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CO₂ Pressure Shift and Broadening of Water Lines Near 790 nm

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Carbon dioxide pressure-broadened ro-vibrational transitions belonging to the $\nu_2+3\nu_3$ band of H₂¹⁶O have been measured with a sensitive cavity ring-down spectrometer. Water vapor of relatively low pressures (<0.5 Torr) was used to limit the self-collisions among water molecules. After the calibration using the precise atomic transitions of Rb and a thermo-stabilized Fabry-Pérot interferometer, 10^{-5} cm⁻¹ frequency accuracy has been achieved. Line parameters are derived from least-squares fitting of the spectra using the “soft” collision model. The retrieved line parameters can be applied in the study of water absorption in the CO₂-rich atmospheres of planets like Venus and Mars.

Key words: Water, Carbon Dioxide, Pressure-induced half width, Pressure-induced line shift, Cavity ring-down spectroscopy

I. INTRODUCTION

The water molecule has an extremely rich spectrum throughout the infrared region. Accurate knowledge of the radiative properties of water vapor is needed in chemical, atmospheric and astronomical studies. Tremendous scientific efforts have been put into both experimental and theoretical studies of the spectrum of water vapor. A huge archive of the transitions can be found in some widely used spectroscopic databases including HITRAN [1], GEISA [2], and HITEMP [3]. The spectroscopic parameters, including the transition frequencies, line strengths, and collision-induced line widths, are widely used in various applications.

The H₂¹⁶O lines near 0.79 μ m, belonging to the $\nu_2+3\nu_3$ and $\nu_1+\nu_2+2\nu_3$ bands, have been extensively studied by Fourier-transform spectroscopy [4–7], intra-cavity laser absorption spectroscopy (ICLAS) [8–10] and cavity ring-down spectroscopy (CRDS) [11]. Using a CRDS calibrated with atomic transitions, we have determined the positions of strong H₂¹⁶O lines ($S>10^{-25}$ cm/molecule) with an accuracy of 3×10^{-5} cm⁻¹ [12]. The line parameters and assignments [13] have been updated in the 2009 edition of HITRAN [1]. However, the collision-induced effects vary largely between different perturbing gases. The CO₂ pressure-induced H₂O line shift and broadening in this spectral region have not been studied, but the information is particularly useful in the study of CO₂-rich gas samples, for example, the atmosphere of Venus.

The atmosphere of Venus consists of 96.5%CO₂ and

3.5%N₂. Though water vapor only contributes less than 0.01% of the atmosphere of Venus, it plays an important role in the climate of Venus [14]. In this case, the spectroscopy of the CO₂ perturbed H₂O lines is essential in the study of Venus. Here we present laboratory measurements of the H₂O lines near 0.79 μ m broadened by CO₂. We select these water lines because they are close to the $\nu_1+5\nu_3$ band of CO₂, which spreads in the 782–789 nm region. The $\nu_1+5\nu_3$ band has also been the first CO₂ band observed from the spectrum of Venus [15, 16], because it is sufficiently strong (but not saturated) and sits in a transparent window of the earth's atmosphere.

II. EXPERIMENTS

Natural carbon dioxide gas samples (stated purity of 99.99 %) with pressures between 50 and 300 Torr were used. The sample pressure was measured with a capacitance gauge (MKS 627B) with an accuracy of 0.15%. Water vapor presented in the sample cell as an impurity of the sample gas. The pressure of the water vapor, being well below 1 Torr, can be estimated from the intensities of its absorption lines observed in the measurements. The spectrum was recorded at room temperature (296 K) with a cavity ring-down spectrometer based on a continuous-wave Ti:Sapphire laser.

The details of the CRDS spectrometer have been presented in Refs.[17, 18] and will be only briefly described here. A laser beam of about 50 mW is coupled into a 1.4 m long ring-down cavity. The cavity mirrors have a reflectivity of 99.995% and one of them is mounted on a piezoelectric actuator. The piezoelectric actuator is driven with a triangle wave from a function generator to repeatedly match the longitudinal mode of the ring-

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TABLE I Line parameters of the H_2^{16}O lines of $\nu_2+3\nu_3$ near $0.79\ \mu\text{m}$ (in cm^{-1}). Values in parentheses are 1σ standard deviations at the last quoted digit.

Line ^a	ν_{HITRAN}^b	ν^c	ν^d	S^e	$\delta_{\text{CO}_2}^f$	$\gamma_{\text{CO}_2}^g$	Γ^h
$2_{11}\leftarrow 2_{12}$	12578.7401	0.739573(15)	0.739523(62)	9.52	+0.00575(24)	0.1893(16)	1.97
$2_{02}\leftarrow 1_{01}$	12609.0728	0.071607(20)	0.071548(36)	31.9	+0.01895(16)	0.2018(09)	1.89
$3_{21}\leftarrow 2_{20}$	12635.5456	0.544696(31)	0.544797(42)	5.00	-0.00295(25)	0.1546(10)	1.78
$4_{14}\leftarrow 3_{13}$	12637.6550	0.654340(23)	0.654286(54)	11.5	-0.00159(24)	0.1257(08)	1.43
$5_{24}\leftarrow 4_{23}$	12667.7514	0.750327(12)	0.750356(42)	17.7	-0.01635(17)	0.1148(09)	1.37
$5_{23}\leftarrow 4_{22}$	12687.0662	0.066076(22)	0.066206(37)	5.19	-0.03078(21)	0.1663(12)	1.85

^a Rotational assignment, given as $J'_{K'_a K'_c} \leftarrow J''_{K''_a K''_c}$.

^b Line position from the HITRAN database [1].

^c Line position from Ref.[12]. Significant digits are omitted.

^d Line position derived from this work.

^e Line strength at 296 K, in $10^{-25}/(\text{cm molecule})$, from the HITRAN database [1].

^f CO_2 pressure-induced line shift coefficient, in $\text{cm}^{-1}\text{atm}^{-1}$.

^g CO_2 pressure-induced line width (HWHM) broadening coefficient, in $\text{cm}^{-1}\text{atm}^{-1}$.

^h Ratio of the CO_2 -broadening coefficient to the air-broadening coefficient, $\gamma_{\text{CO}_2}/\gamma_{\text{air}}$.

down cavity to the laser wavelength. The Ti:sapphire laser is run in a step-scan mode. At each step, typically about 80 ring-down events are recorded. The decay time τ is retrieved from a fit of the exponential decay curve. The sample absorption coefficient can be determined from the equation

$$\alpha = \frac{1}{c\tau} - \frac{1}{c\tau_0} \quad (1)$$

where c is the speed of light, and τ_0 is the ring-down time of an empty cell.

Precise frequency calibration is accomplished by using the longitudinal modes of a 10 cm long thermo-stabilized Fabry-Pérot interferometer (FPI) made of ultra-low-expansion (ULE) glass and installed in a vacuum chamber. The finesse of the ULE-FPI is about 2000 near $0.79\ \mu\text{m}$. Using the precise atomic transitions of ^{87}Rb at 795 nm [19] and 780 nm [20], the absolute frequencies of the longitudinal modes of the ULE-FPI in the region of 780–795 nm have been determined with an accuracy better than 0.6 MHz ($2 \times 10^{-5}\ \text{cm}^{-1}$) [18]. The spectrometer has been applied to measure the absolute line positions of H_2 [21], C_2H_2 [22], and H_2O [12] in this region with relative uncertainty of 10^{-9} .

III. RESULTS AND DISCUSSION

Six well isolated H_2^{16}O lines of the $\nu_2+3\nu_3$ band are studied in this work. They are located in the 788–795 nm region and their strengths vary from $5 \times 10^{-25}\ \text{cm}/\text{molecule}$ to $3 \times 10^{-24}\ \text{cm}/\text{molecule}$. The positions, strengths and rotational assignments from the HITRAN database [1] are given in Table I. For each line, the absorption profile was measured several times under different CO_2 pressures. The spectral profiles

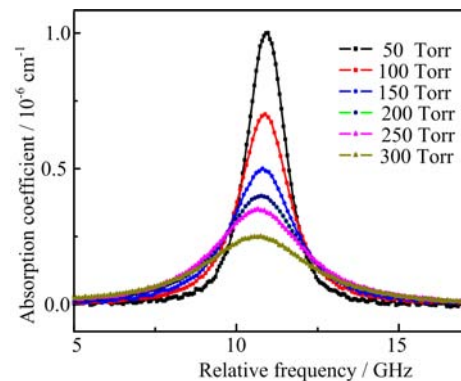


FIG. 1 The normalized profiles of the CO_2 -broadened H_2^{16}O line at $12687.066\ \text{cm}^{-1}$.

of the H_2^{16}O line at $12687.066\ \text{cm}^{-1}$ measured at different CO_2 pressures are presented in Fig.1. Pressure-induced effects including frequency shift and broadening are clearly shown in Fig.1.

Using a least-squares fit of the spectral profile, the line parameters, including the position, intensity, and width, can be derived from each spectrum. Figure 2 shows the spectrum and fitting residuals of the observed H_2^{16}O line at $12635.546\ \text{cm}^{-1}$. As shown in Fig.2 (b) and (e), the conventional Voigt profile cannot fit the observed spectrum well. The “soft” collision model [23], which takes into account the collision effects, was applied in the line-by-line fitting of the recorded spectrum. The Gaussian width was fixed at the calculated value of Doppler broadening width, while other parameters, including the position, intensity, Lorentzian width (half width at half maximum, HWHM) and Dick narrowing coefficient, were derived from the fit. As shown in Fig.2 (c) and (f), the observed line profiles are reproduced with the fitting residuals being at the experi-

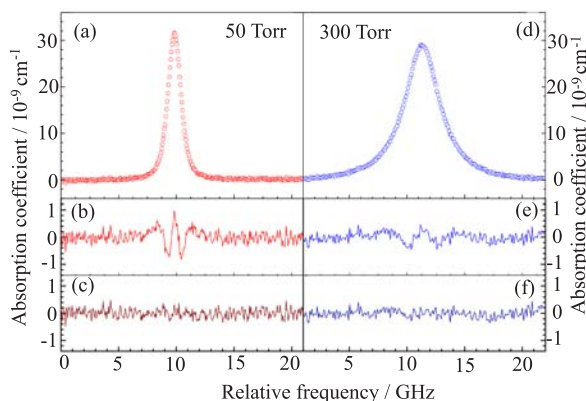


FIG. 2 Fit of the profile of the H₂¹⁶O line at 12635.546 cm⁻¹ broadened by CO₂. (a) Observed spectrum of the 12635.546 cm⁻¹ line broadened by CO₂ of 50 Torr. (b) and (c) are the residuals of the fit of spectrum (a) using the Voigt and Galatry profiles, respectively. (d) Observed spectrum of the H₂¹⁶O line broadened by CO₂ of 300 Torr. (e) and (f) are the residuals of the fit of spectrum (d) using the Voigt and Galatry profiles, respectively.

mental noise level.

The H₂¹⁶O line positions derived from the fitting have a linear dependence on the CO₂ pressure. The results are illustrated in Fig.3. Linear fit of the line positions yields the water line center at zero CO₂ pressure and the collision-induced line shift coefficient. The results are collected in Table I. The obtained line shift coefficients vary considerably from $-0.03 \text{ cm}^{-1}\text{atm}^{-1}$ ($5_{23}\leftarrow 4_{22}$ line at 12687.066 cm⁻¹) to about $+0.02 \text{ cm}^{-1}\text{atm}^{-1}$ ($2_{02}\leftarrow 1_{01}$ line at 12609.073 cm⁻¹). The line positions obtained in this work agree well with our previous measurements using low-pressure pure water vapor [12]. The differences are within the combined standard deviations of both studies, except for the line at 12687.066 cm⁻¹. The position of this line determined in this work differs from our previous study by $1.3 \times 10^{-4} \text{ cm}^{-1}$, which is about 3.5 times of the statistical deviation. It is probably a result of the considerably large CO₂ pressure-induced frequency shift coefficient of this line and the uncertainty of the CO₂ pressure: one Torr difference of the CO₂ pressure will induce a $4 \times 10^{-5} \text{ cm}^{-1}$ difference on the H₂O line position.

The CO₂ pressure-induced half widths, which are also derived from fit of the observed spectra, are shown in Fig.4. The CO₂ pressure-induced broadening coefficients of respective transitions can be derived from a linear fit of the half widths, and the results are listed in Table I. The uncertainty on the γ_{CO_2} values obtained in this work is 0.7% in average. As an comparison, Sagawa *et al.* reported the CO₂-broadening coefficients of water lines in the 18–102 cm⁻¹ region with an average uncertainty of 2.4% using a terahertz time-domain spectrometer [24], and Poddar *et al.* reported the γ_{CO_2} values of 10 for water lines in the 819–833 nm region with an average uncertainty of 2% [25].

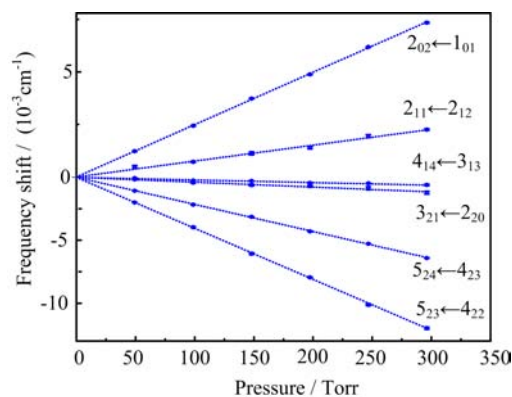


FIG. 3 CO₂ pressure-induced line shifts of six H₂¹⁶O lines of the $\nu_2+3\nu_3$ band.

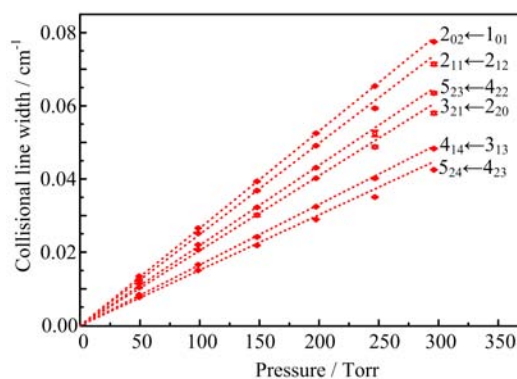


FIG. 4 CO₂ pressure-induced half widths of six H₂¹⁶O lines of the $\nu_2+3\nu_3$ band.

It is worth noting that owing to the high sensitivity of the cavity ring-down spectrometer applied in this work, we are able to obtain sufficient signal-to-noise ratio with relatively low water vapor pressures, which are typically 0.1–0.5 Torr in the present work. Such a low water vapor pressure reduces the interference of the broadening effects from self-collisions among the water molecules. According to the broadening coefficients given in HITRAN [1], the self-broadening coefficients $\gamma_{\text{H}_2\text{O}}$ are typically one order of magnitude larger than the air-broadening coefficients γ_{air} . We have shown that the self-broadening effect can be detectable when the water vapor pressure is over 2 Torr [12]. In Ref.[24], 4 Torr of water vapor was used, and 20 Torr of water vapor was used in Ref.[25]. The ratios of the CO₂-broadening coefficients γ_{CO_2} from this work to the air-broadening coefficients γ_{air} from HITRAN vary from 1.37 to 1.97. It coincides with that of the transitions with the same rotational quantum number J of the bands ν_1 , $2\nu_2$, ν_3 [26], and $2\nu_1+\nu_2+\nu_3$ [25]. Further investigation is needed for a better understanding of the collisions between the water molecule and other perturbing gases.

IV. CONCLUSION

Six CO₂-broadened H₂¹⁶O absorption lines in the 788–795 nm region are studied by a cavity ring-down spectrometer calibrated with precise atomic transitions. The line positions and the pressure-induced frequency shifts have been determined with an accuracy in the order of 10⁻⁵ cm⁻¹. The CO₂ pressure-induced broadening coefficients are determined with an relative uncertainty less than 1%. The measured CO₂-broadening coefficients are found to be 1.37–1.97 times of the air-broadening coefficients. The determined γ_{CO_2} coefficients of H₂O transitions can be useful in the studies of the radiative transfer on Venus and Mars, and also in the modeling of combustion process.

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