

Spectroscopy of thermodynamically inhomogeneous high-temperature water vapor

O.K. Voitsekhovskaya, V.N. Cherepanov,
A.A. Kotov, and A.Yu. Zapryagaev

Tomsk State University

Received June 4, 2003

We consider the state of the art of the research into the IR spectroscopy of high-temperature ($T < 3000$ K) water vapor. Physical models for description (within the framework of direct line-by-line calculations) of absorption coefficient and emissivity of high-temperature water vapor are discussed. A particular attention is paid to the development of the software for compilation of spectroscopic databases of water vapor spectral line parameters based on HOTGAS-H₂O information generation system. Using standard assumptions (radiation diffusion and local thermodynamic equilibrium within one layer), the water vapor emissivity was calculated for various concentrations and temperatures from 300 to 3000 K. The stratified medium was simulated by plane-parallel layers of different thickness. The approximations of absorption coefficients considerably simplifying the calculations were proposed based on direct methods. The values of nonselective component of the water vapor absorption coefficient in the range from 8 to 12 μm and temperatures from 1500 to 3000 K are presented for the first time.

Introduction

Significant attention that is paid to water vapor in spectroscopy of gaseous media is explained by its presence in the planetary atmospheres. Besides, this gas is one of the main products of combustion of various fuels, thus being important for remote monitoring of pollution due to traffic and forest and other fires based on recording spectra of gaseous products of fuel combustion. Therefore, prediction, interpretation, and analysis of emission characteristics of water vapor are a very urgent task. The situation is complicated because of the need to take into account the conditions of radiation propagation through the atmosphere and to solve the corresponding radiative transfer equations.

This paper considers some issues concerning model presentation of the emissivity of heated water vapor that would facilitate calculation and estimation of emission and absorption of high-temperature gases. We have calculated the emissivity of high-temperature water vapor for non-LTE conditions by the exact line-by-line calculation technique using our software package and databases of water vapor spectral line parameters (for $T = 300\text{--}3000$ K) that are generated by the unique HOTGAS-H₂O information retrieval system. The emissivity was calculated of a stratified medium consisting of plane-parallel layers having different concentration and temperature inside the layers of different thickness. In our calculations, we used the commonly accepted assumptions: diffuse radiation and local thermodynamic equilibrium (LTE) inside a layer.

1. State of the art of high-temperature ($T < 3000$ K) water vapor spectroscopy

Since the role of asymmetric top molecules in rotational-vibrational (RV) gas spectroscopy is very significant, the number of studies of the spectra of these molecules at the normal temperature ($T \cong 300$ K) is tremendous (see, for example, Refs. 1–12 and references therein). However, the number of studies made at temperatures from 1000 to 3000 K decreases sharply. This is explained by the fact that experimental and theoretical investigations of spectra of gases at such temperatures are far more difficult. Thus, for example, the spatial distributions of temperature and concentration over the volume of a heated medium are usually unknown. Besides, the molecular dissociation begins at high temperatures, what contributes to the error in determination of the concentration of a gas under study.

In addition, it should be noted that quantitative studies of the processes in a heated gaseous medium are impossible without the knowledge of some physical characteristics, such as probabilities of transitions from excited levels for individual components of the medium studied. It is difficult to determine the intensities of hot transitions experimentally, because at high temperatures different bands overlap and absorption is thus determined by a group of bands rather than a single band.^{13,14}

The temperature dependence of the integral intensities of groups of water vapor bands (1.38, 1.87, 2.7, 6.3 μm) has been widely studied by many investigators.^{15–23} Analysis of the calculated data shows that at very high temperatures (several thousands Kelvin) the intensities of many hot bands become comparable^{22–23} and in calculations of absorption coefficients and emissivities it is necessary to account for the entire sequence of bands.

In absorption spectra of high-temperature gases, quantum transitions between both vibrational and rotational excited states are of principle importance. This leads to the growing role of intra- and intermolecular relaxation and excitation processes. As a result, high-temperature media acquire not only new physical properties, but also become chemically active because of the appearance of radicals.

At the same time, no clear pattern of the hierarchy of physical and chemical processes in such media is available now. This gives rise to two related problems: on the one hand, a theory should be developed to describe adequately the spectra of high-temperature gases (development of such a theory is now far from completion) and, on the other hand, the bulk of spectroscopic and other information (on the number of molecules, spectral line parameters, spectral line shapes, models of a medium, its thermodynamic characteristics, etc.) increase drastically. Therefore, in recent 20–30 years spectral databases, as well as automated systems for calculation of radiation transmission through media with different thermodynamic characteristics (Refs. 13, 24–31) have been intensely developed. The main function of such systems is accumulation of the data on spectral line parameters and models of various media available, their critical analysis, evaluation of reliability, systematization, and storage in a convenient form. In this connection, information systems should allow modifications and include the following tools: database compilation and maintenance; data input and control; data acquisition and correction; dialog interaction.

Recently compilation of the HITEMP high-temperature spectroscopic database has been reported.³¹ This database includes parameters of about $1.3 \cdot 10^6$ spectral lines of water vapor. However, its significant disadvantage is, in our opinion, the compilation principle used. The selection criterion in this database causes the loss of some lines at temperatures higher than 1000 K, because their intensity turns out to be lower than the threshold value specified. The conceptual principles used in the HOTGAS-H₂O information retrieval system generating spectral line parameters for given thermodynamic conditions of a medium based on efficient algorithms and programs for calculation of intensities, positions, and half-widths of water vapor molecular spectral lines allowed us to avoid these troubles.

2. Models for calculating parameters of RV lines

2.1. Technique for calculating intensities and positions of spectral lines of triatomic molecules

Calculation of positions and intensities of RV spectral lines of the H₂O molecule that contribute to absorption and emission at temperatures from 300 to 3000 K is based on the principles formulated in Refs. 32–34. The general approach employs separation of the full rotational-vibrational Hamiltonian into groups of terms:

$$H = \sum_{i=2}^{\infty} H_{i0} + \sum_{i=2}^{\infty} H_{i1} + \sum_{i=0}^{\infty} H_{i2} + \dots, \quad (1)$$

where $\sum_{i=2}^{\infty} H_{i0}$ are the vibrational terms, $\sum_{i=2}^{\infty} H_{i1}$ are the terms describing the Coriolis interaction, and $\sum_{i=0}^{\infty} H_{i2}$ are the rotational terms. This representation

allows one to solve first the vibrational problem (first sum) by calculating energies and matrix elements of vibrational transitions, taking into account all the possible vibrational resonances (through numerical diagonalization of the partitioned matrix with the use of anharmonic potential function), and with the following resolution of the rotational structure (third sum) with the allowance for the terms corresponding to vibrational-rotational interactions (second sum).

In calculating the integral vibrational intensity the HOTGAS-H₂O system takes the vibrational resonances (Fermi resonance and Darling–Dennison resonance) into account. The dipole moment parameters are determined from solution of the inverse problem by the minimization method. The processing involves integral intensities of vibrational absorption bands recorded experimentally at normal temperature ($T \sim 300$ K). Then the matrix elements of the dipole moment are calculated by direct extrapolation in the basis of resonance vibrational wave functions and the integral intensities of the bands are determined. The intensities of RV transitions are calculated as

$$S_{vr} = \frac{S_v \nu}{Q_r \nu_0} L_r F A, \quad (2)$$

where L_r is the rotational line strength; S_v is the integral intensity of a vibrational band; A are the exponential factors; Q_r is the rotational partition function; F is the factor of RV interaction. The latter can be written as a series

$$F = \left(1 + \sum_{i=1}^{\infty} \alpha_i C_i \right)^2, \quad (3)$$

where α_i are the effective constants of a particular vibrational transition; C_i are the known rotational

functions. The system uses both theoretical and semi-empirical values of the F -factor constants.

For calculation of line positions, HOTGAS-H₂O uses the experimental databases of RV energy levels indexed by a set of vibrational quantum numbers. The missing energy levels are calculated by use of standard models of the theory of effective Hamiltonians based on Eq. (1).

Role of high-excited rotational transitions in absorption of radiation. At the temperature higher than 1000 K, the population of rotational levels with large rotational quantum numbers increases, and, consequently, transitions from these levels contribute considerably to absorption. To evaluate the role of such transitions, we have calculated, using the HOTGAS-H₂O system, the water vapor absorption coefficient nearby 850 cm⁻¹ at the temperature ranging from 1000 to 6000 K. This calculation involved all possible RV transitions with the total difference between the vibrational quantum numbers ≤ 2 ($v_i \leq 4$, $i = 1, 2, 3$) that contribute to the spectral range under study. Figure 1 depicts the temperature dependence of the absorption coefficient for different sets of experimental energy levels known from literature.^{52–54,66,67,69} The first set only includes the ground-state energy levels up to $J = 25$ (J is the rotational quantum number). The second set is complemented by the calculated energy levels up to $J = 35$ from Ref. 55 with the assignment corrected according to the calculation by the model of symmetric-top molecule proposed in Ref. 68 for description of high rotational states of the water vapor molecule.

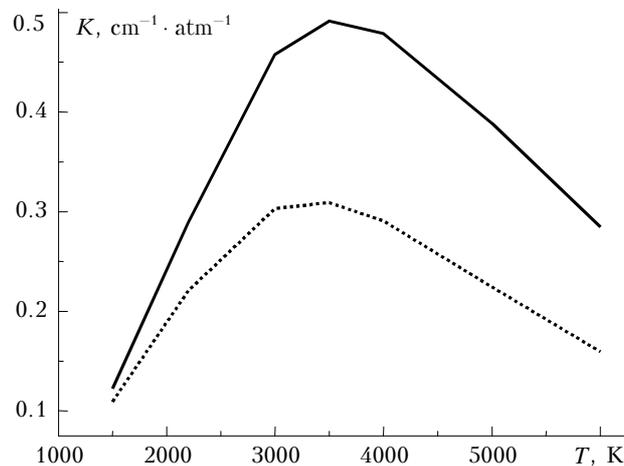


Fig. 1. Water vapor absorption coefficient in the range of (850 ± 20) cm⁻¹. The solid and dashed curves show the values calculated using the first and second sets of the rotational energy levels.

As expected, it is most important to take high energy levels into account in calculating the absorption coefficients within the atmospheric transmission windows free of absorption lines with low values of rotational quantum numbers.⁶⁸ Here it

is worth noting the efficiency of the model of symmetric-top molecule in describing high-excited rotational states of water vapor molecule; for compilation of the archive of RV energy levels with $K_a \sim J$ calculated by simple analytical equations in the Pade form,⁶⁸ and for provision of high predictability (see Tables 1 and 2).

Table 1. Predicted values of rotational energy levels for the ground vibrational state of H₂¹⁶O (cm⁻¹)^{*}

J	K_a	E_{calc}	E_{obs} (Ref. 69)	E_{calc} (Ref. 48)
26	26	14370.0864	14370.22370	14369.7482
27	27	15286.7782	15287.07544	15286.5393
28	28	16219.7036	16220.19037	16219.5958
29	29	17168.1480	17168.81788	17168.1628
30	30	18131.4474	18132.22760	18131.5143
31	31	19108.9875	19109.72107	19108.9555
32	32	20100.2030	20100.777228	20099.7967
33	33	21104.5761	21105.38800	21103.3625
34	34	22121.6356		22119.0377
35	35	23150.9551		23146.1672

^{*} Our assignment.

Table 2. Predicted values of rotational energy levels for the 010 vibrational state of H₂¹⁶O (cm⁻¹)^{*}

J	K_a	E_{calc}	E_{obs} (Ref. 69)	E_{calc} (Ref. 48)
22	22	12914.5109	12914.37782	12914.0420
23	23	13770.7405	13770.28395	13769.8994
24	24	14645.9081	14644.78688	14644.3616
25	25	15539.3255	15537.01552	15536.5335
26	26	16450.3901	16446.13557	16445.5933
27	27	17378.5811	17371.35145	17370.7417
28	28	18323.4549	18311.89961	18311.2137
29	29	19284.6396	19267.04640	19266.2659

^{*} Our assignment.

Effect of vibrational-rotational interaction on water vapor line intensities in the infrared and visible spectral regions. Based on the algorithms developed for calculation of RV line intensities and the estimated contributions of higher-order terms of the perturbation theory to the matrix element of dipole moment, let us discuss the calculated results on RV line intensities for some H₂O bands in the IR and visible spectrum. The parameters of the F -factor for water vapor rovibrational bands have been determined in Refs. 35–42. Note that it was for the first time that most complete treatment of experimental results with the use of F -factor for RV bands with $\Delta v \leq 2$ was carried out in Ref. 42, in which the parameters of the F -factor determined were used to reconstruct RV line intensities and the accuracy of the order of the experimental uncertainty was obtained. At the same time, in parallel to our studies, the RV line intensities for the fundamental bands and bands of the first (100, 001, 002) and second (110, 011, 030) triads were treated with the model effective operator of dipole moment obtained by contact transformations in Refs. 43–45, where it was shown that the correct allowance for the intramolecular

interactions gives the error of 8–11% as compared with the experimental data.

Reliable prediction of the intensities of water vapor RV lines in the visible and infrared spectrum is a more complicated problem. In this region, the H₂O spectrum is determined by the combination and overtone RV bands characterized by large values of vibrational quantum numbers. As follows from the estimates presented, the effect of intramolecular interactions in this region is significant even for lines formed by transitions between states with small values of rotational quantum numbers.

Region of 1.5 μm. This spectral region includes RV bands of the first hexad of H₂O interacting states (021, 101, 120, 200, 002, 040). Note that non-resonance RV interaction affects the intensities of the RV lines of the 000–021 band stronger as compared to the lines of the 000–120 band. The experimental RV line intensities^{46,47} treated in Ref. 6 by the scheme developed in Refs. 43–45 made it possible to achieve close agreement with the experiment ($\leq 10\%$ on the average).

Region ~ 1 μm. The line intensities of H₂O RV bands $\nu_1 + \nu_2 + \nu_3$ and $\nu_2 + 2\nu_3$ lying nearby 1 μm were processed, for the first time, within the three-parameter model of the *F*-factor in Ref. 39. The parameters of the *F*-factor determined provided for a good agreement with the experimental data and good prediction of line intensities in these bands. It is important to note that later on a more correct processing of these intensities with the allowance for resonance interactions⁶ gave almost the same results (error within 30%) as in Ref. 39 except for several weak lines. This circumstance indicates that the proposed simple model to take into account the RV interactions can be efficiently used for solution of a wide range of problems.

Visible spectrum. The number of papers concerning the visible spectral region (Refs. 48–58) increases recently, but the attention paid to analysis of the intensities of individual RV lines is still insufficient. Based on the estimated contributions of RV interactions to the matrix element of the dipole moment, we have studied the effect of RV interaction on the intensities of RV lines under condition $\kappa J \sim \kappa$ (κ is the small expansion parameter) for seven H₂O bands lying in the visible region: 000 → 103 ($\lambda = 0.69 \mu\text{m}$), 202, 221, 301 ($\lambda = 0.715\text{--}0.732 \mu\text{m}$), 321, 401, 302 ($\lambda = 0.59 \mu\text{m}$) [Ref. 41]. As a result, it was shown that the equation for the *F*-factor (3) is suitable for quantitative estimation of the RV interactions in this case too (the mean calculated error is ~20%). In conclusion, we would like to mention Ref. 7, which generalizes recent experimental and theoretical data on water vapor.

Figure 2 depicts the results of calculation of H₂O absorption coefficients at the temperatures from 1000 to 3000 K. It can be seen that the account of the rotational-vibrational interaction leads to a better agreement with the experiment.⁶⁵

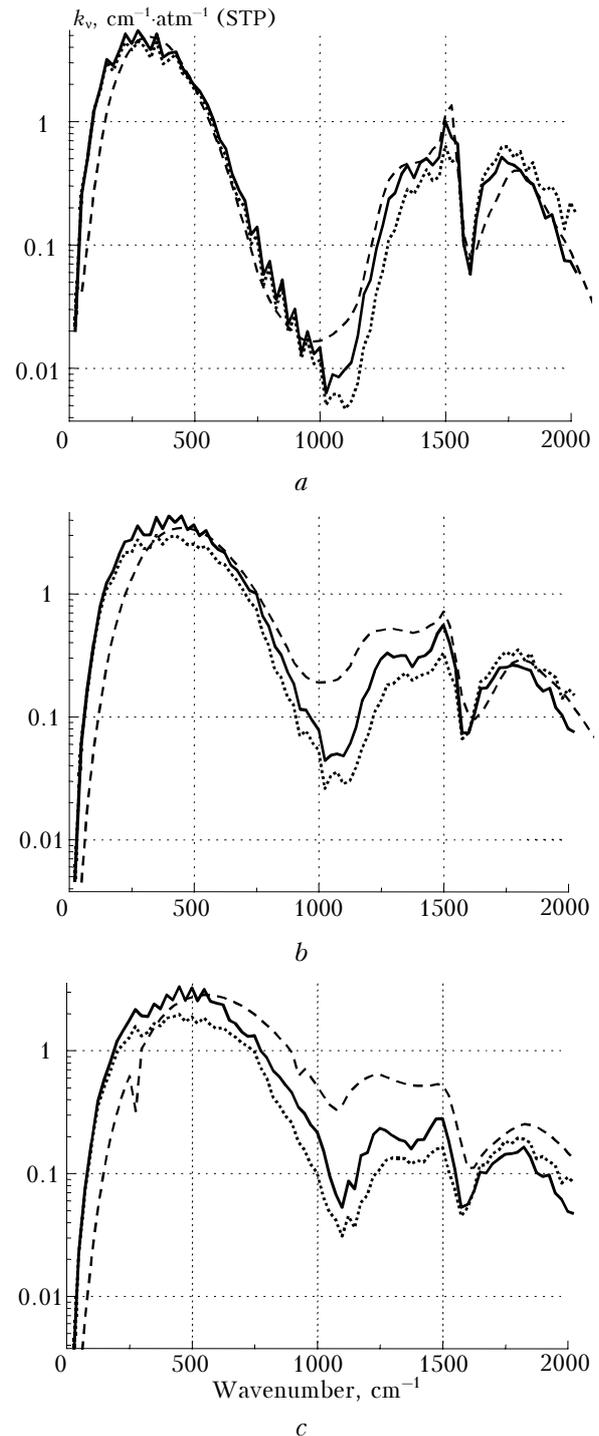


Fig. 2. Water vapor absorption coefficients: experiment⁶⁵ (dashed line), calculation by the rigid-top model (dotted line), calculation with the allowance for rotational-vibrational interaction (solid line); $T = 1000$ (a), 2000 (b), 3000 K (c).

2.2. General approach to calculation of halfwidths of RV lines

In HOTGAS-H₂O, H₂O line halfwidths are calculated by a semiempirical technique.⁵⁹ This is

connected, first, with the fact that line halfwidth calculations at high temperatures are very complicated and no experimental data enough for a comparison are available. Besides, the existing calculation algorithms based on the quantum-mechanics approach are rather cumbersome and do not guarantee the accuracy needed. It seems to be most acceptable to approximate the line halfwidth, as a function of rotational quantum numbers, by the polynomial

$$\gamma \cong \sum_{i=1} a_i J^i + \sum_{k=1} b_k \Delta \tau^k, \quad (4)$$

where J is the rotational quantum number of the lower state of the transition; $\Delta \tau$ is the difference between pseudoquantum numbers of the transition. The values of the polynomial coefficients in Eq. (4) for particular vibrational transitions are presented in Ref. 59. These polynomial coefficients are determined for the normal temperature $T_0 = 300$ K. To pass on to a particular temperature, we used the relation

$$\gamma(T) = \gamma_0 \left(\frac{T_0}{T} \right)^n, \quad \text{where } n = -0.5. \quad \text{The water vapor line}$$

halfwidths calculated by the semiempirical equation (4) agree well with the measurement results from Ref. 70.

3. Technique for calculation of emission characteristics

Homogeneous gas volume. At high temperatures (about 1000 K and higher) a gas volume emits its own radiation. According to Ref. 63, it can be found in the following way:

$$I(\nu, T) = \int_{\nu_1}^{\nu_2} B(\nu', T) E_{\nu'}(T) d\nu'. \quad (5)$$

Here $B(\nu, T)$ is the Planck's function, and the emissivity of the heated air medium in the LTE approximation is determined by the equation

$$E_{\nu}(T) = 1 - \exp(-k_{\nu} \rho L), \quad (6)$$

where k_{ν} is the gas absorption coefficient ($\text{cm}^{-1} \cdot \text{atm}^{-1}$); T , ρ are the temperature (K) and the partial pressure of the gas under study (atm) that are constant all over the path; L is the path length, in cm. The line profile was assumed to be the Lorentz one in calculations of the absorption coefficient.

Inhomogeneous gas volume. The model of the medium in this case is formed in the following way. The entire gas volume is divided into a series of layers, inside which the gas parameters (temperature, concentration, absorption coefficient) are constant. This approach called stratification model is widely used in calculations of radiation propagation through the atmosphere.⁶⁴ Assuming that the radiation propagates normally to the layer, the radiation intensity in the first layer is determined as

$$I(\nu, T) = \int_{\nu_1}^{\nu_2} B(\nu', T_0) (1 - e^{-k_1 \rho_1 L_1}) d\nu'. \quad (7)$$

The subscripts of medium parameters correspond to the layer number. Radiation extinction in the second layer is calculated with the allowance for emission as follows:

$$I(\nu, T) = \int_{\nu_2}^{\nu_2} B(\nu', T_0) (1 - e^{-k_1 \rho_1 L_1}) e^{-k_2 \rho_2 L_2} d\nu' + \int_{\nu_1}^{\nu_2} B(\nu', T_1) (1 - e^{-k_2 \rho_2 L_2}) d\nu'. \quad (8)$$

With the further increase of the number of layers, similar calculations are performed for each layer (an example of thus calculated emissivity is shown in Fig. 3).

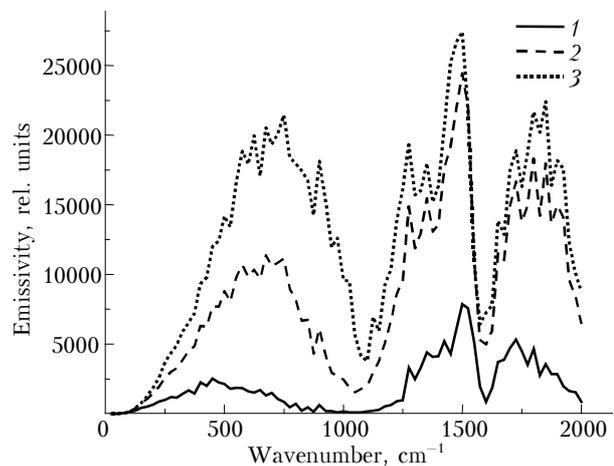


Fig. 3. Water vapor emissivity (rel. units): $T = 1000$ (1), 2000 (2), 3000 K (3).

For simpler calculations, the absorption coefficient is approximated by the spline

$$k_{\nu}(T) = \sum_{i=0 \dots 3} p_i(T) \nu^i, \quad (9)$$

where the polynomial coefficients p_i are determined for the temperatures of 300, 600, 1000, 1500, 2000, 2500, and 3000 K. For the intermediate values of temperature, the coefficients p_i are calculated using linear interpolation:

$$p_i(T) = p_i(T_1) + [p_i(T_2) - p_i(T_1)] (T - T_1) / (T_2 - T_1), \quad (10)$$

where T_1 and T_2 are the boundaries of the interpolation grid. The reconstruction of the absorption coefficient by these equations gives the error no higher than 5%, on the average. Then the emissivity is calculated by Eqs. (5) – (8).

4. HOTGAS-H₂O high-resolution spectroscopic information retrieval system

In development of the HOTGAS-H₂O high-resolution spectroscopic information retrieval system, we implemented the ideas formulated earlier when developing the ATLAS system for formation and management of the database of spectral line parameters (SLP)⁶⁰⁻⁶² with the allowance made for

the requirements considered above. The conceptual, logical, and functional schemes tested in the ATLAS system are now used in HOTGAS-H₂O, as shown in Figs. 4 and 5.

The SLP database management system includes SLP sorting, SLP merge into databases, contents compilation, and search.

The interface is shown in Fig. 5. The HOTGAS-H₂O is oriented at calculation of H₂O spectral line parameters in the temperature range from 300 to 3000 K and the spectral region of 0 to 10000 cm⁻¹.

Fig. 4. Flow chart of calculation of spectral line parameters.

Fig. 5. Flow chart of the HOTGAS-H₂O system.

(The calculation can be performed up to 20000 cm⁻¹, but the reliability of these data calls for separate analysis). A feature of HOTGAS-H₂O is the fact that it generates the SLP database in a preset spectral region at the given pressure and temperature. In contrast to other banks of spectral data,²⁴⁻³¹ this allows all lines at the given temperature to be taken into account automatically by entering the

minimum value of intensities for the lines to be included.

The HOTGAS-H₂O is developed for Windows 98/NT/XP and has a friendly user interface with both text and graphical forms, which allow plots and tables generated in HOTGAS-H₂O to be used in other Windows applications, such as, for example, Word and Excel (Fig. 6).

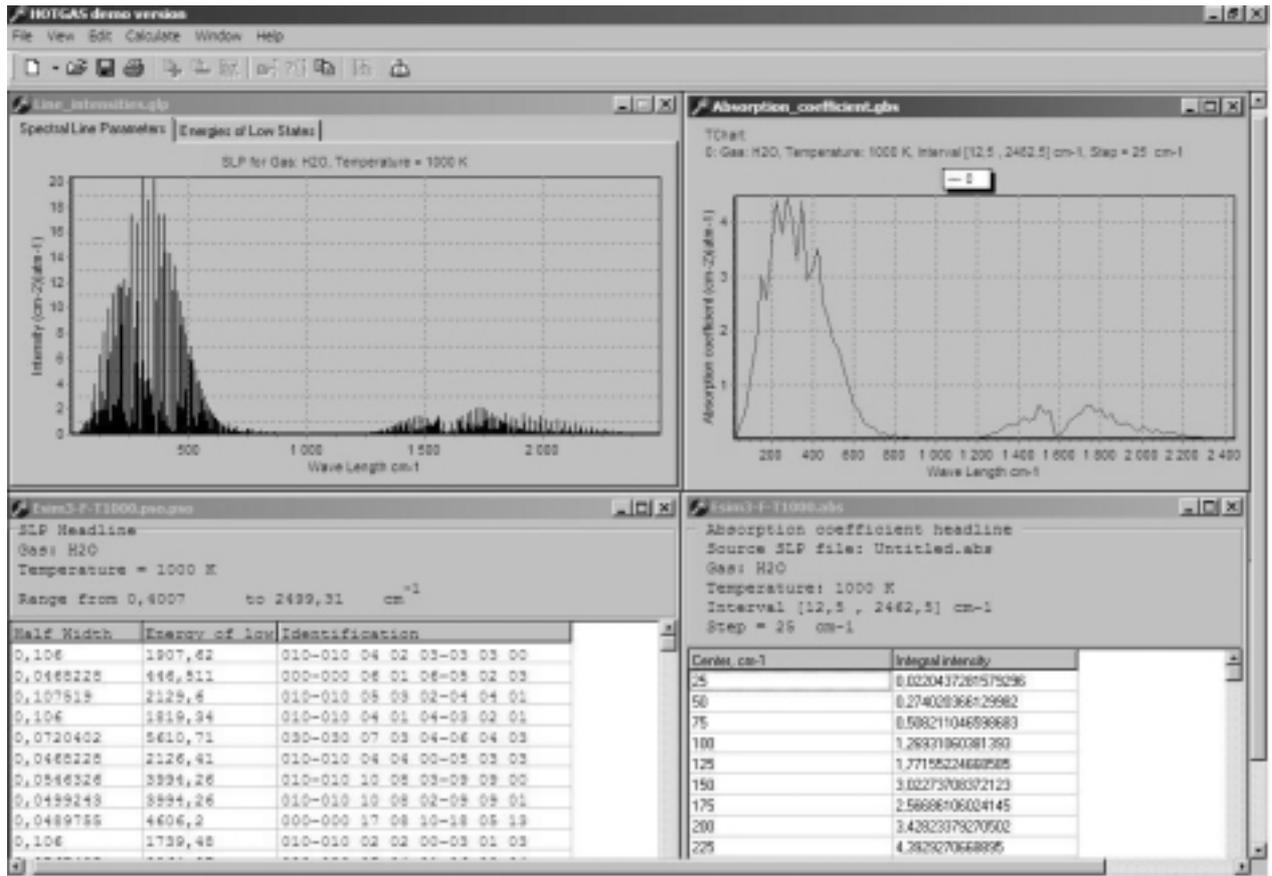


Fig. 6. HOTGAS-H₂O menu.

5. Determination of temperature dependence of nonselective absorption in the 8–12 μm transmission window

As follows from Fig. 2, the known discrepancy between the values of experimentally recorded water vapor absorption in the 8–12 μm window¹¹ and that

Table 3. Nonselective absorption coefficients in 8–12 μm region for temperatures from 1500 to 3000 K

Wavenumber, cm ⁻¹	T, K			
	1500	2000	2500	3000
800	0.00	0.16	0.42	0.76
825	0.03	0.24	0.52	0.87
850	0.00	0.19	0.47	0.80
875	0.03	0.23	0.52	0.87
900	0.01	0.19	0.50	0.87
925	0.04	0.20	0.45	0.59
950	0.02	0.14	0.34	0.65
975	0.02	0.13	0.29	0.54
1000	0.02	0.13	0.26	0.46
1025	0.05	0.17	0.26	0.40
1050	0.04	0.16	0.24	0.32
1075	0.05	0.17	0.25	0.30
1100	0.07	0.20	0.28	0.33
1125	0.10	0.23	0.35	0.42
1150	0.14	0.30	0.41	0.47
1175	0.19	0.36	0.46	0.53
1200	0.24	0.40	0.50	0.54

calculated by the Lorentz profile keeps true at high temperatures as well. Since the data in Ref. 65 were obtained by approximation of measurements, the value of nonselective absorption is determined as the difference between the absorption coefficient calculated by the considered technique and using data from Ref. 65. Table 3 presents the water vapor nonselective absorption coefficients in the 8–12 μm transmission window for the temperature ranging from 1500 to 3000 K.

These data can serve the basis for determining the temperature dependence of the water vapor intermolecular interaction potential and for studying the nature of water vapor nonselective absorption.

Conclusion

Solution of problems connected with the emission of heated gases is now based on the LTE approximation, in which thermodynamic characteristics of a medium are assumed constant within a gas volume considered and the Kirchhoff law is fulfilled, because it is practically difficult to check the homogeneity of the gas volume analyzed. At the same time, development of HOTGAS system provides the information support to spectroscopic studies of water vapor taking into account its actual temperature inhomogeneity, which opens additional possibilities for solving inverse problems in optics of gas media.

The results given by the HOTGAS system can be used in processing the results of spectral measurements of burning, analysis of exhausts of the internal combustion engines, monitoring of industrial production, as well as ecological monitoring of the Earth's atmosphere.

Acknowledgments

The support from the Russian Foundation for Basic Research under Grant No. 01-01-00770 is acknowledged.

References

1. M.A. El'yashevich, Tr. GOI **12**, No. 106, 3-134 (1938).
2. E.B. Wilson, J.C. Decius, and P.C. Cross, *Molecular Vibrations* (McGraw Hill, New York, 1955).
3. G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand, 1959).
4. G. Herzberg, *Electronic Spectra and Electronic Structure of Polyatomic Molecules* (D. Van Nostrand, 1967).
5. V.I. Starikov and V.I.G. Tyuterev, *Intramolecular Interactions and Theoretical Methods in Spectroscopy of Nonrigid Molecules* (Spektr, Tomsk, 1997), 232 pp.
6. A.D. Bykov, Yu.S. Makushkin, and O.N. Ulenikov, *Vibrational-Rotational Spectroscopy of Water Vapor* (Nauka, Novosibirsk, 1989), 296 pp.
7. A.D. Bykov, L.N. Sinitsa, and V.I. Starikov, *Experimental and Theoretical Methods in Spectroscopy of Water Vapor Molecules* (SB RAS, Novosibirsk, 1999), 376 pp.
8. S.S. Penner, *Quantitative Molecular Spectroscopy and Gas Emissivities* (Addison-Wesley, Reading, 1969).
9. K.Ya. Kondratyev and V.I. Moskalenko, *Planetary Thermal Radiation* (Gidrometeoizdat, Leningrad, 1977), 264 pp.
10. L.M. Sverdlov, M.A. Kovner, and E.P. Krainov, *Vibrational Spectra of Polyatomic Molecules* (Nauka, Moscow, 1970), 650 pp.
11. L.I. Nesmelova, O.B. Rodimova, and S.D. Tvorogov, *Spectral Line Contour and Intermolecular Interaction* (Nauka, Novosibirsk, 1986), 213 pp.
12. P.R. Bunker, *Molecular Symmetry and Spectroscopy* (Academic Press, New York, 1979).
13. O.K. Voitsekhovskaya, A.V. Rozina, and N.A. Trifonova, *Information System for High-Resolution Spectroscopy* (Nauka, Novosibirsk, 1988), 150 pp.
14. V.A. Kamenschikov, Yu.A. Plastinin, V.M. Nikolaev, and L.A. Novitskii, *Radiative Properties of Gases at High Temperatures* (Mashinostroenie, Moscow, 1971), 440 pp.
15. I.V. Avilova, M.M. Biberman, V.S. Vorob'ev, V.M. Zamalin, G.A. Kabzev, A.N. Larionov, A.Kh. Mnatsakanyan, and G.E. Norman, *Optical Properties of Hot Air* (Nauka, Moscow, 1970), 355 pp.
16. A. Gutman, J. Quant. Spectrosc. Radiat. Transfer **2**, No. 1, 1-15 (1962).
17. R. Goldstein, J. Quant. Spectrosc. Radiat. Transfer **4**, No. 2, 343-352 (1964).
18. M.V. Vol'kenshtein, L.A. Gribov, A.A. El'yashevich, and B.I. Stepanov, *Molecular Vibrations* (Nauka, Moscow, 1972), 700 pp.
19. M.P. Lisitsa and V.L. Strizhevskii, Opt. Spektrosk. **10**, No. 1, 48-54 (1961).
20. J.C. Breese, C.C. Ferriso, C.B. Ludwig, and W. Malkmus, J. Chem. Phys. **42**, No. 1, 402-406 (1965).
21. A.A. Kon'kov and A.V. Vorontsov, Opt. Spektrosk. **36**, No. 4, 649-653 (1974).
22. S.J. Yao and J. Overend, Spectrochimica Acta **A 32**, No. 5, 1059-1065 (1976).
23. O.K. Voitsekhovskaya, Yu.S. Makushkin, and V.N. Cherepanov, "Intensities of excited vibrational transitions of the water vapor molecule in the temperature range of 300-6000 K," Dep. VINITI No. 1017-77, Tomsk (1977), 28 pp.
24. L.S. Rothman, A. Goldman, R.H. Tipping, C.P. Rinsland, M.A.H. Smith, D.C. Benner, V.M. Devi, J.-M. Flaud, C. Camy-Peyret, A. Perrin, A. Goldman, S.T. Massie, L.R. Brown, and R.A. Toth, J. Quant. Spectrosc. Radiat. Transfer **48**, No. 5-6, 469-507 (1992).
25. L.S. Rothman, C.P. Rinsland, A. Goldman, S.T. Massie, D.P. Edwards, J.-M. Flaud, A. Perrin, C. Camy-Peyret, V. Dana, J.-Y. Mandin, J. Schroeder, A. McCann, R.R. Gamache, R.B. Watson, K. Yoshino, K.V. Chance, K.W. Jucks, L.R. Brown, V. Nemtchinov, and P. Varanasi, J. Quant. Spectrosc. Radiat. Transfer **60**, No. 5, 665-710 (1998).
26. R.A. McClatchey, W.S. Benedict, S.A. Clough, D.E. Burch, R.F. Calfu, K. Fox, L.S. Rothman, and J.S. Garing, AFCRL-TR-0096, E.R.P. No. 434 (1973), p. 78; L.S. Rothman and R.A. McClatchey, Appl. Opt. **15**, No. 11, 2616-2617 (1976).
27. L.S. Rothman, Appl. Opt. **17**, No. 22, 3517-3519 (1978); L.S. Rothman, Appl. Opt. **20**, No. 5, 791-795 (1981); L.S. Rothman, A. Goldman, J.R. Gillis, R.H. Tipping, L.R. Brown, J.S. Margolis, A.S. Maki, and L.D.G. Yong, Appl. Opt. **20**, No. 8, 1321-1328 (1981).
28. L.S. Rothman, R.R. Gamache, A. Barbe, A. Goldman, J.R. Gillis, L.R. Brown, R.A. Toth, J.-M. Flaud, and C. Camy-Peyret, <http://www.opticsinfobase.org>; L.S. Rothman, A. Goldman, J.R. Gillis, R.R. Gamache, H.M. Picket, R.L. Poynter, N. Husson, and A. Chedin, Appl. Opt. **22**, No. 11, 1616-1627 (1983).
29. A. Chedin, N. Husson, N.A. Scott, Bull. d'Inform. Du Centre de Donnies Stellaires **22**, 121-124 (1982); N. Jacquinet-Husson, N.A. Scott, A. Chedin, and A.A. Chursin, Atmos. Oceanic Opt. **16**, No. 3, 256-261 (2003).
30. A.A. Mitsel', K.M. Firsov, and B.A. Fomin, *Transfer of Optical Radiation in Molecular Spectroscopy* (SST, Tomsk, 2001), 444 pp.
31. L.S. Rothman, C. Camy-Peyret, J.-M. Flaud, R. Gamache, D. Goorvitch, A. Goldman, R.L. Hawkins, J. Schroeder, J.E.A. Selby, and R.B. Wattson, J. Quant. Spectrosc. Radiat. Transfer (in press).
32. O.K. Voitsekhovskaya, Atm. Opt. **3**, No. 6, 533-539 (1990).
33. O.K. Voitsekhovskaya, N.N. Trifonova, and M.V. Kuz'mina, Atmos. Oceanic Opt. **5**, No. 5, 296-300 (1992).
34. O.K. Voitsekhovskaya, A.A. Peshkov, M.M. Tarasenko, and T.Yu. Sheludyakov, Izv. Vyssh. Uchebn. Zaved., Fizika, No. 8, 43-51 (2000).
35. O.K. Voitsekhovskaya, Yu.S. Makushkin, and O.N. Sulakshina, in: *Intramolecular Interactions and Infrared Spectra of Atmospheric Gases*, ed. by V.E. Zuev (IAO SB AS USSR Publishing House, Tomsk, 1975), pp. 78-87.
36. O.K. Voitsekhovskaya, V.E. Zuev, I.I. Ippolitov, and Yu.S. Makushkin, Zh. Prikl. Spektrosk. **17**, No. 1, 164-167 (1972).
37. O.K. Voitsekhovskaya, I.I. Ippolitov, and Yu.S. Makushkin, Opt. Spektrosk. **35**, No. 1, 42-47 (1973).
38. O.K. Voitsekhovskaya, I.I. Ippolitov, and Yu.S. Makushkin, Opt. Spektrosk. **33**, No. 1, 78-83 (1972).

39. V.N. Cherepanov, V.P. Kochanov, Yu.S. Makushkin, L.N. Sinitsa, A.M. Solodov, O.N. Sulakshina, and O.K. Voitsekhovskaya, *J. Mol. Spectrosc.* **111**, 173–178 (1985).
40. K.A. Aganbekyan, O.K. Voitsekhovskaya, G.A. Gulyaev, V.V. Kulikov, and N.N. Trifonova, *J. Mol. Spectrosc.* **130**, 258–261 (1988).
41. O.K. Voitsekhovskaya and V.N. Cherepanov, *Izv. Vyssh. Uchebn. Zaved., Fizika*, No. 7, 118–119 (1983).
42. O.K. Voitsekhovskaya, Yu.S. Makushkin, O.N. Sulakshina, and V.N. Cherepanov, in: *Abstracts of Reports at Sixth All-Union Symposium on High and Ultrahigh Resolution Molecular Spectroscopy*, Tomsk (1982), pp. 131–136.
43. J.M. Flaud and C. Camy-Peyret, *J. Mol. Spectrosc.* **55**, No. 1, 278 – 310 (1975).
44. C. Camy-Peyret, J.-M. Flaud, and R.A. Toth, *J. Mol. Spectrosc.* **67**, No. 1, 117–131 (1977).
45. C. Camy-Peyret and J.-M. Flaud, *J. Mol. Spectrosc.* **32**, No. 2, 523 – 537 (1976).
46. C. Camy-Peyret, J.-M. Flaud, and J.-P. Maillard, *J. Phys. Lett.* **41**, No. 2, 123–126 (1980).
47. J.-Y. Mandin, J.-P. Chevillard, C. Camy-Peyret, and J.-M. Flaud, *J. Mol. Spectrosc.* **118**, No. 1, 96–102 (1986).
48. H. Partridge and D.W. Schwenke, *J. Chem. Phys.* **106**, No. 11, 4618–4638 (1997).
49. U.G. Jorgensen and P. Jensen, *J. Mol. Spectrosc.* **161**, No. 1, 219–242 (1993).
50. V.I. Tyuterev, V.I. Starikov, S.A. Tashkun, and S.N. Mikhailenko, *J. Mol. Spectrosc.* **170**, No. 1, 38–58 (1995).
51. V.I. Starikov and S.N. Mikhailenko, *J. Phys. B* **33**, No. 11, 2141–2151 (2000).
52. R. Lanquetin, L.H. Coudert, and C. Camy-Peyret, *J. Mol. Spectrosc.* **195**, No. 1, 54–67 (1999).
53. O.N. Polyansky, N.F. Zobov, S. Viti, J. Tennyson, P.F. Bernath, and L. Wallace, *J. Mol. Spectrosc.* **186**, No. 2, 422–447 (1997).
54. R. Lanquetin, L.H. Coudert, and C. Camy-Peyret, *J. Mol. Spectrosc.* **206**, No. 1, 83–103 (2001).
55. D.W. Schwenke, *J. Mol. Spectrosc.* **190**, No. 2, 397–402 (1998).
56. A.G. Csaszar, J.S. Kain, O.N. Polyansky, N.F. Zobov, and J. Tennyson, *Chem. Phys. Lett.* **293**, Nos. 3–4, 317–323 (1998).
57. J.S. Kain, O.N. Polyansky, and J. Tennyson, *Chem. Phys. Lett.* **317**, Nos. 3–5, 365 – 371 (2000).
58. A. Jenouvrier, M.F. Merienne, M. Carleer, R. Colin, A.-C. Vandaele, P.F. Bernath, O.N. Polyansky, and J. Tennyson, *J. Mol. Spectrosc.* **209**, No. 2, 165–168 (2001).
59. G.V. Antukh, O.K. Voitsekhovskaya, and N.N. Trifonova, *Atmos. Oceanic Opt.* **5**, No. 2, 143–146 (1992).
60. O.K. Voitsekhovskaya, V.E. Zuev, Yu.S. Makushkin, A.I. Popkov, A.V. Rozina, O.N. Sulakshina, N.N. Trifonova, V.N. Cherepanov, and N.E. Yakovlev, “*Automatic database management system for database of spectral line parameters of atmospheric and trace gases*,” Preprint No. 3 (Tomsk, 1985), 54 pp.
61. O.K. Voitsekhovskaya, Yu.S. Makushkin, A.I. Popkov, V.P. Rudenko, N.N. Trifonova, N.E. Yakovlev, O.N. Sulakshina, and V.N. Cherepanov, *Computer Enhanced Spectrosc.* **2**, No. 3, 101–107 (1984).
62. O.K. Voitsekhovskaya, Yu.S. Makushkin, O.N. Sulakshina, N.N. Trifonova, and V.N. Cherepanov, *Computer Enhanced Spectrosc.* **3**, 13–21 (1986).
63. M.P. Esplin, R.B. Wattson, M.L. Hoke, and L.S. Rothman, *J. Quant. Spectrosc. Radiat. Transfer* **60**, No. 5, 711–739 (1998).
64. V.E. Zuev, *Propagation of Visible and Infrared Waves in the Atmosphere* (Sov. Radio, Moscow, 1970), 496 pp.
65. C.C. Ferriso, C.B. Ludwig, and A.L. Thomson, *J. Quant. Spectrosc. Radiat. Transfer* **6**, No. 3, 241–273 (1966).
66. R.A. Toth, *J. Mol. Spectrosc.* **190**, No. 2, 379–396 (1998).
67. J.-M. Flaud, C. Camy-Peyret, and J.-P. Mandin, *Mol. Phys.* **32**, No. 2, 499–521 (1976).
68. O.K. Voitsekhovskaya, A.A. Kotov, and V.N. Cherepanov, *Izv. Vyssh. Uchebn. Zaved., Fizika* **44**, No. 8, 24–28 (2001).
69. J. Tennyson, N.F. Zobov, R. Williamson, O.L. Polyansky, and P.F. Bernath, *J. Phys. Chem. Ref. Data* **30**, No. 3, 735–831 (2001).
70. J.M. Hartmann, J. Taine, J. Bonamy, B. Labani, and D. Robert, *J. Chem. Phys.* **86**, No. 1, 144–156 (1987).