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KINETIC COEFFICIENTS FOR ELECTRONS IN AIR IN AN HF ELECTRIC

FIELD

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The characteristics of a low-temperature air plasma created by an hf electric field are calculated.

The form of the electron distribution over energy and values of the related electron kinetic coefficients in air in an hf field are of interest in connection with studies of air breakdown by an hf field, interaction of hf radiation with the ionosphere, etc. [1-3]. The present study will calculate kinetic constants in dry air (i.e., a mixture  $N_2:0_2 = 8:2$ ) for the case where the frequency of field variation  $\omega$  is significantly higher than the transport frequency of electron interaction with molecules v. The calculation was performed for a wide range of the parameter  $E/\omega$ , where E is the intensity of the electric field. The effect of oscillatory excitation of oxygen and nitrogen molecules on the results obtained was studied.

The Boltzmann equation was solved numerically for the zeroth harmonic of the electron energy distribution function f(u), which for the case  $\omega >> \nu$  can be written in the form

$$\left(\sum_{j} y_{j}k_{ij} - 0, 2k_{ad}\right) f u^{1/2} \left(\frac{2e}{m}\right)^{-1/2} - \frac{1}{3} \frac{2e}{m} \left(\frac{E}{\omega}\right)^{2} \times \\ \times \frac{\partial}{\partial u} \left(u^{2} \frac{\partial f}{\partial u} \sum_{j} y_{j}Q_{it}\right) - \frac{\partial}{\partial u} \left[u^{2} \left(f + \frac{kT}{e} \frac{\partial f}{\partial u}\right) \sum_{j} y_{j}Q_{jt}\right] = St_{1}f + St_{2}f.$$

$$(1)$$

.

The electron energy u is expressed in eV. The collision integral St<sub>1</sub>f describes inelastic collisions which do not lead to a change in the number of electrons (excitation of rotational, oscillatory, and electron levels, collisions of the second type), while Staf describes processes leading to change in the number of electrons (ionization and dissociative adhesion of electrons to an oxygen molecule):

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$$St_{2}f = \sum_{i} y_{i} \left[ Q_{ii} \left( u + u_{ii} \right) \left( u + u_{ii} \right) f \left( u + u_{ii} \right) - Q_{ii} \left( u \right) uf \left( u \right) + \delta \left( u \right) k_{ii} \left( \frac{2e}{m} \right)^{-1/2} \right] - 0.2Q_{ad} \left( u \right) uf \left( u \right).$$
(1')

The constants kij and kad in Eqs. (1) and (1') are averaged over the energy distribution function, i.e., are independent of energy. The form of  $St_2f$  assumes that secondary electrons are generated with zero energy. The validity of this assumption was evaluated in [4]. The first term on the left of Eq. (1) is also related to appearance and disappearance of electrons. The form of Eq. (1) and the necessity of considering electron multiplication were considered in greater detail in [4].

The distribution function is normalized to satisfy the condition

$$\int_{0}^{\infty} f(u) u^{1/2} du = 1.$$

We will also note that the integral criterion for applicability of expansion over harmonics, in the framework of which Eq. (1) was derived, is the condition  $u \gg u_0$ , where u is the mean electron energy and  $u_0$  is the energy of electron oscillations.

The sections for electron interaction with nitrogen molecules were chosen as in [4], while the sections for oxygen were taken from [5]. It should be noted that at present there exists a high degree of uncertainty in the normalization of the sections for oscillatory excitation of nitrogen. The sections used in the present study were taken from [6]. Later studies [7, 8] proposed increasing the value of these sections by 1.9 times, as compared to [6]. Such an increase could have a significant effect on the dependence of the rate constants of processes with a high threshold on the degree of oscillatory excitation. However, the grounds for such an increase are still not sufficiently convincing. Moreover, study of the effect of the value of the sections on kinetic coefficients is a separate problem, beyond the scale of the present study.

In describing collisions of electrons with oscillatorily excited nitrogen molecules transitions between various oscillatory levels were considered ( $N_2$  (v = i)  $\neq N_2$  (v = j),  $i = 0, 1, \ldots, 8, j = i + 1, \ldots, 8$ ) together with elastic scattering on oscillatorily excited molecules. Values of the corresponding sections were taken from [9]. For oxygen molecules, in light of the smallness of the oscillatory sections only transitions  $O_2$  (v = 0)  $\neq O_2$  (v = j), j = 1, 2, 3 were considered, and sections of the reverse processes were found from the principle of detailed equilibrium. The population distribution over oscillatory levels was considered Boltzmann-like with a specified oscillatory temperature  $T_v$ .

The energy distribution function determined in this manner was used to calculate constants for dissociative adhesion of electrons to oscillatorily excited  $O_2$  molecules and to  $O_2$  in the state  $b^1\Sigma_g^+$ . The sections for these processes were taken from [10]. The constant for nitrogen ionization from the state  $A^3\Sigma_u^+$  was also calculated. This section was taken from [11]. The method used for numerical solution of the Boltzmann equation with consideration of electron multiplication in the ionization process was described in detail in [4]. Consideration of electron adhesion to oxygen and collisions with oscillatorily excited molecules leads to the addition of new terms to the equation, which do not change its form in principle. Therefore, the method described in [4] was used to solve Eq. (1) numerically.

Table 1 presents values of the rate constants for the most important processes of electron interaction with N<sub>2</sub> and O<sub>2</sub> molecules as a function of the parameter  $E/\omega$ . For processes with a high threshold results are presented only for T<sub>v</sub> = 300°K, since their dependences on T<sub>v</sub> are identical in character (see below). We will consider in more detail the calculated dependence of the air ionization constant  $k_i = 0.8 k_i (N_2) + 0.2 k_i (O_2)$ . An expression for the ionization frequency  $v_i$  which appears widely in the literature (see, for example, [1]) is

$$v_i = 8,35 \cdot 10^{-4} \, p \left( E_e / p \right)^{5,34},\tag{2}$$

where p is the pressure in mm Hg,  $E_e = Ev/(\omega^2 + v^2)^{1/2}$ ,  $v = 5.3 \cdot 10^9$  p. Equation (2) was first proposed in a somewhat different form in [2] and is based on experimental results. An expression proposed in [2] also describes the dependence of  $v_i$  on nitrogen oscillatory temperature (it is assumed that  $T_v = T$ ):

$$v_i(T_v) = v_i(300) \left[ 1 - \exp\left(-\frac{3395}{T_v}\right) \right]^{-2.67},$$
 (3)

TABLE 1. Rate Constants of Certain Processes,  $cm^3/sec$ , vs Parameter E/ $\omega$ , V·sec/cm, for Various Values of T<sub>v</sub>. The Notation 5.0 (-10) Denotes 5.0·10<sup>-10</sup>

T <sub>v</sub>	Ε/ω								
	5 (-10)	f1 (→9)	2 (-9)	5 (9)	1 (-8)	2 (8)	5 (8)	7 (8)	
$N_2 + e \rightarrow N_2 (A^3 \Sigma_{\mu}^+) + e$									
300	3,6(-23)  7,9(-18)  1,6(-13) 5,5(-11) 3,3(-10) 9,3(-10) 1,1(-9)   1,0(-9)								
	$N_2 + e \rightarrow N_2^+ + e + e$								
300	[ 0	0	2,0(—19)	2,9(-13)	2,9(-11)	8,1(-10)	1,2(8)	2,0(-8)	
			$N_2 (A^3 \Sigma_{\mu}^2)$	$(-) + e \rightarrow N$	$\frac{1}{2} + e + e$				
300	0	1,2(-20)	5,4(-15)	1,4(-11)	2,0(-10)	1,5(-9)	7,6(9)	1,0(8)	
			$O_2 + $	$e \rightarrow O_2 (B^3)$	$(\overline{z_u}) + e$				
300	1,3(14)	4,5(—13)	2,4(-12)	5,0(-11)	[1,0(—9)	2,1(9)	2,3(-9)	2,1(9)	
300	1 0	13.9(-19)	$0_2 + 14,8(-14)$	$e \to O_2 (^{\circ}II)$ 15,3(-11)	(g) + e (5.3(-10)	2,7(-9)	1,0(8)	1,2(8)	
		1., ( - )	O <sub>9</sub> -	$+e \rightarrow 0^+_0 -$	- e + e	,			
300	0	1 0	[9,2(—18)	4,0(—13)	) 1,8(-11)	3,6(10)	6,0(9)	1,0(8)	
$O_2 + e \rightarrow O_2 (a^1 \Delta_g) - e$									
300 3000	1,4(-12) 3,0(-12)	1,4(-11)  7,5(-12)	$ ^{2,6}(-11) _{2,3}(-11) _{2$	1,7(-10) 2,1(-10)	4,6(-10)   4,9(-10)	6,4(-10) 6,5(-10)	5,8(-10) 5,8(-10)	5,4(-10) 5,4(-10)	
5000	1,4(-11)	2,0(-11)	4,9(-11)	2,6(-10)	5,1(-10)	6,5(-10)	5,8(-10)	5,4(-10)	
$O_2 + e \rightarrow O_2 (b^1 \Sigma_g^+) + e$									
300 3000	1,4(-14)  2,1(-13)	$ _{6,4(-13)}^{4,5(-13)}$	$ ^{2,5}(-12) _{4,0(-12)}$	5,0(-11) 6,2(-11)	1,3(-10) 1,4(-10)	1,9(-10) 1,9(-10)	1,8(-10) 1,8(-10)	1,6(-10) 1,6(-10)	
5000	2,5(-12)	3,9(-12)	1,2(-11)	7,7(—11)	1,5(—10)	1,9(-10)	1,8(10)	1,6(-10)	
300	(9.3(-23))	1.1(-17)	$O_2(v = 3,7(-14))$	$(0) + e \rightarrow 0$	2.9(-11)	3,4(-11)	11.9(-11)	[1,6(-11)]	
000	5,8(-17) 8,6(-15)	5,9(-15) 1,5(-13)	3,8(-13)	1,3(-11) 1,6(-11)	3,1(-11) 3,2(-11)	3,4(-11) 3,4(-11)	1,9(-11) 1,9(-11)	$1, \delta(-11)$ 1, 6(-11)	
			$O_2 (v =$	= 1) + <i>e</i> → (	0-+0		,		
300 3000	4,9(-22)	$ _{1,5(-16)}^{1,5(-16)} _{7,0(-14)}$	6,8(-13)	[6,0(-11)]	1,5(-10)	1,6(-10) 1,6(-10)	9,1(-11) 9,1(-11)	7,3(-11) 7,3(-11)	
5000	2,5(-13)	1,7(-12)	1,2(-11)	1,0(-10)	1,7(-10)	1,6(-10)	9,1(-11)	7,3(-11)	
000	10.07 00	17.0( 10)	$O_2(v = 10)$	$= 2) + e \rightarrow 0$	O= -¦- O	11 6 ( 10)	10 17 11	17 97 11)	
3000	3,9(-22) 2,3(-14)	1,2(-16) 2,2(-13)	1,3(-12) 5,0(-12)	1,0(-10)	1,7(-10)	1,6(-10)	9,1(-11) 9,1(-11)	7,3(-11) 7,3(-11)	
5000	11,6(-12)	4,4(-12)	2,0(-11)	(1,2(-10))	) 1,9(—10) ∩− ⊥ ∩	(µ, <b>0(</b> →10)	19,1(11)	µ1,3(—11)	
300	[5,6(-21)	4,7(-15)	3,3(-12)	$-37 + e^{-10}$	2,7(-10)	2,5(-10)	1,3(10)	[1,0(-10)]	
3000 5000	$ _{6,7(-12)}^{1,5(-13)}$	8,2(-13)  1,3(-11)	1,1(-11)   4,2(-11)	1,7(-10)   2,1(-10)	12,9(-10)   3,0(-10)	2,5(-10)   2,5(-10)	1,3(-10)   1,3(-10)	1,0(-10) 1,0(-10)	
$O_2(b^1\Sigma_a^+) + e + O^- + O$									
300	[8.0(-22)	[8,7(-16)]	2,0(-12)	1,4(10)	$[3,3(-10)]{2,5(-10)}$	[3,3(-10)]	1,8(-10)	(1,4(-10))	
<b>5000</b>	1,8(-12)	6,5(-12)	3,4(-11)	2,3(-10)	3,3(-10) 3,7(-10)	3,3(-10) 3,3(-10)	1,8(-10)	1,4(-10)	

where  $v_i$  (300) is the value of  $v_i$  at  $T_v = T = 300$  °K, i.e., the value obtained by using Eq. (2). Based on an analytical calculation of  $v_i$ , [3] concluded that the dependence  $v_i \sim E^{5 \cdot 34}$  was valid for field intensities up to five times the breakdown value. By breakdown field we understand here the field value at which the ionization frequency is comparable to the dissociative electron adhesion frequency to oxygen molecules (or  $k_i = 0.2k_{ad}$ ). Figure 1 shows a comparison of air ionization constants obtained from Eq. (2) for the condition  $\omega >> v$  and the present calculation. Also shown is the value 0.2  $k_{ad}$ . As follows from the figure, the calculated value of the breakdown field is equal to  $E_b/\omega \approx 7 \cdot 10^{-9}$  V·sec/cm. (Using the expressions of [3],  $E_b/\omega \approx 6 \cdot 10^{-9}$  V·sec/cm). The values of  $k_i$  calculated with Eq. (2) agree with the present calculation up to  $E/\omega \approx 20 \cdot 10^{-9}$  V·sec/cm, i.e., up to three times the breakdown field, not five, as indicated in [3]. On the basis of the calculated data, one can pro-



Fig. 1. Air ionization rate constant and electron dissociative adhesion constant for unexcited oxygen,  $cm^3/sec$ , vs  $E/\omega$ , V·sec/cm,  $T_V = 300^{\circ}K$ : 1)  $k_1$ , calculated with Eq. (2); 2)  $k_1$ , calculation of present study; 3) 0.2 $k_{ad}$ ; points, experiment [12]; dashed curve, recalculation of  $k_1$  from parameter E/N, V·cm<sup>2</sup>, to  $E/\omega$ .

pose another expression which describes  $k_i$  in the range  $5 \cdot 10^{-9}$  V·sec/cm  $\leq E/\omega \leq 50 \cdot 10^{-9}$  V·sec/cm to an accuracy of 10%:

$$k_i = 10^{-5,85-rac{14,88}{\sqrt{\gamma}}}, \quad \gamma = E/\omega \cdot 10^9.$$

Unfortunately, for the range of  $E/\omega$  values considered in the present study experimental data on  $k_i$  in air are practically absent. In the only study known to the present authors [12] in which the case  $\omega \gg \nu$  was realized, the range of  $E/\omega$  values considered overlaps the calculated range only slightly. Difference of the experimental values from calculated ones by a factor of two may have been caused by inaccuracy in the experimental determinations.

We will also consider the problem of recalculating  $k_i$  values upon transition from the parameter E/N to the parameter  $E/\omega$  where N is the number of particles per unit volume. As is well known, if v = const, the results obtained for a constant field at a given E/N coincide with those obtained for  $E/\omega = E/N/v/N$ . But if  $v(u) \neq const$ , as is the case for air, we may then take v = v(E/N), where v is the average value of v for a given E/N. A calculation of the electron energy distribution function for a constant field in air was performed, and the values of v found for each E/N\_were compared with the corresponding  $E/\omega$ . The quantity v was determined from the relationship  $v/N = (e/m)[(E/N)/v_{dr}]$ , where  $v_{dr}$  is the electron drift velocity. Figure 1 shows a conversion scale for E/N and corresponding  $k_1$  values. As is evident from the figure, the recalculated  $k_i$  values and those obtained by calculation for  $E/\omega$ agree well in the range  $10^{-15}$  V·cm<sup>2</sup>  $\leq$  E/N  $\leq$  5·10<sup>-15</sup> V·cm<sup>2</sup>, which corresponds to 7·10<sup>-9</sup> V·sec/  $cm \leq E/\omega \leq 30 \cdot 10^{-9}$  V·sec/cm. This agreement is related to the fact that in the E/N range in question the quantity  $\overline{v}(E/N) \approx \text{const} \approx 1.4 \cdot 10^{-7} \text{ N}$ . The fact that  $\overline{v} \approx \text{const}$  also provides a basis for using the effective field method  $E_e = Ev/(\omega^2 + v^2)^{1/2}$ . As has already been noted, in calculating the energy distribution function electron multiplication in the ionization process was considered. Naturally, such consideration is necessary at high values of  $E/\omega$ . Calculations showed that for air, electron multiplication must be considered beginning at  $E/\omega \approx$  $50 \cdot 10^{-9}$  V·sec/cm. Approximately 30% of the energy is then expended in ionization (see Fig. 2), which agrees well with the results of [1]. The calculation was performed for  $T_{\rm V}$  values from 300 to 5000°K (with T = 300°K). Control calculations were also performed with T =  $T_v$  = 3000°K and T = T<sub>v</sub> = 5000°K. It developed that beginning at  $E/\omega \approx 1-2 \cdot 10^{-9}$  V·sec/cm, the value of T had a weak effect on the calculated constant values.

As in the case of constant fields [9], the dependence of rate constants for processes with a high threshold (excitation of electron levels, ionization) on oscillatory temperature can be described by the general expression

$$k = k_0 \exp\left(\frac{c_1 \varepsilon_{N_2} + c_2 \varepsilon_{O_2}}{\gamma^2}\right), \qquad (4)$$



Fig. 2. Electron energy balance depending on E/N, V·sec/cm: 1) elastic + rotation; 2) vibrational levels of  $O_2$ ; 3) vibrational levels of  $N_2$ ; 4) electron levels; 5) ionization; a)  $T_V = 300^{\circ}$ K; b) 5000. Ordinate, %.



Fig. 3. Mean energy (curves 1-3) and electron oscillation energy, eV (curve 4), vs  $E/\omega$ : 1)  $T_v = 300^{\circ}$ K; 2) 3000; 3) 5000.

Fig. 4. Electron energy distribution function in air  $(E/\omega = 1 \cdot 10^{-9} \text{ V} \cdot \text{sec/cm})$ : 1) T = 300°K; 2) 3000; 3) 5000. U, eV.

where  $\varepsilon_{N_2,0_2} = \exp(-\hbar\omega_{N_2,0_2}/T_v)$ ;  $\hbar\omega_{N_2,0_2}$  are oscillatory N<sub>2</sub> and O<sub>2</sub> quanta, respectively; k<sub>0</sub> is the value of the constant at  $T_v = 300^{\circ}$ K. The values of c<sub>1</sub> and c<sub>2</sub> were found from calculations: c<sub>1</sub> = 18.8, c<sub>2</sub> = 0.53.

It is interesting to compare the  $T_v$  dependence of the constants obtained in this manner with Eq. (3). As is evident from the equations, there is a difference in principle between Eqs. (3) and (4). In Eq. (3) increase in vi with growth in  $T_v$  occurs identically for all values of field intensity, while it follows from Eq. (4) that with increase in the value of  $E/\omega$  the effect of  $T_v$  on the value of the constant becomes weaker. Apparently, the growth in  $v_i$  with increase in gas temperature, which has been observed in experiment and is reflected in Eq. (3), is produced by some mechanism other than increase in the fraction of high energy electrons due to collisions with oscillatory excited molecules.

Figure 3 shows the dependence of mean electron energy on  $E/\omega$  for various  $T_V$ . As follows from the figure, the condition  $u >> u_0$  is satisfied well over the  $E/\omega$  range considered. We will note an interesting feature in the behavior of u at  $0.6 \cdot 10^{-9}$  V·sec/cm  $\leq E/\omega \leq 3 \cdot 10^{-9}$  V·sec/cm: with increase in  $T_V$  from 300 to 3000°K u decreases. A similar result was obtained in [13] for electrons in a constant field in pure nitrogen, and in [14] for electrons in an hf field in nitrogen. This behavior of u is related to the fact that in the indicated  $E/\omega$  range the energy distribution function differs greatly from Maxwellian. This is illustrated

in Fig. 4. At  $T_v = 300$  °K the distribution function drops sharply, beginning at an energy of 1.5 eV, due to the large oscillatory sections of the nitrogen. Increase in  $T_v$  leads to an effective decrease in oscillatory sections, and the distribution function "smears" in the energy range 1-2 eV. The moment of the distribution function corresponding to the mean energy then proves to be smaller.

## NOTATION

e, m, charge and mass of electron; k, Boltzmann's constant; yj, relative concentration of j-th component of air, j = 1, 2; Qjt, transport section for electron interaction with j-th component; Qij, ionization section of j-th component; kij, mean ionization rate constant for j-th component; Qad, section for dissociative adhesion of electron to oxygen molecule; kad, average rate constant for electron adhesion to oxygen molecule; T, air temperature.

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