

# Optical Spectroscopy Techniques

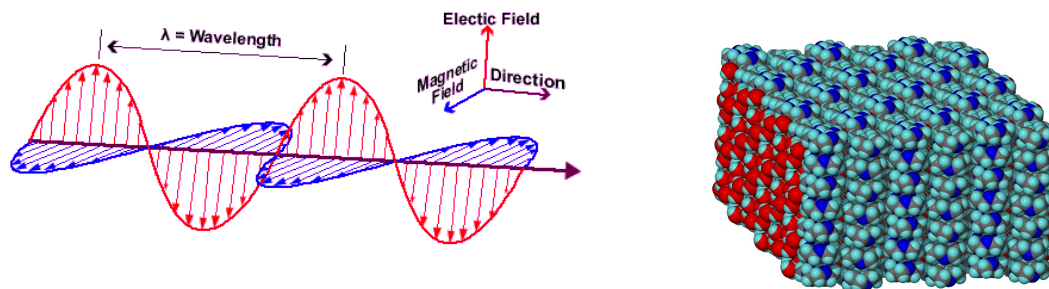
Advanced Solid State Physics, Fall 2010, ETH Zürich

26.11.2010, Runar Sandnes

# Outline

- What is optical spectroscopy?
- Why is optical spectroscopy relevant for solid state physics?
- General considerations on optical spectroscopy
- Ways to measure intensity as a function of frequency,  $I(\omega)$ 
  - Grating spectroscopy
  - Fourier Transform spectroscopy
- Raman spectroscopy
- Summary

# What is optical spectroscopy?



- Measuring the interactions between matter and electromagnetic radiation
  - Electric and magnetic responses or emissions
- Almost zero momentum transfer because of speed of light

$$v_p = \frac{\omega}{k} = c \quad k = \frac{\omega}{c} \rightarrow 0 \quad \Delta k \approx 0$$

- Advantages
  - Wide energy range
  - Able to test bulk properties

# What can optical spectroscopy be used for in solid state physics?

- Measure energy transitions in solids
  - Electronic bandwidth
  - Semiconductor bandgap
  - SDW / CDW / SC bandgap
  - Phonons
  - Plasma frequency
  - Magnons
  - Impurity states in semiconductors

# How can radiation give information about matter?

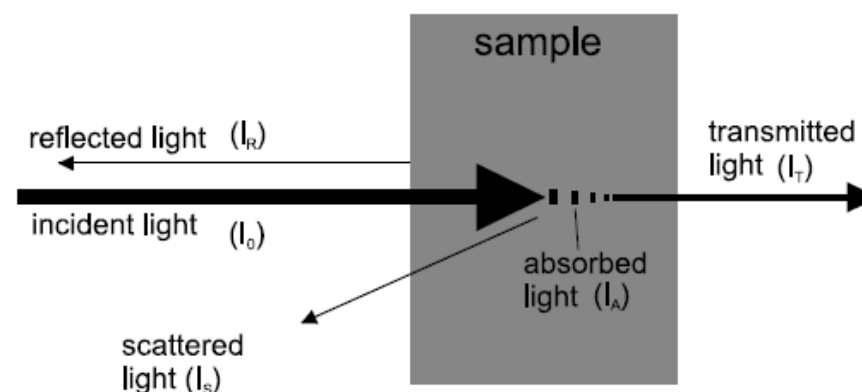
- Absorption spectroscopy

- Neglect scattering

$$I(\omega) \approx T(\omega) + R(\omega) + A(\omega)$$

- Metals

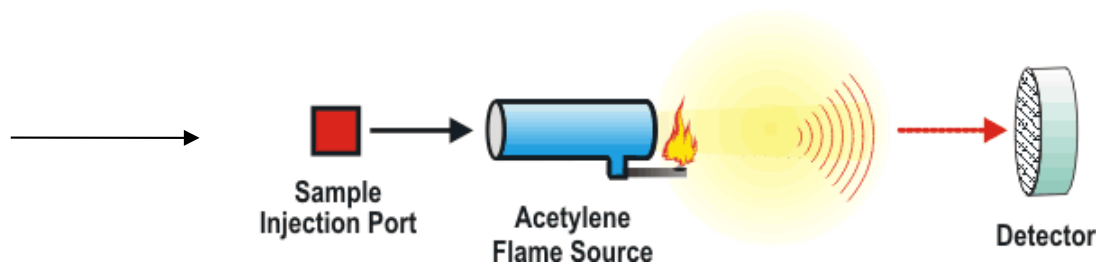
$$I(\omega) \approx R(\omega) + A(\omega)$$



$$I(\omega) = T(\omega) + R(\omega) + S(\omega) + A(\omega)$$

- Scattering spectroscopy

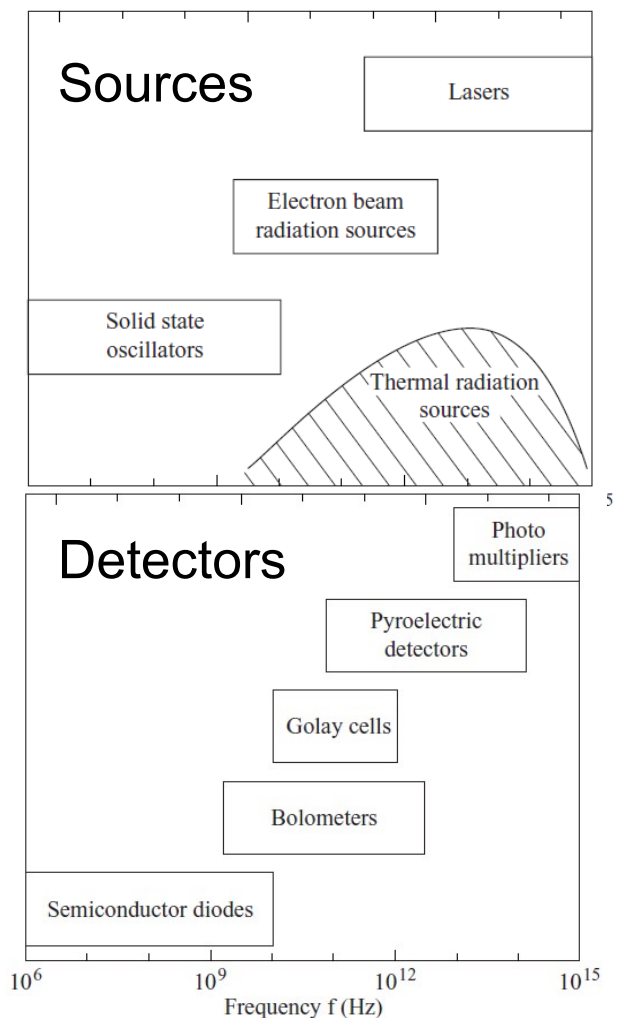
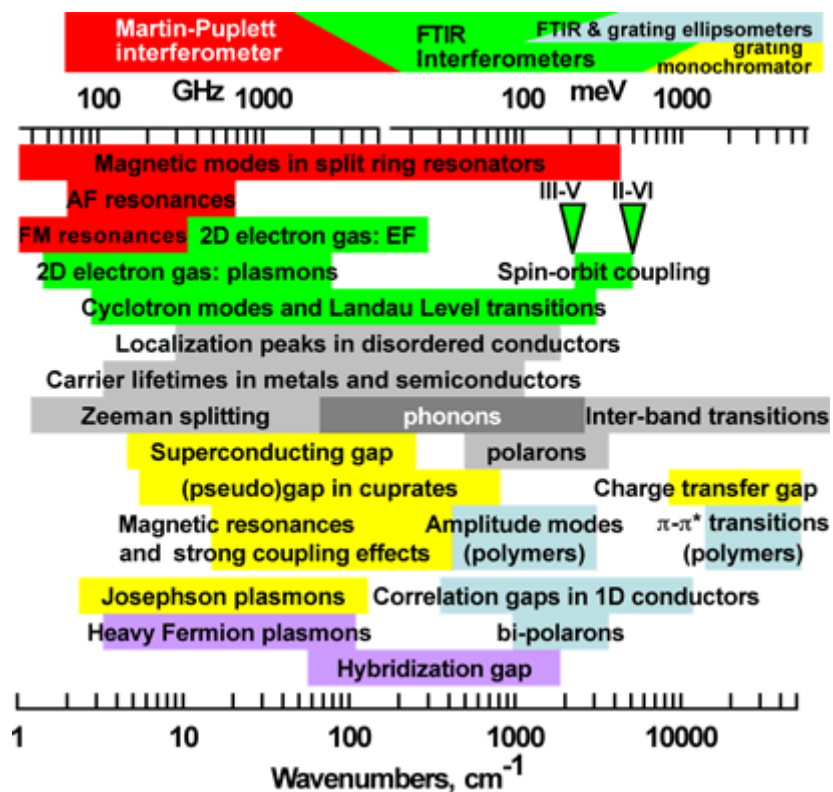
- Emission spectroscopy



# Which energy scales are relevant? Which frequency scales do these correspond to?

<b>Excitation mode</b>	<b>Energy</b>	<b>Frequency range</b>
Electronic bandwidth	1- 10 eV	VIS - UV
Plasma frequency	1- 10 eV	VIS - UV
Semiconductor bandgap	0.1- 5 eV	IR - VIS
SDW / CDW / SC bandgap	< 0.1 eV	FIR - IR
Phonons	~ 10 meV	FIR
Impurity states (semiconductors)	~ 10 meV	FIR
Pinned density wave	→ 0	RF

# Equipment and techniques have limited operational frequency ranges



# Response Functions

- Different techniques, different response functions
- All information about the sample's absorption and phase shifting of light can be gathered in **one** (complex) response function
- Always two components, corresponding to amplitude and phase of response

$$J(\omega) = \sigma(\omega)E(\omega)$$

$$D(\omega) = \varepsilon(\omega)E(\omega)$$

$$\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$$

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

$$N(\omega) = n(\omega) + ik(\omega)$$



# Kramers-Kronig Relations

- Two components of complex response functions
- Only one component measured by spectroscopy techniques
- **Kramers-Kronig relations:** the two components are related by causality

$$\sigma_1(\omega) = \frac{2}{\pi} \text{P} \int_0^{\infty} \frac{\omega' \sigma_2(\omega')}{\omega'^2 - \omega^2} d\omega'$$

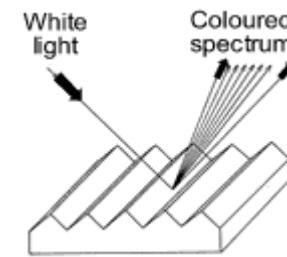
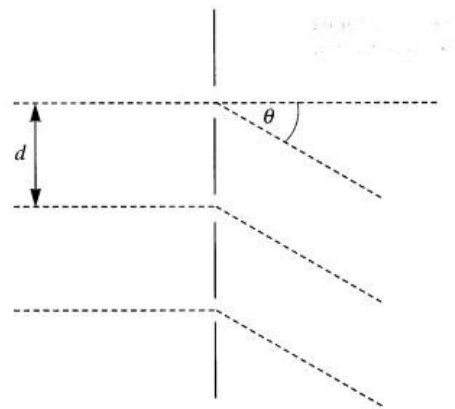
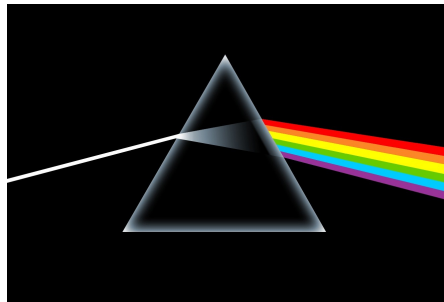
$$\sigma_2(\omega) = -\frac{2\omega}{\pi} \text{P} \int_0^{\infty} \frac{\sigma_1(\omega')}{\omega'^2 - \omega^2} d\omega'$$

$$\theta_r(\omega) = -\frac{2\omega}{\pi} \text{P} \int_0^{\infty} \frac{\ln \left| \sqrt{R(\omega')} \right|}{\omega'^2 - \omega^2} d\omega'$$

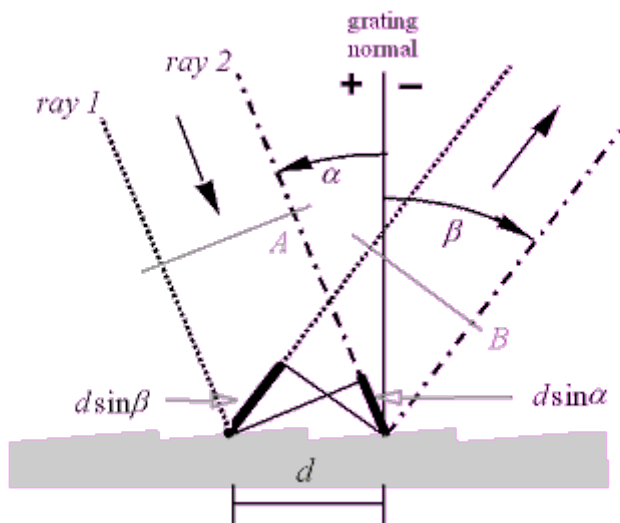
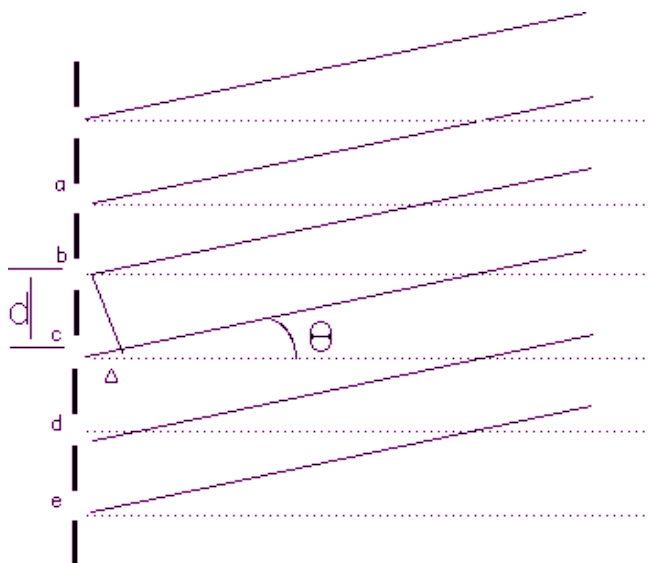
$$\mathfrak{K}(\omega) = \sqrt{R(\omega)} e^{i\theta(\omega)} = \frac{n - 1 + ik}{n + 1 + ik}$$

# Grating Spectroscopy

- Want to find  $R(\omega)$
- Need to decompose the reflectance into its frequency components
- One way to do this: use a dispersive element, such as a **prism** or a **grating**



# Grating Spectroscopy: Principle



- **Diffraction grating** with N slits

$$I = I_0 \left( \frac{\sin b}{b} \right)^2 \left( \frac{\sin Na}{\sin a} \right)^2$$

- Maximum when

$$d (\sin \alpha + \sin \beta) = m \lambda$$

( $m = \text{integer}$ )

- Blazed grating makes first order reflection dominant

$$d (\sin \alpha + \sin \beta) = \lambda \quad (m = 1)$$

# Grating Spectroscopy: Setup

- Selects the frequency components of the reflectance successively by turning the grating – obtain  $R(\omega)$
- Multiple gratings if wide range

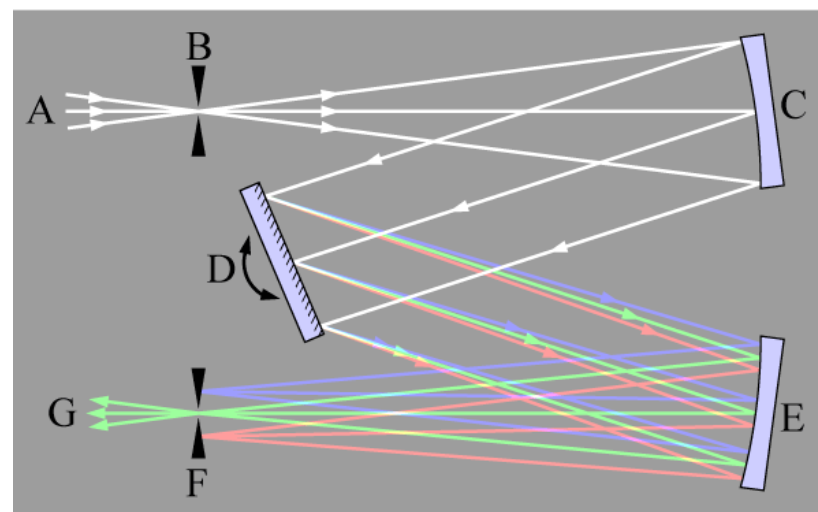
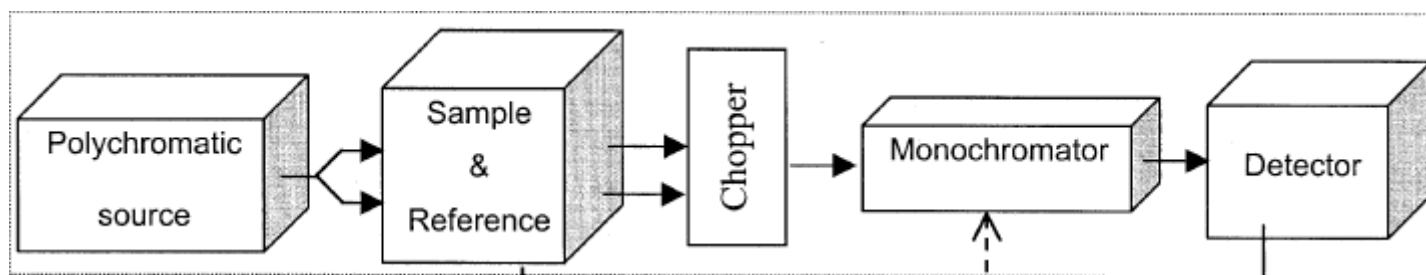


Fig: Czerny-Turner monochromator



# Grating Spectroscopy: Properties

- **Limitations**

Each frequency recorded individually – more time-consuming than FTS

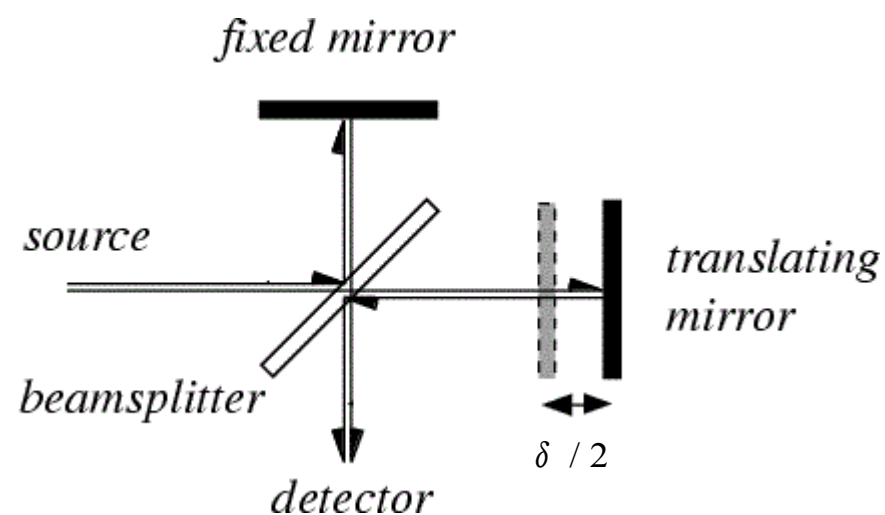
Not possible to make gratings for every frequency range

- **Frequency range**

UV, VIS, NIR, MIR (1 000 000 – 400 cm<sup>-1</sup>)

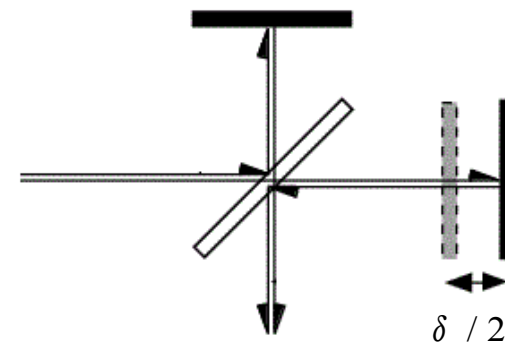
# Fourier Transform Spectroscopy

- Alternative way to measure the frequency dependence of a light beam,  $I(\omega)$  (for us,  $R(\omega)$ )
- **Michelson interferometer** to record  $I(\delta)$  - by Fourier transformation one then obtains  $I(\omega)$
- Faster than grating spectroscopy – determines the whole spectrum  $I(\omega)$  in one «scan»



$\delta$  ... path difference

# Fourier Transform Spectroscopy: Principle



- After Michelson interferometer:

$$E(k) = E_1 + E_2 = E_0(k) \{ \exp i[kx - \omega t] + \exp i[k(x + \delta) - \omega t] \}$$

$$I(\delta, k) \propto I_0(k) [1 + \cos(k\delta)]$$

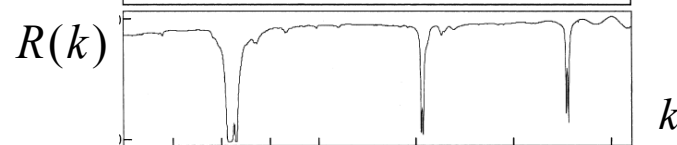
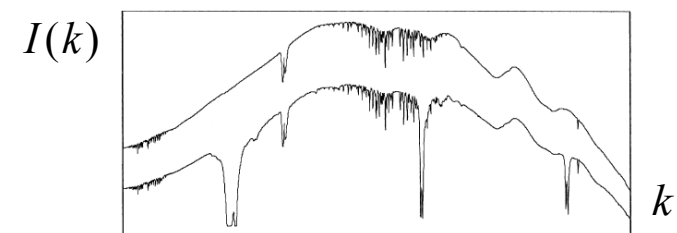
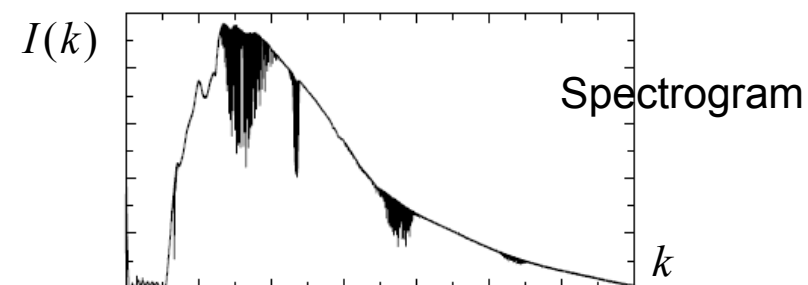
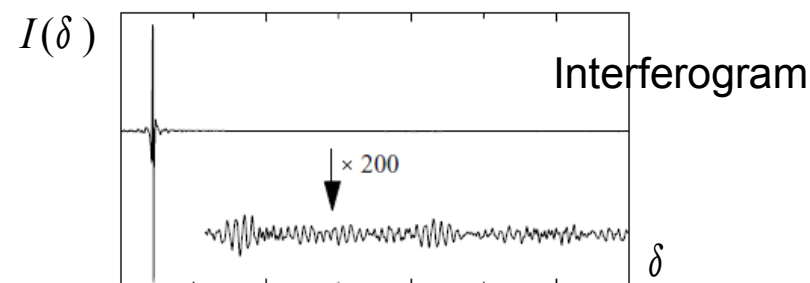
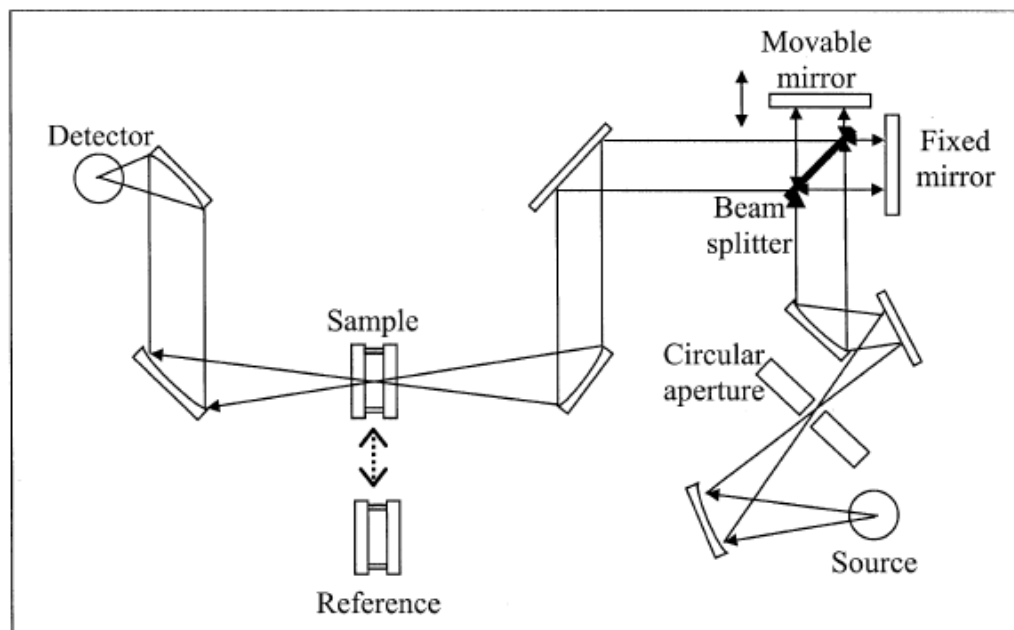
$$I(\delta) \propto \int_0^{\infty} I_0(k) [1 + \cos(k\delta)] dk = \int_0^{\infty} I_0(k) dk + \int_0^{\infty} I_0(k) \cos(k\delta) dk$$

$$\{ I(\delta) - I(\delta = 0) \} \propto \int_0^{\infty} I_0(k) \cos(k\delta) dk \quad \text{Cosine Fourier Transform of } I_0(k)$$

$$I_0(k) \propto \int_0^{\infty} \{ I(\delta) - I(\delta = 0) \} \cos(k\delta) dk$$

→ Convert to  $I(\omega)$

# Fourier Transform Spectroscopy: Principle



Reflectance



# Fourier Transform Spectroscopy: Properties

- **Advantages**

High speed due to ability to obtain full spectrum in one scan

High resolution due to precise mirror displacement technology

- **Limitations**

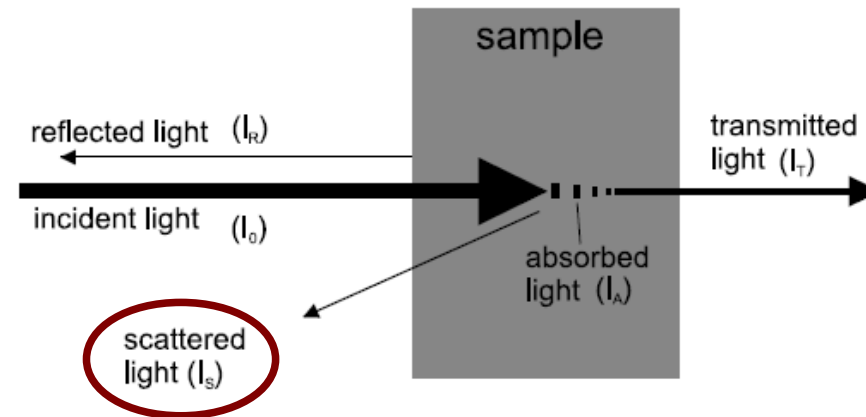
Limited mainly by availability of broadband sources in the low frequency range

- **Frequency range**

VIS to FIR (40 000 – 20 cm<sup>-1</sup>)

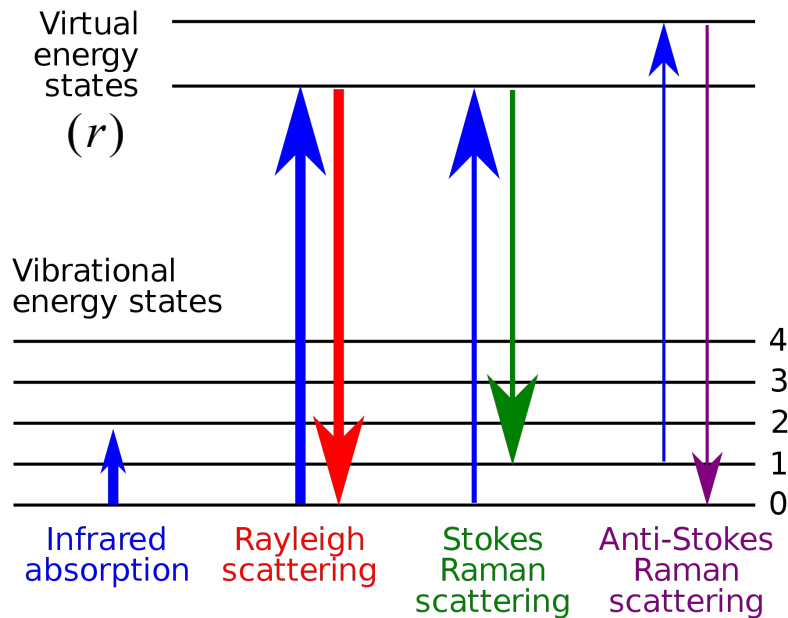
Typical use: Infrared - «FTIR»

# Raman Spectroscopy



- Measures the **inelastically scattered** light intensity
- Change in frequency of the inelastically scattered light interpreted as an energy transition in the sample
- **Complementary** to absorption studies
- In chemistry: studies vibrational and rotational modes in molecules
- In **solid state physics**: probe phonons, plasmons, magnons and other low-frequency excitation modes

# Raman Spectroscopy: QM Theory



- QM perturbation theory

$$P_{nm} = \int \psi_m^* P \psi_n d\tau$$

$$P_{nm} = \frac{1}{\hbar} \sum_r \left( \frac{M_{nr} M_{rm}}{\omega_{rn} - \omega_0} + \frac{M_{nr} M_{rm}}{\omega_{rm} - \omega_0} \right) E$$

$P_{nm}$ ... Induced electric moment (matrix element)

$\omega_0$ ... Electric field frequency

$\omega_{rn,rm}$ ... Frequency difference, state r and n / m

$M_{nr,rm}$ ... Transition moment, state r and n / m

# Raman Spectroscopy: Classical Theory

- QM transition moments  $M_{nr,rm}$  not known in most cases
- Classical treatment in terms of **non-linear polarizability**
- Shows that a Raman active excitation mode must be accompanied by a change in polarizability

$$P = \epsilon_0 \chi E$$

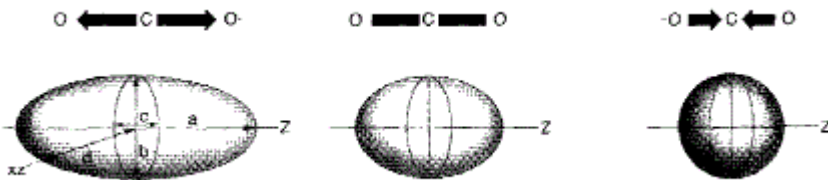
$$\chi = \chi_0 + \frac{\partial \chi}{\partial z} dz + \dots \approx \chi_0 + \frac{\partial \chi}{\partial z} dz$$

$$E = E_0 \cos(\omega t)$$

$$z = z_0 \cos(\omega_m t)$$

$$P = \epsilon_0 \chi_0 E_0 \cos(\omega t)$$

$$+ \frac{\partial \chi}{\partial z} \frac{\epsilon_0 E_0 z_0}{2} [\cos(\omega - \omega_m)t + \cos(\omega + \omega_m)t]$$



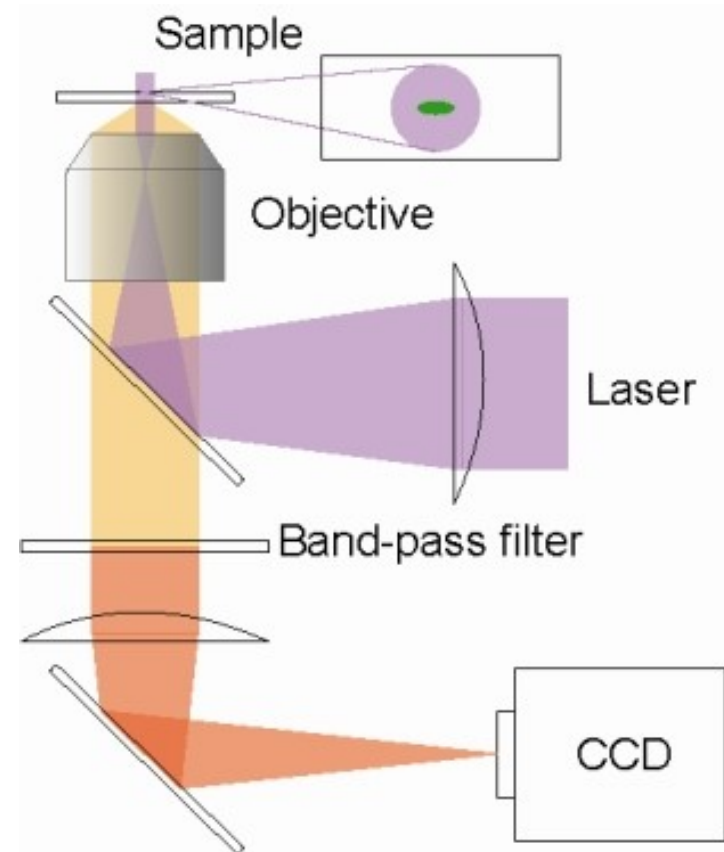
# Raman Spectroscopy: Setup

- Raman scattered light has very low intensity

$$I_{scattered} \approx 10^{-5} I_{incoming}$$

$$I_{Raman(inelastic)} \approx 10^{-2} I_{scattered}$$

- Filter out Rayleigh frequency (= laser frequency)
- Numerous variations: Surface-Enhanced RS, Resonance RS, Stimulated RS, ...



# Raman Spectroscopy: Results

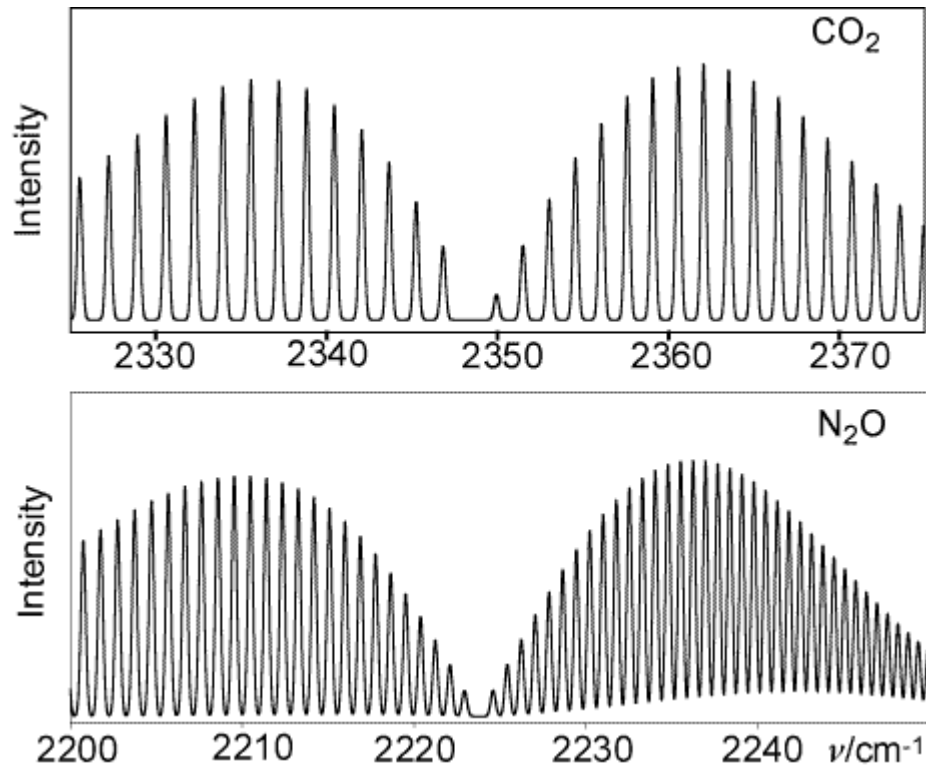


Fig: Infrared vibration-rotation bands of CO<sub>2</sub> and N<sub>2</sub>O.

- Raman spectra are symmetric about the Rayleigh (laser) frequency
- Ratio of Anti-Stokes to Stokes scattering is given by

$$\frac{I_{Anti-Stokes}}{I_{Stokes}} = \frac{(\omega + \omega_m)^4}{(\omega - \omega_m)^4} e^{-\frac{\hbar\omega}{kT}}$$

# Raman Spectroscopy: Properties

- Probed modes must have a nature which leads to a **varying polarizability** – i. e. vibrations, rotations, phonons
- **Complementary** to absorption studies (photon energy transfer processes differ → some frequencies are special to Raman, some to absorption)
- Special equipment needed for detecting the low inelastic scattering intensity → many different Raman techniques
- Very low frequency modes hard to detect because of filtering out of the Rayleigh frequency
- **Frequency range**  
MIR to FIR (10 000 – 10 cm<sup>-1</sup>)

# Summary

- Optical spectroscopy gives information about energy transitions in solids (bandgaps, phonons, plasmons, magnons, impurity states, ...)
- The whole frequency spectrum is important, and different ranges require different techniques and instruments
- If reflectance is measured over a wide frequency range, Kramers-Kronig relations can be used to determine one of the (interconvertible) complex response function
- Ways to measure  $I(\omega)$  : Grating spectroscopy, Fourier Transform spectroscopy
- Raman spectroscopy measures inelastic scattering and is complementary to absorption studies