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Combined quadrupole mass spectrometry and quartz-enhanced photoacoustic spectroscopy for the demonstration of plasma-based ammonia depletion

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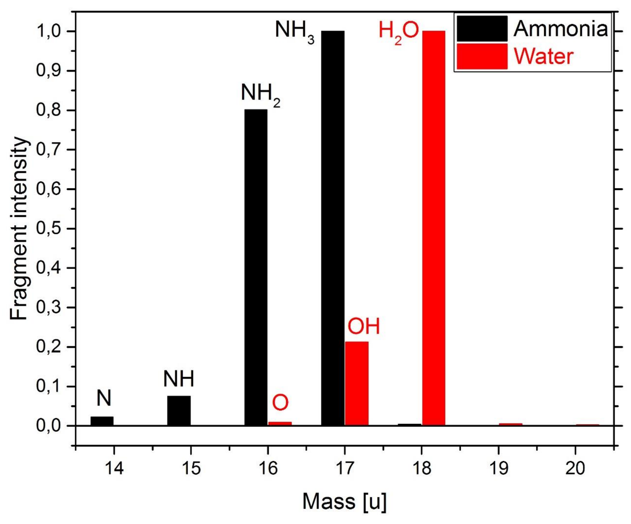
1. Introduction

Reducing ammonia contents in exhaust gas streams is very important for a large number of applications. The main origins of ammonia emissions are livestock feeding and industrial processing, e.g. during the production of rare earth metals. We implemented a highly efficient plasma-based process using a dielectric barrier discharge reactor.

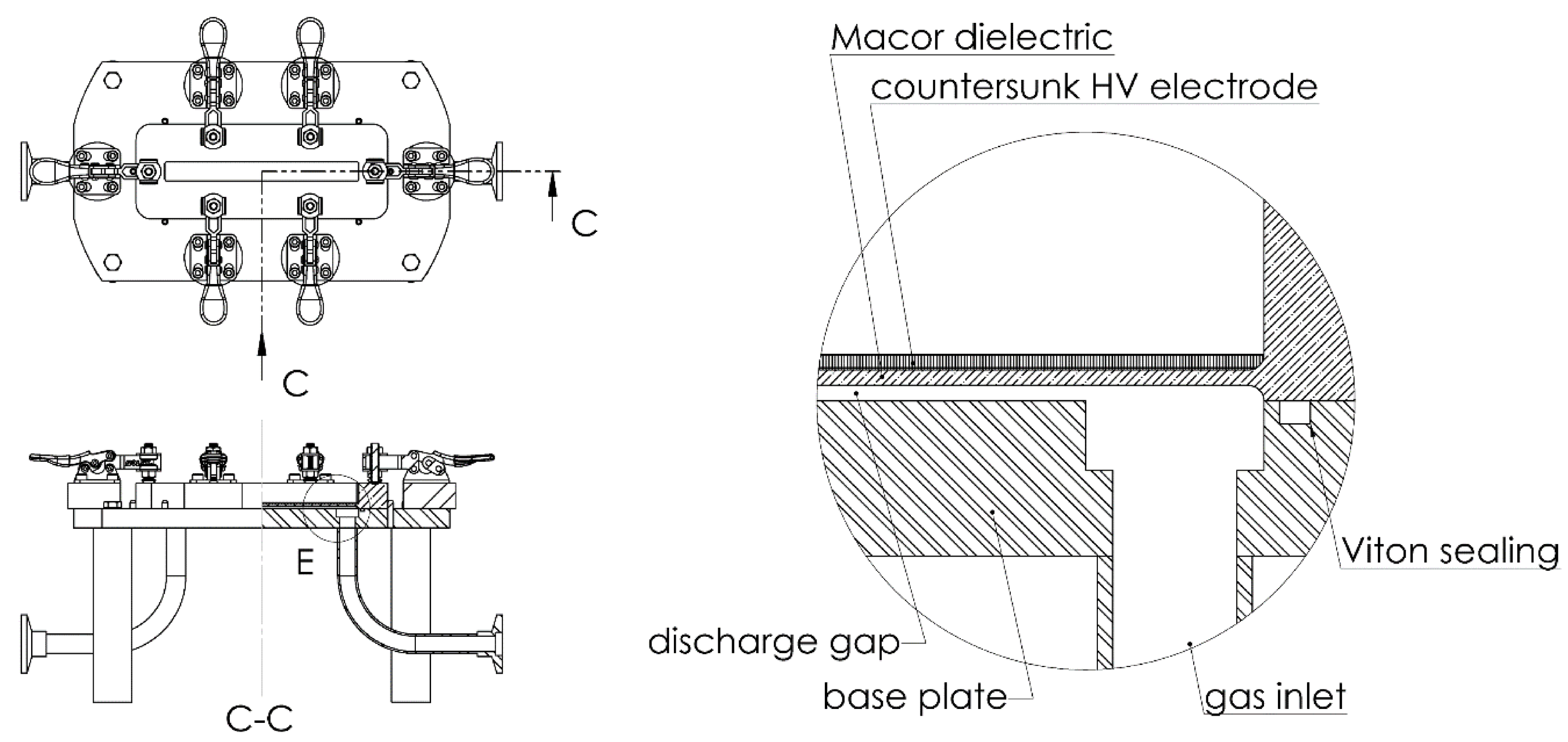


Reference data: NIST Mass Spectrometry Data Center Collection©

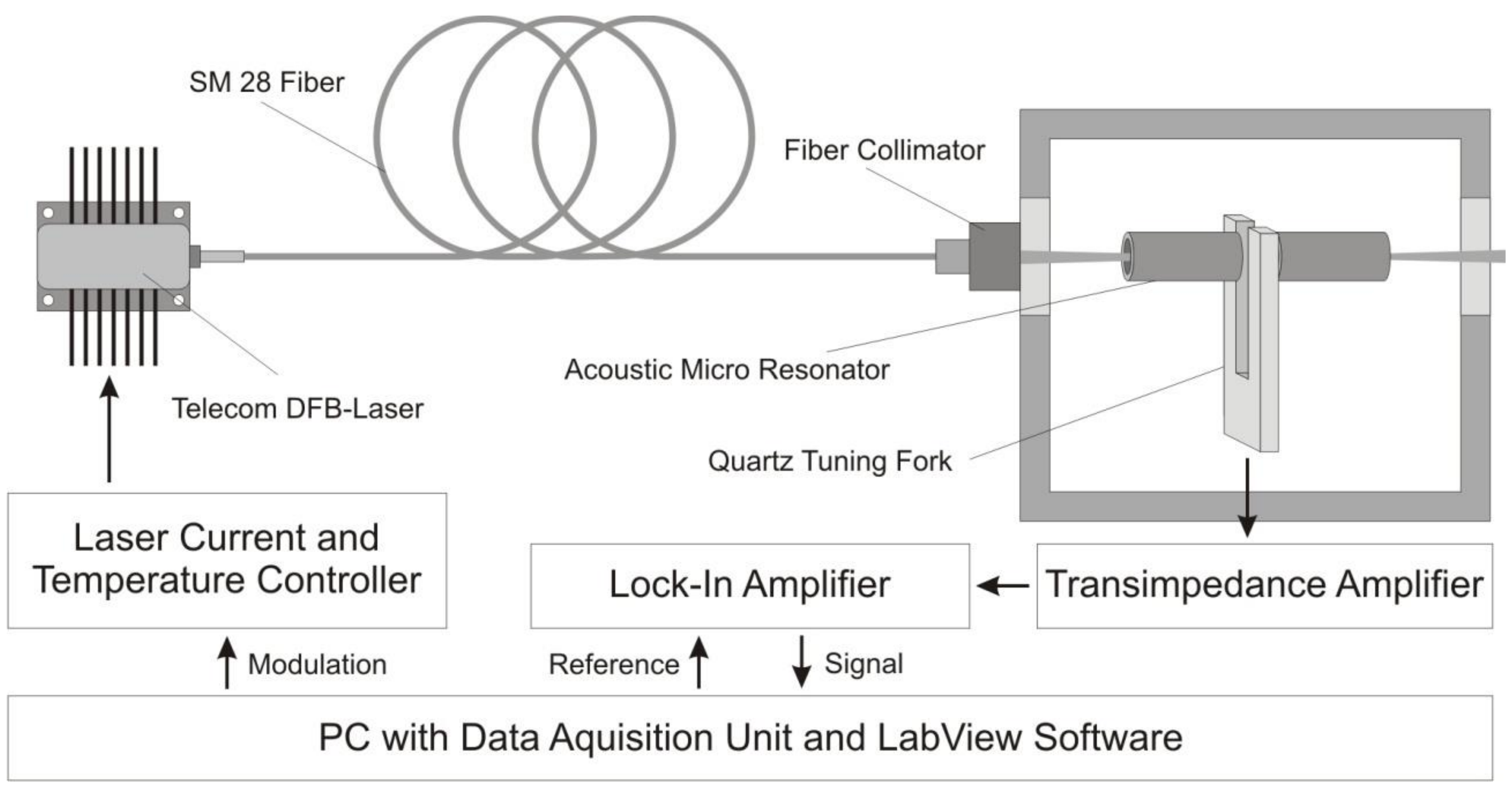
The influence of the plasma discharge on the gas composition was investigated employing quadrupole mass spectroscopy (QMS). Within the mass spectra, fragments of all species are visible. In the presented case, these fragments overlap with other gaseous components, i.e. OH and O overlap with NH_3 and NH_2, respectively. Usually, the components can be well separated employing reference spectra of the pure substances for the analysis of spectra from mixed gases.

Within plasma treated gases, however, fragments of all gaseous components are present at varying concentrations. This leads to difficulties in the interpretation of mass spectra. Therefore, we employed an inline quartz-enhanced photoacoustic sensor (QEPAS) for the determination of the ammonia concentration, while further gas species, especially ozone and NO_x are determined by QMS.

2. Plasma reactor



3. QEPAS setup

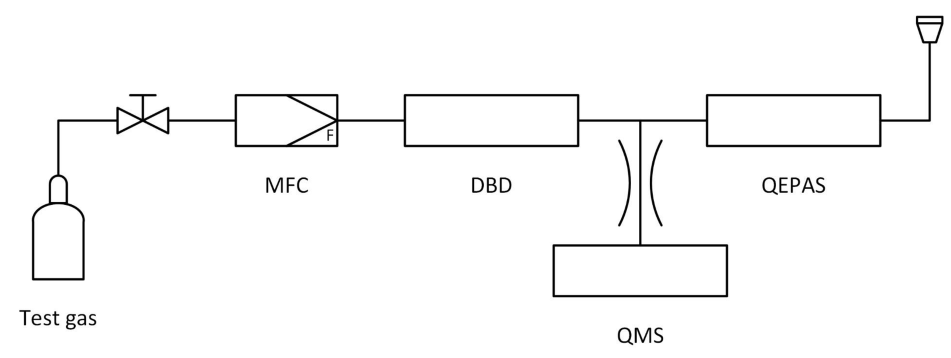


4. Gas flow setup

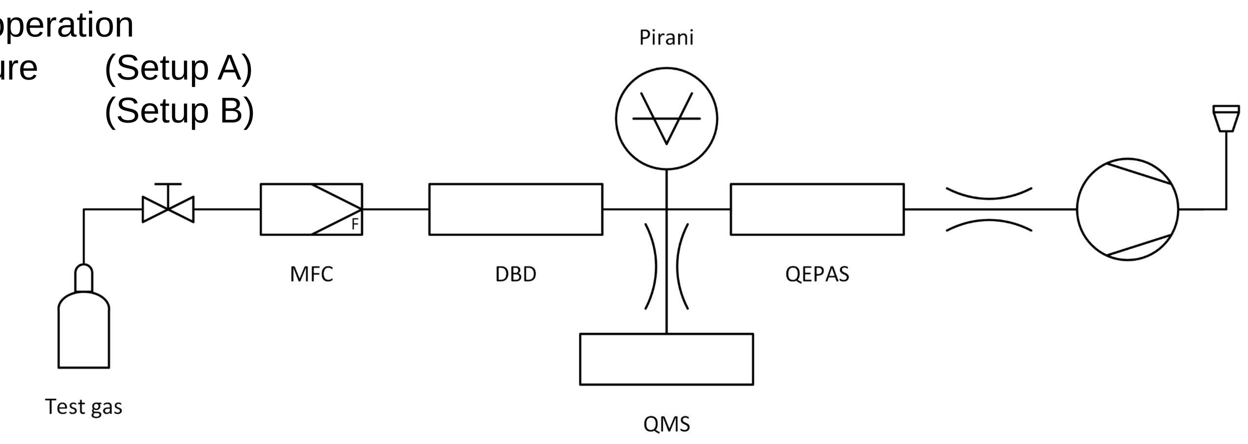
Commercial QMS device
(Multigas Analyzer, MFM Analytical Systems)

- Integrated pumping stage
- Gas inlet via pressure controlled self-adjusting leak valve
→ Avoiding segregation as in microcapillaries

- Two types of setups for operation
  - at atmospheric pressure (Setup A)
  - and at low pressure (Setup B)

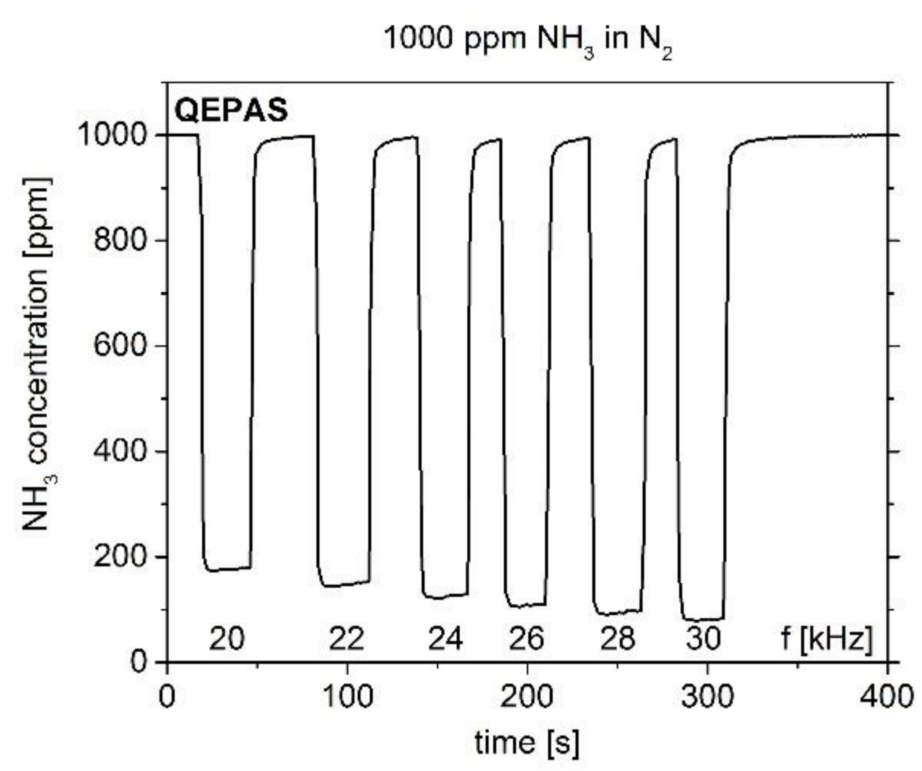


Setup A: Atmospheric pressure operation



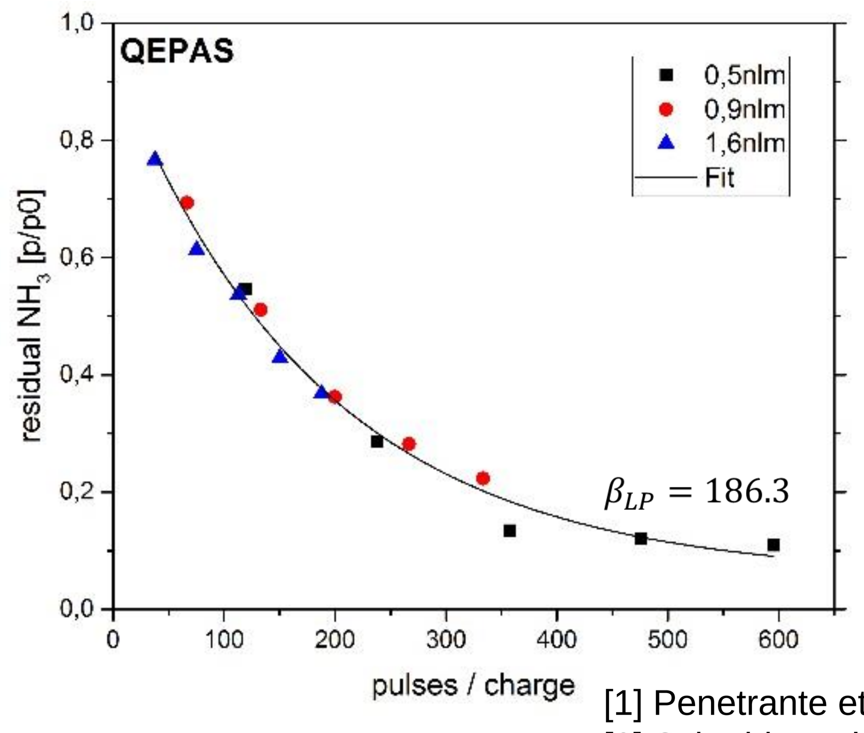
Setup B: Low pressure operation

5. Reaction times



- QEPAS reaction time ≤ 6 s
- QMS reaction time approx. 15 min for the used setup
- QMS spectra (6.c) taken after 45 min

6.a NH_3 depletion – low pressure



Display unit:
Pulses per reactor charge

$$N_V = \frac{f}{q} \cdot V$$

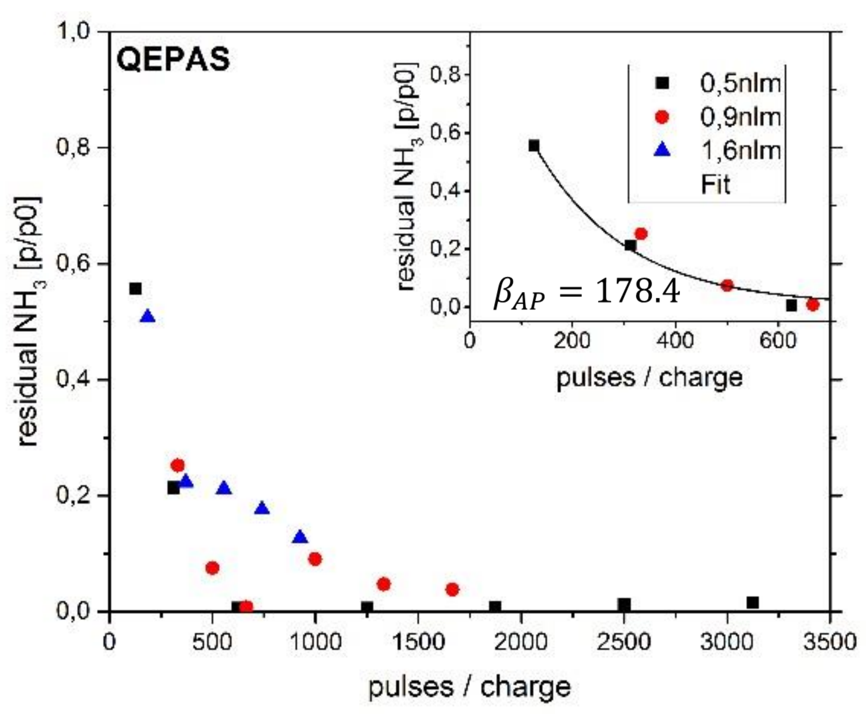
Exponential decay with N_V

$$p_{NH_3}/p_0 \sim e^{-N_V/\beta}$$

Similar behavior as found for other gaseous pollutants, c.f. [1,2] under the assumption of no significant scavenging reactions.

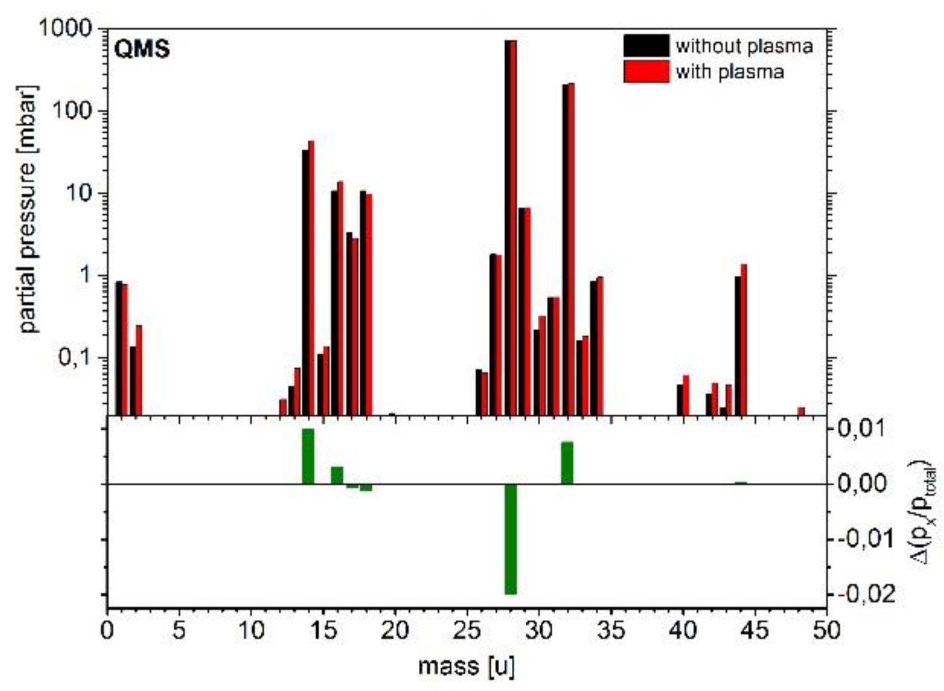
[1] Penetrante et al. 1997 Plasma Sources Sci. Technol. 6:251
[2] Schmidt et al. 2015 Open Chem. 13:477

6.b NH_3 depletion – atmospheric pressure



- Decay constant at atmospheric pressure and small pulse repetition rates comparable to those at atmospheric pressure
- At higher pulse repetition rates, the depletion rate decreases again
- Depletion maxima found at:
  - 10 kHz and 1.6 nlm
  - 15 kHz and 0.9 nlm
  - 25 kHz and 0.5 nlm

6.c NH_3 depletion – mass spectra



- Decrease of water and nitrogen due to dissociation
- Increase of peaks 16u, 32u and 44u, usually corresponding to O, O_2 and CO_2, respectively
→ Formation of hydrazine (N_2H_4)?
- Small amounts of ozone (6 ppm) and NO (100 ppm) found

8. Acknowledgements

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7. Summary

Reaction products from a plasma and fragmentation inside a QMS hinder the interpretation of mass spectra even at simple gas compositions. This problem can be overcome using QEPAS as an additional spectroscopic method that is barely affected by post-plasma gas species. Further, QEPAS has significantly shorter reaction times and is allowing to monitor gas species directly inside the gas stream.

Identifying processes and reactions from the plasma, however, is only possible via a combination of both analytical methods.

Thus, the formation of a significant amount of hydrazine during the depletion of ammonia in synthetic air was identified, as opposed to the dissociation of ammonia in nitrogen, which yielded mainly molecular nitrogen and hydrogen (not shown on this poster).

Plasma-
Enhanced
Reactions

Atom- und Molekülphysik an Oberflächen