

Dissociation of carbon dioxide in pulsed plasma at high electric fields: role of energy exchange with electronically excited species.

Georgy Pokrovskiy

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Dissociation of carbon dioxide in pulsed plasma at high electric fields: role of energy exchange with electronically excited species

Thèse de doctorat de l'Institut Polytechnique de Paris préparée à l'École Polytechnique

École doctorale n°626 (École doctorale de l'Institut Polytechnique de Paris (EDIPP)) Spécialité de doctorat : Optique, Lasers et Plasma

Thèse présentée et soutenue à Palaiseau, le 07/12/2021, par

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Георгий

Résumé de thèse

La thèse est dédiée aux études de la dissociation du dioxyde de carbon aux pressions modérées dans un plasma nanosecond pulsé aux conditions de champ électrique réduit et d'énergie spécifique élevés. L'objectif principal de la recherche a été de se concentrer sur un tel régime de la décharge, qui facilite la domination de l'excitation des degrés de liberté électroniques des espèces actives par rapport aux vibrations.

Les expériences ont été réalisées dans deux types différents des capillaires – les capillaires dits "fin" et "FTIR". Il a été montré que la décharge se développe comme une onde d'ionisation stable (FIW) en CO_2 dans tous les deux types de capillaires. Tout le gaz traversant le réacteur a été traitée par trois impulsions haute tension séparées par 250 ns. Les caracteristiques principales de la décharge telles que le courant électrique, le champ électrique réduit et le dépôt spécifique de l'énergie ont été enregistrées pendant les trois impulsions. La densité électronique a été mesurée dans le capillaire fin. La densité électronique pic s'est avérée être de 2×10^{15} cm⁻³ à première impulsion haute tension. Cette valeur correspond à un degré d'ionisation de 0.5% à la pression de 15.5 mbar.

Puisqu'il était techniquement possible d'enregistrer le profil du champ électrique réduit E/n dans le capillaire fin en fonction du temps, ces mesures précises ont été effectuées. Les valeurs du champ électrique dans le capillaire fin étaient d'environ 1000 Td dans FIW et 300 Td derrière son front. Le dépôt d'énergie spécifique s'est avérée être de ≈ 1.5 eV/particule. Quant au capillaire FTIR, il n'a été possible que d'estimer le champs électrique réduit et le dépôt d'énergie spécifique. Toutefois, il peut être conclu que les deux valeurs sont deux fois plus élevées par rapport au capillaire fin.

Des mesures de valeurs du taux de dissociation α et son efficacité η à leur état stationnaire ont été effectuées à la sortie du capillaire FTIR. FTIR a été utilisé pour les mesures. Les valeurs de α et η étaient proches de 20 % au regime basse cadence des impulsions. Lorsque la cadence augmentait, α atteignait un seuil de 92 %, η du processus était d'environ 8 %.

La spectroscopie d'émission (OES) n'a révélé aucune différence qualitative entre les spectres d'émission acquis dans chacun des capillaires. Les spectres d'émission démontrent une présence abondante des états de CO_2^+ et C électroniquemment excités. Ceux-ci se trouvent entre 18 et 25 eV par rapport à l'état fondamental du CO_2 . Il a été montré que l'excitation des dégres de liberté électroniques domine les degrés de liberté vibrationnels et fournit un taux élevé de la conversion du CO_2 pendant le développement de la décharge. La dissociation du CO en C et O a été aussi remarquée.

Les mesures de profil radial de la densité électronique par ICCD au milieu de la décharge ont été réalisées. Il a été montré que le profil atteint un maximum dans l'axe du capillaire et décroît de la façon monotone en direction des parois. D'ailleurs, le comportement du profil ne changeait pas pendant les impulsions haute tension ni entre elles.

La température du gaz a été enregistrée par OES de l'azote qui avait été adjoint en petites quantités. La pertinence de la température rotationnelle de l'azote pour la température du gaz a été justifiée. Les mesures de la température ont été effectuées dans les deux capillaires. La température au capillaire FTIR a été égale à 2000 K après la troisième impulsion. Le capillaire fin a été chauffé jusqu'au 1100 K. Le phénomène d'échauffement rapide du CO_2 a donc été confirmé.

La modélisation 0D de la décharge a aussi été faite. Elle a montré un bon accord entre les résultats expérimentaux et calculés. Il a été montré que la dynamique temporelle des ions CO_2^+ , O_2^+ and $C_2O_4^+$ et des états électroniques $CO(a^3\Pi)$, $O(^1D, ^1S)$ définit les processus cinétiques plus important ainsi que l'échauffement du gaz pendant et entre les impulsions.

Abstract

The Thesis is devoted to study of dissociation of carbon dioxide at moderate pressure in nanosecond capillary pulsed discharges at high levels of reduced electric field and specific deposited energy. The main purpose of the research was to focus on such a discharge regime that facilitates domination of excitation of electronic degrees of freedom of active species over vibrational ones.

The experimental studies have been done in two different types of capillaries – the so called 'thin' and FTIR' capillaries. It has been shown that the discharge develops as a stable fast ionization wave (FIW) in CO₂ in both types of capillaries. Any portion of gas was being treated by train of three high voltage pulses separated by 250 ns in each experiment. The main discharge characteristics such as electric current, reduced electric field and specific deposited energy have been measured in all three pulses. The electron density as a function of time has been measured in the thin capillary. The peak electron density was found to be 2×10^{15} cm⁻³ in the first high voltage pulse. This value corresponds to the ionization degree of 0.5% at the pressure of 15.5 mbar.

Since it was technically possible to obtain time-resolved profile of the longitudinal reduced electric field E/n in the thin capillary, measurements of E/n as a function of time have been done in it. The values of the E/n in the thin capillary were about 1000 Td in the FIW and 300 Td behind the front of the FIW. Specific deposited energy was found to be about 1.5eV/particle. As for the FTIR capillary, it was only possible to estimate E/n and specific deposited energy. It can be still concluded that both values are two times higher than in the thin capillary.

Measurements of steady-state values of the dissociation fraction α and the energy efficiency of the dissociation η have been done in the FTIR capillary in effluent gas. The FTIR has been used for the measurements. The values of α and η were around 20 % at low frequency pulse regime. When the pulse frequency increased, the α value tended to a saturation threshold of 92 %, η of the process was around 8 %.

Optical emission spectroscopy (OES) in both thin and FTIR capillaries hasn't revealed any qualitative difference between the acquired spectra. The emission spectra demonstrate an abundant presence of electronically excited states of CO_2^+ ion and C atom lying between 18 and 25 eV with respect to the ground state of CO_2 . It has been shown that excitation of electronic degrees of freedom does dominate over vibrational ones and supplies high values of dissociation fraction of CO_2 during the discharge. Presence of dissociation of CO onto C and O has been noticed.

Measurements of radial profile of the electron density by ICCD imaging in the middle of the discharge have been done. The profile has been shown to have a maximum in the axis of the capillary and to monotonously decrease with respect to direction of walls. The behaviour of the profile didn't change within the high voltage pulses and between them.

Gas temperature has been measured by OES of second positive system of nitrogen which has been added to CO_2 as a small admixture. The relevance of rotational temperature of nitrogen and gas temperature of the mixture has been justified. TThe measurements of temperature have been done both in both types of capillaries. The temperature in FTIR capillary was equal to 2000 K after the third pulse. As for the thin capillary, it has been heated up to 1100 K after the third pulse. The phenomenon of fast heating of CO_2 in a nanosecond discharge has been therefore confirmed.

Zero-dimensional numerical modeling of the discharge has been also done. It has shown a good agreement between experimental and calculated results. It has been shown that temporal dynamics of CO_2^+ , O_2^+ and $C_2O_4^+$ ions as well as electronic states $CO(a^3\Pi)$, $O(^1D, {}^1S)$ defines the most important kinetic processes and heating of gas during and between the pulses.

Chapter 1

Literature review

1.1 State of the art of conversion of carbon dioxide

1.1.1 Actual state of the CO₂ problem

Carbon dioxide is one of the main gases presenting in the atmosphere of our planet. Since the beginning of the industrial revolution in the middle of XIX century the antropogenic outcomes of carbon dioxide increased from 250 ppm in the very beginning of the industrial revolution up to 400 ppm in 2014 [1, 2]. The influence of the increase of the antropogenic emission of CO_2 on the greenhouse effect is significant. Nevertheless, the idea that carbon dioxide is a source of secondary fuel rather than a pollutant waste has been acknowledged by scientific community and is developing nowadays. It is considered to be feasible to use different ways of conversion of carbon dioxide combined with other gases like water vapor or hydrogen back to the so called value-added chemicals such as methane and other hydrocarbons and thus to make possible the secondary use of fuels [3, 4]. The concept is illustrated in the Figure 1.1.

Consequently, the extraction and use of fossil fuels could be decreased significantly and the ecological situation could be improved. The problem of conversion of one of the main greenhouse onto value-added chemicals such as CO, CH_4 and oxygen [1, 3] which could act as fuels and an oxidizer is therefore an actual scientific challenge of our time.

An alternative opinion on the problem of pollution of atmosphere of Earth by car-



Figure 1.1 – The concept of waste-free use of fuels with the consequent recycling of carbon dioxide onto value-added chemicals such as methane and other combustible hydrocarbons. The picture is taken from [1].

bon dioxide is suggested in [5]. The idea of the opinion consists on obsolescence of methods which are used for calculation of heat flux caused by carbon dioxide emission. In fact, the calculation of heat flux change used in Paris treaty is based on CO₂ concentration change only and doesn't take into account other molecules like H₂O whose spectral bands overlap with CO₂ spectral bands. Disregard of this fact leads to overestimation of antropogenic global temperature change in 5 times $(\Delta T = 1.5 \text{ K} \text{ instead of } \Delta T = 0.3 \text{ K}).$

On the other hand, the XXI century became the era of space discoveries. For instance, much attention is paid to the exploration and future development of Mars whose atmosphere consists on 96% of carbon dioxide (with approximately 2% Ar and 2% N₂ [6]) and several space missions from different countries are in progress. Currently, there are three automatic stations (rovers) exploring the surface of Mars: "Curiosity" (since 2012, August 6), "InSight" (since 2018, November 26) and "Perseverance" (since 2021, February 19). There are several space projects of a human mission to Mars planned for the next 10-20 years and the question of conversion of the Martian atmosphere to oxygen available for breathing and which could act as an oxidizer for the fuel combustion is of current interest. As for "Perseverance" rover which landed on Mars in the beginning of 2021, a prototype of such a reactor named MOXIE (Mars Oxygen In-Situ Resource Utilization Experiment) has been launched and delivered to the Martian surface with the rover. The MOXIE project has been developed not only for the proof-of-concept that it is possible to supply future Martian astronauts with oxygen necessary to breath but also to understand how to produce fuel and oxidizer which are essential for the delivery of rockets with a sample of Martian soil back to the Earth. The MOXIE reactor is currently (March 2021) operating and is capable to produce approximately 10 grams of oxygen per hour [7]. The MOXIE reactor is based on the principle of the so called solid oxide electrolyzer cell (SOEC) but there are several other ways of conversion of carbon dioxide onto value-added chemicals such as thermal dissociation, photo-electrolysis, bio-fixation or plasma-assisted conversion whose detailed analysis can be found in [1, 3, 8]. The basic principles of the aforementioned mechanisms are described in the next subsection.

1.1.2 Different techniques of CO₂ conversion

As it was mentioned above, there are several techniques of conversion of carbon dioxide and the first one which will be discussed in the current Thesis is the **thermal dissociation** also known as **thermolysis**. It could be noticed that such a mechanism is not very easy to make efficient enough if one take a look at the standard enthalpy of the net reaction of CO_2 conversion [8]:

$$CO_2(g) \longrightarrow CO(g) + \frac{1}{2}O_2(g), \qquad \Delta H^0 = 293 \text{ kJ mol}^{-1}.$$
 (1.1)

It could be seen that a strong thermodynamic barrier has to be overcome in order to make this highly endothermic reaction(1.1) possible. High temperatures are therefore required to shift the thermodynamic equilibrium of the reaction on the right-hand side. [8, 9] report the necessary values of temperature to be at least 2000 K. This fact can be clearly seen in the Figure 1.2 where the dependence of mole fractions of reactants and products of the reaction on temperature is given. An experiment on fully thermal dissociation of carbon dioxide where a rate of the reaction (1.1) was several times increased at T=1300 K with a corundum tube is reported in [10]. The corundum tube was acting as a catalyst. The dissociation fraction at T=1300 K increased more than 3 times (0.02 % with the catalyst instead of 0.006 % without it). The hypothesized mechanism of the catalysis consisted on two main steps: formation of oxygen vacancies in the metal oxide during the heating and the consequent dissociative adsorption of CO₂ on defective surfaces of the catalyst. Nevertheless, despite the fact that the catalyst significantly increased the



Figure 1.2 – Temperature dependence of the mole fractions of reactants and products of the reaction 1.1. The picture is taken from [10].

dissociation fraction, its value is still relatively low. Hence, either a significant increase of temperature or use of other mechanisms of conversion of carbon dioxide is required.

Another possibility to dissociate CO_2 is its **electrochemical reduction** which is a technique using a direct electric current which makes non-spontaneous redox reactions to pass in the gaseous, aqueous or non-aqueous phase with or without a catalyst [1, 8, 11, 12]. The basic principle of any way of electrochemical conversion of pure carbon dioxide without admixtures is the following. The reaction on the cathode can be written as:

$$CO_2 + 2e^- \longrightarrow CO + O^{2-}.$$
 (1.2)

On its turn, the reaction occurring on the anode can be written as follows:

$$\mathcal{O}^{2-} \longrightarrow \frac{1}{2}\mathcal{O}_2 + 2\mathbf{e}^-, \tag{1.3}$$

which results in the net reaction (1.1) occurring in an electrolyte.

The most common way of electrochemical conversion of pure gaseous CO_2 is the so called solid oxide electrolyzer cell (SOEC). A detailed review on this topic can be found in [13]. The main pecularity of the method is use of a dense porous ionic conductor as an electrolyte. The most wide-spread option of the electrolyte is yttria-stabilized zirconia (YSZ) which becomes a conductor for O^{2-} ions at elevated temperatures (around 1000 K). The SOEC concept has been first proposed in 1970 [14] for *in situ* production of CO and oxygen from the Martian atmosphere. Since the beginning of the XXI century, research groups from different countries are developing their exploratory projects on to Mars. As it was mentioned in the section 1.1.1, the MOXIE reactor [7] launched on Mars in 2021 with the "Perseverance" rover is operating successfully. The MOXIE reactor is based on SOEC principle with use of YSZ as an electrolyte.

The main advantages of the electrochemical way of dissociation of carbon dioxide are its controllability by reaction parameters such as temperature or an electrode potential. The reactors are relatively cheap, can be easily integrated with other sources of sustainable energies and can be used for different functions [1, 13]. On the other hand, as it is mentioned in [13], the SOEC technique has several serious disadvantages such as relatively low efficiency of the dissociation and insufficient activity and stability of possible catalysts. In the case of MOXIE, it is neither possible to operate at atmospheric pressure of Mars (≈ 6 mbar) and preliminary gas compression is required. Item, the necessity to heat the reactor cell to relatively high temperatures entails possible recombination of products of dissociation and other technical challenges of operation.

One more possibility of CO_2 conversion is **photochemical dissociation** [1, 9, 15] which can be also combined with the termochemical approach [16]. A detailed review describing the technique of photochemical dissociation of carbon dioxide can be found in [17]. The technique is based on the solar-activated photocatalytic reduction of carbon dioxide with water at room temperature and atmospheric pressure [15]. Briefly, it is possible to describe the mechanism in the following way. When photons of solar radiation illuminate a surface of the catalyst (most generally, TiO_2), they can excite electron-hole pairs in the latter. The electrons are excited in the conduction band of the catalyst and can furthermore reduce CO_2 molecules into CO_2 CH_4 or other fuels. In their turn, the holes excited to the valence band of the catalyst can oxidize water into oxygen. The main advantages of this mechanism are its adaptability for different functions and a relatively low cost. Nevertheless, there are many requirements to be met for a successful operation of a setup. First of all, the electronic band gap of the catalyst material must be low enough for efficient photon collecting from the solar radiation and at the same time high enough such that the excited electrons could have sufficient energy to dissociate an H₂O molecule. Second, the band edges must fit the water electrolysis redox potentials, and the photoelectrode must be resistant to corrosion in water. Several developments of the technique such as doping of TiO_2 by metals or metal oxides can increase [15] the efficiency of the mechanism but still, all aforementioned limitations constrain the efficiency of photochemical conversion of carbon dioxide.

The most 'conventional' and 'well-known' mechanism of **biochemical conversion** of carbon dioxide is photosynthesis. However, mass cultivation of plants directly for processing of carbon dioxide by photosynthesis is difficult due to the fact that a significant part of the arable land is used for the production of crops. Use of microalgae [1, 17, 18] which need only sunlight and freely available raw resources such as freshwater, saltwater or wastewater where the microalgae can be grown might be a reasonable and relatively efficient compromise. The microalgae can hence contribute to the solution of the problem of water overuse. Nevertheless, there is no any common technology which colud be used directly for biological conversion of carbon dioxide by microalgues. Currently, the costs must be shared by several industries such as food, pharmaceuticals and cosmetics industry.

Several approaches to conversion of CO_2 have been briefly reviewed in the current subsection. As it could be seen, all them have their scopes and can be applied for different functions. All them have advantages and disadvantages. The next subsections are devoted to the review of main principles and achievements in the domain of plasma-assisted conversion of carbon dioxide which is the topic of the current Thesis. As it will be seen further, plasma-assisted conversion of carbon dioxide is not an exception and has its own drawbacks and points of superiority.

1.1.3 Theoretical aspects of conversion of carbon dioxide in low temperature plasma

Generally speaking, plasma is a state of matter where the behaviour of electrons, ions and neutral particles is different. Moreover, different internal degrees of freedom of ions and neutral particles might be excited at different stages and this difference depends on many conditions such as gas composition, pressure, electric field etc. This variety entails the fact that plasma in general must be described by several separate temperatures such as temperature of electrons (T_e) , rotational temperature (T_{rot}) , vibrational temperature (T_{vib}) , temperature of ions (T_i) and temperature of neutral gas (T_0) [19, 20, 21]. If the temperature of electrons is equal to the temperature of ions and neutral gas, the plasma is called *thermal* or *equilibrium* plasma since such plasma fits the conditions of thermodynamic equilibrium. In the case of strong inequality of temperatures $(T_e \gg T_{ion} \ge T_0)$ plasma is called *non-thermal* plasma since no thermodynamic equilibrium is established. Another way of classification of plasma is its ionization degree which is defined as the ratio of electron density and total number density of particles:

$$\alpha = \frac{n_e}{n_{total}}.$$
(1.4)

If $\alpha \geq 1$, plasma is classified as *strongly ionized*. In the other limit case, when $\alpha \ll 1$, plasma is called *weakly ionized*. Hereinafter, the case of non-thermal weakly ionized plasma (in most cases, $\alpha < 10^{-2}$) where the average kinetic energy of electrons doesn't exceed significantly the first ionization potential of the gas will be called *low temperature* or *cold* plasma. It is conversion of carbon dioxide by low temperature plasma which is the object of the current literature review and the Thesis.

Dissociation of a CO_2 molecule is a strongly endothermic process. Decomposition of a molecule starts with the following process:

$$CO_2 \longrightarrow CO + O$$
 $\Delta H = 5.5 \text{ eV/mol.}$ (1.5)

Then, the formed O atom can recombine with another O atom or with a CO_2 molecule. According to the section 1.1, the total entalpy required for decomposition of one CO_2 molecule on carbon monoxide and 'a half' of molecular oxygen is equal to E=2.9 eV/mol. Therefore, if the dissociation fraction is defined as:

$$\alpha = \frac{[\text{CO}]}{[\text{CO}] + [\text{CO}_2]},\tag{1.6}$$

the energy efficiency of CO_2 decomposition can be written as:

$$\eta = \alpha \frac{E}{w}.\tag{1.7}$$

Here, E=2.9 eV/mol corresponds to the minimal average energy required for formation of carbon monoxide and molecular oxygen, w is the energy deposited into plasma per one particle. As it will be evident now and further, the counterbalance between dissociation fraction and energy efficiency is an object of essential matter.

There are several mechanisms of conversion of carbon dioxide in low temperature plasma and the first one which will be the object of the discussion is conversion of CO₂ via excitation of the vibrational degrees of freedom. A molecule of carbon dioxide is a triatomic one and it has three different vibrational modes: asymmetric stretching ($\omega = 2396.32 \text{ cm}^{-1}$), symmetric stretching ($\omega = 1354.31 \text{ cm}^{-1}$) and double degenerate bending ($\omega = 672.85 \text{ cm}^{-1}$) [22, 23, 24]. All additional constants such as coefficients of anharmonicity of vibrations are given in [22]. A detailed approach to all vibrational modes of CO_2 and, in particular, to vibrational kinetics of CO_2 will be given in Chapter 9 but it is important to notice that the asymmetric mode plays the most essential role in the vibrational dissociation of carbon dioxide [20].

The Figure 1.3 illustrates the configuration of electronic terms of a CO_2 molecule. It should be noted that since the molecule has 3 atoms, the Figure cannot precisely represent the configuration of terms and the curves should be interpreted as projections of 3D potential surfaces. Nevertheless, this illustrative sketch allows to have an idea about relative position of terms and energy thresholds of various chemical processes.

The vibrational pumping has several steps [25, 26]. First, energy of the applied electric field is transferred to kinetic energy of electrons which reaches 1-3 eV. The electrons accelerated by the electric field transfer their energy to the lower vibrational levels of CO₂ molecules which collide with each other and exchange by vibrational quanta (V-V exchange). Therefore, the vibrationally excited molecules can reach the dissociation threshold (5.5 eV) and decompose onto $CO(X^1\Sigma^+)$ and $O(^{3}P)$ via the $CO_2(^{3}B_2)$ electronic state. The process is illustrated in the Figure 1.3 (orange arrow).

$$\operatorname{CO}_2(^1\Sigma^+, v) \longrightarrow \operatorname{CO}_2(^3B_2) \longrightarrow \operatorname{CO}(^1\Sigma^+) + \operatorname{O}(^3P)$$
 (1.8)

Such process is called *vibrational pumping* and it is the process with the maximal energy efficiency since the energy of electrons is transformed directly to vibrational energy of molecules and not to their translational and rotational energy or energy of their electronic excitation. Moreover, the vibrational pumping is the process which requires the least amount of energy deposited into plasma. However, the gas heating can make this process more difficult for the reason of reverse oxidation of CO back to CO_2 and for the reason of the so called V-T relaxation [20, 25, 26] which is conversion of vibrational energy to translational degrees of freedom by collisions and the dissociation fraction could be hence oppressed.

Another way of CO_2 decomposition emanates from the possibility of electrons with sufficiently high kinetic energy to excite the electronic states of the CO_2 molecule. Since the production of ground states of CO and O by direct electronic impact is spin-forbidden, two processes are possible [27, 28]:

$$\operatorname{CO}_2(^{1}\Sigma^{+}) + e \longrightarrow \operatorname{CO}(^{1}\Sigma^{+}) + \operatorname{O}(^{1}\mathrm{D})$$
 (1.9)



Figure 1.3 – Electronic terms of a CO_2 molecule as a function of the O-CO distance. Dissociation by vibrational pumping is illustrated by the orange arrow. Dissociation by electron impact is illustrated by blue arrows. The red arrow shows the decrease of the activation barrier of the reaction (1.9) by vibrational excitation. According to [23].

which requires the electron energy of 7.0 eV (see Figure 1.3, dash-dotted blue arrow) and

$$\operatorname{CO}_2(^{1}\Sigma^{+}) + e \longrightarrow \operatorname{CO}(a^{3}\Pi) + \operatorname{O}(^{3}P)$$
 (1.10)

requiring the electronic energy above 10 eV (see Figure 1.3, solid blue arrow). A detailed description of both processes as well as their cross-sections are given in [29]. Dissociation of carbon dioxide by direct electronic impact is much less efficient than the dissociation by vibrational pumping for several reasons. First of all, the energy required for the excitation of electronic degrees of freedom of molecules is more than the energy of the CO-O bond and therefore the electron energy losses are inevitable. Second, high electron temperatures ($T_e \gg 1$ eV) are required such that a sufficient

value of dissociation fraction is reached. Finally, the electron energy branching is way more various at these high electron temperatures than in the case of dominance of vibrational pumping and thus the energy efficiency of CO_2 decomposition is decreased. Nevertheless, if the electron temperature is high enough and at the same time the translational degrees of freedom of the molecules are not excited (i.e. the plasma is strongly non-equilibrium) it is possible to reach significant values of dissociation fraction since there is no oppression either by V-T relaxation or back oxidation of CO back to CO_2 . It is possible to combine both vibrational pumping and dissociation by the electronic impact since vibrational excitation. Vibrational excitation of a CO_2 molecule can reduce the activation energy of the reactions (1.9) and (1.10). Thus, the energy efficiency of conversion of carbon dioxide can be improved (see Figure 1.3, red arrow).

CO can be formed in CO_2 plasma by mechanisms of dissociative attachment and dissociative recombination. The first reaction can be written as follows:

$$CO_2 + e \longrightarrow CO + O^-.$$
 (1.11)

This reaction has relatively low energy barrier (3.85 eV [30]). However, the maximal cross-section of the reaction is not significantly high. Therefore, the reaction doesn't increase the dissociation fraction or efficiency quite well. Nevertheless, the reaction is important for general charge balance in plasma. Dissociative recombination of CO_2^+ ions can contribute to formation of CO as well:

$$\mathrm{CO}_2^+ + \mathrm{e} \longrightarrow \mathrm{CO} + \mathrm{O}.$$
 (1.12)

Several variations of the reaction are possible. First, electronically excited states of CO_2^+ can participate the reaction. Second, the products of the reaction are not necessarily CO and O. It is possible to have C+O₂, C+O+O or simply CO₂ again. Formation of electronically excited states of CO and O is possible as well [31, 32]. The reaction (1.12) and its variation plays an important role only in the case of relatively high electron temperatures (20-40 eV [31]) since it is necessary to overcome the ionization potential of CO₂ first which is equal to 13.3 eV. However, there are reasons to assume that such case can take place in the frame of the current Thesis and all the mechanisms mentioned above will be object of detailed discussion in the following chapters.

The Figure 1.4 illustrates the energy branching of electrons in pure CO_2 . The curves in the picture were obtained by the numerical modeling in BOLSIG+ [33] software. The cross-sections of electronic excitation of 10.5 eV state (reaction (1.10)) was taken



Figure 1.4 – Energy loss fractions in pure carbon dioxide as a funcion of reduced electric field modeled in BOLSIG+ [33] software.

from [29]. For the electronic excitation of 7.0 eV state (reaction (1.9)), vibrational excitation of the first level of the asymmetric mode of CO_2 and ionization, the cross-sections were taken from [30]. It can be seen that the vibrational excitation plays the dominant role at relatively low reduced electric fields (up to 70-80 Townsend (1 Td = 10^{-17} V cm²). As the reduced electric field is increased to several hundreds of Td, the vibrational pumping is oppressed by dissociation by direct electron impact. Ionization starts to play an important role approximately at 100 Td.

1.1.4 Experiments on conversion of carbon dioxide in low temperature plasma

The process of dissociation of the CO₂ molecule has been an object of detailed experimental study since the mid-1960s [20, 34]. One of the reasons for the increase of scientific interest at that time was the invention [35] of the carbon dioxide laser which was the first ever source of coherent radiation with a wavelength in the infrared range ($\approx 10,6 \,\mu$ m). In a carbon dioxide laser, a direct current discharge served as a mechanism for creating an inverse population via the mechanism of vibrational pumping. Molecular nitrogen was used as a buffer gas.

More recently, plasma assisted conversion of carbon dioxide has been studied in

different configurations of discharges such as microwave (MW), gliding arc (GA), dielectric barrier discharges (DBD) and nanosecond pulse discharges (whose detailed review is given in the section 1.2). Despite the fact that all types of discharges are different in terms of pressure, deposited energies, reduced electric fields and translational temperatures of neutral particles (T₀), a strong non-equilibrium between T₀ and electron temperature (T_e) is present in all cases.

Microwave discharges (MW) are known as discharges where the energy is delivered into gas through microwaves. Discharge cells usually don't have electrodes and the energy is hence delivered to plasma via surface waveguides [36, 37, 38]. Typical frequencies of microwave discharges are 0.3-10 GHz [1]. Microwave discharges are typically known as systems with the highest gas temperatures (T $_0 \approx$ 1000-3000 K) and with the maximal energy efficiency of CO_2 decomposition among non-equilibrium plasma discharges. In [25] efficiency of 80 % is reported at dissociation fraction of 60 %. It is possible to increase the energy efficiency up to 90 %by introduction of a De Laval nozzle supplying a supersonic expansion of the gas. Such expansion significantly decreases the gas temperature. According to [37, 38], the T₀ before the nozzle was equal to ≈ 1750 K whereas the temperature after the nozzle decreased down to 100-200 K. Such a drastic decrease significantly slows down the V-T relaxation which is the main obstacle for vibrational pumping. Second, low temperatures slow down the reverse oxidation of CO into carbon dioxide. Both effects hence make energy efficiency of CO_2 decomposition higher. In [36] the highest value of energy efficiency was equal to 45 %. However, since the choice of high energy efficiency and the dissociation fraction is always a trade-off at a fixed input power, the lowest value of the dissociation fraction of ≈ 5 % corresponds to the highest value of energy efficiency. As for microwave discharges, energy of the microwave electric field is transferred to kinetic energy of electrons which, in its turn is easily transferred to vibrational degrees of freedom of molecules. Nevertheless, a significant part of the energy of electric field is spent to gas heating which facilitates thermal dissociation [39]. Therefore, a process of pure delivery of energy of the electric field to kinetic energy of electrons only is impossible in the case of use of microwave discharges.

A classical gliding arc discharge (GA) is a discharge in an atmospheric pressure gas flow propagating between two electrodes with increasing distance. When an electric field is applied between the electrodes, the arc is initiated in the narrowest part of the interelectrode gap. Further, the arc is spreading and developing with the gas flow until it disappears when the arc reaches the opposite edge of the electrodes [40, 41]. A new arc is then formed and the process is repeated. There is a modification of the classical configuration which is called gliding arc plasmatron (GAP) where the gas inlet is tangential with respect to the electrodes [42]. The gas flow is further developing on forward or reverse vortices what increases the residence time of the gas and therefore enhances the CO_2 conversion rate. Both (GA and GAP) configurations have their benefits. First, they are sources of a non-thermal plasma where the vibrational pumping is additionally facilitated by an abrupt decrease of the temperature of the gas flow when it leaves the interelectrode zone whereas the electron temperature doesn't drop as abruptly. The energy efficiency of the CO_2 decomposition is therefore enhanced. Second, as a GA operates at atmospheric pressure, it is possible to make it work at large scale. The disadvantages of the configurations are their hard compatibility with the industrial systems and non-uniformity of the arc discharges which limits the conversion fraction.

A dielectric barrier discharge (DBD) consists on two plane-parallel or concentric metal electrodes and a dielectric barrier (made from glass, quartz or a polymer) which prevents the development of the electric current and formation of sparks or arcs. Generally, a DBD operates at pressure about atmospheric or higher and various frequencies of the electric field (10^{1-5} Hz). As a DBD generally has a filamentary structure, the most part of the volume of the discharge cell is not occupied by plasma and acts instead as a buffer absorbing the energy. As it is mentioned in [43], the reduced electric field in DBD are much higher than in MW discharges. Thus, the electron energy is significantly dissipated within electron impact of electronic states of CO₂ molecules what explains relatively low efficiencies of CO₂ conversion [44].

Glow discharges are one of the most conventional sources of low-temperature plasma. The usual configuration of a glow discharge setup consists of a long glass tube with an anode and cathode on two opposite edges of the tube. A simple geometry of a glow discharge makes possible to apply many diagnostics *in situ* such as Raman scattering, FTIR (Fourier Transform Infrared Spectroscopy) and so on. Therefore, glow discharges are an extremely important instrument for study of plasma kinetics, verification of kinetic schemes and theoretical models. An example of an experiment on CO_2 conversion in a millisecond pulsed glow discharge is given in [45]. The experiment has been done in pure CO_2 at 6.7 mbar. The aim of the experiment was to measure *in situ* vibrational and rotational temperature by means of FTIR for which a special algorithm analyzing the transmittance spectra had been developed. As for vibrational temperature, it was measured for all three modes of CO_2 . It was shown that the decrease of the temperature of the asymmetric mode is responsible for increase of the rotational temperature. This fact confirms one more time that the gas flow should be cooled in order to maintain high level of non-equilibrium between temperature of the gas and the vibrational temperature.

Other examples of application of a glow discharge for study of carbon dioxide plasma kinetics are given in [46] and recently published [47]. In [46] measurements of rate coefficients of dissociation of CO_2 by direct electron impact are described. The idea of the experiment consisted on determination of concentration of CO in a glow pulsed discharge by FTIR with consequent derivation of rate coefficients. The rate coefficients of CO_2 dissociation have been measured for reduced electric fields up to 110 Td and are in agreement with rate coefficients published in [29]. As for [47], the experiment similar to ones described previously has been done at 1-5 Torr in two configurations. The first configuration was pure CO_2 at 300 K simulating the 'Earth' conditions and the second one was 96 % CO_2 -2% Ar-2% N₂ at 220 K simulating conditions on Mars. In situ FTIR measurements have confirmed that the Martian conditions of a decreased temperature leads to a stronger degree of non-equilibrium than on Earth. This non-equilibrium increases the dissociation efficiency. A numerical model which is described in details in the paper is in an excellent agreement with measurements of vibrational, rotational temperatures and dissociation fraction of CO_2 which is reported to be as high as 30%. The model will be discussed more thoroughly in the section 1.3.

1.2 Nanosecond discharges. Fast ionization waves. Dissociation of gases in nanosecond discharges.

One of the main messages of the previous section is existence of two competing mechanisms of dissociation of carbon dioxide in a discharge - vibrational pumping and electron impact where the former is more efficient but yields less and the latter requires more energy but can provide bigger values of dissociation fraction. Vibrational pumping is realized at low values reduced electric field (50-100 Td) and electron impact is realized at relatively high values of reduced electric field (> 100 Td). However, as it could be seen in the Figure 1.4 where the energy branching in CO_2 is demonstrated, high values of the reduced electric field facilitate the ionization processes and higher values of electron density and electric current can be reached. Consequently, ionization favours the realization of dissociation of carbon dioxide by electron impact. However, the value of the maximal current is limited by a power of the high voltage generator [48] and the more is the value of E/n to be maintained, the less are the time periods at which it is possible. This limit entails the necessity to shorten the incident high voltage pulse and justifies the motivation of use of **nanosecond discharges** which are powerful source of high reduced electric fields potentially useful for providing of big values of electronically excited species, dissociation and ionization. As the initial and the most important phase of the development of the majority of nanosecond discharges is the propagation of the so called fast ionization wave (FIW) characterized by extremely high electric fields, the first part of the section will be devoted to FIWs.

1.2.1 Fast ionization waves

Fast ionization waves were first experimentally in 1893 by J J Thomson [49] in a 15 m long discharge tube filled by mercury vapor at pressure ≈ 0.7 mbar. The discharge was initiated by an inductance coil and the velocity of propagation of light in the tube measured by a rotational mirror was found to be approximately equal to half of the speed of light. In 1937 a wave of gradient of potential propagating with the same velocity as the glow was discovered [50]. In 1947 it was shown by Mitchell and Snoddy that the current in a FIW is defined by the charge of the capacity of the discharge cell up to the pulse voltage. In 1965, Loeb generalized the experimental knowledge about FIW [51, 52]. After a technological breakthrough in generation of nanosecond pulsed discharges [53, 54, 55] new experimental data such as current, velocity of propagation and amplitude of FIW were gathered and generalized. The term 'fast ionization wave' was therefore established and it is the conventional term since then.

One of the main peculiarities of nanosecond pulsed discharges is the fact that the voltage between the electrodes might be significantly higher than the breakdown voltage. This fact can be described by the parameter of overvoltage $K = U/U_{br}$, where U is voltage between the electrodes and U_{br} is breakdown voltage [56]. Whether the K parameter is high or not, the discharge may develop as a glow or as a spark one. If the overvoltage is high enough (K > 10) for acceleration of high energy electrons such that their energy is significantly contributed to pre-ionization processes, the discharge is developing as a homogeneous glow propagating with $\approx 10^9$ cm/s. Such a discharge is usually called a fast ionization wave (FIW).

A schematic view of the development of a FIW is given in the Figure 1.5. The nanosecond pulse is transmitted to the discharge cell by a coaxial transmission line. The discharge cell is hence a continuation of the central wire of the cable and the metallic screen around the discharge cell is connected to the shielding of the cable. The FIW starts from the high voltage electrode and propagates along the tube. A



Figure 1.5 – Development of a fast ionization wave in a discharge cell. 1 - coaxial transmission line, 2 - high voltage electrode, 3 - discharge tube, 4 - low voltage electrode, 5 - high conductivity plasma after the front of the FIW, 6 - front of the FIW, 7 - lines of the electric field, 8 - metallic screen around the discharge cell. i_{rev} is the reverse electric current flowing in an opposite way with respect to the current in the wave. U - potential distribution along the discharge cell. v_f - velocity of the FIW. Taken from [54]

channel with a high conductivity is formed behind the front of the wave to which the potential of the high voltage electrode is transmitted. The direct conductivity current flows therefore through plasma channel, the reverse current flows backwards in the metallic screen and displacement current establishes the continuity between both [54, 55].

The efficiency of the ionization processes depends exponentially on the reduced electric field E/n and therefore the nanosecond pulsed discharge at high electric fields with FIW propagating in a long discharge tube can be an efficient instrument for ionization. For example, generation of fast ionization waves is used for laser pumping and facilitation of chemical reactions in plasma. Moreover, use of a discharge cell with reduced volume (in particular – a capillary) may increase the specific deposited energy what promotes formation of electronically excited species what might be important for the dissociation processes. The next subsections are therefore devoted to a more detailed review of the experiments on dissociation of various gases by nanosecond capillary discharges where propagation of a fast ionization wave plays one of the dominant roles.

1.2.2 Dissociation of molecular nitrogen and oxygen in nanosecond discharges

A series experiments on dissociation of nitrogen (dissociation energy 9.8 eV/molecule) and oxygen (dissociation energy 5.2 eV/molecule) in nanosecond discharges was done recently at the Laboratory of Plasma Physics, Palaiseau, France. First, a significant dissociation fraction (at least 50-60 %) of oxygen is reported in [48, 57, 58]. Three subsequent high voltage pulses ignited plasma in a discharge capillary. The experiments were conducted in synthetic air (N₂ : O₂ = 4 : 1) at pressures of 24-30 mbar with about 1 eV/particle deposited energy. The measurements of the density of atomic oxygen in the time interval 200 ns-2 μ s after the first incident pulse were done by the xenon-calibrated two-photon absorption laser induced fluorescence (TALIF) technique [59].



Figure 1.6 – Results of TALIF measurements of the density of O atoms in the afterglow of a nanosecond capillary discharge ignited in synthetic air at 27 mbar. Black points and lines correspond to the calculation of O density without taking into account temperature dependence of quenching rates. Red points and lines correspond to the calculation of O density with taking into account temperature dependence of quenching rates. Blue dotted line shows 100% of dissociation. According to [58].

The results of the experiment are given in Figure 1.6. Two options of calculation of the time profile of O atom density are given. The first option takes into account the square root temperature dependence of rate constants of quenching of excited states of O.

$$k_q(T) = k_q(T_0)\sqrt{T/T_0}$$
(1.13)

The other option of calculations is based on the assumption that the quenching rate constants are independent on temperature. According to [58], such discrepancy between two models as well as the thing that the 100% dissociation threshold is exceeded can be explained either by the fact that two-photon absorption cross-section of oxygen is overestimated or by slower increase of the quenching rate with temperature that is proposed in the (1.13).

It can be seen that the oxygen dissociation fraction increases with time and is higher in the afterglow (after 0.5 μ s) than in the discharge (before 0.5 μ s). As there is no any electric field applied after the discharge, there is a mechanism of O₂ dissociation additional to the dissociation by electron impact. Such an additional mechanism was suggest by Popov [60, 61] and can be explained as two-step reaction. First, a metastable N₂(A³ Σ_u^+) state is excited by electron impact from the ground state:

$$N_2(X^1\Sigma_g^+) + e \longrightarrow N_2(A^3\Sigma_u^+) + e.$$
 (1.14)

Second, $N_2(A^3\Sigma_u^+)$ interacts with molecular oxygen:

$$N_2(A^3\Sigma_u^+) + O_2 \longrightarrow N_2(X^1\Sigma_g^+, v) + 2 O(^3P) + \varepsilon$$
(1.15)

Energy of the $N_2(A^3\Sigma_u^+)$ state is therefore distributed for O_2 dissociation, vibrational excitation of $N_2(X^1\Sigma_g^+)$ and gas heating. More recently, argon-calibrated actinometric measurements of density of oxygen atoms were done [62]. It was shown that the decay rate of electron density in the afterglow is an order of magnitude less than it was estimated previously. Therefore, one more channel of additional production of atomic oxygen in the afterglow consists on three-body recombination of positive ions of atomic oxygen with an electron as the third body.

$$O^+ + e + e \longrightarrow O(^3P) + e$$
 (1.16)

To estimate the degree of gas heating, the rotational temperature of the gas was measured by optical emission spectroscopy of $N_2(C^3\Pi_u)$ state. The results of the measurements are given in the figure Figure 1.7. The temperature was measured at three time instant corresponding to three high voltage pulses incident into discharge capillary. The point at 2000 ns corresponds to the measurements of temperature in the afterglow. According to [60, 61, 63], the heating of the gas over sub-microsecond time scales in the afterglow is due to the quenching of nitrogen molecules in excited states $N_2(A^3\Sigma_u^+, B^3\Pi_g, C^3\Pi_u)$ and not due to V-T relaxation of vibrationally excited nitrogen molecules. It can be therefore concluded that excitation of electronic degrees of freedom of nitrogen plays the dominant role both in gas heating and dissociation of oxygen.



Figure 1.7 – Results of rotational temperature temporal profile measurements at gas pressures of 24, 27 and 30 mbar. Taken from [58]

A similar experiment with a nanosecond repetitive pulses discharge in preheated to 1000 K air at atmospheric pressure is described in [63]. An increase of temperature on 900 K as well as an increase of dissociation fraction of oxygen in the first 20 ns are reported. Like in the experiments described previously, a significant role of electronic degrees of freedom of molecular nitrogen in discharge kinetics is shown.

A series of experiments with nanosecond capillary discharges in pure nitrogen at ≈ 27 mbar is described in [64, 65]. It was shown experimentally that the electron

density decay rate is an order of magnitude less than it would be if its main channel had been the typical two-body recombination of electrons with positive N_2^+ ions. The temporal profile of the electron density is presented in Figure 1.8.



Figure 1.8 – Results measurements of electron density in the first incident pulse. Pure nitrogen, p=27 mbar. Blue points: experimental measurements, solid red line: calculations of the electron density with processes of associative ionization, dotted line:calculations of the electron density without processes of associative ionization. Taken from [64].

The so called associative ionization was suggested to be the mechanism of the additional population of the electron density in the discharge afterglow:

$$N_2(A^3\Sigma_u^+) + N_2(a^{\prime 1}\Sigma_u^-) \longrightarrow N_4^+ + e.$$
(1.17)

As it can be seen, the metastable state $N_2(A^3\Sigma_u^+)$ excited from the nitrogen ground state acts as a 'reservoir' responsible for additional formation of the electron density. More recently, TALIF measurements of the temporal profile of the density of atomic nitrogen N(⁴S) showed that significant nitrogen dissociation fraction of almost 10%



is maintained at several milliseconds (ms) after the first nanosecond pulse [66, 67]. The temporal profile of atomic nitrogen $N(^{4}S)$ is given in Figure 1.9.

Figure 1.9 – Time profile of the N-atom density measured using TALIF. Taken from [66].

It was suggested that such significant nitrogen dissociation fraction at several milliseconds is possible provided that two conditions are fulfilled. First, the reaction:

$$N_2(A^3\Sigma_u^+, B^3\Pi_g, C^3\Pi_u) + e \longrightarrow N(^4S) + N(^4S, ^2D) + e$$
(1.18)

must be the dominant mechanism of the dissociative quenching of electronic triplet states of molecular nitrogen. Second, the duration of the discharge pulse must be much longer than the characteristic time of the reaction (1.18) in order to maintain sufficiently high electron temperature for long time.

It was shown theoretically and experimentally that nanosecond discharges act as a source of significant ionization degree and relatively strong reduced electric fields. Both facts entail sufficient degree of excitation of electronic degrees of freedom which can be maintained for relatively long time periods. Since a significant amount of energy is contained in the electronically excited species, it may be transferred to translational degrees of freedom either accelerate the processes responsible for additional dissociation of oxygen and nitrogen. The next subsection is devoted to the review of experimental results in the domain of conversion of carbon dioxide by nanosecond discharge and comparison of processes occurring in CO_2 , N_2 and O_2 .

1.2.3 Dissociation of carbon dioxide in nanosecond discharges

A significant benchmark of experiments on conversion of carbon dioxide by nanosecond discharges is given in [68]. A series of measurements of absolute density of OH radicals by laser induced fluorescence (LIF) on μ s time scale in various CO₂-H₂O-He mixtures is described. Unfortunately, extraction of data about CO_2 absolute density were impossible since the temperature dependence of quenching rates of excited OH-radicals k_{Q0} as well as constants of vibrational energy transfer k_{VET} weren't known. Nevertheless, the experiment has defined the direction of further research in the domain of conversion of CO_2 by nanosecond pulses. First, the pulse rate as well as energy of the pulses is not that important as the fact that the energy should be distributed uniformly on the entire discharge volume. Second, a way of gas cooling in early discharge afterglow should be find in order to slow down back oxidation of produced CO. Finally, an NRP-discharge is not the most efficient source of production of value-added chemicals from CO_2 but is a fruitful instrument for better understanding of plasma kinetics. In addition, various configurations of temporal profiles of incident pulses affecting CO_2 have been studied in [69]. The idea of the work was to look what happens if the same amount of energy is delivered into plasma in different ways such that different dissociation mechanism would be activated. It was shown that the closer in time are the pulses, the higher discharge current is observed. This circumstance is caused by the fact that characteristic recombination time of plasma is comparable between time between pulses. Therefore, the consequent pulses interacted with a perturbed system and a memory effect took place.

The paper [70] is the continuation of the previous work where the gas effluent is analyzed by gas chromatography. Nanosecond pulse discharges in pin-to-sphere configuration were ignited in CO_2/H_2O mixture at pressure close to atmospheric. The maximal value of dissociation fraction shown by gas chromatography was equal to 20 %. The efficiency of dissociation corresponding to this value was 12-14 %. The maximal energy efficiency of dissociation was 30 % at dissociation fraction of 14 %.

To make a step towards better comprehension of gas kinetics by methods of LIF, an assumption of independence on temperature of the ratio k_{Q0}/k_{VET} is made. Such an assumption gave a clue for measurements of temperature profile of dissociation

fraction of CO_2 and gas temperature. Both trends are presented in the Figure 1.10. A significant dissociation fraction of carbon dioxide of 60-70 % can be seen at first 20 μ s after the pulse. An effect of gas heating up to almost 2800 K is presented but the mechanisms responsible for gas heating remain unclear.



Figure 1.10 – Temperature, k_{Q0}/k_{VET} and CO₂ dissociation fraction as a function of the delay after the last pulse of the burst. Gas composition CO2 with 1.35 % H2O, specific energy input (SEI) = 7.2 kJ dm-3. CO2 splitting causes a decrease of the k_{VET}/k_{Q0} ratio. The 12 % CO2 dissociation in the effluent gas measured by GC is designated by a red horizontal line. Taken from [70].

The paper [71] released by the same scientific group describes the measurements of CO_2 treated by NRP-discharges at atmospheric pressure. The time-resolved profile of temperature has been measured in the discharge itself at nanosecond timescale by optical emission spectroscopy of nitrogen which has been added as an admixture of small concentration. The gas has been heated from 300 K to 1500 K during \approx 400 ns. After 2 μ s when the discharge regime is transited to spark one, the gas temperature reaches at least 2000 K. Development of the measurements gave an opportunity to record the gas temperature on nanosecond timescale. By adding a small amount of nitrogen, it was possible to monitor the time evolution of the gas temperature using the Second Positive System bands of N₂ [72].
A relatively recent result in the domain has been reported in [73]. An NRP-discharge in CO₂ at room temperature and atmospheric pressure was studied. To measure the number density of species, a TALIF of CO was applied. 16 % dissociation fraction of CO₂ at 1 μ s time instant is reported. Measurements of temporal and spatial profiles of gas temperature confirm an effect of fast heating of the gas in first 50 ns. At 50 ns after the discharge pulse, the temperature in the middle of the discharge cell was as high as 1200 K and the temperature close to walls was 600 K. After 200 ns the temperature starts to increase and one of the possible mechanisms responsible for that could be V-T relaxation. The temperature measurements are in agreement with previous results of the same research group done by IR-absorption spectroscopy for $10^{-5} - 10^{-4}$ s.

Several scientific experiments on nanosecond discharges in various gases such as nitrogen, oxygen and carbon dioxide have been reviewed above. As for nitrogen and oxygen, it was shown experimentally and justified by numerical modeling that it is population of electronic degrees of freedom of species $N_2(A^3\Sigma_u^+, B^3\Pi_g, C^3\Pi_u)$ by electron impact which is responsible for effects of fast gas heating and additional dissociation of molecular gases in the discharge afterglow. Experiments with nanosecond discharges in carbon dioxide have revealed the same predisposition of carbon dioxide to fast heating in nanosecond pulses. It is demonstrated in recent works [74, 75] encompassing both experiment and detailed kinetic scheme that such species as $CO(a^3\Pi)$ and $O(^1S, ^1D)$ may play the key role both in fast gas heating and CO_2 conversion. However, coexistance of electronic excitation and vibrational pumping competing with each other at nano- and microsecond time scale has to be studied more thoroughly in order to put an end of the discussion about the species and reactions responsible for the aforementioned effects. A detailed numerical modeling could help to find a clue for this issue.

1.3 Numerical modeling of CO₂ discharges

Computer modeling of plasma can be a very useful instrument which could help to evaluate parameters which are difficult to measure and to understand better roles of particular chemical reactions. Therefore, numerical modeling of plasma is a tool which is essential both for predictions of results of an experiment and for underlining the most important chemical reactions in the experiment. One of the most common approaches to model carbon dioxide plasma is the so called state-to-state (STS) modelling which constists on numerical solution of a system of non-linear balance rate differential equations [76]. The most detailed STS approach should take into account the fact that a CO_2 molecule has three vibrational modes and each of them has a certain number of levels. Therefore, if the vibrational modes are coupled, the vibrational states are described by three quantum numbers $v = (v_1, v_2, v_3)$ with a limit that total vibrational energy must not exceed the dissociation threshold of 5.5 eV. Moreover, the reactions should include corresponding V-V' and V-T energy transfer. An example of such a detailed approach with 9018 vibrational levels taken into account is given in [77] where a hypersonic atmospheric flow was modeled. Nevertheless, the amount of the reactions could be reduced to 1224 without a significant decrease of adequacy of the model. Focusing on each vibrational mode helped to understand its own particular contribution into the ensemble of reactions and the modeling has shown that V-T relaxation of bending mode had been the main relaxation channel at the given conditions. Another important result was that vibrational distributions in the bending mode are strongly influenced by excitation of symmetric and asymmetric stretching vibrations what entails strong coupling of vibrational modes of CO_2 .

A detailed state-to-state kinetic scheme which includes all possible vibrational levels of CO_2 , CO and O_2 is a powerful tool which can help to estimate roles of different reactions but it is evident that such expanded kinetic schemes are limited by computational powers. It is therefore necessary to apply reduced kinetic schemes which usually include the vibrational manifold and set of chemical reactions. It is important that a reduced kinetic schemes should be built upon sensitivity and rate analysis of full kinetic schemes. An example of such a 0-D kinetic scheme where all 21 levels of the asymmetric mode are included and the symmetric mode and bending modes are represented only by lower levels is given in [24]. The Boltzmann equation in two-term expansion in Legendre polynomials was being solved to calculate rate constants of reactions with an electron impact. The other examples of STS kinetic schemes where vibrational kinetics is coupled with chemistry of species in ground and electronically excited states could be find in papers published by the groups from Bari [43, 78] and IST Lisbon [79, 80, 81, 47]. Older works developed for the description of CO_2 lasers [82, 83] don't include the vibrational kinetics of CO_2 at all but instead, provide a full set of chemical reactions.

It should be noticed that in the case of nanosecond discharges which is the main topic of the current Thesis the vibrational loss fraction of the electron energy seems to be negligible with respect to the excitation of electronic degrees of freedom because of the relatively high electric fields (see Figure 1.4). In spite of this, it is still necessary to take into account both excitation of electronic and vibrational degrees of freedom of CO_2 for the reason that it the only way to describe the electron energy distribution function (eedf) and, consequently, the experimental results.

An evident drawback of state-to-state models is their elevated requirements for computational power and there should be a way to avoid the detailed STS calculations. An attempt to lump the vibrational levels of CO_2 on three groups is described in [84]. It was demonstrated that the model is able to reproduce the VDF of asymmetric mode of CO_2 . The model gives a good agreement with the full model for electron density and temperature, gas temperature and CO₂ conversion fraction in a range of different pressures between 100 mbar and 1 bar. However, the level lumping was not entirely valid for lower pressures. Another opportunity to make a step away from detailed STS calculations is to replace the vibrational discrete manifold with a continuum using the Fokker-Planck (FP) equation [85, 86]. Nevertheless, as it is mentioned in [86], the FP model requires gas temperature, vibrational temperatures, and number density of a few species as input parameters which are obtained from STS calculations. Therefore, a FP is not a completely isolated model and is more a second iteration of an STS model. Though, provided that the results of the STS model are obtained, the calculations of vibrational distribution function (VDF) are around 3 orders of magnitude faster than in the case of using only an STS model.

One more serious disadvantage of the STS calculations for the particular case of CO_2 molecules consists on the aforementioned fact that a CO_2 molecule has 3 atoms. Therefore, the vibrational and electronic terms of the molecule cannot be represented by potential curves but should be represented as potential 2D surfaces. For this reason, the state-to-state approach may be misleading. One of the implications is that dissociation at 5.5 eV by stepwise excitation requires a modification of the electronic structure. For instance, level 22 of the pure asymmetric-stretching mode is still a bound level. Transitions to the 2D electronic configuration cannot be calculated from STS approach and should use alternative approaches, such as the Rosen-Zener theory which can take into account non-adiabatic transitions [87]. Nevertheless, it should be said that despite this disadvantage of the STS approach it still provides a good agreement between the modeled and experimental results, especially at sub-microsecond timescale where the vibrations do not play a dominant role. The confirmation to this fact will be clearly seen in the Chapter 9 which is devoted to the numerical modeling of the discharge.

1.4 Conclusions of the literature review

The literature review that has been presented above covered several topics. First, it was underlined that the problem of conversion of carbon dioxide is an essential one because of drastic increase of antropogenic outcomes of carbon dioxide since the last 150 years. As the XXI century is the era of space discoveries and knowing the ambition of mankind to make a first step on Martian soil one day, the actuality of the problem of conversion of carbon dioxide becomes even more evident. Second, different techniques of CO_2 conversion such as thermal dissociation, electrochemical and photochemical reduction as well as biochemical conversion have been reviewed. Their advantages and drawbacks have been presented and it was concluded that low temperature plasma may be an efficient tool for conversion of carbon dioxide since mostly electrons, which are way more mobile than atoms and molecules, are affected.

Then, it was mentioned that plasma assisted conversion of CO_2 occurs by two main mechanisms: vibrational pumping and excitation by electron impact where both are competitive with each other in terms of energy efficiency and dissociation fraction. It was shown that dissociation of carbon dioxide by vibrational pumping takes place at relatively low reduced electric fields (≤ 100 Td) and electron impact becomes dominant at higher values of the reduced electric field. Several types of discharges were observed in the literature review and it was underlined that a nanosecond pulsed discharge though may be not a source providing value-added chemicals in the most efficient way but a source which provides their highest yield. A particular case of nanosecond capillary discharge has its signature such as formation of a fast ionization wave and small volume of the reactor. These two facts entail the presence of extremely high reduced electric fields and specific deposited energy. Previous experiments shew that the dissociation fraction of molecular nitrogen and oxygen at such conditions are relatively high with respect to the cases of other discharge configurations. Since a significant amount of energy is contained in electronically excited molecular nitrogen and atomic oxygen, it may either accelerate the processes responsible for additional dissociation of oxygen and nitrogen or to be transferred to the translational degrees of freedom of gas causing the effect of fast gas heating. As the CO_2 and CO both have a plenty of electronic degrees of freedom to be excited, it is worth to expect a similar effect in CO_2 . This fact accentuates again a particular beauty of nanosecond capillary discharges since they are peculiar source of precious and detailed knowledge of fundamental mechanisms of plasma.

Finally, different approaches to numerical modeling have been reviewed. Advantages and drawbacks of state-to-state approach to model vibrational states and plasma chemistry was described in details. It was claimed that the case of nanosecond capillary discharges in CO_2 has its particular complication because the behaviour of both vibrational manifold and electronic degrees of freedom is important at nanosecond time scale.

Having arrived to this point, the problem of the current Thesis will now be formulated.

Problem formulation

It was shown in the literature review that nanosecond pulsed capillary discharges are characterized by relatively high values of reduced electric field (> 200 Td) and specific deposited energy (about 1 eV/particle). Excitation of electronic degrees of freedom of CO_2 and its dissociation products becomes higher than vibrational excitation of at these conditions. Such conditions are rarely represented in the most part of conventional studies described in literature, where vibrational pumping of molecules supplies high values of dissociation energy efficiency but relatively low dissociation fraction. The initial idea of the research was to change the scope and to focus on maximization of gain of dissociation of carbon dioxide via excitation of its electronic degrees of freedom. It has been shown in literature that experiments with nanosecond discharges ignited in $N_2:O_2$ mixtures have revealed a significant role of active species in plasma kinetics. Ions, electronically excited states of atoms and molecules are responsible for dynamics of the main plasma parameters such as electron density, gas dissociation degree and gas temperature. As for the latter, the phenomenon of fast gas heating has been observed in N₂:O₂ nanosecond plasma. Therefore, the research described in the current Thesis should include both thorough experimental and modeling work to define the processes driving the kinetic processes in CO_2 at similar conditions.

The following experimental problems should be solved:

- 1. Measurements of main electric discharge characteristics such as electric current, reduced electric field and specific deposited energy at different pressures.
- 2. Measurements of steady-state dissociation degree and the energy efficiency by means of FTIR (Fourier Transform Infrared Spectroscopy) at various conditions such as different pressures, flow rate and pulse frequency.
- 3. Acquisition of optical emission spectra of the discharge for understanding which active species play the dominant role in plasma processes. Acquisition of temporal profiles of concentrations of the active species.

- 4. Measurements of temporal and analysis of spatial profile of the electron density in high voltage pulses and their afterglow. This set of data is essential for validation of any kinetic model describing the discharge.
- 5. Study of gas temperature by rotational temperature of nitrogen which is added to CO_2 as a small admixture. To study the dynamics of gas heating, the temperature of the mixture should be recorded at several time instants.

Numerical modeling is required to solve the following problems:

- 1. Definition of processes responsible for dynamics of active species in the discharge itself and the afterglow. Understanding of processes responsible for gas heating. Validation of model by comparison the calculation and experimental results.
- 2. Applicability of the kinetic model in prediction of such plasma parameters as CO_2 dissociation fraction, gas temperature at given experimental conditions.

Chapter 2

Experimental methods

In this Chapter the description of the experimental setup configurations and used experimental techniques is given.

2.1 Discharge cell

2.1.1 General observations

Measurements of the main discharge characteristics were done in two different capillaries. First, the so called 'thin capillary' was developed for the spectroscopic measurements and electrical measurements of the discharge. Second, 'FTIR capillary' was developed for measurements of absolute densities of dissociation products in the flowing afterglow by means of FTIR spectroscopy. Both setups were operating at pressures of 10-20 mbar at flow values of 7-37 sccm. CO_2 and N_2 (the latter was used only when gas temperature was being measured) flows were controlled by Brooks Instruments 5850TR mass flow controllers operated from Brooks Instruments Model 0254 control panel. Both setups could be pumped out to 10^{-2} mbar provided that they had not be connected to the gas inlet. The leak rate was estimated to be at the level of 0.05-0.2 mbar/min. The setups were connected to the pump EdwardsXDS5 by the system of tubes and valves which regulated the pressure in the system. The pressure in the system was measured by two pressure gauges Pfeiffer Vacuum CMR 362 installed by two opposite sides of the discharge cell. The mean value of their data was considered to be the real pressure. It was necessary to use two pressure gauges because of high hydrodynamic resistance of the capillary. A schematic view of both setups is presented in the Figure 2.1. The vacuum system is presented by the green color.

The general scheme of the experimental setups and the main experimental equipment are presented in Figure 2.1. The triggering generator (TG) BNC 575 was used to trigger the high voltage generator (HVG) FPG 12-1NM (FID GmbH) and the ICCD camera (PI-MAX 4 1024i, Princeton Instruments) at variable repetition rate. The maximal output voltage of the HVG during the experiment was equal to 9.4 kV, the width of the pulse was 30 ns FWHM and its rise time was 2 ns. It is important to notice that a high voltage pulse sent from the HVG was partially reflected from the discharge cell and then propagated back and forth between HVG and the discharge cell forming 3 consequent pulses in the latter. The amplitudes of the further pulses were negligible with respect to the previous ones.

Despite the effectiveness and simplicity of the thin capillary in which the most part of measurements described in the current Thesis was done, it had several serious drawbacks. First, transportability of the 'thin' capillary was quite poor. Second, the thin capillary wasn't compatible with the main standards of most vacuum details usually used in experiments. Thus, the consumables for the thin capillary couldn't been easily found nor ordered and therefore the development and delivery of the consumables could take a significant amount of time. Third, the thin capillary was connected to the vacuum system via plastic tubes and this plastic couldn't provide a sufficient degree of purity required for the FTIR downstream measurements of absolute density of products of CO_2 dissociation. For those reasons, the so called 'FTIR capillary' was developed which was, in fact, an upgrade of the old one. Sketches of both configurations are given in the Figure 2.2. More information concerning the differences between two configurations is given in the next paragraphs.

Finally, it should be noted that despite the fact that the 'thin' and 'FTIR' capillaries were fabricated from different materials (quartz and glass, respectively), there were no any effect on the discharge caused by this difference.

2.1.2 Thin capillary

The schematic view of the thin capillary is presented in the upper side of the Figure 2.2. The discharge cell was installed in the break of the high voltage cable. The thin capillary with two brass electrodes was made from quartz and had the distance between the electrodes of 75 mm. The length of the capillary was equal to 86 mm. The internal diameter of the capillary was 1.7 mm. The pins of the electrodes were



Figure 2.1 – Sketches of both experimental setups. FC1 and FC2 are mass flow controllers, PG1 and PG2 are pressure gauges. PMT is photomultiplier tube, BCS is back current shunt, CP is capacitive probe. TG is triggering generator, HVG is high voltage generator. Black color designates electrical supplies, green color designates vacuum system and system of gas flow control, blue color designates optical system.



Figure 2.2 – Sketch of two main discharge cell configurations

inserted in the capillary. The other side of the electrodes was flat and could be connected to the central wires of high voltage coaxial cables RG213. The high voltage electrode was connected to the high voltage generator via HV cable, the low voltage electrode was connected to the LV cable under floating potential. The rectangular (48 mm x 60 mm) metal screen surrounding the capillary tube was connected to the shielding of both HV and LV cables. Thus, the high voltage pulse coming from the high voltage generator didn't reflect from the low voltage electrode but could pass instead through the capillary and propagate through the low voltage cable after. Such configuration didn't provide the highest possible deposited energy per particle but made possible measurements of the temporal profile of the electric field by a capacitive probe and additional control of transmitted current. Using of two (instead of one) back current shunts allowed more precise measurements of electric characteristics of the discharge such as electric current and deposited energy. Finally, due to the fact that the thin capillary was made from quartz, it was possible to conduct optical emission spectroscopy (OES) measurements in the 200-300 nm wavelengths range.

2.1.3 FTIR capillary

The schematic view of the thin capillary is presented in the lower side of the Figure 2.2. The FTIR capillary was made from Pyrex glass and had the same interelectrode distance as the thin capillary but its internal diameter was slightly larger and was equal to 2 mm. The total length of the thin part of the capillary was equal to 80 mm. The central wire of the high voltage cable was connected to the high voltage electrode of the discharge cell. The shielding of the high voltage cable was connected to the adhesive copper foil which was glued to the external surface of the capillary. The copper foil was soldered to the low voltage electrode which, in its turn was stuck to a Faraday's cage surrounding the discharge cell. The aim to put a Faraday's cage around the setup was to protect the apparatus from the interference of the discharge which was especially severe at operation at high pulse repetition rate. The maximal possible energy deposited into the discharge system was provided with the configuration described above. Nevertheless, such a configuration makes measurements of the temporal profile of the electric field by a capacitive probe impossible because of the reflection of a fast ionization wave (FIW) back from the grounded electrode. It was neither possible to use two back current shunts instead of one. Therefore, the measurements of the electric current and deposited energy were less accurate than in the case of the thin capillary. Finally, due to the fact that the thin capillary was made from Pyrex glass and not from quartz as the thin capillary, it was possible to conduct optical emission spectroscopy (OES) measurements in the 200-300 nm wavelengths range.

2.2 Electric measurements

2.2.1 Back current shunts and high voltage cables

A back current shunt (BCS) is a device which is used to measure electric voltage in a point of a coaxial cable where the shunt is installed. A BCS is a system of twelve parallel low-inductive KOA Speer CF1/2C2R2J resistors which are installed in the break of the shielding of the high voltage cable. Each resistor of a BCS used in all experiments had a resistance equal to 2.2 Ohm. The shunts were connected to 50 Ohm input of LeCroy WaveRunner 64Xi-A 600 MHz ocilloscope and registered the voltage drop.

Let I be the current in the central wire. Then, there is a current -I flowing in the shielding. It means that the voltage between the shielding and the central wire is equal to

$$U = IZ, (2.1)$$

where Z = 50 Ohm is the wave resistance of the cable. As soon as a BCS replaces a

part of shielding in the cable, the same current -I flows through it. The resistance of the shunt of equivalent resistors is equal to R/N, where N=12 is a total number of the resistors. The voltage which is registered by the oscilloscope is therefore:

$$U_{osc} = \frac{IR}{NK_{att}} \tag{2.2}$$

 K_{att} here is the reducing coefficient of attenuators attached on channels of the oscilloscope. The attenuators were used to keep the oscilloscope in safety. The link between the real voltage propagating in the cable and the voltage registered by the oscilloscope can be found according to following considerations. If the latter is U_{osc} , the real voltage can be expressed in the following way:

$$U = \frac{U_{osc}ZNK_{att}}{R}.$$
(2.3)

The voltage propagates inside a cable with a group velocity:

$$V_g = \frac{c}{\sqrt{\varepsilon}},\tag{2.4}$$

where $\varepsilon = 2.25$ is the dielectric permittivity of the insulator inside the electric cable and c is the speed of light in vacuum. As it can be derived from this formula, the velocity of the propagation of the signal inside the cable is 20 cm/ns. It is important that the signal propagates in a cable without any reflection if and only if the wave resistance is constant along its way. As soon as there is a change of the wave resistance a partial or total reflection of the voltage occurs. In the most general case the reflection coefficient for a voltage can be presented as:

$$k_U = \frac{R-Z}{R+Z}.$$
(2.5)

R here is the resistance of the load. There are two extreme cases here: a short circuit and an infinite load. In the first case with zero load k_U is equal to -1. Signal comes to the end of the long cable and reflects with the different polarity and the same amplitude. At infinite load $k_U = 1$. In this case, signal comes to the end of the cable and is reflected with the same amplitude and doesn't change of the polarity.

2.2.2 Capacitive probe

It was possible to register the temporal dynamics of the longitudinal electric field in the thin capillary. In particular, the time-resolved profile of the electric field of a fast ionization wave propagating in the capillary has been acquired. It was done by the so called capacitive probe. In fact, a capacitive probe is a capacitive divider located above the discharge cell from one side and attached to the input of the oscilloscope from another. The oscilloscope could measure the voltage on the probe as a function of time. The main principle of data acquisition by a capacitive probe is described in [52, 65]. The plasma acts as one plate of the capacitor and the pin of the capacitive probe acts as the other plate. Consequently, when an electric current flows through plasma, an electric potential near the plasma surface is equal to U_{pl} . The potential U_{osc} is registered by the oscilloscope. The scheme of the capacitive probe is given in the Figure 2.3 $C_{coax.cap}$ is known and is equal to 330 pF.



Figure 2.3 – The electric scheme of the capacitive probe. Taken from [65]

Usually, the capacity between the probe's tip and plasma C_{pl-tip} is not known. That's why the probe had to be calibrated. The process of the calibration was the following. A piece of copper foil was inserted in the capillary and a high voltage pulse with known parameters passed through it. Simultaneously, the signal from the capacitive probe was registered. The plasma potential U_{pl} and the signal on the oscilloscope U_{probe} are related by the following expression:

$$U_{pl}(t) = A_{CP}(U_{probe}(t) + \frac{1}{\tau_{CP}} \int_0^t U_{probe}(t')dt').$$
(2.6)

Here, A_{CP} and τ_{CP} are the division coefficient and the response time of the capacitive probe, respectively. They were found in such a way that the measured profile from the capacitive probe and the voltage profile in the coaxial cable acquired by the BCS1 are in agreement. In the described case, the longitudinal electric field can be found with an equation $E(x,t) = -\partial U_{pl}(x,t)/\partial x$. Therefore, a series of measurements by the capacitive probe at different positions was required. After the calibration of the capacitive probe, the signal from the probe was registered in the range of distances to the high voltage electrode from 4 mm to 55 mm with a 1 mm step. To acquire the electric field at the position x_0 the numerical integration of the potential with respect to the spatial coordinate was performed. Here, 10 points before x_0 and 10 points after x_0 were used.

It is important that the measurements of the longitudinal electric field by a capacitive probe were impossible to be done in the FTIR capillary because of reflection of the FIW back from the grounded electrode. Therefore, if a capacitive probe was installed on the discharge cell, the signal registered by the capacitive probe would be superimposed voltages of the incident and reflected FIWs resulting in zero signal. Thus, the only way to estimate the electric field in the FTIR capillary was to use back current shunts.

2.3 Optical emission spectroscopy

Optical emission spectroscopy (OES) is one of the most powerful techniques in plasma physics. First, OES makes possible to answer the question about the main species formed by a discharge capillary. If an additional photomultiplier device is used with a monochromator, it is possible not only to make conclusions about the plasma contents, but to trace the temporal dynamics of electronically excited species as well. The results of such measurements are described in Chapter 5. Another domain where OES technique was indispensable is determination of rotational temperature of the gas which is, at some conditions, related to the translational temperature of the gas. The details and the results of the temperature measurements are given in the Chapter 8.

The Princeton Instruments Acton Series SP-2500i spectrometer acting as a monochromator combined with an ICCD-camera Princeton Instruments PI-Max 4 was used for the registration of the emission spectra of the discharge. The ICCD-camera was attached to the output of the spectrometer. The light was focused to the input slit of the spectrometer by a quartz ultraviolet Uncoated UV Fused Silica Plano-Convex lens with focal distance of 10 cm. Another way to collect and deliver plasma emission to the input slit of the spectrometer was a BF13LSMA01 multimode round optical fiber. The main advantage of the optical fiber was that it didn't require alignment of the optical system. Nevertheless, the losses of signal caused by the optical fiber are more significant than during the use of a lens, especially in ultraviolet region. The width of the input slit of the spectrometer could be varied. The light was decomposed into a spectrum by diffraction gratings (600 lines/mm, blaze 300 nm or 1200 lines/mm, blaze 500 nm and 2400 lines/mm, blaze 240 nm). The ICCD-camera (matrix 1024×1024 pixel) was synchronized with the spectrometer. Both appliances were controlled by a personal computer. The computer software WinSpec was used for the control. The spectrometer was calibrated by the emission lines of mercury and Ar/Ne lamp. After the acquisition of two-dimensional images the averaging of the signal on the part of the matrix where the image had been registered was done. Thus, the dependence of the intensity on the wavelengths was established. The ICCD camera was acquiring the signal during the time gate of 60 ns to get the time-integrated spectra. The camera was triggered by a triggering generator BNC 575m and the acquisition of spectra was started at the time instant corresponding to the propagation of one of the voltage pulses in plasma.

The incidence of light coming from the 2nd order of diffraction to the output slit of the spectrometer has been avoided by use of the following filters:

- 1) In the range of 200-400 any filters haven't been used.
- 2) A Thorlabs FGL400S filter was used in the spectral range of 400-600 nm.
- 3) In the range of 600-900 an orange glass OC-14 was used.

According to the quantum theory of radiation the intensity of any transition between two states n and m at the frequency ν_{nm} is:

$$I_{nm} = h\nu_{nm} \frac{[\mathbf{X}_n]}{\tau_0}.$$
(2.7)

Here, τ_0 is the lifetime of the excited level, $[X_n]$ is the concentration of the particles in the excited state. The intensity of the radiation is thus proportional to this concentration. Consequently, it was possible to establish the temporal dynamics of the concentrations of the excited species using a PMT. The sensitivity of a PMT is strictly dependent on the wavelengths of the registered radiation and it was important that the PMT Hamamatsu H6610 could be used only for the measurements in the range of 200-400 nm. The linearity check of the PMT was performed by means of filters of neutral density attached to the focusing lens. A filter of neutral density decreases the intensity of radiation with a known ratio regardless its wavelengths. The a) side of the Figure 2.4 demonstrates the dependence of the maximal ampli-

tude of the output signal of a PMT on the coefficient of the neutral density filter. The b) side of the Figure 2.4 demonstrates the signals normalized at unity. The dependences are linear and the normalized signals are in good agreement and the PMT can be considered as operating at linear regime.



Figure 2.4 – Linearity check of the Hamamatsu H6610 photomultiplier tube. a) Check by neutral density filters, b) Check by normalization of signal waveforms at different voltages applied to the PMT. Different curves correspond to measurements at various driving voltages.

It is crucial that any optical system has its sensitivity as a function of the registered wavelength. First, the sensitivity of the spectral system is determined by transmission of the optical elements (the material of the discharge capillary, filters, lenses, optical fibers). Second, the sensitivity of the system is determined by quantum efficiency of the diffraction gratings in the monochromator. Third, the sensitivity of the optical system is determined by quantum efficiency of the diffraction gratings in the monochromator. Third, the sensitivity of the optical system is determined by quantum efficiency of the light detector (ICCD camera or a photomultiplier tube). To obtain the absolute sensitivity of the spectral system the absolutely calibrated light source is required. However, in significant part of experiments it is not necessary to have the absolute values of intensity of plasma emission and it is the relation between emission on different wavelengths what matters. In this case, the total relative sensitivity can be calculated according to specifications of the equipment as a product of sensitivities of each optical element and detector in the optical system. The hardware functions are given in the Figures below in the same order as one would trace a light beam propagating from plasma. Figure 2.5 represents the transmission function of the Pyrex glass from



Figure 2.5 – Transmission function of the Pyrex glass from which the FTIR capillary has been fabricated. Transmission function of quartz of the thin capillary is considered to be constant at all wavelengths studied in experiments. Obtained by treating a figure from [88].

which the FTIR capillary has been fabricated. Transmission function of quartz of the thin capillary is considered to be constant at all wavelengths studied in experiments. Transmission function of the Thorlabs FGL400S filter and OC-14 orange glass are given in the Figure 2.6. As for appliances used for collection of the light, transmission function of the Uncoated UV Fused Silica Plano-Convex is given in the Figure 2.7. Transmission function of the BF13LSMA01 optical fiber is considered to be constant at all wavelengths studied in experiments. Then, Figure 2.8 the quantum efficiency of the diffraction grating and the ICCD camera used in the experiments. Finally, quantum efficiency of the Hamamatsu H6610 photomultiplier tube used in the experiments is given in the Figure 2.9.

2.4 Fourier Transform Infrared Spectroscopy(FTIR)

2.4.1 Basic principles of FTIR

FTIR spectroscopy is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high-resolution spectral data over a wide spectral range. It is important that FTIR spectroscopy is only available for study of rovibrational transitions whose dipole moment is nonzero. For instance, it is possible to study the absolute concentrations of molecules of such gases as CO and CO_2 (its bending and asymmetric stretch modes are infrared active) which are object of the scope of the current Thesis. The spectroscopy of absorption should be used for those purposes.

The base of any FTIR spectrometer is a Michelson interferometer where an infrared source of light with a wide continuous spectral range $I_0(\nu)$ is used. A beam is collimated and then is delivered to a beamsplitter with 50 % splitting factor. One of the beams formed by the beamsplitter is then reflected back by a mirror which can be moved (see Figure 2.10). Then, both beams pass through the FTIR diagnostic



Figure 2.6 – Transmission function of the Thorlabs FGL400S filter and OC-14 orange glass. Taken from [89].



Figure 2.7 – Transmission function of the Uncoated UV Fused Silica Plano-Convex. Transmission function of the BF13LSMA01 optical fiber is considered to be constant at all wavelengths studied in experiments. Taken from [89].



Figure 2.8 – (a) Quantum efficiency of the gratings used in the experiments. Red curve corresponds to the grating with 600 lines/mm and blaze 300 nm, green curve corresponds to the grating with 1200 lines/mm and blaze 500 nm, blue line corresponds for the grating with 2400 lines/mm and blaze 240 nm. (b) The quantum efficiency of the ICCD camera PI-MAX 4 1024i. Taken from [90].



Figure 2.9 – Quantum efficiency of the Hamamatsu H6610 photomultiplier tube used in the experiments. The Figure is obtained by treating data from [91].



Figure 2.10 – The principle scheme of a Michelson interferometer. Taken from [92].

cell filled with the object of study. Finally, the beams are captured by a light detector recording a signal $\Phi(x)$ which can be expressed as a function of optical path difference x between two beams. It is linear function of time dependent on the mirror coordinate provided that the mirror is being shifted with a constant speed. An additional laser whose beams are parallel to the beams of the light source is used for measurements of x. The signal $\Phi(x)$ recorded by the light detector is:

$$\Phi(x) = \int_{\nu_1}^{\nu_2} I_{\nu}(\nu) \cos(2\pi\nu x) d\nu.$$
(2.8)

Here, ν_1 and ν_2 are boundary frequencies of the light source, I_{ν} is the spectral intensity of the light source which is the object of the main interest. It can be found by a Fourier Transform which includes integration in the infinite coordinate space. However, in practice the coordinates are limited by the farthest mirror displacement L and the spectral intensity is found as:

$$I_{\nu}(\nu) = 2 \int_{0}^{2L} \Phi(x) \cos(2\pi\nu x) dx.$$
 (2.9)

As it can be deduced from the theory of Fourier transform, the spectral width of the line and therefore the resolution power of the spectrometer is proportional to L. Therefore, the more is possible to maximize the mirror displacement, the better is the resolution power of the spectrometer. Nevertheless, there is another limitation factor which is the aperture of the diaphragm of the light source. If it is too big, non-parallel beams appear and the delay between beams passed through the beamsplitter is varied. Consequently, the spectral width of the line is broadened. On the other hand, the aperture of the diaphragm of the light source shouldn't be too small. Otherwise, the signal-to-noise ratio becomes poorer.

As soon as $I_{\nu}(\nu)$ is obtained, the concentration of gases can be found according to Lambert-Beer law:

$$I_{\nu}(\nu) = I_0(\nu)exp(\sum_i n_i\sigma_i S), \qquad (2.10)$$

where S is the absorption path length, n_i are concentrations of the absorbing molecules and σ_i are cross-sections of the rovibrational transitions of molecules which can be found from databases. The cross-sections depend on the rotational and vibrational temperatures, therefore both can be defined from the analysis of the acquired spectra.

It should be noted that FTIR spectroscopy has two serious advantages compared to others techniques of spectroscopic measurements. The first advantage is the called Jacquinot's advantage which consists on the fact that FTIR aperture can be several orders of magnitude higher than the aperture of a monochromator based on diffraction gratings or on a prism. The second advantage (Fellgett's) arises from the fact that information from all wavelengths is collected simultaneously. It results in a higher signal-to-noise ratio and shorter scan-time for a given resolution.

2.4.2 Experimental procedure and data treatment

FTIR ex situ measurements were performed with a Bruker Vertex 70 FTIR spectrometer. The spectral resolution of the spectrometer was equal to 0.2 cm^{-1} . The spectrometer has been placed in the gas downstream (see Figure 2.1, lower part) and the time delay between the formation of species in plasma and FTIR measurements of their densities had the order of magnitude 1 ms which corresponds to the final gas states when any reaction rate can be considered as negligible. In order to measure the final dissociation fraction corresponding to saturation, each experimental point was obtained by several consecutive measurements of absorption spectra until the spectra stopped changing and became stable. The last measurements had been taken into account as corresponding to saturation of the FTIR bowl by the products of dissociation of CO_2 . It should be noticed that for the reasons of enhancement of signal-to-noise ratio the spectrometer has been cooled by liquid nitrogen during all measurements. For the purity of the signal all the system was purged by diatomic oxygen which is invisible for FTIR diagnostic. The IR spectra studied in the experiments correspond to absorption bands of the asymmetric stretch of CO_2 (between 2200 cm^{-1} and 2400 cm^{-1}) and the CO rovibrational band (between 2000 cm⁻¹ and 2250 cm^{-1}). The background signal was acquired two times. First, it was acquired at the conditions when the FTIR bowl was pumped out. Second, it was acquired at the conditions when the FTIR bowl was filled by the CO_2 at operating pressure. Both background signals were used for calculation of the hardware function of the spectrometer which was necessary for data treatment.

The details of the data treatment and the MATLAB code developed by B.Klarenaar can be found in [93] and [45]. However, the treatment of data acquired in the experiments described in the current Thesis has been simplified by the fact that constant temperature and, therefore, thermal equilibrium are considered to be established at timescale of the experiments, which is wrong for the cases described in the works of B.Klarenaar. The rotational temperature of both CO_2 and CO has been found to be equal to 300 K in all experiments with FTIR which will be described in the Chapter 4. Therefore, only the so called 'equilibrium script' was used for the data treatment. The script fits molecules included in HITRAN database [94] assuming thermal equilibrium. The scipt included several steps. First, rovibrational state distributions at a set dissociation fraction α were calculated from the HITRAN database. Second, the line strengths were calculated. The third step consisted on application of pressure and temperature broadening of the lines. Then, the transmittance was calculated according to the Lambert-Beer law. Finally, instrumental broadening had been applied to calculated spectra which were compared to the experimental ones. Therefore, both dissociation fraction of CO₂ and rotational temperature could be found. An example of fitted absorption spectrum is presented in the Figure 2.11.



Figure 2.11 – An example of fitted absorption spectra with subtracted background. Operating conditions: CO_2 flow rate - 7.4 sccm, pressure - 10.8 mbar, pulse repetition rate - 530 Hz, amplitude of the incident high voltage pulse - 9 kV. Credits: Ana Sofia Morillo Candas.

The author is expressing his acknowledgements for introduction and help in data acquisition and treatment to Dr. Olivier GUAITELLA and Dr. Ana Sofia MORILLO-CANDAS.

2.5 Reconstruction of radial profiles of active species

Plasma is an object with plenty of various species such as electrons, positive and negative ions, atoms and molecules either in ground or electronically excited state. Measurements of concentration of these various species are, in fact, records of their temporal and spatial profiles. Therefore, it was necessary to gather information not only about temporal dependence of concentrations of active species but about the discharge spatial structure as well. As soon as the experiments were conducted in a capillary where a fast ionization wave was propagating, it was assumed that plasma profile is homogeneous along the whole length of the capillary. The problem was therefore to restore the 1D-structure of the radiation (as a function of radius) which is related to the radial distribution of species of interest such as electrons and positive ions.

2.5.1 Experimental procedure

First, it should be noted that the experiments were conducted both in pure CO_2 and in a $CO_2:N_2=10:1$ mixture.

To collect the information about the discharge radial distribution, an ICCD camera with an optical system was required. If the image is obtained by a lens, the data cannot be treated as a spatial distribution of the excited species since plasma isn't a volumetric object, and a set of photons come to the ICCD detector from different regions of the discharge. If each pixel comes to the ICCD matrix from parallel beams only, the reconstruction of radial profile becomes possible. The signal F(y) can therefore be considered as a result of direct Abel transform of the radial profile f(x; y) = f(r) which is the object of our interest. Thereby, in order to restore the f(r) it was necessary to apply inverse Abel transform (IAT) to the signal acquired by the ICCD camera. The details of the procedure can be found in [65, 95].

To gather the data which were consequently treated by the IAT, it was necessary to place the ICCD camera in such a way that the beams coming from the discharge cell could be considered as parallel. This goal could be reached by placing the camera at a distance equal to > 20 radii of the discharge cell. The camera should have been placed in a horizontal and stable way and should have been able to record the entire vertical of the discharge. The gate and delay of the camera could be monitored by the WinSpec software. The gate of the camera should have been as small as possible (<5 ns) and the gate delay was selected according to the time instant of interest. To choose a wavelength of interest corresponding to an atomic or molecular transition

representing the distribution of active species in plasma, a narrow bandpass filter was used. Finally, it was essential to take a photo of the lightened discharge cell (see Figure 2.12). It was necessary for image scaling (in the current case, 1 mm was equal to 18.66 pixels). As soon as the image had recorded, it was necessary to select a vertical line for slicing (see Figure 2.13, red line). The F(y) is the light intensity function along the red line. An input file which was treated by the code was therefore a column with numbers designating the emission intensity. A number of an element in the column is the number of pixel along the vertical line.



Figure 2.12 – An ICCD photo of the lightened capillary



Figure 2.13 – An example of image recorded by an ICCD camera. The vertical (y axis) along which the light intensity F(y) will be treated by the IAT is marked by the red line.

2.5.2 Inverse Abel transform

Mathematical background

As it was mentioned above, an ICCD-camera registers the direct Abel transform of the radial profile of the discharge and it is therefore to reconstruct it by applying the inverse Abel transform to the ICCD-image. In the case of cylindrical symmetry the light intensity F(y) can be written as:

$$F(y) = 2 \int_{y}^{r_0} \frac{f(r)rdr}{\sqrt{r^2 - y^2}},$$
(2.11)

where r_0 is the radius of the capillary and f(r) is the radial profile we want to find. The latter can be expressed by the expression:

$$f(r) = \frac{1}{\pi} \int_{r}^{+\infty} \frac{dF(y)}{dy} \frac{dy}{\sqrt{y^2 - r^2}}$$
(2.12)

which is, in fact, inverse Abel transform. The integral can be taken by part and doesn't seem to pose any problem. However, an analytical solution is only correct if the f(r) tends to zero faster than 1/r, which is not necessarily the case (see [67]). Therefore, the numerical solution of the problem is required. [65, 96]. The f(r) can be written as a polynomial expansion of order n:

$$f(r) = a_0 + a_1 r + a_2 r^2 + \dots + a_n r^n.$$
(2.13)

Thus, the equation 2.11 can be rewritten as:

$$F(y) = 2 \int_{y}^{r_0} \frac{(a_0 + a_1r + a_2r^2 + \dots + a_nr^n)rdr}{\sqrt{r^2 - y^2}};$$
(2.14)

$$F(y) = \sum_{k=0}^{n} a_k I_k(y).$$
 (2.15)

Here, the set of $I_k(y)$ functions acts as set of n basis functions which can be precalculated analytically. a_k are unknown coefficients which are required to be found. The purpose of the code was therefore to find these coefficients by Least Square Method (LSM). Let F(y) be a discrete function which is set at M points known experimentally. Here, M is the total amount of pixels and $i = \overline{1, M}$ is a pixel number. The function F(y) can be projected on the basis functions $I_k(y), k = \overline{0, n}$:

$$(F(y), I_k(y)) = \sum_{i=0}^{M} F(y_i) I_k(y_i).$$
(2.16)

Hereinafter, round brackets will designate the scalar product of vectors. The set of projection can be therefore written in vectorial form:

$$(F, I_k) = \begin{pmatrix} (F, I_0) \\ (F, I_1) \\ \dots \\ (F, I_n) \end{pmatrix} = B$$
(2.17)

On the other hand, it is necessary to find the vector of unknown coefficients X:

$$X = \begin{pmatrix} a_0 \\ a_1 \\ \dots \\ a_n \end{pmatrix}$$
(2.18)

which can be expressed, according to equation 2.15, as a solution of a problem of global minimum research:

$$X = argmin((F - \sum_{k=0}^{n} a_k I_k, I_j)); \quad j = \overline{1, n}.$$
(2.19)

As the scalar product is bilinear, the equation 2.18 can be rewritten as:

$$X = argmin((F, I_j) - (\sum_{k=0}^{n} a_k I_k, I_j)); \quad j = \overline{1, n};$$
(2.20)

$$\sum_{k=0}^{n} (I_k, I_j) a_k \approx (F, I_j); \quad j = \overline{1, n}.$$
(2.21)

the equation 2.21 can be rewritten by introducing the following notion:

$$A = \sum_{k=0}^{n} (I_k, I_j) = \begin{pmatrix} (I_0, I_0) & (I_0, I_1) & \dots & (I_0, I_n) \\ (I_1, I_0) & (I_1, I_1) & \dots & (I_1, I_n) \\ \dots & \dots & \dots & \dots \\ (I_n, I_0) & (I_n, I_1) & \dots & (I_n, I_n) \end{pmatrix}.$$
 (2.22)

Finally, combining equations 2.17, 2.18 and 2.22 one obtains the system of n equations to solve by LSM:

$$AX \approx B$$
 (2.23)

Wall emission estimate

It can be seen in the Figure 2.12 that the quartz walls of capillary emits the light as well as plasma. This light is eventually reflected and refracted on surfaces of the walls. The light then propagates to plasma. Therefore, the signal captured by the ICCD camera should be corrected on wall emission. It has been justified in [65], that the wall emission parallel to the optical axis can be considered as emission from the plasma channel fixed in the free space without any wall in axially symmetric approximation.

To do the correction procedure, it was assumed that the intensity of light scattered in the quartz wall can be written as superposition of two exponential decay functions:

$$W_{quartz}(r) = A_1(exp(-\frac{r-R_{int}}{\alpha}) + A_2exp(-\frac{R_{ext}-r}{\alpha})), \qquad (2.24)$$

where $r \in [R_{int}; R_{ext}]$. If $r \notin [R_{int}; R_{ext}]$, $W_{quartz}(r) = 0$. If one applies direct Abel transform to the function $W_{quartz}(r)$, the estimate of wall emission contribution $I_{estim}(r)$ to the signal recorded by the ICCD camera can be obtained. It is then possible to find the coefficient $A_1 = I_{exp}(R_{int})/I_{estim}(R_{int})$ which is, in fact, a scaling factor between the experimental $I_{exp}(R_{int})$ and predicted $I_{estim}(R_{int})$ intensities of emission taken at position $r = R_{int}$. The other coefficients A_2 and α have been found with a Least Square Method. The program was searching for the best coefficients in a 2D grid which had been preset manually (e.g. $\alpha \in [0.2; 0.9], A \in [0.3; 0.5]$). To do so, the program was running through all possible pairs (α , A_2), calculating the expression of $W_{quartz}(r)$ and its direct Abel transform $I_{estim}(r)$. The optimal pair of coefficients (α , A_2) were the ones whose corresponding function $I_{estim}(r)$ obtained by direct Abel transform of $W_{quartz}(r)$ was the closest to the experimental profile between external and internal wall radii in the sense of the residual sum of squares between two profiles. The correction procedure is illustrated in the Figure 2.14.



Figure 2.14 – Illustration of correction of an experimental profile $I_{exp}(r)$ (black curve) on wall emission $I_{estim}(r)$ (red curve). The corrected profile is designated by the blue curve. Pure CO₂, 11 ns after plasma ignition.

More details of the calculations can be found in [65, 96]. The author is thankful to Dr. Inna OREL and Youssef HAOUCHAT who have developed a reliable and user-friendly Python3 code with a User Interface. The code was used to apply both the correction of signal on wall emission and inverse Abel Transform on the corrected signal by solving the system of linear equations 2.23 by Least Squares Method.

Chapter 3

Electric characteristics of the discharge

The current Chapter is devoted to the description of the electric characteristics of the discharge such as applied electric voltage, electric current flowing through the discharge cell, waveform of the electric field and energy, deposited in plasma. Study of all these parameters are an indispensable initial step because they define all kinetic processes occurring in the discharge and its afterglow.

3.1 Applied voltage and electric current

The first electric characteristics which were recorded in both capillaries were the waveformes of the applied voltage and electric current flowing through the discharge cell. The measurements have been down with the help of back current shunts connected to a digitizing oscilloscope. The details of the acquisition procedure of applied voltage has been described in details in the Chapter 2; as it has been mentioned in the Chapter, both values are related by the equation (2.1). It should be reminded that the main difference between the acquisition procedure in the thin and FTIR capillaries was the number of used back current shunts. Two BCSs were used in the experiments with the thin capillary and a single BCS was used in the experiments slightly different procedures of data treatment.



Figure 3.1 – Waveform of the voltage applied to the thin capillary measured by the BCS1 at pressure of 15.5 mbar. Three incident pulses and their reflections from the discharge cell are noted.

3.1.1 Thin capillary

A typical waveform of the voltage applied to the thin capillary measured be the BCS1 is given in the Figure 3.1. The operated pressure was equal to 15.5 mbar as the amplitude of the transmitted current was the highest and the discharge was the most stable at this condition.

As it has been said before, there were three incident pulses in total. The first one was the pulse created by the HVG. Its parameters were the following: peak amplitude 9.4 kV, rise time 4 ns and width 30 ns FWHM. The first (1^{st} INC) pulse created plasma in the discharge cell, the second and third pulses affected the ionized gas. The origin of the second and the third pulse was the following. Provided that group velocity of propagation of the signal in the high voltage cable was equal to 20 cm/ns (see equation 2.4), the length of the part of the cable between the discharge cell and BCS1 was equal to 11.6 m and the length of the part of the cable between the BCS1 and the HVG was equal to 12.8 m, the first high voltage pulse arrived to

the discharge cell from the HVG after 122 ns. Then, the pulse has been partially reflected from the discharge cell due to mismatch between the impedance of the discharge cell and the impedance of the high voltage cable, Z = 50 Ohm (see equation 2.5). Thus, the 1st REF was formed. After 122 ns the reflected pulse reached the generator whose resistance could be considered as infinitely small value R = 0. According to the equation 2.5 the sign of the voltage changes what can be seen in the Figure 3.1. During this time, impedance of the output of the HVG had been switched to zero. Therefore, the pulse 1st REF was reflected from the generator with inverse polarity forming the 2nd INC pulse which, in its turn, was reflected again from the discharge cell (2nd REF). That repeated one more time and the pulses 3rd INC and 3rd REF had been formed. The time delay between two consequent pulses was equal to 244 ns. For the reason of the decay in the high voltage cables, the amplitudes of the consequent reflections were negligible compared to the first three pulses, thus only them had been taken into account.

As for the electric current flowing in the discharge cell, it has been measured by the BCS2. The waveform of the voltage transmitted through plasma $U_{tra}(t)$ acquired by the oscilloscope has been divided on the wave resistance of the cable Z = 50 Ohm and thus the electric current waveform $I_{tra} = U_{tra}(t)/Z$ has been obtained. The length of the part of the high voltage cable between the discharge cell and the BCS2 was equal to 12.8 m. A typical waveform of the electric current measured at the pressure of 15.5 mbar by the BCS2 is given in the Figure 3.2. Again, such pressure provided the most stable regime of the discharge and the highest transmitted current. In that case, its peak amplitude in the first pulse was equal to 130 A.

The dependence of the maximal current in the first transmitted pulse on the CO_2 pressure is given in the Figure 3.3. It was observed that at low pressures the discharge current increases abruptly as long as the pressure increases. Stability of the transmitted current starts at pressure of 11.1 mbar. As the pressure reaches such value, the maximal current becomes stable and equal to 118 A and deviates on 3% from this value in 15% of shots. At the pressure of 15.5 mbar, the maximal current in the first pulse is equal to 130 A and it deviates on 3% from this value in 9% of shots. As long as the pressure is being increased, the maximal current is being steadily decreased and the rate of deviation from the maximal value becomes higher forming a multi-modal distribution of the passing current. Decrease of the peak current and instability of the discharge at low pressures can be explained by the fact that the value of the radial reduced electric field is too high for development of a FIW. In its turn, increase of the pressure slows down the discharge current since the value of the reduced electric field is not enough for stable production of electrons



Figure 3.2 – Waveform of the electric current flowing in the thin capillary measured by the BCS2 at pressure of 15.5 mbar. Three transmitted pulses are noted.

by ionization. In conclusion, the value of 15.5 mbar has been chosen as the optimal pressure for almost all consequent experiments with the thin capillary.

3.1.2 FTIR capillary

As it was mentioned before, the main difference between the thin capillary and FTIR capillary consisted on the fact that the latter had its low voltage electrode grounded. Consequently, it was possible to measure the electric current and applied voltage by one back current shunt only. The waveform of the voltage applied to the FTIR capillary and recorded by the BCS is given in the Figure 3.4. The first incident pulse (1^{st} INC) was the same as it has been just described for the thin capillary. It can be seen between 0 and 40 ns.

The most important pecularity of the applied voltage waveform consists on the fact that the incident pulse reflects both from high voltage and low voltage electrodes.



Figure 3.3 – Dependence of the peak current in the first pulse on the pressure in the discharge cell. Red points designate absence or instability of the current, black points designate the most stable regime of the discharge, blue points designate bi-modal behaviour of the transmitted current.

The reflection from the latter means that the direction of propagation of the pulse changes its sign and therefore the polarity of the incident pulse is reversed after a certain time instant. The distorted pulse came back to the BCS and thus the 1^{st} REF was formed. In the current case, the change of polarity can be seen in the Figure 3.4 at 121 ns time instant. Then, the 1^{st} REF pulse reflected from the generator. The length of the cable between the discharge cell and the BCS was equal to 10 m; a part of the cable of the same length was between the BCS and the generator. The 1^{st} REF came back to the discharge cell forming the 2^{st} INC pulse. Then, the same behaviour had repeated and consequent pulses were formed. Time delay between two consequent pulses was equal to 200 ns. As in the case of the thin capillary, three incident pulses had been taken into account. The amplitudes of the consequent reflections were negligible with respect to the first three pulses.

Calculations of the electric current flowing in the FTIR capillary were not as simple



Figure 3.4 – Waveform of the voltage applied to the FTIR capillary measured by a back current shunt at pressure of 8.1 mbar. Three incident pulses and their reflections from the discharge cell are noted.

and accurate as it had been for the thin capillary. The reason of the issue was the same - absence of the low voltage cable and another BCS. Thus, it was only possible to estimate the transmitted current. The estimation has been done, according to a suggestion of Dr. Andrey KLOCHKO [97], in the following way, . Let $U_{inc}(t)$, $U_{ref}(t)$ be the waveforms of the incident and reflected pulses, respectively. In fact, the $U_{ref}(t)$ was $U_{inc}(t)$ shifted by 100 ns and multiplied by -1. Therefore, the waveforms have been synchronized as it demonstrated in the Figure 3.5a. As soon as synchronization has been done, it was possible to estimate the waveform of transmitted current $I_{tra}(t) = (U_{inc}(t) - U_{ref}(t))/Z$, where Z=50 Ohm is the wave resistance of the cables. The waveforms of the electric current in FTIR and thin capillaries in the first pulse are presented in the Figure 3.5b. The difference between peak amplitudes of the current of almost 2 times can be observed. It can be explained by the fact that the energy of the high voltage pulse hadn't been spent to charge of the low voltage cable as it had been occurring in the case of the thin capillary. Another observation is that there is a step of 30 A between 100 and 112 ns.
step corresponds to the propagation of a FIW in the discharge cell. In this period of time, the electric current flows from the HV electrode but doesn't reach the LV electrode since the current in the FIW front is circuited on the copper screen by displacement current.

Again, calculation of the electric current flowing in the FTIR capillary can only be rather rough since one doesn't know an amount of energy of the high voltage pulse spent to charge of capacitance of the discharge cell and gone to the ground.

3.2 Electric field

3.2.1 Thin capillary

As it has been previously mentioned, the longitudinal electric field in the thin capillary could be measured in two different independent ways. The first method was based on back current shunts technique. The electric field in the thin capillary could be deduced in the following way. Let $U_{inc}(t)$, $U_{ref}(t)$ and $U_{tra}(t)$ be temporal profiles of incident pulse, the pulse reflected from the discharge cell and the pulse transmitted through the discharge cell, respectively. $U_{inc}(t)$, $U_{ref}(t)$ waveforms were registered by BCS1 and $U_{tra}(t)$ waveform was registered by BCS2. Then, the pulses should have been synchronized according to the lengths of the part of the high voltage cables between the elements of the circuit. Synchronized incident, reflected and transmitted first pulses are given in the Figure 3.6. The difference of the waveforms of the incident and reflected pulses is also given in the Figure. Slight discrepancy between the waveforms of that difference and the transmitted current can be explained by the fact that the part of the electric energy of the high voltage pulse is spent to the charge of the capacitance of the discharge cell system. As in the case of the FTIR capillary, the step between 18 and 30 ns corresponds to the propagation of a FIW in the discharge cell.

As soon as the waveforms are synchronized, the electric field as a function of time can be calculated as the difference of potentials on the electrodes divided on distance d = 7.0 cm between them:

$$E(t) = \frac{U_{inc}(t) + U_{ref}(t) - U_{tra}(t)}{d}$$
(3.1)

The reduced electric field E/n(t) can be obtained by division of the E(t) on concentration of molecules $n = p/k_B T$, where p is gas pressure in the discharge cell, T = 300K is room temperature, k_B is Boltzmann constant.



b)

Figure 3.5 – a) Synchronized waveforms of the incident and reflected pulses b) Synchronized waveforms of the electric current in FTIR and thin capillaries in the first pulse. Pure CO_2 , 8.1 mbar.



Figure 3.6 – Synchronized waveforms of the incident (black), reflected (red) and transmitted(blue) first pulses. The difference of incident and reflected pulses is denoted by the green curve.

The measurements of the temporal profile of the electric field by back current shunts have a serious drawback. Since they may only register the flowing of conduction current, they are insensitive to displacement current between the discharge cell and the metallic cage. Therefore, it is impossible to record the electric field in a fast ionization wave by back current shunts. Such an impossibility leads to the incompleteness of understanding of the ionization dynamics of the discharge and therefore the processes responsible for growth of the electron density can't be taken into account with a sufficient correctness. Consequently, it was necessary to use another method for measuring the reduced electric field - a capacitive probe (CP). The details of the measurements of the electric field by a capacitive are given in the Chapter 2. The synchronized waveforms of the reduced electric field measured by BCSs and CP are given in the Figure 3.7a.

The announced difference between two ways of electric field measurements has been observed. In the waveform of the electric field measured by capacitive probe there is a step at the time period between 0 and 17 ns. The step corresponds to the so called Laplace field which is the field dependent only on the voltage on HVelectrode. Therefore, the Laplace field can exist at the condition of zero spatial discharge. Consequently, the Laplace field is equal to sum of the incident and re-



Figure 3.7 – a) Temporal profiles of the reduced electric field in the first pulse measured by capacitive probe (black curve) and back current shunts (red curve). The waveform of the electric field measured by BCSs multiplied on scaling factor 0.6 is designated by the blue curve. b) Waveforms of the electric current and reduced electric field in the first pulse. Pure CO_2 , 15.5 mbar, thin capillary.

flected pulses multiplied on a scaling factor less than unity. Then, a sharp peak in the period of time of 17-21 ns can be seen. The peak corresponds to the propagation of a fast ionization wave (FIW) near the capacitive probe. [52, 65]. The FIW starts from the HV-electrode and reaches the LV-electrode at the time instant of 27 ns. This is the time instant at which the FIW reaches the LV-electrode and the conduction current starts to flow in the discharge tube (see Figure 3.7b). The reverse wave of the potential starts to develop from the LV-electrode at time instant of 29 ns. This wave causes an increase of the electric field registered by the capacitive probe. At the same time, the potential on the high voltage electrode drops down. When the electron density becomes high enough to establish the conducting regime in the discharge tube the waveforms of reduced electric field measured by the CP and the system of BCSs come to a good agreement (after 30 ns). It can be seen in the Figure 3.7b. As for synchronization of the waveforms of the reduced electric field from CP and BCSs, it has been made in such a way that the left front of the field from BCS multiplied on a scaling less than unity (Scaled Back Current Shunts) in the Figure 3.7a) and the Laplace field from the CP match. In the current case, the scaling factor was found to be equal to 0.6. As soon as the synchronization has been made, the right fronts of the waveforms after 30 ns came to an agreement.

The waveforms of the reduced electric field in the second and the third pulses measured by both capacitive probe and back current shunts are demonstrated in the Figure 3.8. As the fast ionization wave had been already passed in the first pulse, the gas is ionized when the second and third pulses arrive to the discharge cell. Thus, the electric current flowing in the discharge is the conduction current and the measurements of the electric field by back current shunts is correct. Consequently, both ways of measurements are in agreement.

3.2.2 FTIR capillary

As it has been already mentioned, there was no opportunity to use a capacitive probe in the case of the FTIR capillary. Therefore, the only way to estimate the electric field was to use a back current shunt. If $U_{inc}(t)$ and $U_{ref}(t)$ are waveforms of the incident and reflected pulse, respectively, $U_{inc}(t) + U_{ref}(t)$ is voltage on the high voltage electrode. The low voltage electrode is grounded, thus the expression describes the difference of potentials on the electrodes as well. By division on the interelectrode distance d one obtains:

$$E(t) = \frac{U_{inc}(t) + U_{ref}(t)}{d}.$$
 (3.2)



b)

Figure 3.8 – Temporal profiles of the reduced electric field measured by capacitive probe (black curve) and back current shunts (red curve) a) in the second pulse, b) in the third pulse. Pure CO_2 , 15.5 mbar, thin capillary.

The reduced electric field can obtained from E(t) in the same manner as it was described for the thin capillary. The Figure 3.9 represents the temporal profiles of the estimated reduced electric field and electric current in the first pulse at 8.1 mbar.



Figure 3.9 – Waveforms of the electric current (red curve) and the reduced electric field (black curve) in the first pulse. FTIR capillary, pure CO_2 , pressure 8.1 mbar.

The choice was justified by the fact that the maximum deposited energy was reached at this pressure (see 3.3.2). It was said that measurements of the electric parameters of the discharge by one back current shunt only are less accurate than by two BCSs. The reason of the inaccuracy is the fact that a BCS is insensitive to the displacement current. Therefore, the only meaningful part of the E/n waveform is the one after the step in the waveform of the electric current (65 ns and later, corresponds to the establishment and development of conduction current). Nevertheless, it can be concluded that the reduced electric field at 8.1 mbar is at least equal to $E_{max} \approx 1100$ Td which is even higher than E/n in the FIW propagating in the thin capillary at 15.5 mbar. Occurrence of such high reduced electric field can be explained by absence of the low voltage cable since $E_{max} \approx U/ln$, where U=9200 kV is the amplitude of the applied voltage, l = 7.5 mm is distance between electrodes and n is concentration of the gas at 8.1 mbar.

3.3 Deposited energy

3.3.1 Thin capillary

In experiments conducted in the thin capillary it was possible to use data acquired by back current shunts and capacitive probe to calculate the energy deposited into plasma. According to [48, 65], such a way of measurements is more accurate than another way which is based on data acquired by two back current shunts only and in which the capacitive probe isn't used. The reason for this accuracy is that the CP allows to measure deposited energy in the capillary itself and not in the side tubes. In [65] it is mentioned that up to 20% of total energy could be spent to creation of plasma in the side tubes. Let $E_{CP}(t)$ and $I_{tra}(t)$ be temporal profiles of the electric field measured by the capacitive probe and transmitted current, respectively. In this case, the energy W(t) deposited into the discharge can be calculated as follows:

$$W(t) = \int_{t_0}^{t} E_{CP}(t') l I_{tra}(t') dt', \qquad (3.3)$$

where l is the interelectrode distance and t_0 is a time instant corresponding to the beginning of the integration. Temporal profile of specific deposited energy $\omega(t) = W(t)/nV$, where $n = p/k_BT$ is concentration of molecules and V is the volume of the discharge cell; p is gas pressure in the discharge cell, T = 300 K is room temperature, k_B is Boltzmann constant. $\omega(t)$ is presented in the Figure 3.10. Specific deposited energy is expressed in meV per particle. The waveforms of the reduced electric field and electric current are given in the same Figure. It can be seen that the energy starts to be deposited into plasma as soon as the conduction current starts to flow between the electrodes. The total specific deposited energy in the first pulse is approximately equal to 1 eV/particle.

Figure 3.11a demonstrates the specific deposited energy in all three pulses at various pressures. First, it can be seen that the pressure 15.5 mbar is the pressure providing one of the highest values of specific deposited energy delivered into plasma in the first pulse. Along with that, a stable and relatively high peak current at such pressure has been observed. As for the second pulse, an addition of approximately 30% of the first pulse is added into plasma. The specific energy input in the third pulse is negligibly small. Therefore, the total specific energy at 15.5 mbar is around 1.5 eV/particle. However, the pressure 15.5 mbar is not the optimal one it terms of percentage of absorbed energy with respect to pulse energy. It can be seen in the Figure 3.11b that the pulse energy is the better absorbed by plasma, the higher is the gas pressure. Such a behaviour may be explained by the fact that the peak electric current decreases slower than the pressure increases (see Figure 3.3). Consequently, the specific deposited energy which is, in fact, directly proportional to convolution of the waveforms of the electric current and the reduced electric field, increases monotonously with the increase of gas pressure.



Figure 3.10 – Reduced electric field, electric current and specific deposited energy as a function of time. Thin capillary, pure CO_2 , p = 15.5 mbar.

3.3.2 FTIR capillary

The measurements of the deposited energy by the aforementioned combination of the back current shunts and the capacitive probe were impossible in the case of FTIR capillary. The only way to do so was to use the waveform recorded by the BCS1. Let $U_{inc}(t)$ and $U_{ref}(t)$ be temporal profiles of the voltage of incident and reflected pulses, respectively. In this case, the energy W(t) deposited into the discharge can be calculated as follows:

$$W(t) = \frac{1}{Z} \int_{t_0}^t (U_{inc}^2(t') - U_{ref}^2(t')) dt', \qquad (3.4)$$

 t_0 is a time instant corresponding to the beginning of the integration. Specific deposited energy can be found in the same way as for the thin capillary.

Specific deposited energy in all three pulses at various pressures is demonstrated in the Figure 3.12a. It can be seen that the pressure 8.1 mbar and is the pressure providing one of the highest values of specific deposited energy delivered into plasma in the first pulse. As it will be discussed in the Chapter 4, this is the pressure which provides maximal dissociation fraction. As for the second pulse, additional amount of energy of approximately 30-50% of the first pulse is added into plasma. Just like in the case of the thin capillary, specific energy input in the third pulse is negligibly



b)

Figure 3.11 - a) Specific deposited energy in three pulses at various pressures. b) Ratio between the energy deposited into plasma and energy of the pulse. Thin capillary.



b)

Figure 3.12 - a) Specific deposited energy in three pulses at various pressures. b) Ratio between the energy deposited into plasma and energy of the pulse. FTIR capillary.

small. In total, the specific energy at 8.1 mbar is around 5.5 eV/particle which is 3-4 times higher than specific deposited energy in the thin capillary measured at 15.5 mbar. The pressure 8.1 mbar is second optimal one in terms of percentage of absorbed energy with respect to pulse energy. It can be seen in the Figure 3.11b that total absorbance of energy by plasma has an optimum at 10.9 mbar. The similar behaviour is observed for the absorbance of energy in the second pulse. It can be assumed that the gas is well ionized in the first pulse but relatively significant additional ionization processes occur in the second pulse.

3.4 Conclusions

Study of the most essential electrical characteristics of the nanosecond pulsed discharge in pure CO_2 such as applied voltage, electric current, reduced electric field and specific deposited energy has been described in the current Chapter. The measurements have been done both in FTIR and thin capillary at various pressures.

As for the thin capillary, the pressure at which the maximal value of the electric current has been obtained was found to be 15.5 mbar. The value of the electric current was as high as 120 A which is almost 1.5 times higher than the maximal value of the electric current obtained on the same discharge cell in pure air at 27 mbar and described in [48, 98] and 2 times higher than the same parameter in pure nitrogen at 27 mbar [64, 65]. The specific deposited energy in all three pulses at 15.5 mbar in the thin capillary was around 1.5 eV/particle. The same value has been reported for pure air at 27 mbar [48], as for pure nitrogen, a comparable value of 0.9 eV/particle is mentioned in [64]. The measurements of the electric field by a capacitive probe in the thin capillary showed that there was a fast ionization wave (FIW) propagating in the tube from the high-voltage electrode to the low-voltage one. The estimated values of the reduced electric field in the FIW were 1000-1200 Td. It is higher than it have been obtained previously both in pure air (800-900 Td) [98] and pure nitrogen (600-700 Td) [64].

As for the FTIR capillary, it was only possible to obtain the electrical parameters in the first pulse. Moreover, as it wasn't possible to measure the temporal profile of the reduced electric field E/n by a capacitive probe, E/n mean value could only be estimated. Nevertheless, it can be still concluded that the amplitude of the electric current in the first pulse was at least 2 times higher than the same quantity measured in the thin capillary. The pressure optimal for maximization of electric current and specific deposited energy was found to be 8.1 mbar. The total deposited energy in the FTIR capillary was around 5.5 eV/particle which is more than 3 times higher than in the thin capillary. It is therefore straightforward to investigate how such a significant value of specific deposited energy would influence the dissociation of CO_2 . The measurements of dissociation fraction and energy efficiency of dissociation of CO_2 are described in the next Chapter.

Chapter 4

Measurements of CO_2 dissociation fraction and its energy efficiency by FTIR

The results of measurements of absolute densities of CO and CO_2 produced in the FTIR discharge cell and acquired in its downstream are presented in this Chapter. Due to these measurements, it was possible to calculate the dissociation fraction and its efficiency which were the objects of the main interest. These measurements were done at different conditions.

4.1 Dissociation fraction and energy efficiency at different pressures at low pulse frequency regime

First, dissociation fraction and its efficiency was measured at low frequency pulse regime at different pressures. The values of pressure were varied varied between 5 mbar and 35.4 mbar. The flow rate and peak voltage of the incident high voltage pulse were constant and equal to 7.4 sccm and 9.4 kV, respectively. The purpose of these measurements was to find the optimal pressure for both parameters with the least possible change of number of pulses N treating a portion of gas in the discharge cell. Another requirement to the pulse frequency was to maintain N close to unity.

The value N can be found in several steps. First, the actual flow rate can be calculated from the standard flow rate according to the following equation:

$$Q = Q_{st} \frac{p_{st}T}{pT_{st}}.$$
(4.1)

Here, $p_{st} = 1000$ mbar and $T_{st} = 273$ K are pressure and temperature corresponding to standard conditions. p is pressure taken as average between values of two pressure gauges installed upstream and downstream and was varied between 5 mbar and 35.4 mbar. The most interesting value which is an object of discussions is gas temperature T. The simplest way to assume its value is to take the temperature Tequal to room temperature. Let's verify the validity of the assumption. Since it is gas density which influences the N value, it is necessary to calculate the characteristic time τ_{per} of propagation of an acoustic perturbation in the discharge cell which characterizes the time of change of gas density in the discharge cell. It can be found in the following way [99]:

$$\tau_{per} = \frac{l}{c} = \frac{l}{\sqrt{\frac{\gamma RT}{\mu}}}.$$
(4.2)

Here, l = 8 cm is the length of the thin part of the capillary, c is the speed of sound in the CO₂ atmosphere, $\gamma = 7/5$ is the adiabatic index of CO₂, $\mu = 0.044$ kg/mol is its molar mass, R = 8.31 J/mol is the universal gas constant. After all calculations at T=300 K one obtains $\tau_{per} = 2.8 \times 10^{-4}$ s. This value should be compared with the residence time of a gas portion in the discharge cell which depends on pressure. The latter was varied between 5 mbar and 35.4 mbar. Coming back to the equation (4.1) one obtains that the gas residence time τ_{res} :

$$\tau_{res} = \frac{V}{Q},\tag{4.3}$$

where $V = 0.236 \text{ cm}^{-3}$ is the volume of the thin part of the discharge cell. Combining equations (4.1) and (4.3) one obtains that the gas residence time is varied between 8.7×10^{-3} s for pressure of 5 mbar and 6.0×10^{-2} s for pressure of 35.4 mbar. As it could be seen, the residence time exceeds the characteristic time of change of density by 1-2 orders of magnitude which is unacceptable for validation of assumption $T_{gas} =$ 300 K. On the other hand, the main direction of heat flux away from the discharge cell is through its walls. Therefore, it is possible to estimate the diffusion time τ_{diff} of CO₂ molecules from the axis of the capillary to the walls. According to the theory of diffusion, τ_{diff} can be expressed as [99]:

$$\tau_{diff} = \frac{r^2}{2D},\tag{4.4}$$

where r=1 mm is the radius of the capillary, D is diffusion coefficient which can be estimated using Chapman-Enskog theory [100]:

$$D = \frac{AT^{3/2}}{p\sigma^2\Omega}\sqrt{\frac{2}{\mu}},\tag{4.5}$$

where $A = 1.859 \times 10^{-3} \frac{\operatorname{atm} \operatorname{cm}^2 \mathring{A}^2}{\mathrm{K}^{3/2} \mathrm{s}} \sqrt{\frac{g}{mol}}$, *T* is gas temperature in K, $\sigma^2 \approx 10 \ \mathring{A}^2$ is the cross-section of collisions of CO₂ molecules between each other, *p* is gas pressure in atm (0.01 atm has been taken), μ is molar mass of the gas expressed in g/mol, Ω is a temperature-dependent collision integral usually of order of unity. *D* is expressed in $\frac{\operatorname{cm}^2}{s}$. After all calculations one obtains $D = 20.6 \ \frac{\operatorname{cm}^2}{s}$ and $\tau_{diff} = 2.4 \times 10^{-4}$ s. It can be seen that diffusion time τ_{diff} is very close to the characteristic time of change of gas density τ_{per} . It means that if the gas was heated by the discharge only during first hundreds of nanoseconds, the gas will be already cooled down when the gas density will respond to the heating and change. However, chemical reactions of excited species in the discharge afterglow may provide additional heating, as it was the case for oxygen and nitrogen [58]. Therefore, additional study of temperature temporal profile is required. More information about this is given in the Chapter 8. In conclusion, all along the Chapter the number of pulses treating a portion of gas is calculated as if T was constant and equal to 300 K.

The number of pulses treating a portion of gas in the discharge cell N can be found as:

$$N = f\tau_{res}.$$
(4.6)

f here is pulse repetition rate. The measurements were being done at f=33 Hz repetition rate. After the calculations, N=0.3 pulses per portion at p=5 mbar and N=2.1 pulses per portion at p=35.4 mbar are obtained. Both values are close to 1, therefore the results may be considered as representing the dissociation of CO₂ in single pulse regime. The results of the measurements are given in the Figure 4.1. The dissociation fraction and its efficiency have been calculated according to the equations (1.6) and (1.7). The energy deposited into plasma has been calculated as a total integral on a train of three incident pulses (see equation (3.4)). The energy efficiency has been corrected on the number of pulses per portion N which is given in the Figure as numbers near the experimental points.

As it could be seen in the Figure 4.1, both energy efficiency and dissociation fraction decrease slightly within the increase of gas pressure. The decrease of dissociation fraction can be explained by the increase of collision rate between excited molecules, and therefore, to accelerated loss of electronical and vibrational excitation which are both crucial for dissociation of gases in plasma. In addition, number of pulses per portion of gas N increases with the pressure, thus the energy cost increases. On the other hand, it is obvious that dissociation fraction should be low at pressures close



Figure $4.1 - CO_2$ dissociation fraction and its energy efficiency at low frequency pulse regime. Numbers near the experimental points designate the average number of pulses per portion of gas. FTIR capillary.

to zero as there would be nothing to dissociate at such pressures. Thus, there is the pressure optimal for the dissociation. It can be seen in the Figure 4.1 that this pressure is equal to 8.1 mbar. Still, the influence of pressure on dissociation fraction and its energy efficiency doesn't seem to be dramatic at the given pressure range at single pulse regime. Therefore, it was necessary to study the CO_2 dissociation at such conditions which would imply variation of other parameters. The next section is devoted to description of study of dissociation of carbon dioxide at varied pulse frequency.

4.2 Dissociation fraction and energy efficiency at high pulse frequency regime

As it has been just announced, the continuation of study of dissociation fraction in a nanosecond FTIR capillary discharge were the measurements at varied pulse frequency. The motivation of these measurements was to study the influence of number



Figure $4.2 - CO_2$ dissociation fraction and its energy efficiency at high frequency pulse regime. Numbers near the experimental points designate the average number of pulses per portion of gas. The orange rectangular in the right side of the plot shows the area where the gas heating becomes significant and evident.

of pulses per a portion of gas N on the dissociation fraction. The measurements have been down at a constant pressure of 8.1 mbar. The choice of the pressure has been motivated by the fact that it was the pressure which had provided the maximal dissociation fraction at low pulse frequency regime. The flow rate was constant and equal to 7.4 sccm.

The results of the measurements are presented in the Figure 4.2. The number of pulses per a gas portion and the energy efficiency of dissociation have been calculated within the same consideration as it was described previously. It can be seen that the dissociation fraction increases and then reaches a saturation threshold of 92% within the rise of N. In other words, at high pulse repetition rate, almost all CO₂ passing through the capillary is dissociated onto CO and oxygen and isn't oxidized back. Moreover, at low pulse repetition rates the dissociation fraction is proportional

to the number of pulses treating a portion of gas. Another important observation was a significant gas heating at elevated pulse repetition rates. When the pulse repetition rate was higher than 600-700 Hz, a smell of smoke and melting of plastic holders of the discharge cell have been observed. It can be therefore assumed that such a drastic increase of the dissociation fraction α may be caused by the increase of rate of thermal dissociation and the consequent saturation of α is caused by equilibrium between the gas heating rate and the heat transfer to the walls of the capillary. Therefore, further study of the temperature of the gas with the consequent correction of the number of pulses per portion and dissociation efficiency is of great importance.

4.3 Dissociation fraction and energy efficiency at different parameters

The final stage of the study of CO_2 dissociation by the means of FTIR spectroscopy was to measure the dissociation fraction and its energy efficiency at varied flow rates and applied voltages.

4.3.1 Different flow rates

The measurements of CO₂ dissociation fraction has been measured at flow rates varied between 7.4 sccm and 22.2 sccm at low frequency pulse regime (33 Hz). The results of the measurements are given in the Figure 4.3a. It can be seen that the dissociation fraction decreases as the flow rate increases. The explanation to this fact can be the following. As the flow rate increases, the number of pulses per a gas portion N decreases. Thus, less plasma energy is input in the gas. Two facts may witnesses such an explanation. First, the energy efficiency $\eta = \alpha \Delta E/w$ (where $\Delta E =$ 2.9 eV and w is specific deposited energy) is a value which is inversely proportional to N. It can be seen that η is almost constant at the given flow rate range. Second, the dependence of the dissociation fraction on the flow rate seems to be hyperbolic. It can be concluded once again that at low pulse repetition rates the dependence of dissociation fraction on N may be considered as linear one.

4.3.2 Different applied voltages

The measurements of CO_2 dissociation fraction has been measured at applied voltage peak varied from 4 kV and 9.4 kV at high frequency pulse regime (300 Hz). The results of the measurements are presented in the Figure 4.3b. It can be seen that the dissociation fraction decreases with the decrease of applied voltage peak and reaches zero at 4 kV. Such a result can be explained by the fact that at too low applied voltages the electron energy becomes insufficient to overcome the vibrational and electronic threshold of CO_2 molecules. As for the energy efficiency, it slightly increases as the applied peak voltage rises and then tends to a constant value of around 12%.

4.4 Conclusions

The results of measurements of dissociation fraction of $CO_2 \alpha$ and its energy efficiency η by the means of FTIR spectroscopy have been presented in the current Chapter. It was shown that at low pulse frequency regime there is a pressure of 8.1 mbar which is optimal for both α and η . At low pulse frequency pulse regime, the values of α and η are both around 20 %. It should be noticed that such elevated values of α and η are due to high values of electric current and applied electric voltage, as it was shown in the Chapter 3. In their turn, they are due to the configuration of the FTIR discharge where the low voltage electrode is grounded. The obtained values of α and η are comparable with results on dissociation of CO₂ in nanosecond repetitive pulsed discharge (NRP) obtained and published in [68, 70]. As aforementioned 8.1 mbar is the pressure which provides the maximal value of specific deposited energy in the first pulse, it can be assumed that the most significant yield of dissociation of CO_2 occurs in the first pulse. The influence of value of energy, deposited into plasma; number of pulses per a gas portion N and the way of its calculation have been discussed and it was shown that at low values of N the dissociation fraction α is proportional to N and then tends to a saturation threshold of 92%. Therefore, a way to dissociate almost all CO_2 has been found. The energy efficiency of the process at these conditions is around 8%. A significant heating of the discharge cell has been observed at pulse repetition rate higher than 600-700 Hz. Such an observation motivates to initiate a thorough study of gas heating and the mechanisms responsible for it. The first benchmark of this study is to understand which species are formed in the discharge. Optical emission spectroscopy (OES) which is the subject of the next Chapter may give an important clue on this way.



Figure 4.3 – Dissociation fraction and its energy efficiency at various a) flow rates (p=8.1 mbar, peak voltage=9.4 kV, pulse repetition rate=33 Hz; b) applied peak voltage (p=8.1 mbar, flow rate=7.4 sccm, pulse repetition rate=300 Hz). FTIR capillary.

Chapter 5

Study of the discharge by optical emission spectroscopy

The results of optical emission spectroscopy (OES) measurements both in thin and FTIR capillary as well as discussion of these results are presented in the current Chapter.

5.1 Optical emission spectra

5.1.1 Thin capillary

Optical emission spectra in the thin capillary were being recorded by the Princeton Instruments Acton Series SP-2500i spectrometer combined with an ICCD-camera Princeton Instruments PI-Max 4. The emission spectra of the discharge ignited in the thin capillary were acquired in three separate wavelength ranges: 200-400 nm, 400-600 nm and 600-900 nm. The reason to acquire the emission spectra in separate domains was to avoid the influence of the second order of diffraction. The details of this procedure as well as models of the optical filters are given in the 2.3. The radiation of the discharge has been collimated by a focusing UV-lens with a focal distance of 10 cm. The lens was installed in between the discharge cell and the entrance slit of the spectrometer such that the middle of the capillary, the lens and the entrance slit would be in the same line parallel to the optical table and perpendicular to the entrance slit. The time-integrated spectra in all three pulses were obtained. The time gate of the ICCD camera was equal to 60 ns and the signal have been averaged on 300 shots. The so called 'Step and Glue' procedure have been applied to spectra in order to assemble the parts of a spectrum to the unified one. The overlap between two neighbouring parts of a spectrum was 7 nm. To reduce the noise of the signal, spectra of the optical background were being acquired at the same conditions (grating, filter, position of the lens, electric lighting) and without ignition of the discharge. The background spectra were being subtracted from the recorded spectra and the procedures of correction to sensitivity of the system (see 2.3) was done.

Optical emission spectra of the first, second and the third pulses are presented in the Figure 5.1, Figure 5.2 and Figure 5.3, respectively. The time delay between consequent pulses is equal to 250 ns. Three different wavelengths ranges are represented. The intensities of the acquired signals haven't been normalized. The interpretation of spectra was done using different databases [101, 102, 103]. Along with that, the most essential quantum numbers of upper and lower levels of all transitions were found in the sources mentioned above. In the first pulse the 4th positive system of $CO(A^1\Pi \longrightarrow X^1\Sigma^+)$ (200-280 nm) was observed. Relatively strong and stable atomic C line (248 nm, $2p3s \rightarrow 2p2p$) and the bands of CO_2^+ ion were observed in all three pulses. The CO_2^+ ion was represented by the system of CO_2^+ ultraviolet doublet (288.7 nm and 288.9 nm, $B^2\Sigma_u \longrightarrow X^2\Pi_g$) and the so called Fox-Duffendack-Barker system (FDB, 300-440 nm, $A^2\Pi_u \longrightarrow X^2\Pi_q$). As for the infrared range, two lines of atomic oxygen could be observed in all three pulses. The first one was $O(3p^5P)$ $-> 3s^5S$ with the central wavelength 777 nm. As for the second one, it was $O(3p^3P)$ -> 3s³S) with the central wavelength 845 nm. A system of molecular bands of C_2 has been observed in the second and third pulse. It is the so called C_2 Swan system $(d^3\Pi_q \longrightarrow a^3\Pi_u)$. It is unusual that the Swan band has been observed in the same wavelengths range where the Angstrom system of CO ($B^1\Sigma^+ \longrightarrow A^1\Pi$) had been normally observed in similar previous experiments [104, 105, 106, 107]. In the third pulse the lines of the CO_2^+ are not dominant anymore and the third positive system of $CO(b^3\Sigma^+ \longrightarrow a^3\Pi)$ can be observed.

5.1.2 FTIR capillary

Optical emission spectra in the FTIR capillary were being recorded by the Princeton Instruments Acton Series SP-2500i spectrometer combined with an ICCD-canera Princeton Instruments PI-Max 4. Like in the case of the thin capillary, the emission spectra of the discharge ignited in the FTIR capillary were acquired in three separate wavelength ranges: 300-400 nm, 400-600 nm and 600-900 nm. The radiation of the



Figure 5.1 – Optical emission spectra in the first pulse. Thin capillary, pure CO_2 , 15.5 mbar. a) 200-400 nm b) 400-600 nm, c) 600-900 nm. The correspondent atomic lines and molecular bands are designated. The abbreviation FDB is for the Fox-Duffendack-Barker system.



Figure 5.2 – Optical emission spectra in the second pulse. Thin capillary, pure CO_2 , 15.5 mbar. a) 200-400 nm b) 400-600 nm, c) 600-900 nm. The correspondent atomic lines and molecular bands are designated. The abbreviation FDB is for the Fox-Duffendack-Barker system.



Figure 5.3 – Optical emission spectra in the third pulse. Thin capillary, pure CO_2 , 15.5 mbar. a) 200-400 nm b) 400-600 nm, c) 600-900 nm. The correspondent atomic lines and molecular bands are designated. The abbreviations FDB is for the Fox-Duffendack-Barker system and for the third positive system, respectively.

discharge has been collimated by the BF13LSMA01 optical fiber whose transmission function could be considered as constant at all wavelengths studied in experiments. The were several differences between OES in the FTIR and the thin capillaries. The first one consisted on the fact that the FTIR capillary was made from Pyrex glass and not from quartz. Therefore, the recorded spectra should have been corrected on the Pyrex transmission function which starts to be high enough around 300 nm. Along with that, there was no way to record the emission spectra in the FTIR capillary at wavelengths range below 300 nm and the behaviour of atomic C line and CO molecular bands remained unclear. Second, for the reasons of briefness and increase of signal-to-noise ratio, the emission spectra in the FTIR capillary were time integrated throughout all three high voltage pulses and weren't acquired at each high voltage pulse separately as in the case of the thin capillary.

The time integrated optical emission spectra in the FTIR capillary recorded at 10.5 mbar are given in the Figure 5.4. As it can be seen in the Figure, there aren't any essential difference between emission spectra in the FTIR capillary and the thin capillary.

5.2 Temporal behaviour of the main electronically excited species in the thin capillary

In order to better understand the underlying mechanisms of the plasma kinetics, it was necessary to study temporal behaviour of the population of the excited states. To reach that goal, the following transitions have been selected to be studied by the UV-PMT in the thin capillary. The principal quantum numbers of the transitions and their central wavelengths are designated:

- 1. Line of atomic carbon. C(2p3s -> 2p2p), $\lambda_{cent} = 248$ nm.
- 2. The fourth positive system of $CO(A^1\Pi \longrightarrow X^1\Sigma^+)$, the vibrational transition is not resolved), $\lambda_{cent} = 233.6$ nm.
- 3. The UV-doublet of the carbon dioxide ion $\operatorname{CO}_2^+(\operatorname{B}^2\Sigma_u \longrightarrow \operatorname{X}^2\Pi_g), \lambda_{cent} = 288.5$ nm
- 4. The system of Fox-Duffendack-Barker $\operatorname{CO}_2^+(\operatorname{A}^2\Pi_u \longrightarrow \operatorname{X}^2\Pi_g, \text{ vibrational transition } 1 \longrightarrow 0), \lambda_{cent} = 340 \text{ nm.}$

The temporal profiles of the signals normalized on their maximal arbitrary intensities in the first pulse are represented in the Figure 5.5.



Figure 5.4 – Time integrated optical emission spectra in all three high voltage pulses. FTIR capillary, pure CO_2 , 10.5 mbar. a) 300-400 nm b) 400-600 nm, c) 600-900 nm. The correspondent atomic lines and molecular bands are designated. The abbreviation FDB is for the Fox-Duffendack-Barker system.



Figure 5.5 – Temporal profiles of the selected transitions normalized on their maxima in the first pulse. Recorded by the UV-PMT in the thin capillary at 15.5 mbar. Pure CO_2 .

As it has been said before, another remarkable result observed is the presence of Swan band in spectrum and the simultaneous absence of Angstrom band both in the FTIR and thin capillaries. The Angstrom band is usually observed in similar experiments with CO and CO₂. The excitation threshold of $CO(B^{1}\Sigma^{+})$ which is the upper level of Angstrom band is 15 eV with respect to the ground state of CO₂. This is value is significantly lower than the upper level of $C_2(d^{3}\Pi_g)$ which corresponds to Swan band. To resolve this contradiction, it is first necessary to understand how high the excited states are on energy scale and how high are specific deposited energy and the mean electron energy.

5.3 How big is the electron energy?

The relative positions on the energy scale of different species according to [19, 103, 108, 109] observed in plasma are presented in the Figure 5.6. The Table 5.1 demonstrates the main molecular bands and atomic lines observed in the experiment, their wavelengths, excitation thresholds and pulses in which the species have been observed. The energy of $CO_2(X^1\Sigma^+)$ ground state is taken as zero and the energy of $CO(X^1\Sigma^+)$ is taken as 5.5 eV what corresponds to the dissociation threshold of a



Figure 5.6 – Energy thresholds of formation of species observed in plasma.

 CO_2 molecule. The Angstrom band which has been not observed in the main part of the experiment but has appeared at higher pressures is designated by a dashed grey line. Looking on the results presented in the current Chapter as well as at the Figure 5.6 it is possible to notice several important features characterizing the discharge.

First, it can be seen (Figure 5.5) that $CO_2^+(B^2\Sigma_u)$ state is excited before than the underlying $CO_2^+(A^2\Pi_u)$. It can be therefore concluded that the mean energy of electrons in the first is so high that the electrons excite more likely the higher states than the lower ones. The threshold excitation of the $CO_2^+(A^2\Pi_u, B^2\Sigma_u)$ states are around 18 eV which is much higher than the vibrational dissociation threshold of a CO_2 molecule (5.5 eV) and even than the electronic excitation threshold of a CO_2 molecule (7 or 10.5 eV). Thus, it can be assumed that the most significant part of electron energy rather comes to ionization of CO_2 with consequent electronic excitation of CO_2^+ ions than to dissociation of a CO_2 molecule. Another evidence to the proposed assumption is the fact that the intensity of the bands of the 4th positive system of CO are much lower than the molecular bands of the UV doublet and FDB systems of the CO_2^+ ion both in the first and second pulses. As for the third pulse, the mean energy of electrons increases a little bit more and the third positive system of CO (3+, $(b^3\Sigma^+ \longrightarrow a^3\Pi)$) appears instead of the fourth positive system (4+). Still, it can be possible that additional population of highly excited electronic states occurs due to pooling reactions of lower electronic state. The absence of any

Name of the system	Wavelengths, nm	Excitation threshold, eV	Number of pulses
$\rm CO_2^+$ FDB	300-450	17.9	I,II,III
CO_2^+ UV doublet	287-288	18.8	I,II
CO 4th positive	200-275	13.5	I,II
C_2 Swan band	460-570	24.8	II, III
CO 3rd positive	260-360	16.0	III
C atomic line	248	22.3	I,II,III

Table 5.1 – The main molecular bands and atomic lines observed in the experiment. The excitation threshold is given with respect to the ground state of $CO_2(X^1\Sigma^+)$ in an assumption that ground state of $CO(X^1\Sigma^+)$ is 5.5 eV higher than the ground state of $CO_2(X^1\Sigma^+)$ and the state of $C_2(a^3\Pi_u)$ has the same energy as the excited state of C(2p3s).

remarkable difference between OES in the FTIR and thin capillaries indicated than the most part of the electron energy is spent to CO_2 ionization in both capillaries. To recall, the total specific deposited energy in the FTIR capillary (5.2 eV/particle) is more than 3 times higher than in the thin one (1.5 eV/particle). All these observations indicate the further increase of the specific energy at a nanosecond time scale would not enhance the CO_2 dissociation processes via vibrational or electronic degrees of freedom but rather facilitate ionization of CO_2 .

It should be noticed that both C and O atomic lines were observed in all three pulses. These atomic lines are intensive and stable throughout all three high voltage pulses. Therefore, one should assume that CO_2 has been converted not onto CO and O where the products of the dissociation remain stable but CO, in its turn, has been mostly converted onto C and O in the first and the second pulse. The consequent formation of excited diatomic carbon C_2 from the monoatomic carbon whose traces were observed as the Swan band and C atomic line, respectively, may act as an evidence of the aforementioned assumption.

To better justify this point of view, two experiments have been done. First, OES experiments were repeated at higher pressures. The purpose of theses experiments was to decrease the deposited energy per particle and, as a result, to damp the mean electron energy. The decrease of the mean electron energy should slow down the formation of C_2 and increase the formation of $CO(B^1\Sigma^+)$. One expected to observe the Angstrom band of $CO(B^1\Sigma^+ \longrightarrow A^1\Pi)$ appeared instead of C_2 as a signature of mean electron energy damping. The second experiment was to study the temporal behaviour of the C_2 band by a PMT at the conditions where the delay between

pulses is varied. Both experiments have been done in the FTIR capillary. The results of this experiment are presented and discussed in the next section.

5.4 Behaviour of the Swan band in the FTIR capillary

5.4.1 Variable pressures

The Figure 5.7 demonstrates normalized optical emission spectra at various pressures in the FTIR capillary. It can be seen that as the pressure is increased, the Angstrom band of CO appears and dominates over the Swan band of C_2 . At 10.5 mbar there is no any evidence of presence of Angstrom band in any pulse. When the pressure is increased to 15.6 mbar, the Angstrom band appears in the first pulse and disappears in the second pulse. Finally, when the pressure is increased to 22.5 mbar, the Angstrom band intensity in the first pulse increase as well. These observations justify the fact that the decrease of specific energy input facilitates the dissociation of CO_2 . Still, the CO formed in the first pulse is dissociated onto C and O in the consequent pulses and atomic carbon recombines onto excited diatomic carbon.

5.4.2 Varied delay between pulses

One more experiment showing that formation of diatomic carbon takes place in the second pulse was developed. The main idea of this experiment was to trace the emission of Swan band as a function of time by a photomultiplier tube (PMT). The experiment was modified with respect to the previous ones: another high voltage generator (FGP 25-001 NM2C2) was chosen. The reason of using of the other generator was to control the delay between pulses by generation of different series of pulses (I and II in Figure 5.8.) The principle of work of the generator is the following. The generator has three independent inputs which can be connected to a triggering generator. Therefore, if the signal comes to the inputs at different time instants, independent high voltage pulses will be generated. The amplitude of each pulse can be set on the generator. There were two independent pulse series used in the experiment, they are designated as I and II. The number of a pulse reflection is designated by Arabic figures. The amplitudes of I1 and II1 pulses were set to 24 kV and 8 kV, respectively. The delay between I1 and II1 was set to 350 ns.

The arbitrary intensity of the 0-0 transition of Swan band at 515 nm registered



Figure 5.7 – Optical emission spectra at various pressures in the FTIR capillary, pure CO_2 . The spectra are normalized. a) Red curve: 10.5 mbar, all three pulses. Grey curve: 15.6 mbar, first pulse. Blue curve: 15.6 mbar, second pulse. b) Red curve: 10.5 mbar, all three pulses. Grey curve: 22.5 mbar, first pulse. Blue curve: 22.5 mbar, second pulse. The Angstrom band is marked by the black arrow.



Figure 5.8 – The arbitrary intensity of C_2 Swan band (green curve) and specific deposited energy as a function of time measured at 10.5 mbar. Solid black curve: specific deposited energy in the I series. Red curve: specific deposited energy in the I series. Dashed black curve: period between the pulses. Pure CO₂, FTIR capillary. The Roman numerals correspond to the number of series and the Arabic ones to the number of reflection.

by the PMT and the specific deposited energy as a function of time are given in the Figure 5.8. It can be concluded from the experimental results that the Swan band is formed in the second reflected pulse when the deposited energy reaches a certain threshold. As soon as this energy threshold is overcome, a small amount of deposited energy is necessary for further formation of Swan band (see pulse II1 and I3 in the Figure 5.8). In other words, such a behaviour may be named memory effect in a sense that the discharge 'remembers' the ionizing pulse and as soon as the time before the consequent pulse doesn't exceed the time of plasma decay, the consequent pulse impacts the perturbed plasma dissociating the CO and forming the excited state of C_2 .

5.5 Conclusions

The results of study of features of the nanosecond capillary discharge in CO_2 both in FTIR and thin capillary by OES have been presented in the current Chapter. It has been shown that the emission spectra in the FTIR and thin capillary don't have an essential difference and resemble each other qualitatively. The emission spectra demonstrates a significant presence of the energy states lying between 18 and 25 eV with respect to the CO_2 ground state. The electronically excited $CO(B^1\Sigma^+)$ state lying on approximately 11 eV with respect to the CO_2 ground state either don't appear at all or is very dim comparing to the experiments conducted at the same conditions previously. It was shown that at higher pressures and, consequently, at lower specific deposited energies, the Angstrom band $CO(B^1\Sigma^+ \longrightarrow A^1\Pi)$ appears and is more intensive, the higher the pressure is. The first conclusion to make is that the most part of the electron energy is spent to gas ionization and not to excitation of vibrational and electronic degrees of freedom. However, it should be commented here that such a conclusion is purely valid only for the first pulse since the population of highly excited electronic states could be probably due to pooling reactions. The second conclusion is that the specific deposited energy in the aforementioned conditions is too high to maintain dissociated CO in stability during the train of high voltage pulses since the consequent pulses dissociate previously formed CO onto C and O. Nevertheless, it was shown in the previous Chapters that it is a high percentage of pulse energy absorbed by plasma what facilitates the CO_2 dissociation measured downstream of the discharge cell and conversion of CO to C and O during pulses can be in favour of high dissociation fraction.

It is have being said until now that all kinetic processes of the discharge on nanosecond scale are defined by the reduced electric field, electric current and density of electrons in the discharge. It is the electrons that are responsible for the population of the excited species and they define rates of formation and decay of these species. It is therefore indispensable to learn more about their behaviour in plasma in order to pursue profound understanding of chemical processes occurring in the discharge. Thereby, next two Chapters will be devoted to the measurements of the temporal and radial profile of the electron density.

Chapter 6

Measurements of the temporal profile of the electron density in the thin capillary

As it has been just announced, the electron density in the discharge define the kinetic scheme at nanosecond time scale. The current Chapter is devoted to measurements of the temporal profile of the electron density in the thin capillary. The electron density has been measured both in all three high voltage pulses and their afterglow.

6.1 Description of the technique

In the most general case, the electron density temporal profile $n_e(t)$ averaged on the cross section S of a capillary can be found from the definition of the current density j(t) and its relation to the drift velocity of electrons $v_d(t)$:

$$j(t) = \frac{I_{tra}(t)}{S} = en_e(t)v_d(t).$$
(6.1)

Here, e is the charge of an electron, I_{tra} is the current flowing in the discharge. Then, the drift velocity $v_d(t)$ can be expressed as follows:

$$v_d(t) = E/n(t)\mu(E/n(t)).$$
 (6.2)

E/n(t) is the reduced electric field as a function of time, $\mu(E/n(t))$ is the mobility of electrons which is dependent on the value of the reduced electric field. Hereinafter, it will be supposed that the the mobility is calculated using the BOLSIG+ software [33]; the ensemble of the cross-sections for all electron-involving processes in pure
CO_2 is taken from the [28, 30]. Combining both equations (6.1) and (6.2) one finally obtains:

$$n_e(t) = \frac{I_{tra}(t)}{Se\mu(E/n(t))E/n(t)}.$$
(6.3)

The electron density increases during the discharge and the electric current starts to flow. It is the case of all three high voltage pulses and the electric current I_{tra} can be therefore measured by back current shunts and an oscilloscope. The technique of the measurements has been already described in 2.2.1. The waveforms of the electric current $I_{tra}(t)$ in all three pulses have been presented in 3.1, see Figure 3.1. Knowing the $I_{tra}(t)$ due to the BCS2 and the reduced electric field both from BCS1 and BCS2, interpolating the mobility as a function of the reduced electric field to the temporal grid one obtains the temporal profile of the electron density during three high voltage pulses.

As for the afterglow of the discharge, the measurements of the electron density as a function of time become more tricky since the electric current is equal to zero between the high voltage pulses. Nevertheless, it doesn't mean at all that the electron density is zero between the pulses. A solution of the problem has been described in [65, 64], see Figure 1.8. The solution consists in using a reflection of the electric signal transmitted through the plasma from the end of the low voltage cable as a probe pulse. The delay of the probe pulse has been adjusted by choose of the length of the low voltage cable. For instance, if the length of the cable had been changed by 1 m, the time instant at which the electron density is registered was shifted by 10 ns, since the velocity of the voltage pulse propagation is equal to 20 cm/ns and the pulse propagated 1 m twice: to the end of the cable and back after reflection. For adjustment of the length, the cable was being simply chopped so many times as there were experimental points in the temporal profile of the electron density. Like this, it was possible to measure the n_e first in the afterglow of the third pulse and then, as things progress, to move towards the second and the first pulses.

It should be noted that the electric current I_{tra} of the probe pulse should have been, for one hand, high enough for development and maintenance of a self-sustained discharge. For the other hand, the probe pulse shouldn't be too high to perturb the measurements and to create an artificial increase of the electron density. To avoid such an intrusion, a resistor was being soldered to the end od the low voltage cable. According to the equation (2.5), the amplitude of the high voltage pulse drops down in this case. A resistor of 22 Ohm was being used for acquisition of all experimental points. The use of the resistor provided a non-intrusive probe pulse created a self-sustained discharge necessary for calculation of the electron density in all experimental points.

Another point which should be discussed is whether the mobility of electrons between the pulses changes instantaneously with E/n. In other words, the electron density in the afterglow of the pulses can be calculated according to the Eq.6.3 only if the conditions of quasi-stationary approach are fulfilled and the electron energy distribution function follows the changes of E/n. A Θ parameter which describes the swiftness of E/n changes with respect to the effective eedf relaxation frequency ν_{rel} can be expressed in the following way [110]:

$$\Theta = \nu_{rel} \left(\frac{1}{E} \left| \frac{dE}{dt} \right| \right)^{-1} \tag{6.4}$$

If $\Theta > 1$, the regime of the behaviour of eedf can be considered as quasi-stationary. The relaxation frequency of the eedf can be calculated as $\nu_{rel} = v_e/l$, where $v_e = \sqrt{3kT_e/m_e}$ is average electron velocity and l is electron mean free path. According to [21], the mean free path of electrons in CO₂ plasma at the pressure of 15.5 mbar is equal to $2.5 \cdot 10^{-5}$ m. The electric field change in the most drastic way during the propagation of the fast ionization wave (in the first 20 ns). On other hand, the minimal average electron velocity is reached at electron temperature equal to $T_e = 300$ K. After all calculations one obtains minimal possible value of $\Theta \approx 5$ in the fast ionization wave what means that the behaviour of the eedf can be considered as quasi-stationary on the entire timescale. Thereby, the electron density can be calculated by the expression 6.3 in the high voltage pulses as well as between them.

6.2 Experimental results

The results of measurements of electron density in the thin capillary during the high voltage pulses and their afterglow is presented in the Figure 6.1. The values of the electron density in pulses and between them have been obtained according to the equation (6.3) The measurements have been conducted in pure carbon dioxide at 15.5 mbar. The X-error bars of the experimental points correspond to the duration of the period at which the electron density could be assumed as constant during the propagation of the probe pulse. As for the Y-error bars, they have been set according to the noise in the calculated profile of the electron density during the propagation of the probe pulse. The peak amplitude of the electron density in the first, second and the third pulses are as high as 2.0×10^{15} cm⁻³, 1.6×10^{15} cm⁻³ and 1.4×10^{14} cm⁻³, respectively. Knowing that the initial density of the carbon dioxide at 300 K and 15.5 mbar is equal to 3.7×10^{17} cm⁻³, the peak ionization degree in the first



Figure 6.1 – Experimental profile of the electron density. Black solid lines: the temporal profile of the electron density in the high voltage pulses. Black squares: electron density in the afterglow of the pulses. Red circles: the peak electron density in the high voltage pulses. Thin capillary, 15.5 mbar, pure CO_2 .

pulse is approximately equal to 0.5%. A detailed numerical analysis of processes responsible for gain and losses of the electron density as well as comparison of the experiment and model will be thoroughly described in the Chapter 9.

Chapter 7

Analysis of the radial profile of the electron density in the thin capillary on the basis of OES measurements

It has been mentioned previously in 2.5 that capillary discharge is not a 0D object but is a volumetric one. As soon as it is assumed that the discharge has both axial symmetry and homogeneity along its entire length, the discharge can be considered to be a 1D object. Radial distribution of the electrons in the discharge may act as a pronounced signature of kinetic processes occurring on the discharge. Therefore, it is essential to restore the radial distribution of the electron density at different time instants. The procedure of measurements of the radial distribution of the emission has been described in 2.5. The experimental results of the measurements will be given in the current Chapter. Relation between the measured emission distribution and therefore correctness of the measurements will be discussed in the current Chapter as well.

7.1 Experimental setup

The experiments have been conducted in a thin capillary whose parameters were slightly different from the capillary which has been described so far. The length of the capillary was the same (86 mm) as well as the distance between the electrodes (75 mm). However, the internal diameter was equal to 1.5 mm instead of 1.7 mm. The external diameter was equal to 3.0 mm. Therefore, the electric characteristics

of the discharge were slightly different as well. The reduced electric field measured by the capacitive probe and electric current measured by the BCS2 are presented in the Figure 7.1. The presented data have been acquired in a mixture of 10 sccm $CO_2 + 1$ sccm N_2 at 19.4 mbar. Such a value has been chosen because the discharge was operating in the most stable way at this pressure. It should be mentioned that the difference between the given data and experimental profiles of the electric field and current acquired in pure CO_2 (10 sccm) at the same pressure of 19.4 mbar is negligible. That fact has been established experimentally. Thus, it will be assumed hereinafter that the electric characteristics of the discharge developing in the atmosphere of pure CO_2 and the $CO_2:N_2$ mixture are the same.



Figure 7.1 – Experimental profiles of the reduced electric field (black line) and electric current (red line) in all three pulses. Inset: zoomed experimental profiles of the reduced electric field and electric current in the first pulse. Thin capillary, 19.4 mbar, 10 sccm $CO_2 + 1$ sccm N_2 . Zero is referred to the beginning of the electric current flow.

The other electric characteristics such as specific deposited energy and peak electron density in the high voltage pulse were measured by the same manner as it have been described in 3.3 and 6.1, respectively. The mentioned parameters as well as peak

Number of pulse	1	2	3
Peak current, A	58	66	26
$w, \mathrm{eV}/\mathrm{particle}$	0.42	0.6	0.2
Peak N _e , $10^{15} \cdot \text{cm}^{-3}$	0.95	1.14	0.5

Table 7.1 – Main discharge characteristics in all three pulses

current in each pulse are given in the Table 7.1.

7.2 Experimental results

The radial profiles of the emission intensity has been reconstructed by a procedure of numerical application of Inverse Abel Transform (see section 2.5). An example of the raw data to which the procedure has been applied is given in the Figure 2.14. The reconstructed profiles of the emission intensity of the second positive system of nitrogen $(N_2(C^3\Pi_u) \longrightarrow N_2(B^3\Pi_q), 0 \longrightarrow 2)$ are demonstrated in the Figure 7.2. The Figure presents the data taken in all three high voltage pulses in $CO_2:N_2 =$ 10 sccm:1 sccm mixture at 19.4 mbar. The measurements have been done with a narrow bandpass filter with a central wavelength $\lambda_0 = 380$ nm, $\Delta \lambda = 5$ nm. The development of the discharge and its decay can be seen in all three pulses. It is important that the discharge is contracted to axial part of the capillary as maximal intensity is observed for r=0. As the distance from the axis increases, the intensity tends to zero monotonously. Moreover, such a behaviour of the emission intensity is the case not only for the first pulse but for the second and third pulses as well. In other words, the radial distribution of the intensity is restored after interpulse period of almost 250 ns. Thereby, a presence of memory effect in plasma can be stated. A detailed explanation to this fact will be given in the Chapter 11 which is devoted to numerical modeling. The memory effect can be seen even better in the Figure 7.3 where the normalized profiles from the Figure 7.2 are presented. As it can be seen, almost all normalized profiles repeat each other. The only exception is the very beginning of the 2nd pulse (236 ns) which could be explained by the fact that electron density has not be restored yet after the pause between the first and the second pulses.

To prove that the radial distribution of intensity measured in the $CO_2:N_2$ mixture is in agreement with the one in pure CO_2 , the same measurements have been taken in pure CO_2 at the same pressure of 19.4 mbar. Fox-Duffendack-Barker system $(CO_2(A^2\Pi_u) \longrightarrow CO_2 (X^2\Pi_g))$ has been chosen for the measurements. Figure 7.4 represents the profiles taken in all three high voltage pulses in pure CO_2 and normalized at their maxima. The measurements have been done with a narrow bandpass filter with a central wavelength $\lambda_0 = 390$ nm, $\Delta \lambda = 5$ nm.

The behaviour of the discharge rests the same as in the $CO_2:N_2$ mixture except the very last moment in the 3rd pulse. The discrepancy could be explained by the fact that plasma might have been decayed already and the electron density is not enough to maintain a 'centripetal' distribution of the discharge. It can be therefore concluded that the radial distribution of intensity measured in the different mixtures are in agreement and measurements in the $CO_2:N_2$ mixture do represent the situation occurring in pure CO_2 . The next subsection is devoted to explanation of the applicability of the technique for measurements of the electron density. In other words, it will be shown that the recorded normalized profiles in $CO_2:N_2$ mixtures are the same as normalized profiles of the electron density.

7.3 Relation between the emission profiles and the electron density. Validity of gas temperature measurements.

The radial distribution of electron density have been measured by the second positive system (SPS) of N₂ in a CO₂:N₂ = 10:1 mixture. It is therefore necessary to show the correctness of these kinds of measurements by proving the fact that the radial profile of emission intensity of the discharge is directly related to the radial profile of the electron density. To do so, it is essential to verify that the only way of population of N₂(C³Π_u) is direct electron impact from the ground state and the rate of population of the state from N₂(A³Σ⁺_u) :

$$N_2(A^3\Sigma_u^+) + N_2(A^3\Sigma_u^+) \longrightarrow N_2(C^3\Pi_u) + N_2(X^1\Sigma_g^+)$$
(7.1)

is negligible. First, the time-resolved measurements of the intensity of emission of the second positive system at 337 nm by a photomultiplier tube (PMT) have shown that emission between high voltage pulses is at zero level what means that the N₂(C³ Π_u) state is only populated by electrons. However, if the electron density in pulses is high enough, additional processes of population of the N₂(C³ Π_u) by direct electron impact from excited electronic states N₂(A³ Σ_u^+ , B³ Π_g) and not from N₂(X¹ Σ_g^+) are possible:

$$N_2(A^3\Sigma_u^+, B^3\Pi_g) + e \longrightarrow N_2(C^3\Pi_u) + e.$$
(7.2)

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Figure 7.2 – Reconstructed profiles of radial emission intensity of the 2nd positive system of nitrogen in a $CO_2:N_2 = 10:1$ mixture, 19.4 mbar. a) 1st pulse b) 2nd pulse c) 3rd pulse. Gate width: 3ns.



Figure 7.3 – Reconstructed profiles of radial emission intensity of the 2nd positive system of nitrogen normalized at their maxima. $CO_2:N_2 = 10:1$ mixture, 19.4 mbar. Gate width: 3ns.



Figure 7.4 – Reconstructed profiles of radial emission intensity of Fox-Duffenduck-Barker system normalized at their maxima. Pure CO_2 , 19.4 mbar. Gate width: 3ns.



Figure 7.5 – Calculated rate constants of excitation of $N_2(C^3\Pi_u)$ from $N_2(X^1\Sigma_g^+)$, $N_2(A^3\Sigma_u^+)$ and $N_2(B^3\Pi_g)$ as a function of the reduced electric field. According to [33]. The dashed curve shows the ratio between the rate constants of excitation of $N_2(C)$ from $N_2(A^3\Sigma_u^+)$ and $N_2(X^1\Sigma_g^+)$.

The rate constants of excitation of $N_2(C^3\Pi_u)$ from $N_2(X^1\Sigma_g^+) N_2(A^3\Sigma_u^+)$ and $N_2(B^3\Pi_g)$ as a function of the reduced electric field is presented in the Figure 7.5. The constants have been calculated by [33]. The cross sections for the calculations have been taken from [111, 112].

First, the population of the $N_2(C^3\Pi_u)$ state from $N_2(A^3\Sigma_u^+)$ is not significant in the current case. The ratio of the rate constants of excitation of $N_2(C^3\Pi_u)$ by electron impact from the $N_2(A^3\Sigma_u^+)$ and the $N_2(X^1\Sigma_g^+)$ states is approximately equal to 50:1 (see Figure 7.5) at the observed values of the reduced electric field E/n = 150-250 Td. In the current case when $CO_2:N_2 = 10:1$ and E/n = 150-250 Td the role of the reaction (7.2) becomes important only if $[N_2(A^3\Sigma_u^+)]:[N_2(X)] > 2\%$. At given conditions of high values of specific deposited energy the dominating factor responsible for the decay of $N_2(A^3\Sigma_u^+)$ is fast quenching of this state leading to its dissociation [66].

$$N_2(A^3\Sigma_u^+) + e \longrightarrow N(^4S) + N(^2D) + e.$$
(7.3)

The rate constant of the dissociation process at E/n = 150-250 Td is $k_q = (5-10) \cdot 10^{-7}$ cm³/s [66]. Given that the electron density in the 1st and 2nd high voltage

pulses is $N_e \approx 10^{15} \text{ cm}^{-3}$, one obtains frequency of $N_2(A^3\Sigma_u^+)$ quenching $\nu_q = (5-10) \cdot 10^7 \text{ s}^{-1}$. Such a value is much greater than frequency of $N_2(A^3\Sigma_u^+)$ quenching via other canals. The rate constant k_{ex}^A of the excitation of $N_2(A^3\Sigma_u^+)$ from the ground state of nitrogen:

$$N_2(X^1\Sigma_q^+) + e \longrightarrow N_2(A^3\Sigma_u^+) + e$$
 (7.4)

is $k_{ex}^A = (1.1\text{-}1.5) \cdot 10^{-10} \text{ cm}^3/\text{s}$ at E/n = 150-250 Td (see Figure 7.6). Thus, $[N_2(A^3\Sigma_u^+)]/[N_2(X^1\Sigma_g^+)] = k_{ex}^A/k_q = 0.2\text{-}0.3 \%$. It has been mentioned just above that the ratio of the rate constants of excitation of $N_2(C^3\Pi_u)$ by electron impact from the $N_2(A^3\Sigma_u^+)$ and the $N_2(X^1\Sigma_g^+)$ states is approximately equal to 50:1 at E/n = 150-250 Td, one can conclude that the contribution of the population of $N_2(C^3\Pi_u)$ state by electron impact from the $N_2(A^3\Sigma_u^+)$ state doesn't exceed 15 %.



Figure 7.6 – Calculated rate constants excitation of $N_2(C^3\Pi_u)$, $N_2(A^3\Sigma_u^+)$ and $N_2(B^3\Pi_g)$ from as a function of the reduced electric field. According to [33].

Second, it is essential to provide the same argumentation for the $N_2(B^3\Pi_g)$ state. According to [113], the rate of the reaction:

$$N_2(B^3\Pi_g) + CO_2 \longrightarrow N_2(X^1\Sigma_g^+) + CO + O$$
(7.5)

is $k_q^B = 10^{-10} \text{ cm}^3/\text{s}$. The main yield of the Reaction (7.5) is dissociation of CO₂ molecules and not the population of lower electronic state N₂(A³ Σ_u^+). On the other hand, The rate constant k_{ex}^B of the excitation of N₂(B³ Π_g^+) from the ground state of nitrogen:

$$N_2(X^1\Sigma_g^+) + e \longrightarrow N_2(B^3\Pi_g) + e$$
 (7.6)

is $k_{ex}^B = 1.0 \cdot 10^{-9} \text{ cm}^3/\text{s}$ at E/n = 150-250 Td (see Figure 7.6). The rate equation for the N₂(B³ Π_a^+) state may be therefore written as:

$$\frac{d[N_2(B^3\Pi_g)]}{dt} = k_{ex}^B N_e[N_2(X^1\Sigma_g^+)] - k_q^B[N_2(B^3\Pi_g)][CO_2].$$
(7.7)

The concentration of $N_2(B^3\Pi_g^+)$ reach its maximum when the right-hand side of the equation 7.7 is equal to zero. At the given conditions $(N_e \approx 10^{15} \text{ cm}^{-3}, [CO_2] \approx 5 \cdot 10^{17} \text{ cm}^{-3}, [N_2(X^1\Sigma_g^+)] \approx 5 \cdot 10^{16} \text{ cm}^{-3})$ one obtains $[N_2(B^3\Pi_g^+)]/[N_2(X^1\Sigma_g^+)] \approx 1\%$. It can be seen in the Figure 7.5 that the ratio of the rate constants of excitation of $N_2(C^3\Pi_u)$ by electron impact from the $N_2(B^3\Pi_g^+)$ and the $N_2(X^1\Sigma_g^+)$ states is approximately equal to 50:1 at E/n = 150-250 Td, therefore population of $N_2(C^3\Pi_u)$ state from the $N_2(B^3\Pi_g^+)$ state becomes significant if $[N_2(B^3\Pi_g^+)]/[N_2(X^1\Sigma_g^+)] > 2\%$.

It should be noted that the all argumentaion given above is valid not only for demonstrating of relevance of the emission profile of $N_2(C^3\Pi_u)$ and the electron density but also the fact that the rotational temperature of $N_2(C^3\Pi_u)$ 'copies' [65] the rotational temperature of the ground state of nitrogen. Therefore, the measurements of gas temperature by rotational temperature of nitrogen which will be described in the next Chapter are assumed to be valid.

The author is thankful to Dr. Nikolay Popov for his help and participation to the aforementioned discussion.

7.4 Conclusions

Radial profile of the electron density in the thin capillary has been discussed in the Chapter. The thin capillary which has been described in the Chapter is slightly thinner than its homologue described in previous Chapters, but the temporal behaviour of the reduced electric field remained the same. The measurements have been done in $CO_2:N_2 = 10:1$ mixture at 19.4 mbar and the second positive system of nitrogen has been studied. The experiments have been done at different time instants in all pulses. The profile of the emission has a pronounced maximum in the axial part of the capillary and tends to zero as the distance to axis increase. It has

been found that the behaviour of the profile doesn't change within a high voltage pulse and between them. The relation between the emission intensity of the SPS of nitrogen and the electron density has been shown. The demonstration of current relation is also fruitful for further measurements of the gas temperature.

Till now, it was assumed that the temperature in the capillary is constant and equal to 300 K. As it was mentioned in the 4.2, the assumption was experimentally justified to be wrong. Moreover, the similar experiments conducted at the same setup with nitrogen and oxygen mixtures (see 1.2.2) have shown that the fast heating of the gas in which high electronically excited states act as reservoirs of thermal energy. The next Chapter is therefore devoted to the measurements of gas temperature in the discharge.

Chapter 8

Measurements of the gas temperature as the function of time by the means of optical emission spectroscopy

8.1 FTIR capillary

To measure the gas temperature in the FTIR capillary, molecular nitrogen was added into carbon dioxide. The validity of the technique for the conditions of the experiment has been demonstrated in the previous Chapter. The nitrogen flux of 5 sccm was the same for all experiments whereas four different values of the flux of the carbon dioxide were used, 10 sccm, 20 sccm, 30 sccm and 50 sccm. These values correspond to 33%, 20%, 14% and 9% of nitrogen in the mixture respectively. The SLA5850S Brooks Instruments mass flow controller was being used. The pressure was maintained constant and equal to 10.5 mbar. The optical emission spectra of electronically excited nitrogen were recorded in the wavelength range 300-400 nm by a Princeton Instruments Acton SP2500i spectrometer and PI-MAX4 ICCD camera connected to the spectrometer. The grating with 1200 grooves per mm was used. The rotational temperature was then derived from the spectra with the help of a commercial SpecAir [114] code.

An example of the emission spectra in different gas mixtures in the second pulse is given in the Figure 8.1. The ICCD camera gate is equal to the duration of the pulse (about 60 ns). It can be seen that the vibrational transitions of the $N_2(C^3\Pi_u) \longrightarrow$



Figure 8.1 – An example of normalized optical emission spectra in $CO_2:N_2$ mixtures. 0-0 transitions of the second positive system of nitrogen and Violet system of CN are marked. 5 sccm N_2 + various concentrations of CO_2 . 10 mbar, FTIR capillary.

 $N_2(A^3\Sigma_u^+)$ corresponding to the sequences of $\Delta v=1$ (357.7 nm) and $\Delta v=2$ (380.5 nm) are partially or totally overlapped with the bands of CN Violet system produced in the chemical reactions. As a result, 0-0 transition of molecular nitrogen at 337.1 nm was the most representative for definition of the rotational temperature. It can be seen in the Figure 8.1 that the normalized emission spectra of the SPS have the same behaviour regardless the concentration of N₂ admixture. Therefore, the measurements of CO₂ temperature could by N₂ rotational temperature be considered as non-invasive.

After the comparison of the SpecAir fit and the experimental results corrected on slit function and sensitivity of the apparatus, the temperatures in three subsequent pulses separated by 200 ns were found to be equal to 450 K, 1700 K and 2000 K, respectively. Such big values of the gas temperature are a signature of fast gas heating processes occurring in the discharge. However, the temperature measurements were quite rough and have been only done in pulses with a temporal gate width of the ICCD camera of 60 ns. Therefore, the dynamics of gas heating remained unknown. The SpecAir fitting parameter named 'vibrational temperature of N₂' was found to be equal 5000 K in all electric pulses Figure 8.2. It should be mentioned,



a)

Figure 8.2



b)

Figure 8.2



c)

Figure 8.2 – Comparison of the experimental spectra of the $0 \rightarrow 0$ transition of the SPS of N_2 and its SpecAir fit. a) 1st pulse b) 2nd pulse c) 3rd pulse. The fitted values of the rotational and vibrational temperature are given. FTIR capillary, 10.5 mbar.

however, that this fitting parameter is nothing to do with the real vibrational temperature of N_2 since the SpecAir fit cannot take into account the temporal dynamics of vibrational non-equilibrium on the sub-microsecond timescale.

8.2 Thin capillary

The idea and technique of measurements of temperature in the thin capillary was basically the same as for measurements in the FTIR one. However, it was desired to have better temporal resolution by acquisition of spectra with a temporal gate width of the ICCD camera of 10 ns instead of 60 ns. Such experiment could be less rough than the experiment done in the FTIR capillary. Moreover, as the temporal profile of the reduced electric field has been measured by the capacitive probe (what was impossible in the FTIR capillary), there was an opportunity to obtain selfconsisted data of E/n and temperature. This set of experimental data was essential for the numerical modeling and understanding of kinetic processes responsible for gas heating and dynamics of active species. It should be noted that the same thin capillary was used as in the previous Chapter. The experiments in the thin capillary have been done at constant flow rates of CO₂ and N₂ which were equal to 10 sccm and 1 sccm, respectively. The constant pressure of 19.4 mbar was maintained.



Figure 8.3 – Black points: temporal profile of the gas temperature in the thin capillary at 19.4 mbar, $CO_2:N_2 = 10:1$. Red points: temporal profile of the gas temperature in the FTIR capillary at 10.5 mbar, 5 sccm N_2 + various flow rates of CO_2 .

The measurements of the gas temperature in the thin and FTIR capillaries at different time instants are given in the Figure 8.2. As for the thin capillary, it can be seen that gas is significantly heated in the second and the third pulses. The gas temperature in the third is as high as 1100 K. It is almost two times less compared to the FTIR capillary. However, it should be recalled that the specific deposited energy in the FTIR capillary was found to be more than 3 times higher than in the thin capillary. The reason to this was the fact that the low voltage electrode was grounded in the FTIR capillary whereas in the case of the thin capillary the low voltage electrode was attached to a coaxial cable.

8.3 Conclusions

The study of gas temperature in both types of capillaries as a function of time has been demonstrated in the Chapter. As for the FTIR capillary, the values of gas temperature in three subsequent pulses separated by 200 ns were found to be equal to 450 K, 1700 K and 2000 K, respectively. Measurements of gas temperature conducted in the thin capillary with better temporal precision have revealed the gas temperature of 1100 K in the end of the third pulse. In conclusion, it has been

justified experimentally that the phenomenon of fast gas heating does occur in a nanosecond capillary discharge in CO_2 just like it has been previously observed in similar experiments in $N_2:O_2$ mixtures and in pure nitrogen done on the same setup. So far, the experiments as well as the experimental results such as electric and optical characteristics of the discharge, dissociation fraction of CO_2 , gas temperature and so on have been given and discussed. However, an answer to the most essential question about the underlying mechanisms remains unclear still. One of the most powerful instruments to analyse kinetic mechanisms is numerical modeling of plasma. The final part of the Thesis is therefore devoted to description of the numerical model, results of the calculations as well as their comparison with the experimental data and – the most important – a possible explanation of the obtained experimental data will be suggested and discussed in details.

Chapter 9

Numerical modeling of the discharge

The current Chapter is dedicated to application of numerical modeling to analysis of the experimental results. The Chapter is divided into several parts. Basic principles and of the 0D modeling as well as the peculiarities such as input parameters of the model, calculation of gas temperature and electron dynamics will be discussed in the first part. A discussion of the kinetic scheme will be given in the second part. The third part of the Chapter is devoted to validation of the kinetic model.

9.1 Principles of 0D modeling

As it was mentioned before, 0D ZDPlasKin [115] code based on Fortran95 language has been used for calculations. The main task to accomplish by the 0D modeling was to find concentrations of species as a function of time by solving the so called rate equations. Let one have a reaction:

$$aA + bB \longrightarrow a'A + cC$$
 (9.1)

as an example. In this case, the rate equation for the A specie would be written as:

$$\frac{d[A]}{dt} = k(a'-a)[A]^{a}[B]^{b}, \qquad (9.2)$$

where k is the rate constant of the reaction (9.1). Therefore, a system of coupled equation of a type (9.2) was being solved. Two options were possible to set rate constants of reactions. The first option was to take constants from literature and to set them either as constant values or functions of electron and gas temperature. Such an option was chosen if a reaction didn't include electron scattering and the rate constant was independent on the reduced electric field E/n. The second option of calculation of rate constant was used for reactions whose rate constants depend on the reduced electric field. To do so, Boltzmann equation [116] in two-term approximation was being numerically solved by BOLSIG+ [33] solver integrated with the ZDPLasKin code. In fact, Boltzmann equation can be deduced from balance of particles in a point of phase space [21]. It can be written as:

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \nabla f - \frac{e}{m} \vec{E} \cdot \nabla_v f = C[f], \qquad (9.3)$$

where f is electron velocity distribution function (EVDF) in a six-dimensional phase space (which is the main object of interest), \vec{v} is the velocity vector, e is the elementary charge, m is the electron mass, E is the electric field, ∇_v is the velocity-gradient operator, C represents the rate of change in f due to collisions. To solve the Boltzmann equation, it is necessary to use several simplifications. The first one consists on the assumption that the EEDF f is isotropic in velocity space and the only direction which f can be varied along is the electric field direction. Then, the so called two-term approximation consists on expansion of f on Legendre polynomials of $\cos \theta$ (where θ is the angle between the velocity and field direction) and presentation of f as a sum of isotropic part f_0 and anisotropic perturbation f_1 :

$$f(z, v, t, \cos \theta) = f_0(z, v, t) + f_1(z, v, t) \cos \theta.$$

$$(9.4)$$

Variable z designates the coordinate along the vector of the electric field \vec{E} . Therefore, EEDF could be found for any value of the reduced electric field E/n whose temporal dependence was set to the code as an input data. It should be noticed that two-term approximation is only valid if the ratio of inelastic scattering processes to total scattering processes is much smaller than unity. Domination of inelastic processes could be the case at relatively high values of reduced electric fields. Nevertheless, it is shown in [116] that two-term approximation at $E/n \approx 200-500$ Td is still valid. To remind, these are values of E/n which have been measured in experiments described in previous Chapters.

As soon as the electron energy distribution function f is calculated, it was possible to calculate rate constants of processes of electron scattering. If the dependence of cross-sections of a process on electron energy ε is known, the rate constant of the process can be calculated as:

$$k(E/n) = \sqrt{\frac{2}{m_e}} \int_{\varepsilon_0}^{+\infty} f(\varepsilon(E/n))\sigma(\varepsilon)\varepsilon d\varepsilon, \qquad (9.5)$$

where ε_0 is a threshold of a reaction. $f(\varepsilon)$ should satisfy the normalization condition:

$$\int_{0}^{+\infty} f(\varepsilon)\sqrt{\varepsilon}d\varepsilon = 1.$$
(9.6)

Other values describing the ensemble of electron gas can be directly derived from the EEDF as soon as it is calculated for a given time instant. For instance, such parameters could be, electron temperature T_e , drift velocity and mobility of electrons.

It has been shown experimentally that phenomenon of fast gas heating occurs in the high voltage pulses and in between them. Thus, it is essential to take into account the temporal change of gas temperature. There are two reasons for this. The first one is validation of the model which is a matter of both practical and fundamental interest. The second reason consists on the fact that there are rate constants which are dependent on gas temperature. The following equation has been solved for calculation of gas temperature T as a function of time:

$$\frac{dT}{dt} = \frac{\gamma(T) - 1}{n_{gas}} \sum_{j=1}^{j_{max}} \delta \varepsilon_j R_j, \qquad (9.7)$$

where R_j is rate of reaction number j, n_{gas} is gas volume density, $\delta \varepsilon_j$ is energy (expressed in eV) dissipated into system in a unique act. $\delta \varepsilon_j$ was calculated as a difference between energy levels of active species and then set into the equations. It was important to take into account the dependence of adiabatic coefficient as a function of temperature. This dependence was taken from [117] and is demonstrated in the Figure 9.1. It can be seen that variation of $\gamma - 1$ in CO₂ can reach 2 times in 300-3000 K temperature scale, therefore the dependence of γ on temperature plays a crucial role. It is worth to be commented that the adiabatic coefficient of CO₂ given in the Figure 9.1 has been calculated for V-T equilibrium conditions which are evidently not fulfilled at the sub-microsecond timescale. However, the main point of the numerical modeling described in the Chapter is to simulate temperature dynamics at sub-microsecond timescale when the vibrational part of heat capacity does not play an essential role. It will be shown that V-T transfer starts to contribute significantly in heating dynamics only after a time instant of 2 μ s which is beyond the frame of the current discussion.

As it was mentioned before, E/n measured in experiments by a capacitive probe as a function of time has been chosen as the main input parameter of the numerical modeling. The main advantage of the approach is its simplicity and applicability in zero-dimensional case. Numerical models which use electric current as input data are more precise since rate constants of reactions depend exponentially on E/n and



Figure 9.1 – Dependence of adiabatic coefficient of CO_2 at $p = 10^{-2}$ mbar. Taken from [117].

depend linearly on the value of electric current. Another disadvantage of the approach consists on the fact that the E/n between pulses is equal to zero since plasma is not affected by voltage waves. According to the approach which was described previously, all rate constants of electron scattering processes should be equal to zero, the electron temperature should be hence equal to 300 K. It is obvious that such an approach is not valid since instantaneous cooling of electron gas is not physical. Therefore, the following tip to overcome the issue was introduced. There was a 'fictional' constant non-zero E/n set between pulses. The value of the E/n was chosen in such a way that there is an agreement between maxima of the calculated and measured peak values of the electron density in the second and third pulses. To verify the approach, an agreement between vibrational temperature of asymmetric mode of CO_2 and electron temperature between the pulses was verified. The electron temperature was found to be equal to 5000 K between the first and second pulses as well as between the second and the third one. Along with that, it should be noted that the initial electron density $N_e(0)$ was chosen in such a way that the peak electron density in the first pulse is in agreement with the experimental one. $N_e(0)$ was supposed to be equal to $[CO_2^+](0)$. The concentrations of the rest of species were supposed to be equal to zero.

Another disadvantage of 0D modeling is the fact that electron density radial profile is not constant. This fact has been demonstrated experimentally in the Chapter 7. Therefore, the processes of diffusion of electrons along a radius of the capillary cannot be taken into account in the most legitime way. Nevertheless, disregard of losses of electrons due to their diffusion may lead to significant discrepancy between the calculated and measured values of the electron density. An attempt to solve the problem was performed in the following way. An additional term responsible for electron losses has been added to the system of rate equation. The characteristic time of the electron losses can be estimated in the following way. The coefficient of diffusion of electrons in the radial direction at p=15 mbar in CO₂ is $D_e \approx 10^4$ - 10^5 cm²/s [33]. The characteristic time τ_{diff} of diffusion of electrons in a capillary of r=0.1 cm can be calculated as:

$$\tau_{diff} = \frac{r^2}{D_e}.\tag{9.8}$$

After all calculations one obtains $\tau_{diff} \approx 10^{-7} \cdot 10^{-6}$ s. Thus, the rate constant of diffusion of electrons to walls is equal to $k_e = 10^6 - 10^7 \text{ s}^{-1}$. The rate constant of diffusion of electrons to walls has been taken from this range for each series of calculations.

9.2 Kinetic scheme

9.2.1 Set of reactions

The reactions and their constants used in the kinetic scheme have been taken from literature. There were various processes described in literature such as ionization of species, attachment of electrons, electronic and vibrational excitation, formation of cluster and negative ions. Taking into account all these processes may lead to thousands of reactions. Of course, such big amount of reactions may overload the calculations and make them long. That's why choosing the most important reactions is essential to shorten and simplify the calculations. Moreover, it is important to know which reactions and species play the most essential role in a certain parameter. For example, there can be plenty of electronically excited states in plasma but few of them play a real role in fast gas heating and dissociation of CO_2 molecules. Therefore, a build of the so called reduced kinetic scheme is required. To do so, two procedures should be done. The first one is rate analysis which allows to make rough analysis of the kinetic scheme. Rate analysis consists on calculation of rates at different periods of time. A reaction is supposed to be important at a certain

period of time if the rate exceeds a certain threshold (e.g. 10^{22} cm⁻³/s). Such an approach is brief but quite rude since there may be reactions considered as unimportant whereas their combination may lead to formation of clue species despite their rate is lower than the set threshold. Therefore, a finer tool to reduce the kinetic scheme should be applied. Sensitivity analysis of the set of reaction may act as such a tool.

The idea of the procedure of sensitivity analysis is the following. Let α be a parameter of interest, e.g. dissociation fraction of CO₂ or increase of gas temperature. Then, rate constants of each reaction present in the full kinetic scheme are sequentially changed on the same percentage (e.g. 50 %). The sensitivity coefficient ϕ_i of α to change of rate constant k_i of reaction number *i* is then defined as:

$$\phi = \frac{\alpha(1.5k_i) - \alpha(k_i)}{\alpha(1.5k_i)}.$$
(9.9)

The criterion of exclusion of a reaction from the full list is the following. If the sensitivity coefficient of a reaction at any time instant is less than a certain threshold (for example, 10%), the reaction is not included to the reduced scheme.

The author is expressing his deepest acknowledgements to Dr. Elena FILIMONOVA who helped to choose the reactions important for CO_2 dissociation in pulses and between them (sensitivity threshold was set to 10 %) and to Dr. Nikolay POPOV who has done sensitivity analysis of the kinetic scheme for choosing the reactions driving the fast gas heating processes. The set of reactions included on the reduced kinetic scheme has prepared with the closest partipation of Dr. POPOV. He suggested a way to take into account electronic excitation of atoms and molecules participating in reactions of fast gas heating.

The Table 9.1 represents the set of reactions used in the kinetic model. The following species were included in the model: CO_2 , $\text{CO}_2(v)$, $\text{CO}(X^1\Sigma^+)$, CO(v), $\text{CO}(a^3\Pi_r)$, $O(^3\text{P})$, $O(^1\text{D})$, $O(^1\text{S})$, e, CO_2^+ , CO_4^+ , $C_2\text{O}_4^+$, O_2^+ , CO^+ . The rate constants of reactions are given in cm³/s for two-body reactions and in cm⁶/s for three-body reactions. The reactions (R1) - (R9) are processes of electron scattering and their cross-sections have been taken from the Phelps database [111]. If a reaction has an energy defect – in other words, the reaction participates in gas heating – the energy defect expressed in eV is given in the same Table. Several comments should be done here. First, interaction of species with vibrational manifold of CO₂ is not given in the Table 9.1 and CO₂(v) represents a combined set of all levels of vibrationally excited CO₂ species. The same comment is valid for CO(v). Inclusion of various vibrational

levels of CO_2 and the influence on kinetics will be discussed in the next subsection. Second, all reactions given in the table and having either CO_2 or CO in the left-hand side have been repeated with $CO_2(v)$ and CO(v). The cross-sections and rate constants were assumed to be equal to the initial ones. Third, reactions with several electronic states of atomic oxygen in the right-hand side have been assumed to have same rate constants for each specie. Finally, several reactions and choice their constants deserve separate remarks (i-vi).

(i) It has been shown in [123] that the main products of quenching of $N_2(A^3\Sigma_u^+)$ by atomic oxygen are excited O atoms:

$$N_2(A^3\Sigma_u^+, v=0,1) + O(^3P) \longrightarrow N_2(X) + O(^1S).$$
(9.10)

One can notice that the values of excitation energy of $N_2(A^3\Sigma_u^+)$ and $CO(a^3\Pi)$ are close to each other and equal to 6.17 eV and 6.0 eV, respectively. Therefore, it could be assumed that quenching of $CO(a^3\Pi)$ leads to formation of $O(^1S)$ atoms as well:

$$\mathrm{CO}(\mathrm{a}^{3}\Pi, \mathrm{v}=0,1) + \mathrm{O}(^{3}\mathrm{P}) \longrightarrow \mathrm{CO}(\mathrm{v}=0,1) + \mathrm{O}(^{1}\mathrm{S}). \tag{9.11}$$

(ii) Collision of $O({}^{1}S)$ and $O({}^{3}P)$ atoms leads to formation of an excited O_{2}^{*} molecule with excitation threshold of 9.3 eV. The term of the O_{2}^{*} electronic state intersects with the $O_{2}(B^{3}\Sigma_{u}^{-})$ repulsive term which, in its turn, dissociates onto $O({}^{3}P)+O({}^{1}D)$. The energy defect is therefore comes to the gas heating.

(iii) It has been demonstrated in [124] that 44% of energy of $O(^{1}D)$ and CO_{2} is delivered to vibrational excitation of CO_{2} during the reaction (R7):

$$O(^{1}D) + CO_{2} \longrightarrow O(^{3}P) + CO_{2}(v).$$
 (9.12)

It has been therefore concluded that the percentage of $O(^{1}D)$ energy coming to FGH is equal to 56%. Thus, the energy defect in the reaction (R17) is equal to 1.1 eV.

(iv) The same assumption as for (iii) can be applied for the reaction (R18):

$$O(^{1}D) + CO \longrightarrow O^{3}P) + CO(v)$$
 (9.13)

(v) The pre-exponent factor of the rate constant of the reaction (R22) has been taken from [24]. The temperature dependence of the rate constant has been taken as in the reaction [125].

$$N_2 + N_2 + N_2^+ \longrightarrow N_4^+ + N_2 \tag{9.14}$$

N⁰	Process	Constant	Ref	ΔE	Notes
R1	$\rm CO_2 + e \longrightarrow \rm CO_2 + e$	f(E/n)			
R2	$\mathrm{CO}_2 + \mathrm{e} \longrightarrow \mathrm{CO}_2^+ + \mathrm{e} + \mathrm{e}$	f(E/n)			
R3	$\mathrm{CO}_2 + \mathrm{e} \longrightarrow \mathrm{CO} + \mathrm{O}(^1\mathrm{D}) + \mathrm{e}$	f(E/n)			
R4	$\mathrm{CO}_2 + \mathrm{e} \longrightarrow \mathrm{CO}(\mathrm{a}) + \mathrm{O}(^3\mathrm{P}) + \mathrm{e}$	f(E/n)			
R5	$\mathrm{CO}_2 + \mathrm{e} \longrightarrow \mathrm{CO}_2(\mathrm{v}) + \mathrm{e}$	f(E/n)			
R6	$\rm CO + e \longrightarrow \rm CO + e$	f(E/n)			
R7	$\rm CO + e \longrightarrow \rm CO(v) + e$	f(E/n)			
R8	$\rm CO + e \longrightarrow \rm CO^+ + e + e$	f(E/n)			
R9	${ m CO}+{ m e}\longrightarrow { m CO}({ m a}^3\Pi_r)+{ m e}$	f(E/n)			
R10	$\mathrm{CO}(\mathrm{a}^{3}\Pi_{r}) + \mathrm{CO}_{2} \longrightarrow 2 \cdot \mathrm{CO}(\mathrm{v}) + \mathrm{O}(^{3}\mathrm{P})$	$5.0 \cdot 10^{-12}$	[118]	0.55	
R11	$\mathrm{CO}(\mathrm{a}^{3}\Pi_{r}) + \mathrm{CO}_{2} \longrightarrow \mathrm{CO}(\mathrm{v}) + \mathrm{CO}_{2}(\mathrm{v})$	$5.0 \cdot 10^{-12}$	[118]	0.6	
R12	$\mathrm{CO}(\mathrm{a}^{3}\Pi_{r}) + \mathrm{CO} \longrightarrow \mathrm{CO}(\mathrm{v}) + \mathrm{CO}(\mathrm{v})$	$1.1 \cdot 10^{-10}$	[119]	0.6	
R13	${ m CO}({ m a}^3\Pi_r) + { m O}({ m ^3P}) \longrightarrow { m CO} + { m O}({ m ^1S})$	$1.9 \cdot 10^{-10}$	[119]	1.8	(i)
R14	${ m O(^1S)} + { m CO_2} \longrightarrow { m O(^1D)} + { m CO_2(v)}$	$4.0 \cdot 10^{-13}$	[120]	2.23	
R15	${ m O}({}^1{ m S}) + { m CO} \longrightarrow { m O}({}^1{ m D}) + { m CO}({ m v})$	$1.0 \cdot 10^{-13}$	[120]	2.23	
R16	${ m O}({}^1{ m S}) + { m O}({}^3{ m P}) \longrightarrow { m O}({}^1{ m D}) + { m O}({}^3{ m P})$	$5.0 \cdot 10^{-11} \cdot \exp(-301/T_g)$	[121]	2.23	(ii)
R17	${ m O}(^1{ m D}) + { m CO}_2 \longrightarrow { m O}(^3{ m P}) + { m CO}_2({ m v})$	$7.4 \cdot 10^{-11} \cdot \exp(133/T_g)$	[122]	1.1	(iii)
R18	$O(^{1}D) + CO \longrightarrow O(^{3}P) + CO(v)$	$8.0 \cdot 10^{-11}$	[120]	1.1	(iv)
R19	$\mathrm{CO}_2^+ + \mathrm{e} \longrightarrow \mathrm{CO}(\mathrm{v}) + \mathrm{O}(^1\mathrm{D}, ^1\mathrm{S})$	$4.2 \cdot 10^{-7} \cdot \exp(300/T_e)$	[32]	≈ 6	
R20	$\mathrm{CO}_2^+ + \mathrm{O}({}^3\mathrm{P}) \longrightarrow \mathrm{O}_2^+ + \mathrm{CO}$	$2.5 \cdot 10^{-10}$	[24]	1.0	
R21	$O_2^+ + e \longrightarrow O(^3P) + O(^3P, {}^1D)$	$2.0 \cdot 10^{-7} \cdot \exp(300/T_e)$	[110]	5.0	
R22	$\mathrm{CO}_2^+ + \mathrm{CO}_2 + \mathrm{M} \longrightarrow \mathrm{C}_2\mathrm{O}_4^+ + \mathrm{M}$	$3.0 \cdot 10^{-28} \cdot (300/T_e)^{1.7}$	[24]		(v)
R23	$C_2O_4^+ + M \longrightarrow CO_2^+ + CO_2 + M$	$(3-6) \cdot 10^{-14}$	[24]		
R24	$C_2O_4^+ + e \longrightarrow CO(v) + O(^1D) + CO_2(v)$	$1.9 \cdot 10^{-6} \cdot (300/T_e)^{0.33}$	[32]	5.7	(vi)
R25	$O_2^+ + CO_2 + M \longrightarrow CO_4^+ + M$	$5.0 \cdot 10^{-31}$	[120]		

Table 9.1 – The main reduced kinetic scheme used in the model. The rate constants are given in cm^3/s for two-body reactions and in cm^6/s for three-body reactions, ΔE is given in eV.

(vi) The constant of the reaction (R24) was assumed to be equal to the constant of the recombination of $(CO_2)_2(CO)^+$ cluster ion. The products of the reaction (R24) are the same as during the recombination of CO_2^+ ion described in [126].



Figure 9.2 – Dependence of drift velocity on the reduced electric field. Red points: according to experiments given in [127]. Green points: calculations based on cross-sections of reactions of electron scattering.

One of the most essential check of validity of the kinetic scheme and, in particular, of the set of cross-sections of the reactions of electron scattering, is the verification of the so called swarm parameters. Swarm parameters of the electron gas are drift velocity (cm/s) and rate constant of CO_2 ionization expressed in cm³/s. The idea was to compare the experimental values of the swarm parameters [127] and their values obtained by the calculations based on a given set of cross-sections. It can be seen in the Figures 9.2 and 9.3 that the agreement between the experimental swarm parameters and calculations based on the set of Phelps cross-sections is reached. Thus, the choice of Phelps cross-sections for the calculations is legitime.

9.2.2 Vibrational kinetics

• Vibrational excitation and de-excitation by electron impact

The next stage of development of the kinetic model was to introduce the so called vibrational manifold. The manifold included 21 levels of asymmetric mode of CO_2 and four combinations of symmetric modes v_a, v_b, v_c and v_d of CO_2 . The energy levels of the modes are given in the Table 9.2. The cross-sections for excitation of $CO_2(a), CO_2(b), CO_2(c), CO_2(d)$ and $CO_2(0 \ 0 \ 1)$ from the ground state of CO_2



Figure 9.3 – Ratio of the rate constant of the reaction of ionization of CO_2 and drift velocity on the reduced electric field. Red points: according to experiments given in [127]. Green points: calculations based on crosssections of reactions of electron scattering.

were taken from Phelps database [30]. Cross-section of excitation of CO₂ (0 0 n) by electron impact from CO₂ (0 0 m), $n > m; n, m = \overline{1,21}$ have been obtained by scaling the cross-section of the reaction:

$$CO_2 + e \longrightarrow CO_2(0\ 0\ 1) + e$$
 (9.15)

according to the threshold shift approximation [20, 24]. The threshold shift approximation allows to recalculate the cross-sections σ_{mn} of excitation of CO₂ (0 0 n) from CO₂ (0 0 m) by electron impact as a function of electron energy by shifting of electron energies and multiplying them on exponential factor:

$$\sigma_{mn}(\varepsilon) = \exp(-0.5(n-m-1))\sigma_{01}(\varepsilon + E_{01} - E_{mn}), \qquad (9.16)$$

where $E_{01} = E_1 - E_0$ and $E_{mn} = E_n - E_m$.

Dissociation of CO_2 onto $CO(X^1\Sigma^+)$ and $O(^3P)$ by electron impact from any level of the asymmetric mode of vibrations has been taken into account by introduction of a fictional level $CO_2(0\ 0\ 22)$ which was, in fact, equal to $CO(X^1\Sigma^+)$ and $O(^3P)$. The cross-sections of the reactions have been found according to equation (9.16). It

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Level	Energy (eV)
CO_2	0.00
$\operatorname{CO}_2(v_a)$	0.08
$\mathrm{CO}_2(v_b)$	0.17
$\mathrm{CO}_2(v_c)$	0.25
$\mathrm{CO}_2(v_d)$	0.33
$CO_2(0\ 0\ 1)$	0.29
$CO_2(0\ 0\ 2)$	0.58
$CO_2(0 \ 0 \ 3)$	0.86
$CO_2(0\ 0\ 4)$	1.14
$CO_2(0\ 0\ 5)$	1.43
$CO_2(0 \ 0 \ 6)$	1.70
$CO_2(0\ 0\ 7)$	1.97
$CO_2(0\ 0\ 8)$	2.24
$CO_2(0\ 0\ 9)$	2.51
$CO_2(0 \ 0 \ 10)$	2.97
$CO_2(0\ 0\ 11)$	3.03
$CO_2(0\ 0\ 12)$	3.29
$CO_2(0\ 0\ 13)$	3.55
$CO_2(0\ 0\ 14)$	3.80
$CO_2(0\ 0\ 15)$	4.04
$CO_2(0\ 0\ 16)$	4.29
$CO_2(0\ 0\ 17)$	4.53
$CO_2(0\ 0\ 18)$	4.77
$CO_2(0\ 0\ 19)$	5.01
$CO_2(0\ 0\ 20)$	5.24
$CO_2(0\ 0\ 21)$	5.47

Table 9.2 – Energy levels (eV) of symmetric and asymmetric modes of CO_2 . According to [24].

should be noted that since the reactions of vibrational excitation of CO_2 by electron impact are possible, reactions of vibrational de-excitation of CO_2 by electron impact should be taken into account. The rates of de-excitation W_{nm} of CO_2 (0 0 m) from CO_2 (0 0 n), $n > m; n, m = \overline{1, 21}$ can be found from rates of direct reactions W_{mn} according to principle of detailed balance:

$$W_{nm} = W_{mn} \exp\left(-\frac{E_{mn}}{T_e}\right). \tag{9.17}$$

It should be noted that the equation (9.17) is only valid if the detailed balance takes place in the system. A criteria of the presence of detailed balance in a multi-modal model is temperature equilibrium of the electron which, in its turn, may be witnessed by Maxwellian electron energy distribution function. The Figure 9.4 demonstrates EEDF calculated by ZDPlasKin code at t = 6 ns (peak of the electric current in the first high voltage pulse) and t = 15 ns (end of the first high voltage pulse). To understand whether the EEDF satisfies the Maxwellian distribution, Maxwellian fitting curves plotted for $T_e = 4.3$ eV and $T_e = 0.85$ eV are given nearby. The Maxwellian fit of the EEDF has been obtained according to the following formula:

$$f(\varepsilon)\sqrt{\varepsilon} = (T_e)^{-3/2}\sqrt{\varepsilon} \exp\left(\frac{\varepsilon}{T_e}\right),$$
(9.18)

where T_e (in eV) is calculated electron temperature cat a given time instant, ε is energy of electrons (in eV). It can be seen that EEDF at t = 6 ns is not Maxwellian for high energy electrons, nevertheless it satisfies quite well the equilibrium criteria for energies below 5.5 eV which is threshold for dissociation of CO₂. As for the end of the pulse, the EEDF can be considered as purely equilibrium due to e-e collisions. In conclusion, the assumption of principle of detailed balance can be considered as not very far from valid for all calculation timescale since the reduced electric field reaches the maximum in the first pulse. The calculation of cross-sections using the formula (9.17) is therefore legitime.

The author is sincerely thankful to Dr. Elena KUSTOVA for a fruitful discussion of the principle of the detailed balance and the way of taking it into account in the calculations.

• VT-exchange

VT- and VV-exchange in plasma has been introduced according to Schwartz-Slawsky-Herzfeld (SSH) theory, or SSH approximation whose basics have been described in sufficient details in [24]. The SSH approximation has been chosen for the reason of its relative simplicity. The SSH approximation gives a clue for scaling of rate constants from a rate constant of a basic reaction. An act of VT-exchange from an asymmetric vibrational modes can be written as:

$$\operatorname{CO}_2(0\ 0\ m) + \mathcal{M} \longrightarrow \operatorname{CO}_2(0\ 0\ m-1) + \mathcal{M} + \Delta E_{m,m-1}$$
(9.19)



Figure 9.4 – Electron energy distribution functions at t = 6 ns (dashed lines) and t = 15 ns (solid lines) as well as their Maxwellian fits for 4.3 eV and 0.85 eV, respectively. Black: calculations of ZDPlasKin, red: Maxwellian fit.

 $\Delta E_{m,m-1}$ here is difference between energy levels. In fact, VT-exchange (or VTrelaxation) is transition of vibrational energy to translational degrees of freedom. The process leads therefore to gas heating. That's why it is crucial to study is influence on dynamics of the gas temperature. The reactions of transition of vibrational quanta from asymmetric to symmetric modes $CO_2(v_a, v_b, v_c)$:

$$CO_2(0\ 0\ 1) + M \longrightarrow CO_2(v_a, v_b, v_c) + M + \Delta E$$

$$(9.20)$$

whose constants are equal to $k_{VT,a} = 4.25 \times 10^{-1} \exp(-407 T_{gas}^{-1/3} + 824 T_{gas}^{-2/3}) \text{ cm}^3/\text{s}$, $k_{VT,b} = 8.57 \times 10^{-1} \exp(-404 T_{gas}^{-1/3} + 1096 T_{gas}^{-2/3}) \text{ cm}^3/\text{s}$, $k_{VT,c} = 1.43 \times 10^{-5} \exp(-252 T_{gas}^{-1/3} + 685 T_{gas}^{-2/3}) \text{ cm}^3/\text{s}$ were taken as the basic reactions. To find rate constants of processes type Reaction (9.19) the SSH theory has been used for scaling. According to the SSH theory, a rate constant $k_{m,m-1}$ can be written as:

$$k_{m,m-1} = k_{VT,a,b,c} Z_m \frac{F(\gamma_m)}{F(\gamma_1)}.$$
(9.21)

 Z_m here is a scaling factor:

$$Z_m = n \frac{1-\chi}{1-n\chi},\tag{9.22}$$

 χ is the anharmonicity of the energy levels, γ_n is a coefficient showing the adiabaticity of the reaction. The coefficient can be expressed as:

$$\gamma_n = 0.018 (E_m - E_{m-1}) r_0 \left(\frac{\mu}{T_{gas}}\right)^{1/2}, \qquad (9.23)$$

where μ is reduced mass of a CO₂ molecule (in a.m.u.) and $r_0 = 3.94$ Angstrom is the 'radius' parameter of CO₂ Lennard-Jones potential. Function $F(\gamma)$ can be written as:

$$F(\gamma) = \frac{1}{2} \left[3 - \exp\left(-\frac{2}{3}\gamma\right) \right] \exp\left(-\frac{2}{3}\gamma\right).$$
(9.24)

Consequently, a rate constant $k_{m,m-1}$ was a superposition of scaled rate constants $k_{VT,a}$, $k_{VT,b}$ and $k_{VT,c}$. Finally, relaxation of symmetric vibrational degrees of freedom to translational ones can been written as

$$CO_2(v_a, v_b, v_c, v_d) + + M \longrightarrow CO_2(0 \ 0 \ 0) + M + \Delta E.$$
(9.25)

The constants of each reaction were supposed to be equal to each other and to $7.14 \times 10^{-8} \exp(-177 T_{gas}^{-1/3} + 451 T_{gas}^{-2/3}) \text{ cm}^3/\text{s}.$

• VV-exchange

A singular act of VV-exchange between different levels of asymmetric modes when one molecule lowers its vibrational state $(n) \longrightarrow (n-1)$ and another molecule raises its vibrational state $(m) \longrightarrow (m+1)$ has been introduced in a similar way:

$$k_{m,m-1}^{n-1,n} = k_{1,0}^{0,1} Z_m Z_m \frac{F(\gamma_{nm})}{F(\gamma_{11})}.$$
(9.26)

The values of ΔE for calculations of γ_{nm} have been calculated as $\Delta E = |E_m + E_n - 1 - E_{m-1} - E_n|$. The basic reaction to scale the rate constant of, was the reaction:

$$CO_2(0\ 0\ 1) + CO_2(0\ 0\ 0) \longrightarrow CO_2(0\ 0\ 1) + CO_2(0\ 0\ 0)$$
 (9.27)

with the rate constant $k_{1,0}^{0,1} = 1.32 \times 10^{-10} (T_{gas}/300)^{0.5} (250/T_{gas}) \text{ cm}^3/\text{s}.$

• VV'-exchange

An elementary act of a VV'-exchange has been considered as a transfer of energy from asymmetric modes of CO_2 vibrations to its symmetric modes (v_a, v_b) :

$$CO_2(0\ 0\ m) + CO_2(0\ 0\ 0) \longrightarrow CO_2(m-1) + CO_2(v_a)$$
 (9.28)

and

$$\operatorname{CO}_2(0\ 0\ m) + \operatorname{CO}_2(0\ 0\ 0) \longrightarrow \operatorname{CO}_2(m-1) + \operatorname{CO}_2(v_b).$$
(9.29)

The rate constants of the aforementioned processes have been obtained by scaling the rate constants of the basic processes in the similar way as it has been just described above. The basic processes are the following:

$$\operatorname{CO}_2(0\ 0\ 1) + \operatorname{CO}_2(0\ 0\ 0) \longrightarrow \operatorname{CO}_2(v_a) + \operatorname{CO}_2(v_b) \tag{9.30}$$

and

$$\operatorname{CO}_2(0\ 0\ 1) + \operatorname{CO}_2(0\ 0\ 0) \longrightarrow \operatorname{CO}_2(v_b) + \operatorname{CO}_2(v_a) \tag{9.31}$$

with the rate constants $k_{1,ab} = k_{1,ba} = 1.06 \times 10^{-5} \exp(-242 T_{gas}^{-1/3} + 633 T_{gas}^{-2/3}) \text{ cm}^3/\text{s}.$

9.2.3 Vibrational distribution function

Figures 9.5 - 9.8 demonstrate calculations of vibrational distribution function (VDF) at different time instants. The 0 time instant corresponds to the moment when the electric current starts to flow in the discharge cell.

The Figure 9.5 shows VDF at time instants corresponding to the beginning of flowing of the electric current (t = 3 ns) in the capillary, the reach of peak current (t = 8 ns), the end of the high voltage pulse (t = 17 ns) and a time instant in the afterglow of the first high voltage pulse just before the arrival of the second one. Dynamics of increase of population of high vibrational levels can be seen. The very beginning of the high voltage pulse is a too early moment for formation of a stable vibrational manifold and fraction of vibrational excitation of CO_2 is therefore around 0.1 %. As long as the discharge is developing in the capillary, population of the high vibrational levels is increasing and reaches its maximum in the afterglow of the first high voltage pulse. Population of levels 5-13 is almost the same and formation of the so called Treanor-Rich plateau in the VDF can be seen. A transition from a quasi-exponential distribution to the Treanor-Rich plateau is caused by the fact the rate of VT- and VV-relaxation is the faster, the higher is a vibrational level.

As the previous Figure, the Figure 9.6 shows VDF at time instants corresponding to the beginning of flowing of the electric current (t = 228 ns) of the second pulse,


Figure 9.5 – Vibrational distribution function of the asymmetric mode in the first high voltage pulse and its afterglow

the reach of the peak current (t = 244 ns), the end of the second high voltage pulse (t = 17 ns) and a time instant just before the arrival of the third pulse.

The VDF in the second pulse seems to reach the peak of its stability whereas it almost doesn't change within the second pulse except high levels (17-21). The population of these levels is higher increases with the development of the second high voltage pulse in the discharge cell. The plateau in the VDF is quite pronounced as in the first pulse and its afterglow. In contrast to the previous pulse, the VDF starts to relax in the afterglow of the second pulse since population of high vibrational levels drops down. It means that the processes of VT-exchange start to play an important role at this timescale and gas heating by VT-relaxation is expected to start to be significant during the end of the second high voltage pulse and its afterglow.

The processes of VT-relaxation becomes more and more pronounced in the third high voltage pulse (see Figure 9.7). The time instant t = 466 ns corresponds to the beginning of the third pulse, t = 470 ns is the peak current, t = 491 ns is the end of the third high voltage pulse and t = 501 ns is the near afterglow. It can be seen that the VT-exchange is slightly slowed down by the development of the pulse t = 491 ns but the rest part of VDF profiles are the same.



Figure 9.6 – Vibrational distribution function of the asymmetric mode in the second high voltage pulse and its afterglow.

Finally, the Figure 9.8 demonstrates the decay of the vibrational distribution function in the afterglow of the train of pulses. A significant loss of vibrational excitation is seen at the moment of $t = 1\mu$ s. As for $t = 2\mu$ s, the ratio of the CO₂(0 0 1) and CO₂(0 0 0) becomes around 0.1 %. It can be concluded that the characteristic time of VT-relaxation is around 1 μ s. The influence of the vibrational kinetics on gas temperature should be therefore demonstrated and discussed.

The relatively high rate of the processes of VT-relaxation in the third pulse and the afterglow can be explained by the fact that the gas is heated via electronically excited states in the first and the second pulse. Since the rate constant of VTrelaxation increases exponentially with the temperature, the gas heats as a system with a positive feedback: the rate of VT-relaxation increases with the temperature and the faster is the VT-relaxation, the faster gas is heated. It should be mentioned as well that density of gas increases with time due to dissociation processes. Hence, the transfer of vibrational energy to translational degrees of freedom accelerates.



Figure 9.7 – Vibrational distribution function of the asymmetric mode in the third high voltage pulse and its afterglow

9.3 Validation of the model

The current section is dedicated to validation of the 0D model described above by comparison of the calculations and the experimental results.

9.3.1 Calculations of gas temperature profile

The Figure 9.9 represents the calculations of temporal dependence of the gas temperature by 0D model with and without detailed vibrational kinetics. The results of the measurements (which have been given in the Figure 8.3) are represented as well. The model slightly overestimates the temperature in the third pulse. Such a discrepancy can be explained by the fact that it was impossible to take into account the heat transfer within the capillary in the 0D model. A 0D model calculates the temperature as it would be measured directly in the axis of the capillary and not in the entire volume of the capillary. It can be seen that difference between temperature profiles calculated with and without taking into account the detailed vibrational kinetics becomes significant in the afterglow of the second pulse. This difference can be explained by start of VT-relaxation which could be also noticed in the Figure 9.6 by decrease of population of high vibrational levels. The difference



Figure 9.8 – Vibrational distribution function of the asymmetric mode in the afterglow of all pulses

between the profiles becomes more and more significant in the third pulse and the afterglow of the train of pulses. Thus, it can be concluded that vibrations overheat the gas on almost 1000 K on the microsecond timescale.

One of the main ideas of the Thesis was to understand the mechanisms driving the gas heating within the pulses and between them. As it has been said previously, the sensitivity analysis of the kinetic scheme has been done to choose the most important reactions. The most essential mechanisms of gas heating are given in the Figure 9.10. First, $O(^{1}D)$ state is formed due to dissociation of CO_{2} by electron impact (reaction (R3) in the Table 9.1). In its turn, $O(^{1}D)$ is quenched to $O(^{3}P)$ by CO and CO₂ (reactions (R17) and (R18), black curve in the Figure 9.10). The energy of the electronically excited states is partially transferred to the vibratonal degrees of freedom. The rest of the energy goes to the gas heating. Second, it should be noticed that electronically excited $CO(a^{3}\Pi)$ species are formed in pulses due to reactions of dissociation of CO_{2} by electron impact (reaction (R4)). Then, the $CO(a^{3}\Pi)$ species are quenched by CO_{2} , CO and $O(^{3}P)$ (reactions (R10), (R11), (R12) and (R13) between the pulses. In contrast to the previous point, it was considered that the total amount of electronic energy of $CO(a^{3}\Pi)$ is spent both to dissociation of



Figure 9.9 – Temporal dependence of the gas temperature. Blue curve: 0D modeling without detailed vibrational kinetics. Green curve: 0D modeling with detailed vibrational kinetics. Experimental points are designated by the points. p = 19.4 mbar, thin capillary.

CO₂ and excitation of vibrational degrees of freedom of CO and CO₂. Therefore, these reactions didn't contribute to the gas heating. Nevertheless, CO($a^{3}\Pi$) still contributed to fast gas heating processes. It was assumed that quenching of CO($a^{3}\Pi$) on O(³P) atoms (reaction R13, red curve in the Figure 9.10) causes heat transfer to plasma. Moreover, quenching of CO($a^{3}\Pi$) on O(³P) atoms leads to formation of electronically excited O(¹S) atoms which is followed by fast gas heating (reactions (R14) - (R17), blue curve in the Figure 9.10). Finally, the role of heat generation due to the reactions of electron-ion recombination (reactions (R19), (R21), (R24), magenta curve in the Figure 9.10) is important in the first high voltage pulse, but is relatively small between the pulses.

9.3.2 Electron density

Calculations of temporal profile of the electron density and CO_2^+ , $C_2O_4^+$, O_2^+ ions as well as experimental measurements of the electron density in the thin capillary



Figure 9.10 – Temporal dynamics of rates of different reactions responsible for FGH, p = 19.4 mbar, thin capillary

at 15.5 mbar are presented in the Figure 9.11. First, it should be said then calculations of temporal dynamics of electron density is in a good agreement with the experimental measurements. As for the dynamics of ions, CO_2^+ and $C_2O_4^+$ are the dominant agents of electron-ion recombination in the first pulse. However, the dominance of the $C_2O_4^+$ as of a specie of electron-ion recombination stops by the end of the first pulse. At this time instant and following high voltage pulses as well as in their afterglow the $C_2O_4^+$ ions are being converted to O_2^+ ions via processes of charge exchange.

9.3.3 Predictions of CO₂ dissociation fraction and energy efficiency

The results of calculations of temporal dynamics of the main species in the discharge are represented in the Figure 9.12. The calculations have been done for the thin capillary at 19.4 mbar. The dissociation fraction as a function of time is given in the Figure as well. It should be noted than the dissociation fraction has been calculated according to its definition (see equation (1.6)), where concentration of CO_2 has been calculated as sum of concentrations of CO_2 ground state and all vibrationally excited states. As for concentrations of CO, they have been calculated as sum of concentrations of CO in ground state, electronically and vibrationally excited states. The total amount of dissociation fraction at 1μ s is equal to 15.9 %. Since the total of specific deposited energy is equal to 1.22 eV/particle, the energy efficiency of dissociation is equal to (see equation (1.7)) 38 %.

The following analysis of the obtained results can be done. First, the experiment has been done in a thin discharge cell of volume V=0.13 cm³ at pressure p=19.4 mbar. It means that total amount of particles (assuming T = 300 K) is equal to N = pV/kT = $6.3 \cdot 10^{16}$ particles. Second, if specific deposited energy is equal to 1.22 eV/particle, the total amount of energy delivered to plasma is equal to 0.014 J. According to



Figure 9.11 – Calculations of temporal dynamics of electrons (blue curve), CO_2^+ ions (red curve), $C_2O_4^+$ ions (magenta curve) and O_2^+ ions (green curve). Black circles: experimental measurements of peak electron density. Black squares: experimental measurements of electron density between pulses. p = 15.5 mbar, thin capillary

measurements, the gas heating up to the end of the third pulse is equal to $\Delta T = 1200 \text{ K} - 300 \text{ K} = 900 \text{ K}$. The specific heat of CO₂ is equal to $c_1 = 888 \text{ J/mol·K}$ at T=300 K and to $c_2 = 1300 \text{ J/mol·K}$ at T=1200 K (see Figure 8.1). The total mass of the gas inside the discharge cell is equal to:

$$m = \rho V = \frac{pV}{RT}\mu,\tag{9.32}$$

where $\mu = 0.044$ kg/mol is molar mass of CO₂ and R = 8.31 J/mol·K is the universal gas constant. After all calculations one obtains $m = 4.6 \cdot 10^{-9}$ kg. Finally, energy delivered to gas heating is constrained between $Q_1 = mc_1\Delta T$ and $Q_2 = mc_2\Delta T$. After the calculations one obtains such an interval for energy Q_{heat} spent to heating of gas: $Q_{heat} \in [0.0037; 0.0054]$. Again, the total amount of energy delivered to plasma is equal to 0.014 J. Assuming that the energy of high voltage pulses is either spent on CO₂ dissociation or gas heating, one obtains an interval for energy spent to



Figure 9.12 – Calculations of temporal dynamics of the main species in the discharge. Black curve: CO_2 , red curve: CO, blue curve: $O(^3P)$, green: $O(^1S)$, orange: $CO(a^3\Pi)$. Black dashed line: dissociation fraction of CO_2 as a function of time. Thin capillary, 19.4 mbar.

CO₂ dissociation: $E_{diss} \in [0.0086; 0.0103]$ J what corresponds to interval of specific energy [0.85; 1.02] eV/particle. Since the energy threshold of CO₂ dissociation is equal to 5.5 eV, one can divide the interval on the threshold in order to estimate an interval for CO₂ dissociation degree. Therefore, the dissociation degree α is constrained in interval $\alpha \in [15.4; 18.5]$ %. The obtained estimation is in agreement with the calculated value of dissociation fraction of 15.9 %.

9.3.4 Temporal profiles of the electronically excited species

One more series of calculations have been done as an attempt to describe the waveforms of emission of molecular bands whose acquirement have been done by a photomultiplier tube (PMT) and described in the Chapter 5 (see section 5.2). The following systems have been chosen for description:

- The fourth positive system of $CO(A^1\Pi \longrightarrow X^1\Sigma^+)$, $\lambda_{cent} = 233.6$ nm.
- The UV-doublet of the carbon dioxide ion $CO_2^+(B^2\Sigma_u \longrightarrow X^2\Pi_g)$, $\lambda_{cent} = 288.5 \text{ nm}$
- The system of Fox-Duffendack-Barker $CO_2^+(A^2\Pi_u \longrightarrow X^2\Pi_g)$, vibrational transition $1 \longrightarrow 0$, $\lambda_{cent} = 340$ nm.

To do the calculations, a supplementary set of reactions (see Table 9.3) has been added to the kinetic scheme. First, the set of the reactions included dissociative excitation of $\operatorname{CO}_2^+(\operatorname{A}^2\Pi_u, \operatorname{B}^2\Sigma_u)$ ions by direct electron impact from $\operatorname{CO}_2(\operatorname{X}^1\Sigma^+)$ state (reactions (AR1), (AR2)), excitation of high electronic states of CO (AR7) including excitation $\operatorname{CO}(\operatorname{A}^1\Pi \longrightarrow \operatorname{X}^1\Sigma^+)$ state (AR3). Electron impact de-excitation from $\operatorname{CO}(\operatorname{A}^1\Pi)$ to its ground state (AR4) and to $\operatorname{CO}(\operatorname{a}^3\Pi)$ (AR6) has been included as well. Then, the kinetic scheme included radiative decay of species (reactions (AR8) -(AR11)). Finally, for better agreement of measured temporal profiles of $\operatorname{CO}_2^+(\operatorname{A}^2\Pi_u, \operatorname{B}^2\Sigma_u)$ with their calculations additional quenching of the states on electron has been suggested. The rate constants of quenching processes have been chosen in such a way that the profiles are in best agreement (reactions (AR12) - (AR14)). The crosssections of the reactions (AR3) - (AR7) have been taken from Phelps database. It should be said that participation of electronically excited $\operatorname{CO}_2^+(\operatorname{A}^2\Pi_u, \operatorname{B}^2\Sigma_u)$ in the reaction from the main list has been taken into account as well. In fact, the same rate constants of the reactions has been as for the ground state of CO_2^+ .

(i) CO^{*} designates all electronically excited states of CO lying higher than $CO(A^{1}\Pi)$ state.

N⁰	Process	Constant	Ref	Notes
AR1	$\mathrm{CO}_2 + \mathrm{e} \longrightarrow \mathrm{CO}_2^+(\mathrm{A}^2\Pi_u) + \mathrm{e} + \mathrm{e}$	f(E/n)	[128]	
AR2	$\mathrm{CO}_2 + \mathrm{e} \longrightarrow \mathrm{CO}_2^+(\mathrm{B}^2\Sigma_u) + \mathrm{e} + \mathrm{e}$	f(E/n)	[128]	
AR3	${ m CO} + { m e} \longrightarrow { m CO}({ m A}^1 \Pi) + { m e}$	f(E/n)	[129]	
AR4	${ m CO}({ m A}^1\Pi) + { m e} \longrightarrow { m CO} + { m e}$	f(E/n)	[129]	
AR5	${ m CO}({ m a}^3\Pi)+{ m e}\longrightarrow { m CO}({ m A}^1\Pi)+{ m e}$	f(E/n)	[129]	
AR6	${ m CO}({ m A}^{1}\Pi)+{ m e}\longrightarrow { m CO}({ m a}^{3}\Pi)+{ m e}$	f(E/n)	[129]	
AR7	$\mathrm{CO} + \mathrm{e} \longrightarrow \mathrm{CO}^* + \mathrm{e}$	f(E/n)	[129]	(i)
AR8	$CO(A^1\Pi) \longrightarrow CO$		[102]	
AR9	$\mathrm{CO}^* \longrightarrow \mathrm{CO}(\mathrm{A}^1 \Pi)$		[102]	
AR10	$\mathrm{CO}_2^+(\mathrm{A}^2\Pi_u) \longrightarrow \mathrm{CO}_2^+$	$8.3 \cdot 10^6 \text{ s}^{-1}$	[130]	
AR11	$\mathrm{CO}_2^+(\mathrm{B}^2\Sigma_u)\longrightarrow \mathrm{CO}_2^+$	$7.9 \cdot 10^6 \text{ s}^{-1}$	[130]	
AR12	$\operatorname{CO}_2^+(\mathrm{B}^2\Sigma_u) + \mathrm{e} \longrightarrow \operatorname{CO}_2^+(\mathrm{A}^2\Pi_u) + \mathrm{e}$	$1.0 \cdot 10^{-7} \text{ cm}^3/\text{s}$		suggestion
AR13	$\mathrm{CO}_2^+(\mathrm{B}^2\Sigma_u) + \mathrm{e} \longrightarrow \mathrm{CO}_2^+(\mathrm{A}^2\Pi_u) + \mathrm{e}$	$1.0 \cdot 10^{-8} \text{ cm}^3/\text{s}$		suggestion
AR14	$\mathrm{CO}_2^+(\mathrm{A}^2\Pi_u) + \mathrm{e} \longrightarrow \mathrm{CO}_2^+ + \mathrm{e}$	$5.0 \cdot 10^{-8} \text{ cm}^3/\text{s}$		suggestion

Table 9.3 – Additional reactions needed for description of emission of electronically excited species produced in the discharge

The Figure 9.13 demonstrates normalized temporal profiles of $\operatorname{CO}_2^+(\operatorname{A}^2\Pi_u)$ (green line), $\operatorname{CO}_2^+(\operatorname{B}^2\Sigma_u^+)$ (red line) and $\operatorname{CO}(\operatorname{A}^1\Pi)$ (blue line) acquired by PMT in the thin capillary at 15.5 mbar and calculations in the first high voltage pulse based on the combination of the main kinetic scheme with the additional reactions from the Table 9.3. The solid black curve designates calculations of normalized electric current. It can be seen that the calculations and experimental results are in agreement.

9.4 Conclusions

Zero-dimensional numerical modeling of the discharge done by the ZDPlasKin code has been described in the current Chapter. The numerical model used experimentally obtained temporal profile of the electric field as the input set of data. The reduced kinetic scheme has been suggested and validated by several methods. First, the set of cross-sections of the reactions of electron scattering has shown that calculated constant of CO_2 ionization and drift velocity of electrons as a function of the reduced electric field are in agreement with the experimental results given in the literature. The second method of validation was comparison of experimentally obtained temporal profiles of the electron density and arbitrary intensity of emission of electronically excited molecules. Both series of calculations are in agreement with the experimental results.

It has been shown that processes involving electronically excited $CO(a^3\Pi)$, $O(^1S)$, $O(^1D)$ species are responsible for fast gas heating during the discharge and between the pulses whereas, according to analysis of vibrational distribution functions calculated at different time instants, vibrational kinetics starts to play an important role during the afterglow of the second high voltage pulse and further due to processes of VT-exchange. As for electron-ion recombination with CO_2^+ , $C_2O_4^+$ and O_2^+ ions,



Figure 9.13 – Comparison of normalized temporal profiles of $CO_2^+(A^2\Pi_u)$ (green line), $CO_2^+(B^2\Sigma_u^+)$ (red line) and $CO(A^1\Pi)$ (blue line) acquired by PMT and by calculations in the first high voltage pulse. Thin capillary, 15.5 mbar, pure CO_2 . Solid black curve designates calculations of normalized electric current.

it plays a significant role only in the first high voltage pulse.

Two kinetic schemes (with and without taking into account the vibrational kinetics) have been analyzed and have shown a good agreement of calculations of temperature with its experimental measurements. However, taking into account the vibrational kinetics shows that processes of VT-relaxation are responsible for additional gas overheat of gas up to 1000 K.

Finally, calculations of temporal profiles of CO and CO₂ have been done as well as calculations of dissociation fraction of CO₂ and its energy efficiency. At 1 μ s, the dissociation fraction of CO₂ and the energy efficiency of dissociation are equal to 15.9 % and 38 %, respectively.

Chapter 10

General conclusions

Contributions of the present work

The work described in the current Thesis includes experimental study of a nanosecond discharge ignited in CO_2 at moderate pressure at high values of reduced electric fields and specific deposited energy as well as numerical modeling of the discharge.

Measurements of electric characteristic of the discharge such as electric current, specific deposited energy have been done in two different discharge capillaries and have shown that the discharge develops in a stable way in pure CO_2 at moderate pressure. The value of the specific deposited energy is around 1.5 eV in the thin capillary and around 5.5 eV in the FTIR capillary. The measurements of the reduced electric field as a function time in the thin capillary by a capacitive probe have shown that there is a FIW propagating in the capillary from the high-voltage electrode to the low-voltage electrode. The values of the reduced electric field behind the front of the FIW are around 200-400 Td. Measurements of electron density as a function of time have been done in the thin capillary. The values of peak electron density in the first, second and the third pulses have been found to be equal to 2.0 $\times 10^{15}$ cm⁻³, 1.6×10^{15} cm⁻³ and 1.4×10^{14} cm⁻³, respectively. As for the the values of density of negative ions, they are negligible compared to the electron density since the processes of attachment of electrons to atoms and molecules don't play an important role at these values of reduced electric field. Finally, the measurements of the radial profile of the electron density in a $CO_2:N_2$ mixture have shown the presence of radial symmetry of the electron density profile. The measurements have also verified the fact that the electron density reaches the peak value close to the axial part of the capillary and lowers towards the direction of walls. The experiment has been done at different time instants and has revealed the fact that qualitative behaviour of the electron density doesn't change within time.

Measurements of CO_2 dissociation fraction and energy efficiency of CO_2 dissociation by means of FTIR spectroscopy have been done in the exhaust of the FTIR capillary in pure CO_2 . It was shown that pressure of 8.1 mbar is optimal for energy efficiency and dissociation fraction at low frequency pulse regime. Both values are around 20 %. Measurements of energy efficiency and dissociation fraction at high frequency pulse regime have shown the fact that CO_2 dissociation fraction is proportional to number of pulses and then reaches a saturation threshold of 92 %. The energy efficiency of the process at given conditions is approximately equal to 8 %.

Optical emission spectroscopy have been applied to the discharges both ignited in the thin capillary and the FTIR capillary. No qualitative difference has been observed between emission spectra recorded in the capillaries. The emission spectra have demonstrated an abundant presence of energy states lying between 18 and 25 eV with respect to the CO₂ ground state such as electronically excited $\text{CO}_2^+(\text{A}^2\Pi_u, \text{B}^2\Sigma_u)$ ions. The traces of consequent dissociation of CO onto C and O have been observed by presence of electronically excited C line(2p3s - 2p2p) and system of Swan $\text{C}_2(\text{d}^3\Pi_g) \longrightarrow \text{C}_2(\text{a}^3\Pi_u)$. The spectroscopy of the discharge has confirmed the fact that the most part of energy of electrons produced and accelerated by the electric field is spent to electronic excitation.

Gas temperature measurements in the discharge have been conducted both in FTIR and thin capillary. The measurements have been based on acquisition of rotational temperature of N_2 which has been added to CO_2 as an admixture of small percentage. The validity of the approach has been justified. As for the FTIR capillary, whose specific deposited energy was approximately three times higher than for the thin capillary, the values of gas temperature have been found to be equal to 450 K, 1700 K and 2000 K, respectively. Measurements of gas temperature in the thin capillary in the pulses and their afterglow have shown that the gas is heated to 1100 K by the end of the third pulse. Therefore, the phenomenon of fast gas heating in a nanosecond capillary discharge in carbon dioxide has been experimentally justified.

0D numerical modeling of the discharge ignited in the thin capillary and its near afterglow have been done. The calculations of temperature and the temporal profile of the electron density are in good agreement with the experimental results. The calculations have shown that chemical reactions of electronically excited states of $CO(a^3\Pi)$ and $O(^1S, ^1D)$ produced in the high voltage pulses by electron impact are responsible for fast gas heating in the pulses and between them. The processes of VT-relaxation start to play a significant role in the afterglow of the second high voltage pulse and are responsible for additional gas heating on almost 1000 K at the microsecond timescale. According to the numerical modeling of temporal profiles of species, the dissociation fraction of CO_2 and the energy efficiency of dissociation are equal to 15.9 % and 38 %, respectively, at $t = 1 \mu s$.

Perspectives and future work

The described experiments have revealed the fact that dissociation fraction of CO_2 by a nanosecond capillary discharge in a single pulse regime is around 20% as well as energy efficiency of CO_2 dissociation. As for CO_2 dissociation at a high pulse repetition rate, the energy efficiency is less than 10 % whereas the dissociation fraction can exceed 90 %. The obtained values confirm that a nanosecond capillary discharge can be a possible instrument for plasma-assisted CO_2 decomposition. Moreover, since dissociation of CO onto C and O has been observed in the discharge, it can be used not only for production of CO and O_2 , but for production of atomic carbon as well.

Nevertheless, it should be noted that measurements of CO_2 dissociation fraction and numerical modeling of the discharge based on the temporal waveform of the reduced electric field have been done in different discharge cells. Therefore, one of the main experimental challenges is to conduct self-consisted measurements of reduced electric field and concentrations of CO and O. The concentrations should be measured in the discharge, in its afterglow and in exhaust of the discharge cell. The latter can be done by FTIR spectroscopy. The measurements of temporal profile of O atoms in the discharge by Xe-calibrated TALIF are planned for the nearest future.

Finally, mechanisms driving CO_2 dissociation at micro- and millisecond timescales such as oxidation and recombination of CO and O back to CO_2 have not been described by numerical modelling done in the frame of the current Thesis. Hence, further development of a numerical model including dynamics of atoms and molecules in the far afterglow of the discharge is required. The model should have not only a descriptive power, but should give a clue to possible optimization of experimental conditions such as shaping of gas temperature or reduced electric field. For instance, an instantaneous cooling of gas (e.g., by supersonic expansion [37, 38]) can slow down VT-exchange processes and recombination of CO_2 . Relatively high reduced electric fields facilitating dissociation of carbon dioxide by electron impact at nanosecond timescale can be followed by an electric pulse providing values of reduced electric field which can be favorable for consequent dissociation via vibrational pumping. Following development of the kinetic model can make planning of this kind of experiments a way simpler.

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Titre : Dissociation du dioxide de carbon dans les plasmas pulsés aux conditions des champs électriques élevés : rôle de l'échange d'énergie avec les espèces électroniquement excitées

Mots clés : plasma nanoseconde, conversion du dioxyde de carbone, échauffement du gas rapid, conversion assistée par plasma

Résumé : La thèse est dédiée aux études de la dissociation du dioxyde de carbone aux pressions modérées dans un plasma nanoseconde pulsé aux conditions de champ électrique réduit et d'énergie spécifique élevés. L'objectif principal de la recherche a été de se concentrer sur un tel régime de la décharge, qui facilite la domination de l'excitation des degrés de liberté électroniques des espèces actives par rapport aux vibrations. Les processus de la conversion du CO₂ ont été étudiés expérimentalement et par la modélisation numérique. Quant à la partie expérimentale, il s'agissait d'acquisition des caractéristiques de la décharge plus importantes telles que le champ électrique réduit, courant électrique,

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les spectres optiques d'émission et le dépôt de l'énergie spécifique. Après, les mesures des valeurs de la fraction de dissociation et son efficacité quasistationnaires ont été effectuées par des moyens de la spectroscopie infrarouge de la transformée de Fourier (FTIR). Les mesures de la température du gaz à l'échelle sous-microseconde ont montré que le gaz se chauffe jusqu'à 2000 K. Ainsi, l'effet d'échauffement du gaz rapide peut être annoncé. Enfin, la modélisation numérique de la décharge a montré que les espèces CO(a³II), O(¹S) et O(¹D) sont responsables pour l'échauffement du gaz rapide et la conversion élevée du dioxyde de carbone à l'échelle sous-microseconde.

Title : Dissociation of carbon dioxide in pulsed plasma at high electric fields : role of energy exchange with electronically excited species

Keywords : nanosecond plasma, conversion of carbon dioxide, fast gas heating, plasma-assisted conversion

Abstract : The Thesis is devoted to study of dissociation of carbon dioxide at moderate pressure in nanosecond capillary pulsed discharges at high levels of reduced electric field and specific deposited energy. The main purpose of the research was to focus on such a discharge regime that facilitates domination of excitation of electronic degrees of freedom of active species over vibrational pumping of CO_2 . The process of CO_2 conversion was studied both experimentally and numerically. The experimental measurements included acquisition of the most important characteristics of the discharge such as reduced electric field, electric current, optical emission spectra and specific deposited energy. Then, the mea-

surements of steady-state dissociation degree and energy efficiency of CO_2 conversion were done by the means of Fourier Transform Infrared Spectroscopy (FTIR). The measurements of gas temperature at sub-microsecond timescale have revealed the fast heating of carbon dioxide up to temperatures of 2000 K. Formation of active electronically excited species at sub-microsecond timescale is described and discussed in details. It was shown by means of numerical modeling that such species as $CO(a^3\Pi)$, $O(^1S)$ and $O(^1D)$ are responsible both for fast gas heating and elevated conversion of carbon dioxide at submicrosecond timescale.

