Appearance Potential Mass Spectrometry:
A new technique for the detection and quantification of heterogeneous catalytically generated gas phase intermediates

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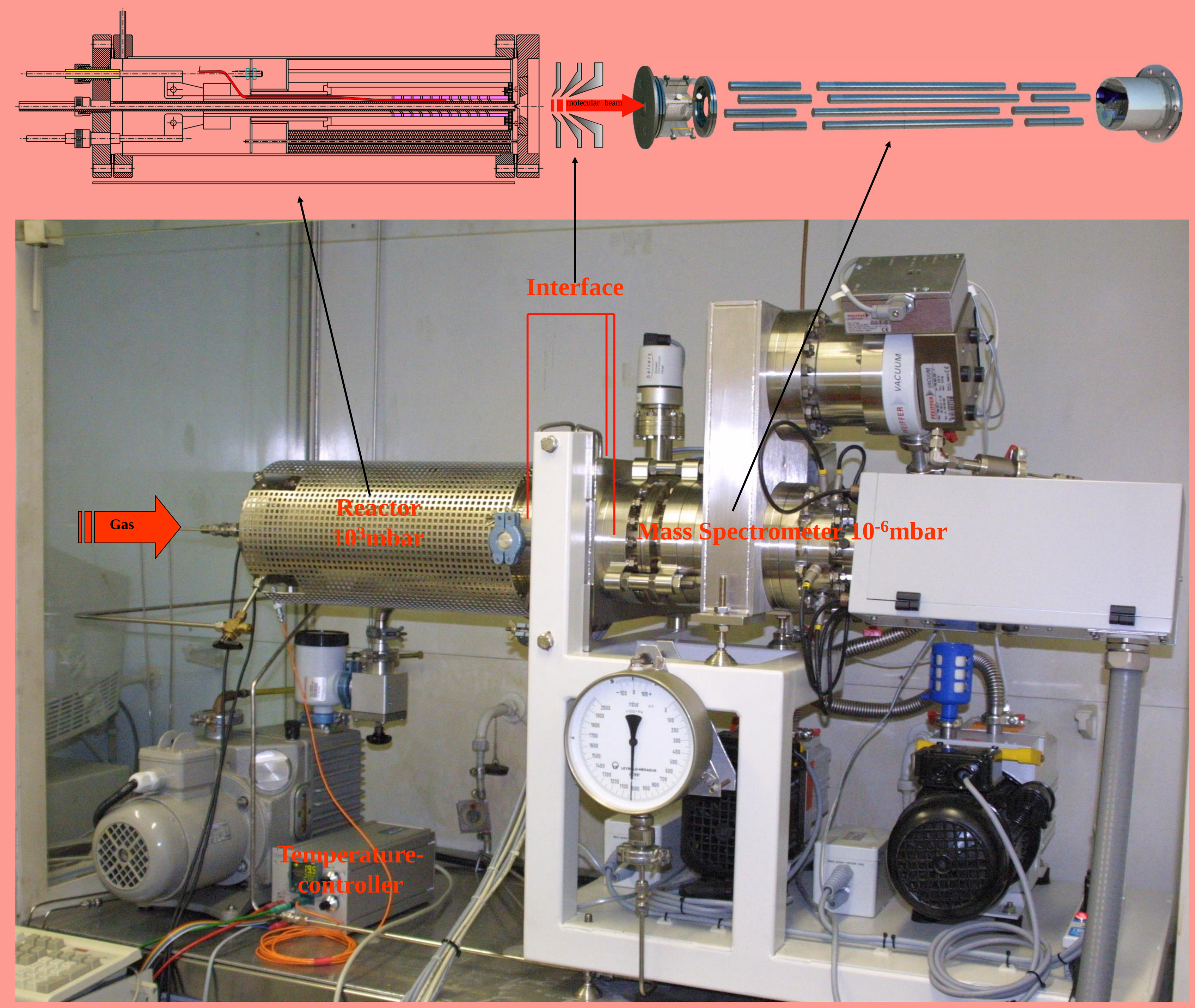
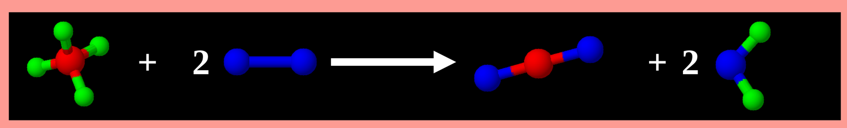
Motivation

In many heterogeneously catalysed reactions, the question arises whether the overall reaction occurs exclusively on the catalyst surface or whether gas phase reactions are involved in the mechanism. To answer this question, one has to probe the gas phase above the catalyst in situ with a very sensitive technique because of the short lifetime of the reactive intermediates and their low concentrations. Spectroscopic methods, as for example Laser Induced Fluorescence Spectroscopy (LIFS), Matrix Isolation ESR (MIESR) and Cavity Ring Down Spectroscopy (CRDS) are applicable but experimentally demanding and very expensive. Appearance Potential Mass Spectrometry is a comparatively cheap method developed in plasma-physics. The idea of AP-MS is to discriminate reactive intermediates from fragments of stable molecules at the same nominal mass by their ionisation or appearance potentials, respectively. The objective of this work is to verify whether AP-MS can be applied successfully to heterogeneous catalysis.

Experimental Setup

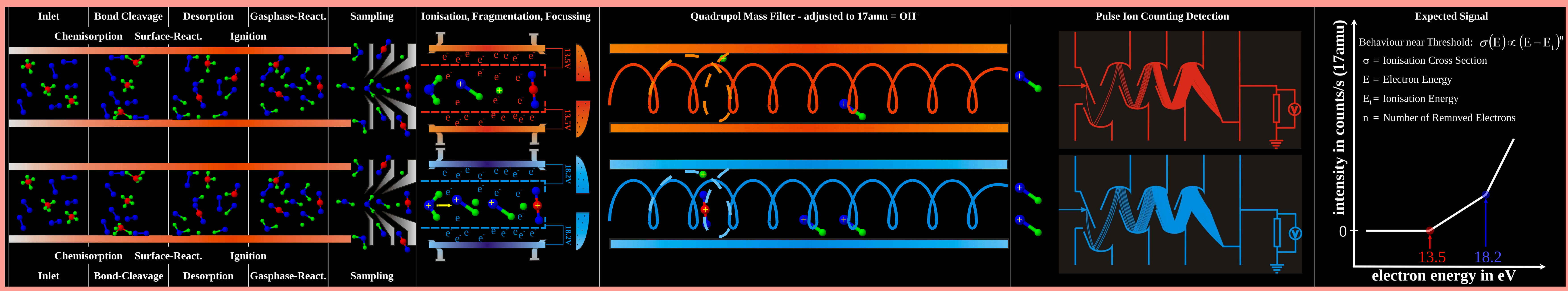


Test Reaction ⇒ Catalytic Combustion of Methane (CCM)



- catalyst → polycristalline platinum
- radical gas phase reactions expected ↔ combustion reaction
- highly exothermic reaction → $\Delta_R H^{\cdot} = -890 kJ \cdot mol^{-1}$

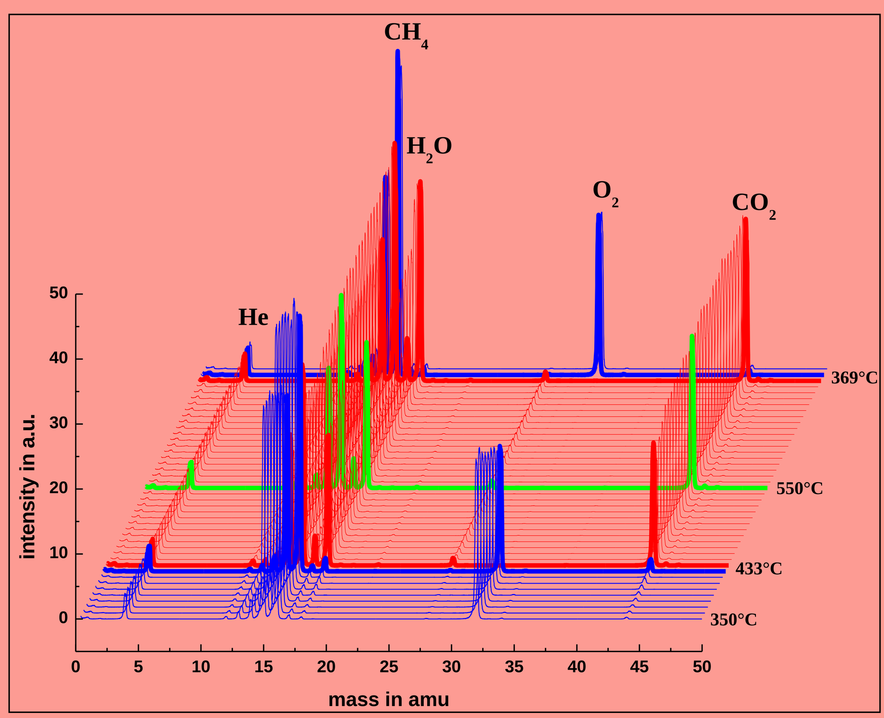
Ideas and Expectations



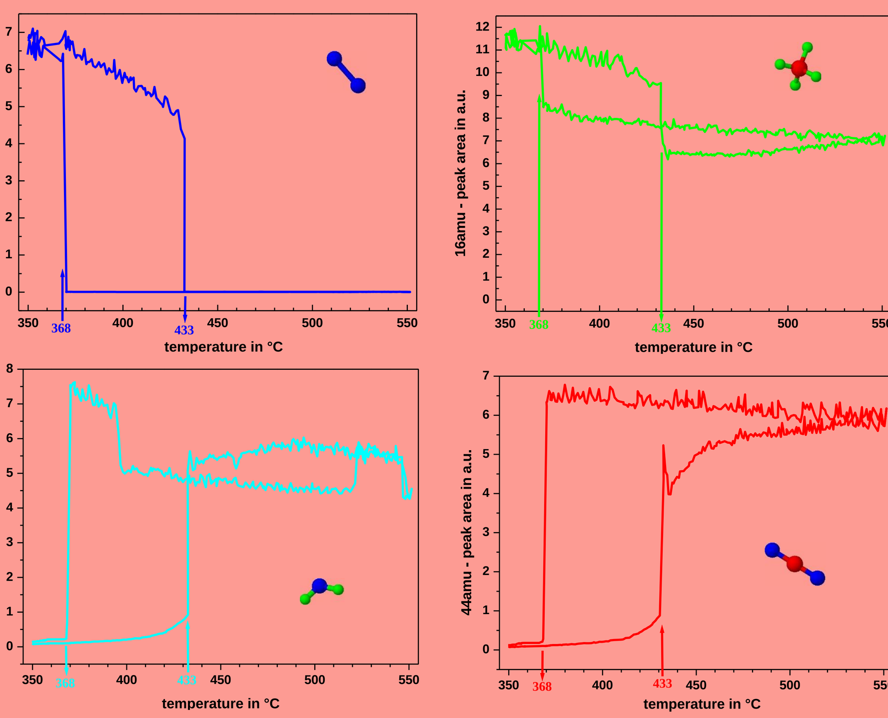
Experimental Verification:

- feed gas:
  49.5% CH_4 / 13.5% O_2 / 37% He
- spectra: 0.40 - 49.99amu, Δm=0.01amu
- temperature program:
  350°C ⇒ 550°C ⇒ 350°C
- temperature resolution:
  ≈ 0.5°C/min ≈ 1°C/spectrum
- internal standard: He

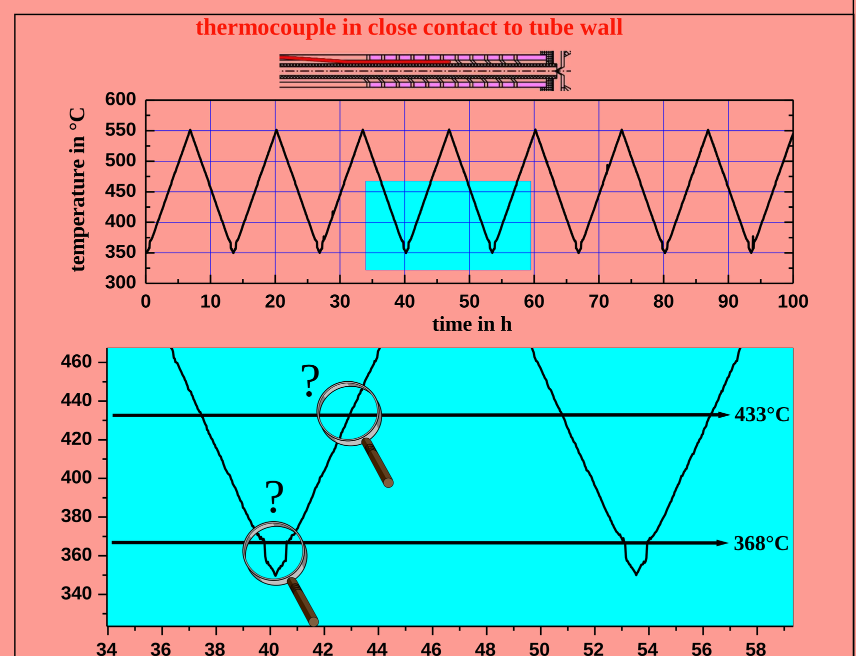
complete spectra

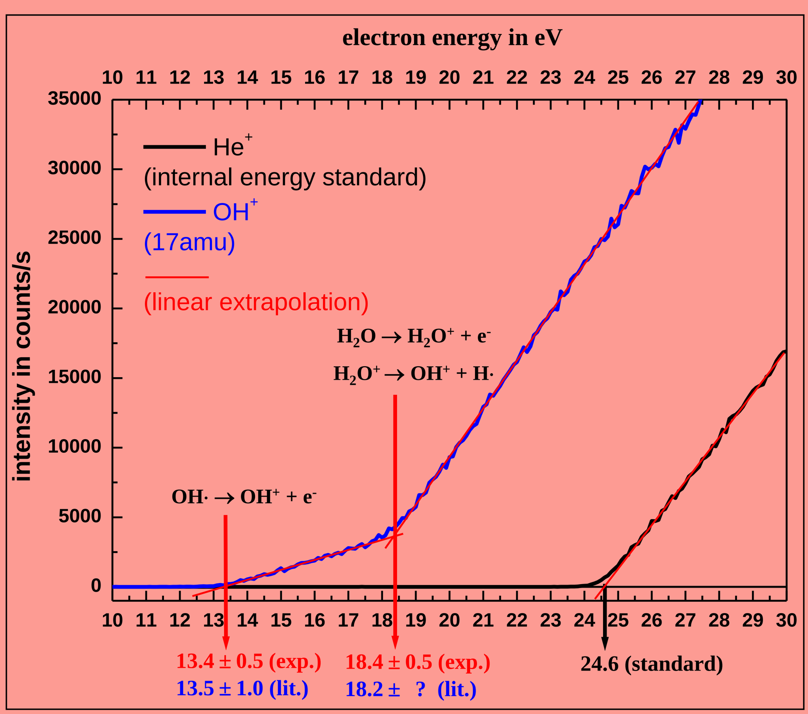


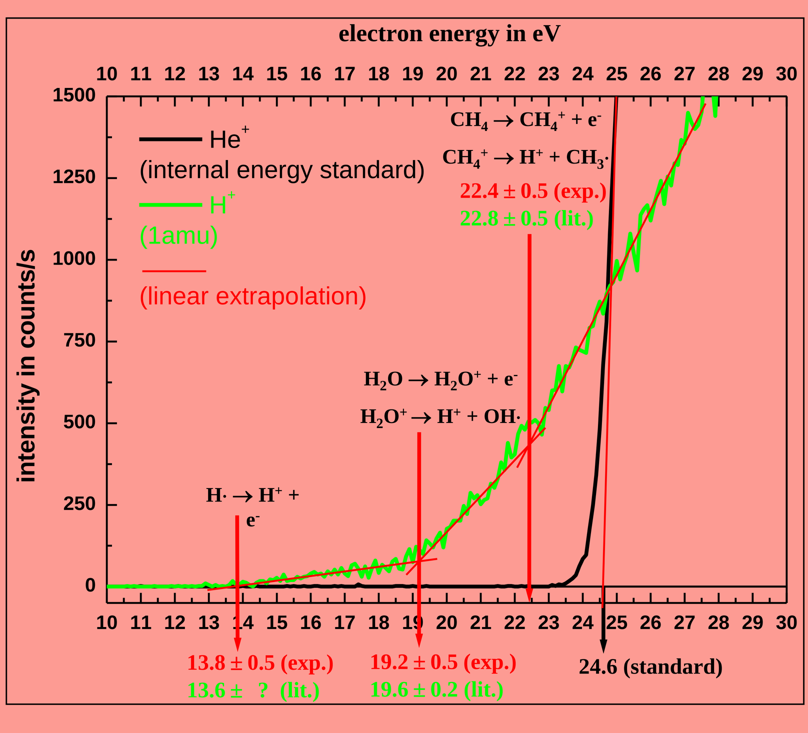
peak areas of O_2, CH_4, H_2O, CO_2



measured temperature program







RADICALS ?

Observations:

Heating:

- conversion starts at 368°C ⇒ instantaneous increase of recorded temperature
- ignition-like complete conversion of oxygen at 433°C ⇒ no change of recorded temperature

Cooling:

- complete oxygen conversion even for temperatures below 433°C
- sudden breakdown of the reaction at 368°C ⇒ instantaneous decrease of recorded temperature

Interpretation:

Heating:

- exothermal surface reaction starts at 368°C ⇒ generation of reactive intermediates (radicals)
- desorption of radicals ⇒ gas phase and surface reaction in parallel ⇒ no gas phase chain reaction below 433°C
- sufficient radical concentration at 433°C ⇒ ignition of gas phase chain reaction ⇒ no heat transport to surface

Cooling:

- the ignited gas phase chain reaction remains operating as long as surface supplies radicals
- breakdown of surface reactions at 368°C ⇒ gas phase chain reactions inhibited