Oxygen dayglow emissions as proxies for atomic oxygen and ozone in the mesosphere and lower thermosphere

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ABSTRACT

The main goal of this study is to propose and then to justify a set of methods for retrieving the [O] and [O_3] altitude distributions from the observation of emissions of the excited oxygen molecules and O(^{1}D) atom at daytime in the mesosphere and lower thermosphere (MLT) region. In other words, we propose retrieving the [O] and [O_3] using the proxies. One of the main requirements for the proxy is that the measured value should be directly related to a variable of our interest while, at the same time, the influence of the proxies on [O_3] and [O(^{3}P)] should be minimal. For a comprehensive analysis of different O_3 and O(^{3}P) proxies, we use a full model of electronic vibrational kinetics of excited products of O_3 and O_2 photolysis in the MLT of the Earth. Based on this model, we have tested five excited components; namely, $O_2(b^1\Sigma_g^+, v = 0, 1, 2)$, $O_2(a^1\Delta_g, v = 0)$ and O(^{1}D) as the [O_3] and [O(^{3}P)] proxies in the MLT region. Using an analytical approach to sensitivity studies and uncertainty analysis, we have therefore developed the following methods of [O(^{3}P)] and [O_3] retrieval, which utilise electronic-vibrational transitions from the oxygen molecule second singlet level ($O_2(b^1\Sigma_g^+, v = 0, 1, 2)$). We conclude that $O_2(b^1\Sigma_g^+, v = 2)$ and $O_2(b^1\Sigma_g^+, v = 0)$ are preferable proxies for [O(^{3}P)] retrieval in the altitude range of 90–140 km, while $O_2(b^1\Sigma_g^+, v = 1)$ is the best proxy for [O_3] retrieval in the altitude range of 50–98 km.

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1. Introduction

The Earth's mesosphere and lower thermosphere (MLT) is important for its physical and chemical processes. Compared to the troposphere, this region is less accessible to observations, while its study is important for the following reasons: (1) the MLT area acts as a gateway between Earth and space, absorbing solar radiance in a number of bands in the region of 200–600 nm [1] and cooling the atmosphere in CO_2, O_3 and H_2O infrared bands (e.g. [2]); (2) the MLT area is considered to be an indicator of greenhouse gas changes and dynamics in the lower atmosphere; (3) most of the infrared satellite observations of the lower atmosphere, both in limb and even in nadir mode, are sensitive to the contribution of the MLT.

Ozone and atomic oxygen are the key components of the middle atmosphere influencing the composition and energy budget of this region in a large number of ways. In particular, atomic O concentration defines the infrared cooling of the MLT [3,4], affecting both

the temperature and height of the mesopause; that is, the stronger the cooling, the colder and higher the mesopause [5].

A comprehensive review of the [O_3] measurement methods is presented in [6]. Currently, the accepted methods for remote sensing of altitude profile of the [O(^{3}P)] in the MLT are the measurements of excited O(^{1}S) green line emission intensity above approximately 90 km and the OH(v', v'') bands intensity measurements below 95 km height, only for the nighttime [7]. For daytime, there are no reliable methods for the remote sensing of the [O(^{3}P)] altitude profile in the MLT [7].

In this study, we set out and justify the methods we set out for retrieving the [O] and [O_3] vertical distributions from the observation of emissions of the electronically–vibrationally excited oxygen molecules and O(^{1}D) atom. In other words, we propose using the proxies to retrieve the [O] and [O_3]. One of the main requirements for the proxy is that the measured value should be directly related to a variable of our interest while, at the same time, the influence of the proxies on [O_3] and [O(^{3}P)] should be minimal.

We have to stress that we are looking for the indirect methods of the [O(^{3}P)] retrieval independently from [O_3] retrieval and vice versa. For this, we introduce a concept of proxies based on our extended photochemical model. The proxies we suggest are

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supposed to allow tracking fast variations of ozone and atomic oxygen concentrations (with characteristic periods from one to tens of minutes) associated with atmospheric dynamics, solar spectrum changes, and so on. Knowing the proxies, one can retrieve [O(^{3}P)] and [O$_3$] from the emissions of electronically–vibrationally excited O$_2$ molecules in the visible and near infra-red spectral region.

The main goal of this study is to identify the optimal proxies for [O$_3$] and [O(^{3}P)] retrieval at daytime in the MLT region. For a comprehensive analysis of these proxies, we use a full model of electronic vibrational kinetics of excited products of O$_3$ and O$_2$ photolysis in the MLT of the Earth (hereafter, YM2011) [8,9]. Here, the traditional kinetics of electronically excited products of O$_3$ and O$_2$ photolysis is supplemented with the processes of energy transfer among electronically–vibrationally excited levels O$_2$(a$^1\Delta_g$, v) and O$_2$(b$^1\Sigma_g^+$, v), excited atomic oxygen O(^{1}D), and the O$_2$ molecules in the ground electronic state O$_2$(X$^3\Sigma_g^-$, v).

Based on the YM2011 model, we tested 5 excited components: O$_2$(b$^1\Sigma_g^+$, v = 0,1,2), O$_2$(a$^1\Delta_g$, v = 0) and O(^{1}D) as the proxies of [O$_3$] and [O(^{3}P)] in the MLT region. Generally speaking, each considered excited level could be a proxy of [O$_3$] and/or [O(^{3}P)], being that each of these 5 excited components depends on O$_3$ and/or O(^{3}P) both in production and in quenching.

The structure of the work is as follows. In Section 2 we present a system of electronic and vibrational levels used in the YM2011 model, which will prove necessary to our discussion. We consider all the significant aeronomical reactions of photoexcitation, radiative quenching and energy transfer processes at collisions with O(^{3}P), O$_2$, N$_2$, O$_3$ and CO$_2$. For collisional reactions, all the possible processes of energy transfer between excited levels have been taken into account, while Appendix A contains an overview of currently available kinetic data. Section 3 is an overview of the methods of [O(^{3}P)] and [O$_3$] retrieval in the MLT.

In Section 4, in the framework of YM2011 model we present the solution of forward problem for every proxy at each altitude, providing the differential kinetic equations for the afore-mentioned excited components in Appendix B. In Section 5, we show the sensitivity of five potential proxies to [O$_3$] and [O(^{3}P)] and to the other parameters of the model. We also provide the results of the sensitivity study for the inverse problem – the [O$_3$] and [O(^{3}P)] retrieval – to proxy concentrations and other parameters of the model. In association with this section, Appendix C contains the analytical formulae for sensitivity coefficients of solutions of forward and inverse problems ([O(^{3}P)] and [O$_3$] retrieval) – using, for example, [O$_2$(b$^1\Sigma_g^+$, v = 1)] as a proxy – to all parameters included in the kinetic equation for [O$_2$(b$^1\Sigma_g^+$, v = 1)].

In Sections 6 and 7 respectively, we present the estimates of photochemical lifetimes and volume emission rates (VER) for each proxy in the MLT. In Section 8, we consider the whole complex of aeronomical reactions influenced on [O(^{3}P)] and [O$_3$] altitude profiles retrieval (Section 8.1). Moreover, in Section 8.2 we discuss the choice of the optimal methods of [O(^{3}P)] and [O$_3$] retrieval for different altitude ranges. Here, we provide recommendations to the community on choosing/using the proxies and explain the optimal altitude intervals for [O$_3$] and [O(^{3}P)] retrieval from these proxies. In Section 8.3 we present the analytical formulae for [O$_3$] and [O(^{3}P)] retrieval using one of the suggested proxies; namely, O$_2$(b$^1\Sigma_g^+$, v = 1). In Section 9, we give the main conclusions of the study and, in summarising our research, provide recommendations for the practical realisation of [O$_3$] and [O(^{3}P)] altitude distribution remote sensing in MLT.

We would like to summarise briefly the new investigations and results of this study:

1. We have used the comprehensive model of electronic-vibrationally kinetics of the electronically–vibrationally excited oxygen molecules and atom O(^{1}D), (YM2011) for the first time, in order to find possible O$_3$ and O(^{3}P) proxies amongst these excited components.
2. We have compiled the experimental data on the rate coefficients of energy transfer processes among electronically–vibrationally excited levels of O$_2$ molecule, as well as quantum yields of the products of these processes, with the measured errors of these factors. In so doing, we have created the database for more than 60 reactions.
3. The model of kinetics YM2011 and the database of experimental data both enable us to work out the analytical methods of sensitivity study and uncertainty analysis for all proposed proxies.
4. These methods, in turn, enable us to work out a new approach to [O$_3$] and [O(^{3}P)] retrieval. In short, O$_2$(b$^1\Sigma_g^+$, v = 1) is the preferable proxy for the whole altitude range 50–100 km for O$_3$; for [O(^{3}P)] retrieval O$_2$(b$^1\Sigma_g^+$, v = 2) is the best proxy in the 90–140 km and the possible proxies above 95 km are O$_2$(b$^1\Sigma_g^+$, v = 0) and O$_2$(b$^1\Sigma_g^+$, v = 1).
5. In the altitude range of 90–105 km, we have worked out a method of [O$_3$] and [O(^{3}P)] altitude profiles simultaneous retrieval, which requires using both of the two proxies.
6. We have determined the restrictions inherent to traditional methods of [O$_3$] retrieval from emissions at 1.27 μm and 762 nm. These could not be made without inclusion in the model of vibrational kinetics.
7. The sensitivity study has enabled us to obtain the approximate analytical formulae for [O$_3$] and [O(^{3}P)] retrieval using proxies O$_2$(b$^1\Sigma_g^+$, v = 1).

2. Model of electronic-vibrational kinetics of the excited products of the O$_2$ and O$_3$ photodissociation in the MLT

2.1. Levels and transitions

Usually, the development of any complex kinetic model passes through a number of iterations and updates. The model of electronic-vibrational kinetics of the O$_2$ and O$_3$ photodissociation products in the MLT is not an exception. Initially, the exploratory variant was presented in [10], while the detailed description of the operative model was given in [1] (YM2006 model), which considered the populations of 35 electronic-vibrational excited states of the O$_2$ molecule and of atomic oxygen O(^{1}D). In this model, we also took into account the photolysis of O$_2$ in the Schumann–Runge continuum and Lyman-α H atom and of O$_3$ in the Hartley band.

In the new extended YM2011 model of O$_2$ and O$_3$ photodissociation in the MLT, the kinetic balance equations were considered for 45 levels: three electronic-vibrationally excited levels O$_2$(b$^1\Sigma_g^+$, $v \leqslant 2$), six levels O$_2$(a$^1\Delta_g$, $v \leqslant 5$), 35 levels O$_2$(X$^3\Sigma_g^-$, $v \leqslant 35$) and level O(^{1}D) [8,9]. Besides the O$_3$ photolysis in spectral Hartley band, we also considered the photolysis in the Chappuis, Huggins and Wulf spectral bands in the interval of 200–900 nm. These channels give rise to the O$_2$(X$^3\Sigma_g^-$, v = 1–35) vibrational levels of ground electronic state, which are then depopulated by V–V and V–T (vibrational–translational) energy exchange processes in collisions with O$_2$, N$_2$, O(^{3}P), O$_3$ and CO$_2$ molecules. The populations of all 45 states are described by the system of kinetic balance equations. Hence, in YM 2011, we have developed the method to solve it.