

## STUDY OF PRESSURE BROADENING AND SHIFTS OF THE 103 BAND OF WATER VAPOR CAUSED BY ATOMIC AND MOLECULAR GASES

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*Measurements of the broadening and shift coefficients of the absorption lines of the 103 band and of H<sub>2</sub>O centered at 694.215, 694.237, and 694.38 nm have been carried out in binary mixtures of atomic and molecular gases with the help of a dual-channel opto-acoustic spectrometer. It was found that in broadening by atomic gases or molecular gases that possess an intrinsic quadrupole moment, the frequency shift of all the lines is negative and comparable in magnitude with the Doppler width. In the case of broadening by the rare gases the shift coefficient for the H<sub>2</sub>O absorption line in contrast with the broadening coefficient is a nonlinear function of the atomic polarizabilities of the gases. In the case of a binary mixture of H<sub>2</sub>O vapor and acetone the pressure-induced shift coefficient for the lines under study differs both in magnitude and sign.*

Measurements of the coefficients of pressure broadening and shifts of spectral lines by foreign gases are of great interest for the study of the interaction between atoms and molecules in gases. In addition, information about broadening and shifts of the H<sub>2</sub>O lines is necessary in order to develop methods for calculating of the propagation of narrow-band optical radiation in the atmosphere and to accurately determine the H<sub>2</sub>O concentration in the atmosphere with the help of lidar systems.

At the present time the experimental and theoretical study of shifts of the H<sub>2</sub>O absorption line caused by nitrogen, oxygen, and air pressure continues to develop apace.<sup>1-9</sup> Nevertheless, in spite of the great amount of data that is available, simultaneous measurements of shifts and broadening coefficients of the H<sub>2</sub>O line as functions of changes in the properties and characteristics of the broadening gases (both atomic and molecular) yet remain to be done. The only work we know of where the shift coefficients of the 010 band of two H<sub>2</sub>O lines broadened by the rare gases (He, Ne, Ar, Kr, and Xe) were measured is Ref. 9. However, for the H<sub>2</sub>O absorption lines corresponding to transitions to high vibrational states (near-IR and visible ranges) such data are not available.

Measurements of the broadening and shift coefficients for the 103 band of the three H<sub>2</sub>O absorption lines centered at the wavelengths 694.215, 694.237, and 694.380 nm, broadened by atomic (He, Ne, Ar, Kr, and Xe) and molecular (N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, and air) gases which possess an intrinsic quadrupole moment, and by acetone (a dipolar molecular gas) are the purpose of this work. These H<sub>2</sub>O lines are interesting because they are working lines in the sounding of humidity profiles using a ruby-laser based DIAL lidar system.<sup>10</sup>

Measurements were carried out using a dual-channel opto-acoustic spectrometer<sup>3,12</sup> with a ruby

laser. The spectral resolution of the spectrometer was  $\leq 0.015 \text{ cm}^{-1}$  the absorption coefficient limiting sensitivity was  $5 \cdot 10^{-8} \text{ cm}^{-1}$ , the frequency tuning region lay between 14397 and 14405  $\text{cm}^{-1}$  the lasing pulse duration was  $(40 \pm 10) \cdot 10^{-9}$  sec, and the pressure of the investigated gas lay in the range 0.1–760 Torr.

The laser beam was transmitted through the cells of two opto-acoustic detectors (OAD-1 and OAD-2) placed one after the other along the optical axis of the laser beam. The cells were connected by a vacuum pump system and a gas bleed-in system. The first cell was filled with pure water vapor at a pressure of  $\leq 5$  Torr, the second – with the same amount of water vapor mixed with a buffer gas,  $P_{buf} \gg P_{H_2O}$ . The shape of the amplitude of the electrical signals from each OAD was recorded as a function of frequency for discrete changes in the lasing frequency of the ruby laser.

Thus, the shapes of the same H<sub>2</sub>O absorption line for two different pressures of the buffer gas were recorded simultaneously. Each series of measurements was repeated three times. Table I lists the average values of the measured shift coefficients  $\Gamma_{sh}$  and broadening coefficients  $\Gamma_b$  of the H<sub>2</sub>O absorption lines.

The values of the broadening coefficient  $\Gamma_b$  were determined from the collisional spectral linewidth  $\gamma_{col}$ , the latter determined from the measured linewidth  $\gamma$  by the expression<sup>11</sup>

$$\gamma^2 = 4B_2^2(0.729 + 0.526 + 0.95 \cdot A^2), \quad (1)$$

where  $B_2 = \gamma_D(2\sqrt{\ln 2})^{-1}$ ,  $A = B_1/B_2$ ,  $B_1 = \gamma_{col}/2$ , and  $\gamma_D$  is the Doppler half-linewidth. Analysis of the experimental data allows us to make the following remarks:

TABLE I. Broadening ( $\Gamma_b$ ) and shift ( $\Gamma_{sh}$ ) coefficients for H<sub>2</sub>O spectral lines measured with the help of a ruby-laser spectrometer.

Line position, nm	Buffer gas	$\Gamma_{sh}$ , MHz/Torr	$\Gamma_b$ , MHz/Torr
694.215	air	$-0.65 \pm 0.02$	$6.9 \pm 0.2$
	O <sub>2</sub>	$-1.04 \pm 0.04$	$5.3 \pm 0.3$
	CO <sub>2</sub>	$-0.51 \pm 0.02$	$10.9 \pm 0.5$
	N <sub>2</sub>	$-0.53 \pm 0.02$	$7.3 \pm 0.3$
	Xe	$-1.66 \pm 0.04$	$8.1 \pm 0.6$
	CH <sub>3</sub> -CO-CH <sub>3</sub>	0	$25.7 \pm 0.5$
694.237	air	$-0.52 \pm 0.04$	$6.9 \pm 0.3$
	O <sub>2</sub>	$-1.05 \pm 0.04$	$5.7 \pm 0.3$
	CO <sub>2</sub>	$-0.04 \pm 0.02$	$8.9 \pm 0.3$
	N <sub>2</sub>	$-0.36 \pm 0.04$	$7.2 \pm 0.3$
	Xe	$-1.50 \pm 0.08$	$8.8 \pm 0.6$
	CH <sub>3</sub> -CO-CH <sub>3</sub>	$+3.04 \pm 0.09$	$20.4 \pm 0.6$
694.380	air	$-0.76 \pm 0.04$	$7.2 \pm 0.4$
	O <sub>2</sub>	$-1.06 \pm 0.04$	$5.2 \pm 0.3$
	CO <sub>2</sub>	$-0.32 \pm 0.04$	$8.1 \pm 0.3$
	N <sub>2</sub>	$-0.67 \pm 0.02$	$7.5 \pm 0.3$
	He	0	$1.9 \pm 0.3$
	Ne	$-0.18 \pm 0.06$	$2.1 \pm 0.3$
	Ar	$-1.39 \pm 0.06$	$4.2 \pm 0.4$
	Kr	$-1.68 \pm 0.04$	$5.9 \pm 0.5$
	Xe	$-1.68 \pm 0.08$	$7.3 \pm 0.6$
	CH <sub>3</sub> -CO-CH <sub>3</sub>	$-0.54 \pm 0.03$	$11.6 \pm 0.3$

1. When the H<sub>2</sub>O vibrational-rotational line was broadened by atomic gases and by small molecules which possess an intrinsic quadrupole moment, the frequency shift of the absorption line center was negative.

2. For broadening by rare gases the shift coefficient  $\Gamma_{sh}$  and the collisional broadening coefficient  $\Gamma_b$  depend in a different way on the polarizability  $\alpha$  of the rare gas atoms (Fig. 1). While the dependence of  $\Gamma_b$  on  $\alpha$  is almost linear, the dependence of  $\Gamma_{sh}$  is a complicated function of  $\alpha$ .

3. When the H<sub>2</sub>O lines are broadened by molecules with a constant quadrupole moment, the coefficient  $\Gamma_b$  increases while the coefficient  $\Gamma_{sh}$  slightly decreases with increase of the quadrupole moment of the perturbing molecule for all three of the measured lines (Fig. 2). According to Ref. 3 this implies that the broadening coefficients are determined primarily by the electrostatic part of the intermolecular potential (the dipole-quadrupole interaction), and the shift coefficient — by the polarizing part of the intermolecular potential, and it is just the latter that introduces a negative contribution to the line frequency shift.

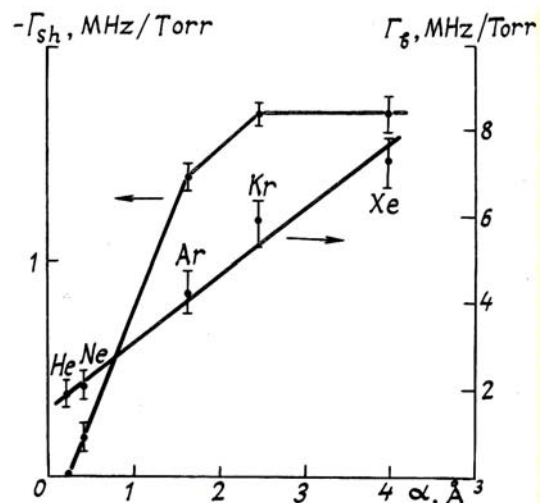


FIG. 1. Shift coefficients  $\Gamma_{sh}$  and collisional broadening coefficients  $\Gamma_b$  of H<sub>2</sub>O absorption line centered at 694.380 nm as a function of the polarizability of the inert buffer gases.

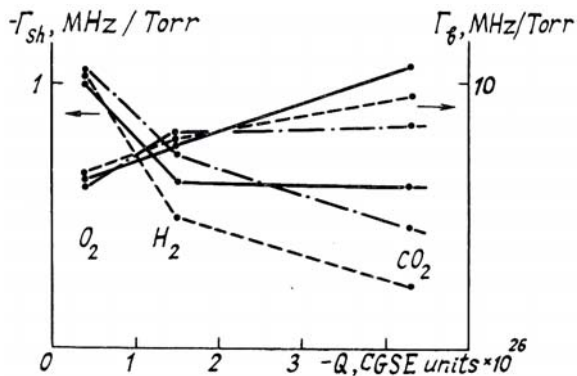


FIG. 2. Shift coefficients  $\Gamma_{sh}$  and collision broadening coefficients  $\Gamma_b$  of the  $\text{H}_2\text{O}$  absorption lines centered at  $694.215 \mu\text{m}$  (solid lines),  $694.237 \mu\text{m}$  (dashed lines), and  $694.380 \mu\text{m}$  (dot-dashed lines) as a function of the magnitude of the quadrupole moment of the molecules of the buffer gases.

4. In the case of  $\text{O}_2$ -broadening all three line shifts has the same magnitude while the differences in the magnitudes of the line shifts is the greatest under conditions of  $\text{CO}_2$ -broadening. This could be attributed to the fact that an increase in the quadrupole moment of molecules results in an increase in the contribution of the dipole-quadrupole interaction and, as a consequence, the dependence of the line shift on the molecular transition frequency becomes more pronounced.

5. Under conditions of air-broadening the values of  $\Gamma_{sh}$  and  $\Gamma_b$  are in good agreement with the values obtained using the empirical relations

$$\Gamma_b^{(\text{air})} = 0.79 \cdot \Gamma_b^{(\text{N}_2)} + 0.21 \cdot \Gamma_b^{(\text{O}_2)}, \quad (2)$$

$$\Gamma_{sh}^{(\text{air})} = 0.79 \cdot \Gamma_{sh}^{(\text{N}_2)} + 0.21 \cdot \Gamma_{sh}^{(\text{O}_2)}. \quad (3)$$

6. In the case of broadening by molecules with constant dipole moment  $\bar{\mu}$  when the dipole-dipole interaction makes the predominant contribution to the

intermolecular potential, the different line shifts can differ both in magnitude and sign. Thus, when the  $\text{H}_2\text{O}$  line broadening was due to acetone ( $\bar{\mu} = 3D$ ), the measured values of the shift coefficients for the lines centered at  $694.215$ ,  $694.237$ , and  $694.380 \text{ nm}$  were approximately  $0.0$ ,  $3.04$ , and  $0.54 \text{ MHz/Torr}$ , respectively. In our opinion, these features are caused by orientation effects in the interaction of the rather large dipolar molecule  $\text{CH}_3\text{-CO-CH}_3$  with the dipolar molecule  $\text{H}_2\text{O}$ .

A study of the temperature dependence of the shift coefficients should provide additional input for a quantitative interpretation of the experimental results, which, however, must be the subject of future work.

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