VIBRATIONAL SPECTROSCOPY STUDIES OF GLASS STRUCTURE: IR spectroscopy

Infrared spectroscopy is widely used in both research and industry as a simple and reliable technique for measurement, quality control, and dynamic measurement.

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Grade:

- Quiz (50%): February 9th
- Homework (50%): *1 pdf/ group* emailed to lpetit@clemson.edu and maffatig@coe.edu before the beginning of the class on Feb 19th

For the group assignment, please email me (lpetit@clemson.edu) as soon as possible.

Group assignment by Monday 5th

OUTLINE

- Definition
- Theory

i) IR and Raman active

ii) Determination of the vibration frequencies

- Sample preparation
- Description of the equipments used for the IR spectrum measurement
- Examples of IR spectra: oxide, sulfide, selenide glasses

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What does this technique measure?

- IR spectroscopy measures the absorption of IR radiation by materials as the atoms vibrate about their bonds
- IR spectroscopy is primarily used to identify bond types, structures, and functional groups in organic and inorganic compounds

Why are IR absorption spectra important?

- Molecules absorb IR radiation at frequencies related to their unique compositions, structures and the numbers, types, strengths and position of their bands.

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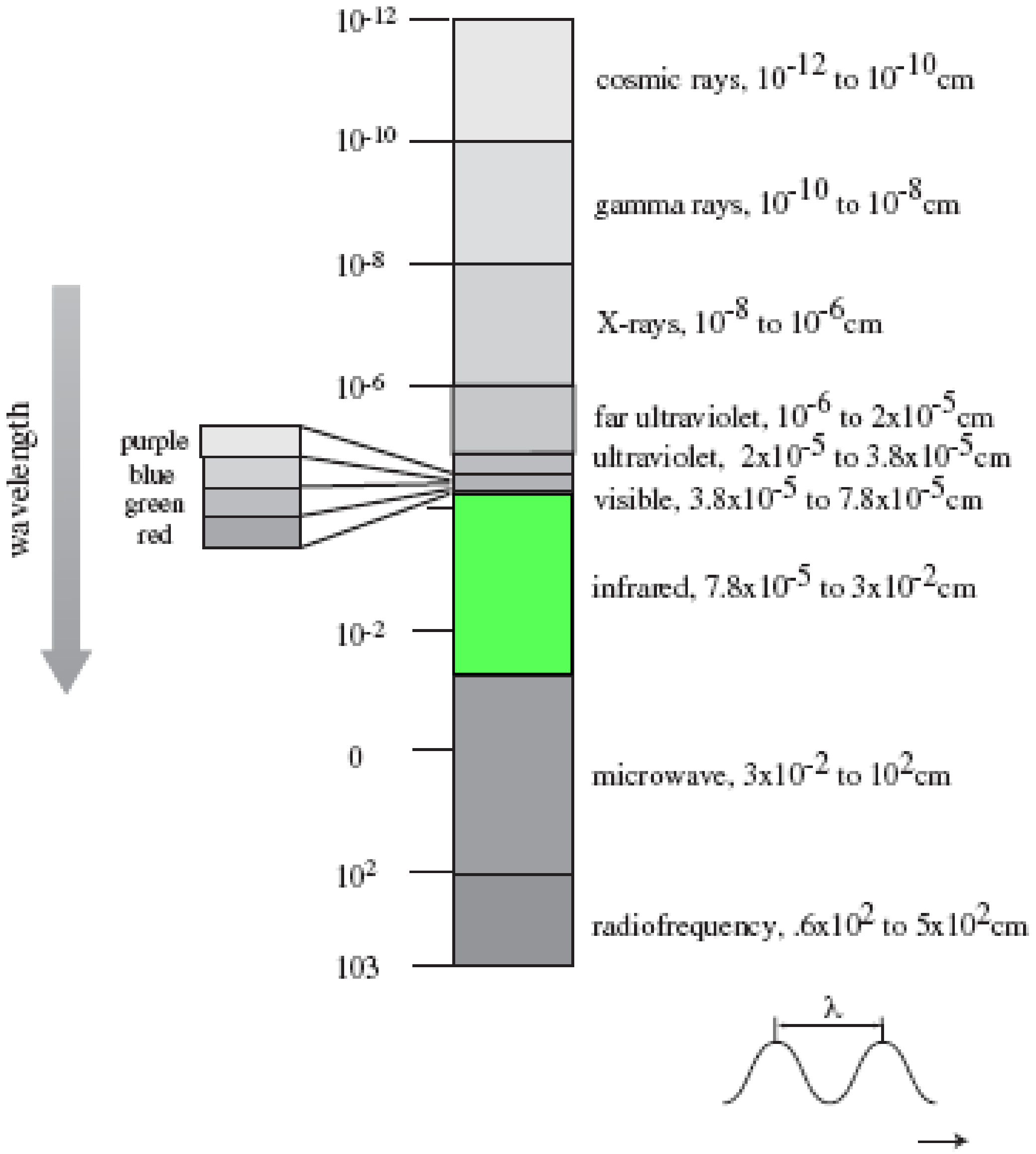
Introduction



Infrared refers to that part of the electromagnetic spectrum between the visible and microwave regions.

Introduction

- The energy of a molecule consists partly of translational energy, partly of rotational energy, partly of vibrational energy and partly of electronic energy.

- **Electronic energy transitions** normally give rise to absorption or emission in the UV and visible regions of the electromagnetic spectrum
- **Pure rotation** gives rive to absorption in the microwave region or the far infrared
- **Molecular vibrations** give rise to absorption bands throughout most of the IR region of the spectrum

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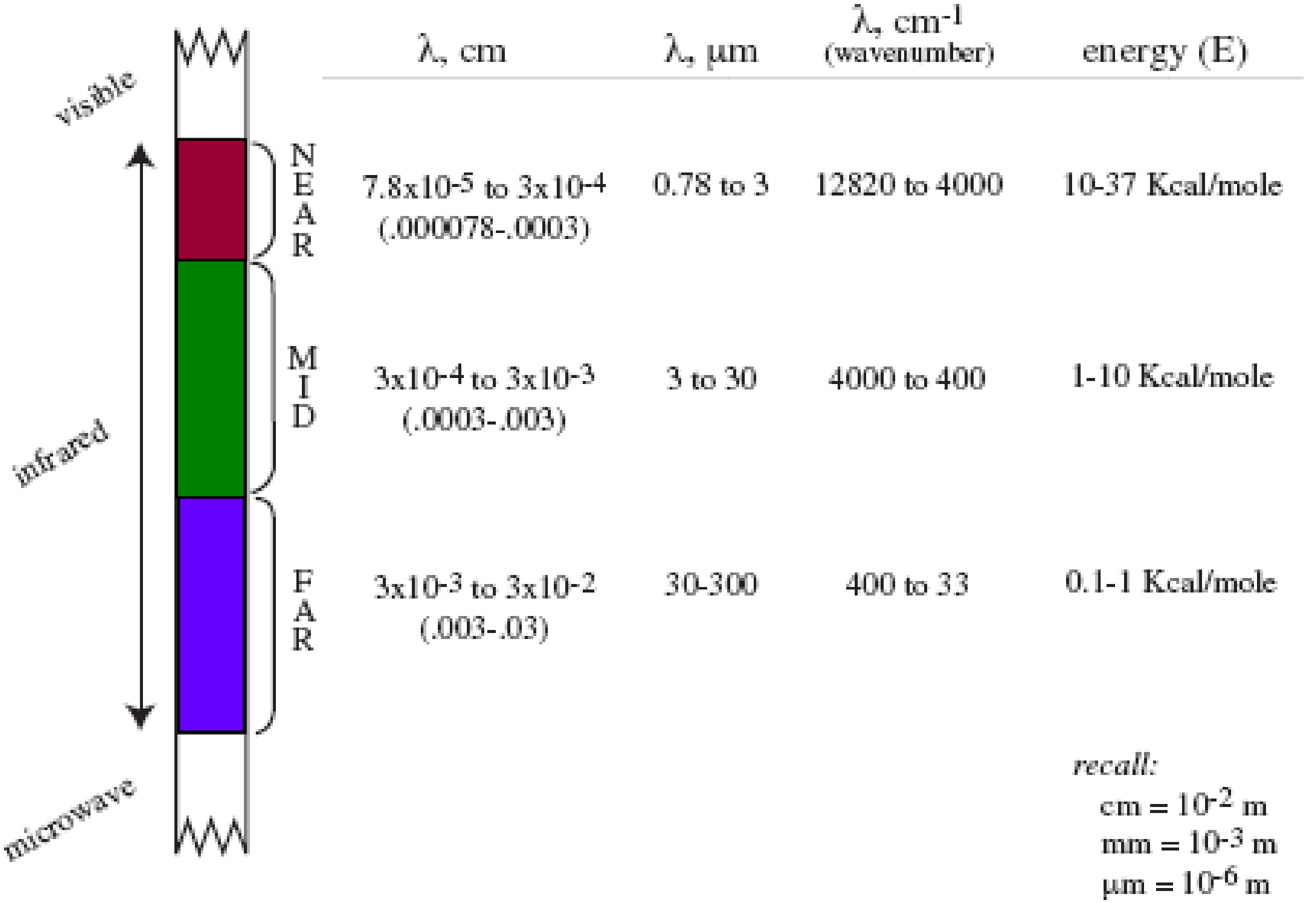
Introduction



	λ, cm	λ, µm	λ, cm^{-1} (wavenumber)	energy (E)
NEAR	7.8×10^{-5} to 3×10^{-4} (.000078-.0003)	0.78 to 3	12820 to 4000	10-37 Kcal/mole
MID	3×10^{-4} to 3×10^{-3} (.0003-.003)	3 to 30	4000 to 400	1-10 Kcal/mole
FAR	3×10^{-3} to 3×10^{-2} (.003-.03)	30-300	400 to 33	0.1-1 Kcal/mole

recall:

cm = 10^{-2} m
mm = 10^{-3} m
µm = 10^{-6} m

The near-IR can excite overtone or harmonic vibrations.

The mid- infrared may be used to study the fundamental vibrations and associated rotational-vibrational structure

The far-infrared, may be used for rotational spectroscopy.

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Definition

- Wavelength and frequency are inversely related:

$$\nu = \frac{c}{\lambda} \text{ and } \lambda = \frac{c}{\nu}$$

where c is the speed of light, 3 x 10^{10} cm/sec

- Energy is related to wavelength and frequency :

$$E = h\nu = \frac{hc}{\lambda}$$

where h = Planck's constant, 6.6 x 10^{-34} joules-sec

- Note that **energy is directly proportional to frequency and inversely proportional to wavelength.**

IR spectroscopy

- IR radiation does **not have enough energy to induce electronic transitions** as seen with UV.

- Infrared spectroscopy works because chemical bonds have specific frequencies at which they vibrate corresponding to energy levels.
- **Infrared radiation is absorbed by molecules and converted into energy of molecular vibration.**
- When the radiant energy matches the energy of a specific molecular vibration, **absorption occurs**.

- **Weaker bonds require less energy, as if the bonds are springs of different strengths.**

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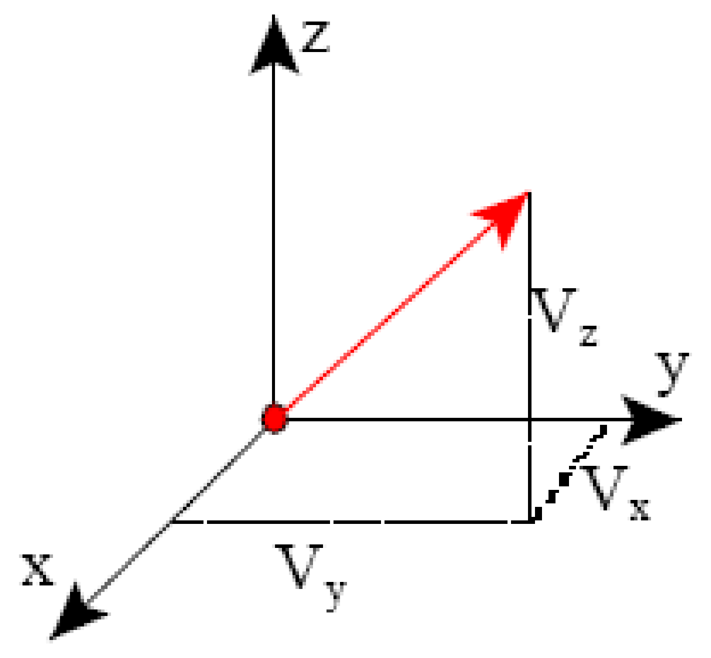
Degrees of Freedom of Molecular Motion



- The vibration of any structure is analyzed in terms of the degrees … ucture possesses.
- Each mass r … define its position suc … sian coodinate . 3 independe … motion in the x, y and z di
- For example

A sphere has … freedom and 0 degrees of r … otation does not result in a perceptibly different state. Note that a single sphere or a single atom does not have vibrational states.

Degrees of Freedom of Molecular Motion

- What about the grouping of 2 spheres?

When two spheres are bonded, the group has **3*2 degrees of translational freedom.**

As a unit, it possesses **3 degrees of translational freedom and 2 degrees of rotational freedom**, since rotation about the axis of the two spheres does not result in a perceptible change.

When considering vibrational states, the degrees of freedom for the grouping are subtracted from the total number of translational degrees of freedom for the individual spheres.

3*2 - (3+2) = 1 degree of vibrational freedom.

Degrees of Freedom of Molecular Motion

- This means that the IR/Raman spectra for a diatomic molecule such as CO will have one absorption band.
- This vibration would involve stretching and compressing of the CO bond.

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Degrees of Freedom of Molecular Motion: Classical model

- If there are N atomic nuclei in the molecule, there will be a total of **3N degrees of freedom** of motion for all the nuclear masses in the molecule
- The center of gravity of the molecule requires 3 coordinates to define its position. It has 3 independent degrees of freedom of motion which are translation of the center of gravity of the molecule.

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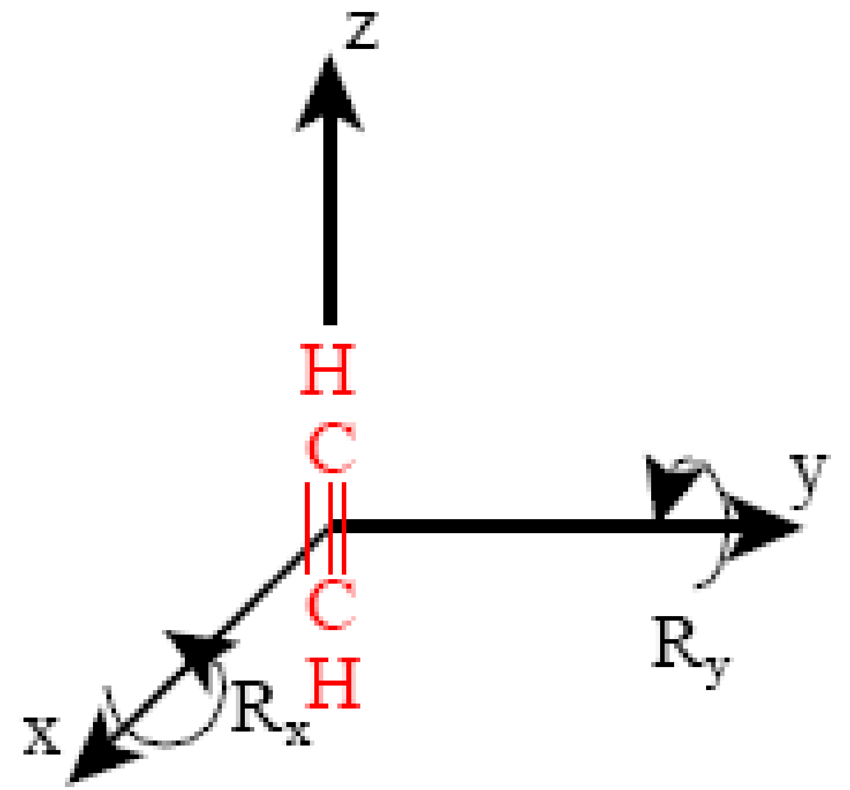
Degrees of Freedom of Molecular Motion: Classical model

- When a non-linear molecule is in its equilibrium
  configuratio **rdinates**
  to specify th the center
  of gravity.
- A linear mol rotational
  degrees of f pendicular
  axes, perpe
- **After subtra rotational**
  degrees of legrees of
  freedom, th es of
  freedom fo 3N-5
  internal degrees of freedom for a linear molecule



Molecule such as water?

- Vibrational states?

3N-6 ⇒ 3*3-6 = 3 vibrational states
which results in three absorption bands in IR and Raman.

The number of *stretching vibrations is N-1* and the number of *bending vibrations is 2N-5*.

Stretching vibrations ⇒ 3-1 = 2: symmetric stretching of the H-0 bonds and asymmetric stretching of the H-O bonds
Bending vibration ⇒ 2*3-5 = 1: 1 scissors bending of the HOH structure.

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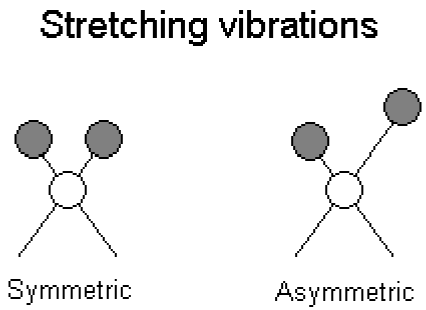
Vibrations

- **Stretching:** Change in inter-atomic distance along bond axis



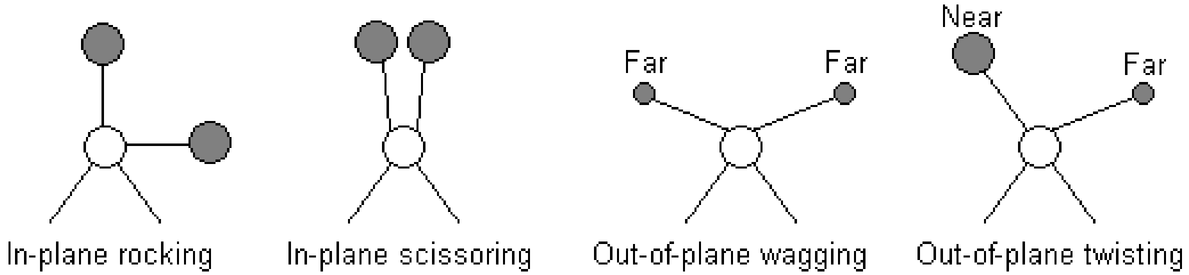
- **Bending:** Change in angle between two bonds. There are four types of bend:

Rocking

Scissoring

Wagging

Twisting



Vibrations

- **The symmetric stretch/bend is an easier deformation than the asymmetric stretch/bend**

- **The bending vibration is much easier than stretching**

Can you find the absorption band related to:

- The symmetric stretch is an easier deformation than the asymmetric stretch

  ⇒ occurs at lower wavenumbers
- The bending vibration is much easier than stretching so it occurs at lower wavenumber

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Compared to Raman spectroscopy

- Infrared (IR) and Raman spectroscopy both measure the vibrational energies of molecules but these method rely only different selection rules.

- For a vibrational motion to be IR active, the dipole moment of the molecule must change.

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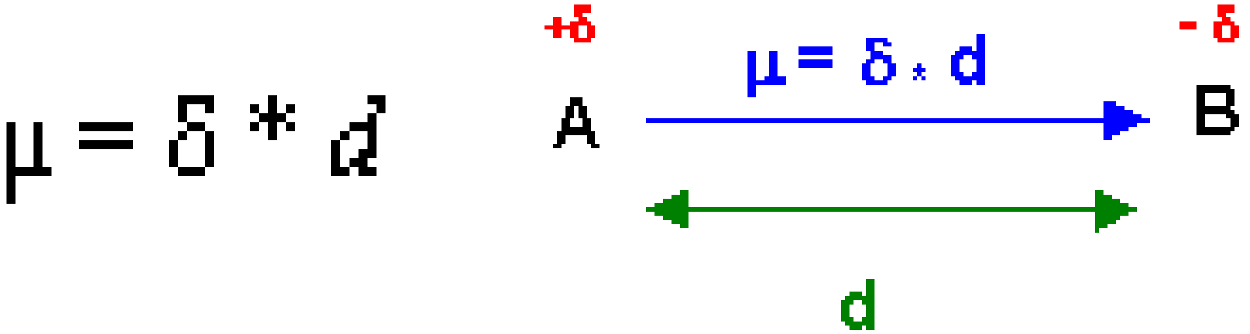
Dipole moment

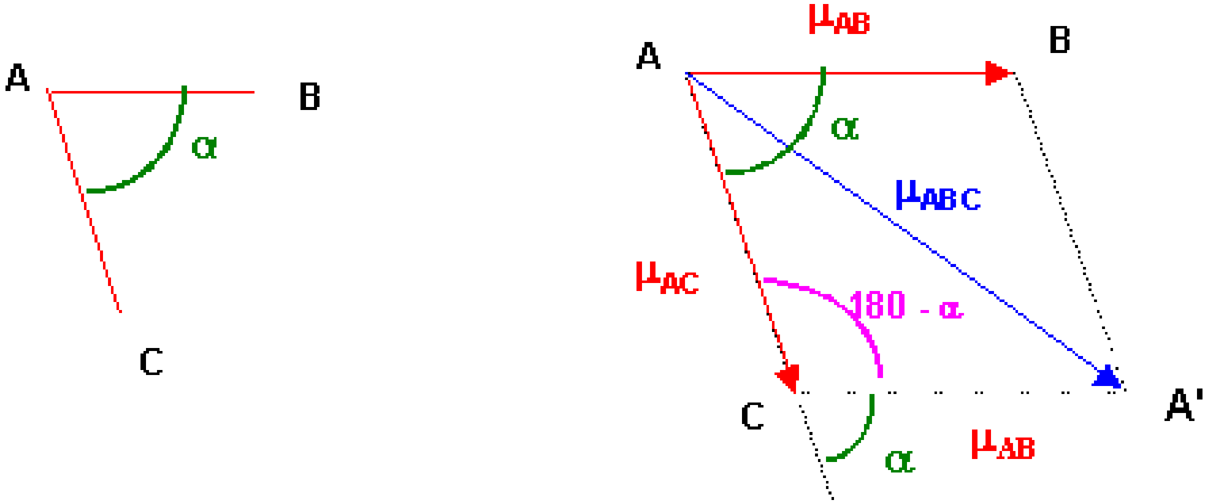
- A dipole moment is a vector quantity - it has both size and direction.



where μ is the bond dipole moment in *coulomb-meters*, δ is the amount of charge at either end of the dipole, given in coulombs, and d is the distance between the charges in meters

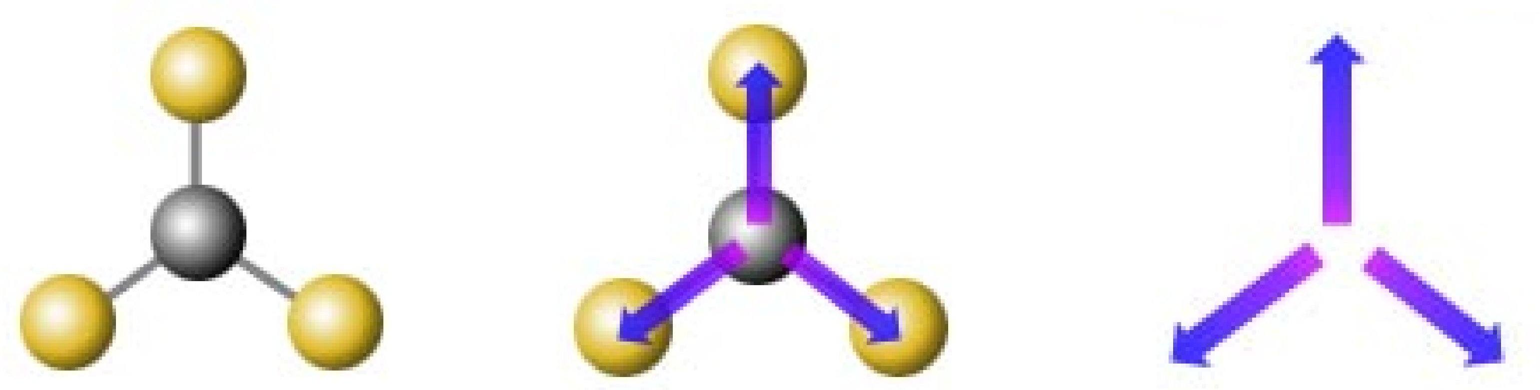
Dipole moment

- Any molecule where the overall centre of the positive charges and the overall centre of the negative charges coincide will have **zero dipole moment**. This happens in molecules with sufficiently symmetric shape.
- **So it is the shape of a molecule that is important in determining whether it has a dipole moment**.
- For a complete molecule the overall dipole moment is calculated as the vector sum of individual dipole moments



Example: what is the dipole moment of BF_3?

- Shape: trigonal planar
- Each BF bond has a dipole moment with a partial negative charge on the fluorine (it is much more electronegative than the boron), but the shape of the molecule is such that the bond dipole moments add up to zero.



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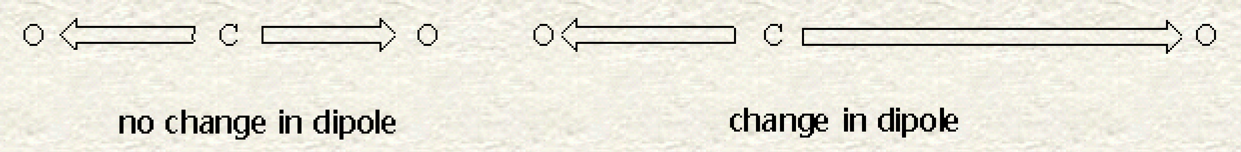
Compared to Raman spectroscopy

- IR sensitive vibrations are associated with changes in dipole moments



- Some of the infrared inactive vibrations (because of the lack of change in dipole moment) are active in Raman spectroscopy because **Raman activity is associated with changes in electronic polarizability**

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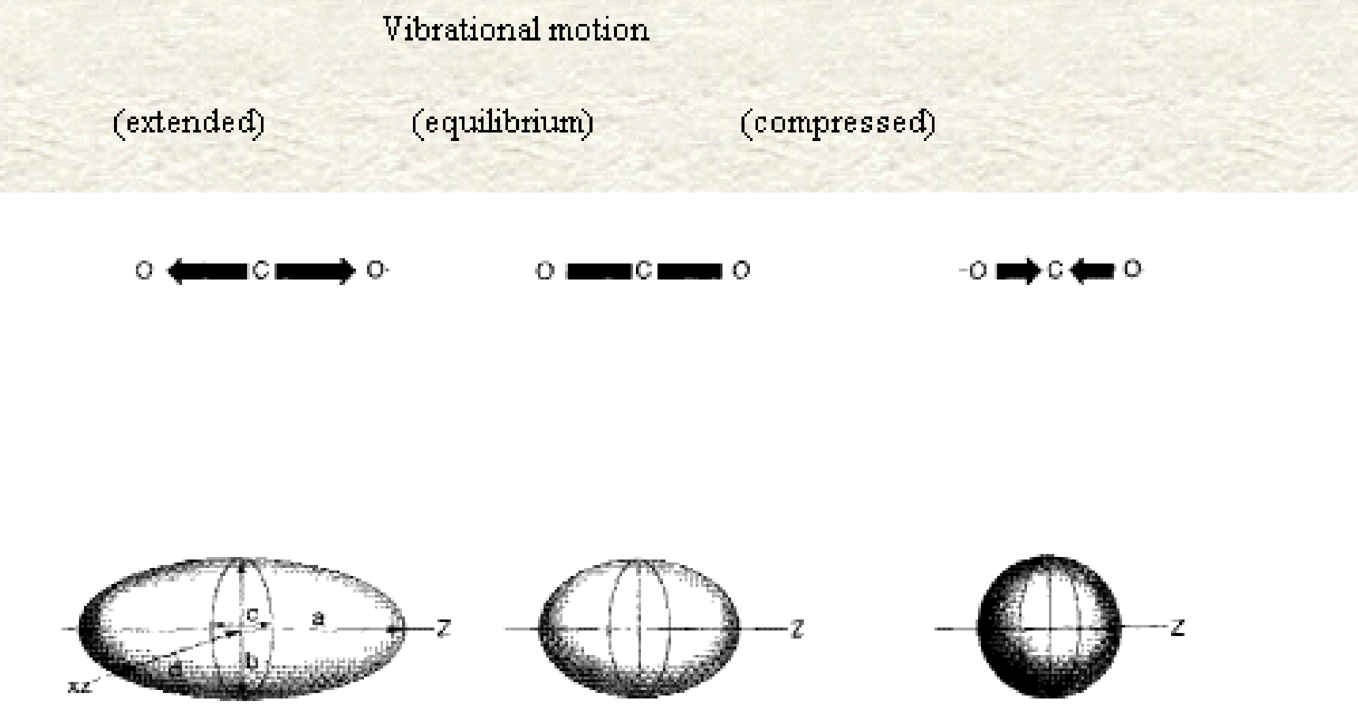
Compared to Raman spectroscopy

- For a transition to be Raman active, there must be a change in polarizability of the molecule.



Molecule such as water?

- 3 absorption bands in IR and Raman

1 symmetric stretching
1 asymmetric stretching
1 Bending vibration.

Are they IR or Raman active?

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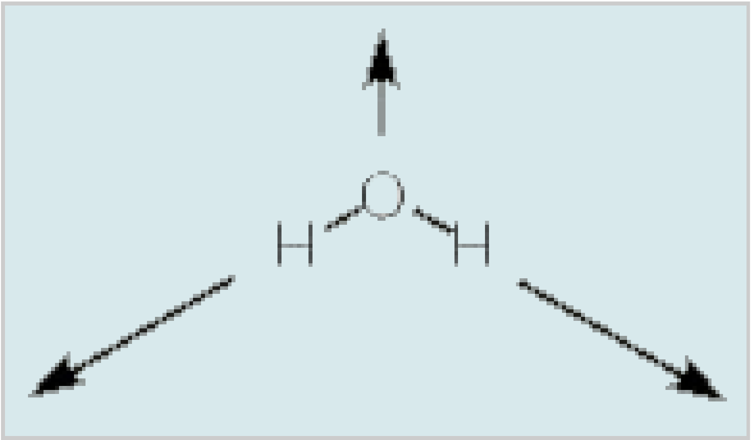
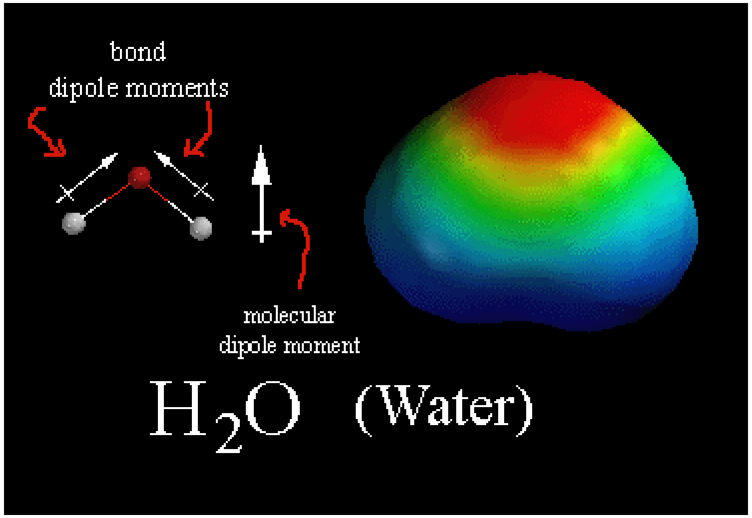
Symmetrical stretch

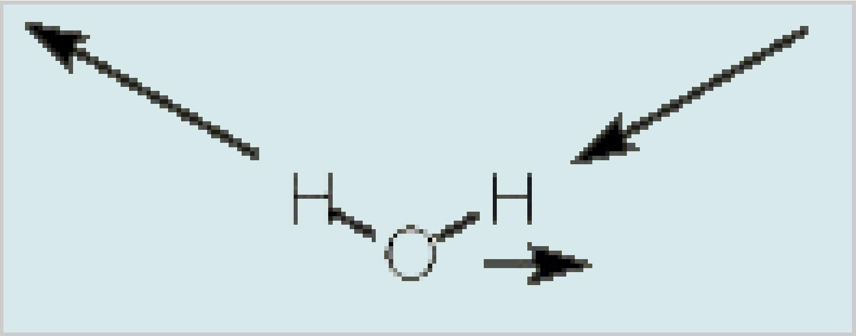
- In this mode the dipole moment for the molecule does not change in direction, but it does change in magnitude. As the molecule stretches, the dipole moment increases. So the dipole moment changes and it does so along the z-axis. **This vibration is IR active**





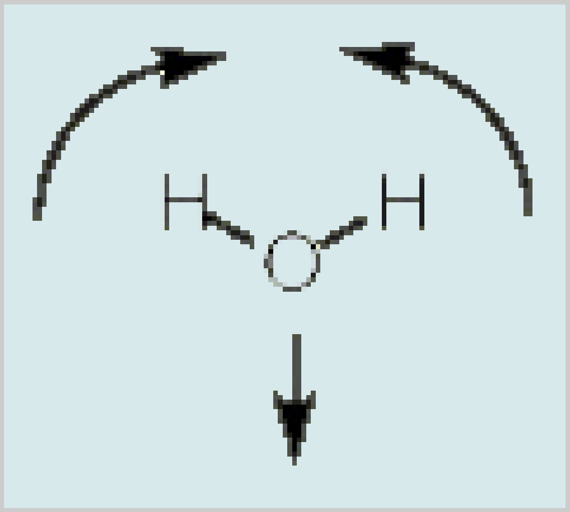
Asymmetric stretch

- In this mode, both the direction and magnitude of the dipole moment are changing. The dipole moment switches from left to right. **This mode is also IR active.**



Bending mode

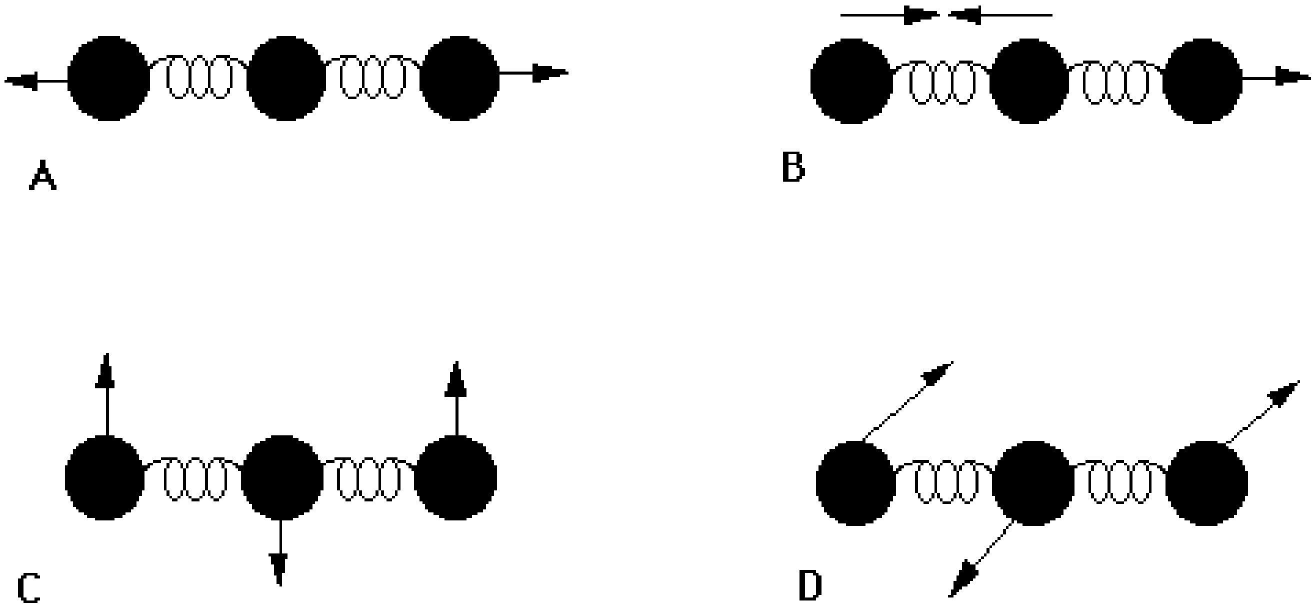
- In this bending (scissoring) mode, the dipole does not change direction. It is still pointed along the z-axis, but it does change in magnitude (increasing with the bend). Thus, **this mode is also IR active.**



What about CO_2?

- Linear Molecule! **O=C=O**

  Vibrational states: 3n-5 = 3*3-5= 4



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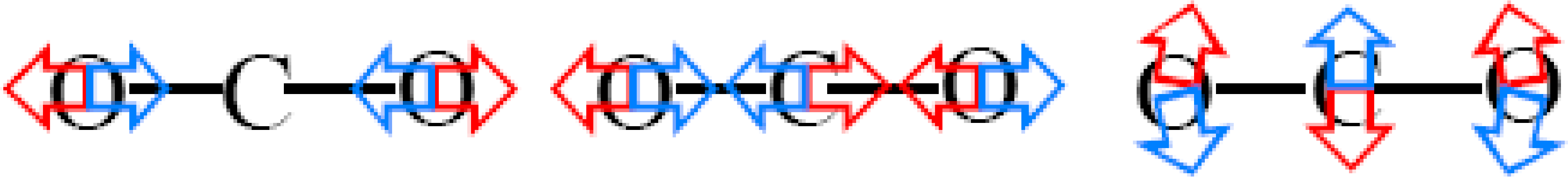
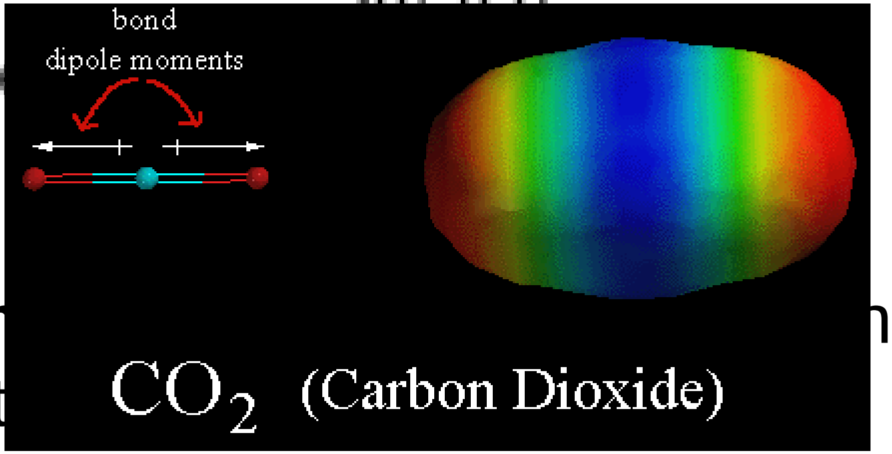
What about CO_2?

- Symmetric and asymmetric stretch and bend: IR and/or Raman active?



dipole moment.



The bending m ndicular to the

molecular axis t

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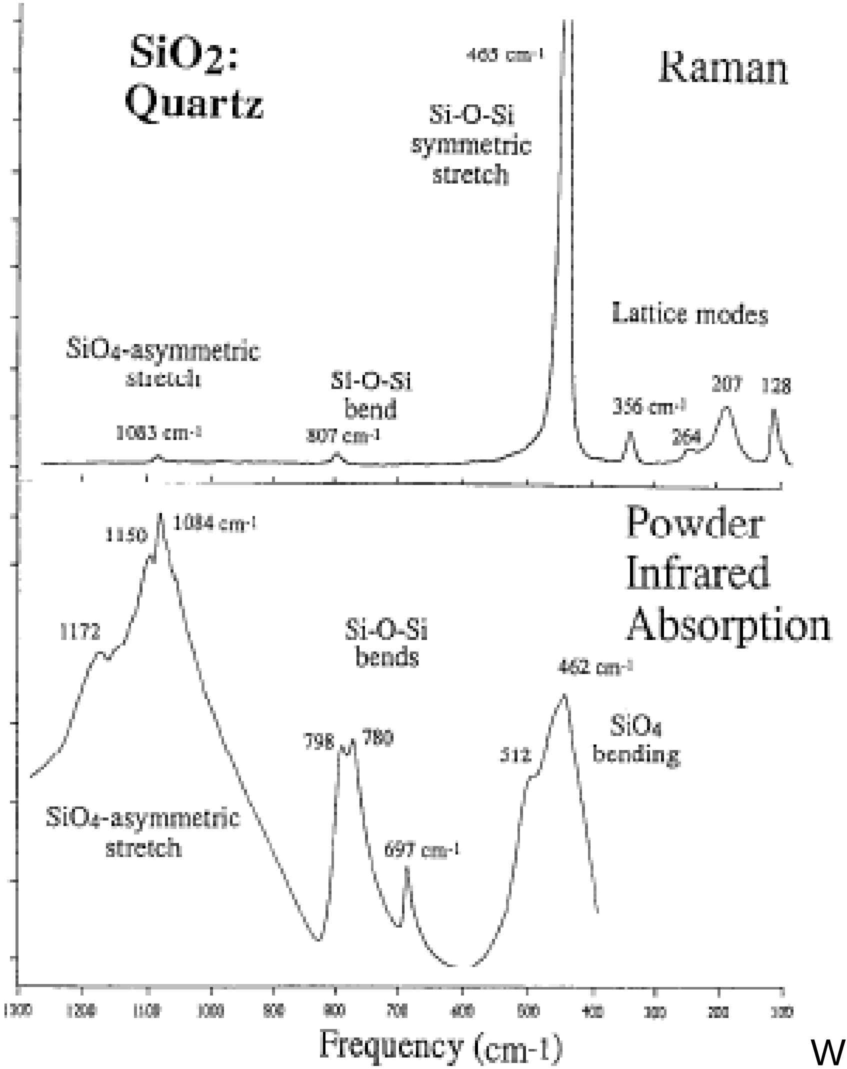
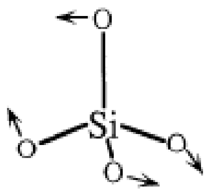
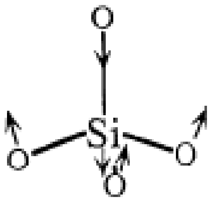
Example: SiO_2

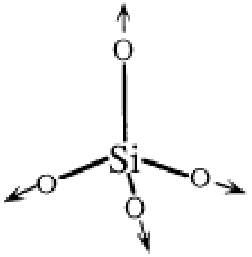




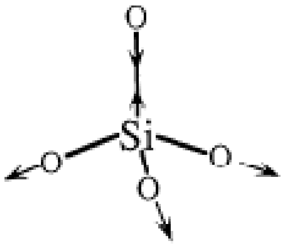
ν_2-symmetric bend
300-500 cm^{-1}
Present in Raman



ν_4-asymmetric bend
400-600 cm^{-1}
Infrared, Raman



ν_1-symmetric stretch
800-950 cm^{-1}
Raman (often strong)



ν_3-asymmetric stretch
850-1200 cm^{-1}
Infrared (strong), Raman

Q. Williams, University of California, Santa Cruz, Institute of Tectonics, Mineral Physics Laboratory, Santa Cruz, CA 95064

Mineral Physics and Crystallography
A Handbook of Physical Constants
AGU Reference Shelf 2

Website: http://www.agu.org/reference/minphys/18_williams.pdf

Theory: Hooke’s law

- the frequency of the vibration of the spring is related to the mass and the force constant of the spring,***k***, by the following formula:

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

where ***k*** is the force constant, ***m*** is the mass, v is the frequency of the vibration

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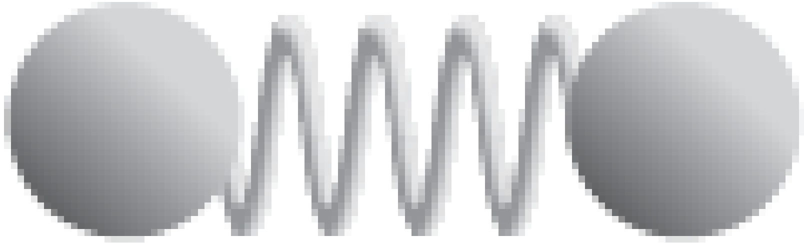
Theory: Hooke's law

- The stretching frequency of a bond can be approximated by Hooke's Law.
- In this approximation, two atoms and the connecting bond are treated as a simple harmonic oscillator composed of 2 masses (atoms) joined by a spring:



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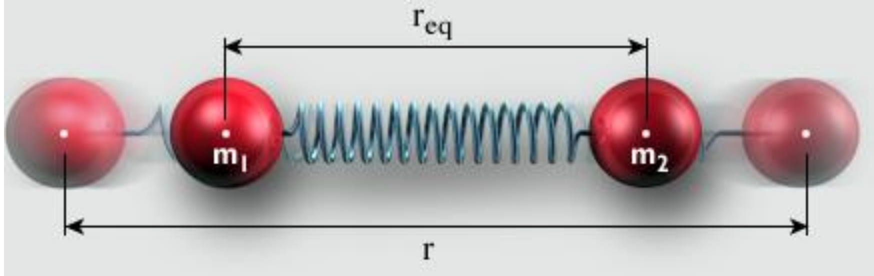
Theory: Classical vibrational Frequency for a diatomic molecule

- Diatomic molecule is represented by 2 masses: m_1 and m_2, connected by a massless spring. *For simplicity, the masses may be allowed to move only along the molecular axis*
- The displacement of each mass from equilibrium along the axis is X_1 and X_2. In this case, (X_2-X_1) is the amount the bond length differs from the equilibrium length.



Theory: Classical vibrational Frequency for a diatomic molecule

- **Each mass will experience a force equal to a constant F.**

$$F(X_2 - X_1) = m_1 \frac{d^2 X_1}{dt^2} \qquad -F(X_2 - X_1) = m_2 \frac{d^2 X_2}{dt^2}$$

Acceleration along the X axis

$$X = \cos(\varpi t) \qquad \frac{dX}{dt} = -\omega \sin(\omega t) \qquad \frac{d^2 X}{dt^2} = -\omega^2 \cos(\omega t)$$

Theory: Classical vibrational Frequency for a diatomic molecule

- If we increase the time t by one period (1/ν) from some initial time t_0 to (t_0+ 1/ν), the cosine function for X will go through 1 cycle and repeat itself. After one cycle:

$$X = \cos(\varpi(t_0 + 1/\nu)) = \cos(\varpi t_0 + 2\pi)$$

- We must add a constant A to define the maximum amplitude of the cosine function and a phase α to define the cosine angle when t = 0

$$X_1 = A_1 \cos(2\pi\nu t + \alpha) \qquad X_2 = A_2 \cos(2\pi\nu t + \alpha)$$

$$\frac{d^2 X_1}{dt^2} = -A_1 4\pi^2 \upsilon^2 \cos(2\pi\nu t + \alpha) \qquad \frac{d^2 X_2}{dt^2} = -A_2 4\pi^2 \upsilon^2 \cos(2\pi\nu t + \alpha)$$

Theory: Classical vibrational Frequency for a diatomic molecule

$$\begin{tikzcd}
F(X_2 - X_1) = m_1 \dfrac{d^2 X_1}{dt^2} \arrow[d] & -F(X_2 - X_1) = m_2 \dfrac{d^2 X_2}{dt^2} \arrow[d] \\
F(A_2 - A_1) = -m_1 A_1 4\pi^2\nu^2 \arrow[d] & F(A_2 - A_1) = m_2 A_2 4\pi^2\nu^2 \arrow[d] \\
\dfrac{A_1}{A_2} = \dfrac{F}{F - m_1 4\pi^2\nu^2} & \dfrac{A_1}{A_2} = \dfrac{F - m_2 4\pi^2\nu^2}{F}
\end{tikzcd}$$

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Theory: Classical vibrational Frequency for a diatomic molecule

$$\begin{tikzcd}
\frac{A_1}{A_2} = \frac{F}{F - m_1 4\pi^2\nu^2} \arrow[dr] & & \frac{A_1}{A_2} = \frac{F - m_2 4\pi^2\nu^2}{F} \arrow[dl] \\
& 16\pi^4 m_1 m_2 \nu^4 - 4\pi^2 F(m_1 + m_2)\nu^2 + F^2 = F^2 \arrow[dl] & \\
\nu^4 = \nu^2\left(\frac{F(m_1 + m_2)}{4\pi^2 m_1 m_2}\right) \arrow[rr] & & \nu = \frac{1}{2\pi}\sqrt{F\left(\frac{1}{m_1} + \frac{1}{m_2}\right)}
\end{tikzcd}$$

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Theory: Classical vibrational Frequency for a diatomic molecule

- Same equation with reduced mass

$$\nu = \frac{1}{2\pi}\sqrt{\frac{F}{u}}$$

with

$$u = \frac{m_1 m_2}{m_1 + m_2}$$

With F the force constant indicating the strength of the bond

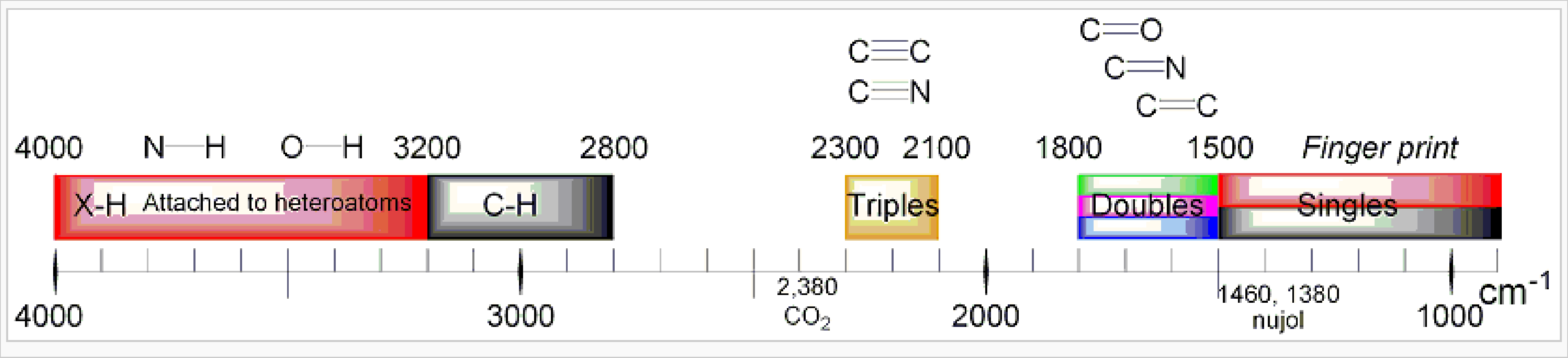
• If there is a high value of F, i.e. **the bond is strong, it absorbs a higher frequency of light.**

• **The larger the two masses, the lower the frequency of light absorbed.**

Examples

- Which molecule has higher vibration?

1. N_2, O_2 or F_2

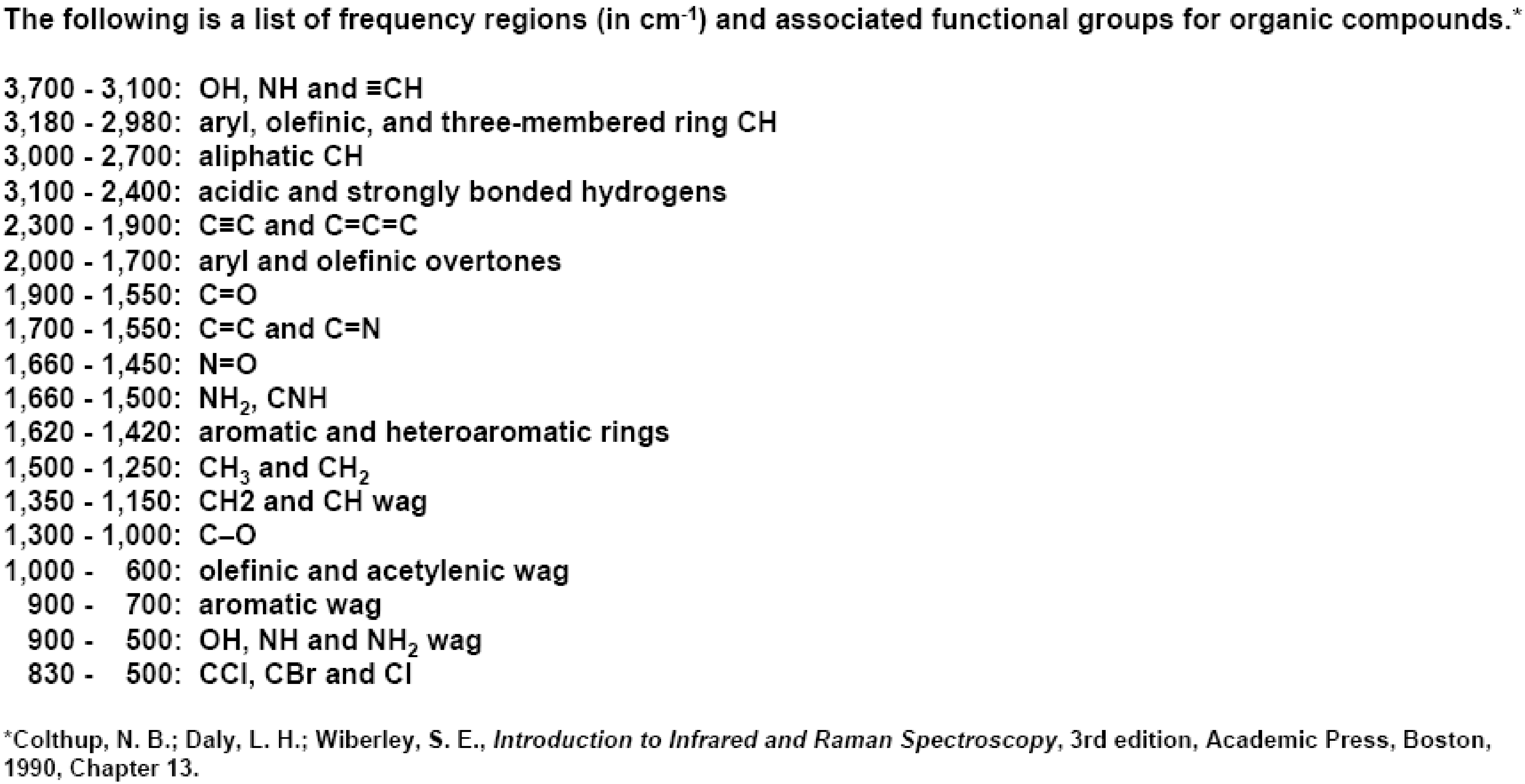


892 cm^{-1}

2. HF is 3,960 cm^{-1} (strong bond) and NaCl is 378 cm^{-1} (weak bond).

Higher!

Examples



The following is a list of frequency regions (in cm^{-1}) and associated functional groups for organic compounds.*

3,700 - 3,100: OH, NH and ≡CH
3,180 - 2,980: aryl, olefinic, and three-membered ring CH
3,000 - 2,700: aliphatic CH
3,100 - 2,400: acidic and strongly bonded hydrogens
2,300 - 1,900: C≡C and C=C=C
2,000 - 1,700: aryl and olefinic overtones
1,900 - 1,550: C=O
1,700 - 1,550: C=C and C=N
1,660 - 1,450: N=O
1,660 - 1,500: NH_2, CNH
1,620 - 1,420: aromatic and heteroaromatic rings
1,500 - 1,250: CH_3 and CH_2
1,350 - 1,150: CH2 and CH wag
1,300 - 1,000: C–O
1,000 - 600: olefinic and acetylenic wag
900 - 700: aromatic wag
900 - 500: OH, NH and NH_2 wag
830 - 500: CCl, CBr and Cl

*Colthup, N. B.; Daly, L. H.; Wiberley, S. E., *Introduction to Infrared and Raman Spectroscopy*, 3rd edition, Academic Press, Boston, 1990, Chapter 13.

In real life!

- If there are more atoms, there will be more bonds. More complex molecules may have many bonds, and vibrations can be conjugated, leading to infrared absorptions at characteristic frequencies that may be related to chemical groups. This will produce a more complicated spectrum.

- When unknown compounds are analyzed, a full spectrum is normally run. The goal is to identify the **presence of a particular functional group and determine its location on a known molecule**

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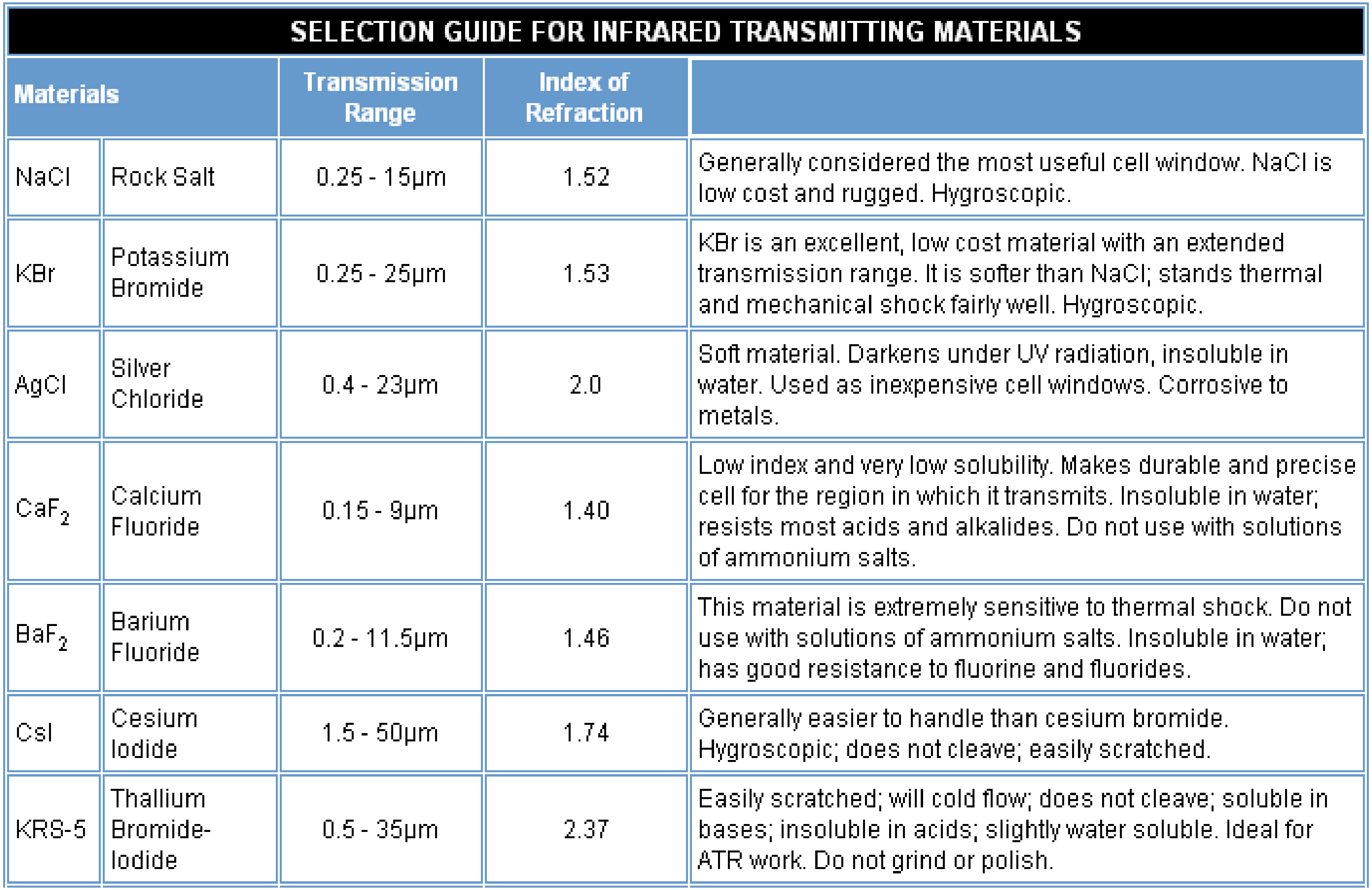
Measurement of IR spectra

- IR spectra are acquired on a special instrument, called an **IR spectrometer**.
- IR is used both to gather information about the structure of a compound and as an analytical tool to assess the purity of a compound or the structure of the glasses
- IR spectra are quick and easy to run
- Cells for holding samples must be made of infrared transmitting material.

Infrared transmitting materials



SELECTION GUIDE FOR INFRARED TRANSMITTING MATERIALS

Materials		Transmission Range	Index of Refraction	
NaCl	Rock Salt	0.25 - 15μm	1.52	Generally considered the most useful cell window. NaCl is low cost and rugged. Hygroscopic.
KBr	Potassium Bromide	0.25 - 25μm	1.53	KBr is an excellent, low cost material with an extended transmission range. It is softer than NaCl; stands thermal and mechanical shock fairly well. Hygroscopic.
AgCl	Silver Chloride	0.4 - 23μm	2.0	Soft material. Darkens under UV radiation, insoluble in water. Used as inexpensive cell windows. Corrosive to metals.
CaF_2	Calcium Fluoride	0.15 - 9μm	1.40	Low index and very low solubility. Makes durable and precise cell for the region in which it transmits. Insoluble in water; resists most acids and alkalides. Do not use with solutions of ammonium salts.
BaF_2	Barium Fluoride	0.2 - 11.5μm	1.46	This material is extremely sensitive to thermal shock. Do not use with solutions of ammonium salts. Insoluble in water; has good resistance to fluorine and fluorides.
CsI	Cesium Iodide	1.5 - 50μm	1.74	Generally easier to handle than cesium bromide. Hygroscopic; does not cleave; easily scratched.
KRS-5	Thallium Bromide-Iodide	0.5 - 35μm	2.37	Easily scratched; will cold flow; does not cleave; soluble in bases; insoluble in acids; slightly water soluble. Ideal for ATR work. Do not grind or polish.

Infrared transmitting materials

- Some of the most useful window materials for the IR are quite soluble in water: NaCl, KCl, KBr, CsBr and CsI

- A typical cell for liquid which is made of NaCl has a transmission that starts to drop at about 700cm^{-1}, is roughly 50% at 600cm^{-1} and is nearly opaque at 500cm^{-1}.

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Sample Requirements

- The detection limit for routine analysis is ~0.1 wt%; under ideal conditions greater sensitivity can be achieved
- Typically only a few milligrams of material are needed for analysis.
- Samples may be in liquid, solid, or gaseous form.

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Preparation of the samples: gas

- Gaseous samples require little preparation beyond purification!
- To obtain an infrared spectrum of a gas requires the use of a cylindrical gas cell with windows at each end composed of an infrared inactive material such as KBr, NaCl or CaF_2. The cell usually has an inlet and outlet port with a tap to enable the cell to be easily filled with the gas to be analyzed.

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Preparation of the samples: liquid

- Sandwiched between two plates of a high purity salt (commonly sodium chloride, or common salt, although a number of other salts such as potassium bromide or calcium fluoride are also used).
- The plates are transparent to the infrared light (not introduce any lines onto the spectra).

Preparation of the samples: solid

- Solid samples can be prepared in two major ways.

1) Crush the sample with a mulling agent (usually nujol) in a marble or agate mortar, with a pestle. **A thin film** of the mull is applied onto salt plates and measured.

2) Grind a quantity of the sample with a specially purified salt (usually potassium bromide) finely (to remove scattering effects from large crystals). This powder mixture is then crushed in a mechanical die press to form a translucent pellet through which the beam of the spectrometer can pass.

Samples dispersed in powder must be homogenously dispersed, with a particle size small enough not to cause scatter (theoretically < 2 microns).

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VIBRATIONAL SPECTROSCOPY STUDIES OF GLASS STRUCTURE: IR spectroscopy

Infrared spectroscopy is widely used in both research and industry as a simple and reliable technique for measurement, quality control, and dynamic measurement.

Lecture #2

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Instruction for the quiz: Feb 9th

- bb.clemson.edu
- Log in between 9am and 6pm (East time)
- Go to Course documents
- Select the test **only if you are ready to begin**
- It is a 1 hour quiz, closed books

- **As soon as you enter in the test, you can not save your data and finish later**

- Don’t forget to submit when you are done
- Email me when you are done

Answer questions: definition mulling agent and nujol

A technique of sample preparation: the sample is ground, then dispersed in an oil or mulling agent. The mixture is then sandwiched between two KBr windows and placed in the infrared beam for analysis.

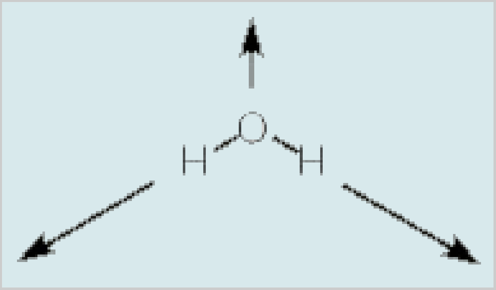
- **A mull** can be described as a suspension of a solid in a liquid. Under these conditions, light can be transmitted through the sample to afford an acceptable infrared spectrum.

Nujol, or mineral oil, is a long chain hydrocarbon. Most solids do not dissolve in this medium but can be ground up in its presence. A small mortar and pestle is used for this purpose..

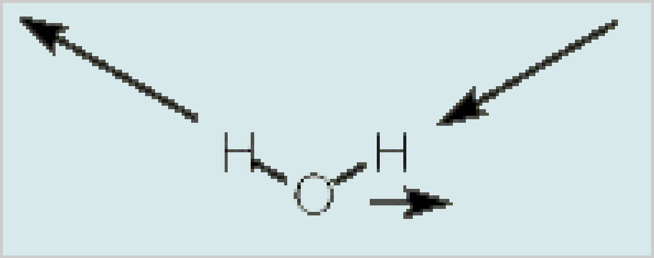
- **The major disadvantage of using a Nujol mull** is that the information in the C-H stretching region is lost because of the absorptions of the mulling agent. To eliminate this problem, it may be necessary to run a second spectrum in a different mulling agent that does not contain any C-H bonds. **Typical mulling agents** that are used for this purpose are perfluoro- or perchlorohydrocarbons. Examples include perchlorobutadiene, perfluorokerosene or a perfluorohydrocarbon oil

Water

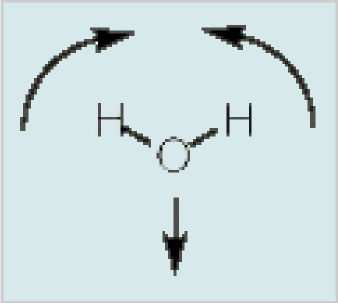
Symmetrical stretch



Asymmetric stretch

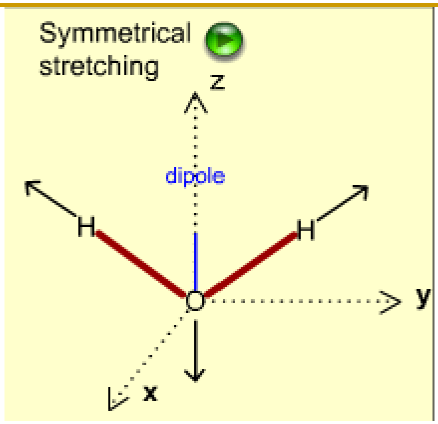


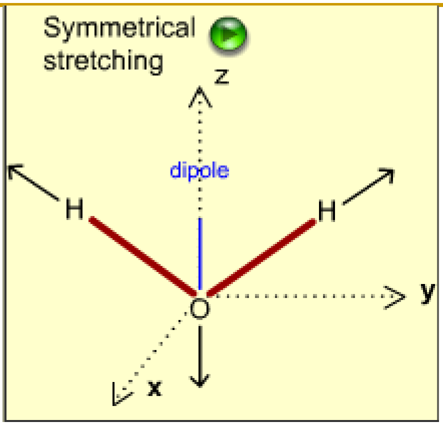
Bending mode

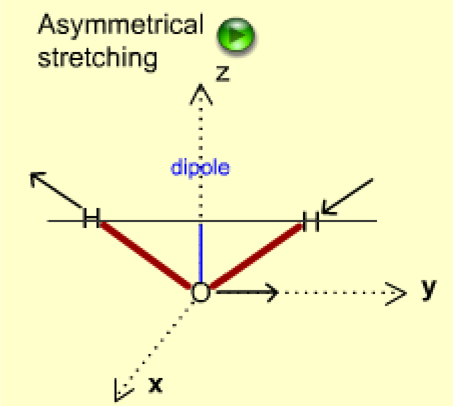


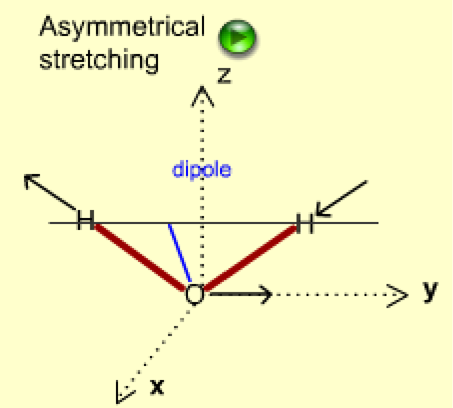
IR active: change of dipole moment
&
Raman active: change in electronic polarizability

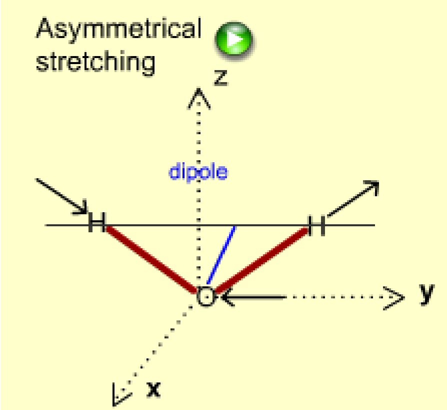
Water

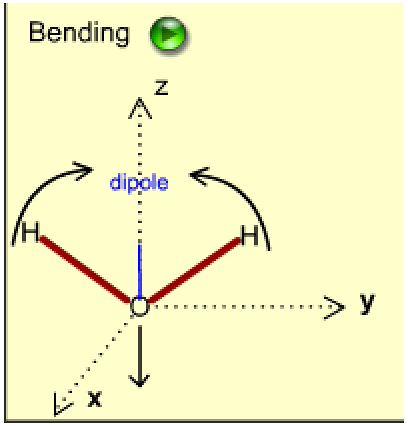


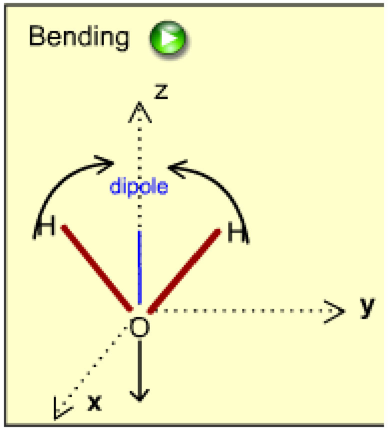












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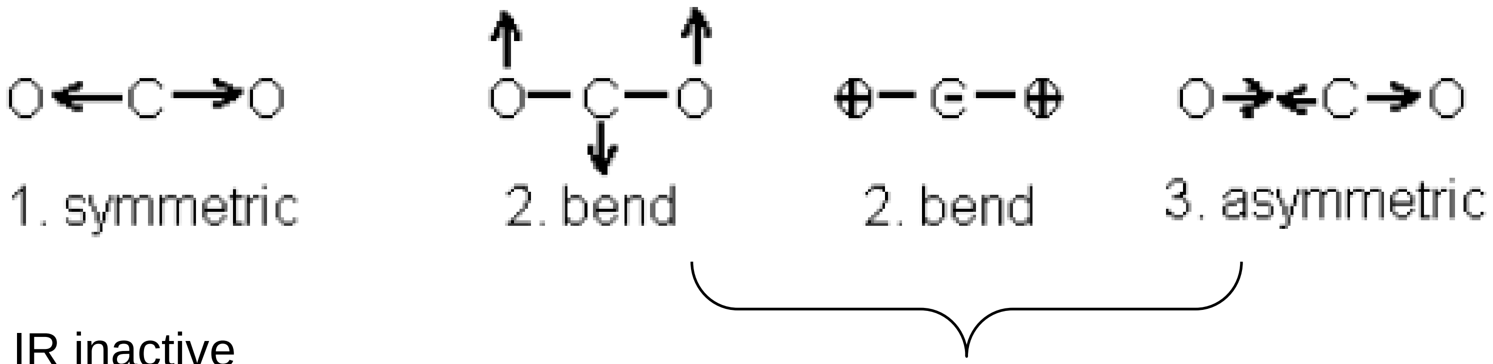
CO_2

- **CO_2 does not have a permanent dipole since the "center of gravity" for the positive charge overlays that for the negative charge.**
- **When a molecule has a center of symmetry Raman active vibrations are those that maintain the center of symmetry.**



IR inactive
Raman active

IR active
Raman inactive

The CO_2 molecule has a center of symmetry located at the carbon atom and so obeys the exclusion rule, “In a centrosymmetric molecule no Raman-active molecule is also infrared-active and no infrared-active vibration is also Raman active.”

Cotton, F. A. *Chemical Applications of Group Theory*, 3rd ed., John Wiley & Sons, Inc., New York: 1990, pages 338-340.

Summary

- Spectroscopy is the study of the interaction of electromagnetic radiation with a chemical substance.
- **When radiation passes through a sample (solid, liquid or gas), certain frequencies of the radiation are absorbed by the molecules of the substance leading to the molecular vibrations.**
- The frequencies of absorbed radiation are unique for each molecule which provide the characteristics of a substance.

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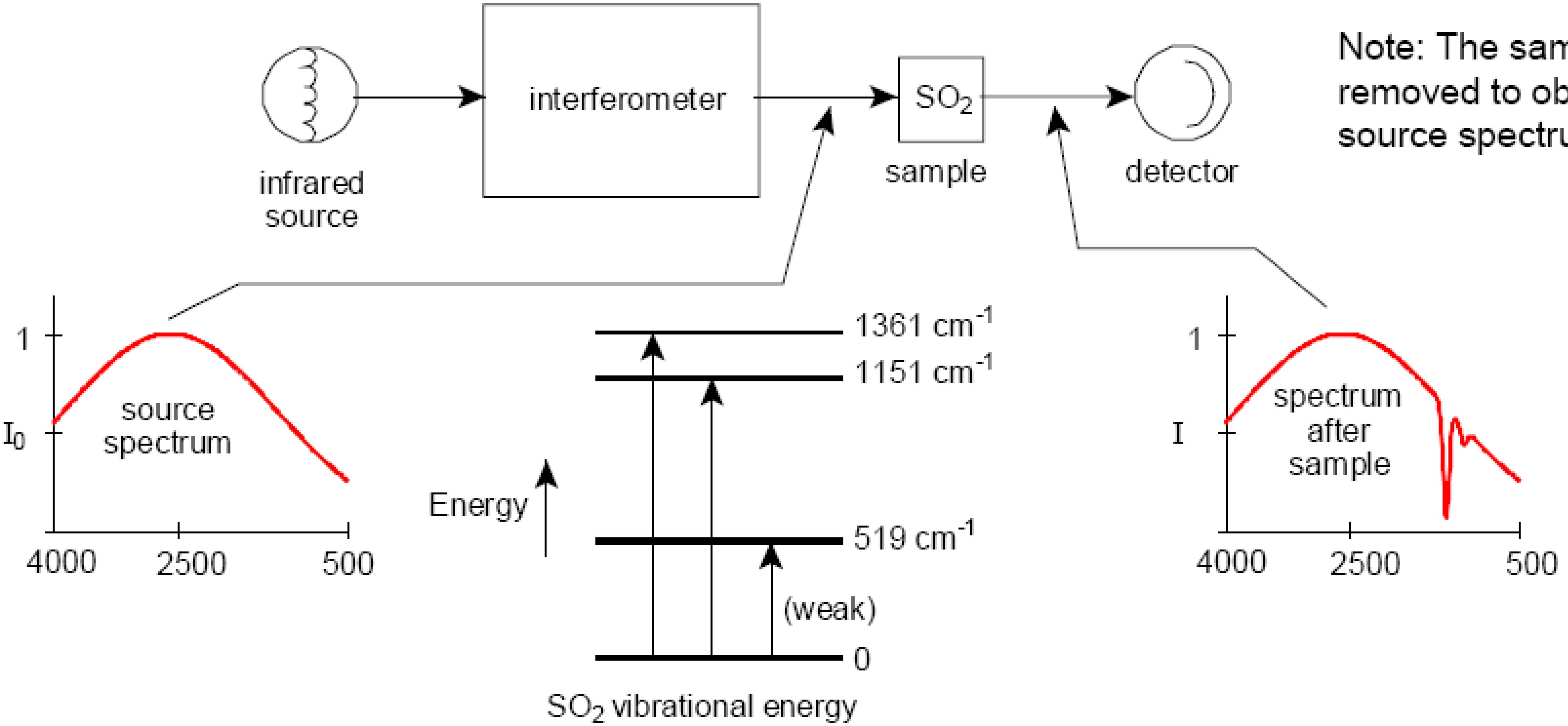
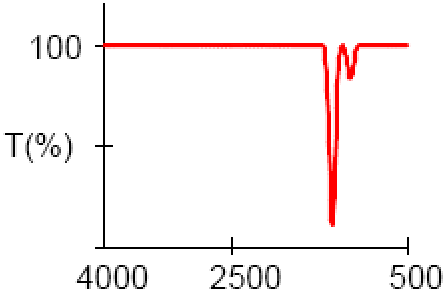
Typical method for transmittance measurement



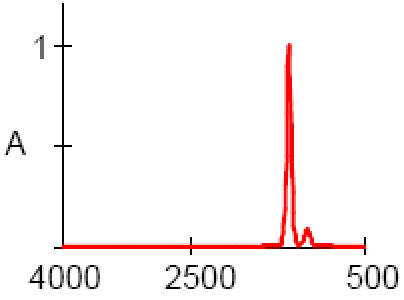
Note: The sample is removed to obtain the source spectrum.

$$T(\lambda) = \frac{I(\lambda)}{I_0(\lambda)}$$



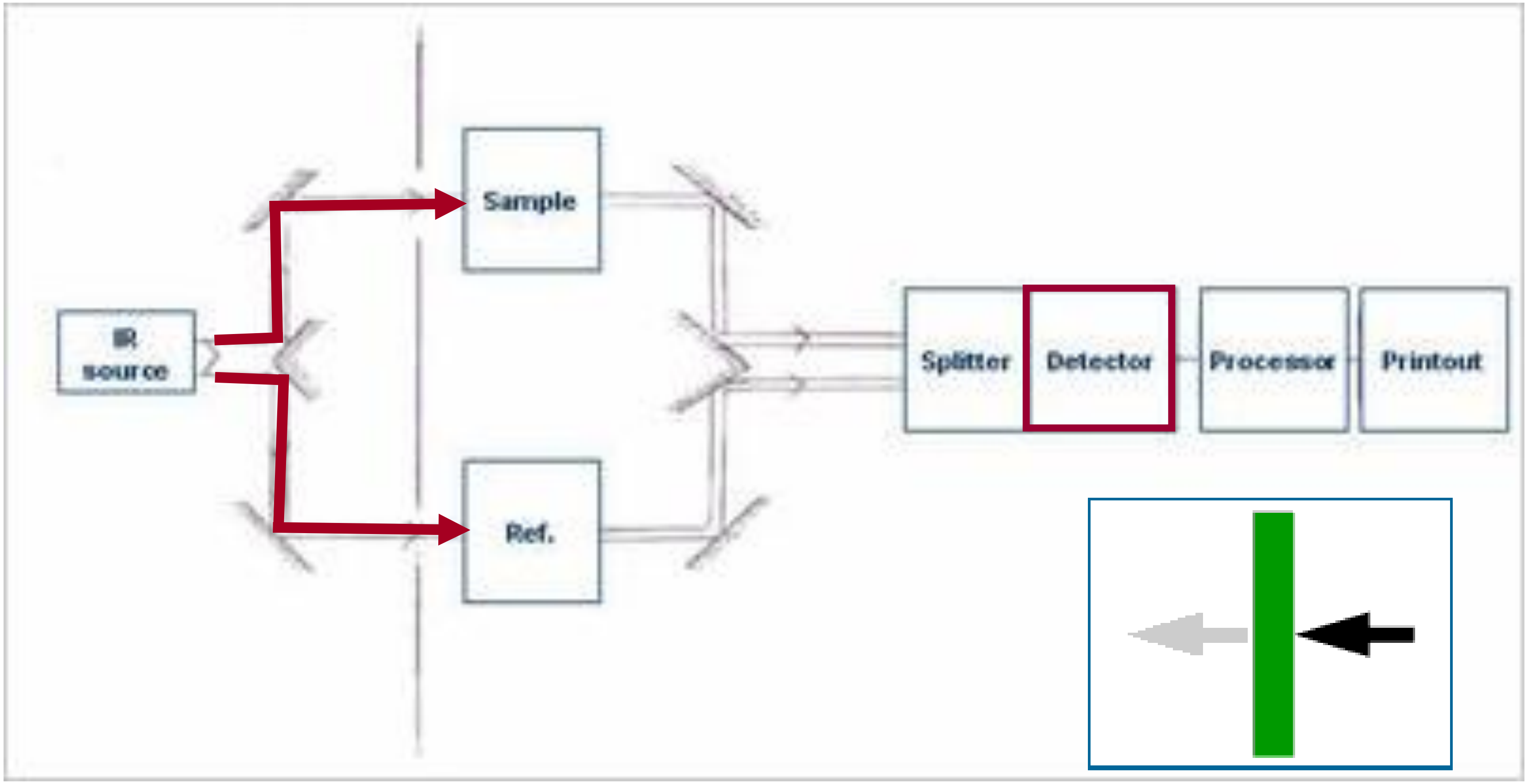
infrared transmission spectrum

$$A(\lambda) = \log\left(\frac{1}{T(\lambda)}\right)$$



infrared absorption spectrum

Typical method for transmittance measurement



Typical method for measurement

- A beam of infra-red light is produced and split into two separate beams. One is passed through the sample, the other passed through a reference which is often the substance the sample is dissolved in.
- **The beams are both reflected back towards a detector,** however first they pass through a splitter which quickly alternates which of the two beams enters the detector. The two signals are then compared and a printout is obtained.
- *A reference can be used for two reasons:*

i) This prevents fluctuations in the output of the source affecting the data

ii) This allows the effects of the solvent to be cancelled out (the reference is usually a pure form of the solvent the sample is in)