

The effect of atmospheric temperature on the calculations of the intensity of oxygen emissions in the framework of the Barth' mechanism: sensitivity study

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Abstract

In the nightglow of the atmosphere in the altitude range of 90–105 km, the Barth' mechanism is the dominant mechanism of excitation of oxygen emissions. The source of oxygen emissions in this altitude range is the three-body reaction of the association of oxygen atoms. The rate coefficient of this reaction, as well as the collision quenching rate coefficients of the excited oxygen components $O(^1S)$, $O_2(b^1\Sigma_g^+)$, $O_2(a^1\Delta_g)$ depend on the kinetic temperature of the gas. The method of sensitivity analysis for complex photochemical systems developed in (Yankovsky et al., 2016) allows one to comprehensively consider the temperature dependence of the processes of excitation and quenching for each excited component. Analytical expressions will be obtained for the sensitivity coefficients of the intensities of these emissions depending on temperature and altitude.

Introduction.

In the nightglow of the atmosphere in the altitude range of 90–105 km, the Barth' mechanism is the dominant mechanism of excitation of oxygen emissions (Krasnopolsky, 2011). The source of oxygen emissions in this altitude range is the three-body reaction of the association of oxygen atoms



The rate coefficient of this reaction, as well as the collision quenching rate coefficients of the excited oxygen components such as atoms $O(^1S)$ or $O(^1D)$, and both molecules $O_2(b^1\Sigma_g^+)$ and $O_2(a^1\Delta_g)$ etc. depend on the kinetic temperature of the gas.

For example, the rate coefficient of the reaction (1) has strong dependence on temperature

$$k(O; O; M) = (4.7 \pm 0.4) \cdot 10^{-33} \cdot (T/300)^{-2} \text{ cm}^6\text{s}^{-1} \quad (2)$$

In the reaction (1), in the general case, any O_2 electronic states can form at different states: $^5\pi_g$, $A^3\Sigma_u^+$, $A'^3\Delta_u$, $c^1\Sigma_u^+$, $b^1\Sigma_g^+$, $a^1\Delta_g$, $X^3\Sigma_g^-$. All of them are below the dissociation threshold of the oxygen molecule. The rate coefficients of these states production as a function of the kinetic temperature were calculated by Wraight in 1982 (Fig. 1, left panel).

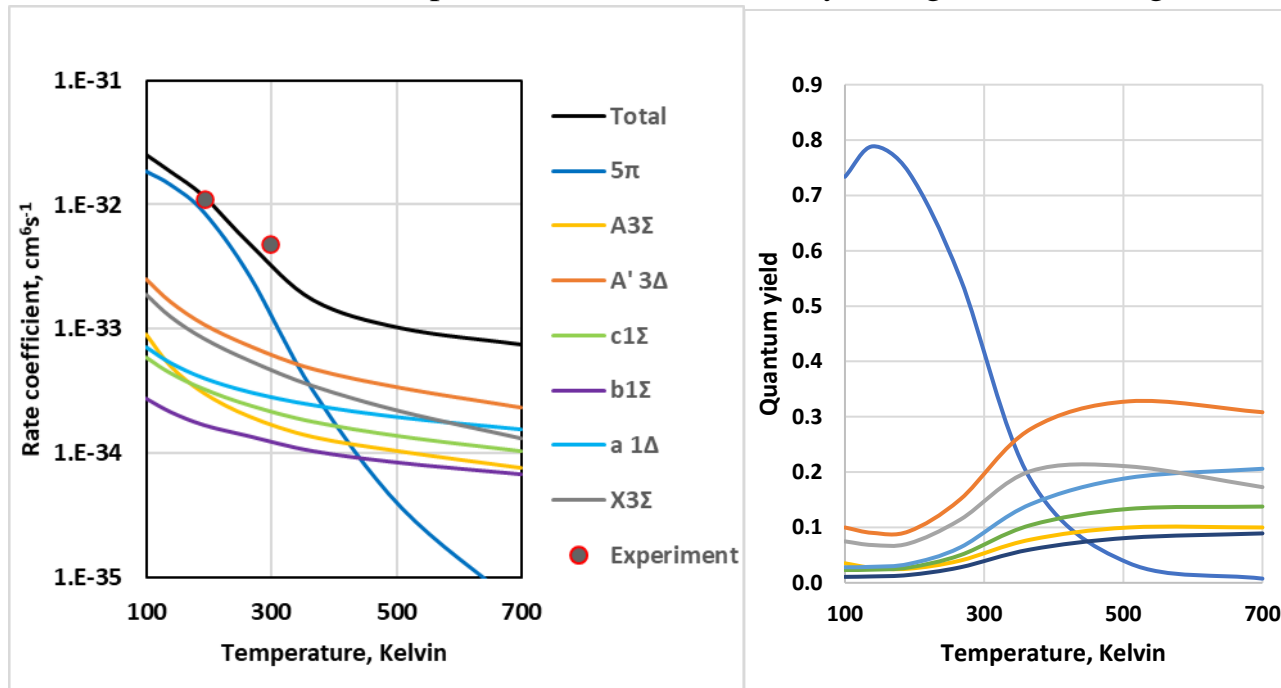


Fig. 1. Left panel - rate coefficients of O_2 electronic states production in the three-body reaction of the association of oxygen atoms (1) depending on the temperature (Wraight, 1982). Right panel - quantum yields of these electronic states based on data from left panel according to the expression (3).

In practice, in most works, the authors use the total rate coefficient (2) and the quantum yields of the products of this reaction. The fixed values of the quantum yields are estimated based on (Wraight, 1982 and Smith, 1984) for the temperature of about 200 K. However, following these works, the quantum yields have a significant temperature dependence. In the right panel of Fig. 1, we present these dependencies calculated on formulae

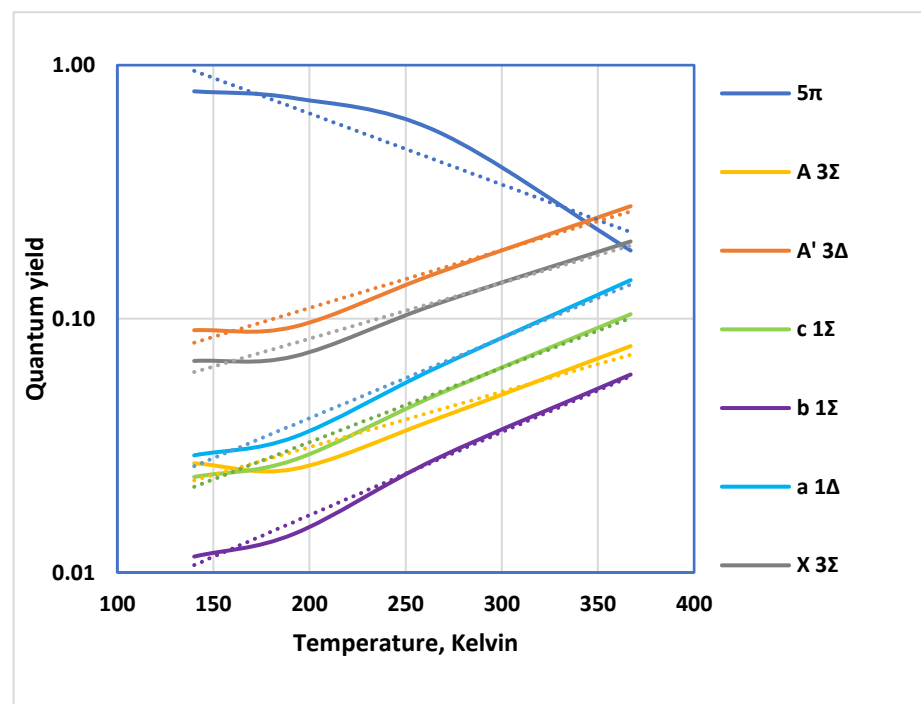
$$F(O_2(\text{precursor})) = \frac{k(O; O; M \rightarrow \text{precursor})}{k(O; O; M \rightarrow \text{Total})} \quad (3)$$

For analytical description of the temperature dependence in the range $T = 140\text{--}370$ K of these quantum yields, we use exponential trends of the next form (see Fig. 2 and Table 1 in full version of paper).

$$F(O_2(\text{precursor})) = \omega \cdot \exp\left(\frac{T}{\theta}\right) \quad (4)$$

This temperature range is chosen by us because the Barth' mechanism dominates at night only in the altitude range 85–110 km.

Fig. 2. Quantum yields of the O_2 electronic states in Barth' reaction (solid lines) and their trends in the temperature range of 140–370 K (dotted lines, see (4) and Table 1).

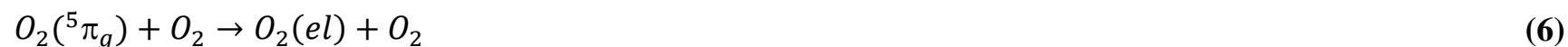


Simultaneous dependence of the rate of the reaction (1) and the quantum yields of the products of this reaction on temperature lead to a significant complication of modeling the Barth' mechanism.

Barth' mechanism fundamentals

The Barth' mechanism includes both direct excitation of an arbitrary electronic level of an oxygen molecule in the reaction (1) and a two-stage formation process of electronical states $O_2(el)$: $A^3\Sigma_u^+$, $A'^3\Delta_u$, $c^1\Sigma_u^+$, $b^1\Sigma_g^+$, $a^1\Delta_g$, $X^3\Sigma_g^-$. The efficiency of a direct one-step process is described by the quantum yield $F(O_2(el))$ (see (3) and Fig. 1, as well as Table 1). The second two-step channel is implemented in two stages. First, the precursor is excited in the reaction (1). This precursor of all $O_2(el)$ is the oxygen molecule $O_2(^5\pi_g)$, which has an excitation threshold just a few hundredths of electron-Volt below the O_2 dissociation threshold of 5.12 eV.

The spin quantum number of this level is 2 and optical transitions to the lower singlet and triplet levels are forbidden from it, therefore, at the second stage of this channel, energy transfers from this level to the lower levels, as it is believed, as a result of collisions with oxygen molecules



Rate coefficient of this reaction is $k(O_2(^5\pi_g); O_2)$ and quantum yield of the $O_2(el)$ production in (6) we denote as $\varphi(^5\pi_g \rightarrow el)$.

So, taking into account (6), the balance equation for the formation of $O_2(el)$ in the two channel Barth' mechanism will be as follows

$$[O_2(el)] = \frac{[O]^2[M] \cdot k(O; O; M)}{Q(O_2(el))} \cdot \left\{ F(O_2(el)) + \frac{\varphi(^5\pi_g \rightarrow el) \cdot F(O_2(^5\pi_g))}{1 + \frac{[O] \cdot k(O_2(^5\pi_g); O)}{[O_2] \cdot k(O_2(^5\pi_g); O_2)}} \right\} \quad (7)$$

In (7) the $O_2(el)$ quenching factor equals to $Q(O_2(el)) = \tau_{el}^{-1} + [O_2] \cdot k(O_2(el); O_2) + [O] \cdot k(O_2(el); O) + [N_2] \cdot k(O_2(el); N_2)$ and τ_{el} is the radiative lifetime of the O_2 excited level. As our analysis in (Yankovsky & Manuilova, 2018)) showed, quenching of the excited O_2 levels in collisions with other components of the atmosphere in the altitude range of 80–120 km is not effective. For analytical description of rate coefficient depending on temperature we use standard Arrhenius form (see details in Yankovsky and Manuilova, 2018).

Sensitivity study

The sensitivity coefficient responsible for the dependence of the concentration of the excited component on the gas temperature (see Yankovsky et al., 2016)

$$S(O_2(el); T) = \frac{T}{[O_2(el)]} \cdot \frac{\partial [O_2(el)]}{\partial T} \quad (9)$$

Using the definition expression (9) and the solution formulae (7), we constructed **the sensitivity coefficient for the Barth' two-channel mechanism:**

$$S(O_2(el); T) = \frac{\left\{ \left(\frac{T}{\vartheta(el)} - 2 \right) F(O_2(el)) + \frac{\varphi(^5\pi_g \rightarrow el) F(O_2(^5\pi_g))}{1 + \frac{[O] \cdot k(O_2(^5\pi_g); O)}{[O_2] \cdot k(O_2(^5\pi_g); O_2)}} \left(\frac{T}{\vartheta(^5\pi_g)} - 2 \right) \right\}}{F(O_2(el)) + \frac{\varphi(^5\pi_g \rightarrow el) \cdot F(O_2(^5\pi_g))}{1 + \frac{[O] \cdot k(O_2(^5\pi_g); O)}{[O_2] \cdot k(O_2(^5\pi_g); O_2)}}} \quad (10)$$

The formulae (10) is correct for the temperature range 140–370 K.

Discussion and Conclusions

If the quantum outputs of the precursor were independent of temperature (i. e., all values of θ from (4) of Fig. 1 tend to infinity), we would get the obvious result from (10), $S(O_2(el); T) = -2$. The temperature coefficient of the triple reaction of the association of oxygen atoms, (1), has just such a temperature dependence.

Next, we consider the results of two rocket experiments, ETON and WADIS2, in which the altitude profile of the concentration of $O_2(b^1\Sigma_g^+)$ was measured and modeled in the framework of the Barth' mechanism. Taking into account the temperature dependence of the precursor quantum yields in reaction (1), the altitude profile of the concentration of $O_2(b^1\Sigma_g^+)$ in the altitude range 85 - 110 km depends on temperature much more than the reaction of the association of oxygen atoms (see Table 2). Approximately this relationship can be described as $[O_2(b^1\Sigma_g^+)] \propto T^{-3}$.

Table 2. Sensitivity of the $[O_2(b^1\Sigma_g^+)]$ altitude profile depending on variation of the temperature for nightglow experiments.

Reference	McDade et al., 1986	Grygalashvyly et al., 2019	
Altitude profile of $[O(^3P)]$ from	MSISE	MSISE	WADIS2
$\varphi(^5\pi_g \rightarrow b^1\Sigma_g^+) \cdot F(O_2(^5\pi_g))$	0.15	0.08	
$k(O_2(^5\pi_g); O)/k(O_2(^5\pi_g); O_2)$	2.9	0.23	
$S(O_2(b^1\Sigma_g^+); T)$	- (2.42 – 3.11)	- (2.72–2.80)	- (2.74–2.81)

Acknowledgments

The author is incredibly grateful to Ekaterina Vorobeva for discussing the results of this work.

This work was supported by the Russian Foundation for Basic Research (grant RFBR No. 20-05-00450 A).

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