Laser-induced fluorescence

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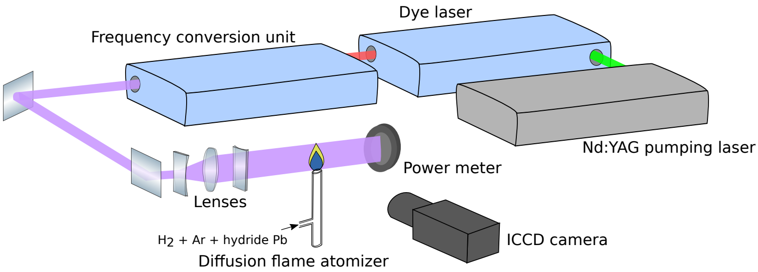
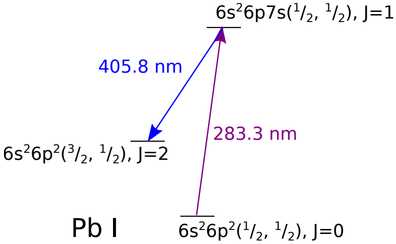
Motivation: methods for detection of reactive particles in plasma

- optical emission spectroscopy (incl. actinometry)
- absorption spectroscopy (incl. cavity ring-down spectroscopy)
- mass spectrometry
- ...

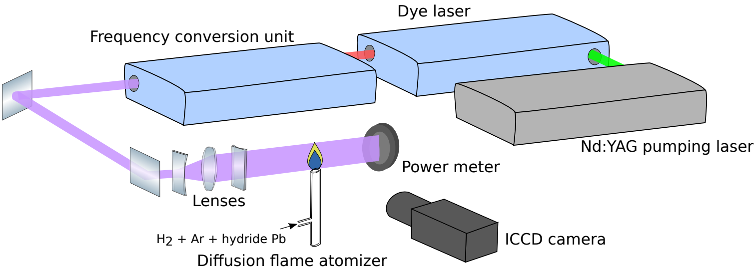
Laser-induced fluorescence



- method for determination of concentrations of various particles in plasma (atoms, molecules, radicals) also in the ground state
- high temporal and spatial resolution
- high sensitivity

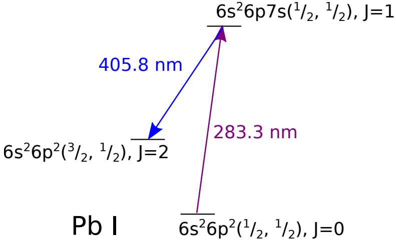


Laser-induced fluorescence



fluorescence signal:

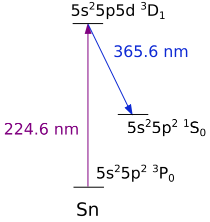
$$f(\vec{r}) = \int_0^\infty A_{32}\, n_3(\vec{r}, t)\, \mathrm{d}t$$

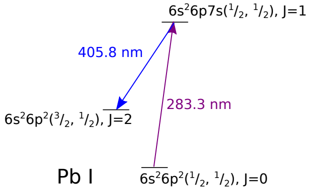


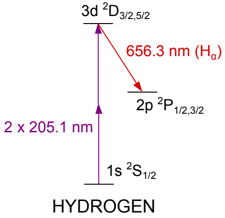
concentration of measured species:

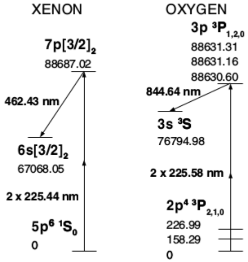
$$n = n_1(0) = n_1(t) + n_2(t) + n_3(t)$$

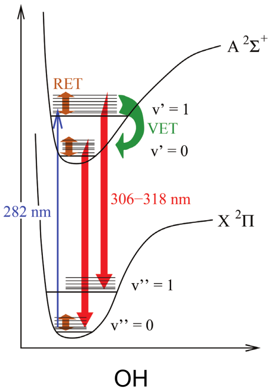
Excitation schemes











Laser-induced fluorescence

Connection between the fluorescence signal and the concentration of excited state is easy:

$$f(\vec{r}) = \int_0^\infty A_{32}\, n_3(\vec{r}, t)\, \mathrm{d}t$$

But what is the connection between n_3 and Σn?

Laser-particle interactions (not only)

- absorption of laser photon
- two-photon absorption
- spontaneous emission
- stimulated emission
- collisional quenching
- amplified spontaneous emission
- atomisation by laser
- ionisation by laser
- ...

Spontaneous emission

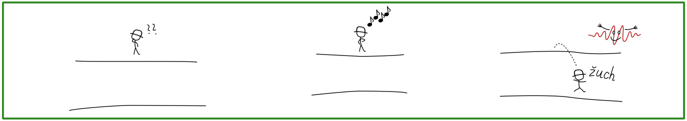
$$\left(\frac{\mathrm{d}n_3}{\mathrm{d}t}\right)_{\mathrm{sp.emission}} = -\left(\Sigma_i A_{3i}\right) n_3$$

solution:

$$n_3 = n_3(0)\,\mathrm{e}^{-\frac{t}{\tau_0}}$$

$$\tau_0 = \frac{1}{\Sigma_i A_{3i}}$$

- A – Einstein coefficient of emission (you can find on NIST)
- τ_0 – radiative lifetime

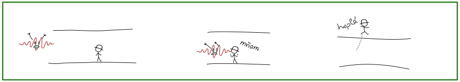


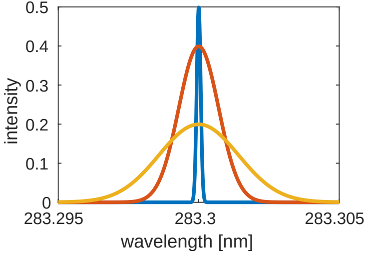
Absorption of laser photon

$$\left(\frac{\mathrm{d}n_3}{\mathrm{d}t}\right)_{\mathrm{absorption}} = \kappa \frac{B_{13}}{c} I n_1$$

- B_{13} - Einstein coefficient of absorption ($B_{13} \sim A_{31}$)
- I – laser intensity
- κ – spectral overlap of laser $I(\nu)$ and absorption line $g(\nu)$

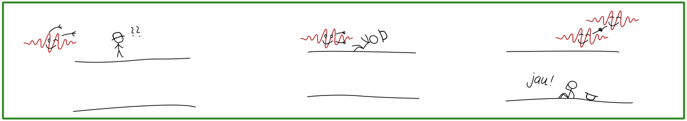
$$\kappa = \int_\nu g(\nu)\, I(\nu)\, \mathrm{d}\nu$$





Stimulated emission

$$\left(\frac{\mathrm{d}n_3}{\mathrm{d}t}\right)_{\text{stim.emission}} = -\kappa\,\frac{B_{31}}{c}\,I\,n_3$$



Collisional quenching

$$\left(\frac{\mathrm{d}n_3}{\mathrm{d}t}\right)_{\text{quenching}} = -\left(Q_{31} + Q_{32}\right) n_3$$

$$Q = \sum_m q_m n_m$$

- Q – effective quenching rate
- n_m – concentration of collisional partner m
- q_m – quenching coefficient for collisions with m

Lifetime of excited state τ:

$$\tau = \frac{1}{\Sigma A + \Sigma Q}$$

Two-photon absorption

$$\left(\frac{\mathrm{d}n_3}{\mathrm{d}t}\right)_{\mathrm{TPabsorption}} = \kappa^{(2)}\, G^{(2)}\, \sigma^{(2)}\, \left(\frac{I}{h\nu}\right)^2 n_1$$

- used in method Two-photon absorption laser-induced fluorescence (TALIF)
- $\sigma^{(2)}$ – two-photon absorption cross section
- $G^{(2)}$ – two-photon statistical factor

Atomisation, ionisation, ... by laser

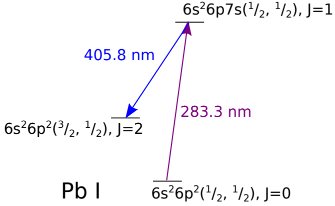
- processes leading to gain or loss of particles in the fluorescence process due to laser
- example for gain: laser causes dissociation of O_3 to O_2 + O
- example for loss: laser causes ionization of O to O^+

Rate equations – simple three-level model

$$
\begin{aligned}
\frac{\mathrm{d}n_1}{\mathrm{d}t} &= -\kappa \frac{B_{13}}{c} I n_1 + \kappa \frac{B_{31}}{c} I n_3 + \\
&\quad (A_{31} + Q_{31})\, n_3 + (A_{21} + Q_{21})\, n_2 \\
\frac{\mathrm{d}n_2}{\mathrm{d}t} &= (A_{32} + Q_{32})\, n_3 - (A_{21} + Q_{21})\, n_2 \\
\frac{\mathrm{d}n_3}{\mathrm{d}t} &= \kappa \frac{B_{13}}{c} I n_1 - \kappa \frac{B_{31}}{c} I n_3 - \\
&\quad (A_{31} + A_{32} + Q_{31} + Q_{32})\, n_3
\end{aligned}
$$

Measured fluorescence signal:

$$f(\vec{r}) = \int_0^\infty A_{32}\, n_3(\vec{r}, t)\, \mathrm{d}t$$



We want to find relation between f and Σn.

Solution: low-intensity approximation – "Linear regime"

assumptions:

- $n_1 \gg n_2, n_3$
- $n_1 \approx$ konst.
- no stimulated emission

solution:

$$n_3(t) = \left(\frac{\kappa}{c} B_{13} I\, n_1 - \frac{\mathrm{d}n_3}{\mathrm{d}t}\right) \tau$$

$$f = A_{32} \int_0^\infty \left(\frac{\kappa}{c} B_{13} I\, n_1 - \frac{\mathrm{d}n_3}{\mathrm{d}t}\right) \tau\, \mathrm{d}t$$

$$f(\vec{r}) = A_{32} \tau\, \kappa\, \frac{B_{13}}{c}\, n_1\, L(\vec{r})$$

- $L(\vec{r})$ – temporal integral of laser intensity, $L(\vec{r}) = \int_0^\infty I(\vec{r}, t)\mathrm{d}t$
- τ – lifetime of the excited state, $\tau = \frac{1}{A_{31}+A_{32}+Q_{31}+Q_{32}}$

Note for the lifetime

What is hapenning to the excited state after the laser pulse?

$$\frac{\mathrm{d}n_3}{\mathrm{d}t} = -(A_{31} + A_{32} + Q_{31} + Q_{32})\, n_3$$

solution:

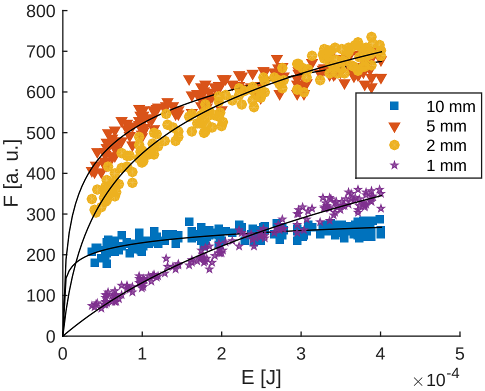
$$n_3 = n_3(0)\, \mathrm{e}^{-\frac{t}{\tau}}$$

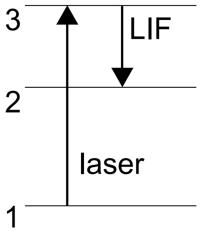
$$\tau = \frac{1}{A_{31} + A_{32} + Q_{31} + Q_{32}}$$

- τ – "real"lifetime of the excited state

A bit more laser intensity?

- the dependence of signal on energy stops to be linear
- reason: stimulated emission and depletion of the ground state





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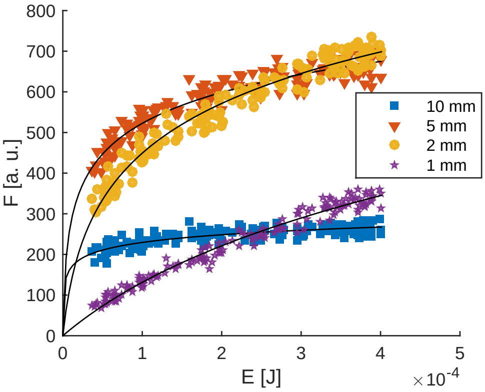
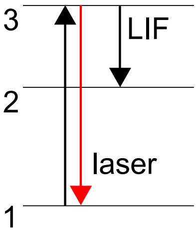
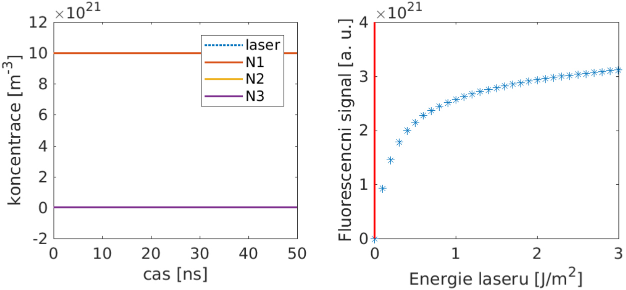




Saturation of LIF

$$
\begin{aligned}
\frac{\mathrm{d}n_1(t)}{\mathrm{d}t} &= -\frac{I_{laser}(t)}{c}B_{13}n_1(t) + \frac{I_{laser}(t)}{c}B_{31}n_3(t) + (A_{31}+Q_3)n_3(t) + \\
&\quad +(A_{21}+Q_2)n_2(t) \\
\frac{\mathrm{d}n_2(t)}{\mathrm{d}t} &= A_{32}n_3(t) - (A_{21}+Q_2)n_2(t) \\
\frac{\mathrm{d}n_3(t)}{\mathrm{d}t} &= \frac{I_{laser}(t)}{c}B_{13}n_1(t) - \frac{I_{laser}(t)}{c}B_{31}n_3(t) - (A_{31}+A_{32}+Q_3)n_3(t)
\end{aligned}
$$

$$F = \int_0^\infty A_{32}\, n_3(t)\, \mathrm{d}t$$



Saturation of LIF

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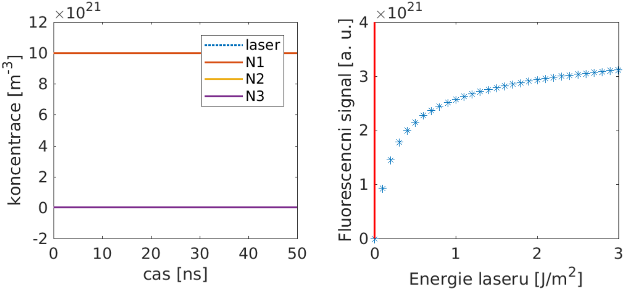
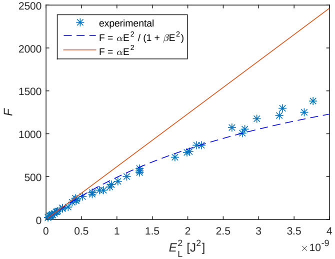
\end{aligned}$$

$$F = \int_0^\infty A_{32}\, n_3(t)\,\mathrm{d}t$$



Saturation: conclusion

Thanks to some modelling, we are able to find "correction factors" which quantificate how many excited species were lost in comparison with ideal linear regime.



How much fluorescence is really detected?

- signal M is integrated from some definite volume V, not only point in space $\vec{r}$
- fluorescence is emitted to all angles, only small part $\frac{\Omega}{4\pi}$ goes to the camera
- wavelength filters have some transmitivity T, camera has some sensitivity C, ...

$$M = T \cdot C \cdot \frac{\Omega}{4\pi} \cdot \int f(\vec{r})\,\mathrm{d}V$$

Calibration

How to obtain $\frac{\Omega}{4\pi}$?

- Let's measure some another signal caused by the exactly same shape of the laser beam, but we know exactly how much signal we should get from it.
    1. Rayleigh scattering of the laser
    2. fluorescence of noble gases with known concentration
- Than compare the theoretical signal and really obtained signal.

Formula for absolute concentration

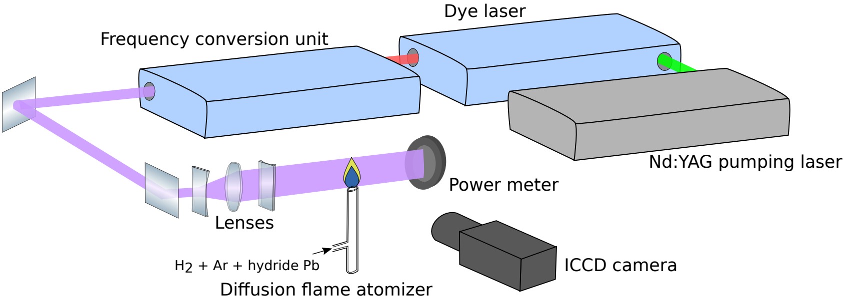
$$n = \frac{M}{E_L}\,\varsigma\,\frac{1}{T\,C}\,\frac{c}{\tau\,A_{32}\,B_{13}\,\kappa}\,\frac{M_{c,theoretical}}{M_c}$$

- n – concentration of measured species
- M – measured fluorescence signal
- E_L – laser pulse energy , $E_L = \iint\limits_{S,t} I(\vec{r},t)\,\mathrm{d}S\,\mathrm{d}t$
- ς – correction factor describing the saturation of signal
- T – wavelength filter transmisivity
- C – camera sensitivity (depends on wavelength)
- c – speed of light
- τ – lifetime of the excited state
- A_{32} – Einstein coefficient of the fluorescence transition
- B_{13} – Einstein coefficient of absorption of laser photon
- κ – spectral overlap of laser and absorption line
- $M_{c,theoretical}$ – theoretical amount of calibration signal
- M_c – really detected calibration signal

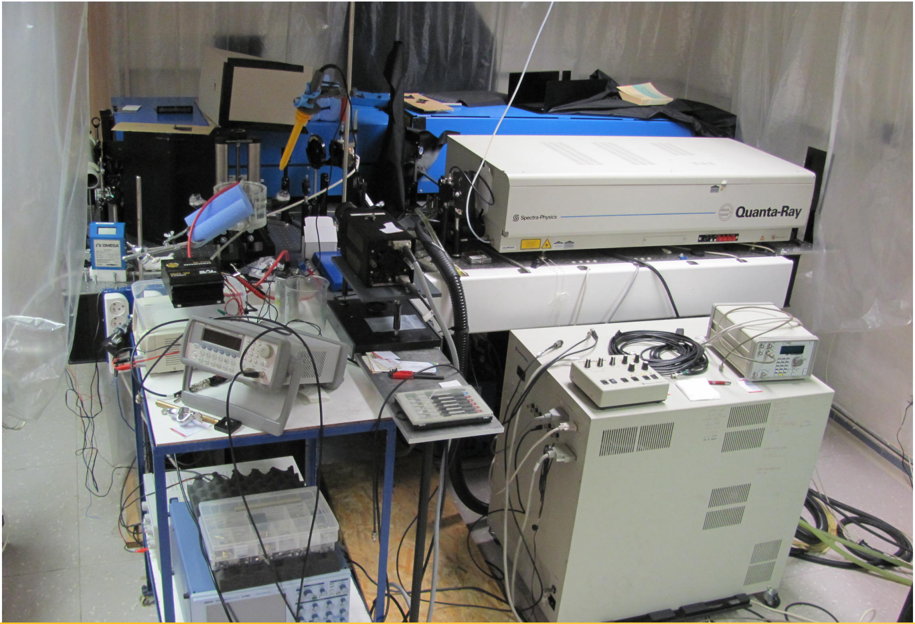
Measurement

- prepare optical path (...)
- set the correct wavelength and find the first fluorescence signal
- check parasitic effects, signal saturation
  - does the signal disappear when the laser wavelength is detuned?
  - does the signal have linear dependence on the laser energy?
- measure the shape of the absorption line ($\rightarrow \kappa$)
- measure the timeshape of the fluorescence ($\rightarrow \tau$)
- nice pictures of the whole fluorescence signal ($\rightarrow M$)
- calibration ($\rightarrow M_c$)
- do not forget to get darkframes and monitor the energy E_L for all the measurements

LIF equipment

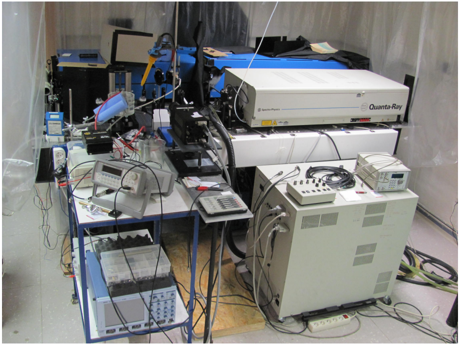


Our LIF laboratory

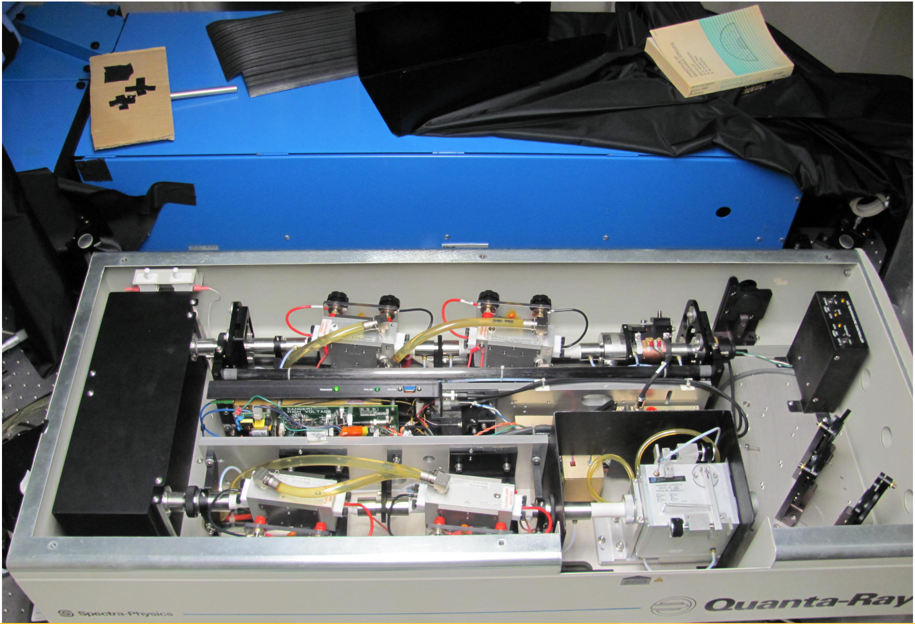


Our laser

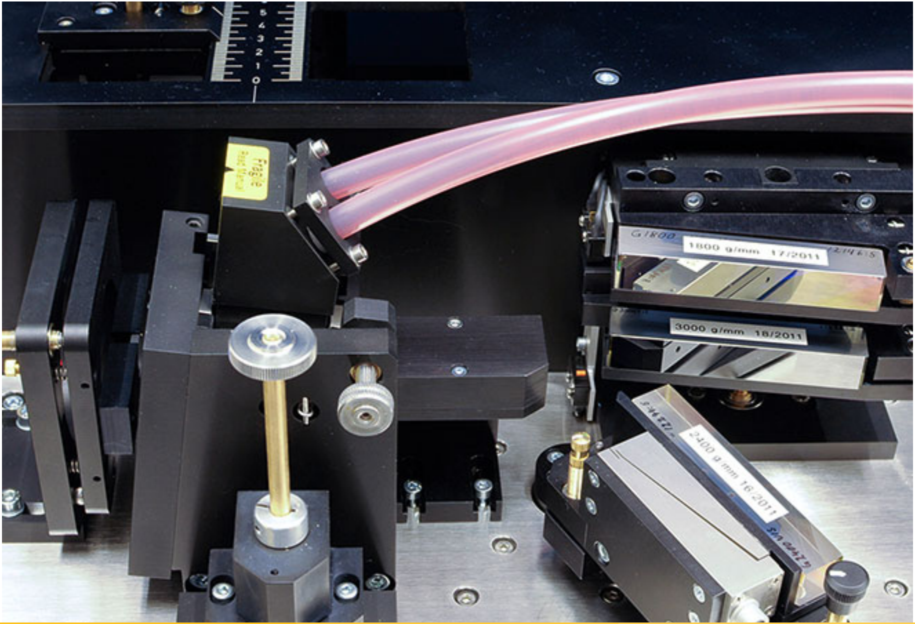
- Nd:YAG pumping laser + dye laser + frequency conversion unit
- pulsed – 10 ns, 30 Hz
- tunable wavelength (1064 nm fundamental; higher harmonics; cca 200 - 900 nm from dye laser and FCU)
- peak power: kW (in UV) - GW (in IR)
    - comparison: laser pointer 20 mW, ELI 10 PW



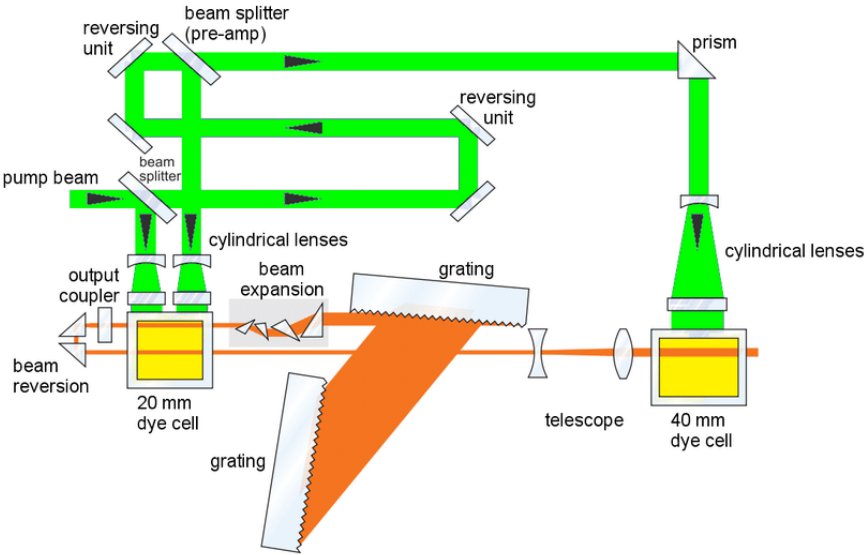
Inside the pump laser



Dye laser



Dye laser



reversing unit
beam splitter (pre-amp)
prism
reversing unit
beam splitter
pump beam
cylindrical lenses
cylindrical lenses
output coupler
beam expansion
grating
beam reversion
20 mm dye cell
telescope
40 mm dye cell
grating

Detector: ICCD camera

- intensified CCD kamera (with microchannel plate)
- gate down to 2 ns
- high sensitivity, both in UV and near IR
- external trigger
- optics: quartz lens, wavelength filter

Practice: LIF of Ge atoms in the diffusion flame atomizer