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Accurate measurements of line strengths and air-broadening coefficients in methane around 1.66 μm using cavity ring down spectroscopy

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Accurate measurements of line strengths and air-broadening coefficients for 10 lines of 12CH4 mostly from the band (2ν2 + ν3) and 2 lines of 13CH4 from the band (2ν4) around 1.66 μm were performed using cavity ring down spectroscopy. Spectra of mixtures of 12CH4 in air and 13CH4 in air with well-defined mole fractions of methane were recorded at pressures between 10 and 90 mbar at 296 K. The values of the line strength for 12CH4 and 13CH4 lines were obtained with the uncertainty 1% and 2%, respectively. The uncertainties of the values of the air-broadening coefficient varied from 2 to 5% depending on the line. The values of the line strength and air-broadening coefficient for two methane isotopes obtained in this work were compared with the corresponding values from different experimental studies, as well as with the data given in HITRAN 2016 database.

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1. Introduction

Methane is an important molecule for atmospheric sciences and ecology. This molecule was found in the atmospheres of the giant planets such as Jupiter, Saturn, Uranus and Neptune [1] and their moons, in particular Titan and Triton [2]. Interpretation of planetary spectra recorded at space crafts and observatories can help to understand the composition of atmospheres and their evolution. Next to carbon dioxide, methane is one of the most important greenhouse gases on Earth. Space and ground-based missions [3–7] are measuring methane concentrations. Spectroscopic methods play an important role in these measurements. For analysis of planetary spectra and for determination of column concentrations of methane in the Earth’s atmosphere accurate data are needed on spectral line parameters of methane in different spectral regions and different temperatures.

A detailed study of the methane spectrum is quite a difficult task. This molecule is highly symmetric; it is characterized by vibrations, which are double and triple degenerate. Moreover, the two stretching vibrational frequencies ν1 and ν3 have close absolute values, at 2917 cm−1 and 3019 cm−1 respectively, and are nearly twice as large as the two deformation vibrational frequencies ν2 and ν4, at 1534 cm−1 and 1306 cm−1 [8]. This results in band overlapping and a very high spectral density, especially in the spectral regions of overtones and combination bands. Next to that, interactions between different vibrational levels make the spectrum even more complicated and the task of line assignment more challenging. The methane spectrum is usually represented by polyads, separated by so-called transparency windows.

Numerous theoretical and experimental studies devoted to the methane spectrum were carried out. The most important ones were summarized in the review of Brown et al. [9], which followed the HITRAN 2012 paper [10], and in the paper related to the latest edition of the HITRAN database HITRAN 2016 [11].

Due to long-term extended theoretical studies [12–21] it became possible to give assignments to the majority of methane lines in the fundamental region around 3.3 μm and great improvement was made in assignments of lines at higher frequencies. Next to theoretical studies numerous laboratory measurements were performed of methane line parameters in different spectral regions. For the measurements of line positions and intensities different spectroscopic techniques were used: Fourier Transform Spectroscopy [22–29], Differential Absorption Spectroscopy [25,30–33], cavity ring down spectroscopy [34–38], Dual Comb Spectroscopy [39], high-intensity Synchrotron radiation combined with Fourier Transform Spectroscopy [40], Intracavity Laser Spectroscopy [41]. In recent years many studies were carried out, devoted to line shape analysis and determination of line parameters such as broadening coefficients, line shifts and line mixing parameters [e.g. 28,42–49].
The numerous laboratory measurements combined with theoretical analysis allowed to improve methane spectral data. For example, in the HITRAN 2012 database more than 70% of methane line parameters were revised: parameters for the known bands were replaced and the new bands were added relative to the HITRAN 2008 edition. In the latest HITRAN 2016 edition the data on line positions and line shape parameters were considerably improved for the methane lines at frequencies higher than 4000 cm\(^{-1}\). Nevertheless, the data for methane are far from being complete: a lot of lines are still not properly assigned, various line parameters are missing and the accuracy of the line data is not very high. For example, typical uncertainties in the line strength values for more intense lines are 2–5%, and for less intense lines they reach 10–20%, or even higher [11]. At the same time, atmospheric calculations need methane line parameters values with an accuracy higher than 1%. Thus, further theoretical modeling is needed, as well as accurate laboratory measurements for validation of theoretical calculations.

In this work, we present the results of traceable measurements of line intensities and air-broadening coefficients in methane in the tetradecad region around 1.66 \(\mu m\), using cavity ring down spectrometry. The results of accurate line strength measurements in carbon dioxide obtained during the validation of the spectrometer are also given. The work was part of the EUROMETRISPEC project carried out by several European metrological institutes, which aim was to draw attention to the problem of traceability of spectral line data and partly to improve the accuracy of these data for several most important atmospheric gases.

2. Experimental

Absorption spectra of methane were recorded using a cavity ring down spectrometer operating around 1.65 \(\mu m\). This spectrometer was described in details in a previous paper, devoted to line strength measurements and relative isotopic ratio measurements in carbon dioxide [50]. Shortly, a continuous wave external cavity diode laser was used, operating in the spectral region of 5800–6250 cm\(^{-1}\) with an output power 20 mW. Having passed through an optical isolator, the laser beam is coupled to a single-mode optical fiber. After the fiber, the beam is divided in a 50/50% beam splitter. One beam is sent to the wavelength monitor to monitor the wavelength during spectra recording. The other beam goes through an acousto-optical modulator (AOM) towards the cavity ring down (CRD) cell. The AOM allows to quickly and efficiently intermit the beam for measurements of the decay curves. A lens between the AOM and the CRD cell is used for mode matching the laser beam to the fundamental transverse mode of the cavity. To determine the optimal focal length and the position of the focusing lens, the actual size of the laser beam was measured and compared to the size of the cavity modes calculated from the parameters of the CRD cell (length of the cell and curvature of the mirrors). The mode matching considerably improved the CRD signal. The CRD cell consists of a 50-cm long stainless steel cell with two highly reflective mirrors (reflectivity \(\approx 99.97\%\)). The decay time in the empty cell is \(\approx 5\) \(\mu s\), corresponding to an optical path length of \(\approx 1.5\) km. One of the mirrors of the cell is mounted onto a piezo to match the laser frequency to the longitudinal cavity modes of the cell. Spectral measurements were performed at room temperature (296 K), while the temperature stability of the cell could be maintained within 1 K. The cell is equipped with a pressure gauge to measure pressures up to 100 mbar, a gas inlet for the gas mixture sample and a gas outlet towards the pump. The gauge was calibrated; its uncertainty in pressure reading did not exceed 0.2%. The light leaking out of the CRD cell is focused onto an avalanche photodetector and the signal from the detector is sent to a computer to calculate the decay time with LabVIEW. The piezo of the external cavity diode laser was used to scan the laser frequency over a measured absorption line. To move to another spectral line of methane we adjusted the position of the grating of the external cavity diode laser.

A spectral line absorption within CRD spectroscopy is given in terms of the decay time \(\tau\) needed for the laser intensity to leak out of the cavity. The decay time \(\tau\) of the laser light with frequency \(\nu\) (here \(\nu\) is the wavenumber, cm\(^{-1}\)) is determined by the loss processes in the CRD cell and can be written as [51]:

\[
\tau = \frac{d}{c} \cdot \frac{1}{\ln(r)} + e_{\nu}d
\]

where \(d\) is the length of the cavity, \(c\) the speed of light, \(r\) the intensity reflectivity of the cavity mirrors and \(e_{\nu}\) the extinction coefficient of the molecules at that frequency. Here, it is assumed that the entire cavity with the length \(d\) is filled with gas. The extinction of light in the cell is determined by absorption and scattering processes. It can be shown that for the wavelengths around 1.66 \(\mu m\) the contribution of the light scattering is very small - for atmospheric molecules at 100 mbar (maximum pressure used in this work) it is of the order of \(10^{-10}\) cm\(^{-1}\). Therefore, we assume that the measured decay time is totally determined by light absorption. Having measured the decaying signal and determined the decay time, one can obtain the absorption coefficient of the molecules \(k_{\nu}\):

\[
k_{\nu} = \frac{1}{\tau_{\nu, C} - \frac{\ln(r)}{d}} = \frac{1}{\tau_{\nu, C} - \frac{1}{\nu C}}
\]

In the last equation the term \(1/(\tau_{\nu, C})\) represents the losses in the empty cavity (baseline signal) and can be determined by measuring the decay time of the laser intensity in the empty cell \(\tau_{\nu, 0}\) (or in the cell filled with a gas transparent in the spectral region studied). During the line strength measurements in methane, spectra of pure nitrogen at pressures corresponding to the pressures of CH\(_4\)/air samples, were used as baseline spectra.

3. Results

3.1. Validation of the cavity ring-down spectrometer: line strength measurements in carbon dioxide

Before starting the measurements with methane, the CRD spectrometer was validated by measuring the strength of the absorption line in carbon dioxide. For this, a calibrated mixture of carbon dioxide in air with mole fraction of CO\(_2\) \((0.2997 \pm 0.0015)\) was prepared in VSL, the Dutch Metrology Institute. Carbon dioxide with natural isotopic abundance was used for this mixture. 25 absorption spectra of the P45e line of 12CO\(_2\) at 6153.6934 cm\(^{-1}\) (01101 \(\rightarrow\) 31113 band) [8] were recorded at 4 different pressures of 20, 40, 60 and 80 mbar at room temperature 296 K.

Spectra of the measured absorption line were analyzed using the software described earlier [50]. Being based on the generalized non-linear method of least squares this software allows fitting the experimental spectral points with a chosen profile and calculating the optimal values of the parameters for this profile, as well as calculating the relative residuals between the experimental data points and their adjusted values. The uncertainties of the measured values of the decay time, frequency and temperature of the sample are taken into account. The value of the temperature is used to calculate the Doppler profile, as the Doppler width is constrained to its theoretical value. Voigt and Galatry profiles were used to fit the spectra of the P45e line of carbon dioxide. The more advanced Galatry profile takes into account Dicke narrowing of spectral lines, resulting from velocity changing collisions. An example of the 12CO\(_2\) absorption line measured using CO\(_2\)/air mixture at 80 mbar and the fitted profile are given in Fig. 1. The difference
between Voigt and Galatry profiles is so small that it can not be seen in the figure.

Spectral analysis showed that Voigt and Galatry profiles give similar description of the P45e line of carbon dioxide measured at different pressures; the values of the line area determined with two profiles did not differ within the uncertainties. The values of the line area were determined with the uncertainty ~0.5% for samples at 80 mbar and 1.5–2% for samples at 20 mbar.

The values of the line area for the P45e line of carbon dioxide, obtained from spectra at different pressures, were used to determine the value of the line strength. The relation between the line area $A$ ($\text{cm}^{-2}$) and the line strength $S$ ($\text{cm/molecule}$) is given by the following equation:

$$ S = \frac{A}{n} \cdot 10^6 $$

where $n$ ($\text{molecule/m}^3$) is the concentration of absorbing molecules. For the experimental conditions used in this work the concentration can be calculated using the ideal gas equation:

$$ n = \frac{p \cdot x}{k_B \cdot T} $$

where $p$ ($\text{Pa}$) is the pressure of the sample, $x$ is the mole fraction of absorbing molecules, $k_B = 1.38065 \times 10^{-23}$ $\text{J/K}$ is the Boltzmann constant, and $T$ ($\text{K}$) is the temperature of the sample. Therefore, the line strength values can be determined from the slope of a straight line fitted to the plotted values of $A$ over $n$. The corresponding plot for the P45e line of carbon dioxide is given in Fig. 2. This plot contains the line area values determined from all 25 absorption spectra of CO$_2$/air mixture at 4 different pressures. During the fitting procedure the uncertainties of the values of the line area (0.5–2%), pressure (0.2%) and temperature (0.3%) of the sample, and mole fraction of CO$_2$ molecules (0.5%) were taken into account. As a result the value of the line strength for the P45e line of CO$_2$ at 296 K was determined with the uncertainty less than 1%: $(5.60 \pm 0.04) \times 10^{-20} \text{cm/molecule}$.

The value of the line strength for the $^{12}$CO$_2$ line obtained in this work was compared with the corresponding value calculated ab initio by Zak et al. [52], which is included in the last edition of the HITRAN database HITRAN 2016. It should be noted that in the line list presented in [52] next to the P45e line a much weaker P23e line of $^{12}$CO$_2$ at $6153.708$ cm$^{-1}$ $(11101 \rightarrow 41113$ band) could be found: $S(P45\text{e line}) = 5.507 \times 10^{-28} \text{cm/molecule}$ and $S(P23\text{e line}) = 1.309 \times 10^{-27} \text{cm/molecule}$. During our spectral measurements and line shape analysis these two close lines of carbon dioxide could not be separated even in the spectra at low pressures, due to Doppler broadening. Hence, we believe that the line strength value obtained in this work, represents the sum of the line strength values of two lines P45e and P23e and should be compared with the corresponding value from Zak et al. [52]: $5.638 \times 10^{-26} \text{cm/molecule}$. It can be seen that the difference between the two values does not exceed 0.7% showing a very good agreement between ab initio calculations and presented experimental data. It should be mentioned that the same agreement between the CRD line intensity measurements and theoretical calculations [52] was already found earlier, for the $^{12}$CO$_2$ and $^{13}$CO$_2$ lines [50].

### 3.2. Line strength measurements in methane $^{12}$CH$_4$ and $^{13}$CH$_4$ around 166 $\mu$m

After validation of the CRD spectrometer, line strength measurements in methane $^{12}$CH$_4$ and $^{13}$CH$_4$ were carried out. For these measurements two calibrated mixtures were prepared in VSL, the Dutch Metrology Institute: a $^{12}$CH$_4$/air mixture with the mole fraction of $^{12}$CH$_4$ 2.00 mmol/mol (uncertainty 0.7%) and a $^{13}$CH$_4$/air mixture with the mole fraction of isotopic methane $^{13}$CH$_4$ 49.5 µmol/mol (uncertainty 1.8%). The mixtures were prepared using cylinders with $^{12}$CH$_4$ (99.9% purity) and with $^{13}$CH$_4$ (99% purity) from Sigma Aldrich.

Absorption spectra of 10 lines of $^{12}$CH$_4$, mostly from the $(2v_2 + v_3)$ band, and 2 lines of $^{13}$CH$_4$ from the $(2v_3)$ band in the spectral region between 5997 and 6046 cm$^{-1}$ were studied. Positions of the measured lines of $^{12}$CH$_4$ and $^{13}$CH$_4$, taken from the HITRAN 2016 database [8], are given in Tables 1 and 2. We used the following measurement procedure. Absorption spectra of each selected methane line were recorded during several days; every experimental day the cavity ring down cell was filled with a new portion of methane/air mixture from the cylinder. Spectra were recorded at 296 K for several pressures of the mixture in the range 10–90 mbar, 3–4 spectra at every selected pressure. As a result for each selected methane line 30–40 spectra were recorded during 3–5 days. Typical CRD spectra of $^{12}$CH$_4$ and $^{12}$CH$_4$ absorption lines are presented in Fig. 3.

Using CRD spectra and the relation between the decay time and the absorption coefficient (2), absorption profiles were determined for every measured spectral line of methane. The absorption lines were then fitted with Voigt and Galatry profiles using the software described in Section 3.1. It should be noted that, due to complexity of methane absorption spectrum, the measured lines cannot be considered as completely isolated. During the line shape

---

**Fig. 1.** Measured values of absorption coefficient and the fitting profile for the P45e line of $^{12}$CO$_2$ at 6153.6934 cm$^{-1}$, recorded at 80 mbar and 296 K.

**Fig. 2.** Determination of the line strength for the P45e line of $^{12}$CO$_2$ at 6153.6934 cm$^{-1}$. 

---
Table 1
The values of the line strength in $^{12}$CH$_4$ compared with ab initio calculation and the HITRAN 2016 database.

<table>
<thead>
<tr>
<th>Line number</th>
<th>Line position, cm$^{-1}$ [8]</th>
<th>Line strength, cm/molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present work 1%</td>
<td>HITRAN 2016 [8]</td>
</tr>
<tr>
<td>1</td>
<td>6009.547</td>
<td>8.20e-24</td>
</tr>
<tr>
<td>2</td>
<td>6014.88474</td>
<td>1.71e-23</td>
</tr>
<tr>
<td>3</td>
<td>6014.939</td>
<td>1.22e-23</td>
</tr>
<tr>
<td>4</td>
<td>6020.737</td>
<td>1.04e-23</td>
</tr>
<tr>
<td>5</td>
<td>6024.208</td>
<td>1.15e-23</td>
</tr>
<tr>
<td>6</td>
<td>6024.356</td>
<td>2.05e-23</td>
</tr>
<tr>
<td>7</td>
<td>6024.59784</td>
<td>2.03e-23</td>
</tr>
<tr>
<td>8</td>
<td>6024.792</td>
<td>3.41e-23</td>
</tr>
<tr>
<td>9</td>
<td>6028.55373</td>
<td>2.56e-23</td>
</tr>
<tr>
<td>10</td>
<td>6045.1057</td>
<td>1.45e-23</td>
</tr>
</tbody>
</table>

Table 2
Line strength values for $^{13}$CH$_4$ lines obtained in the present work (column 2), as well as the corresponding values from other experimental studies (columns 3–5).

<table>
<thead>
<tr>
<th>Line position, cm$^{-1}$ [8]</th>
<th>Line strength, cm/molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present work 2%</td>
</tr>
<tr>
<td>5997.960</td>
<td>5.75e-24</td>
</tr>
<tr>
<td>6008.465</td>
<td>5.82e-24</td>
</tr>
</tbody>
</table>

![Fig. 3](image-url)

Fig. 3. Left panel: CRD spectrum of the $^{13}$CH$_4$ absorption line at 5997.960 cm$^{-1}$ using a 49.5 μmol/mol $^{13}$CH$_4$/air mixture at 60 mbar. Right panel: two $^{13}$CH$_4$ absorption lines at 6014.88474 cm$^{-1}$ and 6014.939 cm$^{-1}$, using a 2.00 mmol/mol $^{13}$CH$_4$/air mixture at 70 mbar.

Analysis, the weaker methane absorption lines next to every selected line were taken into account. The positions and intensities of these weaker lines were taken from HITRAN 2016 [8], and used as input data for the fitting software. Weaker lines were taken into account for the analysis, if they are stronger than 1/100 of the measured methane line.

An example of fitting the absorption spectrum of $^{12}$CH$_4$ around the line at 6024.59178 cm$^{-1}$, using a Voigt and Galatry profile, is shown in Fig. 4. While fitting the line at 6024.59178 cm$^{-1}$, a weaker line of $^{12}$CH$_4$ at 6024.502 cm$^{-1}$, with a ~10 times smaller intensity is taken into account. Although these lines seem to be separate, fitting only the stronger absorption line in a limited spectral interval without the weaker line will lead to overestimation of the area of the line at 6024.59178 cm$^{-1}$ by 2.5%. The difference between Voigt and Galatry profiles is so small that it can’t be seen on the top panel of Fig. 4. Two profiles give a similar description of the recorded absorption spectrum, as could be seen from the relative residuals.

The results of the line shape analysis showed that the Voigt and Galatry profiles give a similar description of the measured absorption profiles for the majority of the measured lines of $^{12}$CH$_4$ and $^{13}$CH$_4$. Only for several lines of $^{12}$CH$_4$, the Galatry profile showed a slightly better fit. For these lines a smaller difference between the measured and the adjusted values of the temperature were obtained for Galatry profile as compared to the Voigt profile. That means that for a more accurate description of the line shape one needs to take into account Dicke narrowing instead of using a simple Doppler profile. Unfortunately, due to limited signal-to-noise ratio the values of the parameters for Galatry profile, in
particular the value of the narrowing coefficient could not be determined reliably. At the same time the values of the line area derived for Voigt and Galatry profiles did not differ within the calculated uncertainties. Thus for further data analysis, line area values were used of the corresponding Voigt profile. The uncertainties of these values depend on the absorption strength and decrease with increasing mixture pressure. While for mixtures recorded in the pressure range between 10–50 mbar the uncertainty was around 2%; for pressures between 50–90 mbar the uncertainty of the line area values was 1–1.5%.

The values of the line strength for the measured methane lines were determined using the linear dependence of the line area on the concentration of absorbing molecules (3). Examples of such plots for several lines of $^{12}$CH$_4$ and $^{13}$CH$_4$ are given in Fig. 5.

![Graph showing line strengths for $^{13}$CH$_4$ and $^{12}$CH$_4$](image)

**Fig. 5.** Determination of the line strength values: for $^{13}$CH$_4$ line at 5997.960 cm$^{-1}$ (left panel) and for $^{13}$CH$_4$ lines at 6014.88474 cm$^{-1}$ and 6014.939 cm$^{-1}$ (right panel).

During the fitting, uncertainties were taken into account of the line area values (1–2%), pressure (0.1–0.3%) and temperature (0.3%), and the mole fraction of absorbing molecules in the mixture (0.7% for $^{12}$CH$_4$ and 1.8% for $^{13}$CH$_4$). As a result, the values of the line strength for 10 lines of $^{12}$CH$_4$ were determined with an uncertainty of 1%, and for the 2 lines of $^{13}$CH$_4$ with an uncertainty of 2%. These uncertainties are largely due to the corresponding uncertainties in the mole fraction of $^{12}$CH$_4$ and $^{13}$CH$_4$ in the mixtures, which were mainly determined by the purity of the available gases. The second largest contribution to the overall uncertainty is the uncertainty in the line area, resulting from the complexity of the methane spectrum. Next to the 12 selected lines of methane the line strength value was also determined for one weaker line of $^{12}$CH$_4$ at 6024.502 cm$^{-1}$ (shown at Fig. 4): $2.1 \times 10^{-24}$ cm/molecule (uncertainty 5%). This value agrees with the corresponding value from HITRAN 2016 [8] $1.847 \times 10^{-24}$ cm/molecule (uncertainty $\geq 20\%$) within the given uncertainties.

The values of the line strength for the selected lines of two main isotopes of methane are given in Tables 1 and 2. The data in these tables relate to the temperature 296 K and natural isotopic abundances of $^{12}$CH$_4$ and $^{13}$CH$_4$.

Table 1 contains also the corresponding line strength values from HITRAN 2016 [8] and from the most recent ab initio calculations of Nikitin and co-workers [20]. The line strength values given in the HITRAN 2016 database originate from a comprehensive study of methane in the tetradecad region between 5500 and 6240 cm$^{-1}$, using Fourier Transform Spectroscopy [24,28]. During this study methane lines with intensities higher than $5 \times 10^{-25}$ cm/molecule were measured and their spectral parameters were retrieved using the Voigt profile. The assignments of the measured lines were considerably improved due to global modeling, performed with an effective operators method, and due to spectral measurements at different temperatures. The work resulted in the line list GOSAT-2014 (“Greenhouse Gases Observing Satellite” Project), which contains methane spectral line parameters for about 12,150 transitions between 5500 and 6240 cm$^{-1}$ [28]. The uncertainty of the line strength values in GOSAT-2014 line list varies from 10% for the strongest lines up to 50% for the weakest lines. In HITRAN 2016 the uncertainty code 3 is used, which corresponds to an uncertainty of $\geq 20\%$ (see Table 1). The theoretical work of Nikitin et al. [20] contains a list of line intensities for more than 5000 strong methane lines in the infrared, for frequencies lower than 6166 cm$^{-1}$. The line strength values were calculated from ab initio potential energy surfaces and dipole moment surfaces, using nuclear motion variational calculations and taking into account the tetrahedral symmetry of the methane molecules. Table 1 shows that the 1%-accuracy line strength values in $^{13}$CH$_4$ are in good agreement with the corresponding values from HITRAN 2016 [8] and Nikitin at el [20].

It is interesting to compare the results on methane line intensities obtained in this work, with recent other experimental studies on methane in this wavelength region. During the last 10 years the group of Campargue in Grenoble performed a detailed, accurate study on methane between 1.26 and 1.71 μm [30–38]. The values of the line parameters, such as frequency and intensity, were determined using two spectroscopic techniques: Cavity Ring Down Spectroscopy and Differential Absorption Spectroscopy. These studies resulted in the empirical methane database known as WKLMC line list [38] containing line parameters for 55,262 lines at 296 K and 72,225 lines at 80 K. The data from this line list were used in the HITRAN 1012 database [10]. In the WKLMC database, the line strengths for $^{12}$CH$_4$ lines around 166 μm which can be compared with the results of the present work, were obtained using Differential Absorption Spectroscopy [32]. The average uncertainty of the line strength values was estimated to be of the order of 3%, while it reached much higher values for weaker lines. Margolis [22] performed methane measurements in the 5500–6180 cm$^{-1}$ wavelength region, using Fourier Transform Spectroscopy. Line positions and intensities were obtained for more than 2000 lines with intensities higher than $1.4 \times 10^{-24}$ cm/molecule. Here, the average estimated uncertainty in the line strength was 3.5%. Margolis [22] used a Doppler profile for spectra analysis as the pressure of methane samples did not exceed 30 mbar. Another detailed study of methane in the wavelength regions of 5891–5996 cm$^{-1}$ (P branch) and 6015–6115 cm$^{-1}$ (R branch) of the (2$\nu_3$) band was performed by Devi and co-workers [47]. These spectra were recorded with a high-resolution Fourier Transform Spectrometer at temperatures between 130 K and 295 K. As a result, line positions, intensities, self- and air-broadening coefficients and shifting parameters with their temperature dependencies, were retrieved for 1517 lines. The uncertainties of the intensity values differ from less than 1% for the lines with intensity in the order of $10^{-22}$ cm/molecule, to several percent for weaker lines [47]. Similar to the present study, line parameters for the majority of lines of $^{12}$CH$_4$ in [32,38 and 47] were retrieved from the observed spectra using a multi-line fitting program, assuming a Voigt profile with a fixed Doppler linewidth. In [47], Dicke narrowing or speed-dependence were considered only for two lines at 6024.59178 cm$^{-1}$ and 6024.792 cm$^{-1}$, showing larger residuals.

In Fig. 6, a comparison is made for the experimental line strengths, determined in the different studies, for 10 lines of $^{12}$CH$_4$. In this figure, the ratios are shown between the values of the experimental line strengths (present work, [22,38,47]) and the corresponding data from HITRAN 2016 [8]. For convenience the $^{12}$CH$_4$ lines are represented by numbers, corresponding to the first
column of Table 1. It should be noted that in the different studies, methane spectra were recorded with different spectroscopic methods: Fourier Transform Spectroscopy [22 and 47], Differential Absorption Spectroscopy [38], and Cavity Ring Down Spectroscopy (present work). The pressures of the samples varied from several mbar to atmospheric pressure. Nevertheless, the values of the line strength from different works for the majority of lines do not differ more than by 5%.

For \(^{13}\text{CH}_4\), the line strength values in HITRAN 2016 database were most probably taken from the work of Campargue et al. [33]. On the HITRAN website [8] one could find as a reference the work of Starikova et al. [19], but we believe that this is not correct. In [33], the absorption spectrum of \(^{13}\text{CH}_4\) was studied in the high energy part of the tetradecad region 5853–6201 cm\(^{-1}\), using Differential Absorption Spectroscopy. Their samples were prepared from 99% \(^{13}\text{C}\) enriched methane. The final line list consists of line positions and intensities for 7207 lines at 296 K, with uncertainties in intensity values larger than 2%. In the HITRAN 2016 database for the two \(^{13}\text{CH}_4\) lines from Table 2, the values of the line strength are given with the uncertainty code 4, corresponding to uncertainty of 10–20%. Lyulin and co-workers [25] performed a detailed study of the \(^{13}\text{CH}_4\) absorption spectrum in the tetradecad region 5850–6150 cm\(^{-1}\), using Fourier Transform Spectroscopy. Their samples were prepared from 90% and 99% \(^{13}\text{C}\) enriched methane. The line list contains line positions and intensities for 3481 lines at 296 K; the uncertainties in the line strength values are larger than 3%. These intensity values were used for the HITRAN 2012 database [10]. In Table 2, the last column contains the line strength values from the GOSAT-2014 line list [28], described earlier in this section. For the GOSAT line list the methane spectra were recorded with a natural abundance for the different methane isoposes. Therefore, the intensity values for the \(^{13}\text{CH}_4\) lines are given with large uncertainty between 10 and 50%. The data for the two specific methane lines in Table 2 show that the line strength values from different studies, obtained using different spectroscopic techniques, do not differ more than by 7%, well within the given uncertainties. Accurate line strength values obtained in the present work agree within 3% with the corresponding values of Lyulin et al. [25], characterized with a relative low uncertainty of \(>3\%\).

3.3. Air-broadening coefficients in methane \(^{12}\text{CH}_4\) and \(^{13}\text{CH}_4\) around 1.66 \(\mu\)m

During the fitting of the measured absorption lines of \(^{12}\text{CH}_4\) and \(^{13}\text{CH}_4\) with Voigt profile, apart from the values of the line area, the values of the Lorentzian width of the lines were obtained. In these calculations theoretical values for the Doppler width were used, corresponding to the temperature of the sample. Lorentzian half-width \(\gamma(p, T)\) of a methane line in a \(^{12}\text{CH}_4\)/air mixture could be determined by the following equation (e.g. [47]):

\[
\gamma(p, T) = p \left[ \gamma_0^\text{self} (p_0, T_0) + \gamma_0^\text{air} (p_0, T_0) (1 - x) \frac{T_0}{T} \right]^{n_1} + \gamma_0^\text{air} (p_0, T_0) \left( 1 - \frac{T_0}{T} \right)^{n_2}
\]

where \(p\) and \(T\) are the total pressure and temperature of the sample, \(\gamma_0^\text{self} (p_0, T_0)\) and \(\gamma_0^\text{air} (p_0, T_0)\) the self- and air-broadening coefficients at \(p_0 = 1\) atm and \(T_0 = 296\) K (cm\(^{-1}\)/atm), \(n_1\) and \(n_2\) the parameters determining the temperature dependence of the line width, and \(x\) the mole fraction of methane in the mixture. Here, all spectral measurements were performed at 296 K, using methane/air mixtures with low mole fractions of methane: 0.2% \(^{12}\text{CH}_4\)/air and 0.00495% \(^{13}\text{CH}_4\)/air mixtures. Under these experimental conditions the Lorentzian half-widths of the methane absorption lines were totally determined by the second term in Eq. (5), with a temperature factor \([T_0 / T]^{n_2} = 1\). For every measured methane line the values of the Lorentzian half-width, obtained from the fits at different pressures, were plotted against the corresponding values of the partial pressure of air in the mixture \(p\_\text{air} = p (1 - x)\). Such a plot is given in Fig. 7 for the \(^{12}\text{CH}_4\) absorption line at 6045.1057 cm\(^{-1}\). The value of the air-broadening coefficient \(\gamma_0^\text{air} (p_0, T_0)\) can be determined from this plot, using the linear dependence of the Lorentzian half-width on the pressure of air in the sample.

The values of the air-broadening coefficient are collected in Table 3, for all measured lines of the two methane isoposes, as well as the corresponding values from HITRAN 2016 [8]. The uncertainties of the values of the air-broadening coefficient determined in this work vary from 2% for the more isolated methane lines to 5% for the more blended lines. To our knowledge, the values of the air-broadening coefficient for the two \(^{13}\text{CH}_4\) lines are the most accurate published experimental values. For the majority of lines in Table 3, the air-broadening coefficients in the
Table 3
Comparison of the measured air-broadening coefficients in $^{12}$CH$_4$ and $^{13}$CH$_4$ with the HITRAN 2016 database. The values are given for $T=296$ K.

<table>
<thead>
<tr>
<th>Line position, cm$^{-1}$ [8]</th>
<th>Air-broadening coefficient, cm$^{-1}$/atm</th>
<th>Present work</th>
<th>HITRAN 2016 [8]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{12}$CH$_4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6009.547</td>
<td>0.064 ± 0.001</td>
<td>0.063</td>
<td></td>
</tr>
<tr>
<td>6014.88474</td>
<td>0.070 ± 0.002</td>
<td>0.0672</td>
<td></td>
</tr>
<tr>
<td>6014.939</td>
<td>0.059 ± 0.002</td>
<td>0.0604</td>
<td></td>
</tr>
<tr>
<td>6020.737</td>
<td>0.060 ± 0.002</td>
<td>0.063</td>
<td></td>
</tr>
<tr>
<td>6024.208</td>
<td>0.061 ± 0.003</td>
<td>0.065</td>
<td></td>
</tr>
<tr>
<td>6024.356</td>
<td>0.065 ± 0.003</td>
<td>0.066</td>
<td></td>
</tr>
<tr>
<td>6024.59178</td>
<td>0.069 ± 0.002</td>
<td>0.066</td>
<td></td>
</tr>
<tr>
<td>6024.792</td>
<td>0.063 ± 0.002</td>
<td>0.066</td>
<td></td>
</tr>
<tr>
<td>6028.55373</td>
<td>0.070 ± 0.004</td>
<td>0.0638</td>
<td></td>
</tr>
<tr>
<td>6045.1057</td>
<td>0.065 ± 0.001</td>
<td>0.0660</td>
<td></td>
</tr>
<tr>
<td>$^{13}$CH$_4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5997.960</td>
<td>0.054 ± 0.001</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>6008.465</td>
<td>0.062 ± 0.001</td>
<td>0.065</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 8. Comparison of the air-broadening coefficients of $^{12}$CH$_4$ lines, normalized to the HITRAN 2016 database data, from the different studies: Lyulin et al. [42], Devi et al. [47], Nikitin et al. [28] and present work. For line numbers see Table 1.

HITRAN 2016 database are represented by values, which are averaged by $J$ (total angular momentum excluding nuclear spin), or are assigned, or estimated, from empirical lower-state energy [8], and hence have an uncertainty $\geq 20\%$ (code [3]). Only for 4 lines of $^{12}$CH$_4$ (at 6014.88474, 6014.939, 6028.55373 and 6045.1057 cm$^{-1}$), the values of the air-broadening coefficient are taken from measurements [42], and have an uncertainty 5 - 10% (code [5]). For all lines of $^{12}$CH$_4$ and $^{13}$CH$_4$, the values of the air-broadening coefficients agree with the HITRAN 2016 database, within the given uncertainties.

Air-broadening coefficients for the $^{12}$CH$_4$ lines near 1.66 $\mu$m were determined in several other experimental studies [28,42,47]. In all these studies the absorption spectra of methane were recorded at different pressures and temperatures, using Fourier Transform Spectroscopy. Fig. 8 gives a comparison of the ratios of the air-broadening coefficients normalized to the HITRAN 2016 database, from this work and the other studies. Ratios are shown for 10 lines of $^{12}$CH$_4$. Similar to Fig. 6, the lines are represented by numbers given in the first column of Table 1. It can be seen that the data from different studies differ by 5–10%, although individual data are presented with uncertainties of several percent [28] or even less than 1% [42,47].

4. Conclusions
In the present work accurate measurements of line intensities and air-broadening coefficients for ten lines of $^{12}$CH$_4$ and two lines of $^{13}$CH$_4$ around 1.66 $\mu$m were performed using cavity ring down spectroscopy. Spectra of mixtures of $^{12}$CH$_4$/air and $^{13}$CH$_4$/air with well-known mole fractions of methane were recorded at room temperature (296 K) in the pressure range 10–90 mbar. Absorption spectra were fitted with Voigt and Galatry profiles. It was concluded that within the experimental uncertainties these two profiles give similar description of the recorded methane lines.

The values of the line strength were determined with 1% and 2% uncertainties for the $^{12}$CH$_4$ and $^{13}$CH$_4$ lines, respectively. To our knowledge, these are the most accurate published experimental values for the twelve studied methane lines. Line strength data for both methane isotopes showed good agreement in comparison with data from other experimental studies [22,25,28,33,38,47], as well as the most recent theoretical calculations [20]. For the majority of the measured lines the difference does not exceed 5%. The good agreement between the line strength values of this work and those in the HITRAN 2016 database [8] may suggest that the uncertainty of the methane line strength values in HITRAN database could be improved.

The accuracy of the air-broadening coefficient values in this work varied from 2 to 5%, depending on the line. For the first time, the air broadening coefficients for two $^{13}$CH$_4$ lines were measured with an accuracy of 2%. But it should be noted that advanced line shape profiles, including line mixing, should be used for accurate description of methane spectrum at pressures close to atmospheric pressure (see Tran et al. [43]). In the present work, a Voigt profile was applied to fit the measured methane lines and to determine line parameters. Because of selection of more or less isolated lines and the use of low pressures (less than 100 mbar) the Voigt profile still gives a good description of the measured lines. At the same time, we realize that the values of the air-broadening coefficient obtained here can be considered as effective values, which can be used to recalculate the line width under limited experimental conditions.

Finally, next to the methane line shape parameters, the line strength of the P45e line of $^{12}$CO$_2$ at 6153.693 cm$^{-1}$ (01101 → 31113 band) was carefully measured. This value was found to be in a very good agreement (within 0.7%) with the corresponding value from theoretical calculations of Zak et al. [52], accepted in HITRAN 2016 database [8].

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