



CHEM F111 : General Chemistry

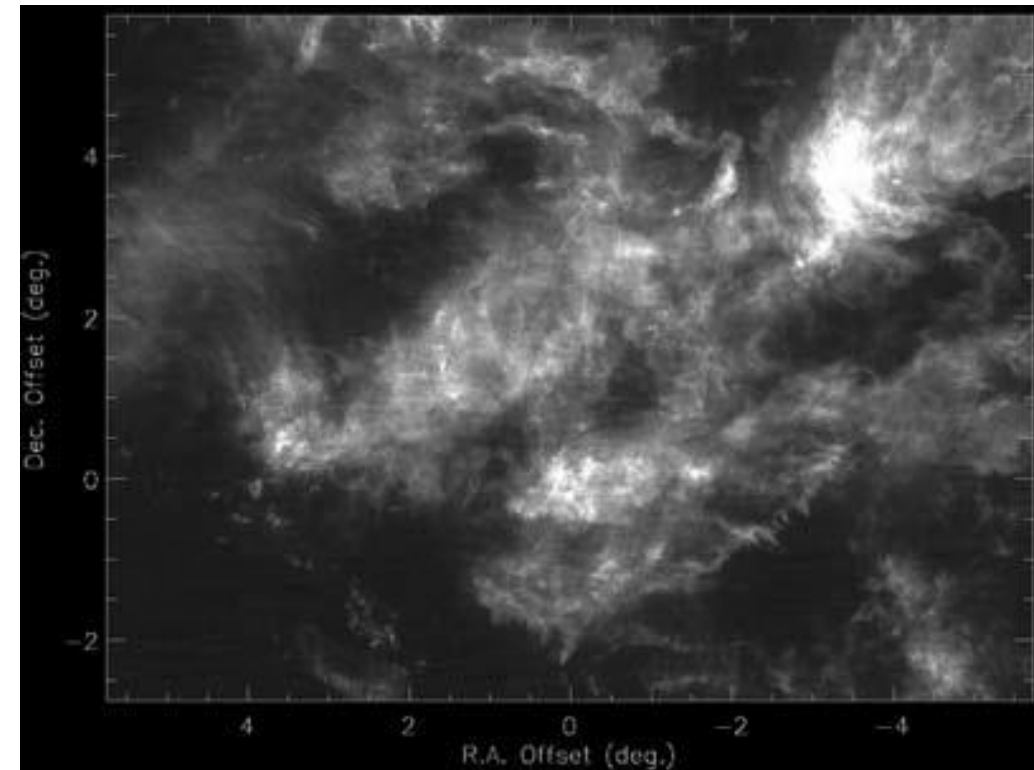
Semester II: AY 2017-18

Lecture-15, 14-02-2018

Mapping clouds of molecules in interstellar medium



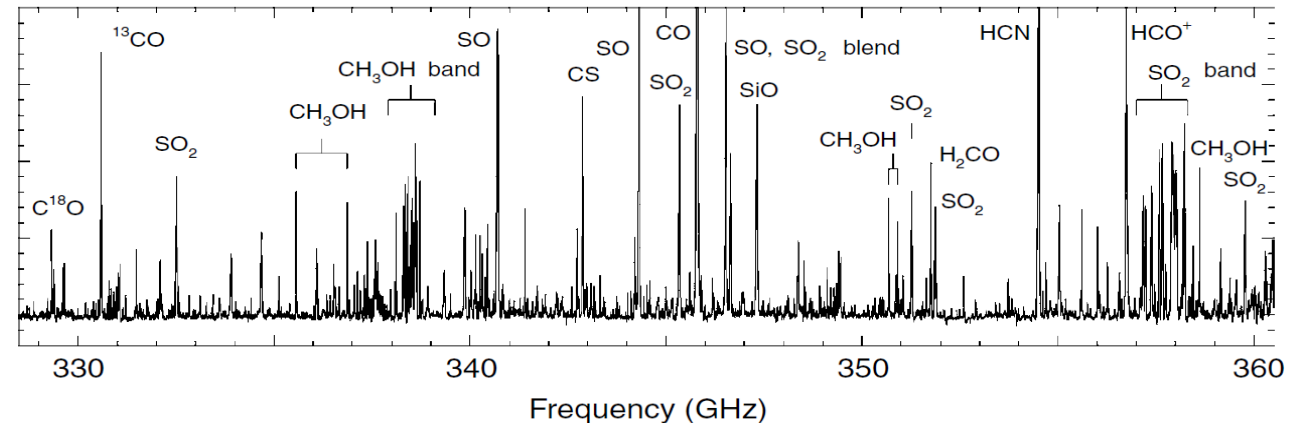
Microwave and millimeter wave astronomy: Microwave identification of molecules



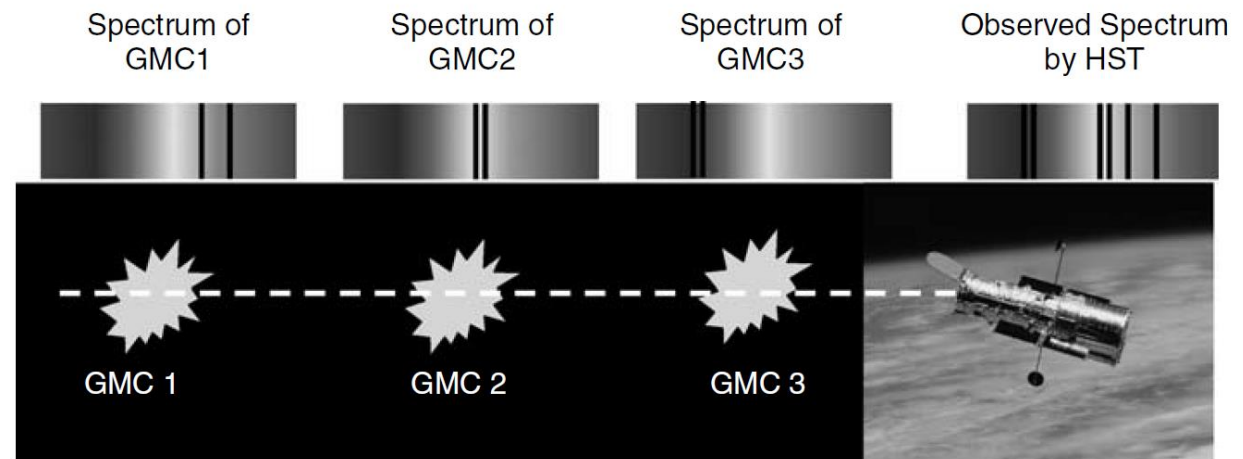
Taurus molecular cloud observed at 115 GHz
 ^{12}CO emission ($J = 1 - 0$)

*****Not part of the Syllabus*****

{Source: Astrochemistry from Astronomy to Astrobiology, by Andrew M. Shaw, Wiley}



Microwave spectrum of the Orion nebula



Line of sight through three Giant Molecular Clouds to the Hubble Space Telescope

Notice for Quiz-02

Quiz-02 will be conducted during **15-02-2018** (Thursday) to **20-02-2018** (Tuesday) in the regular Tutorial Classes.

Syllabus: **L-09 to L-15** according to Hand out, i.e. **Many Electron system to Vibrational Spectroscopy**.

EXTRA CLASS NOTICE for GENERAL CHEMISTRY TUTORIAL SECTION No. 5

- **ROOM NO: 3253**
- **Time 5.00 PM**
- **Date: 15-February 2018 (THURSDAY)**

INSTRUCTOR: Rajeev Sakhuja

Summary: L-14



Boltzmann population distribution:

$$\frac{N_j}{N_i} = \frac{g_j}{g_i} e^{-(E_j - E_i)/kT}, \quad k \text{ is Boltzmann's constant}$$

$N_i \Rightarrow$ Population in the i^{th} state and $g_i \Rightarrow$ degeneracy of the i^{th} state

Population in rotational states:

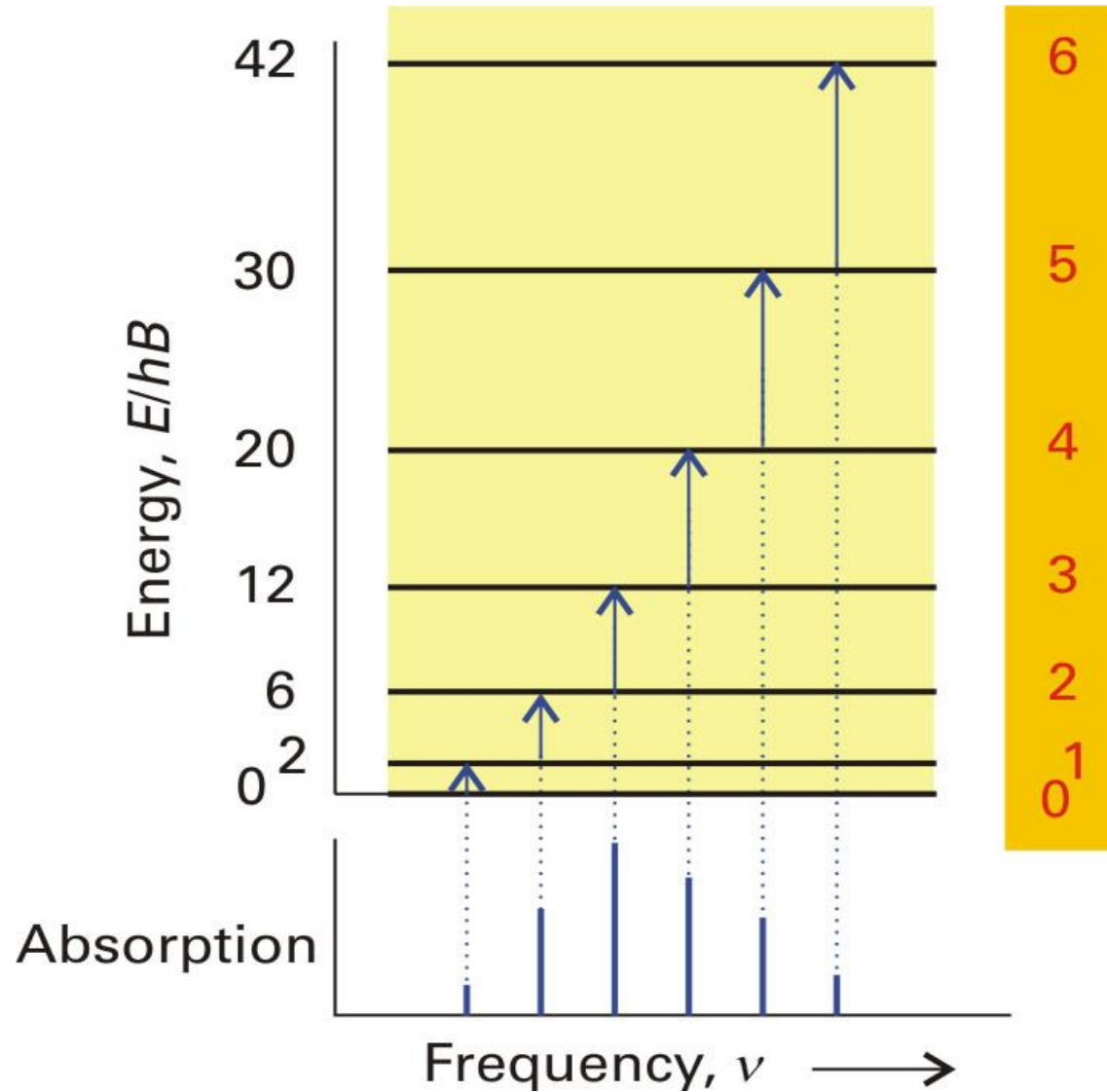
$$P_J = P_0 (2J + 1) e^{-hBJ(J+1)/KT} \quad J_{\max} = \left(\frac{KT}{2hB} \right)^{1/2} - 1/2$$

Rotational transitions – microwave spectroscopy

Gross selection rule: Molecule must be polar.

Specific selection rules: $\Delta J = \pm 1$

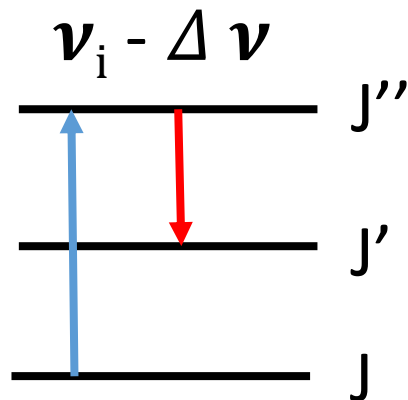
Summary: L-14



Summary: L-14

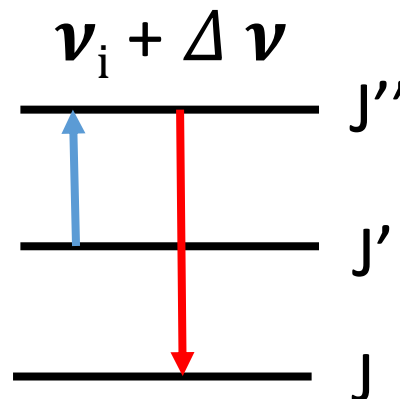


Case-I: Molecule gains energy, ΔE ; State changes from J to J' .



$$\nu' = \nu_i - \Delta \nu$$
$$\Rightarrow \nu_S = \nu_i - \frac{\Delta E}{h}$$

Stokes' radiation



Case-II: Molecule release energy, ΔE ; State changes from J'' to J' .

$$\nu'' = \nu_i + \Delta \nu$$
$$\Rightarrow \nu_{as} = \nu_i + \frac{\Delta E}{h}$$

Anti-Stokes' radiation

Pure rotational Raman Spectroscopy

Gross selection rule: $\frac{d\alpha}{dq} \neq 0$

Specific selection rule: $\Delta J = 0 \text{ or } \pm 2 \text{ only}$

Summary: L-14

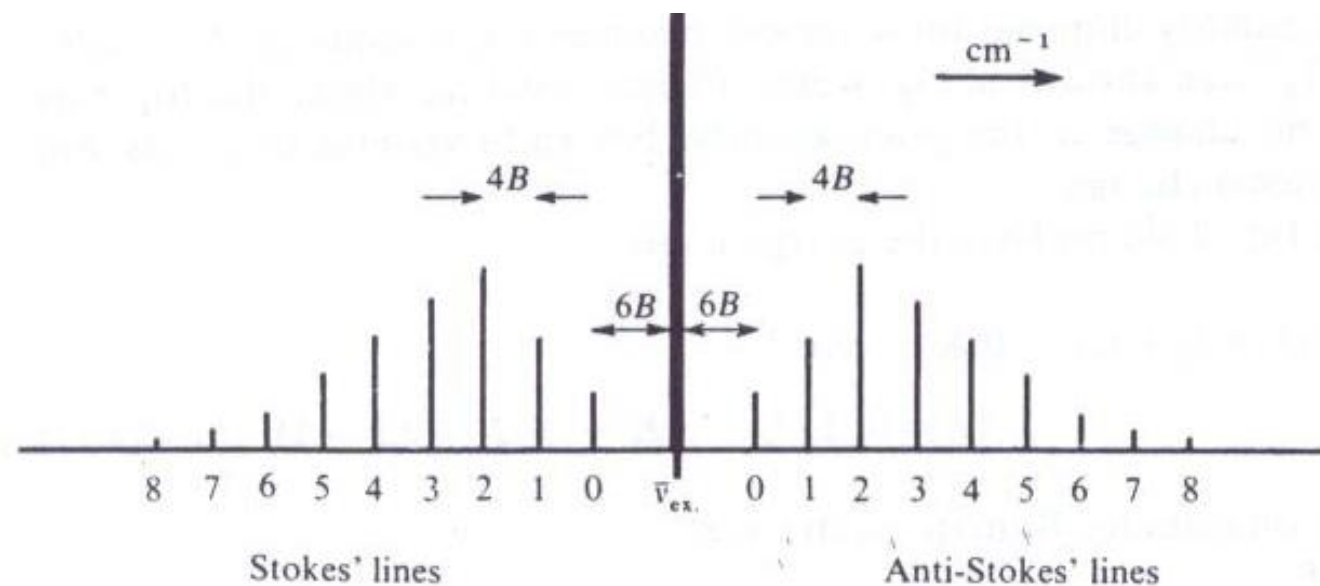
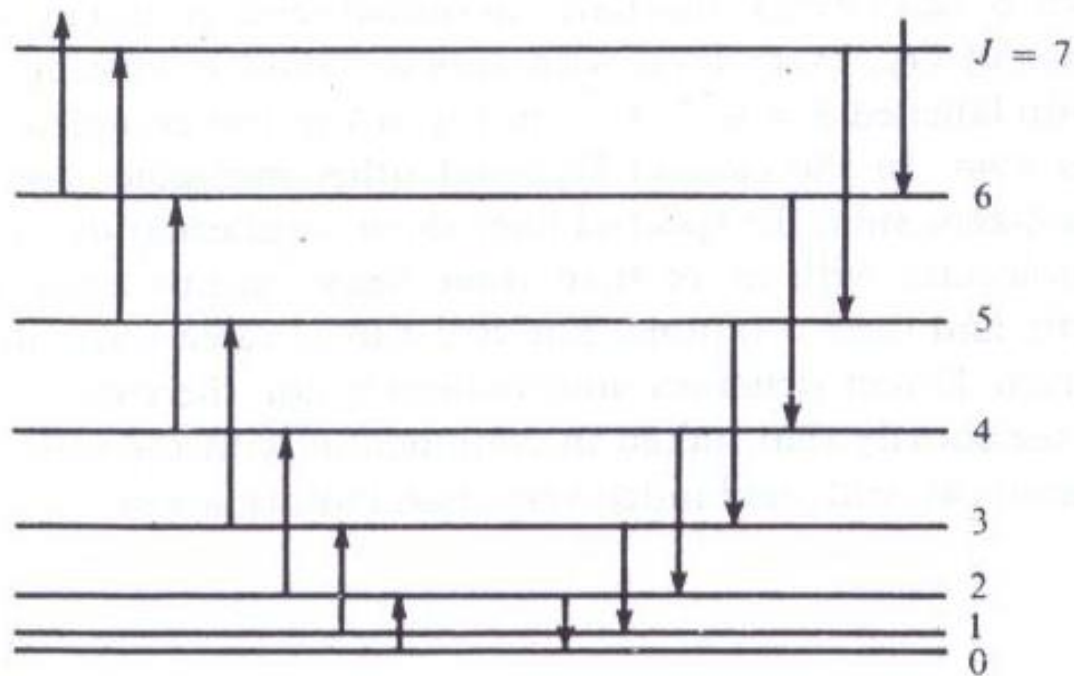
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$$\Delta \bar{\nu}_s = \bar{\nu}_{ex} - B(4J + 6) \text{ cm}^{-1}$$

$$\Delta \bar{\nu}_{as} = \bar{\nu}_{ex} + B(4J + 6) \text{ cm}^{-1}$$



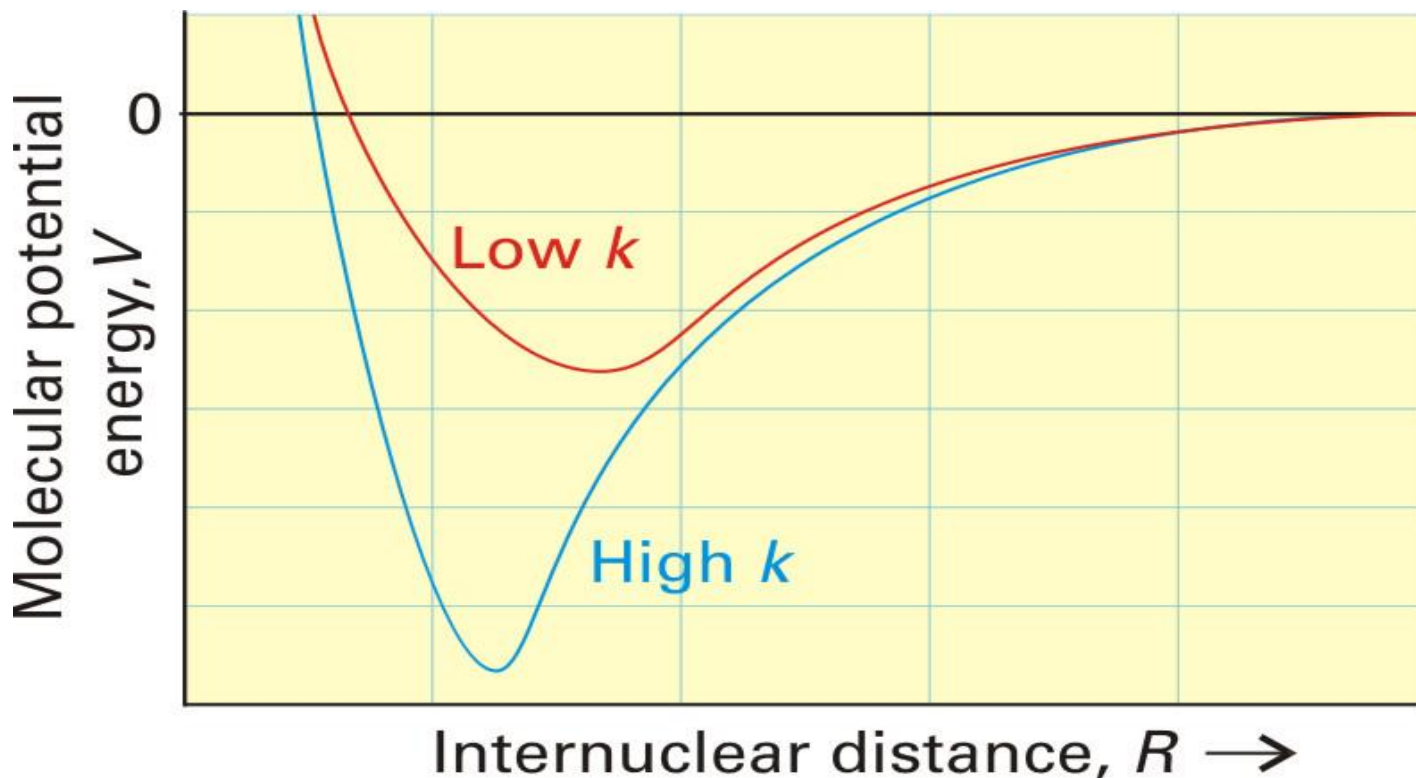
Intensity of Stoke's and anti-Stoke's lines?

Vibrational spectroscopy



Diatomic molecule: A-B $V = \frac{1}{2} k x^2 = \frac{1}{2} k (R - R_e)^2$

K: force constant with dimension N m^{-1}



In the harmonic approximation:

$$E_v = \left(v + \frac{1}{2} \right) h\nu; \quad v = 0, 1, 2, \dots$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}; \quad \mu = \frac{m_A m_B}{m_A + m_B}$$

In terms of wave number:

$$E_v = \left(v + \frac{1}{2} \right) hc\bar{\nu}, \quad v = 0, 1, 2, \dots$$

Vibrational spectroscopy – selection rules



Vibrational transitions: At frequencies of 10^{13} to 10^{14} Hz, infrared spectroscopy.

Transition probability $\propto \left| \int \Psi_n^* \hat{\mu} \Psi_m d\tau \right|^2$

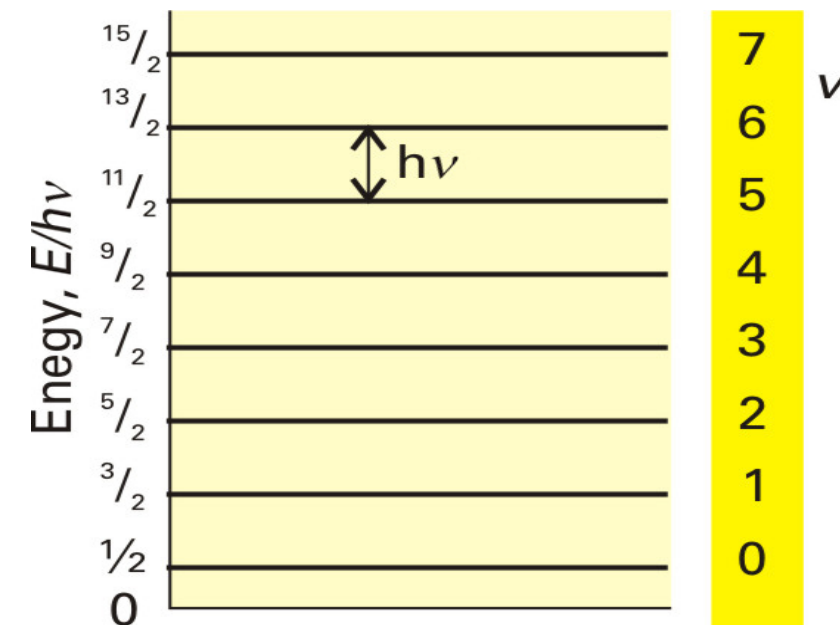
Gross selection rule: The electric dipole moment of the molecule must change during the vibration, $\frac{d\mu}{dq} \neq 0$

Dipole moment change during vibration allows interaction with electromagnetic interaction

Specific selection rule: $\Delta v = \pm 1$

$$\Delta E = h\nu$$

Most important transition from $v = 0$ to $v = 1$.



Homonuclear diatomics are IR inactive as Rotational inactive

Vibrational spectroscopy



A single oxygen atom is attached to a smooth metal surface. The atom vibrates at a frequency of $1.80 \times 10^{13} \text{ s}^{-1}$. Calculate its total energy for $n = 0, 1$, and 2 quantum no. states.

$$E (n=0) = 5.963 \times 10^{-21} \text{ J}$$

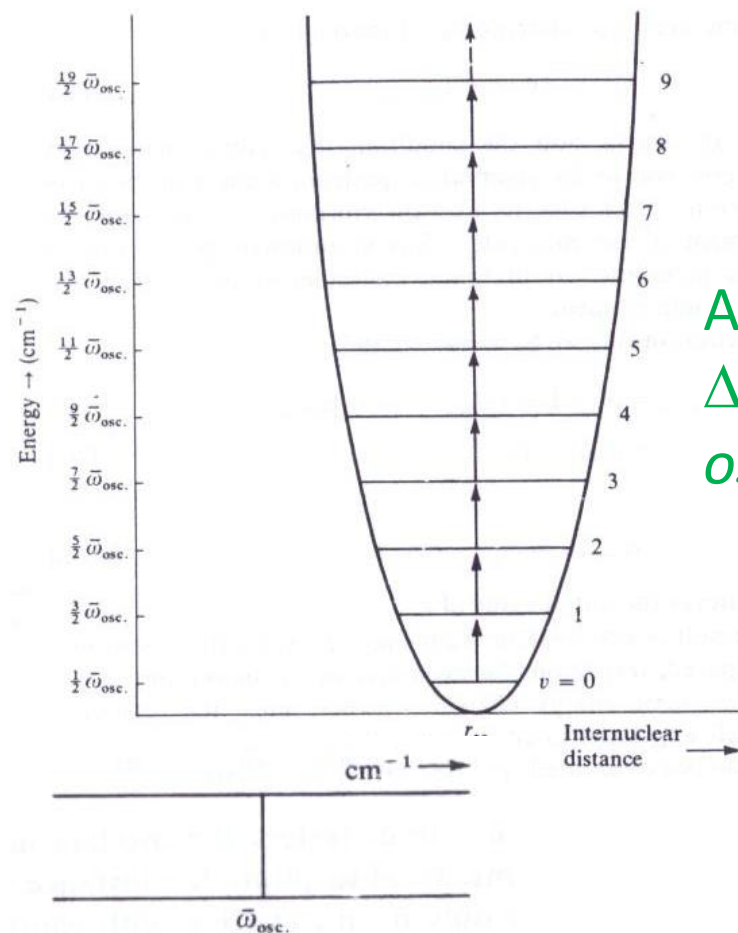
$$E (n=1) = 1.789 \times 10^{-20} \text{ J}$$

$$E (n=2) = 2.982 \times 10^{-20} \text{ J}$$

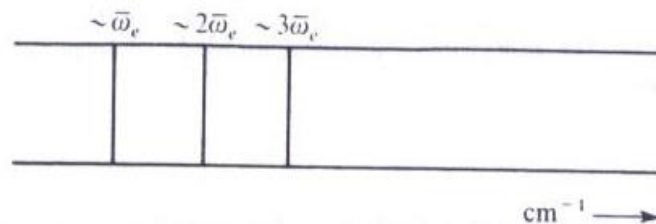
Calculate the wavelength of light necessary to excite a harmonic oscillator from one energy state to the adjacent state in the previous example. $16.66 \mu\text{m}$

Workout: For temperatures of 25°C and 1000°C , calculate the ratio of molecules in the typical excited vibrational energy level to that in the lowest energy level, assuming that the level is 1000 cm^{-1} above the lowest energy level.

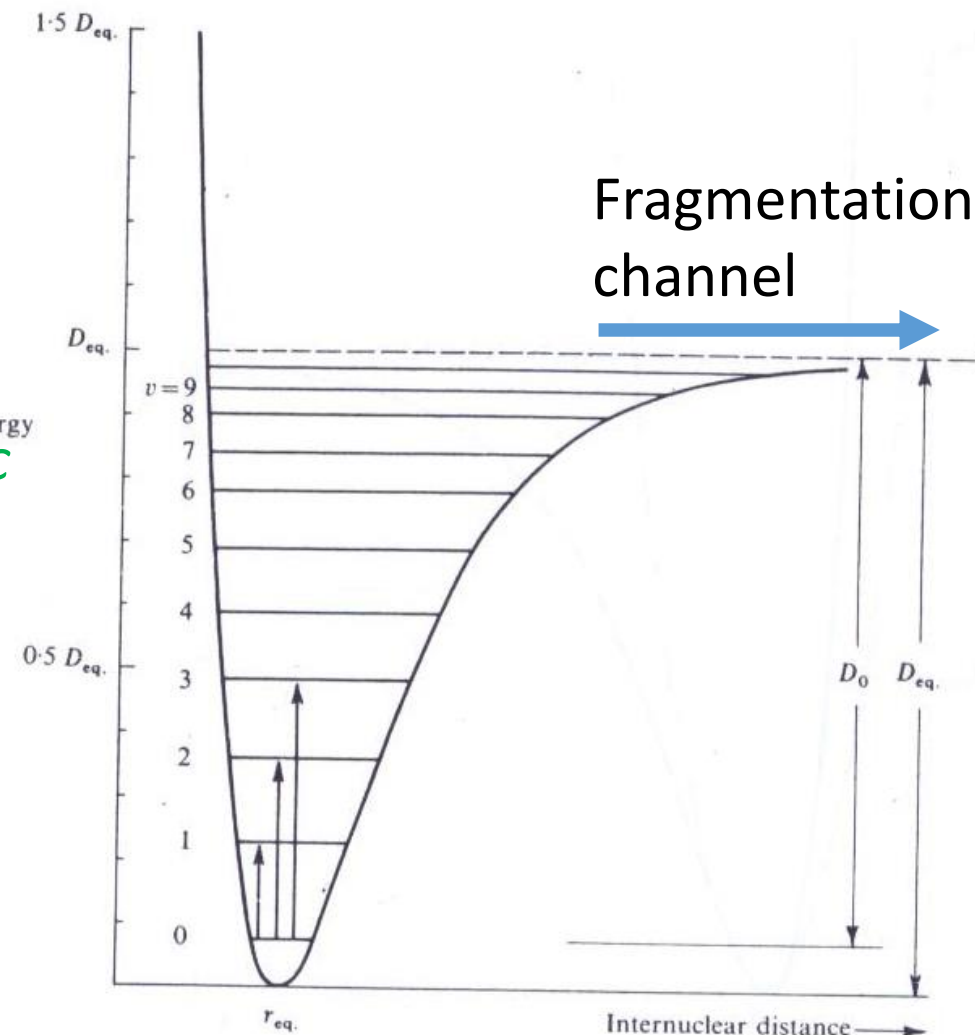
Anharmonicity



We obtain overtones as well



Additional weak transitions:
 $\Delta v = 2, 3, \dots$ for anharmonic oscillator



Anharmonicity:

$$E_v = (v + \frac{1}{2})hc\bar{\nu} - (v + \frac{1}{2})^2 hc\bar{\nu}x_e + \dots$$

x_e is anharmonicity constant

Can not break or make a bond

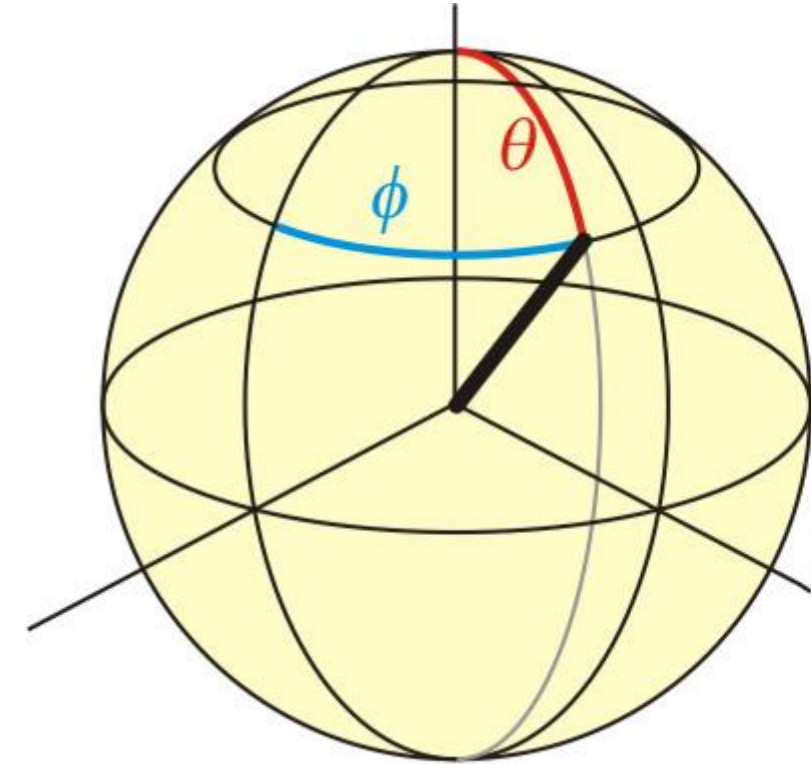
Vibrational spectra: Polyatomic molecules

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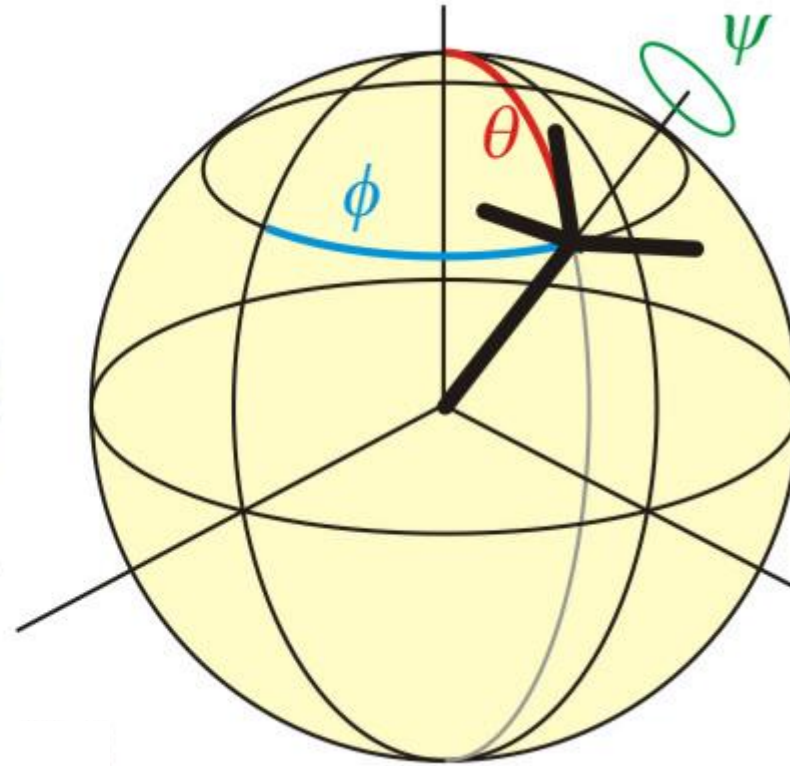
Degrees of freedom



Translational : 3

Rotational : 2 for linear and 3 for nonlinear molecule

Vibrational : $3N - 5$ for linear and $3N - 6$ for nonlinear molecule.



- For a molecule with N atoms, the number of coordinates required to specify the position of all the atoms is $3N$.
- These $3N$ displacements can be thought of in terms of various degrees of freedom.

Normal modes of vibrations



Description of vibration most convenient and simple in terms of normal modes.

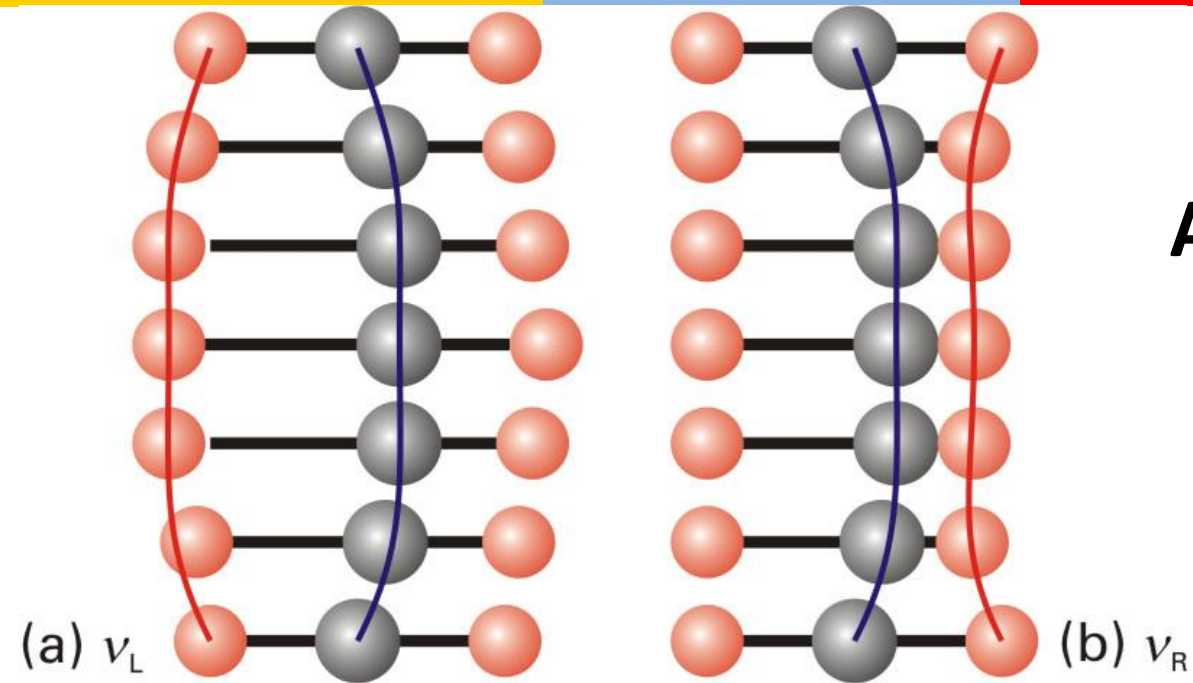
Normal mode – Collective, independent, synchronous motion of group of atoms, that may be excited without exciting any other mode.

Each normal mode may be approximated as a harmonic oscillator with a characteristic frequency and an effective mass.

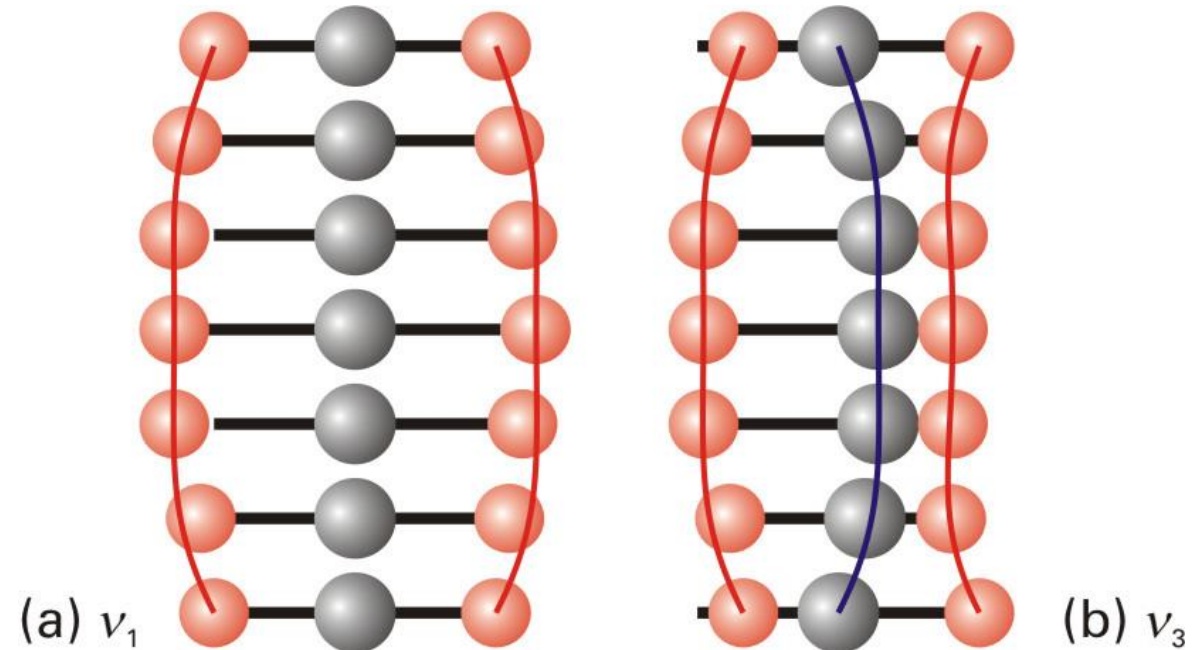
Any arbitrary displacement may be expressed as a superposition of the normal modes.

Vibrational spectroscopy

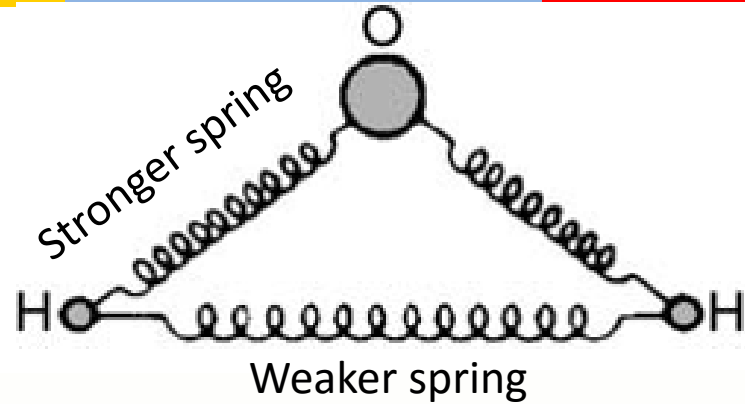
Actual (total) stretching motion



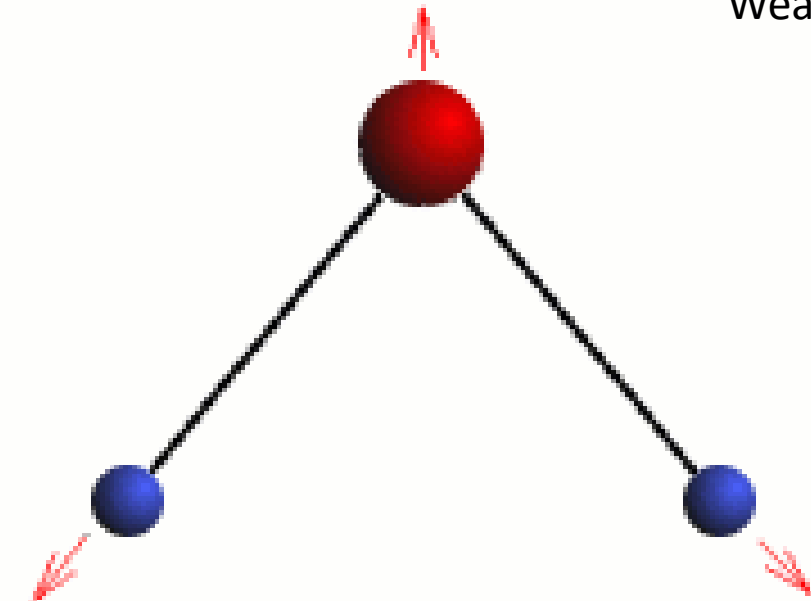
Independent components contributing to the motion (Normal modes): symmetric and asymmetric stretching



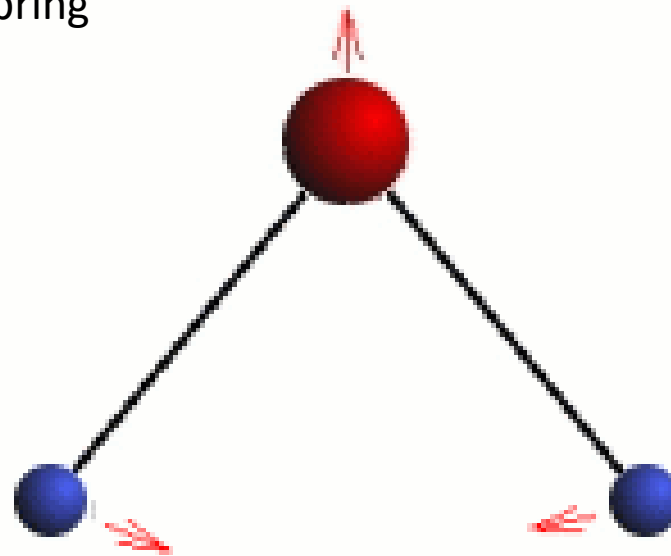
Water: Normal modes of vibrations



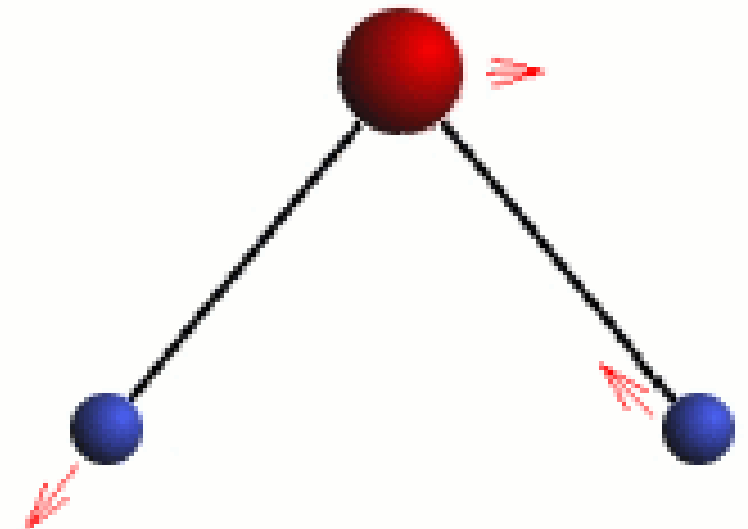
- Ball and spring model for water
- Springs those obey Hooks's law



**Symmetric
stretch**

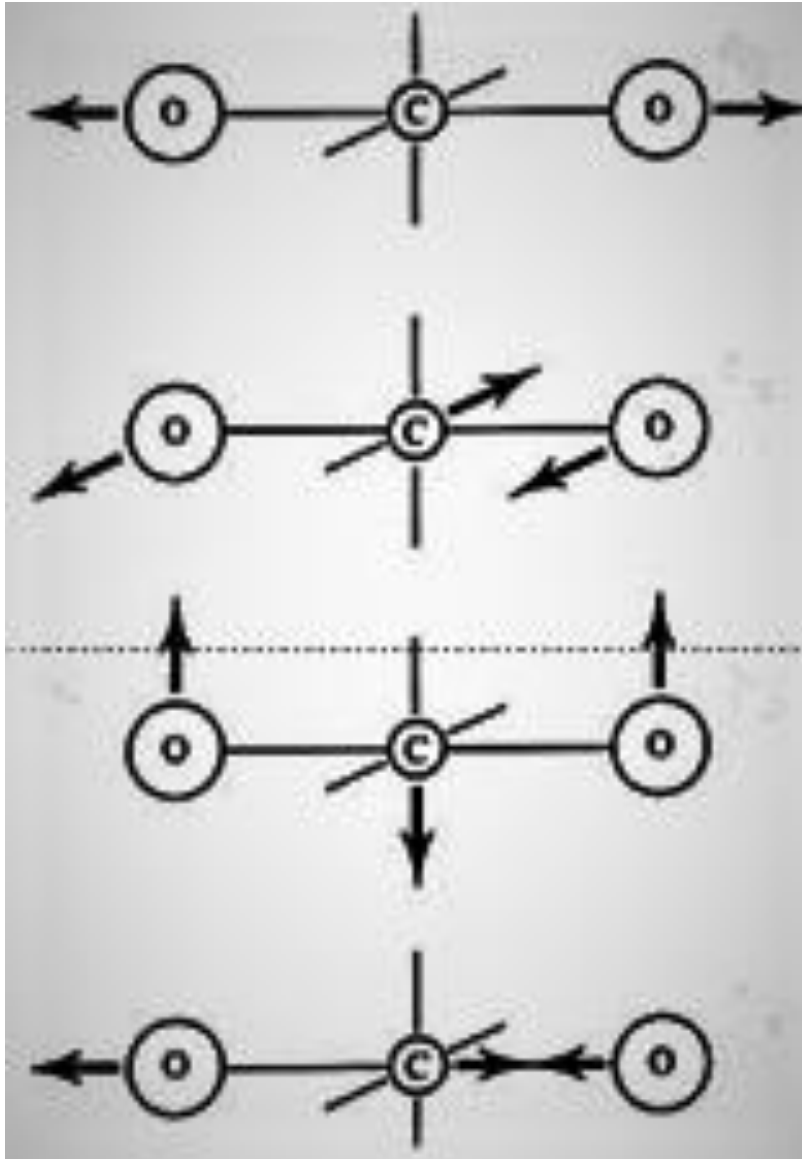


Bend



**Asymmetric
stretch**

Carbon dioxide: Normal modes of vibrations



Symmetric stretch – IR inactive

Why??

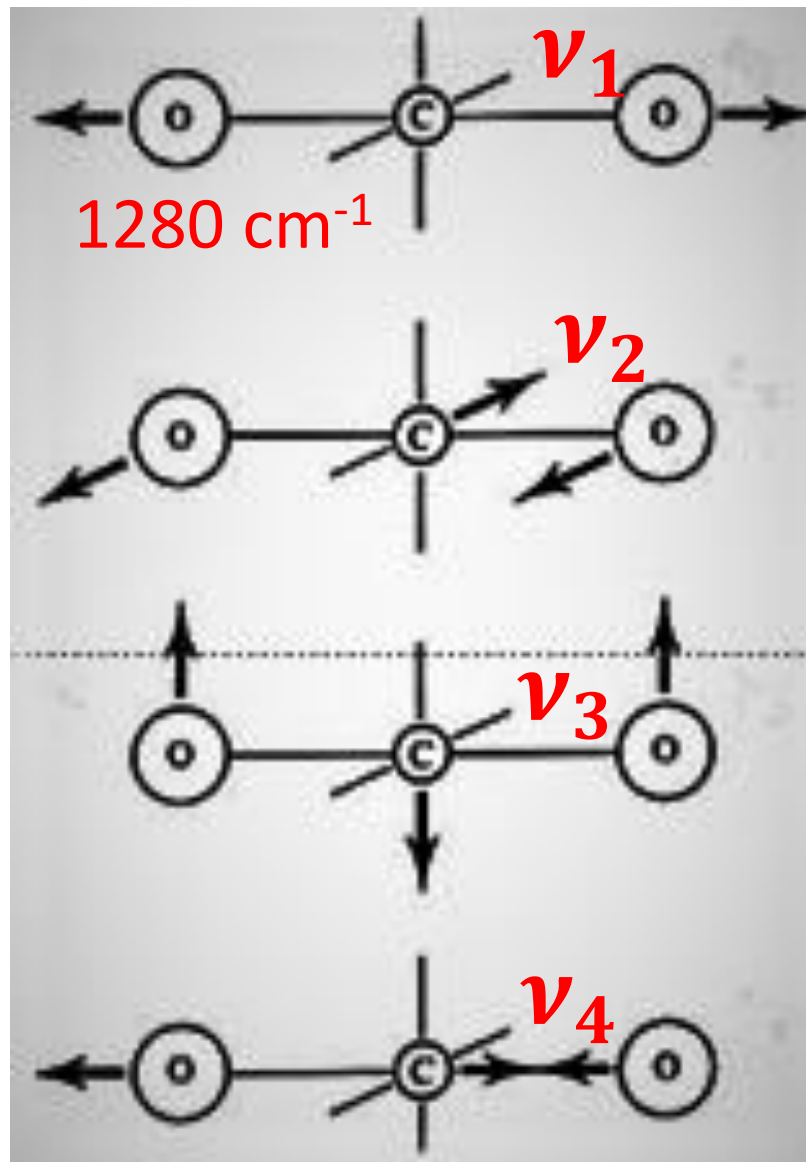
Bend

Bend

Asymmetric stretch

$$\frac{d\mu}{dq} = 0$$

Vibrational transitions in CO₂



$$\psi_1(0)\psi_2(0)\psi_3(0)\psi_4(0)$$

$$\nu_2 \& \nu_3 \quad 580 \text{ cm}^{-1}$$

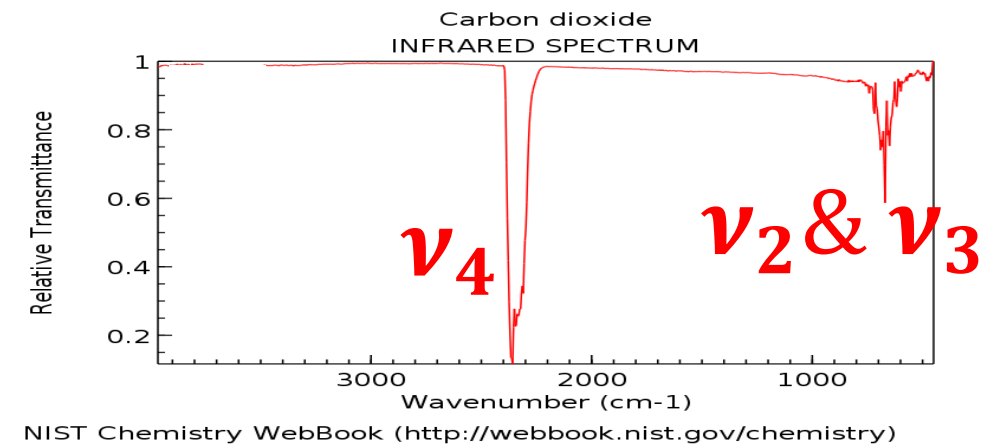
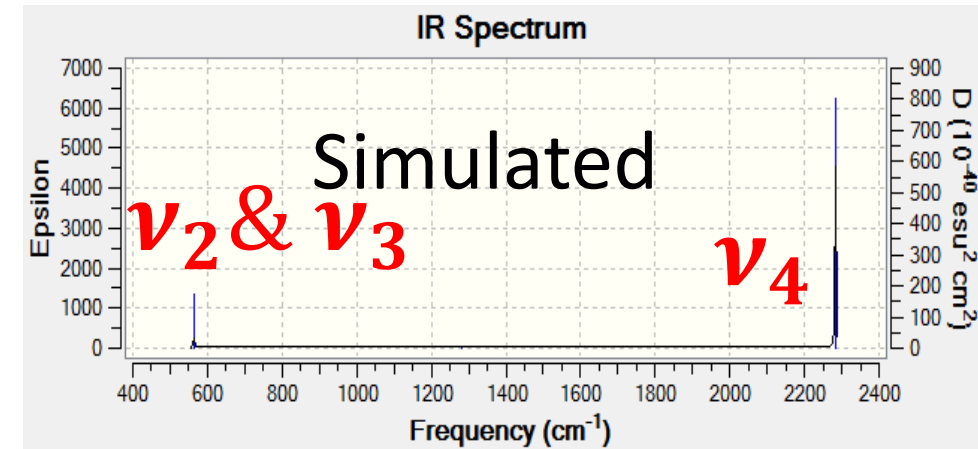
$$\psi_1(0)\psi_2(1)\psi_3(1)\psi_4(0)$$

$$\psi_1(0)\psi_2(0)\psi_3(0)\psi_4(0)$$

$$\nu_4 \quad 2200 \text{ cm}^{-1}$$

$$\psi_1(0)\psi_2(0)\psi_3(0)\psi_4(1)$$

$$\Psi_{vib} = \psi_1(\nu_1)\psi_2(\nu_2)\psi_3(\nu_3)\psi_4(\nu_4)$$



Vibrational spectroscopy



- Infrared spectroscopy powerful tool in identifying organic molecules.
- Some modes essentially motions of individual functional groups.
- Others are collective motions of the molecule as a whole – fingerprint region of spectrum.

Vibrational (IR) spectroscopy



Absorption frequency:

$\nu = 1/2\pi (k/\mu)^{1/2}$ where $\mu = m_A m_B / (m_A + m_B)$ is the reduced mass and k is force constant

Typical range : $10^{13} - 10^{14}$ Hz $\sim 10^2 - 10^3$ cm⁻¹ (Infrared region)

Hence, vibrational (absorption) spectroscopy is also known as IR spectroscopy.

{IR spectrum is generally represented in Transmission mode}

IR frequency calculation



Absorption frequency:

$$\nu(\text{cm}^{-1}) = (k/\mu)^{1/2} / 2\pi c$$

C-H: $k \sim 494 \text{ Nm}^{-1}$; ($\nu \sim 3000 \text{ cm}^{-1}$)

N-H: $k \sim 642 \text{ Nm}^{-1}$; ($\nu \sim 3400 \text{ cm}^{-1}$)

O-H: $k \sim 726 \text{ Nm}^{-1}$; ($\nu \sim 3600 \text{ cm}^{-1}$)

C=C: $k \sim 972 \text{ Nm}^{-1}$; ($\nu \sim 1650 \text{ cm}^{-1}$)

C \equiv C: $k \sim 1650 \text{ Nm}^{-1}$; ($\nu \sim 2150 \text{ cm}^{-1}$)

IR frequencies of functional groups

| GROUP | BOND | FREQUENCY RANGE (CM ⁻¹) |
|---------|------|-------------------------------------|
| Alkyl | C—H | 2853–2962 |
| Alcohol | O—H | 3590–3650 |
| Amine | N—H | 3300–3500 |

**Here the effect is mainly
due to bond strength**

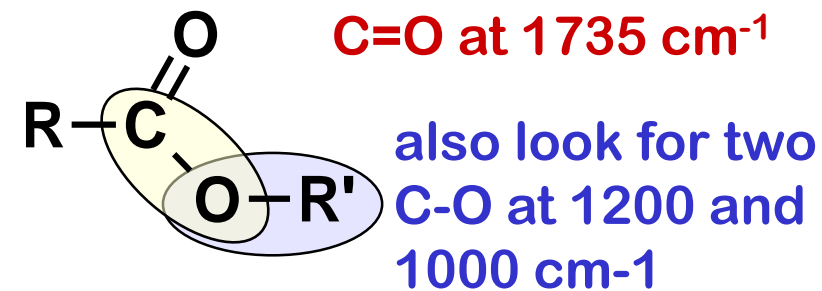
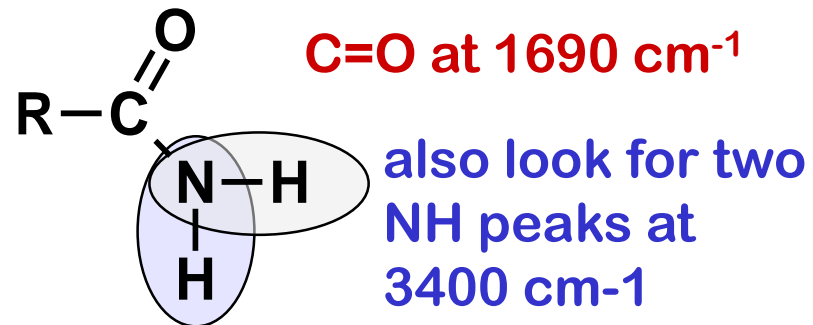
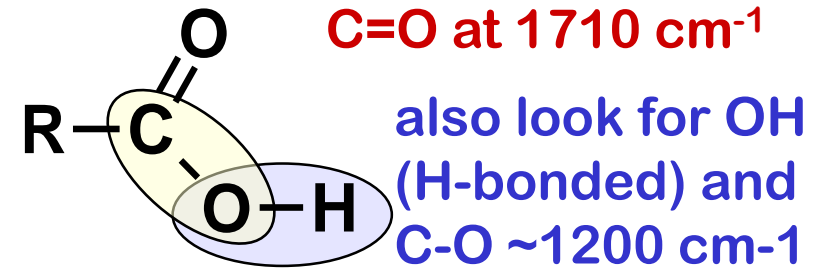
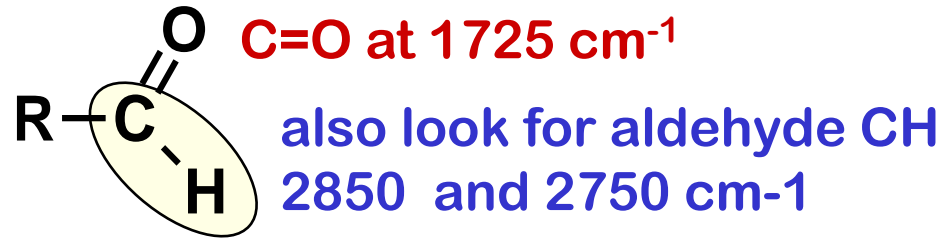
| BOND | FREQUENCY RANGE (CM ⁻¹) |
|------|-------------------------------------|
| C≡C | 2100–2260 |
| C≡N | 2220–2260 |
| C=C | 1620–1680 |
| C=O | 1630–1780 |

Interpreting IR spectra

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Ketones have **C=O at 1715 cm⁻¹** and **no NH, OH, C-O or -CHO**

Anhydrides have **two C=O peaks near 1800 cm⁻¹** and **two C-O**

IR frequency data

| Group | Frequency Range (cm ⁻¹) | Intensity ^a |
|--|-------------------------------------|------------------------|
| A. Alkyl | | |
| C—H (stretching) | 2853–2962 | (m–s) |
| Isopropyl, —CH(CH ₃) ₂ | 1380–1385 | (s) |
| | and 1365–1370 | (s) |
| <i>tert</i> -Butyl, —C(CH ₃) ₃ | 1385–1395 | (m) |
| | and ~ 1365 | (s) |
| B. Alkenyl | | |
| C—H (stretching) | 3010–3095 | (m) |
| C=C (stretching) | 1620–1680 | (v) |
| R—CH=CH ₂ | (out-of-plane C—H bendings) and | 985–1000 (s) |
| | | 905–920 (s) |
| R ₂ C=CH ₂ | | 880–900 (s) |
| | | |
| <i>cis</i> -RCH=CHR | | 675–730 (s) |
| <i>trans</i> -RCH=CHR | | 960–975 (s) |
| C. Alkynyl | | |
| ≡C—H (stretching) | ~ 3300 | (s) |
| C≡C (stretching) | 2100–2260 | (v) |
| D. Aromatic | | |
| Ar—H (stretching) | ~ 3030 | (v) |
| Aromatic substitution type (C—H out-of-plane bendings) | | |
| Monosubstituted | 690–710 | (very s) |
| <i>o</i> -Disubstituted | and 730–770 | (very s) |
| <i>m</i> -Disubstituted | 735–770 | (s) |
| | 680–725 | (s) |
| | and 750–810 | (very s) |
| <i>p</i> -Disubstituted | 800–860 | (very s) |

IR frequency data



E. Alcohols, Phenols, and Carboxylic Acids

O—H (stretching)

| | | |
|--------------------------------------|-----------|------------|
| Alcohols, phenols (dilute solutions) | 3590–3650 | (sharp, v) |
| Alcohols, phenols (hydrogen bonded) | 3200–3550 | (broad, s) |
| Carboxylic acids (hydrogen bonded) | 2500–3000 | (broad, v) |

F. Aldehydes, Ketones, Esters, and Carboxylic

| | | |
|------------------|-----------|-----|
| C=O (stretching) | 1630–1780 | (s) |
| Aldehydes | 1690–1740 | (s) |
| Ketones | 1680–1750 | (s) |
| Esters | 1735–1750 | (s) |
| Carboxylic acids | 1710–1780 | (s) |
| Amides | 1630–1690 | (s) |

G. Amines

| | | |
|-----|-----------|-----|
| N—H | 3300–3500 | (m) |
|-----|-----------|-----|

H. Nitriles

| | | |
|-----|-----------|-----|
| C≡N | 2220–2260 | (m) |
|-----|-----------|-----|

*Abbreviations: s = strong, m = medium, w = weak, v = variable, — = approximately.

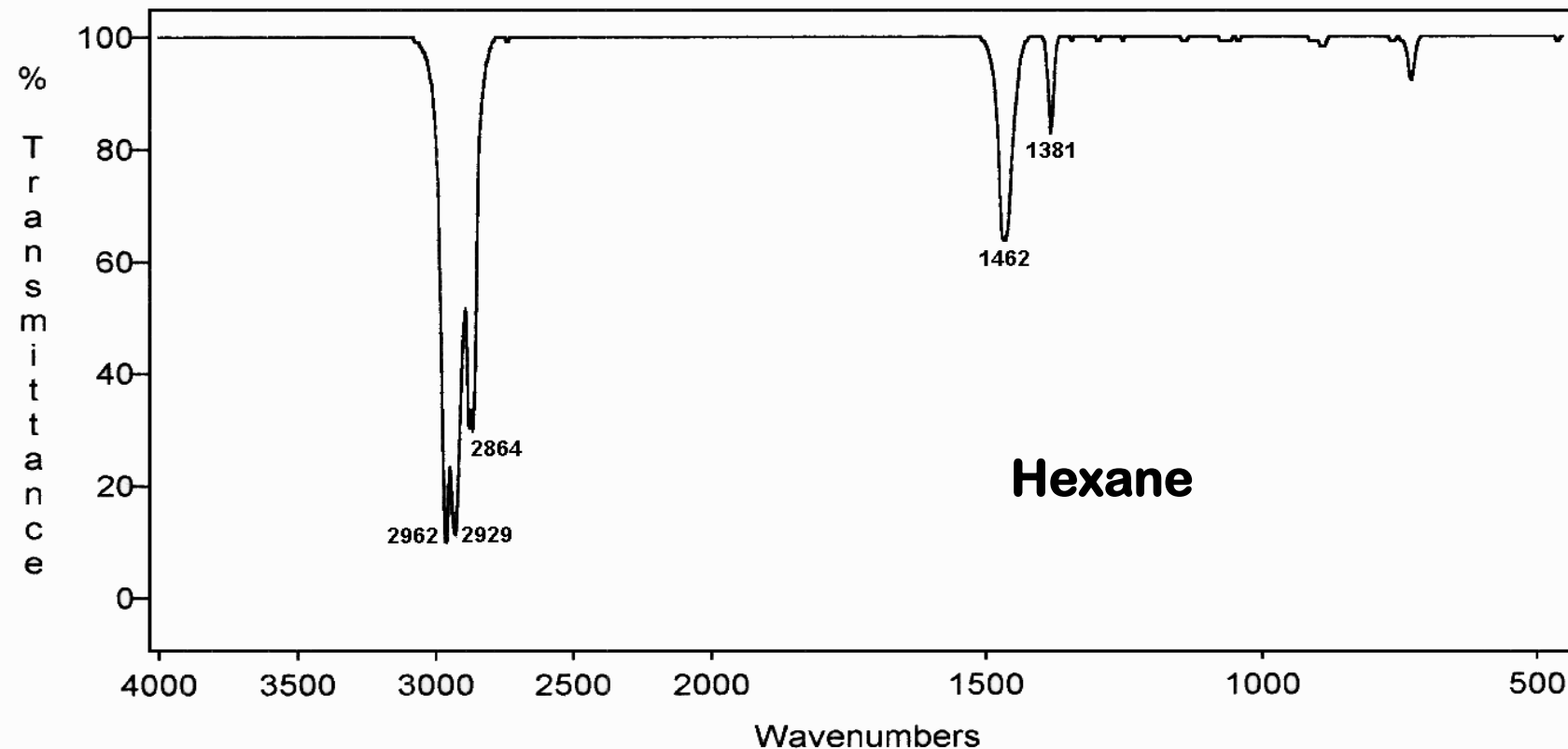
Interpreting IR spectra



C-H stretching frequencies:

$<3000\text{ cm}^{-1}$ for sp^3 ; $>3000\text{ cm}^{-1}$ for sp^2 ; $\sim 3300\text{ cm}^{-1}$ for sp ;

Methylene and methyl C-H stretching: $\sim 2850\text{ cm}^{-1}$ (sym); $\sim 2950\text{ cm}^{-1}$ (asym)



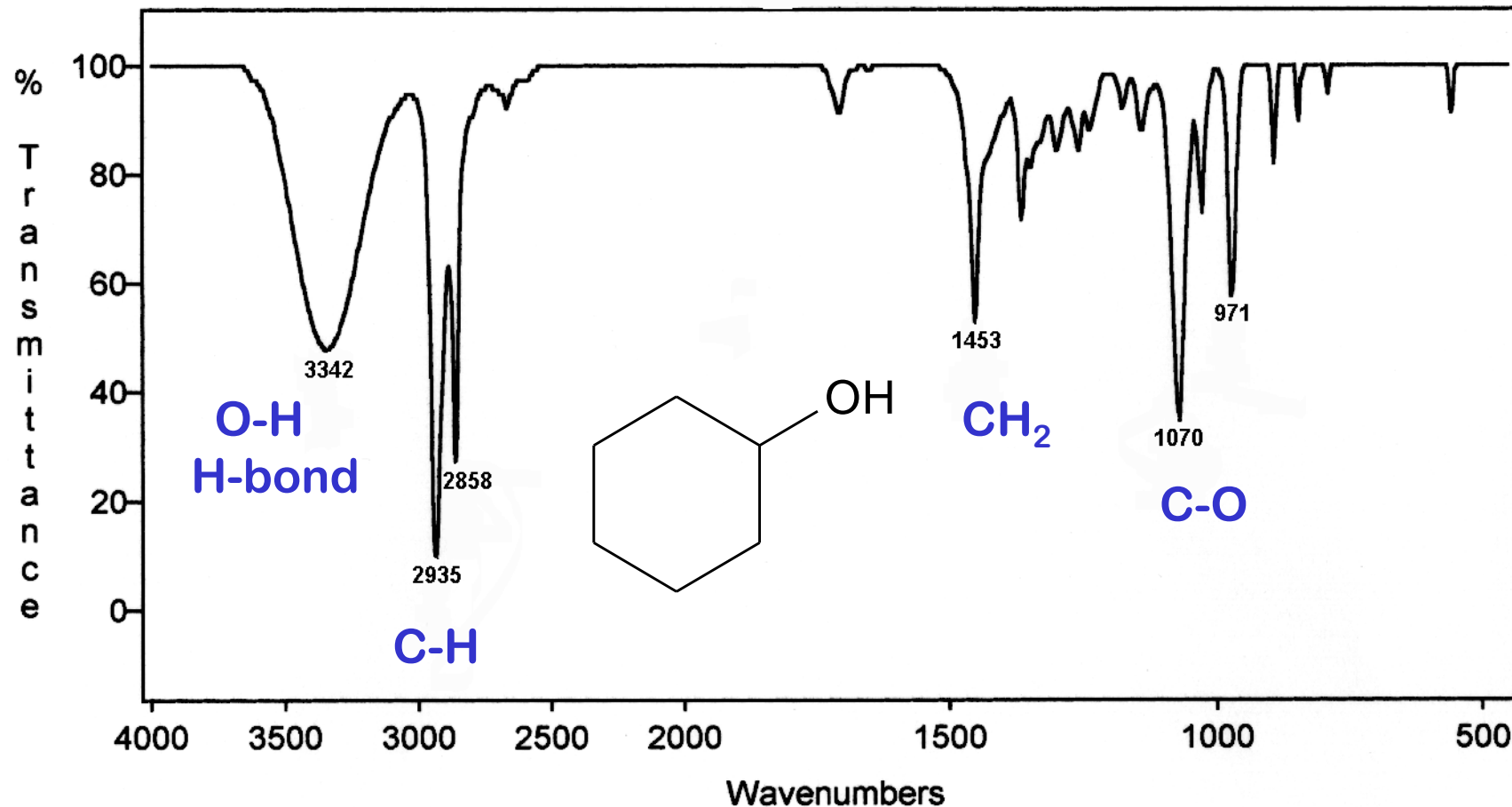
Interpreting IR spectra



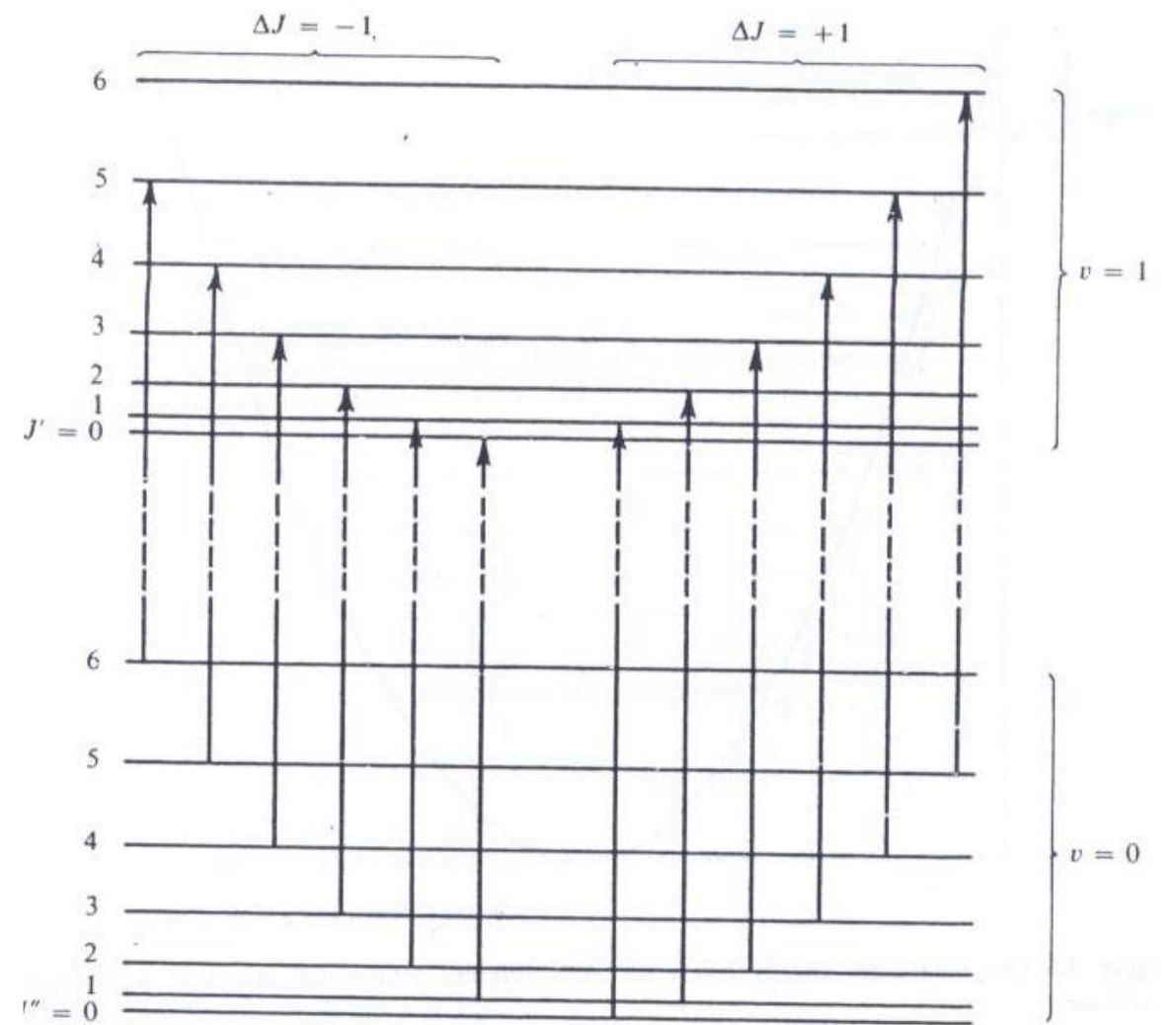
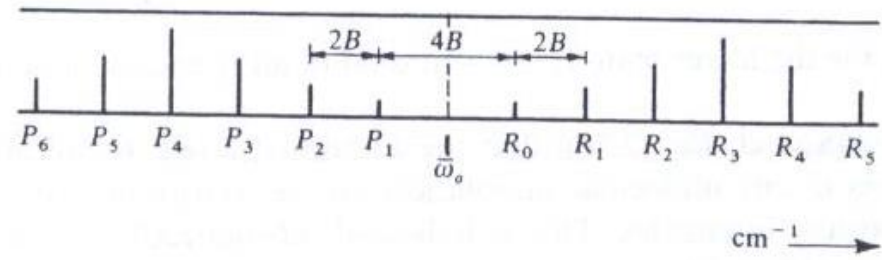
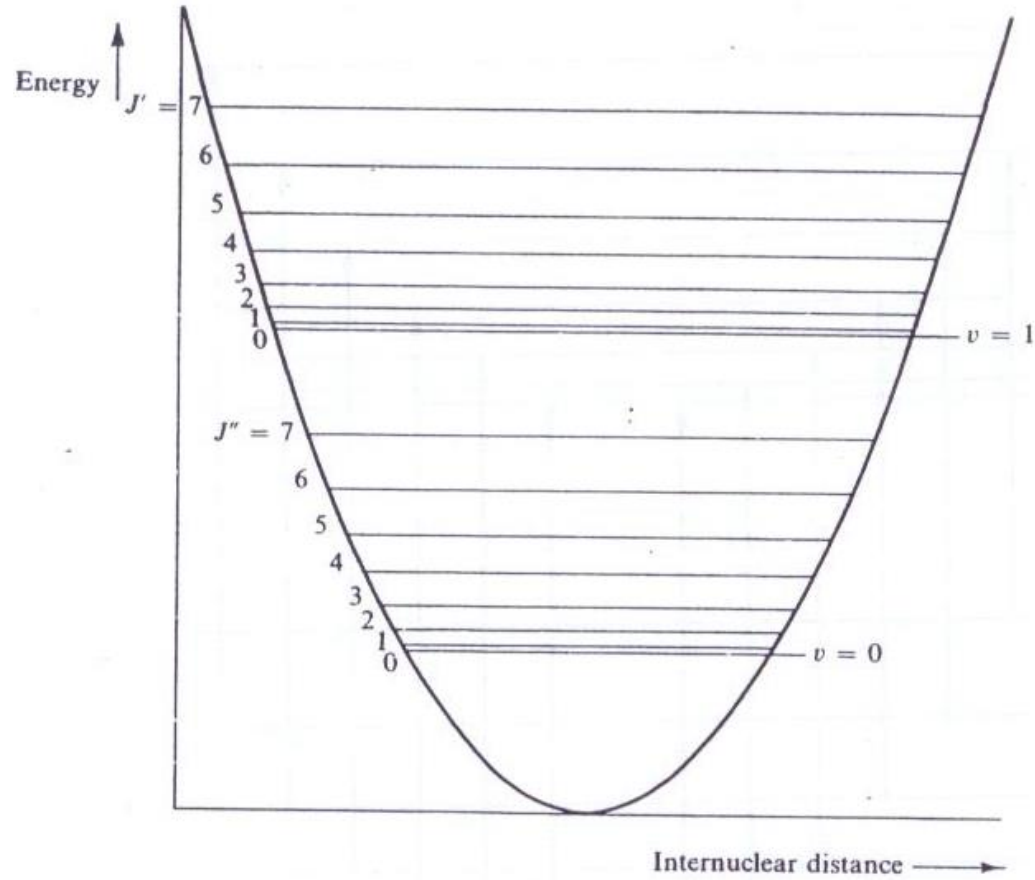
O-H stretching: $\sim 3600\text{ cm}^{-1}$ for alcohols;

brodens and lowers to 3300 cm^{-1} due to H-bonding in alcohols, acids, etc.

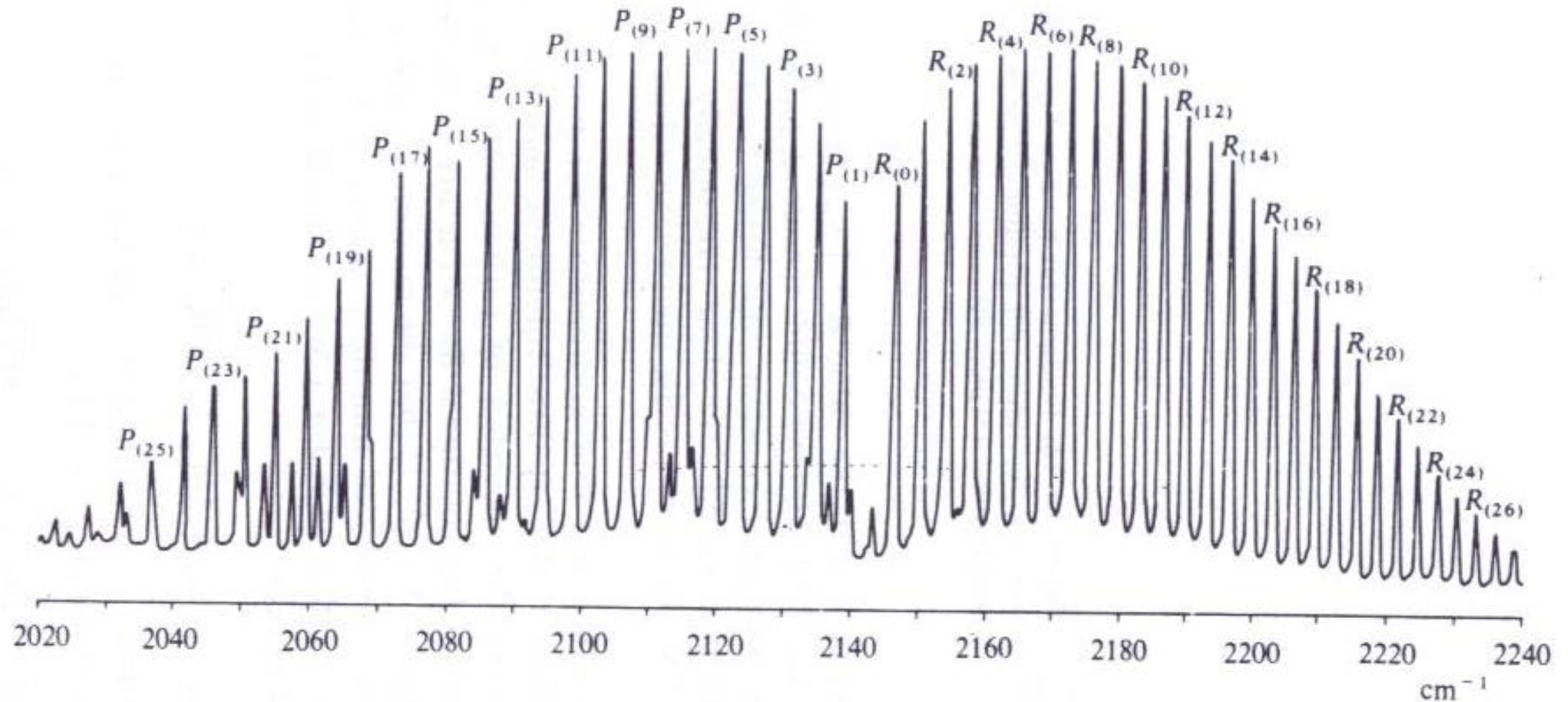
How to distinguish between intramolecular and intermolecular H-bonding?



Diatomic vibrating rotor



Diatomic vibrating rotor: CO

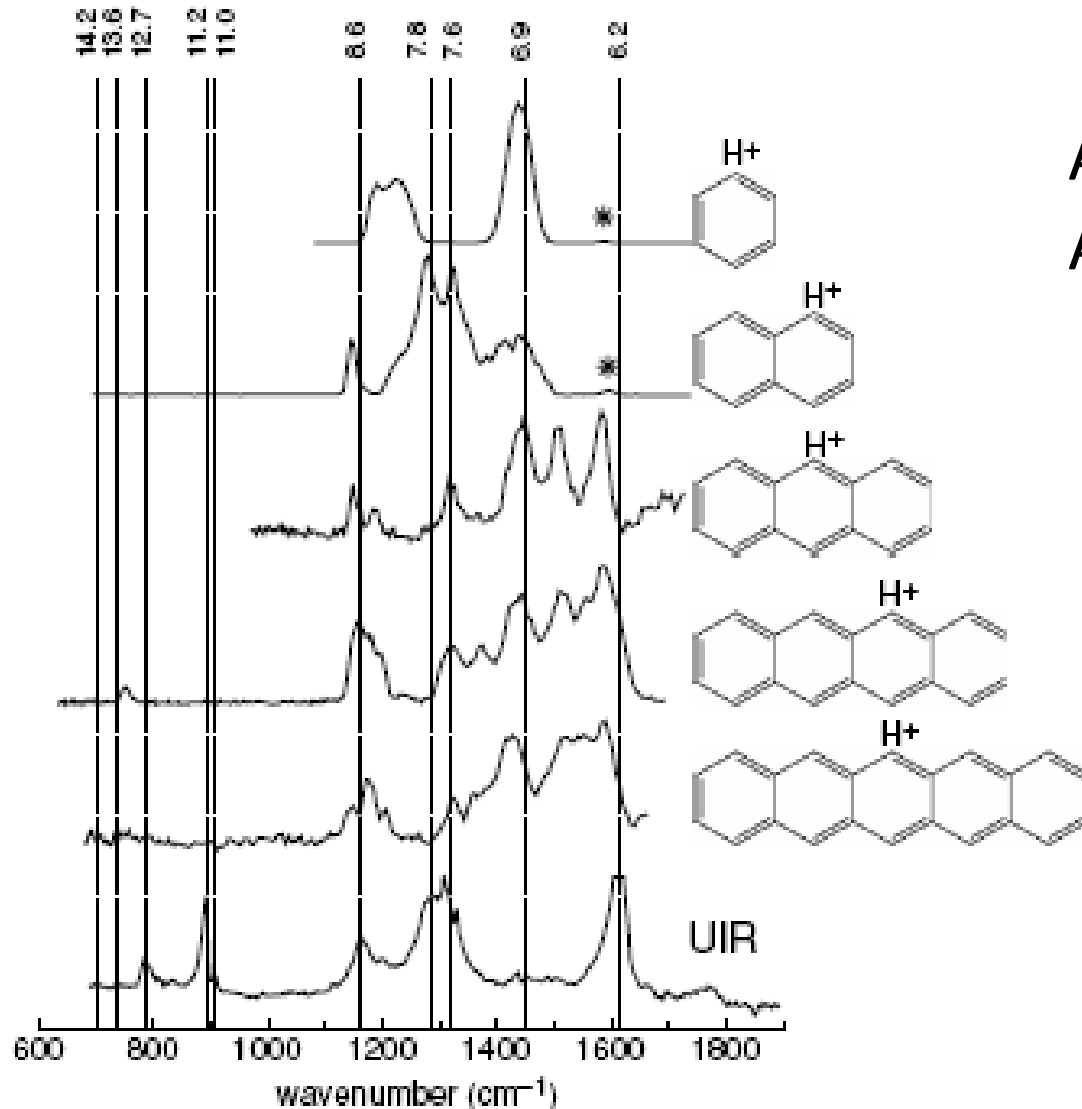


Unidentified Infrared Transitions (UIR)

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Application of IR spectroscopy in Laboratory Astrochemistry

Further information:

- Astrochemistry Laboratory: NASA
{<https://science.gsfc.nasa.gov/solarsystem/astrochemistry/>}
- European Union
{<http://www.astrochemistry.eu/>}
- Astrochemistry Society of India – Established in 2015
{<https://www.prl.res.in/~acsi/>}

Factors affecting absorption frequency

Absorption frequency:

- **Increases** with increase in % of s character: $sp^3 < sp^2 < sp$

e.g. C-H stretching frequencies:

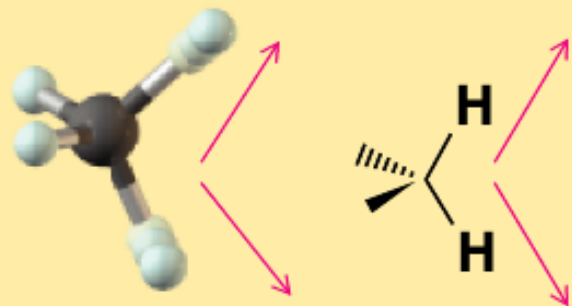
$< 3000\text{ cm}^{-1}$ for sp^3 , $> 3000\text{ cm}^{-1}$ for sp^2 , $\sim 3300\text{ cm}^{-1}$ for sp

- **Decreases** on increase in conjugation

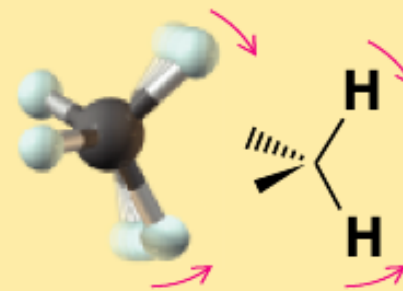
e.g. In aldehydes, ketones and esters, C=O stretching frequency decreases by $25\sim 30\text{ cm}^{-1}$ when conjugated with C=C

- **Is affected** by inductive/resonance/electromeric effects
- **Decreases** due to hydrogen bonding

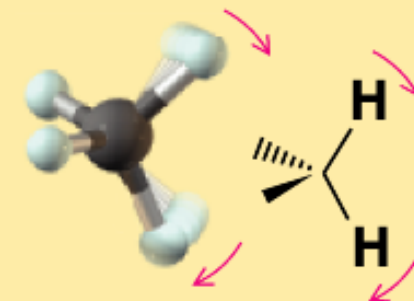
Supporting information: Methane, normal modes of vibrations



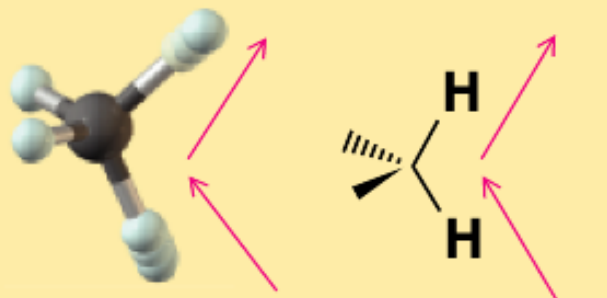
Symmetric stretching



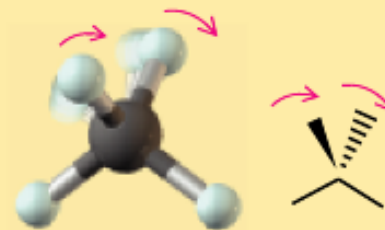
Scissoring



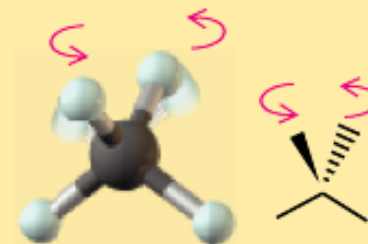
Rocking



Asymmetric stretching
Stretching vibrations



Wagging



Twisting

Bending vibrations

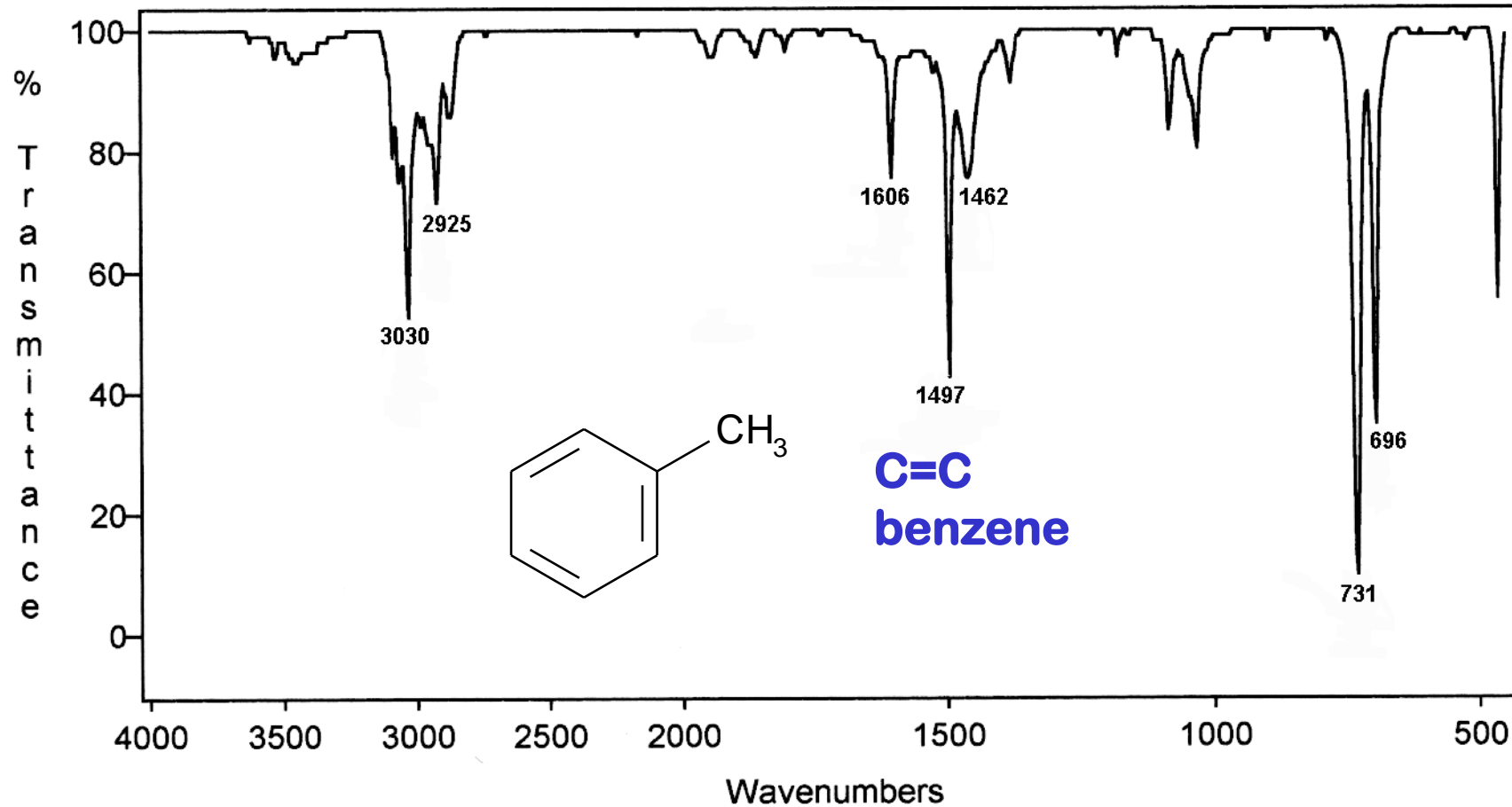
Supporting information: Interpreting IR spectra

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Toluene: Ar-H, CH₂-H, C=C



Supporting information: Interpreting IR spectra

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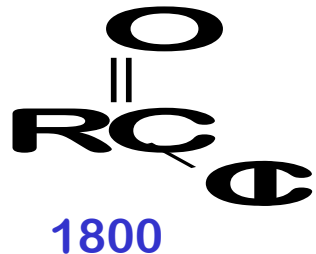
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C=O is highly sensitive to its environment

EACH DIFFERENT KIND OF C=O COMES AT A DIFFERENT FREQUENCY

acid
chloride



ester



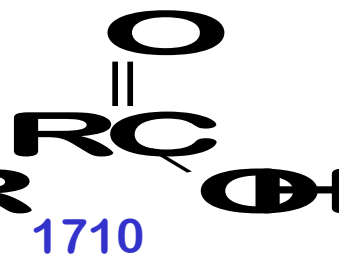
aldehyde



ketone



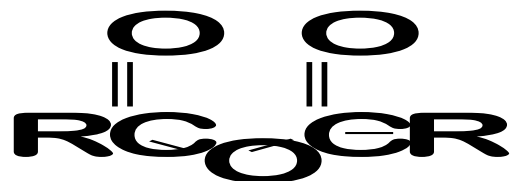
carboxylic
acid



amide



anhydride



BASE
VALUE

THESE VALUES ARE
WORTH LEARNING