

## AN ACCOUNT OF PRESSURE SHIFTS OF THE ABSORPTION LINE CENTERS OF ATMOSPHERIC GASES IN PROBLEMS ON A NARROW-BAND OPTICAL RADIATION TRANSFER

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*This paper analyzes theoretical and experimental results on shifts of absorption lines of atmospheric gases. Results of numerical simulations of an account of influence of line shifts on radiation propagation in the atmosphere obtained for several altitude distributions of the absorbing gases are presented and criteria for assessing the necessity of taking this influence into account are proposed.*

Use of lasers with narrow emission lines and high-resolution instrumentation for active and passive sensing of the atmospheric gaseous components needs for more fine spectroscopic effects to be taken into account. One of such effects is the shift of the molecular absorption line center in the rovibrational spectrum caused by air pressure. In some particular cases<sup>1</sup> it has been already shown that the neglect of the shift can result in a significant systematic error in the solution of inverse problem on laser sensing of water vapor concentration at altitudes above 12–15 km. At present the absorption line shifts have been studied for a number of air molecules of natural and anthropogenic origin. In this connection the problem arises on seeking a universal criterion enabling one to assess the necessity of taking into account the shifts of absorption line centers of minor gaseous components of the atmosphere in such atmospheric optics problems as:

- computation of the atmospheric transmission for the laser and narrow-band optical radiation at the wavelengths of resonance absorption lines along vertical and slant paths,
- determination of integral (over a path) gaseous concentrations by means of ground-based or airborne high-resolution spectrometers, and
- remote sensing of spatial distribution of gaseous components of natural and anthropogenic origin by resonance absorption and scattering technique.

This paper presents an analysis of theoretical and experimental results of studying the absorption line shifts of the minor atmospheric gases and a description of numerical experiments on account of the shift effect on the resonance transmission spectrum for some types of distribution of the absorbing gas concentration over altitudes. Criteria for estimating the influence of the absorption line shift on propagation of a narrow-band radiation in the IR and visible regions.

### SHIFTS OF CENTERS OF ROVIBRATIONAL MOLECULAR ABSORPTION LINES CAUSED BY AIR PRESSURE

Laser and Fourier spectroscopy techniques are now widely used in studying the absorption line shifts of water vapor, CO<sub>2</sub>, O<sub>3</sub>, CH<sub>4</sub>, and a number of other molecules of minor atmospheric components.

The greatest bulk of data on the line shifts is available for water vapor molecule the measurements and calculations for which have been done in different spectral regions from the microwave to visible regions. The results concerning the rovibrational line shifts of the H<sub>2</sub>O molecule can be found in Refs. 2–31. The measurements and theoretical analysis of line shifts for O<sub>3</sub> (Refs. 33 and 34), CO<sub>2</sub> (Refs. 35 and 36) CO (Ref. 37) CH<sub>4</sub> (Refs. 38 and 39) HCl (Ref. 40) NH<sub>3</sub> (Ref. 41), and HF (Ref. 42) molecules were conducted in a more narrow IR region for several vibrational bands. Nitrogen, oxygen, air, light atomic and molecular gases (H<sub>2</sub>, He), inert gases, and polyatomic molecules with large dipole moment were used as broadening gases.<sup>19</sup> In Refs. 1–6, 10, and 31 one can find measurement data on the self-pressure line shifts.

Analysis of the array of experimental and calculational data available allows one to arrive at some general conclusions and to illustrate them. These conclusions are important for understanding some peculiarities on account of the joint effect of the spectral line shifts and broadening on solutions of the direct and inverse problems of optics of inhomogeneous molecular atmosphere.

A comparison of shift coefficients for water vapor absorption lines calculated by the Anderson–Tsao–Curnutte–Frost (ATCF) technique with the experimental ones has shown that this technique gives quite satisfactory results both in the case of broadening by N<sub>2</sub>, O<sub>2</sub>, and air, and self-broadening or broadening by molecules with large dipole moments.<sup>19–24</sup> Analysis of NH<sub>3</sub> absorption line shifts<sup>41</sup> has also shown that ATCF technique is more accurate than the QFT (quantum Fourier transform) technique.<sup>29</sup> All results presented in this paper were obtained using the ATCF technique.

In this approach the line shifts of polar molecules by N<sub>2</sub> or O<sub>2</sub> molecules pressure are described by the imaginary part of the interruption function, which is represented by two terms

$$\begin{aligned} \text{Im}S_{ij2}^{(2)} = & Aq^2 \left( \sum_{i'} d_i^2 D(i, i') P(\omega_{ii'}) - \right. \\ & \left. - \sum_f d_f^2 D(f, f') P(\omega_{ff'}) \right) / b_0^6(j2) \end{aligned} \quad (1)$$

and

$$S_{ifj2}^{(1)} = \frac{B\alpha_2 \left( d_e(d_i - d_f) + \frac{3}{2} \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2} (\alpha_i - \alpha_f) \right)}{b_0^5(j2)}, \quad (2)$$

where  $A$  is a constant,  $d_i$  and  $d_f$  are the dipole moments of the initial and final vibrational states of the transition under study,  $D(i, i')$  and  $D(f, f')$  are the oscillator strengths of the lines of dipole transitions,  $\omega_{ii'}$  and  $\omega_{ff'}$  are the corresponding frequencies of the transitions,  $P(\omega)$  is the odd function of the transition frequencies, which depends also on the frequencies of virtual transitions in a buffer gas molecule,  $q$  is the quadrupole moment either of the  $N_2$  or  $O_2$  molecule,  $b_0(j2)$  is the interruption impact parameter,  $\alpha_2$  is the polarizability either of the  $N_2$  or  $O_2$  molecule,  $\varepsilon_1$  and  $\varepsilon_2$  are the ionization potentials, while  $\alpha_i$  and  $\alpha_f$  are the absorbing molecule polarizabilities in the initial and final states.

Contrary to a line half-width  $\gamma$ , the line shift  $\delta$  depends on the peculiarities of a molecular energy spectrum and is subjected to a strong influence of the intramolecular interactions. The evidence of this fact is, for example, "oscillations" of DCl molecule line shifts, caused by collisions with HCl molecules<sup>32</sup> and the absence of such oscillations in the case of self-broadening of HCl, HF, and of  $H_2O$  absorption lines. Since the line shift is defined as a difference between the shifts of energy levels of the initial and final states of a molecule, i.e., between close values, the shift values are small and can significantly vary in the presence of small additions to one of the summands in Eq. (1) due to intramolecular interactions.<sup>20</sup>

The intramolecular interaction effects on the line shifts were theoretically analyzed in Refs. 19–21, and 24. The role of random resonances in the formation of the  $H_2O$  molecule absorption line shift was discussed in Ref. 13.

The ratio of the  $\text{Im}S_{ifj2}^{(2)}$  to  $S_{ifj2}^{(1)}$  contributions is a very important factor in a description of a general mechanism of line shifts. Actually, if  $S_{ifj2}^{(1)} = 0$  (pure rotational bands of polar molecules) or the  $S_{ifj2}^{(1)}$  value is small in comparison with  $\text{Im}S_{ifj2}^{(2)}$  ( $\alpha_f \cong \alpha_i$ , i.e., weak excitation or a presence of "strong" electrostatic such as the dipole–dipole interaction), then the shift formation is described by the anisotropic component of the intermolecular interaction potential (by dipole–quadrupole interaction in the case of the  $H_2O$  molecule line shift by  $N_2$  molecule pressure).

In this case a sign and a magnitude of the shift coefficient are determined by means of a quite sophisticated procedure from a ratio of contributions of virtual transitions from the initial and final states followed by an increase or a decrease in the internal energy of colliding molecules. Our calculations by the

ATCF technique have shown the existence of approximately equal numbers of lines with positive and negative shift coefficients for  $v_2$  band and the situation, when shifts of centers of adjacent lines of one and the same band have opposite signs and different magnitudes is quite realistic. The same results are obtained for lines of  $v_2$  band broadened by nitrogen<sup>14</sup> and for self-broadened water vapor absorption lines ( $3v_1 + v_3$ ,  $2v_1 + 2v_2 + v_3$  (Ref. 10), and  $v_1 + 3v_3$  (Ref. 31) bands).

Thus obtained data on the line shifts are of a random character what makes it impossible to find some simple relations between the broadening and shift coefficients. However, an analysis of this data array enables one to reveal some regularities in  $J$  and  $K_a$  dependences (for the molecules of water vapor type), band–type dependences, and so on. Alternation of the shift sign for the lines of the  $v_3$ –band with permuted quantum numbers of the initial and final states was experimentally observed in Ref. 11. The case in which the contribution coming into the shift from  $\text{Im}S_{ifj2}^{(2)}$  is dominating can be called "oscillating shift".

If  $|S_{ifj2}^{(1)}| \gg |\text{Im}S_{ifj2}^{(2)}|$  the shift coefficient is negative (at the vibrational excitation ( $\alpha_f > \alpha_i$ ), i.e., at an increase of the polarizability) what means that the shift is formed due to vibrational phase shift. In this case, which can be called the case of "monotonic shifts", the main contribution to shifts comes from the interaction described by the isotropic component of the intermolecular interaction potential. The shift magnitude turned out to be proportional to change of the vibrational quantum number and compared to shifts of lines in lower bands it can increase by an order of magnitude, or change its sign. In the case of absorption lines in the visible region the effect of high energy levels excitation is the decisive one.<sup>19</sup> Table I presents data illustrating the correlation between the energy of an excited vibrational level, its polarizability, and average value of the shift caused by air pressure (according to the data from Refs. 7–20).

As follows from the data presented in Table I in the absorption  $v_2$  band of  $H_2O$  molecule there are both positive and negative line shifts of approximately the same value, while in the  $3v_1 + v_3$  band the shifts are only negative. In the case of "monotonic shifts" the dependence of  $\delta$  on the rotational quantum numbers becomes simpler because only the parameter  $b_0(j2)$  in formula (2) depends on the rotational quantum number. For lines in the near-IR and visible regions there exists an anticorrelation between the half-width and the shift of a line center. As known an increase in  $J$  is accompanied by a decrease in the line half-width (i.e., the decrease of the interruption parameter  $b_0(j2)$ ), at the same time the shift coefficient increases with increasing rotational quantum number  $J$ , what, by the way, is well explained by formula (2).

TABLE I. Measured values of the shift coefficient for H<sub>2</sub>O absorption lines from bands in the IR and visible regions.

$v_1v_2v_3$	$E_v, \text{ cm}^{-1}$	$\mu, D$	$\alpha, A^3$	$\delta, \mu\text{k}/\text{atm}$	Foreign gas	References
010	1594	-1.827	1.493	-11...+ 7	N <sub>2</sub>	7, 8, 14, 26, 27
100	3657	-1.865	1.517	- 6... 0	N <sub>2</sub>	15
001	3755	-1.877	1.499	-11...+ 4	N <sub>2</sub>	15
110	5234	-1.828	1.513	- 8... 0	N <sub>2</sub>	13
011	5331	-1.847	1.563	-22...+ 5	N <sub>2</sub>	13
021	6871	-1.815	1.538	-12...+ 2	N <sub>2</sub>	13
200	7201	-1.869	1.547	-13...+ 3	N <sub>2</sub>	13
101	7249	-1.884	1.535	-15...- 4	N <sub>2</sub>	13, 30
111	8807	-1.852	1.563	-27...- 3	N <sub>2</sub>	13
012	9000	-1.859	1.568	-34...-12	air	19
201	10613	-1.889	1.552	-14...- 8	air	16
221	13652	-1.830	1.593	-18...- 6	N <sub>2</sub>	9
				-22...-11	air	
202	13828	-1.902	1.612	-29...- 5	N <sub>2</sub>	9
				-27...- 6	air	
301	13830	-1.899	1.592	-27...- 6	N <sub>2</sub>	9, 17
				-31...-10	air	
103	14319	-1.909	1.607	-16...- 9	N <sub>2</sub>	18, 19
				-18...-13	air	
401	16899	-1.909	1.617	-30...- 9	air	19

Figure 1 presents the ratio  $\delta/\gamma$  for *P*- and *Q*-branches in the 301 band and for *R*-branch in  $2\nu_1 + 2\nu_2 + \nu_3$  band of the H<sub>2</sub>O molecule as functions of the quantum number *J* in the case of line broadening by air at temperature 296 K.

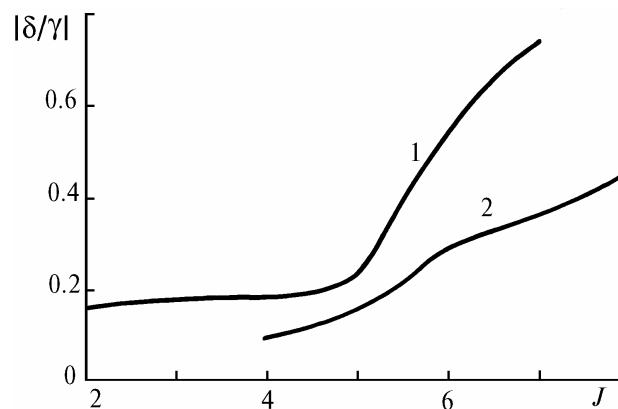


FIG. 1. Dependence of  $|\delta/\gamma|$  on the rotational quantum number *J* at  $T = 296$  K for the absorption lines of H<sub>2</sub>O molecule broadened by air pressure. 1) band 301 ( $\Delta J = 0$ ); 2) band 221 ( $\Delta J = -1$ ) (data from Ref. 9).

And, finally, the temperature dependences of line shifts and widths as well as of oscillating and monotonic shifts differ significantly.

At temperature increase the collisions become more frequent what causes a decrease of the broadening and shift coefficients. These same coefficients increase, on the whole, at decreasing temperature.

Theoretical analysis<sup>22</sup> of the temperature dependence of line shifts of a purely rotational and  $\nu_2$  bands of the H<sub>2</sub>O molecule (oscillating shifts) has shown that it could be nonmonotonic and a decrease of temperature could cause an alternation of the shift sign. Measurement data on  $\delta$  and  $\gamma$

for the HCl molecule obtained at two temperatures 298 K and 163 K are discussed in Ref. 43, in which it is clearly demonstrated, that at 163 K the value of  $|\delta/\gamma|$  is 1.25 times as large as that at 298 K.

Temperature behaviors of the H<sub>2</sub>O molecule line shifts by N<sub>2</sub>, O<sub>2</sub>, and air pressure in the near-IR and visible regions of spectrum (monotonic shifts) are monotonic and approximately inversely proportional to temperature<sup>9,21</sup> due to dominating contributions coming from the first order terms.

Analysis of measurement data on widths and shifts of the absorption lines from the  $3\nu_1 + \nu_3$  band of the H<sub>2</sub>O molecule broadened by air enabled the authors of Ref. 9 to construct empirical formulas for describing temperature behaviors of the linewidth  $\gamma$  and line shift  $\delta$

$$\gamma(T) = \gamma_0(T_0/T)^n, \quad \delta(T) = \delta_0(T_0/T)^{n'}, \quad (3)$$

where  $\gamma_0$  and  $\delta_0$  are the values of  $\gamma$  and  $\delta$  at  $T = 296$  K and

$$n_{\text{air}} = 9.31 \cdot \gamma_{\text{air}} - 0.15, \quad (4)$$

$$n'_{\text{air}} = -52 \cdot \delta_{\text{air}} - 0.15, \quad (5)$$

where  $\gamma_{\text{air}}$  and  $\delta_{\text{air}}$  are the half-width and shift of line in air. The values  $\gamma = 0.0405 \text{ cm}^{-1} \cdot \text{atm}^{-1}$  and  $\delta = -0.0295 \text{ cm}^{-1} \cdot \text{atm}^{-1}$  measured for a line of  $3\nu_1 + \nu_3$  band of the H<sub>2</sub>O molecule corresponding to the (771)–(770) transition, when substituted into relations (4) and (5) give the following temperature dependence of the ratio  $|\delta/\gamma|$ :

$$\frac{\left(\frac{|\delta(T)|}{\gamma(T)}\right)}{\left(\frac{\delta_0}{\gamma_0}\right)} = \left(\frac{T_0}{T}\right)^{1.15}. \quad (6)$$

Naturally, this relation may vary from line to line within a band, but nevertheless, as in the case with HCl molecule, the account for line shifts by air is more critical at low temperatures.

Experimentally observed regularities in the temperature behavior of the shift coefficients, on the whole, well correlate with the data calculated by the ATCF technique.<sup>22</sup>

The value  $\varepsilon = |\delta_0/\gamma_0|$  is the important parameter used in the analysis of the effect of line shifts on the propagation of a narrow-band radiation through the atmosphere as well as in processing of data of active and passive sensing of the gaseous components of the atmosphere.

The next section of this paper presents some results of numerical experiments aimed at illustrating the influence of the absorption line shifts on the propagation of laser and a narrow-band optical radiation with the wavelengths near the absorption line centers along inhomogeneous paths.

**NUMERICAL EXPERIMENTS ON THE PROPAGATION OF OPTICAL RADIATION ALONG VERTICAL PATHS IN THE ATMOSPHERE**

One can find a number of papers in the literature<sup>1,11,44</sup> dealing with the study of influence of an absorption line center shift by air pressure on spectra of the atmospheric transmission along slant paths, but all of them concern with some specific situations. A computer simulation of the process for an isolated line with the Voigt profile has been performed to study the problem in the general case. The volume absorption coefficient ( $\text{km}^{-1}$ ) at the altitude  $h$  and frequency  $\nu$  is

$$\alpha(\nu, h) = \frac{S(h)r(h)}{\pi} \frac{a(h)}{b(h)} \int_{-\infty}^{\infty} \frac{\exp(-x^2)dx}{a^2(h) + (\omega(h) - x)^2}, \tag{7}$$

$$a(h) = \frac{\gamma(h)}{\gamma_D(h)} \sqrt{\ln 2}; \quad b(h) = \gamma_D(h) \sqrt{\pi/\ln 2}, \tag{8}$$

$$\omega(h) = \frac{|\nu - \nu_0 - \delta(h)|}{\gamma_D} \sqrt{\ln 2}, \tag{9}$$

where  $\nu_0$ ,  $S$ ,  $\gamma$ , and  $\gamma_D$  are the center, intensity, Lorentz and Doppler half-widths of the spectral line, respectively;  $\delta(h)$  is the shift of a line center by air pressure; and,  $\rho(h)$  is the partial pressure of an absorbing gas.

Spectral transmission of a slant path through the whole atmosphere at a zenith angle  $\theta$  is determined by the Bouguer law:

$$T(\nu) = \exp[-\tau(\nu, H)],$$

$$\tau(\nu, H) = \frac{1}{\cos(\theta)} \int_0^H \alpha(h)dh, \tag{10}$$

where  $\tau(\nu, H)$  is the optical thickness of the layer 0– $H$ .

Measured value of the atmospheric transmission is determined as

$$T_\nu = \int_{\nu-\Delta\nu}^{\nu+\Delta\nu} T(\nu') g(\nu, \nu') d\nu', \tag{11}$$

where  $g(\nu, \nu')$  is the instrumental function of a spectrometric device normalized by unit. The Gaussian function is a good enough approximation of  $g(\nu, \nu')$  if the width of the latter is comparable by magnitude with the absorption linewidth.

As follows from Eqs.(7)–(11) the profile of the resonance transmission spectrum of an inhomogeneous atmospheric path is determined by the geometrical parameters of the path, altitude profiles of meteorological parameters  $P(h)$  and  $T(h)$  as well as by the type of the dependences of  $S$ ,  $\gamma$ ,  $\gamma_D$ , and  $\delta$  on meteorological parameters. In order to alleviate the analysis and to reveal basic regularities we first consider a simplified case of a vertical path, which is assumed to be isothermal what allows us to exclude temperature dependences of the spectroscopic quantities from the consideration.

Vertical profiles of air pressure and concentration of the absorbing gases were defined in our simulation as

$$P(h) = P_0 \exp(-\beta h);$$

$$\rho(h) = \rho_0 \exp(-m\beta h), \tag{12}$$

where  $\beta = 0.125 \text{ km}^{-1}$ ,  $m = 1, 2, 3$ , and  $P_0 = 1 \text{ atm}$ .

The Lorentz half-width was taken equal to  $0.1 \text{ atm}^{-1} \text{ cm}^{-1}$ . The spectral line intensity was chosen so that the optical thickness of an atmospheric path at the line center was equal to 2.5, what provides for the transmission variation in the range 0.08–1.0. The parameters varied in this model problem were the instrumental contour half-width  $\delta\nu$ , line shift by air pressure  $\delta_0$  at standard temperature and pressure, and the Doppler half-width of a line  $\gamma_D$ . The values of  $\delta\nu$  and  $\delta_0$  varied in the ranges  $0 \leq \delta\nu/\gamma_0 \leq 1$  and  $0.1 \leq \delta_0/\gamma_0 \leq 1$ , and the range of the Doppler half-width variation was  $0.024 \leq \gamma_D/\gamma_0 \leq 1$ .

The calculational results were presented in the form of spectral dependences of the optical thickness and transmission along vertical atmospheric paths within the spectral interval  $\nu_0 \pm 3\gamma_0$  with an increment of  $0.001 \text{ cm}^{-1}$ . The Voigt line profile was calculated using the technique from Ref. 45. At each step of calculations two values were determined: the observed shift of maximum  $\nu^*$  relative to  $\nu_0$  and the asymmetry coefficient  $\chi$  defined by the expression

$$\chi = \frac{\int_{\nu_1}^{\nu^*} [1 - T(\nu)]d\nu}{\int_{\nu^*}^{\nu_2} [1 - T(\nu)]d\nu}. \tag{13}$$

The integration limits  $\nu_1$  and  $\nu_2$  are chosen so that the transmission values  $T(\nu)$  at the boundary points are close to unity.

Tables II–IV present the simulation results for two values of shift, four values of the spectral resolution, and four values of the Doppler half-width.

TABLE II. The line center shift and the asymmetry coefficient along a vertical path for a gas with the vertical distribution of number density  $\rho = \rho_0 \exp(-\beta h)$ .

Absolute value of shifts, $\text{cm}^{-1}$								
$\delta\nu, \text{cm}^{-1}$	$\varepsilon = 0.1$				$\varepsilon = 1$			
	$H, \text{km}$							
	0	10	20	30	0	10	20	30
0	0.004	0.002	0.001	0.000	0.037	0.019	0.007	0.002
0.010	0.004	0.002	0.001	0.001	0.037	0.020	0.011	0.010
0.020	0.004	0.002	0.002	0.002	0.037	0.023	0.018	0.018
0.100	0.004	0.004	0.004	0.004	0.042	0.043	0.044	0.043
Asymmetry coefficient								
$\delta\nu, \text{cm}^{-1}$	$\varepsilon = 0.1$				$\varepsilon = 1$			
	$H, \text{km}$							
	0	10	20	30	0	10	20	30
0	1.00	1.04	1.07	1.13	1.07	1.52	2.23	2.81
0.010	1.00	1.04	1.07	1.08	1.07	1.47	1.85	1.95
0.020	1.00	1.04	1.05	1.05	1.07	1.40	1.61	1.63
0.100	1.00	1.01	1.01	1.01	1.03	1.07	1.07	1.07

TABLE III. The line center shifts and the asymmetry coefficients along a vertical path for a gas with the vertical distribution of number density  $\rho = \rho_0 \exp(-2\beta h)$ .

Absolute value of shifts, $\text{cm}^{-1}$								
$\delta\nu, \text{cm}^{-1}$	$\varepsilon = 0.1$				$\varepsilon = 1$			
	$H, \text{km}$							
	0	10	20	30	0	10	20	30
0	0.006	0.004	0.002	0.001	0.058	0.045	0.037	0.037
0.010	0.006	0.004	0.003	0.003	0.058	0.045	0.038	0.038
0.020	0.006	0.004	0.004	0.004	0.058	0.047	0.043	0.042
0.100	0.006	0.006	0.006	0.006	0.061	0.062	0.062	0.063
Asymmetry coefficient								
$\delta\nu, \text{cm}^{-1}$	$\varepsilon = 0.1$				$\varepsilon = 1$			
	$H, \text{km}$							
	0	10	20	30	0	10	20	30
0	1.00	1.03	1.08	1.11	1.04	1.28	1.50	1.50
0.010	1.00	1.03	1.05	1.05	1.04	1.24	1.37	1.37
0.020	1.00	1.03	1.03	1.03	1.04	1.21	1.29	1.31
0.100	1.00	1.00	1.01	1.01	1.02	1.03	1.04	1.03

The  $H$  value in these tables is the altitude at which the Doppler half-width is equal to the Lorentz one  $\gamma_D = \gamma(H)$ . Since  $\gamma$  is directly proportional to air pressure it decreases with the altitude increase and, consequently, at altitudes below  $H$  the Lorentz profile dominates while at altitudes above  $H$  the Doppler profile does. The data presented in these tables allow us to analyze the role of the line center shift in propagation of radiation along vertical paths in the atmosphere depending on the following factors:

- vertical profile of the absorbing gas concentration,
- spectral range, and
- spectral resolution.

a) The results of calculations have shown that for gases with a rapidly decreasing with height number density the spectrum of resonance atmospheric transmission is symmetric and the line shift is on the order of  $\delta_0$ , while for gases with a uniform altitude distribution of concentration ( $m = 1$ ) the line shift is small and the resonance transmission spectrum of the atmosphere is explicitly asymmetric. Here and below by the center of the resonance transmission spectrum the frequency  $\nu^*$  is meant that corresponds to the maximum absorption observed, and by the shift of a line center the value  $|\nu^* - \nu_0|$  is meant.

TABLE IV. The line center shifts and the asymmetry coefficients along a vertical path for a gas with the vertical distribution of number density  $\rho = \rho_0 \exp(-3\beta h)$ .

Absolute value of shifts, $\text{cm}^{-1}$								
$\delta\nu, \text{cm}^{-1}$	$\epsilon = 0.1$				$\epsilon = 1$			
	$H, \text{km}$							
	0	10	20	30	0	10	20	30
0	0.007	0.006	0.004	0.003	0.069	0.062	0.059	0.059
0.010	0.007	0.006	0.005	0.004	0.069	0.062	0.059	0.059
0.020	0.007	0.006	0.005	0.005	0.069	0.063	0.061	0.060
0.100	0.007	0.007	0.007	0.007	0.071	0.072	0.072	0.072
Asymmetry coefficient								
$\delta\nu, \text{cm}^{-1}$	$\epsilon = 0.1$				$\epsilon = 1$			
	$H, \text{km}$							
	0	10	20	30	0	10	20	30
0	1.00	1.01	1.05	1.08	1.03	1.14	1.20	1.21
0.010	1.00	1.01	1.03	1.04	1.03	1.12	1.17	1.17
0.020	1.00	1.01	1.03	1.03	1.03	1.11	1.14	1.16
0.100	1.00	1.00	1.00	1.00	1.01	1.02	1.02	1.02

b) Doppler half-width of absorption lines is directly proportional to a frequency, therefore in the visible and UV regions it is comparable by magnitude with the Lorentz half-width  $\gamma$  at  $P \sim 1$  atm, whereas in the IR and microwave regions  $\gamma_D \sim \gamma$  only at  $P \ll 1$ . Consequently, the relation between the Doppler and Lorentz half-widths can be considered as a criterion for identifying the spectral range: the UV or the visible range at  $H \approx 0$  and far-IR or the microwave at  $H \approx 20$ –30 km. The analysis of data presented in Tables shows that the largest shift and the smallest asymmetry of the resonance transmission spectrum is observed in the visible and UV regions, other conditions being the same.

c) In all the above-discussed cases one can see a common tendency to a decrease of asymmetry of the transmission spectrum and to an increase of the line center shift for poorer spectral resolution (of course, within the framework of the numerical simulations performed), with the line shift reaching a constant value as the transmission spectrum becomes symmetric. The influence of the instrumental function is minimum in the visible and UV regions whereas in the IR and microwave regions at high resolution the shift of a line center is practically absent and at low spectral resolution the shift is one and the same in all spectral regions. In Fig. 2 one can see the transmission of the vertical atmospheric path calculated using the following values of the parameters:  $\delta_0/\gamma_0 = 0.5$ ,  $\gamma_D = \gamma(h^0)$ , and  $(h^0) = 20$  km that corresponds to the middle IR range at different spectral resolutions; curve 1 corresponds to  $\delta\nu/\gamma_0 = 0$  and curve 2 corresponds to  $\delta\nu/\gamma_0 = 0.3$ . Figure 2 clearly demonstrates strong dependence of the shift value of the resonance transmission spectrum center on the width of the instrumental function for a gas uniformly distributed over the altitude. Therefore, experimental measurements of the line centers in the IR range with different instrumentation can give different values.

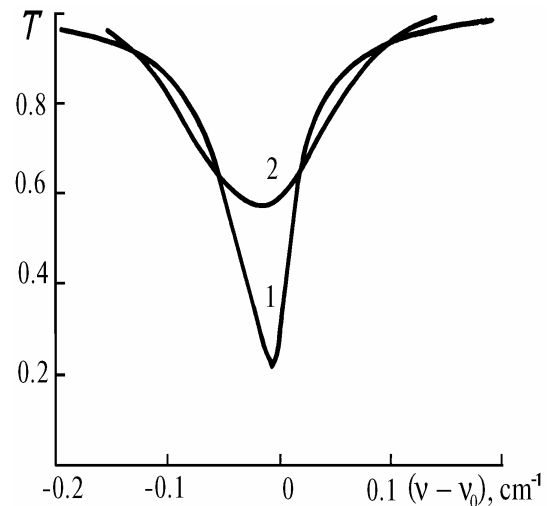


FIG. 2. Transmission of the atmosphere along a vertical path at an isolated absorption spectral line of a gas uniformly distributed over altitude.  $\gamma_D = \gamma(h^0)$ ,  $h^0 = 20$  km, and  $\epsilon = 0.5$ . Curve 1 shows the data for a monochromatic instrumental function ( $\delta\nu = 0$ ) and curve 2 presents the data for the half-width of the instrumental function  $\delta\nu = \gamma_0$ .

#### CALCULATIONS OF THE SHIFT EFFECT IN SPECIFIC CASES

In Table V there are data on some lines of  $\text{H}_2\text{O}$  and  $\text{CH}_4$  molecules with large  $\delta_0$  values. It should be emphasized here that  $\delta_0$  values may only increase (at least for dipole molecules) when passing from the IR to visible regions. The situation, when the value  $\epsilon$  varies from 0.1

to 1.0 is quite realistic in situations when lasers emitting in the visible region are used to detect gaseous components of the atmosphere.

TABLE V. The coefficients of broadening and shift for some absorption lines of water vapor and methane ( $\text{atm}^{-1}\cdot\text{cm}^{-1}$ ) broadened by air.

Gas	Band, transition, $\nu$ , $\text{cm}^{-1}$	$\delta_0 \cdot 10^3$	$\gamma_0 \cdot 10^3$	$\varepsilon =  \delta_0/\gamma_0 $	Refs.
H <sub>2</sub> O	$3\nu_1 + \nu_3$ 771 → 770 13663.5426	-29.5	40.5	0.73	9
	$2\nu_1 + 2\nu_2 + \nu_3$ 818 → 919 13774.4157	-26.5	47.9	0.55	9
	$\nu_2$ 15115 * 16016 15015 * 16016 1879.0190	-3.3	6.9	0.49	7
CH <sub>4</sub>	$\nu_4$ 317 1170.9006	-3.9	17.7	0.22	38
	$\nu_4$ R16 1385.5343	-13.9	48.4	0.29	38
	$\nu_2$ Q15 1563.2483	-4.8	28.8	0.17	38
	$\nu_2$ 317 1170.9006	-11.1	64.7	0.17	38

Quite different situation may take place in the UV spectra formed due to electron–vibrational–rotational transitions in molecules. Transitions of a molecule from the ground state to an excited electron state causes an increase of its polarizability by an order of magnitude. For example, the polarizability of H<sub>2</sub>O molecules in the first and second excited electron states is approximately ten times greater<sup>49</sup> than that in the ground state. In this case the line shift may be much more than the broadening.

The calculations demonstrating the shift effect on the atmospheric transmission were carried out<sup>9</sup> for two isolated lines, i.e., for the line of H<sub>2</sub>O molecule centered at  $\nu_0 = 13775.2987 \text{ cm}^{-1}$  with  $\gamma_0 = 0.0717 \text{ cm}^{-1}$ , and  $\delta_0 = -0.020 \text{ cm}^{-1}$  (see Ref. 9) and for the line of CH<sub>4</sub> molecule centered at  $\nu_0 = 2903.8757 \text{ cm}^{-1}$  with  $\gamma_0 = 0.063 \text{ cm}^{-1}$ , and  $\delta_0 = -0.007 \text{ cm}^{-1}$ . Parameters of the spectral line of the CH<sub>4</sub> molecule were taken from the HITRAN–86 database<sup>46</sup>, while the shift value has been estimated using one of the simplest models. Computations of the transmission functions were performed for mid–latitude summer conditions using the mean zonal models<sup>47</sup> of the meteorological parameters involving the temperature profiles, profiles of pressure and concentrations of absorbing gases, which were obtained by averaging the series of many years observational data on these parameters.

The results of computations presented in Fig. 3 confirm the conclusions drawn in the preceding section that in the case of gases like H<sub>2</sub>O vapor, whose number density rapidly falls off with increasing height, the transmission spectrum is symmetric but its center is strongly shifted from the absorption line center. It can be well seen from this figure, that the neglect of an absorption line center shift can result in significant errors (up to 50 %) of the atmospheric transmission function calculations. In Figs. 4 and 5 one can see the atmospheric transmission spectrum within the contour of an isolated absorption line of the CH<sub>4</sub> molecule, calculated for the instrumental function spectral widths  $\delta\nu = 0$  and  $\delta\nu = 0.06 \text{ cm}^{-1}$ . This line was chosen because, for example, in Ref. 50 it was noted that in the case of a slant atmospheric path the authors observed a shift of its center and experimentally measured the transmission spectrum. Our calculations show that in the case of a transmission spectrum recorded with high resolution its shape should be asymmetric with only a slight shift of its center, whereas at spectral resolution of a recording spectral device with a symmetric instrumental contour width equal to the Lorentz half–width of an absorption line at the earth's surface the shift of a transmission spectrum center becomes already noticeable and the shape of spectrum symmetric.

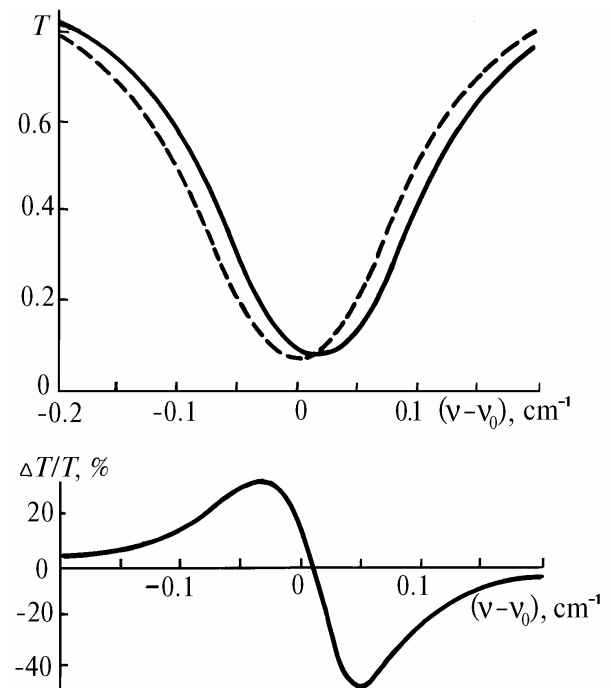


FIG. 3. Spectral transmission of the atmosphere along a vertical path at the H<sub>2</sub>O molecule absorption line with the shift of its center by air pressure taken into account (solid line) and without the account of line shift (dashed line). Relative error due to neglect of the line center shift is given in the lower part of the figure. The line center frequency is  $\nu_0 = 13775.2987 \text{ cm}^{-1}$ . The atmospheric model of mid–latitude summer was used in the calculations.

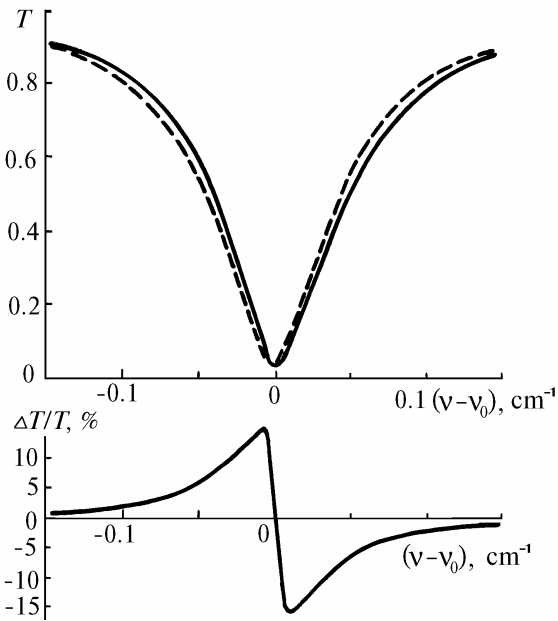


FIG. 4. Spectral transmission of the atmosphere along a slant path at the zenith angle  $85^\circ$  within a  $\text{CH}_4$  molecule absorption line contour calculated with the line center shift by air pressure taken into account (solid line) and without it (dashed line). Relative error due to neglect of the line center shift is shown in the lower part of the figure. The line center frequency is  $\nu_0 = 3903.8757 \text{ cm}^{-1}$ . The atmospheric model of mid-latitude summer was used in the calculations.

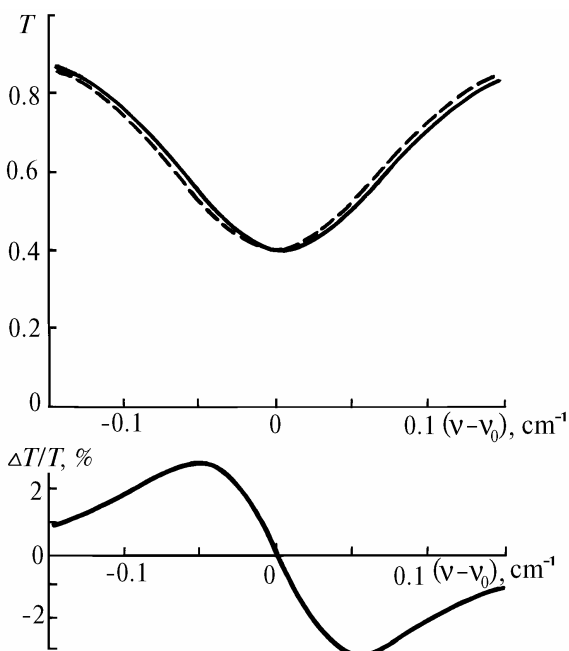


FIG. 5. The atmospheric transmission within the  $\text{CH}_4$  molecule absorption line contour centered at  $\nu_0 = 3903.8757 \text{ cm}^{-1}$  calculated for spectral resolution of  $0.06 \text{ cm}^{-1}$  and for other conditions being the same as in the case presented in Fig. 4.

Behavior of the resonance transmission spectrum recorded by an instrument with the asymmetric instrumental function is more complicated. The spectral line center shifts were studied under laboratory conditions characteristic of homogeneous paths<sup>48</sup> and for asymmetric instrumental function and it was shown that the asymmetry of the instrumental function of a spectral device can cause incorrect values of the shift.

The effect of the shift of an absorption line center by air pressure on the transmission spectrum of a slant atmosphere path is distinctly noticeable in the case of resonance absorption by gases, whose number density rapidly decreases with altitude. Therefore, we had studied the dependence of the maximum error  $\Delta T/T$  (neglecting the line center shift) on the Lorentz-to-Doppler half-width ratio, on the value  $\varepsilon = \delta/\gamma$ , spectral resolution and on the optical thickness  $\tau_0$  at the line center. A set of model curves depicted in Fig. 6 enables one to estimate the necessity of taking into account the shift of a line center by air pressure when studying the transfer of a narrow-band radiation with the wavelength coinciding with an absorption line of an atmospheric gas through the Earth's atmosphere.

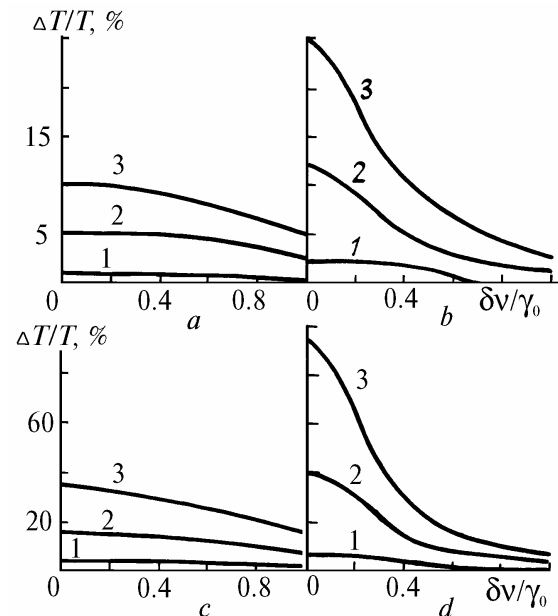


FIG. 6. Dependence of the maximum error in calculations of the atmospheric transmission due to the absorption line shifts by air pressure on the spectral resolution. The concentration profile of the absorbing gas is the model  $\rho = \rho_0 \exp(-\beta h)$ . a) and b) are for the optical thickness of the atmosphere at the line center,  $\tau = 1$ ; c) and d)  $\tau = 3$ ; a) and c)  $\gamma_0 = \gamma_D$ ; b) and d)  $\gamma_D = \gamma$  ( $\varepsilon = 0.1$ ; curve 2 is for  $\varepsilon = 0.5$ ; and curve 3 is for  $\varepsilon = 1.0$ ).

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