PLASMA CHEMICAL PROCESSES IN HIGH-PRESSURE CO_2 LASERS

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Keywords: Laser, Contamination

Compounds: Original mixture: CO_2-N_2, CO_2-He, CO_2-N_2-He
Species produced: CO, NO, N_2O, NO_2

ABSTRACT

The gas composition in closed-cycle, high pressure CO_2 lasers is affected by the preionizing electron beam and the electrical discharge. Contaminants such as nitrogen oxides, produced at high pressure under E-beam irradiation, were measured in an ultra-high vacuum environment. Added oxygen increases the contaminant generation rate considerably. Chemical kinetics modelling supported the experimental results.

1. INTRODUCTION

For many medium and high pressure flowing laser applications, especially where large flow rates, long run times or isotopic mixtures are used, a closed-cycle gas supply will become necessary. However the high energy E-beam used for preionization of the discharge as well as the discharge itself cause plasma-chemical reactions whose products may affect the operation of the laser. These effects have been investigated previously for the low-pressure discharge lasers (1) and more recently for atmospheric pressure TEA lasers (2), but there are no experimental measurements available for atmospheric pressure E-beam preionized lasers. Of particular interest are the generation rates of the various nitrogen oxide compounds, which are known to cause deterioration of the discharge and laser characteristics (1), (3). These compounds can be formed from neutral dissociation products of CO_2 and N_2. They readily form various negative ions (for example $O^- + NO + M \rightarrow NO^- + M$) which can drastically change discharge characteristics and lead to attachment instabilities. Previously it was not known whether they also would be formed in E-beam preionized, atmospheric pressure lasers.

2. EXPERIMENTAL

The purpose of our experiment is to measure the plasma-chemical processes a) without any uncontrolled contributions by the experimental vacuum system and b) using diagnostic methods which allow both a comprehensive survey of gas species and also detailed on-line, time-resolved monitoring of selected species. The first requirement was met with an all stainless steel ultra-high vacuum closed flow loop, with an ultimate pressure in the 10^{-9} Torr range. The gas is circulated with an externally driven blower, connected to its motor via a ferrofluidic rotary feedthrough. The blower speed is variable and can produce a flow speed of up to 20 m/sec. The vacuum system is filled with research grade gases and small sample volumes for remote analysis can be removed using high-vacuum manifolds. The electron beam has a 5x15 cm crossection at total currents to 10 mA and up to 200 keV energy. With these measurements, no sustainer field was used since the high energy electrons were expected to produce most of the dissociation of the gas components. The survey diagnostics are performed off-line using IR absorption spectra with the gas samples in a 20 m White cell and analyzed with an interferometer-spectrometer having a resolution of 0.07 cm^{-1}. Spectral coverage of the instrument is from 2 to 14 microns. This method yields both identity and concentration of infrared active contaminant species. The on-line monitoring of selected species is performed by a diode laser tuned to known absorption lines of the gases of interest. The laser beam is directed through the E-beam irradiated volume via BaF_2 windows. Due to the extremely narrow linewidth of the diode laser and by carefully selecting the spectral region, interference from other gases even in an active discharge can be completely avoided. In summary, the sample IR analysis produces a complete survey of all gas constituents with infrared absorption spectra but will not give proper results for reactive species whereas the diode laser measures on-line, time- and spatially resolved, but only one known species at a time.

3. EXPERIMENTAL RESULTS

Our initial measurements were using E-beam currents of 5 mA, run times of 5-6 hours with a total of about 80 liters of a 3:2:1 mixture of He:N_2:CO_2 at atmospheric pressure. The amount of CO_2 dissociation into CO was unexpectedly small. Less than 1 Torr of CO was measured in the samples. N_2O and NO were detected, and their amounts were also small: 50 and 5 ppm. We then performed on-line measurements of CO concentrations using selected CO absorption lines. Fig. 1 shows the growth of CO absorption as a result of CO_2 dissociation with a CO_2:N_2 mixture, Fig. 2 shows CO absorption for a CO_2:He mixture at two E-beam currents. The generation of CO with the He mixture does not follow a simple exponential curve. This is contrary to expectations since it is improbable that He takes part in the dissociation process. Taking into account the exponential dependence of the absorption on the species density and also the ratio of the small active discharge volume versus the total loop volume, a time constant for the CO generation can be derived. For the CO_2:N_2 case the time constant is 5.5 seconds for 5 mA E-beam current. When the E-beam was switched off, no further changes were observed. The time constants increased with a decrease in E-beam current as is to be expected from a process controlled by electron collisions. To find a reason for the small amount of CO generated, we measured the loss of CO, presumably by dissociation, in an atmospheric pressure N_2 or He background using the same CO absorption lines. From Fig. 3 it can be derived that the time constant for that process is 0.15 sec for 5 mA E-beam current, or 30 times faster than the CO_2 dissociation time constant. The CO loss time constant also is inversely proportional to the E-beam current. Again no change was observed after switching the E-beam off. Spectral analysis of samples indicated that CO_2 was generated, indicating the existence of back-reactions. The fast CO loss rate is probably the reason for the low equilibrium concentration of CO under our E-beam irradiation conditions. To simulate a low quality vacuum system with air leaks, small smounts of O_2 were added. This produced a dramatic increase in dissociation products and a large decrease in the generation time constant of CO. In Fig. 4 the increase of dissociation products is plotted versus the amount of added O_2 for run times of 1 hour. NO_2 also was detected in small amounts in these measurements. Again using small smounts of CO in N_2 background, with added O_2, measurements showed that the CO loss rate decreased by a factor of about 5, indicating increasing back reactions and giving a reason for the much increased CO concentration.

4. MODELLING

Using some of the newer kinetic rates available from ionospheric research (4), we selected 9 neutral species as dissociation products. The original species concentration (3:2:1 $He:N_2:CO_2$ mixture, 1 atm.) was assumed constant. Fig. 5 indicates that within milliseconds of electric discharge operation nitrogen oxides at the ppm level are being generated. When the discharge is switched off (Fig. 6) the gas composition again changes in milliseconds. This illustrates the need for on-line species measurements for the nitrogen oxides, if a true picture of these reactions is to be obtained. The model we used is very incomplete, also leaving out all ion-reactions. An even bigger question is whether the rates used apply to our discharge conditions. Nevertheless the model serves to indicate that nitrogen oxides are produced at high pressures and that neutral reactions take place after the discharge is switched off. An even simpler model is being developed to explain the CO_2 dissociation and O_2 addition measurements. No rates for the back reactions seem to be available.

5. CONCLUSIONS

We have been able to demonstrate the plasma chemical production of nitrogen oxides in atmospheric pressure E-beam discharges. A major increase in the generation of dissociation products was shown to be caused by added O_2. This shows the need to use high-quality vacuum systems if long term closed-cycle operation of this type of laser is desired. Although we have used relatively simple chemical reactions in our modelling, the production of nitrogen oxides as well as composition changes after discharge switch-off could be simulated.

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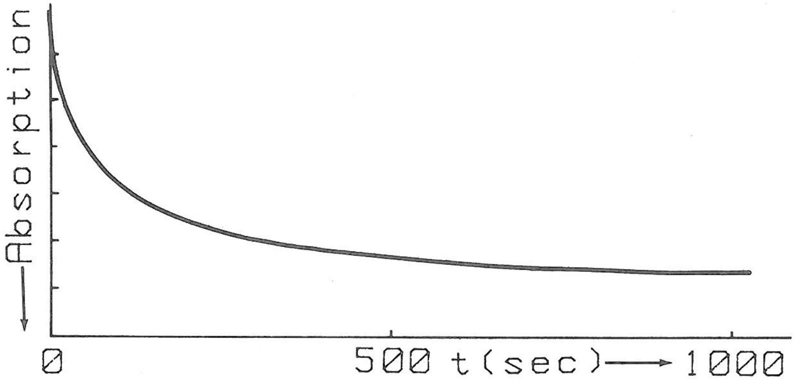

Fig. 1: Measurement of CO generation using diode laser absorption. Initial gas mix of 250 Torr CO$_2$ and 490 Torr N$_2$; E-beam current of 2.5 mA.

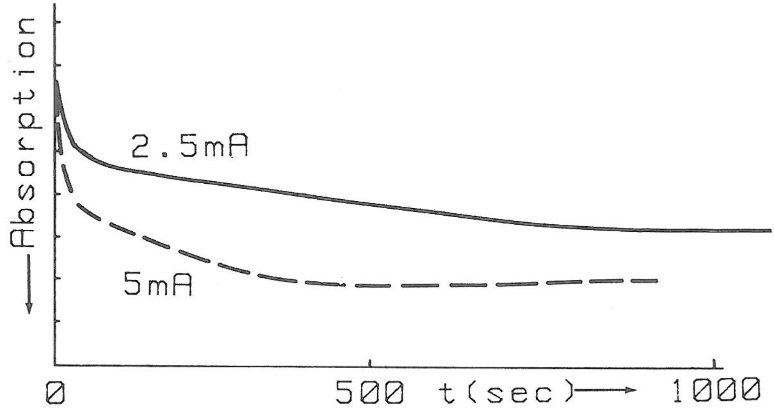

Fig. 2: Measurement of CO generation using diode laser absorption. Initial gas mix of 250 Torr CO$_2$ and 480 Torr He; E-beam current of 2.5 mA.

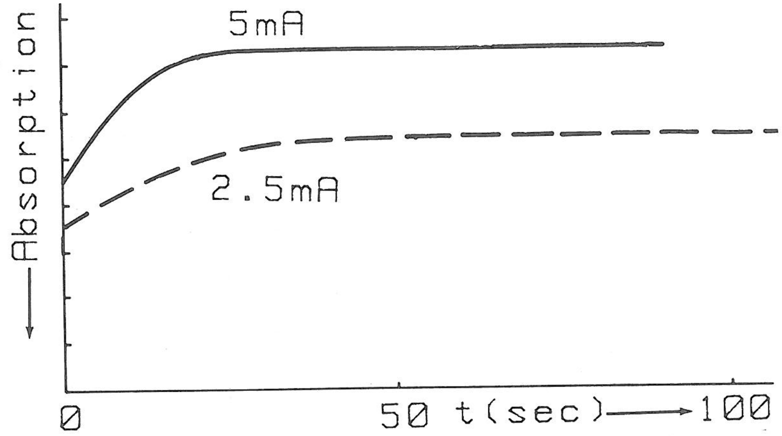

Fig. 3: Measurement of CO loss using diode laser absorption. Initial gas mix of 1 Torr CO and 740 Torr N_2; E-beam current of 5 mA (upper curve), 2.5 mA (lower curve).

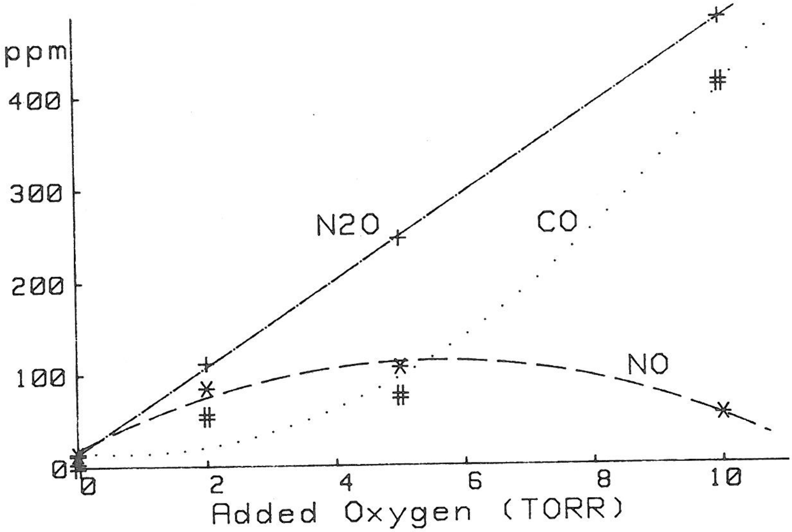

Fig. 4: Dissociation products after 1 hour irradiation. E-beam current 6 mA (CO: arbitrary units).

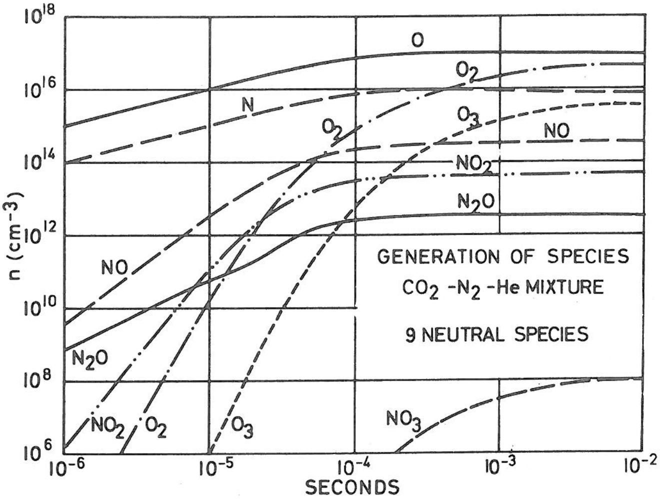

Fig. 5: Kinetic modelling of neutral dissociation products in a 3:2:1 He:N_2:CO_2 mixture at atmospheric pressure and an electron/ion density of 10^{12} cm^{-3}.

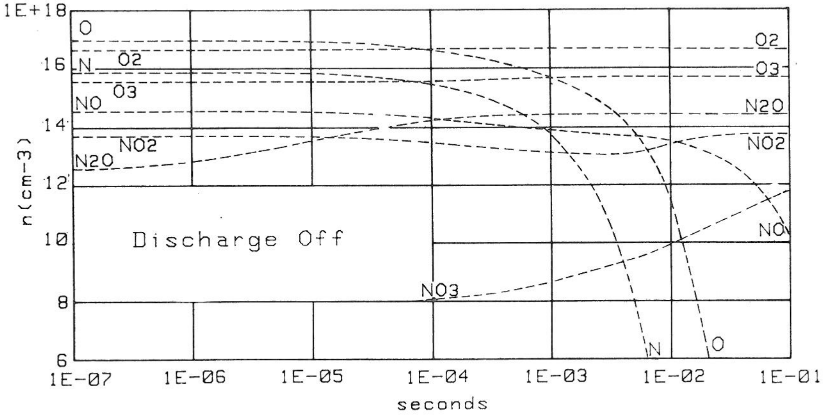

Fig. 6: Kinetic modelling of 9 neutral species. Initial conditions from Fig. 5. Discharge switched off (N_e=N_i=0).