KINETIC CHARACTERISTICS OF ELECTRONS IN HEATED AIR IN A MICROWAVE FIELD

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The dependence of the kinetic coefficients of electrons on the amplitude of a microwave field in air is studied by solving the Boltzmann equation. Heating of the air is found to have only a slight effect on this dependence over a wide range of parameters.

Introduction. In this paper we numerically analyze the electron energy distribution function (EEDF) and calculate the dependence of the kinetic characteristics of electrons on the amplitude E_0 of an electric field in air heated to 500 K at pressures of 0.1-1000 torr. Such conditions occur, e.g., behind a shock wave front in the region of thermodynamic equilibrium. The calculations are carried out over a wide range of field amplitudes, mainly breakdown fields and fields near the threshold. The characteristics of interest to us have been investigated well for cold air [1-4]. Attempts to take account of how heating of the air affects these characteristics and to extend the phenomenological theory for this case to 5000 K resulted in contradictory predictions. Experimental studies [5-8] suggest that the ionization rates in air at 3000-4000 K exceed those in cold air by an order of magnitude or more. The attribution of this discrepancy to the effect of vibrationally excited molecules [5, 6] was not supported by subsequent analytical [4] and numerical [1] estimates. Taylor et al. [2] and others noted that this problem must be tackled by numerically solving Boltzman equations on a computer. The lack of a sufficiently complete and reliable set of cross sections for the elastic and inelastic interaction of electrons with atoms and molecules, however, have hitherto prevented such a study. In the work reported here we investigated the effect that a change in the composition of air during heating has on the EEDF and kinetic coefficients. The air was assumed to consist of N_2, O_2, and NO molecules and O atoms, whose relative concentrations depend on the temperature and pressure of the gas. The numerical analysis technique was similar to that used in [1]. Below we briefly describe it and indicate that change made.

1. Mathematical Model. A computer was used to numerically solve the Blotzmann equation for the zeroth EEDF harmonic $f_0(u)$, which for any relation between the field frequency ω and the momentum transfer rate $\nu_{em}(u)$ has the form

$$\sqrt{\frac{2e}{m}}\, u^{1/2} f_0(u)\frac{dn_e}{dt} + \frac{d}{du}\left[-\frac{n_e}{3}\frac{u\nu_{em}^2(u)}{\sum\limits_x N_x q_{em}^x(u)}\times\right.$$

$$\left.\times\frac{E^2}{\omega^2+\nu_{em}^2(u)}\frac{df_0(u)}{du}\right] + \frac{d}{du}\left\{-n_e u^2\left[\sum_x \frac{2m}{M_x}N_x q_{em}^x(u)\right]\left[f_0(u)+T_m\frac{df_0(u)}{du}\right]\right\} = \mathrm{St}(f_0).$$

Here $E = E_0/\sqrt{2}$; the sign of x determined the component of the air; $q_{em}(u)$ is the transport cross section of the Xth component:

$$\nu_{em}(u) = \sum_x N_x q_{em}^x(u)\, u^{1/2}\sqrt{\frac{2e}{m}};$$

u is the electron energy, eV; and $\mathrm{St}(f_0)$ is the integral of inelastic collisions.

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TABLE 1. Composition of Air as a Function of Temperature and Pressure

T_m, K	P, torr	$\varkappa_{N_2}$	$\varkappa_{O_2}$	$\varkappa_{NO}$	$\varkappa_O$	$\varkappa_N$	$\varkappa_e$
2000	0,1	0,77	0,19	0,03	—	—	1, e—8
2000	100	0,78	0,21	0,001	—	—	1, e—9
3000	0,1	0,64	0,001	0,003	0,34	0,001	4, e—7
3000	10	0,67	0,05	0,02	0,24	—	1, e—7
3000	1000	0,74	0,16	0,04	0,04	—	1, e—7
4000	0,1	0,55	6, e—6	5, e—4	0,32	0,12	2, e—5
4000	10	0,63	6, e—4	0,006	0,34	0,01	7, e—6
4000	1000	0,66	0,03	0,04	0,25	0,001	2, e—6
5000	0,1	0,06	1, e—7	4, e—5	0,22	0,72	2, e—4
5000	10	0,47	2, e—5	0,002	0,31	0,21	9, e—5
5000	1000	0,62	0,002	0,02	0,32	0,02	3, e—5

The distribution function is normalized by the condition

$$\int_0^\infty f_0(u)\,u^{1/2}\,du = 1.$$

The derivation of equations of the form (1) is discussed in [9-11].

Equation (1) is valid when the following conditions are satisfied:

- the air can be considered to be quasihomogeneous;
- the field strength is limited from above by the condition $\bar{u} \gg u_0$, where $\bar{u}$ is the mean electron energy; u_0 is the electron oscillation energy;
- the period $2\pi/\omega$ of the high-frequency component of the field is substantially shorter than the electron energy relaxation ν_u^{-1}; and
- the approximation

$$f(u, t) = n_e(t)\,f_0(u),$$

used in the derivation is satisfied; this approximation is valid if the relaxation time $f_0(u)$ is substantially shorter than the times of the creation-disappearance processes, i.e., ionization, attachment, etc.

The right side of (1) is the integral of inelastic collisions. The contribution from electron-ion interactions is negligible. Electron-electron collisions can make an appreciable contribution if the degree of ionization of molecules exceeds 10^{-5}. The program used makes it possible to take e–e interactions into account, but in order to keep the picture simple we confine the discussion to the range of parameters where they can be disregarded. As seen from Table 1, this makes the range of parameters considered only slighly narrower.

The first term on the left side of Eq. (1) is associated with the appearance and disappearance of electrons. In our case

$$\frac{dn_e}{dt} = (\nu_i - \nu_a)\,n_e,$$

where ν_i and ν_a are the resultant ionization and attachment rates, averaged over the EEDF sought, i.e., Eq. (1) is an integro-differential equation. The form of the equation and the necessity to take the electron multiplication into account are discussed in detailed in [12].

The second term on the left side of (1) describes the energy acquisition by electrons in the field and the third term describes the energy loss in elastic collisions of electrons with atoms and molecules.

The integral of inelastic collisions describes the following processes: excitation of rotational, vibrational, and electronic levels of molecules, and electronic levels of atoms., dissociation of molecules by electron impact, dissociative attachment of electrons to oxygen molecules both in the ground and vibrationally excited states. Moreover, processes of another kind have been taken account collision of electrons with vibrationally excited N_2 and O_2 molecules and electron-excited O atoms. The cross sections for the reverse processes were calculated on the basis of the detailed balancing principle. It was also assumed that a new zero-energy electron appears in the ionization process. The form of the elastic collision

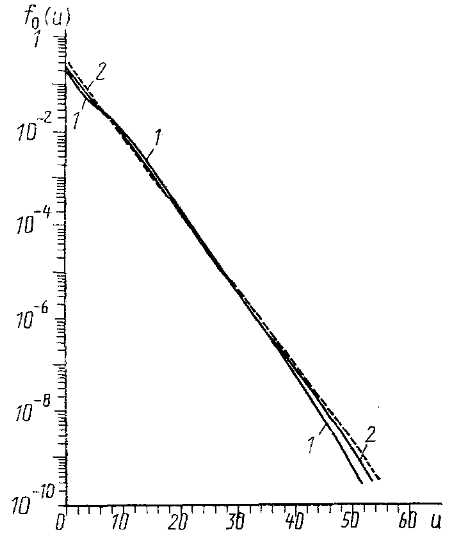

Fig. 1. EEDF in air at $\gamma = 18.7$ V·cm^2, P = 10 tor ;$f_0(u)$, eV$^{-3/2}$; u, eV]: the solid curves represent numerical calculation [1)300 K, 2) 200 K]; the dashed curve represents the Maxwellian EEDF.

integral is described in more detail in, e.g., [1, 9-12]. The level distribution of molecules was assumed to be a Boltzmann distribution with temperature equal to that of the air. The sets of cross sections for N_2 and O_2 were taken to be the same as in [1], those for NO were taken from [13-16], and those for O, from [17]. The relative concentrations of the individual components were taken from tables [18] calculated for air in thermodynamic equilibrium. Their characteristic values as a function of temperature and pressure are shown in Table 1.

Equation (1) was solved by the iteration method described in [12]. From the EEDF found we calculated the electron kinetic coefficients. Calculation of the fraction of energy lost by an electron in an individual collision makes it possible to estimate the contribution of this or some other elementary process to the EEDF. Verification of the energy balance makes it possible to check the accuracy of the calculations.

2. Results. In the case $\omega \simeq \nu_{em}$, as follows from Eq. (1), the EEDF depends on two parameters, e.g., E/N_m and ω/N_m. This causes some inconveniences in representing the results. To avoid a two-parameters dependence, use is made of the effective parameter $\gamma = (E_{ef}/N_m)\cdot 10^{16}$(V·cm^2)($N_m$ is in 1/cm^3), which is analogous to the parameter E/N_m for a constant field:

$$E_{ef} = \frac{E}{\sqrt{1 + \omega^2/\nu^2}},$$

where ν is the effective value of the total momentum transfer rate, which has been introduced in a special way (here, $\nu = 1.6\cdot 10^{-7}$ Nm). The introduction of such a parameter is rigorously substantiated mathematically if $\nu_{em}(u)$ = const. As shown by calculations [1, 12], the value averaged over the EEDF depends on the field for nitrogen and air in the range of γ values considered. This fact makes it possible to use γ in our case.

Gurevich [3] proposes using the parameter E_0/E_k, where

$$E_k = 2.8\cdot 10^4 \left(\frac{N_m}{2.7\cdot 10^{19}}\right) \sqrt{1 + \omega^2/\nu_k^2}\ , \text{ V/cm},$$

is the threshold field in cold air ($\nu_k \simeq \nu$). It can be easily shown that

$$E_0/E_k = (\sqrt{2}/10)\,\gamma, \quad (\text{V}\cdot\text{cm})^{-1}$$

The values γ = 3-70 V·cm^2 and E_0/E_k = 0-10 correspond to the range of parameters studied.

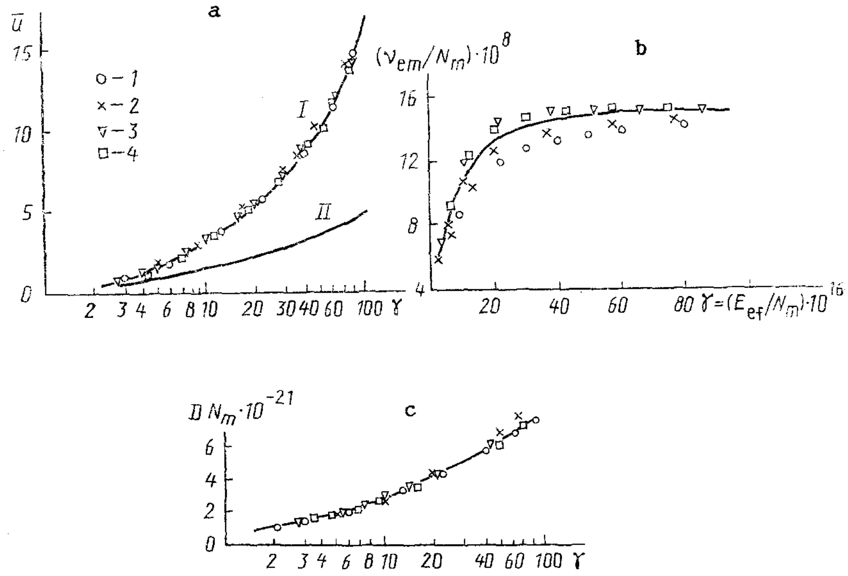

Fig. 2. Dependence of the kinetic coefficients on $\gamma = (E_{ef}/N_m)\cdot 10^{16}$, V·cm^2; the points represent numerical calculation [1)300, 2) 2000, 3) 3000, and 4) 4000 K]: a) means electron energy, eV [1) approximation of the numerical data; II) extrapolation from [20]]; b) diffusion coefficient, (sec·cm)$^{-1}$; c) momentum transfer rate, sec^{-1}.

Fig. 1 shows a typical energy dependence of the EEDF. Calculations shows that the shape of the EEDF is determined by inelastic collisions, mainly with N_2: over the entire temperature range from 300 to 5000 K, pressures, and field amplitudes ($\gamma \geq 3$) 80-90% energy is expended on N_2 excitation (this holds even when the N_2 content is 45%); the reamaining 10-20% of the energy is expanded on O_2 and O excitation; the energy transfer from electrons to NO molecules is negligible. The energy expenditure among the N_2 levels is as follows: no more than 1% of the energy goes for the translational and rotational degrees of freedom; electron multiplication also has little effect on the shape of the EEDF (only starting from γ = 50-70 V·cm^2, a considerable part of the energy, about 30%, goes into ionization). The shape of the EEDF is determined by processes of excitation of vibrational and electronic (including dissociation by electron impact) degrees of freedom of N_2 (vibrational degrees of freedom predominate at $\gamma < 10$ and electronic at $\gamma > 10$) and also by ionization at $\gamma \geq$ 50-70 V·cm^2. The shape of the energy balance is qualitatively analogous to the graph for the case of cold air shown in [1, 19]. The explanation proposed in [5, 6] for the increase observed in [5-8] in the ionization rate when air is heated holds if the growth of the population of the excited levels during heating causes a noticeable change in the EEDF. The calculations indicate that this temperature dependence of the EEDF, which is due to collisions of the second kind between the electrons and vibrationally excited N_2 molecules, is weak. This is because the electron temperature $T_e \gg T_m$ at the values of γ considered. The EEDF graphs for T_m = 300 K and 2000 K shown in Fig. 1 as an example virtually coincide. The comparison in Fig. 1 with the corresponding Maxwellian EEDF illustrates the finding in [12] that the EEDF of the system under study differs from the Maxwellian only in the "tail" of the distribution function at $u \geq 41$. The non-Maxwellian EEDF, therefore, should be taken into account when calculating the kinetic coefficients of the ionization rate type, which are determined by the EEDF tail.

Thus, $f_0(u, \gamma, T_m, \text{composition}) \simeq f_0(u, \gamma)$. This conclusion is supported by the results of calculation of the kinetic coefficients. Their dependence on γ, as is evident from the data given below, is universal with a high degree of accuracy, i.e., is not a function of either the air temperature or pressure. The dependence on the composition has an effect only in the calculation of the resultant constants of the processes, e.g., ionization, $K_i = \Sigma_x \varkappa_x K_i^x$, i.e., via the fraction $\varkappa_x$ of molecules of species x in the air.

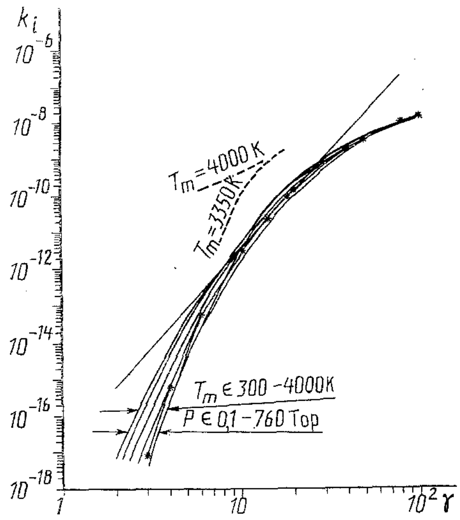

Fig. 3. Dependence of the ionization rate, cm3/sec, on $\gamma = (E_{ef}/N_m) \cdot 10^{16}$, V·cm^2: the dashed curves represent the experimental data of [5, 6, 8] at T_m = 3350 K and 4000 K; the solid curves represent numerical calculation for various T_m and P, encompassing the enter range of parameters studied; the straight line represents $\nu/N_m = 1.5 \cdot 10^{-17} \gamma^{5.34}$; the points represent experiment at T_m = 300 K.

Figure 2a shows the dependence of T_e on γ. The spread of the calculated points does not exceed 2% of the value: the points lie well on the curve approximating them.

$$\frac{3}{2} T_e = \bar{u} = \bar{u}^0 + 0.5\,\gamma^{0.8}, \quad 3 < \gamma < 100, \tag{3}$$

where $\bar{u}^0$ is the initial electron energy. At $\gamma < 3$ the condition $T_e \gg T_m$ is violated and a deviation from the universal dependence of T_e on γ, as found in [1], should be expected. The extrapolation (used by Rogashkova et al. [20]) of the experimental data ($\bar{u} = 0.62\gamma^{0.5}$), represented by curve II in Fig. 2a, gives a value that underestimated by a factor of four.

The expression $u = e^2E^2_{ef}/(m\delta\nu^2)$ [5, 6] suggests that the energy loss by electrons in collisions with heavy particles is determined by the formula

$$\delta = 1.4 \cdot 10^{-3} \gamma^{1.2},$$

which gives values of Δ that differ from the corresponding experimental data [2] by a factor of no more than two.

It is a similar picture for the coefficient of free electron diffusion (Fig. 2b). The calculated points are approximated well by

$$D_f N_m = (20 + \gamma) \cdot 10^{21} \ (\text{sec} \cdot \text{cm})^{-1},$$

which agrees to within 2% with the curve from experiments [22].

Data on the momentum transfer rate are shown in Fig. 2c. The curves corresponding to different compositions of the air coincide to within 10-20%. This is because the constituent molecules of the air have transport cross sections that do not differ markedly. The function

$$\nu_{em} = 1.6 \cdot 10^{-7} N_m (\gamma + 1)/(\gamma + 7.6)$$

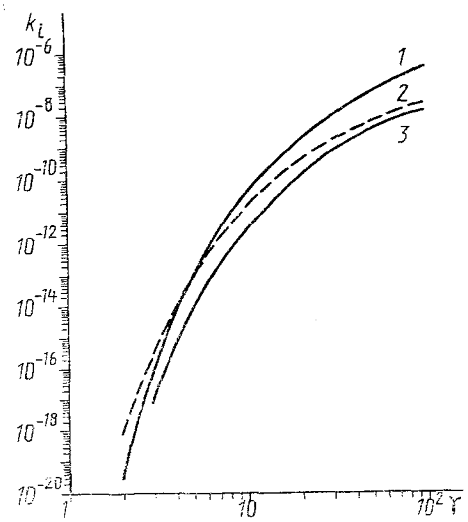

Fig. 4. Dependence of the ionization constant rate, cm^3/sec, on $\gamma = (E_{ef}/N_m) \cdot 10^{16}$, $V \cdot cm^2$, ($T_m = 3000$ K; P = 100 torr): 1) analytical treatment [3]: 2) [19], Maxwellian EEDF: 3) numerical calculations.

describes the dependence of the momentum transfer rate on γ. In their experiments Taylor et al. [7] found that

$$\nu = (1.4 - 1.6) \cdot 10^{-7} N_m,$$

which is in good agreement with the data obtained by calculation with $\gamma \geq 20$.

The variations of the total attachment rate are also attributed to variations in the fraction of O_2 molecules in the air. To within the order of magnitude

$$\nu_a = 2 \cdot 10^{-11} \varkappa_{O_2} N_m.$$

To be more exact, when we take the dependence on γ into account we have

$$\nu_a = 8.25 \cdot 10^{-13} \varkappa_{O_2} N_m \gamma^{1.2}, \quad 3 < \gamma < 30.$$

We go on to discuss the ionization process. It has been determined that the ionization: 1) determined by the contribution from N_2, O, and NO; and 2) takes place from the unexcited ground state of the molecule. The relation $k_iNO \gg k_i^0 \gg k_i^{N2}$ is satisfied at $\gamma < 10$ because of differences in the ionization potentials; if the NO content is high enough, therefore, the total ionization rate is determined by the contribution from NO. At $\gamma > 10$ ionization mainly of N_2 occurs. Charges in the composition do not affect $\nu_i(\gamma)$ enough to explain the aforementioned experimental data and the theoretical predictions. From Figure 3 we seen that the entire family of calculated curves in the shaded region lies roughly an order of magnitude below the experimental data. At the same time the results of a cold-air experi-ment are shown by points in Fig. 3. agree with the corresponding results of calculation.

As already mentioned, the results of the calculations support the conclusion in [1, 4] that excitation of vibrational degrees of freedom of molecules under weak heating has little effect on the ionization constants and also cannot explain the experimentally observed overestimation of the ionization constants, as stated in [5, 6].

Figure 4 compares the results of the analytical treatment [3] (curve 1), in which the EEDF is non-Maxwellian, the treatment of [19] which is characterized by averaging over the Maxwellian EEDF (curve 2), and the results obtained by computer in this study. We note that the expression for ν_i from [19] depends on T_e:

$$\nu_i = CT_e(I_x/T_e + 2)V_eN_x \exp(-I_x/T_e). \tag{4}$$

We used the relation (3) between T_3 and γ to construct the graph (4) in Fig. 4. The relation between the curves shown in Fig. 4 is typical. The results given by treatments of both [3] and [19] are too high by up to an order of magnitude in comparison with direct numerical computation on a computer. In particular, the approximation (used in [3]) with curve 1: $\nu_i=\nu_{am}(E_0/E_k)^{5.34}$, written with (2) taken into account through γ, takes on the form $\nu_i/N_m=9.6\cdot10^{-17}\gamma^{5.34}$ *. The approximation known from the cold-air results of [2], which is also applicable to hot air, according to calculations, is

$$k_i = \nu_i/N_m = 1.5\cdot10^{-17}\gamma^{5.34}.$$

In the range $E_k \leq E_0$ $5E_k$ it is accurate to within a factor of three, as in the case of cold air.

In a wider range of γ than in (5) the value of ν_i can be estimated with the order-of-magnitude approximating expression

$$\nu_i/N_m = 1.0\cdot10^{-8}\exp(-10\,E_k/E_0).$$

The ionization rate can be estimated more exactly (to within a factor of 2-3) with account for the change in composition by using the following expressions which, like those above, were obtained by approximating the results of calculation:

$$k_i^{N_2} = 10^{-7.7-38.1/\gamma};\ k_i^{O_2} = 10^{-8.1-34.5/\gamma};$$

$$k_i^{NO} = 10^{-7.8-24.3/\gamma};\ k_i^{O} = 10^{-8.1-33.3/\gamma};$$

$$k_i = \varkappa_{N_2}k_i^{N_2} + \varkappa_{O_2}k_i^{O_2} + \varkappa_{NO}k_i^{NO} + \varkappa_{O}k_i^{O}.$$

Conclusions. It follows from the calculations that the EEDF, temperature, and coefficient of free diffusion of electrons, and the rate constants of the elementary processes pertaining to individual components of the air depend weakly on the pressure and temperature. They depend only on the effective parameter $\gamma = (E_{ef}/N_m)\cdot10^{16}$, $V\cdot cm^2$, which is calculated using $\nu = 1.6\cdot10^{-7}\,N_m$. Heating of the air manifests itself only when the contribution of each component of the total rate constant of the process under study is taken into account. This is so mainly because in the range of γ under consideration electron energy is lost mainly for excitation of vibrational and electronic degrees of freedom of N_2, whose content varies only slightly.

The calculation are in good agreement with measurements of: 1) the total momentum transfer rate: 2) the energy loss fraction [20]: and 3) the diffusion coefficient. The experimental ionization rate data for cold air are in good agreement with the corresponding results of calculation. The ν_i data for air at 3000-4000 K [5, 6] are roughly an order of magnitude higher than the corresponding calculated results. This has not yet been explained satisfactorily.

Calculation confirm the conclusion [1, 4] that the growth of the population of N_2 vibrational levels when air is heated has little effect on the ionization rate and cannot explain the above-discussed discrepancy between the experimental and calculated data, as was done in [5, 6] on the basis of simplified concepts. This discrepancy is not explained by the change in composition upon heating, in particular the formation of lightly ionized NO molecules or by taking account of the ionization of molecules from the first excited electron

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*The agreement that Gurevich [3] found between his results and the experimental cold-air data of [5, 6] occurs on the logarithmic scale. Our comparision suggests that the results of [3] accord more exactly with the data of [5, 6], which pertain to air at T_m = 3000–4000 K, and are up to an order of magnitude higher than the cold-air data.

level. Analytical methods [3], [22] give results that are an order of magnitude higher than those from direct numerical calculation of the ionization rate. The discrepancy between the results of calculation and the results of [22], which were obtained on the assumption of a Maxwellian electron distribution, means that the non-Maxwellian EEDF has a substantially weaker effect on the form of the dependence of the kinetic coefficients on γ. The resulting dependences of the kinetic coefficients on γ are approximated with analytical functions.

NOTATION

$f_0(u)$ denotes the zeroth harmonic of the electron energy distribution function: u is the electron energy, eV; m, e, n_e, electron mass, charge and concentration; T_m, P, Nm, temperature, pressure, and concentration of air molecules; N_x and M_x, concentration and mass of the xth component of the air: $\nu_{em}(u)$, rate of momentum transfer from electrons of energy u to molecules: ν_{em}, EEDF-averaged momentum transfer rate: ν is the effective value of ν_{em}; ν_u, electron energy relaxation time: ν_i and ν_a, average resultant ionization and attachment rates: E_{ef}, effective field; k_i and k_i^x total and component ionization rates; $\varkappa_x$ fraction of molecules of spices x in the air; T_e, electron temperature, eV; D_i coefficient of free electron diffusion; I_x ionization potential of molecules of species X; V_e, average electron energy; ν_{am} is the maximum value of ν_a; and C, a constant.

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