Contribution of weak water vapor absorption lines to extinction of narrow-band laser radiation in atmospheric microwindows

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The contribution of weak water vapor lines, which are ignored in the HITRAN 2000 database, to atmospheric extinction of narrow-band laser radiation in the range of 9466 cm^{-1} is estimated. Water vapor absorption in this range was studied in some earlier papers. Due to appearance of new *ab initio* calculations of water vapor lines, including those ignored in atlases, the extra contribution of weak water vapor lines can be estimated now. It may prove to be significant and reach 10–20%. Thus the problem of anomalous absorption in this range can be solved.

In some papers (see, for example, Refs. 1 and 2) the contribution of weak water vapor absorption lines to formation of the atmospheric radiative balance was estimated and it was shown that weak H_2O lines can contribute considerably (reaching 1%) to atmospheric absorption in the near infrared and visible regions. In atmospheric microwindows the role of weak lines becomes important, and as was shown in Ref. 2, the contribution can reach several percent.

This paper considers the contribution of weak lines to estimates of water vapor continuum absorption, which is determined traditionally as follows.[3] The measured absorption coefficient is represented as a sum of a selective component formed by the total contribution of neighboring lines and a continuum component formed by far wings of absorption lines. Once selective absorption is subtracted from the measured absorption coefficient, some estimate of continuum absorption is obtained. To calculate the selective component, the data (line positions, intensities, broadening coefficients) of the HITRAN[4] and GEISA databanks are usually used. However, as was shown in Refs. 1 and 2, these databanks contain only limited information about weak H_2O lines, which is obviously insufficient for complete account for selective absorption. This results in overestimation of continuum absorption.

Let us illustrate the effect of weak lines on the absorption in narrow spectral intervals using the following example. The water vapor continuum transmittance in the near infrared range was measured in Ref. 5. Absorption at the Nd:YAG laser frequency (nearby 9466 cm^{-1}) was estimated as more than 0.01 km^{-1}. The spectral width of laser radiation did not exceed 0.01 cm^{-1}, but in Ref. 5 there is no precision measurement of the wavelength. In this spectral range there are no absorption lines in the HITRAN database for all H_2O isotopic modifications. In Ref. 6 the absorption coefficient was calculated with the use of the HITRAN 96 database (the HITRAN 2000 database includes no additional lines for this spectral range). Comparison of calculated and measured data indicates that some extra absorption by an unknown component is present, and this anomalous absorption is observed in both atmospheric[7] and laboratory[12] measurements. In Ref. 12 water vapor continuum absorption at the wavenumber of 9466.1 (laser line width ~ 0.5 cm^{-1}) with the absorption coefficient $6\cdot 10^{-10}$ cm^{-1} (error $\pm 0.9\cdot 10^{-10}$ cm^{-1}) was observed at the H_2O pressure of 16.5 Torr, the N_2 pressure of 760 Torr, and the temperature of 30°C. It is evident that weak lines ignored in the HITRAN database can contribute to the total absorption at this frequency. It should be noted that an experiment was conducted in the region of 9100–9500 cm^{-1} (Ref. 13), and it was shown that molecular absorption in this range varied strongly with the laser frequency and achieved 20%.

We calculated the coefficient of selective absorption of water vapor in the mixture with nitrogen in the range from 9451 to 9471 cm^{-1}, using a more complete database of H_2O absorption lines (Refs. 8 and 9) than the HITRAN DB. It should be noted that this database[8,9] incorporates the results of calculation of the water vapor spectrum by the variational method with the use of precision *ab initio* calculation of the dipole moment function of the H_2O molecule and includes the data on all possible lines, even lines with intensities up to 10^{-30} cm/mol. Figure 1 shows that the HITRAN database includes only four water vapor lines in the range from 9450 to 9475 cm^{-1} and their intensities are determined with the accuracy of 5–10%, whereas the Partridge and Schwenke database[8,9] includes much more lines, and among them six lines lying nearby 9466 cm^{-1}. The positions and intensities of these lines are tabulated below along with rotation–vibration quantum numbers and isotopic assignment.

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In Ref. 10, the data of Ref. 8 were analyzed and compared with experimental observations. It was found that in the studied spectral range the calculated frequencies from Ref. 8 differ from those measured experimentally by no more than 0.1 cm^{-1}. The calculation accuracy for intensities in Ref. 8 may be estimated as tens and even hundreds percent, but we know no one detailed analysis of experimental data and the Schwenke calculations concerning line intensity. For more precision assessment of the selective component of water vapor absorption in the range of 1.054 μm, the calculated line positions from Refs. 8 and 9 were corrected with the use of experimental values of energy levels available from the literature, for example, Ref. 11. The Table gives just the corrected data. From the last column of the Table, it follows that the mean intensity ratio equals 55%, that is, intensities of these lines are overestimated in Refs. 8 and 9 by about 55%. For this reason, the error of the line intensities in the studied range[8] can be estimated as ~50%.

Figure 2 shows the calculated H_2O absorption coefficient in the range from 9450 to 9475 cm^{-1} at the room temperature (because the 10° difference is rather small) and the pressure of 16 Torr. The four lines from the HITRAN DB and the six lines from Ref. 8 nearby 9466 cm^{-1} with the centers refined based on the literature data are depicted. In calculations the Lorentz line profile was used, and halfwidths of all the lines were equal to the mean value for the H_2O–N_2 mixture. Continuum absorption was neglected.

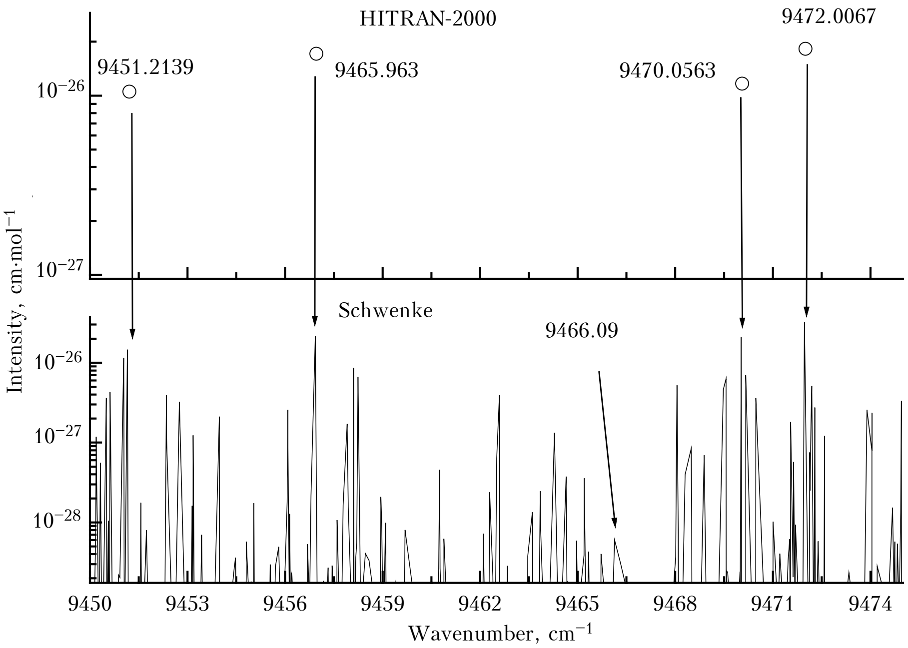

Fig. 1. H_2O absorption lines from the HITRAN database (circles) and lines from the Partridge and Schwenke database (bottom panel). A small peak formed by six absorption lines of different water vapor isotopic species is observed nearby 9466 cm^{-1}.

Table. Absorption lines of $H_2{}^{16}O$(11), $H_2{}^{18}O$(12), and HDO(14) from Refs. 4, 8, 9, and 11

#	$V_1V_2V_3$ $V_1''V_2''V_3''$	J	K_a	K_c	J''	K_a''	K_c''	ν, HITRAN, cm^{-1}	ν, l., cm^{-1}	ν, Schwenke, cm^{-1}	I_{HITRAN}, cm/mol	$I_{Schwenke}$, cm/mol	σ, %
11	(111)–(000)	13	3	11	12	1	12	9451.2139	9451.21011	9451.1529	$1.052\cdot10^{-26}$	$1.46\cdot10^{-26}$	−38.97
11	(012)–(000)	9	3	7	8	0	8	9456.9630	9456.96260	9456.9299	$1.712\cdot10^{-26}$	$2.15\cdot10^{-26}$	−25.46
12	(003)–(010)	3	0	3	2	0	2	–	9465.984	9466.0252	–	$1.70\cdot10^{-30}$	–
14	(032)–(000)	1	1	0	2	1	1	–		9466.0886	–	$1.56\cdot10^{-29}$	–
11	(140)–(000)	7	0	7	7	3	4	–	9466.0129	9466.1343	–	$5.99\cdot10^{-29}$	–
14	(051)–(000)	4	1	3	3	1	2	–		9466.3142	–	$3.10\cdot10^{-29}$	–
14	(051)–(000)	7	0	7	6	1	6	–		9466.5066	–	$1.43\cdot10^{-29}$	–
11	(210)–(000)	17	61	2	16	3	13	–		9466.7724	–	$6.29\cdot10^{-30}$	–
11	(111)–(000)	10	8	2	9	6	3	9470.0563	9470.06117	9470.0289	$1.166\cdot10^{-26}$	$2.09\cdot10^{-26}$	−79.33
11	(012)–(000)	8	5	4	7	2	5	9472.0067	9472.01091	9471/9687	$1.823\cdot10^{-26}$	$3.19\cdot10^{-26}$	−74.98

N o t e : isotopic species are numbered as 11 for $H_2{}^{16}O$, 12 for $H_2{}^{18}O$, and 14 for HDO according to HITRAN encoding; $V_1V_2V_3$, JK_aK_c, $V_1''V_2''V_3''$, and $J''K_a''K_c''$ are the upper and lower vibration and rotation quantum numbers of transitions; ν is the wavenumber; l. denotes line centers refined based on energy levels available from the literature, for example, Ref. 11; $\sigma = [(I_{HITRAN} - I_{Schwenke})/I_{HITRAN}]\cdot100\%$.

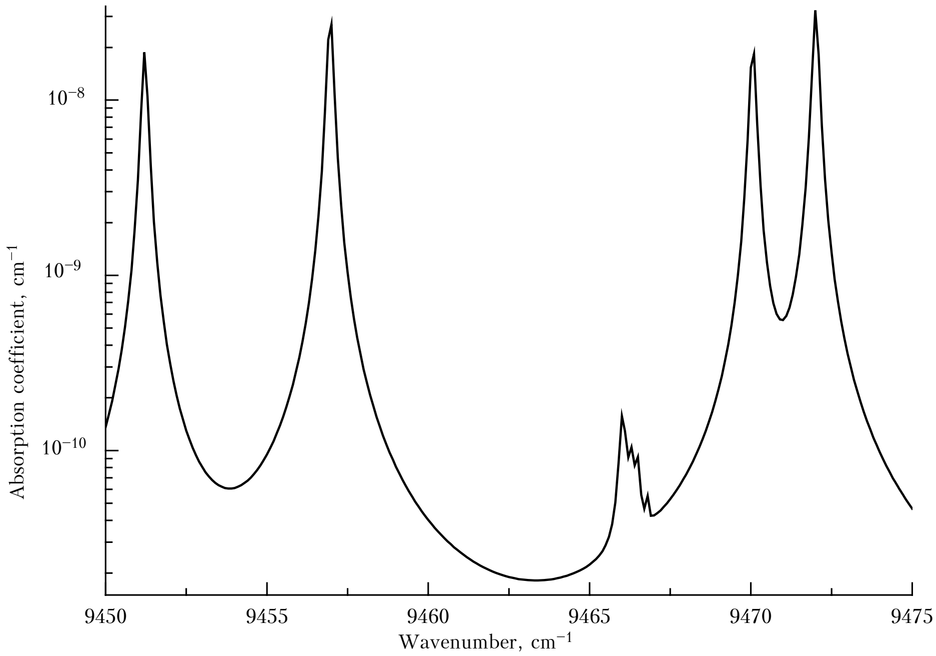

Fig. 2. H_2O absorption coefficient. A peak formed by six water vapor absorption lines from the Partridge and Schwenke database nearby 9466 cm^{-1} is clearly seen in the central part of the plot.

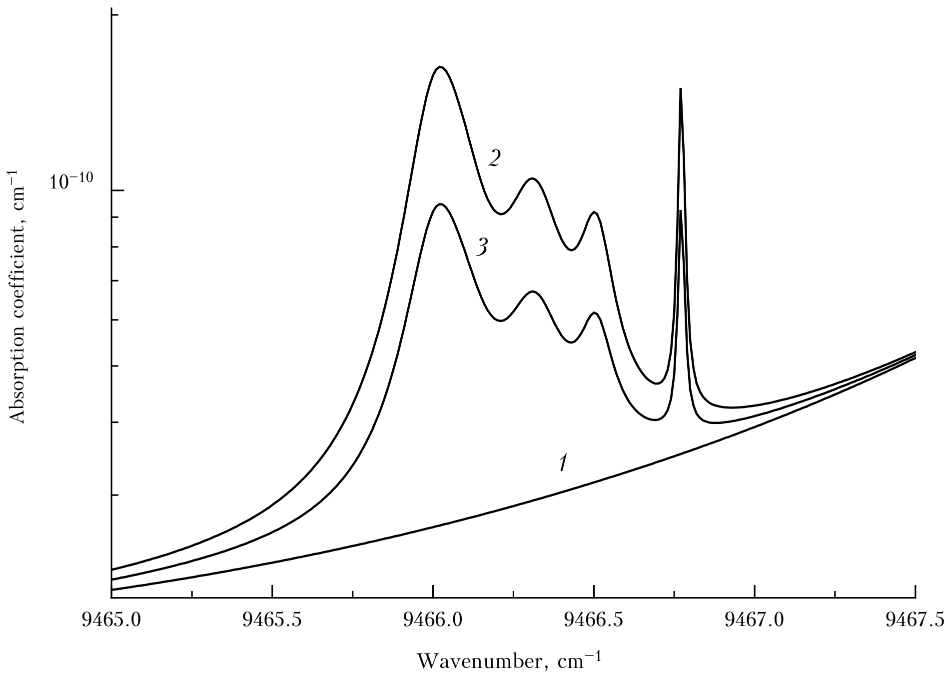

Fig. 3. H_2O absorption coefficient in the range from 9465 to 9467.5 cm^{-1}; absorption by lines from HITRAN-2000 DB (curve *1*), absorption by lines from HITRAN DB and six lines from the Partridge and Schwenke DB[8,9] (*2*), absorption by lines from HITRAN DB and six lines from the Partridge and Schwenke DB with halved intensities (*3*).

Figure 3 shows the H_2O absorption coefficient. Since the lines at 9466.0886, 9466.0252, and 9466.1343 are very close in position, but have far different intensity (the first line is 4 and 35 times more intense than the second and third ones, respectively), they are indistinguishable in the spectrum. It can be seen from Fig. 3 that the absorption coefficient due to weak lines can reach $1.65\cdot10^{-10}$ cm^{-1} in the range of 9466.02 cm^{-1}, that makes up almost one third (27.5%) of the value of $6\cdot10^{-10}$ cm^{-1} (Ref. 12).

Consider now the absorption coefficient in the range of 0.5 cm^{-1} for modeling the experiment from Ref. 12. The range of 9465.9–9466.4 cm^{-1} was taken, since the absorption coefficient due to weak lines is maximal there and it is closest to the description of the experiment from Ref. 12. The absorption in the range of 0.5 cm^{-1} (9665.9–9466.4 cm^{-1}) was $2.7 \cdot 10^{-11}$ cm^{-1} when only lines from the HITRAN DB were considered, $1.1 \cdot 10^{-10}$ cm^{-1} when we considered the lines from the HITRAN DB and Ref. 8, and $7.1 \cdot 10^{-11}$ cm^{-1} when the lines from the HITRAN DB and Ref. 8 were considered, but the latter with the halved intensity (lower boundary of the error). Thus, the resulting absorption by weak lines four times exceeds the absorption by wings of the nearest lines, but reaches only 20% of the absorption measured in Ref. 12.

The allowance for the continuum absorption (or refinement of line centers and intensities) may result in the increase of the calculated absorption and closer agreement with the experiment. Thus, it can be concluded that weak absorption lines of water vapor and its isotopic species, which are absent from the HITRAN DB, should be necessarily taken into account when calculating low absorption coefficients in atmospheric microwindows. The calculations carried out in this paper refine the value of selective absorption, but do not solve the problem of anomalous absorption in the atmosphere. To make estimates more accurate, additional experimental data are needed on both the absorption in atmospheric microwindows and centers and intensities of weak lines.

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