Shifts of water vapor lines of the $\nu_1 + \nu_2$ and $\nu_2 + \nu_3$ bands by oxygen and argon pressure

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Measurements and calculations of the pressure shift coefficients for more than 100 water vapor absorption lines have been performed in the spectral region 5000−5600 cm^{-1} with oxygen and argon as foreign gases. The experimental data on the line shift coefficients were obtained from analysis of H$_2$O−O$_2$ and H$_2$O−Ar absorption spectra recorded at room temperatures in a wide pressure range of the buffer gases using a Fourier spectrometer with the spectral resolution of 0.007 cm^{-1} and an 84.05-m-long optical path. Calculations of the line shift coefficients were performed using semiclassical impact theory by Anderson. The roles of different terms of intermolecular potential for the line shift calculations have been analyzed. In the calculations we used the only parameter for fitting, namely, the mean dipole polarizability of the upper vibrational state. The calculated data quite well agree with the experiment.

Accurate knowledge of the shift coefficients for water vapor absorption lines by the pressure of N$_2$, O$_2$, and other atmospheric gases, is of interest in solving the problems in propagation of laser radiation along vertical and slant paths in the atmosphere[1] as well when retrieving the parameters of the intermolecular potential.[2]

To date numerous measurements of the line shifts of water vapor and its isotopic modifications by the pressure of different buffer gases have been made in a wide spectral range from the microwave to visible region. As to the spectral region under study in this paper the most known so far research in Ref. 3 dealt with measurements of the coefficients of line shift by nitrogen pressure.

In contrast to line broadening, the line shifting processes are more complicated, and many factors, while negligible in the line width formation, become important in the line shifting. This is confirmed, for instance, by the strong dependences of the line shift coefficients on vibrational quantum numbers, type of perturbing molecules, isotopic modification, temperature, and pressure.[2,4,5] Since the pressure shifting is a more sensitive process to fine details of the intermolecular interaction than the line broadening, it can become a promising tool in studies of the molecular collisions. That is why it is necessary to make more detailed analysis of the factors determining the variety of line shift coefficients.

The measurements of water vapor absorption spectra in the 5000−5600 cm^{-1} region, broadened by pressure of oxygen, have been carried out at the National Institute of Standards and Technology of the USA (NIST USA) using a BOMEM DA3.002 Fourier spectrometer. One of the output ports of the spectrometer was optically coupled with a multipass gas cell with the base length of 2 m. This cell was designed to withstand the gas pressure up to 12 atm. A three-mirror White-type optical system of this cell allows one to reach an optical path length inside the cell up to 112 m. All the portions of the beam path from the spectrometer to the cell and from the cell to a detector were evacuated to exclude the influence of the atmospheric water vapor on the measurement results. A calibrated Heise Model 620 pressure gauge was used to measure the pressure of the H$_2$O−O$_2$ and H$_2$O−Ar mixtures inside the cell. Over the 0 to 30 atm pressure range, the uncertainty of the gauge is stated to be ±0.02% or better. All the records of the absorption spectra were made at room temperatures with the spectral resolution of 0.007 cm^{-1} and an optical path length of 84.05 m. A tungsten light source and a HgCdTe detector cooled by liquid nitrogen were used in these measurements.

The pressure of the water vapor varied from 0.56 to 0.88 Torr and the pressure of O$_2$ ranged from 148 to 4000 Torr. In this pressure range eleven absorption spectra at the total pressure of H$_2$O−O$_2$ mixture of 148.57, 294.51, 471.32, 590.87, 734.19, 1186.3, 1856.2, 2478.6, 3095.1, 3800.49 Torr and eight spectra at the total pressure of H$_2$O−Ar mixture of 188.83, 400.62, 647.45, 906.05, 15444.6, 2001.1, 2991.5, and 3983.1 Torr have been recorded. Every absorption spectrum was obtained by recording and averaging of 80 scans and it typically took ~ 4 hours.

The treatment of the spectra obtained was performed in two steps. First the relative line center positions for isolated and overlapping water vapor lines were determined by the least squares fitting of the Voigt profiles to the experimentally measured contours. In this way the values of relative line center positions and their standard deviations for more than

100 water vapor lines at eleven pressures of O_2 and eight of Ar have been obtained. Figure 1 shows a small fraction of a Fourier spectrum recorded near 5119 cm^{-1} in the $\nu_2 + \nu_3$ band of H_2O. This spectrum was recorded at the H_2O partial pressure of 0.56 Torr and the H_2O-O_2 total pressure of 294.51 Torr.
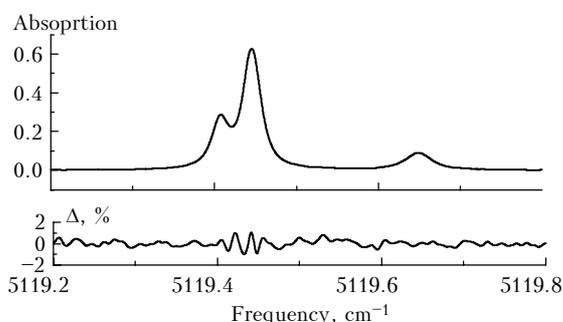
Absoprtion

Fig. 1. A fraction of water vapor absorption spectrum broadened by O_2 recorded with a Fourier-spectrometer. The lower curve shows in percent the difference (Δ) between the measured and theoretical (Voigt contour) value of the absorption.
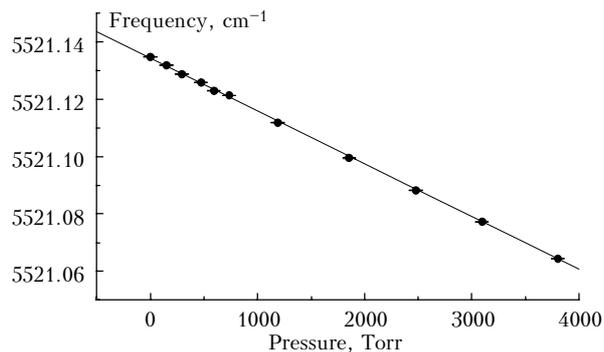
Frequency, cm^{-1}

Fig. 2. The dependence of water vapor absorption line position on the pressure of oxygen.

At the next stage the dependences of line center positions on the pressure of O_2 for each of the spectral lines under study were plotted and fitted again using a linear function (Fig. 2). This latter procedure allowed us to derive the values of shift coefficients due to the oxygen and argon pressure and their standard deviations. A small portion of thus obtained shift coefficients is given in Table 1.

Table 1. The measured and calculated line shift coefficients

Frequency, cm^{-1}	δ_{exp}, 10^{-3} cm^{-1}/atm H_2O-O_2	$\pm 10^{-3}$ cm^{-1}/atm H_2O-O_2	δ_{calc}, 10^{-3} cm^{-1}/atm H_2O-O_2	δ_{exp}, 10^{-3} cm^{-1}/atm H_2O-Ar	δ_{calc}, 10^{-3} cm^{-1}/atm H_2O-Ar	Vib*	$J\ K_a\ K_c$	$J'\ K_a'\ K_c'$
1	2	3	4	5	6	7	8	9
5014.5815	−12.6	0.57	−13.6	−	−	7	4 4 1	5 5 0
5024.6697	−11.1	0.72	−13.5	−	−	7	4 3 2	5 4 1
5032.3866	−13.3	0.75	−13.9	−17.6	−17.4	8	6 1 5	7 3 4
5050.6913	−11.8	0.45	−12.8	−	−	7	3 3 0	4 4 1
5051.1156	−14.3	0.78	−13.8	−	−	7	3 3 1	4 4 0
5072.0754	−10.0	0.43	−10.9	−	−	7	3 2 1	4 3 2
5081.4379	−14.3	0.85	−16.7	−	−	8	10 2 8	11 2 9
5092.3576	−17.9	0.20	−17.1	−18.2	−17.0	8	10 1 9	11 1 10
5092.7870	−15.6	0.33	−16.5	−18.4	−17.3	8	10 2 9	11 2 10
5093.3227	−11.9	0.28	−11.9	−	−	7	2 2 1	3 3 0
5107.0667	−14.2	0.27	−15.7	−17.0	−16.9	8	9 3 7	10 3 8
5116.7920	−14.1	0.28	−12.9	−15.6	−16.3	8	8 2 6	9 2 7
5159.9310	−11.3	0.15	−10,2	−12.7	−13.4	8	6 3 3	7 3 4
5230.8104	−9.68	0.54	−8.9	−12.2	−13.1	8	3 1 2	4 1 3
5231.2230	−9.9	0.46	−7.6	−	−	7	4 2 2	5 1 5
5231.6833	−12.1	0.34	−15.6	−	−	8	4 4 0	5 4 1
5231.8841	−12.3	0.31	−16.5	−	−	8	4 4 1	5 4 2
5303.1485	−9.69	0.37	−10.5	−	−	8	5 2 4	5 2 3
5314.1422	−10.8	0.27	−13.0	−	−	8	7 3 5	7 3 4
5314.5149	−8.47	0.29	−7.3	−	−	7	5 3 2	5 2 3
5513.7305	−11.3	0.31	−11.8	−	−	7	6 4 3	5 3 2
5515.8567	−11.3	0.26	−10.3	−13.7	−14.9	8	7 2 5	6 2 4
5516.6191	−16.8	0.16	−16.3	−17.5	−17.7	8	11 1 11	10 1 10
5518.2836	−13.1	0.27	−10.5	−14.5	−15.4	8	7 3 4	6 3 3
5521.1343	−13.9	0.13	−15.8	−16.1	−16.1	8	7 4 4	6 4 3
5521.8998	−15.1	0.27	−15.8	−16.4	−17.2	8	9 2 8	8 2 7
5523.1289	−14.2	0.21	−15.2	−16.3	−17.2	8	9 1 8	8 1 7
5523.4500	−14.1	0.29	−14.2	−16.3	−15.0	8	7 4 3	6 4 2
5527.8401	−13.7	0.21	−15.3	−16.3	−16.8	8	8 3 6	7 3 5
5531.8082	−10.9	0.35	−10.9	−	−	7	7 4 4	6 3 3
5532.7571	−14.8	0.20	−17.0	−	−	8	7 5 3	6 5 2
5532.9023	−13.8	0.32	−16.9	−	−	8	7 5 2	6 5 1
5536.3032	−13.1	0.18	−11.5	−16.1	−16.6	8	8 2 6	7 2 5
5537.5377	−15.9	0.10	−16.0	−17.3	−16.7	8	10 2 9	9 2 8
5538.1251	−15.3	0.11	−15.8	−17.1	−16.8	8	10 1 9	9 1 8

<div align="right">*Table 1 (continued)*</div>

1	2	3	4	5	6	7	8	9
5547.0789	−15.4	0.26	−15.6	−16.6	−17.0	8	9 3 7	8 3 6
5548.6515	−12.9	0.30	−12.9	−15.3	−15.0	8	8 4 4	7 4 3
5552.4696	−16.6	0.16	−16.2	−17.7	−16.4	8	11 2 10	10 2 9
5552.7575	−15.8	0.18	−16.1	−17.4	−16.4	8	11 1 10	10 1 9
5575.7673	−6.1	0.30	−5.9	−9.3	−9.9	8	5 3 2	4 1 3
5595.5541	−14.5	0.48	−13.6	−15.3	−16.4	8	10 3 7	9 3 6

* 7 denotes band $\nu_1 + \nu_2$, 8 − band $\nu_2 + \nu_3$.

The semiclassical impact theory by Anderson of the spectral line pressure broadening[6] was used to calculate the shift coefficients of water vapor lines. This theory has then been further developed by Tsao and Curnutte.[7] The impact approximation makes simpler interpretation of the collision process and allows one to obtain more reliable results. The well-known general assumptions of the theory are as follows:

1. Collisions are considered to be binary.

2. The duration of a collision is shorter than the time between collisions.

3. Colliding particles are assumed to follow classically prescribed paths.

4. No line mixing effects occur.

In this case the half-width γ_{if} of a spectral line and the line center shift δ_{if} for the transition $i \rightarrow f$ are given by the following formula:

$$\gamma_{if} + i\delta_{if} = \frac{n}{c} \sum_2 \rho(2) \int_0^\infty dv\, v\, f(v) \int_0^\infty db\, b\, S(b), \quad (1)$$

where i and f are the sets of quantum numbers of the initial and final states of an absorbing molecule, 2 are quantum numbers of a perturbing molecule (i, f, 2 are complex indices including magnetic (m_i, m_f, m_2), vibrational (v_i, v_f, v_2) quantum numbers, quantum numbers of angular moment (j_i, j_f, j_2), and other rotational quantum numbers denoted as (r_i, r_f, r_2), for instance, K_a, K_c for asymmetric tops), n is the perturbing particles density, v is the speed of the relative motion of the interacting particles, $f(v)$ is the Maxwell velocity distribution function, ρ_2 is the population of the level 2 of the perturbing molecule, b is the impact parameter.

We can consider the intermolecular interaction as a perturbation in the general Hamiltonian of the system, then

$$S(b) = S_1(b) + S_2(b) + \dots , \quad (2)$$

where $S_1(b)$ and $S_2(b)$ are the known first and second-order terms of the Anderson's theory.

The first-order term $S_1(b)$ is responsible for the adiabatic effect and it is determined by the isotropic part of the intermolecular potential only. In the case of collisions of a polar H_2O molecule with a non-polar molecule N_2, the $S_1(b)$ term can be presented as

$$S_1(b) = -\frac{3\pi}{2\hbar v b^5}\, \alpha_2 \left\{ <V_i|\mu^2|V_i> - <V_f|\mu^2|V_f> + \right.$$

$$\left. + \frac{3\varepsilon\varepsilon_2}{2\,(\varepsilon + \varepsilon_2)}\, [<V_i|\alpha|V_i> - <V_f|\alpha|V_f>] \right\}. \quad (3)$$

In Eq. (3) α, μ, ε are the polarizability, dipole moment, and ionization potential of the H_2O molecule, respectively, α_2 and ε_2 are the polarizability and ionization potential of the perturbing molecule. The dipole moment and isotropic part of the polarizability tensor are the functions of vibrational coordinates and the calculations of mean values with the vibrational wave functions of the initial $|V_i>$ and final $|V_f>$ states allows one to take into account the vibrational perturbation of the molecule. The S_1-term is imaginary and according to Anderson's approach contributes to the line shift only.

As is known, $S_2(b)$ involves three parts:

$$S_2(b) = S_{2i}^{outer}(b) + S_{2f}^{outer}(b) + S_2^{middle}(b), \quad (4)$$

where

$$S_{2i}^{outer}(b) = \sum_{l_1 l_2} \frac{A_{l_1 l_2}}{\hbar^2 v^2 b^{2(l_1 + l_2)}} \sum_{2'} D^2(22'|l_2) \times$$

$$\times \sum_{l'} D^2(ii'|l_1)\, \varphi_{l_1 l_2}(k_{ii'22'}); \quad (5)$$

where l_1 and l_2 denote the type of interaction,

$$D^2(ii'|1) = (r_i\|T_1\| r_i')2/(2j_i + 1) \quad (6)$$

is the transition moment and $(r_i\|T_1\|r_i')$ is the reduced matrix elements of the irreducible tensor operator T_l of the rank $l = 1$, the factors $A_{l_1 l_2}$ are chosen such that $Re\, \varphi_{l_1 l_2}(0) = 1$, $\varphi_{l_1 l_2}(k_{ii'22'})$ are the complex resonance functions, the real parts of which are even and the imaginary parts are odd functions of the adiabatic parameter k

$$\varphi_{l_1 l_2}(k) = f_{l_1 l_2}(k) + i\, If_{l_1 l_2}(k); \quad (7)$$

$$k_{ii'22'} = (2\pi cb/v)(\omega_{ii'} + \omega_{22'}), \quad (8)$$

where $\omega_{ii'}$ and $\omega_{22'}$ are the transition frequencies in the absorbing and perturbing molecules, respectively. The expression for $S_{2f}^{outer}(b)$ is of similar form. Functions $If(k)$ have been calculated according to Ref. 8 for the electrostatic potential (dipole−quadrupole and quadrupole−quadrupole interactions in the case of the H_2O-O_2 mixture), imaginary parts of the resonance functions for induction and dispersion potential (which are the main interaction for H_2O-Ar collisions) were determined in Ref. 9. The expressions for $S_2^{middle}(b)$ are quite similar.

In order to take into account strong interactions, Anderson have suggested the truncation procedure when b_0 is determined from the equation

$$\text{Re } S(b_0) = 1. \qquad (9)$$

$S(b) = 1$ for $b \leq b_0$ and $S(b)$ is determined by Eq. (2) at $b > b_0$.

The H_2O molecular constants, such as dipole moments in the ground and in the first excited vibrational states were taken from Ref. 10, components of quadrupole moments − from Ref. 11, and the dipole polarizability of the molecule in the ground vibrational state from Ref. 12.

The mean dipole moment m_x^V in the upper vibrational states has been determined by formula

$$m_x^V = <V\,|\,\mu\,|\,V> = \mu_e + \mu_1 V_1 + \mu_2 V_2 + \mu_3 V_3 \quad (10)$$

with constants $\mu_e = -1.85498$, $\mu_1 = -0.00508$, $\mu_2 = 0.03166$, $\mu_3 = -0.02246$ taken from Ref. 13. The quadrupole moment transition strengths for H_2O molecule have been calculated in the rigid rotor approximation.

We have also included into consideration the contributions of quadrupole–quadrupole interaction, as well as the induction and dispersion terms of the polarization potential. In the case of the H_2O−O_2 collisions the main contribution to broadening and shifting is due to the interaction between the dipole moment of water vapor molecule and the quadrupole moment of oxygen. For the collisions of water vapor molecule with noble gas atoms the anisotropic part of the polarization potential is most important.

Measured and calculated shift coefficients of water vapor lines in the $\nu_1 + \nu_2$ and $\nu_2 + \nu_3$ bands are presented in Table 1. The values of coefficients are always negative and vary from $-7 \cdot 10^{-3}$ to $-18 \cdot 10^{-3}$ cm^{-1}/atm.

The agreement between the calculated and measured data are well seen from statistics given below and from Fig. 3.

$\Delta \leq 1$	70% of all lines
$1 < \Delta \leq 2$	15%
$2 < \Delta \leq 3$	14%
$3 < \Delta$	1%

$(\Delta = |\delta^{obs} - \delta^{calc}| \cdot 10^{-3}$ cm^{-1}/atm$)$.

Shift coefficient, cm^{-1}/atm

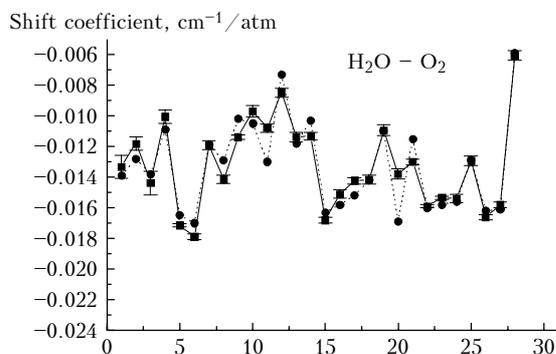**Fig. 3.** The measured (−■−) and calculated (−•−) line shift coefficients for H_2O−O_2 system vs. number of line.

For 70% of all lines the differences between measured and calculated values are within 10^{-3} cm^{-1}/atm.

As was mentioned above the line shifts by pressure of quadrupole molecules and noble gas atoms have different nature. In the first case the dipole–quadrupole interaction is the main factor, while in the second one the induction and dispersion interactions play the decisive role, giving the contribution to the second-order term of the interruption function $S_2(b)$. Nevertheless, from Table 1 one can see that strong correlation exists between the coefficients of line shift by oxygen and argon pressures. This allows one to conclude that the dipole–quadrupole interaction in the case of the H_2O−O_2 collisions and dipole–induced dipole interaction for H_2O−Ar collisions lead to similar line shift effect.

Also it should be noted that in spite of the high pressure of buffer gases used in this experiment (up to 4 atm), measured values of the shifts are linear functions of pressure. Besides, the calculations made in the approximation of linear dependence of a shift on pressure are in a good agreement with measurements. These facts point that the impact Anderson's theory is useful in the above-mentioned pressure region of the buffer gases (argon and oxygen).

Acknowledgments

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