

Dr. Katalin Kamarás (Wigner, SZFI) kamaras.katalin@wigner.hu

Dr. Sándor Bordács (BME, FT) bordacs.sandor@ttk.bme.hu

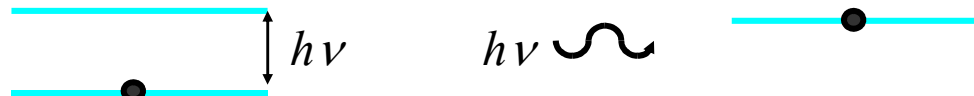
Optical Spectroscopy in Materials Science

Infrared spectroscopy



Spectroscopic processes

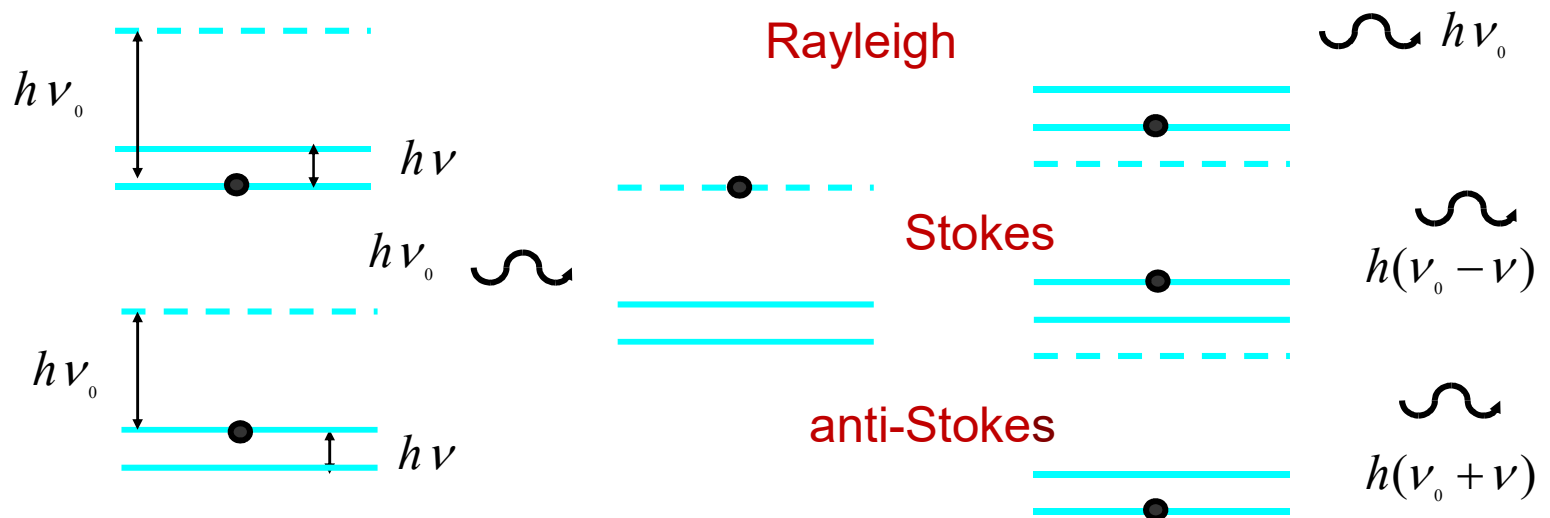
absorption



emission

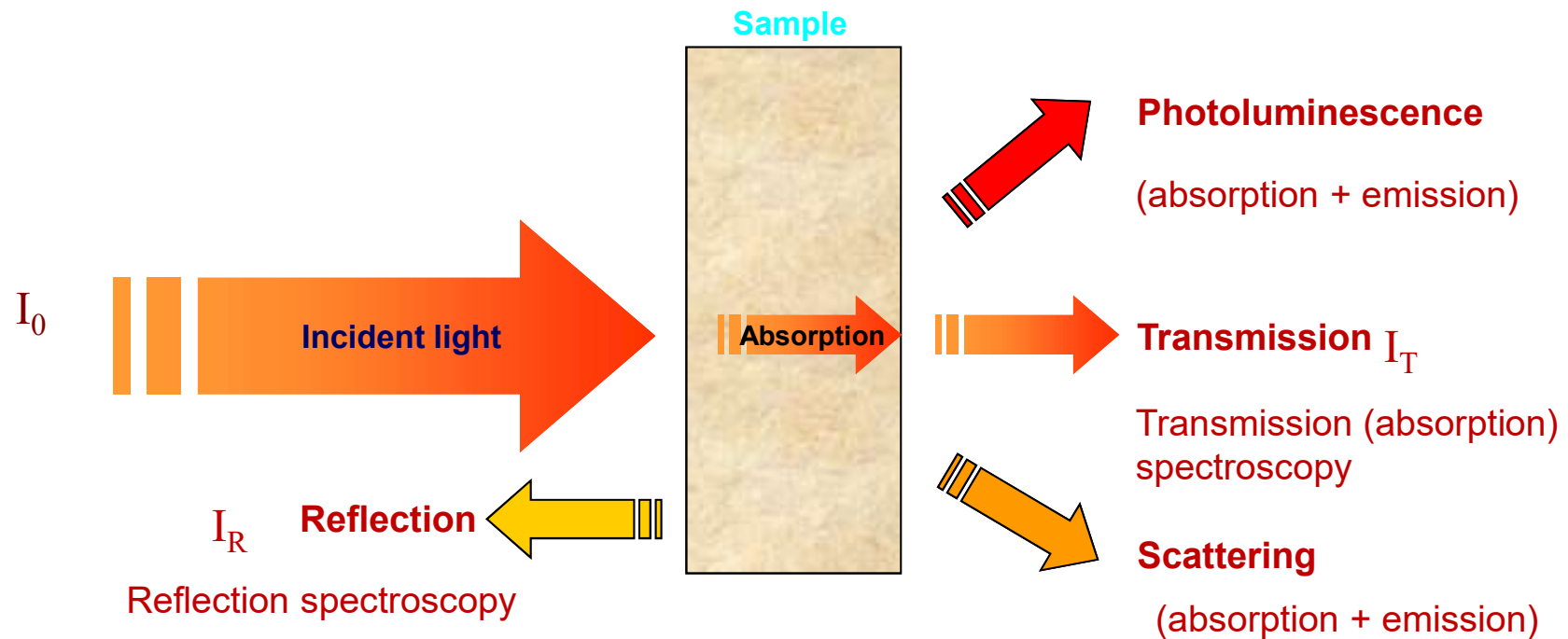


scattering



Experimental arrangements

$$I_0 = RI_0 + (1 - R)I_0e^{-\alpha d} + I_A$$



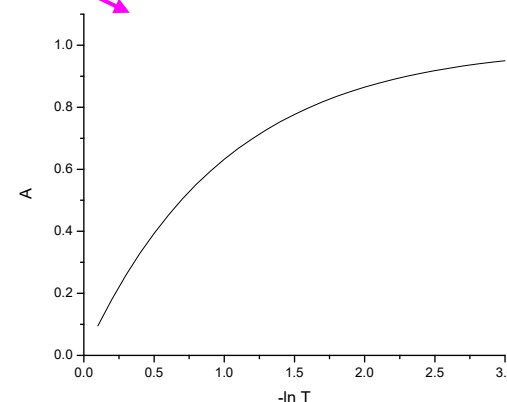
Absorption spectroscopy

$$R \ll 1, \quad T = \frac{I_T}{I_0} \cong e^{-\alpha d} \quad A = 1 - e^{-\alpha d} \cong \alpha d = \varepsilon c d = -\log T$$

Beer's law
Lambert-Beer-törvény
Lambert'sches Gesetz
log, ln?

ε specific (molar) absorption coefficient

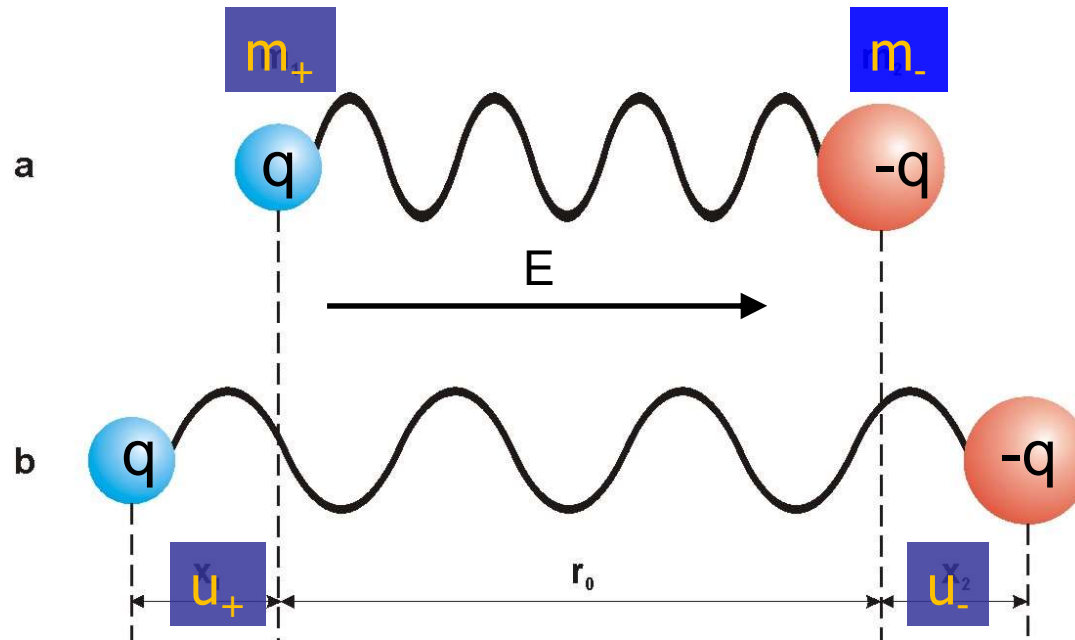
$$[\alpha] = \text{cm}^{-1} \quad [\varepsilon] = 1 / \text{cm} / \text{conc.}$$



concentration determination:
linear ($A < 0.4$) range Beer's law
outside linear range: calibration

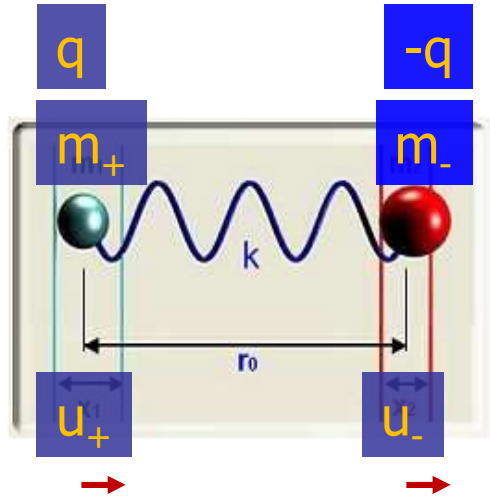
most spectrometer software does not
know the difference!

Molecular vibrations



Mechanical model of a vibrating diatomic molecule

Vibrational spectra



$$\mu = qu_+ - qu_-$$

$$*m_- \quad m_+ \frac{d^2 u}{dt^2} = -\kappa(u_+ - u_-) + qE$$

$$*m_+ \quad m_- \frac{d^2 u}{dt^2} = -\kappa(u_- - u_+) - qE$$

$$m_r = \frac{m_+ m_-}{m_+ + m_-}$$

reduced mass

$$r = (u_+ - u_-)$$

relative displacement

Introducing damping:

$$m_r \frac{d^2 r}{dt^2} + m_r \gamma \frac{dr}{dt} + m_r \omega_0^2 r = qE$$

$$\omega_0 = \sqrt{\frac{\kappa}{m_r}} \quad \text{eigenfrequency}$$

$$E = E_0 e^{-i\alpha t} \longrightarrow r = r_0 e^{-i\alpha t}$$

For a system of volume V, containing N molecules:

$$\frac{m_+ m_-}{m_+ + m_-} \frac{d^2 (u_+ - u_-)}{dt^2} = qE + \kappa(u_- - u_+)$$

$$\mu = \alpha E \longrightarrow \chi = \frac{\alpha N}{V} \longrightarrow \epsilon_{rel} = 1 + \chi$$

$$\epsilon_{rel} = 1 + \frac{Nq^2}{\epsilon_0 m_r V} \frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega}$$

Vibrational spectra – extended charges

For extended charge distribution, an *effective charge* can be defined:

$$\mu = \left(\frac{\partial \mu}{\partial u_+} \right) u_+ + \left(\frac{\partial \mu}{\partial u_-} \right) u_- = Qr \quad Q = \left(\frac{\partial \mu}{\partial u_+} \right) = - \left(\frac{\partial \mu}{\partial u_-} \right)$$

$$\varepsilon_{rel} = \varepsilon_{\infty} + \frac{NQ^2}{\varepsilon_0 m_r V} \frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega} = \varepsilon_{\infty} + \frac{\Omega^2}{\omega_0^2 - \omega^2 - i\gamma\omega}$$

$$\Omega^2 = \frac{NQ^2}{\varepsilon_0 m_r V} \quad \text{oscillator strength (if } Q=0, \text{ no response)}$$

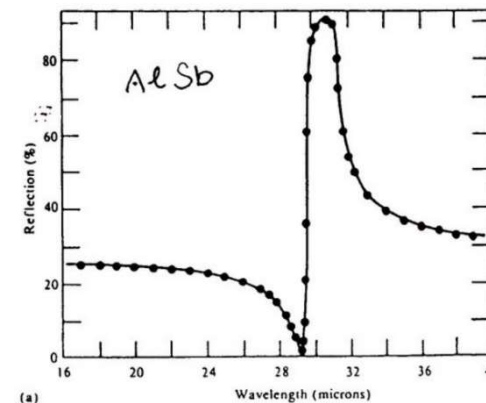
$m_r \gg m_e$ and $Q < e \rightarrow$ usually weaker transitions

Longitudinal excitation if $\varepsilon_{rel}(\omega_l) = 0$:
$$\varepsilon_{rel}' = \varepsilon_{\infty} + \frac{\Omega^2(\omega_0^2 - \omega_l^2)}{(\omega_0^2 - \omega_l^2)^2 + \gamma^2 \omega_l^2} = 0$$

since $\gamma \ll \omega_0 \omega_l$
$$\omega_l^2 = \omega_0^2 + \frac{\Omega^2}{\varepsilon_{\infty}}$$

$\omega_l - \omega_0$: LO-TO splitting (intensity!)

$\omega_l = \omega_{LO}$ longitudinal optical frequency
 $\omega_0 = \omega_{TO}$ transverse optical frequency



Generalized plasma frequency

$$\omega_p^2 = \frac{NQ^2}{\epsilon_0 m_e V} \quad \text{for any excitation } \omega_0$$

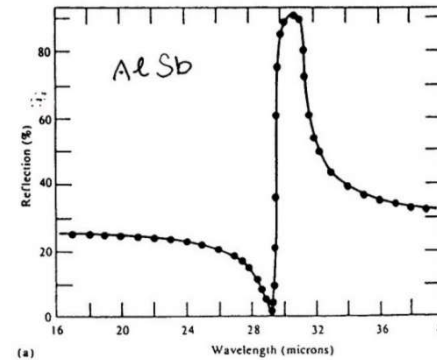
mass can be effective mass m_{eff} ;
N/V charge density involved in excitation

$$\epsilon_{rel} = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega}$$

Frequency of plasma minimum:

$$\epsilon_{rel}'(\omega_m) = 1 + \omega_p^2 \frac{\omega_0^2 - \omega_m^2}{(\omega_0^2 - \omega_m^2)^2 + \gamma^2 \omega_m^2} = 0$$

$$\omega_p^2(\omega_m^2 - \omega_0^2) = (\omega_m^2 - \omega_0^2)^2 + \gamma^2 \omega_m^2$$

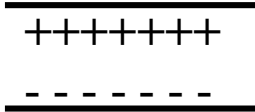


Neglecting $\gamma^2 \omega_m^2$: $\omega_p \gg \omega_0 \gg \gamma$

$$\omega_m^2 = \omega_0^2 + \omega_p^2$$



Plasma oscillations



The oscillations persist in zero external field:

$$\mathbf{E}_{\text{ext}} = \mathbf{D} = \varepsilon \mathbf{E} = \mathbf{0}$$

since $E \neq 0$ (charge separation), $\varepsilon = 0$ ($\varepsilon' = \varepsilon'' = 0$)

Plasma oscillations occur at the frequency where the condition is met, but we do **not** excite the plasma oscillations with light at normal incidence!



(Bulk) plasmons

Plasmons:

longitudinal oscillations of the electron gas
cannot be excited by normal incidence light

they appear if $\varepsilon' = \varepsilon'' = 0$

Detection of plasmons: electron energy loss spectroscopy (EELS)

EELS measures the **loss function**:

$$\text{Im}\left(-\frac{1}{\varepsilon''}\right)$$

T. Pichler, M.Knupfer, M.S. Golden, J. Fink,
A.G. Rinzler, R.E. Smalley:
Phys. Rev. Lett. **80**, 4729 (1998)

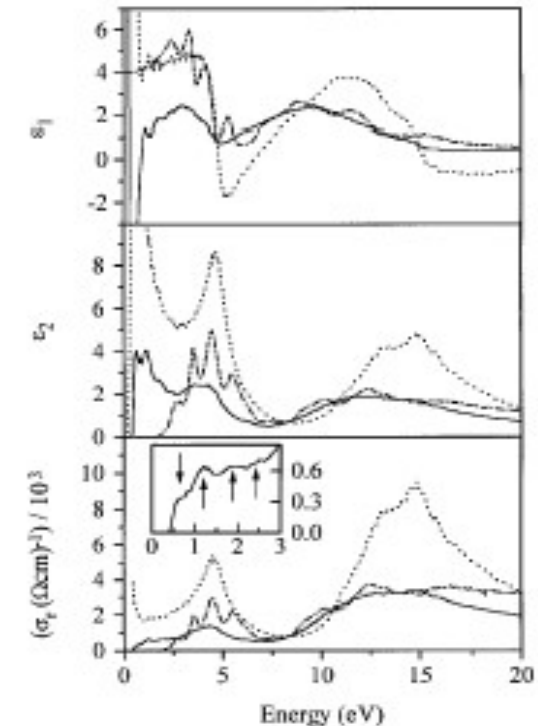


FIG. 3. The real and imaginary parts of the dielectric function (upper panels) and the real part of the optical conductivity (σ_1) at low momentum transfer: SWNTs (—) at $q = 0.1 \text{ \AA}^{-1}$, C_{60} (- · -) and graphite [polarized in plane (- -)] at $q = 0.15 \text{ \AA}^{-1}$, respectively. The inset shows σ_1 for the four lowest-lying interband transitions of SWNTs in an expanded range.

Optical and EELS spectra

$$\omega_{LO}^2 = \omega_{TO}^2 + \frac{\omega_p^2}{\epsilon_\infty}$$

Maximum of the loss function $\text{Im}\left(-\frac{1}{\epsilon(\omega)}\right)$ is at higher frequency than the absorption maximum

X. Liu, T. Pichler, M. Knupfer,
M.S. Golden, J. Fink, H. Kataura,
Y. Achiba:
Phys. Rev. B 66, 045411 (2002)

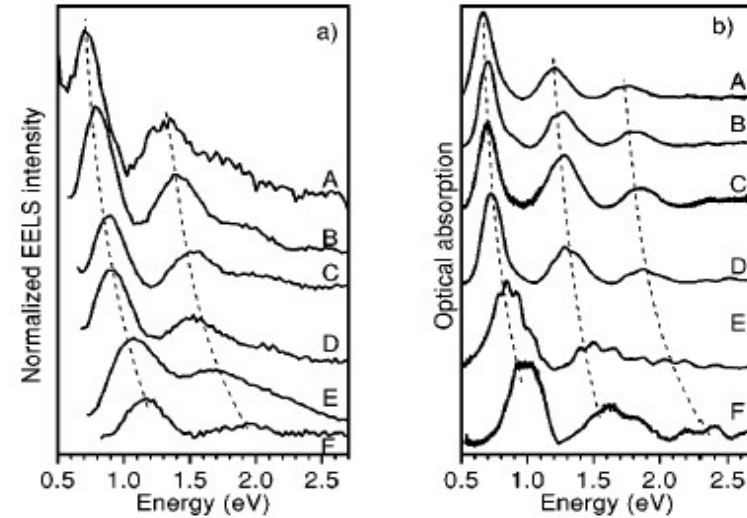


FIG. 4. (a) Loss function in the region of the low-energy inter-band transitions for SWCNT's with different mean diameters recorded with $q = 0.1 \text{ \AA}^{-1}$. (b) Optical absorption spectra (after background subtraction) from SWCNT with mean diameters as indicated.

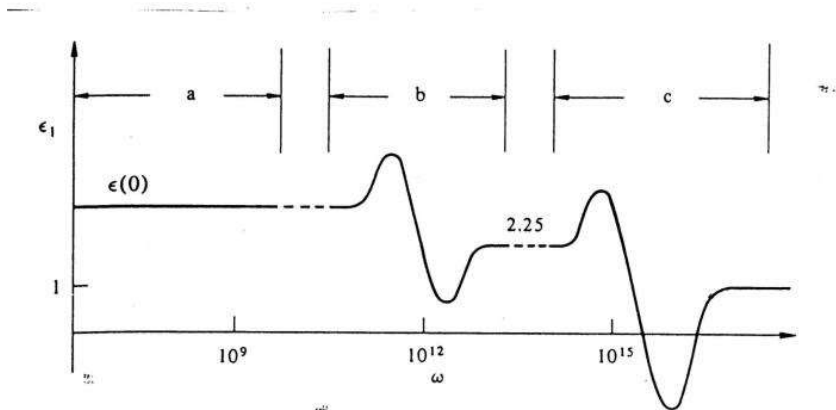
Description of multiple excitations

Drude-Lorentz dielectric function:

$$\epsilon_{rel} = 1 + \frac{e^2}{\epsilon_0 m V} \sum_i N_i \frac{1}{\omega_i^2 - \omega^2 - i\gamma_i \omega} = 1 + \sum_i \frac{\omega_{pi}^2}{\omega_i^2 - \omega^2 - i\gamma_i \omega}$$

Static dielectric constant:

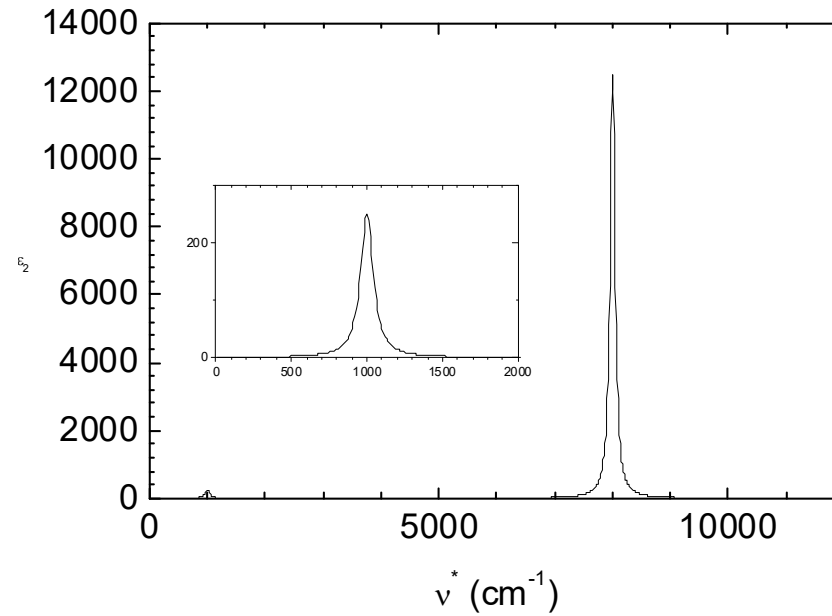
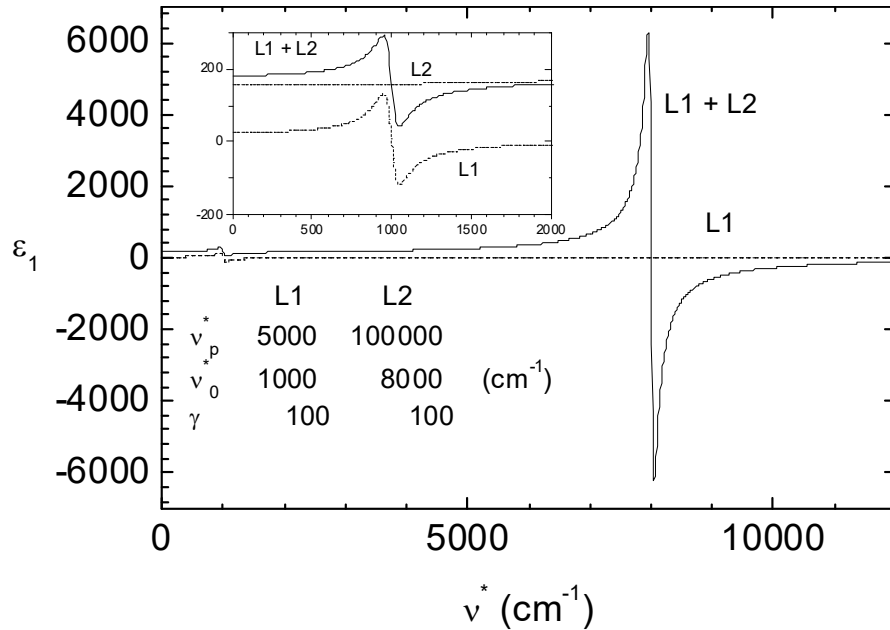
$$\epsilon_{rel}'(0) = 1 + \sum_i \frac{N_i e^2}{\epsilon_0 m V} \frac{1}{\omega_i^2} = 1 + \sum_i \frac{\omega_{pi}^2}{\omega_i^2}$$



If individual excitations are well separated, $\omega_i (i > n) \gg \omega_n$

$$\epsilon_{rel} = \sum_{i>n} \frac{\omega_{pi}^2}{\omega_i^2} + \sum_i \frac{\omega_{pi}^2}{\omega_i^2 - \omega^2 - i\gamma_i \omega} = \epsilon_\infty + \sum_i \frac{\omega_{pi}^2}{\omega_i^2 - \omega^2 - i\gamma_i \omega}$$

Multiple excitations – dielectric function



Special for semiconductors: $\epsilon_{rel}'(0) = \epsilon_{\infty} + \frac{\omega_p^2}{\omega_{gap}^2} = \epsilon_{\infty} + \frac{S}{E_{gap}^2}$ S oscillator strength in energy units

Even more simplified: $\epsilon_{rel}'(0) = 1 + \frac{S}{E_{gap}^2}$ $S = \hbar^2 \omega_p^2$

Static dielectric constant

$$\epsilon_{rel}'(0) = \epsilon_{\infty} + \frac{\Omega^2}{\omega_0^2} \quad (\text{one vibrational transition + electronic excitations})$$

$$\frac{\epsilon_{rel}'(0)}{\epsilon_{\infty}} = \frac{\omega_l^2}{\omega_0^2} = \frac{\omega_{LO}^2}{\omega_{TO}^2} \quad \text{Lyddane-Sachs-Teller relation}$$

For multiple oscillators:

$$\frac{\epsilon_{rel}'(0)}{\epsilon_{\infty}} = \prod_i \frac{\omega_{li}^2}{\omega_{0i}^2}$$

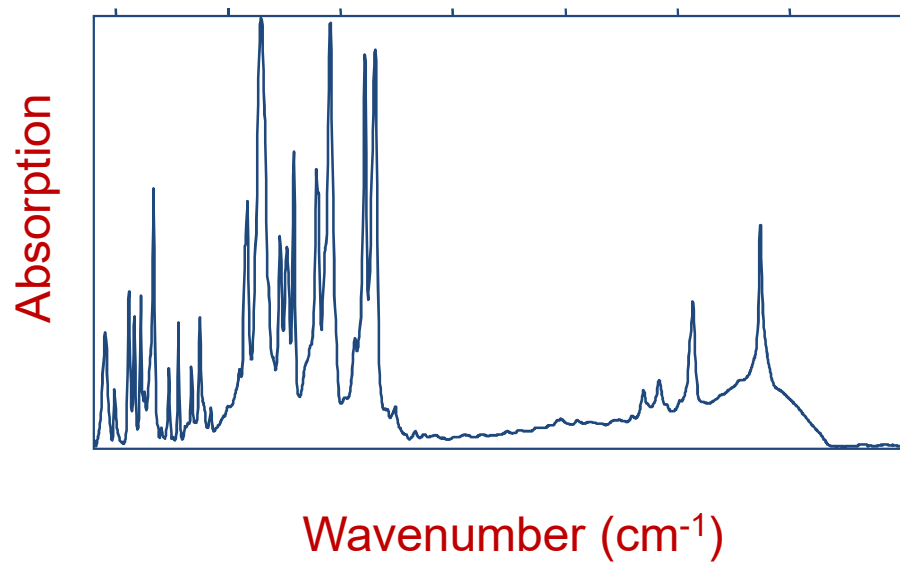
Application:

- is there a vibration below a given frequency? (comparison with dielectric constant)
- Estimation of high-frequency dielectric constant from vibrational spectra and static dielectric constant



Molecular spectra

dilute limit
absorption only



$$\alpha = \frac{2\omega n''}{c} = \frac{\epsilon''_{rel} \omega}{n' c}$$

Vibrations and spectra

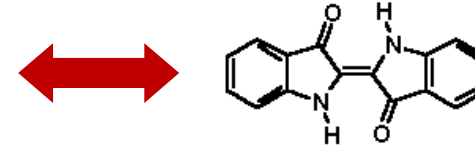
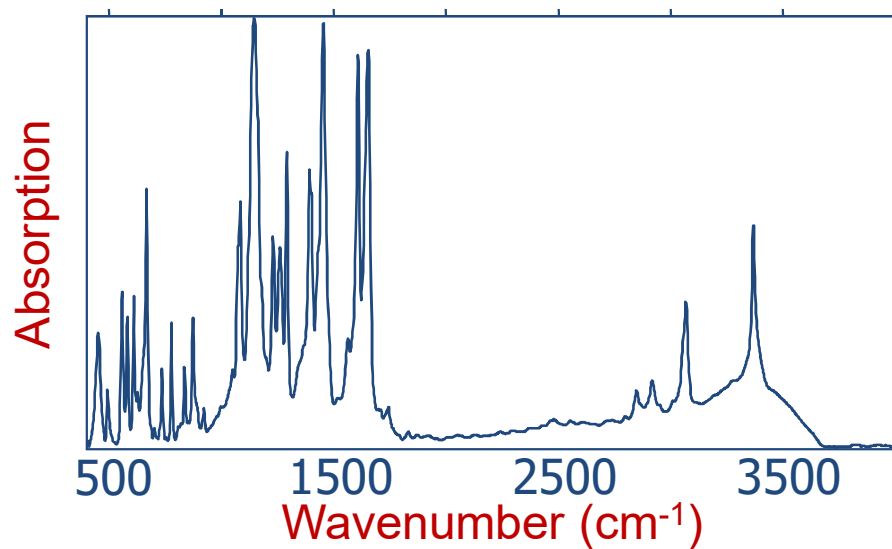
Vibrations need a well-defined energy

$$\text{Frequency: } \omega_0 = \sqrt{\frac{\kappa}{m_r}}$$

κ bond strength (spring constant)

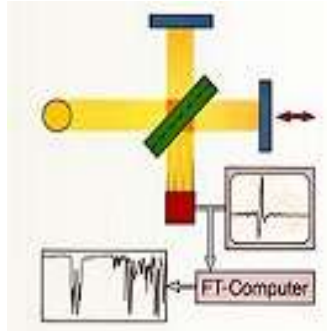
m_r reduced mass

Number of lines: symmetry
complicated structure



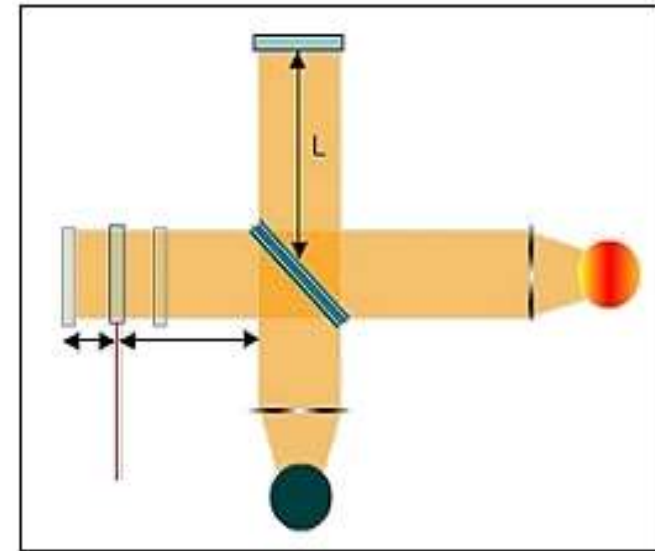
Qualitative analysis

Fourier-transform infrared (FTIR) spectroscopy

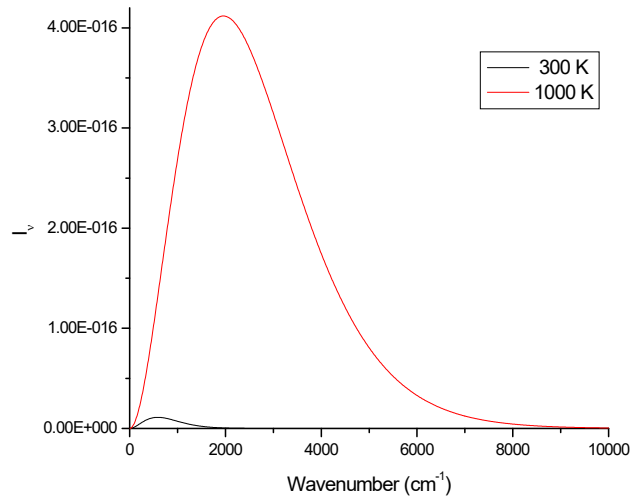
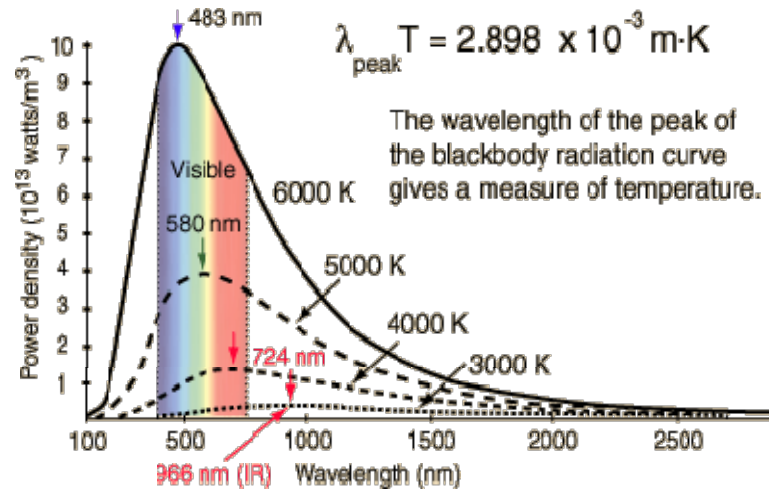


$$I(\nu^*) = \int_{-\infty}^{+\infty} I(x) \cos(2\pi\nu^* x) dx$$

$$i(\nu^*) = \Delta x \sum_{-M}^M I(m\Delta x) \cos(2\pi\nu^* m\Delta x)$$



Why FTIR?



high temperature: intensity grows also at high frequency (short wavelength)

environmental thermal radiation cannot be filtered out

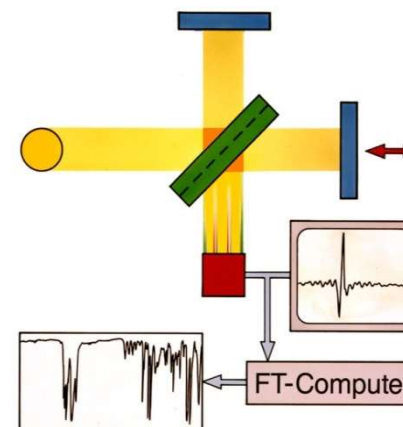
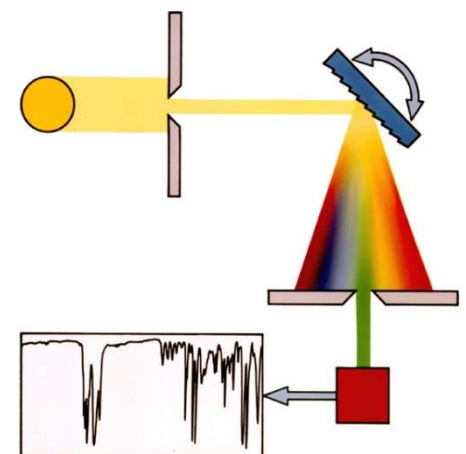
FTIR: only light getting into the interferometer will be modulated

FTIR advantages

Jacquinot's advantage: intensity
no need for narrow slit, as in monochromators
shape of illuminating light spot not critical
(detector: large dynamic range!)

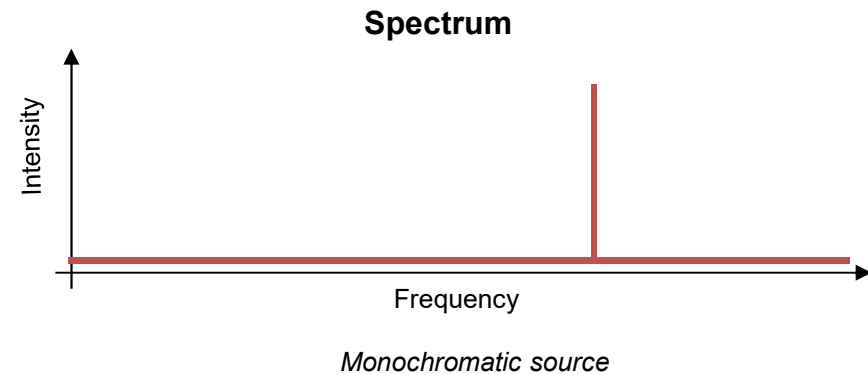
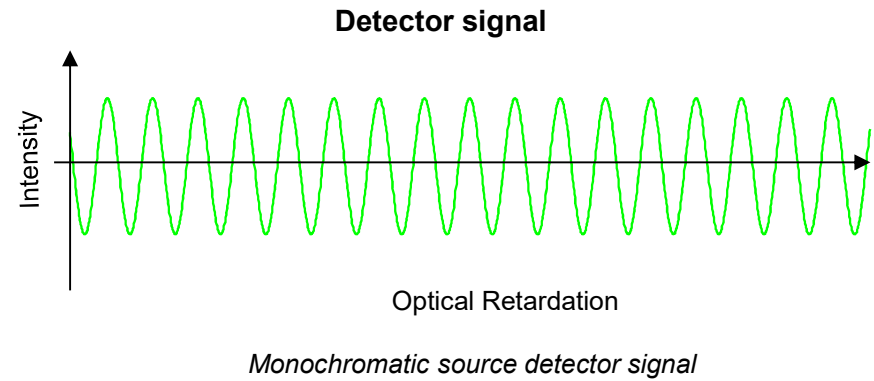
Fellgett's advantage (multiplex):
multiple frequencies in one scan
(in dispersive systems, scan time is determined by
the frequency range with the smallest intensity)
signal-to-noise ratio improves with more scans
time resolution possible on the scale of a few seconds

Dispersive IR spectrometer

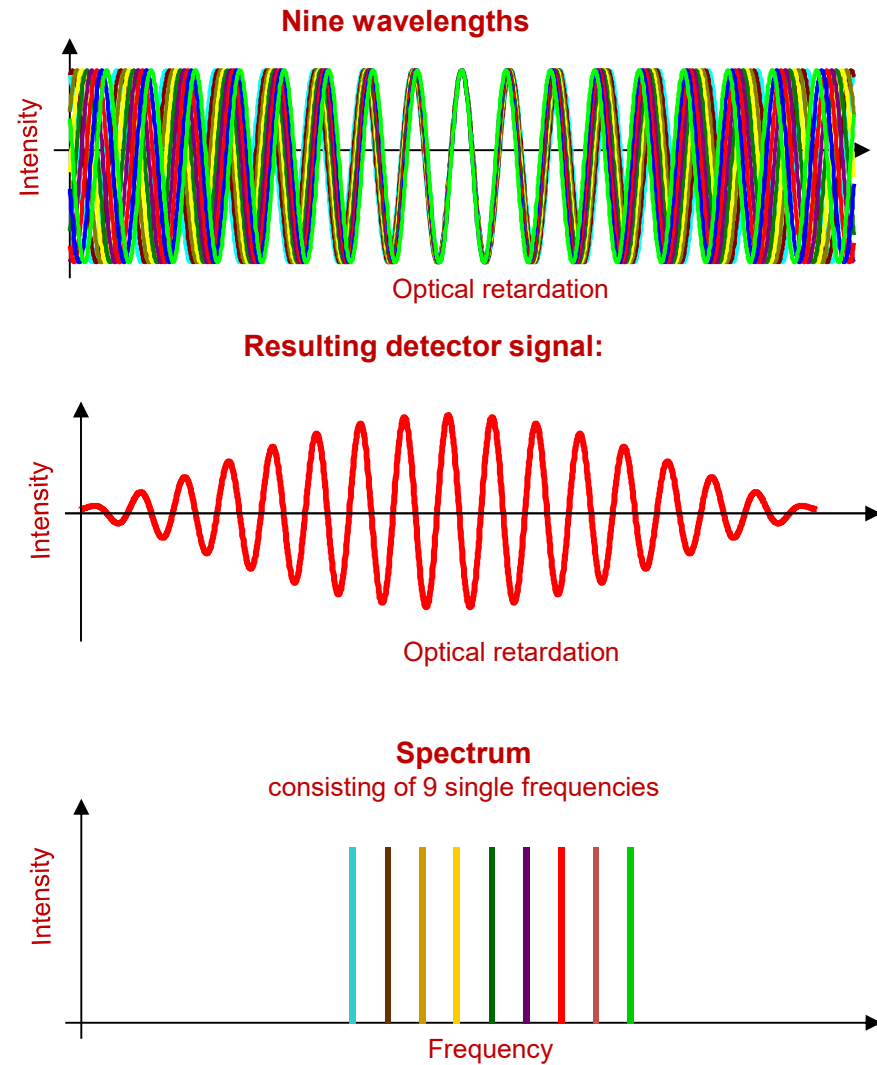


FT-IR spectrometer

Interferogram of a monochromatic source

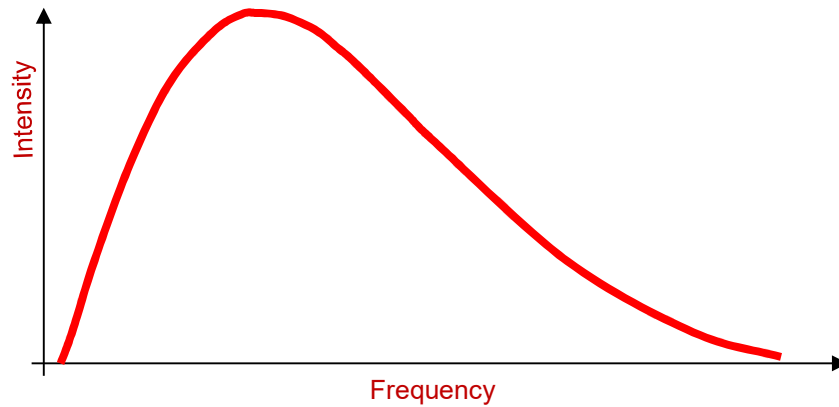


Interferogram of a polychromatic source

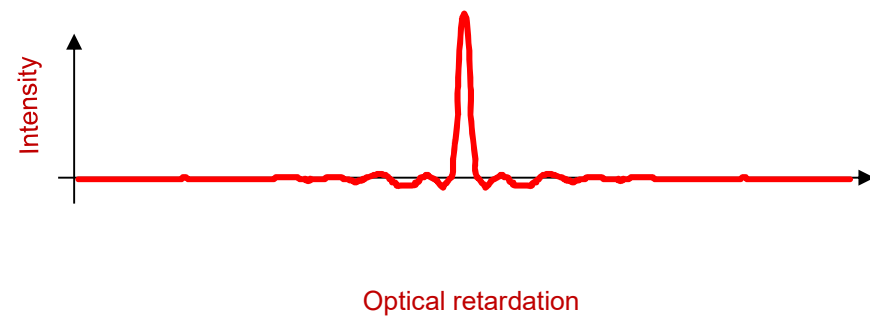


Interferogram of a continuous source

IR-source

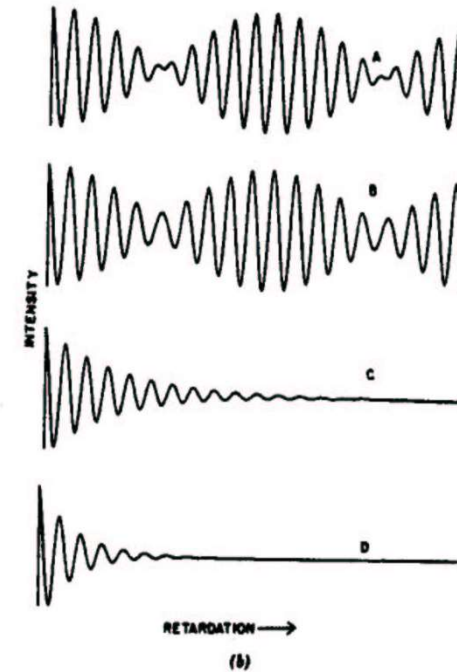
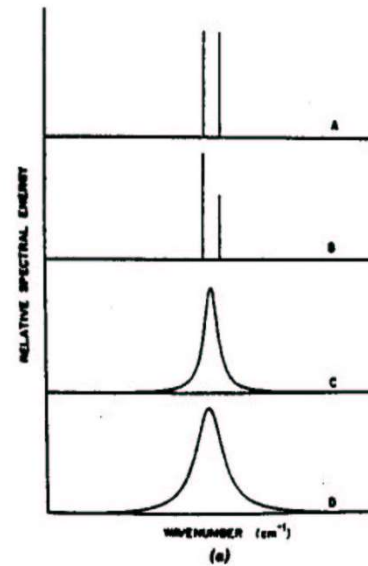


Resulting detector signal



Converting interferograms to spectra

P.R. Griffiths, J.A. de
Haseth:
Fourier Transform
Infrared Spectrometry
Wiley, 2007



Resolution

P.R. Griffiths, J.A. de
Haseth:
Fourier Transform
Infrared Spectrometry
Wiley, 2007

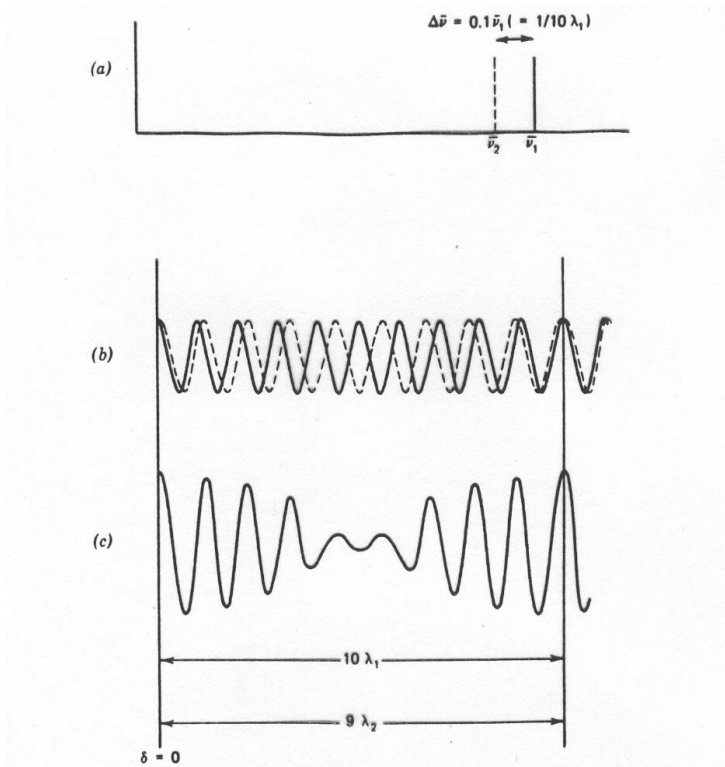


Fig. 1.4. (a) Spectrum of two lines of equal intensity at wavenumbers $\bar{\nu}_1$ (solid line) and $\bar{\nu}_2$ (broken line) separated by $0.1\bar{\nu}_1$. (b) Interferogram for each spectral line shown individually as solid and broken lines, respectively. (c) Resultant interferogram with the first maximum of the beat signal at $10/\bar{\nu}_1$; to resolve these two spectral lines, it is necessary to generate an optical retardation of at least this value.

$$10\lambda_1 = 9\lambda_2$$

$$\nu_2^* = 0.9\nu_1^*$$

$$\Delta\nu^* = 0.1\nu_1^*$$

$$x_{\min} = 10\lambda_1 = \frac{1}{\Delta\nu^*}$$

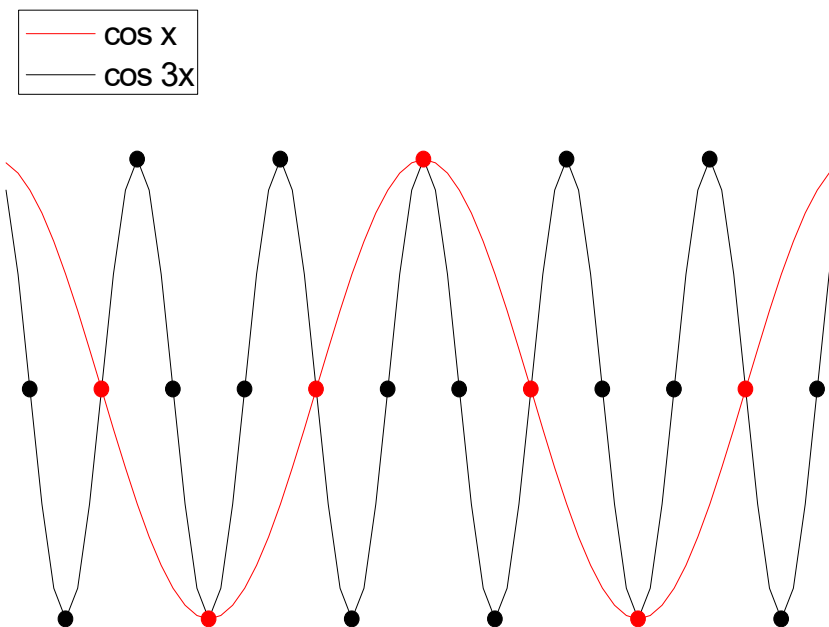
$$\Delta\nu^* = 1\text{cm}^{-1} \rightarrow x = 1\text{cm}$$

$$\Delta\nu^* = 0.01\text{cm}^{-1} \rightarrow x = 1\text{m}$$

Frequency range

Nyquist's theorem: a specific frequency should be distinguished from the harmonics by using appropriate sampling frequency

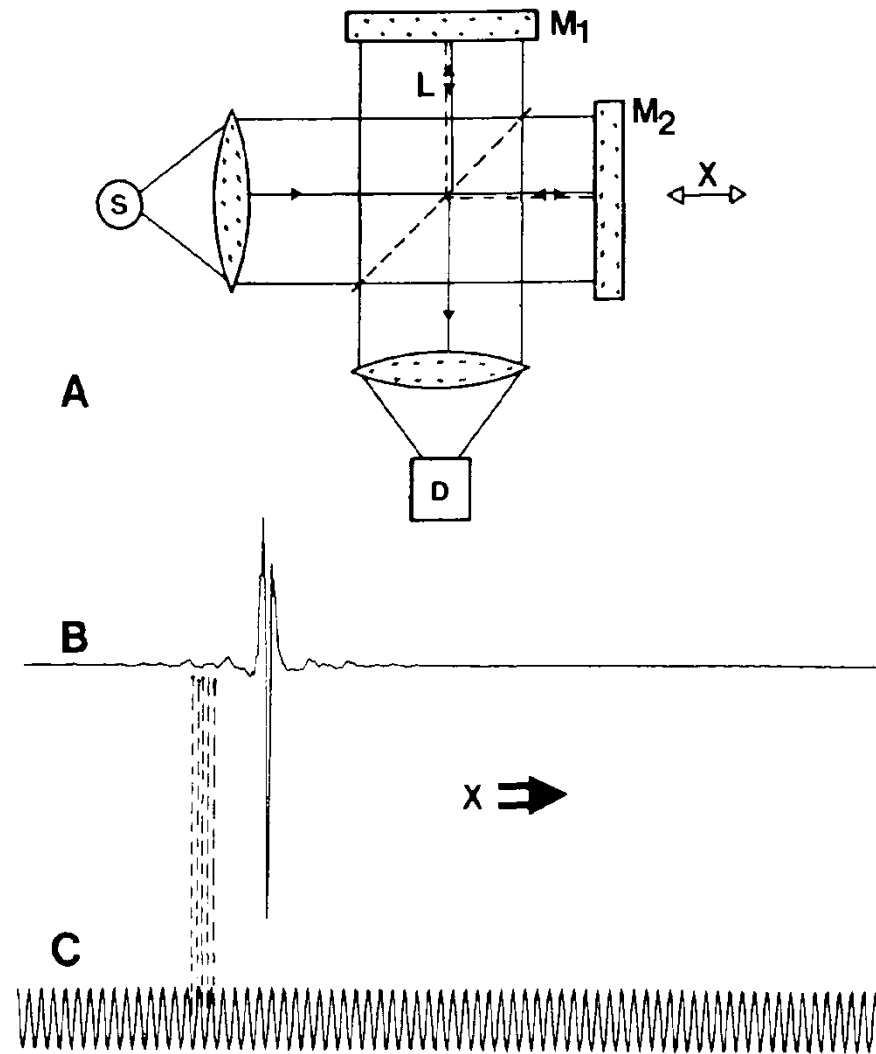
Example:



$$\nu_{\max}^* = \frac{1}{2\Delta x}$$

$$\nu_{\max}^* = 1000 \text{ cm}^{-1} \longrightarrow \Delta x = 5 \mu\text{m}$$

Sampling control: He-Ne laser



Typical parameters

Mirror velocity: 0.5-60 mm/sec

He-Ne laser wavelength: 632.8 nm, wavenumber 15800 cm⁻¹

minimal distance of zero points: 316.4 nm $v_{\max} = 15800 \text{ cm}^{-1}$
632.8 nm $v_{\max} = 7900 \text{ cm}^{-1}$

frequency of signal at detector: $f = 2vv^*$

for $f = 1.58 \text{ mm/sec}$

400 cm⁻¹ $f = 126 \text{ Hz}$

4000 cm⁻¹ $f = 1260 \text{ Hz}$



Signal evaluation

Interferogram

Fourier transformation:

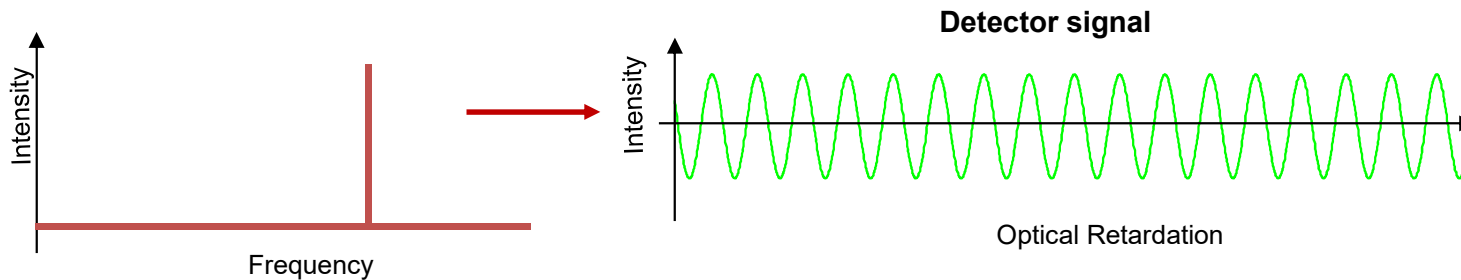
Apodization

Phase correction

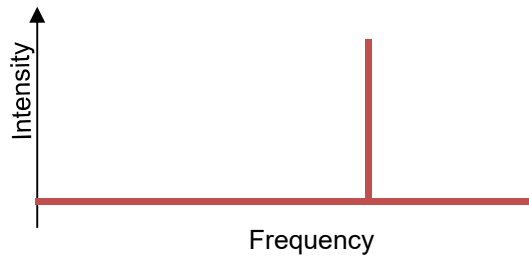
Zerofilling

$$i(\nu^*) = \Delta x \sum_{-M}^M I(m\Delta x) \cos(2\pi\nu^* m\Delta x)$$

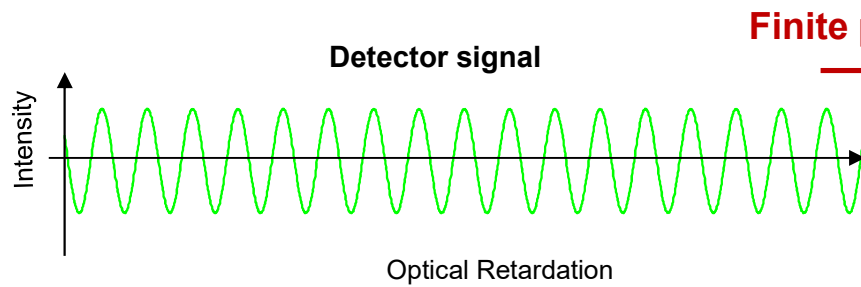
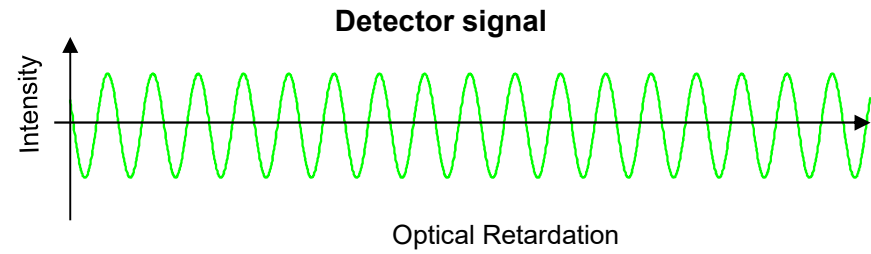
finite, discrete FT



Instrumental lineshape

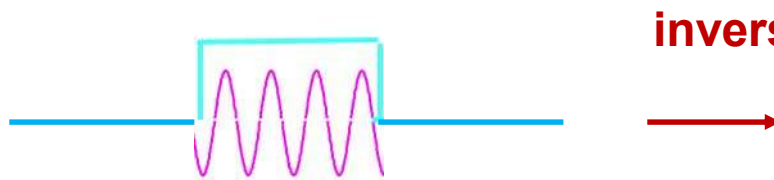
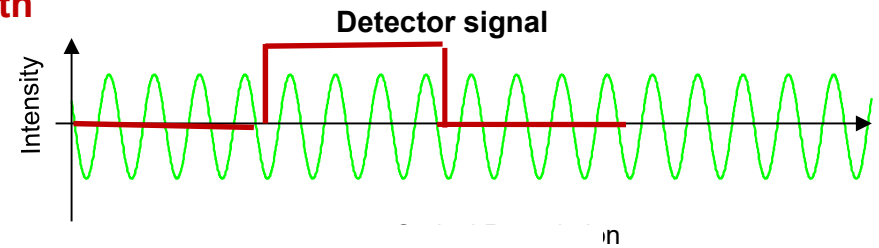


FT
→

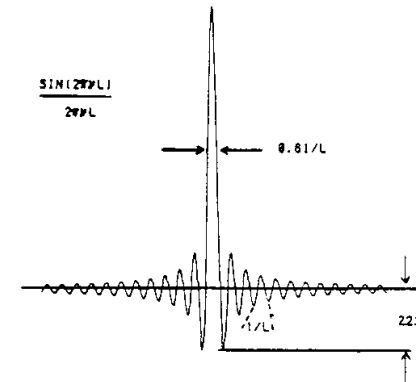


Finite pathlength
→

Boxcar



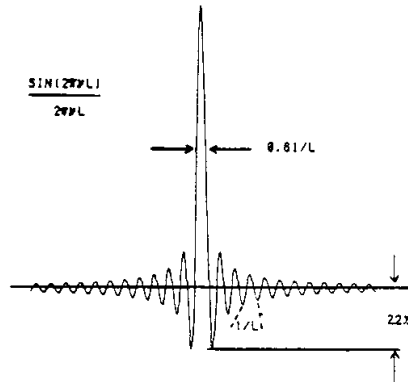
inverse FT
→



Apodization

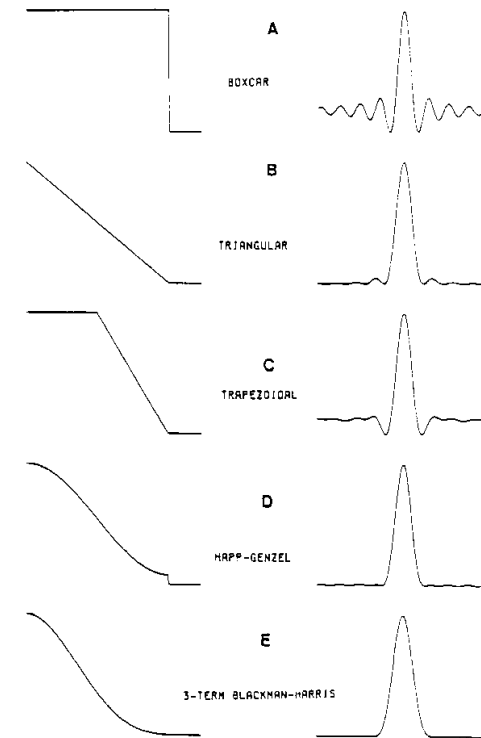
Instrumental lineshape:

$$I(\nu) = 2M\Delta x \frac{\sin(2\pi\nu M\Delta x)}{2\pi\nu M\Delta x} = 2M\Delta x \operatorname{sinc}(2\pi\nu M\Delta x)$$



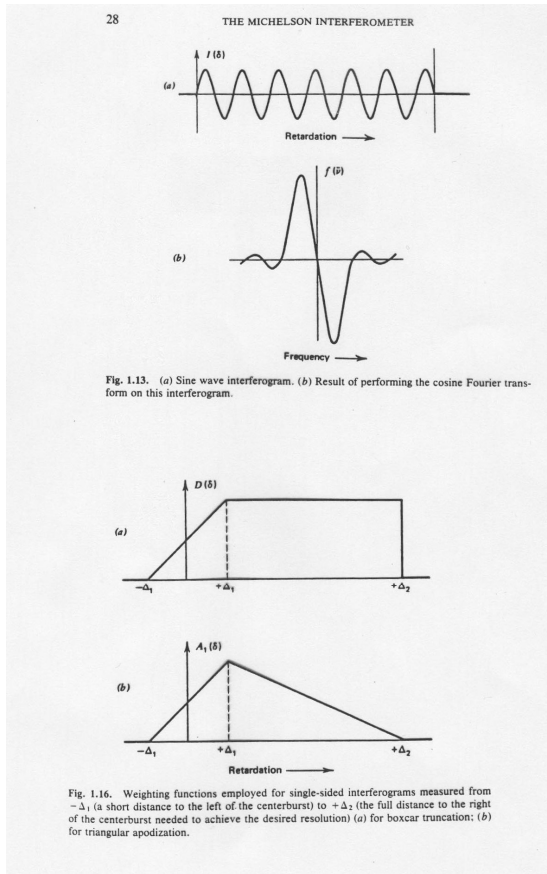
Fourier transform of the boxcar cutoff, known as the sinc function. Largest side lobe is 22 % of the main lobe amplitude. L = Optical Pathlength Difference.

Apodization
(French for
“cutting the feet off”:
convolution with
other functions



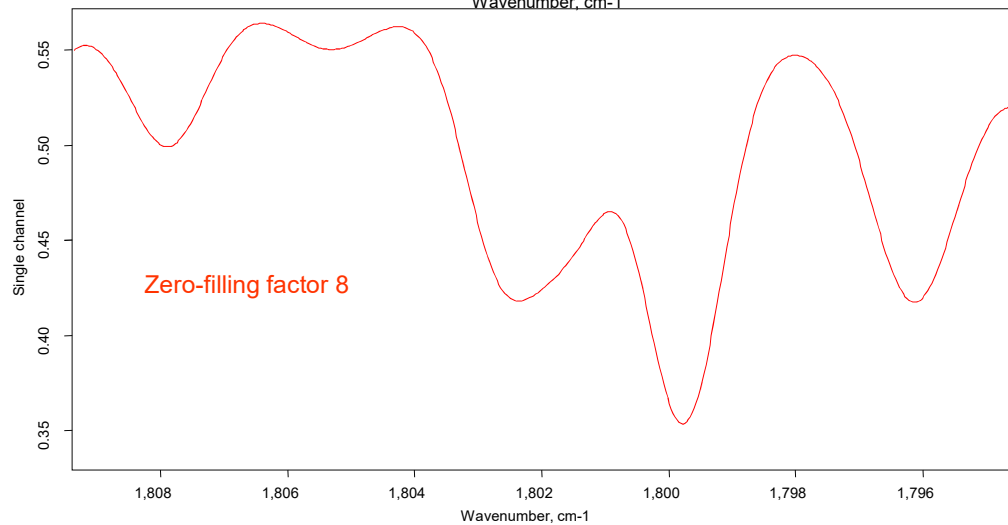
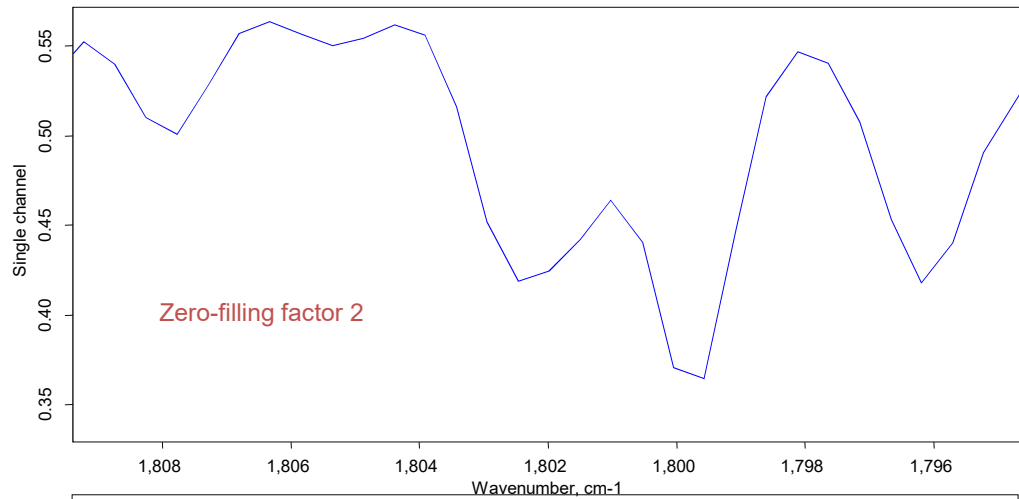
Several apodization functions (left) and the 'Instrumental Lineshape' produced by them (right). The cases A - D are commonly used in FT-IR.

Phase correction



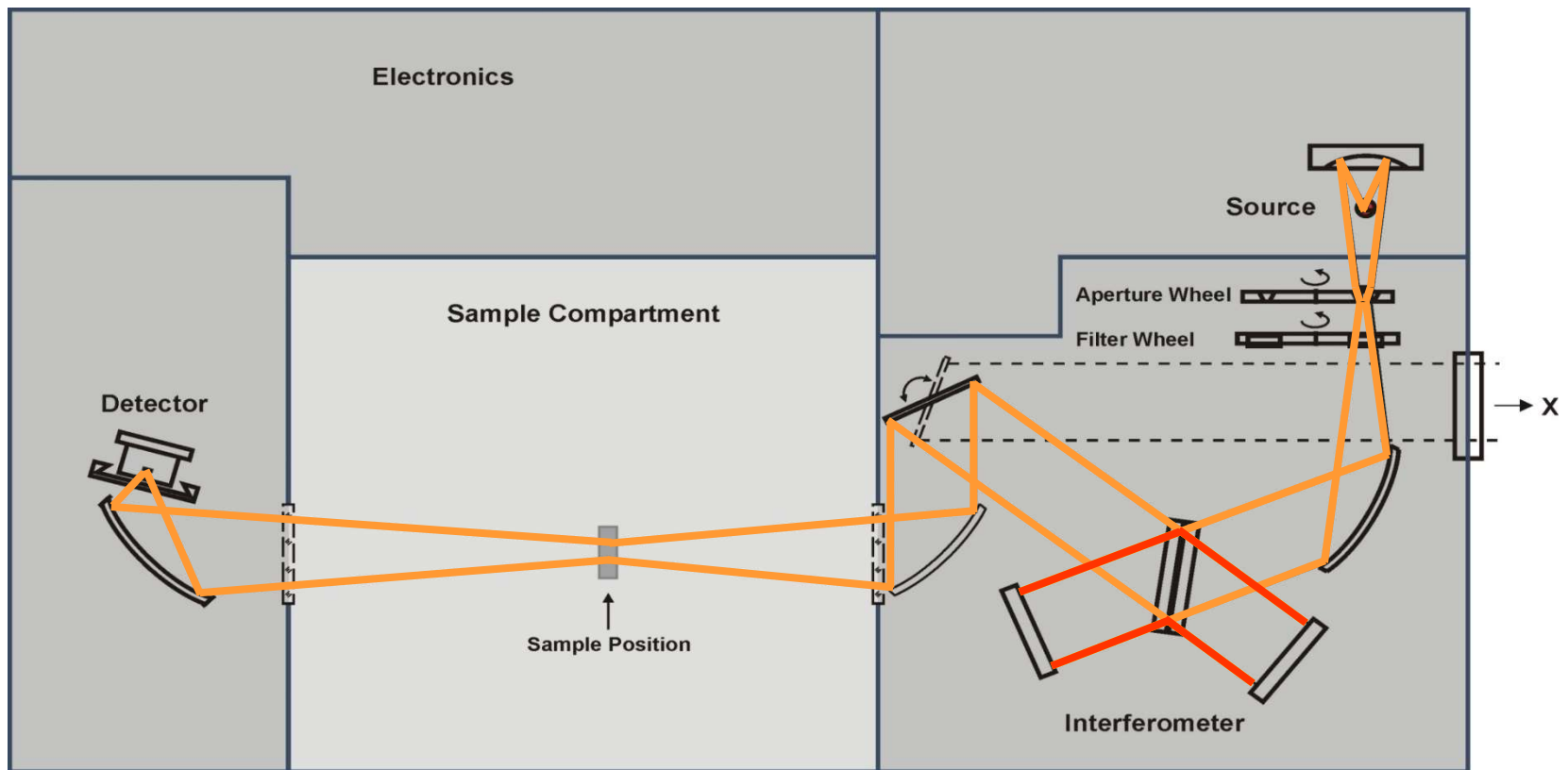
Interferogram contains $\sin(x)$ contributions
Complex Fourier transformation
Determination of phase at chosen frequencies
(real resolution decreases)

Zerofilling

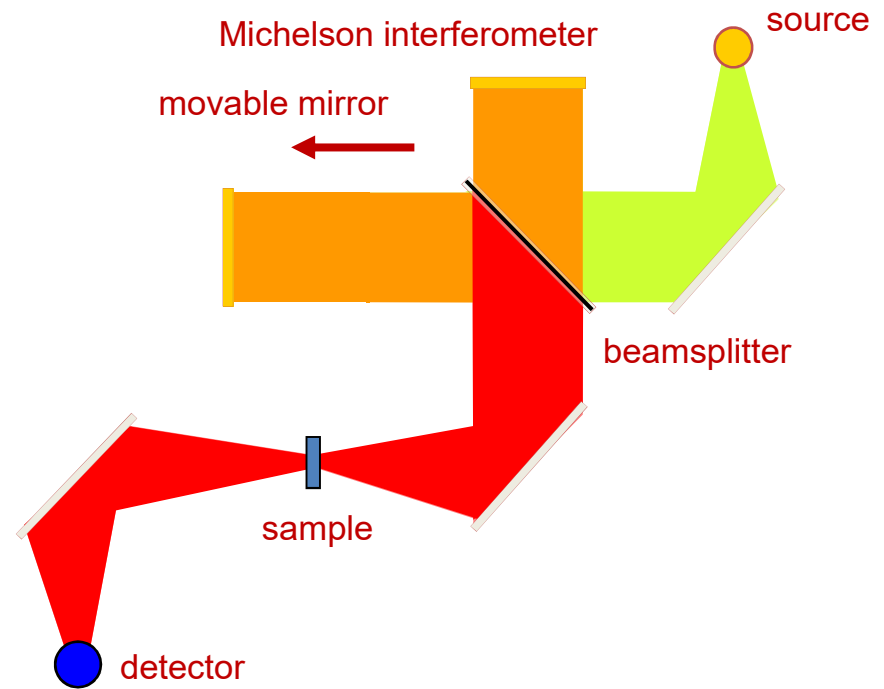
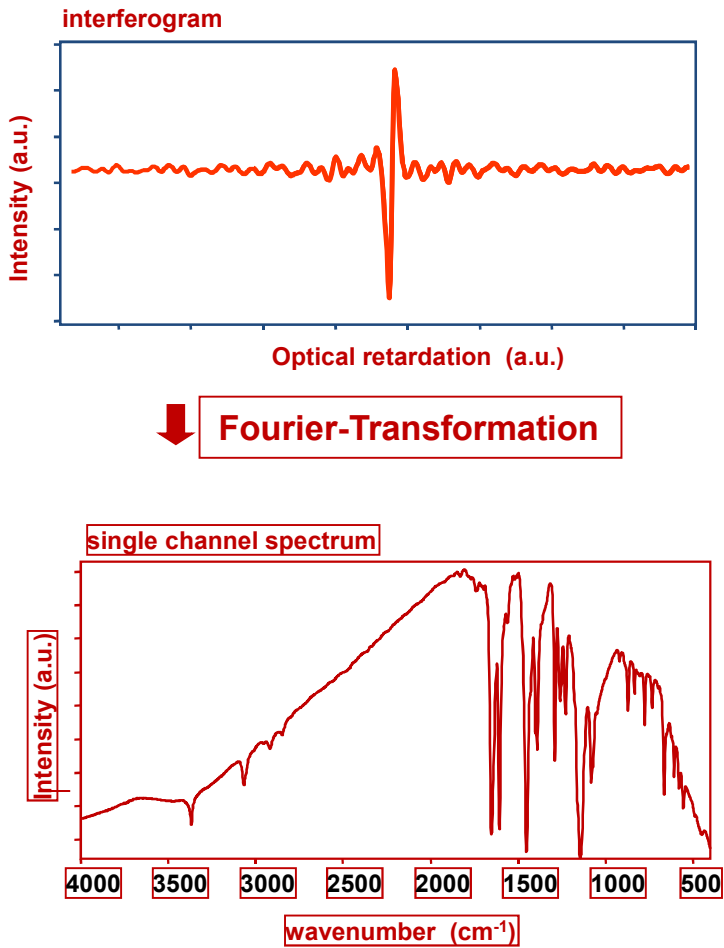


Adding zeroes to end of interferogram
“Spectrum-like” interpolation
Does not replace resolution!

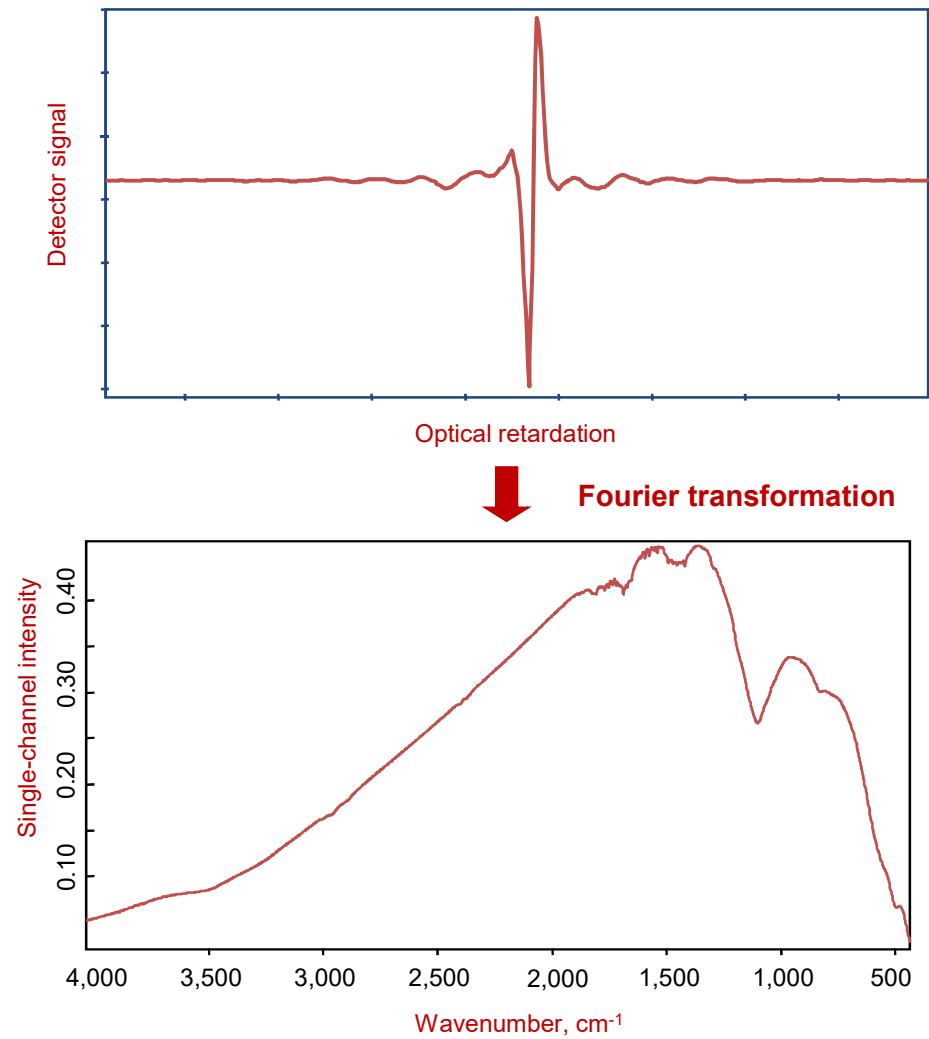
FTIR spectrometer



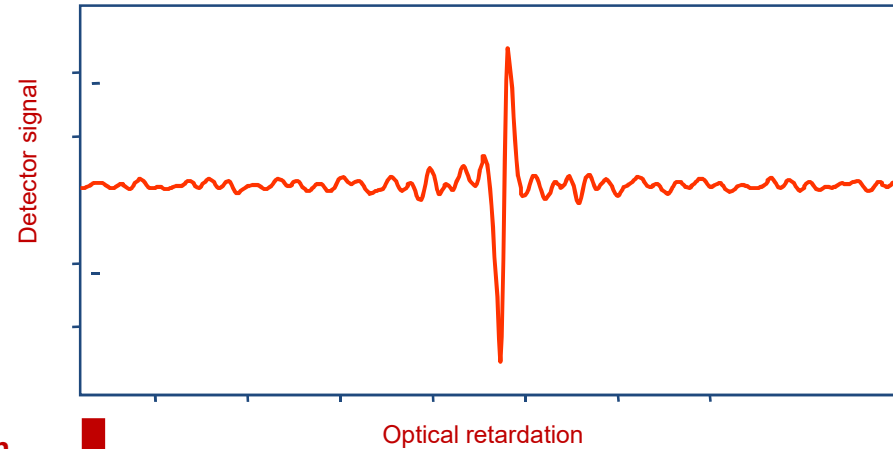
FTIR measurement



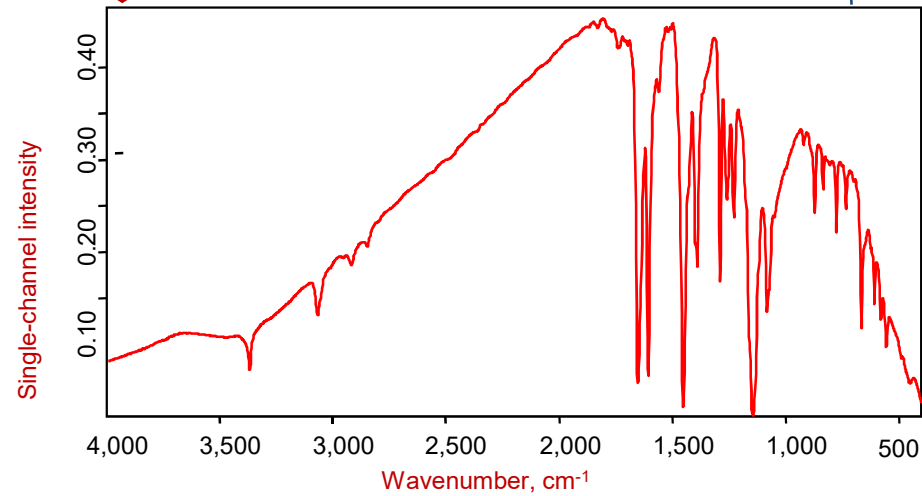
Reference spectrum



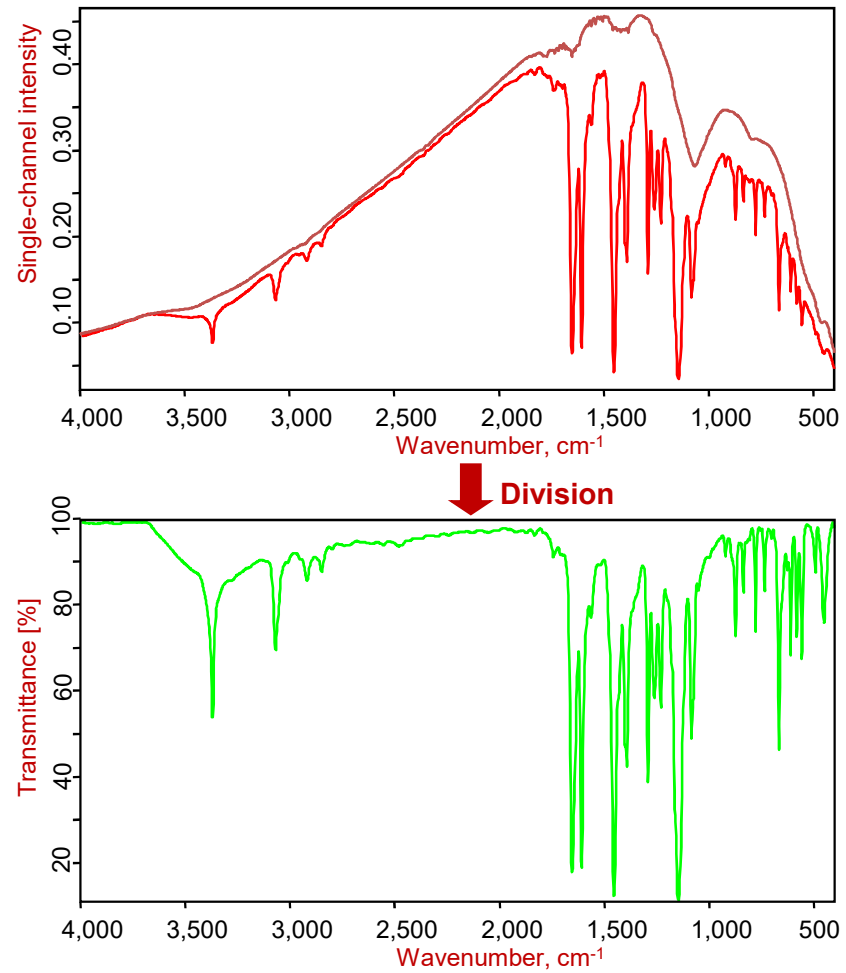
Sample spectrum



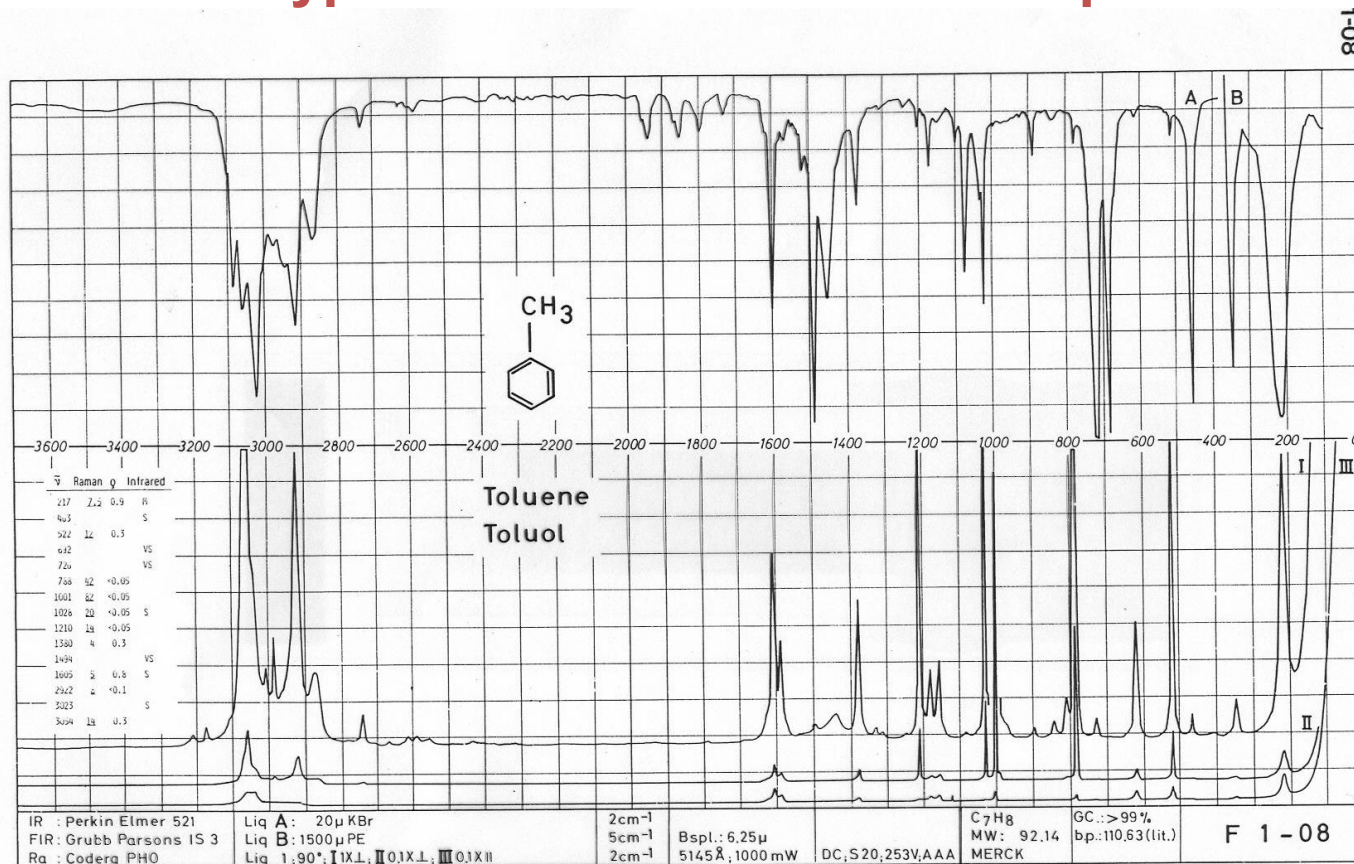
Fourier transformation



Transmission spectrum

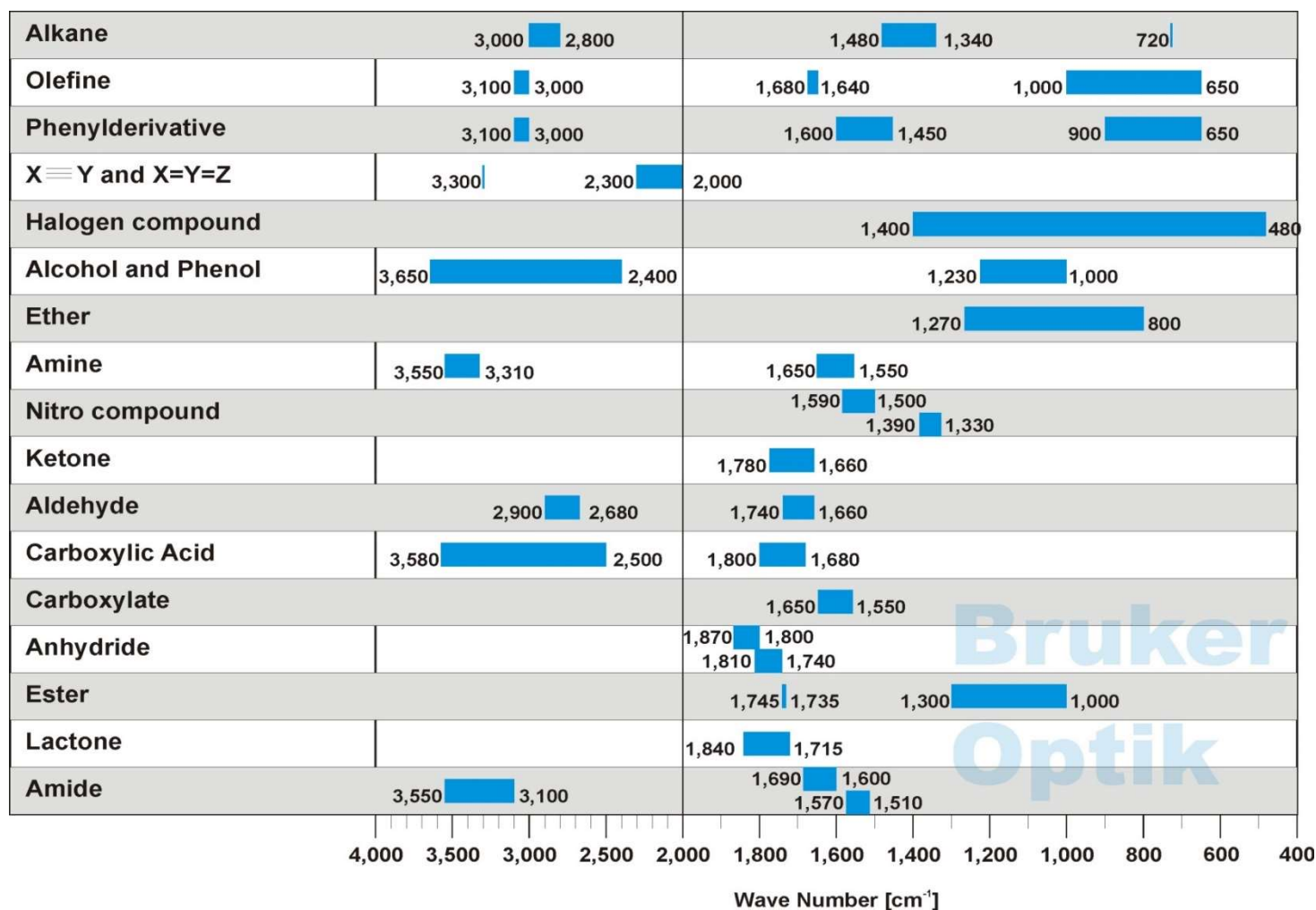


Typical infrared and Raman spectrum



B. Schrader:
Raman/Infrared Atlas
of Organic Compounds.
VCH Publishers, 1989.

Group frequencies



Instruments



FIR/MIR



MIR/NIR



Near field/SNOM

Take-home message

- vibrational spectra: vibrations of atoms, damped harmonic oscillator with reduced mass $m_r = \frac{m_+ m_-}{m_+ + m_-}$ and relative displacement $r = (u_+ - u_-)$
- eigenfrequency of oscillator $\omega_0 = \sqrt{\frac{\kappa}{m_r}}$ κ interatomic interaction strength
- FTIR spectroscopy: Michelson interferometer, $I(\nu^*) = \int_{-\infty}^{+\infty} I(x) \cos(2\pi \nu^* x) dx$
- throughput and multiplex advantage
- interferogram of monochromatic source: cosine function, of continuous source: peaked
- FTIR spectrometer: source – beamsplitter – sample – detector
- measurement: interferogram \rightarrow single-beam spectrum \rightarrow transmission spectrum
- resolution depends on mirror pathlength, frequency range on sampling interval
- signal evaluation from interferogram: apodization, phase correction, zerofilling
- infrared spectral analysis: qualitative (group frequencies), quantitative (Beer's law)



Összefoglalás

- rezgési spektrumok: atomok rezgései, csillapított harmonikus oszcillátor, redukált tömeg $m_r = \frac{m_+ m_-}{m_+ + m_-}$, relatív elmozdulás $r = (u_+ - u_-)$
- sajátfrekvencia $\omega_0 = \sqrt{\frac{\kappa}{m_r}}$ κ az atomok közti kölcsönhatás erőssége
- FTIR spektroszkópia: Michelson interferométer, $I(\nu^*) = \int_{-\infty}^{+\infty} I(x) \cos(2\pi\nu^* x) dx$
- átbocsátás és multiplex előny
- monokromatikus forrás interferogramja: cosinusfüggvény, folytonos forrásé: egy csúcs
- FTIR spektrométer: forrás – nyalábosztó – mintatér – detektor
- mérés: interferogram \rightarrow egysugaras spektrum \rightarrow transzmissziós spektrum
- a felbontást a tükörúthossz, a frekvenciatartományt a mintavétel gyakorisága határozza meg
- jelfeldolgozás: interferogram – apodizáció – fáziskorrekció - zerofilling
- infravörös analízis: kvalitatív (csoportfrekvenciák), kvantitatív (Lambert - Beer törvény)