Estimation of uncertainties of the results of [O(³P)], [O_3] and [CO_2] retrievals in the mesosphere according to the YM2011 model by two approaches: sensitivity study and Monte Carlo method

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Highlights

- Statistical modelling.
- Estimation of the uncertainties of [O(³P)], [O_3] and [CO_2] altitude profiles retrievals.
- Comparison of two approaches: sensitivity study and Monte Carlo method.

1. Outline

The model of kinetics of excited products of O_3 and O_2 photolysis, YM2011, is designed to calculate of the concentrations of electronical-vibrationally excited components O(¹D), $O_2(b^1\Sigma^+g$, v = 0 - 2), and, also, to retrieve of the [O(³P)], [O_3] and [CO_2] in the mesosphere and lower thermosphere (MLT) region from the populations of these components. In forward problem for the all excited components under consideration, we have obtained analytical solutions for balance equations in stationary conditions. In the inverse problem we have obtained several analytical solutions for some altitude intervals using emissions from these excited molecules as individual proxy for each of the target component, [O(³P)], [O_3] and [CO_2].

To estimate the accuracy of solving the forward and inverse problems, we have performed a sensitivity analysis of both problems to the all parameters of the YM2011 model (Fig.1): rate constants, quantum yields of reaction products, rates of photodissociation, kinetic temperature, concentrations of atmospheric gases, etc. [1]. To determine the uncertainties of the calculated values of the target functions, we have used the sensitivity coefficients and the experimentally measured values of the errors of the parameters. We have carried out an alternative investigation of the uncertainties of the target function by Monte Carlo method, using experimentally measured error values for the standard deviations of each parameter.

2. Scheme of YM-2011 model of electronic vibrational kinetics of excited products of O_3 and O_2 photolysis in MLT region of the Earth

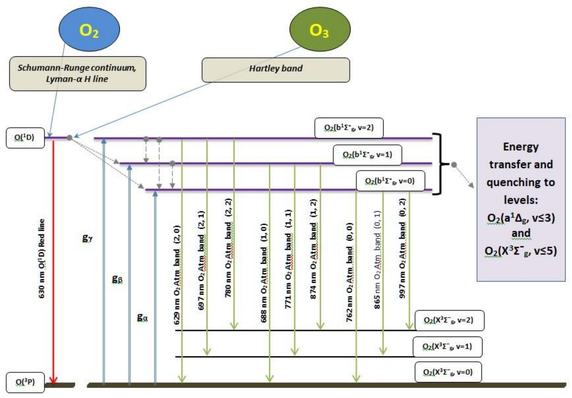

Fig.1. The scheme of electronical-vibrational kinetics of the products of O_2 and O_3 photolysis in the MLT region. Solid blue lines with downwards arrows designate the processes of O_2 and O_3 photolysis. Double blue vertical lines with the arrows pointed upwards designate the processes of solar radiation resonance absorption in the 762 nm (gα), 688 nm (gβ), 629 nm (gγ). Short dashed black inclined lines with arrows present energy transfer from O(¹D) to the $O_2(b^1\Sigma^+g$, v=0, 1) and from $O_2(b^1\Sigma^+g$, v=0 - 2) to $O_2(a^1\Delta g$, v) and $O_2(X^3\Sigma^-g$, v) at collisional quenching. Long dashed black vertical lines with downwards arrows pointed denote collisional V-V transitions. Solid colored (red, green and brown) vertical lines with arrows pointed down designate the processes of radiative emissions from electronic-vibrational levels of O_2 molecule and from excited atom O(¹D).

3. Solutions of the forward and inverse kinetic problems

In general, the kinetic equation for the concentration of excited component, x_m, looks like:

$$\partial[x_m]/\partial t = P(x_m) - [x_m]Q(x_m) \qquad (1)$$

where $P(x_m)$ – production rate of x_m. In this study x_m are O(¹D), $O_2(b^1\Sigma^+_g$, v=0, 1, 2), $Q(x_m)$ – the quenching factor of x_m :

$$Q(x_m) = (\tau_m)^{-1} + [O_2]k(x_m;O_2) + [O(^3P)]k(x_m;O(^3P)) + [O_3]k(x_m;O_3) + [N_2]k(x_m;N_2) + [CO_2]k(x_m;CO_2) \qquad (2)$$

where τ_m – the radiative lifetime of x_m component, $k(x_m; y_j)$ – the rate coefficient of the quenching reaction of component x_m in collision with the main atmospheric components y_j . In this study y_j are O_2, O(³P), N_2, O_3 and CO_2.

A full system of kinetic equations for the forward problem of determining the populations of the excited levels of the oxygen molecule is presented in [1].

In [1] we had developed the methods of retrieval of [O_3] and [O(³P)] altitude profiles in the MLT region using as proxies electronic-vibrationally excited levels of oxygen molecule, namely $O_2(b^1\Sigma^+_g$, v = 0, 1, 2). Furthermore, we had developed new method for retrieval [CO_2] from emissions of the $O_2(b^1\Sigma^+_g$, v=0) molecule. For the certain altitudes intervals we had got the analytical solutions of inverse problems.

4. Example of the inverse problem. Retrieval of [O(³P)] altitude profile using $O_2(b^1\Sigma^+_g$, v = 2) as proxy

In the altitude interval 90 - 140 km it is possible to get simple analytical expression for retrieval of [O(³P)] from solution of kinetic equation for the component $[O_2(b^1\Sigma^+_g$, v = 2)] :

$$[O(^3P)] = \frac{\frac{[O_2]g_\gamma}{[O_2(b,v=2)]} - (\tau^{-1}_{O_2(b,v=2)} + [O_2]k(O_2(b,v=2);O_2) + [N_2]k(O_2(b,v=2);N_2))}{k(O_2(b,v=2);O(^3P))} \qquad (3)$$

where [O(³P)] is the target function, $[O_2(b^1\Sigma^+_g$, v = 2)] is the information source about [O(³P)].

Formula (3) includes the YM-2011 – model's parameters each of which has its own relative error, ξ. The values of the experimental errors of all parameters presented in Table1 were taken from [1].

Let's consider the effect of parameters' relative errors on the uncertainty of retrieved [O(³P)] from (3). We have used two approaches to estimate this effect (sections 5 and 6).

Table 1. Relative errors of parameters used for retrieval of [O(³P)].

Parameter	Relative error, ξ
$k(O_2(b, v=2);O(^3P))$	0.3
$k(O_2(b, v=2);O_2)$	0.07
$k(O_2(b, v=2);N_2)$	0.4
$\tau^{-1}_{O_2(b,v=2)}$	0.1
$[O_2]$	0.01
$[N_2]$	0.01
T	0.01
g_γ	0.01

5. Sensitivity study

If the target function x_m depends on the n parameters z_i then the sensitivity coefficient of the target function to variation of parameter z_i, $S(x_m; z_i)$, is:

$$S(x_m;z_i) = \frac{z_i}{x_m}\frac{\partial x_m}{\partial z_i} \qquad (4)$$

The relative uncertainty of the target function, x_m , connects with the sensitivity coefficients, and also with the relative errors of all parameters which are included in (3), ξ_i:

$$\frac{\Delta x_m}{x_m} = \sqrt{\sum_{i=1}^{n} S^2(x_m;z_i)\xi_i^2} \qquad (5)$$

This approach is schematically presented in Fig.2 by green lines with arrows.

The results of using this approach are shown in Fig. 3a – 3e by a solid green line. It is important to notice that the sensitivity analysis for all of the expressions given below was firstly presented in [1].

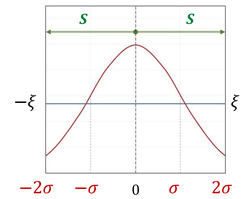

Fig.2. Two approaches to description of the experimental errors. Sensitivity study by (5) – green lines with arrows, Monte Carlo method with the uniform distribution – blue line, with the normal distribution – red line.

6. Monte Carlo method

There is no established point of view on the form of the error distribution for the value of the rate constants for the most known reactions. We have tested two error distribution functions: the uniform distribution within [–ξ, ξ] (Fig. 2, blue line) and the normal distribution, where the limits [–ξ, ξ] correspond to the limits of 2σ (Fig. 2, red line).

Given the errors of parameters, the formula (3) was transformed to

$$[O(^3P)] = \frac{\frac{[O_2]\Lambda_{O_2}g_\gamma\Lambda_{g_\gamma}}{[O_2(b,v=2)]} - \left(\tau^{-1}_{O_2(b,v=2)}\Lambda_\tau + [O_2]\Lambda_{O_2}k(O_2(b,v=2);O_2)\Lambda_{k(O_2(b,v=2);O_2)} + [N_2]\Lambda_{N_2}k(O_2(b,v=2);N_2)\Lambda_{k(O_2(b,v=2);N_2)}\right)}{k(O_2(b,v=2);O(^3P))\Lambda_{k(O_2(b,v=2);O(^3P))}} \qquad (6)$$

where $\Lambda = (1 + \xi \cdot \text{RandomValue})$, $\text{RandomValue} \in [-1; 1]$.

The results of the calculations were compared with the reference value of target function. For the reference value of target function, we have taken the values obtained by (3) (Fig. 3a).

The similar investigation was carried out for the relative uncertainties of the [O_3] and [CO_2] altitude profiles retrievals at using proxies $O_2(b^1\Sigma^+_g$, v = 0 - 2) (Fig. 3b - 3e).

7. Conclusions

- Estimations of the uncertainties of retrieval of the [O(³P)], [O_3], [CO_2] altitude profiles have been performed with various types of proxies.
- The Monte Carlo method gives values of relative uncertainties that are about 1.5 times smaller than the sensitivity study. The sensitivity study overestimates the relative uncertainty values, since it is the result of the product of the sensitivity coefficient by the absolute magnitude of the error of each parameter.
- The values of relative uncertainties calculated by the Monte Carlo method insignificantly depend on the error distribution functions (the uniform distribution or the normal distribution).

Acknowledgments

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References

[1] **Yankovsky V.A., K.V. Martyshenko, R.O. Manuilova, A.G. Feofilov**, "Oxygen dayglow emissions as proxies for atomic oxygen and ozone in the mesosphere and lower thermosphere" , J. Molecular Spectroscopy, 327, 209–231 (2016). doi:10.1016/j.jms.2016.

Results

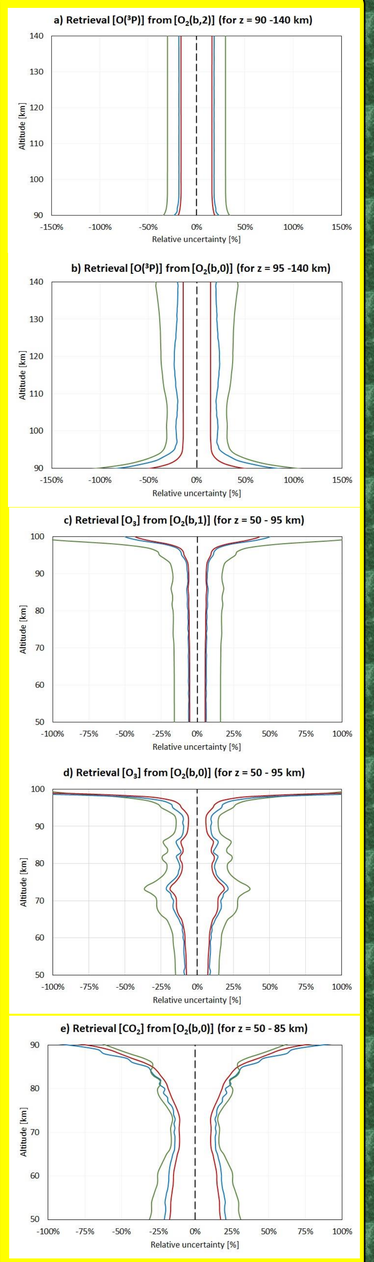

Fig.3. Estimations of the uncertainties of retrieval of the [O(³P)], [O_3] and [CO_2] altitude profiles relative to the standard altitude profiles (dashed line) calculated using two approaches: (1) sensitivity study (green line), (2) Monte Carlo method (1000 runs) for the two error distribution functions, the uniform distribution (blue line), the normal distribution (red line).