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Mass spectrometric investigations in a Ar/CH_4 radio frequency low pressure discharge

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Introduction

As with many other hydrocarbon precursors nanoparticles can be formed in low temperature plasmas from methane. It has been documented, compared to some other gases, that relatively high power densities are required [1,2]. It is, however, increasingly likely to form nano dust only from an argon plasma in a dirty chamber, prior conditioned with a methane plasma [3].

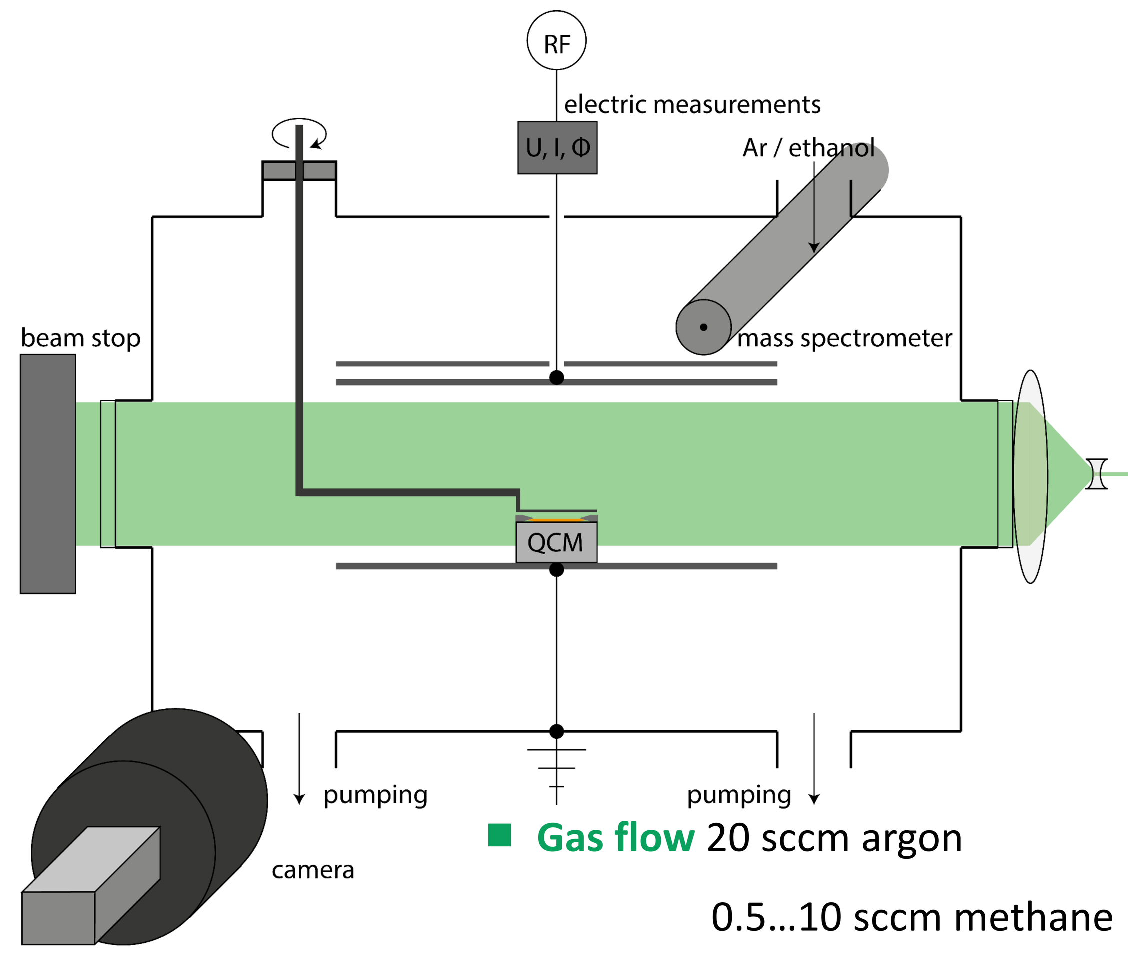
In this work we study by means of mass spectrometry the gas and ion composition of a Ar/CH_4 plasma in a low temperature RF plasma. In particular, the influence of the wall and electrode condition is investigated by the comparison of the respective spectra. Additionally, with a simple rate equation model as introduced in [4] the total dissociation rate of methane is calculated for different plasma parameters.

[1] J. Berndt et al., Dust particle formation in low pressure Ar/CH_4 andAr/C_2H_2 discharges used for thin film deposition, Vacuum **71** (2003) 377–390

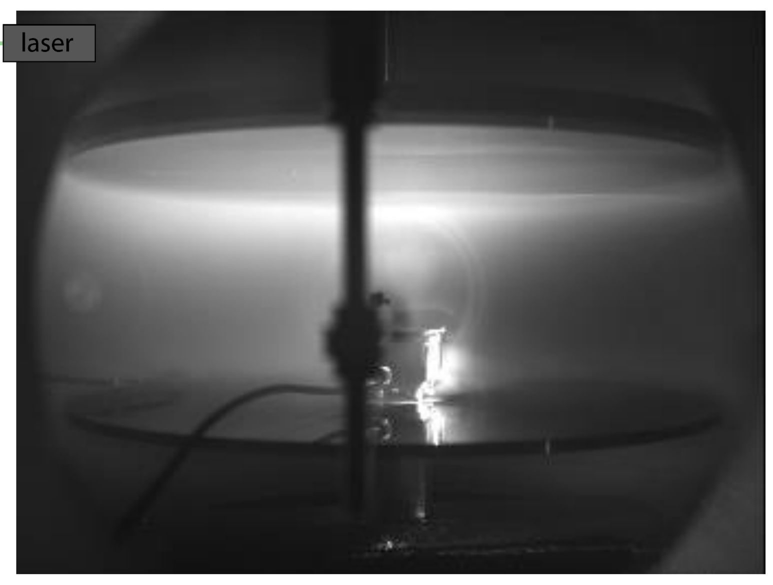
[2] J. Winter et al., Dust formation in Ar/CH_4 and Ar/C_2H_2 plasmas, Plasma Sources Sci. Technol. **18** (2009) 034010 (8pp)

[3,4] see conclusions

Experimental setup



- **Power** 20- 80 W
- **Volume** 0.03 m³
- **Surface area** 0.63 m²



- **Gas flow** 20 sccm argon
  0.5…10 sccm methane
- **Pressure** 0.25…0.5 mbar

Dissociation of methane

Consider uniquely electron impact dissociation processes:

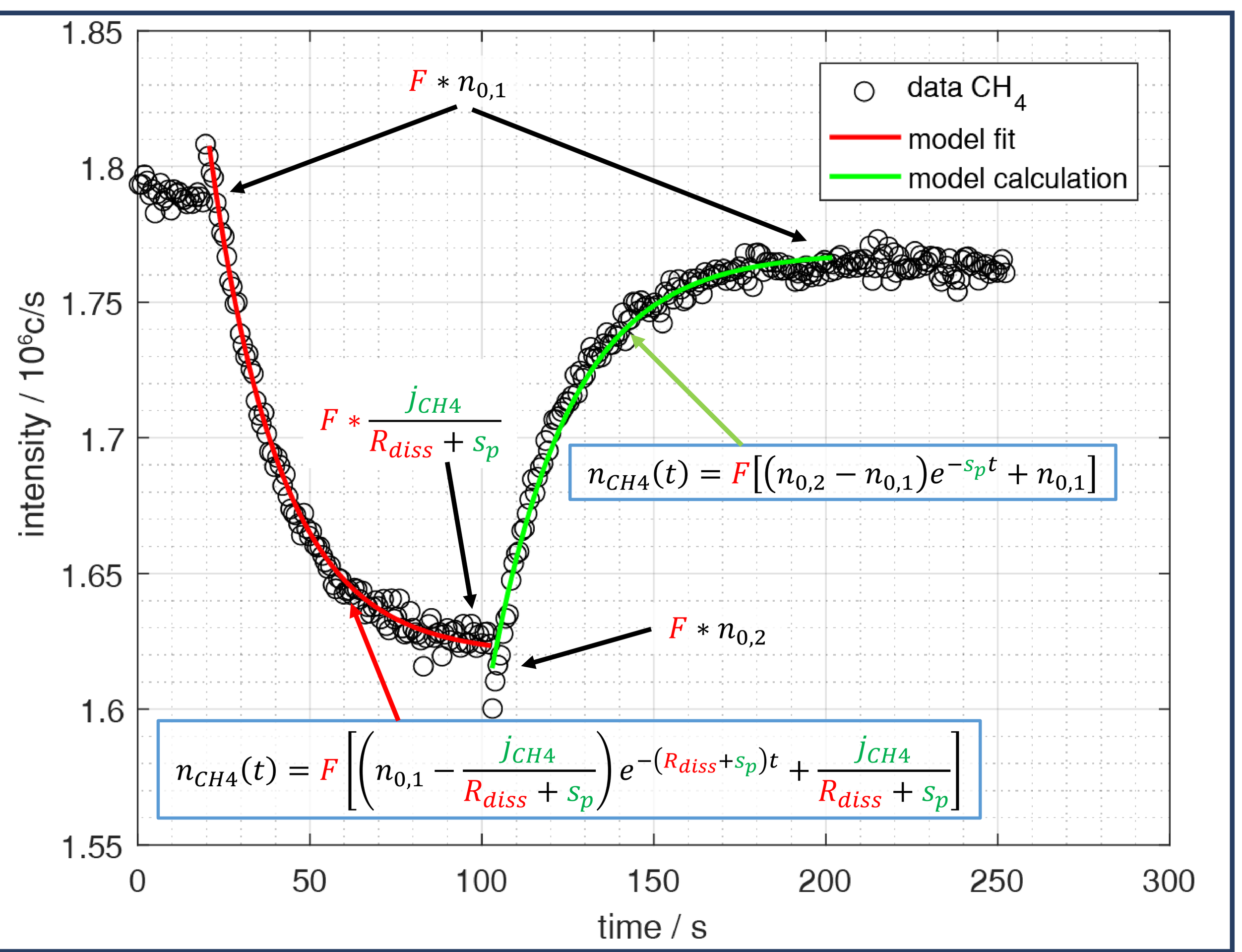
$$CH_4 + e^-_{fast} \xrightarrow{K_{diss,1}} CH_3 + H + e^-_{slow}$$
$$CH_4 + e^-_{fast} \xrightarrow{K_{diss,2}} CH_2 + 2H + e^-_{slow}$$
$$CH_4 + e^-_{fast} \xrightarrow{K_{diss,3}} CH + 3H + e^-_{slow}$$
$$CH_4 + e^-_{fast} \xrightarrow{K_{diss,4}} C + 4H + e^-_{slow}$$
$$CH_4 + e^-_{fast} \xrightarrow{K_{diss,5}} CH_3^+ + H + 2e^-$$
$$\vdots$$

$$\frac{dn_{CH4}}{dt} = j_{CH4} - R_{diss} * n_{CH4} - s_P * n_{CH4}$$

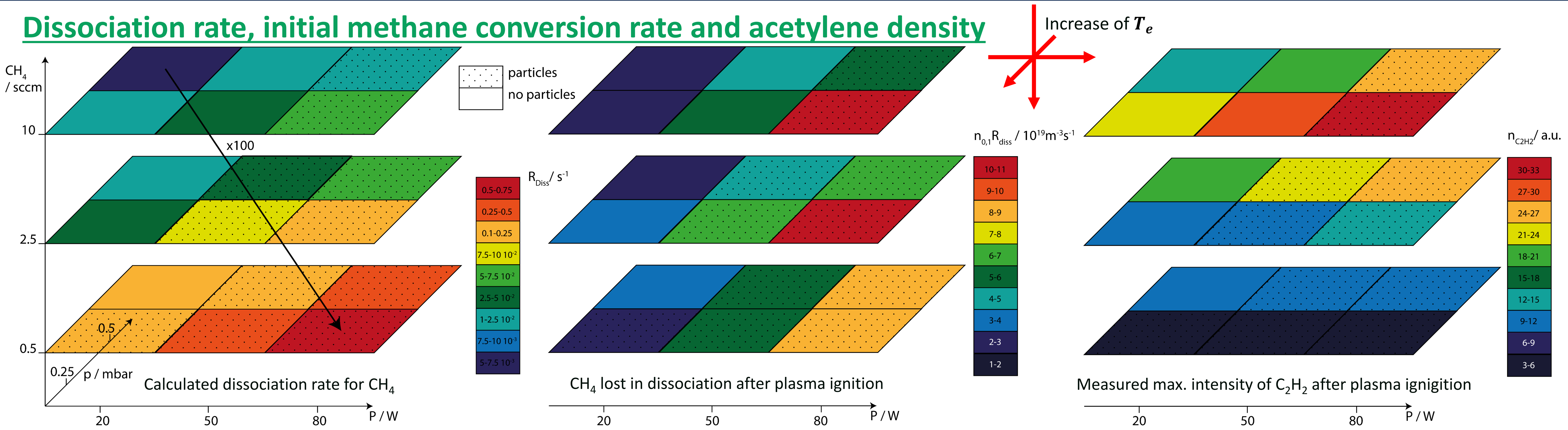
with j_{CH4}, R_{diss}, s_P volumetric methane flow rate, dissociation rate and pumping rate, respectively, and n_{CH4} methane density. More precisely:

$$j_{CH4} = {}^{Q_{CH4}}/_{V}$$
$$R_{diss} \to R_{diss}(n_e T_e) = n_e * \sum_i K_{diss,i}(T_e)$$
$$s_P = (Q_{CH4} + Q_{Ar}) * \frac{k_B T}{pV}$$

- Calculate j_{CH4}, s_P for each set of parameters
- Measure n_{CH4} as a function of time
- Solely fit R_{diss} in model function and sensitivity factor F
- Do not consider $n_e \to n_e(t)$, $T_e \to T_e(t)$



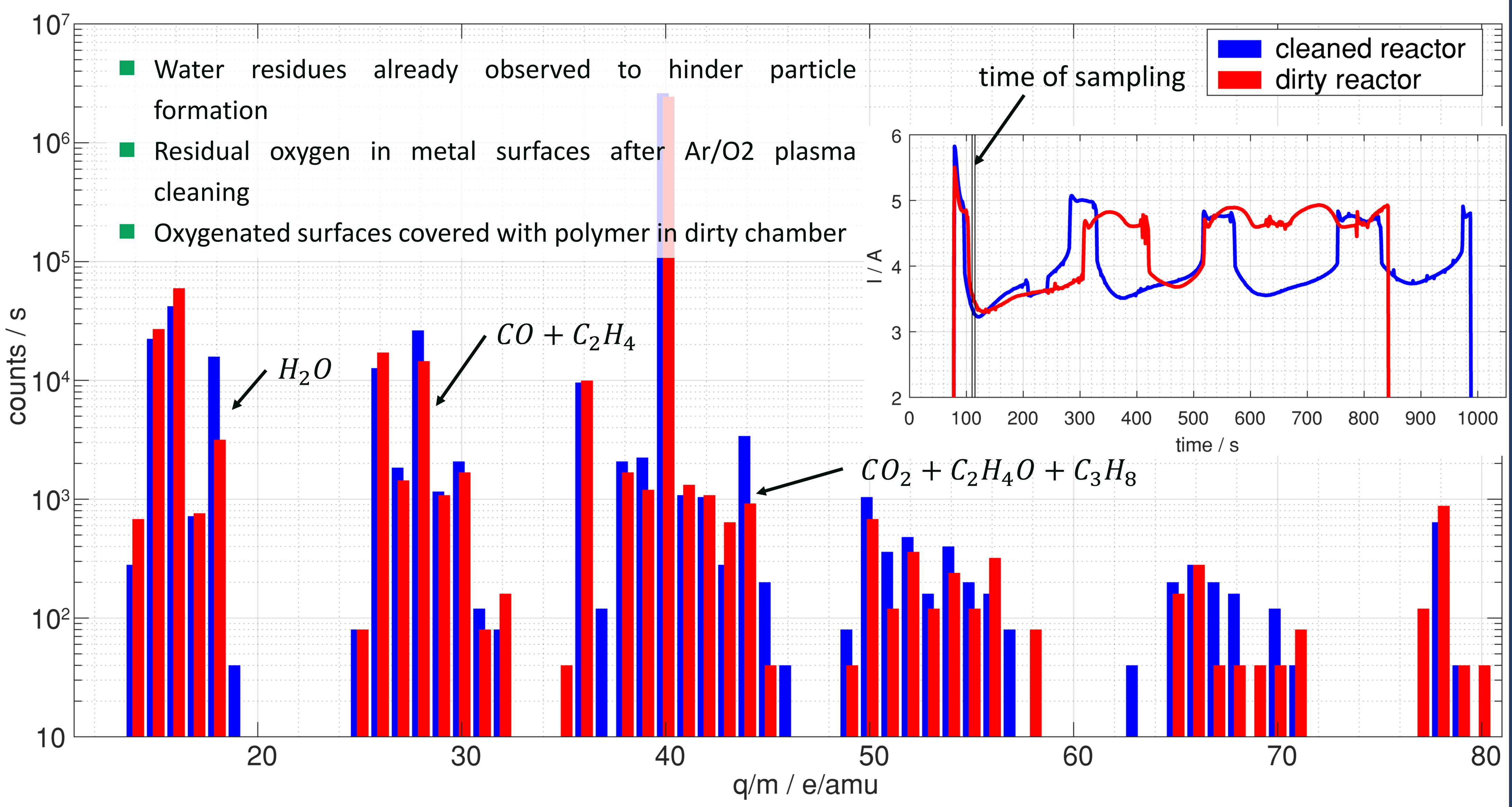
Dissociation rate, initial methane conversion rate and acetylene density



Calculated dissociation rate for CH_4 — CH_4 lost in dissociation after plasma ignition — Measured max. intensity of C_2H_2 after plasma ignigition

Mass spectra for clean and dirty reactor

- Water residues already observed to hinder particle formation
- Residual oxygen in metal surfaces after Ar/O2 plasma cleaning
- Oxygenated surfaces covered with polymer in dirty chamber



Conclusions

- The total dissociation rate has been obtained for a set of parameters, showing a strong increase (factor 100) towards high powers, low pressures and low methane flow rates.
- The increase in the dissociation rate can be explained by a higher ionization degree for high powers and smaller amount of elastic electron collisions for low pressure and methane concentration
- The conversion rate of methane into reactive material has been calculated as a function of available precursor concentration and dissociation rate
- A comparison of neutral mass spectra between a cleaned and a dirty reactor suggests the presence of oxygenated surfaces as a key factor against nanoparticle formation

[3] Géraud-Grenier et al., Plasma chemistry and dust-particle generation in pure methane plasma: Influence of the RF electrode cleanliness, J. Appl. Phys. **126**, 063301 (2019)

[4] J. Berndt et al., Some Aspects of Reactive Complex Plasmas, Contrib. Plasma Phys. **49**, No. 3, (2009) 107 – 133

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