

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

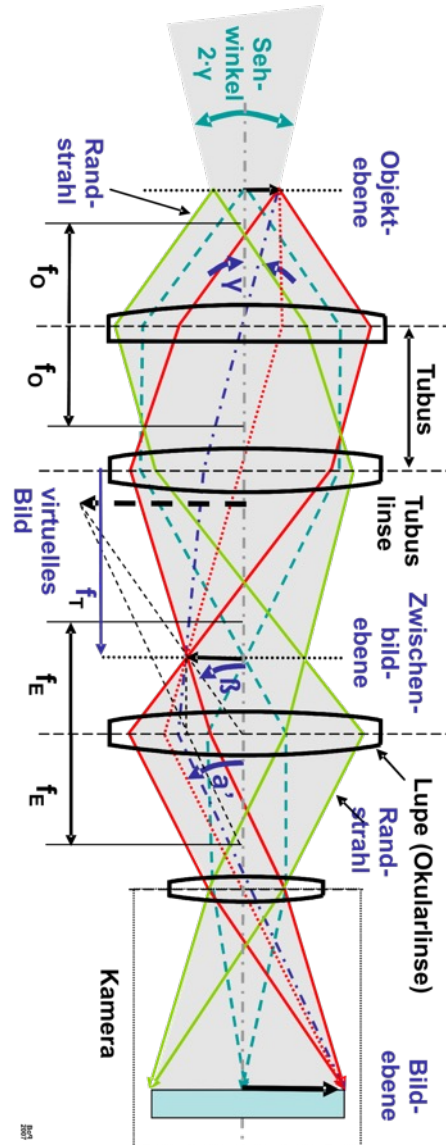
Going towards applications:

However, still focus on some concepts

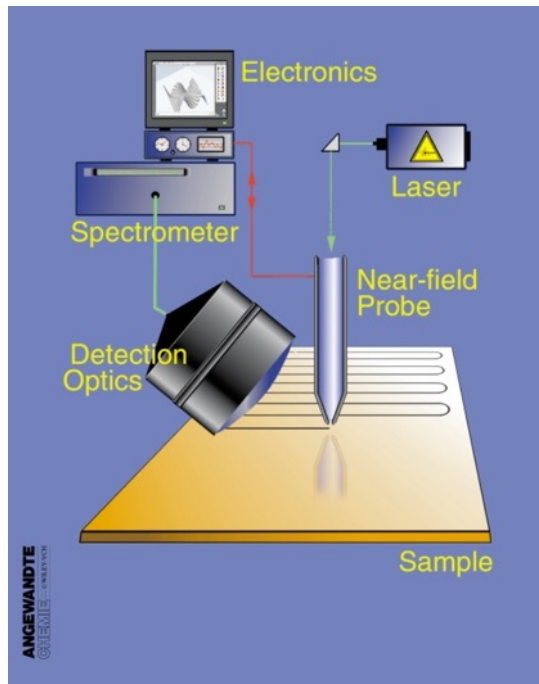
Microscopy – Manipulation - Spectroscopy

Remember: Microscopy

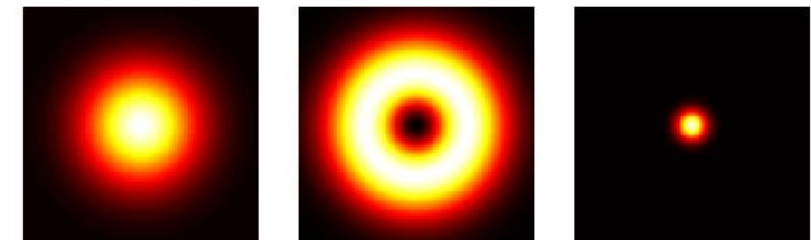
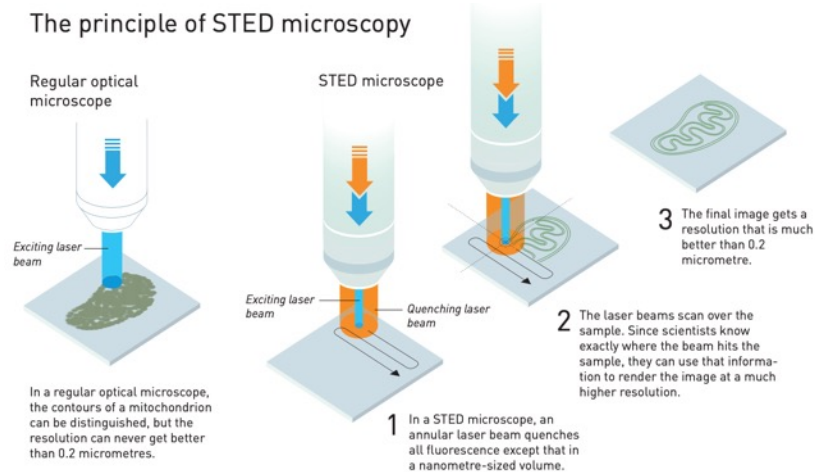
Classical microscope



Near-field approaches

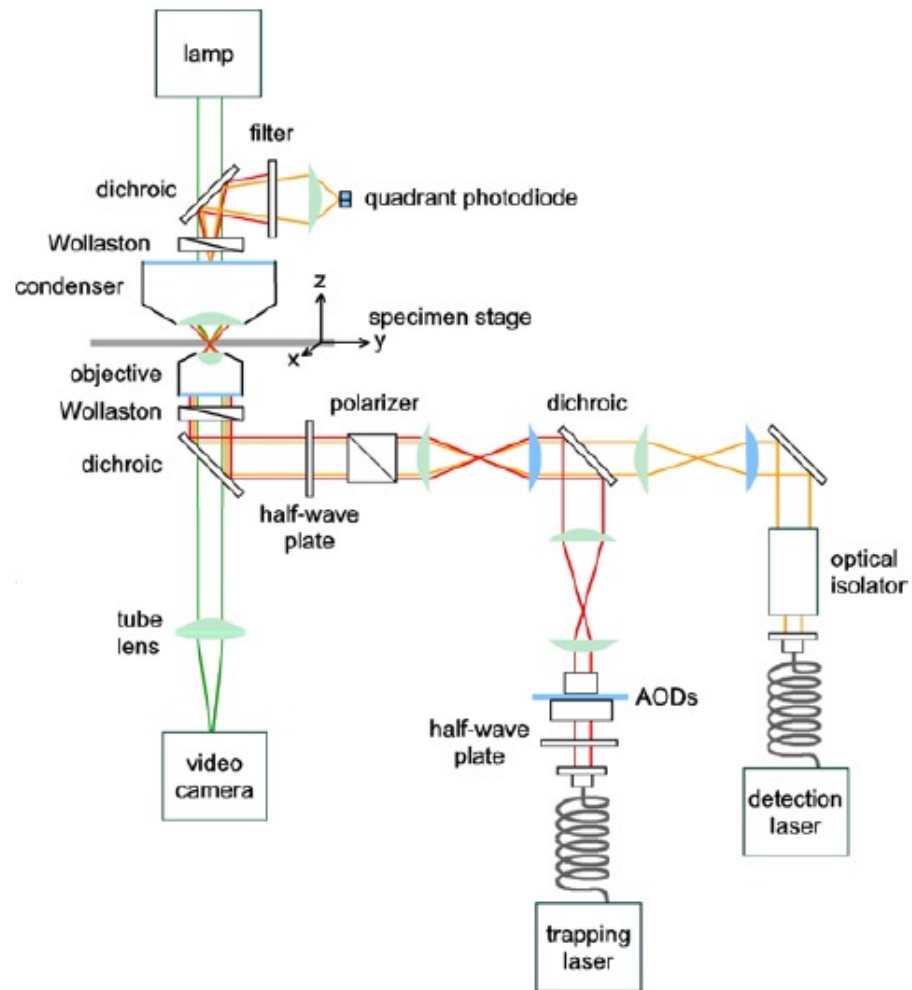


Stimulated emission depletion approach



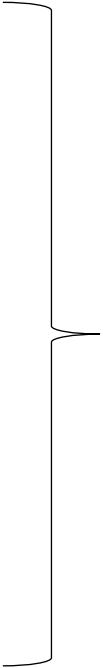
Remember: Manipulation

Manipulation of particles: optical tweezers



Today: Spectroscopy

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



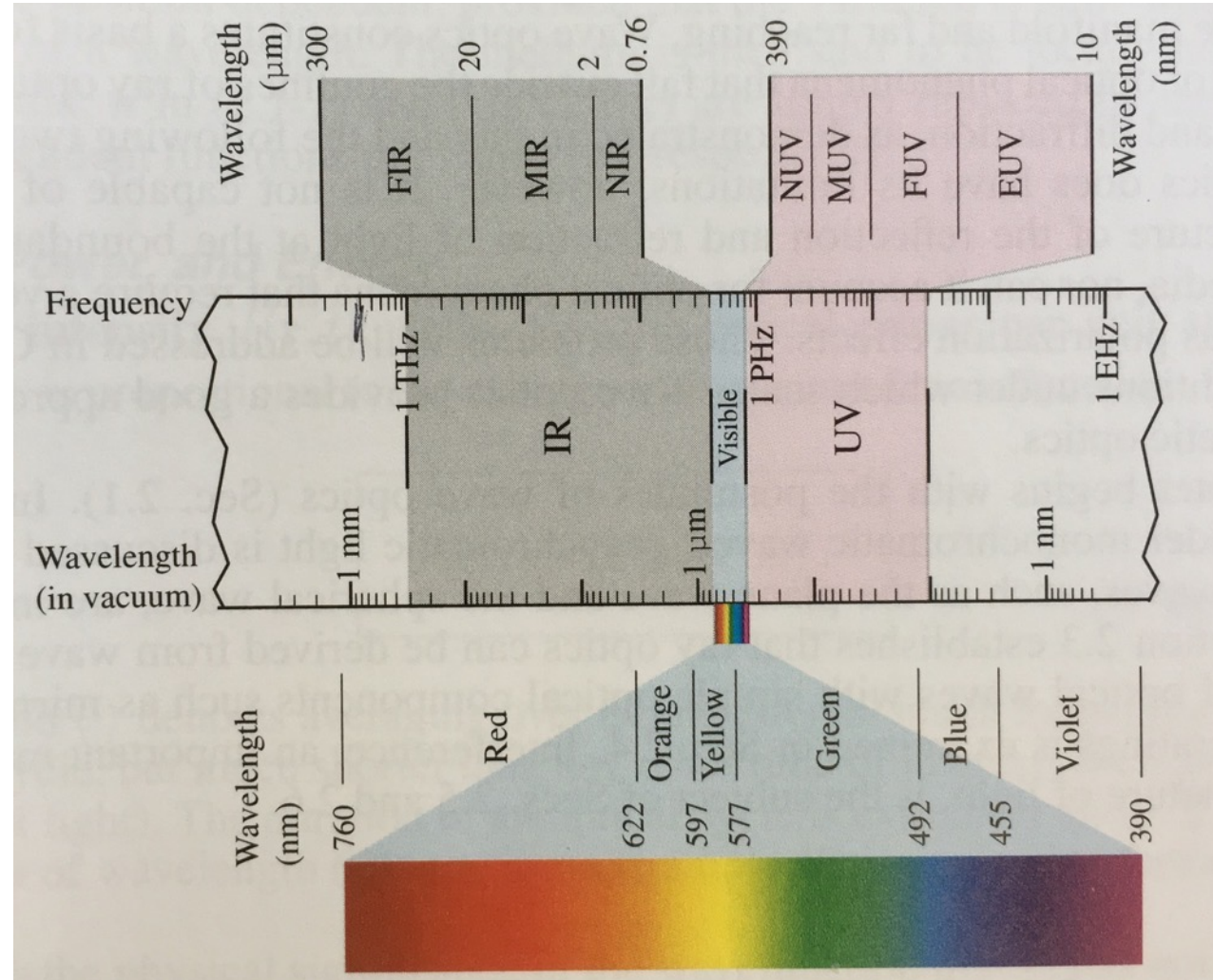
I assume (I know) you have dedicated lessons about these topics, including Quantum Chemistry, Spectroscopy, etc

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

A quick reminder about electromagnetic spectrum



The “classic approach” to spectroscopy

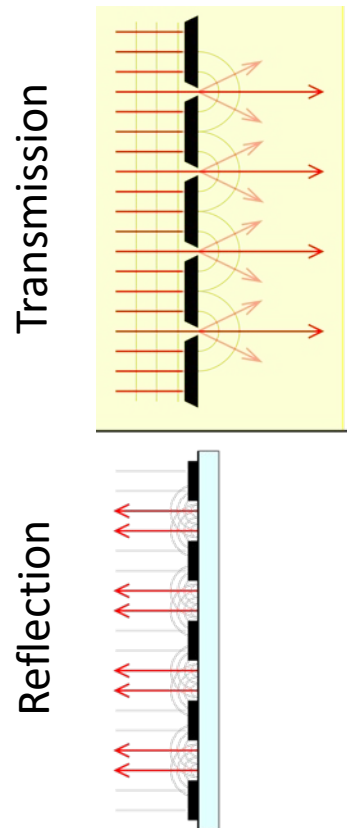
Version 1

Version 2

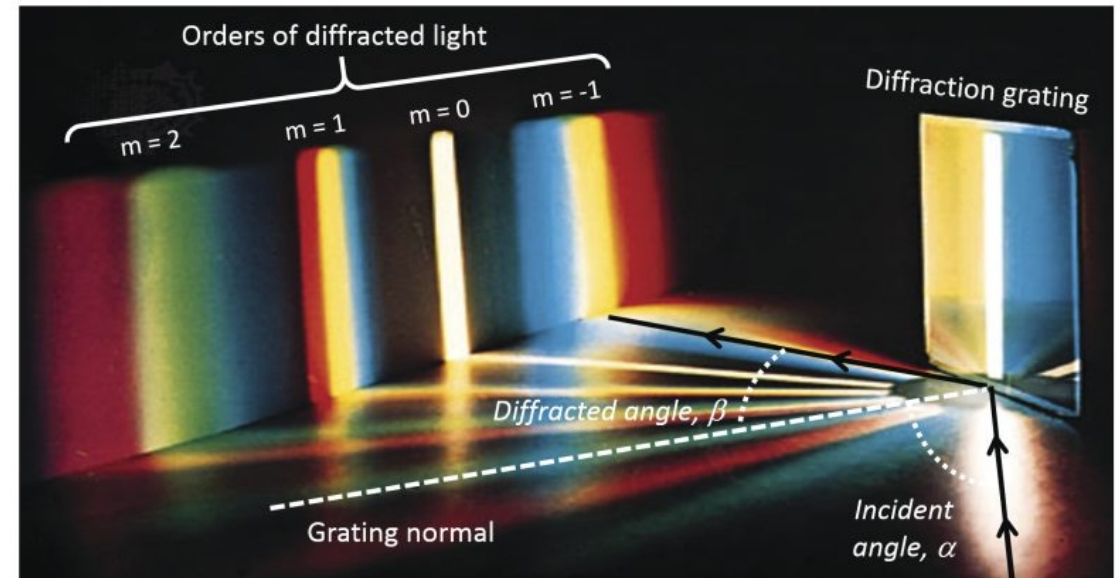
Short note on gratings

- Remember single slit, double slit, Babinet's Theorem
- Grating is extension.

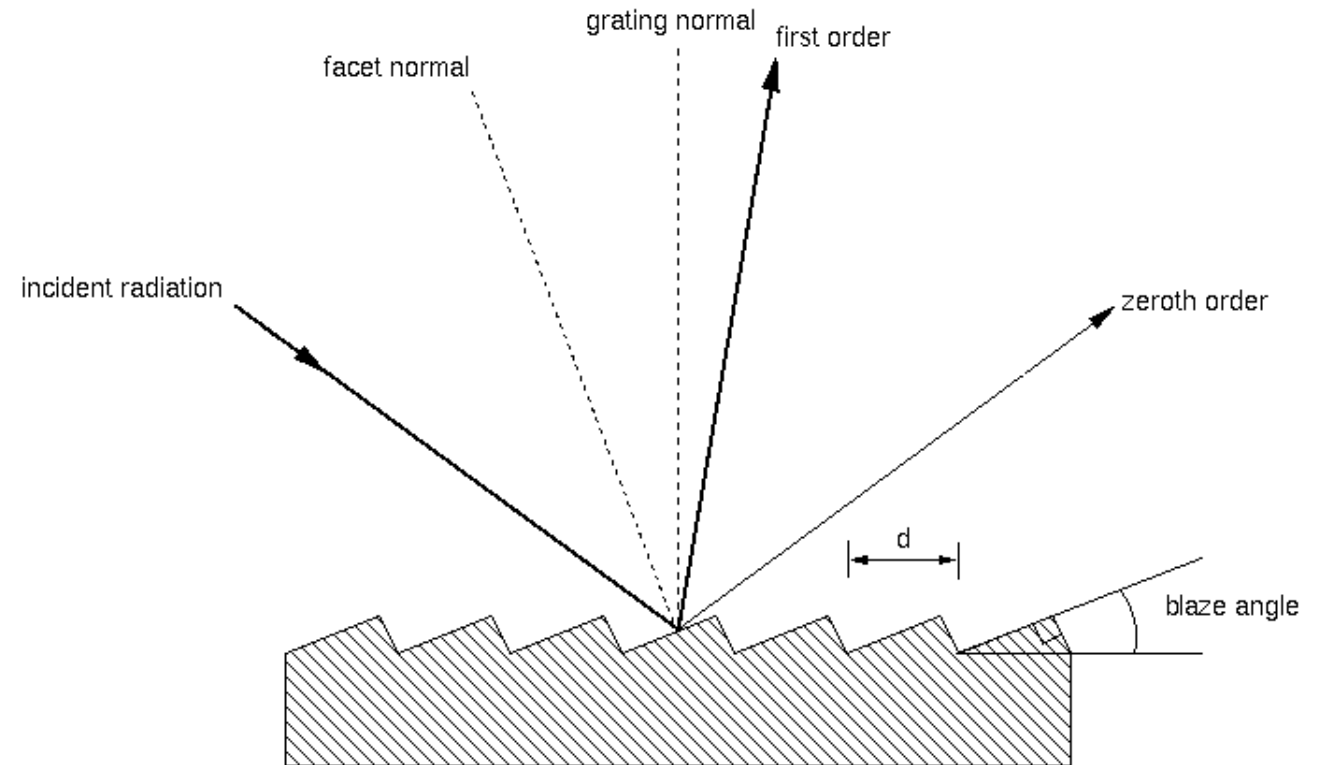
Amplitude grating



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



Blazed grating



Littrow configuration:

Incident angle = diffraction order

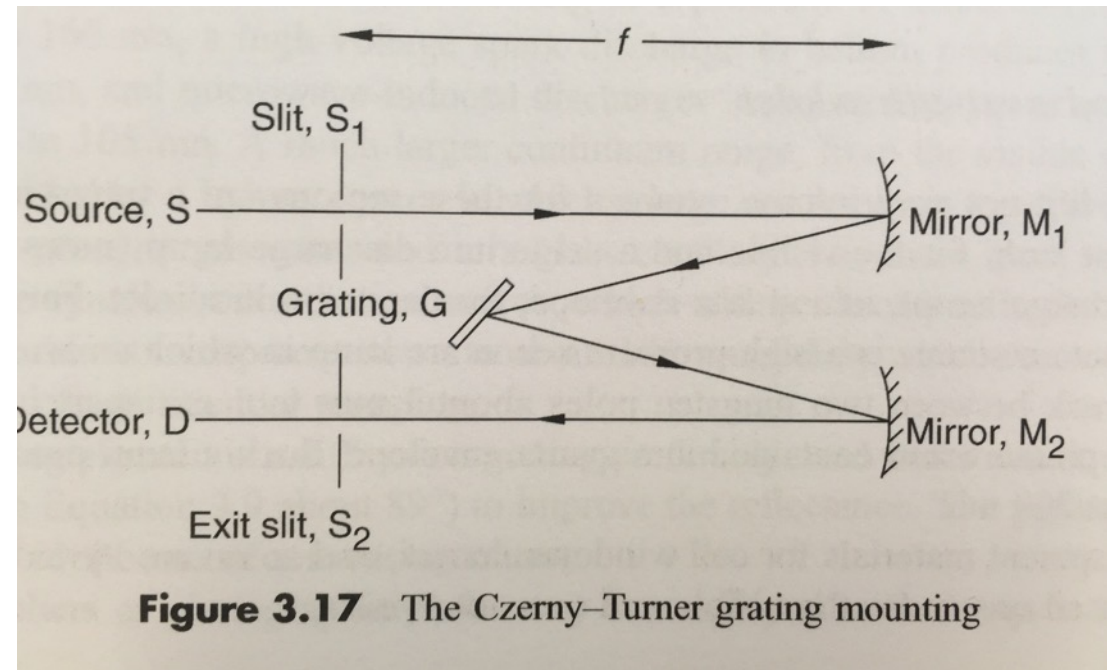
→ Laser cavity

Grating spectrometer

Common use in (far) infrared spectroscopy not restricted to this regime

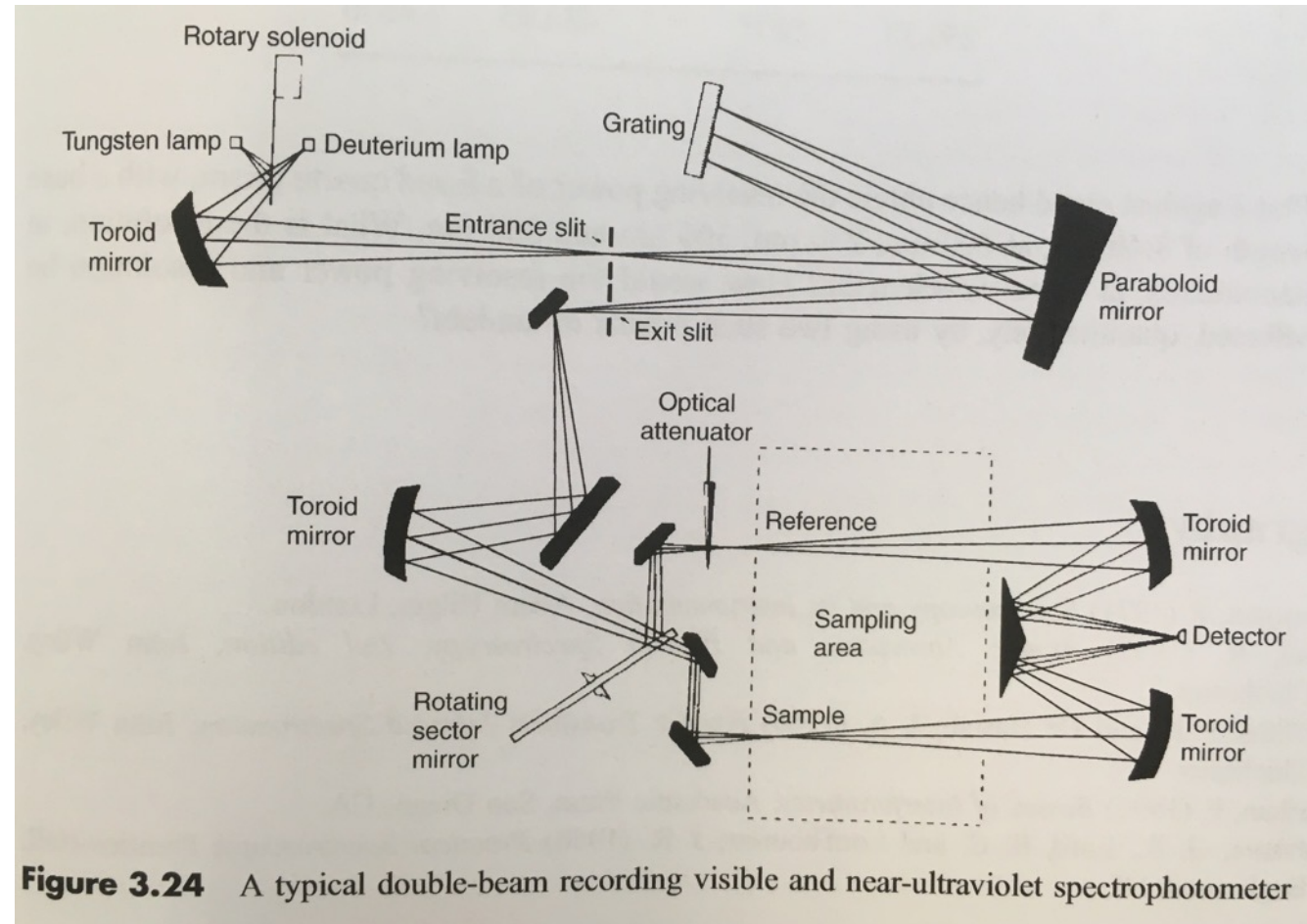
Note strong absorption of water, work in “dry conditions”

Excitation source can be mercury discharge lamp



Spectrophotometer

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

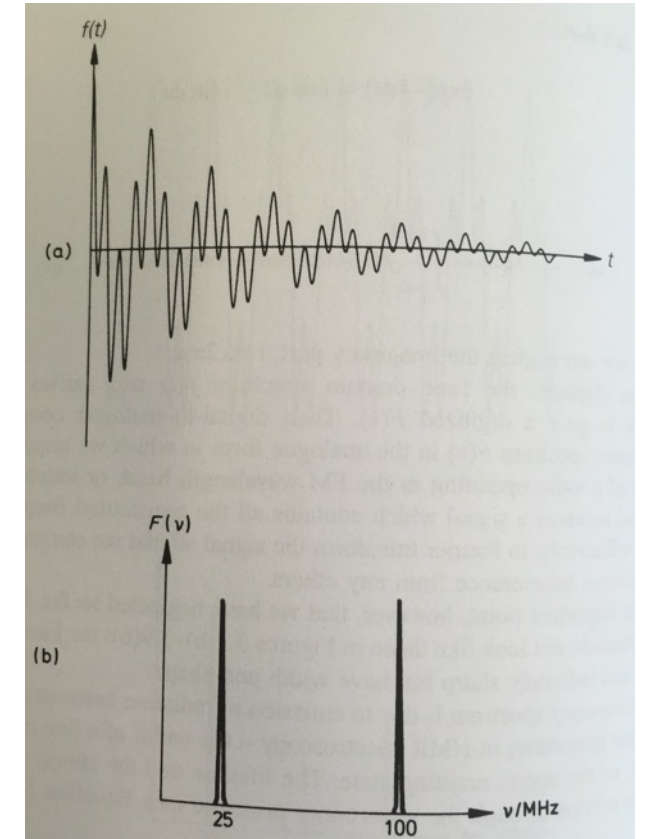
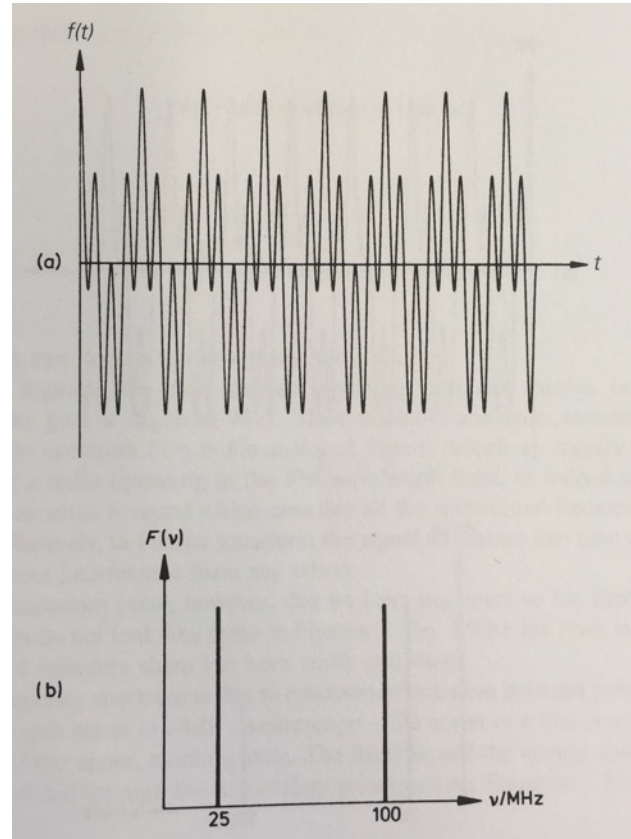
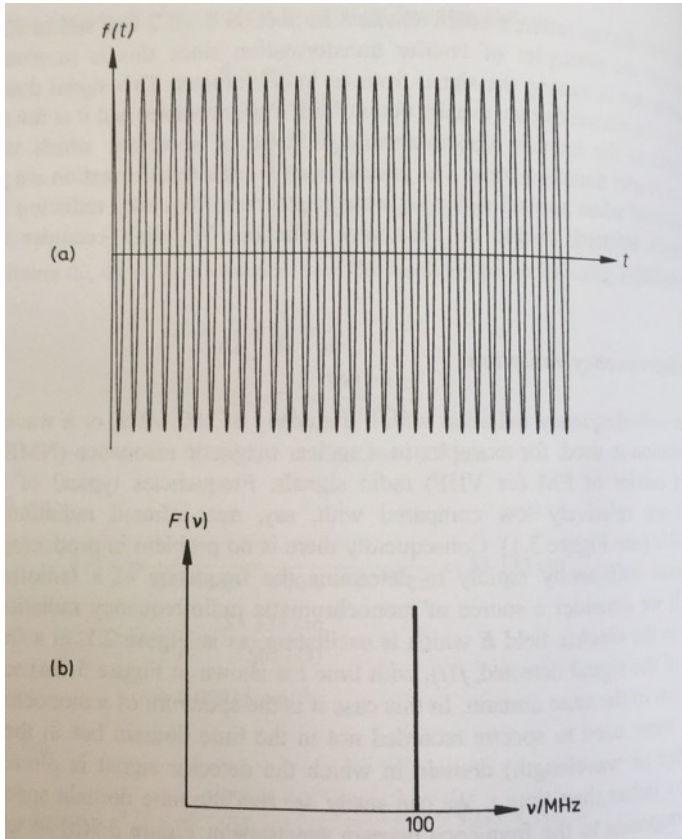


Alternative approach: Fourier Transform (Infrared) Spectrometer

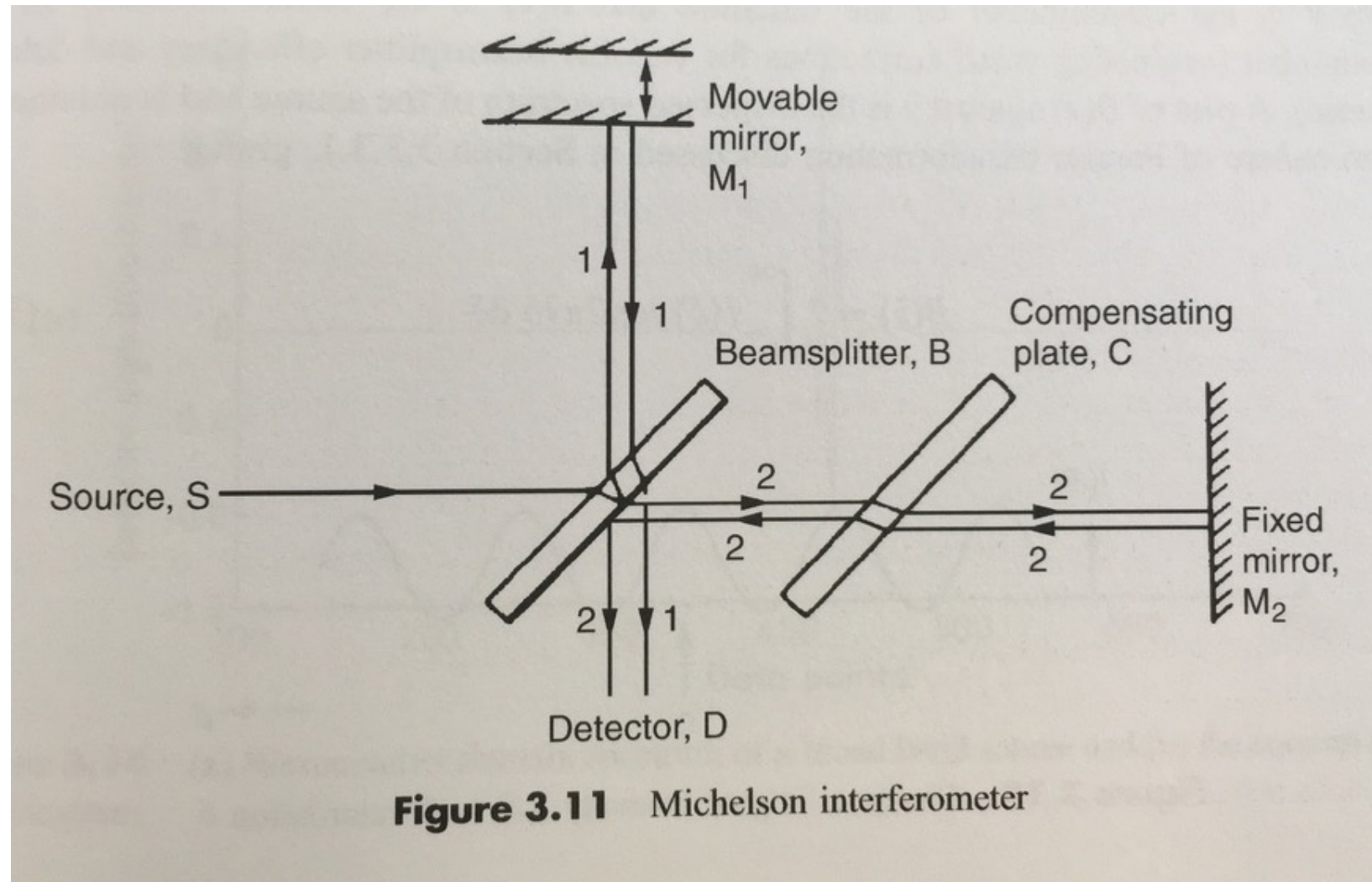
- Not a dispersive measurement but based on interferometry
- Use all wavelength at the same time
- Manipulation in x - cm (real space) to get information in wave numbers $x^{-1} - \text{cm}^{-1}$ (frequencies)
- Measure interferogram, Fourier transform into spectrum



Remember some properties of Fourier Transform



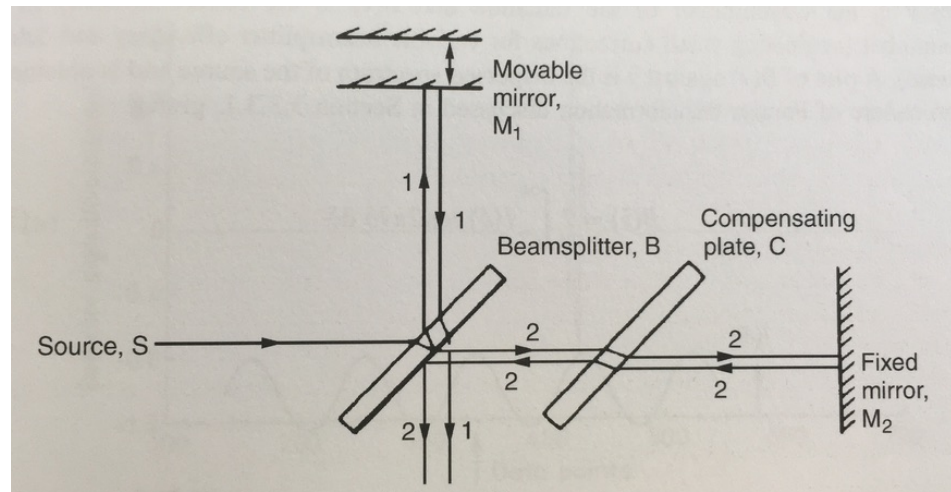
Basics of Michelson interferometer (mono)



Interferometer: Condition for constructive interference with single frequency

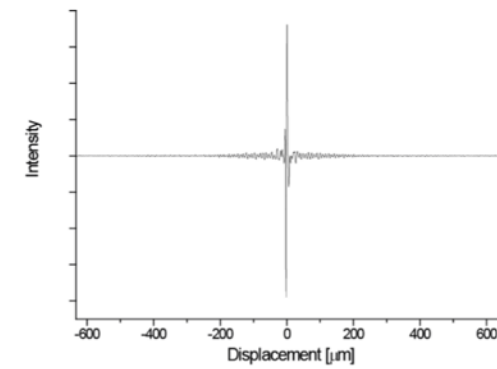
Interferometer: From single frequency to broad band

Measuring an interferogram

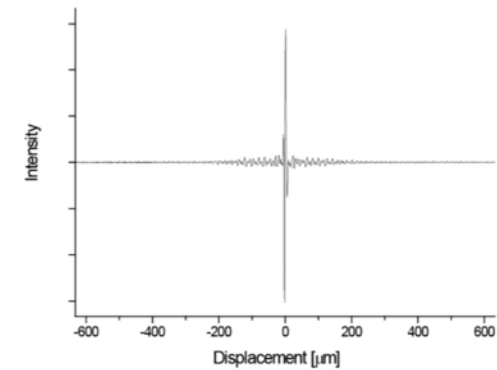
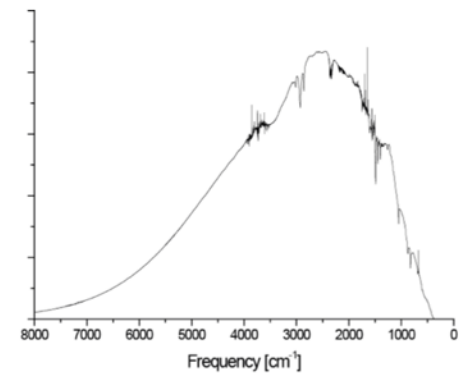


Sample

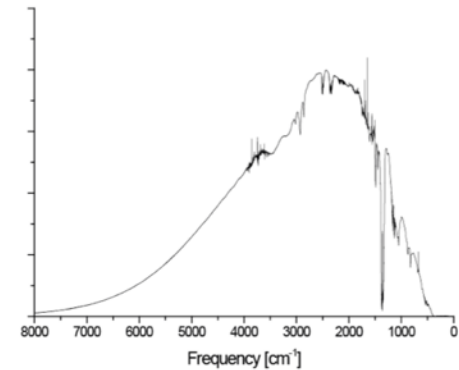
Detector



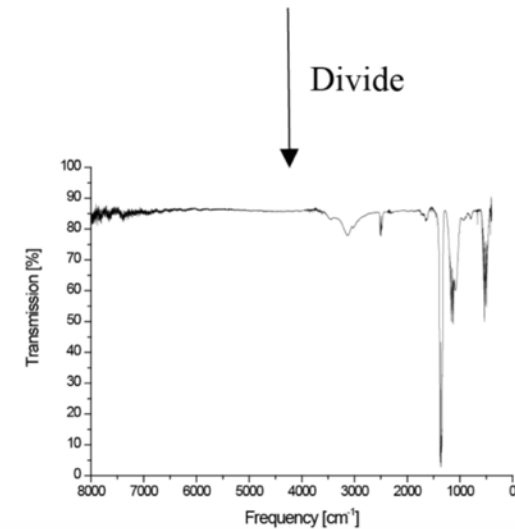
Empty Cell
FT



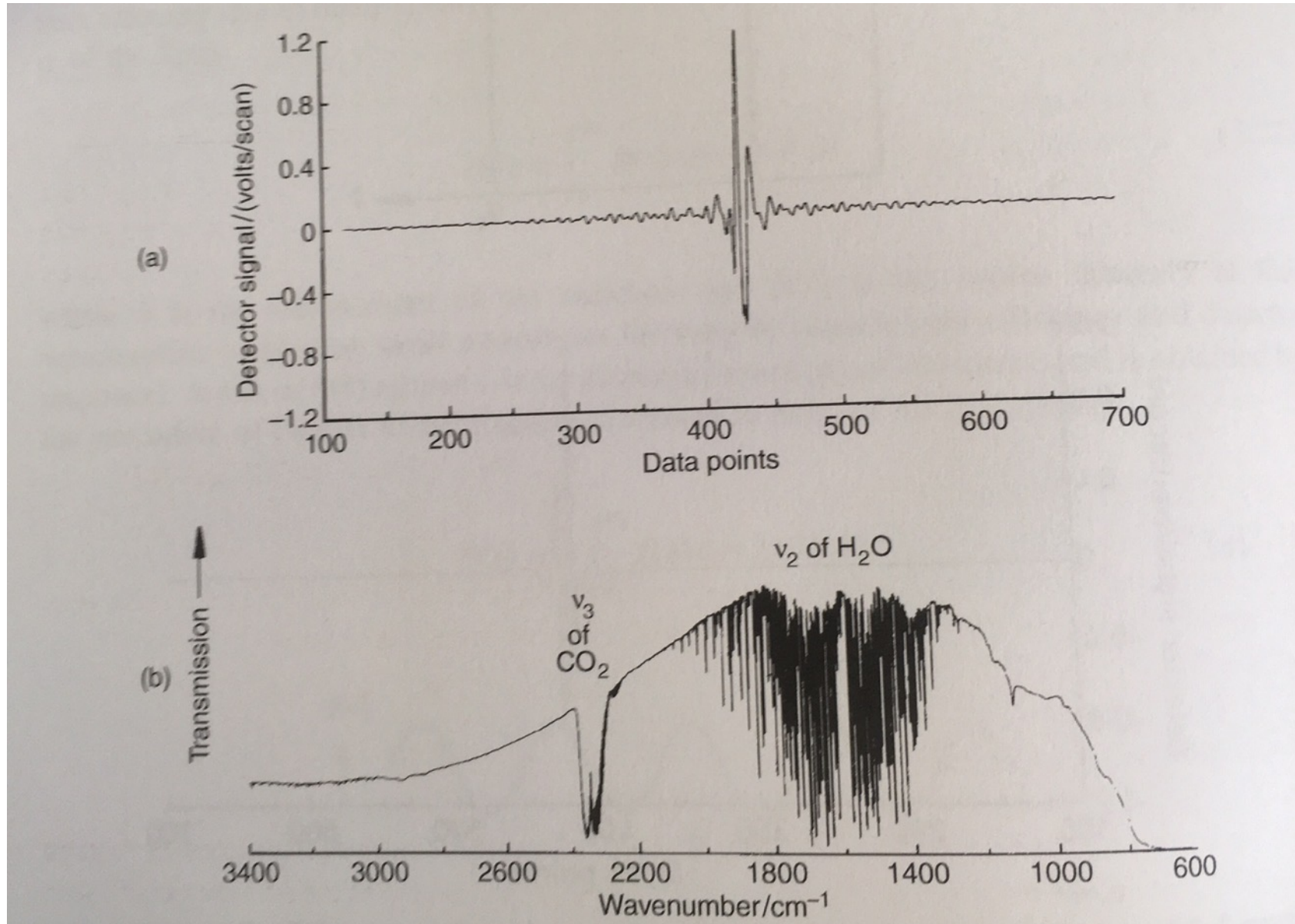
Filled Cell
FT



Divide



Example: Interferogram and spectrum of air



Line shapes

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
 - Typically restricted to IR measurements
 - Accuracy determined by mirror travel distance
- Video by Bruker 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

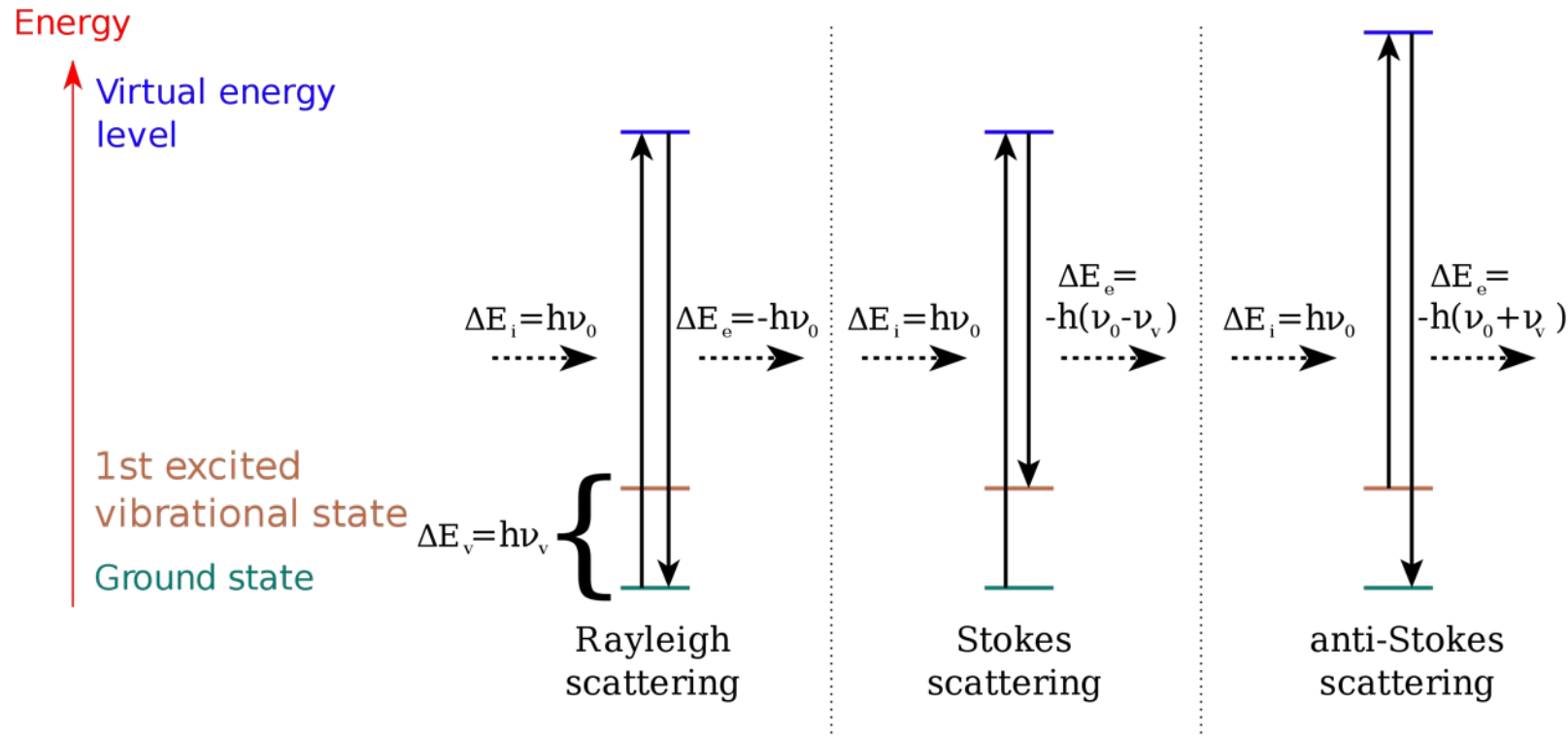


Photo from the Nobel Foundation archive.

Sir Chandrasekhara Venkata Raman

Early potential for chemical sciences



Letter | Published: 07 July 1928

The Negative Absorption of Radiation

C. V. RAMAN & K. S. KRISHNAN

Nature 122, 12–13(1928) | [Cite this article](#)

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

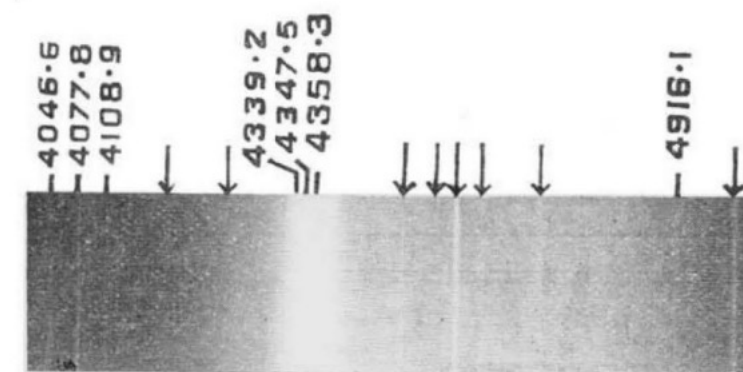
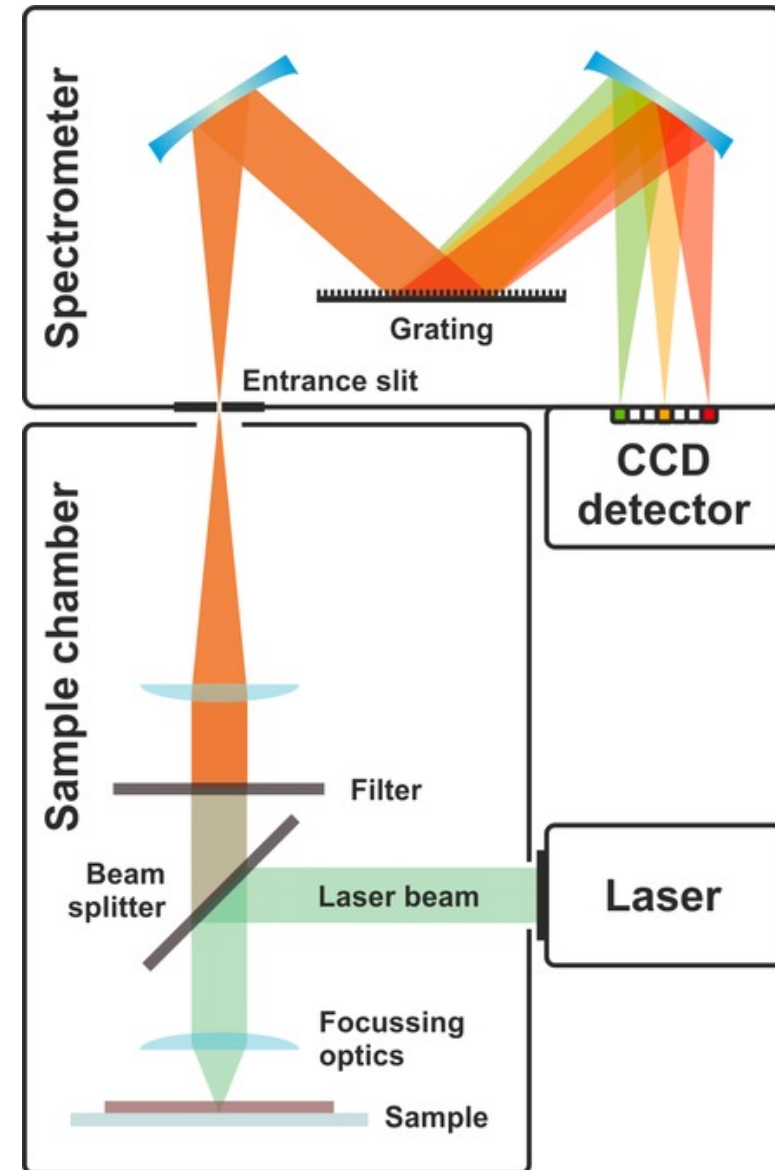
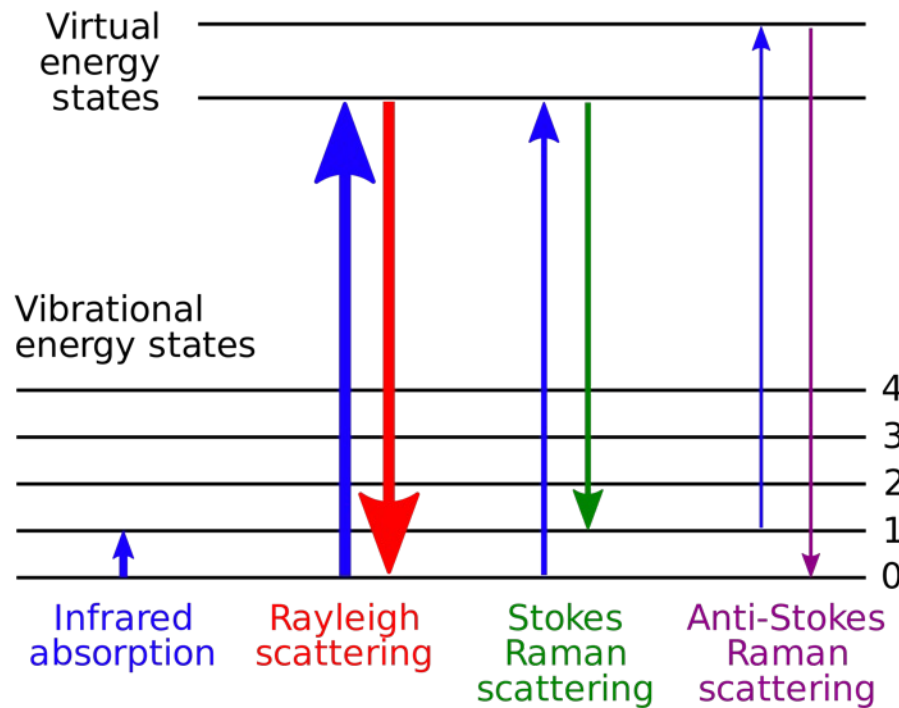


FIG. 1.

spectrogram of the scattering by liquid benzene, of the light of the mercury arc from which practically everything except the 4358 Å. group of lines had been filtered out. In the spectrogram, the wave-lengths in the incident radiation are marked in Å., 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 Å., and their frequencies are determined by the infra-red absorption lines at $16.55\ \mu$, $11.78\ \mu$, $10.10\ \mu$, $8.51\ \mu$, $6.27\ \mu$, and $3.267\ \mu$. (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

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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.

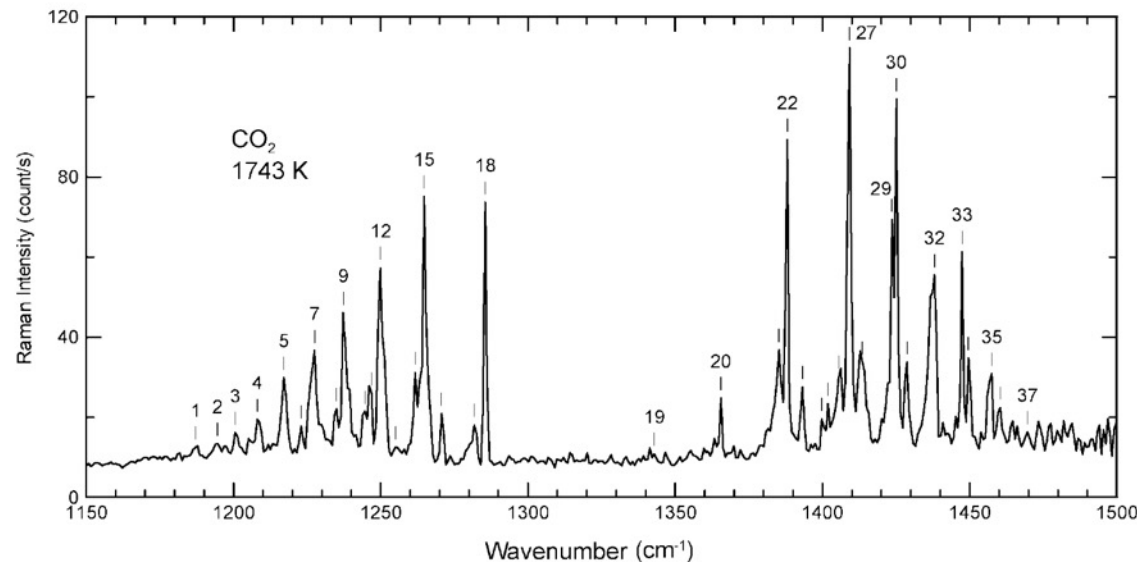
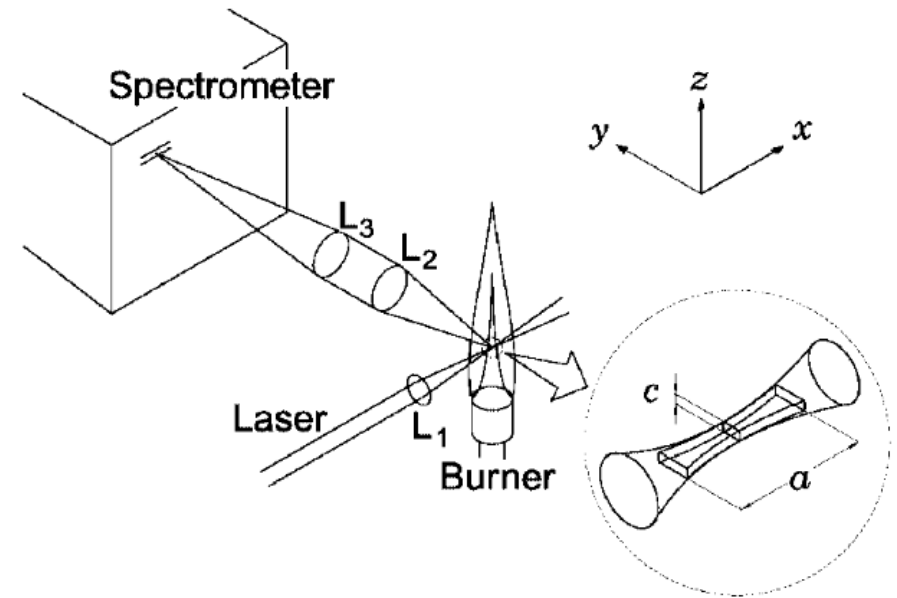


Figure 8. Raman spectrum of CO₂ in the methane/air flame at $z = 30$ mm on the flame axis. Entrance slit was 250 μm , equivalent to a resolution of ~ 1.2 cm^{-1} ; total acquisition time 10 min. The assignment of peaks is given in Table 3. Most peaks above 1460 cm^{-1} are due to the Q-branch of O₂.



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.