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PLASMA INVESTIGATIONS

The Possibility of Local Nonperturbing Diagnostics of the Electron Component in a Glow Discharge Plasma in Nitrogen by CARS Spectroscopy

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Abstract—The possibility is considered of restoring the electron energy distribution function (EEDF) in the interval of electron energies $0 < \varepsilon < 5$ eV from measurements of the electric field strength and of gas and vibrational temperatures by the coherent anti-Stokes Raman scattering (CARS) method in a positive column of a glow discharge in molecular nitrogen at $20 < E/N < 80$ Td and dissociation degree $\alpha \leq 10^{-3}$, when a considerable fraction of electron energy goes to excitation of vibrational degrees of freedom. The results of calculation of drift velocity and electron temperature and of the ratio of transverse diffusion coefficient to electron mobility and EEDF have demonstrated that the model proposed to restore the EEDF is in good quantitative agreement with the experiment depending on the variation of the parameter E/N and vibrational temperature.

INTRODUCTION

At present, the problems of diagnostics of the electron component of a low-temperature weakly ionized plasma at gas pressures $p \geq 0.1$ torr assume considerable importance in view of the development of plasmochemical reactors and lasers. For measurements of parameters of the electron component, the probe methods [1] and the spectral ones [2, 3], as well as microwave interferometry [4], are conventionally used. In [5], the optical interferometry method was proposed for determination of electron concentration.

The properties of discharge plasma at low pressures and a moderate degree of ionization are largely defined by electron collisions with gas molecules. One of the most important characteristics of a low-temperature weakly ionized plasma of molecular gas is the electron energy distribution function (EEDF).

The electric probe method is one of the most commonly used for experimental determination of EEDF. However, in recovering the EEDF, the interpretation of the volt-ampere characteristics obtained by probe measurements is complicated by the effects of electron sink to the probe [6] and of finite plasma resistance [1]. The theory of probe measurements for discharges in molecular gases at average pressures ($p > 10$ torr) is not yet fully developed, and quantitative measurements are, as a rule, estimatory.

In this study we investigate the possibility of restoring the EEDF in the interval of electron energies $0 < \varepsilon < 5$ eV based on its relationship with the vibrational-rotational molecule distribution function (VDF) of nitrogen in a glow discharge plasma, derived experimentally by the coherent anti-Stokes Raman scattering (CARS) method. The form of EEDF is defined by numerical solution of the Boltzmann equation. To recover the EEDF correctly, information about populations of vibrationally excited molecules is required, whose concentrations are included in electron–molecule collision integrals describing inelastic impacts of the first and second (superelastic) kind. Populations of vibrationally excited molecules were determined by CARS spectroscopy. Note that this method allows one to determine the VDF in plasma by direct measurements with high reliability [7–12].

1. EXPERIMENTAL CONDITIONS AND METHODS OF MEASUREMENTS

1.1. Discharge

A direct-current longitudinal glow discharge was initiated in a quartz tube with the inner diameter of 3.6 cm and length of 98 cm. A high-voltage stabilized power source was connected to ring titanium electrodes inserted in the discharge tube. The distance between the electrodes was 60 cm. The tube had a water cooling loop. The evacuation and admission of a gas was performed through holes in end flanges. Quartz mirrors of optical quality were attached to the flanges. The current in the discharge was maintained at 50 mA.

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The value of E/N (E is the average electric field strength in the positive column, and N is the molecule concentration at the discharge axis, defined with due regard for the drop of density as a result of heating) varied from 40 to 80 Td, when the pressure was varied from 3.5 to 9.5 torr at the positive column length of 58 cm.

1.2. CARS Spectroscopy

The following methods were used for direct measurements of the degree of vibrational-translational nonequilibrium in a discharge: the scanning version of CARS; and the two-wave version of CARS, when the intensities of two superposition-free lines of the Q-branch are measured.

Figure 1 shows diagrammatically the setup used in the scanning version of CARS. The setup includes an automatic system of data acquisition and processing. Its laser system consists of a single-mode AIG : Nd^{+3} laser with frequency doubling and of a narrow-band tuned dye laser pumped by the radiation of the second harmonics of the AIG : Nd^{+3} laser. The emission of the second harmonics of the AIG : Nd^{+3} laser with the duration of 25 to 30 ns and energy of up to 70 mJ together with the emission of the dye laser with the energy of up to 3 mJ was directed into the discharge tube along its axis. A useful CARS signal was separated from the background radiation of lasers and plasma by wide-band filters and a monochromator and was registered by a photomultiplier tube or OMA-III optical multi-channel receiver. The spectral resolution of the CARS spectrometer is defined by the spectral widths of radiation of the second harmonic of the AIG : Nd^{+3} laser (up to 0.01 cm^{-1}) and of the dye laser (up to 0.08 cm^{-1}) and is equal to 0.1 cm^{-1}.

In the two-wave version of CARS, a 2-λ-CARS spectrometer was used, whose scheme is shown in Fig. 2. Its laser system consists of a single-mode YAG : Nd^{+3} laser with frequency doubling and a dye laser generating the two-wavelength radiation (for this purpose, the resonator scheme was used with a common diffraction grating and two "plug" mirrors tuned separately). The master oscillators work in the pulse-periodic mode with the repetition frequency of 10 Hz and generated pulse duration of 25 ns. In the course of the experiment, the intensities of nonoverlapping Q-lines were measured that correspond to two vibrational-rotational transitions $v, J = 6 \longrightarrow v+1, J = 6$, and $v, J = 16 \longrightarrow v+1, J = 16$ (v and J are the vibrational and rotational quantum numbers). To normalize the radiation intensities of the CARS signals obtained simultaneously in two different transitions of the Q-branch, a reference channel was used in experiments. The CARS signals, corresponding to the two above-mentioned transitions and obtained in the investigated and reference channels, were filtered by the monochromator and registered by the optical multi-channel receiver. Procedures of data acquisition and processing were automated on the basis of an IBM PC and were described in detail in [12].

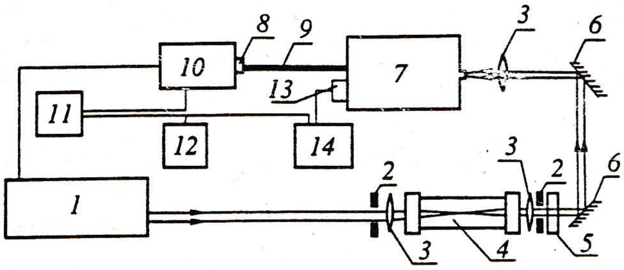

Fig. 1. The experimental setup for CARS spectroscopy: (*1*) system of lasers; (2) diaphragm; (*3*) lens; (*4*) gas-discharge cell; (*5*) wide-band filter; (*6*) mirror; (*7*) monochromator; (*8*) photomultiplier; (*9*) light guide; (*10*) controller; (*11*) IBM PC; (*12*) printer; (*13*) OMA-III optical multi-channel receiver; (*14*) interface unit.

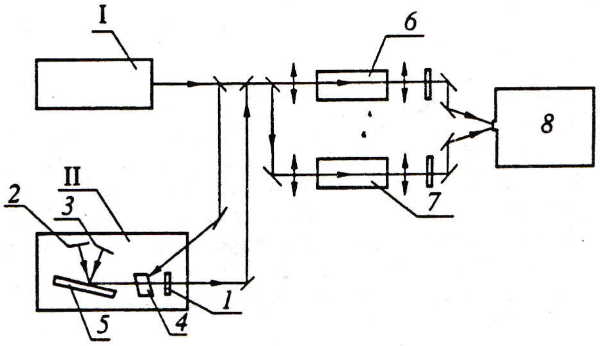

Fig. 2. Sketch of a 2-λ-CARS spectrometer: I, YAG : Nd^{+3} laser; II, dye laser; (*1*) exit mirror; (2, *3*) "plug" mirrors; (*4*) cell; (*5*) diffraction grating; (*6*) measurement channel cell; (*7*) reference channel sell; (*8*) spectrograph with a multi-channel optical receiver.

For investigations of vibrational-rotational distribution of nitrogen molecules in the ground state $X^1\Sigma_g^+$, the CARS spectroscopy method with a collinear scheme of beam convergence was used. After registration on a dichroic mirror, laser beams were passed through a diaphragm and focused by a lens into the central region of a positive column. In such a scheme, the wave vectors of initial and secondary radiations are parallel. With the Gaussian distribution of radiation intensity of the pumping lasers, 75% of the energy of CARS signal is generated in the focal region bounded by a cylinder of diameter D and length S [13],

$$D = 4\lambda f/\pi d, \quad S = 6L, \tag{1}$$

where λ is the radiation wavelength of the AIG : Nd^{+3} laser; f, the focal length of the lens, which focuses laser beams into the discharge tube; d the diameter of beams in the lens plane; and $L = \pi D^2/2\lambda$ is the confocal parameter. The dimensions D and S define the spatial resolu-

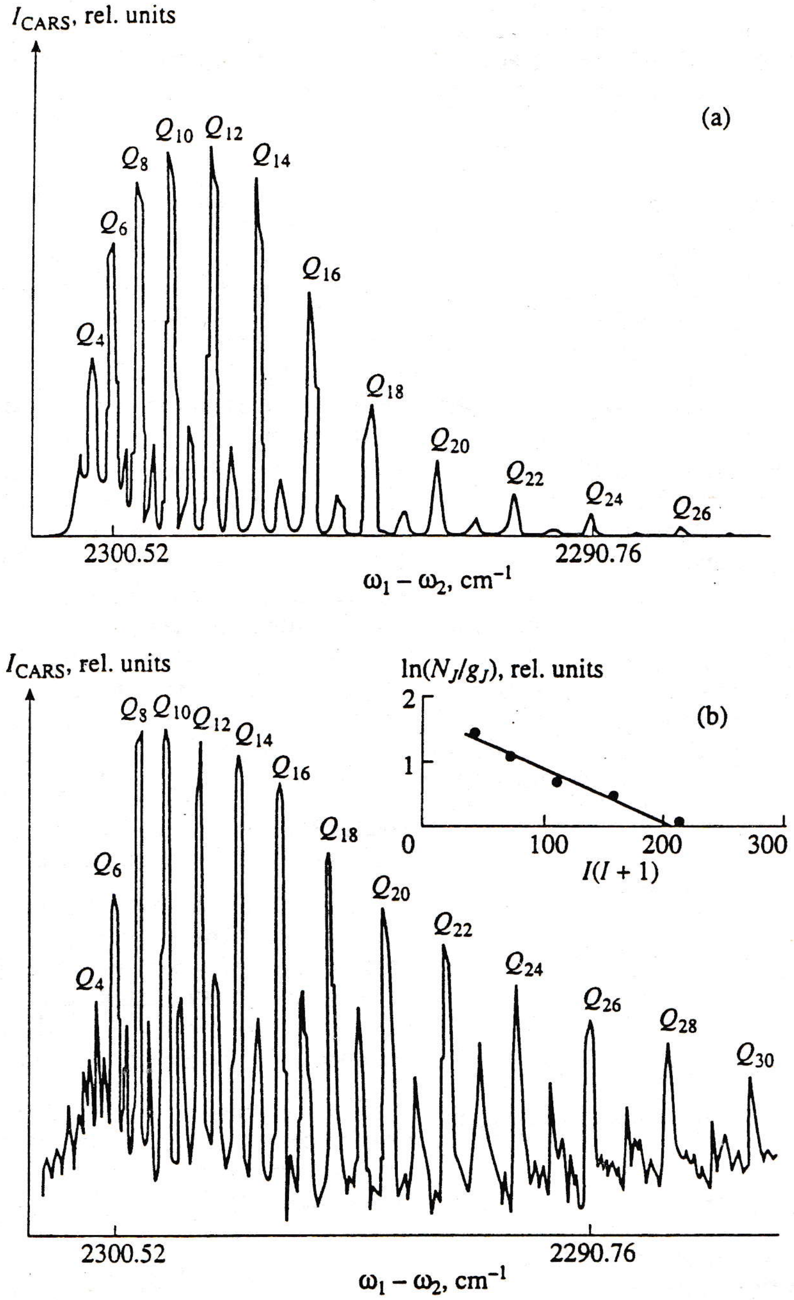

Fig. 3. Distribution of radiation intensity in CARS spectra of the Q-branch of the transition $v = 1 \longrightarrow v = 2$ of a nitrogen molecule in the ground electron state $X^1\Sigma_g^+$ in a glow discharge at the pressure 9.5 torr and current 50 mA. (a) Calculation at $T = 600$ K; (b) measurement results. The solid line indicates the equilibrium $J(J + 1)$ dependence of $\ln(N_J/g_J)$ at temperature 600 K.

tion. In our case, $d = 0.7$ cm and $f = 50$ cm, so that $D =$ 50 mcm and $S = 4$ cm.

Registered in the experiment were distributions of intensity in the spectra of Q-branches of vibrational transitions 0–1, 1–2, 2–3, 3–4, 4–5. In order to interpret and process the obtained CARS spectra, their calculation was performed. Figure 3 illustrates typical measured and calculated spectra with allowed structure of the Q-branch of the 1–2 vibrational transition for a nitrogen molecule in the ground electron state $X^1\Sigma_g^+$. Based on the experimental spectrum, the $J(J + 1)$ dependence of $\ln(N_J/g_J)$ was restored (N_J is the population of rotational level with the quantum number J, and g_J is the multiplicity of its degeneracy), which is shown in Fig. 3b. The derived distribution functions over rotational levels appeared to be the Boltzmann ones in the entire range of the current and pressure values and were characterized by temperatures that may be assumed to coincide with the gas ones under the conditions of our experiment.

2. BASIC EQUATIONS

2.1. Boltzmann Equation for the Electron Energy Distribution Function

In the treated interval of electron energies, the form of EEDF is mainly defined by the increase of their energy under the effect of electric field, and by its losses due to excitation of the lower vibrational levels (v = 0–10) of nitrogen molecules. At high values of vibrational temperature, the form of EEDF is strongly affected by inelastic collisions of the second kind (superelastic ones), in which electrons gain energy upon de-excitation of vibrational levels of nitrogen molecules.

The electron energy distribution function $f(\varepsilon)$ was determined by solving the Boltzmann equation in view of elastic collisions of electrons with nitrogen atoms and molecules; excitation of rotational levels of nitrogen molecules by electron impact; inelastic collisions of the first and second kind between vibrationally excited nitrogen molecules and electrons in the processes,

$$e + \mathrm{N}_2(X^1\Sigma_g^+, v) \longrightarrow e + \mathrm{N}_2(X^1\Sigma_g^+, s); \qquad (2)$$

excitations of electron Y-states of nitrogen molecules

$$e + \mathrm{N}_2(X^1\Sigma_g^+, v) \longrightarrow e + \mathrm{N}_2(Y), \qquad (3)$$

where $Y = A^3\Sigma_u^+,\ B^3\Pi_g,\ C^3\Pi_u,\ B'^3\Sigma_u^-,\ a'^1\Sigma_u^-,\ a''^1\Sigma_g^+,\ a^1\Pi_g,\ w^1\Delta_u$; excitation of electron Y-states of nitrogen atoms

$$e + \mathrm{N}(^4S) \longrightarrow e + \mathrm{N}(Y), \qquad (4)$$

where $Y = {}^2P,\ {}^2D$; and dissociation and ionization of nitrogen molecules by electron impact.

The equation for EEDF [14] was complemented with the integral taking into account collisions of the second kind,

$$\frac{E^2\varepsilon}{3\sum_l N_l\sigma_{ml}(\varepsilon)}\frac{df(\varepsilon)}{d\varepsilon} + \sum_l \frac{2m}{M_l}N_l\varepsilon^2\sigma_{ml}(\varepsilon)\left[f(\varepsilon) + \frac{T}{e}\frac{df(\varepsilon)}{d\varepsilon}\right] + NB_e\varepsilon\sigma_{\mathrm{rot}}(\varepsilon)\left[f(\varepsilon) + \frac{T}{e}\frac{df(\varepsilon)}{d\varepsilon}\right] \qquad (5)$$

$$= -\sum_l N_l \sum_{i,j} \int_{\varepsilon}^{\varepsilon+\varepsilon_{ij}} \sigma_{ij}(\varepsilon')\varepsilon' f(\varepsilon')d\varepsilon' - \sum_{i,j} N_j \int_{\varepsilon}^{\varepsilon-\varepsilon_{ij}} q_{ij}(\varepsilon')\varepsilon' f(\varepsilon')d\varepsilon'.$$

Here m, e, and M_l are the mass and the charge of an electron and the mass of a molecule ($l = 0$) and atom ($l = a$) of nitrogen, respectively; ε, the electron energy; ε_{ij}, the energy lost by an electron in inelastic collisions with molecules and atoms; B_e, the rotational constant; $\sigma_{ml}(\varepsilon)$ denotes the transport cross sections of electron scattering by a nitrogen molecule [15] and an atom [16]; $\sigma_{\mathrm{rot}}(\varepsilon)$ is the excitation cross section of nitrogen molecule rotational levels by electron impact [17]; $\sigma_{ij}(\varepsilon)$ denotes the cross sections of dissociation [18, 19], ionization [20], excitation of vibrational, electron levels of a molecule [21] and an atom [22, 23] for direct reactions; $q_{ij}(\varepsilon)$ denotes the cross-sections of superelastic collisions; N_j denotes the concentrations of vibrationally excited molecules; N_a, the atomic concentration; and T is the gas temperature. The superelastic collisions were considered only for the first ten vibrational levels of the state $X^1\Sigma_g^+$. The excitation cross sections necessary for the description of excitation of vibrational levels of $X^1\Sigma_g^+$ by electron impact were borrowed from [24–26]. The normalization coefficient for these cross sections was borrowed from [27]. When solving the equation for the EEDF, the molecule distribution over vibrational levels N_v with v = 1–10 was first assumed to be the Boltzmann one.

The rate constants for electron-heavy particle collision processes and the macroscopic characteristics of the electron component were calculated by $f(\varepsilon)$ using the relations [28]

$$k_{ij}^e = \sqrt{\frac{2e}{m}}\int_0^\infty \varepsilon\sigma_{ij}(\varepsilon)f(\varepsilon)d\varepsilon, \qquad (6)$$

$$T_e = 2/3\int_0^\infty \varepsilon^{3/2}f(\varepsilon)d\varepsilon, \qquad (7)$$

$$V_{dr} = 1/3\sqrt{\frac{2e}{m}}\frac{E}{N}\int_0^\infty \frac{\varepsilon}{\sigma_m(\varepsilon)}\left(-\frac{df(\varepsilon)}{d\varepsilon}\right)d\varepsilon, \qquad (8)$$

$$D/\mu = \int_0^\infty \frac{\varepsilon}{\sigma_m(\varepsilon)}f(\varepsilon)d\varepsilon\Big/\int_0^\infty \frac{\varepsilon}{\sigma_m(\varepsilon)}\left(\frac{df(\varepsilon)}{d\varepsilon}\right)d\varepsilon. \qquad (9)$$

To normalize the EEDF, the condition

$$\int_0^\infty \sqrt{\varepsilon} f(\varepsilon) d\varepsilon = 1 \quad (10)$$

was used.

The Boltzmann equation for EEDF was solved by the iteration method. The distribution function calculated by the method described in [29] was used as the zero-order approximation of $f(\varepsilon)$.

The computer codes for solving equation (5) were tested in different ways. Good agreement of the values of electron drift velocity and D/μ of electrons, calculated by formulas (8) and (9), with those cited in review [30] in the range of variation of the parameter E/N = 20–80 Td is indirect evidence of the validity of the calculation of EEDF.

2.2. *Equations for the Concentration of Vibrationally Excited Molecules*

Populations of the first five vibrational levels of nitrogen molecules in the ground electron state $X^1\Sigma_g^+$ were determined from measured CARS spectra. However, as was discussed above, information about populations of vibrational levels with $v \geq 5$ is also necessary for correct calculation of the EEDF. The approximation of the VDF by the Boltzmann or Trinore distribution may result in considerable errors. Therefore, calculations were carried out of the populations of vibrational levels of nitrogen molecules in a glow discharge plasma under conditions of our measurements and the experiment [31].

In the positive column of a glow discharge plasma, the predominant processes that form the VDF of nitrogen over levels in the ground state $X^1\Sigma_g^+$ at E/N = 20–80 Td are the processes of *VT*- and *VV*-exchange between molecules and the excitation of vibrational levels by electron impact [32, 33]. The kinetics of electron-excited states and of ionization may be ignored. However, this does not relate to the processes of nitrogen molecule dissociation, which may affect the VDF. In the proposed model, we deal with the mechanisms of nitrogen molecule dissociation as a result of direct electron impact and via vibrational excitation. The dissociation via excitation of electron levels with transition to the scattering term [34] is approximately included in the total dissociation cross section.

Therefore, the initial set of equations, which describes the evolution in time of the populations of vibrational levels of ground electron state of nitrogen molecules and of the atomic concentration in the positive column of a glow discharge plasma at constant pressure, has the form

$$\begin{aligned}\frac{\partial X_v}{\partial t} &= N_e \sum_{s=0}^{10} [k_{sv}^e X_s - k_{vs}^e X_v] - k_D^e N_e X_v \\ &+ N[K_{v+1,v}^{VT} X_{v+1} - K_{v,v+1}^{VT} X_v - K_{v,v-1}^{VT} X_v \\ &+ K_{v-1,v}^{VT} X_{v-1}] + N_a[K_{v+1,v}^{VTa} X_{v+1} - K_{v,v+1}^{VTa} X_v \\ &- K_{v,v-1}^{VTa} X_v + K_{v-1,v}^{VTa} X_{v-1}] \qquad (11) \\ &+ N \sum_{s=1}^{s^*} [K_{v+1,v}^{s-1,s} X_{v+1} X_{s-1} - K_{v,v+1}^{s,s-1} X_v X_s] \\ &+ N \sum_{s=0}^{s^*-1} [K_{v-1,v}^{s+1,s} X_{v-1} X_{s+1} - K_{v,v-1}^{s,s+1} X_v X_s] \\ &+ V_v + \frac{1}{2} V_a X_v,\end{aligned}$$

$$\begin{aligned}\frac{1}{2}\frac{\partial X_a}{\partial t} &= k_d^e N_e - K_R^a N_a^2 + K_{s^*,s^*+1}^{VT} N X_{s^*} \\ &+ N \sum_{s=1}^{s^*} K_{s,s-1}^{s^*,s^*+1} X_s X_{s^*} - V_a. \qquad (12)\end{aligned}$$

Here, $K_{v+1,v}^{VT}$, $K_{v+1,v}^{VTa}$, $K_{v+1,v}^{s-1,s}$, k_{sv}^e, k_D^e, and K_R^a are the rate constants of the following processes:

the one-quantum *VT*-relaxation of nitrogen molecules by molecules and atoms

$$N_2 + N_2(v+1) \longrightarrow N_2 + N_2(v), \quad (13)$$

$$N_2(v+1) + N(^4S) \longrightarrow N_2(v) + N(^4S); \quad (14)$$

the one-quantum *VV*-exchanges between nitrogen molecules

$$N_2(v+1) + N_2(s-1) \longrightarrow N_2(v) + N_2(s); \quad (15)$$

the excitation and de-excitation of vibrational levels of the ground state of a nitrogen molecule by electron impact, relation (2);

dissociation of nitrogen molecules from the vibrational level v of the ground state by electron impact,

$$N_2(v) + e \longrightarrow N(^4S) + N(^4S) + e; \quad (16)$$

recombination of nitrogen atoms

$$N(^4S) + N(^4S) + N_2 \longrightarrow N_2^* + N_2, \quad (17)$$

where N_2^* is the electron-excited term of a nitrogen molecule, and $X_v = N_v/N$, $X_a = N_a/N$.

In equations (11) and (12), the vibrational level $s^* + 1$ is assumed to be the level of dissociation of nitrogen molecules via vibrational excitation [32]. The

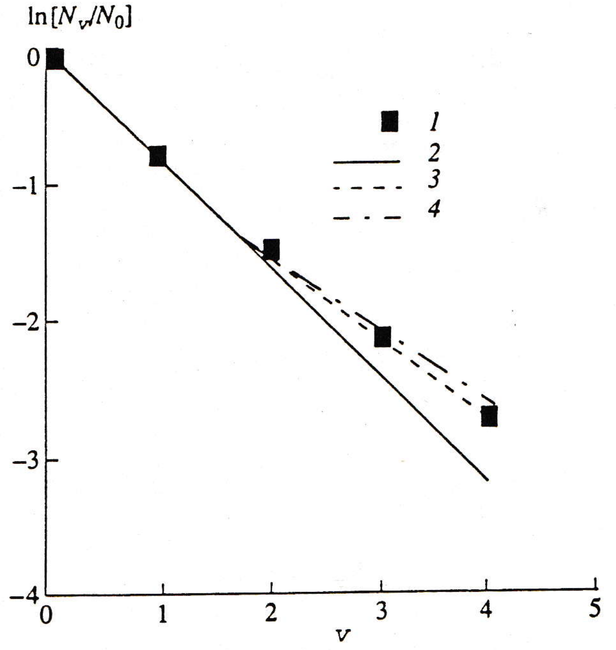

Fig. 4. Vibrational distribution function of nitrogen molecules in a glow discharge plasma by the moment of time t = 15 ms at E/N = 45 Td, p = 7 torr, and current I = 50 mA. The radius of the discharge cell is R = 1.8 cm. (*1*) Experiment T_{vE} = 4250 ± 360 K and T = 530 ± 30 K; (*2*) the Boltzmann distribution at T_v = 4250 K; (*3*) the Trinore distribution at T_v = 4250 K and T = 530 K; (*4*) our calculation for $\gamma_m = 10^{-4}$.

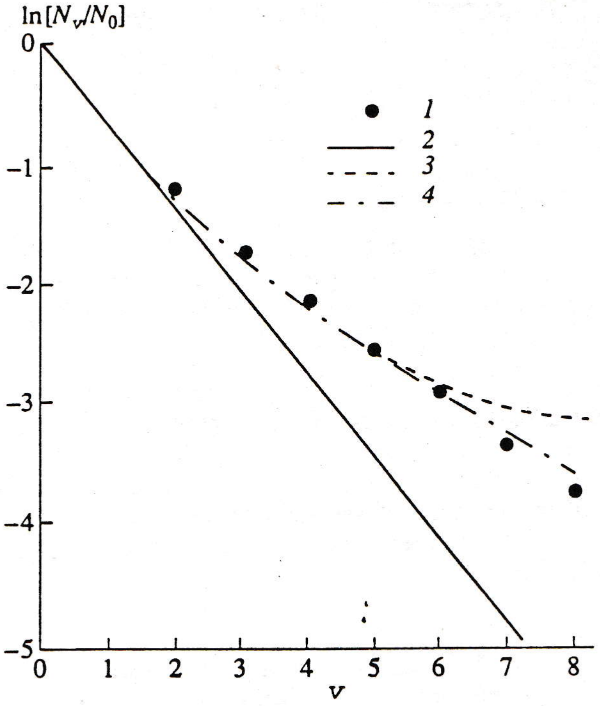

Fig. 5. Vibrational distribution function of nitrogen molecules in a glow discharge plasma by the time t = 11 ms at E/N = 70 Td, p = 2 torr, and current I = 80 mA. The radius of the discharge cell is R = 1 cm. (*1*) Experimental data of [9] at T_{vE} = 5300 ± 350 K and T = 500 ± 30 K; (*2*) the Boltzmann distribution at T_v = 5000 K; (*3*) the Trinore distribution at T_v = 5000 K and T = 500 K; (*4*) our calculation for $\gamma_m = 10^{-4}$.

quantities V_v and V_a express the diffusive drift of vibrationally excited nitrogen molecules and atoms from the plasma followed by the heterogeneous relaxation of molecules and recombination of atoms on the tube walls. The explicit form of these expressions is given in [35].

The rate constants $K_{v,v-1}^{VT}$ and $K_{v,v-1}^{v-1,v}$ of the *VT*- and *VV*-processes for the first nine vibrational levels in the temperature range $300 \leq T \leq 700$ K are borrowed from [36]. For the rate constant K_{10}^{VTa}, the expression was used that is an experimental estimate of the lower limit of the time of vibrational relaxation of nitrogen molecules in collisions with atoms [37],

$$p\tau = 4.7 \times 10^{-11} \exp[176.27 T^{-1/3}] \text{ (atm s)}. \qquad (18)$$

The other rate constants were calculated by the Schwarz–Slavsky–Herzfeld (SSH) formulas [38]. The rate constants of direct and inverse processes are related by the detailed balance equations. The value of the rate constant K_R^a of volume recombination of nitrogen atoms was borrowed from [33].

For the experimental conditions specified above, physical adsorption prevails in the process of heterogeneous relaxation of molecules [33]. In this case, when the tube surface material is quartz and the wall temperature T_w = 300 K, the value of $\gamma_m = 10^{-4}$–10^{-3}, and $\gamma_a = 10^{-4}$, for nitrogen molecules [39].

The set of equations (11) and (12) was solved by Gear's method [40, 41]. Initially, at $t = 0$, the VDF corresponded to the Boltzmann distribution at the gas temperature T measured by us and in [9], and to the atomic concentration $N_a = 0$.

The electron concentration N_e was calculated by the relation for the current density j at the discharge axis

$$j = eN_eV_{dr}. \qquad (19)$$

DISCUSSION OF THE RESULTS

Figure 4 illustrates the populations of vibrational levels with v = 0–4 of the ground electron state $X^1\Sigma_g^+$ of a nitrogen molecule, recovered from the CARS spectra measured by us. The CARS spectra were registered for the following parameters in the axis zone of the positive glow column of a discharge: the pressure p = 7.0 torr, E/N = 45 Td, T = 530 K, $N_e = 1.3 \times 10^{10}$ cm^{-3}.

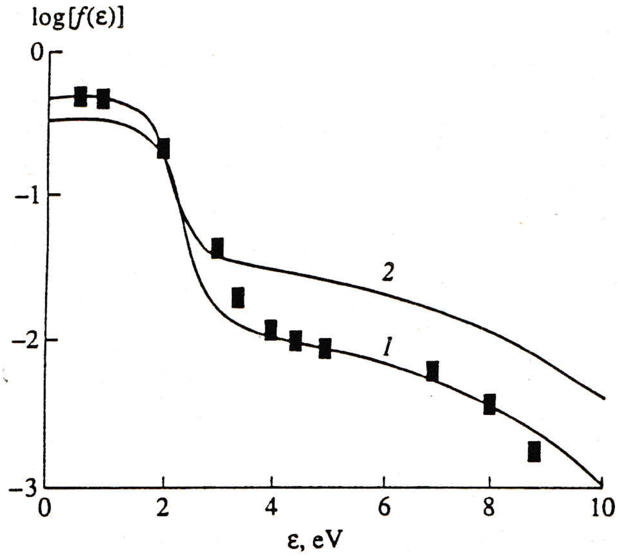

Fig. 6. Electron distribution functions over energy E/N = 70 Td: the lines indicate our calculation; T_v = (*1*) 3000; (*2*) 4000 K; points indicate the experimental data of [31].

The value of vibrational temperature, defined by populations of the first two levels, $T_{vE} = 3400/\ln(N_0/N_1)$, was $T_{vE} = 4250 \pm 360$ K. Figure 4 also shows the Boltzmann (solid line) and Trinore (dashed curve) distributions with the same value of T_v. Figure 5 shows the results of measurements of populations of vibrational levels with v = 0–8 from [9], derived for the following discharge parameters: p = 2 torr, E/N = 60–70 Td, T = 540 K, $N_e = 2 \times 10^{10}$ cm^{-3}. Under these conditions, the value of the vibrational temperature was $T_{vE} = 5300 \pm 350$ K. The time of residence of molecules in the discharge zone was 11 to 15 ms. The curves in Figs. 4 and 5 indicate that the measured values of VDF for v = 0–4 are well approximated by the Trinore distribution. For the vibrational number of $v > 5$, the measured values of VDF lie between the Trinore and Boltzmann distributions.

As was already mentioned, a correct calculation of the EEDF based on equation (5) requires information about the populations of vibrational levels of nitrogen molecules with v = 0–10. In its turn, to solve the balance equations for the concentration of vibrationally excited molecules (to determine the VDF), it is necessary to determine correctly the rate constants of excitation and de-excitation of vibrational levels by electron impact. Therefore, an adequate description of a glow discharge plasma in molecular nitrogen in the range of the parameter E/N = 20–80 Td, where a considerable part of the energy contributed to the discharge is spent for excitation of molecular vibrations [4], may be obtained only by simultaneous solution of equation (5) and the set of equations (11) and (12).

In the first stage, the EEDF, drift velocity V_{dr}, temperature T_e, and the characteristic electron energy D/μ were calculated and compared with the data of [14, 28, 30, 31]. The initial parameters were provided by the experimental data for the gas temperature T, vibrational temperature of the first level T_{vE}, obtained by CARS spectroscopy, and E/N. Note that the method proposed in [42] may be used to determine the electric field strength from the results of CARS measurements.

In the second stage, the VDF and T_v were determined from the solution of the set of kinetic equations describing the balance of vibrationally excited molecules and formation of nitrogen atoms. The gas temperature T and the rate constants, drift velocity V_{dr}, and electron concentration N_e, calculated by the EEDF, were used as the input parameters.

Figure 6 illustrates the results of EEDF probe measurements borrowed from [31] at E/N = 70 Td. Calculation results are also given in Fig. 6. As is seen, good agreement with the experiment is reached at T_v = 2000–3000 K. Note that the values of vibrational temperature T_{v04} = 6000–8000 K (corresponding to the first five vibrational levels) cited in [31] are overestimated for the experimental conditions of that study. The results of direct measurements by the CARS spectroscopy method [8–10, 12] and of the calculations performed both in our study and in [9, 35] for experimental conditions close to those of [31] are listed in the table. As is seen in the table, the values of T_{v04} do not exceed 6000 K (for T_v below 5000 K).

Figure 7 shows the EEDF calculated for the conditions of our measurements (curve *1*), as well as of [9] (curve 2). Dashed curves *3* and *4* indicate the EEDF calculated by the Nighan model, i.e., disregarding the superelastic collisions. Further, the calculated EEDF were used to determine the populations of vibrational levels of nitrogen molecules from the set of balance equations. The VDF calculated in this way are indicated in Figs. 4 and 5 by the dash-dotted lines. It is seen that they are in good agreement with our results (Fig. 4), as well as with the results of [9] (Fig. 5).

A comparison between the experimental and calculated values of the vibrational temperature and EEDF reveals that the information gained from CARS spectra of nitrogen molecules (the vibrational and gaseous temperatures, electric field strength) is sufficient to uniquely restore the low-energy part of EEDF ($\varepsilon \le$ 5 eV) from the solution of the Boltzmann equation. A violation of the above-mentioned agreement for the measured and calculated values of VDF would manifest the presence of additional kinetic processes (e.g., that involving metastable molecules of $N_2(A^3\Sigma_u^+)$ or nitrogen atoms), which affect the EEDF and VDF. This would cause the need for measuring additional discharge parameters. Note that it is only the inclusion of the second-order collisions between electrons and vibrationally excited molecules, as well as of the decrease in the population of ground electron state of nitrogen molecules with $v = 0$, that makes it possible to reach a consistent description of the electron component and vibrational kinetics in the successive solution of the first- and second-stage problems. Qualitative agreement between the calculated and experimental results in V_{dr}, T_e, D/μ, and the EEDF validates the numerical model used by us for determination of the main characteristics of the electron component in a glow discharge plasma in molecular nitrogen. The calculated and measured values of the vibrational temperature are also in good agreement (see the table).

Good agreement between the values of vibrational temperatures T_v and $T_{v\varepsilon}$, as well as of measured and calculated values of EEDF, points to strong correlation between populations of the lower levels of VDF and EEDF in the range of electron energies, where the cross sections of excitation and de-excitation of vibrational levels by electron impact have maxima. Indeed, as is seen in Figs. 6 and 7, an increase in the vibrational temperature leads to an increase in the relative fraction of electrons with energy above 2 eV. Therefore, the form of EEDF in the range of $2 \leq \varepsilon \leq 5$ eV appears to be sensitive to variation of the VDF. The reason is that, for treated values of E/N, when a fraction of electron energy is spent for the excitation of vibrational degrees of freedom, the form of EEDF in the energy range specified above is largely defined by inelastic and superelastic collisions of electron with molecules in states with moderate vibrational numbers $v \leq 10$. As E/N increases, the fraction of high-energy electrons increases, and the variation of the form of EEDF as a function of the VDF becomes less pronounced. For the electron energy of $\varepsilon > 5$ eV, kinetic processes involving nitrogen atoms and molecules in electron-excited states are of importance for the form of EEDF. Therefore, to calculate the latter function correctly, measurements are required of populations of electron-excited states of molecules and atoms.

Figure 8 shows the EEDF for different values of the degree of dissociation of nitrogen molecules in a stationary discharge. The effect of atoms on the EEDF in the electron energy range $\varepsilon < 5$ eV is insignificant at the degree of dissociation $\alpha < 10^{-3}$. In addition, according to the calculations within the framework of the model at hand, as well as to the estimates of [32], *VT*-relaxation of nitrogen molecules by atoms (14) does not affect the VDF of the first eight or ten vibrational levels. Based on this fact, we may assume that, for the discharge conditions, when the degree of dissociation of molecules is $\alpha < 10^{-3}$, atom formation does not considerably affect the degree of vibrational excitation of the lower levels and EEDF. More detailed treatment of the influence of the degree of dissociation on the VDF and EEDF needs additional investigation.

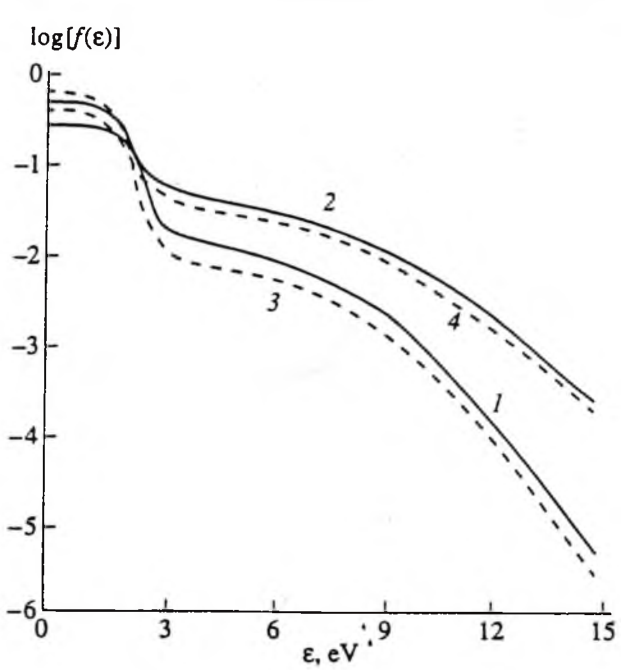

Fig. 7. Calculation of the electron energy distribution functions: (*1*, *3*) at $E/N = 45$ Td; (*2*, *4*) at $E/N = 70$ Td; solid lines indicate calculation including superelastic collisions; dashed curves, without superelastic collisions.

Note that CARS spectroscopy may simultaneously measure the values of electric field strength (and E/N), gas temperature, and populations of vibrationally excited molecules. A set of these values allows one to determine the low-energy part of EEDF in a glow discharge in nitrogen from the solution of the Boltzmann equation. This is true for those conditions when the

Table

Experimental data						Calculation
References	E/N, Td	CARS		2-λ-CARS		T_{v04}, K
		T, K	T_{v04}, K	T, K	T_{v04}, K	
Our paper	80	480 ± 35	4470 ± 350	460 ± 25	4450 ± 220	4415
	45	530 ± 35	4940 ± 360	510 ± 25	4920 ± 245	4750
	60	600 ± 40	4770 ± 370	580 ± 30	4750 ± 240	4700
[9, 10]	70	530 ± 30	6000 ± 350	–		5900

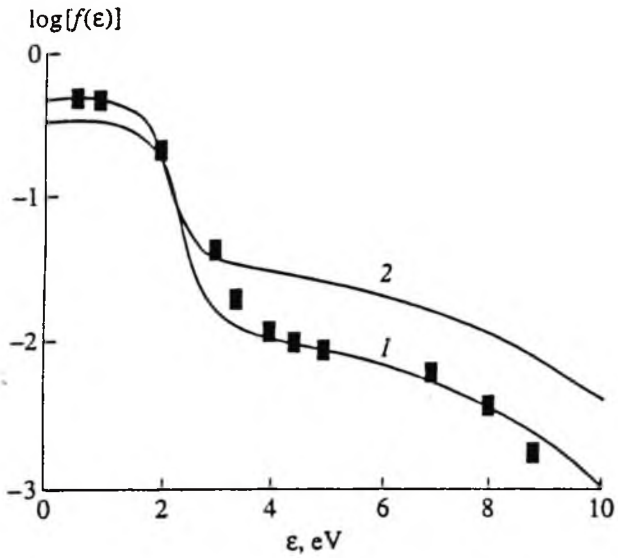

Fig. 6. Electron distribution functions over energy E/N = 70 Td: the lines indicate our calculation; T_v = (*1*) 3000; (*2*) 4000 K; points indicate the experimental data of [31].

The value of vibrational temperature, defined by populations of the first two levels, $T_{vE} = 3400/\ln(N_0/N_1)$, was T_{vE} = 4250 ± 360 K. Figure 4 also shows the Boltzmann (solid line) and Trinore (dashed curve) distributions with the same value of T_v. Figure 5 shows the results of measurements of populations of vibrational levels with v = 0–8 from [9], derived for the following discharge parameters: p = 2 torr, E/N = 60–70 Td, T = 540 K, $N_e = 2 \times 10^{10}$ cm^{-3}. Under these conditions, the value of the vibrational temperature was T_{vE} = 5300 ± 350 K. The time of residence of molecules in the discharge zone was 11 to 15 ms. The curves in Figs. 4 and 5 indicate that the measured values of VDF for v = 0–4 are well approximated by the Trinore distribution. For the vibrational number of $v > 5$, the measured values of VDF lie between the Trinore and Boltzmann distributions.

As was already mentioned, a correct calculation of the EEDF based on equation (5) requires information about the populations of vibrational levels of nitrogen molecules with v = 0–10. In its turn, to solve the balance equations for the concentration of vibrationally excited molecules (to determine the VDF), it is necessary to determine correctly the rate constants of excitation and de-excitation of vibrational levels by electron impact. Therefore, an adequate description of a glow discharge plasma in molecular nitrogen in the range of the parameter E/N = 20–80 Td, where a considerable part of the energy contributed to the discharge is spent for excitation of molecular vibrations [4], may be obtained only by simultaneous solution of equation (5) and the set of equations (11) and (12).

In the first stage, the EEDF, drift velocity V_{dr}, temperature T_e, and the characteristic electron energy D/μ were calculated and compared with the data of [14, 28, 30, 31]. The initial parameters were provided by the experimental data for the gas temperature T, vibrational temperature of the first level T_{vE}, obtained by CARS spectroscopy, and E/N. Note that the method proposed in [42] may be used to determine the electric field strength from the results of CARS measurements.

In the second stage, the VDF and T_v were determined from the solution of the set of kinetic equations describing the balance of vibrationally excited molecules and formation of nitrogen atoms. The gas temperature T and the rate constants, drift velocity V_{dr}, and electron concentration N_e, calculated by the EEDF, were used as the input parameters.

Figure 6 illustrates the results of EEDF probe measurements borrowed from [31] at E/N = 70 Td. Calculation results are also given in Fig. 6. As is seen, good agreement with the experiment is reached at T_v = 2000–3000 K. Note that the values of vibrational temperature T_{v04} = 6000–8000 K (corresponding to the first five vibrational levels) cited in [31] are overestimated for the experimental conditions of that study. The results of direct measurements by the CARS spectroscopy method [8–10, 12] and of the calculations performed both in our study and in [9, 35] for experimental conditions close to those of [31] are listed in the table. As is seen in the table, the values of T_{v04} do not exceed 6000 K (for T_v below 5000 K).

Figure 7 shows the EEDF calculated for the conditions of our measurements (curve *1*), as well as of [9] (curve *2*). Dashed curves *3* and *4* indicate the EEDF calculated by the Nighan model, i.e., disregarding the superelastic collisions. Further, the calculated EEDF were used to determine the populations of vibrational levels of nitrogen molecules from the set of balance equations. The VDF calculated in this way are indicated in Figs. 4 and 5 by the dash-dotted lines. It is seen that they are in good agreement with our results (Fig. 4), as well as with the results of [9] (Fig. 5).

A comparison between the experimental and calculated values of the vibrational temperature and EEDF reveals that the information gained from CARS spectra of nitrogen molecules (the vibrational and gaseous temperatures, electric field strength) is sufficient to uniquely restore the low-energy part of EEDF ($\varepsilon \leq$ 5 eV) from the solution of the Boltzmann equation. A violation of the above-mentioned agreement for the measured and calculated values of VDF would manifest the presence of additional kinetic processes (e.g., that involving metastable molecules of $N_2(A^3\Sigma_u^+)$ or nitrogen atoms), which affect the EEDF and VDF. This would cause the need for measuring additional discharge parameters. Note that it is only the inclusion of the second-order collisions between electrons and vibrationally excited molecules, as well as of the decrease in the population of ground electron state of

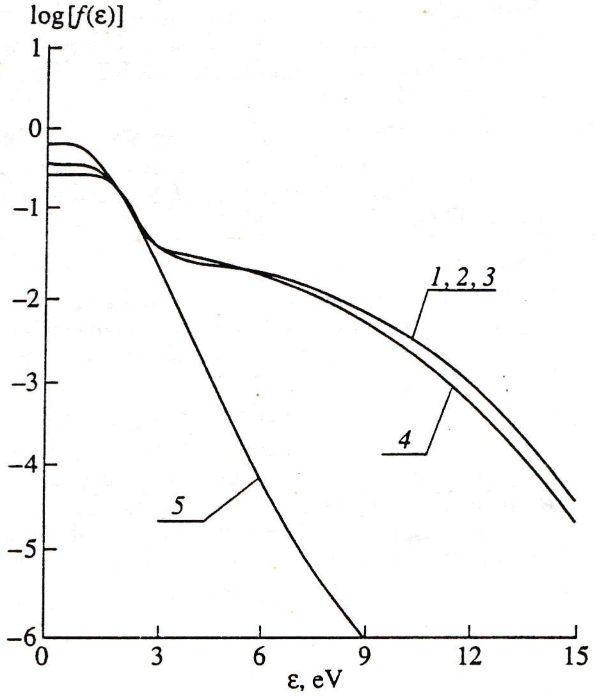

Fig. 8. Calculation of the electron energy distribution functions E/N = 60 Td vs. dissociation degree of molecules α: (*1*) 10^{-6}; (*2*) 10^{-5}; (*3*) 10^{-4}; (*4*) 10^{-3}; and (*5*) 10^{-2}.

EEDF is local in space and the main channel of energy exchange between electrons and molecules at a moderate degree of their dissociation occurs via vibrational degrees of freedom of the electron ground state. Thus, the EEDF restored on the basis of information gained from the CARS-spectra provides an alternative possibility of diagnostics of the electron component in a gas discharge plasma.

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