AIP | Applied Physics Letters

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Citation: Applied Physics Letters **86**, 211501 (2005); doi: 10.1063/1.1935046
View online: http://dx.doi.org/10.1063/1.1935046
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/86/21?ver=pdfcov
Published by the AIP Publishing

APPLIED PHYSICS LETTERS **86**, 211501 (2005)

NO and NO_2 production in pulsed low pressure dc discharge

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(Received 22 December 2004; accepted 11 April 2005; published online 16 May 2005)

Simultaneous measurements of both NO and NO_2 are performed downstream a pulsed low pressure dc discharge in flowing air using tunable diode laser absorption spectroscopy in the infrared region. Pulse duration and repetition rate range from 20 μs to 5 ms and from 50 to 1000 Hz, respectively. The gas pressure is 4 mbar and the peak current is 80 mA. Experimental results show that NO and NO_2 production depends only on the duty cycle ratio, that is, on the average power at a given current. A numerical computation of a simplified kinetics agrees well with experiment results. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1935046]

Due to recent development of plasma based technologies for environmental applications, extensive literature exists on the NO_x ($NO+NO_2$) kinetics in atmospheric pressure discharges.[1–5] In a recent study concerning the potentials of a pulsed microwave discharge at atmospheric pressure for gas treatment and environmental applications, it was shown that the NO_x ($NO+NO_2$) formation depends only on the average power injected in the plasma, and not on the pulse duration itself, i.e., a short pulse (30 μs) with a high repetition rate will lead to the same amount of NO_x as a longer pulse (e.g., 1 ms) with low repetition rate, provided that the averaged power is the same.[5] The use of pulses even as short as 30 μs could not prevent significantly the NO_x formation. However, no straightforward analysis could be performed since the pulsed microwave discharge had strong space gradients. On the contrary, positive columns of dc low pressure discharges are spatially homogeneous and have been extensively studied, both theoretically and experimentally by Gordiets *et al.*,[6] and Rybkin *et al.*,[7] for a wide range of parameters. In this letter we report, experimental results concerning the NO_x formation in a *low pressure* pulsed dc discharge. The simultaneous measurement of NO and NO_2 concentration is very useful to validate reaction schemes occurring in the discharge and in the post-discharge for different pulse duration, repetition rate, and discharge current. NO and NO_2 are measured downstream the plasma region using tunable diode laser absorption spectroscopy (TDLAS) in the infrared region.

The discharge is generated in a 50 cm long and 1.9 cm inside diameter Pyrex tube (Fig. 1). The dc generator is pulsed by a master pulse generator. Pulse duration and repetition rate are adjustable from 20 μs to 5 ms and from 50 to 1000 Hz, respectively; the peak current is set to 80 mA. The gas flow is 20 sccm of dry air-like mixture (N_2/O_2); the gas pressure inside the discharge tube is 4 mbar. The exhaust gas is pumped out of the discharge tube through a multipath cell (optical path length is 100 m), where NO and NO_2 species are simultaneously detected using a two-laser beam infrared system (TOBI) (Fig. 1).[8] The pressure inside the cell was adjusted from 0.1 to 2 mbar, in order to optimize the signal to noise ratio. Essential basics of absorption spectroscopy are the relation between the incident (I_0) and the transmitted (I) intensity of the laser radiation:

$$\ln\left(\frac{I_0}{I}\right) = \int_0^L k_\nu n(z)dz,$$

where k_ν is the absorption cross section at the wave number υ; L is the absorption length, and n is the density of the absorbing species. NO_2 and NO lines, which have been used, are located in the 1626 and 1880 cm^{-1} spectral region, respectively. Absorption lines with different line strengths were used in order to increase the dynamic of the detection sensitivity, from 1 to 10 000 ppm typically.

In Figs. 2 and 3 the influence of the duty cycle ratio (DCR) on the NO and NO_2 production is presented for different pulse repetition rates, respectively. DCR is the ratio of the pulse duration to the pulse period. NO increases monotonously from 40 to 15 000 ppm as the duty cycle ratio increases from 0.1% to 50% (Fig. 2). On the contrary, NO_2 decreases continuously from 160 to 20 ppm (Fig. 3). It is

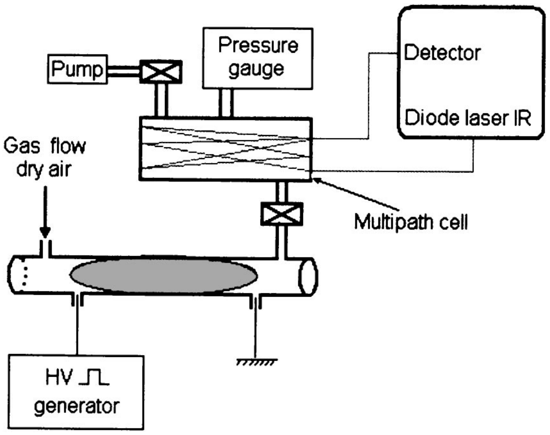

FIG. 1. Experimental set up: pulsed dc discharge, the infrared laser TOBI and the multipath cell.

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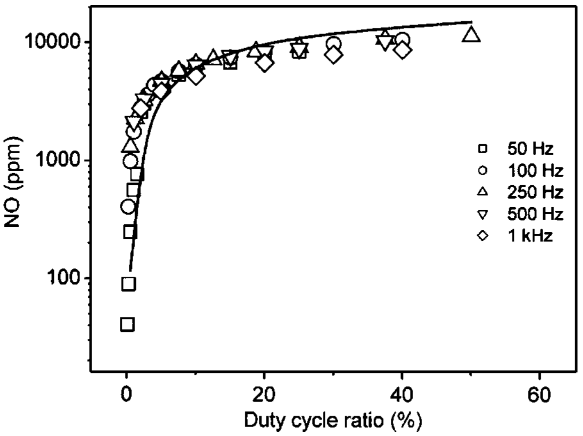

FIG. 2. Influence of the duty cycle ratio, DCR, on the formation of NO for different pulse repetition rates. Peak current 80 mA, 4 mbar, dry air, 20 sccm. The solid line is the computed results from numerical code.

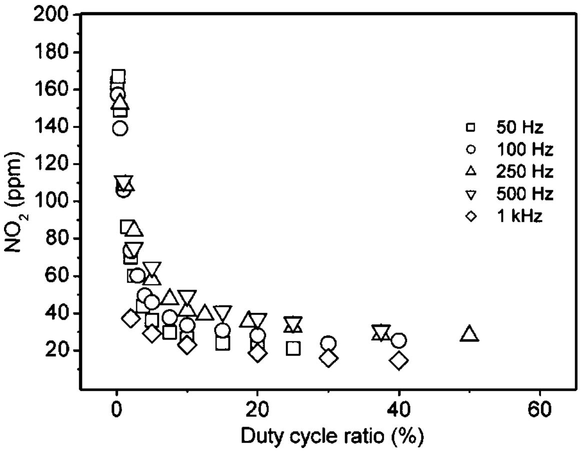

FIG. 3. Influence of the duty cycle ratio, DCR, on the formation of NO_2 for different pulse repetition rates. Labels identical to Fig. 2.

worthwhile to notice that NO and NO_2 depend only on the DCR: the experimental conditions of 4 ms pulse duration at 50 Hz are equivalent, in terms of NO_x production, to 200 μs, 1 kHz (DCR=20%). The scaling of NO_2 concentration with the DCR (Fig. 3) is less remarkable than that of NO; but the discrepancies in NO_2 density are in the range of 10 ppm, which is much less than NO density fluctuations. It is worth noting that DCR is proportional to the time-averaged discharge power for the given current. This shows that NO and $\mathbf{NO_2}$ density scales as a function of the time-averaged deposited power. The peak discharge power P may be found from $P=j\cdot E$, where $j=I/S=2.8\times10^{-2}$ A cm^{-2} is the current density for $I=80$ mA. $E=63$ V cm^{-1} is calculated from the reduced electric field for our discharge conditions $E/N=65$ Td.[9] This corresponds to the peak discharge power $P=1.7$ W cm^{-3} which gives the average discharge power increasing from 0.72 to 360 kJ/l for DCR increasing from 0.1% to 50%, respectively. Recently a similar observation was published for a pulsed microwave discharge near atmospheric pressure where both NO and NO_2 production only depend on the average power.[5]

An extensive analysis of the NO and NO_2 kinetics in a low pressure pulsed dc discharge will be published in a forthcoming paper. However, let us show that a simplified kinetics of NO gives a very good agreement with experimental results. Table I presents reactions taken into account in our model. The related kinetic equations are numerically solved with the following assumptions: (i) the electron energy distribution function (eedf) is computed using a code developed in the Kurchatov Institute (Moscow)[10] with $T_g=500$ K, $T_v=4000$ K, and $E/N=65$ Td. NO density being less than 1.2% is not taken into account for the computation of eedf; (ii) the electron density and E/N are supposed to be constant during the ON phase of the pulse and equal to zero during the OFF phase of the pulse; (iii) no ion kinetics are included in the model; (iv) the computation procedure stands as follows: a

TABLE I. List of reactions taken into account in the numerical model.

No.	Reactions	Rate constant ($cm^3\,s^{-1}$)	References
1	$N_2+e\rightarrow N_2^*(A^3\Sigma_u^+)+e$	5×10^{-11}	10
2	$N_2+e\rightarrow N_2^*(B^3\Pi_g)+e$	7.7×10^{-11}	10
3	$N_2+e\rightarrow N_2^*(a'^1\Sigma_u^-)+e$	4.4×10^{-12}	10
4	$N_2+e\rightarrow N^*(^2D)+N+e$	8.1×10^{-13}	10 and 11
5	$O_2+e\rightarrow O+O+e$	4.3×10^{-11}	10
6	$O_2+e\rightarrow O+O^*(^1D)+e$	2.0×10^{-10}	11
7	$NO+e\rightarrow N+O+e$	3.0×10^{-11}	11
8	$N_2^*(A^3\Sigma_u^+)+O_2\rightarrow N_2+O_2$	$2.5\times10^{-12}\times(T/300)^{0.55}$	12
9	$N_2^*(A^3\Sigma_u^+)O_2\rightarrow N_2+O+O$	$0.65\times k_8$	12
10	$N_2^*(A^3\Sigma_u^+)+O\rightarrow N_2+O$	2.8×10^{-11}	12
11	$N_2^*(A^3\Sigma_u^+)+O\rightarrow NO+N^*(^2D)$	0.4×10^{-11}	13
12	$N_2^*(B^3\Pi_g)+N_2\rightarrow N_2^*(A^3\Sigma_u^+)+N_2$	5.0×10^{-11}	13
13	$N_2^*(B^3\Pi_g)+O_2\rightarrow N_2+O+O$	3.0×10^{-10}	13
14	$N_2^*(a'^1\Sigma_u^-)+O_2\rightarrow N_2+O+O$	2.8×10^{-11}	13
15	$N_2^*(a'^1\Sigma_u^-)+NO\rightarrow N_2+N+O$	3.6×10^{-10}	13
16	$N+NO\rightarrow N_2+O$	3.1×10^{-11}	14
17	$N^*(^2D)+O_2\rightarrow NO+O$	$9.7\times10^{-12}\ e^{-185/T}$	12
18	$O^*(^1D)+N_2\rightarrow O+N_2$	$1.8\times10^{-11}\ e^{107/T}$	13
19	$O^*(^1D)+O_2\rightarrow O+O_2^*$	$3.2\times10^{-11}\ e^{67/T}$	13
20	$O^*(^1D)+NO\rightarrow N+O_2$	1.7×10^{-10}	13
21	$O+O_{ads}\rightarrow O_2$	25.4	For $\gamma=0.5\times10^{-3}$

sequence of n pulse periods is computed, starting from pure N_2/O_2 air like mixture, followed by $t=2$ min. n is defined by the ratio of the experimental residence time of the gas inside the discharge tube 1.2 s to the period; t is the gas averaged residence time between the discharge tube and the multipath cell where infrared measurements are performed; (v) NO_2 kinetics have not been included.

Figure 2 also shows the good agreement between the results of the numerical computation of the model presented above and the experimental results for NO. This agreement covers a wide range of pulse frequency and duration as well as they NO density. NO molecules are formed and destroyed mainly during the plasma pulse. The major process leading to NO formation is the reaction between $N_2^*(A^3\Sigma_u^+)$ molecules and atomic oxygen O (reaction 11). In fact in this reaction two NO molecules are created, because the excited $N^*(^2D)$ atoms, that are produced in reaction (11), collide with O_2 to produce another NO molecule in reaction (17). The destruction of NO occurs by the collision with electrons, $N_2(a'^1\Sigma_u^-)$ molecules and $O^*(^1D)$ atoms (reactions 7, 15, and 20).

The physical reason for the dependency of the NO_x on the DCR may be summarized as follows. The rate of $N_2^*(A^3\Sigma_u{}^+)$ molecules depends mostly on the electron density (process 1), which is constant during the pulse and equal to zero after the pulse; thus the time average value of this rate is proportional to the duty cycle ratio. The same is valid for NO molecule destruction (processes 7, 15, and 20). The destruction of the $N_2^*(A^3\Sigma_u{}^+)$ excited state goes via the collision with O_2 and O (processes 10 and 11), where the time averaged O atom density depends only on the DCR for a given pulse amplitude; as a result NO concentration depends only on the DCR and shows some saturation effect for high DCR corresponding to a high O atom density.

NO_2 kinetics were not included in the kinetic modeling; its density is much lower than the NO density for DCR $>1\%$. NO_2 is formed downstream the plasma region via oxidation of NO by ozone:

$$O_3 + NO \rightarrow NO_2 + O_2,$$

where the O_3 density is strongly reduced with increasing gas temperature above 300 K. This would explain why the NO_2 production decreases with increasing DCR.

In the present study, tunable diode laser absorption spectroscopy has been performed downstream a pulsed low pressure dc discharge in air, in order to measure simultaneously the formation of NO and NO_2 for various pulse durations and repetition rates. It is shown that the NO_x production depends only on the pulse duty cycle ratio, which is proportional to the pulse power. This is similar to recent measurements performed downstream a pulsed microwave discharge near atmospheric pressure. NO density increases with DCR up to about 1.2% for an averaged specific energy equal to 360 kJ/l. A numerical computation, solving a set of 21 kinetic equations including some excited states of N_2 and N, gives a very good agreement with experimental results. NO formation is driven by the time averaged density of $N_2^*(A^3\Sigma_u{}^+)$, which is an increasing function of the DCR.

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