04.1

Synthesis of nitrogen oxides NO_x in atmospheric pressure discharge sustained in the flow of argon-air gas mixture by continuous electromagnetic radiation with frequency 263 GHz

© S.V. Sintsov, A.V. Vodopyanov, E.I. Preobrazhensky, D.A. Mansfeld, A.P. Veselov, A.A. Goryunov, A.P. Fokin, A.A. Ananichev, M.Yu. Glyavin

Institute of Applied Physics, Russian Academy of Sciences, Nizhny Novgorod, Russia
E-mail: sins@ipfran.ru

Received March 11, 2024
Revised March 15, 2024
Accepted March 18, 2024

The results of an experimental study of a plasma torch sustained at atmospheric pressure in a flow of argon−air gas mixture by continuous radiation of a gyrotron with a frequency of 263 GHz are presented. The discharge sustained inside a customised electrodynamic structure having the shape of a truncated cone absorbed up to 80% of the injected millimetre radiation power in some regimes. It is shown that in the realised plasma-chemical process the degree of oxygen conversion into nitrogen oxides (NO_x) can be up to $58 \pm 4\%$.

Keywords: subterahertz radiation, gyrotron, plasma chemistry, nitrogen fixation.

DOI: 10.61011/TPL.2024.06.58487.19917

A gas discharge sustained by electromagnetic subterahertz and terahertz radiation is the least well-studied object in applied plasma physics. Latest advances in the design of vacuum-tube microwave oscillators (gyrotrons) open up new fields of use for the range of electromagnetic radiation frequencies that has earlier remained inaccessible [1–3].

The application of electromagnetic radiation with a frequency of 0.3−3 THz allows one to produce spatially nonuniform weakly collisional plasma ($\nu_{em} \ll \omega$, where ν_{em} is the electron-neutral collision rate and ω is the cyclotron frequency) under near-atmospheric pressures. The average electron concentration in such discharges exceeds the critical value for an electromagnetic field frequency and is equal to $10^{15}-10^{17}\,\mathrm{cm}^{-3}$ [4]. Their specific feature is the formation of plasma filaments with increased electron concentration levels, which may be attributed to nonlinear wave electrodynamics effects [5,6]. The resonance absorption of microwave power in the periphery of plasma filaments, where the electron concentration is near-critical, makes them efficient sources of ionizing ultraviolet radiation. Under the influence of this radiation, a region of non-self-sustained discharge (plasma halo), which may absorb a considerable fraction of the injected microwave radiation power, forms around filaments. A substantially non-equilibrium distribution of temperature characteristics is established in a halo, which constitutes the major part of a gas discharge. Therefore, a halo is a favorable environment for plasma-chemical reactions [7]. In view of this, atmospheric discharges sustained in a gas flow by continuous millimeter and submillimeter radiation are promising sources of non-equilibrium plasma that may find applications in non-equilibrium plasma chemistry.

In the present study, we report the results of experiments on synthesis of NO_x nitrogen oxides in a discharge sustained under atmospheric pressure in an argon−air gas mixture flow by continuous electromagnetic radiation with a frequency of 263 GHz. In future years, the Birkeland−Eyde process in non-equilibrium atmospheric pressure discharges may become an alternative „green“ method for production of nitric acid, which is an essential precursor of synthetic fertilizers [8–10].

The diagram of the experimental setup is shown in Fig. 1. Its two structural parts are upper and lower gas-discharge chambers that are connected hermetically to each other. A gyrotron with an operating frequency of 263 GHz and a power up to 1200 W in the continuous mode was used as a source of electromagnetic radiation [3]. Subterahertz linearly polarized radiation with a Gaussian intensity distribution in the cross section of a beam was introduced into the upper gas-discharge chamber through a polyethylene window. This chamber was fitted with a plasma-forming gas supply system, a parabolic mirror with an adjustment system, a water-flow calorimeter, and an observation window for photographic imaging of a discharge. The parabolic mirror focused a submillimeter beam into a spot 1.2 mm in diameter, which was positioned (see Fig. 1) at the level of the narrow end of a conical electrodynamic structure at the interface between upper and lower chambers. The plasma-forming gas and electromagnetic radiation introduced into the upper chamber could enter the lower chamber only via the conical electrodynamic structure. The apex angle of the truncated conical structure was equal to the angular beam convergence (60°); the base diameters were 5 and 32 mm. The power density at the beam waist was as high as $20\,\mathrm{kW/cm}^2$, and the RMS value of the electric field intensity was 2.7 kV/cm. The lower chamber was fitted with a second water-flow calorimeter, a system for extraction and ejection of used plasma-forming gases, and an observation window for recording of emission spectra. The readings of two water-flow calorimeters indicated that 90% of the

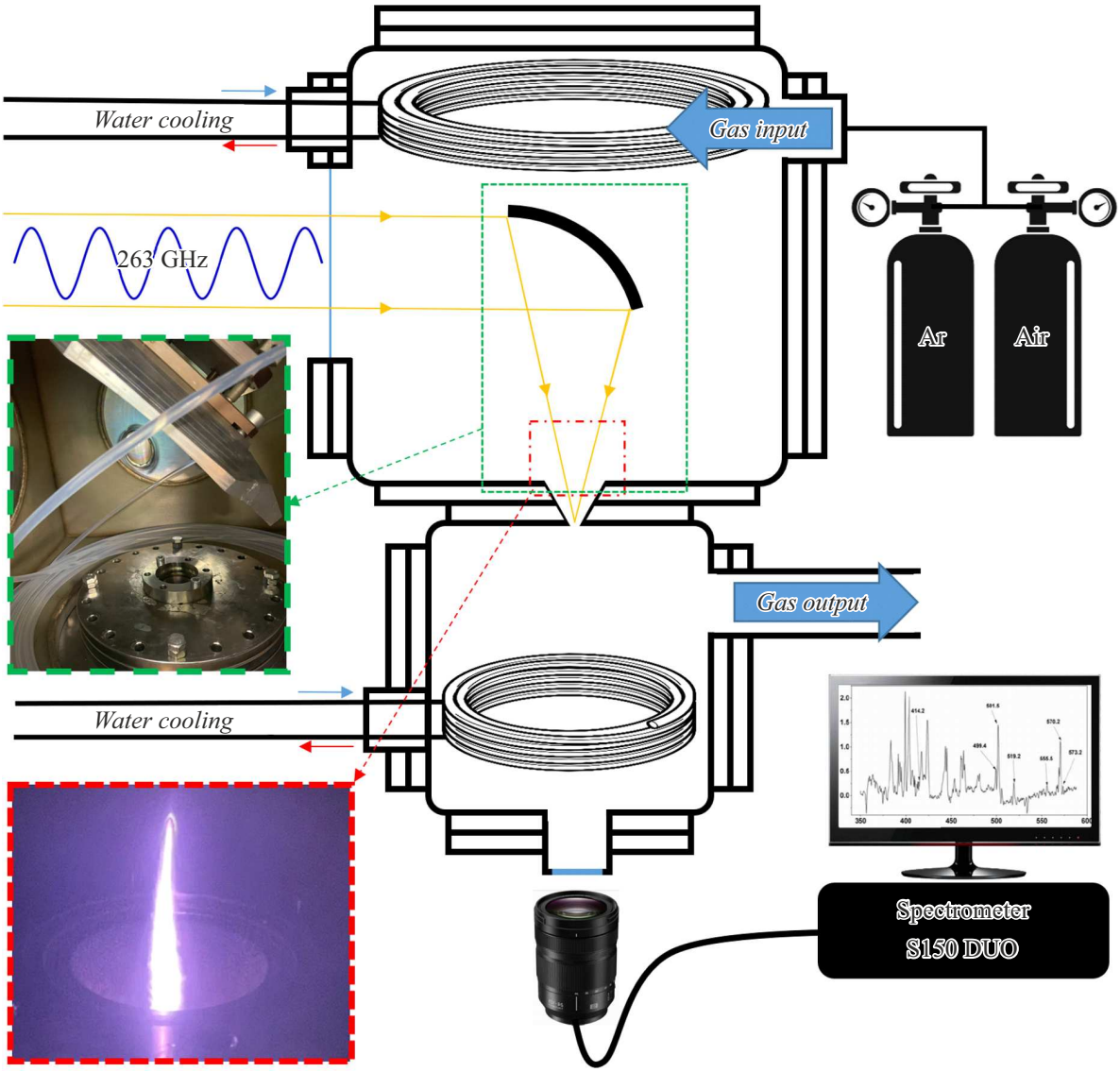

Figure 1. Diagram of the experimental setup.

injected power of submillimeter radiation entered the lower chamber via the conical electrodynamic structure when no gas discharge was initiated. This calorimetric system was used to estimate the microwave power absorbed by plasma in experiments.

High-purity argon (with less than 0.0007% of oxygen) and air (calibration mixture with 20.9% of oxygen) served as working gases. Gas flows were adjusted by Bronkhorst flow regulators with an accuracy of 0.5%. To initiate a gas discharge, the airtight upper chamber was filled with the plasma-forming argon–air mixture under atmospheric pressure. A discharge in gas flowing to the lower chamber via the conical electrodynamic structure was initiated within this structure and extracted toward the convergent microwave beam in the form of a plasma torch (Fig. 2). Its shape and size depended on the microwave power and the ratio of components of the plasma-forming mixture. In a flow of pure argon, a plasma torch 22 mm in length emerged at a minimum subterahertz radiation power of 190 W. When the power was raised to 1200 W, the torch length reached 70 mm. An argon torch consisted of numerous unsteady filamentary channels extending in the beam propagation direction (Fig. 2, *a*). The addition of a molecular gas to the plasma-forming mixture resulted in transformation of a plasma torch into a filament extending toward the microwave beam and surrounded by an unsteady plasma halo. The plasma filament length and the halo volume increased with increasing injected microwave power and decreasing concentration of air in the plasma-forming mixture (Figs. 2, *b–d*). A discharge could be sustained at a maximum air–argon ratio of 0.18; a further increase in the concentration of air in the plasma-forming mixture resulted in extinguishing of the discharge. It was determined by processing the results of calorimetric measurements that a

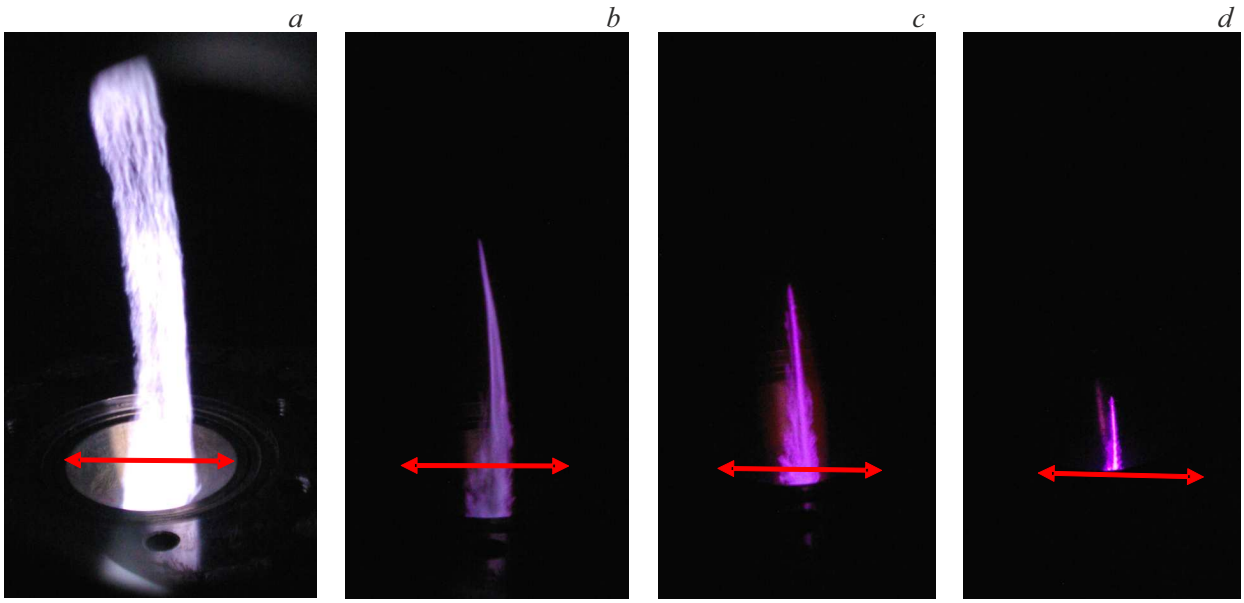

Figure 2. Photographic images of plasma torches sustained under atmospheric pressure in an argon–air gas mixture flow by continuous radiation with a frequency of 263 GHz. *a* — Argon flow: 30 l/min, $P = 820$ W; *b* — argon flow: 21 l/min, air flow: 0.5 l/min, $P = 760$ W; *c* — argon flow: 21 l/min, air flow: 1 l/min, $P = 820$ W; *d* — argon flow: 8.4 l/min, air flow: 0.5 l/min, $P = 680$ W. The arrow is 32 mm in length.

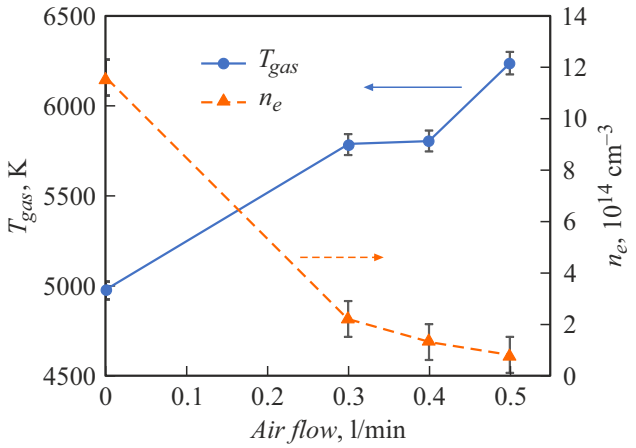

Figure 3. Results of measurement of the gas temperature and the electron concentration in a discharge sustained under atmospheric pressure by continuous microwave radiation with a frequency of 263 GHz at different values of air flow in the plasma-forming argon–air mixture. The argon flow was 21 l/min in all measurements, and the microwave radiation power was 1200 W.

discharge in pure argon absorbs 30–35% of the injected subterahertz radiation power. The addition of 0.5% of air to the plasma-forming mixture resulted in a sharp increase in the absorbed power fraction, which reached 60–65%. As the concentration of air increased further, the coefficient of absorption of microwave radiation by plasma grew approximately to 80%.

Optical emission spectra of a discharge were recorded through the observation window at the bottom of the lower chamber (Fig. 1) by an S150 Duo two-channel spectrometer produced by SOL Instruments. The first channel was used to measure spectra within the 200–1100 nm range for estimating the gas temperature based on the Planck continuum. The second channel with an echelle grating was used to record the shape of the H_α hydrogen line with a resolution of 20 pm. The concentration of electrons in plasma was estimated from the broadening of this line due to the linear Stark effect. A small amount of hydrogen (less than 0.01 l/min) was added to the plasma-forming mixture for these measurements. An objective was used to transfer the image of a discharge at the narrow end of the conical electrodynamic structure to the fiber input of the spectrometer. Therefore, the measured spectra represent integral emission of plasma within the conical electrodynamic structure. Figure 3 present the results of measurement of the gas temperature and the electron concentration at a fixed power of subterahertz radiation (1200 W) and different ratios of components of the plasma-forming air–argon mixture, which vary from 0 to 0.024. As more air is introduced into the mixture, the concentration of electrons in plasma within the conical electrodynamic structure decreases from $12 \cdot 10^{14}$ to $0.8 \cdot 10^{14}$ cm^{-3}, while the gas temperature increases from 4950 to 6250 K. The addition of a molecular gas to argon resulted in a sharp reduction in electron concentration with a transition through a critical value ($8 \cdot 10^{14}$ cm^{-3}) for the given heating field frequency. According to our estimates, this effect, which has been observed for the first time in the previous configuration of the subterahertz gas-discharge system with argon and carbon dioxide gas in the plasma-forming mixture, is

Results of synthesis of nitrogen oxides in a discharge sustained under atmospheric pressure by continuous microwave radiation with a frequency of 263 GHz at different process parameters

Injected power, W	Absorbed power, W	Argon flow, l/min	Argon flow, l/min	Initial concentration of oxygen, %	Concentration of nitrogen oxides, %	Conversion of oxygen, %	Specific energy consumption, MJ/mol
680	460 ± 20	8.4	0.5	1.1	0.20 ± 0.05	18 ± 5	35 ± 8
760	560 ± 20	21.0	0.5	0.5	0.20 ± 0.05	43 ± 8	17 ± 4
820	610 ± 20	21.0	1.0	0.9	0.40 ± 0.05	46 ± 5	9 ± 2
940	710 ± 20	11.2	0.5	0.8	0.50 ± 0.05	58 ± 6	16 ± 2

probably attributable to the emergence of channels of loss of electrons in plasma due to their sticking to oxygen atoms [11]. With the overall energy deposition into a discharge remaining virtually constant, an increase in gas temperature with increasing air concentration in the plasma-forming mixture is compensated by a simultaneous plasma volume reduction (Figs. 2, *b*–*d*).

Gas sampling for subsequent component analysis with an Agilent 6890/MSD 5973N gas chromatograph/mass spectrometer was performed in the system for ejection of plasma-forming gases in the lower chamber. The results of measurement of the NO_x concentration in the used plasma-forming mixture and estimation of the degree of conversion of O_2 into NO_x and the energy costs of synthesis in different discharge regimes are listed in the table. The characteristic concentration of NO_x in experimental studies into plasma synthesis of nitrogen oxides under atmospheric pressure is as high as 5.5% [10]. The concentrations of nitrogen oxides and the energy costs of synthesis presented here are nowhere near record-high levels; however, these parameters are limited in our experiment by the concentration of oxygen in the plasma-forming argon–air mixture. The degree of conversion of O_2 into NO_x is as high as 46–58% in certain regimes; i.e., approximately one half of oxygen introduced into the plasma-forming mixture is involved in the formation of nitrogen oxides, indicating that the process of plasma synthesis in the examined type of a subterahertz discharge is substantially non-equilibrium in nature.

Funding

This study was supported financially by the Russian Science Foundation (project 22-72-00073).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] M.Yu. Glyavin, G.G. Denisov, V.E. Zapevalov, A.N. Kuftin, A.G. Luchinin, V.N. Manuilov, M.V. Morozkin, A.S. Sedov, A.V. Chirkov, J. Commun. Technol. Electron., **59** (8), 792 (2014). DOI: 10.1134/S1064226914080075

[2] Y.K. Kalynov, I.V. Bandurkin, I.V. Osharin, A.V. Savilov, IEEE Electron Dev. Lett., **44** (10), 1740 (2023). DOI: 10.1109/LED.2023.3307161

[3] M.Yu. Glyavin, M.V. Morozkin, A.I. Tsvetkov, L.V. Lubyako, G.Yu. Golubiatnikov, A.N. Kuftin, V.E. Zapevalov, V.V. Kholoptsev, A.G. Eremeev, A.S. Sedov, V.I. Malygin, A.V. Chirkov, A.P. Fokin, E.V. Sokolov, G.G. Denisov, Radiophys. Quantum Electron., **58** (9), 639 (2016). DOI: 10.1007/s11141-016-9636-3

[4] A.V. Sidorov, J. Phys. D: Appl. Phys., **55** (29), 293001 (2022). DOI: 10.1088/1361-6463/ac5556

[5] V.B. Gildenburg, S.V. Golubev, E.D. Gospodchikov, S.V. Sintsov, A.V. Vodopyanov, Phys. Plasmas., **31** (2), 023507 (2024). DOI: 10.1063/5.0173489

[6] M. Fukunari, S. Tanaka, R. Shinbayashi, Y. Yamaguchi, Y. Tatematsu, T. Saito, Sci. Rep., **9** (1), 17972 (2019). DOI: 10.1038/s41598-019-54333-5

[7] N.A. Bogatov, S.V. Golubev, V.G. Zorin, Fiz. Plazmy, **12** (11), 1369 (1986) (in Russian).

[8] B.S. Patil, Q. Wang, V. Hessel, J. Lang, Catal. Today, **256** (Pt 1), 49 (2015). DOI: 10.1016/j.cattod.2015.05.005

[9] N. Cherkasov, A.O. Ibhadon, P. Fitzpatrick, Chem. Eng. Process.: Process Intensif., **90**, 24 (2015). DOI: 10.1016/j.cep.2015.02.004

[10] S. Kelly, A. Bogaerts, Joule, **5** (11), 3006 (2021). DOI: 10.1016/j.joule.2021.09.009

[11] S.V. Sintsov, D.A. Mansfeld, A.P. Veselov, A.P. Fokin, A.A. Ananichev, M.Yu. Glyavin, A.V. Vodopyanov, Tech. Phys. Lett., **49** (1), 44 (2023). DOI: 10.21883/TPL.2023.01.55347.19398.

Translated by D.Safin