Available online at www.sciencedirect.com

ScienceDirect

Journal of Molecular Spectroscopy 240 (2006) 14–25

Journal of MOLECULAR SPECTROSCOPY

www.elsevier.com/locate/jms

Preliminary analysis of CH_3D from 3250 to 3700 cm^{-1}

A.V. Nikitin [a,*], J.-P. Champion [b], L.R. Brown [c]

[a] *Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, Russian Academy of Sciences, 634955 Tomsk, Russia*
[b] *Laboratoire de Physique de l'Université de Bourgogne, UMR CNRS 5027, 9 Avenue A. Savary, BP 4780, F-21078 Dijon Cedex, France*
[c] *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA*

Received 5 June 2006; in revised form 12 July 2006
Available online 5 August 2006

Abstract

The infrared spectrum of CH_3D from 3250 to 3700 cm^{-1} was studied for the first time to assign transitions involving the $\nu_2+\nu_3$, $\nu_2+\nu_5$, $\nu_2+\nu_6$, $\nu_3+2\nu_6$ and $3\nu_6$ vibrational states. Line positions and intensities were measured at 0.011 cm^{-1} resolution using Fourier transform spectra recorded at Kitt Peak with isotopically enriched samples. Some 2852 line positions (involving over 900 upper state levels) and 874 line intensities were reproduced with RMS values of 0.0009 cm^{-1} and 4.6%, respectively. The strongest bands were found to be $\nu_2+\nu_3$ at 3499.7 cm^{-1} and $\nu_2+\nu_6$ at 3342.5 cm^{-1} with integrated strengths, respectively, of 8.17×10^{-20} and 2.44×10^{-20} (cm^{-1}/molecule · cm^{-2}) at 296 K (for 100% CH_3D). The effective Hamiltonian was expressed in terms of irreducible tensor operators and adapted to symmetric top molecules. Its present configuration in the MIRS package permitted simultaneous consideration of the four lowest polyads of CH_3D: the Ground State (G.S.), the Triad from 6.3 to 9.5 μm, the Nonad from 3.1 to 4.8 μm and now the Enneadecad (19 bands) from 2.2 to 3.1 μm. The CH_3D line parameters for this interval were calculated to create a new database for the 3 μm region.

Keywords: CH_3D; Monodeuterated methane; Hot bands; Line positions; Line intensities; Database

1. Introduction

Monodeuterated methane (CH_3D) is often used to determine the H/D ratios in planetary atmospheres [1,2]. The 3 μm region is important for outer planet studies because it is a "window" free of strong CH_4 absorption [3]. New observations from spacecraft (such as VIMS [4] on Cassini), aircraft platforms (such as SOFIA [5]) and high-resolution ground-based telescopes [6] have revealed the need for 3 μm CH_3D line parameters because its features can overlap those of other planetary molecules such as NH_3, PH_3, HCN, C_2H_2 and C_2H_6.

Appropriate theoretical models for such symmetric tops [7,8] are already available from formalisms developed for spherical rotors [9,10]. Accurate representation of the positions and intensities of this molecule requires that the polyad scheme be used. The six fundamentals of CH_3D are grouped into two polyads; the Triad (6–10 μm) is composed of the three lowest fundamentals (ν_6, ν_3, ν_5) [11] while the Nonad (3–5 μm) contains the three upper fundamentals (ν_2, ν_4, ν_1) with three combination bands ($\nu_3+\nu_6$, $\nu_5+\nu_6$, $\nu_3+\nu_5$) and three overtones ($2\nu_6$, $2\nu_3$, $2\nu_5$) [12]. The common effective Hamiltonian is developed so that vibrational states within each polyad can be treated simultaneously in order to account for numerous interactions between the energy levels.

The CH_3D spectrum between 2.2 and 3 μm has not been studied previously partly because the region is so complicated. In Fig. 1, a laboratory spectrum is shown between 3000 and 5000 cm^{-1}. The spectral interval has a polyad of 19 interacting states of CH_3D and is designated as the Enneadecad. Its bands are essentially the Triad quanta combined with the Nonad states: $\nu_1+\nu_3$, $\nu_1+\nu_5$, $\nu_1+\nu_6$, $\nu_2+\nu_3$, $\nu_2+\nu_5$, $\nu_2+\nu_6$, $\nu_3+\nu_4$, $\nu_4+\nu_5$, $\nu_4+\nu_6$, $3\nu_3$, $2\nu_3+\nu_5$, $2\nu_3+\nu_6$, $\nu_3+2\nu_5$, $\nu_3+\nu_5+\nu_6$, $\nu_3+2\nu_6$, $3\nu_5$, $2\nu_5+\nu_6$, $\nu_5+2\nu_6$ and $3\nu_6$. These 19 vibrational states are in fact comprised of 37 separate vibrational sublevels, most

---

[*] Corresponding author. Fax: +7 3822 59086.
E-mail address: avn@lts.iao.ru (A.V. Nikitin).

0022-2852/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jms.2006.08.002

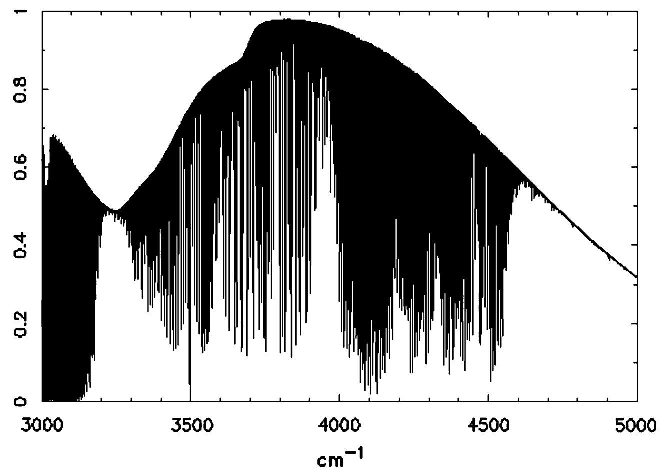

Fig. 1. Observed absorption spectrum of the CH_3D from 3000 to 5000 cm^{-1}. The vertical axis is on an arbitrary scale. The optical path is 150 cm, and the pressure is 20 torr with a 98% enriched sample at 294 K. The scan was recorded in a 70 min period at 0.012 cm^{-1} resolution using the McMath-Pierce FTS at Kitt Peak. The full bandpass of the spectrum is from 1850 to 5200 cm^{-1}. The 19 bands of the Enneadecad fall in the interval from 3200 to 4800 cm^{-1}. The strong features between 3650 and 3950 cm^{-1} due to residual H_2O mask the four weakest CH_3D bands. The features near 3000 cm^{-1} are the upper portion of the Nonad.

of which ultimately give rise to infrared absorption from the ground state. Although the Enneadecad of CH_3D corresponds to the Octad of CH_4 from 2.1 to 2.8 μm [13], the detailed comparison of corresponding bands is not obvious. The Enneadecad of CH_3D contains 12, 7 and 18 sublevels of symmetry A_1, A_2 and E, respectively, while the Octad of CH_4 contains 4, 2, 5, 5, 8 sublevels of symmetry A_1, A_2, E, F_1, F_2, respectively. In both cases the overall vibrational degeneracy is 55.

The complexity of the Enneadecad states is illustrated in Fig. 2. This schematic shows the 19 vibrational levels designated by the number of quanta for each fundamental υ_1, υ_2, υ_3, υ_4, υ_5, υ_6 (e.g., 010001 is $\nu_2+\nu_6$, 011000 is $\nu_2+\nu_3$ and 000003 is $3\nu_6$). The vibrational symmetry of $\nu_2+\nu_5$ and $\nu_2+\nu_6$ is E, while $\nu_2+\nu_3$ is A_1. The states drawn with doubled lines have multiple sub-components; for example, $3\nu_6$ has three (A_1, A_2 and E) sub-levels, and $\nu_3+2\nu_6$ has two (A_1 and E). The vibrations are redrawn in the three other columns to show the expected Fermi and Coriolis interactions based on prior studies of the Triad [11] and Nonad [12]. As a preliminary approach, the Enneadecad polyad can be grouped into three sets. The lowest section between 3250 and 3700 cm^{-1} contains five bands which are essentially the Triad plus ν_2 or $2\nu_6$ ($\nu_2+\nu_6$, $3\nu_6$, $\nu_2+\nu_3$, $\nu_3+2\nu_6$ and $\nu_2+\nu_5$) while the upper portion between 4000 and 4700 cm^{-1} has 10 bands (Triad plus upper Nonad: $2\nu_3+\nu_5$, $2\nu_5+\nu_6$, $\nu_1+\nu_6$, $\nu_4+\nu_6$, $\nu_3+2\nu_5$, $\nu_1+\nu_3$, $\nu_3+\nu_4$, $3\nu_5$, $\nu_1+\nu_5$ and $\nu_4+\nu_5$). The middle set of four bands from 3700 to 4000 cm^{-1} ($2\nu_3+\nu_6$, $\nu_5+2\nu_6$, $3\nu_3$ and $\nu_3+\nu_5+\nu_6$) all involve three quanta of the Triad excited states and are thus expected to be much weaker than the "two quanta" bands in the upper and lower intervals. In our laboratory spectra, only weaker transitions with intensity stronger than 5×10^{-24} (cm^{-1}/molecule · cm^{-2}) are visible, and so the lines in the middle part are not generally observed.

In this article, only the five lowest bands of the Enneadecad are directly analyzed because of the immediate usefulness to planetary astronomy. With the theoretical model, it is possible to predict the approximate location of upper state energy levels as shown in Fig. 3. In the upper panel, the predicted values of reduced upper state energy levels in cm^{-1} are plotted vs the upper state J (the lower panel has the levels that have been assigned in the present study). Many of the interactions between the observed states and the higher sub-vibrational levels are nevertheless included in the model because we used as fixed constants the corresponding interactions within the Triad and Nonad. The vibrational pattern of the entire Enneadecad shown on Fig. 3a illustrates how the main Coriolis and Fermi interactions are extrapolated from the Triad and the Nonad. In particular, the lower Enneadecad has interactions with the middle part due to strong Coriolis terms already known from our previous analysis of the Triad. Similarly the interaction terms active in the Nonad also apply to corresponding states of the Enneadecad. The major advantage of our model is that all the terms and corresponding constants (diagonal or not) obtained in our previous analyses of the lower polyads (Triad and Nonad) can be directly included in the Enneadecad model. In the present work, all major interactions within the Enneadecad are thus considered. This provides an excellent starting prediction for assigning the unexplored region. One interesting aspect of the present study is to discern effects of higher order interactions between the lower and middle portions of the Enneadecad.

2. Experimental details

The spectral data for the present study came from our previous analysis of the Nonad [12], and so experimental details are only briefly repeated here. The spectra were recorded at 0.011 cm^{-1} resolution using the McMath-Pierce Fourier Transform Spectrometer configured with InSb detectors. The spectral band pass covered both the Nonad and the present region simultaneously. Enneadecad positions and intensities at 3 μm could be measured in eight spectra; these involved pure samples of 98%-enriched CH_3D at room temperature in five different absorption cells (with optical paths ranging from 10 to 239 cm). The gas sample conditions are shown in Table 1, and an expanded spectral plot of the measured region is shown in Fig. 4.

The line positions were initially obtained by peak finding of the apodized spectra and later by curve-fitting of the unapodized spectra. The measured line positions and intensities were retrieved using nonlinear-least squares [14] in which the parameters of a synthetic spectrum were adjusted