# Heating of the middle atmosphere as a result of quenching of the products of $O_2$ and $O_3$ photodissociation

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## ABSTRACT

The main product of $O_2$ photodissociation in Schumann - Runge continuum and in Ly $\alpha$ line and also $O_3$ photolysis in Hartley band is the excited atom of oxygen $O(^1D)$. Electronic energy of this metastable level is redistributed at collisional and radiative processes in various channels. The suggested by us modern photochemical model of $O_2$ and $O_3$ photodissociation in the middle atmosphere includes in consideration transfer of electronic energy of atoms $O(^1D)$ to electronic-vibrationally excited molecules $O_2(b^1\Sigma^+_g, v\leq1)$ with the subsequent transfer of energy to the molecules $O_2(a^1\Delta_g, v\leq3)$. Except for it, we took into account formation of the molecules $O_2(a^1\Delta_g, v\leq5)$ in the ozone photolysis. The energy of $O_2(a^1\Delta_g, v\leq5)$ is transferred to the molecules $O_2(a^1\Delta_g, v=0)$ and further to the $O_2(X^3\Sigma^-_g, v)$. At all stages of energy transformation the radiative and collisional losses of energy are possible thus the part of energy thermalizes. The obtained results essentially differ from the previous model of energy transfer, in which the kinetics of electronic-vibrationally excited oxygen molecules were not considered.
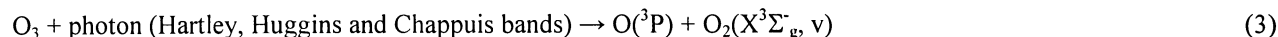
**Keywords:** electron-vibrationally excited metastable products of $O_2$ and $O_3$ photolysis, heating of the middle atmosphere

## 1. INTRODUCTION: SYNOPSIS OF THE PROBLEM

The energy budget of the mesosphere and lower thermosphere is determined by several key mechanisms of heating and cooling, including absorption of a solar radiation, IR radiation transfer, dissipation of tidal and gravity waves, thermal conduction, chemical reactions and others. In this set the photodissociation of molecular oxygen in Schumann - Runge continuum (SRC) and Lyman $\alpha$ (Ly $\alpha$) must be considered as primary

$$O_2 + photon\ (SRC,\ Ly\ \alpha) \rightarrow O(^1D) + O(^3P) \qquad (1)$$

also as the photolysis of ozone

$$O_3 + photon\ (Hartley\ band) \rightarrow O(^1D) + O_2(a^1\Delta_g, v) \qquad (2)$$

$$O_3 + photon\ (Hartley,\ Huggins\ and\ Chappuis\ bands) \rightarrow O(^3P) + O_2(X^3\Sigma^-_g, v) \qquad (3)$$

These both channels (1 and 2) should be considered simultaneously because they have an identical output product – the metastable atom $O(^1D)$, and, that is important, these channels dominate at different altitude intervals, but there is an extensive altitude range where they are essential simultaneously.

In the primary photolytic act (1) the part of energy of the absorbed quantum after process of a photodissociation of molecule $O_2$ and excitation of atom $O(^1D)$ goes into kinetic energy. "Hot" atoms $O(^1D)$ and $O(^3P)$ lose "extra-thermal" kinetic energy, practically for several collisions [1]. However the basic "reservoir" of energy intended for the subsequent thermalization is concentrated in energy of excitation of atom $O(^1D)$.

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In the other photolytic act (2, 3) all energy of the absorbed solar radiation does not go into a kinetic energy, but wholly in excitation of products of a photolysis: $O(^1D)$, $O_2(a^1\Delta_g$, v=0-5) and $O_2(X^3\Sigma^-_g$, v=0-35).

Finally efficiency of transformation of energy of the excited products of photodissociation $O_2$ and $O_3$ in kinetic energy (the process of thermalization) depends on all complex of aeronomical reactions in which these components take part.

A similar consideration were done for a long period of time. In the beginning of 70th there was an attempt to estimate heating of the atmosphere, assuming, all absorbed solar radiation heats the atmosphere [2]. From the beginning of 80th and till nowadays this frequently used assumption is that all absorbed energy goes in heating of the atmosphere except for energy of radiative quenching of $O(^1D)$ in the line of 630 nm, $O_2(b^1\Sigma^+_g$, v=0) in the band of 762 nm, $O_2(a^1\Delta_g$, v=0) in the band of 1.27 μm [3].

Table. 1. Reaction set for the task of calculation of heating of the middle atmosphere as a result of quenching of the products of $O_2$ and $O_3$ photodissociation.

1. $O(^1D) + O \rightarrow 2O$
2. $O(^1D) + O_2 \rightarrow O_2(b^1\Sigma^+_g$, v=1) + O
3. $O(^1D) + O_2 \rightarrow O_2(b^1\Sigma^+_g$, v=0) + O
4. $O(^1D) + O_2 \rightarrow O_2(X^3\Sigma^-_g$, v=0) + O
5. $O(^1D) + O_3 \rightarrow 2O_2$
6. $O(^1D) + N_2 \rightarrow O + N_2$
7. $O(^1D) + N_2 \rightarrow O + nN_2(v=1)$ (where n=1-7)
8. $O_2(b^1\Sigma^+_g$, v=2) + O $\rightarrow O_2(X^3\Sigma^-_g$, v=0) + O
9. $O_2(b^1\Sigma^+_g$, v=2) + $O_2 \rightarrow O_2(X^3\Sigma^-_g$, v=2) + $O_2(b^1\Sigma^+_g$, v=0)
10. $O_2(b^1\Sigma^+_g$, v=2) + $N_2 \rightarrow O_2(b^1\Sigma^+_g$, v=0) + $N_2$(v=1)
11. $O_2(b^1\Sigma^+_g$, v=1) + O $\rightarrow O_2(b^1\Sigma^+_g$, v=0) + O
12. $O_2(b^1\Sigma^+_g$, v=1) + $O_2 \rightarrow O_2(X^3\Sigma^-_g$, v=1) + $O_2(b^1\Sigma^+_g$, v=0)
13. $O_2(b^1\Sigma^+_g$, v=1) + $N_2 \rightarrow O_2(b^1\Sigma^+_g$, v=0) + $N_2$
14. $O_2(b^1\Sigma^+_g$, v=0) + O $\rightarrow O_2(a^1\Delta_g$, v=0) + O
15. $O_2(b^1\Sigma^+_g$, v=0) + O $\rightarrow O_2(X^3\Sigma^-_g$, v=0) + O
16. $O_2(b^1\Sigma^+_g$, v=0) + $O_2 \rightarrow O_2(a^1\Delta_g$, v=0) + $O_2(X^3\Sigma^-_g$, v=3)
17. $O_2(b^1\Sigma^+_g$, v=0) + $O_2 \rightarrow O_2(a^1\Delta_g$, v=1) + $O_2(X^3\Sigma^-_g$, v=2)
18. $O_2(b^1\Sigma^+_g$, v=0) + $O_2 \rightarrow O_2(a^1\Delta_g$, v=2) + $O_2(X^3\Sigma^-_g$, v=1)
19. $O_2(b^1\Sigma^+_g$, v=0) + $O_2 \rightarrow O_2(a^1\Delta_g$, v=3) + $O_2(X^3\Sigma^-_g$, v=0)
20. $O_2(b^1\Sigma^+_g$, v=0) + $N_2 \rightarrow O_2(a^1\Delta_g$, v=0) + $N_2$
21. $O_2(b^1\Sigma^+_g$, v=0) + $O_3 \rightarrow O_2(a^1\Delta_g$, v=0) + $O_3$
22. $O_2(b^1\Sigma^+_g$, v=0) + $O_3 \rightarrow O + 2O_2(X^3\Sigma^-_g$, v=0)

23. $O_2(b^1\Sigma^+_g$, v=0) + $CO_2 \rightarrow O_2(a^1\Delta_g$, v=0) + $CO_2$
24. $O_2(a^1\Delta_g$, v=1-5) + M $\rightarrow O_2(a^1\Delta_g$, v=0) + M (where M=$O(^3P)$, $O_2$, $N_2$)
25. $O_2(a^1\Delta_g$, v=0) + O $\rightarrow O_2(X^3\Sigma^-_g$, v=0) + O
26. $O_2(a^1\Delta_g$, v=0) + $O_2 \rightarrow O_2(X^3\Sigma^-_g$, v=5) + $O_2(X^3\Sigma^-_g$, v=0)
27. $O_2(a^1\Delta_g$, v=0) + $O_2 \rightarrow O_2(X^3\Sigma^-_g$, v=4) + $O_2(X^3\Sigma^-_g$, v=1)
28. $O_2(a^1\Delta_g$, v=0) + $O_2 \rightarrow O_2(X^3\Sigma^-_g$, v=3) + $O_2(X^3\Sigma^-_g$, v=2)
29. $O_2(a^1\Delta_g$, v=0) + $O_3 \rightarrow O_2(X^3\Sigma^-_g$, v=0) + $O_3$
30. $N_2$(v=1) + O $\rightarrow N_2$ + O
31. $N_2$(v=1) + $N_2 \rightarrow N_2 + N_2$
32. $N_2$(v=1) + $O_2 \rightarrow N_2 + O_2$
33. $N_2$(v=1) + $O_2(X^3\Sigma^-_g$, v=0) $\leftrightarrows N_2$(v=0) + $O_2(X^3\Sigma^-_g$, v=1)
34. $CO_2(v_3=1)$ + O $\rightarrow CO_2$ + O
35. $CO_2(v_3=1)$ + $N_2 \leftrightarrows CO_2 + N_2$(v=1)
36. $CO_2(v_3=1)$ + $O_2(X^3\Sigma^-_g$, v=0) $\rightarrow CO_2 + O_2(X^3\Sigma^-_g$, v=1)
37. $CO_2(v_3=1)$ + $O_2 \rightarrow CO_2 + O_2$
38. $O(^1D) \rightarrow O$ + photon(630 nm)
39. $O_2(b^1\Sigma^+_g$, v=2) $\rightarrow O_2(X^3\Sigma^-_g$, v=0) + photon (629 nm)
40. $O_2(b^1\Sigma^+_g$, v=1) $\rightarrow O_2(X^3\Sigma^-_g$, v=0) + photon (688 nm)
41. $O_2(b^1\Sigma^+_g$, v=0) $\rightarrow O_2(X^3\Sigma^-_g$, v=0) + photon (762 nm)
42. $O_2(a^1\Delta_g$, v=1) $\rightarrow O_2(X^3\Sigma^-_g$, v=0) + photon (1,06 μm)
43. $O_2(a^1\Delta_g$, v=0) $\rightarrow O_2(X^3\Sigma^-_g$, v=0) + photon (1,27 μm)

In work 4 the channel (1), and destiny $O(^1D)$ have been considered only was determined by a competition between collisions with $N_2$ (reactions 6, 7 Tables 1) and with $O_2$ (reactions 3, 4 Tables 1), and also radiative quenching $O(^1D)$ in a line of 630 nm. It has been shown, that efficiency of a thermalization varies from 100 % at altitude of 60 km (all energy of excitation $O(^1D)$ passes in kinetic energy of gas), to 76 % at altitude of 100 km and increases up to 79 % at altitude of 150 km. It is emphasized, however, that with increase altitude the opportunity of nonlocal thermalization of excitation energy grows due to dynamic processes and heat conduction. The approach in Harris [4] is based on many simplifications, but from our point of view has two basic disadvantages:

1. One channel of $O(^1D)$ formation, namely (1) though the vertical profile of number density $O(^1D)$ used in work has been compiled from the experimental and modeling data for a mesosphere and the lower thermosphere was meant only, id est is certainly, depend also on a photodissociation of ozone in the channel (2).

2. The relaxation of the products of reaction 3 Tab. 1 is completely ignored

$$O(^1D) + O_2 \rightarrow O_2(b^1\Sigma_g^+, v) + O(^3P),$$
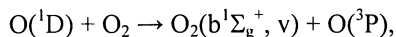
so the mechanism of a thermalization of energy of molecules $O_2(b^1\Sigma_g^+)$ was not considered.

The following stage in a problem of an estimation of efficiency of atmospheric heating due to photolysis $O_2$ and $O_3$, was done in Mlynczak et al [5-8], where the new model of the ozone photodissociation was developed.

In this model not only the direct excitation of the $O_2(a^1\Delta_g)$ molecules in the ozone photolysis, was considered but also the collisional processes of energy transfer from the $O(^1D)$ atoms to the $O_2(b^1\Sigma_g,^+)$ molecules and then to the $O_2(a^1\Delta_g)$ molecules were included.

This lengthening of a chain of reactions of transfer of energy from one metastable component to another

$$O(^1D) \rightarrow O_2(b^1\Sigma_g^+, v=0) \rightarrow O_2(a^1\Delta_g, v=0) \rightarrow O_2(X^3\Sigma_g^-, v=0) \qquad (4)$$
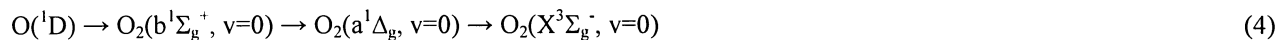
results in increase of the effective time of existence of the "inhibited" energy of the metastable components.

In model of $O_3$ photodissociation in the atmosphere Mlynczak et al [6] the singlet channel (2) has been taken into account, and it was supposed, that molecules $O_2(b^1\Sigma_g^+)$ and $O_2(a^1\Delta_g)$ are formed without vibrational excitation. An addition $O_2(a^1\Delta_g)$ - one more intermediate component in the process of transfer of energy (4) results in essential reduction of the energy going on a thermalization, because of radiating losses of molecule $O_2(a^1\Delta_g)$. In the analysis of the atmospheric heating Mlynczak considered mainly mesosphere in contrary with Harris [4].

From our point of view this approach also is not consecutive, because Mlynczak et al does not take into account:
   a) the triplet channel (3) of the ozone photodissociation, which has quantum yield about 0.1;
   b) the fact that main part of molecules $O_2(a^1\Delta_g)$ in the singlet channel (2) is formed in the highly vibrational-excited state;
   c) the vibrational excitation of molecules $O_2(b^1\Sigma_g^+)$, forming in reaction 3, 39, 40 from Table 1.

## 2. THE MODEL OF A THERMALIZATION PROPOSED IN THE GIVEN WORK. RESULTS

We presented [9] the new self-consistent model of photodissociation $O_2$ and $O_3$, added by processes of energy transfer between electronic-vibrationally excited states of the molecules of oxygen $O_2(a^1\Delta_g, v\geq1)$, $O_2(b^1\Sigma_g^+, v\geq1)$ and the molecules of oxygen in ground electronic state $O_2(X^3\Sigma_g^-, v\geq1)$.

The scheme of the chemical processes of formation and loss of the oxygen molecules in singlet metastable states $O_2(a^1\Delta_g, v)$ and $O_2(b^1\Sigma^+_g, v)$, under our consideration is presented in Fig.1.

The model gives the opportunity to calculate not only vertical profiles of number density $O_2(a^1\Delta_g, v=0)$ and $O_2(b^1\Sigma_g^+, v=0)$, but also the profiles of $[O_2(b^1\Sigma_g^+, v=0, 1, 2)]$, $[O_2(a^1\Delta_g, v=1 - 5)]$ and $[O_2(X^3\Sigma_g^-, v=1-35)]$. As was shown in [9], at some altitudes the consideration of the vibrational-electronic kinetics changes the calculated concentrations of the

metastable oxygen molecules by 30% and even more [9].

In the presented study, using this model of photodissociation $O_2$ and $O_3$, we have calculated efficiency of a thermalization of energy for all set above mentioned electronical-vibrational products of photodissociation $O_2$ and $O_3$.
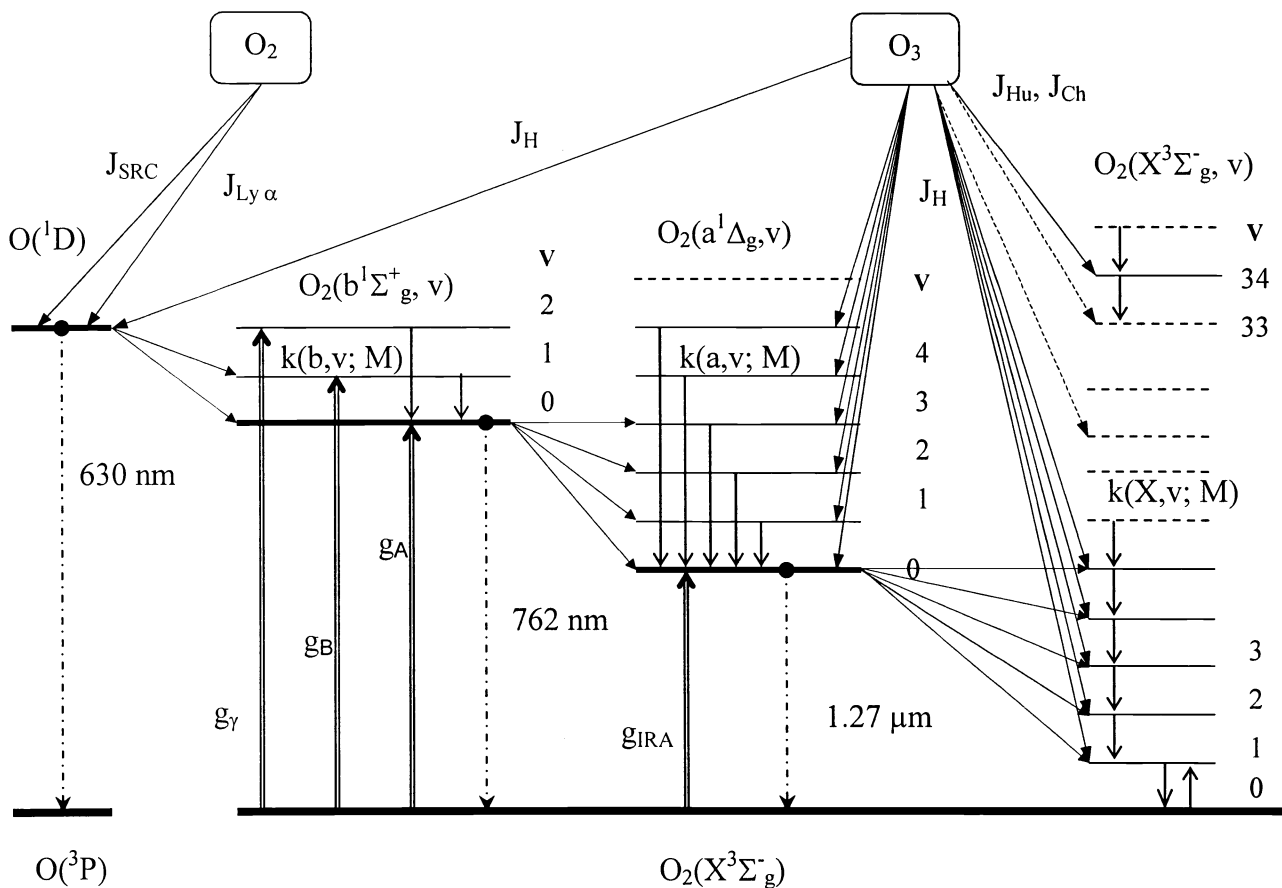


Fig.1. Scheme of the processes for calculation of number densities of $O(^1D)$, $O_2(b^1\Sigma^+_g$, v=0-2), $O_2(a^1\Delta_g$,v=0-5), $O_2(X^3\Sigma^-_g$, v=1-35) in the middle atmosphere.

Basic difference of our calculation (we name our model - "multi-level model" in difference from "two-level" approach, using only two electronically-excited levels $O_2(b^1\Sigma^+_g$, v=0) and $O_2(a^1\Delta_g$, v=0) without vibrational excitation, that were realized in works Mlynczak et al [4-8]) from all previous consists in detailed consideration of transformation of energy $O(^1D)$ not only in primary reactions (1 - 7) Tab. 1, but also and in all subsequent reactions (8 - 29) Tab. 1.

Results of redistribution of primary energy $O(^1D)$ in channels of thermalization and excitation of metastable molecules of oxygen are calculated for the our model in the altitude range 60 – 120 km with step 5 km. The calculations were made with using the computer codes and RateConstantsDataBase (RCDB), developed by Yankovsky V. A. with participation Kuleshova V. A. and Semenov A. O. (St. Petersburg State University). In Fig. 2 the results of redistribution of primary energy $O(^1D)$ in significant channels of thermalization and excitation of metastable molecules of oxygen are presented for altitude 90 km. At calculations the standard model of atmosphere is used for the following conditions: average

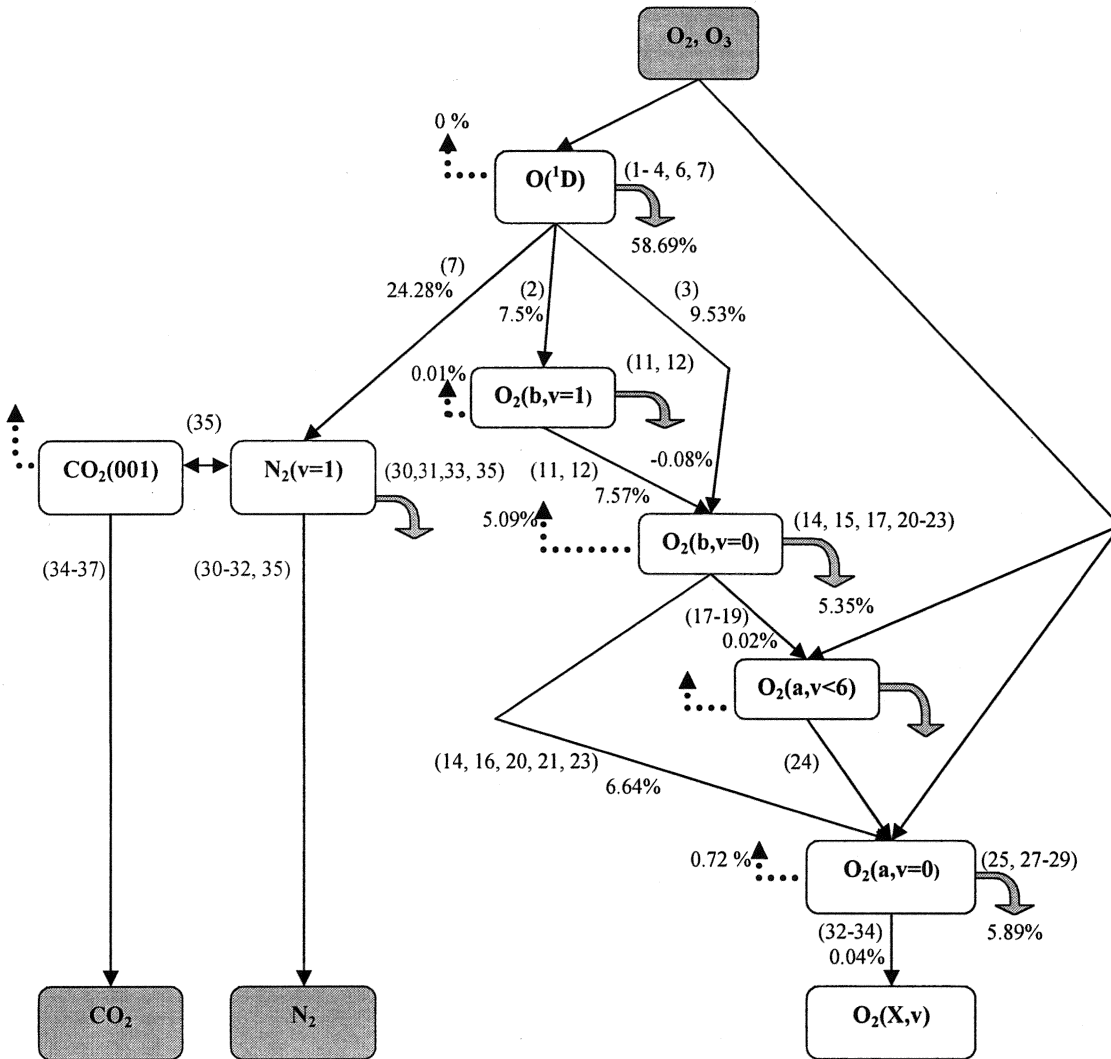latitudes, an equinox, midday, average solar and magnetic activity (MSIS90 with additions).



Fig. 2. Scheme of transformation of $O(^1D)$ energy in the different channels of $O_2$ and $O_3$ photodissociation calculated in percent of initial $O(^1D)$ energy for 90 km. The numbers of reactions from Table 1 are shown in brackets. Solid lines – channels of energy transfer in correspondence with Fig.1, dotted lines – losses of energy in radiative processes, shaded arrows – thermalized energy.

In Fig. 3 comparison of total efficiency of thermalization of $O(^1D)$ energy is given within the framework of the given model, and also within the frameworks of the models offered of Harris [4] and Mlynczak [6]. In the same figure the "overstated" estimation of efficiency of thermalization of $O(^1D)$ energy is shown when all energy of sunlight quanta goes in thermalization except for radiative deexcitation of $O(^1D)$, $O_2(b^1\Sigma_g^+, v=0)$ and $O_2(a^1\Delta_g, v=0)$.
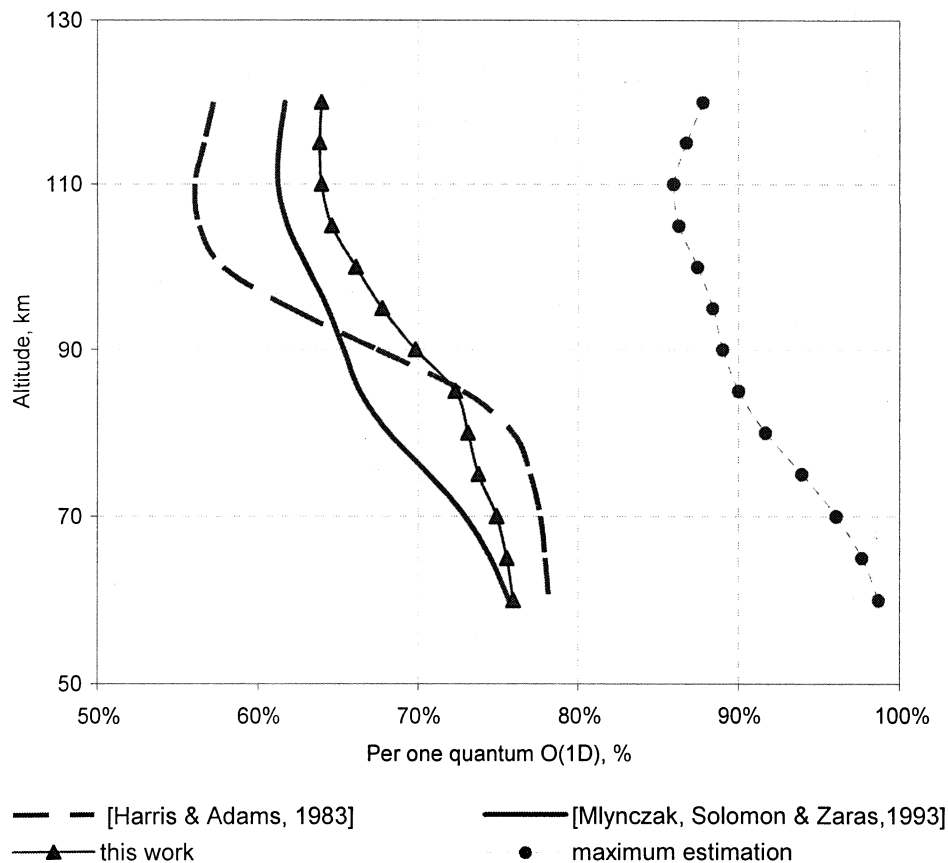
Fig. 3.   The total efficiency of O($^1$D) energy thermalization calculated with using different models (see text).

## 3. CONCLUSIONS

Taking into account electron-vibrationally excited products of $O_3$ and $O_2$ photodissociation leads to essential differences between the obtained results and results obtained from the previous "two-level" models of energy transfer (as it is shown in Fig. 3) . Using simplified approach ("maximum estimation" in Fig. 3) for calculation of energetic balance of the atmosphere could lead to significant errors in the estimation of heating rate due to processes of $O_3$ and $O_2$ photolysis.

## ACKNOWLEDGMENTS

## REFERENCES

1.   Matsumi Y., Chowdhury A.M.S., *Translational relaxation and electronic quenching of hot O($^1$D) by collisions with $N_2$*. J. Chem. Ph., V.104, N.18,P. 7036-7044, 1996

2.   Park J.H., London J., *Ozone photochemistry and radiative heating of the middle atmosphere*. J. Atmos. Sci., V.31, P.1898-1916,1974

3.  Torr M.T., Torr D.G., *The role of metastable species in the thermosphere.* Rev. Geoph. Spa. Ph., V.20, N.1, P.91-114, 1982

4.  Harris R.D., Adams G.W., *Where does the O($^1$D) energy go?* J. Geoph. Res. A, V.88, N.A6, P.4918-4928, 1983

5.  Mlynczak M.G., Solomon S.C., *On the efficiency of Solar heating in the middle atmosphere.* Geoph. Res. Let., V.18, N.7, P.1201-1204, 1991

6.  Mlynczak M.G., Solomon S.C., Zaras D.S., *An updated model for $O_2(a^1\Delta_g)$ concentrations in the mesosphere and lower mesosphere and implications for remote sensing of ozone at 1.27 mkm.* J. Geoph. Res. D, V.98, N.D10, P.18639-18648, 1993

7.  Mlynczak M.G., Olander D.S., *On the utility of the molecular oxygen dayglow emissions as proxies for middle atmospheric ozone.* Geoph. Res. Let., V.22, N.11, P.1377-1380, 1995

8.  Mlynczak M.G., Marshall B.T., *A reexamination of the role of solar heating in the $O_2$ atmospheric and infrared atmospheric bands.* Geoph. Res. Let., V.23, N.6, P.657-660, 1996

9.  Yankovskii V.A. and Manuilova R.O., *New self - consistent model of daytime emissions of $O_2(a^1\Delta_g, v \geq 0)$ and $O_2(b^1\Sigma_g^+, v=0, 1, 2)$ in the middle atmosphere. Retrieval of vertical ozone profile from the measured intensity profiles of these emissions.* Atmos. Oceanic Opt., V.16, No.7, 2003