04

Optical emission spectroscopy of a discharge in an argon-nitrogen mixture sustained by terahertz radiation from a free-electron laser

© A.V. Sidorov[1], V.V. Kubarev[2], A.P. Veselov[1], A.V. Vodopyanov[1], O.A. Shevchenko[2], Ya.I. Gorbachev[2]

[1] Federal Research Center A.V. Gaponov-Grekhov Institute of Applied Physics of the Russian Academy of Sciences, Nizhny Novgorod, Russia
[2] Budker Institute of Nuclear Physics, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia
E-mail: alexsv@ipfran.ru

Received July 8, 2025
Revised July 30, 2025
Accepted August 11, 2025

This paper describes the results of a study of a discharge in an argon-nitrogen mixture created by a focused beam of radiation at a wavelength of 130 μm from the Novosibirsk Free Electron Laser (NovoFEL). The results of a study of the population of nitrogen molecules in a fixed electronic-vibrational state under various discharge conditions are presented. Possible mechanisms for the observed population distribution are discussed.

Keywords: terahertz radiation, gas discharge, ultraviolet radiation.

DOI: 10.61011/TPL.2025.11.62209.20435

The progress in design of high-power sources of terahertz (THz) radiation [1,2] has paved the way toward the study of interaction of electromagnetic radiation of this frequency range with plasma. These studies are of interest primarily from an applied standpoint, since dense THz-discharge plasma may serve as an intense source of optical, ultraviolet, and extreme ultraviolet radiation [3].

One of the key issues with discharges in a focused beam of electromagnetic waves at the Novosibirsk Free Electron Laser (NovoFEL) in pure inert gases is that a discharge shifts toward heating radiation away from the focus of the beam, increasing significantly the volume of plasma and reducing the maximum temperature achieved in the discharge [3]. In the present study, nitrogen was added to the discharge volume, which had a significant negative influence on the breakdown conditions outside the focus of heating radiation. This made it possible to confine the discharge to the focal spot of NovoFEL radiation. Data on the ranges of background gas pressures and gas injection rates supporting the development of a discharge were obtained. In contrast to [3,4], where the glow of inert gases was investigated, the present study is focused on the features of population of rotational levels of nitrogen molecules in a fixed electronic-vibrational state under various discharge conditions. Possible mechanisms behind the observed population distribution are discussed.

The diagram of the NovoFEL optical discharge setup is shown in Fig. 1. NovoFEL radiation *2* (wavelength, 130 μm; pulse duration, 100 ps; pulse repetition rate, 5.6 or 11.2 MHz) was introduced along channel *1* via rotating mirror *3* into discharge chamber *4* through diamond window *5* positioned at the Brewster angle in the focal waist of the mirror introducing radiation into the chamber. The optical system in the discharge chamber, which featured three parabolic (*6*–*8*) mirrors and a single planar one (*9*), then focused FEL radiation to a spot between mirrors *7* and *8* with a minimum transverse size (the width at half maximum of a Gaussian beam for radiation with a wavelength of 130 μm was close to 0.3 mm). Experiments were carried out at two NovoFEL pulse repetition rates: 5.6 and 11.2 MHz (specific rate values are defined by the parameters of the setup; see [1] for more details). An

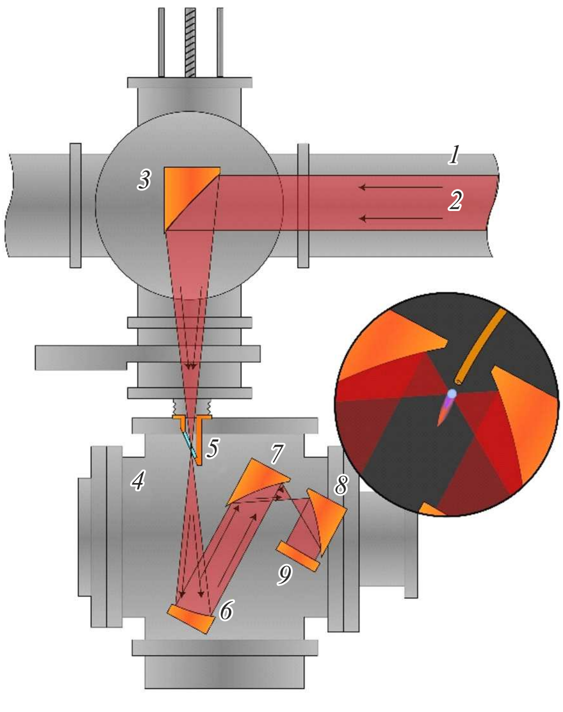

Figure 1. Discharge chamber and diagram of NovoFEL radiation input into it. *1* — NovoFEL radiation channel, *2* — THz beam, *3* — rotating mirror, *4* — discharge chamber, *5* — input window made of CVD diamond, *6* — 30° rotating mirror, *7* and *8* — 90° focusing mirrors, and *9* — planar mirror.

increase in pulse repetition rate translated into an increase in average power of radiation heating the discharge. At half the maximum average power level, exact proportionality between the average power and the pulse repetition rate was achieved easily (the average power increased from 120 W at 5.6 MHz to 240 W at 11.2 MHz). The same proportionality is planned to be established at maximum average powers.

Vacuum discharge chamber *4* was evacuated to pressures at the level of 10^{-4} Torr and filled with working gas (argon with added nitrogen). A high-voltage spark discharge ignited near the focal spot of electromagnetic radiation was used to initiate a discharge if the intensity of electromagnetic radiation was insufficient for self-breakdown.

The discharge was ignited in a gas (argon) jet introduced into the discharge chamber volume in the region of the focal waist (see the inset in Fig. 1) through a hole with an approximate diameter of 1 mm in a copper tube cooled with water (hereinafter referred to as the gas target). The gas jet was introduced into the discharge volume under a high pressure (2 bar). The pressure in the discharge volume was adjusted by altering the rate of gas injection and pumping. In the discussed experiments, this pressure was 1 bar. The flow rate of injected gas was regulated and monitored within the range of 2–10 l/min with the use of a flow meter. Nitrogen was introduced via a separate injection line directly into the atmosphere of the discharge chamber. Its injection rate was varied within the 0.1−1.2 l/min range.

The discharge luminosity was examined within different wavelength ranges using an MS 5204i monochromator spectrograph produced by SOL Instruments (1800 1/mm grating). The instrumental line width calibrated against a mercury lamp was 0.7 Å. Diagnostics of the discharge glow was carried out through an optical quartz glass window in the discharge chamber. Radiation was focused by a quartz lens and directed to the input of a light guide connected to the entrance slit of a monochromator. Almost the entire light output of point discharge *5* (Fig. 2) made its way to the light guide.

To optimize the discharge conditions further, the discharge glow was examined as a function of argon and nitrogen flows introduced into the discharge chamber. The ratio of intensities of the Ar III lines, which are located within the range of 250−280 nm, and continuous radiation was chosen as a parameter characterizing the discharge. It appears that continuous radiation comes primarily from the cold halo of discharge plasma, while line radiation is confined to the hot discharge „core" with an approximate diameter of 1 mm. As the plasma temperature increases, line radiation of the plasma core intensifies, while recombination radiation of the cold plasma halo becomes weaker. Therefore, the ratio of intensities of line radiation and continuous radiation is a fine qualitative indicator of the discharge temperature. It was found that each argon flow level has a corresponding optimal nitrogen flow level at which this ratio is maximized. As the argon flow increases, the optimal nitrogen flow also increases.

Figure 2 presents a typical photograph of a discharge in an argon jet (imaged in the same plane as the inset in Fig. 1) injected into the volume filled with an argon–nitrogen mixture. In addition to the discharge itself, a red-orange „tail" is seen clearly behind it in the direction of gas flow. It appears that gas passing through the periphery of the discharge is heated and, propagating through the background volume of gas, excites the first positive system of the vibrational-rotational spectrum of nitrogen. This induces an orange glow along the hot gas path. As the gas (argon) flow rate increases from 6 to 12 l/min, plasma of the main discharge becomes increasingly dispersive for the gas jet, which cannot pass through it [3]. This results in strong deviations of the jet from the original direction of propagation and even bifurcation of the luminous tail of excited atoms.

The glow of the second positive nitrogen system from the main discharge volume was used to estimate the temperature of this gas.

As is known, the population of rotational levels in molecules is often used to estimate the temperature of gases [5]. In the present study, we investigated the population of rotational states of ground vibrational level (vibrational quantum number $v = 0$) of the $C^3\Pi$ state. The lines of branch R of the second positive system $C^3\Pi{-}B^3\Pi$ (specifically, bands (0-2) and (0-0) with their edges positioned at wavelengths of 380.49 and 337.1 nm, respectively) were used for this purpose.

Figure 3 shows the dependence of the relative population (on a logarithmic scale) of rotational levels in a fixed electron-vibrational state of a nitrogen molecule on the energy of the rotational level ($B_v(J'+1)J'$, where J' is the

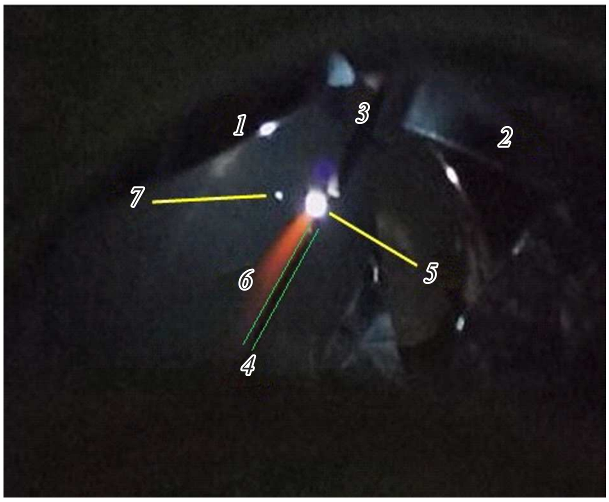

Figure 2. Photographic image of the THz discharge in an argon−nitrogen mixture. *1,2* — 90° focusing mirrors, *3* — gas injection tube, *4* — high-voltage spark discharge ignition electrode (outlined in green for contrast), *5* — main discharge, *6* — orange discharge „tail", and *7* — central part of the main discharge (two reflections of the main discharge in the output window). A color version of the figure is provided in the online version of the paper.

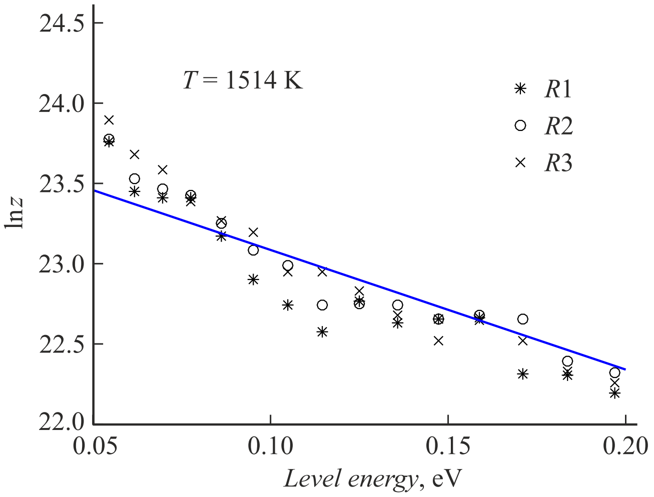

Figure 3. Population distribution over rotational states in a fixed electronic-vibrational state of a nitrogen molecule $N_2(C^3\Pi)$. A discharge was initiated in a mixture of argon and nitrogen. The flow rate of argon and nitrogen was 6 and 0.4 l/min, respectively. The NovoFEL power was 120 W.

rotational quantum number). The relative population was calculated based on the intensity of lines corresponding to branch R- of band (0-2) of the second positive nitrogen system as $\ln z = \ln(I_{J'J''}/S_{J'J''}\nu^4_{J'J''})$, where $\nu_{J'J''}$ is the $J'-J''$ transition frequency and $S_{J'J''}$ is the intensity factor in the rotational structure [5]. A temperature coefficient of population, which was calculated as $T_r = B_v(J'+1)J'/\ln z$ and specified the slope of the dependence of population on the level energy, was introduced in order to characterize this population. In the case of a Boltzmann population distribution, it corresponds to the so-called rotational temperature. The slope of the dependence of relative populations was approximated for levels with $J' > 15$ (this corresponds to an energy of approximately 0.05 eV), since the lines of branch R then do not overlap with the lines corresponding to branch P.

The temperature coefficient of population was reconstructed from the slope of the population dependence plot. Depending on the conditions, this coefficient varied from approximately 1200 to 2000 K. It was virtually independent of both the flow rate of argon introduced into the discharge and the average NovoFEL power (when this power was set to 120 or 240 W). At the same time, the temperature coefficient of population decreased with increasing nitrogen flow from approximately 2000 K at 0.1,l/min to 1200 K at 1.2 l/min. The same is true for the vibrational temperature determined from the ratio of intensities at the peak of bands (0-2) and (1-3) (see, e.g., [5]). It matched, within a measurement error of 20 %, the temperature coefficient of population of rotational levels and also depended only on the nitrogen flow rate, decreasing as it increases. It is important to note that only the lines for J' up to 30 may be observed for band (0-2). To track the population of higher rotational levels, we used the (0-0) band of the second positive nitrogen system, which allows for observation up to $J' = 91$ [6].

Figure 4 shows the dependence of the relative population of levels on their energy reconstructed based on the (0-0) band. While the temperature coefficient was roughly (with an accuracy of 20 %) equivalent to the one reconstructed based on band (0-2) within the range of rotational numbers from 15 to 30, the slope of the dependence of relative populations of rotational levels became significantly smaller at higher rotational numbers (see Fig. 4) and corresponded to a temperature of approximately 9000 K, which differs significantly from the populations of levels with $15 < J' < 30$. As the nitrogen flow rate increased, the indicated temperature dropped approximately to 6000 K.

This non-Boltzmann population distribution has already been observed in various discharges in nitrogen and mixtures of nitrogen with other gases. These studies were reviewed in [5]. Specifically, the presence of two groups of rotational levels with different temperature population coefficients was revealed in [7]: a cold group (with lower J') and a hot one (with higher J'). It was also demonstrated that the temperature of the cold group corresponded to the gas temperature (apparently, this is also observed in the present study) determined both from the populations of rotational levels of other molecules (CO) and directly with the use of a thermocouple. It is interesting to note that the rotational temperature of gas passing through the periphery of our high-temperature laser discharge is higher than the rotational temperature of gas in discharge plasma in a low-frequency electric field [8] by approximately the same factor ($\sim 2-3$) as the temperature of plasma at the periphery of our laser discharge compared to

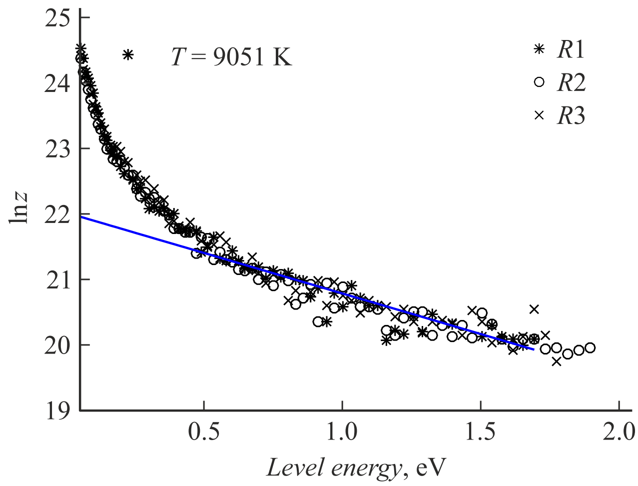

Figure 4. Population distribution over rotational states in a fixed electronic-vibrational state of a nitrogen molecule $N_2(C^3\Pi)$. A discharge was initiated in a mixture of argon and nitrogen. The flow rate of argon and nitrogen was 8 and 0.2 l/min, respectively. The NovoFEL power was 120 W.

the temperature of the hottest electrons in the electric discharge (~ 1 eV). Therefore, the rotational temperature of gas may apparently serve as an auxiliary qualitative probe of the temperature of main plasma of our laser discharge.

It appears that the increased population of levels with high J in our experiments is attributable to collisions of nitrogen molecules in the ground state with excited argon atoms, which occur, e. g., in reaction

$$N_2(X^1\Sigma) + \mathrm{Ar}(3p^5 4s) \rightarrow N_2(C^3\Pi) + \mathrm{Ar}(3p^6\,{}^1S_0). \quad (1)$$

This reaction has been studied extensively as a source of highly excited levels of nitrogen molecules in the $C^3\Pi$ state (see, e. g., [5] and references therein). However, the excess energy released in it does not exceed 0.8 eV, but higher-energy levels are also seen in Fig. 4. The high-pressure THz discharge discussed here is characterized by high concentrations of both neutral particles and electrons (at the critical concentration level; i. e., on the order of $10^{17}\,\mathrm{cm}^{-3}$ at 2.3 THz), which is typical of this discharge type, and a high specific energy input into the discharge (on the order of $100-200\,\mathrm{kW/cm}^3$, when averaged over time under the specified conditions). Therefore, this discharge is an intense source of ultraviolet radiation (up to vacuum ultraviolet), which may excite argon atoms not only to the $3p^5 4s$ state, but also to the higher $3p^5 4p$ state with a roughly 2 eV energy excess above the $C^3\Pi$ level of a nitrogen molecule.

In fact, precisely the inert gas atoms excited by ultraviolet radiation of the discharge are the reason why a THz or microwave discharge [9] in pure inert gases has the capacity to spread into the region of essentially prebreakdown fields that are significantly weaker than the breakdown fields for a cold gas (without a discharge), since the ionization of inert gas atoms from an excited state requires a significantly lower electron energy (just $2-4$ eV for argon). In our experiments, the discharge with added nitrogen could be maintained only in the focal region of THz radiation and, in contrast to a discharge in pure argon, did not shift toward heating radiation. This provides an indirect indication of effective quenching of excited argon atoms in collisions with nitrogen molecules.

Funding

This study was supported by the Russian Science Foundation, grant No 19-72-20166.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] G.N. Kulipanov, E.G. Bagryanskaya, E.N. Chesnokov, Yu.Yu. Choporova, V.V. Gerasimov, Ya.V. Getmanov, S.L. Kiselev, B.A. Knyazev, V.V. Kubarev, S.E. Peltek, V.M. Popik, T.V. Salikova, M.A. Scheglov, S.S. Seredniakov, O.A. Shevchenko, A.N. Skrinsky, S.L. Veber, N.A. Vinokurov, IEEE Trans. Terahertz Sci. Technol., **5**, 798 (2015). DOI: 10.1109/TTHZ.2015.2453121

[2] S. Sabchevski, T. Saito, M.Y. Glyavin, in *Advances in terahertz source technologies*, ed. by G.S. Park, M. Tani, J.S. Rieh, S.Y. Park (Jenny Stanford Publ., N.Y., 2024), p. 419–459.

[3] V.V. Kubarev, Ya.I. Gorbachev, O.A. Shevchenko, A.V. Vodopyanov, A.V. Sidorov, A.P. Veselov, Plasma Sources Sci. Technol., **32**, 055004 (2023). DOI: 10.1088/1361-6595/accca9

[4] A.V. Sidorov, V.V. Kubarev, A.P. Veselov, A.V. Vodopyanov, O.A. Shevchenko, Ya.I. Gorbachev, Tech. Phys. Lett., **50** (12), 147 (2024). DOI: 10.61011/TPL.2024.12.60378.6563k.

[5] V.N. Ochkin, *Spectroscopy of low temperature plasma* (Wiley, Weinheim, 2009).

[6] A. Lofthus, P.H. Krupenie, J. Phys. Chem. Ref. Data, **6** (1), 113 (1977). DOI: 10.1063/1.555546

[7] V.N. Ochkin, S.Yu. Savinov, N.N. Sobolev, in *Elektronno-vozbuzhdennye molekuly v neravnovesnoi plazme*, Ed. by N.N. Sobolev (Nauka, M., 1985), p. 6 (in Russian).

[8] Q.Y. Zhang, D.Q. Shi, W. Xu, C.Y. Miao, C.Y. Ma, C.S. Ren, C. Zhang, Z. Yi, AIP Adv., **5**, 057158 (2015). DOI: 10.1063/1.4921916

[9] N.A. Bogatov, Yu.Ya. Brodsky, S.V. Golubev, V.G. Zorin, in *Proc. of XVIII Int. Conf. on phenomena in ionized gases* (Swansea, U.K., 1987), p. 864–865.

Translated by D.Safin