

NUMERICAL SIMULATION OF THE FORMATION OF OZONE AND NITROGEN OXIDES IN A PULSED MICROWAVE DISCHARGE IN AIR

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The plasma-chemical evolution of the products of a pulsed microwave discharge in the atmosphere at altitudes of 30–60 km was studied theoretically. It was found that intense dissociation of molecules occurs in the discharge, and the rates of formation of oxygen and nitrogen atoms were found. The main products of chemical evolution at the post-discharge stage are nitrogen oxides and ozone in the ratio $\approx 10^{-2}$. This factor is affected primarily by the temperature of the gas. As the gas temperature increases the concentration of nitrogen oxides increases and the concentration of ozone decreases.

1. Artificial ionization of air by pulsed microwave radiation, here to for studied under laboratory conditions, can be realized in the atmosphere at altitudes of 30–60 km in intersecting beams of radio waves.¹ The acceleration of electrons in the field of a powerful radio wave will result in both ionization microwave discharge, which creates an artificially ionized region (AIR), the composition of the atmosphere will change owing to the formation of chemically active nitrogen atoms N and oxygen atoms O. The main products of the interaction of O and N atoms with atmospheric gases are ozone O₃ and nitrogen oxides NO_x, which can destroy ozone in catalytic reactions² as well as prevent the destruction of ozone.³ The production of ozone by a discharge in pure oxygen was studied theoretically and experimentally in Ref. 4. One possibility of formation of nitrogen oxide NO was studied in Ref. 1. Laboratory investigations of discharges produced in air by a long train of microwave pulses have shown that nitrogen oxides are formed more efficiently, and they have raised the question of the ecological consequences of such experiments in the atmosphere.⁵ The purpose of this work is to investigate the plasma-chemical processes accompanying the production and maintenance of an AIR and the possibilities for optimizing the parameters of the discharge in order to reduce the production of nitrogen oxides.

2. We shall study the following problem of the chemical evolution of the air mixture in AIR. At the first stage the primary breakdown pulse, for which the optimal conditions of ionization are satisfied (the frequency of the radiation $\omega \approx 1.7 \cdot 10^{-7} N_m$, the amplitude of the electric field $E_1 \approx 5E_c$, N_m is the number density of air molecules in cm⁻³, and E_c is the critical field at which breakdown occurs), creates over a short time interval τ_1 an electron density n_e ,

averaged over the volume of the AIR, of about 0.1 of the critical value n_c for the frequency ω .¹ At the second stage the maintenance microwave pulse of width τ_2 and amplitude $E_2 \sim E_c$ acts on the AIR. The hot electrons excite, dissociate, and ionize the main molecular constituents of air N₂ and O₂. At the third stage, after the maintenance pulse ends, rapid cooling occurs and the free electrons disappear,¹ and chemical evolution of the gas mixture with participation of the products of the discharge, resulting in the formation of ozone and nitrogen oxides, continues. The evolution of the composition of the mixture is described by the system of equations of chemical kinetics for the ground states of the components O, N, O₃, NO, NO₂, NO₃, and the excited states O²(¹Δ_g), N(⁻²D), which interact with N₂, O₂, and one another in 17 reactions, which are most responsible for the formation and destruction of O₃ and NO_x. The list of reactions is given in Table 1.

The rate of excitation, dissociation, and ionization was calculated from the solution of the kinetic equation for the electron energy distribution function in the high-frequency approximation¹⁰ using cross sections from Refs. 11 and 12. Figure 1 shows the rates of formation of the atoms $v_{N,O}$ and their formation energy $W_{N,O}$ as a function of the electric field. We note that the rate of formation of O atoms accompanying the dissociation of molecules by electron impact via the excitation of the Schumann-Runge and Tertsberg continua is much higher than the rate of formation of O accompanying dissociative attachment.

The energy of formation is defined as the ratio of the energy absorbed from the microwave field to the number of atoms produced. One can see from Fig. 1 that when $E < E_c$ it is very difficult for N atoms to form; this reflects the difference of the dissociation energy threshold of N₂ (≈ 10 eV) and that of O₂ (≈ 5 eV).

TABLE I.

List of the reactions employed and the rate constants (in units of $cm^3 \cdot s^{-1}$ for bimolecular reactions and $cm^6 \cdot s^{-1}$ for trimolecular reactions).

Reaction	k_i	References
$O + O_2 + M \Rightarrow O_3 + M$	$1.1(-34) \cdot e^{510/T}$	[6]
$O + O + M \Rightarrow O_2 + M$	$4.7(-33) (300/T)^2$	[7]
$O + O_3 \Rightarrow 2O_2$	$1.9(-11) \cdot e^{-2300/T}$	[4]
$O_3 + O_2(^1\Delta_g) \Rightarrow O + 2O_2$	$5.2(-11) \cdot e^{-2840/T}$	[4]
$O_2 + O_2(^1\Delta_g) \Rightarrow 2O_2$	$2.2(-18) \left(\frac{T}{300}\right)^{0.8}$	[4]
$N + O_2 \Rightarrow NO + O$	$5.5(-12) \cdot e^{-3220/T}$	[6]
$N + NO \Rightarrow N_2 + O$	$8.2(-11) \cdot e^{-410/T}$	[6]
$O_3 + N \Rightarrow NO + O_2$	$5(-12) \cdot e^{-650/T}$	[6]
$O + NO_2 \Rightarrow NO + O_2$	$3.2(-11) \cdot e^{-300/T}$	[2]
$O_3 + NO \Rightarrow NO_2 + O$	$2.1(-12) \cdot e^{-1450/T}$	[6]
$O_3 + NO_2 \Rightarrow NO_3 + O_2$	$1.2(-13) \cdot e^{-2450/T}$	[6]
$N(^2D) + O_2 \Rightarrow NO + O$	6 (-12)	[8]
$N(^2D) + O_2 \Rightarrow N + O_2$	6 (-12)	[8]
$N(^2D) + NO \Rightarrow N_2 + O$	1 (-10)	[9]
$O + NO + M \Rightarrow NO_2 + M$	$4(-33) \cdot e^{940/T}$	[2]
$N + N + M \Rightarrow N_2 + M$	$8.3(-34) \cdot e^{500/T}$	[2]
$N + O + M \Rightarrow NO + M$	$9.1(-33) \left(\frac{300}{T}\right)^{1.5}$	[7]
	$(-n) = 10^{-n}$	

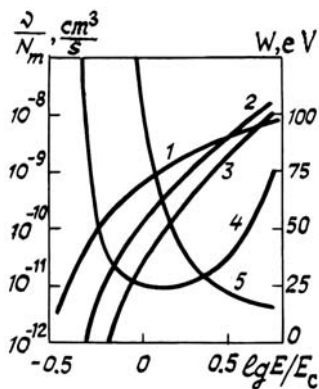


FIG. 1. The dependence of the rate of formation v (O (1), $N(^4S)$ (2), and $N(^2D)$ (3)) and the energy of formation W of an oxygen atom (4) and a nitrogen atom. (5) on the field strength E .

When the electrons interact with the gas for a sufficiently long period of time they transfer to the neutrals energy comparable to the internal energy of the neutrals. On the one hand this can change the electron energy distribution function and on the other it can substantially affect the rate of chemical reactions, both owing to the participation of excited molecules in the reactions and owing to the increase in the translational temperature T as the excited levels are quenched. The temperature dependences of the coefficients k_i are such that as the temperature T increases the rates of the main reactions in which O_3 is formed decrease while those in which NO_x are formed increase. An increase in the vibrational temperature of the molecules also leads to a similar result.¹ Thus in order to minimize the production of nitrogen oxides the width of the maintenance pulse must be less than the heating time of the molecules τ_h . We shall define τ_h as the time over which the electrons transfer to the molecules energy equal to 10% of the kinetic energy of the molecules:

$$\tau_h = \frac{N \epsilon_m}{\delta_e \nu_e n_c \epsilon_e} \tag{1}$$

Where $\epsilon_{e,m}$ are the average kinetic energy of the electrons and the molecules and ν_e and δ_e are the electron collision frequency and the average relative energy transferred in a collision. For $E = E_c$ and $T = 220$ K, according to Eq. (1), $\tau_h \approx 10^{29} / N_m^2$.

The computing time in the post-discharge stage did not exceed 200 s, which is sufficient time for all direct products of the discharge to react. However this time interval is too short to neglect the effect of photolysis by solar ultraviolet radiation and interaction with minor constituents of the atmosphere such as OH , CH_4 , Cl , and others.

3. The system of equations of chemical kinetics that describes the processes studied previously was integrated with different values of the parameters ω , E_2 , τ_2 , and T . We shall characterize the relative efficiency of formation of nitrogen oxides and ozone by the quantity

$$\delta = [NO_x] / [O_3],$$

where $[NO_x]$ is the sum of the concentrations of NO , NO_2 , and NO_3 . In the average atmosphere $\delta = 10^{-2} \div 10^{-3}$ (Ref. 1). Figure 2 shows an example of the time dependence of the concentrations of different components at an altitude of 40 km; the calculations were performed with $E_2 = E_c$, $\tau_1 + \tau_2 = \tau_H = 30 \mu s$, $T = 240$ K. One can see that the atomic oxygen forming when O_2 dissociates is completely transformed into O_3 (curves 5 and 1). Atomic nitrogen partially transforms into NO , which completely transforms into NO_2 (curves 6, 2, and 3, respectively). At the completion of the post-discharge stage $\delta = 1.5 \cdot 10^{-2}$.

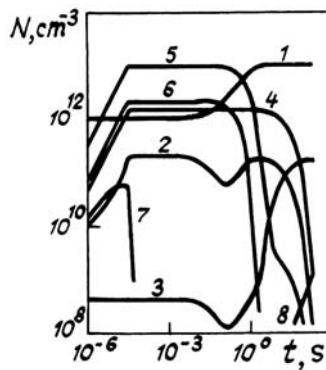


FIG. 2. The evolution of the concentrations of the constituents of the gas mixture: O_3 (1), NO (2), NO_2 (3), $O(2\Delta^1)_g$ (4), O (5), $N(S^4)$ (6), $N(2D)$ (7), and NO_3 (8).

Based on the dependences $W(E)$ shown in Fig. 1 one would expect that when $E_2 < E_c \delta$ will decrease. However the calculations performed for $E_2 < E_c$ as well as for other values of the parameters did not give a significant decrease of δ . Moreover, when the temperature increases significantly (up to $T \sim 500$ K) atomic oxygen is only partially converted into ozone, and the efficiency of the conversion of atomic nitrogen into nitrogen oxides increases sharply. In addition $\delta \gg 1$ and according to preliminary results obtained in Ref. 13 complete annihilation of ozone is possible.

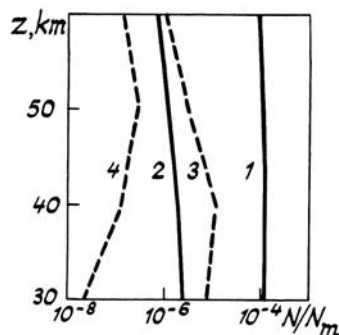


FIG. 3. The altitude dependence of the relative concentrations of ozone and nitrogen oxides formed in the discharge (curves 1 and 2, respectively) and existing under natural conditions (O_3 (3) and NO_x (4)).

Figure 3 shows the altitude dependence of the concentrations of NO_x and O_3 normalized to N_m . This dependence was calculated for the optimal values of the parameters of the ionizing pulse and $E_2 = E_c$ and $\tau_1 + \tau_2 = \tau_h$.

One can see from the figure that the relative concentrations change insignificantly at altitudes of 30–60 km. For comparison the figure also shows these quantities under natural conditions based on data presented in Ref. 1.

For qualitative analysis of the system of equations of chemical kinetics the reactions employed can be divided into several basic groups.

First, there are fast reactions in which excited nitrogen atoms participate $R12$ – $R14$. They occur already at the stage at which the discharge is maintained and can significantly affect $[NO]$. In the group of reactions involving pure oxygen $R1$ – $R5$ the main reactions are $R1$ and $R3$, whose effect is described by the system of equations studied in the Appendix. At the comparatively low temperatures in the natural atmosphere the relation (A4) is satisfied and atomic oxygen is completely converted into ozone. As the temperature increases the rate of the reaction $R3$ increases rapidly and ozone is annihilated by atomic oxygen. As a result the ozone content settles at some low level and then, if nitrogen oxides are present, ozone can be completely annihilated.

The main reactions in which atomic nitrogen is converted into nitrogen oxides are the reactions $R6$ – $R8$, whose effect is also described by the system (A1) (under the condition that the ozone concentration remains constant). Since the conditions (A3) are satisfied the asymptotic value of the concentration is established:

$$[NO] = \frac{k_6}{k_7} [O_2] + \frac{k_8}{k_7} [O_3]. \quad (2)$$

One can see from the relation (2) that $\delta > k_8/k_7 \approx 2 \cdot 10^{-2}$ at $T = 220$ K. As the temperature increases the ratios k_6/k_7 , k_8/k_7 , and together with these ratios δ also increase rapidly. The value of δ can decrease somewhat owing to the fact that the conversion of atomic oxygen into ozone is slower than the conversion of atomic nitrogen into ozone. This difference increases with altitude, since the reaction $R1$ is a three-body reaction and its characteristic time is inversely proportional to the squared neutrals concentration. As one can see from Fig. 3, however, the gain here is not too significant.

Comparing the results of qualitative analysis with those obtained by numerical modeling shows that the remaining reactions presented in Table I introduce quantitative corrections to the NO_x and O_3 content without changing fundamentally the ratio of their concentrations under the conditions studied here.

The efficiency of the dissociation of O_2 and the formation of O can be increased significantly with collisional deactivation of excited molecular nitrogen.^{14,15} Since the deactivation time at the altitudes studied is of the order of 10^{-6} – 10^{-4} s, the effect of the excited N_2 molecules can be taken into account by increasing v_0 . The existing experimental data on the possible channels for deactivation of the excited states of N_2 are insufficient for studying in detail their contribution to the plasma-chemical processes. If it is assumed that the deactivation of each nitrogen molecule in the states $A_3\Sigma_u^+$ and $B^3\Pi_g$ results in the formation of two oxygen atoms, then the rate v_0 is 2 to 2.5 times higher at $E_2 = E_c$. The basic results of the chemical evolution of the mixture remain the same: atomic oxygen is almost completely converted into

ozone and nitrogen oxides with a relative content $\delta \sim 10^{-2}$ are formed.

4. The results obtained show that the temperature of the gas is the main factor determining the formation of NO_x and O_3 accompanying microwave breakdown of the atmosphere. To minimize the formation of nitrogen oxides in the process of producing and maintaining the AIR, conditions under which there is not enough time for the field to heat up the gas must be maintained. Estimates show that in the regime studied in Ref. 1, in which the AIR is maintained by a train of microwave pulses, the total time of interaction of the radiation and the gas during the period when the gas is removed by wind from the volume of the AIR is shorter than the heating time τ_H for $z \geq 40$ km. Calculations modeling the maintenance of AIR by a train of pulses with simultaneous removal of the gas by wind were performed. For realistic values of the characteristic parameters and for interaction distributed in time virtually the same results are obtained as in the case where one wide pulse interacts with the gas followed by chemical relaxation. It is useful to make a detailed study of the plasma-chemical processes as a function of the repetition frequency and width of the maintenance pulses and the rate of removal of the gas by wind when choosing specific values for the parameters of the excitation setup.

Analogous calculations of the chemical composition of AIR can also be performed for other methods of generating the AIR. In particular, the possibility of artificial ionization of the atmosphere at altitudes of 60–70 km by pulses in the VR range, which are emitted by the same ground-based installation, was studied in Ref. 16. The characteristic features of the process in this case are that an electron density significantly lower than the critical density is established and the duration of the interaction of the radiation with the atmosphere in order to maintain the AIR is much shorter than the heating time. Under these conditions for creating an AIR the concentration of the ozone and nitrogen oxides formed is lower than their concentration under natural conditions.

The results obtained above can be used as the initial conditions for studying long-time chemical evolution of the products of a discharge in the atmosphere. In so doing a more complete system of equations should be used and transport processes should be taken into account.

5. In conclusion we shall summarize the main results.

At the temperatures existing in the atmosphere at altitudes of 30–60 km the atomic oxygen formed as a result of a microwave discharge is completely converted into ozone. Nitrogen oxides with concentration $[\text{NO}_x] \geq 10^{-2}[\text{O}_3]$ are formed simultaneously. The ozone concentration reached with an excitation time equal to the heating time of the gas is $[\text{O}_3] \approx 10^{-4} N_m$.

The increase in the temperature of the gas accompanying absorption of the exciting radiation decreases the efficiency of formation of ozone and gives rise to an increase of the concentration of nitrogen

oxides. When the temperature increases up to $T \sim 500$ K complete annihilation of ozone is possible.

The results of this work could be useful in evaluating the ecological consequences of the formation of an AIR in the atmosphere by intense radio waves.

Application. The change in the concentrations $x(t)$ and $y(t)$ of the reacting components (O and O_3 in the reactions R1 and R3 and N and NO in the reactions R6–R8) is described by the system

$$\begin{aligned} \frac{\partial x}{\partial t} &= - (a + by) \cdot x \\ \frac{\partial y}{\partial t} &= (a - by) \cdot x \end{aligned} \quad (\text{A1})$$

$$x|_{t=0} = x_0; \quad y|_{t=0} = y_0; \quad a, b > 0; \quad x, y \geq 0.$$

Since the coefficients a and b and the functions x and y are positive it is obvious from Eqs. (A1) that the functions x and y sought are monotonic and that in the limit $t \rightarrow \infty$ $x \rightarrow 0$ and y approaches an asymptotic value y_∞ .

Dividing the equations of the system [A1] by one another and integrating the result we obtain the trajectory of the system in the (x, y) plane:

$$y - y_0 + \frac{2a}{b} \ln \frac{a - by}{a - by_0} = x - x_0. \quad (\text{A2})$$

The value of y_∞ can be obtained from Eq. (A.2) by setting $x = 0$. If the relation

$$x_0 \gg y_0, \quad a/b, \quad (\text{A3})$$

is satisfied, then we find from Eq. (A.2) that in the limit $t \rightarrow \infty$ $y_\infty \approx a/b$. If

$$y_0 < x_0 \ll a/b \quad (\text{A4})$$

the component x is converted completely into y and $y_\infty \approx x_0$.

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