Fundamental Spectroscopy:
Open Chemical Eyes

基礎光譜学:

開啓化学之眼

1. What is light?

1.1 Electromagnetic wave (電磁波)

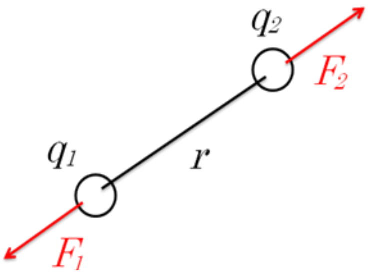
a) Maxwell Equation in vacuo

Equation holds among four quantities ***E***, ***D***, ***B***, ***H***.

- ***E*** : electric field (電場) $\mathrm{NC^{-1}}$
- ***D*** : electric flux density (電通密度) $\mathrm{Cm^{-2}}$
- ***B*** : magnetic flux density (磁通密度) T
- ***H*** : magnetic field (磁場) $\mathrm{Am^{-1}}$

Electric field (電場) *E*

Coulomb law



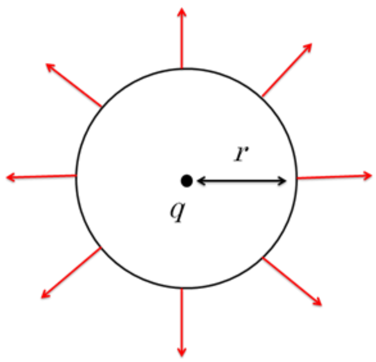
$$F_1 = \frac{q_1 q_2}{4\pi\varepsilon_0 r^2} = q_1 E_1$$

ε_0 : permittivity (電容率) in vacuo $8.854 \times 10^{-12}\ \mathrm{C^2N^{-1}m^{-2}}$

$$F = \underbrace{\frac{q_2}{4\pi\epsilon_0 r^2}}_{E} \cdot q_1$$

$$E = \frac{q}{4\pi\varepsilon_0 r^2}$$

$$\varepsilon_0 E = \frac{q}{4\pi r^2} \longrightarrow D$$



Electric flux density (電通密度) $\boldsymbol{D} = \varepsilon_0 \boldsymbol{E}$ （in vacuo）

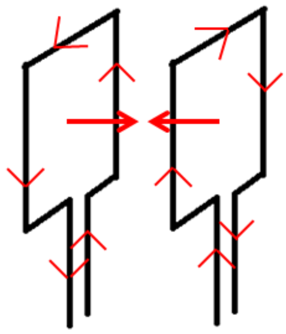
$$\mathrm{div}\,\boldsymbol{D} = \rho$$ ρ: charge density

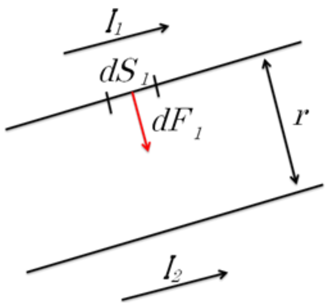
Magnetic flux density (磁通密度) ***B***

Biot-Savart law

$$dF_1 = \frac{\mu_0}{2\pi}\cdot\frac{I_1 I_2}{r}dS_1 = BI_1 dS_1$$

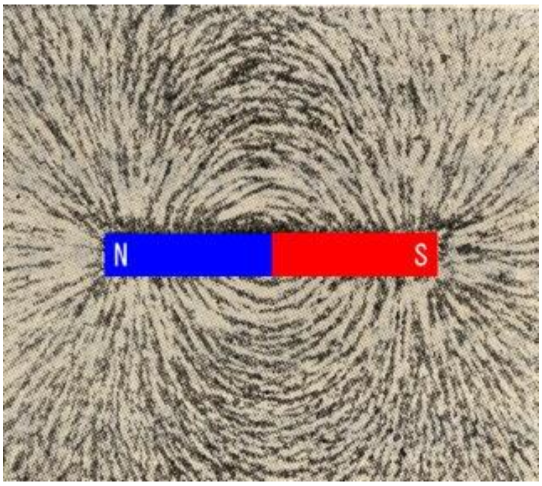
μ_0 : magnetic permeability (導磁率) $1.257\times10^{-7}\ \mathrm{NA^{-2}}$





$$B = \frac{dF_1}{IdS_1} = \frac{\mu_0}{2\pi}\cdot\frac{I_2}{r}\quad \mathrm{NA^{-1}m^{-1}}$$

$$\mathbf{F} = q\mathbf{E} + q(\underbrace{\mathbf{v}\times\mathbf{B}}_{\boldsymbol{I}})$$



http://ji6rcy.canaryyellow.info/top/junk_cology/circuit_tips/making/inductance/magnet1.jpg

Magnetic field (磁場) ***H***

$$\boldsymbol{B} = \mu_0\boldsymbol{H}$$

Maxwell equation in vacuo

$$\left\{\begin{aligned} \mathrm{rot}\boldsymbol{E} &= -\frac{\partial \boldsymbol{B}}{\partial t} \\ \mathrm{rot}\boldsymbol{H} &= \frac{\partial \boldsymbol{D}}{\partial t} \\ \mathrm{div}\boldsymbol{D} &= 0 \\ \mathrm{div}\boldsymbol{B} &= 0 \end{aligned}\right. \quad \Rightarrow \quad \left.\begin{aligned} \varepsilon_0\mu_0\frac{\partial^2 \boldsymbol{E}}{\partial t^2} - \Delta\boldsymbol{E} &= 0 \\ \varepsilon_0\mu_0\frac{\partial^2 \boldsymbol{H}}{\partial t^2} - \Delta\boldsymbol{H} &= 0 \end{aligned}\right\}$$

Wave equation for waves propagating with velocity $\dfrac{1}{\sqrt{\varepsilon_0\mu_0}}$

$$\begin{aligned} \varepsilon_0\mu_0 &= 8.854\times 10^{-12}\quad \mathrm{C^2N^{-1}m^{-2}} \\ &\quad \times 1.257\times 10^{-6}\quad \mathrm{NA^{-2}} \qquad \mathrm{A} = \mathrm{Cs^{-1}} \\ &= 11.129\times 10^{-18}\quad \mathrm{m^{-2}s^2} \end{aligned}$$

$$\begin{aligned} \frac{1}{\sqrt{\varepsilon_0\mu_0}} &= 2.98\times 10^{8}\quad \mathrm{ms^{-1}} \\ &= c_0 \end{aligned}$$

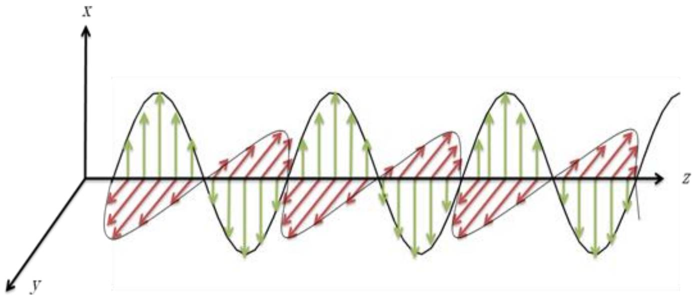
C_0: velocity of light (光速度) in vacuo

$$\left\{\begin{aligned} E_x &= E_{x0}\cos 2\pi\nu\left(\frac{z}{c_0} - t\right) \\ E_y &= E_{y0}\cos 2\pi\nu\left(\frac{z}{c_0} - t\right) \\ E_z &= 0 \end{aligned}\right.$$

$$\left\{\begin{aligned} H_x &= -\sqrt{\frac{\varepsilon_0}{\mu_0}}E_{y0}\cos 2\pi\nu\left(\frac{z}{c_0} - t\right) \\ H_y &= \sqrt{\frac{\varepsilon_0}{\mu_0}}E_{x0}\cos 2\pi\nu\left(\frac{z}{c_0} - t\right) \\ H_z &= 0 \end{aligned}\right.$$

"Electromagnetic waves with velocity c_0 are inherently contained in Maxwell equation."

b) Plane electromagnetic wave（平面電磁波）

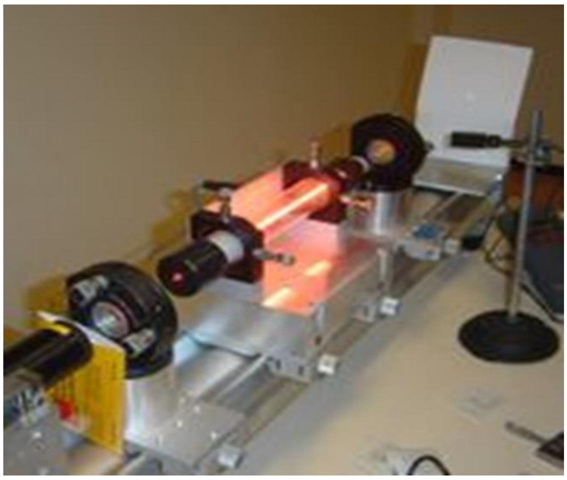


$$E_x \neq 0, E_y = E_z = 0$$
$$H_y \neq 0, H_x = H_z = 0$$

$$\begin{cases} E_x = E_{x0} \cos 2\pi\nu\left(\dfrac{z}{c_0} - t\right) \\ E_y = E_{y0} \cos 2\pi\nu\left(\dfrac{z}{c_0} - t\right) \\ E_z = 0 \end{cases}$$

$$\begin{cases} H_x = -\sqrt{\dfrac{\varepsilon_0}{\mu_0}} E_{y0} \cos 2\pi\nu\left(\dfrac{z}{c_0} - t\right) \\ H_y = \sqrt{\dfrac{\varepsilon_0}{\mu_0}} E_{x0} \cos 2\pi\nu\left(\dfrac{z}{c_0} - t\right) \\ H_z = 0 \end{cases}$$

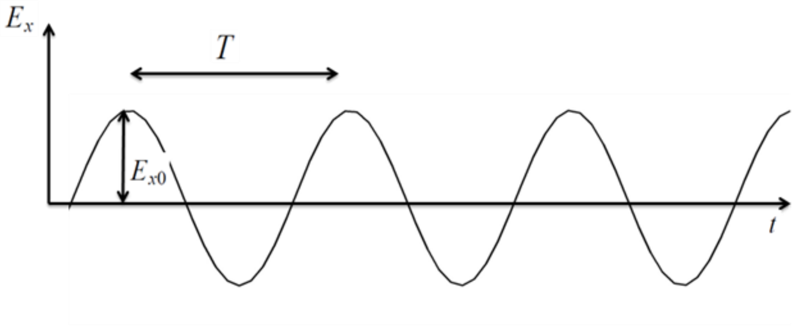
"Linearly polarized laser light is very close to a plane wave."



Ar^+laser (left, 488.0 nm) and He-Ne laser (right, 632.8 nm)

c) Frequency ν, angular frequency ω, wavenumber k

Electric field E_x(t) at z=0



Period (周期)

T s

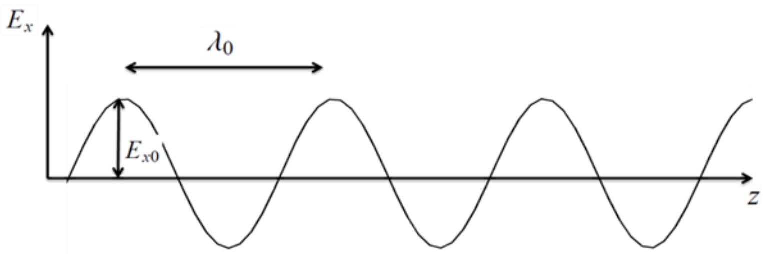
Frequency (頻率)

$$\nu = \frac{1}{T} \quad s^{-1}, Hz$$

Angular frequency (角頻率)

$$\omega = 2\pi\nu$$

Electric field E_x(x) at t=0



Wavelength (波長) λ_0

Wavenumber (波数) $\tilde{\nu}$ cm^{-1}

Number of waves in 1cm

$$\tilde{\nu}_0 = \frac{1}{\lambda_0}$$

Fundamental equation of electromagnetic wave

$$\lambda_0 = \frac{c_0}{\nu}$$

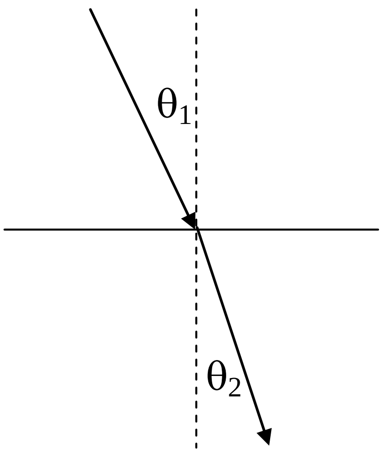
Electromagnetic wave in a medium

$$\varepsilon_0 \rightarrow \varepsilon \quad \mu_0 \rightarrow \mu \quad c = \frac{1}{\sqrt{\varepsilon\mu}}$$

refractive index (折射率) n

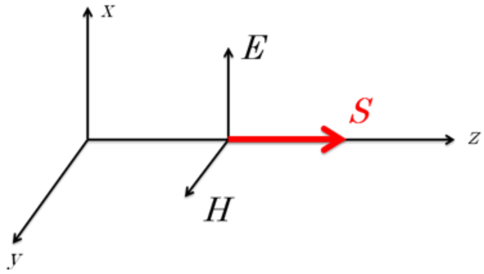
$$n = \frac{c_0}{c} = \sin\theta_1/\sin\theta_2 \geq 1$$

$$\lambda = \frac{\lambda_0}{n} \qquad \tilde{\nu} = n\tilde{\nu}_0$$



d) Intensity of electromagnetic wave（電磁波的強度）

Poynting vector $\boldsymbol{S} = \boldsymbol{E} \times \boldsymbol{H}$



X polarized light propagating along z axis

$$E_x = E_{x0} \cos 2\pi\nu\left(\frac{z}{c} - t\right) \qquad E_y = E_z = 0$$

$$H_y = \sqrt{\frac{\varepsilon}{\mu}} E_{x0} \cos 2\pi\nu\left(\frac{z}{c} - t\right) \qquad H_x = H_z = 0$$

$$S_x = S_y = 0 \qquad S_z = \sqrt{\frac{\varepsilon}{\mu}} E_{x0}{}^2 \cos^2 2\pi\nu\left(\frac{z}{c} - t\right) = c\varepsilon E_{x0}{}^2 \cos^2 2\pi\nu\left(\frac{z}{c} - t\right)$$

$$\begin{cases} c & \mathrm{ms^{-1}} \\ \varepsilon & \mathrm{C^2N^{-1}m^{-2}} \rightarrow \mathrm{Nm^{-1}s^{-1}} \rightarrow \mathrm{Jm^{-2}}s^{-1} \\ E_{x0}^2 & \mathrm{N^2C^{-2}} \end{cases}$$

S_z $\mathrm{Jm^{-2}s^{-1}}$: Electromagnetic energy flowing per unit area per second

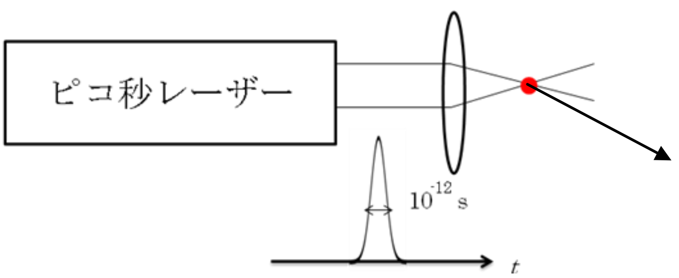
Intensity of electromagnetic wave *I* （電磁波的強度）

$$I = \bar{S_z} = \frac{1}{2} c\varepsilon E_{x0}{}^2 \qquad \mathrm{Jm^{-2}s^{-1} = Wm^{-2}}$$

Laser power : Energy emitted from a laser in 1 s. $\mathrm{W = Js^{-1}}$

Picosecond laser pulse with 1mJ average power

$$\text{Peak power} = \frac{10^{-3}}{10^{-12}} = 10^9 \mathrm{W}$$



$0.01(\mathrm{mm})^2 \sim 10^{-10}\ \mathrm{m}^2$

$$I = \frac{10^9}{10^{-10}} = 10^{19} \mathrm{Wm^{-2}}$$

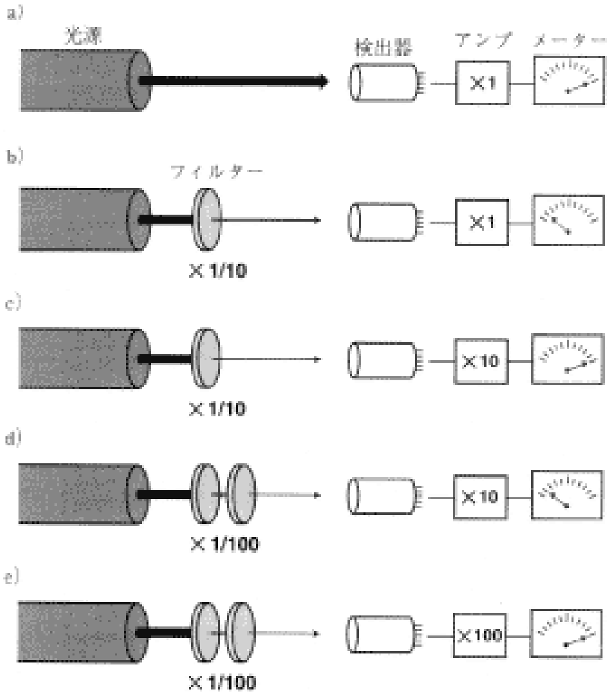
$E_{x0} = 8.5 \times 10^{10}\ \ \mathrm{Vm^{-1}}$

"A focused picosecond laser beam produces a gigantic electric field."

1.2 photon（光子）

Wave–particle duality of light（光的二重性）

“Light is electromagnetic wave as well as photon.”（光是電磁波、并且是光子）



What happens if we repeat attenuation 15 times and make the gain 10^{15}?

Einstein-de Broglie formula: the magic that the Planck constant does

$$E = h\nu$$

E : photon energy → quantity of photon

ν : frequency of electromagnetic wave → quantity of electromagnetic wave

h : Planck constant 6.626×10^{-34} Js

λ = 600 nm He-Ne 632.8 nm

$$\nu = \frac{c}{\lambda} = \frac{3\times10^{8}}{600\times10^{-9}} = 5\times10^{14}\mathrm{s}^{-1}$$

$$E = h\nu = 3.3\times10^{-19}\mathrm{J}$$

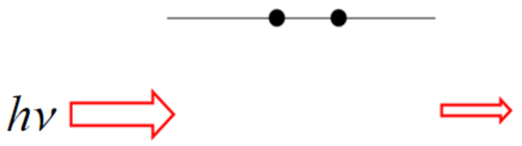
5mW He-Ne laser 5×10^{-3} Js^{-1} → 10^{16} photon s^{-1}

1.3 Laser (雷射)

<u>L</u>ight <u>A</u>mplification by <u>S</u>timulated <u>E</u>mission of <u>R</u>adiation

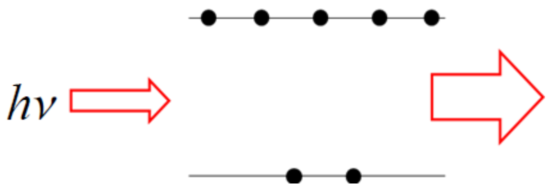
Ideal light source for spectroscopy

2-level model



Light attenuation (absorption)

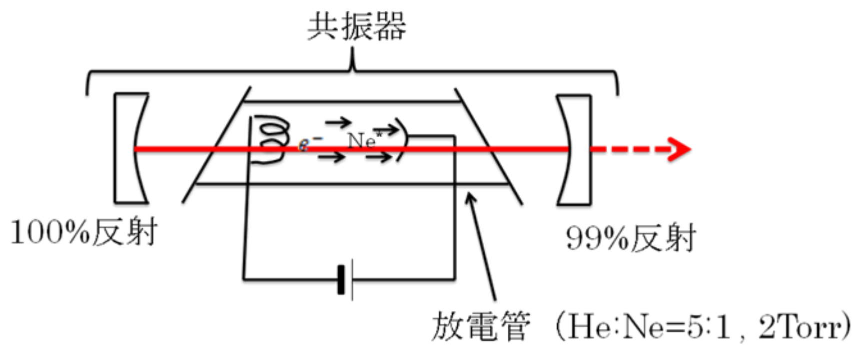
Normal distribution ($T > 0$)



Light amplification (emission)

Inverse distribution ($T < 0$)

He-Ne laser



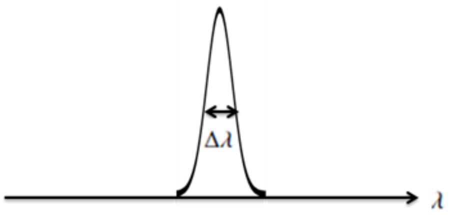
TEM00 TEM10 TEM11

transverse modes

$$\begin{cases} e^- + \mathrm{He} \rightarrow \mathrm{He}^* + e^- \\ \mathrm{He}^* + \mathrm{Ne} \rightarrow \mathrm{He} + \mathrm{Ne}^* \\ \mathrm{Ne}^* \rightarrow h\nu + \mathrm{Ne} \end{cases}$$

Characteristics of laser light

a) Monochromaticity （単色性）： high spectral purity

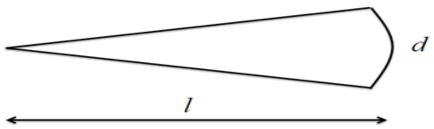


$$\frac{\Delta\lambda}{\lambda} \backsim 10^{-12}$$

High resolution spectroscopy resolution 10^{12}

b) High directionality（指向性）

Divergence angle ～1mrad $\frac{d}{l} \backsim 10^{-3}$

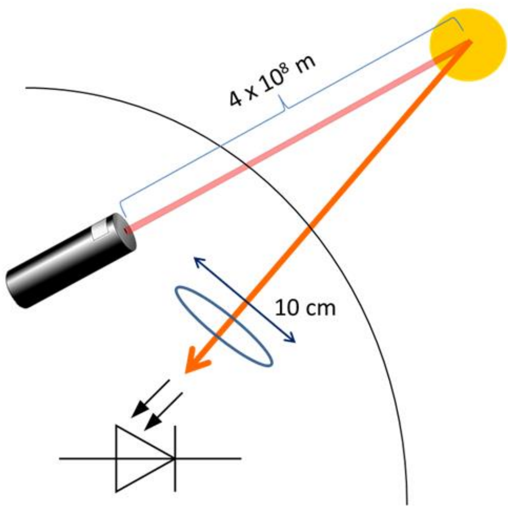


Sending laser light to moon and see the reflected light

$$d = 4 \times 10^8 \times 2 \times 10^{-3} \sim 10^6 \text{ m}$$

Focusing the reflected light with a 10 cm lens

$$10^{16} \times \frac{(10^{-1})^2}{(10^6)^2} = 10^2 \text{ 個}$$

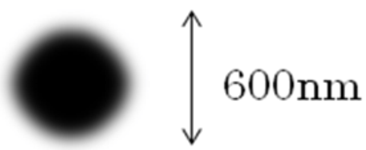


c)

d) High focusing capability（収束性）

Easy to focus into sub-micrometer scale

Suitable for microspectroscopy

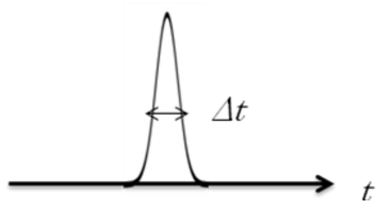


e）High brightness（高亮度）

High light energy can be put into a small solid angle

High intensity laser field

f）High speed（高速性）

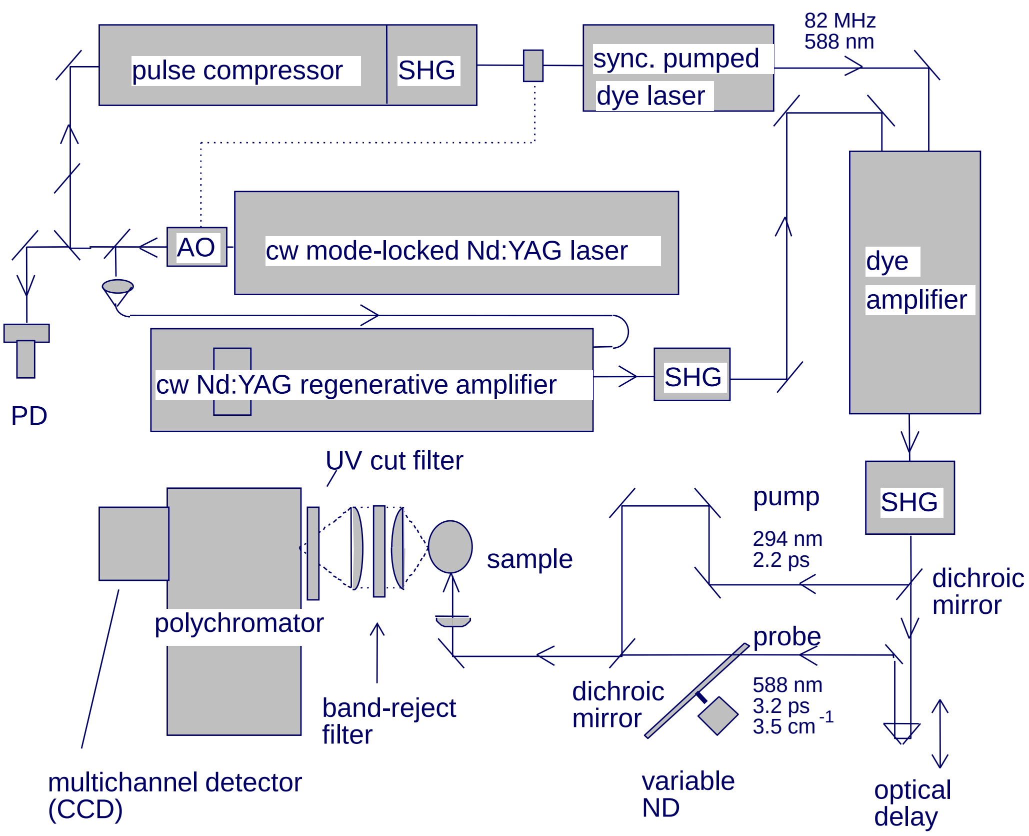


Ultra-fast pulsed oscillation

Q-switing → nanosecond 10^{-9} s

Mode locking → Picosecond ~ femtosecond 10^{-12} ～ 10^{-15} s

Ultrafast time-resolved spectroscopy（超高速時間分解分光）

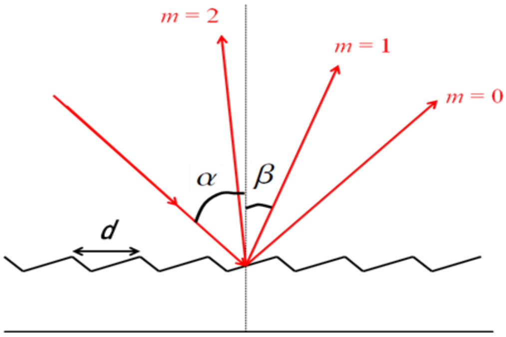


1.4 Spectrometer （光譜儀）

a) Spectrometer

- Dispersive monochromator/polychromator
  （diffraction grating）　UV,　VIS,　Raman
- Fourier-transform spectrometer
  Interferogram ——Fourier transformation——▶ Spectrum　FT-IR

b）Diffraction grating （回折格子）



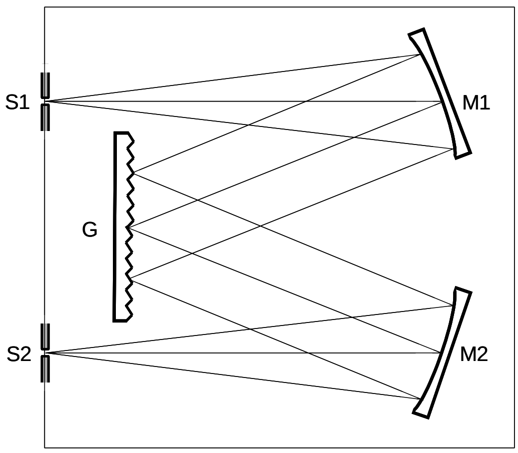
Diffraction formula

$$d(\sin\alpha + \sin\beta) = m\lambda$$

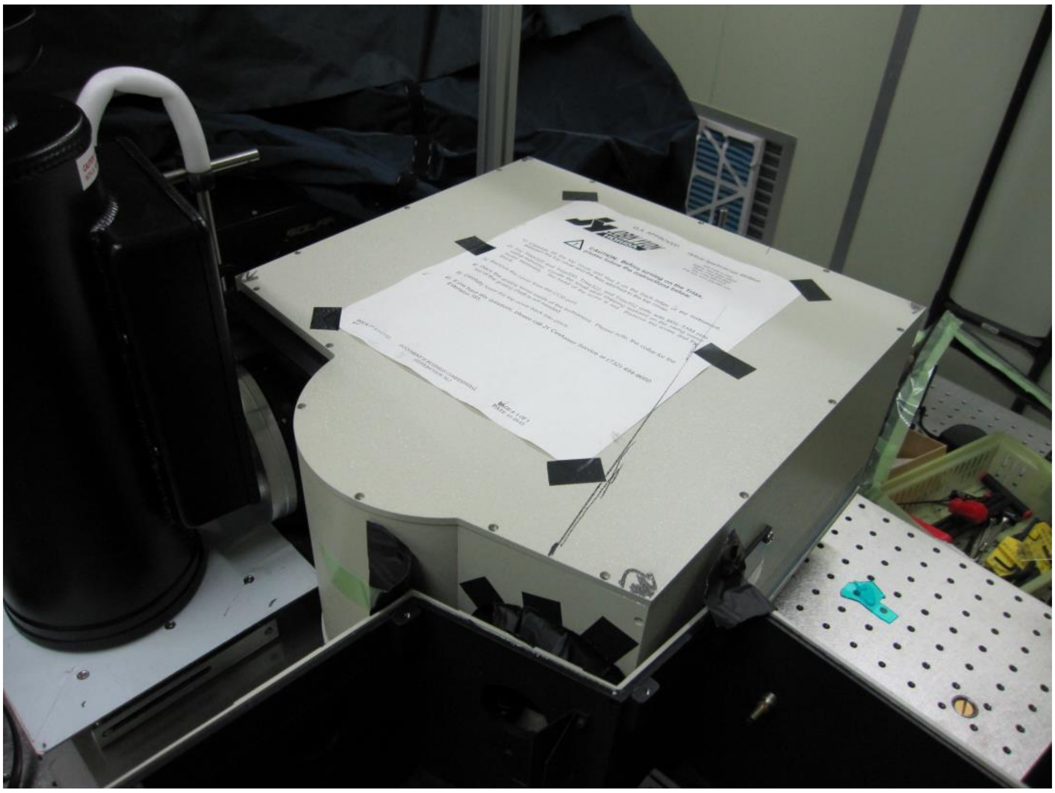
m=0　0^{th} order light　$\beta = -\alpha$

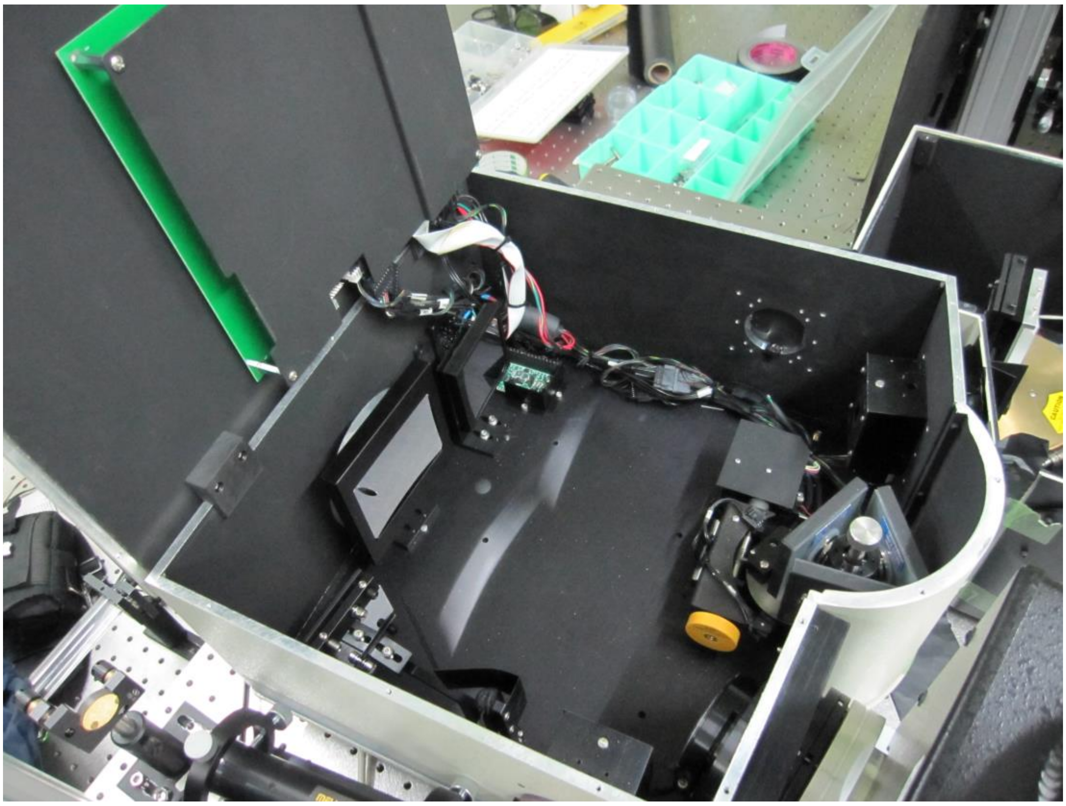
m=1　1^{st} order diffracted light　$\sin\beta = -\sin\alpha + \frac{\lambda}{d}$

m≧2　m^{th} order diffracted light　$\lambda = \frac{d}{m}(\sin\alpha + \sin\beta)$



A Czerny-Turner monochromator





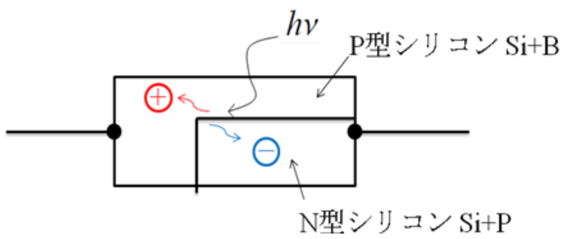
1.5 Light Detector （探測器）

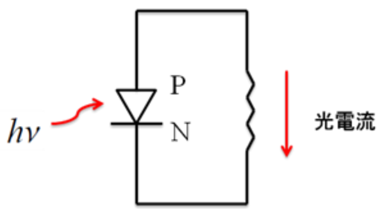
a) Light detector

Single-channel　photodiode, photomultiplier (PMT)
→ monochromator with an exit slit
Multi-channel　CCD (Charge Coupled Device)
→ polychromator

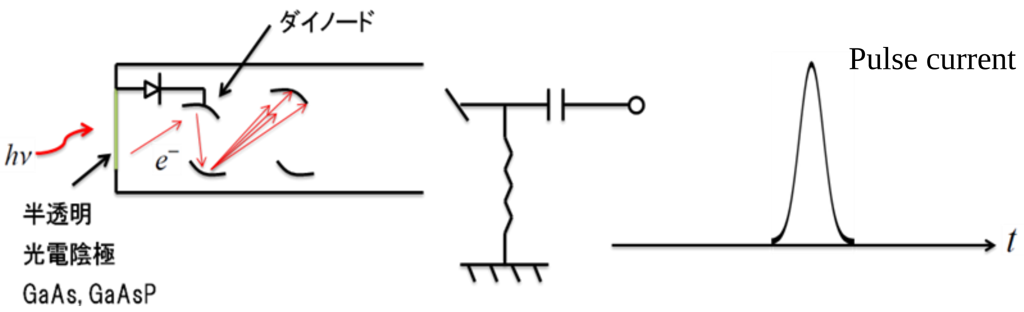
b）Photodiode （光二極管）

PNjunction





c）Photomultiplier （光電倍増管）



One photon → 10^6 photoelectrons　photon counting!