DETECTION OF NONLINEAR PRESSURE BEHAVIOR OF THE H₂O ROVIBRATIONAL LINE SHIFT CAUSED BY H₂ PRESSURE

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The values of broadening and shift coefficients induced by H_2 *pressure for the* H_2O *absorption lines centered at* 694.38 nm *for* $4_{14}-5_{15}$ *transition of* 000-103 *band were measured. Deviation of the* H_2O *absorption line center shift dependence on* H_2 *pressure from linear behavior at pressure increasing beyond* 450-500 Torr *was recorded in the experiment. This phenomenon had not been observed earlier for none of the mixtures of* H_2O *with atomic (* Ne, Ar, Kr, Xe *) and molecular (* N_2, O_2, *air) gases.*

Measuring the broadening and shift coefficients induced by foreign gases pressure for H_2O absorption lines is of current interest for the investigation of the intermolecular interaction processes in gases as well as for solving direct and inverse problems of optics of planetary atmospheres.

The broadening and shifting coefficients of the H_2O rovibrational absorption line shifts induced by nitrogen, oxygen, and air pressure have been studied experimentally and theoretically for a great number of lines in the near, middle IR, and visible regions.[1–7] The connection between the magnitudes of H_2O line shifts in the 000–103 band and electrooptical characteristics of atoms (He, Ne, Ar, Kr, Xe) and small molecules (N_2, O_2, CO), i.e., between the polarizability and the quadrupole moment has been investigated in Ref. 8. The advanced ATCF method (Anderson – Tsao – Curnutte – Frost) proposed by A.D. Bykov et al.[9] and used for interpreting the obtained experimental data[1–4,7] enables one to calculate the value of a line center shift with an error less than 20% for 70–80% of all measured lines in the IR and visible regions.

Investigation of the behavior of H_2O spectral line broadening and shifting by such light gases as H_2 and He is of great interest. The qualitative information about shift coefficients in the H_2 and He atmosphere may be used to estimate collisional cross sections of the vibrationally excited H_2O molecules with H_2 molecules and He atoms and to study light induced drift (LID) processes in the stellar atmospheres. Moreover, in contrast to collisions of H_2O molecules with heavy enough N_2 or O_2 molecules, some new peculiarities of the behaviour of H_2O line center shift may be expected at collisions of H_2O molecules with H_2 due to the increase of contribution of short–range acting part of the intermolecular interaction potential and influence of forces of the hydrogen bond between the oxygen atom in H_2O molecule and hydrogen atoms of H_2 molecule.

This paper presents measurement data on the values of broadening and shifting coefficients of an individual H_2O absorption line centered at 694.38 nm for $4_{14}-5_{15}$ transition in the 000–103 band induced by H_2 pressure. These measurements continue the previous ones[8] aimed at observation of the influence of electrooptical parameters

of a buffer gas particles on the magnitude of broadening and shifting coefficients of the H_2O absorption line used as the reference line in sounding the concentration of H_2O molecules in the atmosphere.[10]

The measurements have been carried out using the dual–channel opto–acoustic spectrometer with frequency–tuned ruby laser providing the spectral resolution 0.015 cm⁻¹, absorption coefficient threshold sensitivity ∼ 5·10⁻⁸ cm⁻¹, and the frequency tuning region from 14397 to 14405 cm⁻¹.

The laser radiation passed through the cells of the opto–acoustic detectors OAD–1 and OAD–2 placed one after another on the optical axis of the laser beam. The first cell was filled with a pure water vapor under pressure ≃ 5 Torr, the second with a mixture of water vapor and buffer gas, where $P_{buf} \geq P_{H_2O}$.

The absorption line shapes of the pure water vapor and water vapor in a binary mixture with buffer gas under condition in which the ruby laser frequency generation varied from pulse to pulse were recorded simultaneously in the experiment. Monitoring the frequency variation was carried out with the help of a Fabry–Perot interferometer with the resolution ∼ 0.002 cm⁻¹.

The values of broadening coefficients were determined from the measured linewidth γ of the H_2O absorption line in the second cell by the formula[11]

$$\gamma^2 = 4B_2^2(0.729 + 0.526A + 0.95A^2) \, ,$$

where $B_2 = \gamma_D\left(2\sqrt{\ln 2}\right)^{-1}$; $A = (B_1/B_2)$; $B_1 = (\gamma_{col}/2)$, γ_D and γ_{col} are the Doppler and collisional widths of the H_2O absorption line, respectively. The magnitude of the shift was measured directly from the shift of the line shape maximum of a gas mixture in the second cell with respect to the pure H_2O line shape maximum under low pressure.

The shift and width values of the H_2O absorption line of interest measured under condition of H_2 pressure increase are presented in Figs. 1 and 2 together with the interval of measurement errors. Figure 1 presents also the plot of the same H_2O line shift by air pressure.

The behavior of the H_2O line center shifts broadened by air distinctly differs from that broadened by H_2.

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Starting with the pressure of 450–500 Torr the dependence of shift on H_2 pressure becomes nonlinear. In contrast to shift, the dependence of the H_2O absorption linewidth on the H_2 pressure is exactly linear (Fig. 2).
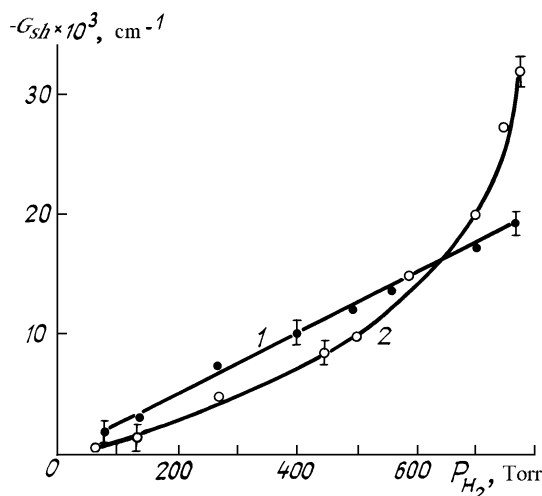

FIG. 1. Dependence of the shift (G_{sh}) of H_2O absorption line centered at 694.38 nm on pressure of a broadening gas (curve 1 for H_2 and curve 2 for air).
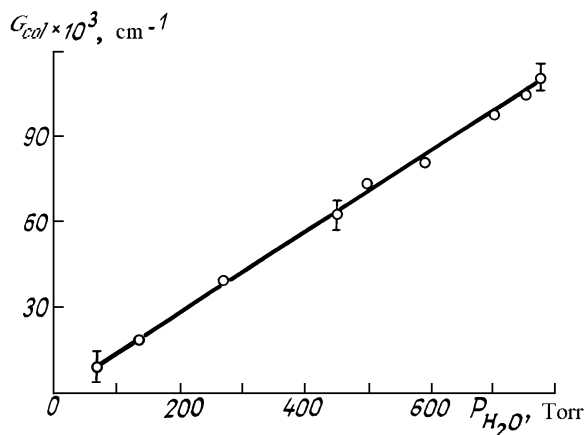

FIG. 2. Plot of the collisional width (G_{col}) of the H_2O absorption line shape (694.38 nm) vs H_2 pressure.

TABLE I. Shifting and broadening coefficients of absorption line (694.38 nm) of H_2O mixed with diatomic molecules.

Broadening gas		Shifting coefficient G_{sh} MHz/Torr	Broadening coefficient G_{col} MHz/Torr
The molecule type	The value of the molecule quadrupole moment		
O_2	−0.39	−1.06 ± 0.04	5.2 ± 0.3
N_2	−1.52	−0.67 ± 0.02	7.5 ± 0.3
H_2	+0.651	−0.59 ± 0.04*	4.4 ± 0.4

* The magnitude of G_{sh} for H_2 molecule is averaged in the 200–500 Torr pressure interval.

The table presents the values of broadening and shifting coefficients of the H_2O absorption line centered at 694.38 nm induced by diatomic molecules possessing the quadrupole moment. The shifting coefficient is determined for the H_2 pressure interval up to 500 Torr. In this interval the shift can be considered linearly dependent on pressure within the experimental error.

Nonlinear behavior of the H_2O absorption line center shift discovered in the experiment with further increase of H_2 pressure have never been observed for any of the atomic (Ne, Ar, Kr, He) and molecular (N_2, O_2, air) broadening gases.

The theory[7,9] fails to explain the H_2O shifts by diatomic symmetrical molecules observed in our experiments.

One of possible physical explanations of such a nonlinear dependence could be the increase of interaction time of H_2O and H_2 molecules moving along spiral paths and being involved in the interaction with another molecule of H_2 buffer gas.

The future supplementary experiments which clarify the interaction mechanism and explain the observed effect could be the following:

— comparison of the dependences of the H_2O absorption line shifts on H_2 and He pressures for various rovibrational bands and

— careful measurements of the absorption line shifts of H_2O in a mixture with CO_2 in which the deviations from linearity can occur due to the strong interaction (at certain orientations) between H_2O and CO_2 molecules leading to formation of H_2CO_3 complex.

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