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Retrieval of daytime [O_3] altitude profile from measurements of 1.27 μm O_2 emission in the mesosphere: a comparison of methods

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ABSTRACT

The altitude profiles of ozone concentration are retrieved from measurements of the volume emission rate in the 1.27 μm oxygen band in the TIMED-SABER experiment. In this study we compare the methods of retrieval of daytime [O_3] altitude profile in the framework of two models: electronic-vibrational kinetics and a purely electronic kinetics of excited products of ozone and oxygen photolysis. In order to retrieve the [O_3] altitude profile from the measurements of the intensity of the O_2 band in the region of 1.27 μm correctly, it is necessary to use the photochemical model of the electronic-vibrational kinetics of excited products of ozone and oxygen photolysis in the mesosphere and lower thermosphere.

Keywords: ozone, molecular oxygen emissions, mesosphere, electronic-vibrational kinetics

1. INTRODUCTION

In the framework of the model of the electronic-vibrational kinetics of excited products of ozone and oxygen photolysis in the mesosphere and lower thermosphere (MLT) of the Earth, YM2011 [1], we consider the problem of retrieval of the [O_3] altitude profiles from the measurement of atmospheric radiation in the 1.27 μm band (formed by the transition $O_2(a^1\Delta_g, v = 0 \rightarrow X^3\Sigma_g^-, v = 0)$ in the TIMED-SABER experiment. Measuring the ozone concentration in the mesosphere and lower thermosphere is one of the most important tasks included in the TIMED satellite program, namely, the investigation of the energy balance of the MLT. The satellite has been operating successfully since 2001, and now a huge amount of data on the [O_3] altitude-latitude distribution for day and night conditions has been accumulated. In 2013, a systematic comparison of the altitude profiles of [O_3] in MLT (60 – 100 km), retrieved from measurements of the intensity of the IR emission in the two channels of the SABER experiment (1.27 μm band and ro-vibrational 9.6 μm O_3 band), and also from the data obtained from eight other satellite experiments on coordinated days and time was carried out [2]. The method of [O_3] remote sensing from measurements of the intensity of the 1.27 μm band in the SABER

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experiment is based on the O_3 and O_2 photodissociation model in the mesosphere and the lower thermosphere suggested by Mlynczak M.G., Solomon S., Zaras D.S. [3], further referred to as the MSZ model. The MSZ model considers two lower metastable levels of the O_2 molecule and the first excited level of atomic oxygen, $O(^1D)$. In addition to direct excitation of the molecules $O_2(a^1\Delta_g, v = 0)$ at photolysis of ozone in the Hartley band, collisional processes of energy transfer from the $O(^1D)$ atoms to the molecules $O_2(b^1\Sigma_g^+, v = 0)$ and further to the molecules $O_2(a^1\Delta_g, v = 0)$ with a quantum yield equal to unity were also taken into account. Besides of that, in the MSZ model, the reactions populating the $O_2(b^1\Sigma_g^+, v = 0)$ and $O_2(a^1\Delta_g, v = 0)$ levels due to the resonance absorption of solar radiation by oxygen molecules in the 762 nm and 1.27 μm bands, and the photolysis of oxygen in the Schumann-Runge band and H Lyman α line were also considered. In this study, we compare the $[O_3]$ altitude profiles retrieved in the YM2011model framework from the measurements of atmospheric radiation in the 1.27 μm band in the TIMED-SABER experiment with interpretation of the same measurements in the MSZ model framework.

2. METHODOLOGY: YM2011 – THE MODEL OF ELECTRONIC-VIBRATIONAL KINETICS OF EXCITED PRODUCTS OF OZONE AND OXYGEN PHOTOLYSIS IN THE MLT

In the YM2011 model [1] we solved the system of 45 kinetic equations for populations of electronically-vibrationally excited levels of the oxygen molecule $O_2(X^3\Sigma_g^-, v = 1 – 35)$, $O_2(a^1\Delta_g, v = 0 – 5)$, $O_2(b^1\Sigma_g^+, v = 0, 1, 2)$ and the excited oxygen atom $O(^1D)$. In this study we consider the part of YM2011 model that describes only the processes populating $O_2(b^1\Sigma_g^+, v = 0 – 2)$ and $O_2(a^1\Delta_g, v = 0 – 5)$ levels. The metastable atoms $O(^1D)$ are formed at ozone photolysis in the Hartley band (λ = 200–320 nm). As a result of aeronomical reactions, energy transfer from the $O(^1D)$ atom to the singlet excited levels $O_2(b^1\Sigma_g^+, v = 1)$ and $O_2(b^1\Sigma_g^+, v = 0)$ takes place. It should be emphasized that above the mesopause and in the lower thermosphere the main part of the $O(^1D)$ atoms is formed not from ozone, but as a result of photodissociation of O_2 molecules in the Schumann-Runge continuum (λ = 120 – 174 nm) with the quantum yield of 1.0 and in the H Lyman-α line. The resonant absorption of solar radiation in the 762, 688, 629 nm and 1.27 μm bands leads to an additional population of the electronic - vibrational levels $O_2(b^1\Sigma_g^+, v = 0, 1, 2)$ and $O_2(a^1\Delta_g, v = 0)$ correspondingly. As a result of binary collisions with O_2, the $O_2(b^1\Sigma_g^+, v>0)$ molecules lose their vibrational excitation and pass to the ground vibrational state $O_2(b^1\Sigma_g^+, v = 0)$, and only from this level the energy transfers to the $O_2(a^1\Delta_g, v = 0 – 3)$ levels. The $O_2(a^1\Delta_g, v)$ levels can be populated not only due to the energy transfer from $O_2(b^1\Sigma_g^+, v = 0)$, but also as a result of the ozone photolysis in the Hartley band with subsequent processes of vibrational relaxation. In our model we took into account about 50 aeronomical reactions of population and deexcitation of the levels under consideration, including the energy transfer and deexcitation processes in collisions with all basic atmospheric components such as $O(^3P)$, O_2, N_2, O_3, and CO_2. A database of all reaction rate constants depending on the gas temperature, with experimental errors, is given in [1]. It should be noted that the YM2011 model of kinetics of the electronical-vibrationally excited products of ozone and molecular oxygen photolysis includes the MSZ model as a special case. In the MSZ model, energy is transferred in accordance with the simplified scheme $O(^1D) \rightarrow O_2(b^1\Sigma_g^+, v = 0) \rightarrow O_2(a^1\Delta_g, v = 0)$, in which contribution of

$O_2(b^1\Sigma_g^+,\ v\geq1)$ and $O_2(a^1\Delta_g, v\geq0)$ to the population of $O_2(a^1\Delta_g, v = 0)$ is totally disregarded. In this connection, the ozone concentration values should be increased to provide the observed intensity of the 1.27 μm band.

To retrieve $[O_3]$ altitude profile one should solve the inverse problem for the altitude profiles of O_3 concentrations in the YM2011 model framework in the MLT region. In order to do it correctly we carried out the sensitivity study of the YM2011 model to all parameters (rate constants, quantum yields, kinetic temperature and other atmospheric parameters) [1]. As a result, we identified the group of proxies for $[O_3]$: $O_2(a^1\Delta_g, v = 0)$, $O_2(b^1\Sigma_g^+, v = 0)$, $O_2(b^1\Sigma_g^+, v = 1)$. The sensitivity study and analysis of uncertainties are described in details in [1]. Here we give the main definitions:

1) The sensitivity coefficient of the target function φ with respect to the variation of the parameter x_i equals to the ratio of logarithmic derivatives

$$S(\varphi; x_i) = \frac{\partial(\ln(\varphi))}{\partial(\ln(x_i))}\ , \qquad (1)$$

where φ is concentration of proxy or one of retrieved components, O_3 or $O(^3P)$, and x_i are the number densities of proxy, atmospheric components $O(^3P)$, O_2, N_2, O_3, and CO_2,, kinetic temperature, rate constants of the production or quenching reactions, and quantum yields of the products ($i = 1, 2, \ldots\ldots N$).

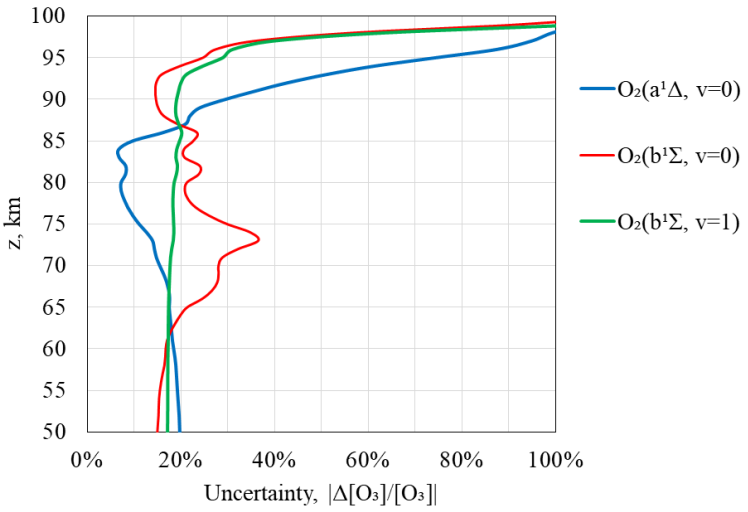

Fig. 1. The altitude profiles of the absolute value of uncertainties of $[O_3]$ retrieved in the YM2011 model framework for three proxies $O_2(a^1\Delta_g, v = 0)$, $O_2(b^1\Sigma_g^+, v = 0)$, $O_2(b^1\Sigma_g^+, v = 1)$.

2) The relative uncertainty of retrieved values of $[O_3]$ for inverse problem can be estimated from formula [1]:

$$\frac{\Delta\varphi}{\varphi} = \sqrt{\left(\sum_{i=1}^{N} \left(S(\varphi; x_i)\right)^2 \left(\frac{\Delta x_i}{x_i}\right)^2\right)} \qquad (2)$$

where $\varphi = [O_3]$, $\frac{\Delta x_i}{x_i}$ - relative error of the *i*-th parameter of the YM2011 model.

So, using the sensitivity study of the model YM2011, it is possible to calculate the uncertainties of retrieved values of $[O_3]$ depending on altitude.

3. COMPARISON OF METHODS OF THE $[O_3]$ ALTITUDE PROFILES RETRIEVALS

In this study, we present some results of analysis of the $[O_3]$ altitude profiles retrievals which we obtained in the YM2011 model framework from 100 SABER measurements of the altitude profiles of the volume emission rates in the 1.27 μm band. We compare the $[O_3]$ altitude profiles with the $[O_3]$ altitude profiles that were retrieved from the same measurements in the MSZ model framework and presented on the website of TIMED-SABER and discuss the reasons for the differences in the altitude profiles of $[O_3]$ reaching 50–70% in the region of 60 – 85 km. To compare the two models, we present the $C_{v,O3}$ profile averaged over 50 $C_{v,O3}$ profiles for 50 TIMED-SABER events during one day. Fig. 2 (a) shows $C_{v,O3}$ for the day of the vernal equinox 2010 (Day = 79, 2010, in the interval of latitudes from 74°S to 45.0°N and the interval of Solar Zenith Angles (SZA) from 38° to 80°). Fig. 3 (a) shows $C_{v,O3}$ for the day of the summer solstice 2010 (Day = 172, 2010 in the interval of latitudes from 35°N to 75.0°N and the interval of Solar Zenith Angles (SZA) from 68° to 84°). In Fig.2 (a) and Fig. 3 (a) the solid bold red curve is the $C_{v,O3}$ profile averaged over 50 $C_{v,O3}$ profiles retrieved in the YM2011 model framework for one day and the solid thin red curves denote the mean altitude profiles of uncertainties of $C_{v,O3}$ connected with uncertainties of the YM2011 photochemical model. The calculations of the mean altitude profiles of uncertainties of $C_{v,O3}$ were based on averaging the altitude profiles of uncertainties of $C_{v,O3}$ calculated for all 50 $C_{v,O3}$ profiles (formula (2) and Fig. 1) for the both days under consideration. In Figs. 2 (a) and 3 (a) the bold dashed black curve is the $C_{v,O3}$ profile averaged over 50 $C_{v,O3}$ profiles which were retrieved in the MSZ model framework for the same SABER events and presented on SABER website (V2.0, http://saber.gats-Inc.com/data.php).

As can be seen from Fig. 2 and 3, the difference between the altitude profiles of ozone concentration retrieved from the same SABER data in the framework of two models (YM2011 and MSZ) is about 50% at 60 km and reaches 100% at 90 km. The complexity of the electronic-vibrational kinetics of excited oxygen considered in the YM2011 model does not allow one to specify strictly the physical processes whose absence in the MSZ model leads to such discrepancies. Nevertheless, the analysis of the methods of $[O_3]$ retrieval based on the YM2011 and MSZ models [4] leads to the following conclusion: the main reason for the discrepancies is that the MSZ model does not take into account the electronic-vibrationally excited states of the oxygen molecule $O_2(a^1\Delta_g, v = 1 – 5)$. Note that at the peak of the cross section of the Hartley band (254 nm) all these levels are excited, whereas in the mesosphere collisional relaxation of $O_2(a^1\Delta_g, v\geq1)$ takes place without radiation losses and the energy transfer occurs from all overlying levels $O_2(a^1\Delta_g, v\geq1)$

to the lowest level $O_2(a^1\Delta_g, v = 0)$. Thus, taking into account exclusively electronic kinetics in the MSZ model framework leads to systematic errors in the retrieval of the $[O_3]$ altitude profiles from the intensity of 1.27 μm band.

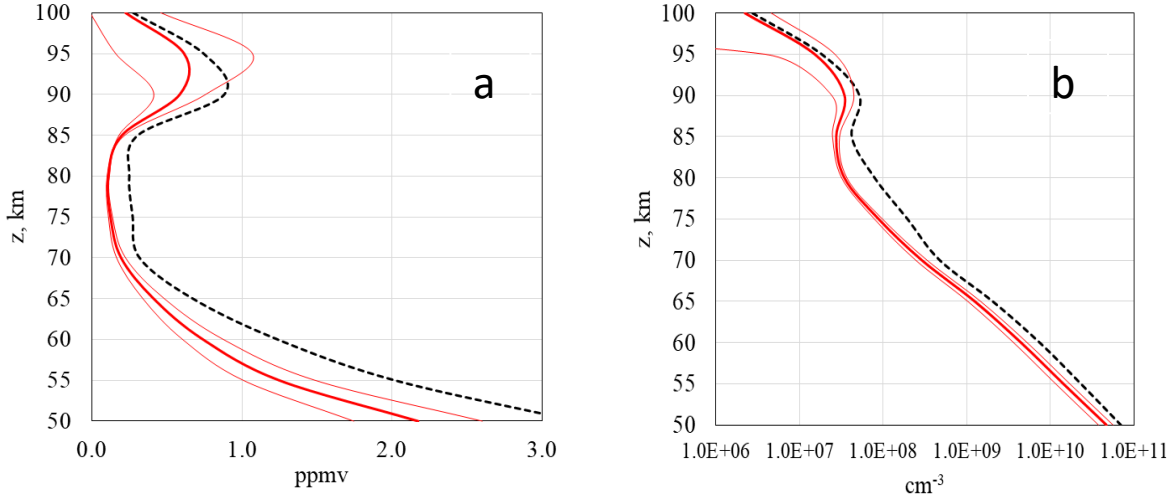

Fig. 2. The altitude profile of O_3 volume mixing ratio, $C_{v,O3}$, retrieved from SABER measurements of the volume emission rates in the 1.27 μm band formed by transition $O_2(a^1\Delta_g, v = 0 \rightarrow X^3\Sigma_g^-, v = 0)$ for the day of the vernal equinox 2010: (a) The solid bold red curve is the averaged $C_{v,O3}$ profile which was obtained in the YM2011 model framework, and the solid thin red curves denote the uncertainties of the $C_{v,O3}$ profile connected with uncertainties of the YM2011 photochemical model. The bold dashed black curve is the $C_{v,O3}$ profiles obtained in the MSZ model framework for the same SABER events. (b) The altitude profiles of O_3 number densities retrieved from the same SABER measurements. All designations and characteristics of the altitude profiles are the same as in panel (a).

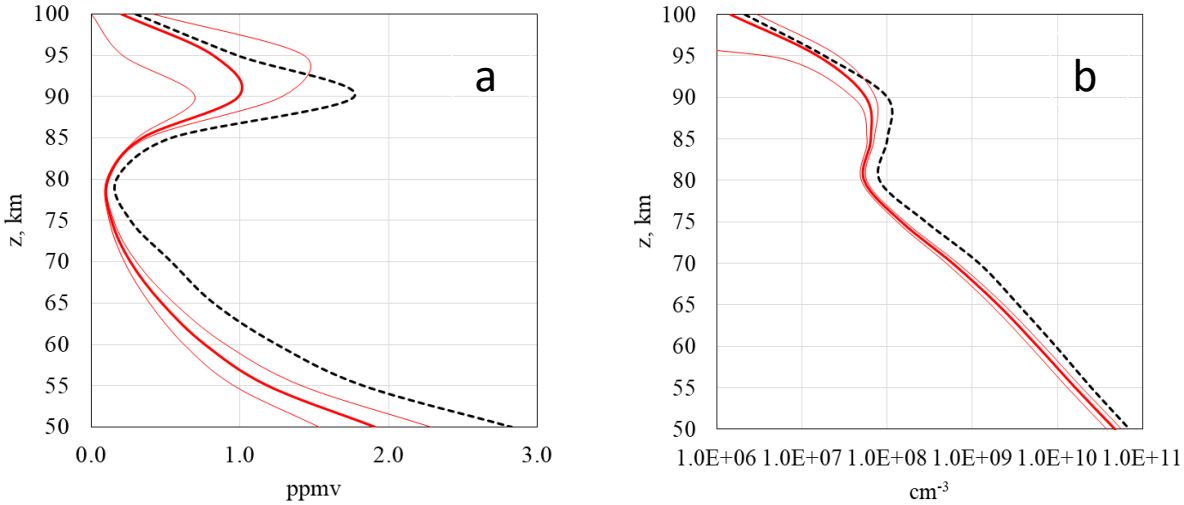

Fig. 3. The same as in Fig. 2, but for SABER measurements on the day of the summer solstice 2010.

Fig. 2 and 3 clearly demonstrate that above 85 km the measurements of the O_2 intensity in the 1.27 μm band should not be used to retrieve the [O_3] altitude profile, since the retrieval errors reach 50-70% already at 88 km (see also Fig. 1). As was shown in [1], this can be explained by the fact that above 85 km the contribution of ozone photodissociation to the formation of $O(^1D)$ sharply decreases in comparison with the contribution of O_2 photodissociation. In addition, atomic oxygen plays the role of the main quencher, for which the quenching rate constants are known with an error of more than 100% [1].

In 2013, a systematic comparison of the daytime altitude profiles of [O_3] in MLT (60 – 100 km), retrieved from measurements of the intensity of the IR emission in the two channels of the SABER experiment (1.27 μm band and ro-vibrational 9.6 μm O_3 band), and of the data from eight other satellite experiments on coordinated days and time was carried out [2]. In addition to the data of the two channels of the SABER experiment, we have selected, from [2], the daytime data (SZA ≤80°) obtained by the following instruments: High Resolution Doppler Imager (HRDI) on the UARS satellite; Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) on the Envisat satellite; the SMILES superconducting submillimeter radiometer at the International Space Station.

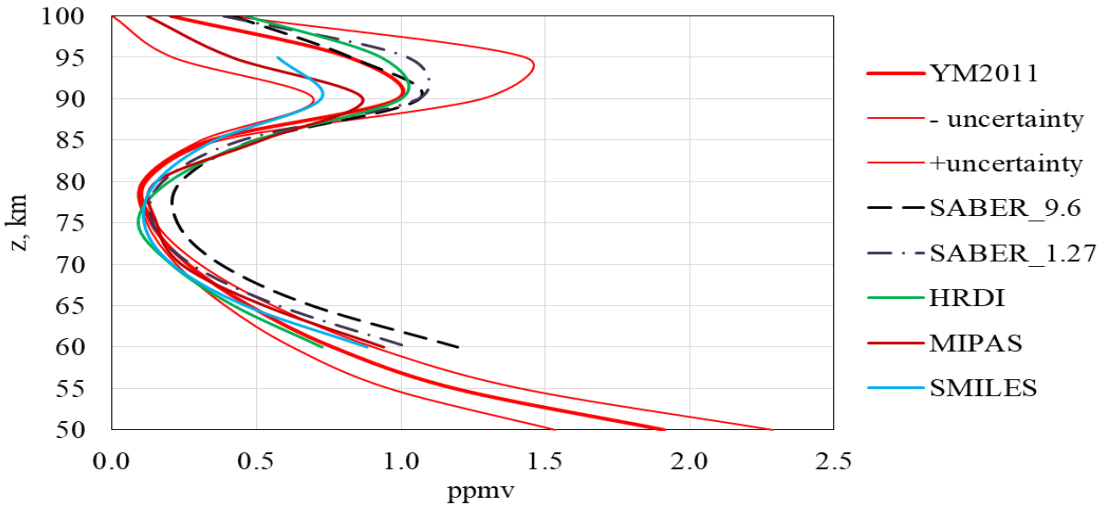

Fig. 4. The daytime altitude profile of O_3 volume mixing ratio, $C_{v,O3}$. The red curves present the same altitude profiles as in Fig. 3 (a): The bold red curve presents the mean $C_{v,O3}$ altitude profile which was obtained by averaging over 50 $C_{v,O3}$ profiles for the day of the summer solstice 2010 (Day = 172) retrieved in the YM2011 model framework from SABER measurements of the volume emission rates in the 1.27 μm band. The thin solid red curves denote the mean altitude profiles of uncertainties of $C_{v,O3}$ connected with uncertainties of the YM2011 photochemical model. For comparison, the global annual mean daytime altitude profiles $C_{v,O3}$ obtained from the measurements of HRDI (green line), MIPAS (brown line), SMILES (blue line) and from SABER in the channels 9.6 μm (black long dashed line) and 1.27 μm (black dot-dashed line) from [2] are presented.

In Fig. 4 we compare our $C_{v,O3}$ altitude profiles retrieved from 1.27 μm emission (Fig. 3 (a)) with the mean daytime $C_{v,O3}$ profiles presented in Fig. 12 [2] which were averaged over the entire period for each instrument. It is impossible to compare such different data directly, because of both the measurement techniques and those parameters on which ozone concentration depends, namely: day, local time, latitude [2]. Nevertheless, a qualitative comparison of the mean $C_{v,O3}$ altitude profile which was obtained for the day of the summer solstice 2010 in the framework of the YM2011 model from SABER measurements of the volume emission rates in the 1.27 μm band and the global annual mean daytime $C_{v,O3}$ altitude profiles obtained from measurements of HRDI, MIPAS, SMILES and of SABER in the 9.6 and 1.27 μm channels [2] reveals the most characteristic features. Within the limits of uncertainties of the photochemical model YM2011, our data for $C_{v,O3}$ are close by value to those for $C_{v,O3}$ retrieved from the data of SMILES and HRDI in the altitude range 60 – 70 km. In the same altitude range, the MIPAS data are by 20% higher than our data, and the SABER data are larger than our data in the 1.27 channel by 30 – 40% and in the 9.6 μm channel by 60 – 70%. In the range 70 – 80 km the values of $C_{v,O3}$ are close for all methods, excluding $C_{v,O3}$ retrieved from the data of SABER in the 9.6 μm channel for which the excess reaches 70 – 80%. Above 75 km the errors of all experiments increase sharply (as indicated in [2]); on the other hand, our method gives the significant increase of the mean values of the $C_{v,O3}$ uncertainty above 85 km (for proxy $O_2(a^1\Delta_g, v = 0)$ in Fig. 1). Above 80 km the values of our and SMILES $C_{v,O3}$ are smaller by magnitude than $C_{v,O3}$ retrieved from measurements of MIPAS, HRDI and of SABER in the channels 9.6 and 1.27 μm by 40 – 60%. In the altitude range of the second ozone concentration peak near 92 km, $C_{v,O3}$ retrieved from the data of both channels of SABER, HRDI and our $C_{v,O3}$ are close to each other, and $C_{v,O3}$ retrieved from the data of SMILES and MIPAS become smaller than ours by 20 – 30%. At 95 km $C_{v,O3}$ retrieved from the data of the 1.27 μm SABER channel reaches the largest values and exceeds our value of $C_{v,O3}$ by 30%.

As one can see from Fig. 2, 3 and the qualitative estimations of Fig. 4, $O_2(a^1\Delta_g, v = 0)$ can be recommended as $[O_3]$ proxy only in the interval 70-80 km. Fig.1 shows the altitude profiles of uncertainties of $[O_3]$ retrieved in the YM2011 model framework for three proxies $O_2(a^1\Delta_g, v = 0)$, $O_2(b^1\Sigma_g^+, v = 0)$, $O_2(b^1\Sigma_g^+, v = 1)$. As can be seen from Fig. 1, $O_2(b^1\Sigma_g^+, v = 1)$ is the best $[O_3]$ proxy in the whole altitude range 50 – 95 km with uncertainty of $[O_3]$ retrieval about 20%, $O_2(a^1\Delta_g, v = 0)$ is suitable as $[O_3]$ proxy not higher than 85 km. An alternative variant of proxy, $O_2(b^1\Sigma_g^+, v = 0)$, can be used, but the uncertainty of $[O_3]$ retrieval varies in the range from 15 to 37% (Fig. 1).

4. CONCLUSIONS

1. The difference between the altitude profiles of ozone concentration retrieved from the same SABER data in the framework of two models (YM2011 and MSZ) is about 50% at 60 km and can reaches 100% at 90 km. In order to retrieve the $[O_3]$ altitude profile from measurements of the volume emission rate of 1.27 μm O_2 band correctly, it is necessary to use the photochemical model of the electronic-vibrational kinetics of the excited products of oxygen and ozone photolysis in the mesosphere and lower thermosphere, as realized in the YM2011 model.
2. A qualitative comparison of the mean $C_{v,O3}$ altitude profile which was obtained for the day of the summer solstice 2010, shows that in the range 60 – 80 km the differences between the values of $C_{v,O3}$ are less than 20% for all

methods (HRDI, MIPAS, SMILES) excluding the $C_{v,O3}$ values retrieved from the data of both SABER channels, which exceed our $C_{v,O3}$ values, e. g., by 70 - 80% for the SABER 9.6 μm channel and from 0 up to 40% for the SABER 1.27 μm channel.

3. We have shown that above 85 km the measurements of the O_2 intensity in 1.27 μm band should not be used to retrieve the $[O_3]$ altitude profile, since for our method the mean values of the $C_{v,O3}$ uncertainties reach 50–70% already at 88 km. As was shown in [1], this can be explained by the fact that above 85 km the contribution of ozone photodissociation to formation of $O(^1D)$ sharply decreases in comparison with the contribution of O_2 photodissociation. In addition, atomic oxygen plays the role of the main quencher, for which the quenching rate constants are known with an error of more than 100%. The new method of $[O_3]$ altitude profile retrieval from measurements of volume emission rate in the 771 or 689 nm bands formed by transitions from $O_2(b^1\Sigma_g^+, v = 1)$ proposed by us in the framework of the YM2011I model [1, 4] enables one to retrieve the $[O_3]$ altitude profile in the altitude range 50 – 95 km (Fig. 1).

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