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Analysis and analytical modeling of Air shifting coefficients of water vapor lines in the visible range

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An analytical model $\delta(sur)$ is proposed for calculations of air shift coefficients of water vapor lines in the visible range. The model $\delta(sur)$ depends on the fitting parameters and linearly depends on the line broadening coefficient. Two sets of 642 and 3241 experimental values of δ were identified, obtained for lines from the ranges $10150-14000\,\mathrm{cm}^{-1}$ and $10150-22637\,\mathrm{cm}^{-1}$. The average accuracy of the coefficients by using the $\delta(sur)$ model is 16.9 and 22.9% for the first and second sets, respectively. Calculations based on $\delta(sur)$ model are compared with calculations based on the semiclassical method and with the HITRAN database.

Keywords: water vapor, shifts, air, analytical representation.

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Introduction

Knowing how the centers of the water vapor molecule lines are shifted by atmospheric gas pressure in the visible region of the spectrum is essential for atmospheric applications. In [1], for example, it was shown that neglecting the shift of the center of line $\lambda = 634.38$ nm resulted in an error of 10 and 20% when sounding the vertical profile of atmospheric humidity at altitudes up to 10 and 20 km. To date, a large set of experimental and calculated data has been obtained for the broadening coefficients (γ) and shift factor (δ) of vibrational-rotational (VR) absorption lines of water vapor by air pressure. The most comprehensive data on these coefficients may be found in HITRAN database [2].

The experimental data (including search of erroneous values) analyzed for the coefficients γ for the lines of H_2O molecule within the range $380-22593\,\mathrm{cm}^{-1}$ is given in [3]. The analytical model $\gamma(sur)$ („*sur*“ stands for a „surface“) is also proposed there, which allows calculating coefficients γ for lines of any vibrational band $(0, 0, 0) \rightarrow (\upsilon_1, \upsilon_2, \upsilon_3)$ from the specified range; υ_1, υ_2, υ_3 — vibrational quantum numbers. Dependence of model $\gamma(sur)$ on the rotational quantum numbers J, K_a, K_c of H_2O is non-linear. Paper [4] gives an insight on experimental data on the broadening coefficient γ and shift factor δ of the lines of 4 vibrational bands of H_2O with the upper oscillatory state $(\upsilon_1, \upsilon_2, \upsilon_3) = (3, 0, 1)$, (2,2,1), (2,0,2) and (1,4,1) in the spectral range $13338-13966\,\mathrm{cm}^{-1}$. When analyzing these data, empirical relations were found in [4] linking the coefficients δ and γ for lines widened by the pressure of air, nitrogen, oxygen and argon. For the broadening of lines H_2O by air pressure, this ratio has the form

$$\mathrm{Sh} = 0.363\Gamma - 0.0476. \qquad (1)$$

Here, the shift factor (Sh) and broadening coefficient (Γ) are defined in cm^{-1}/atm.

The purpose of this work is to 1) using the analytical model $\gamma(sur)$ from [2] for the broadening coefficients γ, obtain an analytical ratio for the shift factors $\delta(sur)$, similar to the ratio (1), but applicable to a wider spectral range, 2) to analyze the compatibility of experimental data for the shift factors. To broaden the water vapor lines with nitrogen and oxygen pressure, a similar problem was solved in [5].

Analytical model for coefficients δ and analysis of experimental data compatibility

The analytical ratio $\delta(sur)$ for the shift factors δ is expressed as

$$\delta(sur) = q_1\gamma(sur) + q_2(1 + q_3\upsilon_1 + q_4\upsilon_2 + q_5\upsilon_3) \qquad (2)$$

and is introduced as a generalized formula (1). In this formula $\gamma(sur)$ defines the broadening coefficients for H_2O line and is expressed as [3]

$$\gamma(sur) = x_2\{1/\mathrm{Cosh}[x_3(K_i - x_4)] + 1/\mathrm{Cosh}[x_3(K_f - x_4)]\}, \qquad (3)$$

in which

$$x_2 = (x_{20} + x_{26}|K_{ai} - K_{af}| + x_{27}(J_f - K_{cf})) \times f_1(\upsilon)/\mathrm{Cosh}[(x_{21}(J_i + J_f) + x_{22}(K_{ci} + K_{cf}) + x_{23}(K_{ci} + K_{cf})^2 + x_{24}(J_i + J_j)(K_{ci} + K_{cf}) + x_{25}(J_i + J_f^2))f_2(\upsilon)],$$

$$x_3 = x_{30} + x_{31}(J_i + J_f),$$

Table 1. Parameters of model $\gamma(sur)$ (3)–(5)*

x_{20}	$0.4892\ (25)\cdot 10^{-1}$	x_{30}	$0.2387\ (36)$
x_{21}	$0.2972\ (367)\cdot 10^{-1}$	x_{31}	$-0.1697\ (225)\cdot 10^{-2}$
x_{22}	$-0.9190\ (464)\cdot 10^{-1}$	t_{121}	$0.2560\ (115)\cdot 10^{-1}$
x_{23}	$-0.5114\ (404)\cdot 10^{-2}$	t_{122}	0.0
x_{24}	$0.3692\ (361)\cdot 10^{-2}$	t_{123}	$0.2002\ (169)\cdot 10^{-1}$
x_{25}	0.0	t_{221}	$-0.2767\ (340)\cdot 10^{-1}$
x_{26}	$0.1349\ (75)\cdot 10^{-2}$	t_{222}	$0.1638\ (392)\cdot 10^{-1}$
x_{27}	0.0	t_{223}	$-0.4953\ (506)\cdot 10^{-1}$

*Parameters x_{20} and x_{26} have a size of cm^{-1}/atm, all other parameters are dimensionless, in formula (3) $x_4 = 0$.

$$x_4 = 0, \tag{4}$$

and functions

$$f_1(v) = 1 + t_{121}v_1 + t_{122}v_2 + t_{123}v_3,$$

$$f_2(v) = 1 + t_{221}v_1 + t_{222}v_2 + t_{223}v_3 \tag{5}$$

define the oscillatory dependence $\gamma(sur)$. Indices i and f relate to the initial and final state in transition $i \to f$. For convenience of using the ratio (2) all parameters from the formulae (3)–(5) are summarized in Table 1 (the table is taken from [3]).

In [3] the parameters of model $\gamma(sur)$ were found from adjusting by formulae (3)–(5) 4110 of measured ($T = 296\,\mathrm{K}$) broadening coefficients of H_2O lines by air and nitrogen pressure of 76 vibrational bands H_2O within the spectral range $380-22593\,\mathrm{cm}^{-1}$.

Formula (2) for $\delta(sur)$ depends on five variable parameters q_i ($i = 1-5$). Initially, the model $\delta(sur)$ was tested with adjustment of the experimental shift factors $\delta(\mathrm{exp})$ found in [3–12] for the lines within $380-22593\,\mathrm{cm}^{-1}$, to the expression (2). This test showed that the (2) model can be applied for lines approximately lying above $10000\mathrm{cm}^{-1}$. In particular, it does not describe positive line shifts in bands with a small increase in vibrational quantum numbers. For this reason, the line shifts for the vibrational bands above $10000\mathrm{cm}^{-1}$ are analyzed later in this section.

The compatibility analysis of the experimental shift coefficients was carried out by directly comparing the coefficients $\delta(\mathrm{exp})$ measured for the same lines in different studies and determining the parameter $R_{[a],[b]} = \delta[a]/\delta[b]$, in which $\delta[a]$ and $\delta[b]$ — the measured shear factors $[a]$ and $[b]$, respectively. The highest amount of such lines were identified for the bands $3\nu_1 + \nu_3$, $2\nu_1 + 2\nu_2 + \nu_3$ and $2_1 + 2\nu_3$ in papers [4] and [12]. For 72 lines from the band $3\nu_1 + \nu_3$ the ratio $R_{[12],[4]} = \delta[12]/\delta[4]$ varies from 0.67 to 2.19, average value of $\langle R_{[12],[4]}\rangle$ for 72 lines is 2.18. For the 21 lines in $2\nu_1 + 2\nu_2 + \nu_3$ $1.1 < R_{[12],[4]} < 1.58$ band the average value of $\langle R_{[12],[4]}\rangle = 1.31$ will be the same. All data from [12] exceed the values from [4] by approximately 30% for the band$2\nu_1 + 2\nu_2 + \nu_3$. Finally, for the five bands from $2\nu_1 + 2\nu_3$ $0.85 < R_{[12],[4]} < 1.2$ and $\langle R_{[12],[4]}\rangle = 1.31$. Thus, the data from [12] and [4] are very different. The average difference between $\delta[12]$ and $\delta[4]$ for 98 lines makes 28.8%.

In general, more than 4000 values of $\delta(\mathrm{exp})$ were analyzed. $\delta(\mathrm{exp})$ have been removed from this list, which, in our opinion, are erroneous. These include positive values $\delta(\mathrm{exp})$ from [12] and those values $\delta(\mathrm{exp})$ that differ from $\delta(\mathrm{exp})$ for lines from neighboring oscillatory bands by more than 30%. For the range under consideration, for all lines from [4,6,10,11], the values $\delta(\mathrm{exp})$ are negative. They are also negative in calculations using the semi-classical Anderson–Tcao–Carnata (ATC) method [13]. In these calculations (see, for example, [3]), the obtained coefficients δ change by no more than 10% when the vibrational quantum numbers change by one. Changes of 30% in the coefficients $\delta(\mathrm{exp})$ are considered erroneous in this work.

Thus, the set of 3241 values of $\delta(\mathrm{exp})$ was formed. This set is clearly divided into two sets. One of them (set 1) consists of 642 values $\delta(\mathrm{exp})$ for the lines from range $10150-14000\,\mathrm{cm}^1$ measured in [4,6,10,11], the second one (set 2) — consists of 2599 values of $\delta(\mathrm{exp})$ for the lines from $13000-22637\,\mathrm{cm}^{-1}$, measured in [12]. In the spectral range from 13000 to $14000\,\mathrm{cm}^{-1}$ both sets contain values $\delta(\mathrm{exp})$ for the same lines, and these values systematically differ from each other by approximately 30%. Therefore, parameters $q_1, \ldots, q_5$ for the model $\delta(sur)$ (2) were determined separately for each data set by fitting them to the formula (2). For the first set, the parameters are given in the second column of Table 2, for the second set — in the third column of the same table. Parameters of model $\gamma(sur)(3)-(5)$ from formula (2) corresponded to the values from Table 1. The last lines of Table 2 show the values of statistical quantities

$$rms = \sqrt{\sum_{i-1}^{N} \frac{(\delta_i(\mathrm{calc}) - \delta_i(\mathrm{exp}))^2}{N}}, \tag{6}$$

$$\chi_{av} = 100\% \sum_{i=1}^{N} |1 - \delta_i(\mathrm{calc})/\delta_i(\mathrm{exp})|/N, \tag{7}$$

characterizing the quality of adjustment N — number of used data. The values of rms and χ_{av} for individual data sets are shown in Table 3.

The quality of shift factors δ based on model $\delta(sur)$, characterized byrms and χ_{av} is comparable to the quality of calculating the same factors using the semi-classical ATC method applied to lines from the range below $10000\,\mathrm{cm}^{-1}$ [3,9,14].

Results from HITRAN database and ATC analysis, compared

The shift factors δ found using model $\delta(sur)$ (2) with analysis using conventional ATC method and using HITRAN database [2] were compared for the two vibrational bands $(0, 0, 0) \to (3, 0, 1)$ and $(0, 0, 0) \to (3, 6, 3)$ localized within $10150-14000\,\mathrm{cm}^{-1}$ and above $25000\,\mathrm{cm}^{-1}$. Fig. 1, 2 shows the dependence of the calculated δ on the

Table 2. Parameters of model $\delta(\text{sur})$ (2), found from adjustment of 642 and 3241 values of the lines centers shift factors $\delta(\text{exp})$ of H_2O molecule by air pressure ($T = 296$ K) for the two sets of experimental data *

Parameter	Set 1, 10150–14000 cm^{-1}	Set 2 10150–22637cm^{-1}
q_1	0.2374 (90)	0.2811(62)
q_2	$-0.2889\,(97)\cdot 10^{-1}$	$-0.9355(638)\cdot 10^{-2}$
q_3	$0.7127\,(861)\cdot 10^{-1}$	0.9791 (730)
q_4	0.0	0.4075(329)
q_5	$0.9586(1068)\cdot 10^{-1}$	1.0917 (833)
N	642	3241
rms	$3.2\cdot 10^{-3}$	$6.8\cdot 10^{-3}$
χ_{av},%	16.9	22.9

* Parameters q_1, $q_3 - q_5$ — are dimensionless, parameters q_2 and rms are found in cm^{-1}/atm.

Table 3. The values of rms (6) and χ_{av} (7) found for individual experimental data sets with parameters from the second column of Table 2

$v_1\,v_2\,v_3$	N	rms, 10^{-3} cm^{-1}/atm	χ_{av},%	Source
003, 022, 102, 121, 201, 300	423	3.1	17.1	[6]
301, 221, 202, 103	114	3.3	16.3	[10,11]
301, 221, 202	105	3.3	15.2	[4]

rotational quantum numbers J and K_a for two rotational series in the vibrational band (0, 0, 0) → (3, 0, 1).

The first series of transitions in Fig. 1 defines δ versus the rotational quantum number J for the fixed quantum numbers K_{ai} and K_{af}. The second series in Fig. 2 delineates δ versus rotational quantum number $K_a = K_{ai}$ for the fixed J_i and J_f. Here and further, the parameters from the second column of Table 2 are used in calculations based on model $\delta(sur)$ (2). In the analysis by ATC method the values of the dipole moment $\mu(v_1, v_2, v_3)$ for the upper vibrational state (3,0,1) were taken from jcite15, and for the highly excited vibrational state (3,6,3) they were obtained by interpolating $\mu(v_1, v_2, v_3)$ from jcite15 for this state using a polynomial model with respect to v_1, v_2, v_3. Polarizability $\alpha(v_1, v_2, v_3)$ (in Å^3) also required to calculate the coefficients δ, was found from the formula

$$\alpha(v_1, v_2, v_3) = 1.4613 + 0.045v_1 + 0.021v_2 + 0.043v_3\ \text{Å}^3, \qquad (8)$$

given in [16].

Figure 1 shows satisfactory agreement between calculations based on models $\delta(sur)$ and ATC for $J \le 11$, consistency between $\delta(sur)$ and HITRAN database is observed only for $J \le 5$. For the quantum numbers $J > 8$ the coefficients δ in HITRAN database are equal — 0.04 cm^{-1}/atm. Figure 2 shows a satisfactory (with the exception of one transition) agreement between $\delta(sur)$ and ATC, and a very unsatisfactory coincidence of these calculations with data from HITRAN database.

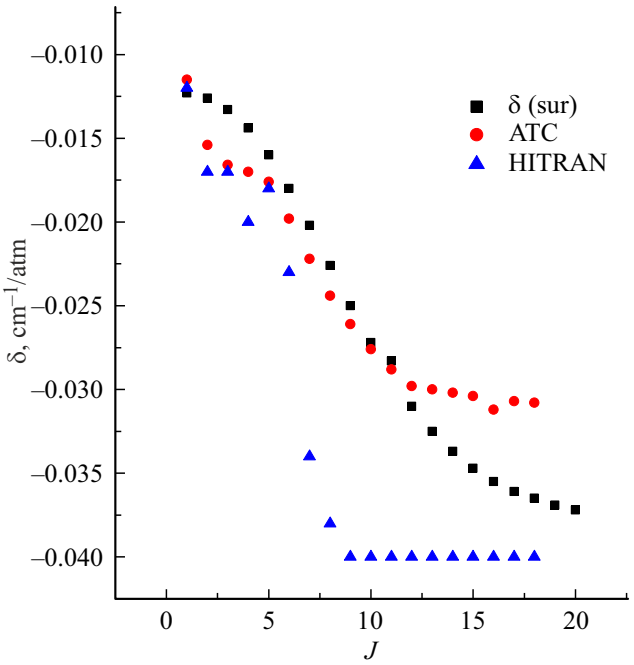

Figure 1. Comparison of the shift factors δ from HITRAN database and factors δ analyzed using model $\delta(sur)$ (2) and ATC method for a series of transitions $[J+1\,K_a = 0\,J+1] \rightarrow [JK_a = 0\,J]$ in $3v_1 + v_3$.

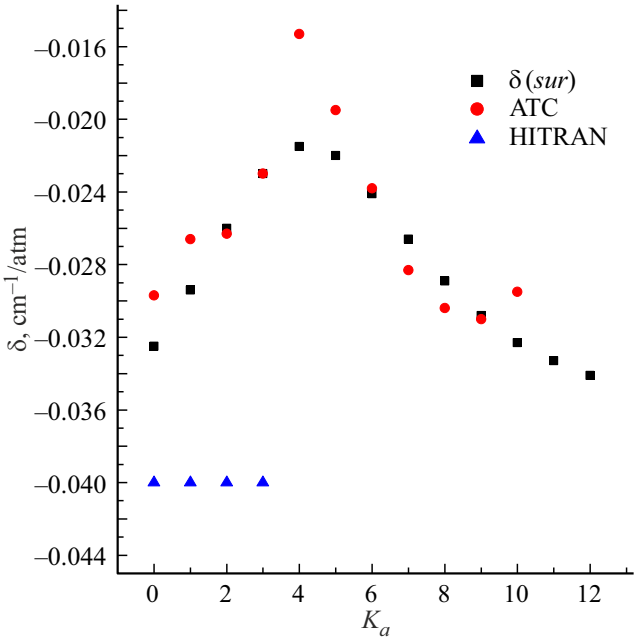

Figure 2. Similar to Figure 1, but for transitions $[J = 13\,K_aK_c = 13 - K_a] \rightarrow [J = 12\,K_aK_c = 12 - K_a]$.

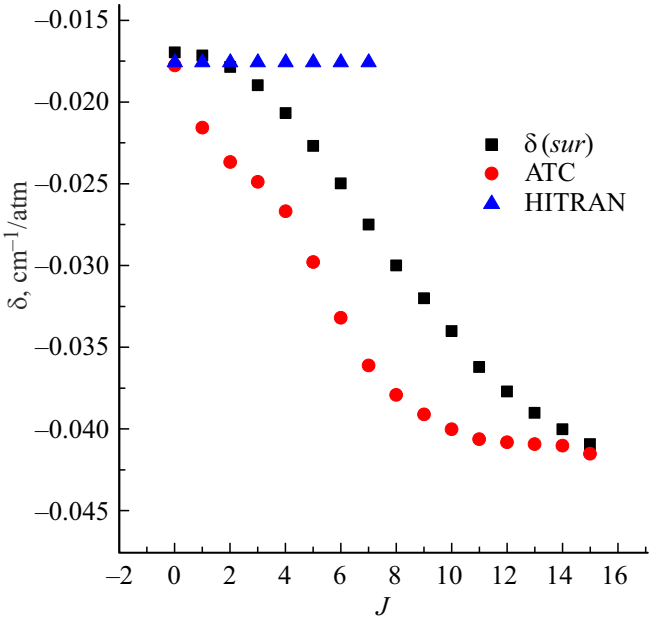

Figure 3. Comparison of the shift factors δ from HITRAN database and factors δ analyzed using model $\delta(sur)$ (2) and ATC method for a series of transitions $[J\,K_a = 0\,J] \rightarrow [J+1\,K_a = 0\,J+1]$ in the band $(0, 0, 0) \rightarrow (3, 6, 3)$.

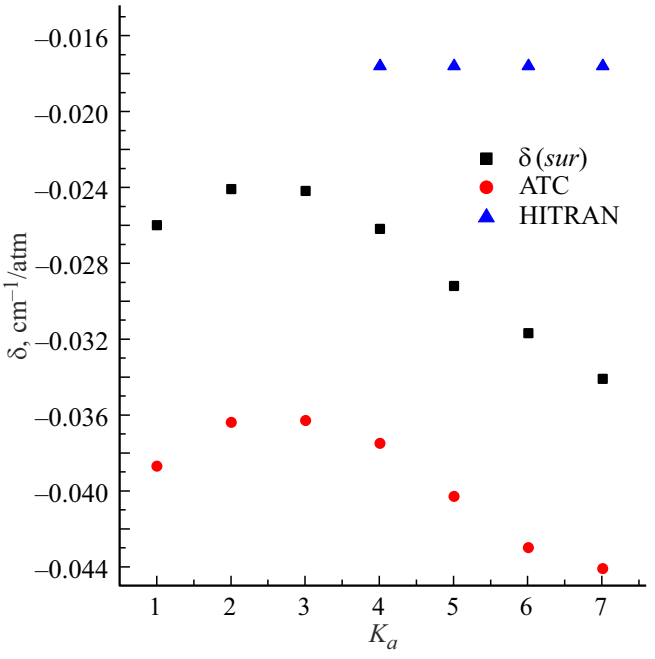

Figure 4. Similar to Figure 3, but for transitions $[J = 8\,K_a K_c = J - K_a + 1] \rightarrow [J = 9\,K_a + 2\,K_c = 9 - Ka - 1]$.

Figures 3, 4 show the dependence of δ on the quantum numbers J and K_a for the two series of rotational transitions in the rotational band $(0, 0, 0) \rightarrow (3, 6, 3)$ localized above 25000 cm^{-1}.

Again, there is a drastic difference between calculations using model $\delta(sur)$ (2) and ATC method from the values of δ from HITRAN database. The shifts of the lines considered in this database do not depend on the rotational quantum number K_a. In the asymptotic at J, $K_a \rightarrow \infty$, when using model $\gamma(sur)$ (3)–(5) the obtained broadening coefficients γ are turned into zero, thus, the model $\delta(sur)$ (2) for large quantum numbers J and K_a leads to a permanent shift of the lines centers $q_2(1 + q_3 v_1 + q_4 v_2 + q_5 v_3)$ for each band.

Conclusion

Experimental data are analyzed for the shift factors $\delta(\mathrm{exp})$ of the centers of lines of $H_2^{16}O$ molecule by air pressure in the range 10150–22637 cm^{-1}. For the considered vibrational bands, the maximum values of vibrational quantum numbers $v_1 = 7$, $v_2 = 9$ and $v_3 = 4$, and the maximum values of rotational quantum numbers in transitions $J = 15$ and $K_a = 8$ for the lower vibrational state. It was found that the experimental data $\delta(\mathrm{exp})$ from different studies may vary greatly. Two optimal sets of 642 and 3241 coefficients $\delta(\mathrm{exp})$ have been formed. The first set was obtained for the lines in 10150–14000 cm^{-1}, the second one — for the range 10150–22637 cm^{-1}. In the range 10150–14000 cm^{-1} both sets contain experimental values $\delta(\mathrm{exp})$, which relate to the same lines, but systematically differ from each other by approximately 30%. Therefore, these sets cannot be used simultaneously to determine the parameters of any analytical model for the shift factors or to determine from these factors the vibrational dependence of the polarizability or the dipole moment of H_2O molecule.

The major finding from this study is shown in Table 2 illustrating the parameters of model $\delta(sur)$ (2) for the two optimal sets of experimental data. Using these parameters (and the parameters from Table 1 for the model $\delta(sur)$(3)–(5)), the broadening coefficients (γ) and shift factors (δ) can be calculated simultaneously for any absorption line of water vapor from the considered range. Thus, for line $[642] \rightarrow [533]$ in the band $2v_1 + 2v_3$ with a frequency of $\nu = 14400.071\ \mathrm{cm}^{-1}$ (corresponds to the wavelength $\lambda = 634.38$ nm where [1] the profile of atmospheric humidity was measured), calculated value $\gamma = 0.0828\ \mathrm{cm}^{-1}$/atm, and $\delta = -0.0188\ \mathrm{cm}^{-1}$/atm, experimental[1] value of the shift of this line is equal $-0.017 \pm 0.006\ \mathrm{cm}^{-1}$ at pressure of 755 Torr.

Average precision of calculating the broadening coefficients γ based on model $\gamma(sur)$ (3)–(5), defined by χ_{av} (7) (in this formula the symbol δ is replaced by γ), and makes 7.2%. χ_{av} for the data sets 1 and 2 for the coefficients $\delta(\mathrm{exp})$ make 16.9 and 22.9%. The respective values *rms* (6) are equal $3.2 \cdot 10^{-3}\ \mathrm{cm}^{-1}$/atm and $6.8 \cdot 10^{-3}\ \mathrm{cm}^{-1}$/atm. Therefore, it is preferable to use the second column of parameters from Table 1 in calculating the shift coefficients. It especially relates to the range 10150–14000 cm^{-1}.

The values $rms = 3.2 \cdot 10^{-3}\,\mathrm{cm}^1/\mathrm{atm}$ are comparable to the values of rms, which were found in calculations using ATC method in [3,9,14] for the lines located below $10000\,\mathrm{cm}^{-1}$.

Comparing $\delta(sur)$ for individual rotational series above $25000\mathrm{cm}^{-1}$ with HITRAN database shows that in some cases there is a significant difference in the coefficients δ (as well as in the values γ). For many transitions, δ and γ from HITRAN database are assigned the values independent of the rotational quantum number K_a, which is incorrect.

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Conflict of interest

The author declares that he has no conflict of interest.

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