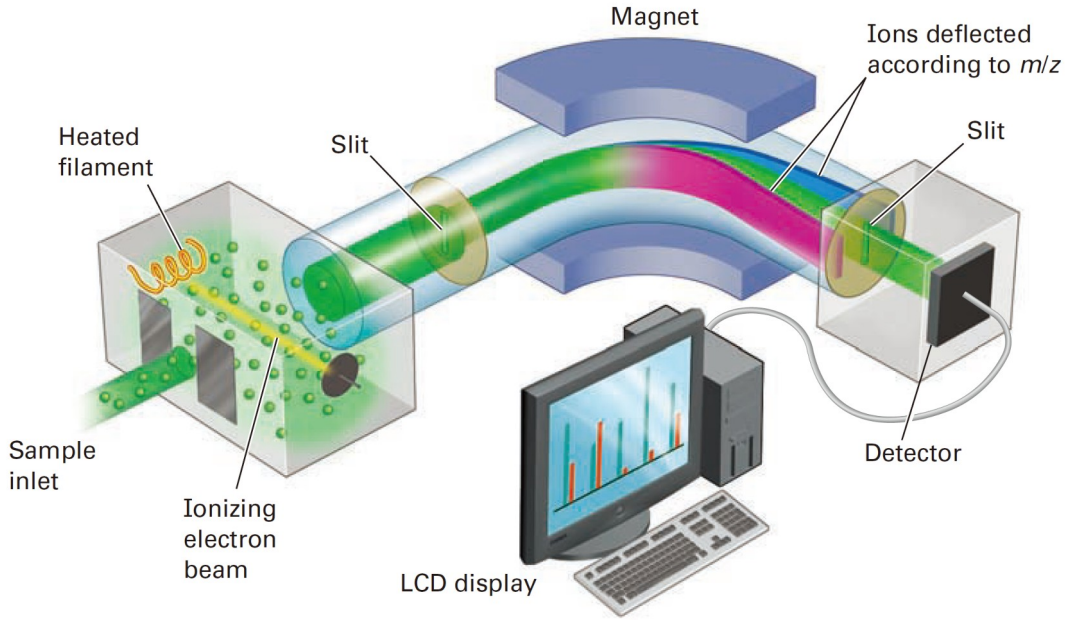


12
结构鉴定：质谱和红外

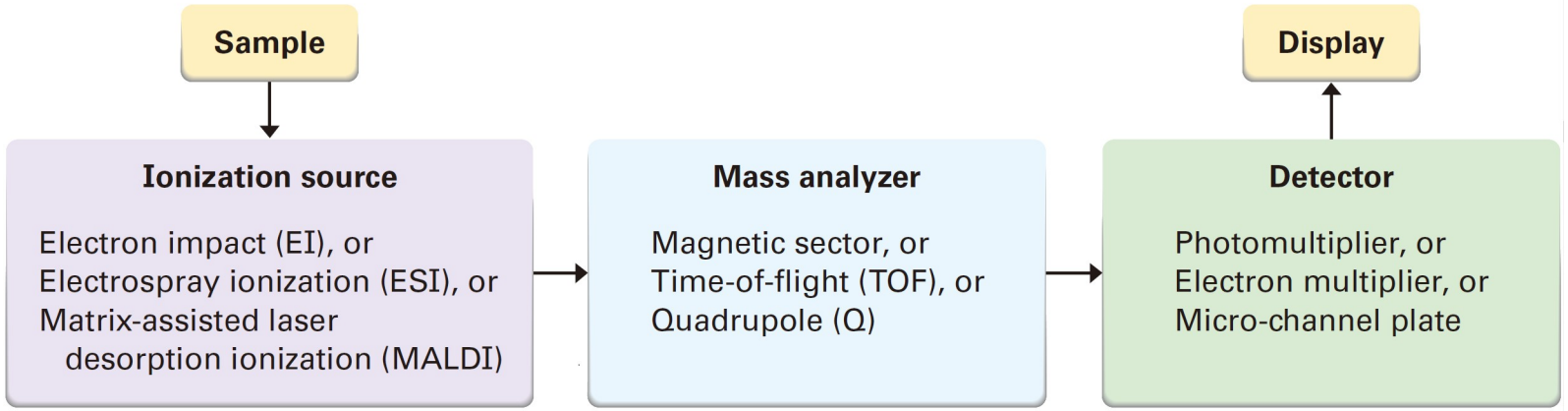
12.0 四大谱学

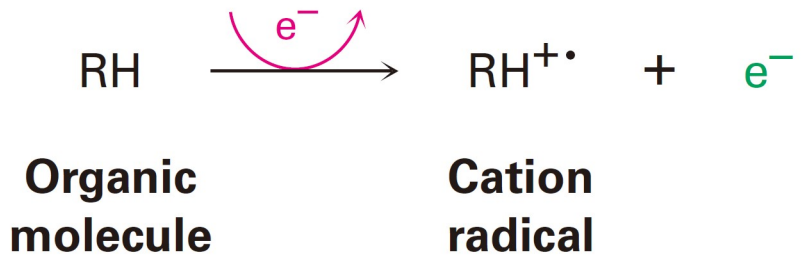
- 质谱，红外，紫外，核磁

Mass spectrometry	What is the size and formula?
Infrared spectroscopy	What functional groups are present?
Ultraviolet spectroscopy	Is a conjugated π electron system present?
Nuclear magnetic resonance spectroscopy	What is the carbon–hydrogen framework?

12.1 质谱仪

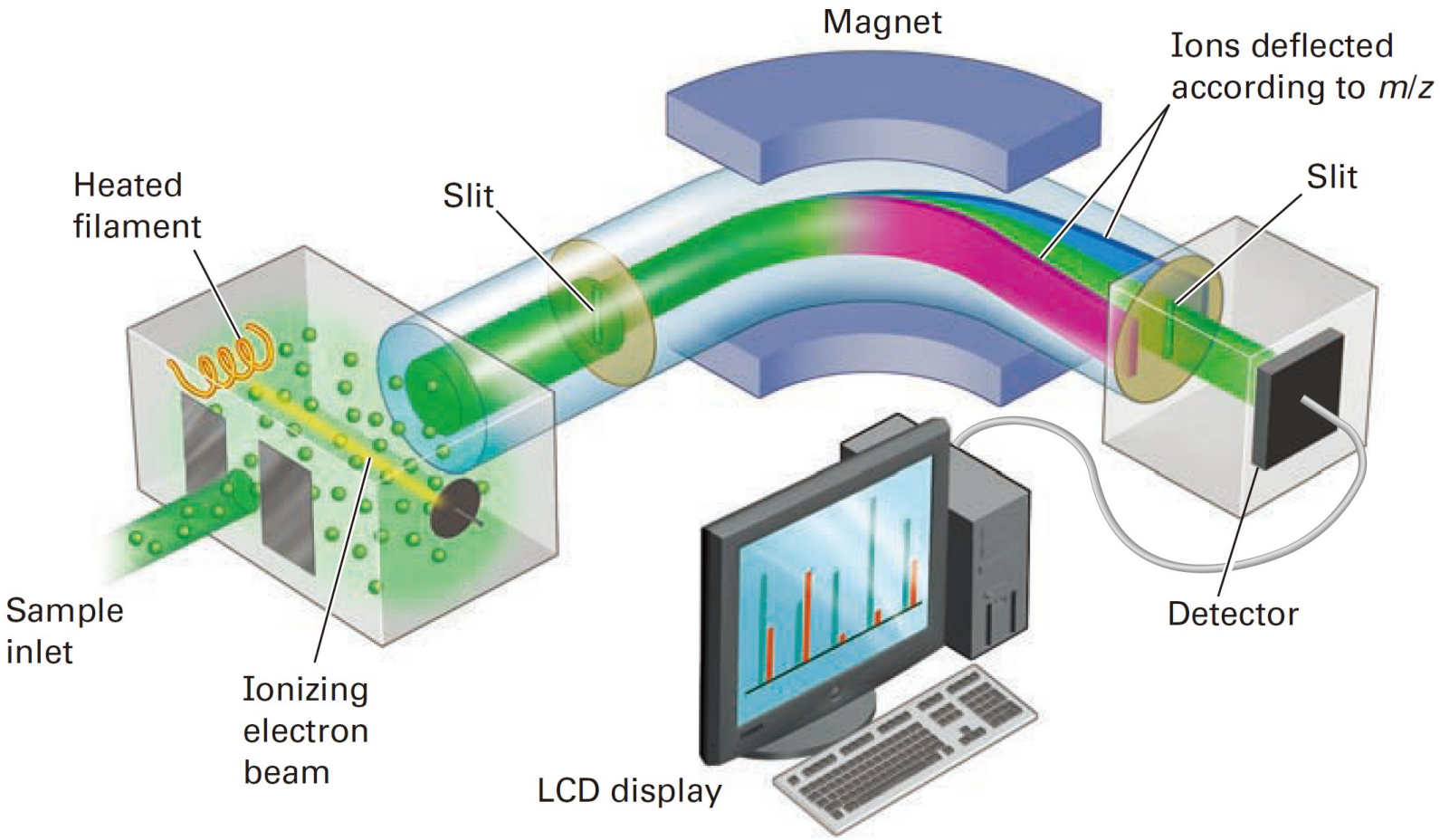
- 质谱（Mass Spectrometry ，缩写： MS）是一种电离化学物质并根据其质荷比（质量－电荷比）对其进行排序的分析技术。





12.1 质谱仪

- 工作原理


Magnet
Ions deflected according to m/z
Heated filament
Slit
Slit
Sample inlet
Ionizing electron beam
LCD display
Detector

12.2 质谱图

- 质谱图能告诉我们什么？分子离子峰、碎片峰、特征离子峰

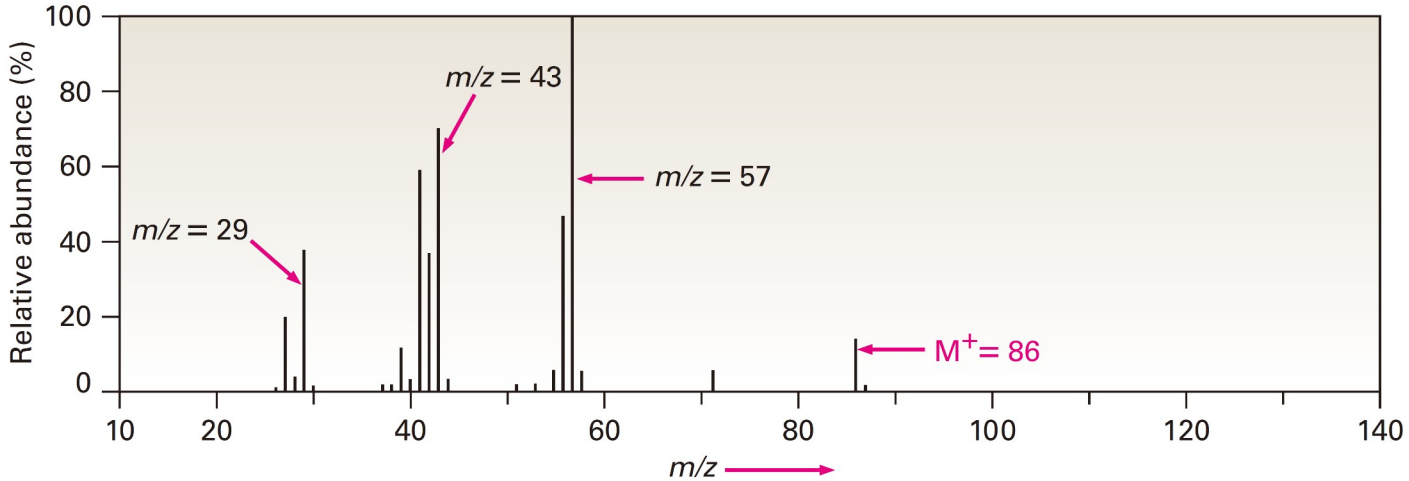


Figure 12.4 Mass spectrum of hexane (C_6H_{14}; MW = 86). The base peak is at $m/z = 57$, and numerous other ions are present.

$CH_3CH_2CH_2CH_2CH_2CH_3$

Hexane

e^-

$[CH_3CH_2CH_2CH_2CH_2CH_3]^{+\cdot}$

Molecular ion, M^+ ($m/z = 86$)

	$CH_3CH_2CH_2CH_2CH_2^+$	$CH_3CH_2CH_2CH_2^+$	$CH_3CH_2CH_2^+$	$CH_3CH_2^+$
m/z:	71	57	43	29
Relative abundance (%):	10	100 (base peak)	75	40

12.2 质谱图

- 有些化合物分子离子峰很弱，甚至看不见，这取决于化合物的结构

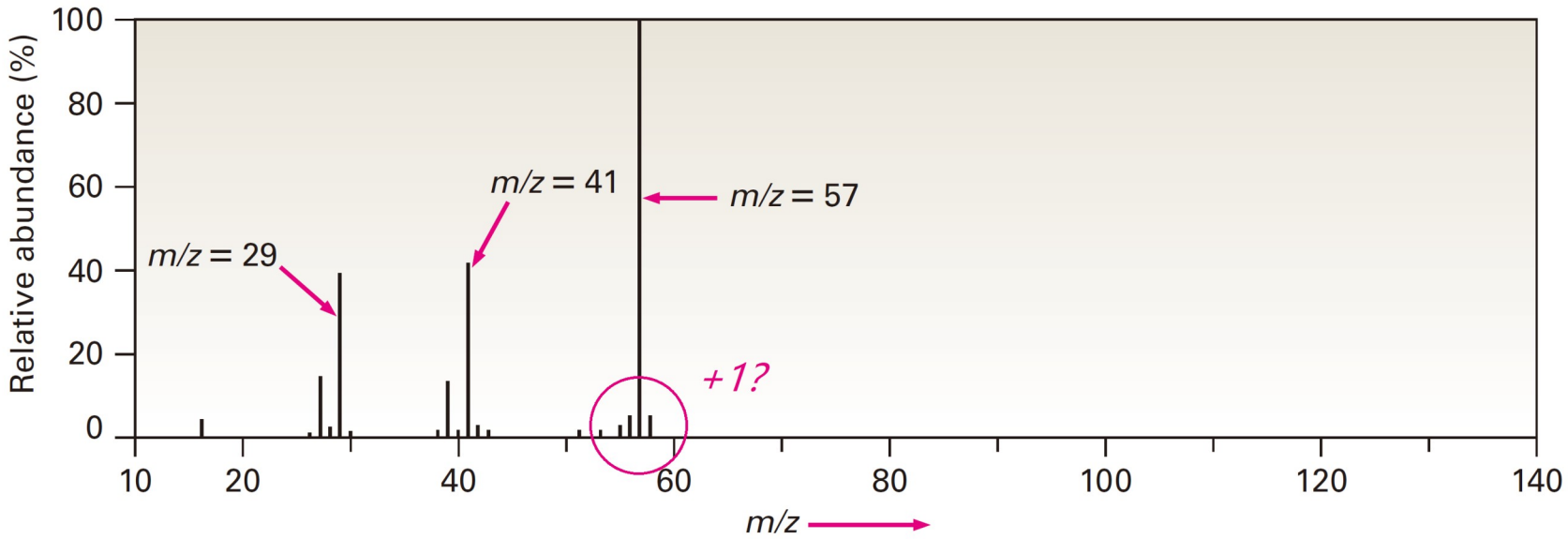
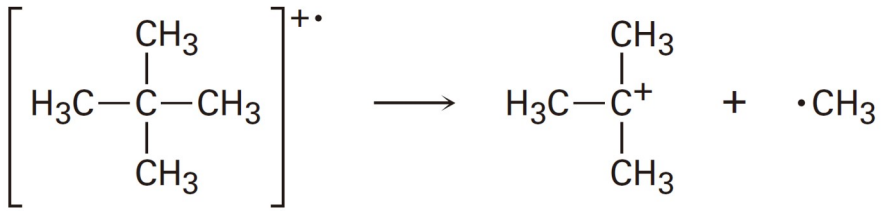


Figure 12.3 Mass spectrum of 2,2-dimethylpropane (C_5H_{12}; MW = 72). No molecular ion is observed when electron-impact ionization is used. What do you think is the formula and structure of the M^+ peak at $m/z = 57$?



$m/z = 57$

12.2 质谱图

- 实例

Using Mass Spectra to Identify Compounds

Worked Example 12.1

Assume that you have two unlabeled samples, one of methylcyclohexane and the other of ethylcyclopentane. How could you use mass spectrometry to tell them apart? The mass spectra of both are shown in **Figure 12.6**.

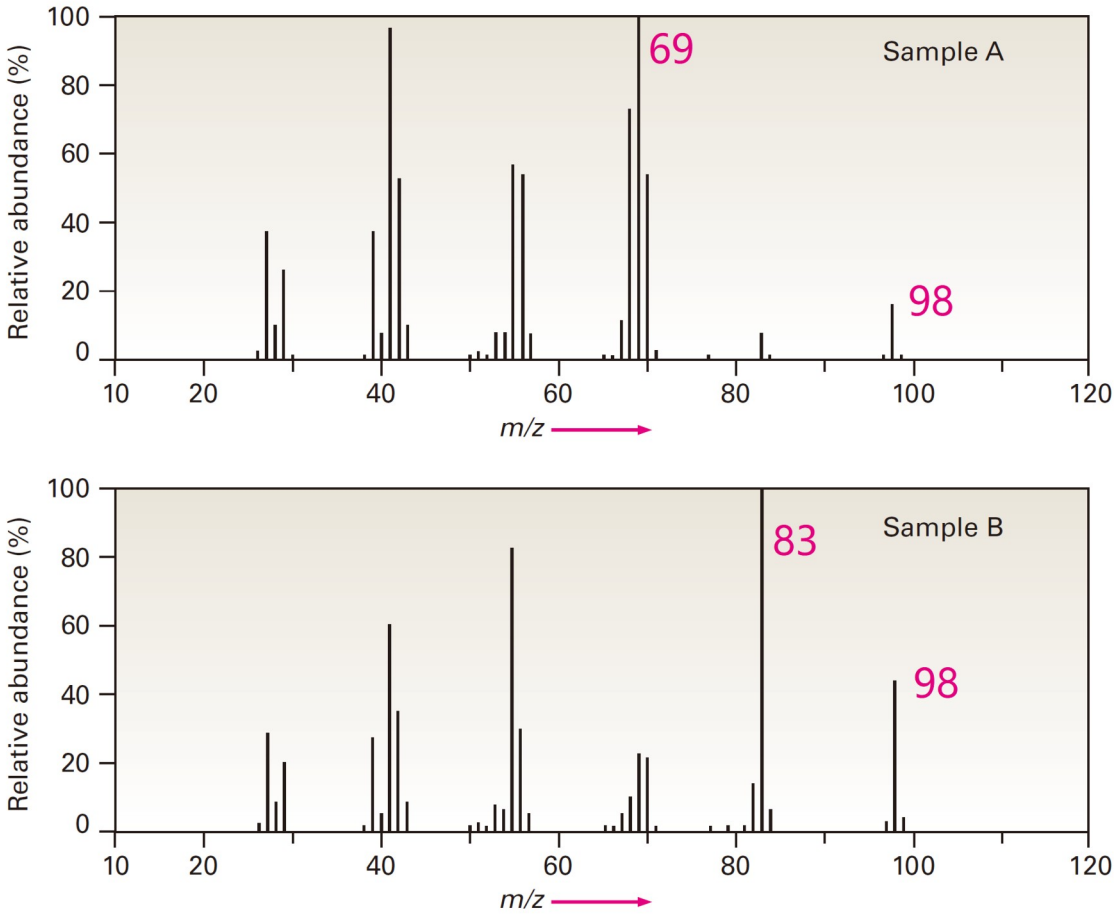
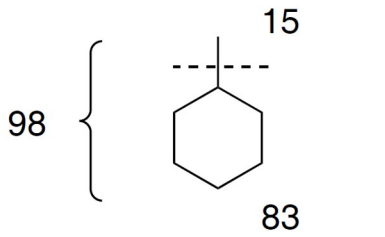
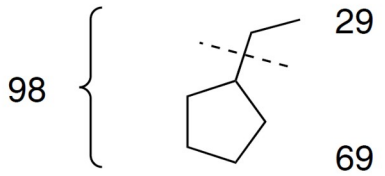


Figure 12.6 Mass spectra of unlabeled samples **A** and **B** for Worked Example 12.1.





12.2 质谱图

- 课堂练习

Problem 12.1

The male sex hormone testosterone contains only C, H, and O and has a mass of 288.2089 amu as determined by high-resolution mass spectrometry. What is the likely molecular formula of testosterone?

Problem 12.2

Two mass spectra are shown in **Figure 12.7**. One spectrum is that of 2-methyl-2-pentene; the other is of 2-hexene. Which is which? Explain.

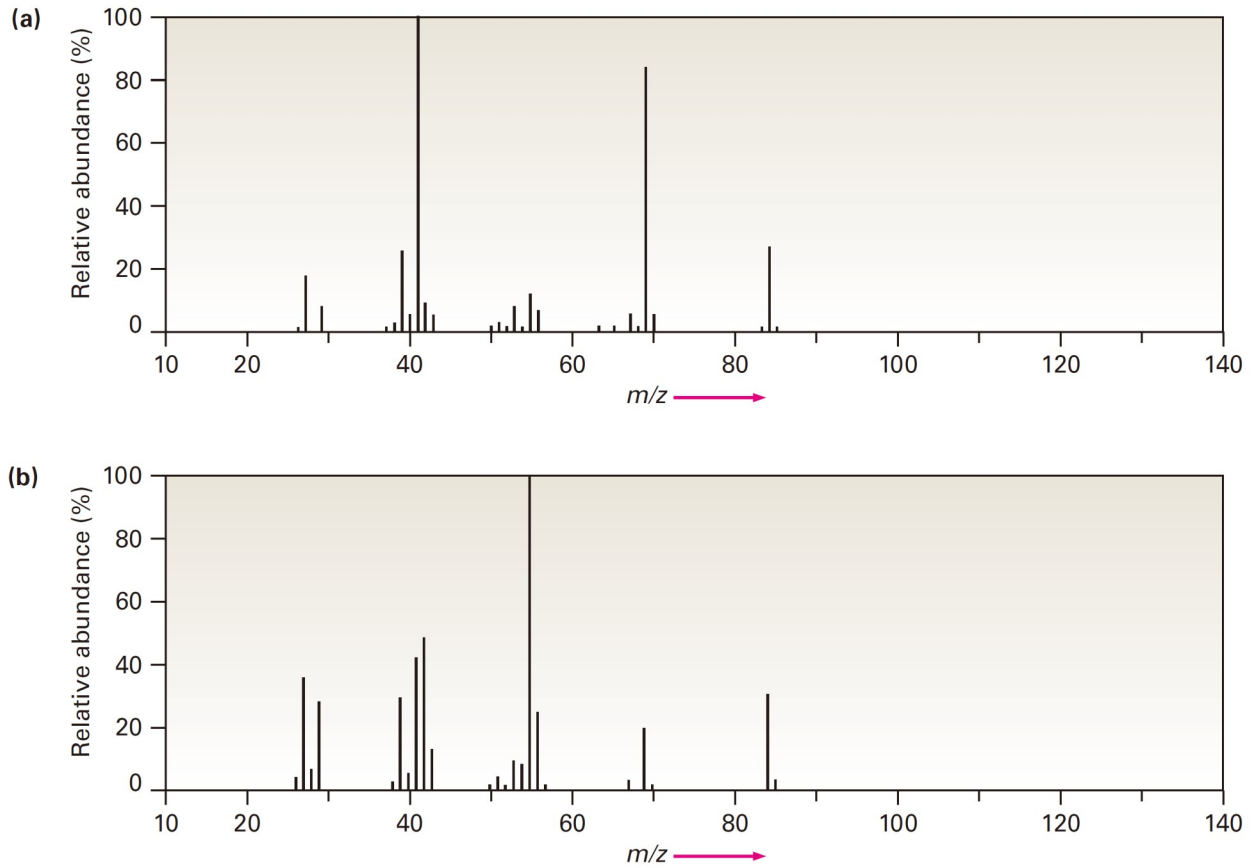
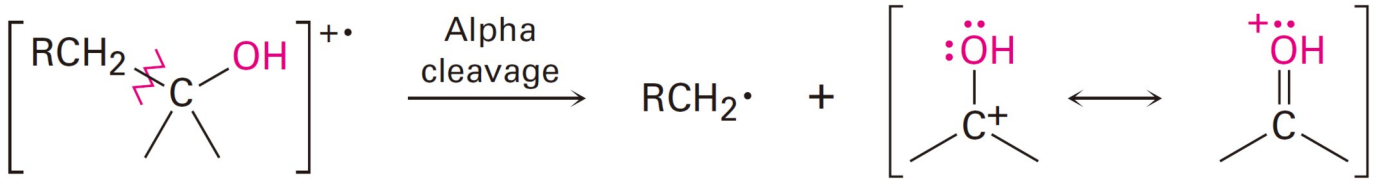


Figure 12.7 Mass spectra for Problem 12.2.

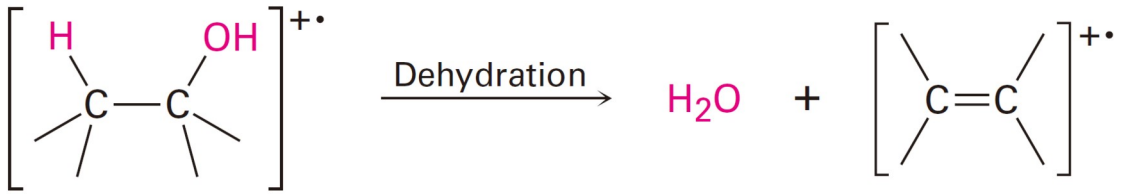
12.3 常见官能团的质谱

Alcohols

Alcohols undergo fragmentation in the mass spectrometer by two pathways: *alpha cleavage* and *dehydration*. In the α-cleavage pathway, a C–C bond nearest the hydroxyl group is broken, yielding a neutral radical plus a resonance-stabilized, oxygen-containing cation.



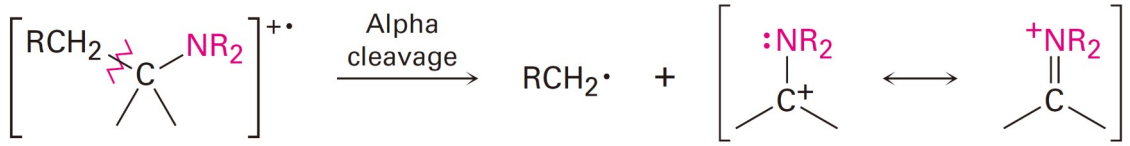
In the dehydration pathway, water is eliminated, yielding an alkene radical cation with a mass 18 units less than M^+.



12.3 常见官能团的质谱

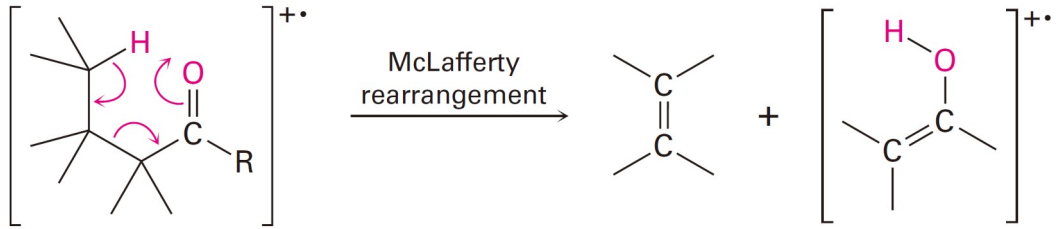
Amines

Aliphatic amines undergo a characteristic α cleavage in the mass spectrometer, similar to that observed for alcohols. A C–C bond nearest the nitrogen atom is broken, yielding an alkyl radical and a resonance-stabilized, nitrogen-containing cation.



Carbonyl Compounds

Ketones and aldehydes that have a hydrogen on a carbon three atoms away from the carbonyl group undergo a characteristic mass-spectral cleavage called the *McLafferty rearrangement*. The hydrogen atom is transferred to the carbonyl oxygen, a C–C bond is broken, and a neutral alkene fragment is produced. The charge remains with the oxygen-containing fragment.



12.4 生物大分子的质谱方法

- **电喷雾电离** electrospray ionization (ESI) **和基质辅助激光电离** matrix-assisted laser desorption ionization (MALDI)

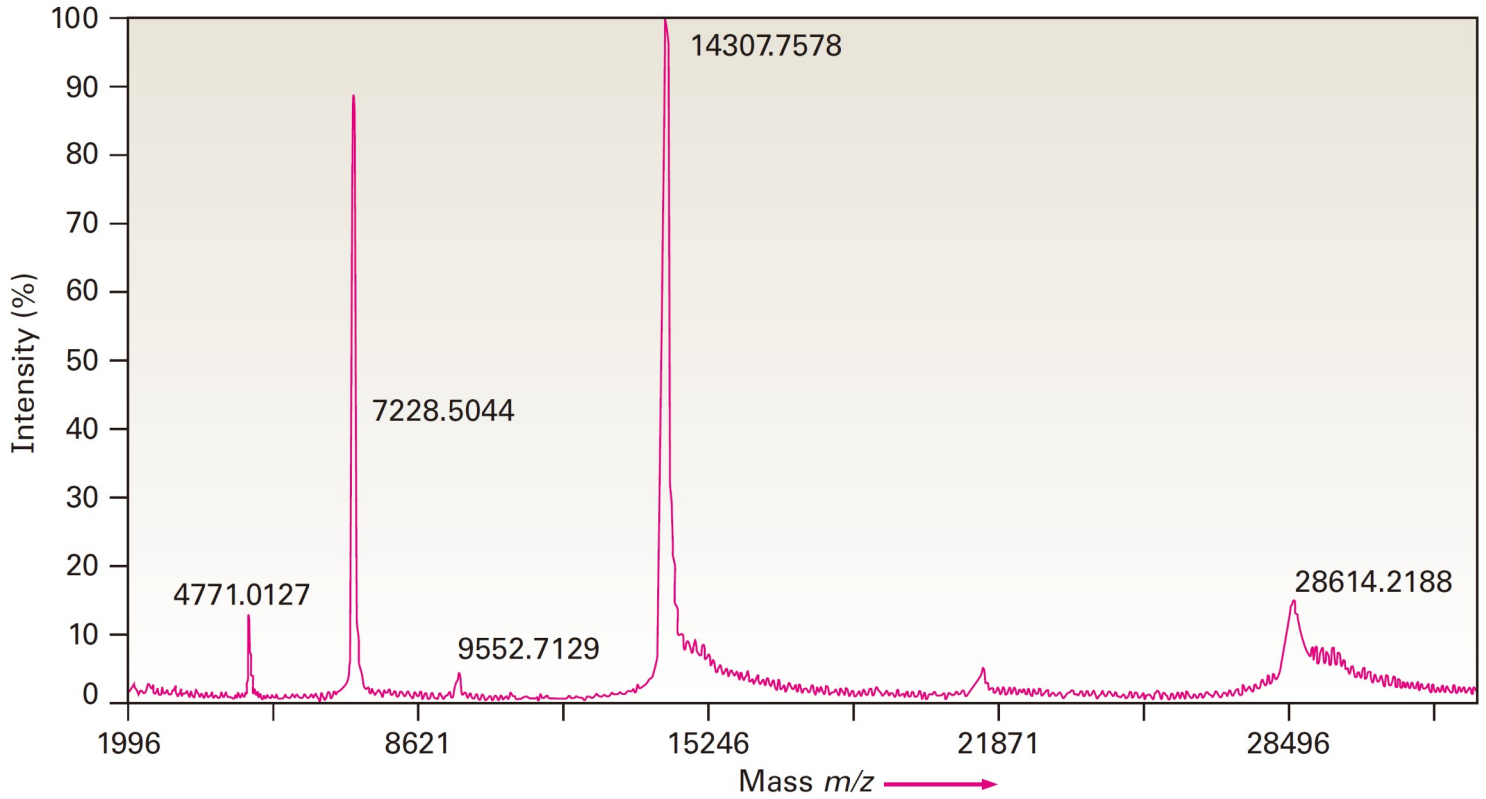


Figure 12.9 MALDI–TOF mass spectrum of chicken egg-white lysozyme. The peak at 14,307.7578 daltons (amu) is due to the monoprotonated protein, $M+H^+$, and the peak at 28,614.2188 daltons is due to an impurity formed by dimerization of the protein. Other peaks are various protonated species, $M+H_n^{n+}$.

12.4 生物大分子的质谱方法

- 田中耕一：一位本科学历的诺奖获得者

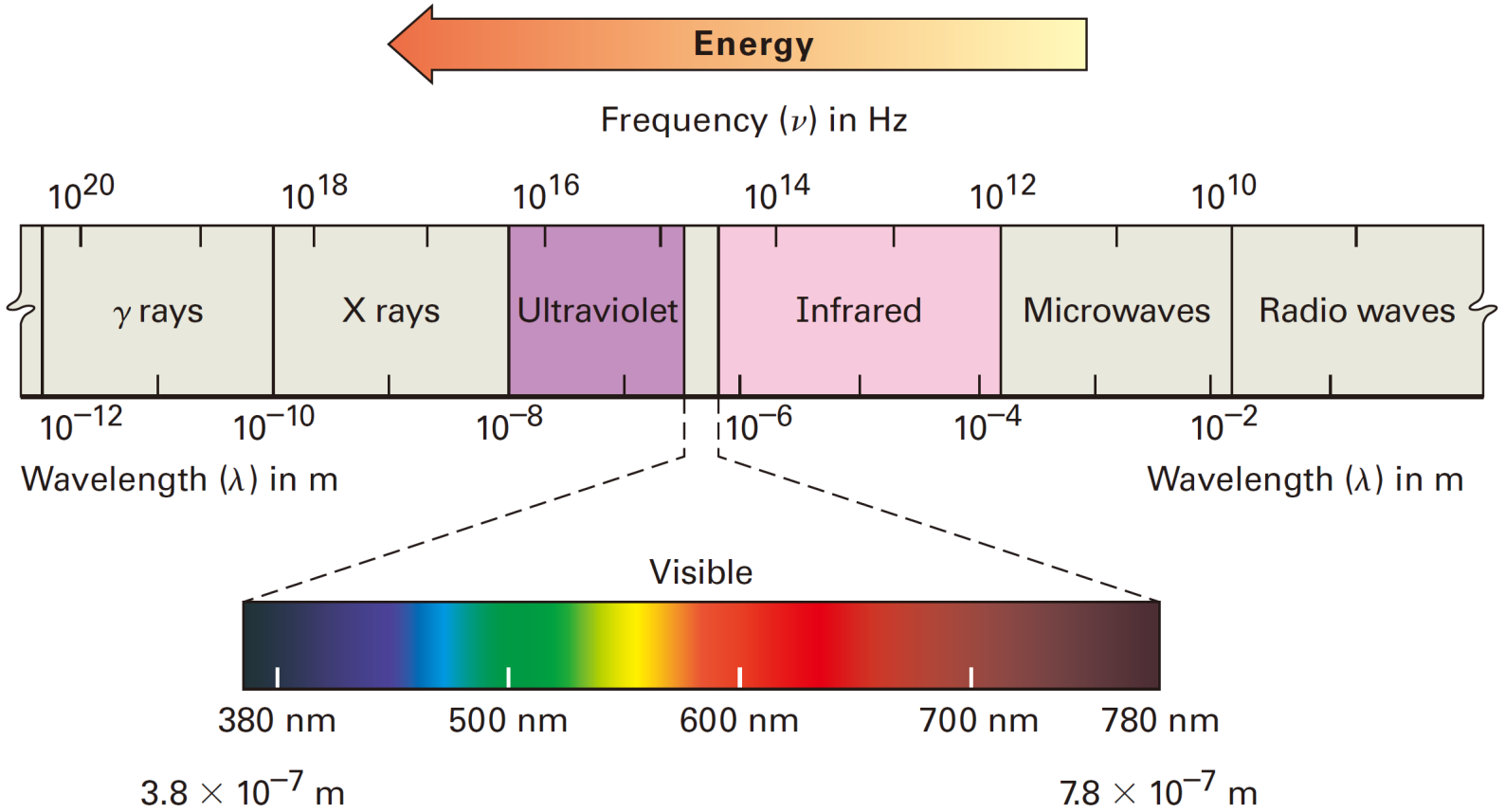


✓ 母校东北大学破例授予他博士学位。田中是这样表达感谢的：**现在我有博士学位了，以后坐飞机就可以免费换到商务舱了。**

✓ 延伸阅读：https://www.zhihu.com/question/24884218

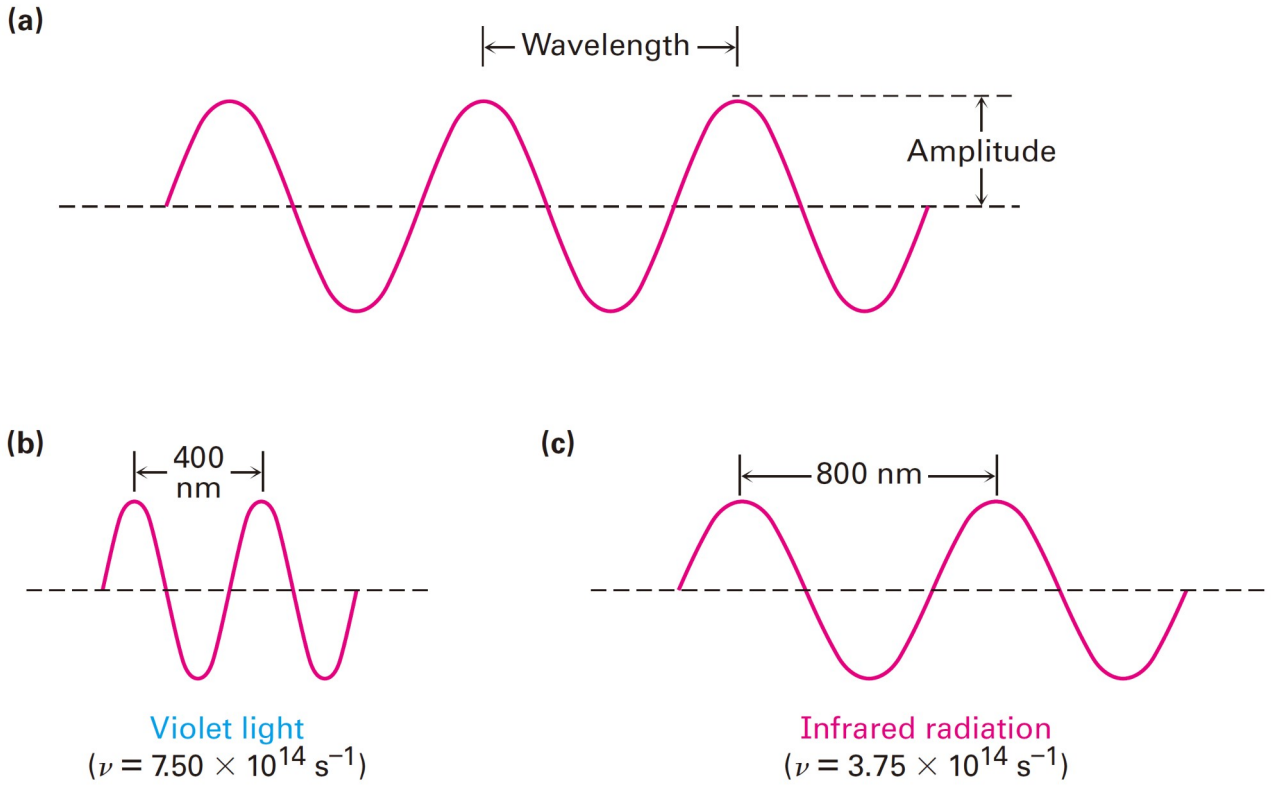
12.5 光谱分析

- 红外，紫外以及核磁与质谱不同，他们是基于分子与电磁波的相互作用机制从而解析结构的。
- 可见光，X 射线，微波，无线电波等都是电磁波，它们频率不同。



12.5 光谱分析

- 电磁波的参数和性质



$$\text{Wavelength} \times \text{Frequency} = \text{Speed}$$

$$\lambda\ (\text{m}) \times \nu\ (\text{s}^{-1}) = c\ (\text{m/s})$$

$$\lambda = \frac{c}{\nu} \quad \text{or} \quad \nu = \frac{c}{\lambda}$$

$$\varepsilon = h\nu = \frac{hc}{\lambda}$$

where h = Planck's constant

$$(6.62 \times 10^{-34}\ \text{J} \cdot \text{s} = 1.58 \times 10^{-34}\ \text{cal} \cdot \text{s})$$

12.6 红外光谱

- 分子的振动能级正好落在红外光谱范围，因此可以通过分子的红外光谱吸收确定分子内一些典型结构单元。

$$\text{Wavenumber:} \quad \tilde{\nu}\,(\text{cm}^{-1}) = \frac{1}{\lambda\ (\text{cm})}$$

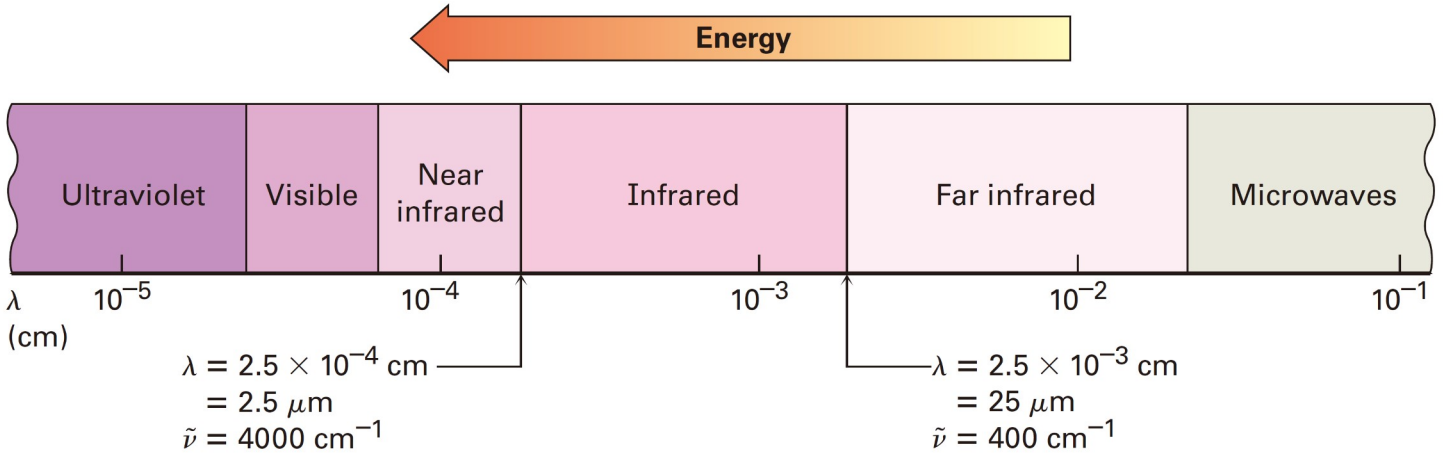
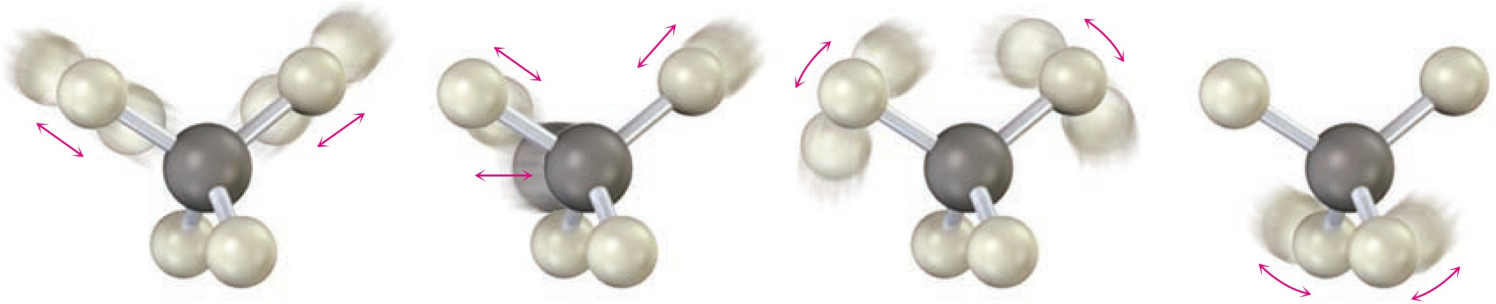
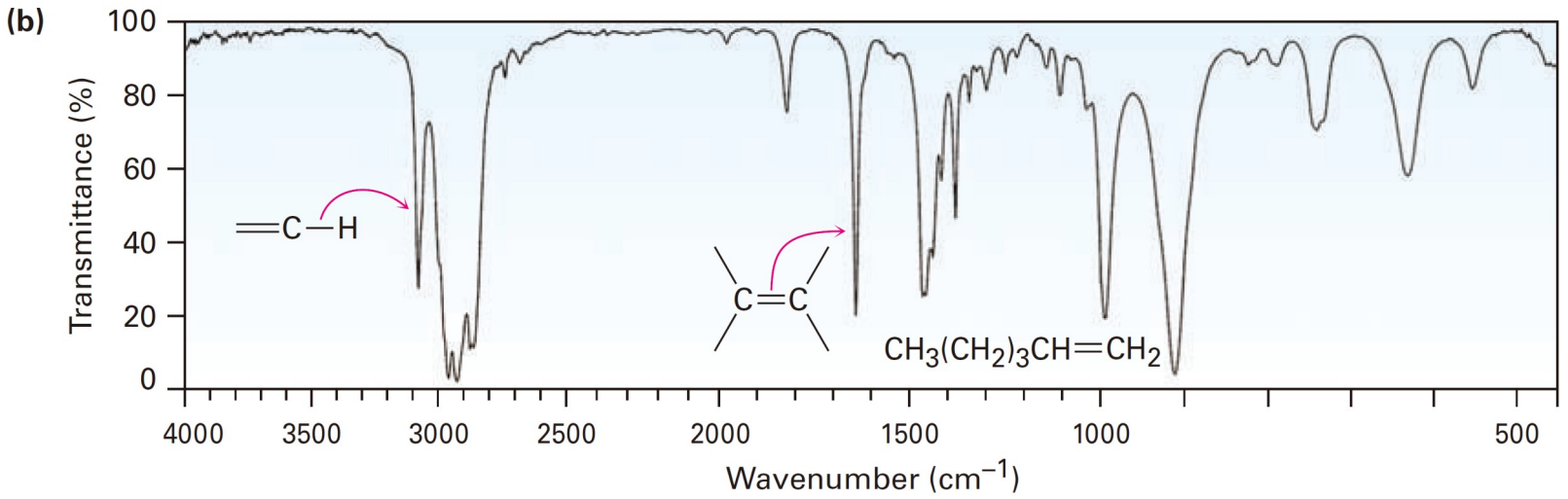


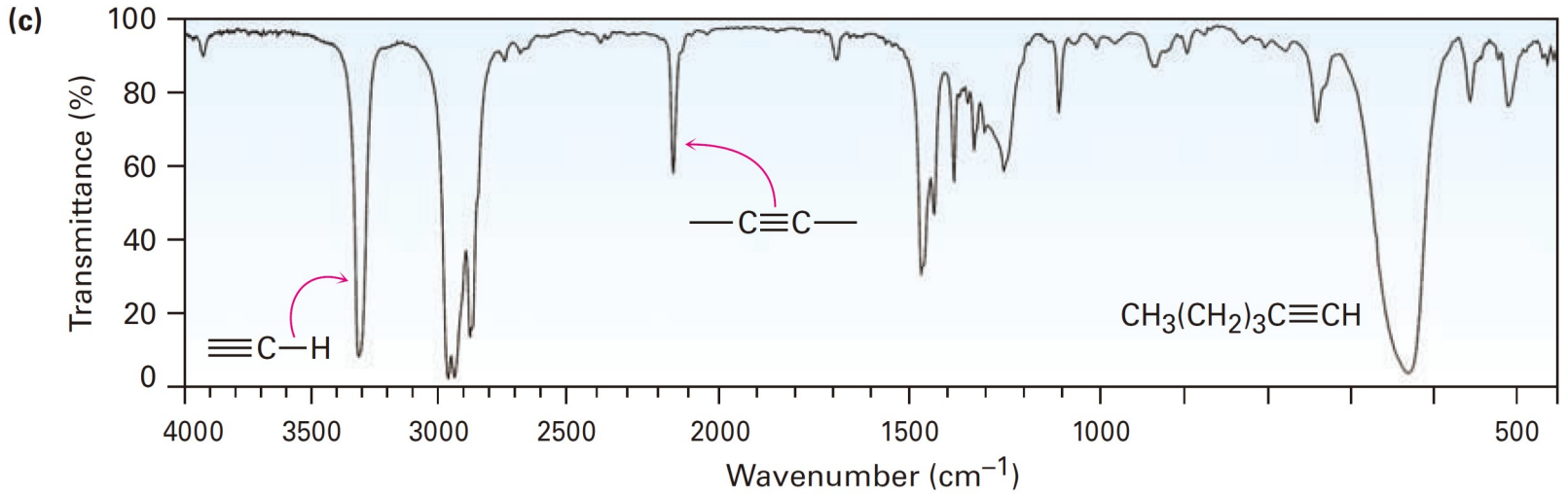
Figure 12.13 The infrared and adjacent regions of the electromagnetic spectrum.



Symmetric stretching | **Antisymmetric stretching** | **In-plane bending** | **Out-of-plane bending**

12.7 红外光谱图


(b)
100
80
60
40
20
0
Transmittance (%)
=C—H
C=C
CH3(CH2)3CH=CH2
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm−1)


(c)
100
80
60
40
20
0
Transmittance (%)
≡C—H
—C≡C—
CH3(CH2)3C≡CH
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm−1)

12.8 常见官能团的红外吸收

Table 12.1 Characteristic IR Absorptions of Some Functional Groups

Functional Group	Absorption (cm^{-1})	Intensity
Alkane		
C–H	2850–2960	Medium
Alkene		
=C–H	3020–3100	Medium
C=C	1640–1680	Medium
Alkyne		
≡C–H	3300	Strong
C≡C	2100–2260	Medium
Alkyl halide		
C–Cl	600–800	Strong
C–Br	500–600	Strong
Alcohol		
O–H	3400–3650	Strong, broad
C–O	1050–1150	Strong
Arene		
C–H	3030	Weak
Aromatic ring	1660–2000	Weak
	1450–1600	Medium
Amine		
N–H	3300–3500	Medium
C–N	1030–1230	Medium
Carbonyl compound		
C=O	1670–1780	Strong
Aldehyde	1730	Strong
Ketone	1715	Strong
Ester	1735	Strong
Amide	1690	Strong
Carboxylic acid	1710	Strong
Carboxylic acid		
O–H	2500–3100	Strong, broad
Nitrile		
C≡N	2210–2260	Medium
Nitro		
NO_2	1540	Strong