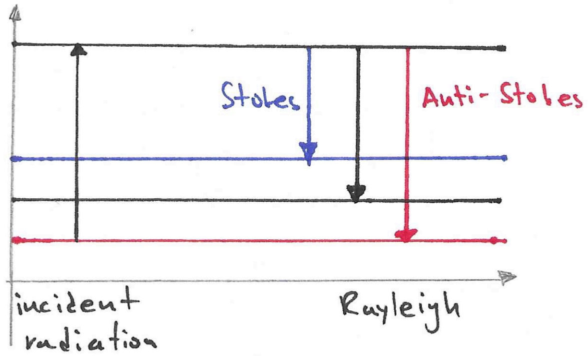
Raman Spectroscopy

- in absorption spectroscopy net absorption of radiation passing through sample is monitored since radiation can also stimulate emission of photons
- in Raman spectroscopy frequency of radiation scattered by molecules is analysed to determine changes in molecular states

frequency: ν wavenumber: $\tilde{\nu} = \frac{\nu}{c}$ wavelength: $\frac{c}{\nu}$

Bohr frequency condition: $h\nu = E_u - E_1$

- sample is exposed to monochromatic radiation so all incident photons are of same E
- most photons are scattered elastically (with no change in energy) called Rayleigh scattering
- 1 in 10^7 are scattered inelastically. Stokes scattering γ loose energy and in anti-Stokes scattering photon gains energy from the molecule
- this gives information about the molecular vibrations + rotations
- rotational, vibrational, electronic transitions
  (microwave, IR, UV/vis)



- Beer-Lambert Law
  ↳ when EM radiation passes through sample of length L and molar conc J the incident and transmitted intensities are

$$I = I_0 10^{-\varepsilon J L}$$

ε - molar absorption coefficient (extinction coefficient)

$[\varepsilon] = dm^3 mol^{-1} cm^{-1}$
or $m^2 mol^{-1}$ (mollar crossection)

- in gas samples Doppler broadening occours

$$\nu = \left(\frac{1-\frac{s}{c}}{1+\frac{s}{c}}\right)^{\frac{1}{2}} \nu_0$$

s - peed relative to an observer

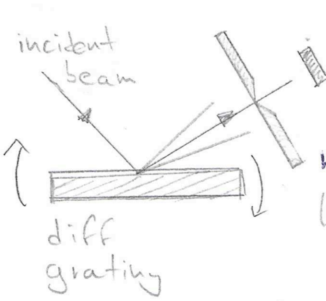
$\delta\nu_{obs}$ - doppler broadening

$$\delta\nu_{obs} = \frac{2\nu_0}{c}\left(\frac{2kT\ln 2}{m}\right)^{\frac{1}{2}}$$

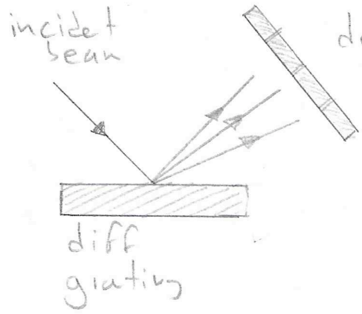
m - mass of molecule

- Lifetime broadening
  - ↳ molecules exist in states but the states change eg when molecules collide
  - ↳ lifetime of states: τ. schrödinger equation used to analyse states with lifetime τ gives energy E uncertain to the extent $\delta E \approx \frac{\hbar}{\tau}$ so spectral lines have uncertainty $\delta \frac{E}{h} = \frac{1}{2\pi\tau}$

    the shorter the lifetime the broader the line

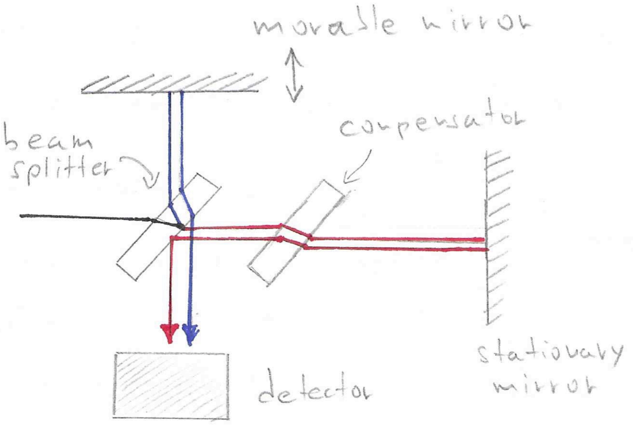
- 

monochromator (narrow slit)



polychronator (no slit)

- Fourier transform spectrometer
  - ↳ uses a Michelson interferometer



splits beam and movable mirror changes the path length of one of the beams to result in constructive or destructive interference of one wavelength component of the initial polychromatic beam

I - intensity of incident

$\tilde{I}$ - resultant intesity

$\tilde{\nu}$ - wavenumber

p - path length difference

$$\tilde{I}(p) = \sum_i I(\tilde{\nu})\,(1+\cos(2\pi\tilde{\nu}p))$$

- Raman spectroscopy setup: