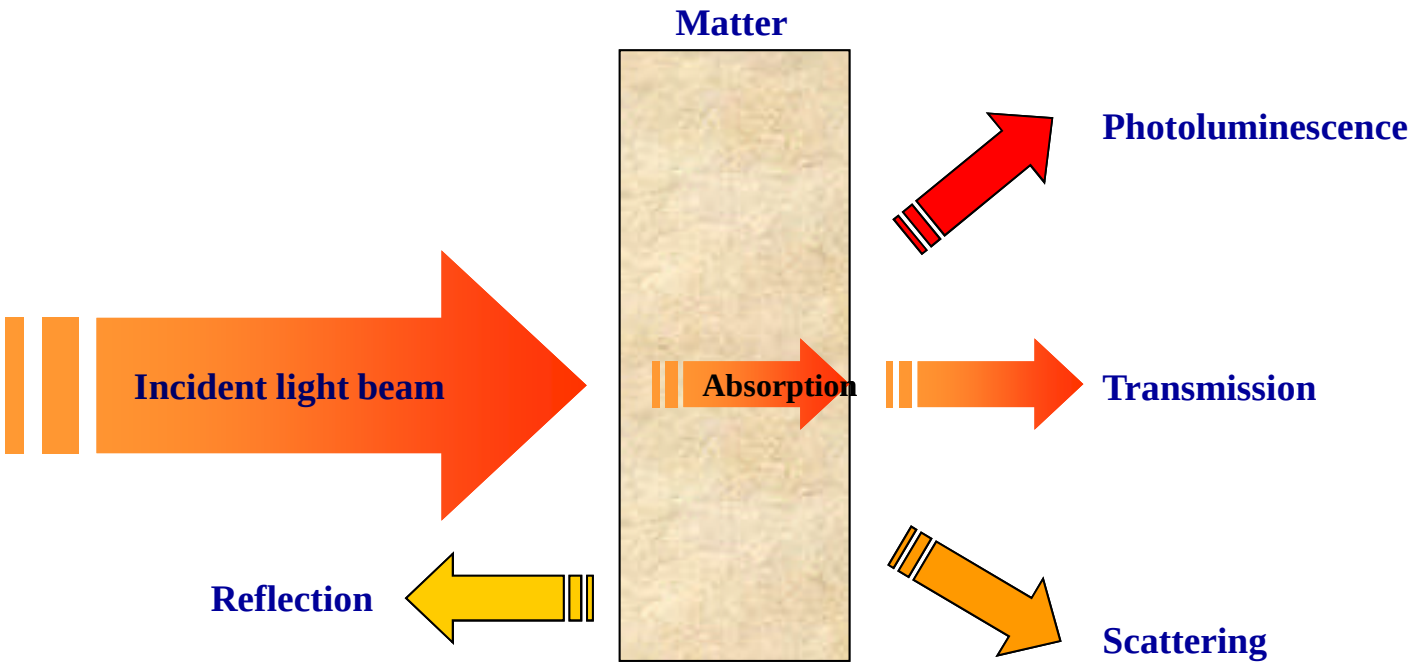
Principles of Spectroscopy

Interaction of radiation and matter

If matter is exposed to electromagnetic radiation, e.g. infrared light, the radiation can be absorbed, transmitted, reflected, scattered or undergo photoluminescence. Photoluminescence is a term used to designate a number of effects, including fluorescence, phosphorescence, and Raman scattering.



Electromagnetic Spectrum

Type of Radiation	**Frequency Range (Hz)**	**Wavelength Range**	**Type of Transition**
Gamma-rays	10^{20}-10^{24}	$<10^{-12}$ m	nuclear
X-rays	10^{17}-10^{20}	1 nm-1 pm	inner electron
Ultraviolet	10^{15}-10^{17}	400 nm-1 nm	outer electron
Visible	4-7.5x10^{14}	750 nm-400 nm	outer electron
Near-infrared	1x10^{14}-4x10^{14}	2.5 μm-750 nm	outer electron molecular vibrations
Infrared	10^{13}-10^{14}	25 μm-2.5 μm	molecular vibrations
Microwaves	3x10^{11}-10^{13}	1 mm-25 μm	molecular rotations, electron spin flips*
Radio waves	<3x10^{11}	>1 mm	>1 mm

The complement of the absorbed light gets transmitted.

The color of an object we see is due to the wavelengths transmitted or reflected. Other wavelengths are absorbed.

The more absorbed, the darker the color (the more concentrated the solution).

In spectrochemical methods, we measure the absorbed radiation.

Table 16.1

Colors of Different Wavelength Regions

Wavelength Absorbed (nm)	Absorbed Color	Transmitted Color (Complement)
380–450	Violet	Yellow-green
450–495	Blue	Yellow
495–570	Green	Violet
570–590	Yellow	Blue
590–620	Orange	Green-blue
620–750	Red	Blue-green

The distance of one cycle is the wavelength (λ).

The frequency (ν) is the number of cycles passing a fixed point per unit time.

$\lambda = c/\nu$ (c = velocity of light, 3 x 10^{10} cm s^{-1}).

The shorter the wavelength, the higher the energy: $E = h\nu$

This is why UV radiation from the sun burns you.

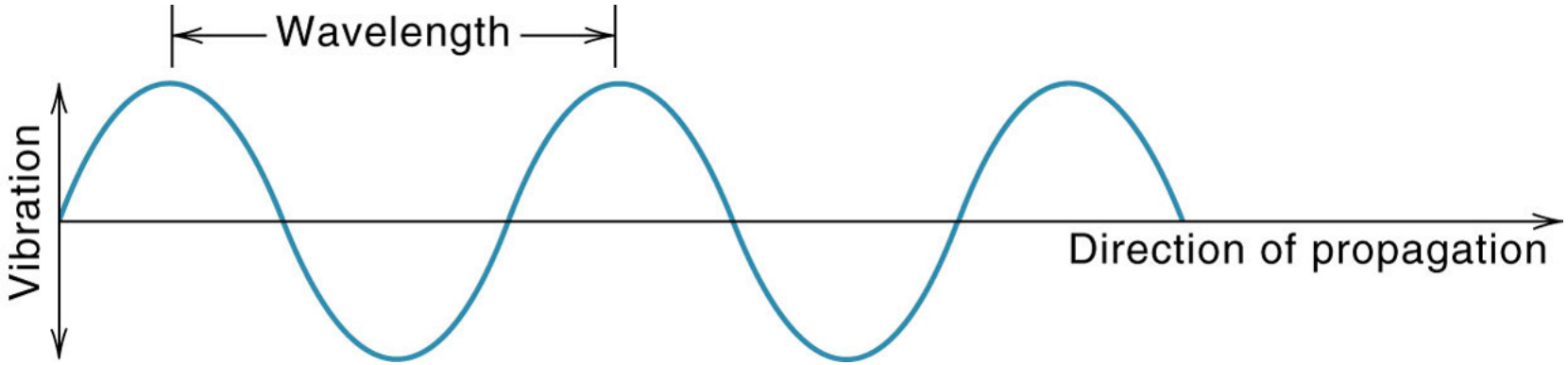


Fig. 16.1. Wave motion of electromagnetic radiation.

We see only a very small portion of the electromagnetic spectrum .

In spectrochemical methods, we measure the absorption of UV to far IR radiation.

UV = 200-380 nm

VIS = 280-780 nm

IR = 0.78 μm-300 μm

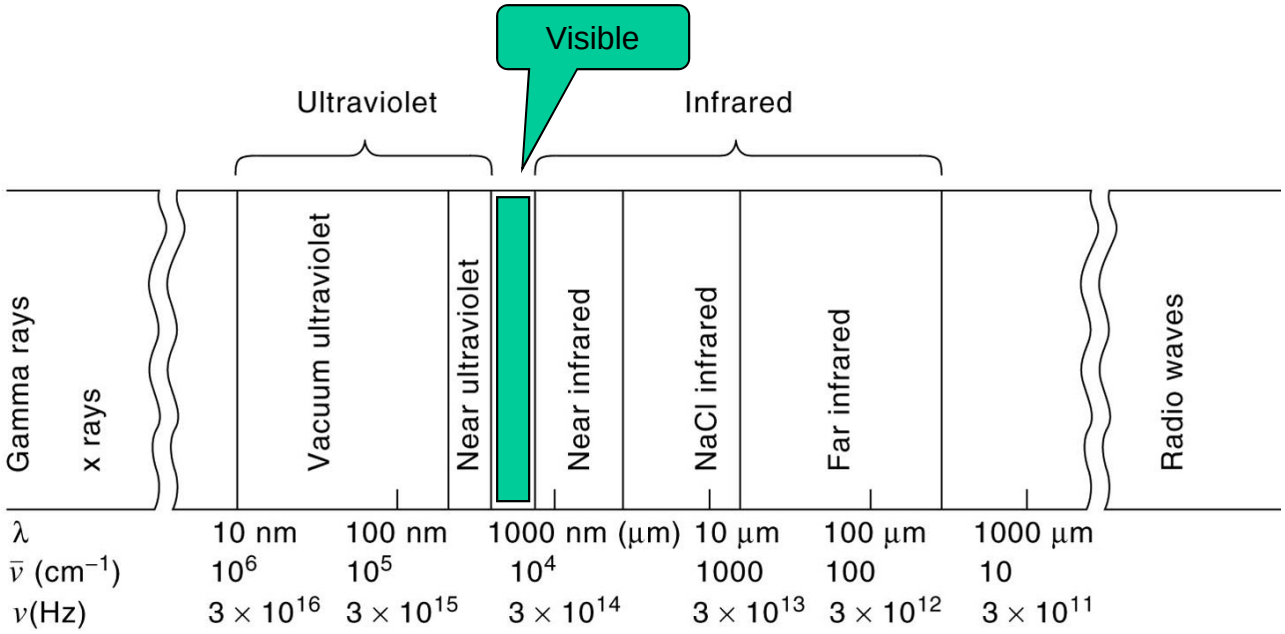
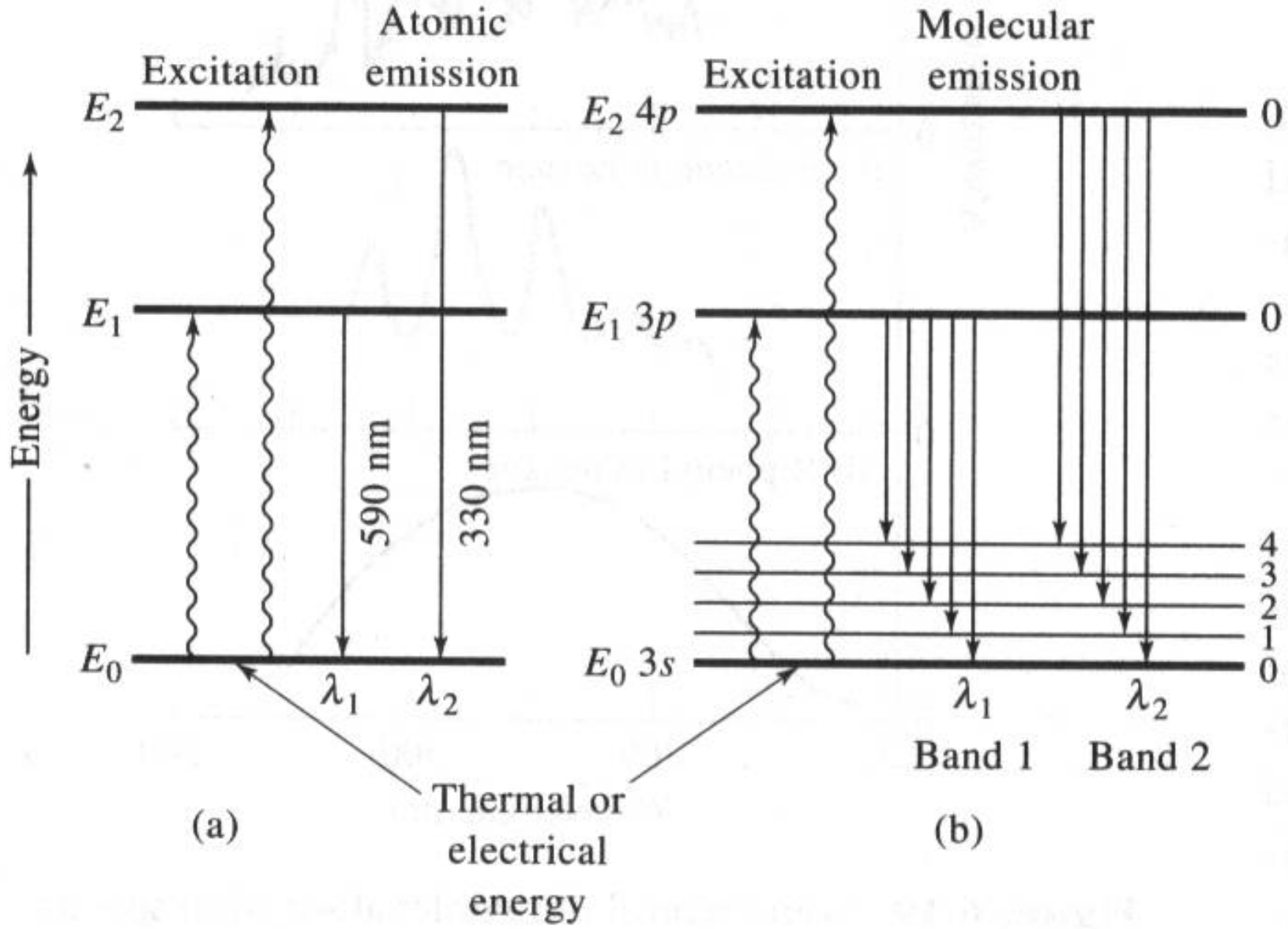


Fig. 16.2. Electromagnetic spectrum.

TYPES OF OPTICAL INSTRUMENTS

- Spectroscope: uses human eye as a detector
- Spectrograph: photographic emulsion used as detector
- Spectrometer: has photoelectric readout
    1. Monochromator: one exit slit, Greek for "one color"
    2. Polychromator: multiple exit slits
- Spectrophotometer:electronics takes ratio of two beams (%T), may be at same or different wavelengths, may be single beam or double beam

Atomic versus Molecular Transitions



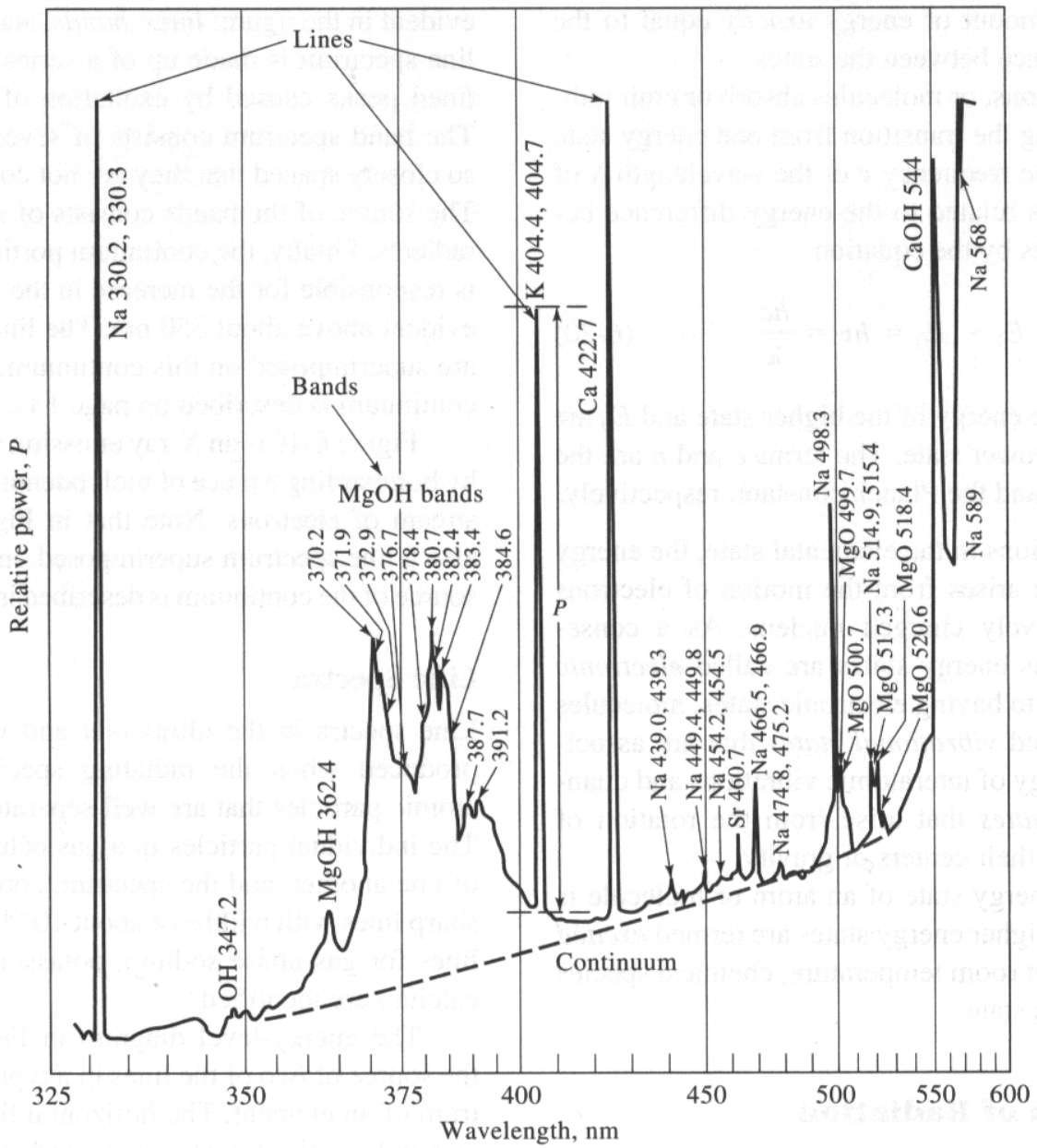


Figure 6-15 Emission spectrum of a brine obtained with an oxyhydrogen flame. *(F. Hermann and C. T. J. Alkemade,* Chemical Analysis by Flame Photometry, *2nd ed., p. 484. New York: Interscience, 1963. With permission.)*

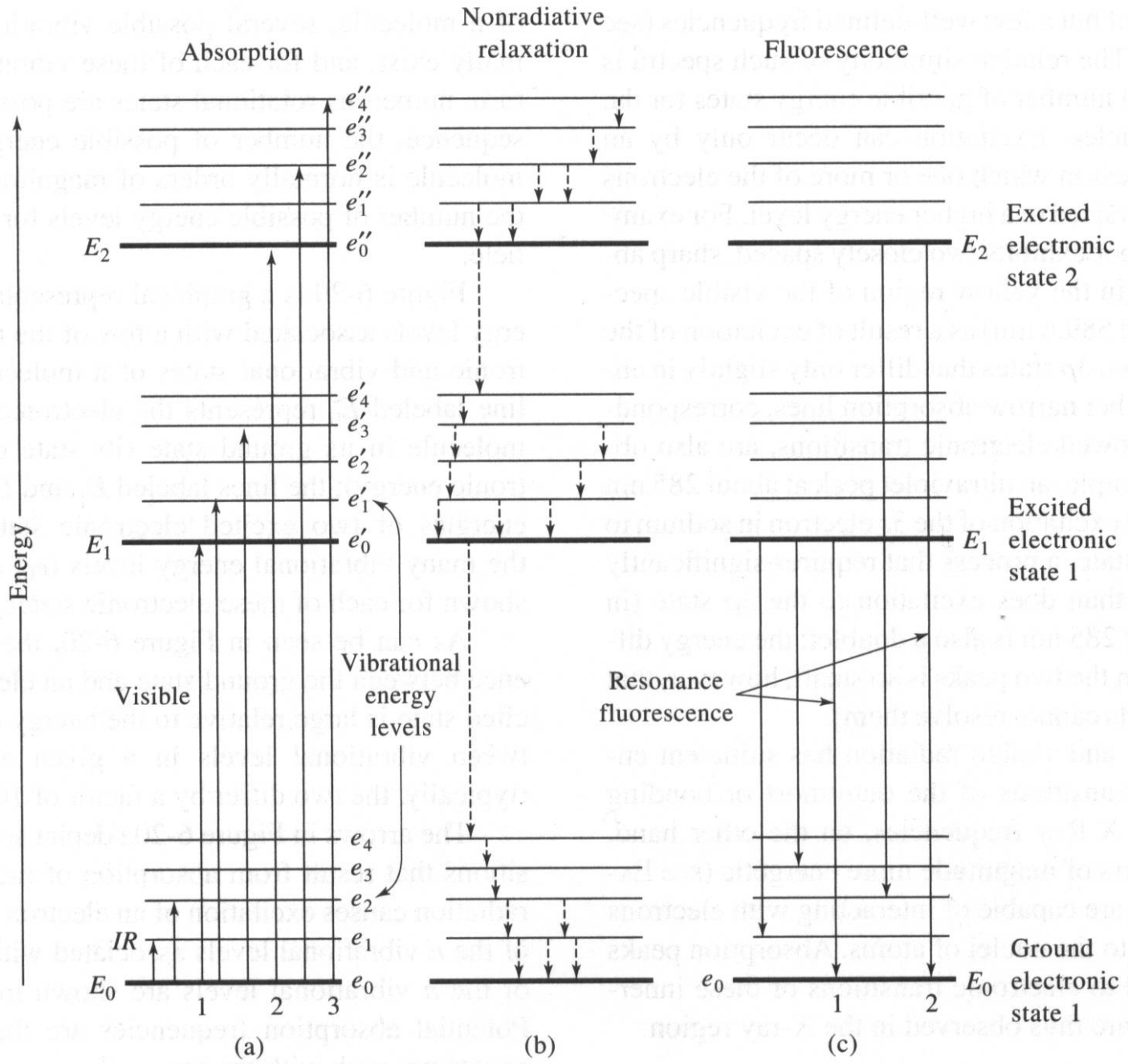
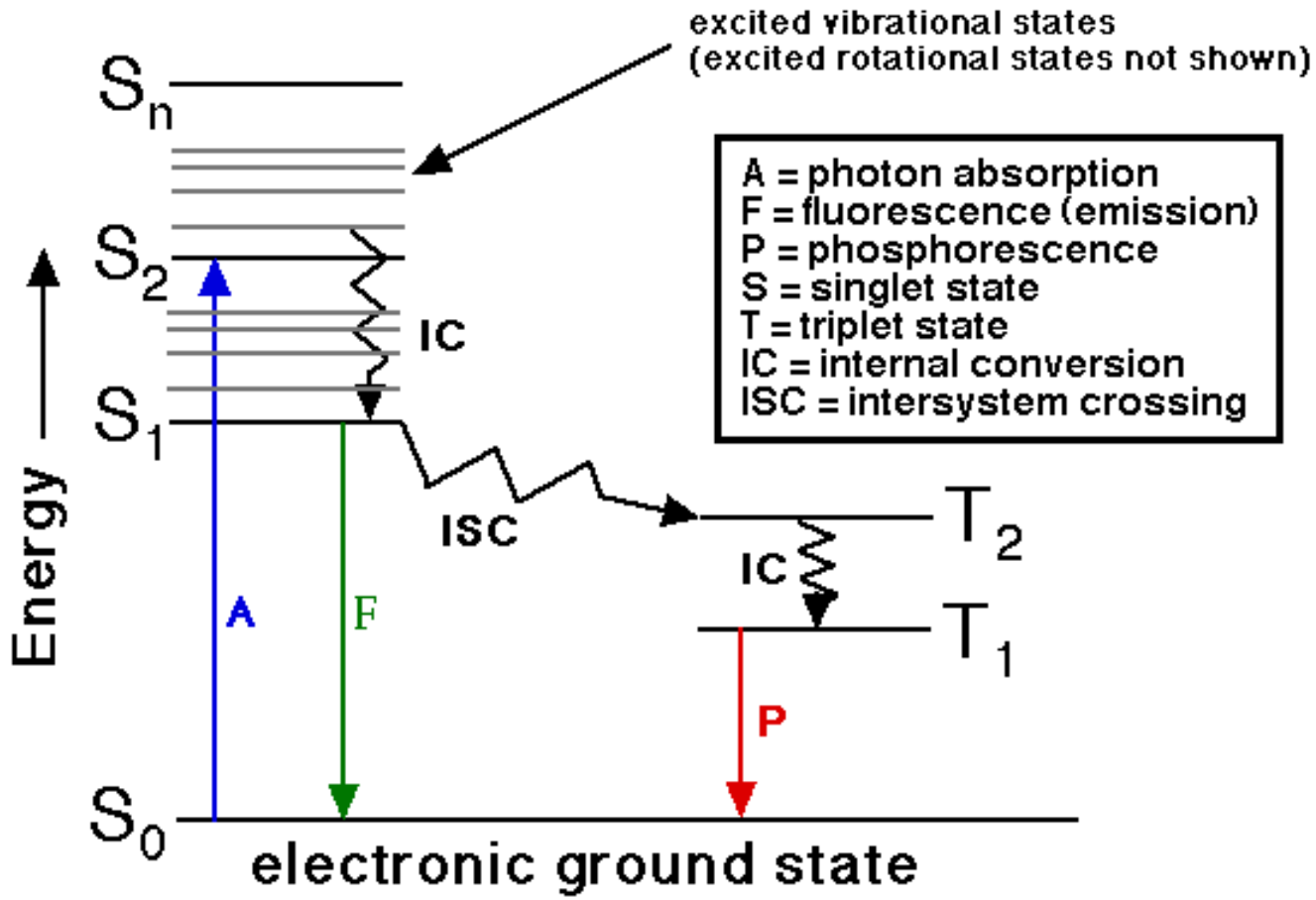


Figure 6-20 Partial energy-level diagrams for a fluorescent organic molecule.

Various Relaxation (de-excitation) Modes

- **Relaxation by emission of the same wavelength**
  - **atomic**
  - **refer back to the emission spectra of brine**
- **Non-radiative**
  - **molecular usually**
- **Fluorescence**
  - **molecular usually**
- **Phosphorescence**
  - **molecular usuall**

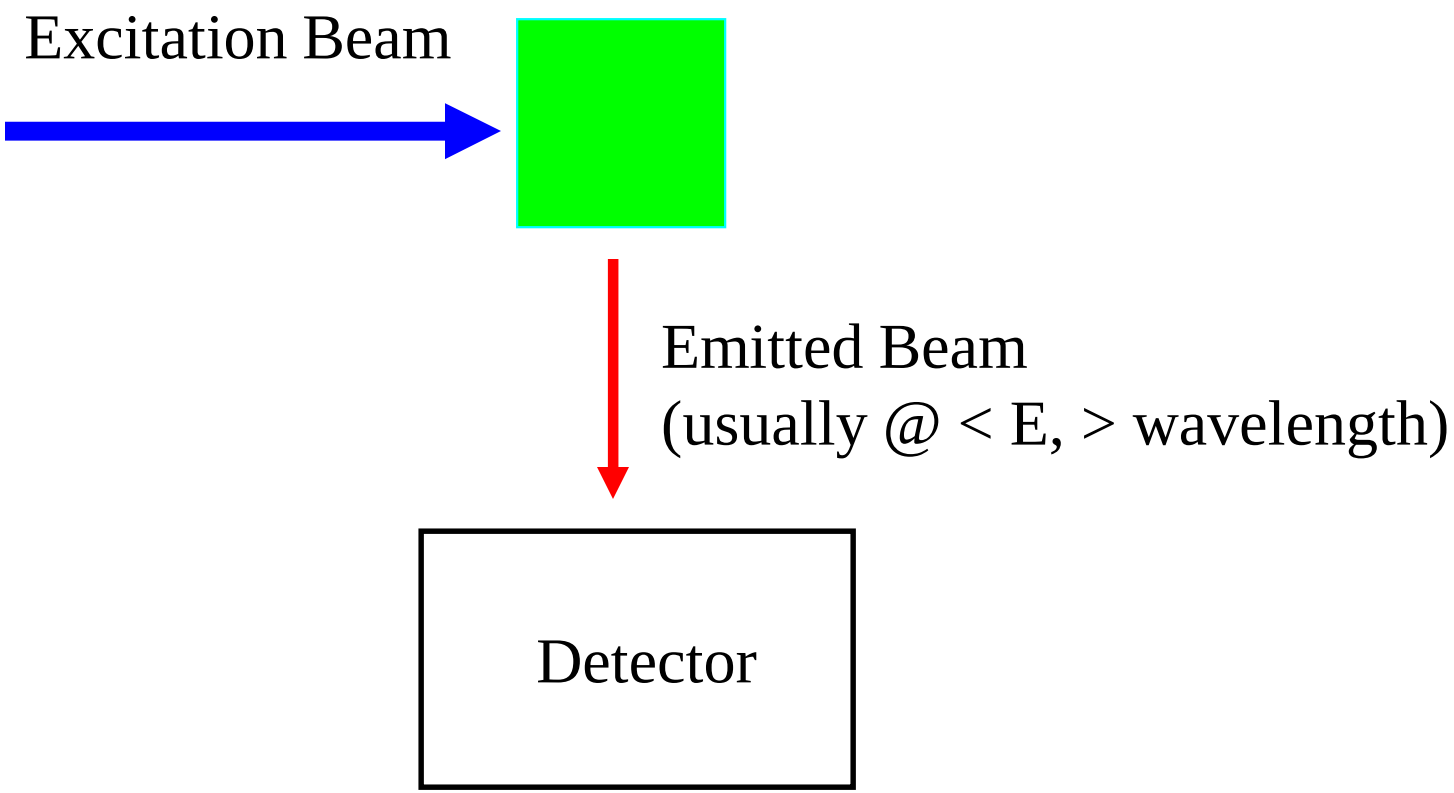

excited vibrational states
(excited rotational states not shown)
S_n
S_2
S_1
S_0
IC
ISC
IC
T_2
T_1
A
F
P
Energy
electronic ground state
A = photon absorption
F = fluorescence (emission)
P = phosphorescence
S = singlet state
T = triplet state
IC = internal conversion
ISC = intersystem crossing

Phosphorescence

- **A molecule is excited by EM radiation**
- **A transition takes place from some state (usually ground) to an excited state**
- **Relaxation back to that ground state takes place over relatively long periods**
  - **The excited state is actually a metastable state, meaning that it is more stable than an excited state but still less stable (thermodynamically) than the ground state**
  - **E-5 seconds to minutes or hours after excitation**

- **Chemiluminescence**
  - **light sticks, etc……**

Fluorescence and Phosphorescence Instruments…..



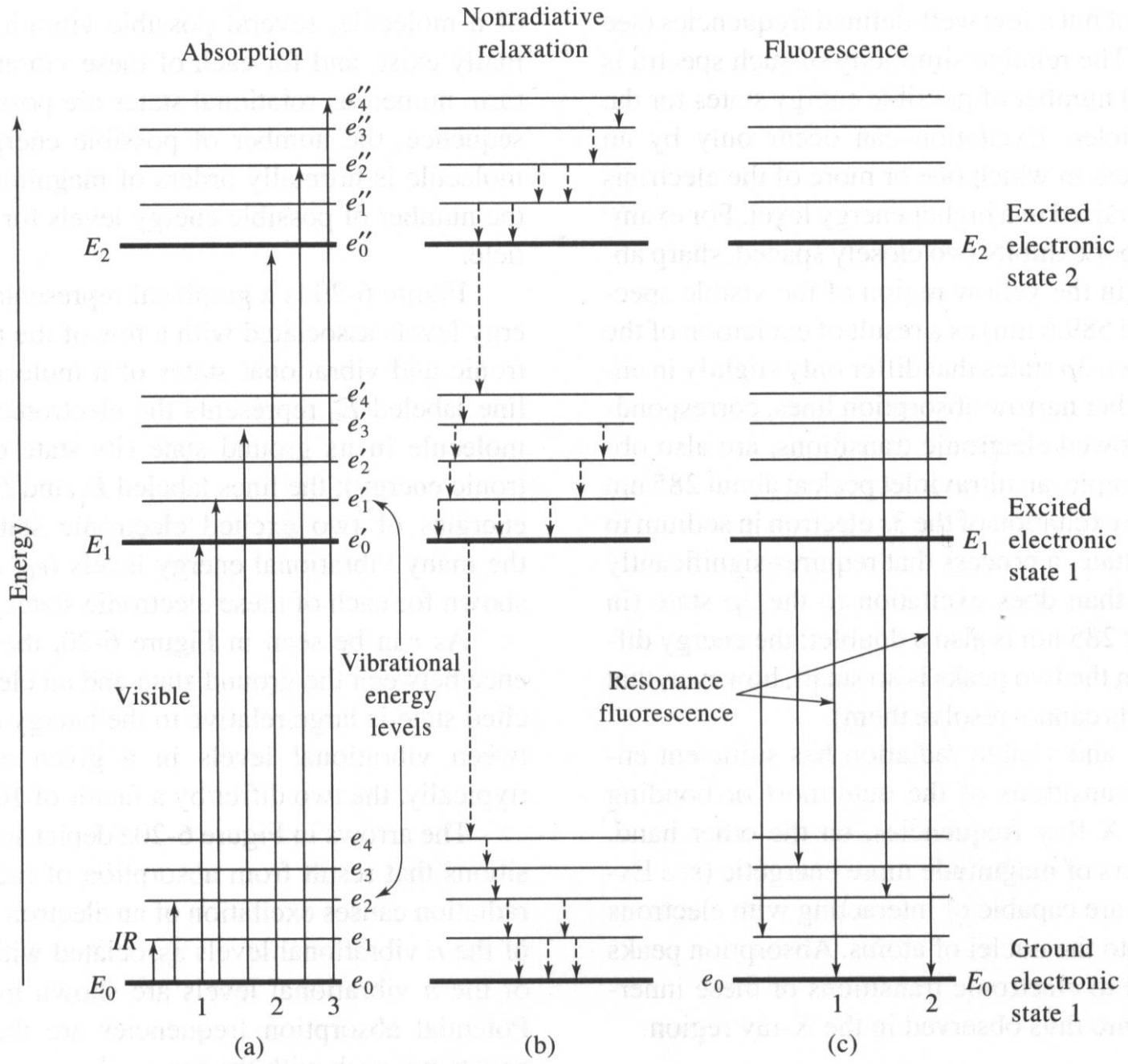
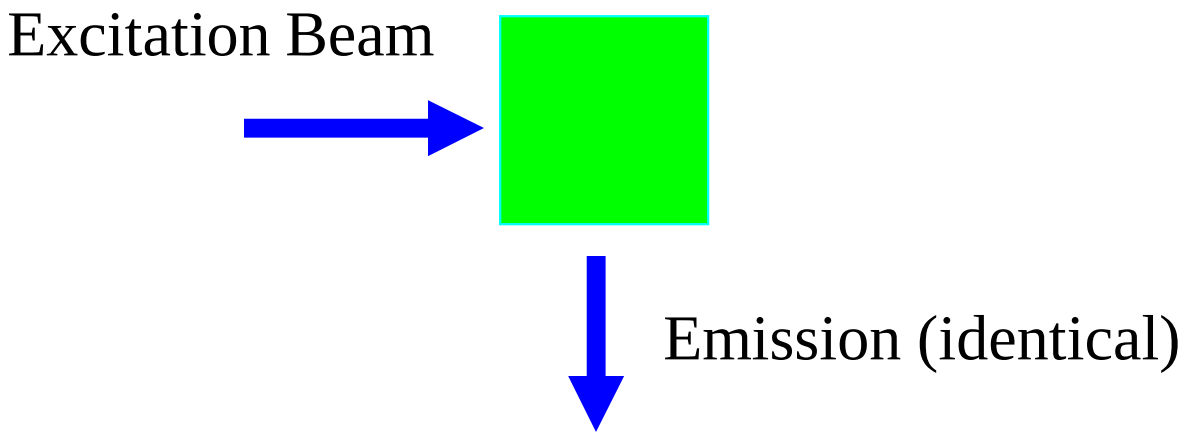


Figure 6-20 Partial energy-level diagrams for a fluorescent organic molecule.

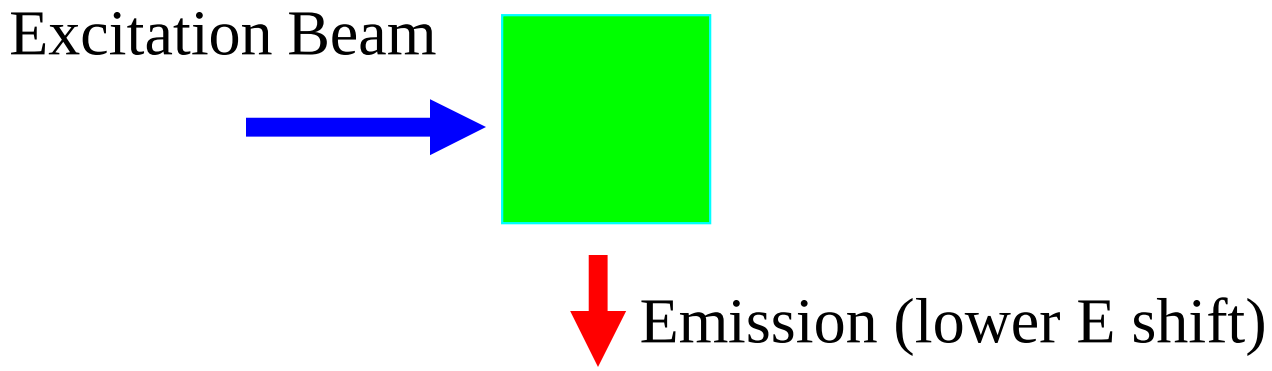
Fluorescence

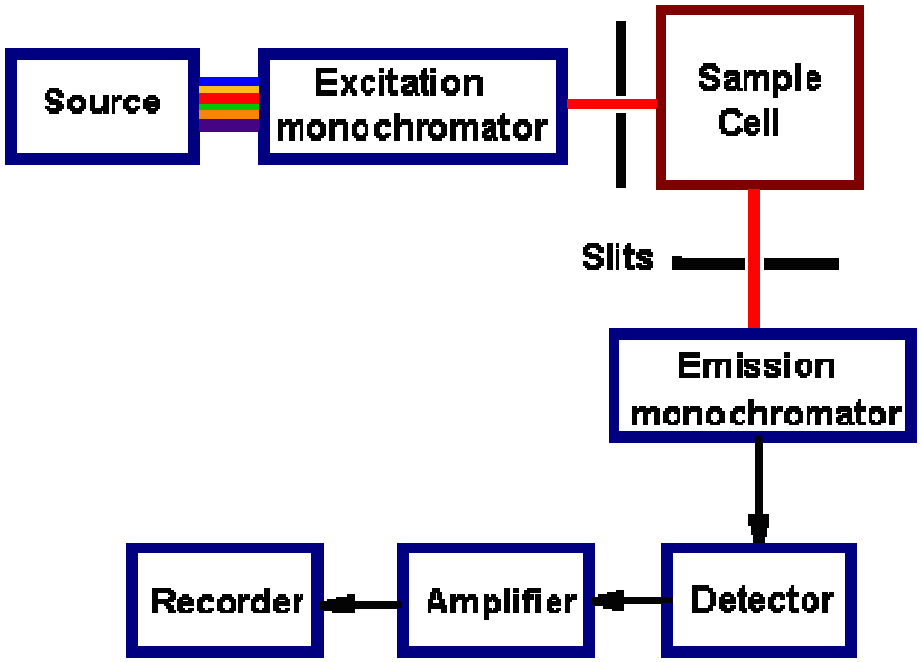
- **Resonance Fluorescence**
  - **Usually atomic**
  - **Emitted light has same E as excitation light**
  - **Simpler, atomic systems with fewer energy states (vs molecules) undergo resonance fluorescence**
- **Not as widely used in analytical chemistry as non-resonance fluorescence**
  - **Hg analysis is one example**

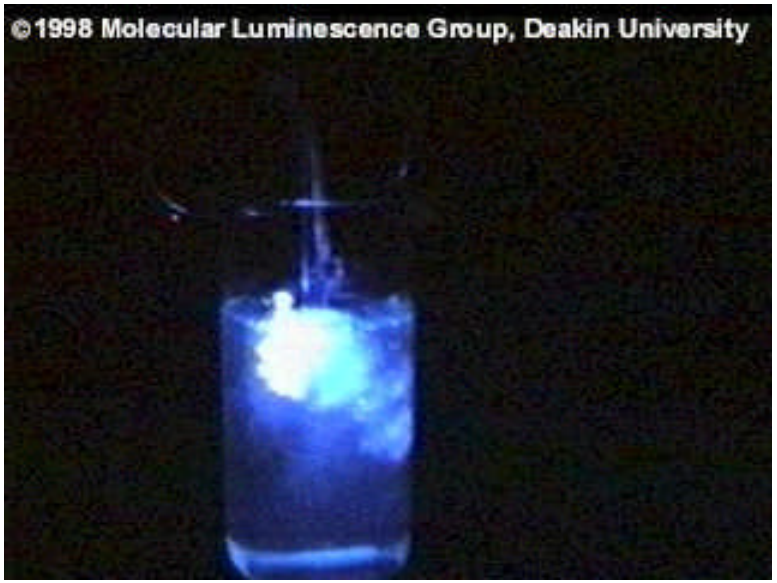


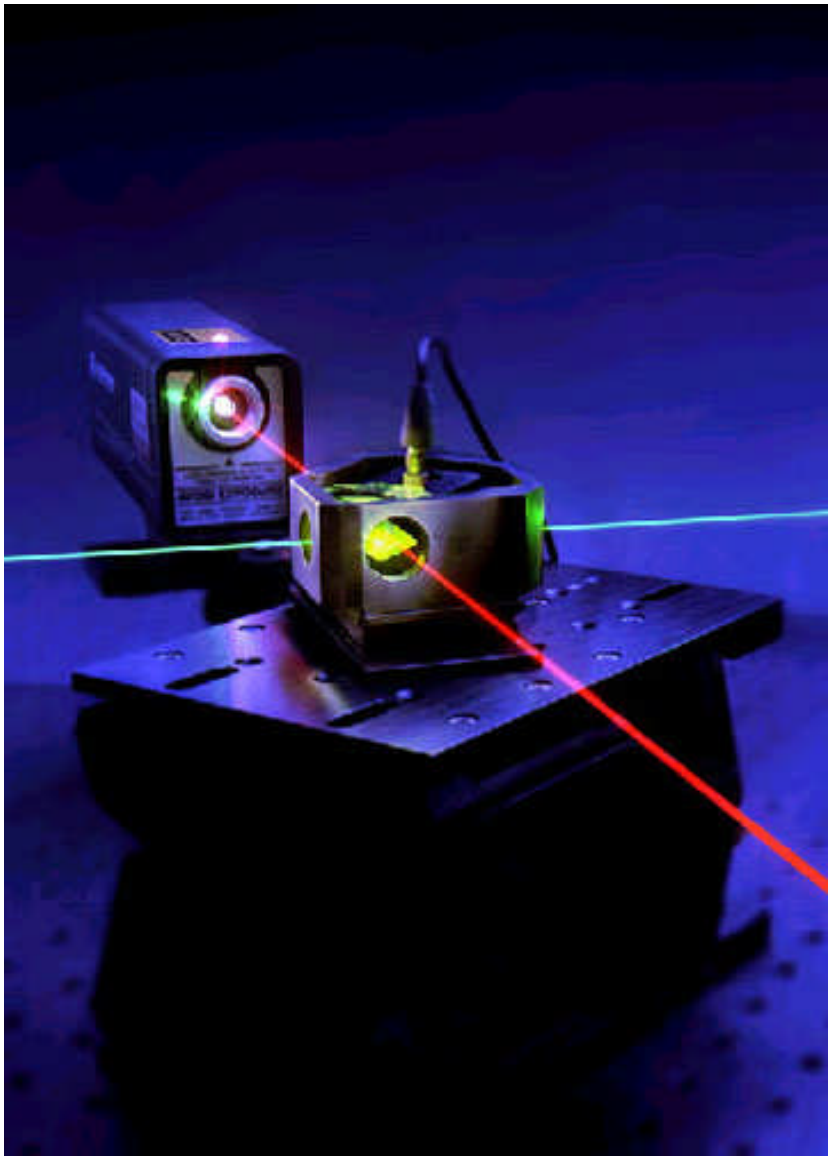
Non-resonance Fluorescence

- **Typical of molecular fluorescence**
- **Large number of excited states**
  - **rotational**
  - **vibrational**
  - **etc..**
- **Molecules relax by ‘stepping’ from one state to another**
- **Resulting emitted light “shifts” to lower energies**
  - **longer wavelengths**
  - **Stokes Shift**




Source
Excitation monochromator
Sample Cell
Slits
Emission monochromator
Recorder
Amplifier
Detector

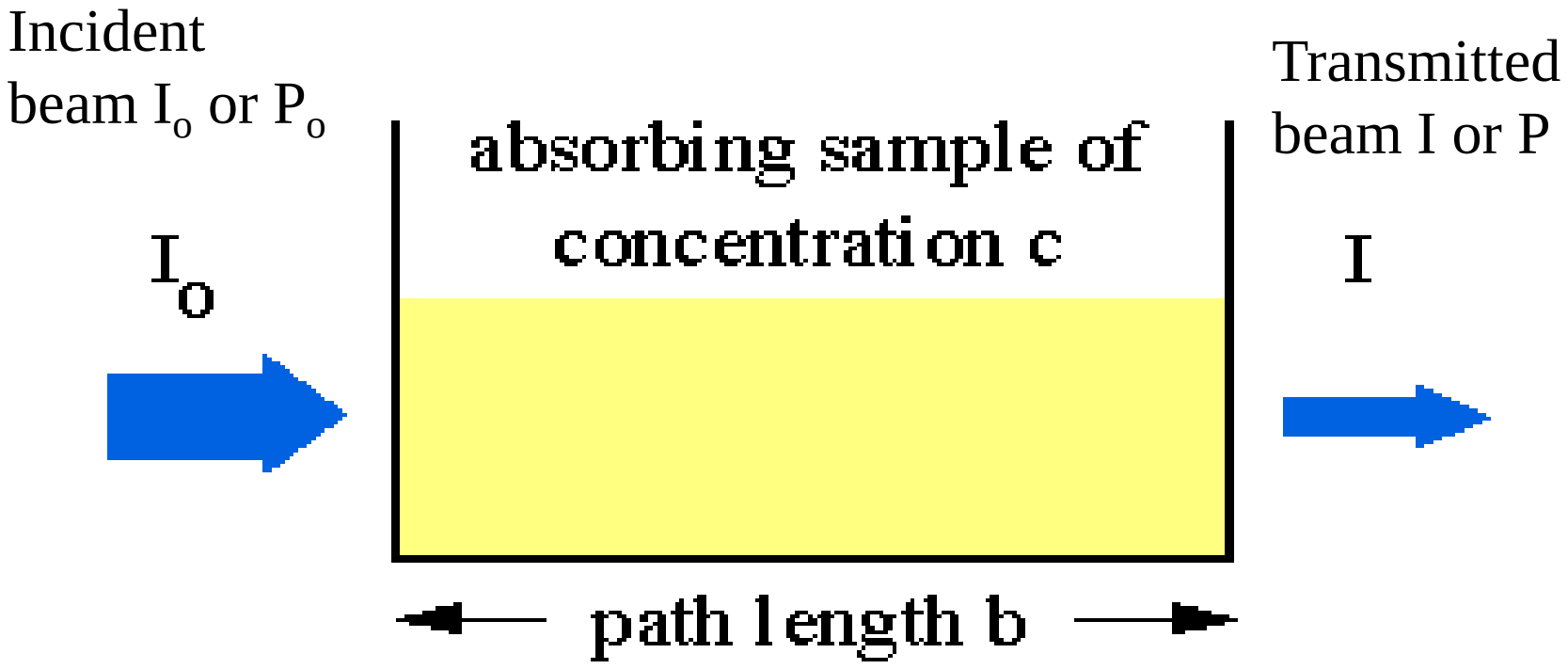

©1998 Molecular Luminescence Group, Deakin University



Some Basic Concepts…...

- **Why are even "line" spectra not truly lines?**
  - **They are really broad distributions that are just over a range of about 1 nm or less.**
- **Some of this (especially with respect to lines) is due to the uncertainty principle!**
- **Remember, than an atom or molecule does not go from one distinct energy state to another**
  - **it goes from some "high probability' state to another "high probability" state**
  - **we can never know the exact energy**
  - **limited by $h/\Delta t$**
  - **Heisenberg's Uncertainty Principle in action!**

Absorption of Light by a Sample in UV-Vis and IR Spectroscopy



Quantitative Relationships for Optical Spectroscopy

- **Beer's Law (you should know)**
- **Definitions: P_0 = incident light intensity, P = transmitted light intensity**
- **Transmittance:**

$$T = \frac{I}{I_o} \qquad \%T = 100 \text{ x } T$$

- **Absorbance**

– A = abc "c" in gm/l

– A= εbc "c" in moles/l

• bC = cm*mol/1000 cm3 = mol/1000 cm^2

• a units cm2/gm ε unit = cm^2/mol

• (old literature often dm^2/gm)

$$A = -\log T = \log\left(\frac{I_o}{I}\right) = \varepsilon bc$$

Limitations of the Beer-Lambert law

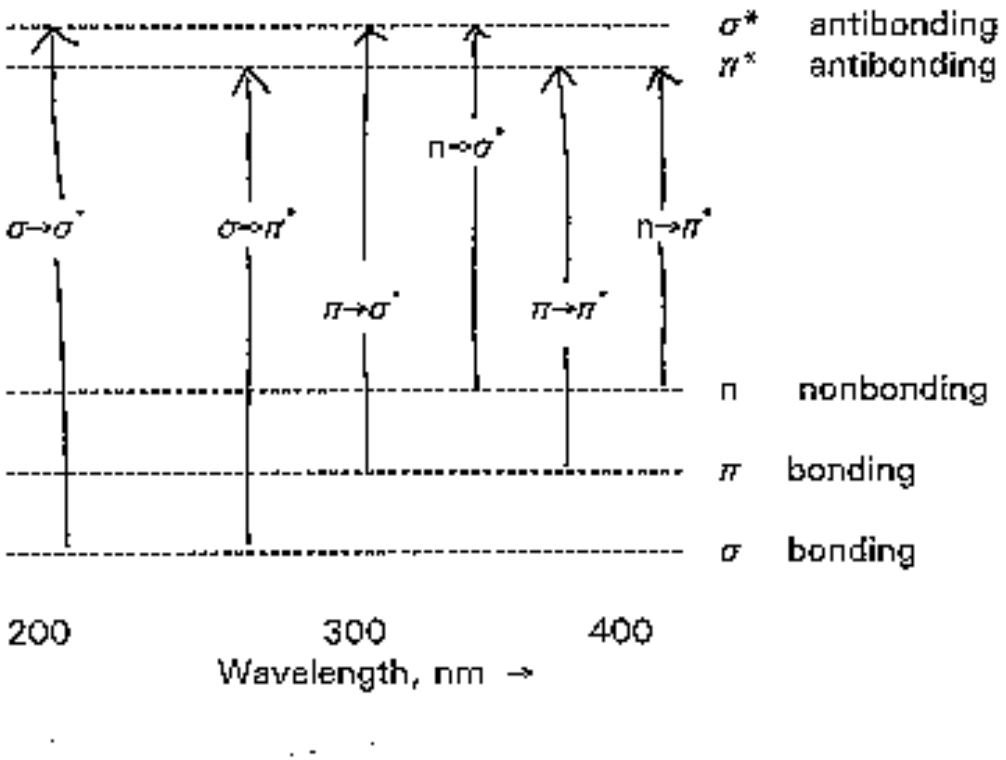
The linearity of the Beer-Lambert law is limited by chemical and instrumental factors. Causes of nonlinearity include:

- deviations in absorptivity coefficients at high concentrations (>0.01M) due to electrostatic interactions between molecules in close proximity
- Interaction with solvent: hydrogen bonding
- scattering of light due to particulates in the sample
- fluoresecence or phosphorescence- a positive deviation in % T and negative deviation for A
- changes in refractive index at high analyte concentration
- shifts in chemical equilibria as a function of concentration
- non-monochromatic radiation, deviations can be minimized by using a relatively flat part of the absorption spectrum such as the maximum of an absorption band
- stray light

Chromophores and Auxophores

Group	ν ($10\ cm^{-1}$)	λ (nm)	ε ($L\ mol^{-1}cm^{-1}$)
C=C	55	182	250
	57.3	174	16,000
	58.6	170	16,500
	62	162	10,000
	58	172	2,500
C=O	34	295	10
	54	185	Strong
C=S	22	460	Weak
$-NO_2$	36	277	10
	47.5	210	10,000
-N=N-	28.8	347	15
C6H5	>38.5	<260	Strong
	39	255	200
	50	200	6,300

Energy Levels in UV-Vis Molecular Spectroscopy



Electronic Transitions in UV Region

Wavelength	**Functional Group**	**Transition**
177 nm	-C=C-	pi -----> pi*
178	C≡C	p i-----> pi*
280	-C=O	n ----->sigma *, n-----> pi *
204	-COOH	n -----> pi *
214	-CNO (amide)	n -----> pi *
339	-N=N-	n -----> pi *
280	$-NO_2$	n -----> pi *
270	$-NO_3$	n -----> pi *

Chromophores and auxophores

Group	ν (10 cm^{-1})	λ (nm)	ε (L $mol^{-1}cm^{-1}$)
-Cl	58	172	-
-Br	49	204	1800
-I	38.8 49.7	258 201	- 1200
-OH	55 67	183 150	200 1900
-SH	43	232	160
-NH2	46.5 52.5	215 190	580 3200
-S-	44 46.5 49.3	228 215 203	620 700 2300

These groups absorb in the UV or visible regions.

Table 16.2

Electronic Absorption Bands for Representative Chromophores[a]

Chromophore	System	λ_{max}	ϵ_{max}
Amine	$-NH_2$	195	2,800
Ethylene	$-C=C-$	190	8,000
		195	1,000
Ketone	$C=O$	270–285	18–30
Aldehyde	$-CHO$	210	Strong
		280–300	11–18
Nitro	$-NO_2$	210	Strong
Nitrite	$-ONO$	220–230	1,000–2,000
		300–400	10
Azo	$-N=N-$	285–400	3–25
Benzene		184	46,700
		202	6,900
		255	170
Naphthalene		220	112,000
		275	5,600
		312	175
Anthracene		252	199,000
		375	7,900

[a] From M. M. Willard, L. L. Merritt, and J. A. Dean, *Instrumental Methods of Analysis*, 4th ed. Copyright © 1948, 1951, 1958, 1965, by Litton Educational Publishing, Inc., by permission of Van Nostrand Reinhold Company.

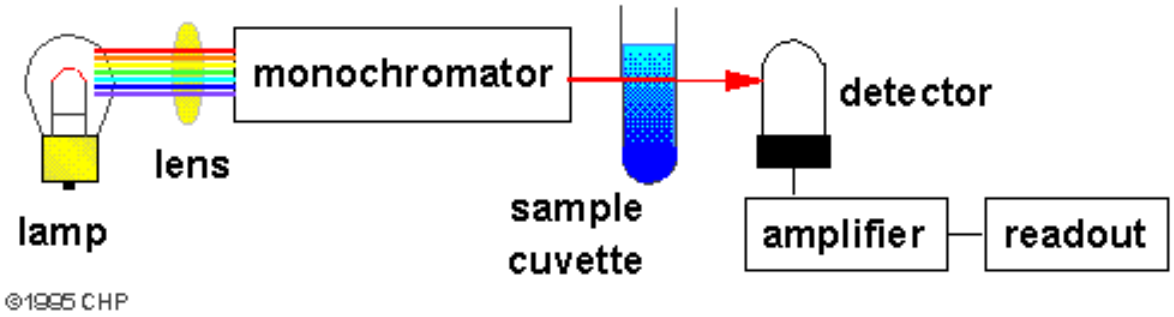
Absorption Characteristics of Aromatic Compounds

Compound		E_2 Band		B Band	
		λ_{max} (nm)	ε_{max}	λ_{max}(nm)	ε_{max}
Benzene	C_6H_6	204	7,900	256	200
Toluene	$C_6H_5CH_3$	207	7,000	261	300
M-Xylene	$C_6H_4(CH_3)_2$	------	------	263	300
Chlorobenzene	C_6H_5Cl	210	7,600	265	240
Phenol	C_6H_5OH	211	6,200	270	1,450
Phenolate ion	$C_6H_5O^-$	235	9,400	287	2,600
Aniline	$C_6H_5NH_2$	230	8,600	280	1,430
Anilinium ion	$C_6H_5NH_3^+$	203	7,500	254	160
Thiophenol	C_6H_5SH	236	10,000	269	700
Naphthalene	$C_{10}H_8$	286	9,300	312	289
Styrene	$C_6H_5CH{=}{=}CH_2$	244	12,000	282	450

Effect of Ligands on Absorption Maxima Associated with d→d Transitions

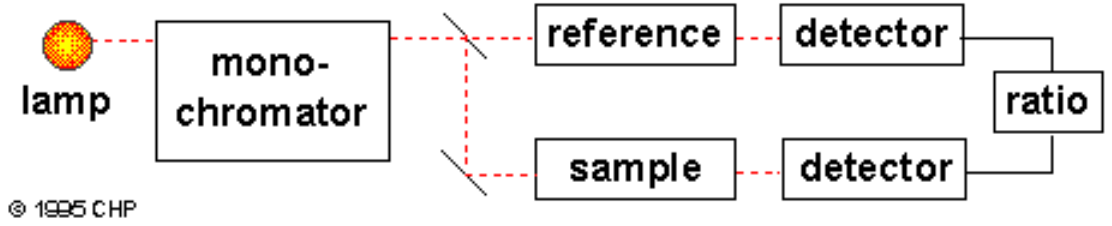
Central Ion	**λmax(nm) for the Indicated Ligands**				
	Increasing Ligand Field Strength →				
	$6Cl^-$	$6H_2O$	$6NH_3$	3en	$6CN^-$
Cr(III)	736	573	462	456	380
Co(III)	----	538	534	428	294
Co(II)	----	1345	980	909	-----
Ni(II)	1370	1279	925	863	-----
Cu(II)	----	794	663	610	-----

PMT: Photomultiplier Tubes



Single Beam

Double Beam



Absorption Measurements

- Procedure

  1) Set 0 % T to record dark current---- block light path

  2) Set 100 % T --- record pure solvent

  3) Measure sample signal --- determine T or % T or A

- Problems

  1) Scattering

  2) Reflection

  3) Inhomogeneities

  4) Stray light

Theory of Vibrational Spectroscopy

The model of molecular vibrations is given by the **anharmonic oscillator**. The potential energy is then calculated by the Morse equation, and is asymmetric. The energy levels are no longer equally spaced, and are given by:

$$E_v=(v + ½) h \bullet \nu - (v + ½)^2 x_{Gl} h \bullet \nu$$

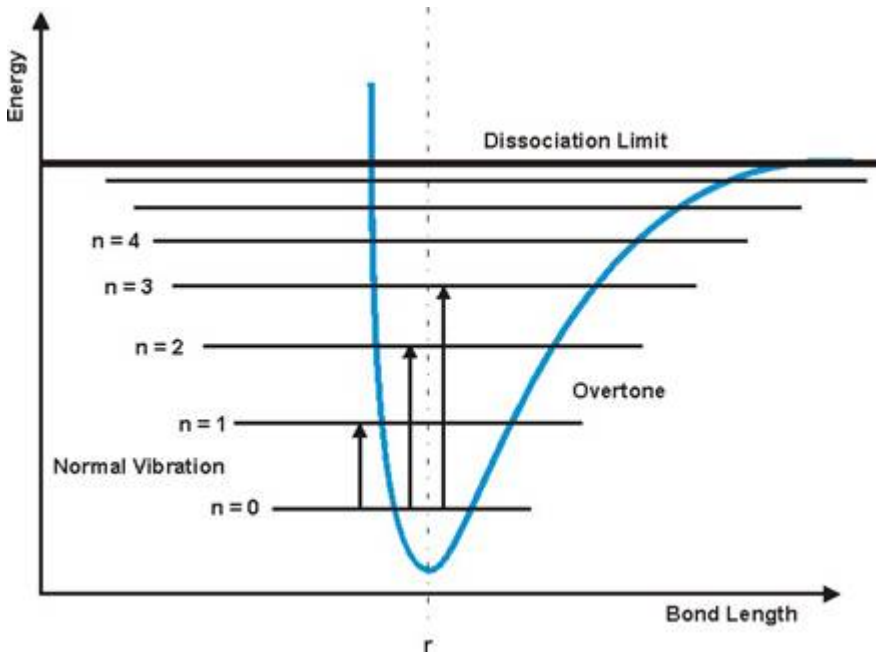
where x_{Gl} is the anharmonicity constant.

The anharmonic oscillator model allows for two important effects:

1) As two atoms approach each other, the repulsion will increase very rapidly.

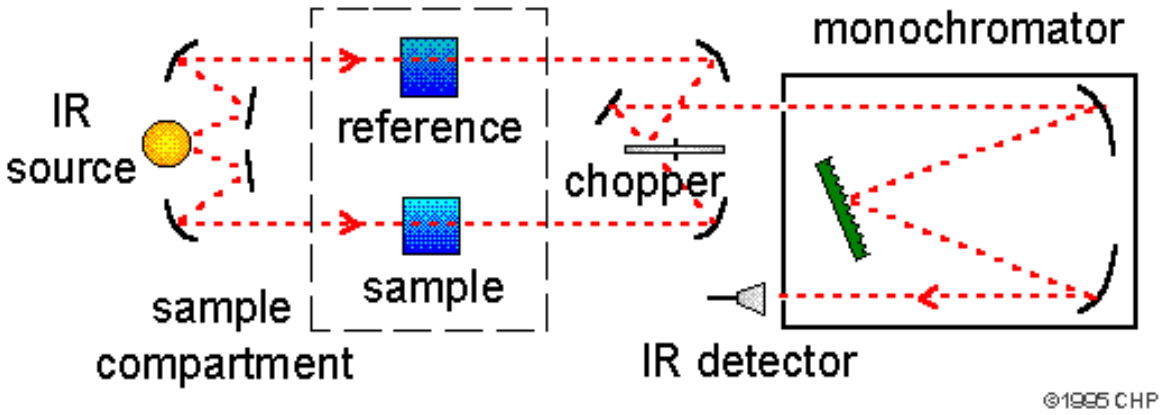
2) If a sufficiently large vibrational energy is reached the molecule will dissociate (break apart). This is called the dissociation energy.

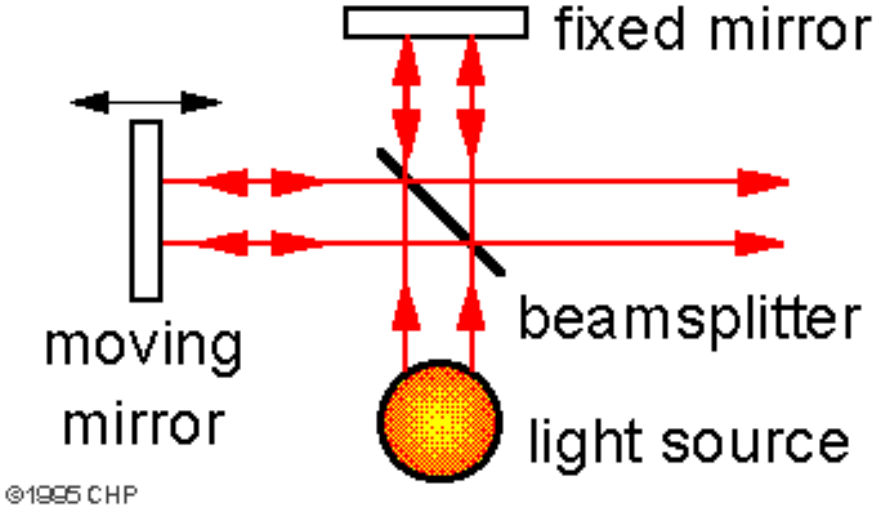
In the case of the anharmonic oscillator, the vibrational transitions no longer only obey the selection rule $\Delta v = \pm 1$. This type of vibrational transition is called **fundamental vibration**. Vibrational transitions with $\Delta v = \pm 1, \pm 2, \pm 3, ...$ are also possible, and are termed **overtones**.



Potential energy curve for an anharmonic oscillator

Infrared Spectrometer Designs





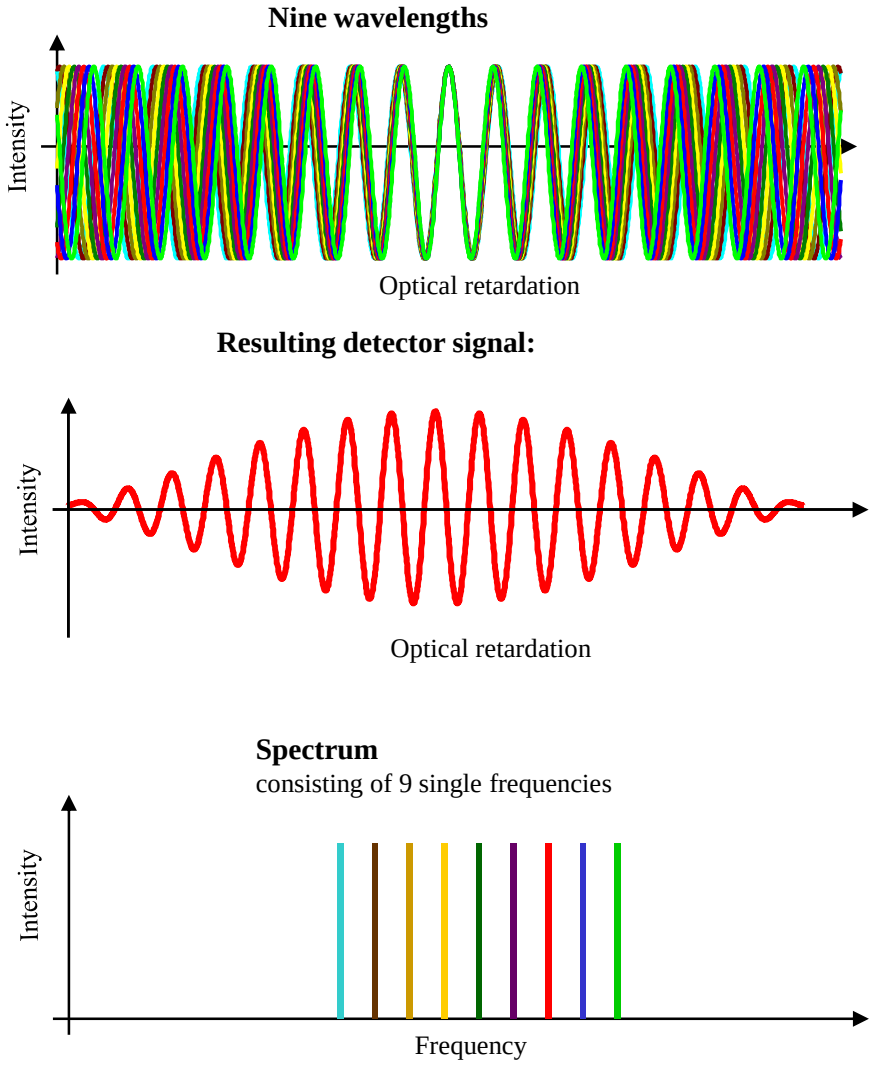
Dispersive IR (top)
Michelson Interferometer
For FTIR (bottom)

Origin of the interferogram

Since spectrometers are equipped with a polychromatic light source (i.e. many wavelengths) the interference already mentioned occurs at **each** wavelength, as shown in the upper figure on the right. The interference patterns produced by each wavelength are summed to get the resulting interferogram, as shown in the second figure.

At the zero path difference of the moving mirror ($\Delta x=0$) both paths all wavelengths have a phase difference of zero, and therefore undergo constructive interference. The intensity is therefore a maximum value. As the optical retardation increases, each wavelength undergoes constructive and destructive interference at different mirror positions.

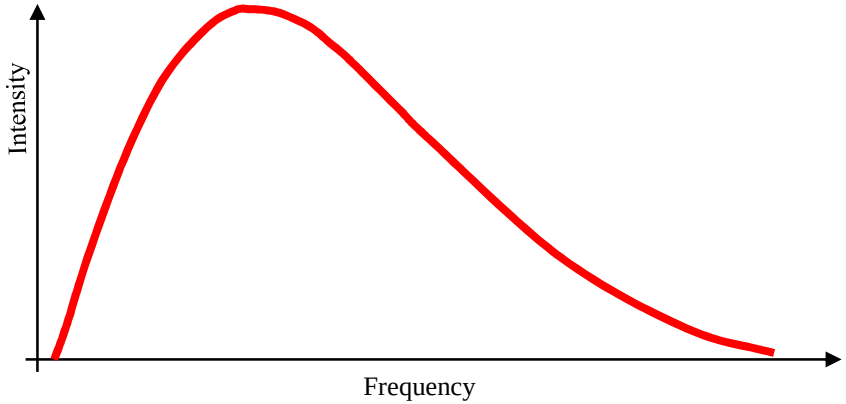
The third figure shows the intensity as a function of frequency (I.e. the spectrum), and we now have nine lines.



Origin of the interferogram

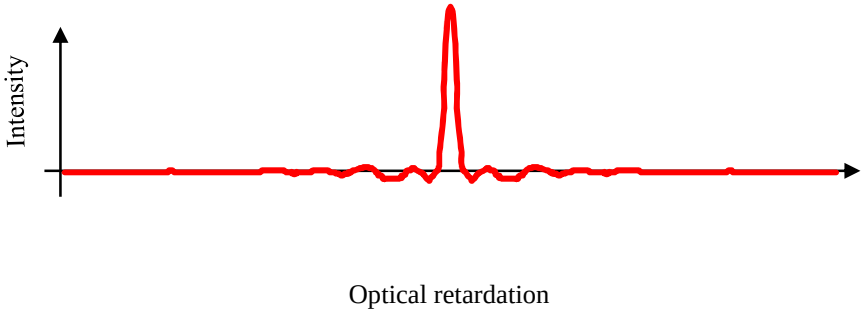
Spectrometers are equipped with a broadband light source, which yields a continuous, infinite number, of wavelengths, as shown in the figure on the left. The interferogram is the continuous sum, i.e. the integral, of all the interference patterns produced by each wavelength. This results in the intensity curve as function of the optical retardation shown in the second figure. At the zero path difference of the interferometer ($\Delta x=0$) all wavelengths undergo constructive interference and sum to a maximum signal. As the optical retardation increases different wavelengths undergo constructive and destructive interference at different points, and the intensity therefore changes with retardation. For a broadband source, however, all the interference patterns will never simultaneously be in phase except at the point of zero path difference, and the maximum signal occurs only at this point. This maximum in the signal is referred to as the "centerburst"

IR-source



Frequency distribution of a black body source

Resulting detector signal



Resulting interferogram (detector signal after modulation by a Michelson interferometer)

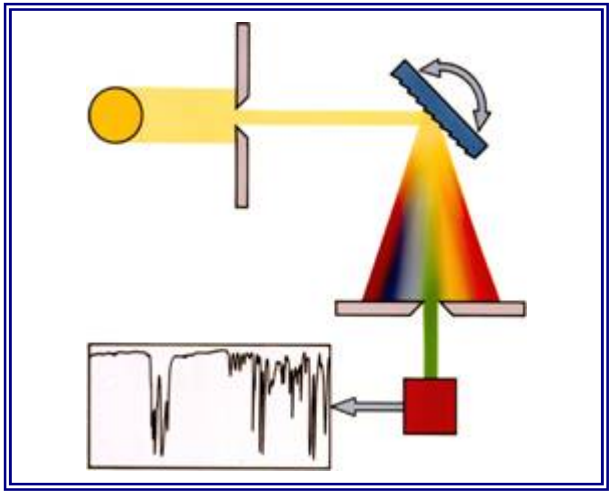
Advantages of FTIR spectroscopy

1) The sampling interval of the interferogram, δx, is the distance between zero-crossings of the HeNe laser interferogram, and is therefore precisely determined by the laser wavelength. Since the point spacing in the resulting spectrum, δ , is inversely proportional to δx, FT-IR spectrometers have an intrinsically highly precise wavenumber scale (typically a few hundredths of a wavenumber). This advantage of FT spectrometers is known as **CONNES' advantage**.

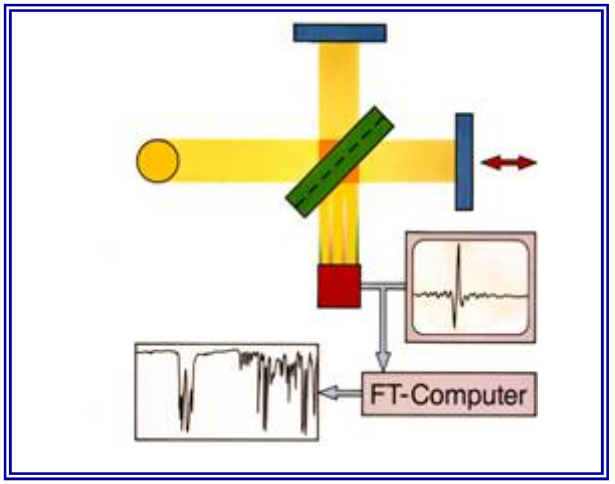
2) The **JAQUINOT advantage** arises from the fact that the circular apertures used in FTIR spectrometers has a larger area than the slits used in grating spectrometers, thus enabling higher throughput of radiation.

3) In grating spectrometers the spectrum S(ν) is measured directly by recording the intensity at successive, narrow, wavelength ranges. In FT-IR spectrometers all wavelengths from the IR source impinge simultaneously on the detector. This leads to the multiplex, or **FELLGETT'S, advantage**.

The combination of the Jaquinot and Fellgett advantages means that the signal-to-noise ratio of an FT spectrometer can be more than 10 times that of a dispersive spectrometer.



Dispersive IR spectrometer



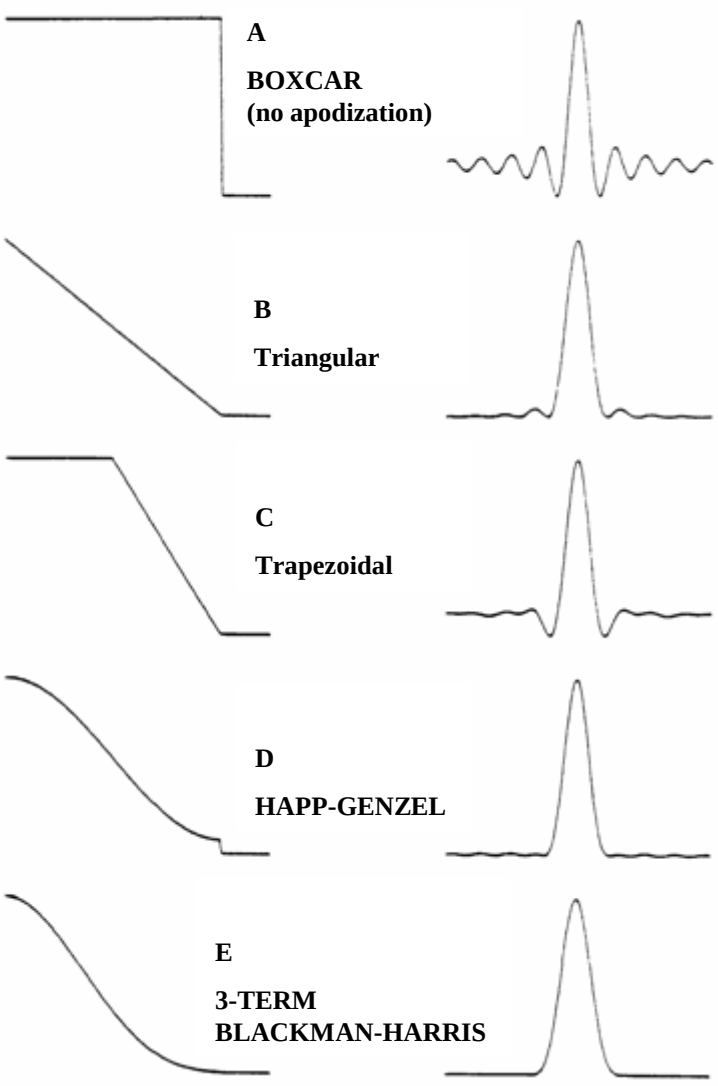
FT-IR spectrometer

Apodization

In a real measurement, the interferogram can only be measured for a finite distance of mirror travel. The resulting interferogram can be thought of as an infinite length interferogram multiplied by a boxcar function that is equal to 1 in the range of measurement and 0 elsewhere. This sudden truncation of the interferogram leads to a sinc( ) (i.e. sin( )/) instrumental lineshape. For an infinitely narrow spectral line, the peak shape is shown at the top of the figure on the right. The oscillations around the base of the peak are referred to as "ringing", or "leakage".

The solution to the leakage problem is to truncate the interferogram less abruptly. This can be achieved by multiplying the interferogram by a function that is 1 at the centerburst and close to 0 at the end of the interferogram. This is called apodization, and the simplest such function is a ramp, or "triangular apodization".

The choice of a particular apodization function depends on the objectives of the measurement. If the maximum resolution of 0.61/*L is required*, then boxcar apodization (i.e no apodization) is used. If a resolution loss of 50% (compared to the maximum resolution of 0.61/*L*) can be tolerated, the HAPP-GENZEL or, even better, 3-Term BLACKMAN-HARRIS function is recommended.



Transmission spectrum

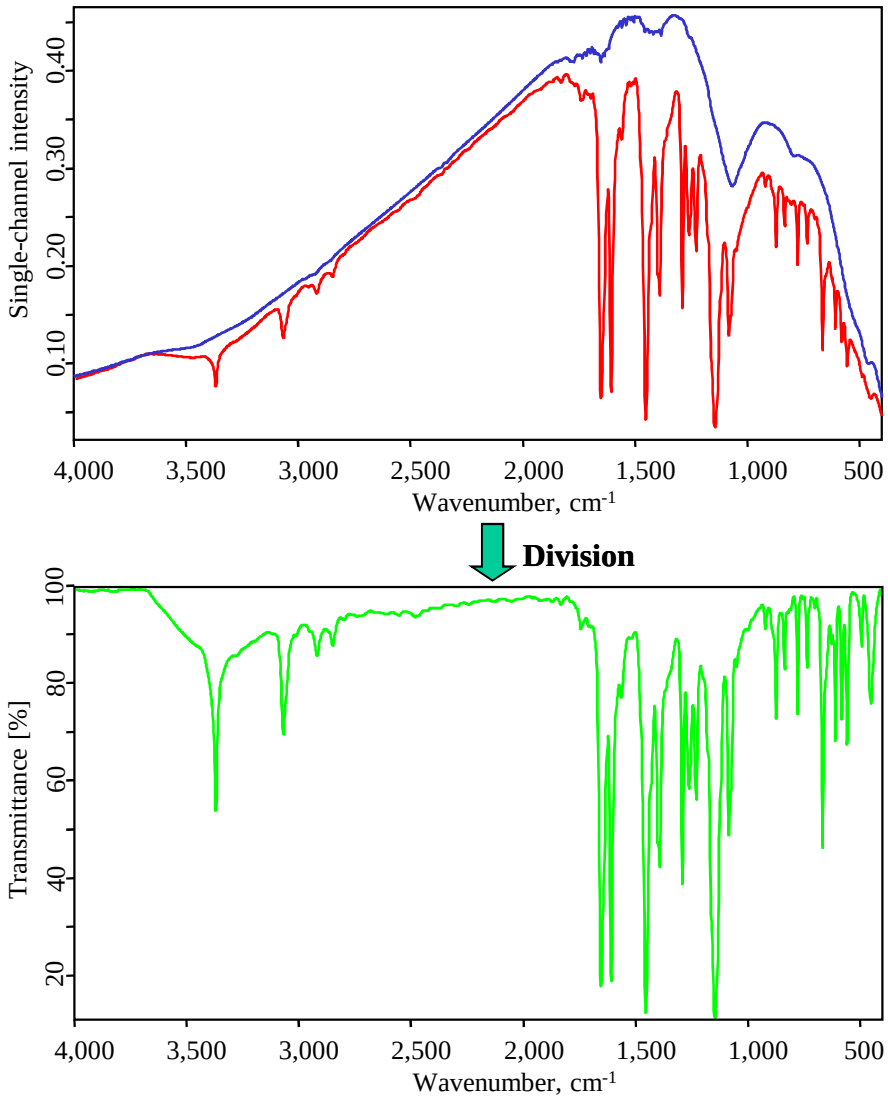
To calculate the transmission spectrum the following steps need to be performed:

- an interferogram measured without any sample in the optical path is Fourier transformed. This results in the so-called single-channel reference spectrum (ν).

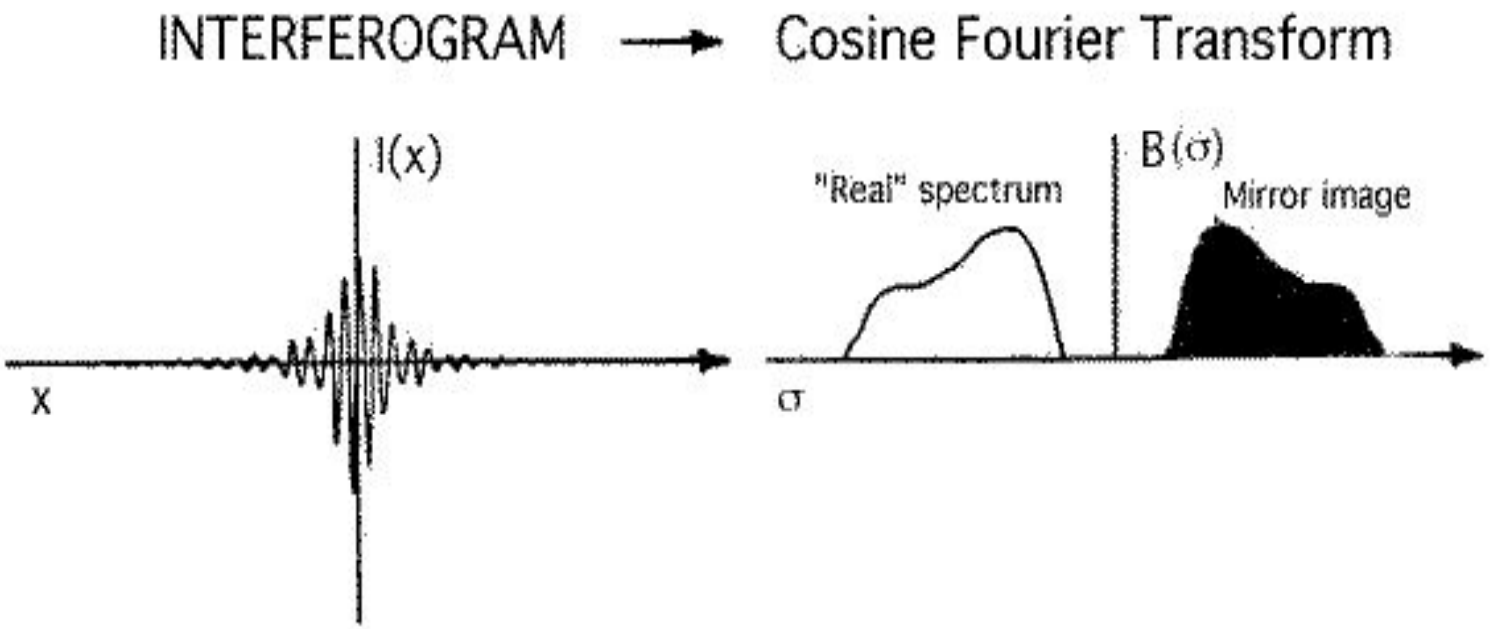
- A second interferogram, measured with the sample in the optical path, is Fourier transformed. This results in the single-channel sample spectrum S(ν). S(ν) looks similar to the reference spectrum, but shows less intensity at those wavenumbers where the sample absorbs radiation.

- The final transmission spectrum T(ν) is obtained by dividing the sample spectrum by the reference spectrum:

T(ν) = S(ν)/R(ν)

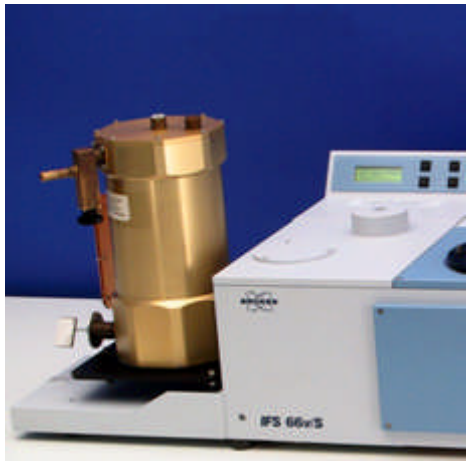


Fourier Transform



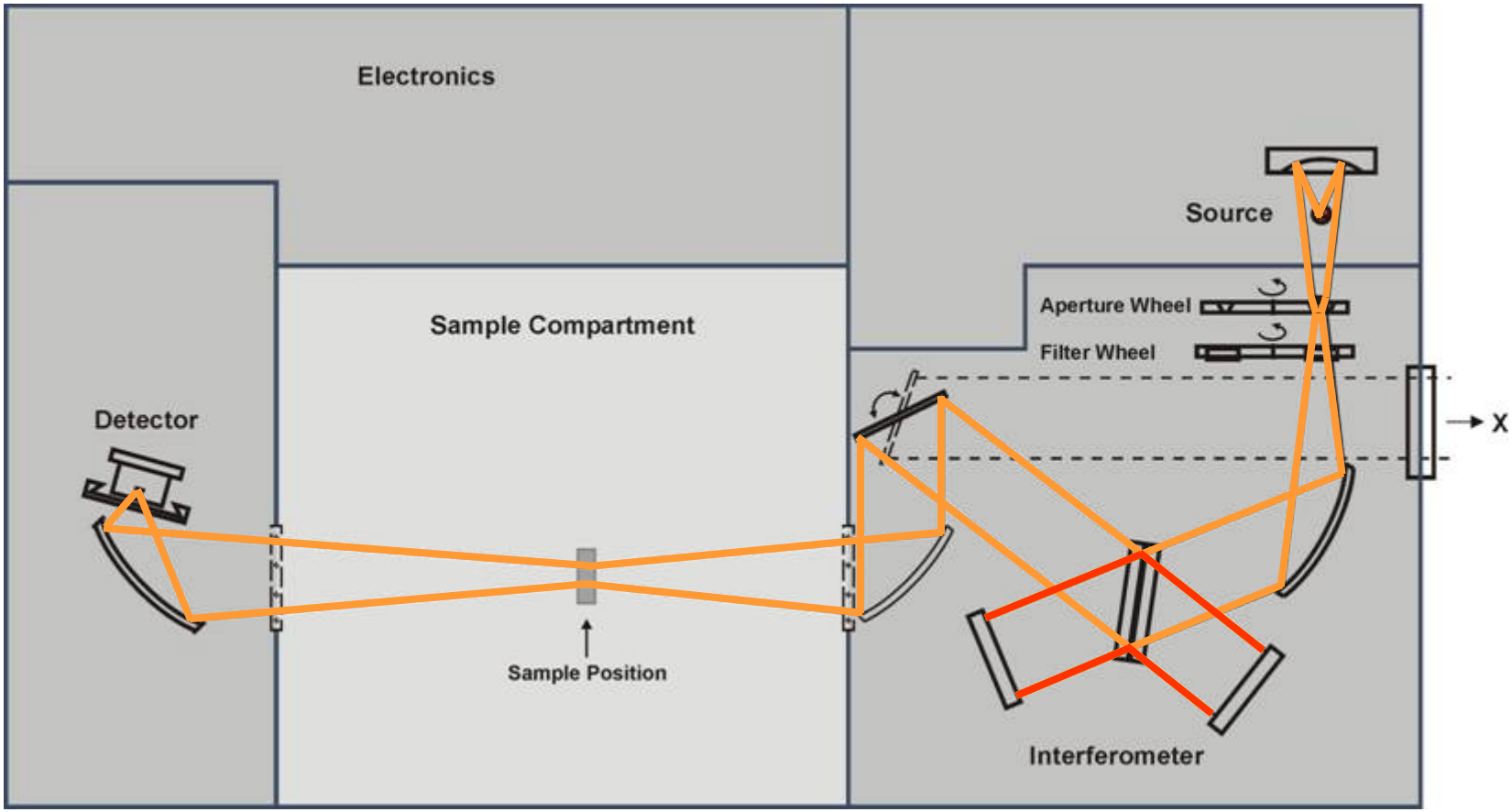
Infrared Spectral Ranges

The mid-infrared, or MIR, is the spectral range from 4,000 to 400 cm^{-1} wavenumbers. In this range fundamental vibrations are typically excited. In contrast, in the 'near-infrared', or NIR, spectral range, which covers the range from 12,500 to 4,000 cm^{-1} wavenumbers, overtones and combination vibrations are excited. The far infrared', or FIR, spectral range is between 400 and about 5 cm^{-1} wavenumbers. This range covers the vibrational frequencies of both backbone vibrations of large molecules, as well as fundamental vibrations of molecules that include heavy atoms (e.g. inorganic or organometallic compounds).



The working principle of an FT-IR spectrometer

Infrared light emitted from a **source** (e.g. a SiC glower) is directed into an **interferometer,** which modulates the light. After the interferometer the light passes through the **sample compartment** (and also the sample) and is then focused onto the **detector**. The signal measured by the detector is called the **interferogram.**

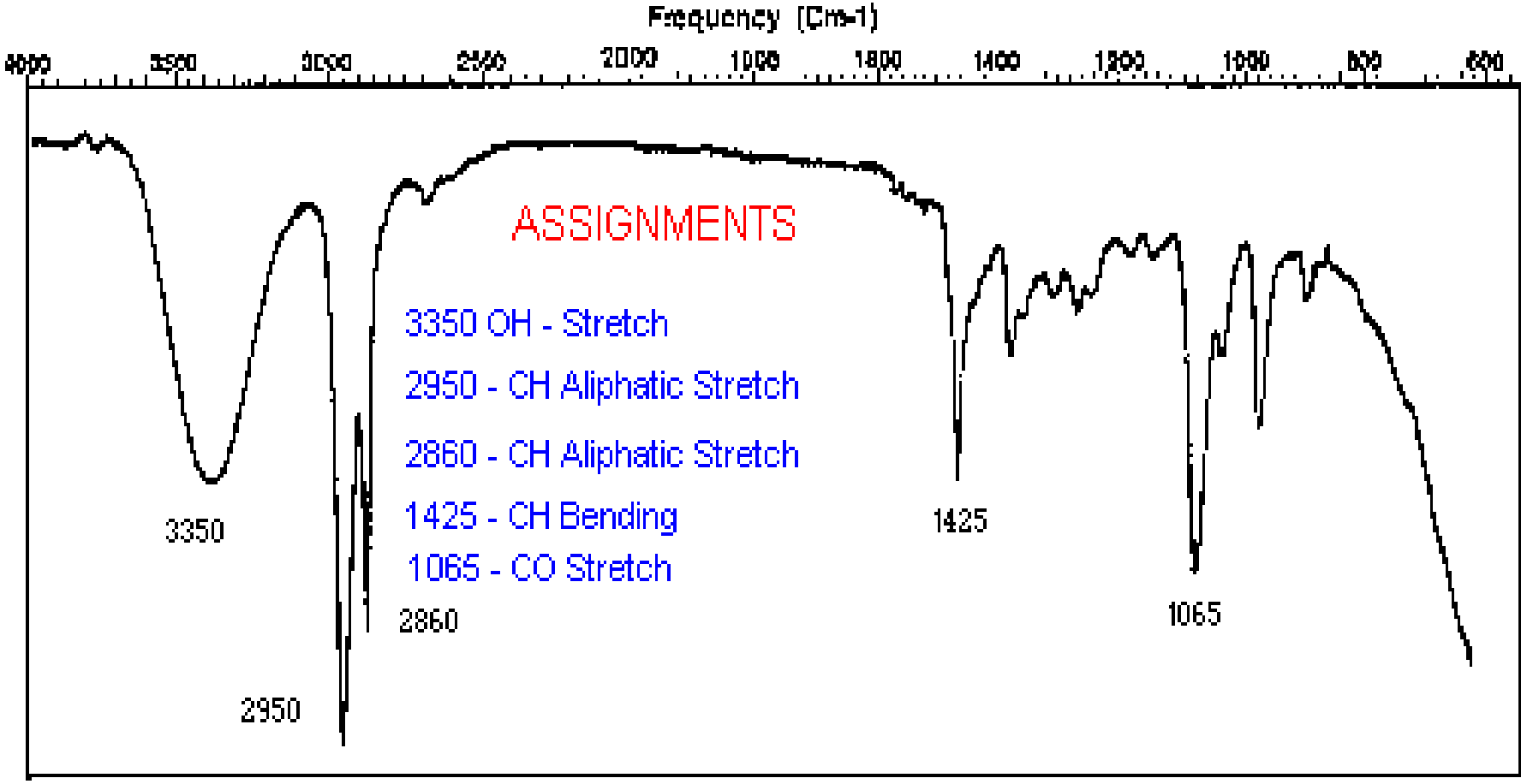


General FT-IR spectrometer layout

Table of Characteristic IR Bands

Group	Bond	Energy (cm^{-1})
hydroxyl	O-H	3610-3640
amines	N-H	3300-3500
aromatic rings	C-H	3000-3100
alkenes	C-H	3020-3080
alkanes	C-H	2850-2960
nitriles	C=-N	2210-2260
carbonyl	C=O	1650-1750
amines	C-N	1180-1360

IR yields good fingerprint spectra



Absorption in the 6- to 15-μm region is very dependent on the molecular environment.

This is called the fingerprint region.

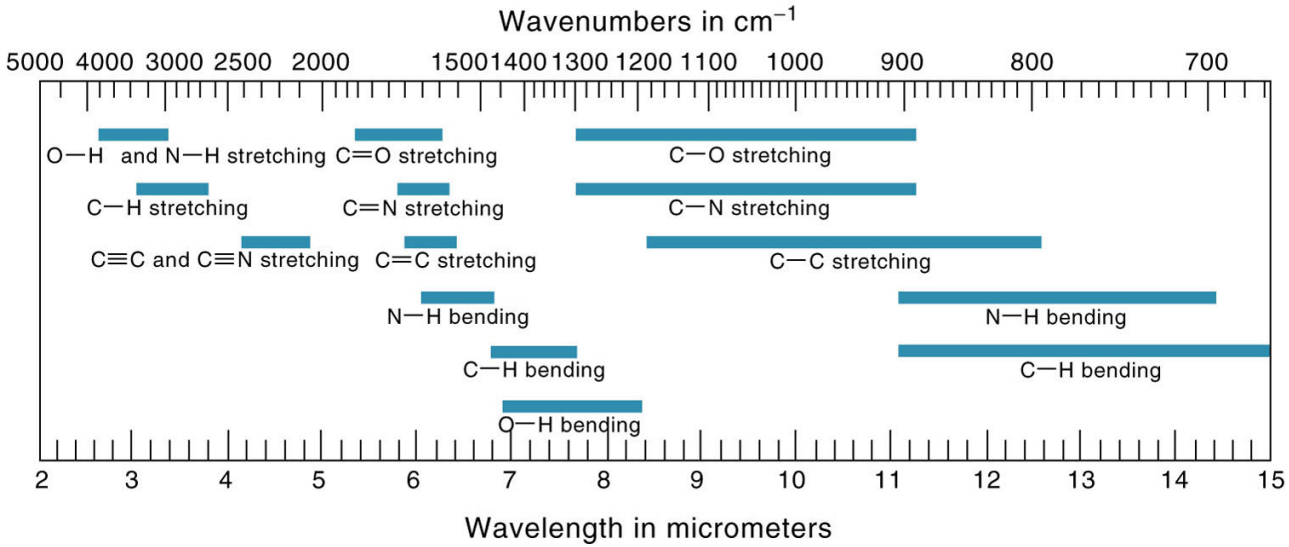
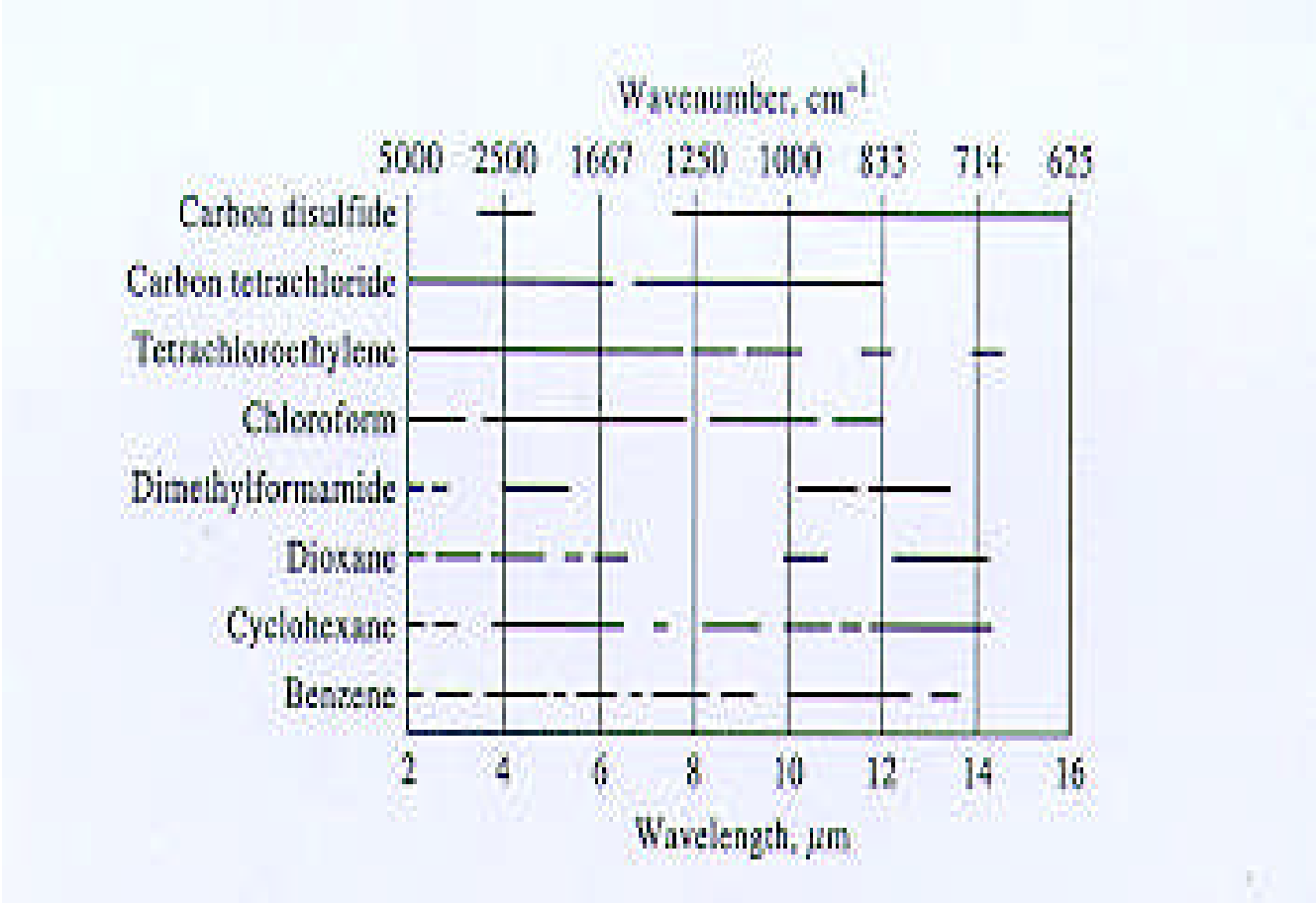


Fig. 16.8. Simple correlation of group vibrations to regions of infrared absorption.

Transmission of solvents in the infrared

Water has strong absorptions and attacks alkali halides



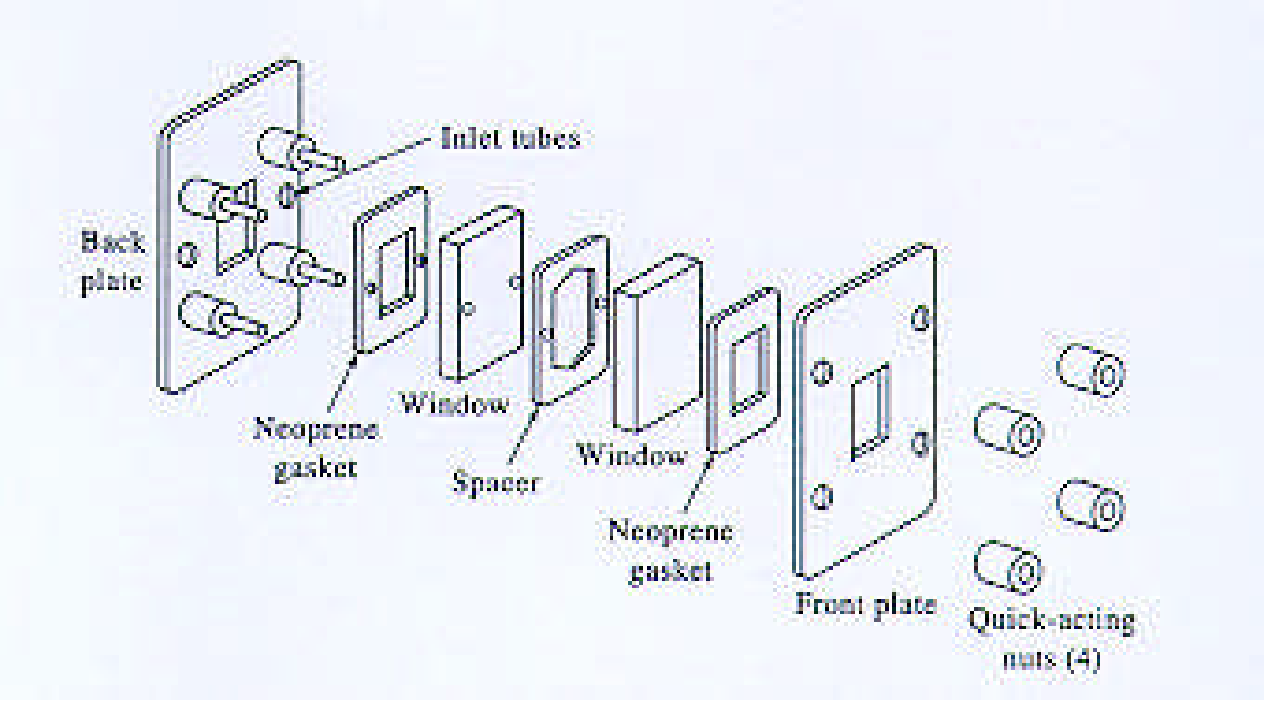
Horizontal lines show useful regions

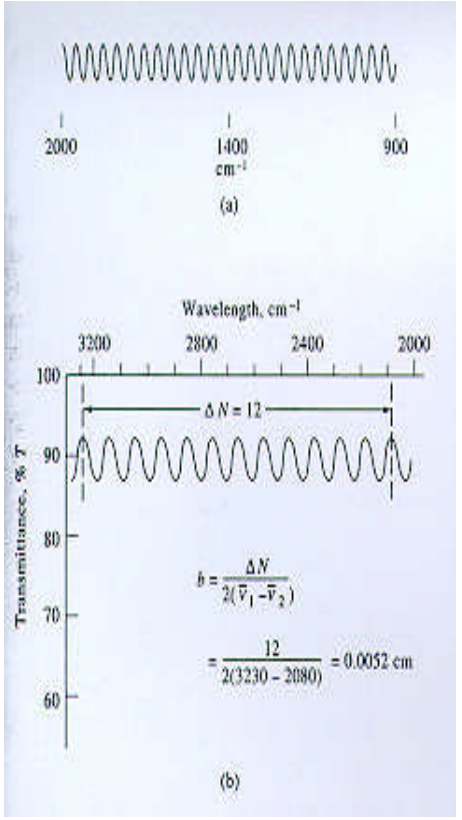
Conventional Techniques use IR transmission

Gases: Introduce into long-pathlength gas cell

Liquids: (i) place as a film between halide plates;

(ii) use a fixed pathlength cell. Determine pathlength, *b*, when empty by counting interference fringes.





Teflon spacers from 0.015 to 1 mm

Dessicator for IR Cell Storage

Dessicator

Water-free Environment for Water-sensitive Salt Plates.

Assembling a Transmission Cell

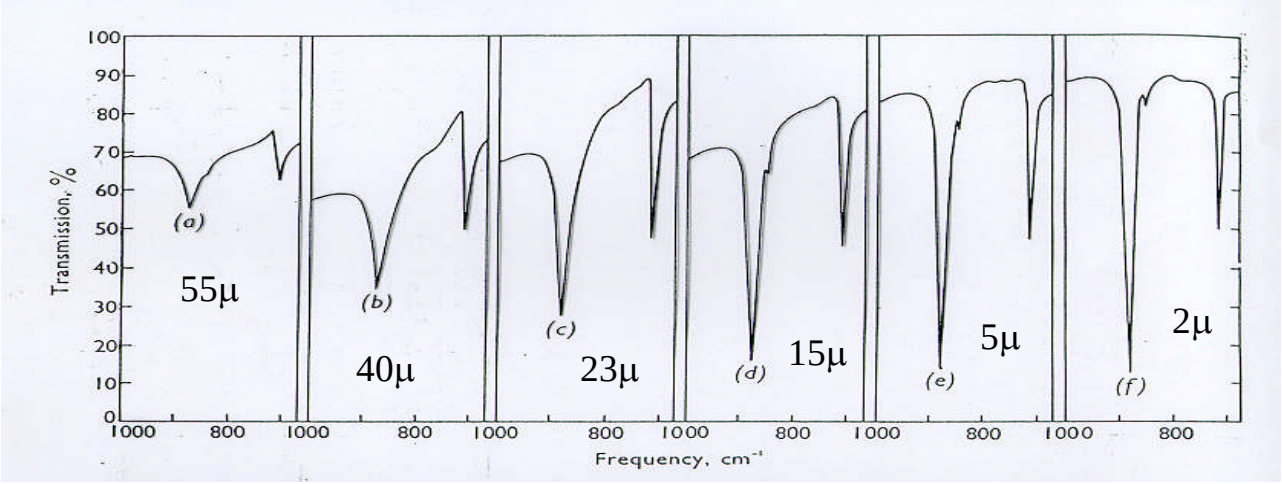
- A second salt plate is placed on top of the first one such that the liquid forms a thin film "sandwiched" between the two plates.

Positioning Transmission Cell

- The salt plates are cleaned by rinsing into a waste container with a suitable organic solvent-commonly cyclohexane; NEVER WATER!
- Cloudy plates must be polished to return them to a transparent condition.
- To polish cloudy windows, rotate salt plate on polishing cloth.

Solids: (i) make a mull with nujol, fluorolube and/or hexachlorobutadiene, so that mulling agent bands do not overlap sample bands.

(ii) Make a KBr disc (1-3 mg sample in 250-300 mg KBr). This may present artifacts.

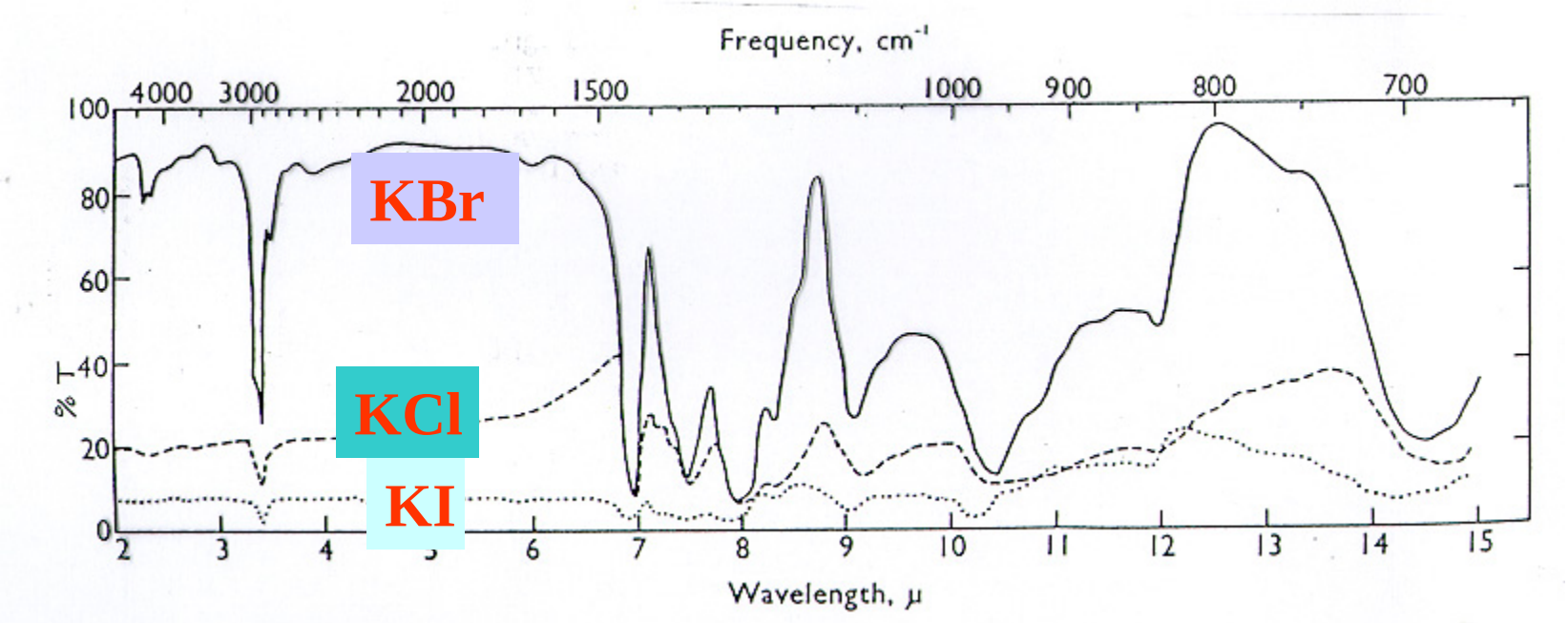


$CaCO_3$ in KBr, showing the mean diameters of the absorbing particles

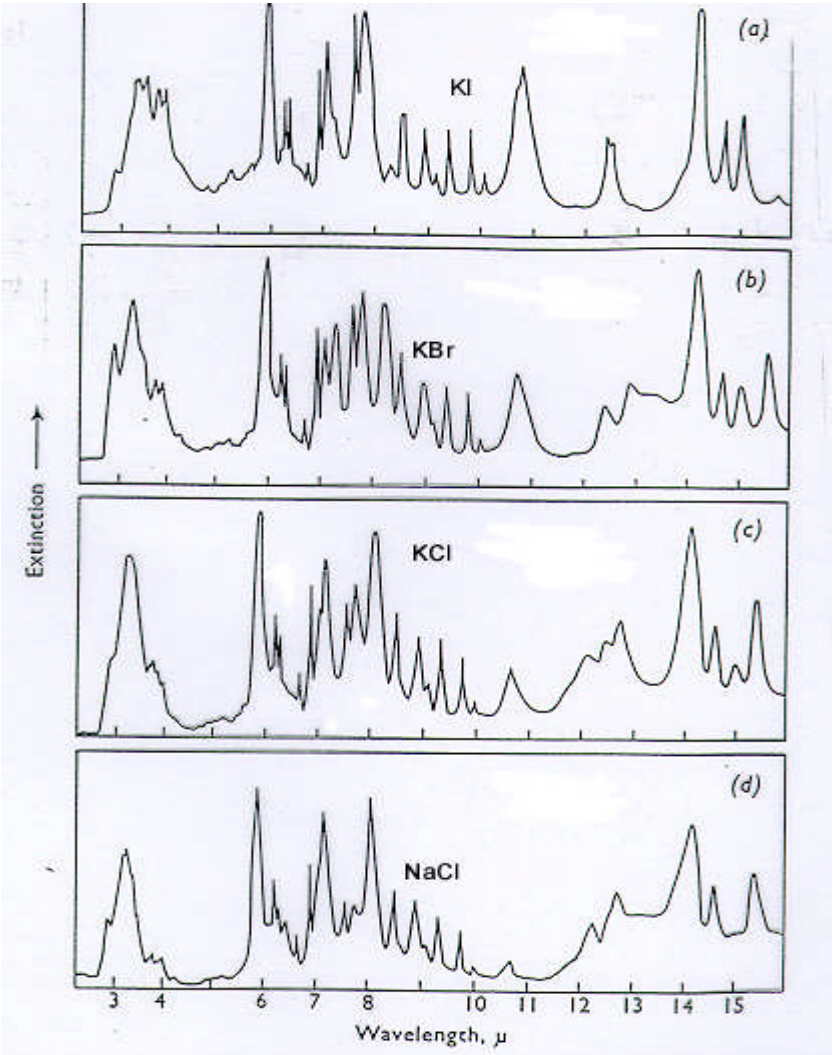
(a) increase of light loss from reflection and scattering by large particles.

(b)matching of sample and medium RI to prevent scattering.

e.g. PVC (n_D = 1.548) dispersed in KBr (n_D = 1.56), KCl and KI.



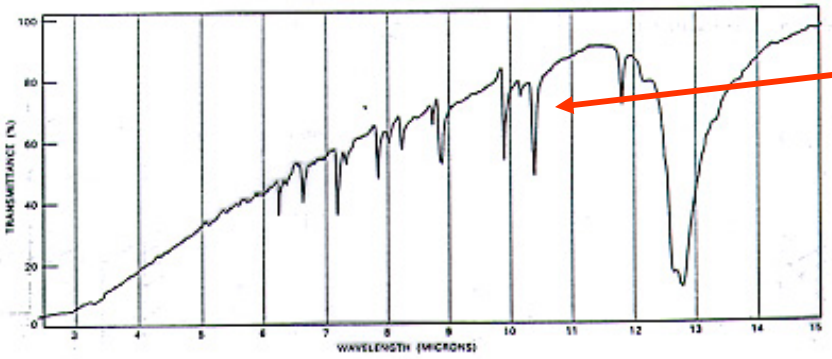
(c) Chemical and physical factors such as chemical reaction with the halide, or adsorption.



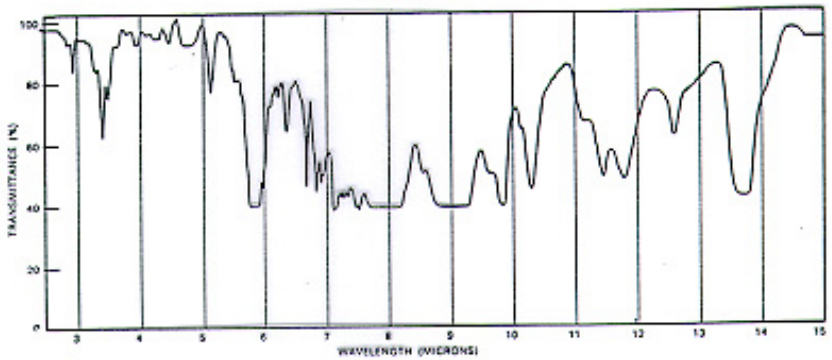
Spectra of benzoic acid in alkali halide discs.

NaCl spectrum is similar to benzoic acid monomer forming hydrogen bonds to dioxan; NaI spectrum is similar to free benzoic acid molecules

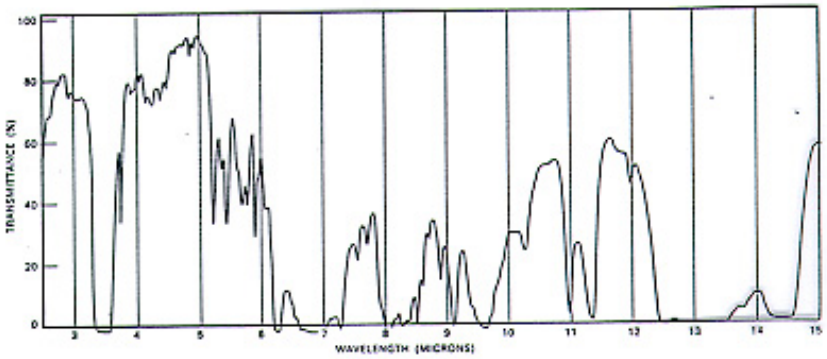
Some problems with spectra



Spectrum 1

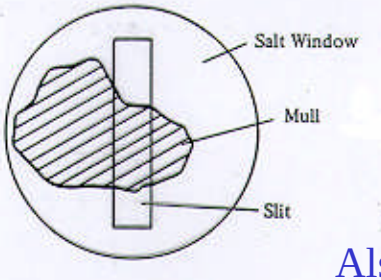


Spectrum 2



Spectrum 3

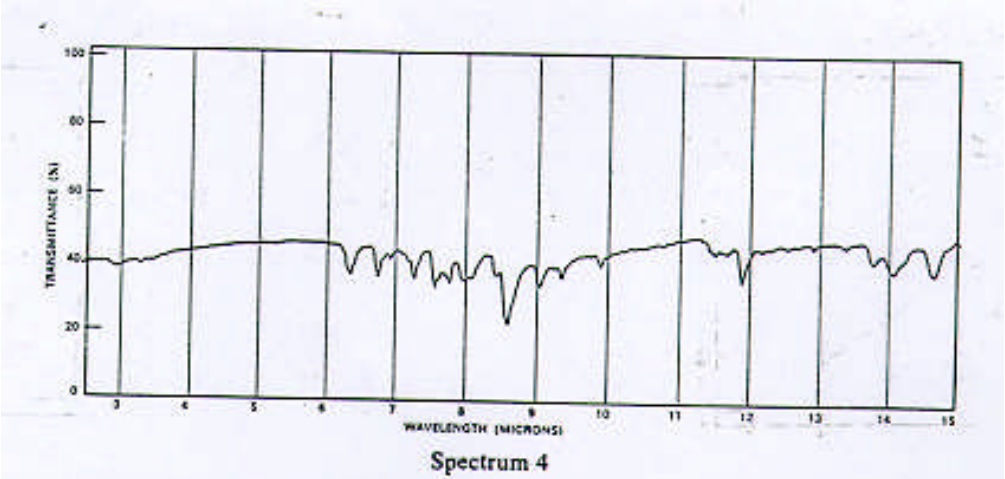
Asymmetric, sloping bands. Badly ground.



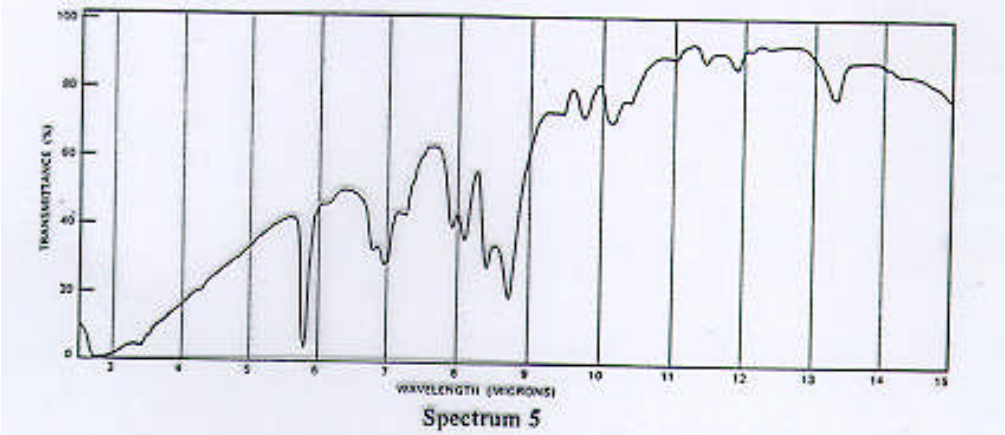
Sample does not cover beam.

Also for air bubble in liquid cell; polymer film with hole or crack

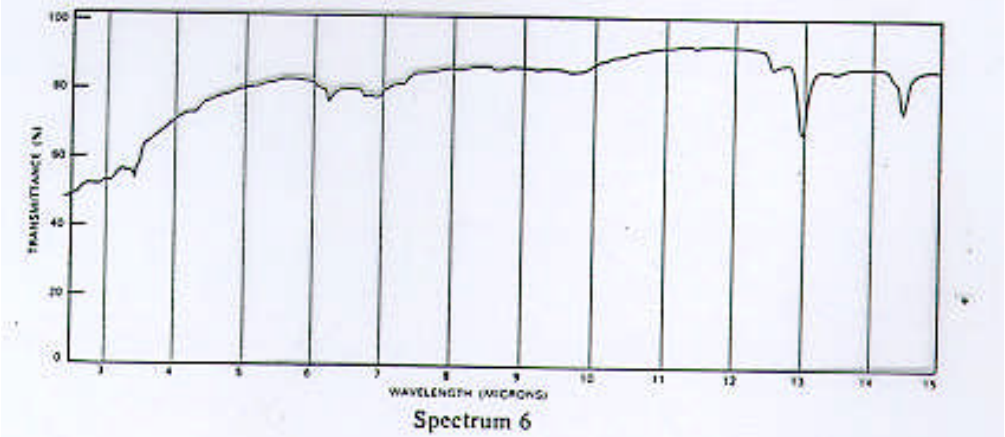
Sample (mull) too thick



Spectrum 4



Spectrum 5



Spectrum 6

Liquid evaporated between KBr plates

Wet sample. Sloping to high energy. Water bands.

Sample too thin

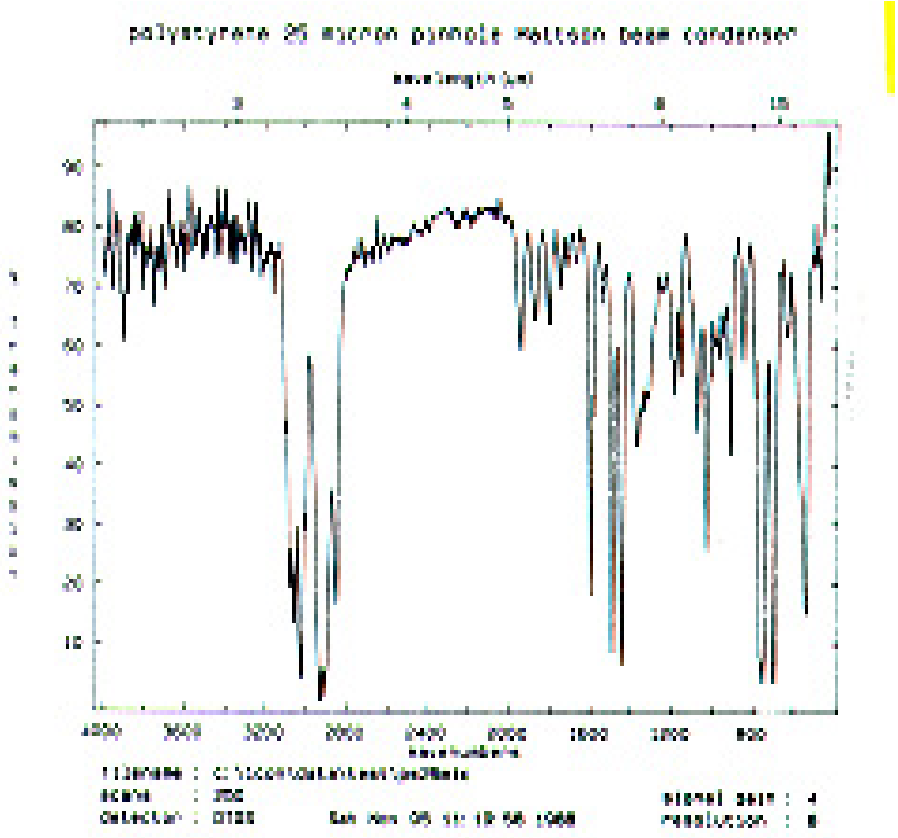
KBr disc problems:

Problem	Reason
Clear disc becomes cloudy	No vacuum used when pressing the disc. H_2O vapour entrained.
Disc is cloudy in centre	Anvil faces not flat or parallel.
Water of crystallization bands of sample have variable intensity from one spectrum to another	(Partial) dehydration occurs on pressing disc.

Beam condenser **reflecting or transmitting beam condensers can reduce source image x6. Normal FTIR instrument can analyze samples 0.5 mm diameter. With beam condenser, samples 25-50 μm can be analyzed**

Example of use of beam condenser:

25 μm polystyrene sample



IR Microscope:

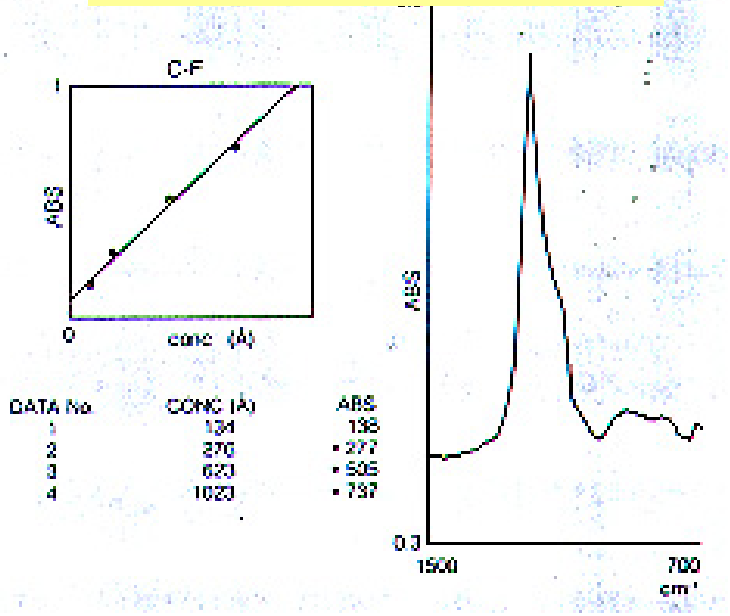
(a) Fit into sample compartment and use normal detector;

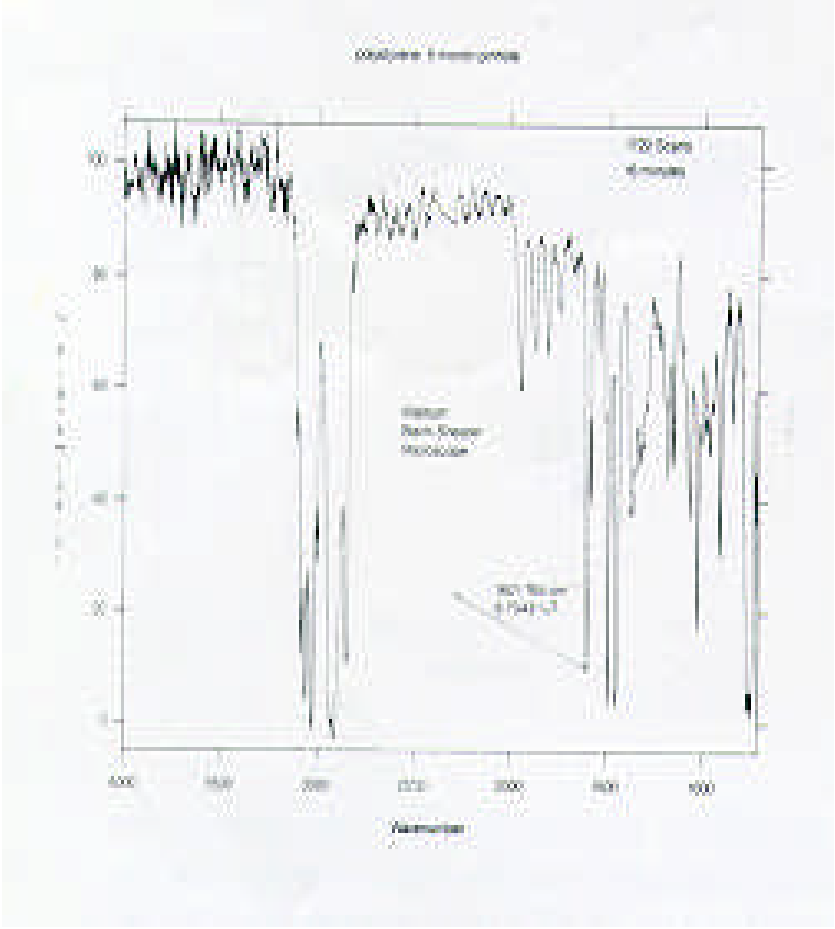
(b) Bolt on to exterior and use high sensitivity MCT detector.

analysis of samples 5-10 μm x 5-10 μm.

Examples of analysis:

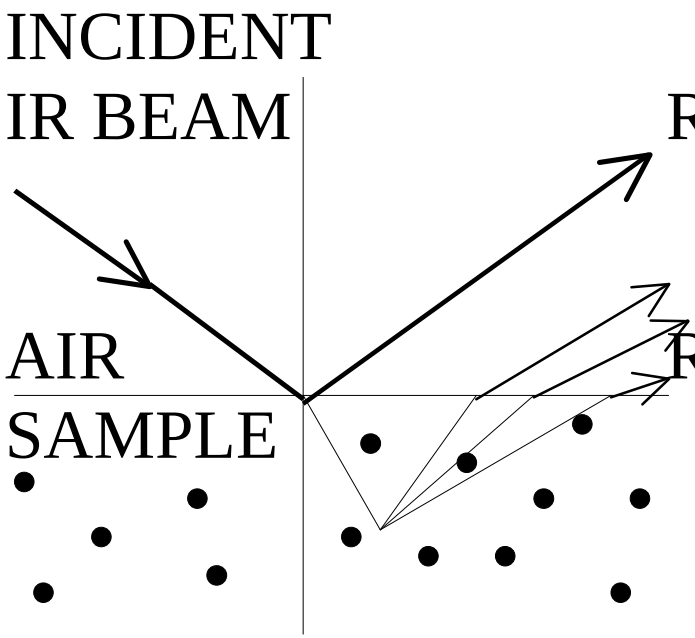
Film thickness (~100 Å) of fluorine system lubricant on Si wafer by transmission





Polystyrene 5μm pinhole

Reflectance spectroscopy



SPECULAR REFLECTANCE COMPONENT

angle *i* = angle *r*

DIFFUSE REFLECTANCE COMPONENT

angle i ≠ angle r

Reflection occurs from (solid) sample surface, or from underlying reflective substrate.

SPECULAR = mirrorlike reflectance from a surface; well defined angle of reflection.

Analysis of films or coatings on reflective surfaces

e.g. polymer coatings on food containers.

Can obtain qualitative analysis of film, and its thickness (smaller angle *i* gives longer sample pathlength).

Pure specular reflectance spectrum largely shows how RI changes with wavelength, and is transformed to transmittance using Kramers-Krønig relation. Specular reflection through surface coatings is 'double transmittance".

DIFFUSE (DRIFTS) = reflected radiant energy that has been partially absorbed, transmitted and partially scattered by a surface, with no defined angle of reflection.

Applications: strongly absorbing samples, e.g. coal, pharmaceuticals, plastics...

Small, irregular samples, powders.

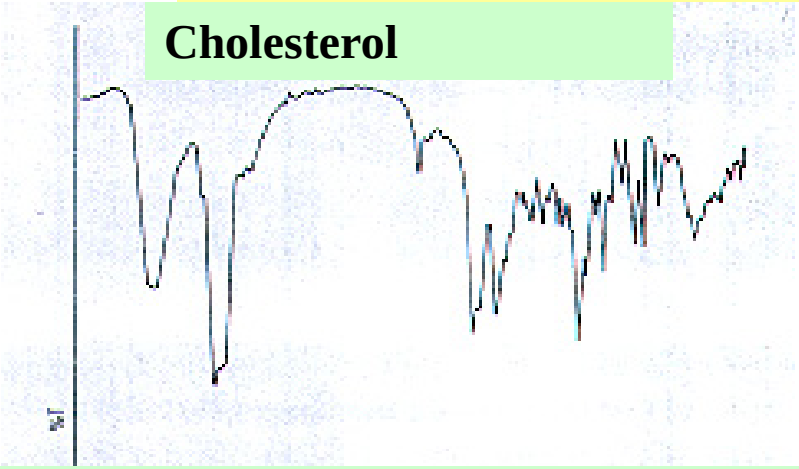
Advantages:

Minimal sample preparation; sample not destroyed

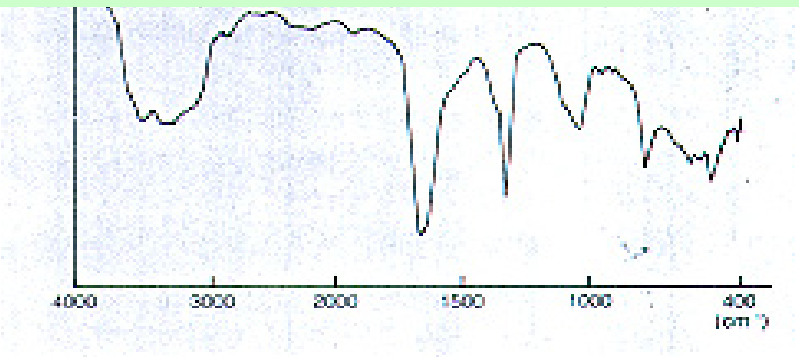
Example of micro-DRIFTS:

analysis of calculus

Cholesterol



Calcium oxalate and calcium phosphate

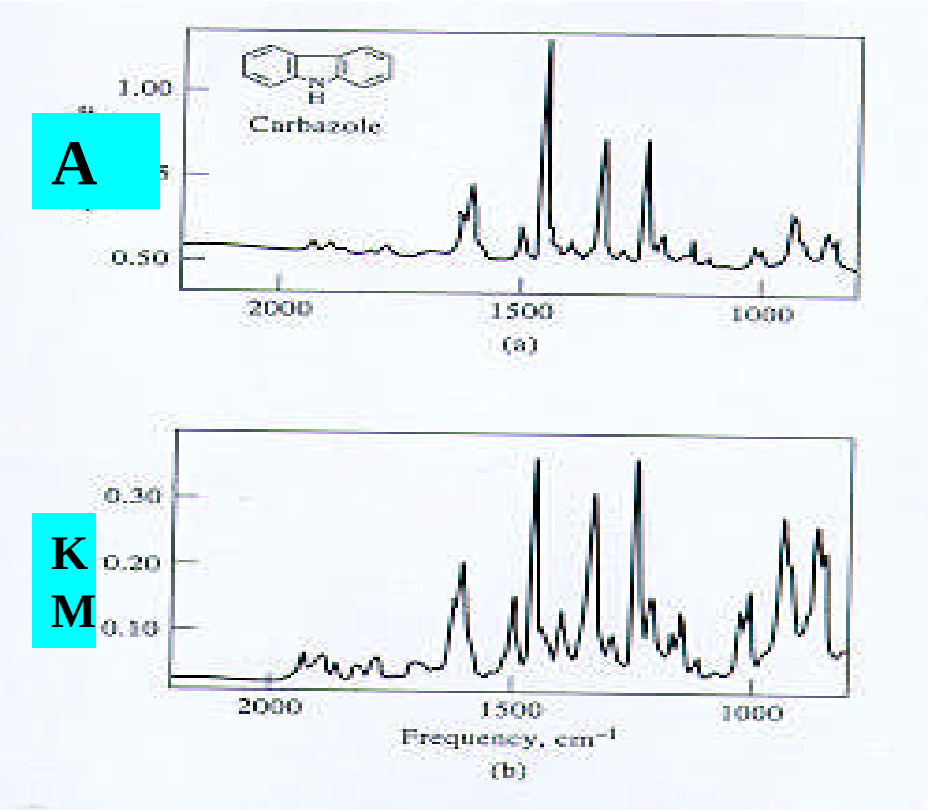


Principle of DRIFTS:

Measure intensity of 'reflected' radiation from sample surface (I), generally reported as percent reflectance (%R) and compared with intensity of radiation reflected from some "standard" nonabsorbing, reflecting surface (I_o): %R=100 I/I_0.

Kulbelka-Munk (KM) units are proportional to concentration (just like A):

$A_{KM}=\{1-(S/R)\}^2/2(R/S)$, where R=nonabsorbing reference, S='deep' sample single beam response.



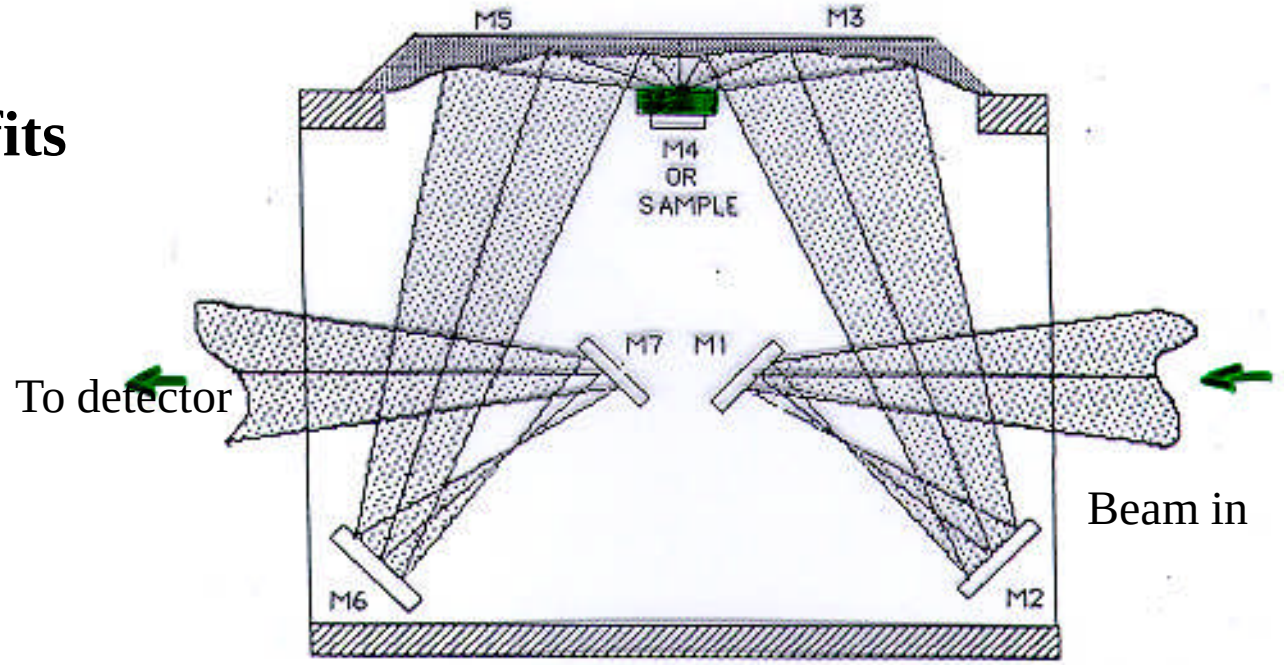
Comparison of absorption and DRIFTS spectrum of carbazole

Construction of DRIFTS accessory:

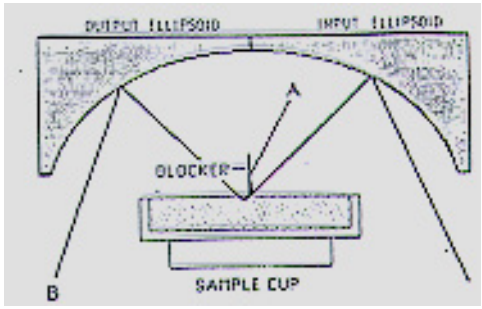
Sample placed in cup. Integrating sphere permits collection of diffusely-reflected light, blocking specular component. Definite fraction reflected to exit slit and detector.

Reference is KBr, Al_2O_3, MgO….

DRIFTS accessory fits into sample compartment

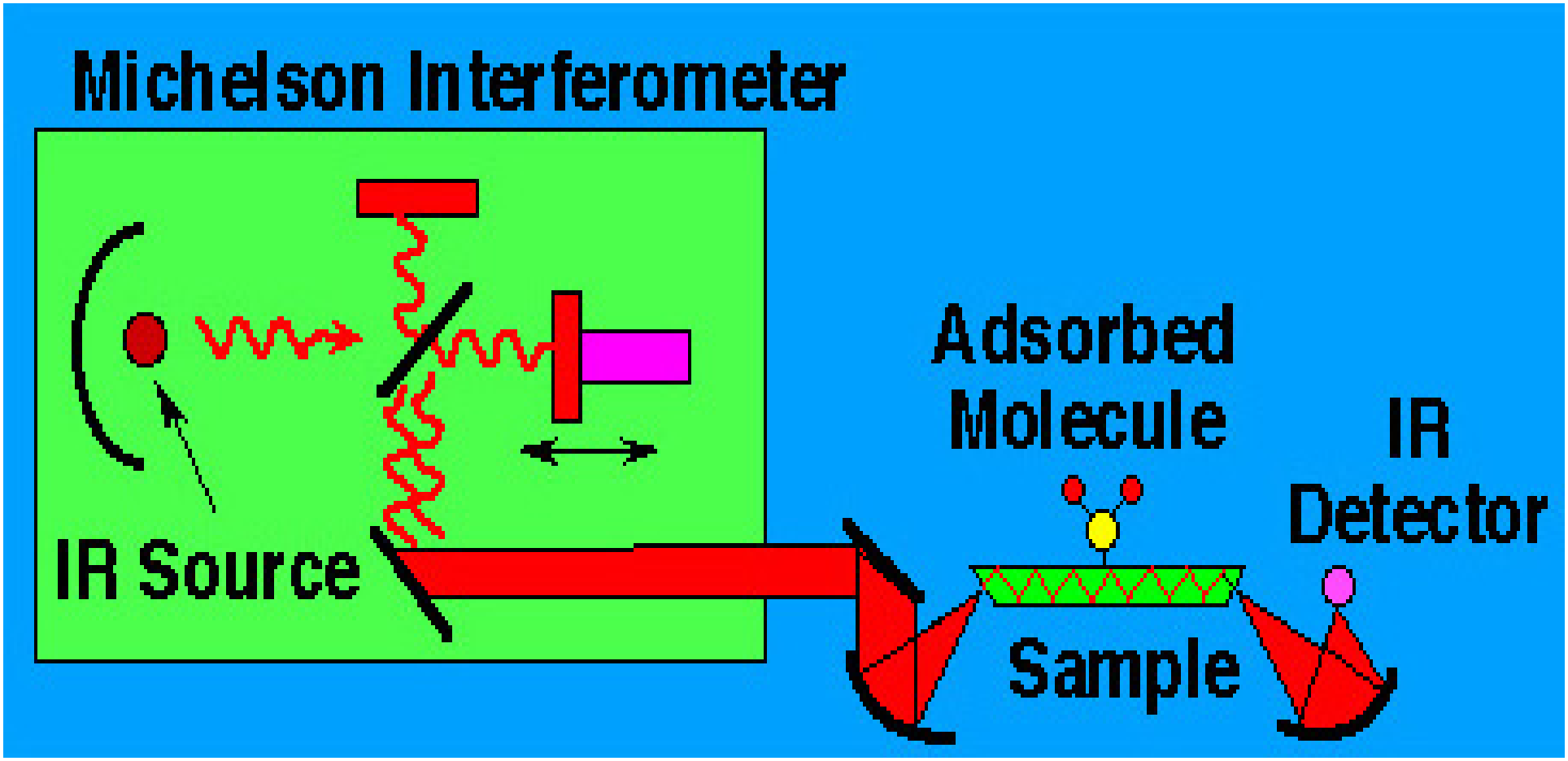


Specular component is blocked



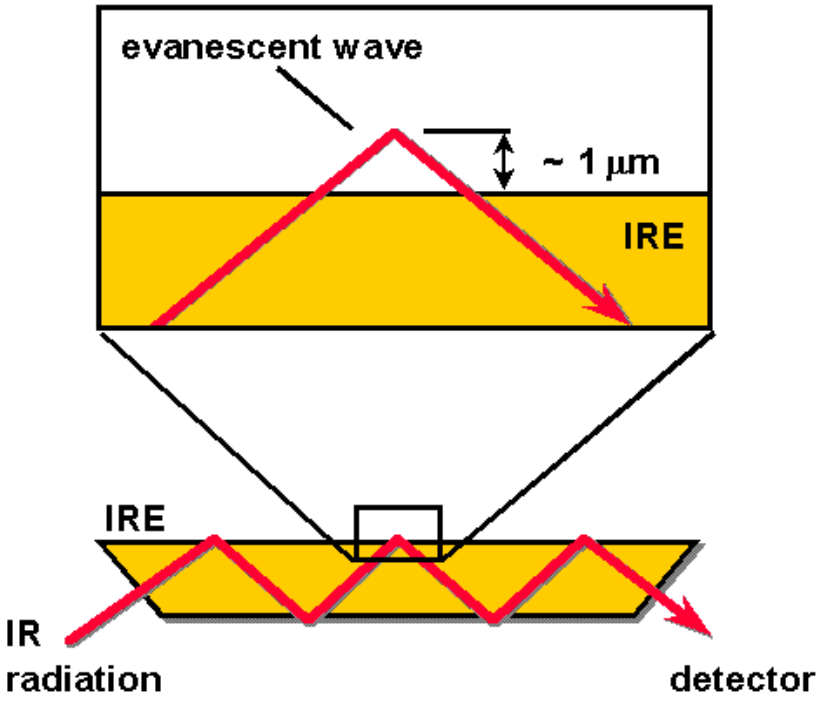
DRIFTS normally carried out on well-ground diluted samples (in nonabsorbing KBr matrix) to obtain transmission rather than specular reflection from sample.

FTIR with ATR Accessory



ATR-IR
How does it work?

- ATR-IR reflects infrared light off of the surface of a sample and measures the angle of reflectance.
- ATR-IR can be used on aqueous phase samples or solids.
- Surface analysis of solids (coatings on paper, ink on cardboard).
- Spectra from strongly absorbing samples (textiles, fibres, foods, rubbers, minerals, adhesive tapes, paint).
- Viscous liquids, or aqueous solutions.

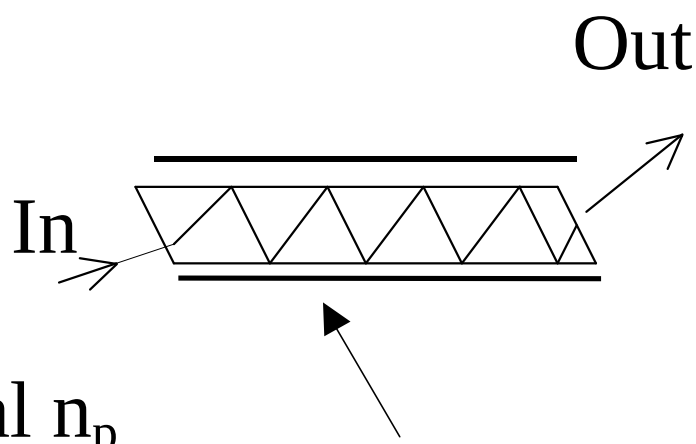


Attenuated total reflection ATR-FTIR

$\sin \theta_c = n_s / n_p$

Total internal reflection, TIR:

Radiation strikes an interface with a medium of lower RI, with an angle > θ_c.



Radiation actually penetrates sample and is partially absorbed

Penetration of a sample is independent of its thickness; Interference and scattering do not occur in a sample; Absorbance in a sample is independent of direction.

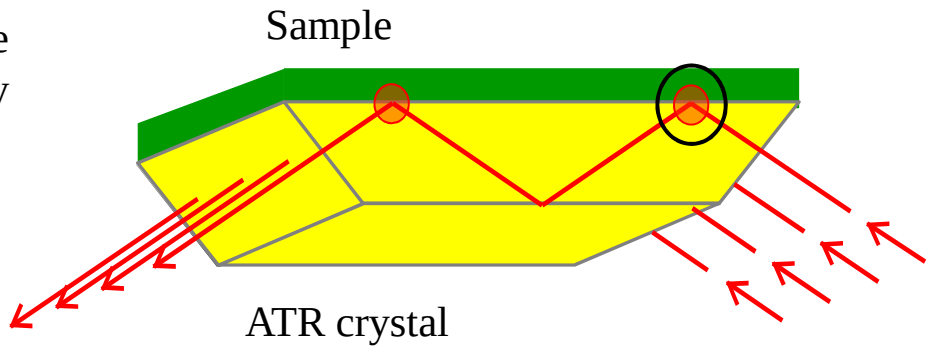
Depth of penetration at ATR

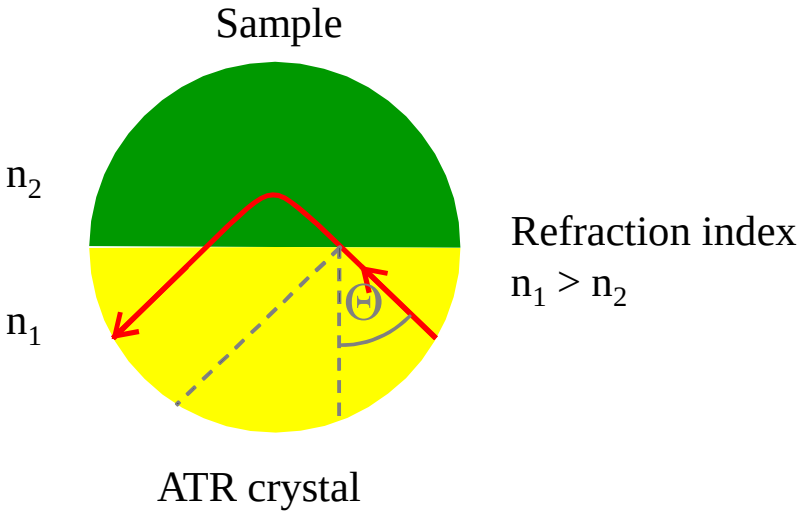
The IR light beam penetrates the sample and the depth of penetration D_P can be quantitatively described by the Harrick approximation:

$$d_p = \frac{\lambda}{2\pi n_p(\sin^2\theta - n_{sp}^2)^{1/2}}$$

- λ = wavelength
- n_p = refraction index, crystal
- θ = incidence angle
- n_{sp} = refraction index ratio between sample and crystal

Dp is defined as the distance between the sample surface and the position where the intensity of the penetrating Evanescent wave dies off to $(1/e)^2$ or 13.5%, or its amplitude has decayed to 1/e.





Depth of Penetration

The depth of penetration depends on different parameters:

1.) Incidence angle: Tthis angle is determined by the design of the ATR accessory and is constant for most ATR accessories. There are ATR accessories which have the capability to vary the angle of incidence. This can be helpful for depth profiling near the surface of a sample (within the 0.5-2.0 micron range).

:

2.) **Refraction index** of the ATR crystal: a higher index of refraction yields more shallow depth of penetration. ATR units with replaceable crystals can also be used for depth profiling of the sample (within the submicron range).

Calculated depths of penetration for some typical ATR crystals

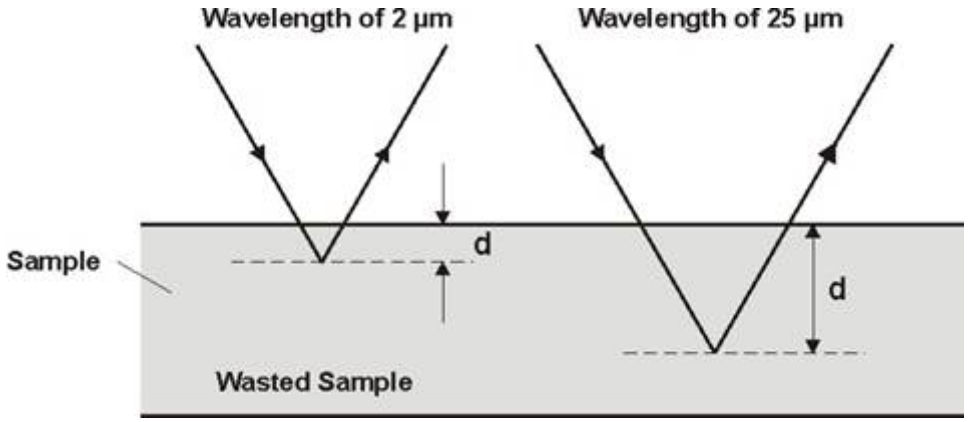
Material	Refraction index at 1,000cm^{-1}	Depth of penetration* at 45°	Depth of penetration* at 60°
Diamond	2.4	1.66	1.04
Ge	4.0	0.65	0.5
Si	3.4	0.81	0.61
ZnSe	2.4	1.66	1.04
AMTIR**	2.5	1.46	0.96

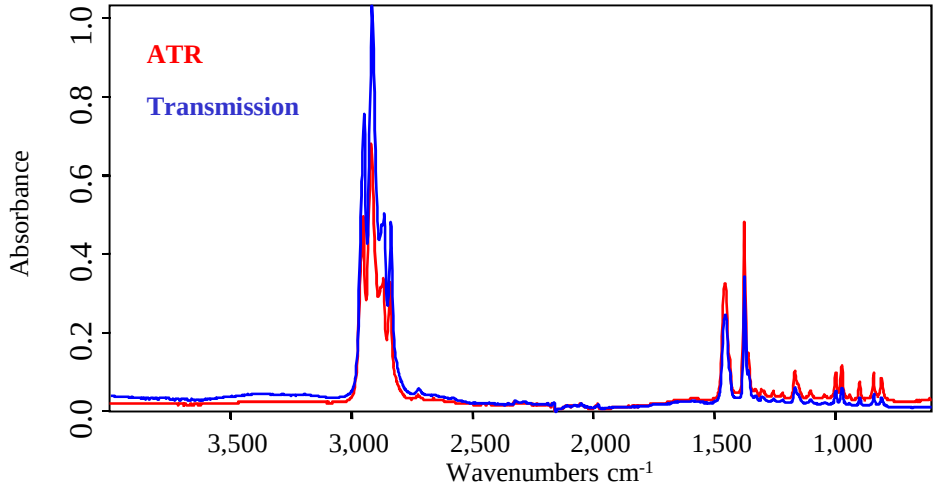
*: The depth of penetration was calculated for a sample with a refraction angle of 1.4 at 1,000cm^{-1}.

**: AMTIR: $Ge_{33}As_{12}Se_{55}$ glass

Depth of Penetration

3.) **Wavelength** of light: the longer the wavelength of the incident light (lower wavenumber), the greater the depth of penetration into the sample. This yields an ATR spectrum that differs from the analogous transmission spectrum, where band intensities are higher in intensity at longer wavelength. However, the ATR spectrum is readily converted to absorbance units by selecting the "convert spectrum" option in the "manipulate" pull down menu in OPUS.





Selecting an Adequate ATR Crystal

When selecting the proper crystal for ATR analysis, sample hardness must be taken into account as well as the desired depth of penetration and spectral range. Diamond has a very high degree of hardness, but very distinctive lattice bands totally absorb between 2,500 and 1,600 cm^{-1}. Most compounds do not have vibrations in this area.

Material	Spectral range	Refraction index	Hardness***
ZnSe	20,000 - 500 cm^{-1}	n = 2.4	130
ZnS	50,000 - 770 cm^{-1}	n = 2.3	250
Ge	5,000 - 550 cm^{-1}	n = 4.0	780
Si	8,333 - 33 cm^{-1}	n = 3.4	1,150
Diamond	50,000 - 2,500 cm^{-1} 1,600 - 0 cm^{-1}	n = 2.4	9,000
KRS-5*	17,000 - 250 cm^{-1}	n = 2.4	40
AMTIR**	11,000 - 725 cm^{-1}	n = 2.5	170

*: KRS-5: TlI/TlBr

**: AMTIR: $Ge_{33}As_{12}Se_{55}$ glass

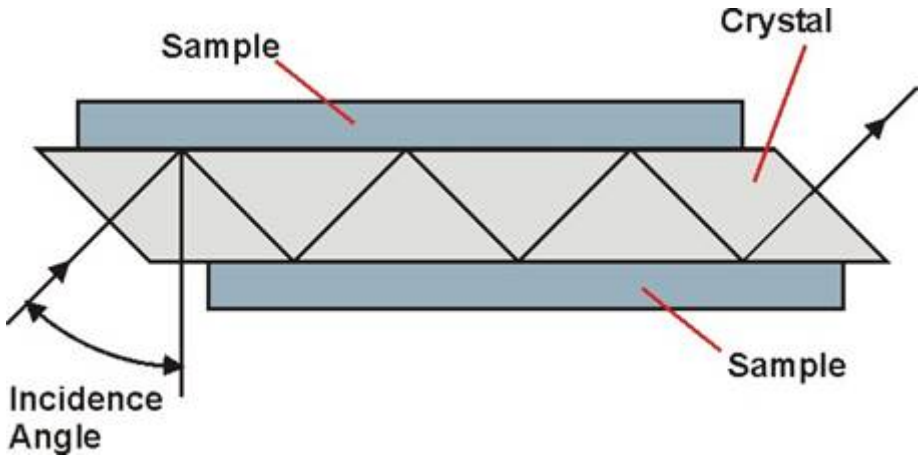
***: Knoop hardness

Number of Reflections - Effective Path Length

The number of reflections depends on the crystal type, the dimensions of the ATR crystal, and the incidence angle of the IR beam. A parallelogram-shaped crystal which contacts the sample on two sides can be described by:

$N = l / (d \bullet \tan\Theta)$

N = Number of reflections
l = Crystal length
d = Crystal thickness
Θ = Incidence angle



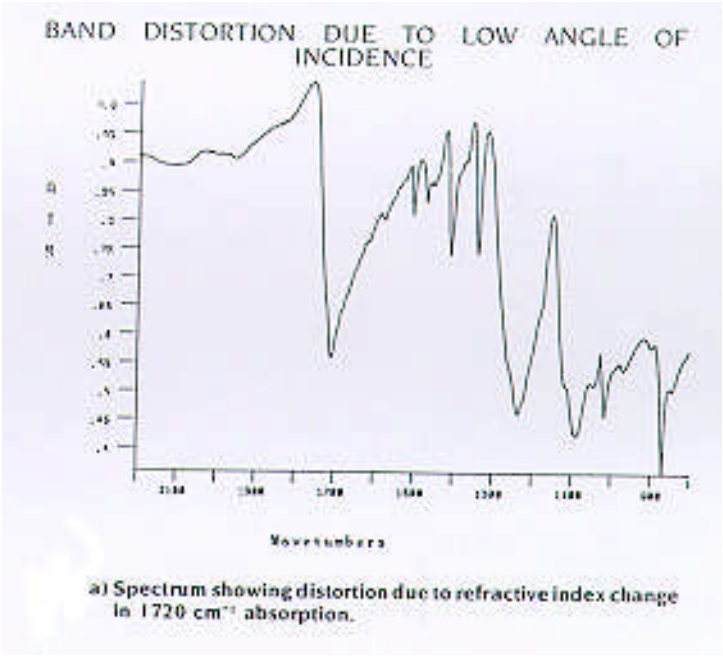
A ZnSe crystal with a length of 80 mm, a thickness of 4 mm and an incidence angle of 45° yields N = 20 reflections.

The equation for the effective path length (D_E) is:

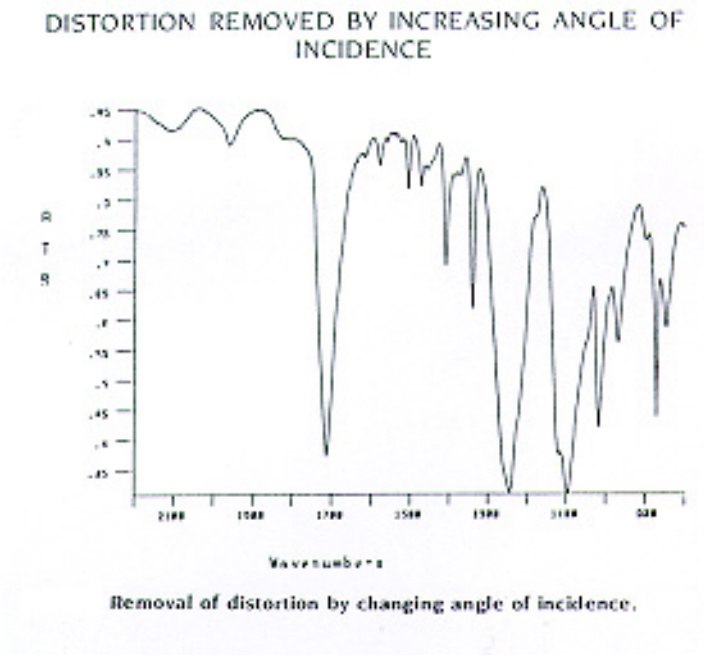
$D_E = N \bullet D_P$

Effect of Refractive Index (RI) and Angle of Incidence

RI of a substance changes with frequency, especially where absorption occurs. Changes in sample RI in the region of intense absorption bands can sometimes change the value of θ_c for a particular crystal/sample combination. If the new value of θ_c becomes > than angle of incidence, then TIR no longer occurs, and the absorption band becomes distorted: usually a high degree of peak asymmetry and baseline drift occur. These distortions may be removed by (a) increase angle of incidence; (b) use a crystal of higher RI.



a) Spectrum showing distortion due to refractive index change in 1720 cm^{-1} absorption.



Removal of distortion by changing angle of incidence.

ATR-FTIR of China Clay Filled Polyester Film

Effect of Angle of Incidence

d, 1/e depth of penetration ($\approx \lambda$)

$$d = \lambda / 2 \pi n_p [\sin^2\theta - (n_s / n_p)^2]^{1/2}$$

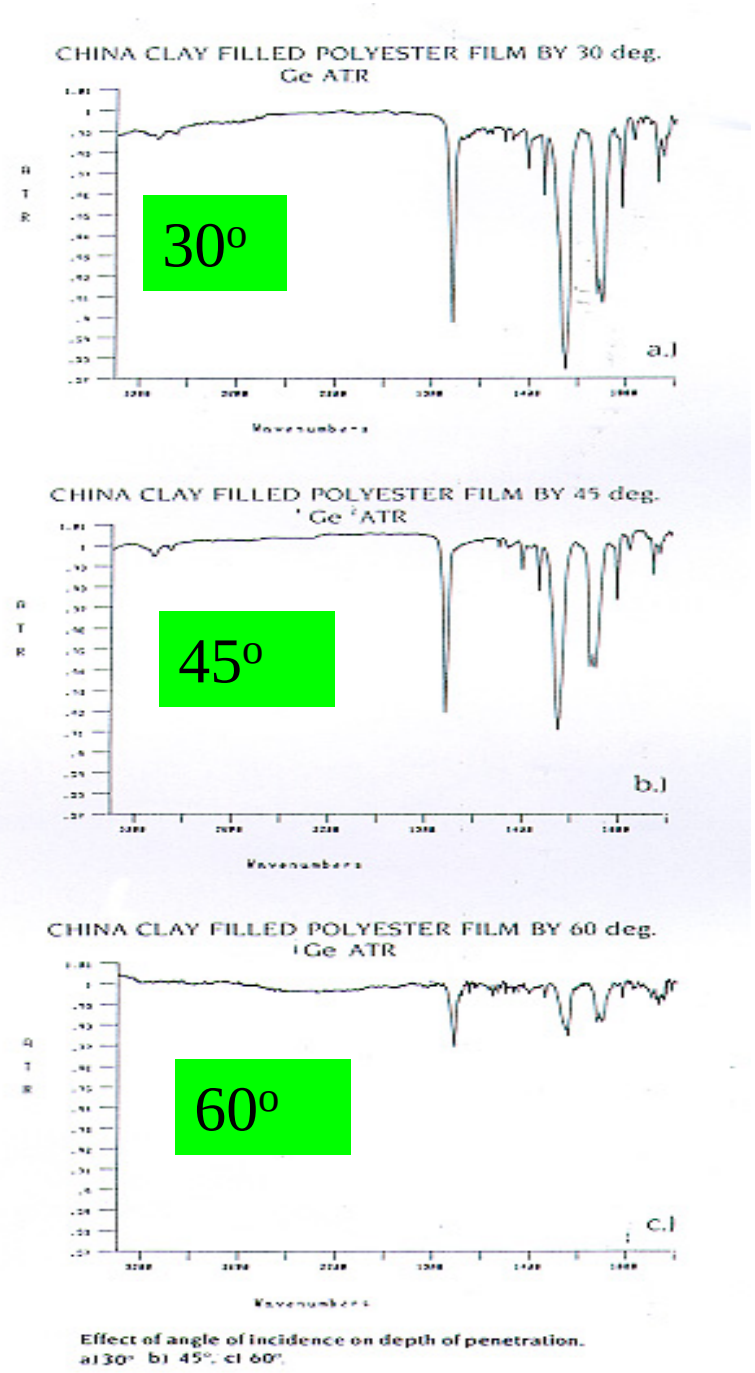
n_p RI of crystal; n_s RI of sample

θ = angle of incidence; varying from

30^o - 60^o decreases d by factor ~10.

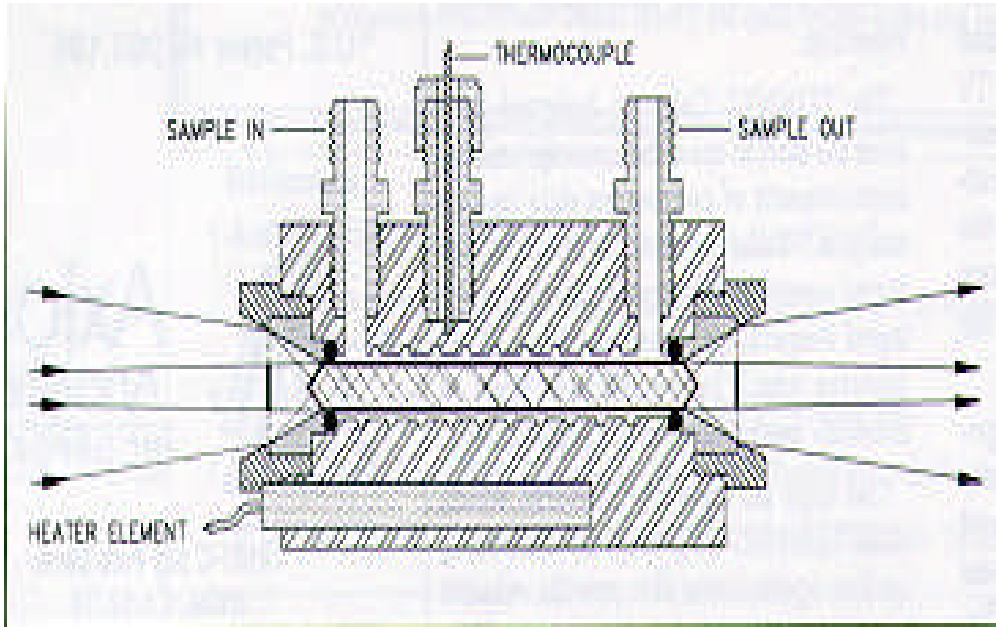
Can depth profile by changing θ.

Smaller angle, deeper penetration



Effect of angle of incidence on depth of penetration.
a) 30° b) 45°, c) 60°

ATR with aqueous solutions:
Axiom Tunnel Cells



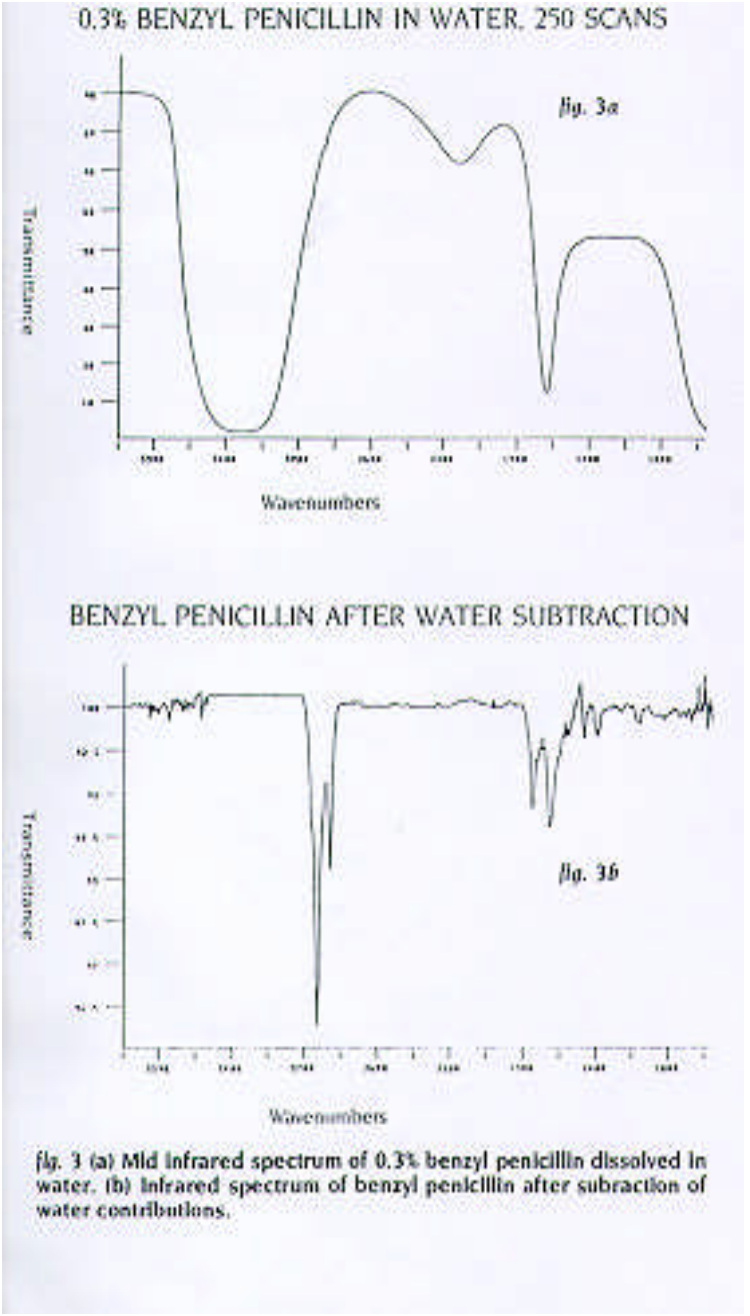
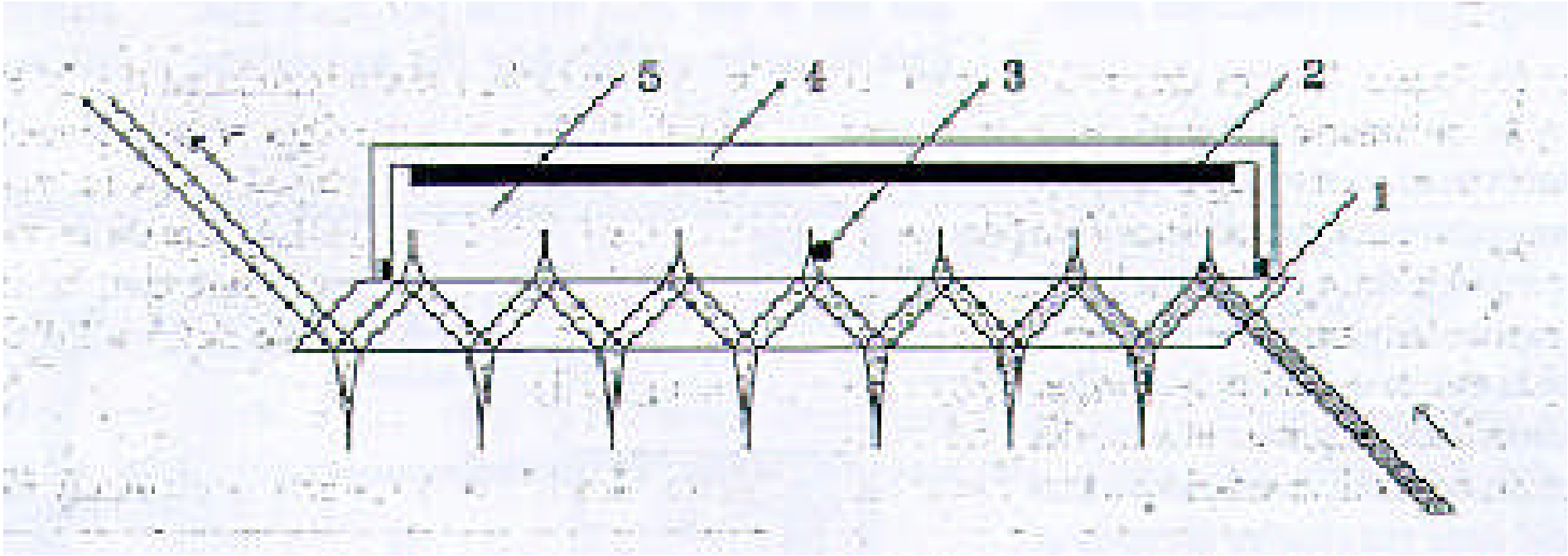


fig. 3 (a) Mid infrared spectrum of 0.3% benzyl penicillin dissolved in water. (b) Infrared spectrum of benzyl penicillin after subtraction of water contributions.

ATR-FTIR at electrode surfaces

Incident ray is totally reflected at electrolyte-ATR element (Ge) interface. Part is absorbed by electrolyte.

1. Ge ATR element, 2. Pt-counter electrode, 3. Reference electrode, 4. PMMA main body of cell, 5. Electrolyte.

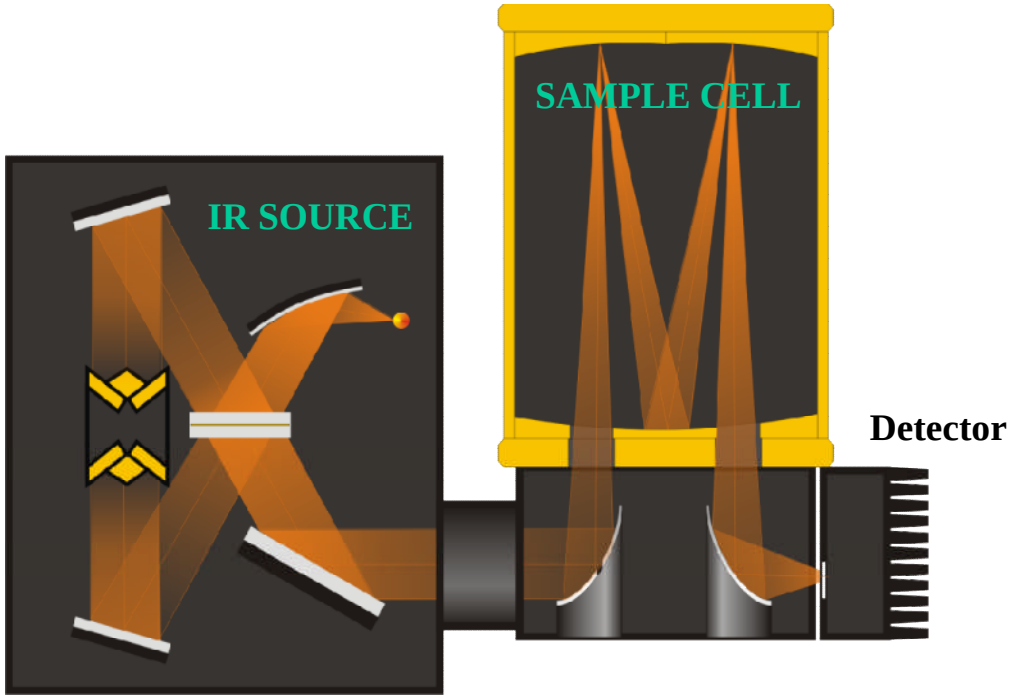


A Quick-Reference Table For Choosing FT-IR Sampling Accessories

Sample Type	Discs and Mulls	Specular Reflectance	ATR	Diffuse Reflectance	PAS	FT-IR Microscopy
Organics (white powders)	Y	N	N	Y	Y	Y
Inorganics	Y	N	N	Y	Y	Y
Tablets	Y	N	N	Y	Y	Y
Fabrics	S	N	S	Y	Y	Y
Individual fibers	N	N	S	S	S	Y
Paints, inks (liquid)	N	S	Y	N	N	N
Paints, inks (dry)	S	Y	Y	Y	Y	Y
Plastics	S	S	Y	Y	Y	Y
Highly filled plastics and rubbers	N	N	Y	Y	Y	S
Plastic foams	N	N	S	Y	Y	S
Non-aqueous liquids	Y	S	Y	N	N	N
Aqueous systems	N	N	Y	N	N	N
Minerals	Y	Y	N	Y	Y	Y
Oils	Y	Y	Y	N	Y	N

Key: Y = yes, straightforward; S = suitable for some samples; N = not normally suitable

Extractive FTIR with Gas Cells



FTIR spectrometer

IR source

Broad band infrared radiation

Interferometer

Modulated infrared radiation

Sample cell

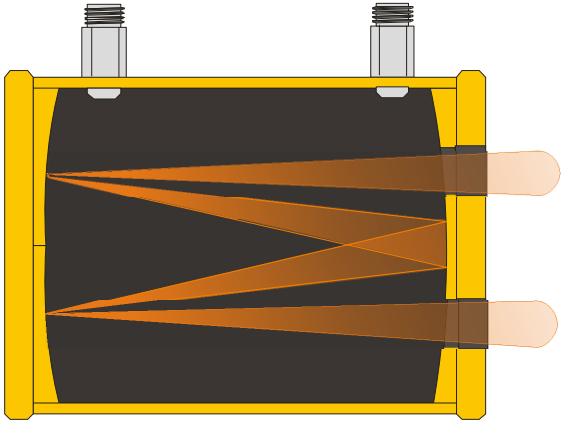
Transmitted infrared radiation

Detector

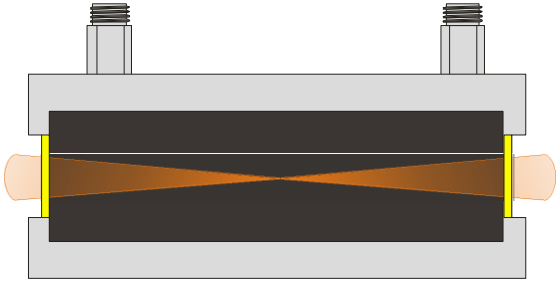
Measured signal

Signal and data processing

Sample cells and optical path length

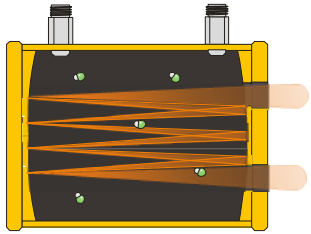


High Sensitivity (Multipass) Sample Cell
V = 0.4 l
L = 60 … 980 cm
T_{90}< 10 sec (4 lpm)

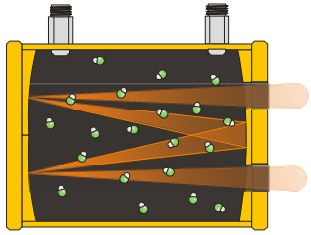


Single pass cell
V = 0.013 … 0.031 l
L = 1, 4, or 10 cm
T_{90} < 1 sec (4 lpm)

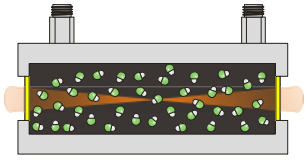
Different path lengths for different measurement ranges



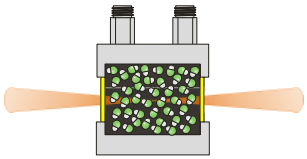
L = 9.8 meter
c = 10 ppm
A = 0.0047 a.u



L = 2.5 meter
c = 39 ppm
A = 0.0047 a.u



L = 10 centimeters
c = 980 ppm
A = 0.0047 a.u



L = 4 centimeters
c = 2450 ppm
A = 0.0047 a.u

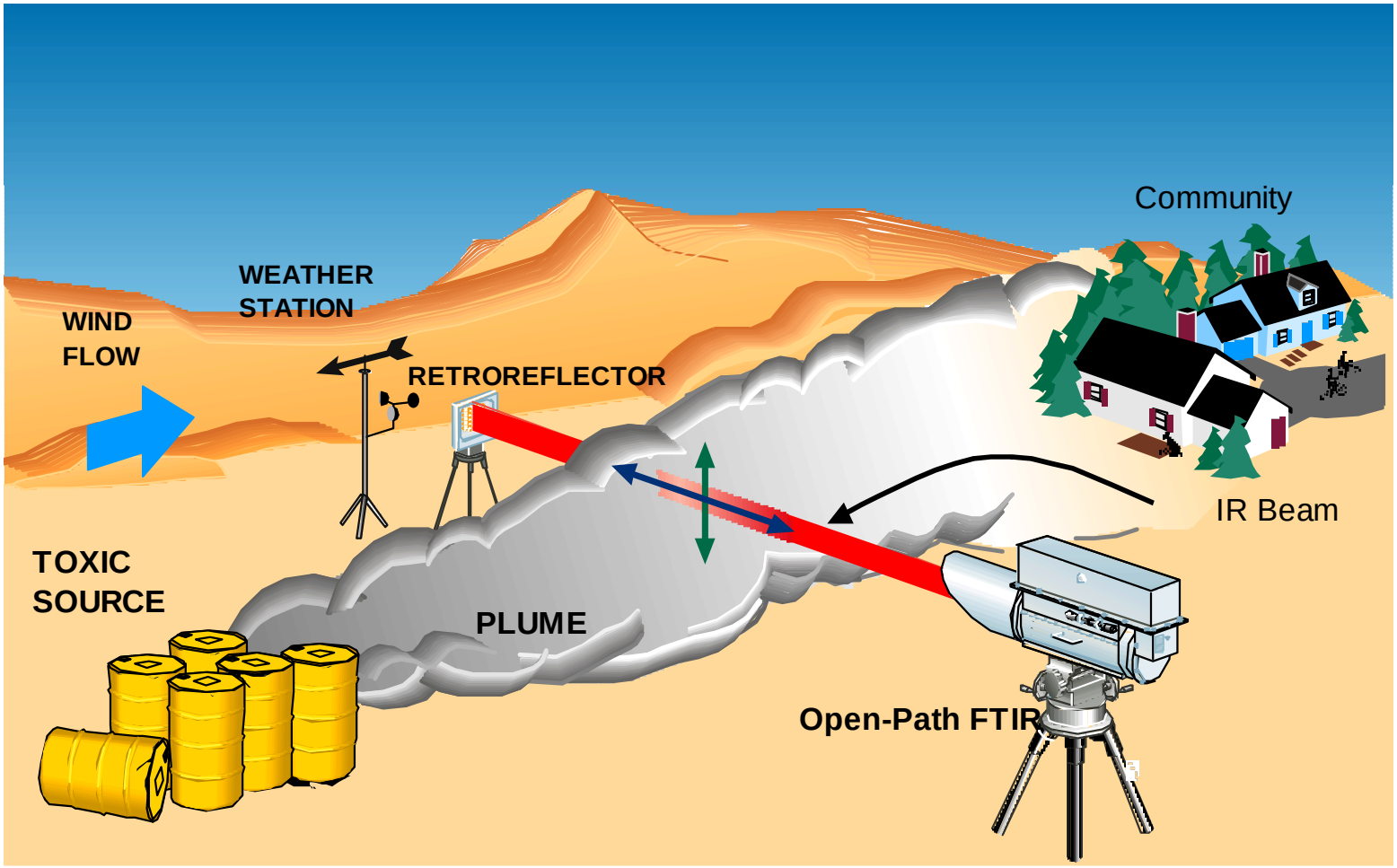
Examples of Infrared Gas Analysis with a 10-meter Cell for OSHA Compliance

Compound	Allowable Exposure, ppm	Wavelength,μm	Minimum Detectable Concentration, ppm
Carbon disulfide	4	4.54	0.5
Choloroprene	10	11.4	4
Diborane	0.1	3.9	0.05
Ethylenediamine	10	13.0	0.4
Hydrogen cyanide	4.7	3.04	0.4
Methyl mercaptan	0.5	3.38	0.4
Nitrobenzene	1	11.8	0.2
Pyridine	5	14.2	0.2
Sulfur dioxide	2	8.6	0.5
Vinyl chloride	1	10.9	0.3

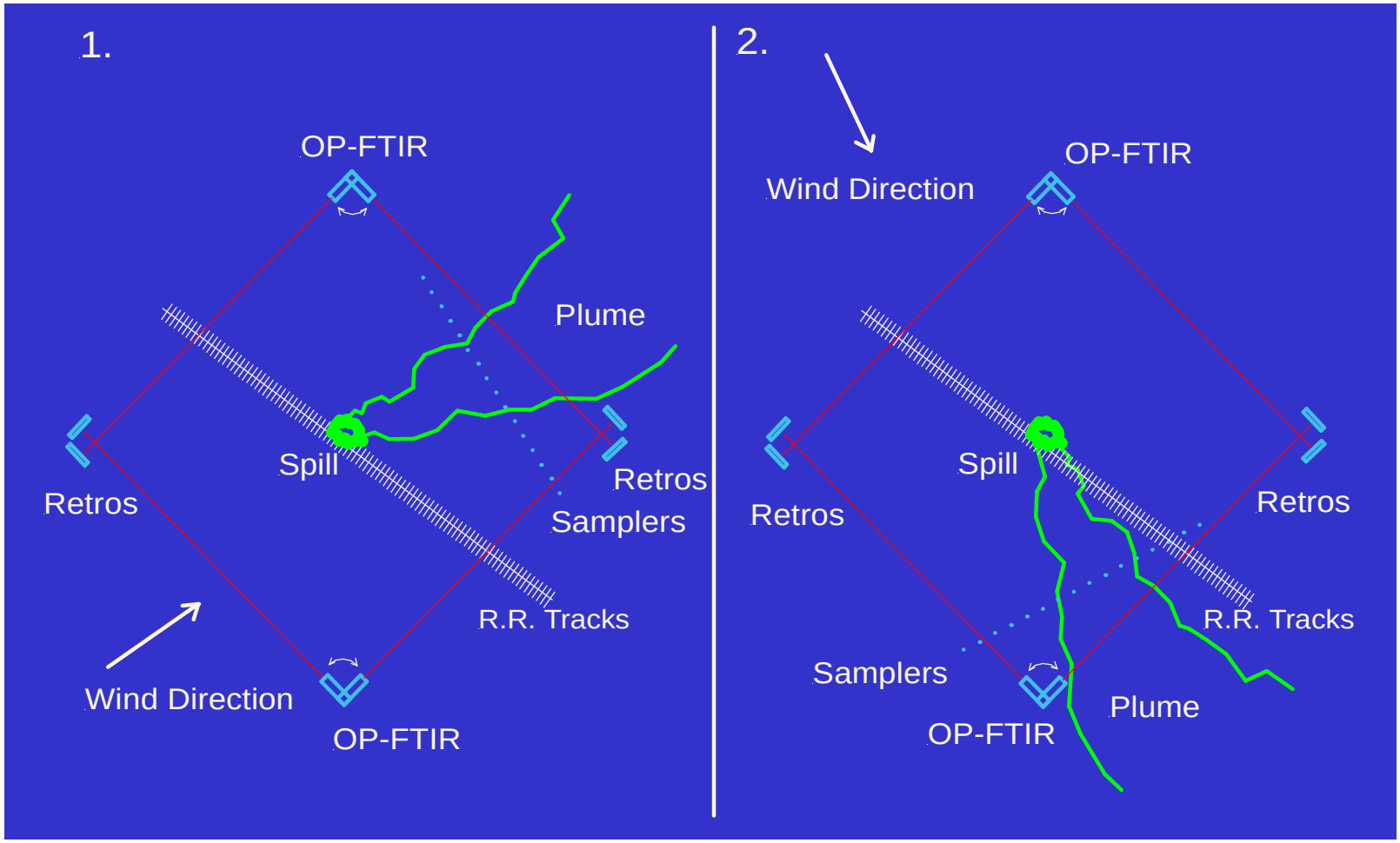
Formaldehyde - Extractive FTIR Versus Other NIOSH Methods

NIOSH Method	Description	Max. Flow rate (L/min.)	Min Volume (L)	Min Time	Detection Limit	Minimum Concentration
2016	DNPH treated silica gel tubes- HPLC	1.5	1	40 sec	0.23 ug	0.2 ppm
2541	HMP treated XAD-2 tubes-GC	0.1	1	10 min	3 ug	2.7 ppm
3500	Impinger, bisulfite-colorimetric	1.0	1	1 min	2 ug	1.8 ppm
3800	Extractive FTIR-direct reading	NA	NA	1 min to fill gas cell (Miran SapphIRe)	0.4 ppm (10 meter gas cell)	0.4 ppm

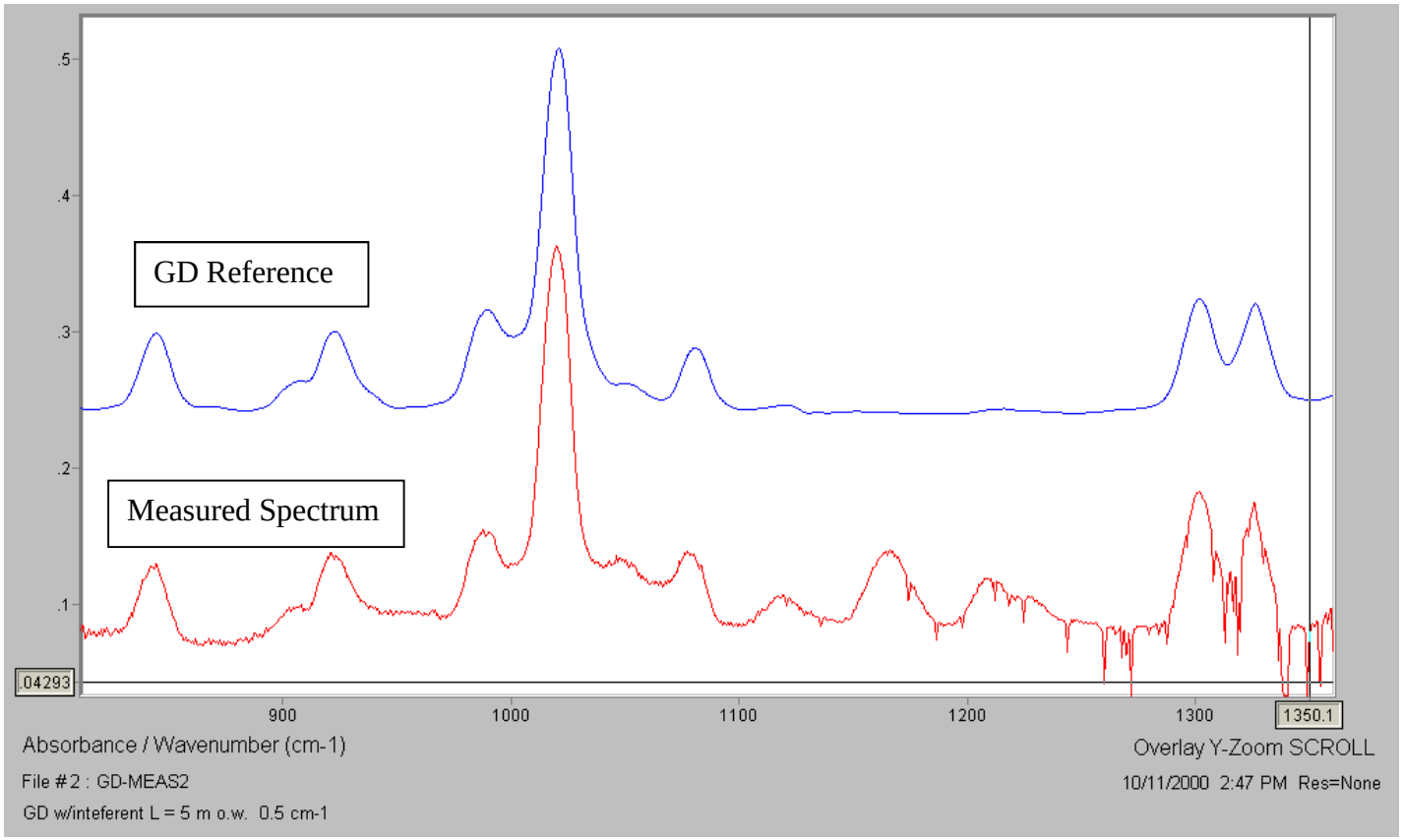
OP-FTIR Measurement



Tomographic Monitoring Scenario at Chemical Accident



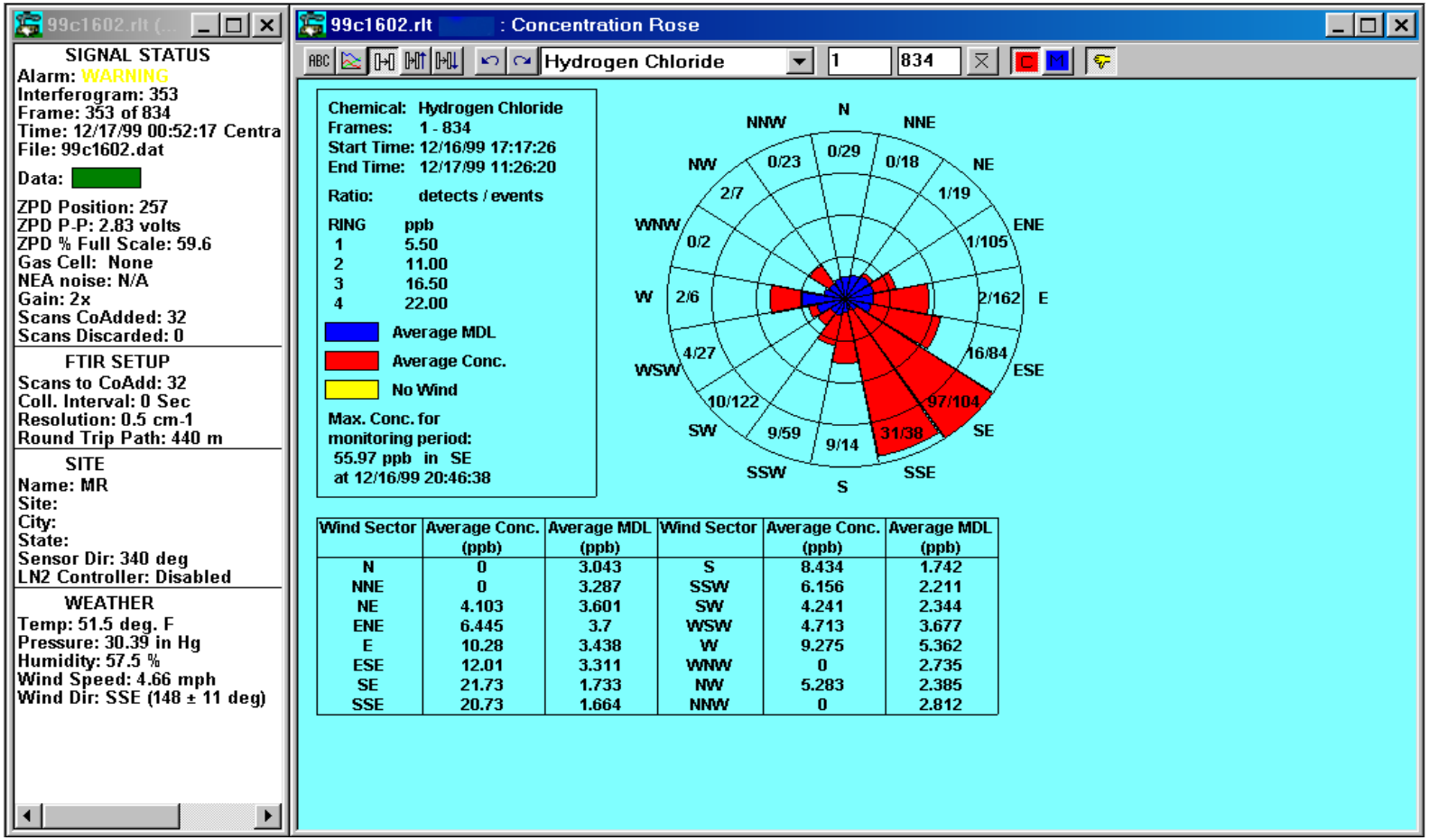
Comparison of Measured Spectrum to GD reference



Open-Path FTIR Detection Limits for Chemical Warfare Agents

Chemical Agent	MDL (100 to 500 m) Meas. time = 2 sec	MDL (200 meters) Meas. time = 1 min
	(ppb)	(ppb)
GA	1.2	0.3
GB	0.7	0.2
GD	1.1	0.3
GF	0.9	0.2
HD 186	3	0.8
Lewisite	4	1.0
VX 22	16	4

Concentration-Rose Points to Emission Source



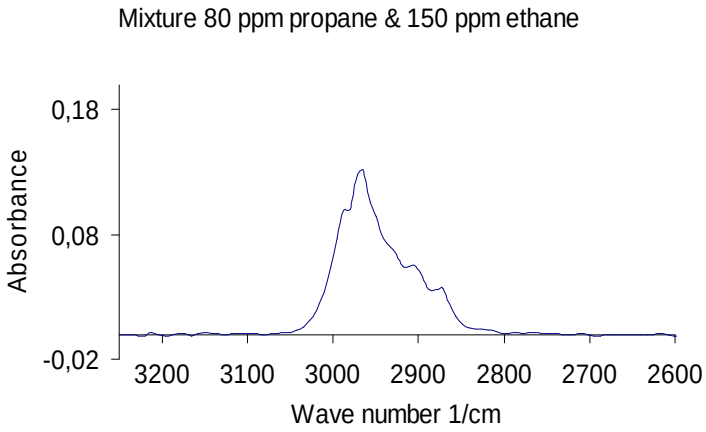
Wind Sector	Average Conc. (ppb)	Average MDL (ppb)	Wind Sector	Average Conc. (ppb)	Average MDL (ppb)
N	0	3.043	S	8.434	1.742
NNE	0	3.287	SSW	6.156	2.211
NE	4.103	3.601	SW	4.241	2.344
ENE	6.445	3.7	WSW	4.713	3.677
E	10.28	3.438	W	9.275	5.362
ESE	12.01	3.311	WNW	0	2.735
SE	21.73	1.733	NW	5.283	2.385
SSE	20.73	1.664	NNW	0	2.812

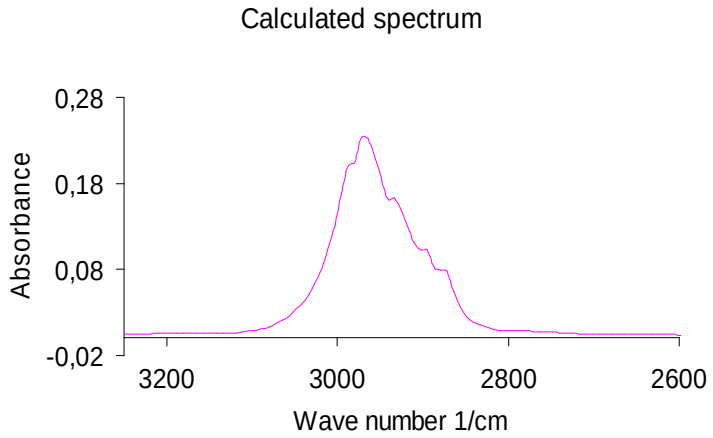
Classical Least Squares Analysis (CLS)

CLS analysis is an iterative process

- At each step every individual reference spectrum is given a coefficient (**k**)
- Model spectrum is calculated as a sum of reference spectra weighted by coefficient (**k**)
- The difference between measured spectrum and model spectrum is called **residual spectrum** (residual)
- The residual is calculated in every data point of the selected analysis area
- The CLS algorithm searches for smallest possible residual by changing the **k** values
- When the minimum residual is found, the concentrations in the sample spectrum are **k** times concentration of the reference spectra

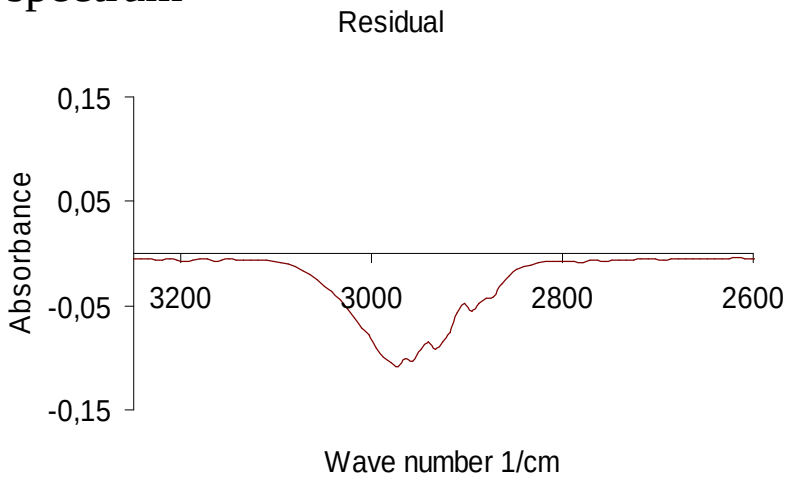
Initial quess: Propane = 100 ppm, ethane = 100 ppm



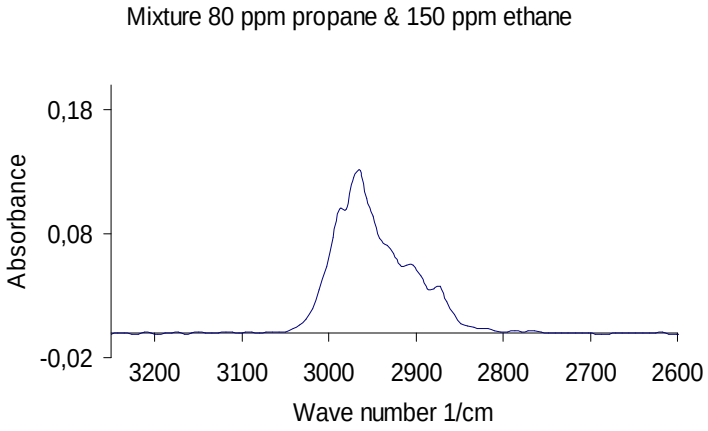


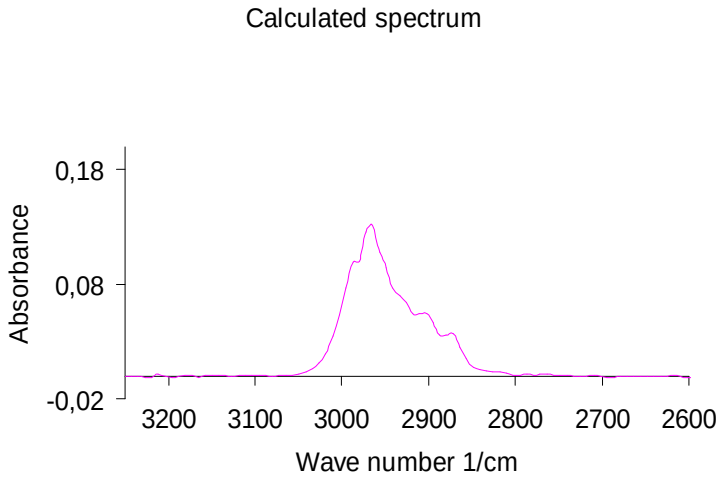
Residual = Sample spectrum – Calculated spectrum

Residual not in minimum
-> optimisation continued



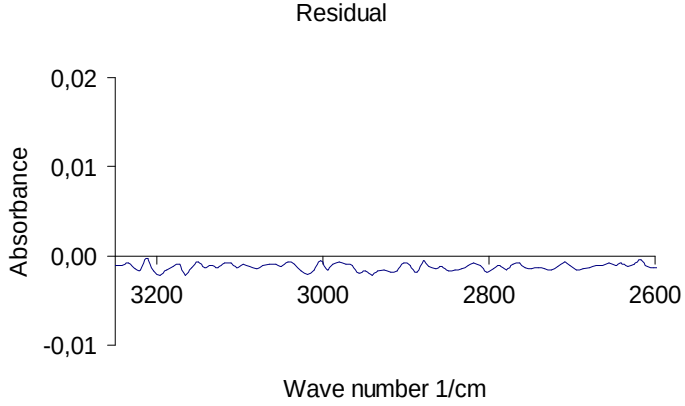
The optimisation stops when:
- k for ethane is 1.5
- k for propane is 0.8



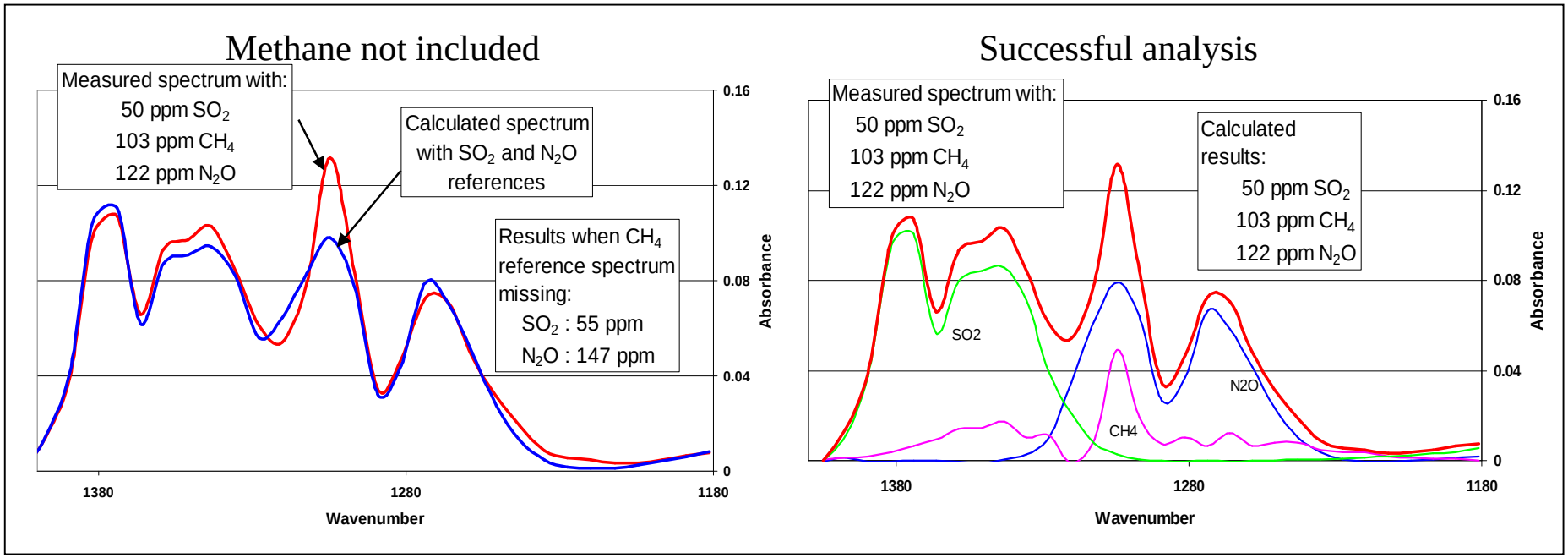


Residual is only noise:
Succesful analysis!

Concentrations:
Ethane = 1.5 X 100 ppm = 150 ppm
Propane = 0.8 X 100 ppm = 80 ppm



Cross interference correction



- Cross interference occurs when one or more gases are missing from the library
- Incomplete library leads to large difference between measured and calculated spectrum → analysis error
- Cross interference may be avoided by selecting suitable analysis areas avoiding the interfering absorption if the library cannot be expanded.

Advantages of the Open Path FTIR

- Can monitor many compounds simultaneously
- Produces near-real time, continuous results
- Can cover a broad range of concentrations
- Can monitor long, multiple open-air paths
- Rugged design applicable to industrial monitoring at industrial fencelines
- Cost effective for large area survey analysis
- Data can be correlated to air dispersion modeling

Materials for Spectroscopic Instruments

	Mirrors	Lenses	Windows
Ultraviolet	aluminum	fused silica, sapphire	fused silica, sapphire
Visible	aluminum	glass, sapphire	glass, sapphire
Near infrared	gold	glass, sapphire	glass, sapphire
Infrared	copper, gold	CaF_2, ZnSe	NaCl, BaF_2, CaF_2, ZnSe

Reflection Losses

substance	refractive index
Glass	1.5
Air	1.0
Water	1.3

$f = [(n_1 - n_2) / (n_1 + n_2)]^2$ = fraction reflected

Examples: for thin glass plate = 92 % T

for an empty cell = 85 % T

for liquid filled cell = 91.3 % T

Prevention: 1) run blank with solvent

2) use matched cells

Slits

	Wide slits	Narrow slits
Throughput	High	Low
Resolution	Low	High
Quant	Good	Poor
Qual	Poor	Good

- Slits are used to limit the amount of light impinging on the dispersing element as well as to limit the light reaching the detector.

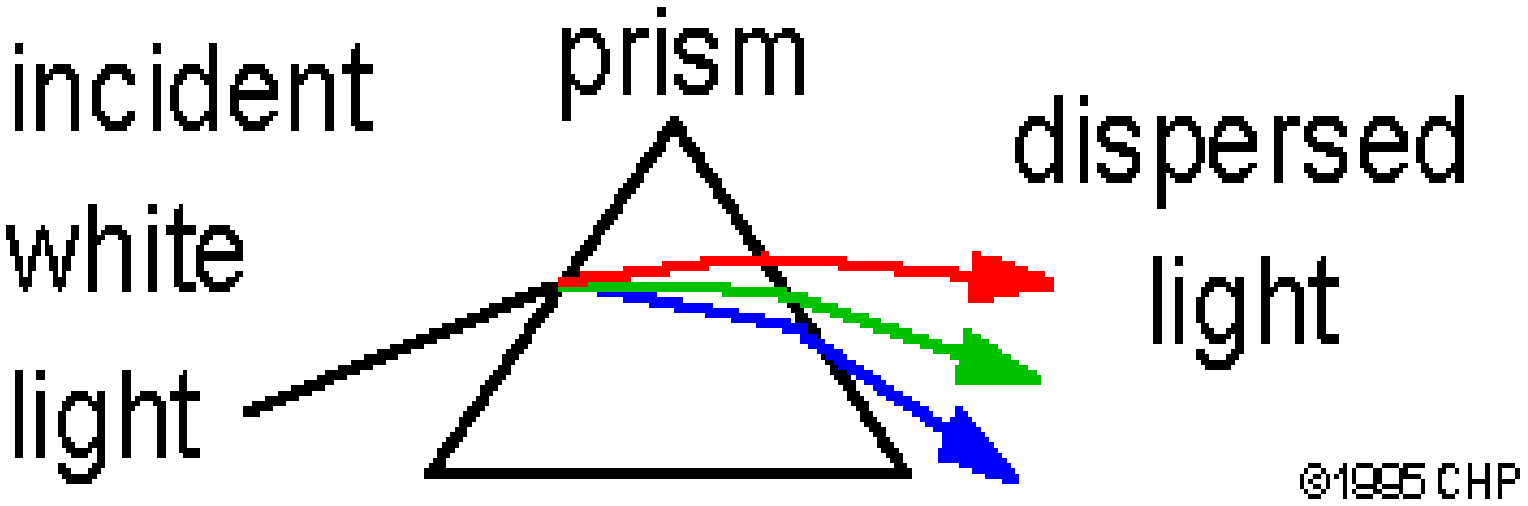
- There is a dichotomy between intensity and resolution.

Voltage regulation required as radiant power varies

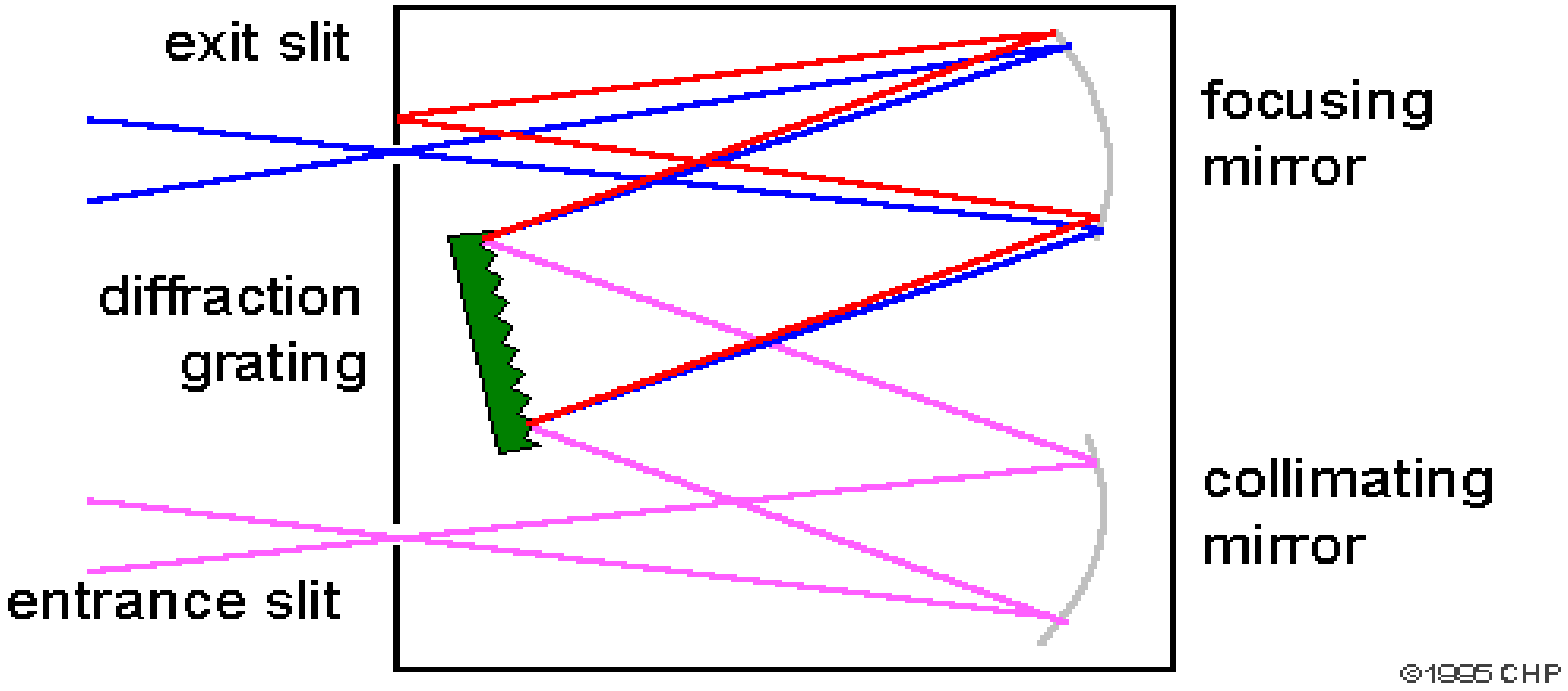
exponentially with voltage

Continuum Sources	
Ar Lamp	VAC UV
Xe Lmp	VAC UV, UV-VIS
H_2 or D_2 Lamp	UV
Tungsten Lamp	UV-Near IR
Nernst Glower	UV-VIS-Near IR-IR
Nichrome Wire	Near IR-Far IR
Globar	Near IR-Far IR
Hollow Cathode Lamp	UV-VIS
Lasers	UV-VIS-Near IR

Polarizing prisms: made of birefringent materials



Czerny-Turner:
two mirrors used to collimate and focus

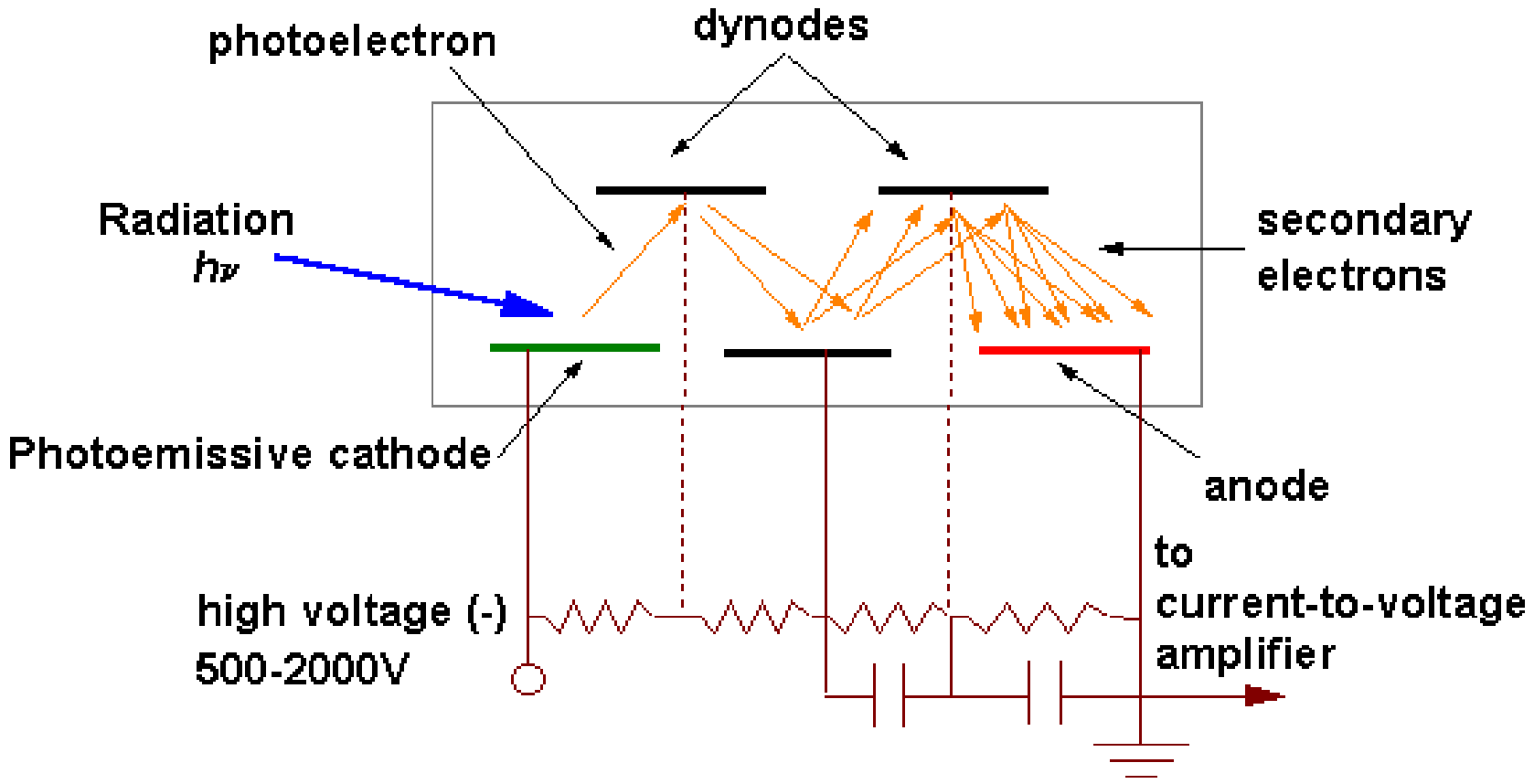


SAMPLE CONTAINERS

Spectral Region	Material
UV	Fused silica
VIS	Plastic, glass
NaCl	IR

- Required of all spectroscopic methods except emission spectroscopy
- Must be made of material that is transparent to the spectral region of interest

Photomultiplier Tubes



Spectral Range of UV-Vis Detectors

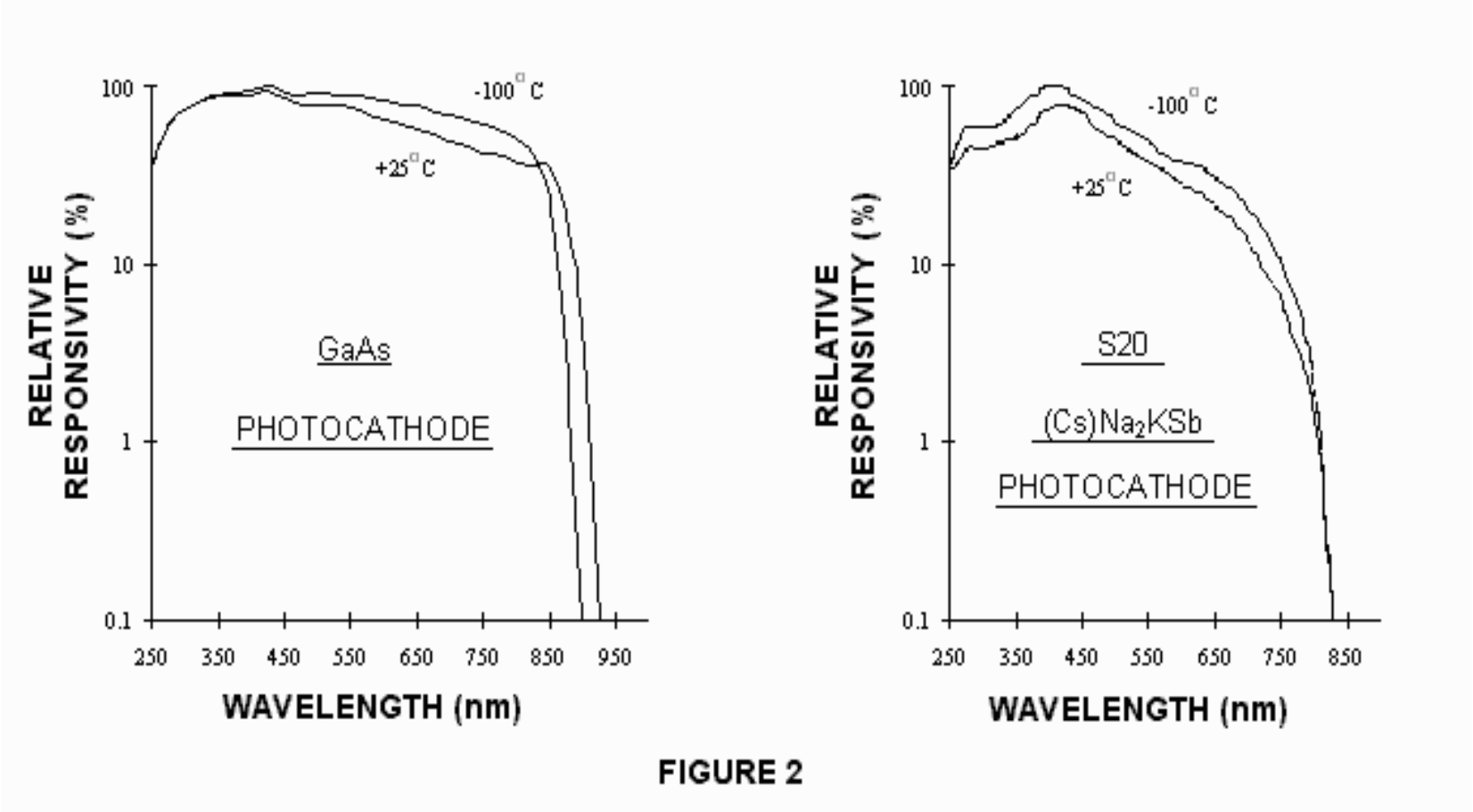


FIGURE 2

Thermionic emission: energy available since PMT is not at absolute zero (0 K)

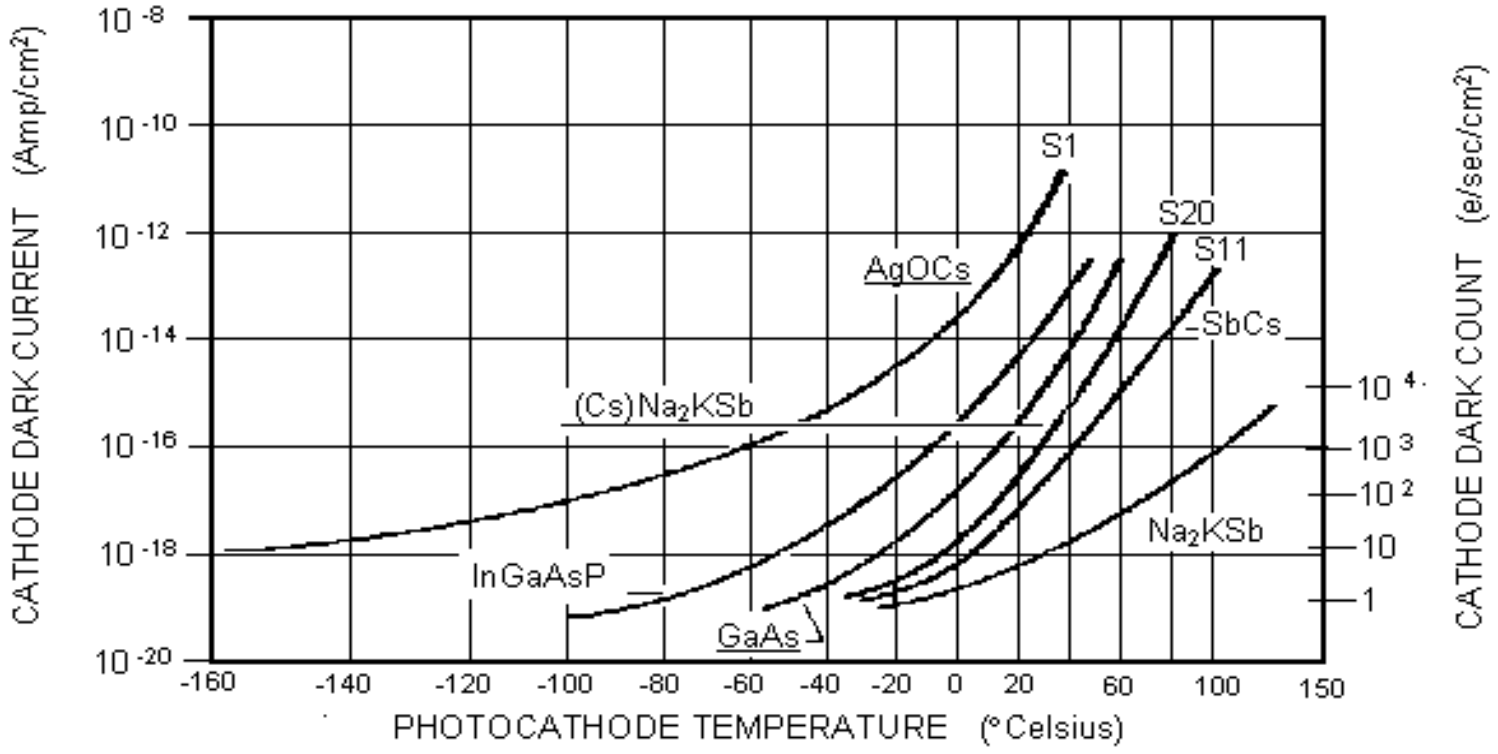
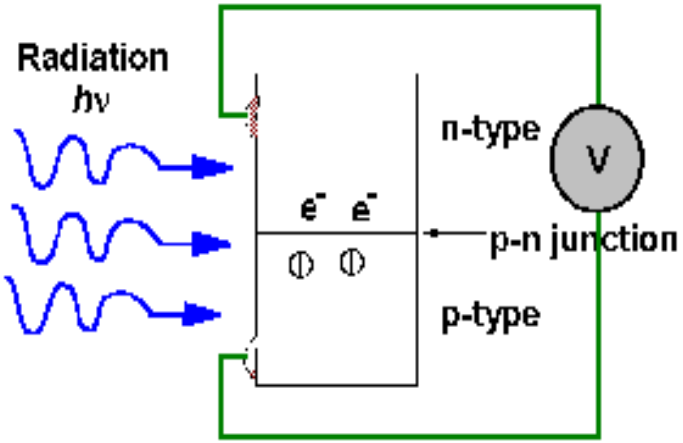


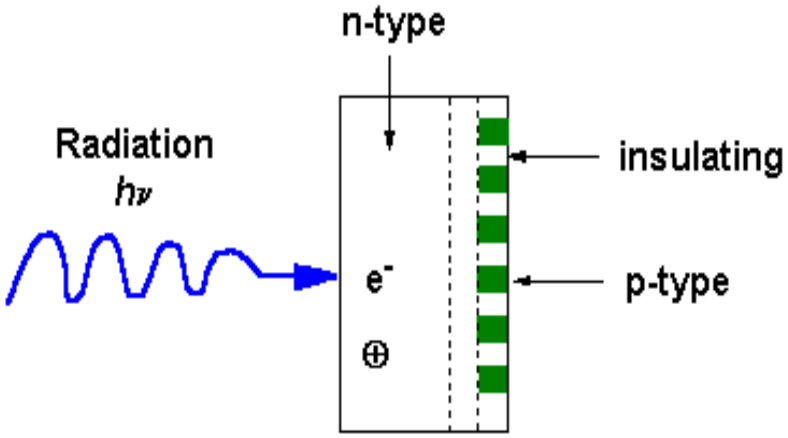
FIGURE 1

ARRAY DETECTORS

- An "electrical photographic plate"
- Detect differences in light intensity at different points on their photosensitive surfaces
- Fabricated from silicon using semiconductor technology
- Originally conceived as television camera sensing elements
- Placed at focal plane of polychromator in place of the exit slit
- Sensitive for detection of light in 200-1000 nm range
- Major advantage is simultaneous detection of all wavelengths within range
- Types
    1) SIT : silicon intensifier target
    2) PDA : photodiode array
    3) CCD : charge-coupled device
    4) CID : charge injection device



PHOTODIODE ARRAYS (PDA)

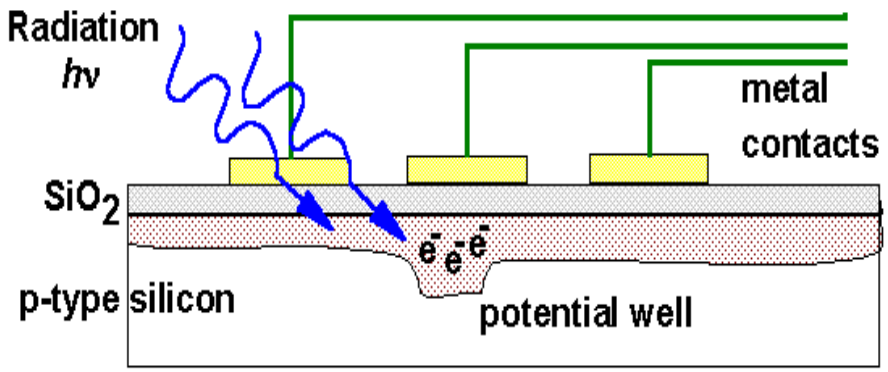


Process

- Each diode in the array is reverse-biased and thus can store charge like a capacitor
- Before being exposed to light to be detected, diodes are fully charged via a transistor switch
- Light falling on the PDA will generate charge carriers in the silicon which combine with stored charges of opposite polarity and neutralize them
- The amount of charge lost is proportional to the intensity of light

Charge-Coupled Devices (CCD)

- Invented in 1970
- Potential well formed by an electrode as in CID
- p-type material, however, used to store charges as electrons
- After exposure to light charge packets are transferred along the row to special
- low-capacitance readout diode
- Passage of charge induces a voltage change proportional to amount of charge
- Small pixels are not well-suited to ordinary dispersive spectroscopy



- Summation is done on the chip rather than in memory after the readout, thus only one read
- operation required for all the pixels to be summed, thus lower readout noise per pixel is achieved

COMPARISON OF OPTICAL DETECTORS FOR THE VISIBLE AND ULTRAVIOLET

- Three most important factors
  1. Sensitivity: Sensitivity of Si > than photocathode materials in PMT
  2. Noise sources

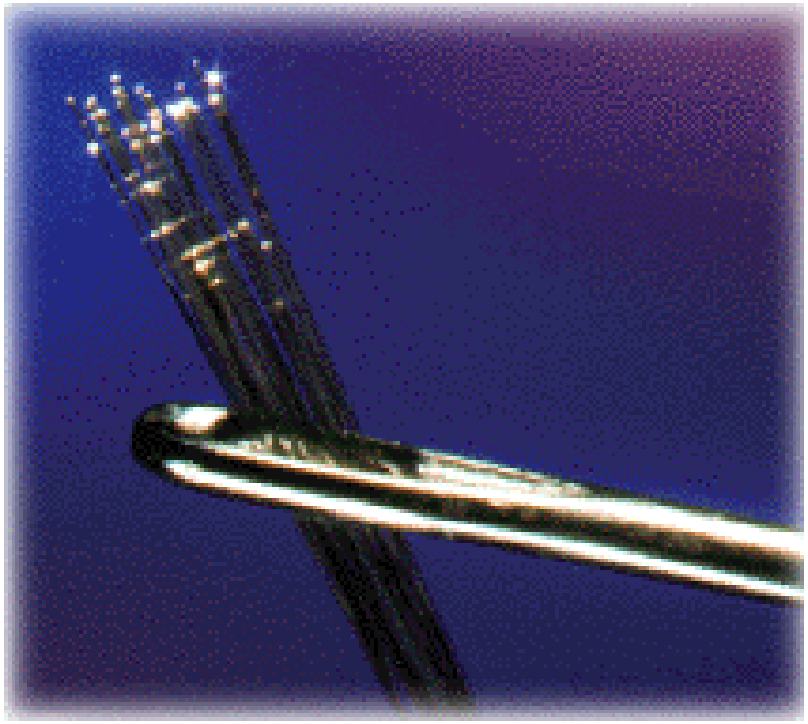
     Dark current in solid Si due to thermally generated electron-hole pairs

     Readout noise generated due to reading amounts of charge stored by detector elements
  3. Dynamic range

     PMTs have dynamic ranges of 10^5-10^6

     Charge transfer devices have single pixel dynamic ranges of about 10^4
- Costs
  1. Array detectors k$25-50
  2. PMT advantage when spectrum acquisition time not important
  3. Array readout times 0.5 ms (1000 diode PDA) - 5 s (520x312 pixel CCD)

FIBER OPTICS



- Properties of Optical Fiber
  transmission of this light depends on the total internal reflection
- Fiber-Optic Sensors
  optrodes- consist of a reagent phase immobilized on the end of a fiber optic
- Fiber Optics for Time
  Discrimination among Signals- use strands of different lengths signal delay of 50 ns per 10 m of fiber that it transverses