红外和Raman光谱学

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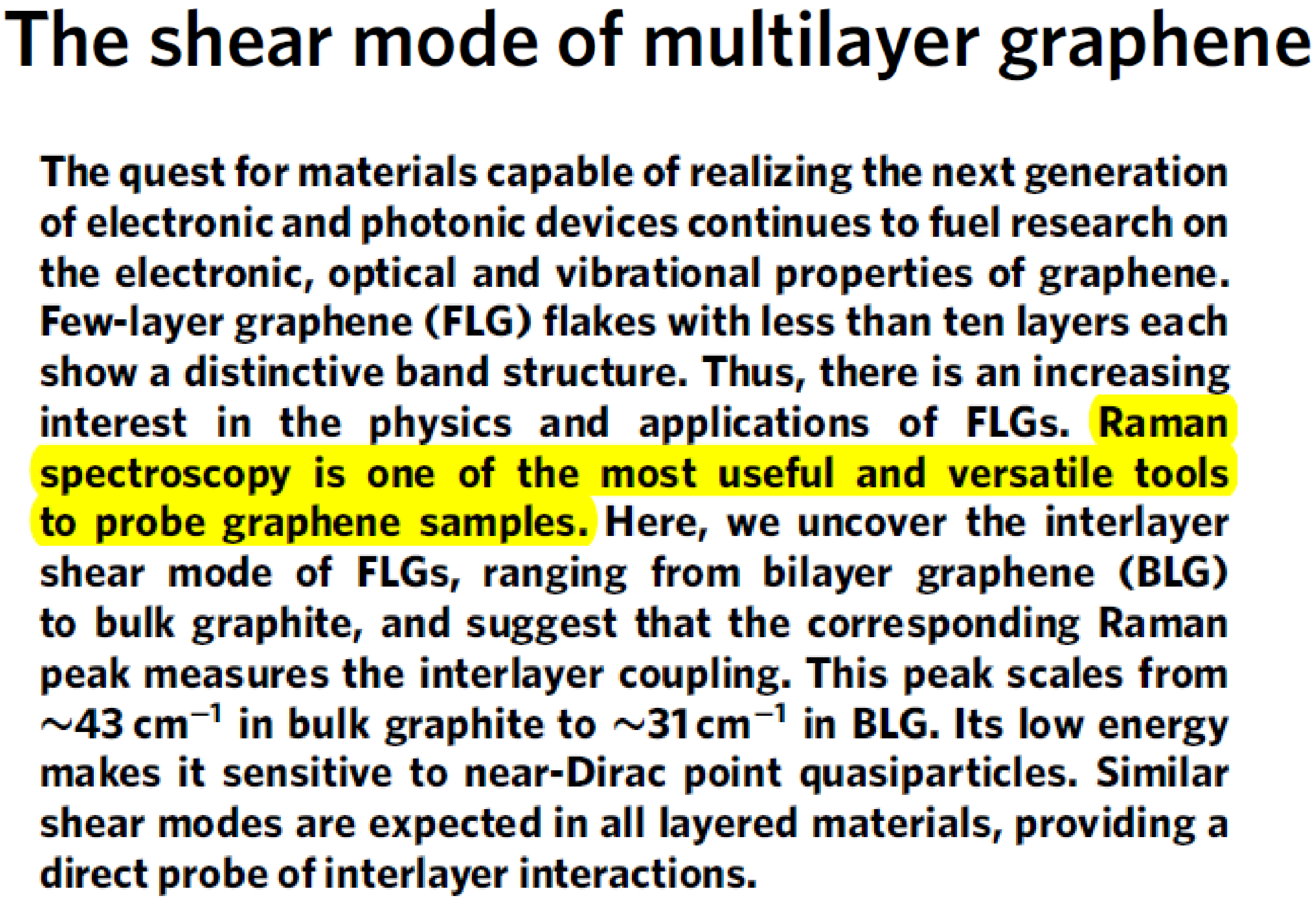
第一章：红外和Raman光谱介绍

- 什么是红外光谱？什么是Raman光谱
- 红外谱仪和 Raman谱仪
- 红外光谱和Raman光谱方法的特点
- 红外光谱和Raman光谱研究的基本问题

红外和Raman光谱举例



The shear mode of multilayer graphene

The quest for materials capable of realizing the next generation of electronic and photonic devices continues to fuel research on the electronic, optical and vibrational properties of graphene. Few-layer graphene (FLG) flakes with less than ten layers each show a distinctive band structure. Thus, there is an increasing interest in the physics and applications of FLGs. Raman spectroscopy is one of the most useful and versatile tools to probe graphene samples. Here, we uncover the interlayer shear mode of FLGs, ranging from bilayer graphene (BLG) to bulk graphite, and suggest that the corresponding Raman peak measures the interlayer coupling. This peak scales from $\sim$43 cm^{-1} in bulk graphite to $\sim$31 cm^{-1} in BLG. Its low energy makes it sensitive to near-Dirac point quasiparticles. Similar shear modes are expected in all layered materials, providing a direct probe of interlayer interactions.

nature materials

2012 | DOI: 10.1038/NMAT3245

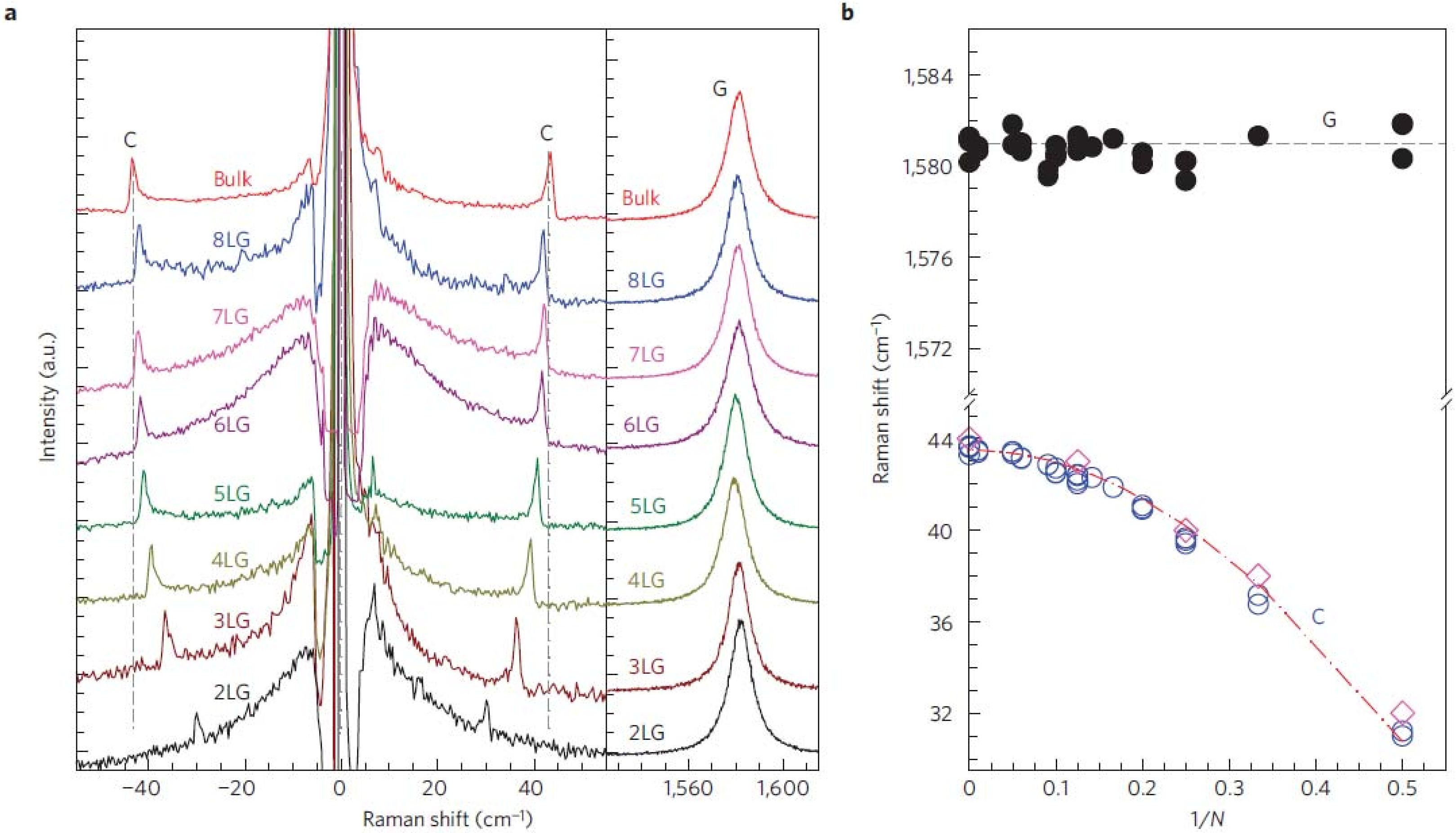
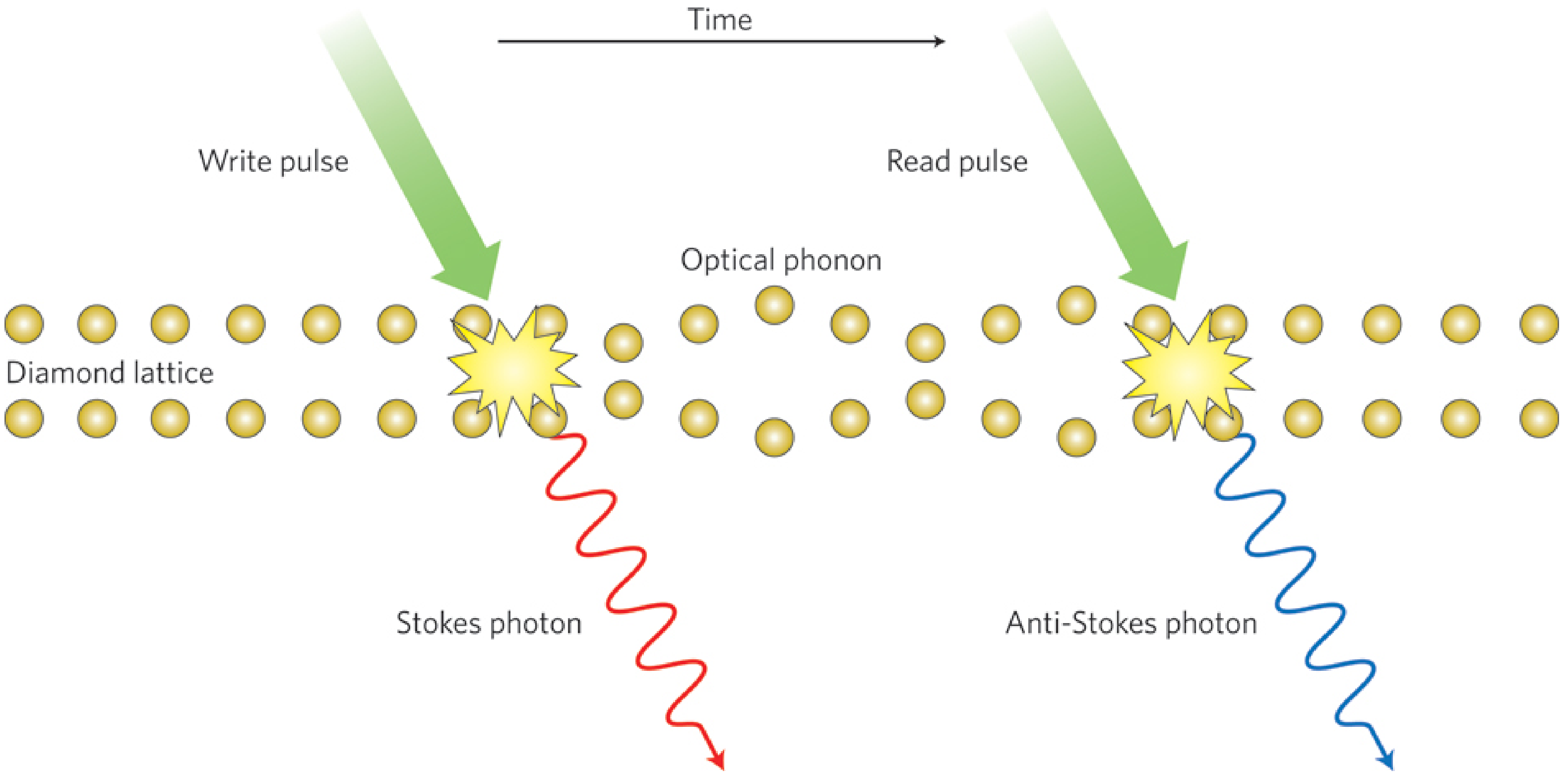


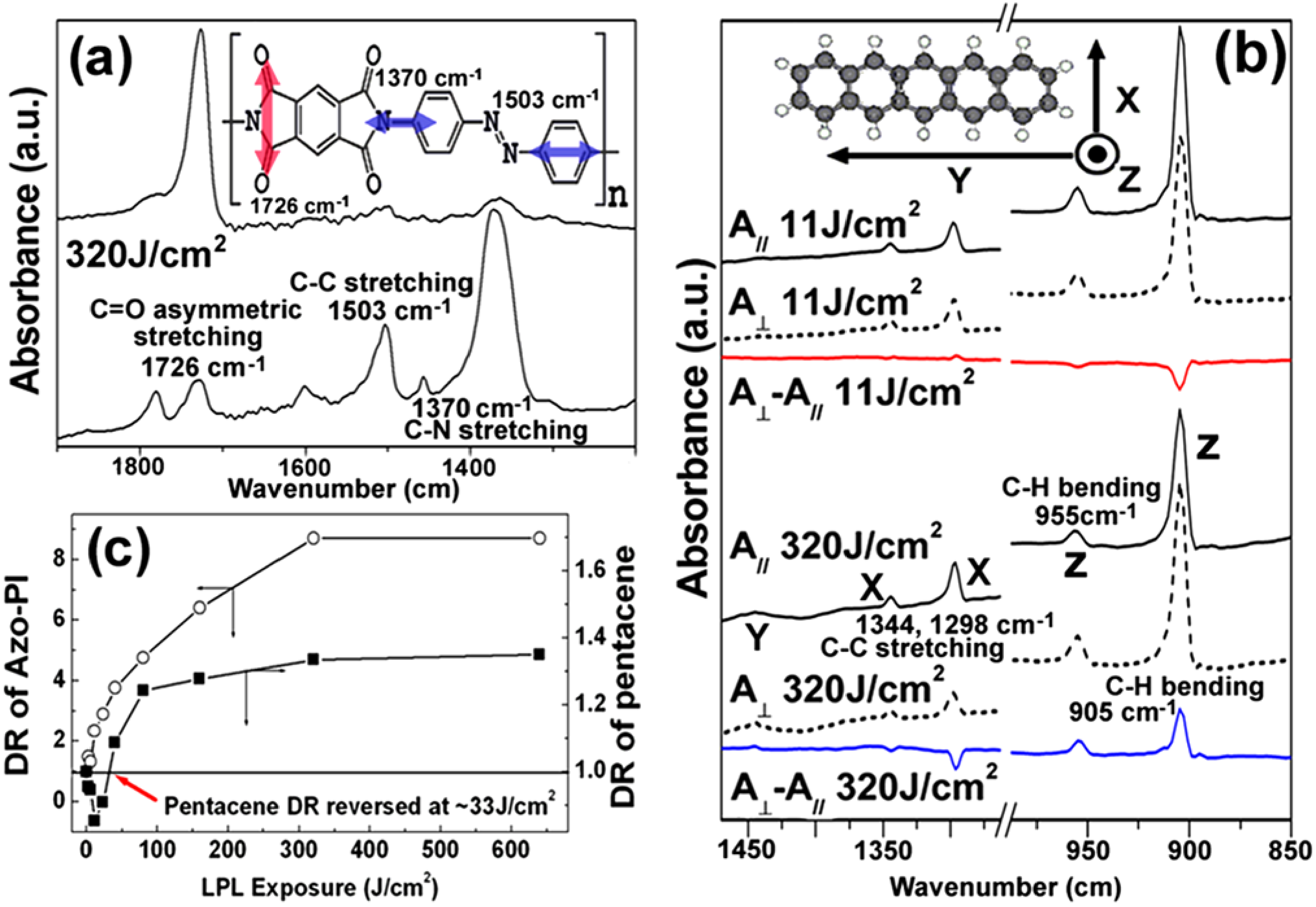
Figure 2 | Raman spectra and fits of the C and G peaks as a function of number of layers. a, S/AS Raman spectra for the C peak spectral region (left) and S Raman spectra for the G peak spectral region (right). **b**, Peak positions Pos(G) (filled black circles) and Pos(C) (open blue circles), as a function of inverse layer number. The red dash-dotted line is a plot of equation (2), open diamonds are DFT calculations. Vertical dashed lines in **a** and the horizontal line in **b** are guides to the eye.

Quantum memory: Phonons in diamond crystals

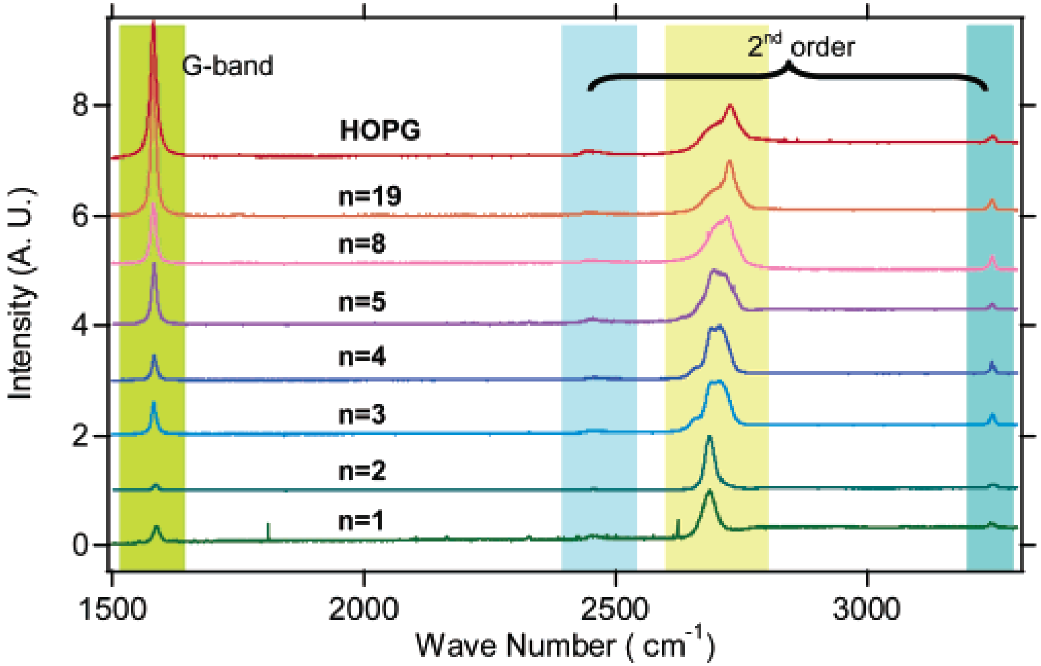

Time
Write pulse
Read pulse
Optical phonon
Diamond lattice
Stokes photon
Anti-Stokes photon

Through Raman scattering, a 'write' laser pulse creates a lower-energy Stokes photon (red) and an optical phonon in the diamond lattice. The optical phonon is a single excitation of a vibration mode in which nearest-neighbour carbon atoms move in opposite directions. A 'read' laser pulse then converts this phonon into an anti-Stokes photon (blue).

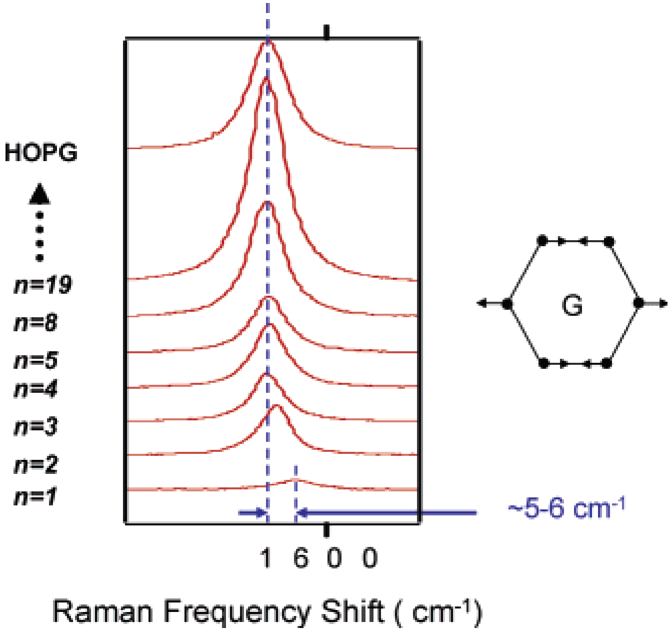
Nature Photonics, **6**, 10 (2012)



(a) Polarized IR spectra of the Azo-PI film with a LPL exposure of 320 J=cm^2. (b) Polarized IR spectra of the pentacene films on 11 J=cm^2 and 320 J=cm^2 exposed Azo-PI. (c) LPL exposure dependence of DR ($A_{\perp}/A_{/\!/}$) of the Azo-PI films (1370 cm^{-1} band) and the pentacene films (905 cm^{-1} band). (**Phys. Rev. Lett., 101**, 236103 (2008))



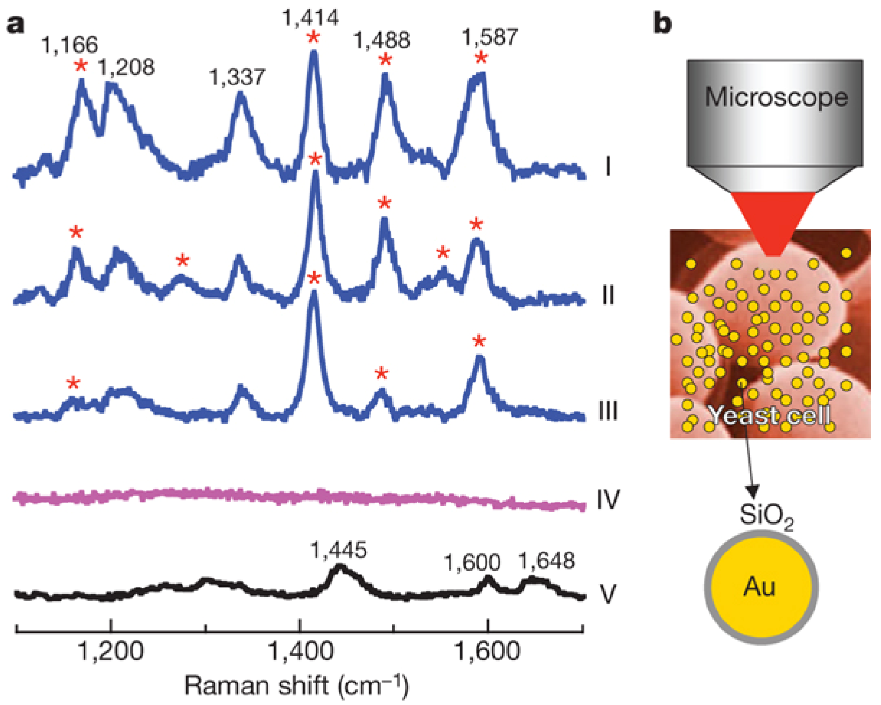
High-frequency first- and second-order micro-Raman spectra of *n*GL films supported on a SiO2:Si substrate and HOPG



First order-allowed Raman G-band for supported *n*GL films vs number of layers *n*.

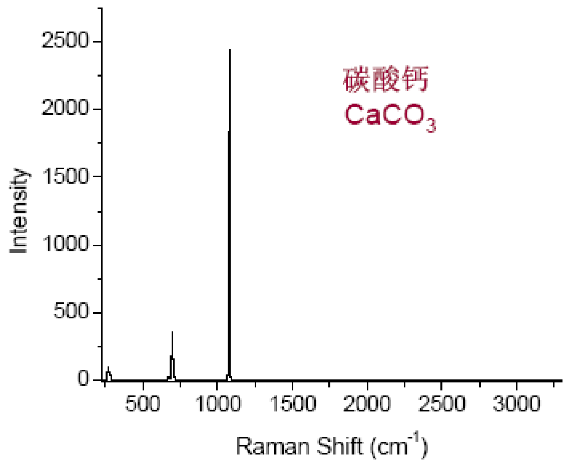
***Nano Lett.*, 6 (**12), 2667(06)

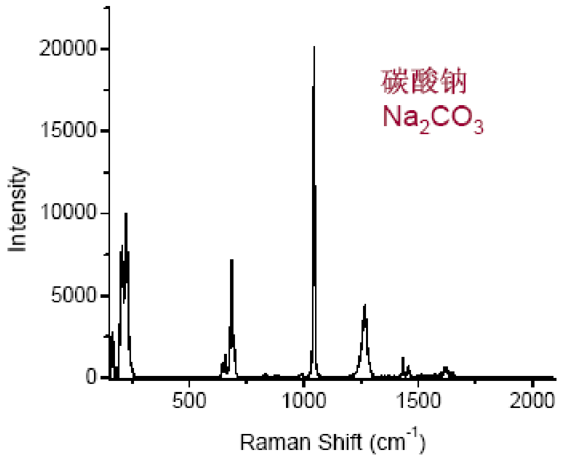
In situ probing of biological structures by SHINERS.

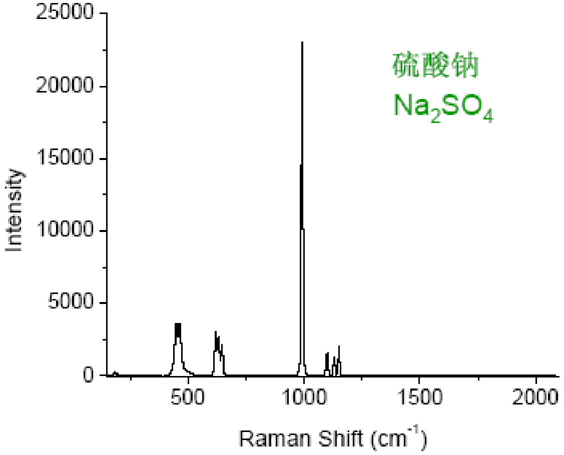


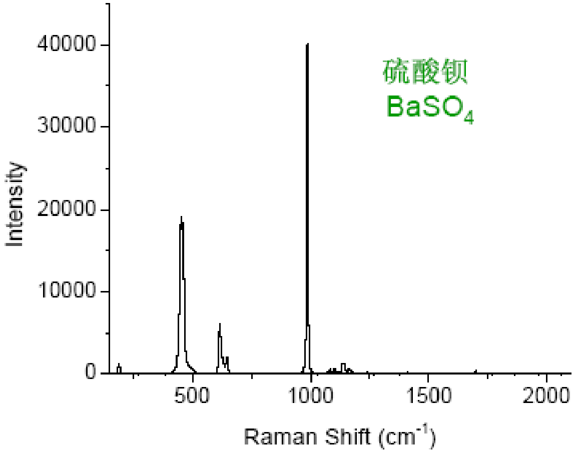
JF Li *et al.* *Nature* **464**, 392-395 (2010) doi:10.1038/nature08907

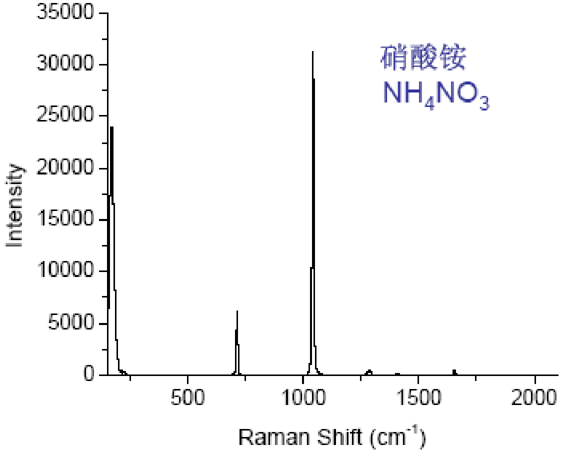
nature

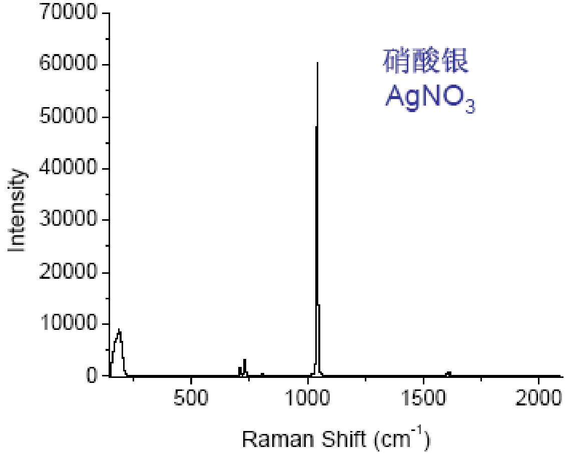

碳酸钙
CaCO3
Intensity
2500
2000
1500
1000
500
0
500
1000
1500
2000
2500
3000
Raman Shift (cm-1)

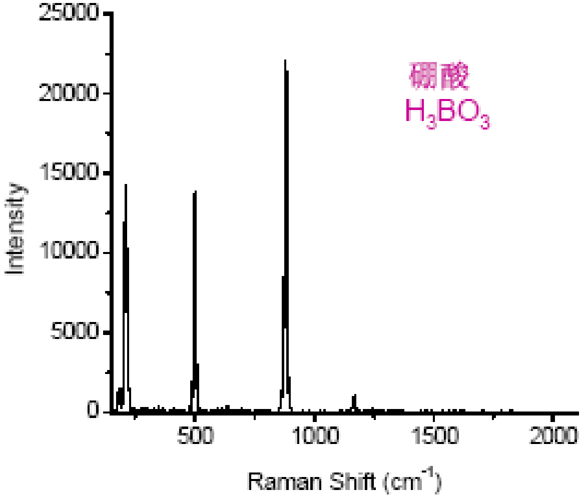

碳酸钠
Na2CO3
Intensity
20000
15000
10000
5000
0
500
1000
1500
2000
Raman Shift (cm-1)

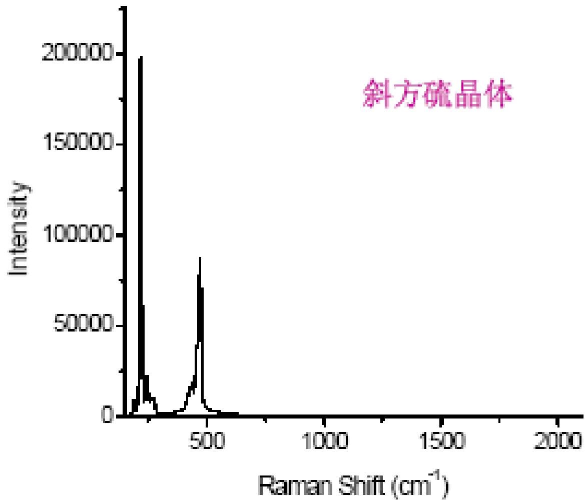

硫酸钠
Na2SO4
Intensity
25000
20000
15000
10000
5000
0
500
1000
1500
2000
Raman Shift (cm-1)

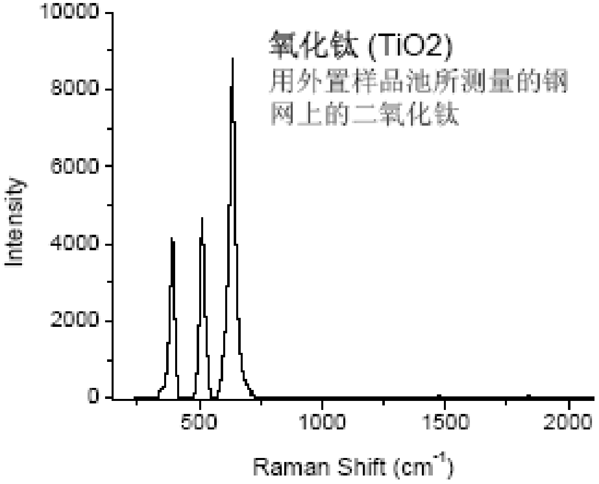

硫酸钡
BaSO4
Intensity
40000
30000
20000
10000
0
500
1000
1500
2000
Raman Shift (cm-1)

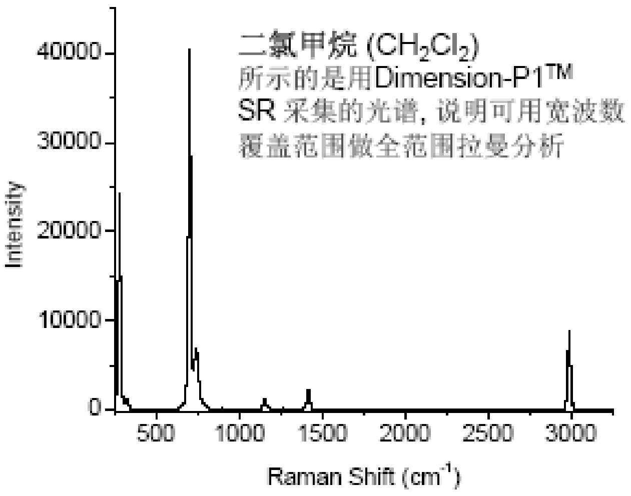

硝酸铵
NH4NO3
Intensity
35000
30000
25000
20000
15000
10000
5000
0
500
1000
1500
2000
Raman Shift (cm-1)


硝酸银
AgNO3
Intensity
70000
60000
50000
40000
30000
20000
10000
0
500
1000
1500
2000
Raman Shift (cm-1)

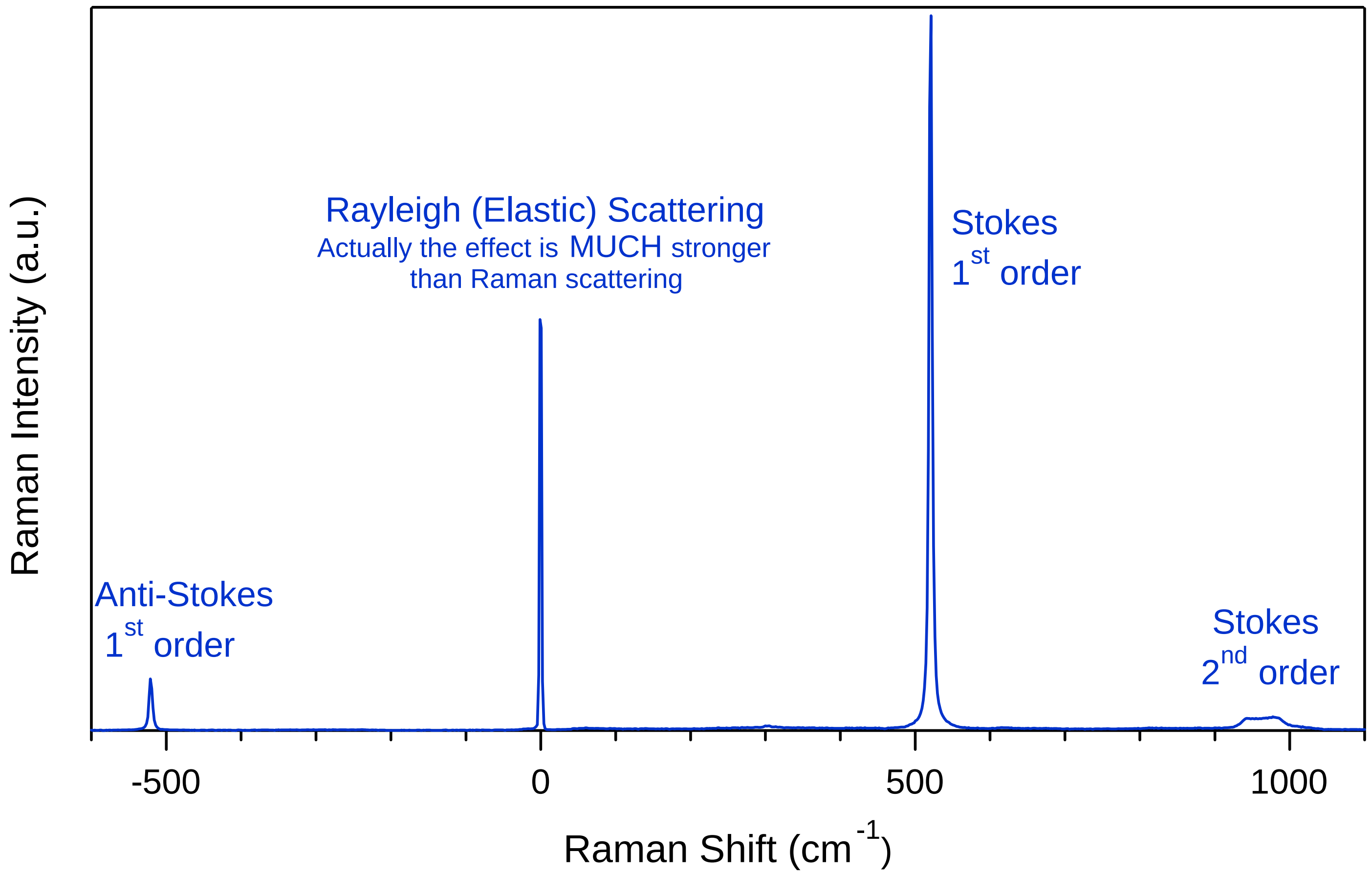

硼酸
H_3BO_3


斜方硫晶体


氧化钛 (TiO2)
用外置样品池所测量的钢网上的二氧化钛

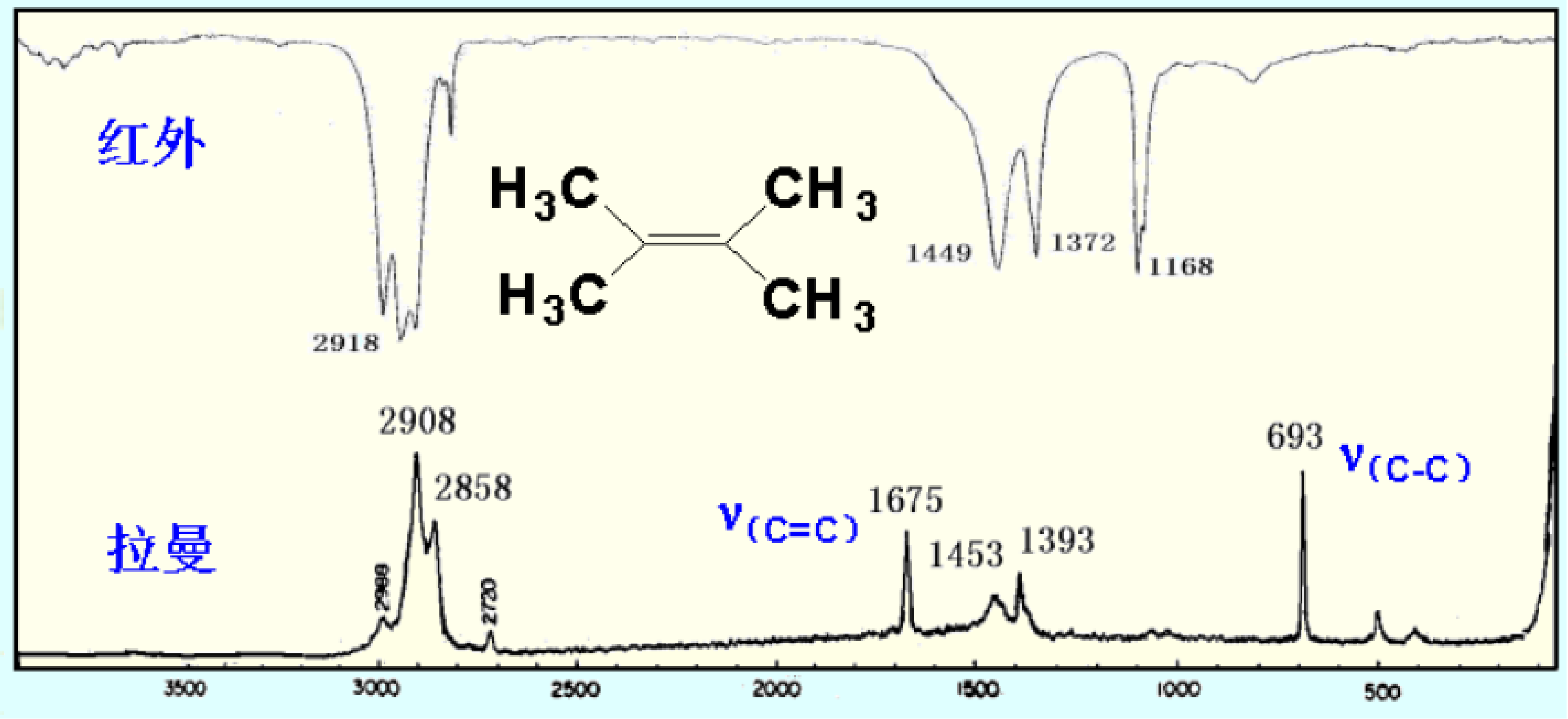

二氯甲烷 (CH_2Cl_2)
所示的是用Dimension-P1^{TM} SR 采集的光谱，说明可用宽波数覆盖范围做全范围拉曼分析

Raman Spectrum of Si (300 K)

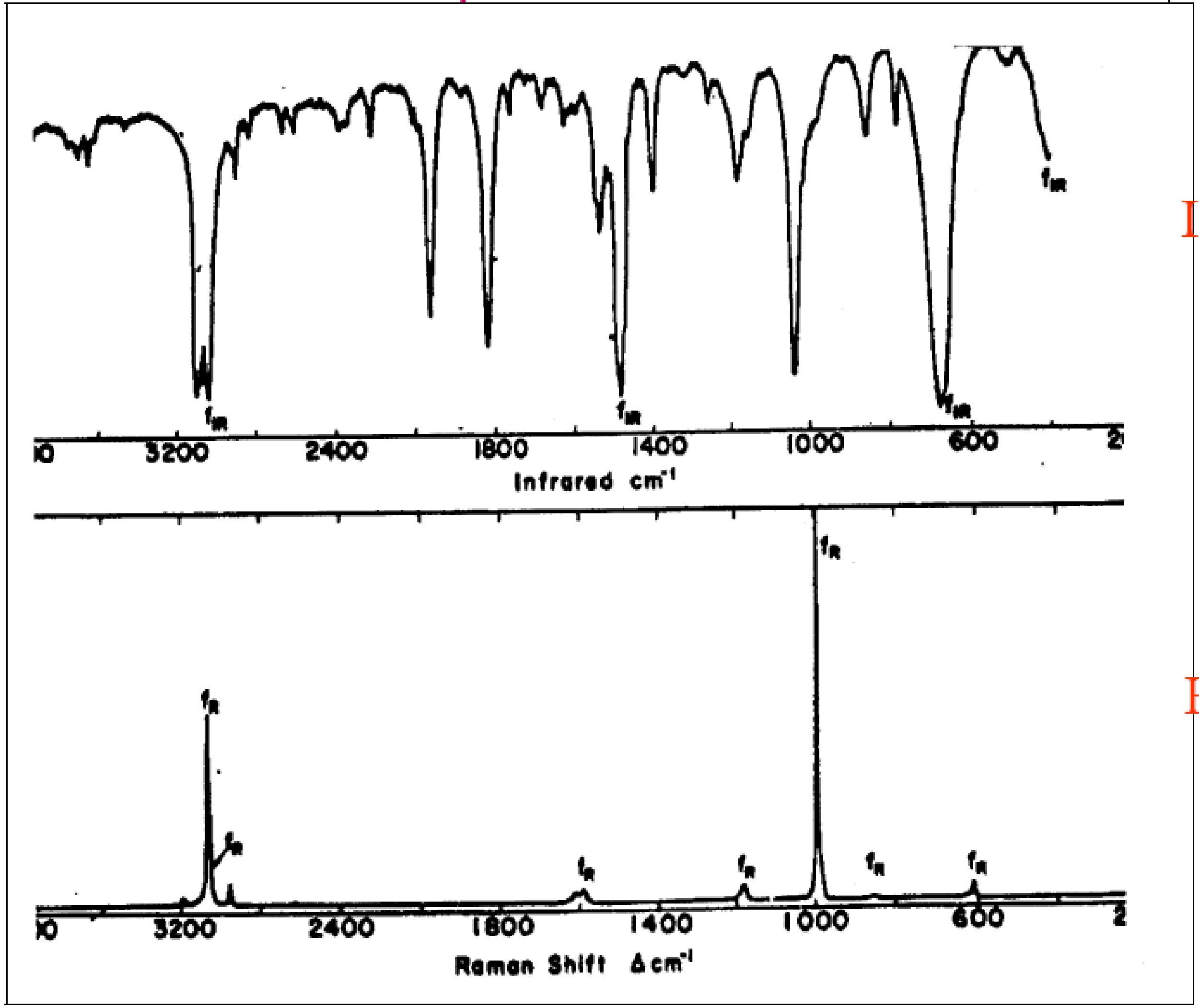


更全面了解Raman Spectrum

红外和Raman光谱的比较



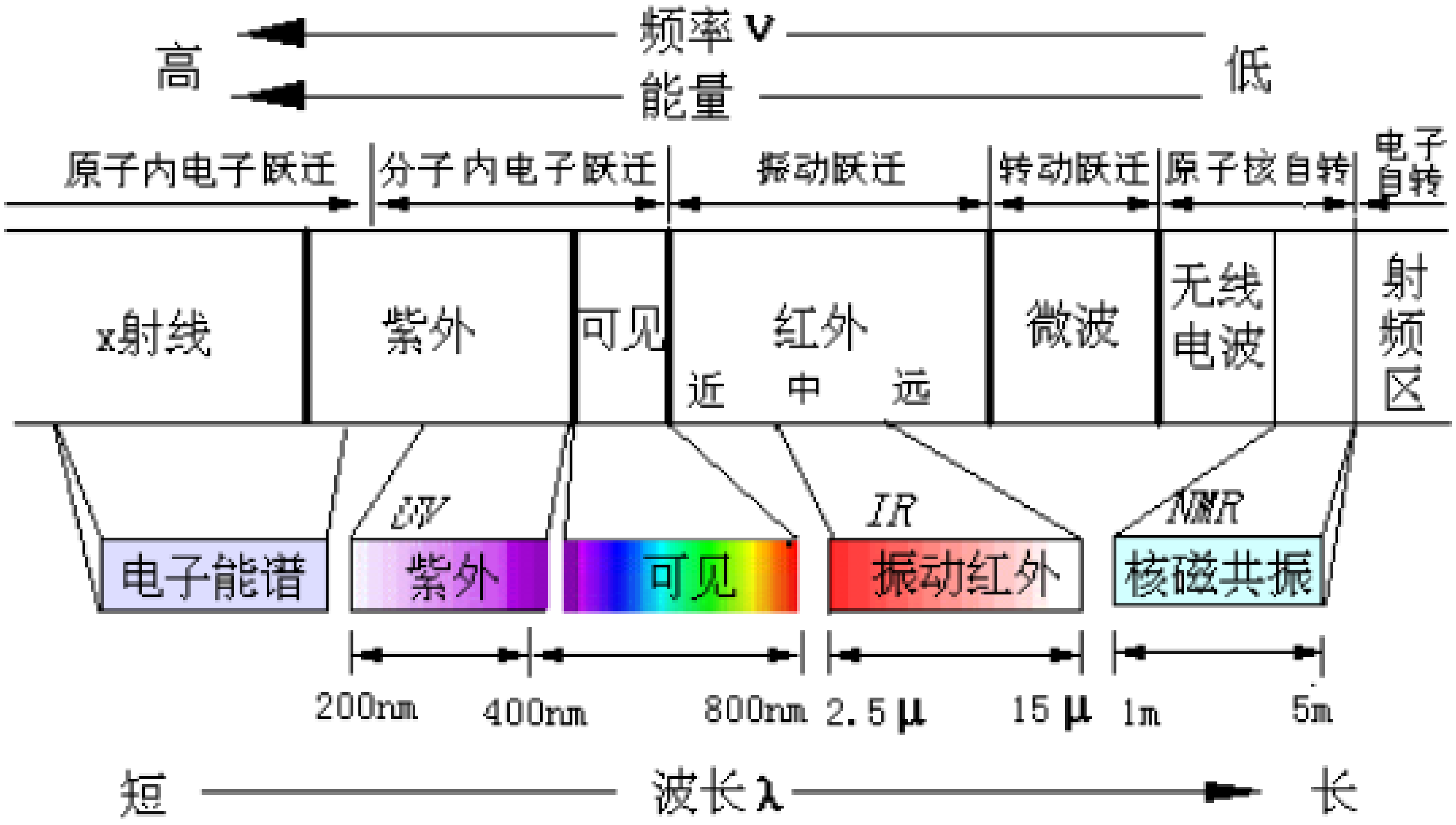
Infrared and Raman Spectra of Benzene



IR

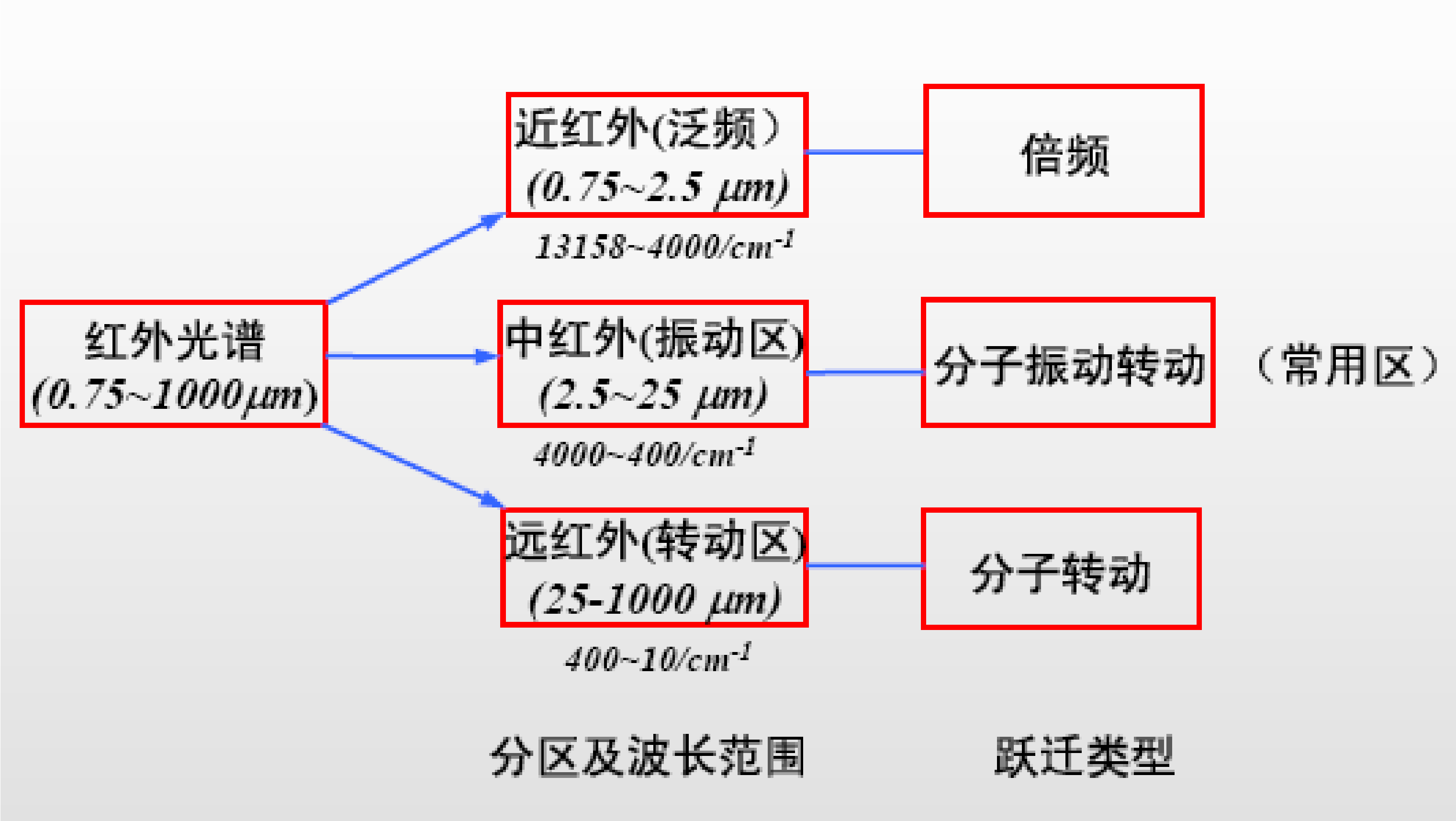
Raman

电磁波波段


频率 ν
能量
高
低
原子内电子跃迁
分子内电子跃迁
振动跃迁
转动跃迁
原子核自转
电子自转
x射线
紫外
可见
红外
近
中
远
微波
无线电波
射频区
UV
IR
NMR
电子能谱
紫外
可见
振动红外
核磁共振
200nm
400nm
800nm
2.5 μ
15 μ
1m
5m
短
波长 λ
长

光波谱区及能量跃迁相关图

红外光波段



红外光谱
(0.75~1000μm)

近红外(泛频）
(0.75~2.5 μm)
13158~4000/cm^{-1}

中红外(振动区)
(2.5~25 μm)
4000~400/cm^{-1}

远红外(转动区)
(25-1000 μm)
400~10/cm^{-1}

倍频

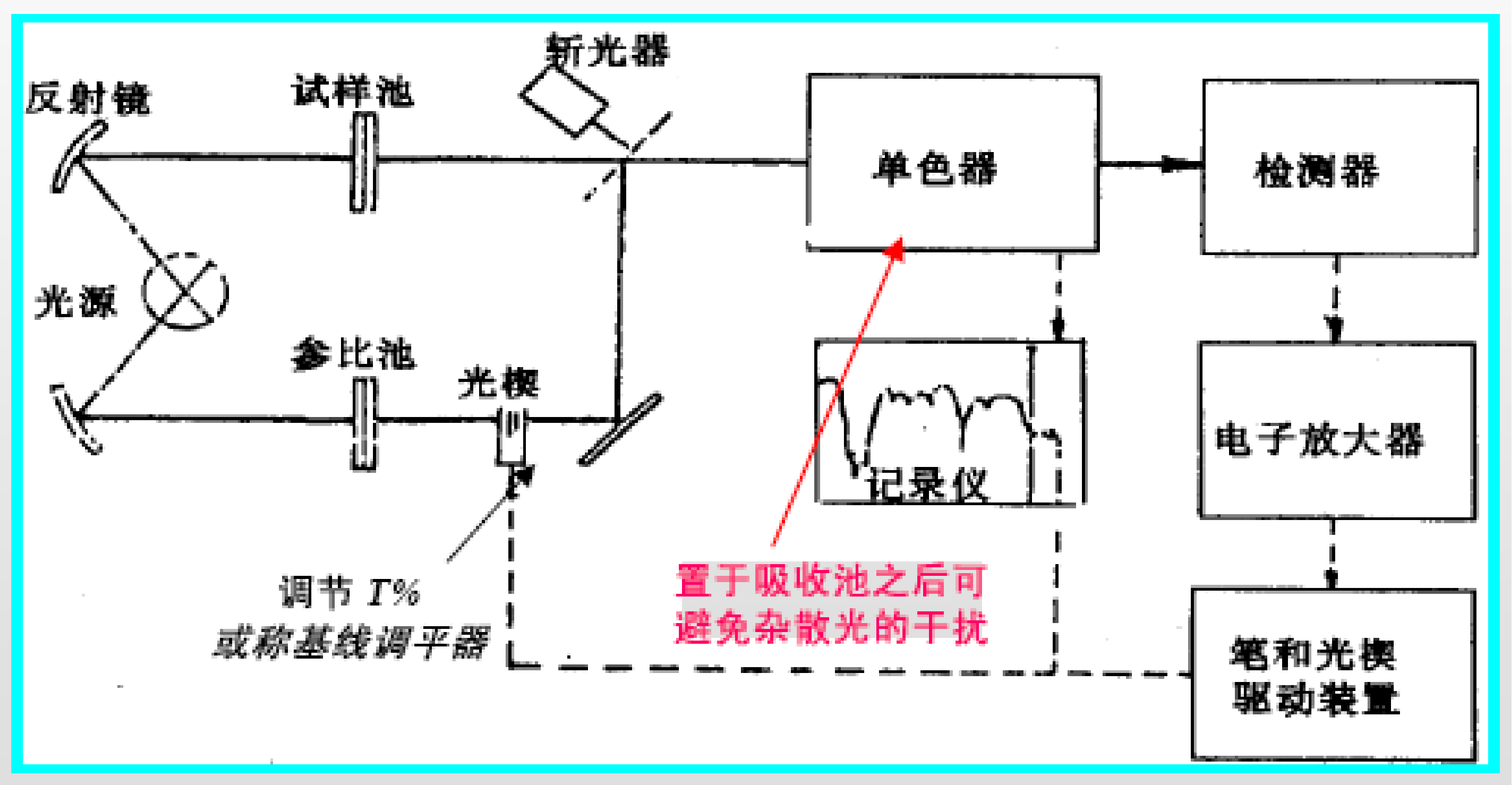
分子振动转动 （常用区）

分子转动

分区及波长范围

跃迁类型

红外和Raman光谱测量

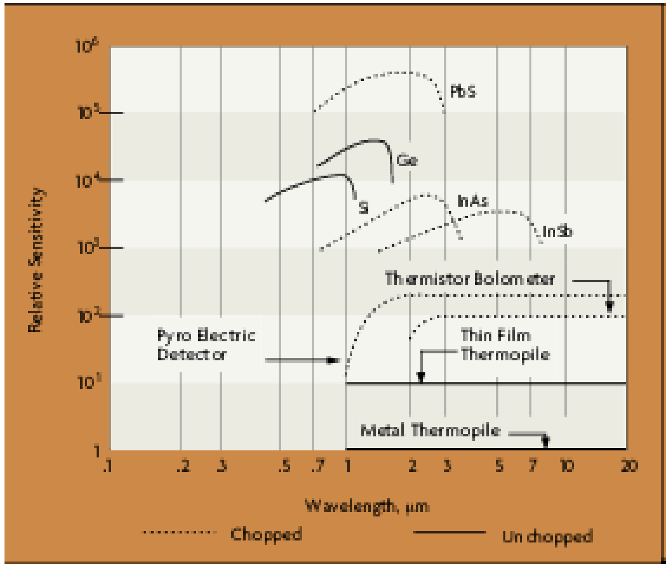

斩光器
反射镜
试样池
单色器
检测器
光源
参比池
光楔
记录仪
电子放大器
调节 T%
或称基线调平器
置于吸收池之后可
避免杂散光的干扰
笔和光楔
驱动装置

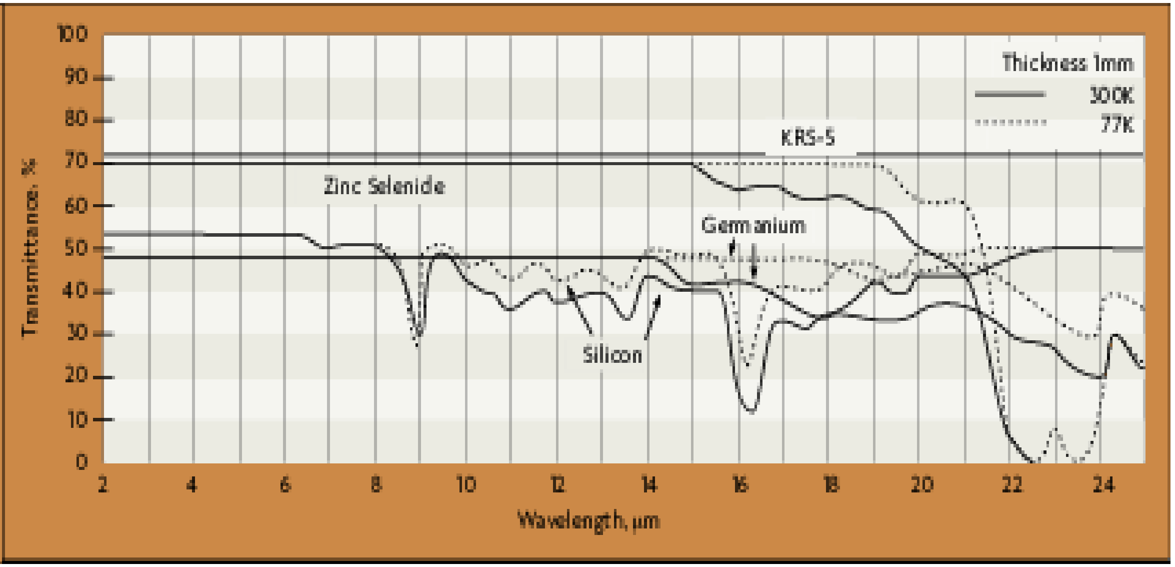
红外光谱仪光路示意图

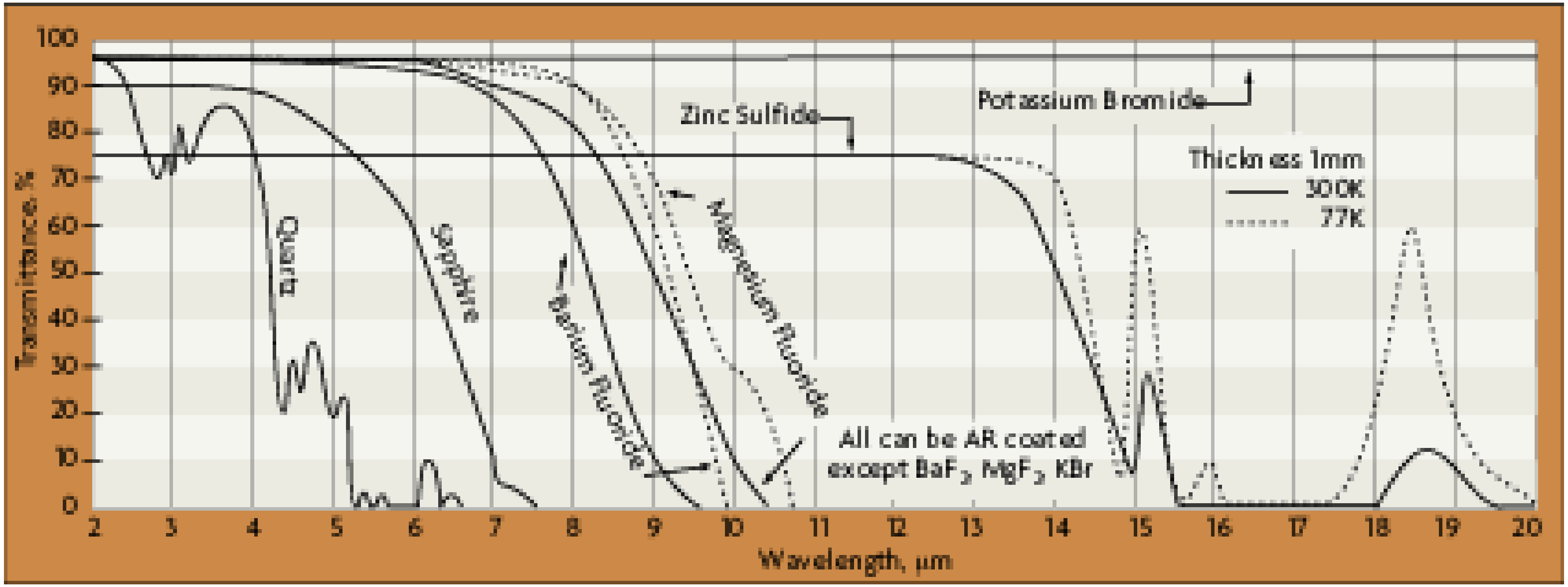
红外谱仪中使用的元器件

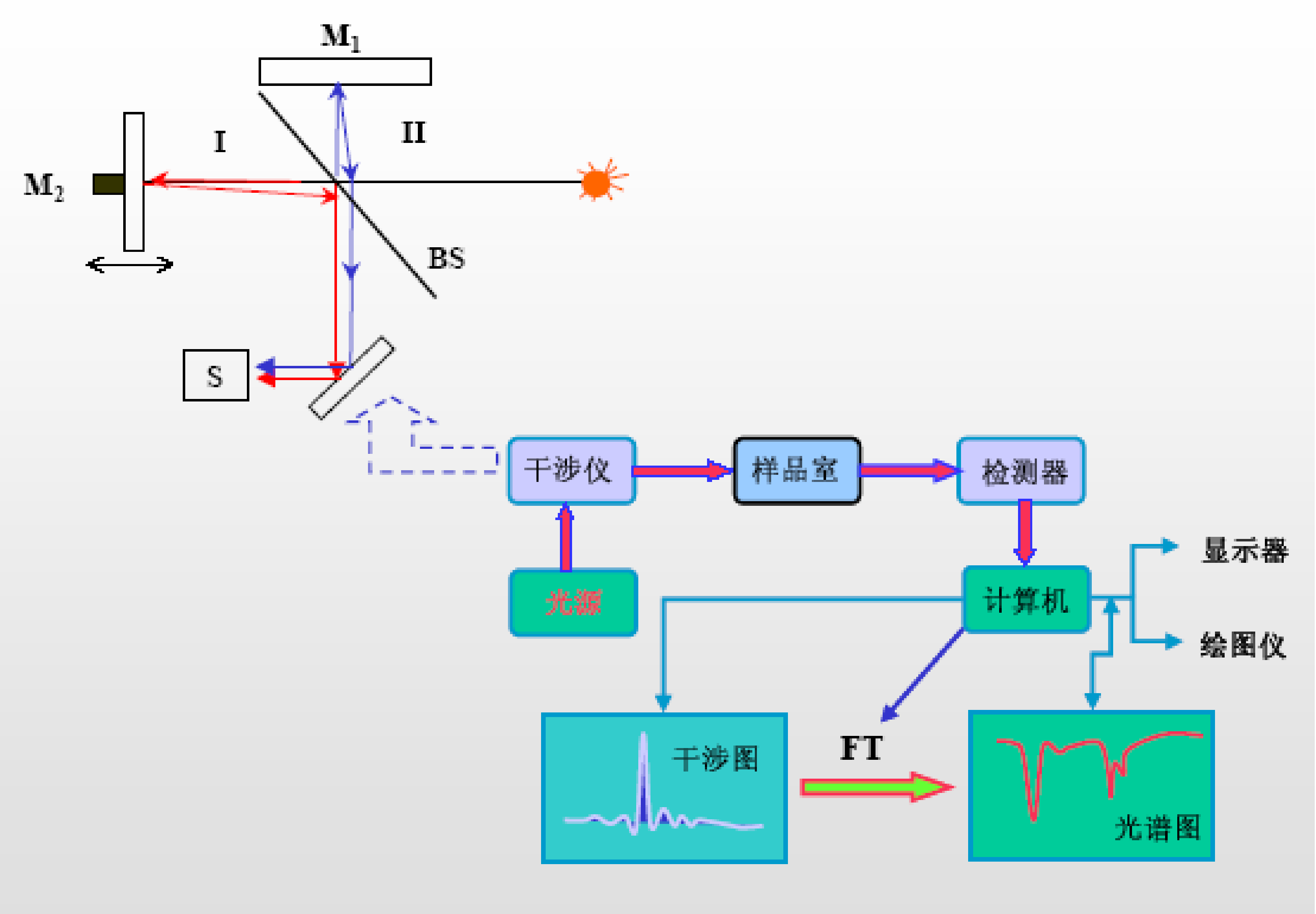
红外测量最主要的特点是特殊元件的需要，包括光源、分光元件和光学窗口等。（大多数材料对红外光有强烈的吸收）

- 光源：钨灯用于近红外、电热棒用于中红外、高压水银弧光灯用于远红外波段。（同步辐射光源）
- 分光元件——反射式光栅
- 红外光学窗口和反射式光学元件


Relative Sensitivity
10⁶
10⁵
10⁴
10³
10²
10¹
1
PbS
Ge
Si
InAs
InSb
Thermistor Bolometer
Pyro Electric Detector
Thin Film Thermopile
Metal Thermopile
.1
.2
.3
.5
.7
1
2
3
5
7
10
20
Wavelength, µm
Chopped
Un chopped

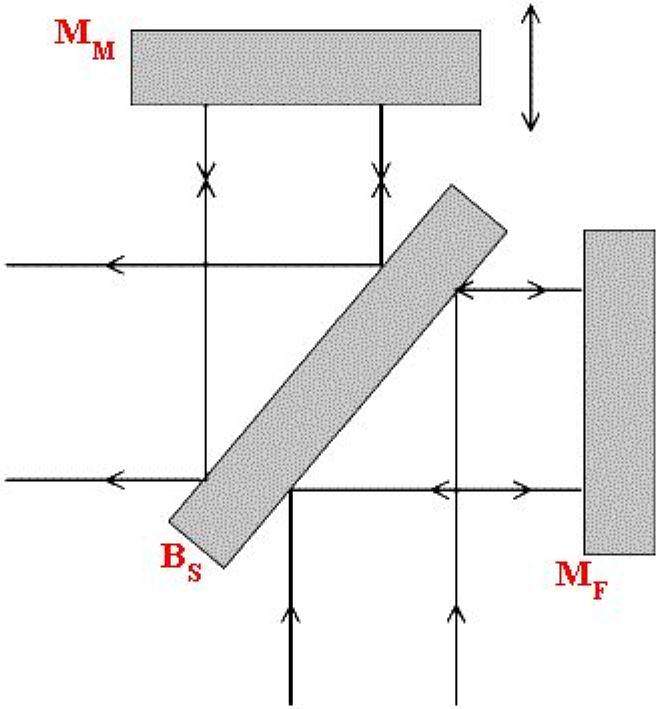

Transmittance, %
100
90
80
70
60
50
40
30
20
10
0
Thickness 1mm
300K
77K
KRS-5
Zinc Selenide
Germanium
Silicon
2
4
6
8
10
12
14
16
18
20
22
24
Wavelength, µm

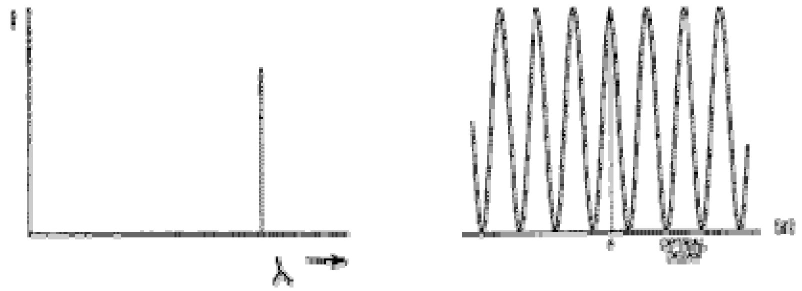

Transmittance %
100
90
80
70
60
50
40
30
20
10
0
Potassium Bromide
Zinc Sulfide
Thickness 1mm
300K
77K
Quartz
Sapphire
Barium Fluoride
Magnesium Fluoride
All can be AR coated except BaF₂, MgF₂, KBr
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
Wavelength, µm


M_1
I
II
M_2
BS
S
干涉仪
样品室
检测器
光源
计算机
显示器
绘图仪
干涉图
FT
光谱图

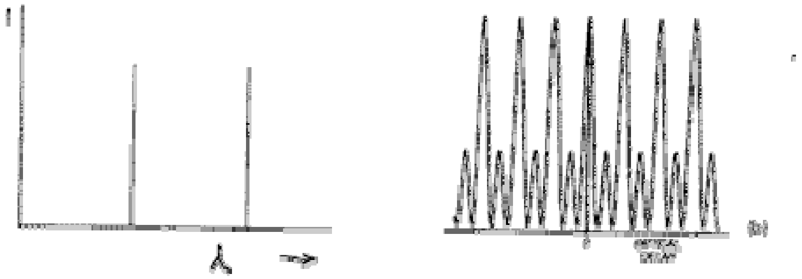
FT-IR谱仪基本框图

FT-IR谱仪的基础——Michelson干涉仪

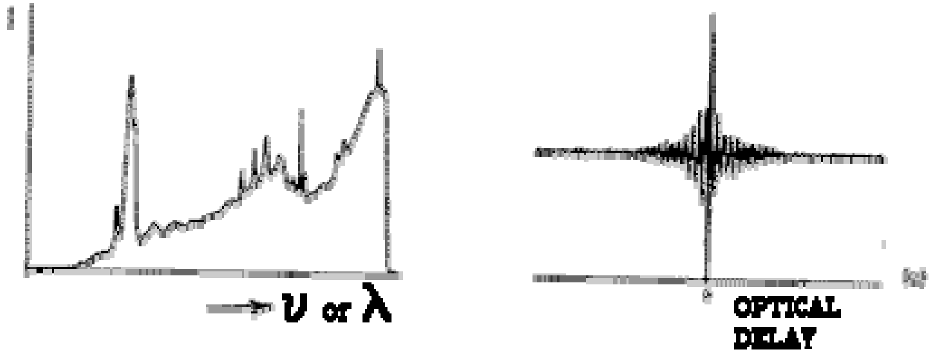




单色光λ入射，干涉强度的变化



两列单色光λ_1 、λ_2入射，干涉强度的变化



普通光入射后，干涉强度的变化

传统红外光谱仪和FTIR谱仪特点

- 传统透射式红外谱仪适合中红外波段应用。
- FTIR谱仪更适合在远红外波段应用，但现在也已经普遍应用于中红外波段。
- FTIR使用的光学元件较少，不用狭缝，因此光通量大。此外，测量比较节约时间。

其它红外光谱测量方法

- 红外光谱的测量有很多方法，这些方法可分为：色散法、FTIR和非色散法（滤波法）。

- 非色散法多用于特定的检测。例如用于气体的分析等。优点是方便使用，缺点是参数变动困难。

- 针对特殊的样品和特殊的需要，有很多特殊的红外测量方法。如光电导法、辐射量热法、光声光谱法、光热光谱法、反射式、内反射式、消逝波式等

反射测量方法

光学常数之间彼此不是独立的，通过一组光学常数的测定可以得到另外的光学常数。而K-K关系告诉我们，一组光学常数也不是彼此独立的。

- **Things we want to know about a sample:**
  - Index of refraction: $N(\omega) = n + ik$
  - Conductivity: $\sigma(\omega) = \sigma_1 + i\sigma_2$
  - Dielectric function: $\varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2$

(All complex functions)

- These are all related:

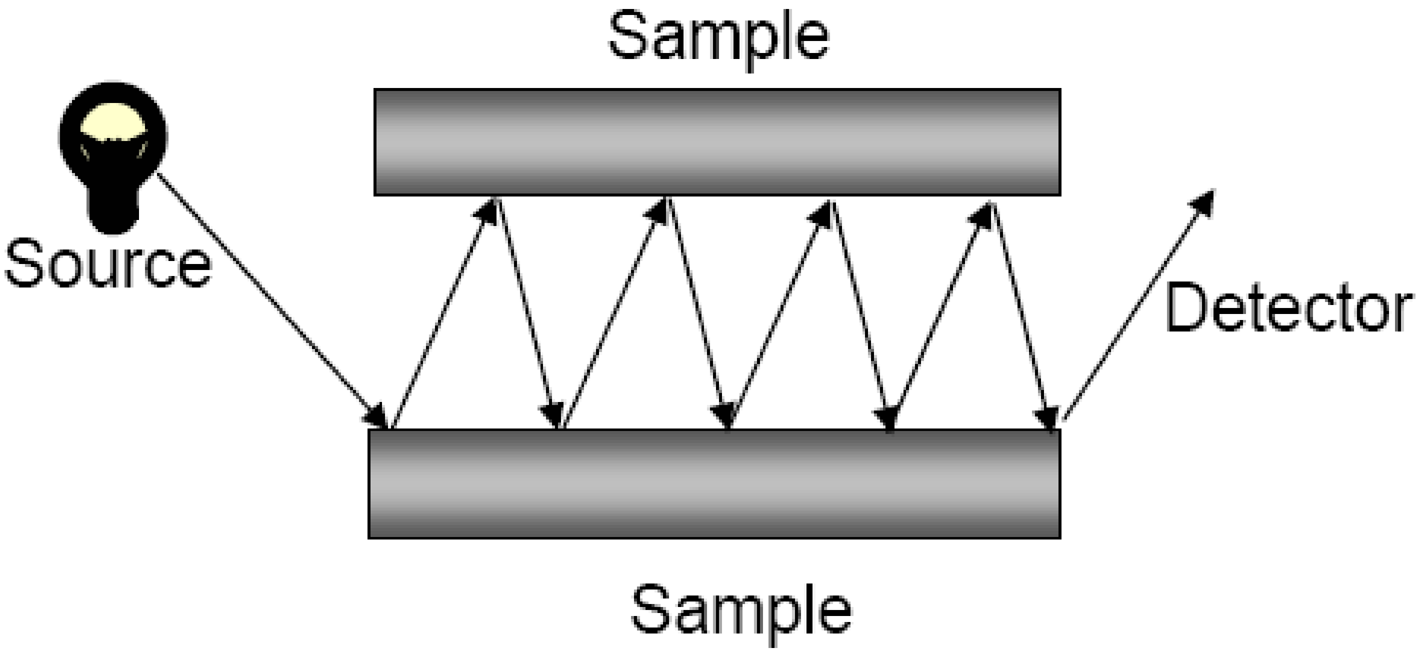
$$\varepsilon(\omega) = 1 + \frac{4\pi i}{\omega}\sigma(\omega) \qquad N(\omega) = \sqrt{\varepsilon(\omega)}$$

- Kramers-Kronig relations hold:

$$\sigma_2(\omega) = -\frac{2\omega}{\pi}\int_0^\infty \frac{\sigma_1(\omega')d\omega'}{\omega'^2 - \omega^2}$$

- **Optical measurements:**
  - Reflectivity: $R(\omega) = \left|\frac{\sqrt{\varepsilon} - 1}{\sqrt{\varepsilon} + 1}\right|^2 = \frac{(1-n)^2 + k^2}{(1+n)^2 + k^2}$
  - Transmission: $T(\omega) = |t(\omega)|^2 = \left|\frac{4N(\omega)}{(1+N(\omega))e^{-2\pi i d N\omega} - (1-N(\omega))e^{2\pi i d N\omega}}\right|^2$

红外内反射测量方法


Sample
Source
Detector
Sample

光电导方法和量热法

- 光电导测量：样品吸收光导致电导率的变化

- 量热法：样品吸收光转化为热

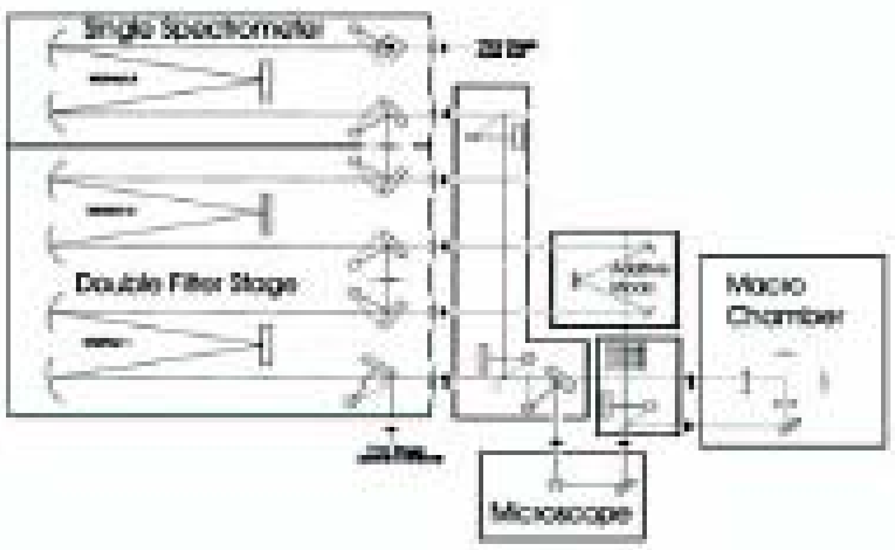
1-辐射量热法

2-光声光谱法

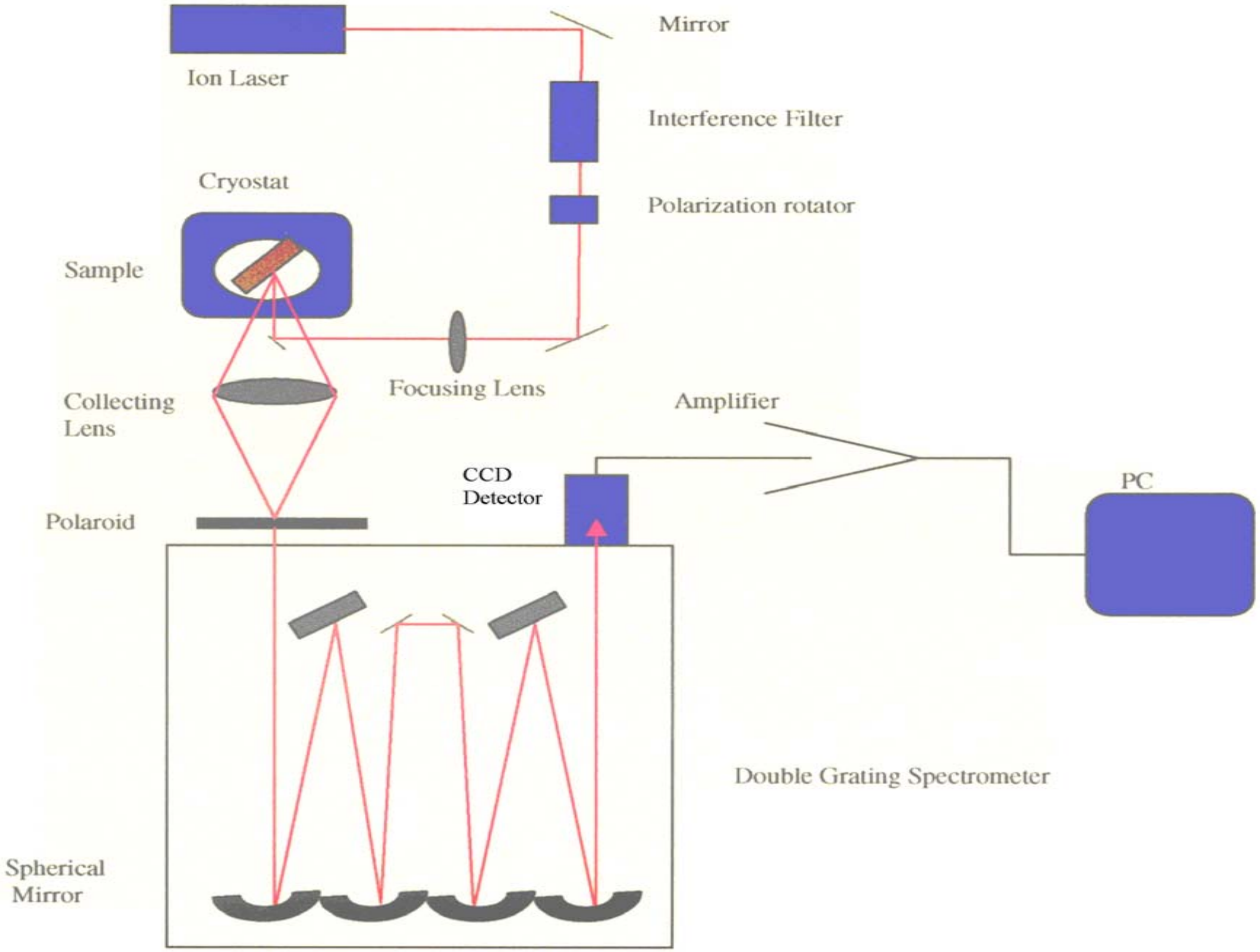
3-光热偏转光谱法

Raman谱仪

HORIBA JOBIN YVON T64000


Single Spectrometer
Double Filter Stage
Macro Chamber
Microscope

Raman Spectrometer(Schematic)


Mirror
Ion Laser
Interference Filter
Cryostat
Polarization rotator
Sample
Focusing Lens
Collecting
Lens
Amplifier
CCD
Detector
PC
Polaroid
Double Grating Spectrometer
Spherical
Mirror

Raman谱仪结构框图

Physics of Infrared (IR) Absorption

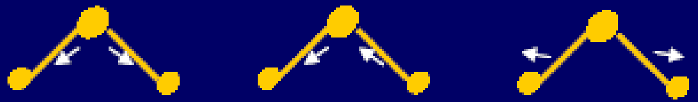
Molecular Energy

$$E = E_{electron} + E_{vibration} + E_{rotation} + E_{translation}$$

Normal Mode Description

3N – 6 (nonlinear)
3N – 5 (linear)

H_2O vibration modes



Symmetric stretching mode

Asymmetric stretching mode

Bendin
g mode

Selection Rule

IR absorption: A change in dipole moment during the vibration
Raman scattering: A change in polarizability during the vibration

Infrared Spectroscopy from Phonons

phonons = lattice vibrations

total number of phonon modes: dn N

N → number of unit cells in crystal

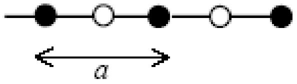
n → number of atoms in unit cell

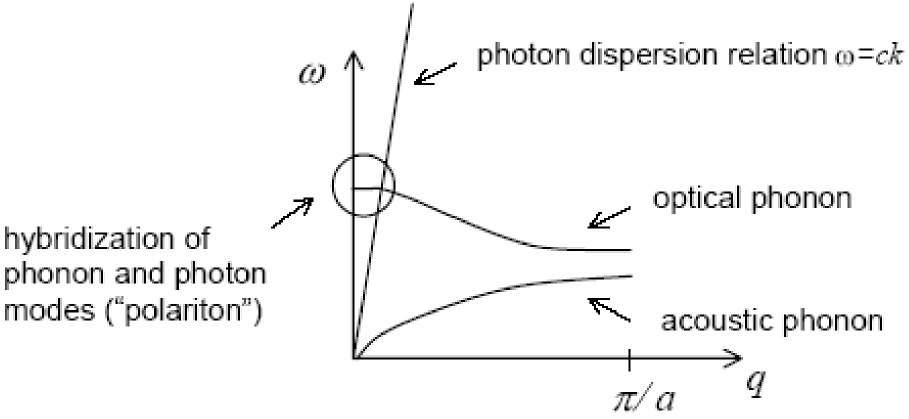
d → dimensionality

arranged in dn branches: d acoustic branches

d (n-1) optical branches

example: diatomic chain



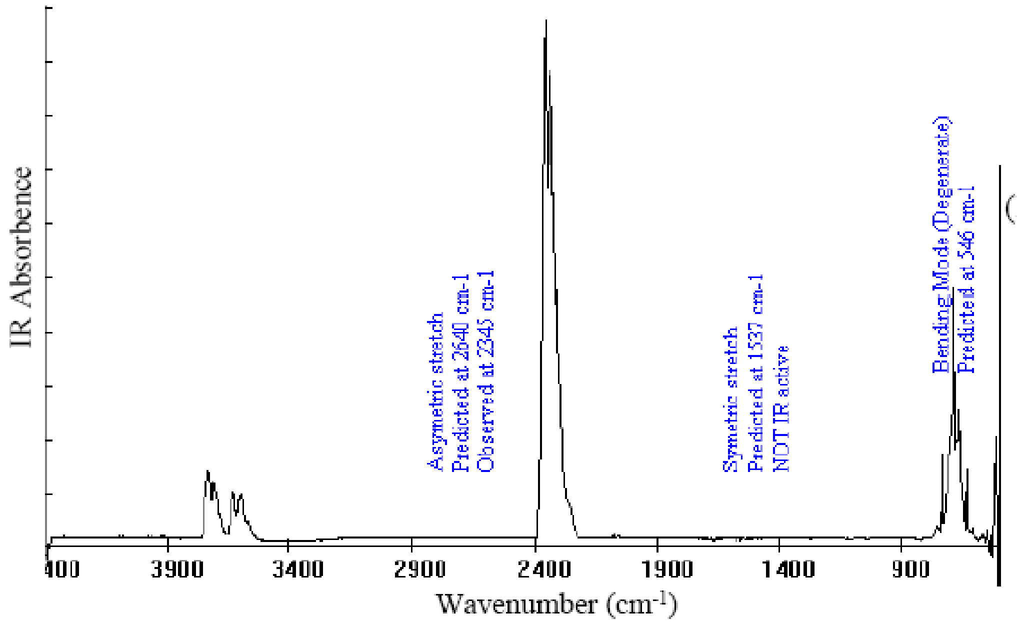

ω
photon dispersion relation ω=ck
optical phonon
hybridization of phonon and photon modes (“polariton”)
acoustic phonon
π/a
q

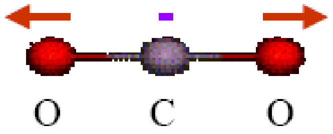
红外光谱能够得到的信息

- **Atoms vibrate with frequencies in the IR range**
- **Chemical Analysis:**
  - Match spectra to known databases
    - Identifying an unknown compound, Forensics, etc.
  - Monitor chemical reactions *in-situ*
- **Structural ideas:**
  - Can determine what chemical groups are in a specific compound
- **Electronic Information:**
  - Measure optical conductivity
    - Determine if Metal, Insulator, Superconductor, Semiconductor
    - Band Gaps, Drude model

分子振动模式

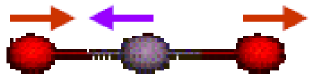
An Example: CO_2





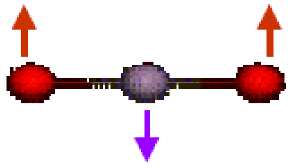
Symmetric Stretch

(Dipole moment = 0 so **not** IR active)



Asymmetric Stretch

(Has dipole moment so IR active)

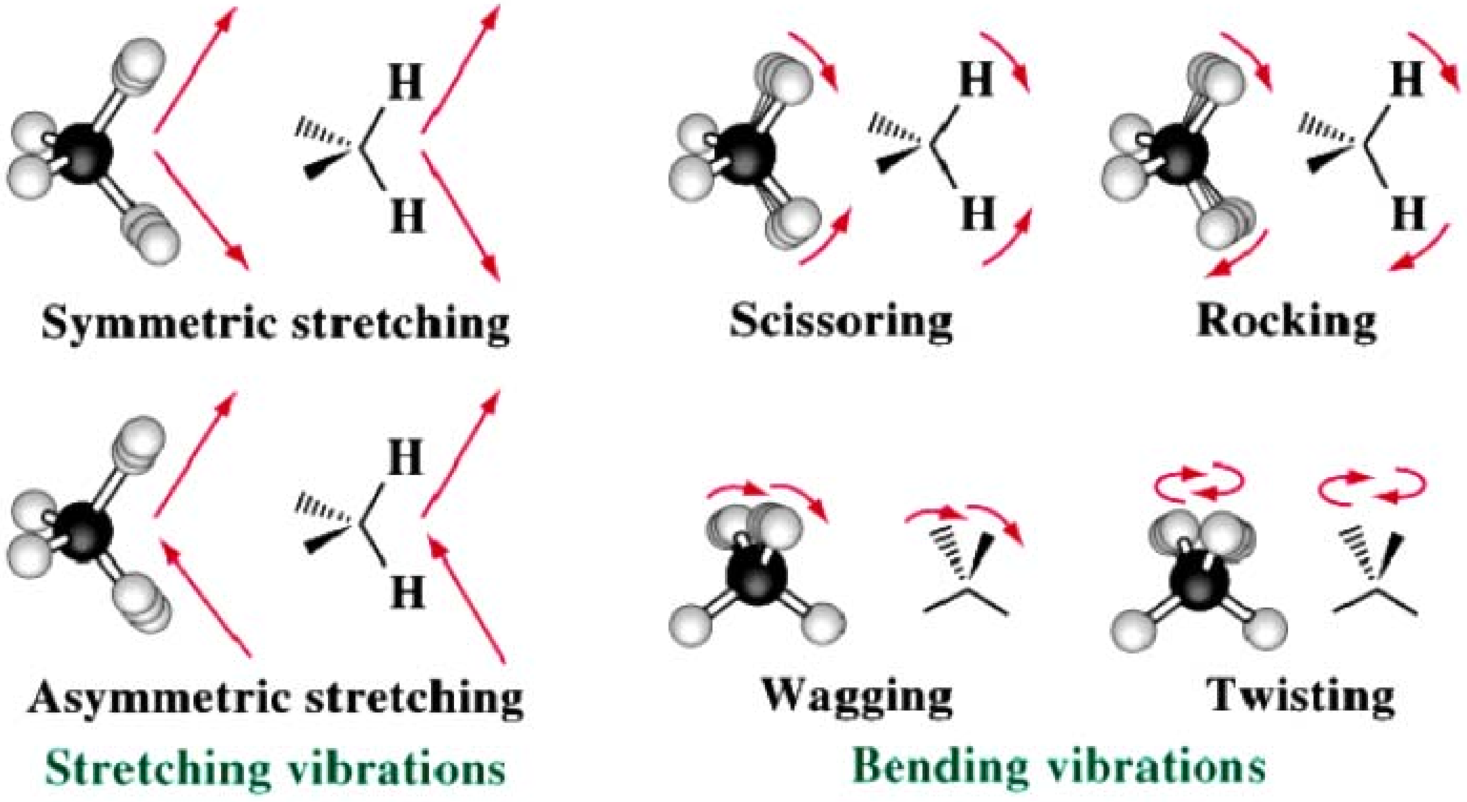


Bending Mode

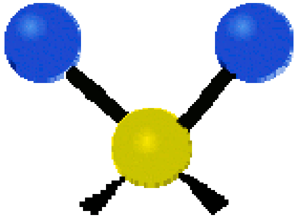
(Has dipole moment so IR active)

A Dipole Moment = charge imbalance in the molecule

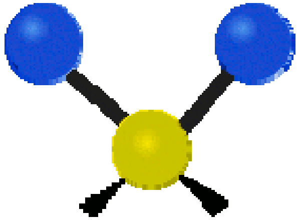
分子振动模式


H
H
Symmetric stretching
H
H
Scissoring
H
H
Rocking
H
H
Asymmetric stretching
Stretching vibrations
Wagging
Twisting
Bending vibrations

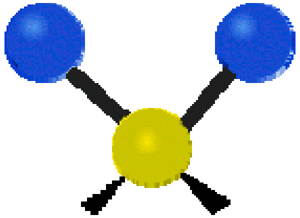
CH$_2$分子团的振动模式



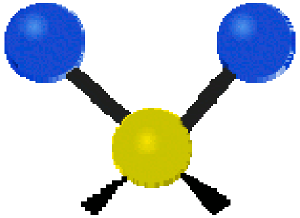
对称伸缩
Symmetric stretching



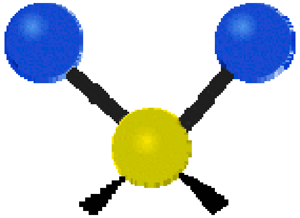
反对称伸缩
Asymmetric stretching



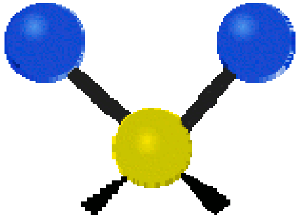
剪刀式摆动
Scissoring



左右摇摆
Rocking



上下摇摆
Wagging



扭摆
Twisting

（来源于维基百科）

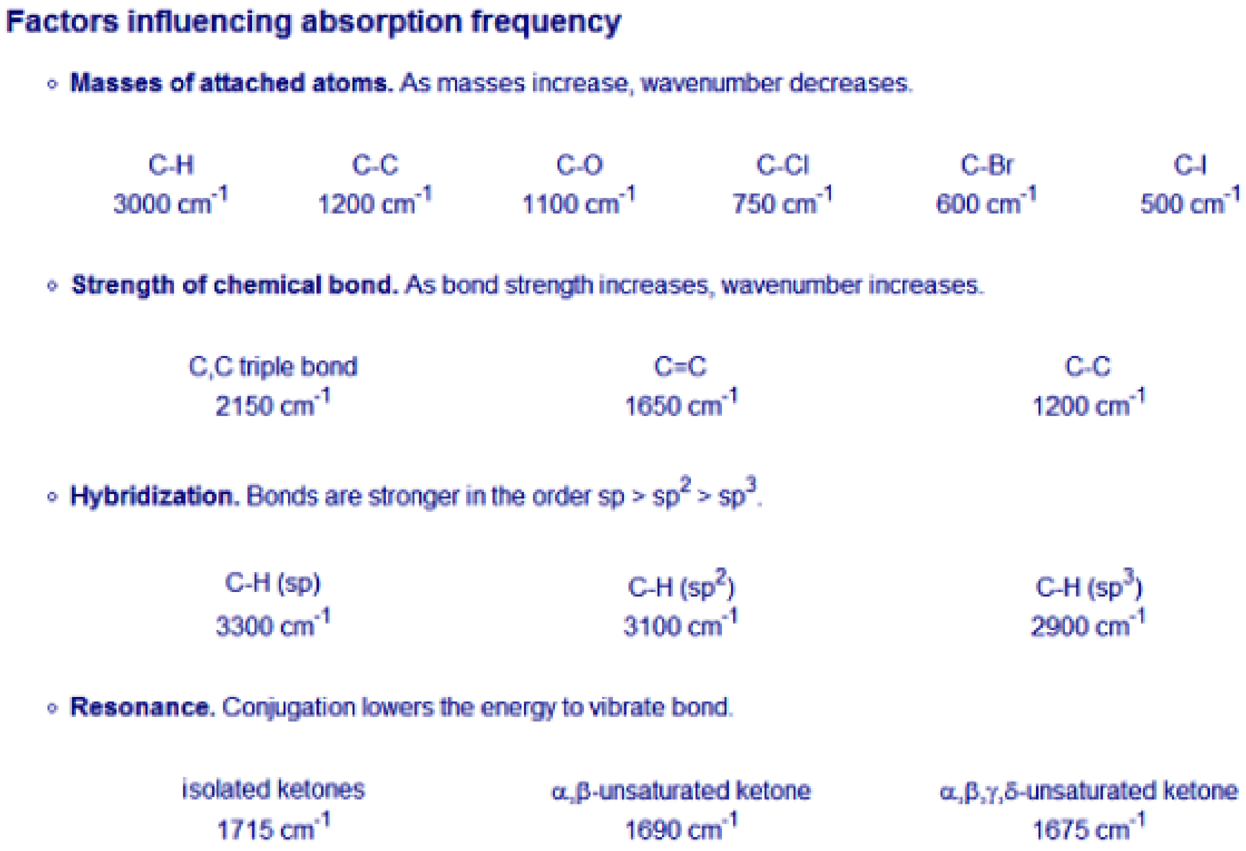
分子振动频率

分子振动可以看成谐振子振动，频率为：

$$\omega=(k/\mu)^{1/2}$$

k为力常数，决定于化学键的强度。
μ为折合质量。（同位素效应）

Factors influencing the absorption frequency



Factors influencing absorption frequency

- **Masses of attached atoms.** As masses increase, wavenumber decreases.

C-H	C-C	C-O	C-Cl	C-Br	C-I
3000 cm^{-1}	1200 cm^{-1}	1100 cm^{-1}	750 cm^{-1}	600 cm^{-1}	500 cm^{-1}

- **Strength of chemical bond.** As bond strength increases, wavenumber increases.

C,C triple bond	C=C	C-C
2150 cm^{-1}	1650 cm^{-1}	1200 cm^{-1}

- **Hybridization.** Bonds are stronger in the order sp > sp^2 > sp^3.

C-H (sp)	C-H (sp^2)	C-H (sp^3)
3300 cm^{-1}	3100 cm^{-1}	2900 cm^{-1}

- **Resonance.** Conjugation lowers the energy to vibrate bond.

isolated ketones	α,β-unsaturated ketone	α,β,γ,δ-unsaturated ketone
1715 cm^{-1}	1690 cm^{-1}	1675 cm^{-1}

红外吸收和Raman散射的基本原理

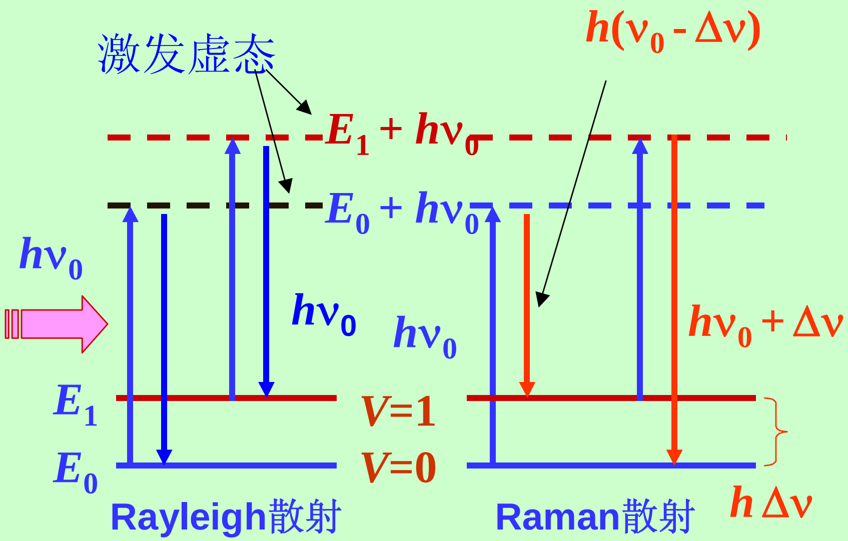
Raman散射基本原理

Rayleigh散射：

弹性碰撞；无能量交换，仅改变方向；

Raman散射：

非弹性碰撞；方向改变且有能量交换；



激发虚态
$h(\nu_0 - \Delta\nu)$
$E_1 + h\nu_0$
$E_0 + h\nu_0$
$h\nu_0$
$h\nu_0$
$h\nu_0$
$h\nu_0 + \Delta\nu$
E_1
E_0
V=1
V=0
Rayleigh散射
Raman散射
$h\Delta\nu$

E_0基态，E_1振动激发态；$E_0 + h\nu_0$，$E_1 + h\nu_0$激发虚态；获得能量后，跃迁到激发虚态.

（1928年印度物理学家Raman C V 发现；1960年快速发展）

1. Raman散射

Raman散射的两种跃迁能量差：

$\Delta E=h(\nu_0-\Delta\nu)$

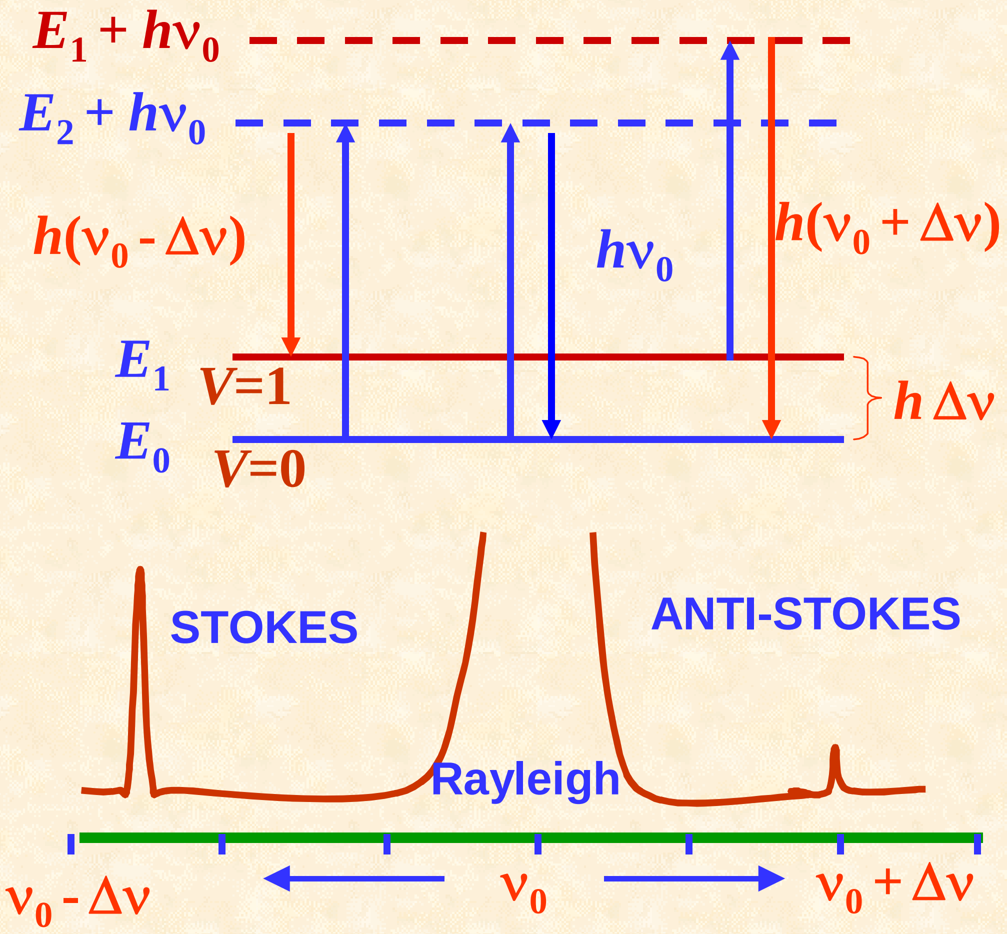
产生stokes线；强；基态分子多；

$\Delta E=h(\nu_0+\Delta\nu)$

产生反stokes线；弱；

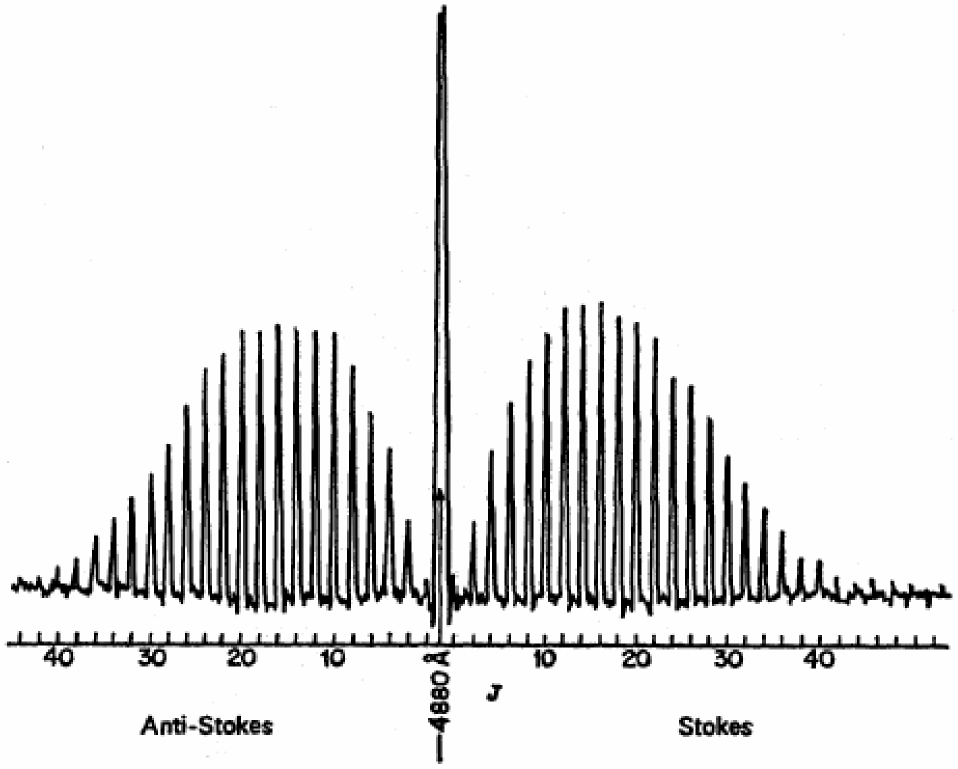
Raman位移：

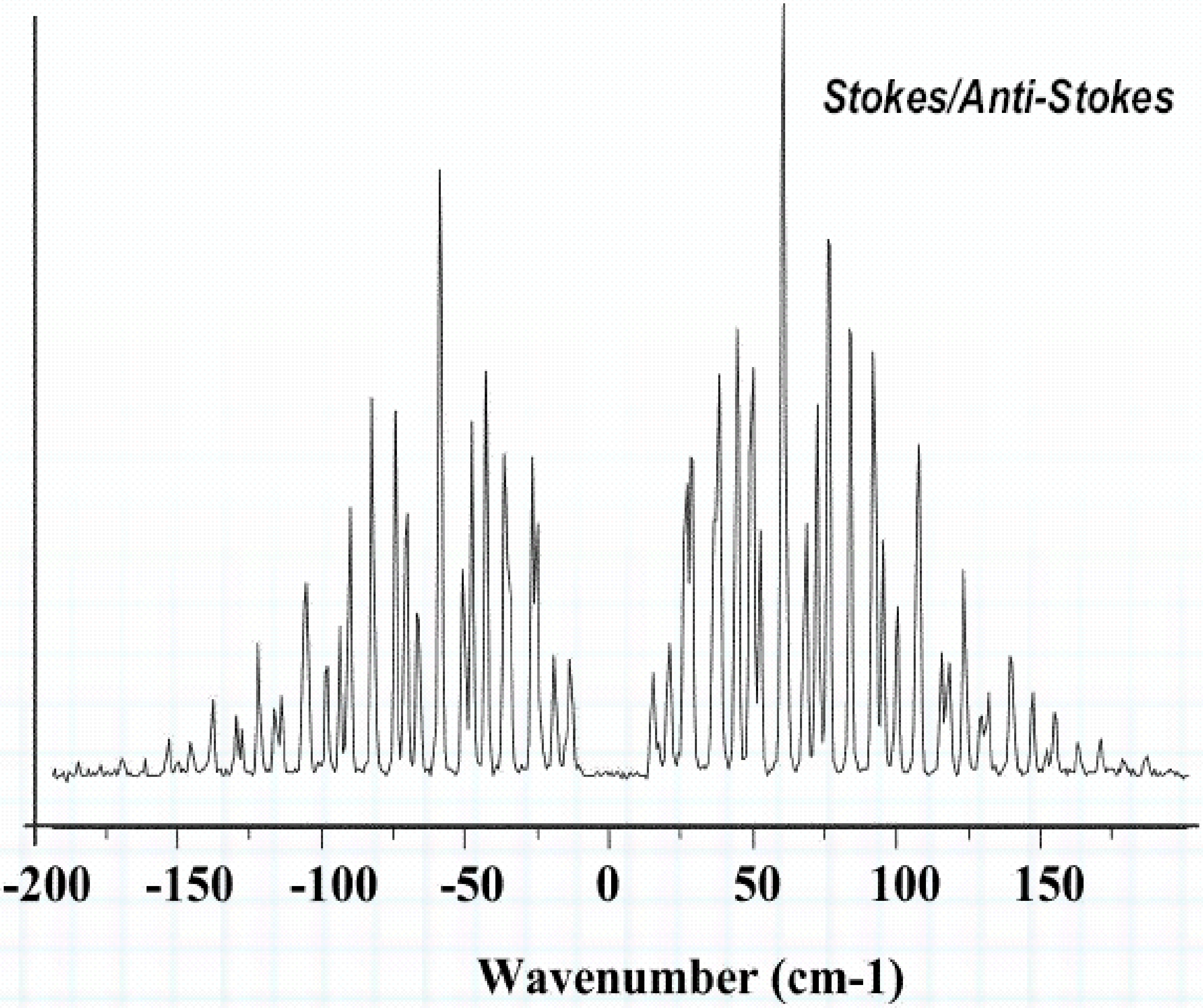
Raman散射光与入射光频率差$\Delta\nu$；



$E_1+h\nu_0$
$E_2+h\nu_0$
$h(\nu_0-\Delta\nu)$
$h\nu_0$
$h(\nu_0+\Delta\nu)$
E_1
$V=1$
E_0
$V=0$
$h\Delta\nu$
STOKES
ANTI-STOKES
Rayleigh
$\nu_0-\Delta\nu$
ν_0
$\nu_0+\Delta\nu$

Pure rotational Raman spectrum of CO_2




Stokes/Anti-Stokes
-200
-150
-100
-50
0
50
100
150
Wavenumber (cm-1)

2. Raman位移

对不同物质：$\Delta\nu$不同；

对同一物质：$\Delta\nu$与入射光频率无关；表征分子振-转能级的特征物理量；定性与结构分析的依据；

Raman散射的产生：光电场E中，分子产生诱导偶极距ρ

$$\rho = \alpha E$$

α 分子极化率；

Raman散射的经典理论

isotropic solid with electrical susceptibility χ

$$P = \varepsilon_0 \chi E \qquad D = \varepsilon_0 \varepsilon E \quad \Rightarrow \quad \varepsilon = 1 + \chi$$

D $\downarrow$ electric displacement

P $\downarrow$ polarization, electric dipole moment per unit volume

incident electromagnetic wave induces polarization:

$$\vec{E}(\vec{r},t) = \vec{E}_i^{\,0} \cos\left(\vec{k}_i \cdot \vec{r} - \omega_i t\right)$$

$$\vec{P}(\vec{r},t) = \chi\, \vec{E}_i^{\,0} \cos\left(\vec{k}_i \cdot \vec{r} - \omega_i t\right)$$

χ is modified by thermally excited phonons with atomic displacements

$$\vec{u}(\vec{r},t) = \vec{u}_0 \cos\left(\vec{q} \cdot \vec{r} - \omega_0 t\right)$$

$\vec{u}_0$ small compared to lattice constant $\Rightarrow$ expand

$$\chi = \chi_0 + \frac{\delta\chi}{\delta\vec{u}}\vec{u}(\vec{r},t)$$

$$\vec{P}(\vec{r},t) = \left[\underbrace{\chi_0}_{(1)} \underbrace{+ \frac{\delta\chi}{\delta\vec{u}}\vec{u}(\vec{r},t)}_{(2)}\right] \vec{E}_i^{\,0}\cos\left(\vec{k}_i\cdot\vec{r} - \omega_i t\right)$$

(1) in phase with incident radiation ⇒ elastic scattering
(2) frequency shift due to phonon ⇒ inelastic scattering

$$\vec{P}_{in}(\vec{r},t) = \frac{\delta\chi}{\delta\vec{u}}\vec{u}_0\cos\left(\vec{q}\cdot\vec{r} - \omega_0 t\right)\vec{E}_i^{\,0}\cos\left(\vec{k}_i\cdot\vec{r} - \omega_i t\right)$$

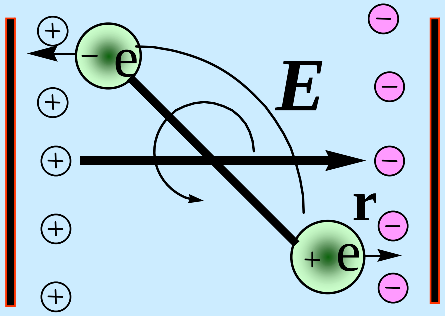
$$= \frac{1}{2}\frac{\delta\chi}{\delta\vec{u}}\vec{u}_0\,\vec{E}_i^{\,0}\left[\cos\left(\left(\vec{k}_i + \vec{q}\right)\cdot\vec{r} - \left(\omega_i + \omega_0\right)t\right) + \cos\left(\left(\vec{k}_i - \vec{q}\right)\cdot\vec{r} - \left(\omega_i - \omega_0\right)t\right)\right]$$

inelastically scattered light contains two waves:

$\vec{k}_f = \vec{k}_i - \vec{q}, \quad \omega_f = \omega_i - \omega_0$ "Stokes" process, phonon creation

$\vec{k}_f = \vec{k}_i + \vec{q}, \quad \omega_f = \omega_i + \omega_0$ "anti-Stokes" process, phonon absorption

3. 红外活性和拉曼活性振动



①红外活性振动

i 永久偶极矩；极性基团；

ii 瞬间偶极矩；非对称分子；

红外活性振动—伴有偶极矩变化的振动可以产生红外吸收谱带.

②拉曼活性振动

诱导偶极矩　　$\rho = \alpha E$

非极性基团，对称分子；

拉曼活性振动—伴随有极化率变化的振动。

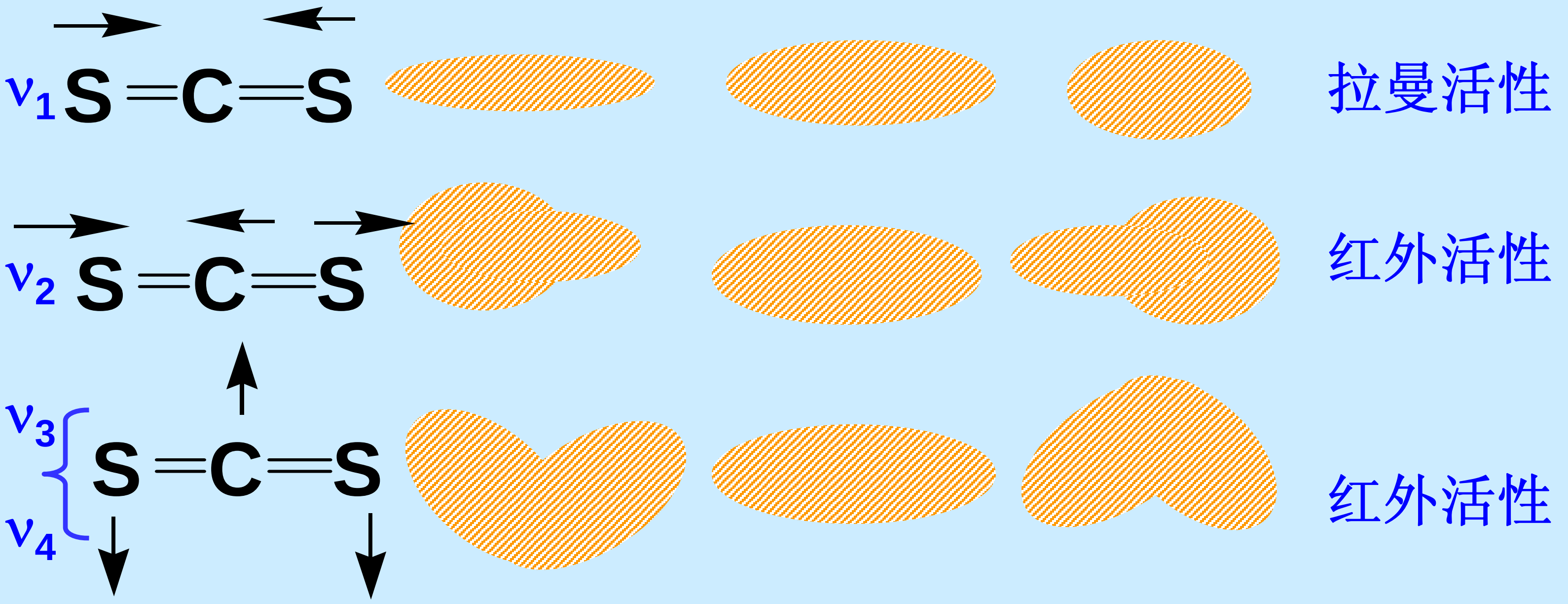
对称分子：

对称振动→拉曼活性。

不对称振动→红外活性

4. 选律

振动自由度：**3N- 4 = 4**



ν_1 S=C=S 拉曼活性

ν_2 S=C=S 红外活性

ν_3 ν_4 S=C=S 红外活性

红外光谱—源于偶极矩变化　　**Raman**光谱—源于极化率变化

对称中心分子CO_2, CS_2等，选律不相容。

无对称中心分子（例如SO_2等），三种振动既是红外活性振动，又是拉曼活性振动。

Raman光谱应用

由Raman光谱可以获得分子和固体材料振动谱特征，由此可以获得分子各种结构信息和固体材料结构、组分等各种信息。

对于有机分子，Raman可以用来进行研究，但是红外相对于Raman的优点是前者方便定量化。

1）同种分子的非极性键S-S，C=C，N=N，C≡C产生强拉曼谱带， 随单键→双键→三键谱带强度增加。

2）红外光谱中，由C ≡N，C=S，S-H伸缩振动产生的谱带一般较弱或强度可变，而在拉曼光谱中则是强谱带。

3）环状化合物的对称呼吸振动常常是最强的拉曼谱带。

4）在拉曼光谱中，X=Y=Z，C=N=C，$O=C=O^-$这类键的对称伸缩振动是强谱带，反这类键的对称伸缩振动是弱谱带。红外光谱与此相反。

5）C-C伸缩振动在拉曼光谱中是强谱带。

6）醇和烷烃的拉曼光谱是相似的：I. C-O键与C-C键的力常数或键的强度没有很大差别。II. 羟基和甲基的质量仅相差2单位。 III.与C-H和N-H谱带比较，O-H拉曼谱带较弱。

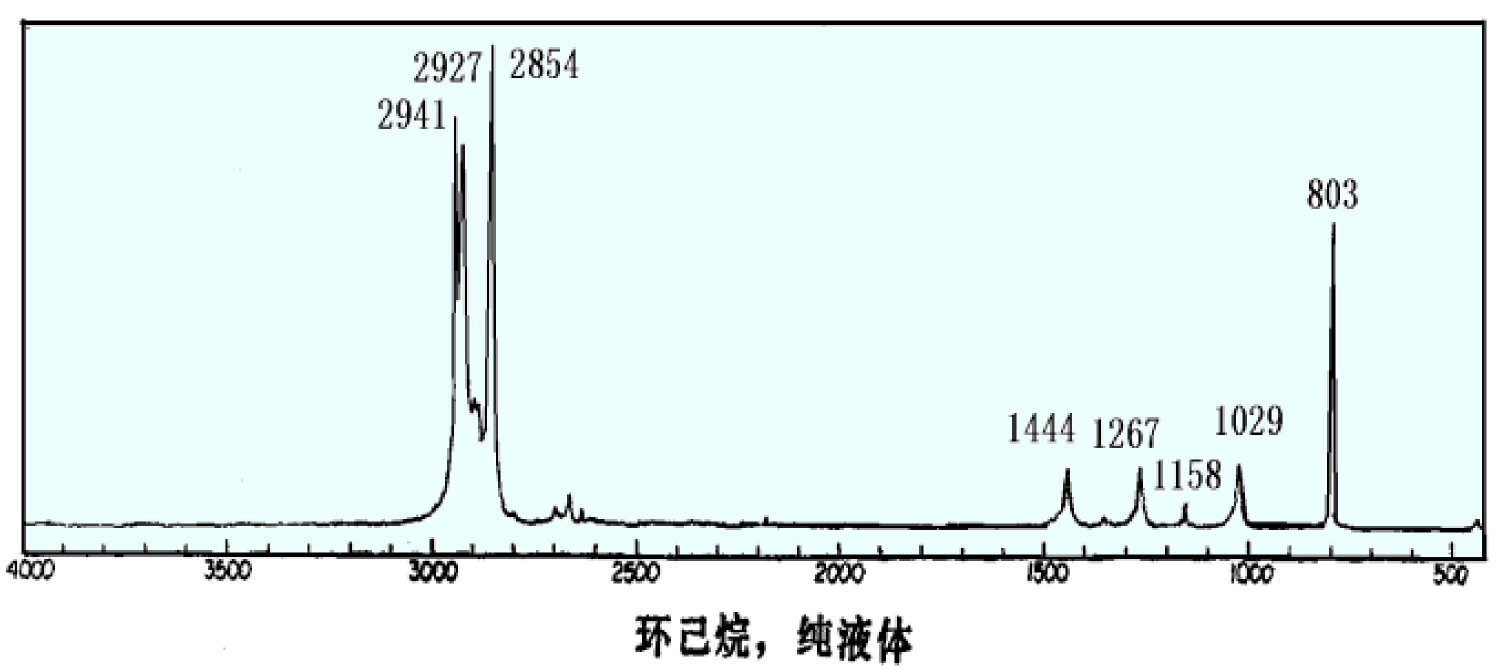
7）有些材料尽管可以用红外谱研究，但Raman谱研究也许更方便，或者能提供补充信息。

- Raman光谱更适合研究生物分子，因为红外对水特别敏感，不能用水溶液。而Raman可以。

- 共振Raman散射对于研究有机分子常常更有优势。

- 无机材料Raman光谱比红外光谱更适宜用于振动谱研究。

- 特别是很多无机材料溶于水。



环己烷，纯液体

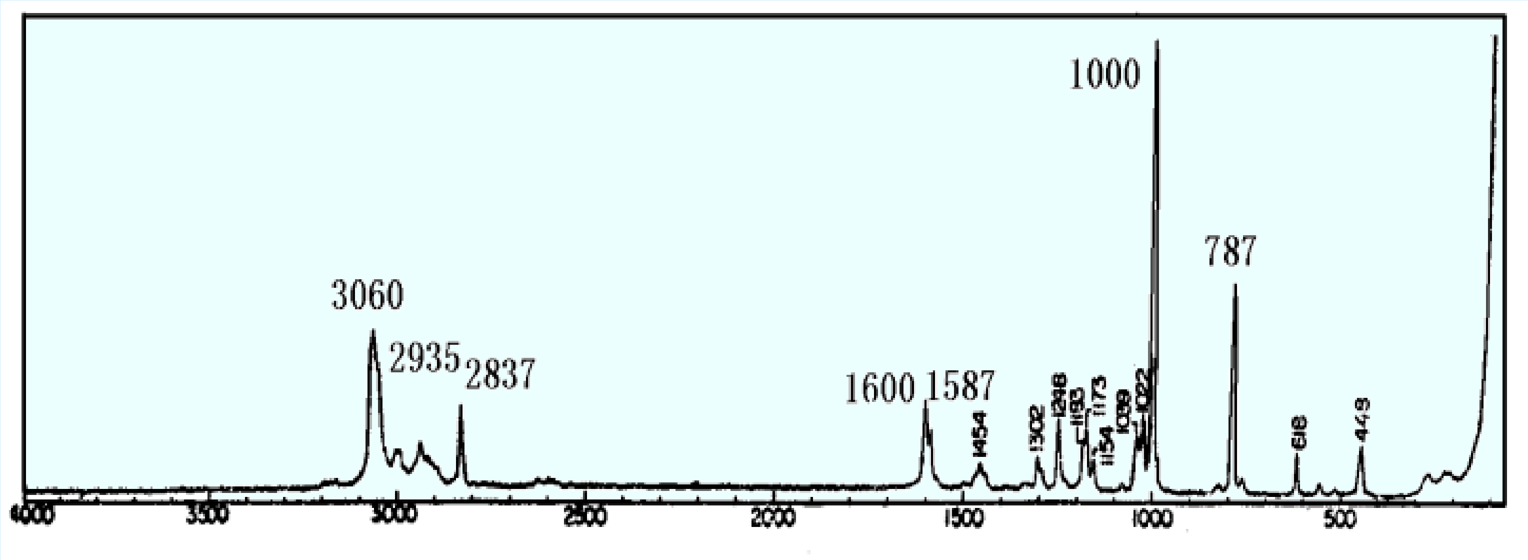
2941，2927cm^{-1} $\nu_{AS}CH_2$

2854cm^{-1} $\nu_{S}CH_2$

1444，1267 cm^{-1} δCH_2

1029cm^{-1} $\nu_{(C\text{-}C)}$

803 cm^{-1}环呼吸



苯甲醚，纯液体

3060cm^{-1} $\nu_{(Ar-H)}$

1600,1587cm^{-1} $\nu_{(c=c)}$苯环

1039, 1022cm^{-1}单取代

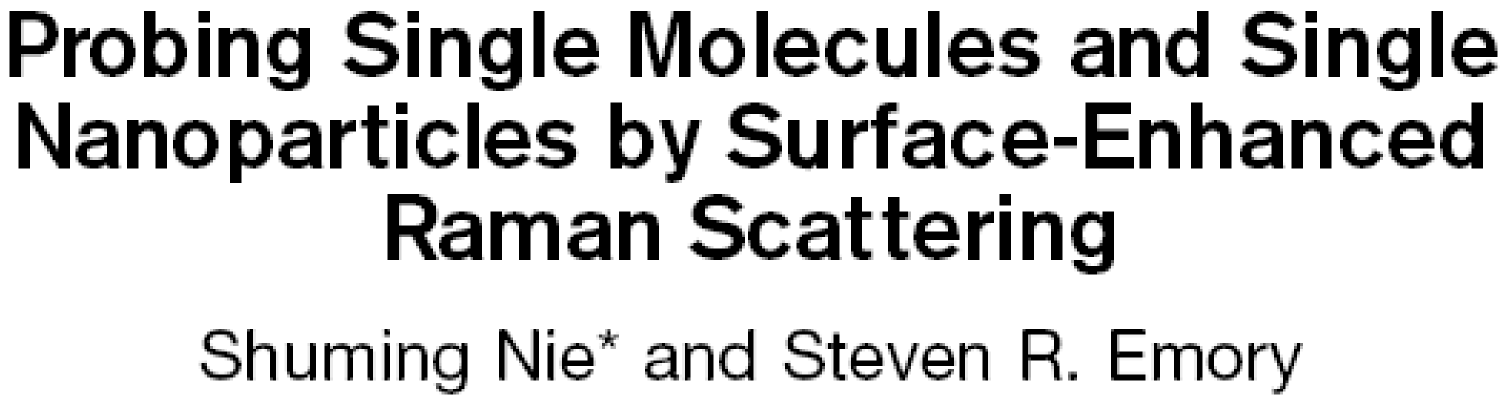
1000 cm^{-1}环呼吸

787 cm^{-1}环变形

各种Raman散射

- 共振Raman散射
- 电子共振Raman散射
- 表面增强Raman散射
- 受激Raman散射
- 超Raman散射
- 逆Raman散射
- 相干反Stokes Raman散射（CARS）
- ……

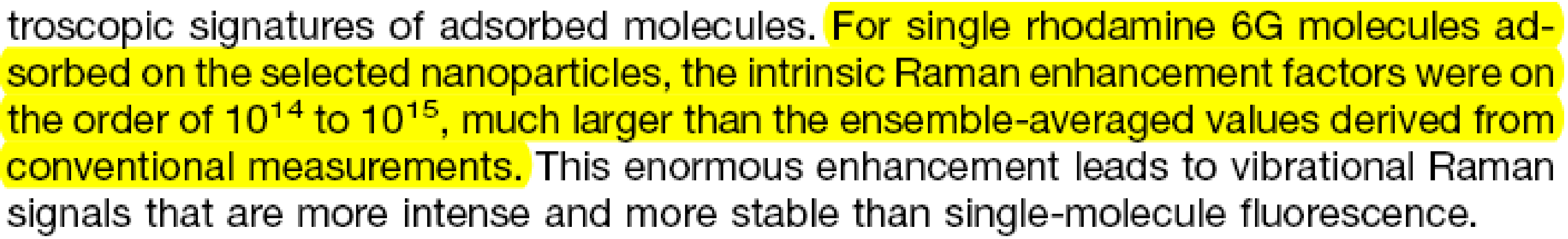
SERS (Surface Enhanced Raman Scattering)



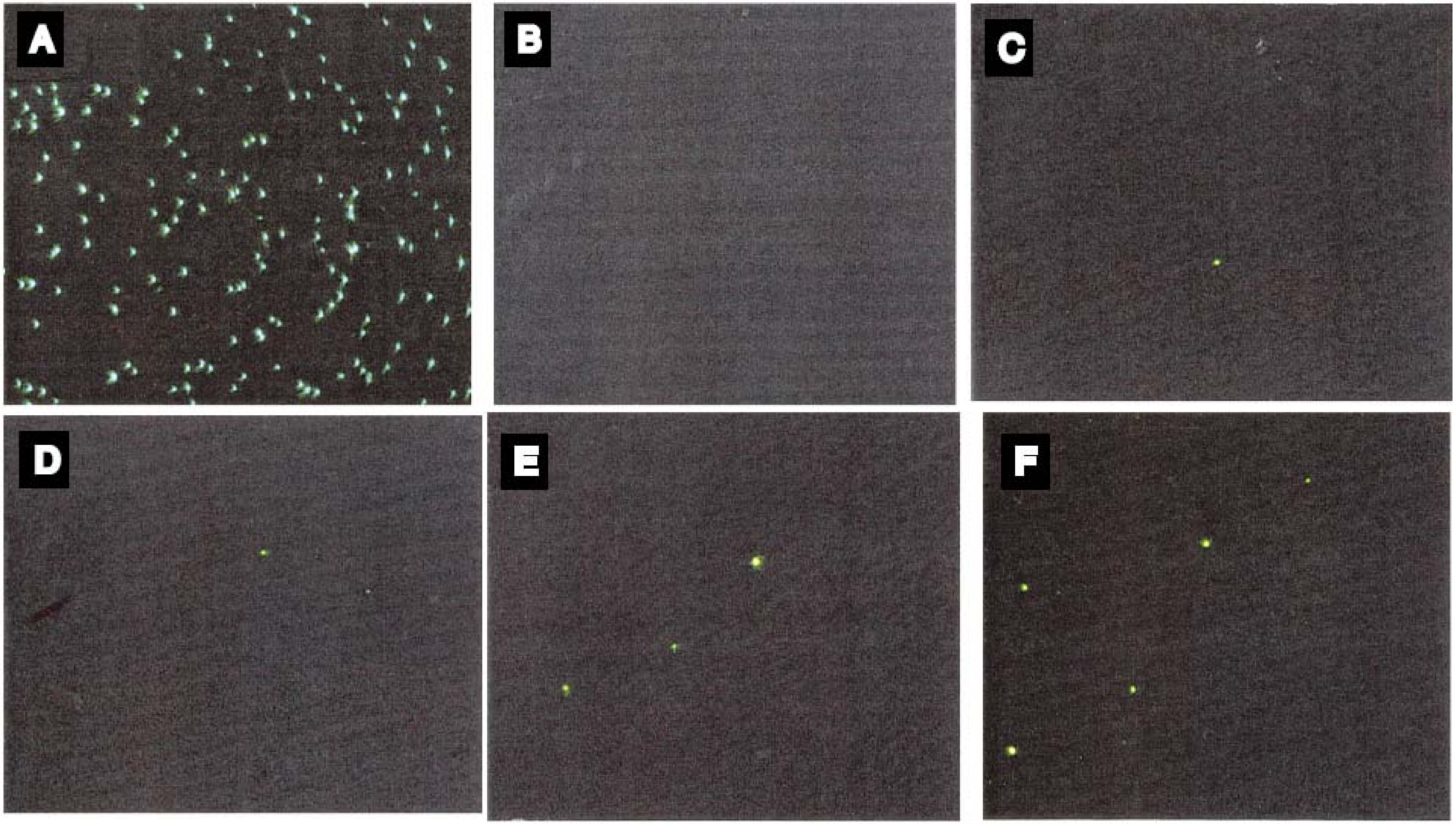
Probing Single Molecules and Single Nanoparticles by Surface-Enhanced Raman Scattering

Shuming Nie* and Steven R. Emory

Science, 275, 1102(1997)



troscopic signatures of adsorbed molecules. For single rhodamine 6G molecules adsorbed on the selected nanoparticles, the intrinsic Raman enhancement factors were on the order of 10^{14} to 10^{15}, much larger than the ensemble-averaged values derived from conventional measurements. This enormous enhancement leads to vibrational Raman signals that are more intense and more stable than single-molecule fluorescence.



(A) Unfiltered photograph showing scattered laser light from all particles immobilized on a polylysine-coated surface. (B) Filtered photographs taken from a blank Ag colloid sample (incubated with 1 mM NaCl and no R6G analyte molecules). (C) and (D) Filtered photographs taken from a Ag colloid sample incubated with 2 3 10211 M R6G. These images were selected to show at least one Raman scattering particle. Different areas of the cover slip were rapidly screened, and most fields of view did not contain visible particles. (E) Filtered photograph taken from Ag colloid incubated with 2 3 10210 M R6G. (F) Filtered photograph taken from Ag colloid incubated with 231029MR6G. A high-performance bandpass filter was used to remove the scattered laser light and to pass Stokes-shifted Raman signals from 540 to 580 nm (920 to 2200 cm21). Continuous-wave excitation at 514.5 nm was provided by an Ar ion laser. The total laser power at the sample was 10 mW. Note the color differences between the scattered laser light in (A) and the red-shifted light in (C) through (F).

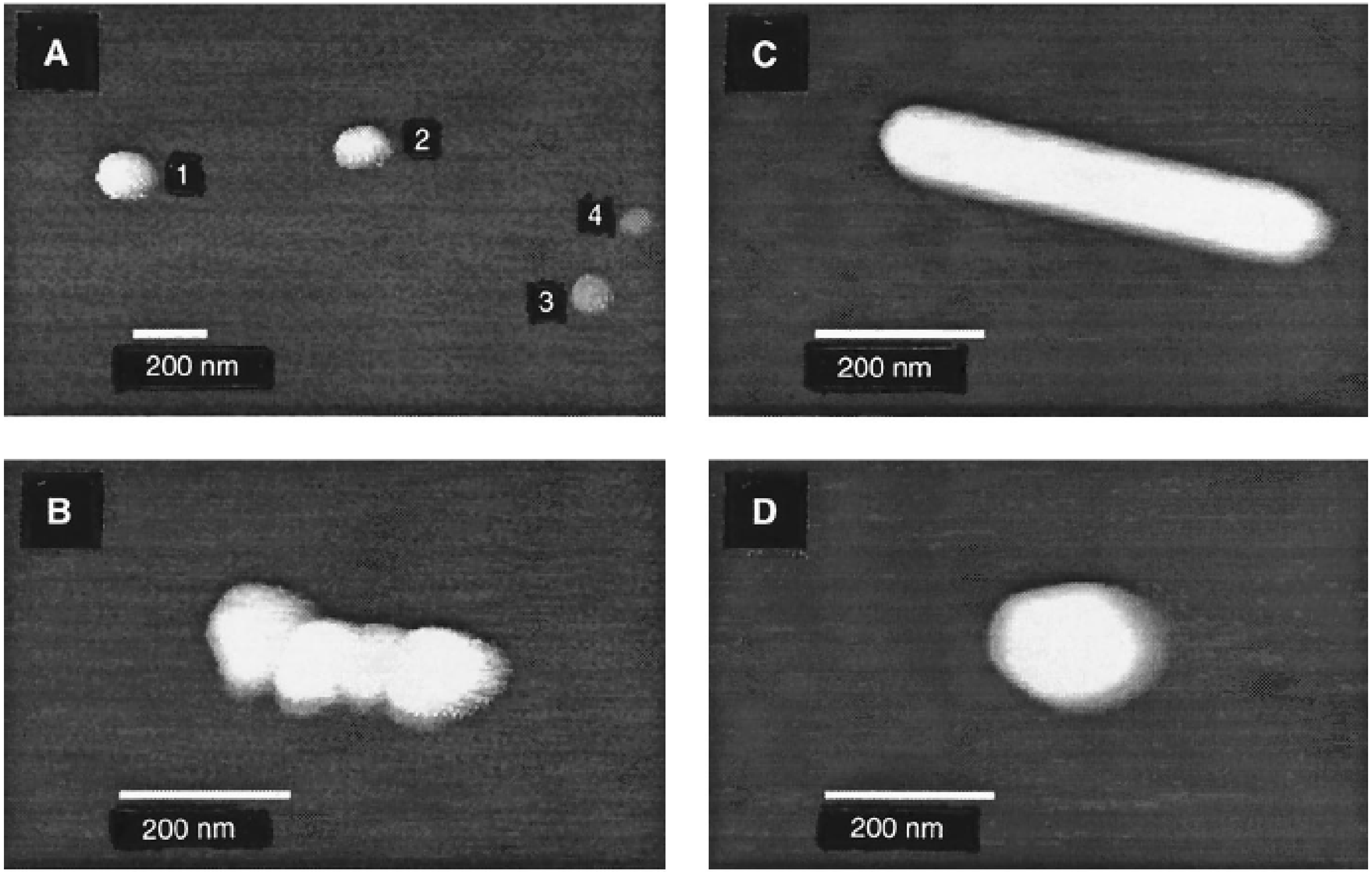


Fig. 2. Tapping-mode AFM images of screened Ag nanoparticles. (**A**) Large area survey image showing four single nanoparticles. Particles 1 and 2 were highly efficient for Raman enhancement, but particles 3 and 4 (smaller in size) were not. (**B**) Close-up image of a hot aggregate containing four linearly arranged particles. (**C**) Close-up image of a rod-shaped hot particle. (**D**) Close-up image of a faceted hot particle.

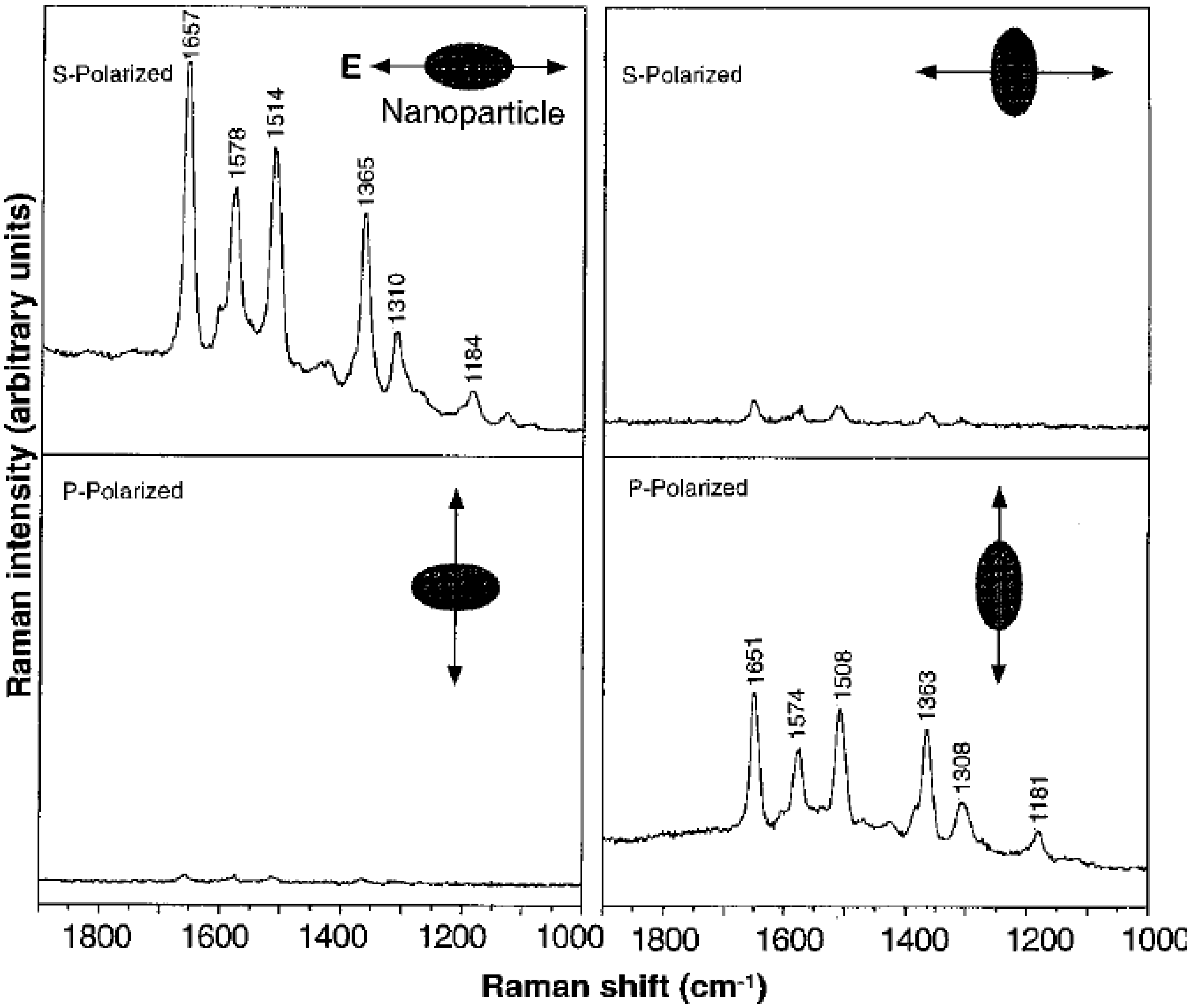
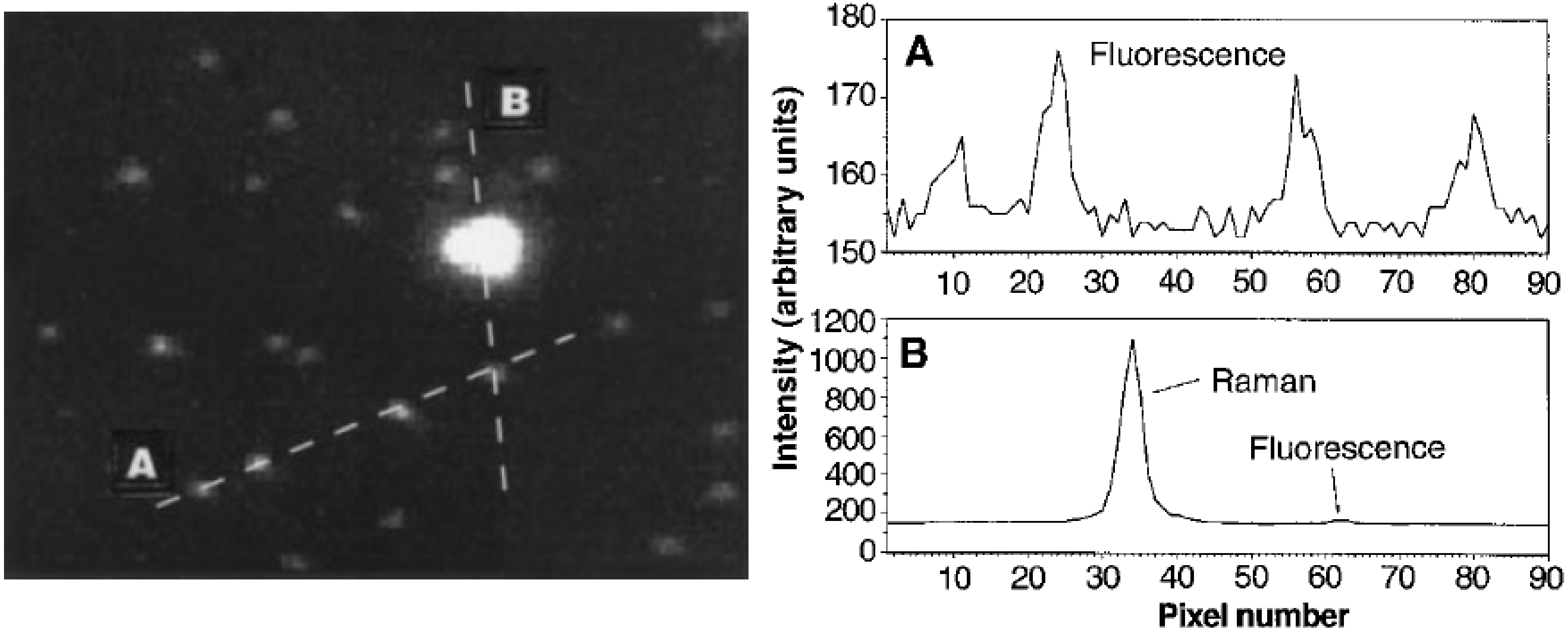


Fig. 3. Surface-enhanced Raman spectra of R6G obtained with a linearly polarized confocal laser beam from two Ag nanoparticles. The R6G concentration was 2×10^{-11} M, corresponding to an average of 0.1 analyte molecule per particle. The direction of laser polarization and the expected particle orientation are shown schematically for each spectrum. Laser wavelength, 514.5 nm; laser power, 250 nW; laser focal radius, ~250 nm; integration time, 30 s. All spectra were plotted on the same intensity scale in arbitrary units of the CCD detector readout signal.



Direct comparison of laser-induced fluorescence and SERS of a single R6G molecule. Note that single-molecule fluorescence signals were observed as diffraction-limited spots (~500 nm in diameter or 6 pixels). The integrated Raman signal appeared much larger in size, but its full width at half maximum was similar to that for fluorescence. Detailed signal intensities and widths are shown for lines (**A**) and (**B**). Laser wavelength, 514.5 nm; excitation power, 10 mW; integration time, 5 s.

CARS (相干反Stokes Raman散射)

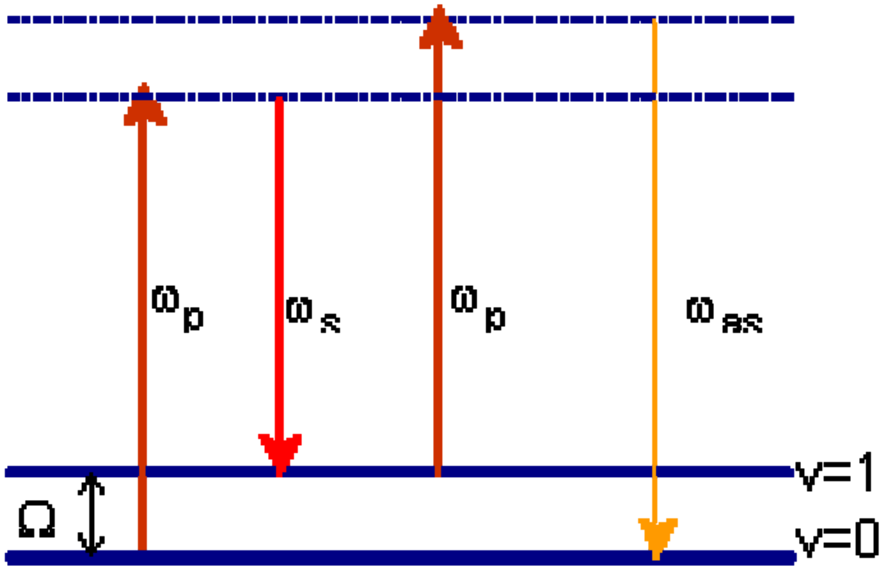
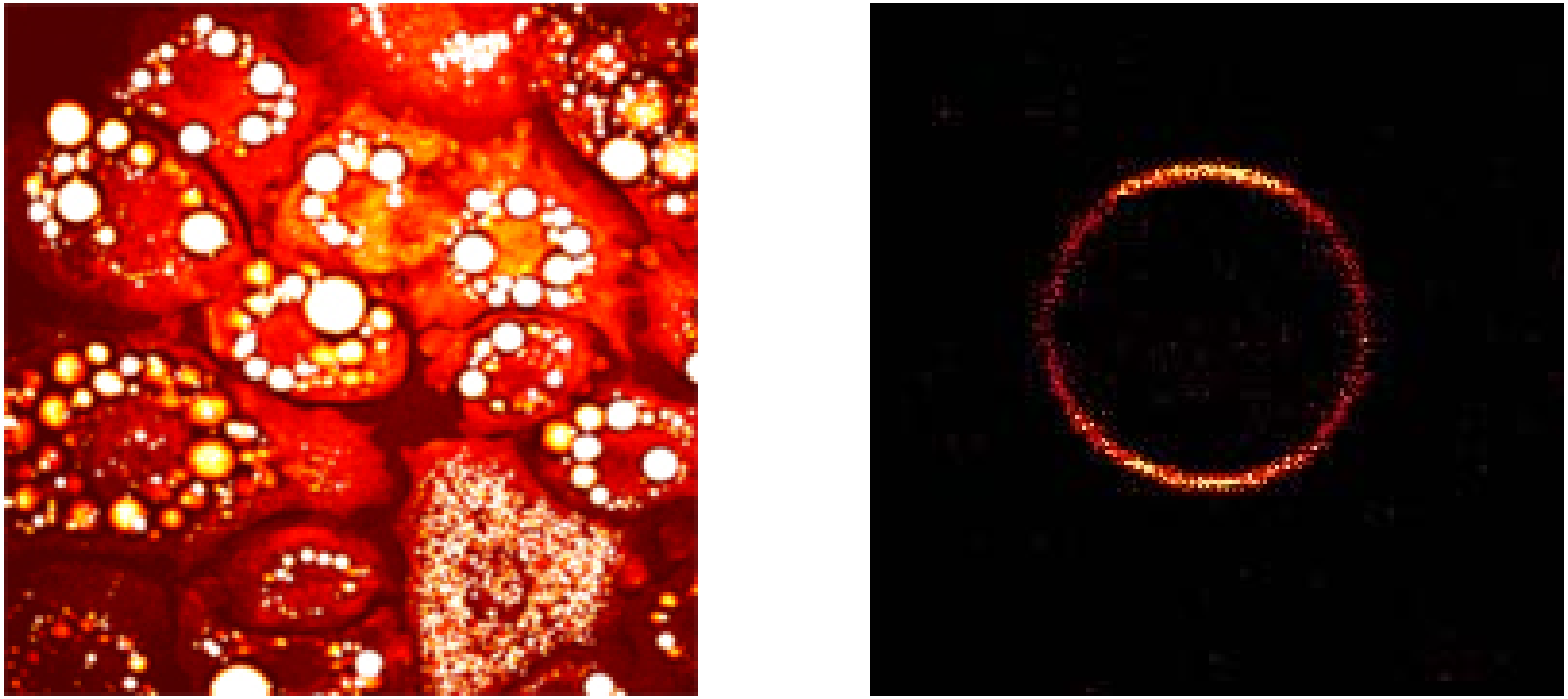


Fig.1 Energy diagram of CARS

Coherent anti-Stokes Raman scattering is a four-wave mixing process in which a pump beam at frequency *wp* and a Stokes laser beam at frequency *ws* interact with a sample to generate an anti-Stokes signal at frequency *was*=2*wp*-*ws*. The energy diagram of CARS is shown in Fig. 1.

The CARS signal is enhanced when the frequency difference between the pump and Stokes beams, *wp*-*ws*, is tuned to a vibrational frequency W, providing the vibrational contrast for CARS microscopy.



[Left] CARS image of **fibroblast cells** that are stimulated to synthesize lipids. The lipid droplets can be visualized with CARS when tuning to the aliphatic C-H vibration. Image was taken in 2.7 seconds and measures 100 by 100 um. ***[Right]*** F-CARS image of a natural single lipid bilayer (erythrocyte ghost) at 2845 cm-1, taken with parallel polarized beams along the x axis (note the polarization dependence). Image size is 15 x 15 um.

拉曼光谱与红外光谱分析方法比较

拉曼光谱	红外光谱
光谱范围40-4000Cm^{-1}	光谱范围400-4000Cm^{-1}
水可作为溶剂	水不能作为溶剂
样品可盛于玻璃瓶，毛细管等容器中直接测定	不能用玻璃容器测定
固体样品可直接测定	需要研磨制成 KBR 压片

红外光谱测量样品准备

气体样品：

1. 金属或者玻璃容器，两端带有红外窗口。
2. 真空和阀控保证气体样品的正确导入。
3. 因为气体吸收一般较弱，光学长程池的应用。
4. 低气压下转动光谱精细结构的分辨。

液体样品：

液体：带有红外窗口的吸收池；液膜法——如滴入两片NaCl平板之间制样。

溶液：对于溶液样品来说，红外测量是个需要仔细考虑问题，因为多数常用的溶剂都吸收红外光，因此只能根据波段选择溶剂。

较好的溶剂有CCl_4, CS_2,氯仿等，红外不激活。

水肯定不是好的溶剂。吸收和溶解光学窗口

固体样品：

晶体样品：

大块晶体样品只要适当切割成合适的薄片就可以。厚度的选择取决于材料的吸收系数。表面粗糙度小于红外光波长。

粉末样品：

直接压片：首先要经过较好研磨，粒度小于红外光波长。

混入有机液体涂片（如NaCl片）

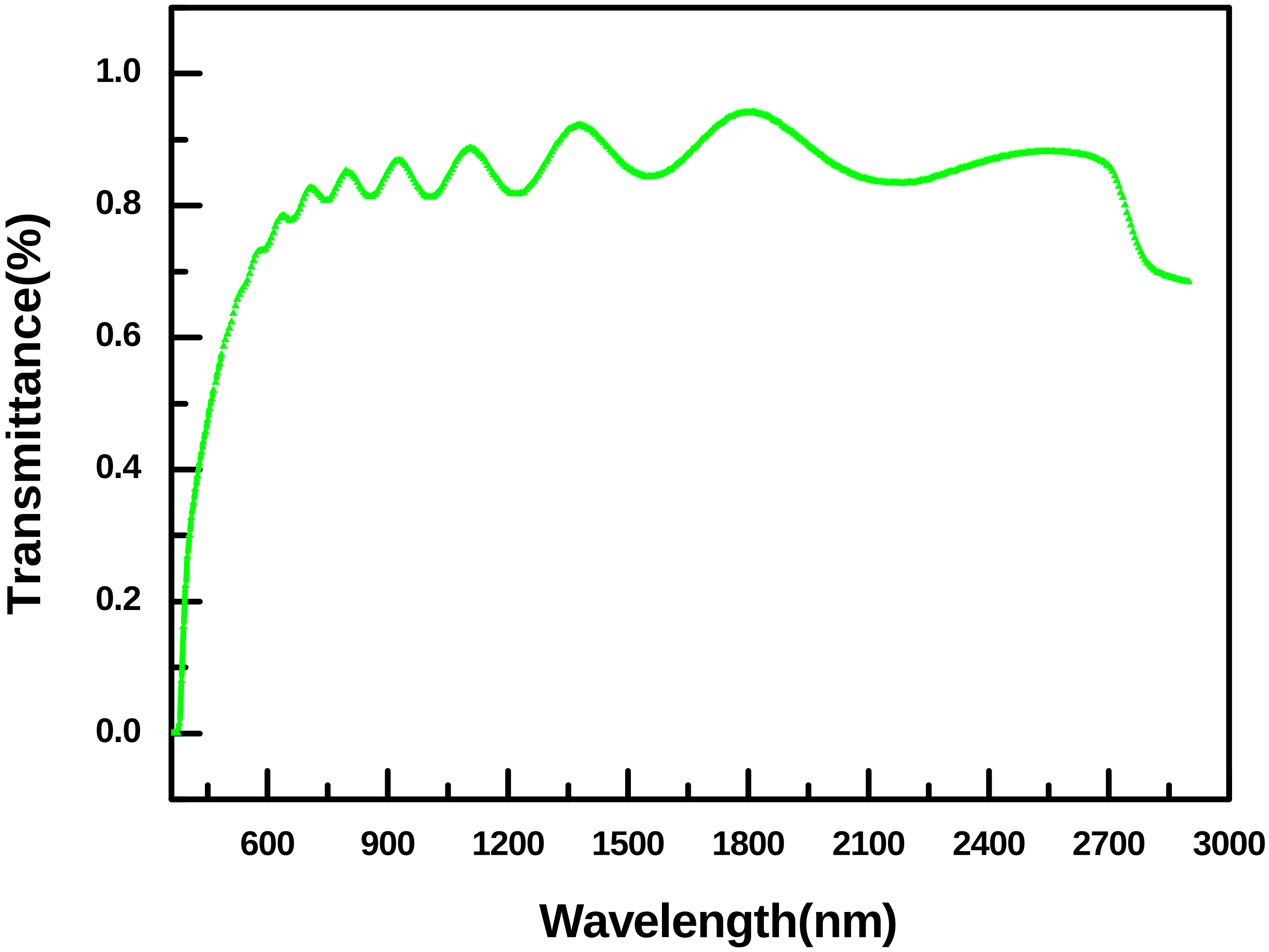
KBr压片：KBr是常用的压片辅助剂，因为到25微米它仍然有很好的红外的通过率。

薄膜样品：

要选择合适的衬底。普通玻璃不是合适的衬底，而c-Si, c-Ge是就是比较好的衬底（到10微米左右），NaCl是更好的选择。

对于薄膜样品有时要故意进行表面粗糙处理，让衬底，同时也是让薄膜不要产生等厚干涉。两个相邻干涉极大值位置满足下式。

$$2nd = \frac{1}{\dfrac{1}{\lambda_2} - \dfrac{1}{\lambda_1}}$$



薄膜的透过率曲线，从中可以看到等厚干涉条纹

Raman光谱测量样品准备

气体样品：

1. 一般来说气体的Raman散射非常困难得到。需要强的激发和灵敏的探测。

2. 相应的样品池的准备同红外，但不同的是不需要红外窗口。

液体样品：

液体：样品池（同样不需要红外窗口，只要光学窗口就可以），一般采用90°散射配置。

溶液：有机溶液和水溶液都可以，根据需要选择。

固体样品：

晶体样品：

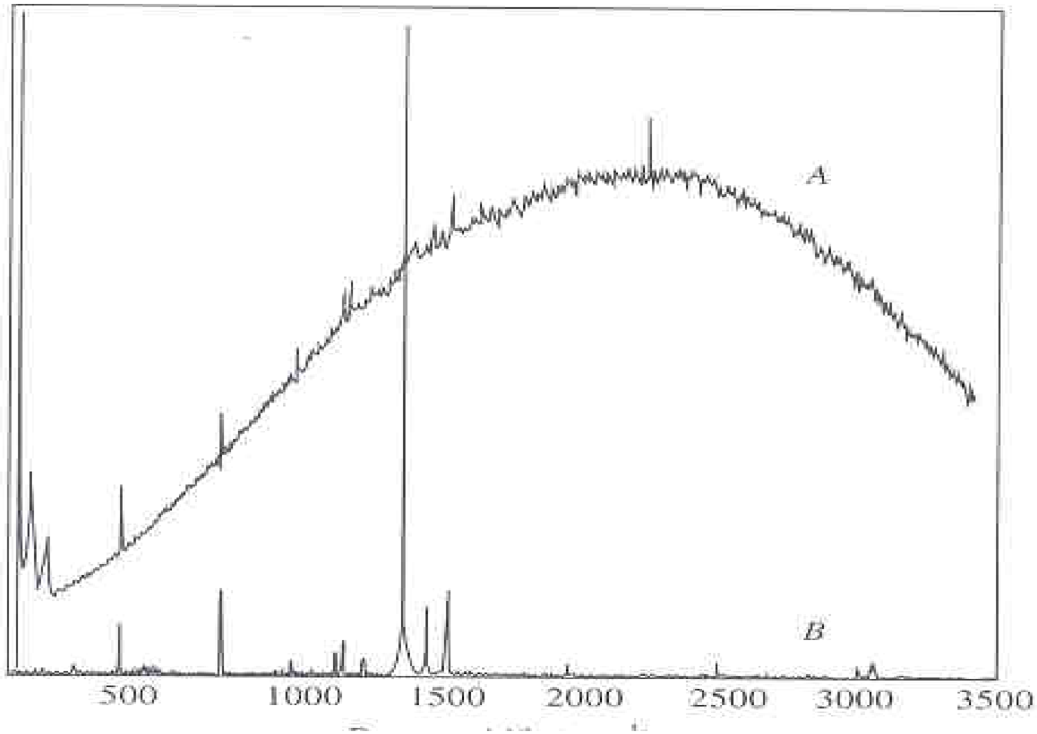
最好有光学平面，越是光滑的平面越有利于Raman光谱的测量。（SERS除外）

粉末样品：

微区Raman光谱仪可以容许直接做数微米大小的样品。当然，压片和涂片也是常见的做法。

荧光背底的抑制

Raman散射一个重要的实验技术是抑制荧光背底。

方法：光滑的平面、改变激发波长等。