THE CHEMICAL COMPOSITION OF RF DISCHARGES IN METHANE: DIAGNOSTICS AND ANALYSIS

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**Introduction**

In the last decades radio-frequency (RF) plasmas became an object of extensive investigations, encouraged by successes in development of surface technologies. These plasmas are typically non-thermal systems, where electrons possess energies in the range of few electron volts, while the mean energy of atomic and molecular components does not rise far above the room temperature. The ability of RF low temperature plasmas to modify the properties of surfaces is highly appreciated, for example, in the semiconductor manufacturing industry or for biomedical coatings. Particularly, a lot of attention has been paid to the hydrocarbon based plasmas, because of still growing interest in the fabrication of so called diamond-like films and amorphous hydrogenated carbon (a-C:H) films, first mentioned 1971 [1].

These kinds of coatings contain carbon and hydrogen and can exhibit different structures, from polycrystalline to amorphous, resulting in combinations of unique properties [2, 3, 4, 5, 6, 7]. For example, C:H layers are often used for wear-resistant coatings, due to their extreme hardness, or as infrared-transparent coatings for optical components, due to their transparency in this spectral region [8,9].

In hydrocarbon plasmas molecules are dissociated and ionized and the radicals and ions impinging on the surface of the substrate give rise to film growth. Therefore, in the deposition process, the properties of the produced material are strongly bound to the chemical composition of the plasma and the plasma-surface interaction.

The description of the plasma composition is a complex problem, which encloses the consideration of chemical and physical processes involving electrons, ions and neutral particles in the plasma bulk and at the surfaces. Lots of both, experimental and theoretical works are dedicated to the problems of understanding and controlling of the plasma parameters and processes [10, 11, 12, 13, 14, 15, 16, 17, 18, 19]. A great number of numerical approaches and simulations were elaborated by research groups all over the world as well [20, 21, 22, 23, 24, 25]. Although a huge amount of experimental information is collected and theoretical background is developed [26, 27], the explanation and prediction of trends in the plasma composition remain complicated and sometimes unreliable.

In the calculation of chemical compositions the main problems are the lack of data for the rate coefficients for reactions in the plasma and for the cross sections of the surface reactions, respectively. A determination of the dissociation frequencies of molecules requires information on the internal parameters of the plasma, such as the electron density and the electron energy distribution function (EEDF).

Experimental determination of internal parameters of reactive gas plasmas is a challenging task. Microwave and far infrared (FIR) interferometers yield line-integrated electron densities and for a correct interpretation, information on the density profile is needed [32, 28]. Thereby, the sensitivity of these methods is paid by reduced spatial resolution [29].

The traditional way to determine the electron density and the EEDF as well is the Langmuir probe technique [30, 31, 32]. Due to the deposition of a carbon coating on the probe surface, some additional technical improvements (like heating of the probe or short-time measurements) must be involved to keep the results reliable. Other possible diagnostics, e.g. based on Thomson scattering [33], involve sophisticated and expensive laser and detection systems and are usually limited to relatively high electron densities, because of weak signals in the presence of bright background radiation.

The EEDF can be found by solving Boltzmann’s equation [26, 34, 35], which is essentially a continuity equation for the particle density in the six-dimensional phase space with sources and sinks of particles by elastic and inelastic collisions. The numerical treatment of Boltzmann’s equation in its full form involves the solution of a time-dependent six-
Dimensional partial integro-differential equation, which is an extremely difficult task. One of the approaches is the numerical solution of Boltzmann’s equation under some simplifications with the electric field as input parameter [36, 37].

In the recent years, a number of fluid models (based on the continuity equations obtained from the moments of Boltzmann’s equation) were developed [24, 38, 39]. These models differ from each other in the way they treat the electron dynamics and the number of species and reactions taken into account.

For example, the self-consistent fluid model described in [24] comprises the balance equations for the densities of various species in the plasma (electrons, positive and negative ions, radicals and stable molecules) and the energy balance equation. The fluxes of the neutral and ionic species are calculated in the model by the drift-diffusion approximation: the diffusion term describes the transport of the species due to the density gradient, while the drift term determines the transport of the charged species under the influence of the electric field. Equations are coupled with the Poisson equation to obtain the electric field.

A more accurate approach is to handle the electrons in a fully kinetic treatment, by following their trajectory in the plasma by Newton’s equation of motion, and by treating collisions with a Monte Carlo algorithm [40]. The self-consistent description of the behaviour of the electrons, molecules, ions and radicals with the solution of Poisson’s equation leads to the particle-in-cell Monte Carlo (PIC-MC) method [21, 41]. PIC-MC models are the most accurate, but this approach is very time consuming.

Having obtained the distribution function and the electron density, all important electron-dependent parameters (such as ionization and dissociation frequencies) are determined, if cross-sections for the processes are known.

The reaction rates of the dissociation processes are especially important for the determination of the chemical composition of the plasma, since the chain of the chemical reactions starts with the formation of highly reactive radicals from the source gas molecules via collisions.

A complete analytical definition of the reaction kinetics in the hydrocarbon plasmas is not possible because of the vast number of plasma components and interactions between them. However, this problem can be solved numerically more or less successful. Several groups have developed plasma-chemistry models [36, 37, 42, 20].

The plasma chemistry block in these models needs the EEDF as an input, which can be found from the previously described models or it has to be assumed [37, 43, 44, 45]. Different authors include different numbers of considered species and reaction paths; in any case, it is always tens of reactions between molecules and molecules and ions [46, 47, 48], and for all of them reaction coefficients must be known, which are functions of the gas temperature. Thus accompanying measurements are required. A very common problem is that the values of the reaction rate coefficients given in the literature can differ by several times for different publications [49]. In addition to this, the reactions of particles with the surfaces are characterized by the sticking coefficients of the species to the materials used in the reactor chamber. The sticking coefficients are not always available. For a validation of the results obtained by the computation, a comparison of the calculated species concentrations with experimental data is indispensable.

The benefit of chemistry models is obvious: they allow us to predict concentrations of the species, including those, which are present in very small amounts (like radicals), and are difficult to measure directly but are important for applications. On the basis of one algorithm many combinations of parameters can be tested, providing data for further physical interpretation. Sometimes, temporal evolution and spatial resolution (both in radial and axial directions for reactors with cylindrical symmetry) are possible [50].
Admitting the evident profits of chemistry models, one should keep in mind that sometimes inaccuracy of the input information and time consumption can depreciate the convenience of the numerical investigations. Additionally it must be noted that the output of model calculations must be always verified experimentally before a conclusion on the plausibility of results can be secured.

In the present work an alternative approach to the treatment of the chemical composition of the plasma was developed: a simple analytical interconnection between the chemical composition and the internal parameters of the plasma for methane plasmas produced in RF discharges has been established exemplarily.

The idea is based on a comparison of experimentally obtained concentrations of some species with analytical dependencies on the time and/or electron density.

The selection of the investigated molecules is based on several intentions. From the literature [20, 22] several stable components were found to be present in the plasma in relatively large amounts. It means that they define the properties of the gas mixture; knowing the approximate composition of the plasma, it is possible to estimate its internal parameters by the method, described in this work.

The absorption spectroscopy with diode lasers as light sources was chosen as a sensitive method for determination of the concentrations of neutral species, since hydrocarbons possess a strong spectrum in the infrared region.

The main advantage of the tunable diode laser absorption spectroscopy (TDLAS) is the capability of a reliable determination of the gas temperature and the absolute values of the concentrations of the single species [51, 52, 53, 54]; the diagnostic permits to perform time resolved measurements. Other attractive features of TDLAS-based methods are i) their non-intrusive character, ii) usage of relative changes of signal, allowing simple calibration and iii) straightforward evaluation of obtained spectra.

Since in the experiment the concentrations are measured as functions of the input power or as functions of the time at a certain input power, a relation between the electron density and the input power is needed. This relation was found from experiments performed in our group by means of a Langmuir probe [55] and microwave and far-infra red (FIR) [29] interferometers.

The analytical expressions for the concentrations of the chosen species can be found under the assumption that among all processes, responsible for their production and consumption, only a limited number of the most important ones can be selected. Then the rate equation system becomes tractable for analytical solution and the concentrations of particles can be found as functions of electron density and mean energy.

In this sense, the present work is a step backwards in comparison with sophisticated plasma models, taking into account tens of processes and predicting the behaviour of concentrations of many species. At the same time the apparent simplicity of considerations given in this work is based on - and was only possible because of - the substantial experience in plasma investigations carried out in different groups including ours.

There are several basic suppositions made in this work. Firstly, as already mentioned, the huge number of the chemical and physical processes, taking place in the plasma volume and regions near to the surfaces, was reduced to only a few of them being the most important ones.

Secondly, essential assumptions concern the treatment of the electron impact processes. In the literature, devoted to the EEDF determination in methane plasmas under similar conditions, Druyvesteyn-like EEDF rather than Maxwellian EEDF are reported [10]. In this work both Druyvesteyn and Maxwellian EEDFs are considered.
The obtained analytical solutions of the rate equations can be fitted to the experimental data with the rates of processes as fitting parameters. The adequacy of the approximation serves for the examination of conformity of the presupposed set of the processes taken for consideration.

The straightforward fitting procedure allows us to obtain valuable information on the rate coefficients of the processes and the concentrations of those plasma species, which were not measured from the fitting parameters. The information on the dissociation rate coefficients permits the estimation of the mean electron energy.

Therefore, the elaborated method gives opportunity to describe analytically the trends of the plasma chemistry dependence on the external and internal parameters and to establish simple practical interconnections between external and internal plasma parameters.

After a brief description of the plasma sources (Chapter 1) the principle scheme of tunable diode laser spectrometers and the background of the method are given in Chapter 2. The main results of the electron density measurements are given in Chapter 3.

Chapter 4 is devoted to the discussion of the selection of the system of processes included in the analysis of the neutral species concentrations. In Chapter 5 and 6 results for the dependencies of the species concentrations on time and electron density are shown.

Finally, in the conclusion it is discussed, which information can be obtained from the measurements of the concentrations of neutral plasma species. Advantages and limitations of the methods, using the time resolved or steady state concentrations, are outlined.
Chapter 1. RF discharges

A detailed description of the physical principles of gas discharges can be found in books of Raizer [27, 56] or Lieberman [26]. Hence, only a few details, which are related to the measurements presented in this work, are mentioned here.

Plasma is produced when the electromagnetic energy released in a discharge is sufficient to ionize the gas and maintain a certain density of charged particles. RF discharges are excited by applying an oscillating electromagnetic field across a discharge gap. The final state of the produced plasma and its parameters is determined by a balance between the input and loss power and a particle balance [26, 57].

Under regulations set up by the International Telecommunication Agreements (ITA) the standard frequency, used in commercial RF generators is 13.56 MHz and its higher harmonics to avoid interference with communication channels. Differing in the way a RF field is induced in the discharge volume, RF discharges can be subdivided into inductively coupled plasma (ICP) and capacitively coupled plasma (CCP). The sketches of the equivalent electrical circuits can be found, for example, in PhD works of I. Möller [37] or V. Kadetov [57].

Inductive methods are based on electromagnetic induction so that the created electric field is a vortex field with closed line of force. In an inductively coupled discharge the RF current from an external source passes through a coil which may have a few turns in practice. The magnetic field of the coil is alternating and directed along the coil axis. Consequently, a circular electric field is induced with its lines of force are concentric with the primary RF current. This electric field can initiate and maintain a gas discharge. Usually the magnetic field is introduced in the reactor chamber trough a dielectric window. Inductively coupled discharges are principally electrodeless, but in many reactors a reference electrode is mounted under the coil, acting as substrate holder in deposition processes.

At low input power the longitudinal electrostatic field between the powered coil and the grounded electrode and between turns of the coil can sustain low-density plasma. This mode is called E-mode. Increasing the input power above a certain threshold, a drastic increase of luminosity is observed. The induced azimuthal electric field is responsible for sustaining of the plasma. This regime is called H-mode. The electron density increases by orders of magnitude.

In capacitive methods, the voltage from an RF generator is applied to the electrodes, the lines of force strike them and the resulting field is essentially a potential field [56].

A capacitive RF discharge can be operated in two modes [27]. Visually, these modes differ in the brightness and the distribution of the glow region along the discharge gap, but they essentially differ in the ionization processes.

The plasma modes are result of the mechanisms by which the energy transfer can be achieved. Because of their large mass, the ions are too immobile to follow the applied RF fields so that the energy is coupled to the electrons, leading to a strong non-thermal situation with energetic electrons and cold ions and neutrals.

Plasma can be separated of the into the bulk and sheaths regions. The number of ions is about the same as number of electrons, net charge density is zero and plasma is quasi-neutral. It is joined to the surfaces across thin positively charged layers, called sheaths. Origin of the sheath is based on the large difference between electron and ion thermal velocities. In plasma initially confined between grounded surfaces, at first, electric field and potential are zero everywhere. Reaching the surface, fast moving electrons are lost. Thin positive ions sheaths form near each wall, resulting in profile of potential, which is positive within the plasma and sharply falls to zero near surfaces.
Chapter 1. RF discharge

For small electrode voltages and particle pressures the basic heating mechanism is ohmic heating. The RF electric fields in the plasma bulk cause the electrons to oscillate, and phase mixing collisions with neutrals allow the electrons to become heated, until they are energetic enough to sustain the discharge. The ionization takes place mainly in the plasma bulk region. This mode of plasma heating is called the \( \alpha \)-regime. The plasma is bright in the layers adjacent to the electrodes, and the space in the centre of the discharge remains dark.

At higher values of the voltage applied to the electrodes, secondary emission of electrons from the electrode surface starts to play an important role and discharge switches to the so-called \( \gamma \)-mode. Then bright emission from the region between electrodes appears. Since here the heating mechanism depends on the energetic electrons being produced in the sheaths, self-consistency has to be achieved including both bulk plasma and the sheaths.

Another heating mechanism, which can be important at low gas pressures (less than 1 Pa) is called stochastic heating [26]. In this mode electrons collide with the discharge sheaths and, on the average over an RF cycle, gain more energy than they lose, thus resulting in heating.

In this work reactors of both types were used. The parameters are chosen in such a way that the CCP discharge is maintained in the \( \alpha \)-regime. Ohmic heating is assumed to be dominant for both discharges in majority of the measurements. All experiments performed in the ICP are related to the operation in H-mode. Measurements, performed in this works mainly are related to the plasma bulk region.

Since one of the purposes of this work is to establish an interconnection between internal and external parameters of reactive plasmas using the chemical composition as a link, the conditions were chosen to cover a wide range of electron densities. The concentrations of several plasma species (source gas methane CH\(_4\), methyl radical CH\(_3\) and three stable products – ethane C\(_2\)H\(_6\), ethylene C\(_2\)H\(_4\) and acetylene C\(_2\)H\(_2\)) were measured for a set of the external plasma parameters such as input power, flow rate and pressure (Table 1 “Experimental Conditions”). The source gas is always pure methane, supplied into the chamber with controlled flow rates of 1 - 60 sccm (standard cubic cm pro minute). The CCP reactor operates at input powers from 0 to 60 W and at pressures of about 100 Pa (1 mbar), whereas in the ICP reactor the gas pressure is at least one order of magnitude lower and the input power is up to 1 kW. In all considerations in this work the difference between the output power of the RF generator and reflected power is taken as “input power”. The investigated plasma is weakly ionized (the degree of ionization is about \( 10^{-2} \) – \( 10^{-5} \% \)) with the electron densities in the range of \( 10^{15} \) to \( 10^{16} \) m\(^{-3}\) and electron temperatures of \(~1\) eV. A detailed description of the reactor chambers is given in the following sections.

<table>
<thead>
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<th>Table 1. Experimental conditions</th>
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<tr>
<td><strong>CCP</strong></td>
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<td><strong>Power</strong></td>
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<td><strong>Pressure</strong></td>
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<td><strong>Flow rate</strong></td>
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<td><strong>Electron densities</strong></td>
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<td><strong>Electron temperature</strong></td>
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<tr>
<td><strong>Measured species</strong></td>
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1.1. Capacitively coupled plasma (CCP) chamber

The CCP reactor used in this work is described in detail in the PhD thesis of C. Busch [36]. Only a brief description is given here.

The configuration of the reactor chamber is shown in Fig. 1. The cylindrical chamber is made of stainless steel with an inner diameter of 30 cm and a height of 30 cm. The two parallel disk aluminium electrodes have a diameter of 7 cm, a thickness of 1 cm and a separation of 4 cm.

A RF generator (Dressler LPGC 131) with a stabilized frequency of 13.56 MHz is used to provide input powers in the range up to 60 W. The power is supplied through the lower electrode via a matching network to minimize the reflected power. For insulation glass plates are placed below the powered electrode. Both the upper electrode and reactor walls are grounded.

The vacuum system consists of a rotary vane pump only. The operation pressure is about 100 Pa and no high vacuum pumping is necessary. The source gas is supplied via a mass flow system (four flow rate control units MKS 179 and one four-channel readout MKS 247) with a maximum flow rate of 10 sccm. During discharge operation a gas-independent capacitive pressure gauge (MKS 121) is used. The condition of constant total operation pressure is achieved by means of a manually stabilized outflow, under a constant source gas inflow. Although both connections to the gas flow system and pump are placed in the upper part of the reactor chamber, the asymmetry in gas injection and exhaust is not significant because of very slow convection due to the low pressures and flow rates.

**Fig. 1.**
*The CCP chamber*
1.2. Inductively coupled plasma (ICP) chamber

Fig. 2 shows the drawing of the ICP reactor. Detailed description can be found in Diploma thesis of C. Scharwitz [58].

The RF power with the frequency of 13.56 MHz is supplied to the plasma via a double three-turn planar coil (water-cooled copper tubing) with the diameter of 12.5 cm, constructed after a prototype, which is in detail described in the PhD thesis of V. Kadetov [57]. The coil is placed outside the vacuum chamber in a quartz cylinder. The power source consists of a signal generator (Rohde & Schwarz, SMY 02) and an amplifier (Bonn Electronic). The power is coupled to the coil through an automatic matching network (Dressler).

Dimensions of the plasma chamber greatly exceed those of GEC reference cell. The cylindrical stainless steel reactor has an inner diameter of 60 cm and a height of 35 cm. The water-cooled grounded electrode has diameter of 18 cm and height of 8.3 cm and is placed 8.2 cm below the quartz window.

The gas supply is realized in analogy to the CCP reactor by means of an MKS mass flow system. In order to achieve a more uniform gas flow a ring-shaped gas inlet is used. The vacuum system consists of a rotary vane and a turbomolecular pumps (Pfeifer Vacuum), allowing to pump the cell to pressures as low as $10^{-5}$ Pa; typical working pressure was in the range of 5-20 Pa. The constant pressure is controlled by an MKS electronic butterfly valve and capacitive pressure gauge.
Chapter 2. Tunable diode laser absorption spectroscopy (TDLAS)

The experimental investigation of the chemical composition of molecular plasmas is a relatively complicated task. The method is based on absorption spectroscopy in the infrared region and was successfully used in our group for measurements of molecular species in RF plasmas in mixtures of methane and oxygen as source gases [36, 37, 59]. A comprehensive representation of the technique is given in the PhD work of C. Busch including a discussion of the difficulties accompanying the application of the TDLAS methods to RF discharges in reactive plasmas and illustrational intermediate results. C. Busch in his turn recommends the review of Webster [60] for an introduction to the subject. Review of D. Brassington [61] contains a lot of very useful information for practical applications.

In this work measurements of hydrocarbon molecules were performed essentially by the same methods as in [36] and [37] (some additional simplifications in the data evaluation are based on the assumptions, proved in [36]). Therefore, in this chapter the main attention is focused on the aspects, which are directly related to this work and the general principles are only mentioned briefly.

The principle of TDLAS is detection of the single isolated line of the species. Gaseous chemicals generally have strong fundamental absorption bands in the mid-infrared (MIR, 5-16 μm) spectrum. The absorption of light by these fundamentals provides means for detecting and quantifying them down to very low concentrations. The near-infrared (NIR, ~ 1 μm) can also be used for identifying and quantifying these chemicals. However, absorption in this region is due to overtone or combination bands with line strengths (see below) that are typically two orders of magnitude weaker than those of the mid-infrared fundamentals and hence, minimum detectable concentrations are several orders of magnitude higher in this case.

A simple tunable diode laser instrument uses a diode to generate light within a narrow frequency range that contains a relatively unique absorption wavelength of the chemical of interest. Multiple chemicals can be monitored by multiplexing the instrument with more than one diode (usually up to four) [62].

The detection limits are dependent on the transition properties and the path length through the absorbing medium. Instrument performance and technical noise (e.g., unintended etalon effects) will also affect the detection limits that can be achieved. One of the ways to increase the signal-to-noise ratio is using a multipass cell to enhance the absorption path. Another possible tool to improve of the detection limit is the usage of modulation spectroscopy (see below).

Besides species identification and concentration measurement, TDLAS allows one a convenient means for determination of the gas temperature which is a very important parameter for fundamental research of the discharges and for applications.

From the industrial point of view the control of the gas temperature in the plasma chamber is necessary for the estimation of the applicability of the plasma treatment of heat-sensitive objects. In spectroscopic measurements information on the temperature is needed for the calculation of the line intensity and the line shape factor, which are functions of the translational and ro-vibrational temperatures. Further, the gas temperature is a very important parameter in the plasma chemistry, because rate coefficients of the reactions between molecular species are dependent on the translational temperature.

Briefly, the main features of TDLAS, which make it such a valuable technique for concentrations measurements, are as follows:

- As a high-resolution spectroscopic technique it is almost immune to interferences by other species - a problem that plagues most competing methods.
Chapter 2. Tunable diode laser absorption spectroscopy (TDLAS)

- It is a general technique. The same instrument can easily be converted from one species to another by changing the laser system and calibration cells. Similarly it is easy to construct an instrument which will measure several species simultaneously by multiplexing the outputs of several lasers.
- Time resolved measurements are possible. The temporal resolution of TDLAS can be traded off against sensitivity. Absorption as low as $10^{-4}$ with a temporal resolution of a few milliseconds was reported recently [63].

One principle limitation of the capability of the diagnostic for investigation of a discharge must be mentioned. Typically, the discharge plasma is spatially inhomogeneous, while the TDLAS yields data which are line-integrated over the whole absorption path and in case of using multipass cells even over a major part of the plasma volume. Although the reconstruction of the concentration profile is principally possible by measurements over several single paths through the plasma and application of the Abel inversion procedure [64], in practice it turns out to be problematic to apply this method correctly, because of the limited size of the viewing ports. Nevertheless, attempts to estimate possible influence of the species space distribution on the precision of the measurements are made in the current work, as will be discussed below.

In the following sections the spectroscopic background of the method and a description of the main components of the tunable diode spectrometer are given.

### 2.1. Diode lasers

Compared to other types of sources of coherent monochromatic radiation, tunable diode lasers are compact devices, consuming low energies. The diode crystal itself has dimensions of tenths of millimetre. Laser radiation is emitted due to the inversion of the population, which is created in the active zone of a p-n junction, when the supported current exceeds the threshold value.

The simplest form of tunable diode laser consists of a crystal of a lead-salt semiconductor such as Pb$_{1-x}$Sn$_x$Se on which a p-n junction is formed by diffusion of a salt of different stoichiometry into the top surface. The front and rear facets form the laser cavity and do not need any reflective coating because the Fresnel reflection is sufficiently strong. If electrodes are deposited on the top and bottom surfaces and a current of a few hundred mA is passed through the junction, lasing action takes place at a wavelength determined by the energy gap of the semiconductor. This energy gap is temperature-dependent and a typical laser can be temperature-tuned over about 100 cm$^{-1}$. The energy gap is also dependent on the alloy composition so that lasers with different wavelengths can be obtained either by varying the stoichiometry of the salt or, for wider tuning, by using different constituents e.g. PbSnTe or PbSSe.
Chapter 2. Tunable diode laser absorption spectroscopy (TDLAS)

The simple laser described above is known as a diffused homojunction laser and has many disadvantages, such as poor mode structure, low power, and the need to operate below liquid nitrogen temperatures. Lasers produced currently have a more sophisticated structure and can be roughly divided into operating below and above 77 K (i.e. the temperature of liquid nitrogen).

The first ones are based on PbSnTe, PbSSe, or PbSnSe. They are homojunction devices formed by a diffusion process but differ from the simple laser described above in using a special structure to confine the active region laterally. This results in a better mode structure and a higher operational temperature. These lasers are available for wavelengths between 3000 and 400 cm\(^{-1}\) and operate at temperatures between about 20 and 70 K. The output powers vary between 100 µW and 2 mW.

Lasers operating at temperatures above 77 K are more complex devices. They are double heterostructure (Fig. 3) or buried heterostructure constructions and are formed by molecular beam epitaxy with PbEuSeTe or PbSnTe active layers. The advantage of this structure is a much better optical and carrier confinement in the active region compared to diffused homojunctions. Lasers of this type are available for wavelengths between 3050 and 900 cm\(^{-1}\) with single-mode operation available over a broad part of this range.

Diode lasers, emitting in the visible and NIR below 3000 cm\(^{-1}\), are based on III – V group materials (InGaAs). Due to their more complicated design they can operate at much higher temperatures and have lower threshold currents. The temperature stabilization can be achieved by a simple thermo-electric element (Peltier element). The distributed feedback (DFB) diode design uses diffractive feedback grating, distributed along the entire cavity. The grating spacing determines the wavelength that is reflected back into the active area. The speciality of DBF diode lasers is the effective longitudinal mode selection, which leads to the single mode emission.

Diode lasers are tuned by varying the temperature of the active region. This can be done either by varying the temperature of the cold stage on which the diode is mounted or by varying the laser drive current, which varies the Ohmic heating of the active region. Variation of the base temperature will tune the laser over its entire range. Variation of the driving current gives a more restricted tuning range of about 20 cm\(^{-1}\), but allows high-frequency modulation of the laser frequency. In practice the two methods are used in combination.

The use of diode lasers as light sources for the absorption spectroscopy is a very successful solution due to their excellent spectroscopic properties: a narrow spectral width (10\(^{-7}\) cm\(^{-1}\)), allowing Doppler-resolved measurements, simple tunability, and the ability of fast modulation (up to GHz) of the wavelength. Nowadays, diode lasers are available in a wide range of wavelengths covering the spectra of most species which are of interest for plasma chemistry. On the other hand, the continuous tunability of a single laser is usually limited to tens of cm\(^{-1}\), allowing a simultaneous detection of several molecules only in rare cases.

Several types of laser diodes with corresponding mountings were used in this work.

- A homojunction lead-salt laser diode (FCC-780-GMP, Laser Components) was used for detection of C\(_2\)H\(_2\) and C\(_2\)H\(_6\) in the spectral range around 800 cm\(^{-1}\) (12 µm). The controller system (Mütek Infrared Laser Systems) maintains the operating temperature of 45 K. The cryogenic temperature is archived by placing the diode inside a cryostat with a closed cycle Gifford McMahon cryocooler (TLS260 Laser source module, Mütek Infrared Laser Systems). Operating current is around 750 mA and averaged laser power at these parameters is ~ 0.1 mW.

- A second laser of this type (FCC-606-GMP, Laser Components) was used for CH\(_3\) detection at 600 cm\(^{-1}\) (operating temperature 32 K, threshold current around 300 mA, laser power ~ 0.1 mW)
Chapter 2. Tunable diode laser absorption spectroscopy (TDLAS)

- A heterostructure lead salt diode laser was used for measurements of C$_2$H$_4$ using the absorption lines at ~1870 cm$^{-1}$ (IR-1840 GMP, Laser Components). The laser operates at temperatures above 77 K, therefore a liquid-nitrogen Dewar was used for cooling (OLS 150 Laser Head and collimator, TLS 150 Laser Controller from Mütek Infrared Laser Systems). In this work operating parameters were the following: temperature ~ 96 K, current ~ 540 mA, power ~ 0.2 mW.

- A distributed feedback (DFB) laser diode (Specdilas D-1648 Laser Components) was used for detection of methane lines at 6067 cm$^{-1}$ (1.67 µm). The typical working temperature is 32°C, driving current ~ 100 mA and power up to 10 mW.

Table 2 shows data about wavelengths of the lines of the measured molecules and the corresponding working parameters of the diode lasers.

### Table 2. Operational parameters of diode lasers used

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Wave length, µm</th>
<th>Line strength at 300 K, cm/molecules</th>
<th>T, K</th>
<th>Current, mA</th>
<th>Power mW</th>
<th>Diode type</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>1.67</td>
<td>8 x 10$^{-22}$</td>
<td>305</td>
<td>66</td>
<td>10</td>
<td>InGaAS DFB</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>16.5</td>
<td>8 x 10$^{-19}$</td>
<td>32</td>
<td>1500</td>
<td>0.1</td>
<td>Homojunction Lead salt</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>12</td>
<td>10$^{-21}$</td>
<td>45</td>
<td>500</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>12</td>
<td>10$^{-21}$</td>
<td>45</td>
<td>500</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>5</td>
<td>10$^{-22}$</td>
<td>96</td>
<td>540</td>
<td>0.2</td>
<td>Heterostructure Lead salt</td>
</tr>
</tbody>
</table>

#### 2.2. Spectrometer set-up

![Spectrometer set-up diagram](image)

**Fig. 4.**

*Principle scheme of the experimental equipment*

A device for tuneable diode laser absorption spectroscopy consists, in general, of three parts: a source of laser radiation with a tuneable wavelength, guiding optics and a detection system.
The optical layout of the spectrometer used in this work can be found in [36] and [37]. A sketch of the principle design is shown in Fig. 4. Driving current and temperature, corresponding to the wave number of the centre of the absorption line, are given by the controller system. After stabilization of the appropriate temperature, tuning over the line is achieved by ramping the current via an external modulation from the waveform generator (HP/Agilent Technologies). In the present work the scanning period was between 1 and 10 seconds, depending on the desired signal-to-noise ratio. The emitted radiation is guided through the reactor chamber and finally to the detection and acquisition system.

**Optics**

Unlike almost all other laser sources, because of the small size of their active region tunable diode lasers generally produce a rather divergent (up to 30°) laser beam which requires collimating. This is achieved by using off-axis paraboloidal reflectors (Kugler). For the reduction of the beam diameter the optics includes a telescope. For beam guiding, mirrors with gold coating were chosen because of the high reflectance in the infrared region. The entrance window of the multipass cell is made of NaCl (Korth).

To simplify the adjustment of the infrared beam, an additional laser emitting in the visible region and a pellicle beam splitter (Melles Griot) are used.

In case of using diode lasers, emitting in multi-mode regime, a monochromator is needed for the selection of a single mode. In the present work it was always possible to obtain single mode generation in the wavelength region of interest.

**Multipass cell**

Depending on the detection limit of the species, the absorption length can be extended using mirrors to fold the optical path. Two configurations of multipass cells are commonly used: Herriott [65, 66] and White [67, 68] type cells. Advantages and drawbacks of both designs are discussed in [37]. In this work a Herriott cell was used, which is described in detail in [69].

The Herriott cell (Fig. 5) features two spherical mirrors separated by a distance less than their diameter of curvature. Light enters through a hole in one mirror and completes a number of passes before it exits through the same hole. The beam bounce path and length is...
adjusted by changing the distance between the mirrors. Herriott cells can support more than one light source by providing different entrance and exit holes in the mirror.

In this work a set of two traditional Herriott cells was used. The distance between the mirrors was chosen in dependence on the geometry of the reactor chambers, the focal length was fitted to the realization of 40 passes through the chamber. The number of passes was chosen in accordance with the sensitivity demands. The mirrors have protected gold coatings (the reflection is higher than 97% for 1.6 µm, DoroTEK). The multipass cell installed in the CCP chamber has mirrors with a focal length 37 cm, placed at a distance of 62 cm. The overall absorption path is ~ 25 m. The cell in the ICP chamber, also calculated for 40 passes, has focal length 50 cm and the distance between the mirrors is ~ 84 cm. The absorption path is ~ 34 m. In both cells the diameter of the entrance hole is 0.7 cm. The hole is placed 3 cm beside the mirror centre.

Only one laser beam at once was introduced into the chamber. To measure concentrations of different molecules, a replacement and new adjustment of the diode laser was necessary.

Detection and data acquisition system

The radiation leaving the chamber is focused on the detector, which is essentially a semiconductor compound which exhibits a wavelength cut-off depending on the alloy composition. Photons with the energy greater than the semiconductor band-gap energy excite electrons into the conduction band, thereby increasing the conductivity of the material. The peak response wavelength depends on the material’s band-gap energy and can be varied by changing the alloy composition. Two types of detectors were used in current work.

For the registration of wavelengths in the region around 1.6 µm (for the detection of methane molecules) a standard photodiode (Hamamatsu) was used. The absorption lines of ethylene were detected in the region of ~5 µm, ethane and acetylene lines were measured at ~ 12 µm and methyl lines lie at 16 µm. Correspondingly, to detect these species three HgCdTe detectors (Grasby Infrared) were used, which require cooling with liquid nitrogen to reduce the noise level. The signal of the detector is forwarded to a lock-in amplifier (EG&G/Perkin Elmer Instr. 7265 DSP).

In general, the lock-in amplifier acts as a phase-sensitive filter and is used to increase the signal-to-noise ratio. The primary advantage of the lock-in amplifier is “narrowing” of the detection bandwidth. Additionally, lock-in amplifier allows obtaining harmonics of the detected signal.

Lock-in amplifiers apply a technique known as phase-sensitive detection to single out one component of the signal at a specific reference frequency and phase (for details see, for example, [70]). The lock-in amplifier multiplies the signal with an internally generated sine wave with the reference frequency \( \omega_{\text{ref}} \) and phase \( \Theta_{\text{ref}} \). Suppose, the signal is described by a sine wave with some frequency \( \omega_S \) and phase \( \Theta_S \). Then the product of multiplication is two cosines with the frequencies (phases), which are the difference \( \omega_{\text{ref}} - \omega_S (\Theta_S - \Theta_{\text{ref}}) \) and sum \( \omega_{\text{ref}} + \omega_S (\Theta_S + \Theta_{\text{ref}}) \) of the frequencies (phases) of the signal and the reference waves. The amplitudes are proportional to the signal amplitude. In the following a low pass filter removes AC signal, so the output signal is zero unless the frequencies \( \omega_{\text{ref}} \) and \( \omega_S \) are exactly the same. The low pass bandwidth determines the bandwidth of detection.

In case if the input signal is not a sine wave, it can be represented as a sum of sine waves of different amplitudes, frequencies and phases (Fourier transformation). Than the product of multiplication yields a DC output signal proportional to the component of the signal, whose frequency is exactly the reference frequency. Simultaneously, the phase difference between waves must be constant in time. Lock-in amplifiers generate internal
reference signal usually by a phase-locked loop locked to the external reference. In our set-up, reference frequency and phase are given by an optical chopper (SCITEC Instruments LTD), used for the modulation of the input signal.

Lock-in amplifier also performs an averaging of the signal over the time, defined by a time constant. The averaging time constant should be chosen by means of trade-off between time resolution and noise level.

In case of applying the modulation technique, lock-in amplifier serves for the generation of a high frequency sine and detection of the higher harmonics of the signal. It will be described more detailed later (see Section 2.5. Modulation technique).

Transfer of the data to a personal computer through a GPIB connection and to an oscilloscope enables the recording and real time observation of the absorption spectrum.

2.3. Spectroscopic principles of TDLAS

Absorption spectroscopy is based on the decrease of intensity of the light while passing the medium, which contains the species of interest. Absorption occurs when the wavelength of the testing light coincides with a molecular spectral line. The wavelength of the spectral line gives information for species identification whereas its shape is defined by gas temperature, pressure and properties of the transition (and external fields if they are sufficiently strong). The intensity of the testing radiation must be low enough to avoid perturbations of the population distribution and saturation effects [36]. In the present work transitions between rotational levels, belonging to the different vibrational levels of the ground state are considered. The theory of the origination and properties of the transitions between vibrational and rotational levels of molecules is well developed but rather complicated. It can be found in the classical monographs of G. Herzberg [71, 72] and therefore is not given here.

Mathematically, the intensity of monochromatic radiation with the wave number \( \nu \) transmitted through a medium containing an absorbing species is expressed by Beer-Lambert’s law:

\[
I(\nu) = I_0 \exp\{-\int_0^L \alpha(\nu) \cdot ndl\}
\]

where \( I_0 \) is the transmitted intensity in absence of an absorbing species, \( L \) is the optical path-length, \( n \) is the absorbing species concentration, \( \alpha \) is the absorption coefficient which is a product of the lineshape function \( g \) (depending on the broadening mechanisms involved) and the line strength \( S \) of the specific transition.

Under the assumption of a constant absorption coefficient and a constant concentration \( \tilde{n} \) over the absorption length \( L \), the integral in equation (2.3.1) is easily found, yielding:

\[
I(\nu) = I_0 \exp\{-g(\nu) \cdot S(\nu_0) \cdot \tilde{n} \cdot L\}. \tag{2.3.2}
\]

The assumption of a homogeneous distribution of the concentration is very restrictive and can cause large uncertainties in the calculations. Moreover, the lack of knowledge about the distribution of the species concentrations makes it impossible to define the absorption length. In this work an attempt to estimate the concentration profiles of the stable molecules
was made (Section 2.7). It was found that the stable species are distributed almost uniformly all over the reactor chamber. For the concentration of the methyl radical in the CCP a strong decrease with the radial distance from the centre of electrode is reported in literature [73, 77]. Therefore for the calculation of the methyl concentration the absorption length was taken to correspond to the electrode diameter.

The relative absorption is defined as:

\[
A = \frac{I_0(v) - I(v)}{I_0(v)} = 1 - \frac{I(v)}{I_0(v)},
\]

which together with equation (2.3.2) yields the mean concentration of the absorbing particle:

\[
\tilde{n} = \frac{-\ln (1-A)}{g(\nu) \cdot S(\nu_0) \cdot L}.
\]

One of the advantages of the diagnostics is immediately obvious: only relative values of the transmitted intensities are required. More details about the determination of the concentration from the absorption measurements together with the methods for the calculation of the line strength and the line shape function are given in the following sections.

**Line shape function**

From the equations (2.3.2) and (2.3.3) follows:

\[
A(\nu) = 1 - \exp\{-g(\nu, T_{in}) \cdot S(\nu, T_{in}) \cdot L \cdot \tilde{n}\}.
\]

In the case of small absorption the equation (2.3.5) can be simplified:

\[
A(\nu) \approx g(\nu, T_{in}) \cdot S(T_{in}) \cdot L \cdot \tilde{n}.
\]

It is easy to see from the simple graphs shown in Fig. 6 that equation (2.3.6) is valid up to absorption is of about 10%. From equation (2.3.6) it follows that in case of small absorption the profile of the absorption line is described by line shape function \(g(\nu)\).

The saturation of the absorption can influence the line shape, leading to a flat central part of the line profile. Fig. 7 shows the experimental spectrum of acetylene at 95 Pa (grey line). The absorption of the strong line only slightly exceeds 10%. In all measurements, performed in this work, absorption was lower than this value. The same is valid for the other measured particles. Therefore in all further considerations the approximation valid for a small absorption is used.

In the pressure range up to 200 Pa the dominating broadening
mechanism of a spectral line is the thermal movement of the particles. Only an increase of the pressure up to 1000 Pa leads to a significant contribution of the collisional broadening of the line shape. Due to the Maxwellian distribution of the velocity of the molecules, the absorption profiles exhibit a Doppler-broadening [74]. In this case the line shape function is a Gaussian function:

\[
g(x) = \frac{1}{\gamma_D} \sqrt{\ln 2 \pi} e^{-\ln 2 x^2}
\]

\[
x = \left( v - v_0 \right) / \gamma_D.
\]

\[
\gamma_D = \frac{v_0}{c} \sqrt{\frac{2kT \cdot \ln 2}{m} } \approx 3.57 \cdot 10^{-7} \cdot v_0 \sqrt{\frac{T}{M}}
\]

(2.3.7)

where \( v_0 \) [cm\(^{-1}\)] is the position of the centre of the line, \( \gamma_D \) is the half width of the line at half maximum (HWHM), \( m \) and \( M \) are the particle mass in [kg] and [a.m.u.] respectively, \( T \) [K] is the translational temperature, \( c \) [m/s] is the speed of light and \( k \) [J/K] is the Boltzmann constant. The line profile function \( g(x) \) is normalized to give unity for the area under the curve. An approximation of the experimental line profile with the Gaussian function is shown in Fig. 7 as dashed line.

Fig. 7.
Experimental spectrum of \( C_2H_2 \) from the reference cell at 95 Pa and fitting with the Gaussian function

Since a ramping of the injection current of the laser diode makes it possible to scan the line profile with a high resolution, the measurements provide information on the translational temperature from the HWHM of the absorption line. In Table 3 values of the HWHM for the Doppler broadening for some of the measured species are listed. Compared to these values, the natural line width is much smaller: typical values in the infrared region are \( 10^{-9} \) cm\(^{-1}\) for vibrational transitions and \( 10^{-11} \) cm\(^{-1}\) for rotational transitions. The same can be stated about the line width due to collisional broadening: for methane at 100 Pa the HWHM is \( \approx 7.9 \cdot 10^{-5} \) cm\(^{-1}\) [37].
Chapter 2. Tunable diode laser absorption spectroscopy (TDLAS)

Table 3. HWHM for Doppler broadening at 300 K

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Mass, amu</th>
<th>( \nu ), cm(^{-1} )</th>
<th>( \gamma_b ), 10(^{-4}) cm(^{-1}), 300K</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)</td>
<td>15</td>
<td>606</td>
<td>9.7</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>16</td>
<td>6067</td>
<td>94</td>
</tr>
<tr>
<td>C(_2)H(_2)</td>
<td>26</td>
<td>( \sim )800</td>
<td>9.7</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>28</td>
<td>( \sim )1870</td>
<td>21.9</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>30</td>
<td>( \sim )800</td>
<td>9</td>
</tr>
</tbody>
</table>

An additional “instrumental” broadening can be introduced by the application of a modulation technique (see below).

### Line strength

The line strength \( S \) is related to the probability of the transition between two levels separated by energy difference \( h\nu \) (here \( h \) is the Plank constant, \( c \) is speed of light and \( \nu \) is the wavenumber). It is proportional to the Einstein coefficient for the absorption and the difference between the populations of the levels involved in the transition. In [36] an expression for the line intensity assuming a Boltzmann distribution of the population of the rovibrational levels is given:

\[
S_{mn}(T) = \frac{8\pi^3}{3h^2c} \frac{h\nu_{mn}}{Q(T)} |R_{mn}|^2 \exp \left\{ -\frac{E_m}{kT} \right\} \left[ 1 - \exp \left\{ -\frac{h\nu_{mn}}{kT} \right\} \right], \quad (2.3.8)
\]

where \( R \) is the transition dipole moment, and \( \nu \) the transition wavenumber in cm\(^{-1}\), \( Q \) the internal partition sum, \( T \) the rovibrational temperature and \( E_m \) the energy of the lower level of the transition. The partition sum is a function of the rovibrational temperature and the distribution of the population of the levels.

If available, the line strengths used in this work are taken from the HITRAN database [75]. This database contains information about the wavelength positions, the transition probabilities and other molecular parameters for many species. The line strengths given there are normalized to the reference temperature \( T_{ref} = 296 \) K:

\[
S_{mn}(T) = S(T_{ref}) \frac{Q(T_{ref})}{Q(T)} \exp \left\{ -\frac{E_m}{kT} \left( \frac{1}{kT} - \frac{1}{kT_{ref}} \right) \right\} \times \left[ 1 - \exp \left\{ -\frac{h\nu_{mn}}{kT} \right\} \right] \left[ 1 - \exp \left\{ -\frac{h\nu_{mn}}{kT_{ref}} \right\} \right], \quad (2.3.9)
\]

In the HITRAN database the dependence of the partition sum on the temperature is approximated by a 3\(^{rd}\) order polynomial:

\[
Q(T) = a_1 + a_2 \cdot T + a_3 \cdot T^2 + a_4 \cdot T^3, \quad (2.3.10)
\]
and the coefficients $a_i$ are also available for most of the investigated species.

Methods for the determination of the rovibrational temperature are described below.

Fig. 8 shows the data taken from the HITRAN database for the line strength of one C$_2$H$_6$ line, which belongs to the $\nu_{12}$ fundamental band (corresponds to CH$_3$ rock band; band centre near to 821 cm$^{-1}$) and one C$_2$H$_2$ line (CH bend; fundamental band $\nu_5$ with centre near 729 cm$^{-1}$) at different temperatures. One can see, that in a very broad range of temperatures (300K – 600K) the line strength of acetylene changes by less than 40%, whereas the line strength of C$_2$H$_6$ changes by a factor of ~3. However, only a slight increase of the temperature up to 350 K was found in our discharges. This increase influences the line strengths by less than 10%. Consequently, the value of the line strength at room temperature can be taken for the calculation of the concentration of the species in the discharge. This observation is very useful, when the experimental spectrum can not be identified properly and a dependence of the line strength on the temperature is not known.

![Graph showing line strength vs. temperature for C$_2$H$_6$ and C$_2$H$_2$ lines](image)

Fig. 8. Dependence of the line strength of C$_2$H$_6$ and C$_2$H$_2$ lines on the temperature, taken from HITRAN database

**Measurement of rovibrational and translational temperature**

Generally, one has to distinguish between translational and rovibrational temperatures, but both, the measurements performed in this work in the CCP of pure methane and the data, reported in [36, 37] for the CCP and the GEC-like ICP in different mixtures of oxygen and methane, are evidence of their coincidence with respect to the error bar.

**Rovibrational temperature**

In [36] two methods were applied for the determination of the ro-vibrational temperature. In both cases several lines related to the different energy levels have to be measured.
1. If all the molecular parameters (like quantum numbers and statistical weights of the involved states) are known, the technique of the Boltzmann plot can be used, which gives an information on the internal state distribution of the molecules of interest.

According to the Maxwell-Boltzmann distribution law, in the thermal equilibrium the number of the particles in state $N_m$ of the total energy $E_m$ and of the total degeneracy $g_m$ is proportional to $g_m \exp\{-E_m/kT\}$ [71]. The idea of the method is to plot the normalized population density versus the energy of the lower level on a semi-logarithmic scale. In case of local thermodynamic equilibrium this plot is a straight line with the slope $-1/kT$.

The Boltzmann plot was performed in [36] for four lines of the methyl radical, belonging to the Q-branch of the $\nu_2$ fundamental band. The obtained rovibrational temperature was $362 \pm 38$ K at an input power of 60 W and a pressure of 100 Pa in the CCP.

2. In the case of unidentified transitions in methane another procedure was applied. This procedure is based on the numerical fitting of the ratio of the product of the concentration and the line strength $(Tsn \cdot S(T))$ and the line strength at the reference temperature $(S(T_{ref}))$ to the experimentally obtained data. The fitting procedure results in a value of 337 K for the rovibrational temperature at 25 W and 100 Pa (CCP cell). For the GEC-like ICP cell this procedure gives a temperature of $346 \pm 40$ K at 500 W and 10 Pa. [37, 69]

**Translational temperature**

The translational temperature can be easily determined from the measurement of the HWHM of the absorption line under the assumption that the broadening due to the Doppler effect dominates over all other broadening mechanisms. The sensitivity of the method can be estimated from equation (2.3.7): the increase of the translational temperature by 10% leads to the increase of the HWHM of $\sim 5\%$. In Fig. 7 the experimental spectrum of acetylene taken from the reference cell is shown. The fitting of the line profile with the Gaussian function provides the value for the HWHM with an error bar of $\sim 3\%$. For the spectra obtained under “real” experimental conditions in the plasma, the error bars are typically lower than then 10% (see Section 2.7), which means that the accuracy of the temperature determination is better than 20%.

For the stable components the rise of the translational temperature can be estimated by a direct comparison of the HWHM for the conditions with and without plasma in case if the drift of the wavelength of the diode laser due to temperature fluctuations of the crystal is insignificant.

The measurements carried out in the CCP chamber in a mixture of the oxygen and methane and in pure methane, show very small increases of the translational temperature above the room temperature. In the ICP cell the temperature is slightly increased only in the H-mode (320 K) [36, 37].

In this work the translational temperature was measured for all considered conditions in both the CCP and the ICP reactors. Within the error bars of $\pm 20\%$ no increase of the translational temperature above the room temperature was registered.

Measurements of the HWHM, performed after different periods of time after the discharge was switched on show very good reproducibility and therefore temperature stability. This way of the evaluation of the experimental data allows a fast and convenient determination of the concentrations.
2.4. Calculation of the species concentrations

For the calculation of the mean concentration the peak relative absorption can be used [36] (see equation (2.3.6); Doppler broadening and small absorption are assumed):

\[
A(v_0) = 1 - \frac{I(v_0)}{I_0(v_0)} \approx \frac{1}{\gamma_D} \sqrt{\frac{\ln 2}{\pi}} \cdot S(v, T_r) \cdot L \cdot \bar{n}.
\]  

(2.4.1)

The second possibility is to calculate the total absorption as the area under the absorption line:

\[
A_{tot} = \int_{0}^{\infty} A(v) \, dv \approx \int g(v, T_r) \cdot S(T_r) \cdot L \cdot \bar{n} \cdot dv = SL\bar{n}.
\]

(2.4.2)

Obviously, both the peak absorption and total absorption are directly proportional to the concentration.

The most accurate method is a fitting of the numerically obtained line profile, which has the absorption area and the line width as parameters, to the measured profile. Fig. 9 shows the calculated and experimental spectra of methane, consisting of four lines located close to each other.

Depending on the quality of the concretely considered measurements, all three techniques were used in this work.

Naturally, the procedures described above are applicable only if an absorption line belongs to an identified transition, for which the line position and the line strength are known from a database or from the literature. Moreover, information about the positions of two or more neighbouring lines is desirable or a concomitant spectrum with the using of the etalon and the reference cell is needed for the precise calibration of the wavenumber scale. Unfortunately, this is not always the case. For the measurements of the stable species a more direct calibration procedure can be applied.

As described in the previous section, under the conditions, used in this work, both rovibrational and translational temperatures are only slightly higher than the room temperature. This fact allows one to compare the absorption to a reference value \(A_{ref}\), which is obtained by filling the corresponding gas at some known pressure \(p_{ref}\) and temperature into the chamber without the discharge, i.e. at the room temperature \(T_{ref} \approx 300\) K:

\[
\frac{A}{A_{ref}} \approx \frac{g(v, T_{ref}) \cdot S(T_{ref}) \cdot L \cdot n}{g(v, T_r) \cdot S(T_r) \cdot L \cdot n_{ref}} \approx \frac{n}{n_{ref}},
\]

(2.4.3)

\[
n_{ref} = \frac{p_{ref}}{kT_{ref}}
\]
where the reference concentration $n_{ref}$ is defined from the ideal gas law.

In principle, this method can introduce an uncertainty in the concentration since the temperature dependencies of the line strength is neglected. This uncertainty can be estimated from the given above considerations for the sensitivity of the line strength to an increase of the rovibrational temperature.

The method does not require information about the spectroscopic parameters of the transition. It was applied for evaluation of the measurements of $\text{C}_2\text{H}_6$, $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_2$, which spectra were not identified and no information on the line positions and the line strength was available.

In general, a minimum detectable absorption of 1% is assumed. This limit can be decreased by one order of magnitude by means of modulation technique (following section). In Table 4 line strengths and minimum detectable concentrations are listed for the measured molecules for CCP under the assumption of a minimum detectable absorption of 1% for direct spectroscopy and 0.1% for modulation spectroscopy. Measurements of $\text{C}_2\text{H}_6$ and $\text{C}_2\text{H}_2$ concentrations were performed with using of the multipass cell only; whereas $\text{CH}_4$ and $\text{C}_2\text{H}_4$ concentrations were investigated with the single pass configuration as well (details are given in Section 2.7). The absorption path length for $\text{CH}_3$ was taken to be 40 times diameter of the electrode. Discussion on the reliability of line-averaged results is given in Section 2.7.

### Table 4. Minimal detectable concentrations in CCP

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Line strength $S$, cm/molecule</th>
<th>Absorption path $L$, cm</th>
<th>Detectable concentration $n$, molecule/m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Direct spectroscopy</td>
</tr>
<tr>
<td>$\text{CH}_4$</td>
<td>$8 \times 10^{-22}$</td>
<td>40x62</td>
<td>$10^{20}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40*</td>
<td>$10^{22}$</td>
</tr>
<tr>
<td>$\text{CH}_3$</td>
<td>$8 \times 10^{-19}$</td>
<td>40x7**</td>
<td>$10^{17}$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_2$</td>
<td>$10^{-21}$</td>
<td>40x62</td>
<td>$10^{18}$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_4$</td>
<td>$10^{-21}$</td>
<td>40x62</td>
<td>$10^{19}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>$10^{21}$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_6$</td>
<td>$10^{-22}$</td>
<td>40x62</td>
<td>$10^{19}$</td>
</tr>
</tbody>
</table>

**Notes**

* single pass configuration
** 40 passes through the distance equal to the electrode diameter, due to the sharp concentration (Section 2.7)
2.5. **Modulation Technique**

The technique of modulation spectroscopy was previously applied in our group [36, 37]. It was used in this work as well; therefore the main features are mentioned here.

The idea of the method is to observe the higher harmonics of the signal. The main benefit of the modulation spectroscopy compared to the conventional methods, described so far, is the following. A signal observed in modulation spectroscopy is directly proportional to the species concentration, rather than the small change in a large signal which occurs with a conventional absorption measurement.

There are two types of the modulation spectroscopy employed in TDLAS systems: wavelength modulation spectroscopy (WMS) and frequency modulation spectroscopy (FMS). These terms are somewhat misleading since in both cases it is the wavelength of the laser that is modulated. The difference is that FMS uses modulation frequencies of MHz to GHz while WMS uses frequencies in the kHz-range [61].

In our experiment a small 1 kHz sinusoidal current is superimposed on the ramped injection current of the diode laser, thereby providing a modulation of the laser wavelength and of the transmitted signal. The principle scheme of the set-up is shown in Fig. 10. The difference between this and the previous one (Fig. 4) is that now instead of using the reference frequency from the chopper, the lock-in amplifier itself is used to produce a sine, which is applied for the laser current modulation, and to detect higher harmonics of the signal.

Mathematically this technique can be described as follows. The modulation of the laser wave number
can be written as

\[ \tilde{\nu}(t) = \nu_1 + a \cdot \cos(\omega t) = \nu_1 + m \cdot \gamma \cdot \cos(\omega t), \tag{2.5.1} \]

with the central laser wave number \( \nu_1 \), which is shifted around the central position of the absorption line \( \nu_0 \) by ramping of the diode laser current; \( a \) is the modulation amplitude, and \( m = a \gamma \) - the modulation parameter, which is the modulation amplitude, normalized on the HWHM of the line.

If the modulation amplitude is less than the HWHM of the absorption line profile, the transmitted intensity can be expanded in a Taylor series around the central diode laser wave number. Then the transmitted intensity can be written as:

\[ I(\nu_1 + a \cdot \cos(\omega t)) = I(\nu_1) + a \cdot \frac{dI}{d\nu_1} \cdot \cos(\omega t) + \frac{1}{4} a^2 \cdot \frac{d^2I}{d\nu_1^2} \cdot [1 + \cos(2\omega t)] + ... \tag{2.5.2} \]

With the help of the lock-in amplifier harmonics of the signal on the frequencies \( \omega, 2\omega \) and etc. can be detected, yielding DC output signal, proportional to the \( dI/d\nu_1, d^2I/d\nu_1^2 \) and so on.

In the case of low absorption, linearized form of the transmitted intensity is

\[ I(\nu) = I_0 \cdot (1 - g(\nu) \cdot L \cdot S \cdot \tilde{n}), \tag{2.5.3} \]

and the first derivative in the case of dominating Doppler broadening of the absorption line is:

\[ \frac{dI}{d\tilde{\nu}} = I_0 \cdot L \cdot S \cdot \tilde{n} \cdot \frac{dg}{d\tilde{\nu}} = I_0 \cdot L \cdot S \cdot \tilde{n} \cdot g(\tilde{\nu}) \cdot \left\{ -\frac{2 \ln 2}{\gamma_D^2} (\tilde{\nu} - \nu_0) \right\}. \tag{2.5.4} \]

One can see that the detection of the first derivative of the transmitted intensity permits to avoid the problem of a small useful signal on the large background, since the obtained signal is directly proportional to the line shape function of the absorption line of the molecule of interest. At points where \( \nu - \nu_0 = \pm \gamma_D \sqrt{2 \ln 2} \) (maximums of first derivative of the signal)

\[ \left. \frac{dI}{d\tilde{\nu}} \right|_{\nu - \nu_0 = \pm \gamma_D \sqrt{2 \ln 2}} = \pm \text{const} \cdot I_0 \cdot L \cdot S \cdot \tilde{n}. \tag{2.5.5} \]

Therefore, measurement of the distance \( \Delta x \) between peaks of the first derivative of the transmitted intensity contains information about the gas temperature. The peak value is linearly proportional to the product of the incident intensity and the species concentration. This fact allows a calibration of the obtained signal. In Fig. 12 the normalized 1st harmonic signal for the same four lines of CH\(_4\) as in Fig. 9 is shown.

Up to a certain value the harmonic signal rises with the modulation amplitude that makes

\[ \Delta x \]

\[ 1 \text{st harmonic signal} \]

wave number, 1/cm

\[ 6067, 6067.05, 6067.1, 6067.15, 6067.2, 6067.25 \]

\[ \text{Normalized 1st harmonic of the spectrum of CH}_4: \text{simulation and experiment} \]
Chapter 2. Tunable diode laser absorption spectroscopy (TDLAS)

It is possible to improve the signal-to-noise ratio. However, with an increase of the modulation amplitude with respect to the HWHM of the line, an “instrumental” broadening arises, since the modulation averages over neighbouring spectral points. In [36] it is recommended to switch in this case to an expansion of the line shape in a Fourier series. C. Busch also provides the results of calculations of the influence of the modulation parameter on the first and second harmonics of a Gaussian line profile. In this work the influence of the increase of the modulation amplitude on the HWHM of the signal was checked experimentally before performing measurements. All measurements were carried out with the modulation amplitude smaller than HWHM of the line, giving possibility to neglect the “instrumental” broadening compared with the Doppler broadening.

2.6. The spectra of C$_2$H$_6$, C$_2$H$_2$ and C$_2$H$_4$

It was possible to measure C$_2$H$_2$ and C$_2$H$_6$ simultaneously because the lines of both molecules in the MIR (about 800 cm$^{-1}$) were accessible within the tunability range of one diode laser. However, calculations of the concentrations were hampered by the fact that information on the position and line strength of the absorption lines of C$_2$H$_2$ and C$_2$H$_6$ in this region given by the HITRAN database (Fig. 13) does not match the experimentally observed spectrum (Fig. 14, above). The data found in the alternative spectral database GEISA [76] do not coincide either. Moreover, these two databases show discrepancies between each other. No suitable gas was found to exhibit isolated identified absorption lines within the tunability range of the laser in this spectral region. Therefore an exact identification of the wavelength of the measured C$_2$H$_2$ and C$_2$H$_6$ absorption lines was not possible; only the wave number region of 790 – 800 cm$^{-1}$ could be allocated. Consequently, no information on the line strength of the obtained lines was available.

Nevertheless, since both C$_2$H$_2$ and C$_2$H$_6$ are stable, long-living molecules the simple calibration procedure, described by equation (2.4.3) can be applied in order to get the absolute concentrations from the absorption measurements (under the assumption that both the rovibrational and the translational temperature are close to the room temperatures at the any input power level in the plasma).

\[ \text{HITRAN and Geisa databases data for the C}_2\text{H}_6 \text{ line positions and the line strengths} \]
The product of the line strength and the Gaussian line shape at the top of the line $S \cdot g(v_0)$ was determined using a reference cell (length $L' = 30$ cm) filled with a known concentration $n'$ of $\text{C}_2\text{H}_6$ and $\text{C}_2\text{H}_2$ at room temperature and using Beer-Lambert’s law in linearized form (2.5.3):

$$S \times g(v_0) = \frac{1 - I'}{I_0} \cdot \frac{1}{n' \cdot L'}.$$  \hspace{1cm} (2.6.1)

The quantity $S \cdot g$ is plotted for several lines in Fig. 14 (below) and is used further for the calculation of the concentrations of $\text{C}_2\text{H}_2$ and $\text{C}_2\text{H}_6$ in the discharge.

There is no information at all on the lines of $\text{C}_2\text{H}_4$ in the region around 1870 cm$^{-1}$ in both databases, although the observed spectrum indicates high line strengths of the absorption lines.

In case of $\text{C}_2\text{H}_4$ measurements in the single path configuration (absorption length 40 cm) modulation spectroscopy was applied. As mentioned above (equation (2.5.4)) the first derivative of the absorption signal is proportional to the incident intensity. After every new adjustment and before performing measurements the slope of the dependence of the detected signal on the $\text{C}_2\text{H}_4$ concentration was defined. This was done by filling ethylene in the reactor chamber under known pressure and performing the calibration procedure. In the measurements with the single pass at 1 Pa the absorption was about $\sim 0.1\%$. With the multipass configuration it was about 1% and could be measured by means of direct absorption spectroscopy.

Fig. 14.
$\text{C}_2\text{H}_6$ lines around 800 cm$^{-1}$:
Upper graph - experimental absorption spectrum; lower graph - value of $S \cdot g$, determined from measurements
2.7. Estimation of the spatial distribution of species

In the case of using a multipass cell, the absorption path length was taken to be 40 times the distance between the two Herriott–cell mirrors. Hence, the concentrations of the stable products, which are fed from outside and deplete inside the plasma bulk, could be overestimated. By contrast, the stable products which are produced inside the plasma bulk could be underestimated. For the species which are produced and destroyed in the plasma an over- or underestimation can not be predicted. Moreover, the geometry of the beam path in the multipass cell usually leaves an important region between the electrodes untouched. In addition, the relatively small size of the “hot” plasma region (for example, in the CCP the diameter of the electrodes is 7 cm) combined with the relatively large size of the chamber (diameter 30 cm) results in the fact that mainly the background gas outside the plasma bulk is detected.

In some cases in the CCP a combination of the relatively high concentrations of species and line intensities of the spectral lines allowed us to avoid using the multipass cell. Then the signal remains line-averaged over the way through the plasma but more precise information on the species concentrations and the temperature is available. A comparison of the measurements performed with the single pass and the multipass configurations reveals an influence of the spatial distribution of the concentration on the quality of the data.

The “spatial” sensitivity of the measurements is discussed further. The application of the Abel inversion technique is hampered by the geometry of the viewing port: the effective window diameter is 8 cm. Due to the low value of absorption, a detection of particles without the multipass cell is only possible for the source gas and the stable products, which were assumed previously to be distributed relatively uniformly inside the reactor.

The CCP chamber is equipped with eight viewing ports located symmetrically around the chamber circumference. Only five from them are drawn in Fig. 16 for simplicity.

The single pass measurements were carried out for the source gas (CH₄) and one stable product...
(C$_2$H$_4$) in the CCP discharge. Measurements of the CH$_4$ concentrations were performed over several different absorption paths, which are schematically shown in Fig. 15. The system of paths ‘a’ belongs to planes, parallel to the surface of the electrodes. Two planes, positioned at distances of ~1 cm from the lower and upper electrodes were scanned. Also a set of measurements was performed in the plane perpendicular to the electrode surface. The laser beam was guided through the centre of the viewing port at different distances from the electrode. For investigation of the background gas composition, the paths ‘b’ and ‘c’, passing the chamber outside the centre region were used. In this case the laser beam leaves the cell through the viewing ports, neighbouring the ones through which it enters.

These data can be compared to the measurements by means of the multipass arrangement. In figs. 16 to 19 the measurements, performed over different absorption paths are presented. The measurements, denoted as “outside long” and “outside short” are performed over the absorption paths ‘b’ and ‘c’. The measurement denoted as “one pass” was done over one of the absorption paths ‘a’ through the center of the viewing port near to the upper electrode.

Obviously there is no significant change in the line-averaged concentration neither in the horizontal nor in the vertical planes. In Fig. 16 the error bars for the ‘outside’ measurements are taken to be 7% of the values, which is more than one order of magnitude larger than the “real” statistic uncertainties (reasons for such error bars are explained below). There is clearly

\[\text{Fig. 17.}\]
\textit{Line integrated measurement of the CH$_4$ concentration on the different distances from the powered electrode}
no significant difference between the data obtained at the different configurations. This leads to the conclusion that there are no large non-uniformities in the CH$_4$ concentration profile within the sensitivity limit mentioned above.

One should keep in mind that the processes leading to the change of the concentrations are usually several orders of magnitude slower than diffusion. In the case of stable molecules, assumed to have a sticking coefficient, which is very close to zero (or very small compared to the one for radicals), diffusion leads to the mixing of the gas components and smoothing of the concentration profiles over the chamber volume.

Measurements of the concentration of C$_2$H$_4$, which is produced and consumed in the plasma, were performed only over the absorptions paths “a” between the electrodes. The concentration of C$_2$H$_4$ is shown in Fig. 19. Fig. 20 shows the HWHM of the C$_2$H$_4$ absorption line, normalized to the HWHM at room temperature. The absorption is measured along the paths, which lie in a plane parallel to the electrode surfaces, and concentrations are averaged. The position “0” corresponds to the middle of the discharge; there the beam crosses the “hot” plasma region along the longest path, whereas at the positions “±3” only a small part of the plasma region is touched (the diameter of the beam is about 0.5 cm). The error bars are comprised of the statistical errors of the single measurements as well as uncertainties introduced by the calibration procedure. After every measurement a new adjustment of the laser beam was performed to achieve a shift of the laser path in the horizontal plane.

The HWHM of the spectral line helps to estimate an increase of the translational temperature in the discharge region. One can see that there is no noticeable broadening inside the error bars. The line
Chapter 2. Tunable diode laser absorption spectroscopy (TDLAS)

averaged concentration represents a relatively flat distribution.

Several remarks on the spatial sensitivity can be made. For an estimation of the influence of the small plasma region on the measured concentration the following consideration can be applied. The measured concentration gives the line-averaged mean value

\[
\tilde{n} = \frac{\int_0^L n(l) dl}{L}.
\]  

(2.7.1)

For a first approximation we assume a rectangular profile of the concentration, with its lower level in the centre of the plasma. Then we can divide the beam path into two parts: one through the background gas \( l_2 \) and the other one through the plasma \( l_1 \):

\[
\tilde{n} = \frac{n_1 l_1 + n_2 l_2}{L}.
\]  

(2.7.2)

Here \( L \) is the whole path of the laser beam through the chamber. The diameter of the reactor chamber is 30 cm, and the distance from the chamber wall to the surface of the viewing port is 5 cm, which yields \( L = 40 \) cm.

It is rather difficult to estimate a “plasma diameter” since no experimental data on the electron density profile in methane discharges are available under the chosen conditions. From the experiments and calculations carried out in other groups in similar CCP in Ar \([31, 83]\), \( \text{CH}_4 \) \([21]\) and mixtures of \( \text{CH}_4\text{-Ar-H}_2 \) \([50]\) it follows, that at pressures higher than 10 Pa the electron density decreases sharply with the distance from the centre of the electrode and is negligible outside the region between the electrodes; more details are given in Chapter 3. Light emission, resulting from the electron impact excitation of molecules, can serve as an indirect indication for the presence of electrons. In our set-up the diameter of the electrodes is 7 cm. At 100 Pa a relatively bright light emission is observed from the area of ~ 1.5 cm around the electrode. Therefore, for simplicity we take the plasma diameter as 10 cm. This gives us

\[
\tilde{n} = \frac{10}{40} L \cdot n_1 + \frac{30}{40} L \cdot n_2 = \frac{1}{4} n_1 + \frac{3}{4} n_2,
\]  

(2.7.3)

with the \( n_1 \) and \( n_2 \) being the methane concentrations in the plasma and in the background region, respectively.

The concentration in the background region was measured by using a single path, passing outside of the plasma (Fig. 16). Therefore, the concentrations measured over the whole path can be compared to the ones measured over the background path:

\[
\tilde{n} = \frac{1}{4} n_1 + \frac{3}{4} n_2 = \frac{a + 3}{4} n_2,
\]  

(2.7.4)

\[a = \frac{n_1}{n_2}.
\]
The coefficient $a$ is the ratio of the concentrations inside and outside the plasma. The results, shown in Fig. 16 help us to estimate the depth of the profile for the simple case of a rectangular distribution. With $a = 0$ (methane dissociates in the plasma completely and the concentration is measured from the background region only) the concentration measured over the whole path would differ from the outside measurements by 25%. From Fig. 16 one can see that the real difference between the measurements, performed over different paths coincide within an error bar of less than 7%. This uncertainty corresponds to the difference between the concentrations of less than ¼ of the “outside” value. In other words, the quality of the measurements proves, that the methane concentration inside the plasma region is at least ¾ of the concentration in the background region ($a \geq 0.75$).

This rough estimation is done under the assumption of a rectangular profile of the concentration. An analytical description requires the solution of a corresponding diffusion equation. Under a set of certain simplifications this was done in [59]. On the basis of the obtained analytical functions, describing the distribution of the concentration over the chamber radius, the calculation of the profile for different diffusion lengths was performed. From the calculation follows that for a diffusion length which is longer than 8 cm, the concentration of methane changes over the radius of the chamber by less than 15%.

At the same time the concentrations of unstable species (for example, $\text{CH}_3$ radical) can exhibit a profound profile. Indeed, production of radicals is mainly ascribed to the electron impact ionization of stable molecules and thus takes place in the plasma region; in the region outside the plasma bulk radicals are effectively lost due to their typically high rates of losses in chemical reactions and interactions with surfaces. It was proved by means of modelling [50, 77] and experiments [63] that the methyl concentration can be neglected outside the plasma region. Results shown in [63] demonstrate even more narrow profile of the $\text{CH}_3$ concentration compared to the electron density profile. Therefore, in the case of measurement of the density of $\text{CH}_3$ radical the absorption path length of the laser beam was defined as the diameter of the electrode (7 and 20 cm in CCP and ICP, correspondingly).

**Summary**

The properties of a hydrocarbon discharge (i.e. a big number of the species, low concentrations, changes of the gas temperature and a non-uniform spatial distribution of the particle concentrations over the reactor chamber) make the measurements a challenging task. The tuneable diode laser absorption spectroscopy is a very suitable diagnostic for the determination of the concentrations and temperatures of the plasma species since it allows fast, robust and sensitive measurements of single components. Although the measured data are principally line-of-sight or even volume integrated, an introduced error is not significant in the case of the stable molecules because of their flat concentrations profiles. Usage of a multipass cell and a modulation technique makes it possible to enhance the detection limits.

As an advantage of the method, it can be mentioned that only the ratio of the measured quantities is needed. Moreover, for the stable plasma components a simple calibration procedure is applicable.
Chapter 3. Electron density measurements

The electron density is one of the most important quantities, characterizing the plasma and enhancing the plasma chemistry. Highly reactive radicals, important for both, surface deposition processes and the rise of longer reaction chains are produced by inelastic collisions of the electrons with stable particles. On the other hand, inelastic collisions with the electrons are one of the strongest lost channels for neutrals. In this work, molecule concentrations are measured as functions of the input power. For further analysis on the base of rate equations, an interconnection between the input power and the electron density is necessarily needed, and reliable measurements are of special importance.

3.1. Langmuir probe

Several methods are well known for obtaining the electron density in the discharge. The very powerful Langmuir probe technique \[78, 79, 80, 81\] works by inserting one or more electrodes into the plasma, with a constant or time-varying electric potential between the various electrodes or between them and the surrounding vessel. The measured currents and potentials in this system allow the determination of physical properties of the plasma, such as electron temperature, electron and ion densities and EEDF, which can be found from the second derivative of the current-voltage characteristic of the Langmuir probe \[82\].

Unfortunately, principle necessity to insert the probe in the plasma bulk is a weak point of this technique. The presence of a probe in the plasma affects its properties. In case of reactive plasmas fast changes in the device characteristics due to the contamination or etching of the probe must be taken into account. For this reason this technique is most popular for investigations of noble gases plasmas. The advantage of the method is the possibility to perform local measurements at relatively low cost and high flexibility compared to other techniques (Thomson scattering, optical emission spectroscopy or microwave interferometry).

In the CCP cell used in this work, measurements of the electron density by means of the Langmuir probe technique were made by V. Singh in argon \[55\]. He obtained electron density and EEDF as functions of the input power at pressures of 1 and 2 mbar. Measurements have been made in the middle of the electrode gap and 2 cm outwards from the centre of the discharge cell. Some of his results are shown in Fig. 21. The electron density increases by one order of magnitude with an increase of the input power from 5 to 60 W. At the highest input power level the electron density for 1 mbar is \(1.8 \times 10^{11}\) cm\(^{-3}\). It is known, that electron density in argon is typically one order of magnitude higher than in methane. This
assumption gives a first and very rough estimation of the electron density in a methane discharge.

### 3.2. Microwave interferometers

Interferometric methods [28, 83, 84] have advantage over the Langmuir probe technique because they are non-invasive. Their second important advantage is that almost no model assumptions are necessary to infer the electron density, since this quantity is directly connected to the plasma frequency and therefore to the refractive index. However, the phase difference which develops between the radiation field propagating through the plasma and the corresponding reference radiation field increases linearly with increasing wavelengths for fixed plasma conditions. Hence, in the case of low electron densities the wavelength of the probing radiation should be sufficiently large in order to produce sizeable phase shifts. Therefore, the microwave (tens of GHz) region is used to improve the sensitivity.

The measured quantity is the phase shift caused by a transparent phase object introduced into one of the two arms of the interferometer.

An ordinary wave propagating through an unmagnetized homogeneous plasma sees an index of refraction $N$, which is a function of the plasma’s electron density:

$$N^2 = 1 - \frac{\omega^2}{\omega_p^2} = 1 - \frac{n_e}{n_c},$$

$$n_c = \frac{\omega_p^2 m e_0}{e^2}$$

where $\omega = 2\pi f$ is the frequency of the probing wave, $\omega_p$ is the plasma frequency, $n_e$ is the electron density and $n_c$ is the cut-off density for the probing wave. Typical values for the electron density in the CCP and ICP discharges are $10^9$ and $10^{11}$ cm$^{-3}$, correspondingly; this gives a cut-off frequency of 0.3 and 3 GHz, respectively.

A change of the refraction index results in a phase shift $\Delta \Phi$ of the probing wave relative to the wave travelling in free space. For small electron densities $\Delta \Phi$ can be written as:

$$|\Delta \Phi| = \frac{e^2}{4\pi cm e_0 f} \int n_e dl,$$

(3.2.1)

where $\int n_e dl = n_L$ is the electron density integrated over the line of sight.

The chosen frequency of the probing wave has to satisfy two opposite conditions. The wavelength should be as small as possible in order to avoid uncontrolled reflections from metallic surfaces (e.g. the electrodes) which could lead to modifications of the phase to be measured. At the same time, one can see from equation (3.2.1) that the phase-shift increases with decrease of the frequency. Going to a shorter wavelength in order to improve the spatial resolution is paid by a smaller phase shift which is therefore harder to detect.

The principal disadvantage of the method is that the signal is integrated over the distance between transmitter and detector of the testing wave; moreover, due to the relatively large diameter of the microwave beam the information on the phase shift is collected from a
large volume. However, the electron density is not spatially uniform neither in axial, nor in radial direction. Additionally, this non-uniformity is pressure dependent.

In the present work measurements were carried out by means of a super heterodyne microwave interferometer with the frequency of 35 GHz, which corresponds to wavelength of about 8.6 mm. The diameter of the beam inside the chamber was estimated to be a few cm.

Unfortunately, in the CCP in methane experimental determination of the distribution of the electron density in space was not possible under our conditions. Results of the investigations performed in other groups have been used for an estimation of the spatial distribution of electrons. The results described in [63] concern a CCP discharge in CH$_4$-Ar-H$_2$ mixture at the total pressure of 100 Pa. The profile of the electron density was obtained by means of a space-resolved microwave interferometer (wavelength of 1 mm, beam diameter ~ 6 mm) and consequently applied Abel inversion technique. It was found that the electron density decreases rapidly with the distance from the axis of the discharge; on the edge of electrode it is about 50% of its value in the centre of the chamber. Earlier [83] this technique was used for the investigation of the electron density profile in CCP in Ar and was compared with the Langmuir probe results; very close agreement was reported. Simulations of methane CCP discharge performed using the fluid model [50] and the particle-in-cell Monte Carlo collision model [21] show sharp decrease of the electron density on the distances, longer than the electrode radius as well.

The investigations of the electron density profile in the ICP by means of plasma absorption probe are reported in by C. Scharwitz in his Master thesis [58]. His results for the pure CH$_4$ discharge and different mixtures with Ar are shown in Fig. 22 for the pressure of 5 Pa and power of 100 W. The densities are normalized on the density in argon in the centre of discharge. One can see that in case of pure CH$_4$ the electron density on the distance from the axis of the discharge equal to 17 cm is about factor 5 smaller than its value in the centre.

![Radial profiles of the electron density in the ICP in mixture Ar/CH$_4$ [58]](image)
Chapter 3. Electron density measurements

In the current work electron density was measured in the CCP (input power 10 - 60 W, in argon and methane discharges at total pressures of 50 and 100 Pa and 1 and 10 sccm gas flow rate) and in the ICP (input power 100 – 650 W, pressure 10 Pa, gas flow rate 10 and 60 sccm).

The discussion on the real shape of the electron density profile goes out of the scope of this work, since the matter is very complicated and is the subject of separate intense investigations. For example, a solution of the diffusion equation with the assumption of the electron temperature constant over the plasma volume would result in an electron density profile, described by Bessel function. The changes of the electron temperature in space lead to the profile, consisting of the several Bessel functions [95]. Moreover, calculations and experiments performed for CCP in [50] and [31], correspondingly, reveal the profile with the slight decrease in the centre of discharge and narrow peak near to the electrode edge.

In this work for simplicity a rectangular profile was assumed for the calculation of the absolute electron densities. Simple estimations prove that using a rectangular profile instead of the Bessel profile leads to the disagreement in the mean electron density by factor less than 1.5. The plasma length $L$ was taken to be 10 cm for the CCP and 30 cm for the ICP according to the chamber geometries (diameters of the electrodes and coil are 7 cm and 12.5 cm, respectively).

At pressure of 5 Pa approximately the same phase shift was detected by the microwave interferometer. The interpretation of the measurements at low pressure was hampered because of the lack of information on the electron density profile, since it can not be taken as rectangular any more. The value of $10^{15}$ m$^{-3}$ was taken as upper limit estimation.

The results are shown in Fig. 23 and 24. In all cases the dependence of the electron density on the input power is almost linear. Depending on the input power the electron density in methane plasmas covers a range of $10^{15}$ m$^{-3}$ to $10^{16}$ m$^{-3}$ in the CCP discharge and $10^{16}$ m$^{-3}$ to $10^{17}$ m$^{-3}$ in the ICP (H-mode).

Absolute values of electron density in the argon discharge (Fig. 23, right) can be compared to the

Fig. 23. Electron density in CCP (left: CH$_4$, right: Ar) at 100 Pa

Fig. 24. Electron density in the ICP at 10 Pa
measurements of V. Singh and coincide relatively well.

The reliability of the measurements in methane in the CCP was checked by C. Pargman [29] applying a microwave interferometer on the base of a far-infrared laser with a wavelength of 432.6 µm (beam diameter ~ 8 mm). His results, obtained over the line of sight passing in the middle of the distance between the electrodes, at 60 W in methane are in good agreement with the heterodyne microwave interferometer.

The obtained dependencies of the electron density on the input power in methane discharges are used further for the analysis of the plasma species production and loss channels, originating from interactions of neutral molecules with electrons.

**Summary**

Both Langmuir probe and microwave interferometer register an increase of the electron density with an increase of the input power. The discrepancy between the results given by both methods is a factor less than 2. The discussion about the reasons for this disagreement is beyond the scope of this work. The interested reader may look for details in publication of L. J. Overzet, devoted to the comparison of these two techniques on the example of argon discharge in GEC reference reactor [32].

The electron density measured in CCP and ICP discharges by means of different diagnostics, exhibits almost a linear dependence on the input power. This dependence was used in the following analysis of the plasma chemical composition. The link between the electron density and the input power is very important since it makes it possible to consider the evolution of the plasma composition apart from a particular geometry of the reactor.
Chapter 4. Plasma chemistry

In numerical approaches to the investigation of the composition of reactive plasmas, tens of chemical reactions are usually taken into account. In order to replace a numerical calculation of the plasma chemistry with an analytical description the manifold processes, occurring in hydrocarbon RF discharges, must be reduced to the most efficient ones. The aim of this chapter is to find a tractable system of rate equations for the concentrations of the selected species, which can be solved for steady-state conditions but also to yield temporal evolutions.

In this chapter some of the physical and chemical processes responsible for the production and consumption of the measured plasma components are discussed.

4.1. Reaction paths

For the determination of the chemical composition of the plasma one needs to solve a system of differential rate equations for the concentration $n_i$ of every component:

$$\frac{dn_i}{dt} = Q + \sum k_{ij} n_j n_i - \sum k_{ji} n_i n_j - v n_i . \tag{4.1.1}$$

The first term $Q$ is the incoming flow rate of the feed gases, the second term corresponds to the chemical reactions between molecules, radicals or ions and reactions with electrons, leading to the production of the component. The third term is related to the consumption of the component in inelastic collisions with electrons and chemical reactions, while the last term represents losses due to diffusion, pumping and sticking to the surfaces.

The efficiencies of the reactions of electrons, ions and neutrals with each other are characterized by the product of the corresponding rate coefficient and the concentrations of the considered reactants. A more detailed consideration will be given below, while here only a brief enumeration of the main dependencies is given.

The rate coefficients for neutral-neutral and ion-neutral reactions are functions of the gas temperature, which can be expressed by Arrhenius’ law. Additionally, they are functions of the gas pressure. A compilation of values, obtained by numerous research groups in different experiments can be found in the literature or in databases [47, 48, 46, 49, 85]. For a broad range of temperatures, sometimes parameters of the temperature dependence are given as well. In this work the gas temperature is of about room temperature (Section 2.3), and for this value all desirable data are available.

The rate coefficients corresponding to the interaction with electrons are functions of the cross sections and the EEDF.

Sticking to the surface is characterized by sticking coefficients, investigated by some groups experimentally [14]. Diffusion is described by a diffusion coefficient, depending on the mobility of the component in the gas mixture, in other words, on the plasma composition. For radicals diffusion in combination with sticking to the surfaces is an important loss channel, since the diffusion brings them to the chamber walls or electrodes. For stable molecules diffusion plays a different role: it is responsible for the smoothing of the concentration profiles and for bringing particles to the pump junction.

Finally, the incoming flow rate and the pumping frequency are defined by the experimental conditions and thus, are the parameters, which are obtained most easily.
From the above description one can see, that the task of plasma composition definition is very complicated. First, a lot of information on the plasma parameters is needed: gas and electron temperatures, electron concentration and energy distribution function, etc.

Moreover, in reactive plasmas the source gas dissociates to radicals and thereby initiates a complicated chain of chemical reactions. In this case, due to the huge number of processes involved, the system of equations (4.1.1) can be solved only numerically. Such calculations were performed by many groups, including ours. Elaborated codes allow one to involve tens of reactions into consideration and provide values of many plasma components. An extended list of sticking coefficients and rate coefficients for numerous chemical reactions can be found in the previous works performed in our group [36, 37, 95]. Unfortunately, by this treatment, the mechanisms, resulting in a certain gas composition, tend to be of little evidence. The reasonability of the results received from simulations should always be confirmed by an experiment.

In the present work an attempt was made to analyze the trends in the plasma composition analytically in dependence on the external (input power, pressure, flow rate, reactor geometry) and internal (electron density and energy distribution function) parameters. The cost of using simplified analytical expressions for measured densities is the limitation of the involved processes to keep the system (4.1.1) tractable.

The most important processes in the plasma chemistry can be chosen by selecting the reactions with relatively high rate coefficients and/or concentrations of reactants. Also, the choice of the considered processes was influenced by the wish to get by with only those species, for which experimentally obtained concentrations were available.

It is obvious, that dissociation and ionization of the source gas in collisions with electrons are the fundamental processes, responsible for the creation of the plasma and giving rise to chains of subsequent reactions. Since for hydrocarbon molecules the threshold energies for ionization are higher than for dissociation, the losses of the investigated molecules due to inelastic interactions with electrons are ascribed to the total and partial dissociation processes:

\[
\begin{align*}
\text{CH}_4 + e & \rightarrow \text{CH}_3 + e + H & (1) \\
\text{CH}_4 + e & \rightarrow \text{CH}_2 + e + \text{H}_2 & (2) \\
\text{CH}_4 + e & \rightarrow \text{CH} + e + 3\text{H} & (3) \\
\text{C}_2\text{H}_6 + e & \rightarrow \text{C}_2\text{H}_4 + e + \text{H}_2 & (4a) \\
\text{C}_2\text{H}_6 + e & \rightarrow \text{C}_2\text{H}_2 + e + 2\text{H}_2 & (4b) \\
\text{C}_2\text{H}_4 + e & \rightarrow \text{C}_2\text{H}_2 + e + 2\text{H} & (5) \\
\text{C}_2\text{H}_2 + e & \rightarrow \text{C}_2\text{H} + \text{H} + e & (6)
\end{align*}
\]

The related rate coefficients can be calculated if information on the EEDF and the cross-sections of the processes is available. To gain some insight into the efficiency of the dissociation processes the value of $10^{-18} \text{ m}^3 \text{s}^{-1}$ can be taken for the rate coefficient of the total dissociation of methane. Anticipating the consideration, given in section 4.3, we notice here that this value corresponds to an electron temperature of about 1 eV if a Maxwellian EEDF is assumed. The product of the rate coefficient and the electron density gives the value of 0.1 s\(^{-1}\) for the frequency of the total dissociation of methane at the highest power level used in the ICP.

Although this is a very rough approach, ion-neutral reactions are neglected in this work. No experimental data on the concentration of ions was available. The following argumentation helps to estimate the corresponding process frequencies.
Because of quasi-neutrality of the plasma the sum of the concentrations of all ions is equal to the electron density. Since in the considered plasmas the degree of ionization is not higher than a tenth of a percent, even the total concentration of all ions is much lower than the concentrations of neutral particles; the concentration of every type of ions is lower than the density of electrons. In [50], on the base of output data of a fluid model CH$_3^+$, CH$_4^+$, CH$_5^+$, C$_2$H$_5^+$ ions are reported to be dominant in the methane plasma. To cause the losses of neutral particles, comparable with the ones due to the interaction with electrons, the rate coefficients of ion-neutral reactions must be as high as $10^{-16}$ m$^3$s$^{-1}$. The values given, for example, in [86] for reactions of methane with the above mentioned ions are close to this estimation and even higher. Nevertheless, the lack of the reliable data on the ion concentrations hampers an implementation of the ion-neutral reactions. Exclusion of the losses, due to the interactions with ions, from the balance between production and consumption channels results in an overestimation of the efficiency of the loss channels due to inelastic electron impacts. This is most crucial in the case of methane, since methane reactions with ions involve most abundant ones.

A wide list of reactions between radicals or between radicals and stable molecules is commonly included in numerical simulations of the plasma kinetics. Among them, reactions of molecules with radicals such as CH$_3$, CH$_2$, CH have rate coefficients of the order of $10^{-17}$ m$^3$s$^{-1}$. However, the concentrations of the radicals are typically very low [20, 42, 50, 102, 103].

In this work only the concentration of the methyl radical (which is as high as $\sim 10^{17}$ m$^{-3}$) was obtained experimentally (Section 6.2). Concentrations of other radicals were not measured. Results of experimental or numerical investigations of other groups indicate that they are even lower than the one of methyl by several orders of magnitude. Hence, reactions with radicals are relatively weak loss channels for molecules and reactions between radicals are too inefficient to be considered as significant production channels.

Only one reaction of this type, namely the reaction between two methyl radicals, was taken into account as a production channel of the ethane molecule:

$$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6 \quad (7)$$

with the rate coefficient (at room temperature)

$$k_{\text{ch}_3\text{ch}_3} = 5 \cdot 10^{-17} \text{ m}^3\text{s}^{-1} \quad [99] .$$

Nevertheless, neglecting reactions with radicals can in some cases lead to an underestimation of the production or consumption of all species.

It was found experimentally that the reproducibility of results on the measured plasma components does not depend on the prehistory of discharge. Indeed, changes of the properties of the surfaces of the electrodes and chamber walls due to deposition of hydrocarbon layers happen in very short time after discharge was switched on. It is also known from the literature that the sticking coefficients for stable molecules to surfaces are very low. Therefore interactions of all measured species, except of methyl with surfaces are neglected.

In Table 5 the processes involved in the analysis of the dependencies of the concentrations on the plasma parameters are listed together with the corresponding rate coefficients.
Chapter 4. Plasma chemistry

Table 5 Considered processes

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Production</th>
<th>Losses</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>dissociation of CH₄</td>
<td>kₑch₄, k₆ch₃</td>
</tr>
<tr>
<td>CH₄</td>
<td>External inflow</td>
<td>Q</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>CH₃ radicals</td>
<td>k₆ch₃n₃</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>dissociation of C₂H₆</td>
<td>kₑ₂b₆</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>dissociation of C₂H₄</td>
<td>kₑ₂b₄</td>
</tr>
<tr>
<td>All stable</td>
<td>Pump</td>
<td>v_p</td>
</tr>
</tbody>
</table>

Assuming a fast production of the electrons [87, 88] and a relatively fast (100 ms) formation and reaching of the steady state concentration of the methyl radical [103], the system of the rate equations for the measured species can be written as follows:

- **CH₄**:

  \[
  \frac{dn}{dt} = Q - (kₚ CH₄ nₑ + ν + v_p) n, \quad n=n_0 \text{ at } t=0
  \]

  where \( ν \) is the frequency of all loss processes, which are different from the pumping and interactions with the electrons. \( t=0 \) corresponds to the concentration before the discharge is ignited. Since methane is used as source gas, its initial concentration is defined by pressure and flow rate conditions.

- **CH₃**:

  \[
  \frac{dn}{dt} = kₑ ch₃ n₃ - k₆ ch₃ n₃ - v_ch₃ n₃, \quad n=0 \text{ at } t=0
  \]

- **C₂H₆**:

  \[
  \frac{dn}{dt} = k₆ ch₃ n₃ - (kₑ₂b₆ nₑ + v + v_p) n, \quad n=0 \text{ at } t=0
  \]

- **C₂H₄**:

  \[
  \frac{dn}{dt} = kₑ₂b₆ nₑ - (kₑ₂b₄ nₑ + v + v_p) n, \quad n=0 \text{ at } t=0
  \]
Chapter 4. Plasma chemistry

- For C₂H₂:

\[
\frac{dn}{dt} = k \nu_{ec2h6} n_e n_{C_2H_6} + k \nu_{ec2h4} n_e n_{C_2H_4} - (k \nu_{ec2h2} n_e + \nu_p) n, \quad (4.1.6)
\]

\n\text{n=0 at } t=0.

4.2. Time scales of pumping, incoming flow and diffusion

In addition to the changes of the concentrations due to chemical reactions there are processes like gas inflow \( Q \), pumping losses \( \nu_p \) and diffusion.

Diffusion plays an important role as a loss channel in case of radicals, by bringing them to the chamber walls, where they easily stick to the surface and disappear for the further consideration. In the case of stable molecules, diffusion is responsible for the “mixing” of the components produced in the active plasma region, with the background gas.

Gas inflow \( Q \) and pumping losses \( \nu_p \) are known parameters of the gas flow system and can be defined from the condition of constant pressure \( p \) at constant flow rate before the discharge is ignited:

\[
\frac{dn}{dt} = Q - \nu_p \cdot n = 0. \quad (4.2.1)
\]

An increase of concentration due to the inflow \( Q \) can be calculated as follows. A flow rate \( \Phi \) of 1 sccm (standard cubic cm per minute) results in an injection of \( 4.48 \times 10^{17} \) particles per second in plasma chamber volume \( V \). This yields:

\[
Q \left[ \frac{\text{molecule}}{m^3 \cdot \text{sec}} \right] = 4.48 \cdot 10^{17} \left[ \frac{\text{molecule}}{\text{sccm} \cdot \text{sec}} \right] \cdot \Phi \left[ \text{sccm} \right] \cdot \frac{V \left[ m^3 \right]}{V \left[ m^3 \right]}. \quad (4.2.2)
\]

Without a discharge, the gas temperature inside the plasma is exactly the room temperature and the concentration can be defined from the ideal gas law:

\[
n = \frac{p}{kT}, \quad (4.2.3)
\]

According to this, for the pump loss frequency \( \nu_p \) we have:

\[
\nu_p = \frac{Q}{n} = \frac{4.48 \cdot 10^{17} \cdot \Phi \cdot k \cdot T}{V \cdot p}. \quad (4.2.4)
\]

Values for \( Q, \nu \) and convection (or residence) time

\[
\tau_c = \frac{1}{\nu_p}, \quad (4.2.5)
\]
calculated for most typical experimental conditions, are listed in the Supplement. The pumping time can be defined as a time, in which concentration changes by factor \( e \approx 2.71828 \ldots \) (Euler number), under the conditions, when the pump is the only loss channel and no producing channels are active. In Fig. 25 pumping times calculated from time resolved absorption of different molecules in the CCP chamber are plotted for different flow rates together with the calculated residence time (4.2.5). The measured pumping times are approximately the same for the measured species and coincide with the calculated residence time with satisfactory accuracy.

The diffusion frequency is

\[ \nu_D = \frac{D}{\Lambda^2}, \]

where \( D \) is the diffusion coefficient and \( \Lambda \) is an diffusion length. The diffusion length depends on the reactor geometry and, for a cylinder, is given by [89]

\[ \frac{1}{\Lambda^2} = \left( \frac{\pi}{h} \right)^2 + \left( \frac{2.405}{R} \right)^2, \]

where \( h \) and \( R \) are the chamber height and radius, correspondingly. Taking the diffusion coefficient to be \( D = 2.5 \times 10^{-2} \text{ m}^2/\text{s} \), which is the value for methane at 100 Pa, for the CCP chamber, the diffusion frequency can be estimated to be \( \sim 10 \text{ s}^{-1} \). It is immediately obvious that convection due to the gas inflow and pumping is much slower than diffusion. This is in agreement with the flat profiles of concentration, reported in Section 2.7.

Fig. 25. Pumping times of the different species in CCP
4.3. Inelastic electron collisions

Dissociation via inelastic collisions with electrons is one of the most important production and/or loss channels for plasma species. It takes place in several possible ways, having different threshold energies. The corresponding cross sections $\sigma$ are functions of the kinetic energy $\varepsilon$ (or velocity $v$) of the electrons. Rate coefficients are given by the cross sections of an electron impact reaction, averaged over the velocity distribution function of the electrons:

$$k_e = \left\langle \sigma \left( v_e \right) \cdot v_e \right\rangle_v.$$

(4.3.1)

Denoting the normalized electron velocity distribution function as $f(v)$, equation (4.3.1) can be written as follows:

$$k = \int \sigma \left( v \right) \cdot f \left( v \right) \cdot v \, dv.$$

(4.3.1a)

So, for the calculation of a certain rate coefficient, one must acquire information about the dependencies of the cross sections on the electron velocity (or electron kinetic energy $\varepsilon = mv^2/2$) and the electron velocity distribution function (or electron energy distribution function).

Cross sections

The analytical dependence of the cross sections on the electron energy for many inelastic processes with hydrocarbons can be found in the literature, for example in [90, 91]. On the basis of extensive compilation of experimental and theoretical data performed by different groups, authors provide a complete set of cross sections for the methane and ethane families of hydrocarbons.

According to these references, the total electron impact dissociation cross-section of CH$_4$ to neutral fragments is represented by the following simple analytic expression:

$$\sigma_{DE}^{\text{tot}} \left( \varepsilon \right) = 44.634 \left( 1 - \frac{E_{th}}{\varepsilon} \right)^3 \cdot \frac{1}{\varepsilon} \ln(\varepsilon + 0.15\varepsilon) \times 10^{-16} \text{ cm}^2,$$

(4.3.2a)

and similarly for C$_2$H$_y$ ($y=2, 4, 6$) molecules by:

$$\sigma_{DE}^{\text{tot}} \left( \varepsilon \right) = 34.6 \cdot (1.35 + 0.177 y) \left( 1 - \frac{E_{th}}{\varepsilon} \right)^3 \cdot \frac{1}{\varepsilon} \ln(\varepsilon + 0.15\varepsilon) \times 10^{-16} \text{ cm}^2.$$

(4.3.2b)

Here $E_{th}$ and $\varepsilon$ are the threshold and collision energies, respectively, expressed in eV and $\varepsilon$ is again the Euler number. The partial cross section for a particular neutral dissociation channel $A$ of C$_x$H$_y$ is given by

$$\sigma_{DE} \left( \varepsilon, A \right) = R_{DE} \left( A \right) \cdot \sigma_{DE}^{\text{tot}} \left( \varepsilon \right),$$

(4.3.3)
where $R_{DE}(A)$ is the value of the branching ratio for each channel. Partial cross sections for $C_2H_y$ can be found in a similar way. Data for threshold energies and branching ratios taken from [90,91] are listed in Table 6. For the calculation of the total dissociation rate coefficient the lowest threshold energy must be taken.

One can see that almost all dissociation channels for the molecules born in the plasma have threshold energies lower than the source gas methane.

Table 6. Neutral dissociation channels of C$_x$H$_y$ [90, 91]

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Products</th>
<th>Threshold energy, eV</th>
<th>Mean Total energy of the products, eV</th>
<th>Branching ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>CH$_3$</td>
<td>8.8</td>
<td>4.4</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>CH$_2$</td>
<td>9.4</td>
<td>4.7</td>
<td>0.144</td>
</tr>
<tr>
<td></td>
<td>CH</td>
<td>12.5</td>
<td>4.5</td>
<td>0.073</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>14</td>
<td>6</td>
<td>0.023</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>C$_2$H$_4$ + H$_2$</td>
<td>4</td>
<td>2.57</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_2$ + 2H$_2$</td>
<td>6.2</td>
<td>2.93</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>CH$_3$ + CH$_3$</td>
<td>6.38</td>
<td>2.65</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>CH$_4$ + CH$_2$</td>
<td>6.95</td>
<td>2.86</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_5$ + H</td>
<td>7.45</td>
<td>3.07</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_3$ + H$_2$ + H</td>
<td>9.4</td>
<td>3.13</td>
<td>0.04</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>C$_2$H$_2$ + H$_2$</td>
<td>5.8</td>
<td>2.4</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_2$ + 2H$_2$</td>
<td>6.5</td>
<td>2.1</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_3$ + H</td>
<td>6.9</td>
<td>2.1</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>C + CH$_4$</td>
<td>8.1</td>
<td>2</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>C$_2$H + H$_2$ + H</td>
<td>8.4</td>
<td>1.8</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>CH$_3$ + CH$_2$</td>
<td>8.7</td>
<td>1.6</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>CH$_2$ + CH$_2$</td>
<td>8.9</td>
<td>1.5</td>
<td>0.06</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>C$_2$H + H</td>
<td>7.5</td>
<td>2.6</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td>C$_2$ + H$_2$</td>
<td>8.7</td>
<td>2.3</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>C + CH$_2$</td>
<td>9.8</td>
<td>0.7</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>CH + CH$_2$</td>
<td>10.6</td>
<td>0.6</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>C$_2$ + 2H</td>
<td>11.38</td>
<td>0.5</td>
<td>0.11</td>
</tr>
</tbody>
</table>
**Distribution function**

The distribution function can be calculated from Boltzmann’s equation [26] which is an equation for the temporal evolution of the phase space distribution (properly a density) function \( g(\vec{r}, \vec{p}, t) \), where \( \vec{r} \) and \( \vec{p} \) are position and momentum, respectively. The distribution is normalized in a way that \( g(\vec{r}, \vec{p}, t) d^3r d^3p \) is the number of particles inside a six dimensional phase-space volume \( d^3r d^3p \) at \((\vec{r}, \vec{p})\) at time \( t \). The Boltzmann equation can be written as:

\[
\frac{\partial g}{\partial t} + \frac{\vec{p}}{m} \cdot \frac{\partial g}{\partial \vec{r}} + F \cdot \frac{\partial g}{\partial \vec{p}} = \left. \frac{\partial g}{\partial t} \right|_{\text{coll}} .
\]

\( F(\vec{r}, \vec{p}, t) \) is the force field acting on the particles, and \( m \) is the mass of the particles. The term on the right hand side is added to describe the effect of collisions between particles.

Experimentally the EEDF can be found from the second derivative of the current-voltage characteristic of the Langmuir probe, to which it is proportional (Chapter 3).

A Maxwellian electron energy distribution function \( f_M(\varepsilon) \) results from a constant collision frequency (independent on the energy) corresponding to thermal equilibrium of the electrons with one common temperature \( T_e \). One of the forms of a Maxwellian EEDF is:

\[
f_M(\varepsilon) d\varepsilon = 2\sqrt{\frac{\varepsilon}{\pi}} \left( \frac{1}{T_e} \right)^{3/2} \exp \left\{ -\frac{\varepsilon}{T_e} \right\} d\varepsilon ,
\]

where the electron energy \( \varepsilon \) and the electron temperature \( T_e \) are in units of electron-volts (eV). For any non-Maxwellian distribution function only an effective temperature \( T_{\text{eff}} \) can be determined, based on the definition of the mean electron energy \( \langle \varepsilon \rangle \):

\[
\langle \varepsilon \rangle = \int_0^{\infty} \varepsilon f(\varepsilon) d\varepsilon ,
\]

\[
T_{\text{eff}} = \frac{\langle \varepsilon \rangle}{3}.
\]

The assumption of a constant momentum transfer cross section (hard-sphere interaction), which implies an increase of the collision frequency with increasing velocity, leads to the so-called Druyvesteyn distribution function \( f_D \):

\[
f_D(\varepsilon) d\varepsilon = A_D \sqrt{\varepsilon} \exp \left\{ -B_D \left( \frac{\varepsilon}{T_e} \right)^2 \right\} d\varepsilon ,
\]

\[
A_D = \frac{4 \left[ \Gamma \left( \frac{1}{4} \right) \right]^4}{\pi \left( 12 \sqrt{2\pi} T_e \right)^{1.5}} .
\]
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\[ B_D = \frac{\Gamma(1/4)^4}{72\pi^2} \approx 0.243, \]

where \( \Gamma \) is the gamma function [92].

The exponent in the Maxwellian distribution function is proportional to the electron energy, while in the Druyvesteyn distribution function it is proportional to its square. As a result the Druyvesteyn distribution function strongly decreases at higher electron energies compared to the Maxwellian distribution function. In Fig. 26 both functions, normalized on the electron density, are plotted for the same value of the mean energy.

In reactive plasmas deviations from the Maxwellian and towards Druyvesteyn-like distribution functions are often observed [10, 93].

\[ f_{M}(e) \text{ (solid line) and } f_{D}(e) \text{ (dashed line)} \]

EEDFs for the same mean energy of 3eV

Rate coefficients

With the given EEDF and cross section, the rate coefficients can be calculated from the expression (4.3.1). In Figs. 27 to 29 rate coefficients for the partial processes (1)-(6) in Section 4.1 and the total dissociation are presented as functions of the effective electron temperature (4.3.5) for Maxwellian and Druyvesteyn distributions. In other words, a relation between rate coefficient and effective temperature can be established for a given shape of the EEDF.

In the present work rate coefficients can be obtained from the experimental data (see following chapters). Therefore, if the electron temperature or mean electron energy is unknown, it can be estimated from the obtained dissociation rate coefficients, assuming some EEDF.

As mentioned above, Druyvesteyn-like distribution functions were found in reactive plasmas. Unfortunately, since the values of the rate coefficient are averaged quantities, a simple chemistry analysis does not permit a determination of the shape of the distribution function. Nevertheless, it is possible to choose between certain assumed shapes and to figure
out the corresponding parameters. Such a technique of EEDF investigation by comparing of the experimental data to plasma chemistry model results was reported in [37].

In this work, dissociation rate coefficients for several molecules were estimated from the dependencies of the concentrations on the internal parameters of the plasma. For this purpose an approximation of the experimental results with analytical approach, obtained from the simplified system of differential rate equations was used. This straightforward method enables a fast and easy appraisal of the rate coefficients. From the Fig. 27 to 29 one can notice that an increase of the electron temperature of 0.3 eV corresponds to a change of the rate coefficients by a few orders of magnitude for the considered energies. Therefore, even relatively imprecise guesses about the rate coefficients gives credible information about the electron temperature or mean electron energy.

The approach was applied to the concentrations of CH₄, C₂H₆, C₂H₂ and C₂H₄ in order to check the plausibility of the chosen set of reactions taken into account and to illustrate the capability of the method.

**Fig. 27.**
Dissociation rate coefficient of C₂H₂ for Maxwell and Druyvesteyn EEDFs

**Fig. 28.**
Dissociation rate coefficients of C₂H₆ for Maxwellian and Druyvesteyn EEDFs
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Summary

Several points were discussed in this chapter.

Restricting ourselves to a very narrow list of considered processes, we could form a system of simplified rate equations for the concentrations of the plasma species. For the source gas the incoming flow is assumed to be the only production term. Electron impact dissociation is considered as one of the most important loss and production channels for the stable neutral components of the plasma. Assuming a shape of the EEDF, the rate coefficients for different dissociation channels of the species can be calculated if the cross-sections of the processes are known. In the current work the cross-sections from [90, 91] have been used.

In Section 2.7 flat spatial distributions of the concentrations of stable molecules were discussed. It was mentioned that diffusion processes are much faster than production and loss channels under the considered experimental conditions (low ionization degree, low flow rates and pressures).

Indeed, for example for CH\textsubscript{4}, the loss frequency, determined by collisions with electrons is the product of the total dissociation rate coefficient and the electron density. In the CH\textsubscript{4} discharge at 100 Pa, assuming a Maxwellian EEDF with 1 eV it has a value of:

\[ v_{el} = k_{e} n_e \sim 10^{-18} \cdot 10^{16} = 10^{-2} \text{s}^{-1} \]

for a maximum input power 50 W.

The incoming flow at the highest used flow rate of 10 sccm is

\[ v_{in} = \frac{Q}{n} \sim 10^{-2} \text{s}^{-1}, \]

whereas the diffusion is \( v_D \sim 10 \text{s}^{-1} \) which is much faster than the main processes responsible for increasing or decreasing the CH\textsubscript{4} concentration.

The same is valid for other measured stable species. Experimentally obtained pumping constants for different neutral plasma components are very close to each other and to the residence time. The rate coefficients for the dissociation for other hydrocarbons are as low as the rate coefficients for methane or even lower. Diffusion coefficients for ethane, ethylene and acetylene are about the same as the one for methane and can be found, for example, in [37].

Fig. 29.

Dissociation rate coefficients of CH\textsubscript{4} for Maxwellian and Druyvestein EEDFs
The role of diffusion is the distribution of the feed gas inside the chamber and the transport of the species, produced in the discharge, towards the chamber walls, resulting in smooth profiles of the stable species concentrations. Interaction of radicals with the walls leads to sticking of the particle; stable species are assumed to reflect back in the chamber and/or to be pumped out.

Returning to the collisions of neutrals with electrons, one can easily see that the EEDF is very important for the plasma chemistry. Under the assumption of Maxwellian and Druyvesteyn shapes, the electron mean energy can be found as follows. Since solutions of equations (4.1.2) - (4.1.6) yield dependencies of the species concentrations on the electron density or the time, with the rate coefficients as parameters, a comparison of calculated data with experimental results makes it possible to determine the rate coefficients and the mean electron energy from the curves presented in Fig. 27-29. This procedure can be performed for every investigated neutral plasma component with a reliability that depends on the accuracy of the chosen rate equation.

Solutions of equations (4.1.2) - (4.1.6) will be obtained and compared to experimental results in the following chapters.
Chapter 5. Time dependencies

Analytical solutions of the rate equations provide the dependence of the species concentration on time, hence a comparison with the experimental data makes it possible to estimate the frequencies of the loss and production processes.

The analysis is performed for the source gas CH\textsubscript{4} and for ethane (C\textsubscript{2}H\textsubscript{6}), which is the stable product of the chain of reactions. Since interactions with electrons are included in the loss channels for both species, the effective electron temperature can be determined from the analysis of any of these two. This can be done under different experimental conditions (pressure, flow rate, input power), in other words, for different plasma-chemical compositions. As the composition of the plasma itself is a function of time, it is also possible to observe changes in the process frequencies.

5.1. Methane (CH\textsubscript{4})

The benefit of performing measurements of the methane concentrations is that CH\textsubscript{4} is a feed gas, and even at the highest input power level used in our investigations, its concentration is high enough to provide large absorbance measurements with a high signal-to-noise ratio. Therefore a short integration constant in the acquisition procedure can be used and a time resolution of a few seconds can be achieved.

For the purpose of analytical description, the rate equation for the CH\textsubscript{4} concentration can be reduced to a relatively simple one which can be solved for equilibrium conditions and as a function of time as well. The main reaction paths are listed in Table 5. Because they involve interactions with electrons, the mean electron energy can be determined from a single expeditious experiment and an uncomplicated analysis procedure if a Maxwellian or Druyvesteyn EEDF is assumed.

General remarks on temporal behaviour

![Time evolution of the CH\textsubscript{4} concentration in the CCP (left) and the ICP (right)](image)

Fig. 30. Time evolution of the CH\textsubscript{4} concentration in the CCP (left) and the ICP (right)

The experimentally obtained time dependence for the CCP is shown in Fig. 30 (left). On the right hand side of Fig. 30 the time dependence for the ICP is presented. Regarding the general behaviour several steps in the temporal evolution of the methane concentration can be noticed. After the discharge is initiated, the concentration decreases with time, following an exponential decay law. After the first few tens of seconds for the CCP and after less than one second for ICP changes in the decay time are noticeable. In this first stage of the chemistry
development about 20% of the initial CH₄ concentration is consumed. During this time the plasma composition changes drastically due to the formation of radicals and new products (see following section). The time constant of the second exponent is more than one order of magnitude larger than the one of the first exponent. After some time the concentration does not change any more; a so-called steady state is reached, where the concentration is determined by the combination of flow rate, pressure and input power.

After the discharge is switched off the concentration undergoes a fast change. It is increased by ~10% of the initial level within less than half a second. After that the chamber is refilled with the source gas follows, which has a time constant equal to the residence time, defined by pressure and flow rate.

In the following sections a mathematical description of the concentration behaviour is given.

### Discharge switching ON and OFF

Before the discharge is switched on, the methane concentration is defined by the external inflow and the pumping (see equation (4.2.1)) and can be found from the ideal gas law:

\[
n = \frac{Q}{v_p} = n_0 = \frac{p}{kT},
\]

where \(p\) is the pressure, \(k\) is the Boltzmann constant and \(T\) is the gas temperature in Kelvin, which is exactly the room temperature without a plasma.

After the voltage is applied to the electrodes, the electron density increases within a very short time (compared to the changes in the chemical composition) until a steady state is reached. Since no changes of the electron density on a timescale of seconds was observed in measurements with microwave interferometer, changes of the methane concentration after the plasma is switched on, can be written on the base of a simplified list of reactions as given by (4.1.2) (Chapter 4). The solution of equation (4.1.2) yields the following time dependence

\[
n(t) = \frac{Q}{k_{e,CH_4} n_e + v + v_p } \left( \frac{Q}{k_{e,CH_4} n_e + v + v_p } - n_0 \right) \times \exp\left\{ - \left( k_{e,CH_4} n_e + v + v_p \right) t \right\}
\]

One can see that, after a long time of discharge operation, CH₄ dissociates to the steady state value of its concentration \(n_{st}\) which is different from zero:

\[
t \to \infty, n = \frac{Q}{k_{e,CH_4} n_e + v + v_p } = n_{st}.
\]

The influence of the different processes can be estimated by a consideration of two contrary situations.

1. \(Q \ll k_{e,CH_4} n_e + v + v_p\).
In this case the losses are much larger than the incoming flow. This can be realized experimentally at low flow rates and high input powers. The time dependence of the CH$_4$ concentration will follow a simple exponential decay with the loss frequency $k_{eCH_4} n_e + \nu + \nu_p$:

$$n(t) = n_0 \cdot \exp\left\{- (k_{eCH_4} n_e + \nu + \nu_p) t\right\}.$$  \hspace{1cm} (5.1.4)

2. $Q >> k_{eCH_4} n_e + \nu + \nu_p$.

Experimentally this occurs at low input powers and high flow rates. If $k_{eCH_4} n_e + \nu + \nu_p \to 0$ then $n \to n_0$ and dissociation is not observed.

In the intermediate case the concentration can be approximated by the expression

$$n(t) = B_{ON} + C_{ON} \cdot \exp(-A_{ON} \cdot t),$$  \hspace{1cm} (5.1.5)

where the fitting parameter $B_{ON}$ is the steady-state concentration, $C_{ON}$ is the difference between steady-state and initial concentration and $A_{ON}$ is the frequency of all loss processes:

$$B_{ON} = \frac{Q}{k_{eCH_4} n_e + \nu + \nu_p} = n_{st},$$  \hspace{1cm} (5.1.6)

$$C_{ON} = n_0 - n_{st},$$

$$A_{ON} = k_{eCH_4} \cdot n_e + \nu + \nu_p.$$

Sometimes it is more convenient to consider the reciprocal value of the loss frequency $\tau = 1/A$, which is a characteristic time constant for the loss process.

In these terms the degree of dissociation of methane is

$$\alpha = \frac{n_0 - n_{st}}{n_0} = \frac{C_{ON}}{B_{ON} + C_{ON}}.$$

As mentioned above that the time constant (or loss frequency) changes during the dissociation of methane and the formation of new particles. In this section an attempt is made to perform fitting of the evolution of the methane concentration until steady state is reached with only one time constant. Such consideration leads to a time-averaged value for the loss frequency. Further effort to estimate and explain the changes in the time constants will be done in the following section.

An approximation with function (5.1.6) was performed for the experimental results from the CCP cell.

![Fig. 31. Evolution of the CH$_4$ concentration after discharge is switched on at ~10 s: dots – experiment, lines – fitting](image)
under several sets of external parameters. An example of the output of the fitting procedure is presented in Fig. 31 and the fitting parameters are listed in Table 7a. The error bars are taken from the fitting procedure.

Table 7a. Fitting parameters for the CH₄ concentration, measured in the CCP after the discharge is switched on

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Flow Rate</th>
<th>Exponent A₂</th>
<th>Steady State Concentration B₂</th>
<th>Temporal Behaviour C₂</th>
<th>Dissociation Time τ₂</th>
<th>Total Power A₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 Pa 1.5 sccm multipass</td>
<td>10 W</td>
<td>7.78 ± 0.03</td>
<td>6.4 ± 0.2</td>
<td>22.0 ± 1.1</td>
<td>4.5 ± 0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30 W</td>
<td>2.18 ± 0.04</td>
<td>17.78 ± 0.03</td>
<td>20.3 ± 0.4</td>
<td>4.9 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>100 Pa 1.5 sccm multipass</td>
<td>10 W</td>
<td>1.68 ± 0.03</td>
<td>7.5 ± 0.5</td>
<td>144 ± 24</td>
<td>7 ± 1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30 W</td>
<td>0.96 ± 0.04</td>
<td>14.8 ± 0.5</td>
<td>179 ± 16</td>
<td>5.6 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>50 Pa 5 sccm single pass</td>
<td>5 W</td>
<td>0.980 ± 0.002</td>
<td>2.64 ± 0.03</td>
<td>89 ± 3</td>
<td>11.2 ± 0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30 W</td>
<td>0.514 ± 0.006</td>
<td>8.3 ± 0.2</td>
<td>88 ± 4</td>
<td>11.4 ± 0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50 W</td>
<td>0.345 ± 0.003</td>
<td>10.3 ± 0.1</td>
<td>82 ± 2</td>
<td>12.2 ± 0.3</td>
<td></td>
</tr>
</tbody>
</table>

Some comments on the values obtained from the fitting parameters can be made:

- As follows from equations (5.1.5) and (5.1.6), the quantity \( k_e n_e \), describing an interaction with electrons, is contained in both the exponent \( A_{ON} \) and in the term \( B_{ON} \), influencing both, the temporal behaviour and the absolute value of the methane concentration.
- The parameter \( B_{ON} \) has the physical meaning of a steady state concentration i.e. the concentration of CH₄ which remains in the reactor after the equilibrium between inflow, dissociation and pumping is reached. With increasing input power the value of \( B_{ON} \) decreases. This means that at higher electron densities the dissociation of methane is more pronounced. The sum of the parameters \( B_{ON} \) and \( C_{ON} \) is the concentration at the initial state and corresponds to the total pressure before the input power is applied. These values are close to the experimental data and match relatively well. A more detailed analysis of the steady-state concentration is described in the following chapter.
The parameter $A_{ON}$ represents the combination of losses caused by pumping, sticking and dissociation via collisions with electrons (see equation (5.1.6)). Since electron impact dissociation is a function of both, electron temperature and density (section 4.3), the loss frequency $A_{ON}$ is a complicated function of the internal plasma parameters.

Information on the dissociation rate coefficient $k_{ech4}$ can be obtained from the total loss frequency if the electron density and the frequencies of other loss processes are known. In order to separate losses caused by collisions of methane molecules with electrons from pumping losses, time resolved measurements after the plasma is switched off were carried out. After the discharge is switched off the source gas refills the reactor chamber, and a mixture of the source gas and the stable products is pumped out. Assuming that electrons disappear much faster than the concentrations of the molecular species undergo significant changes, the equation for the CH$_4$ concentration in the afterglow can be written as:

$$\frac{dn}{dt} = Q - (v + v_p)n,$$

(5.1.7)

with the loss frequency $v + v_p$, caused by processes different from collisions with the electrons. The term $-vn$ originates from reactions between methane and some species produced in the discharge and is, strictly speaking, a function of time.

After a certain time CH$_4$ completely refills the chamber, which leads to the condition $n = n_0$ for $t \to \infty$. Another condition is that in the moment before switching off the concentration is at its steady state value, defined in the “switching-on” experiment: $n = n_{st}$ for $t = 0$. The solution of equation (5.1.7) yields the time dependence

$$n(t) = \frac{Q}{v + v_p} \left( \frac{Q}{v + v_p} - n_{st} \right) \exp \left\{ -(v + v_p)t \right\}.$$

(5.1.8)

Therefore, the fitting of the experimental results can be done with the same analytical function (5.1.5), as for the “switching on” measurements, but the fitting parameters have a different meaning:

$$n(t) = B_{OFF} + C_{OFF} \cdot \exp (-A_{OFF} \cdot t),$$

$$A_{OFF} = v + v_p,$$

$$B_{OFF} = \frac{Q}{v + v_p} = n_0,$$

$$-C_{OFF} = n_0 - n_{st},$$

$$B_{OFF} + C_{OFF} = n_{st}.$$

(5.1.9)

The sum of the parameters $B_{OFF}$ and $C_{OFF}$ represents the steady-state concentration $n_{st}$, reached in the discharge. Since $n_0 < n_{st}$ the parameter $C_{OFF}$ is negative.
Approximations of the experimental data with function (5.1.9) were performed for a data from measurements at the CCP cell at the same flow rates, pressures and initial input powers as in the “switching-on” case. The result of the fitting of the experimental data from the CCP at 5 Pa and 30 W is presented in Fig. 32. The fitting parameters are listed in Table 7b.

Table 7b. Fitting parameters for the CH₄ concentration measured in the CCP after the discharge is switched off

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Flow rate</th>
<th>n₀</th>
<th>Q</th>
<th>ν</th>
<th>B_{OFF}, 10^{20} m⁻³</th>
<th>C_{OFF}, 10^{20} m⁻³</th>
<th>τ_{OFF}, s</th>
<th>A_{OFF}, 10^{-2} s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 Pa 1.5 sccm multipass</td>
<td>10 W</td>
<td>1.21 · 10^{21} m⁻³</td>
<td>3.2 · 10^{19} m⁻³ s⁻¹</td>
<td>2.65 · 10^{-2} s⁻¹</td>
<td>12.8 ± 0.1</td>
<td>-6.8 ± 0.1</td>
<td>45.7 ± 2.3</td>
<td>2.2 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>30 W</td>
<td>9.14 ± 0.04</td>
<td>-7.98 ± 0.05</td>
<td>42.6 ± 0.8</td>
<td>2.35 ± 0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 Pa 1.5 sccm multipass</td>
<td>10 W</td>
<td>2.42 · 10^{22} m⁻³</td>
<td>3.2 · 10^{19} m⁻³ s⁻¹</td>
<td>1.32 · 10^{-3} s⁻¹</td>
<td>2.30 ± 0.04</td>
<td>-6.3 ± 0.4</td>
<td>235 ± 48</td>
<td>4.26 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>30 W</td>
<td>2.4 ± 0.2</td>
<td>-17 ± 2</td>
<td>485 ± 100</td>
<td>2.1 ± 0.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 Pa 5 sccm single pass</td>
<td>5 W</td>
<td>1.21 · 10^{22} m⁻³</td>
<td>10.7 · 10^{19} m⁻³ s⁻¹</td>
<td>8.83 · 10^{-3} s⁻¹</td>
<td>1.296 ± 0.006</td>
<td>-2.4 ± 0.1</td>
<td>190 ± 7</td>
<td>5.3 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>30 W</td>
<td>1.49 ± 0.07</td>
<td>-7 ± 1</td>
<td>230 ± 24</td>
<td>4.4 ± 0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50 W</td>
<td>1.28 ± 0.03</td>
<td>-150 ± 20</td>
<td>170 ± 11</td>
<td>5.9 ± 0.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The conclusions are as follows:

- Parameter $B_{OFF}$ is the concentration of CH₄ after all gaseous components produced in the discharge are pumped out of the reactor chamber and the chamber is completely refilled with methane. Naturally, this concentration is the same as before the discharge was started and must correspond to the total pressure. The disagreement between the values $B_{OFF}$ for different values of the input power at the same pressure and flow rate in the case of 5 Pa is explained by the fact that in the case of 30 W the experiment was not carried out long enough to reach its initial state $n₀$. At 50 Pa, 30 W and 5 sccm $B_{OFF}$ is slightly higher than the concentration corresponding to the total pressure. This is caused by small variations of the flow rate due to an inappropriate position of the pump valve. In general, the fitting parameters $B_{OFF}$ and $C_{OFF}$ describe the methane concentration reasonably well for all chosen experimental conditions.

- Compared to the “switch-on” measurements, the loss frequency $A_{OFF}$ is about half of $A_{ON}$. This reflects the vanishing of the loss channels depending on electrons. The
disagreement between the loss frequency values for different initial input powers is within the error bar.

A further separation of the loss channels can be made: the losses due to the pump can be calculated from the residence time or measured separately (see Section 4.2, Fig. 25). At low pressure (5 Pa) the whole loss frequency is of the same order as the frequency of pumping losses $v_p$:

$$A_{OFF}\big|_{t_{OFF}} = \frac{1}{t_{OFF}} = v_p + v_p \sim v_p.$$ 

However, at a pressure of 100 Pa the loss frequency $A_{OFF}$ is several times higher than $v_p$. This indicates that at high pressures some unknown loss processes take place besides the pumping after the discharge is switched off. Since we assume that the electron density drops drastically in very short times after the plasma is switched off, these processes are assumed to be independent of the collisions with electrons. Under these assumptions, the difference of the loss frequencies obtained from time resolved measurements after the plasma is switched on and off, is a product of the electron density and the dissociation rate coefficient, yielding

$$k_{ech} = \frac{A_{ON} - A_{OFF}}{n_e}.$$  

(5.1.10)

For the determination of the rate coefficient $k_{ech}$ the electron density measurements reported in Chapter 3 were used. The calculated dissociation rate coefficients for two different pressures and input powers are listed in the Table 8.

### Table 8. Temporal evolution of the methane concentration at 1.55 sccm in the CCP

<table>
<thead>
<tr>
<th></th>
<th>5 Pa, 1.55 sccm</th>
<th>100 Pa, 1.55 sccm</th>
<th>measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 W</td>
<td>30 W</td>
<td>10 W</td>
</tr>
<tr>
<td>$A_{ON}$, 10^{-2}$ s^{-1}$</td>
<td>4.5</td>
<td>4.9</td>
<td>0.7</td>
</tr>
<tr>
<td>$A_{OFF}$, 10^{-2}$ s^{-1}$</td>
<td>2.2</td>
<td>2.35</td>
<td>0.426</td>
</tr>
<tr>
<td>$v_p$, 10^{-2}$ s^{-1}$</td>
<td>2.65</td>
<td>2.65</td>
<td>0.132</td>
</tr>
<tr>
<td>$k_{ech}n_e$, 10^{-2}$ s^{-1}$</td>
<td>1.8</td>
<td>2.2</td>
<td>0.3</td>
</tr>
<tr>
<td>$n_e$, m^{-3}$</td>
<td>$\sim 10^{15}$$ \ast$</td>
<td>$\sim 10^{15}$$ \ast$</td>
<td>$\sim 10^{15}$</td>
</tr>
<tr>
<td>$k_{ech}$, m^{-3} s^{-1}$</td>
<td>$2 \cdot 10^{17}$</td>
<td>$2 \cdot 10^{17}$</td>
<td>$3 \cdot 10^{18}$</td>
</tr>
<tr>
<td>$T_{Maxwell}$, eV$\ast$$ \ast$</td>
<td>1.6</td>
<td>1.6</td>
<td>1.2</td>
</tr>
<tr>
<td>$T_{Druyvesteyn}$, eV$\ast$$ \ast$</td>
<td>2.4</td>
<td>2.4</td>
<td>2.1</td>
</tr>
</tbody>
</table>

$\ast$upper limit (estimation from measurements)

$\ast\ast$Sensitivity: at the considered electron energy ranges the variation of the rate coefficient $\delta k_{ech} \sim 10 m^3 s^{-1}$ corresponds to the $\delta T_{maxwell} \sim 0.1 \cdot 0.3$ eV (see Section 4.3)

The value of the dissociation rate coefficient corresponding to the pressure of 5 Pa is higher than the one at 100 Pa. For the same pressure the dissociation rate coefficient for 10 W
exceeds the one for 30 W. These trends can be caused by the dependence of the electron temperature on the gas pressure and composition as discussed below.

In Section 4.3 the dissociation rate coefficients as functions of the electron temperature, assuming Maxwellian and Druyvesteyn EEDFs, are presented. According to these calculations, the obtained dissociation rate coefficient corresponds to an electron temperature $\sim 1$ eV at 100 Pa; for 5 Pa the electron temperature is slightly higher. Although there are a lot of intermediate uncertainties in the rate coefficient evaluations, even a rough estimation of the order of magnitude provides information on the electron temperature within an error bar of less than 0.3 eV.

The results listed in the Table 8 are in good agreement with the electron temperature obtained by heated Langmuir probe [10], where it was found that at the pressure of $\sim 30$ Pa, power of 5 W and flow of 3 sccm, the EEDF is close to the Druyvesteyn EEDF with the mean energy of 4.4 eV (effective temperature $\sim 2.93$ eV). This shows that, the determination of the electron temperature by the analysis of the methane dissociation provides reasonable data with good sensitivity. In the following sections the described method is used to investigate the temporal evolution of the electron temperature and to trace its dependence on external parameters, such as pressure, power and flow rate.

**Description with two exponentials**

A more precise approximation of the decay of the methane concentration can be performed with function, containing two exponents:

$$n(t) = B + C_1 \exp(-t/\tau_1) + C_2 \exp(-t/\tau_2).$$

In this form the dissociation process is divided into two time periods, in which the decay constants and, consequently, the loss frequencies are different. An illustration is shown in Fig. 33.

First, the concentration is described by the exponential function with the shorter time constant $\tau_1$, which means strong losses. Then, after a certain time the losses are getting weaker and the temporal development of the concentration follows an exponential decay with the longer time constant $\tau_2$.

As before, keeping the restricted list of possible processes, it is natural to explain the change of the decay constant by a change of the product of dissociation rate coefficient and electron density $k_e n_e$. The experimentally obtained electron density is independent of time (on a timescale of seconds). Therefore it must be a change of the EEDF which leads to the decrease of the decay frequency.
Indeed, the first stage of the discharge operation takes place in practically pure methane. Only significant changes of the plasma composition due to the formation of heavier molecules (like ethane, acetylene etc.) after tens of seconds of plasma operation. For simplicity, supposing that the shape of the EEDF remains Maxwellian or Druyvesteyn, we come to the conclusion that the electron mean energy decreases with time. Unfortunately, to the author’s knowledge, there is no direct experimental investigation of the temporal evolution of EEDF.

Exact calculations are beyond the scope of this work; nevertheless, a relatively simple estimation of this effect can be made on the base of the global model, developed by Lieberman [26, 94].

In this model the electron temperature is defined by the balance of charged particles, which is the balance between the total volume ionization and the total surface particle loss. In its turn the ionization rate coefficient depends on the ionization potential of the gas, and the electron temperature is a function of the cell dimensions, the pressure and the kind of gas. The ionization potentials of the new components differ from that of methane; therefore an alteration of the EEDF can happen. While a calculation of the electron temperature in pure methane is not very complicated, it becomes too difficult in the case of a mixture of many components. Nevertheless, an important trend can be pointed out: one could expect that, due to the contribution of the components with a lower ionization potential than that of methane, the electron mean energy decreases.

As mentioned above, it is possible to estimate the electron temperature from the charged particle balance before the composition of plasma has changed significantly. Fig. 34 presents a rough estimation of the electron temperature for a pressure 100 Pa in the CCP, based on the global model. The curves correspond to the frequencies of the production of

![Fig. 34.](image)

*Calculated frequencies of loss processes (straight line) and ions production in pure methane (dash dot line) and in the mixture of gases (dash line; see the text) in the CCP at 100 Pa*
charged particles (ions) in the plasma volume (dashed line) and losses on the surface (solid line) during the “hot” stage of discharge operation (the first tens of seconds). The main ion was assumed to be \( \text{CH}_5^+ \) [20, 95]. The plasma volume \( V \) is the product of the electrode surface \( S \) and the distance between the two electrodes \( d \). Under these assumptions, the charged particle balance can be written in a similar way as was done in [96]:

\[
Vn_0k_i = S \sqrt{\frac{k_BT_e}{M}} \\
\text{or} \\
n_0k_i = \frac{1}{d} \sqrt{\frac{k_BT_e}{M}}
\]

Here \( n_0 \) is neutral particle concentration, \( k_i \) the ionization rate coefficient, \( k_B \) the Boltzman constant, \( T_e \) the electron temperature, \( M \) the \( \text{CH}_5^+ \) ion mass and \( d \) the distance between the electrodes. The ionization rate coefficient is calculated in a way similar to the calculation of the dissociation rate coefficient (Section 4.3). The ionization cross sections are taken from [97]. For the calculations a Maxwellian EEDF is assumed.

In equation (5.1.12) the left-hand side describes the production of ions by electron impact ionization of neutral molecules. The dependence on the electron temperature is included via the ionization rate coefficient. The right hand side describes the loss of ions, moving to the surfaces with the Bohm velocity \( \sqrt{k_BT_e/M} \). The electron temperature is determined by the balance between production and losses of charged particles.

The calculated dependence of the electron temperature on the methane pressure under the same assumption for the EEDF and the main ion is shown in Fig. 35. It is easy to see, that the charged particle balance is reached at an electron temperature of \( \sim 1.6 \) eV at 100 Pa and \( 2.4 \) eV at 5 Pa. These values are compared further with the electron temperature, obtained from experimental data.

After new neutral components are created in the plasma, equation (5.1.12) is not valid anymore. Firstly because of new ions, which concentrations can dominate over the \( \text{CH}_5^+ \) concentration; secondly because in the left part of the balance equation the ionization rate coefficient of methane must be replaced with the one, corresponding to the mixture of the species. In Fig. 34 the production and loss frequencies are shown for the mixture of hydrocarbons at a total gas pressure of 100 Pa. The following composition was chosen for the calculation of the ionization rate coefficient on the base of the

<table>
<thead>
<tr>
<th>Ionization potentials</th>
<th>( I ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>14.25</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>11.43</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>10.51</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>11.40</td>
</tr>
<tr>
<td>H</td>
<td>15.43</td>
</tr>
</tbody>
</table>
experimental data, obtained in this work: 50% of CH\(_4\), 10% of C\(_2\)H\(_6\), 10% of C\(_2\)H\(_2\), 5% of C\(_2\)H\(_4\). The remaining 25% of the gas is ascribed to molecular hydrogen.

The ionization cross-sections are again taken from [97]. The ionization potentials are listed in the Table 9. Since the dependence of the ion velocity on the mass is very weak and methane remains the main component of the gas mixture, the same ion mass as before was used in the right hand side of the balance equation.

A slight decrease of the electron temperature from \(\sim 1.6\) eV in pure methane down to \(\sim 1.45\) eV in the gas mixture can be noticed from the comparison of the curves, presented in Fig. 34. This trend is in agreement with the qualitative consideration of the changes of the loss frequency with time.

The estimations, presented in Fig. 34 and 35, are based on the assumption of a Maxwellian EEDF, although it was ascertained that in molecular plasmas the distribution function has rather a Druyvesteyn-like shape [10]. However, due to the formation of hydrogen during the alteration of the chemical composition of the plasma the shape of the distribution function might undergo changes towards a Maxwell-like one (in pure hydrogen plasmas a Maxwellian EEDF was obtained [57]). This argumentation is also in agreement with the observed decrease of the dissociation frequency, since for the same fraction of high energetic electrons the mean electron energy is higher for the Druyvesteyn-like EEDF than for the Maxwellian one.

Measurements performed in the present work show that, depending on the experimental conditions, methane dissociates down to 10% - 60% of the initial concentration and that the concentrations of C\(_2\)H\(_6\), C\(_2\)H\(_2\) and C\(_2\)H\(_4\) rise in the plasma in quantities, comparable with the one of methane (see the following sections). So, generally speaking, the first time constant corresponds to the electron temperature, necessary for the maintenance of the discharge in pure CH\(_4\), while the second time constant is defined by the chemical composition, and the corresponding electron temperature is expected to be lower than the one in methane.

A similar effect was noticed in [98] by investigation of the EEDF in different molecular gases by means of heated Langmuir probe: plasmas of gases with lower ionization cross sections exhibit higher electron temperatures. The chemical composition plays an important role: for example, while the peak ionization cross section of CF\(_4\) is larger than the one of Ar, CF\(_4\) plasmas have a higher electron temperatures due to the formation of radicals like CF\(_3\) and CF\(_2\) with ionization cross-sections smaller than the one of CF\(_4\).

Following the method described in the previous section, the mean electron energies can be found from the fitting of function (5.1.11) to the experimental results. Unfortunately, the number of data points in the short “hot” period of the concentration evolution is barely sufficient for accurate fittings.

Analyzing the data from the CCP (5 Pa, 1.55 sccm, 10 W and 30 W) with function (5.1.11), the information listed in Table 10 was obtained. For 10 W the fitting procedure

Table 10. Time evolution of methane concentration at 5 Pa in the CCP

<table>
<thead>
<tr>
<th>Condition</th>
<th>(\tau_1), s</th>
<th>(\tau_2), s</th>
<th>(A_{ON1})</th>
<th>(A_{ON2})</th>
<th>(v_p), s(^{-1})</th>
<th>(n_e), m(^3)</th>
<th>(k_{eln_e}), s(^{-1})</th>
<th>(k_{elN_e}), s(^{-1})</th>
<th>(k_{el}), m(^3) s(^{-1})</th>
<th>(k_{el'}), m(^3) s(^{-1})</th>
<th>(T_{eMaxwell1}), eV</th>
<th>(T_{eMaxwell2}), eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 Pa 1.55 sccm</td>
<td>2 ± 2</td>
<td>4 ± 2</td>
<td>0.5</td>
<td>0.25</td>
<td>0.043</td>
<td>10(^{15})</td>
<td>~ 0.5</td>
<td>~ 0.22</td>
<td>5 · 10(^{-16})</td>
<td>2 · 10(^{-16})</td>
<td>2.3</td>
<td>2.1</td>
</tr>
<tr>
<td>10 W</td>
<td>23 ± 2</td>
<td>22 ± 1</td>
<td>0.043</td>
<td>0.045</td>
<td>0.02</td>
<td>2 · 10(^{-17})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>30 W</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


supplies data with error bars of 100 % because of the low time resolution of the measurements.

Using the same notation as in the previous section, the loss frequencies are defined as

\[ A_{ON,2} = \frac{1}{\tau_{1,2}} = k_{e,2} n_e + \nu_p. \]

An increase of the input power influences both the dissociation rate coefficient \( k_e \) (via electron temperature alteration due to the changes of the chemical composition) and the electron density \( n_e \). As mentioned above, a value of \( 10^{15} \text{ m}^{-3} \) was taken as an upper limit for the electron density for a pressure of 5 Pa. Several conclusions can be drawn.

For both input power levels the product of dissociation rate coefficient and electron density \( k_e n_e \) is higher for the first stage of the discharge operation, when only a small part of methane is dissociated. This observation is in accordance with the above argumentation. Assuming the electron density to be the same as for 100 Pa, the electron temperature can be evaluated. The values are very close to the ones, following from the balance equation (5.1.12). This confirms the assumption of the weak dependence of the electron density on the total gas pressure in the range of 5 – 100 Pa in the CCP.

The second time constant is the same for both cases, apparently, because the further changes of the chemical composition due to collisions with electrons are not significantly influencing the electron temperature.

### Dependence on external parameters

The combination of external parameters, such as input power, pressure and flow rate defines the electron density and chemical composition of the plasma and thus the electron mean energy. For the investigation of the influence of the flow rate on the plasma parameters, measurements of CH
\(_4\) concentrations after the plasma is switched on and off are performed at flow rates of 5 and 2 sccm at 30 W and 100 Pa. Table 11 contains the data received from the fitting. In Fig. 33 approximations of the concentrations with function (5.1.11) are presented.

#### Table 11. Time evolution of the methane concentration at 100 Pa 30 W in the CCP

<table>
<thead>
<tr>
<th></th>
<th>5 sccm</th>
<th>2 sccm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First exponent</td>
<td>Second exponent</td>
</tr>
<tr>
<td>( \tau ), s</td>
<td>15.94 ± 0.68</td>
<td>154.71 ± 4.13</td>
</tr>
<tr>
<td>( A_{ON} ), 10(^3) s(^{-1})</td>
<td>62.7</td>
<td>6.5</td>
</tr>
<tr>
<td>( A_{OFF} ), 10(^3) s(^{-1})</td>
<td>4.6</td>
<td>4.6</td>
</tr>
<tr>
<td>( \nu_p ), 10(^3) s(^{-1})</td>
<td>4.42</td>
<td>4.42</td>
</tr>
<tr>
<td>( k_{e,CH4} n_e ), 10(^3) s(^{-1})</td>
<td>~ 58</td>
<td>~ 2</td>
</tr>
<tr>
<td>( n_e ), m(^3)</td>
<td>~ 5 · 10(^{15})</td>
<td></td>
</tr>
<tr>
<td>( k_{e,CH4} ), m(^3) s(^{-1})</td>
<td>~ 1 · 10(^{17})</td>
<td>~ 4 · 10(^{19})</td>
</tr>
<tr>
<td>( T_{e,Maxwell} ), eV</td>
<td>1.4</td>
<td>1</td>
</tr>
<tr>
<td>( T_{e,Dr} ), eV</td>
<td>2.2</td>
<td>1.8</td>
</tr>
</tbody>
</table>
In both cases more than half of the methane dissociates with a slight dependence of the concentration and the time constant on the flow rate.

The time constants, obtained from the measurements after the plasma was switched off are close to the residence time, proving that pumping is the dominant loss process in the absence of electrons.

One can see that the loss frequency corresponding to the short time constant is much higher than the one for pumping, thus no significant difference due to the flow can be expected under the chosen experimental conditions. The long time constant is comparable to the pump losses.

One should keep in mind that the accuracy of the estimation of the mean electron energy is about 0.2 eV. Nevertheless, for both flow rates differences in the mean electron energy in the beginning of the discharge operation and after some time can be noticed.

The electron temperatures corresponding to both stages of the discharge development are similar for 2 and 5 sccm. This can be explained by the fact that the difference in the chemical composition due to the flow rate under theses conditions is not sufficient to influence the mean electron energy significantly.

The influence of both the input power and the pressure on the short and long time constants can be seen from the data, listed in Table 12. At the same flow rate of 5 sccm results were obtained for two different pressures and several levels of the input power.

<table>
<thead>
<tr>
<th>Table 12. Time evolution of methane concentration at 5 sccm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>( \tau_1 ), s</td>
</tr>
<tr>
<td>( A_{ON1} ), ( 10^3 ) s(^{-1} )</td>
</tr>
<tr>
<td>( A_{ON2} ), ( 10^3 ) s(^{-1} )</td>
</tr>
<tr>
<td>( n_e ), m(^{-3} )</td>
</tr>
<tr>
<td>( v_p ), ( 10^3 ) s(^{-1} )</td>
</tr>
<tr>
<td>( k_{el} n_e ), ( 10^3 ) s(^{-1} )</td>
</tr>
<tr>
<td>( k_{el} n_e ), ( 10^3 ) s(^{-1} )</td>
</tr>
<tr>
<td>( k_{el} ), m(^3) s(^{-1} )</td>
</tr>
<tr>
<td>( k_{el} ), m(^3) s(^{-1} )</td>
</tr>
<tr>
<td>( T_{eff1} ), eV</td>
</tr>
<tr>
<td>( T_{eff1} ), Maxwellian EEDF</td>
</tr>
<tr>
<td>( T_{eff2} ), eV</td>
</tr>
<tr>
<td>( T_{eff2} ), Druyvesteyn EEDF</td>
</tr>
</tbody>
</table>

Due to the low time resolution and the relatively fast “hot” stage of the discharge the fitting procedure gives large error bars for the short time constant; for this reason, no reliable data is available for an input power of 5 W.
Chapter 5. Time dependencies

There is only a weak influence of the input power on the long scale time constant; as mentioned before, a possible reason for this can be the relatively smooth behaviour of the higher hydrocarbons concentration with the changes of the electron density.

**ICP**

The same procedure as described above was applied on the data from the ICP. Typically, due to the higher electron densities, the decay times of methane are shorter in the ICP compared to the CCP. In order to increase the time resolution, the laser wavelength was fixed on the top of the absorption line and no scan over the profile was applied. Therefore the time resolution is defined by the averaging constant of the lock-in amplifier and was limited to a few tens of milliseconds by the signal-to-noise ratio. This method is less accurate, because of possible fluctuations of the frequency of the emitted diode laser radiation.

Measurements were carried out at 300W, flow rates of 0-60 sccm at pressures of 5 Pa, 10 Pa, 15 Pa and 20 Pa after the plasma was switched on and off. A typical behaviour of the measured methane concentration is shown in Fig. 36.

For the analysis of the time constants the same argumentation as before was used. The electron density was taken from microwave interferometer measurements (Chapter 3). Unfortunately the latter are not precise enough to trace the dependence of the electron density on flow rate and pressure, mainly because the spatial distribution is changing with pressure whereas only a line integrated signal is available from the interferometer measurements. So only a rough estimation was possible.

Independent of the pressure and flow rate the same two-exponential decay as in the CCP was observed for the methane concentration after the plasma was switched on. As before, changes of the electron temperature due to the creation of new chemical components are assumed. Approximately the same values for the rate coefficients at different pressures and flow rates are obtained. A similar calculation as in the previous section gives a value of $10^{-17} \text{m}^3/\text{s}$ for the dissociation rate coefficient at the beginning of the discharge, corresponding to an electron temperature of ~1.4 eV, assuming a Maxwellian EEDF and an effective

\[ \text{Fig. 36.} \]

*The time evolution of the methane concentration in the ICP.*

*Plasma was switched on at ~10 s and switched off at ~290 s.*

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electron temperature ~ 2.3 eV for a Druyvesteyn EEDF. The second exponent gives a dissociation rate coefficient ~ $10^{-18}$ m$^3$/s and temperatures ~ 1.1 eV for a Maxwellian and ~ 1.9 eV for a Druyvesteyn EEDF, correspondingly.

In [98] ICPs of different molecular gases (H$_2$, N$_2$, O$_2$, H$_2$O, CO$_2$, CF$_4$) were investigated under various experimental conditions. It was found that at pressures above ~ 5 Pa the EEDFs in different molecular gases show rising influence of the inelastic cross sections of the gases, and change towards non-Maxwellian shape with increasing pressure. An increase of the effective electron temperature with the decrease of the pressure was observed as well. In the region ~ 5 – 15 Pa an effective electron temperature of ~ 1–3 eV was found. As in the case of the CCP, our data exhibit good coincidence, proving the applicability of the described approach to the ICP as well.

The electron temperatures are very close to the ones found in the CCP reactor. This can be the result of highly effective energy losses due to the numerous inelastic collisions of electrons with neutrals. In both reactors the source gas dissociates to radicals. Further on heavier particles are created during the discharge chemical development. The concentrations of the new particles are comparable with the methane concentration. As will be discussed in the following chapter, with the increase of the electron density or temperature the ratio between the concentrations of the plasma components can be shifted but in any case both light and heavy hydrocarbons have ionization potentials lower than methane. These relatively low ionization potentials of the plasma components can be an explanation for the ineffective heating of the plasma.

5.2. Ethane (C$_2$H$_6$)

As was mentioned before, higher hydrocarbon molecules represent products of chains of physical and chemical reactions. Consumption and production channels of C$_2$H$_2$, C$_2$H$_4$ and C$_3$H$_6$ are listed in Table 5 (Section 4.1).

Fig. 37 shows the temporal evolution of the concentration of ethane and acetylene after the discharge is switched on (left) and off (right). One can see, that in the CCP at 100 Pa and 10 sccm the concentrations rise significantly after a few tens of seconds. According to the analysis of the methane concentration behaviour given in the previous section, during this time the electron temperature changes.
Chapter 5. Time dependencies

After about 100 seconds the balance between the loss and production channels is reached and the concentration does not change any more. This steady state is analysed in the following chapter.

Immediately after the discharge is switched off the concentration of ethane exhibits a drastic increase while the concentration of acetylene decreases. After that both concentrations decrease due to pumping, following an exponential decay with a time constant close to the residence time.

Switching of the discharge ON and OFF

The changes of the \( \text{C}_2\text{H}_6 \) concentration with time are given by equation (4.1.4). Without losses due to pumping and collisions with electrons, the concentration of ethane would increase linearly with time. The presence of consumption paths leads to reaching a state, where the concentration does not change any more. This so-called “steady-state” is considered in Chapter 6.

The solution of equation (4.1.4) leads to the time dependence

\[
n(t) = \frac{k_{\text{ch}3\text{ch}3} \cdot n_{\text{e}}^2}{k_{e\text{c}2\text{h}6} \cdot n_{\text{e}} + \nu + \nu_p} \left[ 1 - \exp \left( - \left( k_{e\text{c}2\text{h}6} \cdot n_{\text{e}} + \nu + \nu_p \right) t \right) \right],
\]

which can be approximated with the function

\[
n(t) = B \left[ 1 - \exp \left( - At \right) \right].
\]

The fitting parameters are:

\[
A = k_{e\text{c}2\text{h}6} \cdot n_{\text{e}} + \nu + \nu_p,
\]

\[
B = \frac{k_{\text{ch}3\text{ch}3} \cdot n_{\text{e}}^2}{k_{e\text{c}2\text{h}6} \cdot n_{\text{e}} + \nu + \nu_p}.
\]

The temporal evolution of the concentration and the result of the fitting at 30W, 10 sccm and 100 Pa in the CCP are shown in Fig. 37a. The values of the fitting parameters and the related coefficients and densities at some typical experimental conditions are listed in Table 13. As in the case of methane, the fitting parameters are combinations of production and consumption terms. One can notice that, independent on the exact choice of reactions involved, parameter \( B \) is the ratio of production and losses and parameter \( A \) is the loss frequency. The only demand is that the process is sufficiently fast compared to the timescale of the \( \text{C}_2\text{H}_6 \) concentration changes, in order to treat them as constants.

The fitting parameters allow us to estimate the rate coefficients of these processes. \( B \) is the steady state concentration. Its value can be used for the validation of the fitting procedure. By comparing it to the experimental data one can see good agreement. The product of the fitting coefficients gives the production channel for the \( \text{C}_2\text{H}_6 \) formation:

\[
A \cdot B \bigg|_{10\text{scm}30\text{W}} \sim 6 \cdot 10^{19} \text{ m}^3\text{ s}^{-1}.
\]
In our approximation the only chosen production channel is the reaction between two methyl radicals. This reaction has been the subject of a large number of both experimental and theoretical works (see, for example, [99] and references therein). The rate coefficient for this reaction depends on pressure and temperature. Currently available experimental measurements span the range from 200 to 1700 K with pressures ranging from ~ 13 to ~ 1.3·10^7 Pa. The rate coefficient given in [99] for this reaction at a temperature of 296 K and a pressure of about 100 Pa is $k_{\text{ch3ch3}} \sim 5 \cdot 10^{-17} \text{ m}^3 \text{s}^{-1}$.

The radical concentration measured by C. Busch [36] is $n_{\text{CH3}} \sim 4 \cdot 10^{17} \text{ m}^{-3}$ at 10 sccm. Based on this, the production term can be estimated:

$$k_{\text{ch3ch3}} \cdot n_{\text{CH3}}^2 \bigg|_{10 \text{sccm} 30 \text{ W}} \sim 0.8 \cdot 10^{19} \text{ m}^3 \text{s}^{-1}.$$  (5.2.6)

The disagreement of about a factor of 6 can be explained by the following argumentation. The simplest reason is the large error of the methyl concentration measurements due to different factors like, for example, the lack of information on the radial distribution in the line integrated absorption. Further, the value of rate coefficient differs by factor of 4 in different publications (from 2.15·10^{-17} m^3 s^{-1} [100] to 8.93·10^{-17} m^3 s^{-1} [101]; for details refer to the compilation of the data, presented in the NIST Chemical Kinetics Database [49]). Additionally, one should keep in mind that the simplicity of the consideration was paid by the reduction of all possible production paths to only one.

### Table 13. Results for the time resolved C2H6 concentration measurements

<table>
<thead>
<tr>
<th>Parameter</th>
<th>10 sccm 30 W</th>
<th>1 sccm 30 W</th>
<th>1 sccm 10 W</th>
<th>origination</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$, 10^21 m^-3</td>
<td>2 ± 0.1</td>
<td>2 ± 0.8</td>
<td>2 ± 0.8</td>
<td>from fitting procedure</td>
</tr>
<tr>
<td>$A$, 10^2 s^-1</td>
<td>3.1 ± 0.9</td>
<td>0.8 ± 0.07</td>
<td>0.8 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>$\tau$, s</td>
<td>140 ± 2</td>
<td>-</td>
<td>-</td>
<td>experimental value</td>
</tr>
<tr>
<td>$\nu$, 10^3 s^-1</td>
<td>7.1 ± 0.1</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$\nu_p$, 10^3 s^-1</td>
<td>8.83</td>
<td>0.883</td>
<td>0.883</td>
<td>from condition of constant pressure</td>
</tr>
<tr>
<td>$n_e$, 10^15 m^-3</td>
<td>5</td>
<td>5</td>
<td>1</td>
<td>experimental value</td>
</tr>
<tr>
<td>$n_{\text{CH3}}$, 10^{17} m^-3</td>
<td>4</td>
<td>~ 3*</td>
<td>~ 2*</td>
<td>literature review [49, 99]</td>
</tr>
<tr>
<td>$k_{\text{ch3ch3}}$, 10^{-17} m^3 s^-1</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>$k_{\text{ec2h6}}$, 10^{-18} m^3 s^-1</td>
<td>4.4</td>
<td>1.7</td>
<td>7</td>
<td>calculation</td>
</tr>
<tr>
<td>$T_{\text{emax}}$, eV</td>
<td>~ 0.6</td>
<td>~ 0.6</td>
<td>~ 0.6</td>
<td>from calculated $k_{\text{ec2h6}}$</td>
</tr>
<tr>
<td>$T_{\text{effD}}$, eV</td>
<td>~ 0.9</td>
<td>~ 0.9</td>
<td>~ 0.9</td>
<td></td>
</tr>
<tr>
<td>$\langle e \rangle_{\text{Dr}}$, eV</td>
<td>~ 1.4</td>
<td>~ 1.4</td>
<td>~ 1.4</td>
<td></td>
</tr>
</tbody>
</table>

* assumed, based on the measurements of [36]

**Notes:**

a) All measurements are performed in CCP at 100 Pa
b) The pump speed is assumed to be independent of gas; experimental results for the pump frequency for different flow rates of different molecules are given in Section 3.2.
c) The electron density is assumed to be independent of flow rate
Knowing the electron density $n_e$ and the pumping loss frequency $\nu_p$, the dissociation rate coefficient $k_{\text{ec}2h_6}$ can be calculated in the same simple way as it was done for methane. Assuming that the electrons disappear immediately after the plasma is switched off and that the CH$_3$ radical decay time is very short as well (~100 ms) [102, 103] the equation for the C$_2$H$_6$ concentration in the afterglow is a simple exponential decay from the steady state value $n_{st}$, due to pumping and processes, which are independent of electrons:

$$n(t) = n_{st} \cdot \exp\left(-\frac{t}{\tau}\right),$$

$$\nu + \nu_p = \frac{1}{\tau}.$$  \hspace{1cm} (5.2.9).

The measurements and the fitting curve for 10 sccm and 100 Pa are shown in fig 37b. From the fitting the time constant of the exponential decay $\tau$ (and the loss frequency $\nu + \nu_p$) is

$$\tau = 140 \pm 2 \text{s},$$

$$\nu + \nu_p = (7.1 \pm 0.1) \cdot 10^{-4} \text{ s}^{-1} \approx \nu_p.$$

The pump losses are assumed to be independent of the molecule. Measurements of the pumping constants for different species at different flow rates are shown on Fig. 25. In case of methane the time constant obtained in Section 4.2 is close to the residence time at 10 sccm and 100 Pa (see Supplement: Parameters of gas system), thus losses can be related to the pump just as in the case of methane. For the following calculations the reciprocal value of the residence time was taken for the loss frequency.

The information on the electron density and the frequencies of losses which are independent of interactions with electrons makes it possible to calculate the dissociation rate coefficient from the fitting parameters $A$ or $B$:

$$k_{ec2h_6} = \frac{1}{n_e} \cdot B \left(\frac{k_{ch3ch3} \cdot n_{ch3}^2}{B} - \nu_p\right)$$

or

$$k_{ec2h_6} = \frac{1}{n_e} \cdot (A - \nu_p)$$  \hspace{1cm} (5.2.10)

The second equation was chosen for the calculation because it requires less information. The results of the calculation are presented in the Table 13.

Exactly as in the case of methane, regarding the dependence of the rate coefficient calculated in section 3.3 for Maxwell and Druyvesteyn EEDFs, it is possible to estimate the electron temperature (mean energy). The sensitivity with which the rate coefficient depends on the mean electron energy is about the same as for methane: in the region around 1 eV an increase of the effective electron temperature of 0.2 - 0.3 eV leads to a change of the rate coefficient by one order of magnitude. Determined in this way, the effective electron temperature for the given conditions was found to be ~ 0.6 eV for a Maxwellian and ~ 1.4 eV for a Druyvesteyn distribution function. These values are lower than the ones obtained using the methane concentration analysis. The reason can be related to the incompleteness of the system of reaction paths considered. The neglect of additional production terms leads to an underestimation of the efficiency of the loss channels and the estimated electron temperature turns out to be lower as expected.
One more indication for this can be found by attempting to analyse the sharp changes of the concentrations after the discharge is switched off (Section 5.4).

5.3. Ethylene ($C_2H_4$) and acetylene ($C_2H_2$)

The experimentally obtained temporal behaviour of $C_2H_2$ is shown in Fig. 37 and Fig. 38.

For $C_2H_4$ and $C_2H_2$ the differential equations (4.1.5) and (4.1.6) are more complicated even if the number of the considered processes is limited. Nevertheless these equations can be solved for the steady state condition $dn/dt = 0$. An attempt to analyze the concentrations in dependence on the electron density (input power) for this steady state condition is done in the following chapter.

5.4. Jumps and drops of species concentrations

Considering the dependence of the concentrations on time after discharge is switched off more closely (Fig. 31 in Section 5.1, Fig. 37 and Fig. 38), one can notice a strong increase of CH$_4$ and C$_2$H$_6$ and a decrease of C$_2$H$_2$. After that described exponential decay due to pumping is observed. Both, the jump and the drop of the concentrations are of about 10% of the initial concentrations. Measurements with higher time resolution (Fig. 38, right-hand side) show that fast changes of the concentrations occur within timescales shorter than 2 seconds.

A consideration of the production and loss channels can explain the drop and jump of the concentrations in the moment when the discharge is switched off. For the case of methane the concentration increases by $\sim 1.5 \cdot 10^{21}$ m$^3$ within $\sim 5$ seconds:

$$\frac{\Delta n}{\Delta t} \approx \frac{1.5 \cdot 10^{21}}{5} = 3 \cdot 10^{20} \text{ m}^3 \text{s}^{-1}. \quad (5.4.1)$$

This increase can be related to the fast disappearance of the electrons, thus

$$- k_e n_e n_{CH_4} = 0$$
in equation (4.1.2). Taking a dissociation rate coefficient, which corresponds to an electron temperature of 1 eV and the electron and methane concentrations from the experiment, the loss channel related to interactions of methane with electrons can be estimated:

\[ k_e n_e n_{ch4} \sim 4 \times 10^{-19} \cdot 5 \times 10^{15} \cdot 1 \times 10^{22} = 2 \times 10^{19} m^{-3}s^{-1}. \]  

(5.4.2)

This is lower than the experimentally observed rate for the increase of the concentration. However, taking an electron temperature of 1.3 eV one receives a dissociation rate coefficient which is approximately one order higher than the one used in (5.4.2) and the obtained value for the speed of change of the concentration is sufficient to explain the jump shown in Fig. 31. The electron temperature of 1.3 eV is close to the value calculated from the particle balance for the CCP discharge in the gas mixture.

The same argumentation can be applied to the temporal behaviour of the concentration of ethane. After the discharge is switched off the term

\[ -k_{e 2h6} n_e n_{2h6} \]

in equation (4.1.4) for C_2H_6 vanishes. This leads to a jump of concentration due to a shift of the balance between the production and consumption channels.

The disappearing term can be estimated using the data from the CCP discharge listed in Table 13:

\[ -k_{e 2h6} n_e n_{2h6} \sim 4 \times 10^{-18} \cdot 5 \times 10^{15} \cdot 2 \times 10^{21} = 0.4 \times 10^{19} m^{-3}s^{-1}. \]  

(5.4.3)

Although the time resolution is obviously too low, it is possible to estimate the speed of change of the ethane concentration. Assuming that the concentration is changing by \(0.2 \times 10^{21} m^3\) in 2 seconds or faster one receives

\[ \frac{\Delta n}{\Delta t} \geq \frac{0.2 \times 10^{21}}{2} = 10^{20} m^3s^{-1}. \]

This value is higher than the one calculated from equation (5.4.3). The reason could be the underestimation of the dissociation rate coefficient. Indeed, the electron temperature obtained by using the fitting parameters of the approximation of the results of C_2H_6 measurements is lower than the temperature received from the same procedure for methane. The temporal evolution of the concentration is governed by the balance between production and consumption channels. As mentioned above, the additional channel for C_2H_6 production might be of the same importance as the reaction between two methyl radicals. Neglect of this term can lead to an underestimation of the losses caused by collisions with electrons.

For C_2H_4 the disappearing term is

\[ k_{e 2h4} n_e n_{2h4} \]

and several situations can be discussed. In the case if

\[ k_{e 2h6} n_e n_{2h6} - k_{e 2h4} n_e n_{2h4} = 0, \]

no sharp changes should be observed, whereas if
a drop of the concentration is expected, which was never found in the experiment. Instead, a small increase of the concentration is noticed, leading to the assumption that

\[ k_{eC_2H_6} \cdot n_e \cdot n_{C_2H_6} - k_{eC_2H_4} \cdot n_e \cdot n_{C_2H_4} > 0 \]

which means that the production of \( C_2H_4 \) from ethane is smaller than the losses due to inelastic collisions with electrons. A process considered additionally is the pumping, which is also responsible for species consumption. Hence, one more production channel independent from interactions with electrons should exist to reach the balance between consumption and production of ethylene - probably it might be a reaction between radicals.

In the rate equation for acetylene, the term depending on the electrons is

\[ k_{eC_2H_6} \cdot n_e \cdot n_{C_2H_6} + k_{eC_2H_4} \cdot n_e \cdot n_{C_2H_4} - k_{eC_2H_2} \cdot n_e \cdot n_{C_2H_2} \]

In all experiments the concentration of \( C_2H_2 \) drops sharply after the discharge is switched off. Thus, the production of \( C_2H_2 \) due to electron impact interactions with ethane and ethylene exceeds the losses. Pumping may be a candidate for the additional loss term in order to provide the balance and the reaching of the steady state.

**Summary**

The study of the temporal behaviour of the neutral species gives a key to the determination of the electron temperature (or electron mean energy) which is an important internal parameter of the plasma. The electron temperature can be estimated from the experimental results if the electron density and the shape of the EEDF are known.

The measurements show that under the considered experimental conditions which are characterized by relatively low electron density and long convective time, changes in the chemical composition proceed on a time scale of tens of seconds. The formation of new neutral plasma components happens during the first tens of seconds of discharge operation.

Analysing the dependence of the methane concentration on time, two regions can be identified, which can be distinguished by the loss frequency. Assuming that the decrease of the loss frequency is caused by changes of the dissociation rate coefficient, two electron temperatures could be determined. However, to the author’s knowledge, there is no experimental evidence of this effect despite the fact that nowadays the temporal resolution of the diagnostics is sufficiently high.

In the first stage of the discharge evolution the degree of dissociation of the source gas is very low. The discharge runs practically in a pure methane plasma. The corresponding electron temperature in the CCP of about 1.4 ± 0.2 eV at 100 Pa (assuming a Maxwellian EEDF) does not show a strong dependence on flow rate and the input power. Probably, there is a dependence on the pressure, but experimental results on the electron density were not available at lower pressure. Assuming that the electron density at 5 Pa is the same or lower than the one at 100 Pa, the estimated electron temperature is ~ 2 eV or higher. Since the “hot” stage of the discharge operation is comparatively short, only a small amount of experimental data points is available. Therefore the fitting procedure has a relatively low quality.

Nevertheless, the presence of two stages of the discharge operation can be confirmed by simple calculations, based on the charged particle balance. The balance equation for pure
methane ionization allows us to determine the electron temperature, required for maintaining the discharge. The calculation shows, that the electron temperature is as high as \(~1.6\) eV at 100 Pa and \(~2.4\) eV at 5 Pa. The agreement between the data obtained from the experiment and the results of the global model approves the assumption of a small influence of the gas pressure on the electron density in the CCP for a pressure range of 5 – 100 Pa. Measurements done with the microwave interferometer (Chapter 3) show very small changes of the electron density with a decrease of the pressure from 100 Pa down to 50 Pa.

After the concentrations of new components are grown enough to influence the properties of the gas mixture, a change of the loss frequency of the methane dissociation is observed. The corresponding electron temperature is \(~1 \pm 0.2\) eV at 100 Pa and \(~1.6 \pm 0.2\) eV (or higher) at 5 Pa if a Maxwellian EEDF is assumed. Similar values are obtained for the evolution of the electron temperature in the ICP discharge.

The analysis of the temporal behaviour of the ethane concentration using the same method gives an electron temperature corresponding to the “cold” stage of the methane dissociation. The estimated temperature is \(~0.6 \pm 0.2\) eV which is lower than the one obtained from methane. A possible reason is the reduced number of reaction paths taken into account (neglection of some production terms can lead to an underestimation of the losses by electron-neutral interactions).

Some conclusions about the completeness of the used system of rate equations can be drawn by considering the sharp changes of the concentrations after the discharge is switched off. Keeping the same list of processes as was used before, these changes must be related to the fast vanishing of the loss (for CH\(_4\) and C\(_2\)H\(_6\)) or production (for C\(_2\)H\(_2\)) channels, caused by dissociation due to collisions with electrons. An electron temperature of 0.6 eV can not explain the significant (~ 10% of the initial value) decrease or increase of the concentrations, whereas a value ~1.3 eV describes the jumps and drops reasonably well.

Generally speaking, the analysis of time resolved measurements does not necessarily require information on the absolute values of concentrations since the effective electron temperature can be determined from the decay constant. On the other hand, to obtain a function, approximating the temporal behaviour of the concentrations, the corresponding rate equation must be solved. This is a relatively simple task for methane, but it turns out to be a problem for the case of higher hydrocarbons. However, these equations can be solved for steady state conditions which will be done in the following chapter together with a further discussion of the balance between loss and production channels.
Chapter 6. Power dependencies

In the previous chapter the temporal behaviour of the concentrations of the neutral plasma species was discussed. For the quantitative analysis the rate equations, derived on the base of the confined list of the processes involved in plasma chemistry (section 4.1), must be solved. The solution can be easily found for the dependence of the methane concentration on time; however, in case of the heavier hydrocarbons the rate equations are too complicated for analytical treatment. Nevertheless, they can be solved for steady state conditions.

The obtained solutions describe the dependence of the species concentrations on the electron density. These functions can be used for analytical approximations for the experimental data with the combinations of the frequencies of the processes as fitting parameters.

The quality of the fitting procedure can serve for appraisal of the conformity of the system of the considered processes. Information about the fitting parameters permits to find out the relative importance of the considered processes under certain experimental conditions and to calculate the dissociation rate coefficients. Assuming a Maxwellian or Druyvesteyn energy distribution function (Section 4.3) the electron temperature can be evaluated from the dissociation rate coefficients (for example, from the curves, presented in Fig. 27-29 (Section 4.3)). As before, the sensitivity can be estimated from the slope of the rate coefficient dependence on the electron temperature in a region, which is characteristic for the considered plasma source: an increase of the rate coefficient in one order of magnitude corresponds to an increase of the electron temperature by about 20%.

Unfortunately, the precision of the fitting procedure is limited not only by the quality of the concentration measurements but by the error bars in the dependence of the electron density on the input power as well. Moreover, one should always keep in mind that the convenience of treatment of the limited number of processes has to be paid by a loss of accuracy of the interpretation of the dependencies.

In this chapter an attempt to analyze the dependence of the concentrations of some molecules created in the discharge in methane on the internal plasma parameters (electron temperature and density) will be made. Analytical expressions will be received for the source gas (methane), the methyl radical and some stable products (ethane, ethylene and acetylene).

Measurements were done in the ICP and CCP chambers under steady state conditions, i.e. after the concentrations achieved some stable values. A variety of experimental parameters (pressure, flow rate, power and power input mechanism) was used. Since the measured concentrations are typically functions of the input power, the link between the electron density and the input power is needed. For interconnection of the external and internal parameters of the discharge the measurements of the electron density, described in Chapter 3, were taken.

From the practical point of view, determination of the dissociation rate coefficients from the steady state concentrations is an alternative way to the method, described in the previous chapter. The advantage of the procedure applied in this chapter is that no time resolved measurements are required and a better signal-to-noise ratio can be achieved.
6.1. Methane (CH$_4$)

**CCP discharge**

The data for the CH$_4$ concentration for a flow rate 2 sccm were obtained with the same experimental equipment (section 1.1) as was used in [36]. The measurements show a very good reproducibility. Therefore, the data for the analysis at 10 sccm was taken from [36].

**Approximation of the concentration with an analytical function**

In comparison with equation (4.1.2) in [36] the simplified rate equation for the methane concentration contains an additional production term:

$$\frac{dn}{dt} = Q - k_{ch4}n_e n - v_p n + k_1 n_e,$$

with the rate coefficient $k_1$ of chemical reaction leading to the CH$_4$ production, depending on the electron density, and the other quantities as defined before (Chapter 5). In steady-state, when balance between the loss and production channels is achieved:

$$\frac{dn}{dt} = 0,$$

the methane concentration is defined as follows:

$$n = \frac{Q + k_1 n_e}{k_e n_e + v_p} = \frac{Q / v_p + k_1 / v_p \cdot n_e}{k_e / v_p \cdot n_e + 1}.$$  \hspace{1cm} (6.1.3)

This dependence can be approximated with the function

$$n(n_e) = \frac{a + c n_e}{b n_e + 1},$$ \hspace{1cm} (6.1.4)

with the fitting coefficients

$$a = \frac{Q}{v_p} = n_0,$$

$$b = \frac{k_e}{v_p},$$ \hspace{1cm} (6.1.5)

$$c = \frac{k_1}{v_p}.$$

Obviously, the parameter $a$ is the initial CH$_4$ concentration, while $b$ and $c$ represent ratios of the frequencies of the processes involved. Since the pump losses are known from the
condition of constant pressure, this kind of fitting makes it possible to define $k_1$ and $k_e$ which are responsible for CH$_4$ production and dissociation, respectively.

When fitted to the data of C. Busch [36] the function (6.1.4) yields the fitting parameters that are listed in Table 14.

<p>| Table 14. Results of the fitting of the methane concentration in the CCP at 100 Pa and 10 sccm |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>$a$, $10^{22}$ m$^{-3}$</th>
<th>$b$, $10^{16}$ m$^{-3}$</th>
<th>$k_e$, $10^{-18}$ m$^{-3}$/s</th>
<th>$c$, $10^5$</th>
<th>$k_1$, $10^3$ s$^{-1}$</th>
<th>$T_{es}$, eV Maxwell</th>
<th>$T_{eff}$, eV Dryusvesteyn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fitting with function (6.1.4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.3 ± 0.1</td>
<td>2.0 ± 0.8</td>
<td>1.7 ± 0.7</td>
<td>8 ± 10</td>
<td>7</td>
<td>1.2</td>
<td>2</td>
</tr>
<tr>
<td>Fitting with function (6.1.6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.3 ± 0.1</td>
<td>1.3 ± 0.1</td>
<td>1.10 ± 0.01</td>
<td>-</td>
<td>-</td>
<td>1.1</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Notes

$Q = 2.13 \times 10^{20}$ m$^3$/s, $v_p = 8.83 \times 10^3$ s$^{-1}$

The following comments can be made.

1. Parameter $a$ describes the initial concentration well.
2. Parameter $b$ gives a value of the rate coefficient, corresponding to an electron temperature of ~1 eV, assuming a Maxwellian distribution function. This value is related to the “cold” stage of the methane dissociation (section 5.1) and is close to the one obtained from the time resolved measurements. In contrast to the measurements, described in section 5.1, which were performed for single values of the input power, here the electron temperature is assumed to be the same for the whole range of electron densities. Since in time resolved experiments no dependence on the input power was observed, the applicability of the fitting procedure with function (6.1.4) for the estimation of the electron temperature is valid.
3. The losses due to collisions with the electrons at the highest input power (60 W, $n_e \sim 10^{16}$ m$^{-3}$):

$$k_e n_e \sim 2 \cdot 10^3 \text{[sec}^{-1}]$$

are comparable with the losses due to the pump at 10 sccm.

Unfortunately, the fitting procedure gives error bars of more than 100% for the fitting parameter $c$, which is related to the rate coefficient $k_1$ and a further estimation of this channel is not reasonable. Therefore, a further simplification of the differential equation is to neglect the production term $k_1 n_e$ in comparison with the incoming flow $Q$. This leads to equation (4.1.2) and in this case (6.1.4) transforms to

$$n(n_e) = a \frac{a}{bn_e + 1}.$$ (6.1.6)

The values of the fitting parameters and the corresponding rate coefficients are listed in Table 14. As mentioned above, the error bars have a different origin. The error bars in the definition of the rate coefficient arise from fitting procedure. One can see that the exclusion of the production term does not influence other terms with respect to the error bars. Both fitting curves are presented in Fig. 39a together with the experimental data points.
Although at a flow-rate of 2 sccm the electron density can be slightly different from the one at 10 sccm, the same dependence of the electron density on the input power is used for further analysis.

For 2 sccm and 100 Pa the measurements were performed for different absorption paths: in a multipass configuration and in single paths through the centre of the plasma and along two different chords (see section 2.7). The results are presented in Table 15. In the case of single pass measurements functions (6.1.4) and (6.1.6) give approximately the same values for the fitting parameters within the error bars, originating from the fitting procedure. Hence the dissociation rate coefficient is the same, without dependence on the position inside the chamber. The electron temperature for both 2 and 10 sccm is the same with respect to the error bars and is close to the one determined in section 5.1.

Table 15. Results of the fitting of the methane concentration in the CCP at 100 Pa and 2 sccm

<table>
<thead>
<tr>
<th>Note</th>
<th>$a$, $10^{22}$ m$^{-3}$</th>
<th>$b$, $10^{16}$ m$^{-3}$</th>
<th>$k_e$, $10^{19}$ m$^3$/s</th>
<th>$T_e$, eV</th>
<th>$T_{\text{eff}}$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>[36]: multipass</td>
<td>2.01 ± 0.05</td>
<td>2.5 ± 0.2</td>
<td>4.4 ± 0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single pass along diameter (&quot;a&quot; Fig. 15)</td>
<td>2.30 ± 0.79</td>
<td>4.2 ± 0.4</td>
<td>7.4 ± 0.7</td>
<td>~1</td>
<td>~1.8</td>
</tr>
<tr>
<td>Single pass along long chord (&quot;b&quot; Fig. 15)</td>
<td>2.5 ± 0.1</td>
<td>4.7 ± 0.6</td>
<td>8 ± 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single pass along short chord (&quot;c&quot; Fig. 15)</td>
<td>2.47 ± 0.08</td>
<td>3.3 ± 0.3</td>
<td>5.9 ± 0.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For 2 sccm and 100 Pa the measurements were performed for different absorption paths: in a multipass configuration and in single paths through the centre of the plasma and along two different chords (see section 2.7). The results are presented in Table 15. In the case of single pass measurements functions (6.1.4) and (6.1.6) give approximately the same values for the fitting parameters within the error bars, originating from the fitting procedure. Hence the dissociation rate coefficient is the same, without dependence on the position inside the chamber. The electron temperature for both 2 and 10 sccm is the same with respect to the error bars and is close to the one determined in section 5.1.

Fig. 40b shows the concentration of methane versus input power at a pressure of 5 Pa. The electron temperature is about 1.6 eV or higher, which is in agreement with the value calculated in section 4.1 from the time resolved measurements.
Table 16. Results of the fitting of the methane concentration in the CCP at 5 Pa 1.55 sccm

<table>
<thead>
<tr>
<th>$a_1$ $10^{21}$ m$^3$</th>
<th>$b_1$ $10^{16}$ m$^3$</th>
<th>$k_{pe}$ $10^{17}$ m$^3$/s</th>
<th>$c_1$ $10^4$</th>
<th>$k_{f1}$ $10^3$ s$^{-1}$</th>
<th>$T_{pe}$ eV</th>
<th>$T_{eff}$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.22 ± 0.03</td>
<td>7 ± 1</td>
<td>2</td>
<td>8 ± 4</td>
<td>2</td>
<td>~1.6</td>
<td>~2.4</td>
</tr>
</tbody>
</table>

Notes

$Q = 3.2 \times 10^{19}$ m$^3$/s, $v_p = 2.65 \times 10^{-2}$ s$^{-1}$.

Electron density supposed to be the same as for 100 Pa.

Recalling the meaning of the fitting coefficients (6.1.5), function (6.1.6) can be rewritten in a form suitable for simple interpretation:

$$n = \frac{n_0}{k_{pe} n_{pe} + 1}.$$  

(6.1.7).

It is immediately obvious that the concentration of methane is directly proportional to the initial concentration. With increase of the electron temperature (influencing the dissociation rate coefficient) or the electron density the dissociation is more pronounced. Finally, the increase of the flow rate leads to an increase of the concentration, because pure methane is supplied as feed gas and the whole mixture of the feed gas and products of the plasma chemistry is pumped out. All these obvious phenomena are reflected in the results summarized in Tables 14-16.

**Direct calculation of the dissociation rate coefficient**

The dissociation rate coefficient $k_{pe}$ can be estimated from the particular steady state values as a function of input power (or electron density):

$$k_{pe} = \left( \frac{Q}{n v_p} - n_{pe} \right) \frac{1}{n_{pe}}.$$  

(6.1.8).

Fig. 40 shows this kind of dependence for the data at 2 and 10 sccm. One can notice, that the values for 10 sccm are close to

$$k_{pe} \sim 1 \cdot 10^{18} \text{ m}^3\text{s}^{-1},$$

except for the first point. This result is in agreement with the one obtained from the fitting, meaning that the dissociation rate coefficient can be determined from a single measurement of the concentration.

The same calculation for 2 sccm gives a dissociation rate coefficient of

$$k_{pe} \sim 6 \cdot 10^{19} \text{ m}^3\text{s}^{-1},$$

which is again in reasonable agreement with the data described above.
Both results yield an electron temperature \( \sim 1 \text{ eV} \), which is in coincidence with the results from fitting and from time resolved measurements.

The result of the application of the fitting procedure (equation (6.1.6)) to the data obtained in the ICP chamber at 10 Pa and 60 sccm are shown in Fig. 41a, together with the experimental data points. The parameters of fitting are as follows:

\[ a = (2.5 \pm 0.1) \cdot 10^{21} \text{ m}^{-3}, \]
\[ b = (3.4 \pm 0.4) \cdot 10^{-17} \text{ m}^{-3}. \]

Again, fitting parameter \( a \) is very close to the steady state concentration, and parameter \( b \) provides the dissociation rate coefficient and an estimation for the electron temperature:

\[ k_{\text{echo}} \sim 5 \cdot 10^{-18} [\text{m}^{3} \text{ sec}^{-1}], \]
\[ T_{\text{maxwell}} \sim 1.3 \text{eV}, \]
\[ T_{\text{effDryanov}} \sim 2.2 \text{eV}, \]
\[ <\varepsilon> \sim 3.3 \text{eV}. \]  

This temperature is close to the one, which follows from the time constant \( \tau_2 \) obtained in section 5.1.

Fig. 41b shows the dissociation rate coefficient, calculated from the experimental data measured in the ICP chamber at 10 Pa and a flow rate of 60 sccm by means of equation (6.1.8). The values are very close to the rate coefficient (6.1.9), determined from the fitting procedure. Therefore, one can see that in both CCP and ICP discharges, changes of the plasma composition with increase of the input power are not strong enough to influence the electron temperature. The dissociation rate coefficient can be calculated from particular measurements.
6.2. Methyl (CH₃)

In the current work it is assumed that methyl is produced mainly from CH₄ via collisions with electrons. Losses are ascribed to sticking to the surface and production of ethane (section 4.1). A corresponding simplified rate equation (4.1.3) is given in Chapter 4.

The solution of equation (4.1.3) for the steady state yields the concentration of the methyl radical:

\[
    n_{ch₃} = \sqrt{\left(\frac{v_{ch₃}}{2k_{ch₃ch₃}}\right)^2 + \frac{2k_{ch₄}'}{k_{ch₃ch₃}} n_{ch₄} n_e - \frac{v_{ch₃}}{2k_{ch₃ch₃}}} - n_e.
\]  

(6.2.2)

The rate coefficient \(k_{ch₃ch₃}\) and the loss frequency \(v_{ch₃}\) are not directly dependent on the plasma parameters like electron density or temperature. Their ratio depends in a complicated way on the gas pressure \(p\) for two reasons: \(i\) the reaction between two methyl radicals is a three-body reaction and \(ii\) diffusion is a function of the mean free path. In the considered pressure range the rate coefficient \(k_{ch₃ch₃}\) is supposed to be constant. The input power is proportional to the electron density and the dissociation rate coefficient is a complicated function of the electron temperature. Therefore, equation (6.2.2) may be re-written as follows:

\[
    n_{ch₃}(n_e, T_e, p) \propto \sqrt{\int f^2(p) + \frac{k_{ch₄}'}{n_{ch₄} n_e} n_e + f(p)},
\]  

(6.2.3)

where \(f(p)\) is some function of pressure.

In expression (6.2.3) there is still a dependence on the methane concentration, which itself is a function of the electron density and temperature. Keeping in mind the approximation (6.1.6) for the methane concentration we obtain the methyl concentration as a function of not only the internal plasma characteristic but also of the external experimental parameters pressure \(p\) and flow rate \(\Phi\):

Fig. 41

a) Experimental data and fitting curve for the methane concentration in the ICP at 10 Pa and 60 sccm; b) calculated rate coefficient for total dissociation of methane.
If pumping is faster than dissociation via electron impact \( (k_{e,\text{ch}_4}n_e/v_p \ll 1 \) as can be realized experimentally at low input power and large flow), equation (6.2.4) can be simplified to

\[
n_{\text{ch}_3}(n_e, T_e, p, \Phi) \propto \sqrt{f^2(p) + \frac{Q}{v_p} + k_{e,\text{ch}_4} \cdot n_e + f(p)}, \tag{6.2.5}
\]

where \( n_0 \) is the methane concentration before the discharge is switched on. There is a weak dependence on the initial methane concentration and the electron density.

At higher input power levels, when losses due to the dissociation dominate over pumping \( (k_{e,\text{ch}_4}n_e/v_p \gg 1) \) equation (6.2.4) can be written as:

\[
n_{\text{ch}_3}(n_e, T_e, p, \Phi) \propto \sqrt{f^2(p) + \frac{Q}{v_p} + k_{e,\text{ch}_4} \cdot n_e + f(p)}.	ag{6.2.6}
\]

For this case a further simplification is possible. In the calculation of the rate coefficients for the total dissociation and the dissociation to CH\(_3\) by equation (4.3.1a) the analytical formulas (4.3.2a) for total \( (k_{\text{ch}_3})\) and (4.3.3) for partial \( (k_{\text{ch}_3})\) cross-sections were used. They show that the ratio \( k_{\text{ch}_3}/k_{\text{ch}_4} \) is a constant, independent of the electron temperature. This leads to the following expression for the description of the CH\(_3\) concentration in the case of high input powers or slow flow rates:

\[
n_{\text{ch}_3}(p, \Phi) \propto \sqrt{f^2(p) + Q + f(p)}.	ag{6.2.7}
\]

One can notice that there is no dependence on the electron density anymore; only a relatively weak dependence on the flow rate and a yet unknown dependence on the pressure remain.

\[
\]

**Fig. 42.**

CH\(_3\) concentration in the CCP. Data are taken from [36]
The data for the methyl radical concentrations in the CCP chamber were taken from [36]. In the ICP chamber measurements were carried out under different experimental conditions, such as pressure, input power and flow rate. Results from [36] and the data from the present work are shown in Fig. 42 and Fig. 43.

It is obvious, that although the electron density at the lowest input power in the CCP is about two orders of magnitude smaller than at the highest input power in the ICP, the methyl radical concentration is approximately the same ($\approx 5 \cdot 10^{17} \text{ m}^{-3}$). So, the dependence on the electron density is very weak. In the CCP the electron density is relatively low and thus function (6.2.5) should be used, which predicts a slight increase of the methyl concentration with input power (see Fig. 42).

Contrarily, the electron density in ICP is higher and consequently here the results are described better by function (6.2.7). Indeed, the dependence of the concentration on the input power is almost flat for input power levels higher than 180 W, where the discharge operates in the H-mode. Comparing the results for different pressures and flow rates (Fig. 43), we find that for the same flow rate the concentration is higher at higher total pressure and for the same pressure it is higher for faster flow. The latter can be explained by a decrease of the residence time and therefore, a probability for longer chains of reactions.

6.3. Ethane ($\text{C}_2\text{H}_6$), ethylene ($\text{C}_2\text{H}_4$), acetylene ($\text{C}_2\text{H}_2$)

Fitting of steady state concentrations

As before, in steady state we have

$$\frac{dn}{dt} = 0. \quad (6.3.1)$$

Using the restricted number of processes discussed before, solutions of the differential equations (4.1.4), (4.1.5) and (4.1.6) in steady state provide dependencies of the hydrocarbon concentrations on the electron density (input power).
Chapter 6. Power dependencies

For $\text{C}_2\text{H}_6$:

$$\begin{equation}
n(n_e) = \frac{k'_{\text{c2h6}} n_{\text{c2h6}}^2}{k_{\text{ec2h6}} n_e + v_p}, \quad (6.3.2)
\end{equation}$$

for $\text{C}_2\text{H}_4$:

$$\begin{equation}
n(n_e) = \frac{k'_{\text{c2h6}} n_{\text{c2h6}} n_e}{k_{\text{ec2h6}} n_e + v_p}, \quad (6.3.3)
\end{equation}$$

and for $\text{C}_2\text{H}_2$:

$$\begin{equation}
n(n_e) = \frac{(k'_{\text{c2h6}} n_{\text{c2h6}} + k'_{\text{c2h4}} n_{\text{c2h4}}) n_e}{k_{\text{ec2h2}} n_e + v_p}. \quad (6.3.4)
\end{equation}$$

Here $k'_{\text{c2h6}}$ and $k'_{\text{c2h4}}$ are the rate coefficients of dissociation of ethane to ethylene and acetylene, and $k'_{\text{ec2h4}}$ is the rate coefficient of dissociation of ethylene to acetylene, respectively. The dependencies (6.3.3) and (6.3.4) can be written as functions of the electron density and the measured concentrations:

for $\text{C}_2\text{H}_6$

$$\begin{equation}
n(n_e) = \frac{A \cdot n_{\text{c2h6}}^2}{B \cdot n_e + 1}, \quad (6.3.5)
\end{equation}$$

$$\begin{align*}
A &= \frac{k_{\text{c2h6}}}{v_p}, \\
B &= \frac{k_{\text{ec2h6}}}{v_p}.
\end{align*}$$

For $\text{C}_2\text{H}_4$

$$\begin{equation}
n(n_e) = \frac{C \cdot n_{\text{c2h6}} n_e}{D n_e + 1}, \quad (6.3.6)
\end{equation}$$

$$\begin{align*}
C &= \frac{k_{\text{ec2h6}}}{v_p}, \\
D &= \frac{k_{\text{ec2h4}}}{v_p}.
\end{align*}$$

For $\text{C}_2\text{H}_2$

$$\begin{equation}
n(n_e) = \frac{(E \cdot n_{\text{c2h6}} + F \cdot n_{\text{c2h4}}) n_e}{G n_e + 1}, \quad (6.3.7)
\end{equation}$$

$$\begin{align*}
E &= \frac{k'_{\text{c2h6}}}{v_p}, \\
F &= \frac{k'_{\text{c2h4}}}{v_p}, \\
G &= \frac{k_{\text{ec2h2}}}{v_p}.
\end{align*}$$
Again, the fitting parameters are ratios of rate coefficients of corresponding production and consumption processes.

**CCP discharge**

**Ethane (C\textsubscript{2}H\textsubscript{6})**

Using values from a previous work [59] for the CH\textsubscript{3} concentration, we obtain the curves shown in Fig. 44\textsubscript{a} from a fit of equation (6.3.5). The absolute concentrations as well as the dependencies on the input power and the flow rate are nicely reproduced. The fitting parameters are listed in Table 17.

The knowledge of the rate coefficient \(k_{\text{ch3ch3}} = 5 \times 10^{-17} \text{ m}^3/\text{s} [99]\) makes it possible to calculate \(n_p\) from the fitting parameter \(A\). The results are shown in Table 17. The corresponding time \(\tau = 1/n_p\) is large compared to the convective time (see Supplement). However, it should be noted that \(v_p\) is obtained from a simplified rate equation neglecting all production processes except recombination of CH\textsubscript{3}. Additionally, as was mentioned above (section 5.2), there is a large uncertainty in the value of the rate coefficient given in different publications. For example, taking the product of the fitting parameter \(A\) and pumping loss frequency \(v_p\) corresponding to the convection time, one obtains the rate coefficient \(k_{\text{ch3ch3}} \sim 8.9 \times 10^{-17} \text{ m}^3/\text{s}\), which is close to the value given in [101].

Since the value of \(v_p\) is higher for 10 sccm than for 2 sccm and the methyl concentration has a very weak dependence on the flow rate, the C\textsubscript{2}H\textsubscript{6} concentration decreases with an increase of the flow rate at the same input power (electron density). This fact is in agreement with the assumption that pumping is a very important process.

With the help of equation (6.3.2) the dependencies of the C\textsubscript{2}H\textsubscript{6} concentration on the electron density (input power) at different flow rates can be analyzed. At high flow rates \(k_{\text{ce2h6}n_e}\) is small compared to \(v_p\), and because of \(k_{\text{ce2h6}n_e} / v_p < 1\), the C\textsubscript{2}H\textsubscript{6} concentration follows the slight increase of the CH\textsubscript{3} concentration:
At low flow rates \((k_{ec2h6}n_e / \nu_p) \gg 1\) the inelastic impact processes become important leading to the saturation and decrease of the concentration at higher electron densities:

\[
n_{c2h6} \sim \frac{k_{ch3ch3}}{\nu_p} \cdot n_{ch3}^2 \cdot n_e.
\]

A more detailed analysis is difficult because of a rather complicated dependence of the CH\(_3\) concentration on the electron density. Nevertheless, several remarks can be made: the experimentally observed dependencies of the concentrations can be well approximated for both flow rates with the same analytical function by using the measured concentrations of CH\(_3\). The fitting parameters provide information about the ratios between production and loss processes.

The definition (6.3.5) leads to a relationship between the efficiency of inelastic electron impact processes and losses by pumping, diffusion and surface processes:

\[
k_{ec2h6} \cdot n_e = B \cdot \nu_p \cdot n_e.
\]

At a flow rate of 2 sccm we have

\[
k_{ec2h6} \cdot n_e \sim 1.5 \cdot 10^{-16} \nu_p \cdot n_e.
\]

and for \(n_e \sim 10^{15} \text{ m}^{-3}\) we obtain

\[
k_{ec2h6} \cdot n_e \sim 0.1 \nu_p.
\]

This shows that the losses due to electron impact processes are one order of magnitude smaller than the losses due to pumping. For higher electron densities \((\sim 10^{16} \text{ m}^{-3})\) the efficiencies of both processes are comparable. This simple consideration does not require
exact knowledge of the values of $k_{ec2h6}$ and $v_p$ and confirms the qualitative explanations of the behaviour of the $C_2H_6$ concentration given above. For higher flow rate (10 sccm) the fitting parameter $B$ is much smaller, which shifts the balance of these two processes to higher values of the electron density.

The ratio $A/B$ of the fitting parameters allows us to estimate the rate coefficient $k_{ec2h6}$ describing the inelastic electron impact processes. As was mentioned above, the accurate calculation of this coefficient requires additional information about the EEDF and is a rather challenging task. In our work we find $k_{ec2h6} \sim 5 \times 10^{-19} \text{ m}^3\text{s}^{-1}$. The effective electron temperature, corresponding to this value of the dissociation rate coefficient is $\sim 0.5 \text{ eV}$ if a Maxwellian EEDF is assumed.

Just as in the case of time resolved measurements described in the previous chapter, this value for the effective electron temperature is lower than the one obtained from the analysis of the methane concentration. As already mentioned, this disagreement originates in the limitation of the processes, included in the rate equation. In contrast to methane, which is assumed to originate from the incoming flow only, ethane is a product of reactions and thus exhibits a more indirect connection to the plasma parameters.

Taking the experimental data for the methyl and ethane concentrations and assuming $v_p$ to be inversely proportional to the residence time, it is possible to calculate the dissociation rate coefficient for particular values of the electron density (input power) without a fitting procedure:

$$k_{ec2h6} = \frac{1}{n_e} \left( \frac{k_{ch3ch3} \cdot n_{ch3}^2}{n(n_e) - v_p} \right).$$

(6.3.8)

The results for a flow rate of 2 sccm are shown in Fig. 44b. There is no obvious dependence on the input power. The calculated values are very close to the dissociation rate coefficient obtained from the fitting procedure.

**Ethylene ($C_2H_4$)**

An obvious indication of the limitation of the applicability of the simplified system of rate equations appears in an attempt to analyze the behaviour of the ethylene concentration. Compared to ethane, ethylene is a product of a longer chain of reactions among stable molecules, radicals and electrons. It was found that successful fitting of the ethylene concentration as a function of input power needs a modification of equation (6.3.6). Namely, one more production term (for simplification independent of the electron density) should be added:

$$n(n_e) = \frac{C \cdot n_{c2h4} n_e + C'}{Dn_e + 1}.$$  

(6.3.9)

The result of the fitting is shown in Fig. 45 together with the experimental data points. The parameters of the fitting curve are listed in Table 18.

Both dissociation coefficients $k_{ec2h4}$ and $k'_{ec2h6}$ are not known a priori. As was
shown in Section 4.2 (Fig. 25) the pumping speed is independent of the gas, among the species considered in this work. Thus the value for pump losses was taken from the condition of constant pressure (Section 4.2). This information allows one to estimate both coefficients and an additional production source:

\[ k_{ec2h4} = D \cdot \nu_p \sim 5 \cdot 10^{-20} m^3 s^{-1}, \]
\[ k'_{ec2h6} = C \cdot \nu_p \sim 3 \cdot 10^{-20} m^3 s^{-1}, \]
\[ production = C' \nu_p \sim 1 \cdot 10^{18} m^3 s^{-1}. \]

(6.3.10)

Table 18. Results of the fitting of the ethylene concentration in the CCP at 2 sccm and 100 Pa

<table>
<thead>
<tr>
<th>parameter</th>
<th>origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C, 10^{17} m^3 )</td>
<td>1.7 ± 0.9</td>
</tr>
<tr>
<td>( C', 10^{20} m^3 )</td>
<td>7.4 ± 0.1</td>
</tr>
<tr>
<td>( D, 10^{17} m^3 )</td>
<td>3 ± 2.2</td>
</tr>
<tr>
<td>( \nu_p, 10^3 s^{-1} )</td>
<td>1.77</td>
</tr>
<tr>
<td>( k_{ec2h4}, 10^{20} m^3 s^{-1} )</td>
<td>5</td>
</tr>
<tr>
<td>( T_{Maxwell}, eV )</td>
<td>0.6</td>
</tr>
<tr>
<td>( T_{eff\text{Druyvesteyn}}, eV )</td>
<td>1.1</td>
</tr>
<tr>
<td>( k'_{ec2h6}, 10^{20} m^3 s^{-1} )</td>
<td>3</td>
</tr>
<tr>
<td>( T_{Maxwell}, eV )</td>
<td>0.7</td>
</tr>
<tr>
<td>( T_{eff\text{Druyvesteyn}}, eV )</td>
<td>1.1</td>
</tr>
</tbody>
</table>

The production rate of the unknown channel turns out to be comparable with the production due to the ethane dissociation:

\[ k'_{ec2h6} \cdot n_{ec2h6} \cdot n_e \sim 10^{18} m^3 s^{-1}. \]

The effective temperature can be obtained from the rate coefficient for the total dissociation of ethylene or the partial dissociation of ethane to ethylene. Values of effective temperatures, calculated from these processes, are very close and agree with the values obtained from the analysis of the ethane dissociation; hence they are lower than the ones obtained from the methane dissociation.

**Acetylene (C\(_2\)H\(_2\))**

An approximation of the experimentally obtained concentration of acetylene with function (6.3.7) was done for 2 sccm and 100 Pa. For the ethylene concentration the experimental data (Fig. 45) were taken. The fitting parameters \( E, F \) and \( G \) are listed in Table 19.

The rate coefficients for C\(_2\)H\(_6\), C\(_2\)H\(_4\) and C\(_2\)H\(_2\) dissociation were calculated as usual. The effective electron temperature can be estimated from any of the three processes: from the
total dissociation of acetylene or from the partial dissociation of ethane or ethylene. All obtained values are in good agreement. They are close to the data calculated from the methane concentrations and consequently higher as the result from ethane and acetylene. This can be interpreted as a sign for an appropriate choice of processes, defining the balance between the production and loss channels of acetylene.

As was noticed in the previous section, the dependence of the ethylene concentration on the electron density is very weak (see Fig. 45). Therefore, equation (6.3.7) can be rewritten as follows:

$$n(n_e) = \frac{(E \cdot n_{c2h6} + F') \cdot n_e}{Gn_e + 1},$$

(6.3.11)

with the new fitting parameter $F'$, which includes the concentration of ethylene as some constant:

$$F' = \frac{k'_{c2h4}}{v_p} \cdot n_{c2h4}.$$

By an approximation of the experimental data for 2 sccm with function (6.3.11) the parameters $E$ and $G$ remain the same within an error bar of less than 10%. The parameter $F'$ is shown in Table 19. The approximation of the concentration with function (6.3.11) was performed for the measurements at 10 sccm as well. The fitting curves are presented in Fig. 46 together with the experimental data points.

Having obtained the effective electron temperature from the total dissociation of acetylene or partial dissociation of ethane, the partial dissociation rate coefficient of ethylene to acetylene $k'_{c2h4}$ can be found and, consequently, the ethylene concentration $n_{c2h4}$ can be estimated from the fitting parameter $F'$:

$$n_{c2h4} = \frac{F' \cdot v_p}{k'_{c2h4}}.$$

(6.3.12)

Both, the experimental and the calculated values of the ethylene concentration at 2 sccm are shown in Table 19. One can see that they coincide with an accuracy of 25%. This opportunity to estimate the unknown concentration was used for the case of 10 sccm. The dissociation rate coefficient was assumed to be the same as in the case of 2 sccm.
Parameter $G$ is the ratio of the dissociation rate coefficient and the pumping frequency. Correspondingly, the product of the parameter $G$ and the electron density gives the relative efficiency of both loss processes. Regarding the fitting parameter $G$ it is possible to conclude that the pumping loss channel is comparable with dissociation process in the case of 2 sccm at low input powers:

$$ G \cdot n_e = \frac{k_{\text{ec2h6}} \cdot n_e}{v}, $$

(6.3.13)

$$ G \cdot n_e \sim 10^{-15} \cdot 10^{15} \sim 1. $$

At higher electron densities the dissociation starts to play a more significant role, but nevertheless the efficiencies of both processes remain comparable. In the case of 10 sccm pumping dominates for any input power level:

$$ G \cdot n_e \sim 10^{-16} \cdot 10^{15} \sim 0.1. $$

(6.3.14)
ICP discharge

Ethane (C\textsubscript{2}H\textsubscript{6})

The above described procedure, performed on the results of measurements in the ICP, leads to the results, which are shown in Fig. 47. Unfortunately, the fitting with two parameters was not successful. Therefore, parameter \( A \) was fixed to the ratio of the rate coefficient and the pump frequency for the ICP chamber:

\[
A \bigg|_{10 \text{ sccm} 10 \text{ Pa}} = \frac{k_{\text{ch}3\text{ch}3}}{v_p} \bigg|_{10 \text{ sccm} 10 \text{ Pa}} = \frac{5 \times 10^{-17}}{2.26 \times 10^{-2}} = 2.21 \times 10^{-15} \text{ m}^3,
\]

\[
A \bigg|_{60 \text{ sccm} 10 \text{ Pa}} = \frac{k_{\text{ch}3\text{ch}3}}{v_p} \bigg|_{60 \text{ sccm} 10 \text{ Pa}} = \frac{5 \times 10^{-17}}{1.36 \times 10^{-1}} = 3.7 \times 10^{-16} \text{ m}^3.
\]

The fitting parameters and the value of the dissociation rate coefficient, calculated from equation (6.3.5), are listed in Table 20.

Assuming the concentration of CH\textsubscript{3} to be independent of the input power or electron density (this is actually true as soon as some small, but finite value of input power is reached - see Chapter 6.2), equation (6.3.5) can be simplified in a similar way as it was done for the acetylene concentration analysis:

\[
A' = \frac{k_{\text{ch}3\text{ch}3}}{v_p} \cdot n\text{ch3}.
\]

In this case fitting parameter \( A' \) contains the concentration of the methyl radical. The result of the fitting is shown in Fig. 48. Fitting was performed from the point, where the CH\textsubscript{3} concentration is assumed to be already independent of the electron density. The parameters are listed in Table 20. Unfortunately, the error is relatively large: 50%. From parameter \( A' \) one can estimate the CH\textsubscript{3} concentration (see Table 20). The result of the calculation is very close to the averaged experimental value (see Section 6.2). This gives the opportunity to estimate the CH\textsubscript{3} concentration in the case when it is not known experimentally.

\[
n(n_e) = \frac{A'}{B \cdot n_e + 1},
\]

\[
A' = \frac{k_{\text{ch}3\text{ch}3} \cdot n\text{ch3}}{v_p}.
\]
for 10 sccm and 20 Pa fitting of the experimental data with function (6.3.16) leads to the following values:

\[
A' \sim 10^{21} \text{ m}^3, \\
B' \sim 10^{-16} \text{ m}^3, \\
k_{ec2h6} \sim 10^{-18} \text{ m}^3 \text{s}^{-1}, \\
n_{ch3} \sim 10^{17} \text{ m}^3.
\]

### Table 20. Results of the fitting of the ethane concentration in the ICP at 10 Pa

<table>
<thead>
<tr>
<th>parameter</th>
<th>60 sccm</th>
<th>10 sccm</th>
<th>origination</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A), (10^{-15}) m(^3)</td>
<td>0.37</td>
<td>2.2</td>
<td>Reaction between methyl radicals</td>
</tr>
<tr>
<td>(B), (10^{-16}) m(^3)</td>
<td>0.53 ± 0.07</td>
<td>2.8 ± 0.5</td>
<td>Dissociation</td>
</tr>
<tr>
<td>(v_D), (10^2) s(^{-1})</td>
<td>13.6</td>
<td>2.26</td>
<td>Pump</td>
</tr>
<tr>
<td>(k_{ec2h6}), (10^{16}) m(^3) \text{s}^{-1})</td>
<td>7.2</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>(A'), (10^{20}) m(^3)</td>
<td></td>
<td>8 ± 4</td>
<td></td>
</tr>
<tr>
<td>(B'), (10^{-16}) m(^3)</td>
<td></td>
<td>1.8 ± 0.9</td>
<td></td>
</tr>
<tr>
<td>(n_{ch3}), (10^{17}) m(^3)</td>
<td>6</td>
<td>6</td>
<td>Fitting</td>
</tr>
<tr>
<td>(T_{eMaxwell}), eV</td>
<td>0.6</td>
<td>0.6</td>
<td>Dissociation rate coefficient</td>
</tr>
<tr>
<td>(T_{efDruyvesteyn}), eV</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

### Fig. 48.
Results of the fitting of the ethane concentration in the ICP with function (6.3.16)
Acetylene (C\textsubscript{2}H\textsubscript{2})

For the analysis of the acetylene concentration in the ICP equation (6.3.11) was applied in the same way as in the case of the CCP. The results are shown in Fig. 49 and listed in Table 21.

The effective electron temperature can be found from the rate coefficient for the total dissociation of acetylene or from the rate coefficient of the partial dissociation of ethane. With the known effective electron temperature the concentration of ethylene can be estimated in a similar way as it was done in Section 6.3.

Table 21. Results of the fitting of the acetylene concentration in the ICP at 10 Pa

<table>
<thead>
<tr>
<th>Parameter</th>
<th>60 sccm</th>
<th>10 sccm</th>
<th>origination</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$, 10\textsuperscript{-17} m\textsuperscript{3}</td>
<td>1 ± 0.7</td>
<td>5.8 ± 1.3</td>
<td>Partial dissociation of C\textsubscript{2}H\textsubscript{6}</td>
</tr>
<tr>
<td>$F^+$, 10\textsuperscript{3} s\textsuperscript{-1}</td>
<td>3.6 ± 1.4</td>
<td>7 ± 4</td>
<td>Partial dissociation of C\textsubscript{2}H\textsubscript{4}</td>
</tr>
<tr>
<td>$G$, 10\textsuperscript{16} m\textsuperscript{3}</td>
<td>0.14 ±0.05</td>
<td>1.9 ± 0.8</td>
<td>Total dissociation of C\textsubscript{2}H\textsubscript{2}</td>
</tr>
<tr>
<td>$v_p$, 10\textsuperscript{2} s\textsuperscript{-1}</td>
<td>13.6</td>
<td>2.26</td>
<td>Pump</td>
</tr>
<tr>
<td>$n_{c2h4}$, 10\textsuperscript{20} m\textsuperscript{3}</td>
<td>1</td>
<td>0.5</td>
<td>Estimation</td>
</tr>
<tr>
<td>$k''_{ec2h6}$, 10\textsuperscript{-18} m\textsuperscript{3} s\textsuperscript{-1}</td>
<td>1.4</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>$T_{eMaxwell}$, eV</td>
<td>1</td>
<td>1</td>
<td>Dissociation of C\textsubscript{2}H\textsubscript{6} to C\textsubscript{2}H\textsubscript{2}</td>
</tr>
<tr>
<td>$T_{effDryvesteyn}$, eV</td>
<td>1.6</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>$k_{ec2h2}$, 10\textsuperscript{18} m\textsuperscript{3} s\textsuperscript{-1}</td>
<td>1.9</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>$T_{eMaxwell}$, eV</td>
<td>1</td>
<td>1.1</td>
<td>Total dissociation of C\textsubscript{2}H\textsubscript{2}</td>
</tr>
<tr>
<td>$T_{effDryvesteyn}$, eV</td>
<td>1.7</td>
<td>1.8</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 49
Results of the fitting of the acetylene concentration in the ICP
6.4. Implementation of additional reactions

As mentioned in section 4.1, ion-neutral reactions and reactions of the species with radicals can be important because of relatively high rate coefficients.

In the case of methane the rate coefficients for the reactions with $\text{CH}_4^+$, $\text{CH}_5^+$, $\text{CH}_2$ and CH are highest. The implementation of the reactions with ions leads to the inclusion of terms of the form $-k_in_i$ (where the $k_i$ and $n_i$ are the reaction rate coefficients and the specific ion concentrations, respectively) in the rate equation (4.1.2). The implementation of the loss channels due to the reactions with radicals results in additional terms of the same type: $-k_Rn_R$ ($k_R$ and $n_R$ are the reaction rate coefficients and radical concentrations, respectively). The solution for the steady state condition (6.1.3) then reads as follows (without discharge $n_i = n_e = 0$):

$$n = \frac{Q + k_i n_e}{k_e n_e + k_i n_i + k_R n_R + v_p} = \frac{k_R n_e}{v_p + k_i n_i + k_R n_R + v_p} + \frac{k_i n_e}{v_p + k_i n_i + k_R n_R + n_e + 1}.$$  \hspace{1cm} (6.4.1)

Therefore, assuming for simplicity that the concentrations of ions and radicals do not depend on the electron density, we still can approximate the concentration of methane with function (6.1.4), but the fitting coefficients (6.1.5) now include one more term in the denominator:

$$a = \frac{Q}{v_p + k_i n_i + k_R n_R},$$
$$b = \frac{k_e}{v_p + k_i n_i + k_R n_R},$$
$$c = \frac{k_i}{v_p + k_i n_i + k_R n_R}.$$  \hspace{1cm} (6.4.2)

The fitting procedure performed in Section 6.1 gives a value of the parameter $a$, which is very close to the initial methane concentration, corresponding to the ratio of the incoming flow to the pumping rate $Q / v_p$. This means that $k_i n_i + k_R n_R \ll v_p$ and the addition of loss channels due to the reactions with ions and radicals has no significant influence on the fitting parameters.

A more accurate analysis can be performed if the specific ion concentrations are taken as fraction $\alpha$ of the electron density:

$$n = \frac{Q + k_i n_e}{(k_e + \alpha \cdot k_i) n_e + k_R n_R + v_p}.$$  \hspace{1cm} (6.4.3)

In this case parameter $b$ would look like:

$$b = \frac{k_e + \alpha \cdot k_i}{k_R n_R + v_p}.$$  \hspace{1cm} (6.4.4)
Unfortunately, the lack of experimental data on the ion fraction and radical density prevent this improvement.

Of course, the same argumentation is valid for the treatment of the temporal behaviour of the methane concentration as well. In a similar way some of the neutral-ion reactions and reactions of species with radicals could be implemented in the rate equations for the concentrations of other measured molecules, if respective concentrations are available.

Summary

In this chapter analytical approaches, following from the solutions of equations (4.1.2) – (4.1.6), have been examined for their applicability for the description of the dependences of the concentrations of hydrocarbons on the internal plasma parameters (electron temperature and density). It was found, that simple expressions reproduce the trends in the behaviour of the concentrations very well for all investigated species over a wide range of experimental conditions. The results of the measurements, carried out at both, ICP and CCP chambers, can be approximated with the same functions, where the fitting parameters are ratios of rates of the corresponding production and loss channels (such as dissociation, pumping or incoming flow).

More precisely, the analysis of the fitting coefficients permits to reveal the relative importance of the involved processes under certain combinations of external parameters (flow rate, pressure, input power).

Fitting of the experimental data with analytical functions helps to analyze the conformity of the chosen system of reactions and in some cases to reconstruct missing information on the species concentrations (like methyl or ethylene concentrations).

Furthermore, the fitting coefficients contain information about the effective electron temperature. The latter can be found from the dissociation rate coefficient of any of the tested components if a certain EEDF is assumed. Similar to chapter 5, the calculations from the rate coefficients of total and partial dissociation for all stable measured species were performed assuming Druyvesteyn and Maxwellian EEDFs. The obtained effective electron temperatures are very close to each to other and to the results calculated from the time resolved measurements in the “cold” stage of the discharge development (Chapter 5).

Calculations from methane and acetylene data give an electron temperature of ~ 1 eV for a Maxwellian EEDF and an effective electron temperature of about 1.6 eV for a Druyvesteyn EEDF for 100 Pa in the CCP and 10 Pa in the ICP. At lower pressures (5 Pa) in the CCP the effective electron temperature is slightly higher. It reaches 1.6 eV for an assumed Maxwellian EEDF and ~ 2.4 eV for a Druyvesteyn EEDF.

The effective electron temperatures obtained from ethane and ethylene are slightly lower. This discrepancy can arise from the incompleteness of the considered system of reactions (see chapter 5).

The dissociation rate coefficient can be calculated directly from measured concentrations for any input power (electron density), if the other parameters are known. Examples of such calculations from methane and ethane concentrations are in good agreement with the data provided by the fitting procedure. No strong dependence of the dissociation rate coefficient on the input power is observed except at low input power levels for methane. This means that under the tested conditions the changes of the chemical composition are not sufficient for a significant influence on the EEDF.
Conclusion and outlook

Plasma chemistry in methane discharge is a very complicated phenomenon due to the great number of processes and species involved. Concentrations of the different components are dependent upon each other and upon rate coefficients, which are in their turn functions of the gas pressure and temperature (in case of neutral-neutral and ion-neutral interactions) and of the EEDF (in case of electron-neutral interactions). Additionally, processes of diffusion and sticking to the surfaces exert influence on the absolute values of concentrations and spatial distributions of the plasma species. For the quantitative description of the chemical composition of molecular plasmas an extended system of differential equations for the concentrations of every component must be solved. Differential equations for different components usually are interrelated since they include terms which correspond to the production and consumption channels, originating from the interactions between species. Naturally, in a more or less full form this system of equations can be solved only numerically.

In this work an approach for establishing simple relations between internal plasma parameters (like electron mean energy and electron density) and concentrations of the dominant neutral components was made exemplarily for radio frequency (13.56 MHz) discharges in methane. The consideration is based on the analysis of the experimentally obtained data in dependence on the external parameters.

As plasma sources capacitively and inductively coupled plasma (CCP and ICP) reactors were used with pure methane as source gas. The chosen operational parameters resulted in a range of electron densities from $10^{15} \text{ m}^{-3}$ to $10^{17} \text{ m}^{-3}$. The electron density as a function of the input power was measured by means of a microwave interferometer. The results were corroborated by a Langmuir probe and a far-infrared interferometer. The measurements show an almost linear dependence of the electron density on the input power.

Measurements of the neutral plasma components were performed by means of tunable diode laser absorption spectroscopy (TDLAS), which provides information on the molecular concentrations and the gas temperature. For improvement of the detection limit a multipass arrangement (Herriott type) and a modulation technique were applied. The obtained data are integrated over line in-sight or even over a major part of the chamber volume; however, in our case of low temperature, low density plasmas the introduced uncertainty is insignificant due to the relatively uniform distribution of the stable species inside the reactor, which was confirmed experimentally.

The gas temperature was determined from the broadening of the absorption lines. It was found that the translational temperature does not rise much above room temperature in the whole range of applied input powers. On the basis of previous investigations, performed in our group, the rovibrational temperature was taken to be close to the translational temperature.

Concentrations of the source gas (methane), the most abundant radical (methyl) and three stable products (ethane, ethylene, acetylene) were measured in a wide range of external parameters as functions of the time and/or input power. It was found that, despite of dissociation, the fraction of methane in the gas mixture is still significant in both types of discharges: from 10% to 50%. The concentration of methyl in both the ICP and the CCP is a few orders of magnitude smaller than the concentration of methane. In the CCP the fractions of ethane and acetylene are about 10% and 8% (in the ICP both are about 5%), and the ethylene fraction is about 3%. The rest of the gas consists conceivably of hydrogen and small amounts of other heavy hydrocarbons and radicals.
As expected, dissociation of methane is more pronounced at higher levels of the input power (or electron density) whereas the concentration of the methyl radical shows a very weak dependence on the external parameters. The concentrations of ethane and acetylene exhibit growth with increasing input power at low power levels; the dependence shows a maximum, which position is defined by the ratio of the production and loss frequencies. With further increase of the input power a decay of the concentrations is observed. Ethylene is formed already at low input powers; further increase of the input power does not influence the concentration.

The time scale of the chemistry development is of about tens of seconds in the CCP and of about seconds in the ICP for stable molecules. During this time methane decays to its steady state level of concentration, and other species form in amounts comparable with methane. The timescales for the formation and disappearance of methyl are much shorter and were beyond the temporal resolution of the diagnostics.

The aspiration to explain the observed trends in the concentration behaviour leads to the study of the processes, which govern the plasma composition.

Since the aim of this work was to find analytical expressions, which connect the internal parameters of the methane plasma with its chemical composition, the extensive list of processes and components was reduced in order to keep the rate equations as simple as possible. The analysis concerned only the experimentally observed components, allowing to reconstruct the concentrations of species, which were not measured in some cases.

The losses of the molecules due to inelastic interactions with electrons are ascribed to total and partial dissociation processes. In the selected system of rate equations, the partial dissociation of methane leads to the production of methyl, and the partial dissociation of ethane results in the formation of acetylene and ethylene. Acetylene is supposed to be produced by the dissociation of both ethane and ethylene. Therefore, both the production and the consumption channels of the measured hydrocarbons are functions of the electron density and the EEDF. The related rate coefficients can be found if the corresponding cross-sections and the EEDF are known. In this work Maxwellian and Druyvesteyn distributions were considered, although the real shape of the distribution function in reactive gases can differ from both.

The decision on the efficiency of chemical reactions was based on the analysis of the rate coefficients and/or reactant concentrations. Thus ion-molecular reactions are neglected in this work. Among neutral-neutral reactions only one, namely the reaction between two methyl radicals, was used as production channel of the ethane molecule. Interactions of all measured species, except methyl, with surfaces are neglected.

This is a very rough approach, since disregard of the reactions with radicals and ions can lead to a serious underestimation of the production or consumption of species. In principle, these reactions can be relatively easily implemented in the analytical consideration of the plasma chemistry if the corresponding concentrations of ions and radicals are known; unfortunately, in practice this is rarely the case. Nevertheless, the method allows one to obtain reasonable results.

These assumptions made it possible to set up a system of simplified rate equations for the concentrations of all measured species, which could be solved analytically, yielding dependencies of the species concentrations on time or electron density.

The time dependencies were found for the concentration of methane only, because the rate equations for the concentrations of ethane, ethylene and acetylene were still too complicated for a straightforward solution. However, they can be solved for steady state conditions, i.e. after the concentrations had reached some stable values. In this case the solutions provide the dependencies of the species concentration on the electron density. The
obtained solutions were used for the approximation of the experimental data, using the rate coefficients as fitting parameters.

The fitting procedure revealed that despite the simplicity of the rate equations used, the obtained functions match the concentrations of methane, ethane and acetylene fairly well. Generally, both the temporal behaviour and the dependence of the concentrations on the electron density were reproduced within experimental error bars for a wide range of the parameters in the CCP and the ICP as well. In some cases the fitting functions can be corrected by introducing additional fitting parameters, related to unknown production or loss channels. For example, an unidentified production channel, independent of the electron density, must be included for a successful approximation of the concentration of ethylene.

From the fitting parameters characteristic constants of the involved processes, such as rate coefficients for total and partial dissociation, were found. This is of course very advantageous, since, as a matter of fact, direct calculation of dissociation rate coefficients requires information on the EEDF and cross sections. Whereas cross sections can be found in literature, the calculation of EEDF implies the solution of Boltzmann’s equation.

Assuming a Maxwellian or Druyvesteyn shape of the EEDF, the dissociation rate coefficients were calculated for different values of the electron mean energy. By comparing the calculated rate coefficients with the ones following from the fitting parameters, information on the effective electron temperature was obtained. The procedure was applied to the steady state concentrations of all measured components, except methyl.

Moreover, since in the case of ethane and methane the efficiencies of the other involved processes were known, the fitting procedure could be replaced by a direct calculation of the dissociation rate coefficients from the analytical expression for the concentration dependence on the electron density. In that way the effective electron temperature was found for every input power value independently. Only a very slight dependence of the dissociation rate coefficients on the input power (electron density) was observed in both reactors. This fact proves the possibility to find the effective electron temperature from single measurement.

Rate coefficients, acquired from the analysis of methane and acetylene data at 100 Pa in the CCP and 10 Pa in the ICP, corresponded to an electron temperature of ~ 1 eV for a Maxwellian EEDF and an effective electron temperature of ~ 1.6 eV for a Druyvesteyn EEDF. Ethane and ethylene concentrations gave slightly lower values. The reason for this disagreement may be attributed to a neglect of production terms, leading to an underestimation of the loss terms and thus lower values of the rate coefficients and electron mean energies.

The determination of the rate coefficients from time-resolved measurements gave an opportunity to trace the change of the mean energy with time, which could be explained by an alteration of the EEDF due to changes in the plasma chemical composition from pure methane to a mixture of different hydrocarbons. It was found that the discharge went through a “hot” stage during the first seconds (ICP) or first tens of seconds (CCP) after the plasma is switched on. The effective electron temperature in this stage was of about 0.5 eV higher than in steady state. Estimation of the changes of the electron temperature due to the formation of new species, performed by the particle balance equation following from a global model, was in agreement with the observed effect.

Besides this attractive possibility to observe the temporal evolution of the EEDF, the analysis of the time resolved measurements has one more benefit: information on the mean electron energy can be obtained already from the time constant of the concentration changes
regardless of the absolute values. Unfortunately, however, time resolved measurements typically have a lower signal-to-noise ratios compared to the experiments in steady state. In addition, this approach can be used for the concentration of the source gas (in our case methane) only, because the production of other dominant components takes a relatively long time.

Generally, the simple analytical approach elaborated in this work describes the trends in the concentration of the dominant species of the rf methane plasma reasonably well in a wide range of external and internal parameters; moreover, a fair estimation of the mean electron energy is possible.

In order to improve the performed analysis a higher time resolution of the measurements is desirable. It would allow us to gain insight on the processes accompanying the formation and disappearance of the short-lived particles (radicals and electrons) and sudden changes of the stable species concentrations (for example, in the moment after the discharge is switched off.).

Information on the spatial distribution of the species is of special interest as well since it can serve for correction of the line-of-sight averaged measurements. This is important especially in the case of electrons and radicals, because an inhomogeneous distribution can introduce significant uncertainties in the determination of the absolute concentrations.

On the other hand, the rough analysis carried out in this work can be done much more accurately by including ion-molecular and radical-molecular reactions, if reliable data on the species concentrations are available. In the first place, these are reactions between species measured in this work with i) \( \text{CH}_2 \) and \( \text{CH} \) radicals and ii) \( \text{CH}_3^+, \text{CH}_4^+ \) and \( \text{C}_2\text{H}_5^+ \) ions. Most of these reactions are independent from each other, therefore the structure of rate equations will not become more complicated and analytical solutions still will be possible.

Concentrations of radicals are typically very low compared to the concentrations of long-lived neutral components. Nevertheless, in principle, the sensitivity of the TDLAS methods is good enough even for measurements of the \( \text{CH}_2 \) and \( \text{CH} \) radicals. At the same time, the detection of ions is more difficult, since their concentrations are very low and only very little information on the spectral properties of their transitions is available; however, TDLAS can be useful ions diagnostic as well [104].

Other methods for obtaining the ion concentration demand the use of expensive sophisticated devices, such as mass-resolved energy analyzers (plasma monitors) [105, 106] or retarding field analyzers [107, 108]. Interpretation of the data obtained from these instruments requires non-trivial calibration procedures. An alternative solution could be the use of pertinent results of numerical approaches.
Supplement

In Section 4.2 equations (4.2.2), (4.2.4) and (4.2.5) are given for gas inflow $Q$, pumping frequency $\nu$ and residence time $\tau$. Taking the volume of the ICP chamber (~ 82 l) and the volume of the CCP chamber (~ 21 l), these values were calculated for the typical experimental condition.

### Parameters of gas system

#### CCP

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<th>Flow (sccm)</th>
<th>$Q_{10}^{10^{16}}$ m$^{-3}$s$^{-1}$</th>
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#### ICP

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Thank you!

I must say, I feel, I’m very happy person. Because the happiness for me – is to be surrounded by people, who, I believe, are my friends. That I had all my time I spent in Bochum. Since the very first days after my arrival I was given every support and care from all of my colleagues in the Institute for Experimental Physics V. I mean not only the help in the solving of all my problems – scientific questions and every-day-life troubles – but something more: the feeling that I’m not alone, that I always have someone, who will try to understand me, from whom I can constantly learn. That is the thing I’m thankful for most of all – for being with me these years and accepting me so as I’m: from time to time asocial, depressive and gloomy.

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Hiermit versichere ich, daß die vorliegende Dissertation von mir selbständig angefertigt und verfaßt wurde, dass von mir keine anderen als die angegebenen Hilfsmittel und Hilfen benutzt wurden und daß die Dissertation in dieser oder ähnlicher Form noch bei keiner anderen Fakultät der Ruhr-Universität Bochum oder bei einer anderen Hochschule eingereicht worden ist.

Bochum, den 02.03.2006