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Influence of nitrogen on thermodynamic properties and plasma composition in discharge tube of CO-laser

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Abstract The role of the addition of nitrogen to the discharge plasma of CO lasers on thermodynamic properties and composition of the laser active medium is discussed here. It is shown that nitrogen addition improves laser characteristics and changes the composition of the laser active medium. The addition of nitrogen significantly decreases CO dissociation level and concentrations of C atoms created in plasma-chemical reactions of laser discharge.

Keywords: CO-laser; Vibrational kinetics; Dissociation; Plasma-chemistry; CN molecules; C_2; Electron kinetics

1 Introduction

The processes of molecular dissociation and following plasma-chemistry, changing the composition of laser active-medium and laser characteristics, determine the long-term and effective operation of molecular sealed-off lasers (working without the gas exchange in the laser discharge tube).

These processes are extremely important for a CO-laser operation. The vibrationally excited $CO(X^1\Sigma,v)$ molecules, involved in the laser-radiation

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generation, hardly relax during collisions with initial component of the active mixture, however the ratio of their relaxation could significantly increase when collision partners are some products of the above mentioned plasma-chemical processes [1]. It is well known (see e.g. [2] and the references therein), that sealed-off CO-lasers usually apply mixtures with significant concentrations of nitrogen, which support better energy-characteristics and improve long-life performance of the laser.

Addition of nitrogen molecules to the laser active-mixture results in the increase of population of vibrationally excited CO molecules due to vibrational-vibrational (VV′) relaxation processes, where V′ denotes vibrations of other molecule. However, there are some important indicators pointing to the fact that improvements of CO-laser operation after nitrogen addition does not necessary result from additional mechanism of CO states excitation. An addition of nitrogen to He-CO mixture leads to a significant change in plasma-chemical products. Firstly, some new nitrogen-containing products appear: N atoms, molecules CN, NO, etc. Secondly, the nitrogen and nitrogen-containing products influence plasma composition of initial He-CO mixture.

Up to now the influence of nitrogen on plasma-chemistry of CO laser has rarely been investigated. There is a lack of comprehensive models for plasma-chemistry of He-CO-N_2 mixtures (except some common feature with plasma of CO_2 laser [3–5]), which would help to estimate the level of degradation of the initial laser mixture. However, it has been shown in [5] that a CO_2 laser plasma with a high nitrogen content, $30\% < [N_2] < 50\%$, ensuring proper storage of the vibrational energy in CO_2 lasers, is characterized by a low electron temperature and thus, small chemical reactivity, i.e., a small level of CO_2 dissociation. From the investigations it follows that mixture decomposition decreases with an increase of N_2 content in the CO_2 laser mixtures. In contrast, electron temperature does not decrease after nitrogen additions to He-CO plasma. The temperature is constant or even slightly increases (up to 15%).

However, there is a small amount of experimental data on products of plasma-chemistry in such discharges and on products' dependence on experimental conditions and discharge time-duration. The concentrations of CN molecules have been measured in flowing $He = CO - N_2$ discharges [6–8] and in sealed-off systems, and theoretically determined based on a model of plasma-chemical processes – see [9]. Unfortunately, dependence of other plasma-chemical products in CO-laser medium on experimental

conditions were not studied. In order to proceed with the development of plasma-chemistry models for CO-laser-medium and to estimate how plasma-chemistry products influence CO-vibrational-state populations it is important to determine the parameters of active mixtures including temperatures (gas and vibrational) and CO-vibrational-state populations.

Thus, the aim of this work is to determine the influence of nitrogen additions to He-CO mixtures on thermodynamic characteristics, CO-vibrational-states populations and products of plasma-chemistry in laser tube discharges. The experiments were performed under conditions typical for discharge tubes of CO-laser working in sealed-off and gas flowing regimes.

2 Experimental set-up

Experimental set-up has been described already in a previous work [9]. The water-cooled discharge tube from molybdenum glass, 17 mm in diameter, was used in the experiment. The lengths of discharge zone was 50 cm. Hollow cylindrical electrodes from tantalum were installed in the side branches of the discharge tube at a distance of 4 cm from its axis. A discharge was excited using DC currents of 10–100 mA. The experiment was performed for initial He-CO and He-CO-N_2 mixtures. The relative CO and N_2 concentrations were varied in the range 3–15%. Gas pressure was set at 0.67–2 kPa. The setup can work in sealed-off and gas-flowing regimes (gas velocities 1–3 m/s were applied).

Initially, the gas mixtures used in the experiments were carefully purified by using a system of traps with silica-gel and zeolite. The mixture composition in the discharge tube was analyzed with a MSC-6 time-of-flight mass-spectrometer [7]. Periodically repeated gas probing from the discharge tube enabled the control of time evolution of stable product concentrations in the laser-discharge plasma.

The emission spectra from the discharge positive-column was registered using a spectrometer in the range 300–6000 nm, in order to determine the respective populations of vibrationally excited states of CO($X^1\Sigma$) and gas temperature along the symmetry axis of the discharge tube as well as its radial profile. The determination was done by analysing the rotational structure of CO vibrational bands. The emission spectra also enabled the determination of electronically excited particles in the plasma of the gas discharge.

The vibrational distribution of CO molecules in the ground electronic

state ($X^1\Sigma$) was determined from the spectra of IR (infrared) molecular emission at the (v$\rightarrow$ v-1) fundamental frequency, and the first (v$\rightarrow$ v-2) overtone.

The analysis of the emission spectra enabled the determination of the gas and vibrational temperatures as well as the concentrations of the electronically excited particles in the gas-discharge plasma. During the experiment the overtones emission was registered from neighbourhood of symmetry axis ($\sim$ 3 mm) in the discharge positive column. The spectra were studied using a Czerny-Turner monochromator with a diffraction grating of 300 and 1200 lines/mm. Cooled (by liquid nitrogen) photoresistors HgCdTl and uncooled InSb were used as photodetectors.

Lack of cataphoresis significant influence during measurements in systems without gas flows was proved. It was confirmed by registering He line intensities and CO molecular band at various points along the symmetry axis of the discharge tube using an optical waveguide.

The electric field in the discharge was determined by measuring the voltage drops across the discharge gap and the electrode sheaths. The electrode sheath voltages were found from the voltage measurements in experiments with different discharge lengths. A typical electrode sheath voltage was 350–400 V. The estimated value of the reduced electric field E/N (where E is electric field and N is concentration of neutral particles) was (2.1–3.2) 10^{-16} V cm^2.

For determination of absolute emission intensities, etalon lamps SI-8-220U and SR-2-32-RM were used. The plasma radiation was collected from the central region of discharge 2–3 mm in diameter.

The concentration of carbon atoms in the ground state was determined from absolute values of population of electronic excited states [1]. The method is based on knowledge of population of electrically excited states, which under experimental conditions applied here are excited mainly by direct collision from ground state and decay in radiation processes. Thus concentration of carbon in ground state can be determined from the simple balance equation:

$$[M_0] = [M^*]A/(n_e K_1) \ ,$$

where: M^* – a molecule in an excited state, A – Einstein coefficient for excited state, n_e – electron density in plasma discharge, and K_1 is the rate constant for carbon excitation by electron impact. Symbol [...] stand for concentration and asterisk (*) denotes excited state. For carbon atoms we used state $2p3p\,^1P_1$ by measuring 1.45 μm IR line intensity.

The population of CN in ground state was calculated from absorption spectra [9]. We have employed the method of two identical light sources. As a light source we used a discharge identical to the one we were investigating. It allows for a complete overlap of emission and absorption contours of both systems. The line of R-band of $K'' = 9$ transition (0,0) violet system CN($B^2\Sigma \rightarrow X^2\Sigma$) was used as in [2], where K'' is rotational quantum number.

Measurements of discharge concentrations of (CO, CO_2, C, CN, N_2) species and their dependence on experimental conditions were compared with results of calculations. The electron energy distribution functions (EEDF) were calculated for our conditions by Kochetov using the method described in [10].

The values of reduced electric field E/N and gas temperature was assumed in the model from experimental data. Electron density was determined from current and calculated value of electron drift velocity.

The measurements where performed for CO-laser-generation regime and without laser-radiation generation. In order to enforce laser generation a resonator in flat/spherical configuration was applied. A fully reflecting metallic mirror (from steel covered with gold) had 5 m curvature radius. The exit mirror (with transmission 85–95%) was a flat plate from CaF_2 or ZnSe covered by dielectric multilayer. Laser energy characteristics under the gas-flow regime were: power 0.4 W and electro-optic efficiency $\eta = 10\%$; under sealed-off regime 0.2 W and $\eta = 4.8\%$, respectively. The resonator was not optimised for the generation conditions.

3 Results and discussion

Measurements showed that a nitrogen addition to the He-CO laser medium results in substantial increase of CO vibrational temperatures. This should be related to transfer of vibrational energy from nitrogen to carbon oxide due to VV′ exchange. As a result a stationary state is realised in the laser medium, with a high level of vibrational energy in CO molecules.

Table 1 presents results of vibrational temperature (T_1) determination:

$$T_1 = E_1 / \ln(N_0/N_1), \tag{1}$$

where: E_1 – energy of the first excited vibrational state, N_0 and N_1 – populations of the ground and first excited vibrational state of CO molecule. The normal font numbers correspond to measurements in the gas flowing

regime, while numbers in bold font to sealed-off regime. As can be seen, the values for both regimes are relatively close. Reproducibility of the results was estimated as 10%.

Table 1: The CO vibrational temperature under different conditions.

Pressure	0.67 kPa			1.33 kPa		
Mixture/Current	50 mA	60 mA	70 mA	50 mA	60 mA	70 mA
He-CO=95:5	1750/1700	1800	1950	1700/1600	1850	1800
He-CO=91:9	1700	1700	1800	1700	1800	1800
He-CO-N_2 = 95:3:2	2850/2700	2800	2800	2700/2600	2750	2750
He-CO-N_2 = 95:4:1	2450/2400	2400	2500	2500/2400	2650	2650

Nitrogen in the mixture increased populations of CO excited vibrational-states, and this effect grows with the considered nitrogen concentrations. The laser generation was observed in He-CO-N_2 mixtures (at the level 0.4 W) but it wasn't observed when nitrogen was absent in the mixture under any considered experimental conditions.

It was found that a decrease of CO vibrational states-populations in the mixtures containing nitrogen proceeds under much higher energy inputs (currents) than in the mixtures without nitrogen. Figure 1 presents CO vibrational energy distributions for mixtures He-CO and He-CO-N_2 for different currents. It can be seen that populations in the He-CO-N_2 mixture fall with current value significantly slower. The populations fall when current value exceed 20 mA, the optimal current value under considered conditions.

It should be pointed out that the gas temperatures measured (near symmetry axis) in both mixtures He-CO and He-CO-N_2 were similar and vary in the range 360–480 K. These temperatures do not depend on gas flow.
One of the main causes of the smaller decrease of CO vibrational states-populations under increase of current value in the mixtures with nitrogen is probably related to lower CO-dissociation level (measured value) and lower concentrations of plasma-chemical products. Level of dissociation 15 min. after discharge was commenced is shown in Fig. 2. ($\Delta[CO]/[CO]_0$, where $[CO]_0$ is the concentration of CO molecules in initial mixture, and $\Delta[CO]$ is the change of CO concentration in discharge). A significantly lower CO-dissociation level is registered after nitrogen addition. Besides, it can be seen that the experimental values of CO dissociation level are

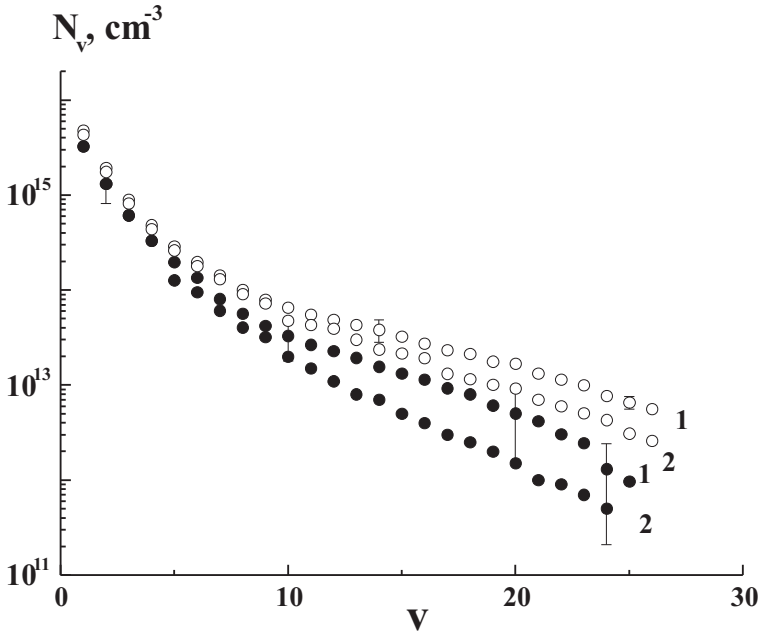

Figure 1: Populations of CO vibrational states in He-CO and He-CO-N_2 mixtures without laser-radiation generation at various discharge currents: black full circles – He:CO = 91:9 mixture; open circles – He:CO:N_2 = 91:4:5 mixture; curves 1 – current I = 25 mA, 2 – I = 40 mA; pressure P = 1.6 kPa.

significantly lower than those determined by calculation. At the same time, the calculated values of CO dissociation level for both mixtures are close to each other (full and dotted curves in Fig. 2). It is well known that the balance of CO concentrations in sealed-off discharge regimes should take into account three basic processes [1]:

- CO dissociation

$$\mathrm{CO} + e \rightarrow \mathrm{C} + \mathrm{O} + e \,, \tag{2}$$

$$\mathrm{CO} + \mathrm{CO}(a^3\Pi) \rightarrow \mathrm{CO_2} + \mathrm{C} \,, \tag{3}$$

- heterogeneous recombination of oxygen and carbon atoms

$$\mathrm{C} + \mathrm{O}^w \rightarrow \mathrm{CO} \quad \text{or} \quad \mathrm{O} + \mathrm{C}^w \rightarrow \mathrm{CO} \,, \tag{4}$$

where index w describes atoms adsorbed at the wall.

The process of CO dissociation in collisions with metastable He states

$$\mathrm{He}(m) + \mathrm{CO} \rightarrow \mathrm{He} + \mathrm{C} + \mathrm{O} \tag{5}$$

could be neglected under our case conditions, as the concentration of He atoms in metastable states is small.

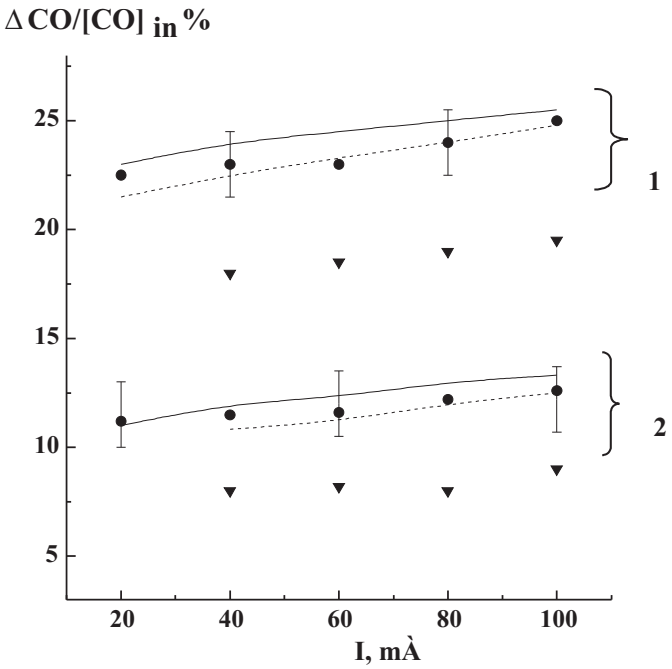

Figure 2: CO dissociation level as function of current 15 min after discharge turned-on: 1 – pressure P = 0.8 kPa, He-CO=95:5 mixture, full black circles – experiment, full curves – calculations; He-CO-N_2 = 95 : 3 : 2 mixture, full black triangles – experiment, dotted curves – calculations; 2 – pressure P = 1.33 kPa, He-NO=91:9 mixture – full black circles – experiment, full curves – calculations; He-CO-N_2 = 91 : 3 : 6 mixture, full black triangles – experiment, dotted curves – calculations.

The rates of dissociation in processes (2) and (3) do not change when nitrogen is added to the mixture, i.e., decrease in the CO dissociation level can be explained by rates for heterogeneous recombination (4). Such change of rates for process (4) could result from change of conditions on discharge-

tube-wall surface under nitrogen addition. It could be related partly to CN-molecules and C_nN_m polymers deposit on the walls.

The concentration of CO_2 molecules, which are created in laser discharge plasma, does not strongly depend on nitrogen addition and under the conditions considered here it was 5–10% of [CO] concentration. The CO_2 molecules in discharge plasmas of He-CO and He-CO-N_2, under the conditions considered here, are created in process (3) and destroyed in dissociation by electron impact

$$CO_2 + e \rightarrow CO + O + e \, . \tag{6}$$

Measurements showed that after nitrogen addition, the concentration of atomic carbon in discharge plasma decreases by 30–50%. They are created during the process (2) and (3) but are removed from plasma by diffusion to the wall.

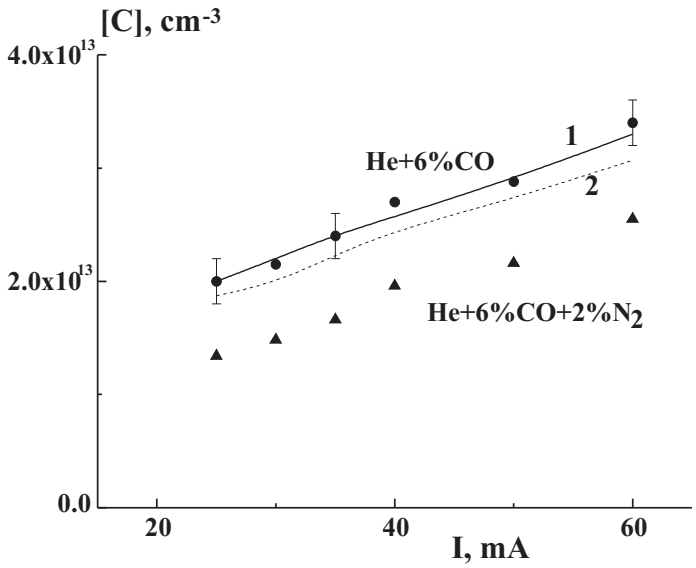

Figure 3: Carbon atom concentration as function of discharge 15 min after discharge turned-on: pressure P =1.6 kPa; symbols – experimental data, curves – calculations.

Figure 3 presents atomic C concentration measured in plasma and calculated using experimental data on concentrations of CO molecules. It is clearly seen that experimental data (points) for nitrogen-free mixtures agree well with calculated values (full curve). For the mixtures containing

nitrogen, experimental data are significantly lower than those calculated (dotted curve). Decrease of atomic carbon concentration after nitrogen additions in the He-CO mixture, can result from existence of additional processes with participation of atoms and carbon molecules. These include the following reactions:

$$C + N_2 + M \rightarrow \text{ products} , \tag{7}$$

$$C + NO \rightarrow \text{products} . \tag{8}$$

The rate constant of reactions (7) and M = Ar equals $K_7 = 3{\times}10^{-33}$ cm^{-6}/c [11]. These values for reaction (7) are large enough to influence the rate of carbon losses in the discharge.

Process (8) has an even more pronounced effect on atomic carbon, as its rate is close to a gasdynamic one (collision rate) [12,13]. In order for reaction (8) to significantly influence carbon losses it is sufficient that the concentration of NO molecules is of the order $5{\times}10^{11}$ cm^{-3}. The NO was not registered in the experiment mass spectra but method sensitivity to NO does not exceed $2{\times}10^{12}$ cm^{-3}, i.e., their existence in large enough quantity could not be excluded.

Besides, in He-CO-N_2 discharge plasmas CN molecules appear. Their concentration varies in the range $8{\times}10^{12}$ – $3{\times}10^{13}$ cm^{-3} under the conditions considered here. Figure 4 presents the measured and calculated values of CN concentrations as a function of discharge current. It can be seen that the measured and calculated values agree very well. Plasma-chemical processes determining CN concentration are described in [9] in detail. It was found that the CN molecules under conditions characteristic for discharge plasma of CO lasers are produced in processes

$$CO(X^1\Sigma) + N_2(A^3\Sigma^+, v \geq 2) \rightarrow CN(X^2\Sigma) + NO(X^2\Pi) , \tag{9}$$

$$CN(A^2\Pi) \rightarrow CN(X^2\Sigma) + h\nu , \tag{10}$$

The $CN(X^2\Sigma)$ molecule is lost due to diffusion and deposition on the wall-surface as well as in reaction with nitrogen atoms:

$$CN(X^2\Sigma) + N \rightarrow C + N_2 . \tag{11}$$

The CN molecules is excited to $A^2\Pi$ state in processes

$$CN(X^2\Sigma) + e \rightarrow CN(A^2\Pi) + e , \tag{12}$$

$$N_2(A^3\Sigma) + CO(X^1\Sigma\,, v \geq 6) \rightarrow CN(A^2\Pi) + NO(X^2\Pi)\,. \qquad (13)$$

In sealed-off systems the influence of heterogeneous processes on [CN] concentration is highly probable but there is a lack of data on their rates. However, the good agreement between experimental and theoretical results related to CN concentrations point to the fact that at the initial phase of discharge the heterogeneous processes do not influence CN concentration in discharge plasma of CO lasers.

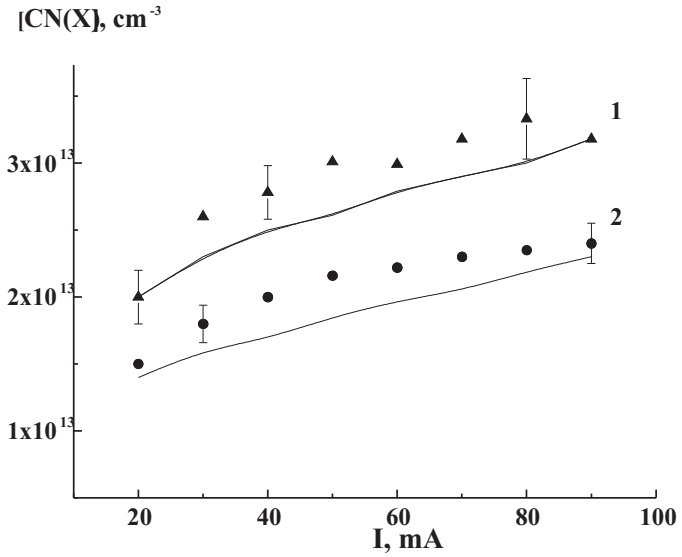

Figure 4: Concentrations of CN molecules as functions of discharge current, 15 min after discharge turned-on: 1 – He:CO:N_2 = 96:2:2, pressure P = 2.13 kPa; 2 – He:CO:N_2 = 91:6:3, pressure P = 0.67 kPa; symbols – experimental data, curves – calculations.

4 Conclusions

The performed measurements under conditions characteristic for discharge plasma in CO laser showed that nitrogen addition to the He-CO mixture leads to:

1. Significant increases in CO vibrational temperature as well as populations of CO excited states. A reduction of CO highly-excited vibrational-states populations with current is smaller in the case of mixtures with nitrogen additions.

2. The CO dissociation level in discharge plasma decreases 20–30%, which could result from changes in heterogeneous recombination of atomic oxygen and carbon and CO production.
3. The C atom concentration decreases 30–50%. This may result from additional channels with participation of nitrogen and possibly NO, which increase [C] losses.
4. The CN molecule concentrations are in the range $8\times10^{12} - 3\times10^{13}\mathrm{cm}^{-3}$ under the considered conditions.

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