The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

IAEA International Atomic Energy Agency

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Winter College on Optics in Environmental Science

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Laser spectroscopy fundamentals
Parts I and II

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ICTP Winter College 2009

Fundamentals of Laser Spectroscopy

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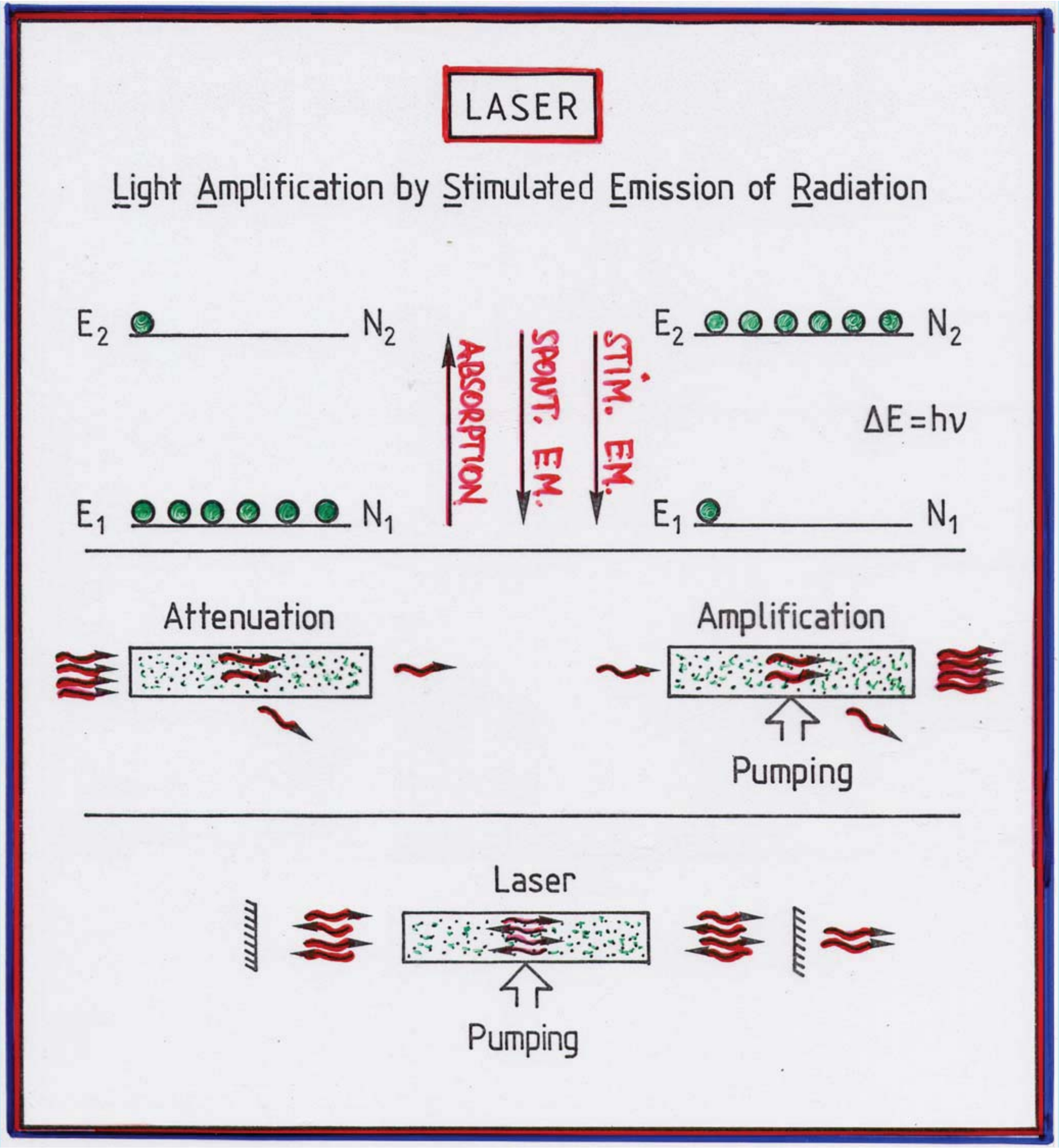
Sweden

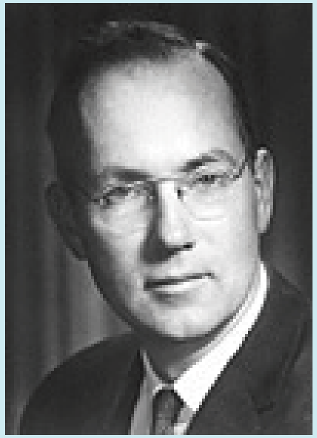
Why is laser spectroscopy special ?

Table 9.1. Comparison between a conventional light source (RF discharge lamp) and a single-mode dye laser

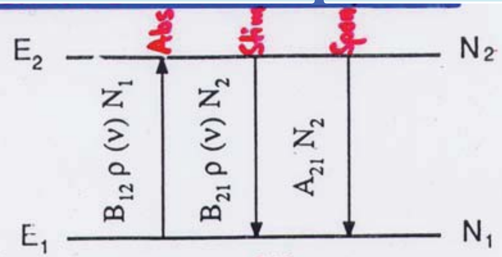
	Conventional line source (RF discharge lamp)	Continuous single-mode dye laser
Linewidth	1000 MHz	1 MHz
Total output of line	10^{-1} W	10^{-1} W
Power within a useful solid angle	10^{-2} W	10^{-1} W
Irradiated area (depends on focusing)	$10\ \mathrm{cm}^2$	$10^{-4}\ \mathrm{cm}^2$
$I(\nu)$ power density per unit frequency	$10^{-6}\ \mathrm{W/(cm^2 \cdot MHz)}$	$10^{3}\ \mathrm{W/(cm^2 \cdot MHz)}$

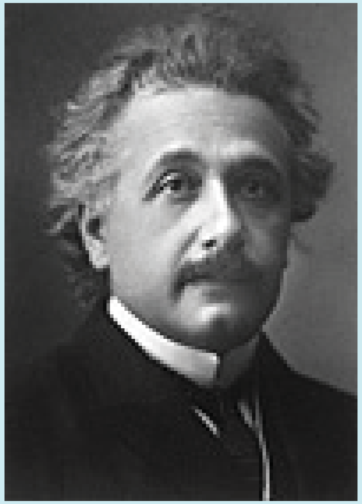
Stimulated emission (Einstein 1917)





Radiative processes





Thermodynamic equilibrium:

$$\frac{dN_1}{dt} = -\frac{dN_2}{dt} = -B_{12}\rho(\nu)N_1 + B_{21}\rho(\nu)N_2 + A_{21}N_2 \qquad (4.21)$$

where $\rho(\nu)$ is the energy density of the radiation field per frequency interval, and $\nu = (E_2 - E_1)/h$. At equilibrium we have

$$\frac{dN_1}{dt} = \frac{dN_2}{dt} = 0 \qquad (4.22)$$

yielding

$$\rho(\nu) = \frac{A_{21}}{B_{12}(N_1/N_2) - B_{21}} . \qquad (4.23)$$

We now assume the system to be in thermodynamic equilibrium with the radiation field. The distribution of the atoms is governed by Boltzmann's law

$$\frac{N_1}{N_2} = \exp\left(\frac{h\nu}{kT}\right), \qquad (4.24)$$

Boltzmann

$$\rho(\nu) = \frac{A_{21}}{B_{12}(\exp\frac{h\nu}{kT}) - B_{21}} .$$

$$\rho(\nu) = \frac{16\pi^2\hbar\nu^3}{c^3}\,\frac{1}{\exp(h\nu/kT) - 1} \qquad (4.25)$$

Planck

we obtain the following relations between the three coefficients

$$B_{12} = B_{21}$$

Indep. of $\rho(\nu)$!

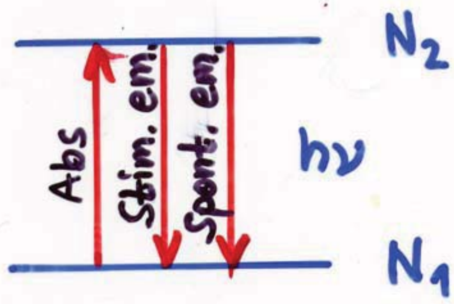
$$\frac{A_{21}}{B_{21}} = \frac{16\pi^2\hbar\nu^3}{c^3}$$

$A_{21} \sim B_{21}\nu^3$

$$A_{ik} = \frac{32\pi^3}{3}\,\frac{\nu^3}{4\pi\epsilon_0\hbar c^3}\,|\langle i|er|k\rangle|^2$$

Saturation

$$\frac{dN_1}{dt} = -\frac{dN_2}{dt} = 0$$



$$\frac{N_2}{N_1} = e^{-\frac{h\nu}{kT}}$$

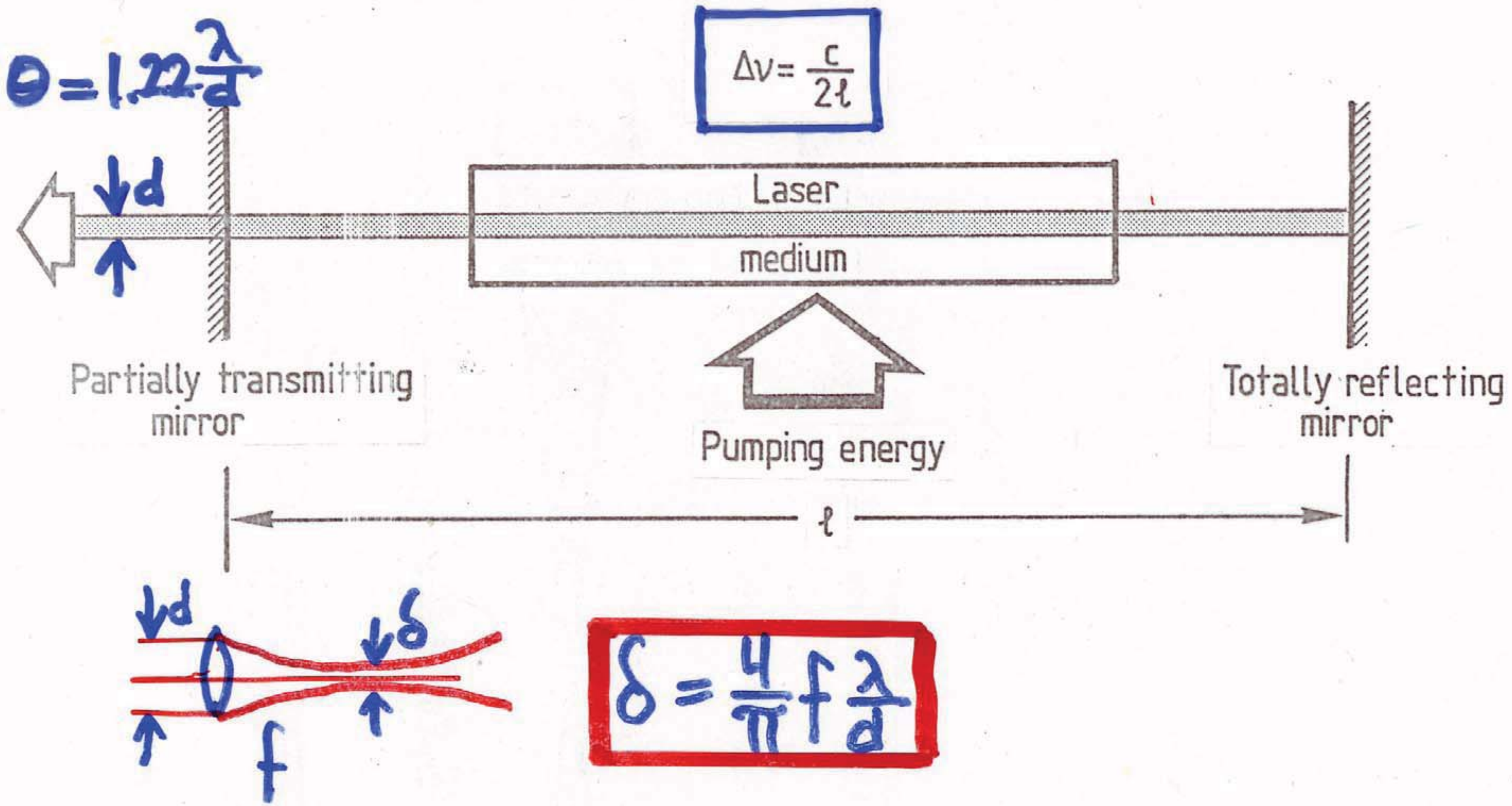
$$-B_{12}\rho(\nu)N_1 + B_{21}\rho(\nu)N_2 + A_{21}N_2 = 0$$

$$\frac{N_2}{N_1+N_2} = \frac{1/2}{1 + A/2B\rho(\nu)} \approx \frac{1}{2} \text{ for } B\rho(\nu) \gg A$$

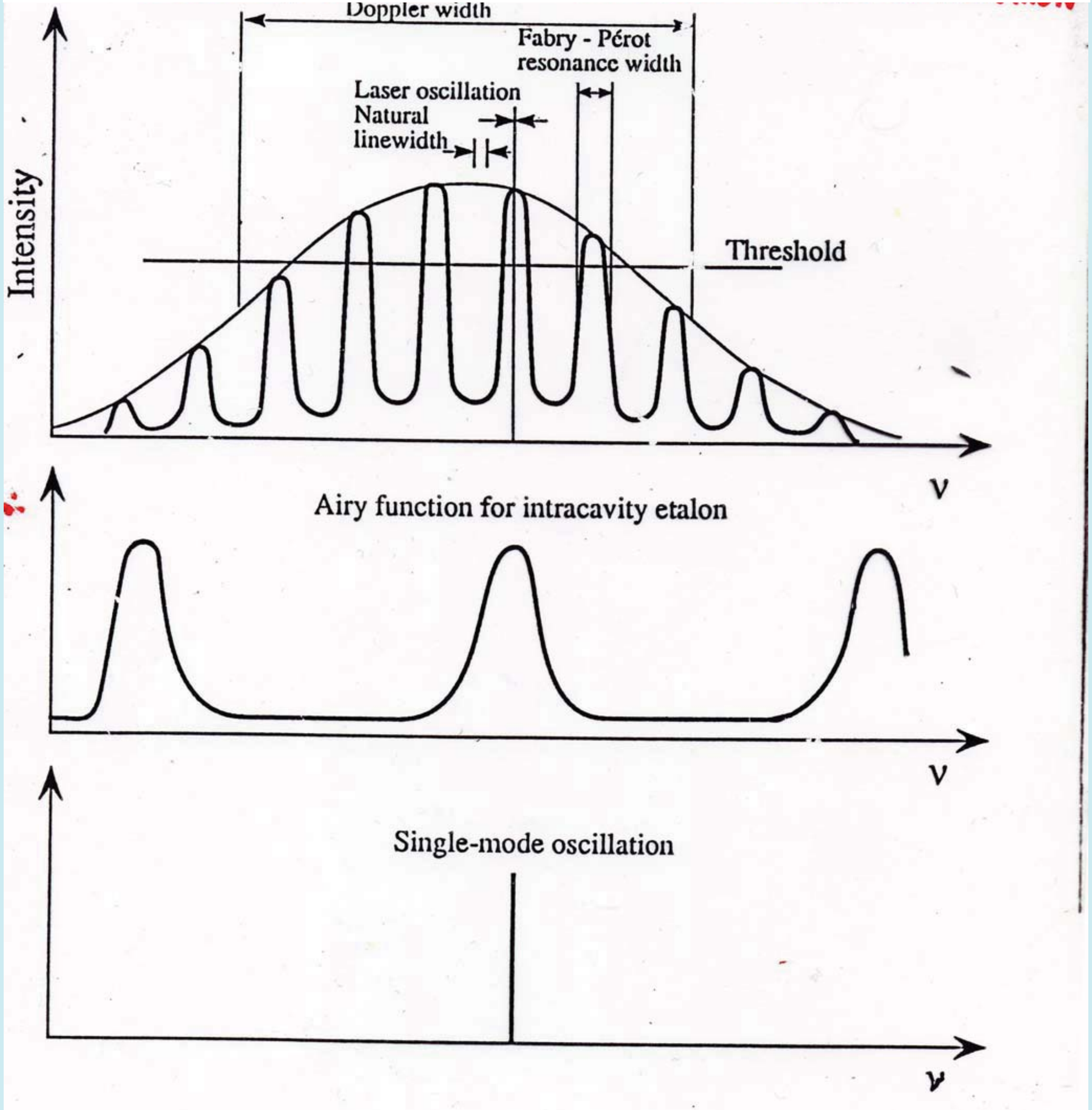
$$I(\nu) = c\rho(\nu)$$

$$I(\nu) \gg c\frac{A}{B} = 16\pi^2 \frac{\hbar c}{\lambda^3} \approx \frac{mW}{cm^2\,MHz}$$

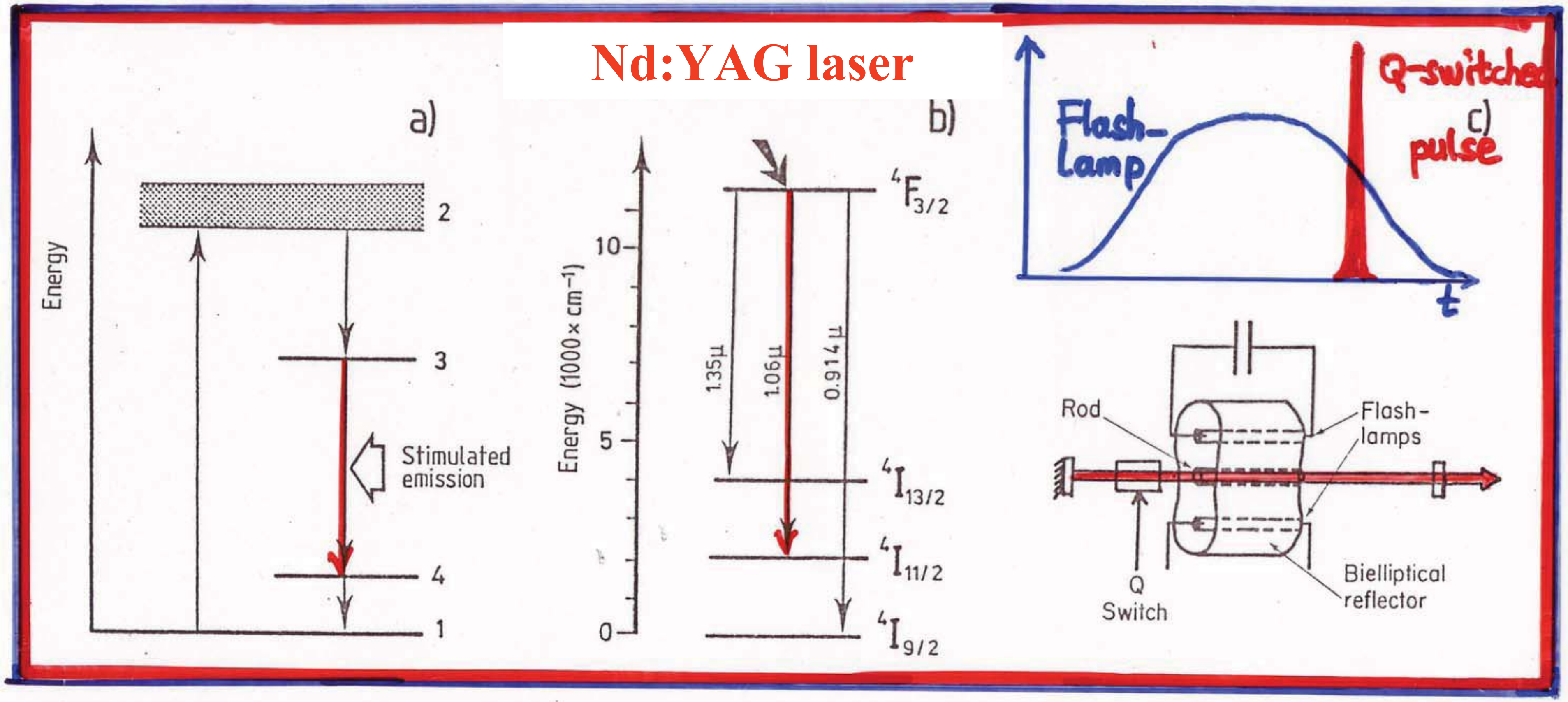
Laser Cavity



Single-mode generation

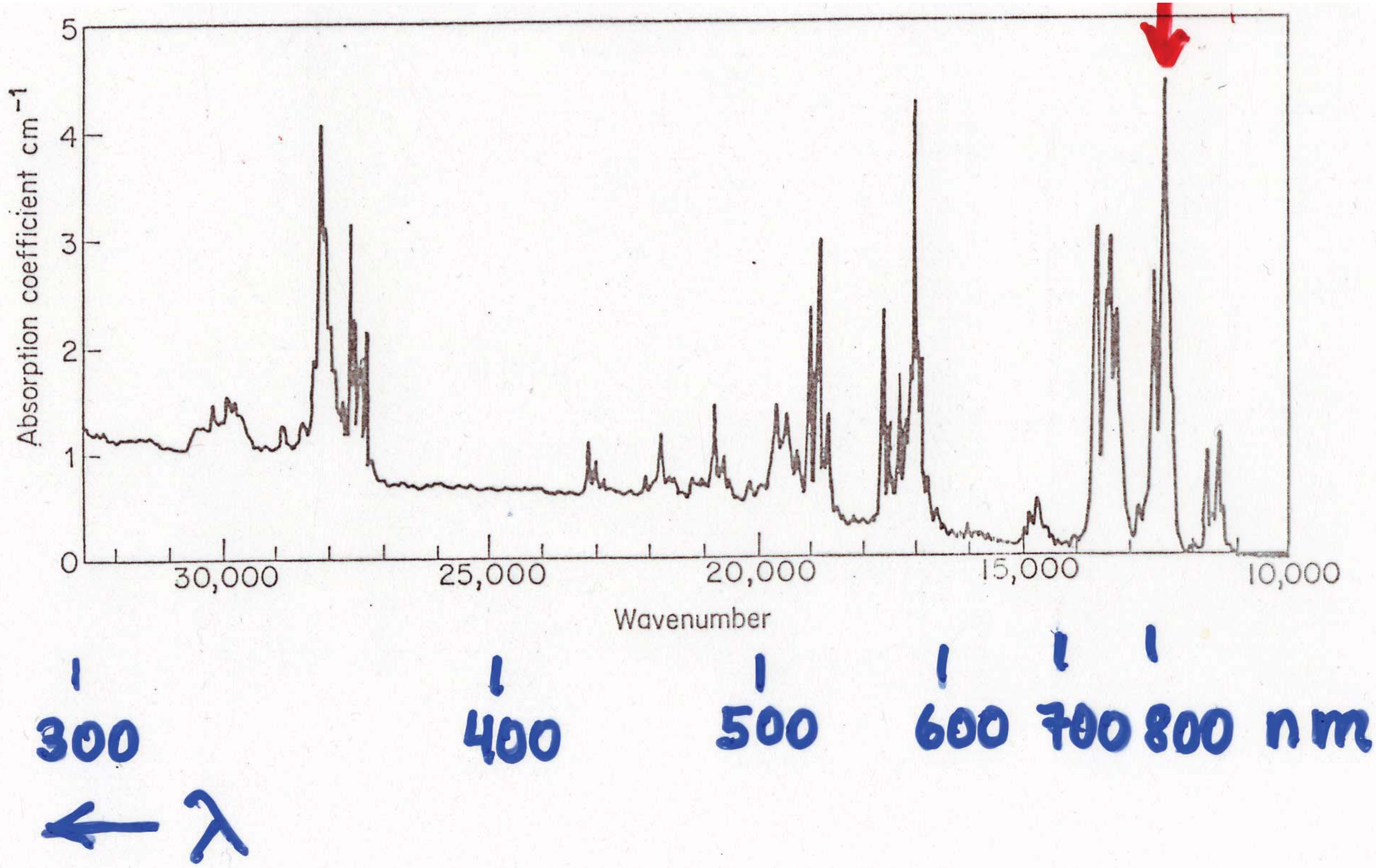


Nd:YAG laser

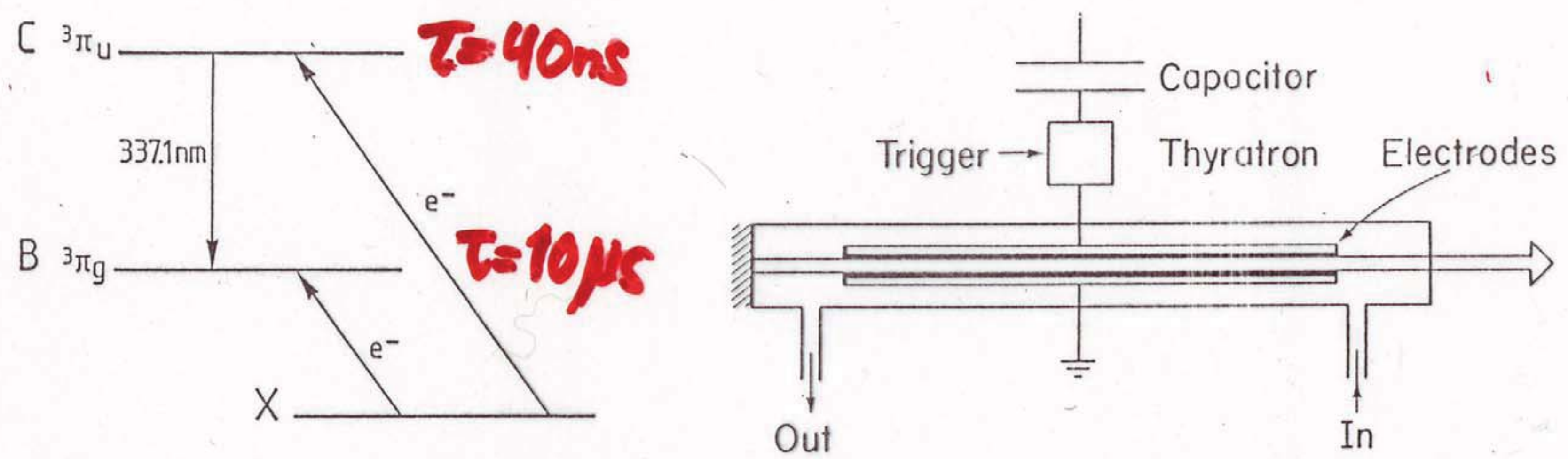


a)
Energy
2
3
Stimulated emission
4
1
b)
Energy (1000 × cm⁻¹)
10
5
0
⁴F3/2
1.35μ
1.06μ
0.914μ
⁴I13/2
⁴I11/2
⁴I9/2
Q-switched
Flash-Lamp
c)
pulse
t
Rod
Flash-lamps
Q Switch
Bielliptical reflector

Absorption of YAG 808 nm

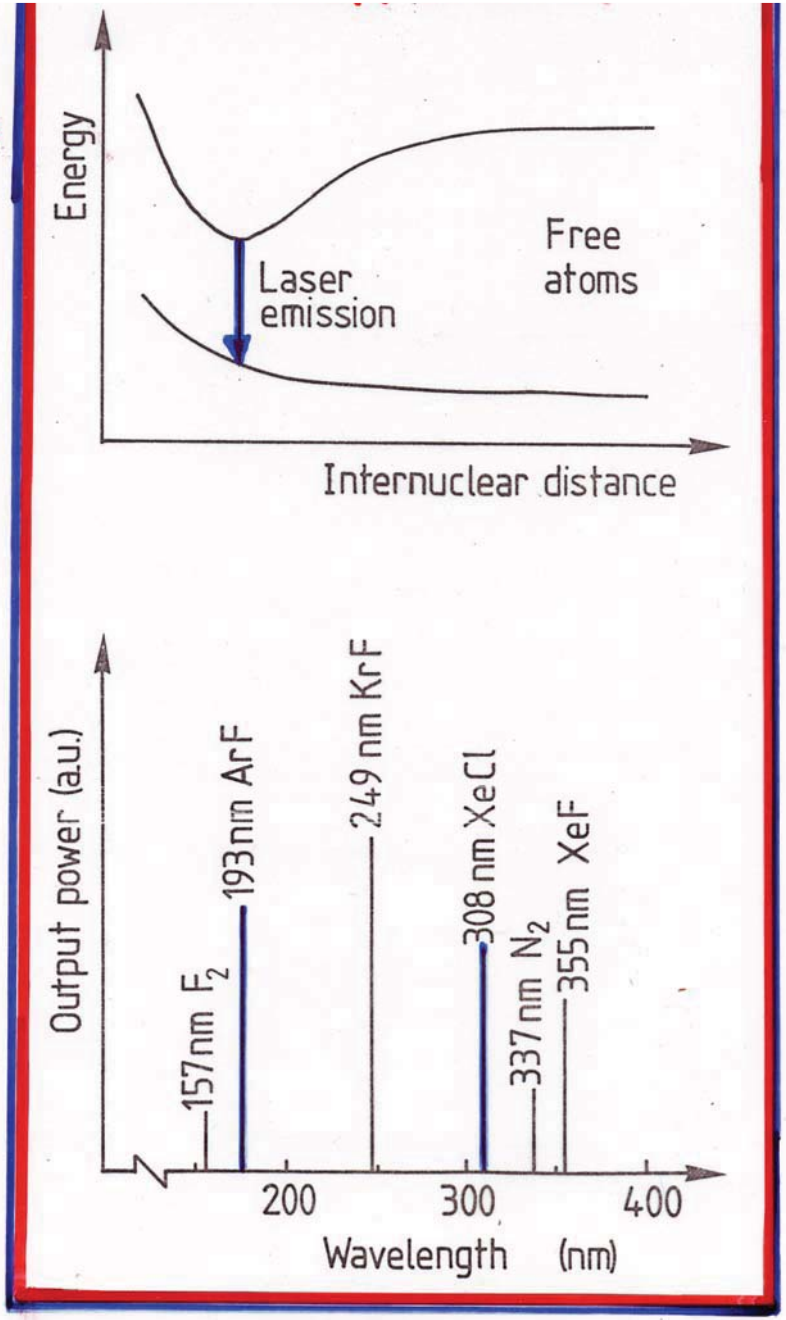


N_2 laser

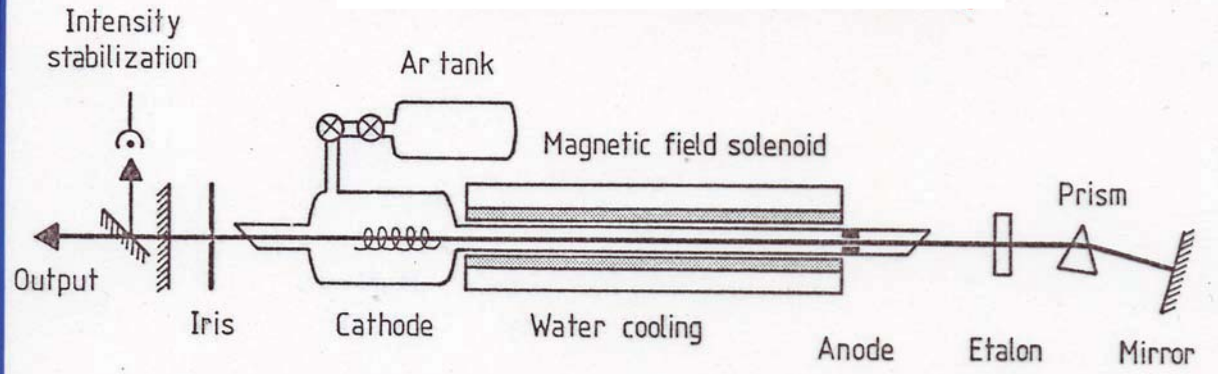


C $^3\pi_u$
B $^3\pi_g$
X
337.1nm
e⁻
e⁻
τ=40ns
τ=10μs
Capacitor
Trigger
Thyratron
Electrodes
Out
In

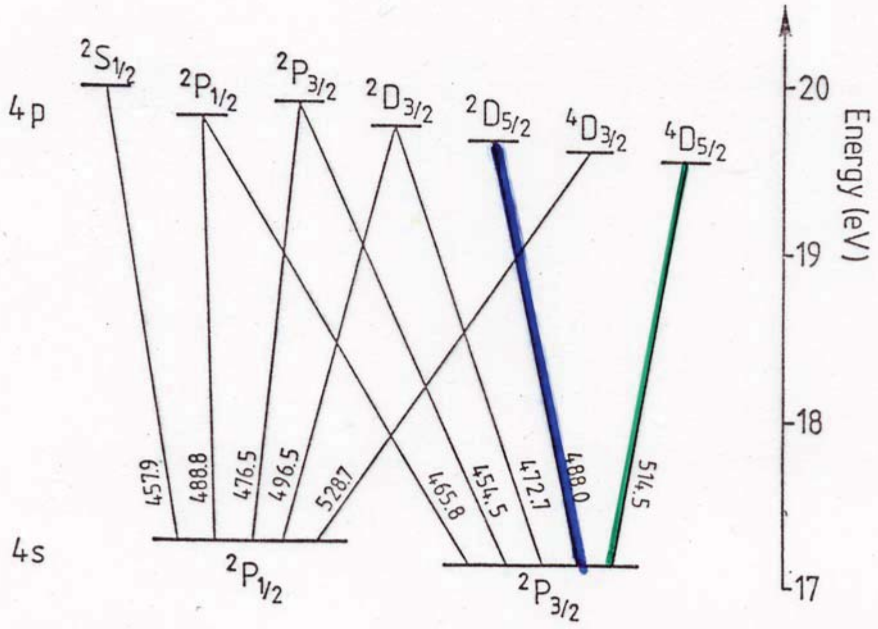
Excimer laser



Ar-ion laser

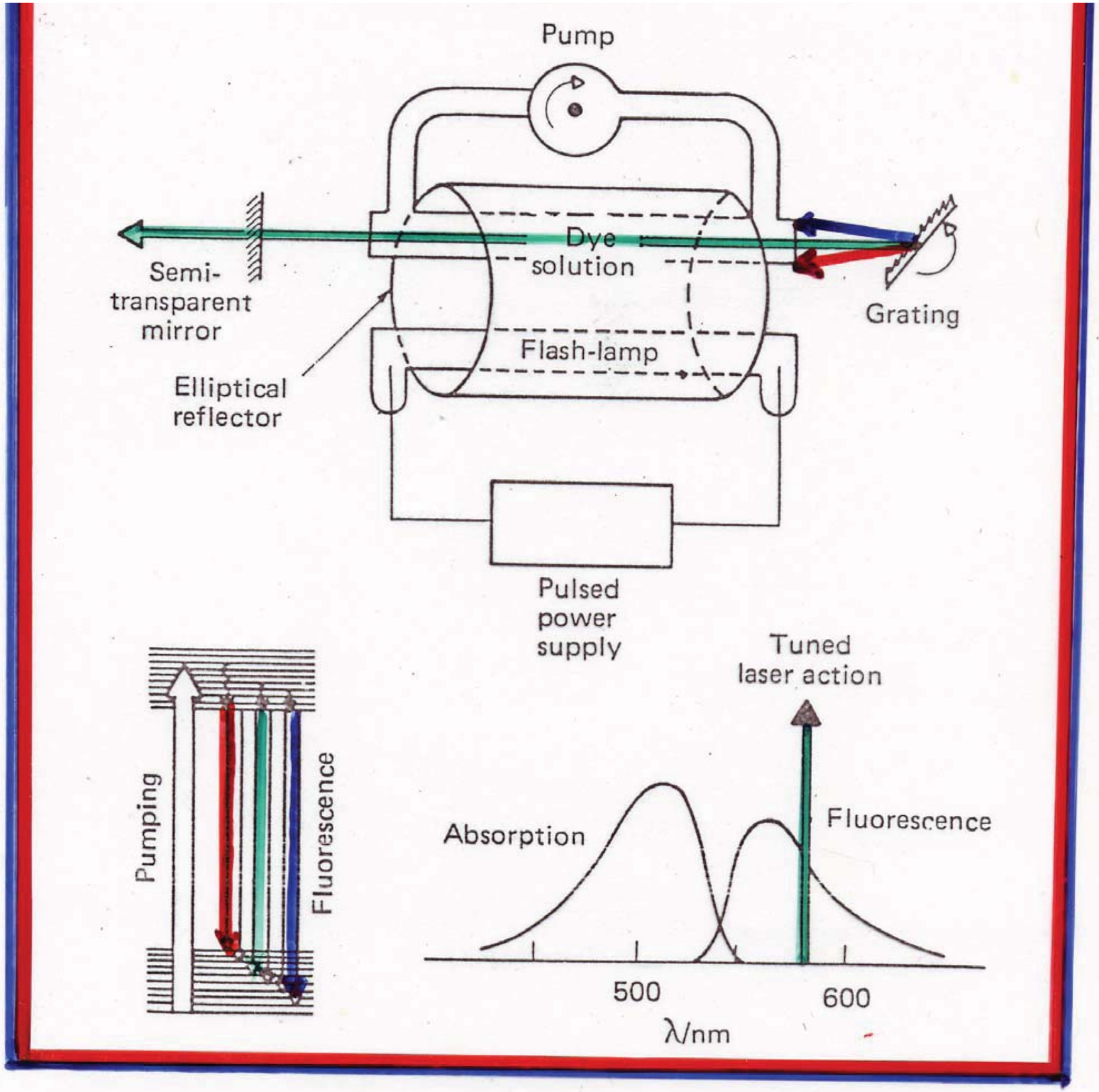


Intensity stabilization
Ar tank
Magnetic field solenoid
Prism
Output
Iris
Cathode
Water cooling
Anode
Etalon
Mirror

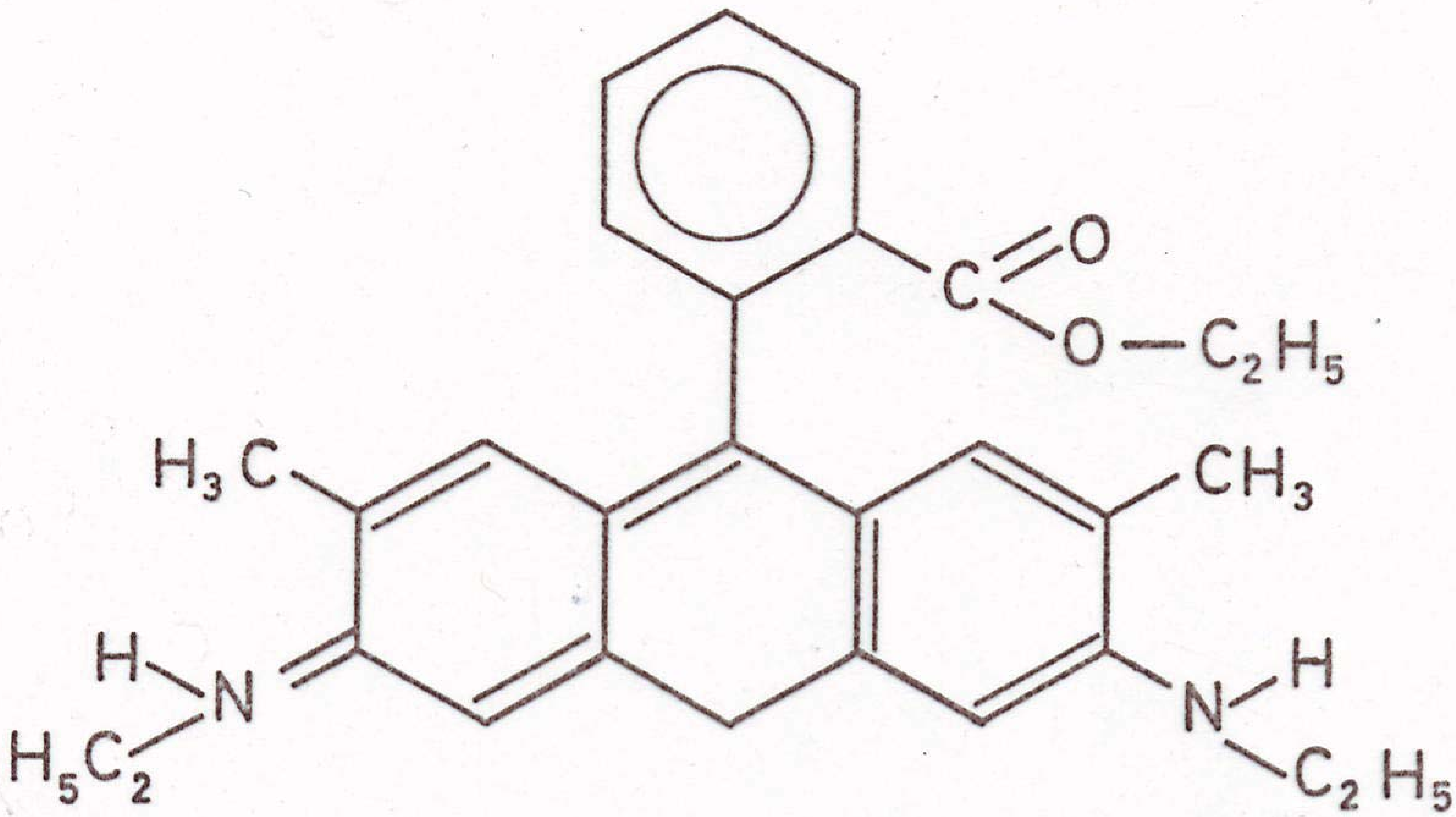


4p
4s
$^2S_{1/2}$
$^2P_{1/2}$
$^2P_{3/2}$
$^2D_{3/2}$
$^2D_{5/2}$
$^4D_{3/2}$
$^4D_{5/2}$
457.9
488.8
476.5
496.5
528.7
465.8
454.5
472.7
488.0
514.5
$^2P_{1/2}$
$^2P_{3/2}$
20
19
18
17
Energy (eV)

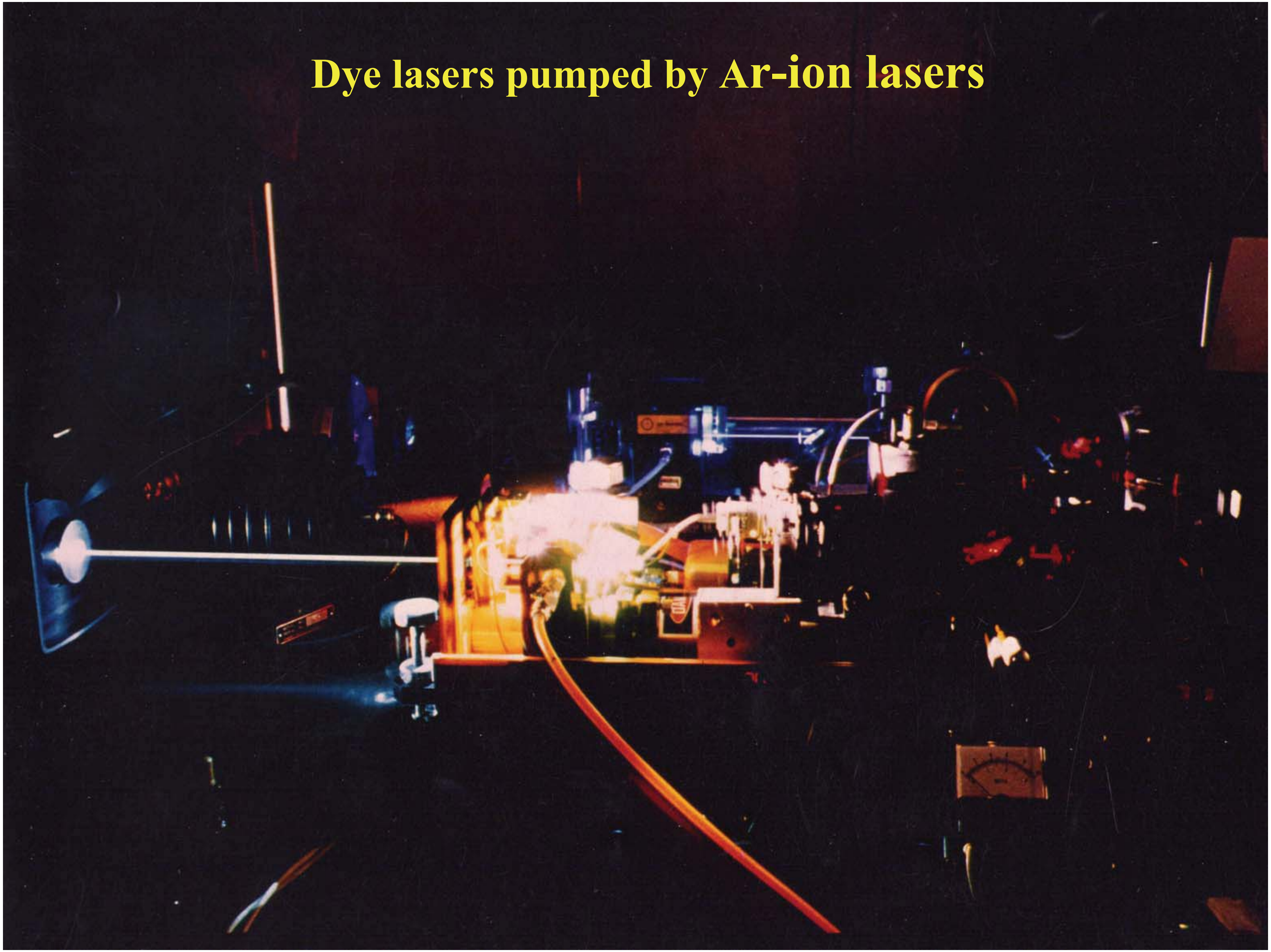
Dye laser

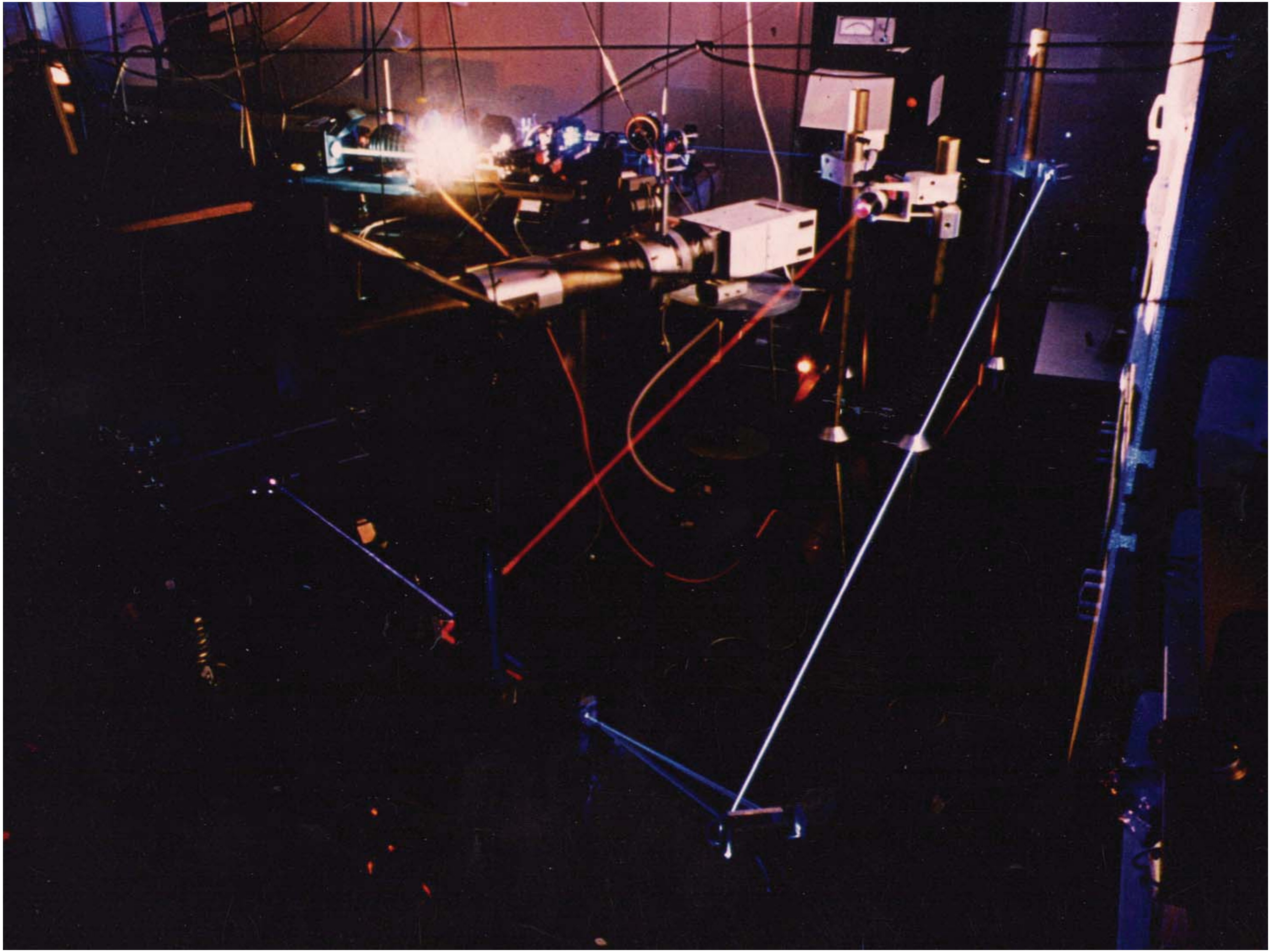


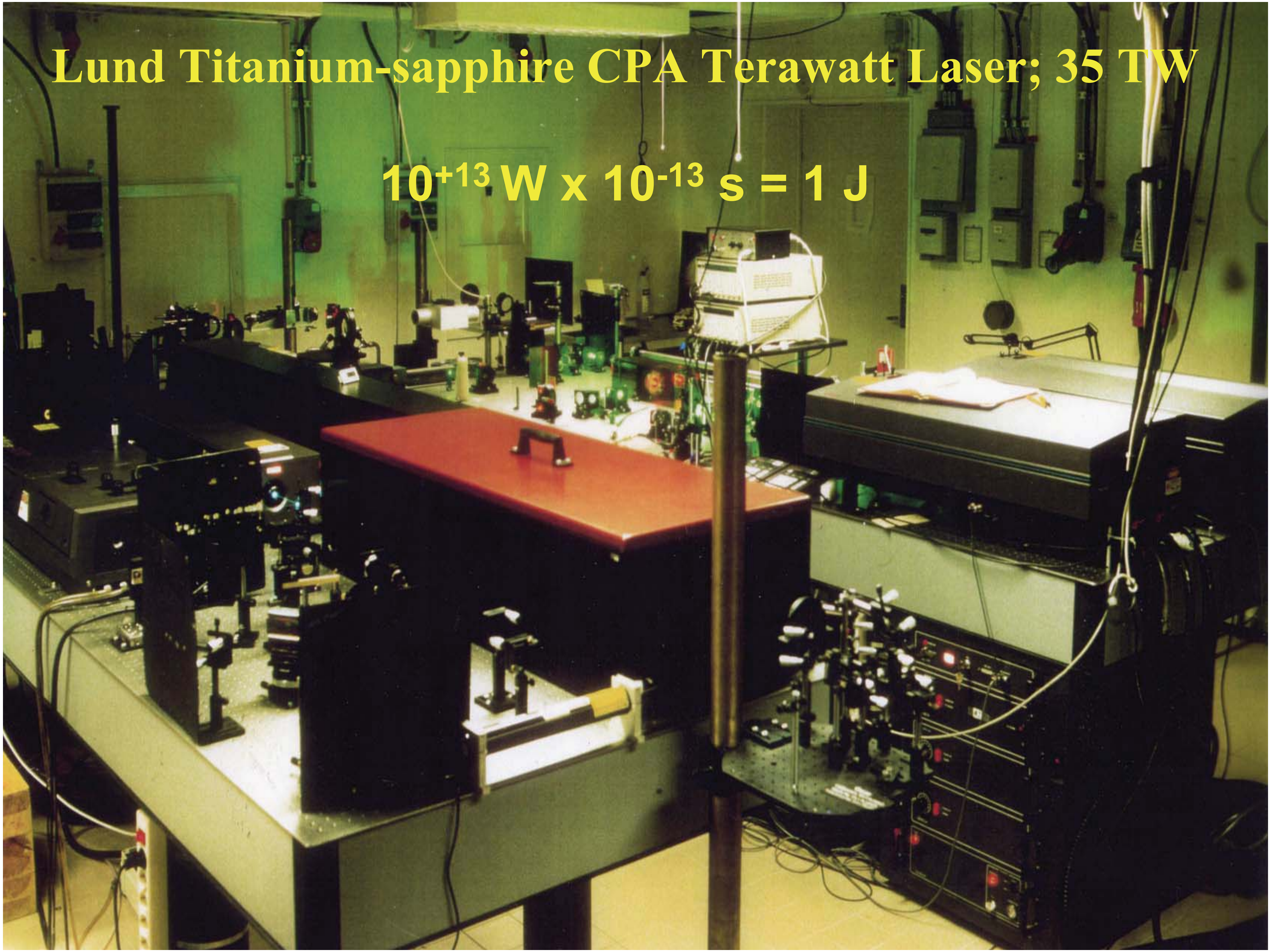
Pump
Dye solution
Semi-transparent mirror
Grating
Flash-lamp
Elliptical reflector
Pulsed power supply
Tuned laser action
Pumping
Fluorescence
Absorption
Fluorescence
500
600
λ/nm



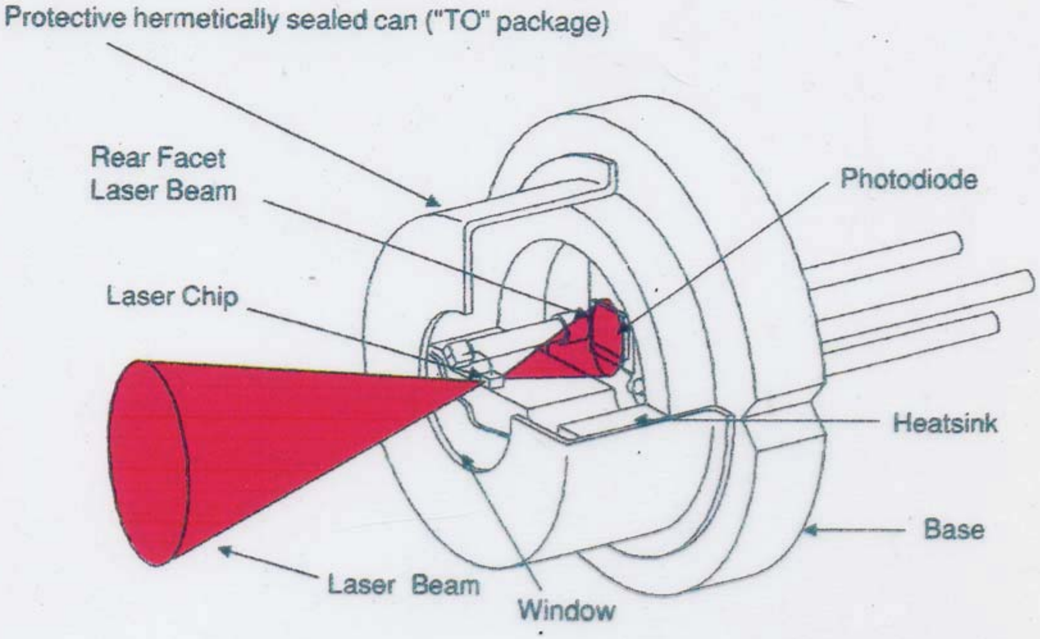
Rhodamine 6G

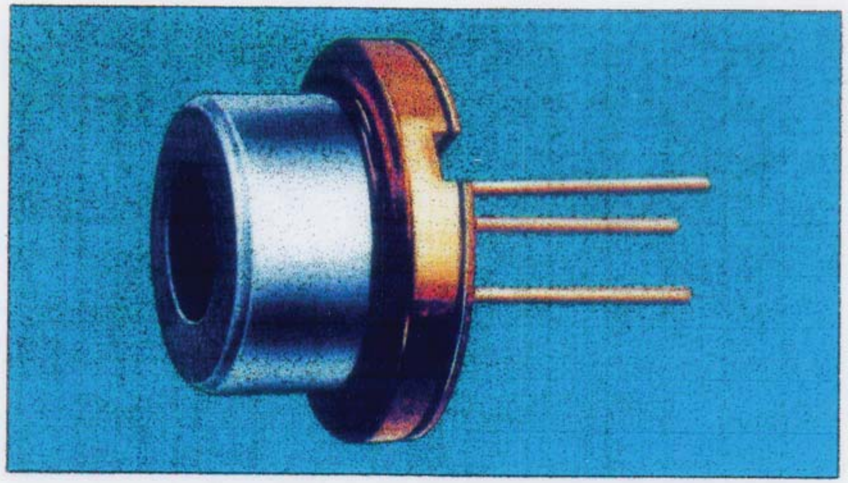

Dye lasers pumped by Ar-ion lasers



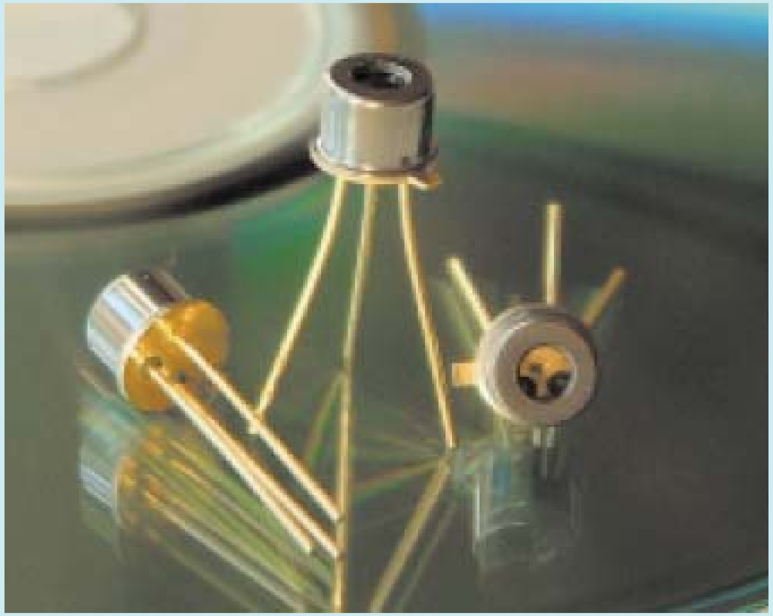

Lund Titanium-sapphire CPA Terawatt Laser; 35 TW
10^{+13} W x 10^{-13} s = 1 J

DIODE LASERS

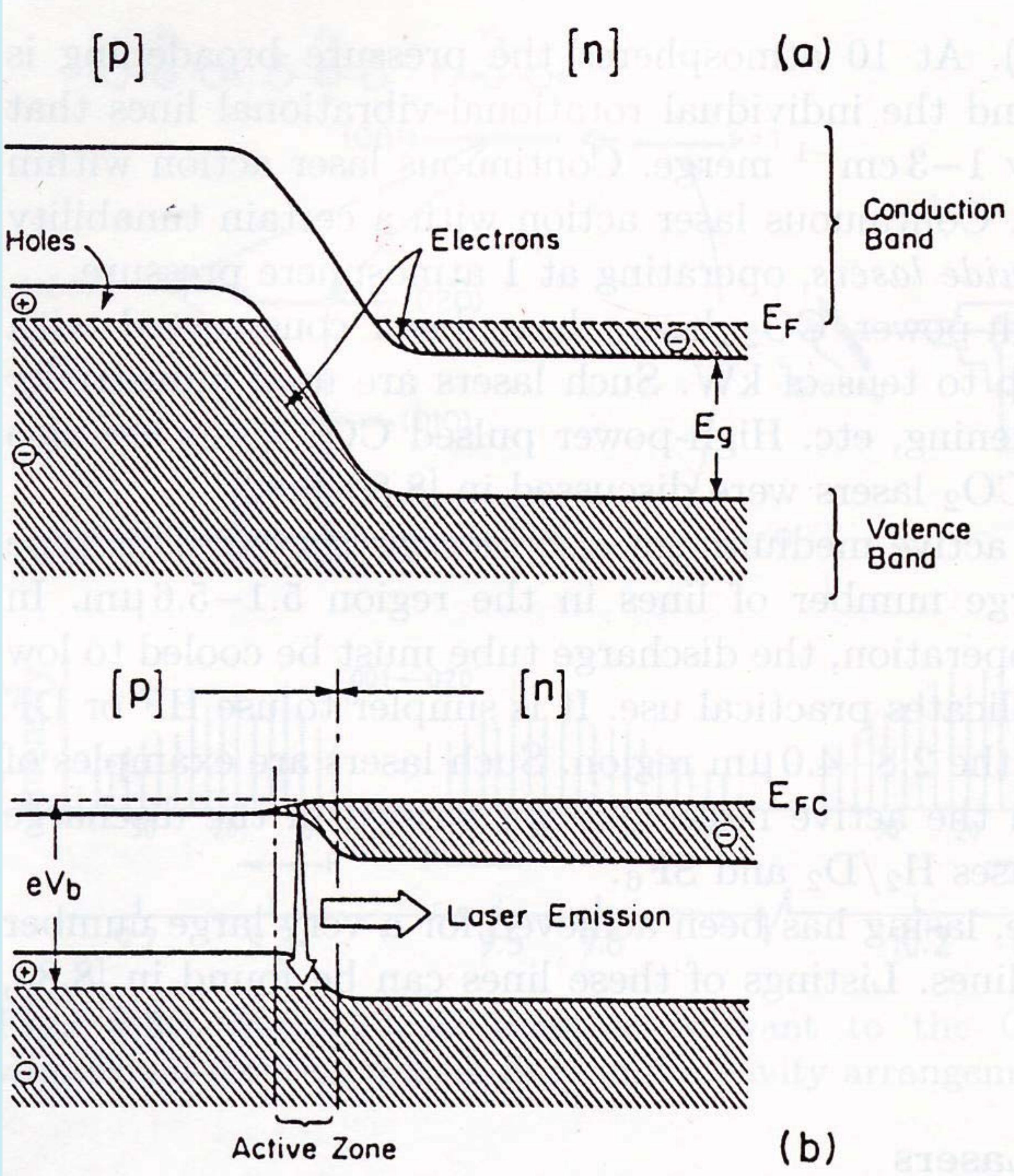




A typical compact disc style laser diode.

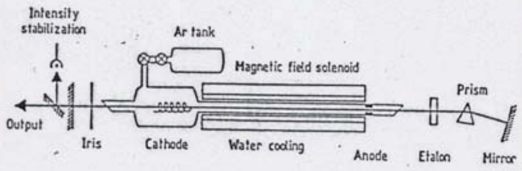


Diode laser



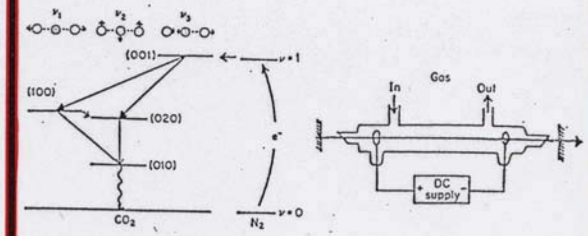
[p]
[n]
(a)
Conduction Band
Holes
Electrons
E_F
E_g
Valence Band
[p]
[n]
E_{FC}
eV_b
Laser Emission
Active Zone
(b)

ARGON ION



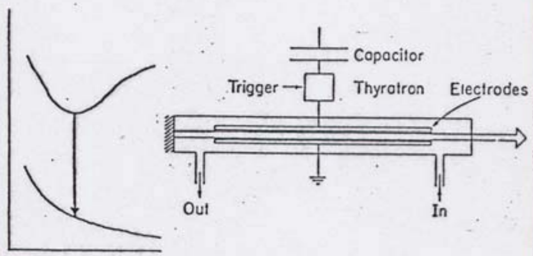
CW — 488, 515 nm

CO_2



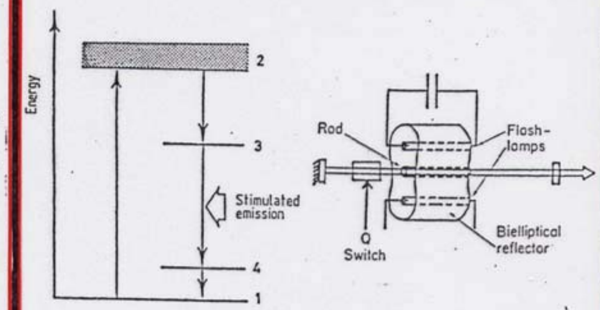
CW, PULSED — 10.6 μm

EXCIMER



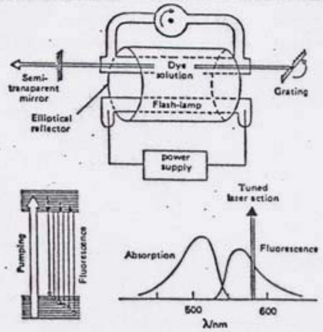
PULSED — 193, 248, 308 nm

Nd:YAG



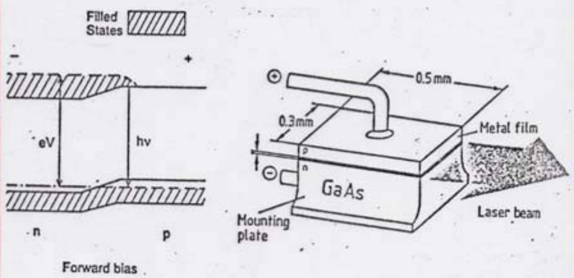
CW, PULSED — 1064, (532, 355) nm

DYE



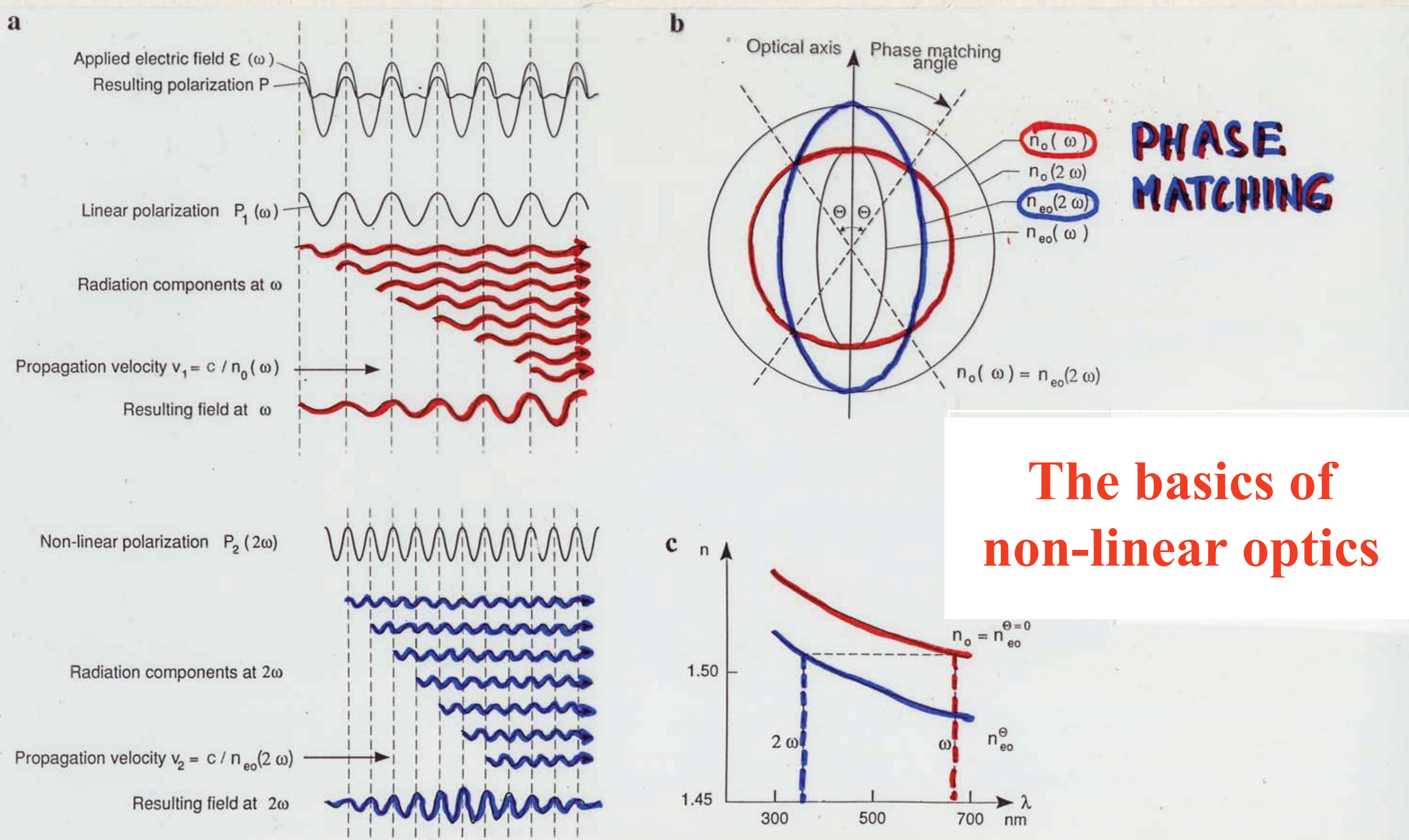
CW, PULSED — 400 – 1000 nm

DIODE



CW, PULSED — 670 – 1500 nm

The basics of non-linear optics

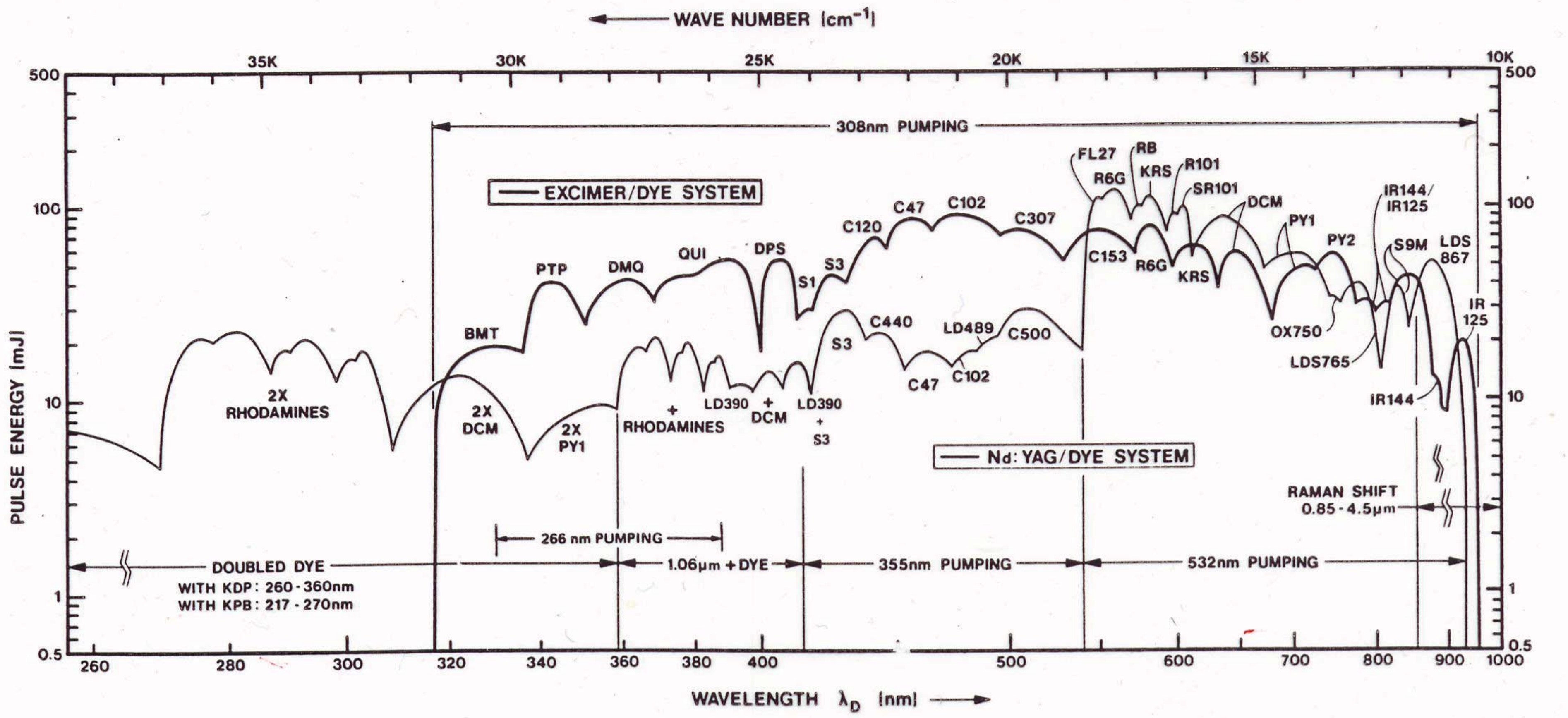


$$P = \chi^{(1)}\mathcal{E} + \chi^{(2)}\mathcal{E}^2 + \chi^{(3)}\mathcal{E}^3 + \dots \qquad \mathcal{E} = \mathcal{E}_0 \sin\omega t$$

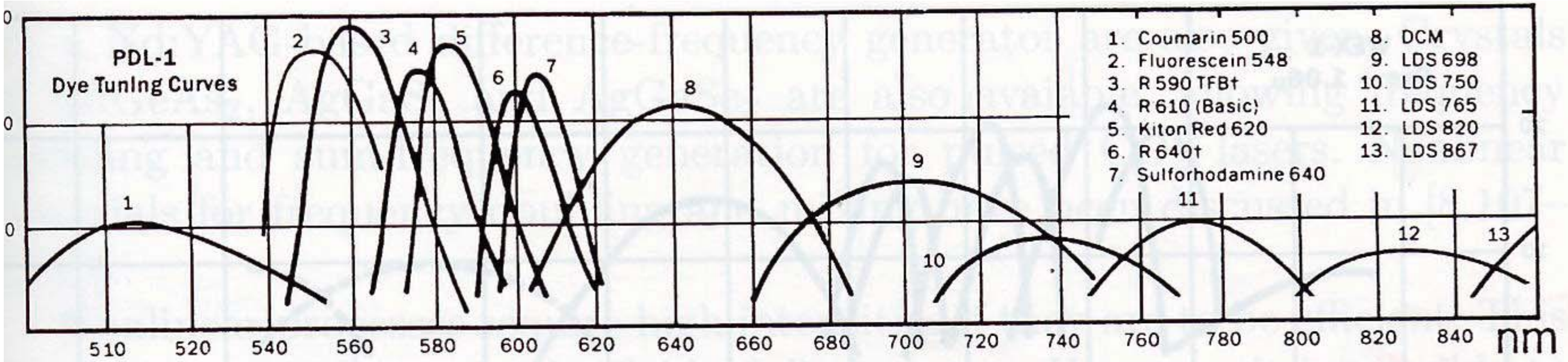
$$P_2 = \chi^{(2)}\mathcal{E}_0^2 \sin^2\omega t = \frac{1}{2}\chi^{(2)}\mathcal{E}_0^2(1 - \cos 2\omega t)$$

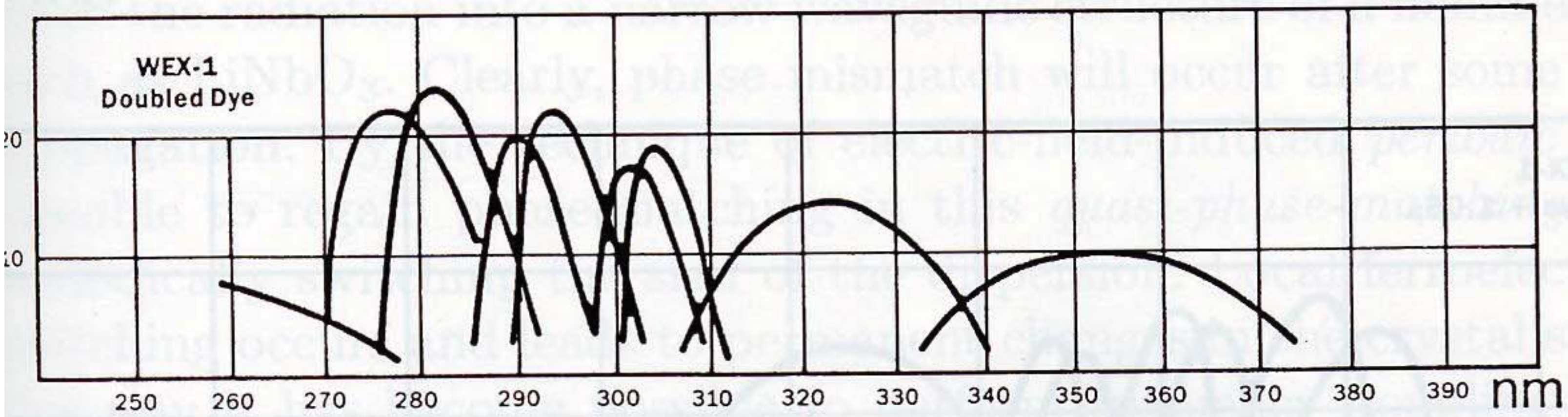
↑ frequency doubling

Pulsed laser tuneability



Tuning ranges – Pulsed dye laser, direct and frequency-doubled





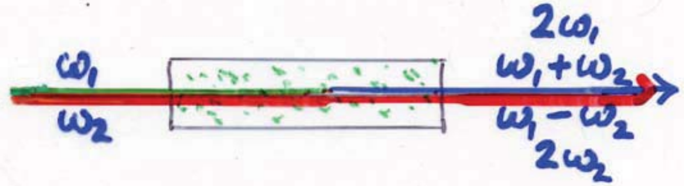
Frequency mixing

$$\mathcal{E} = \mathcal{E}_1 \cos\omega_1 t + \mathcal{E}_2 \cos\omega_2 t$$

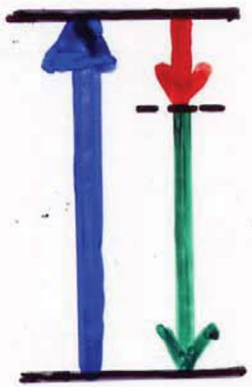
$$P_2 = \chi^{(2)}\left[\mathcal{E}_1^2 \cos^2\omega_1 t + \mathcal{E}_2^2 \cos^2\omega_2 t + 2\mathcal{E}_1\mathcal{E}_2 \cos\omega_1 t \cos\omega_2 t\right]$$

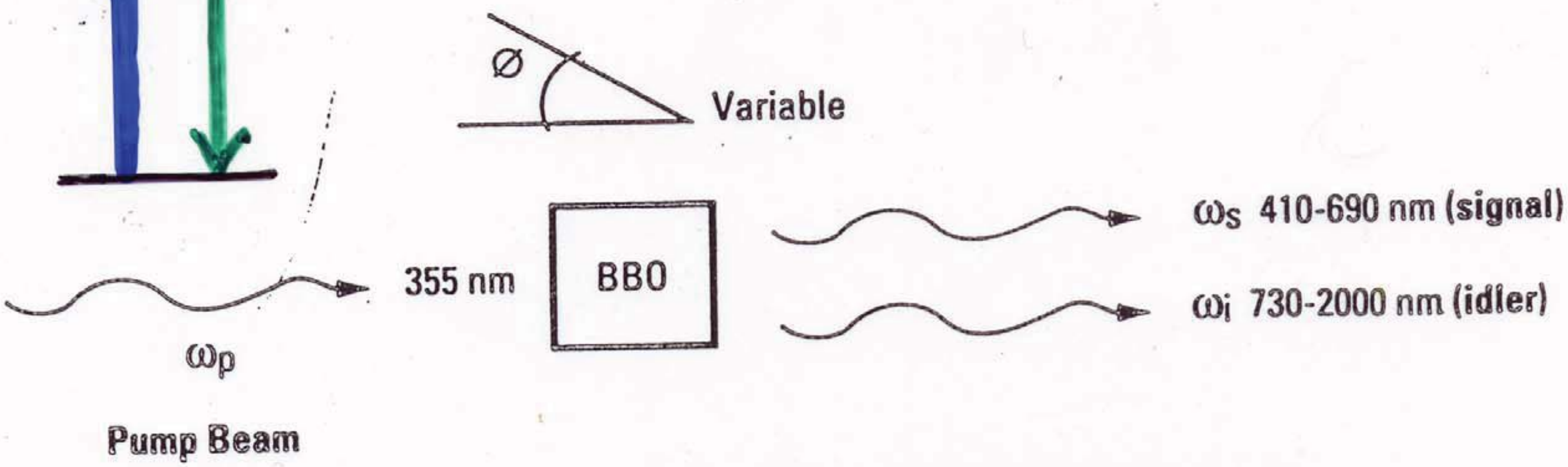
$$= \chi^{(2)}\Big[\tfrac{1}{2}(\mathcal{E}_1^2 + \mathcal{E}_2^2) + \tfrac{1}{2}\mathcal{E}_1^2 \cos\underbrace{2\omega_1}_{2x} t + \tfrac{1}{2}\mathcal{E}_2^2 \cos\underbrace{2\omega_2}_{2x} t + \mathcal{E}_1\mathcal{E}_2 \cos\underbrace{(\omega_1+\omega_2)}_{\text{sum}} t + \mathcal{E}_1\mathcal{E}_2 \cos\underbrace{(\omega_1-\omega_2)}_{\text{difference}} t\Big]$$

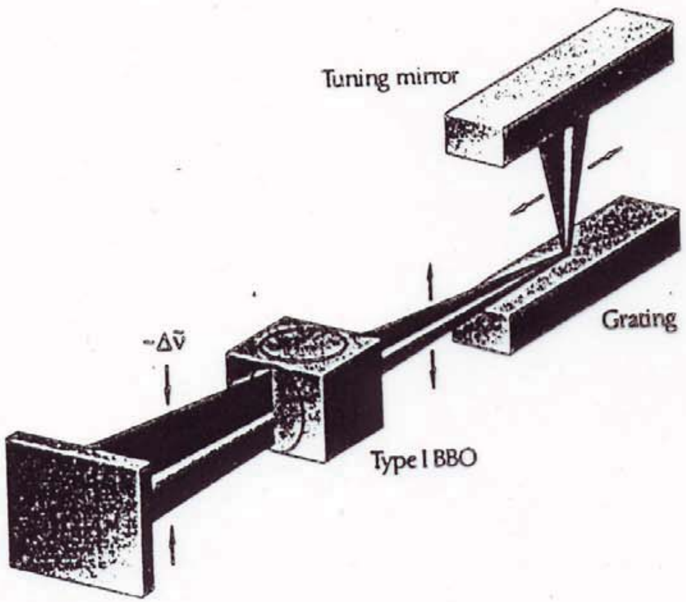
PHASE-MATCHING NEEDED!

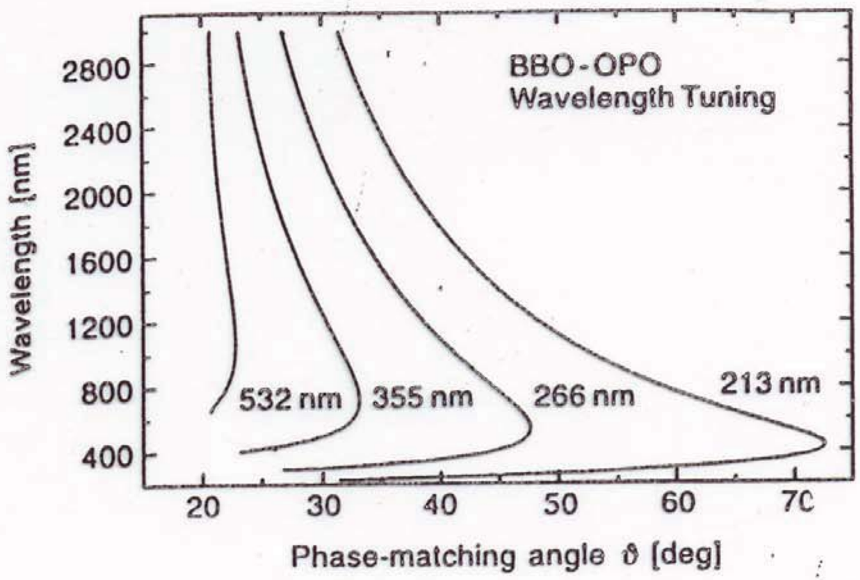


Optical Parametric Oscillator
OPO

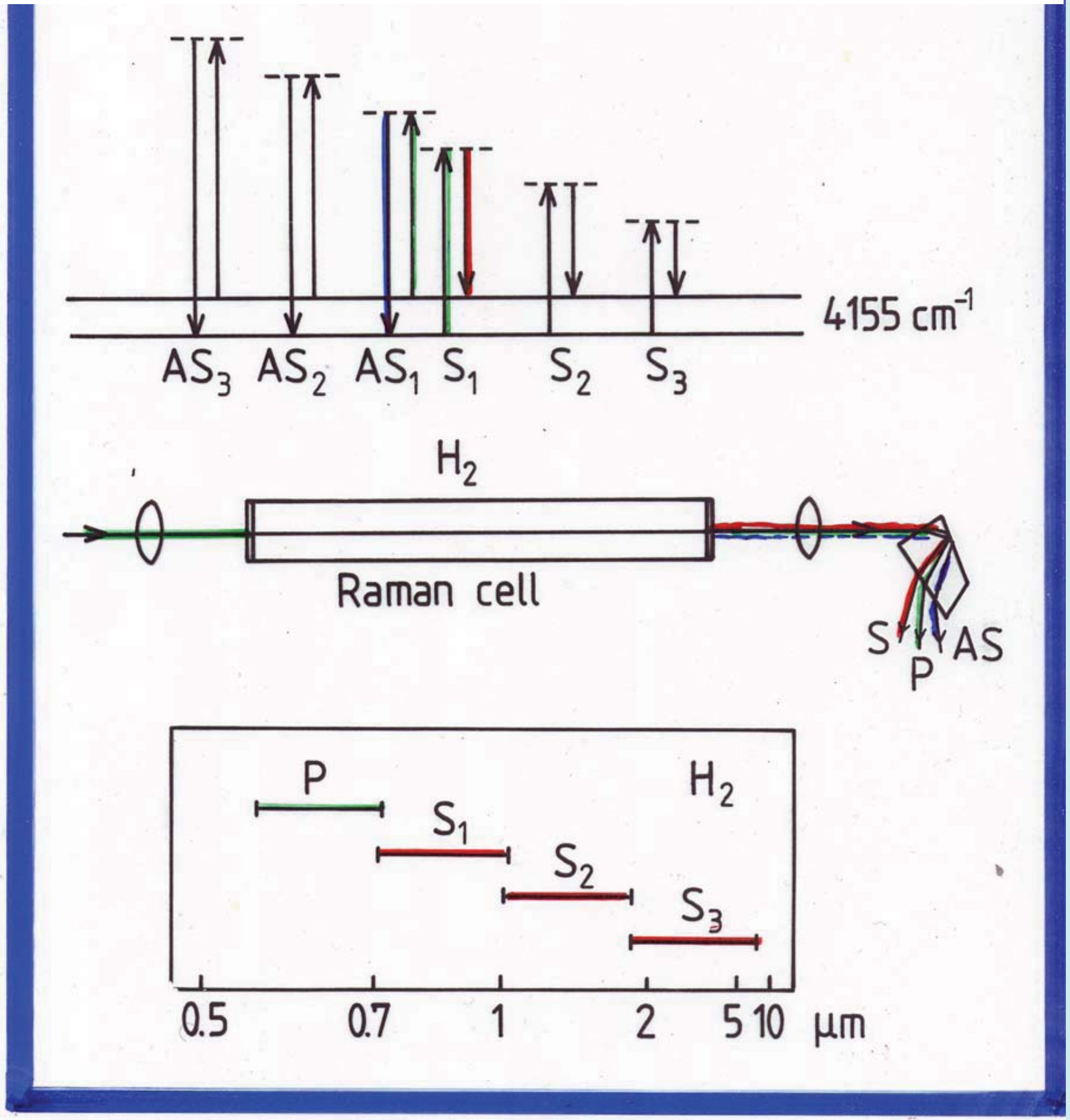




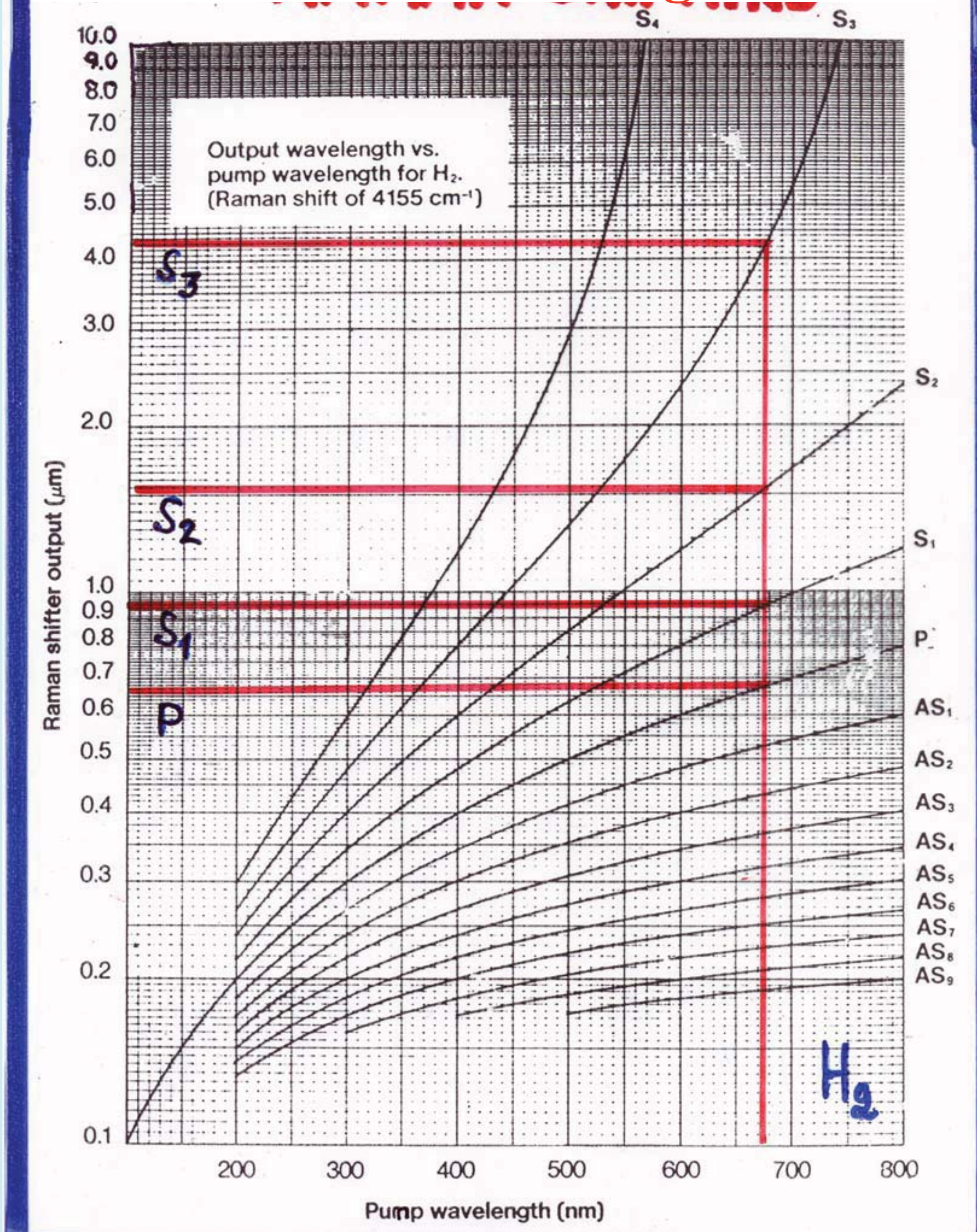




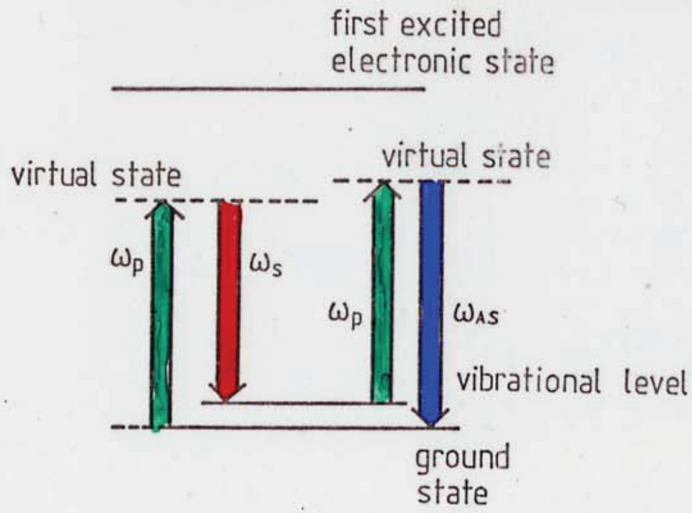
Stimulated Raman Scattering



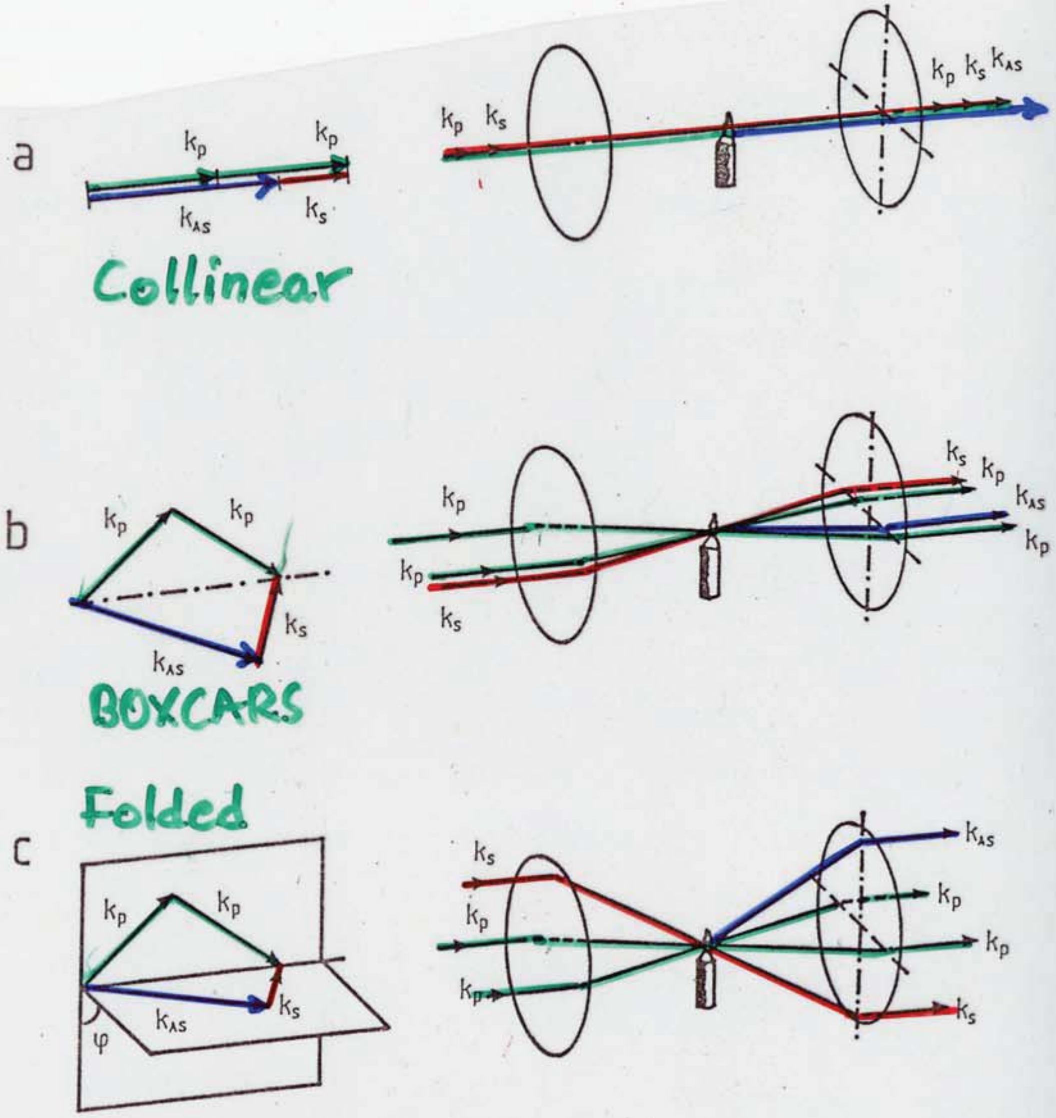
Raman shifting



Coherent Anti-Stokes Raman Scattering CARS



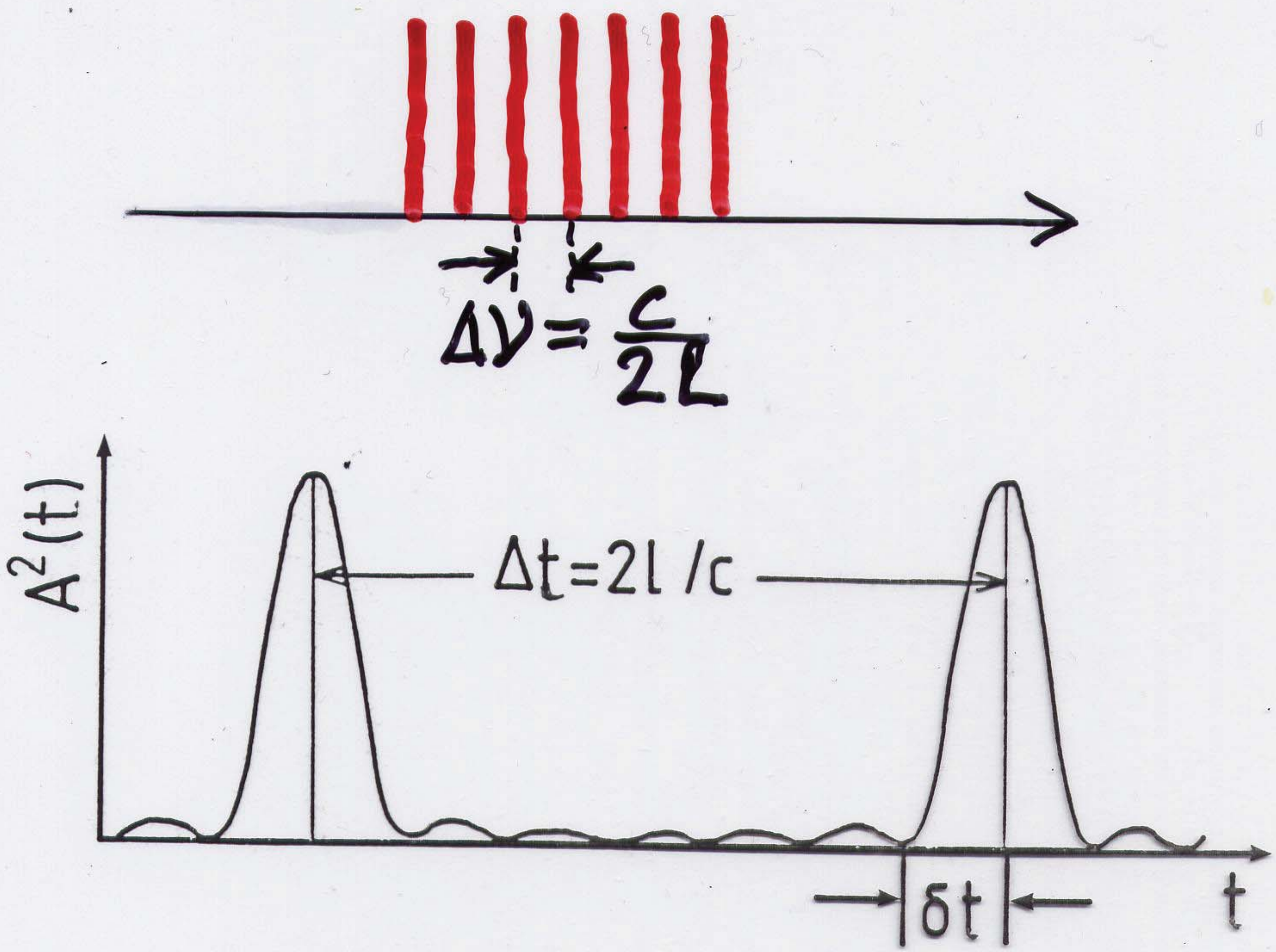
$$\omega_{AS} = 2\omega_p - \omega_s$$



$$\underline{K}_{AS} = 2\underline{K}_p - \underline{K}_s$$

$$|K| = \omega n / c$$

Mode locking



$$E_0 e^{i(\omega t \pm l \Delta\omega t)}$$

$$\begin{cases} \Delta\omega = 2\pi\,(c/2L) = \pi c/L \\ \varphi_K - \varphi_{K-1} = \alpha \end{cases}$$

2N+1 moder

$$E(t) = \sum_{l=-N}^{+N} E_0 \exp\left[i(\omega_0 + l\Delta\omega)t + l\alpha\right]$$

$$E(t) = A(t)\exp(i\omega_0 t)$$

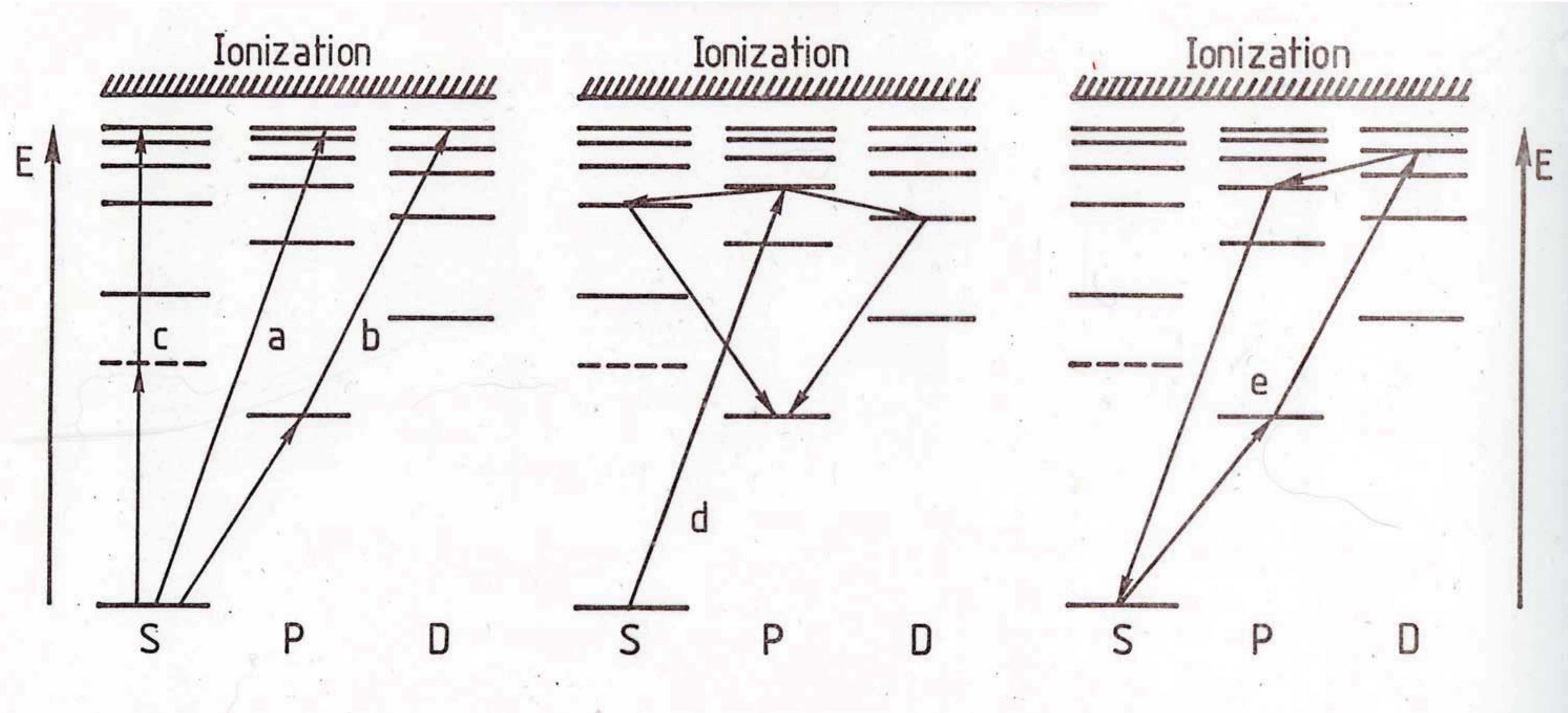
$$A(t) = E_0 \frac{\sin\left[(2N+1)(\Delta\omega t + \alpha)/2\right]}{\sin\left[(\Delta\omega t + \alpha)/2\right]}$$

Repetitiv med perioden $\tau = 2L/c$

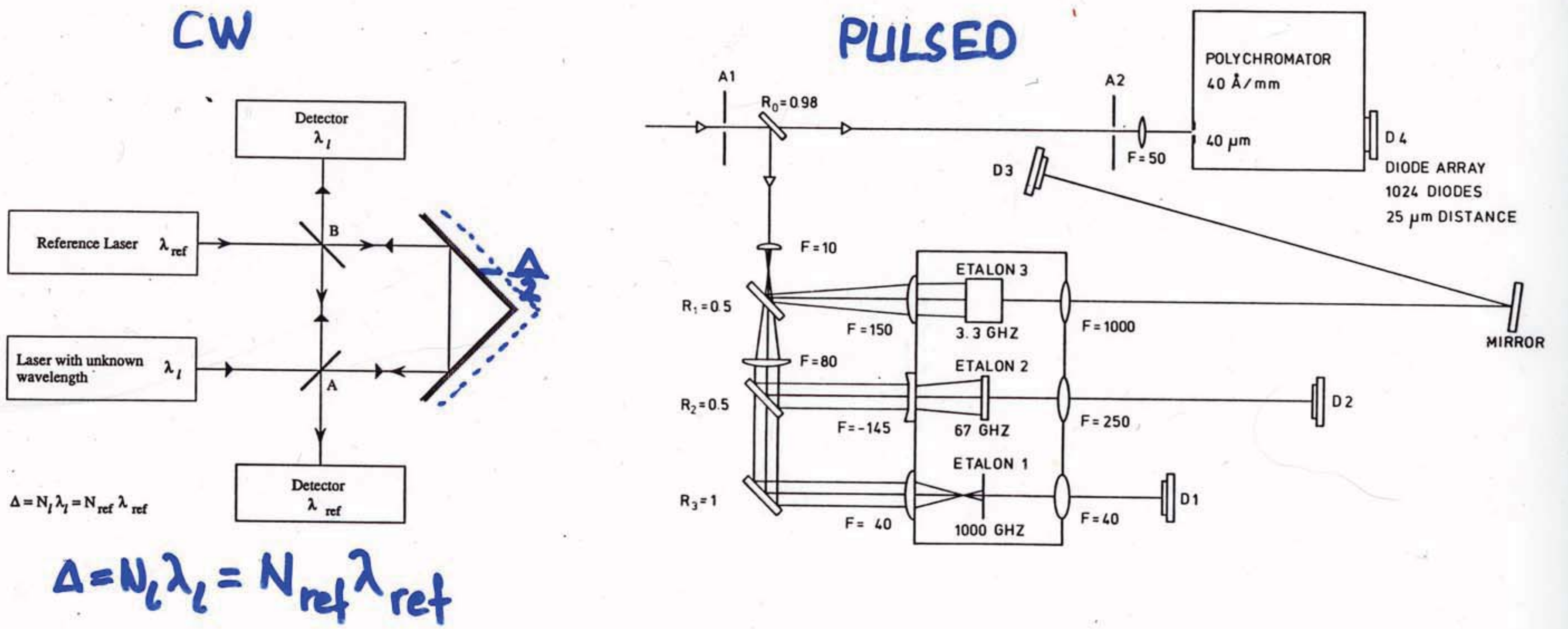
("cavity round trip time")

$$\Delta\tau = \frac{2\pi}{(2N+1)\Delta\omega} = \frac{1}{\nu_{osc}}$$

Excitation schemes

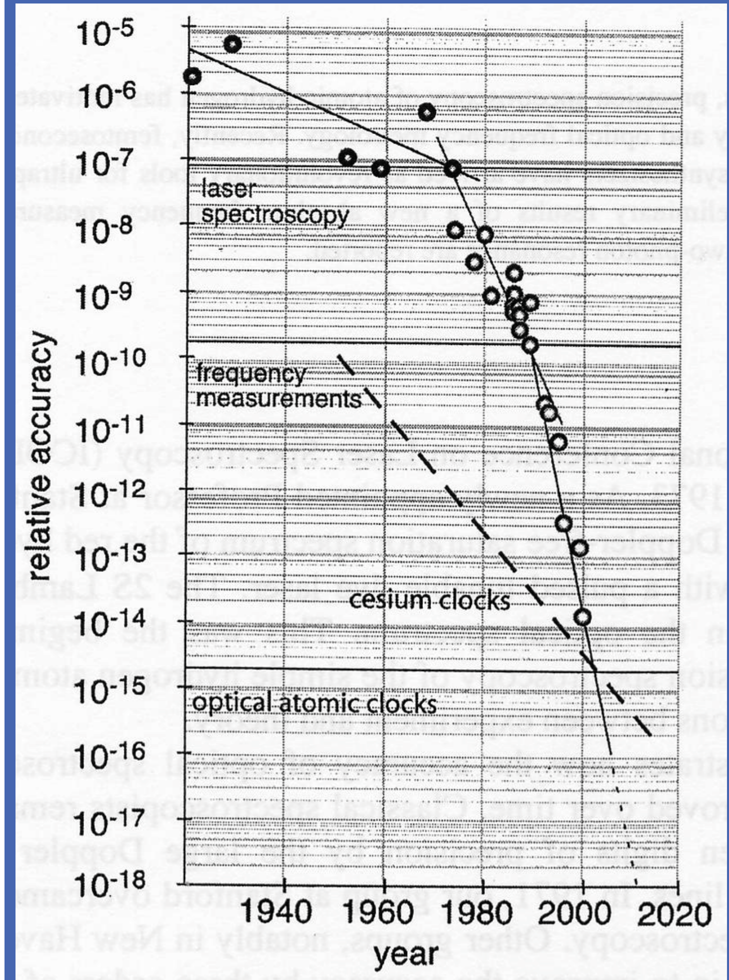


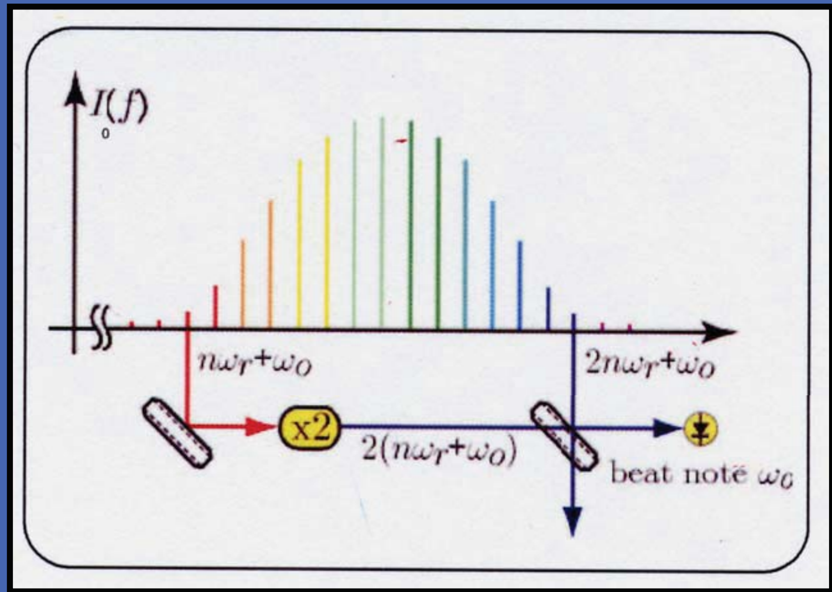
Wave meters


CW
PULSED
Detector λ_l
Reference Laser λ_{ref}
B
Laser with unknown wavelength λ_l
A
Detector λ_{ref}
$\Delta = N_l \lambda_l = N_{ref} \lambda_{ref}$
$\Delta = N_l \lambda_l = N_{ref} \lambda_{ref}$
A1
$R_0 = 0.98$
A2
F = 50
POLYCHROMATOR
40 Å / mm
40 µm
D 4
DIODE ARRAY
1024 DIODES
25 µm DISTANCE
D 3
F = 10
$R_1 = 0.5$
F = 150
ETALON 3
3.3 GHZ
F = 1000
MIRROR
F = 80
$R_2 = 0.5$
F = -145
ETALON 2
67 GHZ
F = 250
D 2
$R_3 = 1$
F = 40
ETALON 1
1000 GHZ
F = 40
D 1

Laser-based precision spectroscopy

Stable lasers, frequency comb techniques
Fundamental measurements





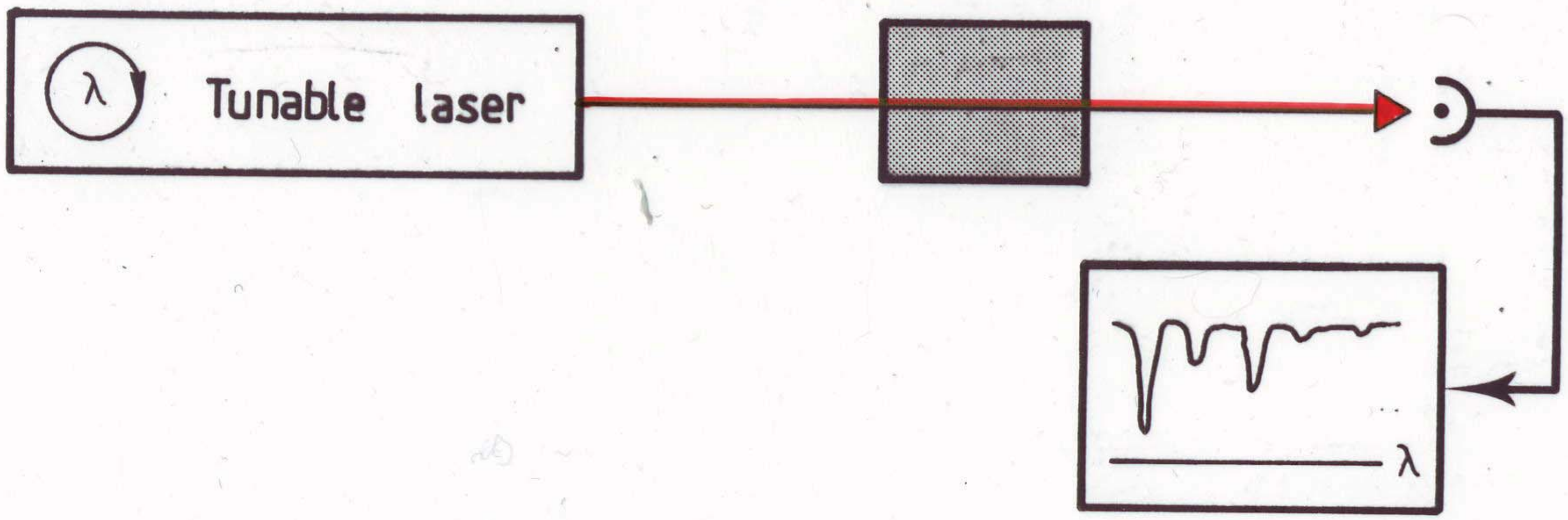
$$\Delta E = hf = h\ c/\lambda$$

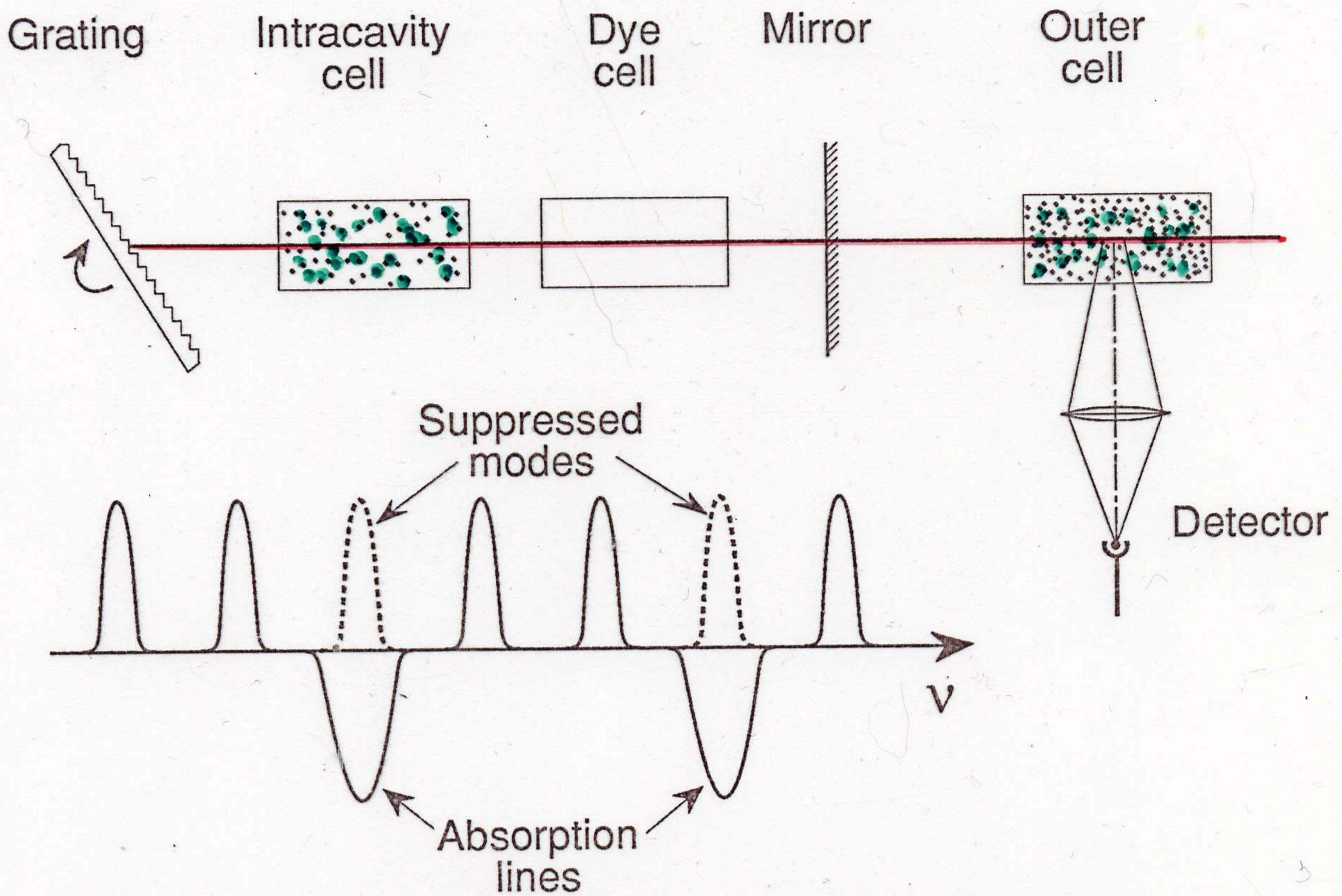
Rydberg constant: f(m,e,h,c)

Fine structure constant: f(e,h,c)

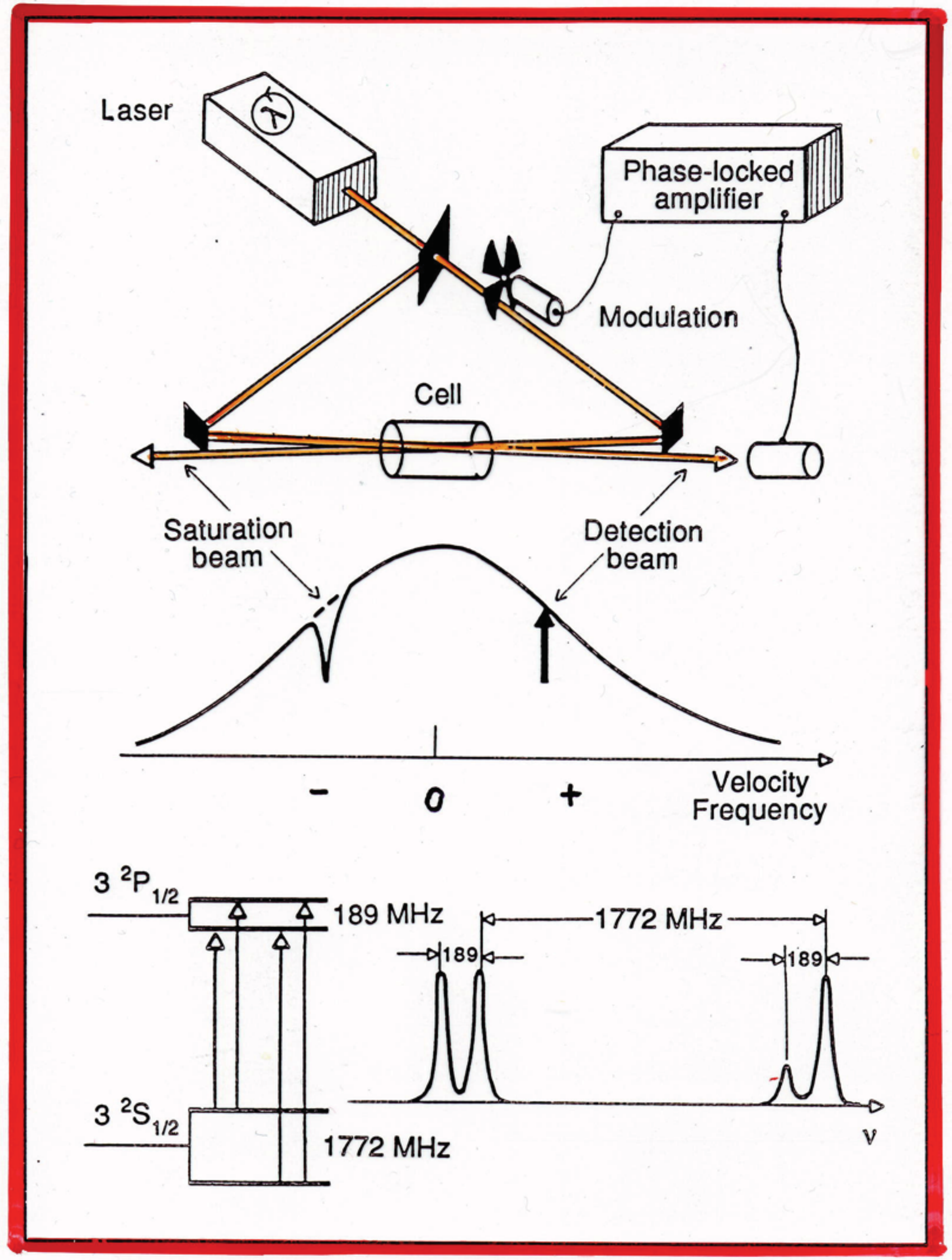
Anti-hydrogen ↔ Hydrogen

Absorption Spectroscopy



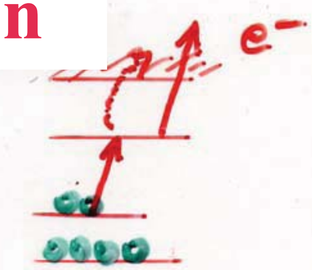


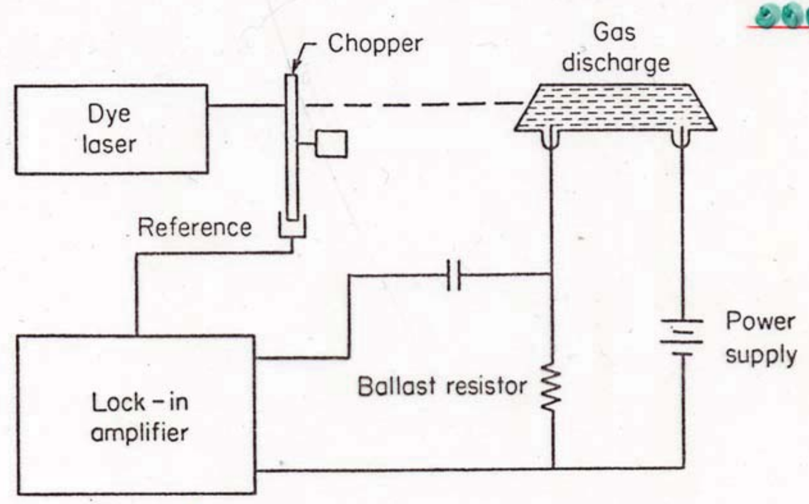
Intracavity absorption

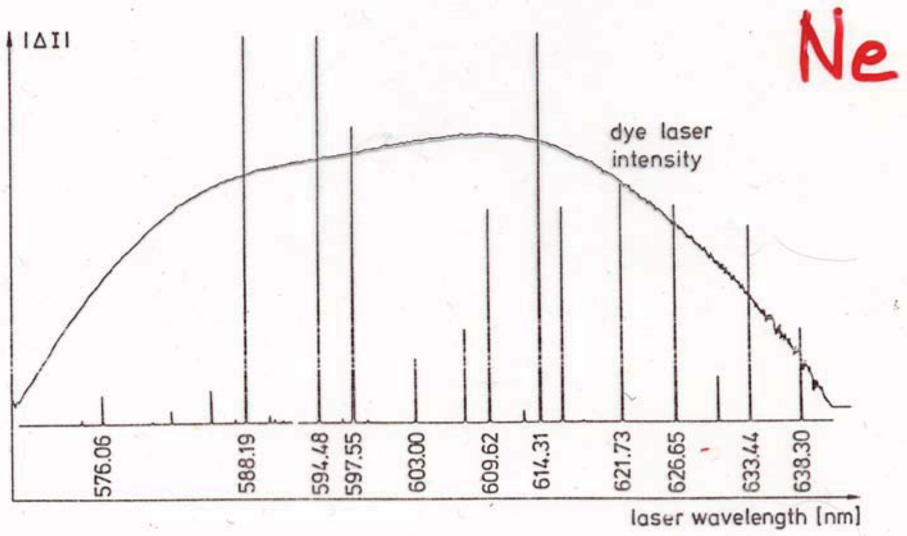


Doppler-free Saturation spectroscopy

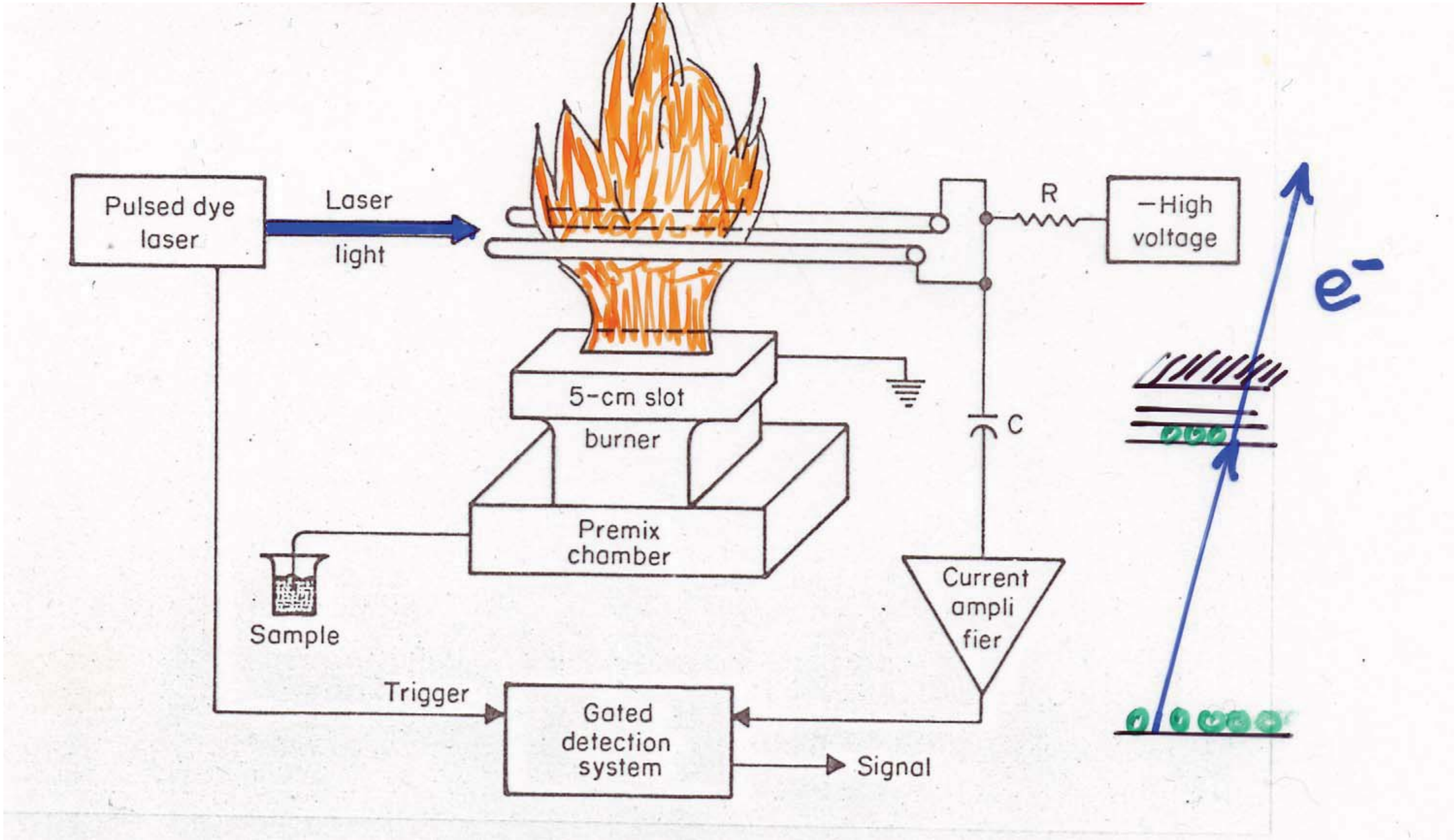
Optogalvanic detection



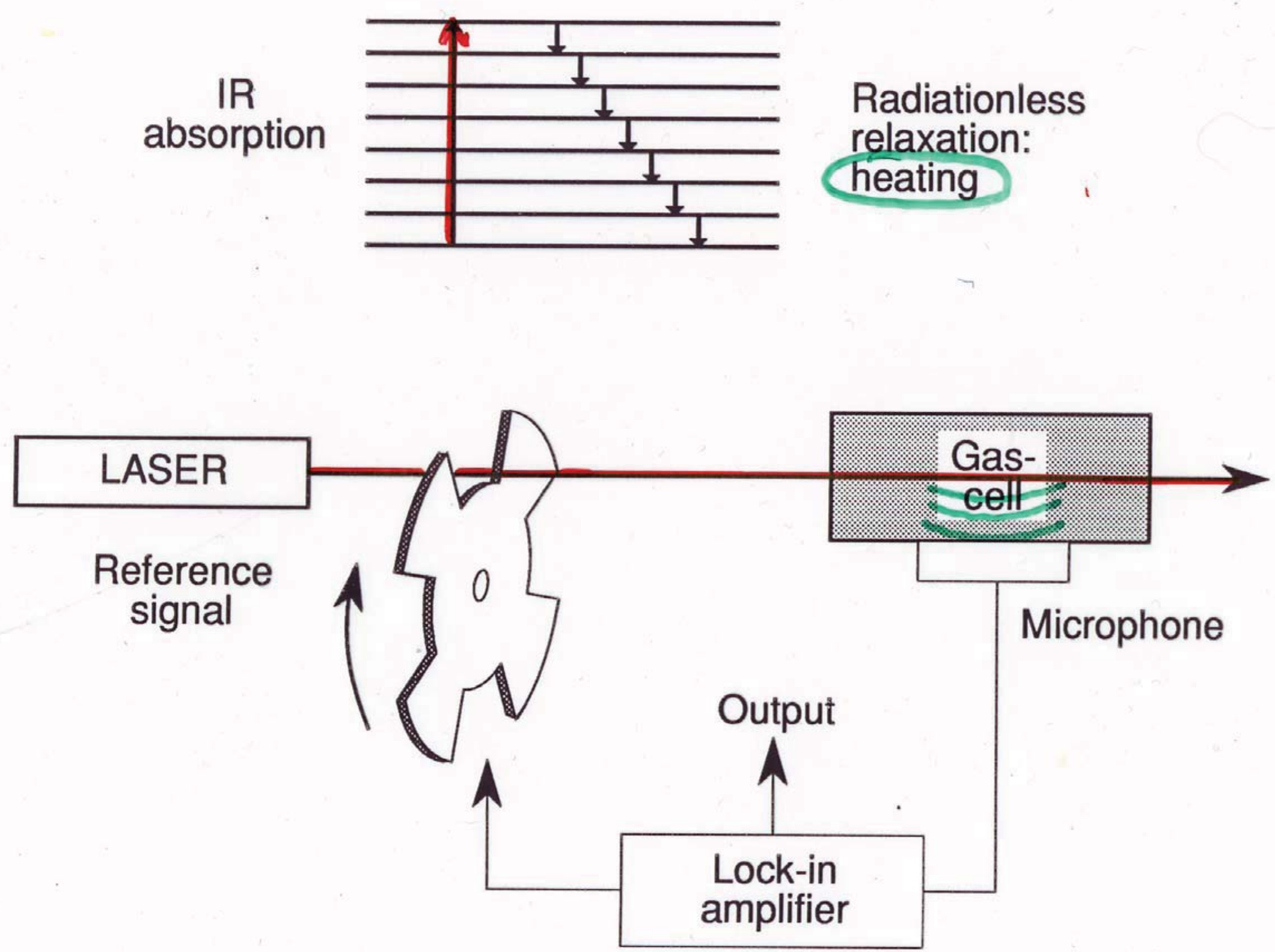


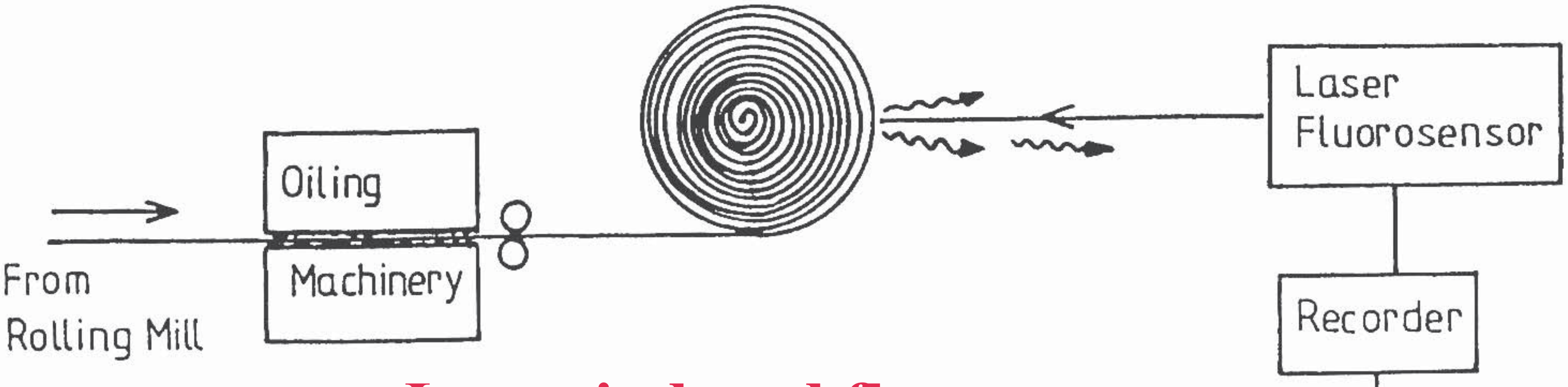


Flame optogalvanic spectroscopy

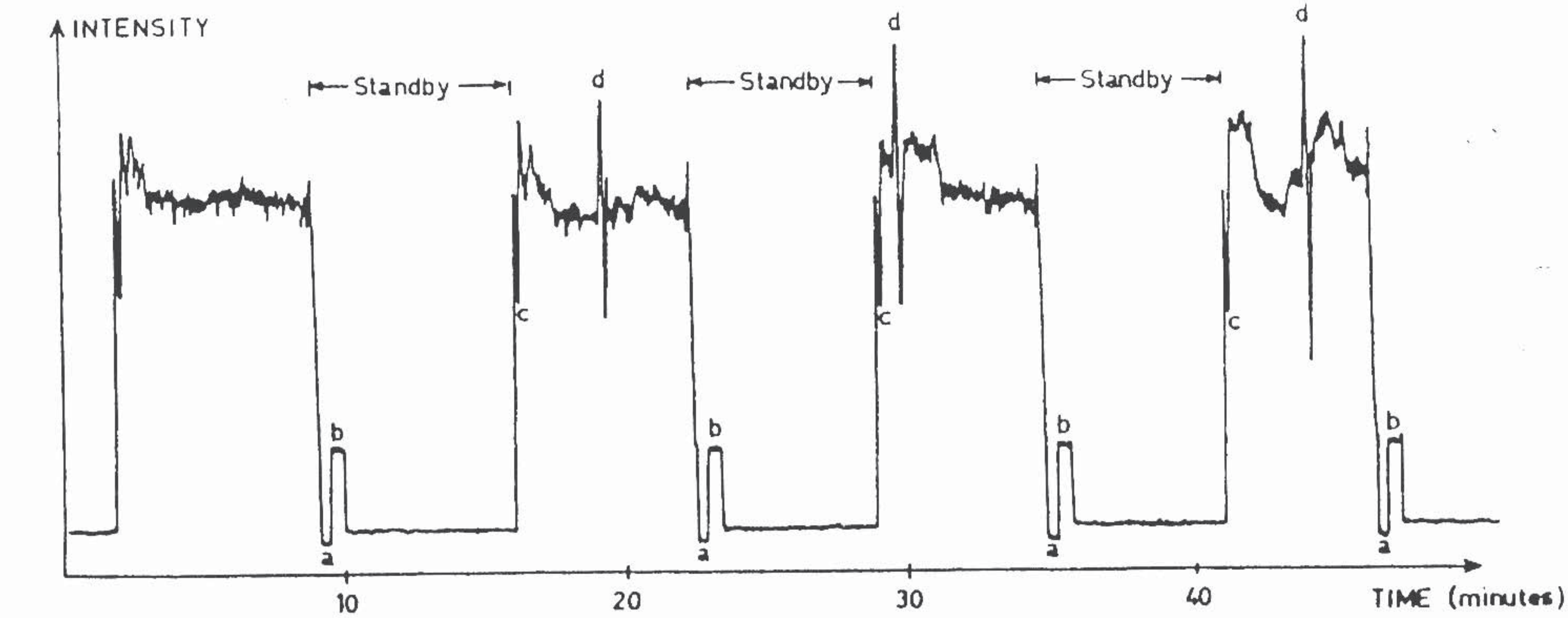


Optoacoustic spectroscopy

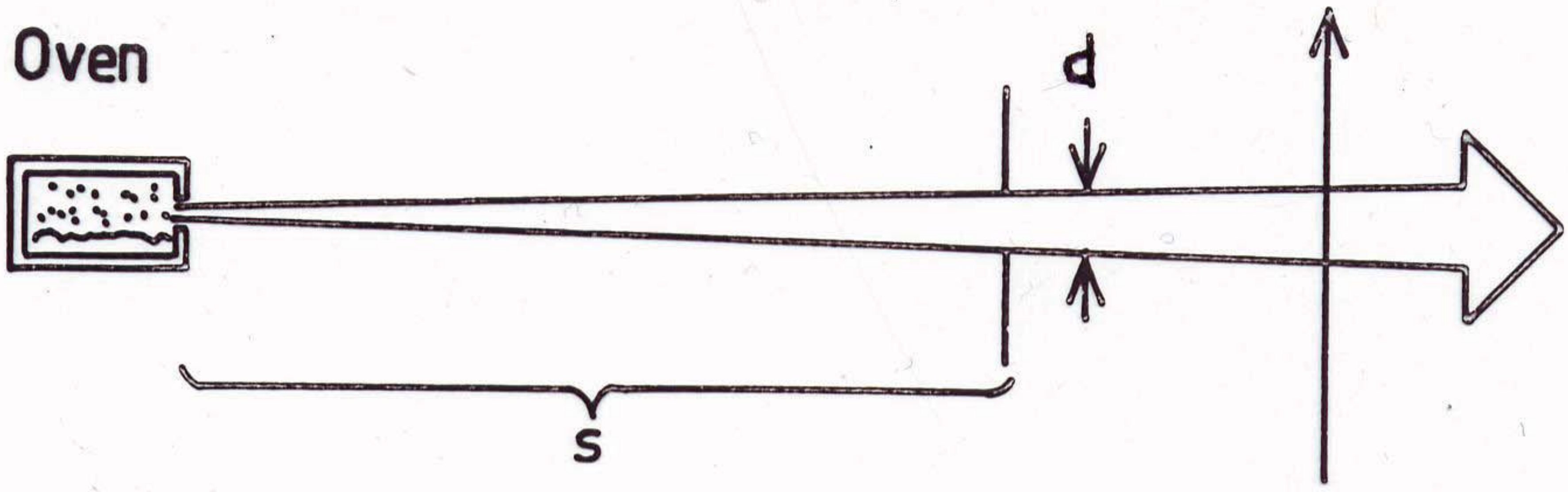




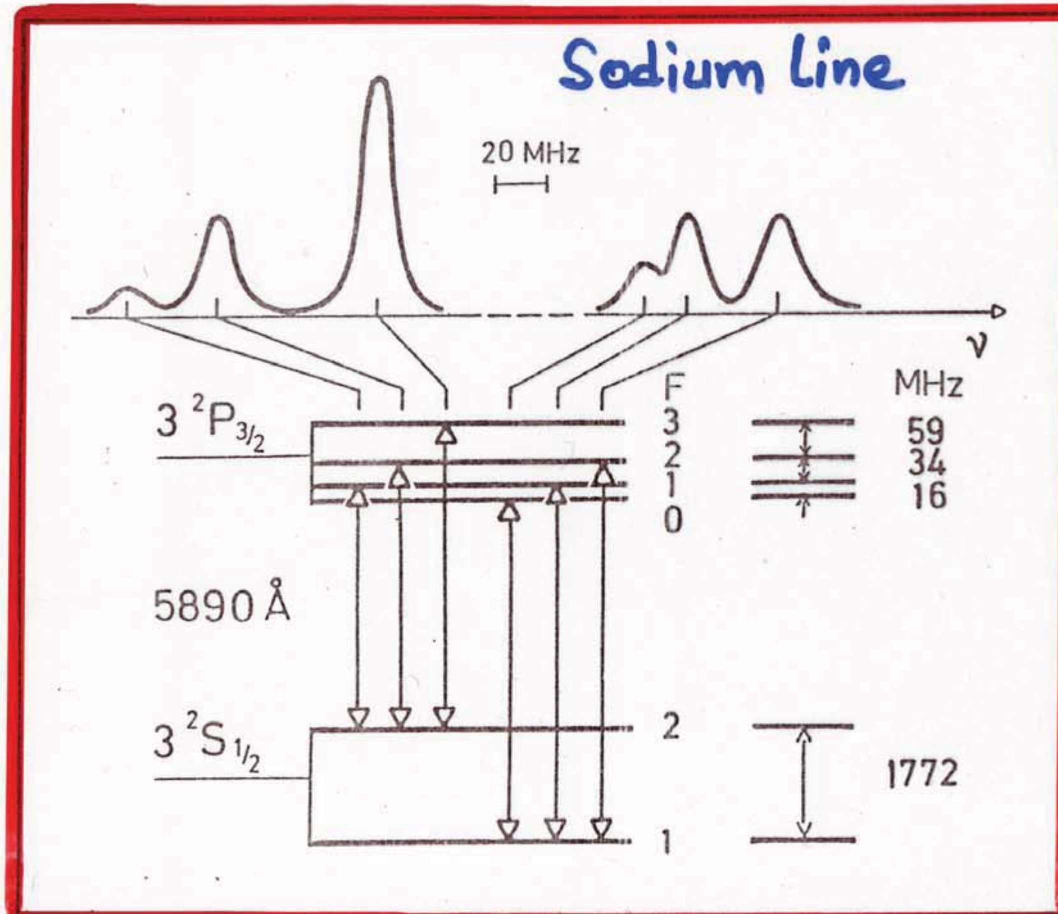
Laser-induced fluorescence
Oil on sheet metal

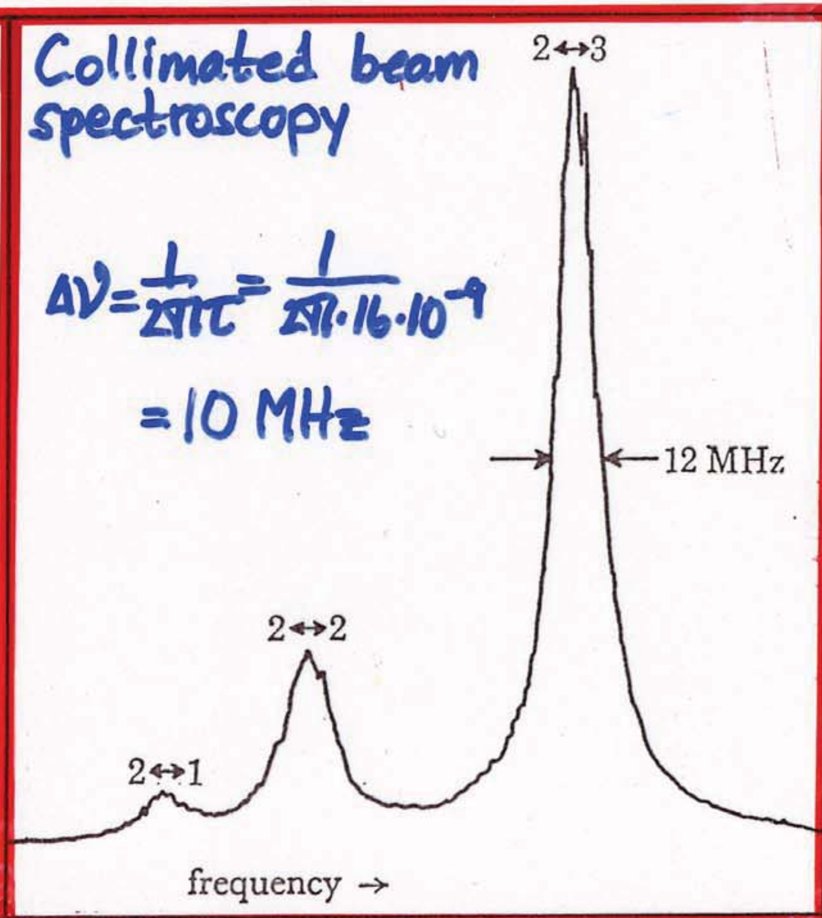


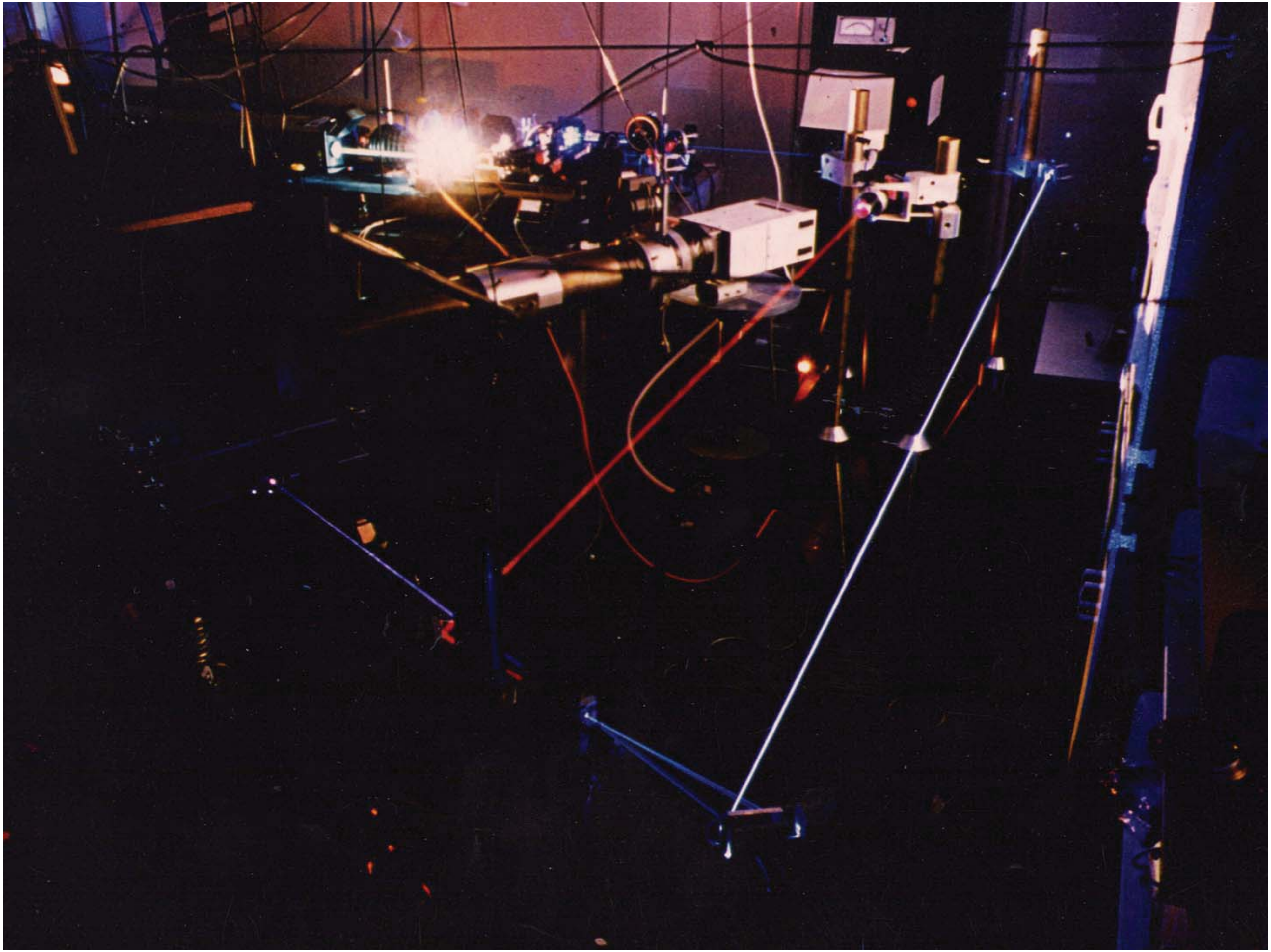
Collimated atomic beam
Laser-indusced fluorescence detection



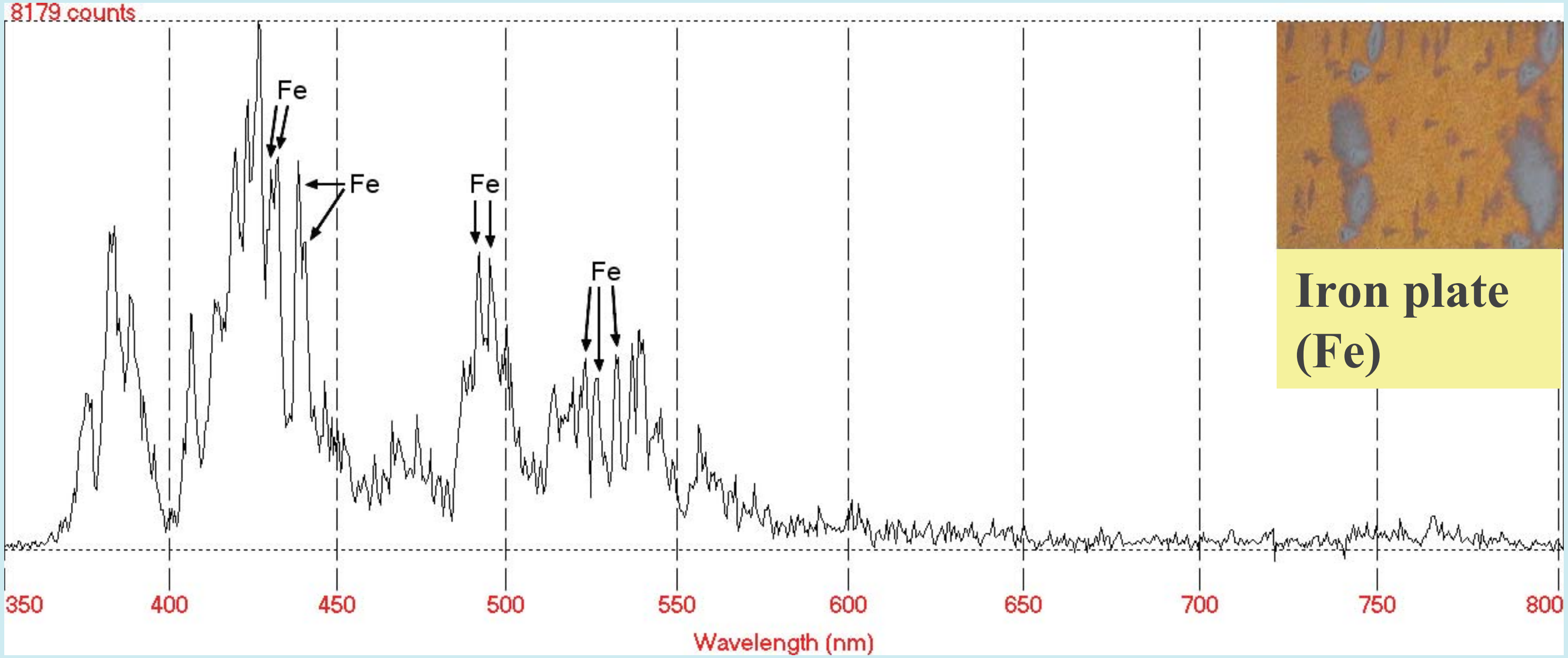
Collimation ratio $C = \frac{s}{d}$

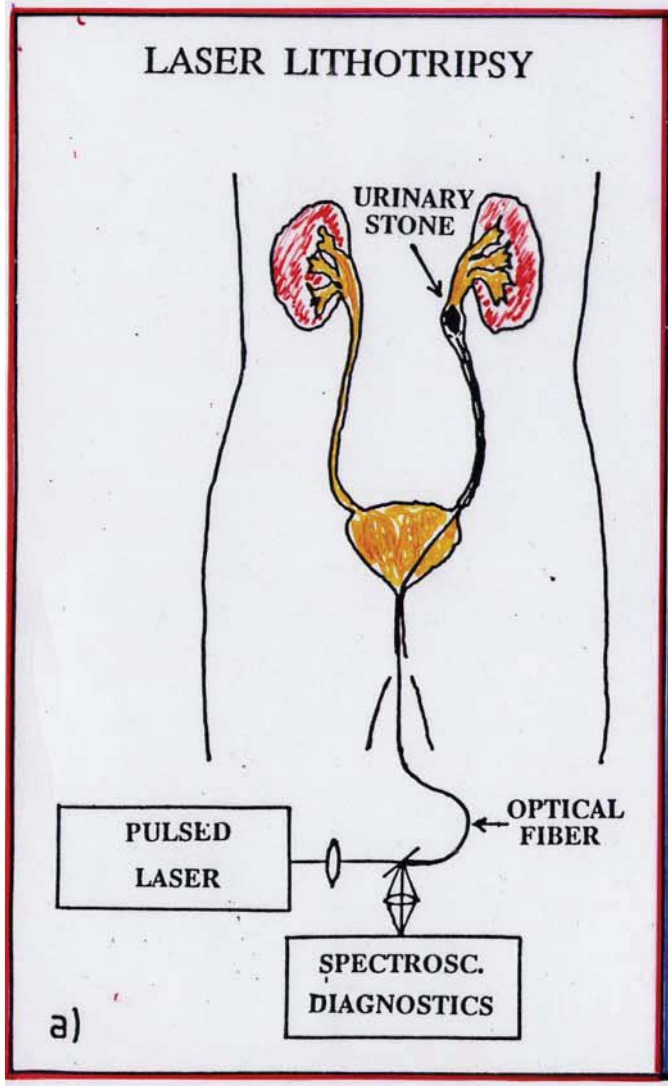

Sodium line
20 MHz
ν
F
MHz
3 ²P3/2
3
2
1
0
59
34
16
5890 Å
3 ²S1/2
2
1
1772

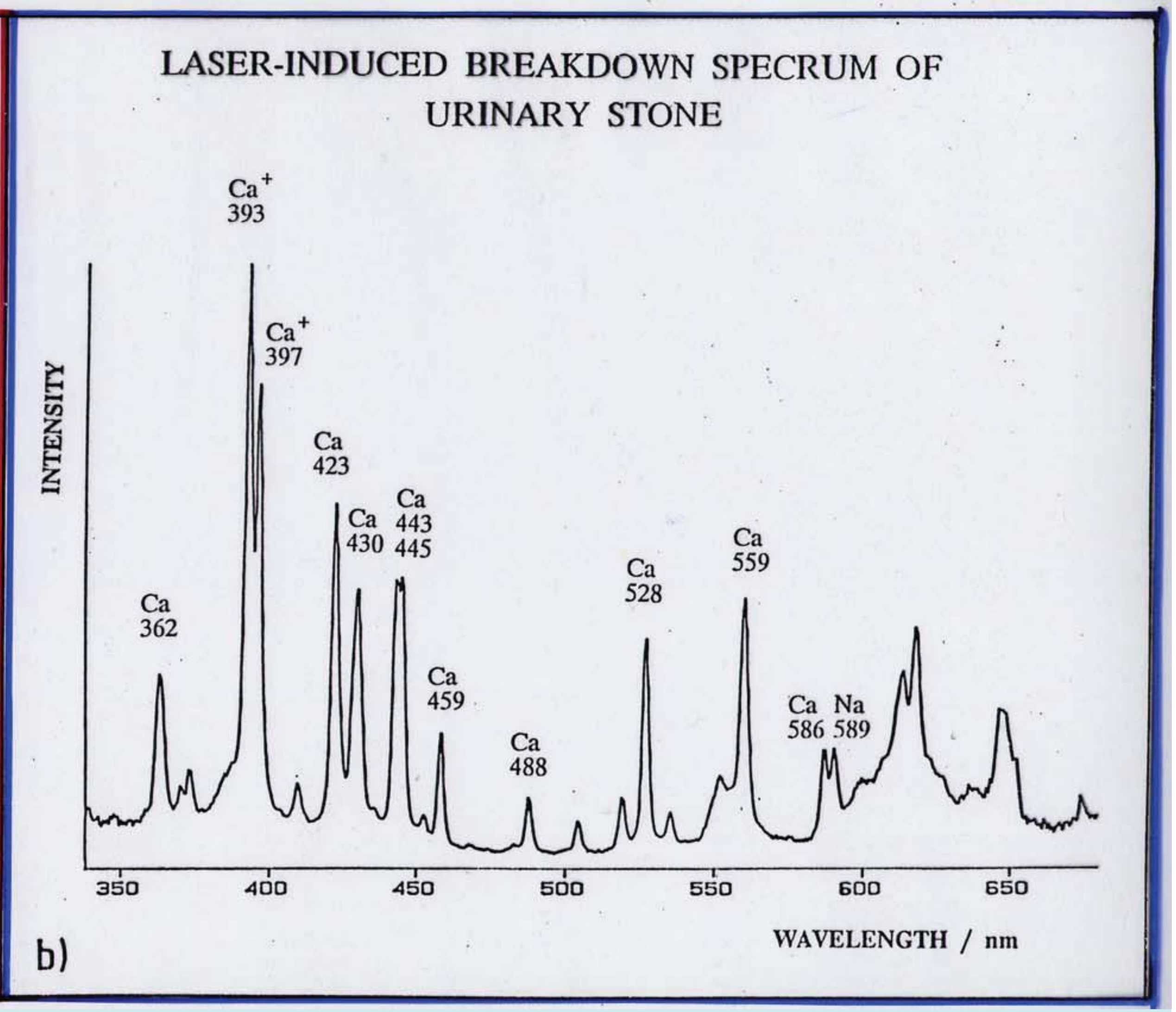

Collimated beam spectroscopy
Δν = 1/2πτ = 1/2π·16·10⁻⁹
= 10 MHz
2↔3
12 MHz
2↔2
2↔1
frequency →



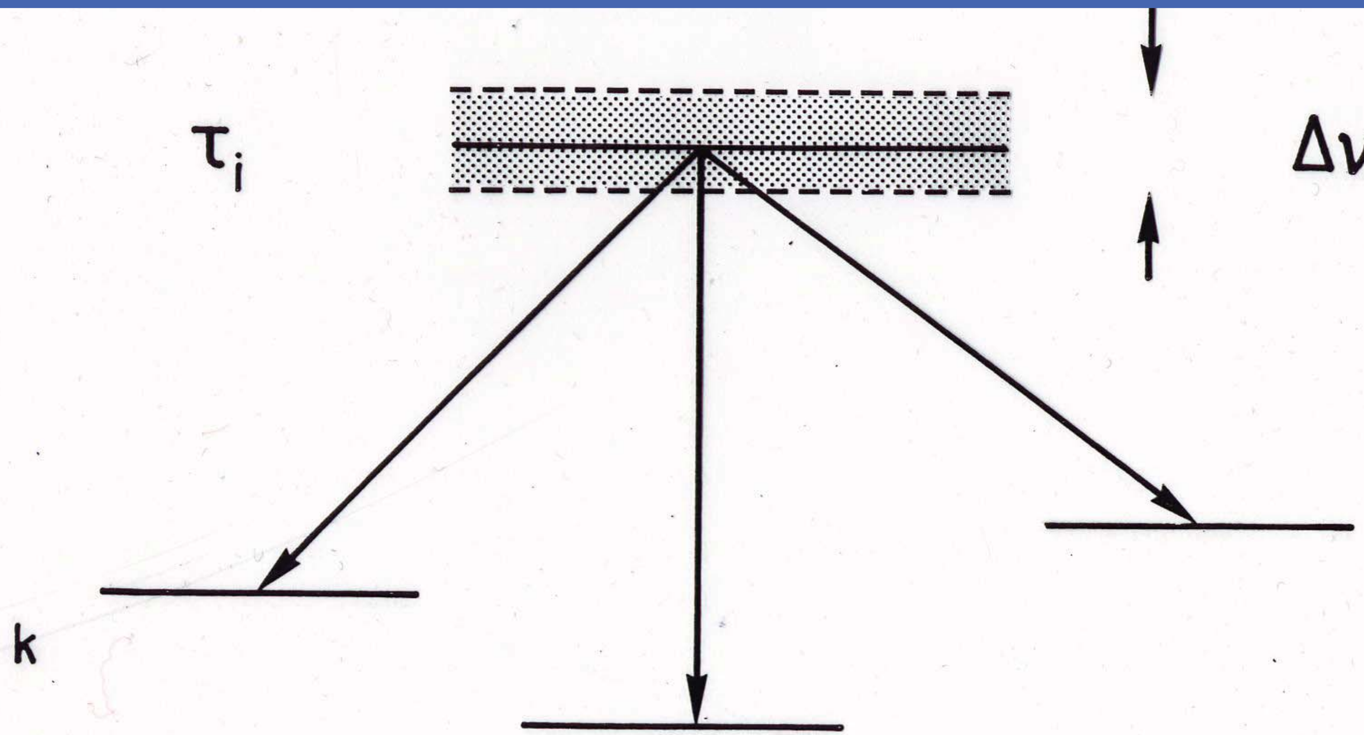
Laser-Induced Break-Down Spectroscopy (LIBS)




LASER LITHOTRIPSY
URINARY STONE
PULSED LASER
OPTICAL FIBER
SPECTROSC. DIAGNOSTICS
a)


LASER-INDUCED BREAKDOWN SPECRUM OF URINARY STONE
INTENSITY
Ca+ 393
Ca+ 397
Ca 423
Ca 430
Ca 443 445
Ca 362
Ca 459
Ca 488
Ca 528
Ca 559
Ca 586
Na 589
350
400
450
500
550
600
650
WAVELENGTH / nm
b)

Relations between radiative properties

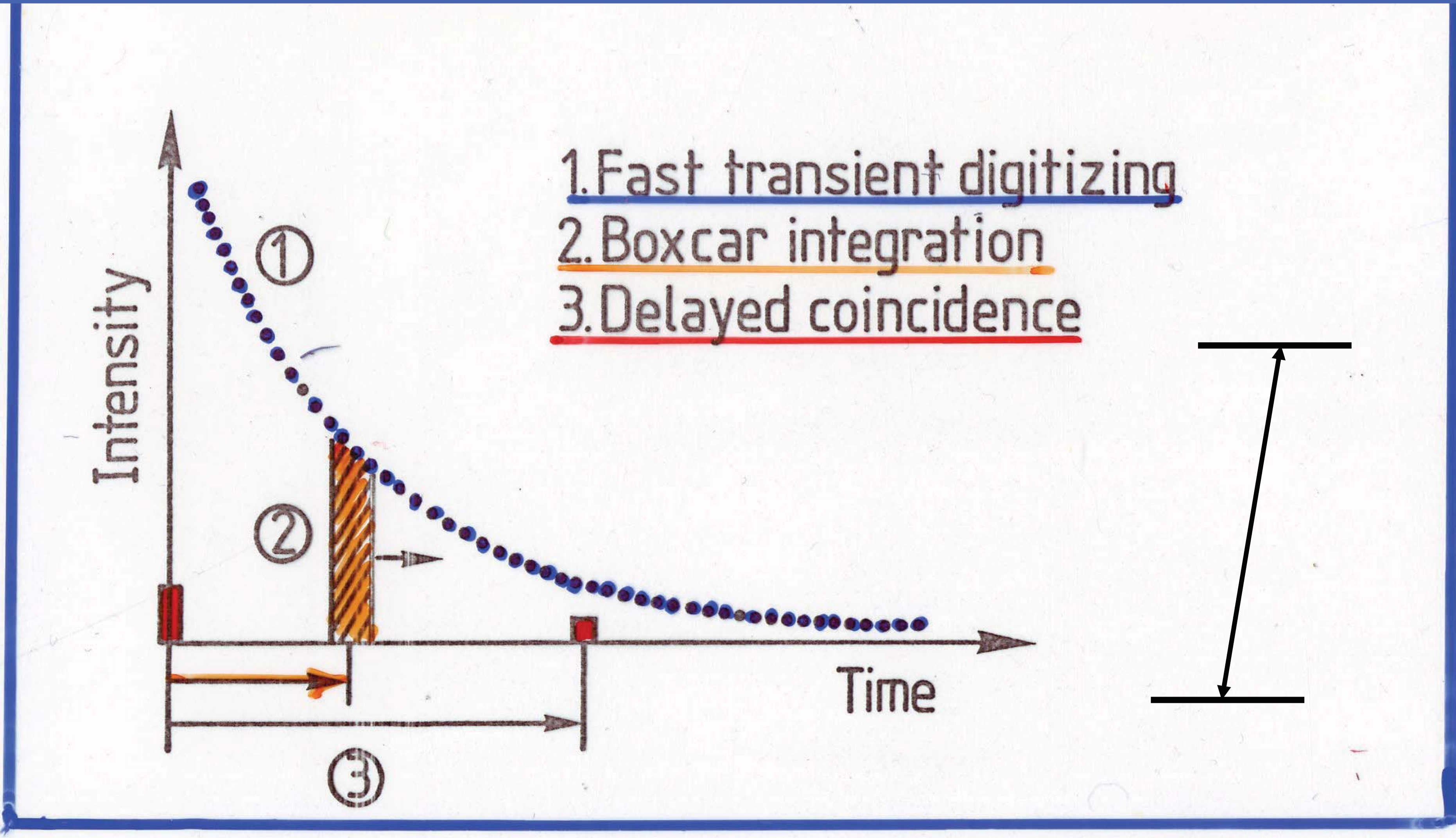


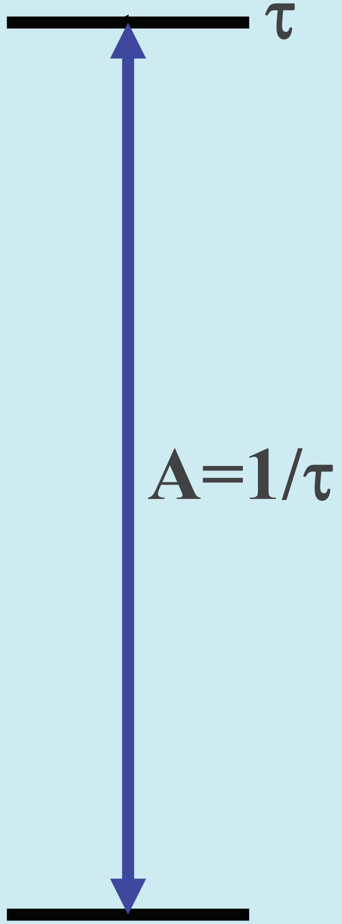
$$\Delta\nu = \frac{1}{2\pi\tau}$$

$$\tau_i = \frac{1}{\sum_k A_{ik}}$$

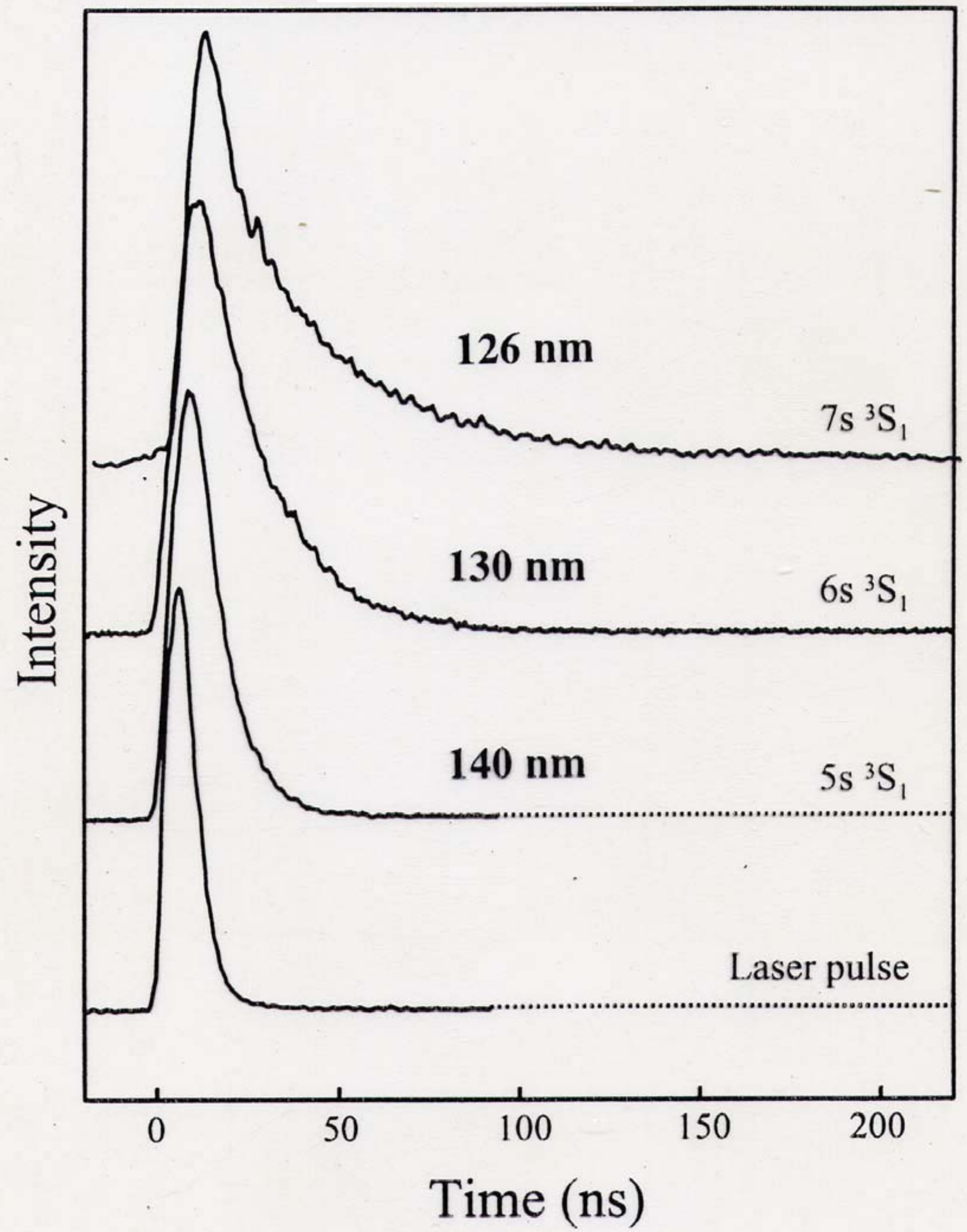
$$A_{ik} \sim |\langle\psi_i \,|\, e\underline{r} \,|\, \psi_k\rangle|^2$$

Electronic recording of transients

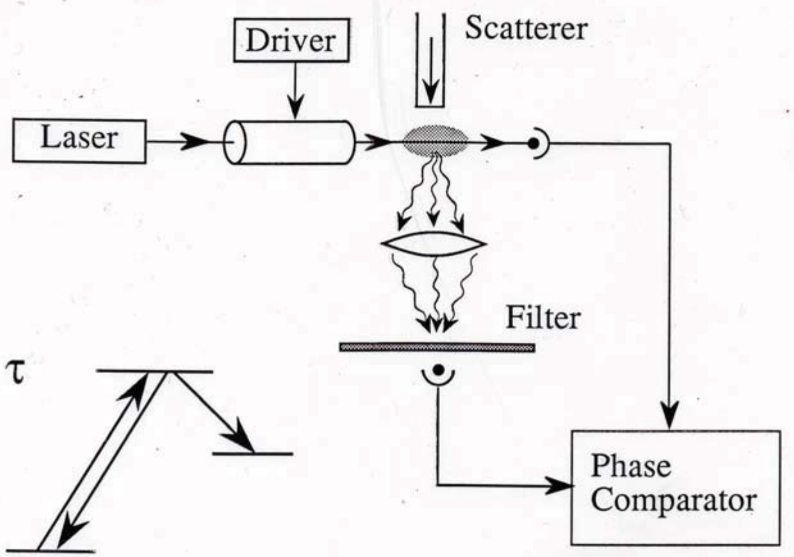


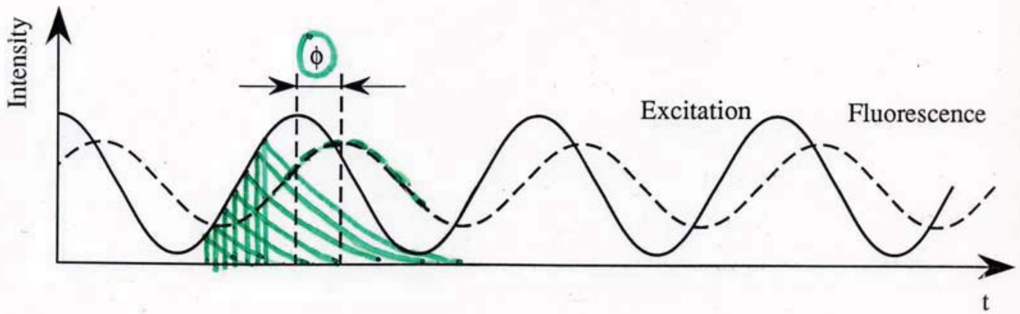

τ
A=1/τ

Sulfur


126 nm
7s ³S₁
130 nm
6s ³S₁
140 nm
5s ³S₁
Laser pulse
Intensity
0
50
100
150
200
Time (ns)

Phase-shift method



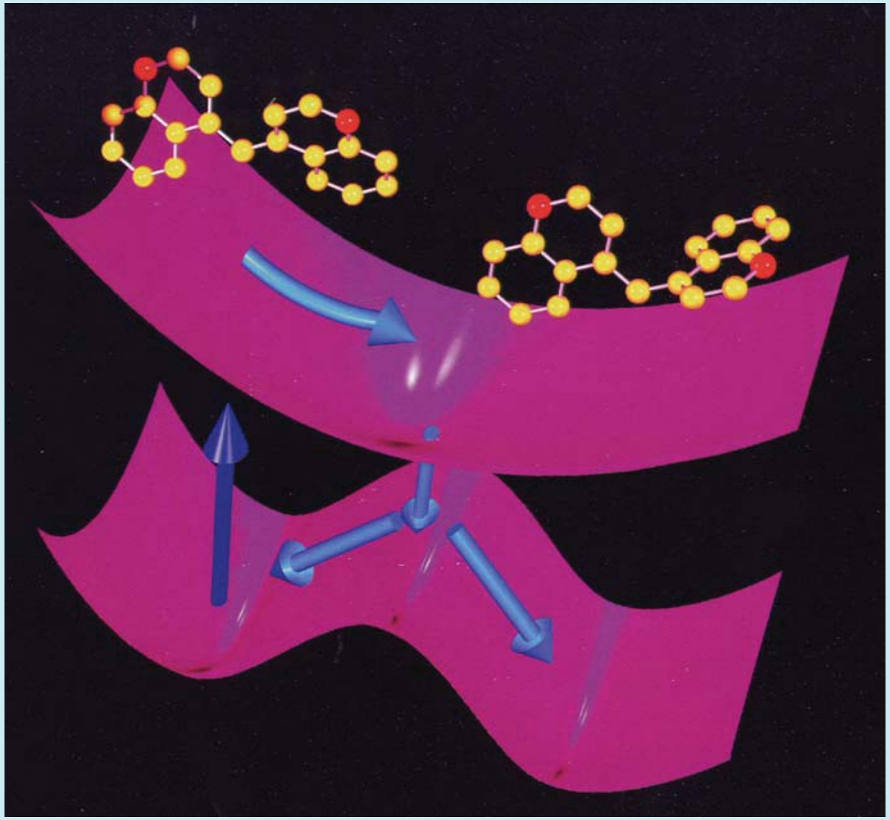


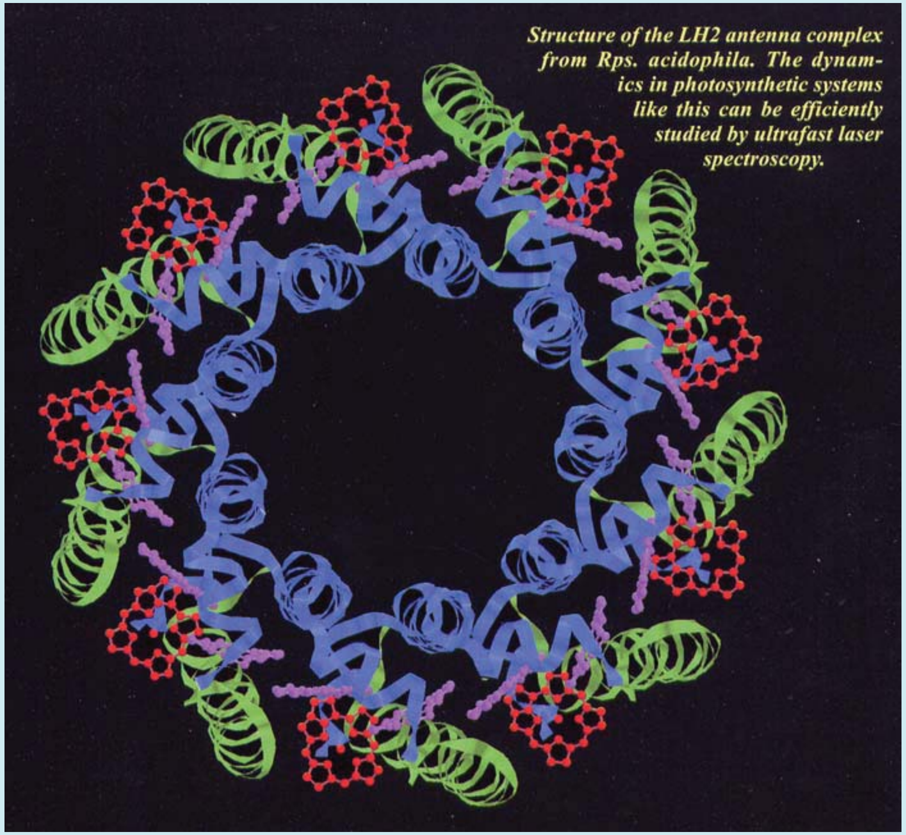
$$I_{exc} = I_0 \, (1 + a \sin \Omega t) \cos \omega t$$

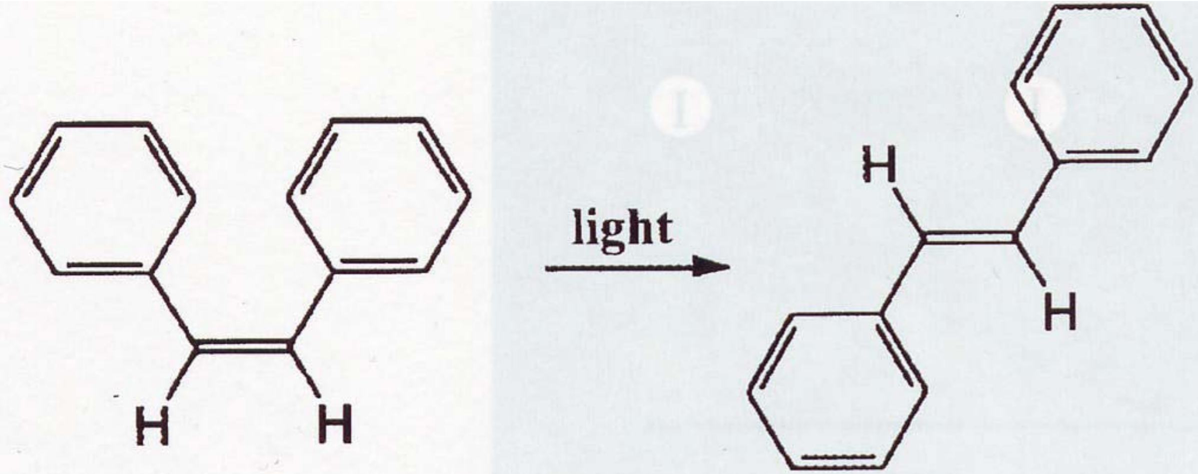
$$I_{fl} = bI_0 \left[1 + \frac{a}{\sqrt{1 + \Omega^2 \tau^2}} \sin(\Omega t + \phi) \right] \cos \omega t$$

$$\tan \phi = \Omega \tau$$

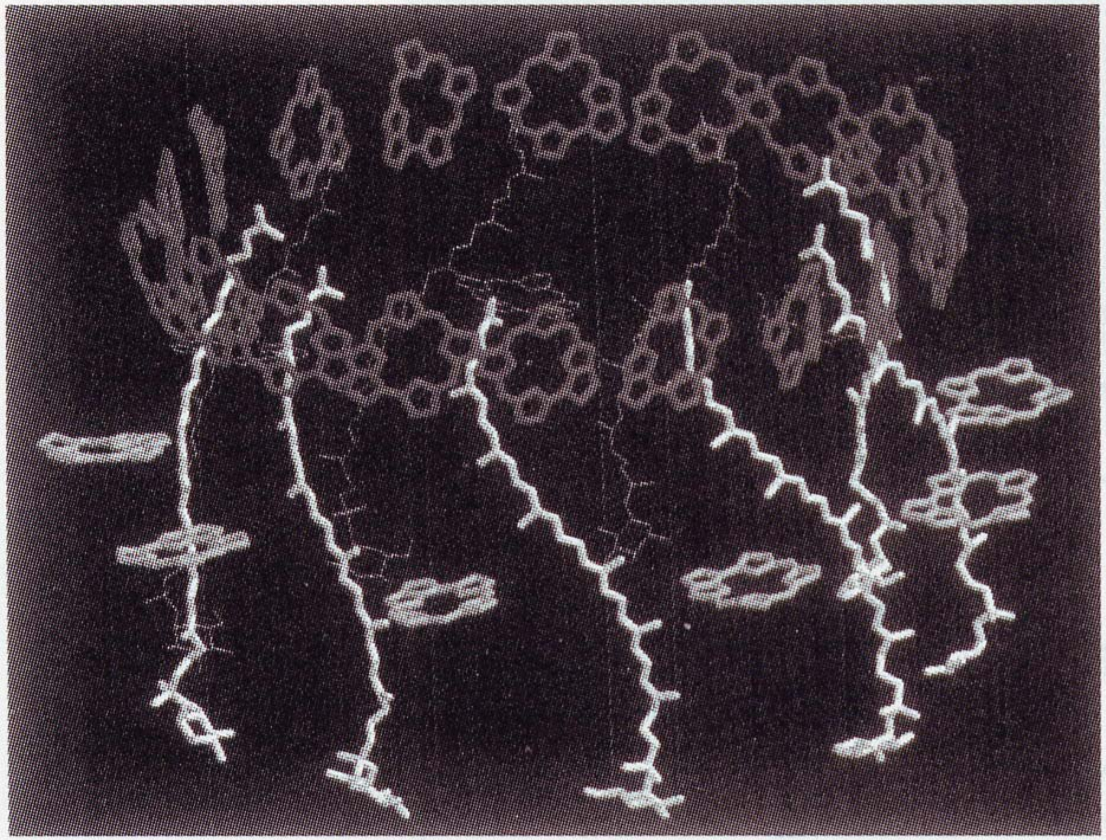
Ultrafast spectroscopy of complex molecules

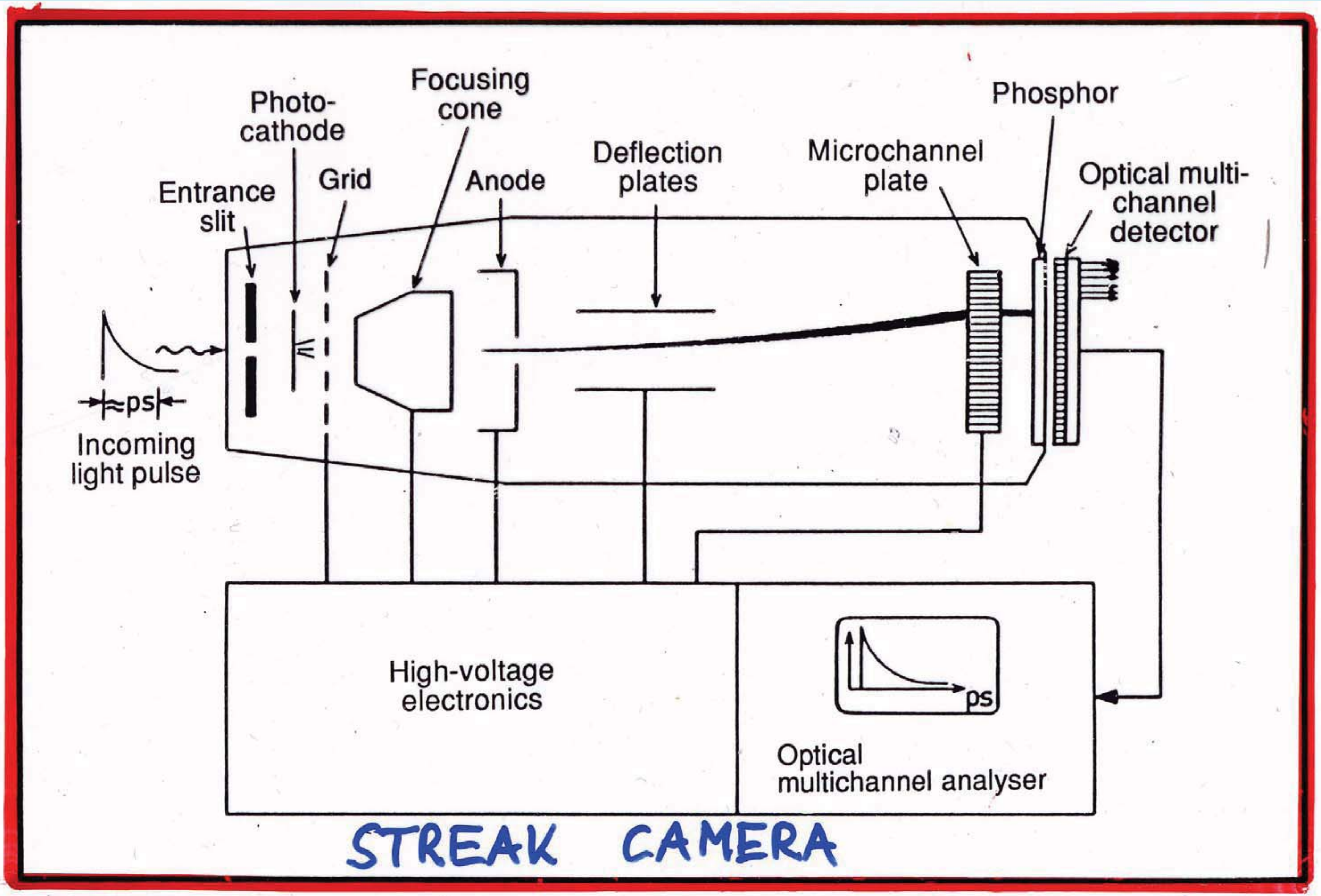




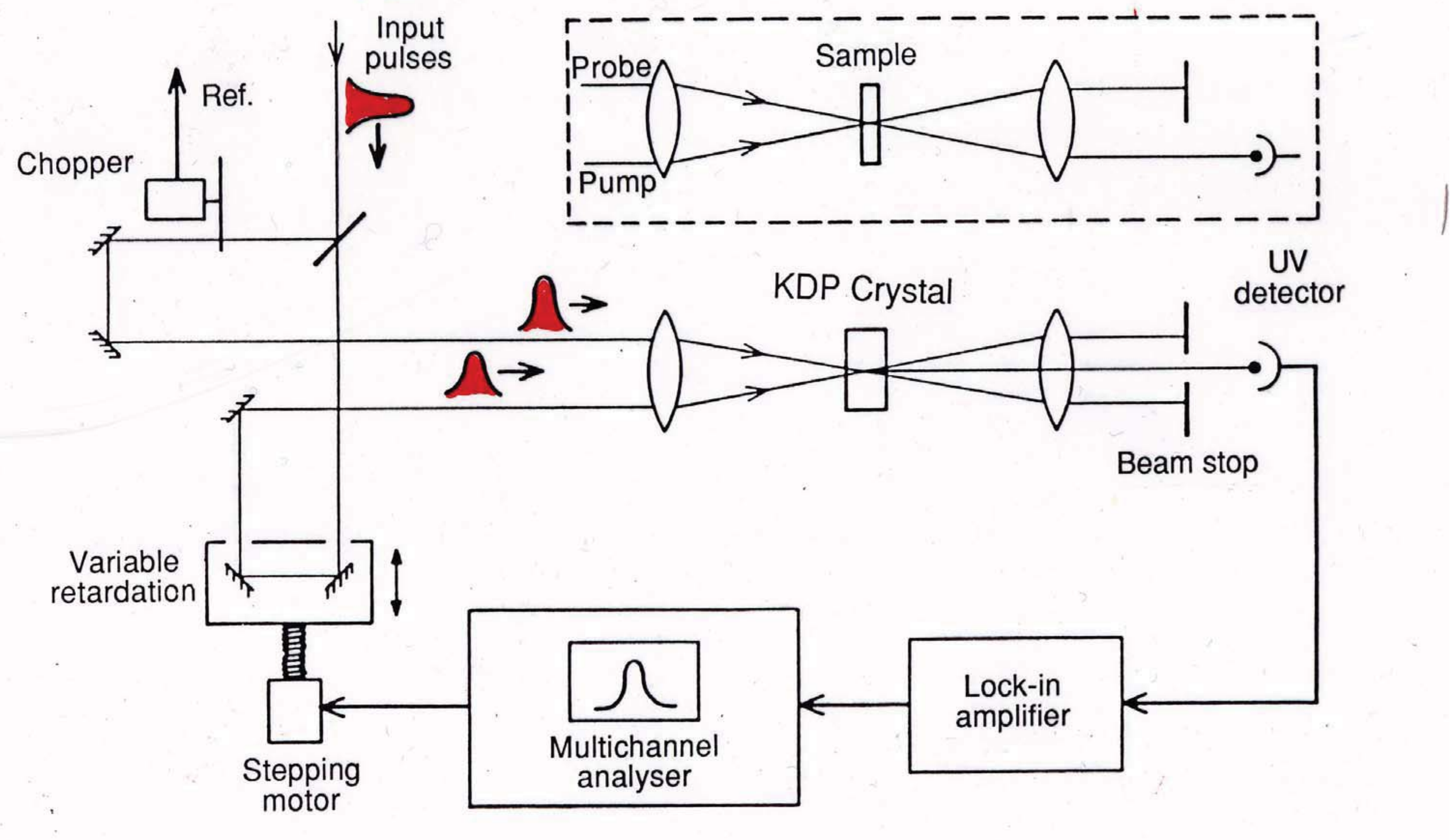


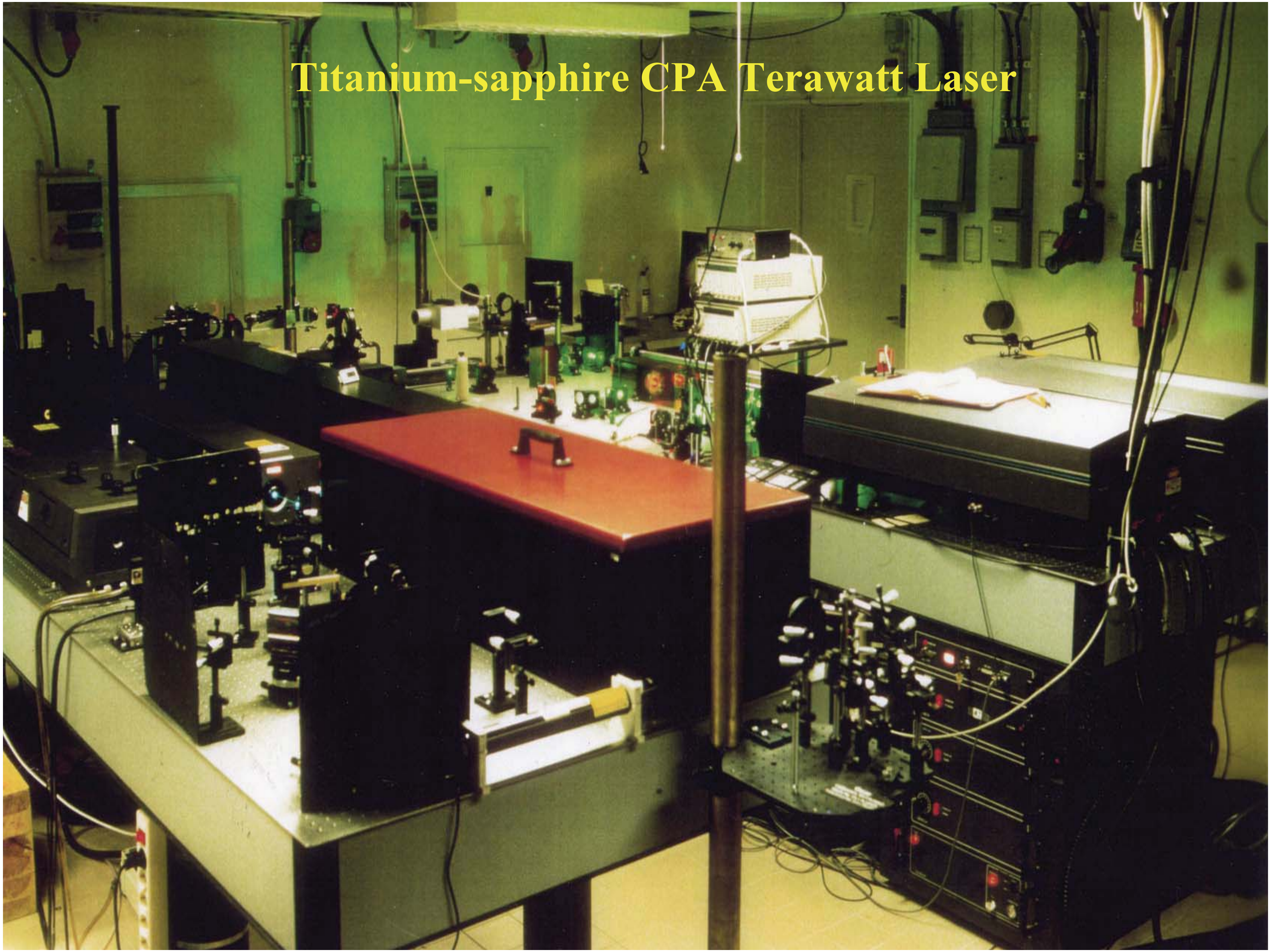
cis-stilbene **trans-stilbene**



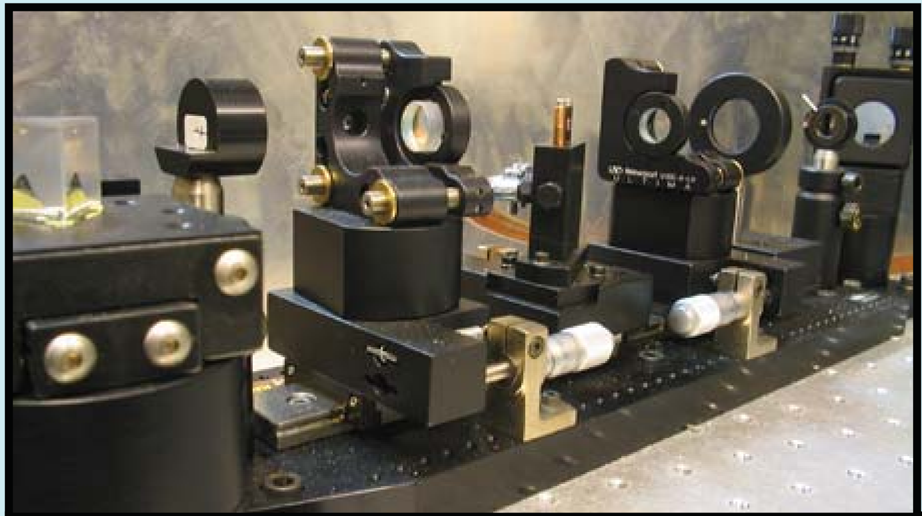

Focusing cone
Photo-cathode
Phosphor
Deflection plates
Microchannel plate
Optical multi-channel detector
Entrance slit
Grid
Anode
≈ps
Incoming light pulse
ps
High-voltage electronics
Optical multichannel analyser
STREAK CAMERA

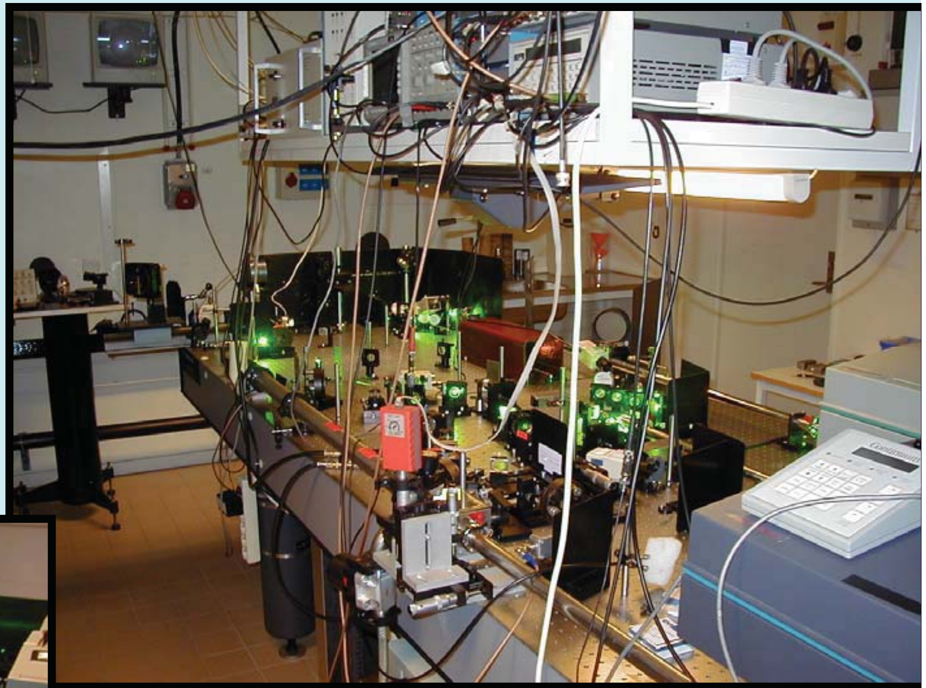
Autocorrelator

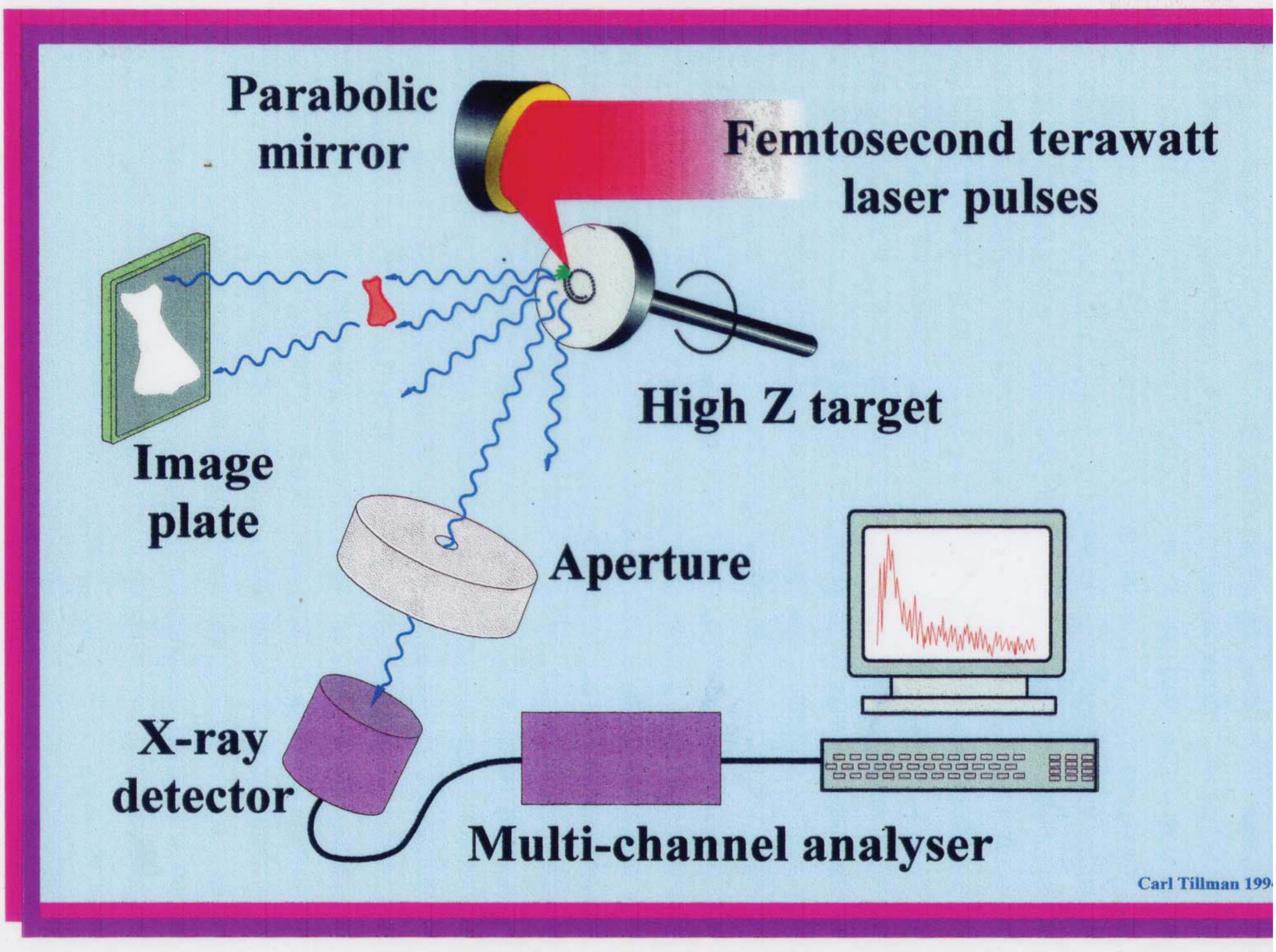



Titanium-sapphire CPA Terawatt Laser

Lund Terawatt Laser
40 TW



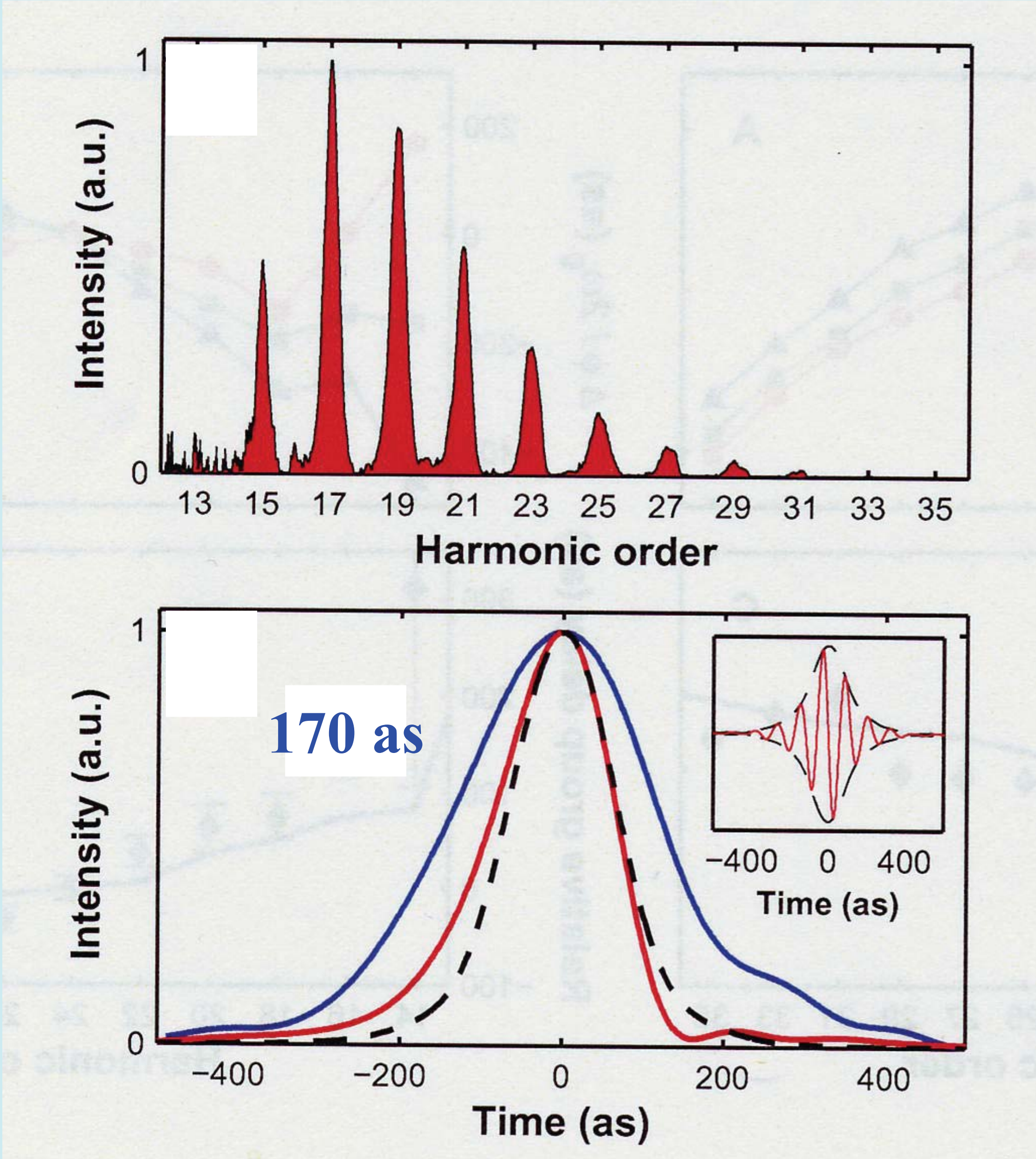


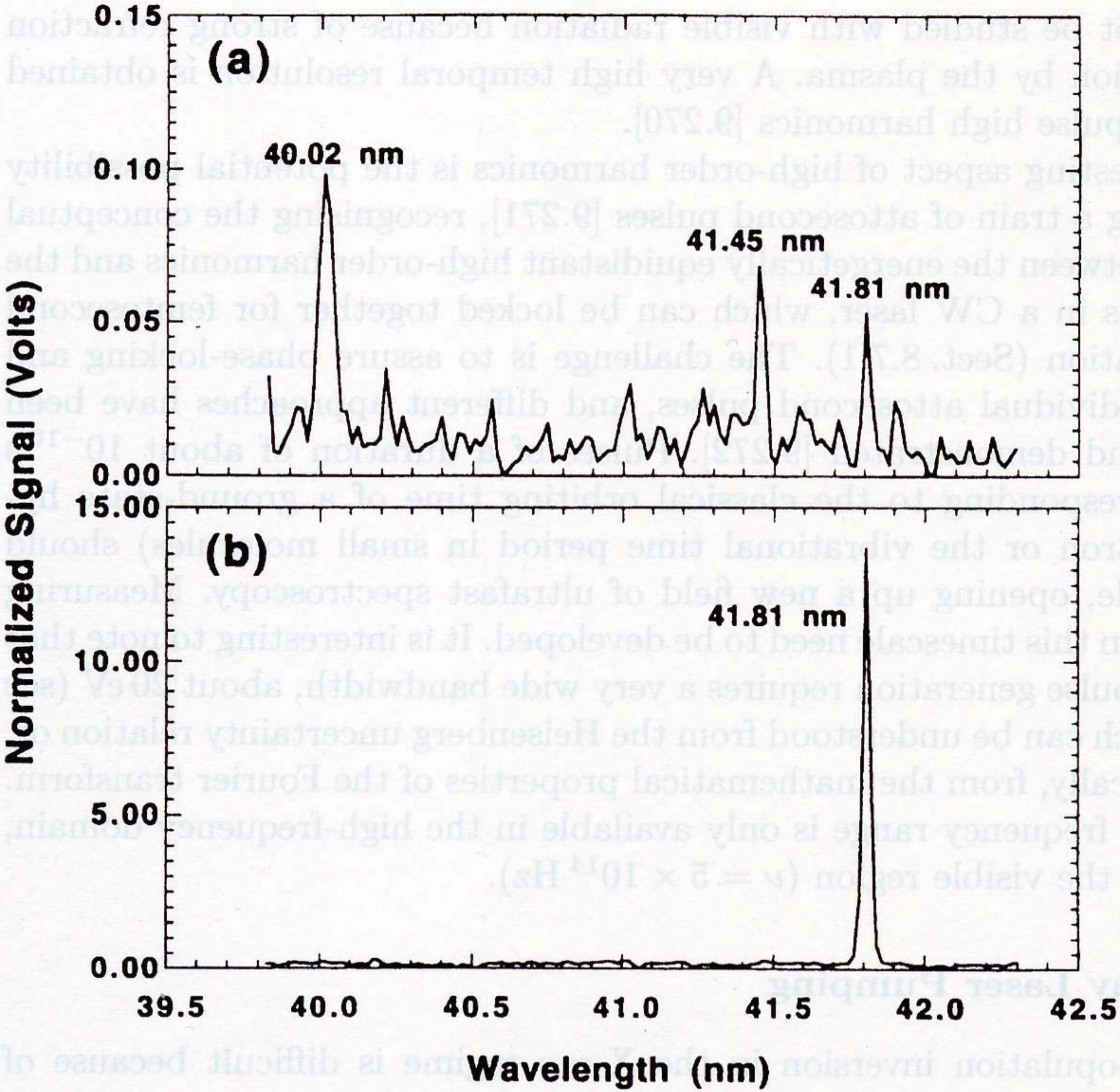

Parabolic mirror
Femtosecond terawatt laser pulses
High Z target
Image plate
Aperture
X-ray detector
Multi-channel analyser
Carl Tillman 199

Rat with contrast agent

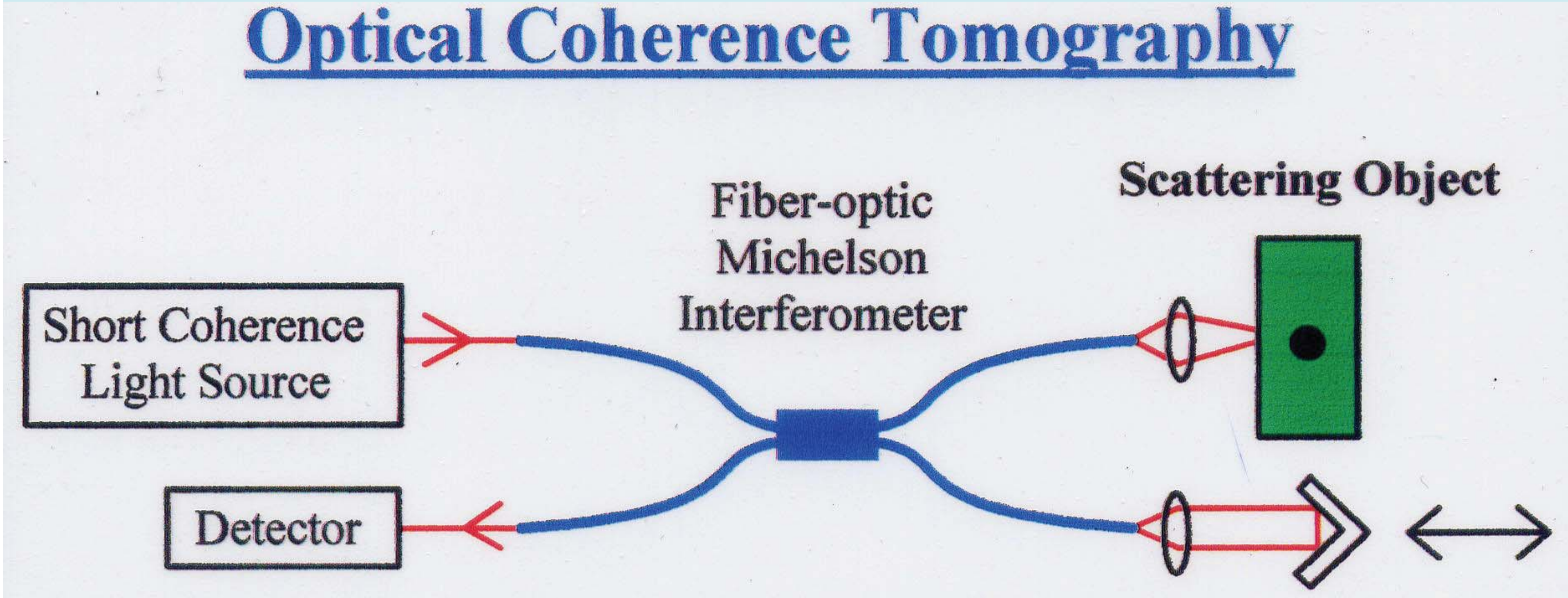
Attosecond pulse generation from high harmonics

A. L´Huillier et al.



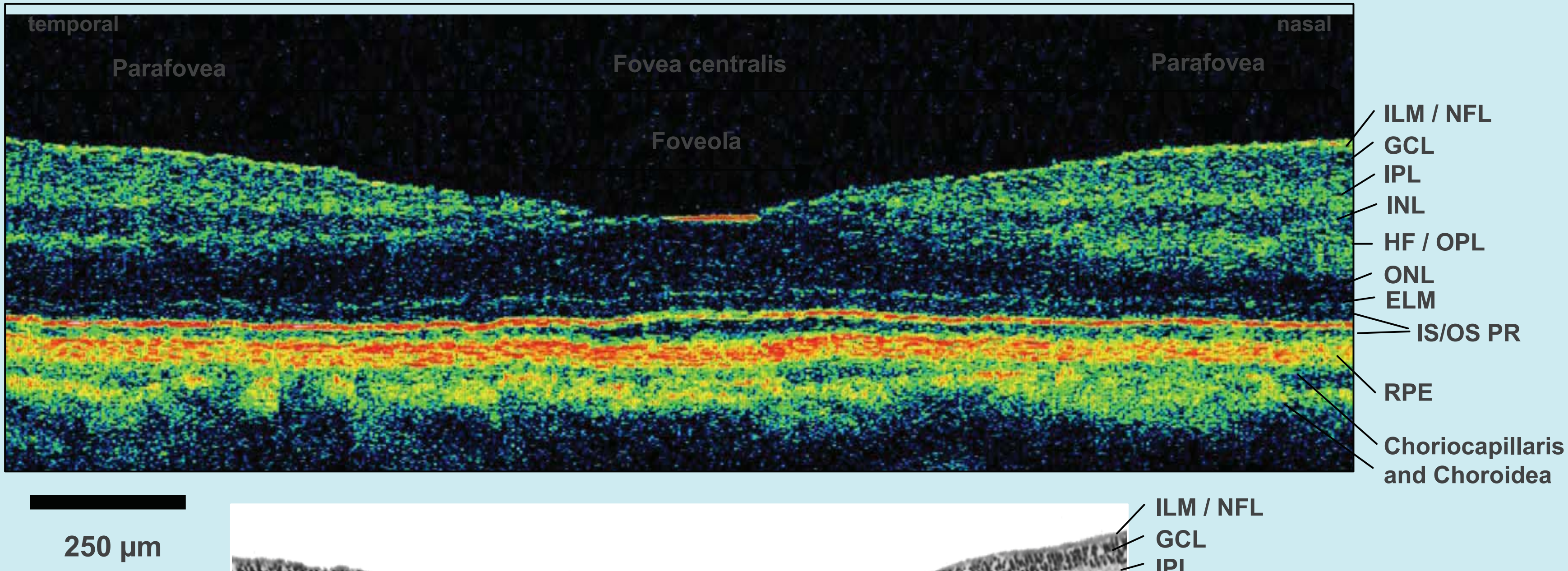


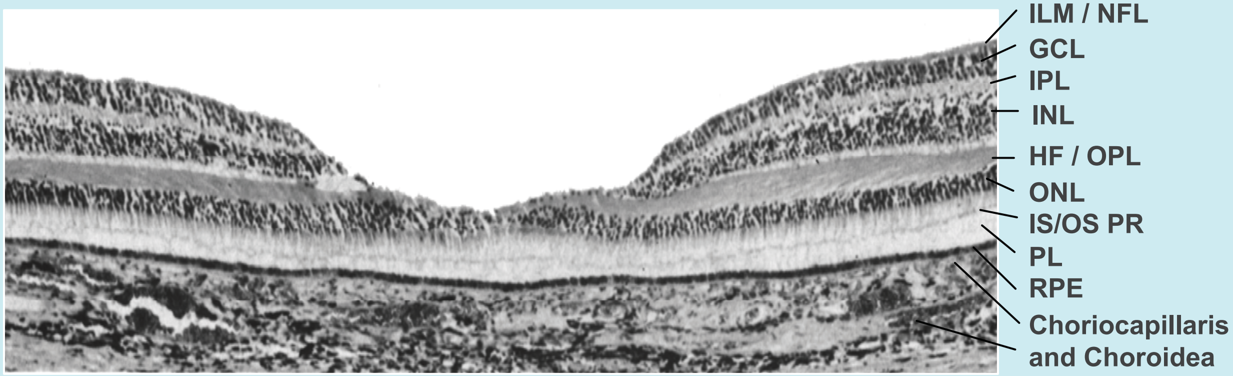
(a)
40.02 nm
41.45 nm
41.81 nm
(b)
41.81 nm
Normalized Signal (Volts)
0.15
0.10
0.05
0.00
15.00
10.00
5.00
0.00
39.5
40.0
40.5
41.0
41.5
42.0
42.5
Wavelength (nm)



J. Fujimoto et al.

In Vivo Ultrahigh Resolution OCT versus Histology





Gass J.D.M., 1997

W. Drexler et al.; Vienna

W. Drexler et al. *Nature Medicine*, Vol 7, No. 4, 502-507, 2001

Collaborative Projects

Workshops in Lund

Diode laser spectroscopy in 85-Rb, 87-Rb Doppler-broadened, Doppler-free 780 nm	A	x5
Compact fibre-optic fluorosensor (395 nm laser)	B	x5
Gas in Scattering Media Absorption Spectroscopy (GASMAS) Oxygen 760 nm	C	x5

LED-based fluorosensors
Multispectral imaging with LEDs (LED microscope)
Photodynamic therapy (PDT)

African Collaboration

University of Cape Coast, Ghana ABC
Paul Buah-Bassuah, Benjamin Anderson

Université Sheik Anta Diop, Dakar, Senegal AB
Ahmadou Wagué, Malik Diop, Almany Konte

University of Nairobi, Kenya ABC
Kenneth Kaduki, Robinson Gathoni, Kimari Wangai

University of Zimbabwe, Harare A C
Manny Mathuthu, Kaitano Dzinavatonga, N. Ndlovu, Louis Olumekor

University of Khartoum, Sudan AB
Ababaker Abdallah

University of Colombo, Sri Lanka C
T.R. Ariyaratne, Hiran Jayaweera

Escuela Politecnica Nacional, Quito, Equador ABC
Edy Ayala, Cesar Costa, Juanita Coloma, Omar Marillo

Sponsors:
Lennart Hasselgren, IPPS, Sweden
Gallieno Denardo, ICTP, Italy

Part of the African-Lund Workshop at the Oncology Department

FROM LEFT TO RIGHT: Malick Diop, Sara Pålsson, Ababakar Abdalla, Kenneth Kaduki, Almamy Konte, K. Dzinavatonga, Jaidane Nejmedinne, Ahmadou Wague, Sune Svanberg, N. Ndolovu, M. Mathuthu, Katarina Svanberg and Niels Bendsoe.

Senegal, Kenya, Zimbabwe, Ghana, Sudan,Tunisia, Equador

ENT department in Dakar

GASMAS
Materials science applications

- Diffusion into building materials
- Moisture in building materials
- Influence of paints
- Ceramics
- Zeolites (catalysts) gas exchange
- Pore size
- Insulators (internal electric fields)

Biological applications

- Meat storage
- Oxygen penetration through plastic films
- Packaging materials
- Fruit maturing (ethylene)
- Food processing
- Foodstuff mixing
- Algae in water

Literature references:

S. Svanberg, Atomic and Molecular Spectroscopy – Basic Aspects and Practical Applications, 4th edition (Springer-Verlag, Heidelberg 2004)

S. Svanberg, Multispectral Imaging – from astronomy to microscopy – from radiowaves to gammarays (Springer Verlag, Heidlberg, to appear)


Thank you for your attention !