

INVESTIGATION OF H₂O ABSORPTION LINE SHIFTS CAUSED BY AIR PRESSURE IN THE VISIBLE

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This paper presents the results of measurements and calculations of the shift coefficients for 170 absorption lines of H₂O from the vibrational-rotational bands. The measurements were made using highly sensitive laser spectrometers with the spectral resolution better than or equal to 0.01 cm⁻¹. The calculations were made using the Anderson-Tsao-Curnutte-Frost technique. Good agreement has been obtained between the theoretical and experimental values of the coefficients of the H₂O absorption line shifts caused by N₂, O₂, and air pressure.

Investigations of H₂O absorption line broadening and shifting is of current interest for the determination of narrow-band optical radiation energy losses along vertical inhomogeneous paths² as well as for the remote sounding of atmospheric humidity fields by the differential absorption method (DIAL).¹ Neglecting the H₂O absorption line shift can lead to systematic errors of from 30 to 100% in retrieving the water vapor concentration at altitudes from 15 to 20 km.¹ Quantitative data on spectral line shifting and broadening coefficients also enable one to obtain information on the characteristics of Intermolecular Interactions in gases, the dynamics of molecular collisions and molecular polarizability in excited vibrational states.³

The paper presents the results of measurements of H₂O absorption line shifts caused by N₂, O₂, and air pressure and the corresponding theoretical results for the visible spectral range. The DIAL systems based on frequency tunable solid state lasers for H₂O profile sounding are presently being developed for use in this spectral range.

EXPERIMENTAL TECHNIQUE AND RESULTS

The experimental data on the H₂O absorption line shifts in the visible range caused by N₂, O₂, and air pressure presented in this paper were obtained using three different high-resolution laser spectrometers.³

The bounds of the spectral intervals under investigation, the values of the spectral resolution, and the identification of the bands corresponding to the H₂O spectral lines are presented in Table I. The same table includes results of IR high-resolution spectrometer measurements used while calculating the line center shifts of the complex bands and their overtones to increase the accuracy of the calculation.

The use of a dual-channel registration scheme is a characteristic peculiarity of our measurement technique. Two White cells with optical path length of up to 120 m are used in the laser spectrometers^{5,6} and two photoacoustic cells with different pressures of the gas mixtures in each of them are used in the photoacoustic spectrometers.^{3,4,7,8} The photoacoustic spectrometer with the two absorbing cells located inside the cavity and with microphone derivative signal control^{7,8} enables one to reach the maximum sensitivity, making it possible to investigate very faint lines with absorption coefficients down to $2 \cdot 10^{-8}$ cm⁻¹ at their maxima. The methods used to take the measurements and process the results are described in detail in Refs. 2–8. As a result of the experiments in the spectral intervals 13000–14000, 14395–14400, and 16100–17540 cm⁻¹, the quantitative data on shifts of more than 180 weak H₂O absorption lines in the (103), (301), (221), (401), and (202) bands with spectral resolution from 0.01 to 0.0001 cm⁻¹ were obtained using air, N₂, O₂, and other buffer gases.

TABLE I. Laser spectrometers used to investigate the pressure-induced H₂O line shifts and profiles of the obtained experimental data. The visible and IR regions.

Type of spectrometer	Spectral region, resolution, investigated bands	Buffer gases	Number of lines for which shifts were measured	References
Two-channel photoacoustic spectrometer with ruby laser	14395-14400 cm ⁻¹ 0.01 cm ⁻¹ (103)	air, N ₂ , O ₂ , CO ₂ , He, Ar, Kr, Xe, CH ₃ -CO-CH ₃	3	[3, 4]
Two-channel photoacoustic spectrometer with dye laser	13700-14000 cm ⁻¹ 0.001 cm ⁻¹ (301), (202)	air	12	[9]
Two-channel spectrophotometer with ring dye laser	13000-14000 cm ⁻¹ 0.0001 cm ⁻¹ (221), (301), (202)	air, N ₂ , O ₂ , H ₂ O, Ar	≈150	[5, 6]
Two-channel photoacoustic intracavity spectrometer with dye laser	16100-17540 cm ⁻¹ 0.001 cm ⁻¹ (401)	air, CH ₃ -CO-CH ₃	10	[7, 8]
Spectrophotometer with ring Nd-glass laser	9240-9250 cm ⁻¹ 0.0001 cm ⁻¹ (012)	air, N ₂ , O ₂	6	[1]
Two-channel spectrophotometer with diode laser	1867-1870 cm ⁻¹ 0.008 cm ⁻¹ (010)	N ₂ , O ₂ , CO, NO, SO ₂	3	[10]
Spectrophotometer with diode laser	1360-1440 cm ⁻¹ 0.001 cm ⁻¹ (010)	N ₂ , CO ₂ He, Ne, Ar, Kr, Xe	4	[11]
Spectrophotometer with diode laser	1946-1979 cm ⁻¹ 0.001 cm ⁻¹ (010)	air, N ₂	9	[12, 13]

THEORETICAL ANALYSIS

Theoretical calculations of H₂O absorption line shifts caused by N₂, O₂, and air pressure, recorded in the above-mentioned experiments, were carried out using the Anderson-Tsao-Curnutte-Frost (ATCF) method.^{15,17} It is known^{5,6,14,18,19} that the dependence of the H₂O absorption line broadening coefficients (Γ_b) on the vibrational quantum number is weak for the majority of absorption bands and only for the nv_2 bending modes can interband variations of the broadening coefficients exceed 10% (Ref. 20). As a consequence of this, the Γ_b values calculated for the pure rotational lines can be used for the corresponding vibrational-rotational transitions. At the same time, the vibrational excitation strongly influences the shift coefficients (Γ_{sh}) and may change not

only the magnitude but also the sign of the shift.²¹ That is why calculations of the line shifts in the vibrational bands must be carried out for each band individually. It is evident that the use of "complex" calculational methods like the Robert-Bonamy,^{22,23} for example, which are based on numerical integration over the impact parameter and account for the repulsive part of the intermolecular potential and the deformation of the collisional trajectory, is a matter of some obvious difficulty. At the same time, a detailed analysis of the data^{22,23} shows that the "simple" ATCF method is valid for the majority of lines of the vibrational-rotational H₂O bands. Spectral lines with large values of the angular momentum quantum number, which are weak in the near-IR and visible spectral ranges and, hence, are absent in the spectra, are an exception.

The modification of the ATCF method required for the correct calculation of the line shift coefficients is described in Ref. 21. Vibrational excitation leads to the growth of the contribution of the isotropic term of the polarization potential to the line shift which strongly depends on the variations of the H₂O molecule polarizability, which, in its turn, determines the value of the dispersion constant C₆ in the intermolecular potential. The polarizability of the H₂O molecule in the excited vibrational state is determined by fitting one or several of the air-broadened absorption lines to the measured shift value. The line shifts of the band caused by the pressure of other gases as well as the shift of other lines of the band are calculated using the found value of the polarizability. A comparison of the calculated data with those obtained experimentally for different spectral intervals and for mixtures of H₂O with different gases is essential for determining the accuracy and validity of the method.

For this reason the present article includes not only the authors' data but also the results of measurements of the line shifts in the ν₂ band using IR laser spectrometers.^{9,10-13} Such a comparison makes it possible to test the predictive property of the ATCF method and to detect lines where the repulsive term of the intermolecular potential contributes significantly to the shift coefficient.

APPLICATION OF THE ATCF METHOD TO THE CALCULATION OF THE H₂O LINE SHIFTS IN THE VIBRATIONAL BANDS

In the ATCF method the spectral line halfwidth γ_{if} and line center shift δ_{if} for the transition i - f, where i and f are sets of quantum numbers of the initial and final states, are given by the following formula:

$$\gamma_{if} - i\delta_{if} = \frac{n}{c} \sum_j \rho(j) \int_0^\infty dv v F(v) \times \left[\int_{b_c(j)}^\infty db b S_{if}(j, b, v) + \frac{b_c^2(j)}{2} \right] \quad (1)$$

where n is the concentration of the buffer gas molecules; c is the speed of light; ρ(j) is the population of the level j of the buffer gas molecules; v is the relative velocity of the colliding molecules; F(v) is the Maxwellian distribution function, and b is the impact parameter. The complex interruption function S_{if}(j, b, v) determines the contribution of the collision (j, b, and v characterize the type of collision) to broadening and shifting, the interruption function in the ATCF method being represented as a sum of the first- and second-order terms of the expansion of the intermolecular potential

$$S_{if}(j, b, v) = S_{if}^{(1)}(j, b, v) + S_{if}^{(2)}(j, b, v) \quad (2)$$

The real part of the interruption function determines the halfwidth and the imaginary part determines the line shift. The interruption parameter is found by solving the equation

$$\text{Re } S_{if}(j, b_0, v) = 1 \quad (3)$$

The smaller of the two values b₀(j) and b_{min} is used to evaluate the integral over the impact parameter

$$b_c(j) = \min\{b_0(j), b_{\min}\} \quad (4)$$

where b_{min} is the "hard sphere" radius associated with the repulsive forces.

The ATCF method gives good results in calculating the H₂O line halfwidths due to the pressure of polar molecules or molecules possessing a large nuclear quadrupole moment.^{22,23} The method is valid for pure rotational line shifts.²⁴ The application of the ATCF method to calculating the H₂O absorption lines of the vibrational bands was described earlier, where the method was shown to be valid if the intermolecular interactions and the contribution of the polarization part of the intermolecular potential are taken into account more accurately. If the broadening is due to N₂ and O₂ and the dipole-quadrupole, induction, and dispersion terms of the intermolecular forces are taken into account, then the interruption function (2) is represented in the form

$$S_{if}^{(1)}(j, b, v) = -i \frac{3\pi}{8\hbar v b^5} \langle V_j | \alpha_2 | V_j \rangle \left\{ \left[\langle V_i | \mu^2 | V_i \rangle - \langle V_f | \mu^2 | V_f \rangle \right] + \frac{3}{2} \frac{e\epsilon_2}{\epsilon + \epsilon_2} \left[\langle V_i | \alpha | V_i \rangle - \langle V_f | \alpha | V_f \rangle \right] \right\} \quad (5)$$

$$S_{if}^{(2)}(j, b, v) = \frac{4}{45\hbar^2 v^2 b^6} \sum_{j'} Q(jj'|2) \times \left\{ \sum_{i'} D(i i' | 1) \varphi_{12}(k_{i i' j j'}) + \sum_{f'} D(f f' | 1) \varphi_{12}^*(k_{f f' j j'}) \right\} \quad (6)$$

In Eqs. (5) and (6) α, μ, and ε are the polarizability, dipole moment, and ionization potential of the H₂O molecule; α₂ and ε₂ are the polarizability and ionization potential of the perturbing molecules. The quantities D(i i' | 1) and D(f f' | 1) are the squares of the reduced matrix elements of the H₂O dipole moment divided by 2J_i ± 1 (or 2J_f + 1). Similarly, Q(jj'|2) is the square of the reduced matrix element

of the nuclear quadrupole moment of the perturbing molecules divided by $2J_2 + 1$. The nonadiabatic function of dipole-quadrupole interaction is written in the form

$$\varphi_{12}(k) = f_{12}(k) + i g_{12}(k), \quad (7)$$

where

$$\begin{aligned} k_{11', JJ'} &= \frac{2\pi cb}{v} \left[E_{1'} - E_{1'} + E_J - E_{J'} \right] = \\ &= \frac{2\pi cb}{v} \left[\omega_{11'} + \omega_{JJ'} \right] \end{aligned} \quad (8)$$

E_i and $E_{i'}$ are the energy levels of the H_2O molecule, E_J and $E_{J'}$ are the energy levels of the buffer gas molecules. The parameters $k_{ffj'}$ are determined analogously as in case (8). The functions $f_{12}(k)$ and $g_{12}(k)$ are given in Refs. 16 and 17. When calculating the line center shift the difference in the molecular parameters of the initial and final vibrational states must be taken into account: the polarizability $\langle V_f | \alpha | V_f \rangle$, the dipole moment $\langle V_f | \mu^2 | V_f \rangle$, the line strength of the rotational transition $D(ff' | 1)$, and the frequency $\omega_{ff'}$.

For absorption lines of the purely rotational spectrum $V_i = V_f$, the contribution of the function $S_{if}^{(1)}(j, b, v)$ is negligible and the line shift is determined only by the imaginary part of (2) $S_{if}^{(2)}(j, b, v)$. The vibrational excitation manifests itself in both the first and the second terms of Eq. (2) and the variation of the isotropic part of the dispersive interaction is responsible for the negative sign of the line shift in the near IR and visible spec-

tral ranges.²¹ The function $S_{if}^{(1)}(j, b, v)$ contributes to a growth of the shift when the difference $\langle V_i | \alpha | V_i \rangle - \langle V_f | \alpha | V_f \rangle$ on the right side of Eq. (5) increases and this growth also influences the behavior of the temperature dependence of the shift.²⁵ Variations of the dipole moment and the rotational and centrifugal constants of the H_2O molecule during the vibrational excitation are very important in calculating the H_2O line shifts.

CALCULATIONS OF THE WATER VAPOR LINE SHIFT COEFFICIENTS IN THE (301), (221), (202), (103), AND (401) BANDS

To calculate the broadening and shifting coefficients of the absorption lines of the above-mentioned bands, it is necessary to determine the energies and the wave functions of vibrational-rotational states, and the dipole moments and polarizabilities of ground and excited states of the H_2O molecule. The energy levels, rotational and centrifugal constants, dipole moment, and polarizability are known for the (000) state.

The vibrational-rotational energy levels for the (301), (221), (202), and (103) states are given in Ref. 26, and for the (401) state — in Ref. 27. The vibrational-rotational wave functions of these states had not been previously determined. We have done this work now. To estimate the rotational and centrifugal constants, we used energy levels up to $J \leq 4$ (Refs. 26 and 27) and the effective rotational Watson Hamiltonian, and the inverse spectroscopic problem was solved without taking into account the Coriolis, Fermi, or Darling-Dennison resonances. This approach makes it possible to estimate rotational (A, B, C) and centrifugal (Δ_k) constants and, hence, to account for the Δk effect in calculating the halfwidth and the line shifts in the band. The spectroscopic constants are given in Table II.

TABLE II. Rotational and centrifugal constants of some vibrational states of H_2O .

Parameter	221	202	301	103
E_v	13652.656	13828.272	13830.938	14318.813
A	31.2880	24.6525	24.6482	24.115
B	14.3505	13.8030	13.7389	13.942
C	8.5066	8.6570	8.6226	8.648
$\Delta_k \cdot 10^2$	8.14	1.8	0.86	6.26
$-\Delta_{jk} \cdot 10^2$	0.47	1.71	0.46	3.18
$\Delta_j \cdot 10^3$	1.72	4.75	1.24	1.24
$\delta_k \cdot 10^3$	4.78	14.24	1.3	1.3
$\delta_j \cdot 10^4$	7.2	5.1	5.1	5.1
$H_k \cdot 10^4$	14.18	1.2	1.2	1.2
$-H_{kj} \cdot 10^5$	—	—	1.4	1.4
$-L_k \cdot 10^7$	39.8	—	6.5	6.5
$P_k \cdot 10^9$	—	—	2.4	2.4

The mean dipole moments $\langle V|\mu^2|V\rangle$ and $\langle V|\mu|V\rangle$ were calculated by formulas taken from Ref. 28. The first and second derivatives of the dipole moment with respect to the normal coordinates and the anharmonic constants were taken from Ref. 29. The Fermi and Darling-Dennison resonances were taken into account in the calculations of the dipole moment matrix elements, and the resonance mixing coefficients were determined according to Ref. 30. The transformed dipole moment operator and its parameters as given in Ref. 29 were used to calculate the line strengths of the dipole transitions $D(i' | 1)$ and $D(ff' | 1)$. The calculated mean dipole moment $\langle V|\mu|V\rangle$ was used to determine the probability of the transitions $D(ff' | 1)$ to the upper vibrational state.

The polarizability of the H₂O molecule in the excited vibrational states was determined by fitting the calculated value of the line shift to that of the measured shift for one or several, lines in the broadening caused by air pressure. These lines are marked with an asterisk in the tables, which contain for comparison both the calculated and measured data. The value of the polarizability, determined in this way, was used to calculate the shift caused by the pressure of other gases as well as for the shift coefficients of other lines of the given band. The molecular constants and N₂ and O₂ parameters needed for the calculations are taken from the literature and are presented in Table III.

TABLE III.

Molecular constants of N₂ and O₂.

Parameter	N ₂	O ₂
Quadrupole moment (D Å ⁰)	3.0	0.7
Polarizability (10 ⁻²⁵ cm ³)	17.6	15.9
Ionization		
potential (10 ⁻¹¹ erg)	2.486	2.003
B ₀ (cm ⁻¹)	1.998	1.4456
D ₀ (10 ⁻⁶ cm ⁻¹)	5.76	4.84
b _{min} (Å ⁰)	3.5	2.645
Nuclear statistic weight		
a) even level	2	1
b) odd level	1	0

COMPARISON OF CALCULATED AND EXPERIMENTAL DATA

A comparison of the calculated and measured values of the line shift coefficients is given in Tables IV–VIII. The first two columns of each table contain the quantum numbers, followed by the tran-

sition frequency, followed by the shift coefficients caused by air, nitrogen, and oxygen. The first row of columns 4–7 gives the measured result, the second one gives the calculated result. The line center shift caused by air pressure is given by the formula

$$\delta_{air} = 0.79 \delta_{N_2} + 0.21 \delta_{O_2} \tag{9}$$

The calculated values of the shift coefficients show satisfactory agreement with the measured values; the sign of the shift is the same for every row, except for the line 4₁₄–3₃₁ of the 2ν₁ + 2ν₂ + ν₃ band. The calculated value of the shift coefficient differs from the measured one by less than 20% for 84.5% of the lines. In general, the agreement between the calculated and measured results is characterized by the following data

	air	N ₂	O ₂	
Δ ≤ 20	85.3	64.7	75.9	% of all the lines
20 < Δ ≤ 30	6.4	24.7	11.2	—"
30 < Δ ≤ 40	3.7	4.7	8.6	—"
40 < Δ	4.6	5.9	6.9	—"
Δ _{max}	62%	123%	60%	

Here $\Delta = \left| \frac{\delta_{exp} - \delta_{calc}}{\delta_{exp}} \right| \cdot 100\%$ and Δ_{max} is the maximum deviation.

TABLE IV.

Water vapor line shift coefficients of the band 3ν₁ + ν₃ (cm⁻¹atm⁻¹).

(J _{K_aK_c) (J_{K_aK_c)'}}	ω _{if} (cm ⁻¹)	air	N ₂	O ₂	air Ref. 9
8 3 6 7 3 5	13580.3677			-0.0304	
		-0.0208	-0.0156	-0.0403	
7 3 4 6 3 3	13601.5250			-0.0261	
				-0.0274	
9 0 9 8 0 8	13602.6515			-0.0377	
				-0.0494	
7 2 5 6 2 4	13611.3631			-0.0263	
		-0.0144	-0.0116	-0.0249	
7 3 5 6 3 4	13612.3790			-0.0283	
		-0.0186	-0.0136	-0.0357	
6 4 2 5 4 1	13628.1702			-0.0164	
		-0.0190	-0.0136	-0.0395	

$(JK_a K_c)(JK_b K_c)$	ω_{1r} (cm ⁻¹)	air	N ₂	O ₂	air Ref. 9
7 1 6 6 1 5	13633.1107	-0.0190		-0.0288	
		-0.0187	-0.0151	-0.0322	
7 2 6 6 2 5	13633.4179	-0.0226		-0.0341	
		-0.0214	-0.0167	-0.0391	
6 3 4 5 3 3	13643.7105	-0.0164		-0.0289	
		-0.0171	-0.0124	-0.0347	
6 2 4 5 2 3	13644.2232	-0.0137		-0.0270	
		-0.0131	-0.0097	-0.0257	
7 0 7 6 0 6	13659.8743	-0.0278		-0.0355	
		-0.0233	-0.0187	-0.0404	
5 4 1 4 4 0	13660.0187	-0.0179			
		-0.0201	-0.0133	-0.0456	
5 4 2 4 4 1	13660.2092	-0.0199		-0.0310	
		-0.0203	-0.0135	-0.0411	
7 1 7 6 1 6	13660.4826	-0.0256		-0.0355	
		-0.0230	-0.0183	-0.0409	
6 1 5 5 1 4	13660.9298		-0.0144	-0.0277	
			-0.0139	-0.0290	
6 2 5 5 2 4	13662.5022	-0.0178	-0.0157	-0.0300	
		-0.0179	-0.0135	-0.0343	
7 7 0 7 7 1	13663.5426	-0.0295			
		-0.0316	-0.0259	-0.0531	
5 3 2 4 3 1	13671.2417	-0.0151	-0.0124	-0.0274	
		-0.0142	-0.0097	-0.0317	
7 1 6 7 1 7	13671.8963	-0.0165			
		-0.0149	-0.0092	-0.0362	
5 3 3 4 3 2	13674.4333	-0.0135			
		-0.0159	-0.0111	-0.0343	
5 2 3 4 2 2	13677.0331	-0.0131	-0.0094	-0.0270	
		-0.0121	-0.0087	-0.0251	
6 1 6 5 1 5	13686.9947	-0.0230	-0.0194	-0.0349	
		-0.0202	-0.0163	-0.0350	
6 0 6 5 0 5	13687.1989	-0.0235	-0.0157	-0.0349	
		-0.0201	-0.0163	-0.0342	
5 1 4 4 1 3	13688.8686	-0.0178	-0.0155	-0.0272	
		-0.0177	-0.0129	-0.0260	
5 2 4 4 2 3	13690.8726	-0.0165	-0.0130		
		-0.0160	-0.0121	-0.0301	

$(JK_a K_c)(JK_b K_c)$	ω_{1r} (cm ⁻¹)	air	N ₂	O ₂	air Ref. 9
7 6 1 7 6 2	13695.7851		-0.0261	-0.0340	
		-0.0292	-0.0229	-0.0527	
4 3 1 3 3 0	13703.1088	-0.0149	-0.0103	-0.0269	
		-0.0140	-0.0089	-0.0334	
4 3 2 3 3 1	13704.1808	-0.0141	-0.0120	-0.0261	
		-0.0151	-0.0097	-0.0352	
6 6 1 6 6 0	13704.5385	-0.0287	-0.0263	-0.0331	
		-0.0305	-0.0245	-0.0530	
4 2 2 3 2 1	13709.5717	-0.0146	-0.0106		
		-0.0125	-0.0091	-0.0255	
5 1 5 4 1 4	13712.7596	-0.0189		-0.0310	
		-0.0174	-0.0140	-0.0304	
5 0 5 4 0 4	13712.9172	-0.0186		-0.0313	
		-0.0174	-0.0136	-0.0295	
4 1 3 3 1 2	13717.1747	-0.0159	-0.0131	-0.0273	
		-0.0126	-0.0095	-0.0241	
5 2 4 5 0 5	13717.6859	-0.0310	-0.0211		
		-0.0188	-0.0151	-0.0328	
4 2 3 3 2 2	13718.5762	-0.0145	-0.0105	-0.0271	
		-0.0147	-0.0110	-0.0287	
4 0 4 3 0 3	13736.1186	-0.0163	-0.0132	-0.0281	-0.015
		-0.0153	-0.0127	-0.0251	0.0032
4 1 4 3 1 3	13737.4161	-0.0163	-0.0133	-0.0277	
		-0.0157	-0.0127	-0.0271	
4 2 3 4 0 4	13737.9024	-0.0199	-0.0164	-0.0287	
		-0.0187	-0.0156	-0.0305	
3 2 1 2 2 0	13741.1540	-0.0135	-0.0110	-0.0247	
		-0.0138	-0.0104	-0.0266	
3 2 2 2 2 1	13745.6006	-0.0099		-0.0226	
		-0.0143	-0.0107	-0.0281	
3 1 2 2 1 1	13745.7853	-0.0125		-0.0259	
		-0.0101	-0.0067	-0.0231	
7 4 3 7 4 4	13754.7927	-0.0236	-0.0211		
		-0.0213	-0.0166	-0.0388	
8 4 5 8 4 4	13758.8791		-0.0263		
		-0.0157	-0.0110	-0.0336	
3 0 3 2 0 2	13759.7148	-0.0153	-0.0125	-0.0257	
		-0.0144	-0.0120	-0.0236	

$(J K_a K_c)(J K_a K_c)'$	$\omega_{1r} \text{ (cm}^{-1}\text{)}$	air	N ₂	O ₂	air Ref. 9
3 1 3 2 1 2 *	13761.5888	-0.0155 -0.0142	-0.0128 -0.0115	-0.0252 -0.0244	
1 1 3 4 1 4	13763.8874	-0.0155 -0.0108	-0.0092 -0.0070	-0.0222 -0.0250	
2 1 1 1 1 0	13774.2119	-0.0095 -0.0092	-0.0070 -0.0057	-0.0227 -0.0226	
5 4 1 5 4 2	13775.2987	-0.0200 -0.0220	-0.0164 -0.0160	-0.0295 -0.0448	
5 4 2 5 4 1	13775.8352	-0.0144 -0.0207	-0.0172 -0.0149	-0.0425	
2 0 2 1 0 1	13783.1795	-0.0164 -0.0147	-0.0126	-0.0234 -0.0224	
5 3 2 5 3 3	13783.8760	-0.0176 -0.0165	-0.0123	-0.0281 -0.0325	
2 1 2 1 1 1	13784.7849			-0.0232 -0.0237	
3 1 2 3 1 3	13788.8892		-0.0097 -0.0116	-0.0220 -0.0240	
4 3 1 4 3 2	13794.5580	-0.0170 -0.0169	-0.0140 -0.0121	-0.0274 -0.0348	
5 3 3 5 3 2	13794.7113	-0.0146 -0.0162	-0.0116 -0.0121	-0.0318	
6 3 4 6 3 3	13794.9029	-0.0137 -0.0158	-0.0105 -0.0119	-0.0280 -0.0303	
4 3 2 4 3 1	13797.5367	-0.0145 -0.0171	-0.0116 -0.0125	-0.0273 -0.0346	-0.013 0.002
3 3 0 3 3 1	13801.2788	-0.0164 -0.0189	-0.0136	-0.0274 -0.0386	-0.016
3 3 1 3 3 0	13801.7317	-0.0160 -0.0189	-0.0139	-0.0272 -0.0377	-0.013 0.001
3 2 1 3 2 2 *	13806.7821	-0.0155 -0.0146	-0.0140 -0.0111	-0.0260 -0.0277	
1 0 1 0 0 0	13807.1435	-0.0113 -0.0112	-0.0091 -0.0084	-0.0226 -0.0218	-0.011
2 1 1 2 1 2	13808.6933			-0.0221 -0.0142	
2 2 0 2 2 1	13815.7375	-0.0148 -0.0158	-0.0128 -0.0124	-0.0241 -0.0288	

$(J K_a K_c)(J K_a K_c)'$	$\omega_{1r} \text{ (cm}^{-1}\text{)}$	air	N ₂	O ₂	air Ref. 9
2 2 1 2 2 0	13818.4083			-0.0233	-0.010
		-0.0143	-0.0106	-0.0284	-0.000
3 2 2 3 2 1	13819.0491			-0.0249	
		-0.0135	-0.0098	-0.0274	
1 1 0 1 1 1	13821.9097			-0.0223	-0.015
		-0.0162	-0.0143	-0.0234	0.0057
4 2 3 4 2 2	13823.1814	-0.0124 -0.0138	-0.0095 -0.0103	-0.0254 -0.0271	-0.013 -0.0009
5 2 4 5 2 3	13830.7879			-0.0263 -0.0146	
		-0.0111		-0.0280	
1 1 1 1 1 0	13832.2508			-0.0179	
		-0.0064	-0.0022	-0.0222	
2 1 2 2 1 1	13839.6550			-0.0202	-0.008
		-0.0097	-0.0062	-0.0231	0.0017
3 1 3 3 1 2	13850.3930	-0.0121 -0.0135	-0.0107	-0.0241	
0 0 0 1 0 1	13853.2706	-0.0128 -0.0130	-0.0109	-0.0210	
4 1 4 4 1 3	13863.4882	-0.0137 -0.0154	-0.0100 -0.0126	-0.0260	-0.009 -0.0013
1 1 1 2 1 2	13866.7312		-0.0101	-0.0228	-0.009 -0.0011
		-0.0113	-0.0083	-0.0228	
1 0 1 2 0 2	13872.6818			-0.0198	-0.003
		-0.0080	-0.0046	-0.0208	0.0038
1 1 0 2 1 1	13876.7795			-0.0229	
		-0.0104		-0.0229	
2 1 2 3 1 3	13882.7586			-0.0096	-0.0226
				-0.0082	-0.0241
2 2 1 3 2 2	13884.0365	-0.0148 -0.0156	-0.0118	-0.0300	
2 0 2 3 0 3 *	13888.0804	-0.0103 -0.0088	-0.0064 -0.0056	-0.0227 -0.0210	
2 2 0 3 2 1	13889.1873	-0.0116 -0.0137	-0.0085 -0.0099	-0.0246 -0.0279	
6 1 6 6 1 5	13890.0672			-0.0275	
		-0.0204	-0.0169	-0.0344	
3 1 3 4 1 4	13897.1062	-0.0159 -0.0119	-0.0123	-0.0253	

$(J_k K_c)(J_k K_c)'$	ω_{1r} (cm ⁻¹)	air	N ₂	O ₂	air Ref. 9
3 2 2 4 2 3	13900.7803	-0.0171	-0.0128	-0.0272	
		-0.0159	-0.0122	-0.0298	
3 0 3 4 0 4	13901.5034	-0.0116	-0.0076	-0.0241	
		-0.0095	-0.0059	-0.0211	
7 0 7 7 2 6	13902.5088		-0.0212		
			-0.0217	-0.0433	
4 3 2 5 3 3	13910.1724			-0.0291	
			-0.0150	-0.0362	
3 2 1 4 2 2	13911.3871			-0.0282	
			-0.0100	-0.0264	
4 0 4 5 0 5	13911.8430			-0.0295	
			-0.0076	-0.0264	
5 4 2 6 4 3	13914.1741	-0.0146			
		-0.0226	-0.0168	-0.0444	
5 1 5 6 1 6	13920.3362		-0.0164		
			-0.0124	-0.0327	
5 0 5 6 0 6	13920.7699		-0.0151		
			-0.0109	-0.0316	
6 1 6 7 1 7	13928.8578			-0.034	
			-0.0159	-0.039	
4 2 2 5 2 3	13931.2178			-0.0280	
			-0.0120	-0.0258	
5 3 2 6 3 3	13935.0703	-0.0145	-0.0116	-0.0271	
		-0.0147	-0.0108	-0.0293	
6 2 5 7 2 6	13935.8416	-0.0216	-0.0195	-0.0309	
		-0.0203	-0.0153	-0.0391	
7 1 7 8 1 8	13936.3758	-0.0278	-0.0272	-0.0339	
		-0.0248	-0.0194	-0.0450	
7 0 7 8 0 8	13936.5789	-0.0290	-0.0265	-0.0349	
		-0.0244	-0.0190	-0.0448	
6 3 4 7 3 5	13937.5048		-0.0200	-0.0303	
			-0.0158	-0.0377	
5 1 4 6 1 5	13937.8679		-0.0106	-0.0243	
			-0.0083	-0.0272	
8 1 8 9 1 9	13943.0026	-0.0200			
		-0.0279	-0.0223	-0.0488	
7 2 6 8 2 7	13943.3957	-0.0290			
		-0.0243	-0.0189	-0.0446	

$(J_k K_c)(J_k K_c)'$	ω_{1r} (cm ⁻¹)	air	N ₂	O ₂	air Ref. 9
7 1 6 8 1 7	13948.3120	-0.0179			
		-0.0186	-0.0134	-0.0381	
8 2 7 9 2 8	13948.8154	-0.0285			
		-0.0269	-0.0212	-0.0485	

Note: experimental uncertainty is equal to ±0.0025 cm⁻¹atm⁻¹

TABLE V. Water vapor line shift coefficients of the 2ν₁ + 2ν₂ + ν₃ band (cm⁻¹atm⁻¹)

$(J_k K_c)(J_k K_c)'$	ω_{1r} (cm ⁻¹)	air	N ₂	O ₂	air Ref. 9
2 1 2 1 1 1	13612.9016	-0.0124		-0.021	
		-0.0122	-0.0098	-0.0217	
1 1 0 1 1 1	13650.0270	-0.0139		-0.0201	
		-0.0154	-0.0139	-0.0210	
3 2 1 3 2 2	13655.8170	-0.0122			
		-0.0112	-0.0076	-0.0248	
2 2 0 2 2 1	13663.2901	-0.0145		-0.0213	
		-0.0115	-0.0078	-0.0256	
5 3 2 5 3 3	13665.0997	-0.0147	-0.0139	-0.0277	
		-0.0142	-0.0098	-0.0309	
2 2 1 2 2 0	13665.8201	-0.0105	-0.0088	-0.0208	
		-0.0101	-0.0060	-0.0253	
2 1 2 2 1 1	13670.1824			-0.0170	
		-0.0087	-0.0056	-0.0204	
4 3 1 4 3 2	13673.3643	-0.0186			
		-0.0150	-0.0104	-0.0323	
4 2 3 4 2 2	13673.8009	-0.0095			
		-0.0118	-0.0084	-0.0245	
7 4 3 7 4 4	13674.7307	-0.0140			
		-0.0206	-0.0160	-0.0381	
4 3 2 4 3 1	13675.7737			-0.0261	
		-0.0146	-0.0098	-0.0327	
3 3 0 3 3 1	13678.4137	-0.0166	-0.0135	-0.0253	
		-0.0180	-0.0127	-0.0379	
3 3 1 3 3 0	13678.5730	-0.0163	-0.0128	-0.0261	
		-0.0176	-0.0124	-0.0373	

$(J_a K_a K_c)(J_b K_b K_c)$	ω_{1f} (cm ⁻¹)	air	N ₂	O ₂	air Ref. 9
5 4 1 5 4 2	13690.0014	-0.0217 -0.0238	-0.0191 -0.0186	-0.0305 -0.0432	
5 4 2 5 4 1	13690.5003	-0.0206 -0.0222	-0.0176 -0.0166	-0.0431	
4 4 1 4 4 0	13695.0327		-0.0105 -0.0355	-0.0468	
1 1 1 2 1 2	13695.2485			-0.0191 -0.0072	
1 1 0 2 1 1	13707.3076			-0.0207 -0.0203	
2 1 2 3 1 3	13711.5933		-0.0084 -0.0100	-0.0217 -0.0215	
3 1 3 4 1 4	13726.4259		-0.0085 -0.0105	-0.0227	
3 0 3 4 0 4	13728.1798		-0.0094 -0.0082	-0.0234 -0.0207	
2 1 1 3 1 2	13730.6507		-0.0152 -0.0120	-0.0206	
2 2 1 3 2 2	13733.0713		-0.0102 -0.0138	-0.0271	
4 1 4 3 3 1	13738.9949		-0.0081 -0.0019	-0.0159 -0.0220	
4 1 4 5 1 5	13739.4403		-0.0139 -0.0119	-0.0268 -0.0253	
4 0 4 5 0 5	13740.3908		-0.0112 -0.0101	-0.0247 -0.0237	
5 1 5 6 1 6	13750.8515		-0.0153 -0.0146	-0.0294 -0.0295	
5 0 5 6 0 6	13751.1356		-0.0151 -0.0131	-0.0291 -0.0284	
3 2 2 4 2 3	13751.5246		-0.0177 -0.0149	-0.0280	
3 1 2 4 1 3	13751.8491		-0.0120 -0.0110	-0.0243 -0.0210	
6 1 6 7 1 7	13761.8064		-0.0236 -0.0181	-0.0331 -0.0349	

$(J_a K_a K_c)(J_b K_b K_c)$	ω_{1f} (cm ⁻¹)	air	N ₂	O ₂	air Ref. 9
3 2 1 4 2 2	13762.0069	-0.0141 -0.0132	-0.0097 -0.0103	-0.0242 -0.0239	
7 1 7 8 1 8	13767.0095		-0.0200 -0.0166		
3 3 0 4 3 1	13772.8714	-0.0167 -0.0185	-0.0140 -0.0138	-0.0361	
8 1 8 9 1 9	13774.4157		-0.0265 -0.0241	-0.0430	
5 1 4 6 1 5	13787.8811		-0.0064 -0.0075	-0.0211 -0.0111	
4 3 1 5 3 2	13794.2500	-0.0157 -0.0156	-0.0080 -0.0117	-0.0216 -0.0305	
6 2 5 7 2 6	13795.4634	-0.0177 -0.0193	-0.0146	-0.0370	
5 3 2 6 3 3	13815.1226	-0.0152 -0.0138	-0.0164 -0.0103	-0.0259 -0.0271	
2 1 2 3 3 1	13884.3369	-0.0058 -0.0000	0.0049	-0.0170 -0.0185	
4 3 2 3 3 1	13581.3161		-0.0136 -0.0082	-0.0244 -0.0338	
3 0 3 2 0 2	13582.5702		-0.0125 -0.0101	-0.0246 -0.0216	

Note: experimental uncertainty is equal to ±0.0025 cm⁻¹atm⁻¹.

TABLE VI. Water vapor line shift coefficients of the 3ν₁ + ν₃ band (cm⁻¹atm⁻¹).

$(J_a K_a K_c)(J_b K_b K_c)$	ω_{1f} (cm ⁻¹)	air	N ₂	O ₂	air Ref. 9
5 2 5 5 1 4	13648.7095			-0.0294	
		-0.0217	-0.0178	-0.0362	
4 2 3 3 1 2	13689.7027	-0.0121 -0.0196	-0.0088 -0.0163	-0.0236 -0.0321	
5 1 4 4 2 3	13705.4437	-0.0118 -0.0119	-0.0060 -0.0070	-0.0303	
5 0 5 4 1 4	13711.0182	-0.0164 -0.0182	-0.0158 -0.0140	-0.0339	

$(JK_a K_c)$	$(JK_a K_c)'$	ω_{1f} (cm ⁻¹)	air	N ₂	O ₂	air Ref. 9
4 0 4 3 1 3		13738.4401	-0.0154	-0.0114	-0.0284	
			-0.0155	-0.0113	-0.0296	
3 0 3 2 1 2		13764.6747	-0.0118	-0.0069	-0.0252	
			-0.0121	-0.0086	-0.0253	
3 1 2 2 2 1		13776.0305		-0.0121		
			-0.0123	-0.0086	-0.0260	
5 2 3 5 3 2		13849.7616	-0.0180			
			-0.0143	-0.0101	-0.0299	
1 0 1 2 1 2		13877.6407			-0.0202	
			-0.0058	-0.0014	-0.0222	
2 0 2 3 1 3		13890.4020			-0.0223	
				-0.0041	-0.0245	
3 0 3 4 1 4		13899.6045	-0.0109		-0.0246	-0.010
			-0.0103	-0.0060	-0.0267	
5 2 4 6 1 5		13919.0867		-0.0110		
			-0.0218	-0.0177	-0.0370	
3 1 2 4 2 3		13931.5358			-0.0246	
			-0.0109	-0.0066	-0.0269	
5 1 4 6 2 5		13942.0505	-0.0118		-0.0261	
			-0.0132	-0.0081	-0.0324	
7 2 5 6 3 4		13644.9348	-0.0211			
			-0.0138	-0.0091	-0.0315	

Note: experimental uncertainty is equal to ± 0.0025 cm⁻¹atm⁻¹.

The considerable disagreement between the calculated and the experimental values of the shift coefficient for a number of the lines may be explained by insufficient accuracy in the values of the vibrational and centrifugal constants and by the fact that the Coriolis, Darling-Dennison, and Fermi resonances are not taken into account in calculating $D(f'f'|1)$. This is confirmed by the fact that the largest deviations Δ are observed, as a rule, for lines with large values of the quantum number K ($K_a \approx 4-6$). Random resonances are known to strongly affect highly excited vibrational-rotational H₂O states.

At the present time it is not possible to adequately take into account resonance effects in the line shift calculations because of the absence of rotational, centrifugal, and resonance constants characterizing the mixing of the wave functions of the states under consideration (i.e., the inverse spectroscopic problem has not yet been solved). For this purpose, the calculational results for lines with large

values of the quantum numbers J and K_a should be considered as a satisfactory.

TABLE VII. H₂O line shift coefficients of the bond $\nu_1 + 3\nu_3$ (cm⁻¹ atm⁻¹).

$(JK_a K_c)$	$(JK_a K_c)'$	ω_{1f} (cm ⁻¹)	air	N ₂	O ₂
4 1 4 5 1 5		14397.364	-0.018	-0.016	-0.026
			-0.016	-0.011	-0.036
4 0 4 5 0 5		14400.328	-0.013	-0.009	-0.026
			-0.014	-0.009	-0.034
3 2 1 4 2 2 *		14400.782	-0.016	-0.013	-0.026
			-0.016	-0.012	-0.026

Note: experimental uncertainty is equal to ± 0.003 cm⁻¹ atm⁻¹

TABLE VIII. H₂O line shift coefficients of the bond $4\nu_1 + \nu_3$ (cm⁻¹ atm⁻¹).

$(JK_a K_c)$	$(JK_a K_c)'$	ω_{1f} (cm ⁻¹)	air	N ₂	O ₂
4 1 4 5 1 5 *		16974.278	-0.016	—	—
			-0.016	-0.010	-0.038
2 1 2 1 1 1		16852.795	-0.009	—	—
			-0.015	-0.011	-0.032
1 1 0 2 1 1		16944.334	-0.014	—	—
			-0.018	-0.015	-0.031
3 1 3 2 1 2		16949.732	-0.018	—	—
			-0.014	-0.009	-0.033
4 1 4 3 1 3		16968.449	-0.008	—	—
			-0.014	-0.009	-0.030
5 0 5 6 0 6		16984.278	-0.018	—	—
			-0.017	-0.011	-0.043
6 1 6 7 1 7		16990.788	-0.030	—	—
			-0.024	-0.016	-0.051

Note: experimental uncertainty is equal to ± 0.002 cm⁻¹ atm⁻¹

TABLE IX.

Parameters of some vibrational states of H₂O.

$V_1 V_2 V_3$	E_v , cm ⁻¹	μ , D	$\alpha \cdot 10^{-25}$ cm ³
0 0 0	0	-1.859	14.69
0 1 0	1594	-1.827	14.93
0 1 2	9000	-1.859	15.68
2 0 1	10013	-1.888	15.52
2 2 1	13653	-1.830	15.93
2 0 2	13828	-1.902	16.12
3 0 1	13831	-1.899	15.92
1 0 3	14319	-1.909	16.07
4 0 1	16899	-1.909	16.17

Note that calculations which do not take the Δk effect into account (i.e., when the rotational constants of the vibrational states are the same as for the ground state) lead to results that strongly differ from the experimental values. The last column of Table IV lists the measured and calculated⁹ results for the H₂O line center shifts caused by air pressure. A comparison of the results of Ref. 9 with the results of the measurements of Ref. 6 and our own calculations shows that the calculated shift values⁹ differ in sign and order of magnitude from the measured results^{6,9} and our calculations. This is due to neglecting the Δk effect and polarization interactions in the calculations.⁹ The trajectory distortion effect of collisions and the short-range part of the intermolecular potential^{22,23} probably have an effect on the shifts of the line centers with $K_a \approx J$. Application of the ATCF method in this case is impossible.

There are no fitting parameters in the calculations of the H₂O line shifts caused by N₂ and O₂ pressure, and hence the results are predictive. These results agree well with experiment, which shows that the polarizabilities, obtained from the shift caused by air pressure, satisfactorily reproduce the intermolecular potential for the binary collisions H₂O–N₂ and H₂O–O₂.

Table IX presents values of $\langle V|\alpha|V \rangle$ for a number of H₂O vibrational states. The polarizabilities of the (010), (012), and (201) states were obtained earlier using the measured shift coefficients given in Ref. 21. An analysis of the data in Table IX reveals that vibrational excitation leads to a nearly linear increase of the polarizability with V . Its maximum increase stands at 10% relative to the polarizability of the (000) state. The vibrational dependence of α can be simply described by the expression

$$\alpha_{V_1 V_2 V_3} = \left[14.69 + \tilde{\alpha}_1 V_1 + \tilde{\alpha}_2 V_2 + \tilde{\alpha}_3 V_3 \right], \quad (10)$$

where $\alpha_{V_1 V_2 V_3}$ is the polarizability of the H₂O molecule in the vibrational state ($V_1 V_2 V_3$) and $\tilde{\alpha}_1$, $\tilde{\alpha}_2$, $\tilde{\alpha}_3$ are the coefficients which describe the vibrational dependence (they are obtained by fitting to the experimental data on the lineshifts using the method of least squares) Their values with 68% confidence intervals are $\tilde{\alpha}_1 = 0.26998 \pm 0.0237$, $\tilde{\alpha}_2 = 0.178 \pm 0.036$, and $\tilde{\alpha}_3 = 0.390 \pm 0.025$. It should be noted that the well-known approximation for the dispersion constant C_6 is used in Eq. (5):

$$C_6 \approx \frac{3}{2} \alpha_1 \alpha_2 \frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2} \quad (11)$$

and the applicability of $S_{if}^{(j, b, v)}$ in Eq. (5) to calculate the line shift depends on the accuracy of Eq. (11) where α_1 and α_2 are the polarizabilities, and ϵ_1 and ϵ_2 are the ionization potentials of the in-

teracting molecules. Therefore the improvement of the accuracy of the polarizability values of the molecules in excited vibrational states increases the predictive power of the calculation method.

In general the results presented show that the ATCF method and approximation (11) enable one to calculate with satisfactory reliability the H₂O absorption line shifts caused by nitrogen, air, and oxygen pressure not only for IR-range bands, but also for the visible spectral range. The available experimental data on the H₂O vibrational-rotational line shifts and the calculational method for applying these data in numerous calculations of shifts in the spectral ranges that are most important for laser gas-analysis make it possible to contribute new information to existing databases of molecule absorption spectra.^{31,32}

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