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GOSAT-2009 methane spectral line list in the 5550–6236 cm^{-1} range

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ABSTRACT

A methane spectral line list for the 5550–6236 cm^{-1} range with the intensity cut off 4×10^{-26} cm/molecule at 296 K is presented. The line list is based on new extensive measurements of methane spectral line parameters performed at different temperatures and pressures of methane and buffer gases N_2, O_2 and air. This spectral line list is prepared in HITRAN-2008 format and contains the following spectral line parameters of about 11,000 lines: position, intensity, energy for lower state (where possible), air-broadening and air-shifting coefficients, exponent of temperature dependence of air-broadening coefficient and self-broadening coefficient.

1. Introduction

Methane (CH_4), like water and carbon dioxide, is an important greenhouse gas. Nowadays many groups in the world are performing continuous monitoring of several greenhouse gases including methane in the Earth's atmosphere. For these purposes in January 2009 the Japanese Greenhouse gases Observing SATellite (GOSAT) was launched. The main aim of this mission is to measure the column amounts and profiles of the concentration of carbon dioxide and methane over the globe from space [1]. Two types of sensors are installed on GOSAT. The Thermal And Near infrared Sensor for carbon Observation Fourier Transform Spectrometer (TANSO-FTS) detects the solar light reflected on the Earth's surface as well as the thermal radiance emitted from the surface and the atmosphere. The TANSO Cloud and Aerosol Imager (TANSO-CAI) is a radiometer to detect optically thick clouds and correct the effects of optically thin clouds and aerosol. Details of GOSAT sensors have already been described in Ref. [2]. The first, preliminary result obtained with GOSAT TANSO-FTS SWIR was reported in Ref. [3].

The absorption band of CH_4 at 1.67 μm is chosen to retrieve the methane column. But, as we discussed in our previous paper [4], the set of CH_4 spectral line parameters contained in the HITRAN-2004 database [5] for this region was not complete and some of the parameters, in particular, the broadening and shifting parameters were not good enough because they were extrapolated from the measurements performed for lower frequency regions. For this reason we have undertaken systematic studies of the spectral line parameters of the methane molecule in the 5550–6236 cm^{-1} range. Based on these studies, in 2008 the GOSAT methane spectral line list was prepared but has not been published. In this paper we publish a slightly modified version of this spectral line list. It should be emphasized that since that time, new measurements of line positions, line intensities and N_2 broadening

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coefficients have been performed in the region under consideration [6–8]. Some of these new results [4,6,7] were used in generating the methane line list for the HITRAN-2008 database [9].

2. Experiment

The spectra were recorded using Bruker IFS 120 HR and 125 HR high resolution Fourier transform spectrometers at Toray Research Center Inc. The spectrometers were equipped with a CaF_2 beam splitter, InSb detector and tungsten lamp as the light source. An optical band-path filter covering the 5500–6200 cm^{-1} region was used to improve the signal to noise ratios (S/N) of the spectra. The unapodized spectral resolution was 0.005 cm^{-1} and no numerical apodization was applied (Boxcar function). This resolution is specified as 0.9/L (L: maximum optical path difference).

The experimental conditions used are listed in Table 1. The measurements have been performed using 2009.9 and 8.75 cm absorption path length cells. The 2009.9 cm absorption path length cell is a coolable White-type multi-pass cell with CaF_2 windows made by Infrared Analysis Inc.; it has been modified for cooling and temperature controlled (± 1 K) experiments utilizing liquid nitrogen. The cell is composed of Teflon-coated stainless steel walls and silver-coated mirrors. The coolable gas cell with an 8.75 cm absorption path length has ZnSe windows.

Transmittance spectra have been obtained using the ratio of the spectral transmittance in the sample spectra to that in the reference spectra. The reference spectrum measurements have been performed for all experimental conditions presented in Table 1. In these measurements the absorption cell was filled with only N_2 for self- and N_2-broadening experiments and with only O_2 for O_2-broadening experiments. The same total gas pressure and the same temperature were used as in the respective broadening experiment. An example of an overview spectrum is presented in Fig. 1.

The gas samples used in this study were purchased from Japan Fine Products (CH_4 of 99.999% purity, O_2 of 99.999% purity) and from Sumitomo Seika (N_2 of 99.9999% purity). These samples were assumed to have the natural abundances of the isotopologues. The air sample was purchased from Japan Fine Products. It contains CO, CO_2, total hydrocarbons less than 0.1 ppm, NO_x, SO_2 less than 0.01 ppm and concentration of H_2O corresponding to saturated water vapor pressure at lower than $-80\,^{\circ}C$. The gas sample pressure was monitored with 10, 100 and 1000 Torr full-scale MKS Baratron pressure gauges (Type 622 A) throughout the acquisition times.

For the 2009.9 cm absorption path length cell, the gas temperature was estimated from the average of the temperatures measured with eight thermocouples at different positions inside the optical absorption cell. In the case of 8.75 cm, the gas temperature was monitored with a thermocouple mounted into the gas cell.

To retrieve the line positions and line intensities of $^{13}CH_4$, the spectrum of ^{13}C-enriched methane sample (99.3% purity, ISOTEC) was utilized [10]. The spectrum was recorded using 8.75 cm absorption path length cell at room temperature and pressure of 15 Torr.

The wavenumber scale has been calibrated using the CH_4 line positions taken from the HITRAN-2004 database [5]. The quantity $\varepsilon=(\nu_{\rm HITRAN}-\nu_{\rm This\ work})/\nu_{\rm HITRAN}$ has been calculated for 340 isolated lines in each of five spectra recorded with pure CH_4 at 296 K and 20.099 m absorption path length cell (spectra 1–5 in Table 1). Then the ε values were plotted versus CH_4 sample pressure averaged over all 340 lines in each spectrum. Assuming linear dependence of ε with pressure, its value at zero pressure has been found. The value of ε obtained was used for calibration of all spectra recorded using the cell with the 20.099 m absorption path length. The experimental setup was not changed between recording of these spectra and the N_2- and O_2-broadened spectra. A similar calibration procedure has been performed for the 8.75 cm absorption path length cell. Spectra 12–16 (see Table 1) were used for calibration. It should be mentioned that data covering the ranges 5550–6180 and 6180–6236 cm^{-1} included in HITRAN-2004 came from two original sources [11,12], respectively. So, the calibration factors obtained are in some degree averaged over these sources.

3. Spectra assignment

The assignment of the spectral line parameters is very important for the different kinds of applications. First of all the assignment gives the energy of a lower state that is used in the equation for the temperature dependence of the line intensity. The assignment can also be useful for modeling line shape parameters. To get the total assignment it is necessary to solve the inverse spectroscopic problem using an effective Hamiltonian model. The upper vibrational states of the cold bands correspond to the spectral region belonging to the tetradecade of interacting vibrational states. This polyad contains 60 vibrational sublevels, so the inverse problem in this case is very complicated. The most advanced solution of this inverse problem has been obtained in Ref. [13]. The authors of Ref. [13] managed to increase the number of completely assigned lines in this region to about 3000 lines. Complementary to their complete assignment, we have managed to give partial assignments (*J* values of the lower levels) for about another 1600 lines. These partial assignments were made using the temperature dependence of the line intensity (a detailed description of the method is presented in Ref. [14]). The GOSAT spectral line list uses these assignments.

The spectrum of ^{13}C-enriched methane was used for assigning the lines of the $^{13}CH_4$ isotopologue in the natural abundance methane sample. The lines of the strongest bands in this spectrum were assigned on the basis of the assigned spectra of the principal isotopologue using the *ab initio* calculated shifts of the band centers due to isotopic substitution [10]. These results allowed us to assign 318 lines of $^{13}CH_4$ in the spectra of the natural sample of methane.