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PRESSURE DEPENDENCES OF LINE PARAMETERS OF THE $\nu_3 + \nu_4$ R(7)F1 TRANSITION OF METHANE DILUTED IN NITROGEN USING THE HARD- AND SOFT-COLLISION MODELS

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Abstract. In this work, the affection of the Dicke narrowing effect on the spectral shape of the $\nu_3 + \nu_4$ R(7)F1 transition of methane diluted in nitrogen was studied using the Hard- and the Soft- collision line-shape models. Room-temperature absorption spectra of CH_4 broadened by N_2 were measured at a wide range of pressure using a difference-frequency laser spectrometer. Measured spectra of the studied transition were then one-by-one fitted with the simple Voigt profile as well as the two line-shape models considered the Dicke narrowing effect at two different assumptions of velocity-changing collisions: hard- and soft- collisions. The obtained results confirmed that using these two models leads to better qualities of fit with respect to the Voigt profile. Pressure-dependences of the line-shape parameters were also observed for the considered transition. The results showed a good agreement with other studies.

Keywords: methane, nitrogen, Dicke narrowing effect, pressure dependence of line parameters.

1. Introduction

Methane (CH_4) is one of the most important greenhouse gases in the Earth's atmosphere. Determination of the concentration of CH_4 in our atmosphere from remote sensing requires precise knowledge of the spectroscopic signature of methane [1].

The spectral line-shape of molecules is governed by different effects related to various physical-mechanisms [2]. For isolated methane lines, the non-Voigt effect on the line-shape is assumed to be entirely due to velocity changing collision, thus considered through the use of the Hard collision [HC, 3] or Soft collision [SC, 4] models [5-7]. It was shown that these two models lead to better qualities of fits than the usual Voigt profile [VP, 8]. Some studies [9-12] reported that the Dicke narrowing parameter obtained by these two models is not directly proportional to pressure, especially at relatively high pressures. The pressure dependences of the collisional half-width and Dicke narrowing

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parameters of the isolated $2\nu_3$ R(0) transition of CH_4 diluted in N_2, O_2, and He at room temperature were shown by *Dufour et al*. [9]. Similar situations were also clearly observed for the isolated ν_4 R(0) line of methane broadened by nitrogen [10], for the doublet $2\nu_3$ R(9)F1-R(9)F2 transitions of CH_4 diluted in N_2, and Ne [12] and for 4 transitions in the P-branch of the $\nu_2 + \nu_4$ vibrational band of CH_4 perturbed by CH_4, N_2, and O_2 [11]. However, the absorption spectra of methane used in these studies [9-12] were recorded at small pressures (from 20 Torr to 250 Torr, from 14 mbar to 128 mbar, from 20 Torr to 100 Torr and from 5 kPa to 35.18 kPa, respectively) which are very low in comparison with the atmospheric pressure condition. In order to fulfill the picture, a spectral shape study of methane at a larger range of pressure is also needed.

The $\nu_3 + \nu_4$ R(7)F1 ($\sigma_0 = 4427.816365$ cm^{-1}) transition of methane is a good candidate for spectral shape study because of its very good isolation with distances to the nearest strong lines of about 1 cm^{-1} and its quite high rotational quantum number (J=7). In this study, the pressure dependence of spectral shape parameters of this transition of methane diluted in nitrogen was therefore firstly investigated at room temperature and at a larger range of pressure, from 19.9 mbar to 945.4 mbar, using the Hard- and Soft- collision models [3, 4] as well as the Voigt profile [8].

2. Content

2.1. Line-shape models used and data analysis

Absorption spectra of the considered transition of methane broadened by nitrogen were measured at room temperature ($T = 298.0 \pm 0.1$ K) using a different frequency laser spectrometer with an absorption path-length of about $L = 180.0$ cm at IEM-CSIC in Madrid, Spain. All detailed information about the spectrometer and the experimental setup was presented in *Le et al.* [13] and references therein, it is therefore only briefly recalled here. The concentration of CH_4 in the mixture is 1.996% and the absorption spectra were consecutively recorded at 8 total pressures of 945.4 mbar, 799.6 mbar, 600.2 mbar, 399.9 mbar, 200.6 mbar, 100.4 mbar, 50.1 mbar and 19.9 mbar (as plotted in the top panel of Figure 1).

To analyze the measured spectra, three different line-shape models (VP, HC, and SC) are considered. The Voigt model [8] is the most widely-used one to represent absorption spectra for the determination of spectroscopic line-shape parameters. This model considered two important physical mechanisms (the Doppler- and the collisional- effects) which significantly affect the molecular absorption line-shapes [2, 8]. The two more accurate line-shape profiles considered the Dicke narrowing effect [14] at different limitations of velocity-changing (VC) collisions are the Hard- and Soft- collision models [3, 4]. In the first limit of VC collisions, one assumes that the velocity memory of the active molecule is lost after each collision. This limiting case corresponds to the so-called hard collision approximation. In contrast to the hard collision approximation, now one assumes that the velocity of the active molecule is not significantly modified after each collision. This limit corresponds to the so-called soft collision approximation. The functional forms of these models were detailly described in the corresponding references [3, 4, 8] and therefore were not presented here.

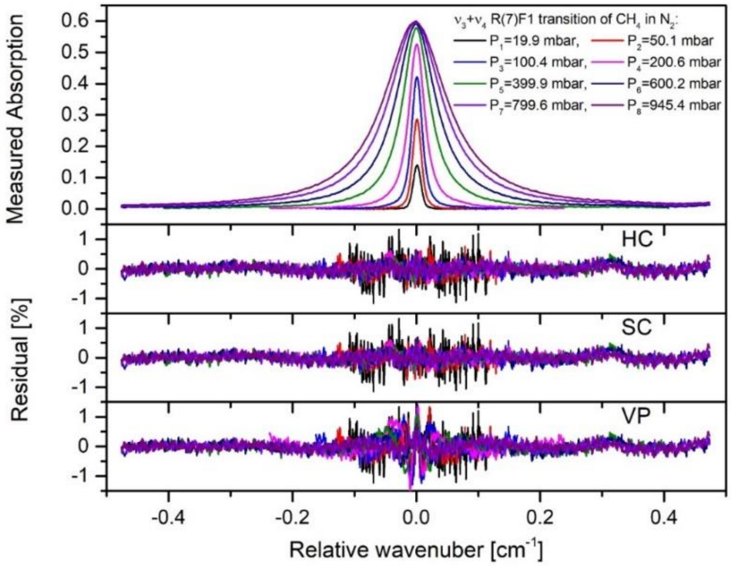

Figure 1. Measured absorption spectra of the considered CH_4 transition broadened by N_2 at room temperature and 8 different pressures. The corresponding residuals obtained from fits of these spectra with the three models (HC, SC, VP) are represented in the lower panels.

The measured spectra were then one-by-one fitted with these three models using the least-squared procedure. The line intensity S, the line-shape parameters (the line-shift Δ, the collisional half-width Γ and the Dicke narrowing B coefficients) and the baseline parameters describing the zero-absorption level were adjusted in the fits. The obtained results were shown and discussed in Subsection 2.2.

2.2. Results and discussions

The residuals obtained from the fits for the considered transition were shown in Figure 1. As can be seen in this figure, among these three considered line-shape models, the Voigt profile leads to the largest residuals. The results obtained from the Hard- and the Soft- collision models are very similar and are at least three times better than those with the Voigt profile at the central parts of the absorption spectra. This observation was previously confirmed in many spectral shape studies not only for methane [5-7, 9-12] but also for other molecular systems [2].

The relative line-shift coefficients Δ (in cm^{-1}) of the considered transition (defined as the displacements of the positions of the absorption peaks at different pressures and those at "zero-pressure" ($\sigma_0 = 4427.816365$ cm^{-1} [15]) were shown in the top panel of Figure 2. The collisional line-shift parameter δ (in cm^{-1}. atm^{-1}) of the transition for each considered model can be derived by using a linear fit of the corresponding Δ respect to the pressure P of the gas mixture. The obtained values of this parameter of the considered transition are the same for the three line-shape models used ($\delta = -3.60(4) \times 10^{-3}$ $cm^{-1}.atm^{-1}$). In order to test the pressure dependence of the line-shift, the values of δ were directly computed as ratios of the line-shift Δ and the corresponding pressure P (i.e., $\delta = \Delta/P$)

and then plotted as a function of pressure in the bottom panel of Figure 2. The results show that the values of δ clearly depend on the pressure at small pressures and then become more constant at high pressures. Note that this pressure dependence of the line-shift parameter is partly caused by the limited accuracy of the determination of the line positions at low pressure. This observation therefore should be confirmed by other studies.

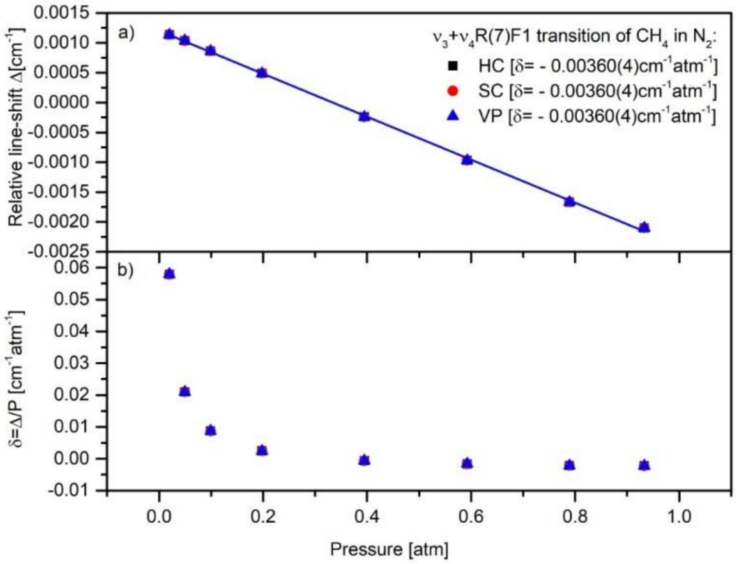

***Figure 2.** a) The relative line-shift coefficients Δ (in cm^{-1}) obtained from the fits using the three models (HC, SC, VP) and b) the corresponding pressure-dependence of the line-shift parameter δ [cm^{-1}. atm^{-1}]*

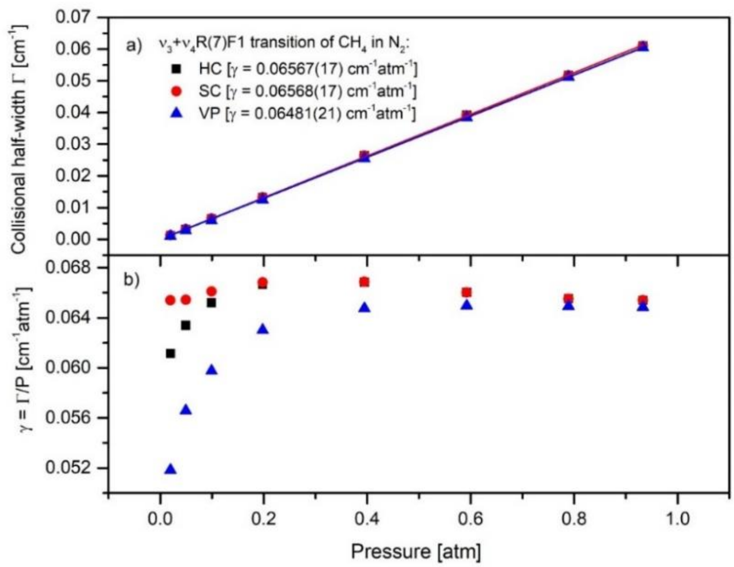

***Figure 3.** The same as Figure 2 but for a) the collisional half-width coefficients Γ [cm^{-1}] and b) the broadening parameter γ [cm^{-1}.atm^{-1}]*

Similarly to the line-shift, the collisional half-width coefficient Γ (in cm^{-1}) and its corresponding parameter γ (in $cm^{-1}.atm^{-1}$) versus the pressure were plotted in Figure 3. As can be seen in the top panel of this figure, the values of γ obtained from HC and SC models are quite the same and higher (about 1.3%,) than those from the Voigt profile. This is caused by the additional consideration of the confinement Dicke narrowing effect in these two models [2]. Pressure dependence of the collisional broadening parameter γ (determined by the formula $\gamma = \Gamma/P$) was observed for the three line-shape models: strongly depend on the pressure at small pressures and then become more constant at high pressures. The values of γ obtained from the HC and SC models are very close together but higher than those from the Voigt profile (up to 15.6%) at small pressures. This result confirmed that the Dicke narrowing effect is more effective at low pressure than at high pressure [2]. Similar situations were also observed for other transitions of methane diluted in different perturbed gases [9-12].

Figure 4 shows the strong pressure dependence of the Dicke narrowing coefficient B [cm^{-1}] and its corresponding parameter $\beta = B/P$ [$cm^{-1}.atm^{-1}$] obtained from the HC and SC models for the considered transition. Similar observations were also reported for other transitions of methane [9-12]. As can be seen in the bottom panel of this figure, the obtained values of β are significantly higher at high pressures in comparison with those at low pressures. This result may be due to the speed dependence effect of the half-width [2, 16] which is not considered in the HC and SC models. As demonstrated in [2], both the Dicke narrowing effect and the speed dependence of half-width lead to a narrower the spectral line-shape of molecules, however, the first one is more dominant at low pressures and the second one is more significant at high pressures. The omission of the speed dependence effect might strongly affect the high-pressure values of the Dicke narrowing parameter. The values of this parameter obtained from the linear-fits (see the top panel of Figure 4 and Table 1) are about 2.5 times the diffusion coefficient calculated for the CH_4-N_2 system ($\beta^{Diff} = 37.9 \times 10^{-3}$ $cm^{-1}.atm^{-1}$ [11]). However, at low pressures (see the bottom panel of Figure 4), the obtained values of β are more comparable with those of β^{Diff}.

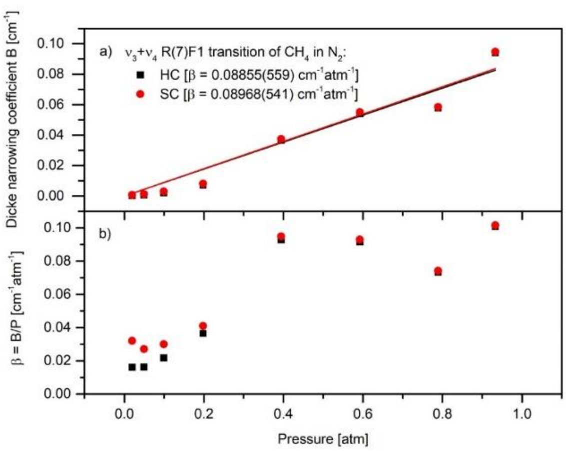

Figure 4. The same as Figure 2 but for a) the "confinement" Dicke narrowing coefficients B [cm^{-1}] and b) the Dicke narrowing parameter β [$cm^{-1}.atm^{-1}$]

The pressure dependence of the measured line intensity S [in 10^{-20}.cm^{-1}/(molecule.cm^{-2})] of the considered transition of methane was shown in Figure 5. Similar to the situations of the line-shape parameters (δ, γ, β), the values of S obtained from the HC and SC models are almost the same and higher (up to 3.1%) than those from the VP. The difference is bigger at the low pressures where the Dicke narrowing effect is more significant. The averaged values of the line intensity obtained from this work are higher in comparison to those from HITRAN database [15] up to 8.4%. This observation might be due to the difference in the used line-shape models and the considered pressure range as well as the uncertainty of the absorption path-length used in this work.

Table 1. *Line parameters of the considered transitions obtained from this work and those of other studies. The values are given in 10^{-3}.cm^{-1}.atm^{-1} for the shifting-, collisional broadening- and Dicke narrowing parameters (δ, γ, β) and in 10^{-20}.cm^{-1}/ (molecule.cm^{-2}) for the integrated line intensity (S). Their uncertainties (in parentheses, in the same unit as the last digit) are estimated as the standard deviations.*

Parameters /Profiles	δ	δ^{Refs}	γ	γ^{Refs}	β	β^{Diff}	S	S^{Refs}
HC	-3.60(4)		65.67(17)		88.55(559)	37.9	0.138502	
SC	-3.60(4)		65.68(17)		89.68(541)		0.138769	
VP	-3.60(4)	-3.6 [15] -3.5(2) [17]	64.81(21)	63.3 [15] 65.5(9) [17]			0.136403	0.128 [15]

In addition, the values of the line-shape parameters obtained from this work for the $\nu_3 + \nu_4$ R(7)F1 transition of methane diluted in nitrogen at room temperature were listed in Table 1. As can be observed from this table, our results are in good agreement with those of the considered transition of methane broadened by air from other studies.

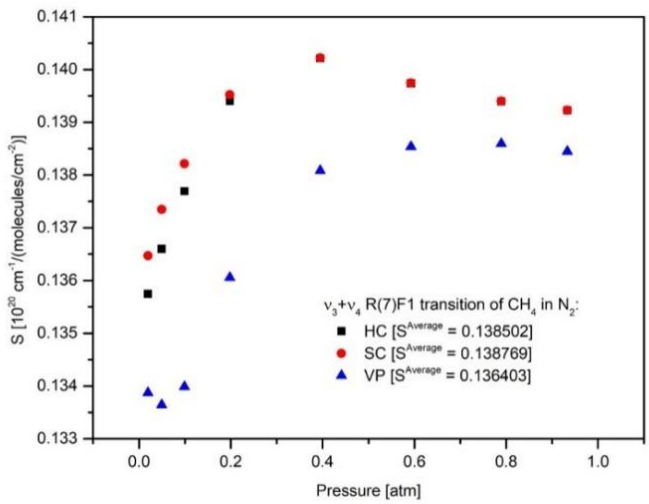

Figure 5. Pressure dependence of the measured line intensity of the considered transition obtained from using three line-shape models (HC, SC, VP)

3. Conclusions

Room temperature absorption spectra of the $\nu_3 + \nu_4$ R(7)F1 transition of methane diluted in nitrogen were recorded with a difference-frequency laser spectrometer at a large range of pressure. The measured spectra were then analyzed using the Hard- and the Soft-collision models as well as the Voigt profile. The results confirmed that the HC and HC models lead to a better agreement with the experiments than the Voigt profile. Pressure dependences of line-shape parameters such as the line-shift, the collisional half-width, and the confinement Dicke narrowing as well as the line intensity were also observed. The result obtained from this work is in good agreement with those of the literatures. In order to get a better representation for experiments, measured spectra should be fitted with a more physical based line-shape model using the multi-spectrum-fitting technique.

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