

IR Spectroscopy

Spectroscopy: Branch of science in which light or other electromagnetic radiation is resolved into its component wavelengths to produce spectra, which are graphs of intensity vs. wavelength or frequency of radiation.

Current usage broadens this definition to include some methods that don't involve electromagnetic radiation, such as mass spectroscopy (also called mass spectrometry), or electron spectroscopy.

This is a useful approach to study matter, since matter will interact with electromagnetic radiation to absorb or emit certain frequencies of radiation which are characteristic of the sample of matter.

As we saw when we studied the H atom, radiation is absorbed or emitted only in the frequency of light matches the energy difference of 2 quantum levels of the sample of matter. $\Delta E = h\nu$

IR Spectroscopy

Tool for examining vibrations in molecules. IR spectra are usually taken in the range $\lambda \sim 2.5 - 15.0 \mu\text{m}$, which corresponds to $4000 - 650 \text{ cm}^{-1}$.

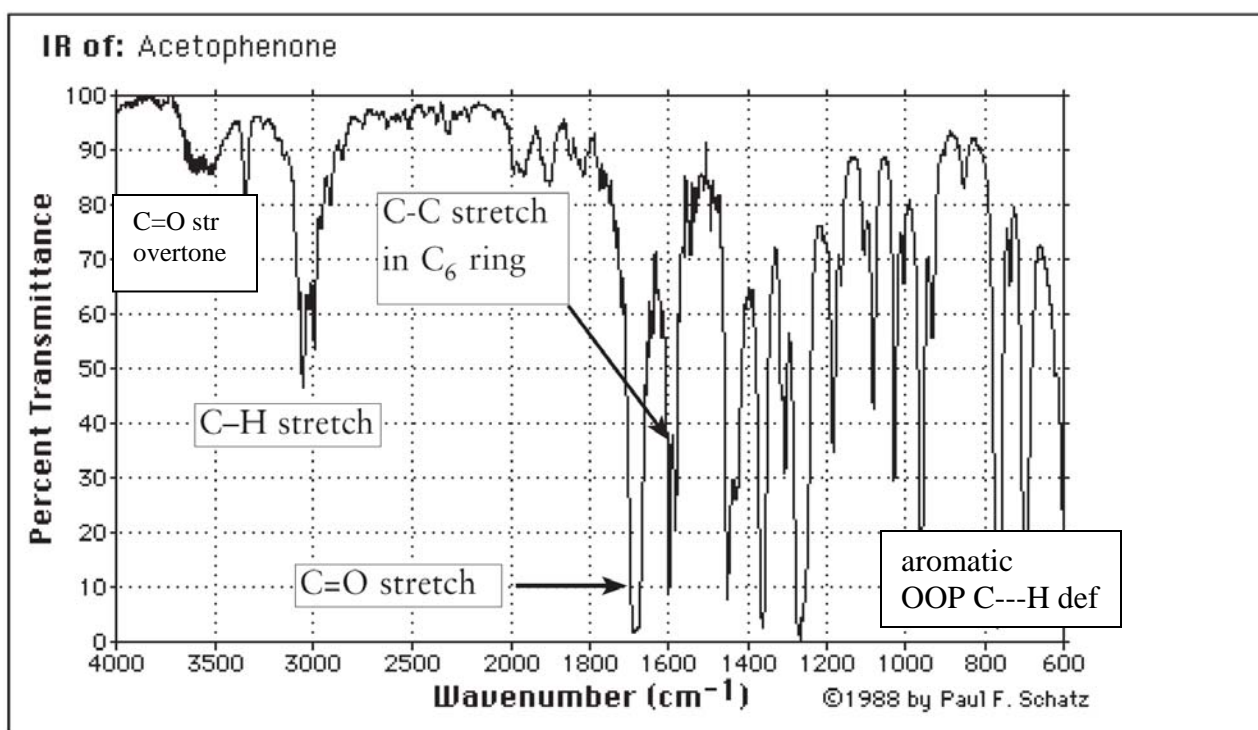
$$\text{(e.g. } 2.5 \mu\text{m} = 2.5 \cdot 10^{-6} \text{ m} = 2.5 \cdot 10^{-4} \text{ cm, } \frac{1}{2.5 \cdot 10^{-4} \text{ cm}} = 4000 \text{ cm}^{-1}\text{)}$$

The whole IR region is considered to be around

$$\lambda \sim 8 \cdot 10^{-5} \text{ cm} (12,500 \text{ cm}^{-1}) \text{ to } 10^{-1} \text{ cm} (10 \text{ cm}^{-1})$$

λ	$\frac{1}{\lambda}$		
190 - 300 nm	52,600 – 30,000 cm^{-1}	ultraviolet	electronic transitions
330 - 800 nm	30,000 – 12,500 cm^{-1}	visible	Electronic transitions often in conjugated molecules
800 - 2500 nm	12,500 – 4,000 cm^{-1}	“near IR”	overtone vibrations
2.5 - 15 μm	4,000 – 650 cm^{-1}	“mid IR”	fundamental vibrations
$1.5 \cdot 10^{-3} - 10^{-1} \text{ cm}$	650 – 10 cm^{-1}	“far IR”	“floppy” vibrations
$10^{-1} - 10 \text{ cm}$	10 – 0.1 cm^{-1}	microwave	Rotations
>10 cm	< 0.1 cm^{-1}	microwave	NMR

- Nearly all molecules absorb IR radiation - some exceptions: N₂, O₂.
- IR spectrum is unique for each molecule – can be used to help identify structure, or test for presence of molecules whose IR spectra are known. Frequently used to test for federally regulated atmospheric pollutants.
- Different types of instruments
 - dispersive spectrometers – light passes through sample, then through a monochromator, then to detector. By selecting different frequencies w/ the monochromator, the whole spectrum can be obtained.
 - fourier-transform spectrometers – high-sensitivity, resolution quicker to take spectrum because all wavelengths are detected simultaneously – they are separated by applying a Fourier transform to the specially modulated source signal.
 - filter photometers – used to detect specific molecules, as in atmospheric pollutants. Come with special filters for molecules of interest.
- All use a heated solid for source of IR radiation, and IR detectors respond to heat rather than photons.



To a first approximation, each bond represents an independent harmonic oscillator w/ a different fundamental frequency (fundamental frequency: transition between quantum levels $\Delta n = 1$) [overtone frequency: transitions between quantum levels $\Delta n = 2$ or higher ... see previous slide for C=O overtone].

Some characteristic IR absorption peaks

<u>Functional group</u>	<u>Cm^{-1}</u>
OH aliphatic aromatic	3600-3000
NH ₂ also secondary and tertiary	3600-3100
C-H aromatic	3150-3000
C-H aliphatic	3000-2850
C≡N nitrile	2400-2200
C≡C alkyne	2260-2100
COOR ester	1750-1700
COOH carboxylic acid	1740-1670
C=O aldehydes & ketones	1740-1660
CONH ₂ amides	1720-1640
C=C- alkene	1670-1610
R-O-R aliphatic	1160-1060

“hot bands”: if the sample has a high temperature, some population of $n=1$, $n=2$, or higher levels will lead to weak absorptions at nearly the same, but slightly lower energy as fundamental. (energy changes because of anharmonicity)

Frequency of C-H stretch will change depending on chemical environment (eg C-H aliphatic 3000-2850, aromatic 3150-3000) The vibrations are not truly decoupled from each other. This is due to anharmonicity. H.O. is a good but not perfect model.

Why are only $\Delta n = 1$ transitions intense? This is a “selection rule” for vibrational spectroscopy. As we’ll discuss in more detail later, when we talk about time-dependent perturbation theory, the interaction of a dipole moment with the electric field of the radiation is $-\vec{\mu} \cdot \vec{E}$. (coupling to magnetic field also happens but is orders of magnitude weaker). This interaction will cause an intense transition between 2 states n and m if $\vec{\mu}_{nm} = \langle \Psi_n | \vec{\mu} | \Psi_m \rangle$ is nonzero. (“transition dipole moment”) We could work out that this implies $n=m\pm 1$ for H.O. using ladder operators or special properties of Hermite polynomials. We would also see that the dipole moment of the molecule must change during the vibration. Molecules with no dipole moment do not have IR spectra! (perhaps Raman spectra though)

High-resolution IR spectra: Note that our example IR spectrum of acetophenone has fairly broad peaks. This is typical of liquid film IR spectra. A gas-phase spectrum can exhibit much sharper peaks (widths $< 1 \text{ cm}^{-1}$), and we can see each peak (“band”) is resolved into many sub-peaks. This fine structure is due to rotational transitions. We’ll discuss this vibrational-rotational spectroscopy later after we’ve dealt w/ rotations.