Absorption Spectrum

What is spectroscopy?

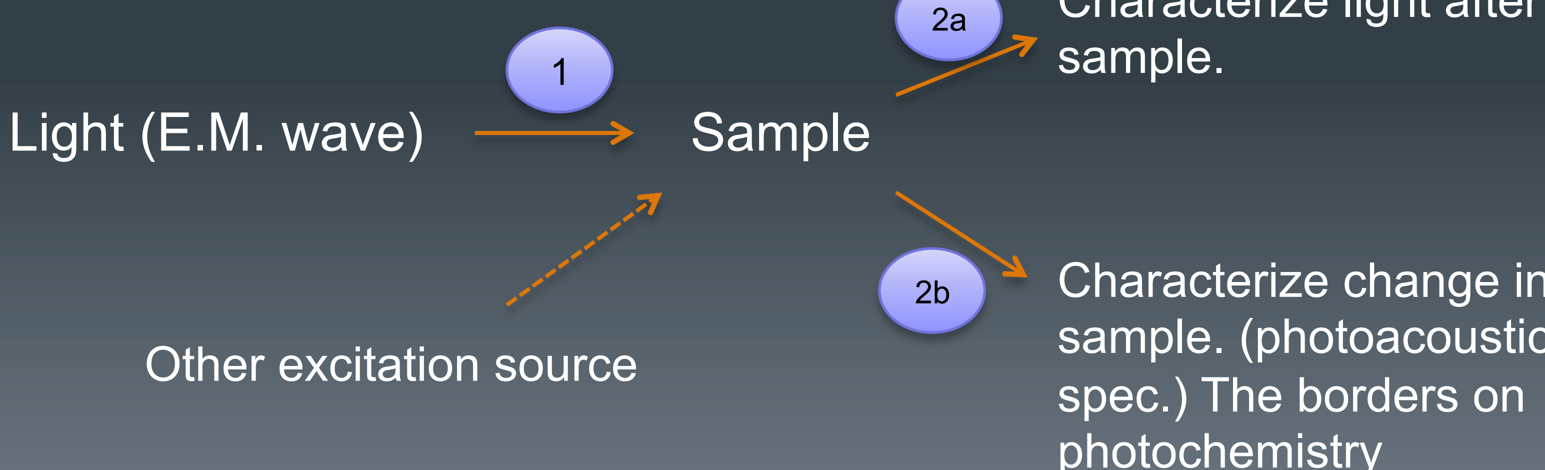
- Studying the properties of matter through its interaction with different frequency components of the electromagnetic spectrum.
- With light, you aren't looking directly at the molecule"the matter" but its –ghost.
- You observe the light's interaction with different degrees of freedom of the molecule. Each type of spectroscopy—different light frequency—gives a different picture → the spectrum.

Spectroscopy

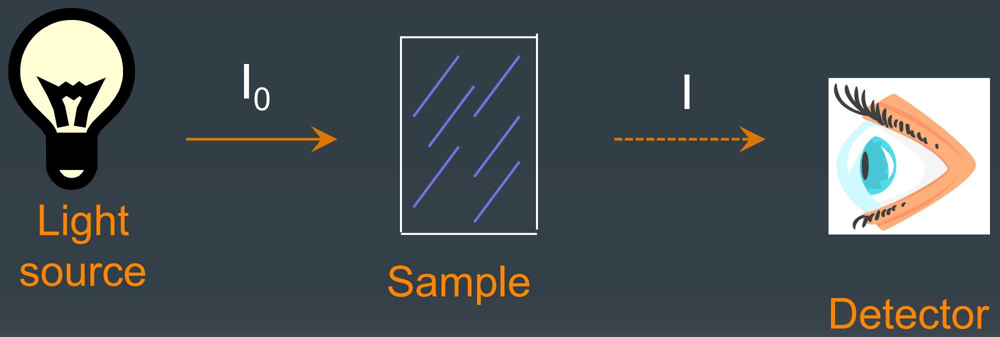
- Is a general methodology that can be adapted in many ways to extract the information you need (energies of electronic, vibrational, rotational states, structure and symmetry of molecules, dynamic information).

What does a spectrum measure?

- Interaction of light with a sample can influence the sample and/or the light.
- Method involves: (1) excitation and (2) detection.
- The basic idea:

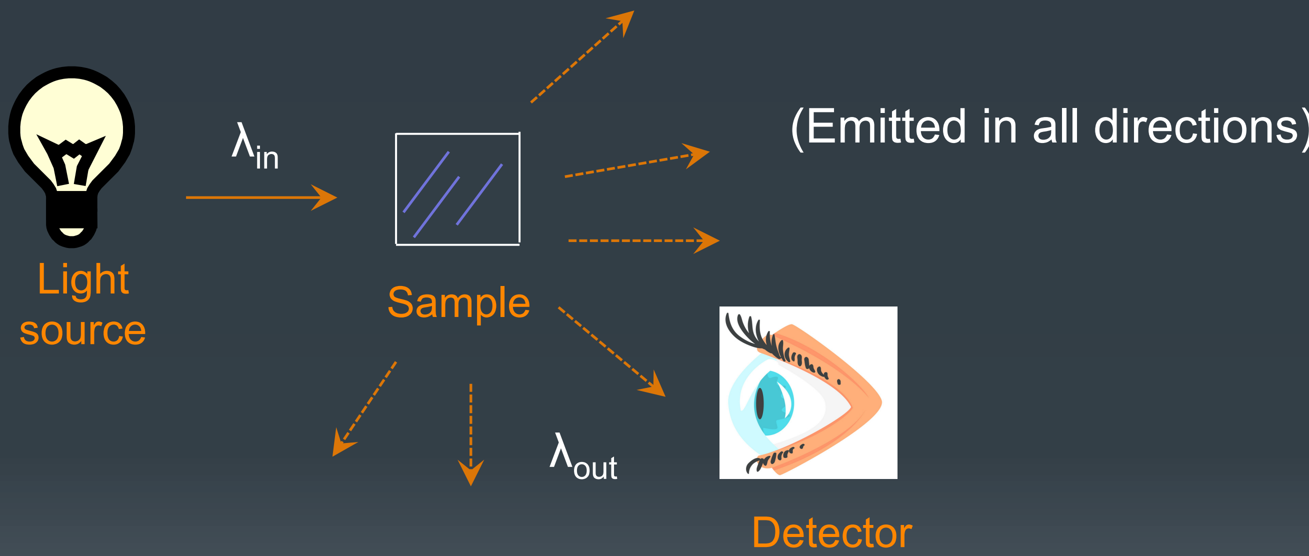


- In most spectroscopies, we characterize how a sample modifies light entering it.
- 1) Absorption:
  - Change in intensity I of incident light
    Sample attenuates light → transmission $T = I / I_0$



- We measure the absorption of light at different frequency or wavelength.

- 2) Emission:
- Excitation induces emission of light from the sample (usually of different frequency).

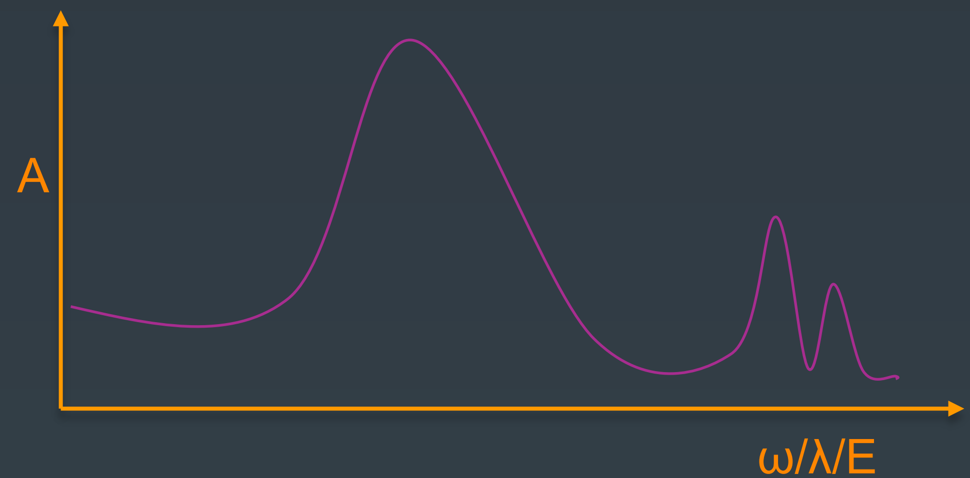


- Includes:

  Fluorescence (emission from excited electronic singlet states)
  Phosphorescence (emission from excited electronic triplet states)
  Raman Scattering (light scattering involving vibrational transition)

- 3) Optical Rotation:
- Change of phase of light incident on sample (rotation of polarization)

A typical absorption spectrum



y-axis:

- Absorption
- $A(v) = \log I_0/I = \varepsilon(v)cL$ (Beer's Law)
- I_0 = light intensity incident on the sample
  I = light intensity after the sample
  ε = molar decadic extinction coefficient ($M^{-1}cm^{-1}$) – the molecular quantity
  c = concentration (M)
  L = sample length (cm)
- This comes from assuming that the fraction of light absorbed as you propagate though the sample is proportional to the distance traversed: $dI/I = -\alpha\, dx$

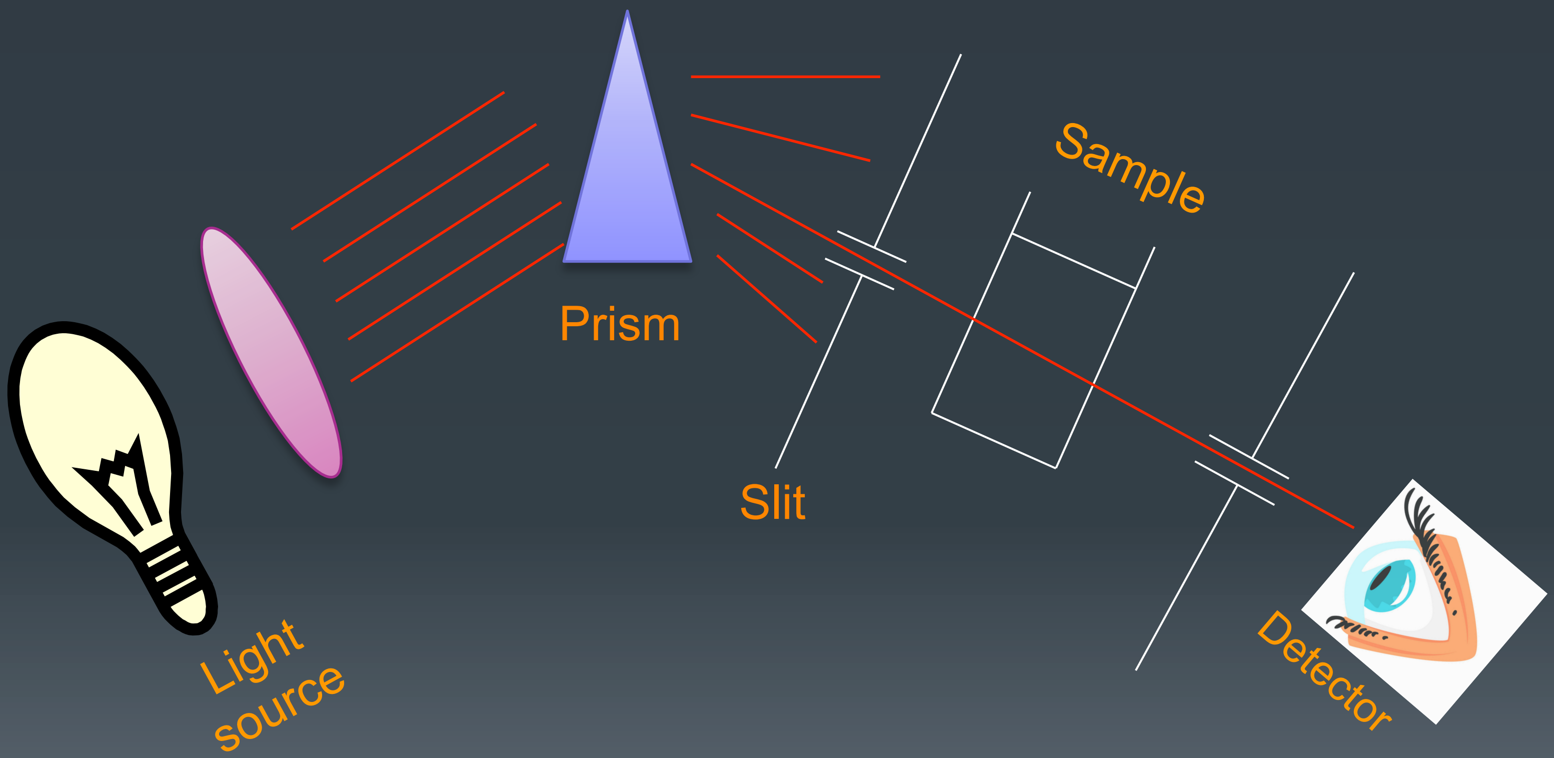
X-axis:

- Characterizes the input light in terms of frequency-wavelength-energy
- Wavelength λ (nm, μm, Å),
  Frequency v (cycles/sec or s-1 or Hz) = $\omega/2\pi = c/\lambda$
  $\omega = 2\pi v$ (rad/sec) (angular frequency)
  $v = \omega/2\pi c = 1/\lambda$ expressed in units of cm-1 (wavenumbers)
- Energy $E = hv$ (expressed as eV or as cm-1 using $E/hc = v/c$)

How do your measure absorption spectra?

- Measure the change of intensity of light at different frequencies as it passes through a sample.
- Two types of spectrometers:
    1) Dispersive
    2) Fourier transform

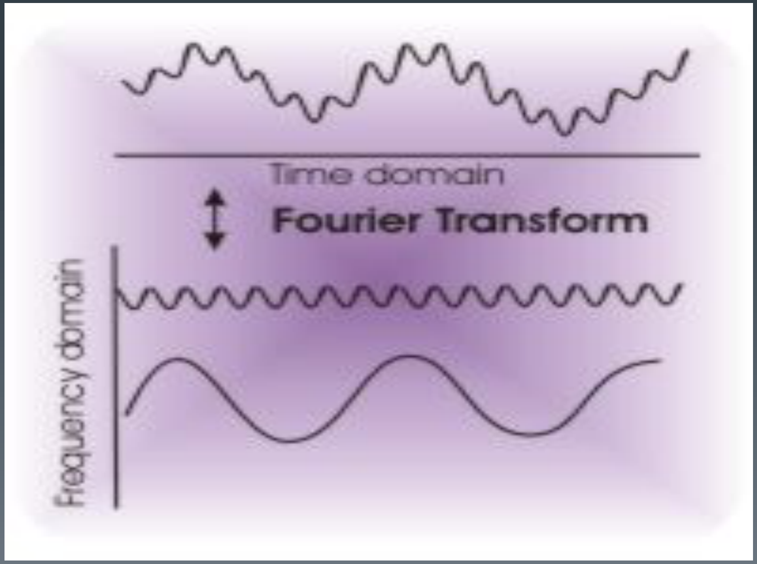
Dispersive spectrometer: Separate different frequency components



This is a way of processing all wavelength/frequencies simultaneously → Infrared/NMR (nuclear magnetic resonance)

Fourier transform

- It decomposes a function of time (a signal) into the frequencies that make it up, in a way similar to how a musical chord can be expressed as the frequencies (or pitches) of its constituent notes.

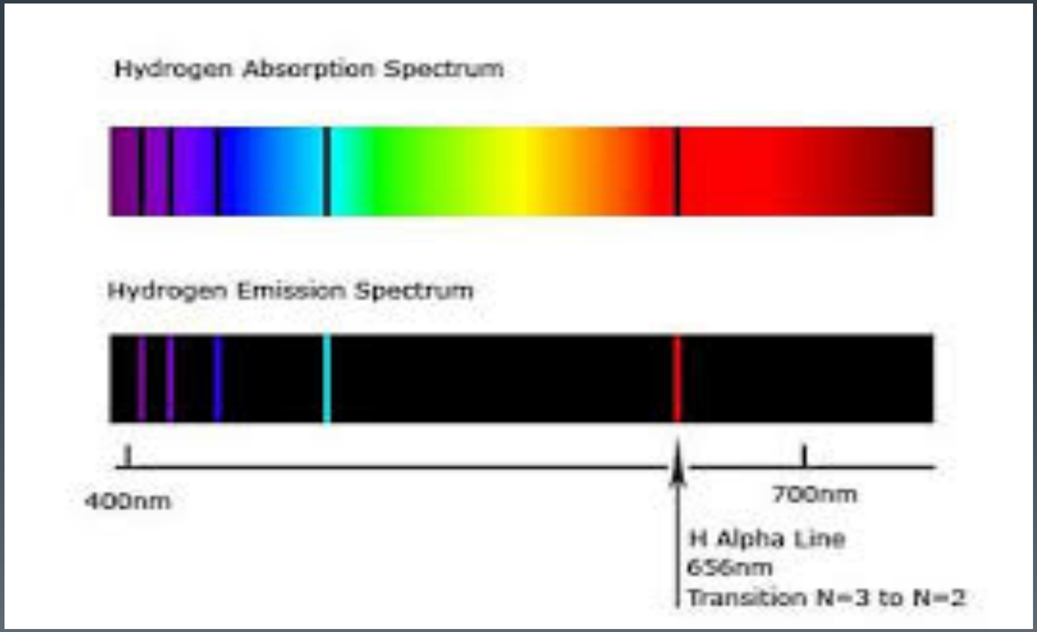


How to obtain absorption spectrum?

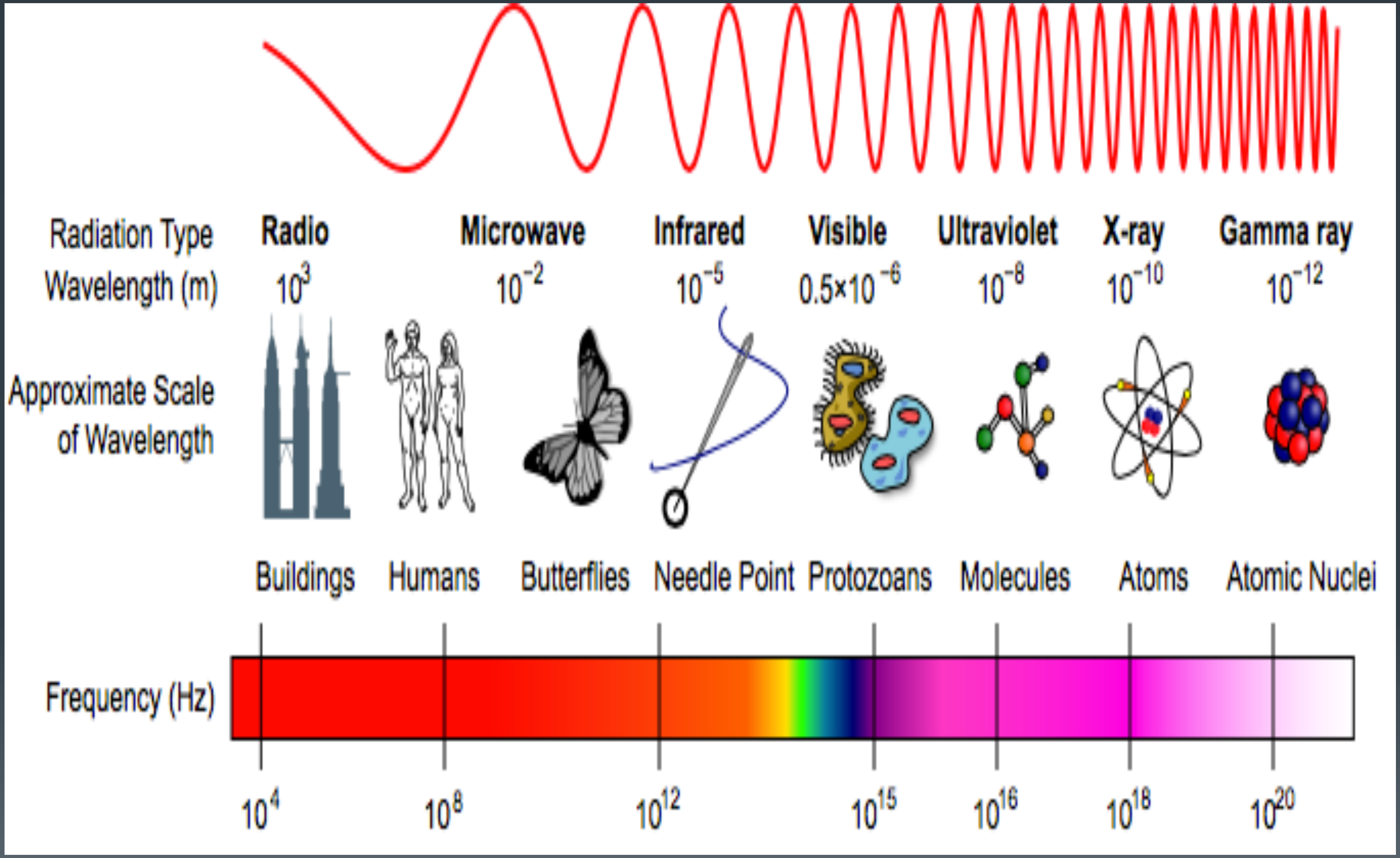
- **line spectrum** observed when a low-pressure gas undergoes an electric discharge. (Electric discharge occurs when the gas is subject to a potential difference that creates an electric field greater than the dielectric strength of the gas.)
- Observation and analysis of these spectral lines is called **emission spectroscopy**.
- This discrete line spectrum contrasts sharply with the continuous rainbow of colors seen when a glowing solid is viewed through the same instrument.
- The wavelengths contained in a given line spectrum are characteristic of the element emitting the light. *The simplest line spectrum is that for atomic hydrogen*.
- No two elements have the same line spectrum, this phenomenon represents a practical and sensitive technique for identifying the elements present in unknown samples.

How to obtain absorption spectrum?

- It is obtained by passing white light from a continuous source through a gas or a dilute solution of the element being analyzed.
- The absorption spectrum consists of a series of dark lines superimposed on the continuous spectrum of the light source.
- The absorption spectrum of an element has many practical applications.



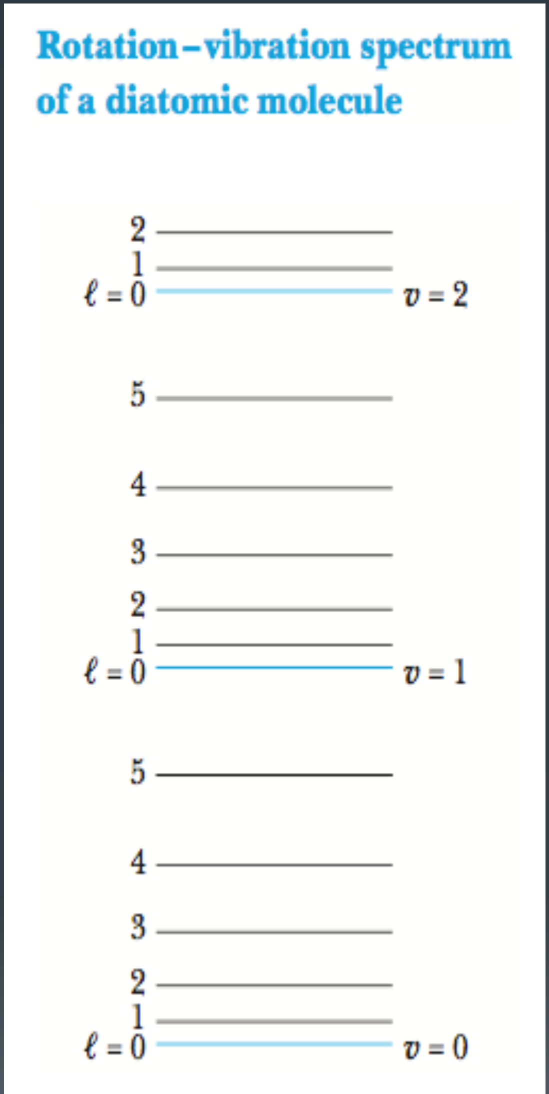
The absorption and emission spectrum for hydrogen.


Radiation Type
Wavelength (m)
Approximate Scale of Wavelength
Frequency (Hz)
Radio
Microwave
Infrared
Visible
Ultraviolet
X-ray
Gamma ray
10^{3}
10^{-2}
10^{-5}
0.5×10^{-6}
10^{-8}
10^{-10}
10^{-12}
Buildings
Humans
Butterflies
Needle Point
Protozoans
Molecules
Atoms
Atomic Nuclei
10^{4}
10^{8}
10^{12}
10^{15}
10^{16}
10^{18}
10^{20}

Molecular spectra

- A molecule can emit or absorb photons, with accompanying electronic transitions among the allowed energy levels of the molecule. The resulting emission or absorption spectrum is different for each molecule and acts as a sort of fingerprint of its electronic structure.
- Molecules also emit or absorb energy in ways not found in atoms. Molecules can rotate, storing energy in the form of kinetic energy of rotation, and they can vibrate, and so possess energy of vibration.

- A molecule rotates and vibrates simultaneously. To a first approximation, these motions are independent of each other



he rotation – vibration levels for a typical molecule. Note that the vibrational levels are separated by much larger energies so that a complete rotational spectrum can be associated with each vibrational level.

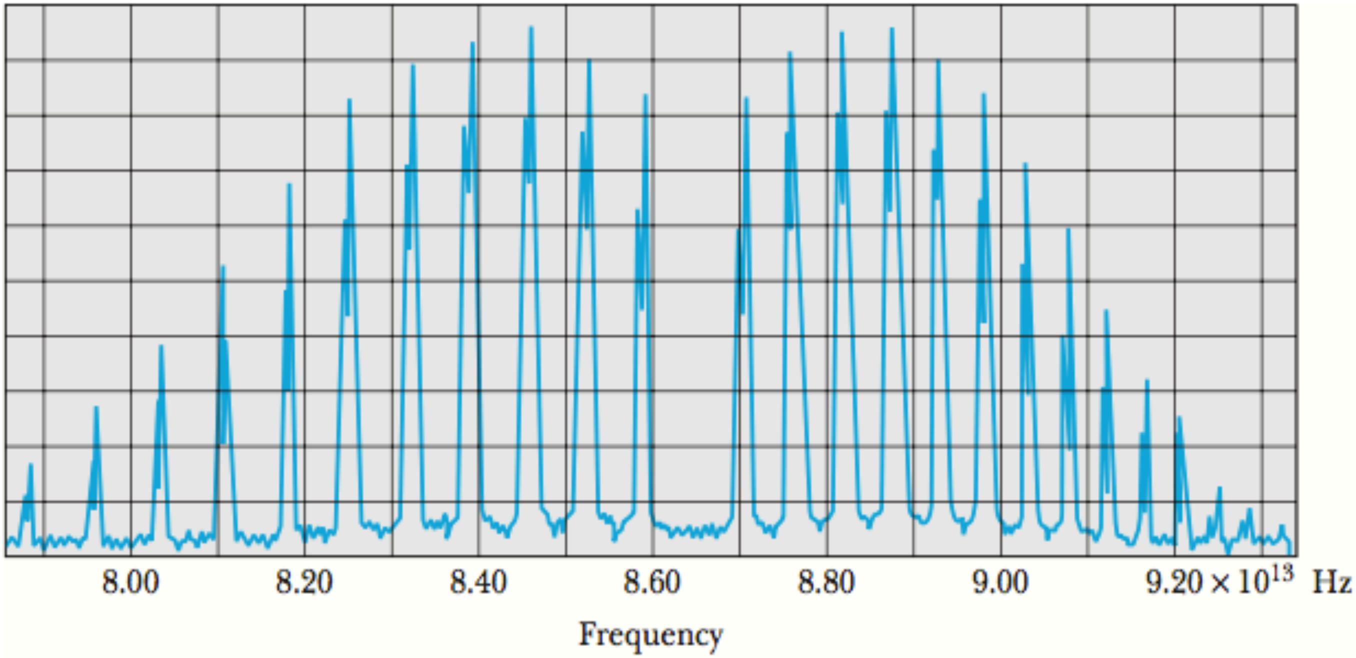


Figure 11.12 The absorption spectrum of the HCl molecule. Each line is split into a doublet because chlorine has two isotopes, ^{35}Cl and ^{37}Cl, which have different nuclear masses. (This is an adaptation of data taken by T. Faulkner and T. Nestrick at Oakland University, Rochester, MI.)