Spectroscopic Methods in Organic Chemistry

CHEM-6124, Organic Chemistry (Minor)

MW & IR Spectroscopy

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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

$$E_J = J(J + 1)\, h^2 / 8\, \pi^2\, I \qquad \rightarrow \text{ eq } 3$$

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

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

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

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

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

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

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

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 = 6.63×10^{-34} J.s

c = velocity of light = 2.998×10^8 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.

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

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

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

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

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

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

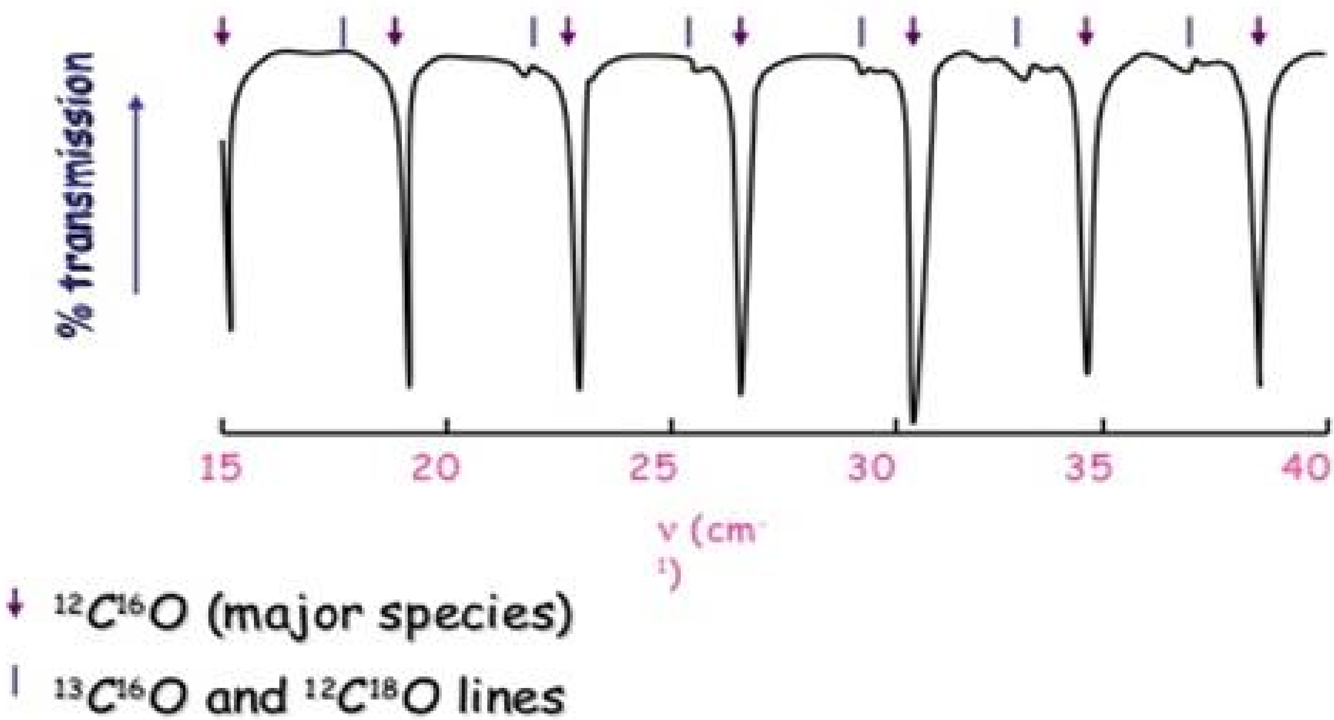
$$r = \left[\frac{6.63 \times 10^{-34}}{8\ (3.1416)^2\ (192.118)\ (2.998 \times 10^{8})\ (1.139 \times 10^{-26})}\right]^{1/2}$$

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

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.



InfraRed Spectroscopy

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

Wavelength (λ) = 0.03 mm to 750 nm

Wave Number ($\acute{\upsilon}$) = 3.33×10^{4} to 0.53×10^{6} m^{-1}

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

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

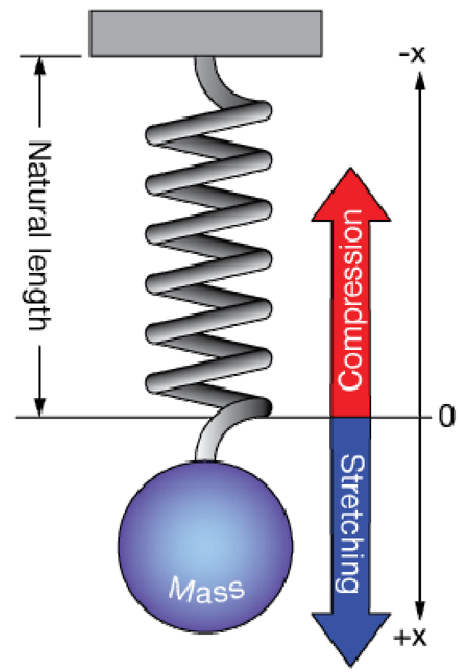
F α (-x)

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

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

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

$E = hc/\lambda$ → eq 5

Since $1/\lambda = \acute{\upsilon}$ so $E = hc\acute{\upsilon}$

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

$hc\acute{\upsilon} = h\,(k/\mu)^{1/2} / 2\pi$ → 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.

$ύ = 1543.3\ cm^{-1} = 154330\ m^{-1}$

$μ = (m_C\ .\ m_O) / (m_C + m_O) × 1 / N_A$

$μ = (0.012 × 0.016) / [(0.012 + 0.016) × 1 / 6.02 × 10^{23}]$

$μ = 1.139 × 10^{-26}\ kg$

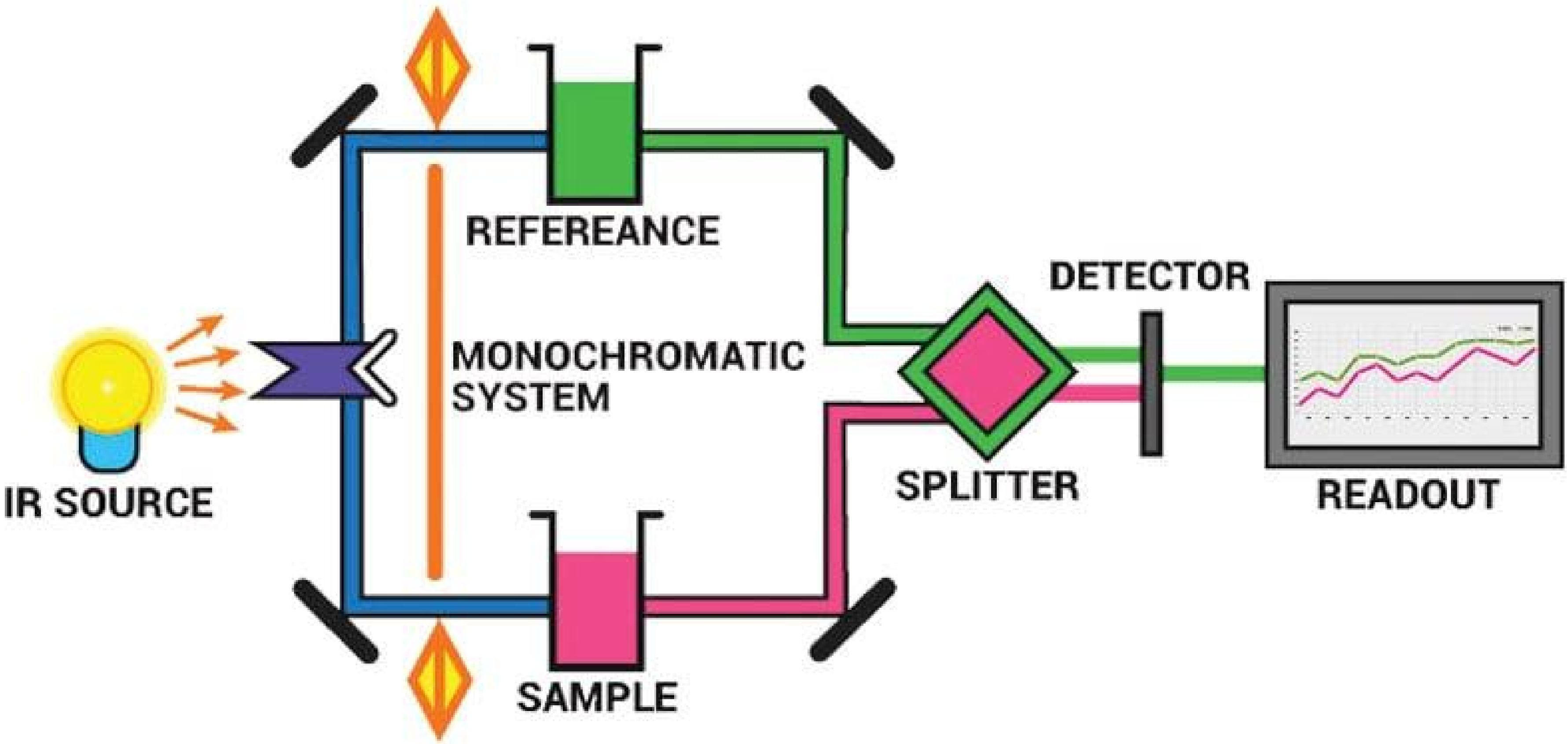
$ύ = (k / μ)^{½} / 2\ π\ c$

$ύ^2 = k / 4\ π^2\ c^2\ μ$ so $k = 4\ π^2\ c^2\ μ\ ύ^2$

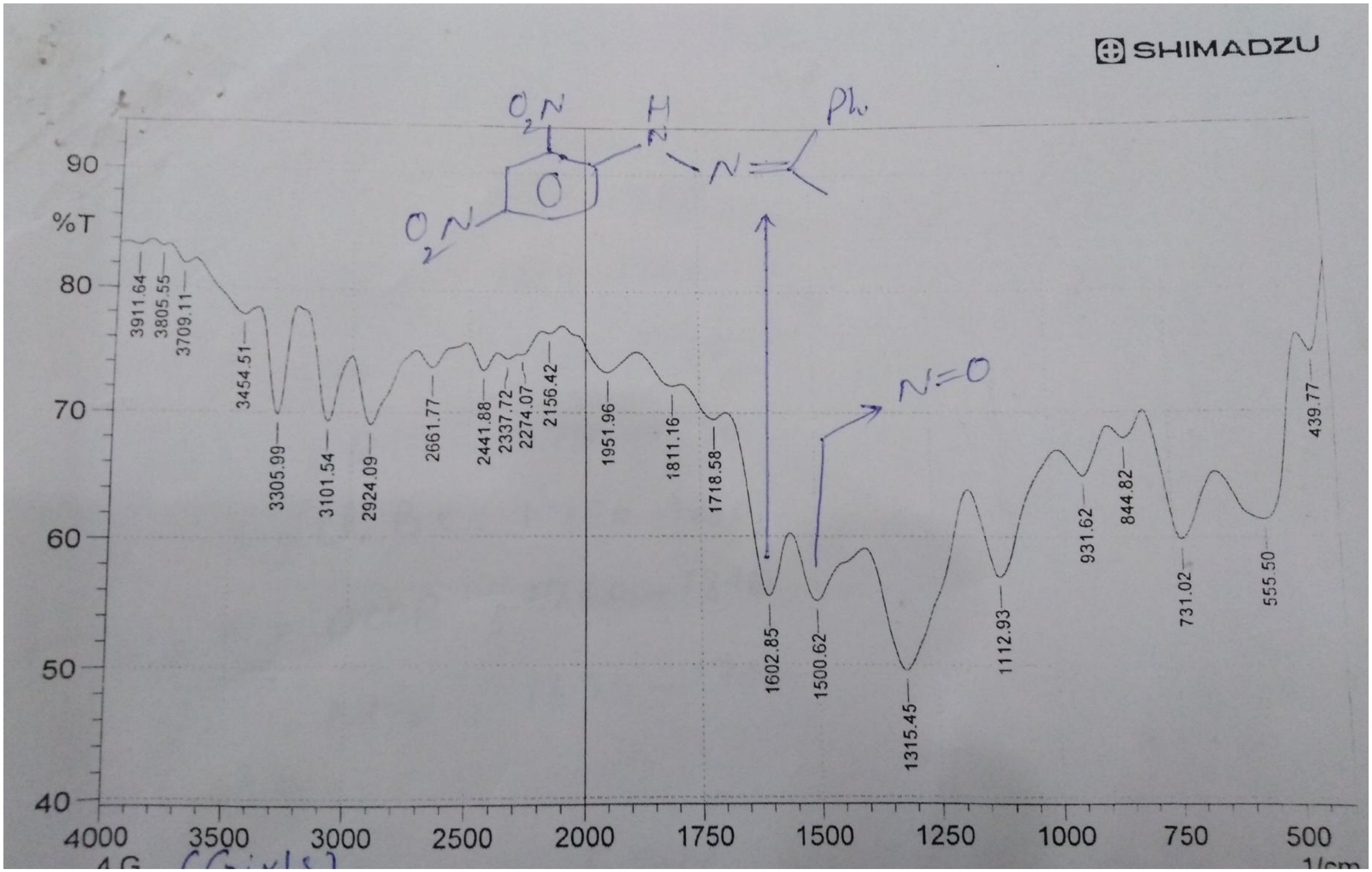
$k = 4 × (3.1416)^2 × (3 × 10^8)^2 × (1.139 × 10^{-26}) × (154330)^2$

$k = 963.94\ N / m$

Instrumentation of IR Spectrophotometer



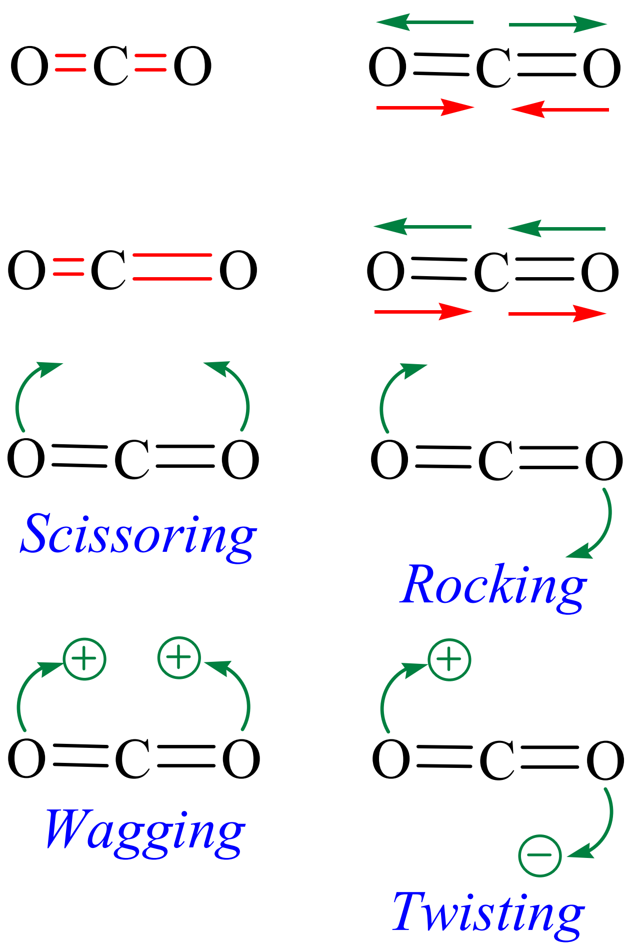
An IR Spectrum



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

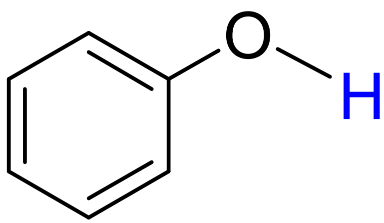
$$\Delta\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad \Delta\bar{\nu} \propto \sqrt{k}$$

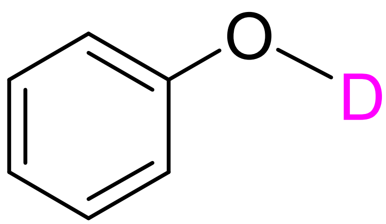
	$\Delta\bar{\nu}$ (cm^{-1})	k ($kg\ s^{-2}$)
C—C	1300-800	5
C=C	1900-1500	10
C≡C	2300-2000	1.5×10^6

Factors affecting IR absorbance

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

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





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

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

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

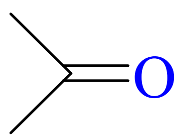
$$\mu = 1.778 \text{ x } 10^{-3} \text{ kg}$$

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

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

Factors affecting IR absorbance

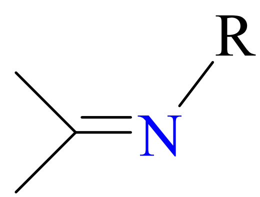
$$\Delta\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad \Delta\bar{\nu} \ \alpha \ \sqrt{\frac{1}{\mu}}$$



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

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

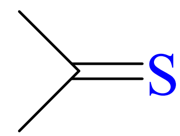
$$\Delta\bar{\nu} = 1700\text{-}1770 \text{ cm}^{-1}$$



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

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

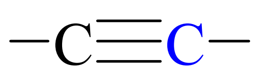
$$\Delta\bar{\nu} = 1640\text{-}1690 \text{ cm}^{-1}$$



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

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

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



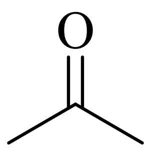
$$\mu = 6.0 \text{ x } 10^{-3} \text{ kg}$$

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

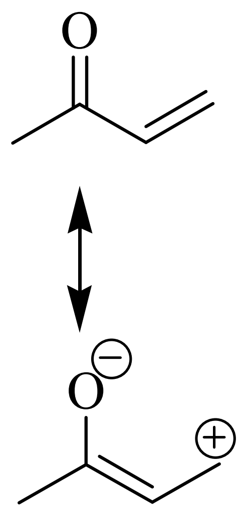
$$\mu = 6.46 \text{ x } 10^{-3} \text{ kg}$$

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

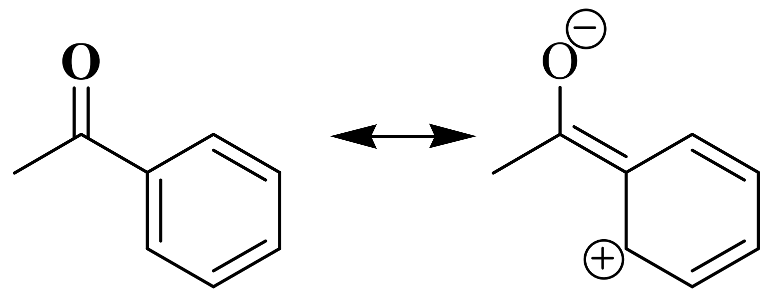
Factors affecting IR absorbance



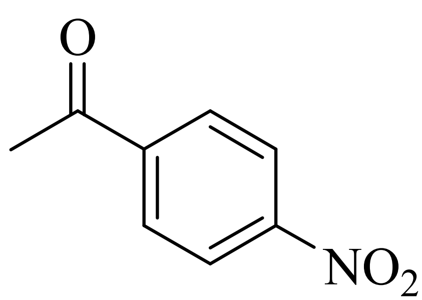
$\Delta\bar{\nu} = 1720\ cm^{-1}$



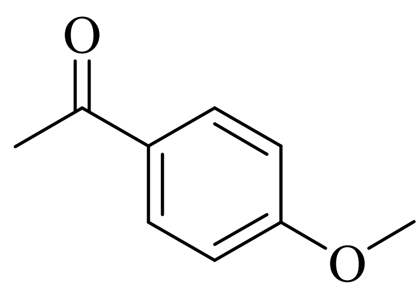
$\Delta\bar{\nu} = 1705\ cm^{-1}$



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



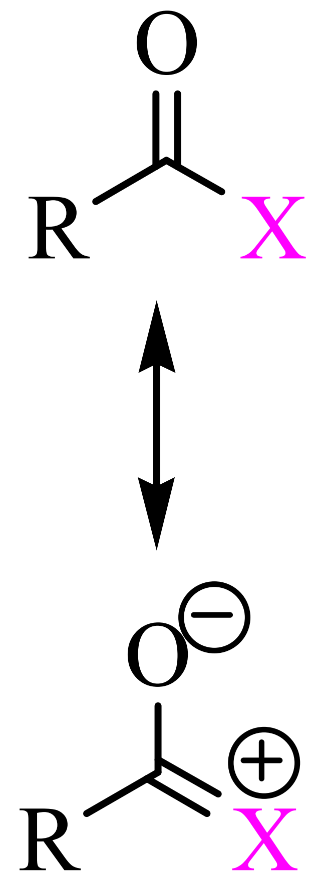
1



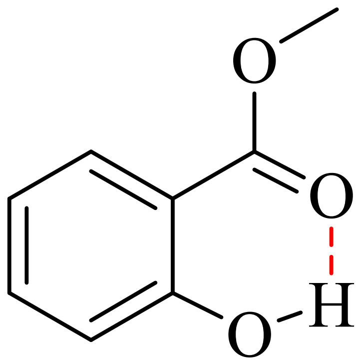
2

Factors affecting IR absorbance

	$\Delta\bar{\nu}$ (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

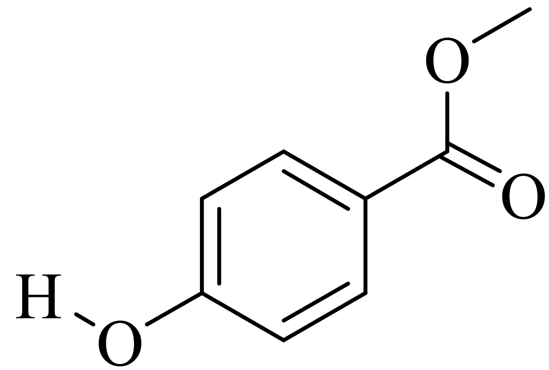


Factors affecting IR absorbance



1 (Intramolecular)

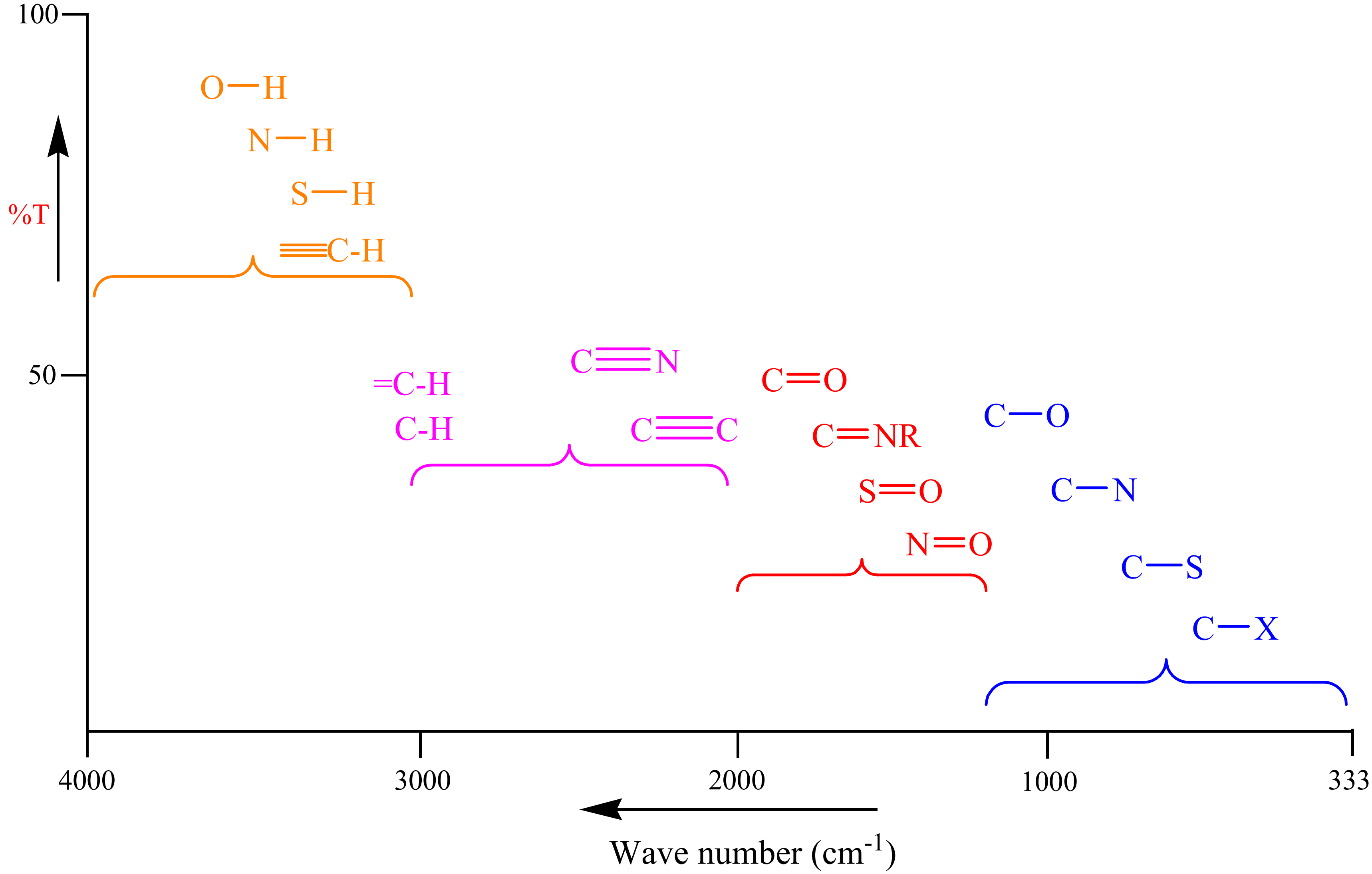
Not affected by dilution



2 (Intermolecular)

Affected by dilution

Division of IR band



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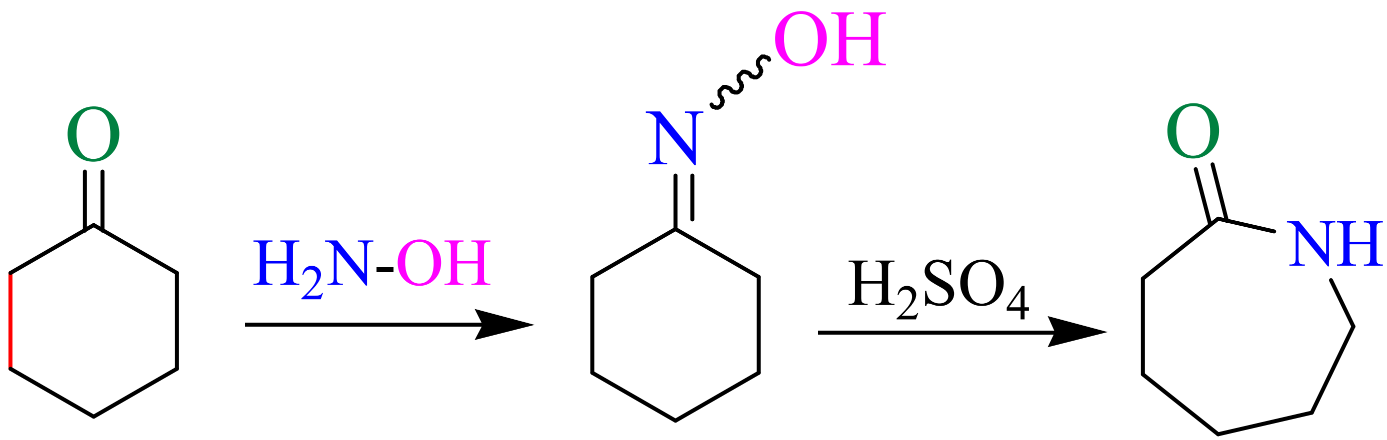
Application of IR Studies



1 **2** **3**

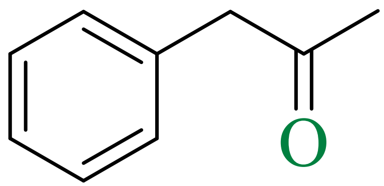
Beckmann's Rearrangement

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

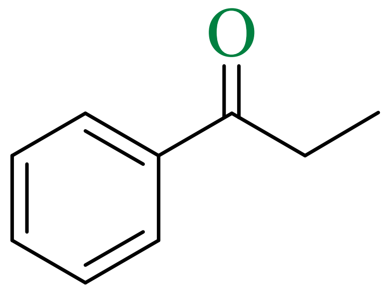
2: $\bar{\nu} = 3355\ cm^{-1}$, $1670\ cm^{-1}$

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

Application of IR Studies

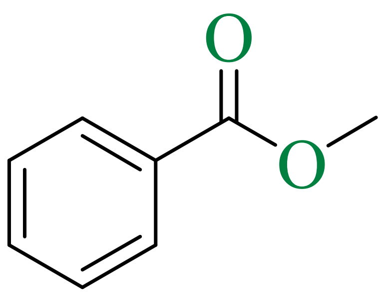


1

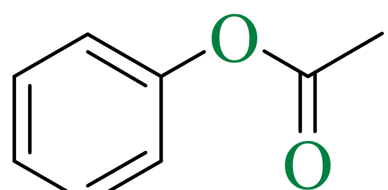


2

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

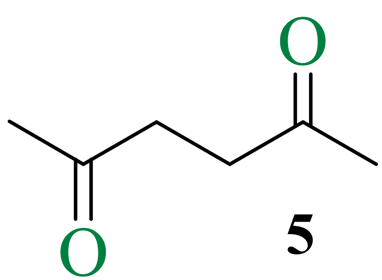


3

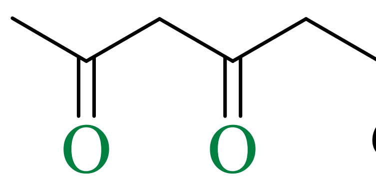


4

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



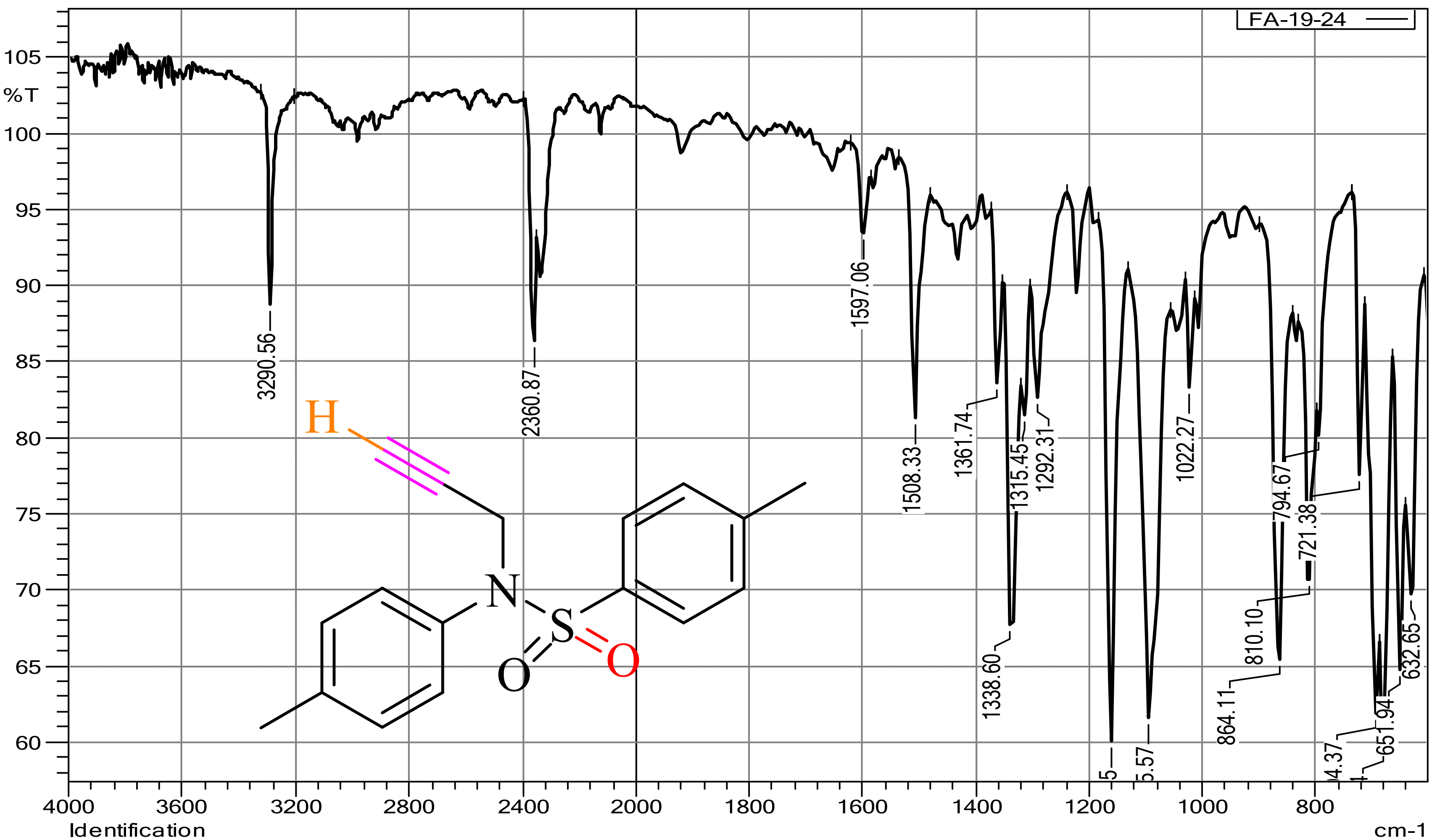
5



6

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

Application



Application