

DATABASE OF THE SHIFT AND BROADENING COEFFICIENTS FOR THE H₂O ABSORPTION LINES IN THE IR AND VISIBLE REGIONS

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Some results obtained in the course of the integrated scientific project "Compilation of an Information Database of the Shift and Broadening Coefficients for Absorption Lines of the H₂O Molecule in the Visible and IR Regions" are presented. Experimental instrumentation and calculational techniques employed for obtaining quantitative data on the shift and broadening coefficients for rovibrational absorption lines of the H₂O molecule in mixtures with N₂, O₂, air, and some other gases are described. A systematic comparison of experimental and calculational data involved into the database is carried out.

Knowledge of spectral line centers as well as of the broadening and shift coefficients and their temperature dependences for molecules of atmospheric gases is now of great interest. The results of investigations of the collisional shifts and broadening of isolated spectral lines of molecular gases are especially important for understanding the nature of intermolecular forces in gases and, in addition, they bear information about cross sections and dynamics of the collisions and on the dependence of the cross sections on the vibrational quantum number, and so on.

Investigations of the absorption line shifts and widths for the case of such molecules as H₂O, O₃, CO₂, and CH₄ are of great practical interest, since just these gases are the main absorbing components of the atmosphere that govern attenuation of radiation in the IR, visible, and UV regions. In addition, variations of these gas concentrations influence on such climatic phenomena as the greenhouse effect and/or the ozone holes.

Numerical data on spectral line parameters of some molecules and dependence of these parameters on pressure and temperature are used for improving techniques for calculating the characteristics of narrow-band optical and laser radiation propagation through the atmosphere as well as for designing optical instrumentation for atmospheric investigations.

The absorption spectra of the H₂O molecules almost entirely overlap the IR, visible, and UV spectral regions, therefore quantitative data on the broadening and shift coefficients of the water vapor spectral lines are needed for solving practically all kinds of the atmospheric optics problems, *in situ* and remote gas analysis.

This paper presents the most important results obtained within the framework of the scientific project "Compilation of the information database of the shift and broadening coefficients for absorption lines of the H₂O molecule in the visible and IR regions". The project has been under permanent development at the Spectroscopy Department of the Institute of Atmospheric Optics of the Siberian Branch of the Russian Academy of Sciences (IAO SB RAS) since 1985.

Most of the measurement data on the half-widths and shifts of the rovibrational absorption lines of H₂O

molecules in air, nitrogen, oxygen, and some other atomic and molecular gases have been obtained using high resolution laser spectrometers, including pulsed diode-laser-based spectrophotometers, intracavity laser spectrometers based on broadband solid-body lasers, and dual-channel optoacoustic spectrometers with cw and pulsed lasers emitting in the visible region. Specifications of these spectrometers are presented in Table I.

The results shown in Figs. 1 and 2 illustrate the dependence of the H₂O spectral line shape on a buffer-gas pressure.

The experimental results obtained at the Institute of Atmospheric Optics as well as the data from Refs. 1–18, 26, and 27 were used to test the calculational results on the shift and broadening coefficients. A series of calculations of the shift and broadening coefficients for the H₂O rovibrational lines and their temperature dependence have been done using an improved Anderson–Tsao–Curnutte–Frost method.^{19–22}

A preliminary analysis of the H₂O absorption line shifts was made to elucidate the influence of different physical factors on the shift magnitude and sign: the short-range intermolecular forces, distribution of molecules over the motion velocities, the trajectory curvatures at the moment of molecular collision, as well as the role of intramolecular resonances and vibrational dependence of the molecular parameters.

As a consequence the dependence of the disperse component of the intermolecular potential on the vibration quantum number was found to be the most important factor that almost entirely explains all experimentally observed features of the water vapor line shift caused by N₂, O₂, and air pressure. In the visible region of spectrum the contribution of this factor is about 90% for the H₂O absorption lines. In the case of pure rotational lines the contribution coming from this factor to the processes forming the line shift vanishes, while its contribution to these processes in the case of absorption lines from H₂O vibrational bands in the IR is comparable with that coming from electrostatic interaction between the dipole H₂O molecules and molecules of foreign gases (either nitrogen or oxygen) possessing quadrupole moment.

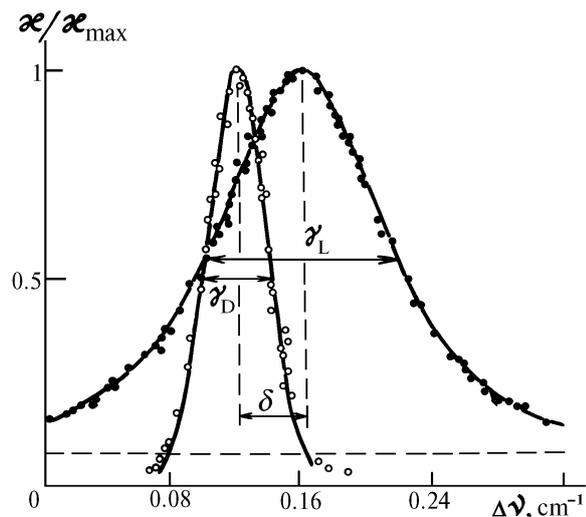


FIG. 1. The absorption line shapes of the pure water vapor at different values of the broadening (argon) gas pressures simultaneously recorded with the dual-channel opto-acoustic spectrometer: open circles at $P_{H_2O} = 5$ Torr, $P_{Ar} = 0$, dots at $P_{H_2O} = 5$ Torr, $P_{Ar} = 760$ Torr, γ_D is the Doppler linewidth; γ_L is the collisional absorption linewidth. Solid curve shows the calculated Doppler and Lorentz shapes and dashed horizontal curve shows the background signal level at recording the absorption line shape for H_2O -Ar mixture.

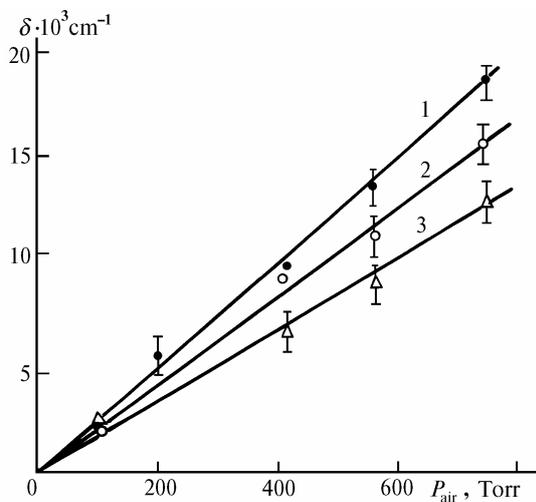


FIG. 2. The H_2O absorption line shifts (centered at 694.38 (1), 694.237 (2), and 694.215 nm (3)) as a function of air pressure. Measurements have been made by V.V. Lazarev using the dual-channel opto-acoustic spectrometer.

The computations we have done quite satisfactorily represent the dependences of the line shifts on the

rovibrational quantum numbers. Data presented in Tables II and III illustrate well the agreement between calculated and observed values of shifts for different rovibrational absorption bands of H_2O molecule in the visible and IR regions. The rotational and centrifugal distortion constants of the vibrational states were obtained from the spectrum of energy levels for $J \leq 4$ using the effective rotational Watson-type Hamiltonian and taking into account random resonances. The polarizability of the H_2O molecule at upper vibrational states was calculated by fitting the line shift coefficients of several lines of a corresponding rovibrational band to the experimental values. The quadrupole moments of N_2 and O_2 were taken to be equal to 3.0 DÅ and 0.7 DÅ, respectively.

The H_2O absorption line shifts were calculated for temperatures 200, 230, 260, and 297 K. The exponents (n_c) and (n_d) of the power law functions describing temperature behaviors of the linewidth and shift were determined for each absorption line using formulas

$$\gamma(T) = \gamma(T_0) (T_0/T)^{n_c};$$

$$\delta(T) = \delta(T_0) (T_0/T)^{n_d}$$

by fitting using the method of least squares.

TABLE I. Specifications of the laser spectrometers developed at the IAO SB RAS and used to measure the broadening and shift coefficients of the H_2O lines.

Laser spectrometer type	Threshold absorption sensitivity, cm^{-1}	Spectral region, μm	Spectral resolution, cm^{-1}
1. Pulse diode laser spectrophotometer	10^{-6}	0.9 ... 6.0	$1 \cdot 10^{-4}$
2. Intracavity laser spectrometer with F-color center LiF laser	10^{-7}	0.9 ... 1.25	$5 \cdot 10^{-2}$
3. Laser spectrophotometer with ring neodymium laser	10^{-7}	1.05 ... 1.07	$1 \cdot 10^{-4}$
4. Dual-channel opto-acoustic spectrometer with ruby laser	$5 \cdot 10^{-8}$	0.6943 ... 0.6945	$1 \cdot 10^{-2}$
5. Dual-channel intracavity opto-acoustic spectrometer with liquid laser	$2 \cdot 10^{-9}$	0.58 ... 0.60	$1 \cdot 10^{-9}$
6. Dual-channel opto-acoustic spectrometer with cw liquid laser	$2 \cdot 10^{-8}$	0.58 ... 0.60	$1 \cdot 10^{-4}$

TABLE II. Data on the H₂O absorption line shifts for the infrared and visible spectral regions.

The bands under study	Number of lines under study	Foreign gas	Refs.	Range of the shift variations mK/atm	Standard deviation of calculation by the ATCF method from experiment, mK/atm
ν_2	126	N ₂ air	11–17,26	–11...+7	1.9
ν_1	6	N ₂	27	–6...	1.3
ν_3	98	N ₂	27	–11...+4	0.2
$\nu_2 + \nu_3$	45	N ₂	18	–22...+5	0.6
$2\nu_2 + \nu_3$	23	N ₂	18	–12...+2	0.7
$2\nu_1$	14	N ₂	18	–13...+3	0.9
$\nu_1 + \nu_3$	30	N ₂	18	–15...–4	0.6
$\nu_1 + \nu_2 + \nu_3$	37	N ₂	18	–27...–3	0.5
$\nu_2 + 2\nu_3$	8	air	3	–34...–12	4.7
$2\nu_1 + \nu_3$	5	N ₂	18	–12...–4	
$2\nu_1 + 2\nu_2 + \nu_3$	6	air	10	–14...–8	1.7
	25	N ₂	15	–18...–6	2.0
	28	O ₂	15	–36...–17	5.9
	30	air	15	–22...–11	1.5
$2\nu_1 + 2\nu_3$	7	N ₂	15	–29...–5	1.1
	9	O ₂	15	–34...–20	4.7
	9	air	15	–27...–6	4.0
$3\nu_1 + \nu_3$	54	N ₂	15	–27...–6	2.5
	79	O ₂	15	–38...–18	5.4
$\nu_1 + 3\nu_3$	72	air	13, 15	–31...–10	3.3
	3	N ₂ , O ₂ , CO ₂	9	–36...–9	1.6
$4\nu_2 + \nu_3$	7	air air	4, 28	–36...–9	4.9

The calculated values of the shift coefficients for the standard temperature 297 K are in a good agreement with the experimental. The list of the rovibrational bands and the numbers of lines, for which the coefficients γ , δ , n_c , and n_d have been calculated, are given in Table II.

TABLE III. Calculated values of the parameters of the H₂O absorption line shifts caused by air pressure in the $3\nu_1 + \nu_3$ band.

f	i	ATCF	ATCF*	ATCID	Experiment ¹⁴
422	523	–0.0089	–0.0099	–0.0099	–0.0094
515	616	–0.0165	–0.0169	–0.0168	–0.0194
505	606	–0.0165	–0.0170	–0.0168	–0.0157
413	514	–0.0132	–0.0141	–0.0130	–0.0155
423	524	–0.0122	–0.0132	–0.0125	–0.0130

TABLE III (continued).

f	i	ATCF	ATCF*	ATCID	Experiment ¹⁴
762	761	–0.0269	–0.0238	–0.0259	–0.0261
330	431	–0.0091	–0.0104	–0.0095	–0.0103
331	432	–0.0098	–0.0111	–0.0105	–0.0105
660	661	–0.0298	–0.0261	–0.0290	–0.0263
321	422	–0.0092	–0.0102	–0.0095	–0.0106
312	413	–0.0097	–0.0107	–0.0103	–0.0131
505	524	–0.0153	–0.0160	–0.0159	–0.0211
322	423	–0.0111	–0.0121	–0.0112	–0.0105
844	845	–0.0116	–0.0129	–0.0114	–0.0263
532	533	–0.0122	–0.0133	–0.0122	–0.0116
633	634	–0.0119	–0.0129	–0.0116	–0.0105
431	432	–0.0125	–0.0136	–0.0122	–0.0116

Comments: Data in columns correspond to calculations by different methods (ATCF, ATCF*, and ATCID). ATCF is the calculation in which the dipole–quadrupole and quadrupole–quadrupole interactions are taken into account. ATCF* – with dipole–quadrupole, quadrupole–quadrupole, dipole–hexadipole, and polarization interactions taken in account. ATCID is the calculation by Cherkasov method²⁵ with dipole–quadrupole and quadrupole–quadrupole interactions taken in account.

Table IV shows some calculational results for illustration.

TABLE IV. Calculated values of the parameters of H₂O absorption line broadening and shift caused by air pressure for $3\nu_1 + \nu_3$ band (cm^{–1}·atm^{–1}).

$(JK_aK_c)(JK_aK_c)'$	γ	δ	n_c	n_d
1	2	3	4	5
6 3 4 7 3 5	0.0773	–0.018	0.43	1.07
5 4 1 6 4 2	0.0719	–0.019	0.48	1.07
6 1 5 7 1 6	0.0821	–0.019	0.44	1.19
6 2 5 7 2 6	0.0729	–0.021	0.33	1.23
5 3 3 6 3 4	0.0801	–0.017	0.48	1.00
5 2 3 6 2 4	0.0956	–0.013	0.75	0.70
6 0 6 7 0 7	0.0693	–0.024	0.15	1.23
4 4 0 5 4 1	0.0641	–0.020	0.45	1.09
4 4 1 5 4 2	0.0629	–0.020	0.42	1.05
6 1 6 7 1 7	0.0687	–0.024	0.15	1.22
5 1 4 6 1 5	0.0921	–0.017	0.58	0.89
5 2 4 6 2 5	0.0813	–0.018	0.42	1.11
7 7 1 7 7 0	0.0385	–0.032	0.45	1.02
4 3 1 5 3 2	0.0859	–0.014	0.66	0.79
7 1 7 7 1 6	0.0701	–0.015	0.24	0.72
4 3 2 5 3 3	0.0806	–0.016	0.51	0.89
4 2 2 5 2 3	0.0960	–0.012	0.76	0.71
5 1 5 6 1 6	0.0801	–0.020	0.30	1.23
5 0 5 6 0 6	0.0817	–0.020	0.32	1.26
4 1 3 5 1 4	0.0975	–0.015	0.67	0.87
4 2 3 5 2 4	0.0877	–0.016	0.50	0.97
7 6 2 7 6 1	0.0460	–0.029	0.33	1.05
3 3 0 4 3 1	0.0803	–0.014	0.57	0.71
3 3 1 4 3 2	0.0779	–0.015	0.50	0.72
6 6 0 6 6 1	0.0421	–0.030	0.40	1.01
3 2 1 4 2 2	0.0954	–0.012	0.71	0.51
4 1 4 5 1 5	0.0901	–0.017	0.46	1.14
4 0 4 5 0 5	0.0927	–0.017	0.51	1.13
3 1 2 4 1 3	0.0992	–0.012	0.69	0.97

TABLE IV (continued).

$(JK_aK_c)(JK_a'K_c')$	γ	δ	n_c	n_d
1	2	3	4	5
5 0 5 5 2 4	0.0855	-0.019	0.41	1.19
3 2 2 4 2 3	0.0915	-0.014	0.57	0.75
3 0 3 4 0 4	0.1001	-0.015	0.66	1.00
3 1 3 4 1 4	0.0970	-0.015	0.60	1.00
4 0 4 4 2 3	0.0933	-0.019	0.55	1.15
2 2 0 3 2 1	0.0948	-0.013	0.66	0.36
2 2 1 3 2 2	0.0935	-0.014	0.61	0.51
2 1 1 3 1 2	0.1016	-0.010	0.67	0.91
7 4 4 7 4 3	0.0763	-0.021	0.47	1.27
8 4 4 8 4 5	0.0816	-0.016	0.56	0.49
2 0 2 3 0 3	0.1042	-0.014	0.70	0.96
2 1 2 3 1 3	0.1003	-0.014	0.70	0.85
4 1 4 4 1 3	0.0987	-0.010	0.66	0.93
1 1 0 2 1 1	0.1061	-0.009	0.65	0.77
5 4 2 5 4 1	0.0674	-0.022	0.44	1.03
5 4 1 5 4 2	0.0680	-0.021	0.47	0.86
1 0 1 2 0 2	0.0082	-0.014	0.70	0.83
5 3 3 5 3 2	0.0858	-0.016	0.62	1.09
1 1 1 2 1 2	0.1020	-0.012	0.72	0.95
3 1 3 3 1 2	0.1009	-0.011	0.71	0.70
4 3 2 4 3 1	0.0817	-0.017	0.58	1.01
5 3 2 5 3 3	0.0863	-0.016	0.65	0.80
6 3 3 6 3 4	0.0885	-0.015	0.66	0.86
4 3 1 4 3 2	0.0820	-0.016	0.61	0.71
3 3 1 3 3 0	0.0763	-0.018	0.51	0.85
3 3 0 3 3 1	0.0762	-0.018	0.52	0.79
3 1 2 3 2 1	0.0972	-0.018	0.68	0.80
0 0 0 1 0 1	0.1061	-0.011	0.70	0.39
2 1 2 2 1 1	0.1175	-0.007	0.75	—
2 2 1 2 2 0	0.0942	-0.015	0.64	0.71
2 2 0 2 2 1	0.0942	-0.014	0.63	1.01
3 2 1 3 2 2	0.0948	-0.013	0.66	1.06
1 1 1 1 1 0	0.1043	-0.016	0.64	0.88
4 2 2 4 2 3	0.0950	-0.013	0.67	1.03
5 2 3 5 2 4	0.0935	-0.014	0.66	0.77
1 1 0 1 1 1	0.1058	-0.006	0.66	0.71
2 1 1 2 1 2	0.1031	-0.009	0.70	0.98
3 1 2 3 1 3	0.1016	-0.013	0.70	0.80
1 0 1 0 0 0	0.1067	-0.012	0.71	1.06
4 1 3 4 1 4	0.0987	-0.015	0.64	0.79
2 1 2 1 1 1	0.1014	-0.011	0.71	0.50
2 0 2 1 0 1	0.1076	-0.007	0.70	0.52
2 1 1 1 1 0	0.1049	-0.013	0.62	0.74
3 1 3 2 1 2	0.0997	-0.011	0.69	0.75
3 2 2 2 2 1	0.0928	-0.015	0.61	1.19
3 0 3 2 0 2	0.1038	-0.008	0.70	0.36
3 2 1 2 2 0	0.0943	-0.013	0.65	1.19
6 1 5 6 1 6	0.0818	-0.021	0.41	1.45
4 1 4 3 1 3	0.0965	-0.012	0.58	0.88
4 2 3 3 2 2	0.0911	-0.016	0.56	1.14
4 0 4 3 0 3	0.0998	-0.009	0.65	0.49
7 2 6 7 0 7	0.0649	-0.026	0.18	1.38
5 3 3 4 3 2	0.0802	-0.019	0.51	1.02
4 2 2 3 2 1	0.0946	-0.013	0.71	0.82

The complete information about the broadening and shift parameters for the absorption lines from all the H₂O absorption bands listed in Table IV is included into the database supplementing the corresponding information from the well-known and widely used databases such as GEISA²³ and HITRAN.²⁴

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