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Yu. V. Voronina, T. Yu. Chesnokova, B. A. Voronin, S. N. Yurchenko, "Contribution of new water vapor absorption lines to the atmospheric transmission in the transparency window 8-12 μm ," Proc. SPIE 11560, 26th International Symposium on Atmospheric and Ocean Optics, Atmospheric Physics, 115600B (12 November 2020); doi: 10.1117/12.2575547

SPIE.

Event: 26th International Symposium on Atmospheric and Ocean Optics, Atmospheric Physics, 2020, Moscow, Russian Federation

Contribution of new water vapor absorption lines to the atmospheric transmission in the transparency window 8-12 μm

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ABSTRACT

The evaluation of the contribution of numerous H₂O absorption lines to the atmospheric transmission in the 8-12 μm transparency window is presented based on different spectroscopic databases of water vapor absorption lines, including the new theoretical data sets POKAZATEL and VoTe, as well as the H₂O data from the popular spectroscopic databases HITRAN and GEISA. Comparison of the atmospheric transmittance calculated using different databases is presented. The contribution of the weak lines is investigated and shown to be important for very long absorption paths.

Keywords: water vapor, atmospheric transmission, absorption line parameters

INTRODUCTION

Water vapor continuum plays main role in the atmospheric transparency window between 8 and 12 μm , with significant influence on radiative fluxes^{1,2}. The H₂O continuum is determined as difference between measured absorption of H₂O and absorption calculated using line parameters from spectroscopic databases. Therefore, precise and full knowledge of H₂O absorption line parameters is important.

Recently, new theoretical H₂O line parameters data set POKAZATEL³ (www.exomol.com) was published. The distinctive feature of the new line list is its completeness. POKAZATEL contains all transitions of H₂O within the ground electronic state between all energy levels up to dissociation ($\sim 40000\text{ cm}^{-1}$) with no intensity, energy or quantum numbers cut-offs. The rotational angular momentum quantum number changes in the range from $J=0$ to $J_{\text{max}}=69$. POKAZATEL contains 810269 states and about 5 billion transitions. The previous extensive water line list BT2⁴ contains only 500 million transitions in the range up to 30000 cm^{-1} with the number of states about 220000. Presently, POKAZATEL is the most complete calculated line list for the H₂O molecule and can be applied in the simulation of absorption and emission spectra over a wide range of temperatures and spectral regions. POKAZATEL is based on the refinement of an *ab initio* potential energy surface by fitting to limited experimental data. The weak point of any empirical line lists is that the accuracy drops outside the spectroscopic region directly used in the empirical refinement. To mitigate this problem, some of the empirically determined line positions in POKAZATEL³ were replaced by the experimental values⁵, where available.

Empirical line lists are found useful in some spectral applications, for example, study of Mars⁶. It is known that the intensity cut-offs have impact in different spectroscopic regions and is especially important at for long wavelengths. For example, HITRAN uses a dynamic intensity cut-off, exponentially increasing for very small values of the frequency. This is illustrated in Fig. 1, which shows intensities of H₂O absorption lines from the POKAZATEL line list in the 800-1250 cm^{-1} transparency window for different values of the intensity cut-offs.

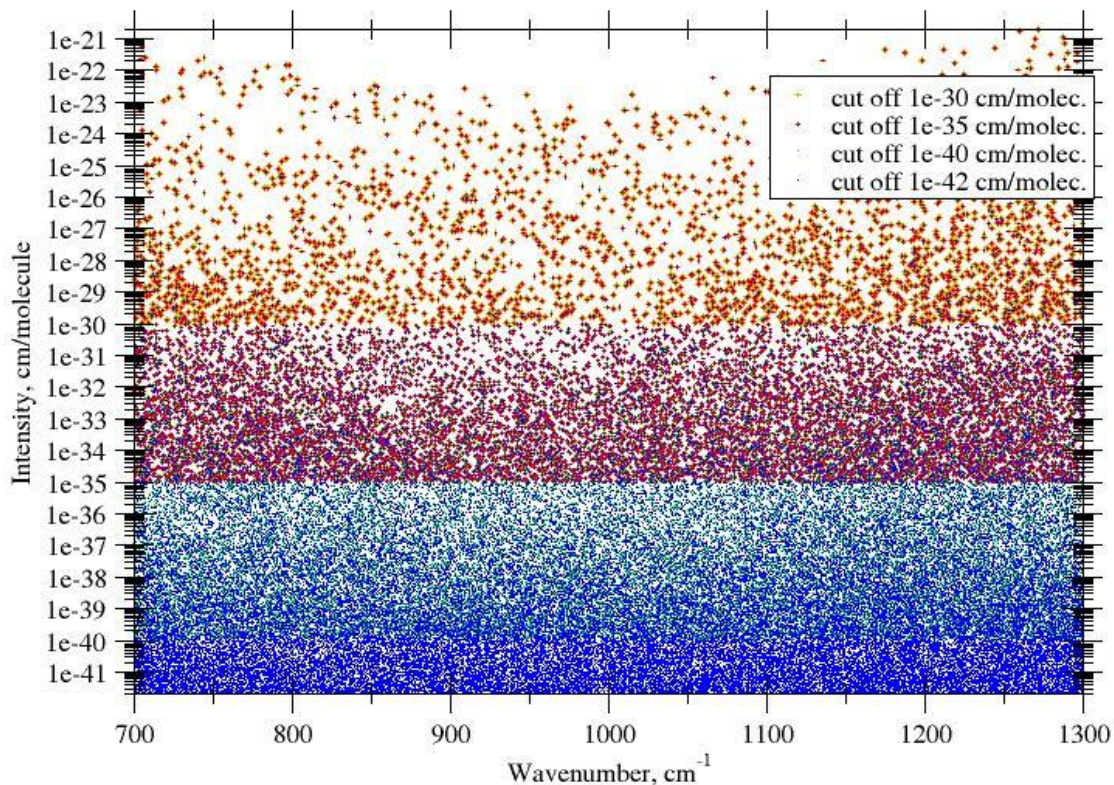


Fig. 1. Intensities of H_2^{16}O absorption lines in POKAZATEL for different values of intensity cut-offs.

It should be noted that in this study we took advantage of the assignment of the water transitions with $J_{\max}=40$ provided by S. Tashkun⁷ with the help of earlier Partridge and Schwenke⁷ calculations and a wave functions analysis.

Recently an H_2O line list VoTe⁸ with $J_{\max}=50$ was produced using the same potential energy surface as for POKAZATEL⁹ but including energy levels only up to 25000 cm^{-1} , where possible, with more accurate wavenumbers.

The aim of this work is to estimate a contribution of numerous weak absorption lines of H_2O , predicted by POKAZATEL and VoTe, to the absorption of thermal radiation for long paths in the atmospheric transparency window $8\text{--}12\text{ }\mu\text{m}$, and to estimate the atmospheric path lengths where this contribution becomes noticeable. Also, it was interesting to compare the results of VoTe and POKAZATEL with the calculations of the atmospheric transmission using the spectroscopic databases HITRAN and GEISA, which are popular in atmospheric applications.

CALCULATION OF ATMOSPHERIC TRANSMISSION WITH DIFFERENT H_2O LINE PARAMETERS DATABASES

The line-by-line calculations of atmospheric transmission requires a set of parameters defining the line shape. The pressure broadening parameters (air- and self-broadening coefficients or temperature-dependence exponent) provided in POKAZATEL have a very limited quantum number dependence (J'' -only). Moreover, a complete rotational-vibrational assignment is provided only for ~ 13000 energy levels out of 800000 reference data⁵. For all other states, POKAZATEL provides J and the symmetry number only. Therefore, in our atmospheric simulations an extended set of line broadening parameters (J'' , and $J'J''$ -dependences) from work¹⁰ was used. The atmospheric transmission was calculated line-by-line¹¹ with the spectral resolution of 0.001 cm^{-1} at a variation of the atmospheric path lengths towards

an integral transmission in the 8-12 μm window. The H_2^{16}O absorption lines from POKAZATEL³, VoTe⁹, UCL08¹² as well as from different versions of HITRAN¹³⁻¹⁵ and GEISA^{16,17} were used in the simulations. The line parameters of other water isotopologues and atmospheric gases were taken from HITRAN2016. The H_2O continuum absorption was taken into account according to the MT_CKD2.5 model¹⁸.

We used the mid latitude summer AFGL model¹⁹ for the vertical profiles of pressure, temperature and concentration of atmospheric gases. The atmosphere was divided into 46 layers from 0 to 100 km with constant values of pressure, temperatures and gases concentrations. The transmissions were calculated at slant path through the atmosphere at zenith angle of 75° . The atmospheric transmission and difference between transmissions calculated using H_2^{16}O line parameters from different spectroscopic databases are presented in Fig. 2. There is a good agreement between the transmissions simulated with latest spectroscopic databases HITRAN2016 and GEISA2015, with the difference not exceeding 0.01.

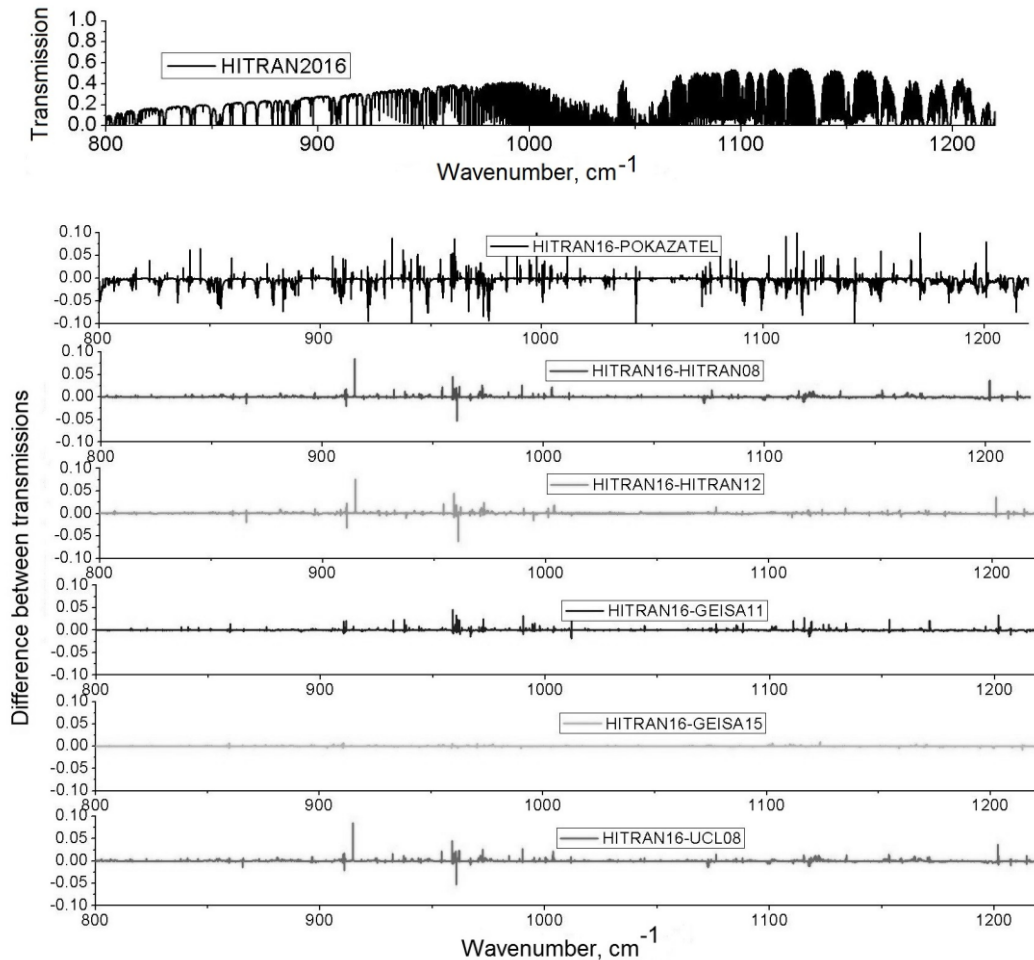


Fig. 2 The atmospheric transmission and difference between transmissions calculated with H_2O line parameters from different spectroscopic databases

The comparison of the integral transmission in the 820-1200 cm^{-1} spectral region, calculated with H_2O line parameters from different spectroscopic databases at vertical and slant paths for the atmospheric models of mid latitude summer and tropics is presented in Tables 1 and 2 (referenced to as POKAZATEL 10^{-42} and VoTe 10^{-42} , respectively). The intensity cut-off value was set to 10^{-42} $\text{cm}/\text{molecule}$ for POKAZATEL and VoTe. As it is shown in Table 2, the relative difference between the integral transmission calculated with HITRAN2016 and POKAZATEL reaches 2.5% for the mid latitude summer model. The difference between the results obtained using HITRAN2016 and other versions of HITRAN and GEISA does not exceed 0.2%.

The same comparison of the atmospheric transmissions was made for a horizontal path of various lengths and illustrated in Table 3-8. The relative difference between the transmissions, calculated using H₂O line parameters from different spectroscopic databases increases by several times at the path length increasing. For example, comparison of the transmissions calculated using last versions of HITRAN2016 and GEISA2015 has shown an increase in the relative difference by an order (0.04% at 1 km length and 0.4% at 100 km).

To estimate the contribution of numerous weak H₂O lines in POKAZATEL and VoTe, we have calculated the atmospheric transmission using two intensity cutoffs, 10⁻⁴² and 10⁻⁴⁰ cm/molecule. The contribution from the VoTe H₂O weak lines to the atmospheric transmission via a horizontal path of 10 km length can reach up to 0.46% (see Table 4). This contribution is less for the POKAZATEL lines, and it is only 0.002% for the atmospheric path of 100 km.

Table 1 The integral transmission in the 820-1200 cm⁻¹ spectral region, calculated with H₂O line parameters from different spectroscopic databases at vertical and slant paths for the atmospheric models of mid latitude summer (MLS) and tropics (TRP).

Atmospheric model	HITRAN 2016	POKAZATEL 10 ⁻⁴²	VoTe 10 ⁻⁴²	HITRAN 2012	HITRAN 2008	GEISA 2011	GEISA 2015	UCL08
MLS, SZA=0 ⁰	0.6116	0.6178	0.6161	0.6110	0.6110	0.6113	0.6112	0.6110
MLS, SZA=75 ⁰	0.2338	0.2397	0.2382	0.2333	0.2334	0.2336	0.2335	0.2334
TRP, SZA=75 ⁰	0.1338	0.1378	0.1368	0.1335	0.1336	0.1338	0.1337	0.1336

Table 2 Relative difference (%) in the integral transmission in the 820-1200 cm⁻¹ spectral region, calculated with H₂O line parameters from the HITRAN2016 and from other spectroscopic databases.

Atmospheric model	POKAZATEL 10 ⁻⁴²	VoTe 10 ⁻⁴²	HITRAN 2012	HITRAN 2008	GEISA 2011	GEISA 2015	UCL08
MLS, SZA=0 ⁰	1.0	0.7	0.1	0.1	0.05	0.06	0.1
MLS, SZA=75 ⁰	2.5	1.8	0.2	0.2	0.08	0.13	0.2
TRP, SZA=75 ⁰	2.9	2.2	0.2	0.1	0	0.07	0.1

Table 3. The atmospheric transmission via a horizontal path, calculated using H₂O line parameters from different spectroscopic databases

L, km	HITRAN2016	HITRAN2012	HITRAN2008	GEISA2011	GEISA2015	UCL08
1	0.7012	0.7007	0.7005	0.7007	0.7009	0.7005
10	0.1066	0.1063	0.1064	0.1065	0.1064	0.1064
100	3.7586E-7	3.7333E-7	3.7445E-7	3.7723E-7	3.7418E-7	3.7325E-7

The difference between the HITRAN2016, POKAZATEL, and VoTe results in Tables 1 and 2 can be explained by the differences in the broadening coefficients used in the simulations. In order to better understand this discrepancies the following schemes of the self- and air-broadened half-widths(γ_{self} and γ_{air}), and temperature dependence exponent (n_t) were tested:

1. HWJJ: γ_{self} , γ_{air} and n_t are calculated using the J²-, J²J²-dependences¹⁰;
2. HWconst: $\gamma_{air}=0.075$; $\gamma_{self}=0.67$ and $n_t=0.4$ as in POKAZATEL³;
3. HWGtKtd: $\gamma_{air}=0.075$; γ_{self} and n_t are calculated using the J²-, J²J²-dependences¹⁰;
4. HWPtashnik: γ_{air} is according to the approximation of Ptashnik et al²⁰; $\gamma_{self}=0.67$ and $n_t=0.4$;
5. HW: $\gamma_{air} = \max(-0.0046875 J''+0.1, 0.024)$; $n_t = \max(-0.0225 J''+0.76, 0.31)$;
 $\gamma_{self} = \max(-0.015625 J''+0.49, 0.24)$.

The atmospheric transmission via a horizontal path, calculated using the schemes of the self- and air-broadened half-widths above is presented in Table 4 for VoTe, and in Table 5 for POKAZATEL. Relative differences between transmissions obtained using these schemes and that using HITRAN2016 is presented in Table 7 and 8 for VoTe and POKAZATEL, correspondingly. The closest results to HITRAN2016 were observed for the VoTe simulation using the HWPtashnik approximation of γ_{air} , where difference in the transmissions was 0.04% for a horizontal path of 1 km. The difference from HITRAN2016 for other schemes of broadening coefficients was 0.4% and higher. For comparison, the transmission calculated with HITRAN2008, HITRAN2012, GEISA2011, GEISA2015, UCL08 differ from the HITRAN2016 results by no more than 0.1% (Table 6).

Table 4. The atmospheric transmission through a horizontal path, calculated with the H₂O line list VoTe using different approximations of the self- and air-broadened half-widths

L, km	VoTe 10 ⁻⁴² HWJJ	VoTe 10 ⁻³⁰ HWJJ	VoTe 10 ⁻⁴² Hwconst	VoTe 10 ⁻⁴² HWGtKtd	VoTe 10 ⁻⁴² HWPtashnik
1	0.7053	0.7053	0.6961	0.6986	0.7009
10	0.1093	0.1098	0.1033	0.1048	0.1065
100	4.2426E-7	4.2423E-7	3.3237E-7	3.5651E-7	3.8280E-7

Table 5. The atmospheric transmission through a horizontal path, calculated with the H₂O line list POKAZATEL using different approximations of the self- and air-broadened half-widths

L, km	Pokazatel 10 ⁻⁴² HWJJ	Pokazatel 10 ⁻³⁰ HWJJ	Pokazatel 10 ⁻⁴² HWconst	Pokazatel 10 ⁻⁴² HW
1	0.7055	0.7055	0.6963	0.7064
10	0.1095	0.1095	0.1034	0.1098
100	4.2522E-7	4.2523E-7	3.3333E-7	4.4041E-7

Table 6 Relative difference (%) in the atmospheric transmission, calculated with H₂O line parameters from the HITRAN2016 and from other spectroscopic databases.

L, km	HITRAN2012	HITRAN2008	GEISA2011	GEISA2015	UCL08
1	0.07	0.1	0.07	0.04	0.1
10	0.3	0.2	0.1	0.2	0.2
100	0.7	0.4	0.4	0.4	0.7

Table 7 Relative difference (%) between atmospheric transmissions, calculated with the HITRAN2016 database and the line list VoTe using different approximations of the self- and air-broadened half-widths

L, km	VoTe 10 ⁻⁴² HWJJ	VoTe 10 ⁻³⁰ HWJJ	VoTe 10 ⁻⁴² Hwconst	VoTe 10 ⁻⁴² HWGtKtd	VoTe 10 ⁻⁴² HWPtashnik
1	0.6	0.6	0.7	0.4	0.04
10	2.5	2.5	3.1	1.7	0.09
100	11.41	11.40	11.57	5.15	1.81

Table 8 Relative difference (%) between the atmospheric transmissions, calculated with POKAZATEL and HITRAN2016.

L, km	Pokazatel 10 ⁻⁴² HWJJ	Pokazatel 10 ⁻³⁰ HWJJ	Pokazatel 10 ⁻⁴² HWconst	Pokazatel 10 ⁻⁴² HW
1	0.6	0.6	0.7	0.7
10	2.65	2.65	3.0	2.9
100	11.608	11.610	11.315	14.66

CONCLUSION

A comparison of the atmospheric transmissions in the 820-1200 cm⁻¹ spectral region calculated using different H₂O line lists is carried out. The relative difference between the results obtained using HITRAN2016 and other versions of HITRAN and GEISA does not exceed 0.2% at slant path with zenith angle of 75° for mid latitude summer. The difference between the integral transmissions calculated using HITRAN2016 and POKAZATEL is about 2.5% which can be partly explained by different approaches using for broadening coefficients.

The atmospheric transmission using different approximations of the self- and air-broadened half-widths and temperature dependence exponents was simulated. It was shown that the closest results to the HITRAN2016 were observed for the VoTe simulation using the HWPtashnik approximation of the air-broadened half-width [20] where the difference in the transmissions was 0.04% for a horizontal path of 1 km. The difference from the HITRAN2016 for other approximations of broadening coefficients was 0.4% and more. According to VoTe, the difference with HITRAN becomes significant for path lengths of 100 km, where using more complete datasets is important.

The contribution of VoTe H₂O weak lines (less than 10⁻³⁰ cm/molecule) to the atmospheric transmission via a horizontal path of the 10 km can reach up to 0.46%.

Acknowledgments

This work was financially supported under the project of the Program of Fundamental Scientific Research of State Academies of Sciences, as well as with partial support of grants RFBR №19-03-00389 and RFBR №18-45-700011 r_a.

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