# QUALITATIVE ANALYSIS OF OXYGEN ATMOSPHERIC MODEL. 1. SMALL SOURCE AND SINK APPROXIMATION

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The steady state of the oxygen atmosphere is shown to be extremely sensitive to the presence of small sources and sinks, except in a narrow region of source and sink parameters at a sink rate well below that of the photochemical molecular oxygen dissociation where only minor deviations from the equilibrium concentrations of ozone and atomic and molecular oxygen are likely to occur.

#### 1. INTRODUCTION

The currently available experimental data on the variations in the stratospheric ozone concentration measured in different geographical areas in recent years<sup>1</sup> have provided ample material for comparison with numerical calculations and theoretical generalizations. These should be preceded, in our view, by qualitative analysis of the relevant system of equations for concentrations of oxygen□containing constituents. Since qualitative analysis is common for sets of equations, in the atmospheric photochemistry it is, in fact, performed for a pure oxygen atmospheric model.<sup>2-4</sup>

If anthropogenic and natural impacts on the atomic oxygen and ozone content in the atmosphere are to be taken into account it is necessary to consider additional chemical reactions between oxygen particles (O,  $O_2$ ,  $O_3$ ) and those of other species that can be approximated by introducing extra sources and sinks into the system of equations for the oxygen atmosphere. In the present paper qualitative changes in the oxygen particle concentrations are examined using the oxygen atmospheric model within the framework of the small source and sink approximation.

Section 2 gives chemical reactions accounted for in analysis of the steady state of the atmosphere and the hierarchy of dimensionless parameters. Sections 3 and 4 describe a basic system of equations and its steady state (standard) solution. Section 5 is concerned with the effect of small sources and sinks on the deviation of the steady state oxygen atmosphere from the standard solution.

## 2. OXYGEN ATMOSPHERE

The number of chemical atmospheric reactions involving oxygen particles is fairly large. However, introducing the concept of the oxygen atmosphere we pick out of this diversity the reactions involving oxygen particles alone or oxygen particles and nitrogen molecules, as well as photochemical processes responsible for destruction of ozone and molecular oxygen. Within the set of reactions chosen we will restrict our consideration to those involving no more than three particles. Reactions of this sort are listed in Table I. The rate constants are given at 30 km altitude and references are made to the papers from which the data are cited. Also included in Table I are the dimensionless quantities

 $\xi_i$  that provide an insight into the hierarchy of the terms involved in the equations of interest. Coefficients of the basic equations defining dynamics of chemical processes in the oxygen atmosphere are linear combinations of the quantities  $\xi_i$ . The oxygen atmospheric model together with all reactions enumerated in Table I will provide a basis for the development below.

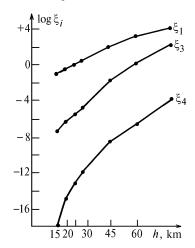


FIG. 1. Values of  $\xi_i$  (i = 1, 3, and 4) vs height in the atmosphere.

The rates of chemical reactions essentially depend on the temperature, the latter being a function of the height in the atmosphere. With these relationships in mind we have calculated the variation of the dimensionless quantities  $\xi_1$ ,  $\xi_3$  and  $\xi_4$  with the height using the data from Ref. 5 as the base. As can be seen from Fig. 1 and Table I, the following inequalities between these quantities are valid at all the heights of interest:

$$\xi_1, \ \xi_2, \ \xi_8, \ \xi_9, \ \xi_{10}, \ \xi_{11} > \xi_3 > \xi_4 > \xi_5, \ \xi_6, \ \xi_7$$
 (1)

where  $\xi_2$ , and  $\xi_5 - \xi_{11}$  are essentially independent of the height, which means that the conclusions to emerge from the qualitative analysis of the oxygen atmospheric model hold good for the 15–80 km range, to say the least.

Our consideration of the oxygen atmospheric model will be restricted to analysis of the steady state found in the neighbourhood of equilibrium concentrations of oxygen particles under natural conditions.

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TABLE I. Basic reactions involved in the oxygen atmosphere ( $H=30~\mathrm{km}$ ).

## 3. BASIC SYSTEM OF EQUATIONS

Let x, y, and z be the molecular and atomic oxygen and ozone concentrations, respectively. The number of nitrogen molecules is assumed to be constant. In the context of the oxygen atmospheric model the system of equations for the time evolution of oxygen particles has the form:

$$\begin{split} d \, x / \, d \, t &= (\, k_{-2}^{\rm N2} \, N + J_3) \, z - J_2 \, x - k_{\rm N2} N \, x \, y \, + \\ &+ k_4^{\rm N2} \, N \, y^2 + (2 \, k_3 + k_{-2}^{\rm O}) \, y \, z + k_{-2}^{\rm O2} \, x \, z + k_{-2}^{\rm O3} \, z^2 \, + \\ &+ (k_4^{\rm O2} - k_2^{\rm O}) \, x \, y^2 - k_2^{\rm O2} \, x^2 \, y + k_4^{\rm O3} \, y^2 \, z - k_2^{\rm O3} \, x \, y \, z + k_4^{\rm O} \, y^3 \, ; \\ d \, y / \, d \, t &= (k_{-2}^{\rm N2} \, N + J_3) \, z + 2 \, J_2 \, x - k_{\rm N2} \, N \, x \, y - 2 \, k_4^{\rm N2} \, N \, y^2 - \\ &- (k_3 + k_{-2}^{\rm O}) \, y \, z + k_{-2}^{\rm O2} \, x \, z + k_{-2}^{\rm O3} \, z^2 - (2 \, k_4^{\rm O2} + k_2^{\rm O}) \, x \, y^2 - \\ &- k_2^{\rm O2} \, x^2 \, y - 2 \, k_4^{\rm O3} \, y^2 \, z - k_2^{\rm O3} \, x \, y \, z - 2 \, k_4^{\rm O} \, y^3 \, ; \end{split} \tag{2}$$

$$d \, z / \, d \, t = - (k_{-2}^{\rm N2} \, N + J_3) \, z + k_{\rm N2} \, N \, x \, y - (k_3 + k_{-2}^{\rm O}) \, y \, z - k_{-2}^{\rm O2} \, x \, z - \\ &- k_{-2}^{\rm O3} \, z^2 + k_2^{\rm O} \, x \, y^2 + k_2^{\rm O2} \, x^2 \, y + k_2^{\rm O3} \, x \, y \, z \, . \end{split}$$

It follows from the law of conservation of the number of oxygen atoms that:

$$2 x + y + 3 z = A, (3)$$

where A is the total number of the oxygen atoms in cm<sup>3</sup> (the numerical value for A is given in Table I). Relation (3) defines the reaction triangle<sup>9</sup> (see Fig. 2). The desired solution of the system of equations is bound to lie in the plane of the triangle.

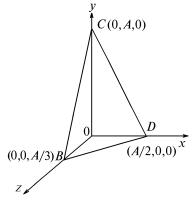


FIG. 2 . Reaction triangle in the space of concentrations x, y, and z.

Qualitative analysis of Eq. (2) is conveniently performed by conversion to Cartesian coordinates (w', u', v') chosen so that the w'-axis is perpendicular to the plane DBC, the u'-axis is directed along the straight line DB and the origin of coordinates is at the point D. In the resultant coordinate system the reaction triangle lies in the plane (u', v') and the highest normalized equilibrium concentration of the oxygen particles is that of the molecular oxygen lying in the vicinity of the origin of coordinates.

The change to the new coordinate system is defined by the following relations:

$$w' = -\frac{A}{\sqrt{14}} + \frac{1}{\sqrt{14}} (2 x + 3z + y);$$

$$u' = \frac{3A}{2\sqrt{13}} + \frac{1}{\sqrt{13}} (-3x + 2z);$$

$$v' = \frac{A}{\sqrt{182}} + \frac{1}{\sqrt{182}} (2 x + 3z - 13y).$$
(4)

For convenient handling of values of different order of magnitude let us introduce the dimensionless time  $t'=t\ k_{\rm N_2}NA$ 

and the dimensionless coordinates

$$u' = A u, \qquad \qquad v' = A v, \qquad \qquad w' = A w . \tag{5}$$

In the coordinate system (u, v, w) the basic set of dynamic equations for the oxygen atmosphere becomes

d w / d t = 0;

$$du/dt = a_0 - a_1 u + a_2 v + a_3 u^2 - a_4 u v + a_5 v^2 + a_6 u v^2 +$$

$$+ a_7 v u^2 + a_8 v^3; (6)$$

$$d v / d t = b_0 + b_1 u - b_2 v + b_3 u^2 - b_4 u v + b_5 v^2 +$$

$$+ b_6 u v^2 + b_7 v u^2 + b_8 v^3$$

subject to the condition that w(0) = 0, which results from Ed. (3).

Eqs. (6) provide a basis for the subsequent analysis of the steady state solution. The coefficients appearing in Eqs. (6) are given in Table II.

Table II. Coefficients of the basic system of equations.

$$\begin{array}{c} a_0 = 3\xi_4/2\sqrt{13} \\ a_1 = (10\xi_3 + 9\xi_4 + 10\xi_5 + 5\xi_7)/13 \\ a_2 = 5/2\sqrt{14} + 3(5\xi_3 - 2\xi_4 + 5\xi_5 + 5\xi_7/2)/13\sqrt{14} + 5\xi_8/4\sqrt{14} \\ a_3 = 10(2\xi_6 - 3\xi_7)/13\sqrt{13} \\ a_4 = (15 + 16\xi_1 - 60\xi_6/13 + 25\xi_7/13 + 10\xi_{13})/2\sqrt{182} + 5(3\xi_8 - \xi_9)\sqrt{182} \\ a_5 = (-10 + 24\xi_1 - 39\xi_2 - 30\xi_7/13 - 45\xi_6/13 + 15\xi_{13})/14\sqrt{13} + 65\xi_{10}/2 + 45\xi_8/2 - 15\xi_9/2 - 39\xi_{11}/2)/14\sqrt{13} \\ a_6 = (135\xi_8/13 + 25\xi_9/13 - 15\xi_{10} + 9\xi_{11} - 6\xi_{12})/14 \\ a_7 = 15(3\xi_8 - 2\xi_9)/13\sqrt{14} \\ a_8 = (110\xi_8/13 + 30\xi_9/13 - 10\xi_{10} + 6\xi_{11} + 9\xi_{12} - 39\xi_{14})/14\sqrt{14} \\ b_0 = \sqrt{14}\xi_4/\sqrt{13} \\ b_1 = \sqrt{14}(2\xi_3 - 6\xi_4 + 2\xi_5 + \xi_7)/\sqrt{13} \\ b_2 = 1/2 + (3\xi_3 + 4\xi_4 + 3\xi_5 + 3\xi_7/2)/13 + \xi_8/4 \\ b_3 = 2\sqrt{14}(2\xi_6 - 3\xi_7)/\sqrt{13} \\ b_4 = (-3 + 2\xi_1 + 12\xi_6/13 - 5\xi_7/13 - 2\xi_{13})/\sqrt{13} + (3\xi_8 - \xi_9)/\sqrt{13} \\ b_5 = (2 + 3\xi_1 - 26\xi_2 + 9\xi_7/13 + 6\xi_6/13 - 3\xi_{13})/\sqrt{182} + 1/(2\sqrt{182})(-13\xi_{10} + 9\xi_8 + 3\xi_9 - 26\xi_{11})/2\sqrt{182} \\ b_6 = -(-27\xi_8/13 + 5\xi_9/13 - 3\xi_{10} - 6\xi_{11} - 4\xi_{12})/\sqrt{14} \\ b_7 = 3(-3\xi_8 + 2\xi_9)/13 \\ b_8 = (-22\xi_8/13 - 6\xi_9/13 + 2\xi_{10} + 4\xi_{11} + 6\xi_{12} - 26\xi_{14})/14 \\ \end{array}$$

The reaction triangle lies in the plane (u, v) as viewed in Figure 3.

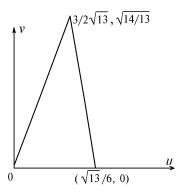


FIG. 3. Reaction triangle in the plane (u, v).

#### 4. STEADY-STATE SOLUTIONS

Before proceeding to the problem of steady state solutions of Eqs. (6) we point out that the coefficients  $a_i$  and  $b_i$  given in Table II are related by the equation

$$a_1 b_2 = a_2 b_1 , (7)$$

which is accurate up to the terms on the order of  $\xi_4 = 10^{-11}$ . Since the free terms are small and the coefficients used with the other terms are around unity, we may seek solutions of Eqs. (6) in the form

$$u_0 = v_0 \, a_2 / \, a_1 + \Delta \,, \tag{8}$$

where  $\Delta \ll v_0 a_2 / a_1$ .

In the search for the steady—state solutions of Eqs. (6) the cubic terms can be omitted because of their small magnitude as compared to the quadratic and linear terms. Substitution of  $u_0$  into Eqs. (6) furnishes steady—state solutions with given accuracy.

$$v_0 = \sqrt{\frac{a_1}{a_2} \frac{a_0 b_1 + b_0 a_1}{a_1 b_4 + a_4 b_1}} = \sqrt{\frac{14 \xi_3 \xi_4}{13(\xi_1 + 15 \xi_8 - 5 \xi_9)}} =$$

$$=\sqrt{\frac{14\,\,\xi_3\,\,\xi_4}{13\,\,\xi_1}}\,\,\alpha\,\,,\tag{9}$$

$$\Delta = \frac{a_0 b_4 + b_0 a_4}{a_1 b_4 + a_4 b_1},\tag{10}$$

$$u_0 = \sqrt{\frac{a_2}{a_1}} \frac{a_0 b_1 + b_0 a_1}{a_1 b_4 + a_4 b_1} = 1/4 \sqrt{\frac{13 \xi_4}{\xi_1 \xi_3}} \alpha.$$
 (11)

$$y_0 = A \alpha \sqrt{\frac{\xi_4 \xi_3}{\xi_1}}, \qquad z_0 = 1/2 A \alpha \sqrt{\frac{\xi_4}{\xi_3 \xi_1}},$$
 (12)

or 
$$z_0 = y_0/2\xi_3$$
 .

The relationship between the ozone concentration and that of the molecular oxygen determined by Eq. (12) is well known.6 In what follows we will refer to Eq. (12) as the standard solution. The calculation of the Lyapunov factors shows the steady-state solution (12) to be stable, and the relaxation times to the steady state are of the order:  $t_1 = 2$  s, and  $t_2 = 0.5 \cdot 10^7$  s.

No other stable solutions in the vicinity of the point  $(x_0, y_0, z_0)$  exist. Eq. (11) states that in the leading order the approximate solution depends on the coefficients  $\xi_4$ ,  $\xi_3$ , and  $\xi_1$ , which allows the general conclusion that when analysing the oxygen atmospheric states approaching the stable state it is vital to take into account the following reactions:

$$\begin{aligned} O + O_2 + N_2 &\to O_3 + N_2 ; \\ O + O_3 + O_2 &\to O_3 + O_3 ; \\ 2O_2 + O &\to O_2 + O_3 ; \\ O + O_3 &\to 2O_2 ; \\ O_3 + hv &\to O + O_2 ; \\ O_2 + hv &\to 2O . \end{aligned} \tag{13}$$

The set of six reactions (13) may be referred to as the Chapman cycle.<sup>7</sup>

In the subsequent discussion, our analysis of systems with a varying number of oxygen atoms will be based on a more general form of Eqs. (6) taking into account a non zero value of w. It is straightforward to show that for analysis of a steady-state solution of this kind of system of equations governing the behaviour of the oxygen atmosphere within the framework of the Chapman model (see reactions (13)), it would suffice to retain the terms whose order is no higher than quadratic.

### 5. SOURCES AND SINKS IN THE OXYGEN ATMOSPHERE

In the upper atmosphere account must be taken of variation of the oxygen particle concentration attributable to the action of sources and sinks along with the chemical reactions described above. Sinks may differ in nature (settlement of oxygen particles on aerosols of volcanic origin or local oxidation processes induced by artificial or natural objects flying by, etc.). Sources may appear as biological processes or oxidant emissions attendant on rocket launches. We will neither go into details of the origin of sources and sinks nor consider their time scale, for we deal with a "point" process, whereas mechanisms acting as local sources or sinks are by no means lacking. The effect of sources and sinks were also discussed elsewhere.8

The sink and source values will be given in equations by the terms  $k_x x$ ,  $k_y y$ ,  $k_z z$  and  $l_i A$ .

In the original coordinate system (x, y, z) the inclusion of sources and sinks gives rise to added linear terms to the basic system of equations in the form of corrections

$$d x/d t = (...) - k_x x + l_x, d y/d t = (...) - k_y y + l_y,$$
  

$$d z/d t = (...) - k_z z + l_z.$$
(14)

With the prior normalization the sinks and sources will be described by the respective  $\lambda_i = k_i/(k_{N2}NA)$  and  $\theta_i = l_i/(k_{N2}NA^2)$ .

In the coordinate system (w, u, v) the linear corrections to the equations associated with sinks and sources have the form:

$$d w / d t = w_0 + \gamma_{11} w + \gamma_{12} u + \gamma_{13} v;$$

$$d u / d t = (...) + u_0 + \gamma_{21} w + \gamma_{22} u + \gamma_{23} v;$$

$$d v / d t = (...) + v_0 + \gamma_{31} w + \gamma_{32} u + \gamma_{33} v.$$
(15)

In Eqs. (16) the following notations are used:

In Eqs. (16) the following notations are used: 
$$w_0 = \frac{1}{\sqrt{14}} (2 \theta_x + 3 \theta_z - \chi_x) , u_0 = \frac{1}{\sqrt{13}} (2 \theta_z + 3 \theta_x - 3\chi_x/2) ,$$

$$v_0 = -\frac{2 \theta_x + 3 \theta_z - 13 \theta_y - c_x}{\sqrt{182}} , \gamma_{11} = \frac{4\chi_x + 9\chi_z + \chi_y}{14} ,$$

$$\gamma_{12} = \frac{6(\chi_x - \chi_z)}{\sqrt{182}} , \gamma_{13} = \frac{4\chi_x - 13\chi_y + 9\chi_z}{14\sqrt{13}} ,$$

$$\gamma_{21} = \frac{6(\chi_x - \chi_z)}{\sqrt{182}} , \gamma_{22} = \frac{9\chi_x + 4\chi_z}{13} , \gamma_{23} = \frac{-6(\chi_x - \chi_z)}{13\sqrt{14}} ,$$

$$\gamma_{31} = \frac{4\chi_x + 9\chi_z - 13\chi_y}{14\sqrt{13}} , \gamma_{32} = \frac{-6(\chi_x - \chi_z)}{\sqrt{182}} ,$$

$$\gamma_{33} = \frac{4\chi_x + 169\chi_y + 9\chi_z}{182} .$$

$$(16)$$

Again, the introduction of the sources and sinks into the analysis raises the question of the number of reactions to be considered for a correct description of the steady-state solution. Since the task was to find solutions approaching the standard solution, our consideration may be restricted to the Chapman approximation. In the coordinate system (w, u, v), with allowance made for the six reactions (13) as well as for sources and sinks, the dynamic equations differ essentially from the relations discussed previously by the non-zero derivative of w, while the structure of the other equations is virtually unchanged, except that the coefficients are renormalized:

$$\begin{split} \mathrm{d} \, w / \, \mathrm{d} \, t &= w_0 + \gamma_{11} \, w + \gamma_{12} \, u + \gamma_{13} \, \mathrm{v} \, ; \\ \mathrm{d} \, u / \, \mathrm{d} \, t &= A_0 - A_{11} \, u + A_{12} \, v + A_{13} \, w - A_{222} \, \mathrm{v}^2 - \\ - \, A_{212} \, u \, \mathrm{v} - A_{233} \, w^2 - A_{213} \, w \, u - A_{223} \, w \, \mathrm{v} \, ; \\ \mathrm{d} \, v / \, \mathrm{d} \, t &= B_0 + B_{11} \, u - B_{12} \, \mathrm{v} - B_{13} \, w - B_{222} \, \mathrm{v}^2 - B_{212} \, u \, \mathrm{v} - \\ - \, B_{233} \, w^2 - B_{213} \, w \, u - B_{223} \, w \, \mathrm{v} \, . \end{split}$$

To find the steady states for Eqs. (17) and test them for stability we eliminate the variable w to derive an equation for the plane in the space of the variables (u, v, v)w), which is an analog of relation (3). The analog is explicitly expressed as

$$w = (w_0 + \gamma_{12} u + \gamma_{13} v) / \gamma_{11} = \delta_0 + \gamma_1 u + \gamma_2 v;$$
 (18)

$$\delta_0 = \sqrt{14} \, \frac{\Omega - \chi_{_{\mathcal{X}}}}{4\chi_{_{\mathcal{X}}} + 9\chi_{_{\mathcal{Z}}} + \chi_{_{\mathcal{Y}}}} \, ; \, \gamma_1 = 6 \, \sqrt{\frac{14}{13}} \, \frac{\chi_{_{\mathcal{X}}} - \chi_{_{\mathcal{Z}}}}{4\chi_{_{\mathcal{X}}} + 9\chi_{_{\mathcal{Z}}} + \chi_{_{\mathcal{Y}}}} \, ;$$

$$\gamma_2 = \frac{1}{\sqrt{13}} - \frac{14}{\sqrt{13}} \frac{\chi_y}{4\chi_x + 9\chi_z + \chi_y} \; ; \; \Omega = 2\theta_x + \theta_y + 3\theta_z \; .$$

Let us pass on to the spherical coordinates in the space of the parameters  $(\chi_x, \chi_y, \chi_z)$ , setting

$$\chi_x = r \sin \varphi \cos \psi, \ \chi_y = r \cos \varphi \cos \psi, \ \chi_z = r \sin \psi.$$

From the explicit form of the quantities  $\gamma_{1,2}$ , it follows that they are independent of the orbital coordinate  $r=\sqrt{\chi_x^2+\chi_y^2+\chi_z^2}$ , i.e. the space of the parameters is isotropic. The dependence on r can be eliminated from the coefficient  $\delta_0$ , setting  $|\chi_x\cdot\Omega|<\xi_4$ .

The elimination of the variable w results in a system of two equations:

$$0 = A A_0 - A_1 u + A_2 v - A_4 u v - A_3 u^2 - A_5 v^2,$$
  

$$0 = B B_0 + B_1 u - B_2 v - B_5 v^2 - B_4 u v - B_3 u^2.$$
(19)

The coefficients of Eqs. (19) involve the corresponding coefficients of Eq. (6) and the corrections linear in  $\gamma_i$ ,  $\delta_\theta$ ,  $\chi_i$ , and  $\theta_i$ .

The introduction of sources and sinks destroys the standard steady—state solution. There may be different destruction mechanisms depending, to a large extent, on the precise interval, out of the four likely intervals determined by the Eq. (1), wherein the parameters  $\chi_i$  and  $\theta_i$  fall.

We will restrict our consideration to the interval  $\chi_i$ ,  $\theta_i \ll \xi_4$  corresponding to the case of small sources and sinks. This approximation permits us to eliminate the terms proportional to  $\chi_i$  and  $\theta_i$  from Eqs. (19).

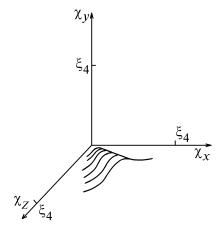


FIG. 4 Range of admissible reaction rates characterizing sinks for which the steady—state solution deviates from the standard solution by  $\leq 10\%$ .

Even though the sources and sinks are small the steady–state solution of Eq. (19) may differ essentially from the standard solution. This is due to the dependence of the coefficients of Eqs. (19) on  $\gamma_i$  and  $\delta_0$ . As Eqs. (18) suggest  $\gamma_i$  and  $\delta_0$  depend on the ratio  $\chi_i/\chi_j$  and on the difference  $(\chi_x - \Omega)$ .

Subject to the condition that  $\delta_0 \ll \xi_4$ , which defines a close relationship between the source and sink rate of the molecular oxygen, consistent analysis of deviations from the steady state will reveal a fold—shaped region in the space of parameters whose widest part is not greater than  $\xi_4$  (see Fig. 4) where the steady states deviating from the standard state by 10% at most are concentrated. The most essential condition wherein small deviations are realized is that the sink rates of molecular oxygen and ozone be nearly the same ( $|\chi_x - \chi_z| \ll \xi_4$ ). Violation of this condition will result in considerable deviations or actually destroy the steady state.

#### 6. CONCLUSION

From the foregoing discussion it follows that the steady state of the oxygen atmosphere is extremely sensitive to the introduction of small sinks and sources. However, in a narrow region of the space of parameters characterizing the sources and sinks only slight deviations from the equilibrium concentrations of the ozone and atomic and molecular oxygen are likely to occur if sink rates are much below the rate of the photochemical dissociation of the molecular oxygen.

#### ACKNOWLEDGMENTS

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