Optical spectroscopy in materials science 6.

Infrared spectroscopy

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Damped harmonic oscillator

(for metals, Drude model was already discussed)
electron of charge -e, mass *m,* in the field of a nucleus of infinite mass

$$\frac{md^2\mathbf{r}}{dt^2}+m\gamma\frac{d\mathbf{r}}{dt}+m\omega_0^2\mathbf{r}=-e\mathbf{E}$$

Look for **r** in the form $\mathbf{r}_0 e^{-i\omega t}$;
using

$$\frac{d\mathbf{r}}{dt}=-i\omega\mathbf{r},\frac{d^2\mathbf{r}}{dt^2}=-\omega^2\mathbf{r}$$

$$\mathbf{r}=\frac{-e\mathbf{E}/m}{\omega_0^2-\omega^2-i\gamma\omega}$$

$$\mathbf{P}=\frac{1}{V}Ne\mathbf{r}=\frac{e^2N}{mV}\frac{\mathbf{E}}{\omega_0^2-\omega^2-i\gamma\omega}=\chi\varepsilon_0\mathbf{E}$$

$$\chi=\frac{e^2N}{\varepsilon_0 mV}\frac{1}{\omega_0^2-\omega^2-i\gamma\omega}$$

$$\boxed{\varepsilon_{rel}=\frac{\varepsilon}{\varepsilon_0}=1+\chi=1+\frac{Ne^2}{\varepsilon_0 mV}\frac{1}{\omega_0^2-\omega^2-i\gamma\omega}}$$

Measuring intensity

$I \sim E^2$

when exiting the medium:

$$I(z) = E(z)^2 = I(0)e^{-\alpha z} = E(0)^2 e^{-\alpha z} = E(0)^2 e^{\frac{-2\omega n'' z}{c}}$$

Hence $\alpha = \dfrac{2\omega n''}{c}$ $\qquad n'' = \dfrac{\alpha c}{2\omega}$ $\qquad \varepsilon_{rel}'' = \dfrac{n'\alpha c}{\omega} = \dfrac{\sigma'}{\omega\varepsilon_0}$ $\qquad \alpha = \dfrac{\sigma'}{n' c \varepsilon_0}$

n” extinction coefficient (amplitude attenuation)

α absorption coefficient (intensity attenuation)

„Crude” division:

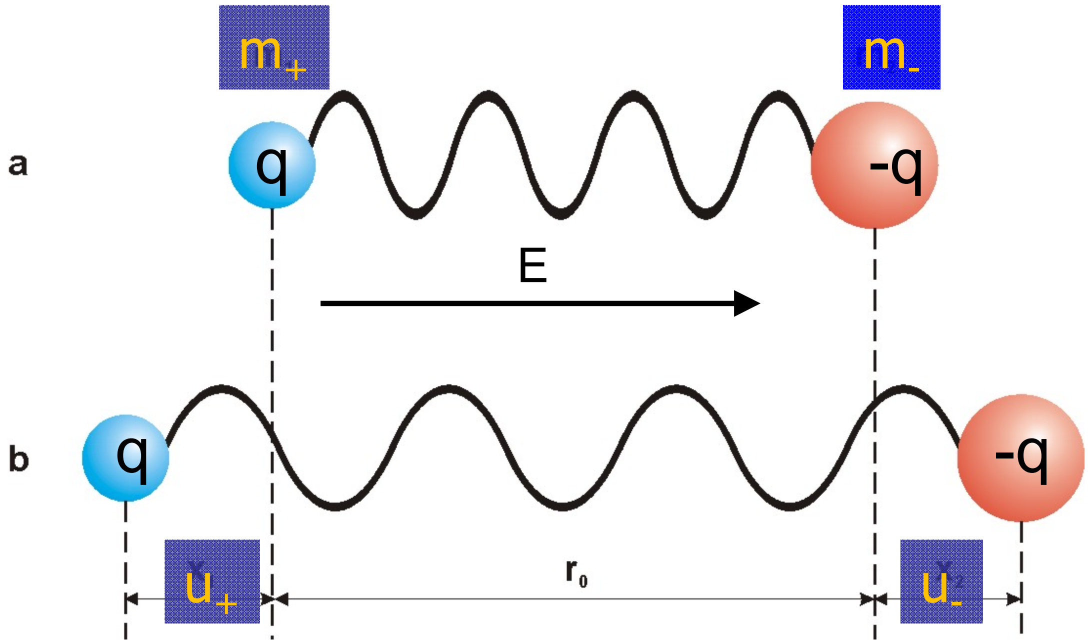
absorption α, n**”, ε”, σ’**

dispersion n’, **ε’, σ”**

Penetration depth: d = 1/α (intensity changes by 1/*e*)

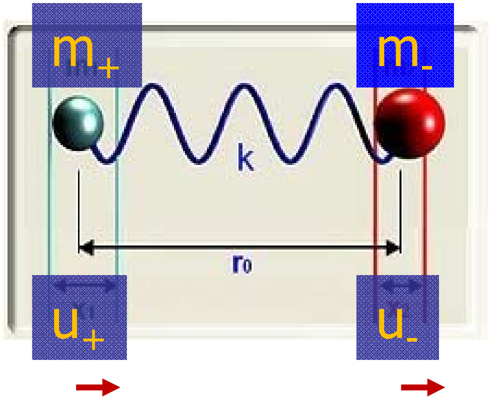
Skin depth (metals): l = 2/α (amplitude changes by 1/*e*)

Molecular vibrations



Mechanical model of a vibrating diatomic molecule

Vibrational spectra



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

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

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

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

$$m_r = \frac{m_+m_-}{m_+ + m_-}$$ **reduced mass**

$$r = (u_+ - u_-)$$ **relative displacement**

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

$$\omega_0 = \sqrt{\frac{\kappa}{m_r}}$$ **eigenfrequency**

$$E = E_0e^{-i\omega t} \longrightarrow r = r_0e^{-i\omega t}$$

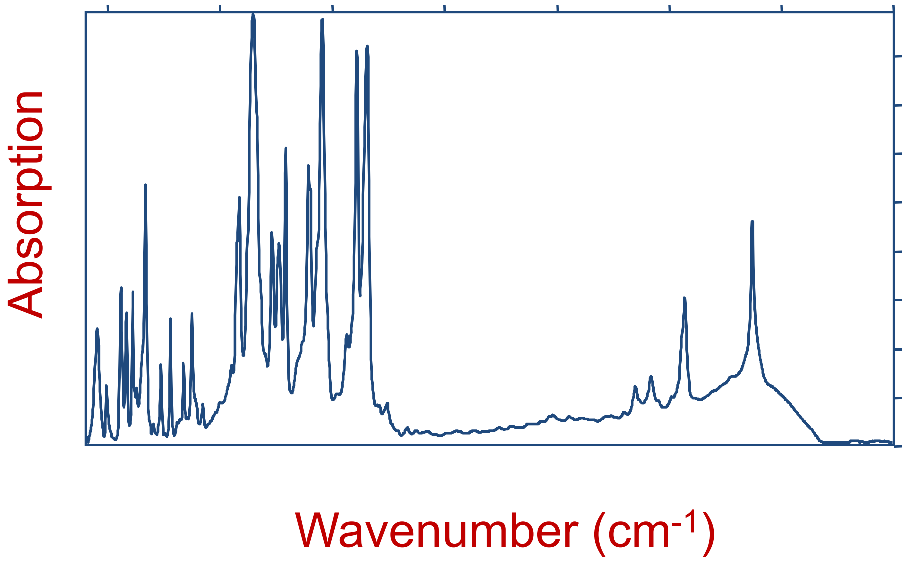
For a system of volume V, containing N molecules:

$$\boldsymbol{\mu} = \alpha\mathbf{E} \rightarrow \chi = \frac{\alpha N}{V} \rightarrow \varepsilon_{rel} = 1 + \chi$$

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

Molecular spectra

dilute limit
absorption only



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

Vibrations and spectra

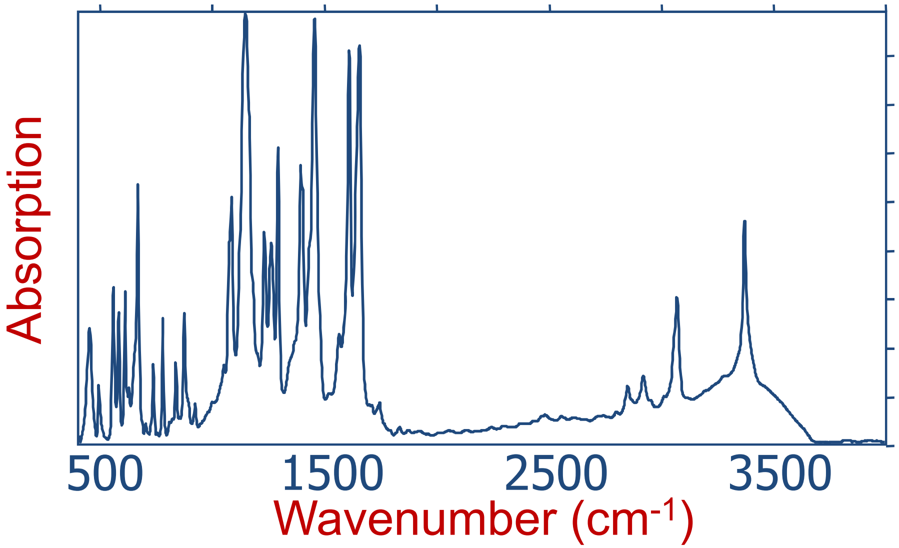
Vibrations need a well-defined energy

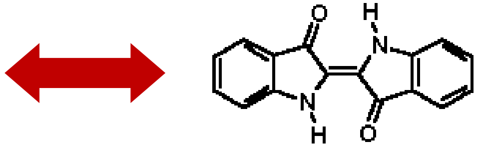
Frequency: $\omega_0 = \sqrt{\frac{\kappa}{m_r}}$

κ bond strength (spring constant)

m_r reduced mass

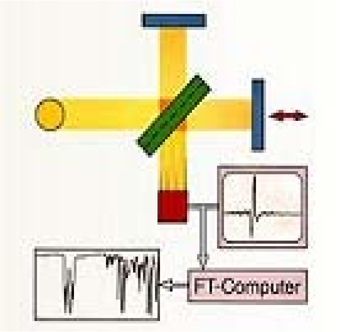
Number of lines: symmetry
complicated structure

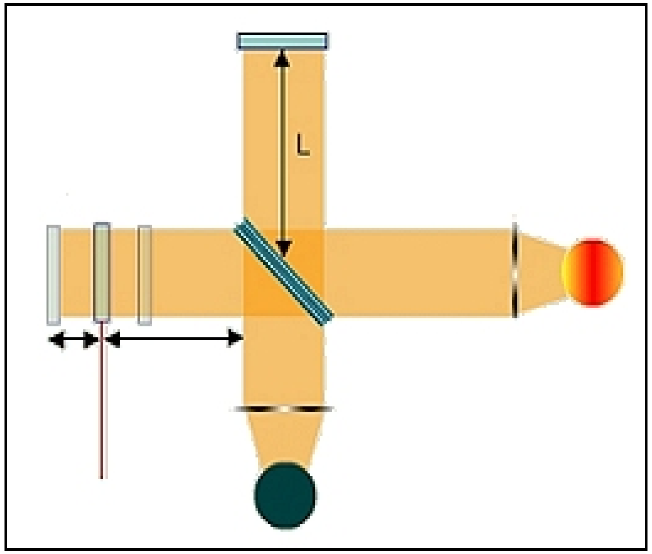




Qualitative analysis

Fourier-transformation infrared (FTIR) spectroscopy

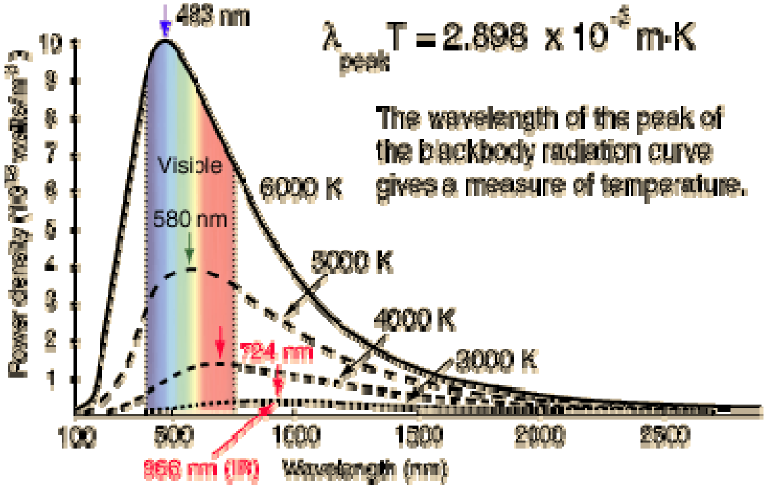


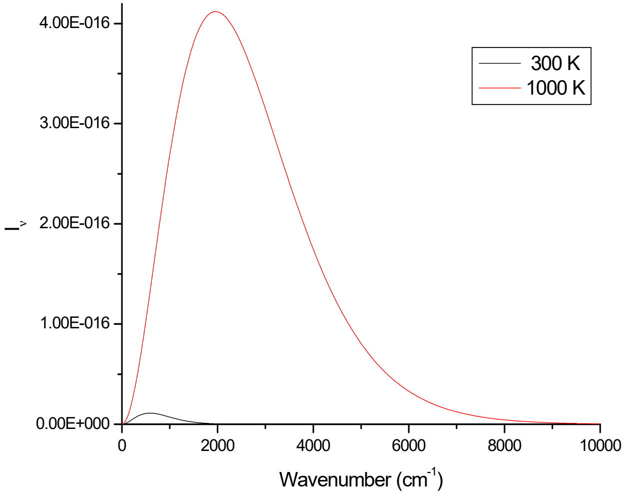


$$I(\nu^*) = \int_{-\infty}^{+\infty} I(x)\cos(2\pi\nu^* x)dx$$

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

Why FTIR?





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

environmental thermal radiation cannot be filtered out

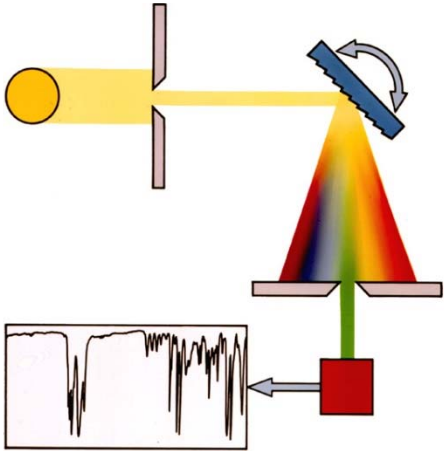
FTIR: only light getting into the interferometer will be modulated

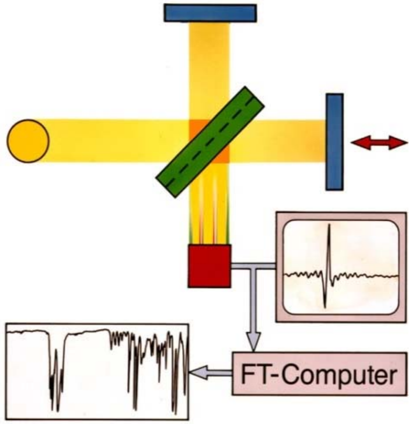
FTIR advantages

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

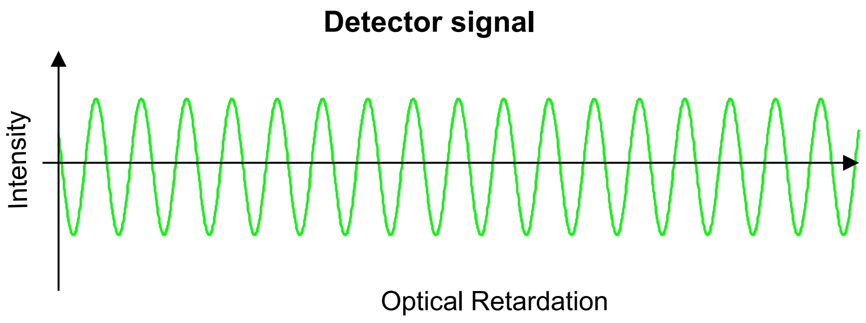
Dispersive IR spectrometer



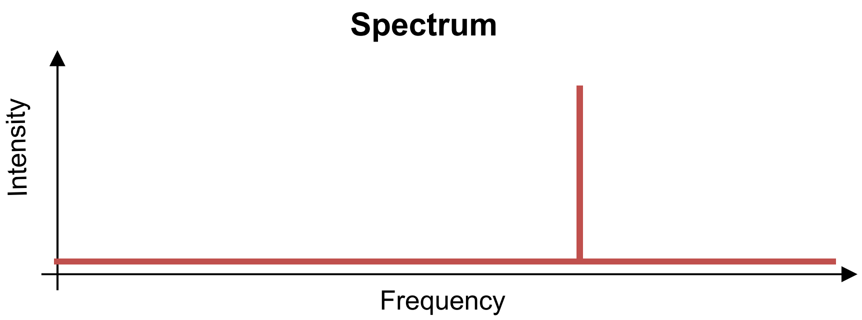


FT-IR spectrometer

Interferogram of a monochromatic source



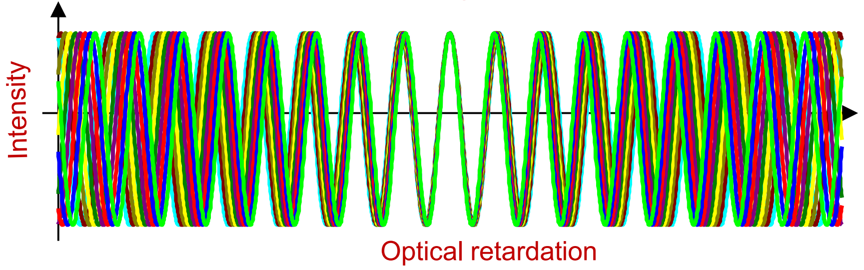
Monochromatic source detector signal



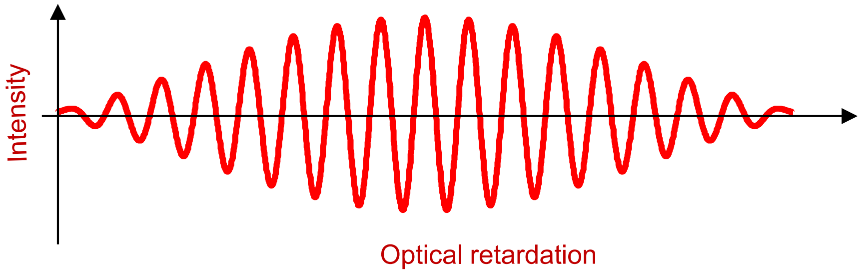
Monochromatic source

Interferogram of a polychromatic source

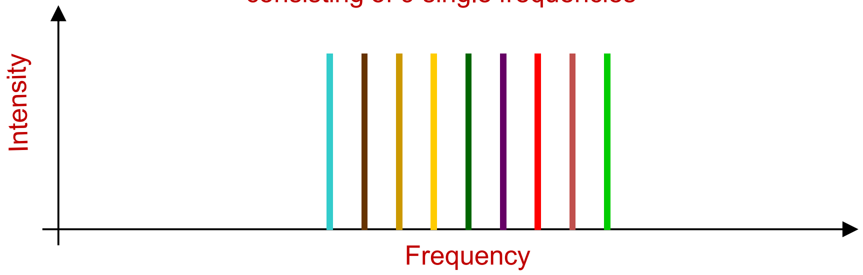
Nine wavelengths



Resulting detector signal:

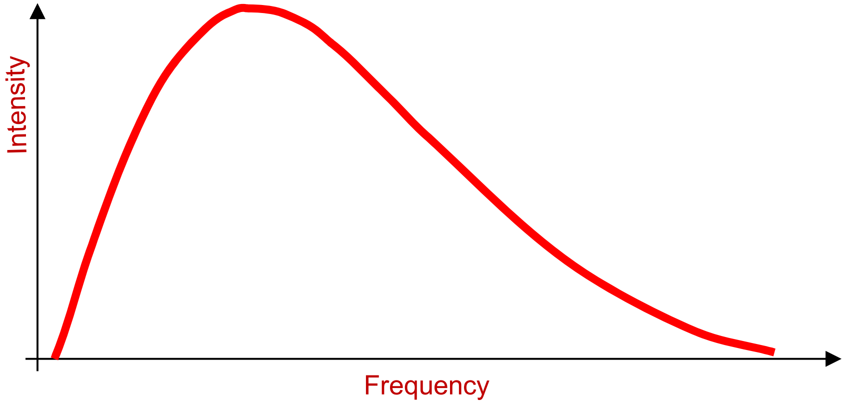


Spectrum
consisting of 9 single frequencies

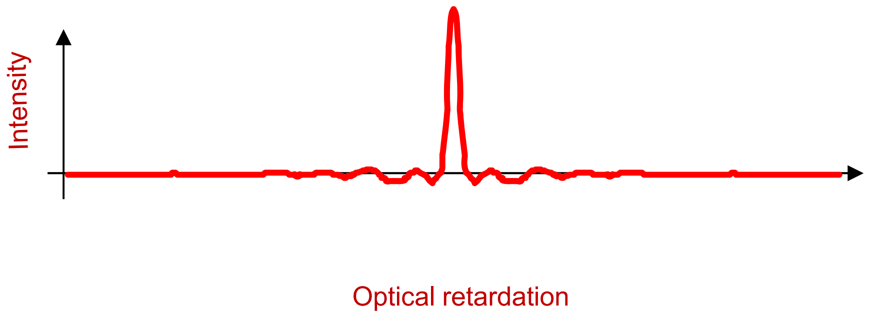


Interferogram of a continous source

IR-source

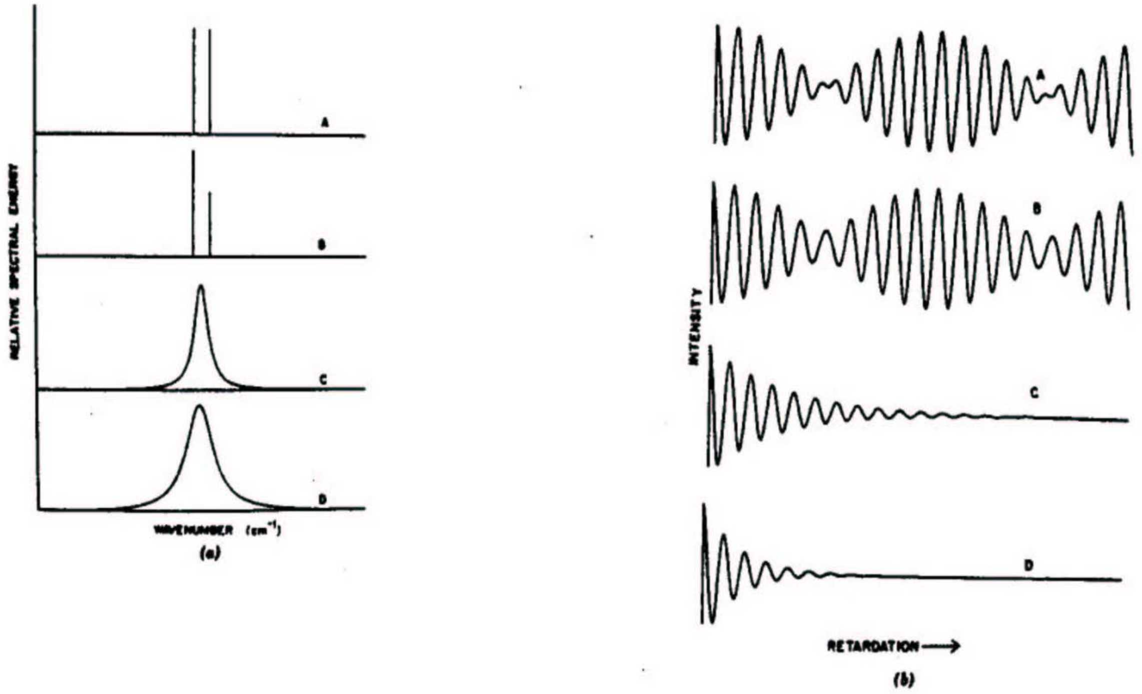


Resulting detector signal



Converting interferograms to spectra

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



Resolution

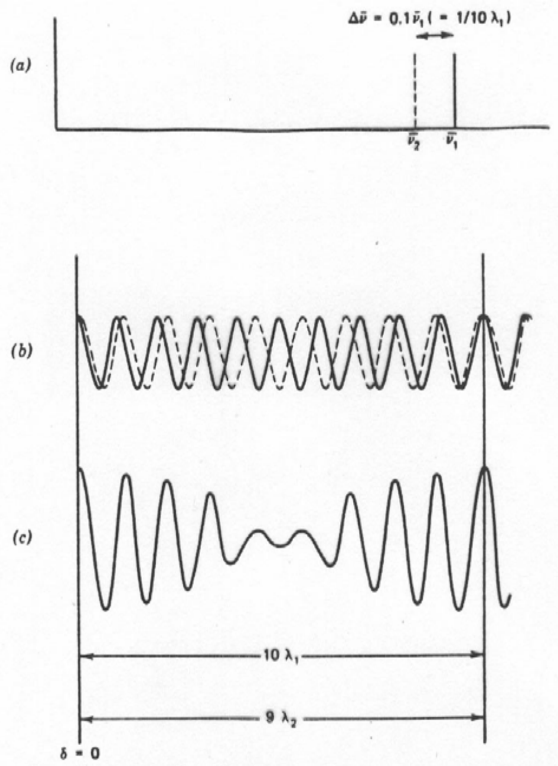


Fig. 1.4. (*a*) Spectrum of two lines of equal intensity at wavenumbers $\bar{\nu}_1$ (solid line) and $\bar{\nu}_2$ (broken line) separated by $0.1\bar{\nu}_1$. (*b*) Interferogram for each spectral line shown individually as solid and broken lines, respectively. (*c*) Resultant interferogram with the 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.

$$10\lambda_1 = 9\lambda_2$$

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

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

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

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

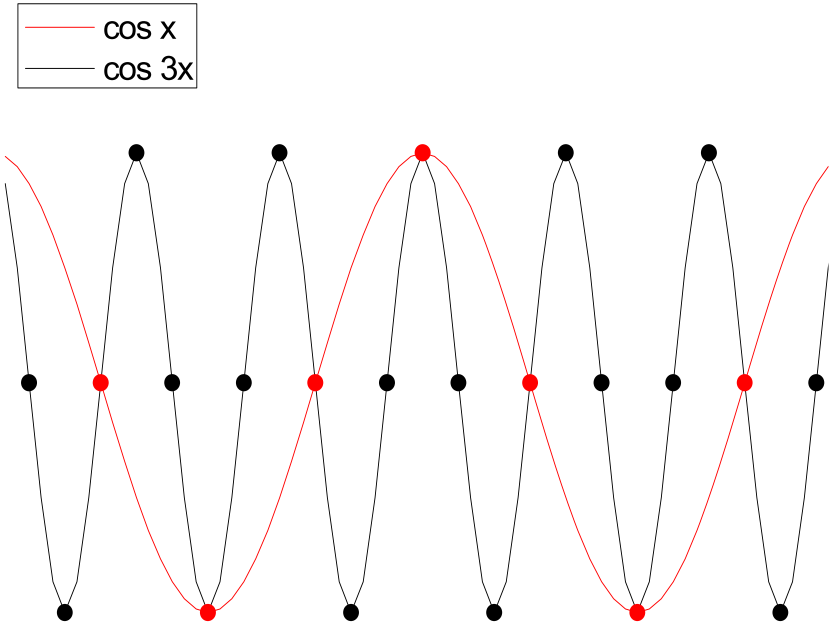
$$\Delta\nu^* = 1cm^{-1} \rightarrow x = 1cm$$

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

Frequency range

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

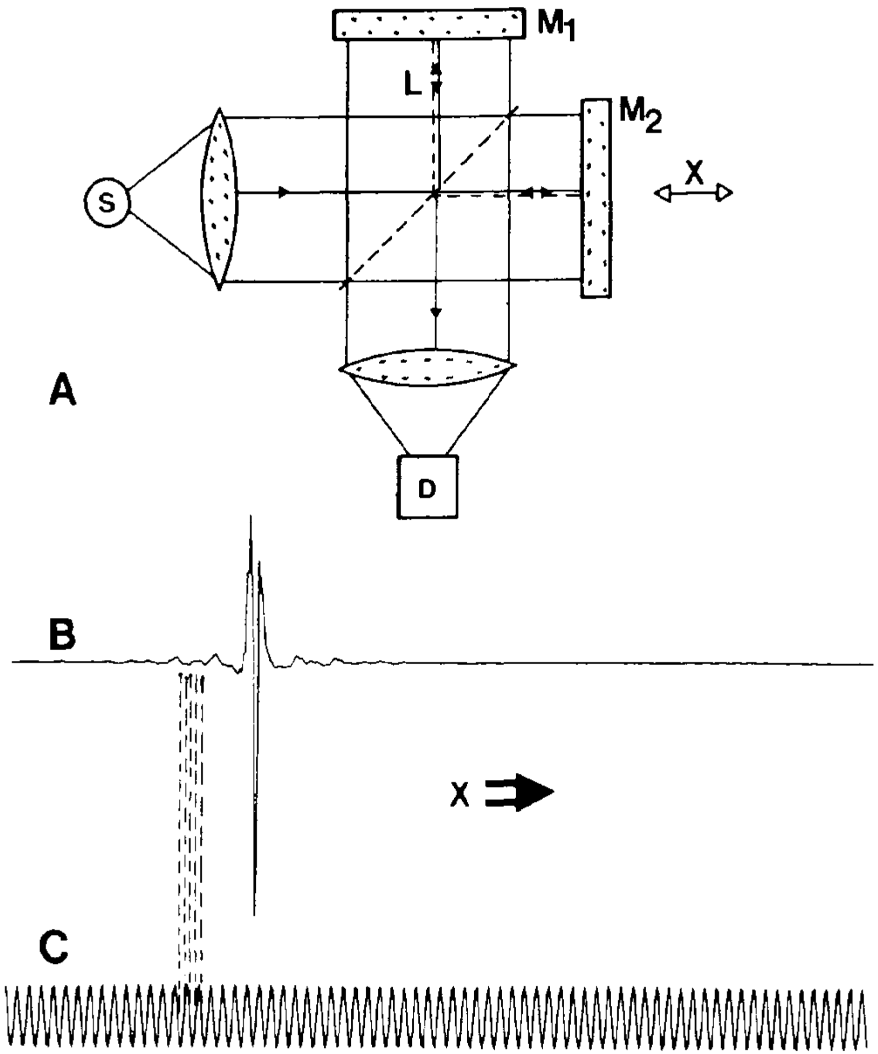
Example:



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

$\nu^*_{\max} = 1000\ \mathrm{cm}^{-1}$ → $\Delta x = 5\ \mu\mathrm{m}$

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 ν_{max} =15800 cm^{-1}
632.8 nm ν_{max}= 7900 cm^{-1}

frequency of signal at detector: $f=2v\nu^{*}$
for f=1.58 mm/sec
400 cm^{-1} f=126 Hz
4000 cm^{-1} f=1260 Hz

Signal evaluation

Interferogram
Fourier transformation:
Apodization
Phase correction
Zerofilling

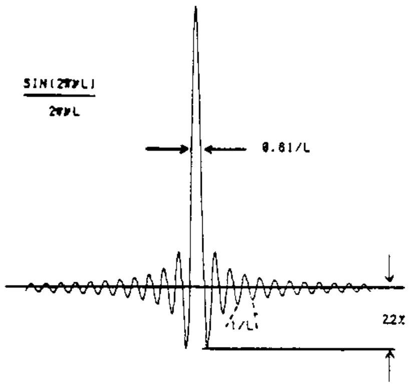
$$i(\nu^*) = \Delta x \sum_{-M}^{M} I(m\Delta x)\cos(2\pi\nu^* m\Delta x)$$

finite, discrete FT

Apodization

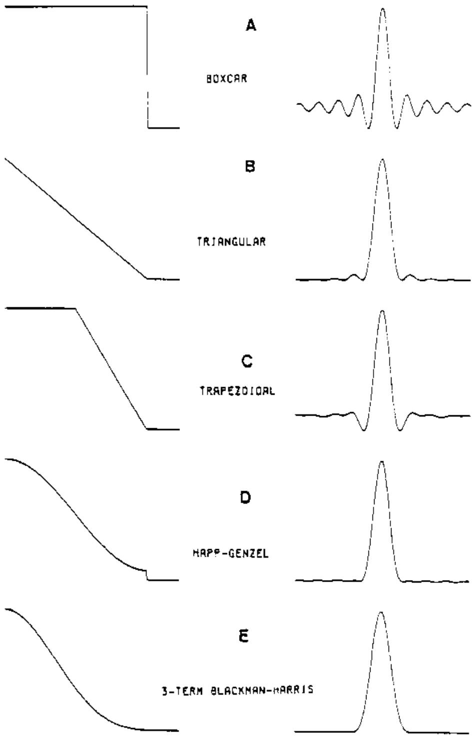
Instrumental lineshape:

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



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

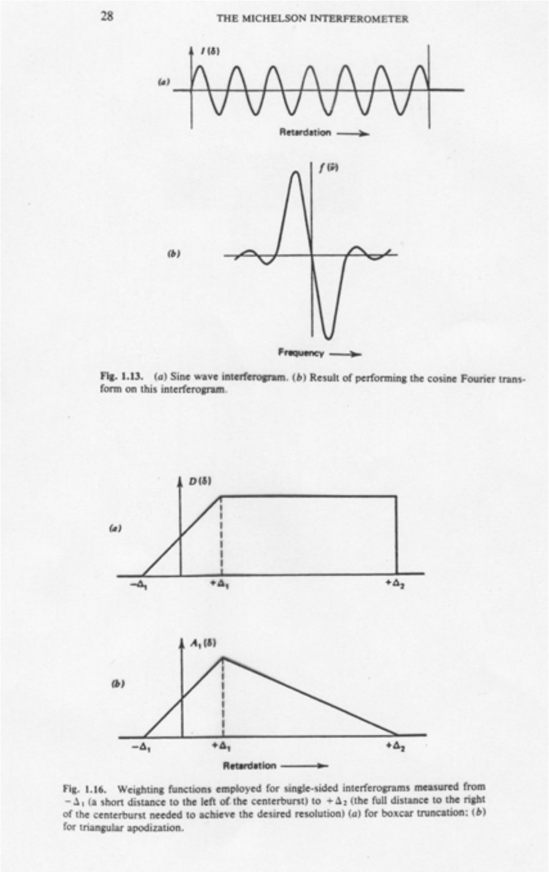
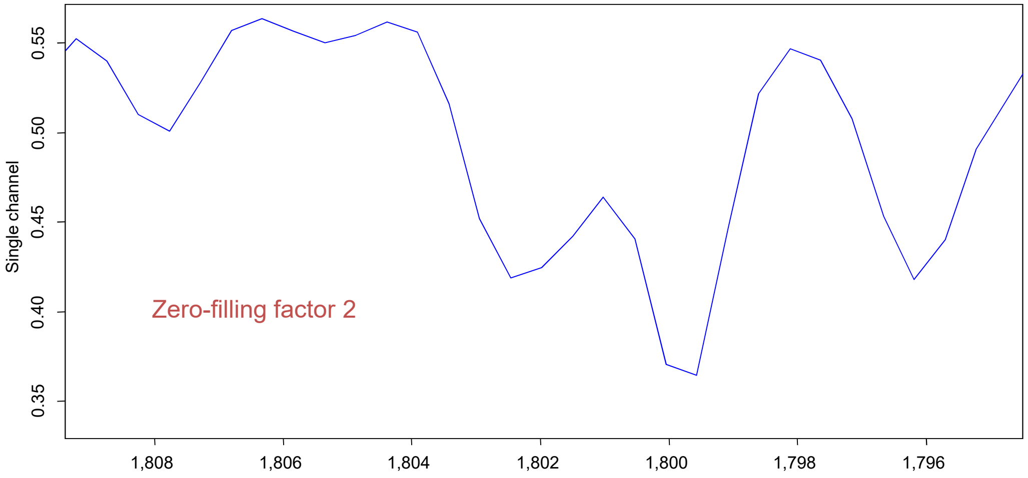

28 THE MICHELSON INTERFEROMETER

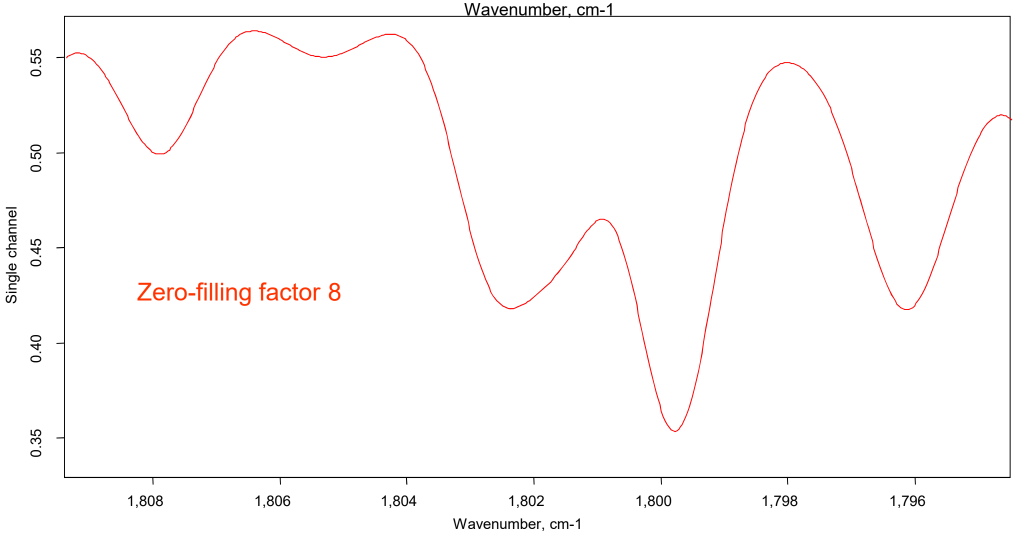
Fig. 1.13. (*a*) Sine wave interferogram. (*b*) Result of performing the cosine Fourier transform on this interferogram.

Fig. 1.16. Weighting functions employed for single-sided interferograms measured from $-\Delta_1$ (a short distance to the left of the centerburst) to $+\Delta_2$ (the full distance to the right of the centerburst needed to achieve the desired resolution) (*a*) for boxcar truncation; (*b*) for triangular apodization.

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

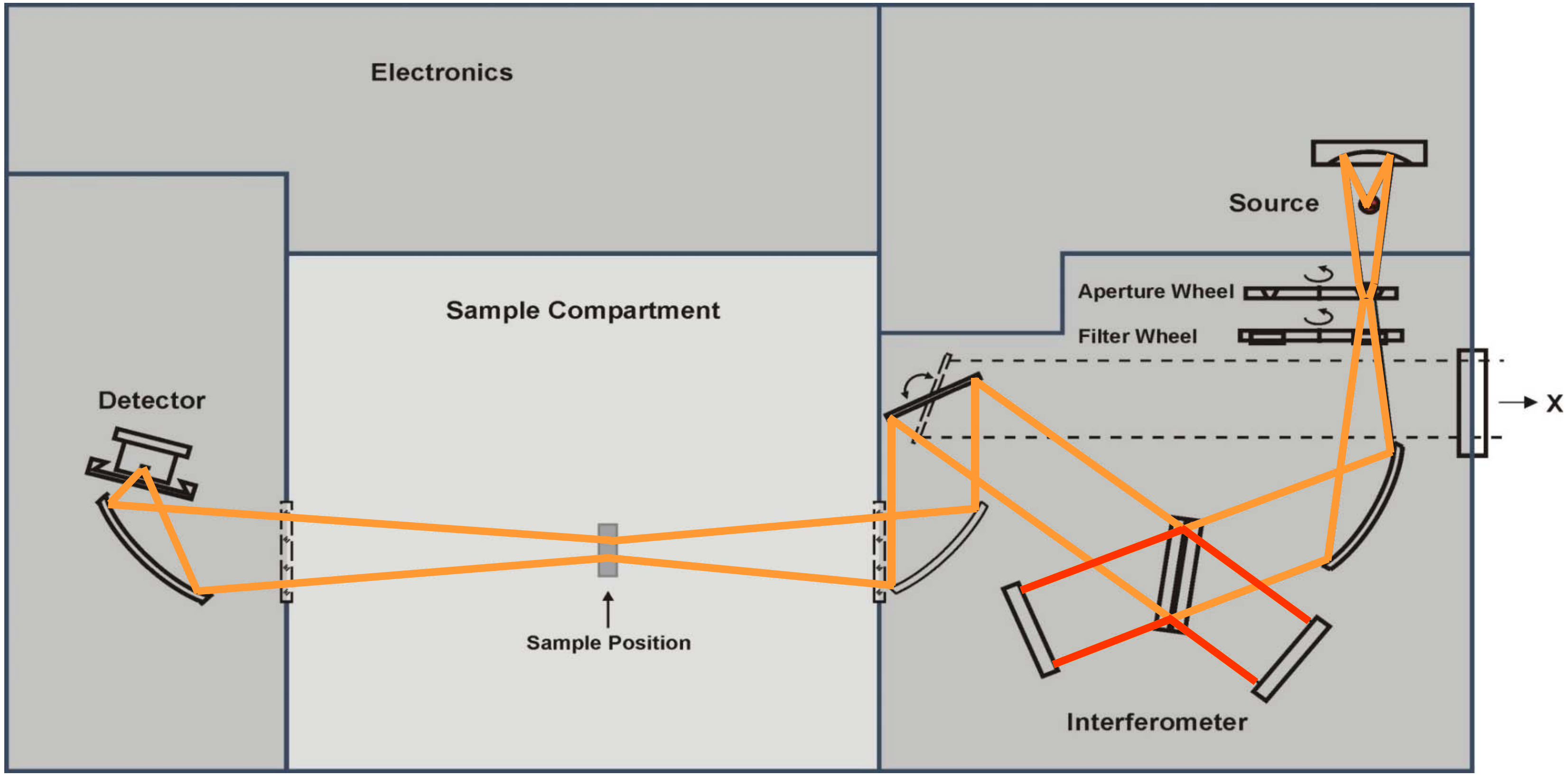
Zerofilling



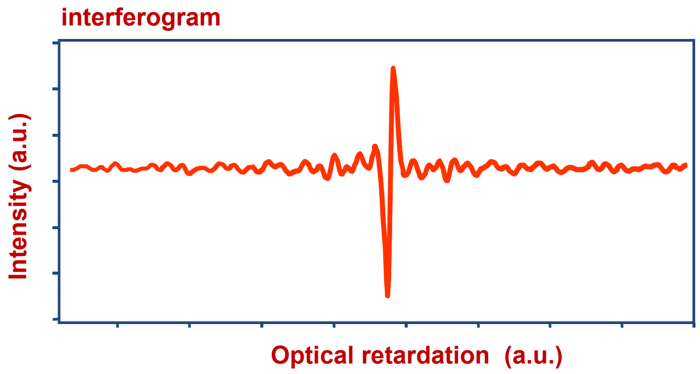


Adding zeroes to end of interferogram
“Spectrum-like” interpolation
Does not replace resolution!

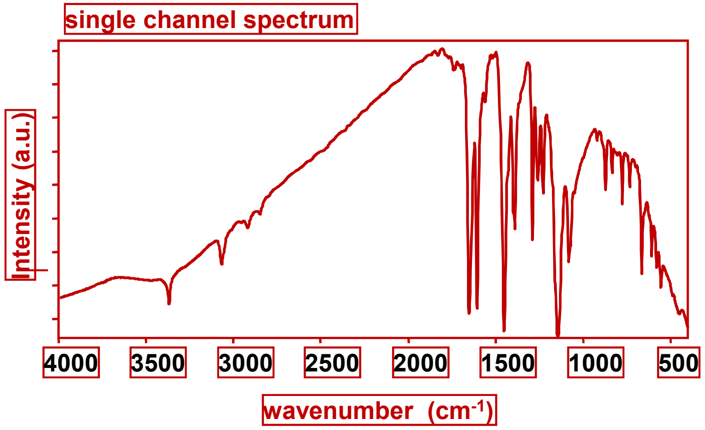
FTIR spectrometer

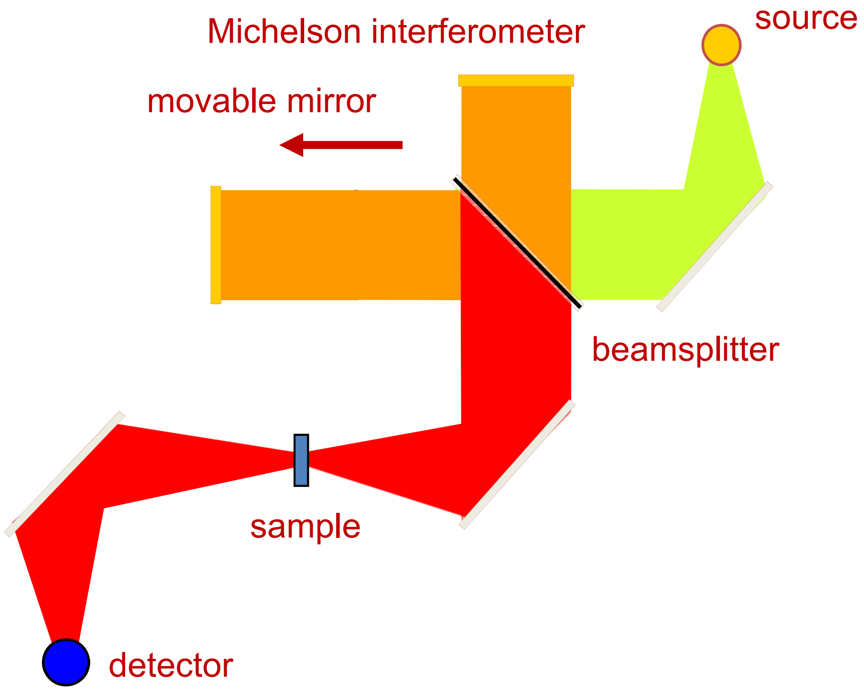


FTIR measurement

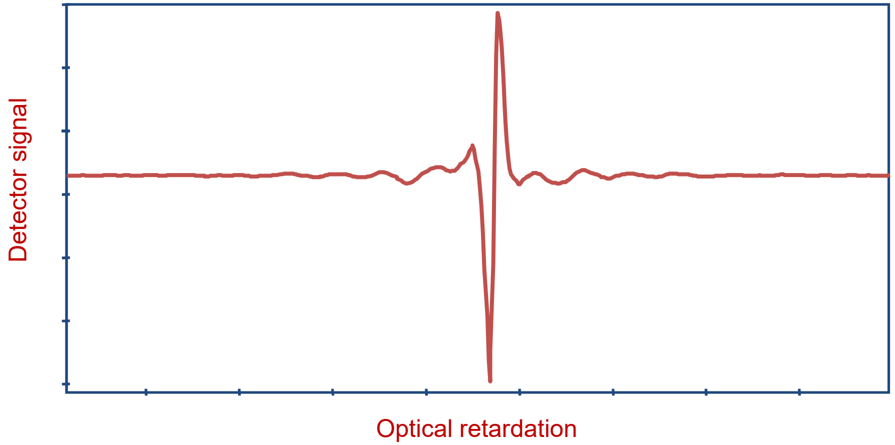


Fourier-Transformation

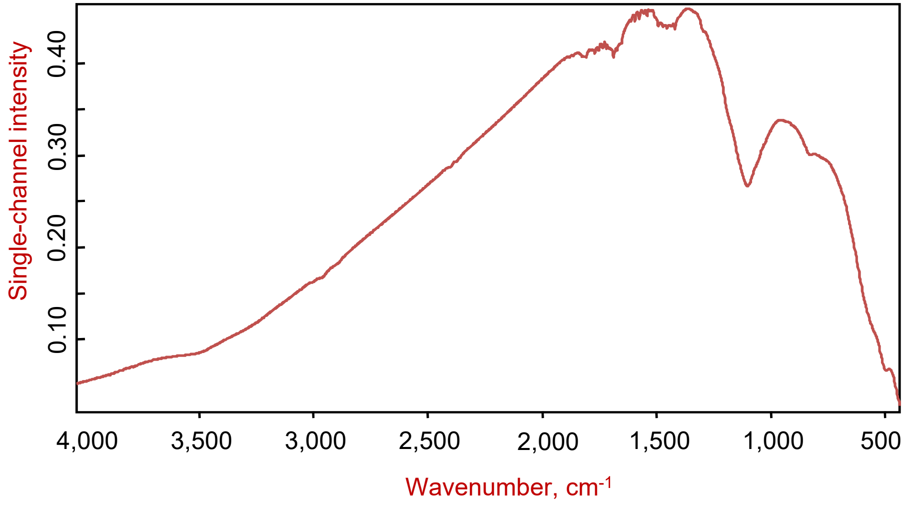




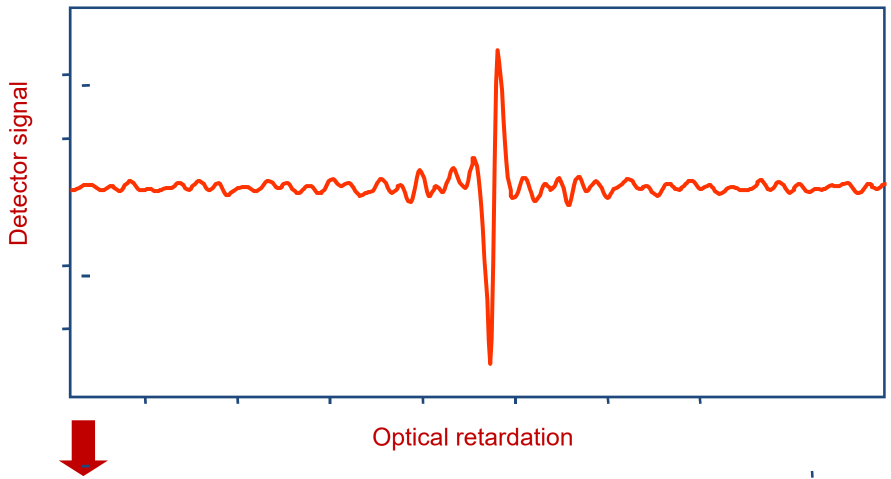
Reference spectrum



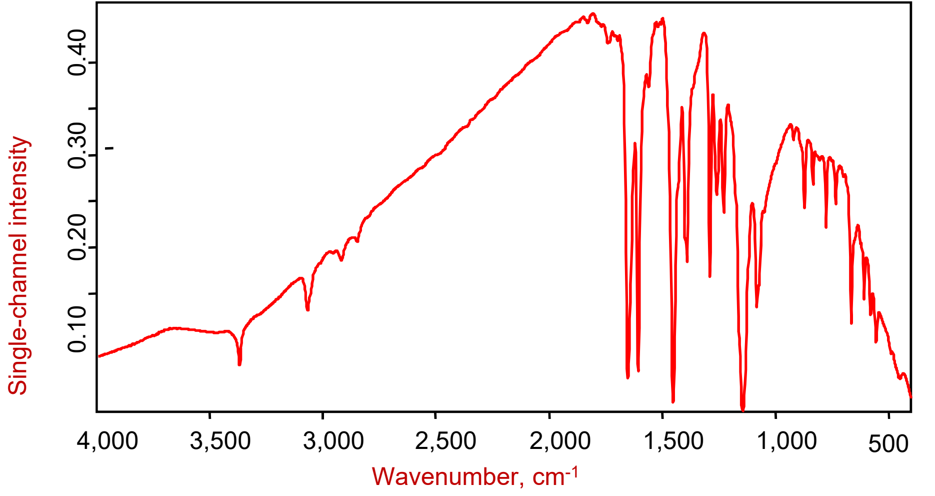
Fourier transformation



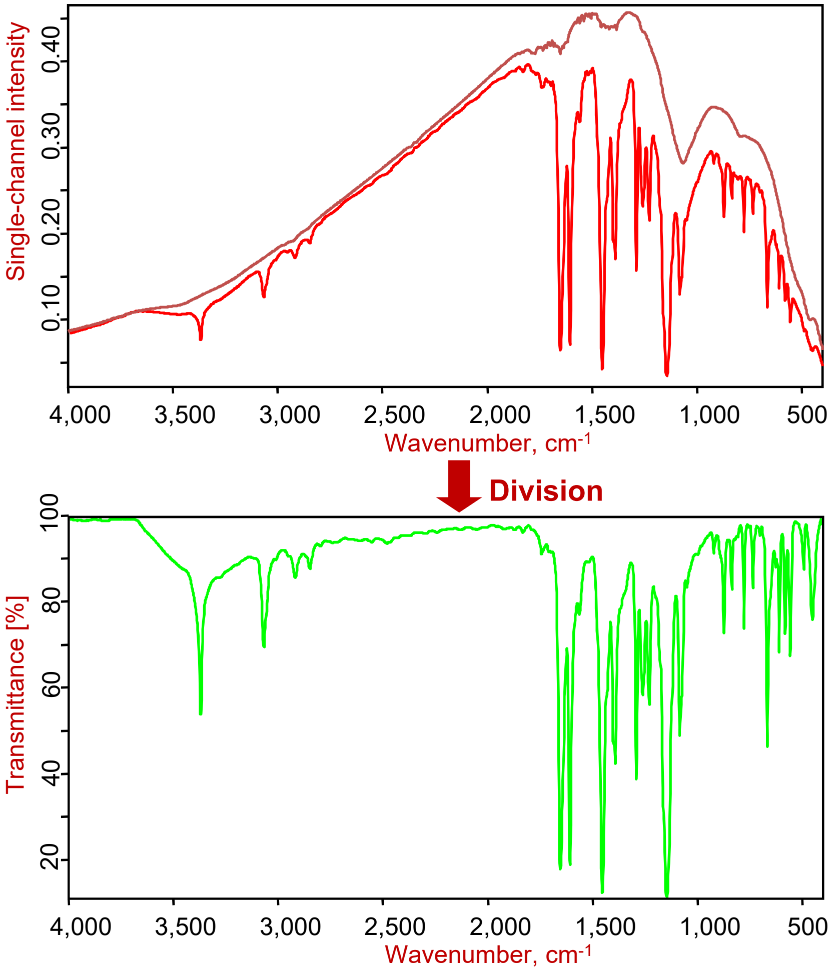
Sample spectrum



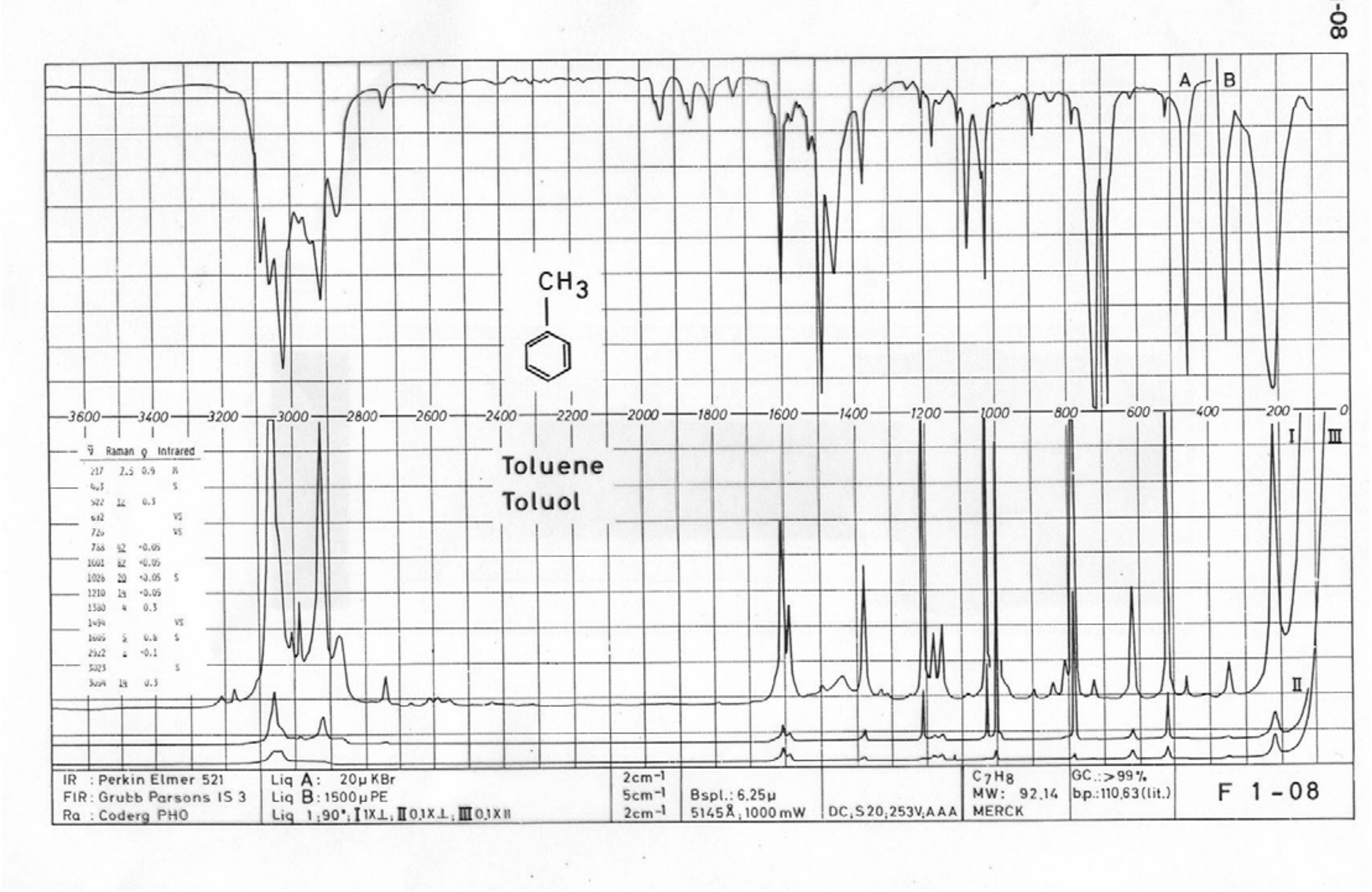
Fourier transformation



Transmission spectrum



Typical infrared and Raman spectrum



$\tilde{\nu}$	Raman	ρ	Infrared
217	7.5	0.9	R
463			S
522	12	0.3	
692			VS
728			VS
788	42	<0.05	
1004	62	<0.05	
1026	20	<0.05	S
1210	14	<0.05	
1380	4	0.3	
1494			VS
1605	5	0.6	S
2922	4	<0.1	
3025			S
3054	14	0.3	

IR : Perkin Elmer 521
FIR: Grubb Parsons IS 3
Ra : Coderg PHO

Liq A: 20µ KBr
Liq B: 1500µ PE
Liq 1; 90°; I 1X⊥; II 0,1X⊥; III 0,1X∥

2cm⁻¹
5cm⁻¹
2cm⁻¹

Bspl.: 6,25µ
5145Å; 1000 mW

DC; S20; 253V; AAA

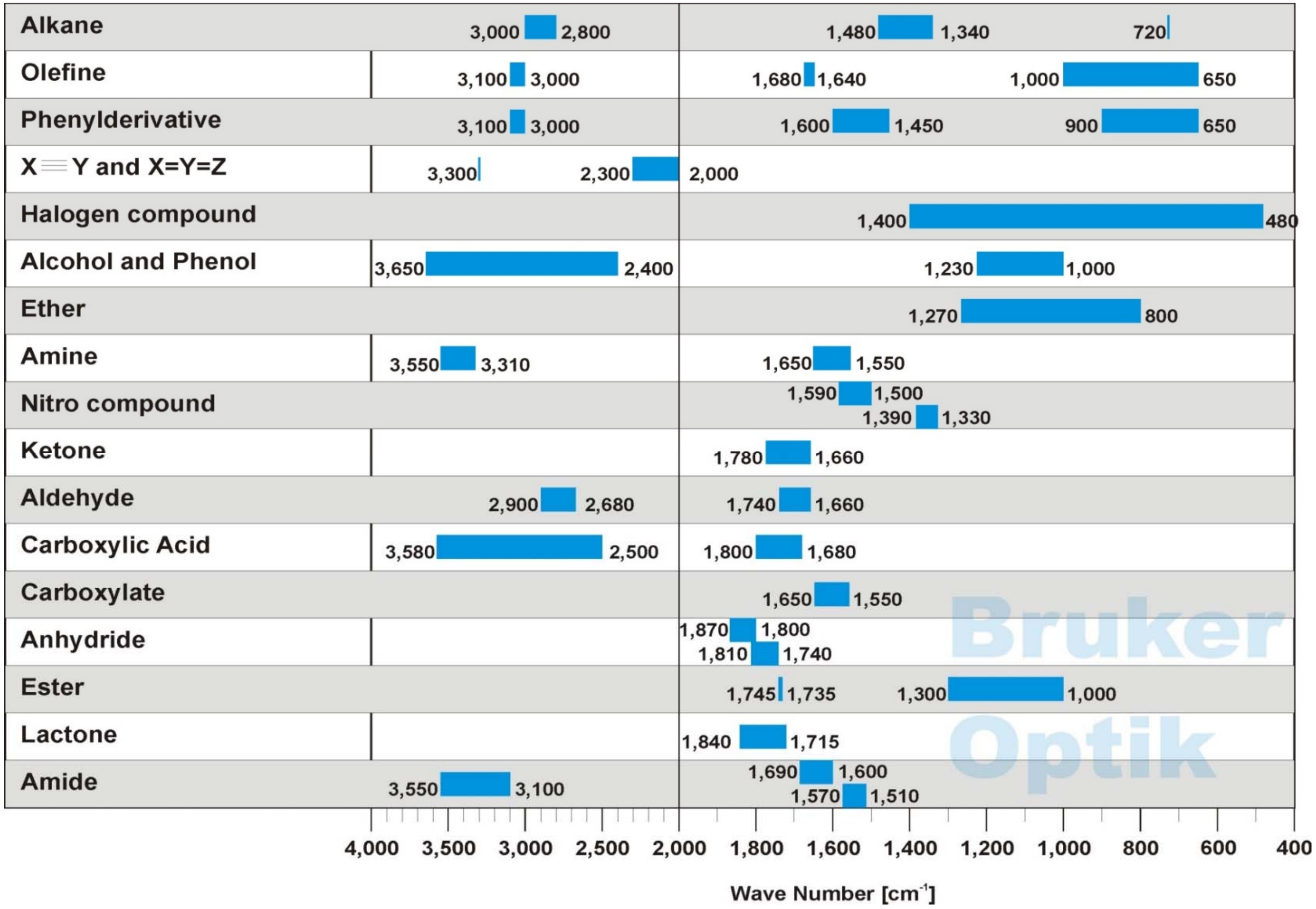
C_7H_8
MW: 92,14
MERCK

GC.: >99%
bp.: 110,63 (lit.)

F 1-08

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

Group frequencies

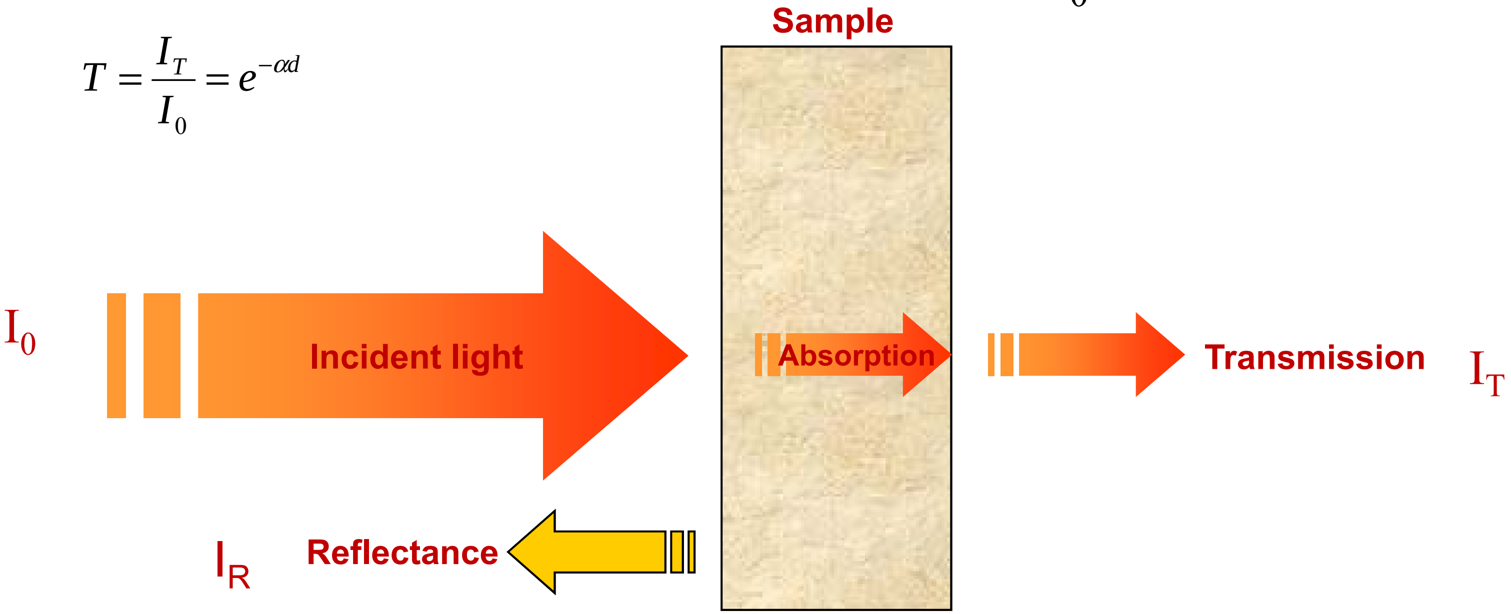


Normal-incidence spectroscopy

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

if R=0: $$I_0 = I_0 e^{-\alpha d} + I_A \qquad A = \frac{I_A}{I_0} = 1 - e^{-\alpha d}$$

$$T = \frac{I_T}{I_0} = e^{-\alpha d}$$



Sample

I_0

Incident light

Absorption

Transmission

I_T

I_R

Reflectance

Reflectance spectroscopy

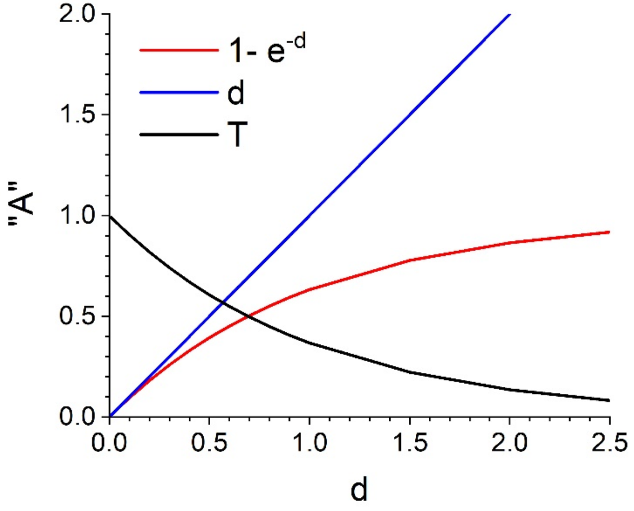
Absorption spectroscopy

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

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

ε specific (molar) absorption coefficient

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



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

most spectrometer software does not know the difference!

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 → single-beam spectrum → 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 → egysugaras spektrum → 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)