

Particle Mass Spectrometry of Soot Particle Formation

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Kinetic studies of soot particle formation and growth have been performed in flat, premixed laminar flames. These flames have comparatively simple flow and temperature fields and allow studies of the combustion process along one single coordinate, the height above burner which is directly related to the reaction time or residence time. The main reaction zone stabilizes a few millimeters above the burner port and looks like a bluish disk. The flow field of the post-flame gases which leave the main reaction zone can be kept uniform by installation of flow stabilizers like wire grids at some distance well above the burner. Ideally, in these flames, the composition of the postflame gases depends on the fuel/oxidizer type and mixture strength, on the temperature, on the pressure and on the height above burner, but radial gradients of temperature and composition are negligible. The mixture strength is often expressed as the molar C/O ratio of the fresh gas before ignition. From thermodynamic considerations, the onset of soot formation would be expected when the C/O ratio exceeds unity, but usually, soot formation starts at lower C/O ratios already, roughly in the range $C/O \sim 0.5 - 0.9$. Developing soot formation is associated with a yellow luminosity in the postflame gases and the critical C/O ratio for soot formation is determined by optical observation usually. The formation of soot particles is investigated under low sooting conditions preferentially, at a C/O ratio slightly above critical.

The measurement of the soot particle size and number density under high temperature, reacting flow conditions is a challenging task and several different measurement methods have been employed and tested. They can be separated into intrusive and non-intrusive methods. Optical methods have the great advantage that they do not require particle sampling and handling. The most commonly used optical techniques are laser light scattering and extinction as well as laser induced incandescence (LII), but they have some disadvantage, in as far they provide information only about integral properties of the particle size distribution, i.e. about the moments of the size distribution function. Direct sampling methods have the potential to measure the particle size distribution, the critical point here being the sampling procedure itself which is liable to distort the temperature field and the flow field of the flame and to induce changes of particle properties in the sampling line due to condensation, coagulation and losses to the wall. Therefore, direct sampling methods need to be optimized for low flame distortion and fast particle extraction. This is best achieved with a molecular beam sampling technique.

In this study, the soot particles were sampled from the hot flame gases by a two stage molecular beam sampling system and transferred into a TOF particle mass spectrometer. The particle mass spectrometer was designed as very compact device and optimized for the high mass range related to particles. It detects the fraction of charged particles present in the flame gases and operates in the mass range $600 - 6 \cdot 10^5$ amu. The particle beam is split into the charged and neutral fractions by a

variable DC deflection voltage. The charged particles are detected at Faraday cups and the intensity is recorded as function of the deflection voltage which is proportional to m/z (mass to charge ratio). In addition, the particle beam is modulated by an AC electric field; the phase shift between trigger point and detector is used to determine the particle velocity. In the soot particle measurements, the mass spectra are converted to size spectra using a soot particle density $\rho = 2 \text{ g/cm}^3$.

The experimental conditions chosen here were flat, premixed acetylene/oxygen flames burning at low pressure (30 mbar) flames and atmospheric ethylene/air flames under low sooting conditions. Parameters were the C/O ratio of the fresh gas, the inlet velocity and the height above burner. Mc Kenna type burners were used in these experiments. The low pressure burner was housed in a steel vessel and the flames could be observed from outside. The flame shape showed some transition from cylindrical to conical. It was very stable and uniform without further stabilization. The atmospheric flames were protected against the surrounding air by a nitrogen shroud and the flow pattern was stabilized to give the flame a cylindrical shape by means of a wire grid which was placed approx. 40 mm above the burner surface.

In the low pressure flames, the number concentration of positively charged particles was higher than that of negatively charged particles. The mass distribution of the positively charged fraction showed three peaks; the negatively charged fraction showed two peaks. The m/z peak separation was by a factor of two in the deflection voltage with one clearly dominating peak which was evaluated for the particle size. The particle diameter was found to increase continuously with increasing height above burner and with increasing C/O ratio, but remained below 10 nm under the present experimental conditions.

In the atmospheric ethylene/air flames, the negatively charged particles dominated the particles with positive charge. The mass distributions were unimodal or bimodal, depending on experimental conditions. The high mass mode corresponds to particles with diameters in the range 3 – 8 nm. The low mass mode covers a mass range from approx. 1500 – 8500 amu (if $z = 1$). Probably, it represents a mixture of polyaromatic hydrocarbons and incipient soot particles up to diameters around 3 nm. The peak intensities were measured as function of the height above burner, as function of C/O – ratio and as function of the inlet flow velocity. The peak intensities showed a different parameter dependence: While the low mass mode peak intensity decreased with increasing C/O – ratio and with increasing height above the burner, the high mass mode intensity increased in contrary. By variation of the inlet flow velocity, it was possible to find conditions when only the low or the high mass peak were detectable.

The low mass mode was observed preferentially at increasing inlet velocity, i.e. at increasing flame temperature, close to the limit of soot formation. This offers three ways of interpretation: (a) The low mass mode could represent some transient high molecular hydrocarbons which do not end up as stable particulates or, (b) the low mass mode could be a result of soot particle decomposition or, (c) it could represent an intermediate species on the way to soot formation. Further experiments are needed to obtain more information about the nature of the low mass mode.

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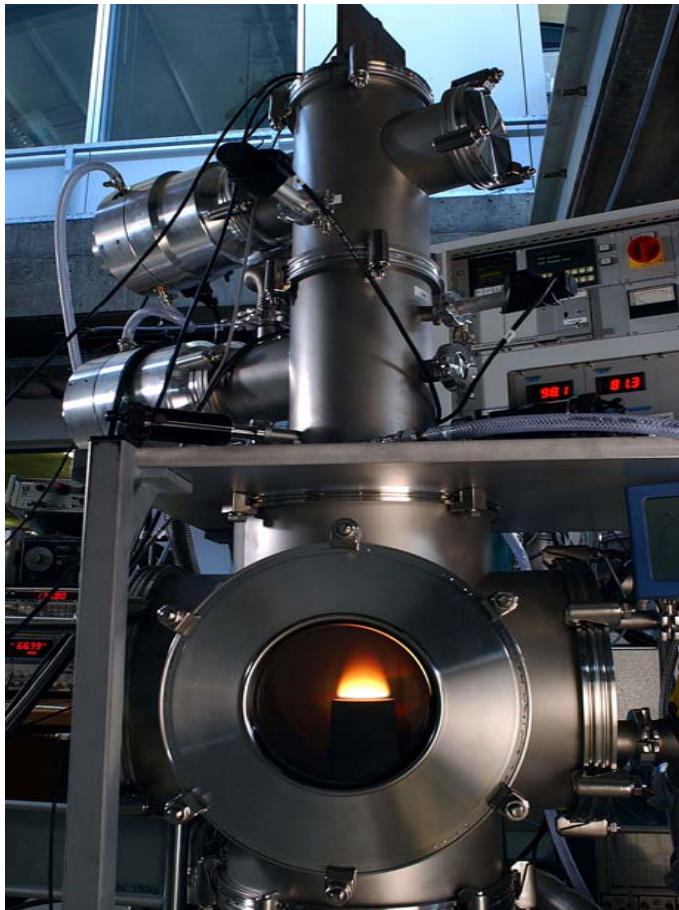
KIT, Institute for Technical Chemistry, Thermal Waste Treatment Division (ITC – TAB)



- 1. Introduction / Experimental and Modelling Tools**
- 2. Particle Sizing / Particle Mass Spectrometer**
- 3. Soot Particles in Low Pressure Acetylene/Oxygen Flames**
 - Mass and Size Spectra**
 - Size Dependence on Parameters**
- 4. Soot Particles in Atmospheric Ethylene/Air Flames**
 - Mass and Size Spectra**
 - Dependence on Parameters**
- 5. Summary**

Experimental Facilities

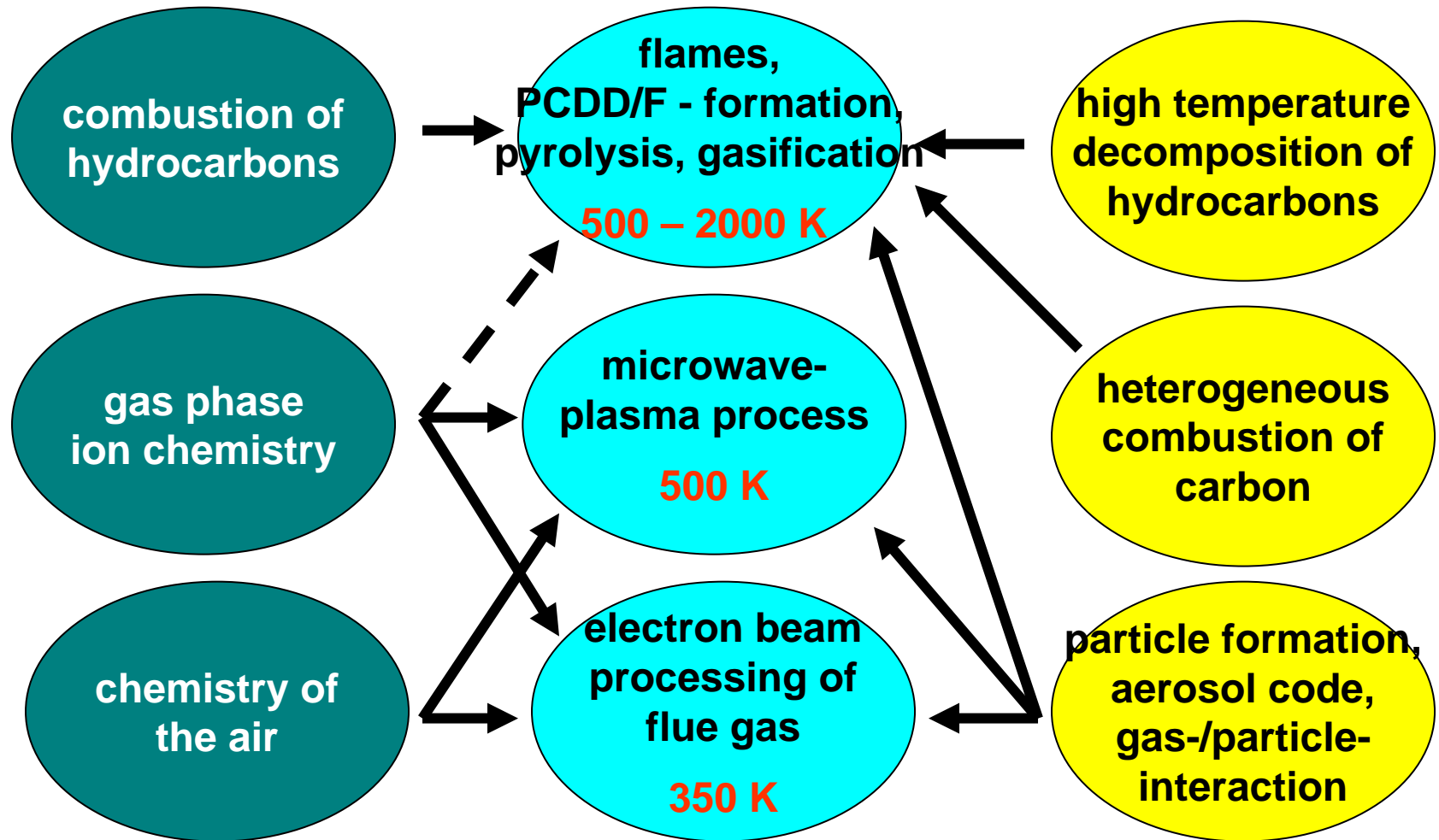
low pressure flame



atmospheric pressure flame



Models of particle formation and aerosol dynamics in technical processes at ITC – TAB (KIT)



gas phase

particulate phase

in – situ techniques

- static light scattering ($N * d^6$)
- extinction ($N * d^3$)
- dynamic light scattering,
autocorrelation (diff-coeff., $1/d$)
- laser induced incandescence (LII)

techniques based on particle sampling

- TEM, REM, BET
- mobility analyzer (SMPS)
- electrical low pressure impactor (ELPI)
- photo acoustic soot sensor (PASS)
- tapered element oscillating microbalance (TEOM)
- particle mass spectrometer (PMS)

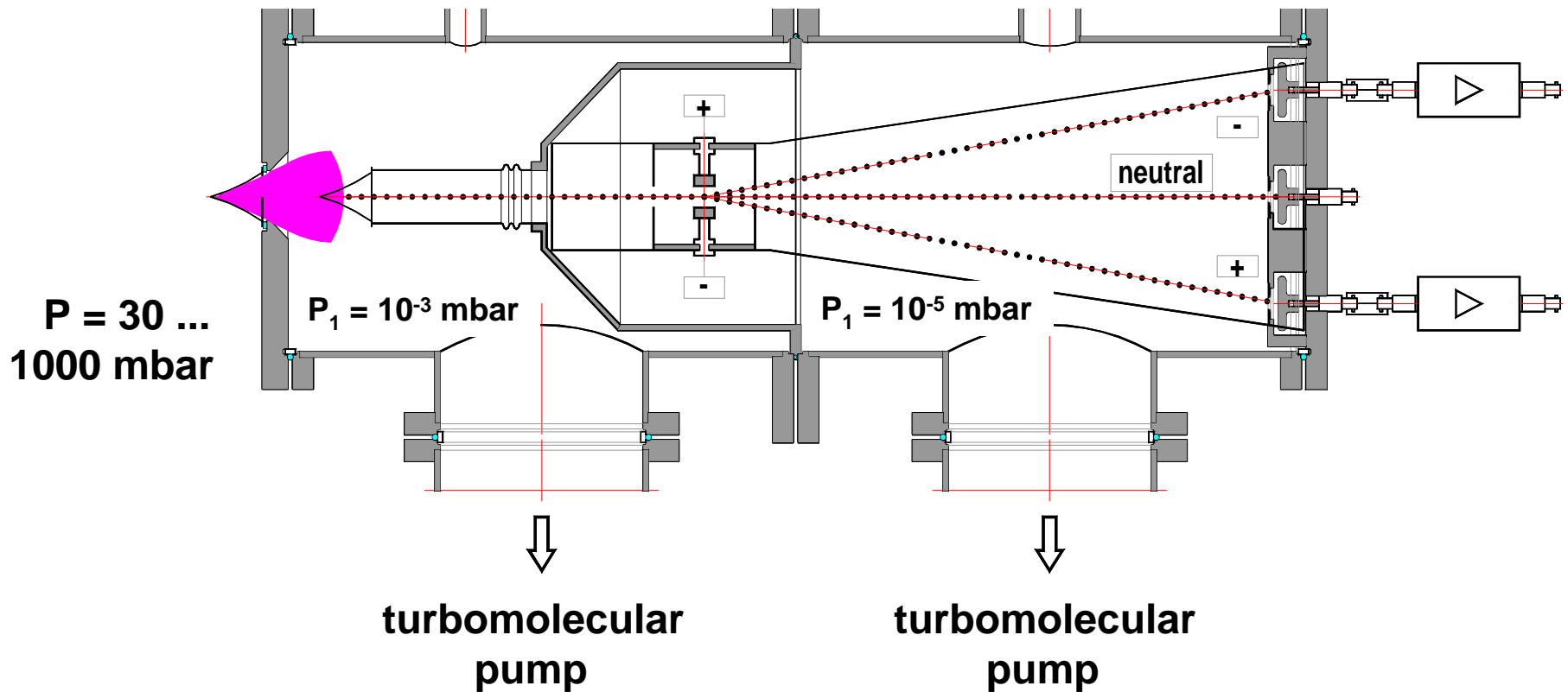
Measurement principle of the Particle Mass Spectrometer

molecular beam
probing

deflection
voltage

charge separated
particle beams

Faraday cups /
amplifier



Application range of PMS

Size range 1 – 30 nm

Concentration $> 10^8$ particles/cm³ without dilution

Detection limit 10^{-14} A [= 10 fA ~ 65000 charges/sec]

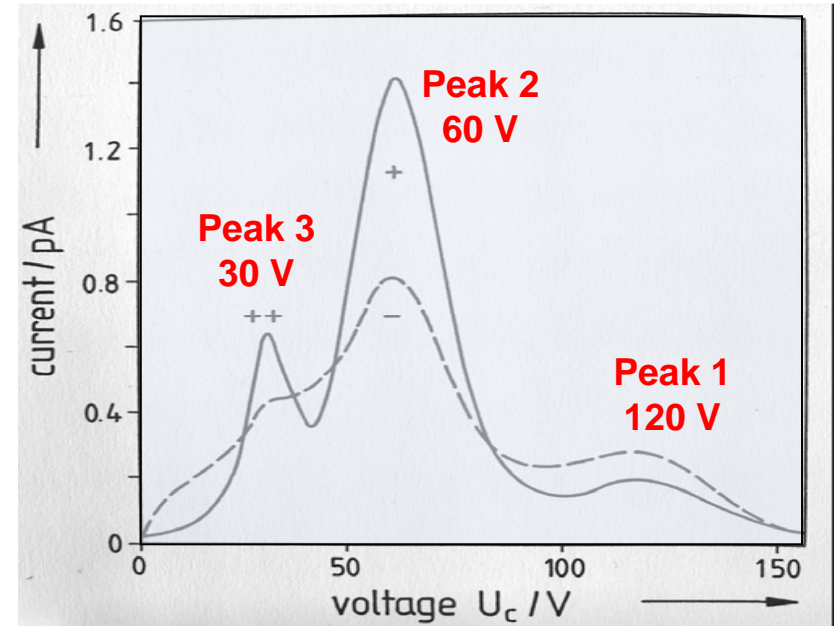
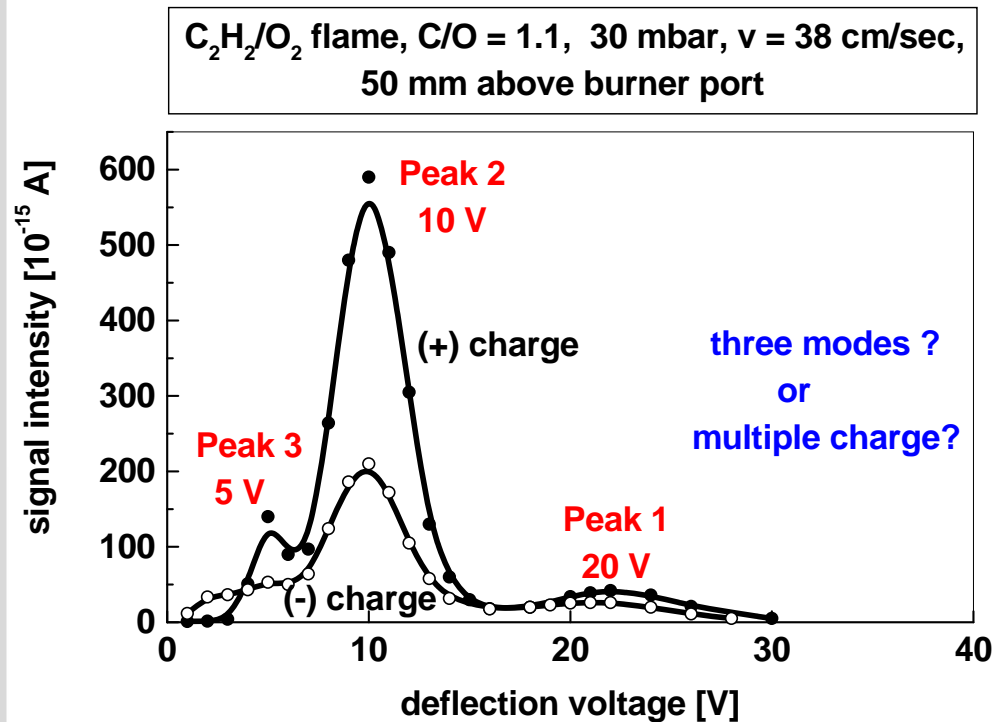
Resolution between 2 – 5 % of particle diameter

Time required approx. 1 – 10 min

The PMS is applicable in basic investigations, e.g. in highly reactive systems, as well as for online process control and for process optimization.

Results *in low pressure flames*

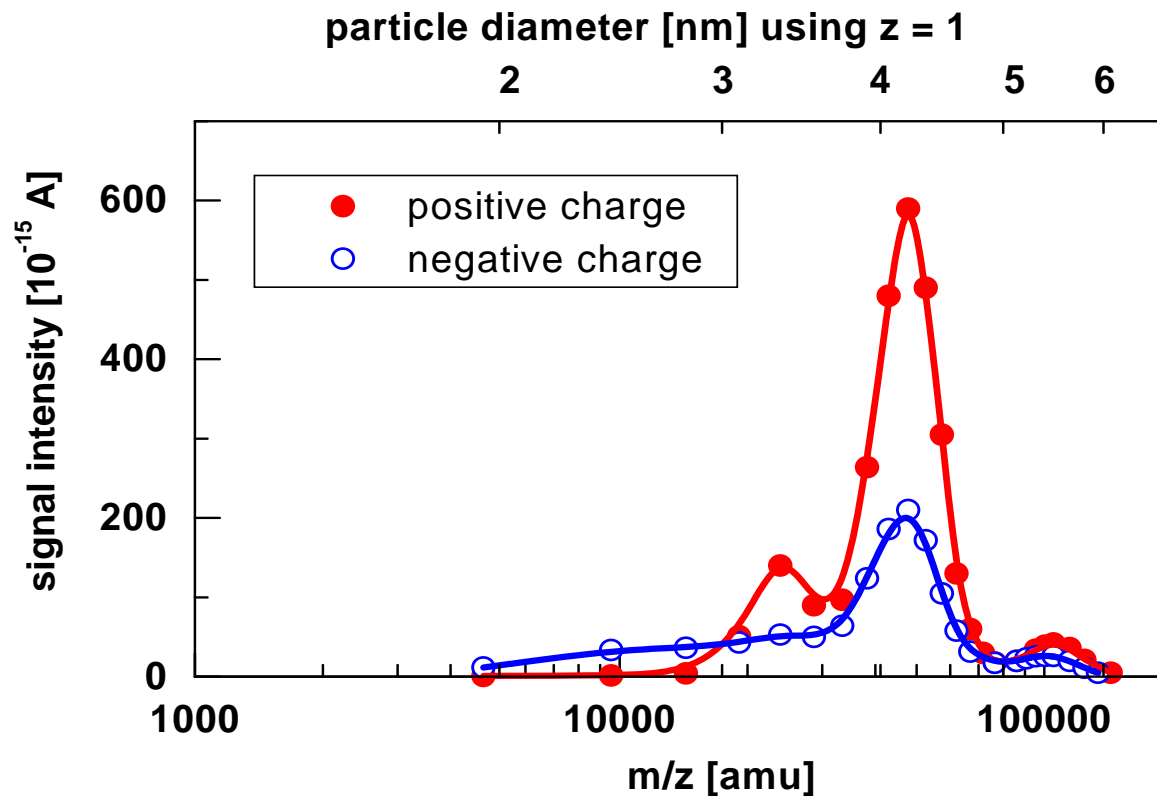
m/z spectra of soot particles in low pressure flames



comparison with P. Roth and A. Hospital,
24th Symposium (International) on
Combustion, p. 981 – 989 (1992)
very similar flame conditions

Mass and size spectra in low pressure flames

**C₂H₂/O₂ flame, C/O = 1.1, 30 mbar, v = 38 cm/sec,
50 mm above burner port**

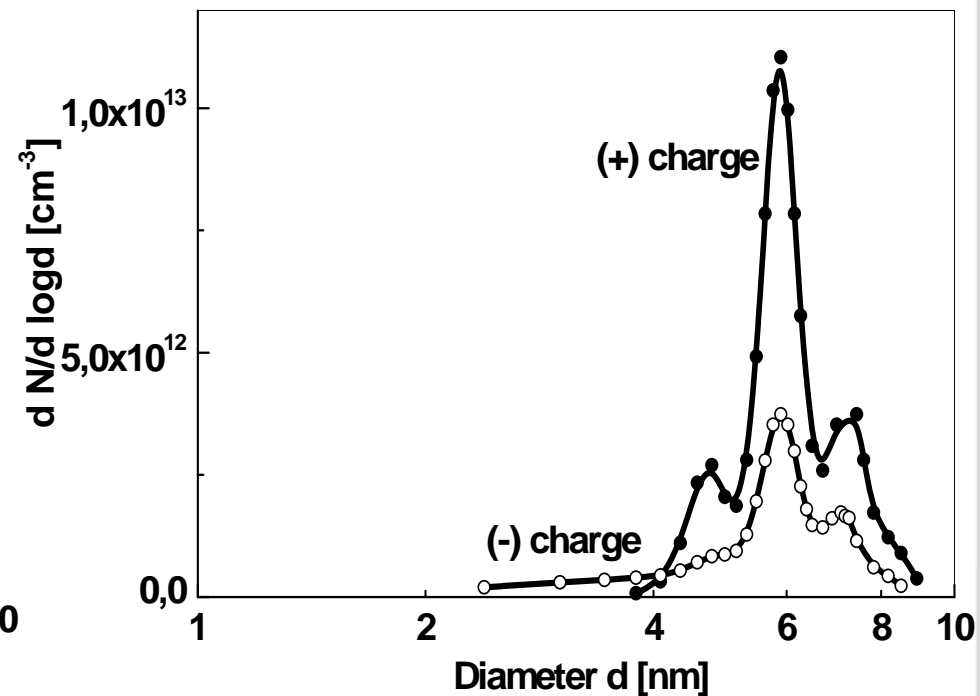
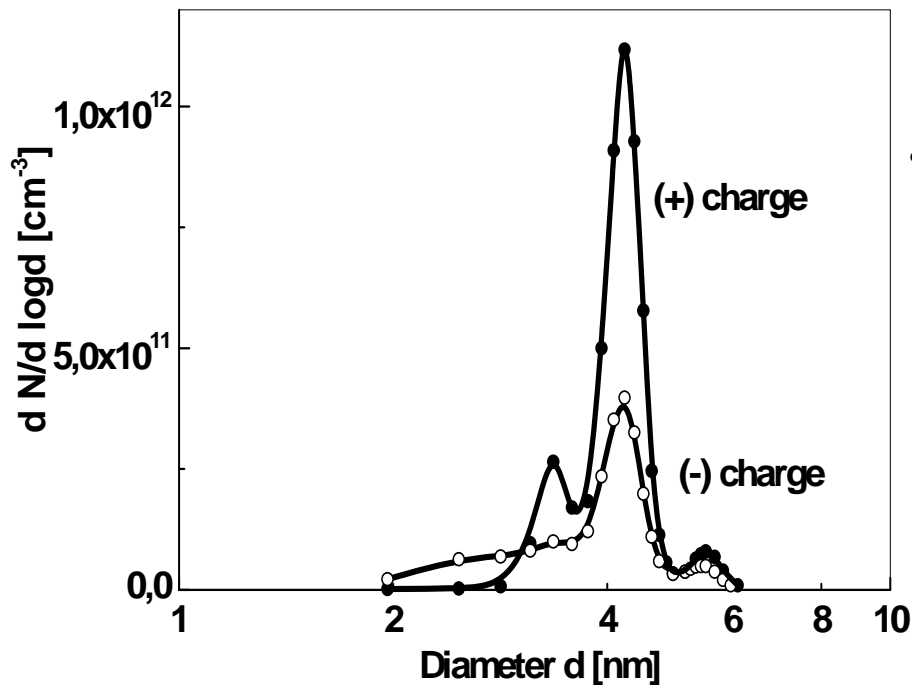


Soot particle size in low pressure flames (single charge assumption)

C_2H_2/O_2 flame, C/O = 1.1, 30 mbar, $v = 38$ cm/sec,

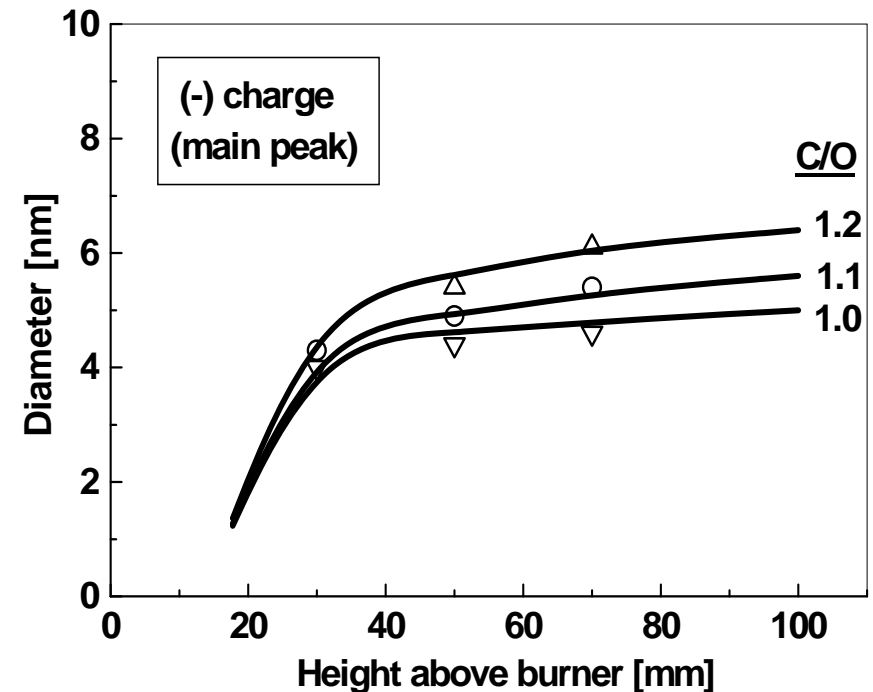
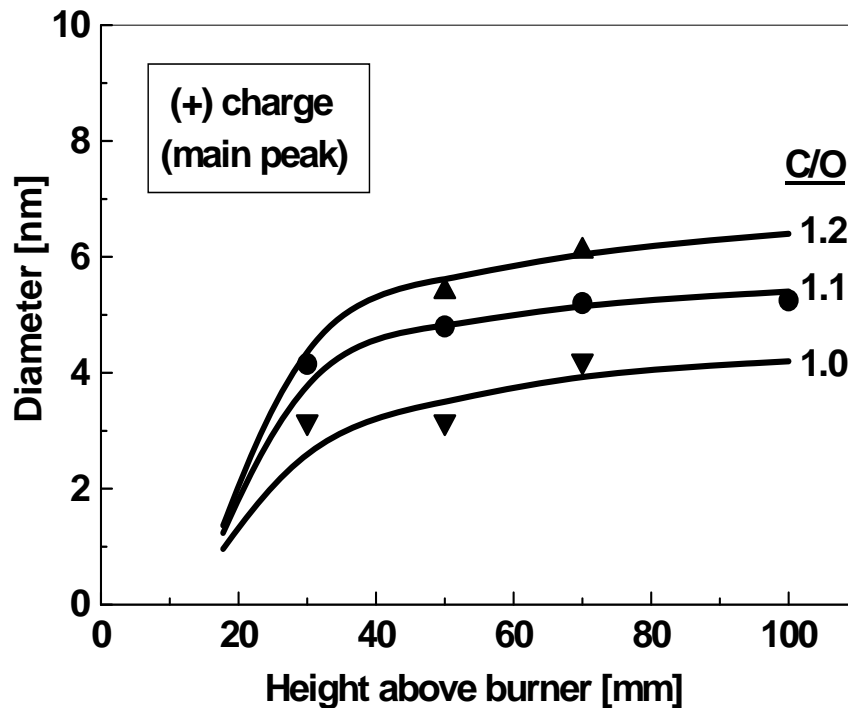
50 mm above burner port

100 mm above burner port



Soot particle size in low pressure flames along height above burner

C_2H_2/O_2 flame, 30 mbar, $v = 38$ cm/sec

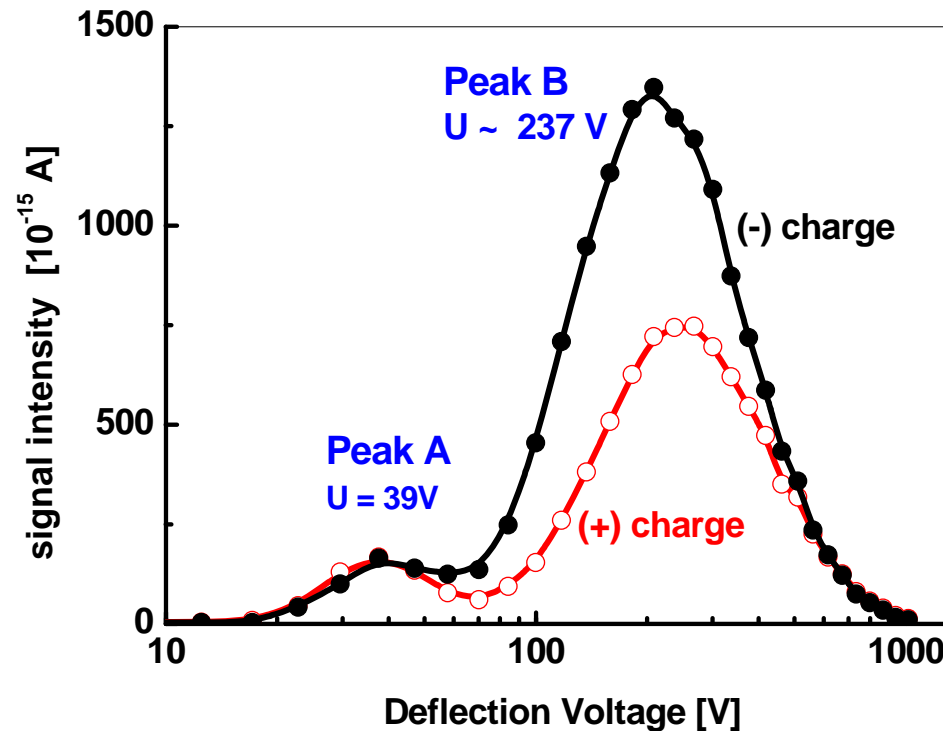


Results

at atmospheric pressure

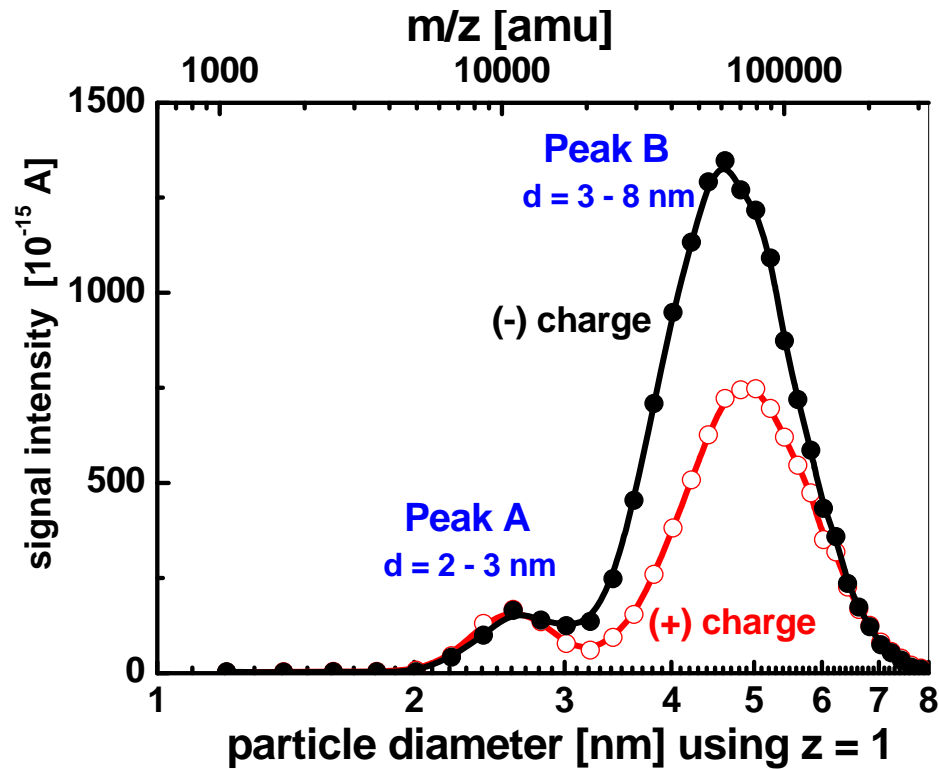
PMS signal in atmospheric flames

C_2H_4 /air flame, 1 atm, $v = 9$ cm/sec, 11 mm above burner port



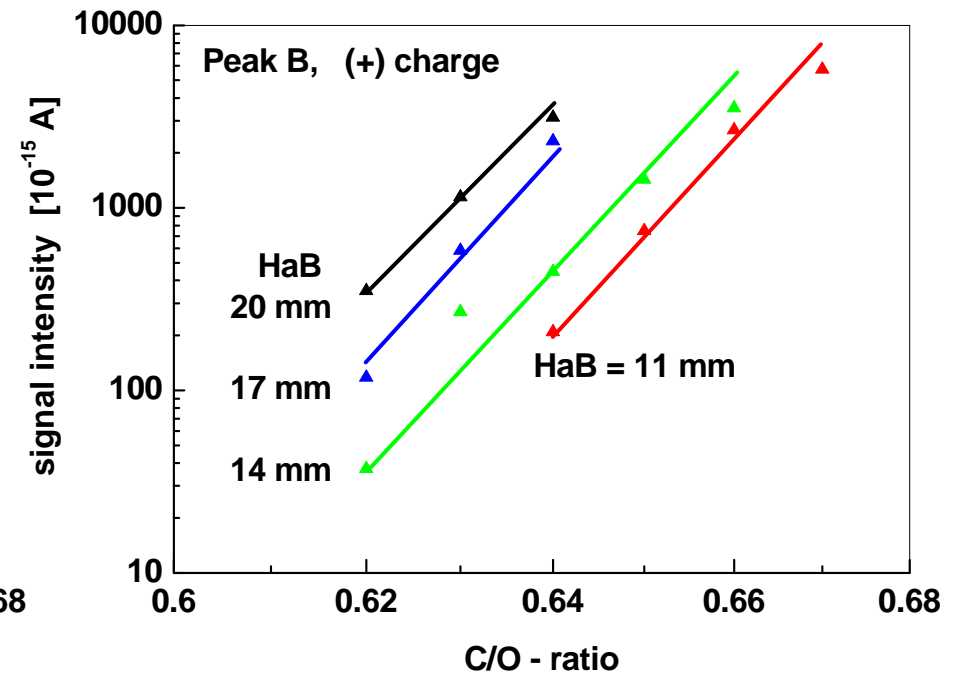
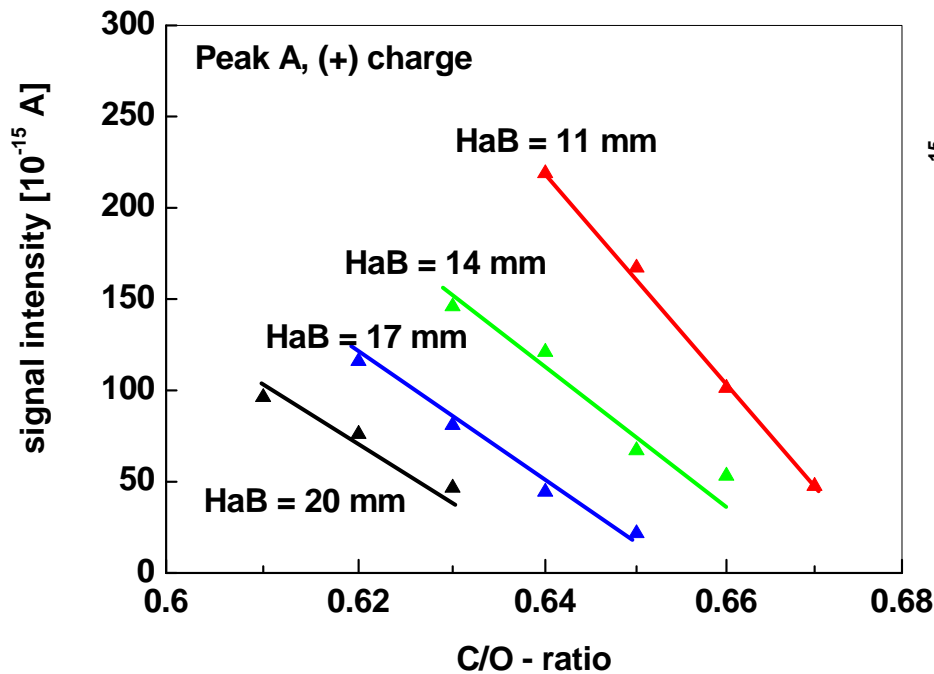
Soot particle mass and size in atmospheric flames

C_2H_4 /air flame, 1 atm, $v = 9$ cm/sec, 11 mm above burner port



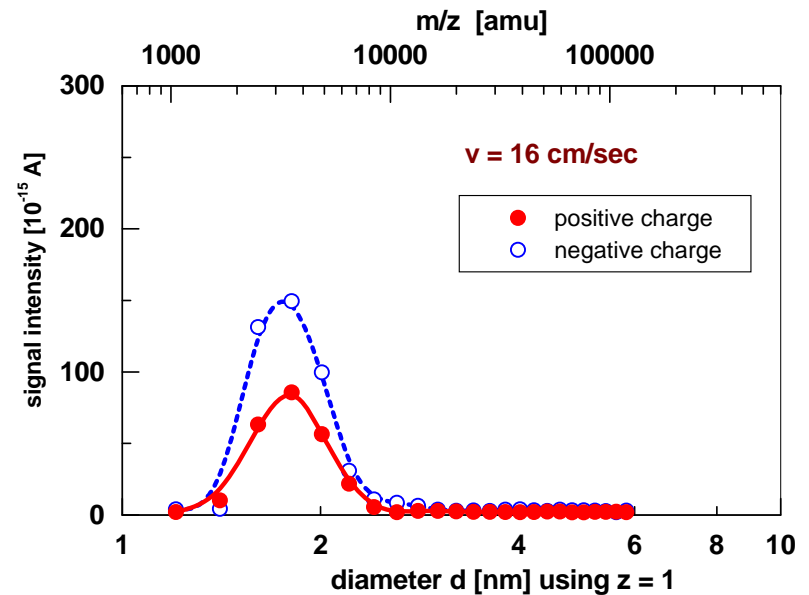
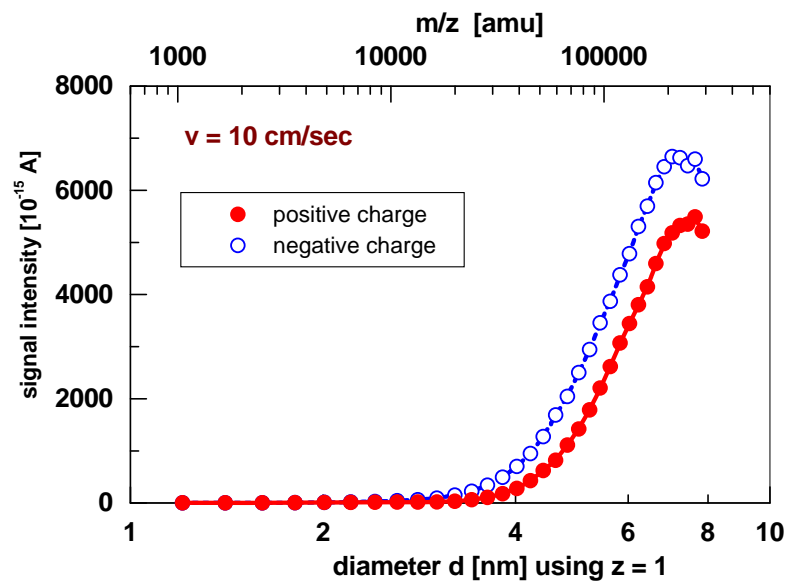
Peak intensity vs. C/O - ratio

C_2H_4 /air flame, 1 atm, $v = 9$ cm/sec



Mass and size spectra at different inlet velocities

C_2H_4 /air flame, 1 atm, C/O = 0.68, 14 mm above burner



The Particle Mass Spectrometer (PMS) has been used to study the very early stages of soot particle formation in flat, premixed flames.

In low pressure acetylene/oxygen flames, a multiple peak structure was observed with one clearly dominating peak, which was attributed to almost monodisperse soot particles.

In atmospheric ethylene/air flames, a bimodal mass distribution was observed. The two modes show a different dependence on temperature. The high mass mode is attributed to soot particles. The low mass mode is in the transition regime from high molecular aromatics to small particles.

Thank you for your attention!