EPSC Abstracts
Vol. 6, EPSC-DPS2011-206, 2011
EPSC-DPS Joint Meeting 2011

A complete line list for methane at 80 K (1.27 -1.71 μm) for planetary applications.

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Abstract

A line list has been constructed for methane at 80 K from spectra recorded by very high sensitivity laser techniques between 1.26 and 1.71 μm. The achieved sensitivity (α_{min}~10^{-10} cm^{-1}) corresponds to a 1 % decrease of the light intensity after a 1000 km absorption pathlength. The WKMC line lists include lower state energy levels allowing accounting for the temperature dependence of the absorption between 80 K and 300 K. It covers the transparency windows at 1.58 and 1.28 μm which are of particular importance for the studies of the giant planets and Titan. The lines due to the CH_3D and $^{13}CH_4$ minor isotopologues have been identified. From simulations of the CH_3D and methane spectra at low resolution, the CH_3D isotopologue in "natural" abundance (5×10^{-4}) has been found to contribute by up to 30% and 80 % of the very weak absorption near 1.58 μm at 296 and 80 K, respectively.

1. Experimental method

The high resolution absorption spectrum of methane has been recorded by high sensitivity laser absorption spectroscopy at room temperature and at 80 K. In the high absorbing regions surrounding the transparency window at 1.58 μm, the spectra were obtained by differential absorption spectroscopy (DAS) using a specifically designed cryogenic cell and several tens DFB diode lasers [1]. This experimental approach provided a sufficient sensitivity (α_{min}~5×10^{-8} cm^{-1}) in the high energy part of the tetradecad (5850-6180 cm^{-1}) [1-3] and in the icosad region (6700-7700 cm^{-1}) [1-6]. In the transparency windows at 1.58 μm (6165-6750 cm^{-1}) and 1.28 μm (7541–7919 cm^{-1}) a much higher sensitivity was achieved by combining the cavity ring down technique (CW-CRDS) with the same cryogenic cell [7-12]. The sensitivity achieved at 80 K and room temperature (α_{min}~1×10^{-10} cm^{-1}) allowed measuring line intensities as weak as 3×10^{-29} cm/molecule i.e. three orders of magnitude smaller than the intensity cut off of the HITRAN line list of methane [7, 8].

2. The WKMC line list for methane at 80 K

A laborious line by line fit of more than 80000 absorption features allowed for the construction of the WKMC (Wang-Kassi-Mondelain-Campargue) line list at 296 and 80 K (Figs. 1 and 2). Intensity values range between 2×10^{-20} and 1×10^{-29} cm/molecule. The low energy values of the transitions observed both at 80 K and at room temperature were systematically derived from the variation of their line intensities [1-12].

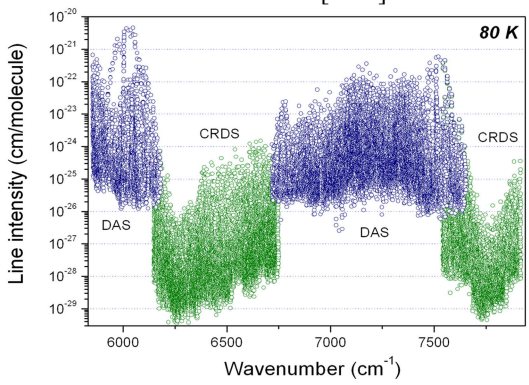

Figure 1: Overview of the WKMC line list for methane at 80 K, constructed from spectra recorded by differential absorption spectroscopy and cavity ring down spectroscopy

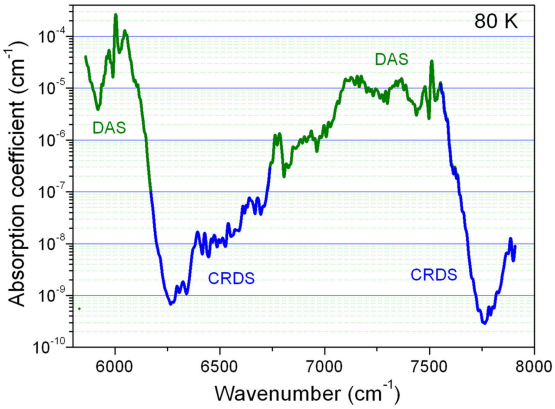

Figure 2: Low resolution simulation (P = 1.0 Torr) obtained from the complete line list (purple) and limited to the CH_3D lines (blue).

The quality of the obtained empirical low energy values is demonstrated by the marked propensity of the empirical low J values of CH_4 to be close to integers. The line lists associated to the low energy values allow accounting for most of the temperature dependence of methane absorption between these two temperatures, over the entire studied region.

3. Importance of the CH_3D contribution in the transparency windows

In the 1.28 and 1.58 μm transparency windows, a number of CH_3D transitions were identified by comparison with a spectrum of CH_3D recorded separately by DAS [9,10,13]. From simulations of the CH_3D and methane spectra at low resolution, the CH_3D isotopologue has been found to contribute by up to 30% and 75 % of the absorption in the 1.58 μm region at 296 and 80 K, respectively. In view of future applications, we point out the importance of taking into account the variation of the CH_3D/CH_4 relative abundance according to the studied absorption medium in order to satisfactorily account for the methane transmission in the considered transparency window [9,10,13].

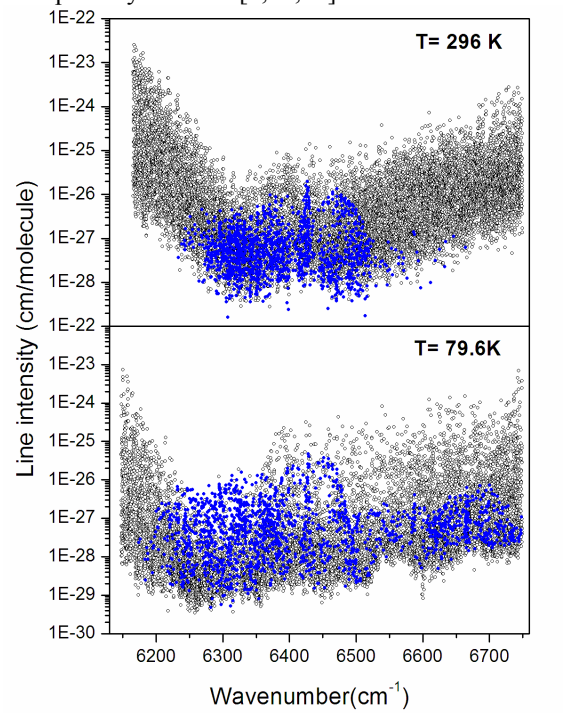

Figure 3: Contribution of the CH_3D transitions to the methane absorption between 6150 and 6750 cm^{-1} at room temperature (upper panels) and 80 K (lower panels). The CH_3D transitions have been highlighted in blue.

4. Conclusion

The final WKMC line lists at 80 K and 296 K (Fig.1), including lower state energy levels and isotopologue identification have already proven to fill a major need for planetary applications in particular for Titan and the giant planets [14]

Acknowledgements

This work is part of the ANR project "CH4@Titan" (ref: BLAN08-2_321467) which is a joint effort among four French laboratories (ICB-Dijon, GSMA-Reims, LSP-Grenoble and LESIA-Meudon) to adequately model the methane opacity. Support of the Groupement de Recherche International SAMIA between CNRS (France), RFBR (Russia) and CAS (China) is acknowledged.

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