Observation of methane nuclear spin isomers in gas phase at low temperature

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A spectroscopic study of methane spectra in the range around 6764 cm \(^{-1}\) was performed at different temperatures (from 55 to 200 K). The recorded spectra were used to increase the precision of transitions lower states energy determination and to retrieve the self-collisional broadening parameter. Both the newly obtained results and the quality of the experimental data were used to evaluate our system in the perspective of nuclear spin conversion measurements.

1. Introduction

Methane is the simplest hydrocarbon molecule having four half-integer spin hydrogen atoms at equivalent positions. As a consequence, three possible configurations differing in the total nuclear spin \(I\) exist. The ground state wave functions of these Nuclear Spin Isomers (NSIs) belong to different representations \((A, F, E)\) of the tetrahedral symmetry group. At the high temperature limit \((>50\,\text{K})\), the mixture ratio between the groups is given by their spin statistics weights: five for meta-CH \(_4\) \((I=2, A)\), nine for ortho-CH \(_4\) \((I=1, F)\) and two for para-CH \(_4\) \((I=0, E)\). As the NSI exist, the change of the total nuclear spin, also called Nuclear Spin (NS) conversion, may occur as well. The conditions leading to the conservation or the conversion of the nuclear spin state of some hydrogenated molecules in different astrophysical, gaseous and solid, environments are currently analysed in the framework of the GASOSPIN project [1]. The first stage in such a project is to spectroscopically identify each isomer, especially since the spectral range of interest, around 6764 cm \(^{-1}\), has already been studied but not fully assigned.

The most recent spectroscopic studies of this region come from the group of Campargue [2,3] as a part of the effort leading to the WKMC (Wang, Kassi, Mondelain, Campargue) empirical line lists for “natural” methane. Initially [2], they compared lines strengths measured at 80 K to room temperature (RT) values from HITRAN [4,5] and GOSAT [6] databases in order to calculate the transition lower state energies. Based on these values the attribution of rotational quantum number \(J\) was performed. To our knowledge there are no published results regarding the lineshape analysis within our range. Closest studies were performed by Menard-Bourcin et al. [7] on the 2v\(_2\) band around 6024 cm \(^{-1}\). They derived the broadening coefficients and the temperature dependence of rotational relaxation at temperatures from 296 down to 100 K. Lyulin et al. [8] recently measured the line profiles of methane transitions at 180, 240 and 296 K between 5556 and 6166 cm \(^{-1}\) and, for the same set of transitions, got similar values to those in [7].

It is the aim of this paper to present the observation and the analysis of a gaseous CH \(_4\) spectra recorded between 6763.458 and 6764.560 cm \(^{-1}\) in a cryogenically cooled (down to 55 K) multi-pass Herriott cell. Together 13 transitions were observed out of 21 present in the WKMC-80K line list [3]. Among them there were two \(^{13}\text{C}H\(_4\) lines (at 6763.70298 and 6764.1999 cm \(^{-1}\)) and one blended \(^{12}\text{C}\(_2\)C\(_\text{e}\) transition (at 6763.94797 cm \(^{-1}\)). In the first part, to evaluate the cell optical properties and its sensitivity, the methane absorption signal was recorded at lowest temperature possible (down to 55 K). Details on the data processing and the rovibrational transitions parameters retrieval are given. The description of the analysis concerning the determination of the transitions lower states energies is in the second part. As already used for ammonia [9] an alternative method to the WKMC “two temperature” approach, is discussed. A comparison of both methods is shown using the methane spectra recorded between 75 and
200 K. In the third part the line broadening measurements at 84 K are described and the collisional broadening coefficients at this temperature are calculated for each observed transition. The comparison of all measurements in order to obtain the temperature dependence of collisional broadening coefficient and the influence of nuclear spin isomers interactions on the spectra are viewed in the last part.

2. Experiment

The experimental setup was essentially that recently used for an ammonia study [9], with the same Extended Cavity Diode Laser (6468–6802 cm$^{-1}$) and the cooled Herriott cell designed by Mondelain et al. [10]. The cryogenic cooling system (CTI-Cryogenics Model 22C Cryodyne cooler coupled with temperature controller Lake Shore Cryogenics Model 331) allows to achieve the sample temperature down to 12.5 K with a spatial gradient and temporal fluctuations less than 0.5 K. Because of a necessary compromise between the strong enough intensities of methane transitions and the possibility to have lines belonging to different NSI groups within the same ECDL mode-hop free scan (about 1 cm$^{-1}$), the 6763.458–6764.560 cm$^{-1}$ spectral range has been selected. Each recorded spectrum was an average of 16 successive scans. The scan contained 50000 points, with a 100 ms scan duration at 10 Hz. The data processing procedure was the same as for NH$\text{\textsubscript{3}}$, except the spectra were fitted with a home made Multifit LabVIEW application [11].

The program used a model composed of Voigt functions representing rovibrational transitions ($\eta \rightarrow \eta'$) and a combination of polynomial and sine functions for the baseline. We also tested the Galatry line shape [12] representing the Dicke narrowing effects [13] as well. Because the obtained correction to the collisional width was smaller than the error given by the quality of our signal we decided to use only the voigt profile in this work. During the fit the Gaussian width of the Voigt function was always fixed to the value calculated for a given temperature. As a result we obtained the position $v_{\eta'\eta}$, the peak surface (intensity) $A_{\eta'\eta}$ and the Lorentz (Collisional) width $w_L$ (full width at half maximum) for each peak. Because we used the WKMC-80K line position to calibrate our spectra, the only independent values we retained for further analysis were $A_{\eta'\eta}$ and $w_L$. Regarding the baseline function its form was chosen to represent the transmittance of empty Herriott cell. The polynomial part was deduced from the reference signal beam containing laser power variations and the absorption outside the cell. The determination of the sine part parameters was more complicated. Following paragraphs are a complement of the description given in Refs. [9,10], dealing in more details with the spectral characteristics of the Herriott cell.

2.1. Sensitivity

Fig. 1 shows CH$_4$ absorbance spectrum recorded at 60 and 55 K. As in our case (regarding the absorption path and transitions line strengths) the methane absorption signal disappeared below these temperatures it represented a good place to evaluate the optical properties and the sensitivity of the setup. The obtained baseline noise was about ±0.001 (peak to peak) on the zl scale, which corresponded approximately to $2 \times 10^{-6}$ cm$^{-1}$. This is a relatively high value when compared to other absorption experiments (e.g. $5 \times 10^{-8}$ cm$^{-1}$ for half of our path-length in [3]). It is clearly visible that most of the noise came from periodic oscillations. The same oscillations were observed also at higher temperatures above the methane freezing point. This suggests their origin to be in the optical components of the cell rather than in the etalon-effect on the thin layer of solid methane.

2.2. Herriott cell

It is known that spectral fringes might appear in a Herriott cell due to the interference between the output beam and the neighbouring reflections on the coupling mirror. Such fringes are observable in the spectra in Fig. 1. McManus and Kebabian showed how the interference fringe free spectral range depends on the beam path pattern in the cell [14]. This pattern is defined by the total number of passes $N$ and the number of orbits $M$ the beam makes before exiting the cell. Based on the hypothesis that the cell belongs to the $N = 4M \pm 1$ family [10] the neighbouring spots numbers are $4$ and $N – 4$. This means that the interferences at frequencies correspond to $4d$ and $(N – 4)d$ with $d$ being approximated by the distance of mirrors centres. In the Fourier transform (FT) spectra of the 55 K signal (Fig. 2) four principal contributions at about 65 cm, 130 cm, 620 cm, 680 cm are clearly recognisable. While the second peak at 130 cm could be explained as the 2f signal from the first one at 65 cm, the positions of first and third peak match our hypothesis for $d \sim 16.5$ cm and $N = 42$. The fourth peak could be explained as $N + d \approx 685$ cm, interference due to the back-reflection on the coupling hole or the entrance mirror.

From the other side we fitted a part of the spectra with no absorption peaks (baseline) with a linear combination of sines functions. The insert graph in Fig. 2 shows such an approach. In this case the best coherence was obtained for interference paths of 66, 623 and 696 cm leading to $d = 16.5$ cm. This corresponds with the
values obtained by FT analysis. To confirm our results we calculated the value of mirror radius of curvature $R$ according to the Herriott cell theory [15]. Using an average value of $d \sim 16.4$ cm, $N = 42$, and $M = 11$ the solution satisfying re-entrant condition exists for $R = 15.26$ cm which is reasonably close to the factory value of 15.05 cm.

Now the total path of the beam through the studied gas inside the cell can be calculated fairly precisely by taking the average $d$ value of 16.4 cm. 1 cm, multiplying it by the 42 passes and adding 0.36 cm for the round trip between the cell entrance hole and the cell entrance/exit window [10]. This gives the absorption path length of $L = 692 \pm 5$ cm. As shown in following section this number is not needed directly for the determination of lower state energy of measured transitions. It is needed for the absolute line strength calculations only. An indirect influence comes through the fitting process where by proper modelling of the baseline our residual noise was one order of magnitude to $4 \times 10^{-7}$ cm$^{-1}$ (calculated as mean of fit residual).

3. Determination of CH$_4$ lower state energy of measured transitions

Such a procedure is based on temperature dependence of line strength $S_{gg}$, which is derived from line intensity $A_{gg}$ according to:

$$S_{gg}(T) = \frac{k_B T}{P} \int \frac{A_{gg}}{T} dx dv$$

where $k_B$ stands for the Boltzmann constant, $xL$ represents the measured absorption signal determined according to the Beer–Lambert law, $T$ and $P$ are the temperature and the pressure of studied gas, and $L$ is the absorption path-length. Combining the data measured at two temperatures $T_1$ and $T_2$, the lower state energy $E_y$ is retrieved as

$$E_y = -\frac{k_B}{1/T_a - 1/T_b} \ln \frac{[S_{gg}(T_b)/Q(T_b)]}{[S_{gg}(T_a)/Q(T_a)]}$$

where $Q(T)$ represent the corresponding rovibrational partition function. As mentioned in the Introduction this approach was widely used for methane by the group of Campargue, e.g. [2,3]. They calculated the lower state energies using their Differential Absorption Spectra (DAS) recorded at liquid nitrogen (LN) temperature. The main limiting factor of this approach was that DAS is a relative measurement method. Therefore besides the quality of the spectra, all the “local measurement parameters” ($p$, $L$, $T$) have strong influence on the precision of $E_y$. This could be seen more clearly if one combines both the Eqs. (1) and (2) and replaces the term $Q(T_a)/Q(T_b)$ with an approximative analytical function ($T_a/T_b$)$^{3/2}$ as proposed by Fox [16]. Such an assumption is eligible as our temperatures fulfilled the condition $T \gg B_0/k_B \approx 7.5$ K for methane, with $B_0 = 5.214$ cm$^{-1}$.

$$E_y = -\frac{k_B}{1/T_b - 1/T_a} \ln [y_{gg}(T_b)/y_{gg}(T_a)]$$

$$y_{gg}(T) = \ln \frac{A_{gg}(T)/(T_b)^{3/2}}{[k_B T_b/P_b]}$$

Several solutions can be brought to increase the precision of $E_y$. Firstly one could try to make the measurements at more than two temperatures. For example Votava et al. [17] used the spectra of supersonic jet expansion (around 25 K) to improve the WKMC identification in the 7070–7300 cm$^{-1}$ region. Another possibility is to perform the measurements on the same experimental setup ($L_0/L_6 \rightarrow 1$) [3] or moreover recording the absorption spectra with the same number of molecules ($\langle p_6 T_6 \rangle/\langle p_b T_6 \rangle \rightarrow 1$). Nevertheless all these approaches reduce the influence of local parameters on the uncertainty of $E_y$ only partially as it still principally depends on their small variations.

Therefore in addition to these two improvements (measuring spectra with the same setup at different temperatures) we proposed a slightly different approach to treat the spectra [9]. The idea consisted in following the temperature dependence of two line intensities ratio $A_{gg}/A_{ee}$ rather than single peak $A_{gg}(T)$. In this case we obtain

$$\Delta E_{yy} = \frac{k_B}{1/T_b - 1/T_a} [y_{gg}(T_b) - y_{gg}(T_a)]$$

$$y_{gg}(T) = \ln \frac{A_{gg}(T)/[A_{gg}(T)]}{[A_{ee}(T)]}$$

with $\Delta E_{yy}$ representing the energy difference between the two transition lower states $E_y - E_a$. Although this gave only a relative energy value, the $p$, $L$ and $T$ parameters principally vanished from the logarithm. As a consequence the uncertainty of the results depends only on the quality of the spectra and on the temperature. The inconvenience of the relative determination of the energy can be simply circumvented by choosing a well resolved, intense enough (high signal to noise ratio) and already assigned line as reference. As our approach deals only with the data treatment in case there are no “reference peaks” present in the spectra one could still use the “two-temperature” method to get the absolute energies. Furthermore one could also use different transitions as the references to increase the precision of result or to identify wrongly assigned reference transition.

It is interesting to quantitatively compare both approaches given by Eqs. (3) and (4). Methane spectra were recorded at different “cold” temperatures: 75, 90, 120, 160 and 200 K (Fig. 3). Before the acquisitions we filled the cell at 75 K with 7 mbar of methane. This was below the methane vapour pressure at this temperature, which is 7.7 mbar according to Thomy and Duval [18]. Once the spectra were recorded we raised the temperature to 90 K. By repeating this cycle we obtained the other spectra up to 200 K. During the process the Herriott cell input valve was closed to keep the number of molecules constant (this also prevented us to measure the pressure inside the cell).

The line intensities were treated according to both methods. The process is represented in Fig. 4a and b with an example for peaks denoted $a$, $b$, $c$, and $d$ on Fig. 3.

Variable $y_{gg}$, displayed on Fig. 4a, represents logarithmic function of $A_{gg}$ which is part of Eq. (3). Similarly, $y_{gg}$, displayed on

Fig. 3. Methane spectra recorded at five different temperatures and their fit residuals. The spectra are plotted with a cumulative offset of 0.1. The black triangles point to the positions of fitted peaks.
Fig. 4b, represents logarithmic function of \( A_{gg} / A_{ee} \) which is part of Eq. (4). The peak at 6763.836 cm\(^{-1}\) (according to WKMC list [3], with \( E_e = 26.886 \) cm\(^{-1}\)) was selected as reference transition \( ee_0 \). For clarity of the figures, both functions are normalised to \( T_a = 200 \) K. The \( E_g \) and \( D_{Eg} \) were retrieved from the slopes of \( y_E \) and \( y_{D_E} \), respectively. Corresponding rotational numbers were calculated according to analytical expression for spherical top molecules

\[
 J_g = \frac{\sqrt{1+4E_g/B_0} - 1/2}{}, \quad \text{with the same } B_0 \text{ for both } ^{12}\text{CH}_4 \text{ and } ^{13}\text{CH}_4. \]

The retrieved values together with all WKMC-80K transitions in the range are listed in Table 1 as function of the WKMC-80K line centre.

### 4. Line broadening measurements

This section aims to provide new experimental data about the line widths measured in the 6763.458–6764.560 cm\(^{-1}\) spectral region. Below, we describe the measurements at variable pressures and constant temperature of 84 K.

Firstly the empty cell was cooled down to the given temperature. The gas was then introduced through a standard 6 mm inox tube (3 mm of inner diameter) welded to the cell with two capacitive diaphragm transmitters (Pfeiffer CMR-361 and CMR-363, with 10 and 1000 mbar ranges and 0.2% accuracy, resp.) placed on the other end of the tube to monitor the pressure. We deduced the value of methane vapour pressure at this temperature from the attained maximal pressure, \( p_{sat} = (44.4 \pm 0.9) \) mbar. At such a temperature the mean free path for the methane molecule (below 0.1 mm) is much smaller than the connecting apertures (tube and valve). Thus the gas was regarded outside and inside the cell in thermal equilibrium and the values of measured pressure correct.

The spectra were recorded during this process at seven different pressures from 1.4 to 44.4 mbar (Fig. 5). Similarly as in [8] we used the multi-spectrum fit procedure (simultaneous fit of spectra recorded at different pressures) to analyse the spectra [11]. Instead of fitting the collisional (Lorentz) parameter independently for each peak in each spectra, the \( \gamma_{sef}(84 \) K) coefficients have been adjusted by the fitting function. The corresponding Lorentz widths were calculated as \( \gamma_{L} = Z\gamma_{sef} \cdot p \), where \( p \) was the measured pressure. The results for peaks with the uncertainty of fitted width less

### Table 1

<table>
<thead>
<tr>
<th>Centre (cm(^{-1}))</th>
<th>Line strength (cm(^{-1}))</th>
<th>( E ) (cm(^{-1}))</th>
<th>( J )</th>
<th>This work</th>
<th>( \gamma_{sef}(84 ) K) (cm(^{-1})/atm)</th>
<th>( \sigma_r ) (cm(^{-1})/atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6763.45866</td>
<td>3.562E–24</td>
<td>102.640</td>
<td>3.95</td>
<td>104.8</td>
<td>3.0</td>
<td>0.25</td>
</tr>
<tr>
<td>6763.47942</td>
<td>2.832E–25</td>
<td>229.529</td>
<td>6.14</td>
<td>216.2</td>
<td>13.0</td>
<td>0.4</td>
</tr>
<tr>
<td>6763.70298</td>
<td>7.167E–26</td>
<td>98.356</td>
<td>3.86</td>
<td>112.9</td>
<td>68.0</td>
<td>0.2</td>
</tr>
<tr>
<td>6763.83627</td>
<td>7.732E–24</td>
<td>26.886</td>
<td>1.82</td>
<td>31.4</td>
<td>2.0</td>
<td>0.23</td>
</tr>
<tr>
<td>6763.84620</td>
<td>9.669E–26</td>
<td>115.960</td>
<td>4.23</td>
<td>189.8</td>
<td>102.0</td>
<td>0.3</td>
</tr>
<tr>
<td>6763.94797</td>
<td>9.728E–26</td>
<td>175.6</td>
<td>116.</td>
<td>53.8</td>
<td>2.8</td>
<td>–</td>
</tr>
<tr>
<td>6763.95844</td>
<td>1.033E–23</td>
<td>28.673</td>
<td>1.89</td>
<td>32.8</td>
<td>3.0</td>
<td>0.25</td>
</tr>
<tr>
<td>6764.00786</td>
<td>9.548E–25</td>
<td>223.767</td>
<td>6.05</td>
<td>222.1</td>
<td>4.0</td>
<td>0.1</td>
</tr>
<tr>
<td>6764.12426</td>
<td>6.631E–25</td>
<td>95.006</td>
<td>3.79</td>
<td>67.1</td>
<td>9.0</td>
<td>0.5</td>
</tr>
<tr>
<td>6764.19994</td>
<td>1.304E–25</td>
<td>125.731</td>
<td>4.42</td>
<td>105.2</td>
<td>26.0</td>
<td>1.1</td>
</tr>
<tr>
<td>6764.43012</td>
<td>1.020E–23</td>
<td>5.774</td>
<td>0.66</td>
<td>11.7</td>
<td>3.0</td>
<td>0.3</td>
</tr>
<tr>
<td>6764.50877</td>
<td>2.122E–25</td>
<td>214.311</td>
<td>5.91</td>
<td>233.0</td>
<td>35.0</td>
<td>6.2</td>
</tr>
<tr>
<td>6764.55970</td>
<td>1.454E–23</td>
<td>59.531</td>
<td>2.91</td>
<td>64.0</td>
<td>2.0</td>
<td>0.25</td>
</tr>
</tbody>
</table>

\( a^{12}\text{C}_2 \)

\( b^{13}\text{C}_2 \)

\( ^c^{12}\text{C}_2 \)

\( ^c^{13}\text{C}_2 \)
At different temperatures. If we look at Table 1 where the WKMC coefficient small misalignment of complex beam trajectory could occur self. As the cell was composed from copper with high thermal coefficient inside the cell. Another issue was the optical path it-pose to ambient temperature which could cause variations of the small space (tube between the cell and injection valve) always ex- periences as well as constant optical path. In reality there was a assumed equal concentration of molecules in the cell for all tem- peratures as well as constant optical path. We obtained a constant value of 6.8 \times 10^{17} \text{cm}^{-3} \text{ with small excursions below 10%.

The results together with data from literature are summarised in Table 2. Even with relatively high uncertainty of our data (around 20%) influenced by pressure calculation we obtained reasonable values for low J peaks in comparison both with Menard et al. [7] or Lyulin et al. [8].

5. Discussion

The new technique for the transition lower state energy calculation described in Section (3) has the advantage to reduce the precise knowledge of fewer parameters, i.e. of the temperature T only. This is visible from the differences in linearities of both functions $y_E$ and $y_n$ on Fig. 4. Indeed due to the design of the experiment we assumed equal concentration of molecules in the cell for all temperatures as well as constant optical path. In reality there was a small space (tube between the cell and injection valve) always exposed to ambient temperature which could cause variations of the concentration inside the cell. Another issue was the optical path it-self. As the cell was composed from copper with high thermal coefficient small misalignment of complex beam trajectory could occur at different temperatures. If we look at Table 1 where the WKMC list [3] data are listed we find that our method offers unambiguous attribution for all but the peaks with intensities close to our sensitivity limits.

Regarding the collisional broadening measurements our precision was mainly limited by the saturated vapour pressure at 84 K. At 44.4 mbar the Lorentz full width is only twice as large as the Gaussian full width of 0.011 cm$^{-1}$. Consequently we could well determine the $\gamma_{\text{ref}}$ at 84 K coefficients only for six most intensive peaks in the spectrum.

To compare these results to values measured for neighbouring bands in [7,8] we have calculated the $\gamma$ at 296 K and the temperature exponent n by fitting the $\gamma_{\text{ref}}$ as a function of a temperature (Fig. 7). According to its definition [4] the $\log[\gamma_{\text{ref}}]$ is expressed as a linear function of $\log[T]$ with the slope equal to n:

$$\log[\gamma(T)] = \log[\gamma(T_{\text{ref}})] + n \cdot \log\left[\frac{T}{T_{\text{ref}}}\right].$$

To obtain the $\gamma_{\text{ref}}$ at different temperatures we combined the spectra used for lower state energies calculations (measured in 75–200 K range) with the collisional broadening measurements at 84 K. As in the first case we did not have pressure measurements. The concentration (and pressure) had to be found from the measured intensities. With the optical path inside the cell of 692 cm (see part 2) and the absolute line strength taken from WKM-80K database we calculated the concentration inside the cell at each temperature. We obtained a constant value of 6.8 \times 10^{17} \text{cm}^{-3} \text{ with small excursions below 10%.

The results together with data from literature are summarised in Table 2. Even with relatively high uncertainty of our data (around 20%) influenced by pressure calculation we obtained reasonable values for low J peaks in comparison both with Menard et al. [7] or Lyulin et al. [8].

5.1. Effect of nuclear spin

At last we were interested how the nuclear spin conversion or conservation affects the $A_{\text{ref}}/A_{\text{ref}}$ dependence described in Section (3), depicted on Fig. 4b. Starting from the definitions of line strength temperature dependence for different NS families: $S(T) \rightarrow S(T, \text{sym})$ [4] the exact expression can be retrieved:

$$S(T) = S_{\text{ref}}(T_{\text{ref}}) \frac{T_{\text{ref}}(T)}{\gamma_{\text{ref}}(T_{\text{ref}})} \Phi_{\text{sym}}^{\text{ns}}(T_{\text{ref}}) \frac{Q_{\text{sym}}(T)}{Q_{\text{ref}}(T)},$$

$$T_{\text{ref}}(T) = \exp[-E_{\text{sym}}/k_B T],$$

$$\Phi_{\text{sym}}^{\text{ns}}(T) = 1 - \exp[-v_{\text{sym}}/k_B T],$$

with $S_{\text{ref}}(T_{\text{ref}})$ the line strength at 296 K as listed in the HITRAN database [4] and $\eta$ in exponent standing for the NS group (meta, ortho or para). $Q_{\text{sym}}$ is the statistic sum for all states together and $Q(T)$ is the sum only for states belonging to given NS group $\eta$, both

![Fig. 6. Broadening coefficient (full width at half maximum) plotted as the function of calculated rotational number.](image)

![Fig. 7. $\gamma_{\text{ref}}$ as function of temperature, obtained from the measurements described in the Section 3 and 4. Line represents the linear fit of log[$\gamma_{\text{ref}}$] function used to determine the n and the $\gamma_{\text{ref}}$ at 296 K.](image)
Table 2
Comparison of the temperature exponent n and the collisional broadening coefficient γ_{c}(296 K) retrieved from our spectra and from the measurements of the 2ν₂ band by [7,8].

<table>
<thead>
<tr>
<th>Source</th>
<th>γ_{c}(296 K) [cm⁻¹ atm⁻¹]</th>
<th>n</th>
<th>T-range (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work, J = 1-4</td>
<td>0.080 (5)</td>
<td>0.88(5)</td>
<td>75–200</td>
</tr>
<tr>
<td>2ν₂, R (0) [8]</td>
<td>0.0809(1)</td>
<td>0.85(7)</td>
<td>180–296</td>
</tr>
<tr>
<td>2ν₂, R (1) [8]</td>
<td>0.0817(1)</td>
<td>0.86(5)</td>
<td>180–296</td>
</tr>
<tr>
<td>2ν₂, J = 1, E [7]</td>
<td>0.081 (9)</td>
<td>0.72(4)</td>
<td>100–296</td>
</tr>
<tr>
<td>2ν₂, J = 1, F [7]</td>
<td>0.08 (1)</td>
<td>0.63(5)</td>
<td>100–296</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.64(6)</td>
<td>100–296</td>
</tr>
</tbody>
</table>

Confidence intervals (1 SD, in unit of the last quoted digit) are given between parentheses.

calculated according the methane rovibrational levels energy database [19]. This is a right expression because the term \( A_{\text{hh}} / \left( L \cdot q \bar{S}_{\text{hh}}(T) \right) \) returns the concentration of all absorbing methane molecules regardless the transition ground state symmetry. The exact expression for \( y_{AE} \) now depends on the symmetries of transitions lower states \( e, g \):

\[
n_{c}y_{AE} = \ln \left( \frac{A_{\text{hh}}}{A_{\text{ee}}} \right) = C - \frac{\Delta E_{cv}}{kT} + \ln \left( \frac{\bar{Q}(T)}{\bar{Q}(T)} \right) + \ln \left( \frac{\Phi_{\text{hh}}(T)}{\Phi_{\text{ee}}(T)} \right), \tag{7}
\]

\[
C = \ln \left( \frac{\Phi_{cv}(T) \bar{Y}_{cv}(T) \bar{S}_{\text{hh}}(T)}{\Phi_{oe}(T) \bar{Y}_{oe}(T) \bar{S}_{\text{ee}}(T)} \right).
\]

When compared to the Eq. (4), considering the terms \( \Phi(T) \) for spectrally close transitions (here spacing is less than 1 cm⁻¹) negligible, the only term representing the influence of NS is \( \bar{Q}(T)/\bar{Q}(T) \).

In Fig. 8 we plotted the \( n_{c}y_{AE} \) function for the \( J = 1 \) peak (at 6764.43012 cm⁻¹) as \( y_{AF} \) and the \( J = 2 \) peak (at 6763.70298 cm⁻¹) as the reference transition \( y_{AE} \). In difference with Fig. 4 we retrieved the \( \ln[\bar{A}_{\\text{ee}}/\bar{A}_{\text{gg}}] \) values from all of our spectra including the low temperature data (from 70 to 55 K) used in the Section (2). As the symmetry of the \( J = 1 \) peak is \( F \), the reference peak with \( J = 2 \) can be \( F \) or \( E \). Looking at Eq. (7) there are two possibilities how \( n_{c}y_{AE} \) evolves with the decreasing temperature. If there is no conversion between different NS groups or if there is a conversion between different NS species and the two peaks have different symmetry (so the reference peak \( J = 2 \) is \( E \)) the NS part of Eq. (7) will be non zero (represented by case B – dashed line on the graph 8).

On the other hand if the reference transition belongs to the same \( F \) symmetry as the \( J = 1 \) peak the NS term in Eq. (7) will become zero and the \( n_{c}y_{AE} \) function linear regardless the NS behaviour.

To better understand the precision needed to distinguish between the two cases we plotted the relative uncertainty of \( \ln(\bar{A}_{\text{gg}}/\bar{A}_{\text{ee}}) \) together with the relative difference \( (\bar{F}_{y_{AE}} - \bar{F}_{y_{AE}})^{2}y_{AE} \) as a function of temperature (Fig. 9). Furthermore a simple model of the experimental error is represented as well. It was calculated by extrapolating the uncertainties of \( \bar{A}_{\text{hh}} \) and \( \bar{A}_{\text{ee}} \):

\[
\frac{\partial y_{AE}}{y_{AE}} \approx \frac{\left( \partial \bar{A}_{\text{hh}} / \bar{A}_{\text{hh}} \right)^{2}}{\partial \bar{A}_{\text{ee}} / \bar{A}_{\text{ee}}} + \frac{\left( \partial \bar{A}_{\text{ee}} / \bar{A}_{\text{ee}} \right)^{2}}{\partial \bar{A}_{\text{hh}} / \bar{A}_{\text{hh}}},
\]

\[
\frac{\partial \bar{A}_{\text{hh}}}{\bar{A}_{\text{hh}}} < 3 \left[ \frac{w_{e}(p,T) + w_{c}(T)}{S_{\text{hh}}(T) \cdot L \cdot n(p,T)} \right] \cdot \sigma_{B}\text{K}
\]

the uncertainty of \( \bar{A}_{\text{hh}} \) was estimated as the product of baseline noise \( \sigma_{B} \) and peak equivalent width, which we guessed as three times the sum of collisional and Doppler widths calculated at given pressure and temperature. On Fig. 9, the experimental error has a minimum around 75 K. There are two reasons for the curve having sharp minimum. First the increase of signal (assuming noise at constant level) is limited by the saturated vapour pressure at given temperature. Another limit is the saturation of the transition where there is no more molecules to absorb the light, the concentration is then kept constant and the pressure follow the law for ideal gas.

6. Conclusion

Although we did not clarify the existence or non existence of the NS conversion mechanism the approach described here is a good step forward as it proposes a method which is much less sensible to the experimental parameters. The lack of sensitivity of our system could be circumvented by the selection of stronger absorption band of methane. Indeed we are investigating a new type of source working at 2.3 μm where methane lines are roughly 1000 stronger and the difference between the NS conversion and conservation should be observable.

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References