Vibrational and chemical kinetics in plasma of CO containing gases

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Abstract. This paper discusses the experimental results pointing to the efficient channel of the CO vibrational to the C2 electron energy transfer. The radiation spectra of $e_3^\Pi$, $C_1^\Pi$, $D_1^\Sigma$ states of C2 molecules were investigated and the relation of their kinetics to vibrational excitation of CO ($X_1^\Sigma, v$) molecules in the He-CO-O2 gas discharge plasma was discussed. The rate constant for VE-process CO ($X_1^\Sigma, v \geq 25$) + C2 $\rightarrow$ CO($X_1^\Sigma$) + C2($D_1^\Sigma$), was estimated, and $k_{VE} \sim 10^{-14}$ cm$^3$/c.

1. Introduction

The low temperature plasma initiated in He-CO-O2 mixture can be characterized by high degree of CO ($X_1^\Sigma$) vibrational excitation. In addition, the steady-state vibrational distributions, CO($X_1^\Sigma, v$), significantly differ from the standard Boltzmann type distribution, due to the fast vibration-vibration (VV) energy exchange processes between vibrationally excited (anharmonic) CO molecules [1]. The difference becomes more pronounced with increasing mismatch between the gas temperature, $T_g$, and the vibrational temperature given by the expression ($T_v = E_1/\ln(N_0/N_1)$), where $E_1$ is the energy of first vibrational level and $N_0$ ($N_1$) denote populations of the ground (the first excited) vibrational states. For a high enough mismatch between $T_g$ and $T_1$, the characteristic plateau on vibrational distribution for levels $v > T_g/2T_1x_e$ ($x_e$ - anharmonicity factor) appears, and the distribution changes slowly, proportionally to $1/(v+1)$. Therefore cryogenic cooling of working gas mixtures was used to increase the overpopulation of high vibrational levels of CO($X_1^\Sigma$).

This leads, in the case of He-CO-O2 discharge plasma with cryogenic cooling, to relatively high values of populations ($[CO(v)] \sim 10^{-2} - 10^{-3} [CO(v = 0)]$) even for levels with $v \sim 10$-15; examples can be found in [2] and [3]. Such high concentration of excited vibrational molecules significantly influences plasma-chemistry of the considered gas mixture, e.g. various VE-processes (energy transfer from vibrational to electronic states) can be observed. For example, the C2 ($d_3^\Pi$, $e_3^\Pi$ and $C_1^\Pi$) excited states were observed, with excitation imposed by energy transfer processes from vibrational to electronic states [4].

Figure 1 presents electronic C2 states and the first 30 vibrational states of CO($X_1^\Sigma$) molecules coinciding energetically. This coincidence and the resulting resonances enable efficient energy transfer from vibrational CO states to electronic states of C2 (V-E process):

$$CO(v) + C_2 \rightarrow CO(v - n) + C_2^*, \quad (1)$$

where C2$^*$ - is an excited state (see Fig. 1).
Here, we continue our investigations of the influence of vibrationally excited CO molecules on electronically excited C₂ clusters [4], including highly excitations e¹Π, C¹Π, D¹Σ (E>4 eV). The vibrational energy transfer to these electronic states has not yet been reported.

Fig.1 Scheme of the energetically-low levels of the electronic excited states of C₂ cluster and the vibrational states of CO molecule. Arrows shows the transitions related to so called Fox-Herzberg (F-H), Deslandres-d’Azambuja (D-A) and Mulliken (M) systems.

2. Experimental set-up and methodology

A molybdenum-glass discharge tube that is 20 mm in radius and 50 cm in length, nitrogen- or water-cooled, was used in the experiments (see details in [4, 6]). The hollow cylindrical electrodes made 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 20 - 100 mA. Gas flowing set-up (v ~2-5 m/s) was applied. The relative CO concentrations in the applied He-CO-O₂ mixtures were varied in the range of 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) 10⁻¹⁶ V cm².

The spectra in the range of 200 - 3000 nm were registered using the Czerny-Turner monochromator with a diffraction grating of 300 and 600 lines/mm. The recorded spectra allowed determination of the 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). Radiation from the discharge plasma was collected from near axis volume 3 mm in radius for visible and UV and 5 mm in radius for IR spectra. HgCdTl photoresistors cooled by liquid nitrogen and InSb photoresistors were used as light detectors in IR region. The sensitivity of this technique allowed us to measured the population of CO(X¹Σ) vibration levels with vibration level numbers up to ν = 29.

The influence of CO vibrational-excitation on the radiation intensities from electronic excited states of C₂ molecules was studied in a discharge tube with an appropriate resonator (enabling CO-laser generation at levels ν > 6-10 - depending on experimental conditions) installed at both ends of the discharge tube. Laser generation led to a rapid decrease of vibrational levels CO(X, ν) population, for levels close to those participating in laser transition. This means that, by covering one mirror of the laser resonator, it was possible to change significantly the vibrational population of CO. It should be mentioned that the laser output was not very high, usually a few Watts. The plasma parameters,
besides vibrational temperatures (i.e. electron and gas temperature, voltage, pressure, etc.) did not vary significantly during the modulation of the laser radiation. For example, it was found that the gas temperature decreased by only 10 K, when the laser was operating. At the same time, E/N was practically constant.

The dependence of the C₂(X^1Σ) concentration on experimental conditions (i.e. discharge current) was determined from absorption spectra. For C₂(X^1Σ) population the Phillips spectral systems (A^1Π- X^1Σ transition) was used. The spectrum was observed using the CW deuterium lamp. The C₂(D^1Σ) population was determined from emission spectra (Mulliken bands).

The laser generation was accomplished using selective (enabling tuning) and non-selective resonators. The non-selective resonator was formed by a highly reflective gold mirror with the curvature radius of 5 m and a plane mirror having transmission of ~ 30%. The tunable laser cavity consisted of 5% transmitting output mirror with radius of curvature 5 m and a metal grating blazed at 5.4 mkm.

3. Results and discussion

The results of experiments [4] showed that changes of populations of high CO vibrational states enforce changes of radiation intensities from the studied e^3Π_g and C^1Π_g electronic states of the C₂ molecule. This can result from a proposed VE process (1). To clarify the contribution of different vibrational states CO(w) to the process (1), the consecutive changes of CO vibrational energy distribution were imposed by an application of a tunable laser resonator to the discharge tube.

![Fig. 2](image)

*Fig. 2* Relative concentrations of C₂(C^1Π_g) (black circles) and C₂(e^3Π_g) (triangles) electronic states (in arb. units) in the discharge plasma (He + 12% CO +1% O₂, p = 13 Torr, I = 30 mA) as a function of the upper vibration level number for lasing transition (CO(w) → CO(w-1)); the number tuned using a selective resonator

Figure 2 shows the measured relative concentrations of C₂(C^1Π_g) and C₂(e^3Π_g) in the discharge plasma as a function of the upper vibration-level number ‘w’ for lasing transition CO(w) → CO(w-1). The concentration [C₂^*] = 1 corresponds to the value of [C₂^*]_0 with lasing absent. It can be seen (from Fig.2) that the CO vibrational levels, which energetically coincide with considered C₂ states affect the concentration of these states mostly. For the C^1Π_g state they are vibrational levels v ~ 17 – 21 and for the e^3Π_g state, vibrational levels v ~ 21 - 27.

The intensity of D^1Σ_u → X^1Σ radiation was to low and its investigation using set-up equipped with selective resonator was not possible. Therefore non-selective resonator was used to study this radiation. Moreover, Mulliken bands (D^1Σ_u → X^1Σ) were not observed in the water-cooled discharge tube, under all considered here conditions. The D^1Σ Mulliken band was registered only in the case of cryogenic
cooled discharge in He-CO-O₂ (with CO ≥ 9% ) mixture without laser generation. The radiation vanishes when the laser operates. Figure 3 presents the spectrum of Mulliken band (Δv = 0) without laser generation (a) and the same spectral region (without band) with laser turned-on (b).

Figure 4 presents the dependence of Mulliken-band intensity and population of CO(X¹Σ, ν = 25) vibrational state (the vibrational state energetically close to C₂(D¹Σ) electronic state). It is clearly seen that the populations of CO(X¹Σ, ν = 25) and C₂ (D¹Σ) states depend on discharge current likewise.

\[ \text{Fig.3} \text{ Spectrum of Mulliken band (0-0) in cryogenic-cooled discharge, He:CO:O}_2 = 88:11:1 \text{ tur p = 10 Torr (a) without laser generation and (b) with laser generation (P = 5W).} \]

\[ \text{Fig.4} \text{ Intensity of (a) Mulliken band radiation (D¹Σ→X¹Σ) and (b) population of CO(X¹Σ, ν = 25) state as function of discharge current in He:CO:O}_2 = 91.5:8.5:0.03 \text{ mixture, p = 12 Torr} \]

It should be mentioned that the C₂(D¹Σ ) state can be populated by VE process with the participation of CO(X¹Σ, ν ≥ 25) states or by a process of direct electron collision. In the second case when C₂(D¹Σ) state would be excited in direct collisional process:

\[ \text{C}_2(\text{X}) + e \rightarrow \text{C}_2(\text{D¹Σ}) + e, \] (2)

the concentration of the C₂(D¹Σ) state should grow with the discharge current. However, from the observed absorption of Phillips spectral system (A¹Π→X¹Σ) it was found that for mixtures with [CO] ≥ 9% the [C₂(D¹Σ)] concentration decrease with the current (Fig. 4). At the same time, there wasn’t any change of [C₂(X)] concentration observed under various discharge currents applied, at least with the achieved precision of 25%.

The observed Mulliken band in cryogenically cooled discharges in He-CO-O₂ mixtures, which vanish when laser operates, can be explained by VE processes of type (1) with the participation of CO(X¹Σ, ν...
\( \geq 25 \) states. This was confirmed by the correlation of \( \text{CO}(X^1\Sigma, v \geq 25) \) and \( C_2(D^1\Sigma) \) states populations presented in Fig. 4.

In addition, as mentioned above, radiation from Mulliken band was observed only for systems with cryogenic cooling. In the system with water cooling the radiation was not observed. Figure 5 shows that in the case of water cooling vibrational states with \( v \), which can participate in VE process leading to the excitation of \( C_2(D^1\Sigma) \) state, are significantly less populated (5 times or more) than in the case with cryogenic cooling. It was also seen that laser generation lead to one order of magnitude lower populations of these states. These low populations of \( \text{CO}(X^1\Sigma, v \geq 25) \) states explain why the Mulliken band was not observed when laser was operating and in water cooled systems.

![Fig.5 Populations of CO vibrational states in discharge (He:CO:O_2 = 91.5:8.5:0.03 mixture, \( p = 12 \) Torr, \( I = 30 \) mA) in (1,2) cryogenic and (3) water cooled set-up; with (2) laser generation and (1,3) laser turned-off](image)

Let us estimate the rate for the process (1) in the plasma of discharge in He:CO:O_2 = 91.5:8.5:0.03 mixture, \( p = 12 \) Torr, \( I = 30 \) mA. Assuming that VE process constitutes the only channel for \( C_2(D^1\Sigma) \)-state excitation, the steady-state balance equation assumes the following form

\[
\Gamma = [C_2]\cdot[\text{CO}(v \geq 25)]\cdot k_{VE} = [C_2(D^1\Sigma)]\cdot A(D^1\Sigma), \quad (3)
\]

where \( A(D^1\Sigma) \) is the probability of spontaneous emission for \( C_2(D^1\Sigma) \)-state [5]. The rate \( \Gamma \) determined from the band intensity was equal to \( 10^{12} \) cm\(^{-3}\)s\(^{-1}\). The population of \([\text{CO}(v = 25)]\) state was determined from IR intensities of \( \text{CO}(v) \) spontaneous emission and under considered conditions was \( \sim 3.4\cdot10^{13} \) cm\(^{-3}\); \([C_2] \sim 3\cdot10^{12} \) cm\(^{-3}\). Finally, the rate constant for VE process is obtained as

\[
\text{CO}(v \geq 25) + C_2 \rightarrow \text{CO}(v-25) + C_2(D^1\Sigma)
\]

\( k_{VE} \sim 10^{-14} \) cm\(^3\)/s.

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