PLASMA-CHEMICAL PROCESSES IN THE ACTIVE MEDIUM OF THE CO SEALED-OFF LASER

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Abstract

Plasma-chemical processes in He-CO, He-CO-Xe mixtures are studied. Experimental concentrations of CO, CO$_2$, C and O in wide range of conditions have been measured. Comparison of the measured and calculated data shows that heterogeneous recombination of C and O atoms is the very important channel of CO reconversion in the sealed-off discharge plasma. It was found that adding of Xe in He-CO mixture may increase dissociation of CO$_2$ molecules due to the reaction of CO$_2$ with metastable Xe atoms: CO$_2$ + Xe$^m$ → CO + O + Xe.

1. Introduction

The CO laser performance depends strongly on plasma-chemical processes in the active medium. This is of prime importance for sealed-off lasers. Up to the present information on these processes is incomplete and contradictory. The aim of this work is experimental and numerical investigation of plasma-chemical mechanisms in a sealed-off CO laser. The most attention has been concentrated on the processes of CO molecules decomposition and reconversion.

2. Experiment

The measurements have been performed with the sealed-off discharge tubes (length-50 cm, internal diameter- 15 mm and 30 mm), which were cooled with flowing water. He-CO and He-CO-Xe mixtures were used. The range of the discharge current was 20-100 mA, the total gas pressure was varied from 3 to 20 Torr.

Gas from the discharge tube was analyzed by mass spectrometer. For spectroscopic studies of the discharge plasma UV, visible and IR emission from the discharge tube was recorded by spectrometer. This allowed to obtain the gas temperature in the discharge tube by analyzing the rotational structure of the CO band systems. Registration of the emission of carbon atoms in the electronic states 2p3s$^1$P$^0$ ($\lambda=247.8$ nm, 2p3s$^1$P$^0$ $\rightarrow$ 2p$^2$ 1S$_0$) and 2p3p$^1$P$^1$ ($\lambda=1454.25$ nm, 2p3p$^1$P$^1$ $\rightarrow$ 2p3s$^1$P$^0$) and oxygen atoms in the electronic state 3p$^5$P ($\lambda=777$ nm, 3p$^5$P $\rightarrow$ 3s$^5$S$_2$) used for estimation the concentration of these atoms in the ground state.
This treatment is possible because in the conditions under study both these electronic states are exited by the direct electron impact and for estimation concentrations of these species in the ground state the simple balance equation must be solved.

This study is the first in which concentrations of CO molecules and of the main plasma-chemical products (CO₂, C and O) have been measured simultaneously. Concentrations of the molecules (CO, CO₂) were obtained by mass spectrometer, concentrations of C and O atoms were found from optical measurements. The electric field strength in the discharge tube was found by measuring the voltage across the discharge tube and, separately, the sum of cathode and anode falls. Theoretical E/N values have been calculated by numerical solution of the steady state diffusion equation for the electron concentration and have been found to be in good agreement with experimental ones.

3. Theoretical model

Experimental values for CO, CO₂, C and O concentrations were compared with theoretical ones. The kinetic equations for concentrations of CO, CO₂, C, O, O₂, C₂O were solved in the model. The rate constants for processes initiated by electrons have been calculated by using the steady state Boltzmann equation for the electron energy distribution function (EEDF)[1]. Changes in mixture composition due to plasma-chemical reactions were taken into account in calculations of EEDF. Plasma chemical processes included in the model (for mixtures without Xe):

1. CO + e → C + O + e
2. CO + CO(a^3Π) → CO₂ + C
3. CO + O + He → CO₂ + He
4. CO + O + CO → CO₂ + CO
5. CO + O + CO₂ → 2CO₂
6. CO + O → CO₂ + ΔE
7. CO₂ + e → CO + O + e
8. CO₂ + CO(a^3Π) → CO + CO + O
9. CO + C + He → C₂O + He
10. CO + C + CO → C₂O + CO
11. C + O → CO + ΔE
12. C + O + He → CO + He
13. C + O₂ → CO + O
14. C₂O + O → 2CO
15. C₂O + O₂ → CO₂ + CO
16. CO(a^3Π) + O₂ → CO₂ + O
17. CO(a^3Π) + O₂ → CO + 2O
18. O₂ + e → 2O + e
19. He + 2O → O₂ + He
20. CO + 2O → O₂ + CO
21. CO₂ + 2O → O₂ + CO₂
22. C₂O + C → C₂ + CO
23. C₂O + e → C + CO + e
24. He + 2C → He + C₂
Heterogeneous reactions:

25. CO + O + wall → CO₂ + wall
26. O + O\(^{\text{w}}\) → O₂ + wall
27. C + wall → products
28. O + wall → products

4. Results and discussion

Reactions (1) and (2) responsible for CO decomposition are very fast and as analysis shows none of the recombination processes in the discharge volume is sufficient to inhibit the drop of the CO concentration in the plasma. Rate constants for these recombination processes (11,12) are too small. This must lead to very fast disappearing of CO molecules in the discharge. CO must be completely decompose within \(t<1\) min.

In experiments concentration were measured at different time intervals: 1 min, 5 min and 20 min. It was found that experimental [CO] decreases but this decreasing is not exceed 5-30% (Fig.1).

![Graph](image)

Fig.1 Dissociation of CO molecules vs discharge current.

\[ \Delta[\text{CO}] = [\text{CO}]_{\text{in}} - [\text{CO}], \] where \([\text{CO}]_{\text{in}}\) is the initial concentration of the CO in the discharge.

\(\tau\) is a duration of the discharge.
Analysis has shown that for agreement between experimental and calculated concentrations of CO molecules and products of plasma-chemical reactions it is necessary to explicitly include in the model heterogeneous recombination of carbon and oxygen atoms leded to CO reconversion:

\[ C + O^+ \rightarrow CO + \text{wall} \]

or/and

\[ O + C^+ \rightarrow CO + \text{wall} \]

Rate constants for these processes are absent in literature. Since in our conditions concentrations of C and O atoms were very closed, it was hard to determine what one of these processes or both of them was responsible of CO reconversion. On the base of comparison of experimental concentrations of CO, CO₂, C and O and results of calculations it was found that the best agreement might be achieved if we assumed that atoms C and O recombine on the wall with the following effective constant:

\[ K_{\text{eff}} = \frac{(k_{\text{n}} \cdot S/V \times k_{\text{at}})}{(k_{\text{n}} \cdot S/V + k_{\text{at}})}, \]

where \( k_{\text{n}} \) is the rate constant of the heterogeneous recombination, \( k_{\text{e}} \approx 6 \times 10^{17}/[\text{CO}] \text{ cm/s} \), \( S/V \) are surface and volume of the discharge tube, \( k_{\text{at}} = D/\Lambda^2 \) is the average time of the atoms diffusion, \( D \) is the diffusion coefficient, \( \Lambda = r/2.4, r \) is the radius of discharge tube.

It is necessary to note that this rate constant depends on the CO concentration in the similar way as it was found for rate constant of O₂ formation by heterogeneous reaction (26):

\[ K_{\text{eff}} = 4 \times 10^{-6}/[\text{CO}] \text{ cm/s} \] [2]. Author [2] proposed that this dependence on the CO concentration is due to higher adsorption probability of CO molecules on the wall of the discharge tube.

Results of calculations showed on the Fig.1-2 were obtained when recombination of C and O on the wall leded to CO molecules formation was taken into account. One may see a good agreement with experimental concentrations. (Accuracy of [CO] and [CO₂] measurements ~ 1%).
Fig. 2 Concentrations of O(1), C(2) and CO$_2$(3) vs discharge current.

Investigations of the behaviour of the [CO$_2$] in different experimental conditions showed that the main process of CO$_2$ formation in the discharge is process (2) and the main loss process is the dissociation in collisions with electrons – (7). Process (8) was found to be inefficient, rate constant $k_8$ was estimated as $<10^{12}$ cm$^3$/s. Experiments with mixtures contained Xe showed that by adding xenon to the working gas mixtures new dissociation process for CO$_2$ molecules may appear in the discharge plasma:

\[ \text{Xe}^{**} + \text{CO}_2 \rightarrow \text{Xe} + \text{CO} + \text{O} \]  \hspace{1cm} (29)

where Xe$^{**}$ is the metastable atom of xenon. The rate constant for this process is high: $k = 4 \times 10^{10}$ cm$^3$/s [4].
Fig.3 Dissociation of CO₂ molecules vs discharge current.
Points – experiment, lines – calculations: 1- without process (29),
2- process (29) is taken into account.

Process (29) was important channel of dissociation (see Fig.3) when discharge tube with small diameter (d=15 mm) was used and E/N values in the discharge plasma was sufficient for effective excitation of low metastable level of Xe atom.

References