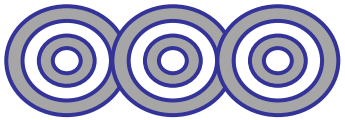
Instrumental Methods of Analysis



Molecular Spectroscopy

Ahmad Aqel Ifseisi
Professor of Analytical Chemistry
College of Science, Department of Chemistry
King Saud University
P.O. Box 2455 Riyadh 11451 Saudi Arabia
Building: 05, Office: 2A/149 & AA/53
Tel. 014674198, Fax: 014675992
Web site: http://fac.ksu.edu.sa/aifseisi
E-mail: aifseisi@ksu.edu.sa
ahmad3qel@gmail.com

AMRC كرسي أبحاث المواد المتقدمة Advanced Materials Research Chair

جامعة الملك سعود King Saud University

Ultraviolet-Visible and Infrared Spectrophotometry

Is the study of the **electromagnetic radiation** absorbed and emitted by **molecules**.

The combination of atoms into molecules leads to the creation of unique types of energetic states and therefore unique spectra of the transitions between these states.

- **Molecular rotations**

(e.g., Rotational and Microwave spectroscopy).

- **Molecular vibration**

(e.g., Infrared and Raman spectroscopy).

- **Electronic states**

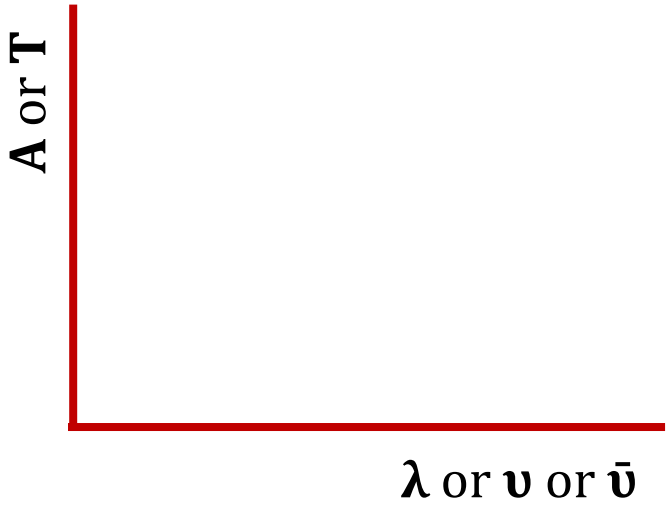
(e.g., Visible, Ultraviolet, and Fluorescence spectroscopy).

Absorption Spectra

An **absorption spectrum** is a plot of absorbance versus wavelength.

Absorbance could also be plotted against wavenumber or frequency.

Older instruments sometimes displayed transmittance and produced plots of T or %T versus wavelength.



One plot of absorbance versus wavelength is called a **spectrum**; two or more plots are called **spectra**.

The absorption spectra vary widely in appearance; some are made up of numerous sharp peaks, whereas others consist of smooth continuous curves.

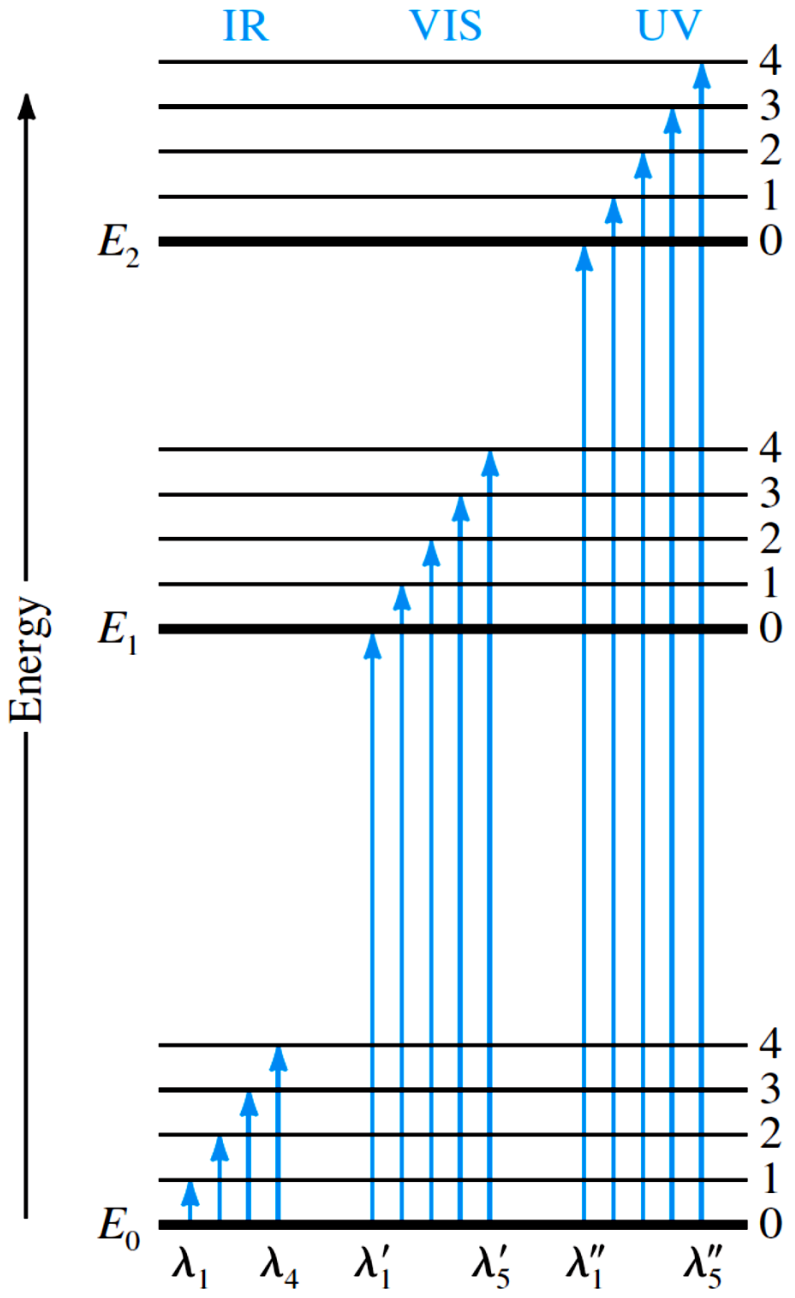
The nature of a spectrum is influenced by such variables as

- The **complexity**,
- The **physical state**,
- The **environment** of the absorbing species.

More fundamental, however, are the differences between absorption spectra for **atoms** and those for **molecules**.

Energy level diagram showing some of the energy changes that occur during absorption of infrared (**IR**), visible (**VIS**), and ultraviolet (**UV**) radiation by a molecular species. Note that with some molecules a transition from E_0 to E_1 may require UV radiation instead of visible radiation. With other molecules, the transition from E_0 to E_2 may occur with visible radiation instead of UV radiation. Only a few vibrational levels (0–4) are shown. The rotational levels associated with each vibrational level are also exist (not shown in this figure), they are too closely spaced.

UV range 10 – 400 nm
Vis range 380 – 750 nm
IR range 700 nm – 1 mm

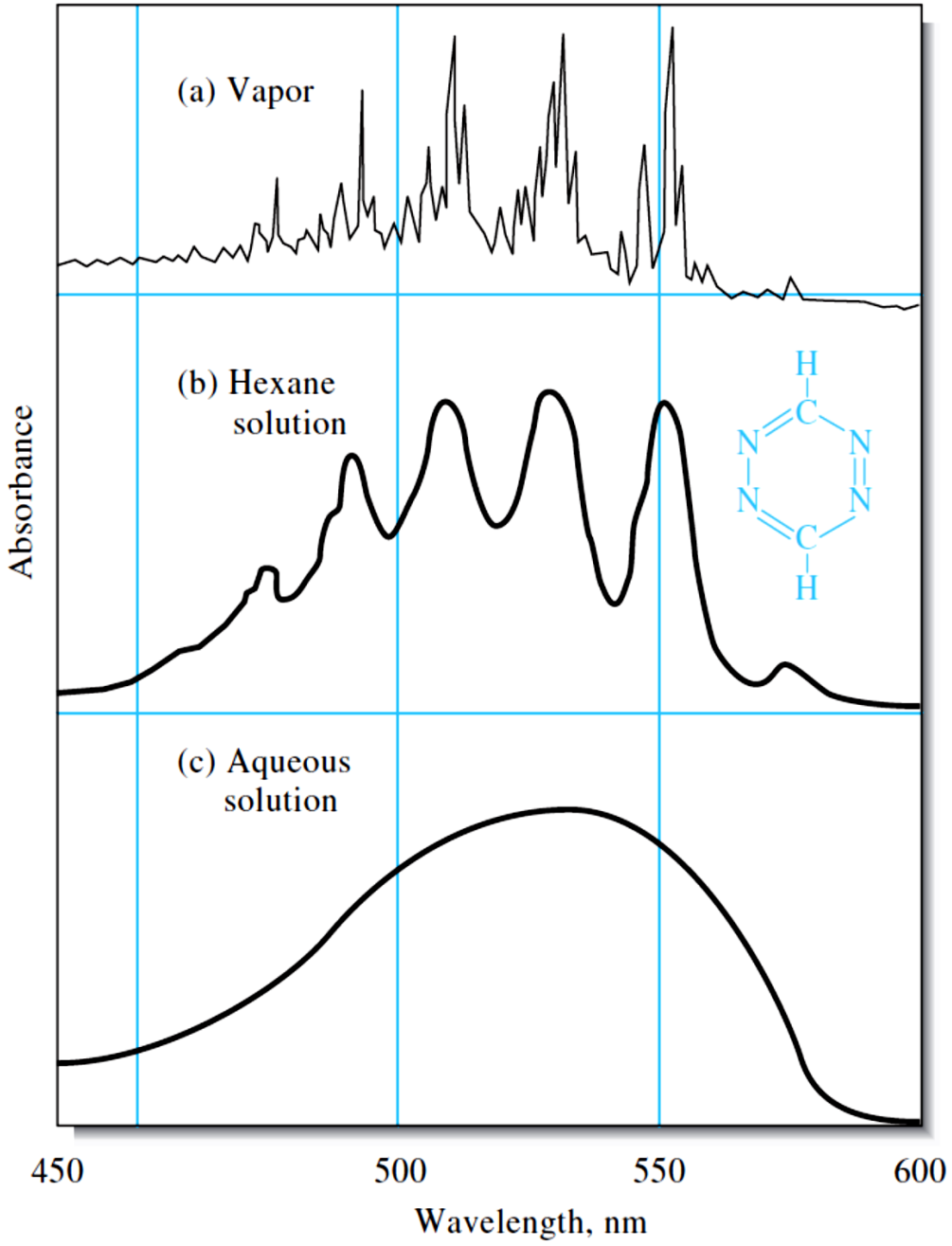


Typical **visible** absorption spectra. The compound is 1,2,4,5-tetrazine.

In (a), the spectrum is shown in the gas phase where many lines due to electronic, vibrational, and rotational transitions are seen.

In a nonpolar solvent (b), the electronic transitions can be observed, but the vibrational and rotational structure has been lost.

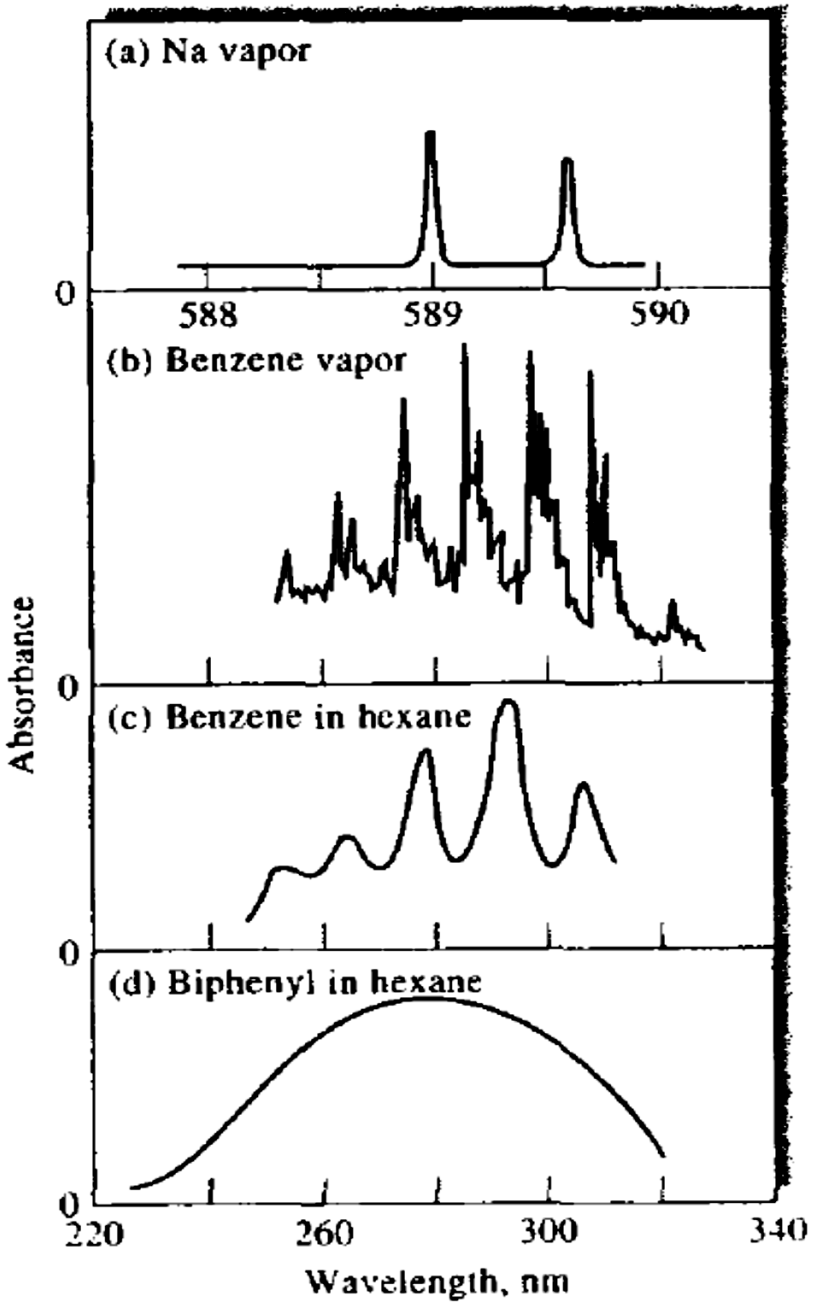
In a polar solvent (c), the strong intermolecular forces have caused the electronic peaks to blend together to give only a single smooth absorption peak.



The Figure suggests that molecular absorption in the ultraviolet and visible regions produces **absorption bands** made up of closely spaced lines.

A real molecule has many more energy levels than can be shown in the diagram. Thus, a typical absorption band consists of a large number of lines.

In a solution, the absorbing species are surrounded by solvent molecules, and the band nature of molecular absorption often becomes blurred because collisions tend to spread the energies of the quantum states, giving smooth and continuous absorption peaks.

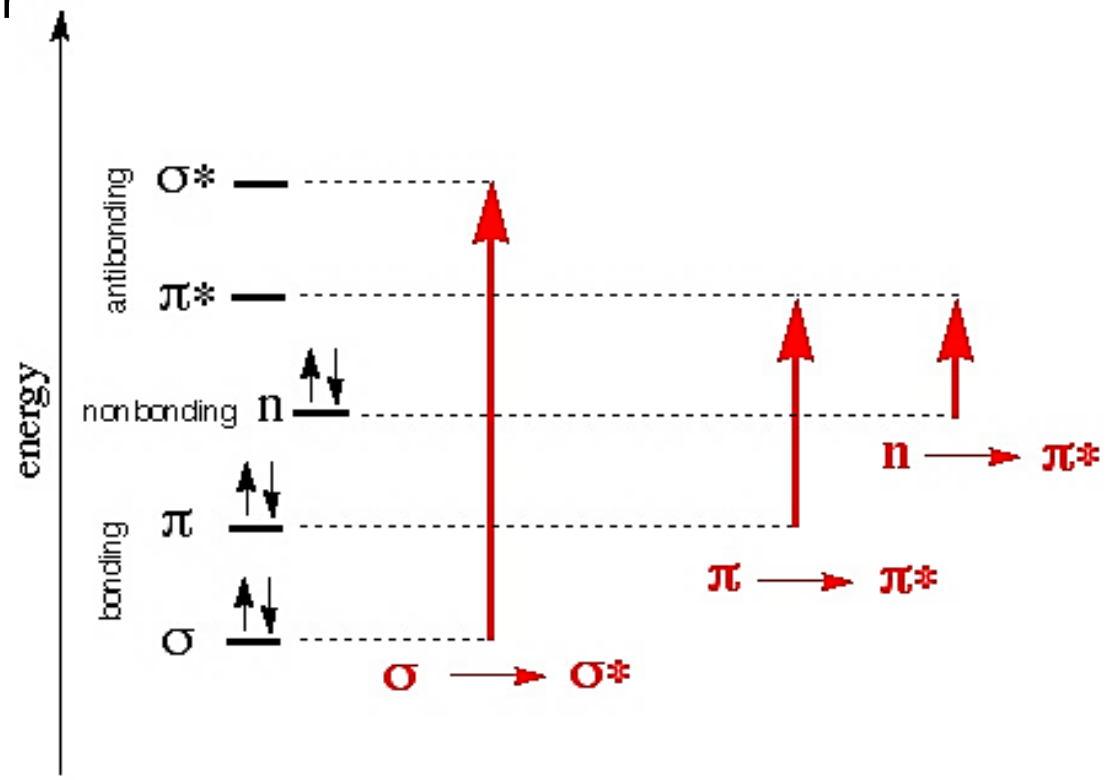


Some typical **ultraviolet** absorption spectra

UV/Vis Spectra for Molecules and Ions

The valence electrons in organic molecules, and inorganic anions such as CO_3^{2-}, occupy quantized sigma bonding, *σ*, *pi* bonding, *π*, and nonbonding, *n,* molecular orbitals.

Unoccupied sigma antibonding, *σ**, and pi antibonding, *π**, molecular orbitals often lie close enough in energy that the transition of an electron from an occupied to an unoccupied orbital is possible.



When a molecule or ion absorbs ultraviolet or visible radiation it undergoes a change in its **valence electron configuration**.

Four types of transitions between quantized energy levels account for molecular UV/Vis spectra.

Electronic transitions involving *n*, *σ*, and *π* molecular orbitals

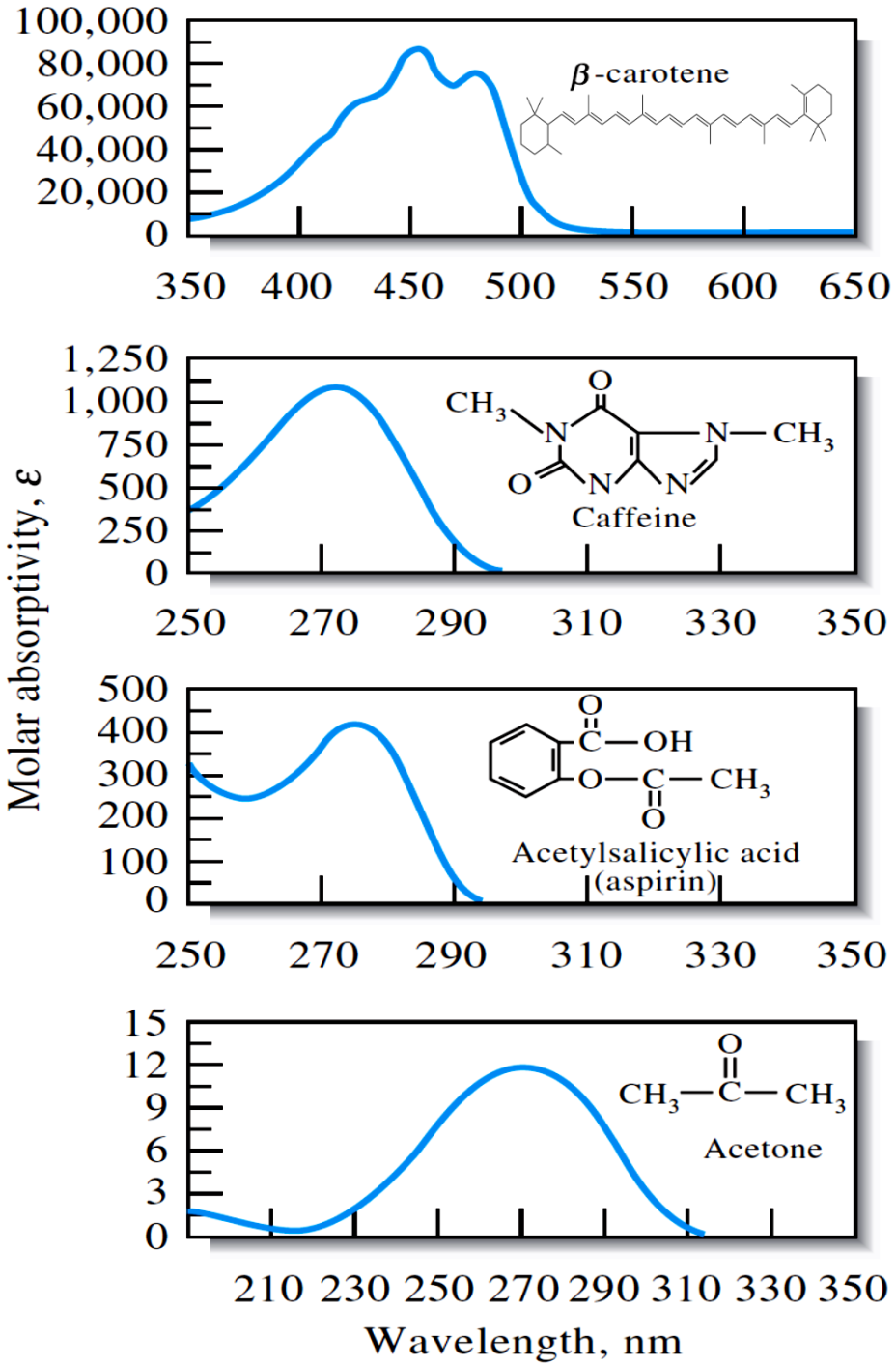
Transition	Wavelength Range (nm)	Examples
$\sigma \rightarrow \sigma^*$	< 200	C—C, C—H
$n \rightarrow \sigma^*$	160–260	H_2O, CH_3OH, CH_3Cl
$\pi \rightarrow \pi^*$	200–500	C=C, C=O, C=N, C≡C
$n \rightarrow \pi^*$	250–600	C=O, C=N, N=N, N=O

Of these transitions, the most important are the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$, because they involve functional groups that are characteristic of the analyte and wavelengths that are easily accessible. The bonds or functional groups in a molecule responsible for the absorption of a particular wavelength of light in ultraviolet and visible radiation are called **chromophores.**

Absorption Characteristics of Some Common Organic Chromophores

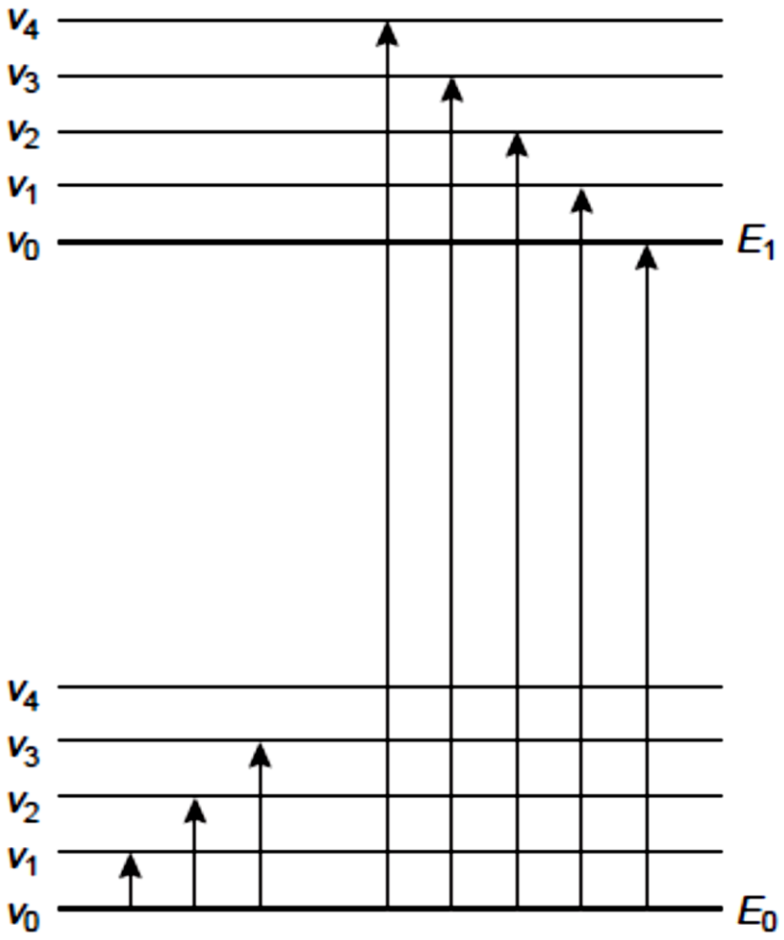
Chromophore	Example	Solvent	λ_{max}, nm	ε_{max}
Alkene	$C_6H_{13}CH{=}CH_2$	*n*-Heptane	177	13,000
Conjugated alkene	$CH_2{=}CHCH{=}CH_2$	*n*-Heptane	217	21,000
Alkyne	$C_5H_{11}C{\equiv}C{-}CH_3$	*n*-Heptane	178	10,000
			196	2,000
			225	160
Carbonyl	$CH_3\overset{\overset{O}{\|}}{C}CH_3$	*n*-Hexane	186	1,000
			280	16
	$CH_3\overset{\overset{O}{\|}}{C}H$	*n*-Hexane	180	Large
			293	12
Carboxyl	$CH_3\overset{\overset{O}{\|}}{C}OH$	Ethanol	204	41
Amido	$CH_3\overset{\overset{O}{\|}}{C}NH_2$	Water	214	60
Azo	$CH_3N{=}NCH_3$	Ethanol	339	5
Nitro	CH_3NO_2	Isooctane	280	22
Nitroso	C_4H_9NO	Ethyl ether	300	100
			665	20
Nitrate	$C_2H_5ONO_2$	Dioxane	270	12
Aromatic	Benzene	*n*-Hexane	204	7,900
			256	200

UV/Vis absorption bands are often significantly broader than those for IR absorption. When a species absorbs UV/Vis radiation, the transition between electronic energy levels may also include a transition between vibrational energy levels. The result is a number of closely spaced absorption bands that merge together to form a **single broad** absorption band.



Infrared Spectra for Molecules and Polyatomic Ions

Infrared radiation generally is not energetic enough to cause electronic transitions, but it can induce transitions in the vibrational and rotational states associated with the ground electronic state of the molecule.

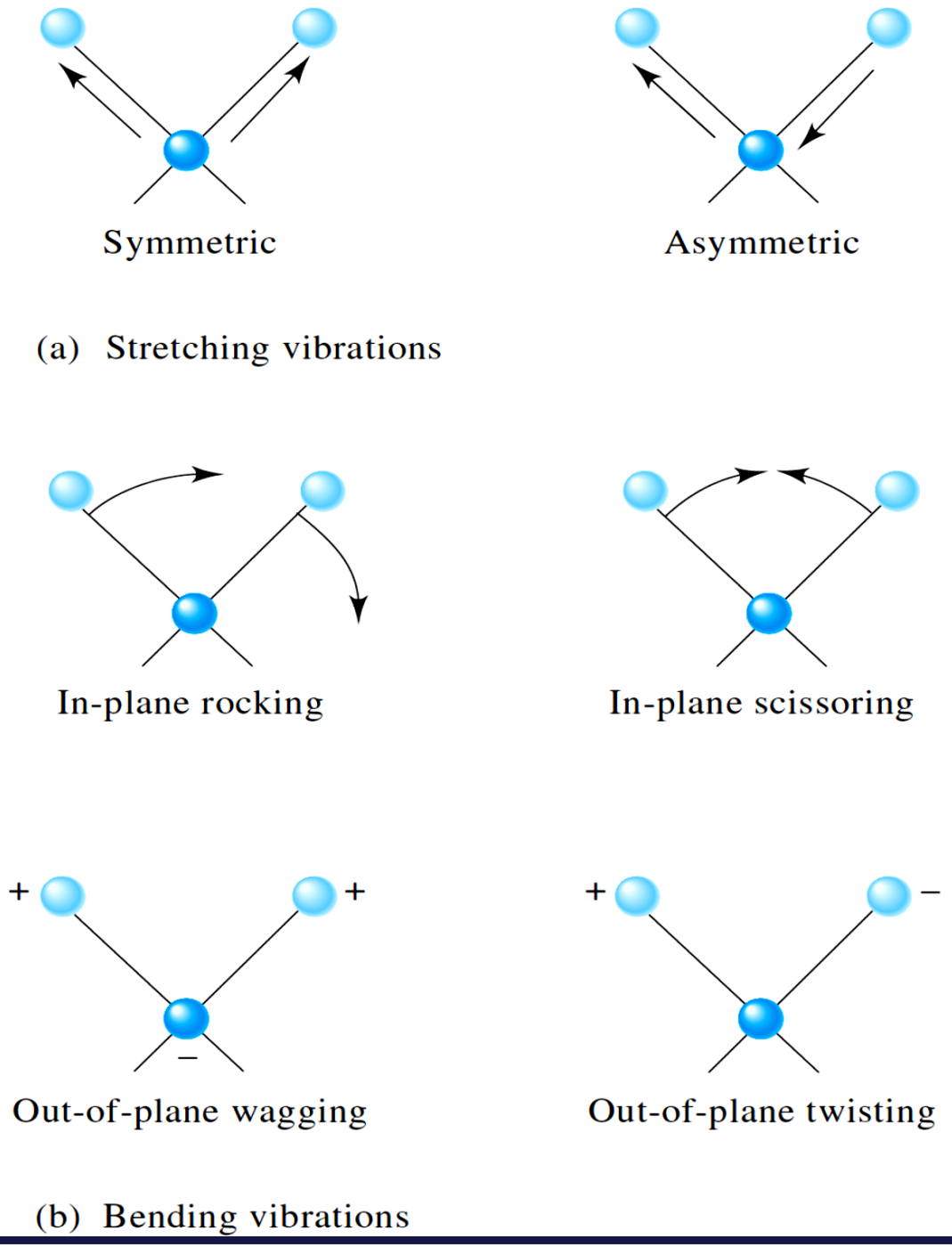


Energy level diagram showing difference between the absorption of infrared radiation (*left*) and ultraviolet–visible radiation (*right*).

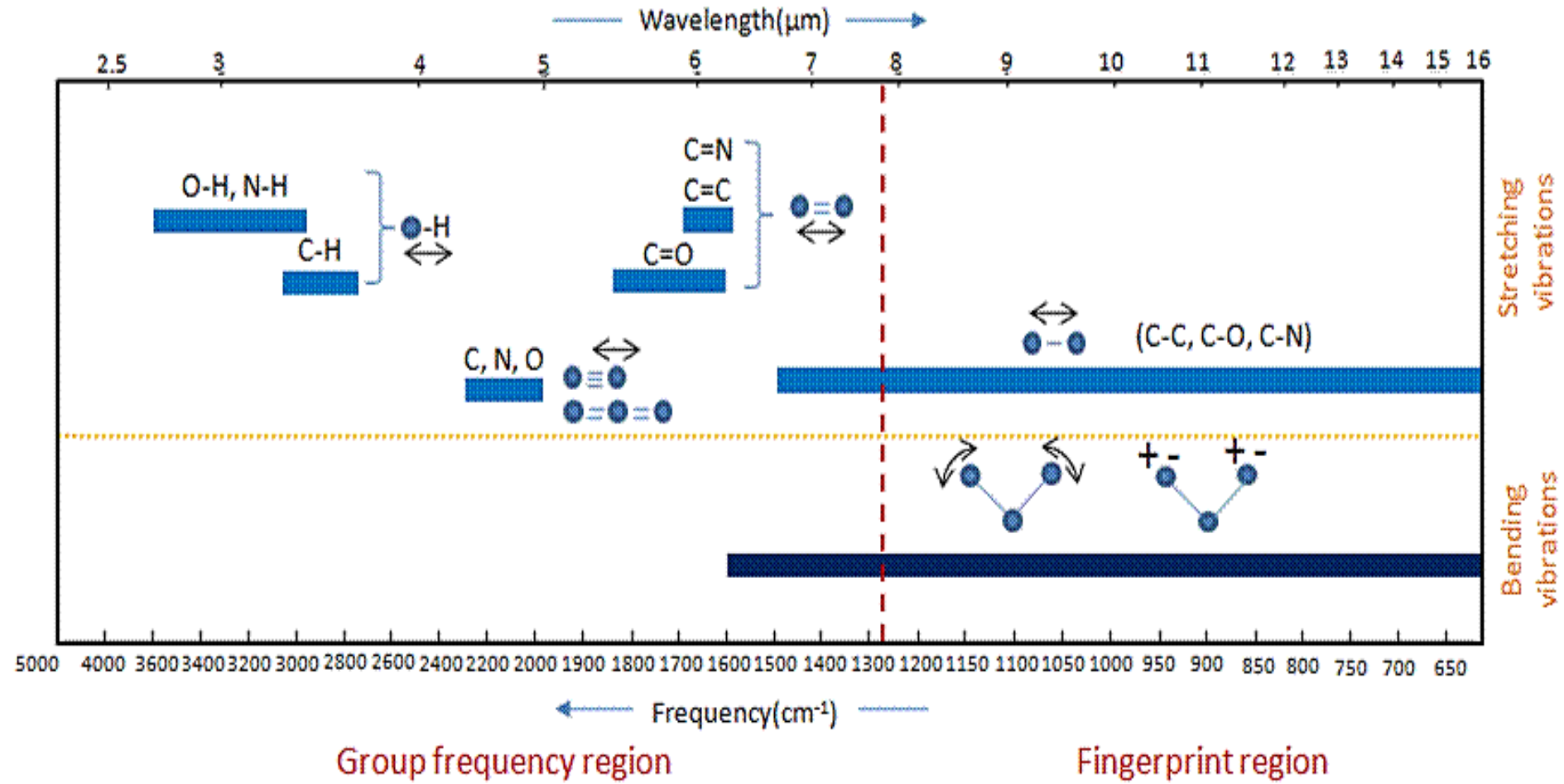
For absorption to occur, the radiation source has to emit frequencies corresponding exactly to the energies indicated by the lengths of the arrows (shown in the figures).

Vibrational energy levels are quantized; that is, a molecule may have only certain, discrete vibrational energies.

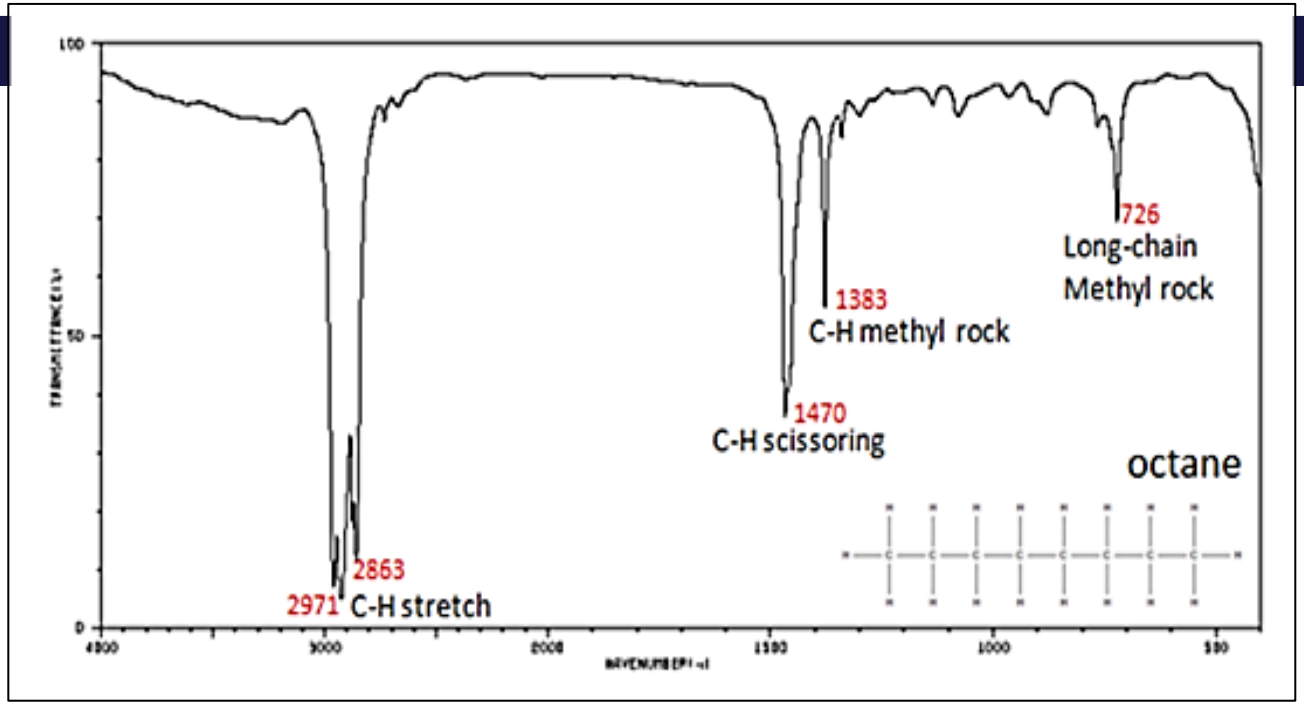
e.g., a carbon–carbon single bond (C—C) absorbs infrared radiation at a lower energy than a carbon–carbon double bond (C=C) because a C—C bond is weaker than a C=C bond.

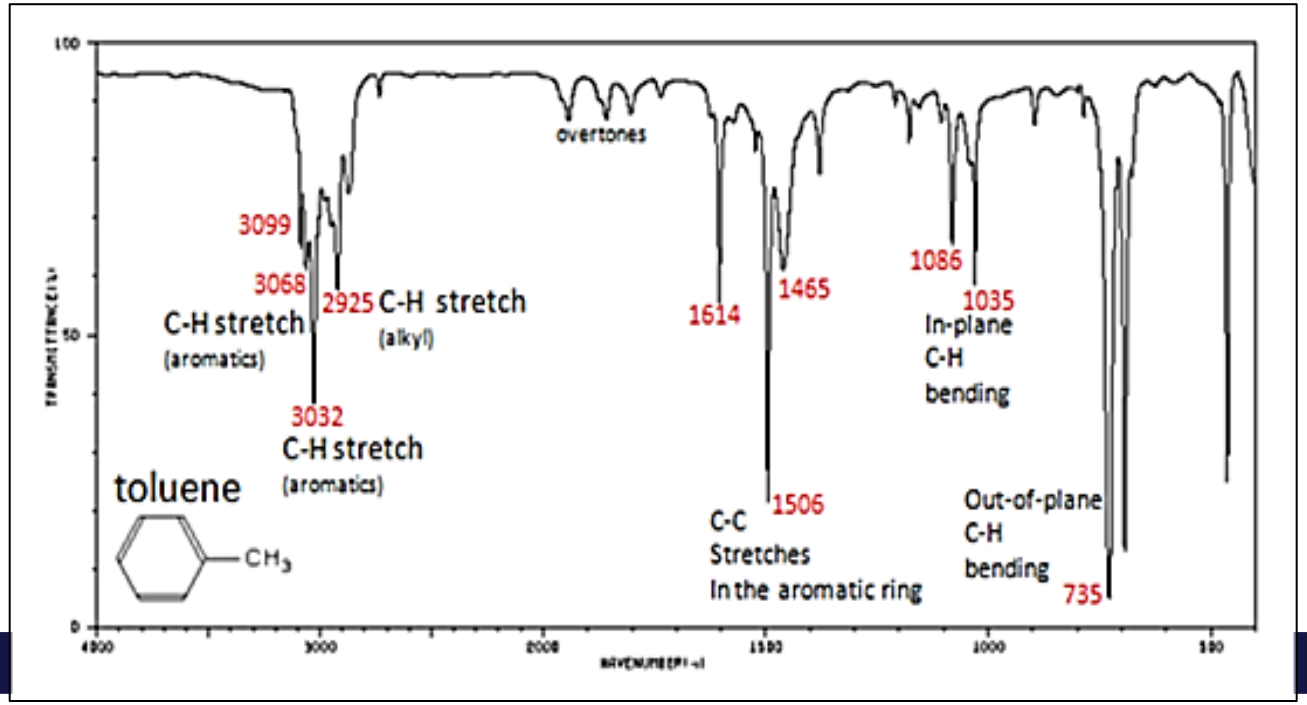


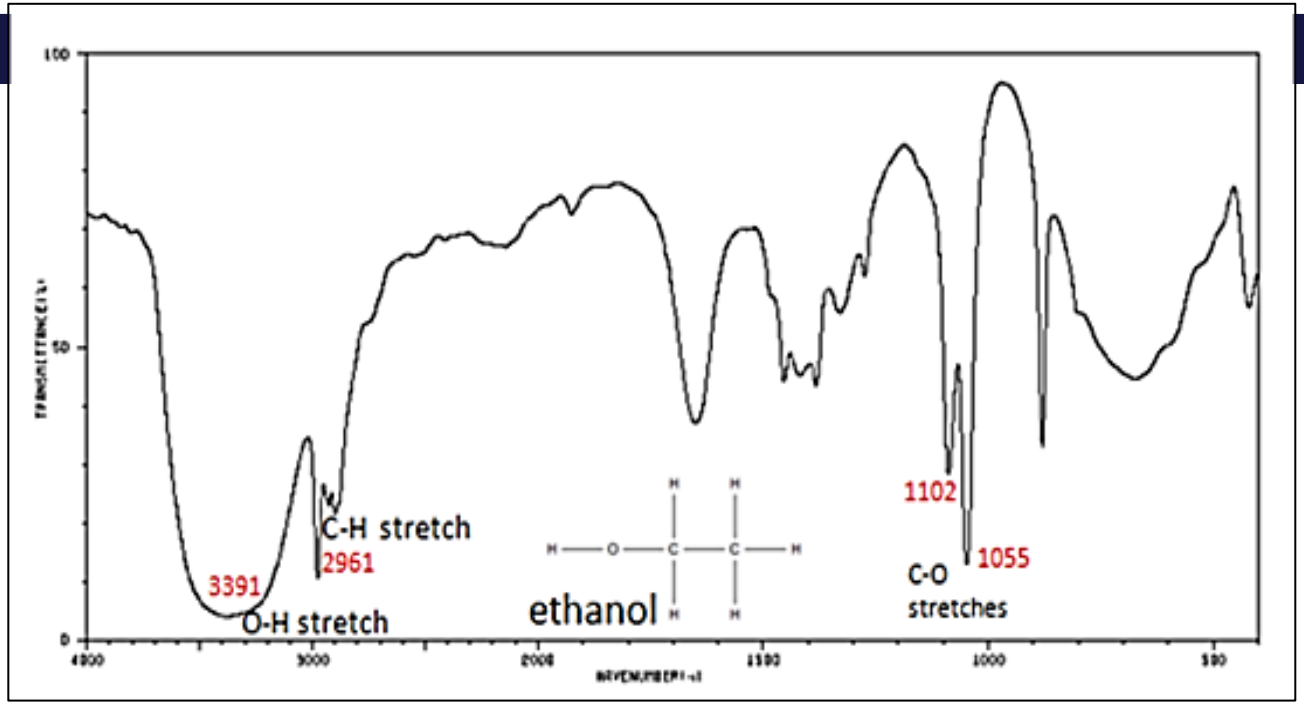
Types of molecular vibrations. The plus sign indicates motion out of the page; the minus sign indicates motion into the page.

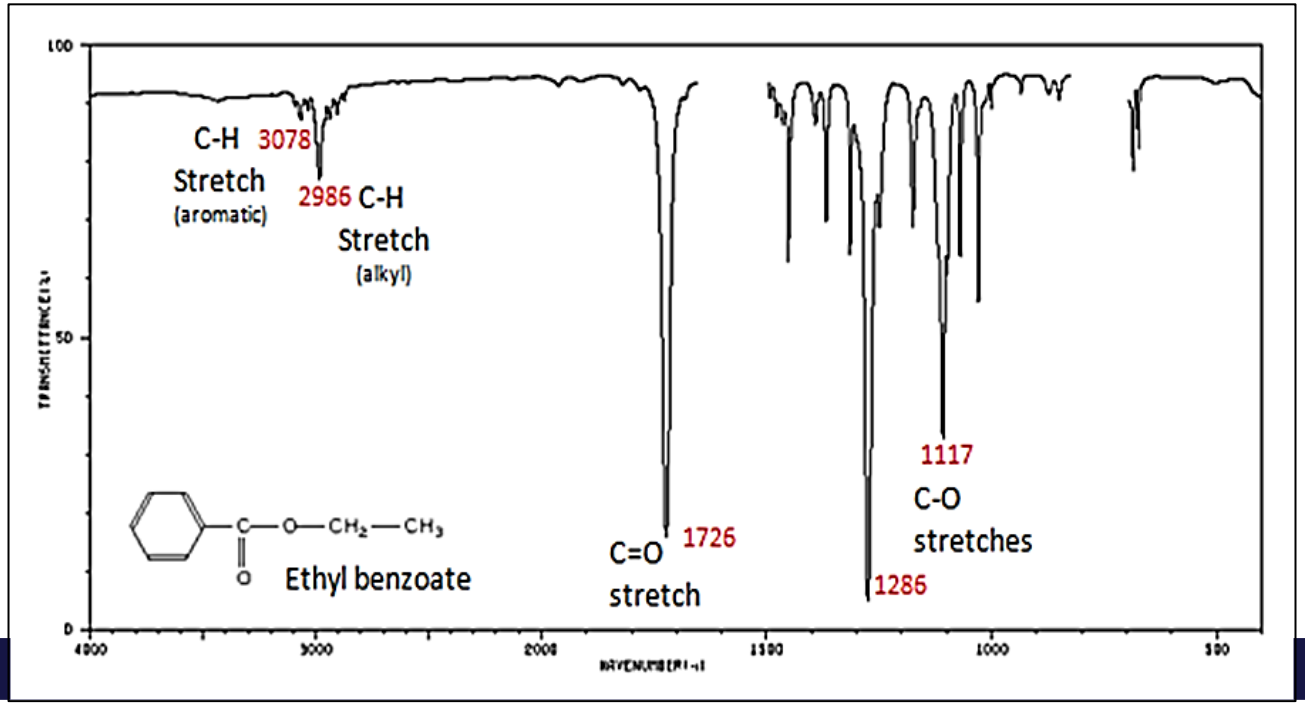


Group frequency and fingerprint regions of the mid-infrared spectrum
400 – 4000 cm^{-1}


726
Long-chain
Methyl rock
1383
C-H methyl rock
1470
C-H scissoring
octane
2863
2971
C-H stretch


overtones
3099
3068
2925
C-H stretch
(aromatics)
C-H stretch
(alkyl)
3032
C-H stretch
(aromatics)
toluene
1614
1465
1086
1035
In-plane
C-H
bending
1506
C-C
Stretches
In the aromatic ring
Out-of-plane
C-H
bending
735


3391
O-H stretch
C-H stretch
2961
ethanol
1102
1055
C-O
stretches


C-H
Stretch
(aromatic)
3078
2986 C-H
Stretch
(alkyl)
Ethyl benzoate
C=O
stretch
1726
1117
C-O
stretches
1286

Some Characteristic Infrared Absorption Peaks

	Functional Group	Absorption Peaks	
		Wavenumber, cm^{-1}	Wavelength, μm
O—H	Aliphatic and aromatic	3600–3000	2.8–3.3
NH_2	Also secondary and tertiary	3600–3100	2.8–3.2
C—H	Aromatic	3150–3000	3.2–3.3
C—H	Aliphatic	3000–2850	3.3–3.5
C≡N	Nitrile	2400–2200	4.2–4.6
C≡C—	Alkyne	2260–2100	4.4–4.8
COOR	Ester	1750–1700	5.7–5.9
COOH	Carboxylic acid	1740–1670	5.7–6.0
C=O	Aldehydes and ketones	1740–1660	5.7–6.0
$CONH_2$	Amides	1720–1640	5.8–6.1
C=C—	Alkene	1670–1610	6.0–6.2
ϕ—O—R	Aromatic	1300–1180	7.7–8.5
R—O—R	Aliphatic	1160–1060	8.6–9.4

Instrumentation

Instrument Designs for Molecular UV/Vis Absorption

Several common terms are used to describe complete instruments.

A **spectrometer** is a spectroscopic instrument that uses a monochromator or polychromator in conjunction with a transducer to convert the radiant intensities into electrical signals.

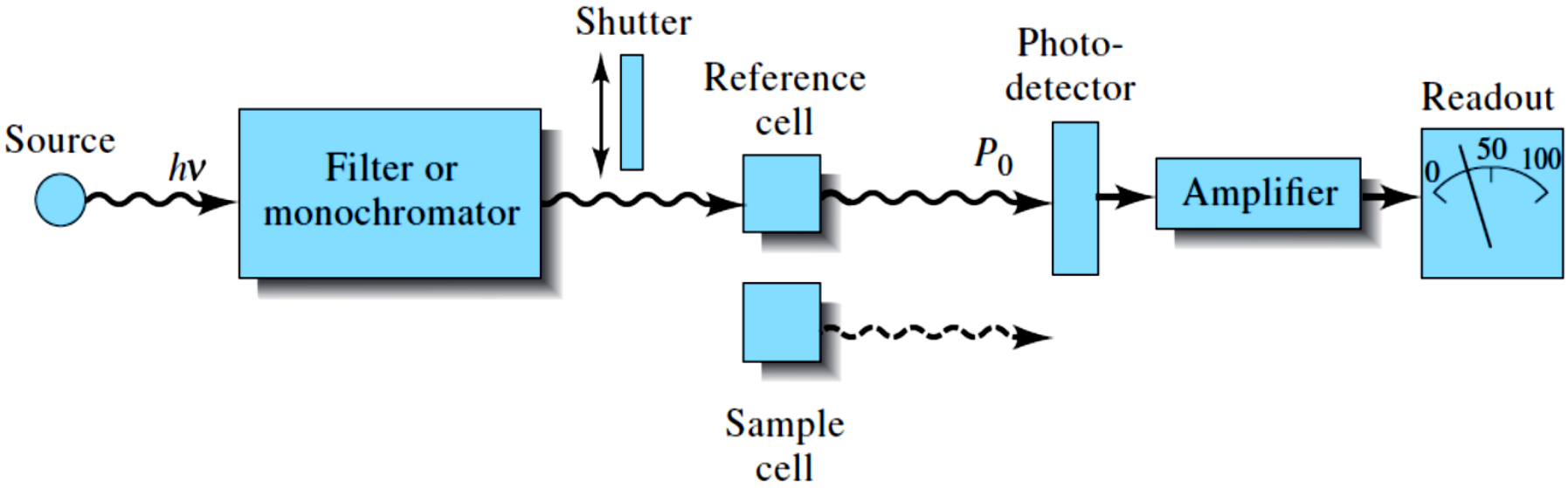
Photometers **(or filter photometer)** use a filter (absorption or interference filters) for wavelength selection in conjunction with a suitable radiation transducer.

Spectrophotometers are instruments for measuring absorbance that uses a monochromator to select the wavelength.

Both photometers and spectrophotometers can be obtained in **single- and double-beam** varieties.

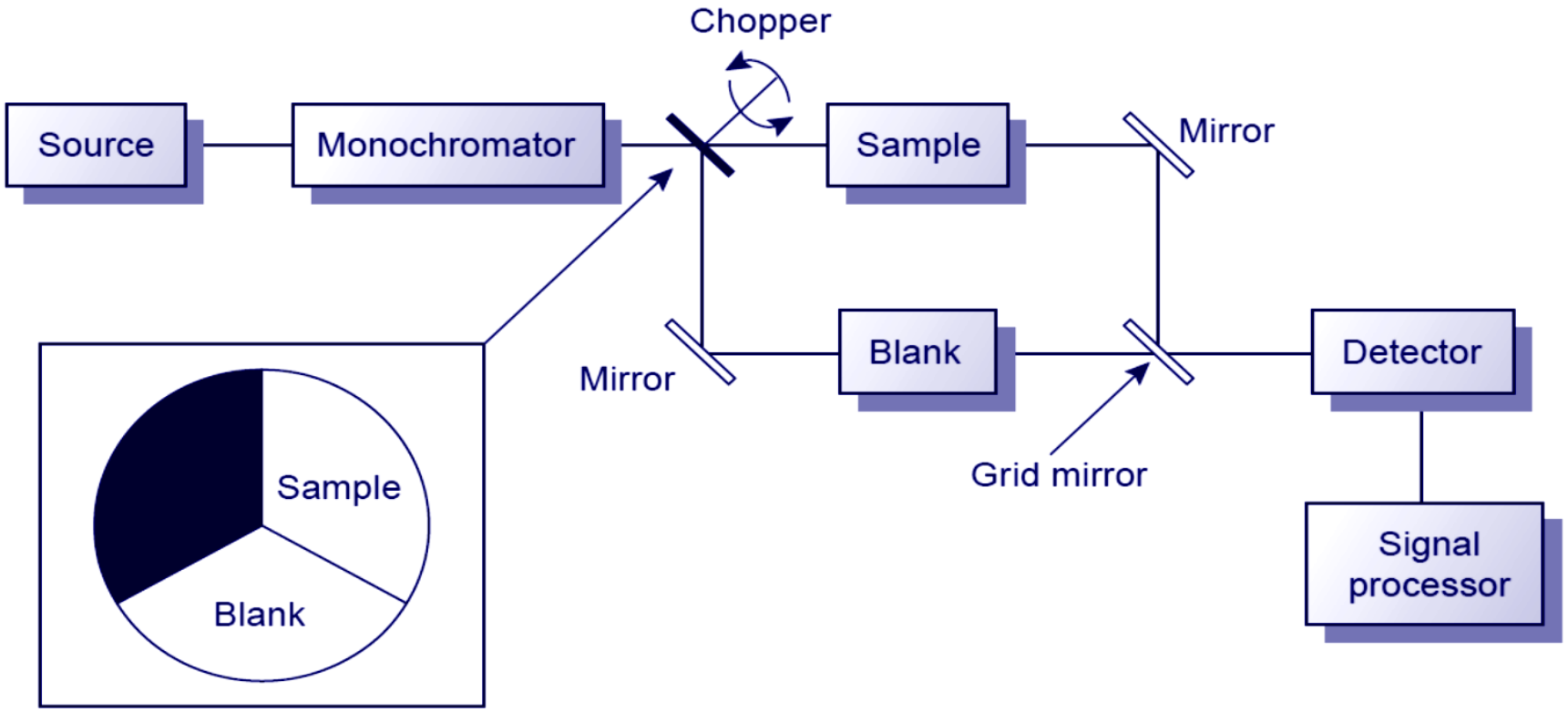
Single-Beam Instruments

A simple and inexpensive spectrophotometer.
Has a single optical path between the source and detector.



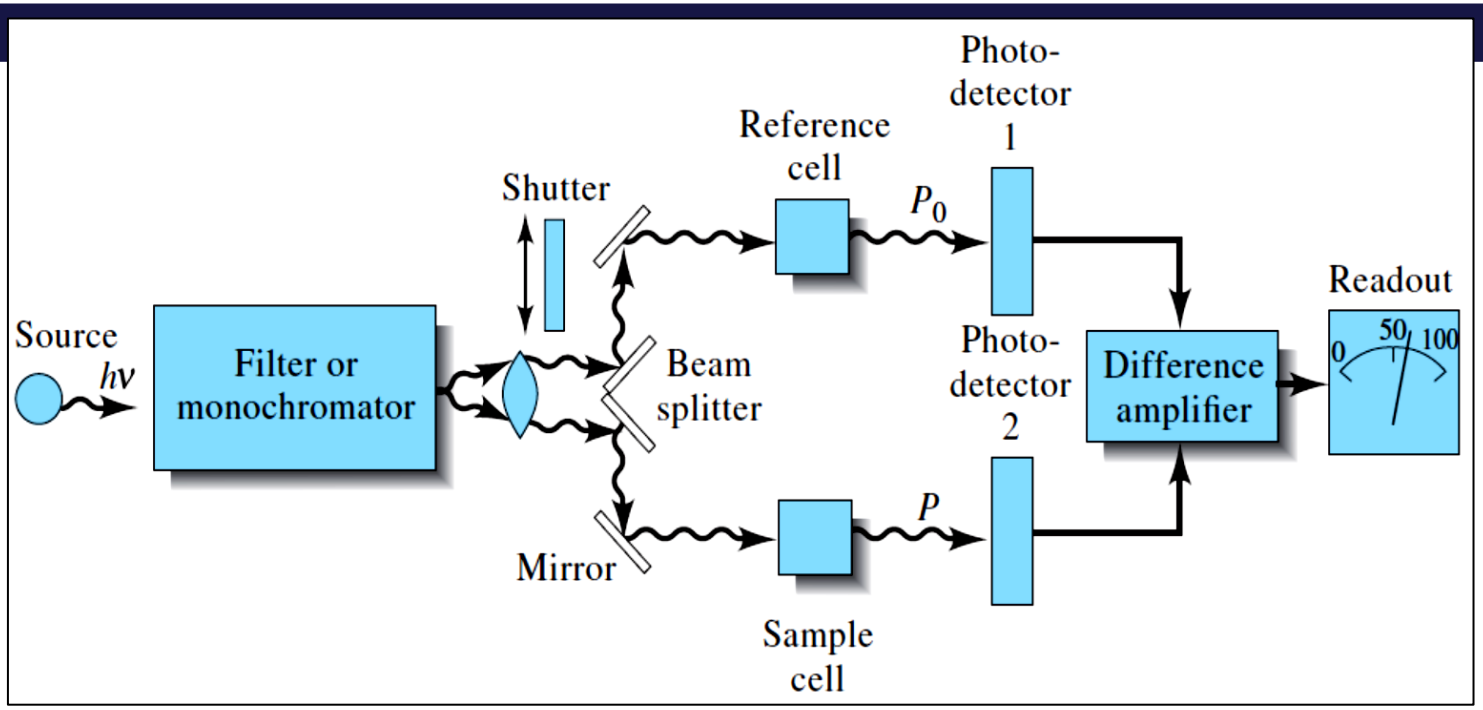
The instrument is calibrated to 0% *T* while using a **shutter** to block the source radiation from the detector. After removing the shutter, the instrument is calibrated to 100% *T* using an appropriate blank. The blank is then replaced with the sample, and its transmittance is measured. Since the source's incident power and the sensitivity of the detector vary with wavelength, the instrument must be recalibrated whenever the wavelength is changed.

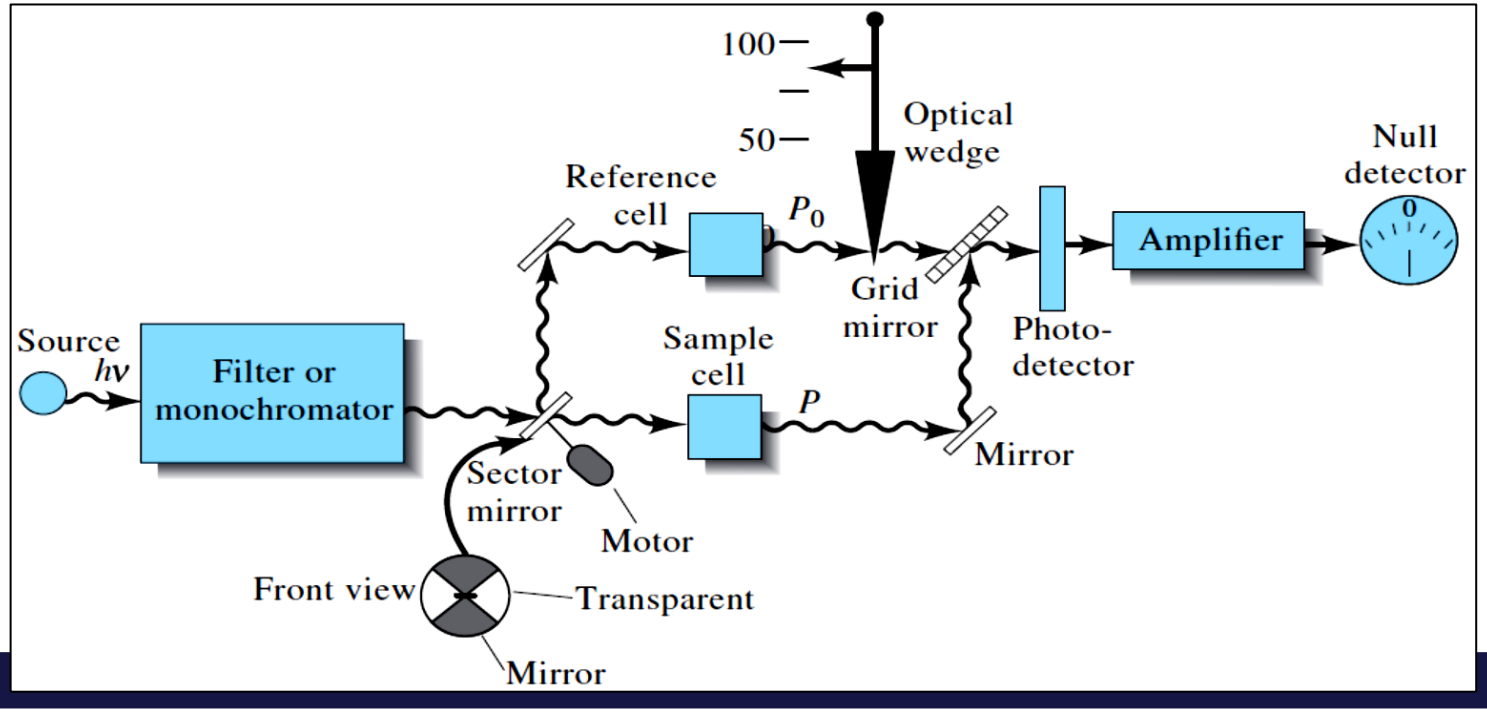
Double-Beam Instruments



Double-beam instruments offer the advantage that they compensate for all but the most rapid fluctuations in the radiant output of the source. They also compensate for wide variations of source intensity with wavelength. Furthermore, the double-beam design is well suited for continuous recording of absorption spectra.

Double-beam-in-space instrument

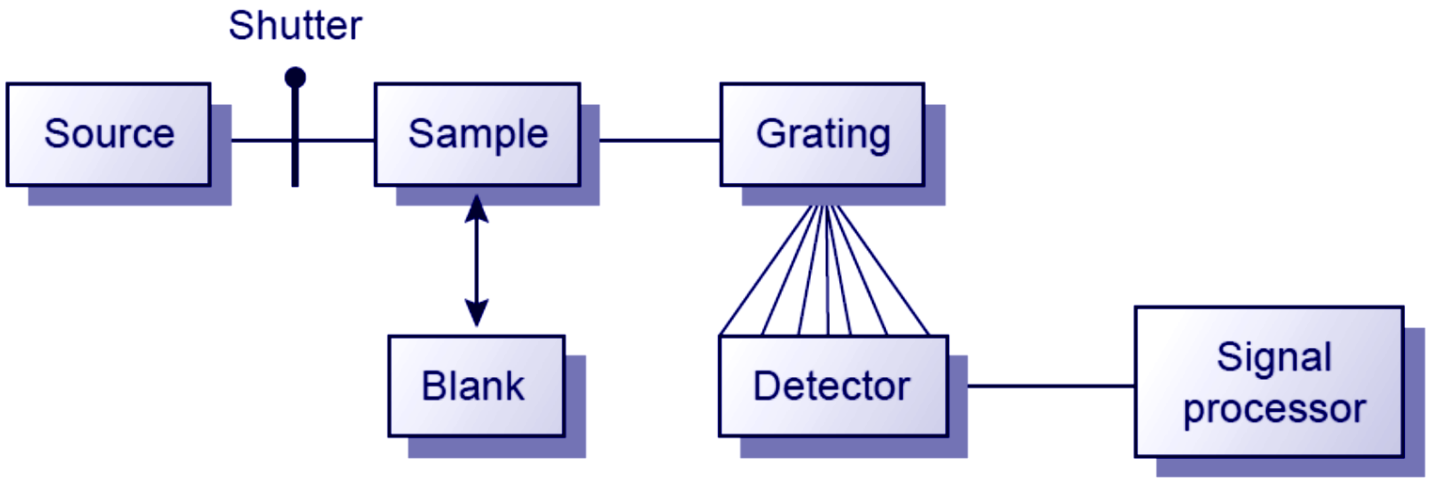




Double-beam-in-time instrument

Multichannel Instruments

A linear photodiode array consists of multiple detectors, or channels, allowing an entire spectrum to be recorded in as little as 0.1 s. Source radiation passing through the sample is dispersed by a grating.



Block diagram for a diode array spectrophotometer

One advantage of a linear photodiode array is the speed of data acquisition, which makes it possible to collect several spectra for a single sample. Individual spectra are added and averaged to obtain the final spectrum. This process of **signal averaging** improves a spectrum's signal-to-noise ratio.


Thank You!