_____ GAS DISCHARGES, __ PLASMA

Investigation of the Glow and Contracted Discharge Plasmas in Nitrogen by Coherent Anti-Stokes Raman Spectroscopy, Optical Interferometry, and Numerical Simulation

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Abstract—The translational temperature in the plasma of glow and contracted discharges is measured using the methods of coherent anti-Stokes Raman spectroscopy and optical interferometry. The current density in the discharge is determined by measuring the electron concentration with optical interferometry and emission spectroscopy. The distribution of nitrogen molecules over vibrational and rotational levels in the ground state, the electron energy distribution, and the time dependence of the gas temperature are numerically found based on a model including the homogeneous Boltzmann equation and balance equations for the concentrations of charged and excited particles and for the gas temperature. The dynamics of transition to the quasi-steady-state distribution of nitrogen molecules over vibrational levels is studied. © 2005 Pleiades Publishing, Inc.

INTRODUCTION

Molecular nitrogen is used as a basic component in a variety of plasma-chemical processes and also as a small additive to various gases in studying the parameters of the gas discharge plasma. The glow discharge plasma in nitrogen is a heavily nonequilibrium weakly ionized gas. The factors responsible for nonequilibrium and affecting the kinetics of processes occurring in the plasma are the disturbance of equilibrium between the vibrational, rotational, and translational degrees of freedom of the molecules, as well as the deviation of the electron energy distribution function (EEDF) from the Maxwell distribution [1–3]. The retarded vibrational relaxation of nitrogen molecules in the discharge causes their high vibrational excitation, and the population of molecular vibrational levels is no longer described by the Boltzmann formula [4]. This greatly complicates experimental and theoretical investigation of the gas heating dynamics, as well as the EEDF and the molecule vibrational-rotational energy level distribution function (hereafter, molecule vibrational distribution function (MVDF)).

Numerical simulation of the process kinetics in the nonequilibrium gas discharge plasma requires experimental verification even if the processes are described in detail (*a fortiori* if they are briefly outlined). However, the published parameters entering into the relevant kinetic equations, such as the rate constants and the cross sections of elementary processes in a gas discharge, are frequently given with an insufficient accuracy, since they are difficult to calculate or measure. For example, the reported cross sections of electronimpact-induced vibrational level excitation in nitrogen molecules differ by a factor of 4 [5], and the scatter in the rate constants for vibrational-vibrational energy exchange (VV exchange) and vibrational-translational relaxation (VT relaxation) differ by one order of magnitude [6]. Therefore, it seems topical to develop efficient plasma diagnostics methods. However, development of diagnostics methods inevitably runs into the problem of gaining insight into elementary processes in the plasma and selecting a model substantiating the means of choice. A reasonable combination of experimental and theoretical studies would make it possible to experimentally verify numerical methods selected, gain lacking data for the rate constants and elementary process cross sections, optimize (with minimal costs) technologies using the plasma of a nonequilibrium gas discharge as an active medium, and comprehensively study its properties in a wide range of critical parameters.

An essential issue in studying the EEDF and MVDF in the nitrogen plasma is kinetic mechanisms behind the interplay between these functions [7–9]. An important parameter characterizing a discharge plasma is the translational temperature, which specifies the routes and rate constants of many plasma-chemical reactions.

The basic processes underlying the interplay between the EEDF and MVDF are electron collisions of the first and second kind with vibrationally excited molecules in the ground state, $N_2(X^1\Sigma_g^+, v)$. In addition, when considering the MVDF formation, one should take into account the processes of VV exchange and VT relaxation. To include these processes, the EEDF was taken by probe methods [10, 11] and the MVDF was obtained by jointly solving the Boltzmann equation and the balance (master) equation [7–9]. The input data, such as the translational and vibrational temperatures, reduced electric field strength, and electron concentration, were measured by the methods of emission spectroscopy, optical interferometry, and coherent anti-Stokes Raman scattering (CARS). The emphasis in this work was on determining the low-energy part of the EEDF. However, reliable determination of the rate constants for high-threshold processes calls for investigation of the high-energy part of the EEDF.

The dynamics of nitrogen heating in the discharge has been the subject of extensive research [12-19]. In this field, a number of reasons makes comparison between measurements and calculations difficult. When nitrogen heats up, it is necessary to take into account not only the interrelation between EEDF and MVDF but also many other processes that may affect their formation in the discharge plasma. Such are electron collisions of the first and second kind with excited particles, relaxation, deactivation of excited molecules and recombination of atoms, thermal losses due to a gas translational temperature gradient, etc. Translational temperature $T_{\rm tr}$ was measured by optical interferometry and CARS. Of special importance in our experiments is a channel of VV energy exchange between nitrogen molecules. It should be noted here that the form of the analytical MVDF is sensitive to the rate constant of VV energy exchange between the molecules [15].

The glow discharge as an object of investigation was chosen for the following reasons. First, in the positive column plasma, equilibrium between the vibrational, rotational, and translational degrees of freedom of nitrogen molecules is noticeably disturbed. Second, the glow parameters, such as electrode potential, cathode drop, and current intensity, which are necessary for finding electron concentration N_e and reduced electric field strength E/N, can be reliably measured. Third, one can use EEDF measurements taken by the probe method.

EXPERIMENTAL

Figure 1 shows the experimental setup used in this work to study the gas heating dynamics, gas density and electron concentration distributions over the cross section of the discharge cell, rotational temperature, and MVDF in a nitrogen glow by the methods of emission spectroscopy, interferometry, and CARS.

A dc longitudinal glow discharge was initiated in a quartz cell at a pressure ranging from 3 to 30 Torr. The cell was cooled by water, and so wall temperature T_w could be kept at 300 K. A weak gas flow was pumped

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Fig. 1. Schematic of the experimental setup: (1) Nd³⁺: YAG laser, (2) dye laser, (3, 17) power suppliers, (4, 5) controllers, (6, 14) photoelectric multipliers, (7) PC, (8) monochromator, (9) discharge cell, (10) filter, (11) lens, (12) lens with focal length f = 150 cm, (13) wedge, (15) camera, (16) voltage dividers, (18) He–Ne laser, and (19) oscilloscope.

through the cell, the flowing gas being prepurified in nitrogen traps. Ring titanium electrodes were mounted flush with the inner surface of the discharge tube. The inner radius of the tube was R = 1.8 cm. Windows at the end faces of the cell were made of different materials depending on optical diagnostics means. For optical interferometry and emission spectroscopy, the windows were made of quartz, which is transparent for the near-UV and visible ranges ($\lambda = 300-700$ nm). When the translational temperature and the populations of nitrogen molecule vibrational levels were measured by CARS, ZhS-17 and SS-5 color filters served as the entrance and exit windows of the cell. The former eliminated the CARS signal due to the nonlinear interaction between the laser beams propagating in the atmosphere toward the cell. The latter filter separated out the CARS valid signal from the total radiation of the discharge and lasers.

Translational temperature T_{tr} and the populations of nitrogen molecule vibrational levels were measured at two stages of the glow. At the first (transient) stage (t = 3-20 ms), T_{tr} was measured optically. It is at this stage of the discharge that its basic parameters (current intensity, T_{tr} , and MVDF) are formed at a constant pressure. The glow discharge was initiated by stepwise increasing the voltage applied to the cell electrodes from a regulated high-voltage power supply. As soon as the discharge was initiated, a voltage drop and current intensity in the discharge gap were displayed and measured on the oscilloscope's screen using resistive voltage dividers.

In the time interval t = 20-25 ms, within which the low-frequency vibrations of the setup deteriorate the accuracy of interferometric measurements, T_{tr} and the MVDF were determined by narrow-band CARS. In addition, T_{tr} and gas density distributions N and N_e over the cross section of the cell were measured by optical interferometry and emission spectroscopy. At this stage, the discharge became quasi-stationary and its current remained at the level $I_d = 20-50$ mA.

From the measured values of p, T_{tr} , and electrode voltage, we found E/N. Electric field strength E in the positive column of the glow was determined with regard to the cathode drop [2], and molecular concentration N at the discharge axis was determined with allowance for a decrease in the gas density as a result of heating. The values of E/N varied from 40 to 80 Td. To take the time dependence of T_{tr} along the axis of the cell and the distribution of this temperature over the cell's cross section, we used a two-pass Michelson interferometer [20, 21].

As a source of monochromatic radiation in the interferometer, a single-mode 632.8-nm He-Ne laser with an output of 50 mW was applied. The laser beam was expanded to 4 cm in diameter with a telescope and then was wedge-split into two, object and reference, beams. The former was directed toward a mirror through the windows, reflected from the mirror, and then (upon being made coincident with the reference beam on the wedge) fell on a lens together with the reference beam reflected from the mirror. Such a double-pass optical scheme was used to improve the sensitivity of the setup at low pressures. Another lens with a focal length of 150 cm placed before the splitter matched the size of the interference pattern to that of the camera frame and to the slit of a photoelectric multiplier (PM). Photographing of the interference pattern provides information on the $T_{\rm tr}$ distribution along the radius of the gasdischarge tube. The maximal displacement of the fringes at the discharge axis was equal to 3.2-8.0 widths of the fringe. The fringe displacement was measured accurate to 0.2 of the fringe width. The axial displacement of the fringes was detected by the PM. The 0.3×4.5 -mm² slit before the PM cathode was placed in such a way that its center was coincident with the center of the interference pattern. The fringes ran parallel to the slit. The signal from the PM was displayed on the screen of the oscilloscope. The time resolution of the PM was 5 µs. The typical waveforms of PM signals and typical interferograms were demonstrated earlier [22, 23]. The fringe displacement measurements were processed by the method described in [20, 21].

The variation of electron concentration N_e at the cell axis in time was calculated from the dependence of the current on the electron drift velocity and discharge cross section S_d ($S_d = \pi R_f^2$, where R_f is the effective radius of the current filament, which is found by the technique described in [14]). The drift velocity was found by solving the Boltzmann equation for the EEDF. As input data, the measured parameters of the glow discharge plasma were used.

It has been experimentally established [14] that, at p = 15-20 Torr in a contracted discharge, the distribution of the radiation intensity from the nitrogen second positive system over the cell's cross section correlates with the electron concentration distribution over the cross section. Therefore, the value of $R_{\rm f}$ was determined from the distribution of radiation intensity $I_{\lambda}(r)$ along cell radius r at wavelengths $\lambda = 337, 354, 358$, and 380 nm of the nitrogen second positive system. Intensity $I_{\lambda}(r)$ was measured with a photoelectric spectral instrument equipped with two 2×2 -mm diaphragms. The spatial resolution along the cell radius was 2 mm. Effective radius $R_{\rm f}$ was determined from the relationship [14]

$$R_{\rm f}^2 = 2 \int_{0}^{R} \frac{I_{\lambda}(r)}{I_{\lambda}(0)} r dr.$$
 (1)

In the stationary glow discharge, the rotational temperature and the populations of nitrogen molecule vibrational levels v = 0-4 in the ground state were measured with a Sopra (France) CARS spectrometer.

The second harmonic of a Nd³⁺ : YAG laser at the frequency corresponding to wavenumber $v_1 =$ 18797 cm⁻¹ (the peak energy is 50 mJ, a pulse width of 25 ns, and a pulse repetition rate of 10 Hz)) and the radiation of a tunable dye laser (the peak energy 1 mJ at the frequency corresponding to wavenumber $v_2 =$ 16475 cm⁻¹) were focused along the positive column of the glow by a lens with a focal length of 50 cm. The populations of the levels at p = 3.5 Torr were measured with the collinear beams. Such a scheme provided a spatial resolution of 250 μ m \times 250 μ m \times 4 cm. When the vibrational temperature was measured at p = 11-20 Torr, the spatial resolution was raised by using sharp focusing of the beams in plane (Planar BOXCARS approach). Such an approach allowed us to improve the spatial resolution to $250 \times 250 \times 500 \,\mu\text{m}$. The valid signal at anti-Stokes frequency ω_{aS} was separated out from the total discharge and laser radiation by wide-band filters and a concave-grating monochromator. The CARS valid signal was recorded in the counting mode with an optical spectrum multichannel analyzer (OSMA).

To find the populations of the vibrational levels, we recorded the intensity distribution in the spectrum of

the *Q* branch of vibrational-rotational transitions from $v = 0 \longrightarrow v = 1$ (Q_{01}) to $v = 4 \longrightarrow v = 5$ (Q_{45}). The MVDF was determined from the CARS spectra by the method suggested in [22]. Rotational temperature T_{rot} was determined from the vibrational-rotational Raman spectrum of the *Q* branch of vibrational transition $v = 1 \longrightarrow v = 2$. From the experimentally found spectrum, the dependence of $\ln(N_J/g_J)$ on J(J + 1) was constructed (N_J is the population of a rotational level with quantum number *J*, and g_J is the order of its degeneracy). When constructing this dependence, we took into account the degeneracy orders of rotational levels and spin degeneracy of the ground state. The rotational temperature was found from the slope of the straight line

$$\ln(N_J/g_J) = \text{const} + J(J+1)\frac{B_e}{kT_{\text{rot}}},$$
 (2)

which was constructed by the rms method under the assumption that the populations of rotational levels obey the Boltzmann distribution. Here, B_e is the rotational constant of a nitrogen molecule and k is the Boltzmann constant. Under our experimental conditions, the translational and rotational temperatures coincide.

KINETIC MODEL

Figure 2 shows the scheme for finding the EEDF and MVDF, as well as for elucidating mechanisms underlying their interplay and gas heating. When finding the MVDF and low-energy part of the EEDF, we varied total (over the first eight vibrational levels) vibrational excitation cross section σ_{Σ} and rate constants of VV exchange in order to achieve the best agreement between the computational results and experimental data. Next, to improve the reliability of extracted quantitative information on the EEDF, MVDF, σ_{Σ} , and rate constants of VV exchange, the number of measured glow discharge plasma parameters used as input data was taken as large as possible.

The EEDF and its basic moments, drift velocity v_{dr} and characteristic temperature D/μ of electrons in the glow discharge plasma, were found by numerically solving the Boltzmann equation. The input data for determining the EEDF were measured values of *E* and T_{tr} . The value of *E/N* was found with regard to the cathode drop and a change in molecular concentration *N* due to gas heating. The cathode drops for various materials used as glow-sustaining electrodes are given in [2].

When comparing the calculated and measured [10, 11] EEDFs in the typical experimental range E/N = 40-80 Td (Table 1), we varied σ_{Σ} and vibrational temperature T_v of the first vibrational level ($T_v = \theta_v/\ln(N_1/N_0)$), where θ_v is the vibrational quantum of a nitrogen molecule).

The EEDF and MVDF were found by iterations from a solution to the Boltzmann equation and kinetic equations that describe the balance of vibrationally



Fig. 2. Block diagram of calculating the discharge kinetics. (1) Comparison of calculated and experimental data for EEDF, v_{dr} , and D/μ ; (2) input experimental data for EEDF, *E/N*, T_{tr} , and T_{v} ; (3) variation of T_{v} and comparison with experiment; (4) EEDF; (5) refinement of cross section σ_{Σ} by comparing calculation and experiment; (6) heating of electrons by electric field E; (7, 21) electron-impactinduced vibrational excitation of molecules; (8) electronimpact-induced ionization of molecules and atoms; (9) electron-impact-induced excitation of Rydberg states of molecules; (10, 23) electron-impact-induced excitation of molecules and atoms; (11) electron-electron collisions; (12) electron-molecule and electron-atom elastic collisions; (13) electron-impact-induced dissociation of molecules; (14) electron-impact-induced rotational excitation of molecules; (15) iterations to determine EEDF, MVDF, vdr, D/μ , $T_{\rm tr}$, and $T_{\rm v}$; (16) reaction rate constants K_i ; (17) input experimental data for heat conduction equation and calculation of MVDF (N, R, N_e, γ_v , γ_{at} , and T_v); (18) MVDF; (19) VT molecule-molecule relaxation; (20) gas heating and heat removal toward the cell wall; (22) VT molecule-atom relaxation; (24) VV molecule-molecule energy exchange; (25) refinement of VV exchange rate constants by comparing calculation with experiment; (26) diffusion of excited molecules and atoms followed by heterogeneous relaxation at walls; (27) dissociation of molecules by electron impact and via vibrational excitation; and (28) comparison of calculated and experimental data for MVDF, T_{v} , and T_{tr} .

excited molecules and variation of the gas chemical composition. This set of equations also included an equation for T_{tr} variation in the isobaric approximation. The exited particle concentration obtained by calculation was used to refine the EEDF, which varies with the chemical composition of the gas and due to electron collisions of the second kind with excited particles. From the EEDF calculated, rate constants K_i , v_{dr} , electron energy losses η_{elas} due to electron—heavy particle elastic collisions, and electron energy losses η_{rot} due to molecule rotational excitation were found. The values

T _{tr} , K		<i>T_v</i> , K		Р,	R cm	t ms	N _e ,	<i>E/N</i> ,	Pefs
experiment	theory	experiment	theory	Torr	R, CIII	1, 1115	cm ⁻³	Td	KC15.
$530 \pm 30^{\text{CARS}}$	470 ($\gamma_v = 10^{-4}$)	$5300 \pm 350^{\text{CARS}}$	4960 ($\gamma_v = 10^{-4}$)	2.0	1.0	11	2×10^{10}	80	[28]
	420 ($\gamma_v = 10^{-3}$)		4250 ($\gamma_v = 10^{-3}$)						
$480 \pm 40^{\text{CARS}}$	512 ($\gamma_v = 10^{-4}$)	$3790 \pm 350^{\text{CARS}}$	3700 ($\gamma_v = 10^{-4}$)	3.5	1.8	20	3.5×10^{9}	45	[22]
G + D 3	470 ($\gamma_v = 10^{-3}$)	G. D.	3475 ($\gamma_v = 10^{-3}$)				10		
$530 \pm 40^{\text{CARS}}$	545 ($\gamma_v = 10^{-4}$)	$4320 \pm 350^{\text{CARS}}$	4255 ($\gamma_v = 10^{-4}$)	7.0	1.8	15	1.2×10^{10}	60	
520 ± 50^{OI}	530 ($\gamma_v = 10^{-3}$)	GADG	4200 ($\gamma_v = 10^{-3}$)				0		
$600 \pm 40^{\text{CARS}}$	610 ($\gamma_v = 10^{-4}$)	$4270 \pm 350^{\text{CARS}}$	4240 ($\gamma_v = 10^{-4}$)	9.5	1.8	15	6×10^{9}	70	
570 ± 50^{01}	605 ($\gamma_v = 10^{-3}$)	GADG	4240 ($\gamma_v = 10^{-3}$)				0		
$395 \pm 15^{\text{CARS}}$	400 ($\gamma_v = 10^{-4}$)	$2850 \pm 100^{\text{CARS}}$	2790 ($\gamma_v = 10^{-4}$)	12.0	0.7	30	∝10 ⁹	<100	[27]
CARS	$360 (\gamma_v = 10^{-3})$		2615 ($\gamma_v = 10^{-3}$)				10		
1000 ± 100^{CARS}	1135 ($\gamma_v = 10^{-4}$)			15.0	1.8	30	2×10^{10}	70	
1140 ± 110^{OI}	1135 ($\gamma_v = 10^{-3}$)						10		
$1200 \pm 110^{\text{CARS}}$	$1230 (\gamma_v = 10^{-4})$			20.0	1.8	30	4×10^{10}	68	This
1230 ± 120^{OI}	$1230 (\gamma_v = 10^{-3})$			• • • •		• •	a to 10		WOIK
$1350 \pm 130^{\text{CARS}}$	$1300 (\gamma_v = 10^{-4})$			30.0	1.8	30	5×10^{10}	67	
1300 ± 350^{OI}	1300 ($\gamma_v = 10^{-3}$)						a a 10		
1150–120001	1170 ($\gamma_v = 10^{-4}$)			20.0	1.0	30	3.9×10^{10}	59	[14]
	1170 ($\gamma_v = 10^{-3}$)								

Table 1

of K_i , v_{dr} , η_{elas} , and η_{rot} thus obtained were then used in calculating the variation of the gas composition in the plasma, N_e , and gas heating dynamics, respectively. Importantly, the rate constants of VV exchange and cross sections σ_{Σ} were refined at each iteration by comparing the calculated and experimental MVDF and T_{tr} , as well as the EEDF and its basic moments. Such a procedure was repeated until the rate constants and cross section started converging.

When determining $N_{\rm e}$ and $T_{\rm tr}$, we took into consideration their nonuniform distribution over the cross section of the cell. In solving the master equation for the composition, allowance was made for particle diffusion toward the walls followed by heterogeneous (*VW*) relaxation in order to estimate the effect of these processes on the MVDF and gas heating.

KINETIC EQUATION FOR THE ELECTRON ENERGY DISTRIBUTION FUNCTION

The homogeneous Boltzmann equation was solved by the two-term approximation method, according to which the EEDF is expanded into a series in spherical harmonics (Legendre polynomials) up to the first two terms, which specify its isotropic part $f(\varepsilon)$ and current characteristics of electrons.

Isotropic part $f(\varepsilon)$ was obtained by solving the equation with regard to (i) electron-atom and electron-molecule elastic collisions; (ii) excitation of $A^{3}\Sigma_{\mu}^{+}$, $B^{3}\Pi_{a}$, $C^{3}\Pi_{u}, B^{\prime 3}\Sigma_{u}^{-}, a^{\prime 1}\Sigma_{u}^{-}, W^{3}\Delta_{u}, a^{1}\Pi_{g}, w^{1}\Delta_{u}, \text{ and } a^{\prime\prime 1}\Sigma_{g}^{+}$ electron and Rydberg rotational and vibrational states, as well as electron-impact-excited (hereafter, impactexcited) states ${}^{2}P$ and ${}^{2}D$; (iii) impact-induced dissociation of molecules in the ground state and also through electron levels with passage to repulsive terms; (iv) ionization of molecules in the ground state due to electronmolecule collisions; (v) impact-induced ionization of atoms from ground state ${}^{4}S$; (vi) collisions of the second kind between vibrationally excited molecules that are in ground $X^1 \Sigma_g^+$ state (only for the first ten levels) and in the impact-excited states listed above (except for state $a''^{1}\Sigma_{g}^{+}$ and electrons; and (vii) collisions of the second kind between electrons and atoms in impactexcited states ${}^{2}P$ and ${}^{2}D$.

In the spatially homogeneous approximation, the equation for the isotropic part of the EEDF has the form [7-9]

$$\frac{E^{2}\varepsilon}{3\sum_{l}N_{l}\sigma_{ml}(\varepsilon)}\frac{df(\varepsilon)}{d\varepsilon} + \sum_{l}2\frac{m}{M_{l}}N_{l}\varepsilon^{2}\sigma_{ml}(\varepsilon)$$

$$\times \left[f(\varepsilon) + \frac{T_{\mathrm{tr}} df(\varepsilon)}{d\varepsilon} \right] + NB_{\varepsilon} \varepsilon \sigma_{\mathrm{rot}}(\varepsilon)$$

$$\times \left[f(\varepsilon) + \frac{T_{\mathrm{tr}} df(\varepsilon)}{d\varepsilon} \right] = -\sum_{l} N_{l} \sum_{i,j} \int_{\varepsilon}^{\varepsilon + \varepsilon_{ij}} \sigma_{ij}(\varepsilon') \varepsilon' f(\varepsilon') d\varepsilon'$$

$$-\sum_{i,j} N_{j} \int_{\varepsilon}^{\varepsilon - \varepsilon_{ij}} q_{ij}(\varepsilon') \varepsilon' f(\varepsilon') d\varepsilon'.$$
(3)

Here, *m* and M_l are the masses of an electron and molecule (l = 0) or atom (l = a); N_l is the concentration of molecules or atoms in the ground state; ε is the electron energy; ε_{ii} is the change in the electron energy due to electron-molecule or electron-atom collisions; $\sigma_{ml}(\epsilon)$ is the transport scattering cross section of an electron by a nitrogen molecule (l = 0) or atom (l = a); $\sigma_{rot}(\varepsilon)$ is the cross section of electron-impact-induced vibrational level excitation; $\sigma_{ii}(\epsilon)$ are the cross sections of dissociation, ionization, vibrational level excitation, and electron level excitation for a molecule or atom in the case of direct reactions; q_{ii} are the cross sections of collisions of the second kind between electrons and molecules or atoms in impact-excited states, which is calculated from the principle of detailed balance; and N_i is the concentration of molecules and atoms, as well as vibrationally excited molecules in electron state $X^1 \Sigma_g^+$ for vibrational levels $1 \le v \le 10$. The set of cross sections is the same as used in [7-9].

The first term in the left of Eq. (3) stands for an increase in the electron energy in field *E*; the second, for energy losses in electron–molecule and electron– atom elastic collisions; and the third, for energy losses due to electron-impact-induced excitation of nitrogen molecule vibrational levels. The right of this equation describes electron–heavy particle inelastic collisions, which change the energy state of the particles (the transition from state *i* to state *j* with energy change ε_{ij} or $-\varepsilon_{ij}$ for electron collisions of the second kind with excited heavy particles). The form of the equation implies that electron–electron collisions are disregarded.

The EEDF is normalized as follows:

$$\int_{0}^{\infty} \sqrt{\varepsilon} f(\varepsilon) d\varepsilon = 1.$$
 (4)

The Boltzmann equation for the EEDF was solved by iterations [9]. The function calculated by the method given in [24] was used as a zeroth-order approximation.

The rate constants for excitation of nitrogen molecule electron states from unresolved higher vibrational levels of ground state $X^1 \Sigma_g^+$ were calculated by relationships derived in [25]. Other rate constants for electron– heavy particle interaction were found by normalizing

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the cross sections of related reactions by the EEDF,

$$K_{i} = \sqrt{\frac{2e}{m}} \int_{0}^{\infty} \sigma_{ij}(\varepsilon) \varepsilon f(\varepsilon) d\varepsilon.$$
 (5)

The values of v_{dr} and D/μ were determined from the relationships [26]

$$D/\mu = \int_{0}^{\infty} \frac{\varepsilon}{\sigma_m(\varepsilon)} f(\varepsilon) d\varepsilon / \int_{0}^{\infty} \frac{\varepsilon}{\sigma_m(\varepsilon)} \frac{df(\varepsilon)}{d\varepsilon} d\varepsilon, \qquad (6)$$

$$v_{\rm dr} = 1/3 \sqrt{\frac{2e}{m}} E/N \int_{0}^{\infty} \frac{\varepsilon}{\sigma_m(\varepsilon)} \left[-\frac{df(\varepsilon)}{d\varepsilon} \right] d\varepsilon.$$
(7)

MASTER EQUATIONS FOR GAS COMPONENTS AND GAS HEATING

The glow discharge positive column is characterized by a complex composition, many kinetic processes, and nonuniform distribution of parameters (molecular, atomic, and electron concentrations; gas temperature; etc.) over the column's cross section. When processing experimental data obtained in this work and in [14, 22, 27, 28], we took into consideration (i) nitrogen molecules in ground state $X^1 \Sigma_g^+$ (47 vibrational levels, among which the level v = 46 was assumed to be a level of dissociation via vibrational excitation) and in impact-excited states $A^{3}\Sigma_{u}^{+}$, $B^{3}\Pi_{g}$, $C^{3}\Pi_{u}$, $B^{\prime3}\Sigma_{u}^{-}$, $a^{\prime1}\Sigma_{u}^{-}$, $W^{3}\Delta_{u}$, $a^{1}\Pi_{g}$, and $w^{1}\Delta_{u}$; (ii) nitrogen atoms in the ground, ${}^{4}S$, and excited, ${}^{2}P$ and ${}^{2}D$, states; and (iii) electrons *e*. The processes and rate constants that were included in describing the glow discharge plasma kinetics are listed in [7, 25].

Furthermore, the master equations for particles and gas temperature must include diffusion and transport phenomena, which greatly complicates the solution of the problems stated. A method was suggested [29, 30] that makes it possible to simplify the partial differential equations. With this method, the set of partial differential equations is reduced to a set of stiff ordinary differential equations for plasma parameters averaged over the cell's cross section. In experiments, however, the discharge parameters are usually measured at the axis of the cell. The approach used in this work allows one to derive a set of stiff ordinary differential equations for the parameters that describe the state of the plasma at the axis of the positive column with regard to heat removal and diffusion of vibrationally excited molecules and atoms from the positive column axis toward the walls with subsequent heterogeneous relaxation of the molecules and recombination of atoms. This approach is based on the assumptions that (i) during the establishment of the gas parameters, the radial profiles of the translational temperature and particle concentration are near-stationary; (ii) pressure p is constant along the positive column; and (iii) the gas flow velocity, as well as the rates of dissociation and ionization, in the positive column are high.

It was also assumed that, in the diffusion- and/or recombination-controlled positive column, energy release $V_T(r)$ and atomic (molecular) concentration $V_{v, at}(r)$ vary along the cell radius by the law

$$V_{x,T}(r) = V_{x,T}(0)(1 - (r/R)^{z}).$$
 (8)

Here, z is an approximation parameter that is determined by comparing the calculated and measured radial temperature profiles $T_{tr}(r)$. Quantities $V_T(0)$ and $V_{v, at}(0)$ express, respectively, heat removal and diffusion of vibrationally excited molecules and atoms from the discharge axis with subsequent heterogeneous relaxation of the molecules and recombination of the atoms at the walls. Under the above assumptions, these quantities as functions of T_{tr} and particle concentration at the cell axis were found by solving the heat conduction and diffusion equations with appropriate boundary conditions [29, 30],

$$\frac{1}{r}\frac{\partial}{\partial r}\left(rD_{x}\frac{\partial N_{x}}{\partial r}\right) = -V_{x}(r), \qquad (9)$$

$$\frac{\partial N_x}{\partial r}\Big|_{r=0} = 0, \quad D_x \frac{\partial N_x}{\partial r}\Big|_{r=R} = \frac{\gamma_x \langle v_x \rangle}{4} N_x \Big|_{r=R}, \quad (10)$$

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\chi\frac{\partial T_{u}}{\partial r}\right) = -V_{T}(r), \qquad (11)$$

$$\frac{\partial T_{\rm tr}}{\partial r}\Big|_{r=0} = 0, \quad T_{\rm tr}\Big|_{r=R} = T_{\rm w}, \quad \chi = \chi_0 (T_{\rm tr}/273)^a.$$
(12)

Here, $\langle v_x \rangle$ (x = v or at) is the mean thermal velocity of molecules or atoms; γ_x is the probability of deactivation of the molecules or recombination of the atoms at the walls; N_x is the concentration of vibrationally excited molecules, $N_2(X^1\Sigma_g^+, v)$, or atoms, $N(^4S)$; D_x is the diffusion coefficient of the molecules or atoms; and $\chi_0 = 2.3 \times 10^{-4}$ W/(K cm) is the thermal conductivity [31]. For nitrogen molecules, $\alpha = 0.84$.

Regardless of vibrational level v, the diffusion coefficients were set equal to [31]

$$D_v = \frac{136.8}{p} (T_{\rm tr}/273)^{1.5}, \ D_{\rm at} = \frac{220.4}{p} (T_{\rm tr}/273)^{1.74},$$
 (13)

where *p* is expressed in Torr.

Under the experimental conditions considered, heterogeneous relaxation of the molecules proceeds largely through physical adsorption [1],

$$W + N_2(X^1 \Sigma_g^+, v+1) \Longrightarrow W + N_2(X^1 \Sigma_g^+, v), \quad (14)$$

$$W + N({}^{4}S) + N({}^{4}S) \Longrightarrow W + N_{2}(X^{1}\Sigma_{g}^{+}, v).$$
 (15)

The value of γ_v was varied from 10^{-4} to 10^{-3} depending on the cell material (quartz, glass, or Pyrex), while γ_{at} was set equal to 10^{-4} [1, 4]. The temperature of the cell walls was taken to be $T_w = 300$ K. Calculations showed that wall (surface) deactivation of impact-excited molecules and atoms is a much weaker process than volume quenching of the excitation and, hence, may be ignored under our experimental conditions [14, 22, 27, 28].

The translational temperature profile taken by optical interferometry is given by

$$T_{\rm tr}(r) = T_{\rm w} \bigg[1 + (1 - (r/R)^2) \frac{(0.25 - (r/R)^2/(z+2)^2)}{(0.25 - 1(z+2)^2)} \times ((T_{\rm tr}/T_{\rm w})^{\alpha+1} - 1) \bigg]^{\frac{1}{1+\alpha}}.$$
 (16)

For such a profile of $T_{tr}(r)$, thermal losses $V_T(0)$ at the axis are expressed (in terms of K/s) as

$$V_T(0) = \frac{4T_w\chi_0}{R^2(1+\alpha)} (T_{tr}/T_w)^{\alpha} \frac{\left[(T_{tr}/T_w)^{\alpha+1} - 1\right]}{\left[1 - \frac{4}{(z+2)^2}\right]}.$$
 (17)

The variation of the concentration of molecules in the state with quantum number v = 0 or atoms due to diffusion from the discharge axis is given by

$$V_{0, \, \text{at}} = \frac{N_{1, \, \text{at}}}{\tau_{\gamma} + \tau_D}.$$
 (18)

In the master equation, this term describes an increment of molecules in the state with v = 0 through VW deactivation of those in the state with v = 1. For atoms, this term describes a decline in the concentration because of wall recombination. The associated relationship for molecules with $v \ge 1$ has the form

$$V_{v}(0) = \frac{N_{v+1} - N_{v}}{\tau_{\gamma} + \tau_{D}}.$$
 (19)

Characteristic times τ_D and τ_γ for diffusion and VW deactivation of molecules (recombination of atoms) at the wall depend on the translational temperature at the cell axis as follows:

$$\tau_{D} = \frac{R^{2}[0.25 - 1/(z+2)^{2}][(T_{\rm tr}/T_{\rm w})^{1+\alpha} - (T_{\rm tr}/T_{\rm w})^{\beta_{\rm v,\,at}}]}{D_{\rm v,\,at}[1 - \beta_{\rm v,\,at}/(1+\alpha)][(T_{\rm tr}/T_{\rm w})^{1+\alpha} - 1]},$$

$$\tau_{\gamma} = \frac{4R(0.5 - 1/(z+2))}{\langle v_{\rm v,\,at} \rangle \gamma_{\rm v,\,at}}.$$
(20)

Thus, in view of the earlier found expressions for $V_{v, al}(0)$ and $V_T(0)$, the simplified master equations for the excited particle concentration and translational temperature in the isobaric approximation have the form of

stiff ordinary differential expressions of type

$$\frac{dN_i}{dt} = \sum_f \sum_j k_{ji}^f N_j - \sum_f \sum_j k_{ij}^f N_i + \sum_f \sum_j k_{ji}^f N_i N_j$$

$$-\sum_{f}\sum_{j}k_{ij}^{J}N_{i}N_{j} + \sum_{f}\sum_{j}\sum_{l}k_{jil}^{J}N_{j}N_{i}N_{l}$$
(21)

$$-\sum_{f}\sum_{j}\sum_{l}k_{ijl}^{f}N_{i}N_{j}N_{l}-\frac{N_{i}dT_{\mathrm{tr}}}{T_{\mathrm{tr}}}+V_{i}(0),$$

$$3.5kN\frac{dT_{\rm tr}}{dt} = \sum_{j} \Delta \varepsilon_{ij} \frac{dN_i}{dt} - V_T(0).$$
(22)

The first two terms in Eqs. (21) and (22) describe one-particle processes responsible for an increase or decrease in the concentration of particles of sort *i* as a result of which a particle of sort *j* disappears or appears (such processes are, for example, radiation-induced processes). The third and fourth terms stand for twoparticle processes, such as impact-induced excitation or de-excitation of molecules or atoms, VT moleculemolecule and molecule-atom relaxation, one-quantum VV exchange, molecular dissociation, and exchange reactions between molecules and atoms in the ground and impact-excited states. The fifth and sixth terms account for three-particle processes: recombination of nitrogen atoms in the ground and impact-excited states. Here, subscripts j and l denote the sort of interacting particles. The last two terms describe the thermal expansion of the elementary volume of the gas and diffusion of excited molecules and atoms toward the cell walls with subsequent VW heterogeneous relaxation. Superscript f indicates the type of reaction between the components, since the same pair of particles may be involved in reactions of several types.

When numerically simulating the MVDF, rate constant K_{10}^{01} of VV exchange was varied until the best agreement between the calculated and measured values of vibrational temperature T_v was achieved.

The basic factors that govern the translational temperature, i.e., are responsible for gas heating in a wallbounded discharge, are (i) VT relaxation of excited molecules on molecules and resulting atoms, (ii) vibrational energy losses due to VV exchange between molecules, (iii) electron-molecule and electron-atom elastic collisions, (iv) excitation of molecular vibrational levels by an electron impact, and (v) thermal losses due to a translational temperature gradient. The model at hand also includes processes with the participation of molecules and atoms in excited states. These processes may noticeably affect the populations of vibrational levels responsible for the MVDF formation and, thereby, indirectly influence the gas heating dynamics. On the other hand, since the amount of energy directly converted to heat via collisions of molecules in ground

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state $X^1 \Sigma_g^+$ and metastable states $A^3 \Sigma_u^+$ and $B^3 \Pi_g$ is not known exactly [6, 17], the direct contribution of these processes to gas heating was not carefully analyzed and so calls for further investigation. Note that gas heating due to ionization of molecules and atoms was not taken into consideration as well.

The set of equations was solved numerically by the method suggested in [32]. At the zero time, the MVDF corresponded to the Boltzmann distribution for $T_{\rm tr} = 300$ K. The concentrations of atoms and molecules in the excited states were set equal to zero. In the course of integration of the equations for particle concentrations, the rate constants for vibrational excitation of the molecules were recalculated according to the variation of the vibrational temperature of the first excited level (300 K $\leq T_v \leq 6000$ K) and translational temperature (300 K $\leq T_{\rm tr} \leq 6000$ K) with time.

RESULTS AND DISCUSSION

Electron energy distribution function. Figs. 3a– 3c compare the calculated EEDF and the EEDF measured by the probe method [10, 11] for the quasi-stationary glow discharge. At E/N = 60-140 Td, the calculation and measurements are in good agreement when $T_v = 3800-4000$ K. It is these values of the vibrational temperature that were obtained by the CARS method under the conditions considered (Table 1).

In the quasi-stationary mode of the glow discharge plasma, near-resonance VV exchange, together with molecule–electron inelastic collisions, plays an essential role in redistribution of populations N_0 and N_1 over vibrational levels. Therefore, T_v depends on rate constant K_{10}^{01} of VV exchange. To provide simultaneous agreement between experimental and calculated data for the MVDF (lower states) and EEDF, σ_{Σ} was varied together with K_{10}^{01} . The former parameter ranged from 3.0 and 13.3 Å² (see [5 and Refs. cited therein]); the latter, from 9×10^{-15} to 1.5×10^{-13} cm³/s [6, 33–36]. For the EEDF, the calculation and measurements are in best agreement when $\sigma_{\Sigma} = 9-10.6$ Å² and $K_{10}^{01} = 9 \times 10^{-15}$ cm³/s, which almost coincides with the values recommended in [5, 6], respectively.

Thus, both the theory and experiment indicate the presence of an additional mechanism behind VV energy exchange between molecules in lower excited states, this mechanism indirectly influencing the form of the EEDF. For the nonequilibrium glow discharge plasma, a consistent description of the electronic component kinetics and vibrational kinetics is only possible if electron collisions of the first and second kind with vibrationally excited molecules and VV exchange in the states with quantum numbers v = 0 and 1 are taken into consideration concurrently.



Fig. 3. EEDF in the glow discharge nitrogen plasma: (a) E/N = 60 Td, $T_v = 3800$ K; (b) E/N = 80 Td, $T_v = 4000$ K; and (c) E/N = 140 Td, $T_v = 4000$ K. Lines, calculation; squares, data points [10, 11].

As follows from calculations, the production of atoms affects the EEDF insignificantly when the degree of dissociation of molecules does not exceed 10^{-3} . *VT* molecule–atom relaxation also remains the MVDF for the first eight to ten vibrational levels and, hence, the EEDF is unaffected.

As E/N exceeds 70 Td, the electron energy is spent mostly on the excitation of electron degrees of freedom, as well as on dissociation and ionization of molecules. At E/N = 80 and 140 Td, variation of the vibrational temperature changes the EEDF only slightly. As follows from Figs. 3b and 3c, good agreement between the calculation and experiment is achieved when T_v is no higher than 4000 K.

The calculated values of drift velocity v_{dr} and characteristic temperature D/μ of electrons are consistent with reference data [26] in the range E/N = 10-85 Td.



Fig. 4. MVDF in the glow discharge. Data points are taken from (**1**) [27], (+) [22], and (**0**) [28]. Computational results are shown by solid lines. Boltzmann distribution: $T_v = (1)$ 5300, (2) 4320, and (3) 2850 K. Treanor distribution: (4) $T_v = 5300$ K, $T_{tr} = 530$ K; (5) $T_v = 4320$ K, $T_{tr} = 530$ K; and (6) $T_v = 2850$ K, $T_{tr} = 395$ K. (7–9) Calculation by the model adopted in this work. v is the vibrational quantum number.

Molecule vibrational distribution function and gas heating. Table 1 and Figs. 4 and 5 compare the computational results for the MVDF, T_{tr} , and T_v with the measurements performed in this work and in [4, 22, 27, 28]. Figure 5 shows the evolution of T_{tr} from its initial (at the time the discharge is initiated) to a steady-state value.

The experimental data listed in Table 1 were obtained in the positive column of the glow discharge plasma at the cell axis. Superscripts OI and CARS indicate that associated $T_{\rm tr}$ and $T_{\rm v}$ were measured by the methods of optical interferometry and CARS, respectively.

Temperatures T_{tr}^{CARS} and T_{v}^{CARS} were found from the populations of rotational and first two vibrational levels that were determined from the CARS spectra. The solid lines in Fig. 4 refer to the MVDFs calculated according to the kinetic model, as well as to the Boltzmann and Treanor distributions.

Residence time t of nitrogen molecules in the discharge zone listed in Table 1 coincides with the time of setting the quasi-stationary values of T_{tr} and T_{v} , which characterize the MVDF in the positive column. The quasi-stationary values of T_{tr} at pressures of 15 and 20 Torr are presented in Table 1 and in Figs. 5a and 5b. Figure 5 also shows the experimental time dependence of the current that was used in calculating T_{tr} . The calculation and measurements of T_{tr} and T_{v} indicate that

the quasi-stationary MVDFs for the first two vibrational levels and quasi-stationary $T_{\rm tr}$ are set within 15– 20 ms.

The setting time for T_{tr} and T_v seems to depend on experimental conditions and is specified, directly or indirectly, by gas pressure p, wall temperature T_w , electron concentration N_e , reduced electric field E/N (which characterizes the discharge-sustaining power supply), probability γ_v of heterogeneous deactivation of the molecule vibrational energy, discharge tube radius R, positive column length L, and gas flow velocity (all the initial parameters are listed in Table 1). This list should be supplemented by other important parameters, namely, reaction rate constants K_i (which are related to the EEDF), T_{tr} , T_v , and elastic and inelastic cross sections.

The parenthetic figures by the values of $T_{\rm tr}$ and T_v in Table 1 are probabilities γ_v of vibrational energy heterogeneous deactivation based on which the temperatures were calculated. The evolution of the MVDF and the gas heating kinetics (Figs. 4 and 5, respectively) were constructed using VV exchange rate constant K_{01}^{10} taken from [6, 25, 33]. In addition, we slightly modified the approximated dependence of VV exchange rate constants on $T_{\rm tr}$ and v (that was suggested in [37]) to achieve a good quantitative fit to experimental data.

Figure 6 demonstrates the MVDF evolution calculated with the aim of analyzing gas heating. Within time interval $t = 10^{-7}-2.0 \times 10^{-3}$ s (solid lines 1-5), the electron energy is spent mostly on the vibrational excitation of molecules in the states with v = 1-10 (eV processes). The populations of these levels obey the Boltzmann distribution with a vibrational temperature markedly differing from temperature T_v of the first vibrational level. The kink in the MVDF curve indicates that the initial stage of the MVDF evolution is due largely to the impact-induced excitation and de-excitation of molecular vibrational states. It should be noted that the results of calculating the MVDF evolution at the initial stage of gas heating in the glow discharge plasma qualitatively agree with those obtained in [25].

From time instant $t \ge 3 \times 10^{-3}$ s (line 6), the redistribution of molecules over lower vibrational levels proceeds via competition of eV processes and near-resonance VV exchange. For lower levels (v = 1-5), the MVDF as a function of $T_{\rm tr}$ and T_v is approximated well by the Treanor distribution, which remains valid with time.

As follows from the calculations in terms of our model, for discharge tube radius R = 1.8 cm and pressures ranging from 3.5 to 9.0 Torr, the effect of *VW* deactivation and diffusion of molecules on the populations of vibrational levels v = 1-5 is insignificant compared with that of resonance *VV* exchange and *eV* processes. At $t \ge 3 \times 10^{-3}$ s, the form of the MVDF for lower vibrational levels turns out to be slightly sensitive to the way of their excitation. This is because the char-

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Fig. 5. Relative current I/I_d and relative gas temperature T_{tt}/T_w vs. time at the stage of discharge formation. Symbols, data points; solid lines, approximation of I/I_d and calculation of T_{tt}/T_w (a) p = 20 Torr, $I_d = 30$ mA and (b) p = 15 Torr, $I_d = 50$ mA.

acteristic times of nitrogen molecule redistribution over lower levels as a result of resonance VV exchange become much shorter than those of VW deactivation and diffusion of the molecules, as well as the times of impact-induced excitation and deexcitation of impactexcited molecules [1]. The Treanor form of the MVDF (curves 4–6 in Fig. 6) and the weak dependence of the vibrational temperature on molecule deactivation probability γ_v when γ_v varies by one order of magnitude (Table 1), are direct evidence for the dominance of VV exchange processes.

Table 2 lists rate constants K_{10}^{01} of VV exchange that were used in comparing the measured and calculated values of quasi-stationary T_v . As K_{10}^{01} grows, vibrational temperature T_v decreases noticeably. Contrasting the experimental and calculated values of the vibra-



Fig. 6. MVDF at the stage of gas heating at p = 7 Torr. Time instants are (1) 10^{-7} , (2) 10^{-6} , (3) 10^{-4} , (4) 10^{-3} , (5) 2×10^{-3} , (6) 3×10^{-3} , (7) 4×10^{-3} , (8) 6×10^{-3} , (9) 7×10^{-3} , (10) 8×10^{-3} , (11) 15×10^{-3} , and (12) 15.5×10^{-3} s.

tional temperature, one can see that they are in quantitative agreement for VV exchange rate constant $K_{10}^{01} = 9 \times 10^{-15}$ cm³/s, which is consistent with measurement and calculations performed elsewhere [6, 25, 33]. Note that the kinetic model in terms of which the EEDF is calculated in our work yields results similar to those obtained in [6], where the EEDF was assumed to be Maxwellian.

The results obtained in terms of the kinetic model are summarized in Table 1. It is seen that the calculated values of vibrational temperature T_v are one order of magnitude higher than the calculated values of $T_{\rm tr}$ As the pressure grows from 3 to 10 Torr, the vibrational temperature varies between 3700 and 4400 K.

The values of the vibrational temperature obtained under experimental conditions [22] far exceed the values measured in [28]. This may be explained by the fact that the electron concentration in [28] is much higher than in the experiment [22]. The fact that, in [28], T_{tr} and T_v appreciably drop with increasing deactivation probability γ_v may be explained by a small radius of the discharge tube used in those experiments (as follows from Table 1). Furthermore, as follows from Fig. 4, the MVDF measured in [28] at v > 6 deviates markedly from the Treanor distribution. In this case, it becomes difficult to discriminate between effects due to *VV* exchange and impact-induced activation/deactivation of molecular vibrational levels and effects due to processes at the discharge cell walls. However, the calculations of T_{tr} and T_v performed for the experimental conditions [22] show that, as the pressure grows, the γ_v dependence of the temperatures becomes less pronounced.

At times far exceeding t = 3 ms (Fig. 6), molecules pass from lower to higher ($v \ge 10$) vibrational levels because of fast VV exchange, forming a plateau in the MVDF (curves 6–12). As the plateau forms, T_{tr} at higher vibrational levels increases (see Fig. 5). The form of the MVDF is specified by competition between nonresonance VV energy exchange between molecules and VT processes. Specifically, the latter form the MVDF tail for $v \ge 15$, which is approximated well by the Boltzmann distribution with a temperature close to the translational temperature. Nonresonance VV exchange plays a significant role in increasing T_{tr} : it transfers a major part of the energy from vibrational to translational degrees of freedom because of molecule vibration anharmonicity.

In the time interval 4–10 ms (curves 7–10), the calculated (using the VV exchange rate constants taken from [6, 25, 33] and the approximation suggested in [37]) and measured rates of rise of $T_{\rm tr}$ are nearly the same, ≈ 50 K/ms. The rate of rise of $T_{\rm tr}$ is related to nonresonance VV energy exchange between molecules in lower and higher (10 < v < 15) vibrational states. For $T_{\rm tr} = 300-500$ K, the contribution of VT molecule–molecule and molecule–atom relaxation to heating is as low as less than several percent of the total energy deposition into translational and vibrational degrees of freedom.

Under our experimental conditions, atoms are produced mainly by direct impact-induced dissociation and also through electron levels with passage to repul-

Experimental data		T_v calculated using published data for $K_{10}^{01} \times 10^{-14}$, cm ³ /s (first row)						
		[6, 25, 33]	[13]	[34]	[35]	[36]		
p, Torr	<i>T_v</i> , K	0.9	2.6	5.0	10	15		
3.5	3790 ± 350	3764	3384	3266	3147	3093		
7	4320 ± 360	4230	3642	3495	3356	3278		
9.5	4270 ± 370	4183	3578	3451	3330	3266		

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sive terms. The effect of molecular dissociation through vibrational excitation and atomic losses due to volume recombination is minor. According to calculations, the fraction of dissociated molecules in the discharge positive column does not exceed 10^{-6} – 10^{-4} by the time t = 10 ms. Thus, at such a low nitrogen molecule dissociation, the significance of channels for VT molecule–atom relaxation is low in terms of our model and, hence, VT relaxation has a negligible effect on the vibrational excitation and gas heating dynamics.

As follows from calculations, the processes involving nitrogen molecules and atoms in impact-excited states (see [25]) also contribute insignificantly to gas heating. For example, the occupation of impact-excited state $B^3\Pi_g$ of a nitrogen molecule through collisions of molecules in states $A^3\Sigma_u^+$ and $X^1\Sigma_g^+$ (3 < v < 15) does not have a considerable effect on the gas heating dynamics. Neither do gas heating reactions involving atoms in metastable state 2P and molecules in states $X^1\Sigma_g^+$ for v > 8, as well as reactions with the participa-

tion of molecules in state $A^3 \Sigma_u^+$.

By the time t = 8-10 ms, thermal losses calculated for our experimental conditions do not exceed 20% of the heat release associated to nonresonance VV exchange.

For $T_{\rm tr} = 600-1000$ K, the contributions of VT molecule-molecule relaxation and VV molecule-molecule exchange become comparable and are roughly compensated by thermal losses. As the pressure rises from 7 to 30 Torr, the values of $T_{\rm tr}$ both calculated for and measured at the quasi-stationary distribution of the glow discharge plasma parameters monotonically grow from 450 to 1300 K. At p > 10 Torr and at the same discharge current (50 mA) and E/N = 50-60 Td, the values of $T_{\rm tr}$ calculated and measured in this work and in [14] diverge only slightly in spite of a large difference in discharge cell radius. This is related to the fact that we are dealing with the contracted discharge. At p > 15 Torr, the glow is filamentary and is observed (localized) at the axis of the discharge cell. In this case, the thermal balance in the quasi-stationary positive column is controlled largely by relaxation processes taking place within a small area near the discharge axis, where the electron concentration is maximal. The wall cooling conditions influence the thermal balance to a small extent. For t > 20 ms, the values of T_{tr} measured in this work and in [14] and calculated using the vibrationaltranslational relaxation rate constants taken from [37] quantitatively coincide, as follows from Table 1.

It should be noted that the use of rate constants and cross sections other than those employed in the kinetic model may cause disagreement with our results. Particular emphasis should be on processes with a high excitation threshold, the correct description of which requires insight into the high-energy part of the EEDF.

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