Homework

- Chapter 11： #3-5

Infrared (IR) and Raman Spectroscopy
红外和拉曼光谱法

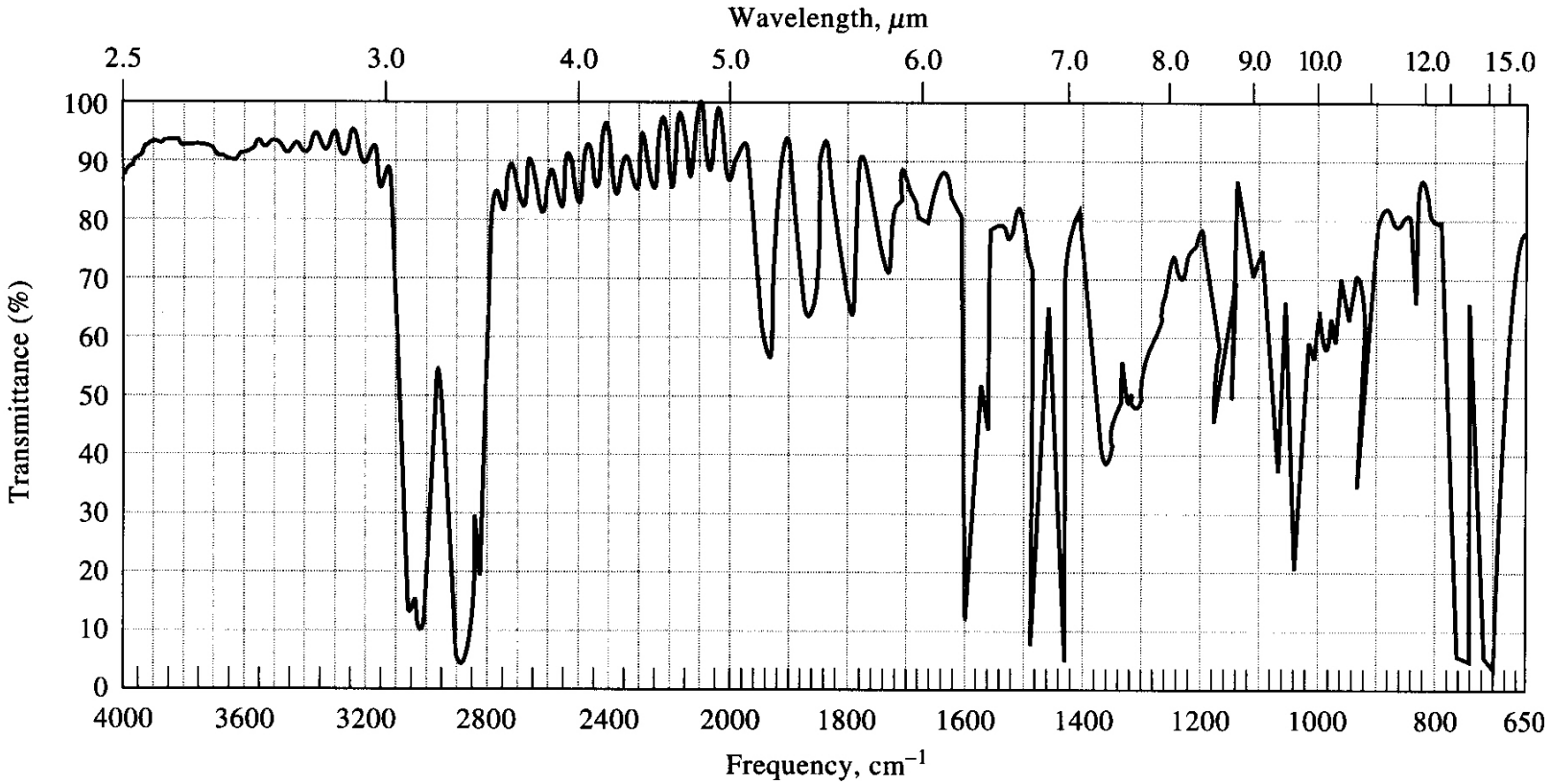
- **Infrared Spectroscopy**
  - **Introduction 简介**
  - **Instrumentation仪器**
  - **Applications应用**
- **Introduction of Raman Spectroscopy拉曼光谱简介**

Sir William Herschel: recognize Infrared, 1800
Abney & Festing: 1882-1900, Spectra vs organic group
W.W. Coblentz: 1908, Measured IR of several hundred molecules

A Few Things to Understand for Infrared

- Why do some molecules absorb infrared light and some not?
- What are the wavelength or better wavenumber (frequency)?
- How to measure absorption spectra in infrared region?

IR Absorption Spectrum of a Thin Polystyrene Film聚苯乙烯薄膜的红外吸收光谱



Note that the abscissa横坐标 scale changes at 2000 cm^{-1}.

Usually wavenumber is used: directly proportional to energy.

横坐标使用波数表示，直接正比于振动能量。

Molecular Dipole Moments分子偶极矩

- Even though the total charge on a molecule is zero, the nature of chemical bonds is such that the positive and negative charges do not completely overlap in most molecules. Such molecules are said to be polar because they possess a permanent dipole moment.
- Examples：
  - With permanent dipole moment ： H_2O
  - With induced dipole moment: N_2, CO_2, CCl_4

Theory of Infrared (IR) Absorption
产生红外吸收的基本理论

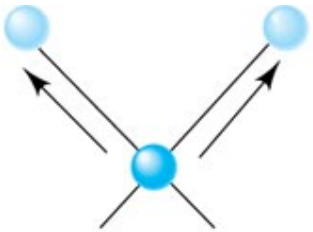
- **The alternating electrical field of the radiation interacts with fluctuations in the dipole moment偶极矩of the molecule. 激发光的电场向量波动与分子的偶极矩的涨落发生作用**
- **Absorption of IR is restricted to a net change in the dipole moment of the molecule associated with the vibrations or rotations**

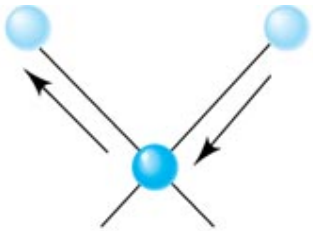
  只有能产生净偶极矩变化的分子振动和转动才能产生红外吸收, 如HCl
- **If the frequency of the radiation matches the vibrational frequency of the molecule then radiation will be absorbed, causing a change in the amplitude of molecular vibration.**

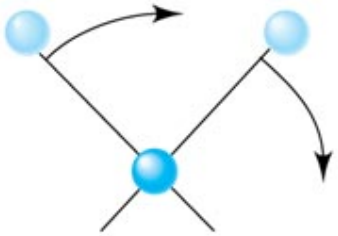
  当光的频率与分子振动频率匹配，则分子吸收该频率的光，振动幅度发生变化

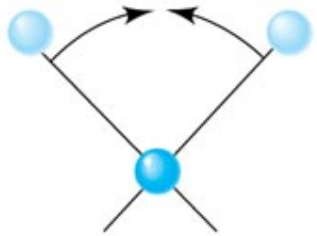
IR transparent molecules: He, Ne, H_2, N_2, O_2

Types of Molecular Vibrations
分子振动类型



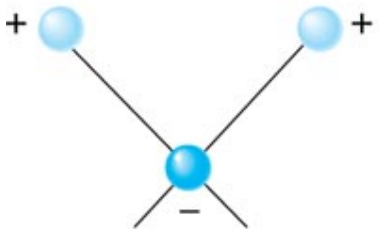


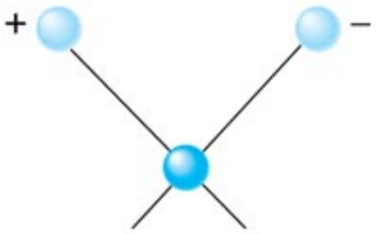




Stretching Vibrations
伸缩振动

“+”面外弯折振动
“-”面内弯折振动



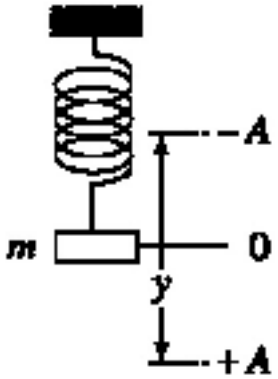


Bending Vibrations
弯曲振动

Mechanic Model as a Stretching Vibration in a Diatomic Molecule
双原子分子伸缩振动的力学模型

***k*: force Constant for the bond**
化学键的力常数

Hooke's law
胡克定律



$$F = -ky$$

Mechanic Model Approximation for the Stretching Vibrationof a Diatomic Molecule双原子分子伸缩振动的力学模型

$$\nu_m = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

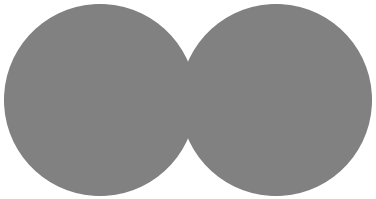
ν_m — natural frequency of the oscillator基频

- Dependent on *k* of the spring and *m* of the attached body基频与力常数和质量有关

力常数(N/cm)：两原子由平衡位置伸长单位长度时的恢复力。

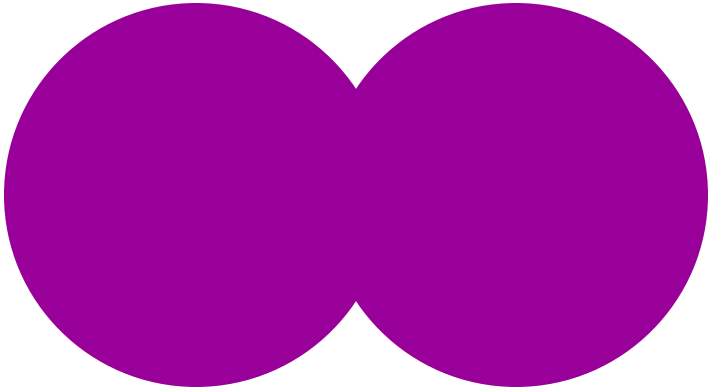
How does the mass influence the vibration?

H_2



MM =2 g/mole

I_2



MM =254 g/mole

The greater the mass - the lower the wavenumber

Diatomic Molecule Stretch Vibration
双原子分子伸缩振动

对于含有两个不同质量的振动体系，使用折合质量(μ)

The mechanical model based equation may be modified to describe the behavior of the system consisting of two masses m_1 and m_2 connected by a spring by substitution of the reduced mass μ for m.

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{thus,} \quad \nu_m = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi}\sqrt{\frac{k(m_1+m_2)}{m_1 m_2}}$$

In wavenumber expression 使用波数表达

$$\bar{\nu} = \frac{\nu}{c} = \frac{1}{2\pi c}\sqrt{\frac{k(m_1+m_2)}{m_1 m_2}}$$

$$\bar{\nu} = \frac{\nu}{c} = \frac{1}{2\pi c}\sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}}$$

- $\bar{\nu}$ —the wavenumber 波数of absorbed light (**cm^{-1}**)
- c — the velocity 速度of light (**$cm \cdot s^{-1}$**)
- m_1 & m_2 — masses of the atoms 1 and 2 (**g**)

  $m=A_r/N_A$(Ar — atomic mass; NA — Avogadro constant)
- k — the force constant for the bond (**$N \cdot cm^{-1}$**)

  (1 N=1 kg ·m/s^2)
  - Single bonds单键: 5 $N \cdot cm^{-1}$(or $5x10^2$ $N \cdot m^{-1}$)
  - Double bonds双键: 10 $N \cdot cm^{-1}$(or $1x10^3$ $N \cdot m^{-1}$)
  - Triple bonds三键: 15 $N \cdot cm^{-1}$(or $1.5x10^3$ $N \cdot m^{-1}$)

Example Calculate the approximate $\bar{\nu}$ and λ of the fundamental absorption peak due to the stretching vibration of C=O

For the O atom: m_1=16 g ·mol^{-1}/6.022x10^{23} mol^{-1}= 2.7x10^{-23} g

For the C atom: m_2=12 g ·mol^{-1}/6.022x10^{23} mol^{-1}= 2.0x10^{-23} g

μ=(2.7x10^{-23}g x 2.0x10^{-23} g)/(2.7x10^{-23}g +2.0x10^{-23} g)= 1.1x10^{-23}g

$$\nu = \frac{1}{2\times 3.14\times 3.0\times 10^{10}\,\mathrm{cm\cdot s^{-1}}}\sqrt{\frac{10\,\mathrm{N\cdot cm^{-1}}}{1.1\mathrm{x}10^{-23}\,\mathrm{g}}}$$

$$= \frac{1}{1.88\times 10^{11}\,\mathrm{cm\cdot s^{-1}}}\sqrt{\frac{10\times 1000\,\mathrm{g}\times 100\,\mathrm{cm\cdot s^{-2}\cdot cm^{-1}}}{1.1\mathrm{x}10^{-23}\,\mathrm{g}}}$$

$$\approx 1600\,\mathrm{cm^{-1}}$$

The carbonyl stretching band is found experimentally to be in 1600-1800 cm^{-1}

Quantum Treatment of Vibrations

$$E = (v + \frac{1}{2})h\nu_m$$

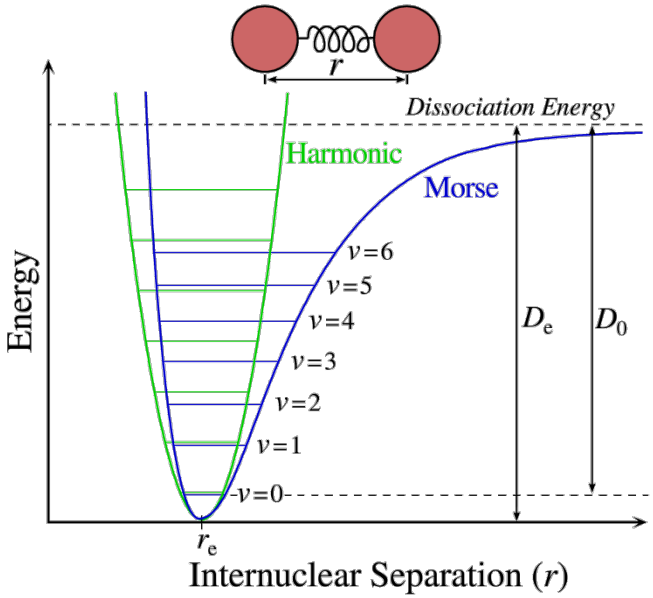
v the vibrational quantum number

Selection Rules: $\Delta v = \pm 1$

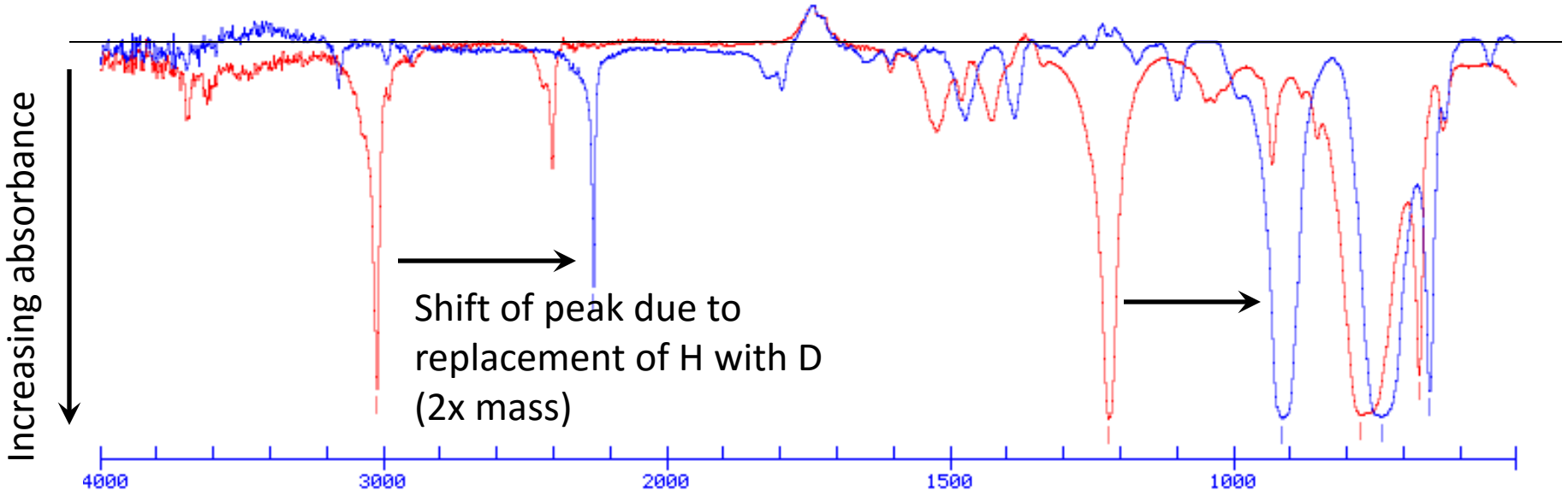
Anharmonicity:

The selection rule is not rigorously followed

Overtones are sometimes observed



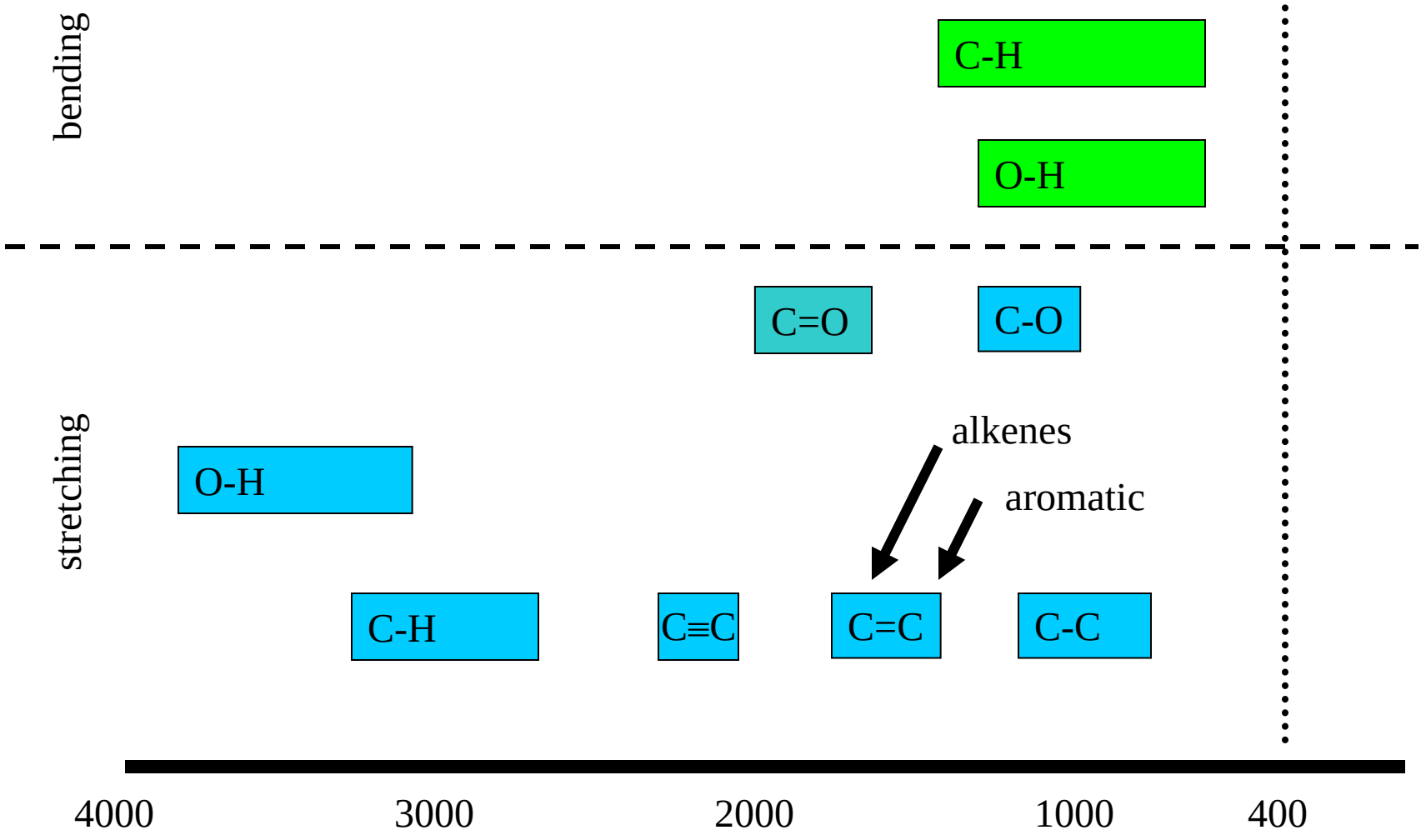
IR Spectra of chloroform and deuterochloroform
氯仿与氘代氯仿的红外光谱



Mode of vibration	$CHCl_3$ Calculated*	$CHCl_3$ Measured	$CDCl_3$ Measured
C-H stretching	3002	3020	2256
C-H bending	1120	1219	912
C-Cl stretching	701	773	737
C-Cl bending	418	671	652

* Spartan '02 AM1 minimization

Basic Functional Groups基本官能团的振动频率



要求！

Announcement

- Homework: chapter 11 6-7
- Final Exam: 7月1日 上午　理教410
- 答疑时间：
  - 6月29-30日 8:30-11:30 AM，2:00-4:00 PM
  - 其他时间答疑请邮件预约

Vibrations in a Polyatomic Molecule
多原子分子的振动

- A molecule containing N atoms has 3N degrees of freedom in motion含有N原子的分子有3N自由度
- Each of the vibrations is called a normal mode 简正振动
  - 3N-6：含有N原子的分子有3N-6个简正振动自由度
  - Linear Molecule 线形分子: 3N-5

Instrumentation for IR Measurement
用于红外范围测量的仪器

- **Dispersive Infrared Spectrometers色散型红外光谱仪**

  The same as UV-vis spectrophotometer with the light source, the dispersive elements and the detector adequately designed for IR

  Drawbacks:缺点

  Slow scan speed, low sensitivity and low resolution

  扫速慢 灵敏度低 光谱分辨率低

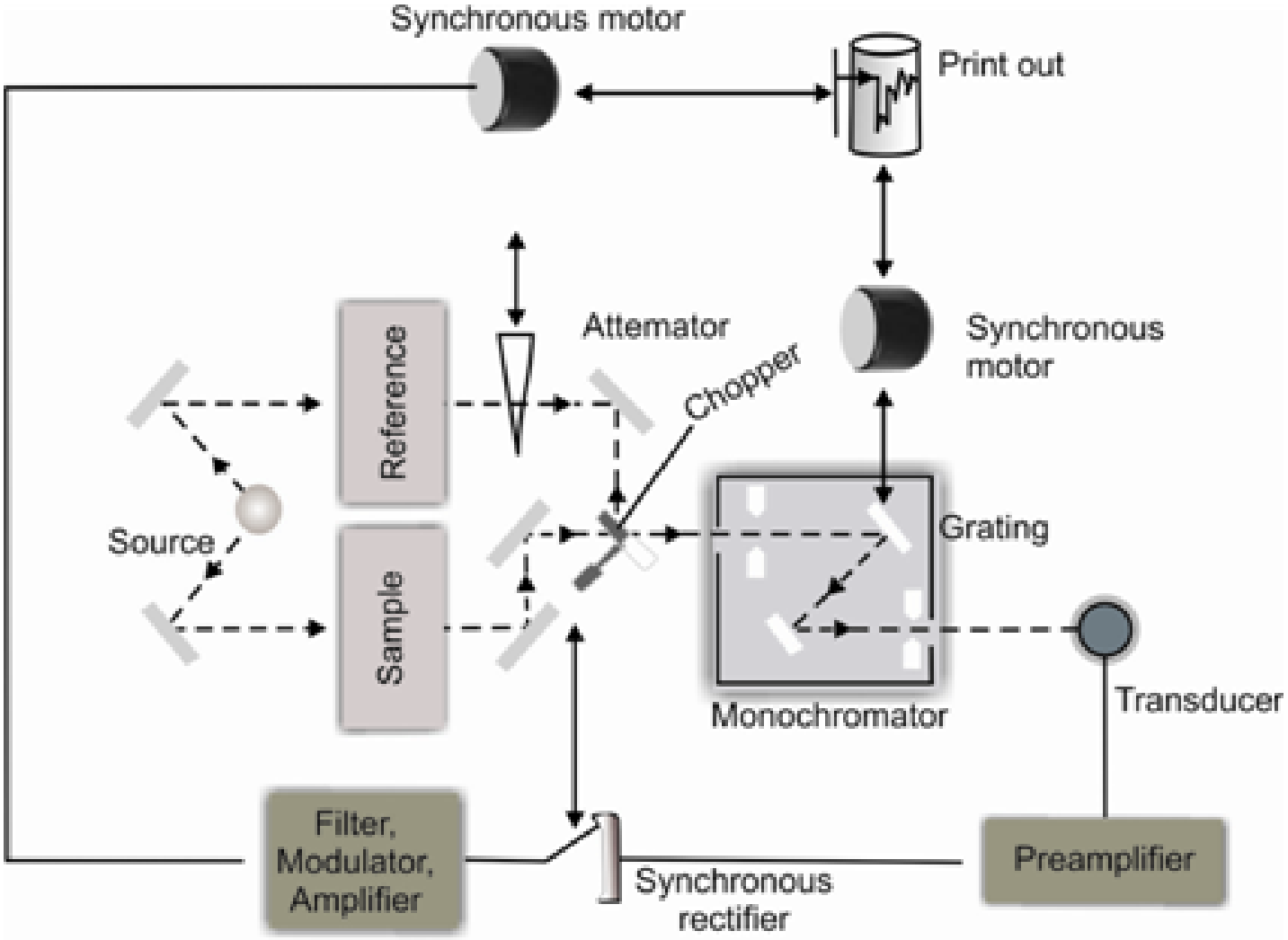
- **Fourier-Transform Infrared Spectrometers**

  傅里叶变换红外光谱仪

  The interference of radiation between two beams to yield an interferogram

  两束光经过干涉产生干涉谱

Dispersive Type色散型



1. Dual beam； 2. Location of sample cell

IR Sources 红外光源

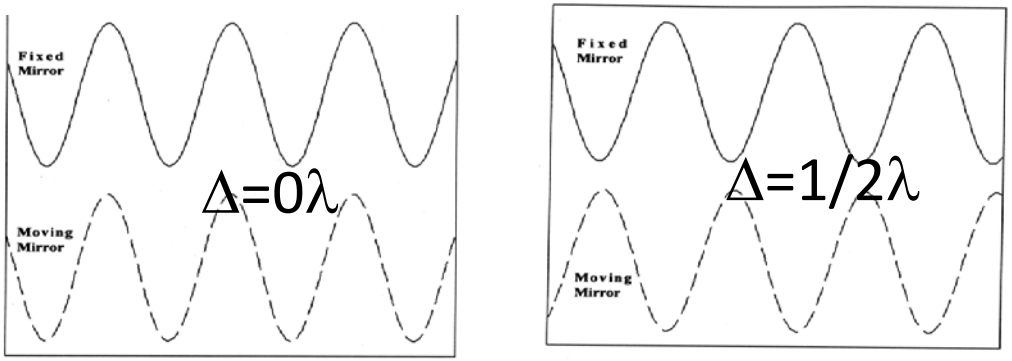
- Need Strong radiation power, for mid-IR
  - By materials根据材质分类
    - Silicon carbide rod (硅碳棒) (glow bar)
    - Rare earth oxide ceramic piece (稀土氧化物陶瓷片）(Nernst filament/Nernst glower)
  - By ways of cooling根据冷却方式分类
    - Water cooled source (Globar), e.g. Silicon carbide rod (硅碳棒)
    - Air cooled source, e.g. Nichrome wire镍铬电热丝 or a small ceramic piece (Air & water)
- CO_2 laser
- Hg arc (Far IR), Tungsten filament (Near IR)

Infrared Transducers红外检测器

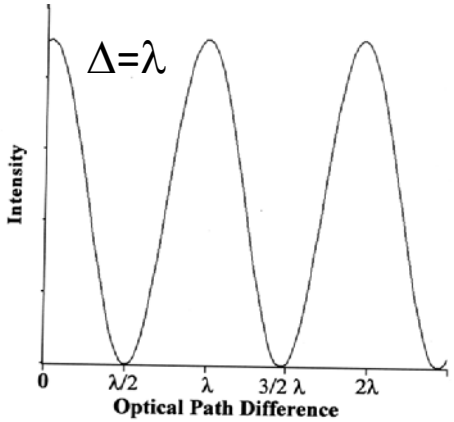
Type	λ, nm
Photon Detectors光子检测器	
Photptubes光电管	150-1000
Photomultiplier Tubes光电倍增管	150-1000
Silicon photodiodes硅光二极管	350-1000
Photoconductive cells光敏电阻器	1000-50000
Thermal Detector热检测器	
Thermocouples热电偶	600-20000
Bolometers辐射热测定器	600-20000
Pneumatic cells气动元件	600-40000
Pyroelectric cells热释电检测器	1000-20000

Optical Path Difference and Interferograms
光程差与干涉谱

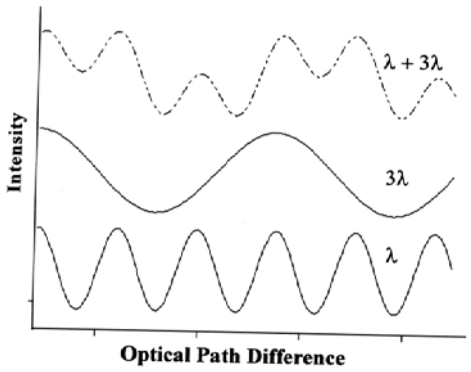
Illustration of Optical Path Difference



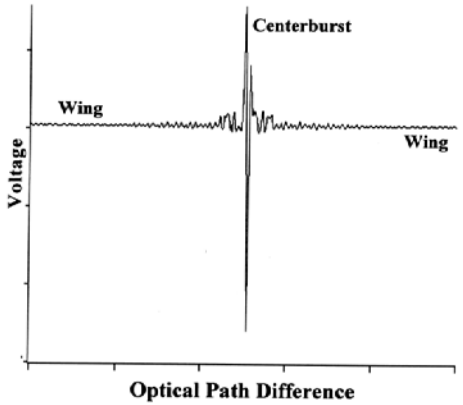
Interferograms



Monochromatic

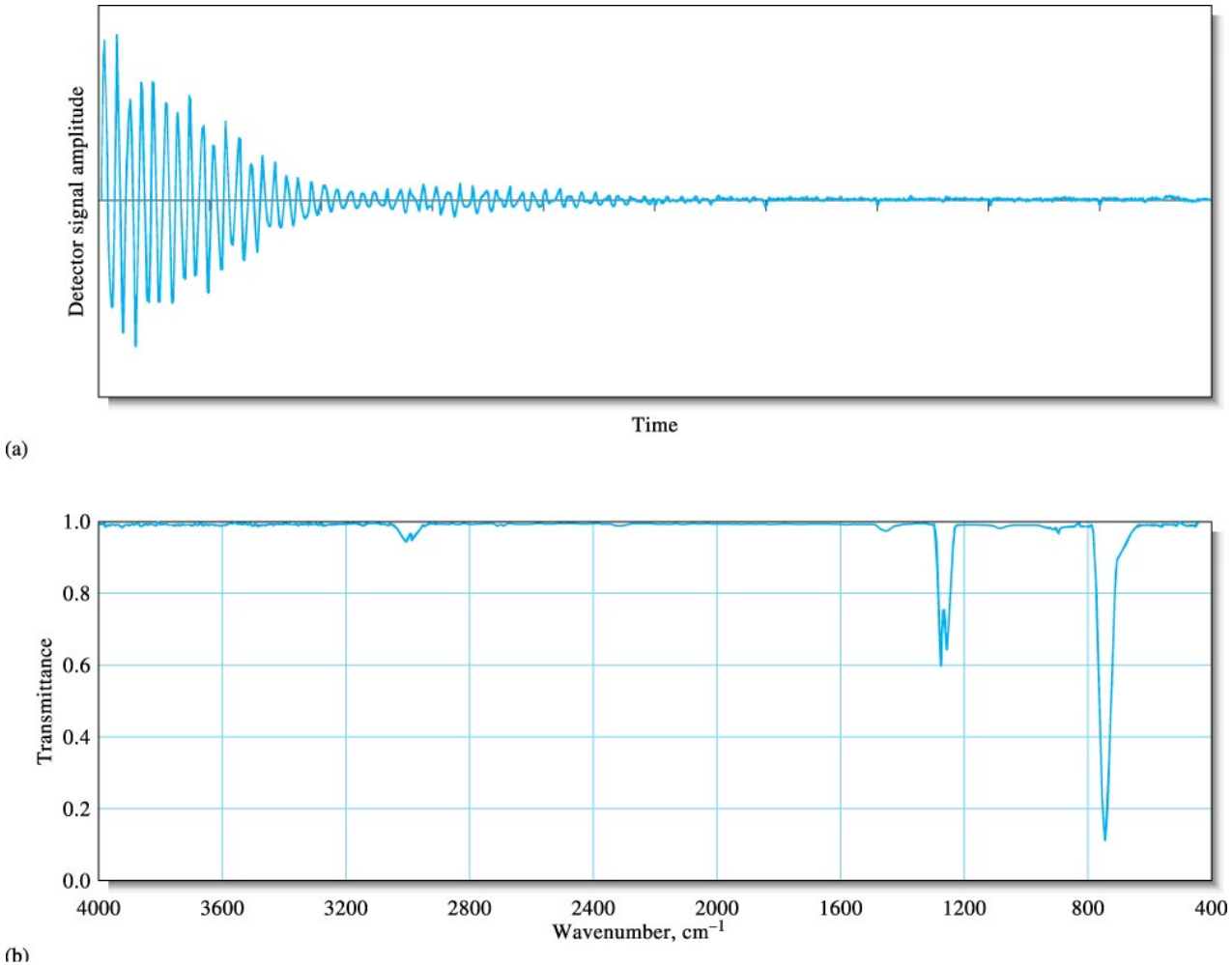


The sum of two wavelength

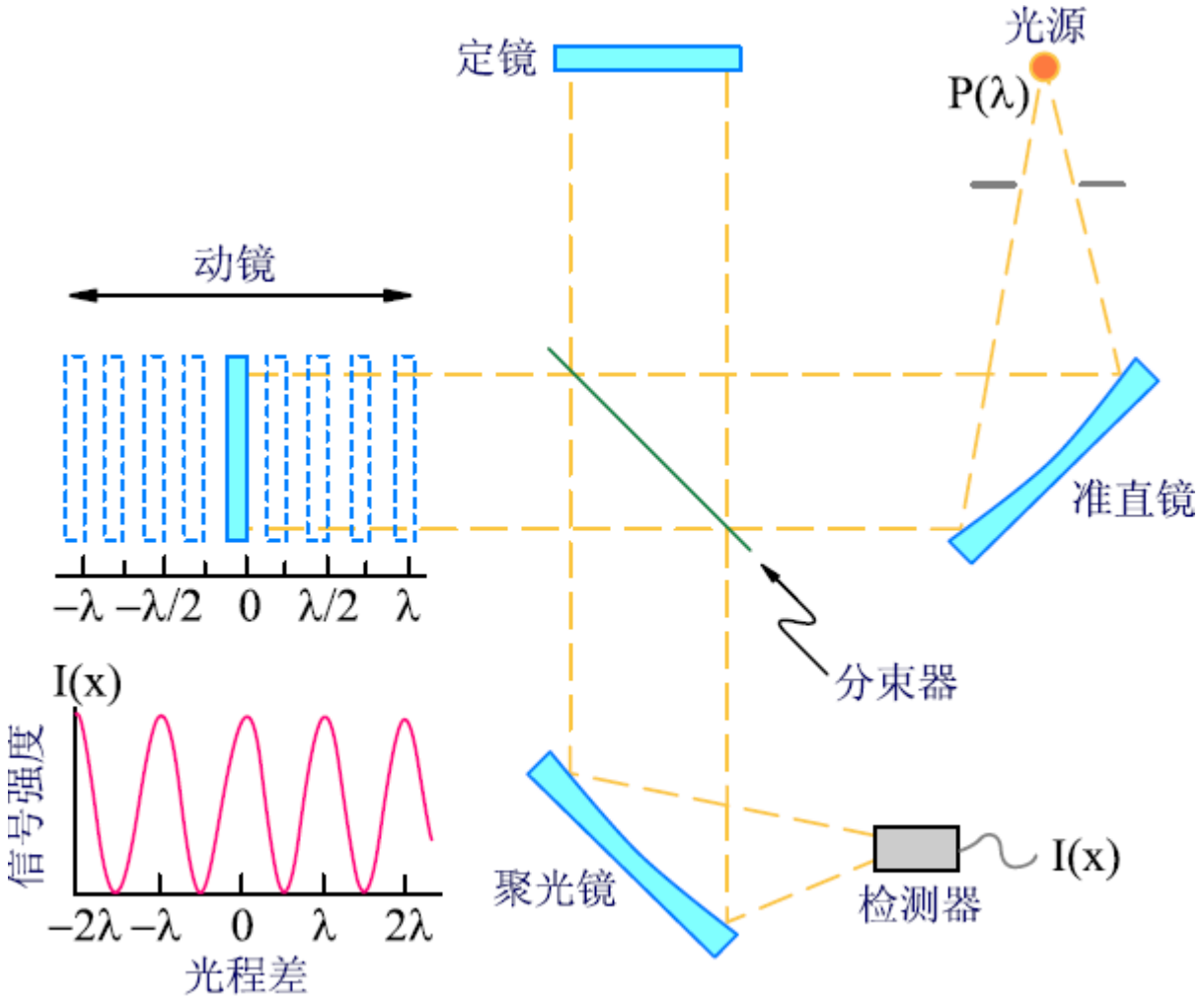


Broadband IR source

Interferogram & IR Spectrum of CH_2Cl_2
CH_2Cl_2的干涉谱和红外谱



Michelson Inferometer迈克尔逊干涉仪



Michelson Interferometer迈克尔逊干涉仪

- ✧Beam splitter 光束分裂器
- ✧Stationary mirror 固定镜
- ✧Moving mirror at constant velocity可动镜
- ✧Motor driven Micrometer screw马达驱动的微米螺杆
- ✧He/Ne laser氦氖激光器: sampling interval, control mirror velocity

Fourier Transform Infrared Spectrometers
FTIR傅里叶变换红外光谱仪

光源
Light source

迈克尔逊干涉仪
Michelson
Interferometer

吸收池
Sample Cell

检测器
Detector

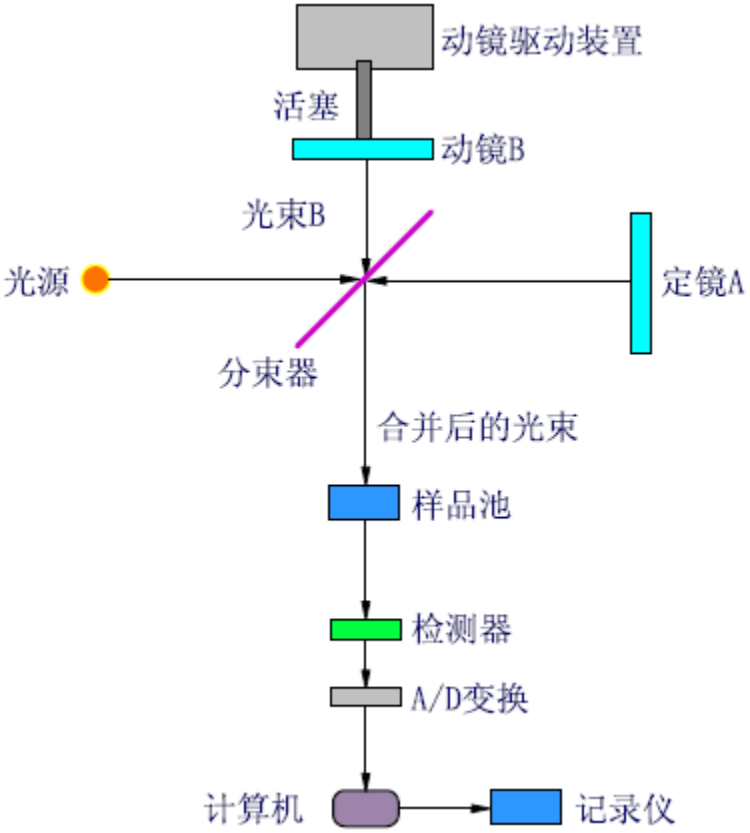
傅里叶变换
Fourier
Transformation

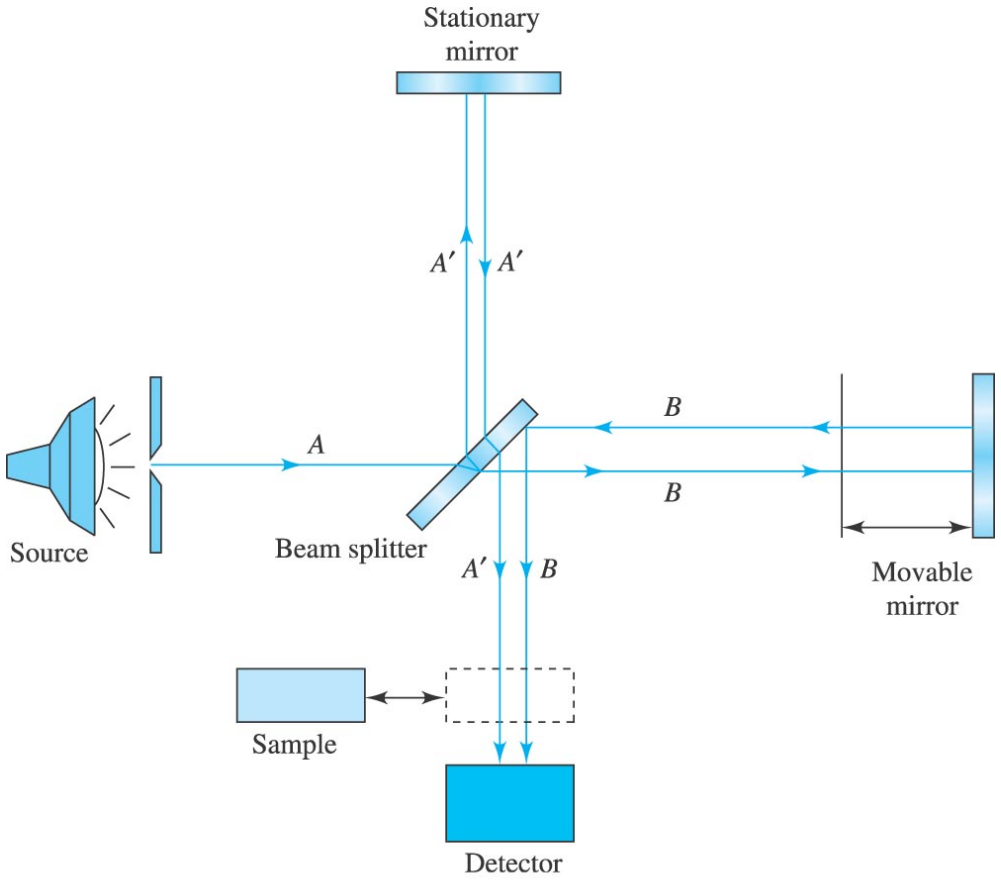
Left: Albert Abraham Michelson, 1907 , the first Nobel Laureate in Sciences in USA

Right: A Michelson Interferometer on a optical table

http://en.wikipedia.org

FTIR Spectrophotometer





Fourier Transform vs Dispersion IR Spectrometer

The Advantages & Disadvantages of FTIR
FTIR的优缺点

- **The throughput (Jacquinot) advantage**

  No slit restriction, energy throughput is high, thus improved SNRs. High sensitivity!

- **High resolving power and wavelength reproducibility**
- **The multiplex (or Fellgett) advantage**

  All source wavelengths are measured simultaneously in an interferometer. High sensitivity and speed!

- **The Connes advantage**:

  Precision of peak position is high with He-Ne laser as a reference for mirror movement.

- **Monobeam – artifacts like H_2O or CO_2 peaks**

Application of FTIR

- **Quanlitative** – Molecular structure, functional group
  - The Sadtler Standard Spectra series
  - Aldrich FT-IR Libraries
  - Sigma Bio-Chemicals FT-IR Library
- **Quantitative**
  - Lambert-Beer's Law

Sample Preparation样品制备

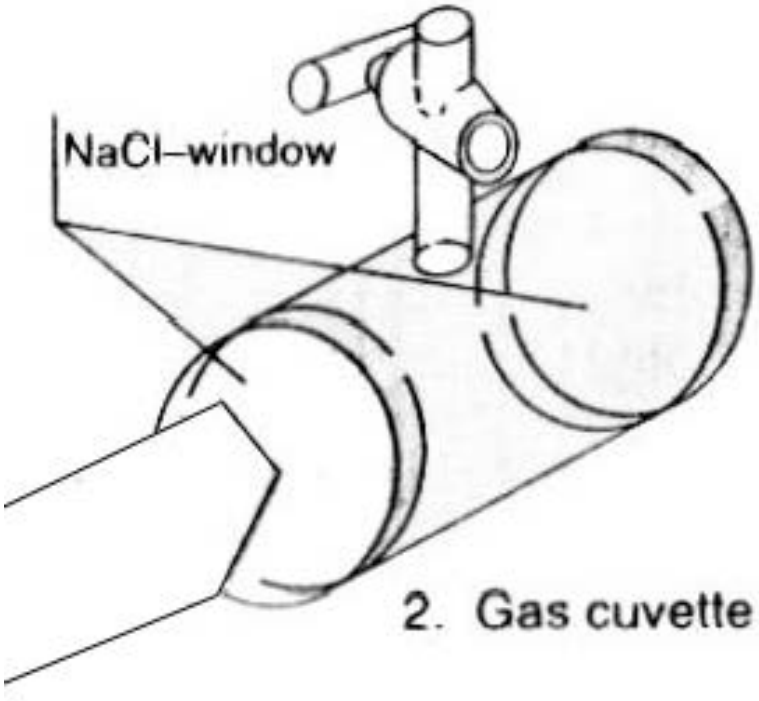
- **Sample forms: Gas, liquid and solid**
  样品形态：气、液、固
- **Sample contains no free water**

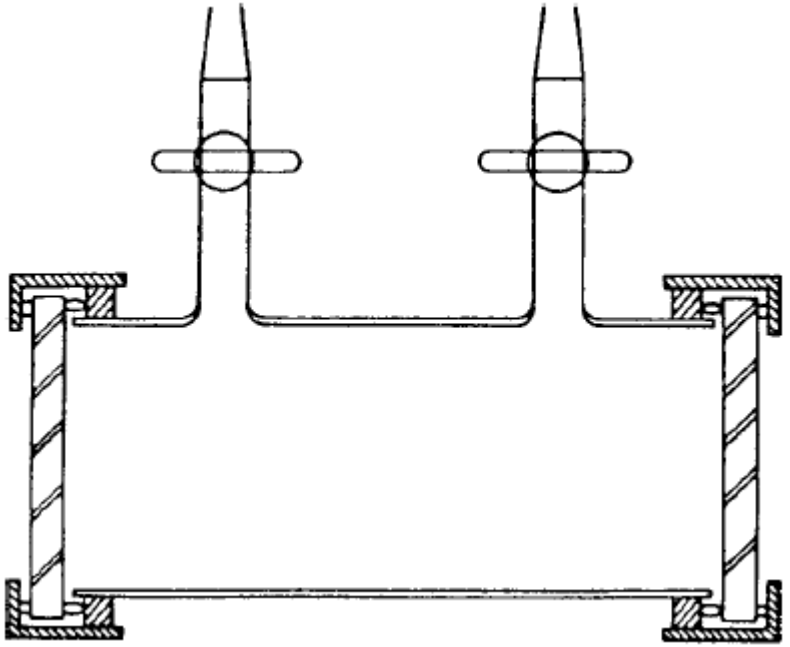
样品中不含水

- **It is desirable that the transmittance is within 10%-80%**

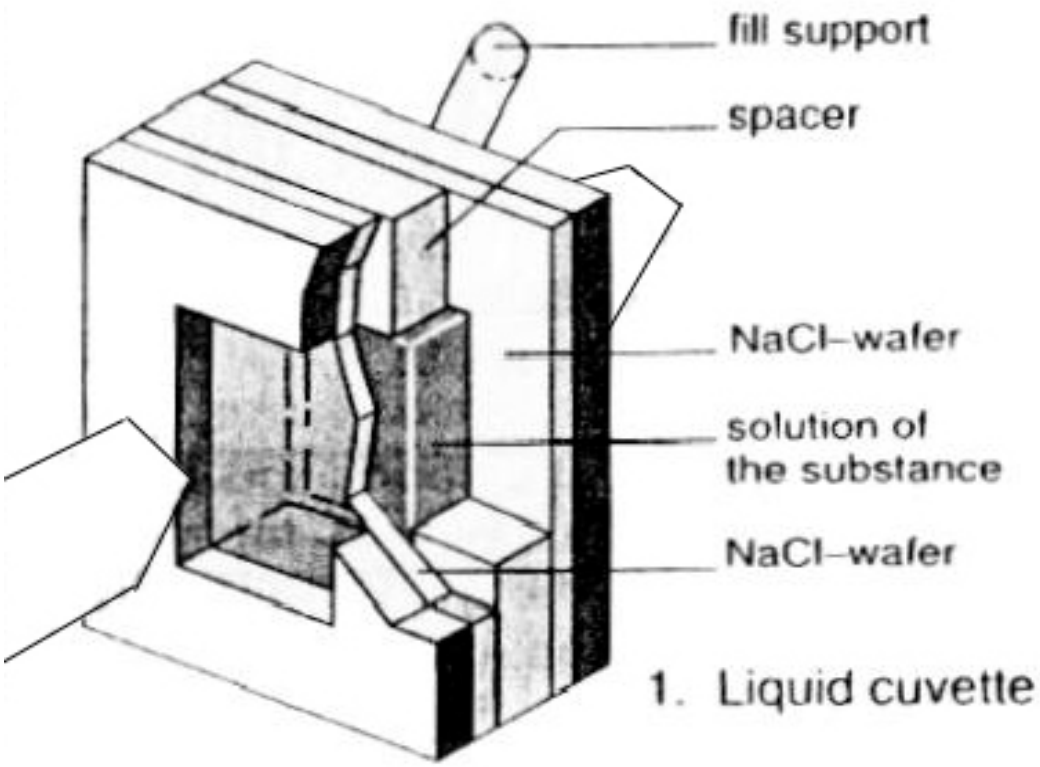
最好透光率在10%-80%之间

Schematic of a Typical Infrared Gas Cell
红外气体池





Liquid Cell液池



Liquid Sample Film Preparation
液体样品膜制备

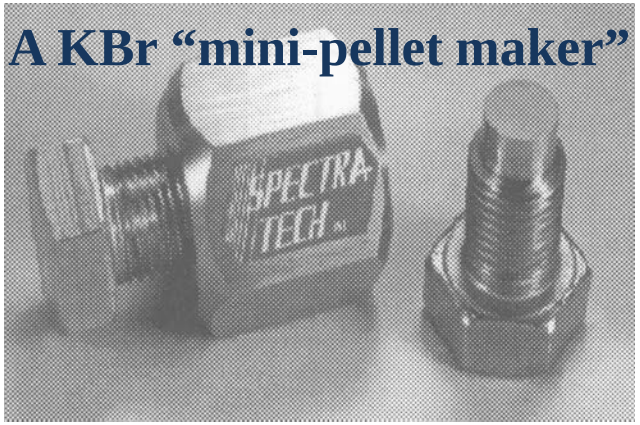
Solid Sample Preparation固体样品制备

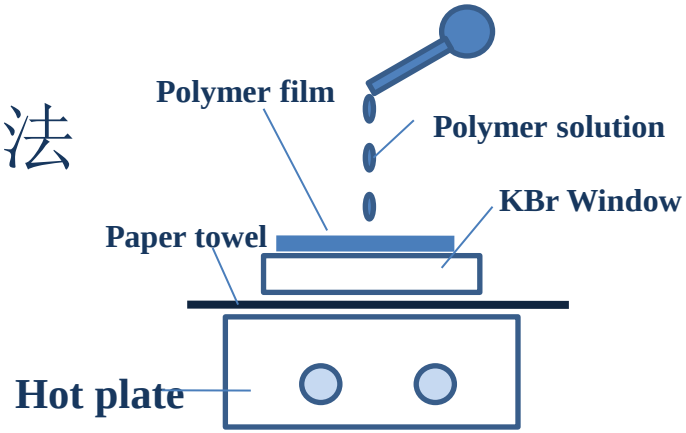
- KBr Pellet (KBr压片法)

  KBr as a support and a diluent(稀释剂)、agate mortar(玛瑙研钵)

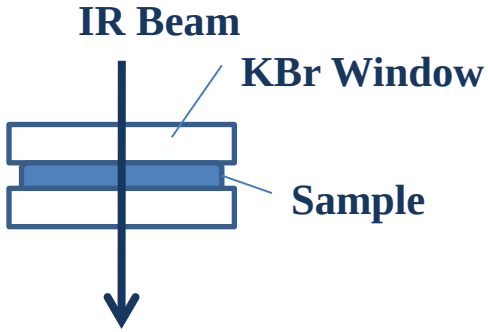
- Mull Sample(石蜡糊法): Nujol as Mulling agent, agate mortar
- Cast films成膜法

  for polymer





A diagram of how to cast a polymer film



A diagram of a mull sample

Raman Spectroscopy, A Brief History

- **1923** Theoretical prediction by the Austrian physicist A.Smekal
  "The quantum theory of dispersion" (Naturwissenschaften 11, p. 873, 1923)
- **1928** Experimental discovery
  - by the Indians C.V. Raman and K.S. Krishnan in Kalkutta

  "The optical analog of the Compton effect" (Nature 121, p.711, 1928)
  - by the Russians G. Landsberg et L. Mandelstam à Moscou

  "A novel effect of light scattering in crystals" (Naturwissenschaften 16, p.557, 1928)
- **1930** Nobel Prize: Sir C.V. Raman (* 1888, +1970)

  "… for is work on light scattering and the discovery of the later called Raman effect ..."

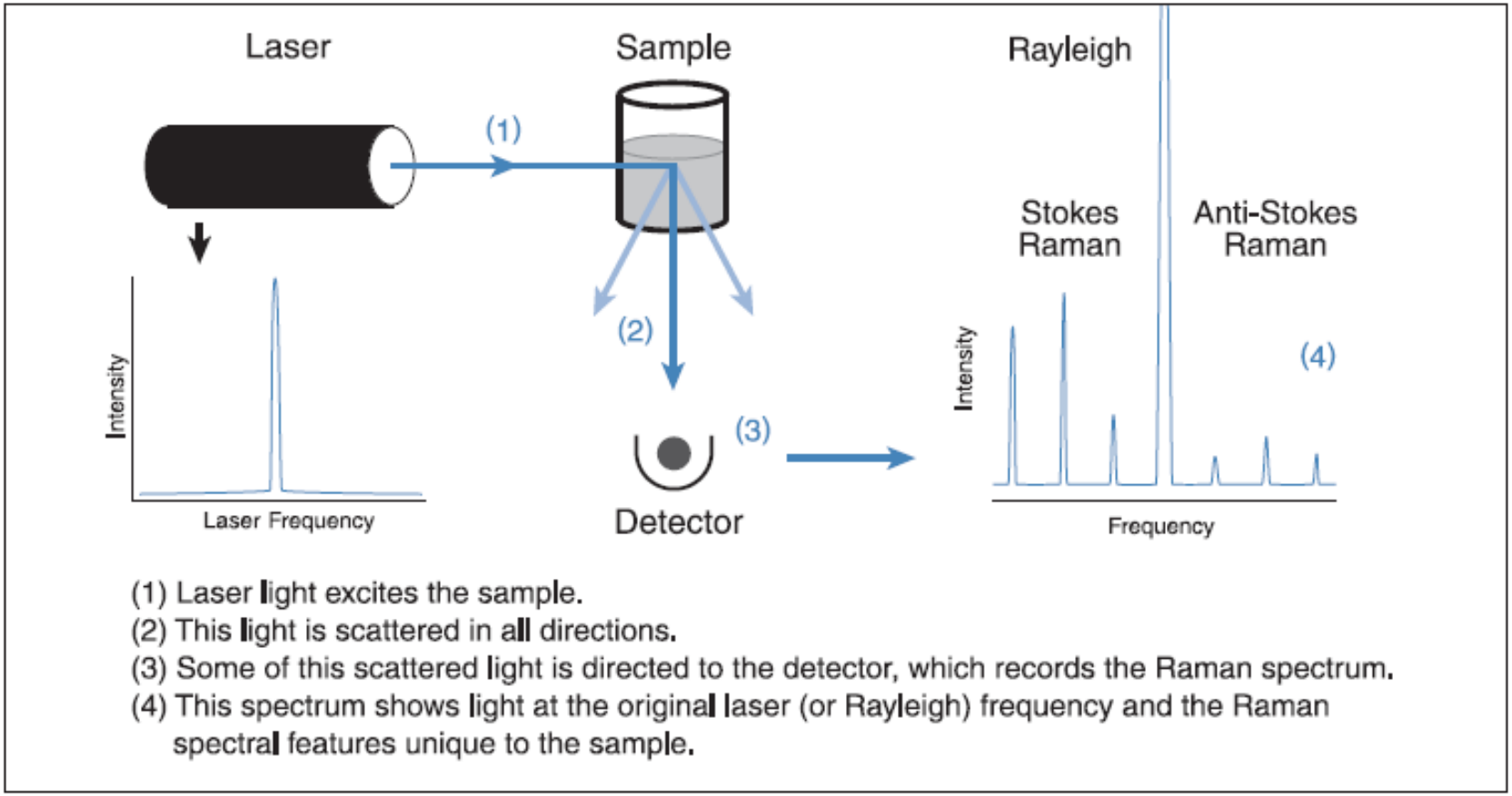
Introduction to Raman Spectroscopy
拉曼光谱简介

- Raman spectroscopy:
  - A spectroscopic technique based on inelastic scattering of monochromatic light. 物质对单色光的非弹性散射
  - The sample is irradiated with a laser source of visible or near infrared monochromatic radiation.

    以单色激光激发样品
  - Stokes and anti-Stokes scattering are measured in infrared region

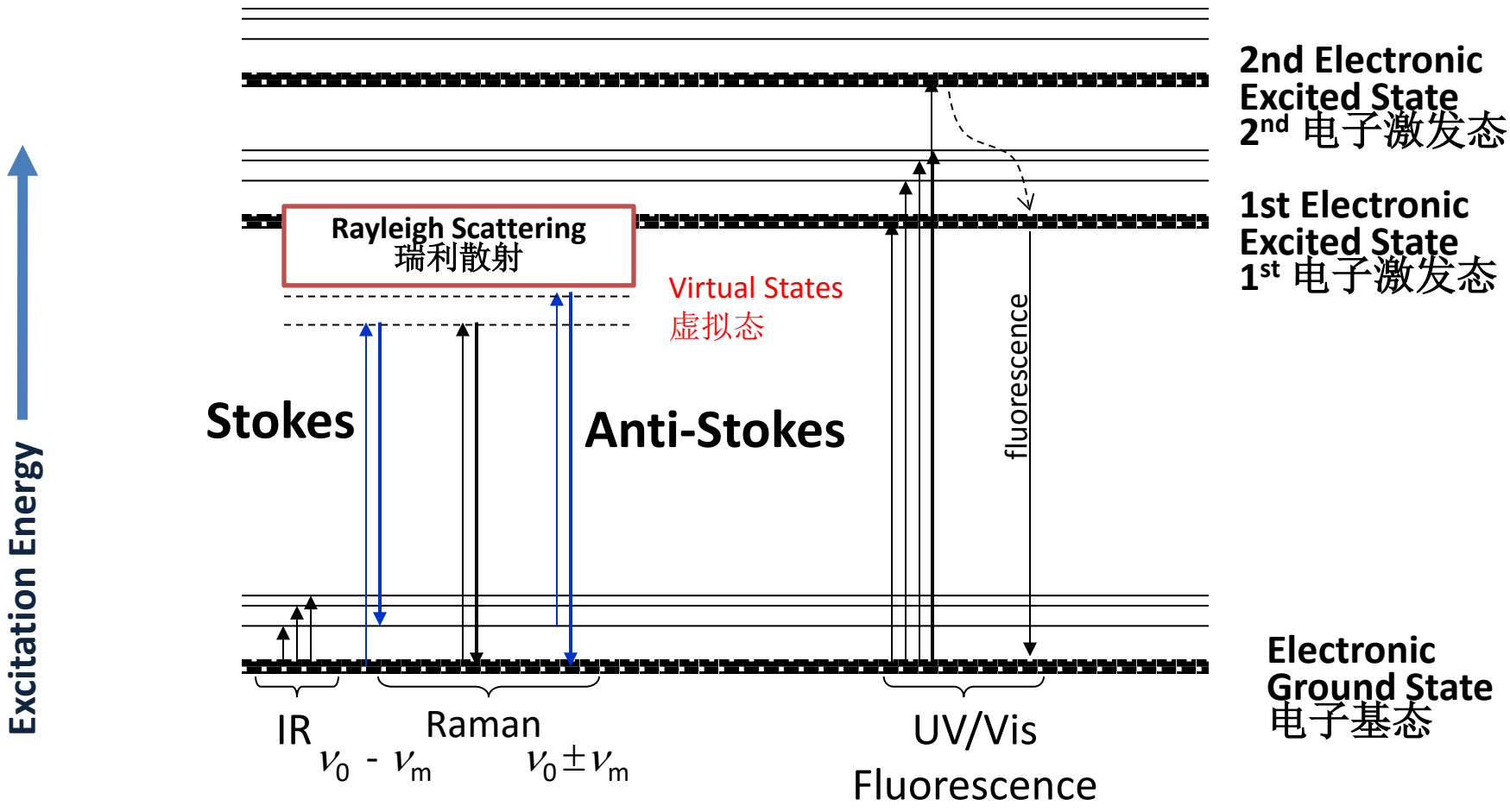
    在红外波长范围测量Stokes和anti-Stokes 散射

Schematic Illustration for Raman Measurement
拉曼光谱测定示意图



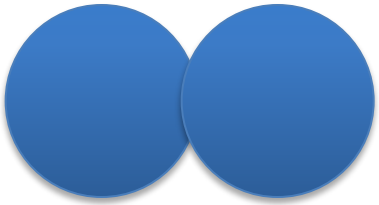
(1) Laser light excites the sample.
(2) This light is scattered in all directions.
(3) Some of this scattered light is directed to the detector, which records the Raman spectrum.
(4) This spectrum shows light at the original laser (or Rayleigh) frequency and the Raman spectral features unique to the sample.

Main Optical Transitions: Absorption, Scattering, & Fluorescence
分子主要跃迁：吸收、散射以及荧光



The virtual state —*a* short-lived distortion of the electron distribution by the electric field of the incident light.

Classical Explanation经典的电磁理论解释



$$\bar{\nu} = \frac{\nu}{c} = \frac{1}{2\pi c}\sqrt{\frac{k(m_1+m_2)}{m_1 m_2}}$$

$$P = \alpha \cdot E \qquad E = E_0 \cos 2\pi \nu_{ex} t, \quad \alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial r}\right)(r - r_{eq})$$

$$r - r_{eq} = r_m \cos 2\pi \nu_v t$$

P – induced dipole诱导偶极矩

α – the polarizability 极化率

A measure of the deformability of the bond in an electric field

α_0 – the polarizability of the bond at the equilibrium internuclear distance r_{eq}

r – *the internuclear* separation at any instant.

Classical Explanation经典的电磁理论解释

$$P = \alpha_0 E_0 \cos 2\pi \nu_{ex} t +$$

$$E_0 r_m \left(\frac{\partial \alpha}{\partial r} \right) \times \cos(2\pi \nu_V t) \cos(2\pi \nu_{ex} t)$$

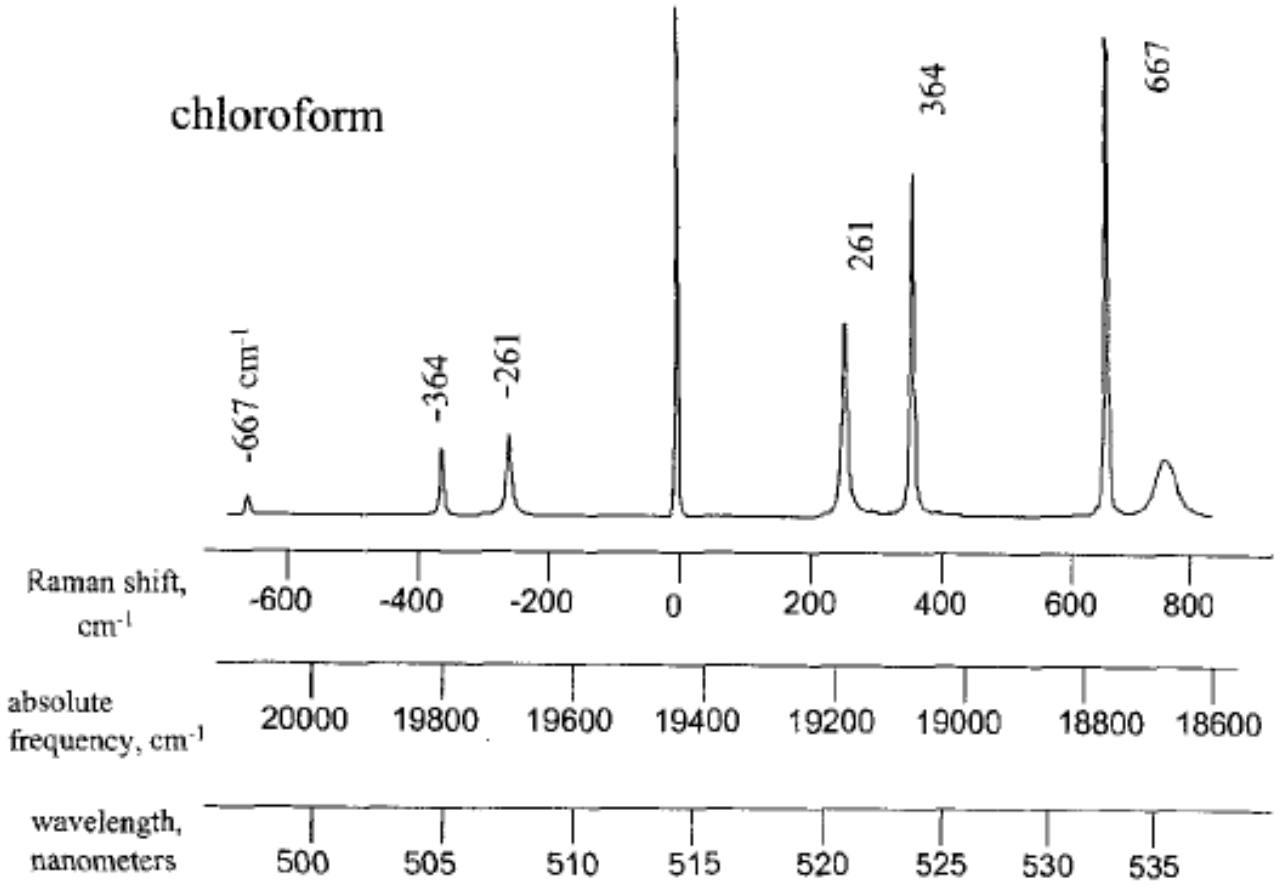
$$P = \alpha_0 E_0 \cos 2\pi \nu_{ex} t +$$

$$\frac{1}{2} E_0 r \left(\frac{\partial \alpha}{\partial r} \right) \times [\cos 2\pi t(\nu_{ex} + \nu_V) + \cos 2\pi t(\nu_{ex} - \nu_V)]$$

Basics for Raman Spectroscopy

- Frequency频率：
  - Rayleigh Scattering瑞利散射: Emitting light with the same frequency as an excitation source ν_0
    散射光频率与激发光频率相等
  - Stokes Frequency (Stokes 频率):Emitting light with $\nu_0 - \nu_m$
    发出光子的频率小了ν_m
  - Anti-stokes Frequency (反Stokes频率): Emitting light with $\nu_0 + \nu_m$ 发出光子的频率大了ν_m
- Intensity强度：
  - Rayleigh Scattering : 99.999% ;Raman Scattering: 0.001%
  - Stokes Intensity >> Anti-Stokes Intensity
- Other Characteristics其他特点
  - Independent of the excitation wavelength与激发波长无关
  - Associated with vibration & rotation energy对应振动和转动能量

Raman Spectrum of Room-Temperature Chloroform ($CHCl_3$) Obtained with 5 14.5 nm Light
以514.5 nm光源获得的氯仿的室温拉曼谱



Raman Spectroscopy for Chemical Analysis. Richard L. McCreery

Comparing IR & Raman

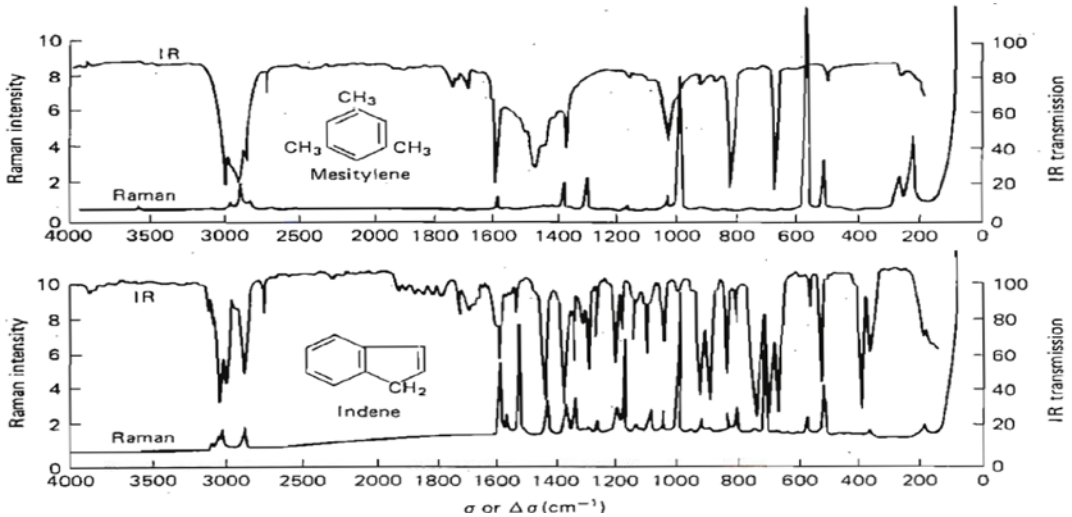
- **Vibrational & Rotational Energy: Same energy/frequency region**
- **Mechanism difference产生光谱的机理**
  - **IR: dipole moment change偶极矩变化**
  - **Raman: momentary distortion of the electrons distributed around a bond in a molecule, then back to normal state by emission**

    分子诱导偶极矩的变化，即分子的电子壳层形变，正负电荷中心相对位移，形成诱导偶极矩

    $\mu = \alpha \cdot E$

    N_2, Cl_2, & H_2 IR transparent
  - **Polarizability of the bond: maximum at maximum distance; minimum at minimum distance**

Comparing Raman and Infrared Spectra



- **IR inactive & Raman active一些振动具有红外和拉曼活性**
- **IR inactive or Raman active –Complementary**

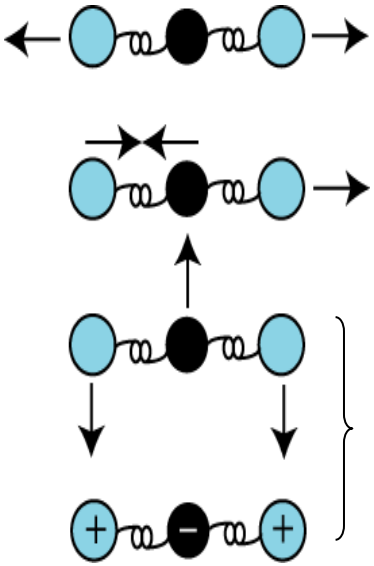
  Each associated with a different set of vibrational modes in a molecule

  一些振动具有红外或者拉曼活性，互为互补，对应于不同的振动模式

DA Skoog, et al Principles of Instrumental Analysis, 1998 Harcourt Brace & Company

Comparing IR & Raman

CO_2

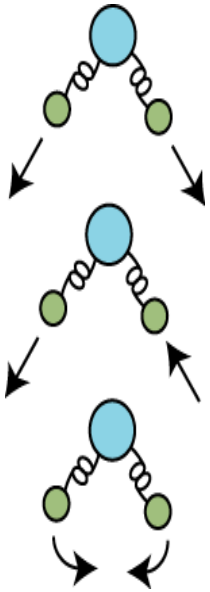


Raman: 1335 cm^{-1}

IR: 2349 cm^{-1}

IR: 667 cm^{-1}

H_2O



Raman + IR: 3657 cm^{-1}

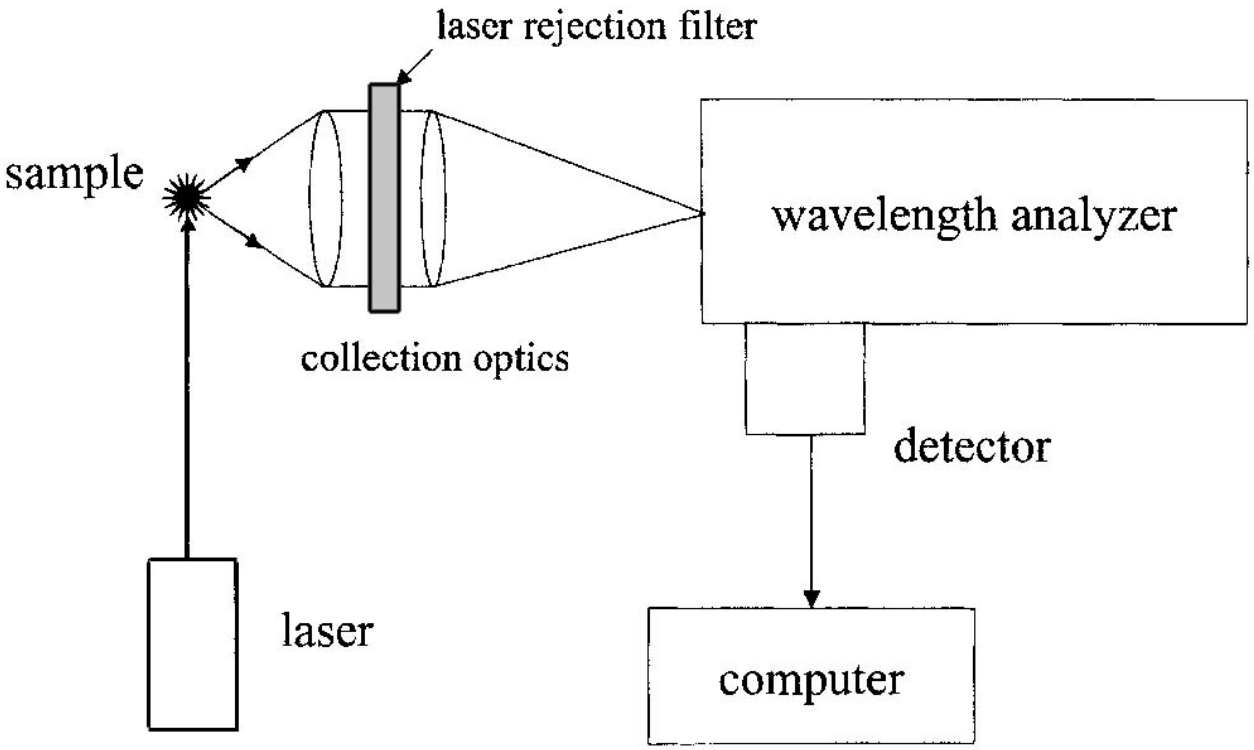
Raman + IR: 3756 cm^{-1}

Raman + IR: 1594 cm^{-1}

Raman Spectroscopy *vs.* Infrared Absorption Advantages & Disadvantages

- Water does not cause interference
  水的拉曼峰弱，不干扰测定
- Glass or quartz cells can be used
  可以用玻璃或石英池
- Need laser需要激光
- Interference by fluorescence from the sample or impurity in the sample样品中的荧光物质干扰测定

Instrumentation for Raman Spectroscopy
拉曼光谱仪

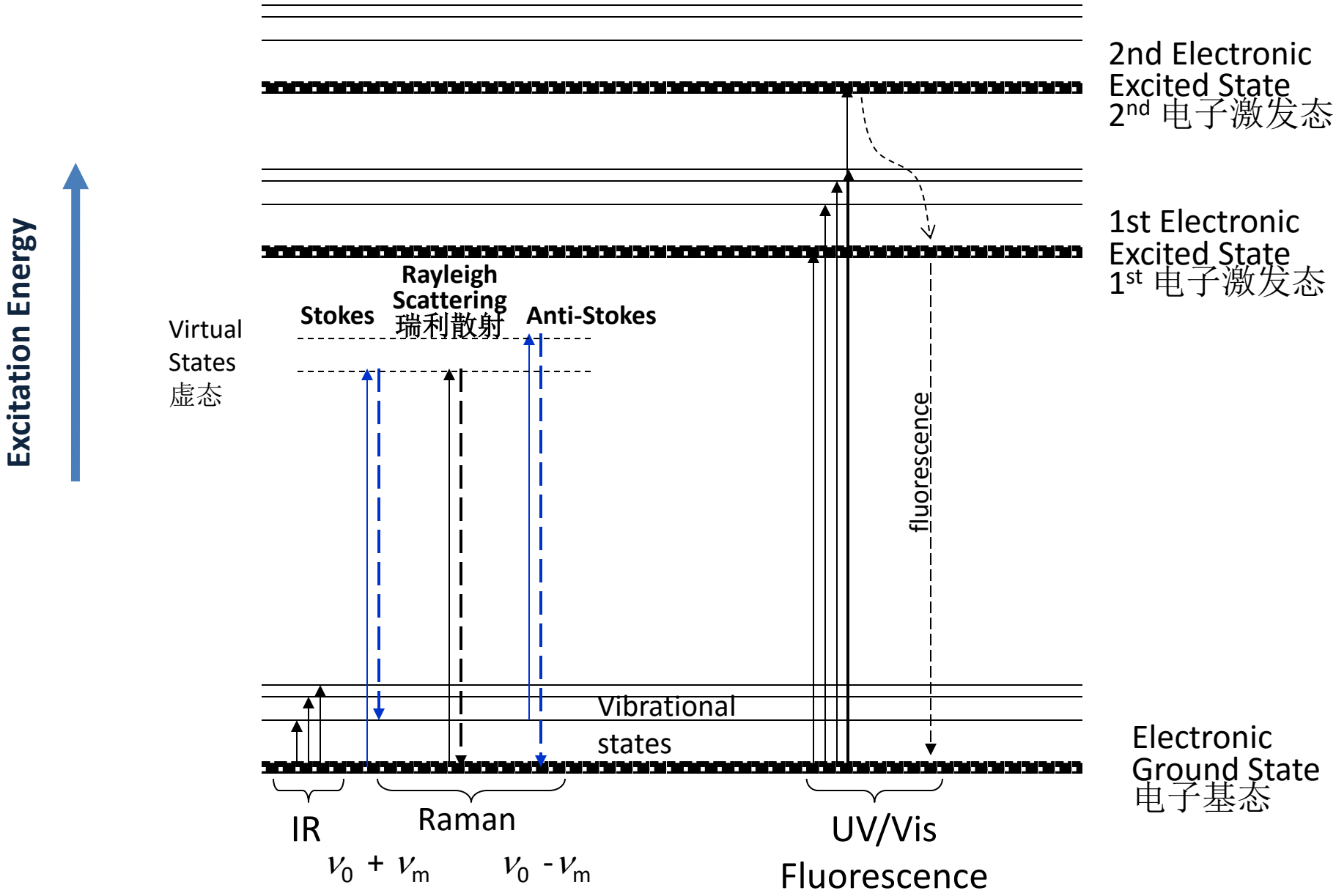


Summary of Molecular Spectroscopy
分子光谱小结

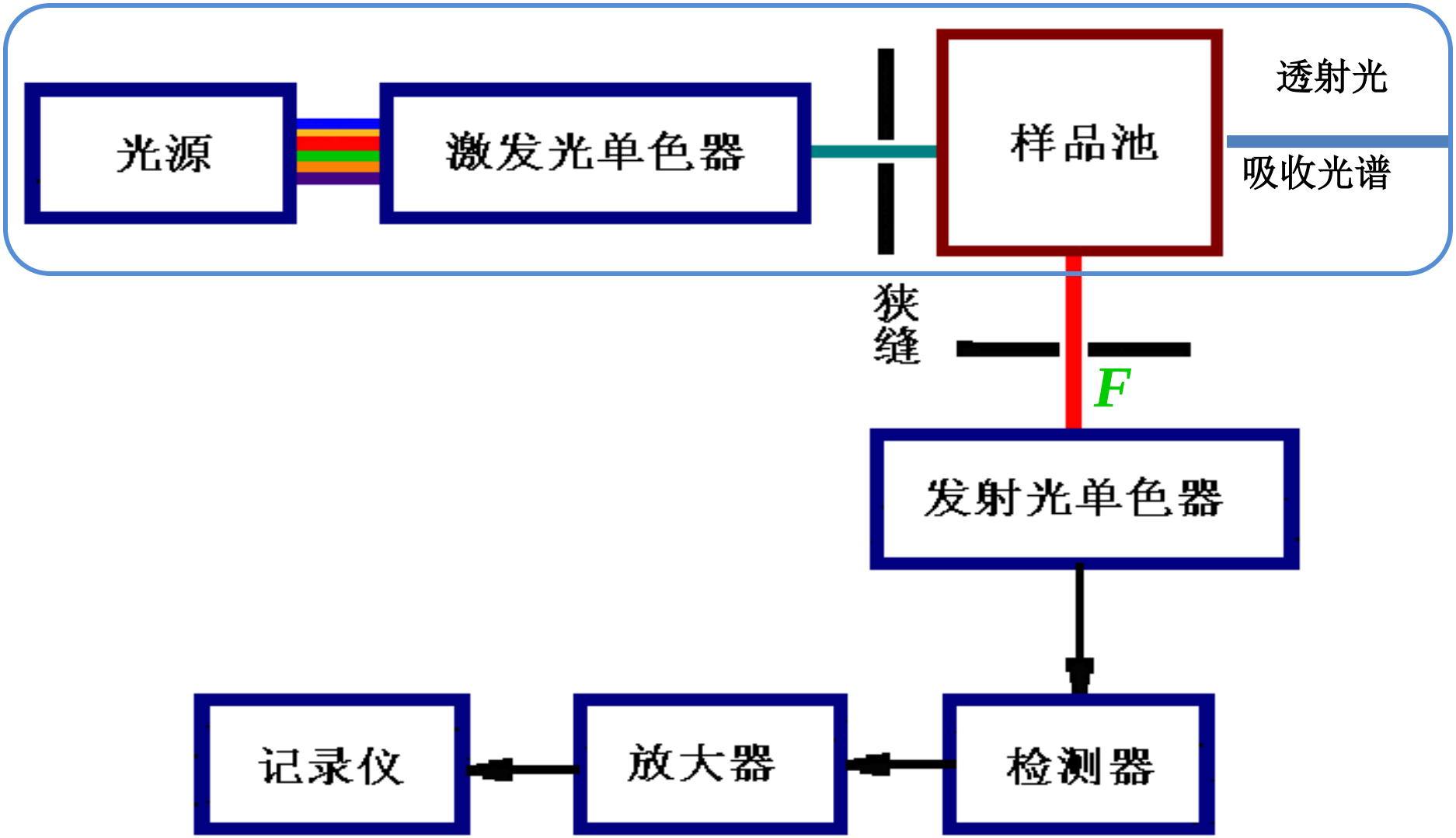
- ***E* field of electromagnetic irradiation interacts with molecule electronic, vibrational, rotational transitions, and other low frequency transition**

  电磁波的电场向量与分子的电子、振动、转动与其他低频跃迁的相互作用产生分子的吸收光谱。当吸收的能量以光的形式释放出来，产生荧光、磷光以及拉曼散射
- **Application in Analytical Chemistry**
  - **Light absorption – UV-vis (to NIR), IR spectrometry**
  - **Light emission – fluorescence, Raman scattering**

Main Optical Transitions: Absorption, Scattering, & Fluorescence
分子主要跃迁：吸收、散射以及荧光



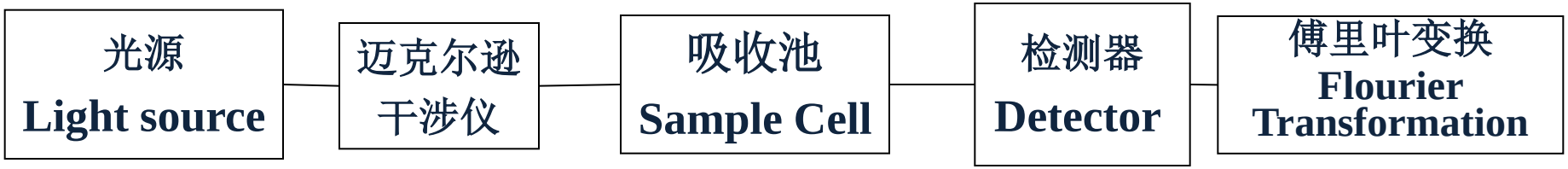
Instrumentations for UV/Vis absorption & Fluorescence
紫外/可见吸收与荧光仪器构造



Instrumentations for Infrared Absorption
红外吸收检测器

色散型

FTIR



Build A Spectrophotometer

Methods	Light Source	Monochromator	Sample Cell	Detector
UV-Visible	Tungsten for visible D_2 for UV	One after light source	Glass for visible Quartz for UV	PMT
Fluorescence	Xenon arc	One after light source One after sample cell	Quartz	PMT, CCD
Infrared	Silicon carbide rod (硅碳棒) Rare earth oxide ceramic piece (稀土氧化物陶瓷片)	One after sample cell for dispersive type Michelson Interferometer for FTIR	Halide salt	Thermocouples热电偶 Pyroelectric cells热释电检测器 MCT (碲镉汞检测器)（又称光电导检测器）
Raman	Monochromatic laser	One after sample cell	Optical glass or quartz	PMT

Sensitivity灵敏度

- Fluorescence vs. UV-visible absorption
  荧光分析法灵敏度高于紫外-可见分光光度法
  - Emitting light in a dark background
    荧光光谱法从黑背景检测光子
  - Source and detection can be adjusted to仪器可以调整
    - PMT
    - Source
  - $I_f = 2.3\phi\varepsilon bcI_0$
    - Molecular structural modification 改造分子结构以提高量子产率, ϕ
    - Solution parameters改变溶液条件提高量子产率, ϕ

分子光谱的要求

- 定量原理
- 定性原理
- 仪器原理、框图、各部分元件名称以及材质要求
- 计算：
  - 波长与频率的换算
  - 基于Beer’s Law 定量
  - 红外光谱中: 振动基频计算
  - Raman中：Raman位移波数→波长的计算