Development of a dielectric barrier discharge source for efficient generation of charged water clusters at atmospheric pressure

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Introduction

Overview:

Water clusters [H+(H_2O)n]$^+$ play a key role concerning proton transfer mechanisms in ambient pressure ionization sources. Various sources have been developed to achieve high cluster concentrations.

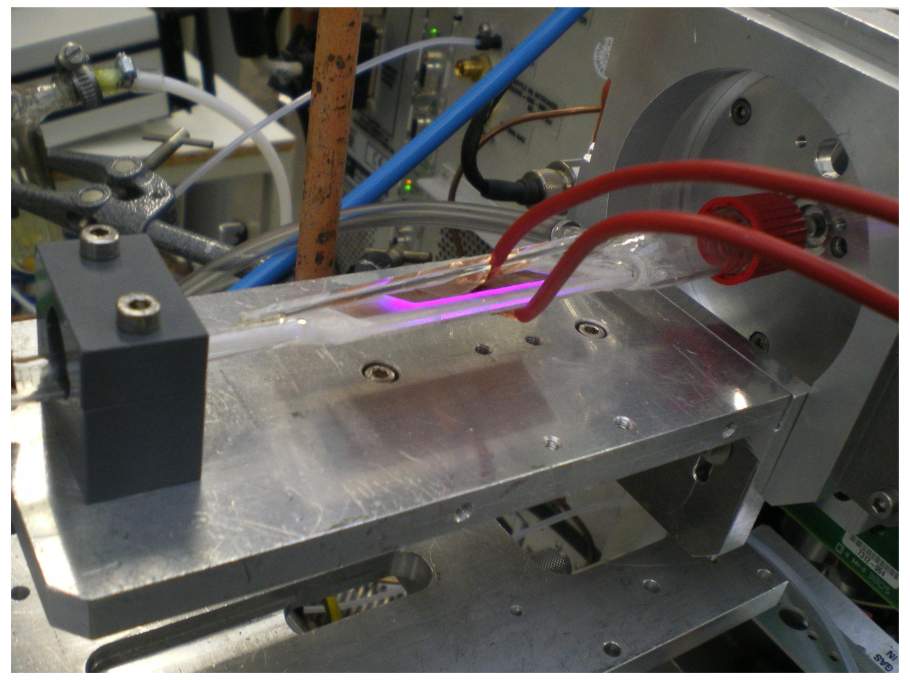
Approach:

The dielectric barrier discharge (DBD) operates far from thermodynamic equilibrium. The plasma consists of numerous non-stationary *streamers* starting randomly on the dielectric surfaces. The efficiency for the generation of ozone, for example, is well established. This study focusses on the DBD as an ionization source for atmospheric pressure MS.

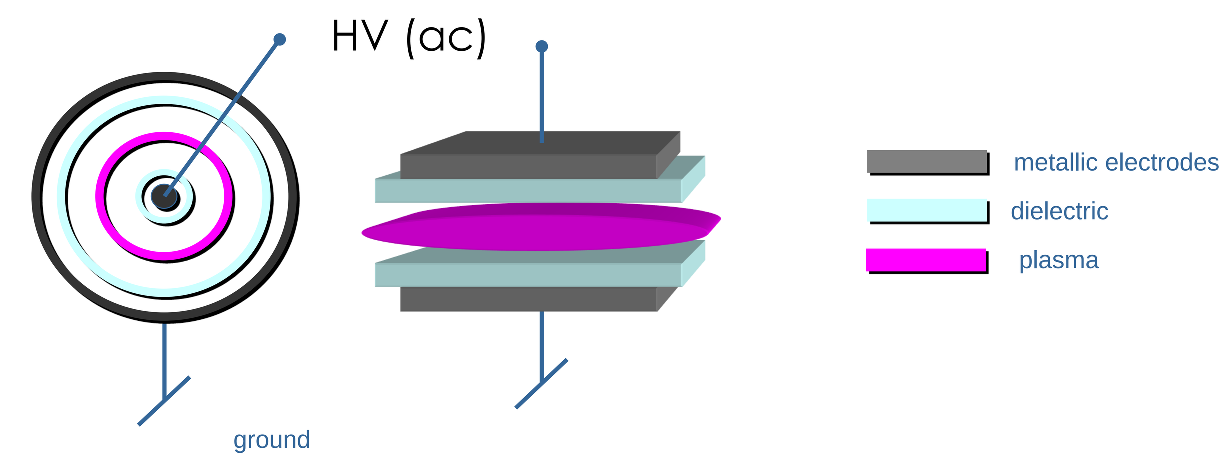
Methods

ionization source	custom dielectric barrier discharge sources - cylindrical design - planar design custom resonant high-voltage ac power supply - sinusoidal voltage - 0-11 kV amplitude - 20 kHz frequency, matched to (mostly capacitive) plasma load
discharge gases	Helium, Neon, Argon, Nitrogen, admixture of water
MS	Esquire 6000 QIT (quadrupole ion trap, Bruker Daltonics, Bremen, Germany) with - transfer capillary, - skimmer, - 2nd pumping stage, - 3rd stage for trap

Dielectric barrier discharge source (DBD)

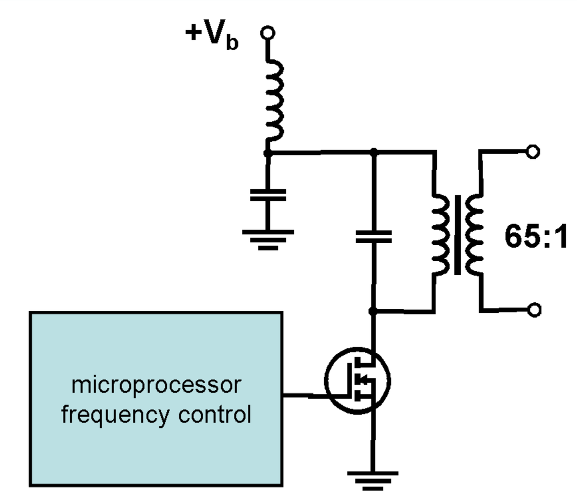


planar DBD source connected to MS



dimensions cylindrical DBDI:
- 25 mm electrode length
- ~4 mm distance

dimensions planar DBD:
- 50 mm x 15 mm area
- ~1 mm distance

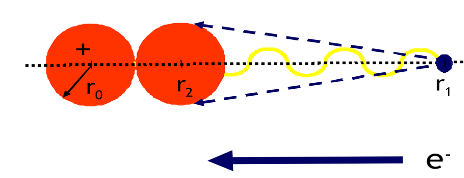


electronic driver circuit for high-voltage ac generation

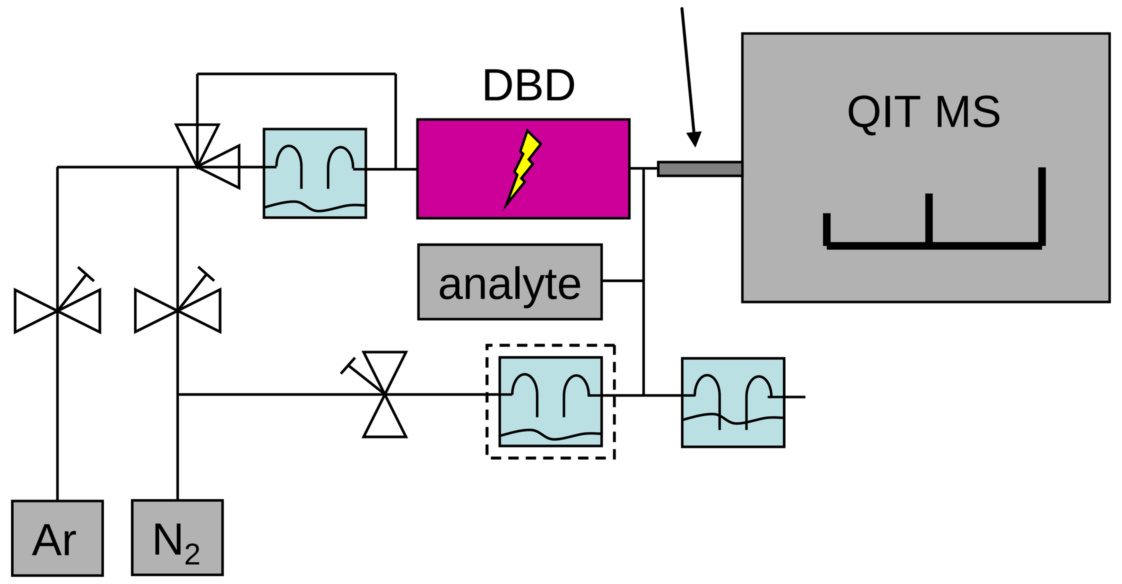
parallel LC resonator with voltage transformer (f = 20 kHz)

plasma operation at 1 bar:
- He: ignites readily at U_{pp} ~1 kV
- Ar: U_{pp} = 3-6 kV
- pure N_2: no ignition at U_{pp} < 11 kV
- N_2/Ar gas mixtures: ignition ~ 8 kV, gas mass flow ratios of up to 2:1

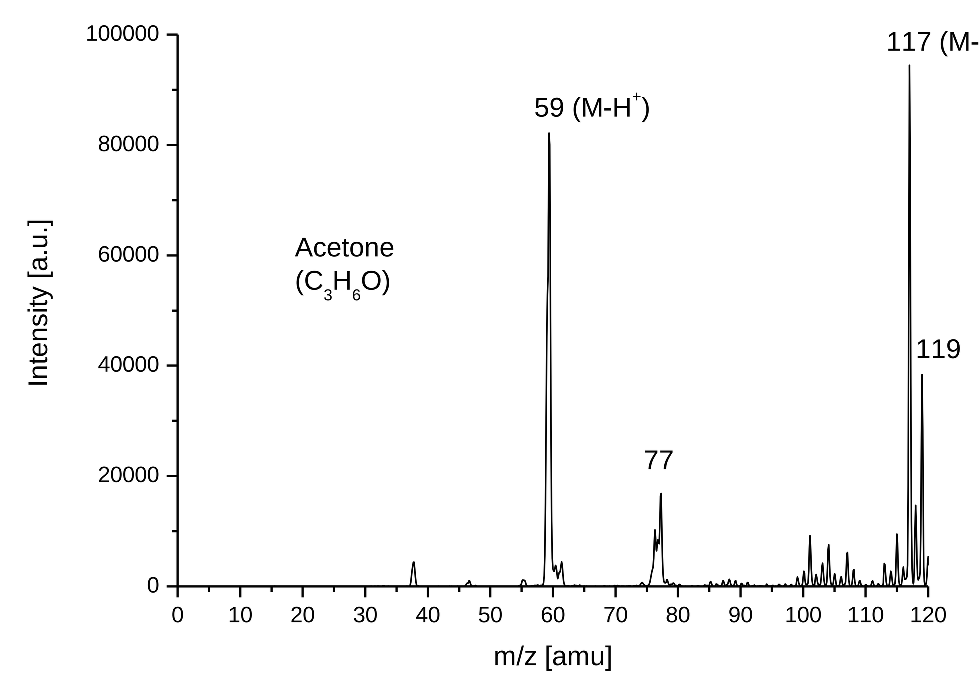
streamer generation dominated by:
- Townsend coefficients
- dV/dt
- electric field geometry [3, 4]



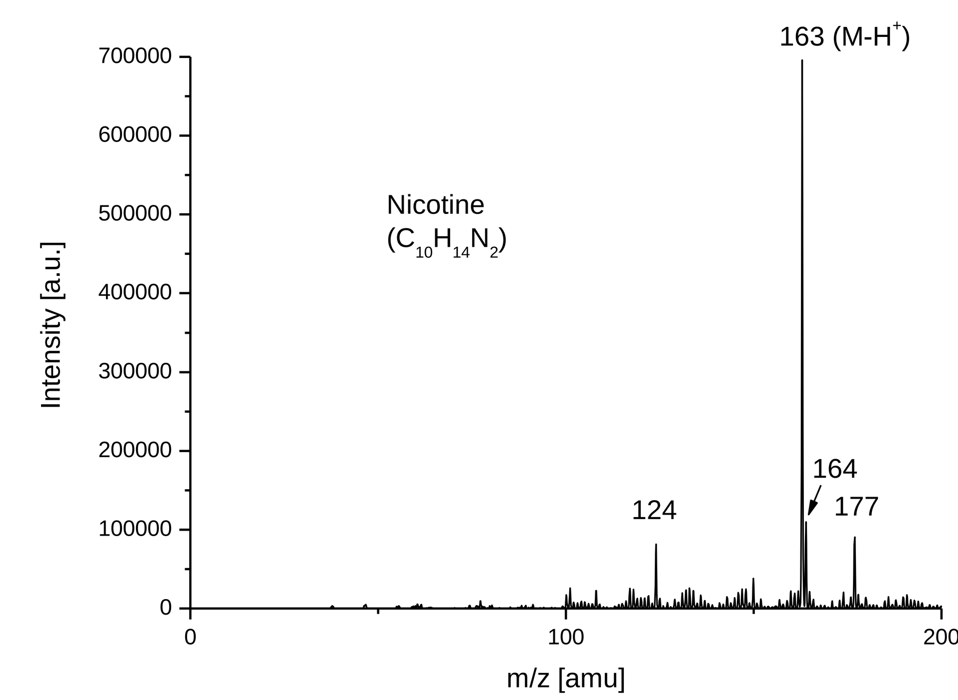
Mass spectra with analyte added downstream from DBD



DBD/MS experimental set-up. Total mass flow of 1.4 slm through transfer capillary enforced. Pressure control by water bubbler (bottom right).



conditions / results:
- only background water present
- N_2/Ar mixing ratio varied (0/1…2/1)
- intensity maximum at 0.1 N_2/Ar mixing ratio
- analyte added by small gas leak to laboratory air
- apparently high sensitivity for acetone (nicotine not determined yet)



[H+ (H_2O)n]$^+$ water cluster generation

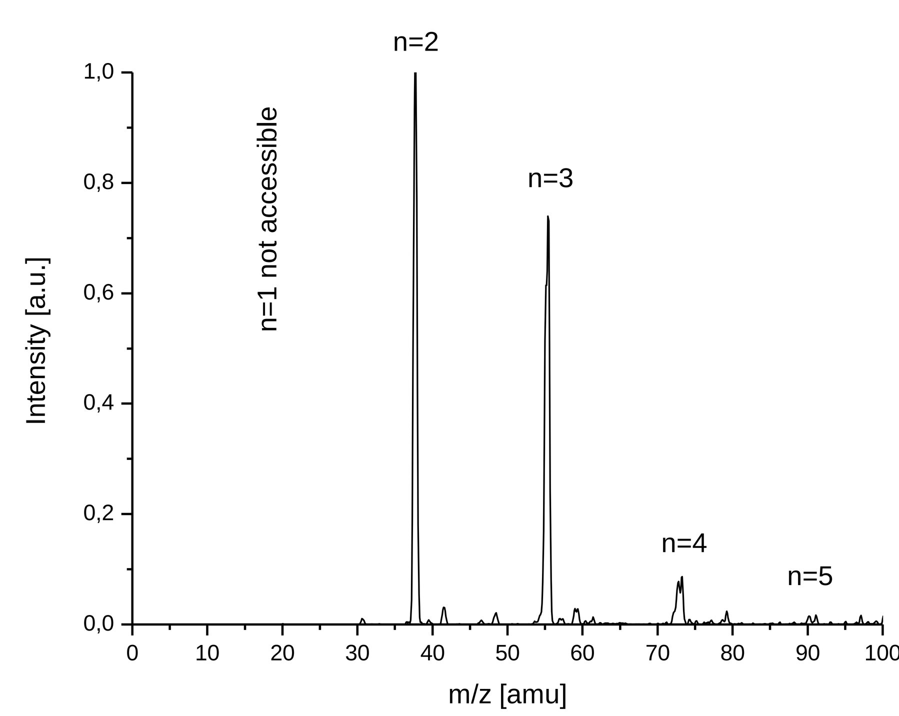
conditions / results:

sensitivity for water cluster detection depends critically on:

- capillary-to-skimmer drift voltage
- RF amplitude at octopole stage
- ion trap storage voltage

DBD effectively generates water clusters; n=2…5 observable, in pure Ar

small water concentration at ambient pressure in the ppmV range is sufficient

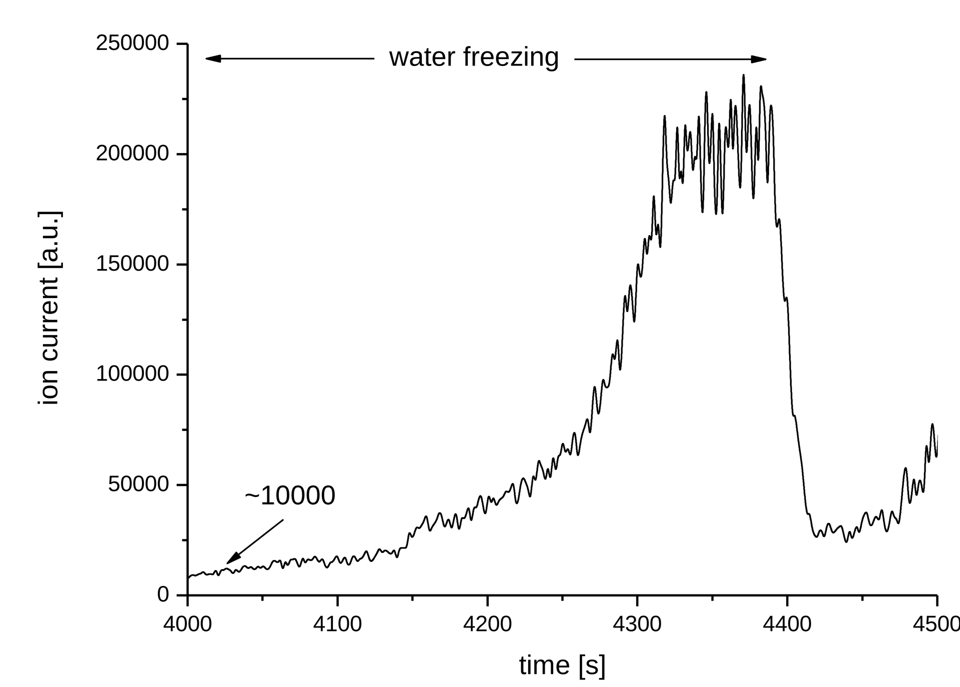


conditions:
water admixture by exposing Ar gas to liquid water reservoir upstream from DBD, then freezing the reservoir

results:
overall ion signal decreases drastically (see right Figure)

but increases again to previous value if cooling is stopped

- adding water to the discharge decreases the plasma density and ionization efficiency
- adding water externally should be done downstream from the DBD



Conclusions

- DBD plasma source is a non-thermal surface discharge that operates without metallic electrodes at ambient pressure
- runs stable in He, Ar, N_2/Ar mixtures for prolonged times
- analyte is typically supplied downstream from the discharge; direct ionization of the analyte within the DBD not useful
- signals increase when small amounts of N_2 (10%) are added to Ar in the plasma zone
- even small N_2 concentrations immediately change the discharge color ⟶ pink afterglow
- detection of water clusters requires careful adjustment of MS parameters
- H_2O gas may be added upstream or downstream from the discharge
- if water is added upstream from the DBD, then the Ar discharge can hardly be ignited and operates only dimly; ion signal decreases drastically
- by adjusting the water mixing ratio added through freezing, the ion signal increases by more than an order of magnitude
- n=2,3,4,5 clusters detected in the downstream configuration
- clusters observed in Ar plasma

References

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