Spectroscopic Methods in Organic Chemistry

CHEM-664/476, Organic Chemistry (Minor)

Online Lectures (MW & IR)

Dr Abdul Rauf Raza

(*Associate Professor*)

Institute of Chemistry

University of Sargodha, Sargodha

Microwave Spectroscopy

Frequency (ν) = 10^9 to 10^{11} Hz
Wavelength (λ) = 30 to 0.3 cm
Wave Number ($\acute{\upsilon}$) = 3.33 to 333 m^{-1}

$K.E. = mv^2/2$ → eq 1 (Born-Oppenheimer approximation)
$K.E. = mv^2/2 \ (m/m)$
$K.E. = m^2v^2/2m = p^2/2m$ p = Linear momentum $j = p \times r$
$K.E. = j^2/2\,m\,r^2$ j = Angular momentum $m\,r^2 = I$ (Inertia)
$K.E. = j^2/2\,I$
$E = J\,(J + 1)\,h^2 / 8\,\pi^2\,I$ → eq 2 (Schrodinger Wave Equation)
$h\,\nu = J\,(J + 1)\,h^2 / 8\,\pi^2\,I$ $\nu = J\,(J + 1)\,h / 8\,\pi^2\,I$
$c / \lambda = J\,(J + 1)\,h / 8\,\pi^2\,I$ $c\,\acute{\upsilon} = J\,(J + 1)\,h / 8\,\pi^2\,I$
$\acute{\upsilon} = J\,(J + 1)\,h / 8\,c\,\pi^2\,I$ $\acute{\upsilon} = B\,J\,(J + 1)$
B (Rotational constant) = $h / 8\,c\,\pi^2\,I$
J = Rotational Energy Levels

Microwave Transitions

$E_J = J\ (J + 1)\ h^2 / 8\ \pi^2\ I$ $\longrightarrow$ eq 3

$E_{(J+1)} = (J + 1)\ (J + 1 + 1)\ h^2 / 8\ \pi^2\ I$ $\longrightarrow$ eq 4

$\Delta E_{(J+1)\ -\ J} = (J^2 + 3J + 2)\ h^2 / 8\ \pi^2\ I - [(J^2 + J)\ h^2 / 8\ \pi^2]$ $\longrightarrow$ A

$\Delta E_{(J+1)\ -\ J} = (2J + 2)\ h^2 / 8\ \pi^2\ I = 2\ (J + 1)\ h^2 / 8\ \pi^2\ I$

$\acute{\upsilon} = 2\ (J + 1)\ h / 8\ \pi^2\ I\ c = 2\ B\ (J + 1)$

$\Delta E_{J\ -\ (J+1)} = [(J^2 + J)\ h^2 / 8\ \pi^2\ I] - (J^2 + 3J + 2)\ h^2 / 8\ \pi^2\ I$ $\longrightarrow$ E

$\Delta E_{J\ -\ (J+1)} = [(J^2 + J)\ h^2 / 8\ \pi^2] - (J^2 + 3J + 2)\ h^2 / 8\ \pi^2\ I$

$\acute{\upsilon} = -\ 2\ (J + 1)\ h / 8\ \pi^2\ I\ c = -\ 2\ B\ (J + 1)$

Application of MW Spectroscopy

$I = m\, r^2$ (Macro Systems)

$I = \mu\, r^2$ (Micro Systems)

$\mu = m_1 \,.\, m_2 / (m_1 + m_2)$

$r^2 = I / \mu$ since $B = h / 8\, \pi^2\, I\, c$

so $I = h / 8\, \pi^2\, B\, c$

r (bond length) $= [h / 8\, \pi^2\, B\, c\, \mu]^{1/2}$

$r = [h\, (m_1 + m_2) / 8\, \pi^2\, B\, c\, (m_1 \,.\, m_2)]^{1/2}$

h = Plank's constant $= 6.63 \times 10^{-34}$ J.s

c = velocity of light $= 2.998 \times 10^{8}$ $m.s^{-1}$

$\pi = 22/7 = 3.1416$

Application of MW Spectroscopy

Q: The line spacing (2B) observed in MW spectrum of CO is 3.84235 cm^{-1}. Calculate the bond length between C and O in CO.

$2B = 3.84235\ cm^{-1} = 384.235\ m^{-1}$

$B = 192.118\ m^{-1}$

$\mu = m_C \cdot m_O / (m_C + m_O) \times 1 / N_A$

$\mu = (0.012 \times 0.016) / (0.012 + 0.016) \times 1 / 6.02 \times 10^{23}$

$\mu = 1.139 \times 10^{-26}$ kg

r (bond length) $= [h / 8\ \pi^2\ B\ c\ \mu]^{1/2}$

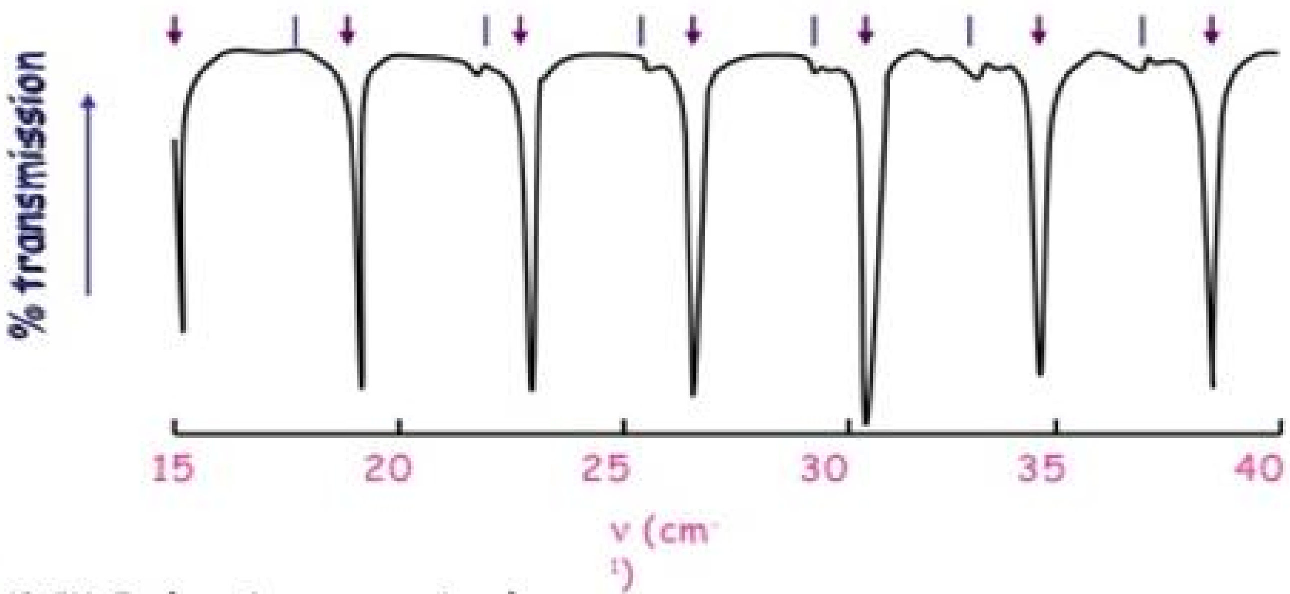
$$r = \left[\frac{[6.63 \times 10^{-34}]}{8\ (3.1416)^2\ (192.118)\ (2.998 \times 10^{8})\ (1.139 \times 10^{-26})}\right]^{1/2}$$

$r = 1.131 \times 10^{-10}\ m = 1.131$ Å

C=O r = 1.20 Å C≡O r = 1.128 Å

MW Spectrum of CO

This is part of the rotational (far infrared) spectrum of CO. You can see that the separation, 2B, is roughly 4 cm^{-1}. Assign the lines.



↓ $^{12}C^{16}O$ (major species)

| $^{13}C^{16}O$ and $^{12}C^{18}O$ lines

InfraRed Spectroscopy

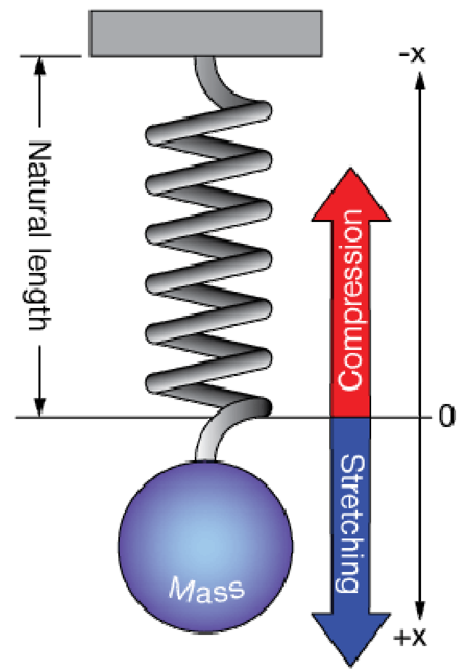
Frequency (ν) = 10^{13} to 1.59×10^{14} Hz

Wavelength (λ) = 0.03 mm to 750 nm

Wave Number (ύ) = 3.33×10^{4} to 0.53×10^{6} m^{-1}

333-4000 cm^{-1} (IR Spectroscopy)

4000-5300 cm^{-1} (Raman Spectroscopy)

F α (-x) F = - k . x Hook's Law F = Force applied x = Displacement k = Hook's (spring / force) constant	

InfraRed Spectroscopy

$E = (V + ½)\, h\, (k / \mu)^{½} / 2\,\pi$ → eq 1 (A solution of Schrodinger Wave Equation)

V = Vibrational Energy Level

h = Plank's constant (6.63×10^{-34})

k = Hook's / force / spring constant

μ = Reduced mass = $(m_1 \,.\, m_2) / (m_1 + m_2)$

$E_1 = (V_1 + ½)\, h\, (k / \mu)^{½} / 2\,\pi$ $V_1 = 0$ (ground state energy)

$E_1 = (0 + ½)\, h\, (k / \mu)^{½} / 2\,\pi = h\, (k / \mu)^{½} / 4\,\pi$ → eq 2

$E_2 = (V_2 + ½)\, h\, (k / \mu)^{½} / 2\,\pi$ $V_2 = 1$ (first excited state energy)

$E_2 = (1 + ½)\, h\, (k / \mu)^{½} / 2\,\pi = 3\, h\, (k / \mu)^{½} / 4\,\pi$ → eq 3

$\Delta E = (E_2 - E_1) = [3\, h\, (k / \mu)^{½} / 4\,\pi] - [h\, (k / \mu)^{½} / 4\,\pi]$

$\Delta E = h\, (k / \mu)^{½} / 2\,\pi$ → eq 4

InfraRed Spectroscopy

$\Delta E = h\,(k / \mu)^{1/2} / 2\,\pi$ $\rightarrow$ eq 4

Since $E = h\,\nu$ and $\nu \times \lambda = c$

$E = h\,c / \lambda$ $\rightarrow$ eq 5

Since $1 / \lambda = \acute{\upsilon}$ so $E = h\,c\,\acute{\upsilon}$

LHS of both equations (4 & 5) are equal; hence

$h\,c\,\acute{\upsilon} = h\,(k / \mu)^{1/2} / 2\,\pi$ $\rightarrow$ eq 6

$\acute{\upsilon} = (k / \mu)^{1/2} / 2\,\pi\,c$

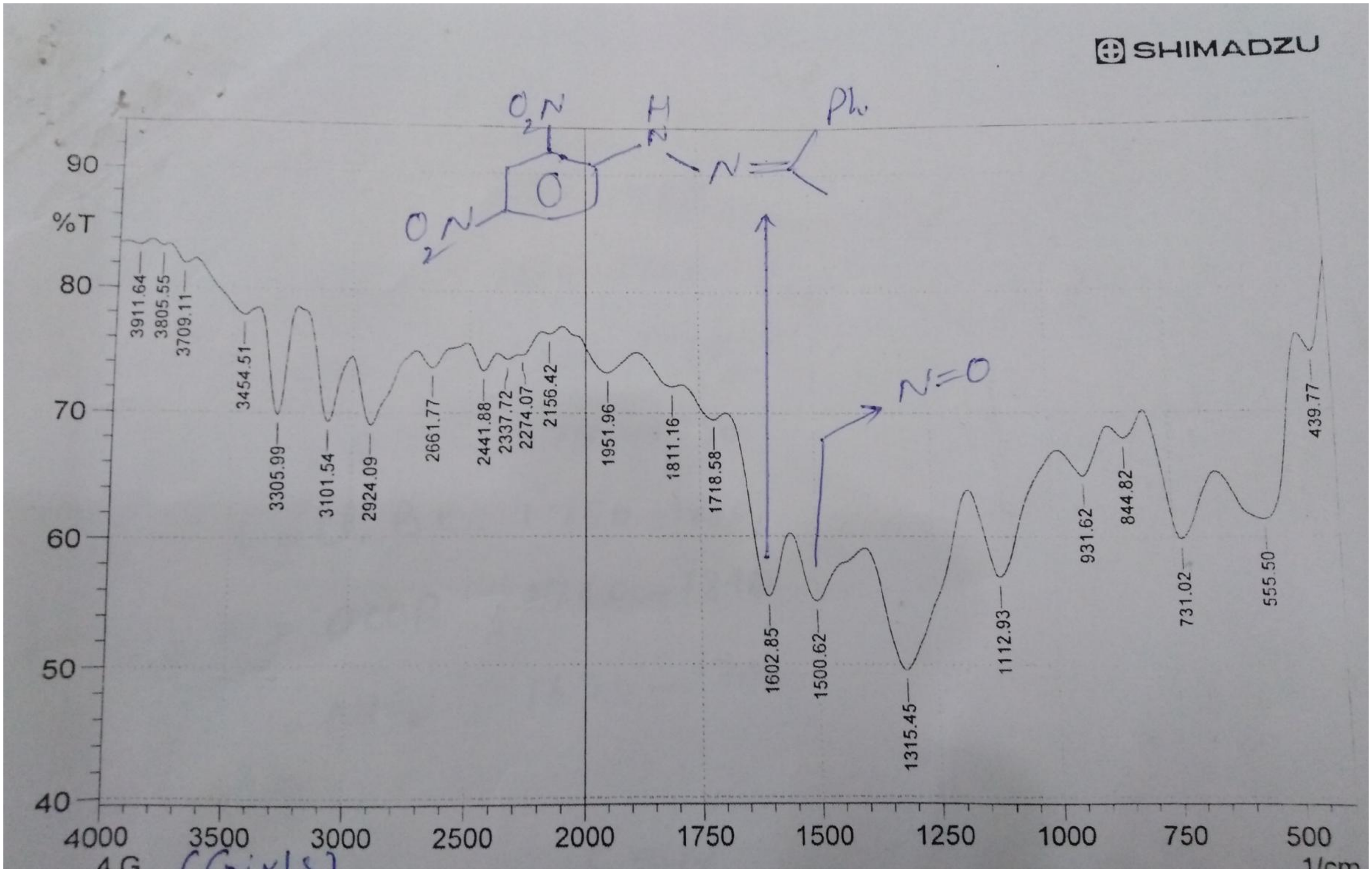
Application of IR

The IR spectrum of CO shows only one absorption at 1543.3 cm^{-1}. Calculate the force constant between C & O.

$ύ = 1543.3\ cm^{-1} = 154330\ m^{-1}$
$μ = (m_C \,.\, m_O) / (m_C + m_O) × 1 / N_A$
$μ = (0.012 × 0.016) / [(0.012 + 0.016) × 1 / 6.02 × 10^{23}]$
$μ = 1.139 × 10^{-26}\ kg$

$ύ = (k / μ)^{½} / 2\ π\ c$
$ύ^2 = k / 4\ π^2\ c^2\ μ$ so $k = 4\ π^2\ c^2\ μ\ ύ^2$
$k = 4 × (3.1416)^2 × (3 × 10^8)^2 × (1.139 × 10^{-26}) × (154330)^2$
$k = 963.94\ N / m$

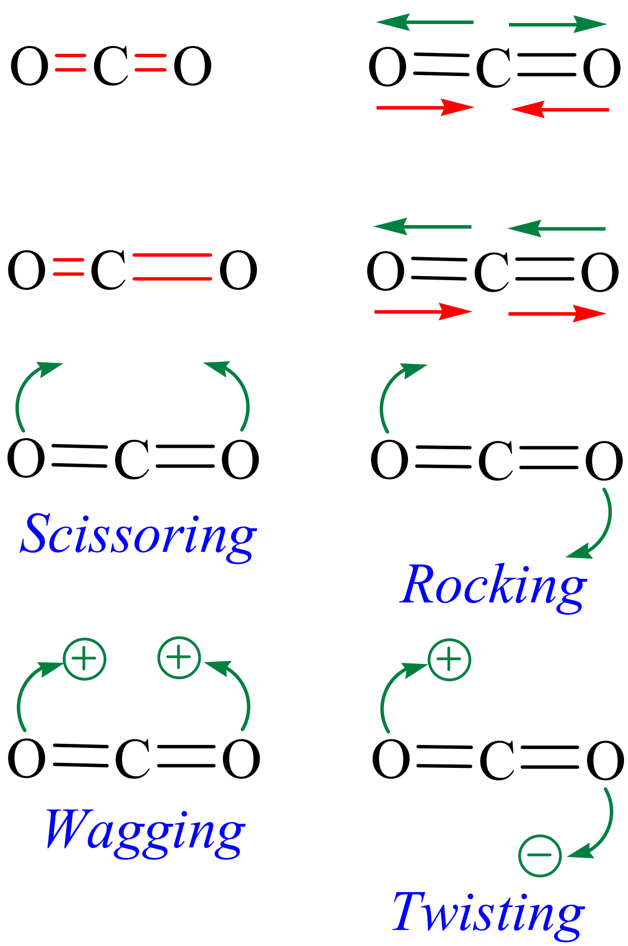
An IR Spectrum



Mode of Vibrations

3N - 5 (Linear molecule)

3N - 6 (Non-linear molecule)



Symmetrical Stretching

Asymmetrical Stretching

In plane bending

Out of plane bending

Factors affecting IR absorbance

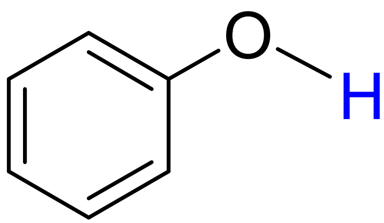
$$\Delta\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad \Delta\bar{\nu} \;\alpha\; \sqrt{k}$$

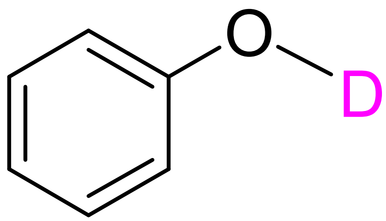
	$\Delta\bar{\nu}$ (cm^{-1})	k ($kg\ s^{-2}$)
C—C	1300-800	5
C=C	1900-1500	10
C≡C	2300-2000	1.5×10^6

Factors affecting IR absorbance

$$\Delta\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

$$\Delta\bar{\nu} \;\alpha\; \sqrt{\frac{1}{\mu}}$$





$$\mu = \frac{(0.001 \text{ x } 0.016)}{(0.001 + 0.016)}$$

$$\mu = \frac{(0.002 \text{ x } 0.016)}{(0.002 + 0.016)}$$

$$\mu = 0.941 \text{ x } 10^{-3} \text{ kg}$$

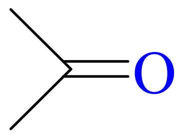
$$\mu = 1.778 \text{ x } 10^{-3} \text{ kg}$$

$$\Delta\bar{\nu} = 3500 \text{ cm}^{-1}$$

$$\Delta\bar{\nu} = 2600 \text{ cm}^{-1}$$

Factors affecting IR absorbance

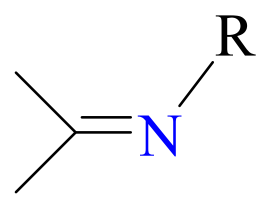
$$\Delta\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad \Delta\bar{\nu}\ \alpha\ \sqrt{\frac{1}{\mu}}$$



$$\mu = \frac{(0.012 \text{ x } 0.016)}{(0.012 + 0.016)}$$

$$\mu = 6.86 \text{ x } 10^{-3} \text{ kg}$$

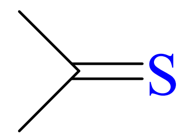
$$\Delta\bar{\nu} = 1700\text{-}1770 \text{ cm}^{-1}$$



$$\mu = \frac{(0.012 \text{ x } 0.014)}{(0.012 + 0.014)}$$

$$\mu = 6.46 \text{ x } 10^{-3} \text{ kg}$$

$$\Delta\bar{\nu} = 1640\text{-}1690 \text{ cm}^{-1}$$



$$\mu = \frac{(0.012 \text{ x } 0.032)}{(0.012 + 0.032)}$$

$$\mu = 8.73 \text{ x } 10^{-3} \text{ kg}$$

$$\Delta\bar{\nu} = 1550\text{-}1600 \text{ cm}^{-1}$$

$$-C\equiv C-$$

$$\mu = 6.0 \text{ x } 10^{-3} \text{ kg}$$

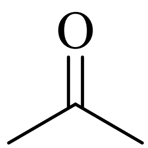
$$\Delta\bar{\nu} = 2100\text{-}2260 \text{ cm}^{-1}$$

$$-C\equiv N$$

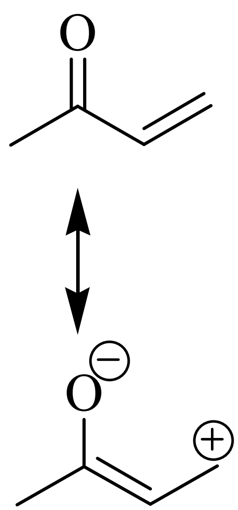
$$\mu = 6.46 \text{ x } 10^{-3} \text{ kg}$$

$$\Delta\bar{\nu} = 2210\text{-}2260 \text{ cm}^{-1}$$

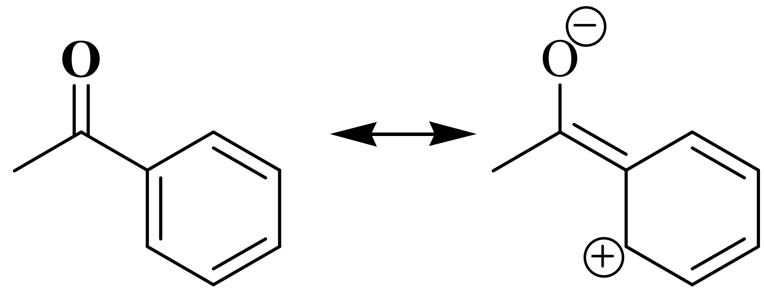
Factors affecting IR absorbance



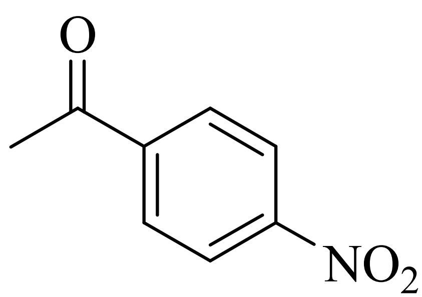
$\Delta\bar{\nu} = 1720\ \mathrm{cm}^{-1}$



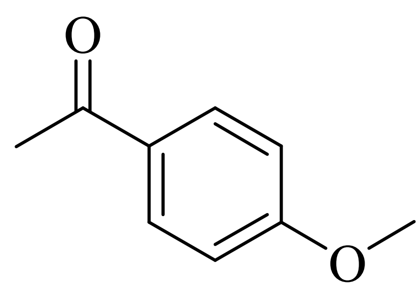
$\Delta\bar{\nu} = 1705\ \mathrm{cm}^{-1}$



$\Delta\bar{\nu} = 1695\ \mathrm{cm}^{-1}$



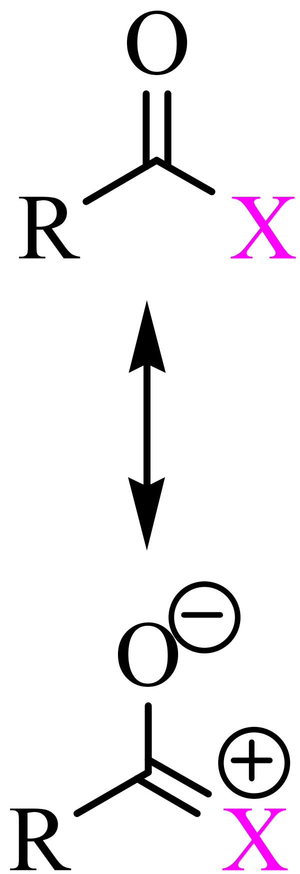
1



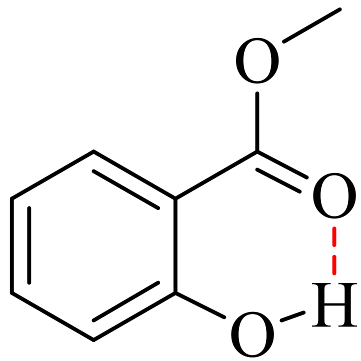
2

Factors affecting IR absorbance

X	$\Delta\bar{\nu}$ (cm^{-1})
H	1680-1740
R / Ar	1665-1725
OH	1680-1720
OR	1710-1750
Cl, Br, I	1750-1850
OCOR	1740-1840
NH_2	1630-1700

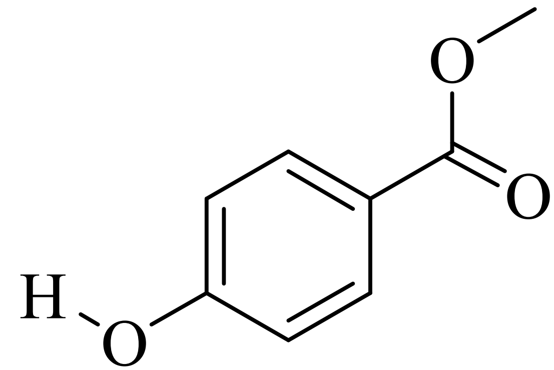


Factors affecting IR absorbance



1 (Intramolecular)

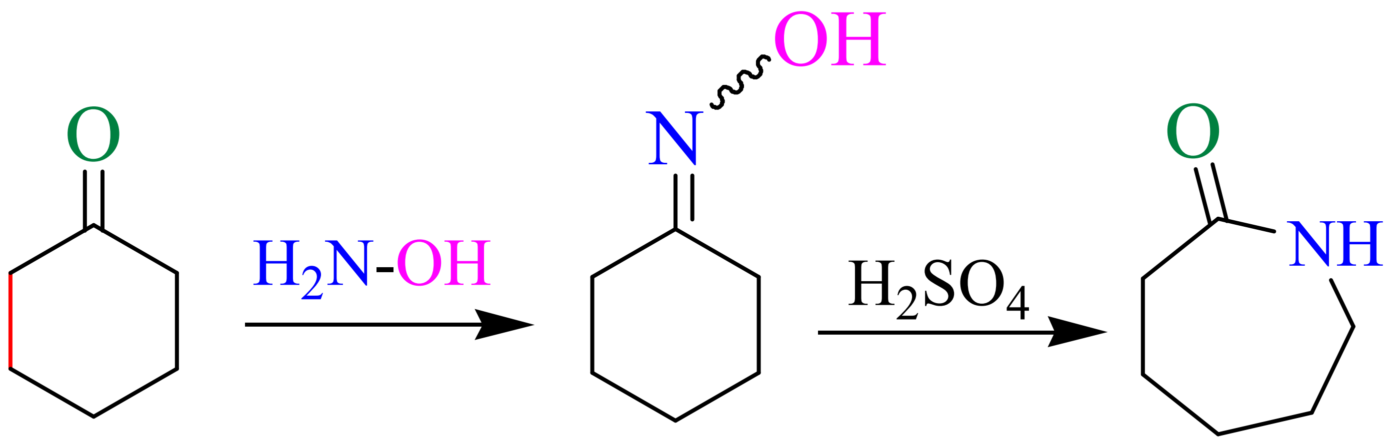
Not affected by dilution



2 (Intermolecular)

Affected by dilution

Application of IR Studies



1 **2** **3**

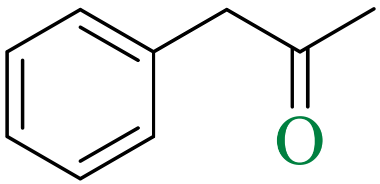
Beckmann's Rearrangement

$\bar{\nu} = 1708\ cm^{-1}$

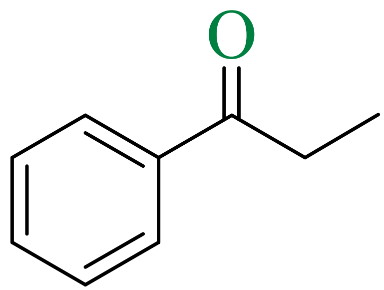
$\bar{\nu} = 3355\ cm^{-1}$
$1670\ cm^{-1}$

$\bar{\nu} = 3310\ cm^{-1}$
$1668\ cm^{-1}$

Application of IR Studies

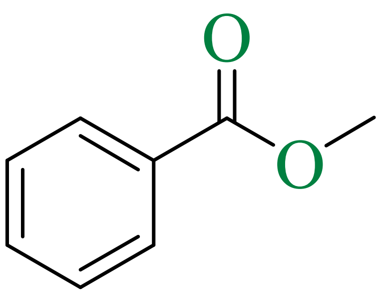


1

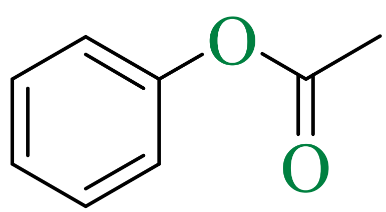


2

$\bar{\nu}$ = 1680 cm^{-1}
1715 cm^{-1}

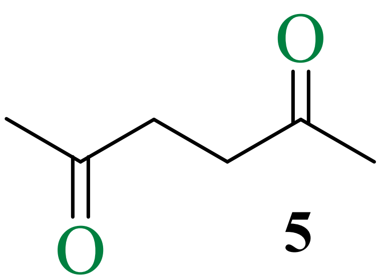


3

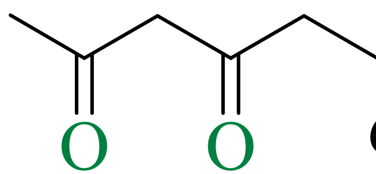


4

$\bar{\nu}$ = 1770 cm^{-1}
1730 cm^{-1}



5



6

$\bar{\nu}$ = 1720 cm^{-1}
1640 cm^{-1}