

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 ($\bar{\nu}$) = 3.33 to 333 m^{-1}

K. E. = $mv^2/2$ $\rightarrow$ 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. = $j^2/2 I$

$E = J(J+1) h^2 / 8 \pi^2 I$ $\rightarrow$ eq 2 (Schrodinger Wave Equation)

$h \nu = J(J+1) h^2 / 8 \pi^2 I$ $\nu = J(J+1) h / 8 \pi^2 I$

$c / \lambda = J(J+1) h / 8 \pi^2 I$ $c \bar{\nu} = J(J+1) h / 8 \pi^2 I$

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

B (Rotational constant) = $h / 8 c \pi^2 I$

J = Rotational Energy Levels

Microwave Transitions

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

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

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

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

$$\nu = 2(J + 1) h / 8 \pi^2 I c = 2 B (J + 1)$$

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

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

$$\nu = -2(J + 1) h / 8 \pi^2 I c = -2 B (J + 1)$$

Application of MW Spectroscopy

$$I = m r^2 \quad (\text{Macro Systems})$$

$$I = \mu r^2 \quad (\text{Micro Systems})$$

$$\mu = m_1 \cdot m_2 / (m_1 + m_2)$$

$$r^2 = I / \mu \quad \text{since } B = h / 8 \pi^2 I c$$

$$\text{so } I = h / 8 \pi^2 B c$$

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

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

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

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

$$\pi = 22/7 = 3.1416$$

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.

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

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

$$\mu = m_{\text{C}} \cdot m_{\text{O}} / (m_{\text{C}} + m_{\text{O}}) \times 1 / N_{\text{A}}$$

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

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

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

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

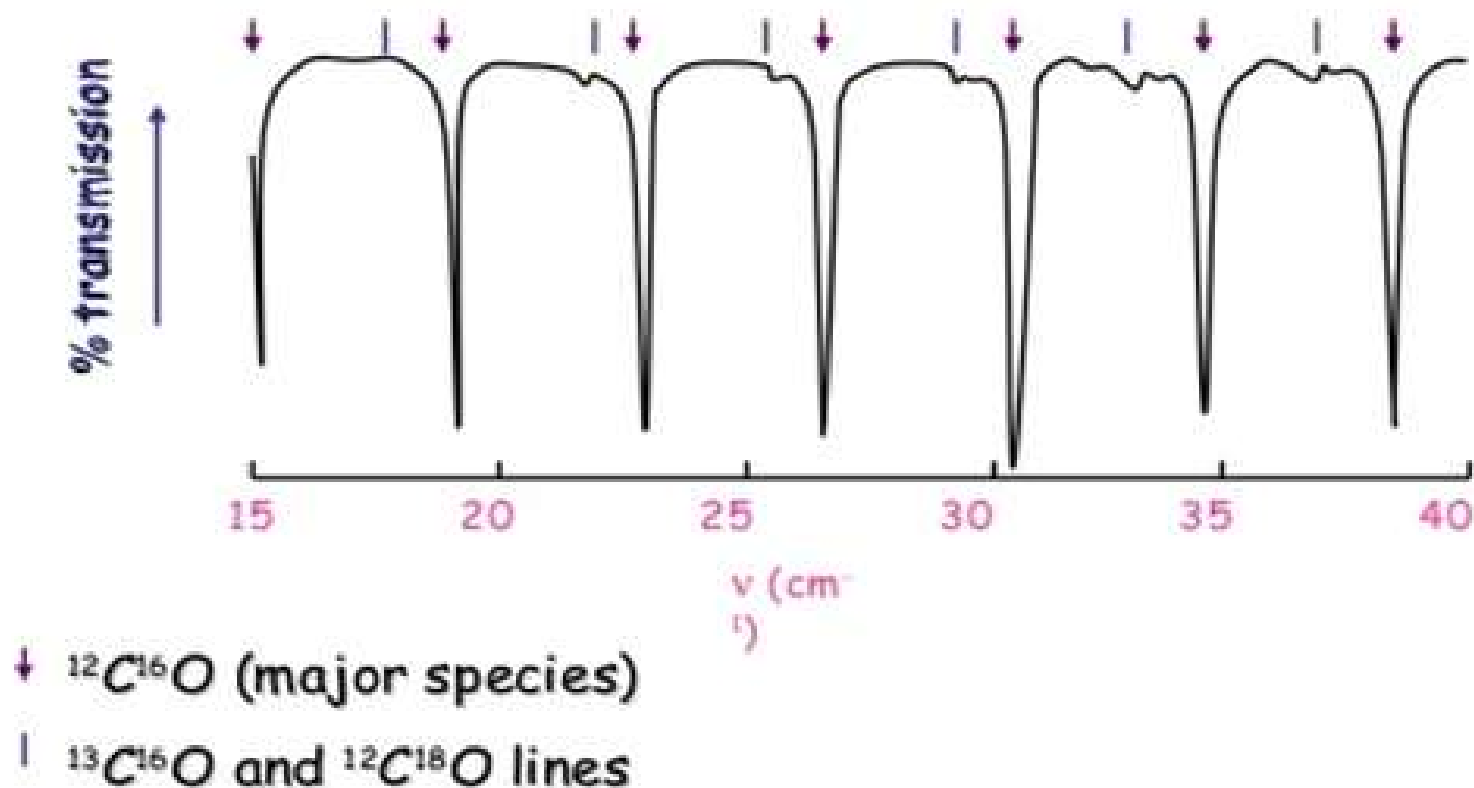
$$r = 1.131 \times 10^{-10} \text{ m} = 1.131 \text{ \AA}$$

$$\text{C=O} \quad r = 1.20 \text{ \AA}$$

$$\text{C}\equiv\text{O} \quad r = 1.128 \text{ \AA}$$

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 ($\bar{\nu}$) = 3.33×10^4 to 0.53×10^6 m^{-1}

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

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

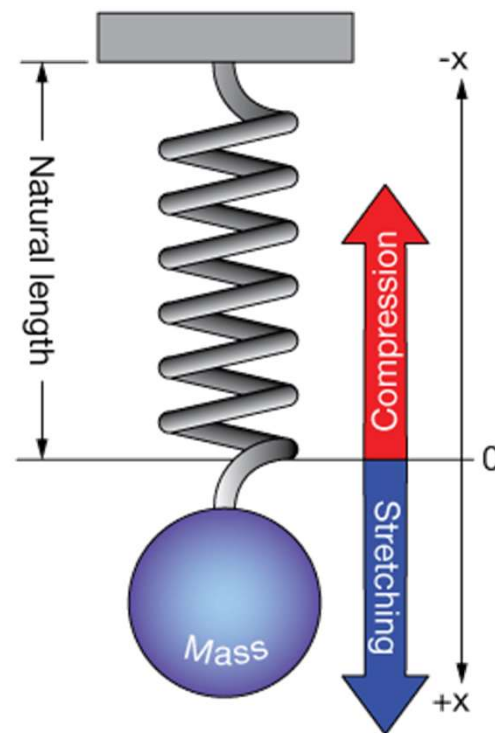
$$F \propto (-x)$$

$$F = -k \cdot x \quad \text{Hook's Law}$$

F = Force applied

x = Displacement

k = Hook's (spring / force) constant



InfraRed Spectroscopy

$$E = (V + \frac{1}{2}) h (k / \mu)^{\frac{1}{2}} / 2 \pi \quad \rightarrow \text{eq 1 (A solution of Schrodinger Wave Equation)}$$

V = Vibrational Energy Level

h = Plank's constant (6.63×10^{-34})

k = Hook's / force / spring constant

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

$$E_1 = (V_1 + \frac{1}{2}) h (k / \mu)^{\frac{1}{2}} / 2 \pi \quad V_1 = 0 \text{ (ground state energy)}$$

$$E_1 = (0 + \frac{1}{2}) h (k / \mu)^{\frac{1}{2}} / 2 \pi = h (k / \mu)^{\frac{1}{2}} / 4 \pi \quad \rightarrow \text{eq 2}$$

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

$$E_2 = (1 + \frac{1}{2}) h (k / \mu)^{\frac{1}{2}} / 2 \pi = 3 h (k / \mu)^{\frac{1}{2}} / 4 \pi \quad \rightarrow \text{eq 3}$$

$$\Delta E = (E_2 - E_1) = [3 h (k / \mu)^{\frac{1}{2}} / 4 \pi] - [h (k / \mu)^{\frac{1}{2}} / 4 \pi]$$

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

InfraRed Spectroscopy

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

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

$$E = h c / \lambda \quad \rightarrow \text{eq 5}$$

Since $1 / \lambda = \nu$ so $E = h c \nu$

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

$$h c \nu = h (k / \mu)^{1/2} / 2 \pi \quad \rightarrow \text{eq 6}$$

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

Application of IR

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

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

$$\mu = (m_{\text{C}} \cdot m_{\text{O}}) / (m_{\text{C}} + m_{\text{O}}) \times 1 / N_{\text{A}}$$

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

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

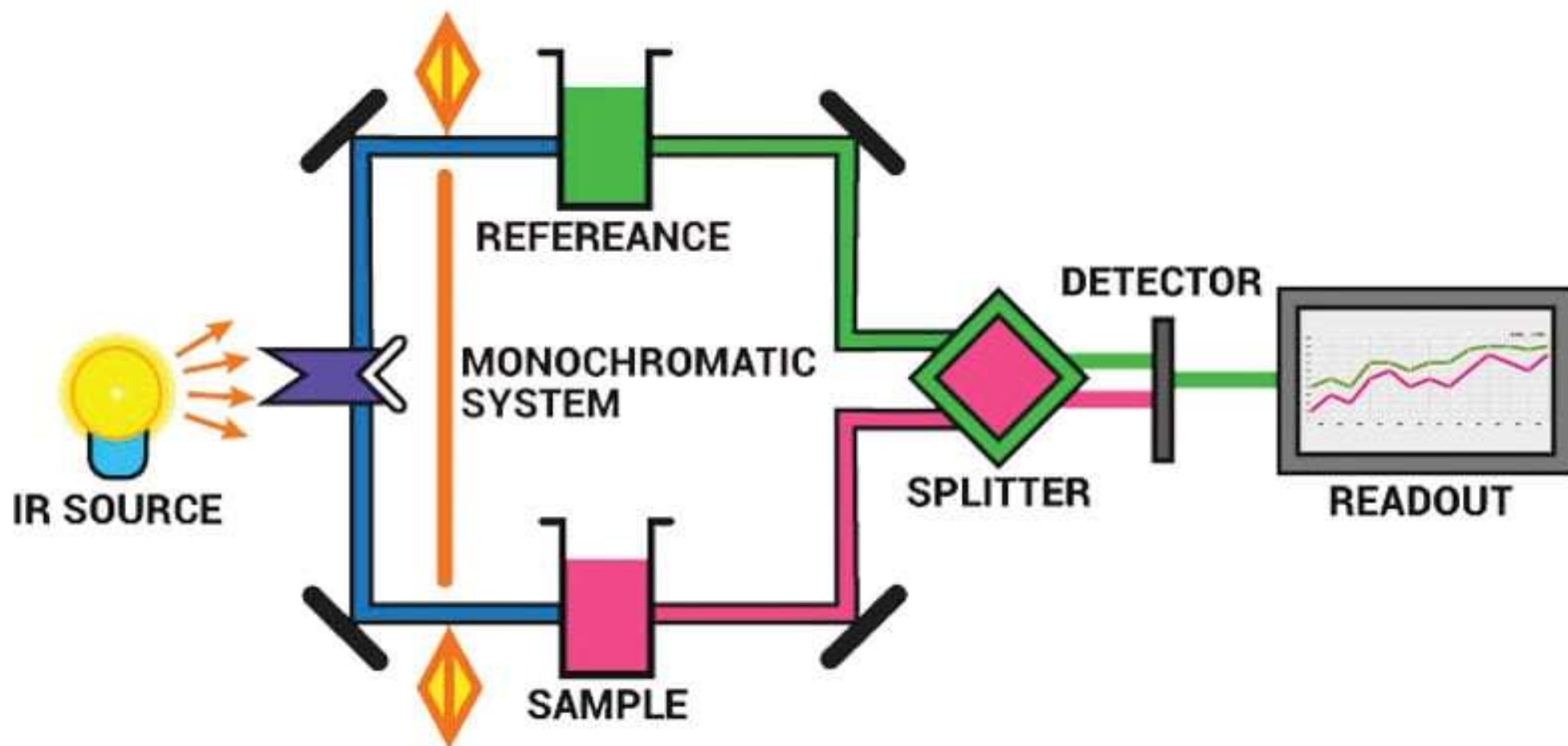
$$\nu = (k / \mu)^{1/2} / 2 \pi c$$

$$\nu^2 = k / 4 \pi^2 c^2 \mu \quad \text{so} \quad k = 4 \pi^2 c^2 \mu \nu^2$$

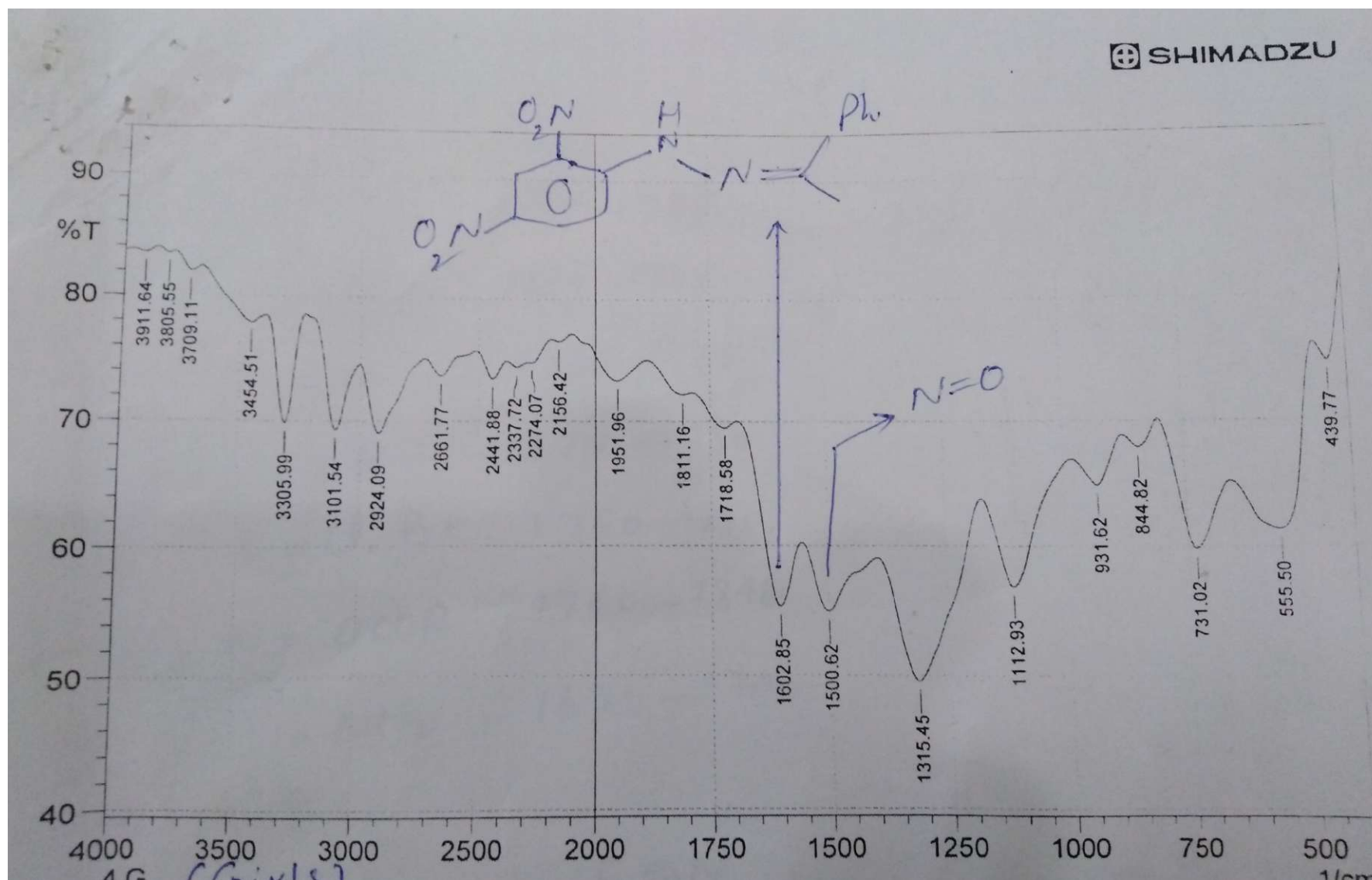
$$k = 4 \times (3.1416)^2 \times (3 \times 10^8)^2 \times (1.139 \times 10^{-26}) \times (154330)^2$$

$$k = 963.94 \text{ N / m}$$

Instrumentation of IR Spectrophotometer



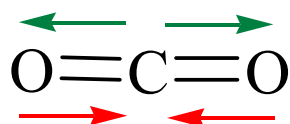
An IR Spectrum



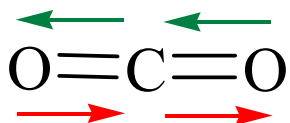
Mode of Vibrations

3N - 5 (Linear molecule)

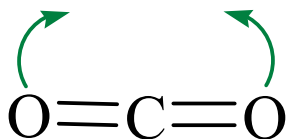
3N - 6 (Non-linear molecule)



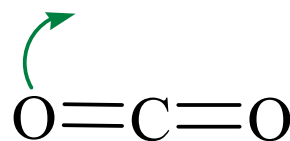
Symmetrical
Stretching



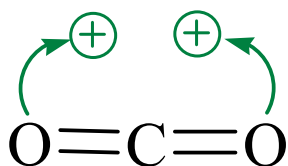
Asymmetrical
Stretching



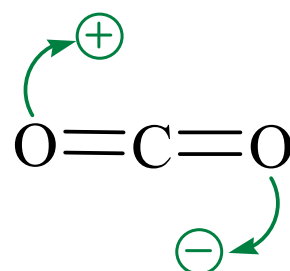
Scissoring



Rocking



Wagging



Twisting

In plane bending

Out of plane bending

Factors affecting IR absorbance

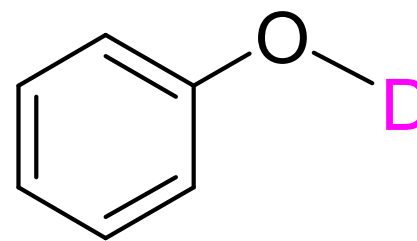
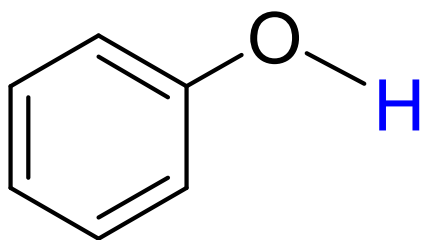
$$\Delta\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \Delta\bar{\nu} \propto \sqrt{k}$$

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

Factors affecting IR absorbance

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

$$\Delta\bar{\nu} \propto \sqrt{\frac{1}{\mu}}$$



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

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

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

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

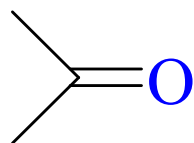
$$\Delta\bar{\nu} = 3500 \text{ cm}^{-1}$$

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

Factors affecting IR absorbance

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

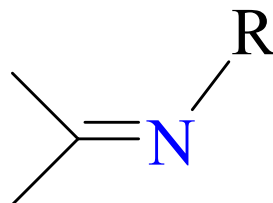
$$\Delta\bar{\nu} \propto \sqrt{\frac{1}{\mu}}$$



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

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

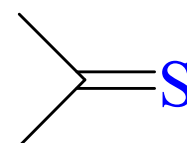
$$\Delta\bar{\nu} = 1700-1770 \text{ cm}^{-1}$$



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

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

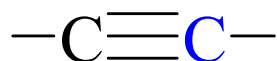
$$\Delta\bar{\nu} = 1640-1690 \text{ cm}^{-1}$$



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

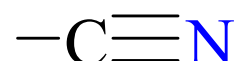
$$\mu = 8.73 \times 10^{-3} \text{ kg}$$

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



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

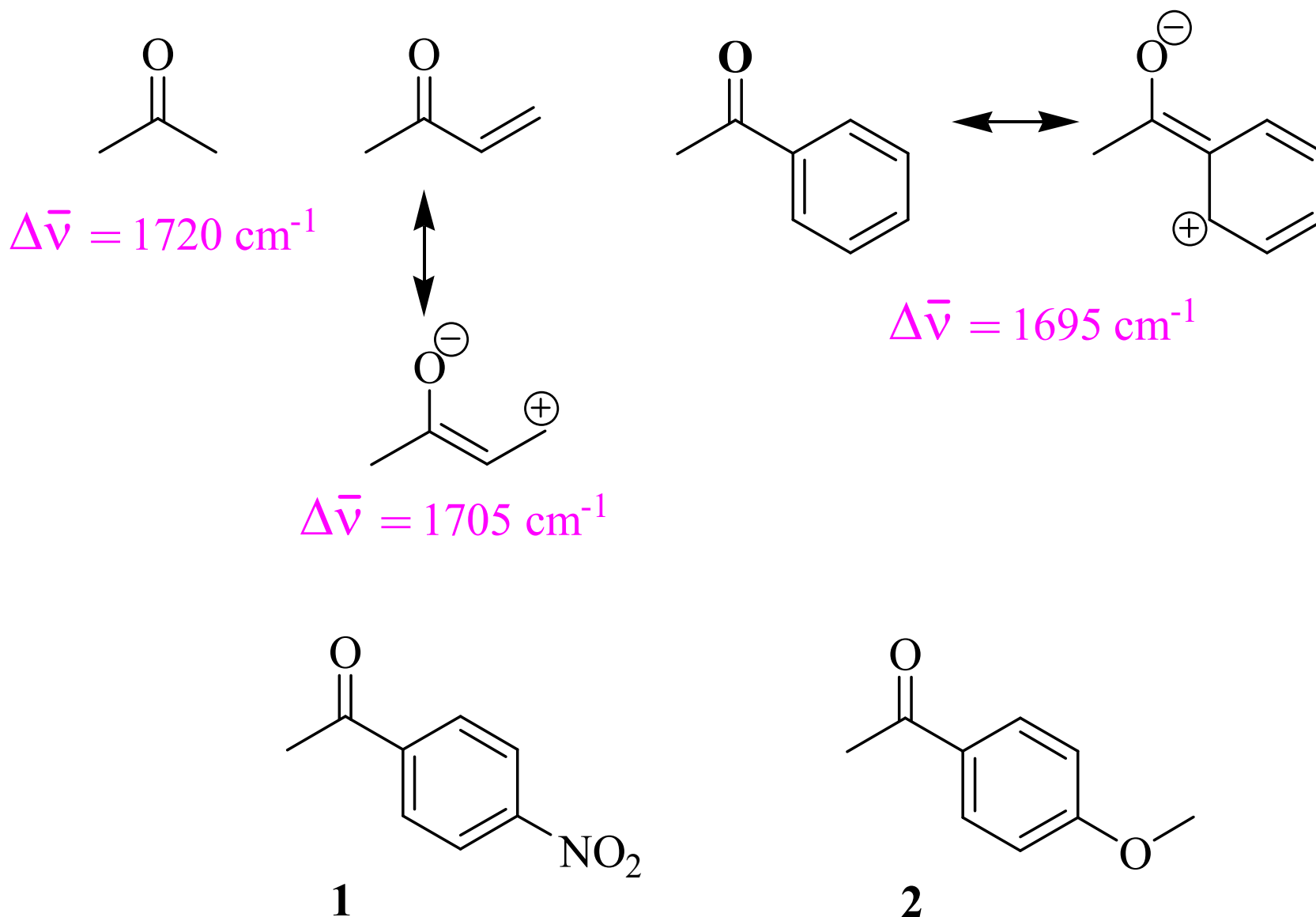
$$\Delta\bar{\nu} = 2100-2260 \text{ cm}^{-1}$$



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

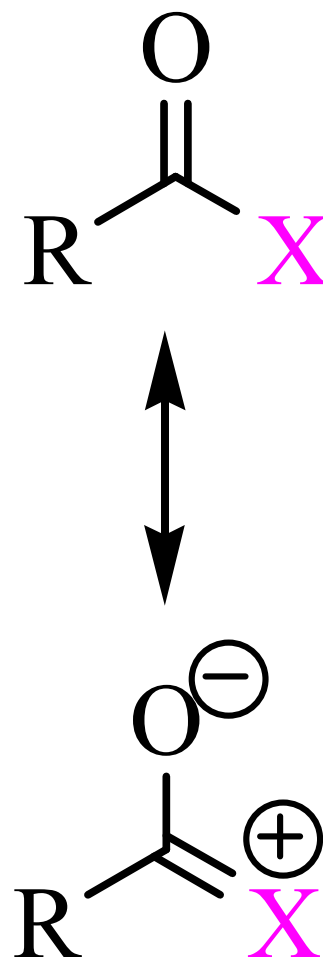
$$\Delta\bar{\nu} = 2210-2260 \text{ cm}^{-1}$$

Factors affecting IR absorbance

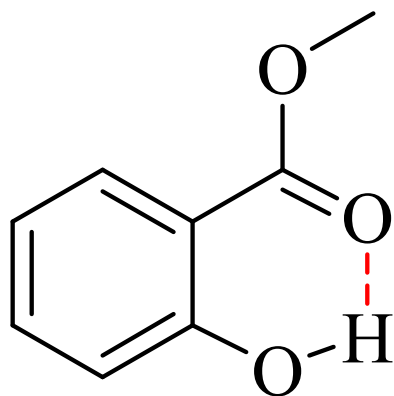


Factors affecting IR absorbance

	$\Delta\bar{\nu}$ (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



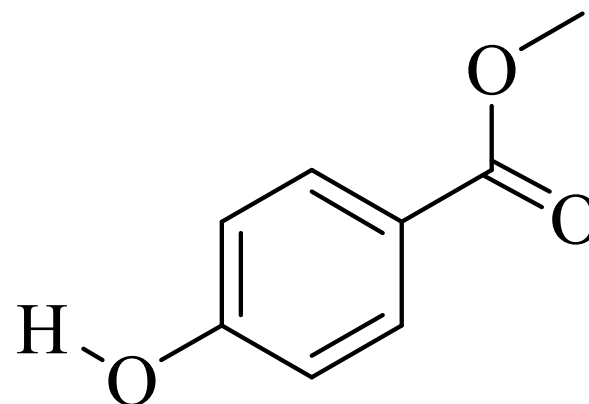
Factors affecting IR absorbance



1 (Intramolecular)



Not affected by dilution

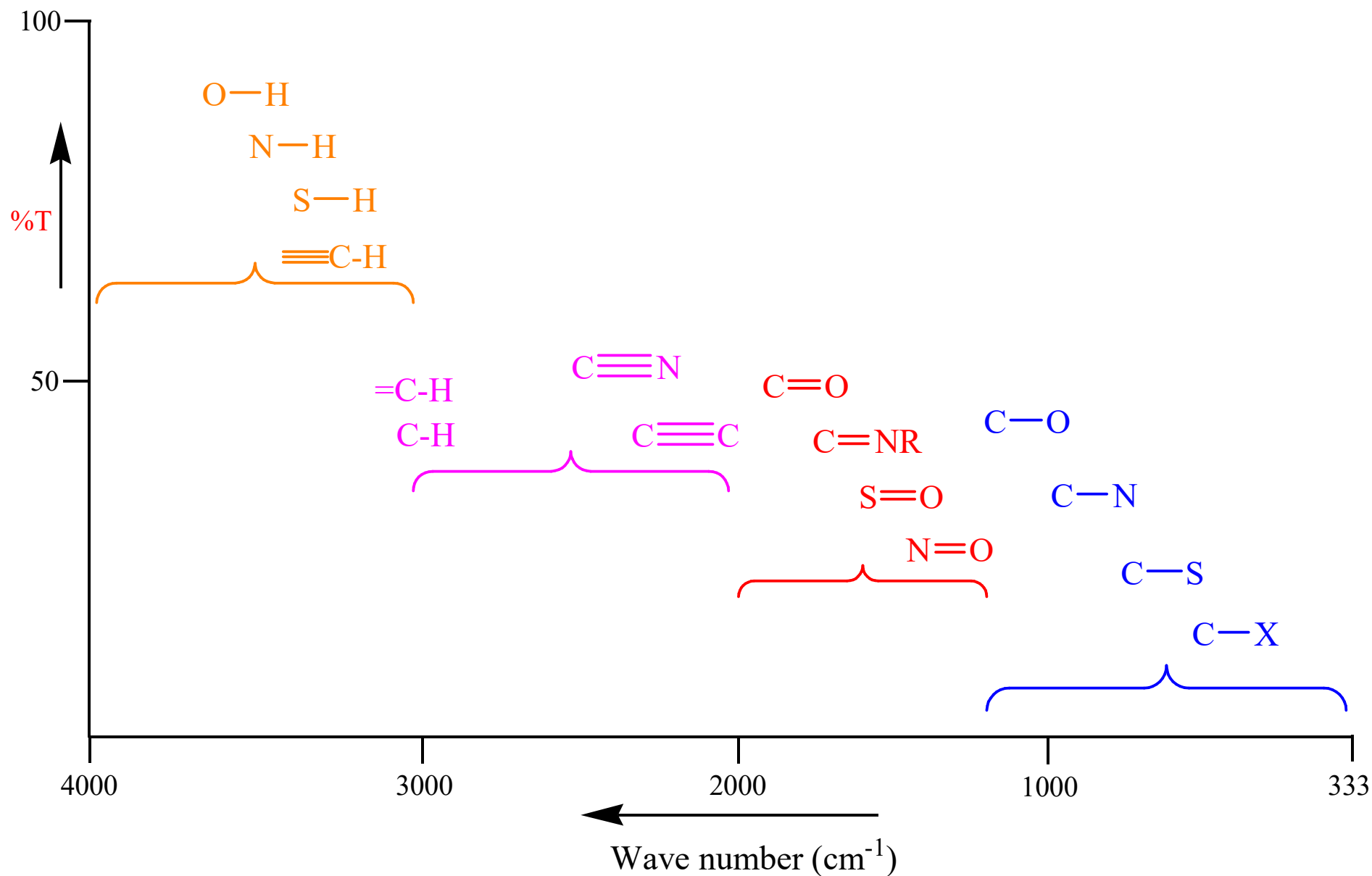


2 (Intermolecular)

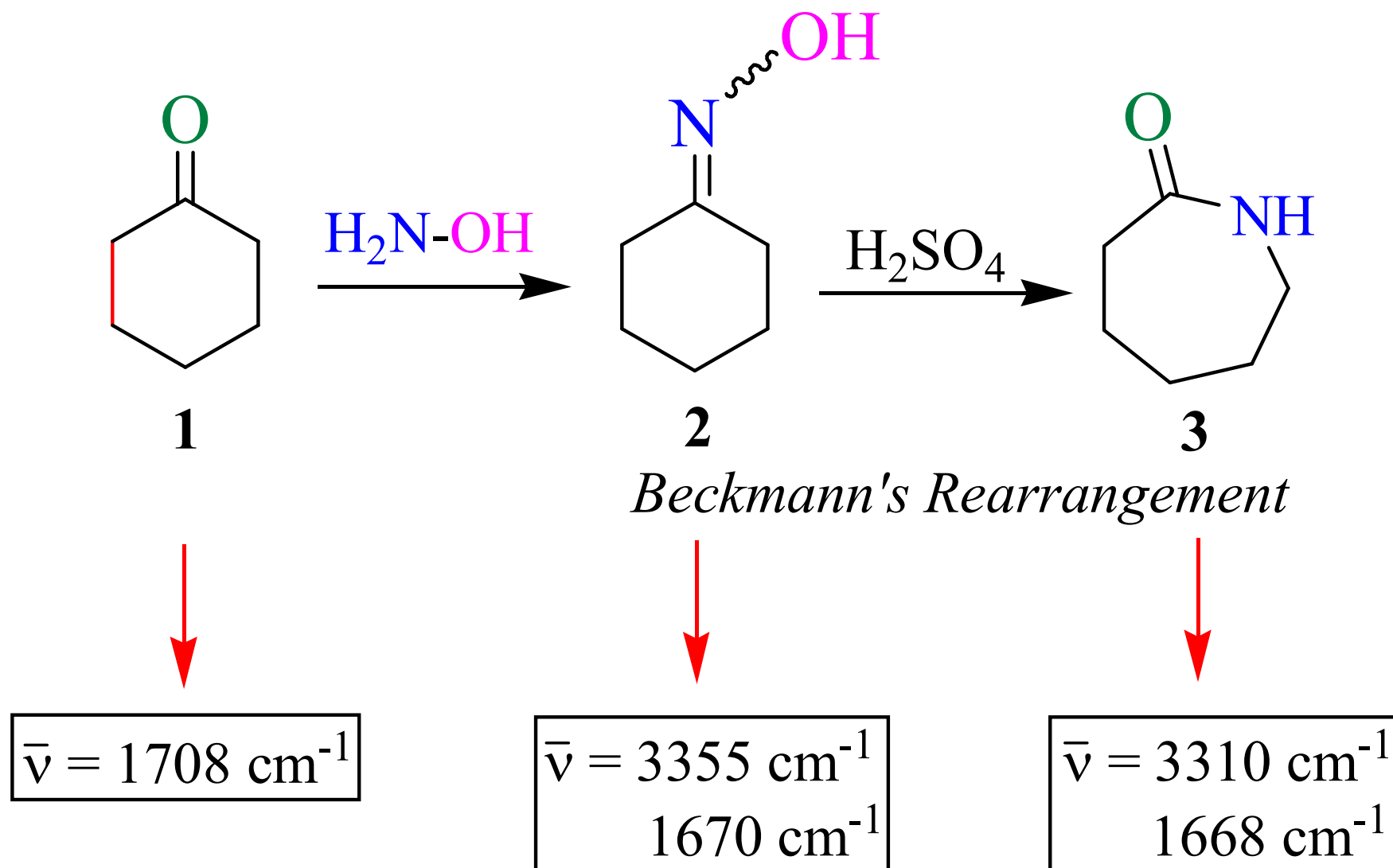


Affected by dilution

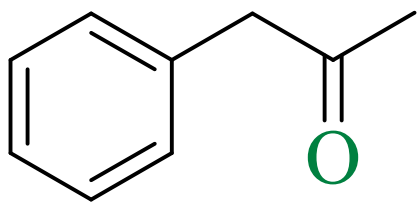
Division of IR band



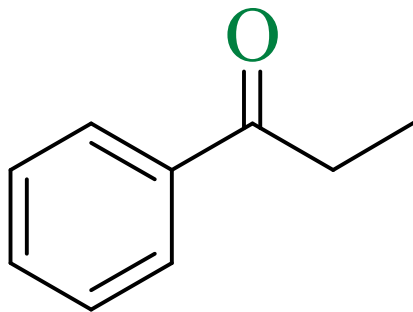
Application of IR Studies



Application of IR Studies

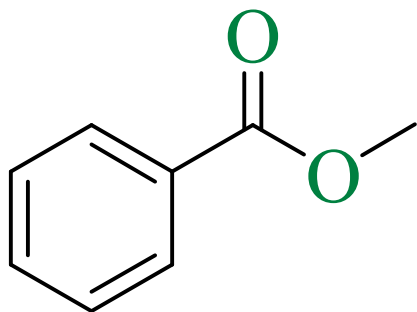


1

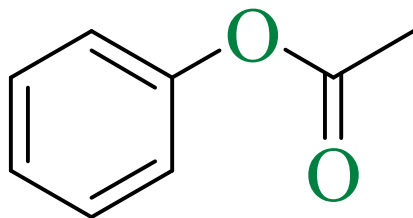


2

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

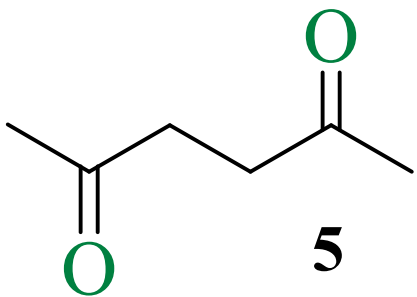


3

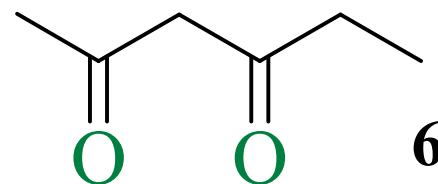


4

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



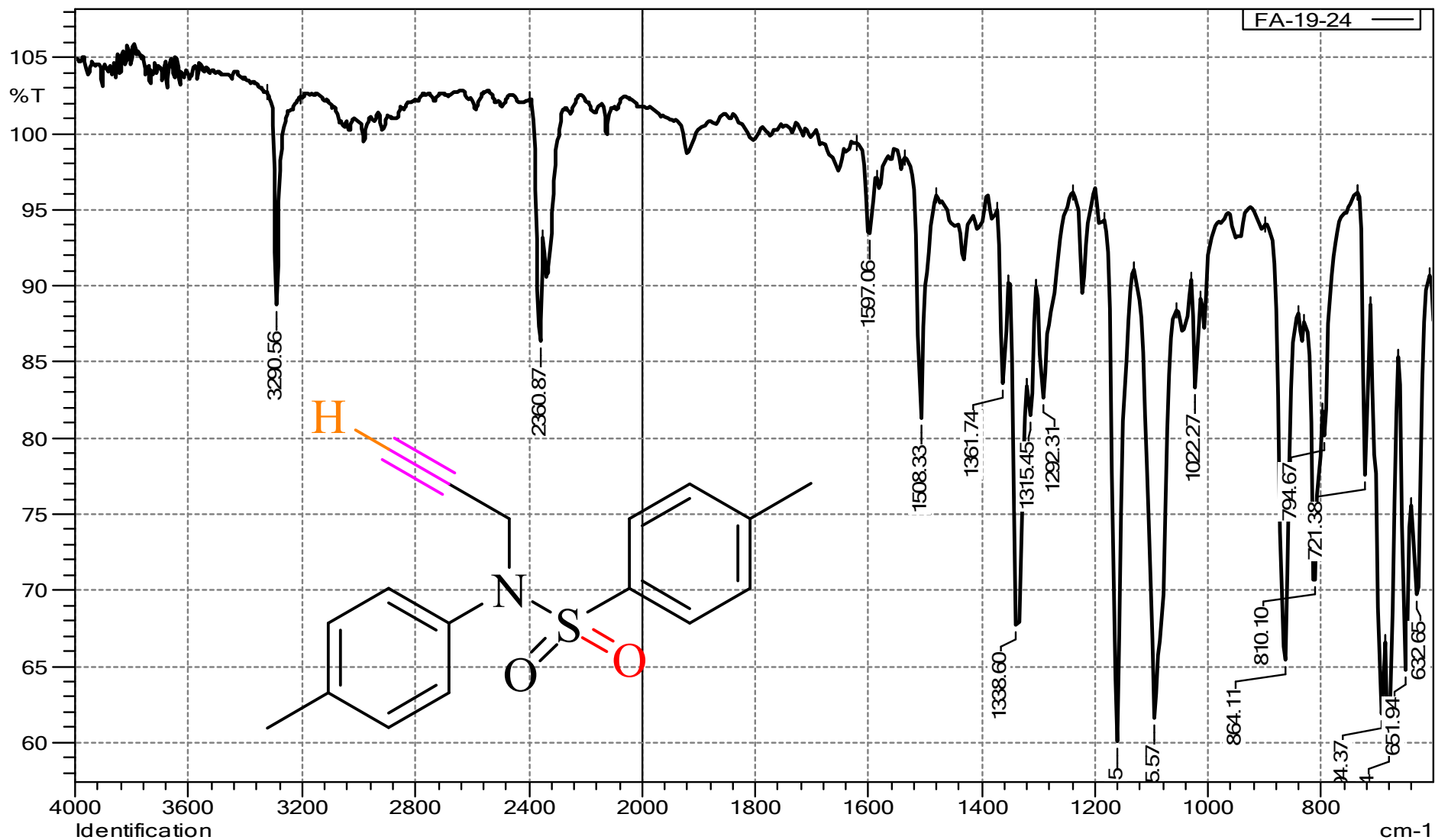
5



6

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

Application



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Application

