

O₂ Absorption Measurements and Modeling. Connection with the Troposphere Temperature

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Ground-based measurements of the A(0,0) and b(1,0) bands of the O₂ atmospheric system are carried out using a spectrometric system designed for direct solar spectrum measurements in the region 3000 – 8000 Å, with a spectral resolution of about 0.3 Å.

Theoretical modeling of the O₂ absorption is performed presuming plane-parallel atmosphere, divided into equal homogeneous parallel layers, and applying line-by-line calculations. The A and b bands intensities are computed at different altitudes and zenith angles. The comparison of the modeled spectra to the detailed measured ones shows that the absorption calculation method is reliable.

The ground-based spectrometric measurements afford opportunities to obtain information for the atmospheric parameters, including the temperature and its change with the height. Up to now methods for temperature profile retrieval using ground-based measurements have not been developed. The creation of such a method would be a contribution to the atmospheric studies because of the importance of the temperature as well as the cheaper implementation of the needed measurements. The temperature profile can be retrieved resolving the non-linear system equations for the equivalent widths of the rotational O₂ lines. Such system equations for the equivalent widths are obtained in both cases - of weak and strong absorption, they are linearized and the systems are resolved towards the temperature in the separate layers, using an iteration method. The solution stability is studied with respect to the deviation of the input initial temperature values from the real ones, as well as with respect to the error in determining the equivalent widths. The system equations are found to be ill-conditioned, and the solution is highly sensitive to the input data. In order to provide the solution stability and a better convergence, a regularization algorithm should be applied. The application limits of the weak and strong absorption equations are studied.

Introduction

The temperature is one of the main parameters, which describes the physical conditions of the atmosphere. The ground-based temperature and the vertical temperature profile are connected with the atmospheric dynamics and the climatic changes, which influence the coefficients of a number of chemical reactions in the atmosphere, the trace gases content and the solar radiation absorption. The presence of temperature profiles is necessary for the more precise determination of the atmosphere species column content from the measured spectra. To determine the temperature profile, balloon [1], satellite [2 - 8] or lidar [9] measurements are usually used, which are very expensive.

The spectrometric methods are a powerful tool for atmospheric research. They afford opportunities to obtain information both for the atmospheric species concentration and for the atmospheric processes and parameters, including the temperature. The ground-based spectrometric measurements are much cheaper than the above-mentioned ones.

This paper presents some first results of an attempt to develop a method for the temperature profile determination by ground-based spectrometric measurements. For this purpose, ground-based measurements and theoretical modeling of the A(0,0) and b(1,0) absorption bands from the O₂ atmospheric system $X^3\Sigma_g^- \rightarrow b^1\Sigma_g^-$ have been used. Up to now methods for temperature profile retrieval by using such measurements have not been reported.

Measurements and theoretical computations

The spectrometric system

Ground-based measurements of the A(0,0) and b(1,0) bands of the O₂ atmospheric system are carried out using a

spectrometric system designed for direct solar spectrum measurements in the region 3000 – 8000 Å. The first configuration of the instrument is described in detail in [10]. Since then, it has been upgraded several times. Presently, the spectrometric system consists of an objective Cassegrain type, the Jobin-Yvon monochromator HR640 type, and a CCD camera TOPICA TP-505A/3 with threshold sensitivity 0.04 Lx. The video signal is registered directly in a PC using a video card. The spectral resolution of the instrument is about 0.3 Å. In the obtained spectra the rotational lines are clearly detached and even some isotopic lines can be observed. The lines with rotational quantum numbers up to J''=27 and J''=19 from the A and b systems, respectively, are present in the detected spectra.

The A(0,0) and b(1,0) O₂ absorption bands modeling

To calculate the O₂ A- and b-band spectra, the atmosphere is treated as plane-parallel and it is divided into 50 parallel, homogeneous layers [11]. The top of the atmosphere is accepted to be at the altitude of 100 km. The line intensity is determined by the line-by-line calculations method [12].

The values of the Lorenz half width αL and the strength of the rotational line or line intensity SJ for every rotational transition under standard conditions, as well as the values of the rotational line centre wave number ν_0 and the lower state energy F'' are from the HITRAN 96 database [13]. The temperature and concentration profiles are taken from the atmospheric model U.S. Standard Atmosphere 1976. The calculations are made for the intervals 12880÷13190 cm⁻¹ and 14280÷14590 cm⁻¹, which completely cover the spectral regions of the A (0, 0) and b (1, 0) O₂ bands, respectively, with a step of 0.01 cm⁻¹. The A-band absorption turned very strong, and most P-lines are saturated already at 16 km altitude. The P-lines absorption in the b-band is much weaker.

The comparison of the modeled spectrum with a detailed measured one [14] and the computations of Mlynczack [15] and Werner et al. [16] show that this method for absorption calculation is reliable.

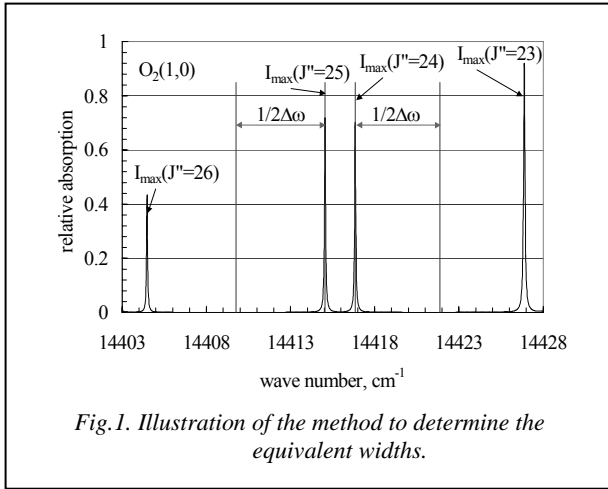


Fig.1. Illustration of the method to determine the equivalent widths.

Determining the equivalent width from the measured spectra

The equivalent width W of a given separate rotational line is defined as the width of the rectangle with height = 1 (full absorption) and with area, equal to the area over the absorption line [17]:

$$W = \int_{\text{line}} s(\nu) d\nu = \int_{\text{line}} \frac{I_{\text{cont}} - I_{\nu}}{I_{\text{cont}}} d\nu \quad (1)$$

In the measured spectra the wings of the adjacent rotational lines are superimposed. To determine the equivalent widths from the measured spectra the intensities from the line maximum to the next following minimum (Fig.1) are summed up to eliminate better the influence of the superimposed line intensities. Finally, the sums are doubled.

The computed spectra are used to evaluate the errors in the equivalent widths of the different lines, obtained as described above. The errors, due to the limitation of the summing interval and to contamination by the other lines of the same branch are examined.

The errors caused by the limitation of the summing interval, are larger for the stronger lines regions, and reach 4% and 16% for the A and b bands, respectively. The errors, due to contamination counterpoise the ones, due to the limitation of the summing interval of each line, especially in the case of strong lines, and their values strongly depend on the relative intensities of the separate lines. The resulting common errors are below 10% and 5% up to $J''=31$ for A and b bands, respectively, and abruptly increase for the weaker lines (with larger values of J'').

Thus, to use equivalent widths, produced by experimental spectra in the described way for the temperature profile retrieval, the large error values should be avoided, possibly by using a theoretical estimate.

The case of weak absorption

The equivalent width in case of weak absorption

For weak absorption, W can be expressed in terms of the optical depth τ :

$$W = \frac{1}{\mu} \int_{\text{line}} \tau(\nu) d\nu \quad (2)$$

The equivalent width W_{ki} of the k^{th} line in the i^{th} homogeneous layer is:

$$W_{ki} = \frac{1}{\mu} \int_{\text{line}} \int_{\text{layer } i} n(z) S(T, z) f(\nu) dz d\nu = \frac{N_i}{\mu} S_j^k(T_i) (z_{i+1} - z_i), \quad (3)$$

From (3) the following expression is obtained for W_{ki} :

$$W_{ki} = c_{O_2} n_i S_j^k(T_s) \frac{T_s}{T_i} \exp\left[\frac{1.439 F_k''(T_i - T_s)}{T_i T_s}\right] \Delta z_i. \quad (4)$$

c_{O_2} is the O_2 mixing ratio (constant up to 100 km), n_i - the air concentration in layer i , $S_j^k(T_s)$ and F_k'' - the intensity and the lower state energy for the rotational line k , respectively, given in the Hitran 96 database [13]. The index S denotes the standard parameters (T_s , p_s , n_s) used in the database. The equivalent width W_k of the observed rotational absorption line k is the sum of the equivalent widths W_{ki} at the separate levels i :

$$W_k = \sum_i W_{ki} = \sum_i c_{O_2} n_i S_j^k(T_s) \frac{T_s}{T_i} \exp\left[\frac{1.439 F_k''(T_i - T_s)}{T_i T_s}\right] \Delta z_i. \quad (5)$$

The system of equations for the temperature profile retrieval

According to the Newton's method, equation (5) can be linearized as follows:

$$W_k(T) = \sum_{i=1}^n W_{ki}(T_{i0}) + \sum_{i=1}^n \frac{\partial W_{ki}}{\partial T_i} \Big|_{T_i=T_{i0}} (T_i - T_{i0}), \quad (6)$$

where the values T_{i0} represent the improved temperature approximation of T_0 .

The following linearized system is obtained:

$$y_k = \sum_{i=1}^n a_{ki} (T_i - T_{i0}), \quad (7)$$

where

$$y_k = W_k - \sum_{i=1}^n c_{ki},$$

$$c_{ki} = c_{O_2} n_i S_j^k(T_s) \frac{T_s}{T_{i0}} \exp\left[\frac{1.439 F_k''(T_{i0} - T_s)}{T_{i0} T_s}\right] \Delta z_i,$$

$$a_{ki} = c_{O_2} n_i S_j^k(T_s) \frac{T_s}{T_{i0}^2} \left(\frac{1.439 F_k''}{T_{i0}} - 1 \right) \times \exp\left[\frac{1.439 F_k''(T_{i0} - T_s)}{T_{i0} T_s}\right] \Delta z_i. \quad (8)$$

The case of strong absorption

The equivalent width formula

In the case of strong absorption, the lines, broadened as a result of the pressure, should follow the square root law:

$$W \approx 2 \left(\frac{\alpha N S}{\mu} \right)^{1/2} = \frac{8\sqrt{2}}{3} (\alpha N S)^{1/2}, \quad (9)$$

where α is the line half-width with the corresponding pressure P and temperature T , N is the column density, and S is the line strength. Hence, the equivalent width W_{ki} of the k^{th} line in the i^{th} atmospheric layer is given by the formula:

$$W_{ki} = \frac{8\sqrt{2}}{3} (\alpha_{ki} N_i S_J^k(T_i) (z_{i+1} - z_i))^{1/2} \quad (10)$$

Taking into account that

$$\alpha_{ki} = \alpha_s \frac{n_i}{n_s} \left(\frac{T_i}{T_s} \right)^{1/2}, \quad (11)$$

and

$$N_i S_J^k(T_i) = c_{o_2} n_i S_J^k(T_s) \frac{T_s}{T_i} \exp\left(\frac{1.439 F_k^*(T_i - T_s)}{T_i T_s} \right), \quad (12)$$

we obtain

$$W_{ki} = \frac{8\sqrt{2}}{3} n_i \left(\frac{\alpha_s c_{o_2}}{n_s} S_J^k(T_s) \Delta z_i \right)^{1/2} \left(\frac{T_s}{T_i} \right)^{1/4} \exp\left(\frac{1.439 F_k^*(T_i - T_s)}{2 T_i T_s} \right) \quad (13)$$

The total equivalent width of the k^{th} rotational line is calculated by the expression:

$$W_k = \sum_{i=1}^n W_{ki} = \frac{8\sqrt{2}}{3} \left(\frac{\alpha_s c_{o_2}}{n_s} S_J^k(T_s) \right)^{1/2} \sum_{i=1}^n n_i (\Delta z_i)^{1/2} \left(\frac{T_s}{T_i} \right)^{1/4} \exp\left(\frac{1.439 F_k^*(T_i - T_s)}{2 T_i T_s} \right) \quad (14)$$

The system of equations for the temperature in case of strong absorption

After the linearization of (14) according to the Newton's method, a system of equations, analogous to the system of weak absorption (7) is obtained, with the following expressions for the coefficients y_k , z_{ki} and a_{ki} :

$$y_k = W_k - \sum_{i=1}^n c_{ki}, \quad (15)$$

$$c_{ki} = \frac{8\sqrt{2}}{3} n_i \left(\frac{\alpha_s c_{o_2}}{n_s} S_J^k(T_s) \Delta z_i \right)^{1/2} \left(\frac{T_s}{T_{i0}} \right)^{1/4} \exp\left(\frac{1.439 F_k^*(T_{i0} - T_s)}{2 T_{i0} T_s} \right), \quad (16)$$

$$a_{ki} = \frac{8\sqrt{2}}{3} n_i \left(\frac{\alpha_s c_{o_2}}{n_s} S_J^k(T_s) \Delta z_i \right)^{1/2} \frac{T_s^{1/4}}{T_{i0}^{5/4}} \left(\frac{1.439 F_k^*}{2 T_{i0}} - \frac{1}{4} \right) \times \exp\left(\frac{1.439 F_k^*(T_{i0} - T_s)}{2 T_{i0} T_s} \right). \quad (17)$$

Application limits of the week absorption equations

A study is carried out to determine the limits in which the absorption may be considered weak. The equivalent width can be presented in this way:

$$W_{ki} = C_i S_J \exp\left[\frac{-B_0 hc J(J+1)}{kT} \right] \quad (18)$$

where

$$C_i = c_{o_2} n_i \frac{T_s}{T_i} \Delta z_i, \quad S_J = S_J^k(T_s) \exp\left[\frac{B_0 hc J(J+1)}{kT_s} \right]. \quad (19)$$

From this formula, the following linear dependency is obtained:

$$\ln\left(\frac{W_{ki}}{S_J} \right) = \text{const} - \frac{B_0 hc}{kT_i} J(J+1). \quad (20)$$

The slope coefficient is obtained to be inversely proportional to the i^{th} layer temperature. Such dependencies are constructed for A and b bands of O₂ for 20 atmospheric layers with thickness of 5 km. Thicker layers are used to diminish the range of the system of equations in order to

make the number of equations commensurable with the maximal number of measured lines of one band. The layers in the high atmosphere are optically thin and the absorption can be considered weak. The dependencies of $\ln(W_{ki}/S_J)$ from $J(J+1)$ can be approximated with straight lines with $R^2 > 0.999$. Such results are obtained for all lines of the A band above 60 km and of the b band above 45 km in the examined 5-km layers. Below these altitudes, the strongest lines in the bands are saturated in the 5-km layers. In the ground layer, the absorption is obtained weak for the lines with $J'' > 31$ and $J'' > 25$ from A and b bands, respectively [18]. Therefore, to retrieve the temperature profile from ground-based measurements, using the weak absorption equations, the following conditions should be present: necessity to measure weak lines, with rotational quantum numbers larger than about 30 (unfortunately, our possibilities doesn't respond to this condition); fulfillment of a compensation of the large error values in the equivalent widths determined on the basis of theoretical evaluations; correct estimate of the remaining errors and application of a regularization algorithm.

Application limits of the strong absorption equations

In the case of strong absorption, the equivalent width can be presented as:

$$W_{ki} = C_i S_J^{1/2} \exp\left(-\frac{B_0 hc J(J+1)}{2kT_i} \right) \quad (21)$$

where

$$C_i = \frac{8\sqrt{2}}{3} n_i \left(\frac{\alpha_s c_{o_2}}{n_s} \Delta z_i \right)^{1/2} \left(\frac{T_s}{T_i} \right)^{1/4},$$

$$S_J^{1/2} = (S_J^k(T_s))^{1/2} \exp\left(\frac{B_0 hc J(J+1)}{2kT_s} \right). \quad (22)$$

The following approximate linear dependency is obtained, from which the layer temperature can be derived:

$$\ln\left(\frac{W_{ki}}{S_J^{1/2}} \right) = \text{const} - \frac{B_0 hc J(J+1)}{kT_i}. \quad (23)$$

Such dependences are built for A and b bands of O₂ for 21 layers with thickness of 5 km, including the atmosphere from the ground to 105 km height. The weakest band lines always follow the weak absorption law. Presence of strong absorption is admitted when two well differentiated courses of the drawn dependencies are observed, and the course of part of the stronger lines is highly linear.

In the ground layer, the absorption can be considered strong for the rotational lines with quantum numbers J of the low state up to 31 and 23, belonging to the (0,0) and (1,0) vibrational bands from the atmospheric system of O₂, respectively.

At 30 km height, in the layer of 5 km thickness, the absorption appears strong for the lines with $J < 17$ and $7 < J < 14$ from the A and b O₂ bands, respectively (Fig.2).

A study is carried out of this dependency using thicker layers in the upper atmosphere, thus obtaining more lines following the law of strong absorption (as in the highest 5-km layers, weak absorption for all lines is present).

Considering the atmosphere from 30 km to 105 km height as one layer, the absorption is obtained strong for the lines with $5 < J < 21$ and $5 < J < 15$ from the A and b bands, respectively (Fig.3).

The following results for the application limits of the strong absorption equations can be specified: layers with thickness 5 km can be used from the ground up to 30 ÷ 35 km

Conclusions

Taking into account the described results for the weak and strong absorption, it can be deduced, that the strong absorption equations system is more suitable for temperature profile retrieval by ground-based measurements. The use of thicker atmospheric layers at higher altitudes or application of a bigger zenith angle in the observations is required. The application of a regularization algorithm to solve the incorrect inverse problem is indispensable.

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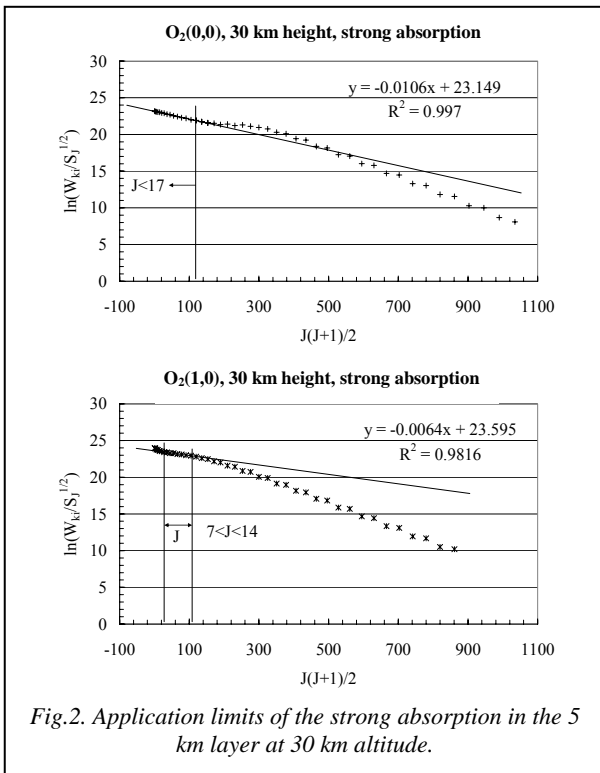


Fig.2. Application limits of the strong absorption in the 5 km layer at 30 km altitude.

height; a thicker layer of 70 ÷ 75 km must be used above this limit in order to provide the presence of strong absorption; the presence of strong absorption is more clearly expressed and a larger number of lines follows the strong absorption law in the A band than in the b band; more layers with strong absorption observed in them can be formed for the computations when using A band, whose lines are stronger than the ones of the b band; the errors in the line separation are smaller for the b band lines.

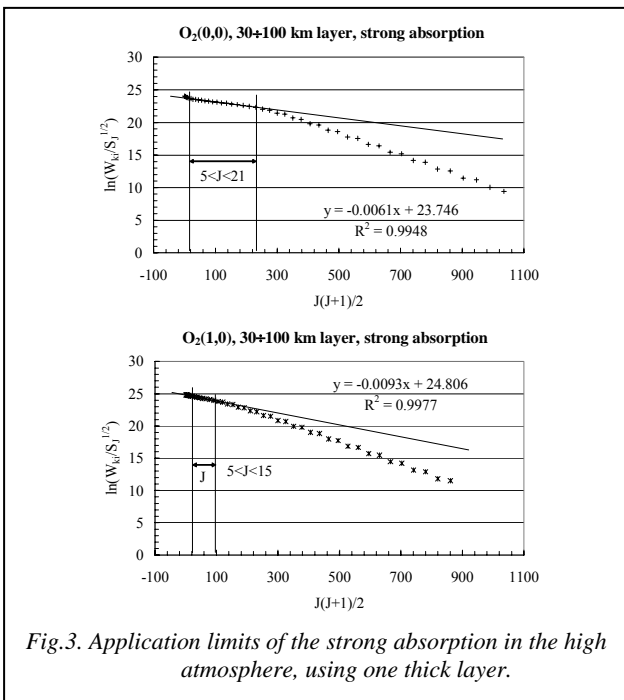


Fig.3. Application limits of the strong absorption in the high atmosphere, using one thick layer.