Line parameters for CO₂ broadening in the ν_2 band of HD¹⁶O

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Abstract

CO₂-rich planetary atmospheres such as those of Mars and Venus require accurate knowledge of CO₂ broadened HDO half-width coefficients and their temperature dependence exponents for reliable abundance determination. Although a few calculated line lists have recently been published on HDO-CO₂ line shapes and their temperature dependences, laboratory measurements of those parameters are thus far non-existent. In this work, we report the first measurements of CO₂-broadened half-width and pressure-shift coefficients and their temperature dependences for over 220 transitions in the ν_2 band. Self-broadened half-width and self-shift coefficients at room temperature are also obtained for majority of these transitions. In addition, the first experimental determination of collisional line mixing has been reported for 11 transition pairs for HDO-CO₂ and HDO-HDO systems. These results were obtained by analyzing ten high-resolution spectra of HDO and HDO-CO₂ mixtures at various sample temperatures and pressures recorded with the Bruker IFS-125 HR Fourier transform spectrometer at the Jet Propulsion Laboratory (JPL). Two coolable absorption cells with path lengths of 20.38 cm and 20.941 m were used to record the spectra. The various line parameters were retrieved by fitting all ten spectra simultaneously using a multispectrum nonlinear least squares fitting algorithm.

The ν_2 and $2\nu_2-\nu_2$ transitions in the 1100–4100 cm⁻¹ region were extracted from the HITRAN2012 database giving 2245 and 435 transitions, respectively. Modified Complex Robert-Bonamy formalism (MCRB) calculations were made for the half-width coefficients, their temperature dependence and the pressure shift coefficients for the HDO–CO₂ and HDO–HDO collision systems. MCRB calculations are compared with the measured values.

1. Introduction

Planetary atmospheres are characterized through spectroscopic observations to derive their chemical compositions, temperatures, and pressures (e.g. see Ref. [1]). Measurements of CO₂-broadened HDO half-width coefficients and their temperature exponents are important for atmospheric remote sensing of Mars, because (a) HDO has been observed to be greatly enhanced in Mars atmosphere (~ 5 times larger than the earth's atmosphere), (b) accurate measurements of HDO abundance is critical to the analysis of Mars climate models, (c) broadening by CO₂ is important due to Mars low temperature where Lorentz broadening becomes dominant over Doppler broadening, (d) currently, no systematic high precision laboratory measurements are available and no temperature dependence of CO₂-broadened half-width coefficients are available covering Mars temperature, (e) theoretical calculations should be validated against measurements and, (f) when both accurate experimental measurements and theoretical calculations are combined, an extensive line list of accurate line parameters can be compiled for application to Mars spectroscopy. For Mars, spectroscopy of H₂O and HDO is essential because D/H ratio is obtained by retrieving the abundances of these two species [2-5]. Recently, Villanueva et al. [6] have given details about Mars atmosphere showing maps of water isotopologues, H₂O and HDO across the Martian globe, from a number of observations obtained with high resolution spectrometers at various ground-based observatories. These maps address the fundamental unknowns such as the current representative D/H ratio in Mars that may provide insight into Mars climate evolution.

The Martian atmosphere is 95% CO₂ at low temperature so that reliable CO₂-broadened half-width coefficients (HDO-CO₂) and their temperature dependence exponents must be applied in analyzing the observed spectra by various NASA missions and other observations, such as, Mars Climate Sounder, Mars Science Laboratory (MSL) and its curiosity rover, Global surveyor, Odyssey, Express, and Reconnaissance Orbiter [7, 8] along with *in situ* devices carried out by Viking, Pathfinder, and the rovers, Spirit and Opportunity, MAVEN (Mars Atmosphere and Volatile EvolutionN) and future Mars 2020 missions.

Despite the low Martian atmosphere surface pressure and temperature (~ 10 mb and ~ 150 - 300 K), past high-resolution measurements obtained with ground-based observations (with TEXES and NIRSPEC) and from orbit (SOIR) have confirmed that pressure broadening of HDO by CO_2 is required to properly interpret atmospheric remote sensing data. Although water vapor (H_2O and HDO) spectroscopy for line positions, intensities and lower state energies are generally well determined up to 4200 cm^{-1} , the knowledge of pressure broadening by CO_2 is “the Achilles heel” in obtaining the Mars D/H ratio.

The measurements of half-width coefficients and their temperature dependence exponents of HDO transitions broadened by CO_2 are important especially in the fundamental bands since HDO transitions in the ν_2 and ν_1 bands have been observed and identified in Mars data [2, 5, 6]. Transitions belonging to the ν_3 band were selected for the TLS (Tunable Laser Spectrometer) instrument led by Webster and Mahaffy at JPL [9] for the MSL (Mars Science Laboratory) mission. The ν_1 lines observed by Villanueva et al. [5] required accurate information on the HDO- CO_2 half-width coefficients and their temperature dependence exponents, the laboratory measurements of which are not available until the present study.

Measurements of room temperature CO_2 -broadened H_2O transitions were reported in 1970 for transitions in the pure rotation band [10] and in 1971 for transitions in the ν_2 band [11]. In 2007, Brown *et al.* [12] reported measurements for several hundred transitions in the pure rotation and ν_2 fundamental regions. Sagawa *et al.* [13] in 2008 reported measurements of room temperature CO_2 -broadened H_2O half-widths for 32 rotation band transitions and in 2009, Dick *et al.* [14] reported CO_2 pressure broadening of the $1_{10} \leftarrow 1_{01}$ transition of water from 17 to 200 K. Until now, no other laboratory measurements of CO_2 broadening of H_2O or HDO are available. Astronomers trying to interpret Mars atmospheric data remotely, rely upon un-validated quantum mechanical predictions of the temperature dependences of pressure broadening for H_2O and HDO that have an uncertainty 20% or greater. Moreover, some of those theoretical predictions indicate that many broadening coefficients may be in error by as much as 40% (and even more for their temperature dependence). Hence accurate knowledge of CO_2 -broadened HDO half-width coefficients and their temperature-dependence exponents are critical for astronomers to properly interpret Mars atmospheric data to determine reliable D/H ratios. Ideally, combined

measurements of HDO and H₂O abundances are the best means to obtain Mars atmospheric D/H ratios. Significant systematic inaccuracies in the knowledge of HDO-CO₂ widths and their temperature dependences can adversely affect the retrievals of the D/H ratio.

In an effort to reduce such errors in abundance determinations, Gamache et al. [15] developed a calculated line list of half-widths, their temperature dependence, and line shifts for both H₂O-CO₂ and HDO-CO₂ collision systems for application to CO₂-rich planetary atmospheres (e.g., Mars and Venus). These authors applied the semi-classical complex Robert-Bonamy (CRB) formalism [16] to determine the line-shape parameters for the HDO-CO₂ and H₂O-CO₂ collision systems. In 2014, Lavrentieva et al. [17] took the *ab initio* HDO database of Voronin et al. [18] (positions, intensities, and lower state energies) for the spectral region 0.00065-25660 cm⁻¹ and made semi-empirical calculations of HDO broadened by CO₂ line parameters for application to the atmospheres of Mars and Venus. Recently, Gamache et al. [19] have published a calculated line list for seven isotopologues of water vapor transitions in the 1100-4100 cm⁻¹ region for application to CO₂-rich planetary atmospheres.

As an example, the potential effects of incorrect half-widths on the retrieved HDO column densities are shown in **Fig.1**, where the curve of growth (integrated line area vs. column density) for a strong (optically thick) HDO transition in the ν_2 band is plotted. In the example shown, using the HDO-CO₂ half-width (**blue curve**) coefficient from this work vs. the air-width from HITRAN (**red curve**) and 1.8×air-width, generally used by researchers as a proxy to HDO-CO₂ width (**dotted green curve**) would cause an error of about +61% in the retrieved column abundance. Also included in **Fig. 1** is the curve of growth corresponding to the MCRB calculated [PS] CO₂-broadened half-width coefficient (**solid green curve**). It is clear that the HDO-CO₂ half-width coefficient measured in this study is very close to the calculated half-width coefficient using the MCRB formalism [PS]. However, the ratio 1.8 used as an example here is dependent upon the particular transition studied (e.g. see Refs. [5, 12, 20-28] for the different ratios used in the literature). Similarly, one can show the effects of using wrong temperature dependence exponents for the half-width coefficients in the retrieved column abundances.

Insert Fig. 1 here

The multispectrum nonlinear least squares fitting algorithm used in this study requires an initial line list of spectral line parameters for starting the analysis. For this, line shape parameters including the new CO₂ broadening were adopted from Ref. [19] while the positions and intensities of H₂O and HDO were taken from HITRAN2012 [29]. For the D₂O transitions, their positions were computed based on the MARVEL energy levels and, their line intensities were computed based on multiple sources including *ab initio* values along with new calculations for CO₂ broadening reported in [19].

In the present high-resolution FTIR laboratory study, we have measured HDO-CO₂ half-width and pressure shift coefficients and their temperature dependences. Over 250 HDO transitions in the ν_2 band region (not all line parameters could be determined for all transitions) that are fairly separated from other strong absorption features of H₂O and D₂O were measured. Since transitions from all three species (H₂O, HDO and D₂O) appear in almost all wavenumber regions, the spectral regions where most of the strong transitions belong to HDO were selected prior to starting the least squares fitting. This procedure of selecting spectral intervals where majority of transitions are from HDO for line shape measurements eliminated most of the strong H₂O and D₂O lines from the fitted intervals. This selective choice, however, limited the number of spectral intervals where broadening of individual HDO lines could be measured. In this study, we recorded several high resolution, high S/N ratio spectra in the 2.7 to 7 μm region (covering the ν_1 , ν_2 and ν_3 regions) using different mixtures of CO₂ in HDO with total gas mixture pressures in the 0.043-0.41 atm range and at temperatures between ~ 230 and 296 K using the Bruker IFS-125HR at JPL and two temperature-controlled gas absorption cells; one short path (20.38 cm) straight cell for the temperature range 296-250 K and the other, a long path multipass (~ 21 m) Herriott cell to reach ~ 230 K. Although the effective vapor pressure of HDO at 230 K was very low (~ 0.0001 atm) we were able to measure line parameters for several strong transitions because of the long path length of the Herriott cell.

A brief summary of line parameters (e.g. line positions, intensities and broadening) available in the mid- and near infrared regions for HDO reported in the literature, measured or theoretically

calculated (extending to very large wavenumber region), are summarized in **Table 1**. For comparison, parameters from present measurements are listed at the top of **Table 1**.

Insert Table 1 here (summary of reported line parameters)

Table 1

A brief summary of published line parameters in the fundamental bands of HDO^a: Measurements and calculations.

Ref.	Author/band/spectral range	Isotopologue	Perturbing gas	Parameter reported	Meas./Calc.
This study ^b	Devi et al. ν_2 and $2\nu_2, \nu_2$ (1236-1492 cm^{-1})	HD ¹⁶ O	Self, CO ₂	Widths, shifts, T-dep. widths & shifts	JPL Bruker 125HR FTS; MCRB calc.
[30]	Toth et al. ν_1 and $2\nu_2$ (2400-3300 cm^{-1})	HDO	none	Positions and intensities	Kitt Peak FTS
[31]	Toth & Brault. $\nu_3, \nu_1+\nu_2$ & $3\nu_2$ (3250-4370 cm^{-1})	HDO	none	Positions and intensities	Kitt Peak FTS
[32]	Devi et al. ν_2 (1260-1360 cm^{-1})	HDO, H ₂ ¹⁶ O, HD ¹⁸ O	Air, N ₂	Widths	TDL
[33]	Rinsland et al. ν_2 (1176-1640 cm^{-1})	HD ¹⁶ O	Air, N ₂ , O ₂	Widths and shifts (over 200 lines)	FTS
[34]	Rinsland et al. ν_1 (2576-2726 cm^{-1})	HD ¹⁶ O, D ₂ O	Air, N ₂ , O ₂	Widths and shifts (48 lines)	FTS
[35]	Toth; ν_2 (969-1892 cm^{-1})	HD ¹⁶ O, HD ¹⁷ O, HD ¹⁸ O	none	Positions and intensities	Kitt Peak FTS
[36]	Toth; several bands (600-3100 cm^{-1})	HD ¹⁶ O, HD ¹⁷ O, HD ¹⁸ O	none	Positions and intensities	Kitt Peak FTS
[37]	Toth; ν_2 & $2\nu_2, \nu_2$ (700–2000 cm^{-1})	HD ¹⁶ O, HD ¹⁸ O, D ₂ O	Air, N ₂	Widths and shifts	Kitt Peak FTS
[38]	Gamache and Fischer	H ₂ ¹⁶ O, H ₂ ¹⁸ O, H ₂ ¹⁷ O, HD ¹⁶ O, D ₂ ¹⁶ O	N ₂ , O ₂	Widths	CRB
[39]	Tennyson et al. (various)	HD ¹⁶ O, HD ¹⁷ O, HD ¹⁸ O		Energy levels and positions	MARVEL procedure
[15]	Gamache et al. (2250-4450 cm^{-1})	HD ¹⁶ O	CO ₂	Width, shifts, T-dep. of widths	CRB
[18]	Voronin et al. (range up to 25000 cm^{-1} and J=50)	HDO	None	Positions and intensities	Ab initio (VTT) database with 700 million transitions
[40]	Voronin et al. (range up to	HD ¹⁶ O	Self, air	Widths and T-	Semi-empirical

	25000 cm ⁻¹ and for J<51)			dep. of air widths	calculations
[5]	Villanueva et al.	H ₂ O and HDO transmittance & Fluorescence model	None	none	Database with theory & empirical lists (500-700 million lines)
[17]	Lavrentieva et al. (0.000065-25660 cm ⁻¹)	HD ¹⁶ O	Self, air and CO ₂	Widths and T-dep. Widths	Variational VTT line list (420000 lines)
[19]	Gamache et al. (1100-4100 cm ⁻¹)	H ₂ ¹⁶ O, H ₂ ¹⁸ O, H ₂ ¹⁷ O, HD ¹⁶ O, HD ¹⁷ O, HD ¹⁸ O, D ₂ ¹⁶ O	Self- and CO ₂	Width, shifts, T-dep. of widths	MCRB

^a Measurements are limited to spectral regions of the ν_1 , ν_2 and ν_3 bands.

^b Line mixing via off-diagonal relaxation matrix formalism and quadratic speed dependence parameters are also measured, where applicable. Data were obtained for all 3 regions of the fundamental bands ν_1 , ν_2 and ν_3 of HDO. The analyzed results for the ν_1 and ν_3 bands will be reported in a forth coming article.

Some nomenclature:

FTS = Fourier transform spectrometer.

TDL = Tunable Diode Laser.

CRB = Complex Robert-Bonamy formalism.

MARVEL = Measured Active Rotational-Vibrational Energy Levels.

MCRB = Modified Complex Robert-Bonamy formalism.

VTT = Veronin, Tennyson, Tolchenov

2. Experimental details

2.1. Experimental setup

High-resolution absorption spectra of H₂O, D₂O and HDO were recorded using the Bruker IFS-125HR Fourier transform spectrometer at the JPL. The spectral resolutions were chosen to be between 0.0032 and 0.0056 cm⁻¹ range depending on the sample conditions and absorption path length. Two custom-built coolable absorption cells were used to keep the sample gases. The sample cells used in the experiment were a 20.38 cm straight path cell [41] and a multipass Herriott cell with a fixed total path length of 20.941 m [42] with a base path length of ~37.5 cm. The cells' construction and performance details are given in Refs. [41, 42]. Details of the general experimental setup are given in **Table 2**.

Insert **Table 2** here (experimental setup)

As seen in **Table 2**, the experimental setup consisted of a Globar as the radiation source, a KBr beam splitter and, a HgCdTe detector for use in the ν_2 spectral region. The effective spectral band pass was limited to 950-1550 cm^{-1} . The aperture size varied from 1.3-2 mm, depending upon the S/N ratios and the cell path lengths. The HDO sample pressures were in the range of 1.83 to 6.94 Torr while the total pressures of HDO+CO₂ varied from 33 to 314 Torr. Except for the one spectrum at 230 K recorded with the multipass Herriott cell for which the S/N ratio was very low (~ 80), all other spectra obtained with the 20.38 cm coolable cell had S/N ratios in the 1000-1500 range.

2.2. Sample preparation and summary of physical conditions of spectra

Pure HDO is not commercially available due to rapid isotopologue exchange reaction, and hence HDO samples were prepared in the laboratory by mixing known quantities of H₂O and D₂O. To maximize the HDO production, a 50%-50% mixture of distilled H₂O and D₂O (99% pure) were prepared resulting in the following approximate fractional amounts of the 3 isotopologues:

Initially, individual spectra of H₂O, D₂O and HDO (a mixture of H₂O, D₂O and HDO) samples were recorded to identify HDO features. For this, three cylindrical glass tubes (~ 15 cm tall and about 5 cm in diameter) each containing one of the three liquid samples and provided with separate vacuum tight valves were attached to the experimental setup. The three samples were connected by appropriate glass/stainless steel bellows to the entire setup such that any one of the 3 samples could be chosen for recording its spectrum. The entire FTS system including the gas absorption cell, the FTS chamber and the sample lines were pumped thoroughly. Next, each water sample (H₂O, HDO and D₂O) was purified removing air, CO₂ and other trace impurities by a repeated freeze-thaw-pump process. This procedure of freeze-thaw-pump was repeated each time a new sample gas was introduced into the absorption cell. The valve was slowly opened to release known amounts of the gaseous sample into the absorption cell, the pressure of which was monitored continually by appropriate pressure gauge read outs. For the CO₂ broadening of HDO, a 99.98% ¹²C-enriched sample of CO₂ without further purification was used. After recording the required pure sample spectra of the HDO mixtures, CO₂ broadened spectra were recorded for

which appropriate amounts of CO₂ were added to the sample cell. CO₂ broadened data were not obtained with pure H₂O and therefore only HDO and, CO₂ broadened HDO spectra were obtained for analysis.

Spectral lines of H₂O and D₂O are ubiquitous, and hence the number of features in the HDO spectra was very dense and complex. Spectra of pure H₂O and D₂O were useful to identify the HDO transitions and to choose spectral intervals with mostly HDO transitions for pressure-broadening measurements. A careful selection of specific spectral intervals prior to starting the least squares fittings was therefore made to perform the fittings of HDO-CO₂ half-width and pressure-shift coefficients. In the CO₂ broadened HDO spectra, absorption features for example, of H₂¹⁶O, HD¹⁸O, D₂O and CO₂ were also observed, complicating the analysis, especially in the ν_3 region of HDO. The details will be discussed in a forthcoming paper reporting the measurements of the ν_1 and ν_3 bands. A summary of the gas sample conditions of the HDO and HDO-CO₂ spectra in the ν_2 band is listed in **Table 3**.

Insert **Table 3** here (Summary of gas sample conditions)

A total of 10 spectra, three with only HDO mixture (containing H₂O, HDO and D₂O) and the remaining seven with HDO broadened by CO₂, at different temperatures, pressures and volume mixing ratios of HDO were recorded. The maximum amount of HDO in the sample is 0.5 (**Eq. 1**) of the total pressure, since for the 50%-50% mixture of H₂O and D₂O, the amounts of H₂O, HDO and D₂O were estimated to be 0.25, 0.5 and 0.25, respectively (**Eq. 1**). In addition to this fractional amount of HDO, one has to determine the individual abundances of the various isotopologues (e.g., H₂¹⁶O, H₂¹⁸O, H₂¹⁷O, HD¹⁶O, HD¹⁸O, D₂¹⁶O and D₂¹⁸O) present in the HDO sample. To calculate the abundances of the various isotopologues in the HDO sample, we used the isotopologue enhancement factors available in HITRAN2012 [29]. In determining the absolute intensities of HDO transitions, these two quantities (HDO fractional amount in the sample as well as the isotopologue abundance of HD¹⁶O in each gas mixture) were determined spectroscopically (from retrieved line intensity) in each fitted spectrum. Initial amounts of the isotopologue abundances from HITRAN2012 database were assumed. Although the fitted spectral regions were selected based upon the presence of well-separated HDO lines, it was not

always possible to avoid the presence of H_2^{16}O , H_2^{18}O , D_2^{16}O , HD^{18}O lines completely in the selected spectral regions. The relative abundances of the various isotopologues were determined initially from fitting a few spectral intervals, and (once determined for each spectrum) the same sets of volume mixing ratios and isotopologue abundances were used to fit the other selected spectral regions. Although a number of H_2^{16}O , H_2^{18}O and D_2^{16}O features that appeared in several of our fitted regions were also measured to minimize the fit residuals, the majority of those transitions were weak and hence not reported in the final list of measurements.

The path lengths of the 20.38 cm and the 20.941 m cells are known to 0.01 and 0.03% uncertainty [41, 42]. Total sample pressures were continually measured and monitored throughout the data acquisition period using a 10 Torr and a 1000 Torr calibrated pressure gauges ($\pm 0.05\%$ of full-scale reading). The sample gas temperatures are known to $\pm 0.02\text{--}0.2$ K [41, 42] and were monitored throughout the data-taking period using recommended calibration factors provided by the manufacturers for the temperature sensors.

The calibration of the wavenumber scales of the spectra were performed relative to positions of the ν_2 lines of water vapor [43]. These lines appeared in the empty cell scans as residual absorption features arising from the “evacuated” FTS chamber. Empty cell scans were taken periodically not only for wavenumber calibration of spectra but also to obtain ratio spectra that were used in the analysis.

To illustrate the quality of the spectra analyzed, compressed plots of the ν_2 band of HDO are shown in **Fig. 2**. The graphs in panels (a)-(c) correspond to the spectrum of HDO at 296 K, HDO+CO₂ at 296 K and HDO+CO₂ at 271.3 K, respectively. For the one spectrum at 230 K recorded with the multipass Herriott cell (**Table 3**) for which an unratiod spectra was used, ratio spectra were used for the remaining nine spectra recorded for this band. Nine of the ten spectra used in the fittings were apodized using the apodization function (A) defined in Bell [44]. The function used is defined as:

$$A = 1 - PP_{max} 22 \quad (2)$$

In Eq. (2), P_{max} is the maximum optical path difference and P is the distance from the center of the interferogram. No channel spectra were observed in the data. It may be noted that the apodization will reduce the spectral resolution slightly (compared to the unapodized resolution listed in Table 2) and for the present measurements it did not affect the quality of the retrieved line parameters.

Insert Fig. 2 here

3. Multispectrum fitting technique

3.1. General description of analysis

The various spectral line parameters were retrieved from the experimental spectra listed in Table 3 using the multispectrum nonlinear least squares fitting technique of Benner et al. [45] which was later modified to perform more accurate and rapid Voigt profile calculations [46] and speed dependent line profiles. In the fitting program, the assumed values of positions, intensities, HDO-CO₂ half-width and pressure shift coefficients, and their temperature dependences were adjusted in the calculated spectra minimizing the differences between the observed and synthetic spectra. In addition to the above line parameters, self-broadened half-width and self-shift coefficients were also determined for the majority of transitions for which CO₂ broadened half-widths and pressure shifts were measured. In addition to these, a quadratic speed dependence (S_d) parameter [47] was also included for the majority of transitions (except for weak transitions for which the speed dependence parameter was fixed to default values that were chosen appropriate for specific fitted intervals). For a number of weak lines the speed dependence parameters was fixed to zero. For a number of specific transition pairs, collisional line mixing via the off-diagonal relaxation matrix formalism of Levy *et al.* [48] was also determined, as appropriate, when high-pressure spectra were added to the fittings. In several instances, where doublet transitions were involved whose positions were separated by small amounts, auxiliary parameters and constraints were used to measure line separations and their relative line intensities [49]. Similarly, in other cases, line parameters (intensities, half-width and pressure-

shift coefficients, their temperature dependences) for the closely-spaced transitions were constrained to be the same [49] in order to obtain the best fit residuals.

As discussed earlier, prior to starting the multispectrum fitting, the wavenumber scales of all spectra were calibrated relative to positions of the ν_2 water vapor lines. The isotopologue abundances of the different species (e.g., H_2^{16}O , HD^{16}O) in each of the fitted spectra were determined from line intensities obtained by analyzing short spectral intervals in individual spectra so that all spectra could be fit simultaneously using the same total and partial pressures and volume mixing ratios in all fitted spectral intervals. The selected multispectrum fitted regions range between ~ 1236 and 1495 cm^{-1} . Each fitted region consisted of short wavenumber intervals extending $\sim 1\text{-}2.5\text{ cm}^{-1}$. To fit the background of all the ten spectra simultaneously, a Chebyshev polynomial expression of order 1-3 (as appropriate) was chosen to fit the 100% transmission level of each spectrum. For the majority of the fitted intervals a first order polynomial (a slope and a straight line) was found adequate to fit the background. Spectra were given weights inversely proportional to the square of their S/N ratios. Except for the 20.941 m Herriott cell spectrum, the other spectra were given weights ranging from 0.5 to 1.0 (1.0 being the maximum weight for a spectrum with the highest S/N). The weight for the Herriott cell spectrum was only 0.02 since, with reference to [42], the use of a 1.3 mm source diameter and the possibility of a slight degradation of the mirror reflectance from 0.994 to 0.985 will degrade the performance of the Herriott cell and transfer optics signal from approximately 22% to approximately 12% of the signal recorded with the single pass short cell.

3.2. Line shape coefficients

By employing the multispectrum fitting technique [45] all ten spectra (**Table 3**) were successfully fitted providing a consistent set of line parameters in a single least squares solution for each fitted region. This fitting technique is flexible and allows determining several line parameters including positions, intensities, broadening and pressure-shift coefficients and their temperature dependences simultaneously. **Eqs. (3)-(5)** listed below were used in this work similar to many of our previous studies [49].

$$b_L = p \times \left[b_{L,CO_2}^0 \times (1 - \chi) \left(\frac{T_0}{T} \right)^{n_1} + b_{L,self}^0 \times \chi \left(\frac{T_0}{T} \right)^{n_2} \right] \quad (3)$$

$$\nu = \nu_0 + p \times [\delta_{CO_2}^0 \times (1 - \chi) + \delta_{self}^0 \times \chi] \quad (4)$$

$$\delta = \delta^0 + \delta' \times (T - T_0) \quad (5)$$

In **Eqs. (3-5)**, bLO and δ^0 represent the pressure broadening and pressure-shift coefficients (in $\text{cm}^{-1} \text{ atm}^{-1}$ at 296 K), respectively. b_L is the Lorentz half-width (in cm^{-1}) of the spectral line at pressure p and temperature T , bL,CO_2O and $bL,selfO$ are the Lorentz half-width coefficient of the line for HDO- CO_2 and HDO-HDO broadening, respectively, at the reference pressure p_0 (1 atm) and temperature T_0 (296 K) of the broadening gas (either CO_2 or HDO), and χ is the ratio of the partial pressure of HDO to the total sample pressure (HDO+ CO_2 in this case) in the cell. Similar to HDO- CO_2 and HDO-HDO half-width and pressure-shift coefficients, temperature dependences of HDO- CO_2 half-width and pressure-shift coefficients were also measured for a number of transitions. No temperature dependences were determined for self-broadened widths or self-shift coefficients since no appropriate low temperature spectra with only HDO were obtained. As shown in **Eq. (5)** a linear model was used for the temperature dependence of pressure-shift coefficients. The term $bL,selfO$ in **Eq. (3)** refers to (water-HDO) broadening coefficients where “water” corresponds to (H_2O , D_2O and HDO) mixture. Similarly the term $\delta selfO$ refers to (water-HDO) pressure-shift coefficient.

Sample multispectrum fits are plotted in **Figs. 3 and 4** for the $1450\text{--}1451.8 \text{ cm}^{-1}$ and the $1468.8\text{--}1470.4 \text{ cm}^{-1}$, respectively. In both these plots, the ten experimental spectra fitted simultaneously are overlaid in the top panel (**a**) while the weighted (observed minus calculated) fit residuals are displayed in the bottom panel (**b**). The horizontal dashed line in (**a**) corresponds to the 100% absorption level. The short vertical lines at the top of (**a**) represent positions of absorption lines included in the least squares fits.

Insert Figs. 3 and 4 here (Sample fittings)

Even though we were able to measure line parameters for over 250 individual transitions, not all parameters were determinable for every transition. Positions and intensities were retrieved for almost all measured transitions, but the number of measurements obtained for Lorentz half-widths, pressure-shifts and the temperature dependences of half-widths and pressure shifts coefficients were less because several of the absorption lines were either weak or blended. Measured parameters and number of HDO-CO₂ and HDO-HDO measurements are listed in **Table 4**.

Insert Table 4 (measured parameters and number of measurements)

A number of weaker lines belonging to other isotopologues (*e.g.*, H₂¹⁶O, D₂¹⁶O) that appeared in some of the fitted intervals were also measured, but those results are not included in **Table 4** (due to weakness of those lines and therefore less accurate) or the **Supplemental file** (*file listing all measured transitions with measured spectral line parameters*) included with this paper.

A sample of measured line parameters is listed in **Table 5**. The table lists the line identification under the first column ($J' K_a' K_c' \leftarrow J'' K_a'' K_c''$) followed by the measured line position (cm⁻¹) and line intensity (cm/molecule at 296 K). The uncertainties associated with measured positions (cm⁻¹) and line intensities (% intensity uncertainty) are also listed next to their values. The two-row format for line shape parameters of each transition provides HDO-CO₂ broadening parameters at the top row and water-HDO broadening parameters at the bottom row. These are the measured broadening coefficient (cm⁻¹ atm⁻¹ at 296 K) for CO₂ and self-broadening, *bLO* (HDO-CO₂) and *bLO* (water-broadened HDO); the temperature dependence exponents (n_1 and n_2) for CO₂ and self-broadening, respectively (no units), CO₂- and self- pressure-shift coefficient (cm⁻¹ atm⁻¹ at 296 K), δQ (HDO-CO₂) and δQ (water-HDO), and the temperature dependence coefficient (in cm⁻¹ atm⁻¹ K⁻¹), $\delta'Q$ (HDO-CO₂), respectively. These are followed by the speed dependence parameter and its % uncertainty given under the last two columns. As noted earlier, no low temperature spectra were recorded with appropriate amounts of HDO since the low temperature spectra with CO₂-broadened HDO do not have enough volume mixing ratios of HDO to retrieve the temperature dependence exponent n_2 . In the multispectrum fittings, the

temperature dependence exponent (n_2) for self-broadened (water-HDO) half-width coefficients and the temperature dependence of self- pressure-shift coefficients δ' (water-HDO) were fixed to 0.75 and 0.0, respectively, as shown in the table.

Insert Table 5 here (sample of measured parameters)

To fit all spectra to their noise levels, it was necessary to include line mixing for select line pairs and speed dependence. Prior to this study, collisional line mixing for two pairs of H₂O transitions, one each in the P and R branch, involving self- and six perturbing gases (H₂, He, CO₂, air, N₂, O₂) in the ν_2 band at room temperature was reported by Brown *et al.* [50]. Details of the equations used for retrieving the off-diagonal relaxation matrix element coefficients determined in this study are given in Brown *et al.* [50]. The present study involves spectra at various temperatures and hence the temperature dependence must also be considered in the measurements of relaxation matrix element coefficients. We have considered the temperature dependence of the relaxation matrix element coefficients following the same power law expression [Eq. (3)] as used for the temperature dependence exponents for the Lorentz half-width coefficients. However, we were not able to determine reliable temperature dependence exponents of relaxation matrix element coefficients and hence their values were fixed to a default value of 0.8 (a value similar to the nominal temperature exponents of half-width coefficients that are usually used when no reliable experimental measurements are determinable) in the least squares fittings. We suspect that the expression used for the temperature dependence of relaxation matrix element coefficients may need modification and at this time we are not aware of any known theoretical expressions available in this regard.

Comparisons of the present measurements with the positions and intensities from Gamache *et al.* [19] line list, and MCRB calculated line shape parameters from this work are shown in **Table 6**. For these specific lines, we also included the line parameters given in the **Supplemental file** of Lavrentieva et al. [17]. In **Table 6**, the first column provides the upper and lower quantum identifications of the transitions, followed by line position (cm⁻¹), intensity (cm/molecule at 296 K), Lorentz half-width coefficient for HDO-CO₂ (cm⁻¹ atm⁻¹ at 296K), temperature dependence exponents of HDO-CO₂ half-width coefficient, n_1 (unit less), HDO-CO₂ pressure-shift

coefficient ($\text{cm}^{-1} \text{ atm}^{-1}$ at 296 K) and, under the last column, the room temperature self-broadened half-width coefficients ($\text{cm}^{-1} \text{ atm}^{-1}$ at 296 K). Line positions and line intensities from present study are experimentally measured values, the Gamache *et al.* [19] line list is from HITRAN2012 [29] and those from Ref. [17] are from *ab initio* calculations. See the original articles for further details. From values listed in **Table 6**, it is apparent that line intensities from the present study are closer to Lavrentieva et al. [17] than the HITRAN2012 values. The HDO- CO_2 half-width coefficients agree well among all three studies, the self-broadened half width coefficients agree better with present MCRB calculated values than those listed in Ref. [17]. The measured temperature dependence exponents, n_l , are much higher than both the present MCRB calculated values and of Ref. [17]. There are no HDO- CO_2 pressure-shift coefficients calculated in [17] and the present HDO- CO_2 pressure-shift coefficients agree reasonably well with MCRB calculations.

Insert **Table 6** here (Comparisons of line parameters)

Collisional line mixing coefficients were measured for eleven sets of transition pairs for both HDO-HDO and HDO- CO_2 systems and their values are listed in **Table 7**.

Insert Table 7 here (off-diagonal relaxation matrix elements)

In **Table 7**, the first column lists the quantum numbers J , K_a and K_c for the transitions involved (upper state quanta first, followed by the lower state quanta). Columns 2-7 correspond respectively, to line position, line intensity, HDO- CO_2 half-width coefficient, its temperature dependence exponent (n_l), HDO- CO_2 pressure-shift coefficient ($CO2o$) and its temperature dependent coefficient ($CO2'$). The last 3 columns list the collisional line mixing (off-diagonal relaxation matrix element coefficients, W_{ij} , in $\text{cm}^{-1} \text{ atm}^{-1}$ at 296 K) for HDO- CO_2 and water-HDO systems followed by the temperature dependence exponents of the relaxation matrix element coefficients (unit less). For the two sets of strong transitions near 1349 and 1451 cm^{-1} , the two components involved in the mixing are fairly well separated and hence the majority of the line parameters for both components were individually determined. For the remaining cases,

positions of both line-mixed components have been adjusted for all sets and intensities of all but two sets of weaker transitions (near 1450 and 1451 cm^{-1}) were retrieved individually. In the majority of cases, the HDO-CO₂ half-width coefficient, its temperature dependence exponent (n_1), HDO-CO₂ pressure shift coefficients ($CO2o$) and its temperature dependent coefficient ($CO2'$) were constrained to be the same (such as for the transitions at 1356.759026 and 1356.773559 cm^{-1}). Adjusting each of those parameters might still provide small fit residuals but the retrieved results might lead to unrealistic and unacceptable values. In most cases the two collision mixed transitions are nearly of equal intensity (see **Figs. 5** and **6**).

Insert Figs. 5 and 6 here (Line mixing)

In **Figs. 5** and **6**, the 10 observed spectra are overlaid in the top panel (**a**). In the middle panel (**b**) the final weighted fit residuals (observed minus calculated) including collisional mixing and speed dependence are plotted on an expanded vertical scale. As seen in (**a**), line mixing occurs between two sets of transitions; lines marked 1&3 and 2&4. Individual line assignment and parameters such as positions, intensities and other line shape values along with line mixing and its temperature dependence exponents are listed in **Table 7**. From this Table it is clear that strong mixing occurs between the closer line pair (1&3) rather than lines 2&4. The weighted fit residuals excluding line mixing in the fit (but with speed dependence included) are plotted in the bottom panel (**c**).

The panels (**a**)-(**c**) in **Fig. 6** follow similar details as in **Fig. 5**. There is only one collisional mixing pair between transitions marked 1 & 2. The strong feature marked “BL” is a blend of at least 3 transitions. In the initial line list used in starting the multispectrum fittings, there were no temperature dependence exponents (n_2 in **Eq. (3)**) for self-broadening, self-shift coefficient or its temperature dependence. Since we did not obtain any high-pressure HDO spectra other than at room temperature, temperature dependences for self-broadened half-width and self- pressure shift coefficients were fixed to 0.75, and 0, respectively. However, room-temperature values for self-broadening and self-shift coefficients were retrieved.

A detailed comparison to all measured and MCRB calculated HDO-CO₂ half-width and pressure-shift coefficients and, HDO-HDO (water-broadened HDO, where water represents all nine isotopologues combined) self-broadened half-width and self-shift coefficients are shown in **Figs. 7-11**.

A quadratic speed dependence model given by **Eq. (6)** was used to describe the Lorentz width as a function of velocity as was used in several of our previous studies [49].

$$bL_0v = bL_0v_m \sqrt{1 + S_d v v_p^2 - 1.5} \quad (6)$$

In the above expression, v is the speed of the molecular collision, v_m is the mean speed of the molecular collision, v_p is the most probable speed of the collision, and S_d is the speed dependence parameter (SD) reported in this study. Please note that the width will be reduced to the Lorentz width when S_d approaches 0. With **Eq. (6)** implemented into the Voigt expression and integrated over all velocities of collision, the resulting real (K_s) and imaginary (L_s) parts for the speed dependent line shape are given by **Eq. 7**.

$$K_{sx,y,S_d} = \frac{2\pi - \infty}{\pi} e^{-v^2} \tan^{-1} \frac{v + x y S_d v^2 - 1.5 + 1}{2v} \quad (7a)$$

$$L_{sx,y,S_d} = \frac{1\pi - \infty}{\pi} e^{-v^2} \ln \frac{v + x y S_d v^2 - 1.5 + 1}{2v} \quad (7b)$$

Where,

$x = \ln 2 / v - v / \alpha D$, $y = \ln 2 b L_0 \alpha D$, and αD is Doppler half-width (cm⁻¹).

Transitions for which speed dependence was not measured, they were fixed to reasonable default values comparable to those for other transitions in the fittings. For several weak lines the speed dependence was fixed to zero. The measured speed dependence parameters are listed in the Supplemental file and examples are listed in **Table 5** along with other measured parameters.

4. Theoretical formalism

The calculations of the line shape parameters, the half-width and line (pressure)-shift coefficients, were made using the formalism of Robert and Bonamy [16] as modified by Ma *et al.* [51] and has the appellation Modified Complex Robert-Bonamy (MCRB) formulation. In this complex values formalism the half-width, γ , and line shift, δ , of a ro-vibrational transition $f \leftarrow i$ are given by (*in the theoretical section, the half-width and pressure-shift coefficients are denoted by γ and δ , respectively, instead of bLO and δ^0 used in the experimental section*):

$$(\gamma - i\delta)_{f \leftarrow i} = \frac{n_2}{2 \pi c} \int_0^\infty v f(v) dv \int_0^\infty 2\pi b db \left[1 - e^{-i\langle S_1 + \text{Im}(S_2) \rangle_{J_2}} e^{-\langle \text{Re}(S_2) \rangle_{J_2}} \right] \quad (8)$$

where, n_2 is the number density of perturbers, v is the velocity, $f(v)$ is the Boltzmann distribution of velocity, $\langle \rangle_{J_2}$ is the average over the states of the perturber, and b is the impact parameter. S_1 and S_2 are the first and second order terms in the successive expansion of the Liouville scattering matrix and depend on the intermolecular potential (*in the experimental section n_2 represents the temperature dependence exponent of self-broadened half-width coefficient*).

The intermolecular potential consists of the electrostatic components (dipole-dipole, dipole-quadrupole and quadrupole-quadrupole), an atom-atom component described by the Lennard-Jones potential [52, 53], and the induction and London dispersion terms give the isotropic components. In order to employ the atom-atom potential in the formalism, the r_{ij} atom-atom distances must be mapped into the center of mass separation, R , using the expansion of Sack [54]. The expansion is described in terms of the Order and the Rank of the Wigner D-matrices for the radiating and perturbing molecule. Here, the atom-atom part of the potential was expanded to 20th order and rank 4 4 for the CO₂-broadening calculations and to 8th order and rank 2 2 for the self-broadening calculations. The isotropic part of the atom-atom potential was used in Hamilton's equations of motion to solve for the trajectories of the collision pairs. The calculations included the real and imaginary components for the half-width and line shift

coefficients and proper averaging over the velocity, both of which have been shown to be important [55-59].

The parameters describing the electrostatic, induction, and London dispersion potentials (dipole moments, quadrupole moments, ionization potentials, etc.) are well known. The Lennard-Jones atom-atom potential is:

$$V_{atom-atom} = \sum_{i,j} 4 \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (9)$$

where, the sum on i and j are over the atoms on the radiating and perturbing molecules. The parameters ϵ_{ij} and σ_{ij} are somewhat in question. There are a number of proposed methods to determine heteronuclear atom-atom parameters from homonuclear parameters [53, 60-65]. Using the different combination rules lead to some differences in the derived ϵ_{ij} parameters greater than 1900% with many combinations different by several hundred percent and differences in the derived σ_{ij} parameters >35%. The atom-atom parameters were determined using the combination rules of Hirschfelder *et al.* [53] and labeled pot00. The effect of these parameters on the line shape calculations was tested by changing, one at a time, the atom-atom ϵ_{ij} and σ_{ij} values by 10%, recalculating the half-width and line shift coefficients and comparing to the pot00 calculations. It was observed that changing the atom-atom parameters had little to no effect on the calculated half-widths and line shift coefficients. This fact is not surprising in that HDO-CO₂ is a strong dipole-quadrupole system and HDO-HDO a strong dipole-dipole system. In the calculations presented here the pot00 parameters listed in **Table 8** were used.

Insert Table 8 here (MCRB constants used)

The ν_2 and $2\nu_2-\nu_2$ transitions in the 1100-4100 cm⁻¹ region were extracted from the HITRAN2012 database [29] giving 2245 and 435 transitions, respectively. The rotational quantum numbers were taken to create a list of transitions for use in the MCRB codes. The half-width and line-shift coefficients were calculated for each transition at 7 temperatures: 200, 225, 275, 296, 350, 500, and 700 K. Given these data the temperature dependence of the half-width coefficient can be determined using the standard power law model:

$$\gamma(T) = \gamma(T_{ref}) \left[\frac{T_{ref}}{T} \right]^n \quad (10).$$

There are a number of studies [66-69] that indicate the standard formula, **Eq. (10)**, used for determining the temperature dependence of the half-width coefficients do not strictly hold for certain collision systems [66] or over large temperature ranges [70], and can vary significantly for different temperature ranges [15, 70, 71]. Here, the emphasis is a line list for application to the atmosphere of Mars, thus, the temperature dependence of the half-width coefficients were determined over the temperature range of 200-350 K with a reference temperature of 296 K. While the actual temperature range of the Martian atmosphere where pressure broadening is important is less than the chosen fit range, the first five T points were used to make a least-squares fit to **Eq. (10)**. It is also noted that the correlation coefficients of the fits were all equal to 1 to four significant figures, implying the power law is valid in the temperature range. It may be noted that the form of **Eq. (10)** is very similar to that of **Eq. (3)**. Although line-shift coefficients were also calculated for each transition at 7 temperatures, no temperature dependence for the line-shift coefficients are reported here since at this time there is no agreed upon theoretical model to compute this parameter.

5. Comparisons of measured and calculated line parameters

In **Fig. 7 (a-c)**, we show comparisons of line positions and intensities between present measurements and the initial input values [19] used in the multispectrum fits. In panel **(a)** the line position differences [PS-HITRAN2012] vs. line position (cm^{-1}) are plotted. For the majority of cases, the position differences lie between $\pm 0.000025 \text{ cm}^{-1}$ except for weak lines where the position differences show large scatter and vary between $\pm 0.0005 \text{ cm}^{-1}$. The mean and standard deviation of measured minus calculated positions are $-0.00005 (14) \text{ cm}^{-1}$. In panel **(b)** the ratios of line intensities [PS/HITRAN2012] are plotted vs. J'' (lower state rotational quanta). The mean and the standard deviation of the intensity ratios are 1.05 and ± 0.7 . In panel **(c)**, the same information as in **(b)** is shown but plotting the ratios of line intensities as a function of line positions. As seen in **Fig. 7(b and c)**, for the majority of cases, the measured intensities are $\sim 5\%$ larger than the calculated values. The higher scatter seen in panels **(b)** and **(c)** are attributed to weaker transitions. Since the calculated positions and intensities do not include uncertainties, no

error bars are plotted in **Fig. 7 (a)** and **(b)**. Comparisons of 225 line positions and intensities of the ν_2 transitions that are common between present study [PS] and Toth [35] gave mean position difference and intensity ratio to be $-0.00004(13) \text{ cm}^{-1}$ and $1.06(7)$, respectively. These values are close to the position difference and intensity ratio shown in **Fig. 7** between [PS] and the HITRAN2012 [29] database.

Fig. 7 (a) - (c) here (Position and intensity comparisons)

The measured and MCRB calculated HDO-CO₂ half-width coefficients and their temperature dependence exponents vs. $K_{\text{max}} + 0.1 \times (J_{\text{max}} - K_{\text{max}})$ are plotted in **Figs. 8(a)** and **8(b)**, respectively, where J_{max} and K_{max} stand for the maximum values of J and K quantum numbers of the transitions. The term $(J_{\text{max}} - K_{\text{max}})$ was used to offset the plot symbols in order to see if there are any trends observed in the variations of measured widths (or its temperature dependence exponents) with respect to J or K quantum numbers. In both panels **(a)** and **(b)** the measured and computed quantities are compared. The means and standard deviations listed in **(a)** and **(b)** indicate that while the calculated HDO-CO₂ half-width coefficients agree with measurements to within a few percent, the measured temperature dependence exponents are generally much higher compared to MCRB calculated values, by 15%-30%. Although MCRB calculations are performed for 200 – 700 K, the results reported in this work correspond to temperature dependence exponents for the 200-350 K (i.e. for Martian applications) range. At this time we are not able to explain the reason for this discrepancy between measurements and calculations. The calculations are consistent and the correlation coefficients of the calculated fits to determine the temperature dependence exponent (n_l) are equal to one to 4 significant figures. Since MCRB calculated values include estimated uncertainties, error bars are shown in both panels **(a)** and **(b)**.

Fig. 8 (a) and (b) here (HDO-CO₂ widths and T-dep.)

Comparisons between the measured and MCRB HDO-CO₂ pressure shift coefficients are plotted in **Fig. 9(a)** as a function of $K_{\text{max}} + 0.1 \times (J_{\text{max}} - K_{\text{max}})$. Similar to pressure-shift coefficients in general, the HDO-CO₂ pressure shift coefficients are also found to be transition dependent and could either be positive or negative. In the present case, the HDO-CO₂ pressure shift coefficients

range between $\pm 0.04 \text{ cm}^{-1} \text{ atm}^{-1}$ at 296 K. An estimated pressure-shift uncertainty of $0.002 \text{ cm}^{-1} \text{ atm}^{-1}$ at 296 K has been assigned to the calculated HDO-CO₂ and HDO-HDO pressure-shift coefficients based on comparisons with measurements. Both the measured and calculated pressure-shift coefficients generally overlap each other. While a number of line shape parameters such as the temperature dependence of widths or pressure shifts could not be measured for weak or blended lines, calculations are performed for all transitions whose positions and or intensities were measured (see the **Supplemental file**). Because of the relatively smaller values for pressure-shift coefficients compared with the Lorentz half-width coefficients, no differences or ratios between measured and calculated pressure-shift coefficients have been computed or plotted. The horizontal black dotted line represents zero pressure-shift coefficients.

Fig. 9 (a) and (b) here (HDO-CO₂ shifts and T-dep.)

In panel **9(b)**, the measured temperature dependences for HDO-CO₂ pressure shift coefficients are plotted vs. $K_{\text{max}} + 0.1 \times (J_{\text{max}} - K_{\text{max}})$. A linear model as given in **Eq. 5** was used in determining the temperature dependence of pressure-shift coefficients. It may be mentioned that a linear model is recommended to warrant continuous representation of the pressure shift values that range from negative to positive for water. The measured values range between $\pm 0.0002 \text{ cm}^{-1} \text{ atm}^{-1} \text{ K}^{-1}$ with the majority of values showing negative temperature dependence coefficient. The horizontal black dotted line corresponds to zero temperature dependence.

The measured and calculated room temperature self-width and self-shift (water-HDO) coefficients are plotted in **Fig. 10(a) and (b)** as a function of $K_{\text{max}} + 0.1 \times (J_{\text{max}} - K_{\text{max}})$ since no adequate low temperature self-broadened spectra were obtained in the present study. However, temperature dependence of self-broadened half-width coefficients was calculated using the MCRB formalism and are listed in the **Supplemental file**.

Insert Figs. 10 (a) and (b) here (self-widths and shifts)

In **Fig. 11(a)-(c)** combined plots showing the measured and MCRB calculated values for HDO-CO₂ half-width coefficients, their temperature dependence exponents and pressure-shift

coefficients vs. line positions are plotted to provide an overall view of the 3 important line shape parameters. The measured and MCRB calculated values are represented by **solid green up triangles** and **open blue circles**, respectively.

Fig. 11 (a) - (c) here (comparisons of obs. and calc. HDO-CO₂ line shapes)

6. Uncertainties

While it is important to know the uncertainties in the Lorentz half-width and pressure-shift coefficients at the reference temperature, 296 K, it is also important to know how these uncertainties propagate to *the temperatures and volume mixing ratios* in the simulations. For example, when one uses a half-width coefficient at 296 K and its temperature exponent from a different source (e.g., HITRAN database), it is usually assumed that the half-width coefficient at 296 K is the best determined value and the uncertainty in its temperature exponent (n) increases the uncertainty in half-width as the gas temperature gets farther from 296 K. In fact, for each line the experimental values of the two half-width parameters, (foreign-broadening and self-broadening) and the two pressure-shift parameters (foreign-shift and self-shift) are highly correlated and the uncertainties as a function of temperature are quite different. Uncertainties and their effect upon the gas sample temperatures have been described in detail in our earlier work on the two CO₂ bands [72].

We examined the above effects on one of the transitions measured in this study and illustrate the results for the HDO transition at 1368.208807(9) cm⁻¹. As discussed earlier, we did not obtain any adequate low-temperature spectra of HDO-HDO and hence the temperature dependence exponents of the water-broadened HDO lines were fixed to 0.75 and the temperature dependence of self-shift coefficients fixed to zero for all measured lines. Thus, the uncertainties in the temperature dependences of self-broadening and self-shift coefficients are zero and we wanted to see how these assumptions could affect the Lorentz self-broadening and self-shift coefficients as a function of the gas sample temperature applicable to Mars atmospheric conditions.

Using only the uncertainties in the water and CO₂ broadening and pressure-shift coefficients, and their temperature dependences can be misleading. These parameters have significant correlations in the least squares solution and alter the uncertainties in ways that are not clear. **Figs. 12** and **13** describe the effects on a specific HDO transition at 1368.208807(9) cm⁻¹, but provide a general guide for unblended lines. The uncertainties depend upon the assumption that **Eqs. 3-5** accurately describe the parameters.

Figure 12 displays the percent uncertainty in the Lorentz half-width coefficient as a function of temperature for four cases. The two red curves are for the case of self-broadening within a gas consisting of pure water vapor for which we have assumed the mixing ratio as one. The solid horizontal red line is what is produced in the fit itself which assumes that the temperature dependence exponent for self-broadening is 0.75 with no uncertainty. This produces a relative uncertainty that is constant with temperature. The dashed red curve displays a more realistic case if a 20% uncertainty in the temperature dependence exponent is considered. It is assumed to have no correlation with the other three parameters. The minimum uncertainty occurs at 296 K where the Lorentz self-broadened half-width coefficient is determined by the multispectrum fit, but rises rapidly away from that temperature. The self-broadened half-width coefficient is only uncertain at the 1% level or less from 278 to 315 K and it remains <6% for the entire temperature range from 200 to 360 K. For better accuracy, analysis using self-broadened spectra at substantially different temperatures than room temperature would be required.

The blue curves in **Fig. 12** are the corresponding percent uncertainties in the Lorentz broadening for a mixture containing 1% water and 99% CO₂. Since the temperature dependence exponent for the CO₂ broadening has been determined, the uncertainties as a function of temperature with and without the (measured) uncertainty added for the broadening are close to the same (solid and dashed blue curves). Over the entire displayed temperature range, the uncertainty is less than about 0.5%. The minimum uncertainty is at about 282 K, within the range of the spectra used to determine the coefficients. The minimum fractional uncertainty of the CO₂ broadening is larger than that of water broadening because of the smaller value of the broadening itself.

Insert Fig. 12 here (% half-width uncertainty plot)

Figure 13 displays the uncertainty of the pressure-shift coefficients in an analogous manner to that of **Fig. 12** for the Lorentz widths. Here the uncertainty in the temperature dependence of the self-shift coefficient is assumed to be $0.0001 \text{ cm}^{-1} \text{ atm}^{-1} \text{ K}^{-1}$. The degradation of self-shifts by the lack of the temperature dependence is less severe than the effect on the Lorentz self-broadened half-width coefficients, only about a factor of two or less over the temperature range graphed. The lack of knowledge of the temperature dependence of the self-shift coefficients has only a very small effect upon the 1% mixture, an effect indistinguishable in the graph. The HDO-CO₂ shift coefficients are better determined than the self-shift coefficients by typically an order of magnitude. Minimum uncertainties are near room temperature. The nature of the curves is highly transition dependent and can be plotted for each measured transition from the knowledge of the appropriate parameter values and the correlation coefficients involved. The correlations among the fitted parameters have been taken into consideration in the present study.

Insert Fig. 13 here (Pressure shift uncertainty)

7. Summary and conclusions

The present study reports not only the first experimental measurements of CO₂-broadened HDO half-width and pressure-shift coefficients and their temperature dependences but also the first experimental results of the off-diagonal relaxation matrix element coefficients for HDO-CO₂ and HDO-HDO collision systems. Quadratic speed dependence parameter for a number of strong and medium strength transitions was also measured. In the process of performing multispectrum fittings, line positions and intensities for over 250 HDO transitions were measured (1236 to 1496 cm^{-1}). All of the parameters were obtained by analyzing 10 high-resolution (3 HDO and 7 CO₂-broadened HDO); high signal-to-noise ratio spectra recorded with the Bruker IFS-125 HR Fourier transform spectrometer at the JPL. The analyses were performed in several short spectral segments extending from $\sim 1\text{-}2.5 \text{ cm}^{-1}$, but fitting all ten spectra simultaneously using a multispectrum fitting technique.

High precisions were achieved in all the measured parameters including line positions, intensities, half-width coefficients and their temperature exponents (see Table 5). We have also generated vibrationally dependent line shape parameters for ν_2 and $2\nu_2$ - ν_2 transitions using the Modified Complex Robert-Bonamy (MCRB) formalism. Figure 14 shows the percent difference between the vibrationally dependent half-widths (this work) and the pure rotation half-widths of Ref. [19] versus line position for the ν_2 (blue x symbol) and $2\nu_2$ (black o symbol) bands. The average percent difference for the ν_2 band is 2.1% and that for the $2\nu_2$ band is -0.6, with maximum differences approaching 30% and 15%, respectively. These differences are quite large compared to what is observed for transitions of H₂O [73] with small changes in vibrational quanta. Room temperature HDO-HDO (HDO-water) width and shift coefficients have also been measured for many of the transitions for which HDO-CO₂ widths and shift coefficients were determined. Finally the measured and calculated data have been combined with previous work [19], which only considered the rotational band line shape parameters, to create an improved database for all HDO transitions between 1100 and 4100 cm⁻¹. The final list will be provided as a Supplemental file with similar results for all 5 bands ν_1 , $2\nu_2$, ν_2 , $2\nu_2$ - ν_2 , and ν_3 bands in a forthcoming article.

Insert Fig. 14 here (vibrational dependence of half-widths)

Systematic errors due to uncertainties in various sources (such as in absorption path lengths, pressure and temperature readings, wavenumber calibration scales, and, deficiencies in the line shape model used) could influence the absolute accuracies in the measured parameters. Such errors could be small compared to uncertainties in the actual volume mixing ratios of HDO in the total sample, errors in the assumed values of parameters that could not be adjusted in the fittings and hence fixed to default values. In the present multispectrum analysis, by combining several spectra obtained at various gas sample pressures, temperatures, volume mixing ratios, and two widely different absorption paths (20.38 cm and 20.941 m), the usual sources of systematic errors affecting the retrieval of spectroscopic line parameters were minimized.

The correlation coefficients between fitted parameters were internally computed in our fitting software and were used in minimizing the random errors in the retrieved parameters and thus

reducing the internal statistical errors associated with the parameters plotted in various figures and listed in **Tables 5-6** and **the Supplemental file**. Best precisions were obtained in the measured parameters by using non-Voigt line shapes including speed dependence and off-diagonal relaxation matrix elements, where appropriate.

Systematic errors in the experiment could influence the absolute accuracies in the retrieved line parameters, mostly affecting the line shapes in general (e.g., widths, shifts, temperature dependence). These systematic error sources include wavenumber scale (dependent upon the calibration standards), the uncertainties in absorption paths (0.01-0.03%), pressure and temperature readings (0.1-0.2% and 0.03-0.06%, respectively); volume mixing ratio determination (not well determinable), background polynomial fits (which is minimal in the present case), and possible model deficiencies (difficult to quantify). In the present study the most challenging aspect of the experiment was to determine the purity of HDO samples and the actual abundances of the various isotopologues in the dataset. As in all of our multispectrum analyses, the residuals due to random errors were minimized by fitting several spectra simultaneously (HDO and CO₂-broadened HDO at room and low temperatures). By employing speed dependence and off-diagonal relaxation matrix elements (when appropriate) in the least squares analysis, we have achieved a high precision as seen, for example, in **Table 5** and **Figs. 7-9**. For the future, similar analyses could be pursued using other new line shape models [74]) and also using spectra with higher amounts of pure HDO at different temperatures.

Based upon our various measurement uncertainties, we estimate the absolute accuracies in our parameters to be $\pm 0.0001 \text{ cm}^{-1}$ for positions, $\pm 2\%$ for intensities, $\pm 2\text{-}3\%$ in Lorentz half-width coefficients, $\sim 10\%$ in the pressure shift coefficients and the temperature dependences in pressure shift coefficients. The errors in the relaxation matrix element coefficients and speed dependence parameters are difficult to estimate; but these are expected to have an upper limit of 10-20%. This work will result in the generation of an improved line list for application to remote sensing observations of Mars and Venus.

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Table titles

1. A brief summary of published line parameters in the fundamental bands of HDO^a:
Measurements and calculations.
2. Experimental setup and physical conditions of HDO and HDO-CO₂ spectra.
3. Summary of experimental conditions of HDO and HDO-CO₂ spectra analyzed in the ν_2 band.
4. Measured line parameters and number of HDO-CO₂ and HDO-HDO measurements.
5. Sample of measured line parameters for self- and CO₂-broadened HDO transitions in the ν_2 band.
6. Comparisons of line parameters from the present measurements, line positions and intensities from Gamache et al. [19] line list, the MCRB line shape parameters from this work and from Lavrentieva et al. [17] for select lines in the ν_2 band of HDO.
7. Off-diagonal relaxation matrix element coefficients, W_{ij} (cm⁻¹ atm⁻¹ at 296 K), for transitions in the ν_2 band of HDO broadened by CO₂ and HDO.
8. Pot00 atom-atom parameters used in the MCRB calculations.

Figure captions

1. As an example, the potential effects of incorrect half-widths on the retrieved HDO column densities are shown in **Fig.1**, where the curve of growth (integrated line area vs. column density) for a strong (optically thick) HDO transition in the ν_2 band is plotted. In the example shown, using the HDO-CO₂ half-width (**blue curve**) coefficient from this work vs. the air-width from HITRAN (**red curve**) and 1.8×air-width, generally used by researchers as a proxy to HDO-CO₂ width (**dotted green curve**) would cause an error of about +61% in the retrieved column abundance. Also included in **Fig. 1** is the curve of growth corresponding to the MCRB calculated [PS] CO₂-broadened half-width coefficient (**solid green curve**). It is clear that the HDO-CO₂ half-width coefficient measured in this study is very close to the calculated half-width coefficient using the MCRB formalism [PS]. See the text for further details.

2. Laboratory absorption spectra of HDO and HDO broadened by CO₂ (HDO-CO₂) in the ν_2 band of HDO between 1200 and 1485 cm⁻¹. The spectra were recorded at 0.0032-0.0056 cm⁻¹ resolution (corresponding to the Bruker defined resolution 0.0056-0.01 cm⁻¹) with the Bruker FTS at JPL. The path length of the absorption cell was 20.38 cm and other experimental conditions are summarized in the legends of panels (**a-c**) and in **Table 3**.

3. An example of a multispectrum fit with 10 spectra (3 HDO and 7 HDO+CO₂) in the 1450–1451.8 cm⁻¹ region. The experimental conditions of all 10 spectra are listed in **Table 3**. All ten observed spectra fitted simultaneously are overlaid in panel (**a**) with the weighted observed minus calculated fit residuals plotted in panel (**b**). The three sets of transition pairs involved in line mixing are marked as 1 1, 2 2 and 3 3 and shown in panel (**a**). A quadratic speed dependence parameter was determined for a number of strong transitions, as appropriate.

4. An example of a multispectrum fit with 10 spectra (3 HDO and 7 HDO+CO₂) in the 1468.8–1470.4 cm⁻¹ region. The experimental conditions of all 10 spectra are listed in **Table 3**. All ten observed spectra fitted simultaneously are overlaid in panel (**a**) with the weighted observed minus calculated fit residuals plotted in panel (**b**). Line identifications for the two strong transitions (no line mixing) are shown in the upper panel (**a**). A quadratic speed dependence parameter was measured for several transitions, as appropriate.

5. Multispectrum fit of ten spectra in the ν_2 band of HDO extending from 1421 to 1423.15 cm^{-1} . There are 3 pure HDO and 7 CO_2 -broadened HDO spectra included in the fit. The 10 observed spectra are overlaid in panel (a). In panel (b), the weighted observed minus calculated fit residuals with off-diagonal relaxation matrix element coefficient coefficients and quadratic speed dependence included in the multispectrum fit are plotted. Panel (c) shows the multispectrum fit residuals with relaxation matrix element coefficients excluded from the fit (but speed dependence included).

6. Multispectrum fit of ten spectra in the ν_2 band of in the 1434 to 1435.5 cm^{-1} range. There are 3 pure HDO and 7 CO_2 -broadened HDO spectra included in the fit. The 10 observed spectra are overlaid in panel (a). In panel (b), the weighted observed minus calculated fit residuals with off-diagonal relaxation matrix element coefficient coefficients and quadratic speed dependence for the $5\ 4\ 2 \leftarrow 5\ 4\ 1$ and $5\ 4\ 1 \leftarrow 5\ 4\ 2$ transition pairs included in the multispectrum fit are plotted. Panel (c) shows the multispectrum fit residuals with relaxation matrix element coefficients excluded from the fit (but speed dependence included). The strong feature marked “BL” is a blend of at least 3 transitions.

7. (a) Comparison of present measured line positions with HITRAN2012 values plotted vs. wavenumber (cm^{-1}). The majority of the differences are within $\pm 0.000025\ \text{cm}^{-1}$, with the mean difference of $-0.00005(14)\ \text{cm}^{-1}$, (b) Measured and HITRAN2012 line intensities vs. J'' , with the ratios of intensities $[\text{PS}]/\text{HITRAN2012}=1.05(7)$, (c) Ratios of measured to calculated line intensities plotted vs. wavenumber (cm^{-1}) (see the text for details).

8. (a) Comparison of measured and calculated CO_2 -broadened HDO half-width coefficients in the ν_2 band of HDO plotted as a function of $K_{\text{max}}+0.1*(J_{\text{max}}-K_{\text{max}})$. The mean and standard deviation of the ratios of PS measured/MCRB calculated half-width coefficients = 1.01(5), while the mean and standard deviation of the ratio of measured/calculated half-width coefficients from Ref. [17] = 1.07(15). (b) Measured and MCRB calculated temperature dependence exponents of the CO_2 -broadened HDO half-width coefficients in the ν_2 band of HDO plotted as a function of $K_{\text{max}}+0.1*(J_{\text{max}}-K_{\text{max}})$. The mean and standard deviation of the PS measured/MCRB calculated temperature dependence exponents = 1.22(9), while the mean and standard deviation of the

measured/calculated values of the temperature dependence exponents from Ref. [17] is 2.00(1.32). No measurements for the $2\nu_2$ - ν_2 band lines were made (See text for details).

9. **(a)** Comparison of measured and calculated HDO-CO₂ pressure-shift coefficients in the ν_2 band of HDO plotted as a function of $K_{\max}+0.1*(J_{\max}-K_{\max})$. Because of the smaller values of pressure-shift coefficients compared to half-width coefficients, ratios of measured to calculated pressure-shift coefficients are not made. Pressure-shift coefficients are measured only for the ν_2 lines while calculated values are obtained for $2\nu_2$ - ν_2 lines also. **(b)** Measured temperature dependence exponents of the HDO-CO₂ pressure-shift coefficients in the ν_2 band of HDO plotted as a function of $K_{\max}+0.1*(J_{\max}-K_{\max})$. No calculations have been performed for the temperature dependence of HDO-CO₂ pressure-shift coefficients (See text for details).

10. **(a)** Measured and calculated self-broadened half-width coefficients are plotted vs. $K_{\max}+0.1(J_{\max}-K_{\max})$ in the ν_2 band of HDO. **(b)** Measured and calculated self-shift coefficients vs. $K_{\max}+0.1(J_{\max}-K_{\max})$ in the ν_2 band of HDO. Estimated error bars are provided for the calculated widths and shifts coefficients. The measured self-width coefficients agree well with the MCRB calculated values. Because of the random nature of pressure-shift coefficients, ratios of self-shift coefficients between measurements and calculations are not made. No measurements are made for the $2\nu_2$ - ν_2 self-width or self-shift coefficients and hence only calculated self-width and self-shift coefficients are plotted in **(b)**.

11. **(a)** Measured (**solid green up triangles**) and MCRB calculated (**open blue circles**) CO₂-broadened (HDO-CO₂) half-width coefficients plotted as a function of positions (cm⁻¹), with the mean and standard deviation of measured to calculated half-width coefficients = 1.01(5). **(b)** Measured (**solid green up triangles**) and MCRB calculated (**open blue circles**) temperature dependence exponents of CO₂-broadened (n_1) (HDO-CO₂) half-width coefficients plotted as a function of positions (cm⁻¹), with the mean and standard deviation of measured to calculated half-width coefficients = 1.22(9). **(c)** Measured (**solid green up triangles**) and calculated (**open blue circles**) HDO-CO₂ pressure-shift coefficients (δ^0 (HDO-CO₂) in cm⁻¹ atm⁻¹ at 296 K, plotted as a function of positions (cm⁻¹). Because of the smaller values and scatter in pressure-shift coefficients, no differences or ratios of measured to calculated pressure-shift coefficients are either plotted or calculated.

12. Percent uncertainty of Lorentz half-width coefficients as a function of temperature for the CO₂-broadened and self-broadened HDO transition at 1368.208807(9) cm⁻¹ (see the text for details).
13. Pressure-shift uncertainty as a function of temperature for the CO₂-broadened and self-broadened HDO transition at 1368.208807(9) cm⁻¹ (see the text for details).
14. Percent difference between vibrationally dependent half-widths minus the pure rotation half-widths versus line position in cm⁻¹ for the ν_2 (blue x symbols) and the $2\nu_2$ (black o symbols) bands.

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Fig. 1

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Fig. 13

Fig. 14

Table 2

Experimental setup and physical conditions of HDO and HDO-CO₂ spectra.

Configuration of the Bruker 125 HR FTS at JPL	
Light Source	Globar
Beam Splitter	KBr
Detector	HgCdTe
Focal length of the collimating lens (mm)	418
Source aperture diameter (mm)	1.3-2.0
Effective filter band pass (cm ⁻¹)	900-1500
Resolution (cm ⁻¹) Unapodized	0.0032–0.0056 (depending on the sample mixture)
Maximum Optical Path Difference (cm)	90 - 155
Pure water sample pressure (Torr) ^a [Mixture (H ₂ O+HDO+D ₂ O)]	1.83-6.94
Total pressure: CO ₂ -broadened HDO (Torr)	~33.6-314
Volume mixing ratios of HDO (HDO and HDO-CO ₂ mixtures)	~0.00022-0.5
Temperature (K)	~297-230
Cell path length (m)	0.2038 and 20.941
Scanning time (h)	~3-12 for data scans and 7-17 for empty cell scans
Signal-to-noise	~80-1500 (varying with absorption path length) ^b
Gas Samples	High-purity distilled H ₂ O, 99% D ₂ O and, 99.98% ¹² C-enriched CO ₂ sample.
Calibration standards	H ₂ O

^a HDO sample is a mixture containing HDO+H₂O+D₂O [see **Eq. (1)**] with nine isotopologues in different amounts. “Water” represents all the isotopologues in the mixture broadening the HDO transitions.

^b The lowest (~230 K) temperature spectrum recorded with the Herriott cell (20.941 m) had the smallest S/N ratio (~80). The S/N of other nine spectra were in the 1000-1500 range.

Table 3

Summary of experimental conditions of HDO and HDO-CO₂ spectra analyzed in the ν_2 band.

Serial #	Spectra ^a	Cell length (m) ^b	Total Pressure (Torr) ^b	Sample temperature (K) ^c	Volume mixing ratio of water ^d
Only HDO (mix of H ₂ O+HDO+D ₂ O)					
1	4375×1200.ars	0.2038	1.83	296.8	1.0
2	4381×1200.ars	0.2038	6.94	296.8	1.0
3	4392×1200.ars	0.2038	2.43	296.8	1.0
CO ₂ broadened HDO ^e					
4	4404×1200.ars	0.2038	153.40	296.8	0.0422
5	4398×1200.ars	0.2038	314.0	296.8	0.040
6	4528×1200.ars	0.2038	122.9	271.3	0.02502
7	4526×1200.ars	0.2038	214.26	271.3	0.0048
8	4533×1200.ars	0.2038	68.10	255.0	0.0066
9	4535×1200.ars	0.2038	39.31	255.0	0.00715
10	4612×1200.aus	20.941	33.55	230.0	0.000215

Notes:

1 atm = 101.3kPa = 760 Torr.

^a Included for the authors' identification purpose.

^b Cell lengths are known with uncertainties of 0.01–0.03% depending on the cell path length (see the text for details).

^b Gas sample pressures are measured with uncertainties of $\pm 0.05\%$ of the full-scale readings of the appropriate pressure heads (10 Torr and 1000 Torr).

^c Cell (gas sample) temperatures are measured with uncertainties of ± 0.02 -0.2 K.

^d “Water” including all nine isotopologues. The volume mixing ratio of water sample is 1, with maximum amount of HDO in the sample being 0.5 of the total pressure (see text for details). In addition to the volume mixing ratio of water, abundances of the major isotopologues (*e.g.*, HD¹⁶O, H₂¹⁶O, D₂¹⁶O) were determined in each spectrum to fit all the spectra simultaneously). See text for further details.

^e A 99.98% ¹²C-enriched CO₂ sample was used for the CO₂-broadened HDO spectra.

Table 4

Measured line parameters and number of HDO–CO₂ and HDO–HDO measurements.

Parameters	Number of measurements	Parameters	Number of measurements
Position (ν) ^a	258	Intensity (S) ^b	258
CO ₂ -broadened HDO half-width coefficient (HDO-CO ₂ width) ^c	226	Self-broadened (HDO-HDO) half-width coefficient (self-width) ^c	247
Temperature dependence of CO ₂ -broadened HDO half-width coefficient ^d (n_1)	164	(HDO-HDO) pressure-shift coefficient ^c (δO_{self})	206
HDO-CO ₂ pressure-shift coefficient ^e (δO_{CO2})	212	Off-diagonal relaxation matrix element coefficients for HDO-CO ₂ and HDO-HDO collisions ^c	11 ^g
Temperature dependence of HDO-CO ₂ pressure-shift coefficient ^e (δ')	130	Speed dependence ^f	169

Notes: The number of measurements for various parameters listed in the above Table includes constrained values also (*e.g.*, widths, shifts and temperature dependence exponents for some individual components in a collision-mixed transition pairs were constrained (fixed) to have identical values). HDO sample is a mixture containing HDO+H₂O+D₂O [see **Eq. (1)**] with nine isotopologues in different amounts. (HDO-HDO) width refers to (Water-HDO) width coefficients where “Water” represents all the isotopologues in the mixture broadening the HDO transitions.

^a Line positions in cm⁻¹.

^b Line intensity in cm/molecule at 296 K.

^c Lorentz half-width and pressure-shift coefficients and, the off-diagonal relaxation matrix element coefficients in cm⁻¹ atm⁻¹ at 296 K.

^d Temperature dependence exponents of HDO-CO₂ half-width coefficients (n_1), and speed dependence parameter (no units). Only room-temperature measurements for self-broadened half-width and self-shift coefficients were measured. Self-broadening means water (all nine isotopologues of water) broadening of HDO transitions.

^e Temperature dependence of HDO-CO₂ pressure-shift coefficients in cm⁻¹ atm⁻¹ K⁻¹.

^f Including constrained values.

^g 11 sets of line-mixed pairs (HDO-CO₂ and HDO-HDO collisions).

Table 5Sample of measured line parameters for self- and CO₂-broadened HDO transitions in the ν_2 band.

Quantum numbers ^a	ν and unc. ^b	Intensity S ^c	(%) unc.	Half-width coefficient (bLO) ^d	% unc.	Temp. dep. (bLO) n^e	% unc.	Press. shift coeff. (δ^0) ^d and unc.	Temp. dep. (δ') ^f and unc.	Speed dependence (SD) ^g	% unc.
6 4 2 ←7 4 3	1325.610702(9)	1.820e-24	0.14	0.12913 0.35674	0.61 0.61	0.7097 0.75(F)	11.9	-0.00574(14) +0.0148(22)	+1.138(354) 0.0(F)	0.1989	5.7
8 3 5 ←8 3 4	1325.661744(9)	2.000e-24	0.13	0.13723 0.43425	0.56 0.53	0.6773 0.75(F)	12.4	+0.01888(16) +0.0023(24)	-0.327(365) 0.0(F)	0.1734	6.8
6 4 3 ←7 4 4	1325.822532(9)	1.823e-24	0.14	0.13046 0.34883	0.58 0.60	1.133 0.75(F)	7.2	-0.00218(13) +0.0045(21)	-1.419(360) 0.0(F)	0.2037	5.4
1 1 1 ←2 2 0	1326.030941(6)	1.353e-23	0.10	0.19477 0.50606	0.23 0.16	0.8656 0.75(F)	1.5	-0.01335(9) +0.0229(19)	+0.397(121) 0.0(F)	0.1824	1.9
7 2 6 ←7 3 5	1326.357260(6)	4.935e-24	0.12	0.12097 0.43453	0.35 0.29	0.7633 0.75(F)	4.1	-0.00957(8) -0.0057(17)	+0.400(136) 0.0(F)	0.1944	2.8
6 1 6 ←6 2 5	1327.948102(6)	7.477e-24	0.12	0.12060 0.45670	0.33 0.24	0.6972 0.75(F)	3.2	-0.00555(8) +0.0401(17)	-0.271(94) 0.0(F)	0.1760	2.9
4 0 4 ←5 1 5	1328.096448(6)	1.354e-23	0.08	0.15713 0.50846	0.21 0.15	0.6883 0.75(F)	2.1	-0.00957(7) +0.0357(18)	+0.240(86) 0.0(F)	0.1881	2.2
5 3 3 ←6 3 4	1328.273447(6)	4.764e-24	0.11	0.12914 0.40282	0.35 0.30	0.8228 0.75(F)	3.9	+0.00090(9) +0.0321(16)	-0.084(14) 0.0(F)	0.1839	3.3
6 2 5 ←6 3 4	1329.931691(6)	6.861e-24	0.11	0.12345 0.44666	0.30 0.24	0.8922 0.75(F)	2.5	-0.00960(8) +0.0022(16)	-0.236(108) 0.0(F)	0.1663	3.1
4 2 2 ←5 2 3	1330.093822(6)	9.513e-24	0.11	0.16279 0.47456	0.26 0.19	0.7761 0.75(F)	3.2	-0.00569(8) +0.0335(17)	-0.195(12) 0.0(F)	0.1654	2.7
4 0 4 ←5 0 5	1332.015221(6)	1.591e-23	0.06	0.15575 0.50615	0.17 0.15	0.6620 0.75(F)	1.8	-0.00754(7) +0.0247(18)	-0.044(78) 0.0(F)	0.1792	1.5
5 2 4	1332.292972(6)	8.357e-24	0.09	0.13056	0.24	0.8099	2.4	-0.00938(7)	-0.147(93)	0.1481	3.2

←5 3 3				0.45234	0.21	0.75(F)		+0.0078(16)	0.0(F)		
7 0 7	1332.578707(6)	5.745e-24	0.10	0.13675	0.31	0.7191	3.8	+0.01379(9)	-1.027(127)	0.1980	2.4
←7 1 6				0.48853	0.29	0.75(F)		-0.0011(18)	0.0(F)		
3 1 3	1355.436729(6)	1.224e-23	0.08	0.16577	0.22	0.8704	1.9	+0.00068(8)	-1.035(105)	0.1491	2.9
←4 0 4				0.50571	0.17	0.75(F)		+0.0020(18)	0.0(F)		
2 1 1	1355.736182(6)	1.398e-23	0.07	0.18755	0.19	1.0125	1.5	+0.00894(8)	-1.029(108)	0.1678	2.2
←3 1 2				0.44736	0.16	0.75(F)		+0.0370(18)	0.0(F)		
8 1 7	1355.988111(7)	4.919e-24	0.11	0.14150	0.36	0.8944	4.4	-0.02799(10)	+0.749(183)	0.1983	3.1
←8 2 6				0.46176	0.30	0.75(F)		+0.0424(19)	0.0(F)		
8 2 6	1356.626204(7)	3.873e-24	0.11	0.13926	0.39	0.6779	7.1	-0.01818(11)	+0.000(F)	0.2084	3.2
←8 3 5				0.43712	0.15	0.75(F)		+0.0103(19)	0.0(F)		
4 4 0	1356.759026(9)	1.743e-24	0.13	0.11664	0.17	0.9216	3.6	-0.00817(7)	+0.456(132)	0.2086	2.0
←5 4 1				0.31211	0.36	0.75(F)		+0.0293(14)	0.0(F)		
4 4 1	1356.773559(11)	1.742e-24	0.14	0.11664	0.17	0.9216	3.6	-0.00817(7)	+0.456(132)	0.2086	2.0
←5 4 2				0.31211	0.36	0.75(F)		+0.0293(14)	0.0(F)		
3 3 1	1421.607154(5)	1.356e-23	0.14	0.13789	0.16	0.8910	1.6	-0.00508(8)	-0.912(73)	0.1457	2.0
←3 3 0				0.39951	0.16	0.75(F)		+0.0448(13)	0.0(F)		
3 3 0	1421.661992(26)	9.140e-24	1.82	0.13789 ^h	0.16	0.8910 ^h	1.6	-0.00508(8) ^c	-0.912(73) ^h	0.1457 ^h	2.0
←3 3 1				0.39951 ^h	0.16	0.75(F) ^h		+0.0448(13) ^h	0.0(F)		

The percent (%) uncertainties listed under various columns correspond to one sigma internal statistical uncertainty obtained from the least-squares fits.

(F) Values were fixed to 0.75 for self-broadened half-width coefficients (n) and to 0.0 for self-shift coefficients (δ').

^a $J' K_a' K_c' \leftarrow J'' K_a'' K_c''$

^b Positions and uncertainties in cm⁻¹.

^c Line intensities (S) in cm/molecule at 296 K.

^d Lorentz half-width coefficients (bLO) and pressure-shift coefficients (δ^0) in cm⁻¹ atm⁻¹ at 296 K.

In the two row format, the numbers in the top row in each column correspond to CO₂-broadening of HDO and the bottom to HDO (water-HDO) broadening.

^e The temperature dependence exponents of broadening coefficients have no units. No low-temperature spectra were obtained with adequate amounts of HDO and hence no measurements for temperature dependences of self-broadening or self-shift coefficients ($\text{cm}^{-1} \text{atm}^{-1} \text{K}^{-1}$) are reported.

^f Temperature dependences of pressure shift coefficients, $\delta'(\text{HDO-CO}_2)$ in units of ($10^{-4} \text{cm}^{-1} \text{atm}^{-1} \text{K}^{-1}$). No $\delta'(\text{HDO-HDO})$ are measured in this study.

^g Speed dependence parameter has no units. The speed dependence parameter for both HDO-CO₂ and HDO-HDO broadening are assumed to be the same and hence only one value for each transition is determined.

^h Values were constrained to be identical to the transition listed just above it; for example $3\ 3\ 1 \leftarrow 3\ 3\ 0$ and $3\ 3\ 0 \leftarrow 3\ 3\ 1$ (see the text for details).

Table 6

Comparisons of line parameters from present measurements, line positions and intensities from Gamache et al. [19] line list, the MCRB line shape parameters from this work and from Lavrentieva et al. [Ref. 17] for select lines in the ν_2 band of HDO.

Line Assignment ^a	ν (cm ⁻¹)	S (cm/molecule) at 296 K	HDO-CO ₂ Width ^b	n_1^c HDO-CO ₂	O^b HDO-CO ₂	HDO-HDO Width ^b
6 2 4 ← 7 3 5	1239.996368	2.6841e-24	0.1652	0.4015	+0.01984	0.4853
	1239.996310	2.4330e-24	0.1526	0.6310	+0.01110	0.4533
	1239.99638	2.6471E-24	0.1451	0.325	n/a ^d	0.4266
6 1 5 ← 7 2 6	1280.695828	3.6919e-24	0.1492	0.7519	-0.01167	0.5149
	1280.695960	3.3160e-24	0.1537	0.6500	-0.00689	0.4589
	1280.69596	3.6662E-24	0.1474	0.294	n/a ^d	0.3978
7 1 6 ← 8 1 7	1284.897872	4.5776E-24	0.1232	0.6213	-0.001909	0.4603
	1284.897930	4.3170E-24	0.1362	0.4410	-0.003720	0.4641
	1284.89797	4.6293E-24	0.1389	0.177	n/a ^d	0.3402
7 1 7 ← 8 1 8	1294.920343	6.5782E-24	0.0954	0.8845	-0.003163	0.4282
	1294.920420	6.0920E-24	0.10537	0.5360	-0.006260	0.4234
	1294.92043	6.7731E-24	0.1179	0.596	n/a ^d	0.3402
5 0 5 ← 6 0 6	1319.433149	1.3005E-23	0.1296	0.6697	-0.007558	0.4960
	1319.433180	1.1940E-23	0.1456	0.4950	-0.014280	0.4913
	1319.43326	1.3391E-23	0.1562	0.059	n/a ^d	0.3225
5 2 4 ← 5 3 3	1332.292972	8.3571E-24	0.1306	0.8099	-0.009376	0.4523
	1332.293000	7.9470E-24	0.1341	0.6130	-0.012310	0.4443
	1332.29306	8.6373E-24	0.1438	0.446	n/a ^d	0.4182
3 2 1 ← 4 2 2	1347.187929	9.5777E-24	0.1630	0.6936	-0.003900	0.4876
	1347.188000	9.0774E-24	0.1654	0.6380	+0.001590	0.4643
	1347.18799	1.0098E-23	0.1705	0.566	n/a ^d	0.4221
8 1 7 ← 8 2 6	1355.988111	4.9185E-24	0.1415	0.8844	-0.027985	0.4618
	1355.988230	4.6390E-24	0.1603	0.6750	-0.019320	0.4549
	1355.98831	4.9400E-24	0.1360	0.256	n/a ^d	0.3612
1 1 1 ← 1 1 0	1402.803698	1.0731E-23	0.2082	0.9176	-0.011229	0.4714
	1402.803700	9.3590e-24	0.2054	0.7190	-0.006940	0.5054
	1402.80375	1.0750E-23	0.2024	0.666	n/a ^d	0.4230
1 1 0 ← 1 1 1	1408.391316	1.0373E-23	0.2050	0.9039	+0.013699	0.4477
	1408.391380	9.4000E-24	0.2043	0.7190	+0.009360	0.5123
	1408.39141	1.0750E-23	0.2025	0.660	n/a ^d	0.4230

^a $J' K_a' K_c' \leftarrow J'' K_a'' K_c''$, where the prime and double prime correspond to the upper and lower vibrational quanta.

^b Lorentz half-width coefficients (bLO) and pressure-shift coefficients (δ^0) are in $\text{cm}^{-1} \text{ atm}^{-1}$ at 296 K.

The numbers in the top row in each column correspond to measurements from this study [PS], the middle row from present MCRB calculations and, the bottom row from Ref. [17]. For the purpose of comparison with present measurements, the line intensities listed in [17] have been scaled to correspond to natural isotopologue abundance of HD^{16}O using the factor $0.310693\text{e-}03$ from HITRAN2012 [20]. For further details see Ref. [17].

^c n_1 are the temperature dependence exponents of HDO-CO_2 half-width coefficients and have no units.

^d n/a stands for not available.

Table 7

Off-diagonal relaxation matrix element coefficients, W_{ij} ($\text{cm}^{-1} \text{ atm}^{-1}$ at 296 K), for transitions in the ν_2 band of HDO broadened by CO_2 and HDO.

Line assignment ^a	ν (cm^{-1})	S^b	HDO- CO_2 Width ^c	n_1 (HDO- CO_2) ^d	(HDO- CO_2) ^c	r (HDO- CO_2) ^e	(W_{ij}) HDO- CO_2 collision ^c	(W_{ij}) HDO-HDO collision ^c	T de (W_{ij})
5 4 2 $\leftarrow$ 5 5 1	1299.218839	1.293e-24	0.1269(2)	0.758(70)	+0.00656(16)	0. 0(F)	0.0166(7)	0.0148(34)	0.8(
5 4 1 $\leftarrow$ 5 5 0	1299.233841	1.293e-24	Cons.	Cons.	Cons.	Cons.			
5 4 1 $\leftarrow$ 6 4 1	1341.232124	2.135e-24	0.1278(3)	1.142(33)	+0.00094(7)	-0.00013(2)	0.0155(2)	0.0058(29)	0.8(
5 4 2 $\leftarrow$ 6 4 3	1341.296894	2.137e-24	0.1271(3)	Cons.	Cons.	Cons.			
3 1 3 $\leftarrow$ 4 1 4	1349.210793	1.623e-23	0.1545(4)	0.610(15)	-0.00734(10)	-0.225(81)	0.0053(2)	0.0116(28)	0.8(
2 0 2 $\leftarrow$ 3 1 3	1349.403111	1.618e-23	0.1938(6)	0.791(14)	-0.01254(10)	-0.189(101)			
4 4 0 $\leftarrow$ 5 4 1	1356.759026	1.743e-24	0.1166(4)	0.922(33)	-0.00817(7)	-0.456(131)	0.0071(7)	0.169(17)	0.8(
4 4 1 $\leftarrow$ 5 4 2	1356.773559	1.742e-24	Cons.	Cons.	Cons.	Cons.			
3 3 1 $\leftarrow$ 3 3 0	1421.607154	1.356e-23	0.1379(2)	0.891(14)	-0.00508(8)	-0.912(73)	0.0311(3)	0.0114(10)	0.8(
3 3 0 $\leftarrow$ 3 3 1	1421.661992	9.140e-24	Cons.	Cons.	Cons.	Cons.			
4 3 2 $\leftarrow$ 4 3 1	1421.658600	1.207e-23	Cons.	Cons.	Cons.	Cons.	0.0158(2)	0..005(F)	0.8(
4 3 1 $\leftarrow$ 4 3 2	1422.034002	7.667e-24	0.1373(3)	0.807(14)	+0.00098(7)	-0.592(65)			
5 4 2 $\leftarrow$ 5 4 1	1434.928772	4.553e-24	0.1261(2)	0.772(17)	-0.00386(5)	-0.888(75)	0.0202(2)	0.0114(10)	0.8(
5 4 1 $\leftarrow$ 5 4 2	1434.960104	4.537e-24	Cons.	Cons.	Cons.	Cons.			
4 2 2 $\leftarrow$ 4 1 3	1451.105039	1.319e-23	0.1820(6)	0.713(20)	+0.00499(12)	-0.125(13)	0.015693)	0.0392(49)	0.8(
5 2 3 $\leftarrow$ 5 1 4	1451.459566	1.199e-23	0.1723(4)	0.714(16)	+0.01803(9)	-0.179(10)			

7 5 3 ← 7 5 2	1450.973657	9.910e-25	0.1105(4)	0.810(F)	-0.00297(10)	-0.100(F)	0.0099(8)	0.0219(23)	0.8(
7 5 2 ← 7 5 3	1450.986900	Cons.	Cons.	Cons.	Cons.	Cons.			
8 5 4 ← 8 5 3	1451.342333	4.717e-25	0.1227(8)	0.7(F)	+0.00208(14)	-0.100(F)	0.0141(9)	0.0098(89)	0.8(
8 5 3 ← 8 5 4	1451.398479	Cons.	Cons.	Cons.	Cons.	Cons.			
4 3 2 ← 3 3 1	1484.311636	3.871e-24	0.1468(4)	0.792(18)	+0.00199(13)	-0.610(82)	0.0155(3)	0.0171(48)	0.8(
4 3 1 ← 3 3 0	1484.470356	3.876e-24	0.1422(6)	Cons.	+0.00247(13)	Cons.			

^a $J' K_a' K_c' \leftarrow J'' K_a'' K_c''$

(F) = Values are fixed.

^b Intensities (S) in cm/molecule at 296 K.

^c Lorentz half-width coefficients (bLO), pressure-shift coefficients (δ^0) and off-diagonal relaxation matrix element (ORME) coefficients (line mixing), W_{ij} , in $\text{cm}^{-1} \text{ atm}^{-1}$ at 296 K. Uncertainties listed in parentheses correspond to parameter values in the last digits quoted.

^d Temperature dependence exponents of HDO-CO₂ half-width coefficients and of the line mixing (off-diagonal relaxation matrix element) coefficients have no units. Uncertainties listed in parentheses correspond to parameter values in the last digits quoted. ***No appropriate low temperature data for HDO-HDO were recorded.***

^e Temperature dependences of pressure-shift coefficients, $\delta'(\text{HDO-CO}_2)$ in ($10^{-4} \text{ cm}^{-1} \text{ atm}^{-1} \text{ K}^{-1}$).

Cons. = Values are constrained to those listed in the line just above or below it (as appropriate) in the least squares fittings.

Table 8

Pot00 atom-atom parameters used in the MCRB calculations.

Interacting pair	ϵ/κ (K)	σ (Å)
HO	24.15	2.84
DO	21.81	2.55
OO	51.80	3.01
HC	32.19	2.81
DC	25.51	2.83
OC	40.43	3.29
HH	11.25	2.68
HD	9.63	2.67
DD	9.20	2.66