H_2O ABSORPTION LINE SHIFTS OF THE $\nu_1 + 3\nu_3$ BAND CAUSED BY PRESSURE OF H_2, CO_2, AND H_2O

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Measurement and calculational results on shifts and widths of the H_2O *absorption lines of the* $\nu_1 + 3\nu_3$ *band caused by self–pressure and by pressure of* H_2 *and* CO_2 *are presented. The measurements have been carried out using a dual–channel optoacoustic spectrometer with a tunable ruby laser. The coefficients of shift and broadening are calculated using the Anderson–Tsao–Curnutte–Frost method. The results are compared to the published data. Some possible physical mechanisms for explaining deviation of measured pressure behavior of the* H_2O *line shift caused by* H_2 *pressure from a linear one are discussed.*

The broadening and shift coefficients of H_2O rovibrational lines for the case of nitrogen, oxygen, and air broadening gases have been already measured for 15 vibrational bands and for more than 600 lines in the visible and IR spectral regions.[1–20] Such measurements were first of all needed for solving direct and inverse problems of the radiation transfer through planetary atmospheres.

The H_2O absorption line shifts in binary mixtures with different atomic and molecular gases could be interesting for studying physics of intermolecular forces in gases. As is noted in Ref. 20, quantitative information about broadening and shifts of spectral lines of the H_2O molecule by such light gases as He and H_2 can be used for estimating cross sections of collision of vibrationally excited H_2O molecules with He atoms and H_2 molecules, which are the basic gaseous components of stellar atmospheres, and for investigating the processes of light–induced drift in stellar atmospheres.

The first measurements of the pressure behavior of the H_2O rovibrational line shift by H_2 pressure in the $\nu_1 + 3\nu_3$ band (visible spectral region) have already revealed its nonlinearity.[8,20] Such a nonlinear behavior cannot be explained within the framework of the ATCF theory[21–23] which only allows one to describe basic regularities in the behavior of the shift coefficients during the collisions of the H_2O molecule with heavier diatomic molecules like N_2 or O_2 (see, e.g., Refs. 24 and 25). When discussing the experimental results we proposed to advance the experimental studies in order to try to elucidate the role of orientational effects, trajectories with torsion, and some other factors.

This paper presents the results of measurements and calculations of shifts and broadening of the H_2O absorption lines of the $\nu_1 + 3\nu_3$ band by self–pressure and by pressure of H_2 and CO_2. The measurements were aimed at obtaining additional information that could be useful for explaining the nonlinear dependence[20] of the H_2O absorption line shifts on H_2 pressure.

A dual–channel optoacoustic spectrometer with a tunable ruby laser was used in these measurements. The spectrometer[1,6] provided spectral resolution about 0.015 cm^{-1} and threshold sensitivity with respect to the absorption coefficient of $5{\cdot}10^{-8}$ cm^{-1}. The range of frequency tuning is from 14397 to 14405 cm^{-1}. Two optoacoustic cells were installed one after another along the axis of the laser beam. The first cell was filled with pure water vapor under a pressure of several Torr, the second with mixture of water–vapor and a buffer gas under a pressure $P_{\rm buff} \gg P_{H_2O}$ or with water vapor under a higher pressure (for measuring self–broadening and self–shift). Thus, in this experiment the contour of pure water vapor absorption line under low pressure with unshifted central frequency was recorded simultaneously with the contour of the same line broadened and shifted by a foreign gas pressure. The laser radiation frequency was tuned discretely from pulse to pulse. The spectral width and variations in the laser radiation frequency were controlled with a Fabry–Perot interferometer providing the spectral resolution of 0.002 cm^{-1}.

The collisional width of an absorption line and the broadening coefficient were found from measurements of the H_2O absorption line contour made in the second optoacoustic cell, while the widths of the H_2O absorption line contours were determined according to the technique taken from Ref. 26. The shift was determined directly as a difference between central frequency of a line contour measured in the mixture of water vapor and a buffer gas (the second cell) and that of a line contour measured in pure water vapor under a low pressure (the first cell). Let us estimate the error in measuring a shift of a maximum of an absorption line contour.[27] In measurements of the absorption line contour shape using a single–channel optoacoustic spectrometer with pulsed lasers the generation wavelength of which is tuned discretely, from pulse to pulse, one records, as a rule, the wavelength shift $\Delta\lambda_i = \lambda_i - \lambda_0$ with respect to the absorption line center λ_0 or to the wavelength of radiation of the first pulse.

In the described experimental setup the wavelength shift of a pulsed ruby laser with narrow spectrum ($\Delta\nu \sim 10^{-2}$ cm^{-1}) was measured using a Fabry–Perot interferometer based on the measurements of diameters of the interference fringes. Relative error of the value $\kappa(\Delta\lambda_i)$ measured in the optoacoustic experiments can be represented in the form

$$\frac{\delta k}{k} = \frac{\delta k_0}{k_0} + \frac{[\partial g(\Delta\lambda)/\partial(\Delta\lambda)]\delta(\Delta\lambda)}{g(\Delta\lambda)}\,, \qquad (1)$$

where κ_0 is the value of the absorption coefficient at the central frequency of a line and $g(\Delta\lambda)$ is the function normalized by unit area that describes the contour shape. The contour of a pure water vapor absorption line is measured at a low (several Torr) pressure in the first OA cell. The absorption line contour is described in this case by a Gaussian distribution

$$g(\Delta\lambda) = \frac{2\sqrt{\ln 2}}{\sqrt{\pi}}\frac{1}{\gamma_\mathrm{D}}\exp\left[\frac{(2\sqrt{\ln 2})^2/\Delta\lambda^2}{\gamma_\mathrm{D}^2}\right]. \tag{2}$$

The error in referring the measured values of κ to the wavelength is described by the second term of Eq. (1) which, after substituting Eq. (2) into Eq. (1), takes the form

$$\alpha_\mathrm{D} = 2(2\sqrt{\ln 2})^2\left(\frac{\Delta\lambda}{\gamma_\mathrm{D}}\right)^2\left[\frac{\delta(\Delta\lambda)}{\Delta\lambda}\right]. \tag{3}$$

For the mixture of H_2O vapor and a buffer gas a total pressure in the second cell corresponds, as a rule, to a collisional mechanism of broadening when the absorption line contour is close to the Lorentzian and is described by the function

$$g(\Delta\lambda) = \frac{1}{2\pi}\frac{\gamma_\mathrm{L}}{(\Delta\lambda)^2 + \gamma_\mathrm{L}^2/4}. \tag{4}$$

By substituting Eq. (4) into Eq. (1) we obtain the equation similar to Eq. (3)

$$\alpha_\mathrm{L} = \frac{2(\Delta\lambda)^2}{(\Delta\lambda)^2 + \gamma_\mathrm{L}^2/4}\frac{\delta(\Delta\lambda)}{\Delta\lambda}. \tag{5}$$

Characteristic diameter D_i of a fringe of an interference pattern formed by a Fabry––Perot etalon used for determining the wavelength shifts from the fringes diameters is about 1 cm. This value is typical of an interferometer with the 2–3 cm spacing and an objective with a focal length of 50 cm. Taking into account that $\delta(\Delta\lambda)/\Delta\lambda$ is approximately equal to $4\,\Delta D_i/D_i$ and $\Delta D_i/D_i$ is about 1% in processing of interferograms with a microphotometer, we obtain the estimate ≤ 4% of the value $\delta(\Delta\lambda)/\Delta\lambda$. When measuring the shifts of maxima of the absorption line contours, it is sufficient to tune the laser radiation wavelength in a relatively narrow wavelength interval $\Delta\lambda \ll \gamma_\mathrm{D}$ or γ_L in the vicinity of the absorption line center. Then for $\Delta\lambda/\gamma_\mathrm{D} = 0.2$ we obtain $\alpha_\mathrm{D} \le 1\%$ and for $\Delta\lambda/\gamma_\mathrm{L} = 0.2$ the value $\alpha_\mathrm{L} \le 1.2\%$, respectively. Thus, total error of measurements of the difference between central frequencies of the absorption line contours measured in both OA cells can be as low as 2.2%. It should also be noted that the self–broadening effect is eliminated when the coefficients of broadening and shift of absorption caused by a foreign gas pressure are measured with a dual–channel optoacoustic spectrometer whose absorbing gas pressures in the measuring cells are equal. The effect of fluctuations of the laser radiation spectrum width and shape from pulse to pulse is also minimized.

When small shifts are measured, e.g., when the shift of H_2O absorption lines caused by its own pressure and the pressure difference in measuring optoacoustic cells is small enough (about 10–15 Torr) it is more convenient to record the derivative of the resonance absorption line contour, with respect to frequency detuning. Depicted in Fig. 1 are the derivatives $d\kappa(\Delta\nu)/d(\Delta\nu)$ for the H_2O line 694.380 nm measured under two different pressures. The distance between the coordinates of the points of the curves intersection with $\Delta\nu$ axis corresponds to the value of the pressure shift of the absorption line (~ 0.003 cm^{-1}). At a pressure difference in the measurement cell below 10 Torr measurement errors do not allow one to detect a line center shift. Measurement results on self–broadening presented in Fig. 1 enable one to estimate the resolution of the experimental instrumentation at the level of 0.001 cm^{-1} when measuring the shift of an isolated absorption line.

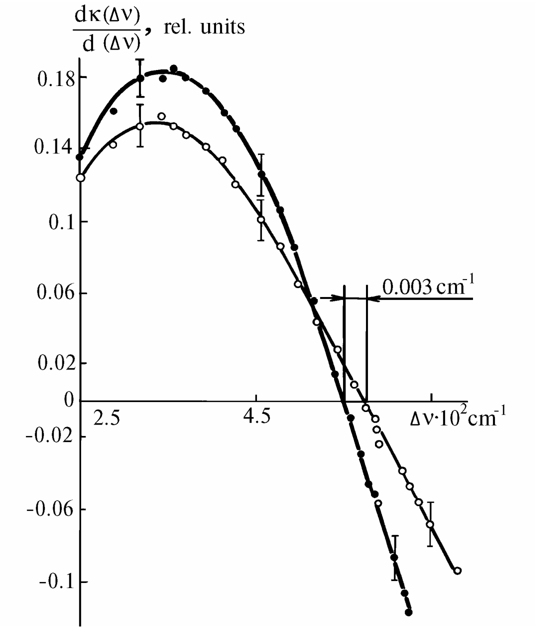

FIG. 1. Derivatives of the 694.380 nm H_2O *absorption line contour for pressures* $P_{H_2O} = 18.8$ Torr *(dots) and* $P_{H_2O} = 0.4$ Torr *(circles).*

Measurement results on the coefficients of shift and broadening of the H_2O absorption lines falling into the wavelength interval of a ruby laser generation are demonstrated in Figs. 2 and 3 and in Table I. Figure 2 shows the shift and line half–width of one of the three H_2O absorption lines as functions of the CO_2 pressure and Fig. 3 depicts a nonlinear dependence of the H_2O line shift with small values of $K_a = 0.1$ on the pressure of a light buffer gas (H_2). The half–widths of all of the three lines have linear dependence on H_2 pressure, provided that the latter is below 400 Torr.

To process the experimental results we used the algorithm for fitting the experimental contour measured over points to the Voigt contour proposed by Belbruno et al.[28] Thus the coefficients of broadening and shift by pressure of each of the buffer gas were determined. Listed in Table I are the coefficients of H_2O line shift caused by H_2 pressure, which were determined for pressures below 400 Torr. When the H_2 pressure increases to 760 Torr the shift of the lines 694.380 and 694.237 nm nonlinearly depends on H_2 pressure.

The same table presents the broadening and shift coefficients calculated using the ATCF method. The calculational method for the case of H_2O molecule collisions with diatomic symmetric molecules is given in detail in Ref. 25. The contributions of dipole–dipole, dipole–

quadrupole, quadrupole–dipole, quadrupole–quadrupole, and polarization (induction and dispersion) interactions were taken into account in calculations of self–broadening and self–shift coefficients. In the case of H_2 and CO_2 broadening, dipole–quadrupole, quadrupole–quadrupole, and polarization interactions were taken into account. The calculated coefficients of self–shift and self–broadening are in a satisfactory agreement with the measured ones.

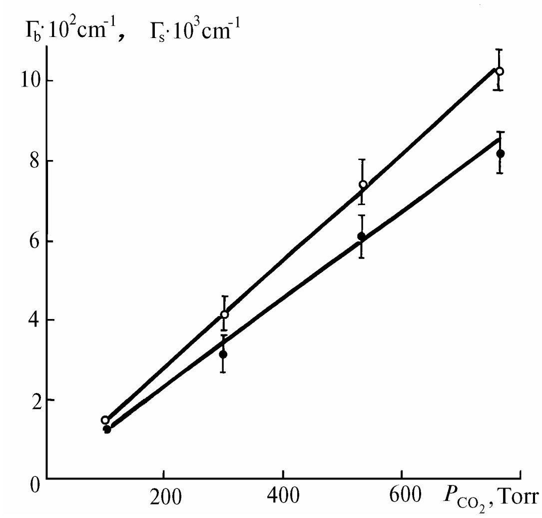

FIG. 2. Half–width Γ_b *(circles) and the* 694.380 nm H_2O *absorption line center shift* Γ_s *(dots) as functions of the carbon dioxide pressure.*

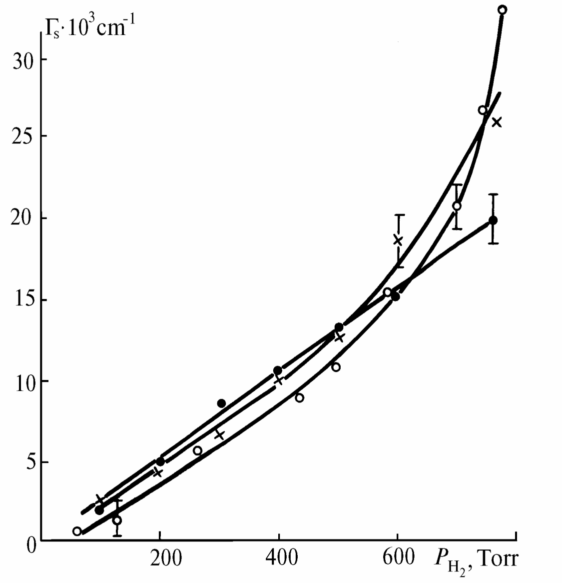

FIG. 3. The absorption line center shifts for 694.380 nm *(circles),* 694.237 nm *(crosses), and* 694.215 nm *(dots)* H_2O *absorption lines as functions of* H_2 *pressure.*

TABLE I. Broadening (Γ_b) *and shift* (Γ_s) *coefficients for* H_2O *absorption lines in the vicinity of* 0.69 μm.

$(J\ K_a\ K_c)\ (J\ K_a\ K_c)$	Frequency, cm^{-1} (wavelength, μm)	Foreign gas	Γ_s, $cm^{-1}\cdot atm^{-1}$ experiment	Γ_s, $cm^{-1}\cdot atm^{-1}$ calculations	Γ_b, $cm^{-1}\cdot atm^{-1}$ experiment	Γ_b, $cm^{-1}\cdot atm^{-1}$ calculations
		H_2O	0.015±0.004	0.014	0.570±0.01	0.600
4 1 4 5 1 5	14397.364	CO_2	−0.008±0.001	−0.010	0.103±0.05	0.114
	(694.380)	H_2*	−0.015±0.001	−0.013	0.056±0.04	0.065
		H_2O	0.010±0.003	0.007	0.554±0.01	0.615
4 0 4 5 0 5	14400.328	CO_2	0.001±0.001	−0.014	0.113±0.07	0.152
	(694.237)	H_2*	−0.018±0.002	−0.011	0.073±0.005	0.082
		H_2O	−0.016±0.006	−0.020	0.585±0.01	0.575
3 2 1 4 2 2	14400.782	CO_2	−0.013±0.001	−0.005	0.138±0.007	0.123
	(694.215)	H_2*	−0.019±0.002	−0.016	0.079±0.005	0.091

* The shift coefficient caused by H_2 pressure was determined in the pressure interval 100 to 400 Torr (see Fig. 3).

Deviations of the pressure behavior of the H_2O absorption line shifts from a linear one observed in these experiments for H_2 as a buffer gas, have not been detected earlier for mixtures of H_2O with other molecular (N_2, O_2, air) and atomic (Ne, Ar, Kr, Xe) gases.[6] The theory developed in Refs. 24 and 25 for describing shifts of H_2O rovibrational lines by pressure of gases composed of diatomic symmetric molecules cannot explain the obtained results.

We think that the anomalous behavior of the H_2O absorption line shift can be explained by several physical mechanisms.

1. The increase in time of interaction between the H_2O and H_2 molecules with their relative motion along spiral trajectories. At such a motion the time of H_2O and H_2 molecule interactions increases that can lead to increase of the probability of collisional interaction for H_2O–H_2 pair with another molecule of H_2. From the physical point of view the appearance of spiral trajectories can be accounted for by an increased contribution of short–range forces and an anisotropic component of the intermolecular interaction potential. The fact that the shift nonlinearity is observed for the lines with low rotational energy (K_a = 0.1) indirectly favours this hypothesis. However the assumption[20] that orientational effects can be noticeable in the line shifts in the H_2O and CO_2 mixtures, in which strongly orientational interaction resulting in formation of H_2CO_3 compound can occur, was not confirmed by the measurements made in Ref. 20. For those absorption lines whose shift in the H_2O–H_2 mixture is linear, in the H_2O–CO_2OH mixture it linearly

depends on CO_2 pressure to 760 Torr. The effect of trajectory curvature of colliding molecules on the spectral line shift was theoretically analyzed in Ref. 29.

2. The nonlinear dependence of the CO absorption line shift in the 0–1 band when the He buffer gas pressure increases to 4 atm is accounted for[30] by the effect of interference of spectral lines. The parameter of cross–relaxation determining the effect under the experimental conditions[30] does not exceed 10^{-2} what makes up about 20% of the width of the corresponding line. The relations between the cross–relaxation parameters for NH_3 in N_2 (Ref. 31) and for a pure rotational spectrum of H_2O in O_2 and N_2 are similar in magnitude.[32] The estimate of the cross–relaxation parameter made under the conditions of our experiment using the algorithm[30] gives the value 0.5 for the investigated H_2O lines what is several times larger than the linewidth. Such a disagreement casts some doubts upon the fact that in our situation the line interference is the basic mechanism of nonlinear dependence of the H_2O absorption line shift on H_2 pressure.

3. It should be also taken into account the possibility of incomplete applicability of the ATCF theory to describing collisions of the H_2O and H_2 molecules, in particular, the need for quantum–mechanical description of relative motion of molecules as well as of the dependence of collision parameters on specific properties of the velocity distribution over the ensemble H_2O–H_2 discussed, e.g., in Ref. 33.

4. It would be reasonable to estimate the influence of the Dicke effect on the pressure dependence of shift as in the case of the H_2O line broadening by N_2 pressure.[34]

In our further investigations of the H_2O absorption line shifts the measurements are planned to be done for different bands at different temperatures and for a wider set of buffer gases.

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