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Determination of concentration of excited oxygen atoms on the basis of ion mobility in atmospheric plasma

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Abstract

A method is developed for determination of the concentration of excited oxygen atoms for a plasma of an upper atmosphere or gas discharge in an excited air with dissociated oxygen. The method is based on the measurement of time-dependencies for the currents of oxygen atomic ions which are formed by pulse corona discharge and move in an electric field in a drift chamber. The accuracy for the concentration of excited oxygen atoms is $\sim 1\%$, if the resolution for the time distribution function of the ion current corresponds to the relative accuracy of the ion mobility better than 1%. Accumulation of current signals by repetition of corona ionization discharge with a frequency of some kHz improves the accuracy of an express analysis for the concentration of excited oxygen atoms.

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Keywords: Ion mobility; Mass spectrometry; Charge exchange process

1. Introduction

Fine physical methods can be a basis of contemporary measuring equipment which give new qualitative possibilities for the analysis of processes and phenomena in other areas of science. In particular, using of the quadrupole mass-spectrometer in 1950's–1960's allowed one subsequently to measure the rate constants of many ion–molecular reactions [1,2]. A general scheme of these measurements [3,4] includes a drift chamber where ions are drifting and partake in some processes, and products of these processes are detected by a quadrupole mass-spectrometer. Measurement of currents of yield ions as a function of a flow velocity and composition of a flowing gas allowed one to determine the rates of ion–molecular processes.

The simplicity and reliability of this scheme allows one to use it for other problems. In particular, the Lindinger device [5–7] on the basis of this scheme gives the possibility to measure the concentrations of certain air admixtures if this concentration is of the order of 1 *ppb* (10^{-9}). The basis of this device is the above flow method and known rate constants of some ion–molecular reactions. The molecular ion H_3O^+ that has a structure $H^+ \cdot H_2O$ is used as the incident one. This ion is located a certain time in a flow and partake in known ion–molecular reactions, and measurements of currents of some ions by mass-spectrometer allows one to restore the concentration of some components in a flowing gas. Usually these components accompany the processes involving organic substances, and examples of these components are allyl methyl sulfide, dimethyl sulfide and acetone [6]. The Lindinger device is useful for the analysis of physiological processes, as breathing, degradation of food products and for aerophysical measurements, as the analysis of tropospheric acetone and methanole which are generated in Earth atmosphere as a result of biological processes by plants. Thus the method of ion drift in a flowing gas can be used for creation of devices for measurement of current content of certain components in air.

There are various schemes of the mobility spectrometers which are focused on certain problems (for example, [8]). We suggest to apply this scheme for measurement of electronically excited oxygen atoms in the upper atmosphere at altitudes ap-

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proximately 100 km where the main components of the atmosphere are molecular nitrogen and atomic oxygen. sun fluxes are of importance in formation of an atmospheric plasma at these altitudes. In particular, dissociation of molecular oxygen and ozone results from Sun radiation, and then along oxygen atoms in the ground state excited oxygen atoms influence on some atmospheric phenomena as glowing of a night sky, polar glowing etc [9]. Excited oxygen atoms $O(^1D)$ and $O(^1S)$ are characterized by the radiation lifetime 140 and 0.8 s correspondingly [10], and their radiation at wavelengths of 630 and 557.8 nm are present in various emission of the upper atmosphere. We below consider a simple method to determine concentration of these atoms on the basis of measurement of drift times for oxygen atomic ions in the drift chamber.

It is of importance for this scheme that atomic oxygen ions are formed both in the ground and in metastable states. Electronically excited ions are separated from ions in the ground state of their different mobility, and this is used for the ion mobility mass spectrometry [11–13] giving additional information about ion interaction with a buffer gas. In the case of drifting of oxygen ions in excited air, ions in the ground and excited states are characterized by an approximately same mobility in molecular nitrogen, but the cross section of resonant charge exchange of these ions and oxygen atoms are different. Then on the basis of the mobility of these ions in an excited air one can obtain information about the presence of excited oxygen atoms in air.

2. Method for determination of concentration of excited oxygen atoms

We apply the drift flow for a current determination of the excited oxygen concentration on the basis of the ion mobility profile detected from the drift camera. The scheme of this method is given in Fig. 1 and the method is as follows. A pulse of atomic ions is formed at entrance to the drift chamber, and then atomic ions are moving under the action of an electric field through a flow of a mixture of oxygen atoms and nitrogen molecules. After the quadrupole mass-spectrometer we obtain the distribution of an ion current in time. From the analysis of this dependence one can determine the concentration of excited oxygen atoms.

In the analysis of an ion current, we take into account that atomic oxygen ions are found in three electron states ($^4S, ^2D, ^2P$), and the quadrupole mass-spectrometer is tuned only on these ions. Next, formed ions partake in processes of elastic collisions with nitrogen molecules and oxygen atoms, so that the electron state of an ion does not change during its drift through the drift chamber under used parameters. Since the cross section of resonant charge exchange depends on the electron state of colliding oxygen ion, a time of passage through the drift chamber is different for different atom and ion states. Therefore, the drift time is different for different ion states and depends on the presence of excited atoms in a flowing gas. This is a basis of express-measurements for the concentration of excited oxygen atoms in a gas.

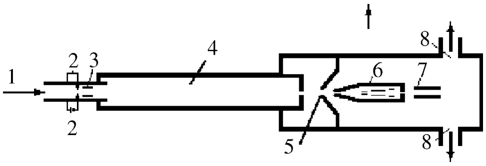

Fig. 1. A scheme of a flow-drift method for the analysis of air: (1) a flow of an atmospheric air containing excited oxygen atoms; (2) pulse ionization of air by corona discharge; (3) collector of electrons; (4) drift tube; (5) exit of the main flow; (6) skimmer and condensed ion lenses; (7) quadrupole mass-spectrometer; (8) collector of ions; (9) exit of a detected flow.

Table 1

The average cross sections of resonant charge exchange σ_{ex} (in 10^{-16} cm^2 at collision energies of 0.1, 1.0 and 10.0 eV the laboratory frame of reference)

Atom, ion state	$O(^3P)$	$O(^1D)$	$O(^1S)$
$O(^4S)$	65, 54, 43	0, 0, 0	0, 0, 0
$O(^2D)$	42, 33, 25	56, 44, 34	0, 0, 0
$O(^2P)$	37, 29, 22	41, 32, 24	57, 46, 35

It is essential in this analysis a remarkable difference between the cross sections of resonant charge exchange involving different ion states. We give in Table 1 these cross sections averaged over electron terms for a given oxygen atom and ion states [14]. It should be noted that the cross sections for excited ion states ($^2D, ^2P$) are lower than the corresponding ones for ground state (^4S). This trend is also qualitatively confirmed by the old calculations in Ref. [15].

A time of passage of the drift camera by an atomic ion of a given type is inversely proportional to the mobility of these ions in a given gaseous mixture. We use for the ion mobility K the Chapman–Enskog formula that has the following form for an one-component gas [16,17]:

$$K = \frac{3\sqrt{\pi T}}{8\sqrt{\mu} N \sigma^*} \tag{1}$$

Here T is the gas temperature that is expressed in energetic units, μ the reduced mass of a ion and atomic particle of a gas, N the number density of atomic particles of the gas, and σ^* is the diffusion or transport cross section for collision of an ion and a gas atomic particle.

For many-component gas it is necessary to change the value $N\sigma^*$ in formula (1) by the value $\sum_i N_i \sigma_i^*$, where N_i is the number density of atomic particles of this component in the gaseous mixture, σ_i^* the transport cross section for elastic collision between a given ion and this atomic particle. Because the mobility is reduced to the normal total number density of atomic particles, we obtain from this for the ion mobility [18,19]:

$$K = \left(\sum_i \frac{c_i}{K_i} \right)^{-1}, \tag{2}$$

where c_i is the concentration of atomic particles of ith component, and K_i is the mobility of ions in a gas that consists of i-th component only.

Since we deal with drift of atomic oxygen ions in atomic oxygen, Table 2 gives the mobilities K_i of this formula for pure atomic oxygen including atoms in a given electron state. In addition to this, the mobility of oxygen ions in molecular nitrogen

Table 2
The mobility (in cm^2/(V s)) of atomic oxygen ions in atomic oxygen if atoms are found in an indicated state at temperatures $T = 300$ and 1000 K (in parentheses)

Atom state, ion state	O(^{3}P)	O(^{1}D)	O(^{1}S)
O(^{4}S)	2.65 (1.60)	–	–
O(^{2}D)	4.07 (2.48)	3.07 (1.87)	–
O(^{2}P)	4.57 (2.81)	4.12 (2.54)	2.98 (1.82)

Table 3
The mobilities (in cm^2/(V s)) of atomic oxygen ions in air defined according to formula (4a) at air temperatures $T = 300$ and 1000 K (in parentheses)

Atom state, ion state	K_0	ΔK_1	ΔK_2
O(^{4}S)	3.02 (2.18)	−1.15 (−0.83)	−1.15 (−0.83)
O(^{2}D)	3.53 (2.97)	0.58 (0.37)	−0.91 (−1.18)
O(^{2}P)	3.63 (3.10)	0.12 (0.14)	0.51 (0.64)

may be determined by the Dalgarno formula [20–22]:

$$K = \frac{36}{\sqrt{\alpha\mu}} \tag{3}$$

where the ion mobility is expressed in cm^2/(V s), the molecule polarizability α is expressed in atomic units (a_0^3), and the reduced mass of colliding ion and molecule μ is expressed in units of atomic mass. Deduction of this formula is based on the assumption that ion–molecule scattering is determined by the polarization interaction of the ion charge with the molecule polarizability. In particular, for collision of an oxygen ion and nitrogen molecule we have $\mu = 10.2$, $\alpha = 11.8$, so that the mobility of an atomic oxygen ion in pure molecular nitrogen is $K = 3.28\,\text{cm}^2/(\text{V s})$ and does not depend on the gas temperature. One can estimate the accuracy of this value using the measured mobilities of other ions in molecular nitrogen [21,22]. The mobility of ions Na^+ in nitrogen is 2.85 cm^2/(V s), the mobility of ions K^+ is 2.55 cm^2/(V s), for ions N^+ this value is 2.97 cm^2/(V s), and for ions N_3^+ it is 2.26 cm^2/(V s). Assuming the interaction of an ion with the nitrogen molecule to be determined only by the ion charge, as well as in the case of atomic oxygen ions, we find the mobility of atomic oxygen ions in nitrogen on the basis of the above measured values as 3.17, 3.23, 2.84 and 2.90 cm^2/(V s) correspondingly, and the statistical average of these values gives the mobility of oxygen ions in nitrogen as (3.0 ± 0.2) cm^2/(V s). Change of this mobility leads to a shift of the mobility (2) of the mixture conserving the relative change of the mobility resulted from a change of the mixture.

3. Mobility of oxygen atomic ions in excited air

We now analyze the character of drift of oxygen ions in air in which oxygen is dissociated. This takes place in the upper atmosphere and for gas discharge in air under certain conditions. Considering air to consist of 80% nitrogen molecules and 20% oxygen molecules, we obtain that after dissociation of oxygen molecules the air includes 2/3 nitrogen molecules and 1/3 oxygen atoms. Denoting by K_0 the mobility of a given oxygen ion in air where all the oxygen atoms are found in the state O(^{3}P), we give the values of K_0 in Table 3. Next we denote as $1 - \xi - \eta$, the part of oxygen atoms in air which are found in the state O(^{3}P), by ξ the part of oxygen atoms in air in the state O(^{1}D), and by η the part of oxygen atoms in air in the state O(^{1}S). This allows us to represent formula (2) for the mobility of a given oxygen ion in the form

$$K = K_0 + \Delta K_1 \xi + \Delta K_2 \eta, \tag{4a}$$

and the parameters of this formula are:

$$K_0 = \left[\frac{2}{3K(\text{N}_2)} + \frac{1}{3K(^3\text{P})}\right]^{-1},$$

$$\Delta K_1 = \frac{K_0^2}{3}\left[\frac{1}{K(^1\text{D})} - \frac{1}{K(^3\text{P})}\right]$$

$$\Delta K_2 = \frac{K_0^2}{3}\left[\frac{1}{K(^1\text{S})} - \frac{1}{K(^3\text{P})}\right] \tag{4b}$$

Here $K(\text{N}_2) = 3.28\,\text{cm}^2/(\text{V s})$ is the mobility of a given atomic oxygen ion in pure nitrogen, $K(^3\text{P})$, $K(^1\text{D})$ and $K(^1\text{S})$ means the mobility of a given oxygen ion in atomic oxygen where all the atoms are found in the states ^{3}P, ^{1} D and ^{1}S correspondingly. Of course, we assume above the concentration of excited oxygen atoms in air to be small:

$$\xi \ll 1, \qquad \eta \ll 1 \tag{5}$$

Table 3 gives the values of the parameters of formula (4a).

4. Drift of oxygen atomic ions in excited air

In considering a general case when several types of ions are moving through a drift chamber [11–13], we find criteria when signals for different ions may be separated. Indeed, diffusion of ions widens individual signals, and in order to resolve these signals, many collisions are necessary during the drift of each ion, so that the ion mean free path in a buffer gas is relatively small. We below obtain this criterion for drift of oxygen ions in an excited air. We will be guided by typical concentrations of excited oxygen atoms in air ξ, $\eta \sim 1\%$, and hence a drifting ion has hundreds collisions with atoms and molecules in the drift camera. Then along with the drift motion, the ion will have a diffusion motion in the drift camera also. As a result, the ion current to a detector at time t in a gas in the case of one sort of ions is given by [23,24]:

$$I(t) = \frac{J_0}{\sqrt{4\pi Dt}} \exp\left[-\frac{(L - wt)^2}{4Dt}\right] \tag{6}$$

Here $J_0 = \int I(t)\,\text{d}t$ is the total number ions detected on a collector, L the distance from the ion source to the detector, D the diffusion coefficient of ions, $w = KE$ the ion drift velocity, so that K is the ion mobility in this gas, and E is the electric field strength (for simplicity, we assume below the ion drift velocity w to be small compared to their thermal velocity v_T, though it is not of principle). In the case of several ion sorts, when collector detects only a ion charge, this formula takes the form:

$$I(t)=\sum_j \frac{J_j}{\sqrt{4\pi D_j t}} \exp\left[-\frac{(L-w_j t)^2}{4D_j t}\right] \tag{7}$$

where an index *j* relates to a certain ion state.

In order to distinguish different ions in the method under consideration, it is necessary to resolve signals from them. In reality, as it follows from Table 2, the mobilities of ions in different states are nearby. Correspondingly, the diffusion coefficients that are expressed through the zero-field mobilities by the Einstein relation $D = KT/e$ (e is the ion charge, and T the temperature expressed in energetic units) are nearby also for ions of different sorts. Taking this into account, we find the criterion when signals for ions of two sorts may be resolved in time. For two ion states formula (7) takes the form:

$$I(t)=\frac{J_1}{\sqrt{4\pi D_1 t}} \exp\left[-\frac{(L-w_1 t)^2}{4D_1 t}\right] + \frac{J_2}{\sqrt{4\pi D_2 t}} \exp\left[-\frac{(L-w_2 t)^2}{4D_2 t}\right] \tag{8}$$

where indices 1 and 2 respect to certain ion states. Evidently, signals from these two ion sorts can be resolved, if the time dependence $I(t)$ has a minimum between two maxima. We below find the criterion when it is realized.

Let us introduce $w = (w_1 + w_2)/2$, $\Delta w = w_1 - w_2$ ($w_1 > w_2$) and take for simplicity $D_1 = D_2 = D$. We account for transport parameters of different ions are nearby, and then $\Delta w \ll w$. In this case, both maxima and minimum are located near $t_0 = L/w$. In order find the minimum of the current (8) under this condition, we introduce the reduced variable x and the reduced constant A according to the relations:

$$x=\frac{2w}{\Delta w}\left(\frac{w}{L}t-1\right), \qquad A=\frac{eEL}{8T}\left(\frac{\Delta w}{w}\right)^2 \tag{9}$$

We consider the case of low electric field strengths E in the drift camera $w = KE$ and the Einstein relation $D = eK/T$. In new variables the relation (8) takes the form:

$$I(t)=C\left\{J_1 \exp\left[-A(1+x)^2\right] + J_2 \exp\left[-A(1-x)^2\right]\right\}, \qquad C=\sqrt{\frac{eE}{4\pi LT}} \tag{10}$$

Let us analyze this expression from the standpoint of resolution of two signals. Evidently, these signals are resolved if the dependence (10) has two maxima with a minimum between them. Then one can relate to an appropriate ion a signal part located at a corresponding side from the minimum. Hence, the possibility to resolve different ion states connects with existence of the minimum for the dependence (10). As it follows from formula (10), the extremum condition for the function $I(t)$ is given by the relation:

$$F(x)=\frac{J_2}{J_1}\frac{1-x}{1+x}e^{2Ax}=1 \tag{11a}$$

and the extrema of the ion current are located in a range:

$$1 \ge x \ge -1 \tag{11b}$$

For simplicity we consider the case $J_1 = J_2 = J$, when due to the symmetric form of $F(x)$ we obtain the relation:

$$F(x)F(-x)=1$$

This gives the solution of this equation $x = 0$, and this solution is a minimum of $I(t)$ if $\mathrm{d}^2I/\mathrm{d}t^2 > 0$. The latter is fulfilled if $A > 1/2$ or:

$$U=EL>U_0=\frac{4T}{e}\left(\frac{w}{\Delta w}\right)^2, \tag{12}$$

where U is the voltage for the drift chamber. As it is seen, the voltage does not depend on the gas pressure. For the data of Table 3 we obtain for ions O(^{2}D) and O(^{1}P) that the parameter U_0 is equal to 170 and 190 V at room temperature and temperature of 1000 K correspondingly. Signals for ions O(^{2}D) and O(^{2}P) consist of two peaks if the drift chamber voltage exceeds the values indicated in the case when excited oxygen atoms are absent in a gas mixture ($\xi = 0, \eta = 0$) and the intensities of ions O(^{2}D) and O(^{2}P) are coincided ($J_1 = J_2$). Note that this estimate relate to weak electric field strengths when the ion drift velocity w is proportional to the electric field strength E. The latter corresponds to the criterion $eE\lambda \ll T$, where λ is the ion mean free path in a gas. Therefore this condition requires the validity of the criterion:

$$\frac{L}{\lambda} \gg \left(\frac{w}{\Delta w}\right)^2, \tag{13}$$

that corresponds to many collisions in the drift camera for a drifting ion. Since the mean free path of ions in a gas is inversely proportional to the number density of gas atoms or molecules N, this criterion requires a small N.

In the case when the intensities of two nearest signals are different, the criterion for the voltage between electrodes of the drift chamber is stronger than that according to (12). Let us consider the limiting case $J_1 \gg J_2$, when according to formula (11a) the function $F(x)$ is zero at $x = 1$ and is close to zero at $x = 0$. The relation (11a) $F(x) = 1$ can be fulfilled in two points which give the minimum and maximum of $I(t)$ in the range $0 < x < 1$. Considering the function $F(x)$ to be almost symmetric in this range with respect to transformation $x \leftrightarrow 1 - x$, we take for existence of the $I(t)$ minimum in this range the criterion $F(1/2) > 1$. This gives the criterion of resolution for currents of different ion states $A > \ln(3J_1/J_2)$ or:

$$U=EL>\frac{8T}{e}\left(\frac{w}{\Delta w}\right)^2 \ln\frac{J_1}{J_2}=2U_0 \ln\frac{J_1}{J_2} \tag{14}$$

From this one can write a general criterion for $J_1 > J_2$ that is transformed into (12) at $J_1 = J_2$ and into (14) if $J_1 \gg J_2$. Such a criterion has the form

$$U=EL>2U_0 \ln\left(\frac{J_1}{J_2}+0.65\right) \tag{15}$$

Thus, we obtain that a certain length of the drift camera or enough high electric field strength is necessary for resolution of

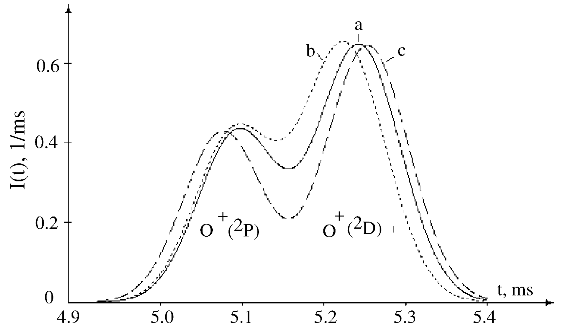

Fig. 2. The time dependence for the current of excited atomic oxygen ions in the states $O^+(^2D)$ and $O^+(^2P)$ which are drifting in air with the concentration 2/3 of nitrogen molecules and 1/3 of oxygen atoms. The population of ion states in the ion current is 75% of $O^+(^4S)$, 15% of $O^+(^2D)$ and 10% of $O^+(^2P)$. The population of oxygen atom states is: (a) 100% of $O(^3P)$; (b) 98% of $O(^3P)$, 2% of $O(^1D)$; (c) 96% of $O(^3P)$, 2% of $O(^1D)$, and 2% of $O(^1S)$.

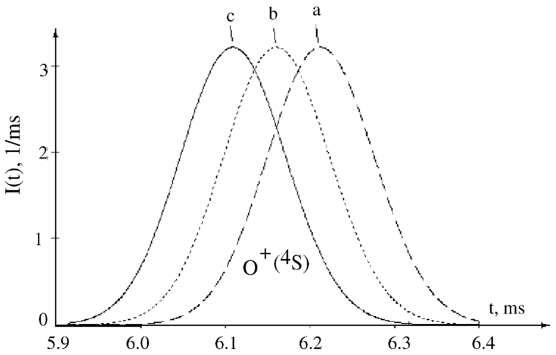

Fig. 3. The time dependence for the current of atomic oxygen ions in the the ground state $O^+(^4S)$ states which are drifting in air with the concentration 2/3 of nitrogen molecules and 1/3 of oxygen atoms. The population of ion states in the ion current is 75% of $O^+(^4S)$, 15% of $O^+(^2D)$ and 10% of $O^+(^2P)$. The population of oxygen atom states is: (a) 100% of $O(^3P)$; (b)98% of $O(^3P)$, 2% of $O(^1D)$; (c) 96% of $O(^3P)$, 2% of $O(^1D)$, and 2% of $O(^1S)$.

currents of different ions in this method, and the criterion to resolve ions in different states is found. A typical time dependence for an ion current to the collector is given in Figs. 2 and 3, when it is possible to resolve currents from each ion state. In treating such dependencies from an experiment, we extract three resonances that allows us to find the populations J_1, J_2, J_3 for different ion states. Next, times of current maxima are the drift times through the drift chamber for ions in different states. The presence of excited oxygen atoms in a gas mixture leads to a shift of appropriate peaks on the time dependence of the ion current. Let us denote by τ_1, τ_2, τ_3 the peak positions for ions $O(^4S)$), $O(^2D)$ and $O(^4P)$. Table 4 contains the relative times of ion drift and the relative shift of these peaks near $\xi = 0$, $\eta = 0$, when excited oxygen atoms are absent in a gas. These data show that for measurement of population of excited states of oxygen atoms with the accuracy up to 1%, it is necessary to determine relative positions of peaks with the accuracy up to 0.3%. Note that the relative shift of two peaks, *i* and *j*, as it follows from the data of Table 4, is ($\tau_i > \tau_j$):

$$\frac{\mathrm{d}\ln(\tau_i - \tau_j)}{\mathrm{d}\xi} = \frac{\tau_i}{\tau_i - \tau_j}\frac{\mathrm{d}\ln\tau_i}{\mathrm{d}\xi} - \frac{\tau_j}{\tau_i - \tau_j}\frac{\mathrm{d}\ln\tau_j}{\mathrm{d}\xi} \qquad (16)$$

and the same expression we have for the shift of signal peaks due to the presence in air the excited oxygen atoms $O(^1S)$.

We believe that this method allows us to find the concentration of excited oxygen atoms with the accuracy ∼ 1% if the measurement of a relative mobility of ions is possible with the accuracy ∼0.01 cm²/(V s).

Table 4
The relative drift time for ions in the drift chamber and its derivatives for the concentrations ξ and η of excited oxygen atoms $O(^3P)$ and $O(^1D)$ in the cases of drifting ions $O(^4S)$, $O(^2D)$ and $O(^2P)$

Ion	$O(^4S)$	$O(^2D)$	$O(^2P)$
τ/τ_1	1	0.855	0.832
$\frac{\mathrm{d}\ln\tau}{\mathrm{d}\xi}$	-3.8×10^{-3}	8.5×10^{-4}	2×10^{-6}
$\frac{\mathrm{d}\ln\tau}{\mathrm{d}\eta}$	-3.8×10^{-3}	-2.9×10^{-3}	1.6×10^{-3}

5. Ion drift in drift chamber filled with air

We below estimate parameters of this method for express-measurements of the concentration of excited oxygen atoms in the upper atmosphere. Note that the criterion (13) requires practically that the ion drift velocity is small compared to a thermal velocities of atoms or molecules, and violation of this criterion is not of principle and requires a change of using formulas. Nevertheless, we will keep this criterion if the gas pressure is not small. Taking for estimations the air pressure to be $p = 0.03$ Torr at temperature of $T = 200$ K (the atmosphere altitude about 90 km), we have the total number density of nitrogen molecules and oxygen atoms in air to be $N = 2 \times 10^{15}\,\mathrm{cm}^{-3}$, and the mean free path of ions is $\lambda \sim 0.1$ cm. Taking according to the data of Table 2 the difference of K_0 for different ion sorts to be 0.1cm²/(V s), we have $(w/\Delta w)^2 \sim 10^3$, and the criterion (13) gives $L \gg 100$ cm. If we take $L = 200$ cm, and the longitudinal electric field strength is taken $E_x = 0.5$ V/cm (the axis x is directed along the drift tube), i.e. the total voltage in the drift chamber is 100 V. Under these parameters we have $eE\lambda \approx 3T$, i.e. the ion drift velocity exceeds a thermal velocity of atoms and molecules, i.e. the criterion $eE\lambda \ll T$ of a drift velocity smallness is violated. Nevertheless, because the ion mobility is determined mostly by scattering on nitrogen molecules, formula for the drift velocity $w = KE$ is fulfilled more or less for this electric field strength, and is valid for more high pressures of a gas. Since we use relative values of the drift velocities, the accuracy of this formula is not of importance.

Under these parameters a time of ion drift through the drift chamber is approximately 6×10^{-3} s, and it is necessary to resolve relative times of ion passage through the drift chamber with the accuracy about 0.3%. This means the the duration of an ionization pulse is shorter than $\sim 1 \times 10^{-5}$ s, i.e. it must be used microsecond ionization by corona discharge. Simultaneously, the ion collector must resolve ion currents during time of several microseconds. Along with a small duration of the ionization pulse (∼ 10 μs), the above accuracy requires a small size of the ionization region below 0.5 cm. In this case, the signals of different ions on the ion collector with not be overlapped.

As a result of a short electric pulse for ionization, different ions are formed, and the population of excited oxygen ions $O(^2D)$ and $O(^2P)$) is less than that of ions in the ground state $O(^4S)$, though these populations are comparable. Along with ions, electrons are formed by ionization of atoms and molecules. They will screen an external electric field where ions are drifting, and this will create a noise. In order to escape a loss of accuracy due to electrons, a collector of electrons is located near the ionization region, and electrons are removed from the gas flow. An electron collector creates an electric field that attracts electrons to the collector and repulses ions. This collector simultaneously focused ions near the center flow.

Because of a noncompensated ion charge in a gas, an additional electric field arises and acts in a different manner on ions before and behind the bunch of ions. Taking the width of this bunch to be $\Delta x = 0.5$ cm and requiring this field to change a time of passage of the drift chamber less than 1%, we obtain the value of this field $E' = 0.06$ V/cm, and the number density of ions $N_i = 1 \times 10^5\,\mathrm{cm}^{-3}$ corresponds to this field. Hence, the total number of ions at an indicated size of the ion bunch is $n_i \sim 10^4$. This amount of ions results from a small input energy that heats a gas where ions are formed by a value of $\Delta T \sim 10^{-7}$ K. Since this bunch of ions is formed in a narrow space region $\Delta x \sim 0.5$ cm and moves through the drift chamber with the drift velocity approximately 2×10^4 cm/s, the repetition of ionization signals is convenient with the repetition frequency below 1 kHz. Then signals of different pulses may be accumulated that can increase the accuracy of the express analysis. Note that in reality an increase of the ion number density, as well as the presence of atomic particles in air, can lead to broadening of the ion current signal, that can be taken into account. Therefore the indicated limit for the ion number density is not of principle.

Though the gas pressure can be different, we are guided by pressures $p \sim 0.1$ Torr. Note that a distance of transversal ion diffusion during ion location in the drift chamber

$$r = \sqrt{4Dt} = \sqrt{\frac{4DL}{w}} \approx \sqrt{\frac{4TL}{eE}}, \tag{17}$$

if we assume the ion drift velocity w to be proportional to the electric field strength E. At room temperature this gives $r \sim 3$ cm.

The above conditions may be fulfilled with using of a microsecond equipment and very low ion currents ∼ 1 pA in each pulse. We give in Figs. 2 and 3 the profiles of ion currents if oxygen atoms are found in the state $O(^3P)$ mostly, and a small admixture of atoms $O(^1D)$ and $O(^1S)$ is present in air. Since the criterion (12) is fulfilled, peaks for ions $O(^2D)$ and $O(^2D)$ are separated. Because the peak for a drift time of ions in the ground state $O(^4S)$ is found far from these ones, we give them in Fig. 3 separately. One can see that it is possible in principle to separate the cases when the concentrations of excited oxygen atoms $O(^1D)$ and $O(^1S)$ differ by ∼ 1%.

Though our task is the determination of the concentration of oxygen atoms and ions in excited states, this method may be used for oxygen atoms in the ground state when their concentration is low. Indeed, the main component of air is molecular nitrogen, and at low temperatures and low degrees of excitation oxygen is present in air in the form of molecules. Scattering of atomic oxygen ions in the ground and excited states on nitrogen and oxygen molecules is almost identical, but resonant charge exchange cross sections in collisions with oxygen atoms are different for the ground and excited oxygen states. When the concentration of oxygen atoms is very small, the mobility peaks are not distinguished for the ground and excited ion states. According to formula (14) these peaks are distinguished in atmospheric air at room temperature and the above parameters of the drift chamber if the concentration of atomic oxygen with respect to the molecular one exceeds 5%.

6. Ion drift in excited atmospheric air

In analyzing drift of oxygen atomic ions in air, we consider above this air to be located in the drift chamber and has a suitable pressure. We now consider one more scheme for such measurements directly in the atmospheric air under a suitable pressure. This scheme is given in Fig. 4, and a pulse of oxygen atomic ions generated by a pulse corona discharge is detected as peaks of the time dependence for the ion current.

There are two methods to measure drift times of atomic oxygen ions between electrodes which are supported at a certain voltage and are located in an atmospheric air. A certain amount of atomic oxygen ions is present in an atmospheric plasma. In the first case drift times of atomic oxygen ions in an atmospheric plasma are detected as the difference of a time of generation of these ions by pulse corona discharge and a time when a corresponding peak is observed. In other version of measurement of ion drift times ions are removed from the region between electrodes and may be inserted in this region from an atmospheric plasma through a shutter near a remote electrode. Then appearance of ions of each type at the collector is observed as a jump in the ion current. The amplitude of each jump gives the number density of ions in a given excited state. It is important that the mobility of ions in the ground state $O(^4S)$ is lower than that for other ion states, so that a more strong jump of the ion current proceeds later than weak jumps due to excited atomic oxygen ions. This improves the method accuracy as well as the repetition of pulses of corona discharge.

Note that an atmospheric plasma contains ions of different types, but the quadrupole mass-spectrometer is tuned on atomic oxygen ions, and other ions does not reach the collector. Though these charged atomic particles do not pass through

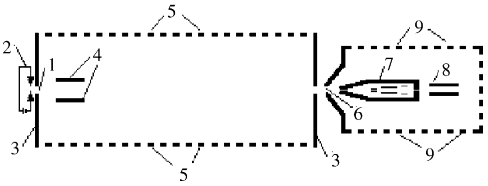

Fig. 4. A scheme for measurement of drift of oxygen atomic ions in an atmospheric plasma: (1) an entrance for charged particles; (2) pulse ionization of air by corona discharge; (3) electrodes with a constant electric field between them; (4) collector of electrons; (5) a grid for protection of interelectrode space from penetration of charged particles; (6) skimmer and condensed ion lenses; (7) quadrupole mass-spectrometer; (8) collector of ions; (9) a grid for protection of gaging equipment.

the quadrupole mass-spectrometer, fields of these particles may lead to distortions and must be taken into account. The method under consideration can be used only in a restricted range of air pressures. Indeed, ions are drifting between electrodes if the following criterion holds true

$$L \gg \lambda, \tag{18}$$

that takes place if the air pressure is $p \gg 10^{-4}$ Torr when $L \sim 100$ cm. In reality the lower boundary of the excited air pressure must be higher in order signals from different types of atomic oxygen ions can be resolved.

In considering ion drift both in the drift chamber and in atmospheric plasma, we assume that excited oxygen atoms and ions are not quenched in collisions during ion drift. This means that location of excited oxygen ions in the drift chamber does not influence on the balance of excited atoms. The rate constant of quenching of excited atoms in collisions with air atoms and molecules is small compared to the gas-kinetic rate constant. Indeed, quenching of excited atoms $O(^1D)$ or $O(^1S)$ by an atom $O(^3P)$ with transition of a colliding atom in the ground state $O(^3P)$ is weak since the total electron spin is conserved during the collision. For the same reason one can expect that transition of excited ions in the ground state $O(^4S)$ is also forbidden in nonrelativistic limit, i.e. such a process is weak.

Nevertheless, according to [25] the rate constant of quenching of excited oxygen atoms $O(^1S)$ in collisions with atoms in the ground state $O(^3P)$ is $7.5 \times 10^{-12}\,\text{cm}^3$ s and relates to transition of an excited atom in the state $O(^1D)$, so that the excitation energy transfers into the kinetic energy of colliding atomic particles. This transition is possible in such a collision at small distances between colliding particles when these particles are found on an attractive electron term, and this term is intersected with a repulsed electron term that corresponds to another excitation of a colliding particle. Therefore though a strict prohibition is absent in this case, one can expect a small rate constant of quenching.

The rate constant of $O(^1D)$ atom quenching in collisions with nitrogen molecules at room temperature is approximately $3 \times 10^{-11}\,\text{cm}^3/\text{s}$ [26]. Though this value is small compared a gas-kinetic rate constant ($2 \times 10^{-10}\,\text{cm}^3/\text{s}$), a typical time of quenching of excited atoms is comparable to a drift time of ions in the drift chamber during that a drifting ion has many collisions.

This fact has to account for the measurement scheme, so that the measurement operation cannot change equilibrium for excited atoms. This means that excited atoms can freely pass inside the drift chamber or leave it without quenching on walls, whereas charged particles of a surrounding atmospheric plasma cannot penetrate inside the drift chamber. This creates special requirements to the drift chamber. In particular, an air compression for a decrease of a time width of signals is not suitable for this case since this intensifies quenching of excited atoms.

Along with this, we assume a weak or measurable quenching of excited atomic ions in the course of their drift. Then measurement of drifting times for oxygen atomic ions in excited air allows one to find both the concentration of excited oxygen atoms in excited air and the concentration of atomic oxygen ions in different states.

7. Conclusions

The method under consideration uses a general concept [11–13] that nonexcited and excited ions interact with a buffer gas in a different way, and they are characterized by different mobilities. Above we analyze this concept for determination of the concentration of excited oxygen atoms on the basis of the ion mobility spectrometry for a drift of atomic oxygen ions in an excited atmospheric air. This air contains oxygen atoms in the ground and metastable states, and the cross sections of resonant charge exchange depend on the ion and atom state. This allows one to separate the currents for passage of ions through the drift chamber, and these signals are connected with the concentration of oxygen ions and atoms in the ground and metastable states. According to the analysis fulfilled, this method allows one to restore the concentrations of oxygen atoms and ions with an accuracy of 1% if the accuracy of relative times of ion passage through the drift camera can be measured with the accuracy of 10^{-3}. In addition, such measurements will deep our knowing of the kinetics and elementary processes involving excited atomic oxygen ions and oxygen atoms.

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