

Line parameters of HDO from high-resolution Fourier transform spectroscopy in the 11 500–23 000 cm^{-1} spectral region

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Abstract

This work presents new measurements of HDO line parameters in the near-infrared and visible regions (11 500–23 000 cm^{-1}). The measurements consist in high-resolution Fourier transform absorption spectra of $\text{H}_2\text{O}/\text{HDO}/\text{D}_2\text{O}$ vapor mixtures, obtained using a long absorption path. Spectra with and without nitrogen as the buffer gas were recorded. Due to the simultaneous presence of the three isotopologues H_2O , D_2O , and HDO, the H_2O lines removal and the D_2O lines identification were two necessary preliminary steps to derive the HDO line parameters. The D_2O contribution was small and confined to the well-known $4\nu_1 + \nu_3$ band. An extensive listing of HDO spectroscopic parameters was obtained, for the first time, by fitting some 3256 observed lines to Voigt line profiles. The list contains calibrated line positions, absorption cross-sections and, for many of the lines, N_2 -broadening coefficients, as well as N_2 -induced frequency shifts. As a result of the low HDO vapor pressures, it was not possible to retrieve the self-broadening parameters. The list is available on the <http://www.ulb.ac.be/cpm> website.

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1. Introduction

Spectroscopy is a privileged tool to study the global properties of the terrestrial atmosphere, notably the evolution of the concentrations of the minor molecular species with altitude. This requires the experimental and theoretical knowledge of the spectroscopic parameters of these species. It is necessary to have precise information not only on the frequencies of the absorption lines and their intensities, but also on the evolution of their shapes with pressure and temperature.

Like the H_2O molecule, the HDO species is of great interest for studying planetary atmospheres. In addition, HDO is an important species in the determination of the

isotopic D/H ratio, which is fundamental to understand the origin and sources of the atmospheric water. It is also used to compare water found in comets or in other solar system bodies [1,2] with terrestrial water.

The deuterated water molecule (HDO) possesses an absorption spectrum fundamentally different to the one of H_2O . Essentially, its structure is simpler because the ν_3 (OH) bands are well-separated [3,4]. This is due to the large difference, about 1000 cm^{-1} , between the two stretching harmonic frequencies ω_1 and ω_3 .

The first extensive study of the HDO spectrum was carried out by Benedict et al. [5] in the 2400–8000 cm^{-1} region with a resolution of 0.25 cm^{-1} . In 1992, Bykov et al. [6] investigated the $5\nu_3$ band centered at 16920 cm^{-1} and the $3\nu_3$ band centered at 10632 cm^{-1} by optoacoustic spectroscopy and intracavity laser absorption spectroscopy (ICLAS) respectively. More recently, the rotational

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analysis in the visible and near infrared overtone bands of HDO has been performed by Fourier transform spectroscopy [7,8] and ICLAS [3,4,9–13]. To the best of our knowledge, experimental data of absorption cross-sections and broadening parameters for HDO in the 11 500–23 000 cm^{-1} spectral range have never been reported. A recent high accuracy ab initio prediction of the line intensities of HDO, derived from improved potential-energy and dipole moment surfaces, was performed by Schwenke and Partridge [14].

In the continuation of our previous work concerning the experimental determination of the line parameters of the H_2O molecule [15–17], this study presents the measured positions and absorption cross-sections of HDO transitions and their corresponding broadening and frequency shifting by N_2 . Measurements were performed in the near infrared and visible regions at 291 K, with $\text{H}_2\text{O}/\text{HDO}/\text{D}_2\text{O}$ samples and in mixtures with dry N_2 at total pressures ranging from 168 to 800 hPa. Spectra were recorded using a Fourier transform spectrometer in the 11 500–23 000 cm^{-1} spectral range at a resolution of 0.06 cm^{-1} . Comparisons with existing literature data have also been carried out.

2. Experiment details

The detail of the experimental set-up has been described elsewhere [15,17]. In brief, a Bruker IFS 120M Fourier transform spectrometer was coupled to a long multiple-reflection absorption cell of 50 m base length. A path length of 600 m was chosen to maximize the signal-to-noise ratio. The temperature in the cell was monitored by three platinum resistance thermometers. All spectra of H_2O and D_2O mixtures were recorded at room temperature (291 ± 3 K). The light source was a 450 W high-pressure Xenon arc lamp (USHIO). After successive reflections on the cell, the light was directed onto the detector, either a silicon or gallium phosphide GaP diode, depending on the investigated spectral region. Several spectra were recorded successively to allow

the monitoring of any change inside the cell, due essentially to a change in the pressure resulting from condensation on the walls of the cell. Each spectrum was the result of the Fourier transformation of 128 co-added interferograms. After a careful comparison of the spectra, they were co-added to improve the S/N ratio. The unapodized resolution was set to 0.06 cm^{-1} , defined as 0.9/maximum optical path difference. No apodization function was used.

Under the chosen experimental conditions summarized in Table 1, signal to noise ratios of 3000 and of 2500 were obtained in the 11 500–22 000 cm^{-1} and 15 800–31 500 cm^{-1} region, respectively. These values result typically from the addition of 2048 and 4096 interferograms, which correspond to a total recording time of the order of 12 and 24 h, respectively.

The sample of D_2^{16}O was purchased from the Commissariat à l'Énergie Atomique (CEA), with a stated purity of 99.9%. A mixture of 42.5% H_2O and 57.5% D_2O , at a total pressure of 13.17 hPa, was introduced into the cell and led to the formation of HDO. At equilibrium, a mixture of $\text{H}_2\text{O}/\text{HDO}/\text{D}_2\text{O}$ in a proportion determined as 19, 48, and 33%, respectively was obtained. The spectra of HDO with N_2 as buffer gas were obtained by introducing progressively N_2 into the cell already filled with the $\text{H}_2\text{O}/\text{HDO}/\text{D}_2\text{O}$ vapor mixture, waiting afterwards sufficiently long to allow for the stabilization of the temperature and pressure. N_2 -broadening parameters and N_2 -induced shifts of the line positions were determined from four spectra with different nitrogen pressures ranging from 155 to 787 hPa (see Table 1). An overview of the HDO spectra labeled A and B in Table 1, is provided in Fig. 1.

3. Spectra analysis

3.1. HDO lines extraction and identification

Due to the simultaneous presence of all three isotopologues in the cell, an original procedure was

Table 1
Experimental conditions for the spectra recorded in this work

Spectrum	Spectral range (cm^{-1})	$P(\text{H}_2\text{O} + \text{D}_2\text{O})$ (hPa)	$P(\text{N}_2)$ (hPa)	T (K)	Detector	Nbr of scans
$\text{H}_2\text{O} + \text{D}_2\text{O}$						
A	15 800–31 500	13.2 ^a	0	292	GaP	16 × 128
B	11 500–22 000	13.1 ^a	0	291	Si	16 × 128
C	11 500–22 000	13.1 ^a	155.3	291	Si	16 × 128
D	11 500–22 000	13.2 ^a	320.9	291	Si	16 × 128
E	11 500–22 000	13.2 ^a	486.5	291	Si	16 × 128
F	11 500–22 000	13.2 ^a	786.8	292	Si	16 × 128
D_2O						
G	11 500–22 000	13.2 ^b	0	293	Si	16 × 128

The path length and resolution for all spectra were 602.32 m and 0.06 cm^{-1} , respectively.

^a With 48% of HDO, 33% of D_2O , and 19% of H_2O .

^b With 29% of HDO, 68% of D_2O , and 3% of H_2O .

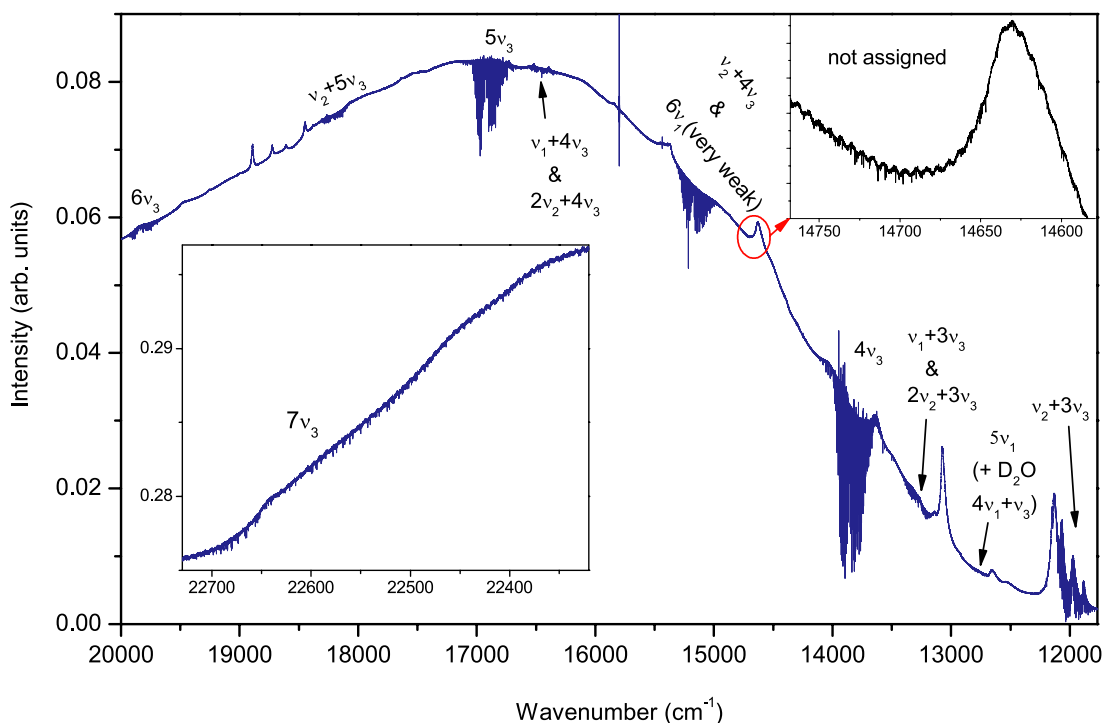


Fig. 1. Overview of the HDO spectrum recorded in this work using a $\text{H}_2\text{O} + \text{D}_2\text{O}$ mixture (pressure = 13 hPa; $T = 291$ K; absorption path length = 600 m) recorded at a resolution of 0.06 cm^{-1} .

applied to extract only the HDO lines. Fig. 2 shows the different steps followed in the treatment of the spectra.

The first step consists in removing the atmospheric contribution due to the absorption within the 6 m external path between the light source and the spectrometer. An atmospheric H_2O spectrum was generated for this purpose using the BR (Brussels–Reims) database (<http://www.ulb.ac.be/cpm/>) and the Winprof program [19] which enables synthesizing a spectrum by applying a Voigt line profile to line positions and intensities. This program also accounts for instrumental effects (truncation, apodization, and field of view) to match as closely as possible the experimental conditions. The atmospheric contribution of the water absorption lines was removed by the division of the observed spectrum by the simulated one. The external contribution to the absorption was about 5% of the integrated surfaces of the water vapor absorption structures, depending on the humidity within the room. It is important for the present work only when a HDO line is overlapped by a strong line of H_2O .

The same strategy was used to remove the atmospheric absorption of the O_2 A bands, $b^1\Sigma_g^+(v=0) - X^3\Sigma_g^-(v=0)$ and $b^1\Sigma_g^+(v=1) - X^3\Sigma_g^-(v=0)$, observed around 13120 cm^{-1} and 14525 cm^{-1} , respectively. The atmospheric O_2 spectrum was simulated using the HITRAN database. This procedure allows to

easily identifying the HDO overlapping lines as shown in Fig. 3.

In the next step, the absorption lines due to the H_2O present in the cell were carefully removed using a simulated spectrum generated from the H_2O BR database. This procedure is illustrated in Fig. 4. It is important to notice here that in addition to the self-broadening effect, the H_2O lines are also broadened by collisions with HDO and D_2O . We assumed that the broadening of H_2O induced by HDO and D_2O was identical to the self-broadening. Then, the H_2O spectrum simulation was performed at the total pressure of the sample with the appropriate mixing ratio.

After these different steps, one is left with a spectrum containing HDO lines, with the addition of a few weak D_2O lines observed between 13125 and 12158 cm^{-1} and belonging to the $4v_1 + v_3$ band. These lines were easily identified by comparing the spectrum with an enriched D_2O spectrum recorded under the same experimental conditions (Table 1). They were also observed and rotationally analyzed by the ICLAS technique [18]. Unlike the H_2O lines, the D_2O lines cannot be eliminated because their parameters are not known in the literature. Fig. 5 shows a portion of a $\text{H}_2\text{O}/\text{HDO}/\text{D}_2\text{O}$ spectrum, where the D_2O lines have been identified. Finally, it has to be noted that a weak unidentified band containing 54 lines is observed around 14675 cm^{-1} . It was not possible to confirm if those lines, which are not observed

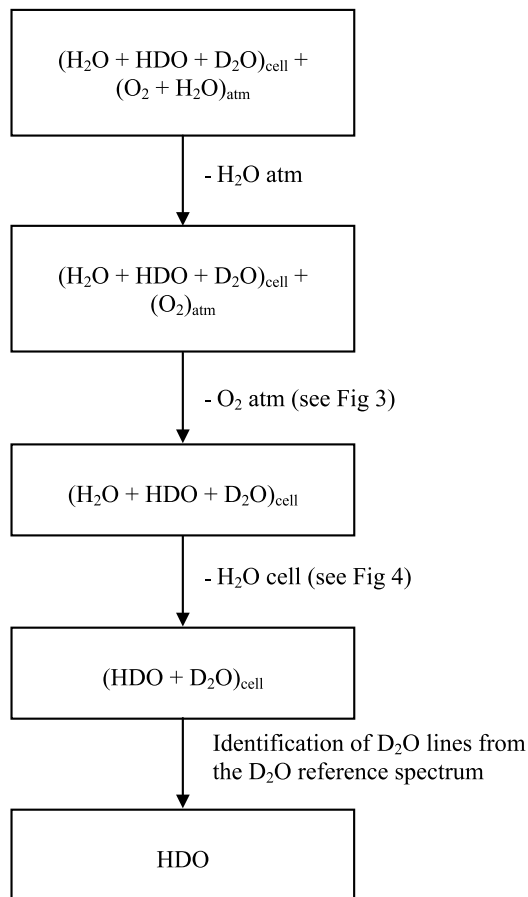


Fig. 2. Description of the different steps applied in the preliminary treatment of the spectra.

by the highly sensitive ICLAS technique [18], are belonging to HDO.

3.2. Partial pressures determination

The H₂O partial pressure was determined on the basis of the intensity of 75 strong and well defined lines. The HDO and D₂O partial pressures were calculated using the equilibrium constant given in [20], $K_{\text{eq}} = 3.86 \pm 0.07$, for the reaction between H₂O and D₂O in gaseous phase:



Values of 6.3 and 4.3 hPa were obtained for the HDO and D₂O partial pressures respectively, and are reported as percentages in Table 1.

3.3. Line fitting and line list construction

A computer program using a non-linear least squares fitting procedure, Wspectra [21], was used to derive the line positions, line areas, and linewidths (Lorentzian width) from the spectra. This program fits

one by one the observed lines to the exponential of a Voigt profile convolved with the instrumental function. The wavenumber scale was calibrated by comparison of the well defined H₂O lines observed in the present spectra with the H₂O vacuum wavenumbers listed in the BR database. The uncertainty on the wavenumber calibration corresponds to better than 0.0033 cm^{-1} accuracy.

The absorption cross-section (S_σ in cm per molecule) for 3256 HDO lines, observed in this work were extracted from spectra using the following relation:

$$S_\sigma = A \frac{P_0 T}{n_L T_0 P_{\text{HDO}} l}, \quad (2)$$

where A is the line area (in cm^{-1}), T is the temperature (in K), l is the absorption path length (in cm), P_{HDO} is the partial pressure of HDO (in atm), $T_0 = 273.15 \text{ K}$, P_0 is 1 atm, and $n_L = 2.68676 \times 10^{19} \text{ molecule cm}^{-3}$ is the Loschmidt number.

The N₂-broadening parameters (γ_{N_2} , in $\text{cm}^{-1} \text{ atm}^{-1}$) and N₂-induced frequency shifts (δ_{N_2} , in $\text{cm}^{-1} \text{ atm}^{-1}$) were determined using the following linear expressions:

$$\Gamma/2 = \gamma_{\text{self}} \times P_{\text{HDO}} + \gamma_{\text{H}_2\text{O}} \times P_{\text{H}_2\text{O}} + \gamma_{\text{D}_2\text{O}} \times P_{\text{D}_2\text{O}} + \gamma_{\text{N}_2} \times P_{\text{N}_2}, \quad (3)$$

$$\tilde{\nu}_{\text{N}_2} = \tilde{\nu} + \delta_{\text{N}_2} \times P_{\text{N}_2}, \quad (4)$$

where Γ is the measured Lorentzian width (full width at half maximum); $\tilde{\nu}_{\text{N}_2}$ and $\tilde{\nu}$ are the line positions in the spectra with and without buffer gas; P_{HDO} , $P_{\text{H}_2\text{O}}$, $P_{\text{D}_2\text{O}}$, and P_{N_2} are the partial pressures of HDO, H₂O, D₂O, and N₂; γ_{HDO} , $\gamma_{\text{H}_2\text{O}}$, and $\gamma_{\text{D}_2\text{O}}$ are the pressure broadening parameters due to HDO, H₂O, and D₂O. The Γ value in Eq. (3) corresponds to the Lorentzian line width caused by HDO–N₂ and HDO–HDO collisions, but also by the collisions with H₂O and D₂O molecules, which contribute to the broadening of the HDO lines. The first three terms in the right-hand side of Eq. (3) are the same for all diluted spectra. In the regression analysis, their sum corresponds to the intercept at zero N₂ pressure. Under the experimental conditions, it is not possible to separate these contributions and to extract the values of γ_{self} from our measurements. Consequently, only γ_{N_2} values, corresponding to the slope of the linear regression, can be obtained. In Eq. (4), $\tilde{\nu}$ corresponds to the line position as measured in the H₂O/HDO/D₂O spectra. It includes the frequency shifts due to the presence of H₂O and D₂O, and the self-induced shift. Due to the difficulty of measuring the pressure dependent parameters for many of the weak lines of the spectrum, a conservative approach was adopted for the line list construction: the values of pressure-dependent parameters were not kept in the list if (a) less than three diluted spectra were used or if (b) the value of the statistical uncertainty (3σ) was greater than the parameter value.

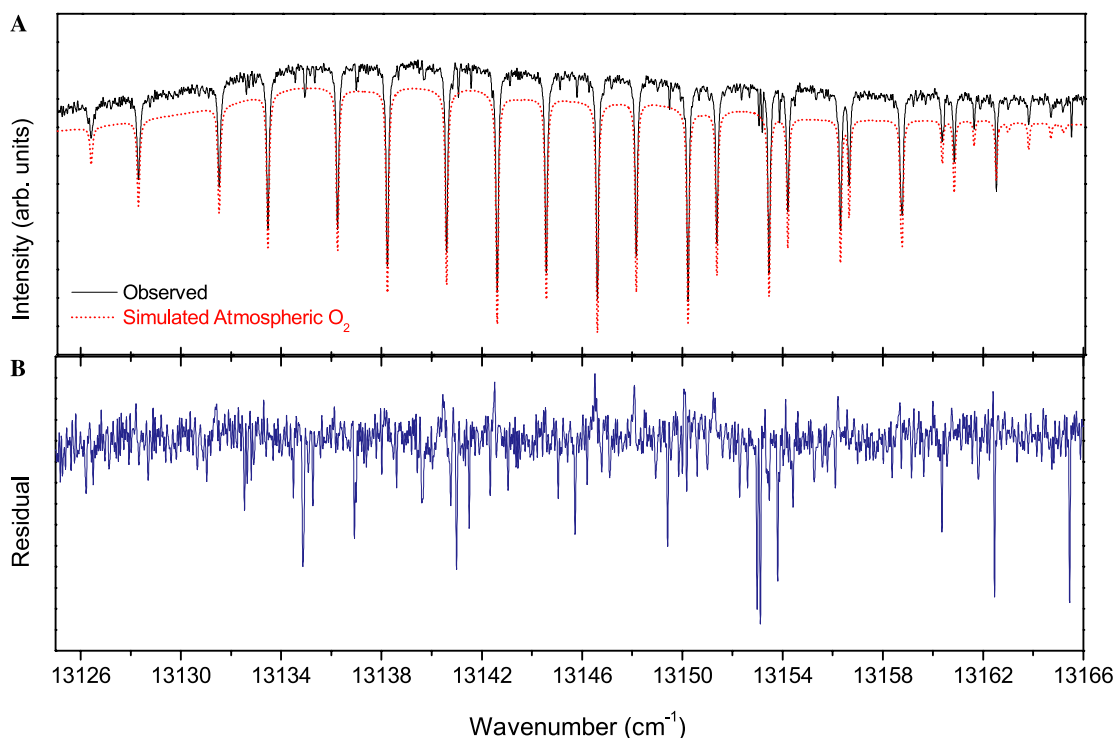


Fig. 3. Removal of the O₂ atmospheric absorption. (A) Experimental spectrum (plain line) and atmospheric O₂ simulated spectrum (dashed line). (B) Residual obtained after the removal of the O₂ contribution.

Table 2 summarizes the results by giving for each vibrational band, the number of observed transitions, the wavenumber limits, the absorption cross-section limits (minima–maxima) and also the band integrated cross-section.

3.4. Error analysis

The possible sources of experimental errors, both systematic and statistic on the derived parameters can be identified as following:

- Systematic uncertainties on the temperature, total pressure in the cell, and on the path length were estimated to be 1, 1, and 0.5%, respectively.
- The error on the partial pressure of HDO was derived by propagating these errors in the determination of the partial pressure. Considering a relative error of 1.8% on the equilibrium constant K_{eq} (Eq. 1), and a 5% uncertainty on the determination of the H₂O partial pressure based on the use of the BR line list [15], the uncertainty on the HDO partial pressure has been estimated to be of the order of 2%.
- From Eq. (2), the systematic error on the cross-sections is estimated to be 4.5%.
- The systematic contribution to the uncertainties on both pressure parameters (γ_{N_2} and δ_{N_2}) has been estimated to be 1%.

- A statistic uncertainty resulting from the fitting procedures (Wspectra and regression analysis) was also taken into account. The 3σ values were considered for each fitted parameter and are mentioned in the complete list of the HDO line parameters obtained in this work. Note that, contrary to the systematic uncertainty affecting all lines in the same way, the statistical uncertainty is different from line to line and generally, is larger for weak or blended lines than for the strong and well isolated lines. For the absorption cross-sections, the statistic uncertainty is of the same order of magnitude as the systematic uncertainty. In the case of the pressure-induced parameters (γ_{N_2} and δ_{N_2}), the statistic uncertainty is the dominant contribution to the overall uncertainty.

4. Discussion

A total of 3256 HDO lines, involving 13 upper vibrational states, have been identified. Their position and absorption cross-section are compiled in a list available on our website <http://www.ulb.ac.be/cpm>. The N₂-induced broadening and shifting parameters (γ_{N_2} and δ_{N_2} in cm⁻¹ atm⁻¹) are given whenever possible. It is worth pointing out that among the identified lines, 47 are unresolved doublets, 181 are superimposed to H₂¹⁶O lines

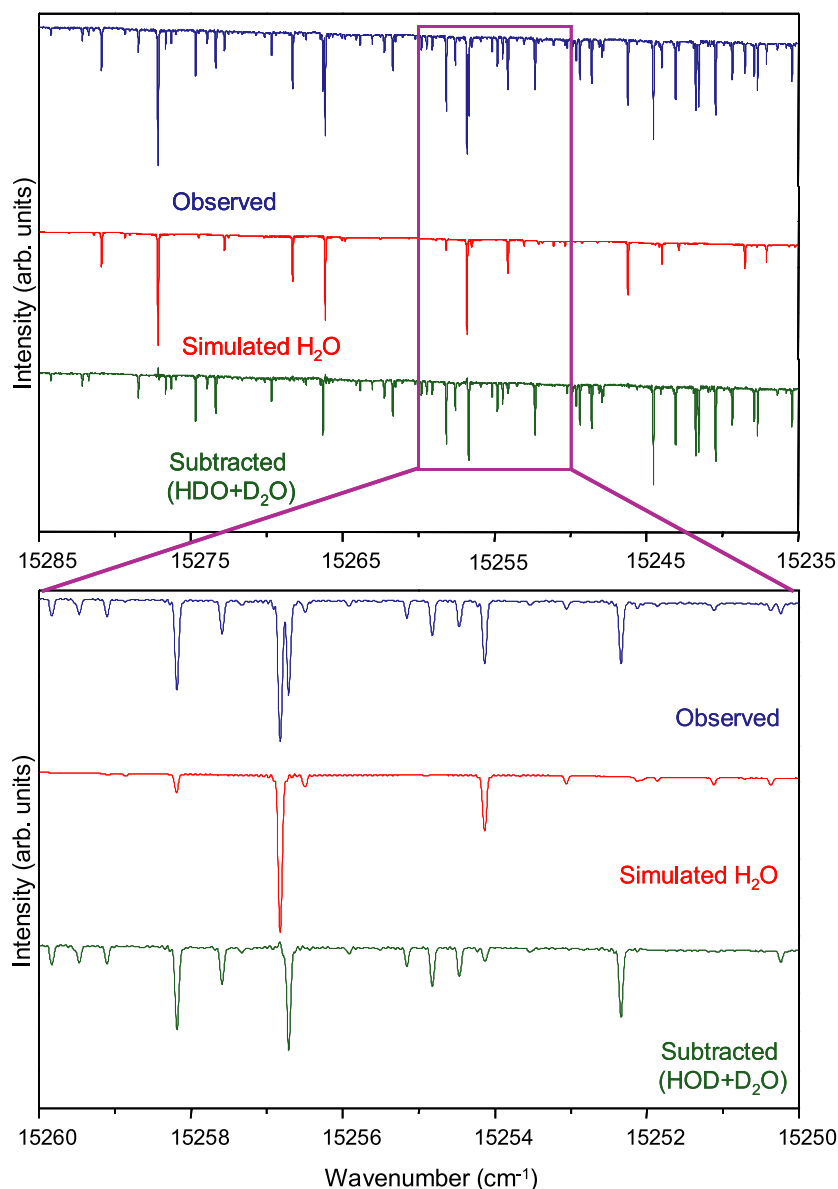


Fig. 4. Removal of the lines of H_2O present in the cell. The bottom panel shows an expanded portion of the spectral interval presented in the top panel. In each case, the top curve represents the experimental spectrum after removal of the atmospheric contributions of H_2O and O_2 ; the middle curve is the simulated H_2O contribution to the absorption in the cell; and finally, the bottom curve is the remaining spectrum, with contributions of only HDO and D_2O (but no D_2O lines are observed in this region).

($|\tilde{\nu}_{\text{HDO}} - \tilde{\nu}_{\text{H}_2\text{O}}| \leq 0.03 \text{ cm}^{-1}$) and 236 are blended by H_2^{16}O lines $0.03 < |\tilde{\nu}_{\text{HDO}} - \tilde{\nu}_{\text{H}_2\text{O}}| \leq 0.07 \text{ cm}^{-1}$. For these latter, the absorption cross-sections are likely less reliable due to an additional error introduced during the removal procedure. These lines are consequently flagged in the list. No saturated lines were observed in our spectra.

4.1. Line positions

In the $11\,500\text{--}12\,300 \text{ cm}^{-1}$ range, the line positions belonging to the $\nu_2 + 3\nu_3$ band can be compared to the Fourier transform spectroscopy data of Naumenko

et al. [8]. The positions of 274 common lines agree within 0.004 cm^{-1} on average, and the wavenumber difference never exceeds 0.025 cm^{-1} .

In the $13\,165\text{--}18\,350 \text{ cm}^{-1}$ range, the line positions can be compared to the data obtained by the ICLAS technique [3,4,9–13]. The agreement with their calibrated wavenumbers was found to be 0.003 cm^{-1} on average for the 1719 common lines, but the calculated maximum wavenumber difference is about twice the one obtained for the $\nu_2 + 3\nu_3$ band. The agreement worsens somewhat (0.008 cm^{-1}) for the $\nu_1 + 3\nu_3$ and $2\nu_2 + 3\nu_3$ bands around $13\,260 \text{ cm}^{-1}$ and the $\nu_2 + 5\nu_3$

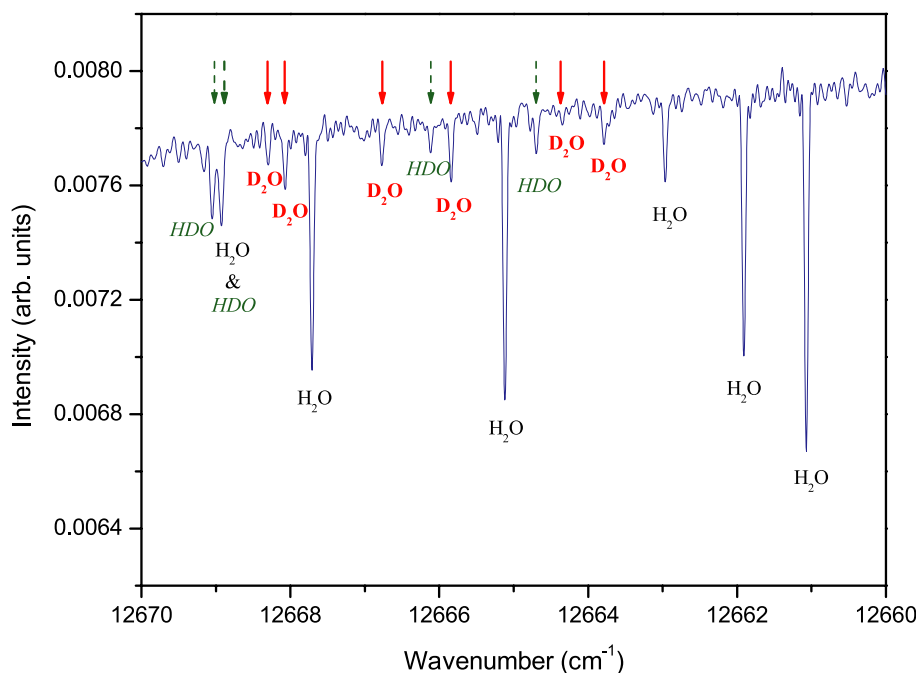


Fig. 5. Part of spectrum showing the D₂O lines, identified according to their relative intensities in relation to spectrum G.

Table 2
Summary of results

Band	Nbr of lines	ν_{\min} (cm ⁻¹)	ν_{\max} (cm ⁻¹)	$S_{\sigma_{\min}}$ (cm molecule ⁻¹)	$S_{\sigma_{\max}}$ (cm molecule ⁻¹)	$S_{\sigma_{\text{int}}}$ (cm molecule ⁻¹)	Nbr of γ_{N_2}	Nbr of δ_{N_2}
$\nu_2 + 3\nu_3$	399	11 749	12 196	2.25×10^{-26}	1.64×10^{-23}	8.34×10^{-22}	213	230
$5\nu_1$	90	12 594	12 845	3.06×10^{-26}	3.66×10^{-25}	9.81×10^{-24}	1	6
$\nu_1 + 3\nu_3$	470	13 017	13 483	1.01×10^{-26}	6.35×10^{-25}	4.95×10^{-23}	120	193
$2\nu_2 + 3\nu_3$								
$4\nu_3$	659	13 500	14 216	6.88×10^{-27}	1.30×10^{-23}	7.89×10^{-22}	445	473
Not assigned	54	14 579	14 768	5.77×10^{-27}	4.13×10^{-26}	8.45×10^{-25}	0	0
$\nu_2 + 4\nu_3$	505	14 916	15 386	3.30×10^{-27}	1.55×10^{-24}	6.09×10^{-23}	232	282
$6\nu_1$								
$\nu_1 + 4\nu_3$	177	16 301	16 605	3.82×10^{-27}	1.15×10^{-25}	4.63×10^{-24}	79	104
$2\nu_2 + 4\nu_3$								
$5\nu_3$	388	16 622	17 163	2.62×10^{-27}	2.36×10^{-24}	8.29×10^{-23}	244	282
$\nu_2 + 5\nu_3$	165	18 010	18 340	3.53×10^{-27}	1.41×10^{-25}	6.30×10^{-24}	88	110
$6\nu_3$	226	19 372	19 967	2.41×10^{-27}	2.38×10^{-25}	1.14×10^{-23}	102	131
$7\nu_3$	123	22 328	22 736	2.63×10^{-27}	2.86×10^{-26}	1.54×10^{-24}	0	0

For each band, ν_{\min} , ν_{\max} , refer to the minimum and maximum wavenumber, $S_{\sigma_{\min}}$, $S_{\sigma_{\max}}$ to the minimum and maximum line integrated absorption cross-section. $S_{\sigma_{\text{int}}}$ is the band integrated absorption cross section. γ_{N_2} and δ_{N_2} are the Nitrogen-broadening and Nitrogen-induced frequency shift, respectively.

band around 18 220 cm⁻¹. The data from Bykov et al. [6] covering the $5\nu_3$ band region around 16 920 cm⁻¹ are not included in this comparison, since Bertseva et al. [9] confirm and significantly extend the older dataset. A total of 2495 transitions belonging to HDO, including 291 unresolved doublet lines, have been measured by ICLAS. Among these, 125 transitions (64 of them are unresolved doublet lines) are not observed in our spectra because they are too weak to be detected under our experimental conditions ($\sim 2.0 \times 10^{-27}$ cm per

molecule). Some 597 HDO lines, which are overlapped by strong H₂O lines, are observed in the present work but not reported by these authors.

In the region above 18 350 cm⁻¹, the $6\nu_3$ and $7\nu_3$ bands were rotationally analyzed in our previous work [7]. This work reports the position of 63 and 30 lines for the $6\nu_3$ and $7\nu_3$ bands respectively, compared to 226 and 123 lines in the present work. The wavenumbers of the 93 common lines agree to 0.002 cm⁻¹ on average.

4.2. Absorption cross-sections

Absorption cross-sections were determined for all observed transitions from the spectra containing only the HDO signature and using Eq. (2). They range from 2.41×10^{-27} to 1.64×10^{-23} cm molecule $^{-1}$, most of them being lower than 2.0×10^{-25} cm molecule $^{-1}$. For some 300 well defined and unblended lines, absorption cross-sections measured from the N₂-diluted spectra agree to within 3% with those measured from the un-diluted spectra. This percentage gives an estimate of the reproducibility of our measurements with respect to this parameter. The integrated absorption cross-section measured within each band is given in Table 2.

As far as we are aware of, there have been no previous measurements of HDO cross-sections in the spectral interval investigated in this work. The present results can, however, be compared with those derived from the ab initio calculations of Schwenke and Partridge [14] (Fig. 6). Except for several lines, laying in majority below 16000 cm $^{-1}$, the agreement between measured and calculated values is generally better than 25%, and mean and median ratios are close to 1.0. A slight tendency of the measurements to overestimate the absorption cross-section is observed for the two bands below 14000 cm $^{-1}$ and the contrary is noticed for the band located around 15000 cm $^{-1}$ (Fig. 6).

4.3. Nitrogen-broadening coefficients and nitrogen frequency shifts

Nitrogen-induced broadenings and shifts have been obtained for most of the HDO lines reported in this

work. These parameters were determined from the four N₂-diluted spectra (C to F in Table 1) and by solving Eqs. (3) and (4) using a general least-squares fit. The statistical uncertainties on these parameters correspond to the RMS values resulting from the least-squares fits. Fig. 7 presents the values of the N₂-broadening coefficient, γ_{N_2} (a) and the N₂-induced frequency shift, δ_{N_2} (b) over the whole spectral range investigated. No analysis of the rotational dependence of the pressure broadening and pressure shift parameters has been attempted in this work. However, we have observed a slight vibrational dependence of these parameters for isolated overtone bands nv_3 ($n = 4-6$). The mean measured values of γ_{N_2} are 0.093, 0.101, and 0.102 cm $^{-1}$ atm $^{-1}$ for the $4v_3$, $5v_3$, and $6v_3$, respectively and those for δ_{N_2} are -0.018 , -0.022 , and -0.023 cm $^{-1}$ atm $^{-1}$, respectively.

5. Conclusion

A new set of HDO line parameters is provided for the spectral region 11 500–23 000 cm $^{-1}$. These data were obtained by recording high-resolution Fourier transform spectra of H₂O/HDO/D₂O mixtures and by using a multiple reflection cell that allows long absorption paths. Spectra of Nitrogen-diluted mixtures were also recorded at different total pressures (155–787 hPa). The original procedure consisting of removing the H₂O interfering lines and identifying the confined D₂O lines are necessary steps prior to the HDO lines investigation. A total of 3256 HDO lines have been identified and fitted. Their positions, absorption cross-sections, and N₂-broadening

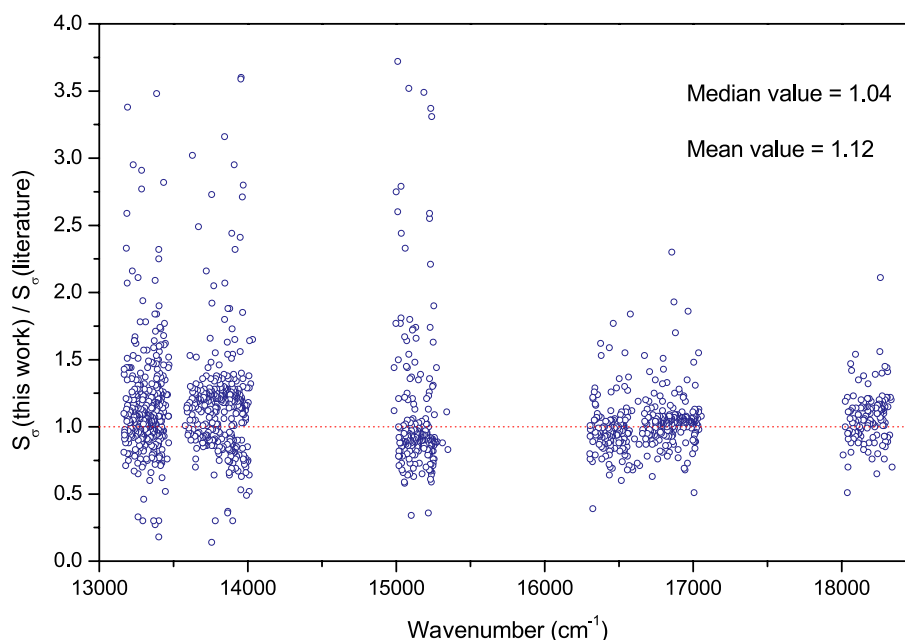


Fig. 6. Comparison of the absorption cross-section measured in this work with the data of [14].

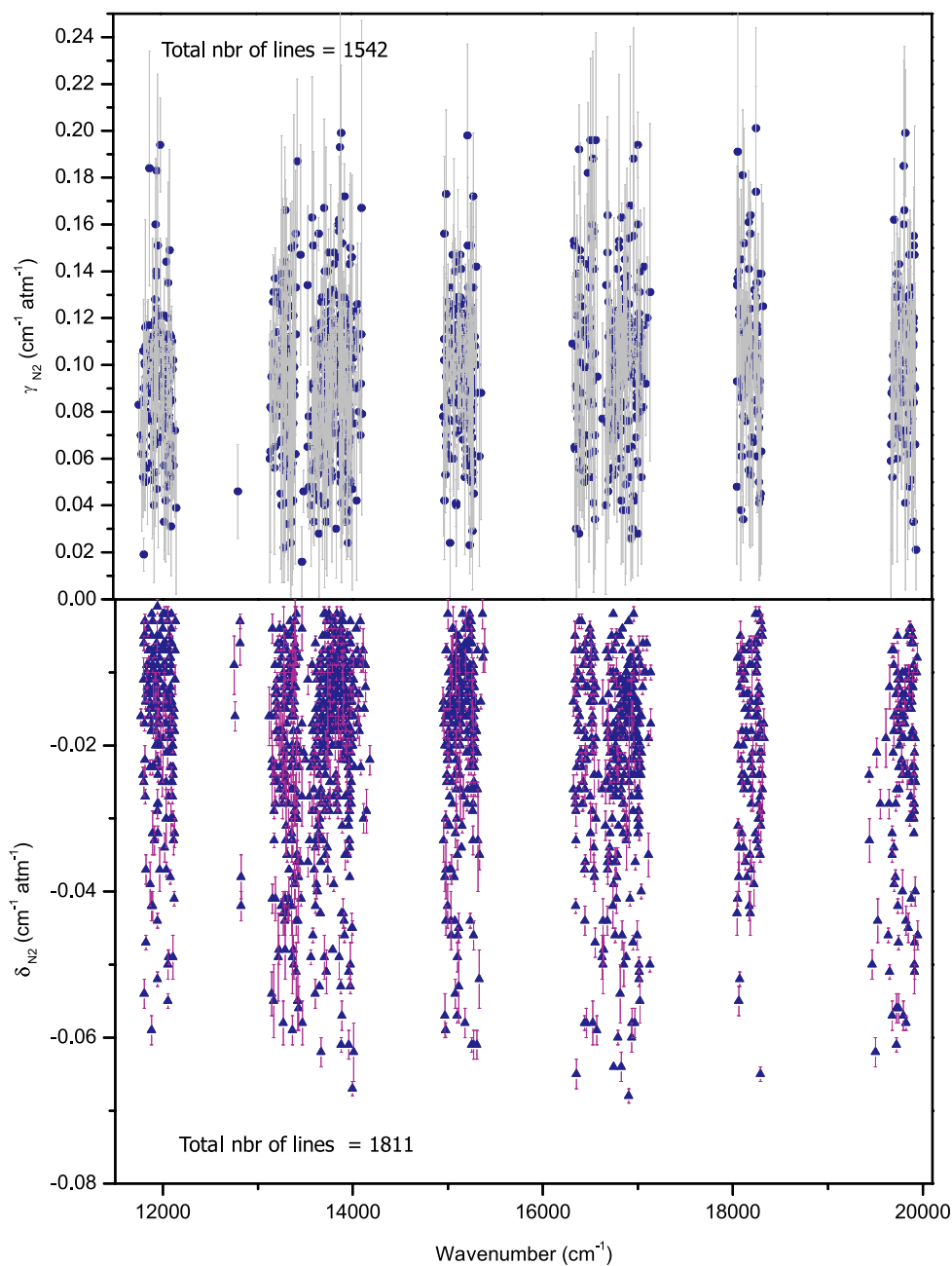


Fig. 7. Overview of the measured N₂-broadening coefficients (top) and the N₂-induced frequency shifts (bottom) of HDO over the spectral region investigated.

and frequency shift coefficients have been determined for the first time. Thirteen bands were observed and identified in the spectral region under investigation. For about 2000 lines in common with previous ICLAS and FTS studies, the calibrated line positions agree to better than $8 \times 10^{-3} \text{ cm}^{-1}$. Absorption cross-sections show a reasonably good agreement with the most recent ab initio calculations. The present study leads to a significant improvement in the spectroscopic parameters of HDO lines, especially in the visible spectral region.

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Appendix A. Supplementary data

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://msa.lib.ohio-state.edu/jmsa_hp.htm).

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