3. General Features of Experimental Methods

reference; J.F. Rabek, "Experimental Methods in Photochemistry and Photophysics."

3.1 The Electromagnetic Spectrum

(1) Spectroscopist's unit for Energy

- Frequency ν : $E = h\nu$ (Hz (=sec^{-1}), kHz, MHz, GHz, ..)
- Wavenumber (number of waves per centimeter) $\tilde{\nu}$

  $E = hc\tilde{\nu}$ (cm^{-1})
- Wavelength λ : $E = \dfrac{hc}{\lambda}$ (cm, nm, μm, Å)

* Frequency is independent of the medium through which the radiation passes. But wavenumber and wavelength are dependent.

$$\lambda_{vac} = \frac{c}{\nu} = \frac{1}{\tilde{\nu}_{vac}}$$

$$\lambda = \frac{v}{\nu} = \frac{c}{n\nu}$$

speed of light in the medium

$$= \frac{\lambda_{vac}}{n}$$

refractive index of the medium

and $\tilde{\nu} = n\,\tilde{\nu}_{vac}$

Electromagnetic Wave	Spectral energy Range
Radio frequency	$\nu < 1\,GHz$
Microwave	$1\,GHz < \nu < 100\,GHz$ $3\,mm < \lambda < 30\,cm$
mm wave	$100\,GHz < \nu < 600\,GHz$ $0.5\,mm < \lambda < 3\,mm$
Far IR	$600\,GHz < \nu < 10\,THz$ $30\,\mu m < \lambda < 500\,\mu m$ $20\,cm^{-1} < \tilde{\nu} < 300\,cm^{-1}$
Mid IR	$2\,\mu m < \lambda < 30\,\mu m$ $300\,cm^{-1} < \tilde{\nu} < 5000\,cm^{-1}$

near IR	$720\,nm < \lambda < 2\,\mu m$ $5000\,cm^{-1} < \tilde{\nu} < 14000\,cm^{-1}$
visible	$400\,nm < \lambda < 720\,nm$ $14000\,cm^{-1} < \tilde{\nu} < 25000\,cm^{-1}$
U.V.	$200\,nm < \lambda < 400\,nm$ $3\,eV < E < 6\,eV$
vacuum U.V.	$50\,Å < \lambda < 2000\,Å$ $6\,eV < E < 240\,eV$
X-ray γ-ray	$120\,KeV < E < 1\,MeV$ $1\,MeV < E <$ 个GeV

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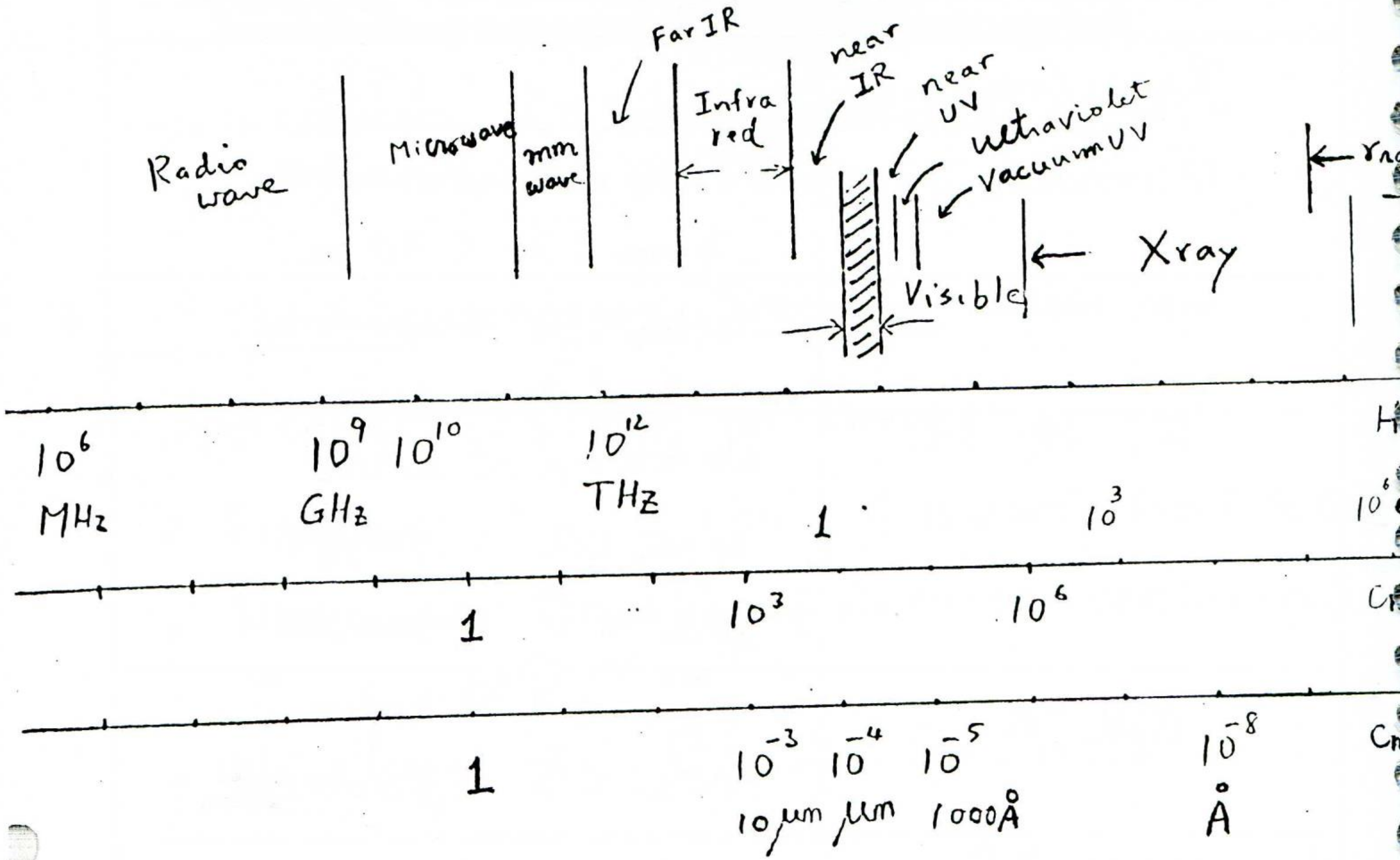
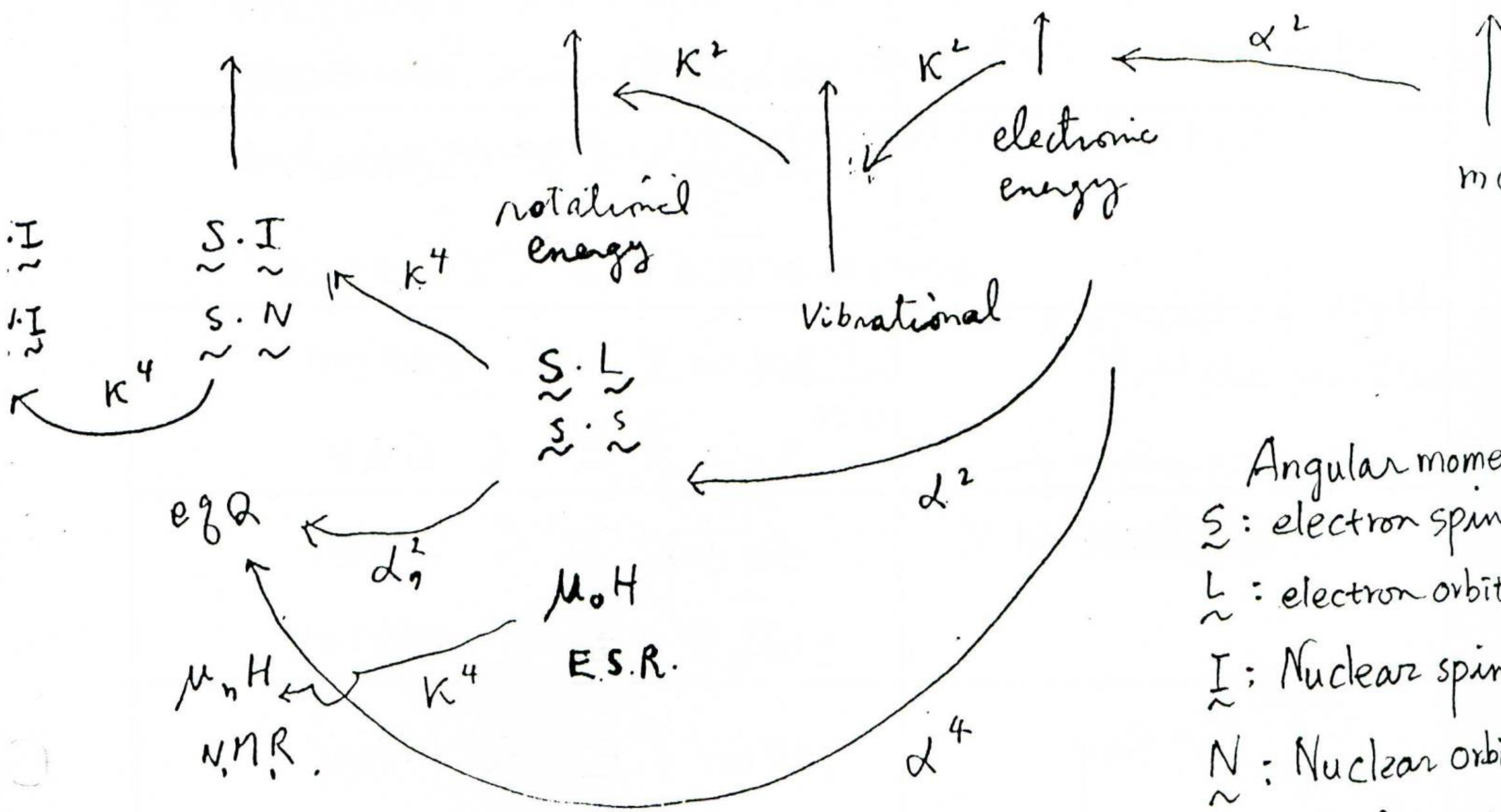

Far IR
near IR
near UV
ultraviolet
Vacuum UV
Radio wave
Microwave
mm wave
Infra red
Visible
Xray
γ ra
H
10^6 MHz
10^9
10^10
GHz
10^12 THz
1
10^3
10^6 e
C
1
10^3
10^6
Cm
1
10^-3
10^-4
10^-5
10^-8
10 μm
μm
1000Å
Å



Angular momen[tum]

$\underset{\sim}{S}$: electron spin

$\underset{\sim}{L}$: electron orbital

$\underset{\sim}{I}$: Nuclear spin

$\underset{\sim}{N}$: Nuclear orbital

$$\alpha = \frac{e^2}{(4\pi\varepsilon_0)\hbar c} \doteqdot \frac{1}{137}$$

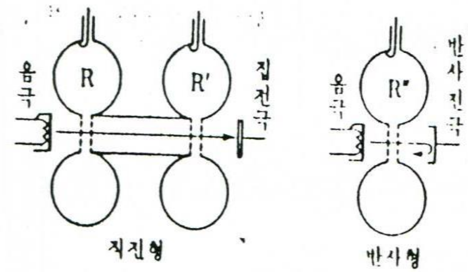
$\kappa^4 \sim \frac{m_e}{\ }$: $\frac{1}{\ }$

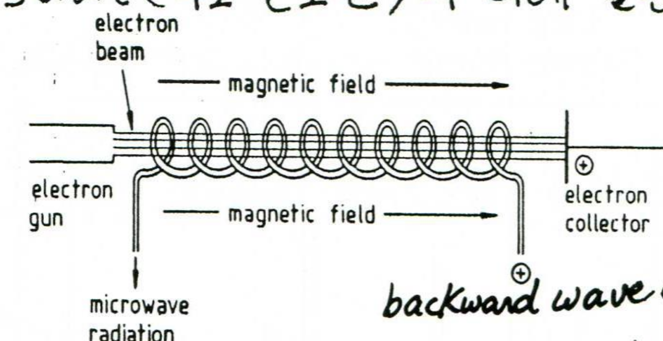
3.2. General Components of an Absorption Experiment

(1) Source of Radiation

Microwave 영역.

1 ~ 100 GHz 에서는 Klystron (속도 변조관)에 의해 발진, 증폭.



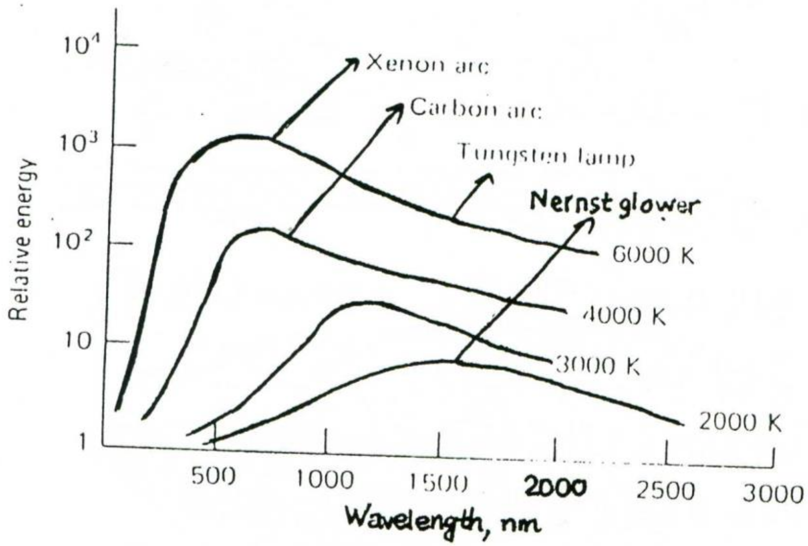


backward wave oscillator

100 ~ 600 GHz 에서는 (millimeter wave) Klyston 의 진동수를 배가, 삼배가 (frequency multiplication)하여 사용.

③ IR 영역.

Thermal radiation 이용, $I(\lambda)d\lambda = \dfrac{hc^3}{\lambda^5[\exp(hc/\lambda kT)-1]}d\lambda$



Globar : SiC 막대에 전류를 흘려주어 1300~1500 K 정도까지 가열

니크롬선 : 1200-1400 K로 가열. 장점 : good stability, 단점 : nonuniform image

Nernst Glower : rare-earth oxides의 혼합물로 만든 막대에 2000 K까지 전류를 흘려줌. 장점 : small size, good efficiency, near-IR에 적합
단점 : preheating 필요, fragile, electrical contact.

Mercury Discharge : Mercury Vapor + red hot silica, 저온/고압에서 작동할수 있게 design하여 Far-IR에 적합.

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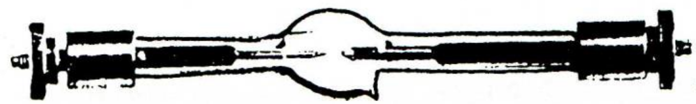
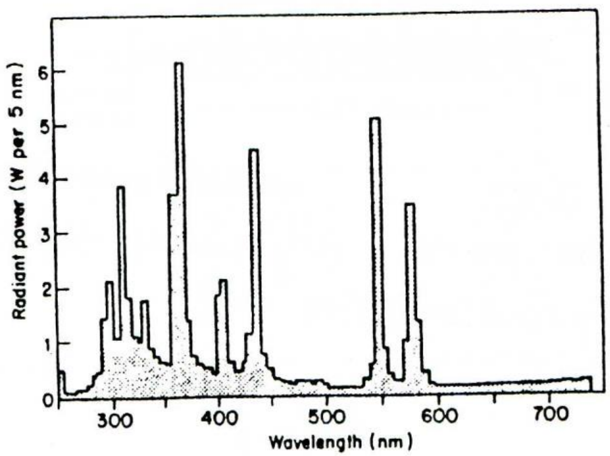
3) UV-Visible 영역.

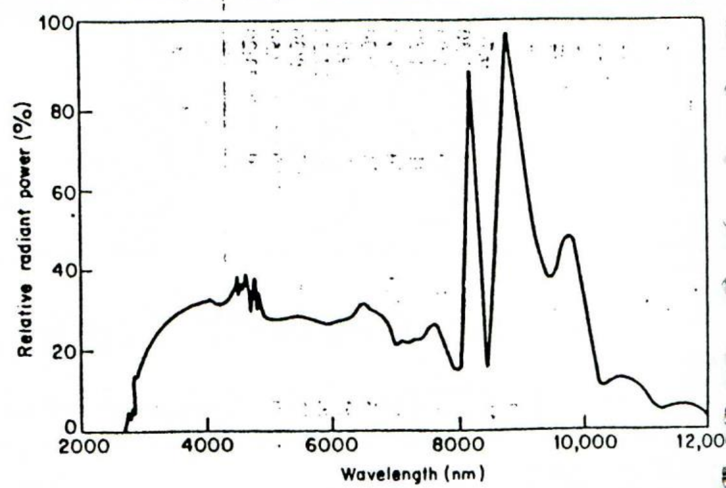
Lamp



(a)



Medium Pressure Mercury Lamp.



Xe-Arc Lamp.

기타: Tungsten Filament, D_2 discharge Lamp. 등

D) Lasers. 주로 UV. visible. 영역에서 cw 혹은 pulse cw

Ar ion laser : 514.5nm (연두색), 488nm (하늘색),

Kr ion laser : 647nm (빨강색), cw

He-Cd laser : 442nm (보라색), 325nm (UV), cw

He-Ne laser : 632.8nm (빨강색), 기타, cw

Ruby laser : 694nm (진빨강색), 펄스형

N_2 laser : 337nm, 펄스형 (UV)

CO_2 laser : 10.6μm, cw 및 펄스 (mid IR)

Dye laser : 400 – 800nm, Tunable, cw 및 펄스 (VISIBLE)

Ti-Sapphire laser : 750 – 1300nm, Tunable, cw 및 펄스 (near IR)

Nd:YAG laser : 1064nm (fundamental), 532nm (초록색) (2nd Harmonic), 355nm (Third Harmonic) 266nm (Fourth Harmonic)

Nd:Glass 레이저 : 1.06μm, 펄스 (near IR)

ArF 엑시머 레이저 : 193nm 펄스 (vacuum UV)

KrF 엑시머 레이저 : 249nm 펄스 (UV)

XeCl 엑시머 레이저 : 308nm 펄스 (near UV)

diode 레이저 (GaAs/GaAlAs, InGaAsP 등), 630nm~1600nm (near IR), CW 및 펄스

* Very narrow bandwidth, tunable in small range.

Synchrotron Radiation. (주로 X-ray 와 Far UV)

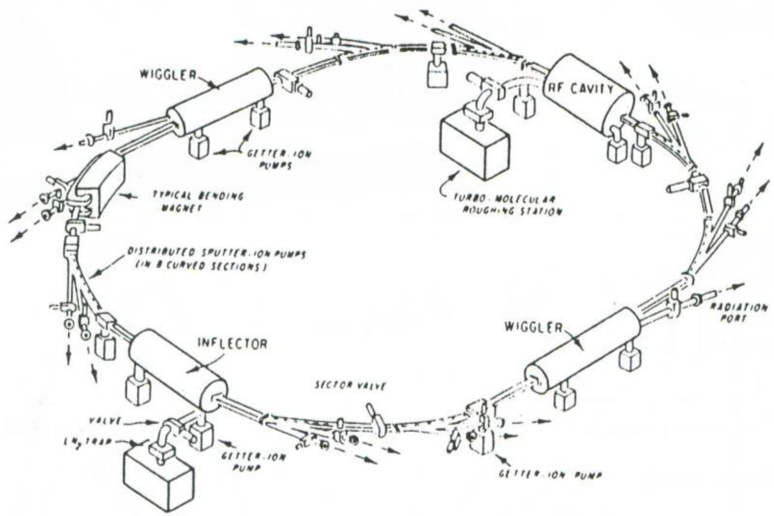


Figure 1. Schematic of an intermediate-energy (0.5-1.0 GeV) electron storage ring designed as a source of synchrotron radiation. Only one bending magnet is shown. Notice the several tangent ports for radiation (courtesy of J. Godell, Brookhaven National Laboratory).

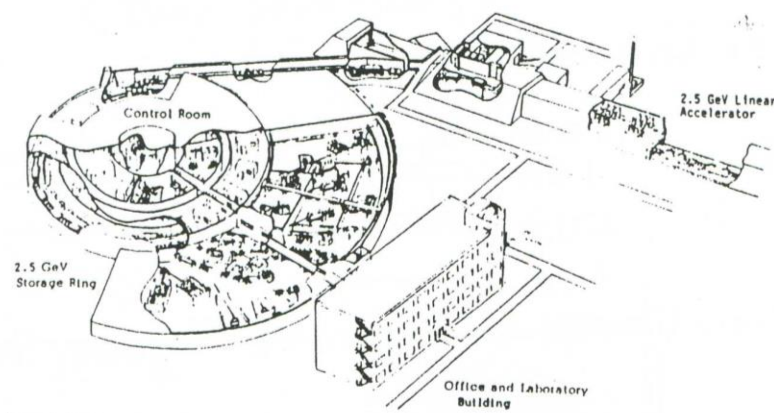


Figure 7. The 2.5-GeV photon factory under construction at KEK, Tsukuba, Japan (courtesy of T. Ohta, KEK).

⑥ Free-Electron laser, 주로 Far IR, millimeter wave 영역에서 개발중.

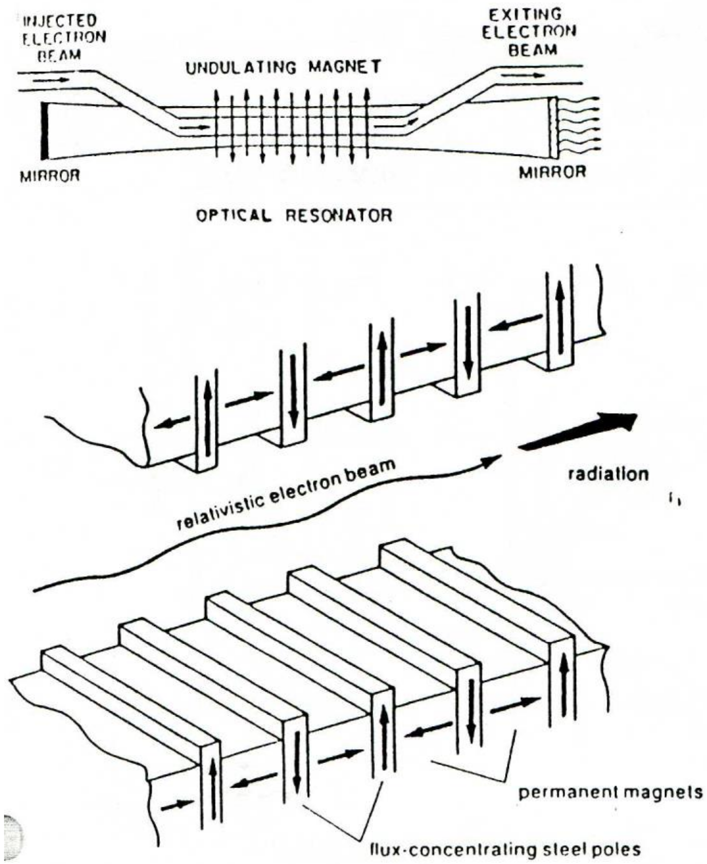
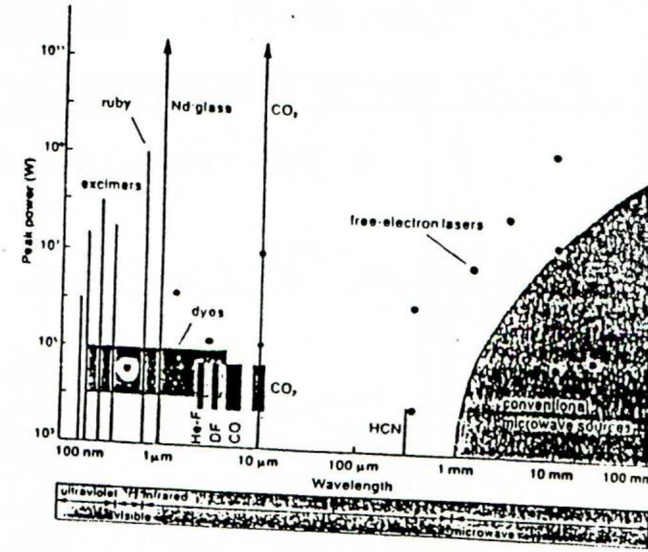
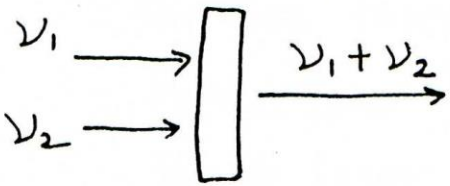


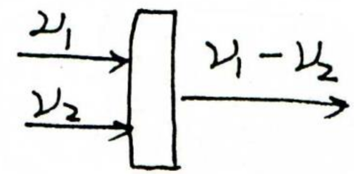
Figure 1: Cumulative energy transfer from an electron beam to a wave is accomplished in the FEL by introducing an undulating beam trajectory.



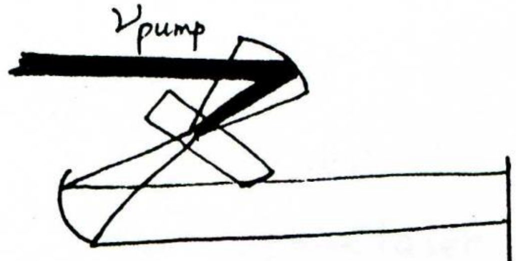
7) Nonlinear Frequency Generation 방법.



Sum Frequency generation



Difference Frequency Generation.



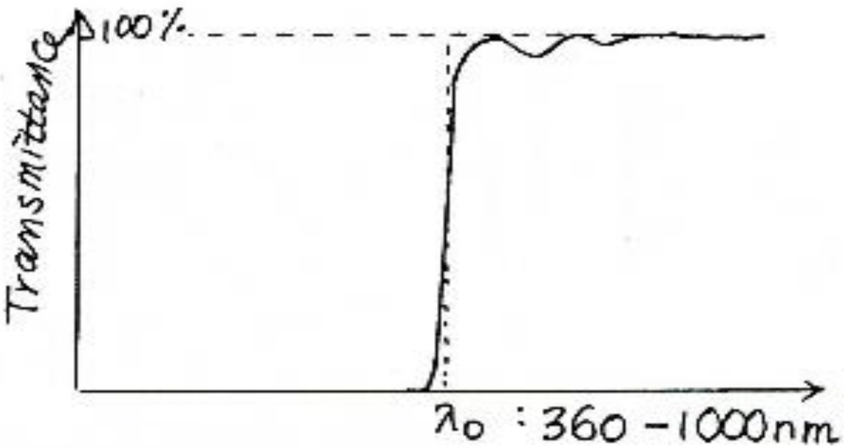
$\nu_{pump} = \nu_{signal} + \nu_{idle}$

↳ 400 nm – 2500 nm Tunable

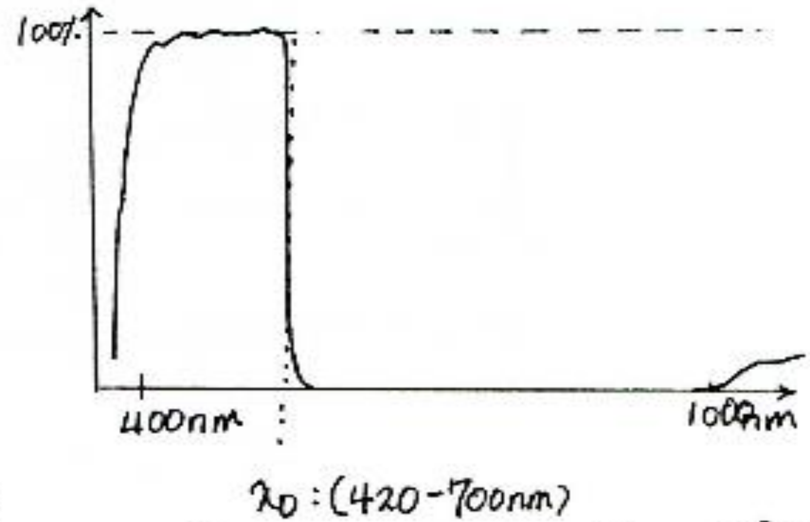
Optical Parametric Oscillator

(2) Dispersing Element

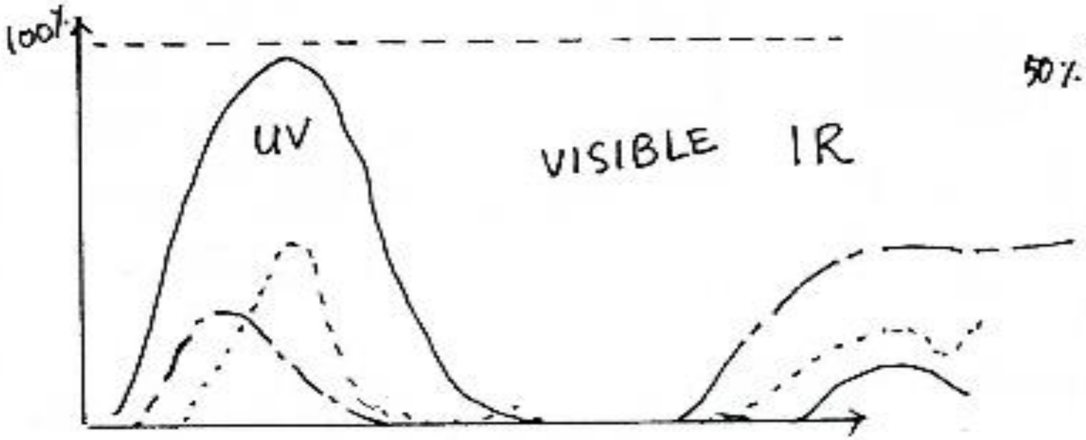
① Filters



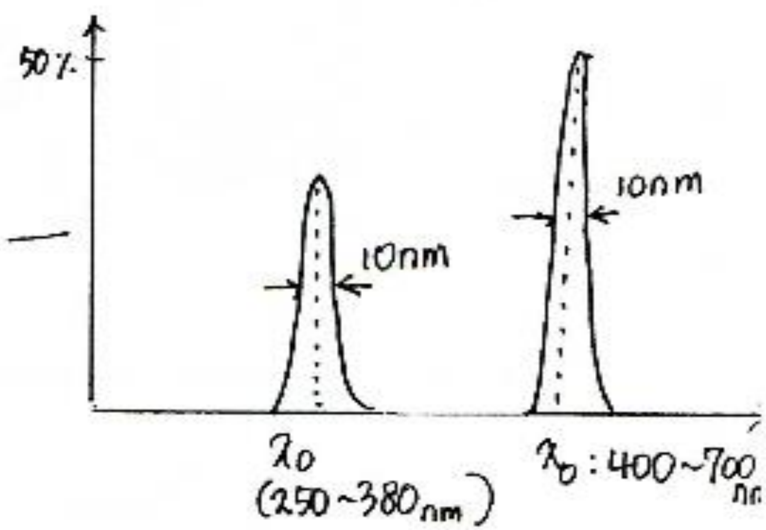
<Long (wavelength) pass filters>

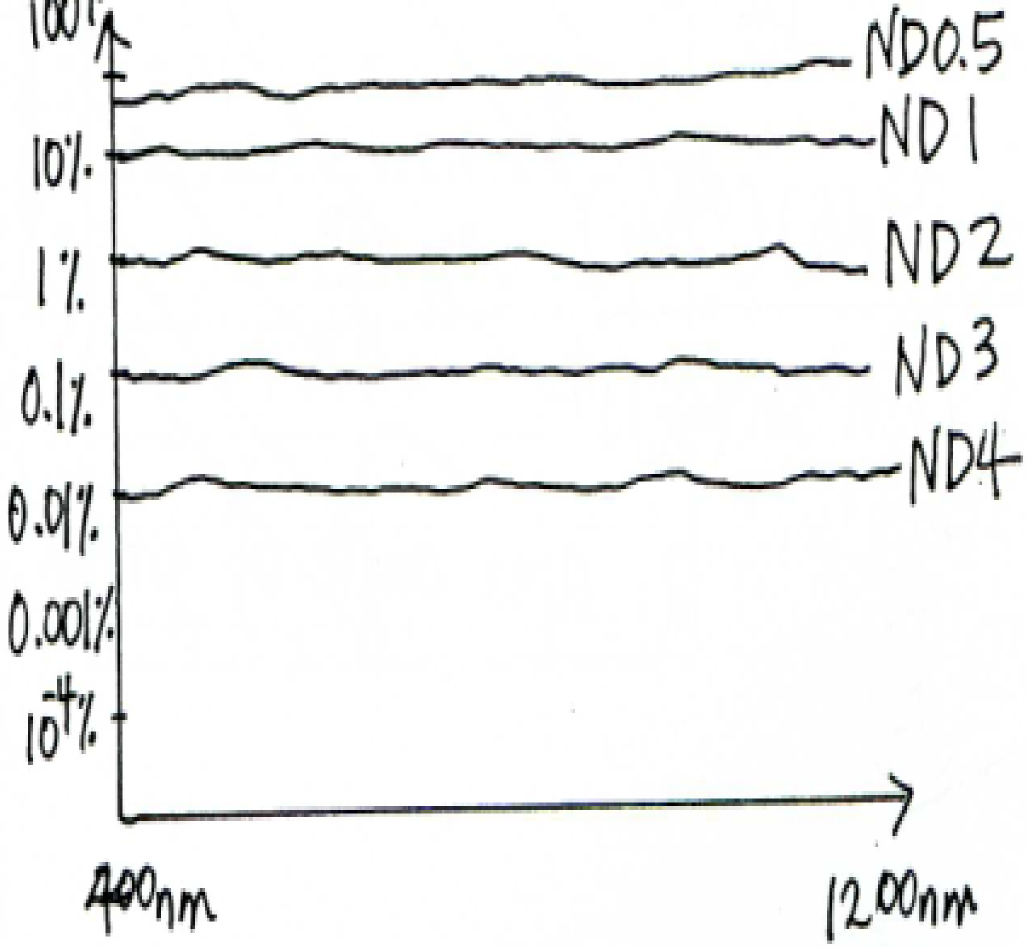


< Short (wavelength) pass filters

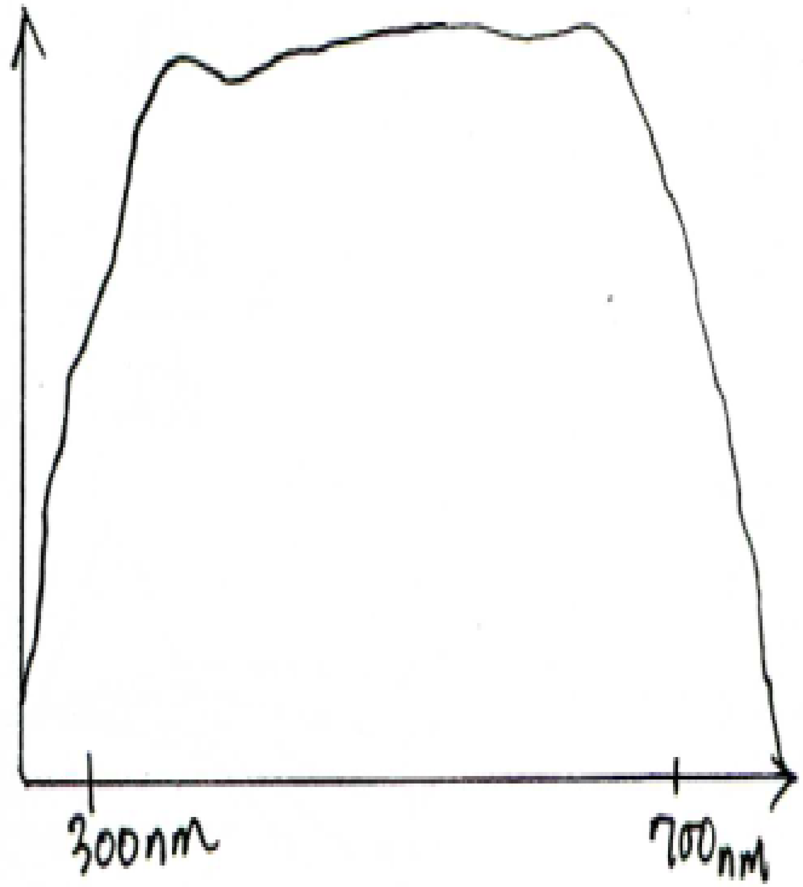


< Band pass filters >



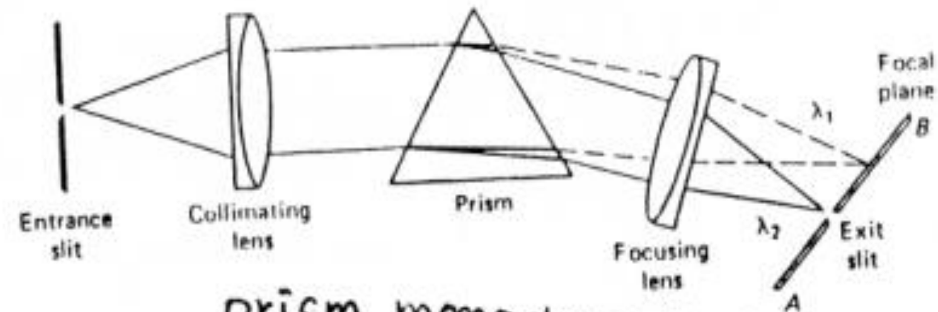


⟨Neutral Density Filters⟩

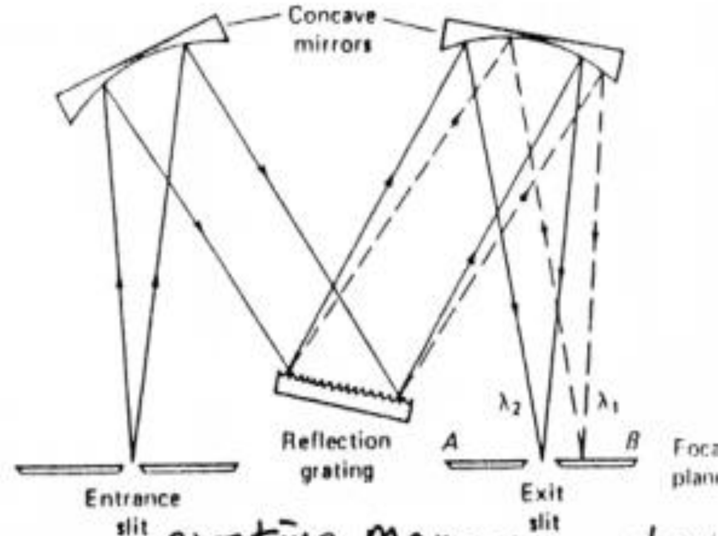


⟨Water Filters⟩

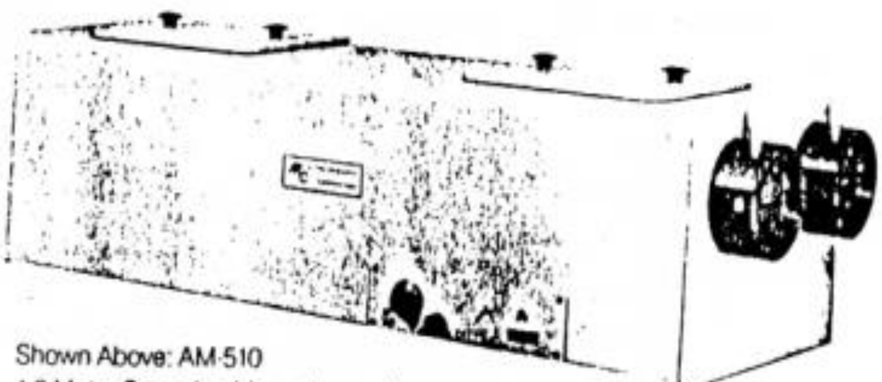
② Monochromator



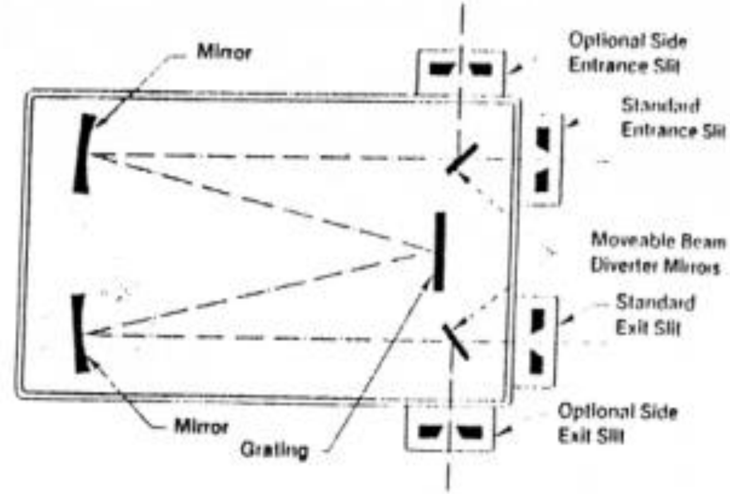
prism monochromator



grating monochromator



Shown Above: AM-510
1.0 Meter Scanning Monochromator



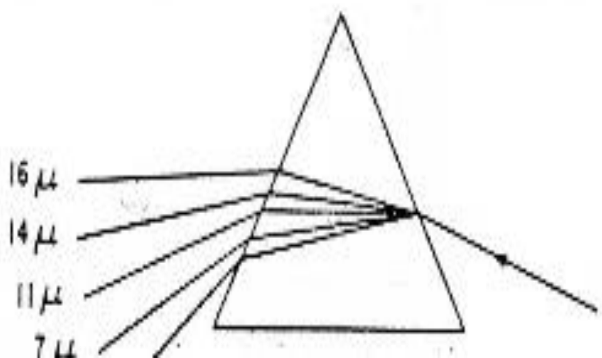
* prism monochromator 의 특성.

Resolving Power

$$R = \frac{\lambda}{d\lambda} = \frac{\nu}{d\nu} = \frac{\tilde{\nu}}{d\tilde{\nu}}$$

$$= \frac{d\theta}{d\lambda} = \frac{2\sin(\alpha/2)(dn/d\lambda)}{[1-n^2\sin^2(\alpha/2)]^{1/2}} = b\,\frac{dn}{d\lambda}$$

α: apex angle of prism



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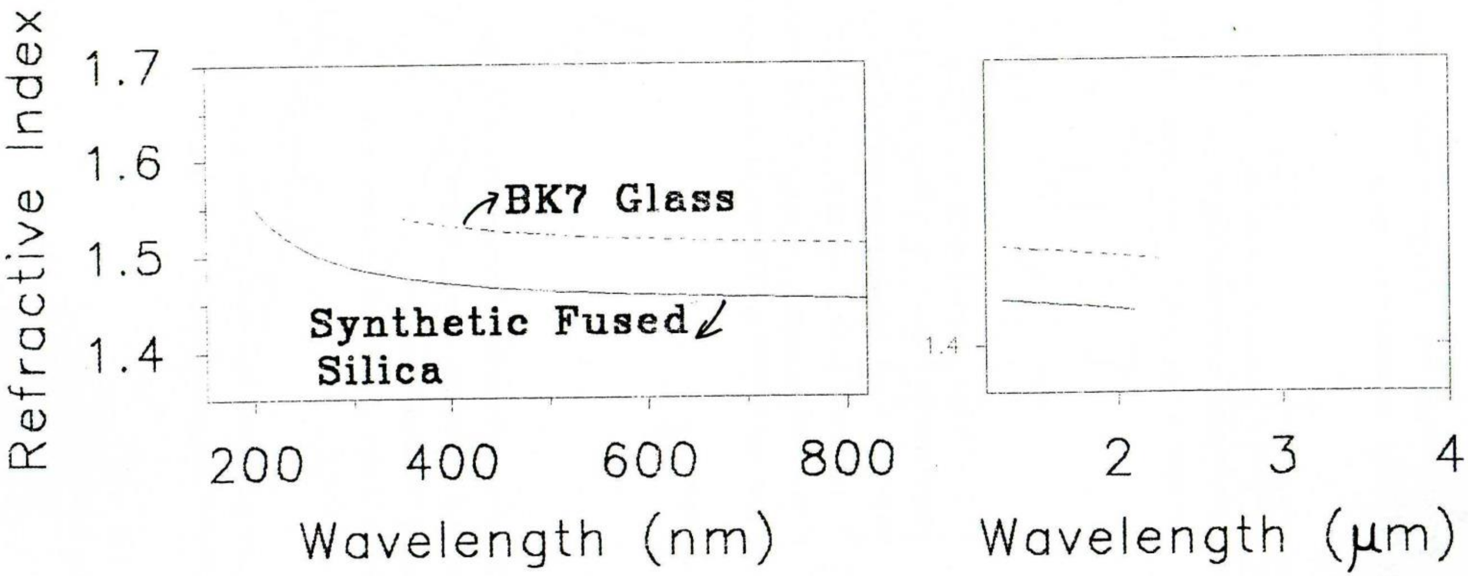
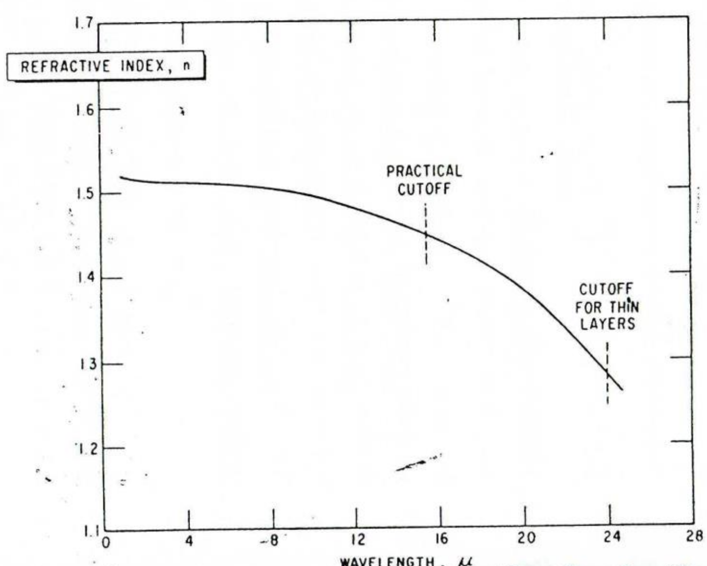
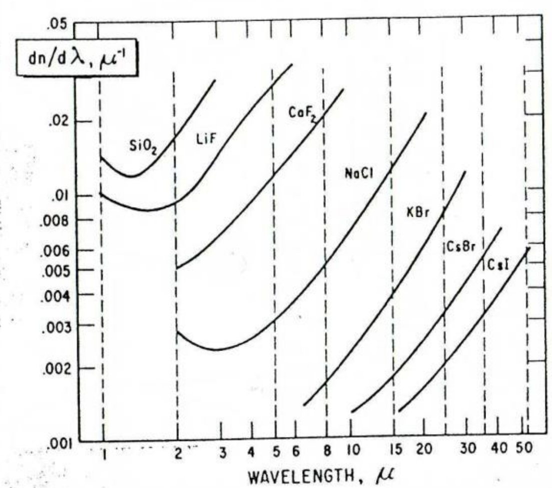
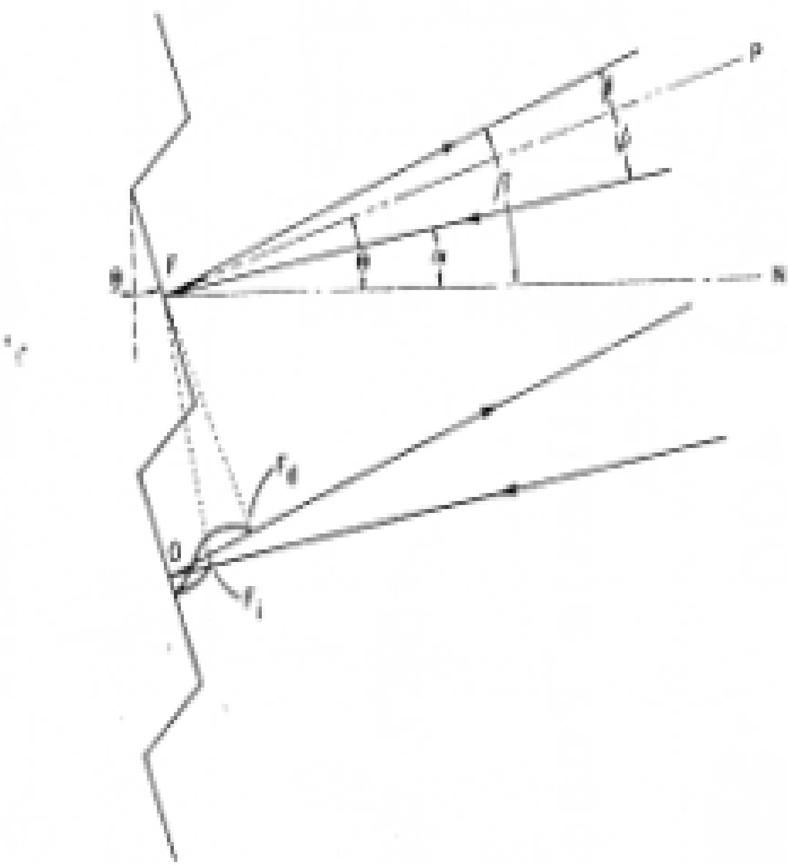
Refractive Index Dispersion Equation : $n^2 - 1 = \frac{b_1 \lambda^2}{\lambda^2 - a_1^2} + \frac{b_2 \lambda^2}{\lambda^2 - a_2^2} + \cdots$







Grating

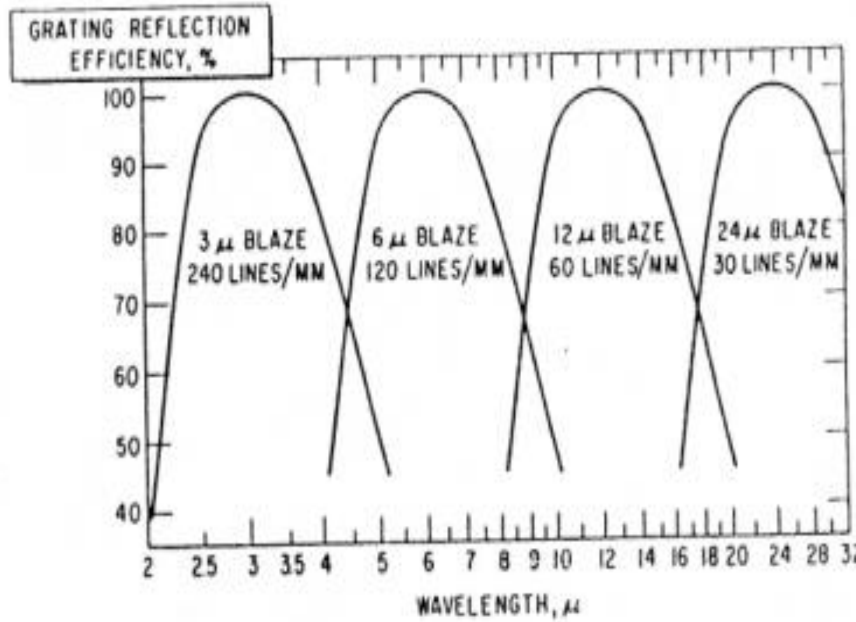


옆 그림에서 diffracted ray가 이루어질 조건은 F와 F_d가 같은 위상을 가져야 한다. 즉 F_i-O-F_d의 길이가 파장의 정수 배여야 한다. 즉,

$$(\sin\alpha + \sin\beta) = \frac{n\lambda}{d}$$

위 식에서 α, β는 각각 incident angle과 diffracted angle을 나타내며, λ는 파장, d는 두 이웃한 홈(groove)간의 거리, n은 F_i-O-F사이에 들어갈 수 있는 파장의 수로서 grating order로 불리워진다. n=0인 diffrated ray는 거울에 반사하듯이 행동한다. n이 커질 때 resolving power는 커지지만 intensity는 감소한다. 짧은 파장에서 더 적어 diffraction됨을 주의 (prism과는 반대).

diffracted light intensity는 위 그림의 ψ와 φ가 같을 때 (specular reflection) 최대가 된다. 주어진 <u>blazing angle</u>, θ에서 diffracted intensity가 최대가 되는 한 λ가 존재하며 이때 이 grating이 이 파장에 대해 "blazed" 되었다 한다. 아래 그림에서 나타난대로 한 grating은 한 brazing wavelength을 중심으로 매우 좁은 파장 영역에서만 쓰인다.



grating order separation : 고정된 각도에 detector 를 놓았을 때 원하는 λ뿐만 아니라 λ/2 (2nd order),λ/3 (3rd order), λ/4 (4th order),... 등도 관측되므로 이들을 분리제거해야 한다. (방법 1:long pass filter사용, 방법 2: 보조 prism 사용)

(Monochromator quality와 performance에 대해 더 자세한 내용은 「W.J. Potts, Jr., *Chemical Infrared Spectroscopy*, p46-p55, John Wiley, 1963」)

3) Fourier-Transform Technique

Detectors.

① IR 영역에선

Photoconductive detectors : photon flux → 전자 flux

여러 반도체 소자(Si, GaAs 등)들을 사용.

장점 : very sensitive

단점 : radiation이 반도체의 bandgap 에너지보다 커야한다. 즉 대부분이 near IR 영역에서만 쓰여진다. longer wavelength의 photodetector 들은 최근 개발 중.

Thermal detectors : photon flux → 온도변화 → 전기신호

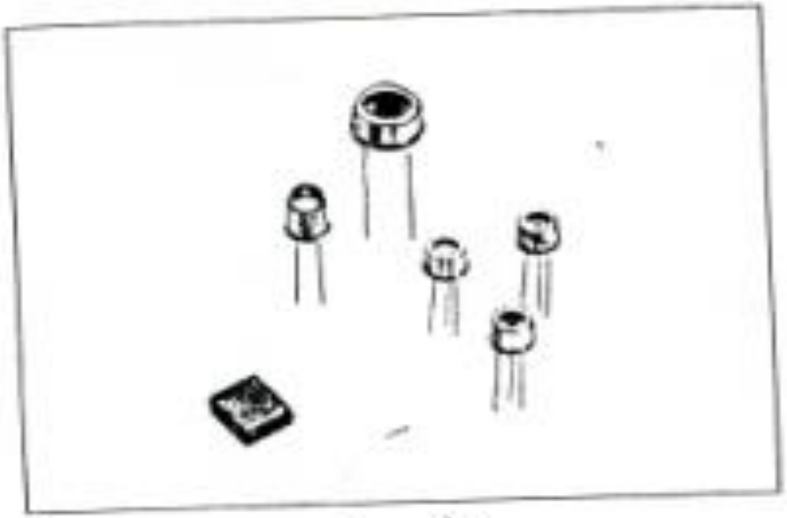
Thermocouple : IR radiation에 의해 온도가 증가한 것을 bimetal의 electrical conductivity를 측정하여 IR intensity를 잰다.

Bolometer : Thermocouple의 bimetal대신 얇은 conductor sheet로서 IR을 측정.

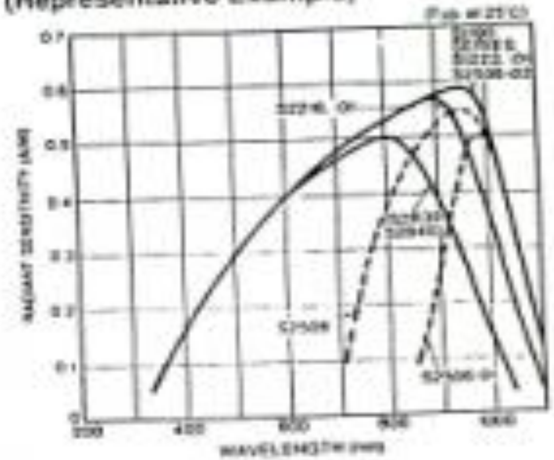
Golay cell : IR radiation이 gas를 데워서 reference light의 optical pathway의 변화 정도를 측정

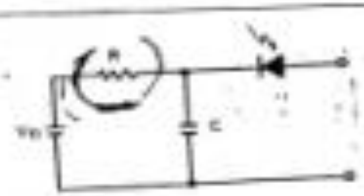
② Visible 영역에선.

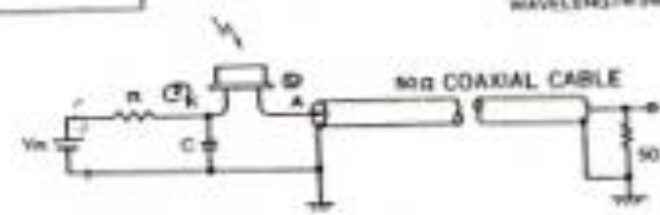
photodiode (visible & near IR).



• Spectral Response (Representative Example)



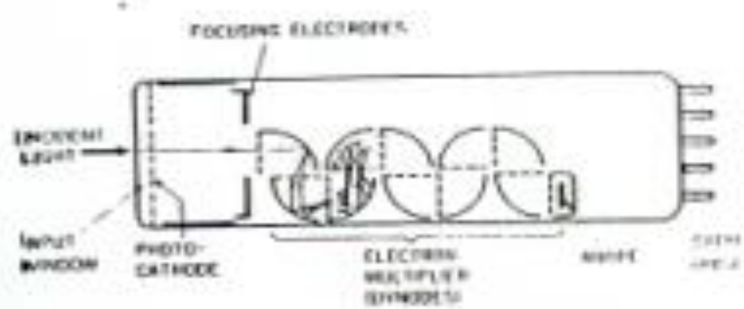




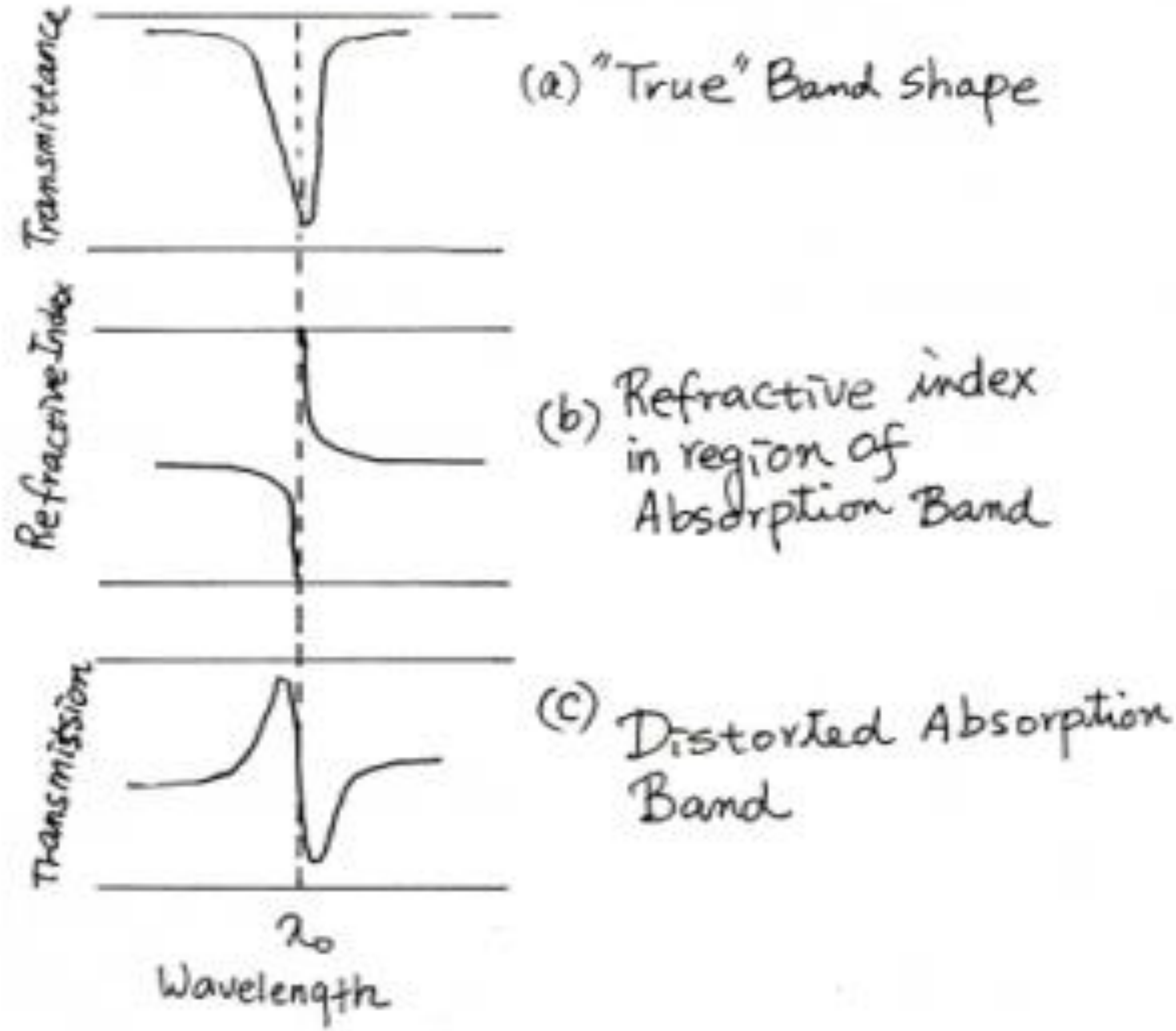
otomultiplier Tube
(PMT)(UV & Visible)

a) Side-On Type

b) Head-On Type



Absorption과 refractive index 와의 관계



and, consequently, χ must be expressed as a tensor. We shall find that the χ tensor of a crystal summarizes most of its optical properties.

6.3 The General Wave Equation

In our study of solid-state optics we shall be concerned only with nonmagnetic, electrically neutral media. Hence $\mathbf{M}$ and ρ are both zero. Maxwell's equations, in the form expressed by Equations (6.1) to (6.4), then reduce to the following:

$$\nabla \times \mathbf{E} = -\mu_0 \frac{\partial \mathbf{H}}{\partial t} \tag{6.10}$$

$$\nabla \times \mathbf{H} = \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} + \frac{\partial \mathbf{P}}{\partial t} + \mathbf{J} \tag{6.11}$$

$$\nabla \cdot \mathbf{E} = -\frac{1}{\epsilon_0} \nabla \cdot \mathbf{P} \tag{6.12}$$

$$\nabla \cdot \mathbf{H} = 0 \tag{6.13}$$

The general wave equation for the E field is obtained by taking the curl of Equation (6.10) and the time derivative of Equation (6.11) and eliminating H. The result is

$$\nabla \times (\nabla \times \mathbf{E}) + \frac{1}{c^2}\frac{\partial^2 \mathbf{E}}{\partial t^2} = \underbrace{-\overbrace{\mu_0 \frac{\partial^2 \mathbf{P}}{\partial t^2}}^{\text{polarization charges}} - \overbrace{\mu_0 \frac{\partial \mathbf{J}}{\partial t}}^{\text{conduction charges}}}_{\text{source terms}} \tag{6.14}$$

The two terms on the right-hand side of the above equation are called *source terms*. They stem from the presence of polarization charges and conduction charges, respectively, within the medium. The way in which the propagation of light is affected by the sources is revealed by the solution of the wave equation when the source terms are included. In the case of nonconducting media the polarization term $-\mu_0\, \partial^2\mathbf{P}/\partial t^2$ is of importance. It turns out that this term leads to an explanation of many optical effects, including dispersion, absorption, double refraction, and optical activity to mention only a few. In the case of metals it is the conduction term $-\mu_0\, \partial\mathbf{J}/\partial t$ that is important, and the resulting solutions of the wave equation explain the large opacity and high reflectance of metals. Both source terms must be taken into account in the case of semiconductors. The result is a rather complicated wave equation and the solutions are somewhat difficult to interpret. Nevertheless, a qualitative description of many of the optical properties of semiconductors is furnished by classical theory. A rigorous treatment of semiconductor optics must await the application of quantum theory.

6.4 Propagation of Light in Isotropic Dielectrics. Dispersion

In a nonconducting, isotropic medium, the electrons are permanently bound to the atoms comprising the medium and there is no preferential direction. This is what is meant by a simple isotropic dielectric such as glass. Suppose that each electron, of charge $-e$, in a dielectric is displaced a distance $\mathbf{r}$ from its equilibrium position. The resulting macroscopic polarization $\mathbf{P}$ of the medium is given by

$$\mathbf{P} = -Ne\mathbf{r} \tag{6.15}$$

where N is the number of electrons per unit volume. If the displacement of the electron is the result of the application of a static electric field $\mathbf{E}$, and if the electron is elastically bound to its equilibrium position with a force constant K, then the force equation is

$$-e\mathbf{E} = K\mathbf{r} \tag{6.16}$$

The *static* polarization is therefore given by

$$\mathbf{P} = \frac{Ne^2}{K}\mathbf{E} \tag{6.17}$$

However, if the impressed field $\mathbf{E}$ varies with time, the above equation is incorrect. In order to find the true polarization in this case, we must take the actual motion of the electrons into account. To do this we consider the bound electrons as classical damped harmonic oscillators. The differential equation of motion is

$$m\frac{d^2\mathbf{r}}{dt^2} + m\gamma\frac{d\mathbf{r}}{dt} + K\mathbf{r} = -e\mathbf{E} \tag{6.18}$$

The term $m\gamma\,(d\mathbf{r}/dt)$ represents a frictional damping force that is proportional to the velocity of the electron, the proportionality constant being written as $m\gamma$.[3]

Now suppose that the applied electric field varies harmonically with time according to the usual factor $e^{-i\omega t}$. Assuming that the motion of the electron has the same harmonic time dependence, we find that Equation (6.18) becomes

$$(-m\omega^2 - i\omega m\gamma + K)\mathbf{r} = -e\mathbf{E} \tag{6.19}$$

Consequently, the polarization, from Equation (6.15), is given by

$$\boxed{\mathbf{P} = \frac{Ne^2}{-m\omega^2 - i\omega m\gamma + K}\mathbf{E}} \tag{6.20}$$

It reduces to the static value, Equation (6.17), when $\omega = 0$. Thus for a given amplitude of the impressed electric field, the amount of polarization varies with frequency. The phase of **P**, relative to that of the electric field, also depends on the frequency. This is shown by the presence of the imaginary term in the denominator.

A more significant way of writing Equation (6.20) is

$$\mathbf{P} = \frac{Ne^2/m}{\omega_0^2 - \omega^2 - i\omega\gamma}\,\mathbf{E} \tag{6.21}$$

in which we have introduced the abbreviation ω_0 given by

$$\omega_0 = \sqrt{\frac{K}{m}} \tag{6.22}$$

This is the *effective resonance frequency* of the bound electrons.

The polarization formula (6.21) is similar to the amplitude formula for a driven harmonic oscillator, as indeed it should be, since it is the displacement of the elastically bound electrons that actually constitutes the polarization. We should therefore expect to find an optical resonance phenomenon of some kind occurring for light frequencies in the neighborhood of the resonance frequency ω_0. As we shall presently see, this resonance phenomenon is manifest as a large change in the index of refraction of the medium and also by a strong absorption of light at or near the resonance frequency.

To show how the polarization affects the propagation of light, we return to the general wave equation (6.14). For a dielectric there is no conduction term. The polarization is given by Equation (6.21). Hence we have

$$\nabla \times (\nabla \times \mathbf{E}) + \frac{1}{c^2}\frac{\partial^2 \mathbf{E}}{\partial t^2} = \frac{-\mu_0 Ne^2}{m}\left(\frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega}\right)\frac{\partial^2 \mathbf{E}}{\partial t^2} \tag{6.23}$$

Also, from the linear relationship between **P** and **E**, it follows from (6.12) that $\nabla \cdot \mathbf{E} = 0$. Consequently, $\nabla \times (\nabla \times \mathbf{E}) = -\nabla^2 \mathbf{E}$, and the above wave equation reduces to the somewhat simpler one

$$\nabla^2 \mathbf{E} = \frac{1}{c^2}\left(1 + \frac{Ne^2}{m\epsilon_0}\cdot\frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega}\right)\frac{\partial^2 \mathbf{E}}{\partial t^2} \tag{6.24}$$

after rearranging terms and using the relation $\boxed{1/c^2 = \mu_0\epsilon_0}$.

Let us seek a solution of the form

$\nabla \times (\nabla \times V) = \nabla\nabla \cdot V - \nabla \cdot \nabla V$

$$\mathbf{E} = \mathbf{E}_0\, e^{i(\mathcal{K}z - \omega t)} \tag{6.25}$$

This trial solution represents what are called *homogeneous plane harmonic waves*. Direct substitution shows that this is a possible solution provided that

$$\mathcal{K}^2 = \frac{\omega^2}{c^2}\left(1 + \frac{Ne^2}{m\epsilon_0}\cdot\frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega}\right) \tag{6.26}$$

#5 2-2

The presence of the imaginary term in the denominator implies that the wavenumber $\mathcal{K}$ must be a complex number. Let us inquire as to the physical significance of this. We express $\mathcal{K}$ in terms of its real and imaginary parts as

$$\boxed{\mathcal{K} = k + i\alpha} \tag{6.27}$$

This amounts to the same thing as introducing a complex index of refraction

$$\boxed{\mathcal{N} = n + i\kappa} \tag{6.28}$$

where

$$\boxed{\mathcal{K} = \frac{\omega}{c}\mathcal{N}} \tag{6.29}$$

Our solution in Equation (6.25) can then be written as

$$\boxed{\mathbf{E} = \mathbf{E}_0 e^{-\alpha z} e^{i(kz-\omega t)}} \tag{6.30}$$

The factor $e^{-\alpha z}$ indicates that the amplitude of the wave decreases exponentially with distance. This means that as the wave progresses, the energy of the wave is absorbed by the medium. Since the energy in the wave at a given point is proportional to $|\mathbf{E}|^2$, then the energy varies with distance as $e^{-2\alpha z}$. Hence 2α is the *coefficient of absorption* of the medium. The imaginary part κ of the complex index of refraction is known as the *extinction index*. The two numbers α and κ are related by the equation

$$\alpha = \frac{\omega}{c}\kappa \tag{6.31}$$

The phase factor $e^{i(kz-\omega t)}$ indicates that we have a harmonic wave in which the phase velocity is

$$u = \frac{\omega}{k} = \frac{c}{n} \tag{6.32}$$

From Equations (6.26) and (6.29) we have

$$\mathcal{N}^2 = (n + i\kappa)^2 = 1 + \frac{Ne^2}{m\epsilon_0}\left(\frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega}\right) \tag{6.33}$$

Equating real and imaginary parts yields the following equations:

$$n^2 - \kappa^2 = 1 + \frac{Ne^2}{m\epsilon_0}\left(\frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}\right) \tag{6.34}$$

$$2n\kappa = \frac{Ne^2}{m\epsilon_0}\left(\frac{\gamma\omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}\right) \tag{6.35}$$

from which the optical parameters n and κ may be found

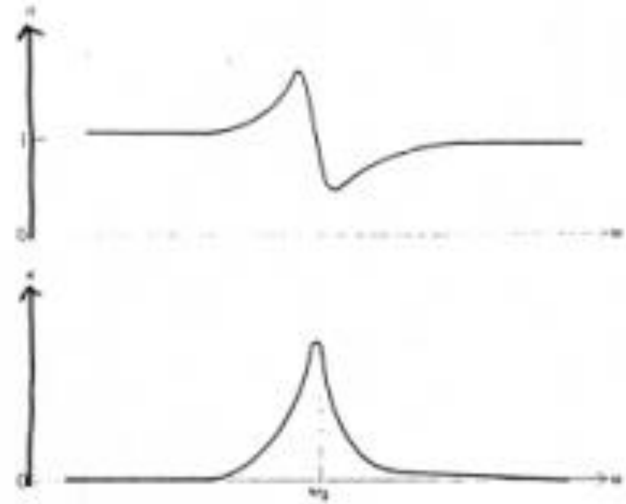


Figure 6.1. Graphs of the index of refraction and extinction coefficient versus frequency near a single resonance line.

Figure 6.1 shows the general way in which n and κ depend on frequency. The absorption is strongest at the resonance frequency ω_0. The index of refraction is greater than unity for small frequencies and increases with frequency as the resonance frequency is approached. This is the case of "normal" dispersion, which is exhibited by most transparent substances over the visible region of the spectrum, the principal resonance frequencies being in the ultraviolet region. At or near the resonance frequency, however, the dispersion becomes "anomalous" in the sense that the index of refraction *decreases* with increasing frequency.

Anomalous dispersion can be observed experimentally if the substance is not too opaque at the resonance frequency. For instance, certain dyes have absorption bands in the visible region of the spectrum and exhibit anomalous dispersion in the region of these bands. Prisms made of these dyes produce a spectrum that is reversed; that is, the longer wavelengths are refracted more than the shorter wavelengths.

Now, in the above discussion it has been tacitly assumed that all of the electrons were identically bound, and hence all had the same resonance frequencies. In order to take into account the fact that different electrons may be bound differently, we may assume that a certain fraction f_1 has an associated resonance frequency ω_1, a fraction f_2 has the resonance frequency ω_2, and so on. The resulting formula for the square of the complex index of refraction is of the form

$$\mathcal{N}^2 = 1 + \frac{Ne^2}{m\epsilon_0}\sum_j \left(\frac{f_j}{\omega_j^2 - \omega^2 - i\gamma_j\omega}\right) \qquad (6.36)$$

The summation extends over all the various kinds of electrons indicated by the subscript j. The fractions f_j are known as *oscillator strengths*. The damping constants associated with the various frequencies are denoted by γ_j. Figure 6.2 shows graphically the gen-

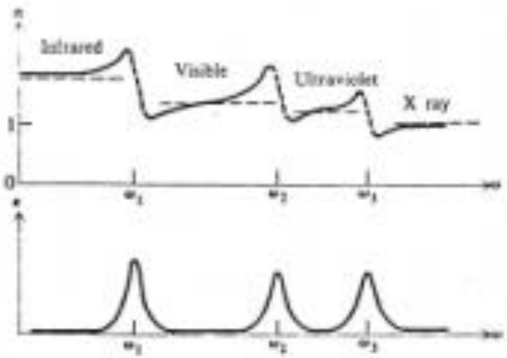


Figure 6.2. Index of refraction and extinction index for a hypothetical substance with absorption bands in the infrared, visible, and ultraviolet regions of the spectrum.

eral dependence of the real and imaginary parts of $\mathcal{N}$ as determined by Equation (6.36). This graph is intended to show qualitatively the case for a substance, such as glass, which is transparent in the visible region and has absorption bands in the infrared and ultraviolet regions of the spectrum. In the limit of zero frequency, the square of the index approaches the value $\boxed{1 + (Ne^2/m\epsilon_0)\,\Sigma f_j/\omega_j^2.}$ This is just the static dielectric constant of the medium.

While this expression is fine for rare media such as gases there is yet another complication which must be dealt with if it is to be applied to dense substances. Each atom interacts with the local electric field in which it is immersed. Yet unlike the isolated atoms considered above, those in a dense material will also experience the induced field set up by their brethren. Consequently an atom "sees" in addition to the applied field $E(t)$ another field,* namely $P(t)/3\epsilon_0$. Without going into the details here it can be shown that

$$\frac{\mathcal{N}^2 - 1}{\mathcal{N}^2 + 2} = \frac{Nq_e^2}{3\epsilon_0 m_e}\sum_j \frac{f_j}{\omega_{0j}^2 - \omega^2 - i\gamma_j\omega}$$

Absorption이 작은 경우

$\omega_{0j}^2 - \omega^2 \gg \gamma_j \omega$

$x \to 0$

$\therefore \frac{n^2-1}{n^2+2} = \frac{Ne^2}{3\epsilon_0 m}\sum_j \frac{f_j}{\omega_{0j}^2-\omega^2}$

(4) Transmitting Optical Materials

Material	Transmission Range	Band	장단점
Glass (BK7, SF11 Crown…) borosilicate	360nm ~ 2.5μm		싸다. 화학적으로 안정. T ~ 99% (주로 visible, near IR에서 사용)
Quartz (Synthetic Fused Silica, Suprasil, …)	200nm ~ 3.5μm	2.2μm 2.7μm	화학적으로 안정 T ~ 99% (uv, visible, near IR에서 사용)
Sapphire	150nm ~ 6μm		단단하다, 비쌈, T ~ 83% (uv, visible, near IR 에서
NaCl	2 ~ 16μm	52μm	비교적 싸고 polishing하기 쉽다 물에 약간 녹으나 금속 등으로 coating 하여 단점보강. IR 에서 가장 많이 사용되

Si	1.3 ~ 8 μm	9 μm	T ~ 50% (IR에서 가끔 사용됨)
CaF_2	? ~ 8.5 μm	23 μm	물에 대해 안정. 고온 고압에서는 불안정 prism material로 많이 사용
KBr	? ~ 25 μm	83 μm	NaCl에 비해 polishing 하기 어렵고 물에 좀 더 녹는다. IR용 lens나 prism material로 쓰인다. 고온고압 상태의 IR sample window로 쓰인다
CsI	? ~ 52 μm	145 μm	물에 잘 녹는다. 잘 깨지지 않는다. 저온의 sample window로서 적당.
polyethylene	20 ~ 1000 μm	125 μm	Far-IR 영역에서 적당.

(5) 종합.

#54

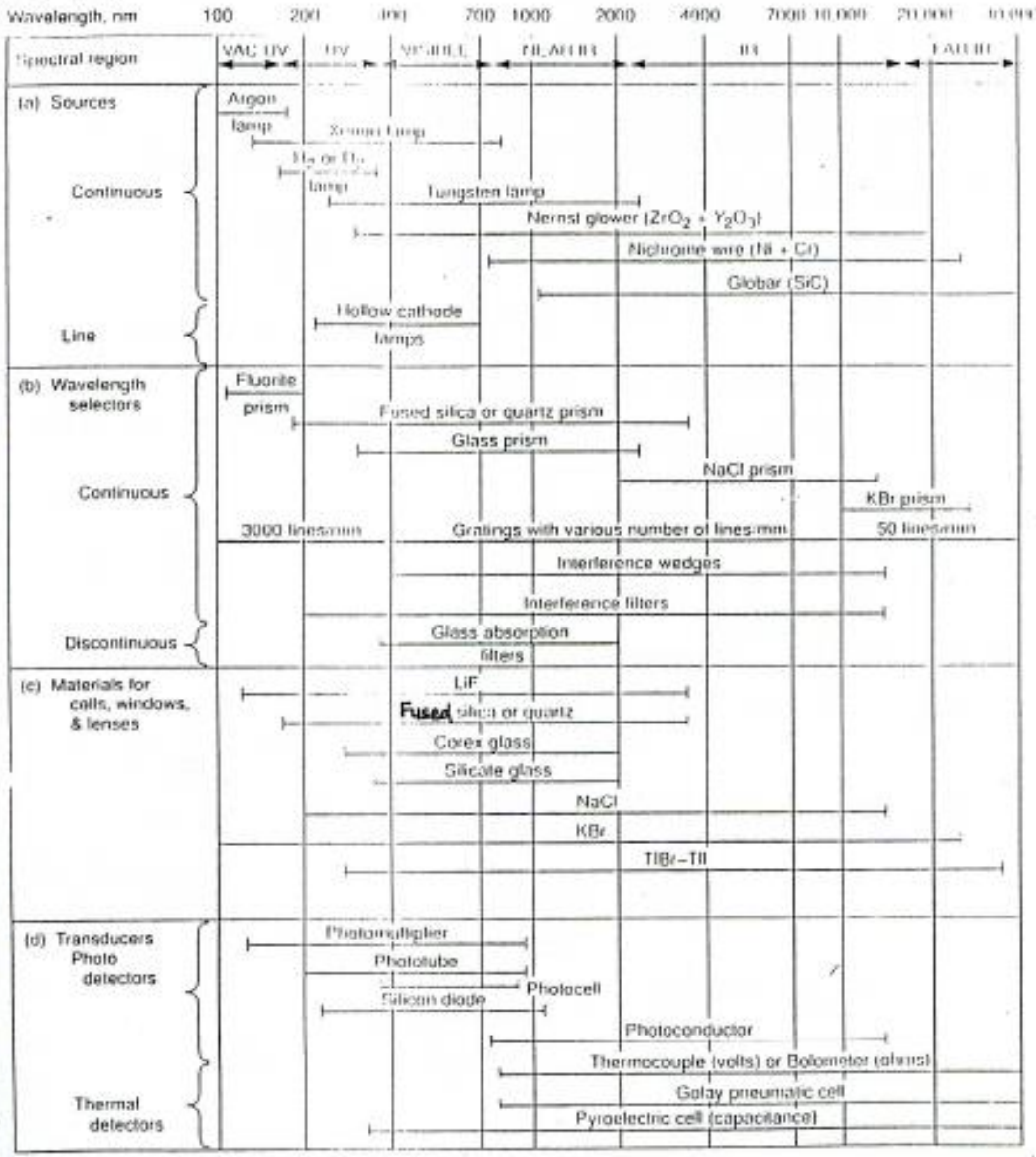


FIGURE 6–2 Components and materials for spectroscopic instruments. (Adapted from a figure by Professor A. R. Armstrong, College of William and Mary. With permission.)

(6) Signal Processor.

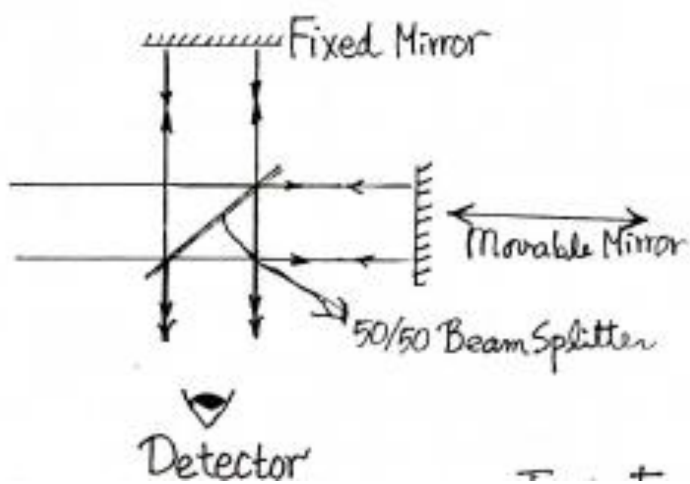
Digital Oscilloscope
Analog-to-Digital Converter
Pulse Counter
Photon Counter
Boxcar Averager

→ Computer

Chart Recorder

< Fourier Transform Technique >

Michelson Interferometer



① Case I. Single Frequency Input

$$\mathcal{E}_{in} = \mathcal{E}_0 \sin 2\pi\nu t \qquad \langle I_{in} \rangle = \mathcal{E}_0^2 \langle \sin^2 2\pi\nu t \rangle = \frac{1}{2}\mathcal{E}_0^2$$

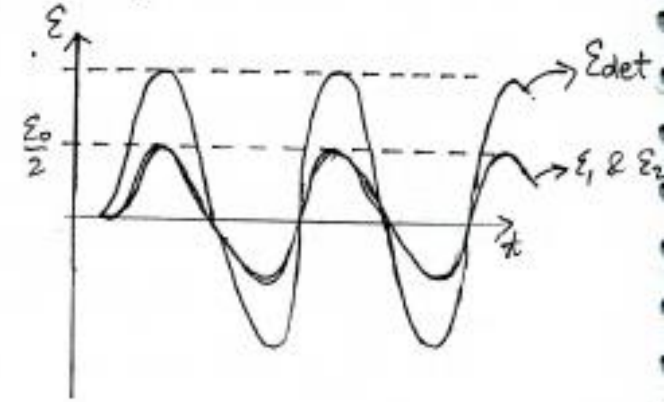
a) p (; path length difference) $= 0$ 일때 즉 $\tau = 0$

↳ arrival time difference

$$\mathcal{E}_{det} = \overbrace{\frac{\mathcal{E}_0}{2}\sin 2\pi\nu t}^{\mathcal{E}_1} + \overbrace{\frac{\mathcal{E}_0}{2}\sin(2\pi\nu t + 0)}^{\mathcal{E}_2}$$

$$= \mathcal{E}_0 \sin 2\pi\nu t$$

$$\langle I_{det} \rangle = \mathcal{E}_0^2 \langle \sin^2 2\pi\nu t \rangle = \frac{1}{2}\mathcal{E}_0^2 = \langle I_{in} \rangle$$



b) $p = \frac{\lambda}{4}$ 일때   즉 $\tau = \frac{\lambda}{4c}$ 일때

$$\mathcal{E}_{det} = \mathcal{E}_1 + \mathcal{E}_2 = \frac{\mathcal{E}_0}{2} \sin 2\pi\nu t + \frac{\mathcal{E}_0}{2} \sin\left(2\pi\nu t + \frac{2\pi P}{\lambda}\right)$$

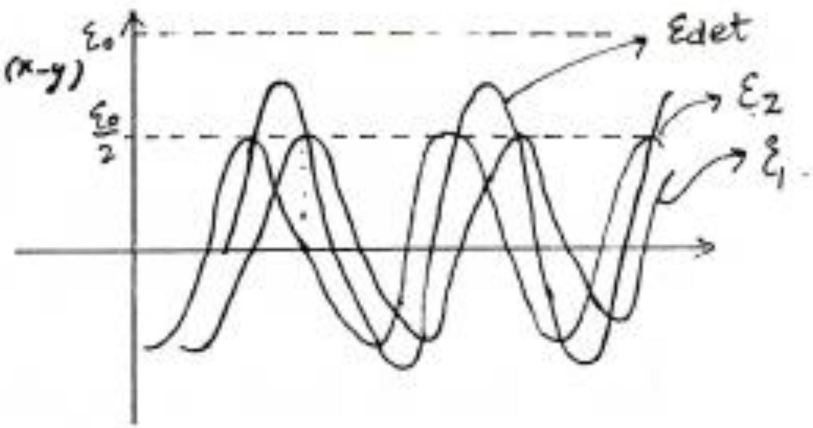
$$= \frac{\mathcal{E}_0}{2}\, 2 \cos\left(\frac{2\pi P}{2\lambda}\right) \sin\left(2\pi\nu t + \frac{\pi P}{\lambda}\right)$$

$$\langle I_{det} \rangle = \mathcal{E}_0^2 \cos^2 \frac{\pi}{4} \cdot \frac{1}{2} = \frac{\mathcal{E}_0^2}{2} \cdot \frac{1}{2} = \frac{1}{2} \langle I_{in} \rangle$$

$$\sin x \cos y = \frac{1}{2}\sin(x+y) + \frac{1}{2}\sin(x-y)$$

$$x = 2\pi\nu t + \frac{\pi P}{\lambda}$$

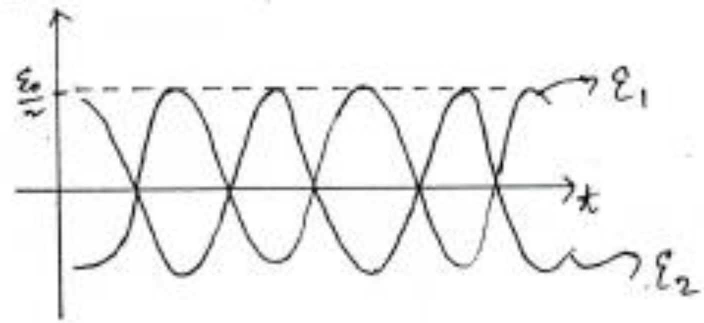
$$y = \frac{\pi P}{\lambda}$$



c) $p=\frac{\lambda}{2}$ 일 때 즉 $\tau = \frac{\lambda}{2c}$ 일 때

$$\mathcal{E}_{det} = \mathcal{E}_1 + \mathcal{E}_2 = \frac{\mathcal{E}_0}{2}\sin 2\pi\nu t + \frac{\mathcal{E}_0}{2}\sin(2\pi\nu t + \pi) = 0$$

$$\langle I_{det}\rangle = \frac{\mathcal{E}_0^2}{2}\cos^2\frac{\pi}{2} = 0$$

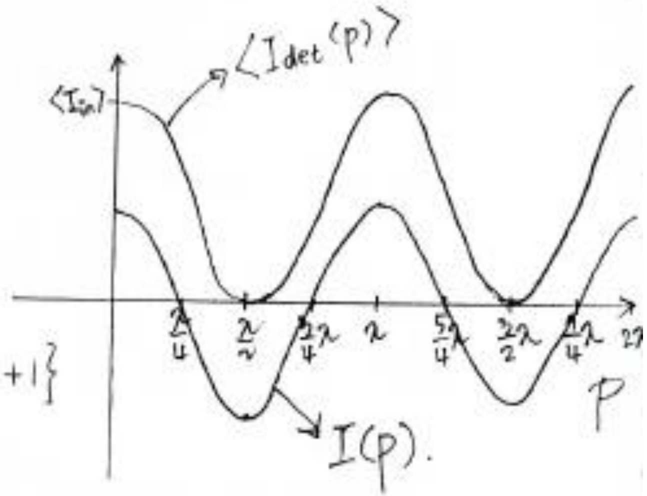


d) $p=\frac{3}{4}\lambda$ 일 때 $\langle I_{det}\rangle = \frac{\mathcal{E}_0^2}{2}\cos^2\frac{3}{4}\pi = \frac{\mathcal{E}_0^2}{4} = \frac{1}{2}\langle I_{in}\rangle$

$$\langle I_{det}(p)\rangle = \frac{\mathcal{E}_0^2}{2}\cos^2\left(\frac{\pi p}{\lambda}\right)$$
$$= \frac{\mathcal{E}_0^2}{2}\cos^2(\pi\nu p/c)$$
$$= \langle I_{in}\rangle \cos^2(\pi\nu p/c)$$

$2\cos^2 x = 1+\cos 2x$

$$= \frac{\langle I_{in}\rangle}{2}\left\{\cos(2\pi\nu p/c)+1\right\}$$

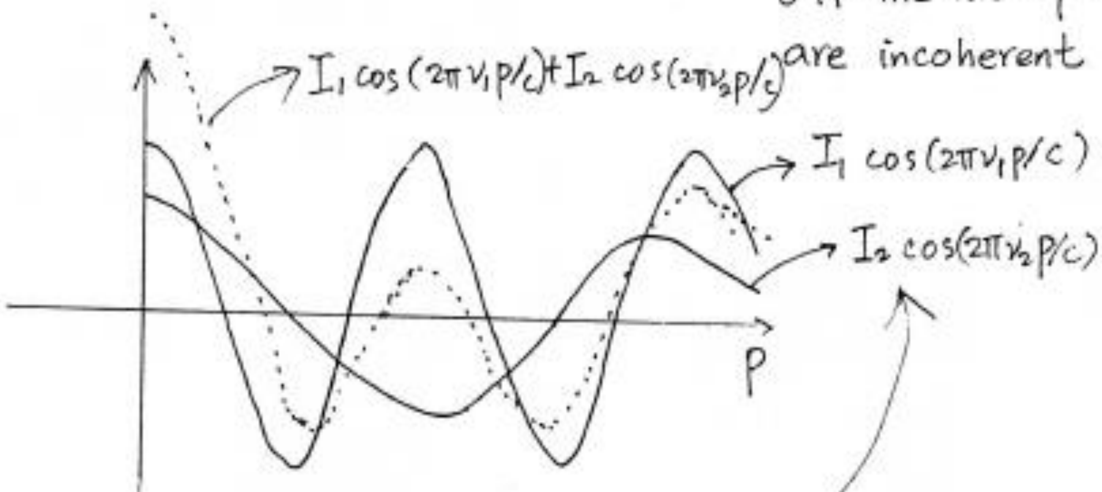


Define
$$I(p) = I_{det}(p) - \frac{1}{2}\left.I_{det}(p)\right|_{max} = \frac{\langle I_{in}\rangle}{2}\cos(2\pi\nu p/c)$$

② Case II. Double Frequency Input

$$E_{in} = \mathcal{E}_{01}\sin 2\pi\nu_1 t + \mathcal{E}_{02}\sin 2\pi\nu_2 t$$ 일 때

$$\langle I(p)\rangle = \frac{\langle I_{in1}\rangle}{2}\cos(2\pi\nu_1 p/c) + \frac{\langle I_{in2}\rangle}{2}\cos(2\pi\nu_2 p/c) + \underbrace{\langle \text{heterodyne term} \rangle}_{=\,0 \text{ if the two inputs are incoherent}}$$



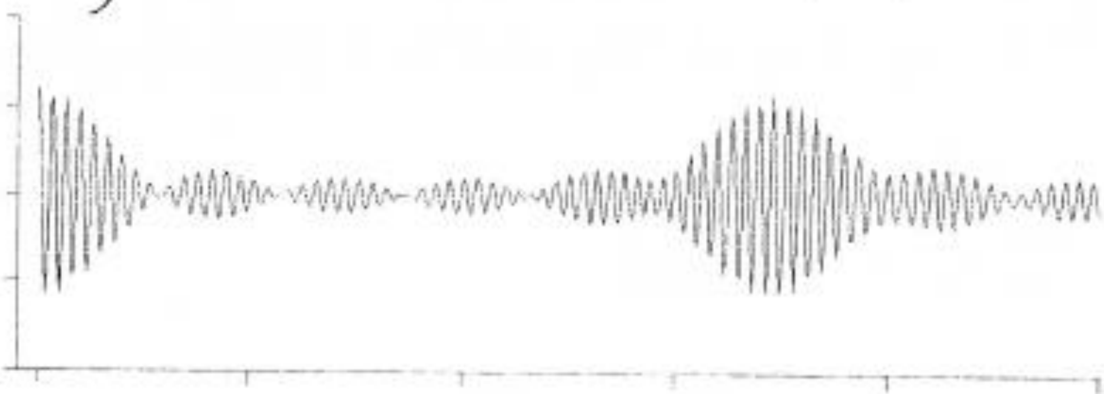
$$I_i = \frac{\langle I_{in\,i}\rangle}{2}$$

③ Case III. Multiple Frequency Input

$$\mathcal{E}_{in} = \sum_i \mathcal{E}_{0i} \sin(2\pi\nu_i t) \text{ 일 때}$$

$$I(p) = \sum_{i=1}^{\infty} I_{0i} \cos(2\pi\nu_i p/c)$$

a) $I_{0i} = 1$ for all i $\lambda_i = 1, 1.02, 1.04, 1.06, 1.08, 1.1$ 일 때



$$I(p) = \int_0^{\infty} I(\nu)\cos(2\pi\nu p/c)\,d\nu$$

$$= R_e \int_{-\infty}^{\infty} I(\nu)\, e^{i2\pi\nu p/c}\, d\nu$$

$$= R_e\, F(I(\nu)) \qquad \text{; Fourier Transform}$$

$$I(\nu) = R_e\, F^{-1}(I(p))$$

$$= R_e \int_{-\infty}^{\infty} I(p)\, e^{-i2\pi\nu p/c}\, dp \quad \text{: Inverse Fourier Transfo}$$

$p = ct$

$$I(t) = \mathrm{Re}\int_{-\infty}^{\infty} I(\nu) e^{i2\pi\nu t} d\nu = \mathrm{Re}\, F\{I(\nu)\}$$

$$I(\nu) = \mathrm{Re}\int_{-\infty}^{\infty} I(t) e^{-i2\pi\nu t} dt = \mathrm{Re}\, F^{-1}\{I(t)\}.$$

Fourier Transform의 중요한 성질

① I(t) 와 I(ν) 과 모두 일반적으로 complex 라할때

$$I(t) = F\{I(\nu)\}$$

$$I(\nu) = F^{-1}\{I(t)\}$$

② $I(\nu)$가 even function이면

$I(t) = F\{I(\nu)\}$는 real function and even function

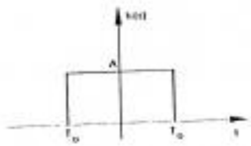
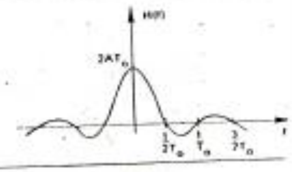
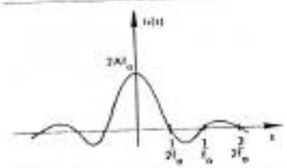
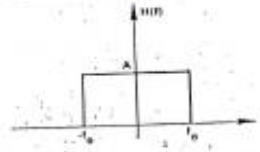
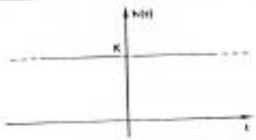
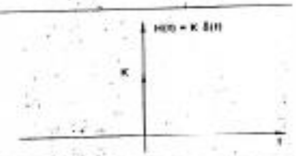
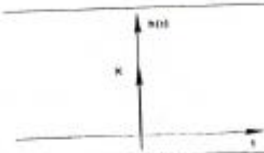
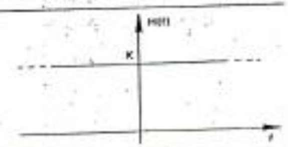
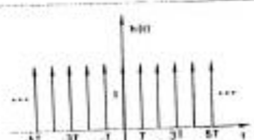
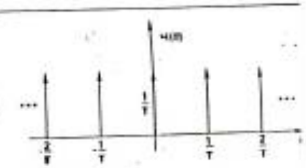
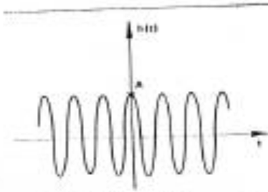
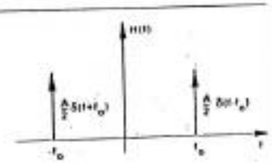
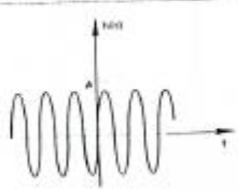
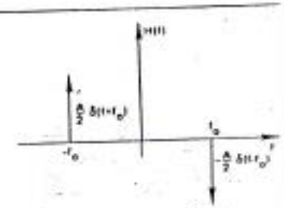
$I(\nu)$가 odd function이면

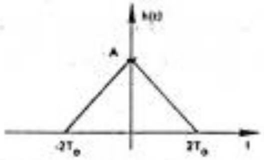
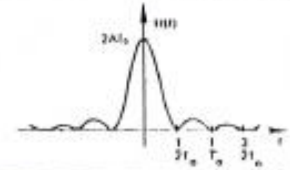
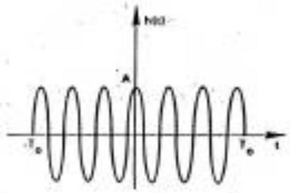
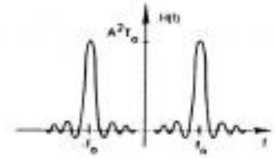
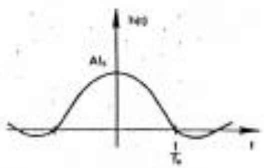
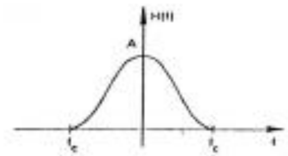
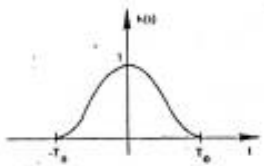
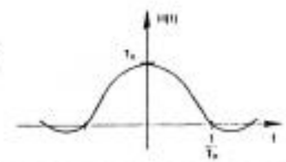
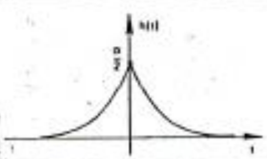
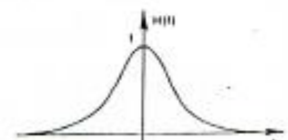
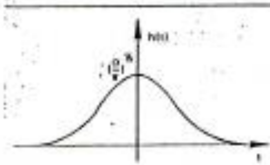
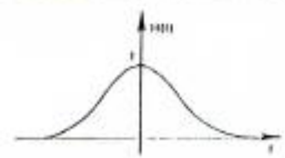
$I(t) = F\{I(\nu)\}$는 imaginary function and even function

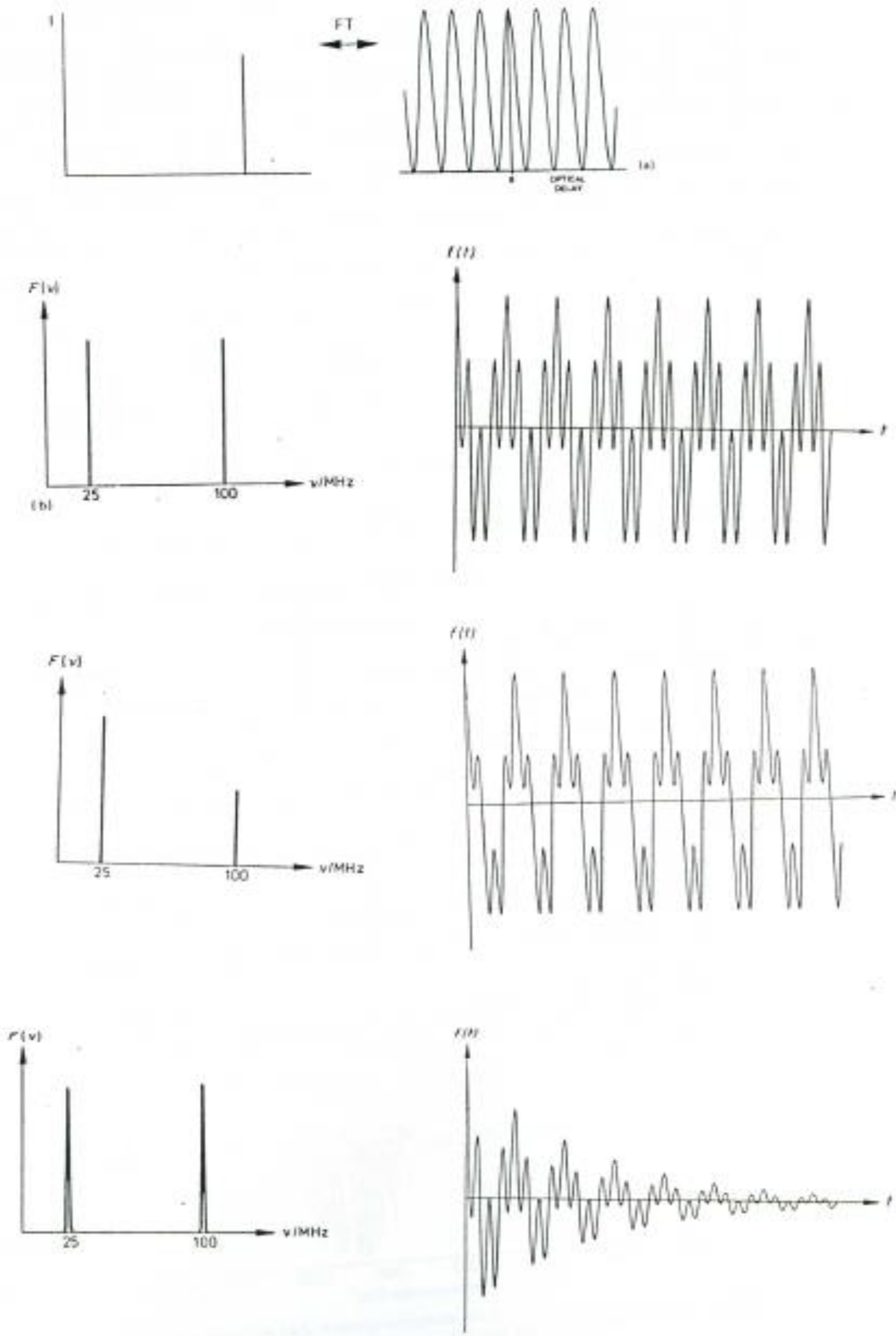
③ Convolution $x(t) \otimes y(t) \equiv \int_{-\infty}^{\infty} x(\tau) y(t-\tau) d\tau$

$I(t) = I_1(t) \cdot I_2(t)$이면 $I(\nu) = I_1(\nu) \otimes I_2(\nu)$

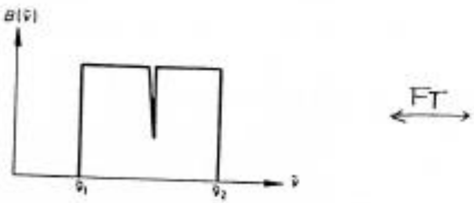
$I(t) = I_1(t) \otimes I_2(t)$이면 $I(\nu) = I_1(t) \cdot I_2(t)$

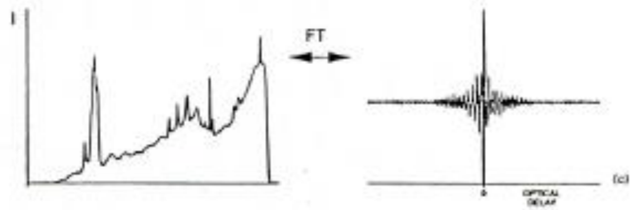
Time Domain		Frequency Domain
	$h(t) = A \quad \lvert t\rvert < T_0$; $\; = \frac{A}{2} \quad \lvert t\rvert = T_0$; $\; = 0 \quad \lvert t\rvert > T_0$ $\Leftrightarrow$ $H(f) = 2AT_0 \frac{\sin(2\pi T_0 f)}{2\pi T_0 f}$	
	$h(t) = 2Af_0 \frac{\sin(2\pi f_0 t)}{2\pi f_0 t}$ $\Leftrightarrow$ $H(f) = A \quad \lvert f\rvert < f_0$; $\; = \frac{A}{2} \quad \lvert f\rvert = f_0$; $\; = 0 \quad \lvert f\rvert > f_0$	
	$h(t) = K \Leftrightarrow H(f) = K\delta(f)$	
	$h(t) = K\delta(t) \Leftrightarrow H(f) = K$	
	$h(t) = \sum_{n=-\infty}^{\infty} \delta(t - nT) \Leftrightarrow H(f) = \frac{1}{T} \sum_{n=-\infty}^{\infty} \delta\left(f - \frac{n}{T}\right)$	
	$h(t) = A\cos(2\pi f_0 t) \Leftrightarrow H(f) = \frac{A}{2}\delta(f - f_0) + \frac{A}{2}\delta(f + f_0)$	
	$h(t) = A\sin(2\pi f_0 t) \Leftrightarrow H(f) = -j\frac{A}{2}\delta(f - f_0) + j\frac{A}{2}\delta(f + f_0)$	

Time Domain		Frequency Domain
	$h(t) = -\frac{A}{2T_0}\|t\| + A$ ⇔ $H(f) = 2AT_0 \frac{\sin^2(2\pi T_0 f)}{2\pi T_0 f}$ $\|t\| < 2T_0$ $= 0 \quad \|t\| > 2T_0$	
	$h(t) = A\cos(2\pi f_0 t)$ ⇔ $H(f) = A^2 T_0 [Q(f + f_0)$ $\|t\| < T_0$ $\quad + Q(f - f_0)]$ $= 0 \quad \|t\| > T_0$ $Q(f) = \frac{\sin(2\pi T_0 f)}{2\pi T_0 f}$	
	$h(t) = \frac{Af_c}{2} q(t)$ ⇔ $H(f) = \frac{A}{2} + \frac{A}{2}\cos\left(\frac{\pi f}{f_c}\right)$ $+ \frac{Af_c}{4} q\left(t + \frac{1}{2f_c}\right)$ $\quad \|f\| \le f_c$ $+ \frac{Af_c}{4} q\left(t - \frac{1}{2f_c}\right)$ $\quad = 0 \quad \|f\| > f_c$ $q(t) = \frac{\sin(2\pi f_c t)}{\pi t}$	
	$h(t) \frac{1}{2} + \frac{1}{2}\cos\left(\frac{\pi t}{T_0}\right)$ ⇔ $H(f) = \frac{1}{2} Q(f)$ $\|t\| \le T_0$ $\quad + \frac{1}{4}\left[Q\left(f + \frac{1}{2T_0}\right)\right.$ $0 \quad \|t\| > T_0$ $\quad \left. + Q\left(f - \frac{1}{2T_0}\right)\right]$ $Q(f) = \frac{\sin(2\pi T_0 f)}{\pi f}$	
	$h(t) = \frac{1}{2}\alpha \exp(-\alpha\|t\|)$ ⇔ $H(f) = \frac{\alpha^2}{\alpha^2 + 4\pi^2 f^2}$	
	$h(t) = \left(\frac{\alpha}{\pi}\right)^{1/2} \exp(-\alpha t^2)$ ⇔ $H(f) = \exp\left(\frac{-\pi^2 f^2}{\alpha}\right)$	



FT
(a)
F(ν)
f(t)
25
100
ν/MHz
(b)
t





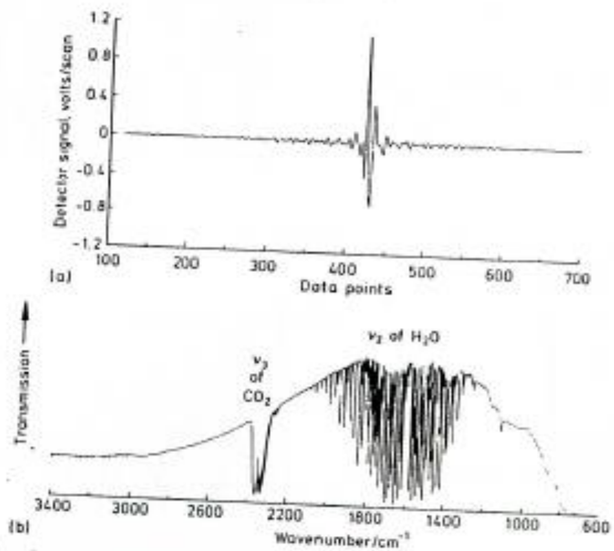


Figure 3.16 (a) Infrared interferogram of the absorption spectrum of air in the 400–3400 cm^{-1} region and (b) the Fourier transformed spectrum.

$\boxed{\text{적용}}$ FT 방법으로 1000 cm^{-1} 의 IR absorption peak를 분석하려면 Movable mirror의 stepper scan size 와 scan length는 어느정도 되어야 하는가? 같은 1000 cm^{-1} 의 peak를 Ar^+ laser의 514 nm (19455 cm^{-1}) line 으로 excitation 시켜 얻은 FT-Raman에서는 어떤가 또 Nd:YAG 의 1064 nm (9398.5 cm^{-1})을 excitation source로 사용하면 어떤가? FT-Raman의 경우 Ar^+ laser 와 Nd:YAG 레이저 중 어느것이 더 좋은 excitation source 인가?

$\boxed{\text{해설}}$ FT-IR의 경우 $\Delta p \doteqdot \frac{1}{1000\ cm^{-1}} = 10\ \mu m$ 즉 최소한 $10\mu m$ 보다 정밀한 Steppor의 Scan size control이 필요.
$1\ cm^{-1}$의 resolution을 갖기 위해선 $P_{max} \doteqdot \frac{1}{1\ cm^{-1}} = 1\ cm$ 이상의 scan length 필요.

FT-Raman의 경우 514 nm를 excitation으로 사용했을때
$\Delta p \doteqdot \frac{1}{20000 cm^{-1}} = 0.5\mu m$, 즉 최소한 $0.5\mu m$의 Scan size control이 필요. $1\ cm^{-1}$의 resolution을 갖기 위해선 $P_{max} \doteqdot \frac{1}{1\ cm^{-1}} = 1\ cm$ 이상의 scan length 가 필요.
1064 nm를 excitation으로 사용했을 때
$\Delta p \doteqdot \frac{1}{10000\ cm^{-1}} = 1\mu m$, 즉 최소한 $1\mu m$ 보다 정밀한 Scan size control이 필요. resolution은 위와 동.

$\therefore$ 1064 nm가 더 좋은 excitation source이다.