

# **Vibrational spectroscopy**

A faint, light purple background image of a balance scale is visible behind the text. The scale has a horizontal beam with two pans hanging from it. The left pan is larger and lower, while the right pan is smaller and higher.

**(IR and Raman spectroscopy)**

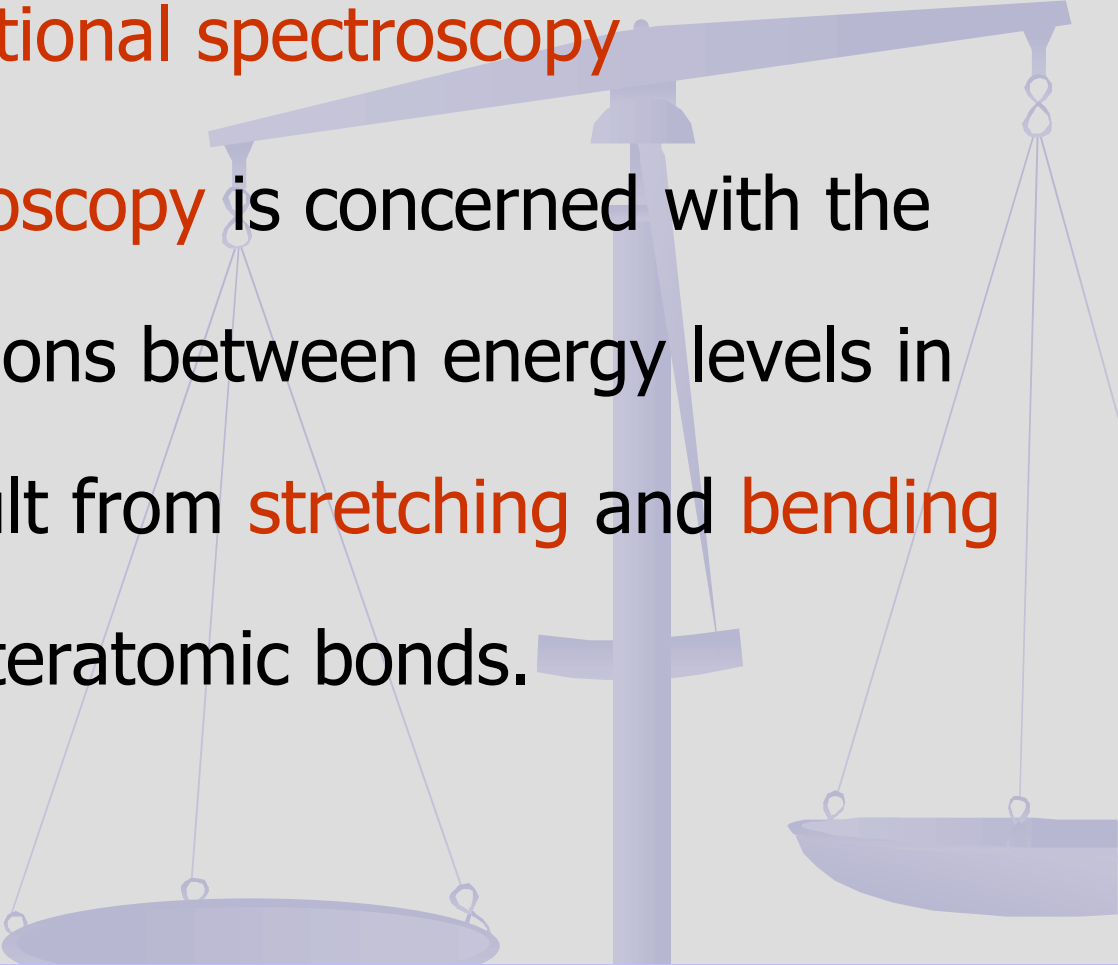
- ❖ 5.1 Fundamental principle
- ❖ 5.2 Instrument
- ❖ 5.3 Sample preparation
- ❖ 5.4 Application



## 5.1 Fundamentals of vibrational spectroscopy

### Definition of vibrational spectroscopy

**Vibrational spectroscopy** is concerned with the detection of transitions between energy levels in **molecules** that result from **stretching** and **bending** vibrations of the interatomic bonds.



# Fundamentals of vibrational spectroscopy

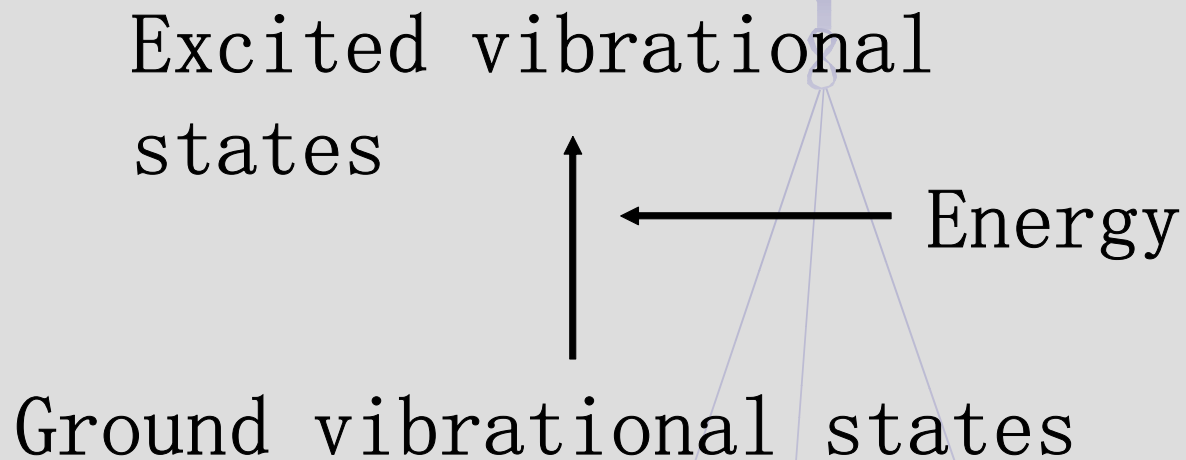
## Vibrational frequencies

- **Be characteristic of particular functional groups in molecules.**
- **Be sensitive to**
  - (1) molecular environment**
  - (2) chain conformations**
  - (3) morphology.**

It is a useful method for the structure analysis of materials.

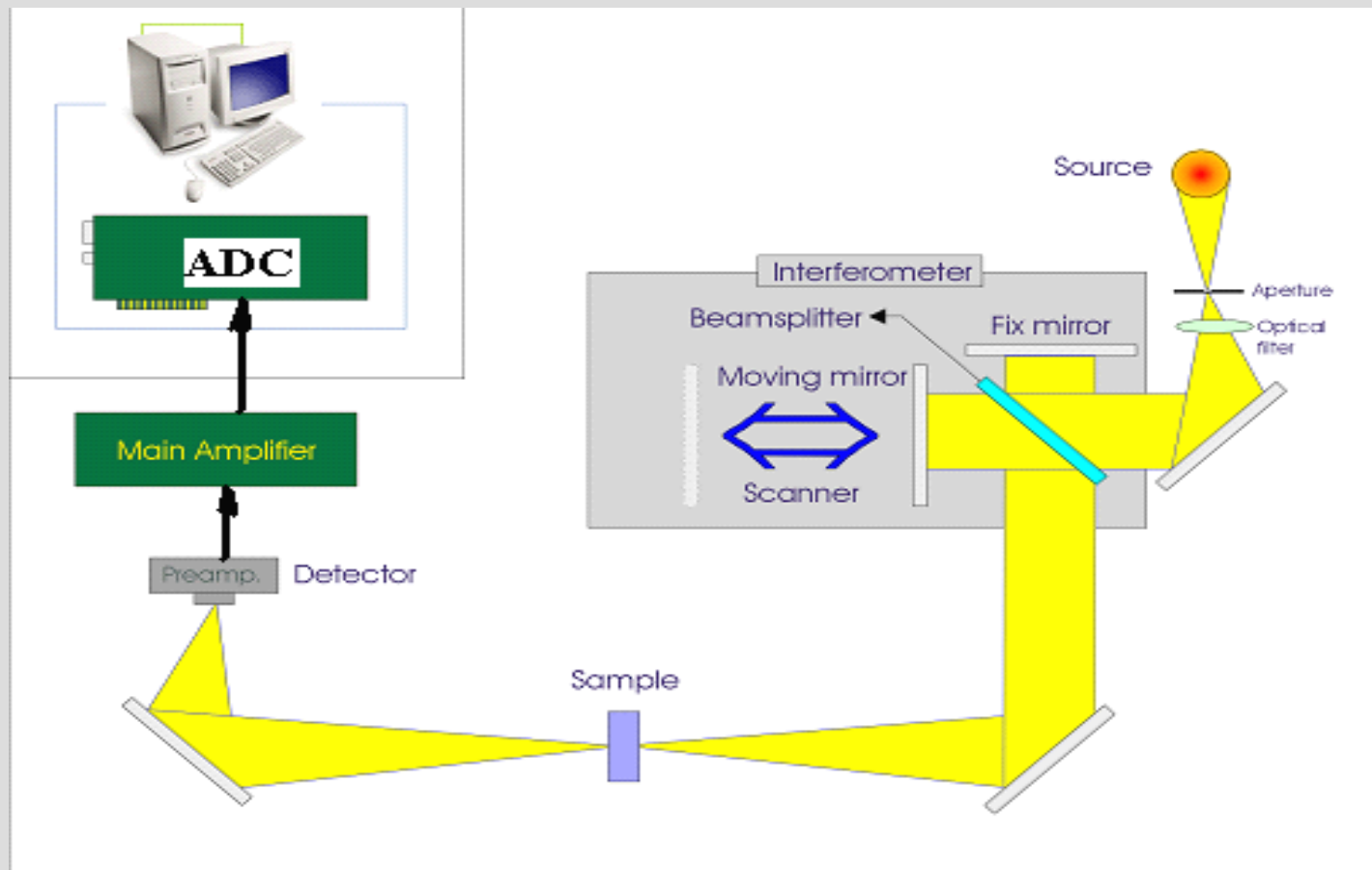
# Fundamentals of vibrational spectroscopy

## State of molecules



**At room temperature, most molecules exist in their ground vibrational states.**

# Fundamentals of vibrational spectroscopy



# Fundamentals of vibrational spectroscopy

## Kinds of vibrational spectroscopy

- Infra-red (Polarized) spectroscopy
- Raman (Non-polarized) spectroscopy

# Infrared spectroscopy

EM radiation of an appropriate frequency

Molecular

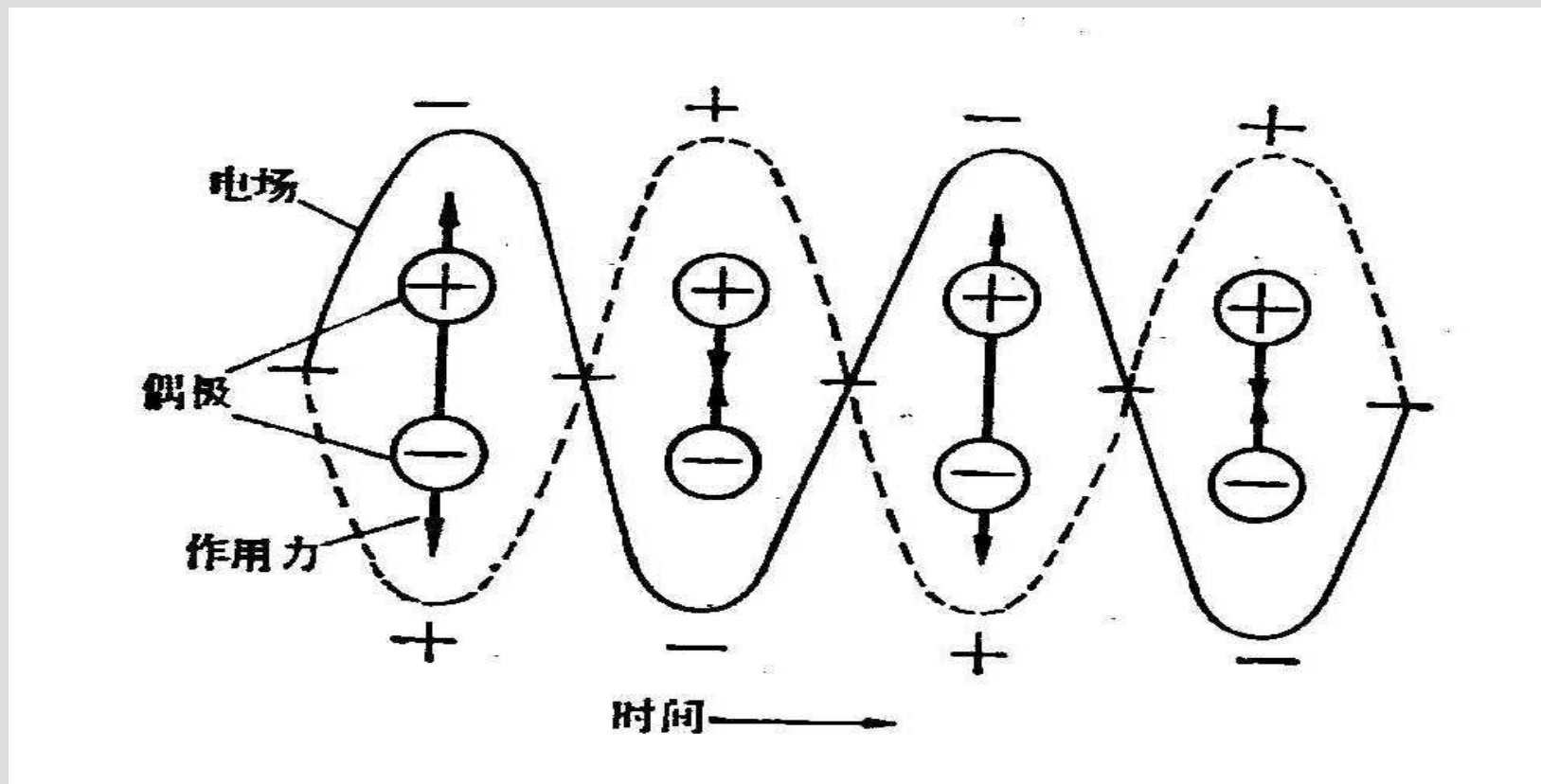
Bond dipole moment

**Infrared absorbance**

When the vibrating dipole is in phase with the electric vector of the incident radiation the vibrations are enhanced and there is transfer of energy from the incident radiation to the molecule.

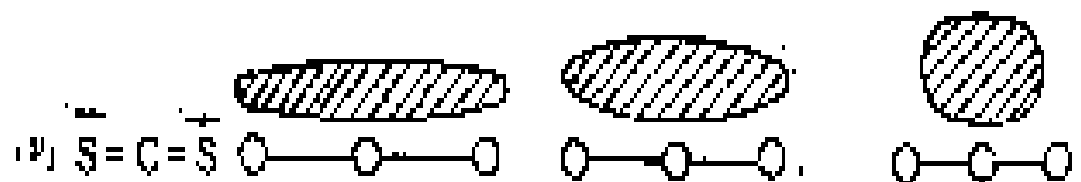


# Infrared spectroscopy

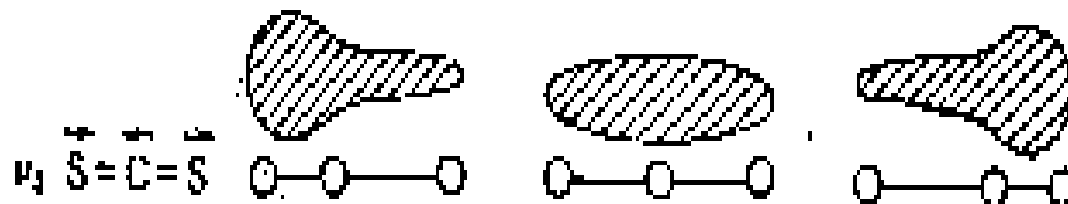


# Infrared spectroscopy

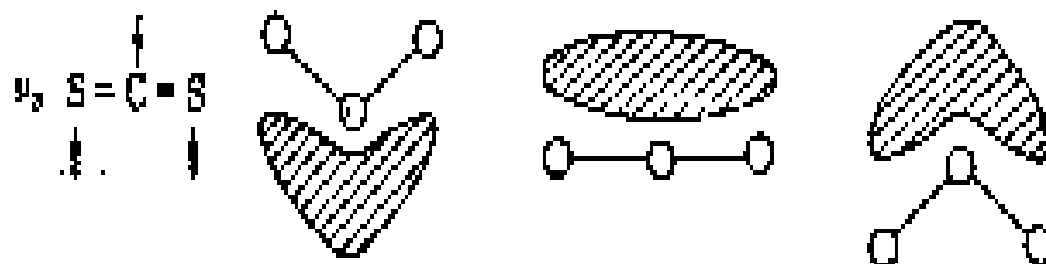
## Vibrating of Disulfide carbon



Symmetrical stretching



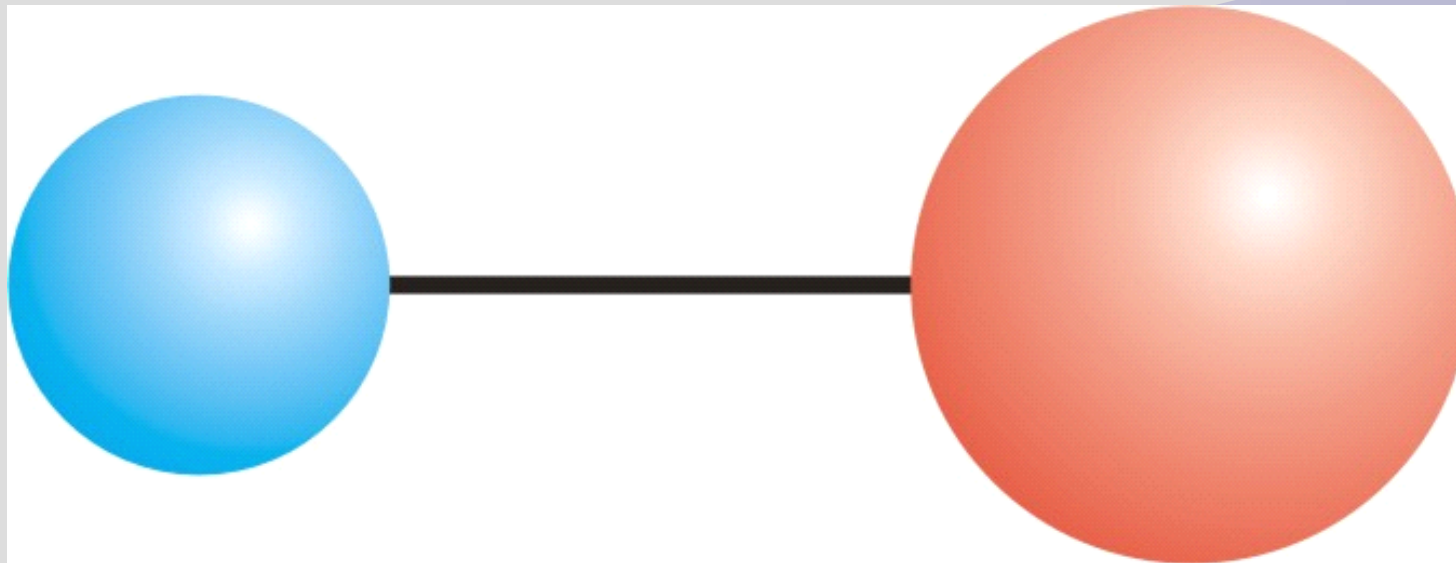
Asymmetrical stretching



Bending

# Infrared spectroscopy

## Diatomic molecule model



$m_1$

$m_2$

# Infrared spectroscopy

## Diatomic molecule model

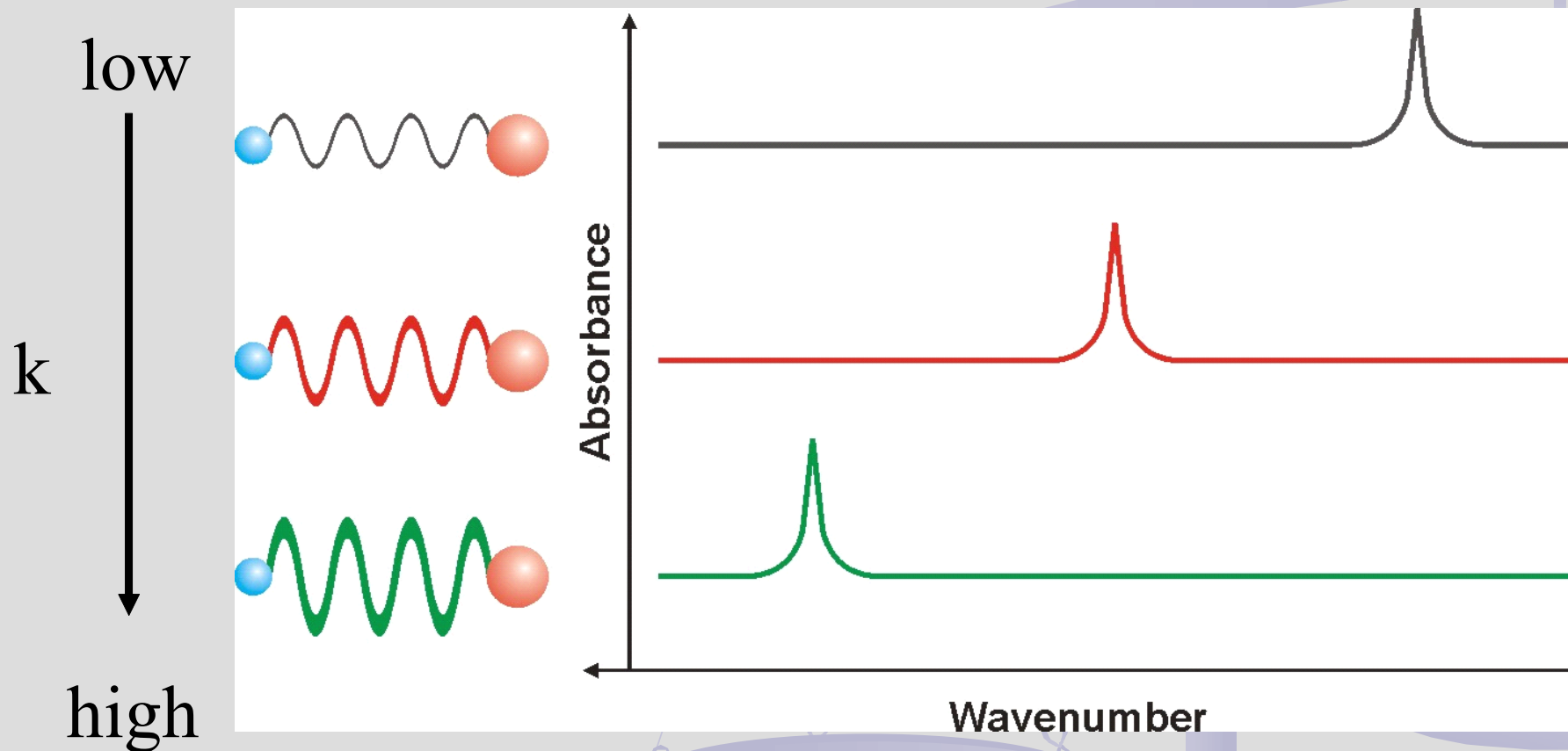
The vibration frequency ( $\nu$ ) is then expressed:

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

where  $k$  is the force constant  
 $\mu = m_1 m_2 / (m_1 + m_2)$ : reduced mass

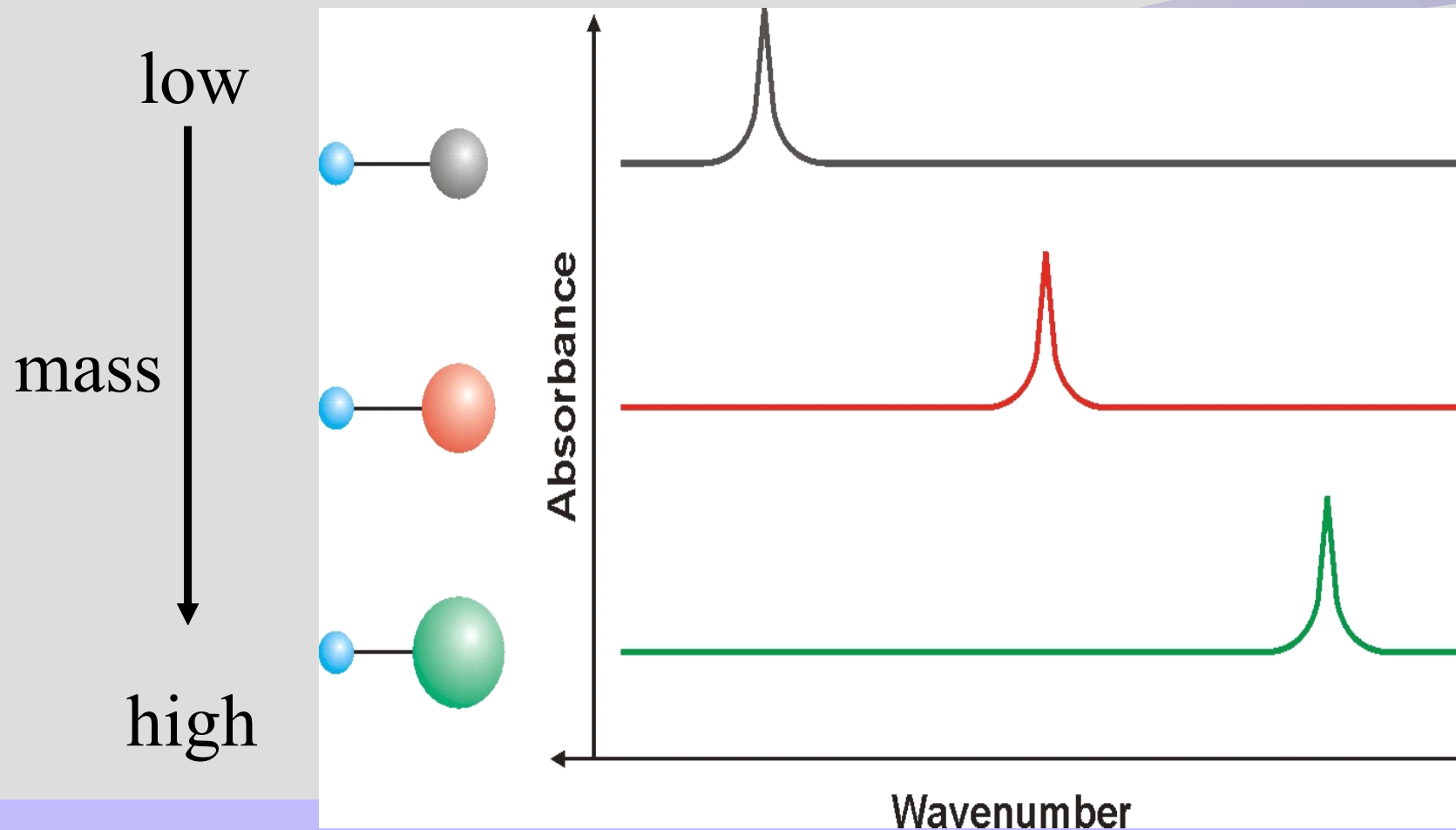
# Infrared spectroscopy

The vibration frequency ( $\nu$ )



# Infrared spectroscopy

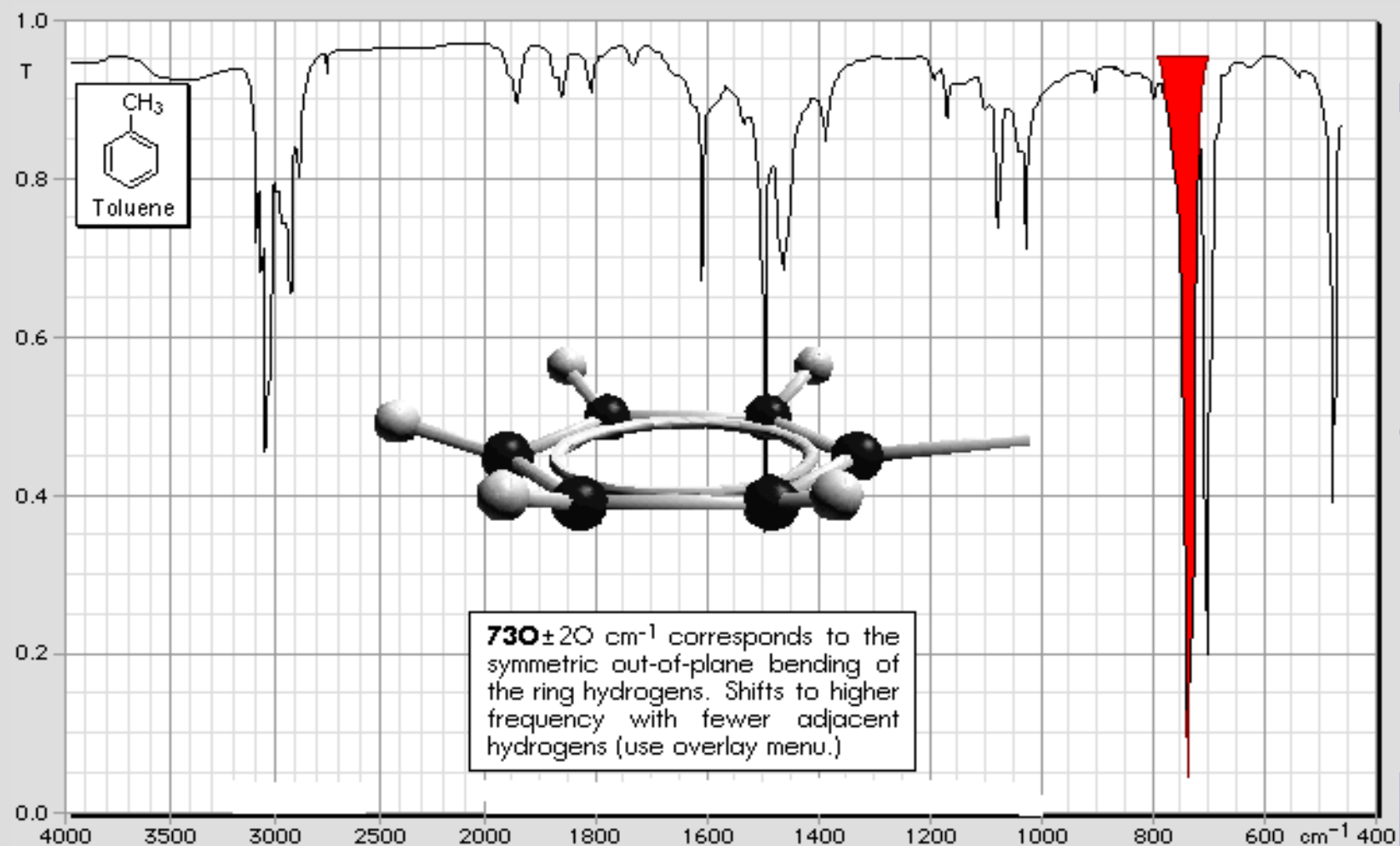
The vibration frequency ( $\nu$ )



# Infrared spectroscopy

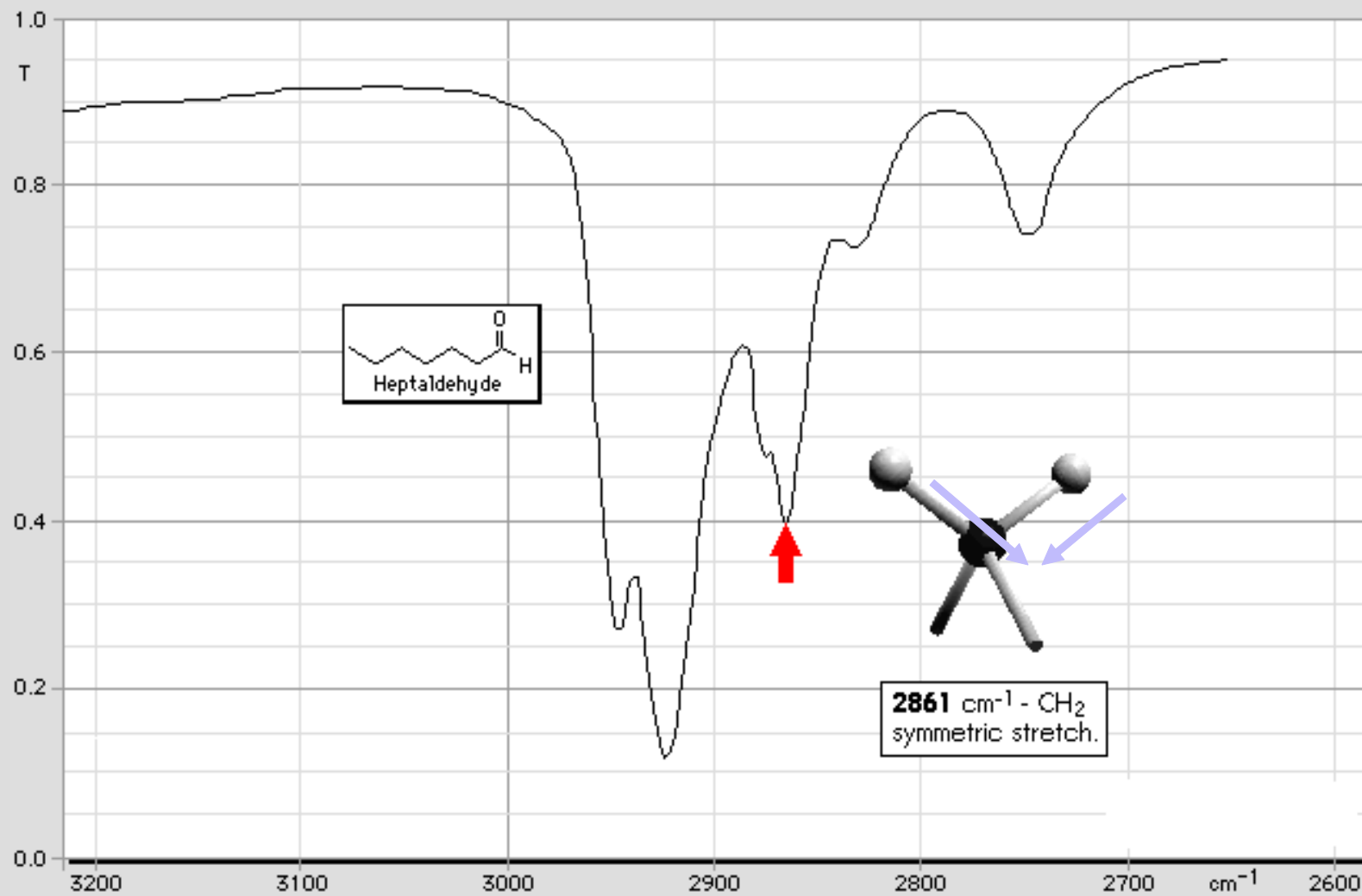
- The detection of the energy absorption constitutes IR spectroscopy.
- In continuous recording spectrometers the spectral transitions are detected by scanning through the frequency whilst continuously monitoring the transmitted light intensity.

# Methybenzene





# 谱图解析——己醛



# Raman spectroscopy

- Raman spectroscopy is concerned with detection of light scattered **inelastically** by molecules interacting with incident monochromatic radiation.

# Raman spectroscopy

- **When EM radiation interacts with matter, a certain fraction of the incident radiation is scattered.**

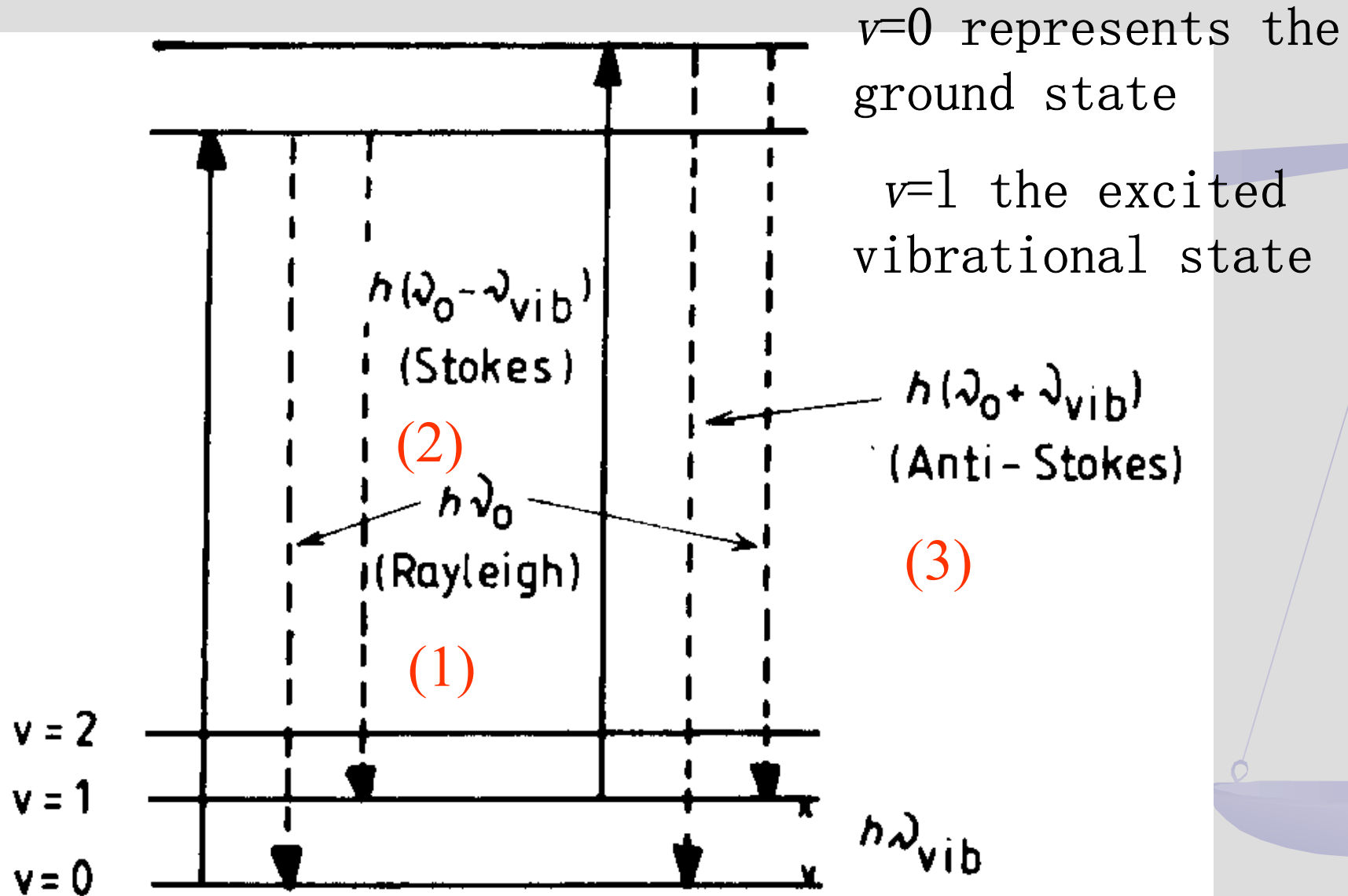
Two kinds of scattering:

Rayleigh: **elastically** (1 in  $10^4$ )

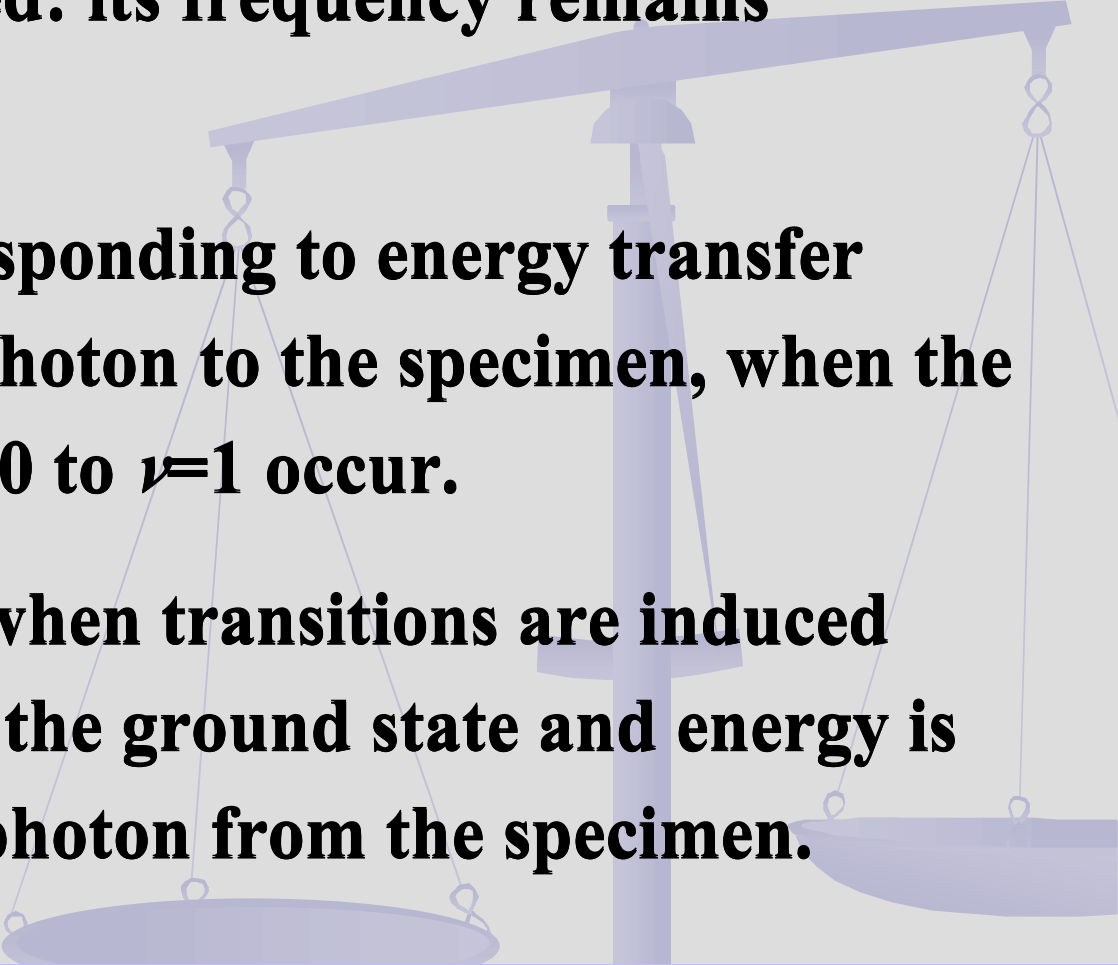
Raman: **inelastically** (1 in  $10^9$ )

**The difference between the wavelengths of the scattered and incident radiation arise due to induced transitions of the vibrational states of the molecules.**

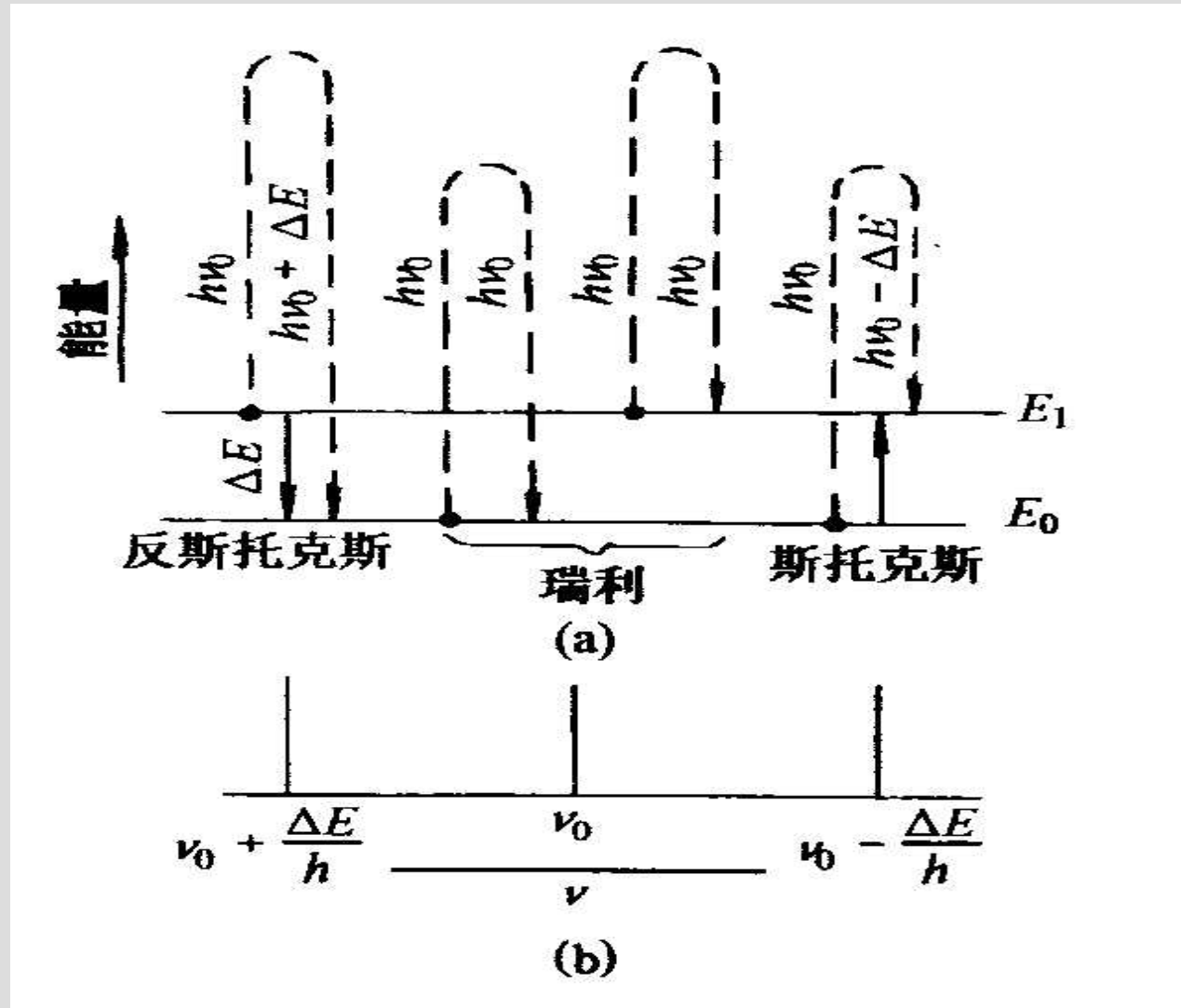
# Raman spectroscopy



# Raman spectroscopy

- 
- ① **Elastically scattered: its frequency remains unchanged.**
  - ② **Stokes lines: corresponding to energy transfer from the incident photon to the specimen, when the transitions from  $\nu=0$  to  $\nu=1$  occur.**
  - **Anti-stokes lines: when transitions are induced from the excited to the ground state and energy is transferred to the photon from the specimen.**

# Raman spectroscopy



# Raman spectroscopy

- Stokes lines:  $\nu_0 - \nu_{\text{vib}}$ , corresponding to energy transfer from the incident photon to the specimen
- Anti-Stokes lines:  $\nu_0 + \nu_{\text{vib}}$ , transitions are induced from the excited to the ground state and energy is transferred to the photon from the specimen.

# Vibrations in Molecules

Degrees of freedom (two atoms rigid molecular)

- 3 translational (平移) degrees of freedom
- 3 rotational (旋转) degrees of freedom



# Vibrations in Molecules

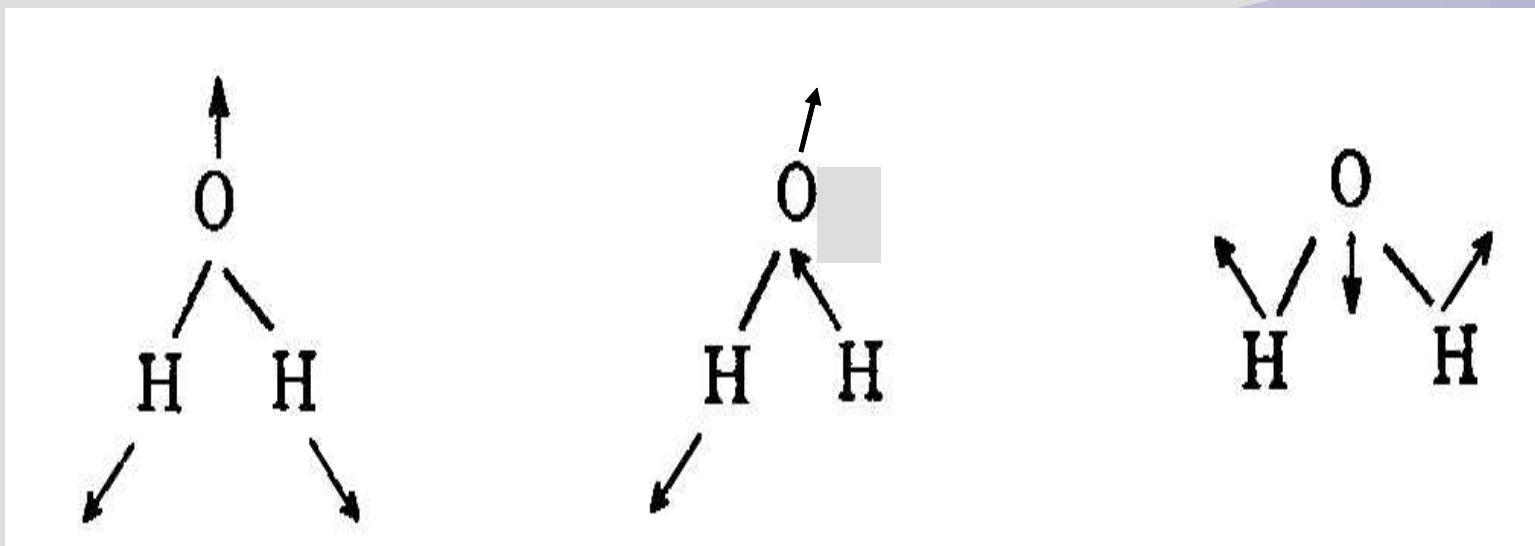
## Degrees of freedom

(molecular consisting of  $n$  atoms)

- Total degrees of freedom is  $3n$
- The number of vibrational degrees of freedom is  $3n - 6$
- For linear molecules, it is increased to  $3n - 5$

# Vibrations in Molecules

Degrees of freedom ( $\text{H}_2\text{O}$ ) :  $3 \times 3 - 6 = 3$



**Symmetrical  
stretching**

$\nu_s$ : **3652 cm<sup>-1</sup>**

**Asymmetrical  
stretching**

$\nu_{as}$ : **3756 cm<sup>-1</sup>**

**Bending**  
 $\delta$ : **1595 cm<sup>-1</sup>**

# Vibrations in Molecules

Degrees of freedom ( $\text{CO}_2$ ) :  $3 \times 3 - 5 = 4$

1) **Symmetrical stretching** :  $\vec{\text{O}} = \text{C} = \vec{\text{O}}$   
C atom is the center of +、- charge.  $d = 0$ ,  
 $\mu = 0$  (dipole moment=0)  
IR inactive.

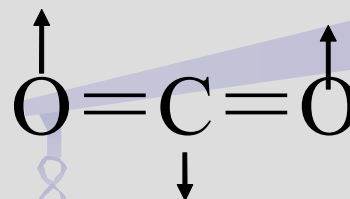
2) **Asymmetrical stretching** :  $\vec{\text{O}} = \text{C} = \vec{\text{O}}$   
 $\nu_{\text{as}}$  :  $2349\text{cm}^{-1}$

# Vibrations in Molecules

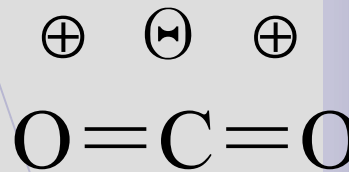
Degrees of freedom ( $\text{CO}_2$ ) :  **$3 \times 3 - 5 = 4$**

3) in-plane bending:

$\delta$  :  $667 \text{ cm}^{-1}$



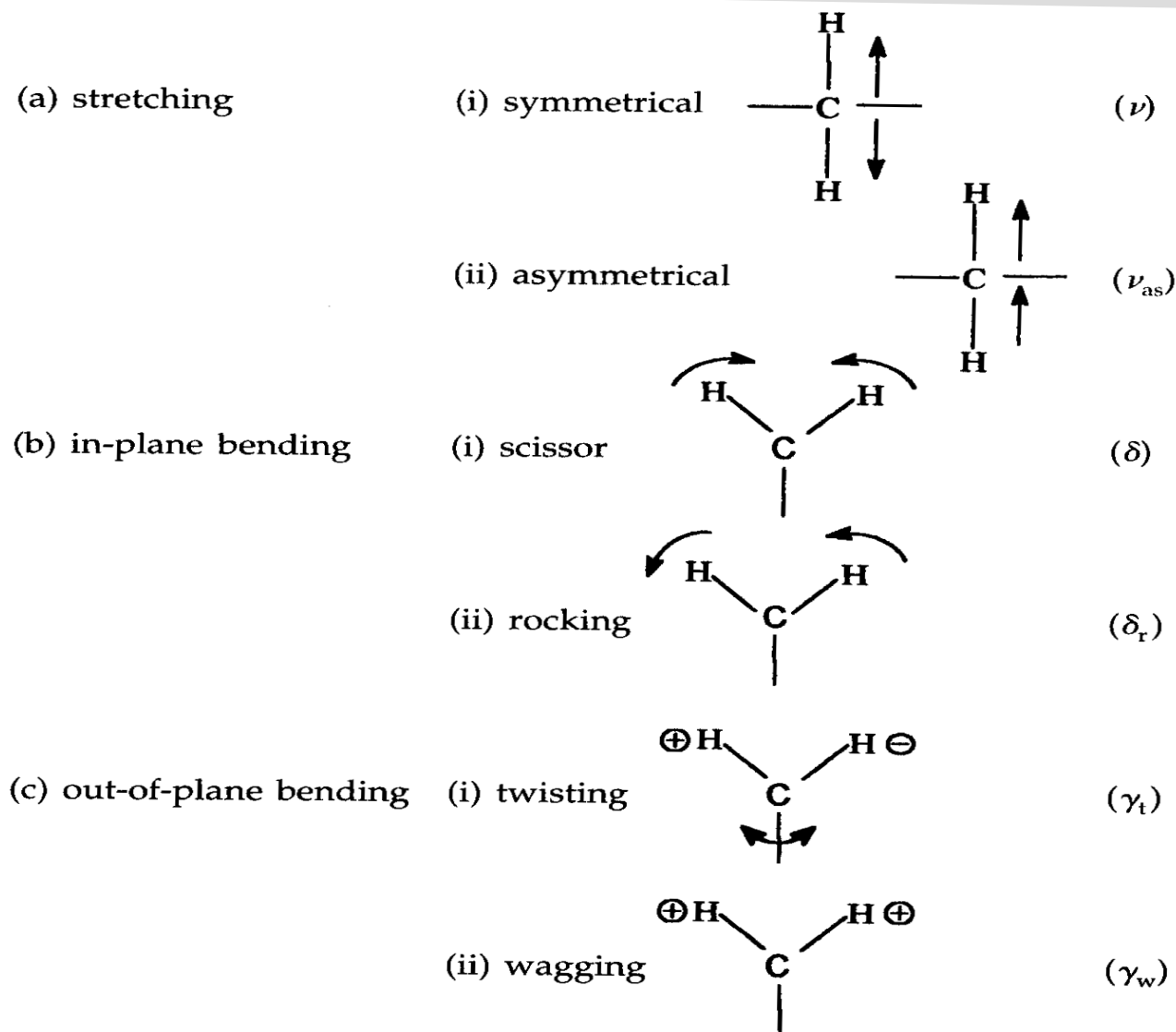
4) out-of-plane bending :  $\gamma$  :  $667 \text{ cm}^{-1}$



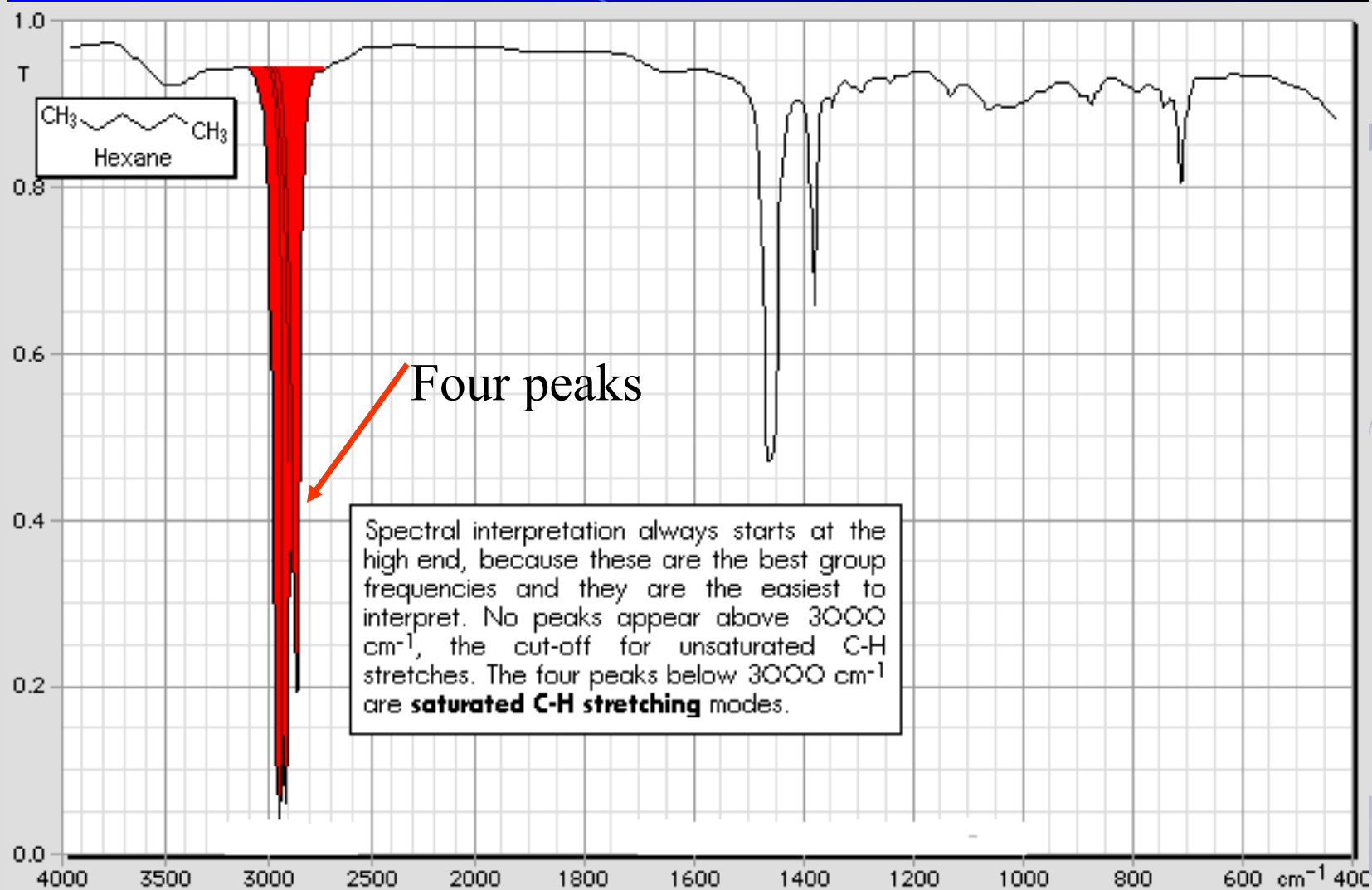
$\oplus$  indicates “out”,  $\ominus$  indicates “in”

The vibrational energy for (3) and (4) is the same.  
So only one absorbing peak at  $667 \text{ cm}^{-1}$

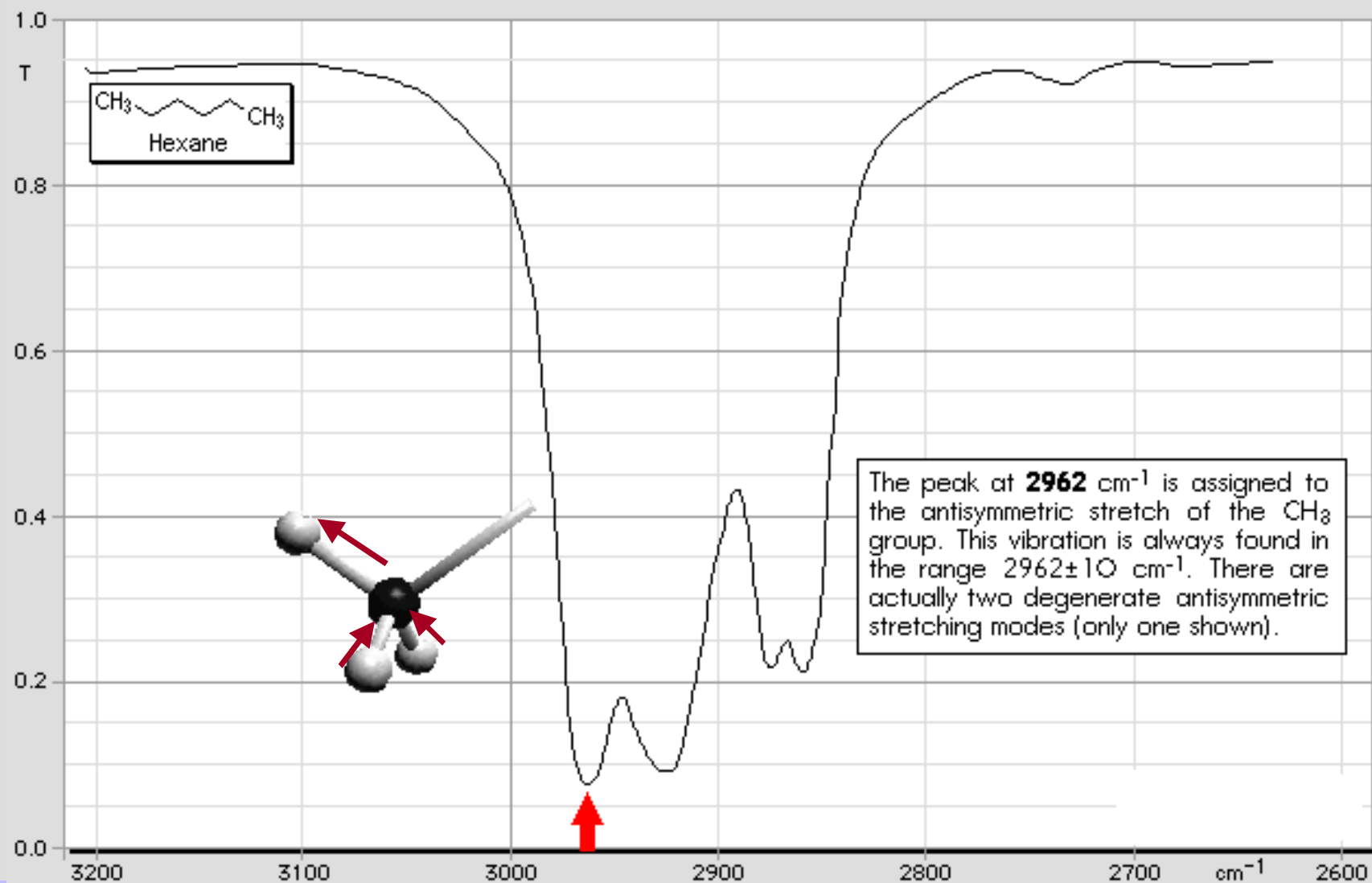
# Vibrational modes (methylene group)



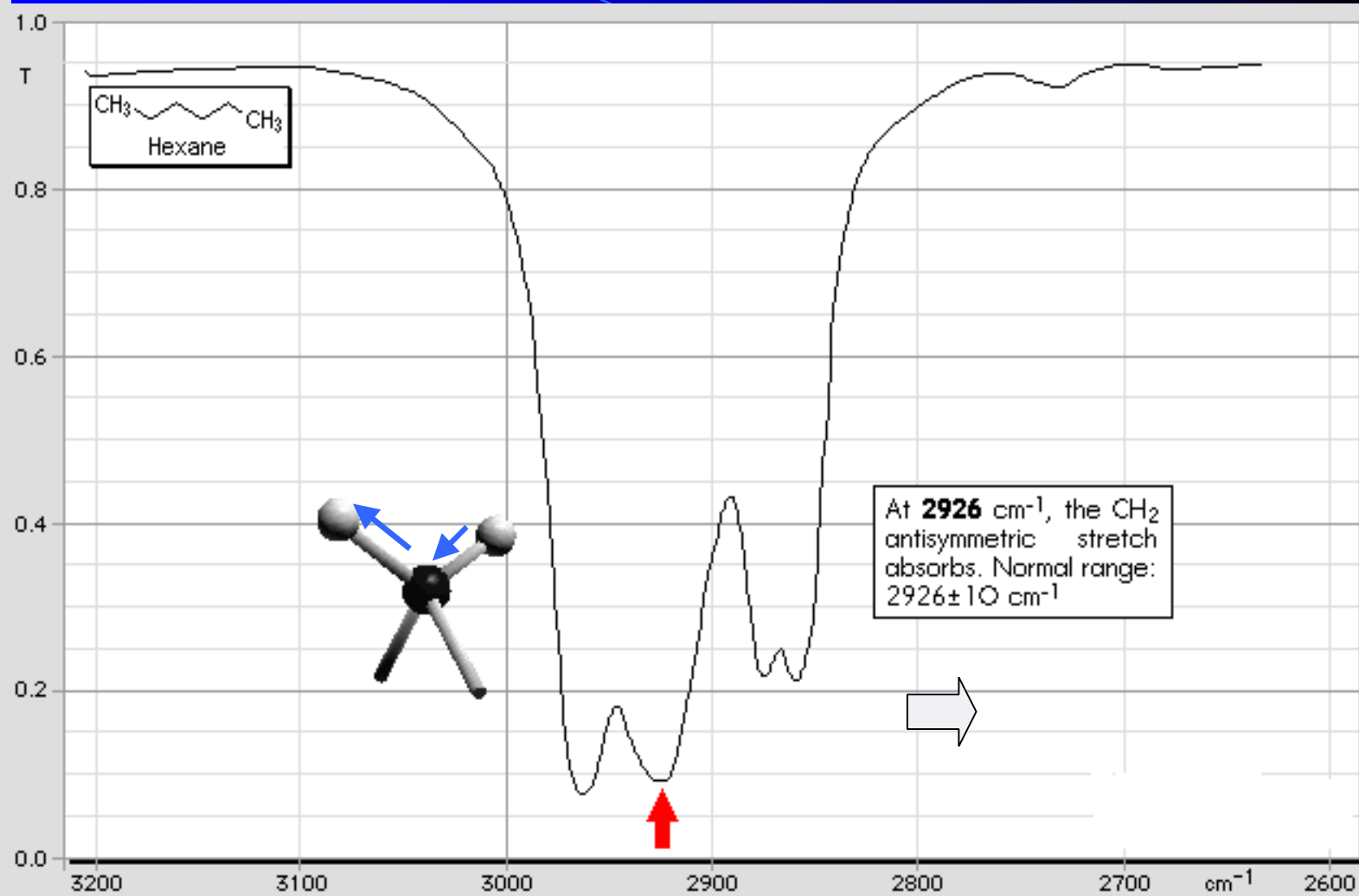
# Hexane



# Hexane



# Hexane

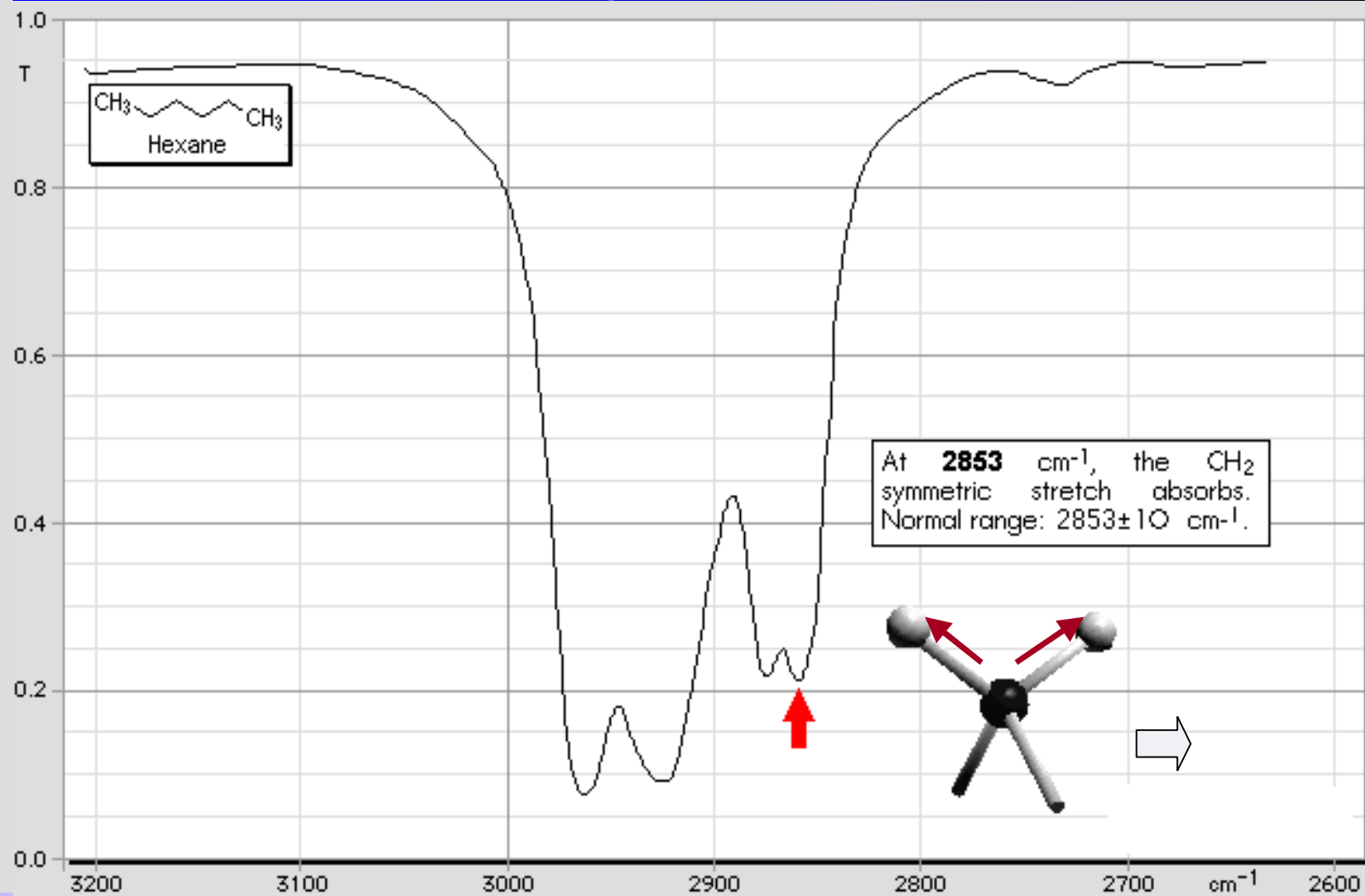




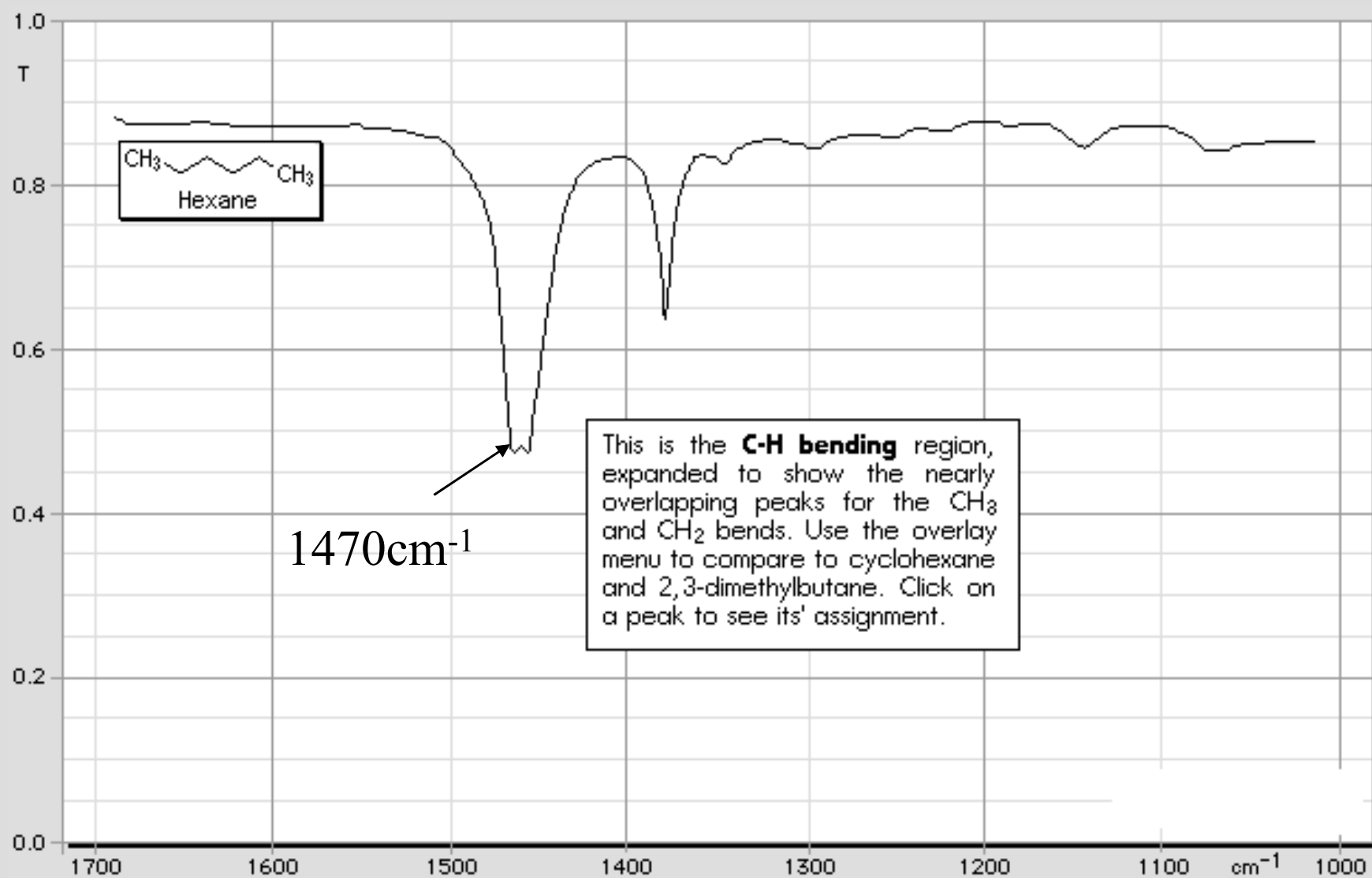
# Hexane



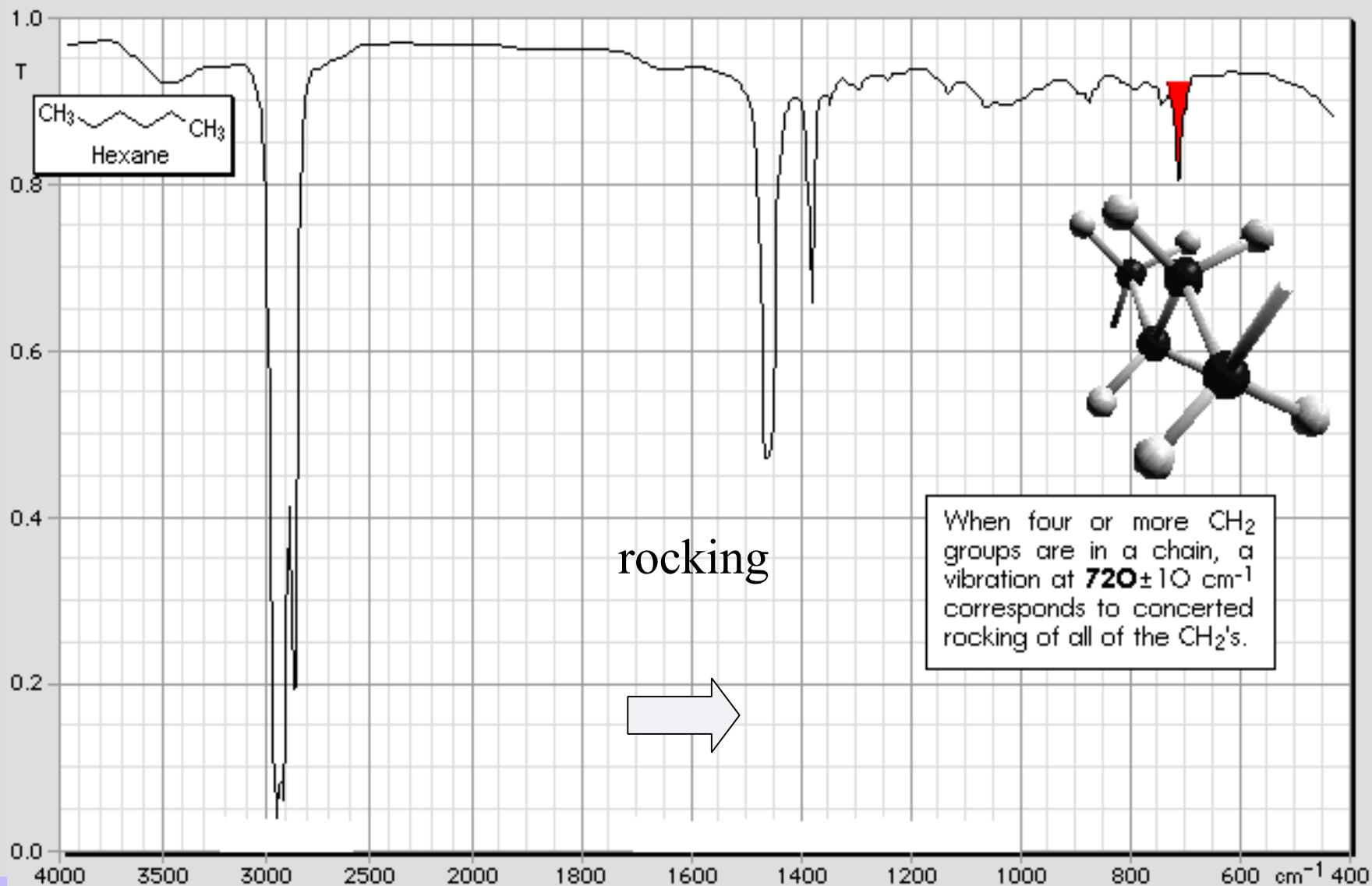
# Hexane



# Hexane

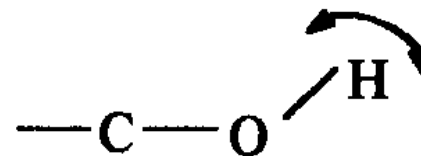


# Hexane



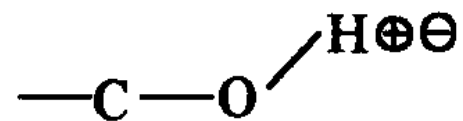
## Vibrational modes of $\text{—OH}$ (hydroxyl)

in-plane bending



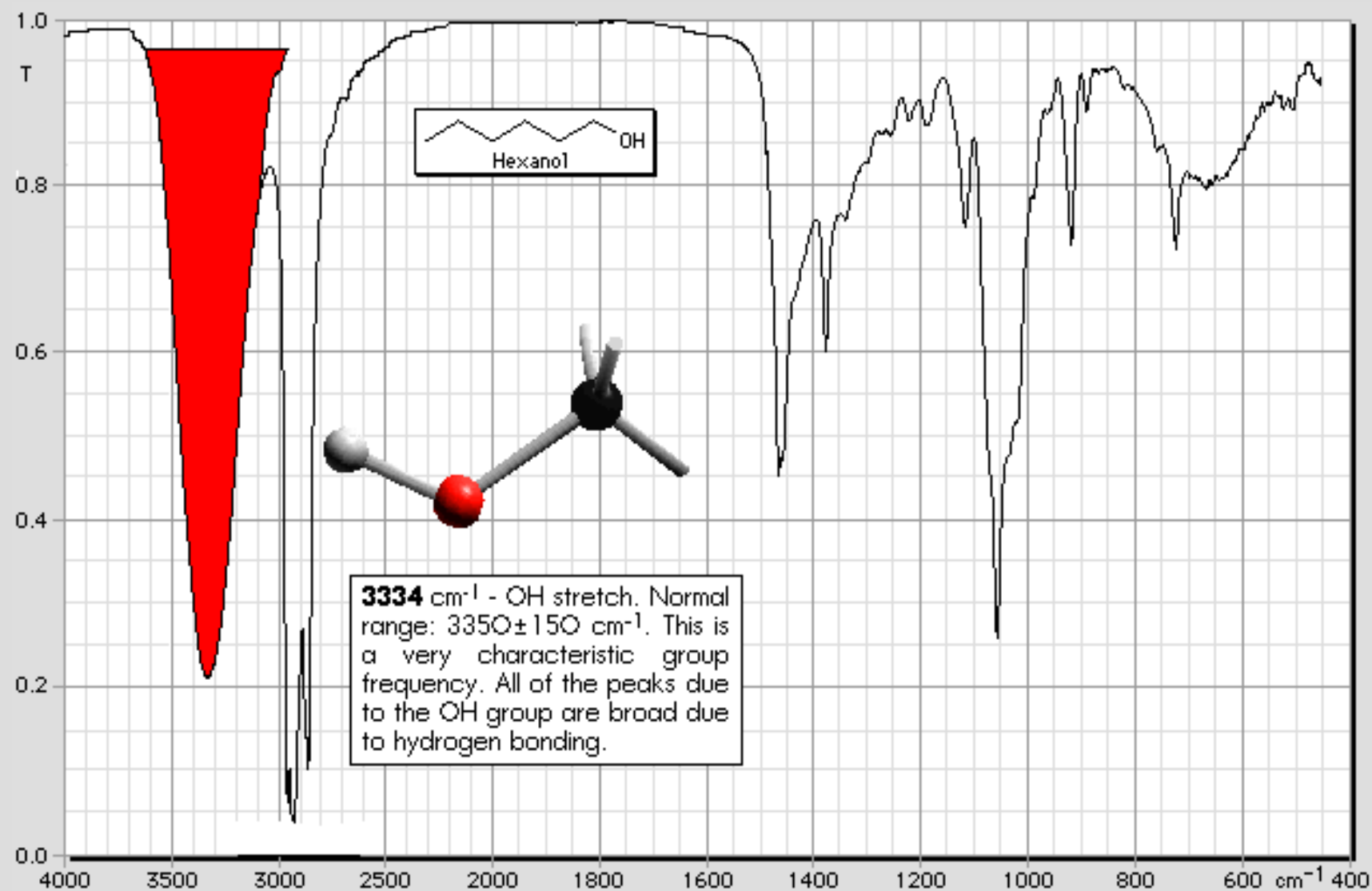
$(\delta)$

out-of-plane bending

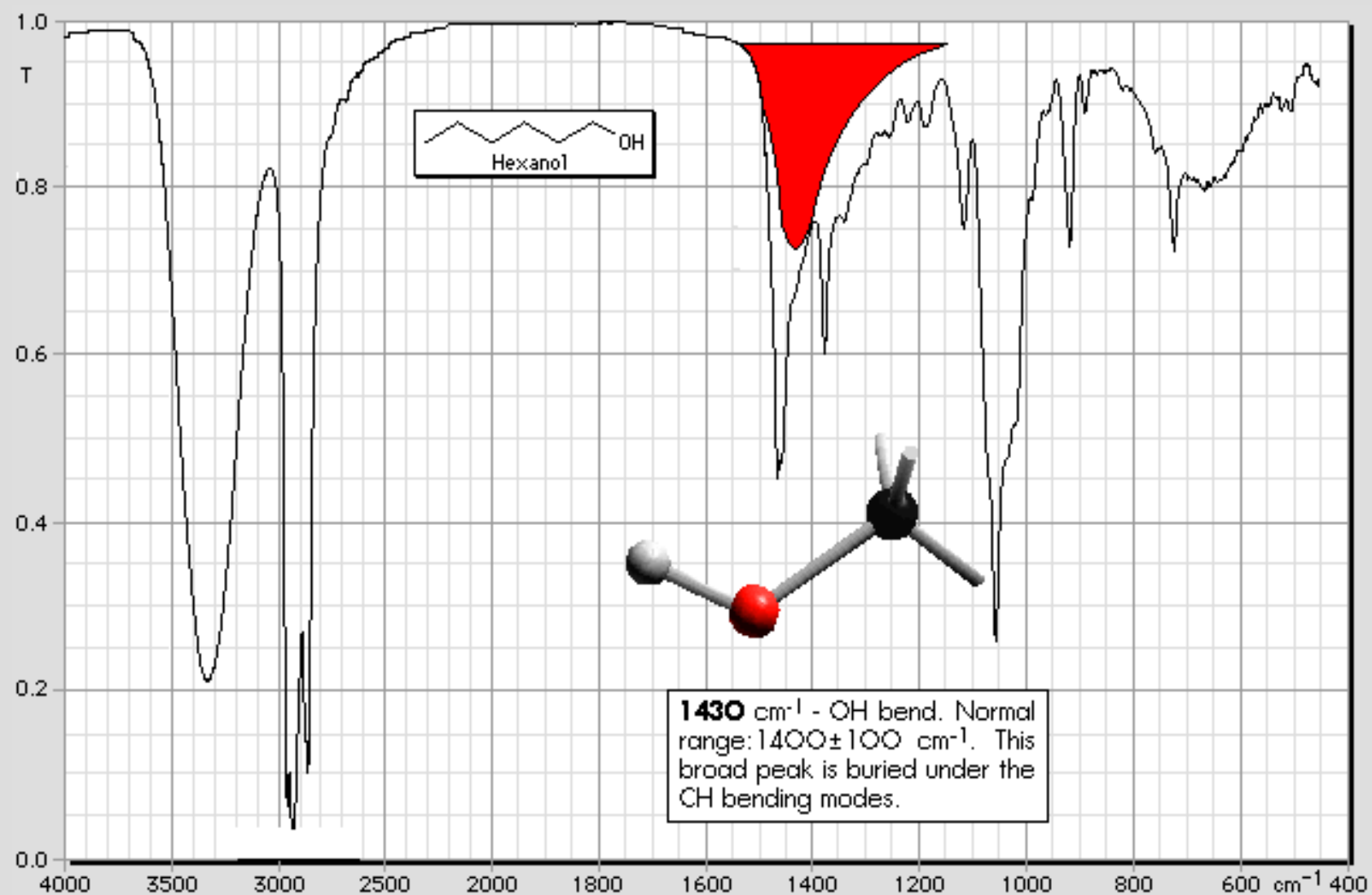


$(\gamma_w)$

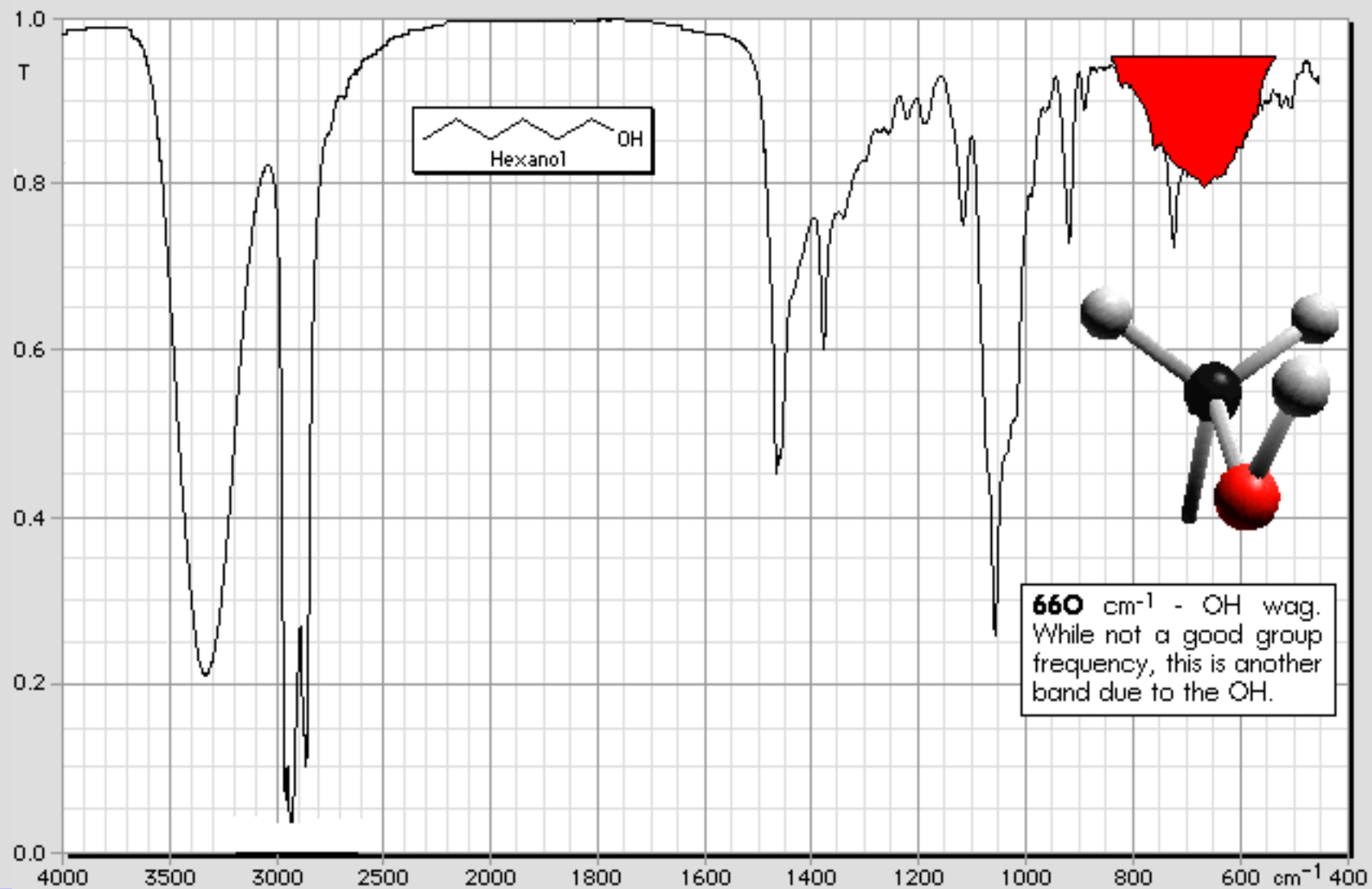
# Hexanol



# Hexanol

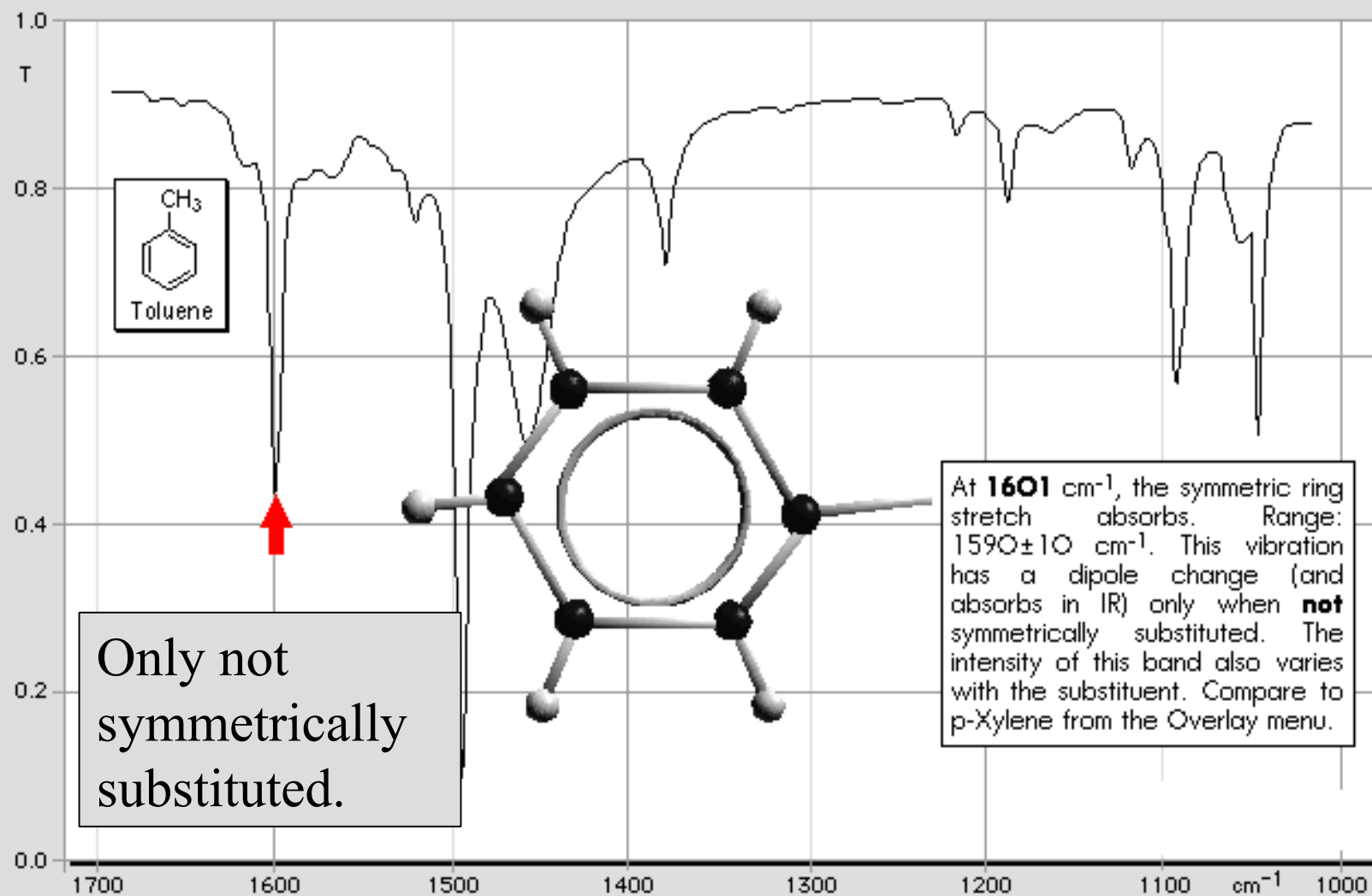


# Hexanol

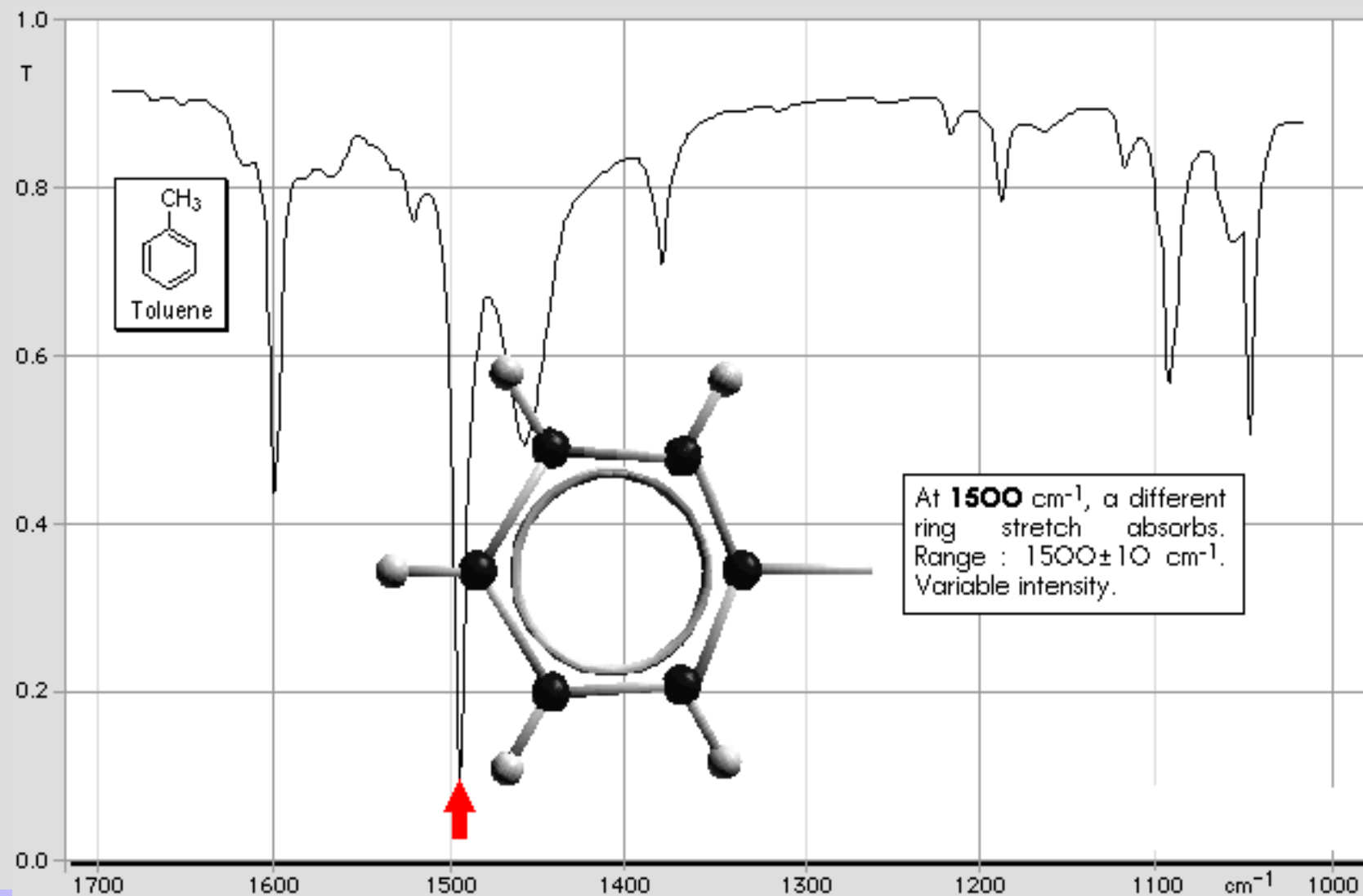




# Aromatic ring expansion (Methylbenzene)



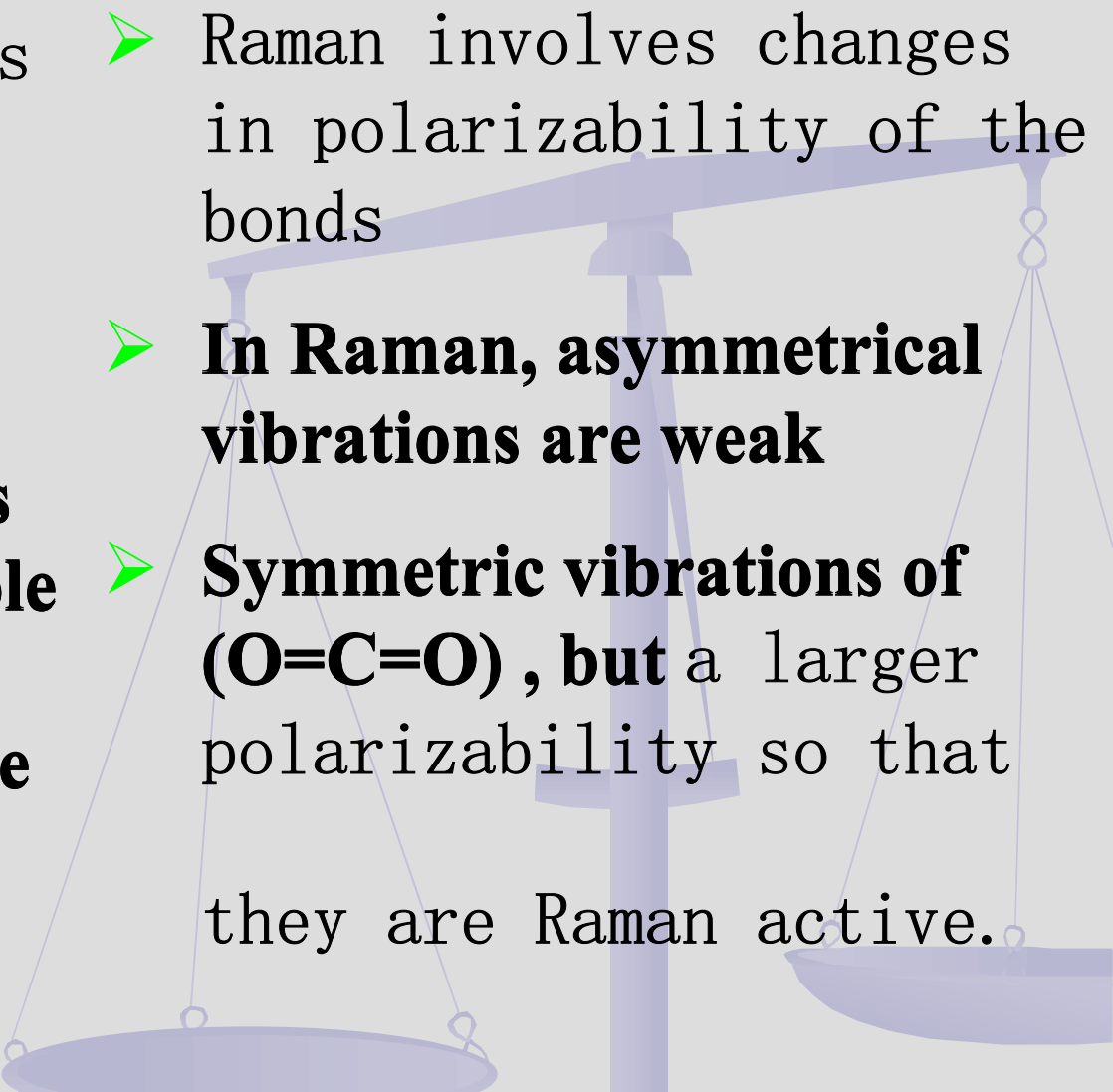
# Aromatic ring expansion (Methylbenzene)



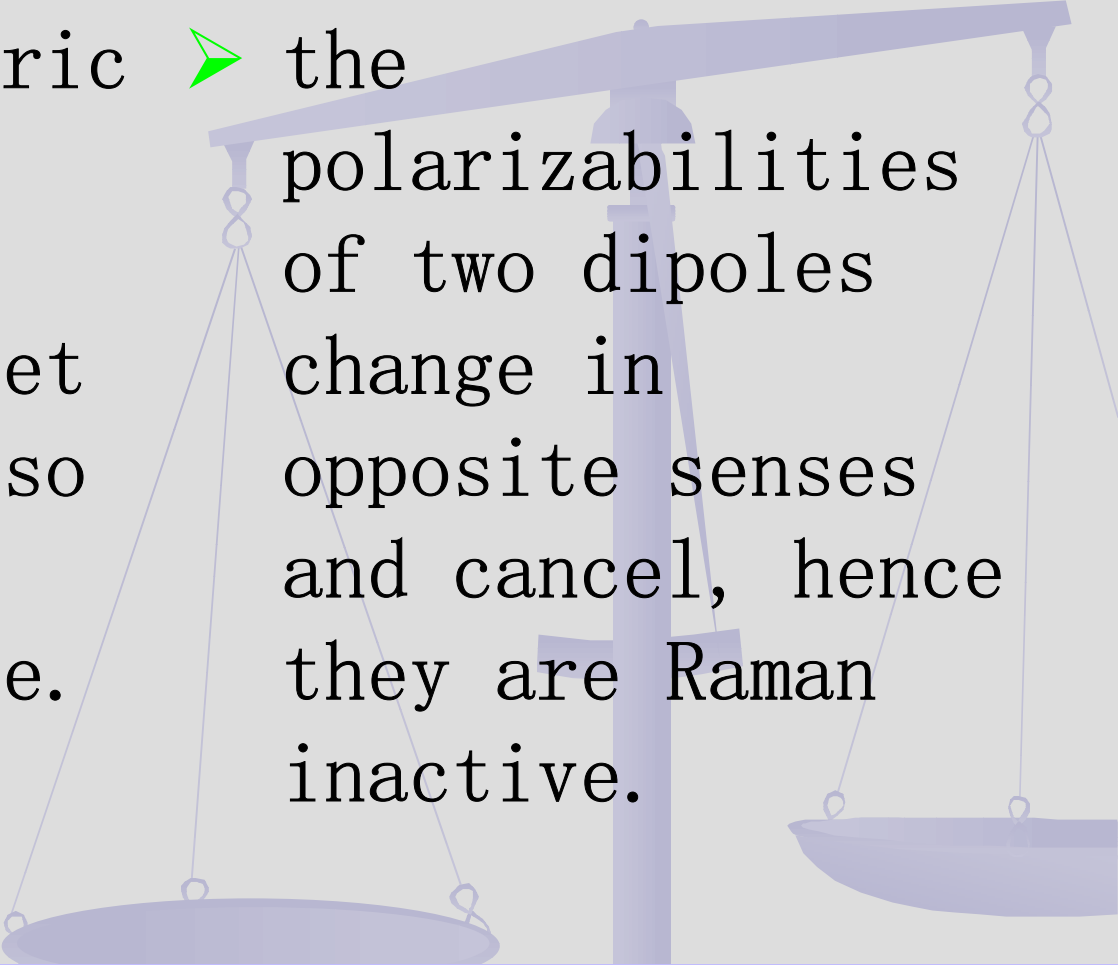
## Use of vibration spectra

- The group theory determine the expected normal vibrations from the symmetry of the molecule
- Predicts whether vibrations are IR active or Raman active.
- The force constants can be estimated for each vibration based on Hook's law.
- Detailed assignments of the absorption peaks can be made by comparison with observed spectra.

## Comparing of IR and Raman Spectroscopy

- 
- IR requires changes in dipole moments
  - **In IR, symmetrical vibrations are weak**
  - **Symmetric vibrations of (O=C=O), no dipole moment change, inactive in the infrared.**
  - Raman involves changes in polarizability of the bonds
  - **In Raman, asymmetrical vibrations are weak**
  - **Symmetric vibrations of (O=C=O), but a larger polarizability so that they are Raman active.**

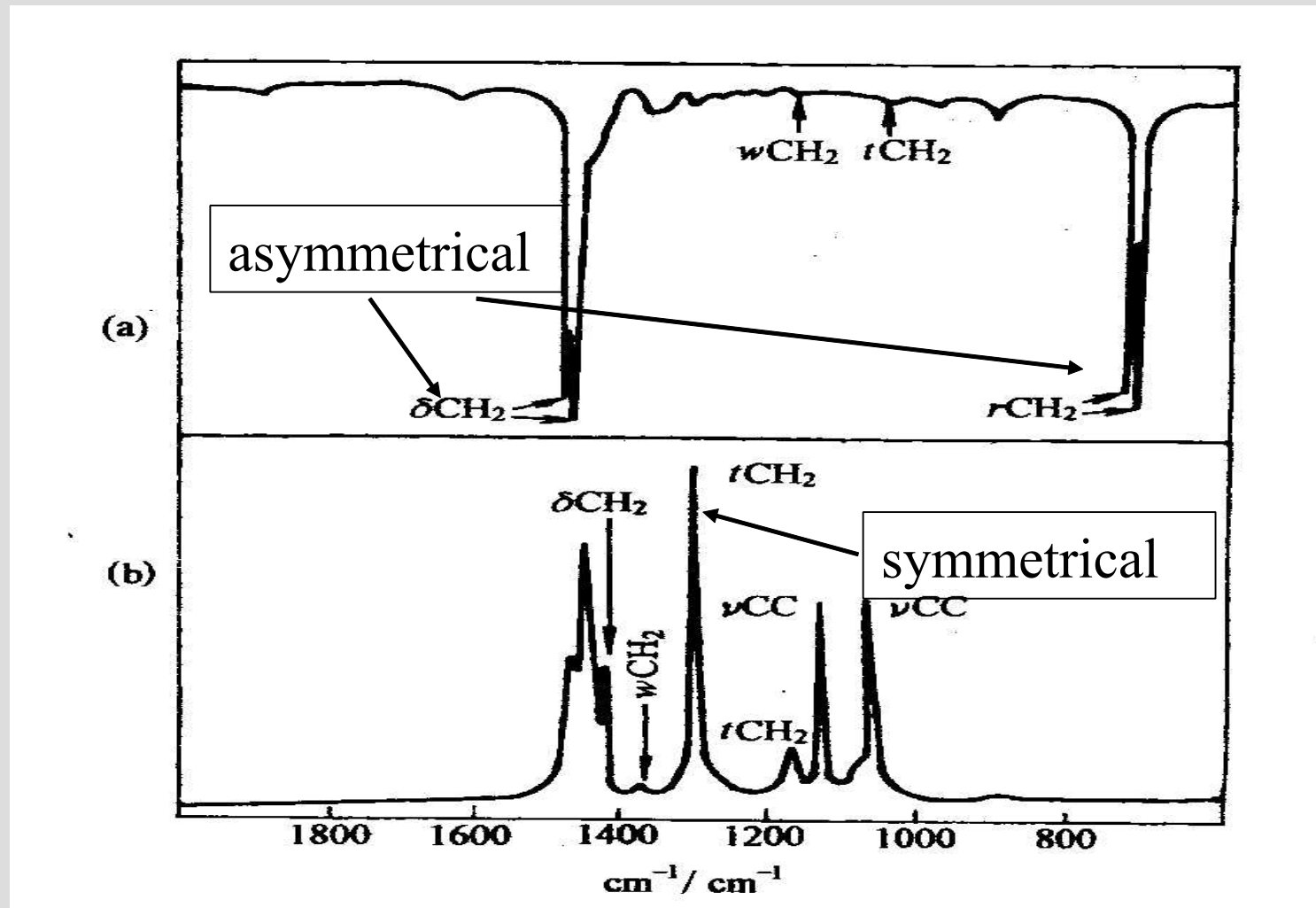
## Comparing of IR and Raman Spectroscopy

- 
- For antisymmetric vibrations the dipoles do not cancel and a net dipole exists so that they are infrared active.
  - the polarizabilities of two dipoles change in opposite senses and cancel, hence they are Raman inactive.

## Comparing of IR and Raman Spectroscopy

- For less symmetrical molecules, some vibrations are IR and some are Raman active.
- For vibrations that are active in both Raman and IR, asymmetric vibrations are strong in IR but give only weak absorptions in Raman.
- Detailed analysis of the vibrational modes in polymers requires complementary use of both IR and Raman spectroscopy.

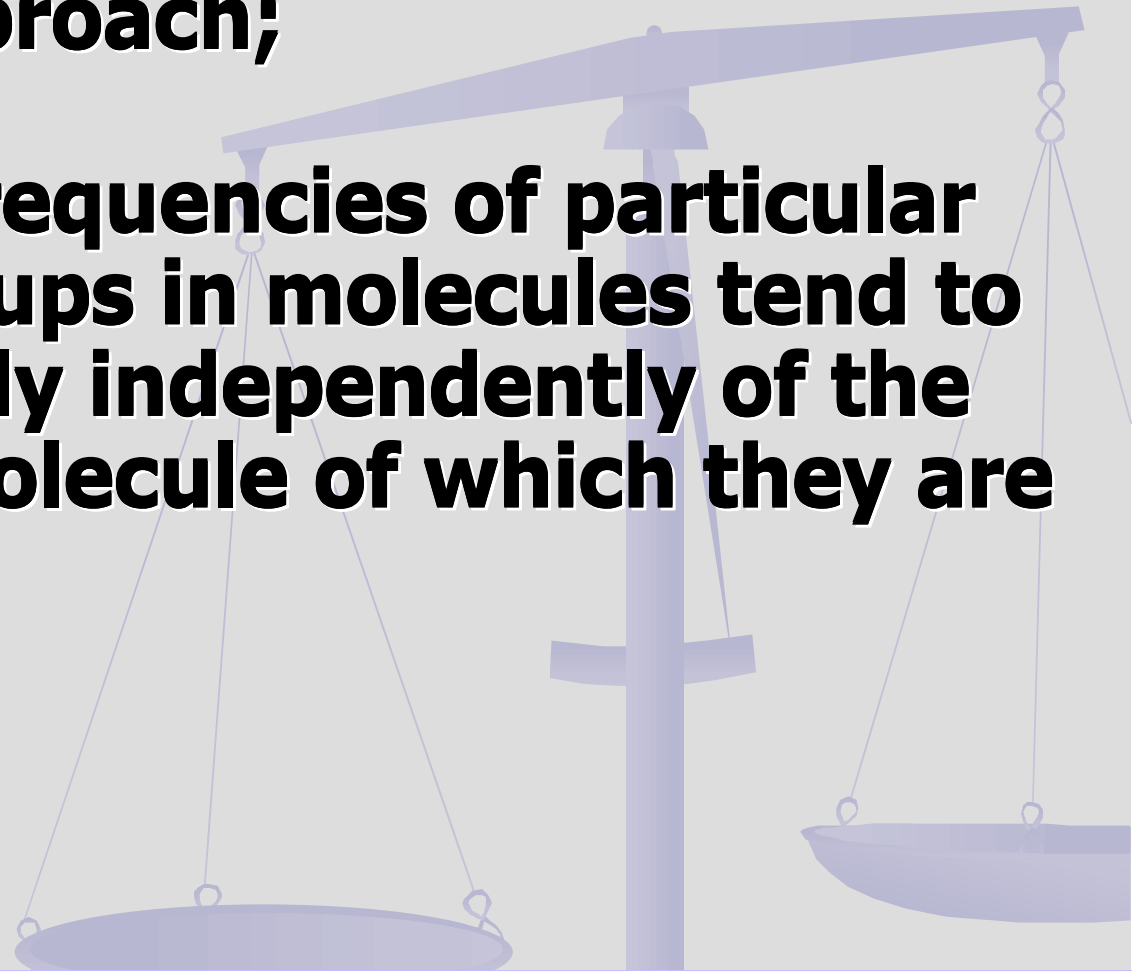
# Comparing of IR and Raman Spectroscopy



**Liner PE: (a) IR, (b) Raman**

# Group frequencies

- **Most investigations rely on a more empirical approach;**
- **Vibrational frequencies of particular chemical groups in molecules tend to behave largely independently of the rest of the molecule of which they are apart;**



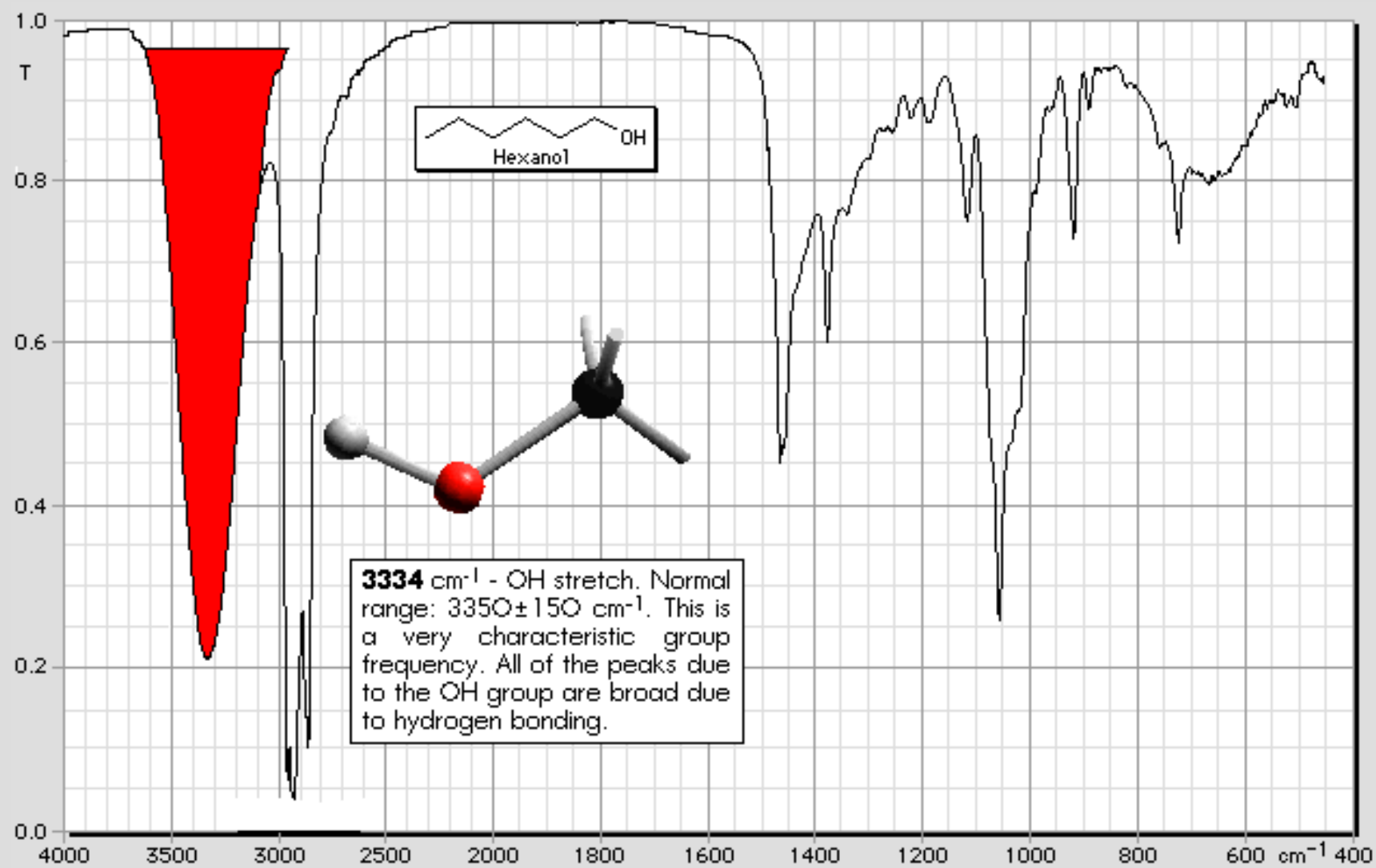


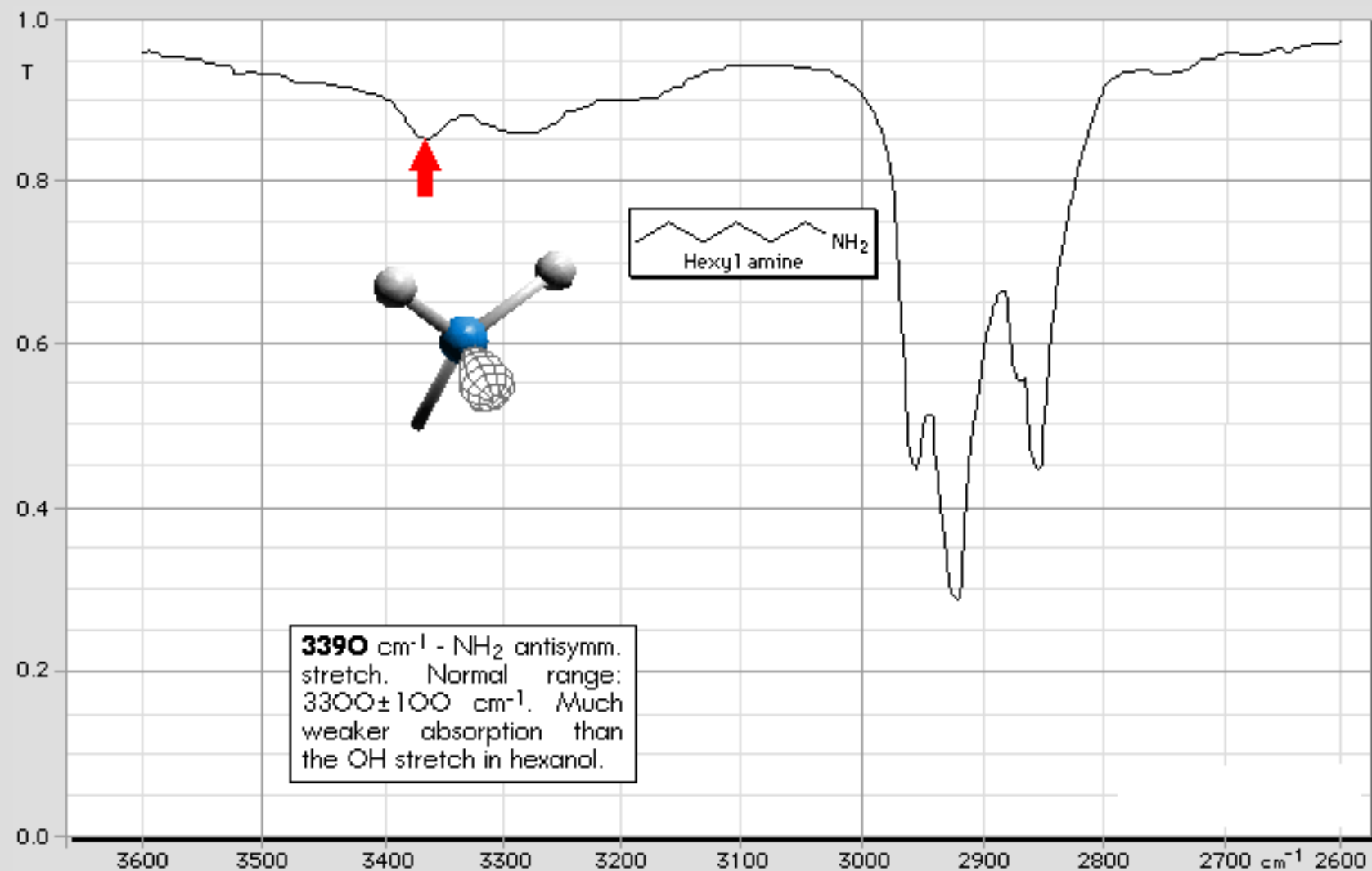
# Group frequencies

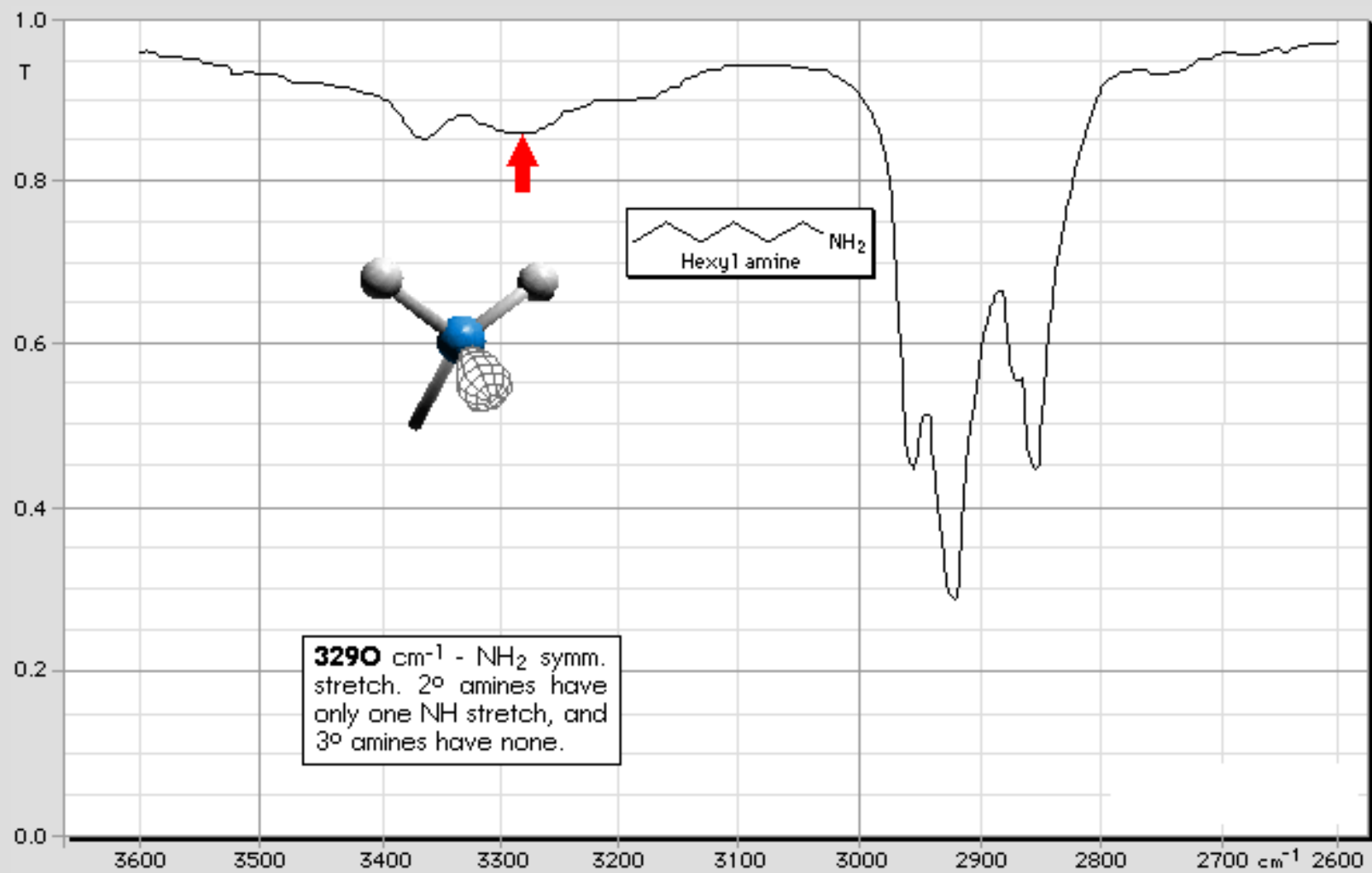
- The absorption frequencies for a particular chemical group are essentially constant;
- Absorption bands appear in roughly the same region of the spectra;
- Assign particular absorption bands to vibrations in the groups by reference to standard correlation tables.
- Computer database---automatic assignment

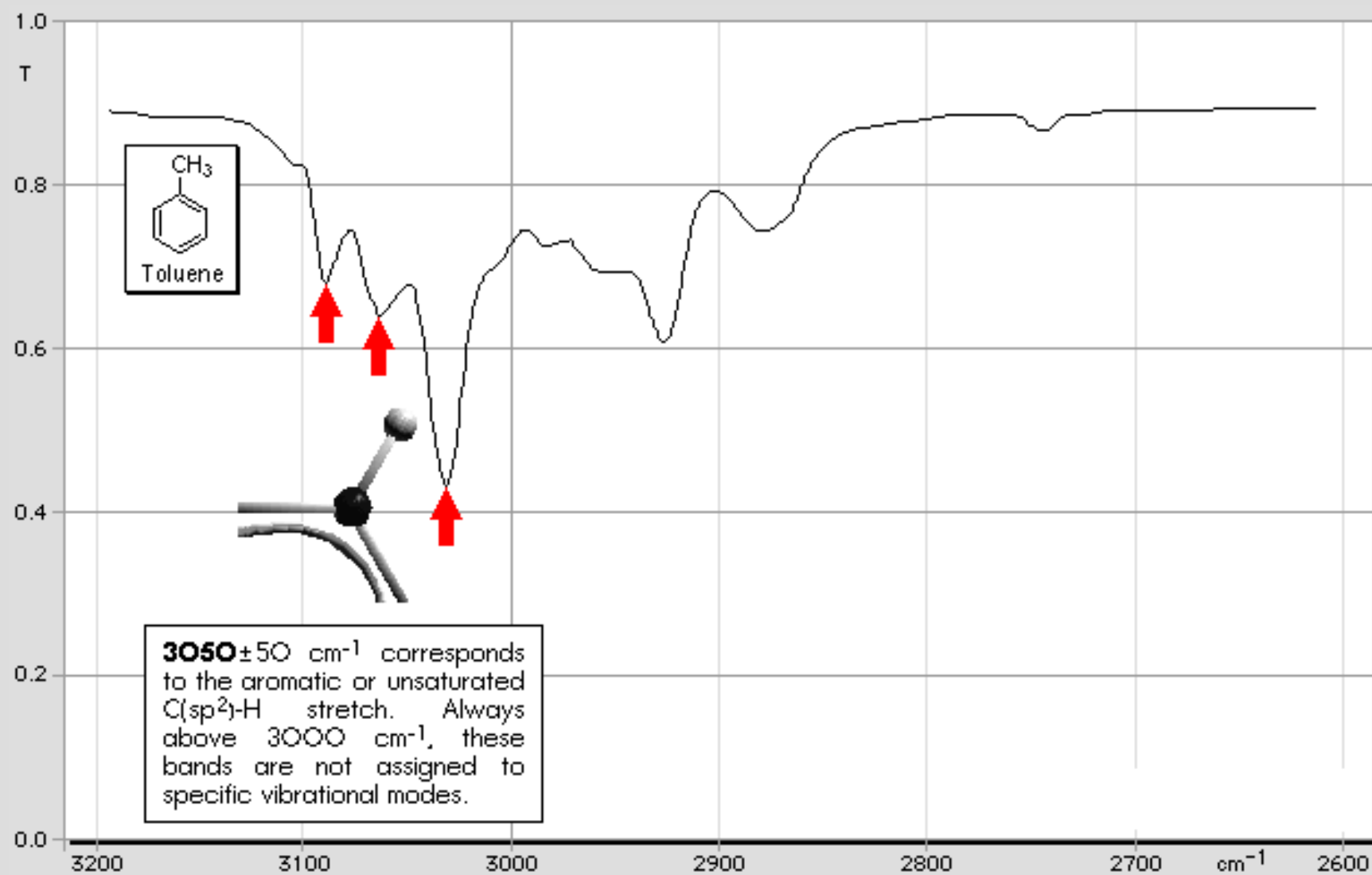
Table 5.1 Characteristic vibration modes for common groupings found in polymers

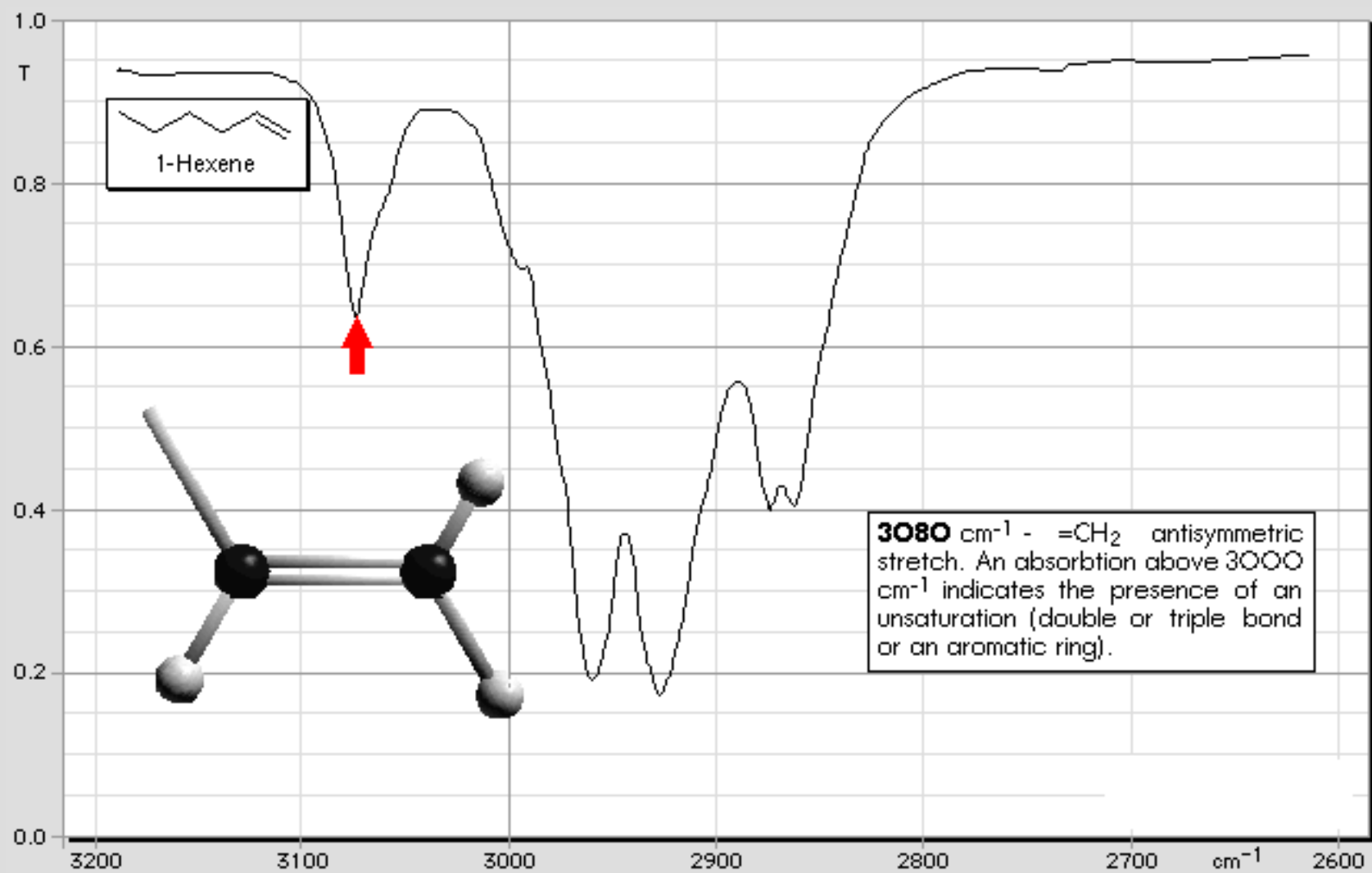
Type of vibration	Characteristic frequencies (cm <sup>-1</sup> )
O—H {stretching}	3650-3000
N—H {stretching}	3500-3300
C—H {stretching}	3200-2800
S—H {stretching}	2600-2550
C≡N {stretching}	2255-2220
C≡C {stretching}	2250-2100

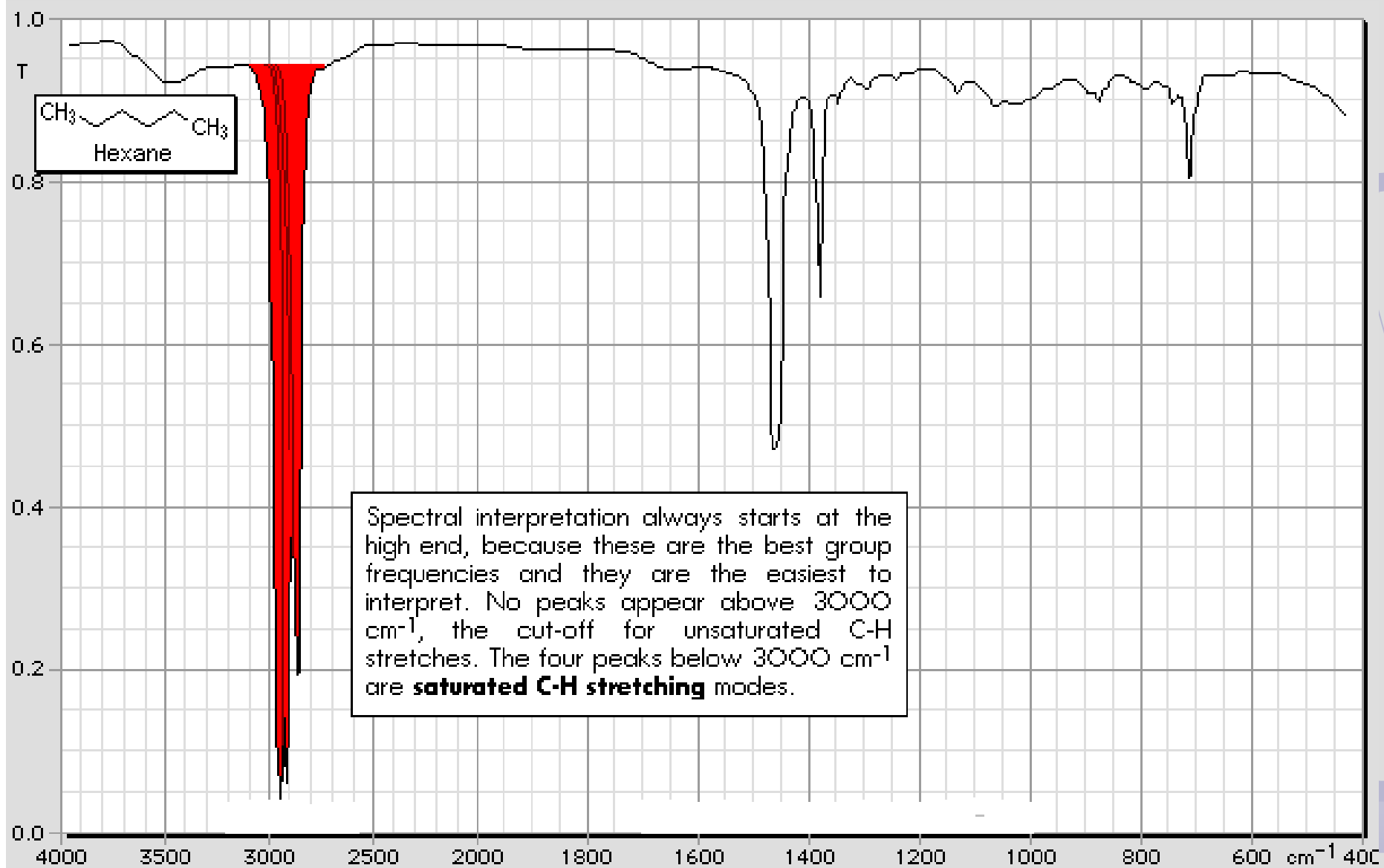




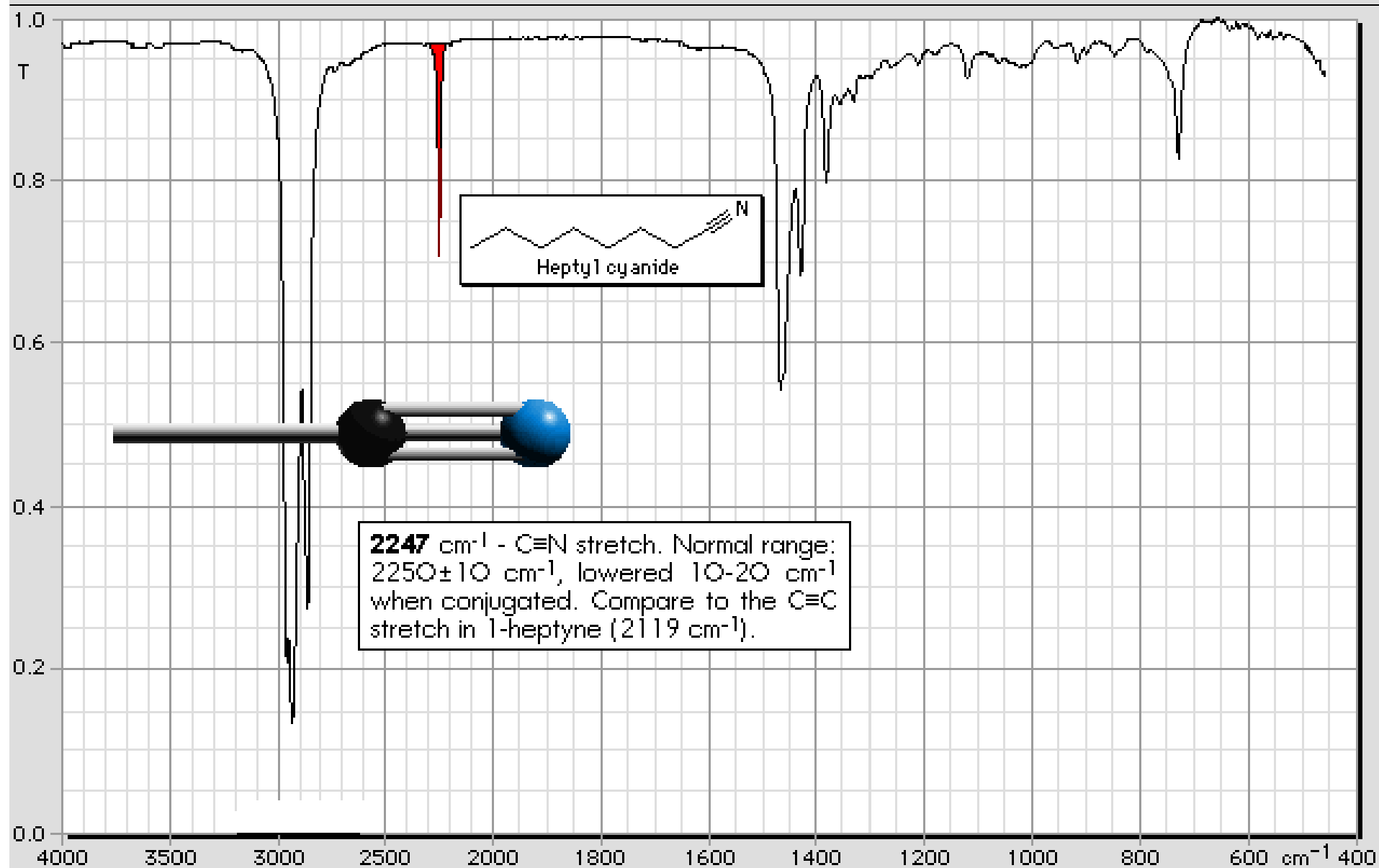


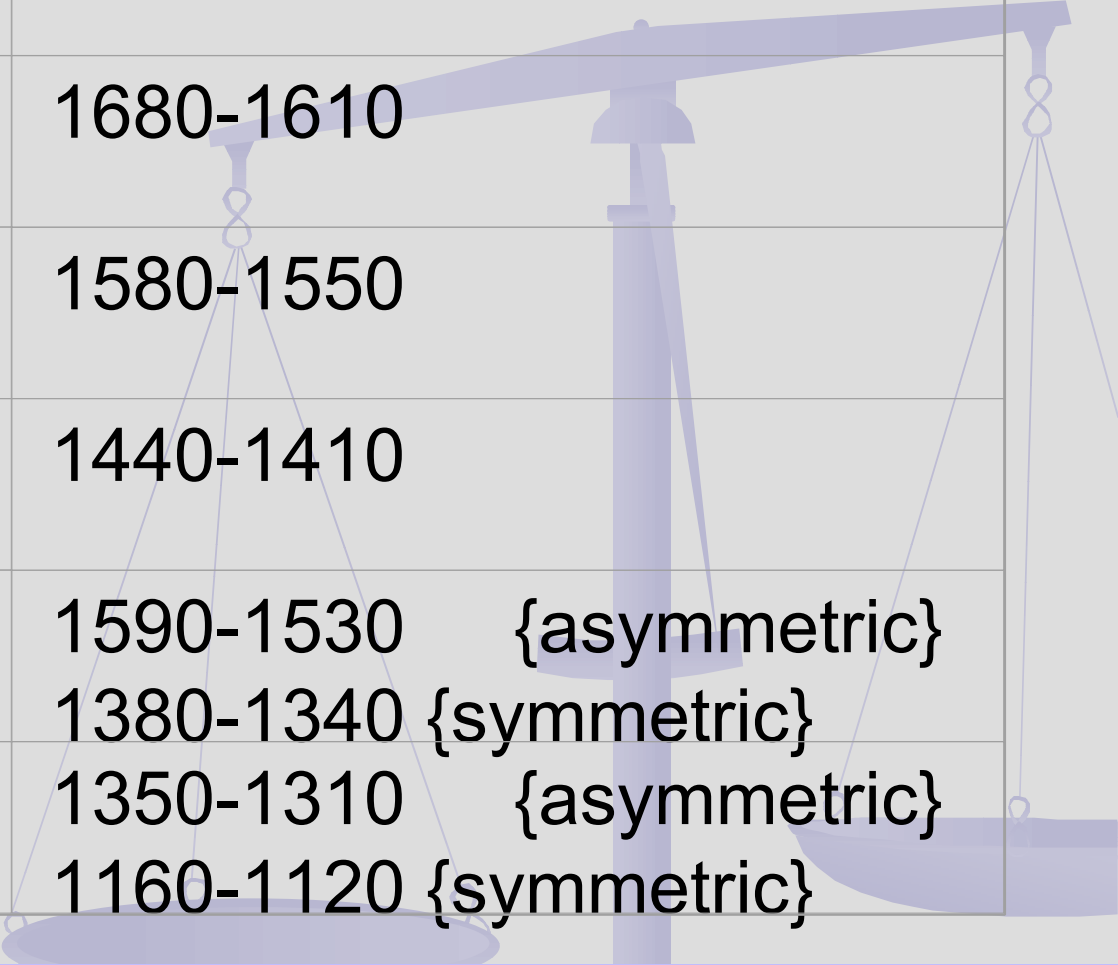




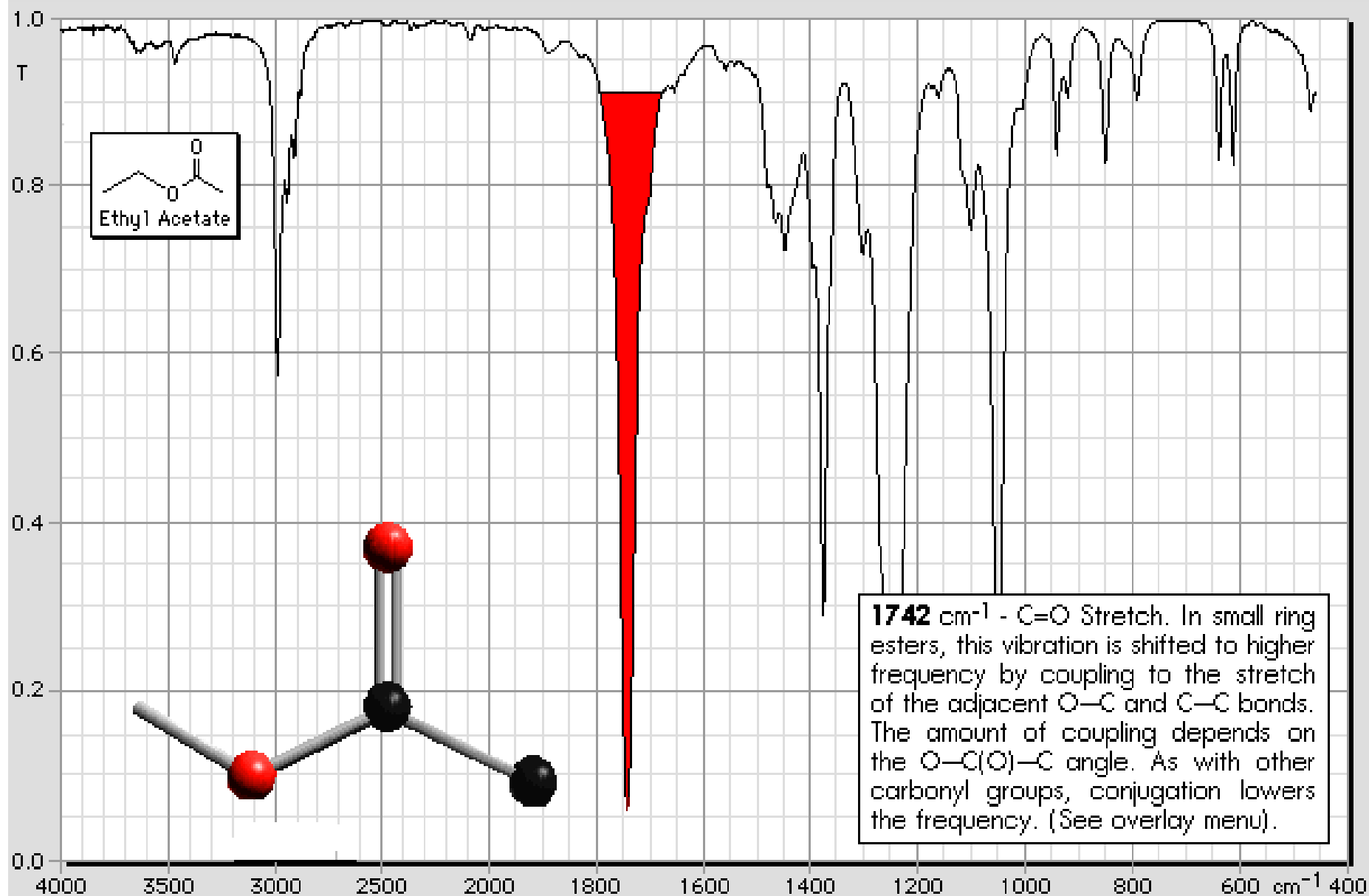


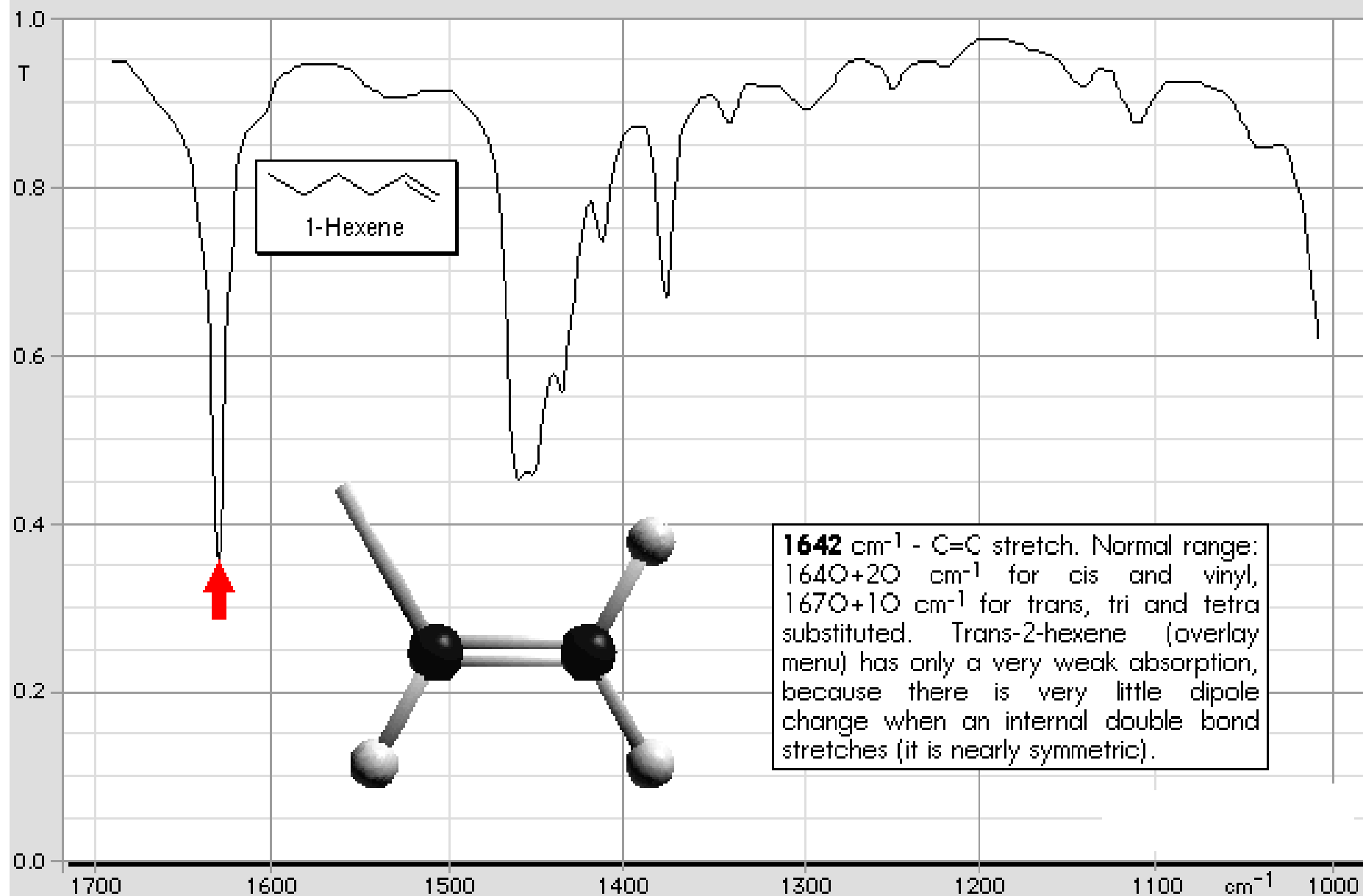


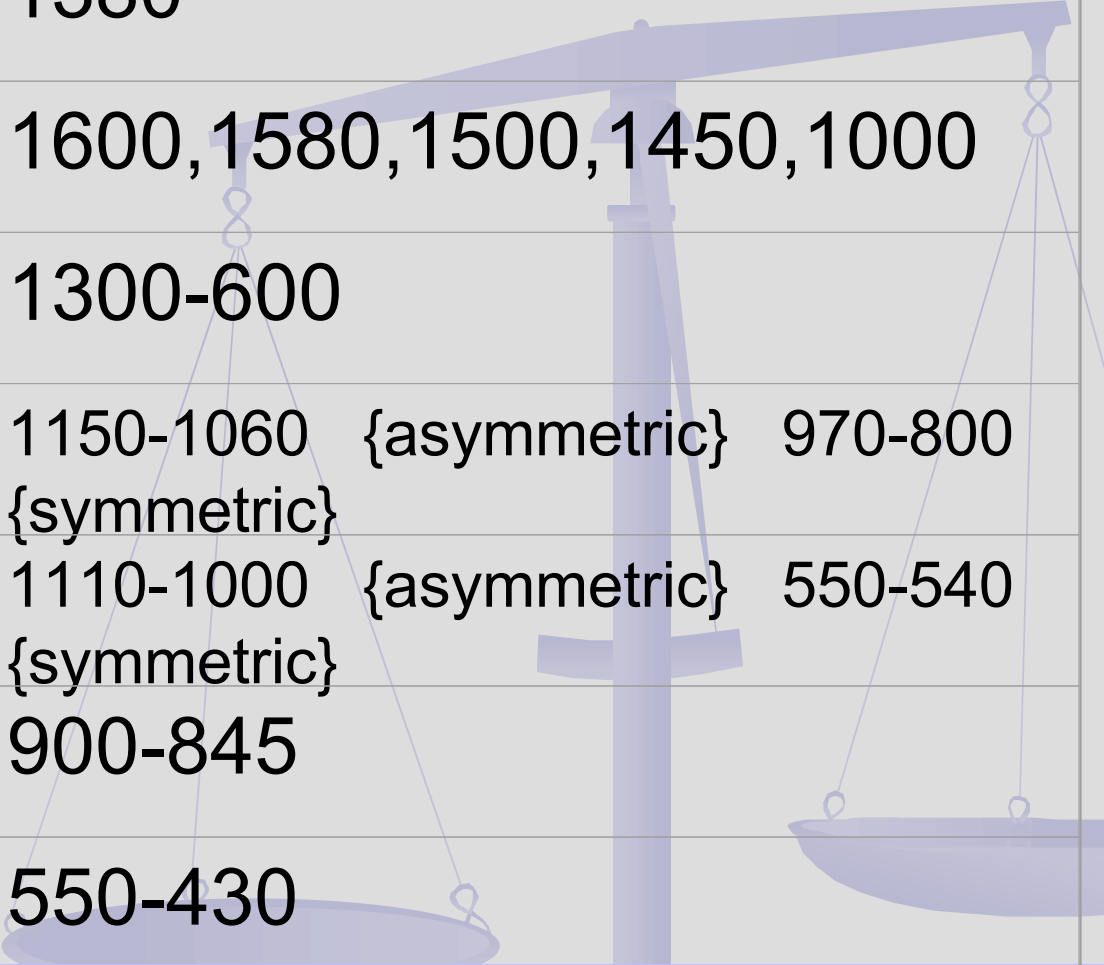




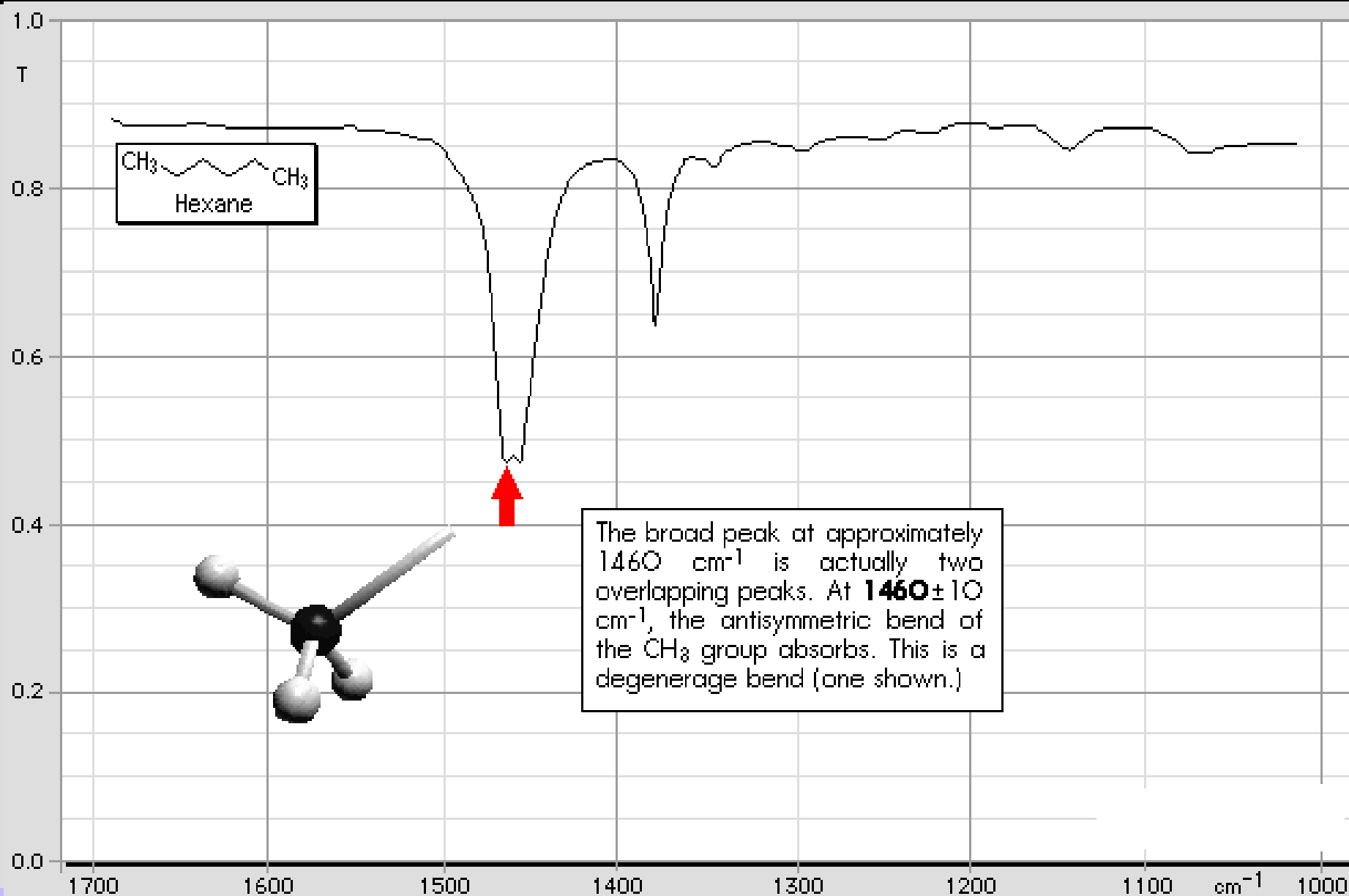
C=O {stretching}	1820-1680
C=C {stretching}	1900-1500
C=N {stretching}	1680-1610
N=N {stretching} — aliphatic	1580-1550
N=N {stretching} — aromatic	1440-1410
C — NO <sub>2</sub> {stretching}	1590-1530 {asymmetric}
	1380-1340 {symmetric}
C — SO <sub>2</sub> — C {stretching}	1350-1310 {asymmetric}
	1160-1120 {symmetric}

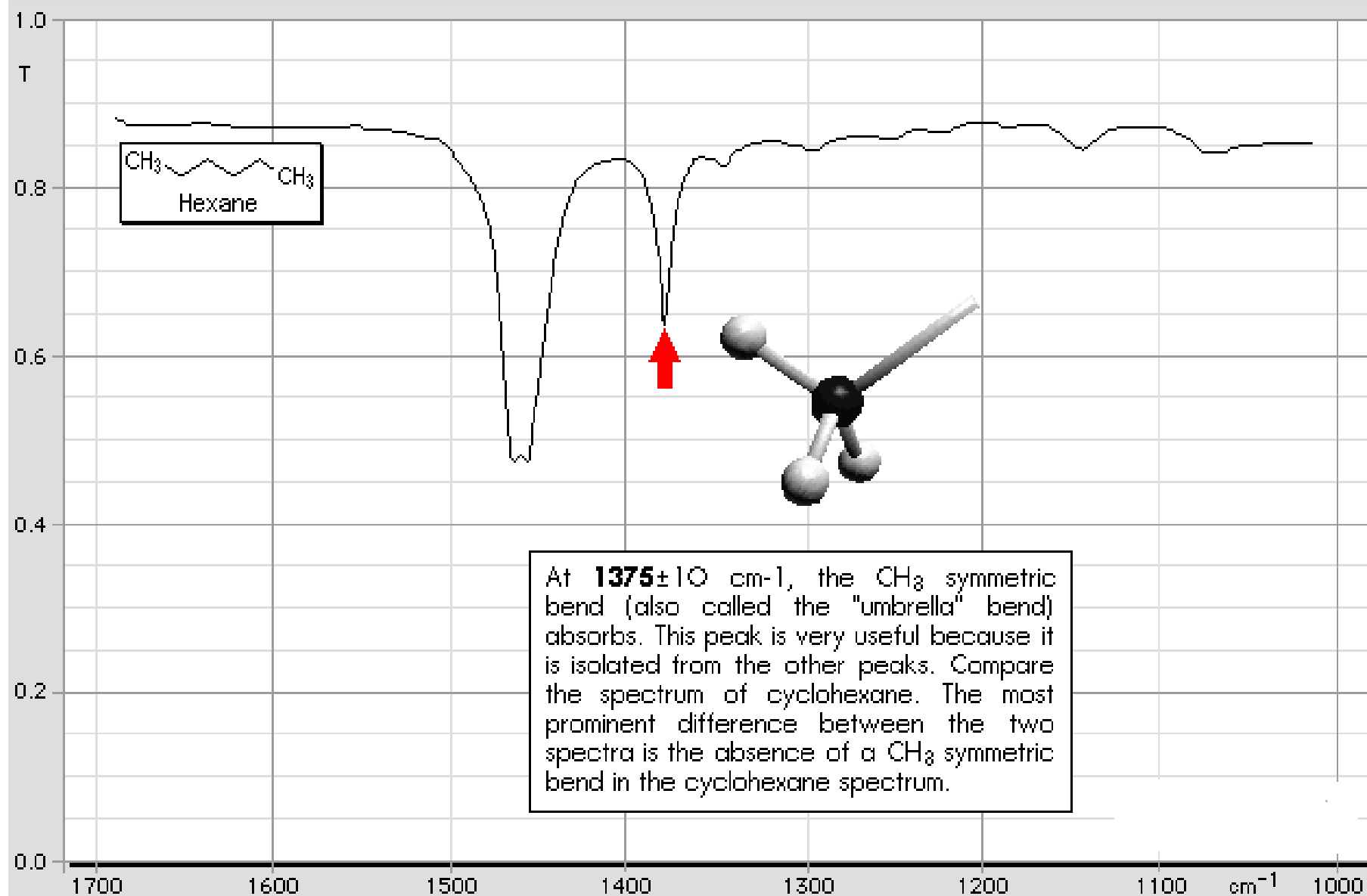


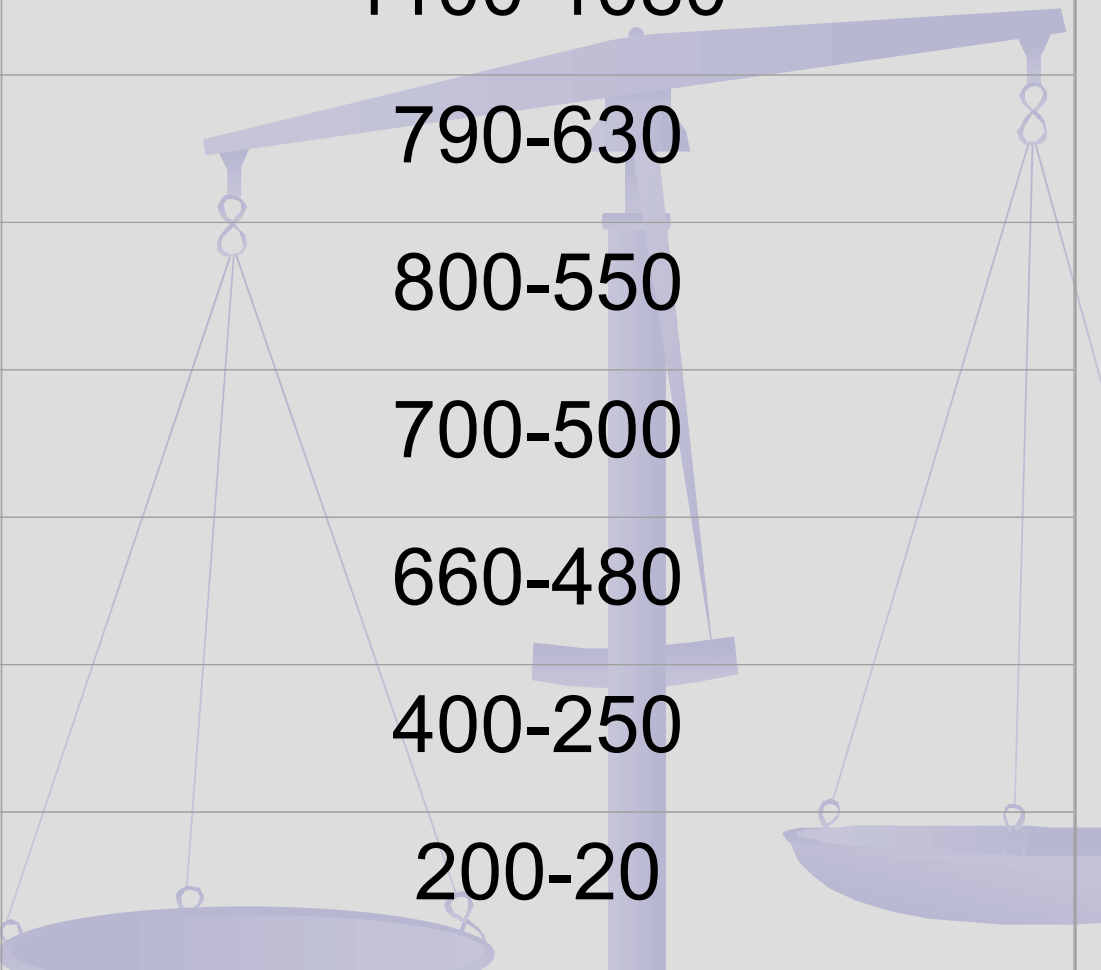




C=S {stretching}	1250-1000
CH <sub>2</sub> {bending}	1470-1400
CH <sub>3</sub> {bending}	1380
C — C {aromatic — stretching}	1600, 1580, 1500, 1450, 1000
C — C {alicyclic — stretching}	1300-600
C—O—C {stretching}	1150-1060 {asymmetric} 970-800 {symmetric}
Si—C—Si {stretching}	1110-1000 {asymmetric} 550-540 {symmetric}
O—O {stretching}	900-845
S—S {stretching}	550-430







Se—Se {stretching}	330-290
C (aromatic) — S {stretching}	1100-1080
C (alicyclic) — S {stretching}	790-630
C—Cl {stretching}	800-550
C—Br {stretching}	700-500
C—I {stretching}	660-480
C—C {blending}	400-250
lattice vibrations — accordion modes	200-20



# Coupling

- **Coupling of groups causes shift of spectra**
- **Shifts of spectra provide valuable information on the molecular environment of the particular chemical group**
- The magnitude of the coupling effect is smallest when the atoms of neighbouring groups have significantly different masses or when the bond vibrations possess relatively large force constants.

# Coupling

- The force constants are greater for bond stretching vibrations than for bending deformations;
- The absorption frequencies for stretching modes are essentially invariant whereas those for bending modes show more significant shifts due to coupling;

## Coupling

- For most hydrocarbons, assignment of specific vibration frequencies to particular group motions is usually possible;
- In case of fluorinated polymers, the coupling of vibration and bending motions leads to group vibrations which are very sensitive to the effects of substitution;

# Quantitative analysis

## Beer-Lambert Law

$$A = \log \frac{I}{I_0} = \varepsilon c l$$

$A$ : Absorbance;

$I_0$ : Incident light intensity;

$I$ : Intensity at a depth  $l$  in the absorbing medium;

$c$ : the concentration of the absorbing species;

$\varepsilon$ : a constant for the material termed the absorptivity or extinction coefficient.

※ Most spectrometers display the spectrum as percentage transmittance *vs* wavenumber.

$A=0$ , no absorption  
( $I=I_0$ )  
 $A=\infty$ , complete  
absorption ( $I=0$ ).

# Quantitative analysis

## Beer-Lambert Law

**Transmittance :**

$$T = I / I_0$$

**Percentage transmittance:**

$$100 \times I / I_0$$

**Absorbance:**

$$A = \log (I / T).$$



# Quantitative analysis

- In principle, if extinction coefficient is known, absorbance can be made by direct application of the **Beer-Lambert Law**
- Quantitative analysis is best carried out in solution with appropriate concentration.
- And more usually there is need to examine polymers in the solid state. (thin film, in the form of KBr discs or Nujol mulls)

# Quantitative analysis

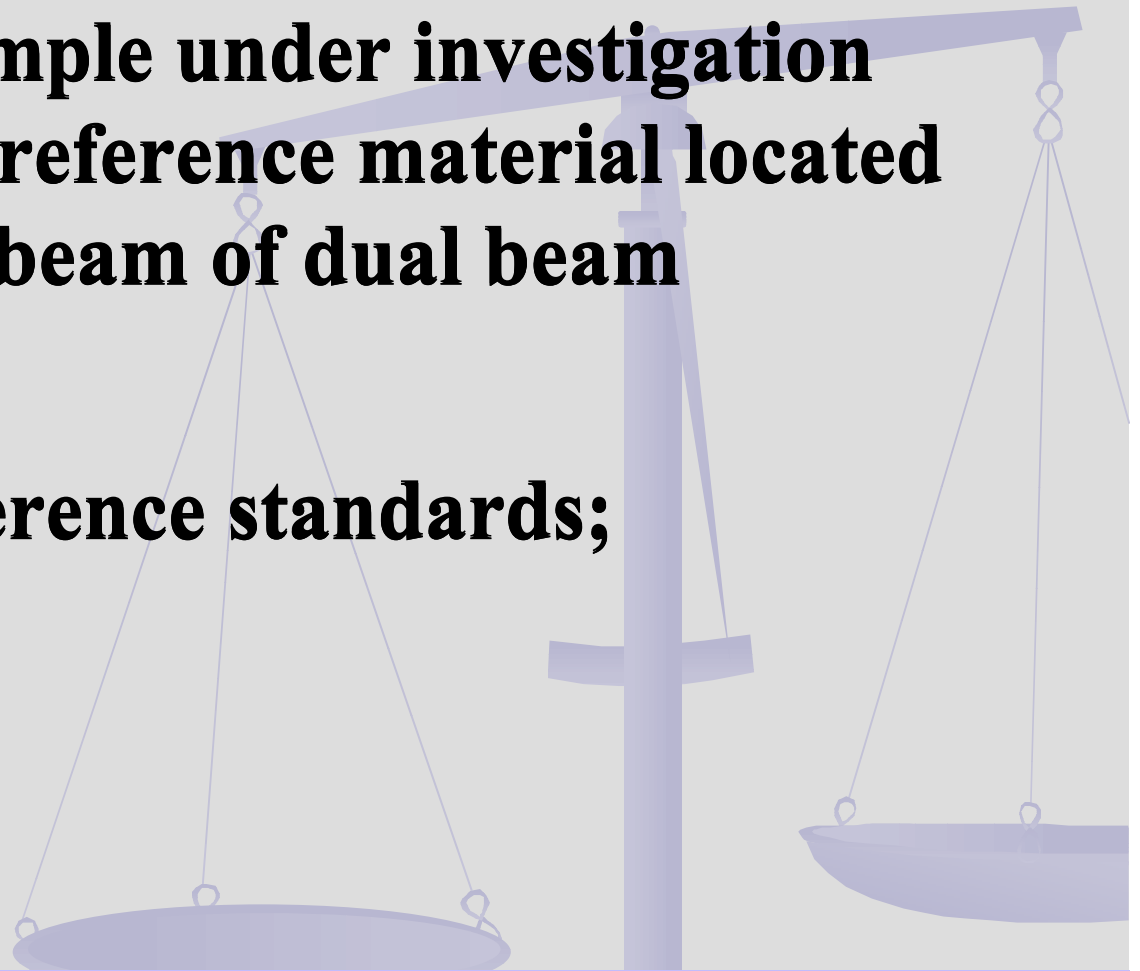
For absolute measurements, there are some problems:

- Uniform film thickness
- Homogeneous distribution of absorbing species (particularly additives)
- Optical effects such as extraneous light scattering

## Quantitative analysis

**More reliable results are usually obtained:**

- **Compare the sample under investigation with a standard reference material located in the reference beam of dual beam spectrometers;**
- **Use internal reference standards;**

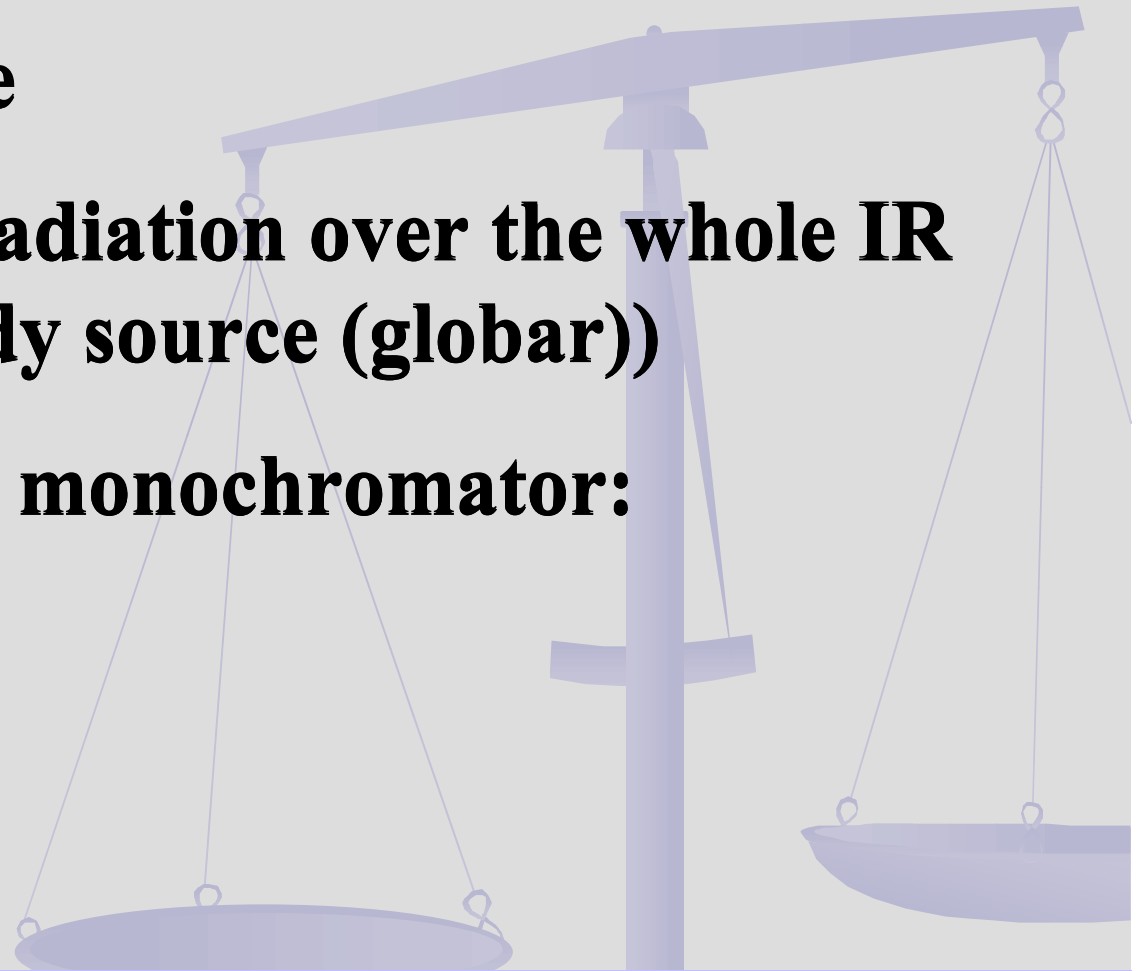




# Instrumentation

## (a) Dispersive infrared spectrometers

- **Double beam mode**
- **The source emits radiation over the whole IR region (a black body source (globar))**
- **Use more than one monochromator:**



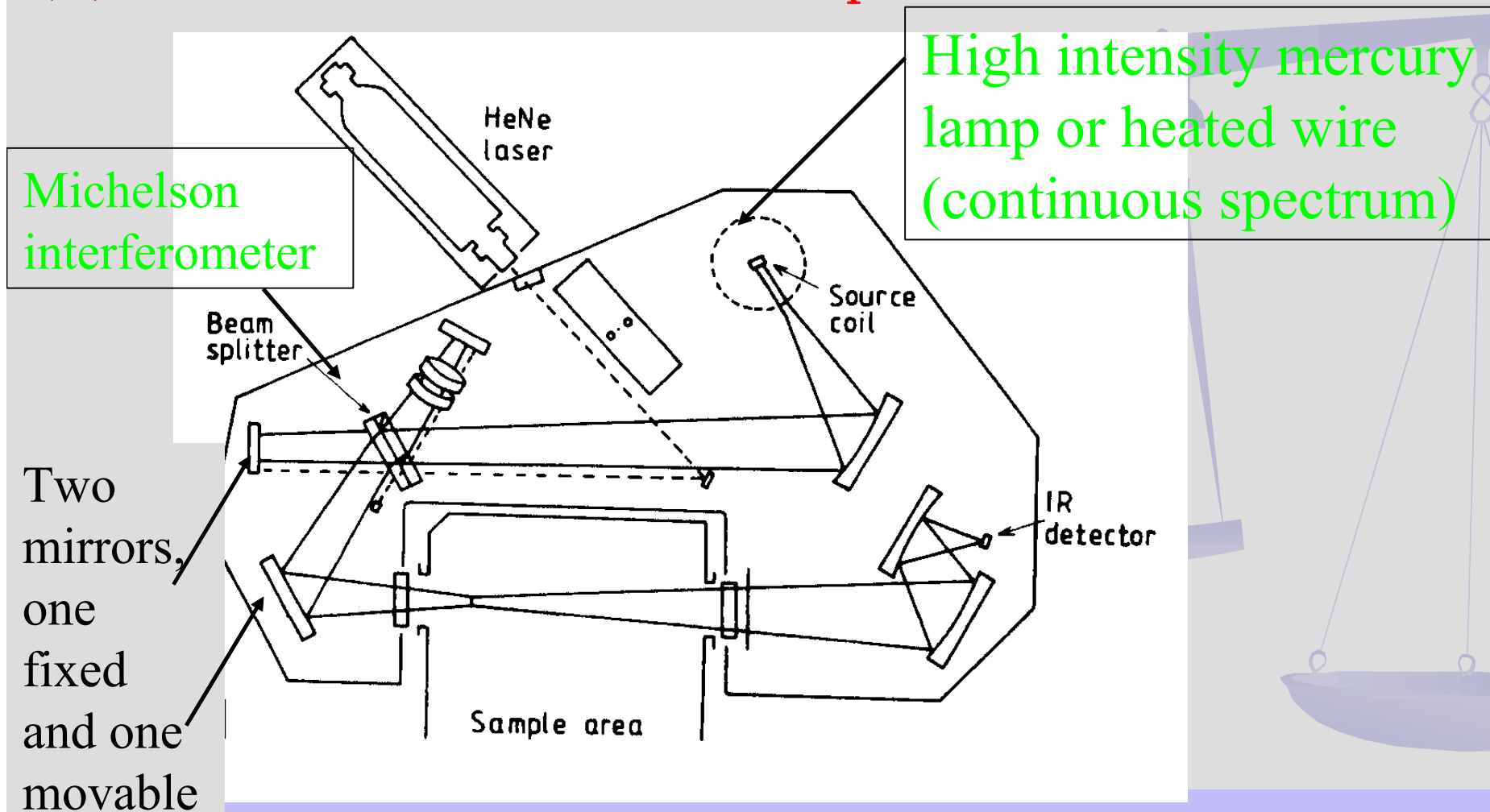
# Instrumentation

## (b) Fourier transform spectrometers

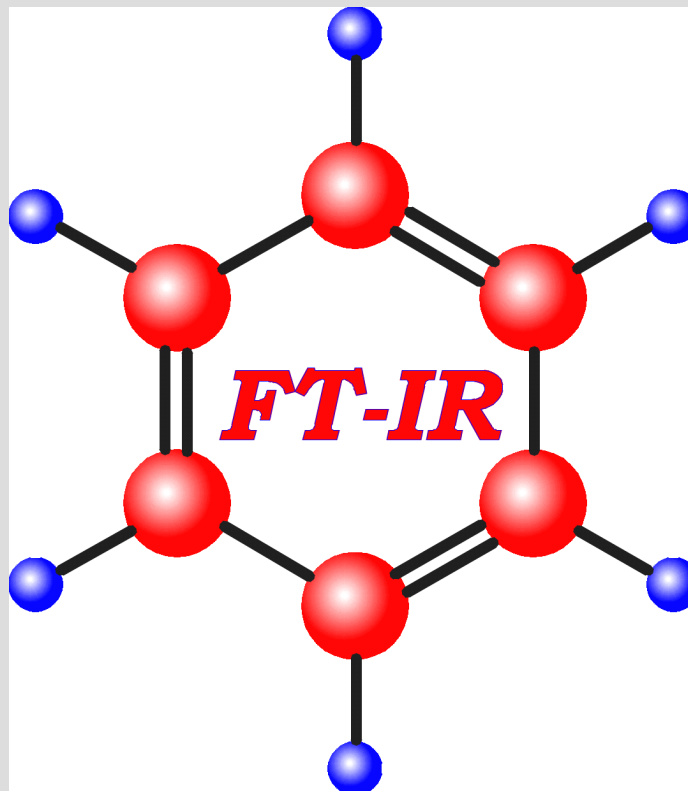
- Whole infrared region
- FTIR instruments have largely replaced the traditional double beam instruments.
- Higher signal-to-noise ratios compared to dispersive instruments
- Capability of complex data handling
- Also permit investigation of transient structural changes during deformation of polymers

# Instrumentation

## (b) Fourier transform spectrometers



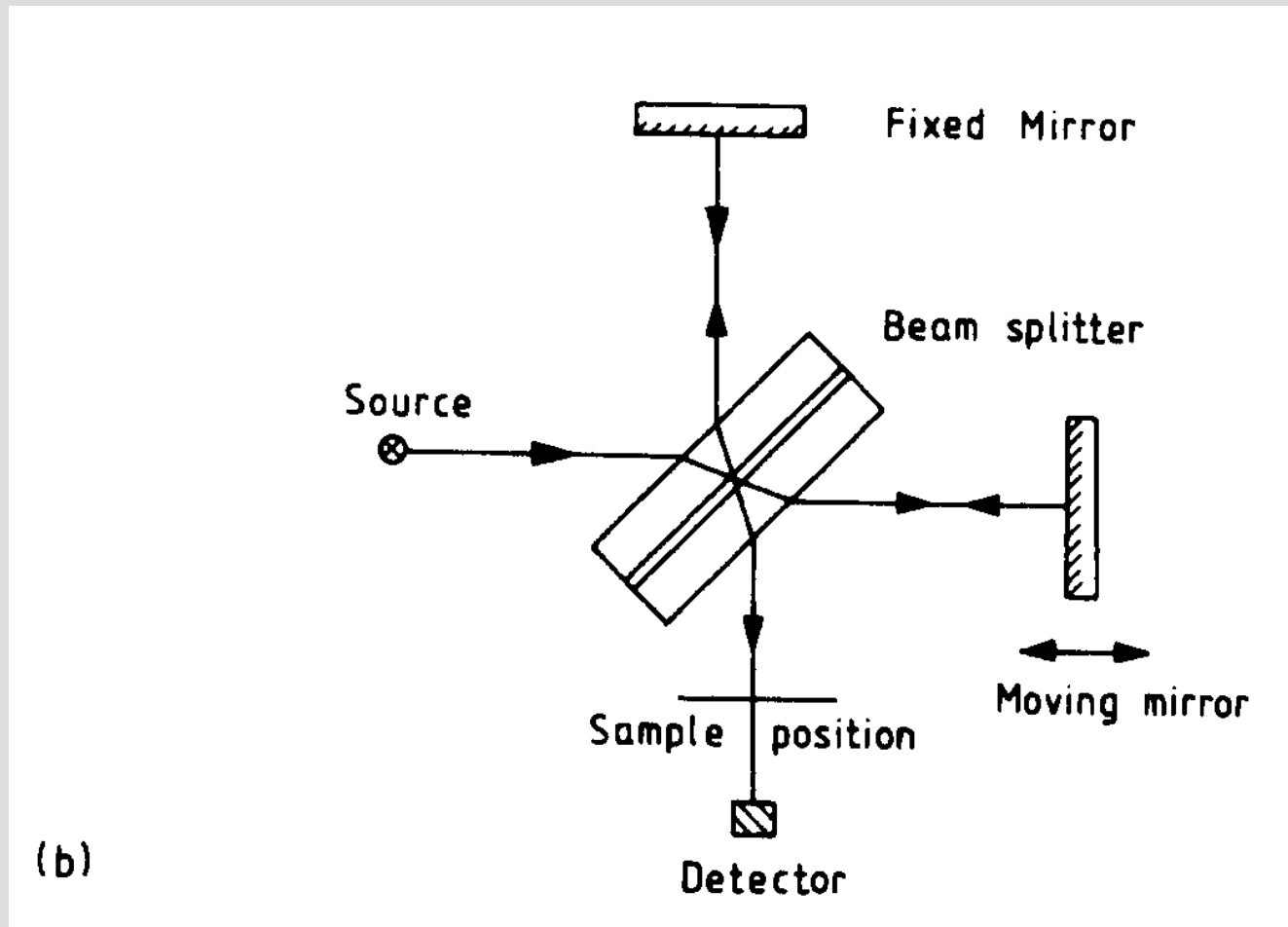
# Instrumentation



布鲁克光谱仪器公司

# Instrumentation

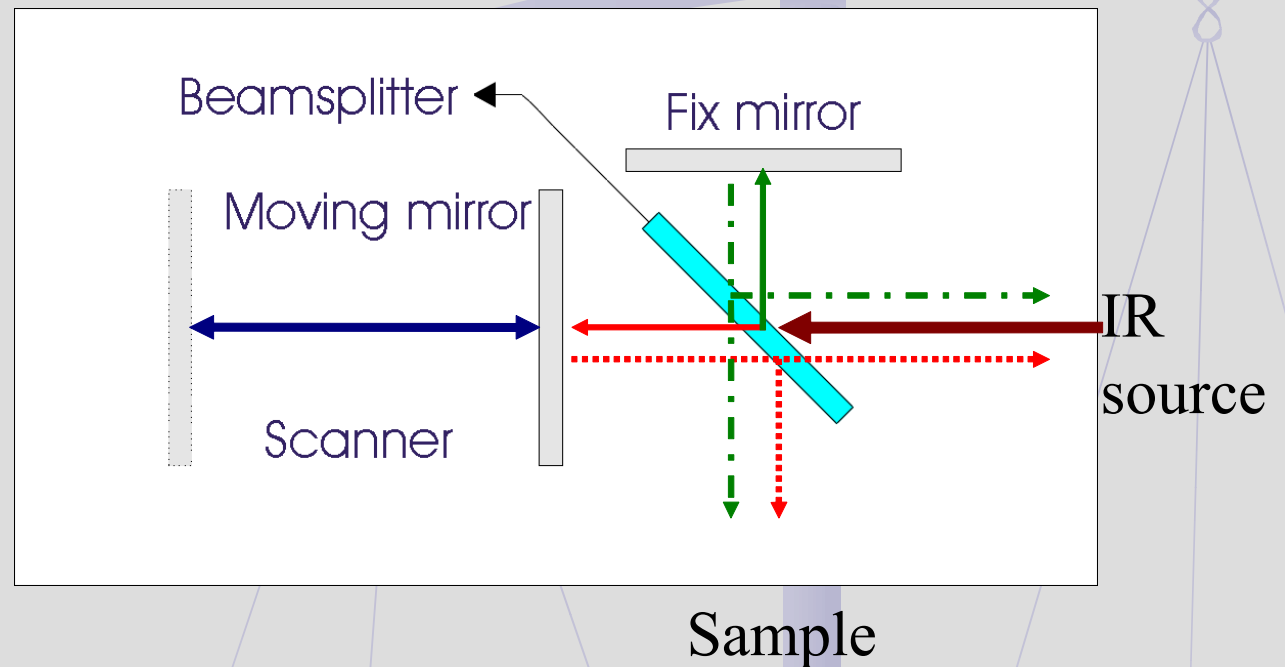
## (b) Fourier transform spectrometers



# Instrumentation

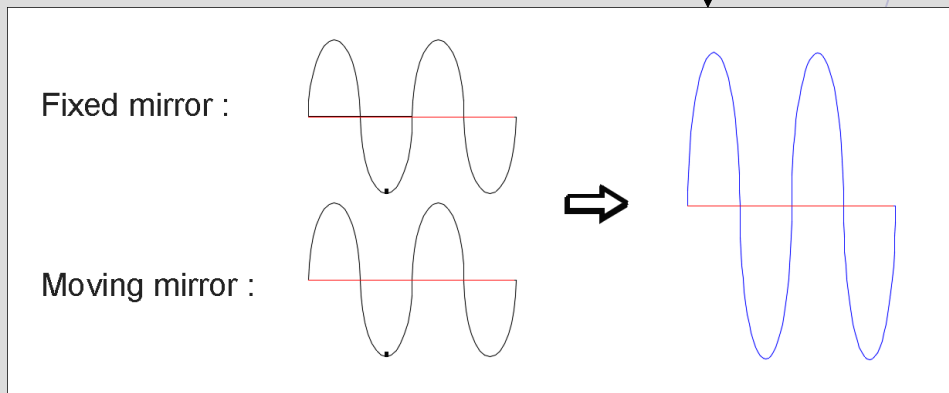
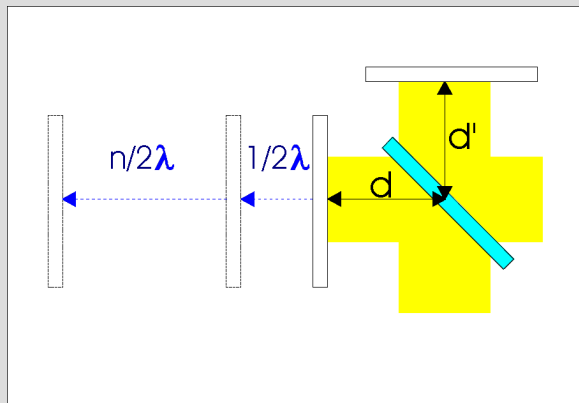
## (b) Fourier transform spectrometers

- **constructive interference.**
- **destructive interference**
- **oscillatory pattern or interferogram**



# Instrumentation

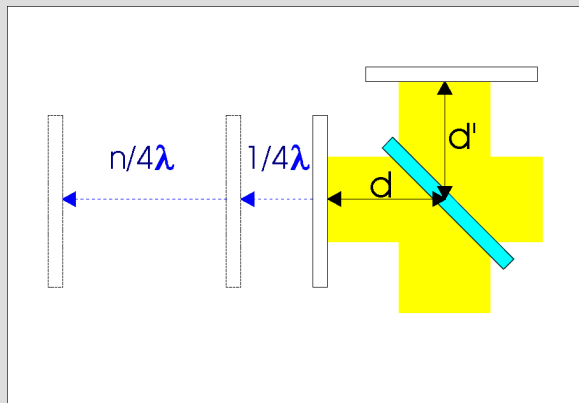
## (b) Fourier transform spectrometers



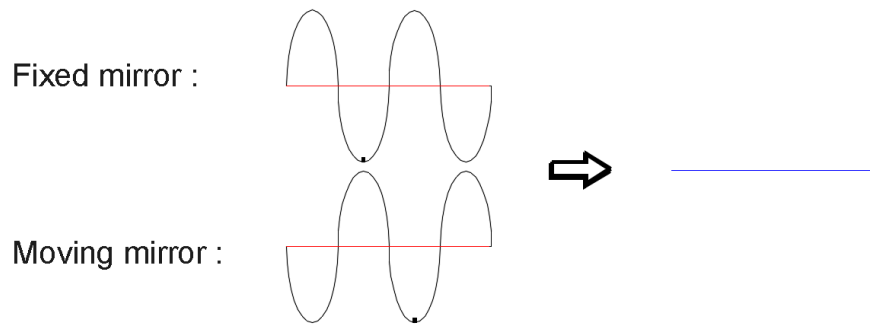
- mirrors are located equidistant, the optical path difference is an Integral number of wavelengths
- the reflected beams are in phase
- produce constructive interference

# Instrumentation

## (b) Fourier transform spectrometers



- the optical path difference is an odd number of half wavelengths
- destructive interference



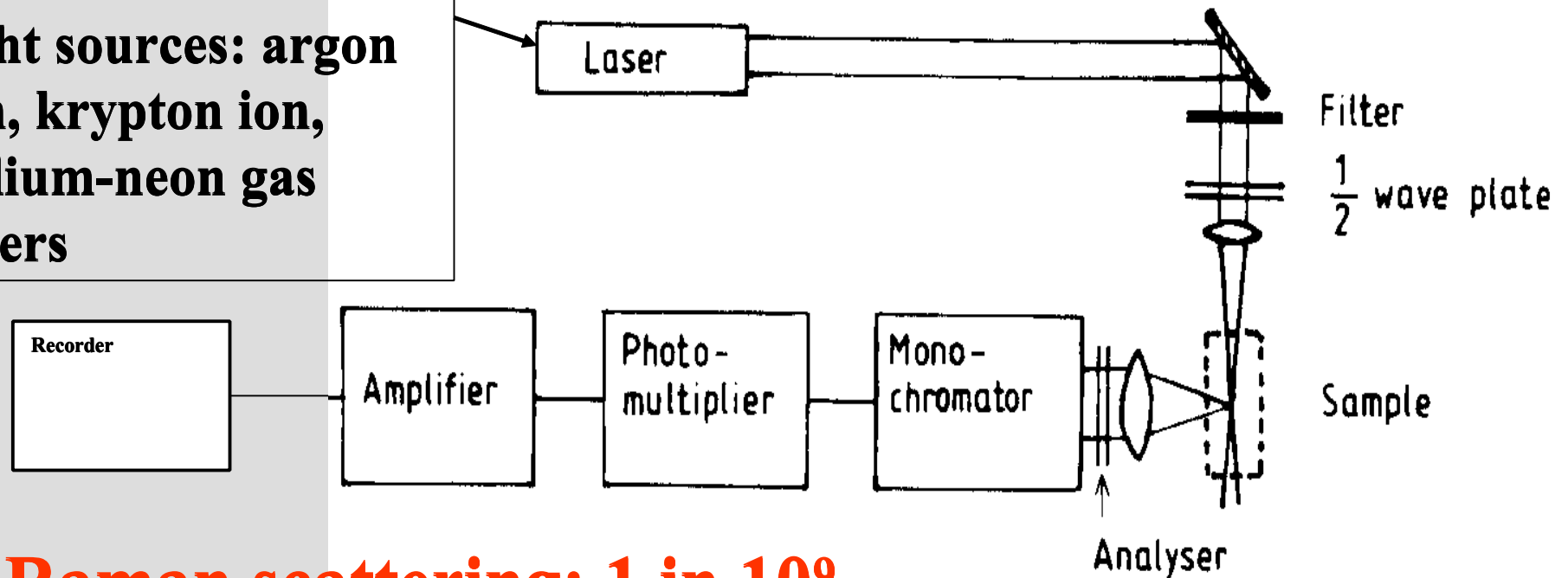


# Instrumentation

*Bruker*光谱仪

## (c) Raman spectrometers

**High intensity monochromatic laser light sources: argon ion, krypton ion, helium-neon gas lasers**



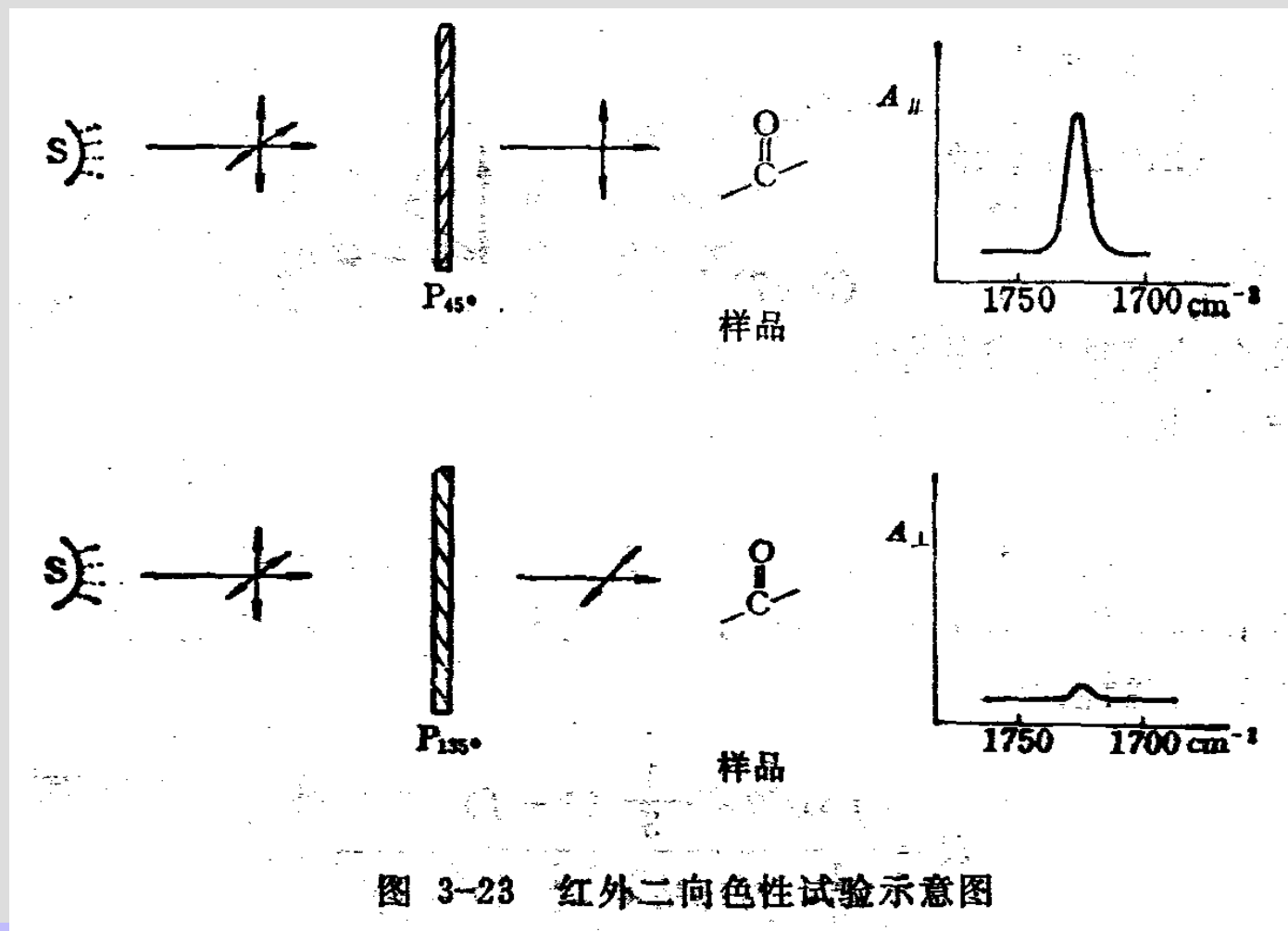
**Raman scattering: 1 in  $10^9$**

The scattered light is usually observed at  $90^\circ$  to the incident beam.

## (d) Attenuated Total Reflectance (ATR)

- IR spectra of surfaces
- Provide information on surface oxidation

# Infrared Dichroism



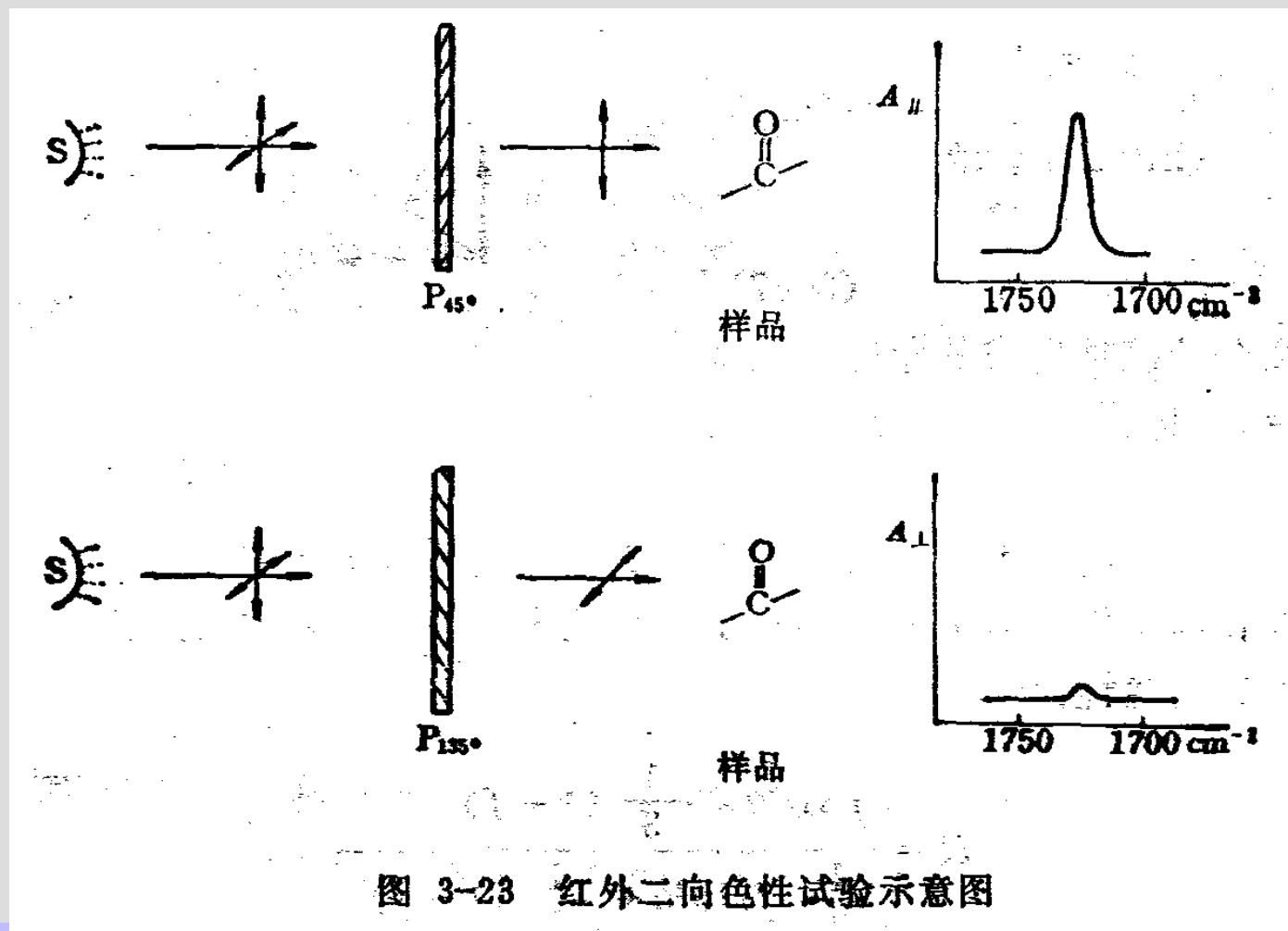
# Infrared Dichroism and Raman Polarization

- Use polarized light source;
- Determine the extent of IR dichroism and/or Raman depolarization
- Provide structural information of molecular chain orientation.

## Infrared Dichroism

- The maximum absorption of IR radiation occurs when the electric vibrating of the incident EM radiation is parallel to the dipole of the vibrating group;
- Absorption of IR radiation is zero in the perpendicular direction.

# Infrared Dichroism



# Infrared Dichroism

Two situations:

➤ Random orientated molecules

(The measured absorbance is independent of the polarization of the incident light.)

➤ Oriented specimens

(The observed spectra will differ depending on the direction of the plane of polarization relative to the molecular orientation.)



# Infrared Dichroism

Dichroic ratio:

$$D = A_{//}/A_{\perp}$$

$$D_0 = 2\cot^2\alpha$$

$$f = [3\langle \cot^2\theta \rangle - 1]/2 = (D-1)(D_0+2)/(D_0-1)(D+2)$$

where  $A_{//}$  and  $A_{\perp}$  are the absorbances defined with respect to a reference axis in the sample, typically the orientation direction.  $f$  is the chain orientation factor.  $\alpha$  is the transition moment angle, which is the angle between the direction of the nitrile group's dipole moment and the chain axis. For PAN, it is  $70^\circ$ . And  $\theta$  is the angle of the molecular segment relative to the fiber axis.

# Raman Polarization

The directional properties of Raman spectra are determined by:

- The symmetry of the vibrations
- The orientation of the molecules relative to the plane of polarization.

# Raman Polarization

For randomly orientated molecules, the intensities of Raman lines are dependent on:

- The polarization of the incident beam;
- The symmetry of the vibrational modes.

## Raman Polarization

For oriented specimens, the intensity of the scattered light is dependent also on:

- The molecular orientation relative to the plane of polarization of the incident radiation;
- The direction and plane of polarization of the scattered radiation.

## Raman Polarization

Polarization effects are expressed quantitatively by **depolarization ratio ( $\rho$ )**

$$\rho = \frac{I_{//}}{I_{\perp}}$$

where  $I_{//}$  is the intensity of the light scattered with its plane of polarization in the same direction as that of the incident light;

$I_{\perp}$  is the intensity of light having its plane of polarization at right angles to that of the incident light.

# Raman Polarization

➤ Depolarization:

$$\rho = 0.75$$

➤ Polarization:

$$\rho < 0.75$$