Inter-Lecture C

Infrared Spectroscopy and Mass Spectrometry

А.И.Соч

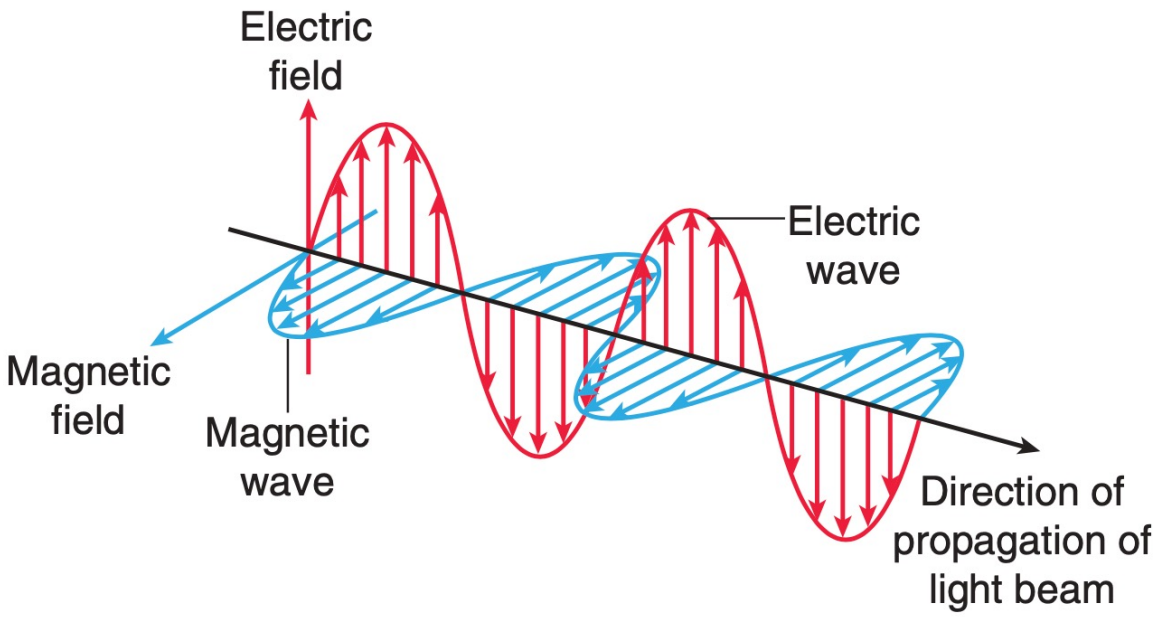
2022/3/16

Infrared Spectroscopy

Introduction to Spectroscopy, Principles of IR Spectroscopy,

Signal Characteristics, Analyzing Techniques

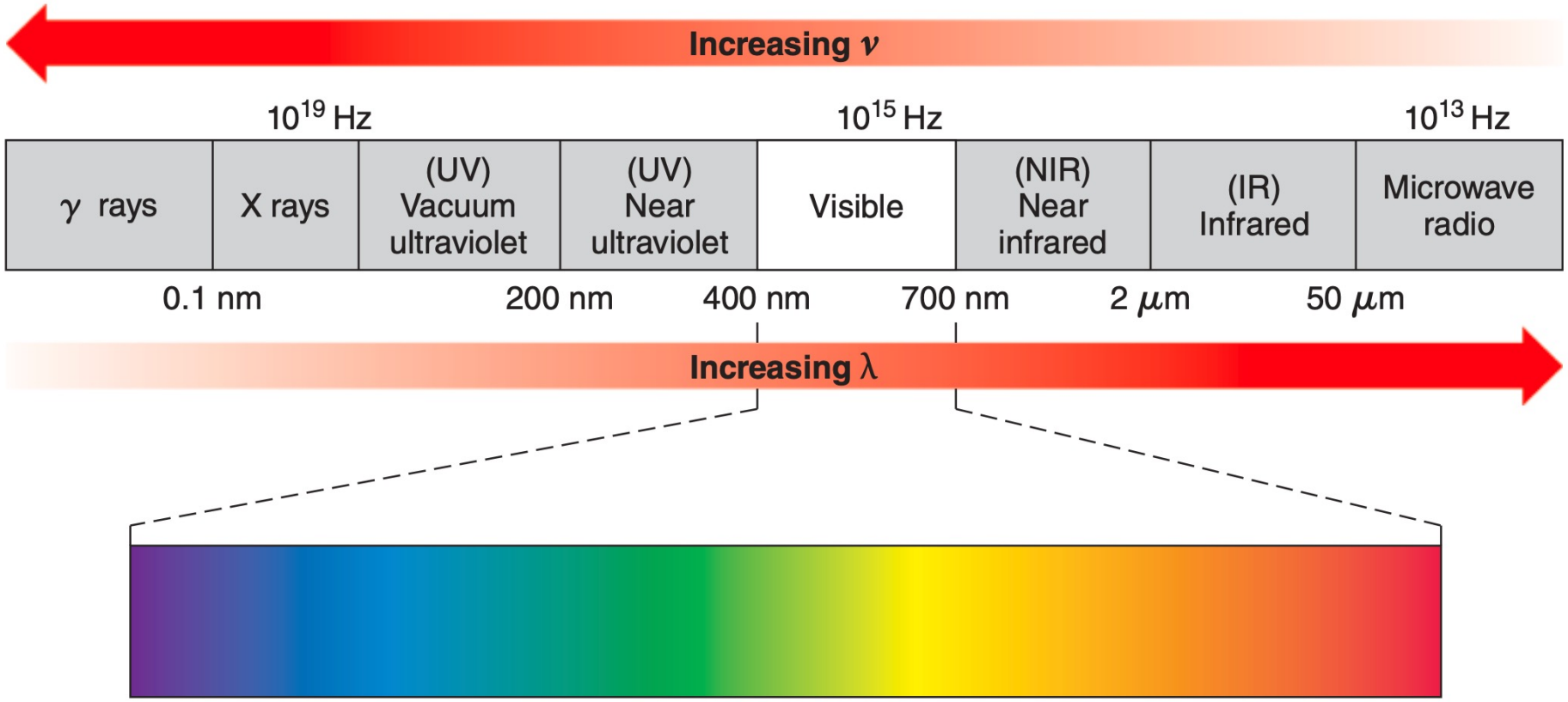
- The nature of light: electromagnetic radiations



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

$$E = h\nu$$

- Electromagnetic spectrum

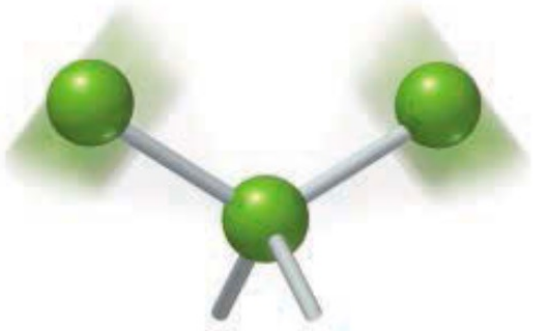


- Some common forms of spectroscopy and their uses

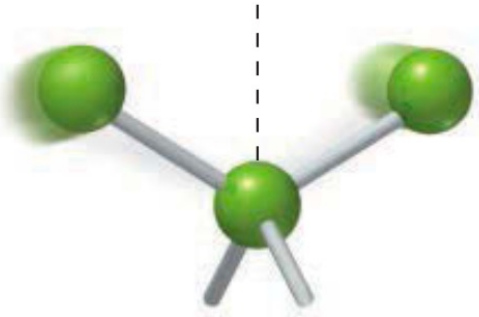
TYPE OF SPECTROSCOPY	REGION OF ELECTROMAGNETIC SPECTRUM	INFORMATION OBTAINED
Nuclear magnetic resonance (NMR) spectroscopy	Radio waves	The specific arrangement of all carbon and hydrogen atoms in the compound
IR spectroscopy	Infrared	The functional groups present in the compound
UV-VIS spectroscopy	Visible and ultraviolet	Any conjugated π system present in the compound

- Vibrational excitation

A stretching vibration

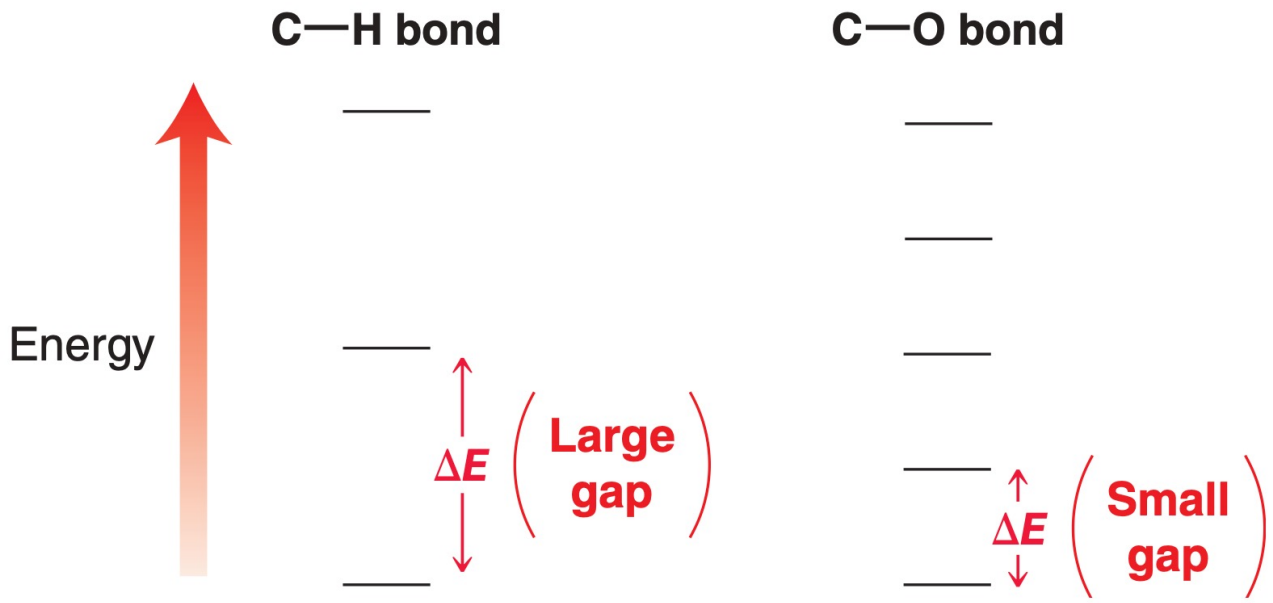


An in-plane bending vibration (scissoring)



An out-of-plane bending vibration (twisting)

- Functional group identification

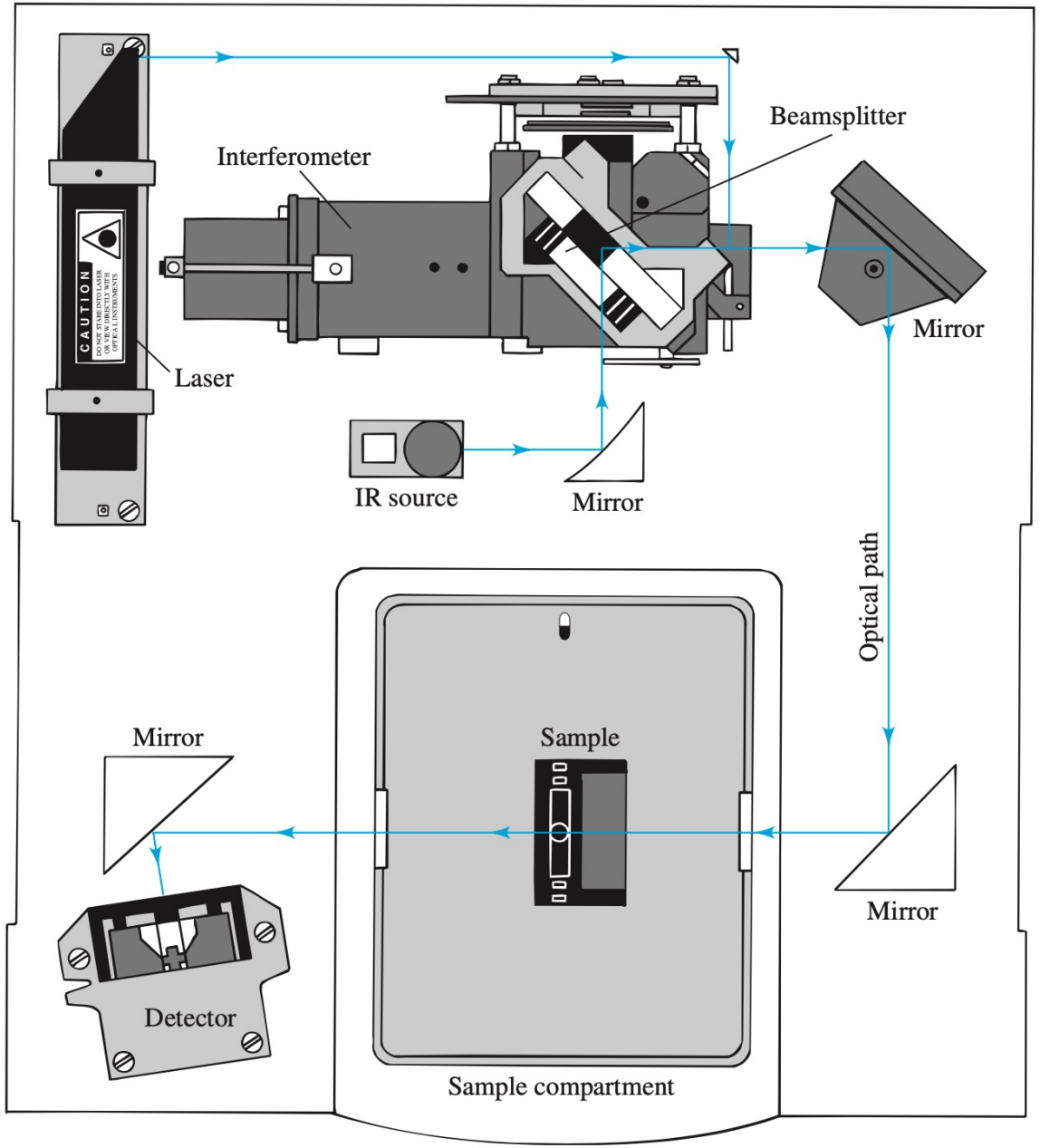


different bonds have different vibrational energy gap

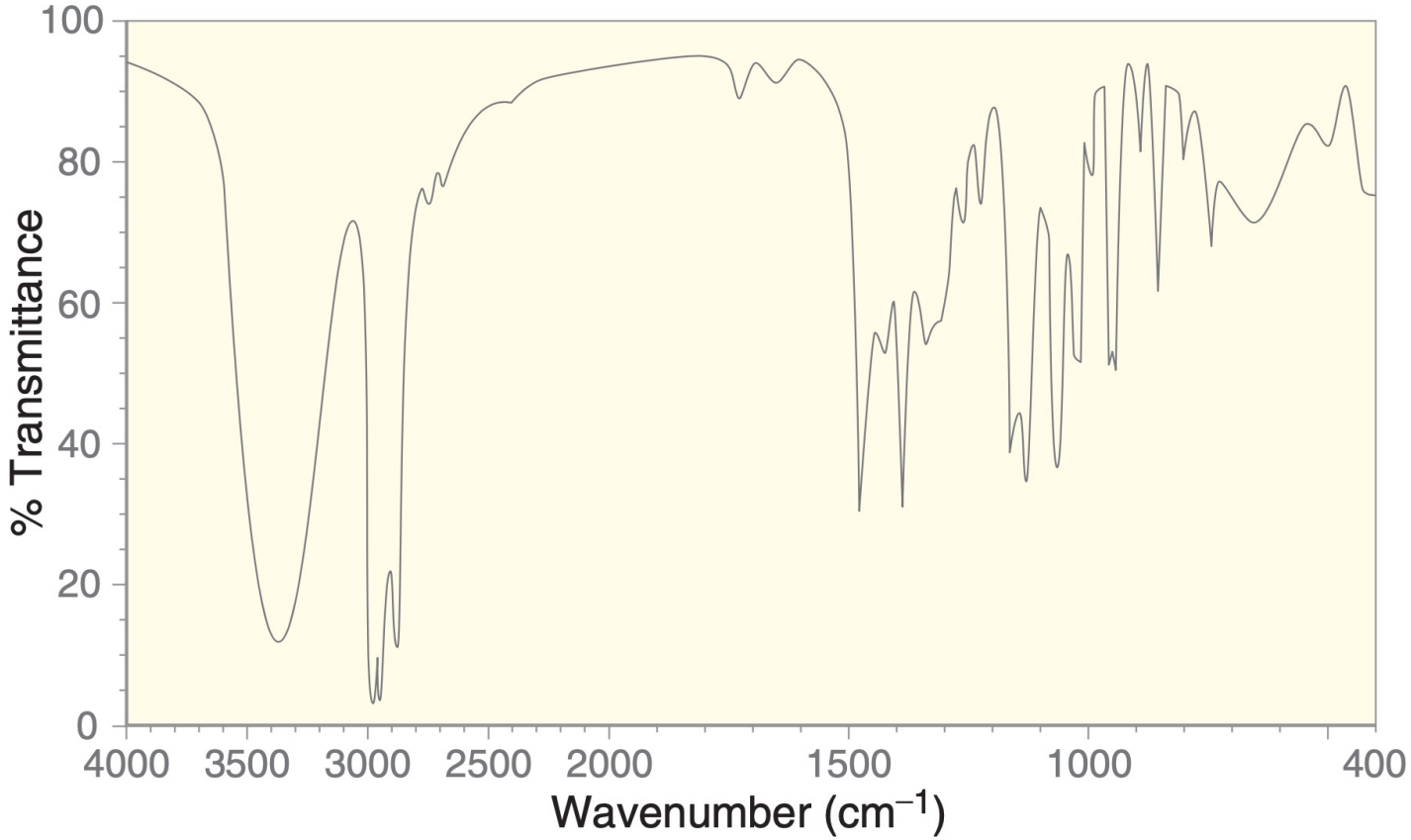
- IR Spectrometer

salt plate (NaCl)

transparent to IR radiation

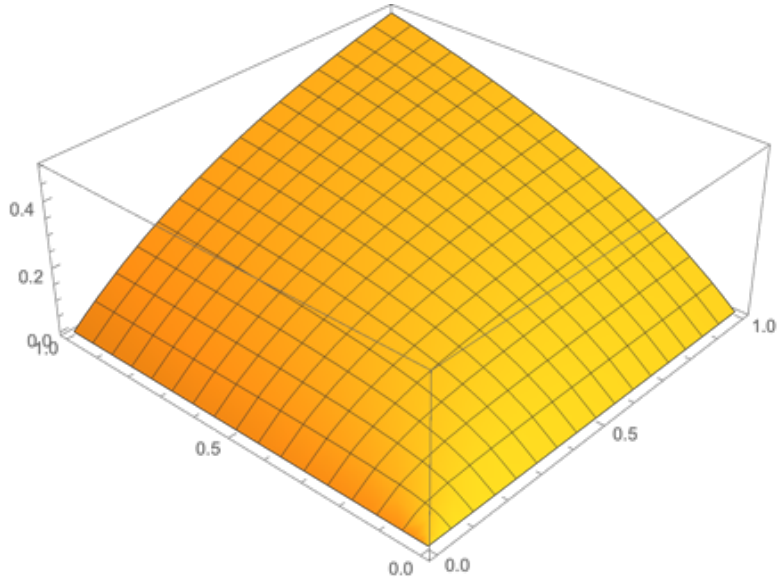


- The general shape of an IR absorbance spectrum



wavenumber: $\tilde{\nu} = \frac{\nu}{c}$

*why not **frequency**?*



- Hooke's law

$$\tilde{\nu} = \left(\frac{1}{2\pi c}\right)\left(\frac{f}{m_{red}}\right)^{\frac{1}{2}}$$

force constant (bond strength)

reduced mass $= \left(\frac{m_1 m_2}{m_1 + m_2}\right)$

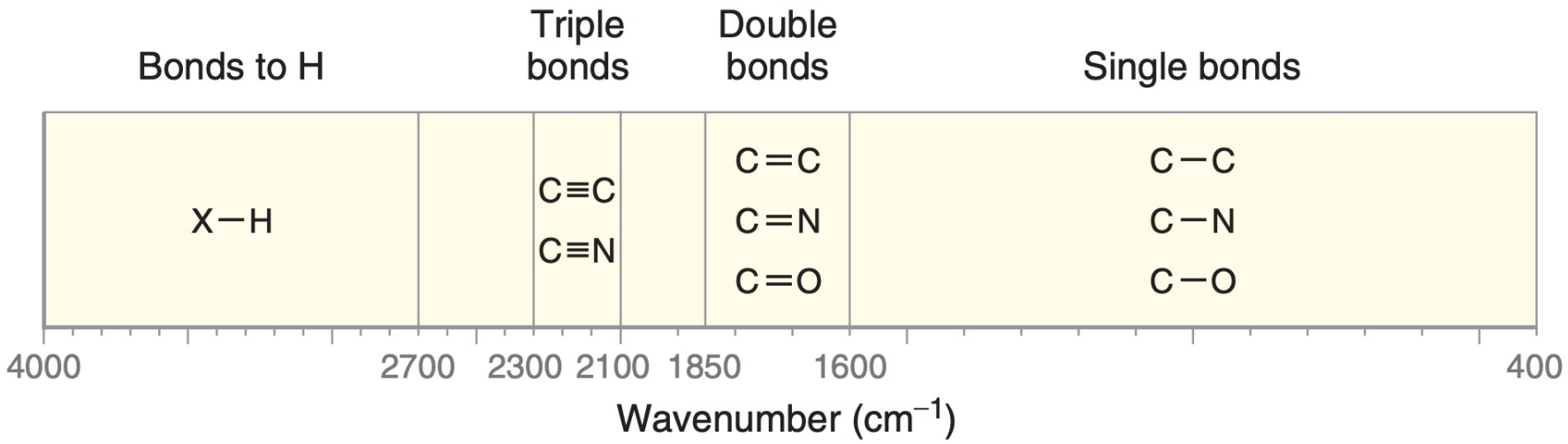
- m_{red} – denominator: smaller mass, higher wavenumber

C—H	C—D	C—O	C—Cl
~3000 cm^{-1}	~2200 cm^{-1}	~1100 cm^{-1}	~700 cm^{-1}

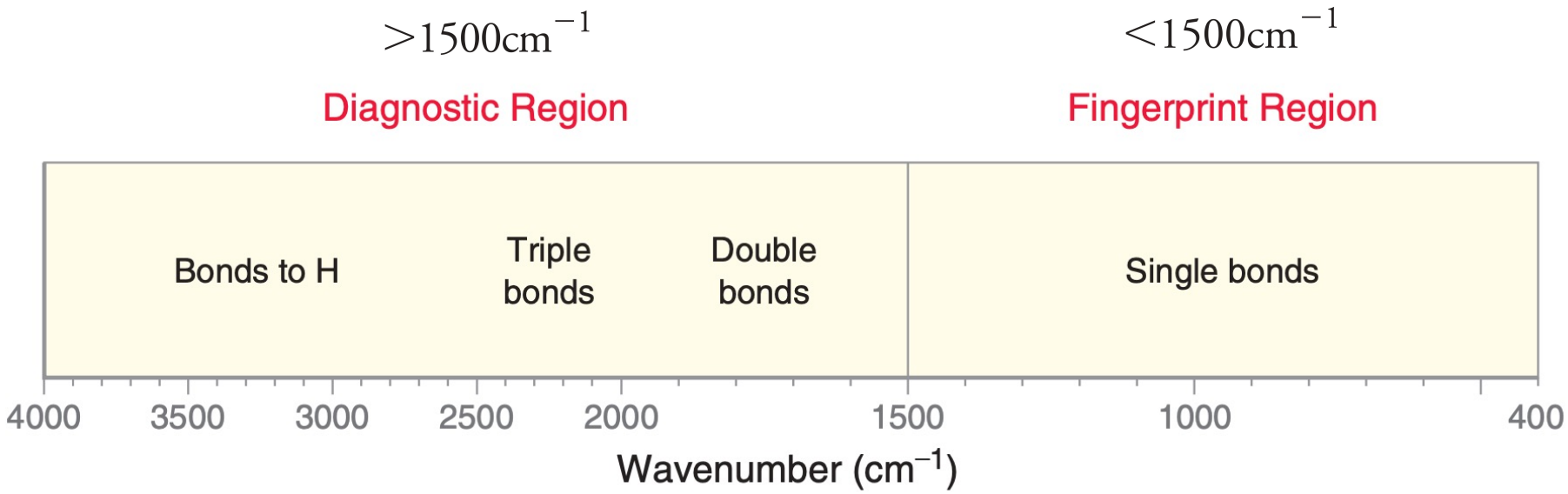
- f – numerator: stronger bond, higher wavenumber

C≡N	C=N	C—N
~2200 cm^{-1}	~1600 cm^{-1}	~1100 cm^{-1}

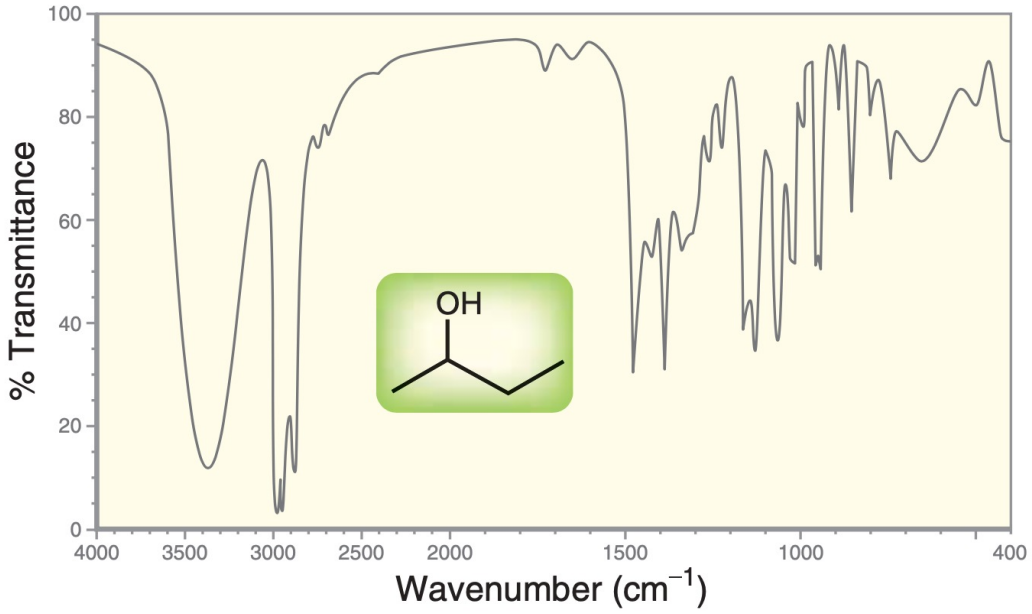
- Different wavenumbers represent different type of bonds

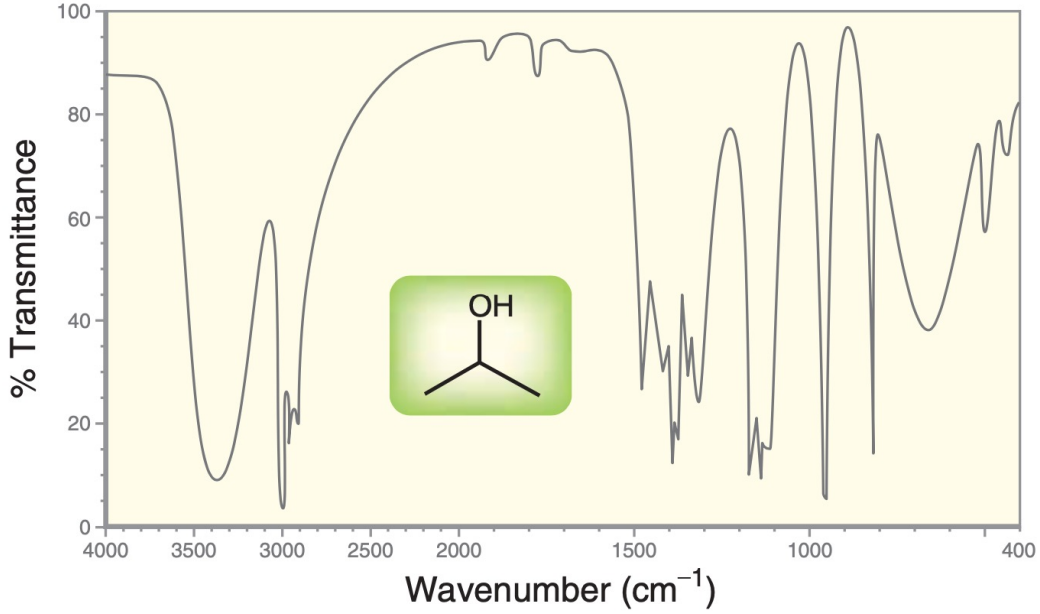


- Diagnostic region and fingerprint region

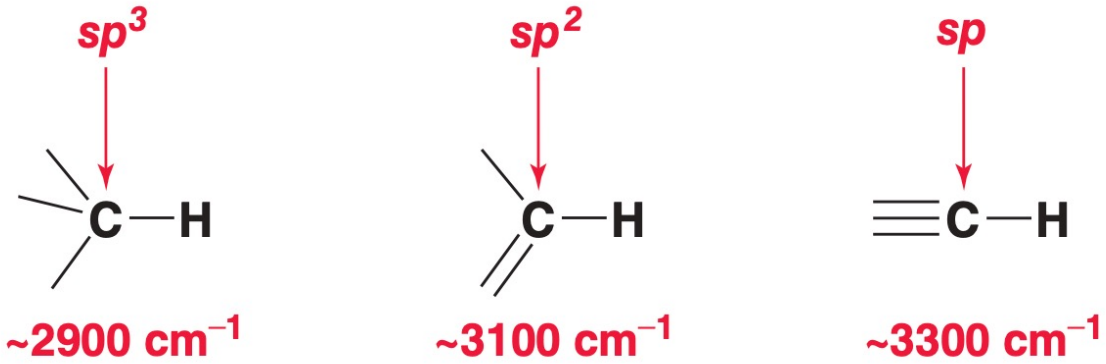


- Slight differences in fingerprint region



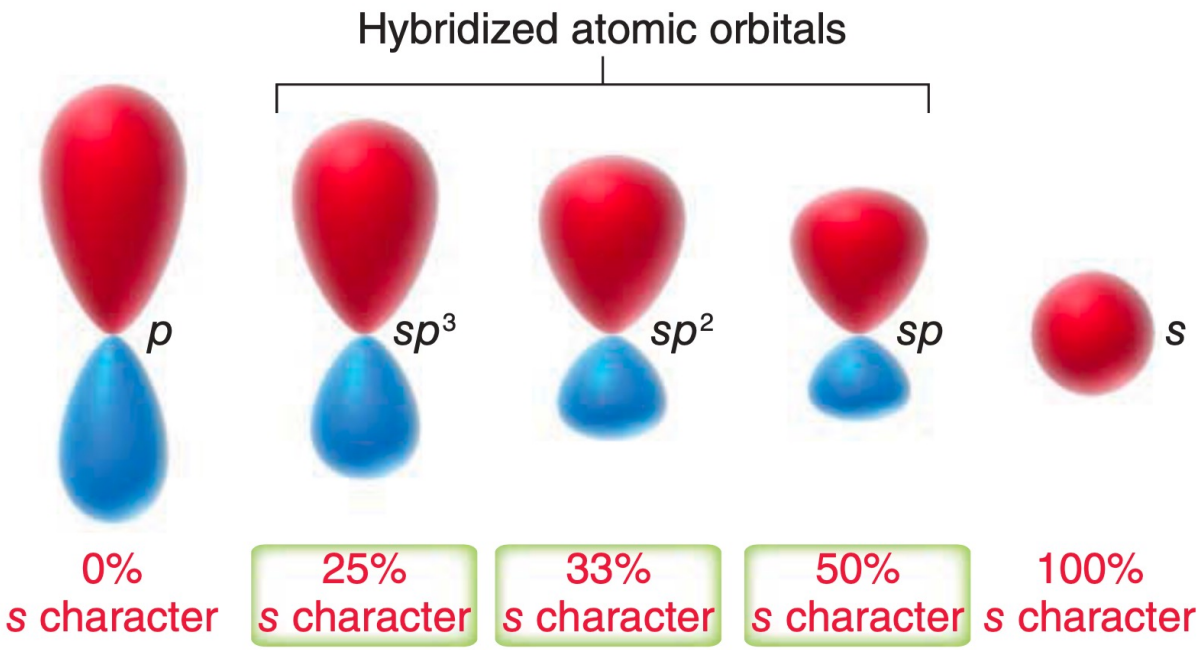


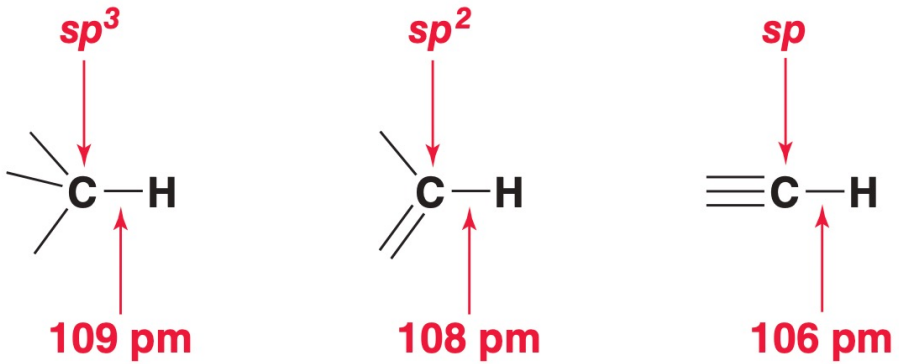
- Effect of hybridization states on wavenumber of absorption



wavenumber increases with the increase of *s* character

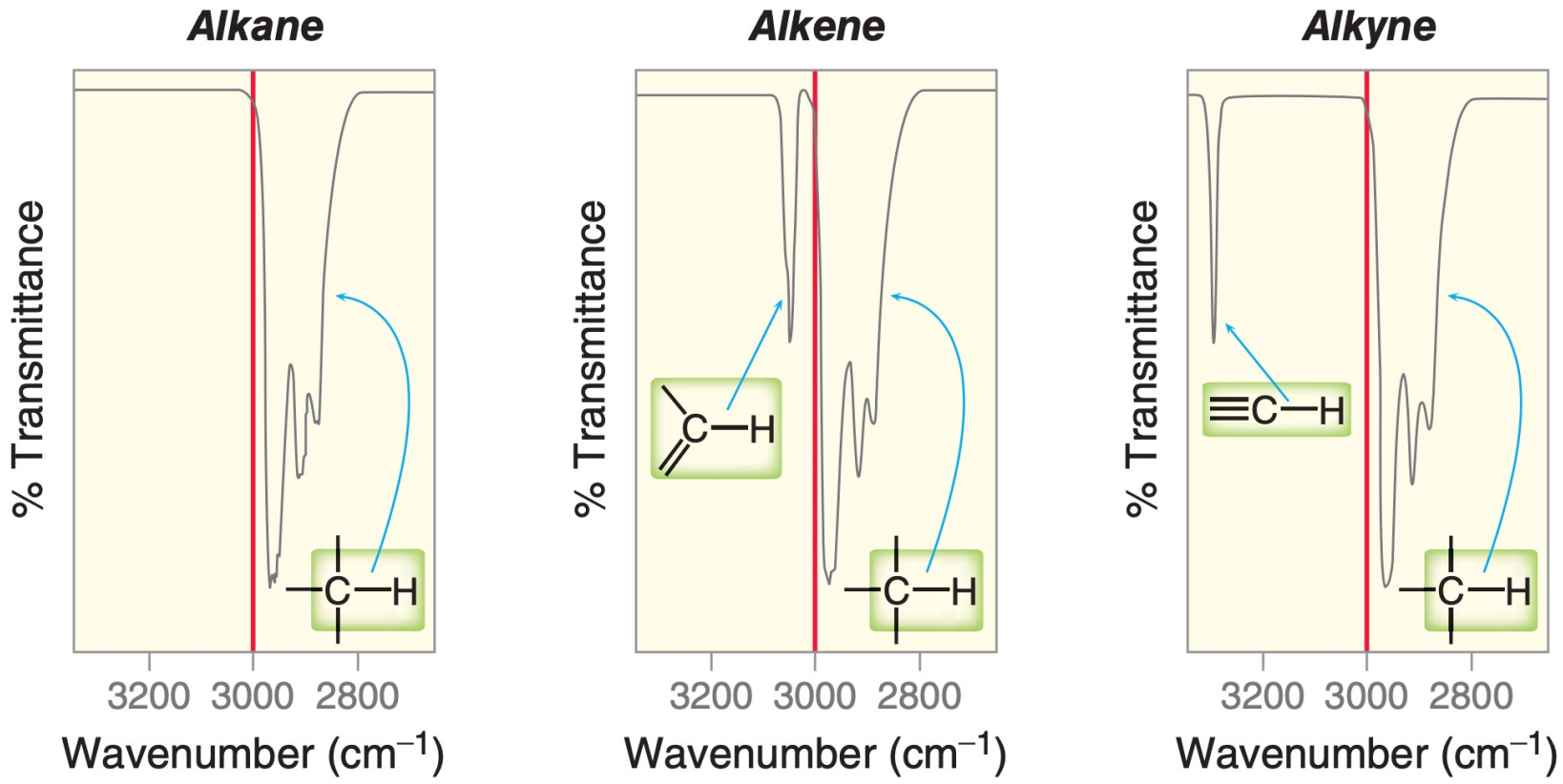
- Hybridization and shape of orbitals



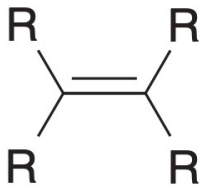


higher % *s* character – closer shape – better overlap – stronger bond

- Spectra for different hybridization C–H bonds



- Absence of C–H bond gives no signal >3000 cm^{-1}



No signal at 3100 cm^{-1}

(no $C_{sp^2}-H$)

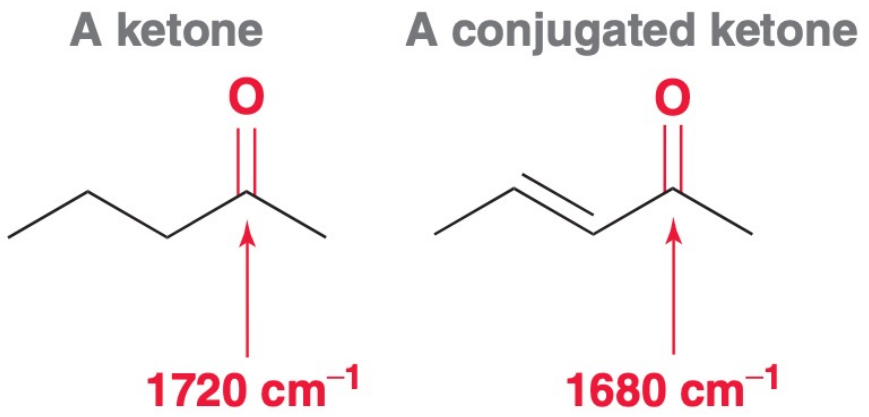
No signal at 3300 cm^{-1}

(no $C_{sp}-H$)

the absence of a signal to the left of 3000 cm^{-1}

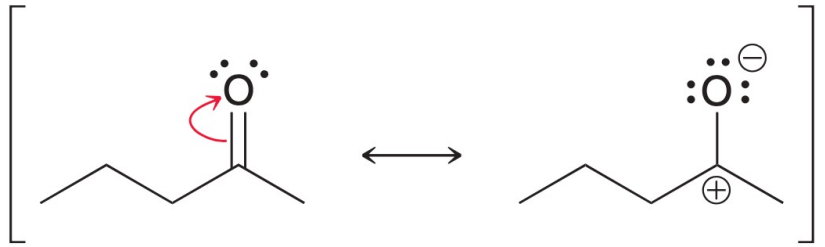
does **NOT** necessarily indicate the absence of a double bond or triple bond!

- Effect of resonance on wavenumber of absorption

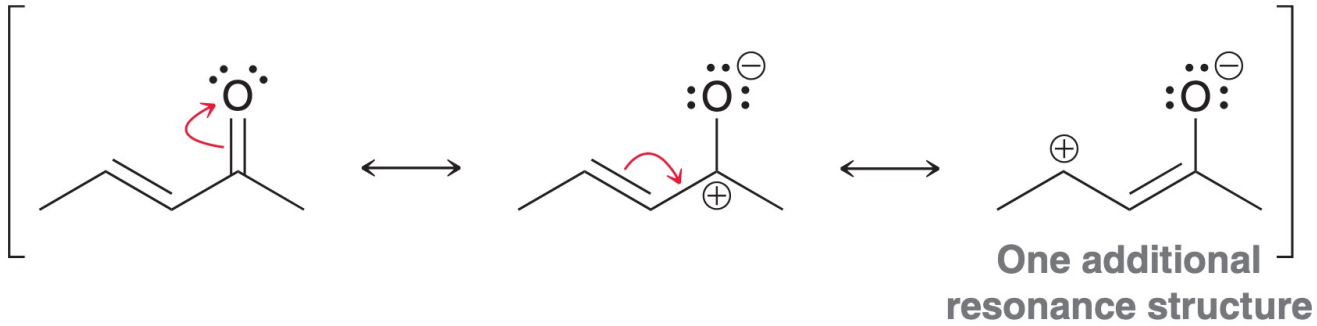


conjugation decreases the wavenumber of carbonyl groups

- More resonance structures contribute more single bond character

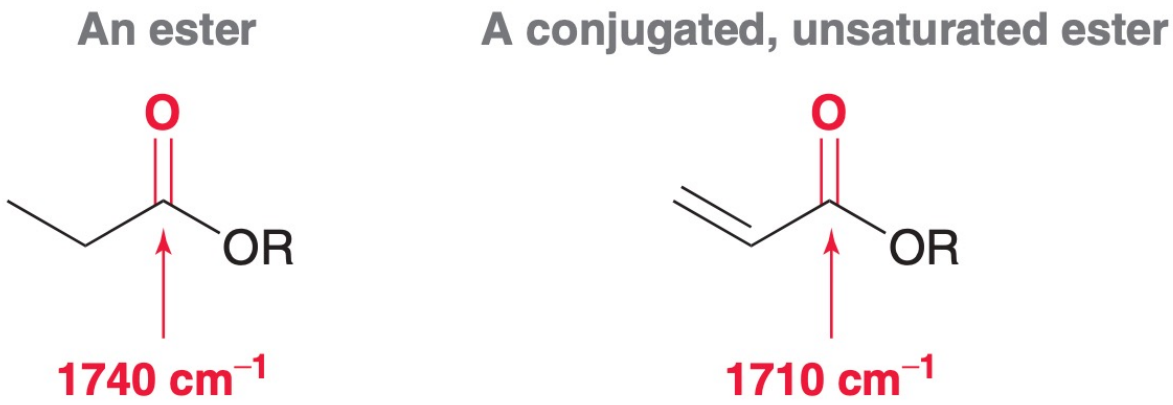


single bond character: 1/2

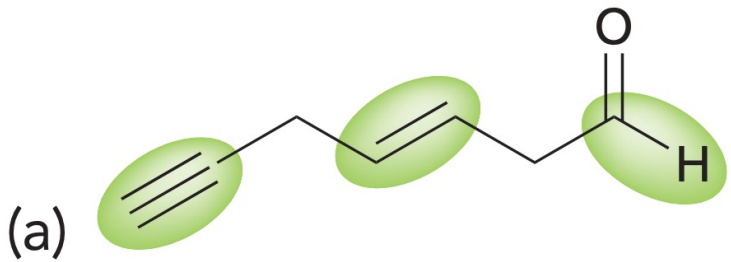


single bond character: 2/3

- Conjugate esters also have lower wavenumbers

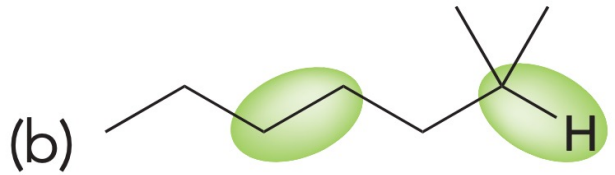


- Practice: for each of the following compounds, rank the highlighted bonds in terms of increasing wavenumber:



Increasing wavenumber

C—H C≡C C=C

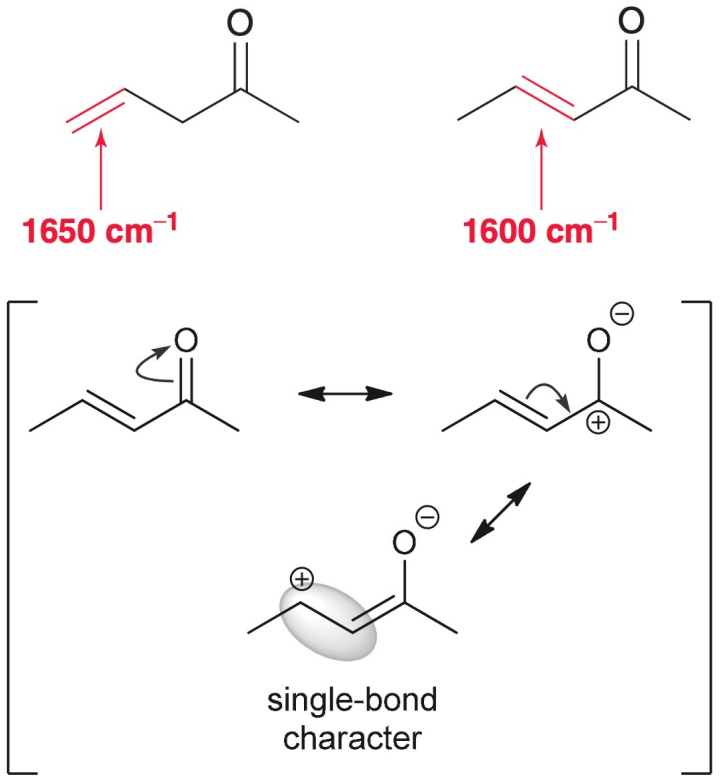


Increasing wavenumber

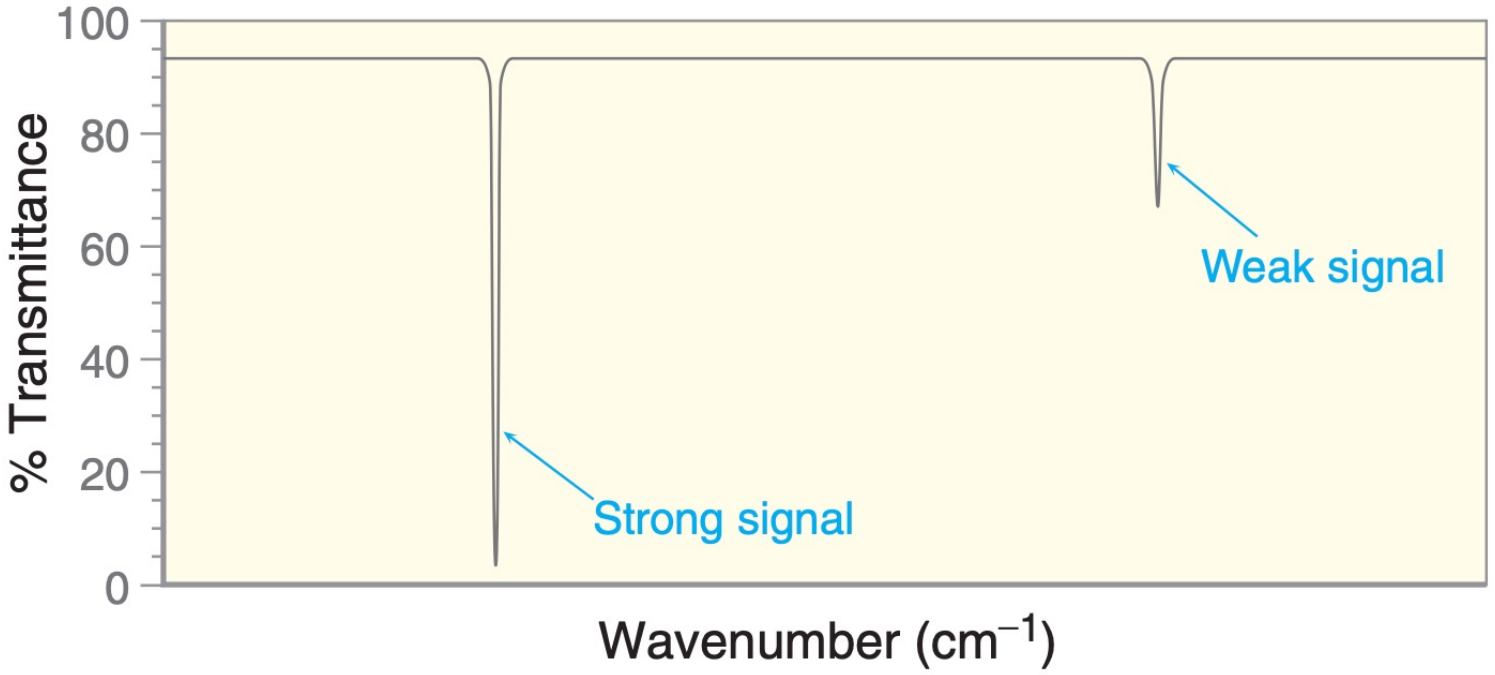
C—H C—C

- Practice

14.4 Compare the wavenumber of absorption for the following two C═C bonds. Use resonance structures to explain why the C═C bond in the conjugated compound produces a signal at lower wavenumber.



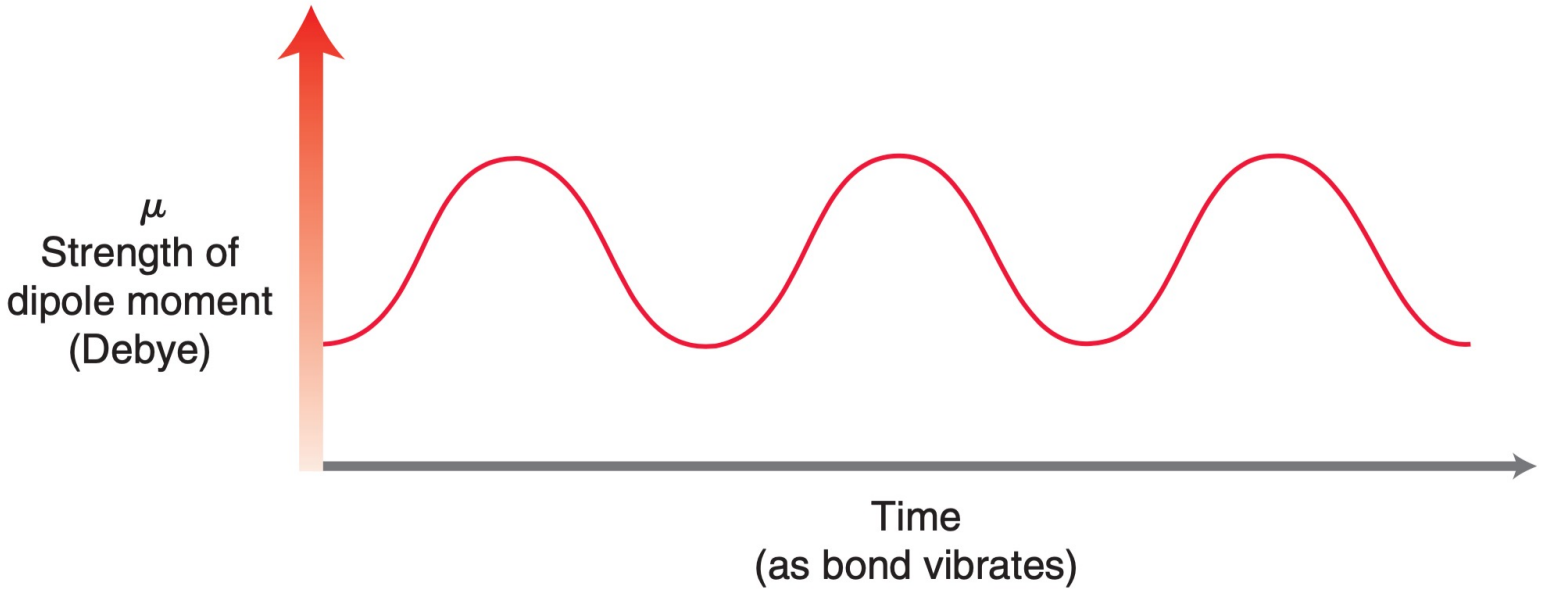
- Intensity of signals



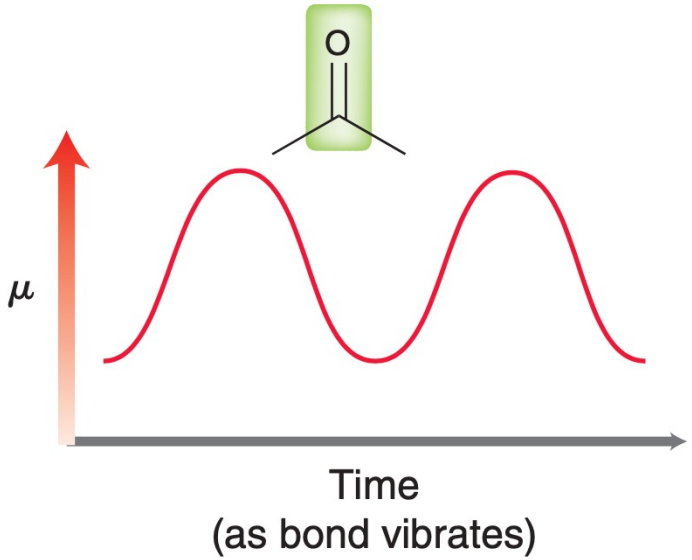
- Intensity and dipole moment

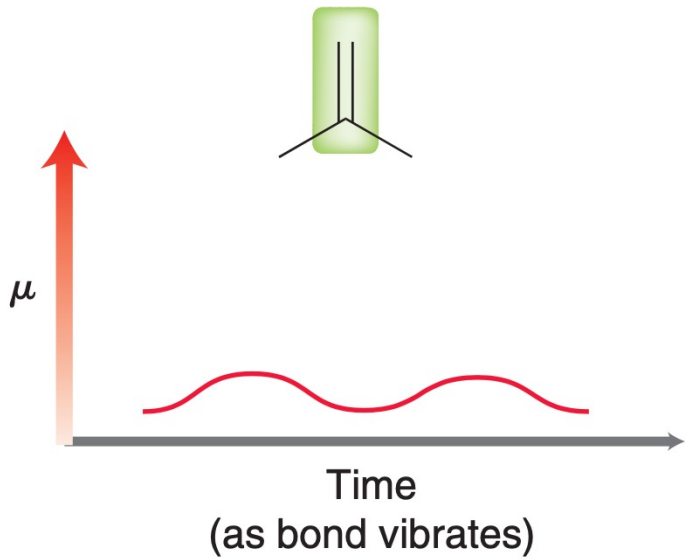
$$\mu = e \times d$$

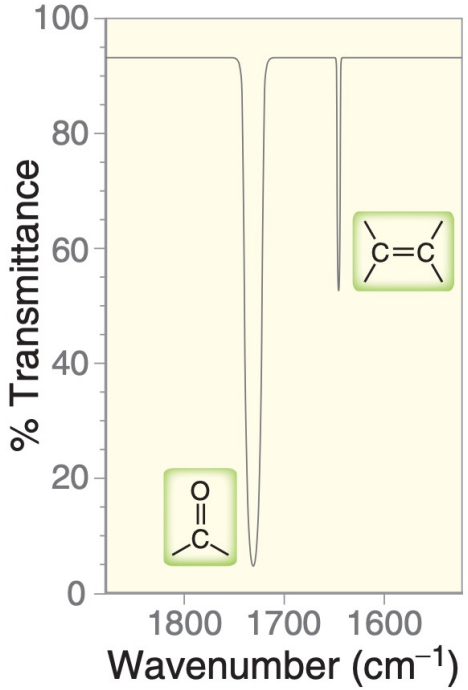
A stretching vibration



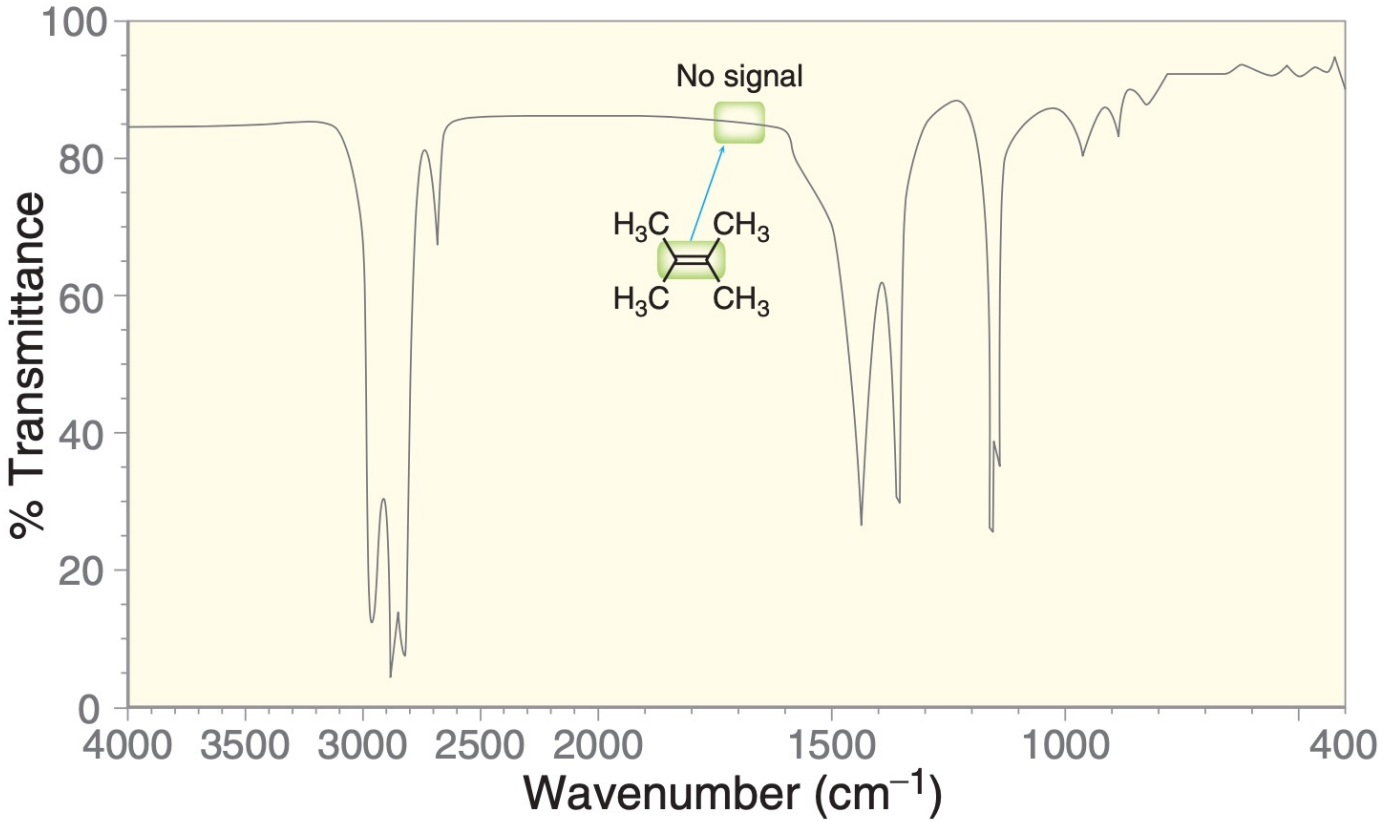
- Larger dipole moment results in greater intensity





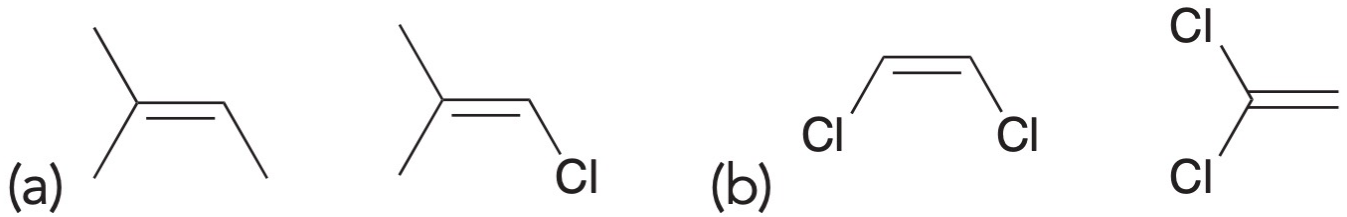


- Symmetrical structure reduces intensity

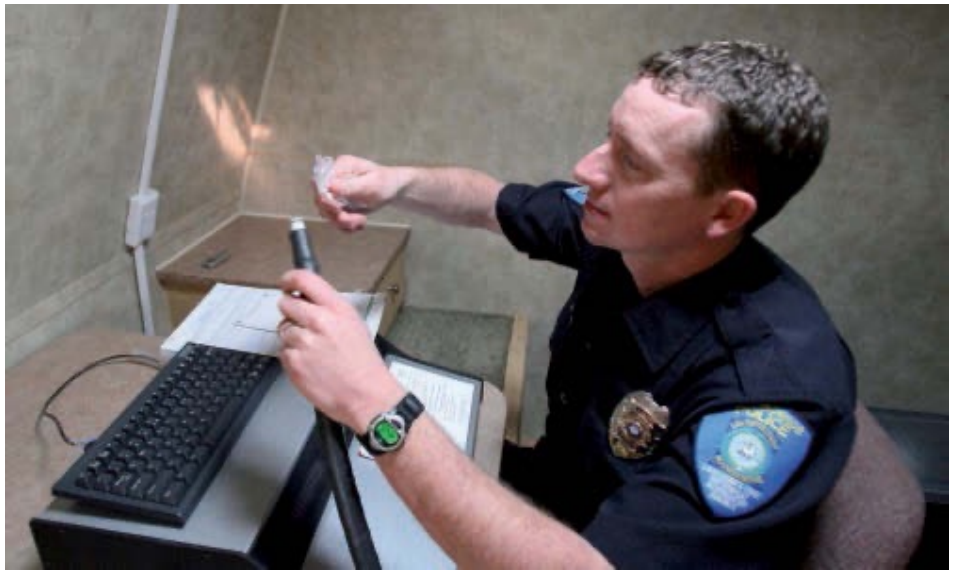


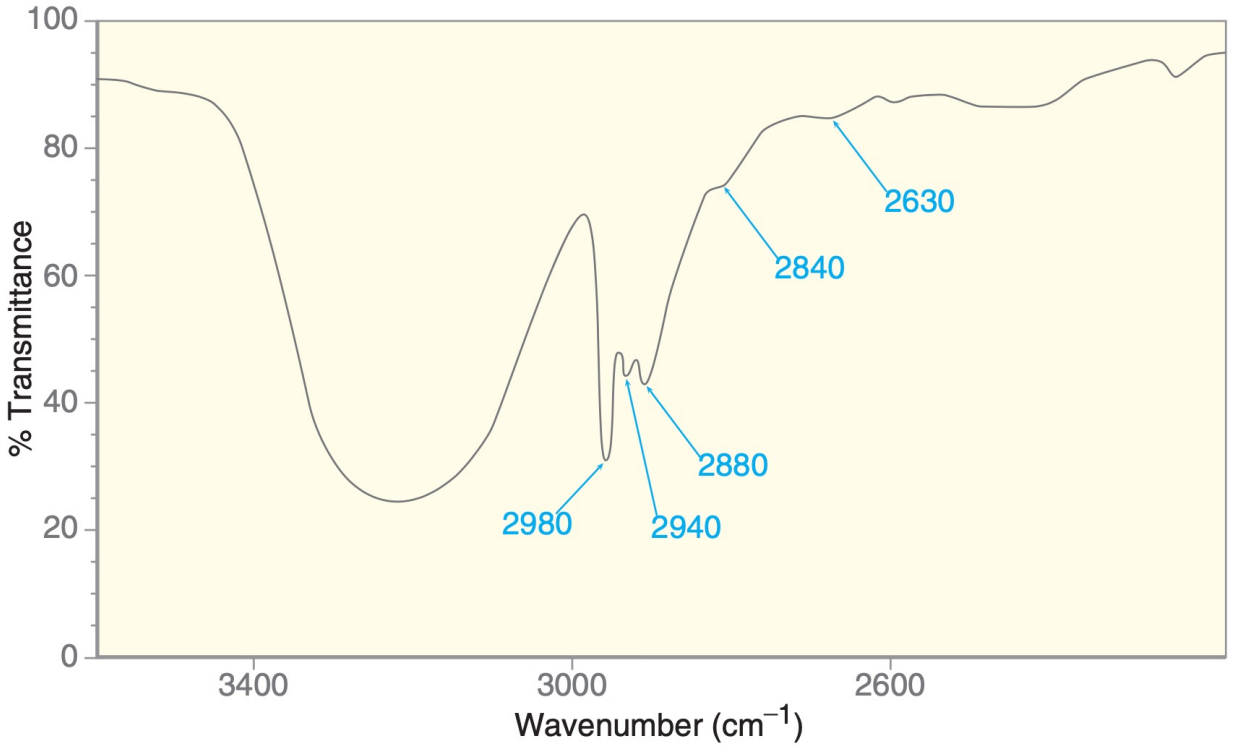
- Practice

14.5 For each pair of compounds, determine which C═C bond will produce a stronger signal.

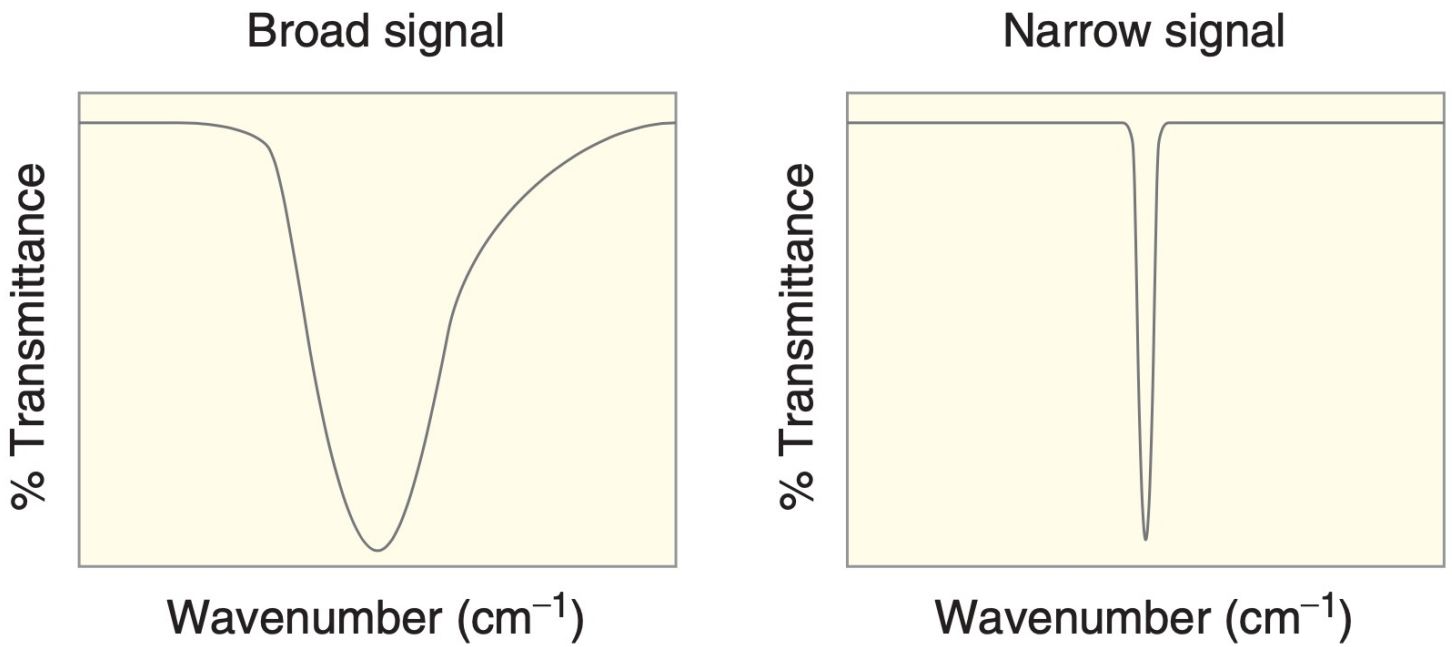


- Quantitative IR spectroscopic analysis: the *Intoxilyzer*

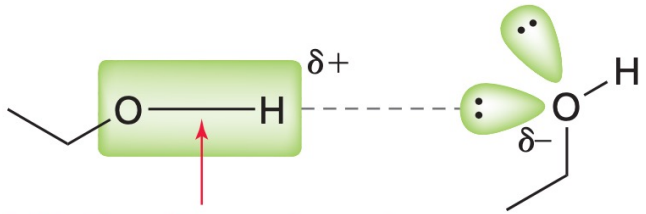




- Shape of signals



- Effects of hydrogen bonding

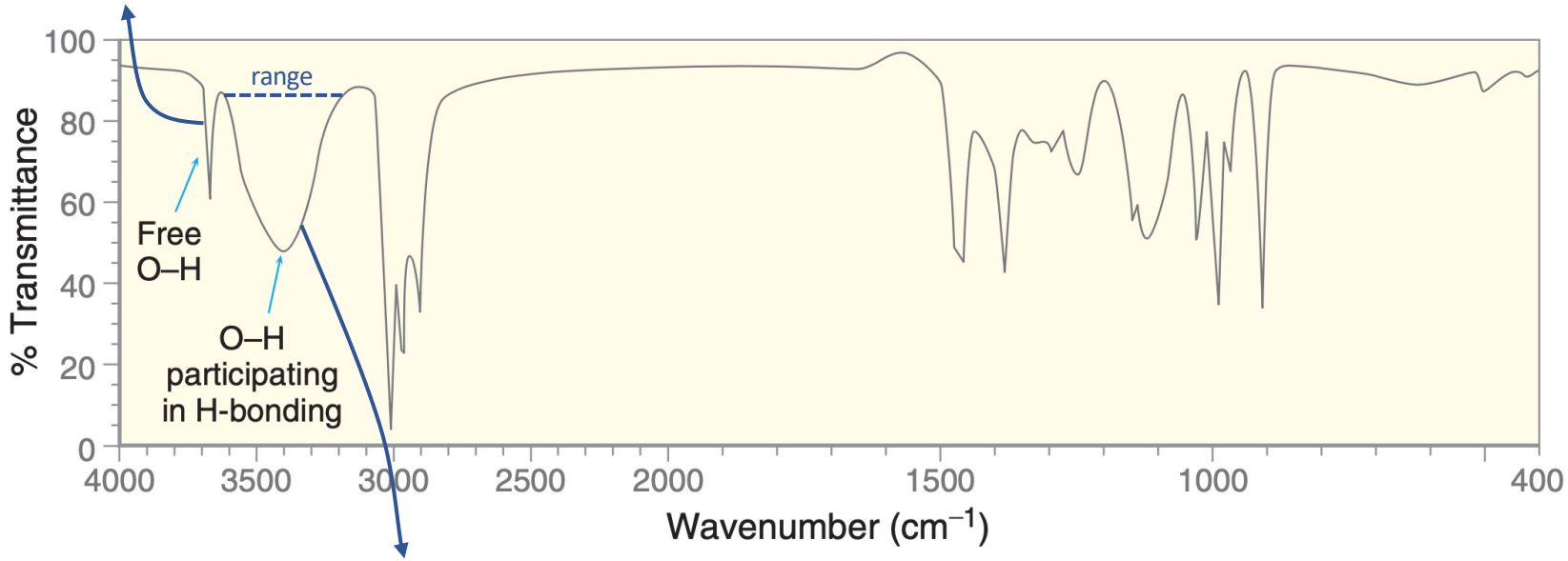


hydrogen bonding can extend the O–H bond

thus weakening the strength

in dilute solution

free O–H peak could appears



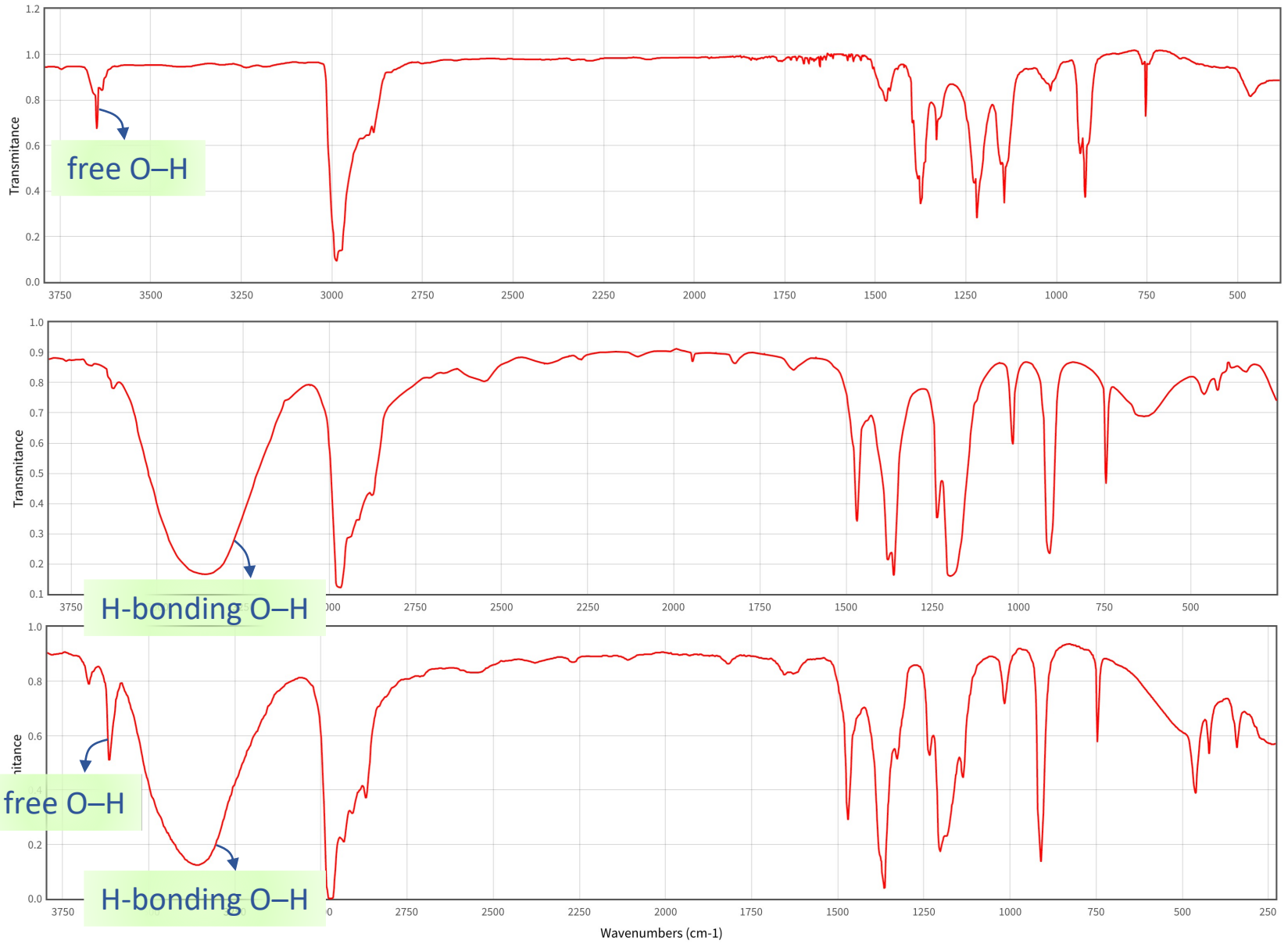
different weakening extent generate a range of bond strength

IR spectra of *tert*-butanol

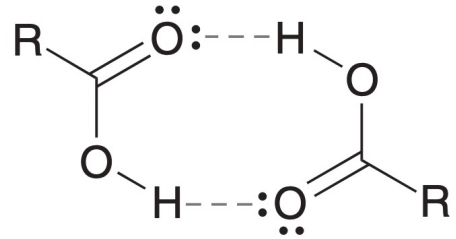
gas

liquid

solution
(10.5% in CCl_4)

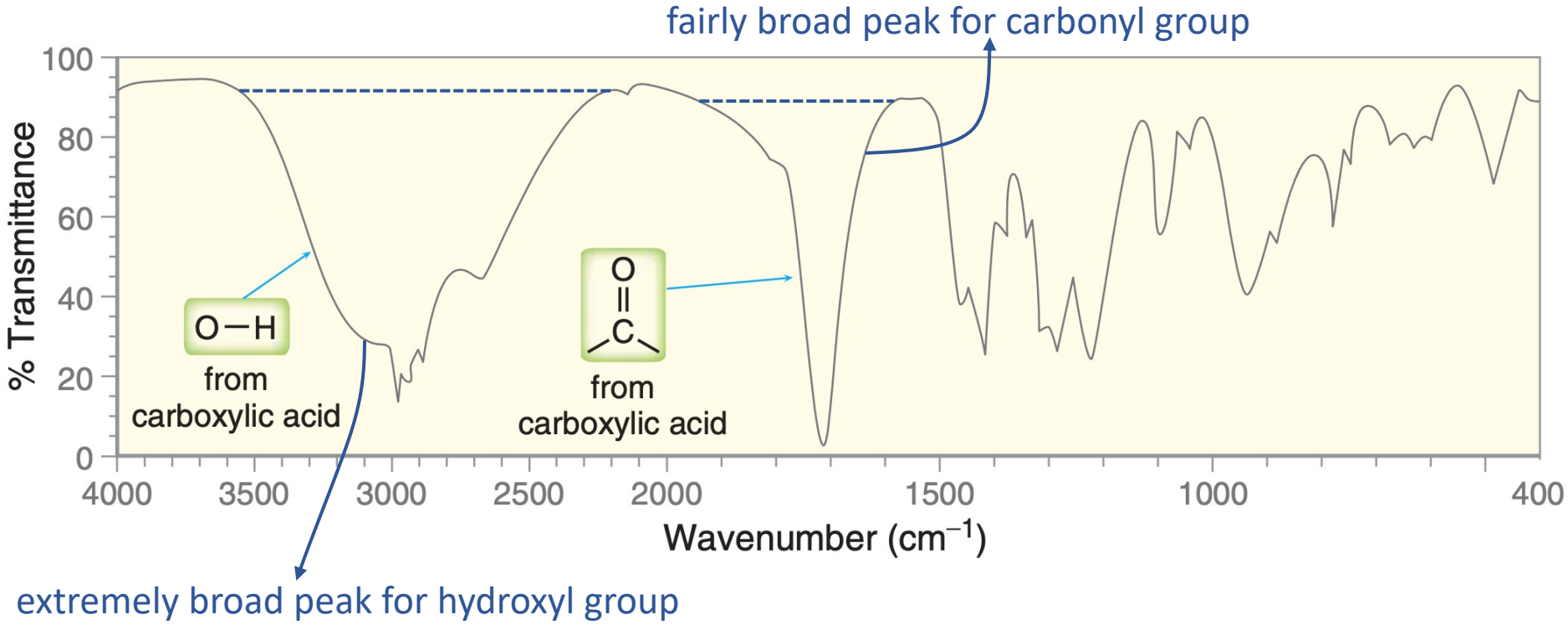


https://webbook.nist.gov/cgi/cbook.cgi?Name=tert-butanol&Units=SI&cIR=on

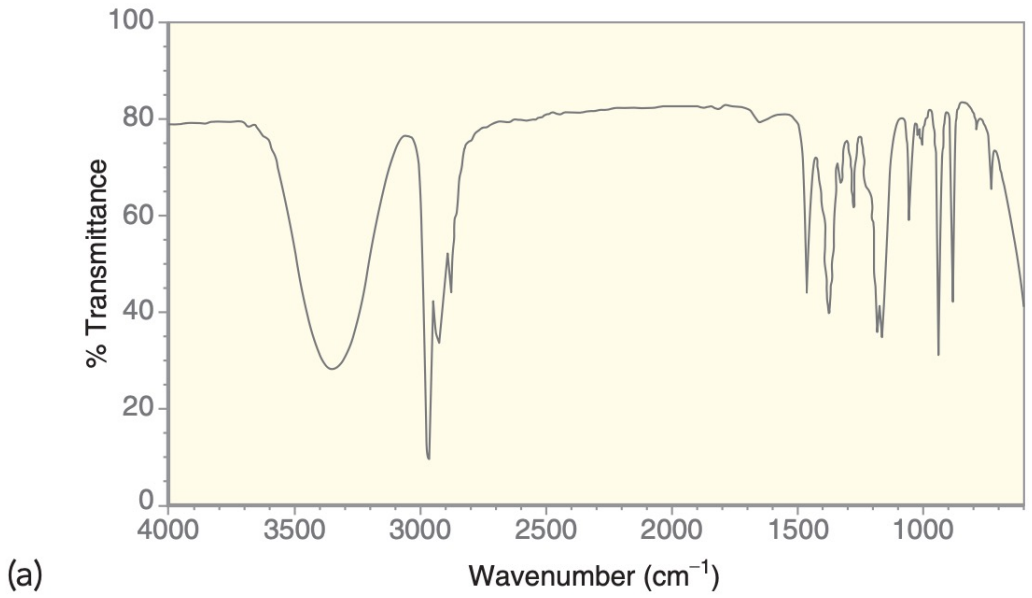


dimerization due to hydrogen bonding

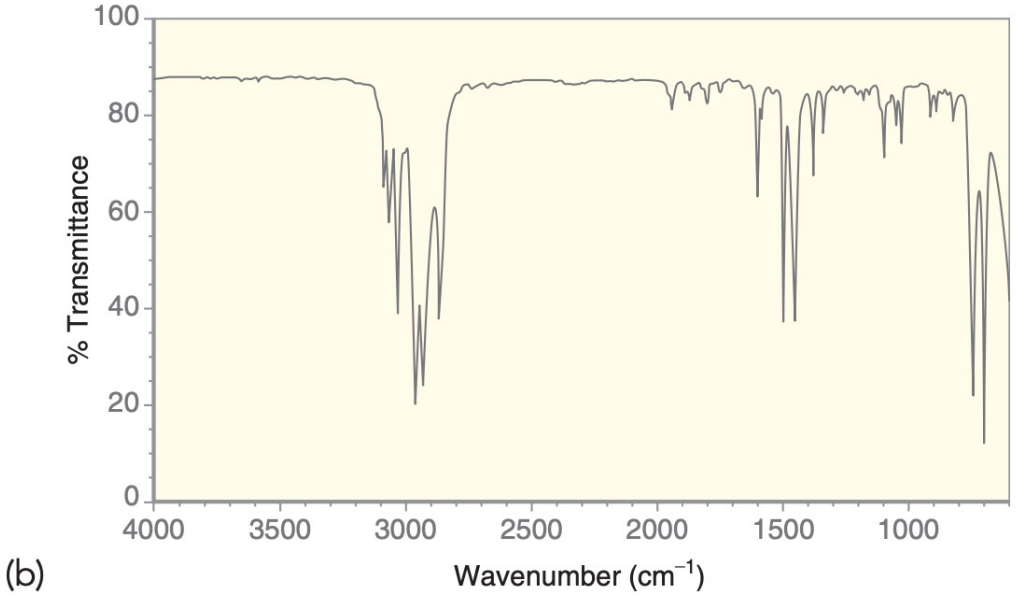
- Carboxylic acids – more pronounced effect



- Practice: for each of the following IR spectra, identify whether it is consistent with the structure of an alcohol, a carboxylic acid, or neither:

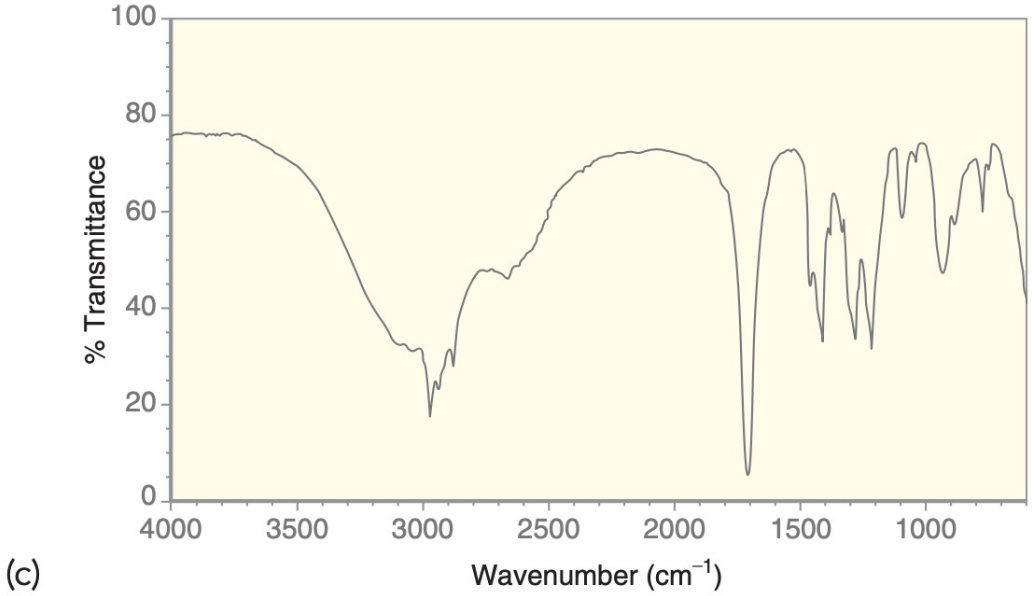


alcohol



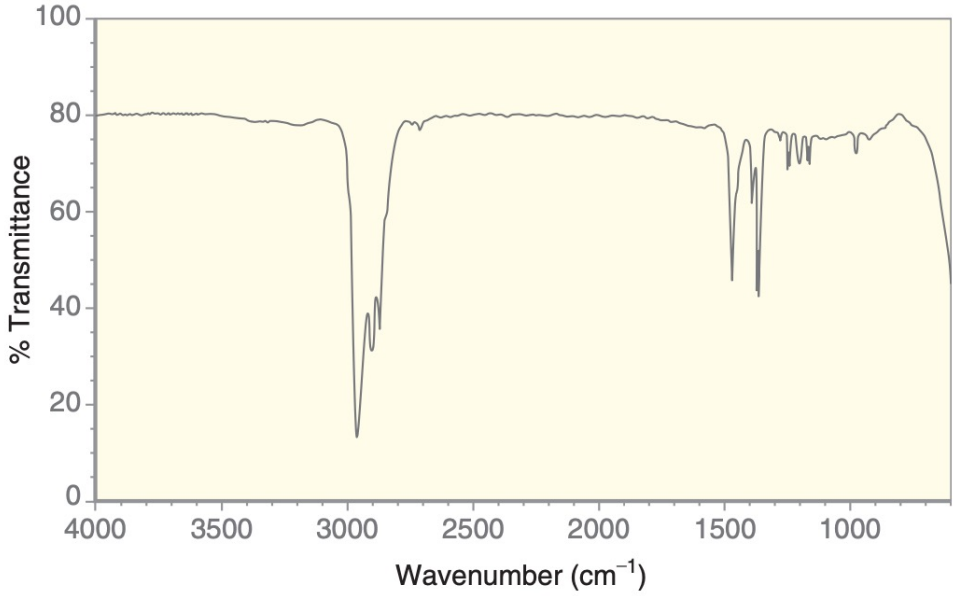
neither

- Practice: for each of the following IR spectra, identify whether it is consistent with the structure of an alcohol, a carboxylic acid, or neither:



(c)

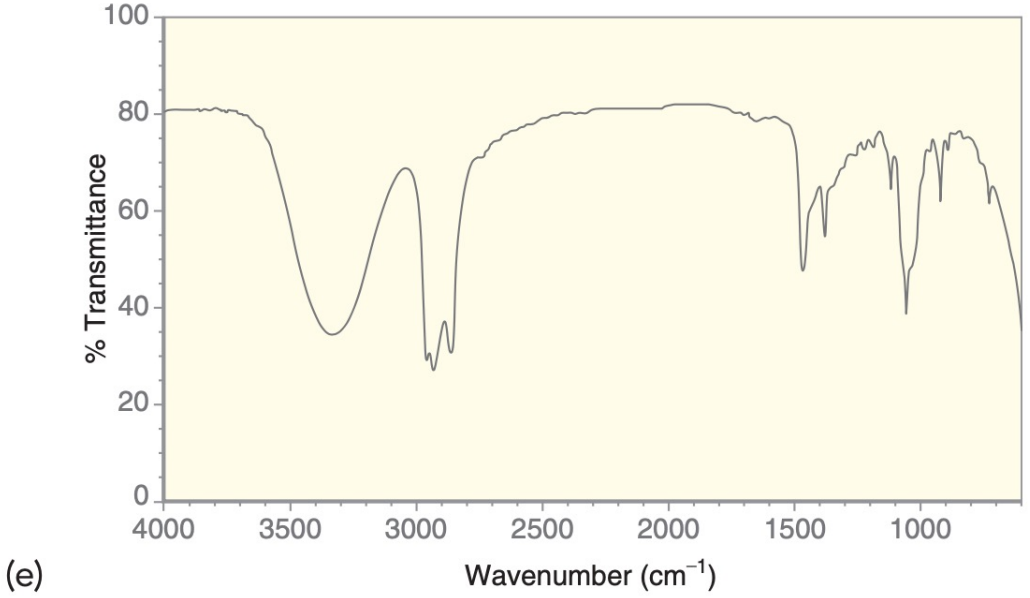
carboxylic acid



(d)

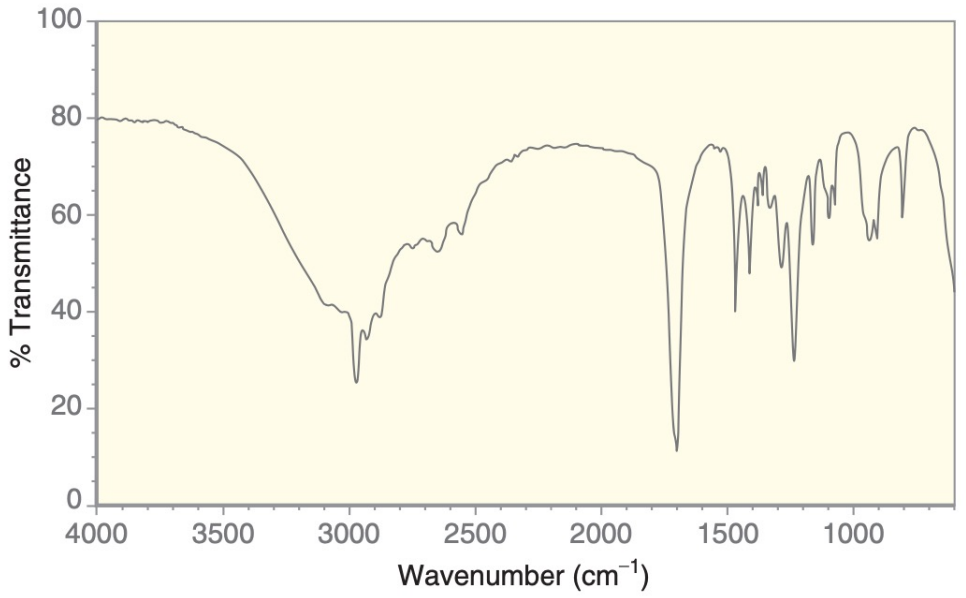
neither

- Practice: for each of the following IR spectra, identify whether it is consistent with the structure of an alcohol, a carboxylic acid, or neither:



(e)

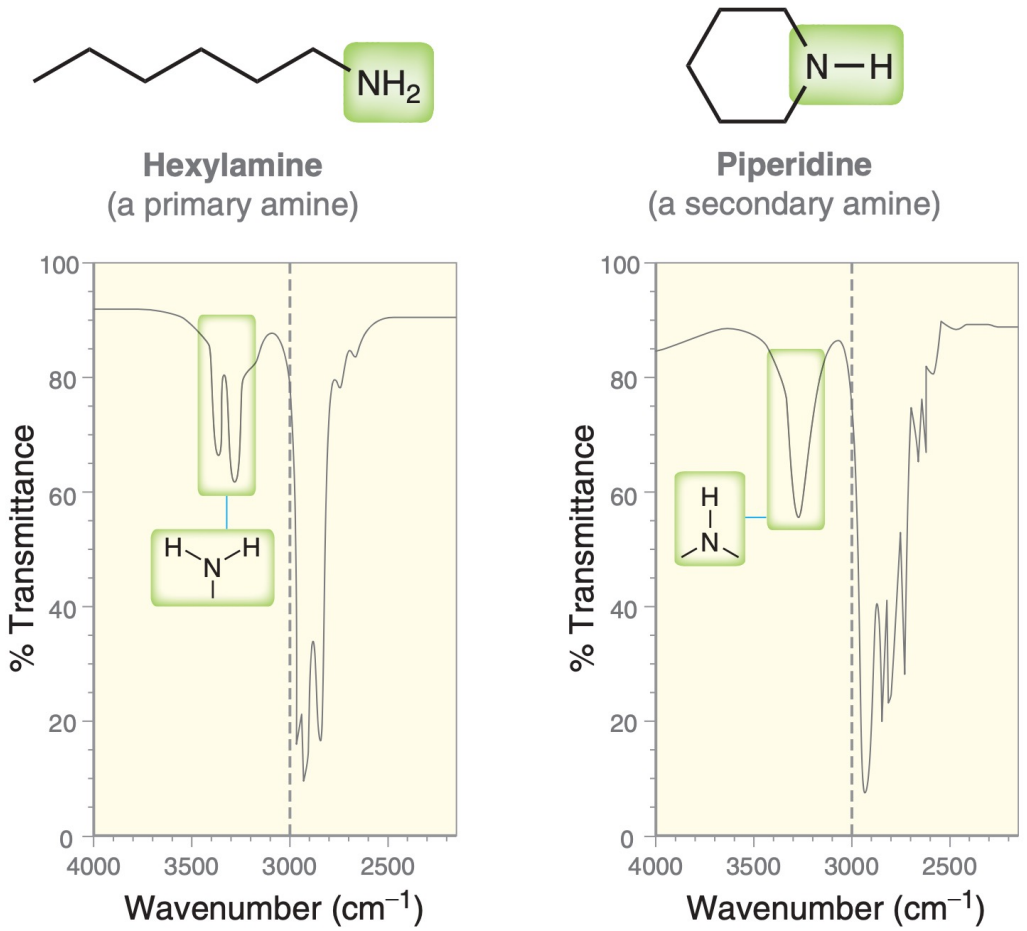
alcohol



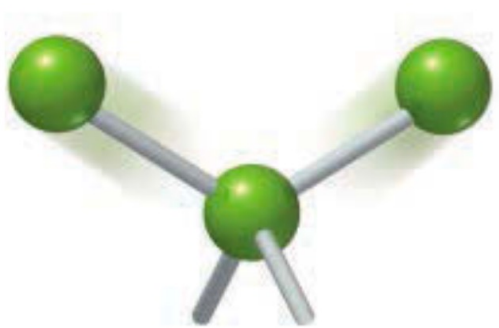
(f)

carboxylic acid

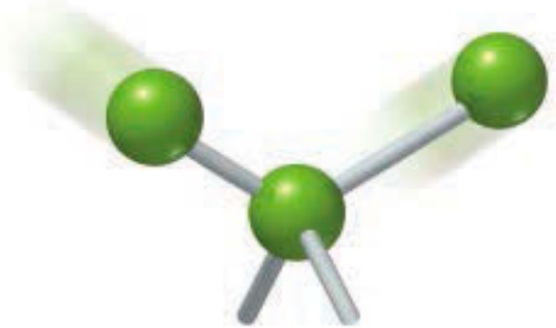
- Amines: symmetrical *vs*. asymmetrical



- Primary amine has two stretching patterns



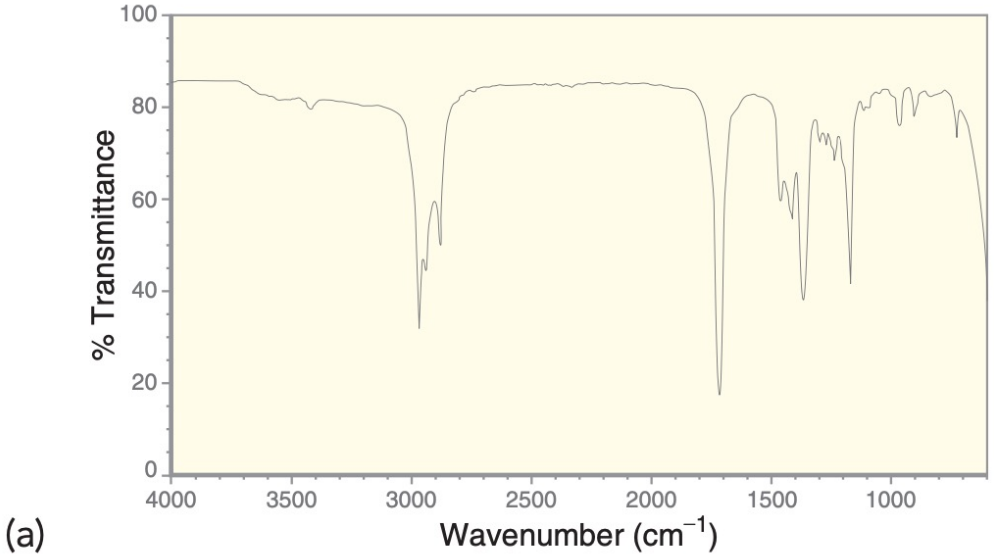
Symmetric stretching



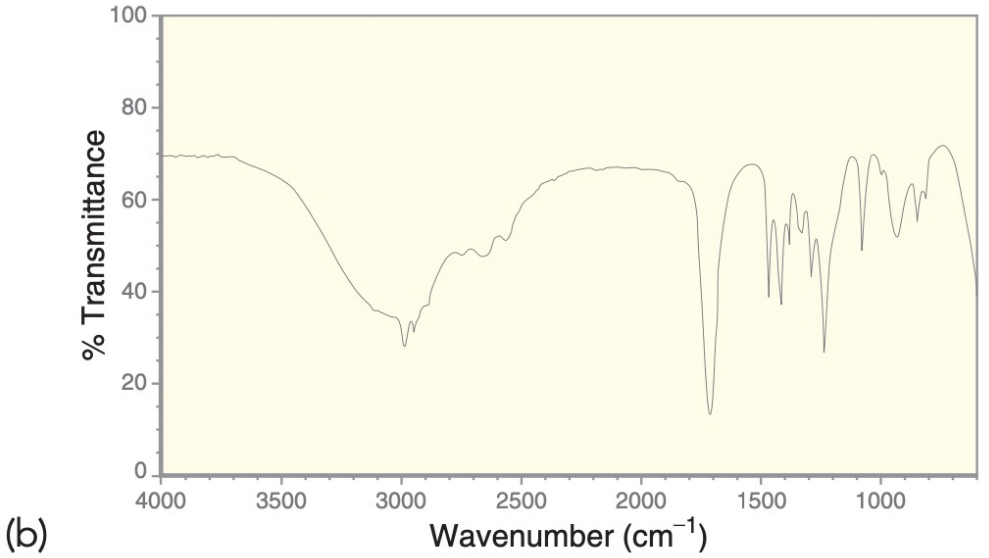
Asymmetric stretching

two ways of stretching – two frequencies – two peaks

- Practice: for each of the following IR spectra, determine whether it is consistent with the structure of a ketone, an alcohol, a carboxylic acid, a primary amine, or a secondary amine:



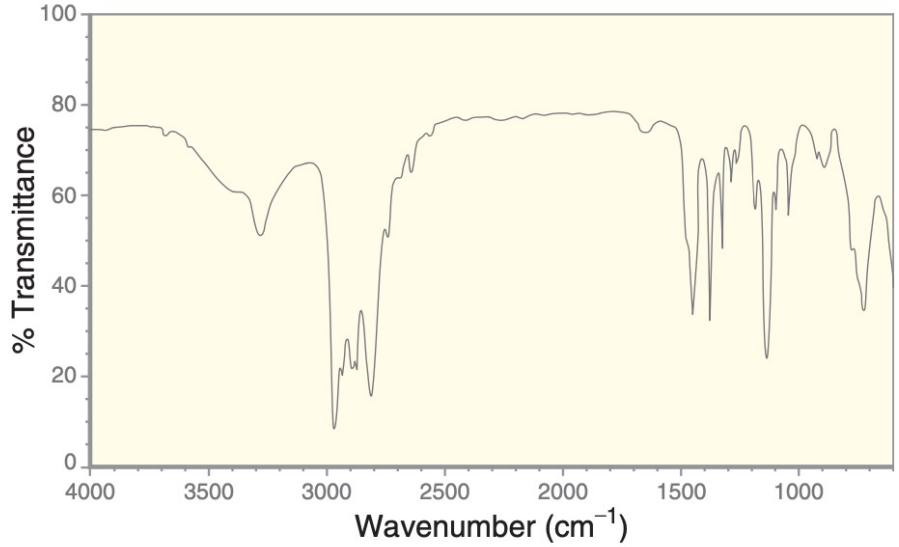
ketone



carboxylic acid

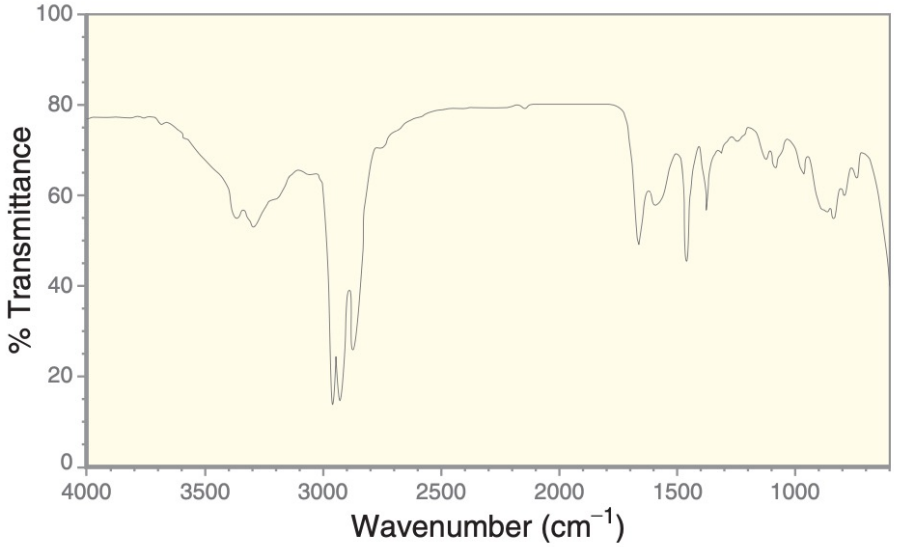
- Practice: for each of the following IR spectra, determine whether it is consistent with the structure of a ketone, an alcohol, a carboxylic acid, a primary amine, or a secondary amine:

(c)



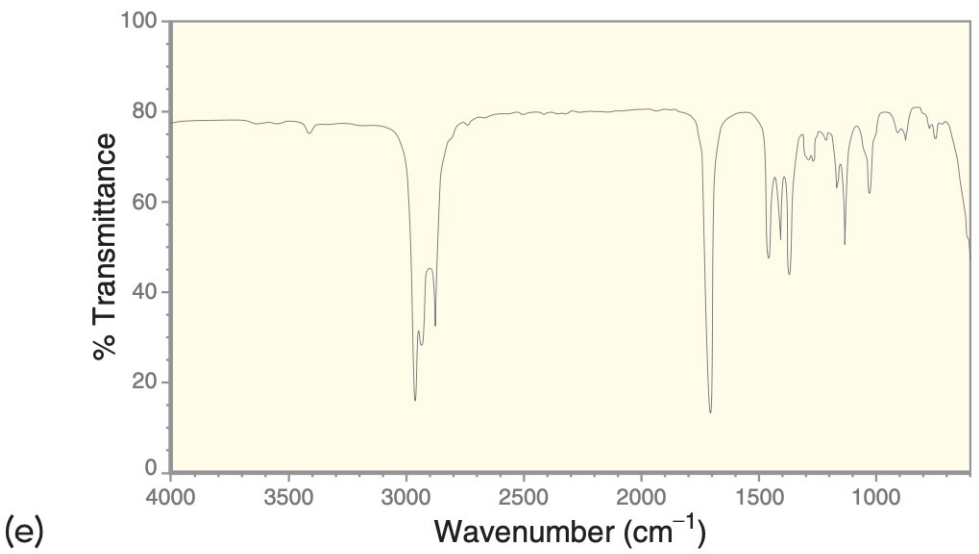
secondary amine

(d)



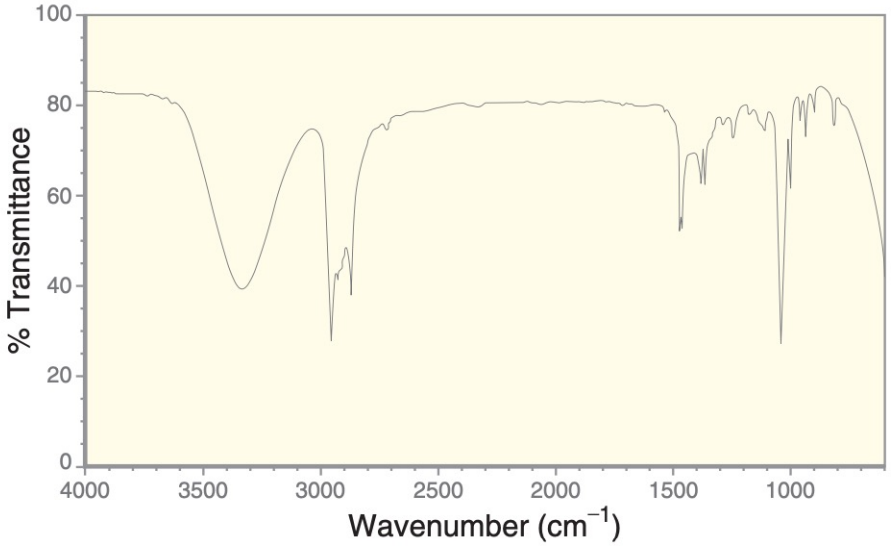
primary amine

- Practice: for each of the following IR spectra, determine whether it is consistent with the structure of a ketone, an alcohol, a carboxylic acid, a primary amine, or a secondary amine:



(e)

ketone



(f)

alcohol

- **Important signals in IR spectroscopy (diagnostic region)**

- Double bonds: 1600–1850 cm^{-1}
- Triple bonds: 2100–2300 cm^{-1}
- X—H bonds: 2700–4000 cm^{-1}

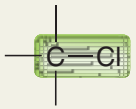
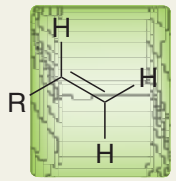
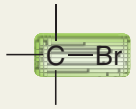
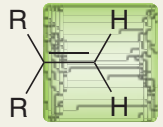
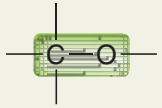
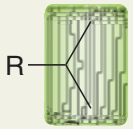
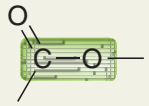
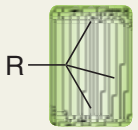
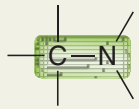
USEFUL SIGNALS IN THE DIAGNOSTIC REGION

STRUCTURAL UNIT	FREQUENCY (cm^{-1})	
Single Bonds (X— H)		
O—H	3200–3600	*s*, sharp (free); *s*, broad (H-bonding)
O, O—H	2200–3600	*s*, very broad
N—H	3350–3500	*m*, two peaks (primary); m, one peak (secondary)
C—H	~3300	*s*
C—H	3000–3100	*m*
C—H	2850–3000	*s*
O, C—H	2750–2850	can be used to distinguish aldehyde and ketone
Triple Bonds		
C≡C	2100–2200	*m*
C≡N	2200–2300	*m*

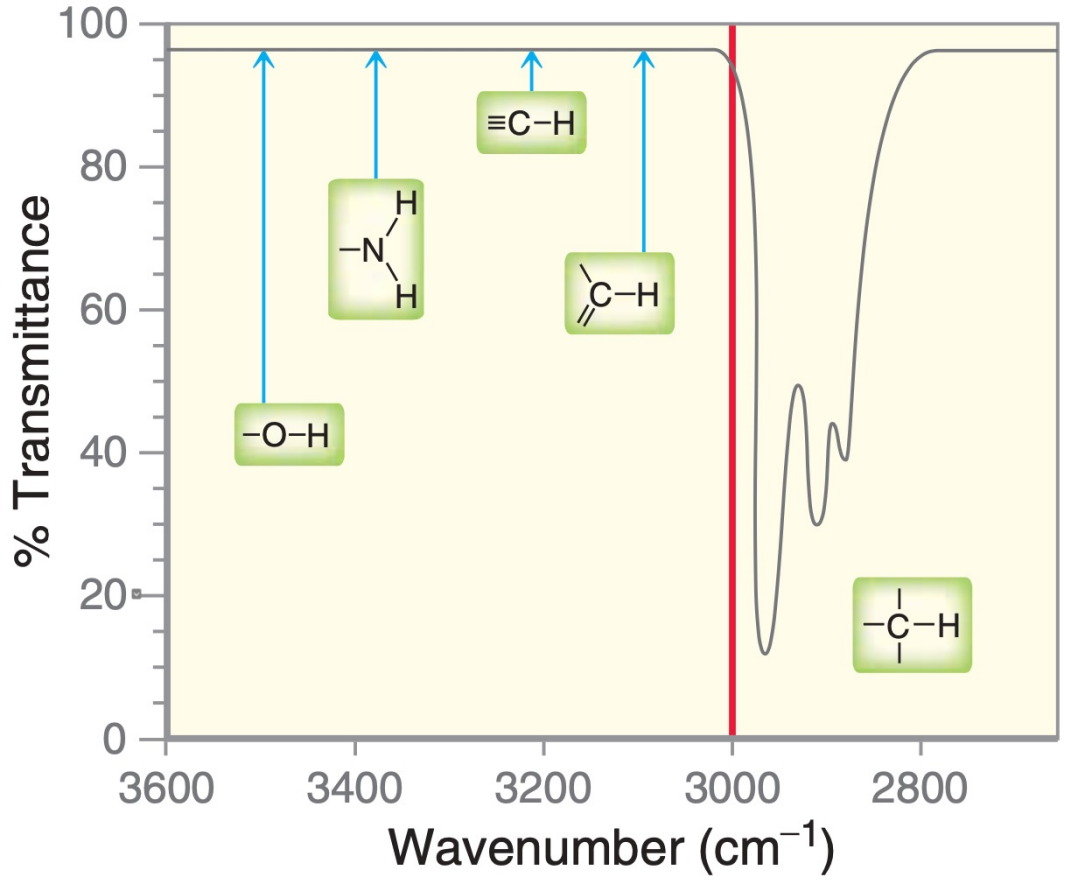
STRUCTURAL UNIT	FREQUENCY (cm^{-1})	
Double Bonds		
Cl, C=O	1750–1850	*s*
RO, C=O, R	1700–1750	*s*
HO, C=O, R	1700–1750	*s*
R, C=O, R	1680–1750	*s*
H_2N, C=O, R	1650–1700	*s*
C=C	1600–1700	*m*
	1450–1600 1650–2000	*m* *w*

s: strong; *m*: medium; *w*: weak

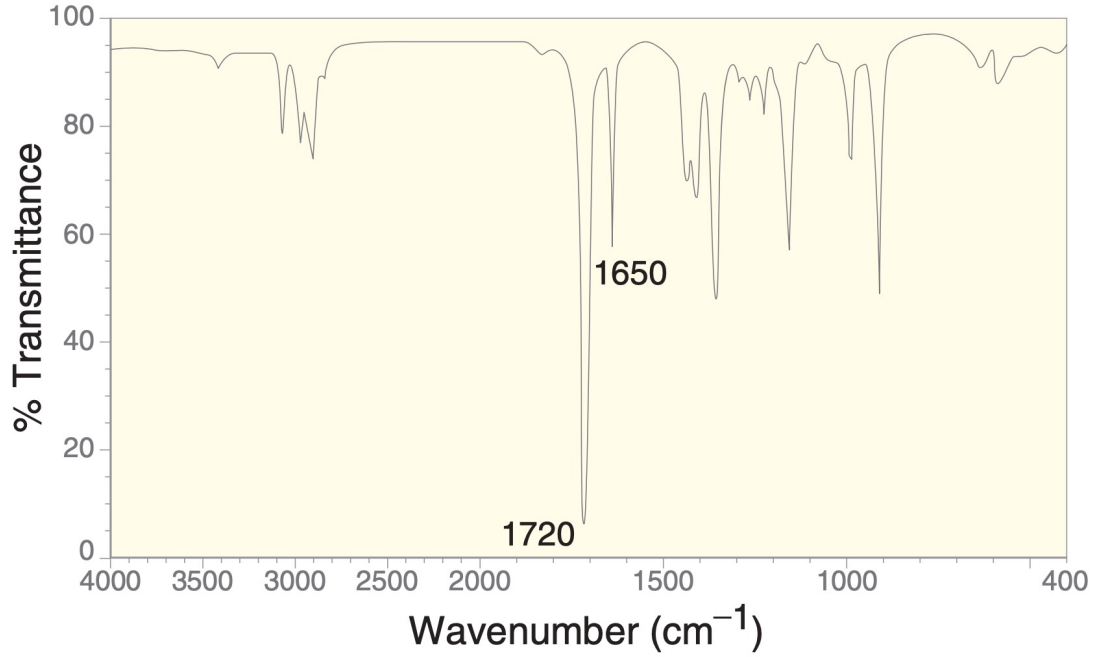
- **Important signals in IR spectroscopy (fingerprint region)**

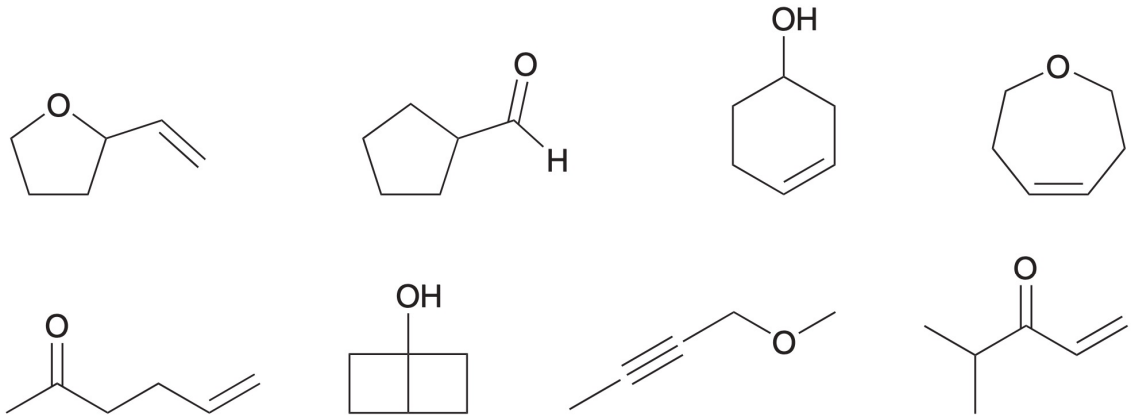
STRUCTURAL UNIT	FREQUENCY (cm^{-1})	STRUCTURAL UNIT	FREQUENCY (cm^{-1})	
USEFUL SIGNALS IN THE FINGERPRINT REGION				
	600–800		900–920 980–1000	*(bending)*
	500–600		880–900	*(bending)*
	1000–1100		1370, 1380	*(bending)*
	1250–1350		1370, 1390	*(bending)*
	1000–1200			

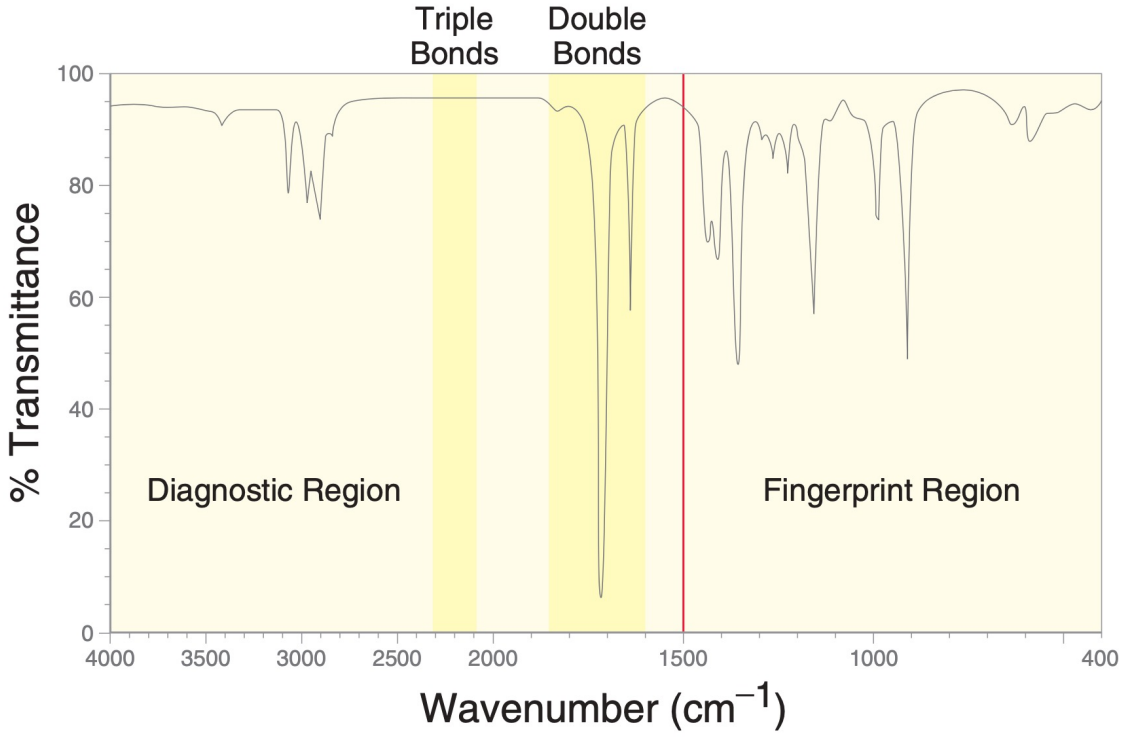
- Draw a line at 3000 cm^{-1} – looking for X–H signals

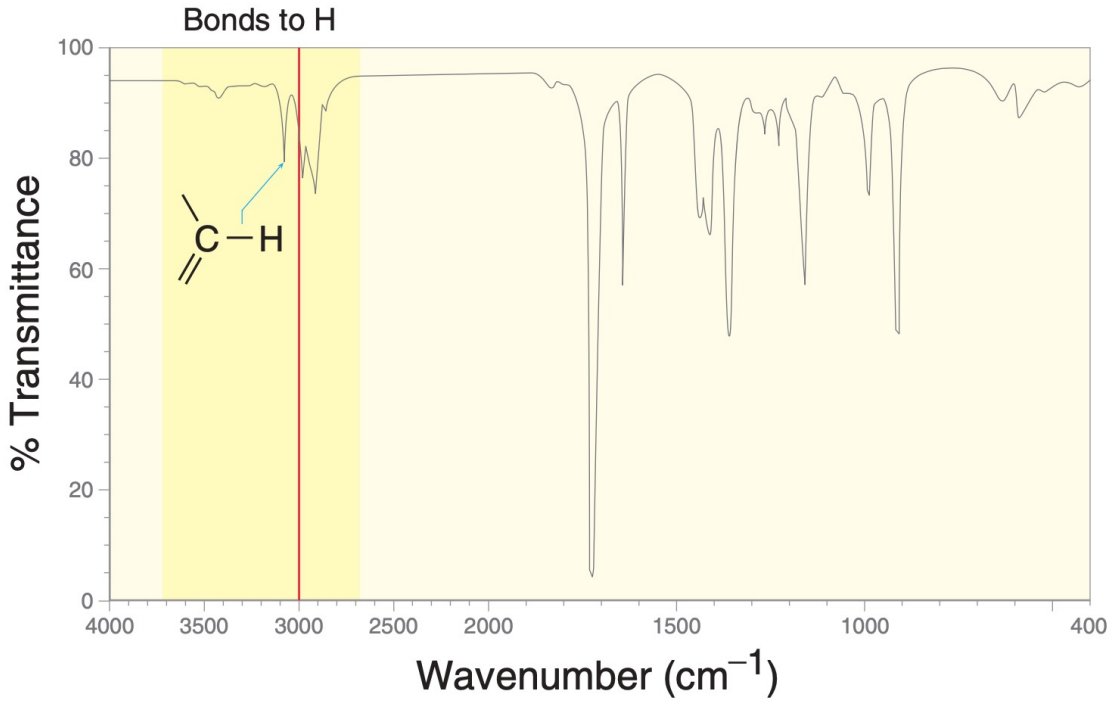


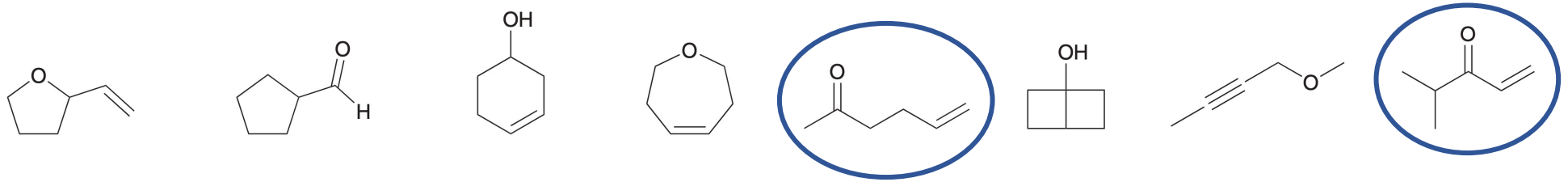
- Practice: a compound with the molecular formula $C_6H_{10}O$ gives the following IR spectrum; identify the structure below that is most consistent with the spectrum:

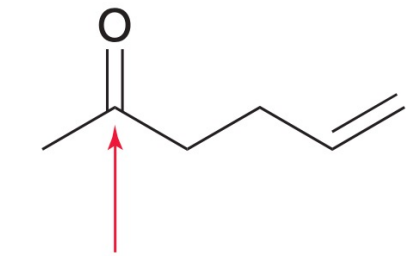




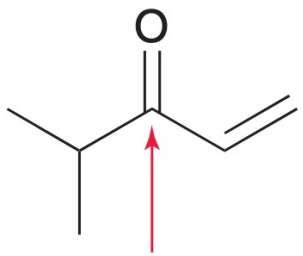

Triple Bonds
Double Bonds
Diagnostic Region
Fingerprint Region
% Transmittance
Wavenumber (cm^{-1})


Bonds to H
C—H
% Transmittance
Wavenumber (cm^{-1})

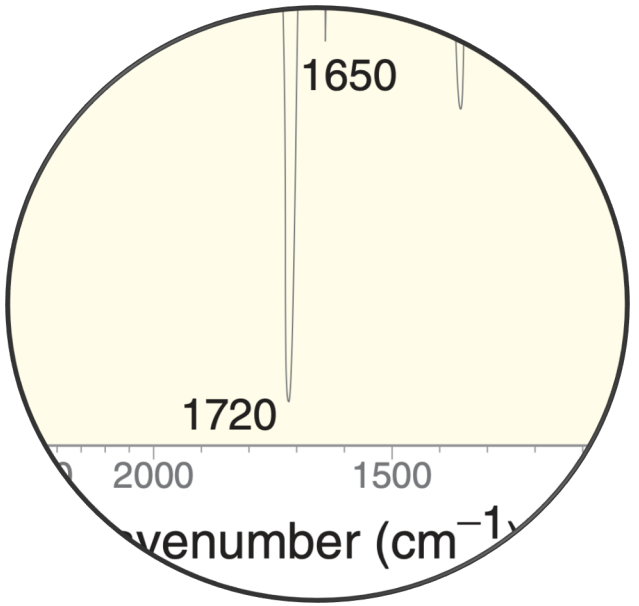

O
O
H
OH
O
O
OH
O
O

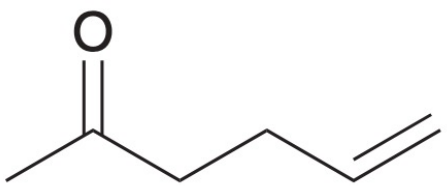


1720 cm^{-1}

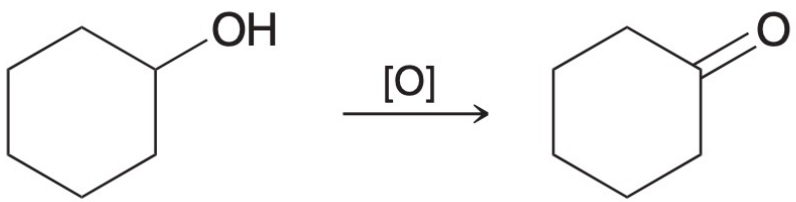


1680 cm^{-1}





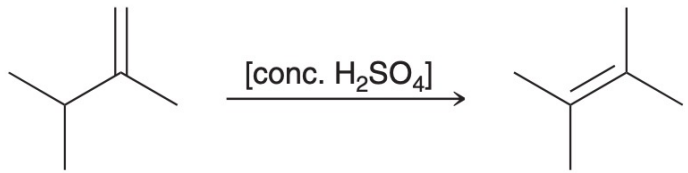
- Using IR to distinguish two compounds

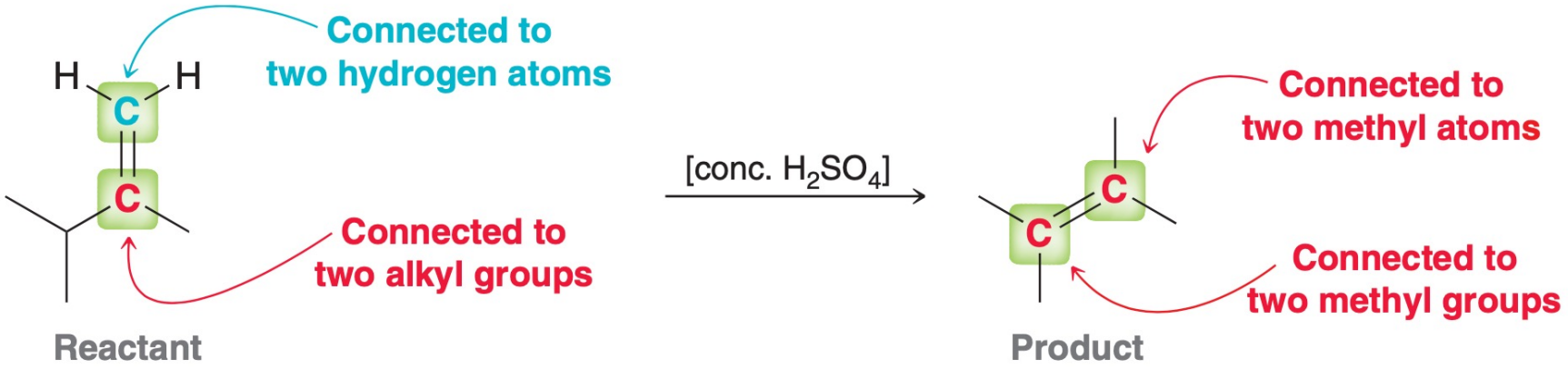


looking for the absence of a hydroxyl signal and the presence of a carbonyl signal

- Practice

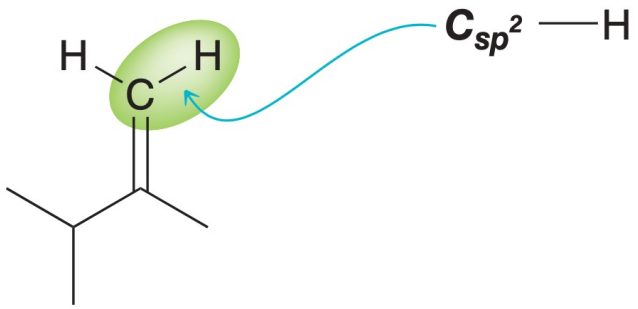
Identify how IR spectroscopy might be used to monitor the progress of the following reaction.



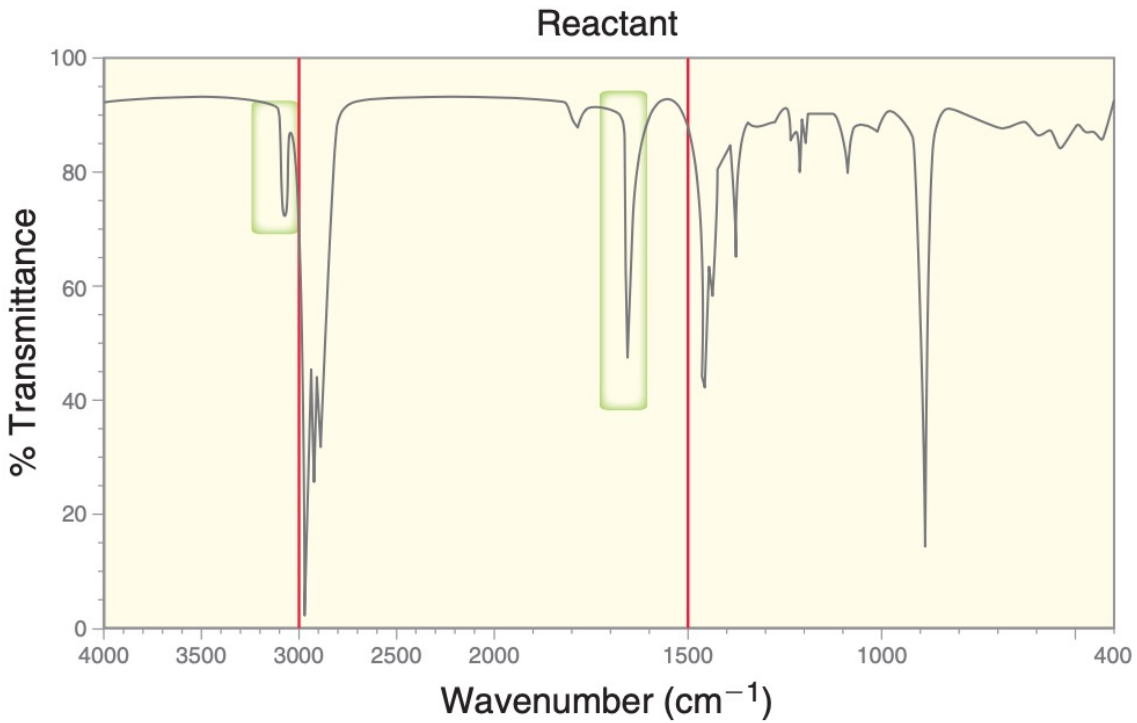


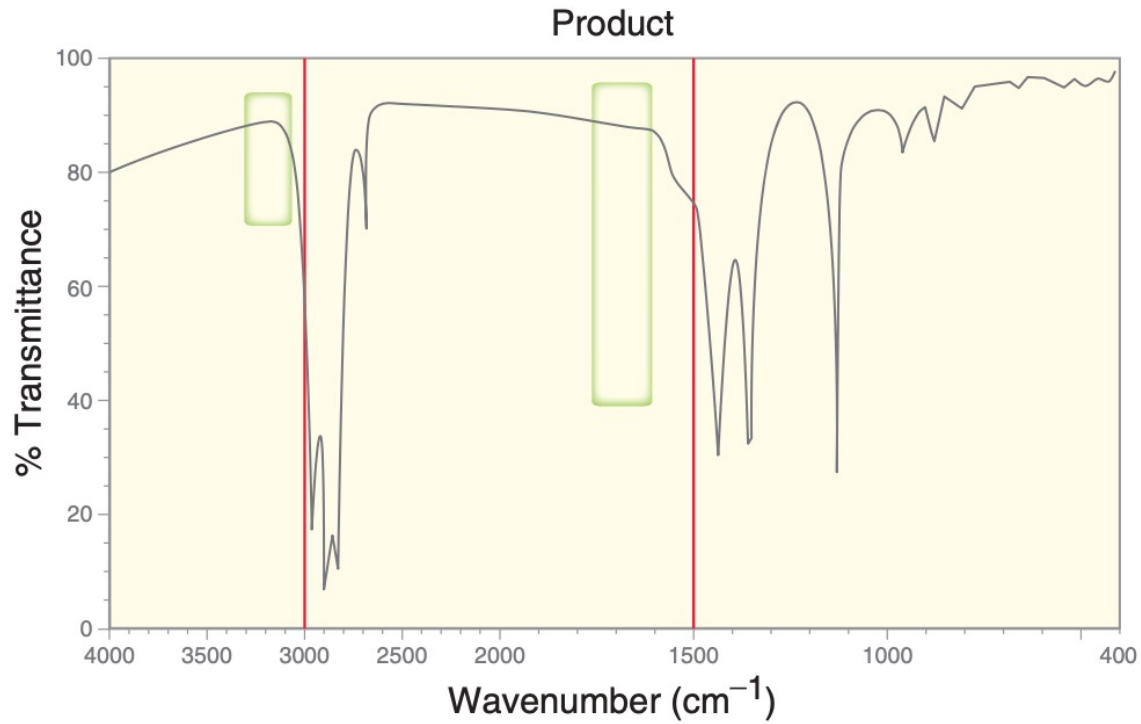
signal of C=C at around 1650 cm^{-1}

no signal for C=C since symmetrical structure



reactant: signal of =C–H bond at around 3100 cm^{-1}


Reactant
% Transmittance
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
400
Wavenumber (cm^{-1})

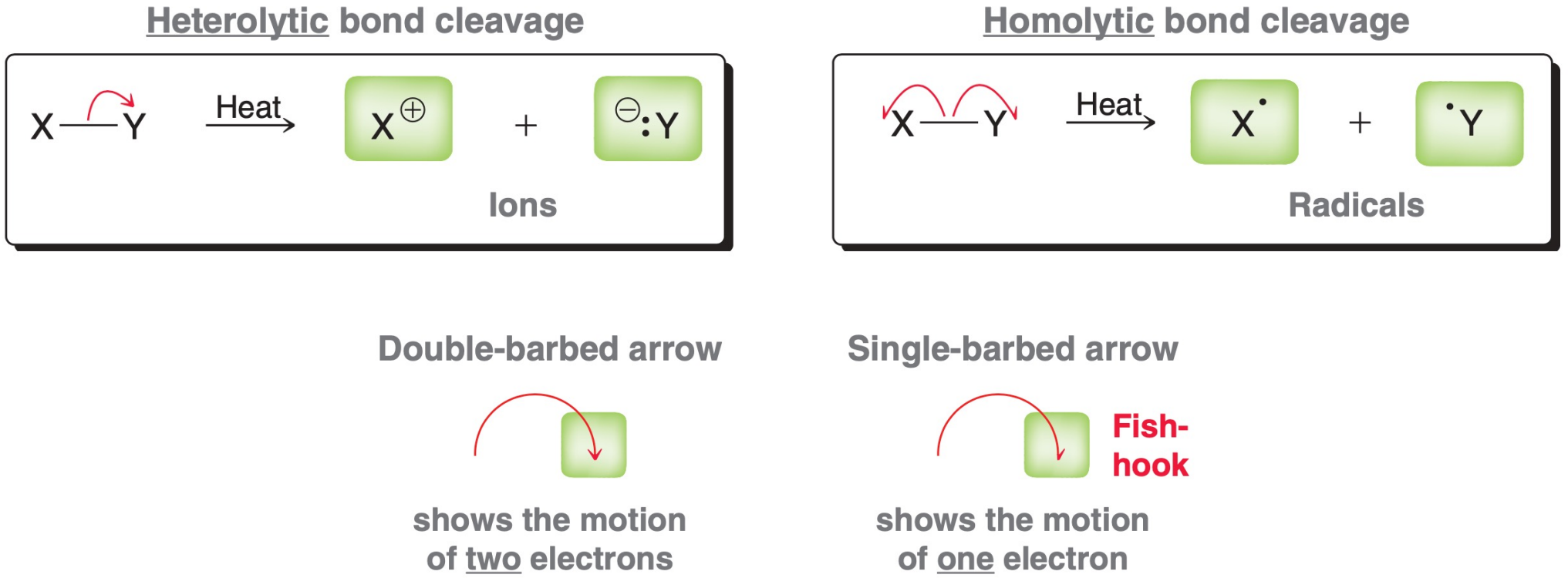

Product
% Transmittance
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
400
Wavenumber (cm^{-1})

Mass Spectrometry

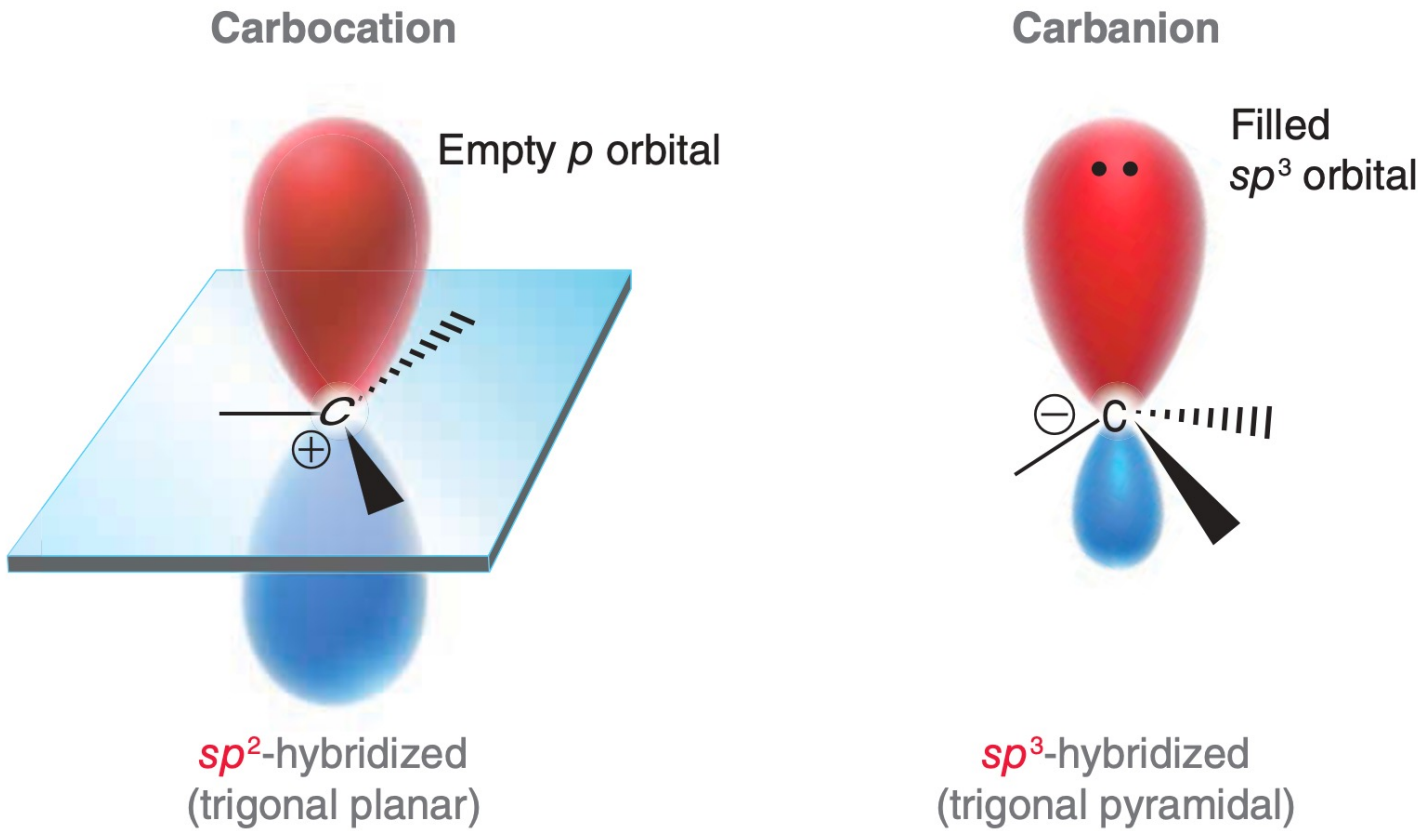
Radicals, Principles of Mass Spectrometry, Characteristic Peaks,

Analyzing Fragments, Further Speaking, Hydrogen Deficiency Index

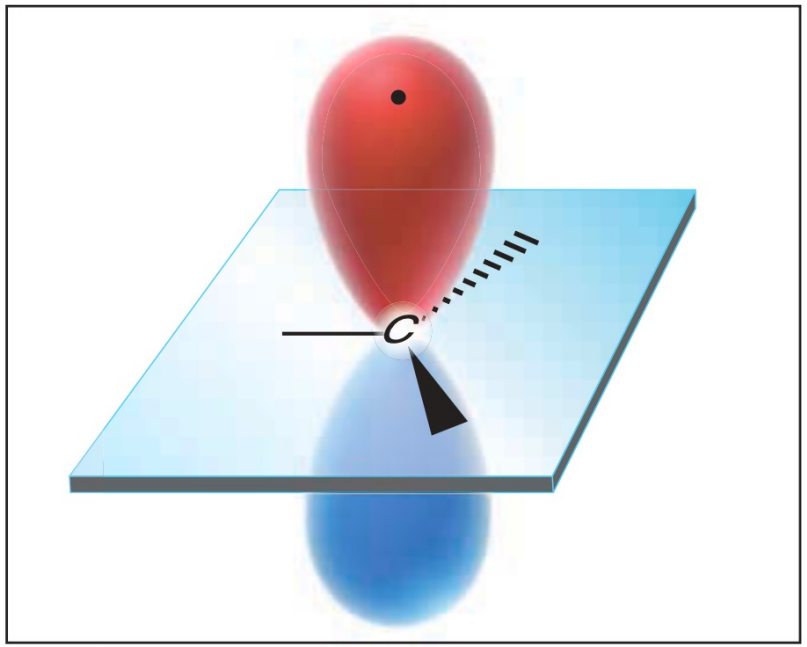
- Homolytic cleavage produces radicals



- Structure and geometry: a comparison to C^+ and C^-

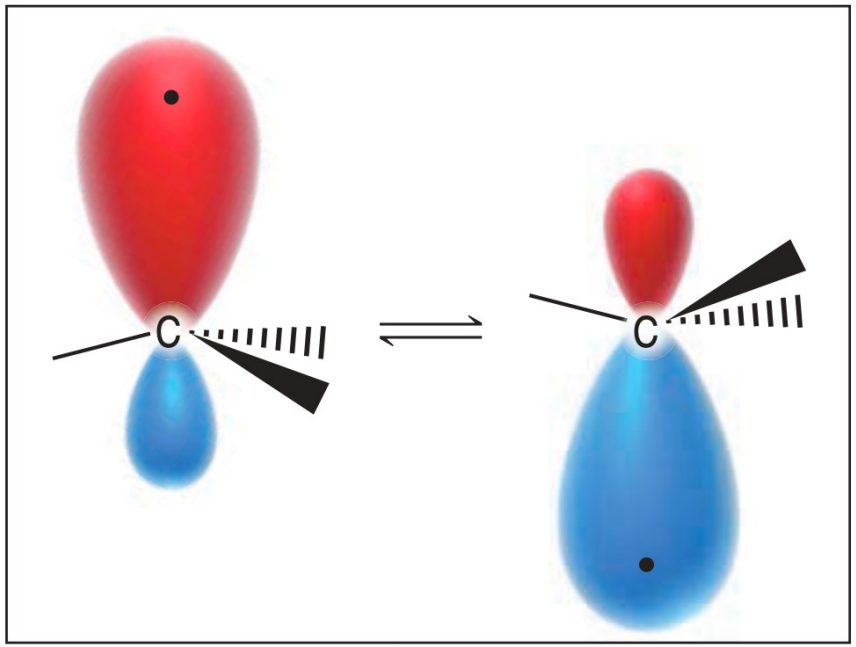


- Structure and geometry of radicals



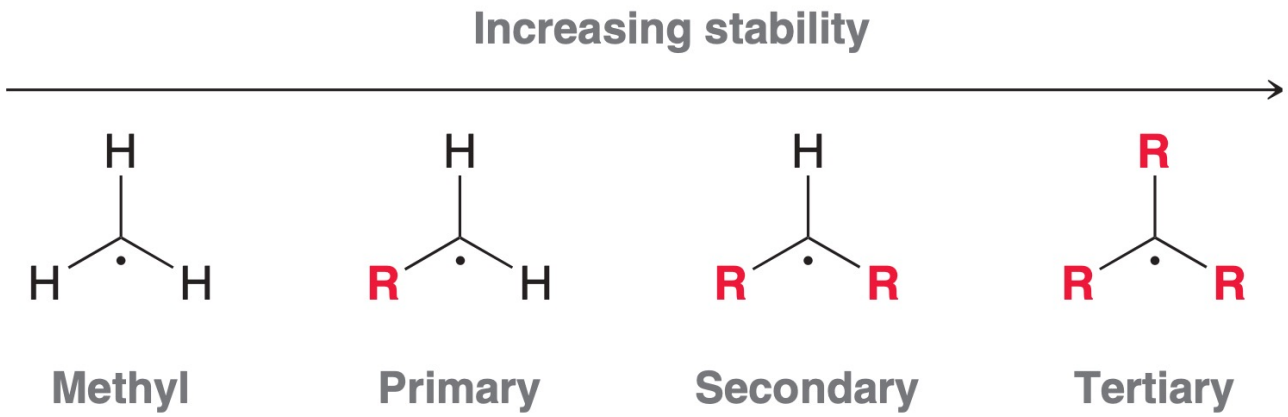
Trigonal planar

or

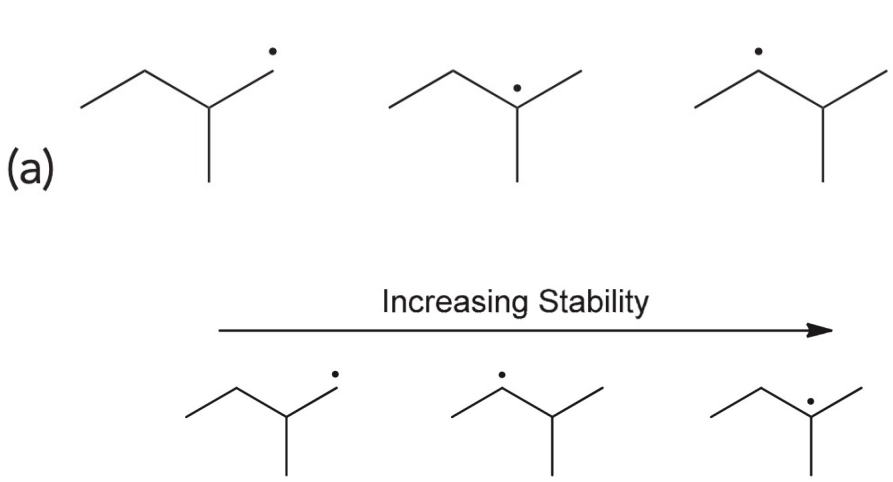


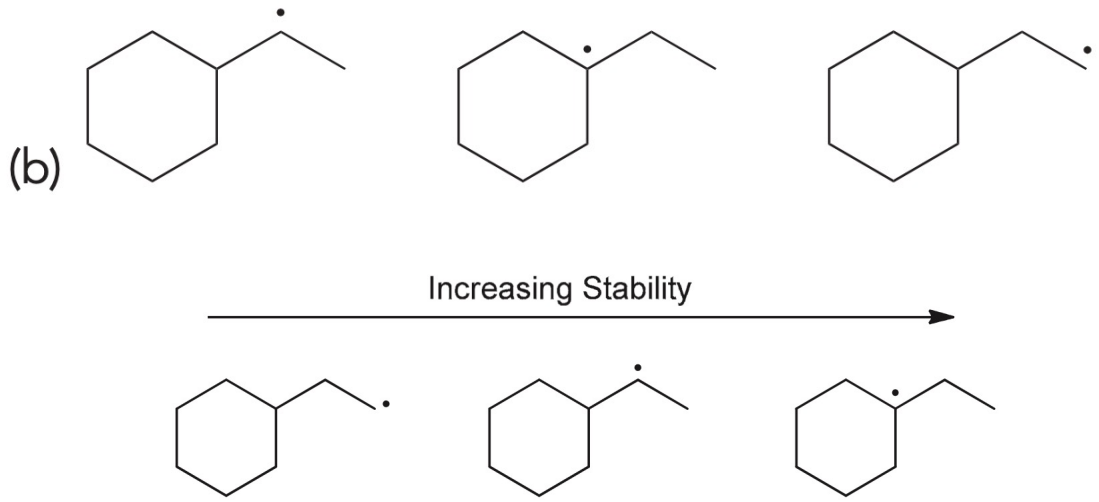
Shallow pyramid
(rapidly inverting)

- The stability of radicals follow the trend of carbocations – hyperconjugation

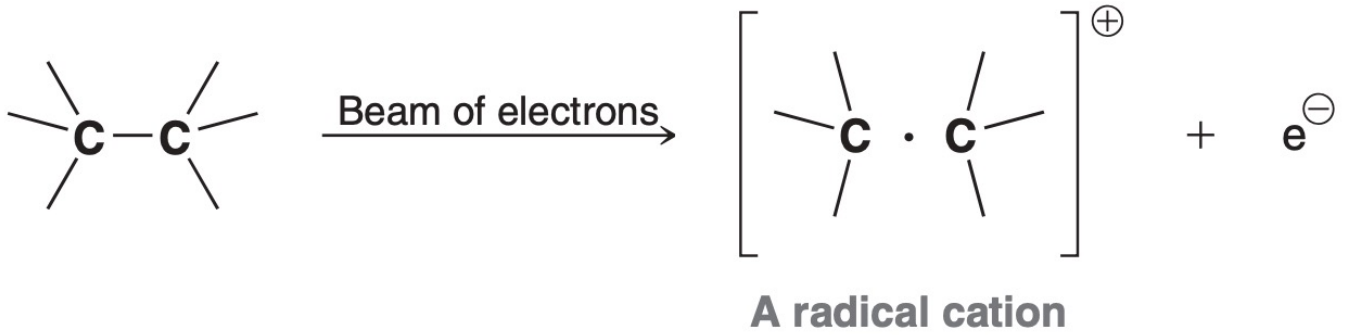


- Practice: rank the following radicals in order of stability:

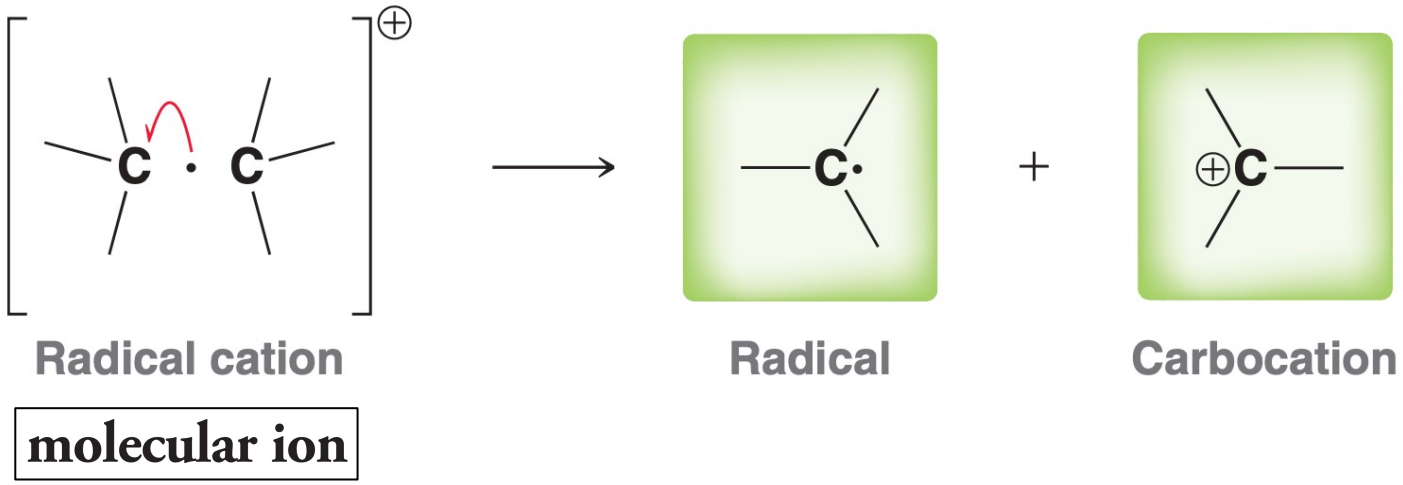




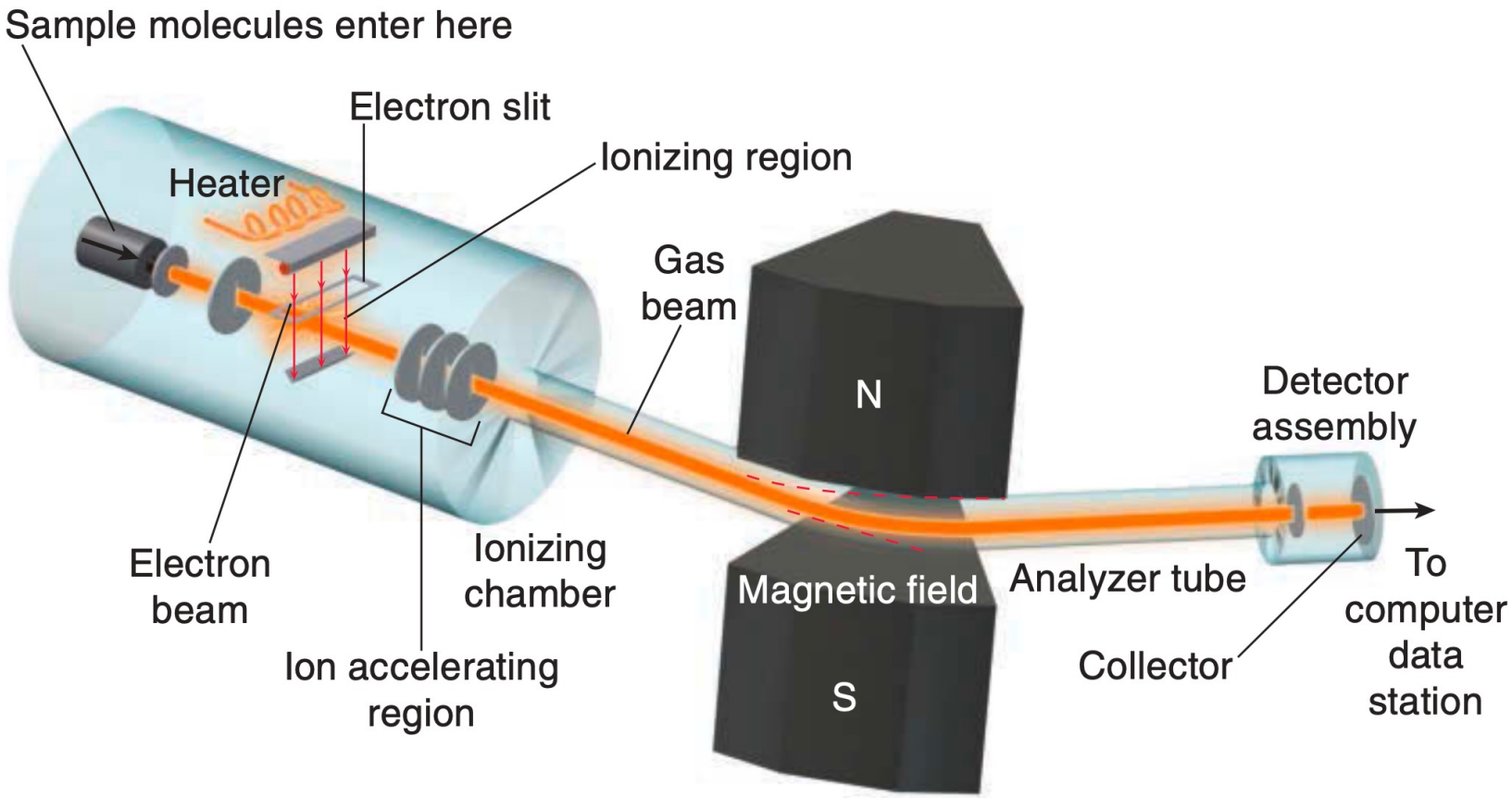
- Electron impact ionization (EI)

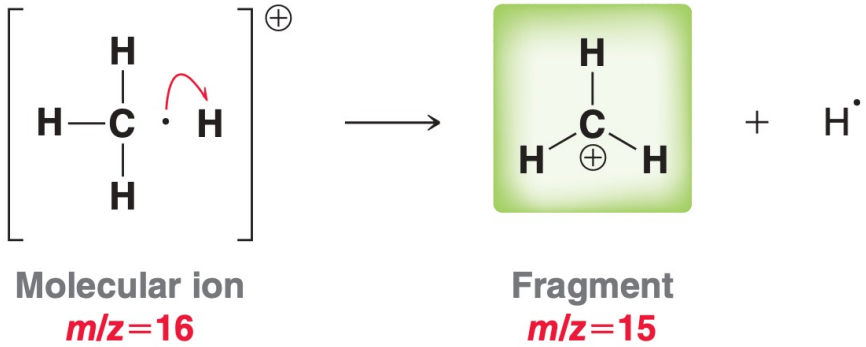


- Molecular ion $(M)^{+\bullet}$ fragmentation



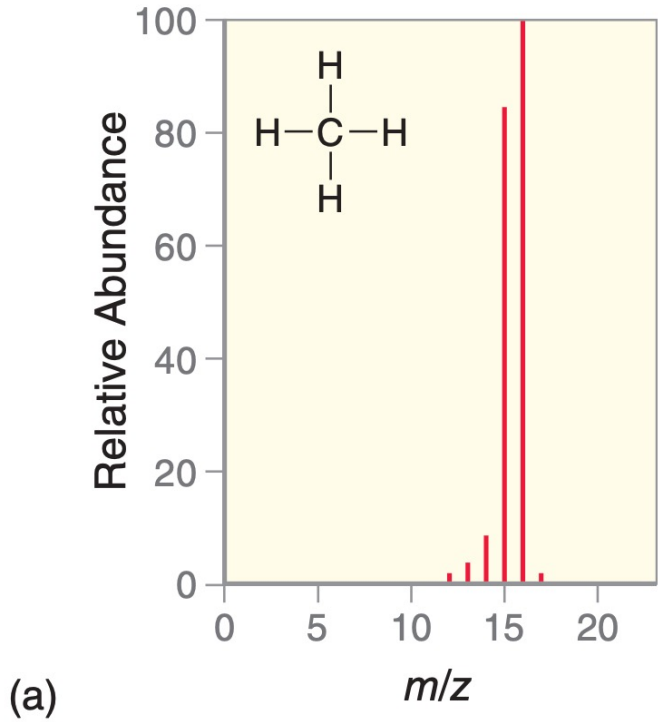
- Mass spectrometer





- Mass spectrum

fragmentation producing peaks below 16



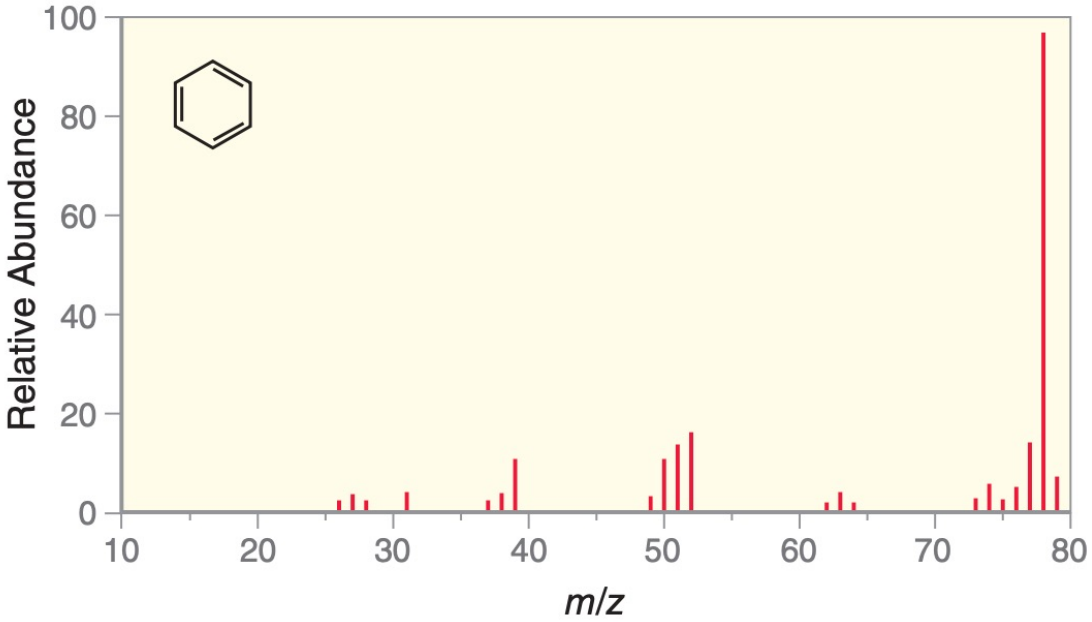
(b)

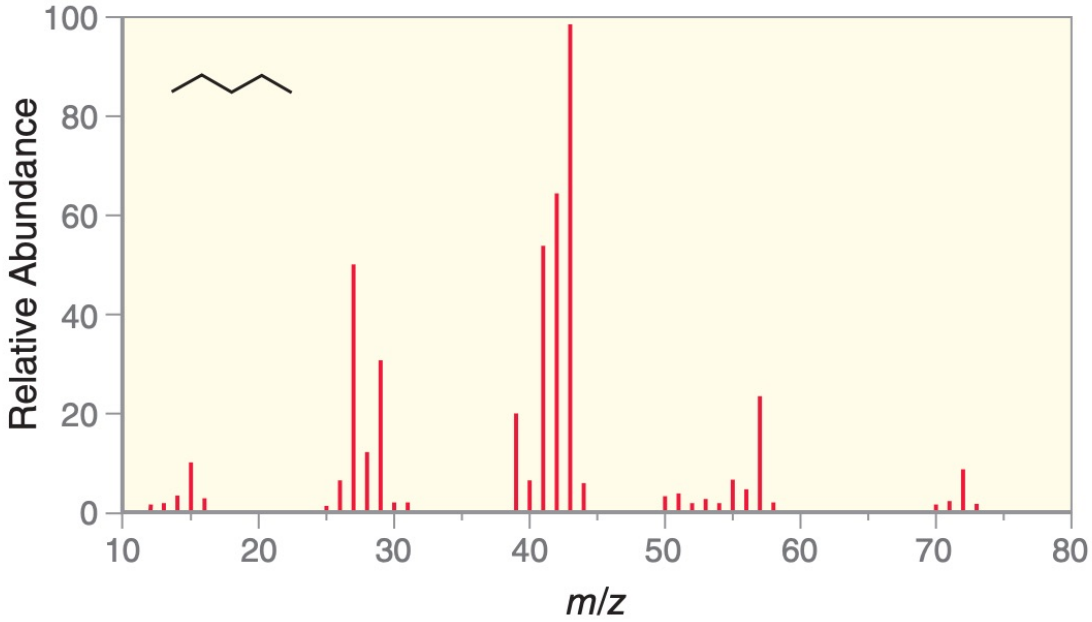
MASS SPECTRUM DATA

m/z	RELATIVE HEIGHT (%)
12	1.0
13	3.9
14	9.2
15	85.0
16	100 (base peak)
17	1.1

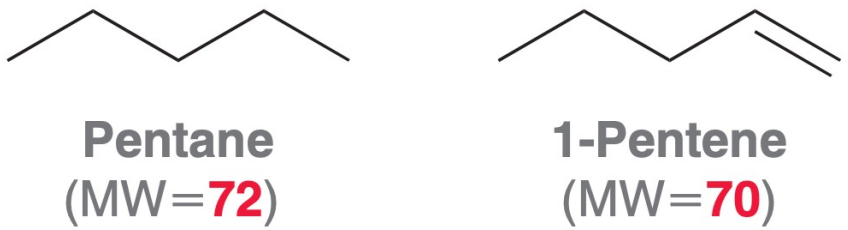
base peak: the highest peak used as a reference

- Analyzing the $(M)^{+\bullet}$ Peak

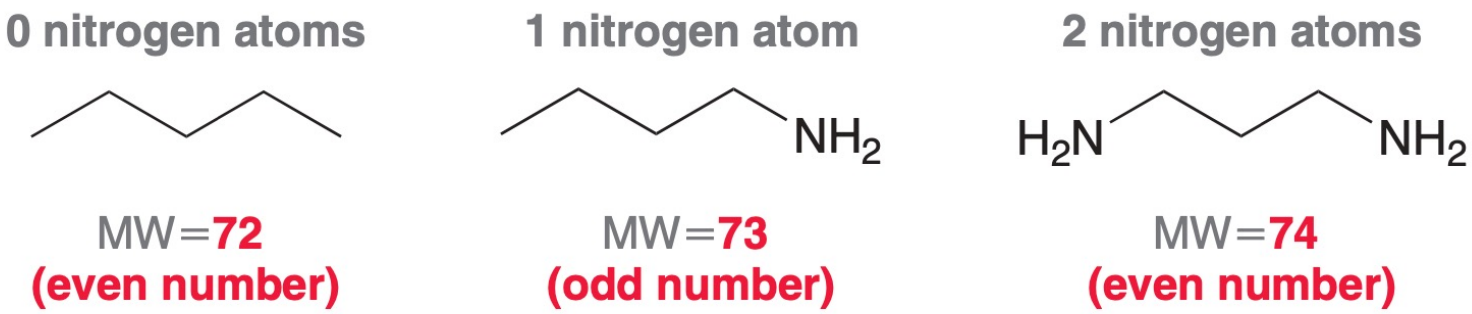




- Molecular weight determination and compound distinguishing



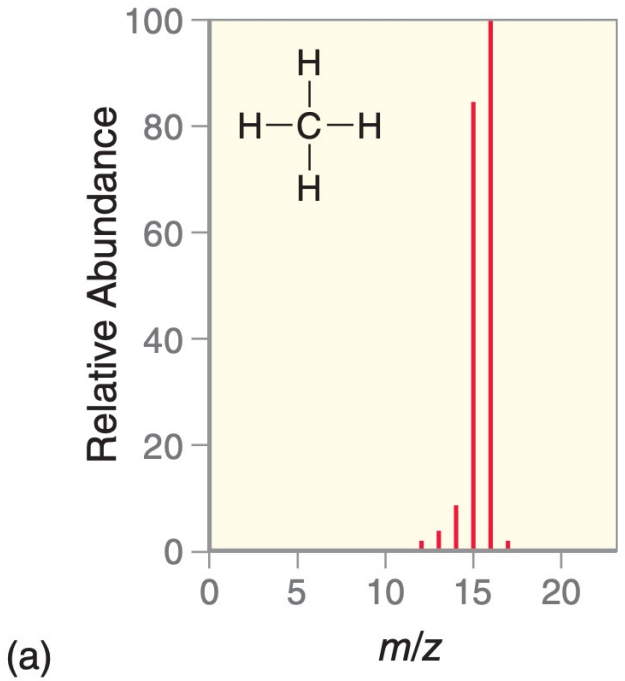
- The nitrogen rule



odd molecular weight – odd number of nitrogen atoms

even molecular weight – absence / even number of nitrogen atoms

- Analyzing the $(M+1)^{+\bullet}$ Peak



(b)

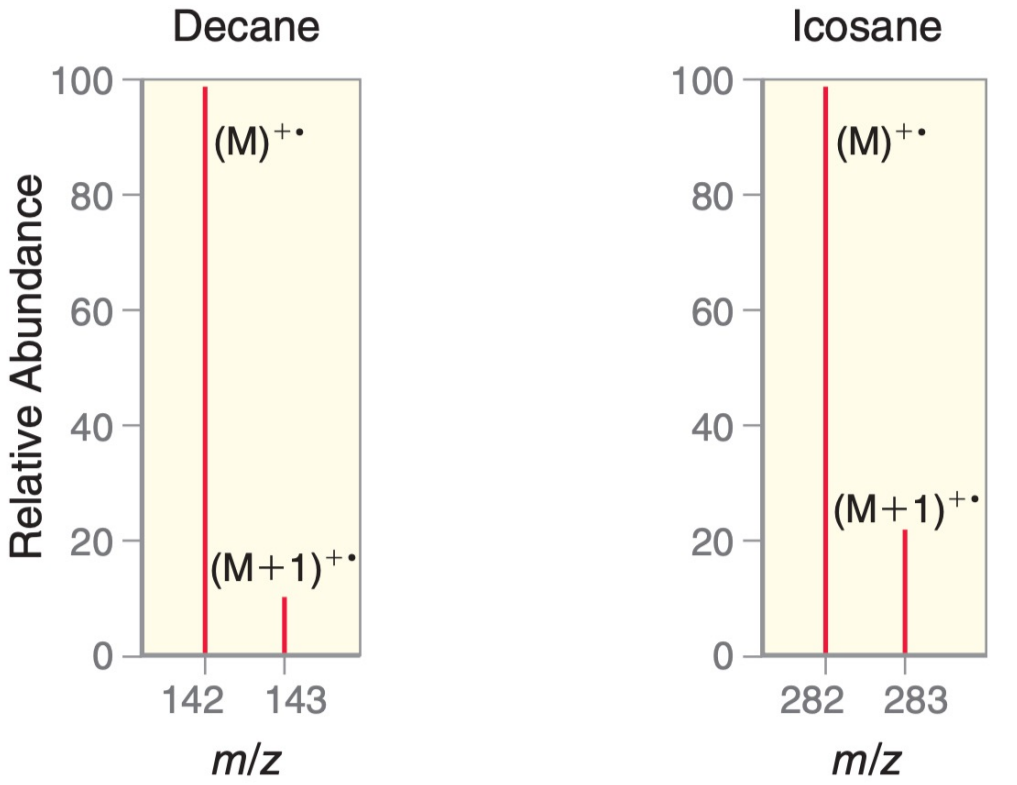
MASS SPECTRUM DATA

m/z	RELATIVE HEIGHT (%)
12	1.0
13	3.9
14	9.2
15	85.0
16	100 (base peak)
17	1.1

^{13}C peak

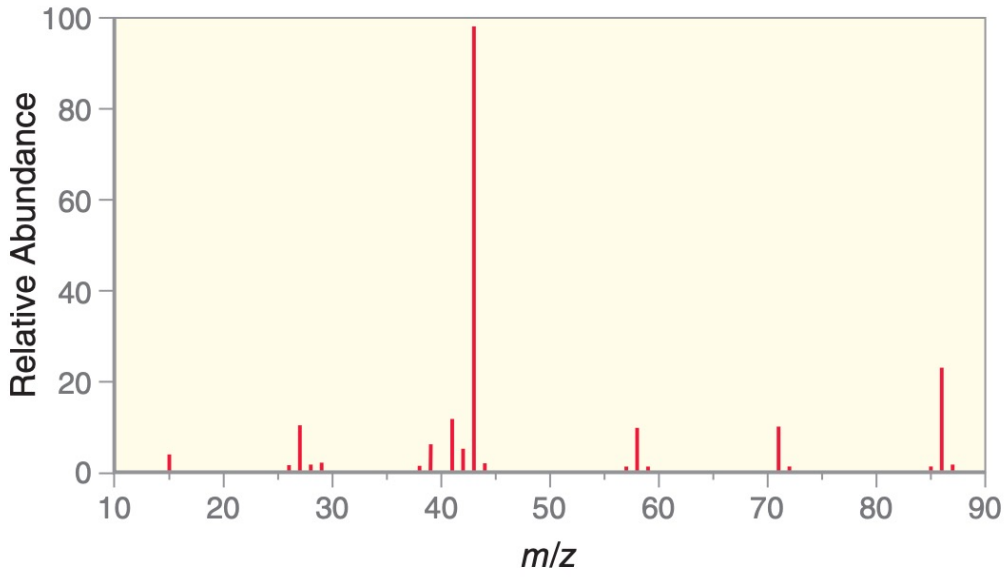
^{13}C abundance: ≈1.1%

- Larger compounds have larger $(M+1)^{+\bullet}$ peak



$(10 \times 1.1\%)$ $(20 \times 1.1\%)$

- Practice: below is the mass spectrum as well as the tabulated mass spectrum data for an unknown compound. Propose a molecular formula for this compound.



MASS SPECTRUM DATA

m/z	RELATIVE HEIGHT (%)	*m/z*	RELATIVE HEIGHT (%)
15	4.8	42	4.0
26	1.3	43	100 (base peak)
27	10.5	44	2.3
28	1.3	58	10.3
29	1.9	71	11.0
38	1.2	86	20.9 ($M^{+\bullet}$)
39	6.3	87	1.2
41	11.9		

86	20.9 ($M^{+\bullet}$)
87	1.2

$$\frac{1.2\%}{20.9\%} \times 100\% = 5.7\%$$

calculate the relative height of $(M+1)^{+\bullet}$

$$\text{Number of C} = \frac{5.7\%}{1.1\%} = 5.2$$

determine the total number of C in the compound

the molecular weight of C: $5 \times 12 = 60$

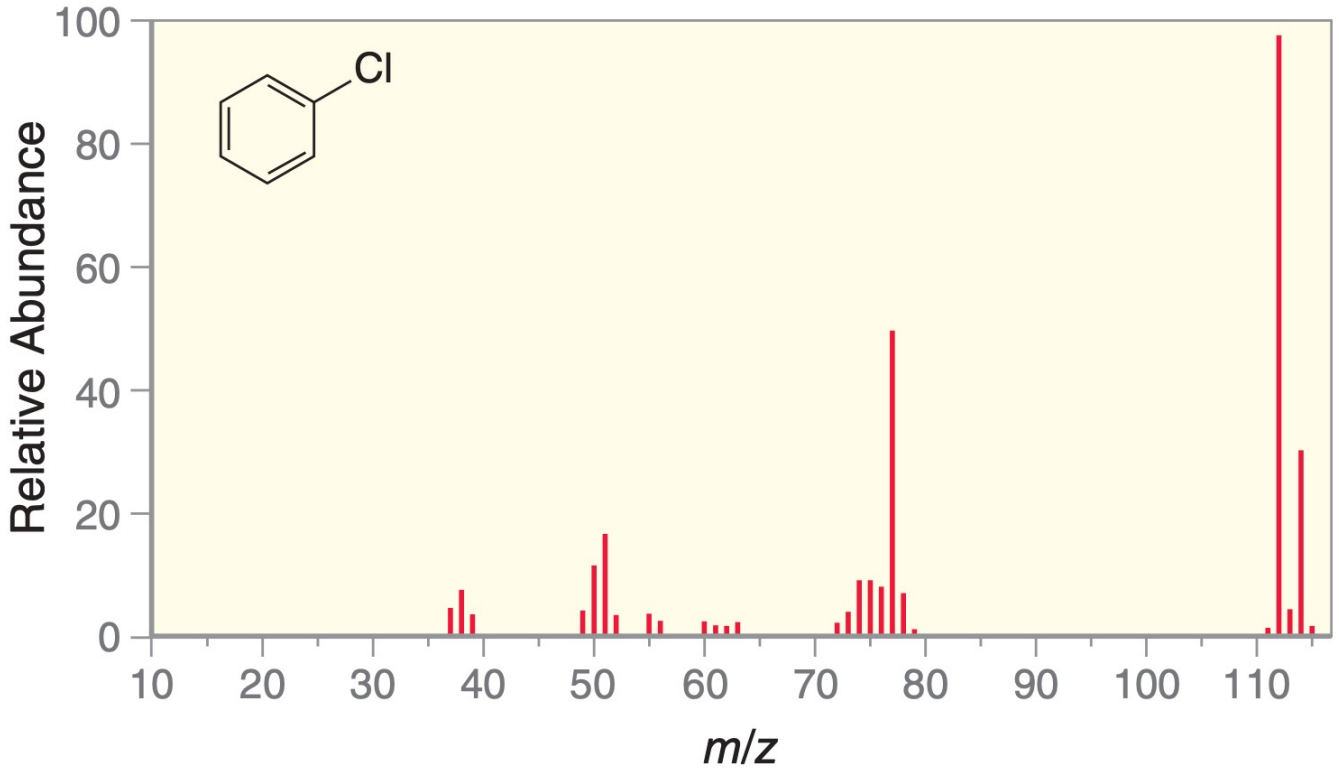
the remaining: $86 - 60 = 26$

consider C, H, O, N

not N – even weight

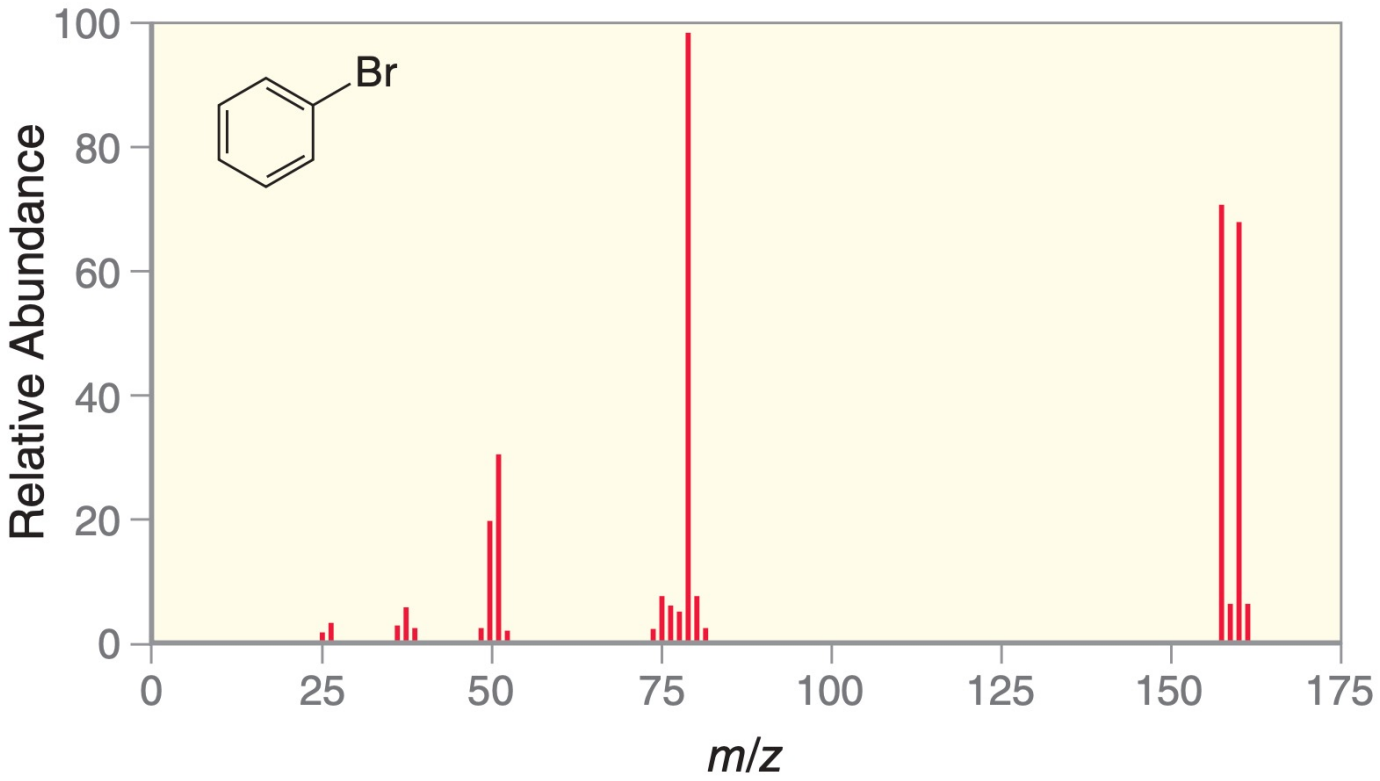
$C_5H_{10}O$

- $(M+2)^{+\bullet}$ Peak: Cl isotopes



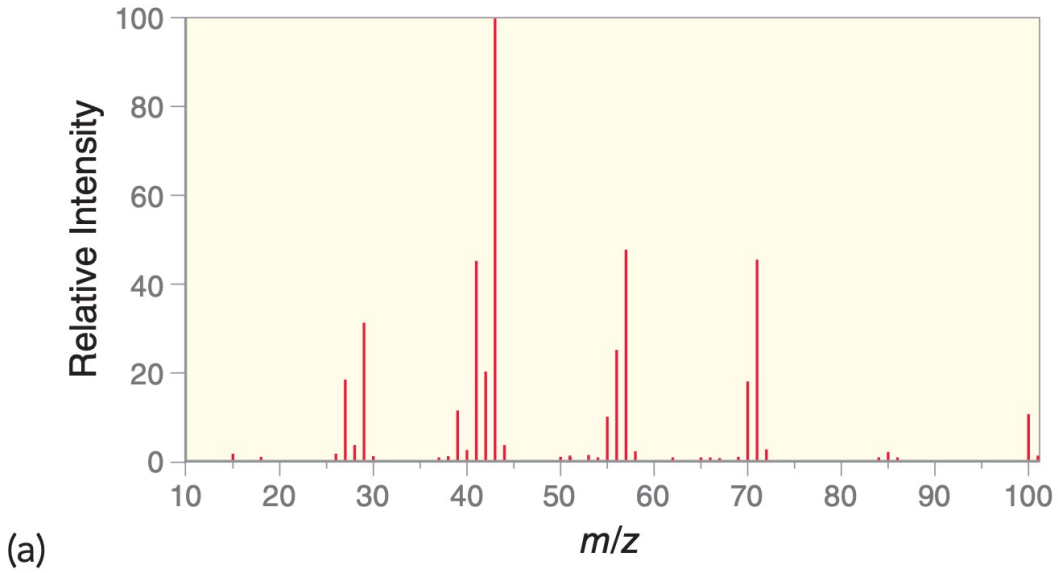
$^{35}Cl : {}^{37}Cl = 3 : 1$

- $(M+2)^{+\bullet}$ Peak: Br isotopes

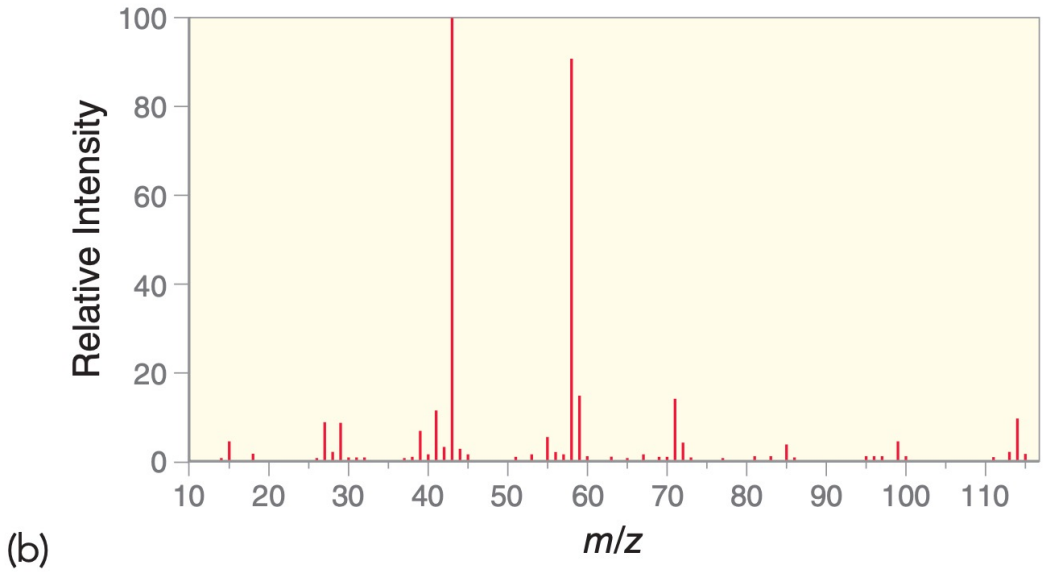


$^{79}Br : {}^{81}Br = 1 : 1$

- Practice: below are mass spectra for four different compounds. Identify whether each of these compounds contains a bromine atom, a chlorine atom, or neither.

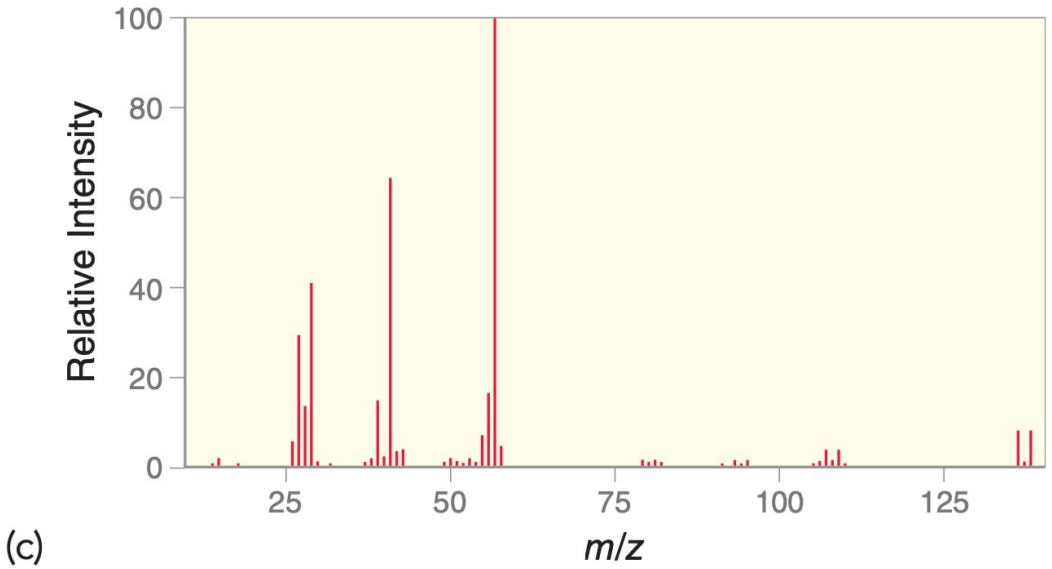


neither



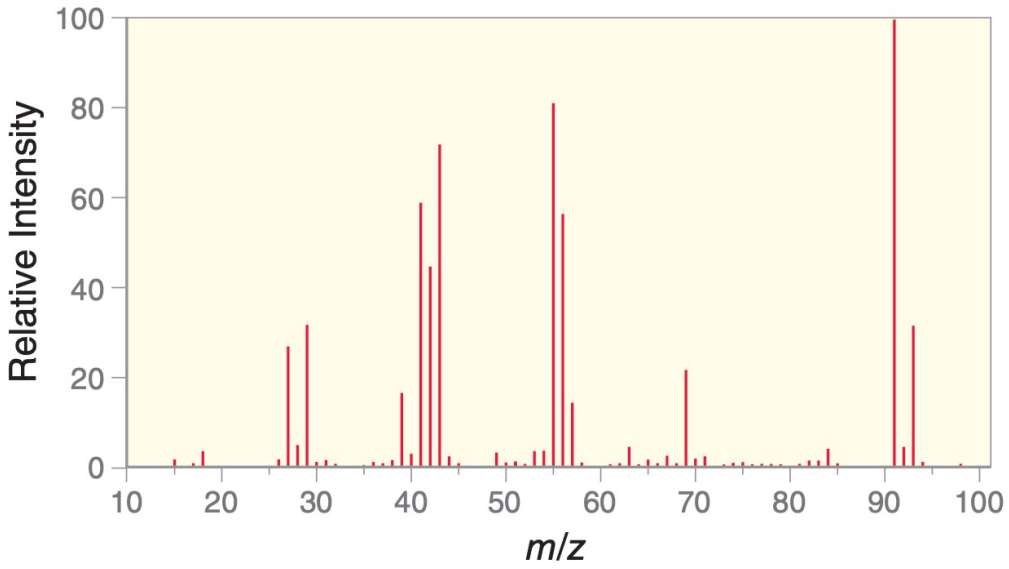
neither

- Practice: below are mass spectra for four different compounds. Identify whether each of these compounds contains a bromine atom, a chlorine atom, or neither.



(c)

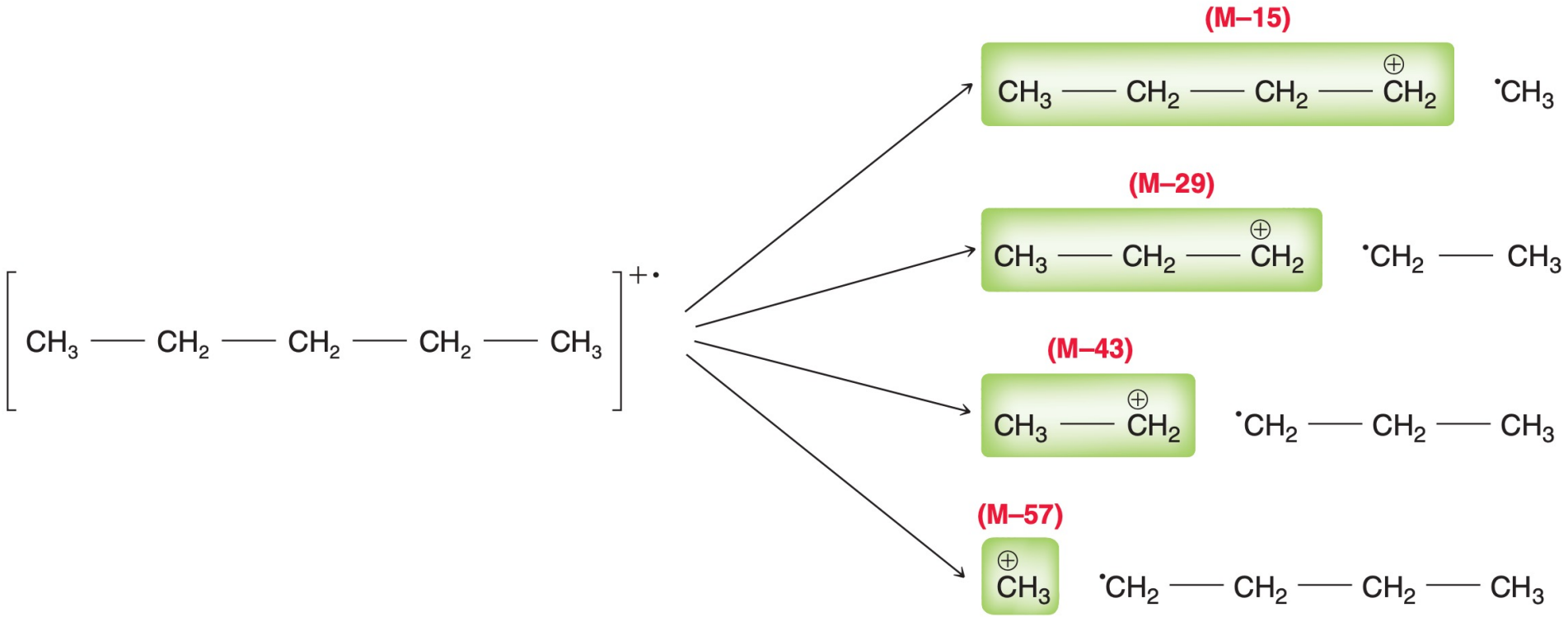
Br



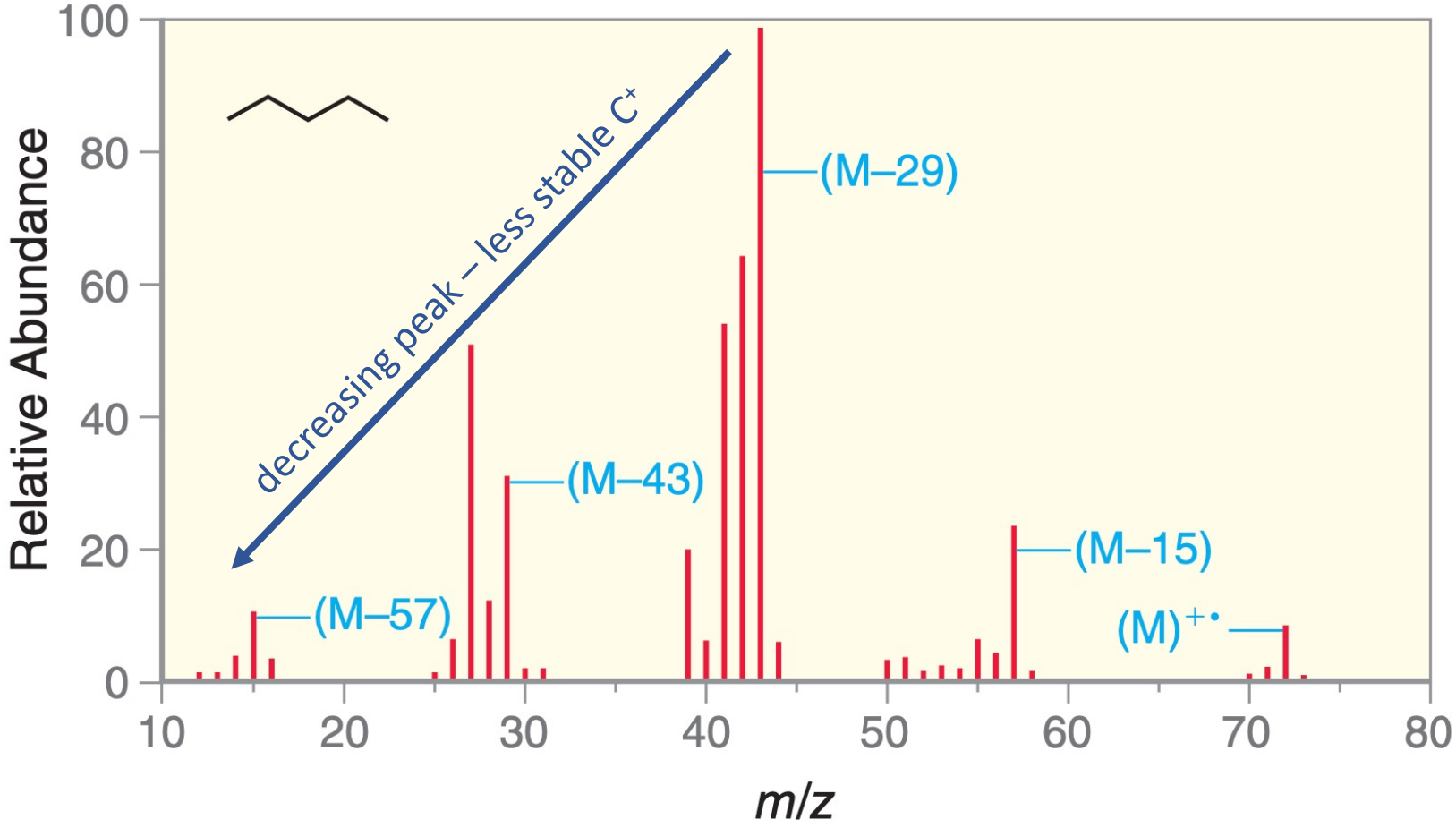
(d)

Cl

- Fragmentation of Alkanes

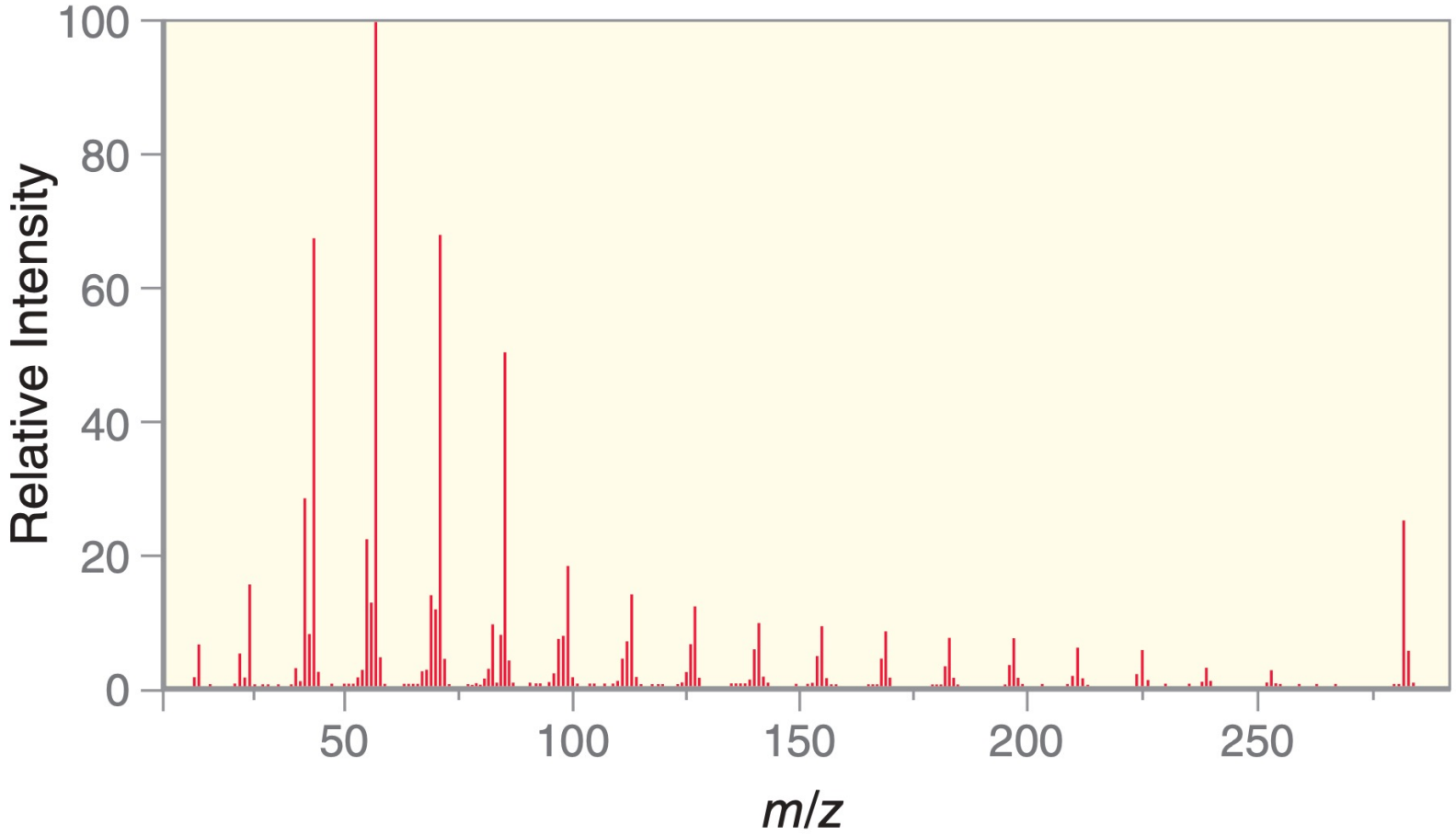


- Characterized peaks decreases with –15(–14) pattern



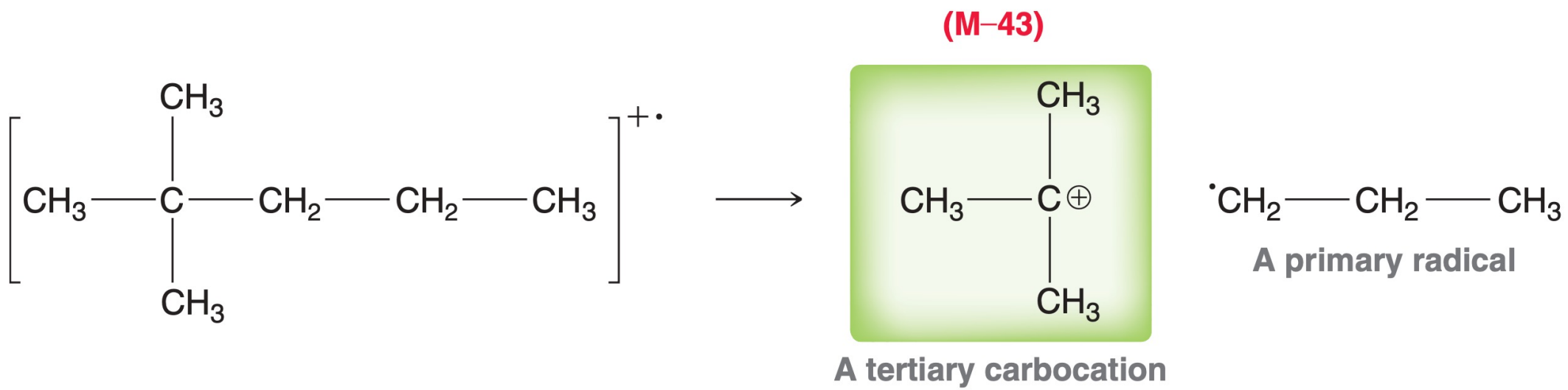
pentane

- Similar pattern – group of peaks for *n*-alkanes

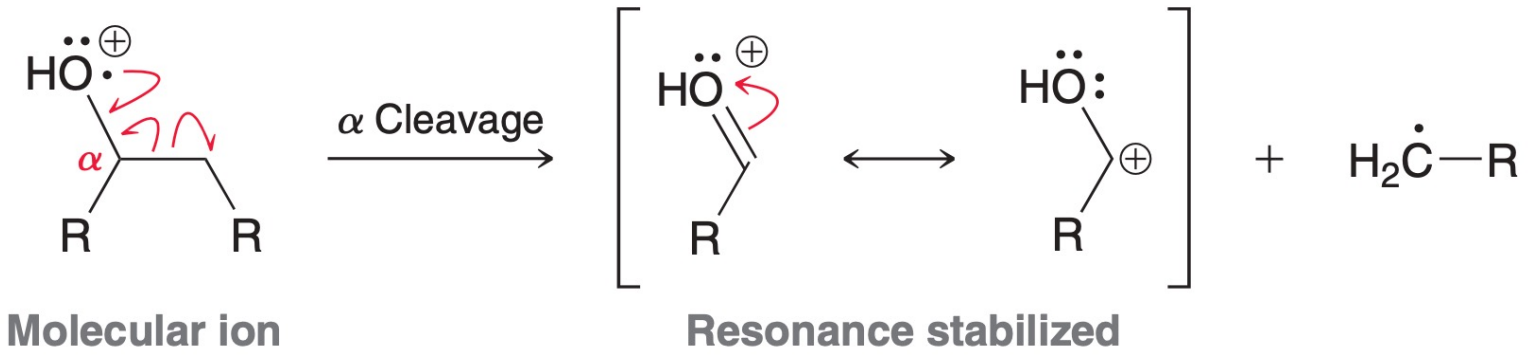


icosane

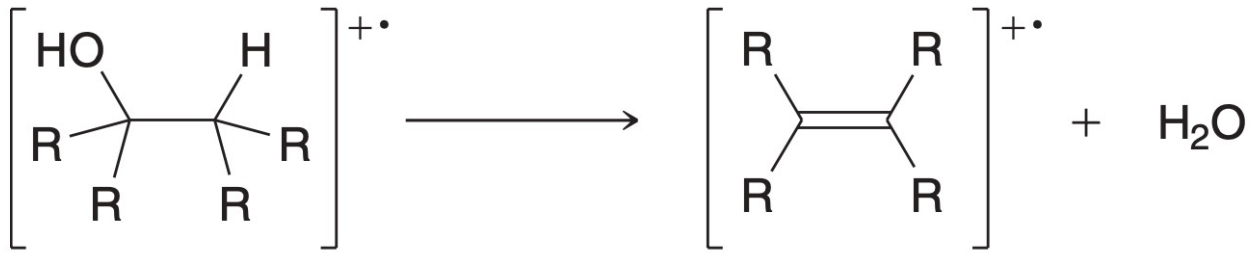
- Branched alkanes



- Fragmentation of alcohols – α cleavage



- Fragmentation of alcohols – dehydration



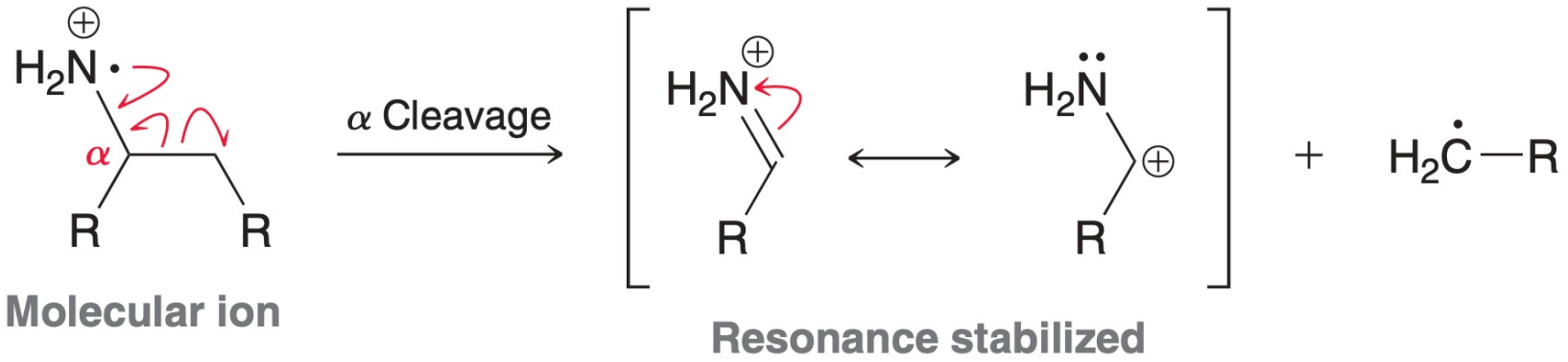
Molecular ion

(M−18)

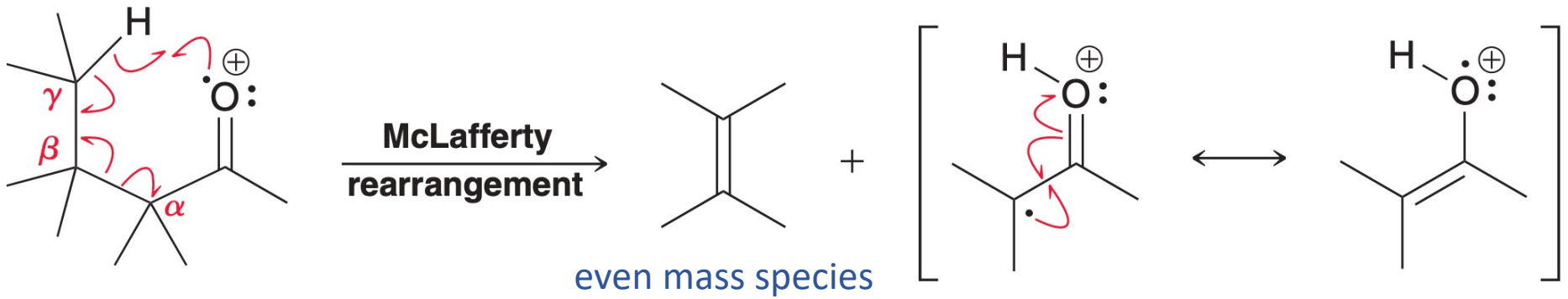
characteristic peak

for alcohols

- Fragmentation of amines



- Fragmentation of ketones and aldehydes



even mass species

characteristic peaks for ketones and aldehydes: $M-x$, where x is an even number

- **Summary: common fragments**

M − 15	Loss of a methyl radical
M − 29	Loss of an ethyl radical
M − 43	Loss of a propyl radical
M − 57	Loss of a butyl radical
M − 18	Loss of water (from an alcohol)
M − *x* (where *x* = even number)	McLafferty rearrangement (ketone or aldehyde)

- Practice

14.24 Although 2,2-dimethylhexane has a molecular weight of 114, no peak is observed at $m/z = 114$. The base peak in the mass spectrum occurs at M−57.

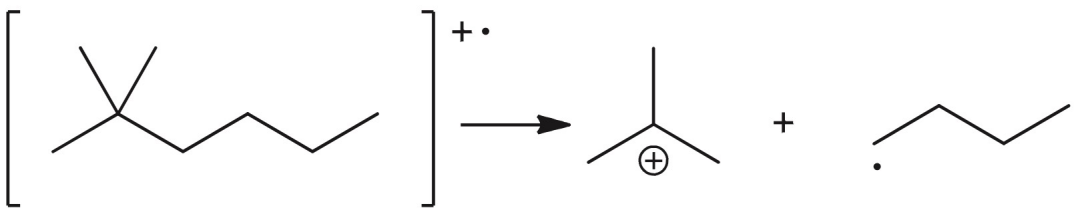
(a) Draw the fragmentation responsible for formation of the M−57 ion.

(b) Explain why this cation is the most abundant ion to pass through the spectrometer.

(c) Explain why no molecular ions survive long enough to be detected.

(d) Can you offer an explanation as to why the M−15 peak is not the base peak?

(a) A peak at M–57 indicates the loss of a four-carbon radical fragment, which can result in the formation of a tertiary carbocation, as shown. This tertiary carbocation is the fragment responsible for the peak at M–57:



(M − 57)

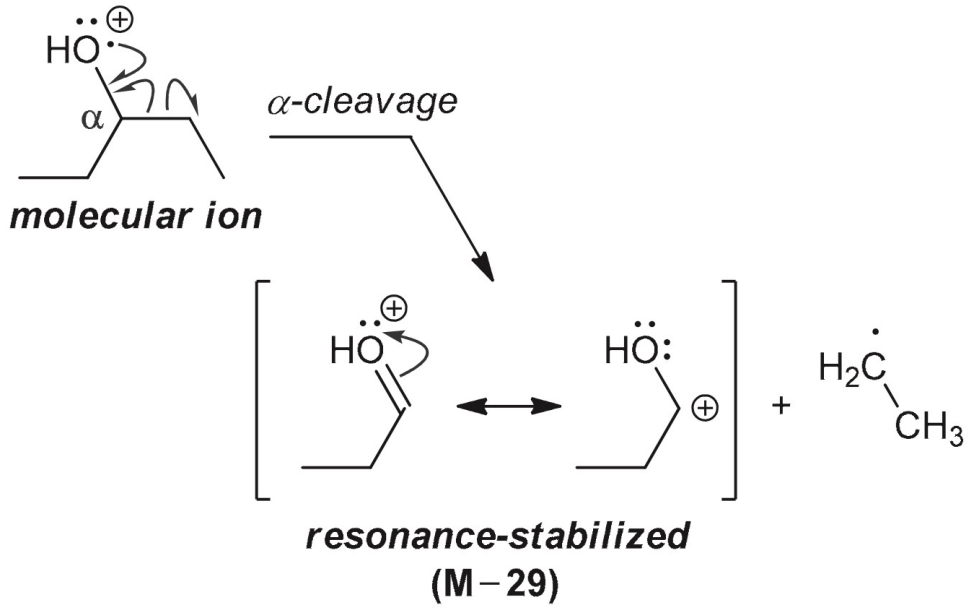
Remember that the radical fragment (the butyl radical) is not detected by the mass spectrometer.

(b) This carbocation is tertiary, and its formation is favored over the other possible secondary and primary carbocations.

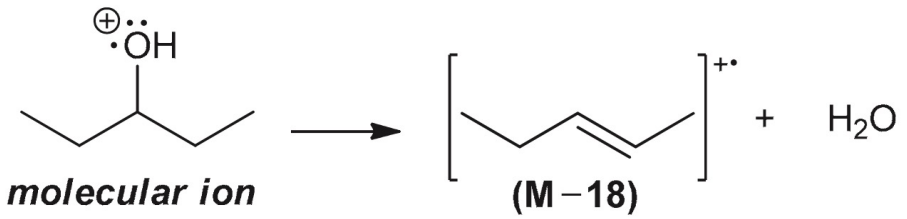
(c) They readily fragment to produce tertiary carbocations.

(d) M–15 corresponds to loss of a methyl group. Indeed, loss of a methyl group would also produce a tertiary carbocation, but that pathway is less favorable because it involves formation of a methyl radical (which is less stable than a primary radical).

- Practice: identify two peaks that are expected to appear in the mass spectrum of 3-pentanol. For each peak, identify the fragment associated with the peak.

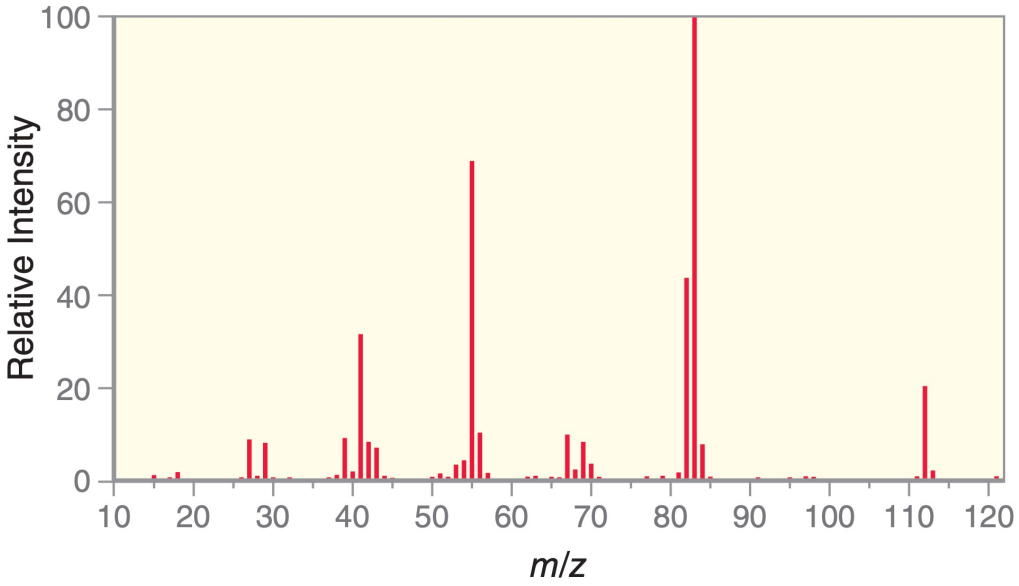


M–29

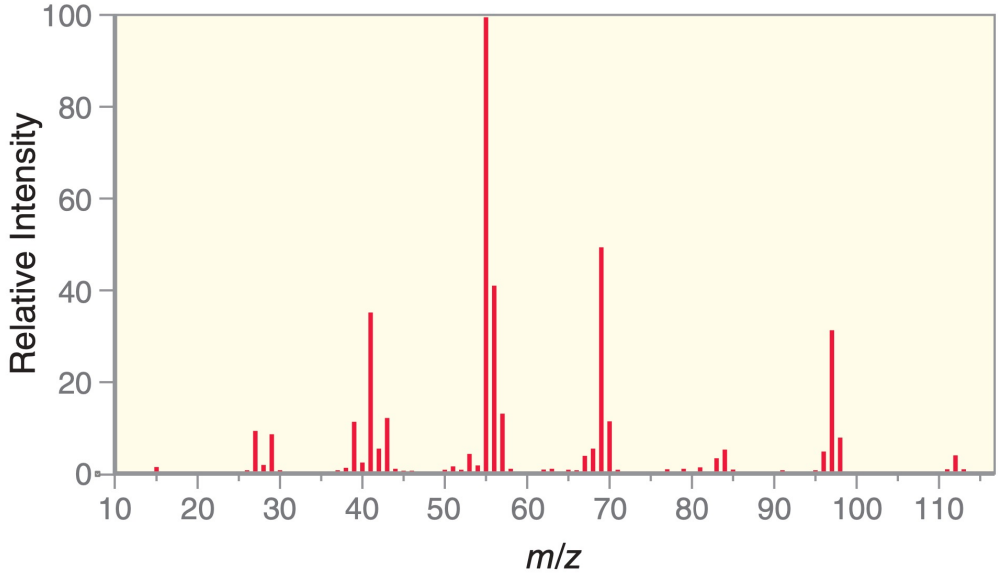


M–18

- Practice: the following are mass spectra for the constitutional isomers ethylcyclohexane and 1,1-dimethylcyclohexane. Based on likely fragmentation patterns, match the compound with its spectrum.



ethylcyclohexane



1,1-dimethylcyclohexane

- Simple approximation of relative mass

ELEMENT	NUMBER OF PROTONS	NUMBER OF NEUTRONS	RELATIVE ATOMIC WEIGHT
H	1	0	1
He	2	2	4
C	6	6	12
N	7	7	14
O	8	8	16

- The inaccuracy of the simple model…
  - Protons do not have exactly the same mass as neutrons

$$\text{one proton} = 1.6726 \times 10^{-24}\ \text{g}$$
$$\text{one neutron} = 1.6749 \times 10^{-24}\ \text{g}$$

  - Two bound protons will have less mass than two individual protons

Relativity – mass defect of bound protons – converted to potential energy

$$E = mc^2$$

- The atomic mass unit (amu)

$$1\ \text{amu} = \frac{1\ \text{g}}{6.02214 \times 10^{23}} = 1.6605 \times 10^{-24}\text{g}$$

Avogadro's number (N_A)

N_A: the number of atoms in exactly 12 g of ^{12}C

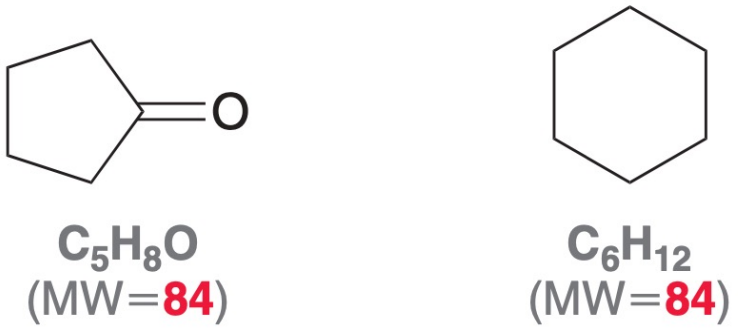
ONLY one atom of ^{12}C has an atomic mass of exactly 12 amu

- Relative atomic mass and abundance of several elements

ISOTOPE	RELATIVE ATOMIC MASS (amu)	ABUNDANCE IN NATURE	ISOTOPE	RELATIVE ATOMIC MASS (amu)	ABUNDANCE IN NATURE
^{1}H	1.0078	99.99%	^{16}O	15.9949	99.76%
^{2}H	2.0141	0.01%	^{17}O	16.9991	0.04%
^{3}H	3.0161	$<0.01\%$	^{18}O	17.9992	0.20%
^{12}C	12.0000	98.93%	^{35}Cl	34.9689	75.78%
^{13}C	13.0034	1.07%	^{37}Cl	36.9659	24.22%
^{14}C	14.0032	$<0.01\%$	^{79}Br	78.9183	50.69%
^{14}N	14.0031	99.63%	^{81}Br	80.9163	49.31%
^{15}N	15.0001	0.37%			

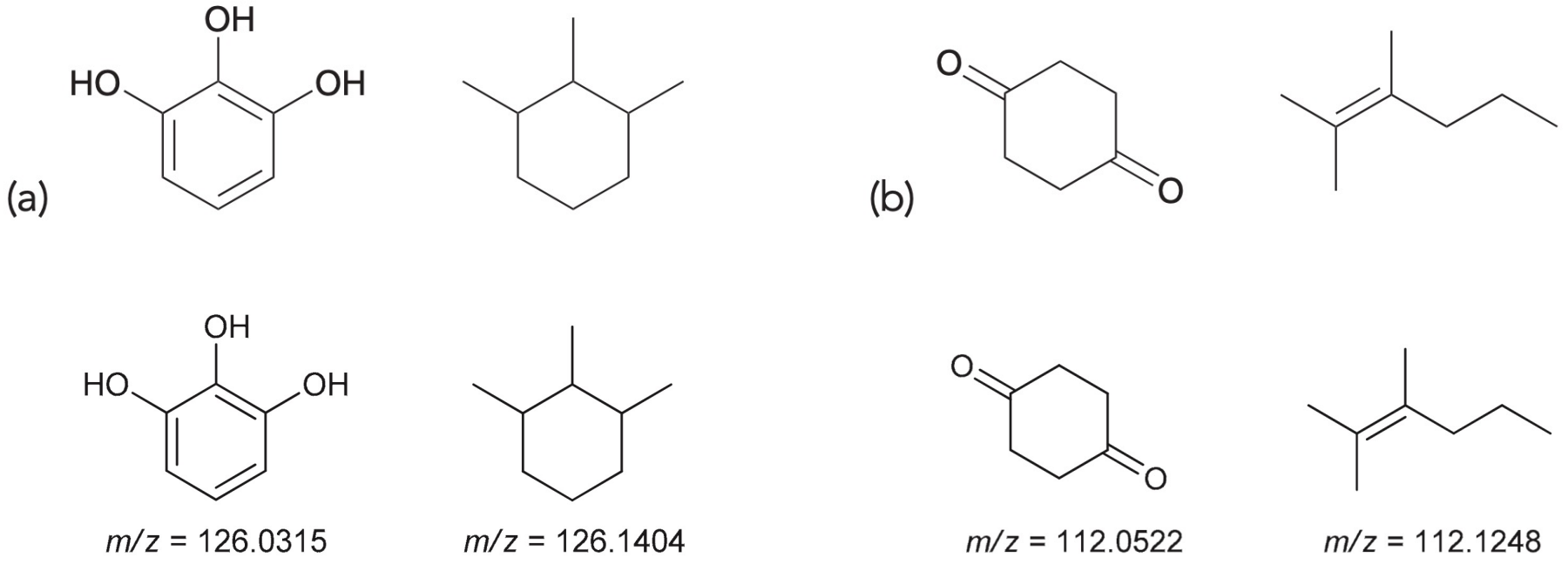
Note: Data obtained from the National Institute of Standards and Technology (NIST).

- Using high-resolution mass spectrometry to distinguish compounds



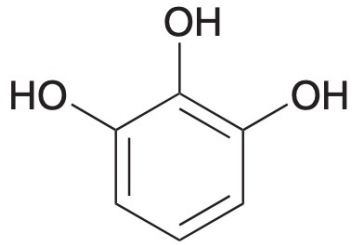
$$C_5H_8O = (5 \times 12.0000) + (8 \times 1.0078) + (1 \times 15.9949) = \mathbf{84.0573}\ \text{amu}$$
$$C_6H_{12} = (6 \times 12.0000) + (12 \times 1.0078) = \mathbf{84.0936}\ \text{amu}$$

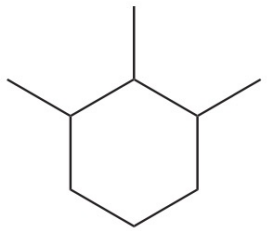
- Practice: how would you distinguish between each pair of compounds using high-resolution mass spectrometry?



- Practice: how would you distinguish between each pair of compounds in the previous problem using IR spectroscopy?

(a)

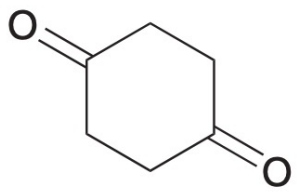




3200-3600 cm^{-1}

for hydroxyl group

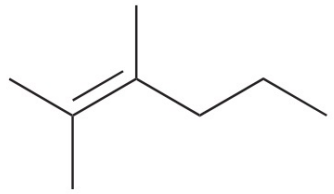
(b)



strong signal

around 1720 cm^{-1}

for carbonyl group

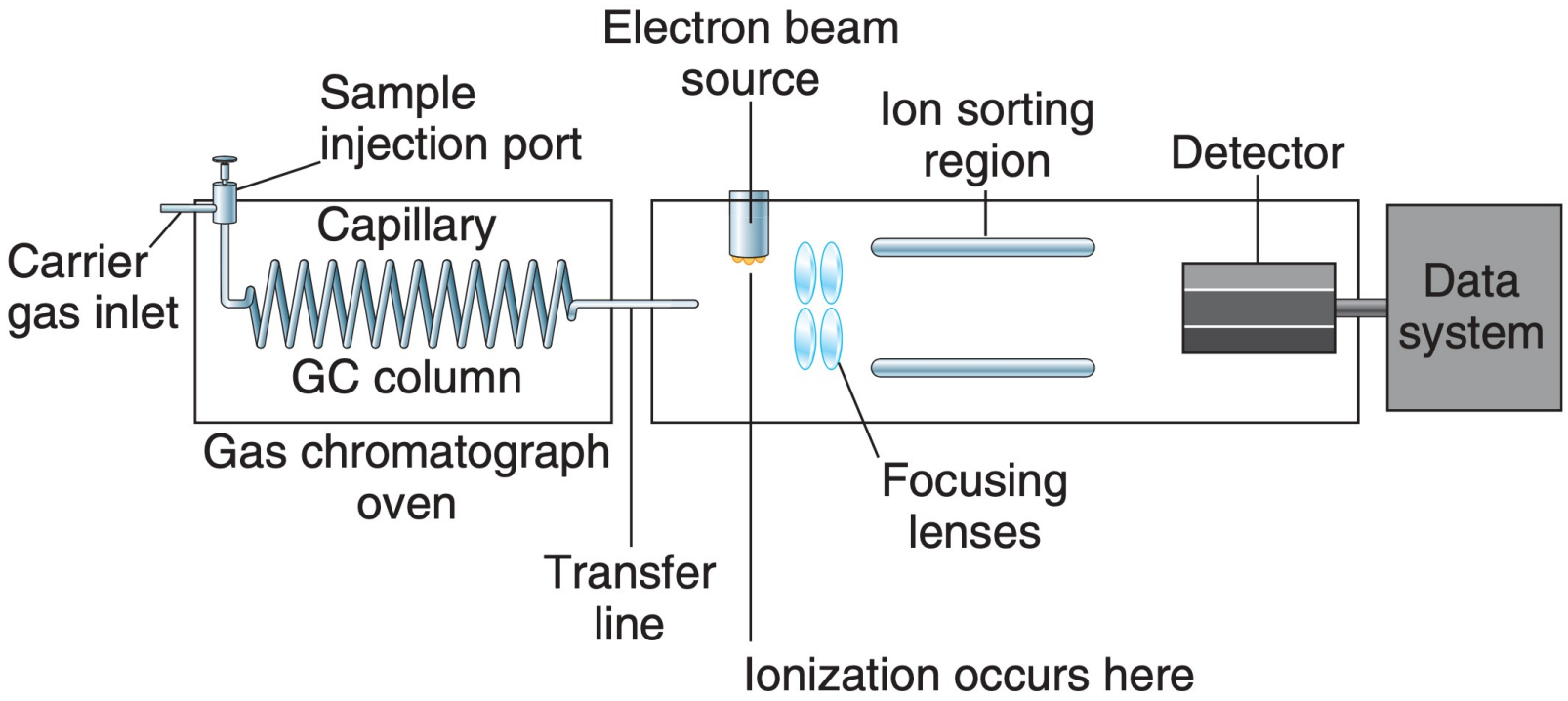


medium-weak signal

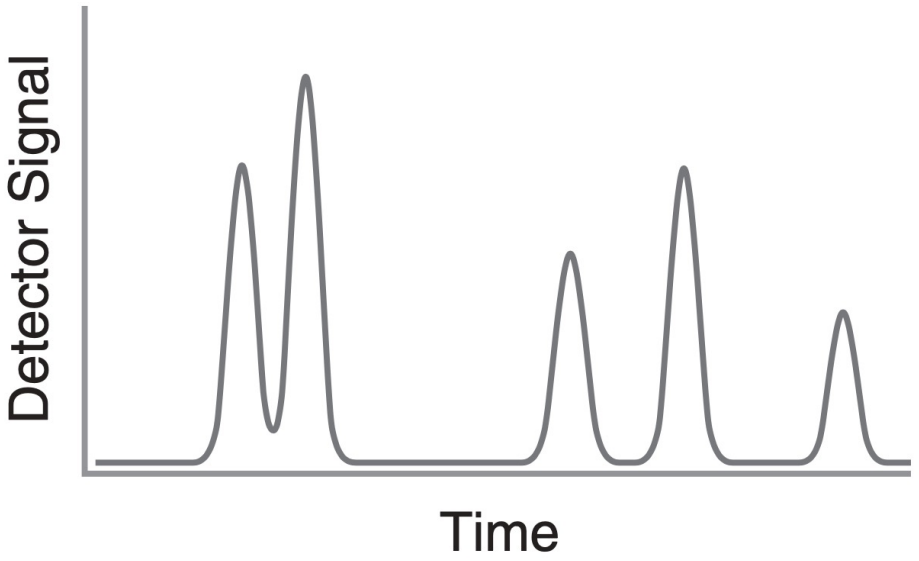
around 1650 cm^{-1}

for double bond

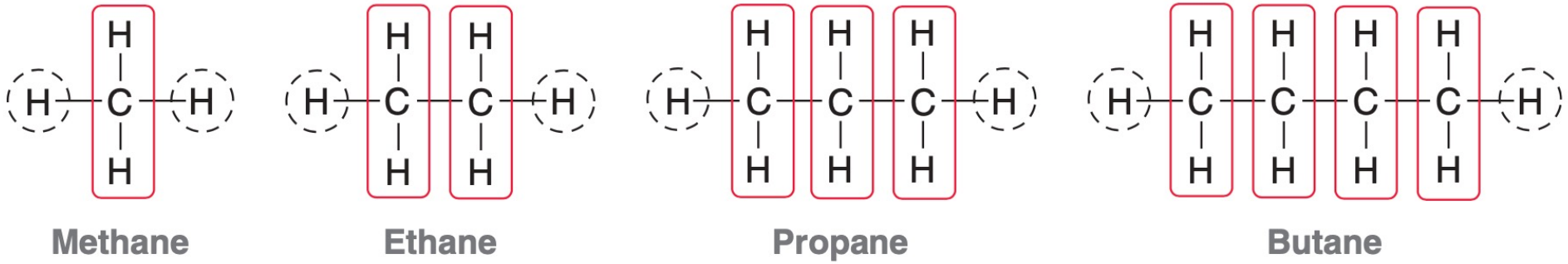
- Gas chromatography-mass spectrometry (GC-MS)



- Chromatograph

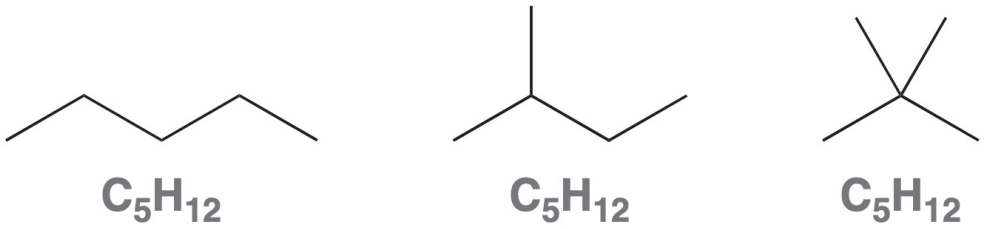


- General formula for alkanes



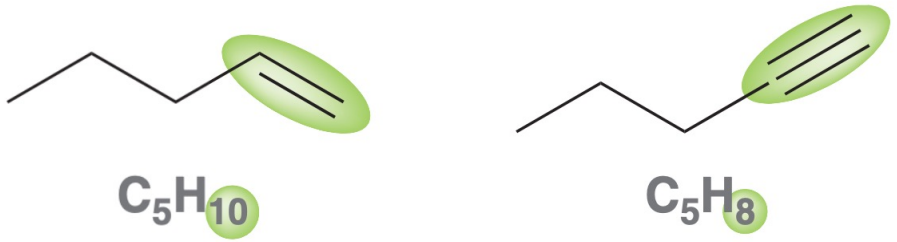
$$H—(CH_2)_n—H$$

- The rule also true for branched alkanes



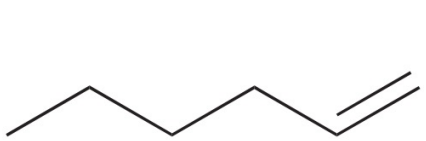
$$C_nH_{2n+2}$$

- Saturated vs. unsaturated

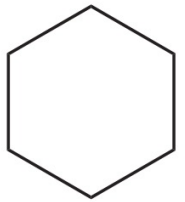


multiple bonds decrease the possibility of # of hydrogen linked – unsaturated

- Rings also contribute to unsaturation



1-Hexene
(C_6H_{12})

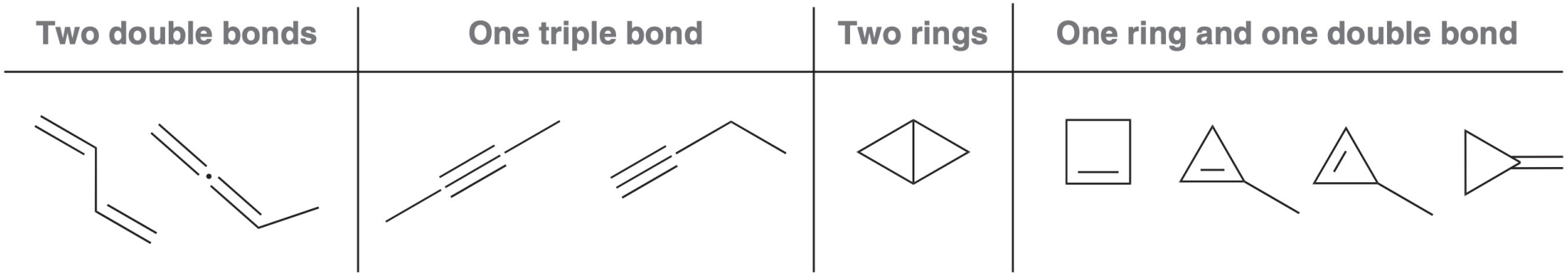


Cyclohexane
(C_6H_{12})

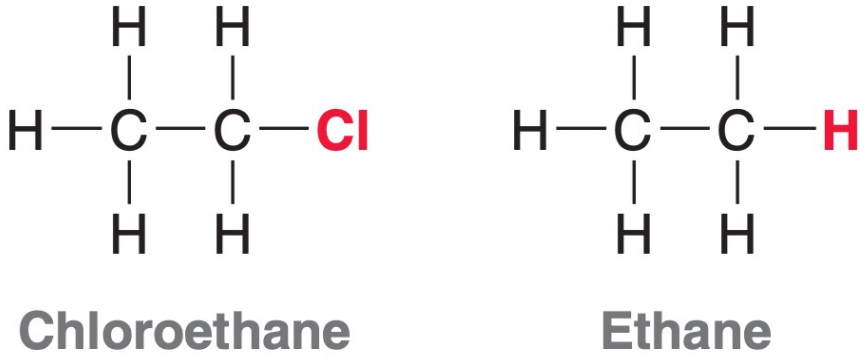
missing two hydrogens – one degree of unsaturation

hydrogen deficiency index (HDI) = 1

- Possible structures of two degrees of unsaturation (HDI = 2)

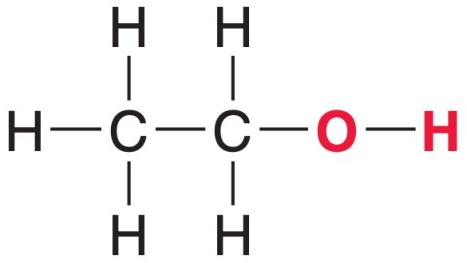


- Elements that affect HDI: halogen
  - Halogen usually has a same valence compared to hydrogen
  - Halogen can be treated as a hydrogen

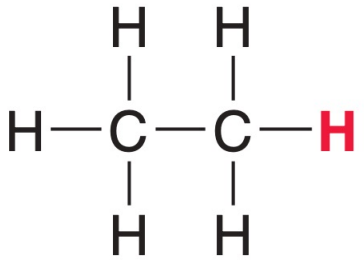


they have the same HDI

- Elements that affect HDI: oxygen
  - Oxygen (–O– structure) can be treated as an “insertion”
  - Oxygen is ignored in HDI calculation



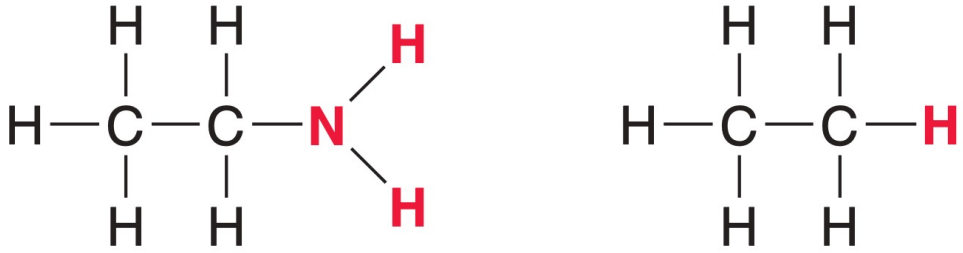
Ethanol



Ethane

they have the same HDI

- Elements that affect HDI: nitrogen
  - Nitrogen allows one more hydrogen linked to the molecule
  - One hydrogen must be subtracted if there is a nitrogen presented



Ethyl amine

Ethane

they have the same HDI

- Summary
  - Halogen: ***add*** one H for each halogen
  - Oxygen: ***ignore***
  - Nitrogen: ***subtract*** one H for each N

$$\mathrm{HDI} = \frac{1}{2}(2C + 2 + N - H - X)$$

- Practice: calculate the HDI for a compound with the molecular formula $C_4H_8ClNO_2$ and identify the structural information provided by the HDI.

$$\text{HDI} = \frac{1}{2}(2C + 2 + N - H - X) = \frac{1}{2}(8 + 2 + 1 - 8 - 1) = \frac{2}{2} = 1$$

HDI = 1: one ring / one double bond