

Measurement of H₂O absorption line shifts induced by pressure of atmospheric gases in the region 1.06 μm

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A technique is developed for measurement of shift coefficients of absorption lines using intracavity laser spectroscopy. Line shifts for the H₂O $\nu_1 + \nu_2 + \nu_3$ and $\nu_2 + 2\nu_3$ bands are measured in the region of 9403–9414 cm⁻¹ with the aid of an intracavity Nd:glass laser spectrometer. The shift coefficients of eight H₂O absorption lines when inducing by pressure of O₂, N₂, and atmospheric air are between -0.004 and -0.029 cm⁻¹/atm.

Introduction

Investigation of line shifts of molecular gases, in particular, water vapor is of significant interest for study of intermolecular interactions in gases, as well as for development of laser sensing methods. Measurements of rotational-vibrational line shifts induced by pressure of atmospheric gases in the near-IR region are important for solution of different problems connected with optical radiation propagation in the atmosphere. In Ref. 1, it was shown that when narrow-band lasers and high-resolution spectral devices are used in sensing the atmospheric composition, absorption line shifts induced by the air pressure in the rotational-vibrational spectrum should necessarily be taken into account.

Water vapor line shifts are usually investigated using spectrometers allowing high-resolution of line profiles, namely, Fourier transform spectrometers, diode laser spectrophotometers, photo-acoustic spectrometers, as well as spectrometers employing a back-wave lamp operating in the microwave spectral range. For example, in Refs. 2 and 3, line profiles of the water vapor ν_2 band broadened by the He, Ne, Ar, Kr, and N₂ pressure were studied with the aid of diode and Fourier transform spectrometers. In Refs. 4 and 5, mass measurements of half-widths and nitrogen-pressure induced shifts of water vapor absorption lines were described.

The technique of intracavity laser spectroscopy, in contrast to other spectroscopic methods, allows shifts of weak lines to be studied both at high temperatures and high pressures. Two papers^{6,7} are now available, which demonstrate the feasibility of using intracavity spectroscopy for investigation of absorption line shifts. In Ref. 6, the nitrogen, hydrogen, and helium pressure induced shift and broadening coefficients of methane were measured in the region 727 nm at temperatures of 77 and 296 K. Reference 7 presents the data on shifts of water vapor

absorption lines induced by the hydrogen, air, and water vapor pressure.

When investigating absorption line shifts, the necessary condition of measurements is the use of frequency references, relative to which the spectrometer frequency scale is corrected. This paper presents the technique developed for correct measurement of shift coefficients of weak absorption lines by the method of intracavity spectroscopy. A temperature-stabilized Fabry–Perot interferometer was used as a frequency reference. Transmission peaks of the Fabry–Perot interferometer were recorded simultaneously with the studied absorption spectrum. In addition, the paper describes the measurement technique and the measured shifts of water vapor absorption lines induced by the pressure of different interfering gases.

Estimated broadening and shift coefficients

Line shift coefficients of the H₂O purely rotational spectrum or fundamental bands are usually small and equal to few percent of a line half-width. For lines in the near-IR and visible regions, shifts of nitrogen, oxygen, and air lines increase by an order of magnitude and can achieve 50% of a line half-width for weak transitions corresponding to large values of the angular momentum quantum number.

If the broadening coefficient far exceeds the shift coefficient, then it is very difficult to ensure sufficiently accurate measurements of a line position. Usually, at the signal-to-noise ratio of about 10, the shift-to-half-width ratio should exceed 0.1 for a line center to be obtained with an acceptable accuracy.

To determine the possibility of line shift correct measurement by the intracavity spectroscopy method, it is necessary to analyze possible ratios of shift coefficients to the broadening coefficients for different interfering gases. For this purpose, we used the known literature data on the simplest estimates

of the broadening and shift coefficients in the approximation of a transition mean frequency.⁸ Table 1 summarizes the calculated data on half-widths and shift coefficients of H₂O lines in the region of 1 μm and, for comparison, the data from Refs. 9 and 10. These data are necessary for assessment of the feasibility of applying intracavity spectrometers to measurement of H₂O line shifts induced by the pressure of different interfering gases. The shift-to-half-width ratio serves a criterion for selection of an interfering gas.

It follows from Table 1 that if nitrogen, acetylene, or carbon dioxide are used as an interfering gases, then the significant broadening of water vapor lines is observed at a small shift of the line center. If hydrogen, oxygen, argon, or krypton are used as interfering gases, then lines are less broadened and the error in determination of line center positions is much smaller than in the previous case.

Measurement technique

To record absorption line shifts in the region of 1.06 μm , we used an intracavity Nd:glass laser

spectrometer. The spectrometer description in more detail can be found in Ref. 11. The spectrometer was based on a pulsed Nd:glass laser operating in the free lasing mode.

The laser cavity was formed by spherical mirrors with the high reflection coefficient in the region of 1.06 μm . A quartz cell of 600 mm in length and 10 mm in diameter was set inside the cavity.

The laser spectrum was recorded with a DFS-8 grating spectrograph with a focal length of 2650 mm and a photodetector based on a linear CCD array. To increase the spectral resolution, a diffraction grating of 150 lines/mm operating in the 12-th dispersion order for a wavelength of 1.06 μm was used in the spectrograph. The spectrometer had the following characteristics:

- 1) spectral range of 9380–9460 cm^{-1} ,
- 2) spectral resolution of 0.035 cm^{-1} ,
- 3) threshold sensitivity for absorption coefficient of 10^{-8}cm^{-1} ,
- 4) error of 0.002–0.005 cm^{-1} in determination of line centers depending on the line intensity,
- 5) accuracy of 1% in measurement of the pressure of gases under study.

Table 1. Half-widths and shift coefficients of H₂O lines in the region of 1 μm calculated in the approximation of a mean frequency of transition

Interfering gas	Dipole (d), quadrupole (q) moments, polarizability (α), ionization potential (ε)	Half-width, $\text{cm}^{-1} \cdot \text{atm}^{-1}$	δ , $\text{cm}^{-1} \cdot \text{atm}^{-1}$	Half-width, $\text{cm}^{-1} \cdot \text{atm}^{-1}$ (experiment, average values)	δ_{exp} , $\text{cm}^{-1} \cdot \text{atm}^{-1}$ (average values)
H ₂ O	$d = 1.85$, $q = 1.4$ $\alpha = 1.76$, $\varepsilon = 15.580$	0.35	−0.001		
N ₂	$d = 0$, $q = 1.4$ $\alpha = 1.76$, $\varepsilon = 15.580$	0.08	−0.0098	0.0927	−0.0133 \pm 0.0054 [Ref. 9]
O ₂	$d = 0$, $q = 0.4$ $\alpha = 1.59$, $\varepsilon = 12.077$	0.05	−0.016	0.0575	−0.0261 \pm 0.0045 [Ref. 9]
CO ₂	$d = 0$, $q = 4.3$ $\alpha = 2.59$, $\varepsilon = 13.79$	0.12	−0.006		
C ₂ H ₂	$d = 0$, $q = 3.0$ $\alpha = 2.0$, $\varepsilon = 11.406$	0.11	−0.005		
H ₂	$d = 0$, $q = 0.651$ $\alpha = 0.767$, $\varepsilon = 15.4261$	0.05	−0.039		
He	$\alpha = 0.205$, $\varepsilon = 24.58$	0.032	−0.021	0.024 \pm 0.006	0 \pm 0.002 [Ref. 10]
Ne	$\alpha = 0.397$, $\varepsilon = 21.565$	0.026	−0.018	0.027 \pm 0.006	−0.005 \pm 0.002 [Ref. 10]
Ar	$\alpha = 1.642$, $\varepsilon = 15.76$	0.040	−0.030	0.0471 0.053 \pm 0.006	−0.0350 \pm 0.0031 [Ref. 9] −0.035 \pm 0.002 [Ref. 10]
Kr	$\alpha = 2.48$, $\varepsilon = 14.00$	0.043	−0.031	0.075 \pm 0.006	−0.043 \pm 0.002 [Ref. 10]
Xe	$\alpha = 4.01$, $\varepsilon = 12.13$	0.050	−0.037	0.093 \pm 0.006	−0.043 \pm 0.002 [Ref. 10]

Note. α in \AA ; q in $\text{D} \cdot \text{\AA}$; ε in eV; d in D.

In measurements of line positions by the intracavity spectroscopy method, there are many sources of measurement errors. A change in geometry of the grating spectrometer at ambient temperature variations influences most strongly the absorption line shift. We have shown experimentally that as the ambient temperature changes roughly by 1° , absorption line centers shift markedly.

To control and take into account distortions of this kind, measurements with the external stabilized interferometer were conducted in series with the main measurements of the laser spectrum. The interferometer was made as a K8 optical glass plane-parallel plate free of a reflecting layer. It was located outside the laser cavity on its axis behind the totally reflecting mirror, whose transmission coefficient was about 0.01. A part of the laser radiation, transmitted by this mirror, was reflected from the interferometer and returned to the cavity. Due to high sensitivity of the intracavity method, abrupt dips in the radiation intensity were observed in the laser spectrum. The distance between these dips depended on the length of the interferometer base. For an interferometer base length of 15.5 mm, the half-width of interference peaks was $\sim 0.04 \text{ cm}^{-1}$. Since the spectral range recorded for one pulse was restricted by the length of the CCD linear array to 14 cm^{-1} , about 70 peaks were observed simultaneously in the intracavity spectrum.

Our estimates of the shift of the interference pattern at temperature variations have shown that if the interferometer temperature is maintained accurate to 0.02° , then the shift of interference peaks does not exceed 0.001 cm^{-1} and is not observed within the experimental error. In this case, we can control the shifts of absorption line centers relative to the positions of interference peaks without using additional reference lines.

To measure the absorption line center shifts induced by the interfering gas pressure, the following procedure was developed:

1. First, the laser spectrum was recorded in the absence of water vapor absorption lines. This spectrum was used as a reference.

2. Then the laser radiation spectrum was recorded together with the interferometer (Fig. 1*a*), and the centers of peaks of the interference pattern were determined.

3. The next step was the recording of the intracavity spectrum with H_2O absorption lines at zero pressure of interfering gas (Fig. 1*b*). For analysis, we used isolated water vapor absorption lines and performed averaging over 30 realizations.

4. The intracavity spectrum of water vapor absorption lines and interferometer reflection peaks (Fig. 1*c*) was recorded; the frequency scale was corrected to the magnitude of interference peak shifts. Since the positions of 60 to 70 peaks were used to determine the shift, rather than of individual

ones, the error in determination of the spectrum shift caused by temperature distortions was by an order of magnitude lower and its value was smaller than 0.001 cm^{-1} . The similar procedure of frequency scale correction was executed after every recording of spectra with different interfering gas pressures.

5. Absorption spectra of the H_2O + interfering gas mixture were recorded (Fig. 1*d*), and the results were averaged over 30 realizations as well. All measurements were conducted at room temperature at the interfering gas pressure between 0 and 1000 mbar.

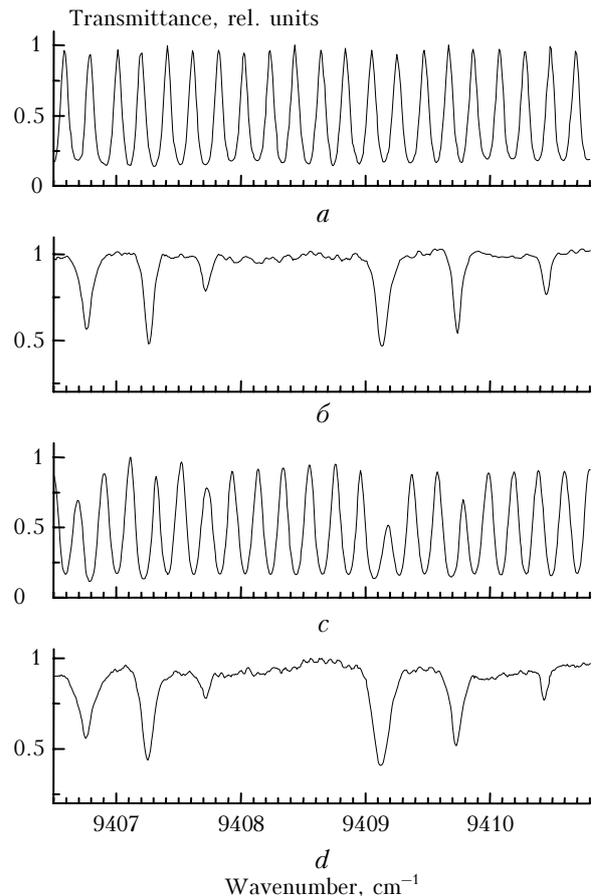


Fig. 1. Intracavity absorption spectrum of water vapor in the region $9406\text{--}9411 \text{ cm}^{-1}$.

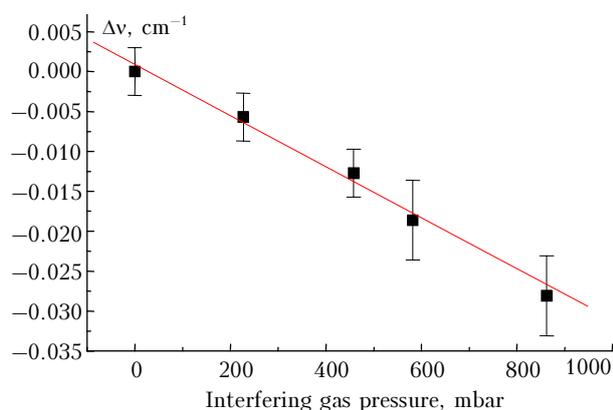
The spectral line centers at the spectrometer frequency scale were determined by the least-square fitting of the theoretical profile to the experimentally recorded one. The Voigt and Lorentz profiles were used for approximation. For each individual line, we plotted the line center position as a function of the interfering gas pressure. The linear approximation of the function yielded the shift coefficient for each spectral line.

In this work, we have determined the shift coefficients for eight water vapor absorption lines shifted by the pressure of nitrogen, oxygen, and dried atmospheric air. Table 2 summarizes the conditions of line shift measurements.

Table 2. Experimental conditions

$P\text{-H}_2\text{O}$, mbar	$P\text{-(H}_2\text{O+N}_2\text{)}$, mbar	$P\text{(H}_2\text{O+O}_2\text{)}$, mbar	$P\text{(H}_2\text{O+air)}$, mbar
21	0	0	0
21	210	217	250
21	425	400	410
21	590	644	640
21	836	870	910

The shift coefficient of an H₂O line for each interfering gas was determined in a series of five measurements at the interfering gas pressure varying from 0 to 1000 mbar. As an example, Figure 2 shows the dependence $\Delta\nu(P)$ for the 10₇₃–9₅₄ line of the H₂O (111) band. The linear dependence is seen.

**Fig. 2.** Shift of the 10₇₃–9₅₄ line of the H₂O (111) band as a function of the nitrogen pressure.

To check the measurement technique, these series were repeated three or more times. The

repeatability of the results is very good; differences between the results obtained in different series are comparable with the error obtained in a single measurement series. To exclude the influence of line self-shifts, all measurements in a series were conducted at the same partial pressure of water vapor.

The measurements were conducted for absorption lines of the rotational-vibrational bands $\nu_1 + \nu_2 + \nu_3$ and $\nu_2 + 2\nu_3$ in the region 9403–9414 cm⁻¹. Table 3 presents the measured line center positions along with their quantum numbers and the shift coefficients.

For all absorption lines, we observed the linear dependence of the line shift on the interfering gas pressure. The shift coefficients ranged from -0.004 to -0.029 cm⁻¹/atm. It should be emphasized that the measurements were conducted for very weak H₂O lines corresponding to transitions to the states with the quantum numbers $J = 8 \dots 12$ and $K_a = 2 \dots 8$. The intensities of these lines range from $1.4 \cdot 10^{-25}$ cm/mol (for the strong (012) 8₃₆–7₀₇ line) to $2.28 \cdot 10^{-26}$ cm/mol (for the weak (012) 10₇₄–9₆₃ line).

The sixth column of Table 3 presents the measured absorption line shift coefficients δ_{exp} in the case of shifts induced by the atmospheric air pressure and the coefficients δ_{calc} calculated according to the partial ratio of the nitrogen and oxygen content in air with the use of data from the fourth and fifth columns.

The comparison of the values presented shows a good agreement between δ_{exp} and δ_{calc} for each H₂O absorption line within the measurement error. This fact additionally confirms the correctness of the measurement technique.

Table 3. Measured H₂O line shift coefficients for the cases of shifts induced by nitrogen, oxygen, and air pressure ($T = 300$ K)

Wavenumber, cm ⁻¹	$V_1 V_2 V_3$	$JK'_a K'_c$	$JK''_a K''_c$	δ_{exp} , cm ⁻¹ /atm (oxygen)	δ_{exp} , cm ⁻¹ /atm (nitrogen)	δ_{exp} , cm ⁻¹ /atm δ_{calc} (air)
9403.971	111	12 2 10	11 0 11	-0.0237(30)	-0.0218(35)	-0.0240(40) -0.021
9406.764	012	11 5 6	10 4 7	-0.0129(25)	<0.004	<0.004
9407.258	111	10 7 3	9 5 4	-0.0270(40)	-0.0245(40)	-0.0240(40) -0.024
9409.129	012	8 3 6	7 0 7	-0.0306(40)	-0.0070(30)	-0.0126(30) -0.01
9409.740	111	10 7 4	9 5 5	-0.0320(40)	-0.0204(40)	-0.0231(40) -0.022
9411.416	012	9 8 2 9 8 1	8 7 1 8 7 2	-0.0265(35)	-0.0287(30)	-0.0291(35) -0.027
9412.407	012	10 7 4	9 6 3	-0.0200(35)	-0.0208(30)	-0.0204(30) -0.02
9412.789	012	8 4 5	7 1 6	-0.0230(40)	<0.004	-0.0070(30)

Conclusions

The measured results and estimates presented allow us to conclude that the application of the technique of intracavity laser spectroscopy to measurement of pressure-induced shift coefficients is quite promising. The proposed technique of measurements with the use of a temperature-stabilized frequency reference allows the spectrometer frequency scale to be corrected and ensures frequency measurements accurate to 0.003 cm^{-1} . This allows the pressure-induced line shift coefficients to be determined accurate to $0.003\text{--}0.004\text{ cm}^{-1}/\text{atm}$. The results obtained for the air-pressure-induced shift coefficients of water vapor can be used in calculations of propagation of narrow-band radiation in the near-ground atmosphere.

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