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Christophe Claveau, A. Valentin. Narrowing and broadening parameters for H₂O lines perturbed by helium, argon and xenon in the 1170-1440 cm⁻¹ spectral range. *Molecular Physics*, 2009, 107 (14), pp.1417-1422. 10.1080/00268970902911404 . hal-00513288

HAL Id: hal-00513288

<https://hal.science/hal-00513288>

Submitted on 1 Sep 2010

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Narrowing and broadening parameters for H₂O lines perturbed by helium, argon and xenon in the 1170-1440 cm⁻¹ spectral range

Journal:	<i>Molecular Physics</i>
Manuscript ID:	TMPH-2009-0016.R1
Manuscript Type:	Full Paper
Date Submitted by the Author:	13-Mar-2009
Complete List of Authors:	Claveau, Christophe; Laboratoire de Physique Moléculaire pour l'Atmosphère et l'Astrophysique, CNRS, Université Pierre et Marie Curie Valentin, A.; Université Pierre et Marie Curie
Keywords:	infrared absorption line profile, line narrowing and broadening, water vapor

**Narrowing and broadening parameters for H₂O lines perturbed by helium, argon
and xenon in the 1170-1440 cm⁻¹ spectral range.**

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Abstract

Collision effects on water vapor at low concentration in mixture with noble gases (helium, argon and xenon) have been studied by Fourier transform spectroscopy in a pressure range where line narrowing by dynamic confinement (Dicke effect) and collision broadening are observable i.e. when the Voigt function cannot reproduce the observed profiles. Precise values of the broadening parameter have been obtained for P and Q branches of the H₂O ν_2 band taking into account the molecular confinement (hard or soft collisions).

The broadening parameter value derived from a Voigt profile for H₂O lines perturbed by helium is too small about 10 % compared with the values determined with the soft or hard collision model. For H₂O lines perturbed by argon or xenon this difference can reach more than 50 % for the narrowest lines.

Keywords: infrared absorption line profile, line narrowing and broadening, water vapor

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1. Introduction

In a previous paper we reported the narrowing and broadening parameters for R branch lines of the H_2O ν_2 band perturbed by noble gases and nitrogen with F.T.S. (Fourier Transform Spectrometer) [1]. In a second paper we reported the narrowing and broadening parameters for P branch lines with F.T.S. and for R branch lines with T.D.L.S. (Tunable Diode Laser Spectrometer) [2] of the H_2O ν_2 band perturbed by nitrogen.

This paper presents precise measurements on absorption lines shapes in the P and Q branches of the H_2O ν_2 band perturbed by helium, argon and xenon. The narrowing parameters determined in this work and in Ref. [1] will be compared.

2. Experiment details

Spectra of water vapor in the $1170\text{--}1440\text{ cm}^{-1}$ region have been recorded using the F.T.S. described elsewhere [3]. In all experiments, water vapor was contained in a multiple reflection cell with a 36-m maximum optical path. Experimental conditions for the different spectra are given in Table 1. The low H_2O vapor pressures were measured with a 0-10 torr capacitance manometer. The total pressure was measured with a 0-1000 torr Bourdon gauge from Texas Instruments. The temperature, measured with a Pt thermistor with an accuracy of 0.3 K, does not vary by more than 0.5 K during the interferogram recording. To reduce the residual absorption by water vapor, the spectrometer tank is pumped below 0.1 torr between each spectrum.

As previously in Refs. [1-2], each experimental spectrum is obtained from the ratio I_t/I_0 between two spectra. For the first one, both absorption cells are empty. For the second one, the multiple pass cell was filled with water vapor in presence of the buffer gas and the second cell, 1.5 m long, with CH_4 at a very low pressure. This method allows improve the base line definition. In order to optimize the signal to noise ratio and reach a value close to 500, a maximum path difference of 2.8 m has been chosen. After numerical apodization the apparatus function width ($3.6 \times 10^{-3}\text{ cm}^{-1}$) is equal to the Doppler line width ($\text{FWHM} \cong 3.6 \times 10^{-3}\text{ cm}^{-1}$) in this spectral

region. For line shape studies an accurate knowledge of the apparatus function is needed; an example of its determination is shown in Figure 1. A low pressure CH₄ line, described as the convolution product of the apparatus function with the CH₄ line shape, described with a Voigt profile, is fitted to the observed line. The self broadening parameter of CH₄ line is fixed to the HITRAN 2004 value [4]. Details about apparatus function are given in Ref. [3].

3. Computations

The observed line $I_t(\tilde{\nu})/I_0(\tilde{\nu})$ is compared in a least squares fit to a synthetic line, convolution product of the apparatus function $A(\tilde{\nu})$ with a theoretical line shape

$$\frac{I_t(\tilde{\nu})}{I_0(\tilde{\nu})} = A(\tilde{\nu}) * \exp(-\ell k(\tilde{\nu}, P_{H20}, P)) \quad (1)$$

where ℓ is the path length and $k(\tilde{\nu}, P_{H20}, P)$ the absorption coefficient at the total pressure P , defines the line profile. In a first approximation it is described by a Voigt profile (given in Ref. [1], Eq. (2) to (4)) convolution product of a Gauss function (Doppler effect) with a Lorentz function (collision broadening).

The narrowing effect of collisions on pure Doppler is taken into account in the soft and hard collision models (developed respectively by Galatry [5] and Rautian *et al.* [6]). The expressions are recalled in Ref. [1] (Eq. (5) to (6)). For the computations, we used line profile expressions in the standardized form initiated by Herbert [7] for the soft collision model and extended to the hard collision model by Varghese and Hanson [8]. We used only symmetric line profiles neglecting the correlations between the phase and velocity changes.

The narrowing parameters β_{soft}^0 and β_{hard}^0 , for respectively a soft and hard collision models, are related to the inverse of the time required for an appreciable change in velocity and have the same physical meaning in both models. In all cases, we will compare the fitted narrowing parameter β^0 to the value of the dynamic friction coefficient β_{diff}^0 deduced from the relation

$$\beta_{\text{diff}}^0 = \frac{k_B T}{2\pi c m_l D_{12}} \quad (2),$$

where D_{12} is the diffusion coefficient of the binary mixture and m_l is the mass of the absorbing molecule.

In the soft and hard collision models, the collision broadening profile is introduced as a single Lorentz function (assuming the relative speed of the partner molecules independent of the absorber speed). The line profile is then equivalent to the convolution of a Lorentz profile with a confinement narrowed profile (hard or soft collision model with collision broadening γ_L set to zéro).

4. Results and discussion

The broadening and narrowing parameter values have been obtained by multfit program introduced in Ref. [9]. This program permits the simultaneous analysis of spectra recorded with different pressures and absorption path length, but at a fixed temperature.

For each spectrum the studied lines have been first compared with synthetic lines involving a Voigt function to describe the H₂O line profile. Deviations of about 1% between observed lines and synthetic lines were always observed. The greatest differences were obtained with the heaviest perturber especially if the pressure broadening is small and the absorption at the peak of the line is strong. The observed deviations can be reduced within the noise limit using soft or hard collision model.

Three parameters are determined: the partial pressure of water vapor, the broadening parameter γ^0 and the narrowing parameter β^0 (soft or hard). The lines intensities are fixed in the fit to the values reported by Toth *et al.* [10].

Although the H₂O concentration is only 1% the contribution of the self broadening is far from being negligible compared with the broadening by the buffer gas. The ratio between γ_{self}^0 and γ^0 for

the perturber i is rarely less than 4 and may reach 20 as it can be deduced from the values reported by Toth *et al.* [10]. The contribution of the self broadening has been removed from the γ_L measurements using the equation

$$\gamma_L = \gamma_{\text{noble gas}}^0 P_{\text{noble gas}} + \gamma_{\text{self}}^0 P_{\text{H}_2\text{O}} \quad (3)$$

with the γ_{self}^0 values reported in Ref. [10]. $\gamma_{\text{noble gas}}^0$ is the broadening parameter ($\text{cm}^{-1} \text{ atm}^{-1}$) for H_2O perturbed by noble gases (helium, argon or xenon) at a partial pressure $P_{\text{noble gas}}$.

The confinement narrowing is easier to observe on "narrow" lines, that is to say if the contribution of the Lorentz profile which describes the collision broadening remains small compared with the profile associated with the Doppler effect for the chosen pressures. This is the case for the H_2O line which is reproduced on Figure 2 perturbed by xenon. The observed line appear narrower than the synthetic line described by a Voigt profile. The residual is reduced within the noise limit if the soft or hard collision models is used to describe the line profile. The narrowing effect is spectacular for the heaviest perturber as xenon where the ratio γ/β is nearby 0.2. In a light buffer gas as helium the molecular diffusion is faster and consequently narrowing effects are weaker and more difficult to observe. Then only narrow lines corresponding to γ/β values equal to about one for helium have been studied.

The broadening and narrowing parameter values are reported in Table 2 for helium, in Table 3 for argon and in Table 4 for xenon as buffer gas. As expected the β_{soft}^0 value is always found greater than the β_{hard}^0 value. However the difference between the corresponding broadening parameters is generally lower than 1%. For the chosen pressures to study the confinement narrowing the Voigt profile does not give a good description of the observed lines, while the soft or hard collision model fits the data within the noise.

The broadening parameters for H₂O lines perturbed by helium (Table 2) show that neglecting the confinement narrowing, the broadening parameter value derived from a Voigt profile is too small by about 10% compared with the values determined with the soft or hard collision model. For H₂O perturbed by argon and xenon (Tables 3 and 4) this difference varies from about 3% and 5% respectively for the broadest lines to more than 50% for the narrowest ones. The broadening parameter value for H₂O lines perturbed by argon can be compared with the only common value at 1361.80 cm⁻¹ measured by Giesen *et al.* [11]. The difference between the two values is about 7 %. Our results can be compared also with our previous work [1] in R branch of the H₂O v₂ band perturbed by argon. We can see generally a good agreement for the same J Ka Kc: the difference is generally about 3 or 4%.

The narrowing parameter mean values obtained for each gas mixture by averaging the β_{soft}^0 or β_{hard}^0 values determined from all the lines are reported in Table 5. They can be compared with the dynamic friction coefficient β_{diff}^0 deduced from the diffusion coefficient D₁₂. The diffusion coefficient has been calculated using the equations given in Ref. [12], considering the only interactions between unlike molecules, and using the combining laws allowing to obtain the force constants which describe the interaction between a polar molecule as H₂O and a non polar molecule from a Lennard-Jones form of the potential. We could expect that the soft collision model would lead to a better agreement with the dynamic friction coefficient for H₂O perturbed by helium. However the measured values of β_{hard}^0 are more close to β_{diff}^0 than β_{soft}^0 . In fact with Helium the narrowing is very weak and difficult to measure. Then the two values are very close and the noise ratio can't permit to choice between hard or soft collision model. For H₂O perturbed by argon and xenon the hard collision model give a better agreement with the dynamic friction coefficient.

In table 5 we have compared also our results with our previous work [1] in R-branch of the $\text{H}_2\text{O } \nu_2$ band perturbed by noble gases. A very good agreement is obtained between the mean narrowing parameter values determined in the two spectral region (5 and 8 μm).

The β^0 mean value of Grossman *et al.* [13] is twice the β^0 values obtained in the previous work [1] and in this study. Nevertheless the precision of narrowing measurements doesn't permit to conclude at a vibrational effect. In fact the uncertainties due to the I_0 line have an important effect: typically a 0.1% variation of I_0 lead a 20% variation of the narrowing parameter of the strong lines (about 50% absorption at the peak) and more for the weakest lines.

Acknowledgements

The authors thank Dr. A. Henry for numerous discussions which have been a precious help in this line profile study. They are grateful to Dr. C. Camy-Peyret who suggested this work and was a source of constant encouragement.

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Table Captions

- Table 1: Experimental conditions
- Table 2: Broadening γ^0 and narrowing β^0 parameters ($10^{-3} \text{ cm}^{-1}/\text{atm}$) for H_2O perturbed by helium deduced by fitting different models to the observed lines.
- Table 3: Broadening γ^0 and narrowing β^0 parameters ($10^{-3} \text{ cm}^{-1}/\text{atm}$) for H_2O perturbed by argon deduced by fitting different models to the observed lines.
- Table 4: Broadening γ^0 and narrowing β^0 parameters ($10^{-3} \text{ cm}^{-1}/\text{atm}$) for H_2O perturbed by xenon deduced by fitting different models to the observed lines.
- Table 5: Dynamic friction coefficient and narrowing parameter mean values ($10^{-3} \text{ cm}^{-1}/\text{atm}$)

Figure captions

- Fig. 1: Determination of the apparatus function: observed spectrum of the line of CH_4 at 1348.04 cm^{-1} at very low pressure (—) and least squares fitted line (----) described by Eq. 1 where the line profile is very close to a Gauss function
- Fig. 2: Observed spectrum of the H_2O line perturbed by xenon (—) and least squares fitted line described by a Voigt profile (----). The (obs-calc) residuals are plotted as plain curves for different least squares fits: Voigt profile, hard and soft collision model.

Fig 1:

Fig 2:

Table 1:

H ₂ O perturbed by	H ₂ O Pressure (torr)	Total Pressure (torr)	Temperature (K)	Pathlength (cm)
Helium	1.00	100.5	297.1	1607
	1.03	100.0		
Argon	0.40	40.1	297.6	1607
	0.75	75.1		
	2.50	250.0		
Xenon	0.48	41.0	297.6	1607

Table 2:

Wavenumber cm ⁻¹	Transition			Broadening Parameter γ^0			Narrowing Parameter β^0	
	J' K _a ' K _c '	←	J K _a K _c	Profile			Profile	
				Voigt	Hard	Soft	Hard	Soft
1266.668	9 6 3		10 7 4	8.8(2)	9.5(1)	9.6(1)	10(2)	11(2)
1317.610	13 0 13		14 1 14	6.4(2)	7.1(1)	7.2(1)	10(2)	11(2)
1317.616	13 1 13		14 0 14	7.3(5)	7.8(3)	7.8(3)	8(3)	10(3)
1344.069	12 2 11		13 1 12	8.1(2)	9.1(1)	9.2(1)	10(2)	12(2)
1352.349	11 2 9		12 3 10	10.0(2)	10.7(1)	10.8(1)	8(2)	9(2)
1361.796	11 2 10		12 1 11	8.8(2)	9.4(1)	9.5(1)	7(1)	8(1)
1369.828	12 1 12		12 2 11	8.6(2)	9.1(1)	9.2(1)	11(1)	12(1)
1369.953	12 0 12		12 1 11	8.7(2)	9.8(2)	9.9(2)	12(2)	13(2)
1388.483	6 1 5		6 4 2	16.0(2)	16.6(1)	16.7(1)	11(2)	12(2)
1411.323	10 4 7		11 3 8	13.3(2)	14.1(2)	14.1(2)	10(2)	11(2)

The digits in parenthesis are two standard deviations in unit of the last digit.

Table 3:

Wavenumber cm ⁻¹	Transition J' K _a ' K _c ' ← J K _a K _c		Broadening Parameter γ^0			Narrowing Parameter β^0	
			Profile			Profile	
			Voigt	Hard	Soft	Hard	Soft
1198.178	7 1 7	8 2 6	32.2(3)	33.4(3)	33.4(3)	27(4)	30(5)
1224.978	9 3 7	10 4 6	23.7(3)	25.6(2)	25.6(2)	32(9)	36(9)
1225.086	6 0 6	7 3 5	30.0(3)	31.1(2)	31.1(2)	44(3)	48(3)
1266.668	9 6 3	10 7 4	9.9(4)	12.2(2)	12.3(2)	28(4)	32(5)
1280.047	9 4 5	10 5 6	19.7(4)	21.2(1)	21.2(1)	37(3)	41(3)
1284.306	3 1 2	4 4 1	35.7(4)	37.2(4)	37.2(4)	36(7)	40(8)
1288.886	8 5 3	9 6 4	2.8(3)	14.3(1)	14.4(1)	36(2)	40(2)
1296.490	8 7 2	9 8 1	6.9(5)	8.4(1)	8.5(1)	36(2)	41(2)
1296.491	8 7 1	9 8 2					
1317.610	13 0 13	14 1 14	1.7(5)	4.6(1)	4.7(1)	31(4)	37(5)
1317.616	13 1 13	14 0 14	1.0(10)	4.7(5)	4.7(5)	35(12)	42(12)
1338.286	7 0 7	7 3 4	38.9(3)	40.5(2)	40.5(2)	31(5)	35(6)
1344.069	12 2 11	13 1 12	3.7(6)	6.8(2)	7.0(2)	45(4)	51(5)
1352.349	11 2 9	12 3 10	9.8(5)	12.6(1)	12.7(1)	37(4)	43(5)
1361.796	11 2 10	12 1 11	5.2(5)	8.2(2)	8.3(2)	36(2)	42(2)
1369.828	12 1 12	12 2 11	7.0(5)	9.0(1)	9.1(1)	33(2)	38(3)
1369.953	12 0 12	12 1 11	5.9(5)	9.2(3)	9.3(3)	40(4)	46(5)
1378.493	7 1 6	7 4 3	28.6(3)	29.8(2)	29.8(2)	31(3)	34(3)
1382.062	10 3 8	11 2 9	12.7(5)	14.5(1)	14.5(1)	40(3)	45(3)
1390.522	5 1 4	5 4 1	34.1(3)	35.0(2)	35.0(2)	32(2)	36(3)
1390.758	11 1 11	11 2 10	9.0(5)	10.8(2)	11.0(2)	40(2)	45(3)
1403.462	9 3 7	10 2 8	16.6(5)	18.6(1)	18.6(1)	33(2)	37(3)
1411.323	10 4 7	11 3 8	19.0(5)	21.4(4)	21.5(4)	35(7)	40(7)

The digits in parenthesis are two standard deviations in unit of the last digit.

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Table 4:

Wavenumber cm ⁻¹	Transition J' K _a ' K _c ' ← J K _a K _c		Broadening Parameter γ^0			Narrowing Parameter β^0	
			Profile			Profile	
			Voigt	Hard	Soft	Hard	Soft
1198.178	7 1 7	8 2 6	53.3(7)	55.9(9)	56.0(9)	62(21)	65(22)
1225.086	6 0 6	7 3 5	45.8(6)	48.3(5)	48.3(5)	61(12)	65(13)
1266.668	9 6 3	10 7 4	16.4(13)	21.9(6)	22.1(6)	77(12)	84(18)
1280.047	9 4 5	10 5 6	28.0(6)	30.7(2)	30.9(2)	50(4)	54(4)
1288.886	8 5 3	9 6 4	19.0(8)	22.7(2)	22.7(2)	59(4)	65(4)
1317.610	13 0 13	14 1 14	0.7(12)	6.7(4)	7.1(4)	55(5)	65(6)
1317.616	13 1 13	14 0 14	0.6(25)	7.6(4)	7.6(4)	52(5)	61(6)
1338.286	7 0 7	7 3 4	60.7(5)	63.2(4)	63.3(4)	48(7)	52(7)
1361.796	11 2 10	12 1 11	5.6(12)	12.3(3)	12.5(3)	62(4)	69(4)
1369.828	12 1 12	12 2 11	8.8(9)	12.9(2)	13.2(2)	50(2)	56(3)
1369.953	12 0 12	12 1 11	7.9(12)	15.2(5)	15.4(5)	64(6)	72(6)
1378.493	7 1 6	7 4 3	42.5(6)	44.9(4)	45.0(4)	50(8)	54(9)
1379.745	2 0 2	3 3 1	71.3(4)	73.4(3)	73.4(3)	48(7)	51(7)
1382.062	10 3 8	11 2 9	17.2(10)	21.4(3)	21.6(3)	66(4)	72(5)
1390.522	5 1 4	5 4 1	50.9(6)	53.4(3)	53.4(3)	48(7)	52(7)
1390.758	11 1 11	11 2 10	12.3(9)	16.8(3)	17.0(3)	52(4)	58(4)
1403.462	9 3 7	10 2 8	23.8(8)	27.8(3)	28.0(3)	54(5)	60(6)
1411.323	10 4 7	11 3 8	28.9(10)	33.4(11)	33.6(11)	52(13)	58(14)

The digits in parenthesis are two standard deviations in unit of the last digit.

Table 5:

H ₂ O perturbed by :	β_{diff}^0 ^a	β_{hard}^0		β_{soft}^0	
		This Work	[1]	This Work	[1]
Helium	08.0	10(2)	10.8(12)	11(2)	12.0(15)
Argon	32.0	35(5)	32.4(48)	40(5)	36.2(55)
Xenon	52.0	56(8)		62(9)	

^a deduced from the diffusion coefficient D_{12} calculated using the equations given in Ref. [12]