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Role of Electron–Ion Dissociative Recombination in CH₄ Microwave Plasma on Basis of Simulations and Measurements of Electron Energy

T. Minea¹ · A. W. van de Steeg¹ · B. Wolf¹ · A. S. da Silva¹ · F. J. J. Peeters¹ · D. C. M. van den Bekerom¹ · T. Butterworth¹ · Q. Ong¹ · M. C. M. van de Sanden¹ · G. J. van Rooij¹

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Abstract

C–H bond activation was studied in low pressure microwave plasma discharges in methane. Electron energy loss channels were analyzed in view of promoting vibrational excitation. The molecular dissociative recombination (DR) channel is concluded to play multiple roles in the hydrocarbon plasma chemistry. DR increases the electron temperature with input power density and simultaneously breaks the hydrocarbon chains. Depending on the ionic species considered, plasma density n_e in the range of $10^{17} - 10^{19} \text{ m}^{-3}$ ($10^{-6} - 10^{-4}$ ionization degree) and the electron mean energy $\langle T_e \rangle$ in the range of 2–4 eV were estimated on basis of a Boltzman solver. $\langle T_e \rangle$ from 2–3 eV measured with Thomson scattering anchored the microwave discharges in a preferential regime for vibrational excitation. The best agreement with experiments was obtained when C^+ is the dominant ion in the CH₄ microwave plasma, formed through successive DR and charge exchange reactions from molecular ions.

Keywords Methane · Plasma · Activation · Thomson · Scattering

Introduction

Methane remains an underutilized raw material for production of fuels and chemicals, with the main industrial use being combustion for heating or power generation [1]. Converting methane to more value added products, e.g. ethylene, has been a challenging topic of study where C–H bond cleavage is considered the rate limit step [2]. An alternative approach to the traditional upgrading schemes is represented by plasma conversion and in particular by the nonequilibrium state of the plasma [3]. The key property of nonequilibrium plasma is that power is more efficiently deposited into vibrational degrees of freedom of the feedstock molecules than to their translational degrees of freedom. The electrons in the plasma are accelerated by the

✉ T. Minea
t.minea@diffier.nl

¹ Non-equilibrium Fuel Conversion, DIFFER, de Zaaie 20, 5612 AJ Eindhoven, The Netherlands

electric field of the standing microwave and decelerated through collisions with neutral molecules. The energy gained between collisions characterizes the type of interaction, as shown in Fig. 1 [4]. In the low energy range, up to 10 eV, the main power loss mechanism is represented by vibrational excitation (elastic scattering does not count in the energy balance). The result is an inequilibrium between the translational (i.e. gas) temperature and the vibrational temperature and hence the term “nonequilibrium plasma”. Control over the electron energy distribution function (EEDF) allows to achieve selectivity in the complex reaction pathway manifold of the plasma phase hence improving energy efficiency: a holy grail within plasma chemistry [5–7].

In the high energy tail of the EEDF, electronic excitation and ionization are the dominant processes. Although, ionization is needed to sustain the plasma it should not consume a significant part of the input energy in view of the high energy cost. Direct electron impact dissociation processes require energies between 9 – 12 eV while the average C–H binding energy is around 4.5 eV. This is an inefficient process with more than half of the energy being lost into heat. A more efficient dissociation process would have a lower activation barrier, mediated by vibrational excitation, as shown in Fig. 2 [8]:

A direct channel for electrons in molecular plasmas is represented by their loss to radical production through the dissociative recombination (DR) of hydrocarbon ions. DR reactions have no energy barrier resulting in very high rates of the process. The rate increases even further with decreasing translational energy of the colliding species [14, 15]. The rate coefficient is similar for hydrocarbon ions being slightly enhanced when vibrational states are taken into account as well [9, 16–18]. This channel depends on which are dominant ionic species in the methane discharges. Methane has the highest ionization potential (IP) among its dissociation products as shown in Table 1. In literature the most dominant ion species were found to be C_2H_5^+ , C_2H_3^+ , CH_5^+ , C_3H_5^+ , C_2H_4^+ and CH_3^+ [19–23]. DR of these ions produces dominantly methyl radicals [24]:

Fig. 1 Electron impact cross sections in methane. Values in brackets represent threshold energies. Vibrational excitation has low energy thresholds of 0.16 and 0.37 eV, while electronic excitation and ionization have high energy thresholds of 7.9 and 12 eV

Fig. 2 Schematic drawing of the potential energy diagram for methane molecule showing dissociation enhanced by vibrational excitation by more favorable Franck Condon overlap, as indicated by the red arrow (Color figure online)

Table 1 Ionization potentials (IP) and electron affinities (EA) for radical and hydrocarbon species presented in the methane discharges [9–13]

Species	IP (eV)
C	11.26
H	13.59
CH	10.63
CH ₂	10.40
CH ₄	12.61
CH ₃	9.84
C ₂	11.41
C ₂ H ₂	11.40
C ₂ H ₄	10.51
C ₂ H ₆	10.52

Studies of fusion divertor plasma (low electron temperature of few eV) learned that successive DR reactions is the dominant process breaking hydrocarbon chains [9, 25]. Carbon has also a long history in the fusion community as the plasma-facing material of choice for the divertor plates. Here the erosion of the carbon target by hydrogen plasma leads to hydrocarbons being formed and ejected back into the plasma [26, 27]. Additionally, charge exchange (CX) reactions have also very high rates, comparable to the DR process [28, 29]:

Together the processes of CX and DR break the hydrocarbon radical chain down to atomic carbon:

The CH radical is of particular importance in the above chain of reactions because it is spectroscopically observable producing a strong emission band around 430 nm ($\text{A}^2\Delta \rightarrow \text{X}^2\Pi$), as shown in an overview optical emission spectrum of microwave methane plasma discharge at 20 mbar Fig. 3 [30, 31]. Similar radical formation mechanism based on CX and DR was also reported in low pressure acetylene and silane plasmas used for *a*-C:H and *a*-Si:H deposition [32–35].

C–H bond activation, i.e. the formation of vibrationally excited methane, was studied by analyzing the electron energy loss channels with the help of a Boltzmann solver. Bolsig+ was used for the evaluation of the electron kinetics as a function of input power density. A complete description of the Bolsig+ solver can be found in the work of Hage-laar and Pitchford [36]. Furthermore, the electron mean energy and density are obtained from a particle and power balance analysis and benchmarked with a set of Thomson scattering measurements.

Measurements of the electron temperature and density are essential in order to assess whether the operational parameter space is preferential for vibrational excitation. Thomson scattering is the diagnostic of choice for in-situ measurements of the plasma parameters for a wide range of plasma sources [37–39]. While it is routinely used in atomic gas discharges it becomes challenging on molecular plasmas since generally molecules emit rotational Raman scattering over the same wavelength range. Methane is a special case because it has a point group symmetry where its depolarization reduces to zero. This means that there is no depolarization of the Rayleigh scattering but also no rotational Raman scattering. It makes methane an ideal molecule for Thomson scattering experiments [40]. However, methane discharge products are rotationally Raman active making the detection of the Thomson signal challenging.

In this work, basic plasma physics in combination with a Boltzmann solver was used to estimate the plasma parameter space and electron energy coupling in low pressure microwave plasma discharges in methane. The influence of the different ionic species on n_e and T_e is considered together with the role of DR processes, or lack thereof. The electron density and temperature were also measured with Thomson scattering diagnostic. Additionally, optical imaging based on spontaneous plasma emission characterized the plasma volume and anchored the measurements in the simulated parameter space by determining the input power density.

Fig. 3 Overview optical emission spectra from methane plasma at 20 mbar. The intense peak at 430 nm represents the CH ($\text{A}^2\Delta \rightarrow \text{X}^2\Pi$) line emission

Experiment and Methodology

The experimental setup consists of a microwave plasma reactor coupled with a laser scattering system, as shown in Fig. 4. A detailed description and operation of the microwave reactor (including video footage) and the laser setup used for Raman scattering together with improvements that facilitated the Thomson scattering measurements can be found elsewhere [40–42]. Here only a brief overview of the experimental setup together with the analysis methodology is given.

Experimental Setup

Steady state microwave discharges are generated in a tubular quartz reactor of 20 cm length and 3 cm inner tube diameter, inserted through the wide faces of a rectangular waveguide (WR-340). This position corresponds to a maximum of the electric field in the center of the tube. The continuous microwave generator supplies up to 1 kW power at 2.45 GHz operating frequency. A three-stub tuner is used for impedance matching of the waveguide with the plasma for maximizing the absorbed input power. Tangential gas injection stabilizes the plasma discharge in the center of the tube. This ensures operation over a wide parameter space while minimizing the heat load on the tube.

A frequency doubled ($\lambda = 532$ nm) Nd:YAG laser (Spectra Physics GCR230) operated at 6 W is used for the laser Thomson scattering. The beam is focused with an $f = 1.7$ m lens in the center of the waveguide. Scattered light is collected at 90° with an achromatic doublet. A 1:1 image is projected onto a fibre bundle ($27 \times 400 \mu\text{m}$) that is used to illuminate a custom-built Littrow spectrometer ($f = 1$ m, lens diameter $d = 100$ mm and 1800 lines/mm grating), equipped with an iCCD (PI-MAX4).

Fig. 4 Schematic drawing of the microwave plasma plug flow reactor. Process gas is injected by means of two tangential injection nozzles connected to the upstream glass-to-metal connector on the quartz tube. The plasma is sustained in the tube by microwave radiation through a rectangular WR-340 waveguide. Axial optical access for the laser scattering is provided by two Brewster windows. A hole in the sliding short permits scattered light to be collected and finally coupled to the spectrometer via a linear fibre bundle

Spontaneous optical emission of the plasma in the microwave reactor was measured with a Manta G-146B camera. A 30 cm lens was used for imaging the active region of the plasma reactor. Additionally, an optical emission spectrometer (HR2000 and HR4000, Ocean Optics) recorded overview emission spectra of the plasma as well.

Thomson Scattering Analysis

In laser scattering experiments stray light rejection is of extreme importance, as is the filtering of the Rayleigh scattered light, which is orders of magnitude stronger than Raman or Thomson scattering. For this purpose a sharp longpass filter is put in front of the fibers. Details about the filter response calibration can be found elsewhere [40].

Thomson scattering represents elastic scattering of photons, i.e. the laser light, on the electrons in the plasma. Scattered power depends on the number of electrons and on the interaction between them. Correlated interaction between electrons occurs above the Debye length λ_D .

The scattered spectrum yields both the electron density and temperature. For Maxwellian electrons and negligible relativistic effects, the electron temperature is calculated from the measured Doppler broadened spectrum:

$$s_T(\lambda) = \frac{1}{\sqrt{\pi}s_T} \exp\left(-\frac{(\lambda - \lambda_0)^2}{s_T^2}\right) \quad (9)$$

where λ is the scattering wavelength, λ_0 the laser fundamental wavelength and s_T the $1/e$ width of the spectrum:

$$s_T = \sqrt{\frac{4k_B T_e}{m_e c^2}} \lambda_0 \quad (10)$$

where c is the speed of light, k_B is the Boltzmann constant and m_e is the electron mass.

Integrating the measured spectrum yields the number of photons collected per spatial element that is proportional to the electron density n_e . Details about the calibration based on the rotational Raman of N_2 at known gas pressure and temperature can be found elsewhere [40].

Spontaneous Emission Analysis

The spatial extent of the discharge is designated by the region of spontaneous optical emission. When spontaneous optical emission is driven mostly by direct electron impact excitation, the correlation between emission intensity and electron density may be assumed to be roughly linear. In this way the emission profile can be related to the electron density profile in the plasma. The plasma emission is found to correspond well with a Gaussian emission profile and is therefore characterized in axial and lateral direction by the Gaussian FWHM [43].

The volume of the discharge is approximated as a cylinder with radius $FWHM_r^2$ and length $FWHM_z^2$. The lateral width $FWGN_r$ can be taken as the radial profile since the Gaussian distribution is projected onto itself under inverse Abel transform with conservation of characteristic width.

Experimental Results

Optical Emission Imaging and Spectroscopy

The plasma volume was estimated on basis of the spontaneous emission imaging of the steady state plasma discharges in order to obtain the input power density. Data was acquired in scans of power, from 90 to 350 W, at three pressures of approximately 15, 25 and 35 mbar and 4 slm gas flows. These settings were selected for being favorable for having low gas temperatures and negligible carbon deposition. The lowest power was close to the minimum input needed to sustain the plasma. The upper limit power was given by the volumetric expansion of the plasma switching to a discharge mode touching the wall (unstable plasma). The low pressure conditions kept the plasma discharge mode in the diffuse regime [44, 45].

Figure 5 illustrates the strong dependence of the optical emission on pressure values. The plasma appears to be widening along the axial distance, the effect being more pronounced for the lower pressure case. This could be attributed to the flow dynamics, where the vortex due to tangential gas injection has a strong swirl decay along the reactor longitudinal axis [46, 47]. Both axially and radially, there is a clear contraction of plasma with pressure that leads to a smaller discharge volume for the same input power. Figure 6a shows the variation in plasma volume, determined based on the optical emission imaging, with input power at three different reactor pressure settings. For the 15 mbar and 25 mbar pressure cases there is a linear increase in plasma volume with input power. This behavior is in line with the microwave propagation in under-dense plasma ($v_e/\omega < 1$) where the electron density is limited to the critical density ($7.5 \times 10^{16} \text{ m}^{-3}$ in the case of the 2.45 GHz driving frequency). The plasma volume is expected to scale linearly with absorbed power [44]. This scenario is confirmed, since Fig. 6b shows a constant power density as function of power (for the 15 mbar and 25 mbar cases). At 35 mbar pressure, a clear deviation from the linear scaling is observed. This indicates the transition to the over-dense regime (v_e/ω) where the electron density is not limited to the critical density and the power density can increase. The same behavior is shown for CO_2 plasmas [44], although it occurs at a higher transition pressure of approximately

Fig. 5 Two optical emission measurements that show at similar input power the difference in plasma volume with pressure **a** 15 mbar and **b** 35 mbar

Fig. 6 **a** Overview of plasma volume change with input power and pressure from optical emission imaging. **b** Estimated power densities as function of input power at three different pressures

120 mbar. The over-dense regime is associated with a power density increase and an accompanying temperature increase.

Thomson Scattering Measurements of n_e and T_e

The electron density and temperature for different reactor conditions (scans in power and pressure) are measured with Thomson scattering, as shown in Fig. 7. For consistency with the non-Maxwellian evaluation of Bolsig+ simulation results, the electron temperature data is plotted as mean energy $\langle T_e \rangle = \frac{3}{2} T_e$. The electron mean energy was found in the range of 2–3 eV with no clear dependence on the pressure of discharges. Additionally, T_e dependence as function of the input power remained rather constant as well. The electron density was found in the range of $10^{19} - 10^{20} \text{ m}^{-3}$ with lowest values corresponding to the lowest pressure discharges. A slight increase with input power was seen at 18 and 25 mbar, but a clear rise was observed at 30 mbar. At 35 mbar the more significant presence of rotational Raman scattering of plasma products made the Thomson scattering measurements challenging. The 30 mbar discharges represented the highest pressure for the Thomson measurements. The lowest pressure setting of is also challenging because plasma expands and can adhere to the reactor's wall [45]. Thus, variations of a few mbar can happen between discharges at these conditions depending on the

Fig. 7 Thomson scattering **a** electron mean energy ($\frac{3}{2} T_e$) and **b** density measurements for different power and pressure conditions in methane discharges

onset for the plasma stability. The uncertainty of the measurements was in the order of 10%. Apart from the general fitting error introduced by the presence of the cut-off filter, there was an additional contribution due to the N_2 calibration procedure for the absolute electron density.

Evaluation of the Electron Energy Distribution in Methane Plasma

Particle and Power Balance Analysis on Basis of Bolsig+ Solver

In this section, the electron energy distribution function (EEDF) simulations are implicitly used to demonstrate the efficacy of promoting the vibrational excitation channels. The non-Maxwellian aspect of the discharges was taken into account by evaluating the electron kinetics with Bolsig+ simulations. The solver takes as input an interval of values for the reduced electric field to solve the Boltzmann EEDF for the electrons. Then the cross sections are convoluted with the EEDF to obtain the reaction rate coefficients. In order to get back the temperature dependence of the rate coefficients a look-up table is made for the reduced electric field and electron energy.

Furthermore, the electron mean energy and density are obtained from a particle and power balance analysis where we used the reaction rates obtained from Bolsig+. Solving the particle and power balance equations for density and temperature can be also done analytically for the Maxwellian case as it is shown in the book of Lieberman [48]. This exercise learns that T_e does not depend on n_e and it is constant with input power. However, this is not the case when there are second order processes in n_e such as DR. As a result, the electron temperature is now coupled with the electron density and implicitly with the input power.

There are two coupled equations that need to be solved. Firstly the electron balance:

$$\Gamma_{loss} = n_e^2 V k_{DR}(T_e) + n_e A_z v_{flow} + n_e A_r c_s \quad (11)$$

where $n_e = n_{ion}$ are the electron and ion densities (assuming only one type of ion here for simplicity), V is the plasma volume (measured with optical emission imaging as shown in Fig. 6), $A_z = \pi d^2/4$ is the radial cross section, $A_r = \pi dl$ is the lateral area, v_{flow} is the flow speed, and $c_s = \sqrt{T_e/M_i}$ is plasma sound speed.

The loss particle flux Γ_{loss} is made of three components: a convective flux due to the flow $\Gamma_{conv} = n_e A_z v_{flow}$, a diffusive flux to the walls $\Gamma_{Bohm} = n_e c_s A_r$ and a particle flux due to dissociative recombination of the hydrocarbon ions. The Bohm flux term indicates wall recombination, i.e. ions reach sound speed c_s at the sheath in forth of the wall. Hence, it can only contribute to the loss process. Similar for the convection term, once the charged particles are generated in the simulated volume they are lost with the flow to the downstream of the reactor. Among the diffusive and convective terms, the diffusive flux is usually dominant, being an order of magnitude higher than the convective term.

For the DR component in Eq. 11, rate coefficients of the hydrocarbon ions are similar varying at most by an order of magnitude between 10^{-7} and 10^{-6} $\text{cm}^3 \text{s}^{-1}$ [17]. Given the similarity of the rate coefficients, it is not necessary to know the dominant molecular ion when considering the effect of the DR process. Assuming that two different types of molecular ions, e.g. CH_3^+ and CH_2^+ to coexist in the plasma, the DR term in Eq. 11 can be expanded to:

$$n_e^2 V k_{DR}(T_e) = n_e (n_{ion_1} + n_{ion_2}) V k_{DR}(T_e) \quad (12)$$

where $n_{ion_1} + n_{ion_2} = n_e$ given the charge neutrality condition and assuming the same DR rate coefficients, which is an approximation.

The produced particle flux is solely caused by ionization:

$$\Gamma_{prod} = n_0 n_e V k_{ion}(T_e) \quad (13)$$

and the particle balance is simply given by

$$\Gamma_{prod} = \Gamma_{loss} \quad (14)$$

The second equation is represented by the power balance made between the input power and a summation over the main loss channels:

$$P_{in} = n_0 n_e V \sum k_i(T_e) U_i, \quad (15)$$

where n_0 and n_e are the neutral and electron density, $k_i(T_e)$ and U_i are the rate coefficients and energy loss by ionization, electronic excitation and vibrational excitation.

Solving the particle and power balance equations together yields the electron mean energy and density as function of the input power density.

Simulation Results for Different Ionic Species

Within the hydrocarbon plasma chemistry the set of DR and CX reactions (Eq. 8) make it difficult to assess what is the dominant ionic species. Figure 8 shows the simulation results where three ion species cases, CH_4^+ (feedstock gas), CH_3^+ (lowest IP) and C^+ (no DR component) are considered to assess their influence on plasma parameters. The calculations are done considering room temperature plasma discharges at 15 mbar, whereas the gas temperature is in excess of 1000 K for this type of microwave discharges [45, 49]. Thus, a direct (quantitative) comparison with the measurements cannot be made but only a qualitative one. The hot plasma case is addressed in the following section. The electron density with input power density is shown in Fig. 8a. The case of C^+ ions show the highest electron density values followed by CH_3^+ and CH_4^+ cases. For the two molecular ions CH_3^+ and CH_4^+ the difference originates from the difference in IP values, as shown in Table 1. Whereas for the atomic C^+ ion the main difference consists in the absence of the DR process. The cut off electron density of $7.5 \times 10^{16} \text{ m}^{-3}$ (based on microwave propagation theory) corresponds

Fig. 8 Particle and power balance calculation of the plasma parameters, n_e and T_e , using Bolsig+ simulations input. **a** Electron density and **b** electron mean energy as function of the input power density. Three ion species cases, CH_4^+ , CH_3^+ and C^+ are considered to show the influence on plasma parameters. The dashed (black) vertical lines border the measured parameter space in the continuous operation mode

to input power densities that are an order of magnitude lower than minimum needed to sustain the plasma as shown in Fig. 6b.

Figure 8b shows the electron mean energy that is set by the particle balance (Eq. 14), as function of the input power density. As seen from Eqs. 11–14, the dissociative recombination term has a square dependence in n_e which makes the electron temperature increase with power. The whole DR process is rendered out when C^+ represents the dominant ion species. Taking off the molecular ionization coupled with a lower ionization potential leads to no DR processes and an even lower electron temperature profile [7].

When compared to the Thomson scattering measurement set, as shown in Fig. 7, the molecular ion results show higher mean energy values and electron densities differing by more than one order of magnitude. The closest agreement, in both electron density and temperature appears to be for the case of atomic C ions. This agreement further improves, i.e. the simulated electron density and temperature increase, when the effect of gas temperature is taken into account as well in the following section.

Hot Plasma Instability Results

So far we have considered room temperature plasma discharges. To look at the effect of gas temperature on the above simulations, we can change the neutral density n_0 assuming constant pressure along the reactor. Solving the two equations for a cold and a hot gas plasma, gives the results plotted in Fig. 9 chosen here for the case of C^+ ions. In the transition from a cold to a hot plasma case we see the electron temperature (and density) increasing to accommodate the same input power. This behavior represents a thermal plasma instability [50]. The instability is due to the exponential dependence of the ionization rate coefficient on the reduced electric field E/n_0 . Higher electron density leads to an increase of gas heating by electron impact. For a constant pressure along the reactor, a gas temperature increase leads to a lower neutral density and to a higher reduced electric field. Finally a higher reduced electric field results in the increase of the electron density making this a positive feedback system.

Similar electron density and temperature increase is also observed for the two molecular ion cases. Their simulated electron temperatures were already higher than Thomson results at room temperature. Hence, the extra increase due to the higher gas temperatures only

Fig. 9 Particle and power balance calculation of the plasma parameters, n_e and T_e , using C^+ as dominant ions for both cold and hot plasmas. a) Electron density and b) electron mean energy ($\frac{3}{2}T_e$) as function of the input power density. The dashed (black) vertical lines border the measured parameter space in the continuous operation mode

adds to the existing difference. The hot plasma case where C^+ represented the dominant ion species was closer to the measured plasma parameter values, as shown in Fig. 7. When C^+ would be the dominant ion, the plasma starts from CH_4 gas, and other (intermediate) ions would be formed as well, finally leading to C^+ ions. Successive CX and DR reactions (Eq. 8) in the core of the plasma discharge are thought to be the mechanism leading to the atomic C formation. These other ions, and their DR reactions, would also affect the electron density. A full model including all the species and their reactions, i.e., all DR and CX reactions, but also other chemistry would be needed to support the above mechanism.

Power Loss Channels in Methane Plasma

The effect of the DR channel, or the lack thereof, on C–H bond activation is assessed on the basis of the power partition analysis in methane microwave plasma. The main power loss channels for methane discharges are shown in Fig. 10. For the operational parameter space studied here, it shows that the preferred vibrational excitation is dominant over direct electron excitation channels. These channels cross over at a rather short mean energy interval with increasing electron temperature and opening up the ionization pathway. In general, the lower the electron temperature, the better as vibrational excitation is dominant in this lower region. Nevertheless, a trade off is most often set by the high energy needed in ionization channel to sustain the plasma. While ionization is important to sustain the plasma it should not become a significant fraction of the input power in view of the high energy expense around 10 eV.

DR has two primary effects on the partition of power in methane plasma. Given the lack of contribution to the electron loss it enables a low mean energy operational parameter space that is preferential for vibrational excitation. Additionally, with decoupling the electron temperature from the input power density it allows for increased chemical conversion. At constant energy loss fractions the reactor can be operated at higher input power densities that enhance the conversion degree but without sacrificing the energy efficiency. Hence, overcoming the compromise given by the trade-off between conversion and energy efficiency degree.

The difference in case of molecular ions is that an increased power density also leads to an increased electron temperature. As a result there is a transition from a preferential regime for vibrational excitation to electronic excitation. Furthermore, there is an increased power deposition in the electronic excitation channel leading to a trade-off between energy efficiency and conversion degree. This behavior was studied in microwave plasma

Fig. 10 Energy loss fractions as function of the electron mean energy. The dashed (black) vertical lines border the measured parameter space

discharges concerning activation of CO_2 (into CO). Seeding of alkali metal traces was proposed to take off the ionization from the molecular ions, i.e. decoupling the plasma activation from the ionization channel [7]. In the case of CH_4 discharges, taking off the ionization from the molecular ions happens through successive DR and CX reactions resulting in a preferential regime for methane activation.

Conclusions

C–H bond activation was studied in low pressure microwave plasma discharges in methane. Within the hydrocarbon plasma chemistry at play the DR channel is seen to drive up the electron mean energy with input power. Together with CX processes they form a system of probable reactions that break the hydrocarbon radical chains down to the atomic carbon.

Taking advantage of the nonpolar character of the methane molecule we measured the plasma electron density and temperature with Thomson scattering. A Boltzman solver aided with the interpretation of the measured plasma parameters by evaluating the electron energy loss channels. Electron mean energies in the range of 2 eV showed that the microwave discharges were in a preferential regime for vibrational excitation. The results could be best explained in the case where atomic C^+ ions accounted for the dominant ion species in the plasma. Essentially, elimination of dissociative recombination channels allows for increased chemical conversion efficiencies by opening vibrational excitation pathway.

Furthermore, when C^+ is the dominant ion in the CH_4 plasma, rather than the molecular ions, it has a beneficial effect for the trade-off between energy efficiency and conversion degree. The fact that the electron temperature is decoupled from the input power density allows for high conversion degrees while maintaining the energy efficiency.

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