Optical methods in chemistry
or
Photon tools for chemical sciences

Session 8:

Course layout – contents overview and general structure

- Introduction and ray optics
- Wave optics
- Beams
- From cavities to lasers
- More lasers and optical tweezers
- From diffraction and Fourier optics
- Microscopy
- **Spectroscopy**
- Electromagnetic optics
- Absorption, dispersion, and non-linear optics
- Ultrafast lasers
- Introduction to x-rays
- Summary

Going towards applications:

However, still focus on some concepts

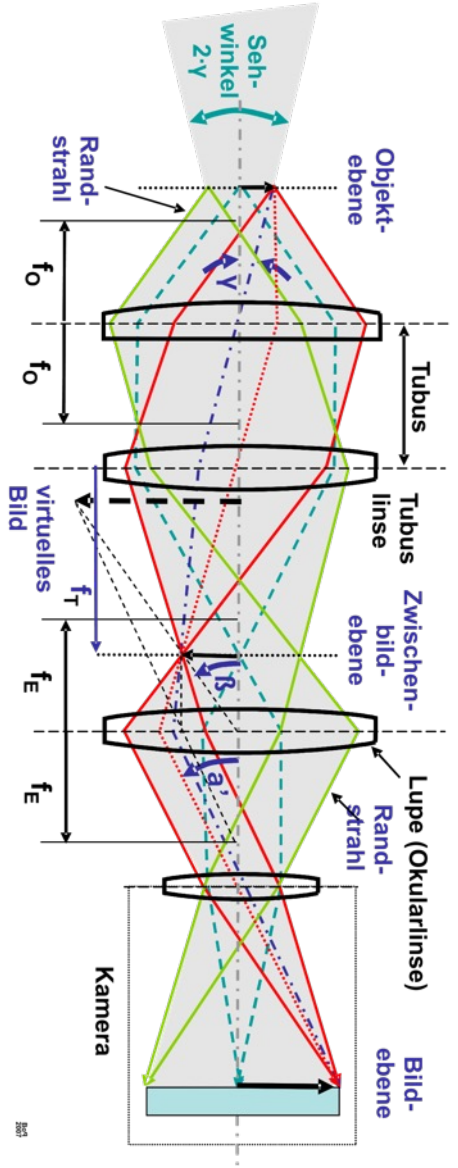
Microscopy – Manipulation - Spectroscopy

Remember: Microscopy

Classical

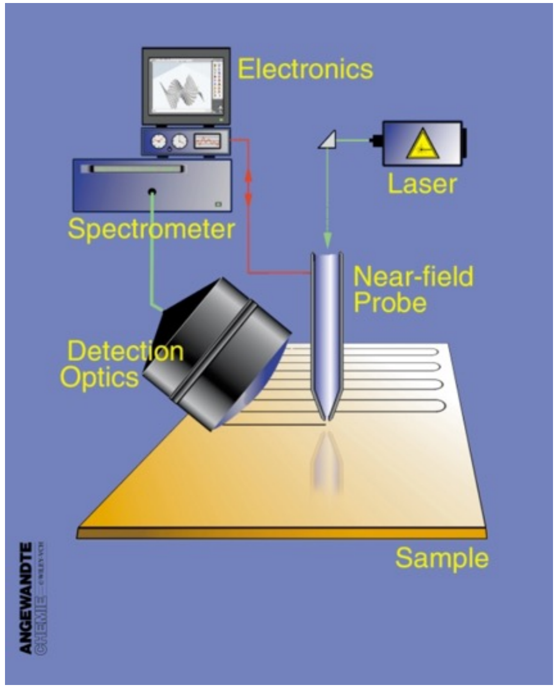
↳ Zernike / phase contrast

Classical microscope



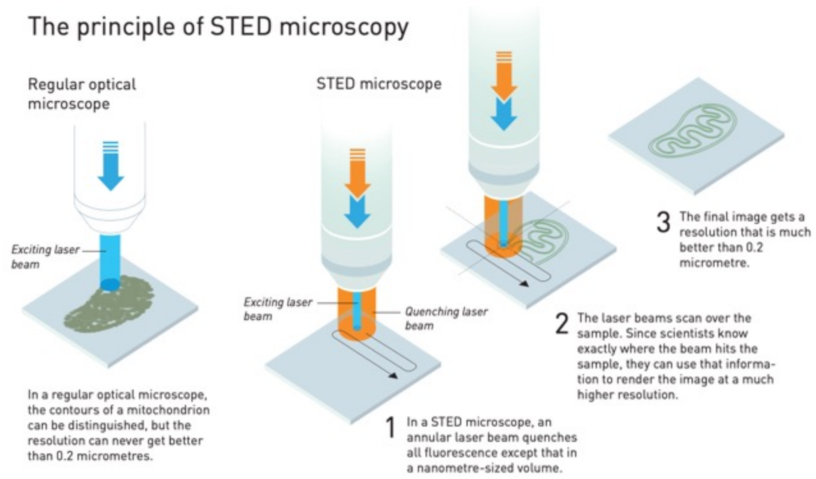
Instead of forming image → Scanning

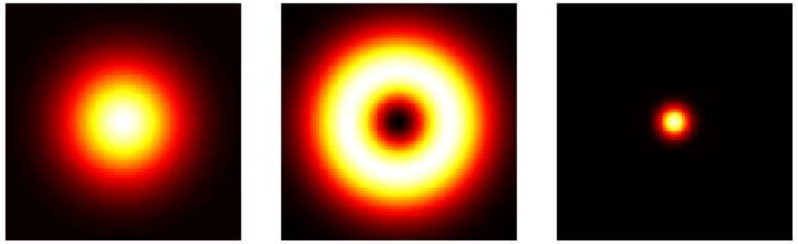
Near-field approaches



Overlap two beams/modes

Stimulated emission depletion approach

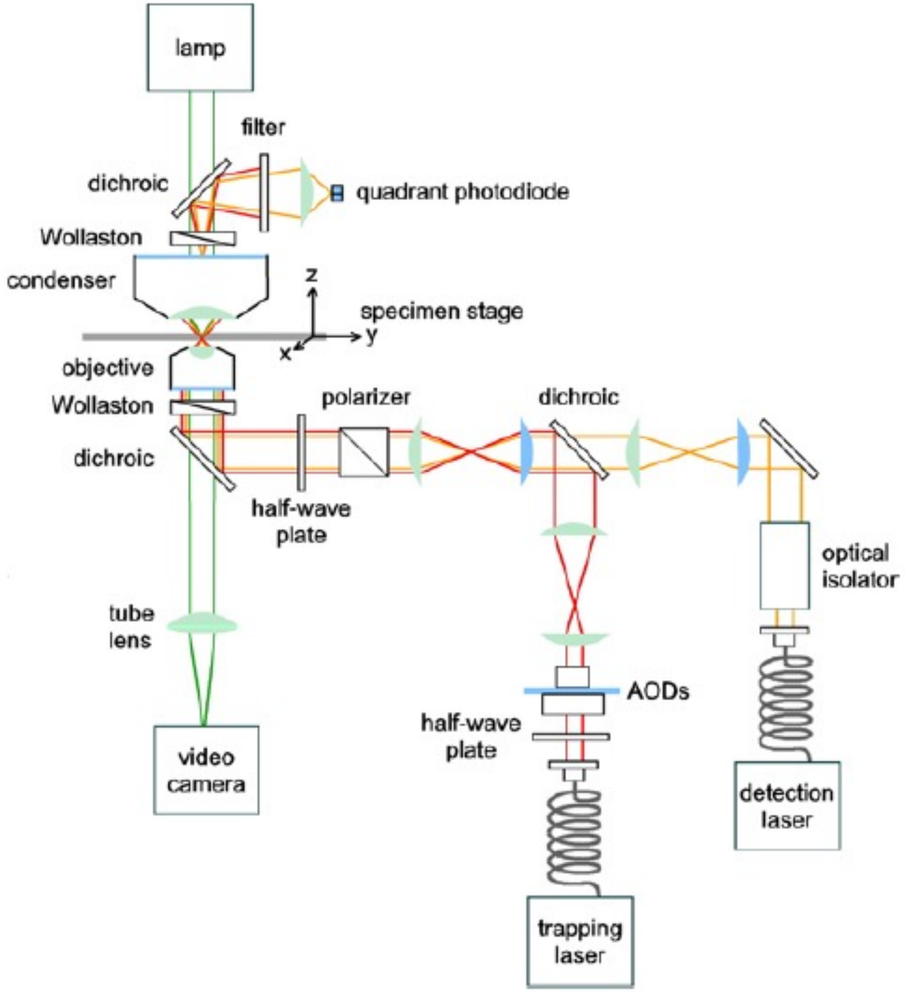




⇒ Appreciate concepts → combination of optic technology advances

Remember: Manipulation

Manipulation of particles: optical tweezers



→ new applications & opportunities for lasers

→ fundamental considerations

photon → momentum

+ Gaussian beam → trap

Today: Spectroscopy

- Molecular symmetry
- Rotational spectroscopy
- Vibrational spectroscopy
- Electronic spectroscopy

I assume (I know) you have dedicated lessons about these topics, including Quantum Chemistry, Spectroscopy, etc

This course is Optical Methods in Chemistry.

Therefore I will focus on concepts and approaches based on the material discussed.

Characteristic fingerprints of a molecule: rotational, vibrational, electronic transitions

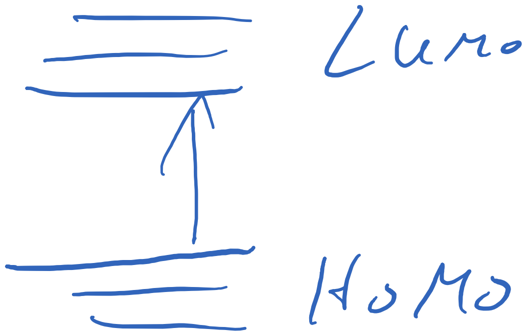
CO_2

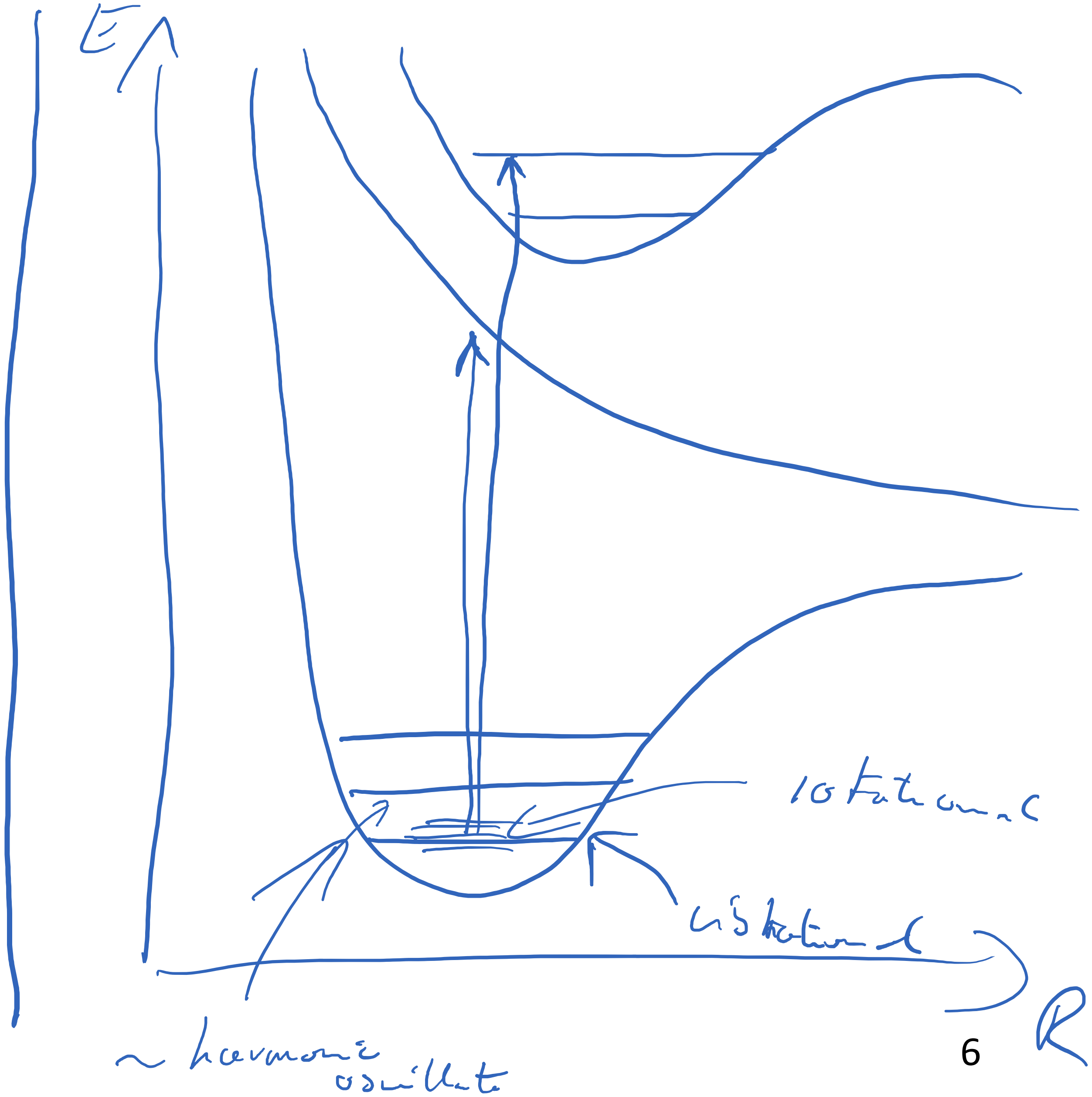
$O = C = O$

Rotation

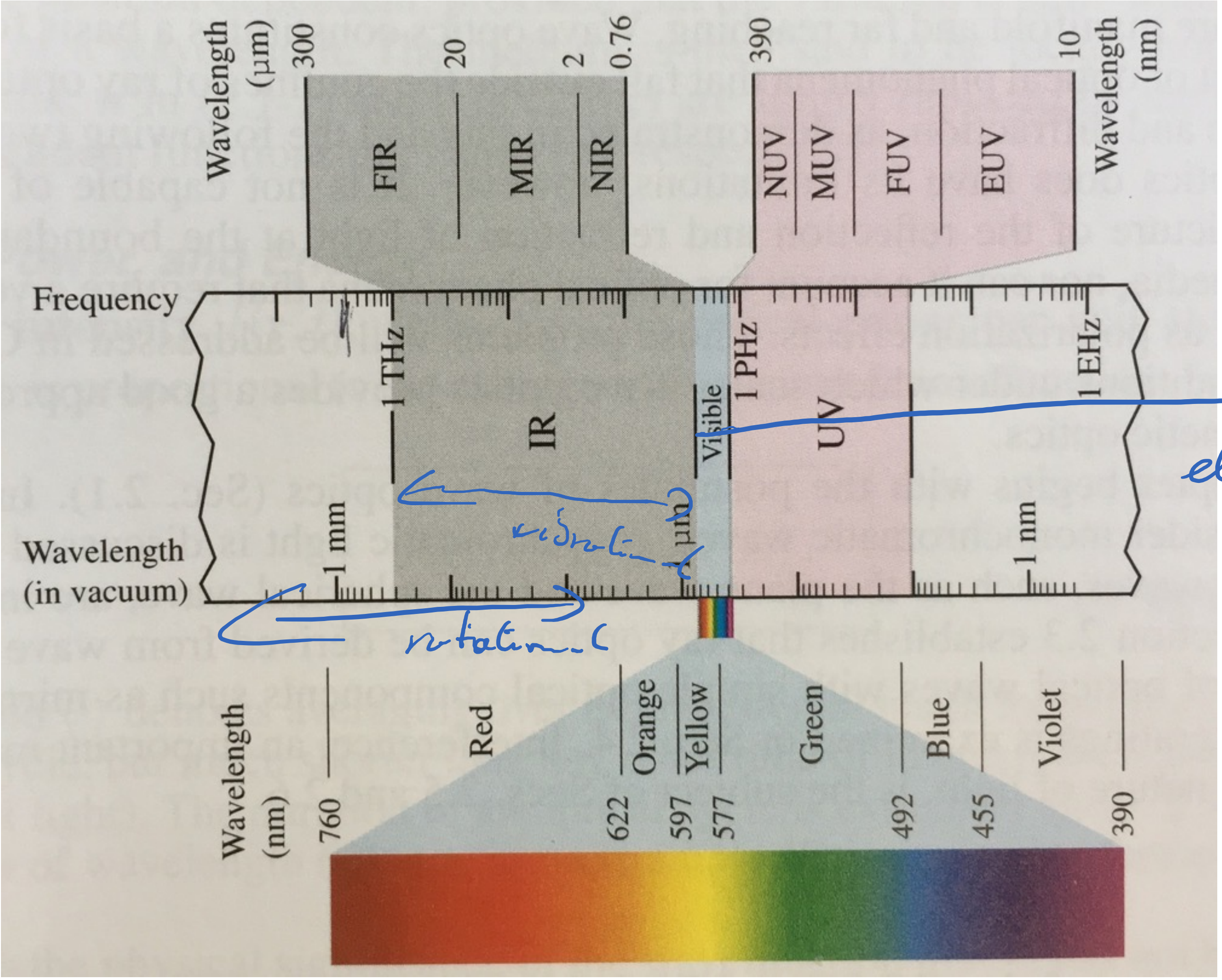
Vibrations

Electronic





A quick reminder about electromagnetic spectrum



electronic →

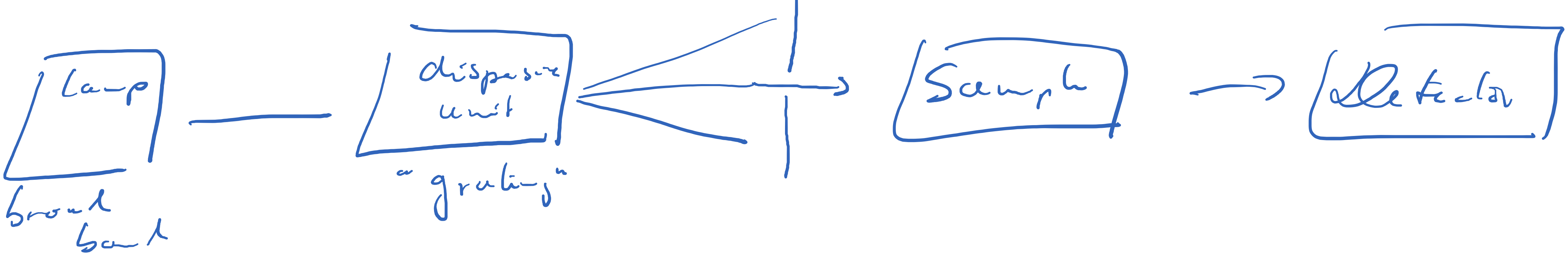
Homo-Lumo
1– 10 eV

Core-level
100 – keV

vibrational excitation → good fingerprint of molecules
technically accessible

The “classic approach” to spectroscopy

Version 1 ~~Version 2~~

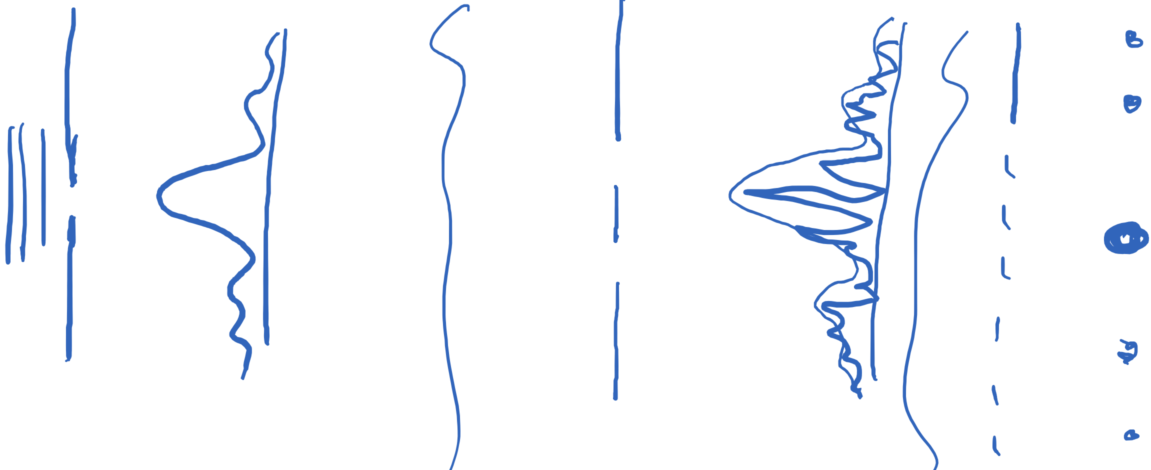


Version

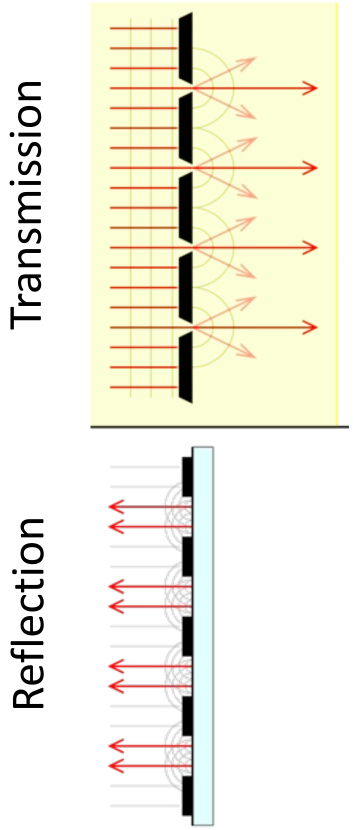
"one wavelength at a time"

Short note on gratings

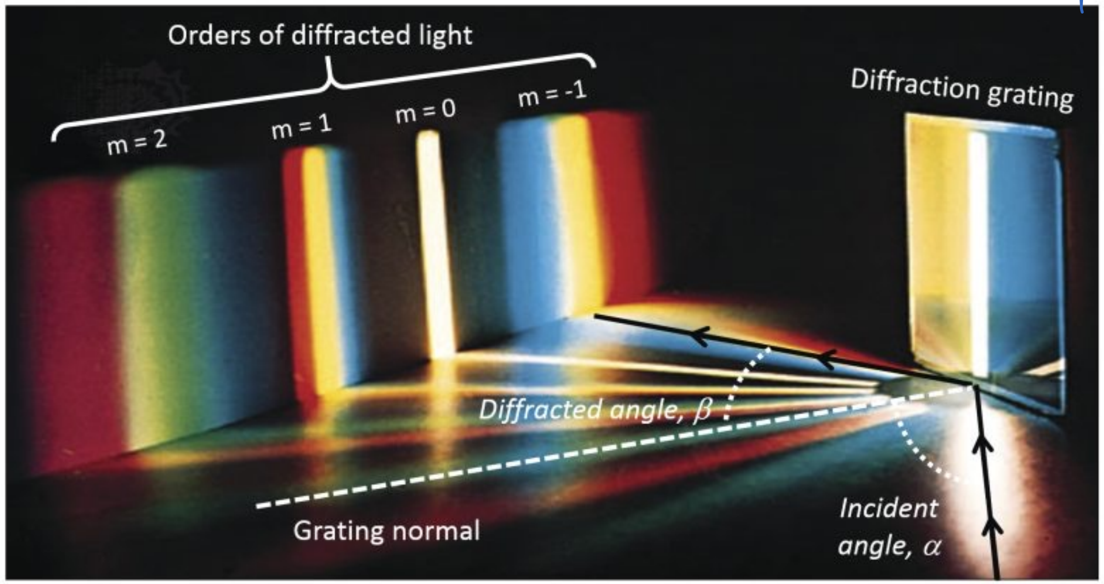
- Remember single slit, double slit, Babinets Theorem
- Grating is extension.



Amplitude grating



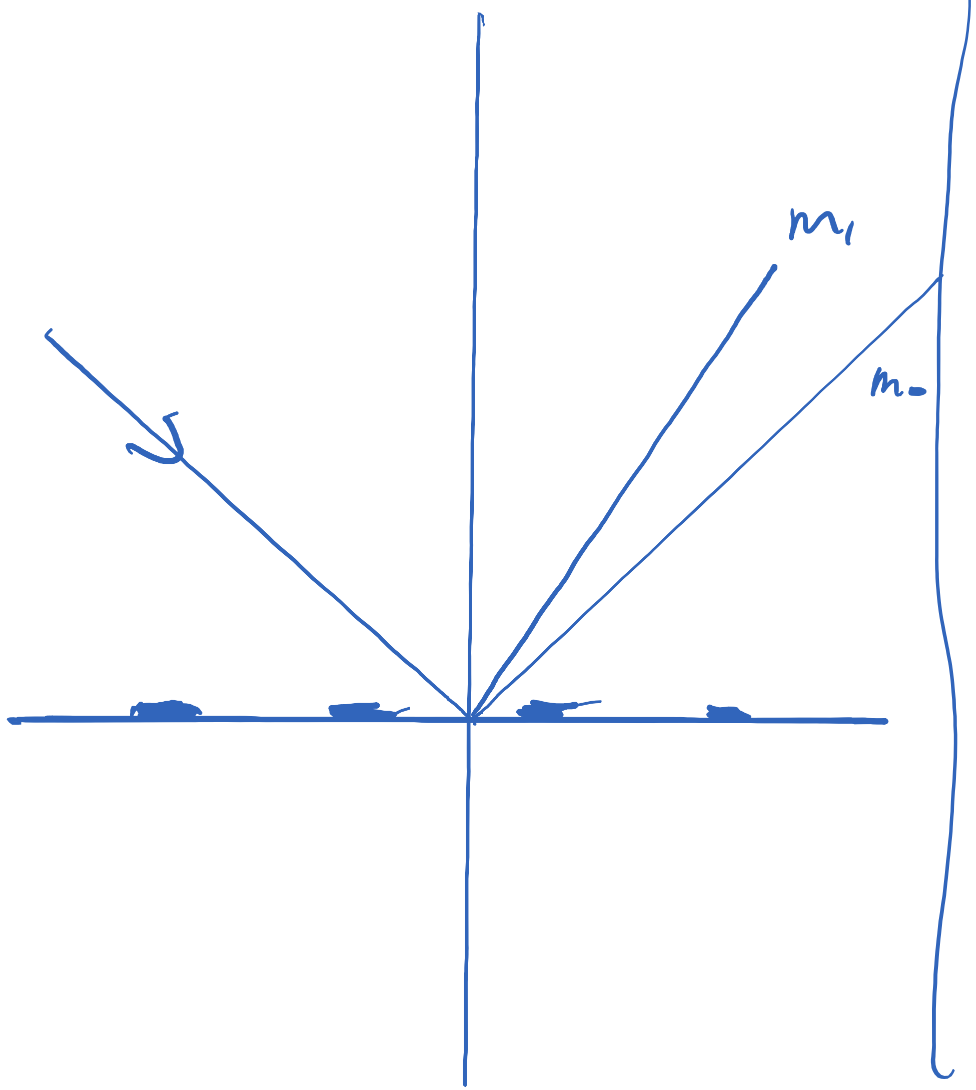
$$m\lambda = d_G(\sin\alpha + \sin\beta_m)$$

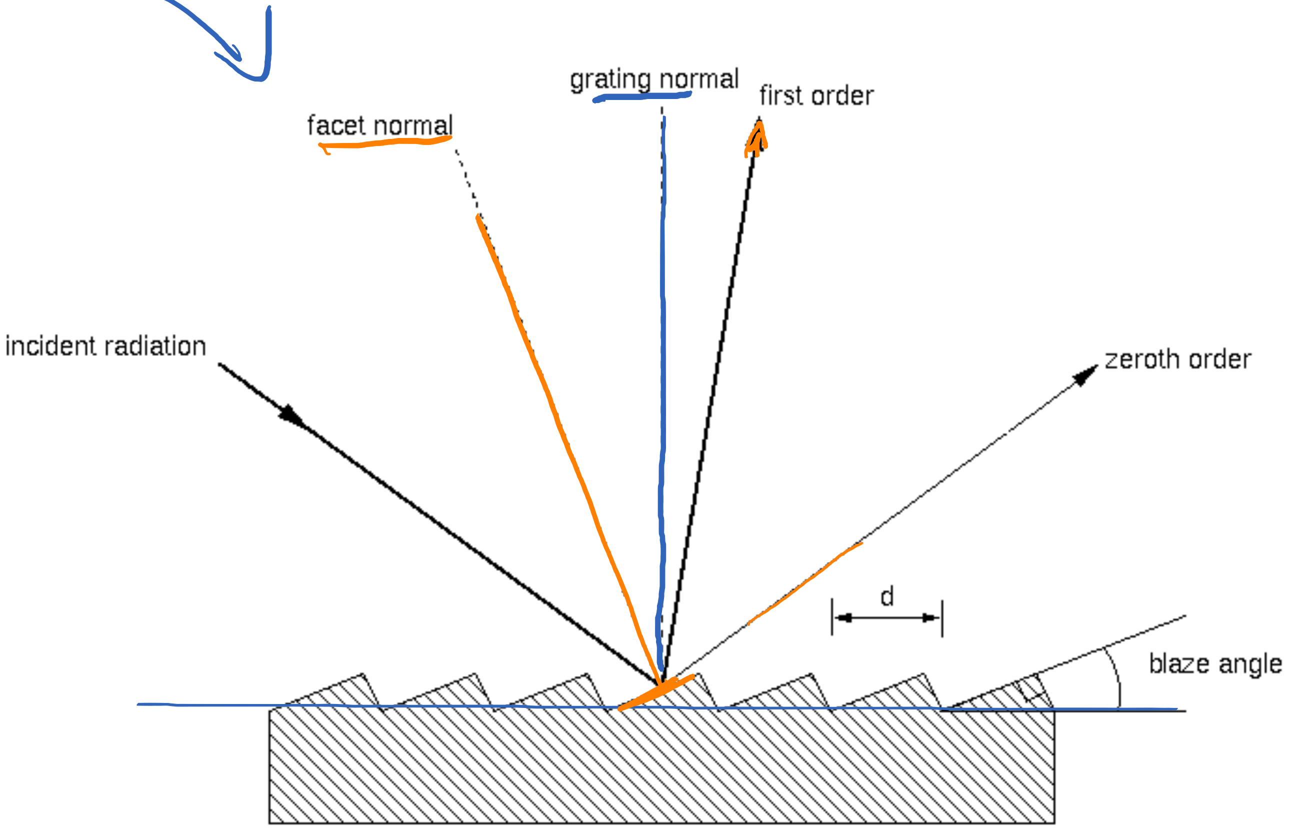


https://www.newport.com/n/diffraction-grating-physics

https://de.wikipedia.org/wiki/Optisches_Gitter#/media/Datei:Gittertypen.svg

Blazed grating





Littrow configuration:

Incident angle = diffraction order

→ Laser cavity

Grating spectrometer

Common use in (far) infrared spectroscopy not restricted to this regime
Note strong absorption of water, work in "dry conditions"
Excitation source can be mercury discharge lamp

Sources in lab setting

- arc lamps
- "black body" emitters
  ↳ could be a classic light bulb
- of course nowadays tunable lasers

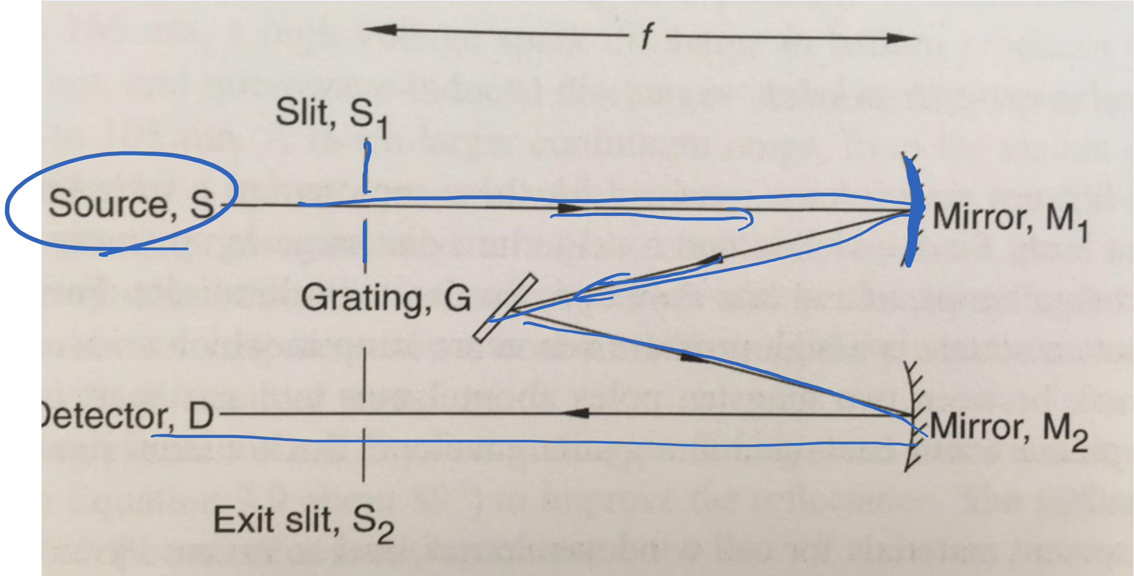


Figure 3.17 The Czerny–Turner grating mounting

Spectrophotometer

Depending on excitation source from IR to visible to near-uv

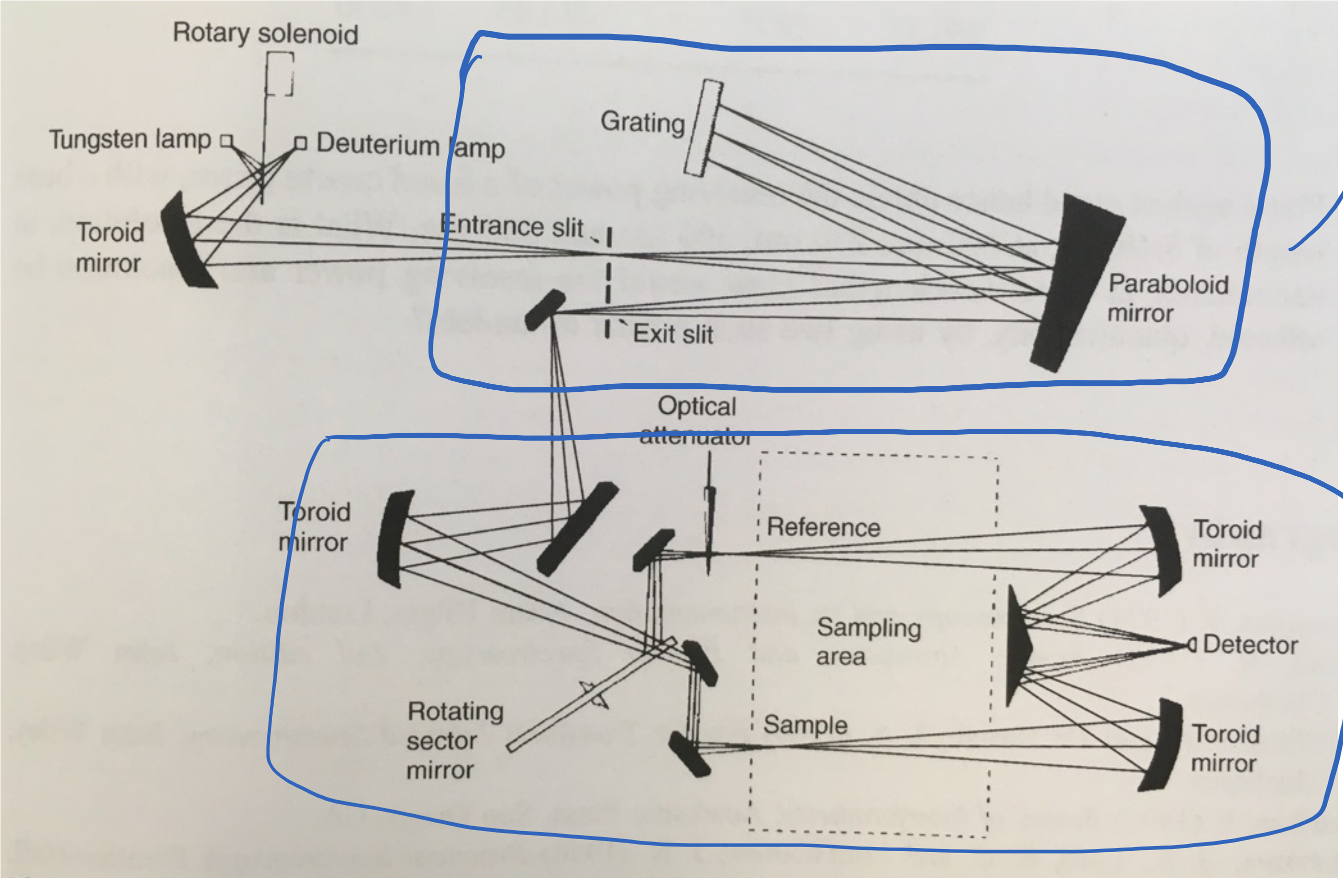


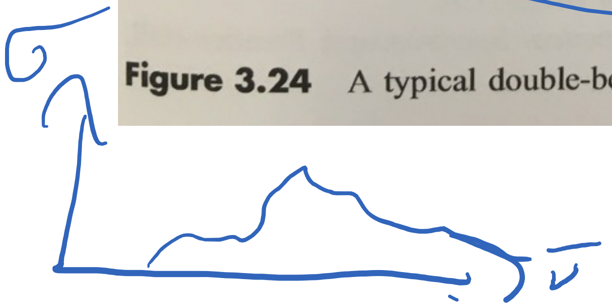
Figure 3.24 A typical double-beam recording visible and near-ultraviolet spectrophotometer

Monochromator

Measurement

absorption

$$\frac{I_{sample}(h\nu)}{I_0(h\nu)} \Rightarrow$$



Alternative approach: Fourier Transform (Infrared) Spectrometer)

- Not a dispersive measurement but based on interferometry
- Use all wavelength at the same time
- Manipulation in x - cm (real space) to get information in wave numbers x^{-1} – cm^{-1} (frequencies)
- Measure interferogram, Fourier transform into spectrum

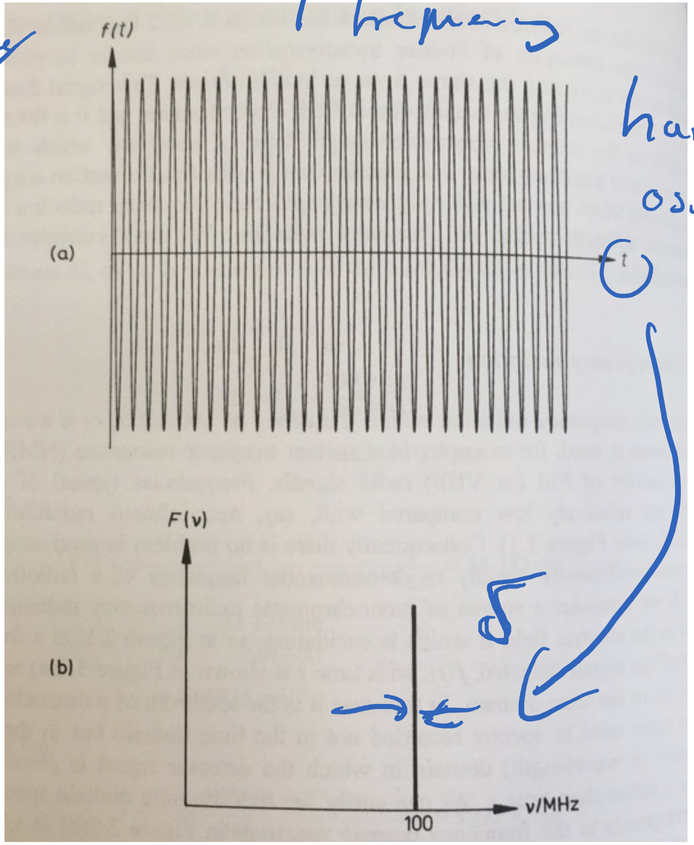
Broad Band source → Interferometer → Sample → Detector → Computer → Spectra

Remember some properties of Fourier Transform

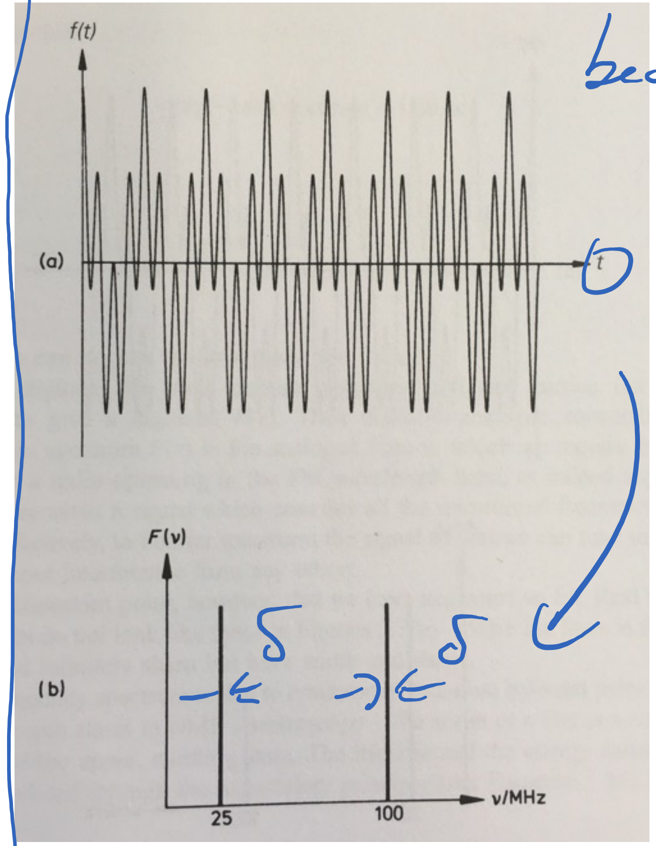
2 frequencies

time

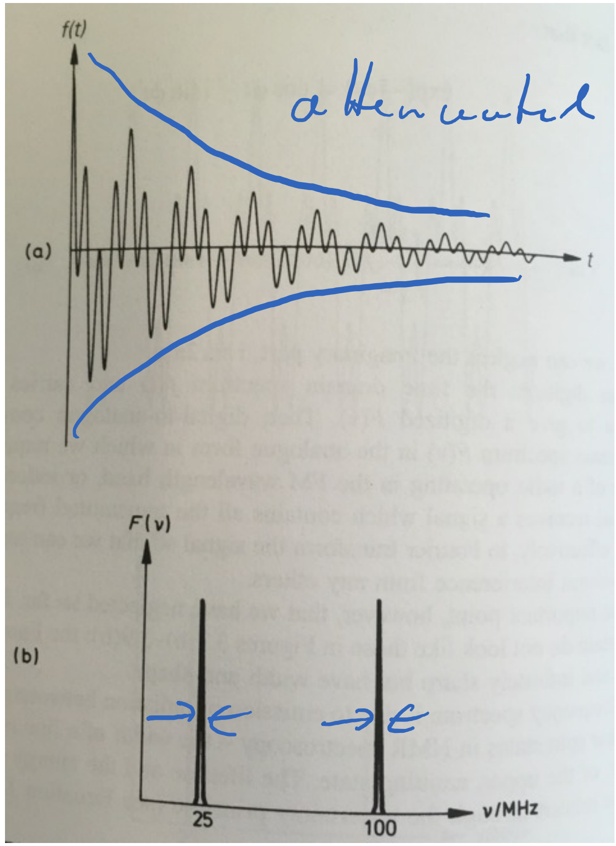
1 frequency



harmonic oscillator



beating



attenuated

δ δ δ

1 frequency

2 frequencies

line width

uncertainty E,t

Basics of Michelson interferometer (mono)

mono light
equal path →
Constructive

=

shifted $\lambda/2$

= $\emptyset$

Constructive
$\Delta = n\lambda$

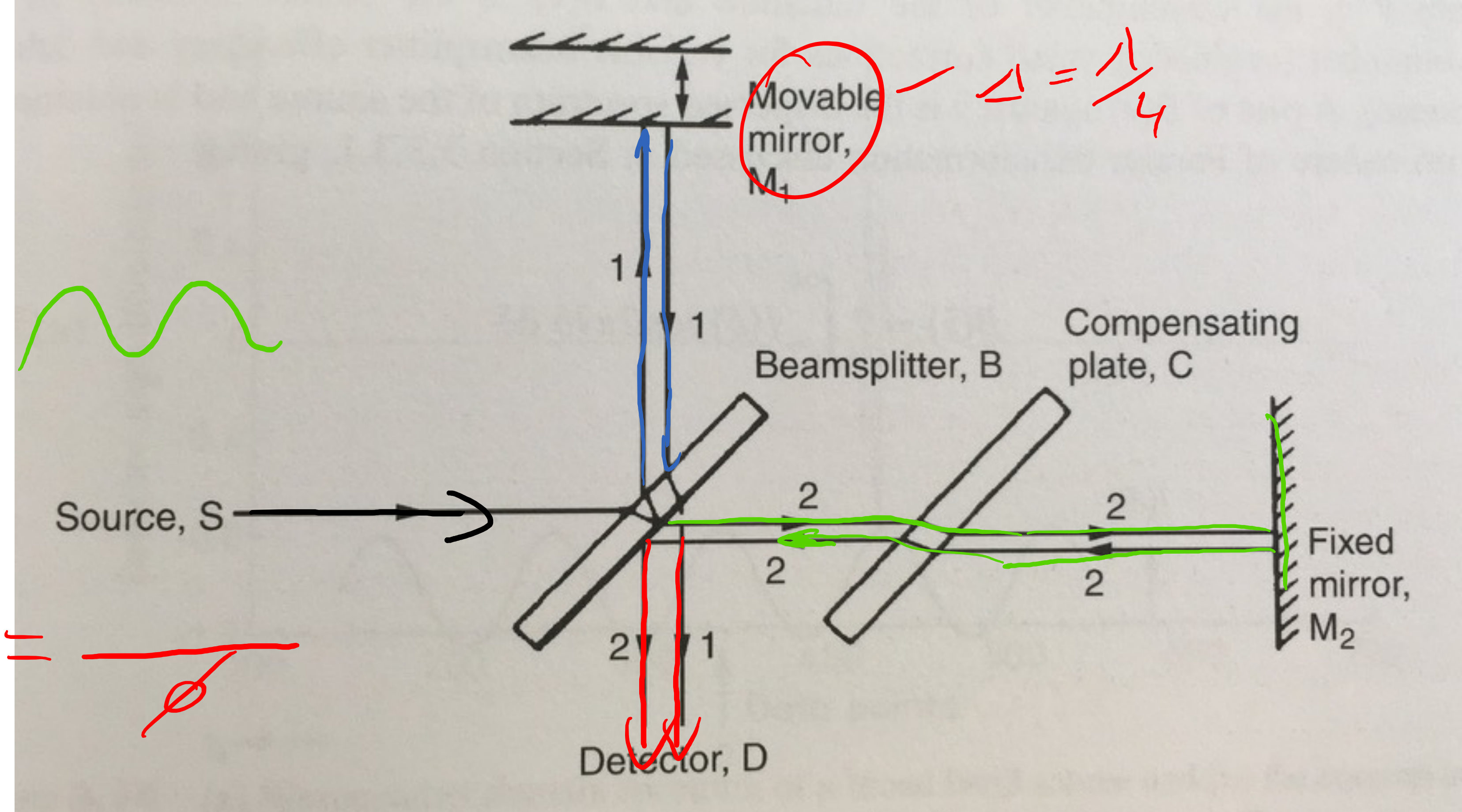


Figure 3.11 Michelson interferometer

Constructive

destructive
interference

Sample

detector

Interferometer: Condition for constructive interference with single frequency

Interfere $\Delta = n\lambda$, more convenient in frequencies $\tilde{\nu} = \frac{1}{\lambda}$ "wave numbers" $\frac{1}{cm}$

Constructive $\delta = n/\tilde{\nu}$

destructive $\delta = \frac{n+\frac{1}{2}}{\tilde{\nu}}$

$\delta \rightarrow$ still displacement in cm

$\delta = \frac{n}{\tilde{\nu}}$

beam splitter $\Rightarrow$ 50%/50% each beam

½ of light in each beam

ij

$\frac{I(\cancel{\tilde{\nu}})}{\cancel{2}} = I$

Intensity at detector $I(\delta) = \frac{I(\tilde{\nu})}{2} + \frac{I(\tilde{\nu})}{2}\cos(2\pi\tilde{\nu}\delta) = \frac{I(\tilde{\nu})}{2}(1 + \cos 2\pi\tilde{\nu}\delta)$

Interference condition $\simeq I(\tilde{\nu})(\cos 2\pi\tilde{\nu}\delta)$ δ = displacement

Interferometer: From single frequency to broad band

V - Interferogram
S - frequency dependent transmission of sample

At detector $I(\delta) = I(\tilde{\nu}) \cos(2\pi \tilde{\nu} \delta)$

with sample in beampath $V(\delta) = I(\tilde{\nu})\, S(\tilde{\nu}) \cos(2\pi \tilde{\nu} \delta)$

frequency dependent transmission

added sample

Now broadband source

$$V(\delta) = \int_{-\infty}^{\infty} I(\tilde{\nu})\, S(\tilde{\nu}) \cos(2\pi \tilde{\nu} \delta)\, d\tilde{\nu}$$

$$= \int_{-\infty}^{\infty} I(\tilde{\nu})\, S(\tilde{\nu})\, e^{-2\pi i \tilde{\nu} \delta} (\delta \tilde{\nu})$$

Interferogram

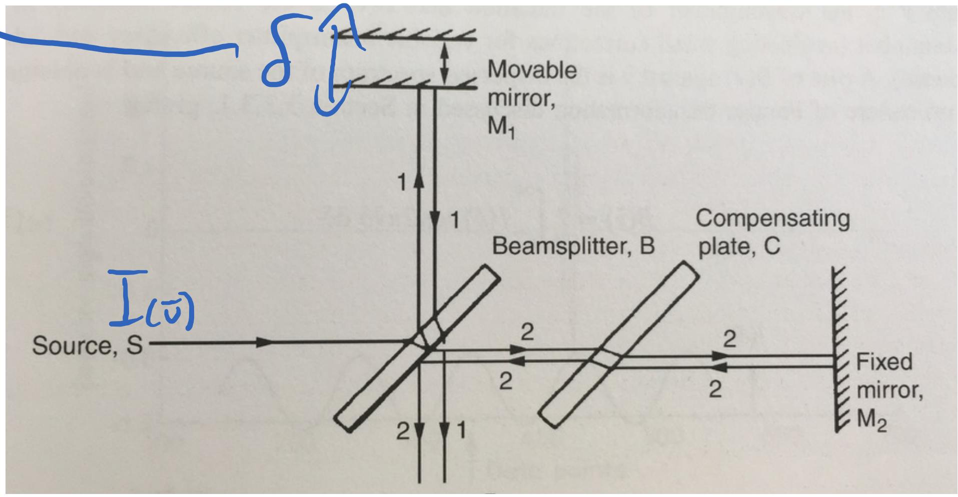
$V(\delta)$ - FT of spectrum $S(\tilde{\nu})$ • Frequency dependence of source

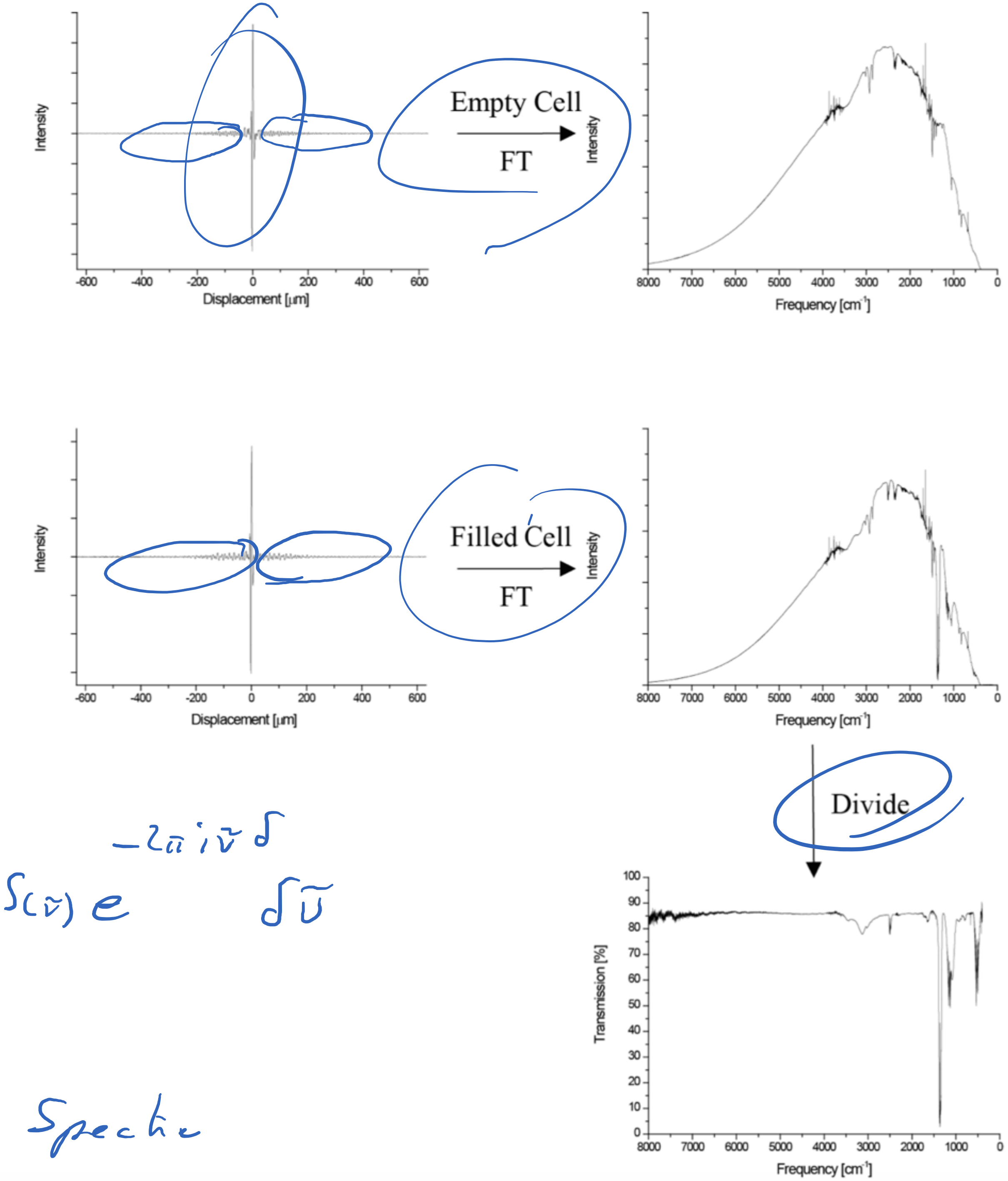
$V(\delta) = FT(I(\tilde{\nu}) \cdot S(\tilde{\nu}))$

$I(\tilde{\nu}) \cdot S(\tilde{\nu}) = FT^{-1}(V(\delta)) \rightarrow$ Interferogram

looks FT!

Measuring an interferogram



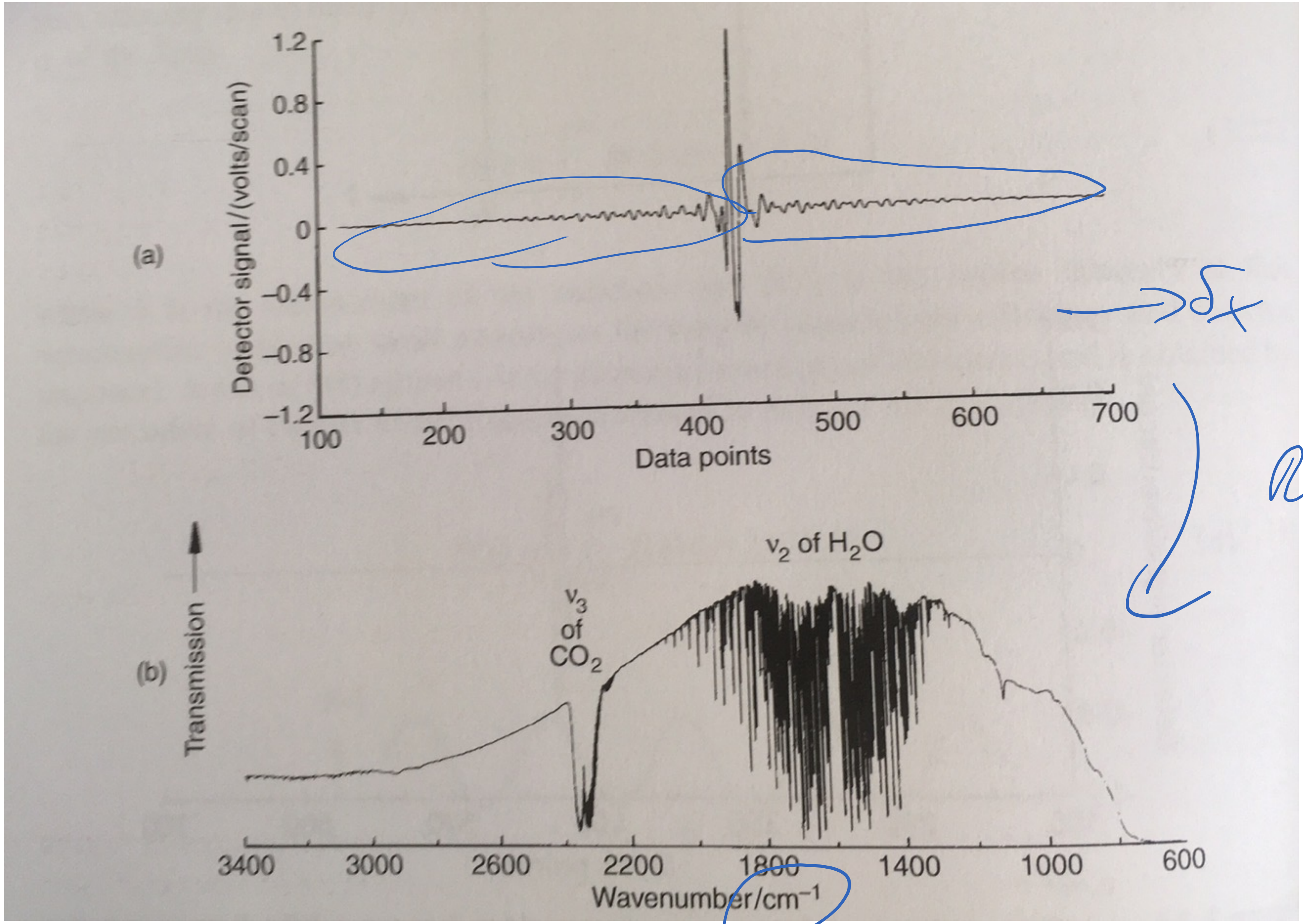


Sample $S(\tilde{\nu})$

Detector ← measure $V_\delta = \int_{-\infty}^{\infty} I(\tilde{\nu}) \cdot S(\tilde{\nu})\, e^{-2\pi i \tilde{\nu} \delta}\, d\tilde{\nu}$

Computer ⟹ FT^{-1} → Spectra

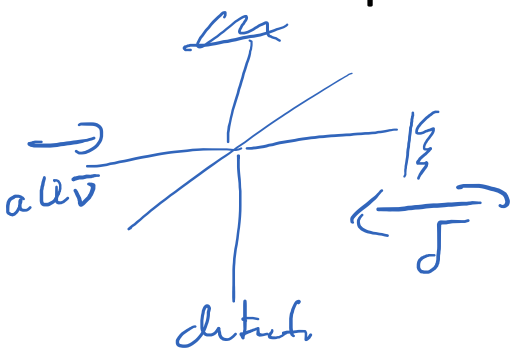
Example: Interferogram and spectrum of air



$\rightarrow \delta x$

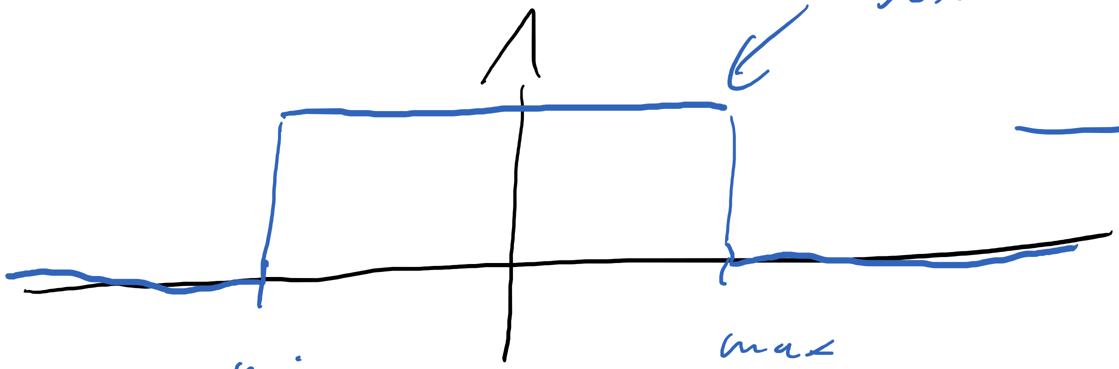
Rich in information

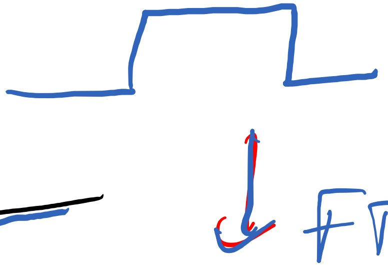
Line shapes



How to do $\int_{-\infty}^{\infty} \dots \, d\delta$

box car fct





FT → Sinc fct

back to FTIR

$$I_{(\tilde{\nu})} S_{(\tilde{\nu})} = \int_{-\infty}^{\infty} V_{(\delta)} e^{\cdots} \, d\delta$$

technically not possible

$$= \int_{-\infty}^{a} V_{(\delta)} A_{(\delta)} e^{\cdots} \, d\delta$$

↳ box car

$$F(f * g) = F(f) \cdot F(g) \rightarrow I_{(\tilde{\nu})} \cdot S_{(\tilde{\nu})} = FT(V(\delta)) \cdot FT(A(\delta))$$

Fourier spectroscopy

- Advantages
  - Higher overall transmission through interferometer compared to spectrometer
  - Multiplexing through use of all frequencies
  - Faster acquisition times and better signal to noise ratio
  - Higher accuracy for measuring mirror travel

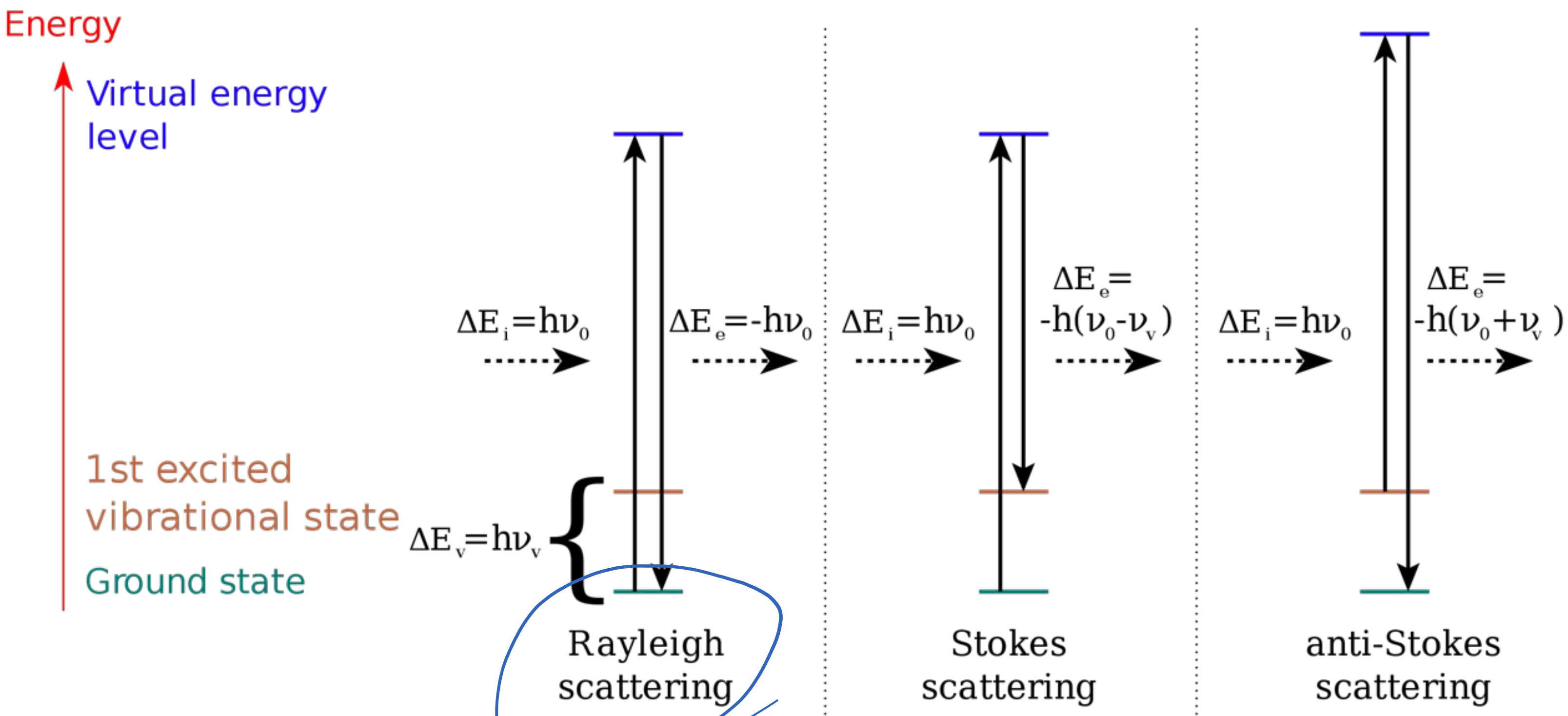
- Limitations
  - Tyipcally restricted to IR measurements
  - Accuracy determined by mirror travel distance

- Video by Brooker company for modern apparatus

https://www.facebook.com/bruker.corp/videos/o.712956095479376/10152856330318129/?type=2&theater

Raman spectroscopy (short introduction)

Raman process: Inelastic scattering of light



elastic | inelastic loss | inelastic gain

The Nobel Prize in Physics 1930

Photo from the Nobel Foundation archive.
Sir Chandrasekhara Venkata Raman

Early potential for chemical sciences

nature

Letter | Published: 07 July 1928

The Negative Absorption of Radiation

C. V. RAMAN & K. S. KRISHNAN

Nature **122**, 12–13 (1928) Cite this article

→ incredible foresight

→ early discussion of vibrational detection

→ really changed with invention of lasers

→ also in x-ray

A definite experimental proof is now forthcoming of the reality of negative absorption. We have discovered (NATURE, April 21, 1928, p. 619) that when a liquid, for example, benzene, is irradiated by monochromatic light, the radiation scattered by the molecules contains several spectral lines of modified frequencies. Careful measurements have shown that the difference between the incident and scattered frequencies is exactly equal to an infra-red frequency of the molecule, so that the process of modified scattering involves the absorption of radiation by the molecule. As the molecule has several characteristic infra-red frequencies, we have an equal number of modified scattered lines. This is seen in the photograph reproduced in Fig. 1, which is from a

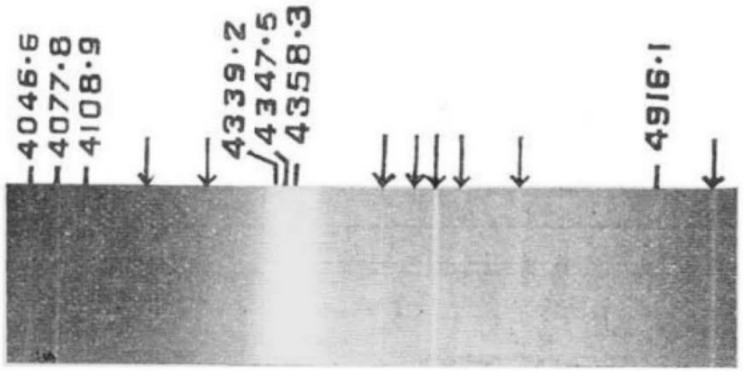
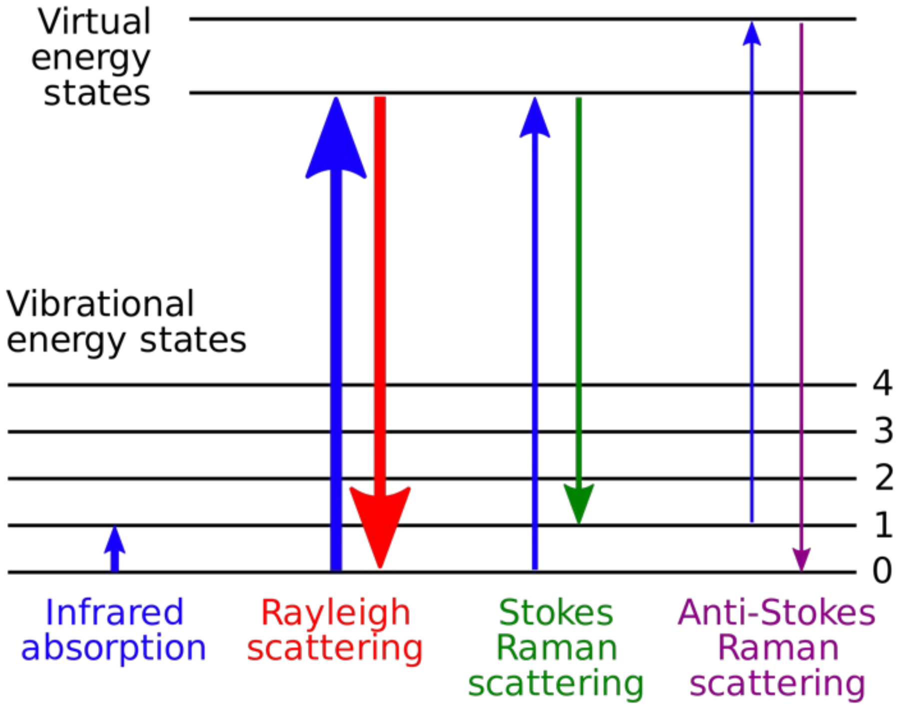
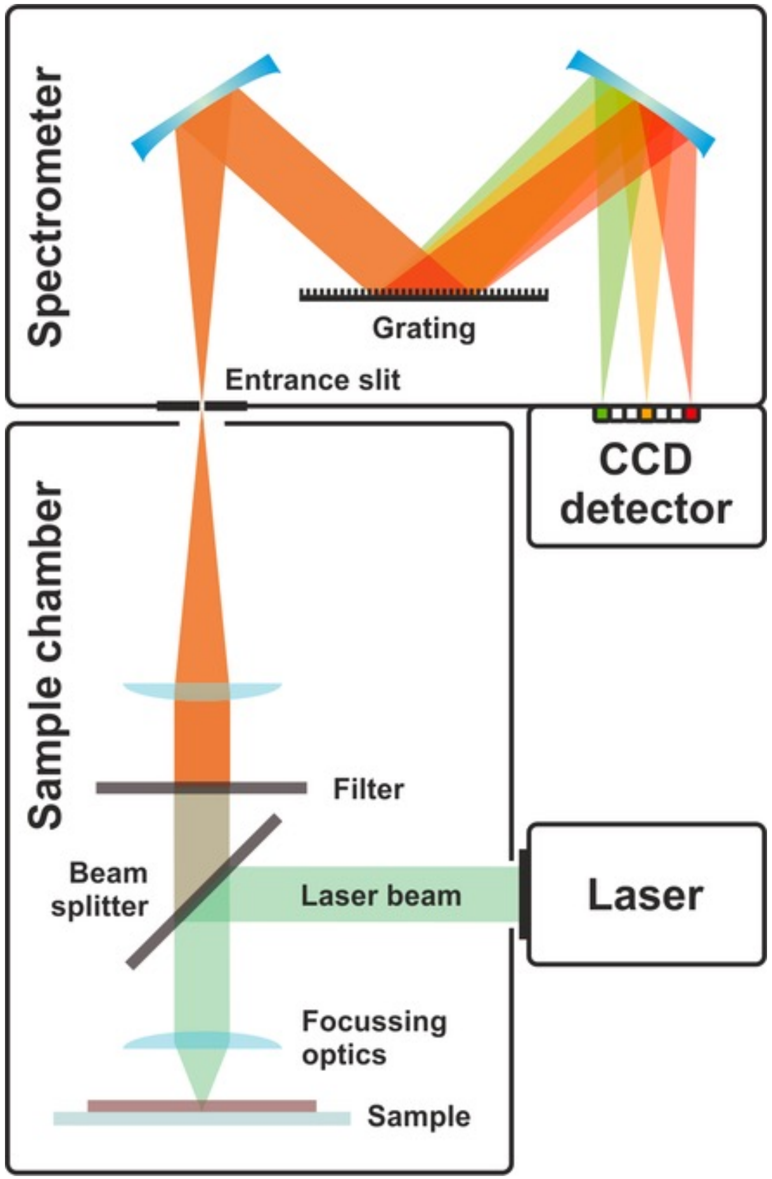


FIG. 1.

spectrogram of the scattering by liquid benzene, of the light of the mercury arc from which practically everything except the 4358 A. group of lines had been filtered out. In the spectrogram, the wave-lengths in the incident radiation are marked in A., and the modified scattered lines are indicated by arrowheads. (It may be mentioned in passing that the benzene had not been completely purified, hence a marked continuous spectrum is also present in the modified scattering.) The brightest modified lines are of longer wave-length than 4358 A., and their frequencies are determined by the infra-red absorption lines at 16·55 μ, 11·78 μ, 10·10 μ, 8·51 μ, 6·27 μ, and 3·267 μ. (These wave-lengths can be determined more accurately in this way than with an infra-red spectrometer.)

Raman spectroscopy





Example of Raman spectrum of CO2 (somewhat random example but still CO2)

JOURNAL OF RAMAN SPECTROSCOPY
J. Raman Spectrosc. 2006; **37**: 175–182
Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/jrs.1462

JRS

Quantitative diagnostics of a methane/air mini-flame by Raman spectroscopy†

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Received 12 April 2005; Accepted 15 August 2005

$(\partial\sigma/\partial\Omega)_0$ is the cross section at a temperature low enough for seen there.

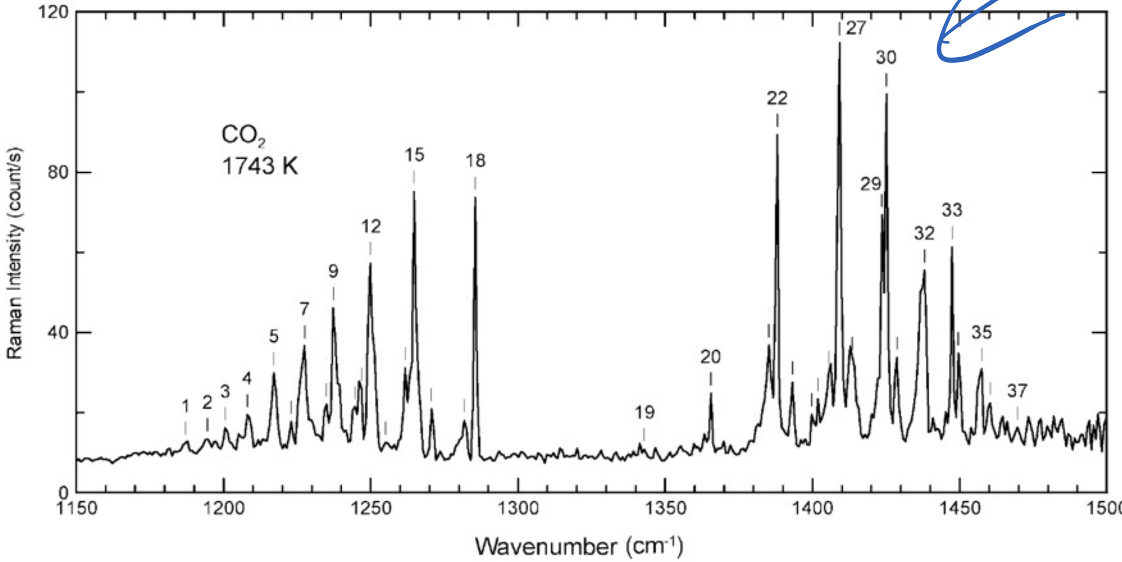
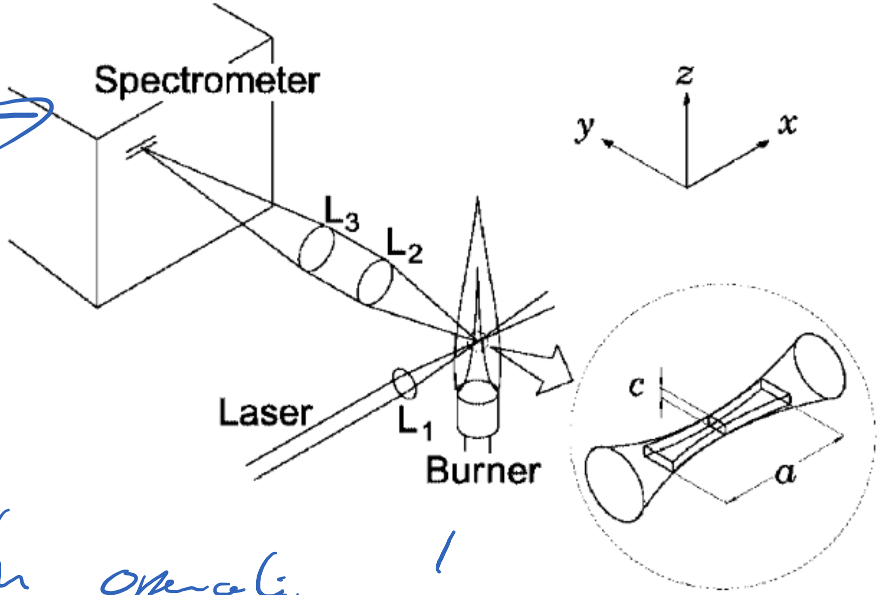


Figure 8. Raman spectrum of CO_2 in the methane/air flame at $z = 30$ mm on the flame axis. Entrance slit was 250 µm, equivalent to a resolution of ~1.2 cm^{-1}; total acquisition time 10 min. The assignment of peaks is given in Table 3. Most peaks above 1460 cm^{-1} are due to the Q-branch of O_2.



In operation!

Sensing / Screening

Today

- We have revisited spectroscopy approaches
- You learned two alternative ideas to the classic approach
  - Fourier spectroscopy based on interferometry
  - Raman spectroscopy based on inelastic scattering

The end.