FTIR Seminar

Chapter 1 Principles and Fundamentals of Infrared Spectroscopy
Chapter 2 Principles of FTIR
Chapter 3 Standard Data Processing Features
Chapter 4 Transmittance Techniques
Chapter 5 Reflectance Techniques
Chapter 6 Quantitative Analysis (Optional Software)
Chapter 7 Infrared Spectrum Analysis Techniques

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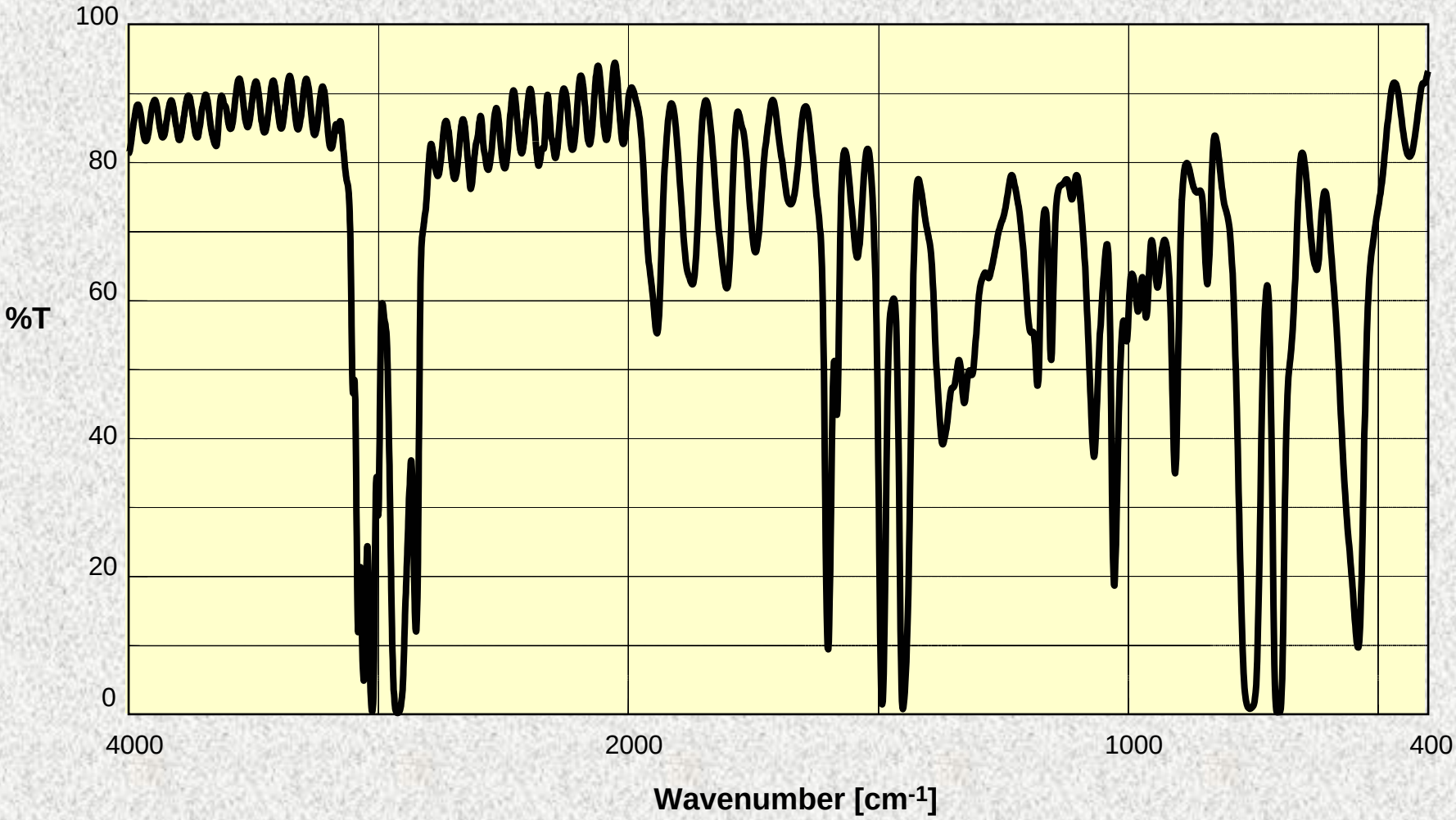
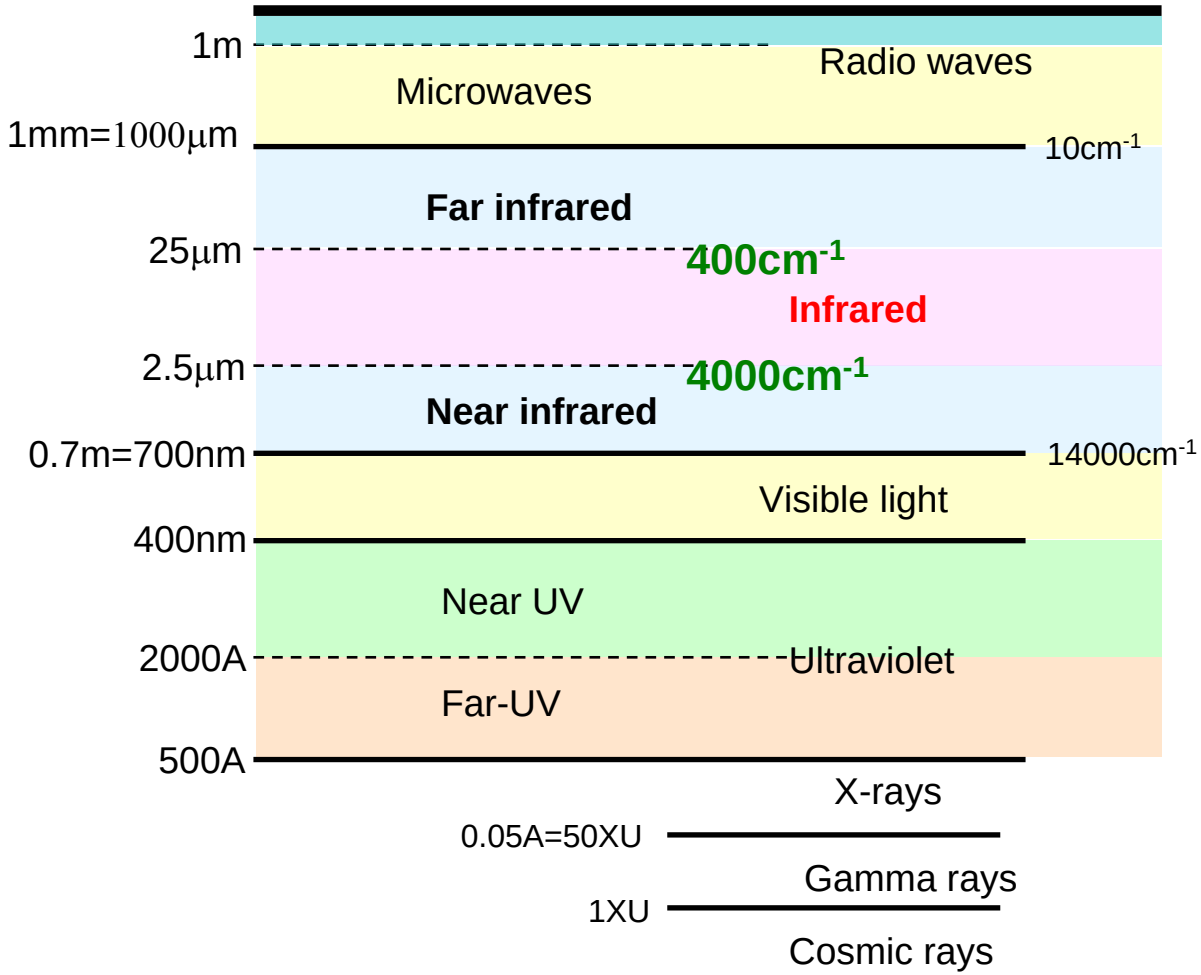
Chapter 1

Principles and Fundamentals of Infrared Spectroscopy

Infrared absorption spectrum

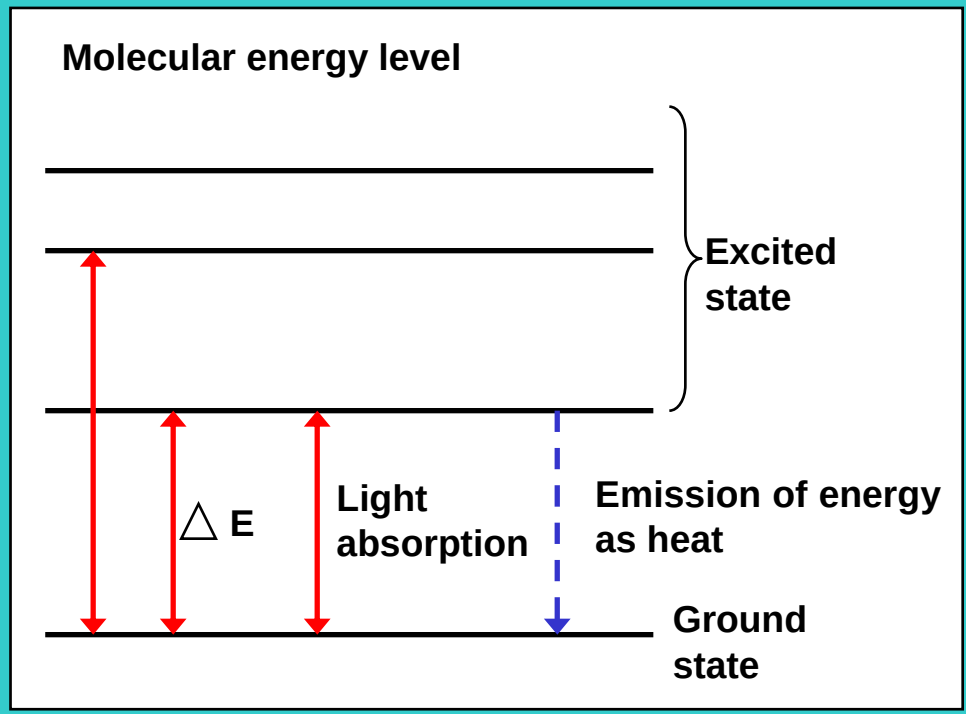


Types of Electromagnetic Radiation



Interaction between Molecular Dynamics and Light

Molecular energy = electronic energy
+ vibrational energy
+ rotational energy



△ E

Electronic energy ≒ Visible light and ultraviolet energy

Vibrational energy ≒ Infrared energy

Rotational energy ≒ Near-infrared energy

Molecular Vibration of Diatomic Molecules

Infrared light and a molecule only interact when the dipole moment of the molecule changes due to vibration

Spring between two spheres

Heteronuclear diatomic molecules : HCl, CO Infrared active

Homonuclear diatomic molecules : O_2, H_2, N_2, and CL_2 Infrared inactive

Vibrational Frequency of Diatomic Molecules

The Vibrational Frequency of a diatomic molecule for which the absorption position, bond strength = spring strength, can be expressed by the following equation

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{f(m+m')}{mm'}}$$

ν is determined by m and m'

f : strength constant (bond constant and bond order)

m and m' : mass number of atom

***C* : Speed of light**

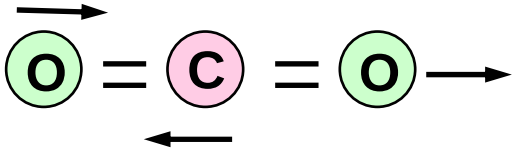
Normal Frequency of Triatomic Molecules (CO_2)

CO_2: linear molecule

(1) Symmetric stretching vibration

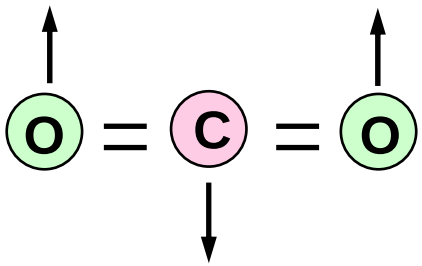
Infrared inactive

(2) Asymmetric stretching vibration

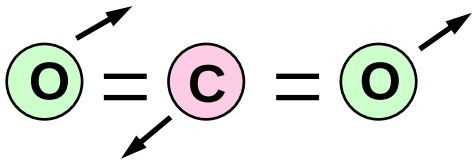


2349cm^{-1}

(3) Deformation vibration



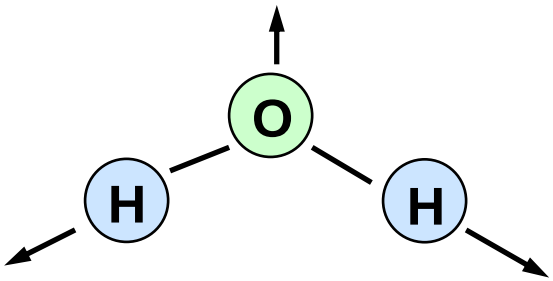
667cm^{-1} Degeneracy



Normal Frequency of Triatomic Molecules (H_2O)

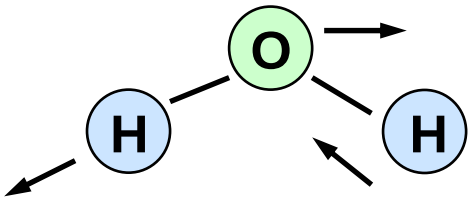
H_2O : nonlinear molecule

(1) Symmetric stretching vibration



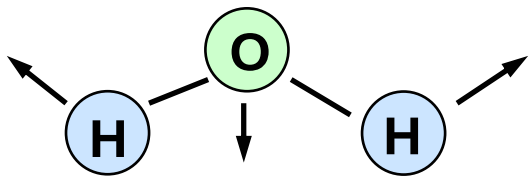
3652cm^{-1}

(2) Asymmetric stretching vibration



3756cm^{-1}

(3) Deformation vibration



1595cm^{-1}

Number of Normal Frequencies

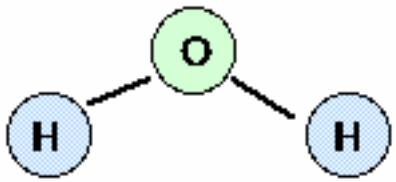
The number of normal frequencies of a molecule consisting of n atoms can be determined by the following calculations:

Linear molecule ····· 3n-5

Nonlinear molecule ··· 3n-6

Example :

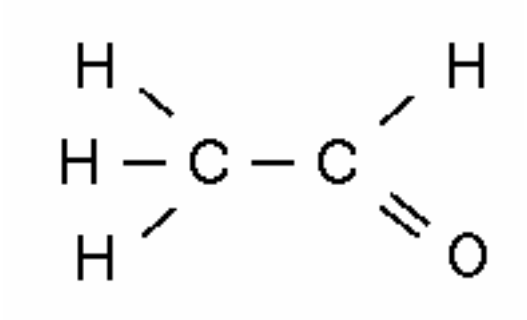
····· 3 x 3 − 5 = 4

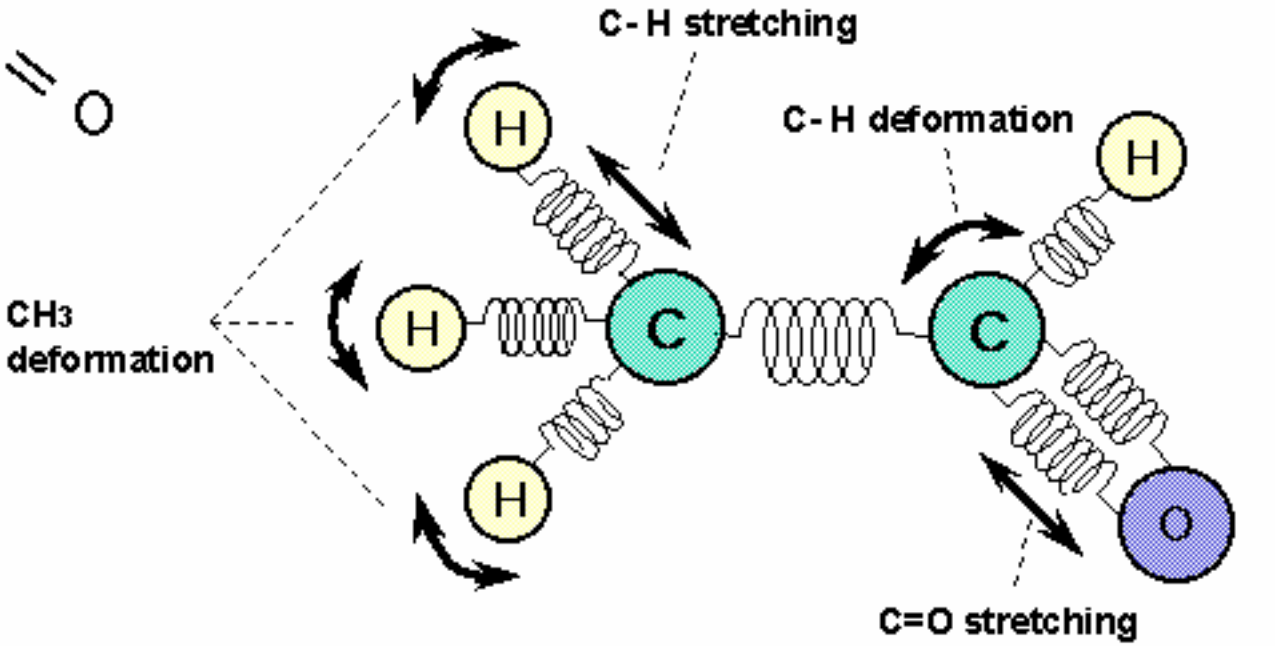


····· 3 x 3 − 6 = 3

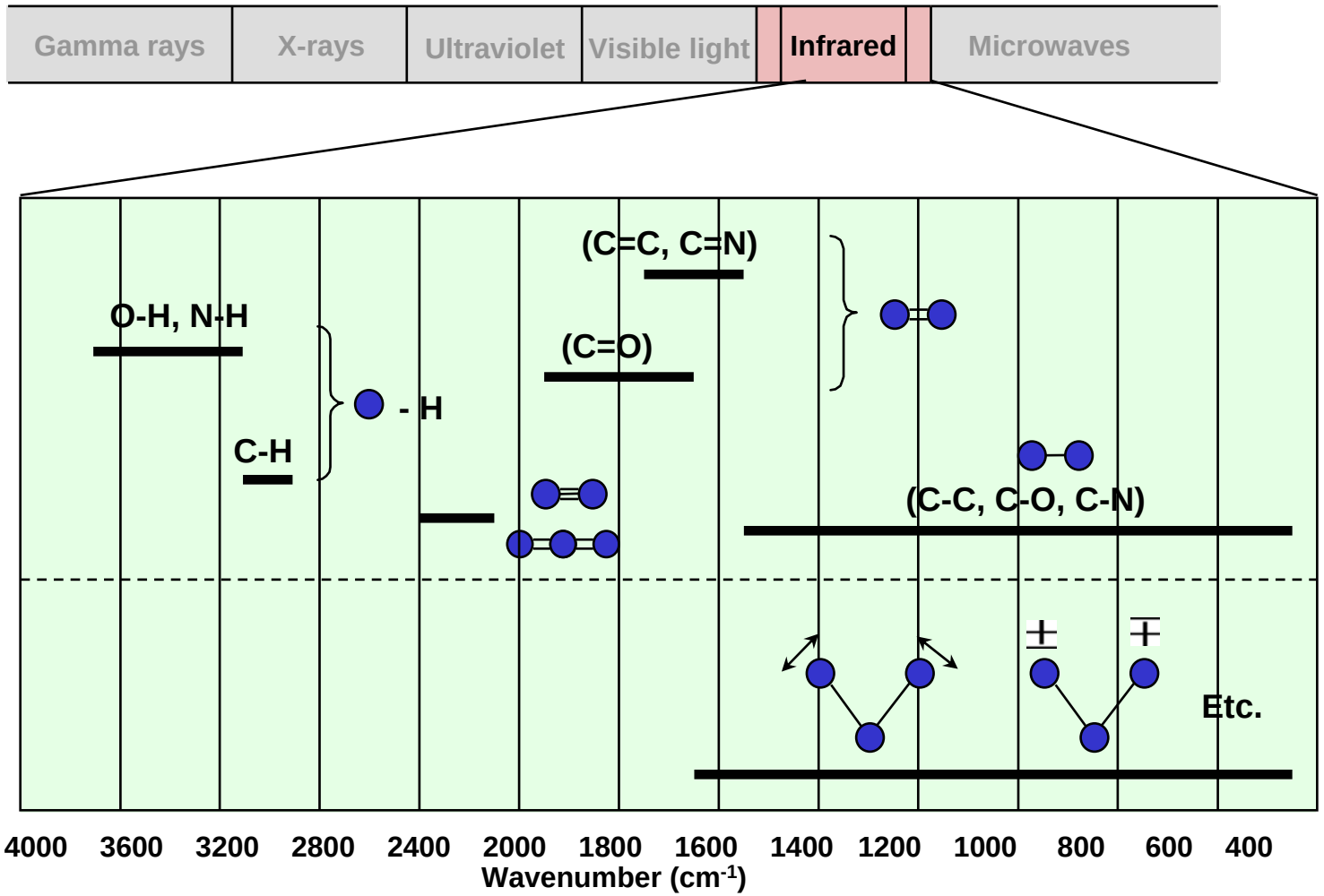
Molecular Vibration of Polyatomic Molecules

Example : Acetaldehyde

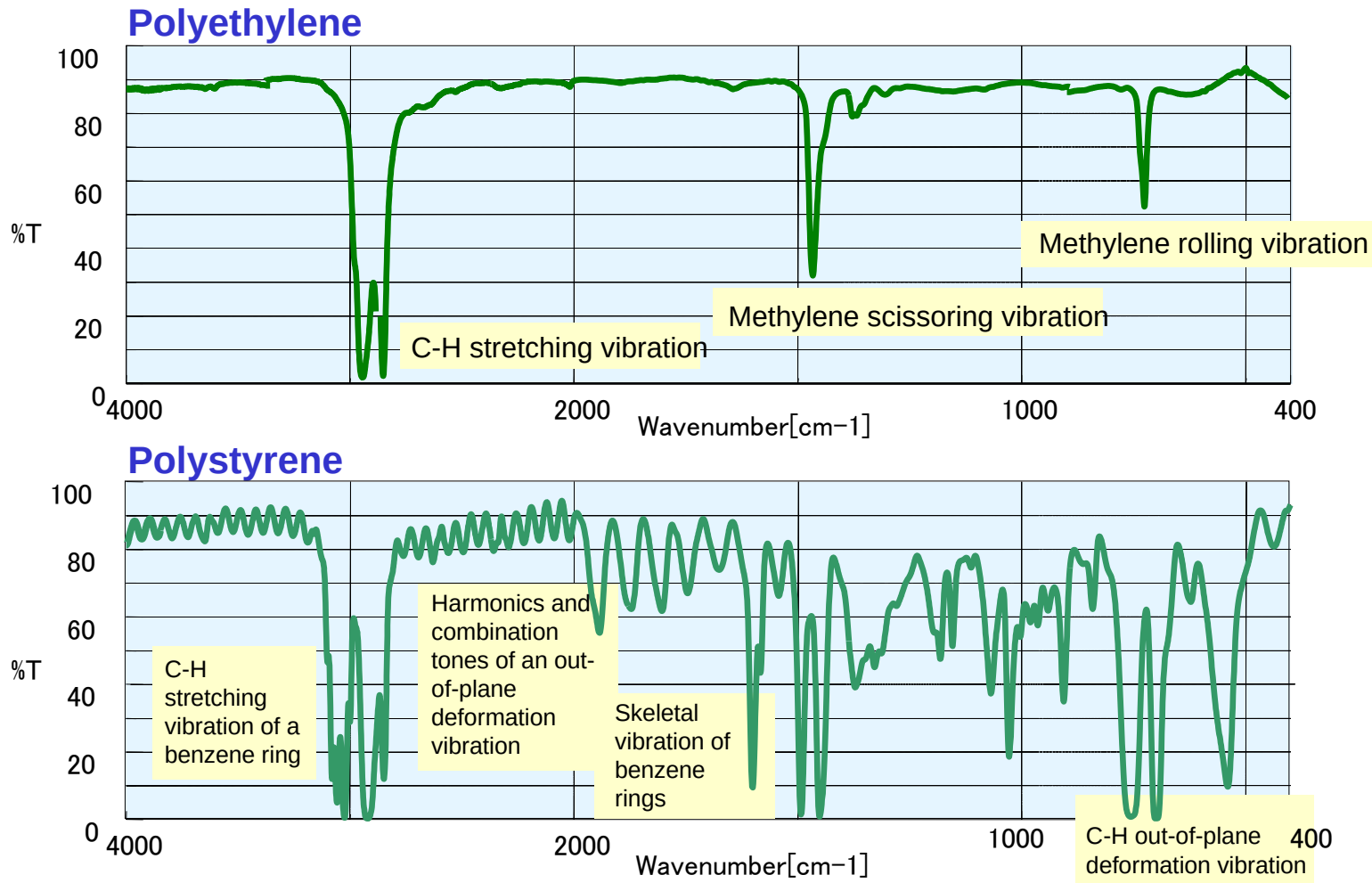




Absorption Position



An Example of Assignment



Absorption Strength

Absorption strength depends on the size of deformation of the dipole moment due to vibration

$$\mu = -\Sigma qiri$$

μ : dipole moment

qi : electric charge of the i-th nucleus

ri : position vector of the i-th nucleus

Deformation of the dipole moment is large : strong absorption C=O, C-X

Deformation of the dipole moment is small: weak absorption C-C

Near-Infrared Absorption Spectrum

Principles of absorption

Harmonics or combination tones of normal frequencies

Primarily **O-H**, **N-H**, and **C-H**

Weak absorption compared to the infrared region

Spectrum shape is complex

Analysis

A recent trend is quantitative analysis by the application of Chemometrics

Main Applications

Nondestructive analysis in agriculture- and food-related fields

Far-Infrared Spectrum

Absorption principles

- **Vibrations of heavy atoms and weak bonds**

  Example : Metals such as copper and tin
  Sulfur and iodide
  Coordinate bonds (complexes)

- **Rotation**

Conclusion of Chapter 1

(1) Region

- **Infrared : 4,000 to 400 cm^{-1}**
  - Produces information on molecular vibration and rotation
- **Near infrared : above 4,000 cm^{-1}**
  - Almost entirely harmonic peaks of normal frequency
  - Samples containing moisture can also be measured
  - Introduced in the fields of processed foods and agriculture
- **Far-infrared : below 400 cm^{-1}**
  - Molecular rotation information
  - Metal oxides, metal compounds, and organic and inorganic metal complexes

Conclusion of Chapter 2

(2) Analysis targets : Organic and inorganic substances

(3) State : Gas, liquid, and solid

(4) Analysis description

Qualitative analysis

Functional group analysis

Determines the existence of functional groups by the presence of specific functional group peaks.

Pattern analysis

Estimates compound materials by comparing standard spectra

Quantitative analysis

The strength (absorbance) of the absorption band is proportional to the amount of the material.

↓

Quantitative analysis is possible.

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Chapter 2

Principles of FTIR

Process up to Obtaining a Spectrum

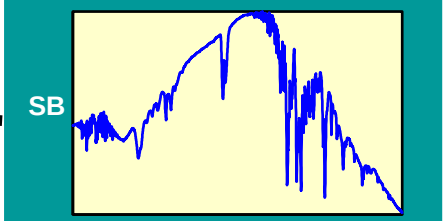
Light source

Interferometer

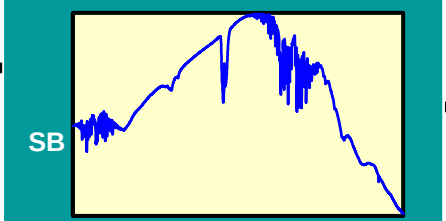
Measurement : Interferogram

Fourier transform process

Sample (S)

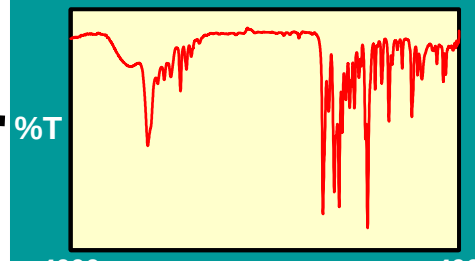


Background (B)

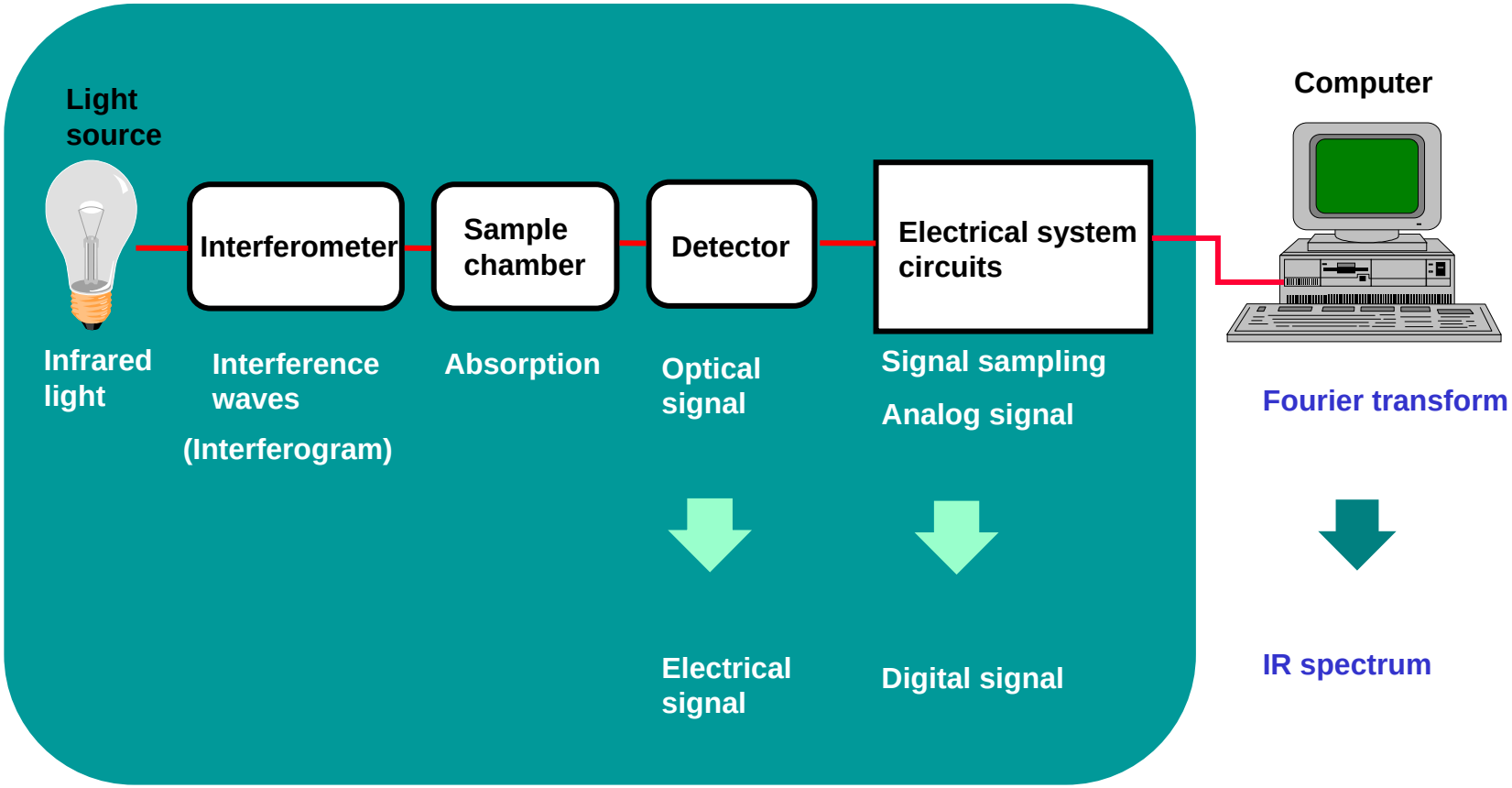


(S) / (B)

Transmission spectrum

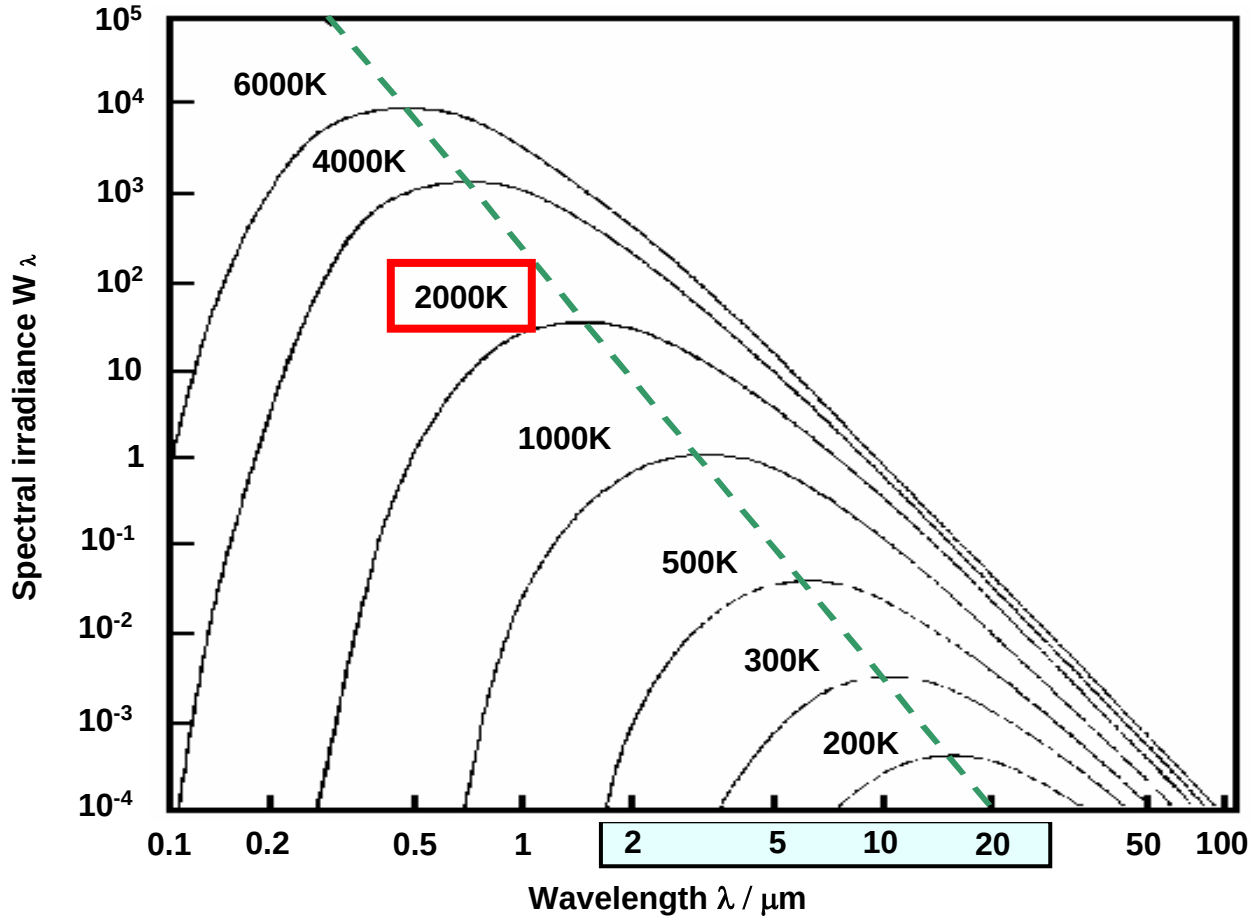


Spectroscope

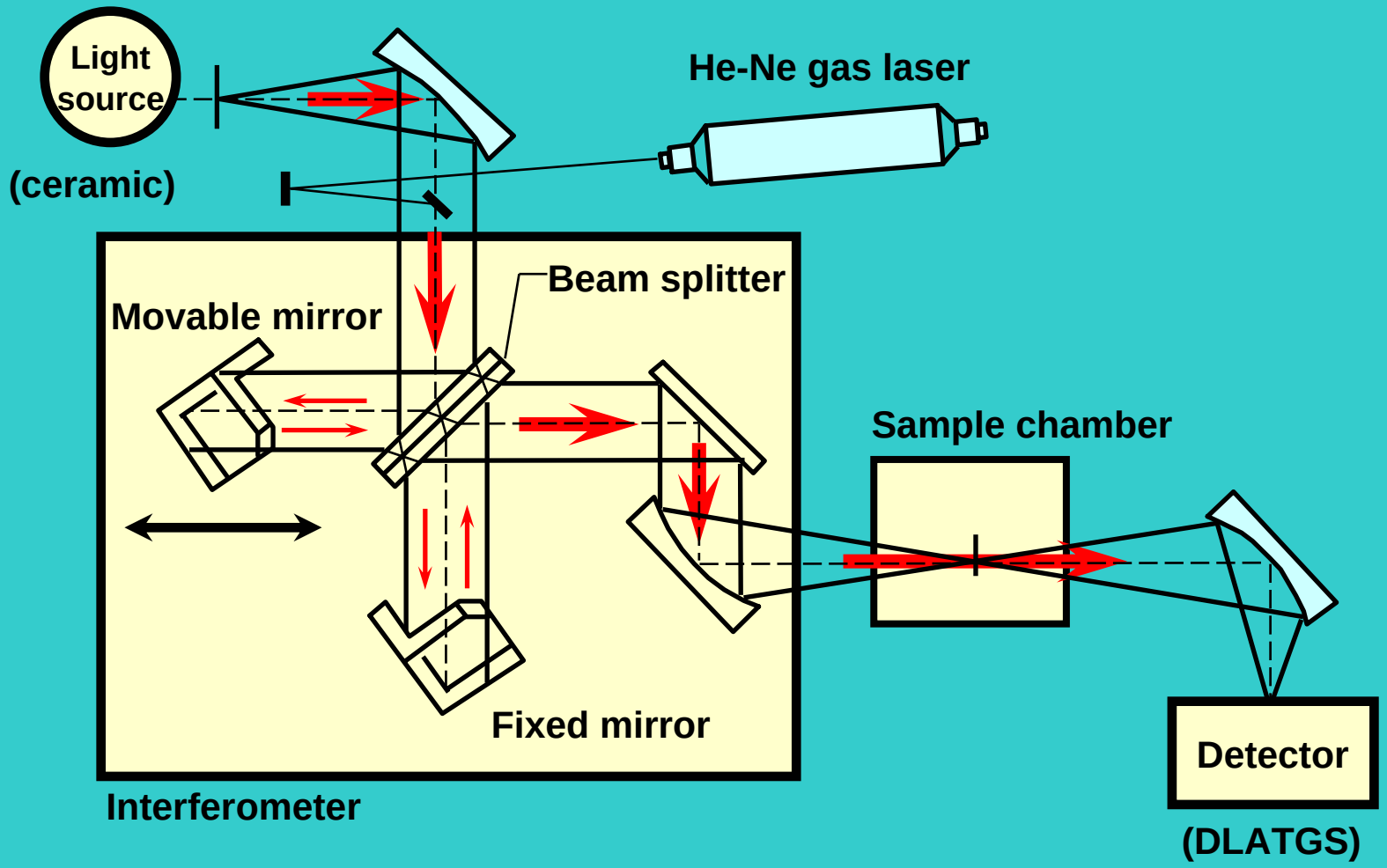


IR light source

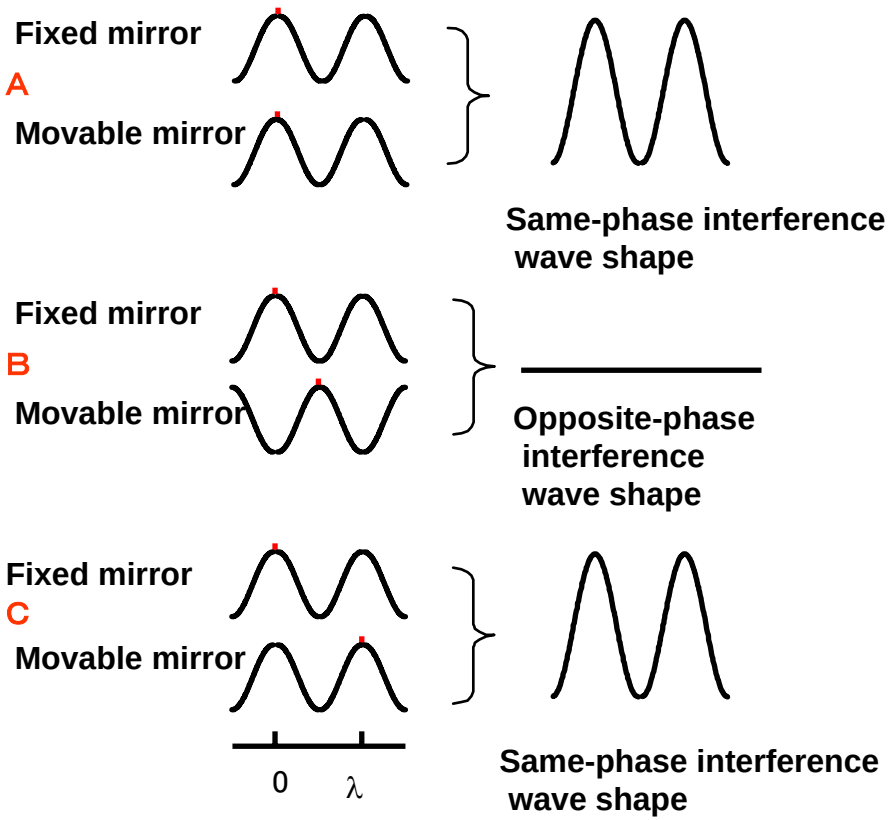
Intensity Distribution and Temperature Dependency versus Wavelength of Black Body Radiation Energy

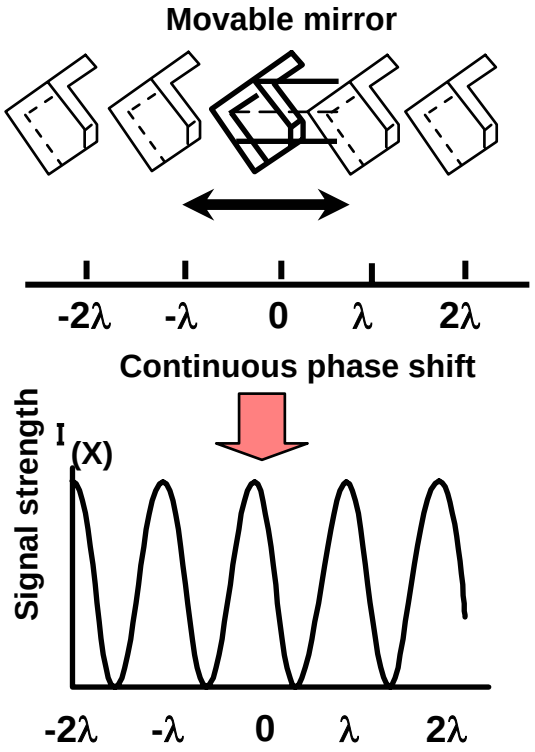


FT Optical System Diagram



Interference of Two Beams of Light





D Interference pattern of light manifested by the optical-path difference

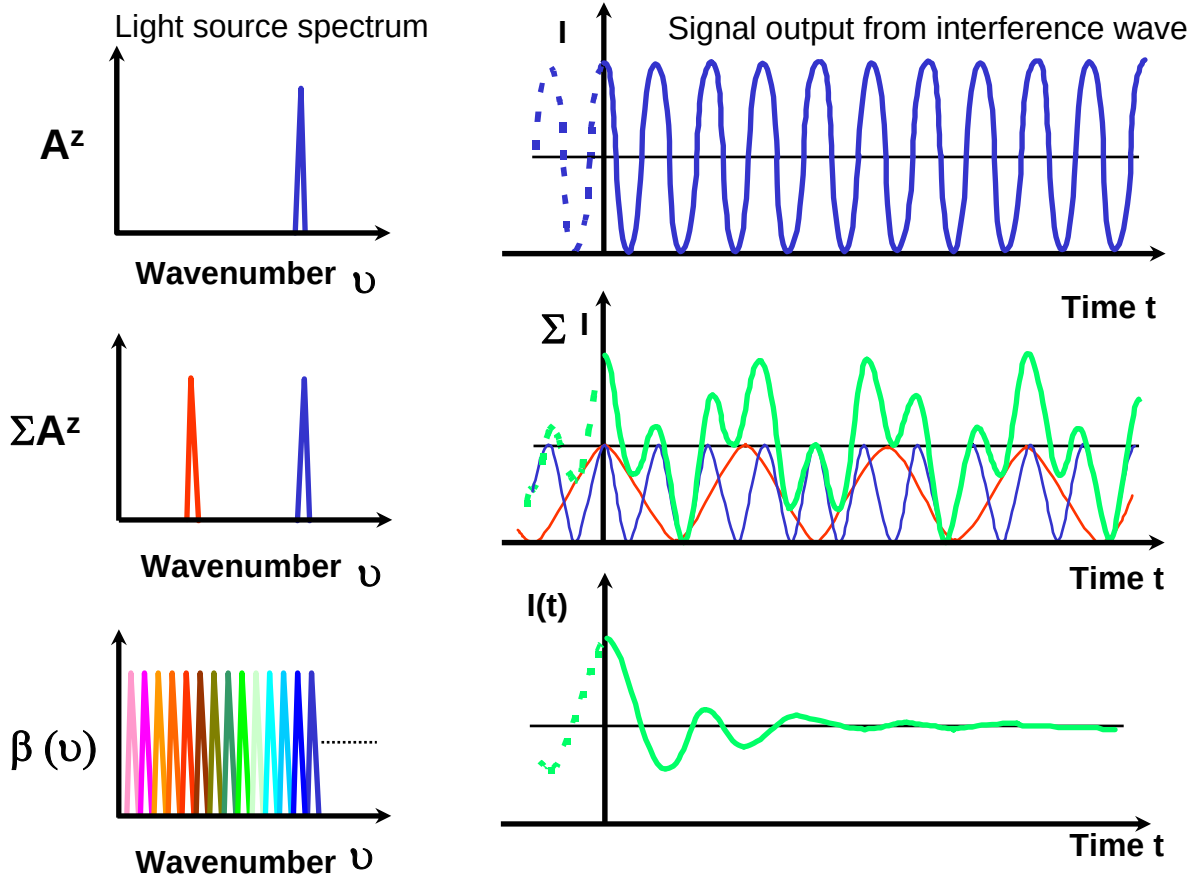
Interference Is a Superpositioning of Waves

Relationship between light source spectrum and the signal output from interferometer

(a) Monochromatic light

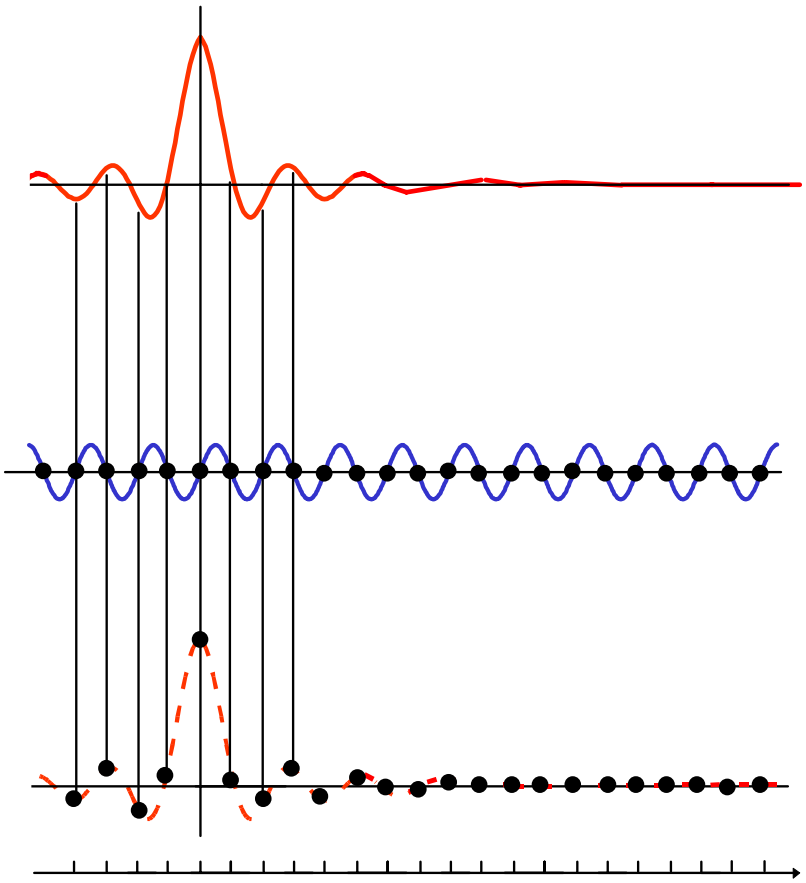
(b) Dichroic light

(c) Continuous spectrum light



- All intensities are standardized.

Sampling of an Actual Interferogram



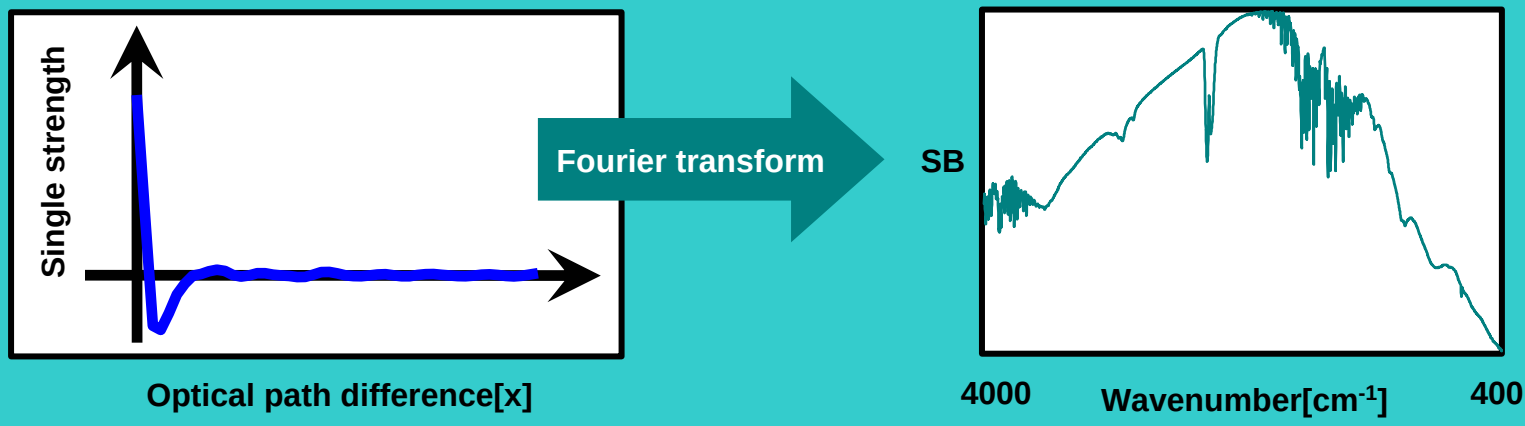
Interferometer interferogram

Output of a Laser interferometer

Primary interferometer interferogram that was sampled

Optical path difference x

Fourier transform

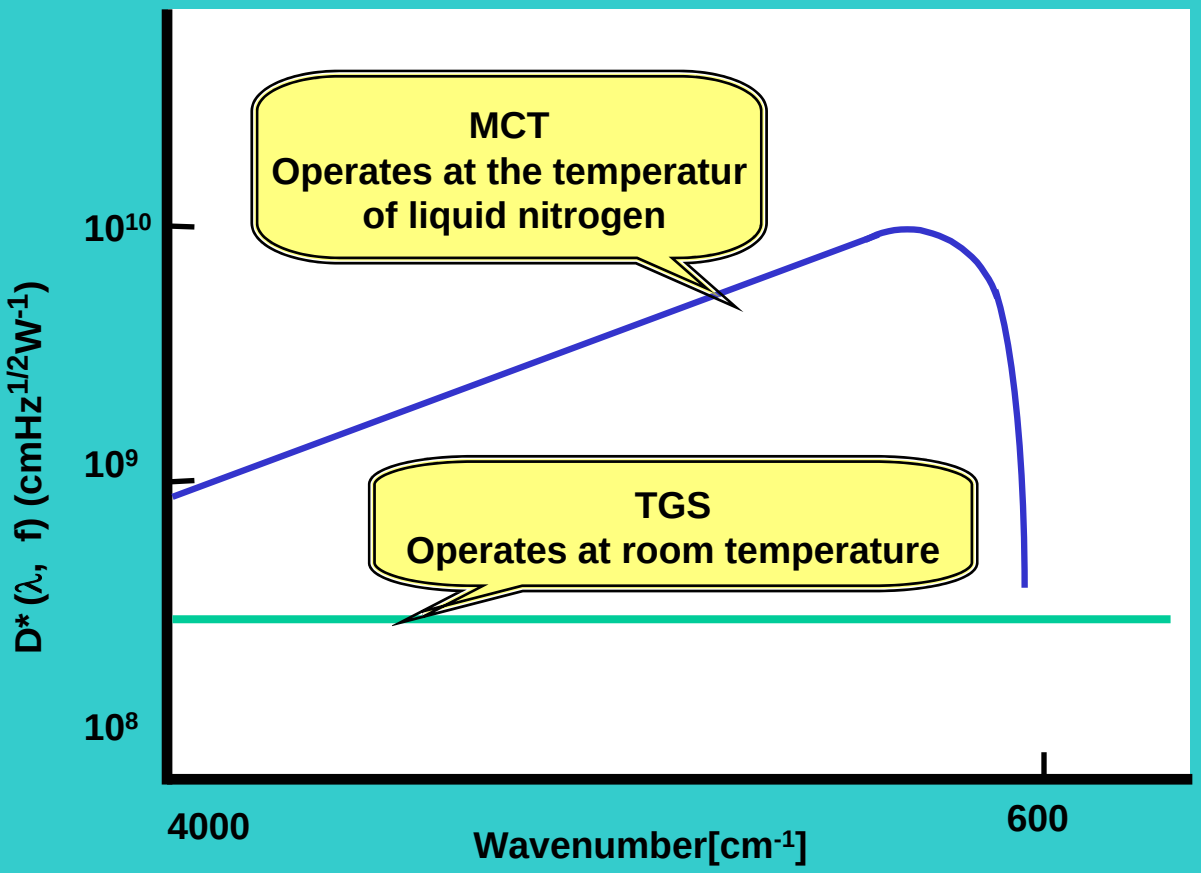


(Interferogram)

(Single beam spectrum)

Time axis by FFT → **Wavenumber**

Detector Properties



Measurement Parameters

Resolution : Fixed, qualitative analysis of liquid sample: Standard 4 cm-1

Gas analysis, peak shift study, and band resolution etc: High resolution
The larger the maximum optical path difference of the interferometer, the higher the resolution

Number of integrations : Approx. ten times normal gain

The goal is to improve the SN ratio. SN ratio improvement can be expected at multiples of the integration count root

Apodization function : Standard Cosine

Since the movable mirror can only move a certain distance, discontinuity arises in the data. Apodization is an operation that treats the end of the interferogram so that there is no difference in level. Apodization is concerned with the shape of peaks (including their sharpness and half-value width)

Zero filling : Interpolation of data (smoothes out data)

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Chapter 3

Standard Data Processing Features

Standard Data Processing Features

Baseline correction :	Fixes curved baselines
Extraneous peak elimination :	Cuts absorption peaks for atmospheric carbon dioxide gas (CO_2)
Smoothing :	Reduces noise by means of computer processing
Difference spectra :	Decomposition of spectra containing multiple components etc.

Peak processing :	Computation of peak position, height, area, and half-value width
Ordinate axis conversion :	%T <-> Abs etc.
KM conversion :	In the diffuse reflectance method, conversion of transmissivity to the y axis proportional to temperature
KK conversion :	Conversion of an abnormal spectrum affected by the sample's refractivity to an absorption spectrum
ATR correction :	Use of ATR to correct spectrum distortion
Mathematical operations :	Mathematical operations for two spectra or a spectrum and constant
Differential :	Differential of spectra

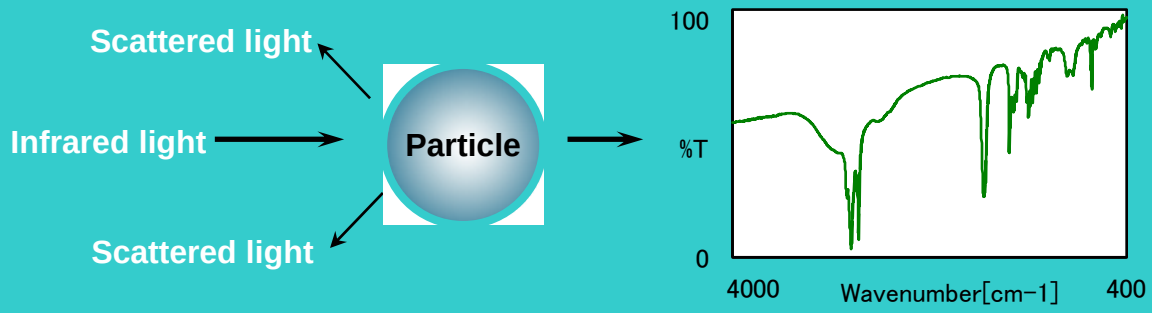
Others

Deconvolution:	Extraction of peak positions in each band
FFT filtering:	Eliminates from spectra only noise possessing a specific cycle
Data cutting:	Cuts measured spectra to any wavenumber region
Curve fitting:	Band decomposition
Validation:	Instrument performance check

Baseline Correction

Relationship of particle size

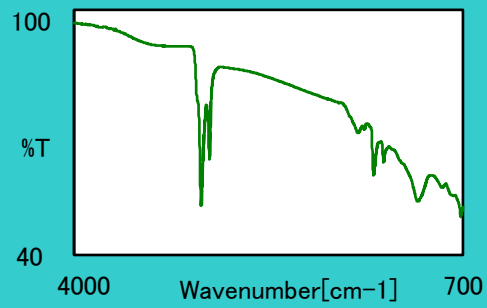
Property of light: Light scatters when it strikes a particle larger than its own wavelength



Effect of sample refractivity

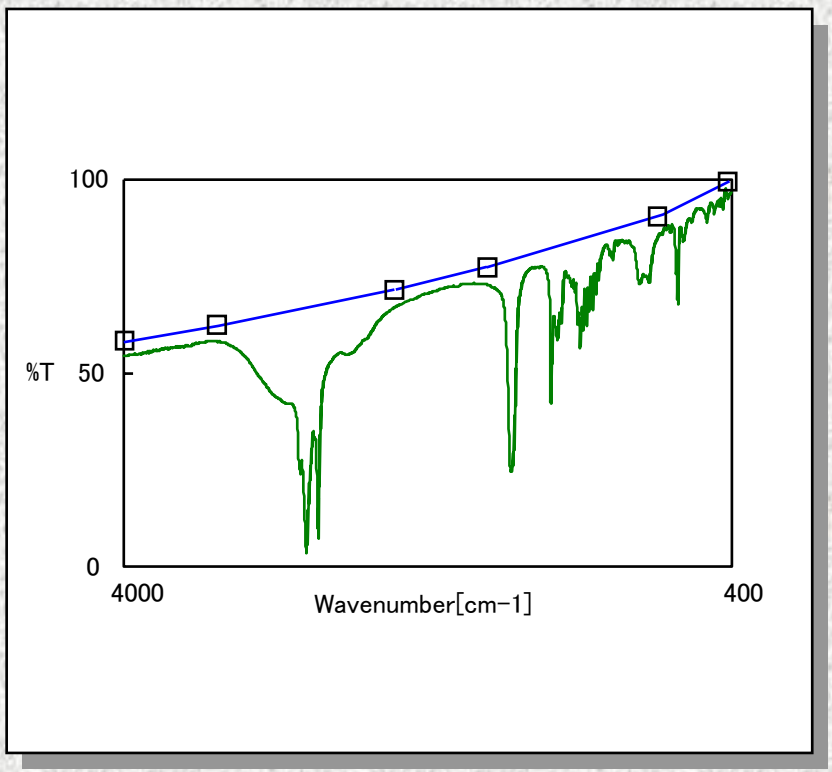
A sample containing carbon has high refractivity

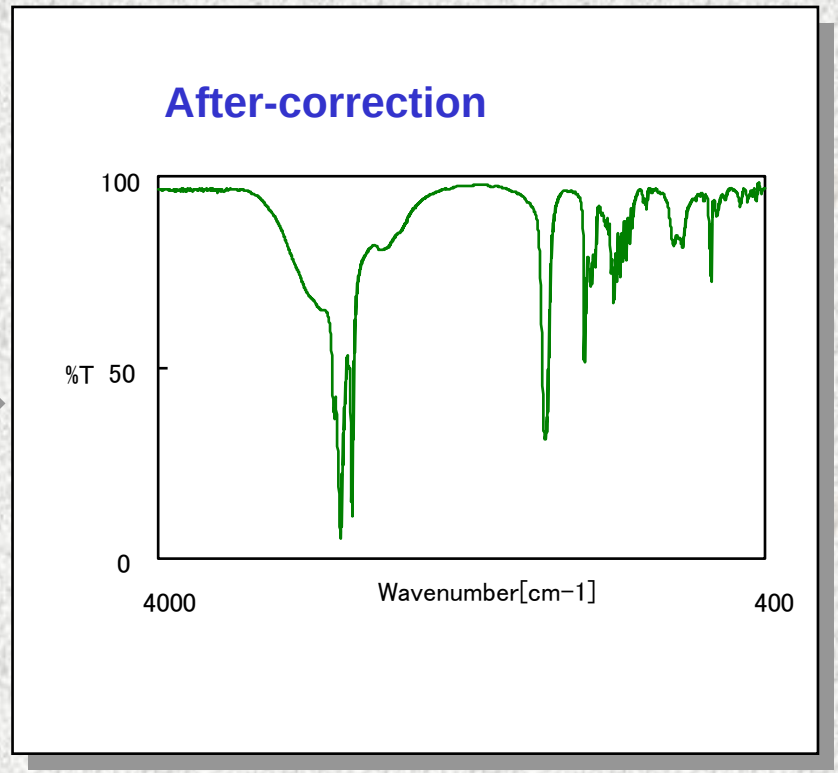
Among the effects of this refractivity is a lower base to the right



Correction Example

Baseline Correction

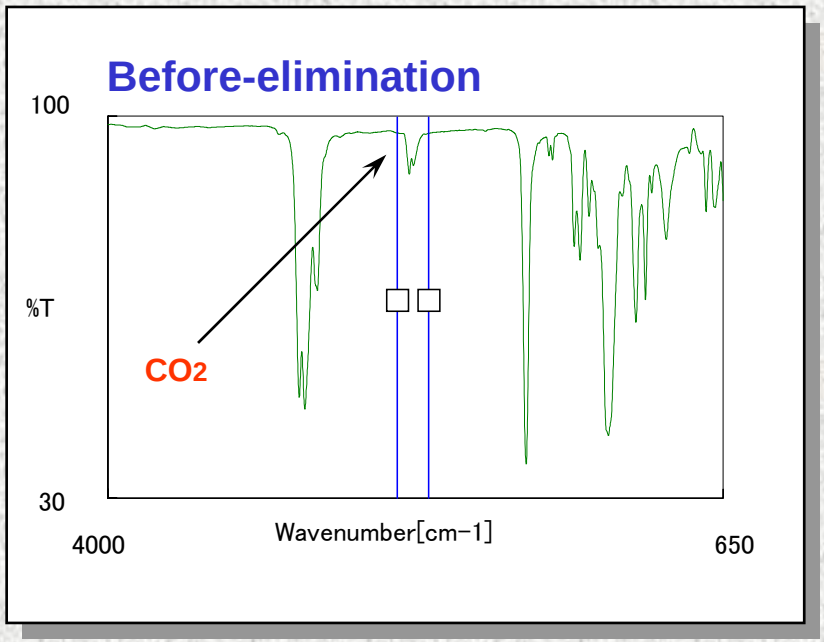


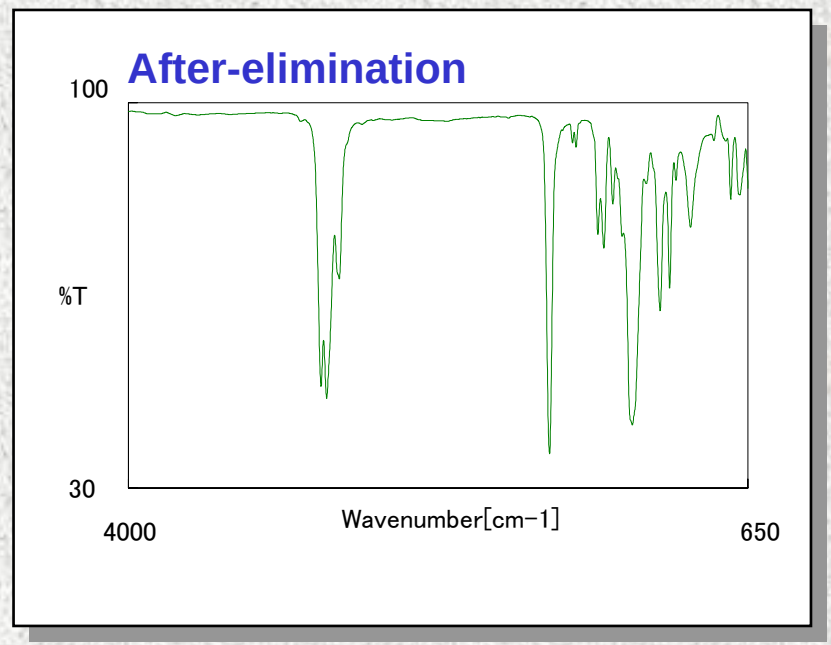


CO_2 Elimination

When a large CO_2 peak appears in a spectrum, mathematical processing is used to eliminate it.

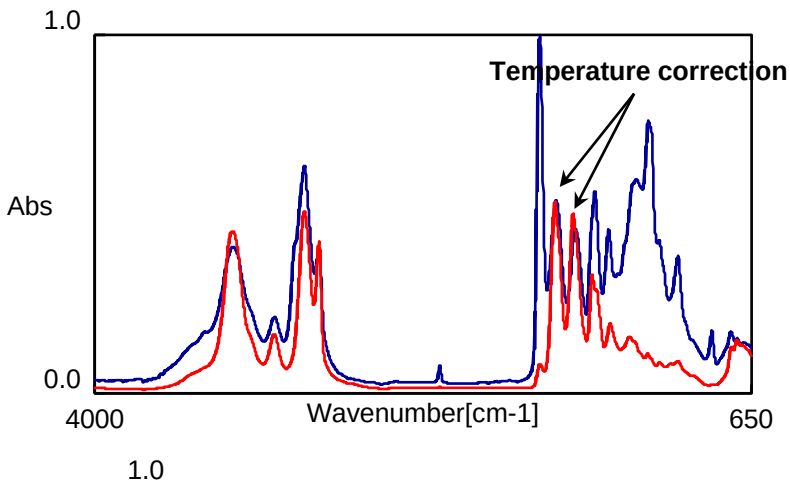
CO_2 absorption peaks appear near 2,350 and 670 cm^{-1}.



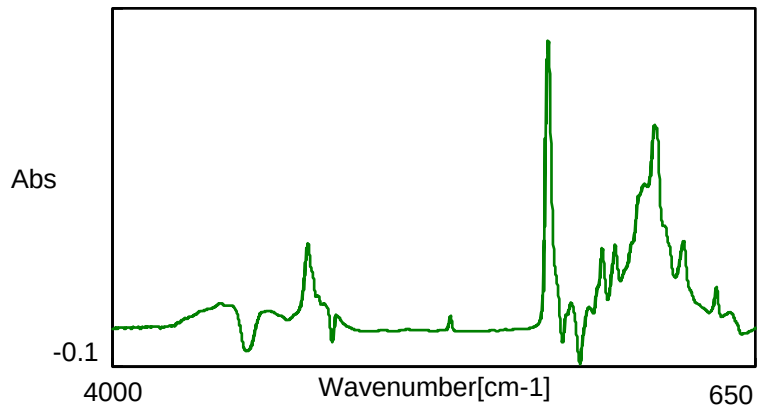


Difference Spectra

(Target component + known component) - known component = target component



Blue line: adhesive
Red line: hot-melt nylon



Adhesive - hot-melt nylon
= acrylic polymer

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Chapter 4

Transmission Techniques

Types of Transmission Technique

Solid samples

- **KBr disk technique** — Primarily qualitative analysis of organic or inorganic substances in powder form or that can be made into powder form
- **Thin-film technique** — Polymeric qualitative and quantitative analysis for substances in film form or that can be made into film form
- **Solution technique** — Primarily qualitative analysis of substances dissolved in solvent (uses liquid cells)

Liquid samples

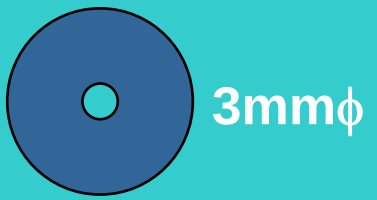
- **Liquid film technique** — Primarily qualitative analysis of viscous and nonvolatile substances (sandwiched between KBr windows)
- **Solution technique** — Primarily qualitative analysis of liquids that dissolve in solvent and nonvolatile substances (uses liquid cells)

KBr Pellet Technique

	Disk press	Microdisk press		
Disk diameter	10 mm ϕ	5 mm	3 mm	2 mm
Sample amount	500 μg	100 μg	Several 10's of μg	Several μg
KBr amount	150 mg	20 mg	10 to 7 mg	5 to 3 mg
Pressure	7 t	1 t	Hand press	Hand press

What You Need

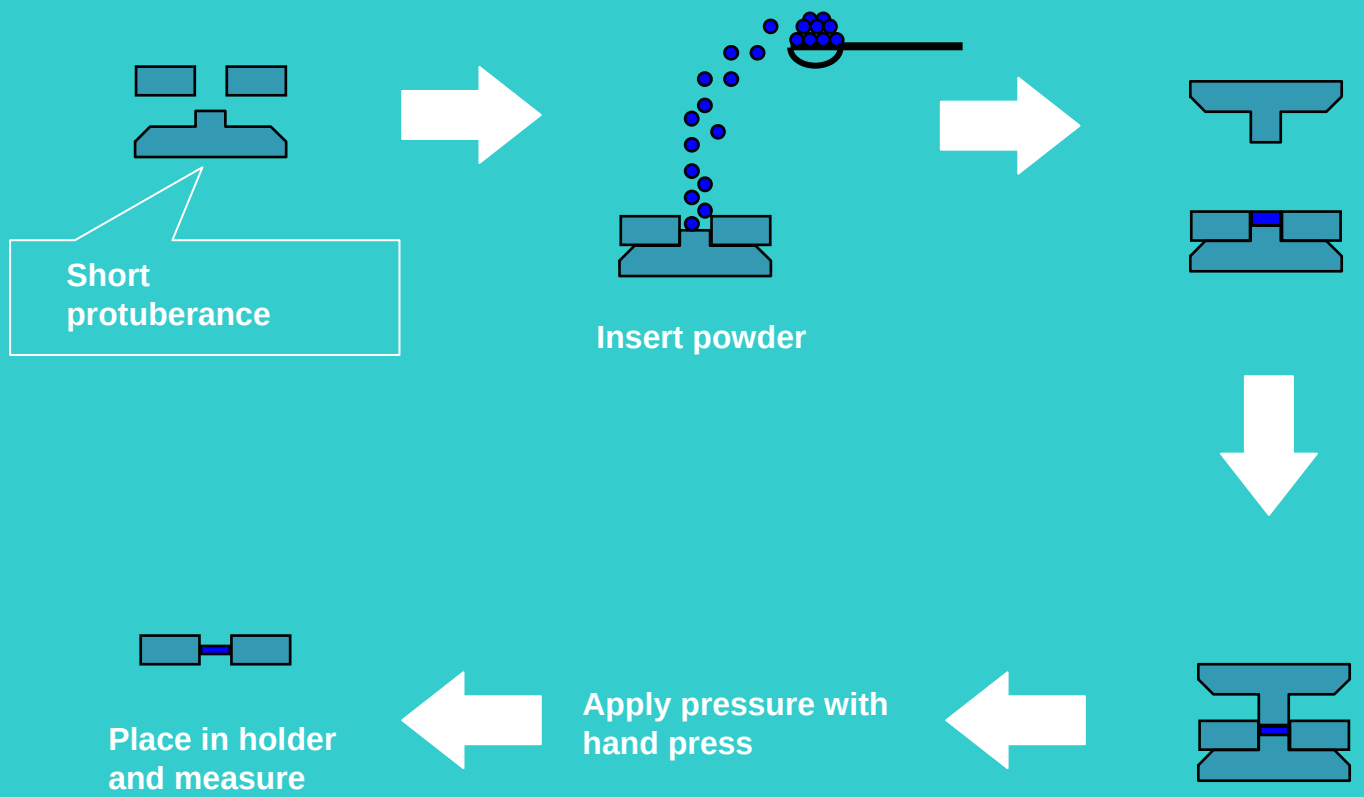
- **KBr crystals (for IR)**
- **Microdisk press**
- **Hand press**
- **Disk holder**



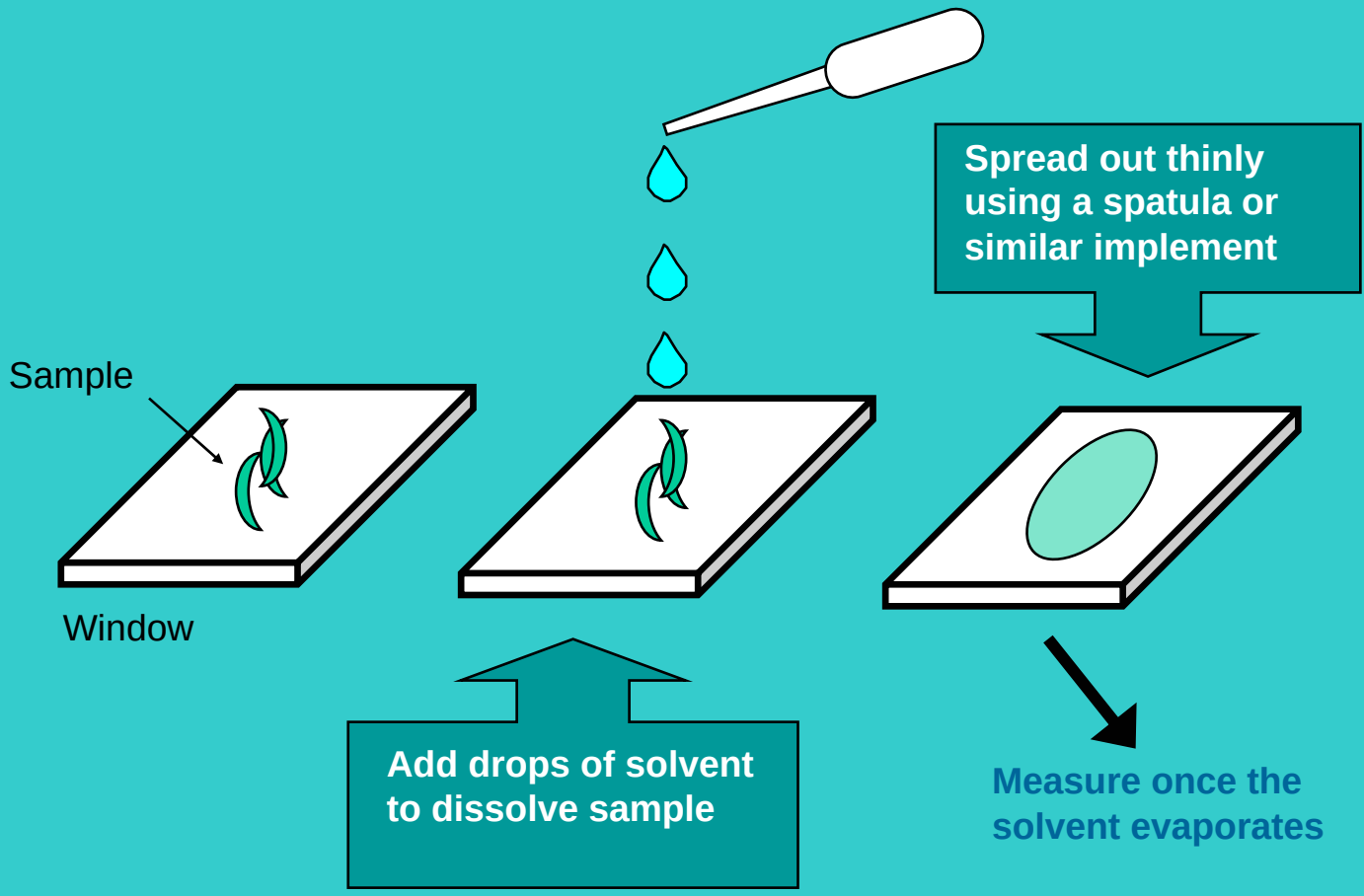
3mmϕ

Protuberance is different!

How to make disks



Thin-film Technique

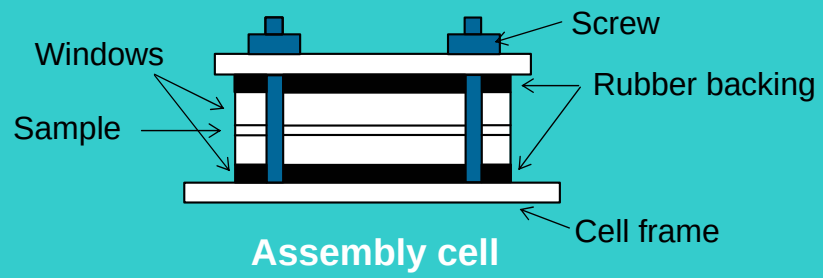


Liquid-film Technique

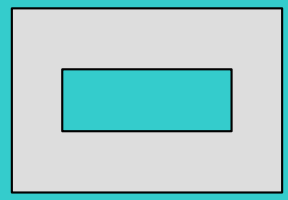
Sandwich the sample between two windows

↓

Place and measure the assembly cell



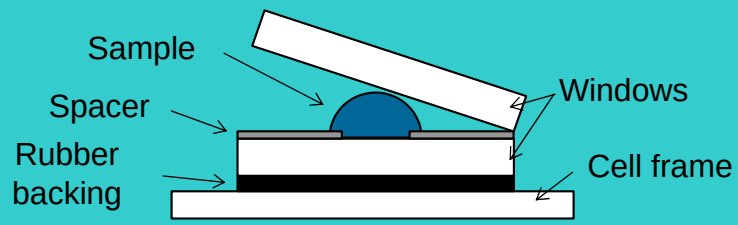
Assembly cell



Spacer (Al or Pb)

What You Need

- Windows
- Assembly cell
- (Spacer)
- Silicone cloth

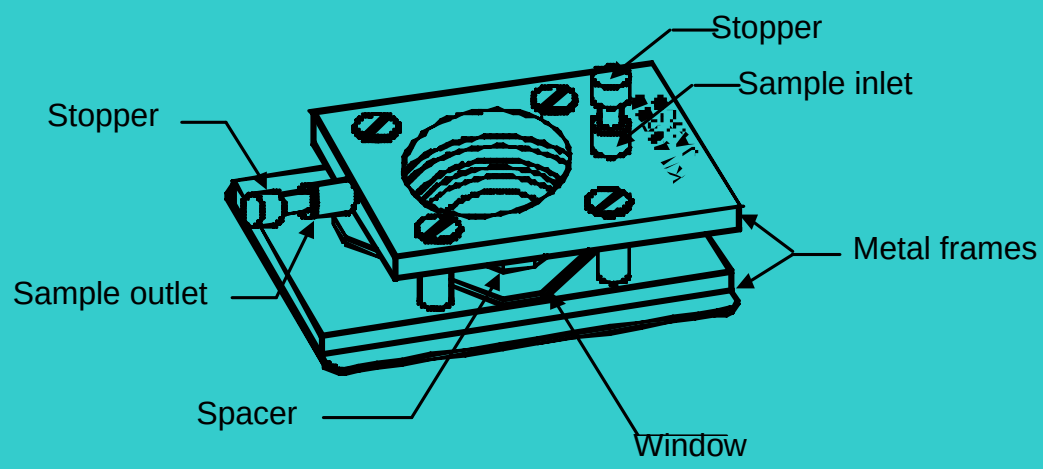


Solution Technique

Dissolve the sample in an appropriate infrared solvent, place it in a fixed liquid cell , and then measure.

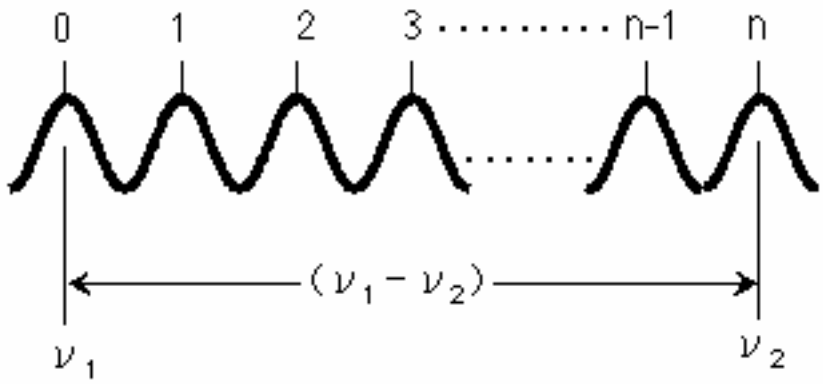
What You Need

- **Fixed cell for liquid**
- **Solvent**
  - Chloroform
  - Carbon tetrachloride
  - Carbon dioxide



How to Determine Cell Thickness

Measure the empty cell to find the interference curve.



$$d = \frac{n}{2\ (\nu_1 - \nu_2)}$$

d	: Cell thickness (cm)
ν_1、ν_2	: Any wavenumber
n	: Number of peaks between ν_1 and ν_2

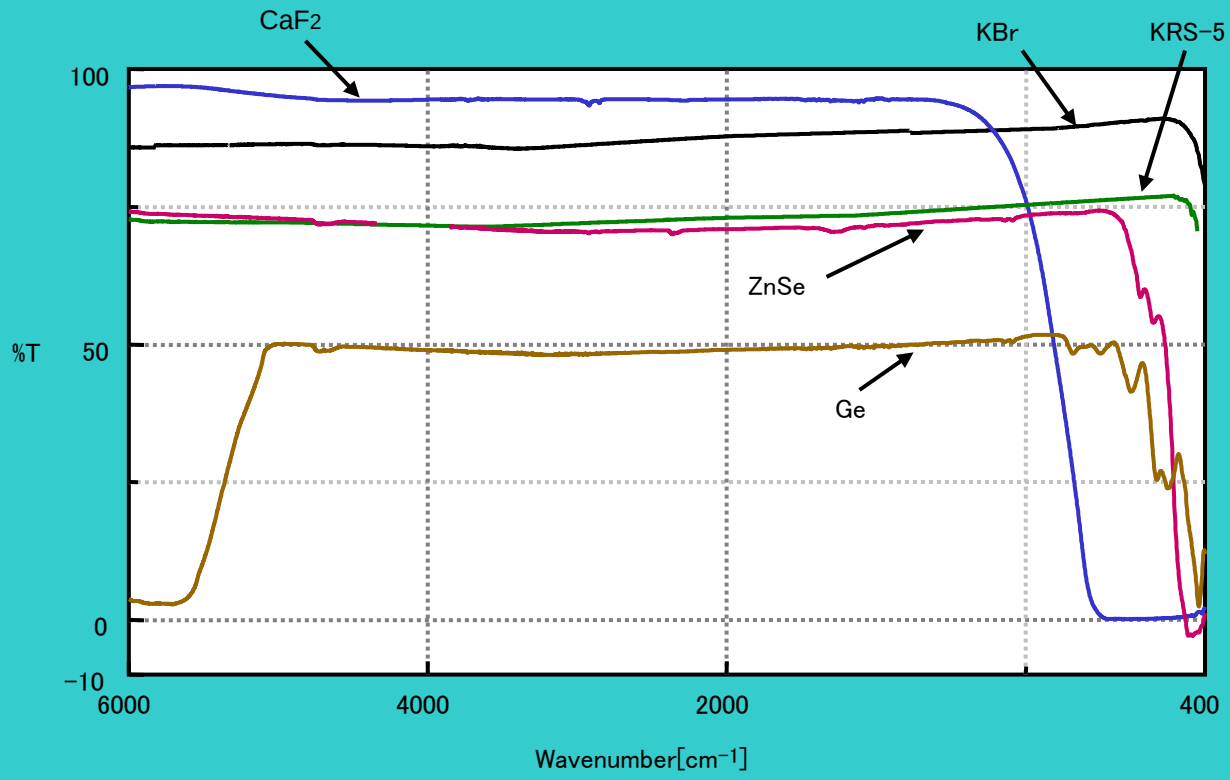
Materials That Transmit Infrared (1)

Materials That Transmit Infrared

Material	Refractivity (Approx.)	Melting Point (oC)	Applicable Range(cm^{-1})	Water-Solubility (g/100g Water)	Notes
KBr	1.5	730	43500 to 400	53.5	No mechanical strength Easily broken
CaF2	1.4	1360	77000 to 1100	0.0017	Dissolved in an ammonia salt solution
KRS-5	2.4	414	20000 to 250	0.05	Affected by acidic solutions Soft and easily damaged
ZnSe	2.4	1100	10000 to 500 (For ATR: up to about 650)	Insoluble	Dissolves in HNO_3 Easily broken
Ge	4.0	936	5500 to 500 (For ATR: up to about 700)	Insoluble	Dissolves in warm sulfuric acid Easily broken

Materials That Transmit Infrared (2)

Materials That Transmit Infrared



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Chapter 5

Reflection Techniques

Types of Reflection Technique

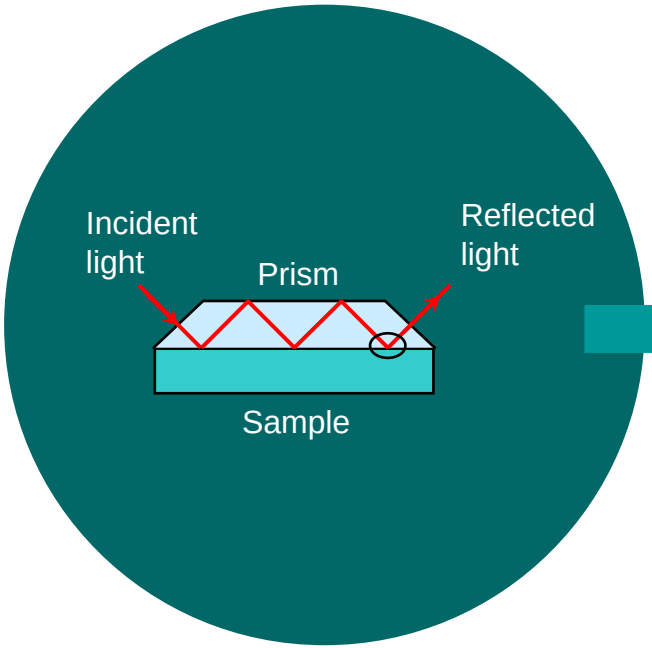
Solid samples

- **ATR technique**
  Elastic and viscous substances that are insoluble, infusible, and difficult to grind up Information of sample surface
- **Diffuse reflectance technique**
  Substances in powder form or that can be turned into powder
  Those with surfaces that are rough.
- **Specular reflection technique**
  Film on a metal substrate (around 0.1 to 5 μm)
  Solids with a smooth surface
- **RAS technique**
  Thin film on a metal substrate (around 10 angstrom to 1 μm)

Liquid samples

- **ATR technique**
  Measurement of aqueous solutions
- **Diffuse reflectance technique**
  Measurement of aqueous solutions (eliminate water)

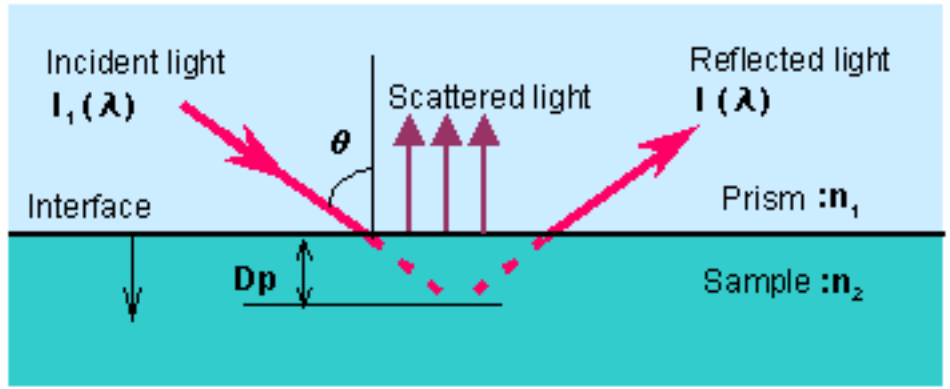
ATR Technique



$$\text{Sin}\,\theta\ (\text{critical angle}) \geq \frac{\text{Sample refractivity } (n_2)}{\text{Prism Refractivity } (n_1)}$$

$$\sin 45^\circ = 0.71$$

$$0.71 \geq \frac{n_2}{2.38} \qquad 1.7 \geq n_2$$



Depth of Light Penetration into Sample

Depth of Light Penetration into Sample

Depth of light penetration into sample is determined by:

1. Wavelength (μm)
2. Incident angle (η)
3. Refractivity of prism (n_1) and sample (n_2)

Proportional to wavelength

$$dp = \frac{\lambda}{2\pi n_1} [\sin^2\theta - (n_2/n_1)]^{-1/2}$$

dp : depth of penetration

Inversely proportional to prism refractivity

Types of ATR Prisms

	Measurable Wavelength Range	n_1	n_2		Measurement Target
			θ=45°	θ =60°	
KRS-5	up to 250	2.4	1.7	2.1	General organic materials
ZnSe	up to 625	2.4	1.7	2.1	General organic materials and aqueous solutions
Ge	up to 700	4.0	2.8	3.5	Rubber containing carbon and extremely thin surfaces

θ : incident angle

n_1 : prism refractivity

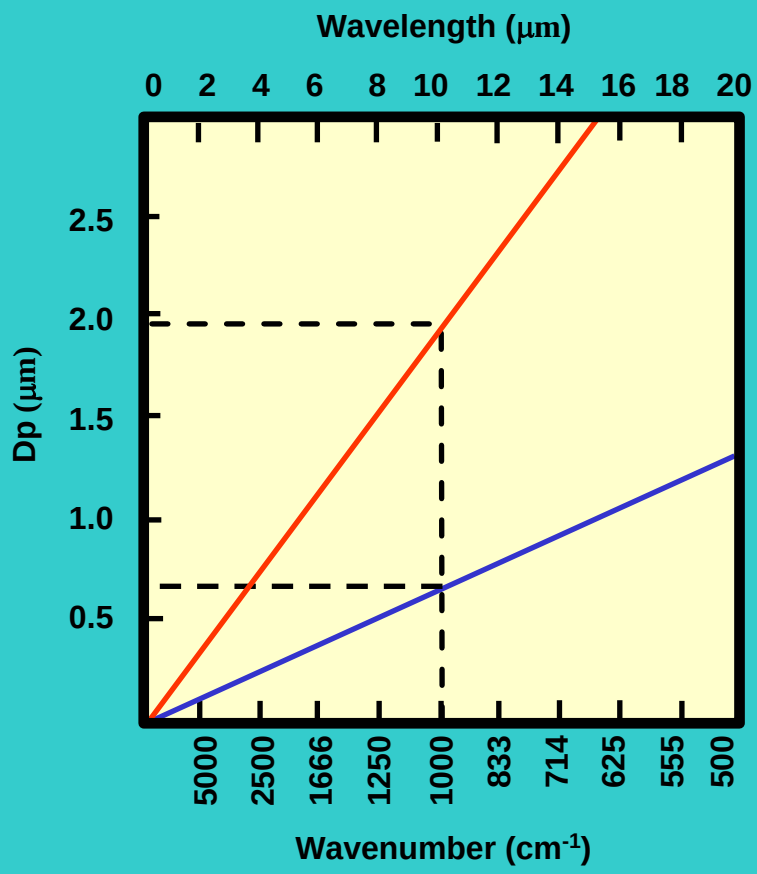
n_2 : sample refractivity

(upper limit of sample refractivity for producing total reflection)

$$\sin\theta \geqq \frac{n_2}{n_1}$$

Relationship between Wavelength and Incident Angle

Relationship between Wavelength and Incident Angle to depth of penetration by prism type



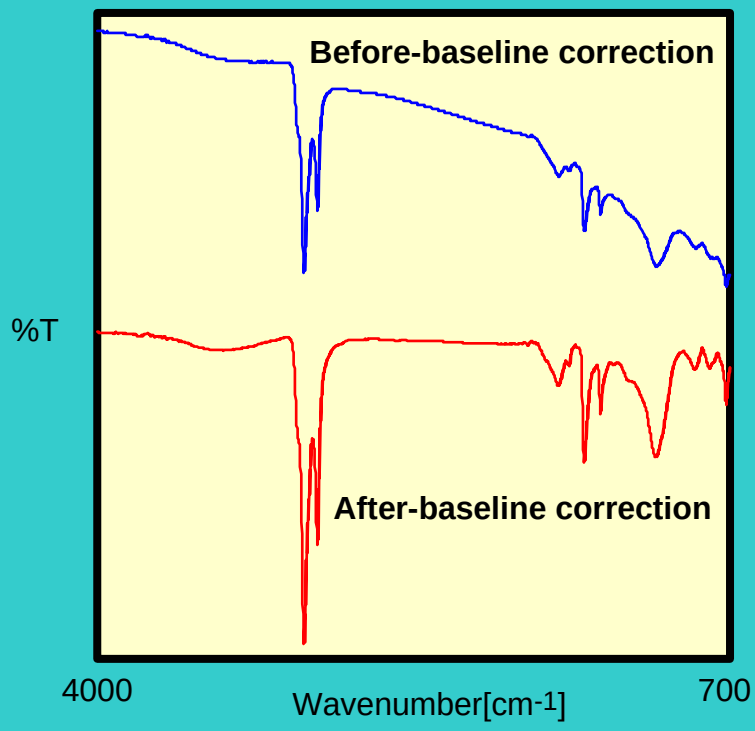
Prism	Refractivity
KRS-5 ZnSe	n_1=2.4
Ge	n_1=4.0

Sample refractivity n_2 = 1.5
Incident angle θ = 45°

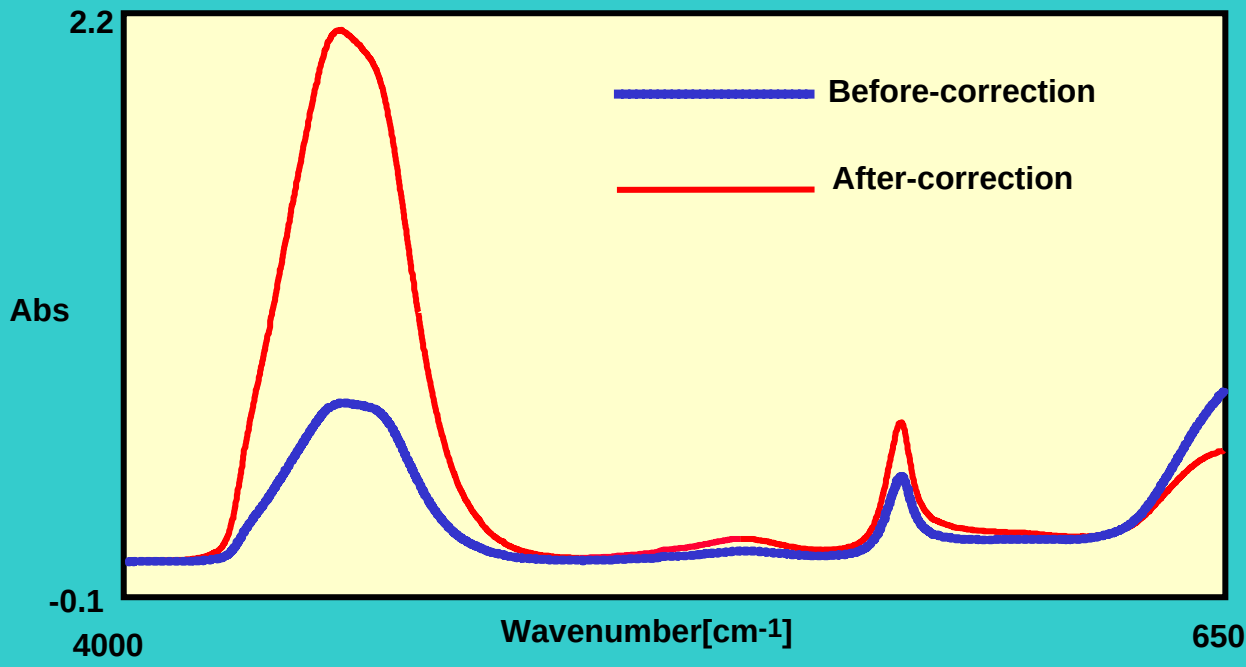
Measurement of Rubber Containing a High Concentration of Carbon

- **Normally, the ATR technique is employed to measure rubber**
- **The material for the prism is selected based on the amount of carbon contained in the rubber**
- **A Ge prism is used when the carbon content is high, and when the baseline is curved it is corrected**

Attachment: ATR-300/H
Prism: Ge
Integrations: 20
Resolution: 4 cm-1
Detector: TGS



ATR Correction



Attachment: ATR-500/M
Integrations: 30
Resolution: 4 cm^{-1}

ATR Technique Features

- Surface layer information can be measured in a nondestructive manner
- No need for sample preparation, and state analysis is possible
- By selecting the correct prism, it is possible to adjust the depth of light penetration into the sample
- Using a holder for liquid allows measurement of aqueous solutions as well

Cautions on Usage

In most cases, the reason for failing to obtain a good spectrum is a poor bond between the sample and prism. Care must be taken with samples lacking a smooth surface and those that are hard because a layer of air can easily form between the sample and the prism during bonding.

Since ZnSe and Ge crystals are fragile, be careful not to apply too much pressure to them or strike or drop them.

Since ZnSe and Ge have absorption in the low wavenumber region, verify the measurable range.

If a ZnSe prism fails to yield a good spectrum when measuring a material such as rubber containing carbon, use a Ge prism instead.

How to clean a prism:
KRS-5 : Rinse the prism with chloroform or similar fluid, being careful not to touch it.
ZnSe and Ge :Dampen a Kimwipe or similar wipe product with solvent and lightly wipe the prism.

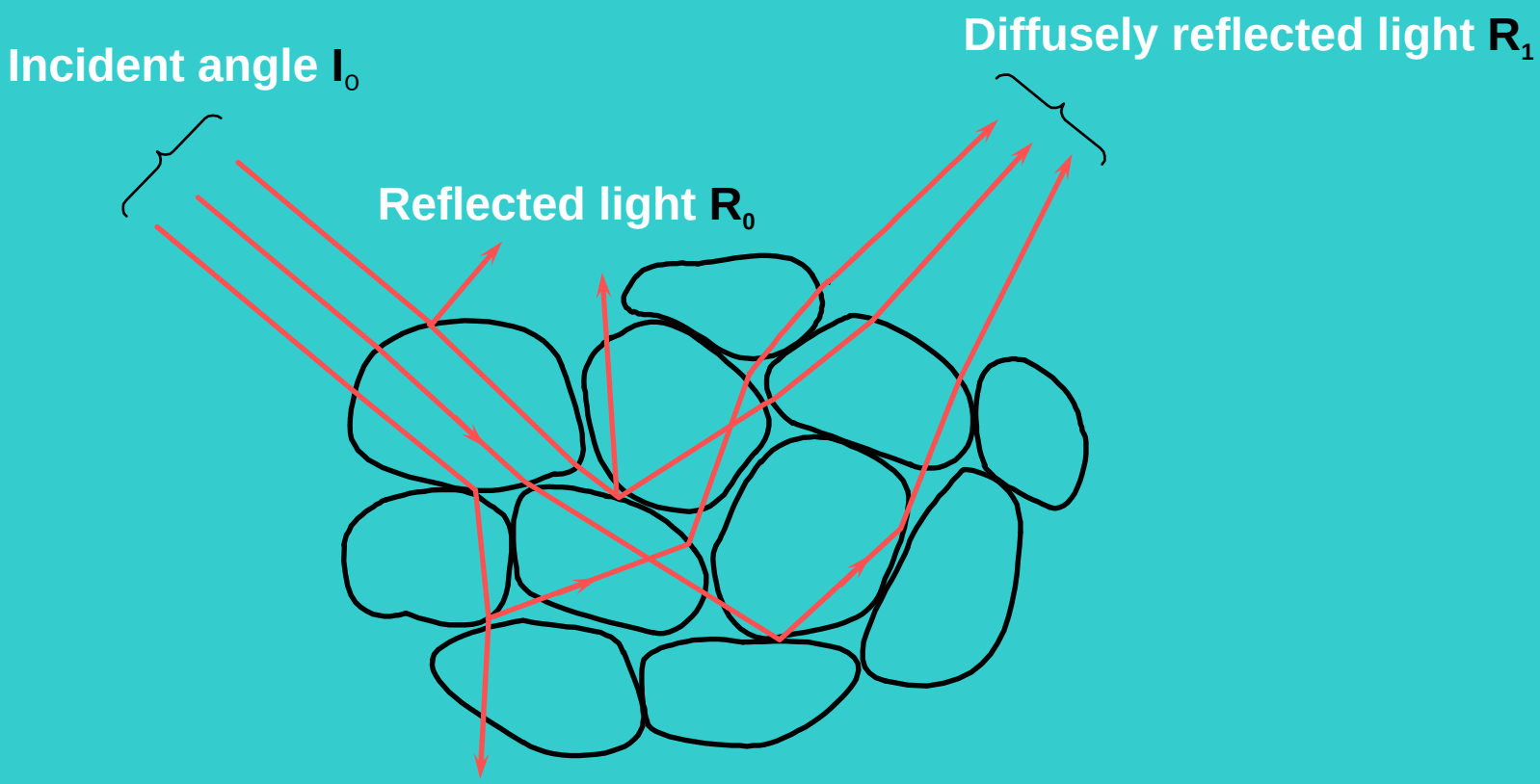
The KRS-5 should be stored in a desiccator

Applications

The ATR technique can be applied to measure the following types of substances:

- **Elastic and viscous substances that are insoluble, infusible, and difficult to grind up**
  Rubber, urethane foam, synthetic leather, and thermoset resin
- **Substances difficult to measure using the thin-film technique**
  Polymeric thin films
- **Surfaces consisting of an extremely thin layer that is difficult to measure**
  Measurement of coatings such as paint, varnish, and lacquer and their change over time
  Measurement of adhesive tape and electrical tape surfaces
  Identification of coating materials such as paper, metal, cloth, and leather
- **Measurement of aqueous solutions**

Diagram of Diffuse Reflectance Principle



Kubelka-Munk Equation

$$f(\gamma^{\infty}) = \frac{(1-\gamma^{\infty})^2}{2\gamma^{\infty}} = \frac{K}{S}$$

γ^{∞} : Ratio of reflected light intensity to incoming light intensity (relative reflectivity)

γ (std) : DR spectrum of KBr powder

γ (Sample) : DR spectrum of sample diluted by KBr

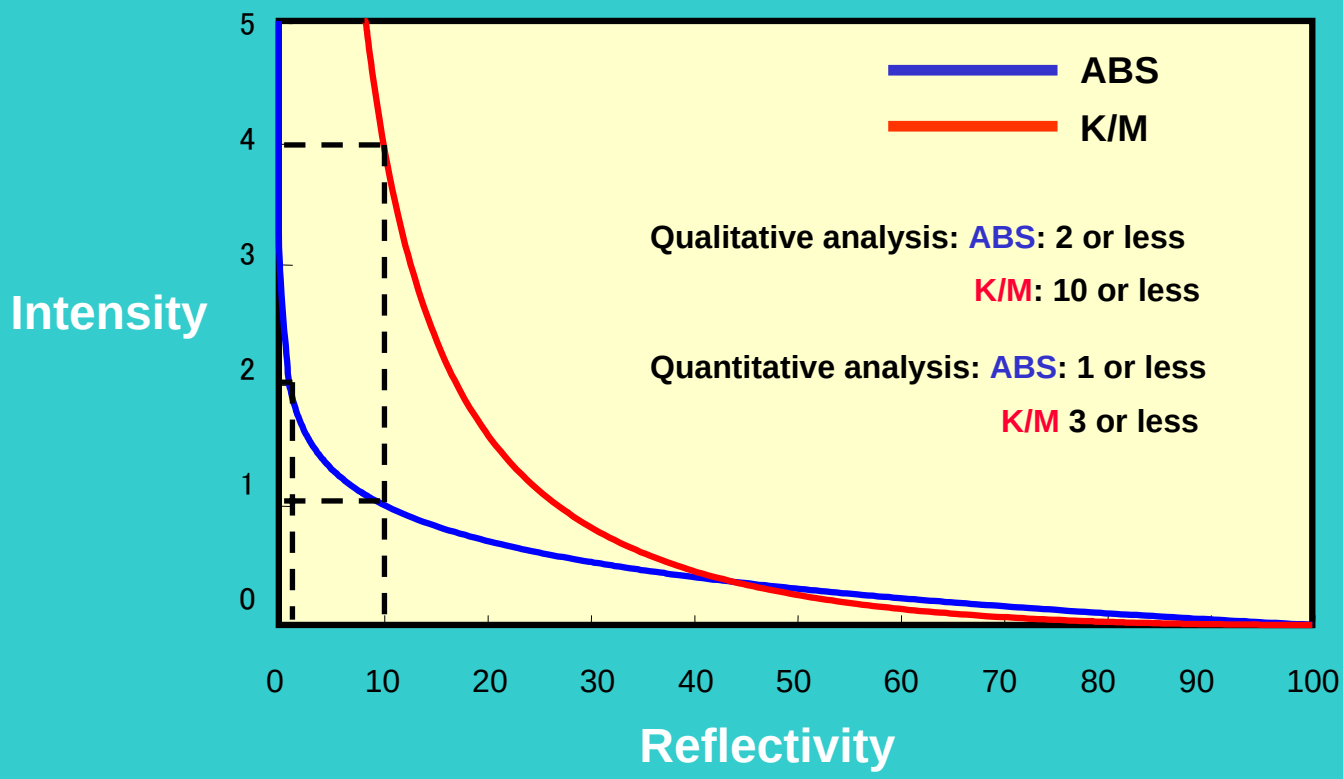
γ^{∞} : γ (Sample) / γ (std)

K : Extinction coefficient of powder layer
(proportional to the product of extinction coefficient and sample concentration)

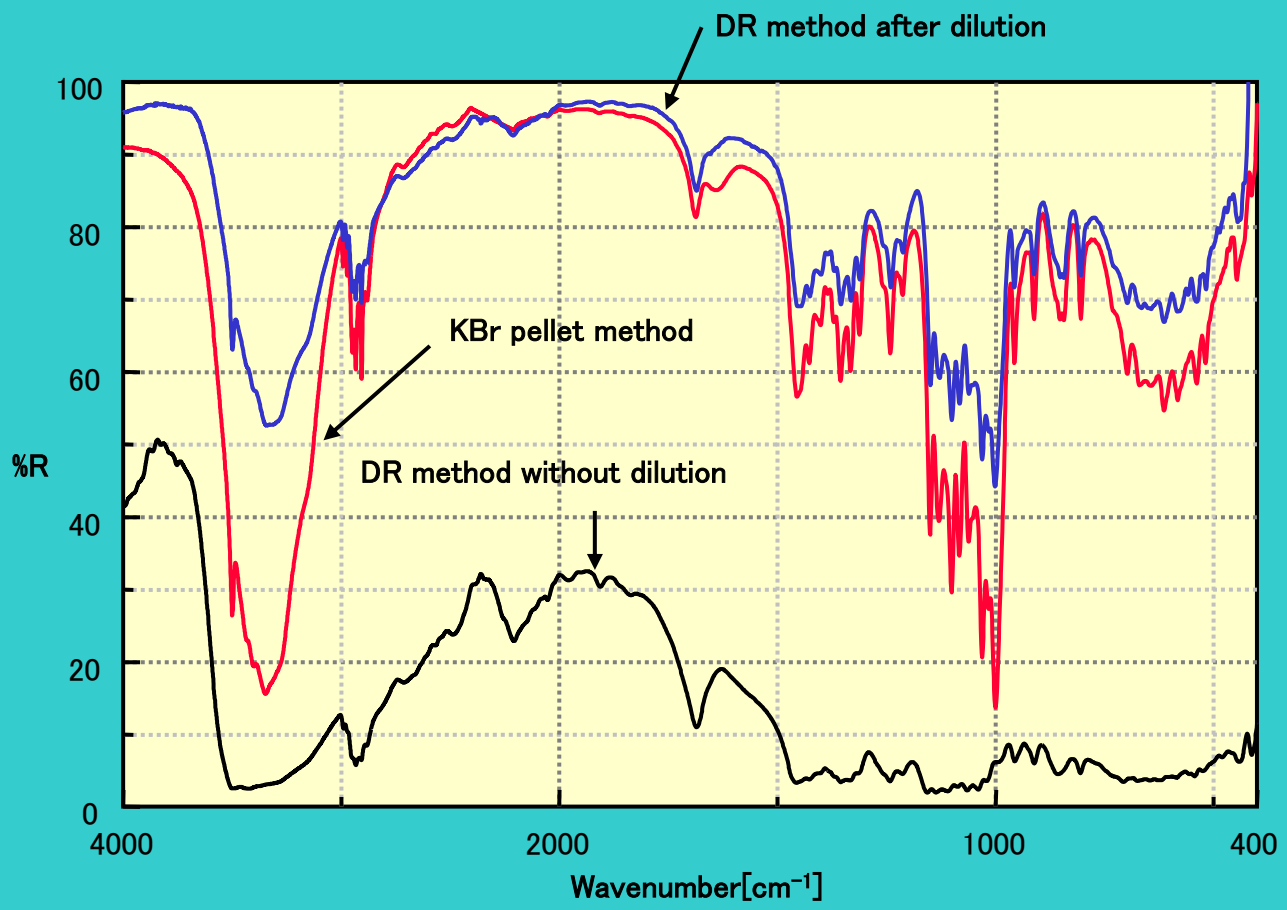
S : Scattering coefficient of powder layer (powder particle size and refractivity)

$f(\gamma^{\infty})$: Kubelka-Munk coefficient (proportional to sample concentration;
Kubelka-Munk equation is equivalent to the Lambert-Beer equation
in the transmission technique)

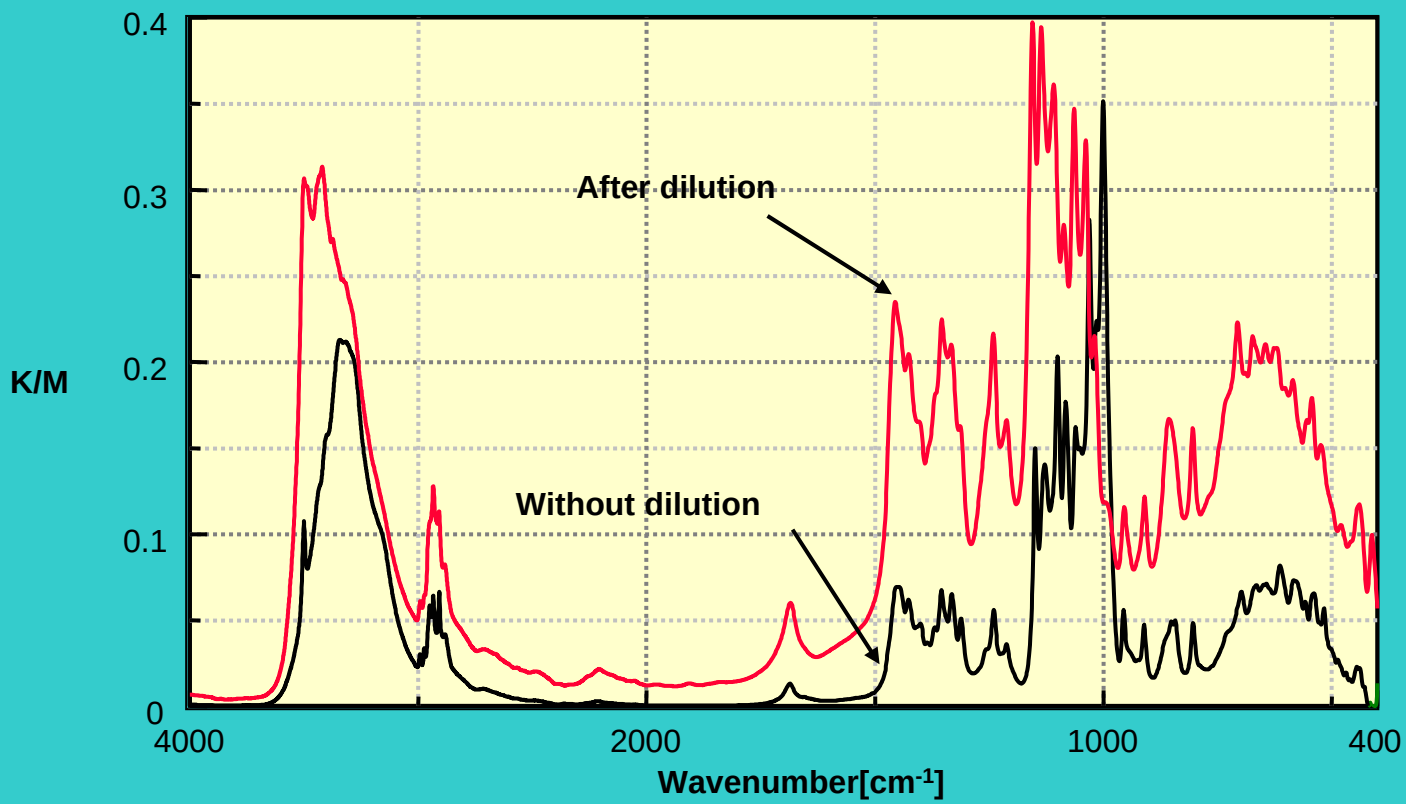
Kubelka-Munk



Spectra of Trehalose



Spectra of Trehalose



Features

(1) Can be used on powder samples and samples with rough surfaces

(2) Obtains a spectrum resembling a transmission spectrum but with a slight difference in the intensity ratio
=> Weak absorption in the transmission spectrum is enhanced by the DR spectrum

(3) Compared to the KBr technique, the sampling operation is easier

(4) Quantitative analysis is also possible by switching to the K/M function (only when the K/M value is 3 or less)

(5) In addition to room temperature, measurement during or after heating is possible. Attachments are available for that purpose

Important Information Concerning the Diffuse Reflectance Technique

(1) **Samples should be in the finest powder form possible (a particle size of 20 µm or less is best)**

- Prevents specular reflection
- Increases number of reflections, thereby enhancing absorption

(2) **Dilute samples with KBr**

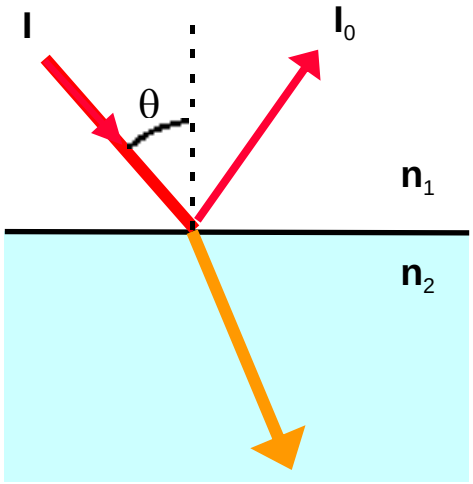
- Dramatically lowers specular reflection
- Enables the dilution ratio to be obtain corresponding to the measurement target (normally, around several percent)

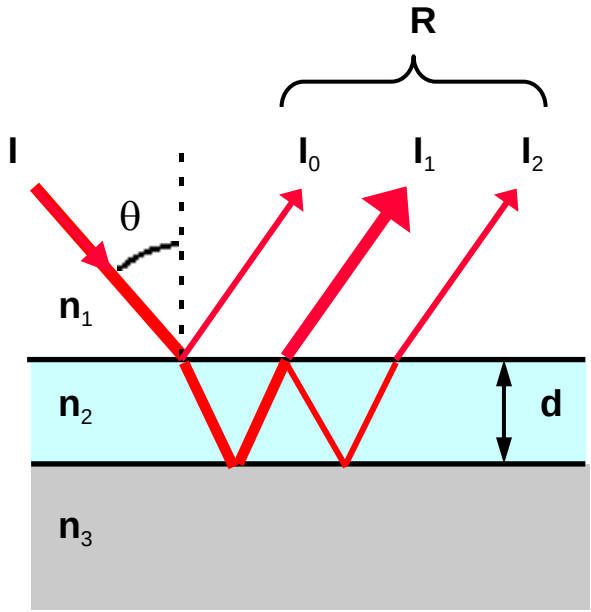
(3) **When focusing on OH groups, use CaF2 powder instead of the highly hygroscopic KBr powder**

Applications

- Substances that can be measured using the normal KBr technique
- Substances difficult to measure using the KBr technique (includes clay, cement, minerals, and pigment)
- Research on adsorption/desorption reactions on catalyst surfaces

Principles of the Specular Reflection Technique



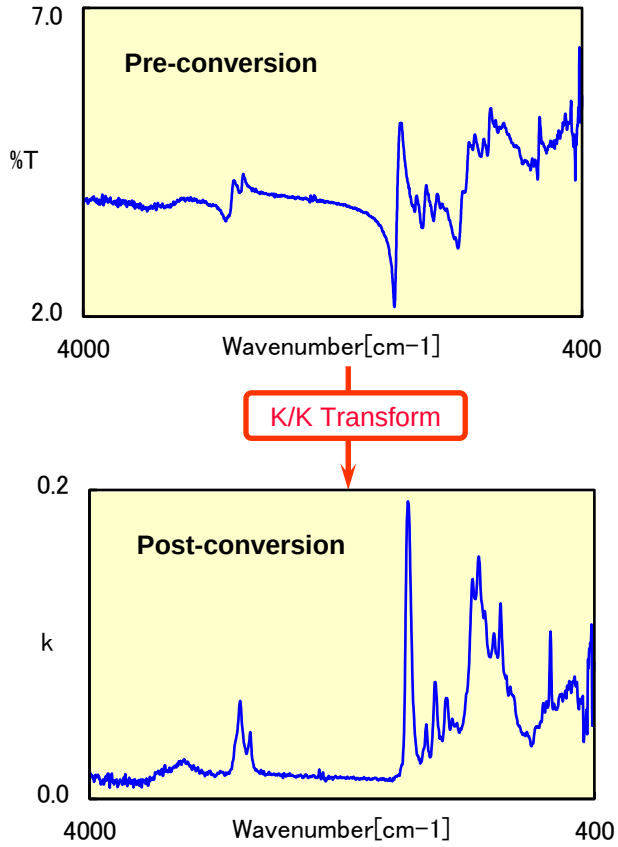


Kramers-Kronig Transform

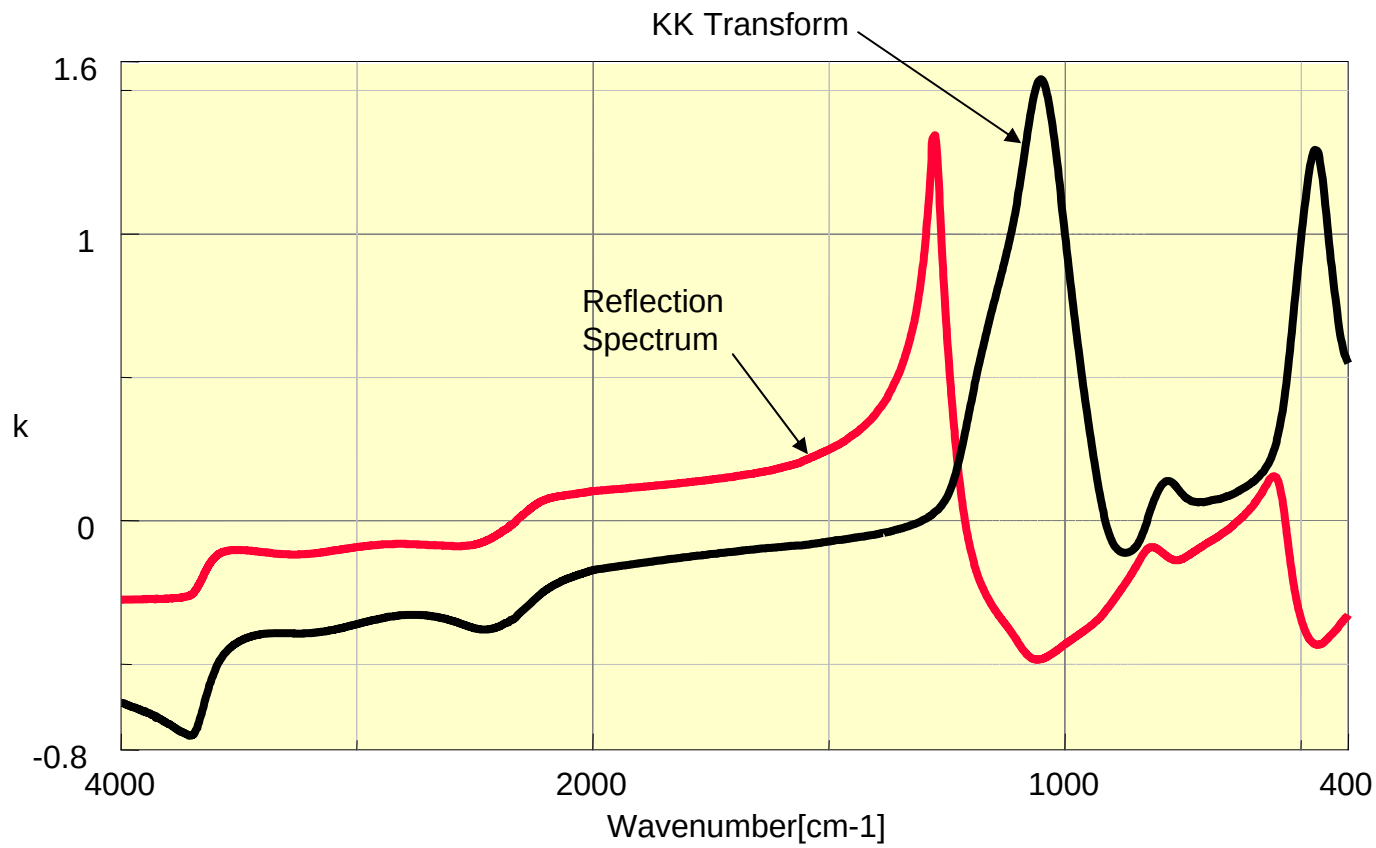
By transforming the surface of a resin or plastic into a specular surface, it is possible to capture faint reflected light and obtain the reflection spectrum.

The reflection spectrum is affected by the sample's refractivity (n), causing its waveform to change.

This example if for software that converts the reflection spectrum into an absorption spectrum.



Kramers-Kronig Transform

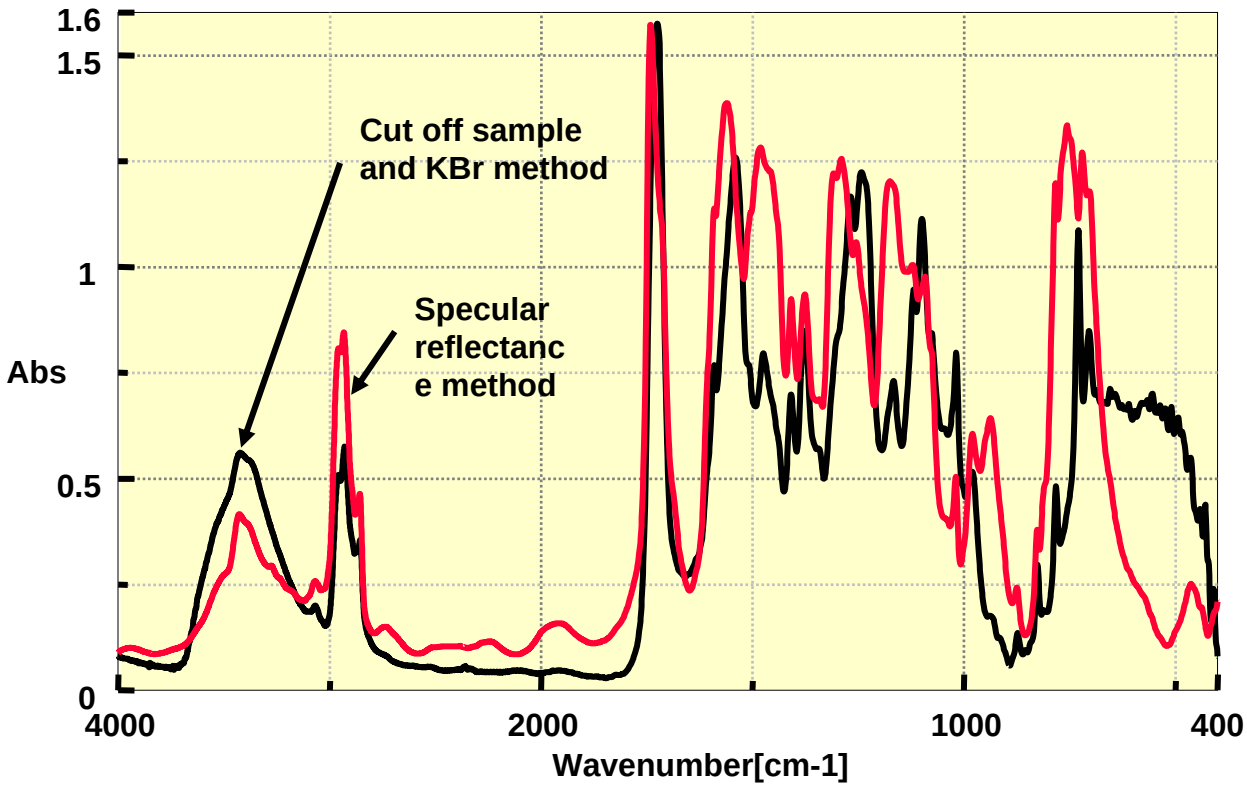


Features

(1) Can obtain spectra simply by placing a sample with a smooth surface. However, the K/K transform is required to contrast with the normal transmission spectrum.

(2) Enables state analysis of thin film (approximately 5 μm or less) on a metal substrate.

Specular reflectance method



Cautions on Usage

(1) The measurement surface must be either a specular surface or smooth surface.

(2) The reference sample should be a substance as close as possible to the sample. When a reference is not available, a mirror can be used instead.

(3) When measuring coating film on a reflective substrate, the film thickness should be between 0.1 and 5 μm.

Applications

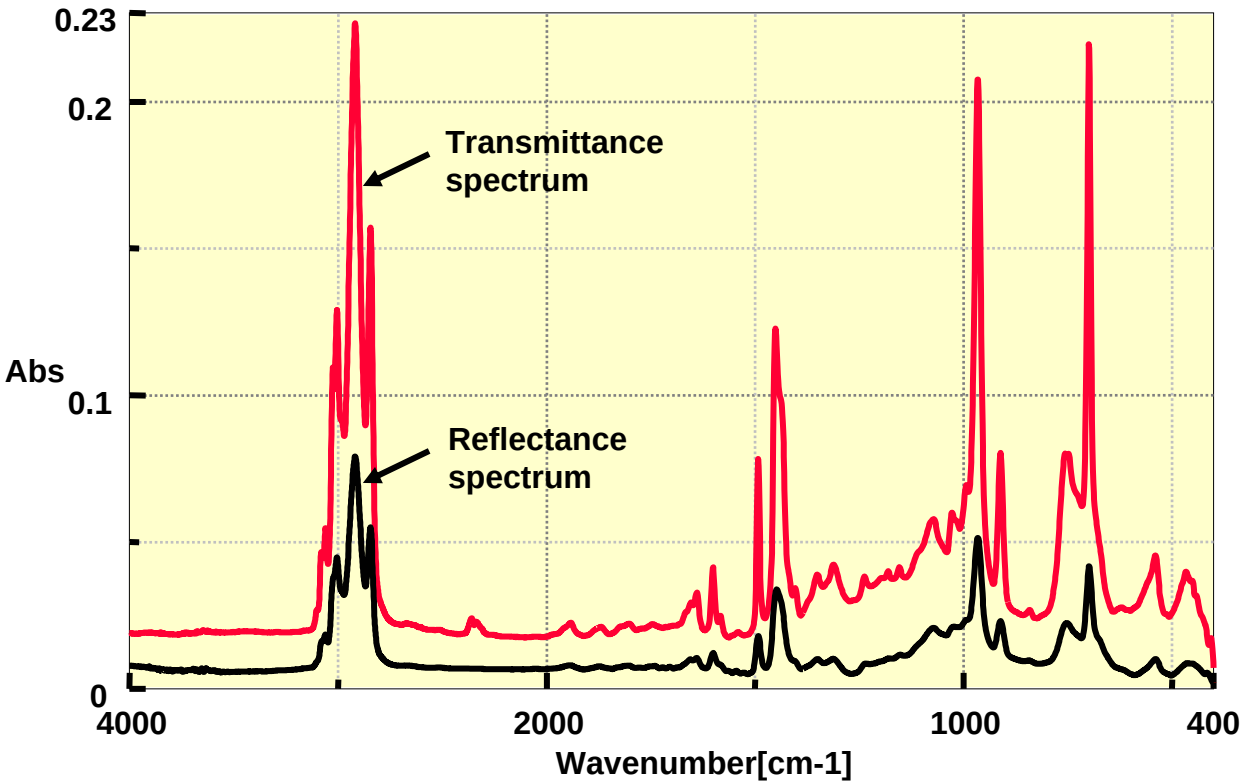
(1) Analysis of film coatings on metal surfaces, deposits, and oxide films

(2) Analysis of samples that have a smooth surface and are difficult to measure using the transmission technique

(3) Measurement of epitaxial layer thickness

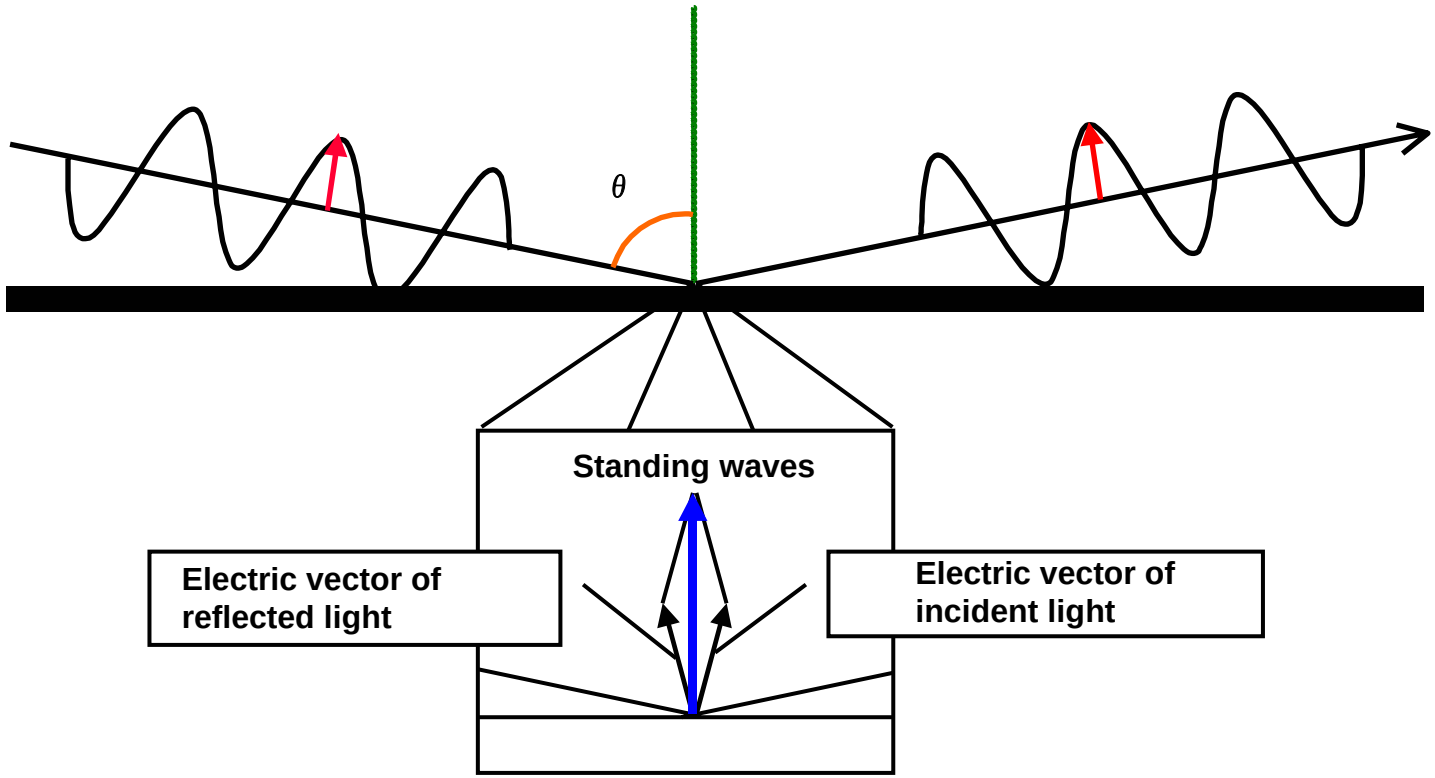
(4) Measurement of relative reflectivity

Applications



High-Sensitivity Reflection Technique

Reflection of linearly polarized light on a metallic surface: In the case of p polarization



Features

(1) Enables the qualitative and quantitative analysis of thin film of around several tens of Å to several μm that has been processed on the surface of a metal substrate.

(2) Absorption increases as the dipole moment approaches 90 degrees.

(3) Most sensitive method for measuring thin-films on the surface of metal substrates.

Cautions on Usage

(1) The transmission spectra and patterns of RAS spectra differ depending on the surface selection ratio.

(2) This technique should be applied to thin films on the surface of smooth metal substrates.

(3) Notes on handing samples:
Handle samples with tweezers (avoid putting fingerprints on samples).
Do not expose the samples to the open air except when measuring
(avoid contamination by airborne debris).

(4) Make sure no absorption exists that will interfere with the reference (unprocessed metal substrate).

Applications

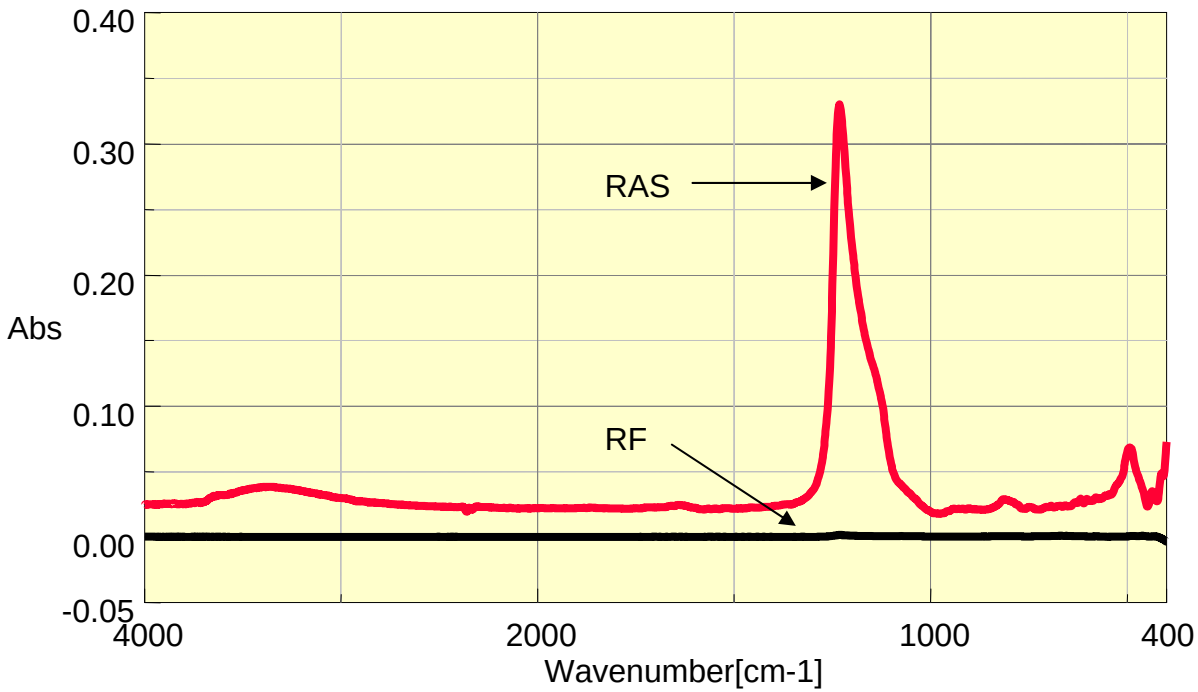
(1) Analysis of surface processing and adsorption of metal substrates and semiconductor substrates

(2) Residue check after washing metal substrates and semiconductor substrates

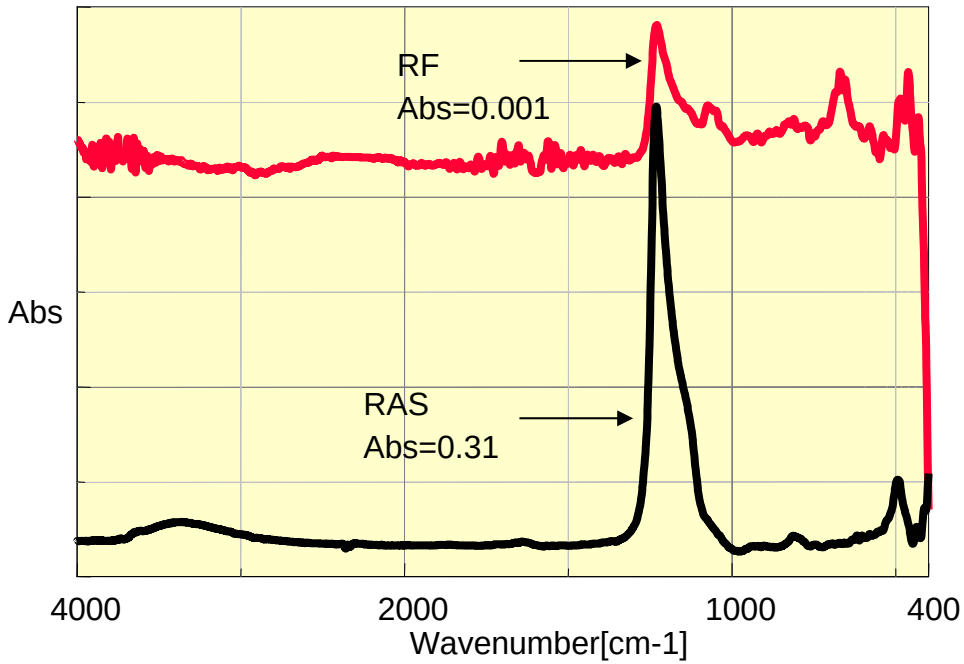
(3) Measurement of LB films

(4) Qualitative analysis of compact disc surface lubricating oil

Applications



Applications



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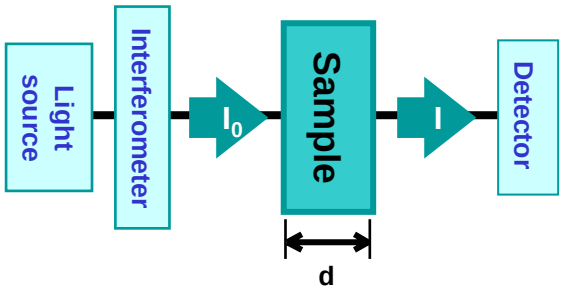
Chapter 6

Quantitative Analysis

Quantitative Handling of Infrared Spectra

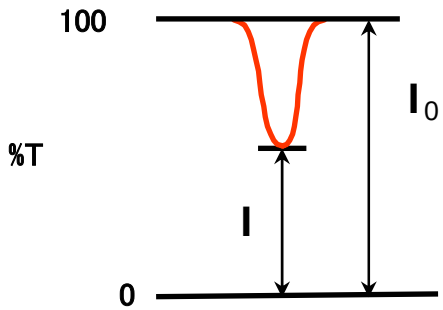


Transmissivity : %T=(I/I_0) x 100

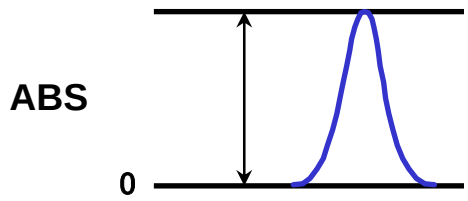
Absorbance : ABS=log(1/T)
=log(I_0 /I)
=ε x d x c

Ordinate axis is proportional to concentration (c)

ε : Molar extinction coefficient
d : Depth
c : Concentration



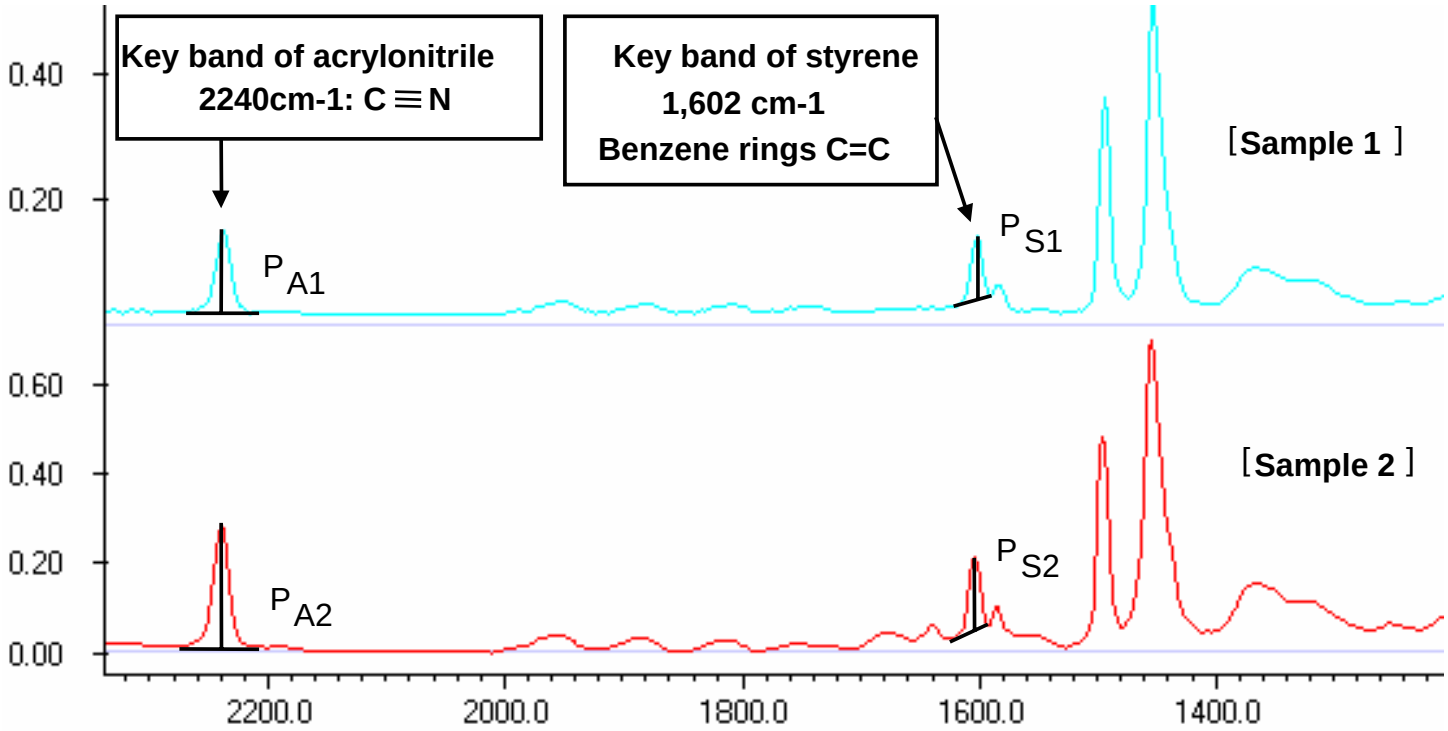
Transmissivity measurement



Absorbance measurement

Application of Quantitative Analysis

Application of Quantitative Analysis



Example: Comparison of component ratios in ABS resin (acrylonitrile/butadiene/styrene)

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Chapter 7

Infrared Spectrum Analysis Techniques

Infrared Spectrum Analysis Techniques

Overview

Substructure analysis: Analysis of functional groups

Spectrum searching: Identification of compounds

Conditions for obtaining spectra suited to analysis

Select a measurement technique which fits the analysis purpose

Optimum concentration: Low

Decrease the number of components as much as possible during preprocessing

Substructure Analysis

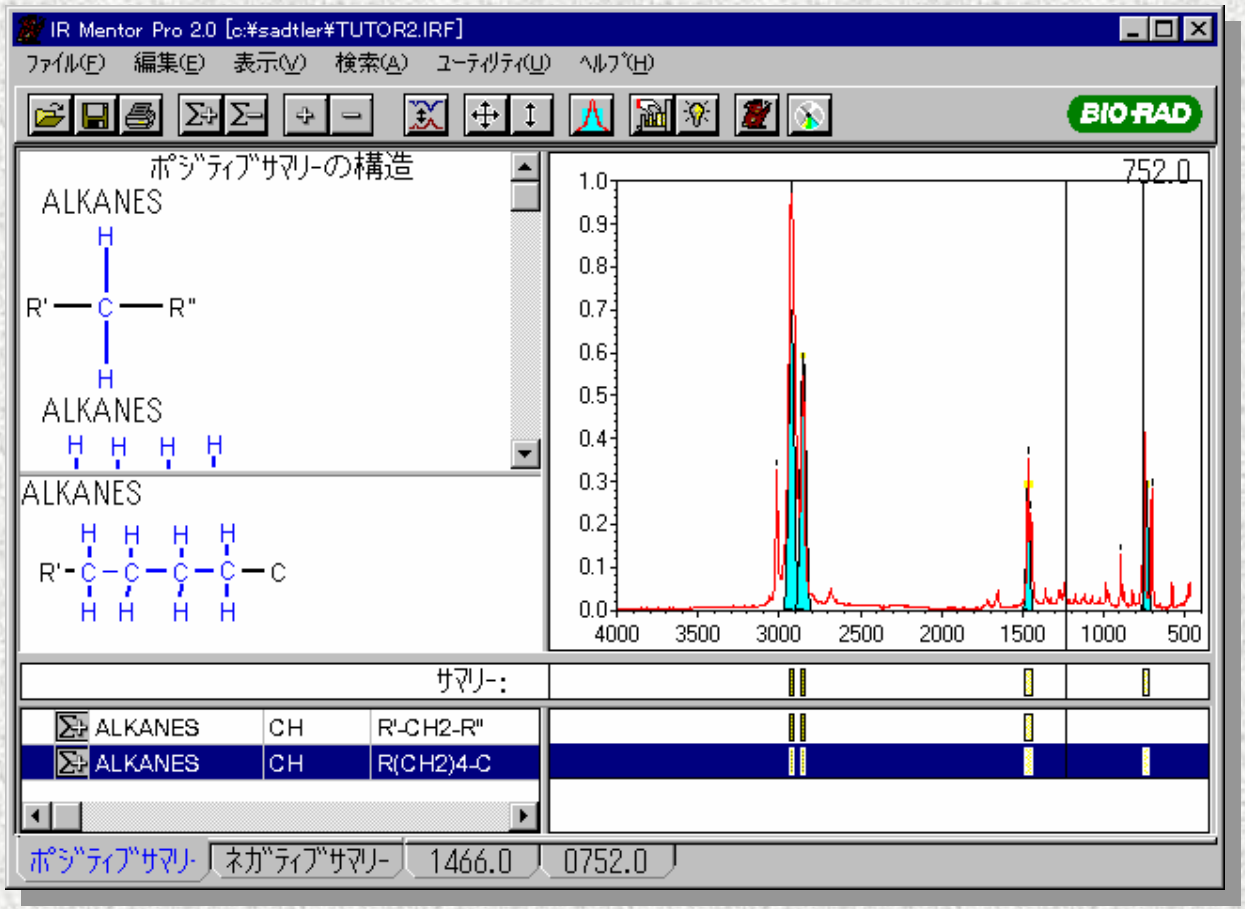
(1) Utilize reference material

(2) IR Mentor (application that assists the analysis of infrared spectra)

- **Finds the functional groups for each absorption band**
- **Finds the functional groups for specified peaks**
- **Finds function groups by compound type**
- **The functional groups that have been entered are limited**

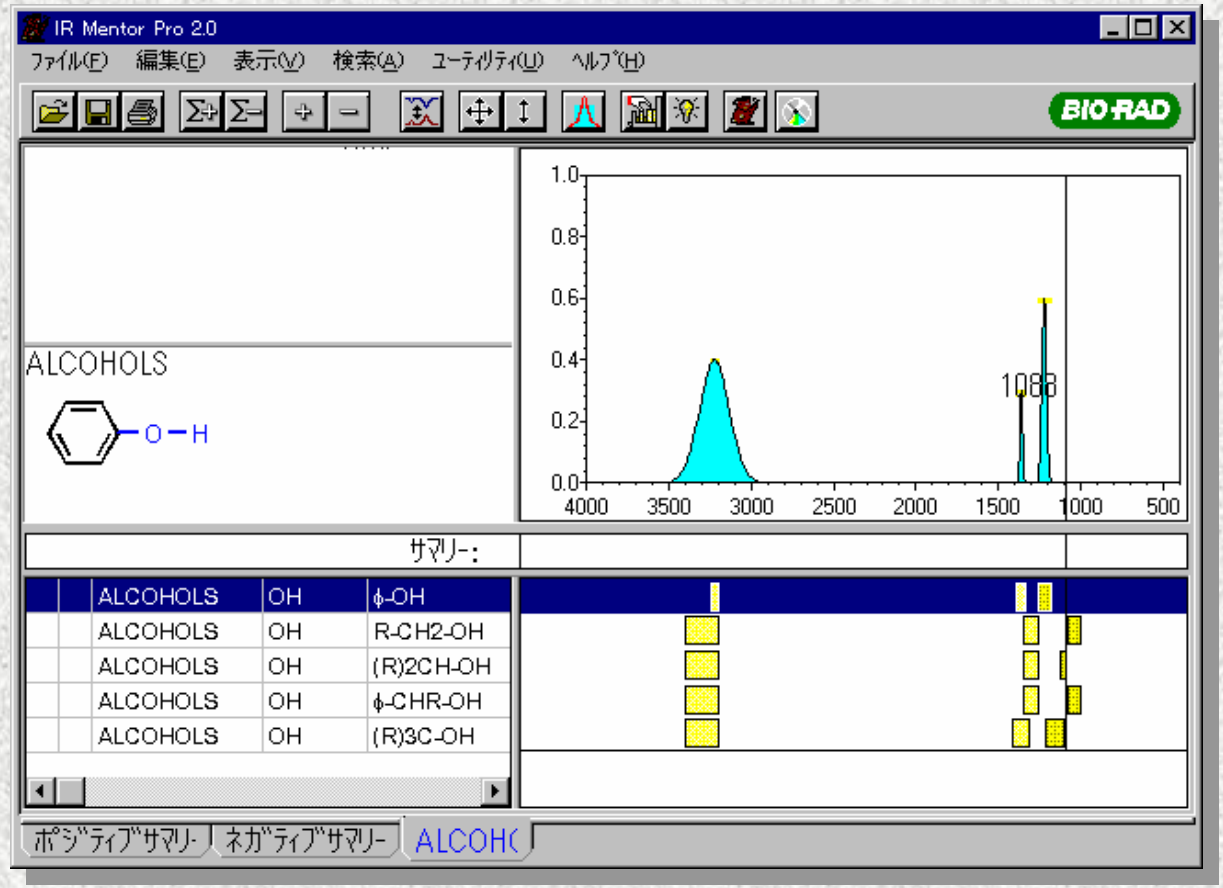
Analysis Example

Search example (1) : Searching by peak



Analysis Example 2

Search example (2): Search by compound classification



Spectral Search

Spectral Search

(1) Compare with standard spectrum collections
(2) Compare with Sadtler databases

Important Information on Searching

Use a search algorithm suited to your purpose

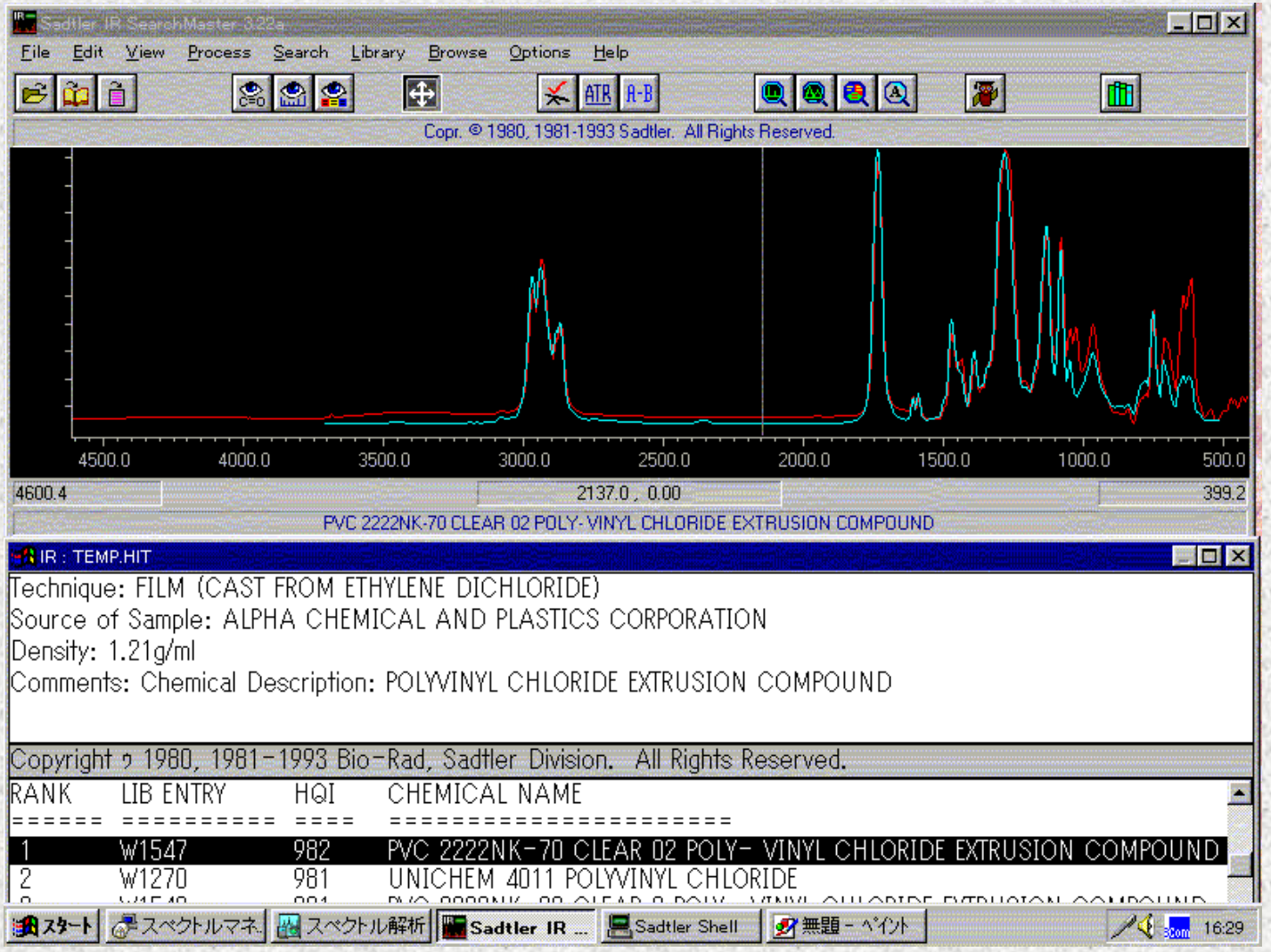
Identify whether the sample is made up of single or multiple components

Judge search results by eye based on their resemblance to a pattern rather than emphasizing evaluation points
(Algorithms can quickly find similar spectra in a large volume of data, but they cannot interpret the spectra they find)

When there are mixtures, the key is to skillfully utilize difference spectra

Obtain other component information in advance whenever possible

Spectral Search Example



Spectral Search Example (Difference Spectrum)