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THE ABSORPTION SPECTRUM OF CH_3D IN THE 1.58 μm TRANSPARANCY WINDOW OF METHANE

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СПЕКТР ПОГЛОЩЕНИЯ МОЛЕКУЛЫ CH_3D В ОБЛАСТИ ОКНА ПРОЗРАЧНОСТИ 1.58 мкм МЕТАНА

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Аннотация. *В настоящей работе было проведено исследование спектра высокого разрешения молекулы CH_3D в диапазоне 6100-6530 $см^{-1}$. Было смоделировано более чем 8000 экспериментальных линий для спектра 294 K. Также были получены эмпирические значения энергии нижнего состояния для более чем 4000 переходов из отношения интенсивностей двух спектров. Анализ спектра 81 K выполнен на основе метода комбинационных разностей основного состояния, метода двух температур и при использовании ab initio данных. В результате анализа шести состояний было найдено порядка 800 новых колебательно-вращательных переходов.*

Introduction. The present work is devoted to the 1.58 μm transparency window of methane, which is a spectral region of low opacity lying between strong absorption regions corresponding to the polyads of vibrational states called tetradecad. This region is of particular importance for the studies of the giant planets and Titan, Ref. [1-3]. It allows one to probe very deep into the atmospheres, down to the troposphere and even to the surface. The quality of methane absorption coefficients used in the inference of the surface albedo is important in all planetary simulations and strongly influences the results.

In 2010-2011 the line list of methane in the range of 6000-8000 cm^{-1} was constructed in LiPhy (Laboratoire Interdisciplinaire de Physique), Grenoble, France [4] for both room temperature (RT) and 81 K. In the present work we continue the construction of the line list of CH_3D for the room temperature spectrum in two ranges that have not been studied before. Moreover, in the present work we provide a ro-vibrational analysis of CH_3D in 6180–6700 cm^{-1} range.

Experimental details. Highly sensitive absorption spectra of the CH_3D molecule (sample purity is about 98%) were recorded by differential absorption spectroscopy (DAS) in the range of 6099 - 6991 cm^{-1} in LiPhy, Grenoble, France. The experimental conditions are presented in Table 1.

Table 1

Experimental conditions for the region 6099 - 6991 cm^{-1} of the infrared spectra of CH_3D molecule

Spectrum	Optical path length, cm	Pressure, Torr	Temperature, K
I	294	10	294
II	294	6	81

Construction of the line list. An interactive multi-line fitting program was used to reproduce the spectrum. A Voigt function of the wavenumber was adopted for the line profile. The local baseline and three parameters of each Voigt profile (line center, integrated absorption coefficient, HWHM of the Lorentzian component) were fitted. The HWHM of the Gaussian component was fixed to its theoretical value for $^{12}CH_4$. Following the described procedure, we could construct two line lists in ranges 6100-6200 cm^{-1} / 6394-6530 cm^{-1} for RT spectrum. As a result of this step, we fitted 8067 lines. After that we combined two new line lists with existing information from Ref. [4] and eliminated lines belonging to $^{12}CH_4$ isotopologue. That way we prepared a global line list for spectral range 6100-6530 cm^{-1} for the RT spectrum. The global line list in the same region for 81 K spectrum was done earlier in 2011, Ref. [4]. Using both global line lists for T_1 = 294 K and T_2 = 81 K we applied the two-temperature method described in details in Ref. [4] and obtained empirical lower state energies for about 4500 transitions.

Assignment of the transitions. The studied range was previously discussed in Ref. [4-7]. According to these articles, the most intensive band in the 1.58 μm region is $3\nu_2$ and this band is the most well studied. Other bands ($\nu_2+2\nu_5+\nu_6$ *E*, $\nu_2+\nu_4+\nu_6$ A_1, $3\nu_2$ A_1, $\nu_1+\nu_2+\nu_6$ *E*) also were partially assigned. We extended the analysis of all mentioned bands, made some corrections and analyzed $\nu_2+\nu_4+\nu_6$ *(E)* band for the first time. For the assignment we used three approaches. First, we used the ground state combination difference method. For that we used the ground state structure of CH_3D is available in Ref. [8] and *ab initio* predicted upper level energies, Ref. [9], as an input to find probable combinations of transitions. After that we verified assigned lines by the two-temperature method.

Conclusion. As a result, we fitted about 8000 lines and constructed a line list with line positions and absolute line intensities for the RT spectrum of CH_3D. Then we estimated about 4500 empirical lower state energies by the two-temperature method. After that we extended the analysis of 81 K spectrum of 5 ro-vibrational bands and analyzed 1 band for the first time (Fig. 1). In total, we assigned about 800 new transitions.

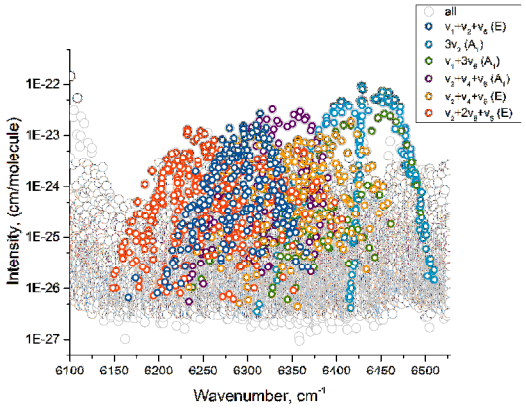

Fig. 1. The whole experimental line list recorded at 81 K (open black circles) and 6 assigned ro-vibrational bands (open colorful circles)

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