Optická emisní spektroskopie atomů

Diagnostické metody 1

Zdeněk Navrátil

Ústav fyziky a technologií plazmatu
Přírodovědecká fakulta Masarykovy univerzity, Brno

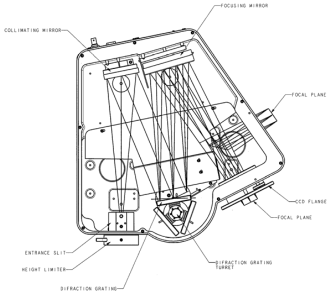
Outline

1. OES
2. CR modelling

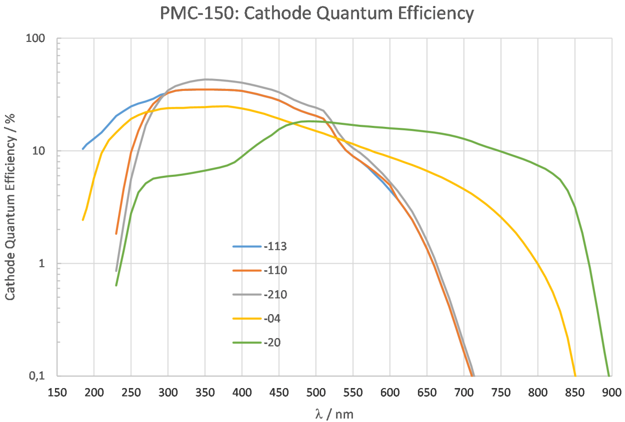
Instrumentation

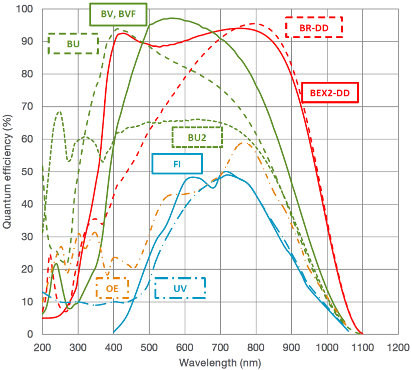
- typically grating spectrometer of Czerny-Turner mounting equipped with CCD/ICCD detector
- typical spectral range 190 – 1100 nm
- sensitivity of detectors (silicon CCD, photocathode of PMT), grating efficiency
- resolution: number of illuminated grating grooves, slit width, pixel size

$$R = \lambda/\Delta\lambda = mN$$



Sensitivities





- grating efficacy, fibre efficacy, windows

Technique overview – how we measure

- collecting the light emitted by plasma (optical emission spectroscopy, OES):
  - non-intrusive
  - sensing the light at the plasma boundary
  - optical probes
- sending the light through the plasma (optical absorption spectroscopy):
  - based on Lambert-Beer law
  - can disturb the plasma, two ports
  - white light, hollow cathode lamps, lasers
- collecting the light emitted and reabsorbed by the plasma (self-absorption methods of OES)

Technique overview – how we measure

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  - sensing the light at the plasma boundary $\rightarrow$ self-absorption can play a role
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Technique overview – what we look at

- line positions = wavelengths: electric, magnetic fields, atom velocities (Stark, Zeeman, Doppler effect)
- lineshapes and linewidths: electron density, gas pressure, density, temperatures (Stark, van der Waals, resonance, Doppler line broadening)
- line intensities: . . . all

Technique overview – what we look at

- line positions = wavelengths: electric, magnetic fields, atom velocities (Stark, Zeeman, Doppler effect)
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- line intensities: . . . all
  - relative – instrument spectral sensitivity is taken into account, no absolute intensity calibration is performed
    output: relative populations of excited states, excitation temperatures etc.
  - absolute – access to absolute densities of excited states, electron density etc.

Absolute intensity measurement

- radiant flux/zářivý tok – energy emitted/incident on surface per unit time

$$\Phi = \frac{\mathrm{d}\mathscr{E}}{\mathrm{d}t}, \quad \mathrm{W} \tag{1}$$

- irradiance – flux density (per unit surface)

$$I = \frac{\mathrm{d}\Phi}{\mathrm{d}S} = \frac{\mathrm{d}^2\mathscr{E}}{\mathrm{d}t\mathrm{d}S}, \quad \mathrm{W\,m^{-2}} \tag{2}$$

  - specified during calibratrion of calibrated light sources (spectral irradiance)
  - optical fibre is not a detector of irradiance (acceptance angle)
  - radiometric irradiance probes, cosine correction diffusers, integrating spheres, ...

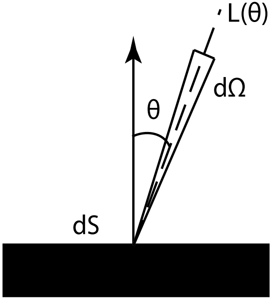
Absolute intensity measurement 2

- radiance (zář) – radiant flux per unit perpendicular surface and unit solid angle

$$L = \frac{\mathrm{d}^2\Phi}{\mathrm{d}S\cos\theta\,\mathrm{d}\Omega} = \frac{\mathrm{d}^3\mathscr{E}}{\mathrm{d}t\,\mathrm{d}S\cos\theta\,\mathrm{d}\Omega}, \quad \mathrm{W\,m^{-2}\,sr^{-1}} \tag{3}$$

- radiance $\times$ irradiance

$$I = \int_{\Omega} L(\theta)\cos\theta\,\mathrm{d}\Omega \tag{4}$$



For constant L (Lambert) radiators $I = \pi L$.

- for description of radiating solid surfaces

Absolute intensity measurement 3

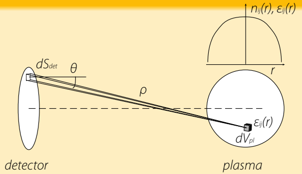
- emission coefficient – radiant power emited by unit volume into unit solid angle

$$j = \frac{\mathrm{d}^3\mathscr{E}}{\mathrm{d}t\,\mathrm{d}V\,\mathrm{d}\Omega}. \tag{5}$$

- all quantities have their spectral densities, e.g. $j(\lambda)$

emission coefficient of transition

$$j_{ij} = \frac{1}{4\pi} n_i A_{ij} h\nu_{ij}$$



$$I_{ij} = \frac{1}{S_{\mathrm{det}}} \int_{V_{\mathrm{pl}}} \int_{S_{\mathrm{det}}} \frac{j_{ij}(r)}{\rho^2} \mathrm{Acc}(\theta) \mathrm{d}V_{\mathrm{pl}} \mathrm{d}S_{\mathrm{det}}$$

irradation of detector for optical thin plasma condition

Electron temperature from Boltzmann plot?

- density of atoms in excited state

$$n_i = n\frac{g_i}{Q}\mathrm{e}^{-\frac{\mathscr{E}_i}{k_\mathrm{b} T_\mathrm{e}}} \tag{6}$$

2 g_i – statistical weight, $\mathscr{E}_i$ – excitation energy, n – atom density, Q – state sum, T_e excitation ($\stackrel{?}{=}$ electron) temperature

- spectral line intensity

$$I \propto n_i A_{ij} \frac{hc}{\lambda} \tag{7}$$

$$I = C \cdot \frac{g_i A_{ij}}{\lambda}\mathrm{e}^{-\frac{\mathscr{E}_i}{k_\mathrm{b} T_\mathrm{e}}} \tag{8}$$

- Boltzmann plot

$$\ln \frac{I\lambda}{g_i A_{ij}} = -\frac{1}{k_\mathrm{b} T_\mathrm{e}}\mathscr{E}_i + \ln k_1, \tag{9}$$

Possibility of electron temperature measurement

excited level balance

- local thermodynamic equilibrium (LTE) plasma
  - LTE condition

$$n_e \gg 1.6 \cdot 10^{12} \sqrt{T_e} (\Delta E)^3 \quad (\mathrm{cm}^{-3})$$

  - electron temperature from Boltzmann plot
- non-LTE plasma
  - corona equilibrium, excitation saturation phase, . . .
  - low electron density plasma
  - use of Boltzmann-plot leads to erroneous electron temperature
  - CR modelling

non-Maxwellian EDF

- inelastic collisions, beam electrons, non-local EDF

Collisional-radiative modelling

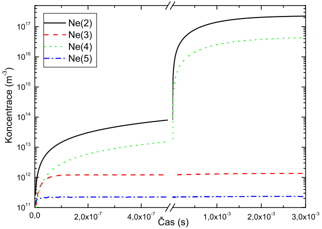
coupled DE for densities of excited states

$$\frac{\partial n_i}{\partial t} + \nabla(n_i \vec{v}) = \left(\frac{\partial n_i}{\partial t}\right)_{\mathrm{c,r}} \quad (10)$$

population and depopulation processes are very fast:

$$\frac{\partial n_i}{\partial t} = \left(\frac{\partial n_i}{\partial t}\right)_{\mathrm{c,r}} = 0 \quad (11)$$

not valid for ground-state atoms, ions, metastables, high pressure



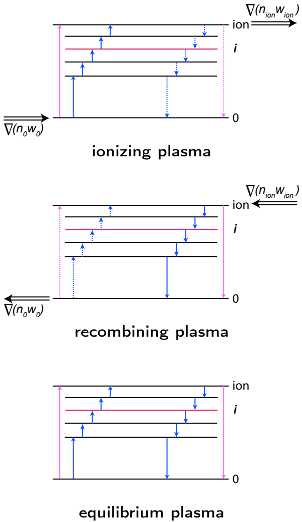
Level balance

$$\frac{\partial n_0}{\partial t} + \nabla(n_0 \vec{v_0}) = -S_{\rm cr} n_{\rm e} n_0 + \alpha_{\rm cr} n_{\rm e} n_{\rm ion}$$

$$\frac{\partial n_{\rm ion}}{\partial t} + \nabla(n_{\rm ion} \vec{v_{\rm ion}}) = +S_{\rm cr} n_{\rm e} n_0 - \alpha_{\rm cr} n_{\rm e} n_{\rm ion}$$

classification of models (plasma state)

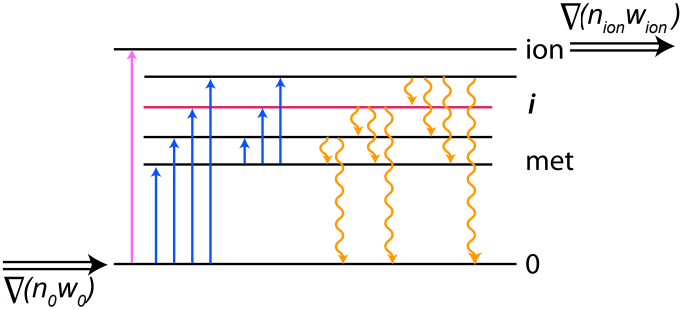
- ionizing plasma $S_{\rm cr} n_{\rm e} n_0 - \alpha_{\rm cr} n_{\rm e} n_{\rm ion} > 0$
  - plasma conducting current, ionizing waves
- recombining plasma $S_{\rm cr} n_{\rm e} n_0 - \alpha_{\rm cr} n_{\rm e} n_{\rm ion} < 0$
  - afterglows, outer regions of flames
- equilibrium plasma $S_{\rm cr} n_{\rm e} n_0 - \alpha_{\rm cr} n_{\rm e} n_{\rm ion} = 0$ (ioniozation-recombination equilibrium)



Excitation phases: corona phase

population by electron impact excitation, radiative deexcitation

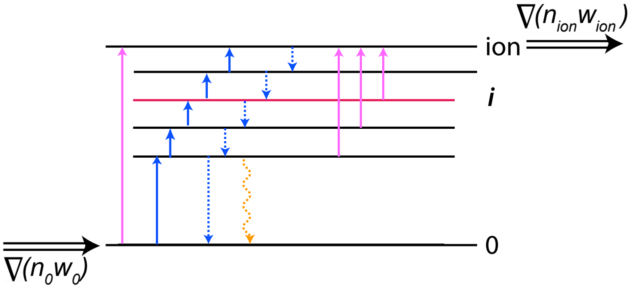
$$k^{\mathrm{el}}_{0i} n_{\mathrm{e}} n_0 + k^{\mathrm{el}}_{\mathrm{m}i} n_{\mathrm{e}} n_{\mathrm{m}} (+ \sum_{j>i} \Lambda_{ji} A_{ji} n_j) = \sum_{j<i} \Lambda_{ij} A_{ij} n_i$$



Excitation phases: excitation saturation phase

population and depopulation by electron impact

$$\sum_{j \neq i} k_{ji}^{\mathrm{el}} n_{\mathrm{e}} n_j + (\alpha_i n_{\mathrm{e}} n_{\mathrm{ion}}) = \sum_{j \neq i} k_{ij}^{\mathrm{el}} n_{\mathrm{e}} n_i + S_i n_{\mathrm{e}} n_i$$

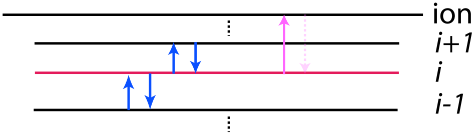


- saturation of the excited state densities with increased n_{e}
- no Saha equilibrium, $S_i n_i \gg \alpha_i n_{\mathrm{ion}}$

Excitation phases: excitation saturation phase 2

- stepwise excitation → ladder-like excitation flow
- coefficients of upward processes are larger (closer upper levels, higher statistical weights of upper levels)

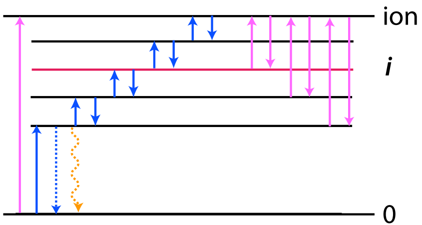
$$k_{i-1,i} n_e n_{i-1} - k_{i,i-1} n_e n_i = k_{i,i+1} n_e n_i - k_{i+1,i} n_e n_{i+1} + S_i n_e n_i$$



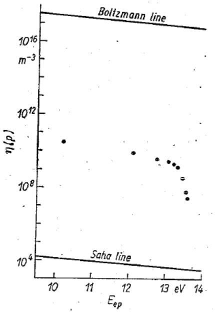
Excitation phases: partial local thermodynamic equilibrium

- 2 equilibria: excited state $\times$ ion state, neighbouring excited states
- ionization $\sim$ recombination $\gg$ excitation flow

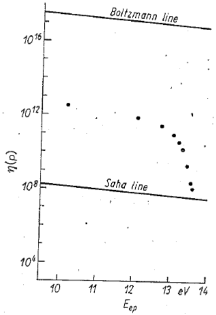
$$k_{i-1,i} n_\mathrm{e} n_{i-1} - k_{i,i-1} n_\mathrm{e} n_i = k_{i,i+1} n_\mathrm{e} n_i - k_{i+1,i} n_\mathrm{e} n_{i+1} - S_i n_\mathrm{e} n_i + \alpha_i n_\mathrm{e} n_\mathrm{ion}$$



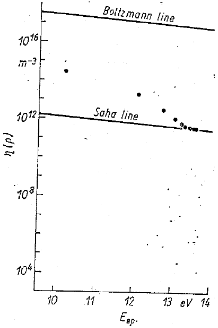
Role of dominant electron collisions



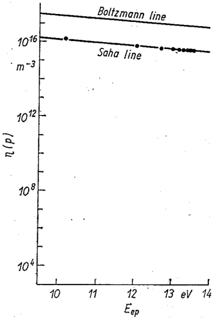
$n_e = 10^{16}\ \mathrm{m}^{-3}$



$n_e = 10^{18}\ \mathrm{m}^{-3}$



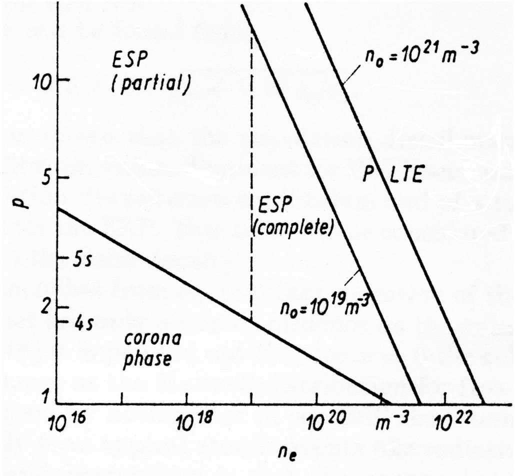
$n_e = 10^{20}\ \mathrm{m}^{-3}$



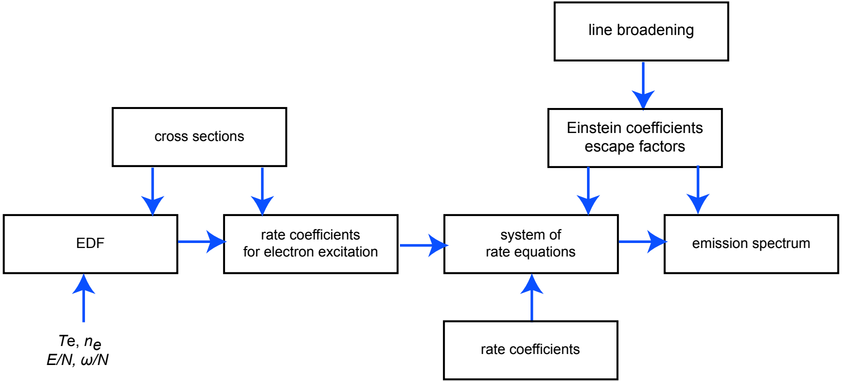
$n_e = 10^{22}\ \mathrm{m}^{-3}$

Boltzmann	$n_i^B = n_0 g_i / g_0 \mathrm{e}^{-E_i/kT_\mathrm{e}}$
Saha	$n_i^S = n_\mathrm{e} n_\mathrm{ion} \frac{g_i}{g_e g_\mathrm{ion}} (h^2/2\pi m_\mathrm{e} k T_\mathrm{e})^{3/2} \mathrm{e}^{E_{ion,i}/kT_\mathrm{e}}$
deviation from B & S	$n_i = r_i^0 n_i^S + r_i^1 n_i^B$

Excitation phases



Collisional-radiative model



Electron distribution function

- Maxwellian EDF
- solution of Boltzmann kinetic equation
- normalization of the EDF

$$\int_0^\infty f(\varepsilon)\varepsilon^{1/2}\mathrm{d}\varepsilon = 1 \tag{12}$$

- mean electron energy

$$\langle\varepsilon\rangle = \int_0^\infty f(\varepsilon)\varepsilon^{3/2}\mathrm{d}\varepsilon, \tag{13}$$

- rate coefficients k, k_{inv} of electron collision with cross section σ and of inverse process

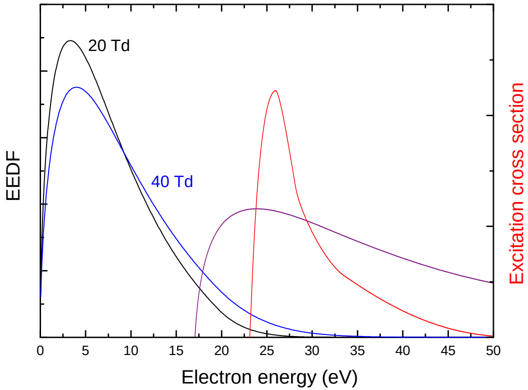
$$k = \sqrt{\frac{2e}{m_{\mathrm{e}}}}\int_0^\infty \sigma(\varepsilon)f_0(\varepsilon)\varepsilon\mathrm{d}\varepsilon$$

$$k_{\mathrm{inv}} = \sqrt{\frac{2e}{m_{\mathrm{e}}}\frac{g_j}{g_i}}\int_{\varepsilon_{ij}}^\infty \sigma(\varepsilon)f_0(\varepsilon-\varepsilon_{ij})\varepsilon\mathrm{d}\varepsilon$$

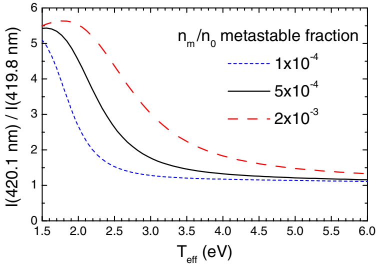
Approaches of OES data processing

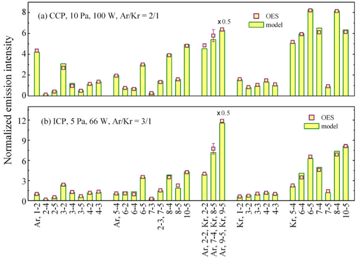
- line ratio methods
  - selection of convenient line pair (sensitivity, model simplicity, ease of measurement)
  - no control of model validity
- „many line fitting“methods

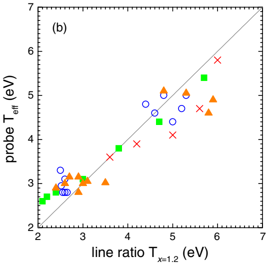
Line ratio method – ideal case

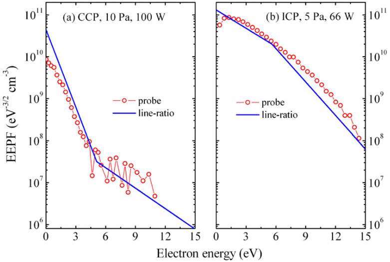


Electron temperature and EDF measurement by OES+CR

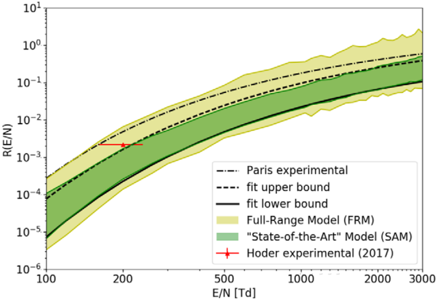


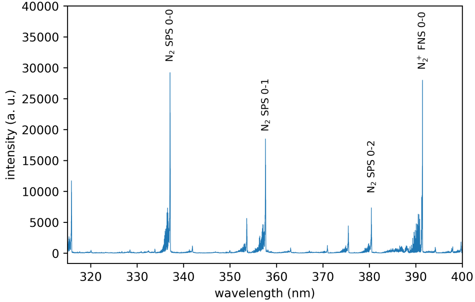






Electric field measurement in air





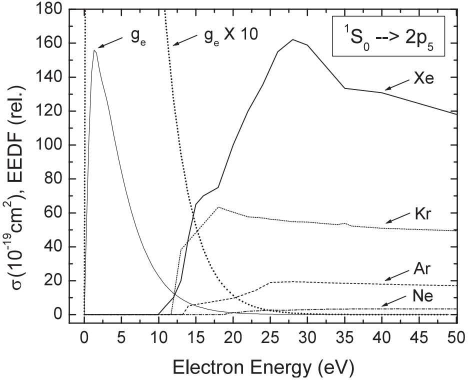
$$R(E/N) = \frac{FNS(0,0)}{SPS(0,0)}$$

Kozlov and Wagner 2001 *J. Phys. D: Appl. Phys.* **34** 3164

Bilek *et al* 2018 *Plasma Sources Sci. Technol.* **27** 085012

TRG spectroscopy

- based on admixing of a small amount of rare gas into plasma
- mapping EDF at specific electron energies
- low pressure, what is small amount?



Helium line ratio method

- ratio of helium singlet lines $R = I_{667}/I_{728}$
  He I 667.8 nm ($2\,^1P - 3\,^1D$)
  He I 728.1 nm ($2\,^1P - 3\,^1S$)

✓ high spectral resolution is not required

✓ sensitive to fields of several kV/cm

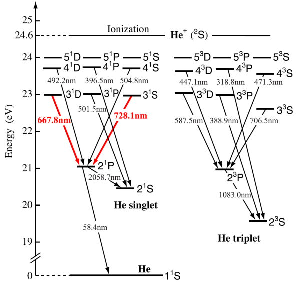
✓ verified at atmospheric pressure

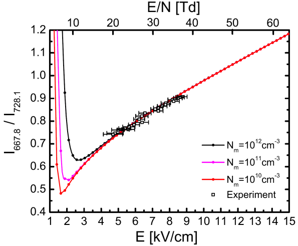
✗ dependence on the gas purity

✗ dependence on metastable density at low field

$$E(R) = 2.224 - 20.18R + 45.07R^2 - 19.98R^3 + 3.369R^4$$
$$[E] = \text{kV/cm, for } 3-40 \text{ kV/cm}, \; T = 310\,\text{K}$$

Ivković et al 2014 *J. Phys. D: Appl. Phys.* **47** 055204

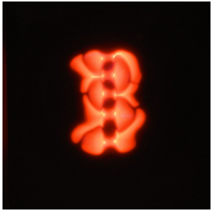




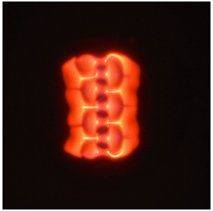
Diffuse coplanar barrier discharge in rare gases

Neon

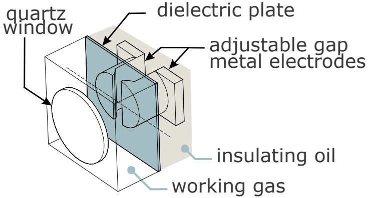
diffuse,
high gas purity



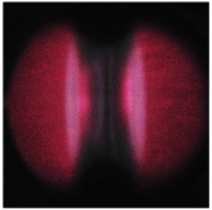
filamentary,
low gas purity



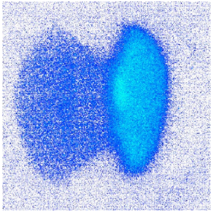
low gas purity,
higher voltage



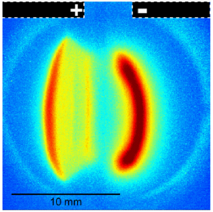
Helium



50 ms



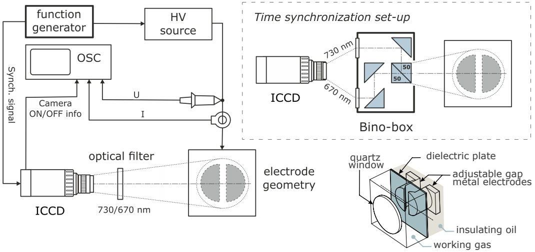
1 µs



100 ns, 10 k

run:I.mp4

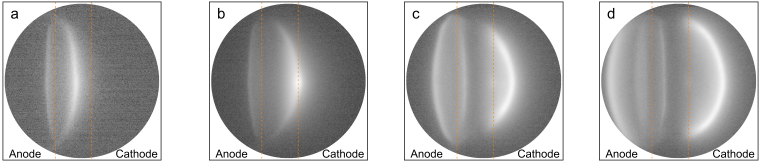
Experimental setup



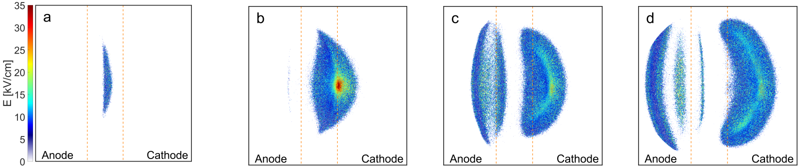
- coplanar DBD, brass electrodes covered with 96% Al_2O_3 (0.63 mm thick),
- parallel gap footprint, electrode distance 4.75 mm,
- helium 5.0 at atmospheric pressure, gas flow 550 sccm
- AC sine-wave high voltage of 1.6 kVmax, 10.3 kHz
- ICCD camera Princeton Instruments PI-MAX3 (time window 50 ns)
- bandpass filters Thorlabs FL670-10 and FL730-10 (670, 730 nm, FWHM 10 nm)

2D resolved electric field development

total light emission



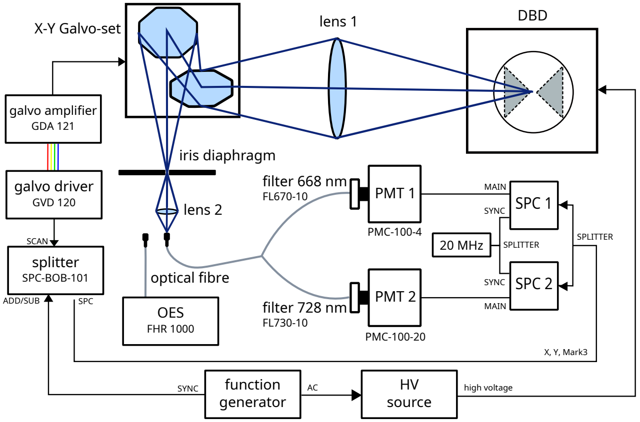
electric field



CDIW: $\sim 10\,\mathrm{kV/cm}$ $\sim 32\,\mathrm{kV/cm}$ $20-25\,\mathrm{kV/cm}$

Čech J *et al* 2D-resolved electric field development in helium coplanar DBD *Plasma Sources Sci. Technol.* **27** 105002

2D resolved simultaneous line ratio measurement



2D resolved simultaneous line ratio measurement