

Vibrational relaxation of highly excited CO molecules on CO₂ molecules in the active medium of a CO laser

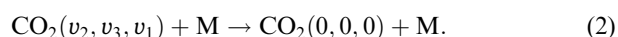
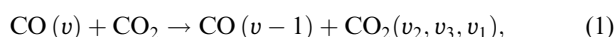
G.M. Grigorian, I.V. Kochetov

Abstract. The stationary vibrational distribution functions (VDFs) of CO molecules are measured in the axial region of a glow discharge in a glass tube at different concentrations of CO₂ molecules. The relaxation constants of CO(*v*) molecules in excited vibrational states colliding with CO₂ molecules are estimated for high vibrational levels with $v = 17 - 29$ by comparing experimental and calculated VDFs of CO molecules. Mechanisms explaining large relaxation rates are discussed. The dependence of the emission spectrum of a CO laser on the concentration of CO₂ molecules is studied experimentally.

Keywords: CO laser, vibrational relaxation, vibrational distribution function of CO molecules.

1. Introduction

During plasma-chemical reactions in the active medium of an electric-discharge CO laser, CO₂ molecules are produced. The concentration of these molecules can vary from several and even tens percent (in sealed-off lasers) of the concentration of CO molecules. There is reason to expect that for such high concentrations of CO₂ in the active medium, the vibrational relaxation of CO molecules in collisions with CO₂ molecules can considerably reduce the population of vibrational levels of CO and impair the energy parameters of the CO laser. The rate constants of the vibrational relaxation of CO(*v*) in collisions with CO₂ molecules were measured for $v < 17$ in papers [1–3]. It is known [4] that the diatomic molecules in excited vibrational states relax in collisions with polyatomic molecules at two stages. First the vibrational–vibrational exchange occurs between molecules, and then the intramode vibrational relaxation of the vibrational excitation of a polyatomic molecule takes place:



The rate constants of the vibrational relaxation of CO in collisions with CO₂ measured by different authors are in good agreement with each other. There is no information in the literature on the relaxation rates of CO(*v*) molecules colliding with CO₂ for $v > 17$. Papers [5–7] devoted to the study of the effect of CO₂ molecules on the operation of a CO laser report rather contradictory data on the admissible concentration of CO₂ molecules in the active medium of the CO laser. Thus, in [5] a considerable decrease in the output power of the CO laser was observed already after the addition of CO₂ in the amount ~ 0.01 [CO], whereas in [6, 7] it was reported that the operation of the CO laser was deteriorated only at considerably higher concentrations of CO₂ molecules ($[\text{CO}_2] > (0.1 - 0.2)[\text{CO}]$).

The aim of this paper is to study experimentally and theoretically the influence of controllable additions of carbon dioxide on the population of the vibrational levels of CO molecules and to investigate experimentally the effect of CO₂ on the spectral and energy parameters of an electric-discharge CO laser.

2. Experimental

Experiments were performed on the setup similar to that described in [8]. We used molybdenum glass discharge tubes of diameter 1.5–2.2 cm that were cooled by running water or liquid nitrogen. The length of the dc discharge region was 50–65 cm. Studies were carried out in the He–CO–O₂ (in the liquid-nitrogen continuous-flow cooling regime) and He–CO–Xe (in the sealed-off water cooling regime) mixtures. The concentration of CO molecules in the mixtures was 4%–12% and the concentration of Xe was 5%–12%. The total gas pressure in a discharge tube was varied from 5 to 20 Torr and the discharge current was 20–80 mA. The gas mixtures used in experiments were preliminarily carefully purified by using a system of traps with silica gel and zeolite.

The experimental setup allowed the addition of CO₂ into a gas mixture in a controllable way. Measurements were performed under conditions when the concentration of other plasma-chemical products was low and they could not noticeably affect the population of vibrational levels. The additional production of CO₂ molecules in plasma-chemical reactions under our conditions did not exceed fractions of percent [7, 9], which is noticeably smaller than the concentration of the added CO₂. The concentration of

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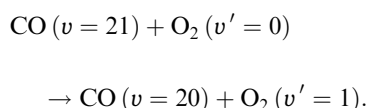
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oxygen atoms was lower than 10^{13} cm^{-3} , while the rate constant of relaxation of vibrationally excited CO molecules in collisions with oxygen atoms was $3.4 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ [10]. The relaxation time of these molecules in collisions with O atoms is noticeably larger than that in collisions with CO_2 molecules. The rates of the VV exchange between high vibrational levels of CO and vibrational levels of O_2 were measured in [3]. For CO ($v = 13$), the rate constant is $4 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$. The resonance appears upon the exchange



Because it is unlikely that the resonance exchange constant can noticeably exceed $10^{-12} \text{ cm}^3 \text{ s}^{-1}$ and that the concentration of O_2 is 0.08 %, this process can be neglected.

The laser could operate in the continuous-flow or sealed-off regimes. Because CO and CO_2 molecules could disappear and form in plasma-chemical reactions, it was necessary to control their concentration during experiments. The concentrations of CO and CO_2 molecules in the active medium were measured with a time-of-flight mass spectrometer and from the IR absorption spectra in the region from 4.5 to 5 μm . Gas samples were taken from the cathode region in the discharge tube (at a distance of ~ 2 cm from the cathode). Gas was supplied either directly into a mass spectrometer or into a special vessel, which was then disconnected from the system to analyse the gas [8]. Mass-spectroscopic and IR absorption measurements gave close results.

The populations of vibrational levels of CO molecules were measured by the emission at their first and second vibrational overtones [11, 12]. The spontaneous IR emission of vibrational overtones from the axial region (~ 0.3 cm) of the positive discharge column selected with an aperture and projected at the entrance slit of a monochromator was recorded in experiments. The gas temperature at the discharge-tube axis and its radial profile were determined from the rotational structure of the Angström system bands of the CO molecule.

The electric field strength E in the discharge was determined by measuring the voltage drop across the discharge gap in near-electrode regions. The near-electrode voltage drops were determined by measuring the voltage between electrodes for different lengths of the discharge region. Typical values of near-electrode voltage drops were 350–400 V. The experimental values of the reduced electric field strength E/N (where N is the mixture concentration) were $(1.4 - 2.2) \times 10^{-16}$ and $(0.9 - 1.5) \times 10^{-16} \text{ V cm}^2$ for the He–CO– O_2 and He–CO–Xe mixtures, respectively.

In experiments in the sealed-off regime, the laser resonator was formed by a highly reflecting gold-coated mirror with the radius of curvature 5 m and a plane output mirror with a multilayer dielectric coating and a reflectivity of 95 %. In the continuous-flow regime (the working mixture flew in the discharge tube at the rate of 3–5 m s^{-1}), the plano-spherical resonator was formed by a gold-coated highly reflecting mirror with the radius of curvature 5 m and a plane mirror with a 0.15-cm hole at the centre. The laser emission spectrum was recorded with a 200-lines mm^{-1} grating monochromator.

3. Numerical model

We considered in the numerical model the axial region in a discharge tube. The reduced electric field E/N and the translational temperature of the gas were specified according to their experimental values. The discharge power density on the axis was determined from the measured discharge current by assuming that the distribution of the electron concentration over the tube radius is described by the Bessel function. The electron drift velocity, a part of energy spent to excite molecular vibrations, and excitation rate constants were determined by solving numerically the stationary Boltzmann equation for the electron energy distribution function (EEDF) in the two-term approximation. It was assumed that the EEDF is determined by the local value of E/N . The Boltzmann equation took into account the electron energy loss in elastic collisions of electrons with atoms and molecules, excitation of rotational and vibrational levels of molecules, excitation of electron levels and ionisation of atoms and molecules. Collisions of electrons with CO molecules in excited vibrational states also were taken into account. The cross sections for scattering by atoms, molecules and vibrationally excited CO molecules used in calculations are presented in paper [8].

The Boltzmann equation for the EEDF was solved taking into account the state-to-state of the vibrational kinetics of CO molecules (50 vibrational levels). This allowed us to calculate the change in the fraction of power spent to excite vibrational levels with increasing the vibrational temperature. The kinetic equations took into account the excitation of vibrational levels by plasma electrons, the vibrational–vibrational exchange between CO molecules (VV exchange), the vibrational–translational relaxation (VT relaxation) on the components of the initial mixture, the spontaneous emission of vibrationally excited CO molecules and their relaxation on the discharge tube wall. We used in calculations the probability of heterogeneous relaxation of $\text{CO}(v)$ molecules on the discharge tube wall $\epsilon = 6 \times 10^{-2}$ [13], which was independent of the vibrational level number v . It was assumed that the diffusion coefficient of $\text{CO}(v)$ molecules was independent of v and the energy of a CO molecule decreased by one vibrational quantum in each collision with the wall. The theoretical model used in calculations is described in more detail in [8].

The rate constants for relaxation of CO molecules ($v < 17$) on CO_2 molecules are taken from paper [1], where the total relaxation rates of the vibrational energy were measured without specifying the vibrational state of CO_2 molecules after relaxation. It was assumed in calculations that the vibrational quantum number of the CO molecule decreases by unity and the energy transferred from the vibrational levels of CO molecules to the vibrational levels of CO_2 molecules transforms to heat.

4. Discussion of the results

Measurements of the vibrational distribution function (VDF) in the active medium of a laser (in the absence of lasing) showed that the addition of CO_2 to the working mixture considerably reduced the population of high vibrational levels of the CO molecule, whereas the low vibrational levels were far less sensitive to the presence of CO_2 in the discharge. Note that the presence of CO_2

molecules ($[\text{CO}_2] < 0.3[\text{CO}]$) did not virtually affect the reduced electric field E/N and the translational temperature of the gas. Figure 1 presents VDFs of CO molecules at

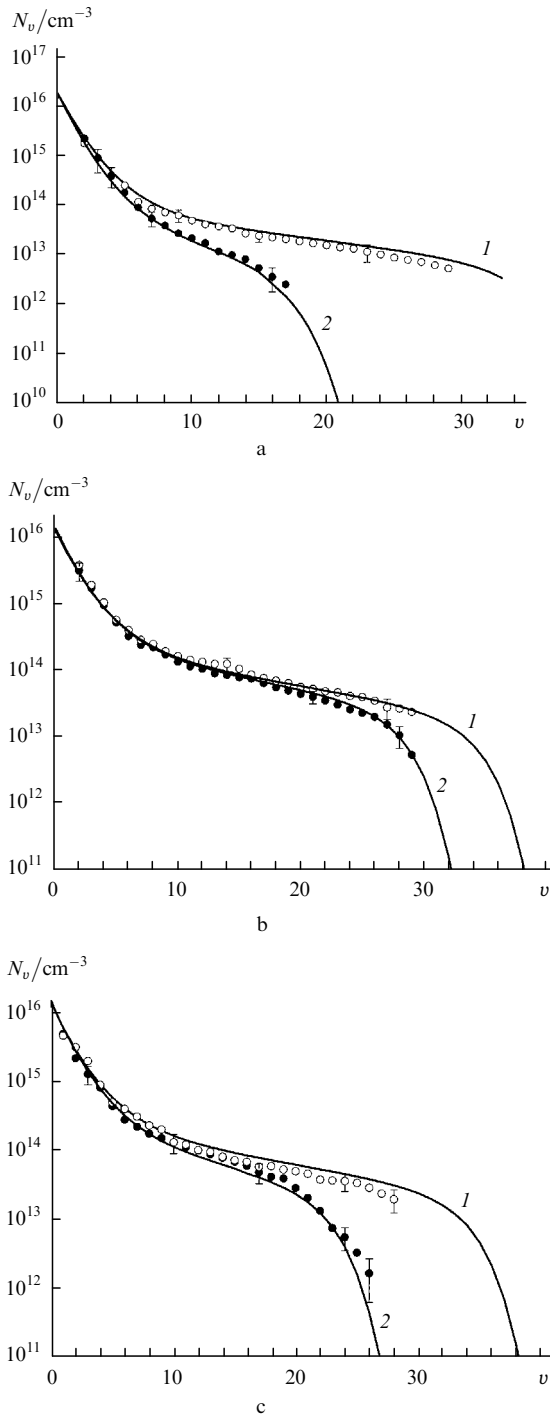


Figure 1. Vibrational distribution functions of CO molecules for the CO laser operating on the continuous-flow regime (a) and in the regime without gas flow (b, c) for $[\text{CO}_2] = 0$ ($[\text{CO}_2] < 0.003[\text{CO}]$) in experiments (1, \circ); $0.3[\text{CO}]$ (a, c), and $0.1[\text{CO}]$ (b) (2, \bullet). Experimental conditions: the mixture pressure $p = 12.3$ Torr, the mixture temperature $T = 310$ K, the discharge current $I = 40$ mA, the discharge tube radius $R = 1.1$ cm, He : CO : O₂ = 91 : 8.92 : 0.08 (a); $p = 16$ Torr, $T = 370$ K, $I = 30$ mA, $R = 0.75$ cm, He : CO : Xe = 73 : 7.5 : 19.5 (b); $p = 15$ Torr, $T = 400$ K, $I = 30$ mA, $R = 0.75$ cm, He : CO : Xe = 73 : 7.5 : 19.5 (c). Circles are experimental data, curves are the results of numerical simulation.

different concentrations of CO₂ for a laser operating in the continuous-flow regime and in the regime without gas flow. One can see that, compared to the population of the vibrational levels of CO for $[\text{CO}_2] = 0$, the population of the vibrational levels of CO for $v = 29$ decreases five times for $[\text{CO}_2] = 0.1[\text{CO}]$ (Fig. 1b) and approximately ten times for $v = 17$ (Fig. 1a) and twenty times for $v = 26$ (Fig. 1c) when $[\text{CO}_2] = 0.3[\text{CO}]$, whereas the concentration of CO molecules on the lower ($v < 5$) vibrational levels changes only slightly. When the VDF of CO molecules was measured without the addition of CO₂ molecules to the working-mixture, the concentration of CO₂ produced in plasma-chemical reactions did not exceed 0.3% of the CO concentration.

As follows from our calculations, such a concentration of CO₂ does not affect the VDF of CO molecules. The calculated value of the total relaxation constant for vibrational states of CO molecules for $v > 16$ depends on the assumed relaxation mechanism. Below, we consider the case when the vibrational quantum number of the CO(v) molecule decreases by unity and it is assumed that the energy transferred to the vibrational states of the CO₂ molecule transforms to heat.

We estimated the relaxation rate constants for vibrational levels with $v > 16$ by comparing the measured and calculated VDFs. The relaxation constants were described by the function $K_v = a_0 \exp(v/b_0)$ of two fitting parameters a_0 and b_0 . The parameters a_0 and b_0 were restricted by the additional condition according to which the constants calculated for $v = 16$ should coincide with those measured in [1]. The values of K_v for $v = 1 - 16$ were taken from experiments [1]. The relaxation constants for $v > 16$ obtained in this way are presented in Fig. 2 [straight line (1)]. Good agreement between experimental VDFs of CO molecules with VDFs calculated for the concentrations of CO₂ molecules equal to $0.1[\text{CO}]$ (Fig. 1b) and $0.3[\text{CO}]$ (Figs 1a, c) for different gas mixtures with added O₂ (Fig. 1a) and Xe (Figs 1b, c) demonstrates the reliability of the determined relaxation constants.

A large value of K_v and its noticeable increase with increasing v is explained, in our opinion, by the increase in the number of possible nearly resonance transitions in

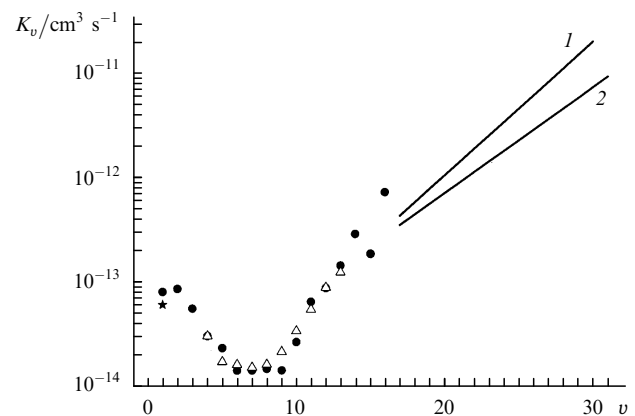
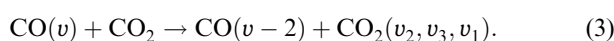


Figure 2. Dependences of the relaxation rate constant for CO molecules colliding with CO₂ molecules on v . Points are the experimental data from [1] (\bullet), [2] (\star), and [3] (\triangle). The straight lines are calculated in this paper by assuming that $\Delta v = 1$ ($a_0 = 2.8 \times 10^{-15}$, $b_0 = 3.4$) (1) and $\Delta v = 2$ ($a_0 = 6.5 \times 10^{-15}$, $b_0 = 4.3$) (2).

CO ($v \rightarrow v-1$) and CO₂ ($0, 0, 0 \rightarrow v_2, v_3, v_1$) molecules. While for $v < 6$ the vibrational energy of CO (v) molecules is transferred predominantly to the vibrational levels of the asymmetric CO₂ ($0, 0, v_1$) mode, due to a noticeable decrease in a vibrational quantum of CO with increasing v , the energy transfer to other modes of CO₂ becomes more energetically advantageous. In particular, the vibrational energy is transferred to a symmetric mode, which in turn is in the Fermi resonance with the deformation mode, and also with combination modes. As for the asymmetric mode of CO₂, for the vibrational levels of CO in the region of $v = 35$, already two-photon vibrational transitions in CO are resonant with this mode.

To estimate relaxation constants taking into account only two-quantum transitions from high CO levels, we calculated the VDF by assuming that for levels with $v > 16$ two vibrational quanta of the CO molecule transfer to the CO₂ molecule:



Straight line (2) in Fig. 2 shows the dependence of the relaxation constant on v calculated by assuming that the relaxation of CO molecules with $v > 16$ involves the transfer of two vibrational quanta.

The calculations of the VV'-exchange rate constants for CO and CO₂ reported in the literature have been performed only for the case of energy transfer to the first vibrational level of the asymmetric CO₂ mode [the CO ($v=1$) + CO₂ → CO ($v=0$) + CO₂ ($0, 0, 1$) transition]. Calculations for other modes are absent. The estimates of the rate constants and even qualitative consideration of their dependences on the vibrational level number of CO molecules is very complicated because a triatomic CO₂ molecule is a very complex vibrational system with different modes coupled with each other due to anharmonicity, the Coriolis interaction, Fermi resonances, etc. The degree of influence of these interactions on the rate constants it is not clear now.

It should not be ruled out that the increase in the vibrational relaxation constants of CO(v) in collisions with CO₂ with increasing the vibrational level number v may be explained by the formation of a long-lived CO-CO₂ complex; the formation probability of this complex should increase with increasing the degree of vibrational excitation of colliding molecules [14].

The measurements of the laser emission spectra showed that, as the concentration of CO₂ molecules in the working mixture increased, the spectral emission range narrowed down due to the shift of the long-wavelength boundary to the shorter wavelengths (corresponding to transitions between lower vibrational levels). This is explained by a noticeable increase in K_v with increasing v , which reduces the emission intensity from the upper vibrational levels of CO. As a result, the degree of influence of CO₂ on the emission parameters of the CO laser proves to be dependent not only on the CO₂ concentration in the active medium but also on particular experimental conditions (mainly on the translational gas temperature and excitation power) determining the VDF form and the numbers of vibrational levels involved in lasing. Therefore, in cases when the output power of a CO laser is mainly determined by transitions from the lower vibrational levels ($v < 7-10$) (which is typical for operation with cryogenic cooling [6, 7]), the influence of CO₂ on the output power is considerably weaker than under conditions when the laser spectrum is

determined by transitions from higher vibrational levels (in particular, in sealed-off CO lasers [5]).

Figure 3 shows the dependences of the intensity of vibrational transition lines of the CO laser on the number of the upper vibrational transition for different CO₂ concentrations in a mixture. The laser resonator had a gold plated mirror with the radius of curvature of 5 m and a plane output mirror with a multilayer dielectric coating and the reflectance 95%. Lasing occurred simultaneously at several (3–5) rotational transitions within one vibrational transition. Because of this the lasing intensity on a vibrational transition was determined as a sum of intensities at all the rotational transitions corresponding to this vibrational transition. For each v , the laser line intensity at the concentration $[\text{CO}_2] = 0.003[\text{CO}]$ was set equal to unity. In this case, the laser efficiency was 17%.

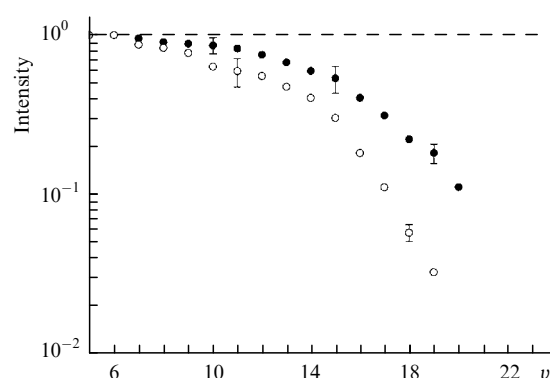


Figure 3. Normalised output intensities of the CO laser as functions of the number of the upper vibrational transition for $[\text{CO}_2] = 0.1[\text{CO}]$ (●) and $0.17[\text{CO}]$ (○); $I = 40$ mA, $p = 16$ Torr, $R = 0.75$ cm, He : CO : Xe = 12 : 1 : 3.

It was found experimentally in [5, 15] that the spectral range of sealed-off CO lasers gradually narrowed down during their prolonged operation: the long-wavelength boundary of the laser spectrum shifted to the blue, while its short-wavelength boundary remained unchanged. Based on the emission spectra of the CO laser obtained at different CO₂ concentrations obtained in our experiments, this fact can be explained by the influence of the relaxation of CO molecules in collisions with CO₂ molecules, whose concentration gradually increases with time during the operation of the sealed-off CO laser.

5. Conclusions

The relaxation constants of vibrationally excited CO(v) molecules colliding with CO₂ molecules have been estimated for the first time for high vibrational levels with $v = 17-29$ by comparing the experimental and calculated VDFs of CO molecules. The increase in the relaxation rate constants with increasing the vibrational level number and their large values for $v = 29$ have been explained by the increase in the number of vibrational transitions in CO₂ molecule resonant with the vibrational transition in the CO molecule.

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