

ON A MECHANISM OF MESOSPHERIC SODIUM NIGHTGLOW

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A mechanism for mesospheric sodium night glow emission owing to the interaction of the surrounding medium with gaseous compounds whose origin is connected with human activity is studied. It is shown that at altitudes of 80–100 km the Na emission intensity and source function could be two to three orders of magnitude greater than the average values of the analogous quantities in the undisturbed atmosphere.

In the last few years a great deal of attention has been devoted to the problem of describing the atmospheric sodium nightglow emission.^{1–3} Significant progress has been achieved in explaining the mechanism of excitation of Na(²P) in nighttime conditions. With its help the characteristics of emission, which together with the correct set of rate constants for the chemical reactions responsible for the excitation of Na(²P) give satisfactory agreement with the observations, have been calculated. At the same time, in spite of the obvious progress achieved, a number of problems connected with determining more accurately the nature of the emission itself as well as with the currently existing possibilities for describing the emission still remain. However these are not the only problems that affect the interpretation of atmospheric data. Factors associated with changes produced in the atmospheric conditions by different types of disturbances, in particular, disturbances caused by anthropogenic effects on the atmosphere, can contribute additional difficulties. In this paper one mechanism for such an effect is studied.

Airplanes eject into the Earth's atmosphere a large amount of gaseous products from the combustion of fuel, including compounds containing Na. The relative fraction of such compounds is equal to

10^{-6} – 10^{-4} (see Table I).^{4,5} The products of combustion mixing with the atmosphere, form a long-lived formation which we shall refer to as the trail. Because nonequilibrium conditions are created some products of combustion interact chemically with separate atmospheric components. Among the reactions occur those in which sodium participates play a special role owing to the fact that the initial concentrations $[Na]_0$ in the trail are significantly higher than the atmospheric concentrations $[Na]_{atm}$. For Na and its compounds the kinetic scheme of reactions occurring in the nighttime trail at altitudes $z = 80$ – 100 km (the region of atmospheric nighttime emission of the NaD line) is not much different from the analogous scheme in the undisturbed atmosphere. Both these situations (the significant difference in the values of $[Na]_0$ and $[Na]_{atm}$ and the similarity of the kinetic schemes in the trail and in the atmosphere) result in the fact that at altitudes z in the range 80 to 100 km the concentration $[Na]$ in the trail will be several orders of magnitude higher than $[Na]_{atm}$ for some period of time. Correspondingly, for some period of time, the emission of the section of the atmosphere containing the trail should also be significantly stronger than the average atmospheric emission at the wavelength 589.3 nm.

TABLE I.

The typical values of the relative concentrations of exhaust gases.⁴

H ₂	CO	H ₂ O	CO ₂	HCl	N ₂	H	OH	Cl	Na	NaCl
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

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

The description of the evolution of the trail is a complicated gasdynamic-kinetic problem. Since we are more interested in the kinetic part of the problem, in what follows we shall use the simplified model of the dynamics described in Ref. 6. Briefly, it consists of the following. It is assumed that in the vertically disturbed

region of space the initial turbulent mixing of the products of combustion with the atmosphere proceeds rapidly, so that at the time $t = 0$ the concentration of atmospheric components in the trail is equal to that in the surrounding space. For simplicity the radial expansion of the trail is assumed to be of the form

$$R^2(t) = R_0^2 \left[1 + \frac{t}{\tau_d} \right], \quad (1)$$

where R_0 is the initial size of the trail. The quantity τ_d characterizes the rate of evolution of the trail. Over long times ($t/\tau \sim 100$), however, strictly speaking, τ_d cannot be regarded as the characteristic time of gas-dynamic processes because it depends on t .

The kinetic equations are constructed not for the concentrations of the reagents per unit volume, as is usually done, but rather for the quantity in the entire volume of the trail with thickness δz . On the one hand,

this approach makes it possible to avoid calculating the gas-dynamic processes; on the other hand, however, it gives an incomplete picture, since it permits determining only the average concentrations of the products of the chemical reactions. The characteristic expansion time of the trail at the initial stage ($t/\tau_d \leq 10-50$) is assumed to be equal to 2.5 s.

The reactions responsible for the change in the sodium-containing components in the trail are presented in Table II. The table also gives the rate constants of the processes and the characteristic lifetimes τ_{chem} for Na and its compounds.

TABLE II

The basic reactions in the nighttime trail involving sodium.

N	Reaction	$k, \text{cm}^{-3}\text{s}^{-1}$	τ_{chem}, s	References
1	$\text{Na} + \text{O}_3 \rightarrow \text{NaO} + \text{O}_2$	$3.1 \cdot 10^{-10}$	20	[7]
2	$\text{Na} + \text{O}_2 + \text{N}_2 \rightarrow \text{NaO}_2 + \text{N}_2$	$6.7 \cdot 10^{-31} \exp\left(\frac{290}{T}\right)$	$10-10^3$	[8]
3a	$\text{NaO} + \text{O} \rightarrow \text{Na} + \text{O}_2$	$3.7 \cdot 10^{-10}$	0.005-0.2	[9]
3b	$\rightarrow \text{Na}(\text{P}) + \text{O}_2$			
4	$\text{NaO} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{OH}$	$2.2 \cdot 10^{-10}$	0.001-0.01	[10]
5a	$\text{NaO} + \text{H}_2 \rightarrow \text{NaOH} + \text{H}$	$2.6 \cdot 10^{-11}$ $\frac{k_{5b} + k_{5c}}{k_5} > 0.2$	0.005-0.05	[10]
5b	$\rightarrow \text{Na} + \text{H}_2\text{O}$			
5c	$\rightarrow \text{Na}(\text{P}) + \text{H}_2\text{O}$			
6	$\text{NaO} + \text{HCl} \rightarrow \text{NaCl} + \text{OH}$	$2 \cdot 10^{-10}$	0.001-0.01	[11]
7	$\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$	$2 \cdot 10^{-10}$	0.001-0.01	[11]
8	$\text{NaO}_2 + \text{HCl} \rightarrow \text{NaCl} + \text{HO}_2$	$2.3 \cdot 10^{-10}$	0.001-0.01	[12]

To estimate τ_{chem} the atmospheric concentrations were employed for $[\text{O}_3]$, $[\text{O}_2]$, $[\text{O}]$, and $[\text{N}_2]$ and the initial concentrations of the products of combustion in the trail, in accordance with the relative fractions given in Table I, were used for $[\text{H}_2\text{O}]$, $[\text{H}_2]$, and $[\text{HCl}]$ (the altitude distribution of the latter is discussed below). All constants were corrected taking into account the latest experimental data. It is interesting that in the trail, unlike the undisturbed atmosphere, there is an additional channel (5c) for excitation of $\text{Na}(\text{P})$. Since the value of k_{5c} has still not been measured this channel is ignored below.

One can see from Table II that the processes 3-8 proceed practically instantaneously with respect to both the reactions 1 and 2 and the turbulent mixing process. As a result of this at the times of interest here ($t \geq \tau_d$) the concentrations are always quasistationary in the fast processes. It is also important that NaOH and NaO_2 are transformed very rapidly into NaCl which is chemically

inert under nighttime conditions. Of course, this affects the rate of decay in the $\text{Na}(\text{P})$ emission intensity, but it substantially simplifies the description of the chemical kinetics, because there is no need to follow the change in the components NaO_2 and NaOH.

Based on the assumptions and remarks made above, the system of equations for describing the kinetics of excitation of $\text{Na}(\text{P})$ in the trail has the form

$$\frac{d\{\text{NaO}\}}{dt} = k_1[\text{O}_3]\{\text{Na}\} - (k_3[\text{O}] + k_4[\text{H}_2\text{O}] + k_5[\text{H}_2] + k_7[\text{HCl}])\{\text{NaO}\}; \quad (2)$$

$$\frac{d\{\text{Na}\}}{dt} = -(k_1[\text{O}_3] + k_2[\text{O}_2][\text{N}_2])\{\text{Na}\} + (k_3[\text{O}] + 0.2k_5[\text{H}_2])\{\text{NaO}\}.$$

In Eq. (2)

$$\{X\} \equiv \int_0^{R(t)} [X(r, t)] 2\pi r dr \delta z$$

is the number of molecules of type X in a volume of the trail with thickness δz and

$$[\overline{Y}] = \frac{[Y]_0 R_0^2}{R^2(t)} \tag{3}$$

is the average concentration of molecules of type Y in the trail at the time t . We note that all $[\overline{Y}]$ in the system (2) depend only on the gas-dynamic processes.

The condition quasistationariness for the first of equations (2) means that $\frac{d[NaO]}{dt} = 0$. This gives immediately

$$\{NaO\} = \frac{k_1 [O_3] \{Na\}}{k_3 [O] + k_4 [H_2O] + k_5 [H_2] + k_7 [HCl]} \tag{4}$$

Using Eq. (1) with a fixed value of τ_d as well as Eqs. (3) and (4) we obtain the solution of the second equation of the system (2):

$$\{Na\} = \{Na\}_0 e^{-k_2 [O_2] [Na] t} \times \left(1 + \frac{t}{\tau_d} \frac{k_3 [O]}{k_3 [O] + k_4 [H_2O]_0 + k_5 [H_2]_0 + k_7 [HCl]_0} \right)^{-\tau_d a}$$

z, km	80	82.5	85	87.5	90	92.5	95	97.5	100
$[Na]_0, \text{cm}^{-3}$	1.0+8	8.4+7	7.2+7	5.8+7	4.2+7	3.5+7	2.8+7	2.2+7	1.5+7

$$a + b \equiv a \cdot 10^b$$

The distribution was obtained with a relative sodium concentration of $2 \cdot 10^{-6}$ in the products of combustion. For comparison we point out that the maximum value of $[Na]_{atm}$ occurs at $z = 90$ km and is equal to $\approx 5 \cdot 10^3 \text{ cm}^{-3}$ (Ref. 1).

The total relative concentration of $[H_2O]_0$, $[H_2]_0$, and $[HCl]_0$ in the range 0.5–0.6 (Ref. 4). This fact together with the data of Table II make it possible to derive the following relation:

$$k_4 [H_2O]_0 + k_5 [H_2]_0 + k_7 [HCl]_0 \approx 4 \cdot 10^{-5} [Na]_0$$

As regards the altitude distributions of $[O]$ and $[O_3]$ the same profile as that used in Ref. 6 was employed for $[O]$, while the $[O_3]$ profile was taken from Ref. 13.

The quantity ε , as a function of z and t , as well as the intensity of the emission of the trail in the NaD line along the z axis is presented in Table III.

where

$$a = \frac{k_1 [O_3]}{k_3 [O]} (k_4 [H_2O]_0 + 0.8 k_5 [H_2]_0 + k_7 [HCl]_0) \tag{5}$$

The average concentrations of $[\overline{Na}]$ and $[\overline{NaO}]$ are determined with the help of Eqs. (4) and (5) according to the formulas

$$[\overline{Na}] = \frac{\{Na\}}{\pi R^2(t) \delta z}, \quad [\overline{NaO}] = \frac{\{NaO\}}{\pi R^2(t) \delta z}$$

The calculation of the characteristics of the emission is connected directly with the calculation of the source function

$$\frac{\varepsilon}{h\nu} = A[Na(^2P)] = k_{3b} [O] [\overline{NaO}],$$

where ε is the energy emitted in the NaD line per unit time per unit volume in all directions; $h\nu$ is the energy of the photon in the optical transition $Na(^2P \rightarrow ^2S)$; and, A is the Einstein spontaneous coefficient. The expression for the intensity of the trail at $\lambda = 589.3$ nm in the direction l in the three-dimensional approximation has the form

$$I = \frac{h\nu}{4\pi} k_3 [O] \int [\overline{NaO}] dl$$

The values of $[\overline{NaO}]$ were determined for the following model distribution of $[Na]_0$ as a function of the altitude z .

The last column gives for comparison the analogous quantities characterizing the atmospheric nighttime emission of Na. The rate constants for the excitation of Na in the channel 3b, required for the calculations, were determined, as customarily done, from the formula $k_{3b} = k_3/6$ (Ref. 13).

One can see from Table III that excited sodium is formed in the trail primarily near $z = 90$ km, like in the atmosphere. The fundamental difference, however, lies in the fact that for the time interval presented the source function in the trail is two to three orders of magnitude larger than the source function in the undisturbed atmosphere. Low altitudes ($z < 85$ km) play a small role for two reasons. First, the removal of Na via the reactions 2 and 8 with the formation of NaCl, which is inert under nighttime conditions, is very efficient at low altitudes. Second, for $z < 85$ km the ratio

$$\frac{k_3[\text{O}]}{k_3[\text{O}] + k_4[\text{H}_2\text{O}]_0 + k_5[\text{H}_2]_0 + k_7[\text{HCl}]_0},$$

characterizing in the reactions 1–8 the degree of the regeneration of atmospheric sodium, is much less than unity. At high altitudes ($z \geq 97.5$ km) these

factors are much less significant, but the rapid decrease in $[\text{O}_3]$ as z increases becomes important. As regard I , it is much greater than the intensity of the atmospheric emission right up to $t = 100$ s (it should be noted that the values of I for $t < 5$ s are not entirely correct — along the z axis the trail is not optically thin during the first several seconds).

TABLE III

The source function $\varepsilon/h\nu$ (photons/($\text{cm}^3 \cdot \text{s}$)) and the emission intensity, $I(R, R \equiv 10^6$ photons/($\text{cm}^3 \cdot \text{s}$)) of the NaD line in the trail

z, km	t, s							Atmo- sphere, [1]
	0	5	10	25	50	75	100	
80	1.6+3	7.7+2	3.7+2	37	0.9	«1	«1	1
82.5	3.0+3	2.7+3	1.9+3	6.3+2	1.1+2	18	3	7
85	1.6+4	1.2+4	1.0+4	4.7+3	1.5+3	5.0+3	2.1+2	23
87.5	2.5+4	1.9+4	1.5+4	8.0+3	3.3+3	1.6+3	8.7+2	87
90	5.0+4	3.3+4	2.4+4	1.3+4	5.7+3	3.3+3	2.2+3	87
92.5	4.0+4	2.8+4	2.3+4	1.2+4	6.7+3	4.3+3	3.3+3	70
95	1.6+4	1.1+4	9.0+3	5.3+3	3.0+3	2.1+3	1.6+3	40
97.5	3.7+3	2.7+3	2.0+3	1.2+3	7.0+2	5.0+2	4.0+2	8
100	1.2+3	6.3+2	4.3+2	2.4+2	1.4+2	1.0+2	70	-
<i>I</i>	4.0+4	3.0+4	2.5+4	1.2+4	6.0+3	3.5+3	2.5+3	1.0+2

Extension of the proposed mechanism to times exceeding 100 s can result in significant errors owing to the fact that $\tau_d \approx \text{const}$ at times such that $t/\tau_d < 100$. Since in this model it is assumed that the products of combustion mix rapidly (relative to kinetic process) with the atmosphere the values of the intensity obtained for the trail are the maximum values. If the limiting stage is the gas-dynamic stage, then the intensities under otherwise equal conditions will be lower than the values presented in Table III.

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