

ON A MECHANISM OF HYDROXYL AIRGLOW EMISSION

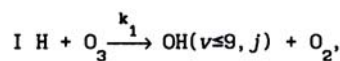
A.M. Samusenko

*Institute of Physics of the Atmosphere,
Academy of Sciences of the Byelorussian SSR, Minsk*

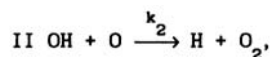
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A mechanism of hydroxyl airglow emission owing to the interaction of the surrounding medium with gaseous compounds, whose origin is connected with human activity, is examined. It is shown that at altitudes of 80–100 km the hydroxyl emission intensity in the region of interaction can be an order of magnitude or more greater than the average intensity of the same emission in the undisturbed atmosphere.

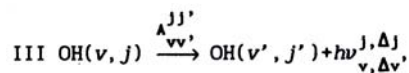
The atmospheric sources of hydroxyl emission are located at altitudes z ranging from 80 to 100 km. The hydroxyl emission is produced primarily by the chemiluminescence mechanism^{1,2}:



$$k_1 = 1.4 \cdot 10^{-10} e^{-\frac{470}{T}} \text{ cm}^{-3} \text{ s}^{-1};$$



$$k_2 = 2.2 \cdot 10^{-11} e^{-\frac{117}{T}} \text{ cm}^{-3} \text{ s}^{-1};$$



where k_1 are the rate constants of the processes I and II and $A_{vv'}^{jj'}$ is the Einstein spontaneous emission coefficient for the transition $vj \rightarrow v'j'$.

This model describes quite accurately the characteristics of hydroxyl emission averaged over a long time interval. However there are significant difficulties in interpreting on the basis of this model the unaveraged observed values ("instantaneous" values). There are several reasons for this. First, the atmosphere itself is subject to rapid and, most importantly, difficult to

predict oscillations of both the dynamic and thermodynamic parameters (for example, the temperature and concentrations of minor components), which affect the hydroxyl layer emission. In this connection the observed "instantaneous" values of the hydroxyl emission intensity which are separated by some time interval often differ by one or two orders of magnitude for no apparent reasons, even for the same location.³ From here there follows the second reason: the mechanisms of excitation and deexcitation of $\text{OH}(v)$ in the atmosphere have not been adequately studied. The third reason is connected not with the lack data on atmospheric processes but rather with the fact that the rate constants are poorly known, even for those mechanisms which are thought to be firmly established. All this leads to the fact that in many cases the computed values of the hydroxyl emission intensity differ by several orders of magnitude from the values which have not been averaged over a long time interval. It is shown below that additional factors, connected with the anthropogenic effects on the atmosphere, can also be added to the factors enumerated above.

An airplane flying through the Earth's atmosphere leaves in its wake a long-lived formation (which in what follows we shall simply call the trail) that moves in space and consists of a mixture of atmospheric gases and the products of combustion of the fuel. The typical composition of the exhaust gases and their content as well as the other required parameters are given in Table I.

TABLE I.

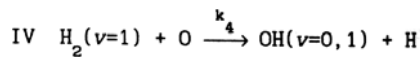
The typical values of the relative concentrations c_{M_i} and temperatures of exhaust gases.^{4,5}

T, K	M _i														Refs.
	H ₂	CO	H ₂ O	CO ₂	HCl	N ₂	H	OH	Cl	Na	NaCl	K	KCl	PbO	
1800	0.29	0.24	0.14	0.02	0.15	0.083	1.3-3	5.5-5	3.7-4	1.7-6	2.0-4	9.6-8	8.0-8	-	[4]
2000	0.19	0.19	0.25	0.042	0.18	0.088	1.4-3	4.0-4	9.0-4	-	-	-	-	-	[4]
1120	0.15	0.4	0.2	0.1	-	0.12	6.0-5	~0	-	-	-	-	-	2.0-3	[5]

Remark: $a - b = a \cdot 10^{-b}$

The products of combustion can react chemically with the active minor components of the atmosphere. Such a situation can occur, in particular, in the mesosphere and lower thermosphere, when the products of combustion of fuel contain molecular hydrogen. Since the initial vibrational temperature of H_2 is ~ 2000 K the jet expands rapidly. The rate of vibrational relaxation of excited hydrogen at pressures below 10^{-5} atm is low^{6-8} and the relative fraction of $H_2(v=1)$ can reach 4% of the total H_2 content in the trail.

It was established recently that at low temperatures the reaction



proceeds many orders of magnitude more rapidly than the same reaction with $H_2(v=0)$. The experiment was performed only at the temperature $T = 302 \pm 2$ K. The measured value is $k_4 = 1_{-0.6}^{+0.9} \cdot 10^{-14} \text{ cm}^{-3} \cdot \text{s}^{-1}$ (Ref. 9). A wider range of temperatures was covered in a series of calculations of K_4 based on the model potentials for the interaction of H_2 and O (Refs. 10–12). The computational results for certain potentials agree well with the experimental value of K_4 . Extrapolation of the results to $T = 200$ K (the characteristic temperature of the atmosphere at altitudes of 80–100 km) gives

$$k_4 \approx 2 \cdot 10^{-15} \text{ cm}^{-3} \cdot \text{s}^{-1}.$$

The reaction IV indicates that compared with the surrounding atmosphere the trail contains an additional source of atomic hydrogen. To find the concentration of $[H]_{\text{add}}$ the dynamic processes involved in the expansion of the trail must be studied together with the processes I–IV. Unfortunately studying these two processes at the same time significantly complicates the problem. The primary goal of this work, however, is to determine the effect of the mechanism IV on the hydroxyl emission of the trail without the factors that complicate the problem. It turns out that in I the approximation of fast turbulent mixing of the products of combustion with the atmosphere this goal can be reached relatively simply, if the change in atomic hydrogen and accompanying radicals is described not per unit volume, as is usually done, but rather in the entire volume of the trail.

For simplicity we shall assume that the trail is cylindrically symmetric and its axis is oriented along the z axis. The radius of the trail is obviously a function of time $R(t)$. At the starting stage of formation of the trail the mixing of the products of combustion with the atmosphere is assumed to be so rapid that on the time scales of interest to us the concentrations of the atmospheric components in the trail and the surrounding space are virtually identical (the question of the effect of the processes I, II, and IV on $[O_3]$ and $[O]$ is studied in the Appendix). For the volume V we shall choose the part of the trail with thickness $6z$ such that the possible displacements of

mass z are insignificant. Then integrating over the trail volume V the kinetic-gasdynamic equations describing the change in the concentrations of the reagents in space and in time gives the following system of equations for the quantities $\int_V [H]_{\text{add}} dV$, $\int_V [OH]_{\text{add}} dV$,

$$\begin{aligned} & \int_V [H_2(1)] dV : \\ & \frac{d}{dt} \int_V [H_2(1)] dV = -k_4 [O] \int_V [H_2(1)] dV; \\ & \frac{d}{dt} \int_V [H]_{\text{add}} dV = k_4 [O] \int_V [H_2(1)] dV + \\ & + k_2 [O] \int_V [OH]_{\text{add}} dV - k_1 [O_3] \int_V [H]_{\text{add}} dV; \\ & \frac{d}{dt} \int_V [OH]_{\text{add}} dV = k_4 [O] \int_V [H_2(1)] dV + \\ & + k_1 [O_3] \int_V [H]_{\text{add}} dV - k_2 [O] \int_V [OH]_{\text{add}} dV. \end{aligned} \quad (1)$$

Since $\frac{k_4 [O]}{k_2 [O] + k_1 [O_3]} \approx 10^{-4}$ and $Z \geq 80$ km

$\frac{k_2 [O]}{k_1 [O_3]} \gg 1$ the solution of the system (1) for $t > 1$ s

can be written in a very simple form:

$$\begin{aligned} \int_V [H_2(1)] dV &= \int_{V_0} [H_2(1)] dV e^{-k_4 [O] t}, \\ \int_V [H]_{\text{add}} dV &= 2 \left(1 - e^{-k_4 [O] t} \right) \int_{V_0} [H_2(1)] dV, \\ \int_V [OH]_{\text{add}} dV &= 2 \frac{k_1 [O_3]}{k_2 [O]} \left(1 - e^{-k_4 [O] t} \right) \int_{V_0} [H_2(1)] dV, \\ V_0 &\equiv \pi R_0^2 \delta z, \quad R_0 \equiv R(t=0). \end{aligned} \quad (2)$$

With the help of Eqs. (2) it is easy to find the average concentrations of the radicals in the trail at a given altitude. For this it is sufficient to divide the integrated number of radicals by the quantity $R^2(t) \delta z$. Since in our case the chemical processes have a small effect on the thermodynamic state of the trail the function $R(t)$ can be found independently by solving the gasdynamic equations. Taking into account the

atmospheric component $[H]_0$ we obtain the following expression for the average concentration $\overline{[H]}$, which is of interest here, in the trail:

$$\overline{[H]} = \overline{[H]}_{\text{add}} + [H]_0 = \frac{2R_0^2}{R^2(t)} \overline{[H_2(1)]}_0 \cdot \left[1 - e^{-k_1[O]t} \right] + [H]_0, \tag{3}$$

where

$$\overline{[H_2(1)]}_0 = \frac{1}{\pi R_0^2 \delta z} \int_{v_0} [H_2(1)] dv$$

The function $R(t)$ is, generally speaking, a complicated function of time.¹³ Initially the trail expands rapidly, but as time passes this process slows down. Ultimately the trail looks like a quasistationary formation, whose further expansion is determined by atmospheric processes.

In spite of the complicated character of the evolution of the trail we shall assume that $R(t)$ is determined by the diffusion law:

$$R^2(t) = R_0^2 \left(1 + \frac{t}{\tau_d(t)} \right). \tag{4}$$

This form is convenient because over relatively short time intervals it can be assumed with good accuracy that $\tau_d(t) = \tau_d = \text{const}$. The complicated character of the expansion of the trail is reflected in the fact that, in contradistinction to classical diffusion, the characteristic time τ_d is a function of t .

Substituting Eq. (4) into Eqs. (3) we obtain for $t > 1$ s and $\tau_d(t) = \text{const}$

$$\overline{[H]}_1 \approx 2\tau_d k_d [O] \overline{[H_2(1)]}_0 + [H]_0. \tag{5}$$

The formula (5) shows that in spite of the expansion of the trail the concentration of atomic hydrogen in it does not decrease with time. In what follows, as a model, we shall assume that for $t \leq 100$ s $\tau_d(t) \approx \tau_d = 2.5$ s.

It is also interesting to study the state of the trail at times of the order of $\sim (k_1[O])^{-1}$. On the one hand, over such time intervals most of $[H_2(v = 1)]$ will be transformed into $[H]$. On the other hand, it should be expected that at $z \sim 80-100$ km at times $t \sim (k_1[O])^{-1} \geq 10^{-3}$ s the trail will evolve very slowly. For this reason it may be assumed with good accuracy that the dimensions of the trail are fixed. For the model chosen to describe the mixing the characteristic value of the quantity $R^2(t)/R_0^2$ for $t \geq 10^3$ s can vary from one to several hundreds. In what follows we shall assume that $R^2(t)/R_0^2 = 200$. Then we obtain

$$\overline{[H]}_2 \approx 10^{-2} \overline{[H_2(1)]}_0 + [H]_0, \quad t \sim (k_1[O])^{-1}. \tag{6}$$

Table II gives the atmospheric concentrations of atmospheric oxygen and hydrogen, the model distribution of $\overline{[H_2(1)]}_0$ as well as the values $\overline{[H]}_1$ and $\overline{[H]}_2$. The model distribution of $\overline{[H_2(1)]}_0$ is determined completely by the dynamics of turbulent mixing of the atmospheric components and the gaseous products of combustion. The upper and lower limits on the concentration of atomic oxygen from existing experimental data are given.^{14,15} Most of these data lie closer to the upper limit. The values of $[H]_0$ presented are typical for theoretical calculations.^{16,17} The experimental data on $[H]_0$ were obtained very recently¹⁸ and they are significantly lower than the tabulated values.

One can see from Table II that for the chosen model the concentration of atomic hydrogen in the trail is for a long time much higher than the atmospheric concentration of atomic hydrogen. We note that the values of $\overline{[H]}_2$ for $z \leq 85$ km could be greatly overestimated. The fact is that for $z \leq 85$ km the characteristic time $(k_1[O])^{-1}$ is of the order 10^4 s. At such long time intervals the dimensions of the trail no longer satisfy the ratio $R^2(t)/R_0^2$ used in deriving Eq. (6).

TABLE II.

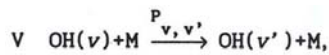
The concentrations (in cm^{-3}) of the active components of the trail.

Components of the trail	z, km							
	82.5	85	87.5	90	92.5	95	97.5	100
$[H]_0$ (10^{-8})	2	3	3	2	1.4	1.0	0.8	0.6
$[O]$ (10^{-11})	0.4	0.6-2	1.5-3	2-6	3-6	3-6	3-7	3-8
$\overline{[H_2(1)]}_0$ (10^{-11})	6.8	5.8	4.8	3.4	2.8	2.3	1.8	1.2
$\overline{[H]}_1$ (10^{-8})	4.7	6.5-15	10-17	10-24	9-18	8-15	7-14	4-11
$\overline{[H]}_2$ (10^{-8})	70	61	51	36	29	24	18.8	12.6

The energy $\varepsilon_{v,\Delta v}^{i,Aj}$ of hydroxyl emission via the transition $vj \rightarrow v'j'$ per unit volume of the trail in all directions per unit time (the source function) in the case of rotational equilibrium is proportional to $[\text{OH}]_v$ ($[\text{OH}]_v$ is the population of the vibrational level v of the hydroxyl radical). ; The system of equations for finding $[\text{OH}]_v$ is constructed based on the schemes I–IV and in principle it is virtually identical to the system of equations usually employed to describe the hydroxyl emission of the atmosphere:

$$\frac{d[\text{OH}]_v}{dt} = k_4 [\text{H}][\text{O}_3] f_v + \sum_{s=v+1}^9 (A_{s,v} + P_{s,v}) [\text{OH}]_s - [\text{OH}]_v \times \sum_{s=0}^{v-1} (A_{s,v} + P_{s,v}) - k_{2v} [\text{OH}]_v \quad (7)$$

In Eq. (7) $P_{s,v}$ is the rate of the transitions $s \rightarrow v$ owing to VT processes



and the function f_v is the starting distribution of OH molecules over vibrational levels in the reaction I.

The characteristic times of the processes represented in Eq. (7) are of the order of fractions of a second. Since we are interest in much longer times, in solving Eq. (7) it is sufficient to restrict the analysis to the quasistationary regime. The corresponding solution was found in Ref. 19 and, in the notation of this problem, has the form

$$[\text{OH}]_v = k_4 [\text{H}][\text{O}_3] \sum_{s=0}^9 f_{s,v} \varphi_{s,v}(0), \quad (8)$$

where $\varphi_{s,v}(0)$ is a special function that depends on the constants P_{sv} , $A_{s,v}$, $k_{2,v}$ and can be calculated with the

help of recurrence relations.²⁰ If the constants are known, it is trivial to calculate $[\overline{\text{OH}}]_v$ and hence $\varepsilon_{v,\Delta v}^{i,Aj}$ also. Unfortunately their uncertainty in the values of the constants is at the present time so large that it is impossible to give a reliable quantitative description of hydroxyl emission either for the atmosphere, as mentioned previously, or for the trail. In this situation it is more appropriate to calculate not the absolute values of $[\text{OH}]_v$ but rather the relative quantity $[\text{OH}]_v/[\text{OH}]_{0,v}$. This approach makes it possible to ignore a number of uncertainties. In particular, the sum $\sum_{s=0}^9 f_s \varphi_{s,v}(0)$, which is the least accurately known cofactor in Eq. (8), can be ignored (assuming, of course, that in the trail extinction occurs in the same manner as in the atmosphere).

The concentration of ozone, like that of the other minor atmospheric components, is still too uncertain, in spite of the fact that several tens of measurements of $[\text{O}_3]$ have been performed. Here there is an uncertainty in the measurements, but the uncertainty in the ozone concentration is due primarily to the great variability of $[\text{O}_3]$ owing to diurnal, seasonal, and latitudinal variations of the upper atmosphere. Transferring from absolute to relative concentrations greatly simplifies the problem, because in so doing we need to know only the altitude profile of $[\text{O}_3]$, whose structure is more stable with respect to atmospheric fluctuations than are the absolute values.

Table III gives the values of the product of $[\text{H}] \cdot [\text{O}_3]$, which, as a function of z , is actually equivalent to the $[\text{OH}]_v$ and $[\text{OH}]_{0,v}$ profiles. This table was constructed using the typical $[\text{O}_3]$ profiles (Refs. 21 and 22 – experiment, Ref. 23 – numerical modeling). The concentrations of $[\text{H}]_1$ were calculated only for the profile with the maximum values of $[\text{O}]$.

TABLE III.

The values of the product $10^{-15} [\text{H}] \cdot [\text{O}_3]$ (in cm^{-6}) for different $[\text{O}_3]$ and $[\text{H}]$ profiles (top row – $[\text{H}] = [\text{H}]_0$, bottom row – $[\text{H}] = [\text{H}]_1$).

Ref's.	z, km							
	82.5	85	87.5	90	92.5	95	97.5	100
[21]	8	21	25.5	18	8.4	2	-	-
	19	105	146	208	108	30	-	-
[22]	18	24	24	16	10	3	0.6	0.1
	42	120	136	184	130	45	8.6	2.1
[23]	8	6	24	60	56	30	8	1.2
	20	30	136	690	736	450	128	21.2

It is obvious from the data in Table III that the hydroxyl emission of the trail is not only much stronger than that of the atmosphere but it is also shifted up to high altitudes. Thus even if VT collisions

are important for calculating the hydroxyl emission they are less important in the trail than in the atmosphere (owing to the drop in the atmospheric pressure as z increases).

The spectral intensity of the emission is an integral of the source function along the line of sight l .

$$I_{\nu} = \int_1 \epsilon_{\nu, \Delta\nu}^{J, \Delta J} \frac{dl}{4\pi} \sim \int_1 [\text{OH}]_{\nu} dl. \tag{9}$$

If V processes are not important, then the trail and atmospheric spectra will have the same form. In the opposite case the lines owing to emission from highly excited vibrational states will be stronger in the hydroxyl spectrum of the trail than that of the atmosphere.

We shall compare the intensities of the hydroxyl emission of the trail and atmosphere along the z axis. For this we shall calculate the integral (see Table IV, δz_i was set equal to 2.5 km in the calculations)

$$\int_z [\text{H}][\text{O}_3] dz \approx \sum_{\delta z_i} [\text{H}][\text{O}_3] \delta z_i.$$

TABLE IV.

The value of $10^{-15} \sum_{\delta z_i} [\text{H}][\text{O}_3] \delta z_i$ (in cm^{-5}) for different $[\text{H}]$ and $[\text{O}_3]$ profiles.

H profile	[O ₃] profile		
	[21]	[22]	[23]
[H] ₀	96	111	202
[H] ₁	635	700	2222

The emission intensity along the z axis intergrated over the spectrum can be found with the help of the formulas (8) and (9) and has the form

$$I = \frac{k_1}{4\pi} \int_z [\text{H}][\text{O}_3] dz \sum_n E_n f_n. \tag{10}$$

The sum in Eq. (10) is the energy of the pumping owing to the chemical reactions. For the process $I \sum_n E_n f_n$ is equal to approximately 3 eV. Substituting into the right side of Eq. (10) the numerical values of the quantities we obtain, for example, for the profile of Ref. 22

$$I_0 \approx 5\text{MR}, \quad I_1 \approx 31\text{MR} \quad (1\text{MR} = 10^{12} \text{ fot/cm}^2).$$

Thus for the chosen mixing model over a period of several minutes (see the Appendix) the hydroxyl emission of the trail is approximately an order of magnitude stronger than that of the atmosphere. In reality the difference can be even larger, since the computed value of I_0 is five times greater than the average observed values of the atmospheric hydroxyl emission intensity.

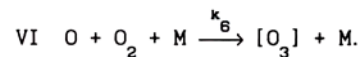
In conclusion, we shall discuss the question of the effect of atomic hydrogen, which is present in the products of combustion of fuels, on the hydroxyl emission (compared with H the other radicals presented in Table can be neglected). At first glance the starting atoms should play an important role: for $C_H = 10^{-3}$ the initial hydrogen concentrations in the trail for $z = 80-100$ km are equal to $5 \cdot 10^{10} \div 7.5 \cdot 10^9$. It should be noted, however, that in Ref. 4 the relative concentration of the radicals is so high only because the temperatures are high (~ 2000 K). Already at $T = 1120$ K (see Table I) the value of C_H drops to such an extent that the radicals affect primarily the earliest stage of expansion of the trail. We recall that prior to mixing with the atmosphere the products of combustion pass through a complicated evolution, in the process of which their temperature drops from ~ 2000 to ~ 200 K. It is obvious that at such low temperatures, the values of C_H presented in Table I cannot be used as reliable data for studying the role of the primary radicals in the hydroxyl emission of the trail. If it is still assumed that the relative fraction of radicals in the trail is the same as in the first two rows of Table I, then at the starting stage of the development of the trail $\tau_{\text{chem}} = (k_1[\text{H}])^{-1} \sim 2 \div 10$ s. This value is comparable to the characteristic turbulent mixing time, and to solve the problem the kinetic and gasdynamic equations must be studied simultaneously.

APPENDIX

We shall determine how the processes I, II, and IV affect the concentrations of $[\text{O}_3]$ and $[\text{O}]$ in the trail. The equation describing the change in $\{O_3\} \equiv \int_v [\text{O}_3] dV$ as a function of time has the form

$$\begin{aligned} \frac{d\{O_3\}}{dt} = & -k_1 [\text{H}]\{O_3\} - \sum_1 k_{M_1} [M_1] \frac{\{O_3\}}{1 + \frac{t}{\tau_d}} + \frac{\pi R_0^2 \delta z}{\tau_d} [O_3] + \\ & + k_6 [O][O_2][M] \pi R_0^2 \delta z \left[1 + \frac{t}{\tau_d}\right]. \end{aligned} \tag{A.1}$$

The first and second terms on the right side of (A.1) describe the loss of ozone in the interactions with atomic hydrogen and the products of combustion of the fuel. The third and fourth terms describe the flow of ozone into the trail owing to turbulent mixing with the surrounding space and the production of ozone by recombination of oxygen via the mechanism



The mechanism VI is a constant source of ozone in both the trail and the atmosphere. For a stationary atmosphere

$$k_1 [\text{H}]_0 [\text{O}_3] = k_6 [\text{O}][\text{O}_2][\text{M}]. \tag{A.2}$$

We shall write out the solution of (A.1), transformed with the help of (A.2), for the case when the effect of the products of combustion can be neglected:

$$\begin{aligned} \overline{[O_3]} = & [O_3] \left[1 + \tau_d k_1 [H]_0 - \frac{[H]_0}{[H]} \right] \frac{1 - \exp(-k_1 \overline{[H]} t)}{k_1 \overline{[H]} (t + \tau_d)} + \\ & + [O_3] \frac{[H]_0}{[H]} \frac{t}{t + \tau_d}. \end{aligned} \quad (A.3)$$

It follows from (A.3) that at times shorter than $(k_1 \overline{[H]})^{-1} \sim (10^{-11} \cdot 10^9) = 100$ s the ozone concentrations in the trail are approximately the same as in the atmosphere. For $t > (k_1 \overline{[H]})^{-1}$ the quantity $\overline{[O_3]}$ decreases from the value of $[O_3]$ to different stationary value equal to $[O_3] [H]_0 / \overline{[H]}$. This happens over a time interval which is the smallest of the quantity $k_1 [H]_0^{-1} \sim 10^3$ s and the characteristic dynamic time interval during which the mixing of the trail and atmosphere stops. However it has not been excluded that for $t \geq 10^3$ s the atmospheric dynamic processes themselves will start to affect the state of the trail.

The second term in Eq. (A.1) is not significant over the characteristic time intervals - during which the value of $\overline{[O_3]}$ changes. Its role reduces primarily to decreasing by a factor of $\overline{[O_3]}$ the stationary value of $\left(1 + \tau_d \sum_i k_{M_i} [M_i] \right)$ given by (A.3).

The estimates presented make it possible to describe qualitatively the temporal evolution of the hydroxyl emission of the trail time. Approximately up to $t \sim (k_1 \overline{[H]})^{-1} \sim 100$ s the sources of emission are $[H]/[H]_0$ times stronger in the trail than in the surrounding medium. As time passes the sources of the hydroxyl emission start to weaken in proportion to the inverse of the time (and this dependence is even stronger because the mixing slows down) and their strength reaches a new stationary value at some time $t \leq 10^3$ s. Since in the new stationary state $k_1 \overline{[H]} \overline{[O_3]} = k_1 [H]_0 [O_3]$, the emission of the trail is equal to the atmospheric emission. This leads to a paradoxical situation: the hydrogen concentrations in the trail (see the values of $\overline{[H]}_2$ in Table II) are one to two orders of magnitude greater than $[H]_0$, but because of the ozone deficiency this in no way affects the hydroxyl emission. Such strong nonequilibrium of the chemical composition can affect the emission only if additional dynamic processes occur in the atmosphere which efficiently mix the atmosphere with the trail.

The parameter $k_1 \overline{[H]}$ plays two roles. On the one hand, it determines the time interval over which the emission of the trail is significantly stronger than that of the atmosphere and, on the other hand, it is directly related with the intensity of the emission of the trail.

These properties of the parameter $k_1 \overline{[H]}$ compete with one another: the higher $k_1 \overline{[H]}$, the stronger the emission of the trail for a fixed value of τ_d is, but the emission process lasts for a shorter period of time, and vice versa.

The equation for $\{O\}$ analogous to (A.1), is

$$\frac{d\{O\}}{dt} = -k_4 [H_2(1)] \{O\} - k_2 \overline{[OH]} \{O\} + [O] \frac{\pi R_0^2 \delta z}{\tau_d}. \quad (A.4)$$

Substituting into (A.4) for $\overline{[OH]}$ the corresponding formula from (2) and solving the equation gives

$$\overline{[O]} \approx \frac{[O]}{\tau_d 2k_1 [O_3] \frac{[H_2(1)]_0}{[O]} + 1} \approx [O].$$

Thus the processes I, II, and IV do not significantly affect the value of $[O]$.

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