Atomic and Molecular Physics

Course Code: PHYS4009

Lecture Topic

Infrared Spectroscopy

By

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Outline

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- *Infrared Spectroscopy*
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- *Selection Rule for Vibrational Transition*
- *IR-Active and Inactive vibrations of* CO_2
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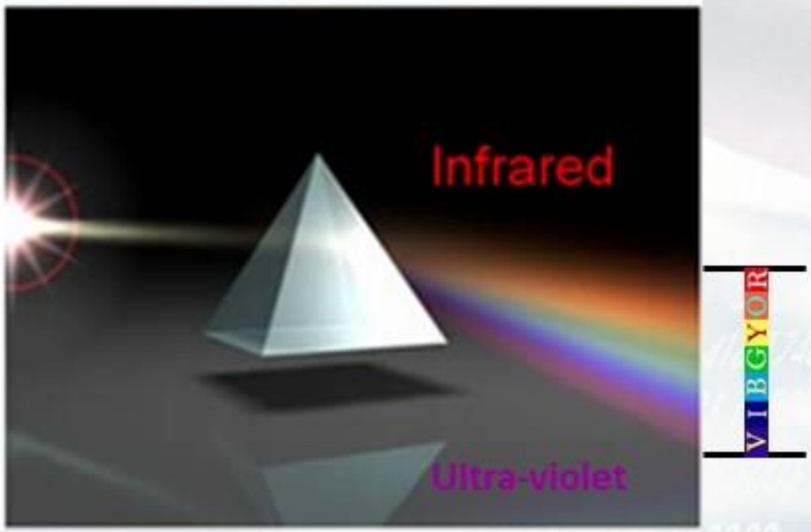
Infrared Radiation

Discovery of IR radiation

In year 1800 the astronomer Friedrich Wilhelm Herschel observed a kind of invisible radiation by directing the sunlight through a glass prism. He called it infrared radiation.



Infrared Spectroscopy

IR spectroscopy measures the infrared light that is absorbed by the substance. The infrared portion of the electromagnetic spectrum is divided into three regions:

Far-infrared : approximately **400 - 5 cm^{-1} (25 - 2000 μm)**, lying adjacent to the microwave region, has low energy and may be used for ***rotational spectroscopy***

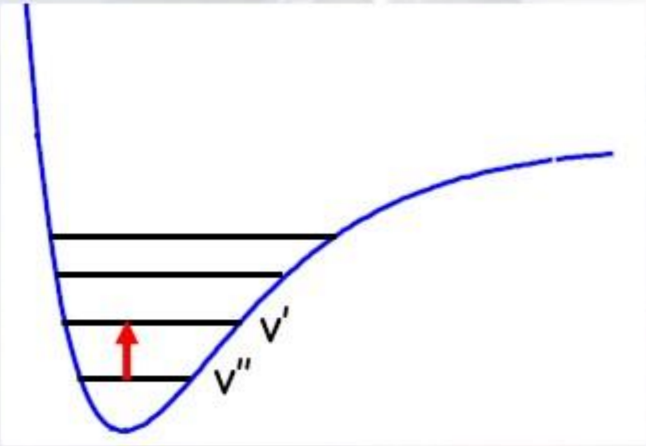
Mid-infrared : approximately **4000 - 400 cm^{-1} (2.5 - 25 μm)** may be used to study the ***fundamental transitions of molecular vibrations*** and associated ***rotational-vibrational structure***

Near-IR : approximately **15000 - 4000 cm^{-1} (0.7 – 2.5 μm)** can excite **overtone or combination bands of molecular vibrations**

Theory of Infrared Spectroscopy

An infrared transition between lower and upper states with vibrational wavefunctions $\psi_{v''}$ and $\psi_{v'}$, respectively, depends on the transition dipole moment, which is given by:

$$\boxed{R_{v'v''} = \int \psi_{v'}^{*} \mu \psi_{v''} dx}$$



The intensity of absorption corresponding to vibrational transition $v' \rightarrow v'$ is governed by the transition dipole moment integral $R_{v'v''}$. where x is (r - r_e), the displacement of the internuclear distance from equilibrium. The dipole moment μ is zero for a homonuclear diatomic molecule, resulting in $R_{v'v''} \rightarrow 0$ and all vibrational transitions being forbidden. For a heteronuclear diatomic molecule m is non-zero and varies with x.

This variation of dipole moment with internuclear separation can be expressed as a Taylor series expansion:

$$\mu = \mu_e + \left(\frac{d\mu}{dx}\right)_e x + \frac{1}{2!}\left(\frac{d^2\mu}{dx^2}\right)_e x^2 + \ \ldots\ldots\ldots$$

where, the subscript 'e' refers to the equilibrium configuration. The transition dipole moment now becomes:

$$R_{v'v''} = \mu_e \int \psi_{v'}^* \psi_{v''} dx + \left(\frac{d\mu}{dx}\right)_e \int \psi_{v'}^* x \psi_{v''} dx + \ \ldots\ldots\ldots$$

Since $\psi_{v''}$ and $\psi_{v'}$ are the eigen function of the same Hamiltonian, they are orthogonal, which means that, when $v' \neq v''$,

$$\int \psi_{v'}^* \psi_{v''} dx = 0$$

therefore, $R_{v'v''} = \left(\frac{d\mu}{dx}\right)_e \int \psi_{v'}^* x \psi_{v''} dx + \ \ldots\ldots\ldots$

Selection Rule for Vibrational Transition

As the vibrational transition dipole moment is given by

$$R_{v'v''} = \left(\frac{d\mu}{dx}\right)_e \int \psi^*_{v'} x \psi_{v''} dx + \;\ldots\ldots\ldots$$

For the infrared active transition, the $R_{v'v''}$ should be non-zero. The above equation has two term; $\left(\frac{d\mu}{dx}\right)_e$ and an integral $\int \psi^*_{v'} x \psi_{v''} dx$. In order to have $R_{v'v''}$ non-zero, both term should be non-zero. Therefore, for infrared active transition, following condition should meet:

$\left(\frac{d\mu}{dx}\right)_e \neq 0$ i.e. there must be **change of dipole moment at equilibrium inter-nuclear separation during vibration** and $\int \psi^*_{v'} x \psi_{v''} dx \neq 0$, the integral is non-zero only when, Δv = ±1, ±2, ±3, ... which constitute the vibration selection rule for infrared transition.

The transition intensities are proportional to $|R_{v'v''}|^2$ and therefore to $\left(\frac{d\mu}{dx}\right)_e^2$.

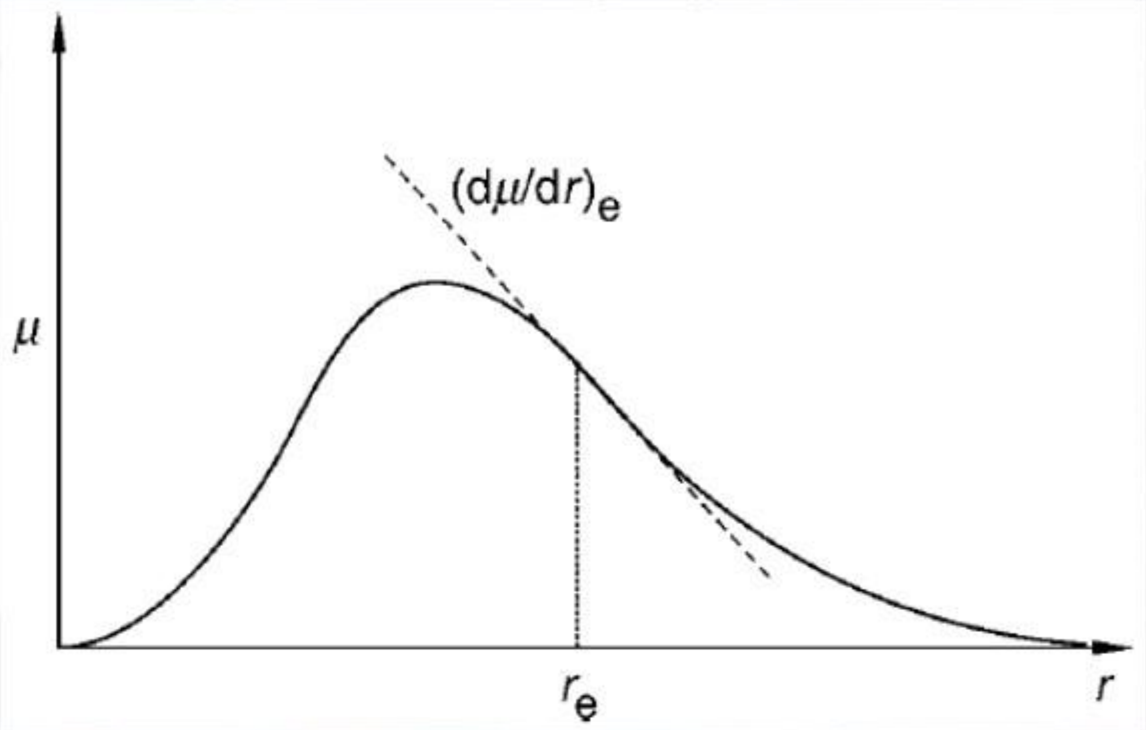


Figure shows variation of dipole moment μ with internuclear distance in a typical heteronuclear diatomic molecule. Obviously, $\mu \to 0$ when $r \to 0$ and the nuclei coalesce. For neutral diatomic molecules, $\mu \to 0$ when $r \to \infty$ because the molecule dissociates into neutral atoms. Therefore, between $r = 0$ and $r = \infty$, there must be a maximum value of μ.

In figure it is shown that the maximum is at $r < r_e$, giving a negative slope $d\mu/dr$ at r_e. If the maximum were at $r >$ re there would be a positive slope at r_e. It is possible that the maximum is at $r = r_e$, in which case $d\mu/dr = 0$ at $r = r_e$ and the $\Delta v = 1$ transitions, although allowed, would have zero intensity.

Hetero-nuclear diatomic

$$\frac{\partial \mu}{\partial r} \neq 0$$

Infrared active

Homo-nuclear diatomic

$$\frac{\partial \mu}{\partial r} = 0$$

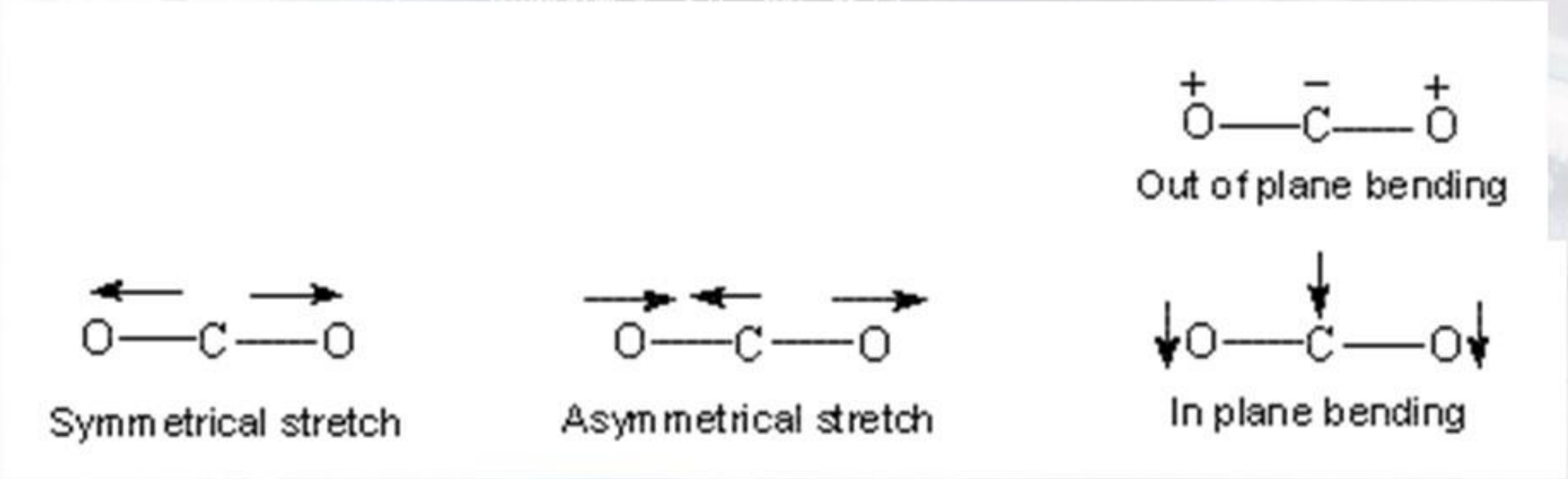
Infrared inactive

In general for polyatomic molecules for transition to be infrared active

$$\frac{d\mu}{dQ} \neq 0$$

where, Q is the normal coordinate of the vibration. For a diatomic: Q = r (bond length).

IR active and inactive vibrations of CO2



$$\frac{d\mu}{dQ} = 0$$

IR inactive
(no change in dipole moment)

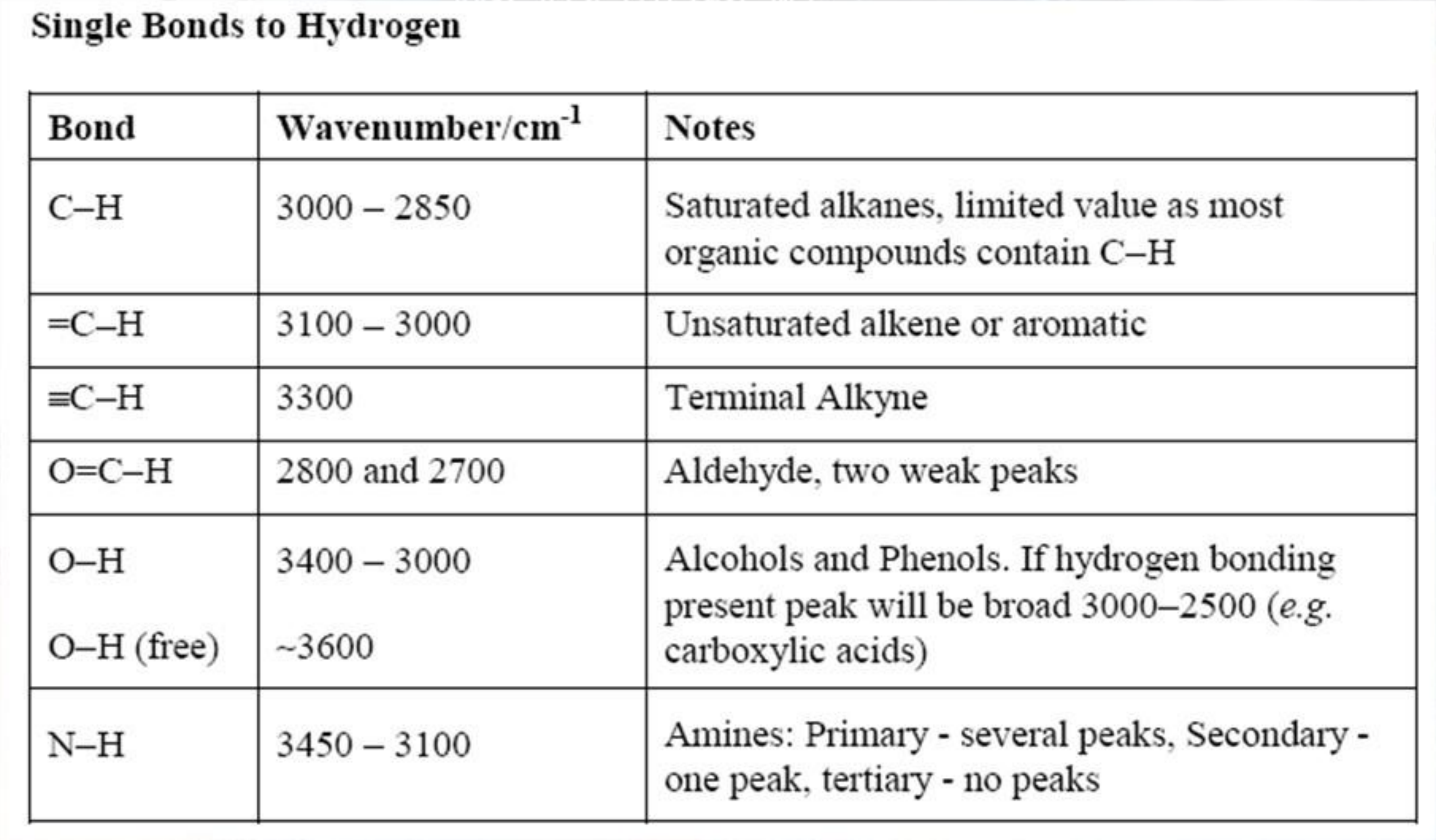
$$\frac{d\mu}{dQ} \neq 0$$

IR active
(change in dipole moment)

$$\frac{d\mu}{dQ} \neq 0$$

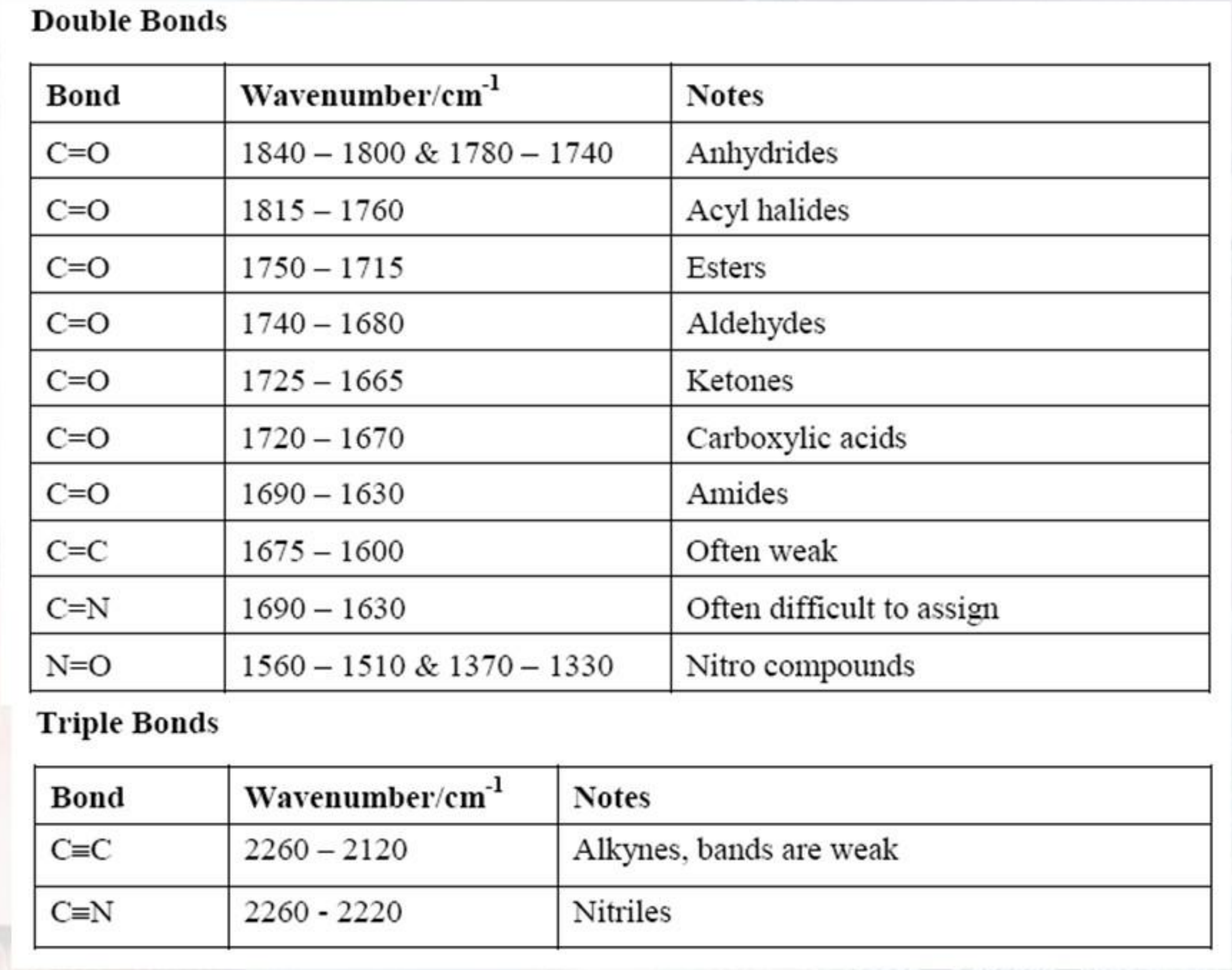
IR active
(change in dipole moment)

Finger print regions of molecular vibrations



Single Bonds to Hydrogen

Bond	Wavenumber/cm^{-1}	Notes
C–H	3000 – 2850	Saturated alkanes, limited value as most organic compounds contain C–H
=C–H	3100 – 3000	Unsaturated alkene or aromatic
≡C–H	3300	Terminal Alkyne
O=C–H	2800 and 2700	Aldehyde, two weak peaks
O–H O–H (free)	3400 – 3000 ~3600	Alcohols and Phenols. If hydrogen bonding present peak will be broad 3000–2500 (*e.g.* carboxylic acids)
N–H	3450 – 3100	Amines: Primary - several peaks, Secondary - one peak, tertiary - no peaks



Double Bonds

Bond	Wavenumber/cm^{-1}	Notes
C=O	1840 – 1800 & 1780 – 1740	Anhydrides
C=O	1815 – 1760	Acyl halides
C=O	1750 – 1715	Esters
C=O	1740 – 1680	Aldehydes
C=O	1725 – 1665	Ketones
C=O	1720 – 1670	Carboxylic acids
C=O	1690 – 1630	Amides
C=C	1675 – 1600	Often weak
C=N	1690 – 1630	Often difficult to assign
N=O	1560 – 1510 & 1370 – 1330	Nitro compounds

Triple Bonds

Bond	Wavenumber/cm^{-1}	Notes
C≡C	2260 – 2120	Alkynes, bands are weak
C≡N	2260 - 2220	Nitriles

Single Bonds (not to Hydrogen)

Bond	Wavenumber/cm^{-1}	Notes
C–C	Variable	No diagnostic value
C–O, C–N	1400 – 1000	Difficult to assign
C–Cl	800 – 700	Difficult to interpret
C–Br, C–I	Below 650	Often out of range of instrumentation

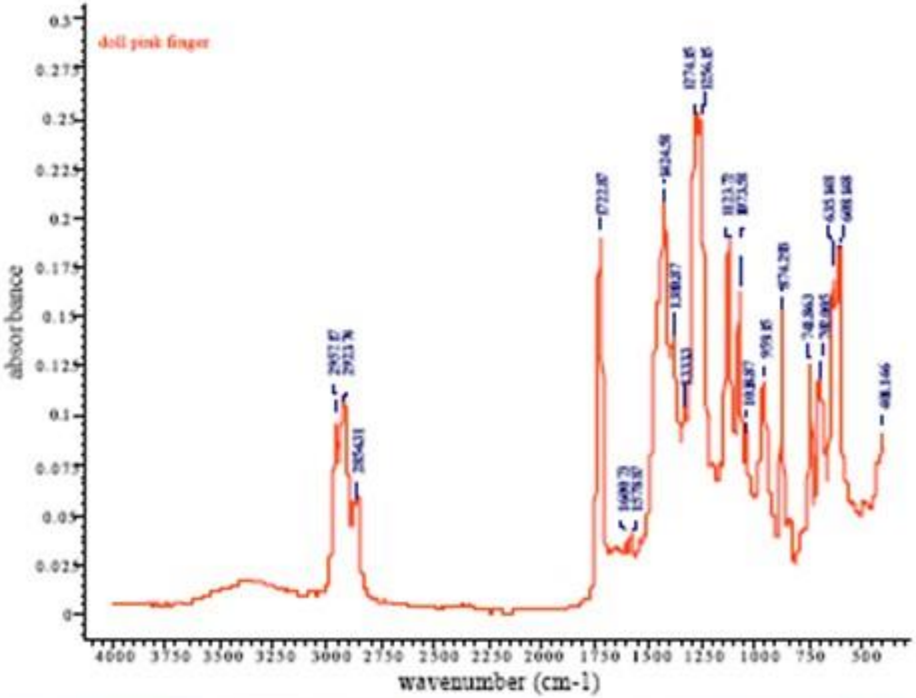
Bending Vibrations

Bond	Wavenumber/cm^{-1}	Notes
R–N–H	1650 – 1500	Take care not to confuse N–H bend with the C=O stretch in amides
R–C–H	1480 – 1350	Saturated alkanes and alkyl groups
R–C–H	1000 – 680	Unsaturated alkenes and aromatics

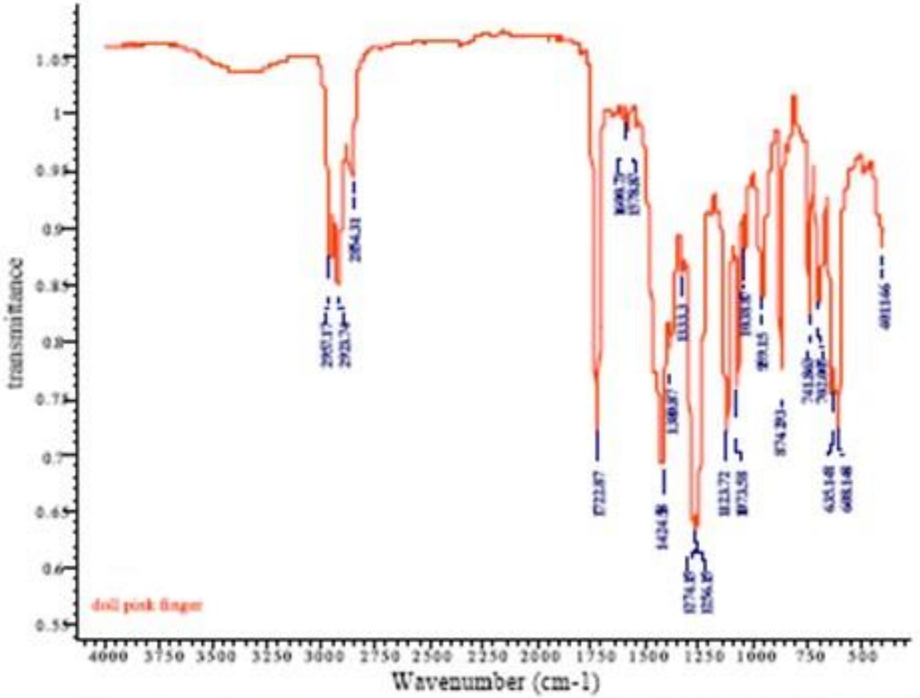
Infrared Spectra

IR spectrum which is a plot of measured IR intensity (absorbance or transmittance) versus wavelength (or wavenumber) of light.

Absorbance



Transmittance



Advantages and Disadvantages of IR Spectroscopy

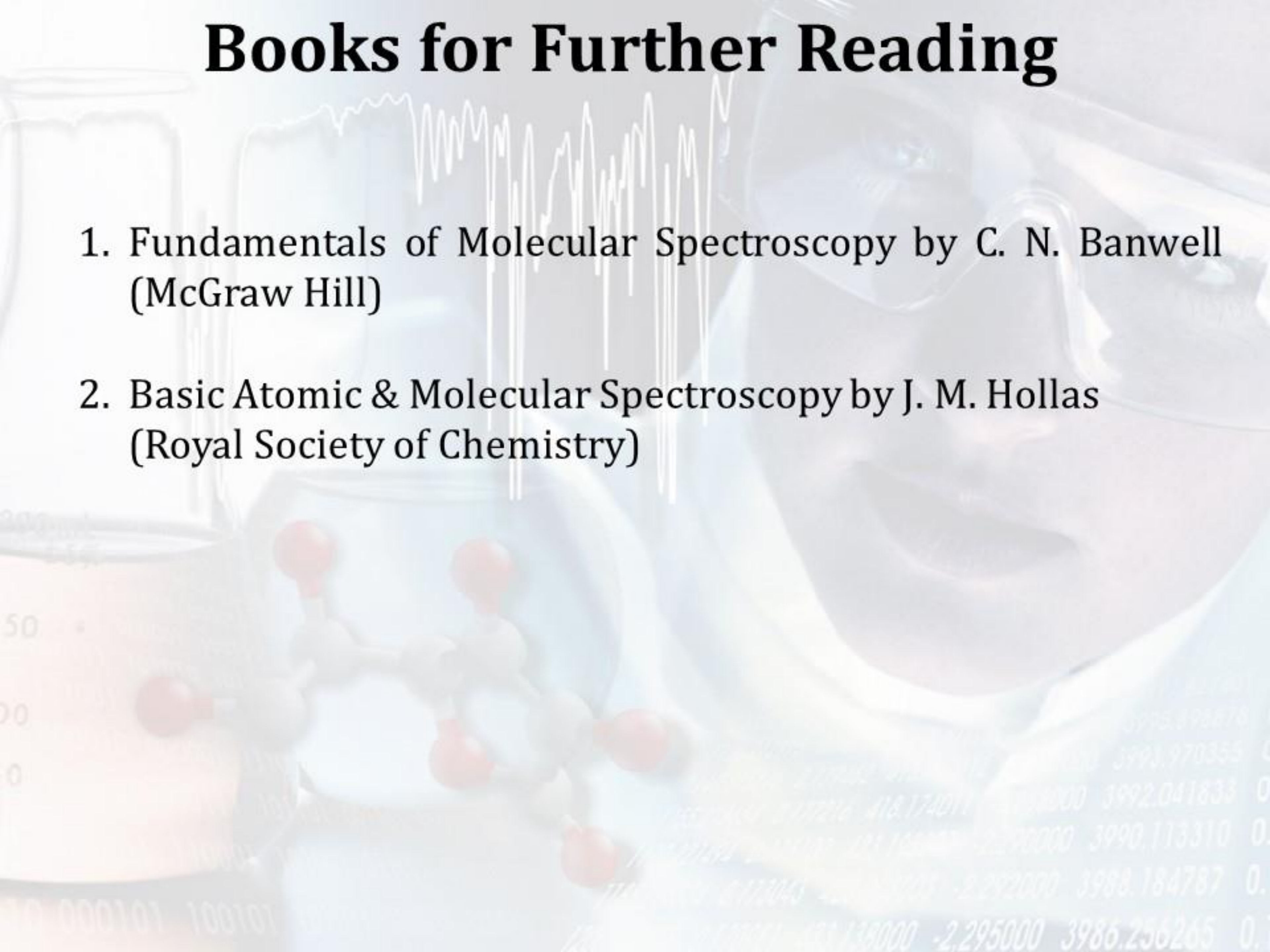
Advantages

- A universal technique i.e. solids, liquids, gases, semi-solids, powders, and polymers can be routinely analyzed.
- IR is relatively fast and easy technique.
- IR is very sensitive. Micro to nano gram quantities can routinely be detected.

Disadvantages

- Homonuclear compounds don't absorb.
- Aqueous solutions difficult to analyze because the strong absorbance of water.
- Some compounds give broad bands that interfere with other compounds.
- Complex mixtures are difficult to analyse
- Dark (black) compounds often absorb the IR beam completely, i.e. 0% transmittance.

Books for Further Reading



1. Fundamentals of Molecular Spectroscopy by C. N. Banwell (McGraw Hill)
2. Basic Atomic & Molecular Spectroscopy by J. M. Hollas (Royal Society of Chemistry)

Thank you