SPECTRAL SHAPE PARAMETERS OF SOME NITROGEN BROADENED METHANE TRANSITIONS AT ROOM TEMPERATURE USING THE SPEED DEPENDENCE-AND DICKE NARROWING-MODELS

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Abstract. In this work, spectral shape parameters of some isolated transitions in the infrared region of methane diluted in nitrogen at room temperature are obtained using two refined line-shape models including the Rautian and the speed dependent Voigt profiles as well as the simple Voigt one. The measured absorption spectra at large pressure ranges were one-by-one fitted with these models using the least-squares method. The obtained result reconfirmed that non-Voigt effects must be taken into account to get a better fit residual and fit quality. Pressure dependence of the Dicke narrowing parameter and the speed dependent components of line width and shift were also obviously observed. The obtained line shape parameters are in good agreement with the literature.

Keywords: methane, nitrogen, Dicke narrowing, pressure dependence of width and shift.

1. Introduction

Methane in large quantities from the Arctic and wetlands is the third most important greenhouse gas in the Earth's atmosphere. Methane contributes about 20% to global warming due to the absorption of long-wavelength radiation by the atmosphere [1]. Currently, there are many satellite-based remote sensing projects to determine the density of CH_4 in the atmosphere according to altitude such as SCIAMACHY [2], TANSO [3], and MERLIN [4]. Based on the absorption spectrum of the atmosphere at different altitudes (measured by spectrometers located on these satellites) and the characteristic spectral parameters of gas molecules (stored in the databases), scientists were able to determine the densities of the gases of interest according to altitude. The accuracy of these measurements therefore depends on the accuracy of the used spectral characteristics of atmospheric molecules in general and of methane in particular.

The spectral features of methane stored in spectral databases such as HITRAN are mainly determined based on the Voigt spectral line model [5]. However, as mentioned in [6], the role of non-Voigt effects needs to be considered in high resolution measurements for isolated methane lines. For that, the Hard collision model, (called the Rautian model, RP, [7])

and the Soft collision model called the Galatry model, GP, [8]) was used to describe the velocity changing collision effect (the Dicke narrowing effect). In order to take into account the speed dependence effect, the Speed dependent Voigt model, SDVP, [9] will be used. This effect has been an interesting subject of many studies [10-15] for many lines of Methane. In the work [6], the study took into account the Dicke narrowing effect only using both Hard and Soft collision models to deduce the pressure dependent on line-shape parameters of $\nu_3 + \nu_4$ R(7)F1 transition. As there is very little difference between the results calculated by each of the two models for the system CH_4/N_2, in this work, following the study by [6], the Rautian model, RP, (the Hard collision in [6]) was used to consider the role of Dicke effect but for more other transitions of CH_4/N_2 gas in order to validate whether it has the same effect as for the considered line in [6]. The difference between calculated results in [6] and other literature was explained as the absence of the speed dependence effect. Furthermore, recently, many researchers have started to consider the role of speed dependent effect on the line-shape [16, 17]. The speed dependent effect of the width and shift now is known as nonnegligible. However, these current studies were done for limited transitions and pressure ranges only due to the difficulty in setting up the measurements. So, it is useful to fulfill the overview of this effect for more transitions and in a larger range of pressure conditions. In this work, together with using the RP to consider the Dicke narrowing effect, the SDVP was also used to consider the speed dependent effect. The study was done for four transitions at room temperature and a large range of pressure. The obtained results were compared with other results from the literature.

2. Content

2.1. Line-shape model used and measured data

In the spectroscopy radiative transfer technique, the Voigt profile [5], VP, is widely used. This profile can be built as a convolution of the Doppler profile and the Lorentz profile. These two profiles take into account the two main effects, the Doppler and the collisional effect. In the Doppler effect, the velocity of molecules in the system leads to the broadening of the line width, and in the Lorentz effect, the velocity of molecules can be changed due to collision between molecules in the system, so it affects the line shape. Considering the two main effects above, one can use the more refined model to analyze the measured spectra by taking into account other effects. In the case of taking into account the Dicke narrowing effect, two models can be used, the Rautian profile [3], and the Galatry (the Soft collision) profile, GP, [8]. The RP was used to describe the hard collision between molecules, which means that the velocity changed after each collision while the GP will be used for the case when the velocity of the active molecule is almost unchanged after each collision. In addition, as the speed dependent effect which leads to the change of molecule velocity is taken into account, the speed-dependent Voigt profile, SDVP [9], will be used. In our work, these two refined effects were considered by using the RP and the SDVP independently.

The experimental data used in this study are part of a data package provided by Dr. José-Luis Doménech, Institute of Structural Materials (Instituto de Estructura de la Materia, Consejo Superior de Investigaciones Cientificas (IEM-CSIC)), located at

Serrano 123, 28006 Madrid, Spain. The group of authors T. Le, J.L. Doménech, M. Lepère and H. Tran used this data package in combination with simulation data by molecular dynamics method to study the broadening of the absorption spectral line of methane (CH_4) disturbed by nitrogen gas (N_2) at room temperature. The spectral model used to describe the absorption spectrum of CH_4/N_2 in this study is the Voigt model [5]. The main results of the study were published by the authors in an article in The Journal of Chemical Physics in 2017 [18]. The detailed information about the spectrometer and experimental conditions when measuring the absorption spectrum of the CH_4/N_2 gas system has been described in detail in [18].

The methane and nitrogen used in the study have a purity greater than 99.995%, provided by the companies Air Liquid and Contse. The density of CH_4 in the CH_4/N_2 gas mixture is about 2% ($P_{CH4}/P \approx 2\%$). With this density, we can roughly ignore the partial methane contribution when determining the parameters that characterize the spectral pattern. The transitions selected in the study are isolated transitions so that the influence of neighboring transitions on their absorption spectrum can be ignored. These transitions are therefore suitable subjects for carrying out studies of spectral line patterns.

In this work, we limited the study of the spectral shape of four isolated transitions of nitrogen-perturbed methane at room temperature. Information about the names and positions of these transitions as well as the experimental conditions in which their absorption spectra (pressure P, temperature T, density P_{CH4}/P, and absorption path length L) are measured is given in Table 1.

Table 1 Experimental conditions. The corresponding wave numbers of the transitions are referenced from the HITRAN database [19]

Trans.	σ_0 (cm^{-1})	T(K)	L (cm)	P (mbar)	P_{CH4}/P (%)	Γ_L/Γ_D
$\nu_3+\nu_4$ P(9)A1	4161.051852	299.0±0.1	180.0	50.8, 98.4, 200.7, 399.2, 599.9	1.790	0.36-5.17
$\nu_3+\nu_4$ P(8)F1	4168.483790	297.3±0.1	180.0	49.9, 99.5, 200.6, 400.1, 599.9	1.990	0.41-5.60
$\nu_1+\nu_4$ Q(1)F1	4324.933076	297.5±0.1	180.0	50.0, 100.8, 200.5, 400.7, 598.7	1.996	0.41-5.69
$\nu_3+\nu_4$ Q(2)F2	4330.107883	297.7±0.1	180.0	49.8, 100.1, 200.4, 399.8, 599.5	1.996	0.43-5.83

In the fitting procedure using the least-squares method, for each line transition, the line intensity S together with the line-shape parameters including spectral shift Δ, Lorentz half-width Γ, speed dependence of half-width Γ_2 and shift Δ_2, narrowing coefficient, B, due to Dicke effect; and the baseline parameter of the zero-absorption level are changed and adjusted simultaneously. From these line-shape parameters at different pressure conditions, by using the linear fitting procedure, one can deduce the line-shape coefficient parameters which are independent with pressure, P: $\gamma = \Gamma/P$; $\delta = \Delta/P$; $\gamma_2 = \Gamma_2/P$; $\delta_2 = \Delta_2/P$; $\beta = B/P$. The obtained results are shown and discussed in Section 2.2.

2.2. Results and discussion

2.2.1. Fit Residuals

As shown in Figure 1 for the $\nu_3+\nu_4$ P(9)A1 transition, results using the speed-dependent Voigt and the Rautian models to fit the experimental spectrum lead to a much better fit than with the Voigt model. VP leads to a maximum residual of about 2%, which is 4 times larger than the error from the SDVP and the RP. These two models lead to an error of only about twice the noise of the experimental spectrum. As can be seen in Figure 1, using the SDVP leads to a better residual in comparison with those of the RP. The same situations were also observed for the other considered transitions of this study and the v4 P(3)A transition of Reference [21]. This implies that the Voigt model is only an approximation in describing the absorption spectral pattern of methane diluted in nitrogen. For a better description, refined effects affecting the absorption spectra such as confinement (Dicke narrowing effect) and the speed dependence of the half-width and shift must be taken into account. This conclusion is also consistent with the research results for some other transitions of the CH_4/N_2 gas system [20, 21].
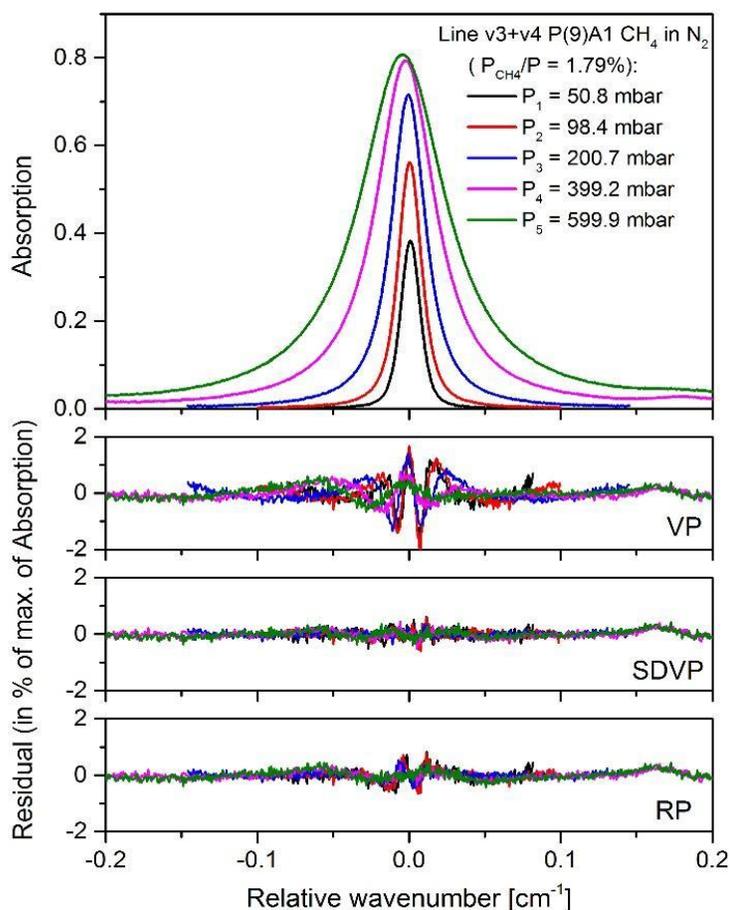

Figure 1. The fitting spectra of Methane diluted in Nitrogen with the corresponding experimental spectra at different pressure conditions using different line-shape models of v3+v4 P(9)A1 (σ_0 = 4161.051852 cm^{-1}) transition at room temperature

2.2.2. The Lorentz width and shift

It can be seen that the spectral shift coefficient δ of each transition when using two line-shape models (VP and RP) is the same and these values are about 6.5% to 11% smaller than the results obtained respectively when using the SDVP for two transitions with large rotational quantum numbers ($\nu_3+\nu_4$ P(9)A1 and $\nu_3+\nu_4$ P(8)F1 (see Figure 2 and Table 2). This can be explained because in the RP, parameter B only characterizes the narrowing of the absorption spectrum without affecting the shift, Δ. In contrast, the speed dependence of the shift described by the parameter Δ_2 in the SDVP may have affected the value of the parameter Δ.
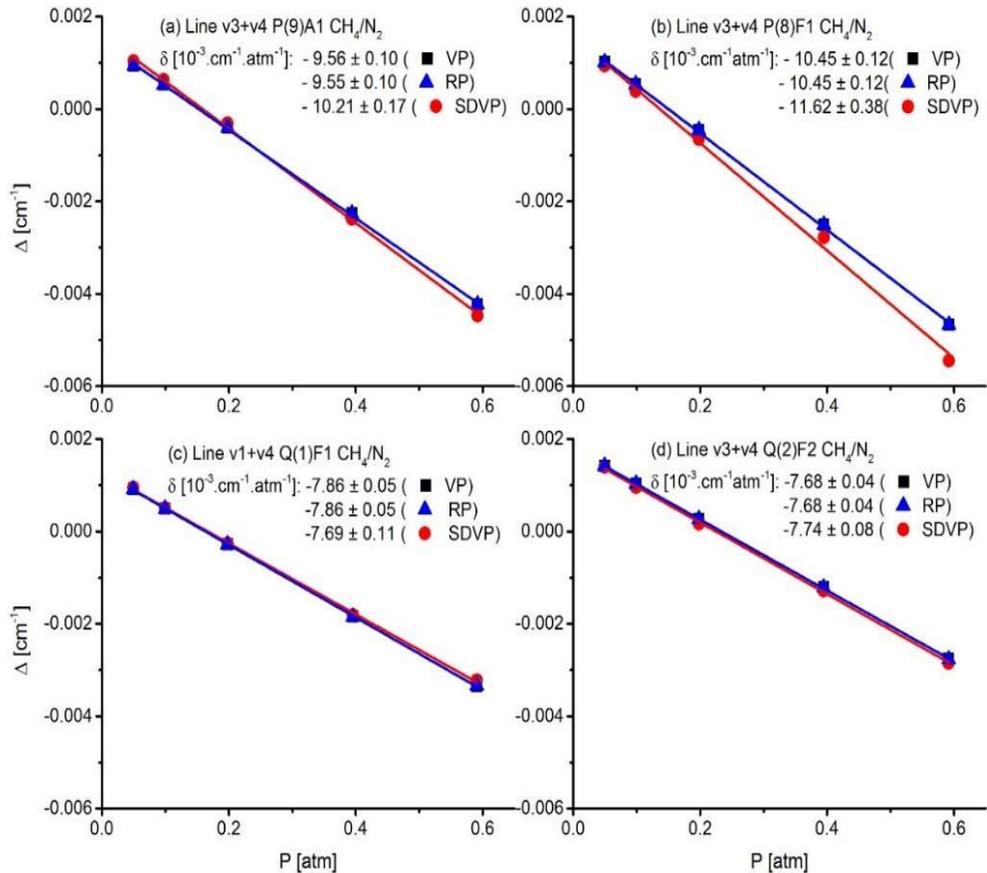

***Figure 2. The calculated shift Δ [cm^{-1}] at different pressure conditions
for different transitions of CH$_4$/N$_2$ using different profiles
(black-square, blue-triangle, and red-circle)***

As shown in Figure 3, the value of the pressure broadening coefficient γ [cm^{-1}.atm^{-1}] when using the speed-dependent Voigt and the Rautian models is equivalent and 2% to 3% larger than the obtained results using the Voigt model range. This difference is because the SDVP and the RP take into account the effects that narrow the absorption spectrum, such as the speed dependence of the half-width (Γ_2) and the Dicke effect (B).

The results for the shift coefficients δ and the line broadening coefficients γ of these transitions obtained using the Voigt model for a wider range of pressures have been published by Le et al. [18]. In this work, we limit the study to a narrower pressure range (see Tables 1 and [18]), but the values of the parameters remain unchanged and are in good agreement with studies by other authors [22]. In Table 2, the results of the line-broadening coefficient of CH_4/N_2 using the RP by [12] and of CH_4/air using a multispectrum procedure with the SDVP [14] and the VP [24] (for different transitions) are shown for comparison.
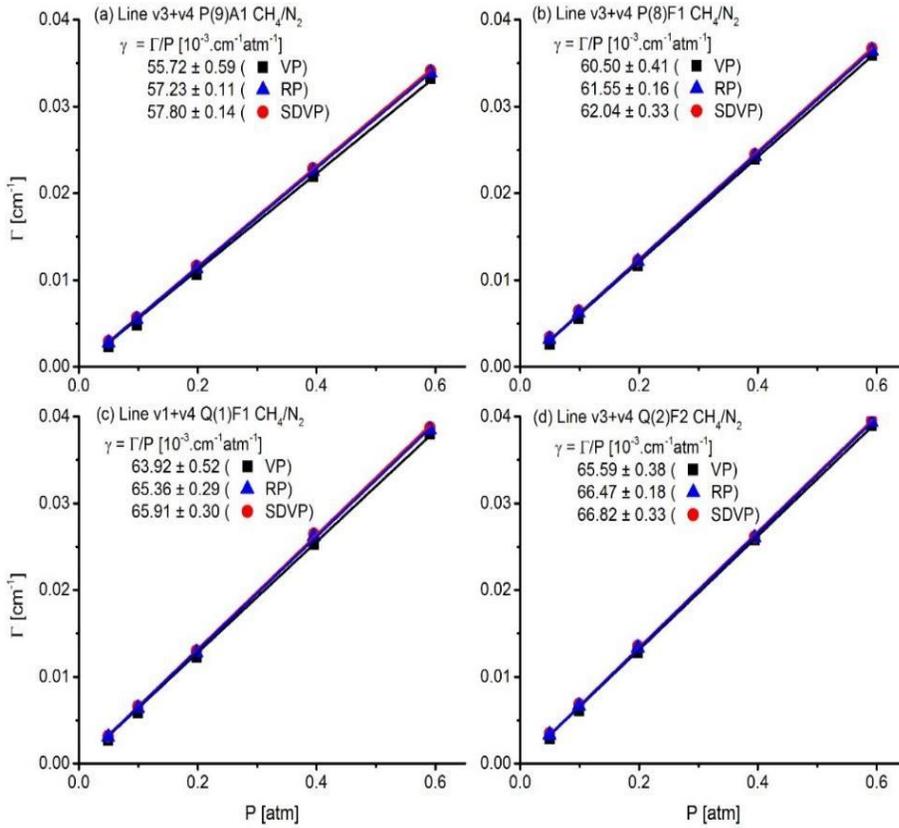

Figure 3. The calculated Lorentz width Γ [cm^{-1}] at different pressures P [atm]
for different transitions using different profiles (black-square, blue-triangle, and red-circle)

2.2.3. The speed dependence of width and shift

Figure 4 shows the dependence of the speed dependence of the shift Δ_2 to pressure P. It can be seen that these dependencies are not linear to pressure, especially with the two transitions with large rotational quantum numbers ($\nu_3+\nu_4$ P(9)A1 and $\nu_3+\nu_4$ P(8)F1). Thus, the value of the pressure-independent coefficient δ_2 [cm^{-1}.atm^{-1}], which characterizes the dependence of the Lorentz half-width on speed, is determined by the gradient of the line passing through it. The origin describes the linear dependence of Δ_2 concerning P, for these two transitions, there will be large errors.
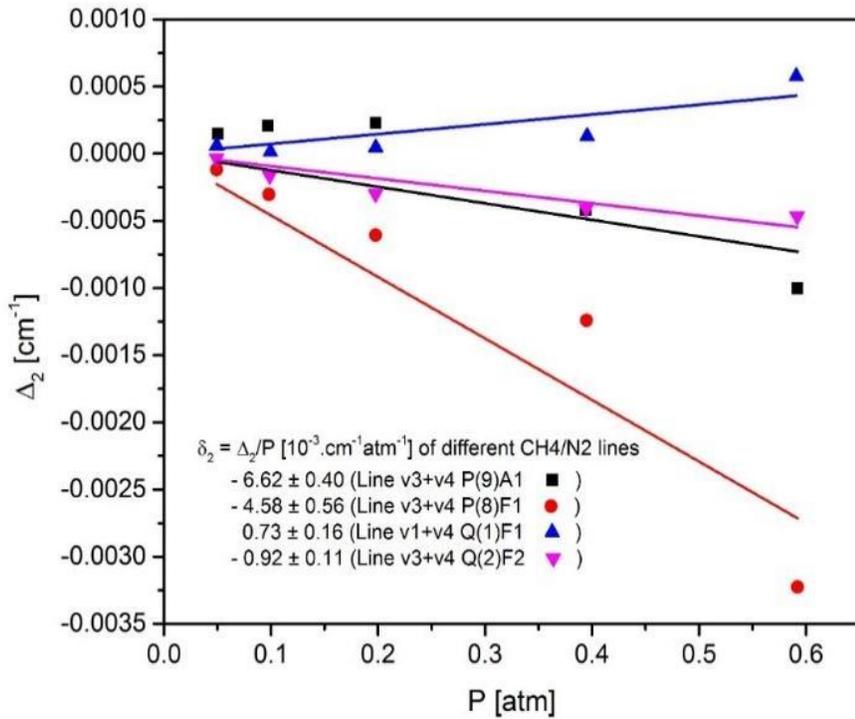
Figure 4. The calculated speed-dependent of the shift Δ_2 [cm^{-1}] at different pressures of CH$_4$/N$_2$ for the considered transitions using SDVP

For the other two transitions ($\nu_1+\nu_4$ Q(1)F1 và $\nu_3+\nu_4$ Q(2)F2), the obtained value of δ_2 is very small. This implies that we can ignore the speed dependence of the shift of these two transitions. This result is also consistent with the result for parameter Δ.

The dependence on pressure P [atm] of the parameter characterizing the speed-dependent of the width Γ_2 [cm^{-1}] of the CH$_4$/N$_2$ gas system for four different transitions is shown in Figure 5. Similar to the case of Δ_2, the dependence of Γ_2 on pressure P is non-linear. This can be explained by the fact that the noise of the experimental spectrum is quite large, especially for the $\nu_3+\nu_4$ P(8)F1 transition. It should be noted, however, that the SDVP also only considers the speed-dependent effects of the shift and the width and does not consider other refined effects, so it is only an approximate model.

The value of the line-broadening coefficient γ_2 [cm^{-1}.atm^{-1}], is determined by the gradient of the line passing through the origin and describes the linear dependence of Γ_2 concerning P, also shown in Figure 5 and Table 3, the value of speed dependence of width for transition v3+v4 Q(2)F2 of CH$_4$ in the air by [14] using the SDVP was also shown for comparison. Note that, to our knowledge, this is the first study of spectral parameters using the SDVP for these transitions of the CH$_4$/N$_2$ gas system. Therefore, another study using this model is needed to confirm the obtained values of the parameters δ_2 and γ_2 in this study.
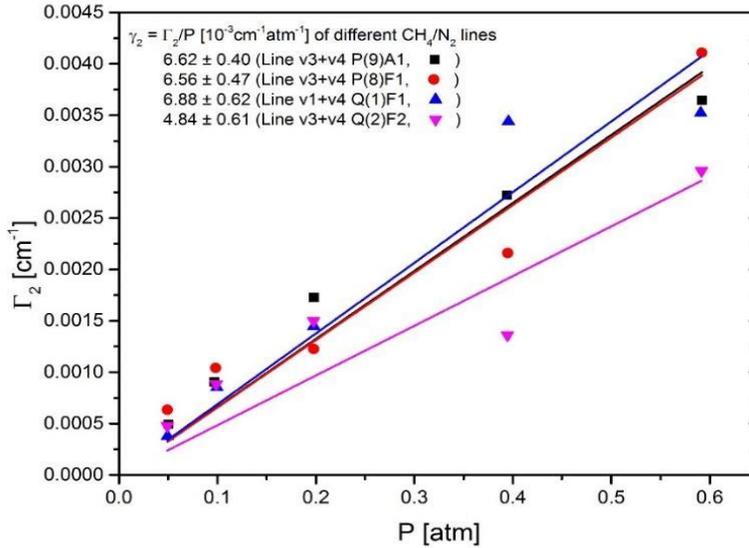
Figure 5. The pressure dependence of speed-dependent of the width Γ_2 [cm^{-1}] of CH$_4$/N$_2$ for four transitions

2.2.4. The Dicke narrowing parameter

The dependence of the Dicke narrowing parameter, B [cm^{-1}], on pressure, is shown in Figure 6. As shown in Figure 6, similar to the case of Δ_2 and Γ_2, the dependence of B on P is non-linear. This can be explained as the low signal to noise ratio (as can be seen in Figure 1, for example) affected B. Another explanation can be given from the used profile. In this case, the Rautian model was used, but only the Dicke narrowing effect was taken into account in this model but some refined effects were neglected. The non-linear dependence on pressure was also observed at some other transitions of system CH$_4$/N$_2$ [20].
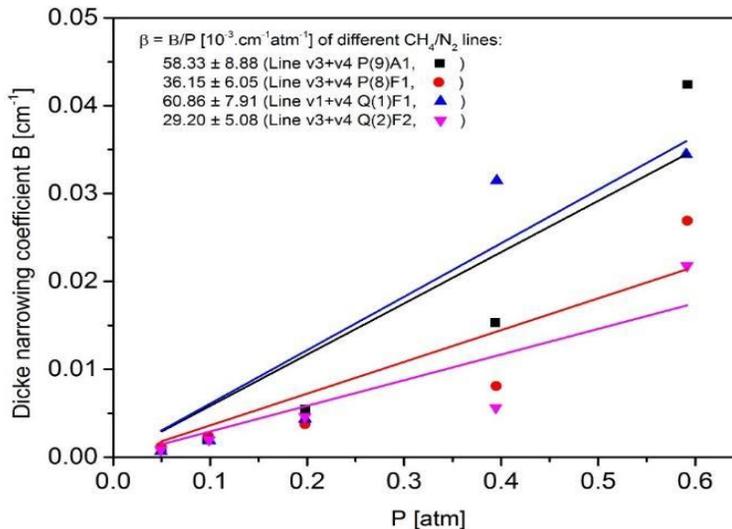

Figure 6. The calculated Dicke narrowing parameter B [cm^{-1}] at different pressures P [atm] of different transitions using RP

For the Dicke narrowing coefficient parameter $\beta = B/P$, it can be seen in Figure 6, that β is strongly influenced by the noise of the experimental spectrum. The average value of this parameter for the 4 studied transitions of the CH_4/N_2 gas system is $\beta^{Mean} \approx$ 46.14±15.83 $[10^{-3}$ cm^{-1}atm$^{-1}]$, which is quite consistent with the research works for other CH_4/N_2 transitions such as Lepere et. al. (β=38.1 $[10^{-3}$ cm^{-1}atm$^{-1}]$, [23]) and Kapitanov et al (β=32.1 $[10^{-3}$ cm^{-1}atm$^{-1}]$], [20]). The results for v3+v4 P(9)A1 using the Hard collision model by Pine (24.5$[10^{-3}$ cm^{-1}atm^{-1}), [10] and by Mondelain et. al. (β= 25.0 $(10^{-3}$ cm^{-1}atm^{-1}), [12] also were listed in Table 2 as a comparison. As can be seen in this table, the values of β in [10] and [12] are quite different compared with our results. This can be explained due to the different ranges of pressure used in the calculation. In [10] and [12], the measurements were made in low pressure conditions (from 20 Torr to 100 Torr in [12]) but in our work, we used a large range of pressure scales (from 45 Torr to 450 Torr which covers almost all atmospheric pressure range).

2.2.5. The line intensity

The pressure dependence P [atm] of the line intensity S [cm^{-1}/(molecule.cm^{-2})] of the transition obtained using different spectral models is shown in Figure 7.

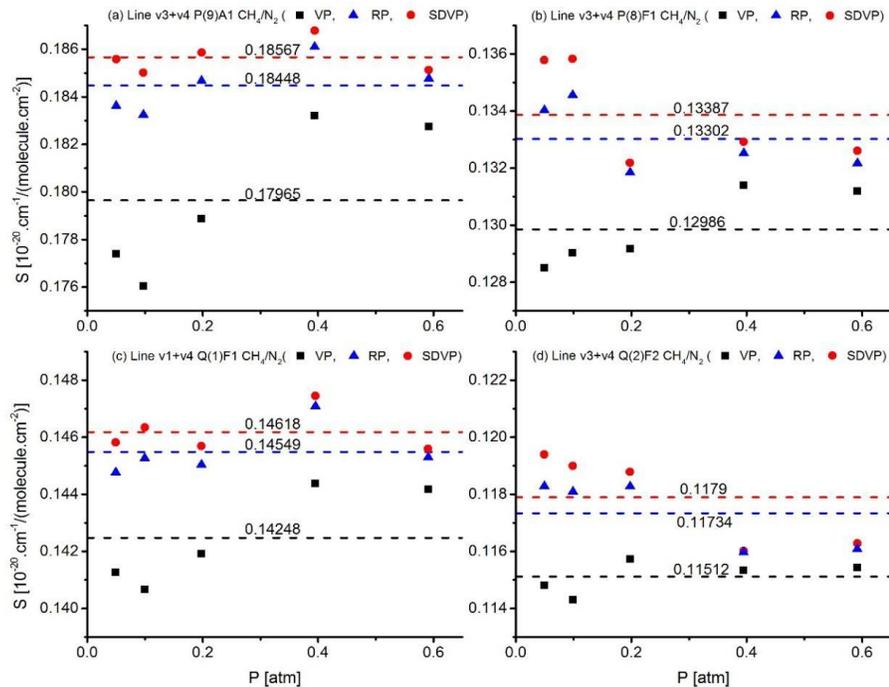***Figure 7. The dependence of line intensity S [cm^{-1}/(molecule.cm^{-2})] to pressure P [atm] for different transitions. The mean value of line intensity of transitions obtained using different line shape models were shown using dashed lines***

The results show that the line intensity S of each transition corresponding to a spectrum varies with the pressure of the CH_4/N_2 gas system. For each transition and at each pressure of the gas system, the SDVP, and the RP show that the value of S is approximately equivalent to and greater than the corresponding value given by the VP. This difference is between 0.6% and 5.7% and can be explained because the SDVP and

the RP take into account the effects of narrowing the absorption spectrum, such as the speed dependence of the width (Γ_2) and the Dicke effect (B). These results lead to the difference between the mean value of S for each transition obtained from using the two models SDVP and RP of 2% to 3% higher than using the VP as can be shown in Figure 7. When compared with the line intensities of these transitions in the 2012 HITRAN database (HITRAN database [19] (see Table 2), the spectral intensities obtained from using the Voigt model of this study are about 5.6% to 8.7% higher. This difference is probably due to the difference in pressure range and also by the noise of the absorption spectra used in the study.

The line-shape parameters for the absorption spectra of the transitions obtained by using three spectral models VP, SDVP, and RP, and also values from other research have been listed in Table 2.

Table 2. Line-shape parameters of some transitions of methane perturbed by nitrogen at room temperature were determined using different line-shape models. The values of these parameters are given in [10^{-3} cm^{-1} atm^{-1}], except for S, which is [10^{-20} cm^{-1}/(molecule.cm^{-2})]. The errors in the quantitiesare taken as the corresponding standard deviation (1σ)

Transition	Model	δ	γ_0	γ_2	δ_2	β	S
v3+v4 P(9)A1	SDV	-10.21 ±0.17	57.80±0.14	6.62± 0.40	-1.23 ±0.45		0.18567± 0.00071
	RP	-9.5 5±0.10	57.23±0.11 62.00[12] (250K)			58.33 ±8.88 24.5[10] 22.0[12]	0.18448± 0.00112
	V	-9.56 ±0.10	55.72±0.59 55.40[24]				0.17965± 0.00320 0.169[19]
v3+v4 P(8)F1	SDV	-11.62 ±0.38	62.04±0.33	6.56± 0.47	-4.58 ±0.56		0.13387± 0.00179
	RP	-10.40 ±0.12	61.55±0.16			36.15 ±6.05	0.13302± 0.00120
	V	-10.45 ±0.12 -10.14[22]	60.50±0.41 64.78[22] 64.00[24]				0.12986± 0.00134 0.123[19]
v1+v4 Q(1)F1	SDV	-7.69 ±0.11	65.91±0.30	6.88± 0.62	0.7 3±0.1 6		0.14618± 0.00077
	RP	-7.86±0.05	65.36±0.29			60.86 ±7.91	0.14549± 0.00092

	V	-7.86±0.05 -8.05[22]	63.92±0.52 66.39[22] 65.60[24]				0.14248± 0.00170 0.131[19]
v3+v4 P(9)A1	SDV	-10.21±0.17	57.80±0.14	6.62 ±0.40	-1.23 ±0.45		0.18567± 0.00071
	RP	-9.55±0.10	57.23±0.11 62.00[12](250K)			58.33 ±8.88 24.5[10] 22.0[12]	0.18448± 0.00112
	V	-9.56±0.10	55.72±0.59 55.40[24]				0.17965± 0.00320 0.169[19]

3. Conclusions

This work presents a study to determine the line-shape parameters of four isolated transitions ($v3+v4$ P(9)A1, $v3+v4$ P(8)F1, $v1+v4$ Q(1)F1 and $v3+v4$ Q(2)F2) of methane perturbed by nitrogen at room temperature. The experimental spectra of these transitions at different pressures are fitted using three spectral line-shape models - the Voigt (VP), the Rautian (RP), and the speed-dependent Voigt (SDVP) profiles by the least-squares method.

The comparison results between the experimental spectrum and the calculated spectrum using different spectral line models indicate that the SDVP and the RP lead to a better fit than the VP. However, the pressure-dependences of the refined parameters $\Delta 2$, $\Gamma 2$, and B observed in this work imply that the SDVP and the RP are also approximate models. In order to solve this problem and to get a better presentation for measured N_2-broadened CH_4 spectra, a multi-spectrum fitting technique and a more physical-based line shape profile which takes into account both the speed dependence of line -width and -shift and the Dicke narrowing effects must be used.

The parameters that characterize the considered transitions such as the line intensity S and the parameters that characterize the spectra corresponding to each line-shape model (such as the shift coefficient δ, line-broadening coefficient γ_0, coefficient describing the speed dependence of the shift, δ_2, and the width, γ_2, the Dicke narrowing coefficient, β) have been determined and are in good agreement with those of other studies realized for the same rotational transition belonging in the same- or other- vibrational bands of the CH4/N2 gas system.

To our knowledge, this is the first study to use the speed-dependent Voigt and Rautian models to determine the line-shape parameters for these transitions of the CH_4/N_2 gas system. Therefore, the results of this study are new and can be added to spectral databases.

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