room temperature from absorption spectra recorded by Fourier transform spectroscopy (l = 13 and 73 m) and at 81 K by differential absorption laser spectroscopy (l = 1.4 m). By applying the two temperature method, empirical lower state energies could be systematically derived, thus extending the assignments obtained by Nikitin et al. [12] on the basis of spectra at 180, 240 and 298 K with a short optical path (0.0875 m). In Fig. 1, we present an overview comparison of the present line lists at 81 and 296 K compared to the assignments reported by Nikitin et al. [12].

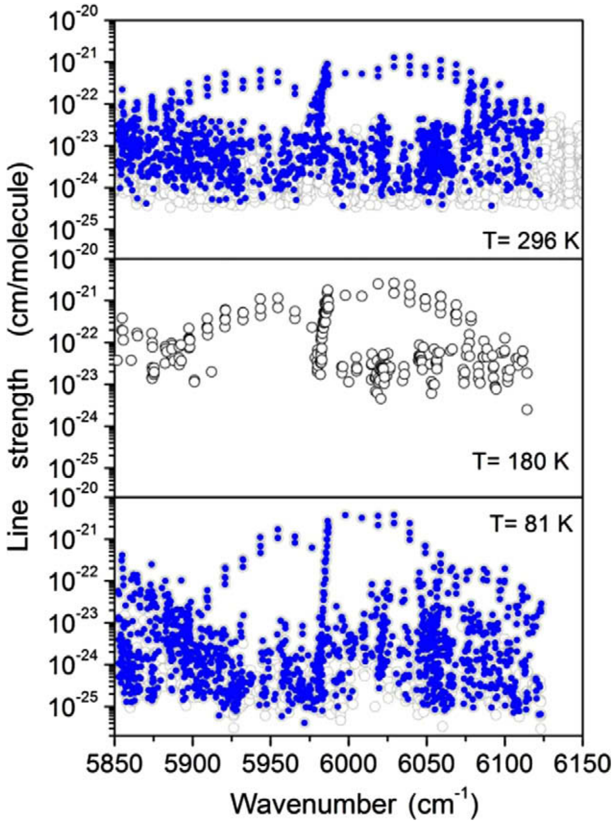

Fig. 1. Overview of $^{13}CH_4$ measurements between 5850 and 6150 cm^{-1}: *Upper panel:* 3481 intensities at 296 K obtained from two FTS spectra (*this work*); *Middle panel:* 267 transitions at 180 K assigned for $\nu_2 + \nu_3 + \nu_4$, $2\nu_2 + \nu_3$ and $2\nu_3$ from Ref. [12]; *Lower panel:* 1629 intensities derived at 81 K by differential absorption spectroscopy (this work). The full circles (*in blue*) highlight the 1196 pairs of transitions observed at 81 and 296 K, for which the lower energy values could be derived (see Section 4 in the text). (For interpretation of the references to color in this figure legend the reader is referred to the web color version of this article.)

In the following sections, we provide the experiment details (Section 2) and describe the construction of the room and cold temperature line lists (Section 3). Then we apply the *two temperature method* (Section 4) to obtain our empirical J values. These results are discussed (Section 5) and compared to known assignments from HITRAN [4] and Nikitin et al. [12].

2. Experiment

The Fourier transform spectrometers (FTS) at the Kitt Peak National Observatory (Tucson, AZ, USA) and a the Bruker 125 HR spectrometer at the Jet Propulsion Laboratory (Pasadena, CA, USA) were used to acquire two $^{13}CH_4$ spectra at room temperature while the differential absorption spectroscopy at Grenoble University (France) provided corresponding data at 81 K. Table 1 provides an overview of the datasets.

2.1. Fourier transform spectroscopy at room temperature

One spectrum at higher optical density was obtained in 1999 with the FTS located at the McMath-Pierce Solar telescope on Kitt Peak Mountain in Arizona. The intended purpose was to identify weak features in normal sample spectra of the octad [17], but the standard near-IR bandpass for this FTS also included the tetradecad region. The experimental set up was similar to that described in numerous other studies involving the 6-m base multipass cell at Kitt Peak (e.g. CH_4, CO_2 and CO [18–20]). As indicated