SPECTROSCOPY
OF AMBIENT MEDIUM

Parameters of Broadening of Water Molecule Absorption Lines by Argon Derived Using Different Line Profile Models

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Abstract—The water vapor absorption spectrum was measured in the spectral region 6700–7650 cm^{-1} with argon as a buffer gas. The room-temperature spectrum was measured using a Bruker IFS 125-HR Fourier Transform Spectrometer with high signal-to-noise ratio, with a spectral resolution of 0.01 cm^{-1}, at argon pressures from 0 to 0.9 atm. The H$_2$O absorption spectral line parameters are derived by fitting two line shape profiles (Voigt and speed-dependent Voigt) to the experimental spectrum. It is shown that the use of speed-dependent Voigt profile provides the best agreement with experimental data.

INTRODUCTION

In many areas of science in recent years, great attention has been paid to obtaining accurate and reliable information on spectral line parameters of gases. This became possible due to the rapid development of experimental techniques such as laser and Fourier transform spectroscopy. Thus, modern spectrometers allow measurements with phenomenal spectral resolution (better than 0.001 cm^{-1}) and high signal-to-noise ratio (10^5 and higher). Many studies have shown that a widely used Voigt (V) profile did not describe sufficiently accurately the real profiles of absorption lines. The largest differences appear near the center and in the wings of spectral lines (see, for example, [1–4]). This leads to errors in deriving such line parameters as intensity and broadening coefficients, which can reach several percent, even for isolated lines. Thus, it became necessary to use line profile models that take into account subtle effects, such as collisional Dicke narrowing of the lines [5, 6], line mixing [7], and the wind effect [8, 9]. Among the most common models, the Galatry [10] and Rautian–Sobel'man [9] profiles can be noted. They consider the Dicke effect, i.e., reduction of the Doppler broadening due to restriction on free movement of absorbing molecules due to collisions. However, the area of applicability of these profiles is limited by a range of broadening gas pressures; the Dicke effect on line parameters is negligible at pressures over 300 mbar.

Another physical mechanism leading to narrowing of spectral lines is the so-called wind effect, which is caused by the dependence of collisional relaxation rate constants on the speed of the active absorbing molecule. The Lorentzian halfwidth and the shift of the center of line are not constant in this case, but depend on the speed of the absorbing molecule. A quadratic dependence on speed [8, 11] is used in the most common models; a hypergeometric dependence is also used sometimes [12]. One of the models, which takes into account this effect, is the speed-dependent Voigt (SDV) profile [3]. In addition, there are models that take into account both the Dicke effect and wind effect: speed-dependent Rautian [11] and Galatry [12] line profiles, and the pCqSDHC (partially Correlated quadratic Speed-Dependent Hard-Collision) model [1, 2].

A fast algorithm for computing the SDV line profile, depending on the speed of molecules, was suggested in [13]. This algorithm has been applied to the processing of atmospheric spectra measured with the satellite ACE-FTS spectrometer, to analyze H$_2$O spectra. The use of the SDV profile made it possible to greatly improve agreement between measured and simulated spectra and the quality of retrieval of the water vapor content in the atmosphere. Currently, this algorithm is widely used in atmospheric applications. For example, it is included in the latest version of the SFIT software designed to address the problems of determining the content of atmospheric gases from
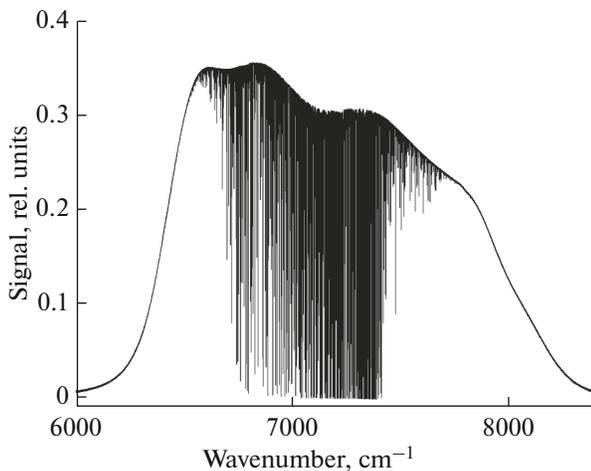
Fig. 1. Outline transmission spectrum of H_2O in the spectral region 6000–8400 cm^{-1} at water vapor pressure of 0.00873 atm and Ar pressure of 0.503 atm.

measurements in the NDACC ground-based network of Fourier spectrometers [14]. Spectroscopic databases contain little information on parameters of H_2O absorption lines for the line profiles that depend on the speed of buffer molecules. Therefore, a study of the SDV profile and determination of its parameters from laboratory spectra under different conditions will be useful for more accurate simulation of atmospheric spectra in the gas-analysis problems.

This paper presents the analysis of the values of broadening and shift coefficients for H_2O absorption lines, obtained from two sets of spectra recorded with different signal-to-noise ratios, when approximated by two different line profiles: the conventional V profile and the SDV profile. Argon was used as a buffer gas, because the mass ratio of the molecules of this gas to the active molecules is about 2.2, which means that this effect will manifest itself well.

EXPERIMENT

The water vapor absorption spectra broadened by argon were measured in the spectral region 6700–7650 cm^{-1} using a Bruker IFS 125HR FT spectrometer. A tungsten light source was used as a radiator; detection of radiation was performed with an InSb detector cooled with liquid nitrogen. A Thermo Electron multipass optical cell with a base of 20 cm, which provides an optical path length of up to 10 m, was mounted inside the sample compartment of the spectrometer. The buffer gas pressure was varied from 0 to 0.9 atm. The pressure of Ar–H_2O mixtures inside the cell was measured with a DVR5 pressure gage having a measurement error of 1%. To improve the signal-to-noise ratio (S/N), an optical filter was used with the maximum transmittance in the region near 7000 cm^{-1}. The S/N ratio reached 20 000 for a number of lines. To

be able to analyze lines with different S/N ratios, two spectra were recorded with a different number of scans for each pressure of the buffer gas: averaging over 200 scans was used to obtain one spectrum (first data set), and averaging over 4000 scans, to obtain the other spectrum (the second dataset). All absorption spectra were recorded at room temperature (296 K) with a spectral resolution of 0.01 cm^{-1} and an optical path length of the beam in the cell of 10 m. A more detailed description of the experimental setup and technique is presented in [15–17]. An outline transmission spectrum of the water molecule is shown in Fig. 1.

DISCUSSION OF THE RESULTS

For the analysis of absorption spectra, we used a program that allows deriving line parameters from their simultaneous fitting to several spectra recorded under different conditions. We derived the following spectral line parameters: line center, intensity, and broadening and shift coefficients. This program can automatically search for the line peaks, split them into groups for simultaneous fitting of the parameters of lines located under one contour. The automatic search for peaks is based on methods of the pattern recognition theory [18, 19]. It is a recognition system that is trained on examples and answers of a "teacher". Examples are spectral points indicated by the "teacher", who also specifies whether or not each given point is a peak of a line. Such an approach allows configuring the system to search for not only the obvious maxima and minima, but also weak lines observed on wings of stronger lines. Training the program is performed once after its installation; however, the system can be additionally trained during further work, based on features of the spectrum in a particular task. A detailed description of the program, methods, and approaches is presented in [20–22].

In the previous version of the program, a V profile was used for approximation of experimental data. A new version of the program includes a SDV profile, which takes into account the quadratic dependence of the broadening coefficients on the speed of an active molecule. For this, a fairly simple algorithm given in [13] was used. Apart from traditionally used spectral line parameters (line position, intensity, and halfwidth) this model uses two additional parameters: collisional narrowing and asymmetry parameters.

For the analysis, we selected 12 absorption lines for which S/N ratio varied within a wide range (from 30 to 16 300). Two profiles were used for the calculations: V and SDV at a fixed Doppler halfwidth. Table 1 shows line parameters of the water molecule: intensity and broadening, shift, and narrowing coefficients. The data were retrieved from the spectra averaged over 4000 scans for each pressure of the buffer gas. During this retrieval, we considered not only the spectral lines analyzed, but also all closely spaced lines, including those with a much lower intensity.

Table 1. Parameters of absorption lines derived using the SDV line profile (averaging over 4000 scans)

ν, cm^{-1} HITRAN	V	$J'K_a'K_c'$	$J''K_a''K_c''$	$I \times 10^{-3}$, cm^{-2} atm^{-1}	γ, cm^{-1} atm^{-1}	δ, cm^{-1} atm^{-1}	β, cm^{-1} atm^{-1}
6726.24882	0 2 1	6 0 6	7 0 7	7.16(2)	0.0287(1)	−0.0213(1)	0.00850(10)
6731.44505	0 2 1	6 3 3	7 3 4	1.99(2)	0.0335(1)	−0.0161(1)	0.00689(15)
6755.02085	0 2 1	4 1 3	5 1 4	13.38(3)	0.0386(1)	−0.0177(1)	0.00734(10)
6761.45207	0 2 1	5 3 2	6 3 3	1.24(1)	0.0321(1)	−0.0158(1)	0.00647(20)
6790.64896	0 2 1	4 3 1	5 3 2	5.55(2)	0.0303(1)	−0.0156(1)	0.00756(16)
6791.88741	0 2 1	3 1 3	4 1 4	22.58(3)	0.0427(1)	−0.0179(1)	0.00958(11)
6949.70384	1 2 0	10 3 8	11 0 11	0.14(1)	0.0210(2)	−0.0183(2)	0.00667(28)
6956.31484	0 2 1	3 1 2	2 1 1	9.45(2)	0.0391(1)	−0.0199(1)	0.00733(16)
6958.77665	2 0 0	4 3 1	5 4 2	2.58(1)	0.0321(1)	−0.0224(1)	0.00684(21)
6963.16829	0 2 1	3 2 2	2 2 1	16.23(2)	0.0390(1)	−0.0157(1)	0.00818(15)
7172.69909	2 0 0	3 3 0	4 2 3	8.12(2)	0.0419(1)	−0.0122(1)	0.00748(11)
7178.44584	1 0 1	6 2 5	6 2 4	3.54(1)	0.0395(1)	−0.0200(1)	0.00665(18)

V is the quantum number of the upper vibrational state; $J'K_a'K_c'$ and $J''K_a''K_c''$ are the quantum numbers of the upper and lower rotational states, respectively; I is the intensity; γ is the broadening coefficient; δ is the shift coefficient; β is the narrowing coefficient. Calculated errors on the last significant digit are shown in parentheses.

Table 2. Comparison of the water molecule absorption line parameters derived using different models of line profile (averaging over 4000 scans)

ν, cm^{-1}	I_{SDV}/I_V	γ_{SDV}/γ_V	S/N	QF_{SDV}	QF_V	$\Gamma_{SDV}/\Gamma_{Dop}$
6726.24882	1.039	1.108	6680	980	290	1.17
6731.44505	1.025	1.054	1590	1070	260	1.39
6755.02085	1.020	1.043	10090	1180	250	1.39
6761.45207	1.033	1.047	1000	740	260	1.33
6790.64896	1.028	1.070	4820	930	170	1.25
6791.88741	1.033	1.065	16350	810	180	1.61
6949.70384	1.052	1.133	182	182	102	1.61
6956.31484	6700	1.041	6810	1090	255	1.48
6958.77665	1.025	1.056	2180	1270	202	1.13
6963.16829	1.026	1.056	11800	1220	225	1.53
7172.69909	1.017	1.037	5730	830	260	1.50
7178.44584	1.019	1.035	2550	280	1090	1.49

S/N ratios and standard deviations of $\Gamma_{SDV}/\Gamma_{Dop}$ (QF) are obtained for argon pressure of 0.273 atm.

On average, for the water vapor pressure of 0.00873 atm, the ratio of the Lorentzian (collisional) halfwidth to the Doppler halfwidth γ/γ_{Dop} varied from 1.41 to 3.55 with the argon pressure varying from 0.273 to 0.9 atm. Line intensities varied from 1.3×10^{-4} to 2.1×10^{-2} cm^{-2} atm^{-1}. For both sets of data, the values of intensities of the water molecule absorption lines and their broadening coefficients obtained with the V profile were smaller than the corresponding values obtained using the SDV profile. The broadening coefficients were smaller by 6%, and intensities, by 3% (Tables 2 and 3). At the same time, the broadening coefficients obtained using different models are quite close.

Figure 2 shows examples of approximation for one of the studied absorption lines of the water molecule at different pressures of the buffer gas. It can be seen that

Table 3. Comparison of the water molecule absorption line parameters derived using different models of line profile (averaging over 200 scans)

| ν, cm^{-1}	I_{SDV}/I_V	γ_{SDV}/γ_V	S/N	QF_{SDV}	QF_V
6726.24882	1.040	1.108	1130	520	160
6731.44505	1.028	1.055	270	240	180
6755.02085	1.019	1.043	1700	1160	286
6761.45207	1.025	1.035	170	169	140
6790.64896	1.031	1.072	815	580	240
6791.88741	1.036	1.083	2770	840	276
6949.70384	1.045	1.121	30	30	29
6956.31484	1.025	1.049	1153	800	335
6958.77665	1.020	1.043	370	311	230
6963.16829	1.023	1.053	2000	700	410
7172.69909	1.016	1.035	970	570	300
7178.44584	1.018	1.035	430	330	230
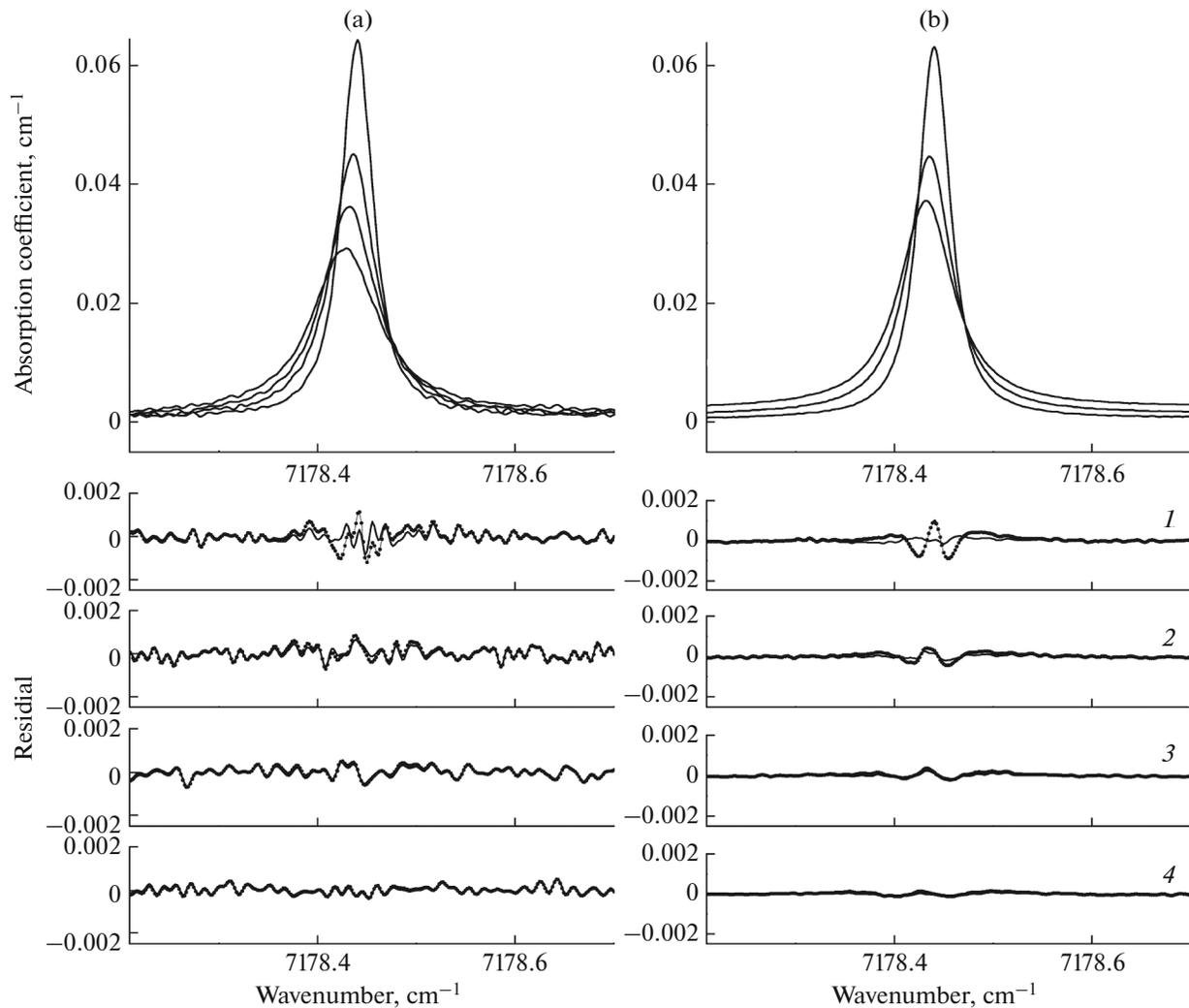
Fig. 2. Example of approximation of the water molecule absorption spectra using (a) Voigt and (b) SDV profiles for two datasets recorded at Ar pressure of 0.273 (*1*), 0.503 (*2*), 0.680 (*3*), and 0.9 atm (*4*). Solid line shows result of fitting using the SDV profile; dash-dot line corresponds to the Voigt profile; the spectrum is obtained by averaging over (a) 200 and (b) 4000 interferograms.

the accuracy of approximation by V profile is much worse, which is especially evident at low argon pressures. At pressures of less than 0.503 atm, the difference between experimental spectra and spectra calculated using the V profile has a clear W-shaped form.

The fitting quality can be estimated by the magnitude of the standard deviation. It was suggested in [2, 23] to use a parameter related to the standard deviation:

$$QF = (K_{\max} - K_{\min})/\sigma_r,$$

where $K_{\max}$ and $K_{\min}$ are the maximum and minimum values of line absorption; and σ_r is the standard deviation. Ideally, when the calculated line profile describes the spectrum within experimental uncertainty, QF should be close to the S/N value. Based on spectral line simulation, it has been shown in [2] that the S/N ratio and the ratio between Lorentzian and Doppler

halfwidths play an important role in the analysis of absorption lines using different profiles.

We derived S/N and QF values for each spectral line (see Tables 2 and 3). Figures 3 and 4 show the main results: dependences of $K = QF/(S/N)$ on S/N for the same absorption lines of the water molecule, but at different pressures of the buffer gas. At an argon pressure of 0.273 atm (Fig. 3), when line halfwidths differ from the Doppler halfwidth on average by a factor of 1.4, the standard deviation, as calculated using the SDV profile, is smaller by a factor of 5 on average than in the case with the V profile. The use of SDV profile for spectral lines with S/N values less than 2000 gives good results: the QF value differs from the S/N ratio by less than a factor of two. However, when S/N ratio is higher than 3000, the SDV profile does not provide a zero residual (i.e., the difference at the noise level), demonstrating a clearly pronounced
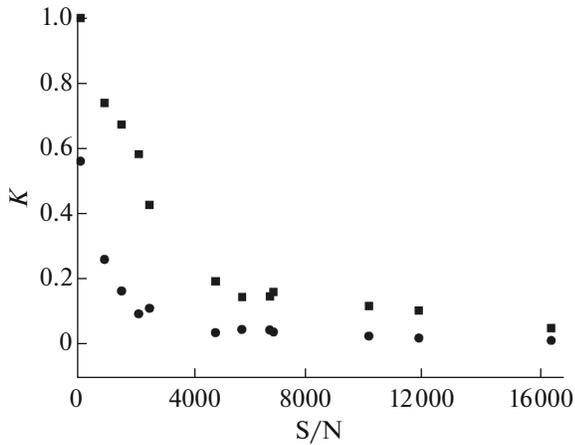
Fig. 3. Dependence of the parameter $K = QF/(S/N)$ on S/N value (Ar pressure is 0.273 atm). Here and in Fig. 4 squares show the data derived using the SDV profile, and circles, using the conventional Voigt profile.
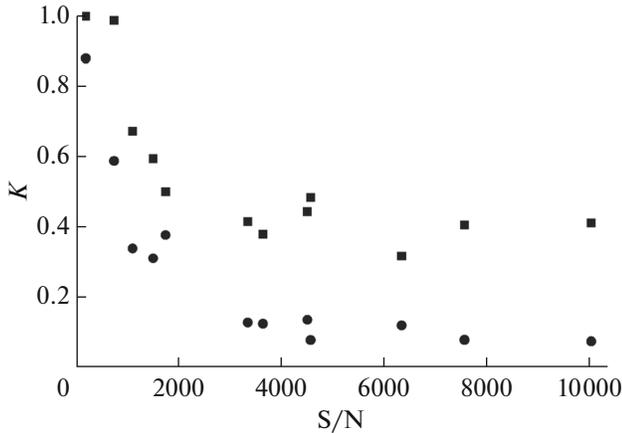

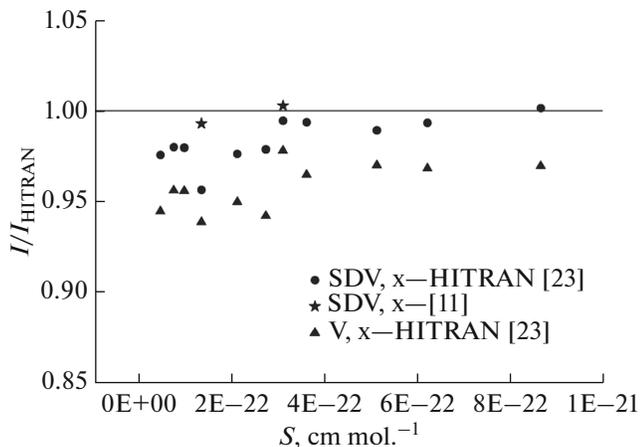**Fig. 4.** Dependence of the parameter K on S/N value (Ar pressure is 0.9 atm).

Fig. 5. Comparison of water molecule line intensities derived in this work with those from HITRAN database.

spectral structure. This suggests that the SDV profile does not fully reflect how the line profile is formed.

An increase in the argon pressure increases the halfwidths of the water molecule absorption lines, which, in turn, increases QF values and decreases K (see Fig. 4). For a S/N ratio of 10000, the value of K is approximately 0.4.

The widely used HITRAN database [24] contains the line centers, intensities, self-broadening and air-broadening coefficients for the water molecule. Figure 5 shows the comparison of line intensities from the HITRAN database with those obtained in this paper. In the case where the SDV profile is used for approximation, the intensity ratio I/I_{HITRAN} was on average 0.983, while for the traditional V profile this ratio was 0.958. For additional verification of the intensity values, Fig. 5 shows a comparison with the data [11], where the intensities of water molecule absorption lines were measured with high accuracy using laser absorption spectroscopy. The difference for these lines does not exceed 1%.

CONCLUSIONS

The water vapor absorption spectra broadened by argon pressure are recorded in the spectral region from 6700 to 7650 cm^{-1} with a high signal-to-noise ratio. The line parameters derived using two different models, the traditional Voigt profile and speed-dependent Voigt profile, are analyzed. To derive these parameters, we used the program that allows a multispectrum fitting. The best agreement with the experimental data is obtained when using the speed-dependent Voigt profile. The analysis of the lines recorded with different signal-to-noise ratios indicated that though the speed-dependent Voigt profile does not provide adequate recovery of experimental profiles in some cases, it is optimal when the S/N ratio < 2000 as a relatively simple profile with a relatively small number of physically clear fitting parameters.

ACKNOWLEDGMENTS

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