Peculiarities of the $\text{C}_2 \; d^3 \Pi \rightarrow a^3 \Pi$ band system intensities in gas discharges through CO-contained mixtures

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Abstract. The paper discusses the experimental results pointing to the efficient channel of the CO vibrational to the $\text{C}_2$ electronic energy-transfer. The radiation spectra of the $d^3 \Pi_g$ electronic state of $\text{C}_2$ molecule are investigated and the relation of their kinetics to a vibrational excitation of CO molecules in the He-CO-O$_2$ plasma is discussed. The changes of CO vibrational energy distribution (VED) were imposed by an application of a laser resonator to the discharge tube under investigation. It was found that the modulation of laser radiation (and VED) led to a similar changes of the spontaneous radiation from $d^3 \Pi_g$ state of $\text{C}_2$ molecules.

1. Introduction

The growing interest observed for the kinetics of the $\text{C}_2$ molecules is related to the carbon nanoparticles production, studies of flame and carbon-containing-plasma properties as well as to the astrophysical investigations. Therefore, an information related to spectral investigations of $\text{C}_2$ molecules is already widely available in literature, see e.g. [1-4]. Even the processes leading to the $\text{C}_2$ production as well as the $\text{C}_2$ excitation-channels in a discharge plasma are not well known. However, the knowledge of kinetic processes with participation of these molecules and their rates is rather scarce.

A population inversion in $v = 6$ has been observed in a lot of experiments. There is general agreement to attribute this inversion to production of $\text{C}_2$ molecules in an electronic state crossing $d^3 \Pi_g$ in the vicinity of $v' = 6$. In [5] a theoretically predicted metastable $^3 \Pi_g$ state of $\text{C}_2$ molecules has been proposes as a candidate for the precursor state.

It was shown in our previous works [6-8], that changes in the CO vibrational population in CO containing plasmas influence intensities of Swan system ($\text{C}_2$: $d^3 \Pi_g \rightarrow a^3 \Pi_u$ transition), the vibrational distribution of $d^3 \Pi_g$ state and the rotational temperature of $v = 6 \; d^3 \Pi_g$. In conditions with high concentration of CO($w$) molecules a population inversion in $v = 6$ of $\text{C}_2 \; d^3 \Pi_g$ disappeared. One of the reasons of this phenomenon may be the changing of the excitation process of $v = 6 \; d^3 \Pi_g$. Figure 1 shows that the electronic state of $\text{C}_2$ corresponds energetically to some vibrationally excited levels of CO($X', \Sigma$, $w$) molecule, with the vibrational quantum numbers $w > 10$. This hints to a possible energy transfer from the vibrational to electronic states between these molecules (V-E processes). Up to date it is unclear which ones of the vibrational levels of CO($X', \Sigma$, $w > 10$) take part in processes followed the disappearing of the selective excitation of $v = 6 \; d^3 \Pi_g \; \text{C}_2$.

In the present work we study the influence of the changes of populations of different vibrational levels of CO($w$) molecules on the concentration of $v = 6 \; d^3 \Pi_g$ state of the $\text{C}_2$. 

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Fig. 1 Scheme of the energetically-low levels of the electronic excited states of C\textsubscript{2} molecule and the vibrational states of CO molecule. Arrow shows the transition related to so called Swan band system.

2. Experimental set-up and methodology

The experimental set-up has been described in detail elsewhere [9]. The discharge was operated in DC mode. The experimental conditions were the typical for the active medium of electrical discharge CO-laser and the discharge tube with an appropriate resonator may work as a CO-laser. The molybdenum-glass discharge-tubes 15-20 mm in radius and 50 cm long, water- or nitrogen-cooled were used in our experiment. The 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 the DC currents of 20 - 100 mA. The relative CO concentrations in the applied He-CO-O\textsubscript{2} mixtures were varied in the range 3 – 15 %. 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 \( E/N \) was \((1.5–2.5) \times 10^{-16} \text{ V cm}^2\).

The spectra in the range 200 - 3000 nm were registered using the Czerny-Turner monochromator with a diffraction grating 300 and 1200 lines/mm. The recorded spectra allowed determination of concentrations of electronic excited species, gas temperature (through the analyses of the vibrational-rotational spectra) as well as vibrational populations of CO molecules (by analyzing the radiation in the first and second vibrational harmonics) - see also [10,11].

The changes of CO vibrational energy distribution were imposed by an application of a laser resonator to the discharge tube (in oscillation regime populations of vibrational levels of CO(v) molecules which take part in generation drastically decrease) – as can be seen in Fig. 2. It should be mentioned that the laser output was not very high, in order of few W. So, we have assumed that the plasma parameters, besides vibrational temperatures (i.e. electron and gas temperature, voltage, pressure, etc.) have not varied significantly during the modulation of the laser radiation. For example, we have found that the gas temperature decreased only by \~ 10 K, when laser was operating. At the same time, \( E/N \) was practically constant.
3. Results and discussion

Strong correlation has been found in experiments between concentrations of vibrationally excited CO molecules and the electronically excited state d^3Π_g of C_2 molecule. In particular, modulation of the intensity of lasing oscillation caused marked modulation of the intensity of the emission from d^3Π_g (Swan bands). Fig.3 illustrates the spectrum of Swan bands of C_2 molecule under conditions of laser generation (a) and turn-off generation (b). Under conditions of laser generation the intensive emission from C_2(d^3Π) was observed showing significant overpopulation of the sixth vibrational level. The population of the level v = 6 was 8 - 15 times larger than populations of lower levels. When lasing was absent the intensity of radiation from [C_2(d^3Π, v < 6)] increased 1.5-2 times. At the same time the transition from [C_2(d^3Π, v = 6)] decreased more than 1 order of magnitude.

It has been shown in [5] that overpopulation of the sixth vibrational level of the d^3Π_g state of C_2 most likely caused processes with participation of the hypothetic quintet ^5Π_g:

\[
\begin{align*}
C_2O + C & \rightarrow C_2(^5\Pi_g, v = 0) + CO \quad (1) \\
C + C + M & \rightarrow C_2(^5\Pi_g, v = 0) + M \quad (2) \\
C_2(^5\Pi_g, v = 0) + M & \rightarrow C_2(d^3\Pi_l, v = 6) + M \quad (3)
\end{align*}
\]

C_2O molecules formed in the gas discharge plasma due to plasma chemical processes.

In conditions when concentration of vibrationally excited CO molecules is high we observe the change of the excitation mechanism [8]. Correlation between concentration of C_2(d^3Π_l) and CO(v>10) may be cased by effective VE-process:

\[
\text{CO}(v>10) + C_2 \rightarrow \text{CO} + C_2(d^3\Pi_l) \quad (4)
\]

The efficiency of these channels increases with the growth of populations of high enough CO vibrational states v > 10, e.g. when the laser radiation declines. The importance of these channels decreases with the fall of CO vibrational populations, when laser is turned-on. In addition, it can be assumed, that vibrationally excited CO molecules may quench metastable quintet ^5Π_g.

To clarify the contribution of different vibrational states of CO molecule to the process (4), the consecutive changes of CO vibrational energy distribution were imposed by an application of a tunable laser resonator to the discharge tube.
It was found that the vibrational levels $12 < w < 20$ of the CO molecules most effect on the concentration of the $C_2$ ($d^3Π_g$). In conditions with low concentrations of CO($w$) molecules (in the lasing regime of the discharge tube) rotational temperature determined from (6,5) band of the $C_2$ Swan system - $T_rC_2(v = 6)$ was $\sim 150$K, but $T_r(v \neq 6)$ was equal to the gas temperature ($\sim 300-400$ K) - $T_g$. Without lasing all rotational temperatures $T_rC_2(v)$ was equal $T_g$ and the inversion on the $C_2$ ($d^3Π_g, v = 6$) was absent.

![Fig.3 The spectrum of Swan bands ($\Delta v=1$) of $C_2$ molecule under conditions of laser generation (a) and turn-off generation (b). He+6%CO+ 0.2%O$_2$, P = 9 Torr, I = 30 mA](image)

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