

Optical spectroscopy in materials science 2.

Infrared spectroscopy

Kamarás Katalin

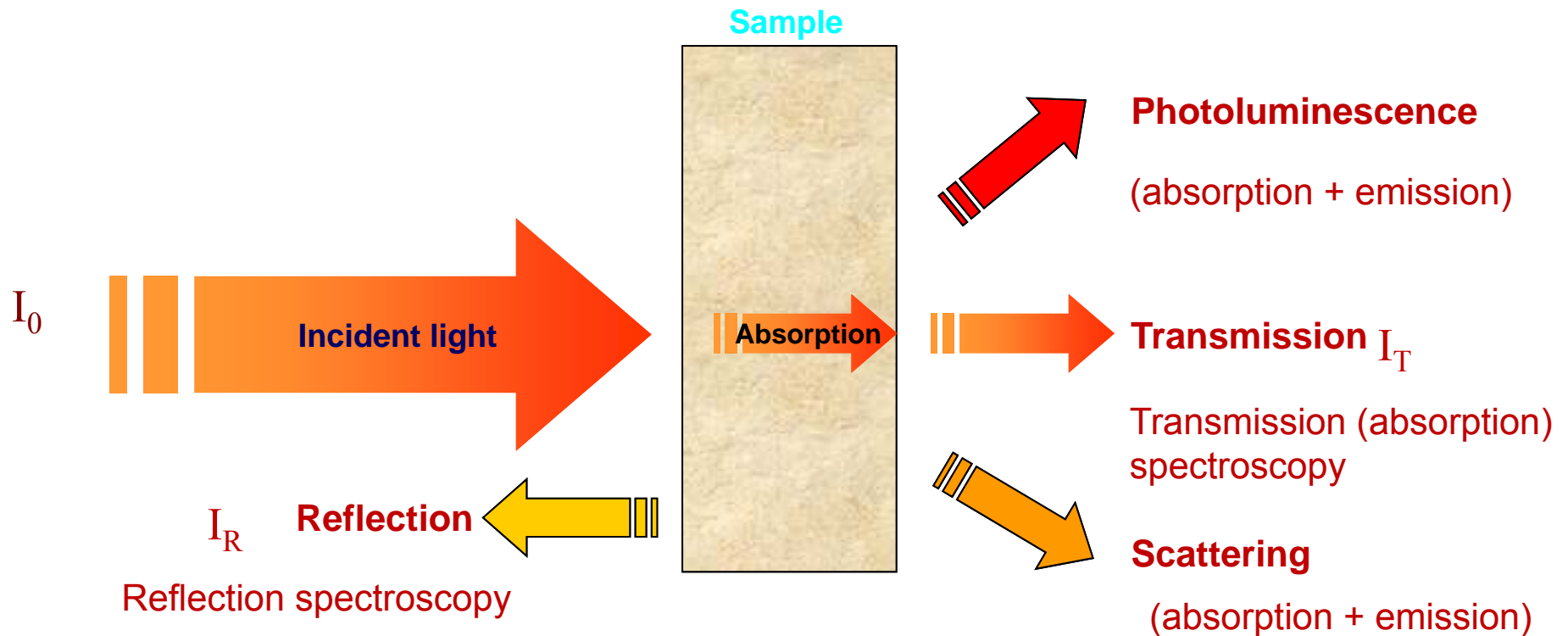
MTA Wigner FK

kamaras.katalin@wigner.mta.hu

Experimental arrangements

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

11.1. egyenlet hibás!



Damped harmonic oscillator

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

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

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

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

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

Frequency dependence of optical functions

$$\varepsilon_{rel}' = n'^2 - n''^2 = 1 + \frac{Ne^2}{\varepsilon_0 m_e V} \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}$$

$$\varepsilon_{rel}'' = 2n'n'' = \frac{Ne^2}{\varepsilon_0 m_e V} \frac{\gamma \omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}$$

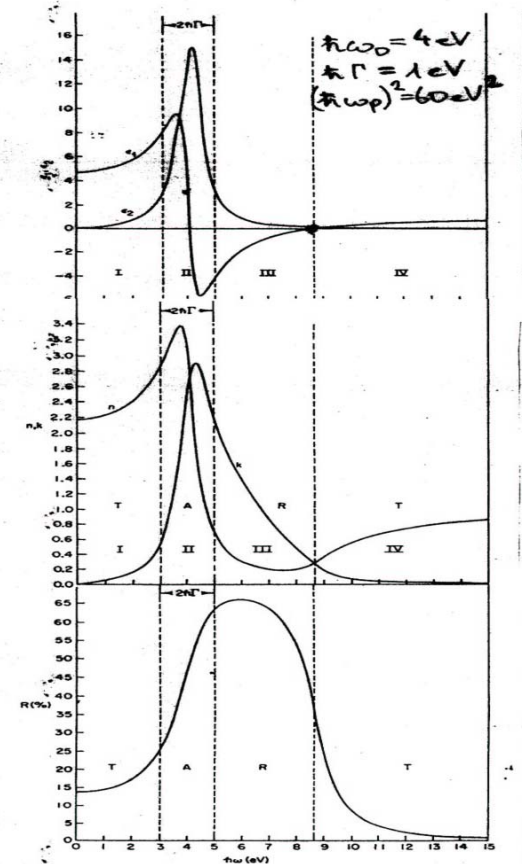
$$\sigma' = \omega \varepsilon_0 \varepsilon_{rel}'' = \frac{Ne^2}{m_e V} \frac{\gamma \omega^2}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}$$

$$\sigma'' = -\varepsilon_0 \omega (\varepsilon_{rel}' - 1) = \frac{Ne^2}{m_e V} \frac{\omega^2 - \omega_0^2}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}$$

$\varepsilon, \varepsilon''$

n', n''

R



$$R = \frac{I_R}{I_0} = \frac{(n'-1)^2 + n''^2}{(n'+1)^2 + n''^2} \quad \text{where} \quad n'^2 = \frac{1}{2} \left[\varepsilon_{rel}' + (\varepsilon_{rel}''^2 + \varepsilon_{rel}'^2)^{\frac{1}{2}} \right] \quad n''^2 = \frac{1}{2} \left[-\varepsilon_{rel}' + (\varepsilon_{rel}''^2 + \varepsilon_{rel}'^2)^{\frac{1}{2}} \right]$$

Real dielectric function

condition: $\gamma \ll \omega_0$

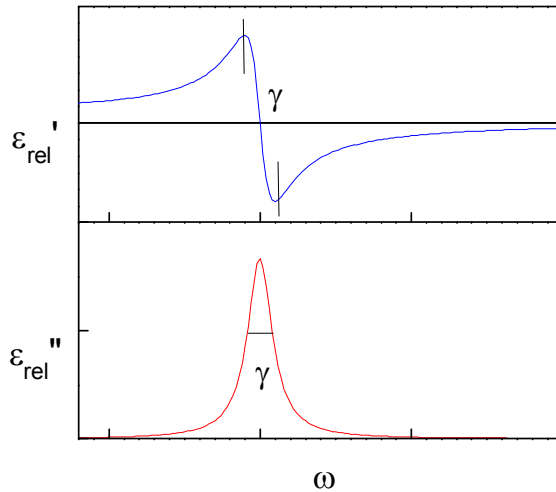
atomic transitions: $\omega_0 \sim 10^4 \text{ cm}^{-1}$, $\gamma \sim 10^{-4} \text{ cm}^{-1}$

$$\epsilon_{rel}' = n'^2 - n''^2 = 1 + \frac{Ne^2}{\epsilon_0 m_e V} \frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}$$

$$\epsilon_{rel}' = 1, \text{ if } \omega = \omega_0 \text{ or } \omega \gg \omega_0$$

normal dispersion: ϵ' increasing with ω
 anomalous dispersion: ϵ' decreasing with ω

Limits of anomalous dispersion region:

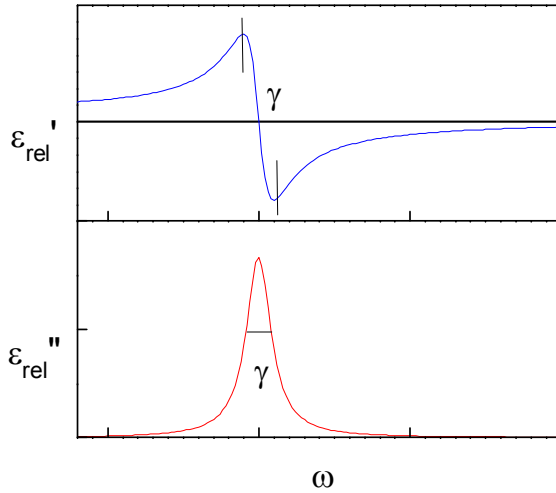


$$\frac{\partial \epsilon_{rel}'}{\partial \omega} = 0 \quad \frac{f(\omega)}{\left[(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2 \right]^2} = 0 \quad \Rightarrow \quad \omega_0^2 - \omega_m^2 = \pm \gamma \omega_0$$

$$(\omega_0 + \omega_m)(\omega_0 - \omega_m) = \pm \gamma \omega_0 \quad (\text{condition}) \quad 2\omega_0(\omega_0 - \omega_m) = \pm \gamma \omega_0$$

$$\omega_m \cong \omega_0 \pm \frac{\gamma}{2}$$

Imaginary dielectric function



$$\epsilon_{rel}'' = 2n'n'' = \frac{Ne^2}{\epsilon_0 m_e V} \frac{\gamma \omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}$$

full width at half maximum:

$$\epsilon_{rel}''(\omega_f) = \frac{\epsilon_{rel}''(\omega_0)}{2} = \frac{Ne^2}{\epsilon_0 m_e V} \frac{1}{2\gamma\omega_0} = \frac{Ne^2}{\epsilon_0 m_e V} \frac{\gamma\omega_f}{(\omega_0^2 - \omega_f^2)^2 + \gamma^2\omega_f^2}$$

condition $\omega_0 \cong \omega_f$

$$\omega_f = \omega_0 \pm \frac{\gamma}{2}$$

$$\epsilon_{rel}'' = \frac{n' \alpha c}{\omega} = \frac{\sigma'}{\omega \epsilon_0}$$

ϵ_{rel}'' can be determined from absorption if $n' \ll n''$

Semiconductors and metals – collective electron system

Harmonic oscillator: here it is an electron of the delocalized electron system, oscillating in the electric field of the atomic cores

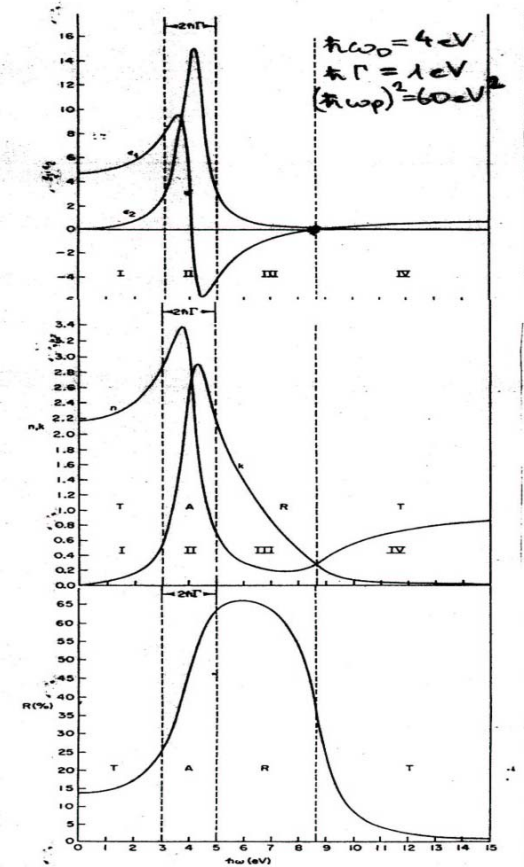
$$\epsilon_{rel} = 1 + \frac{e^2}{\epsilon_0 m_e V} \sum_i \frac{N_i}{\omega_i^2 - \omega^2 - i\gamma_i \omega} \quad \omega_i = \frac{|E_i - E_0|}{\hbar}$$

$E_{i,j}$ energy of bands

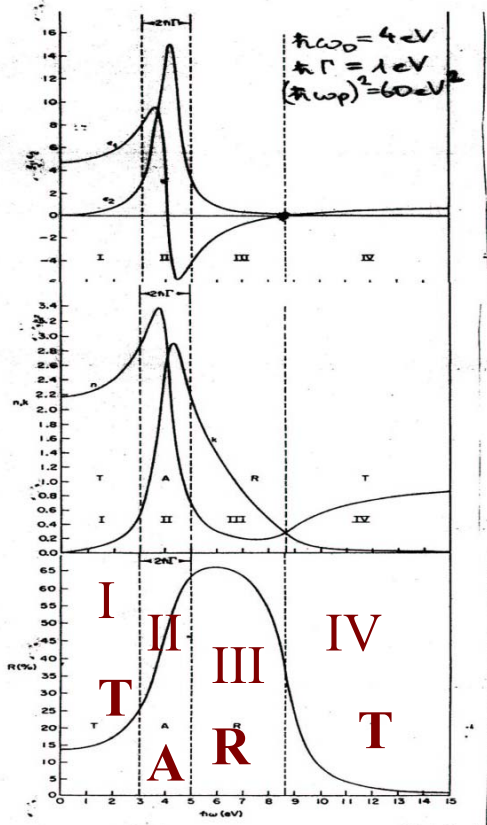
$\omega_i \sim \gamma$, shape of functions can be relevant

Measurement technique: reflectance
(large absorption in bulk)

$$R = \frac{I_{sample}}{I_{mirror}} R_{mirror} \quad R = \frac{I_R}{I_0} = \frac{(n'-1)^2 + n''^2}{(n'+1)^2 + n''^2}$$



Reflectance curve around an excitation



I. Transparent region (T): $\omega < \omega_i$, $\epsilon'' = 0$, $\epsilon_{rel}' > 0$
 absorption small (in semiconductors, below absorption edge)
 R from dispersion, can be large for semiconductors (Si)
 (static polarization)

II. Absorbing region (A): $\omega \sim \omega_i$, ϵ' , ϵ'' , n' , n'' , R large
 anomalous dispersion
 ideal region for reflectance measurements

III. Reflecting region (R): $\omega > \omega_i$ R large
 metallic luster
 semiconductors: electrons in conduction band

IV. Transparent region (T): $\epsilon'' = 0$, ϵ_{rel}' small
 limit: plasma frequency (ω_p) $\epsilon' = \epsilon'' = 0$

Metals

Drude model:

damped harmonic oscillator without restoring force
($\omega_0=0$)

$$\epsilon'_r = 1 - \frac{Ne^2}{\epsilon_0 m V} \frac{1}{\omega^2 + \gamma^2} \quad \epsilon''_r = \frac{Ne^2}{\epsilon_0 m V} \frac{\gamma}{\omega(\omega^2 + \gamma^2)}$$

$$\gamma = \tau^{-1} \text{ (}\tau \text{ relaxation time – transport) } l = v_F \tau$$

Optical conductivity:

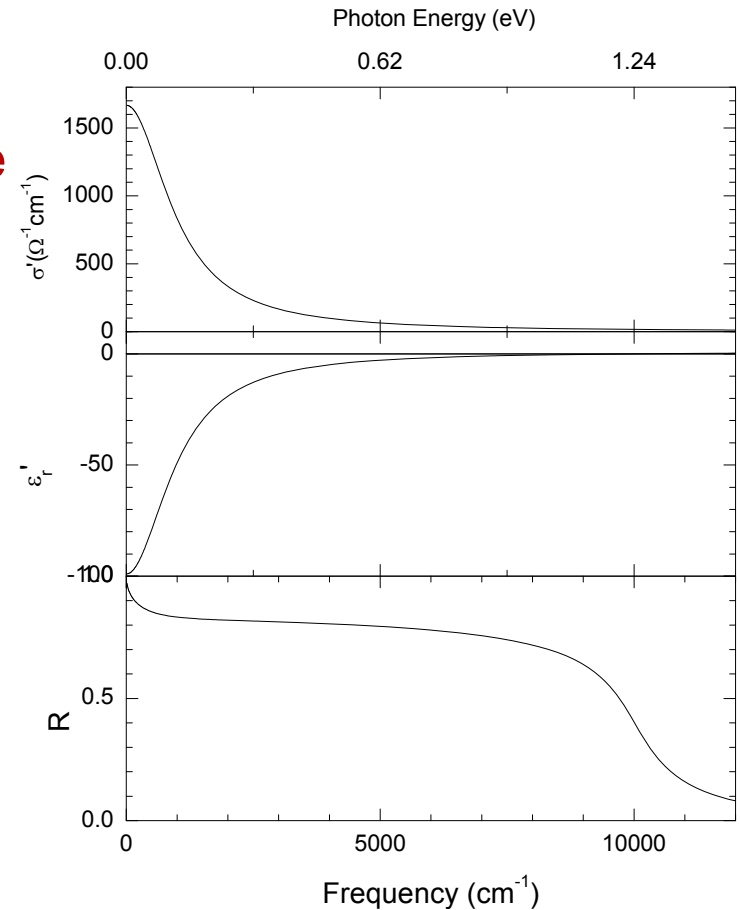
$$\sigma' = \omega \epsilon''_r \epsilon_0 = \frac{Ne^2}{mV} \frac{\gamma}{\omega^2 + \gamma^2}$$

dc conductivity:

$$\sigma'(0) = \sigma'_{dc} = \frac{Ne^2}{mV\gamma}$$

Full width at half maximum:

$$\sigma'(\omega_x) = \frac{Ne^2}{2mV\gamma} = \frac{Ne^2}{2mV} \frac{\gamma}{\omega_x^2 + \gamma^2} \longrightarrow 2\gamma^2 = \omega_x^2 + \gamma^2 \longrightarrow \omega_x = \gamma = \tau^{-1}$$



Plasma frequency in metals

$$\varepsilon'(\omega_p) = 0$$

$$\varepsilon_{rel}' = 1 - \frac{Ne^2}{\varepsilon_0 m_e V} \frac{1}{\omega_p^2 + \gamma^2} = 0$$

$$\frac{Ne^2}{\varepsilon_0 m_e V} = \omega_p^2 + \gamma^2$$

Neglecting γ^2 :

$$\frac{Ne^2}{\varepsilon_0 m_e V} \cong \omega_p^2$$

$$\omega_p \gg \gamma$$

Reflectance around ω_p (plasma edge):

$$\varepsilon_{rel}' = 0, \varepsilon_{rel}'' = 0 \rightarrow R = 1$$

$$\varepsilon_{rel}' = 1, \varepsilon_{rel}'' = 0 \rightarrow R = 0$$

$$R = \frac{I_R}{I_0} = \frac{(n'-1)^2 + n''^2}{(n'+1)^2 + n''^2}$$

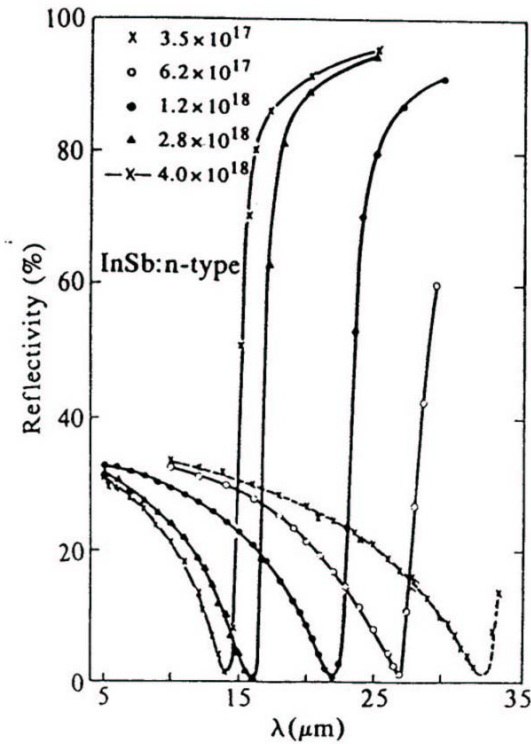


Fig. 13-13 Reflectivity spectra for n-type InSb samples with different numbers of free electrons. [From W. G. Spitzer and H. Y. Fan, Phys. Rev. 106, 882 (1957).] See the comment about the ε_{∞} effect in Section 13-3 and the caption of Fig. 13-5.

The plasma edge shifts with charge carrier concentration

Generalized plasma frequency

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

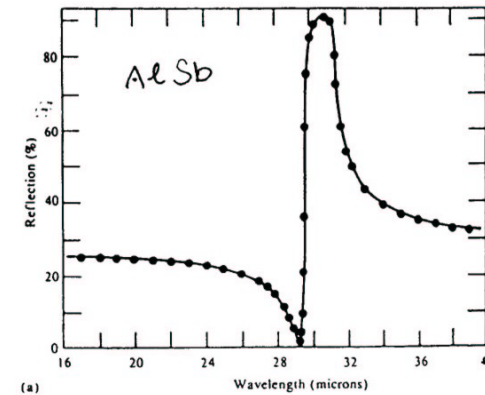
mass can be effective mass m_{eff} ;
 N/V charge density involved in excitation

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

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

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

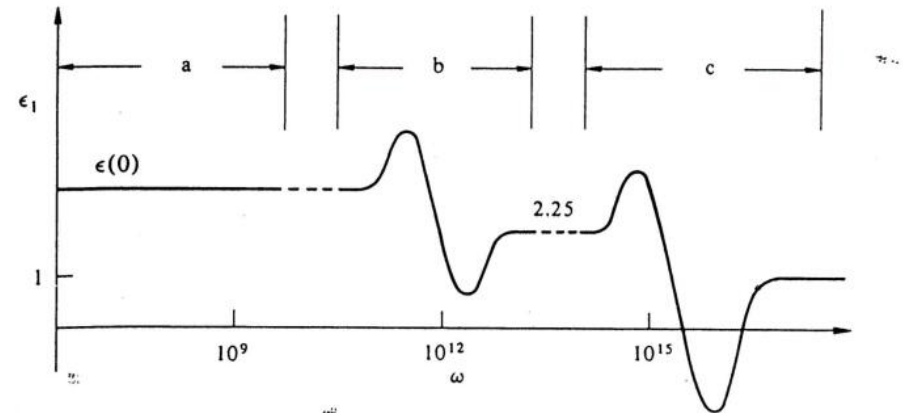
Description of multiple excitations

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:

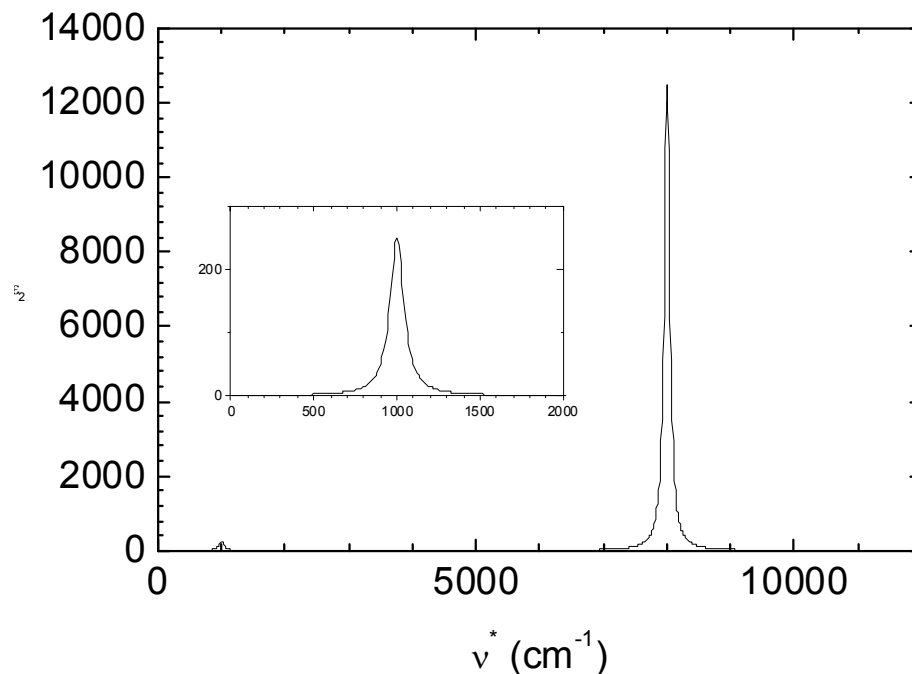
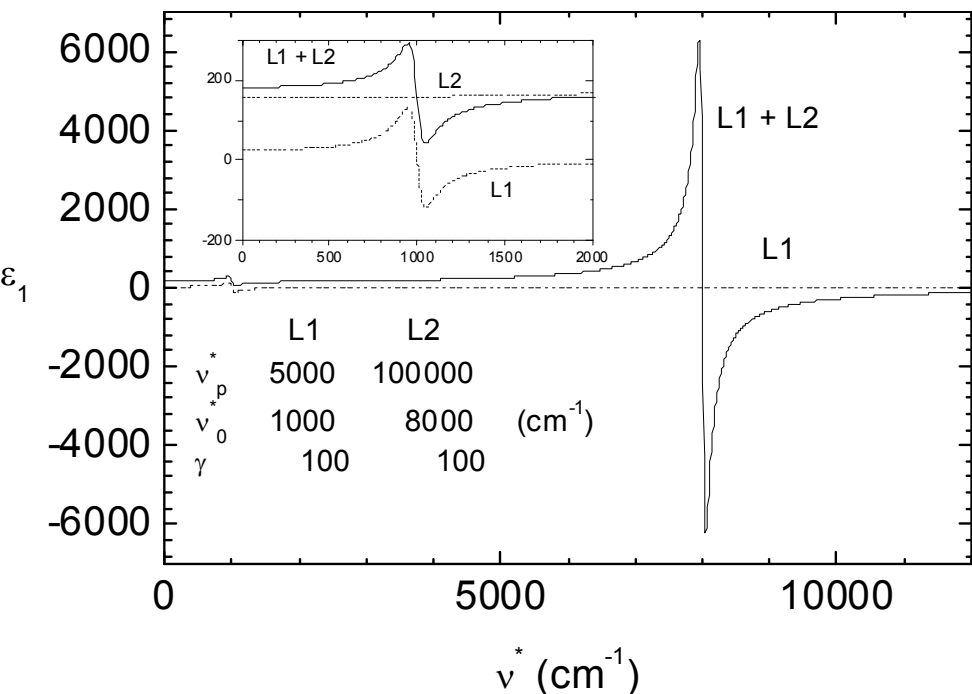
$$\epsilon_{rel}'(0) = 1 + \sum_i \frac{N_i e^2}{\epsilon_0 m V} \frac{1}{\omega_i^2} = 1 + \sum_i \frac{\omega_{pi}^2}{\omega_i^2}$$



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:

$$\epsilon_{rel}'(0) = \epsilon_{\infty} + \frac{\omega_p^2}{\omega_{gap}^2} = \epsilon_{\infty} + \frac{S}{E_{gap}^2}$$

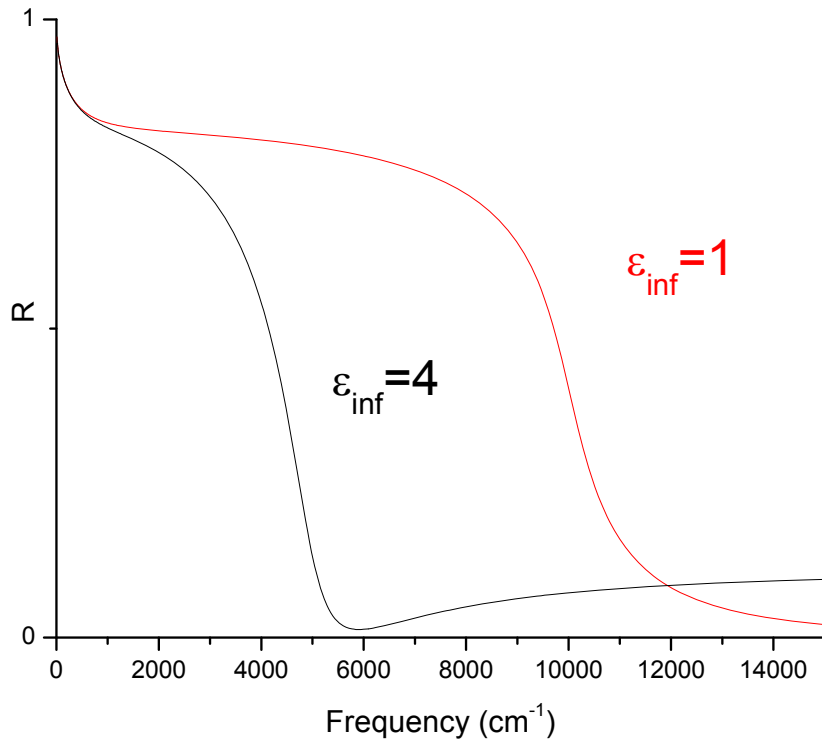
S oscillator strength
in energy units:

Even more simplified:

$$\epsilon_{rel}'(0) = 1 + \frac{S}{E_{gap}^2}$$

$$S = \hbar^2 \omega_p^2$$

Shift of metallic plasma edge



$$\epsilon_{rel}' = \epsilon_{\infty} - \frac{\omega_p^2}{\omega_{pm}^2 + \gamma^2} = 0$$

$$\epsilon_{\infty}(\omega_{pm}^2 + \gamma^2) = \omega_p^2$$

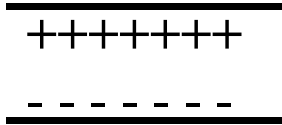
because $\omega_{pm} \gg \gamma$, $\omega_{pm} = \frac{\omega_p}{\sqrt{\epsilon_{\infty}}}$

ω_{pm} : screened plasma frequency

$$\omega > \omega_{pm} : \epsilon_{rel}' = \epsilon_{\infty} \quad \epsilon_r'' = 0$$

$$R = \frac{(\sqrt{\epsilon_{\infty}} - 1)^2}{(\sqrt{\epsilon_{\infty}} + 1)^2}$$

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 $\epsilon' = \epsilon'' = 0$

Detection of plasmons: electron energy loss spectroscopy (EELS)

EELS measures the **loss function**:

$$\text{Im}\left(-\frac{1}{\epsilon_2}\right)$$

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

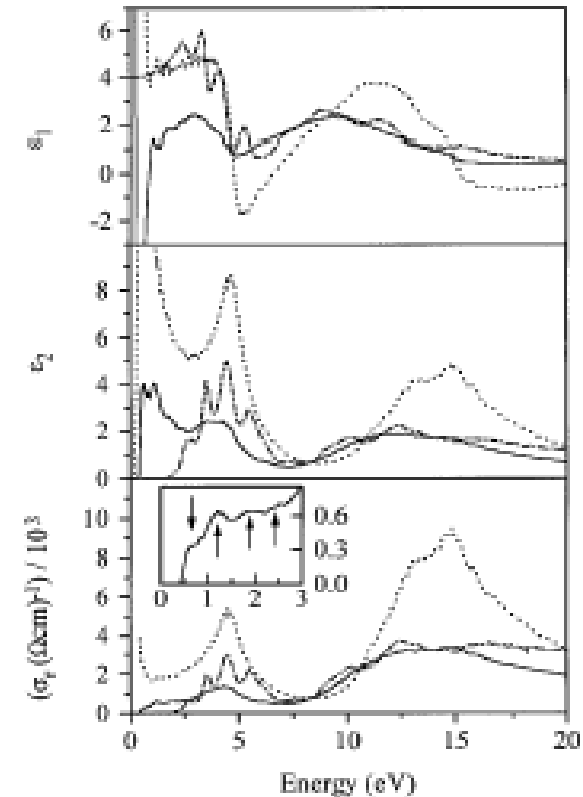


FIG. 3. The real and imaginary parts of the dielectric function (upper panels) and the real part of the optical conductivity (σ_1) at low momentum transfer: SWNTs (—) at $q = 0.1 \text{ \AA}^{-1}$, C_{60} (- · -) and graphite [polarized in plane (- -)] at $q = 0.15 \text{ \AA}^{-1}$, respectively. The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

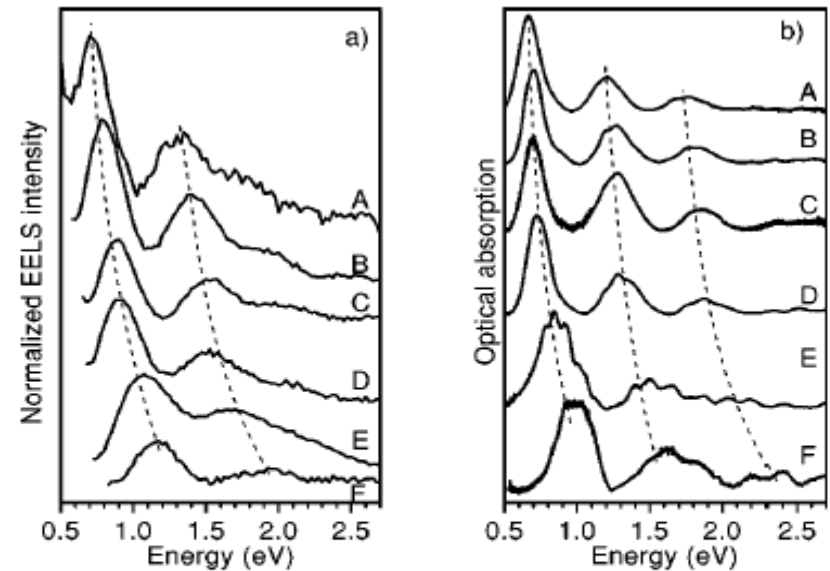
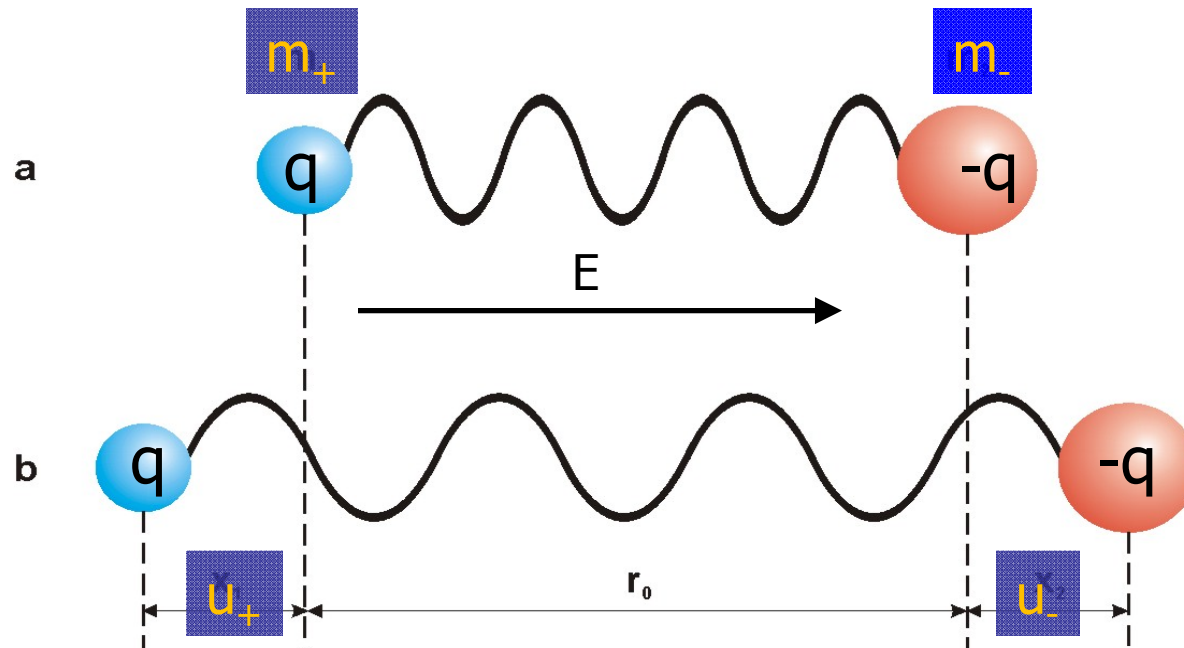


FIG. 4. (a) Loss function in the region of the low-energy inter-band transitions for SWCNT's with different mean diameters recorded with $q=0.1 \text{ \AA}^{-1}$. (b) Optical absorption spectra (after background subtraction) from SWCNT with mean diameters as indicated.

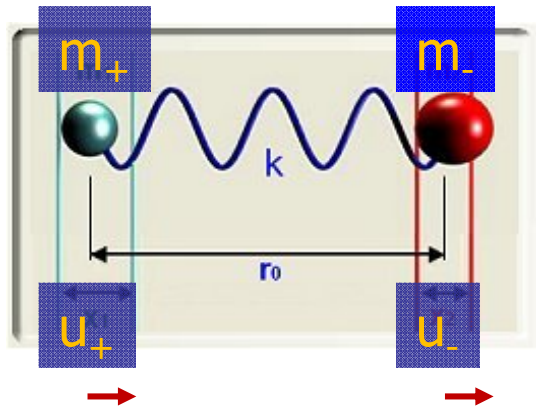
X. Liu, T. Pichler, M. Knupfer,
M.S. Golden, J. Fink, H. Kataura,
Y. Achiba:
Phys. Rev. B 66, 045411 (2002)

Molecular vibrations



Mechanical model of a vibrating diatomic molecule

Vibrational spectra



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

reduced mass

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

relative displacement

Introducing damping:

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

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

eigenfrequency 38. old. sajtóhiba!

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

For a system of volume V, containing N molecules:

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

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

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

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

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

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

4.5., 4.6. egyenlet: sajtóhiba! (m_+ , m_- felcserélve)

Vibrational spectra – dielectric formalism

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

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

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

$$\Omega^2 = \frac{NQ^2}{\epsilon_0 m_r V} \quad \text{oscillator strength (if } Q=0, \text{ no response)}$$

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

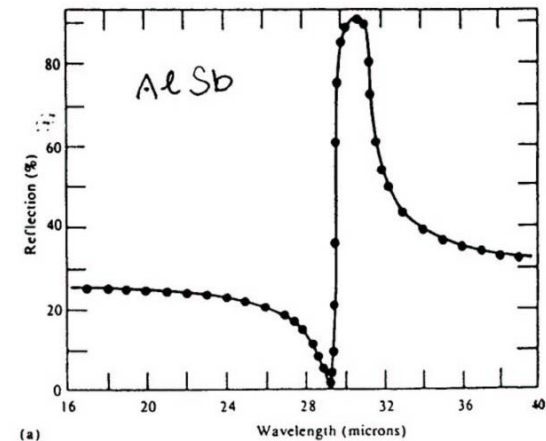
Longitudinal excitation if $\epsilon_{rel}(\omega_l) = 0$:
$$\epsilon_{rel}' = \epsilon_\infty + \frac{\Omega^2(\omega_0^2 - \omega_l^2)}{(\omega_0^2 - \omega_l^2)^2 + \gamma^2 \omega_l^2} = 0$$

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

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

$\omega_l = \omega_{LO}$ longitudinal optical frequency

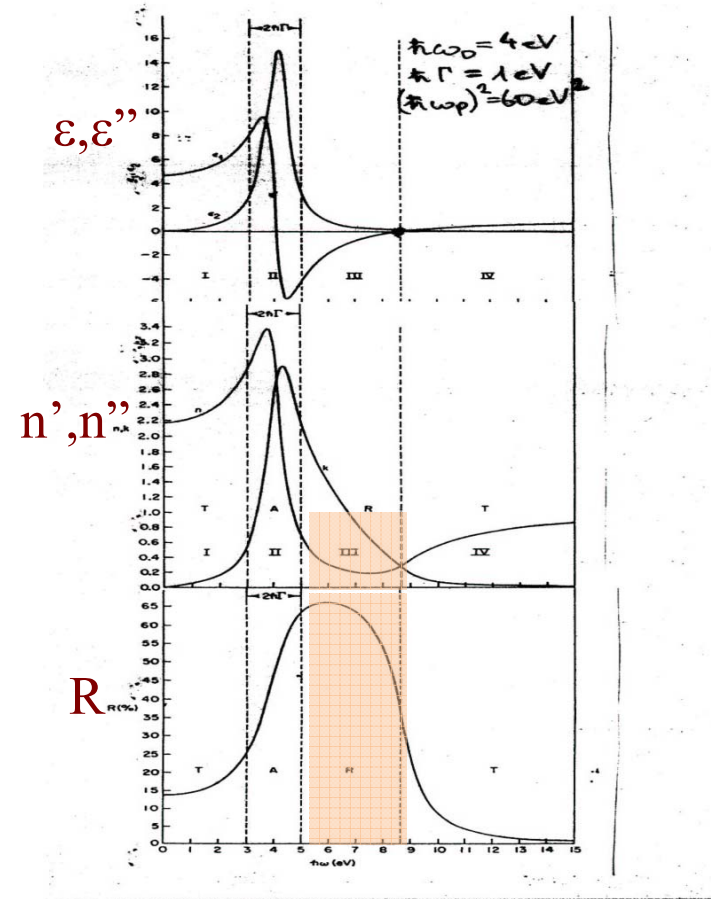
$\omega_0 = \omega_{TO}$ transverse optical frequency



Reststrahlen

“Reststrahlen” (residual rays) – frequency filter

“Reststrahlen” region $n' < 1$



Static dielectric constant

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

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

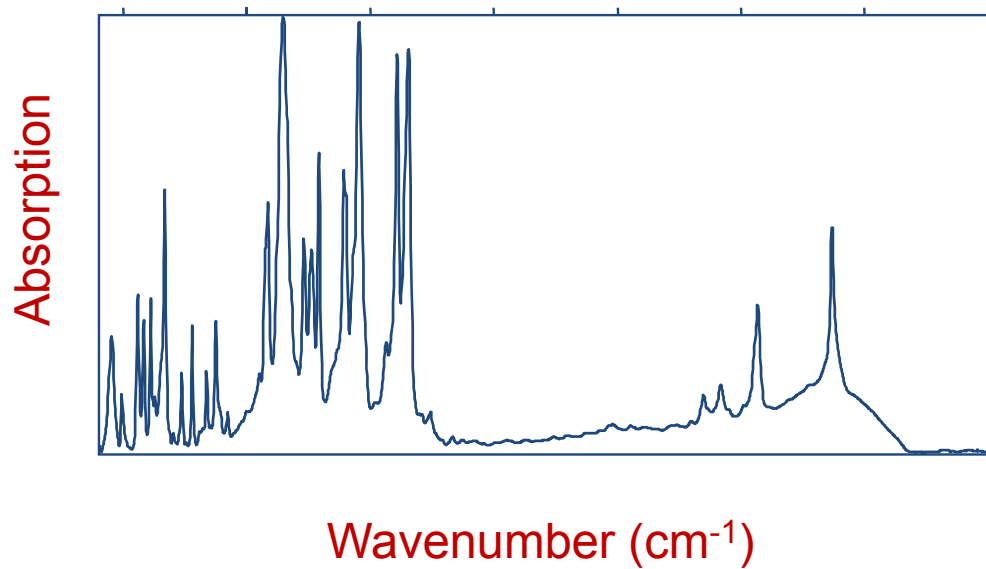
For multiple oscillators:

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

Application:

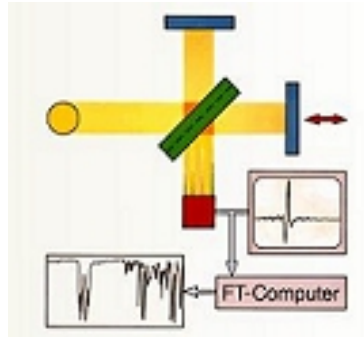
- is there a vibration below a given frequency? (comparison with dielectric constant)
- Estimation of high-frequency dielectric constant from vibrational spectra and static dielectric constant

Molecular spectra



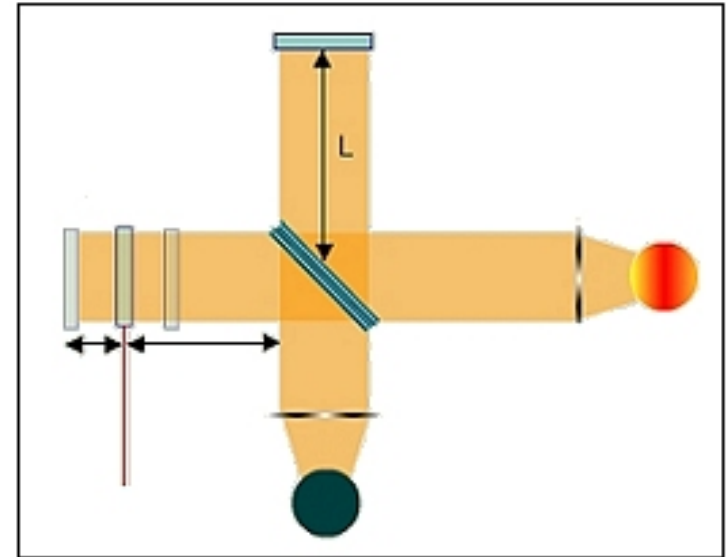
$$\alpha = \frac{2\omega n''}{c} = \frac{\varepsilon''_{rel} \omega}{n' c}$$

Fourier-transformation infrared (FTIR) spectroscopy

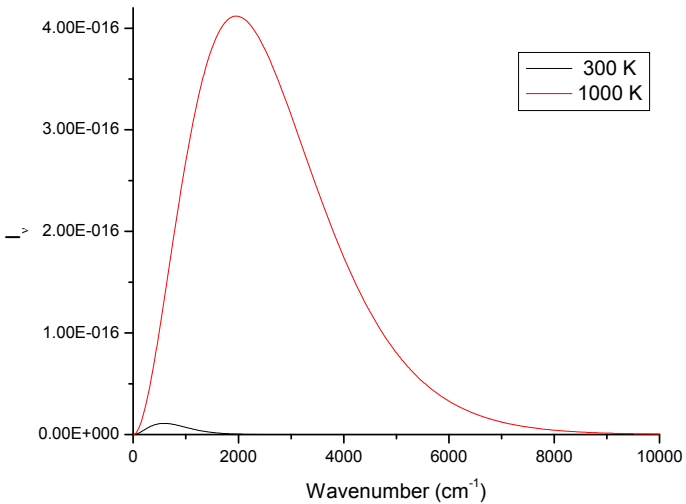
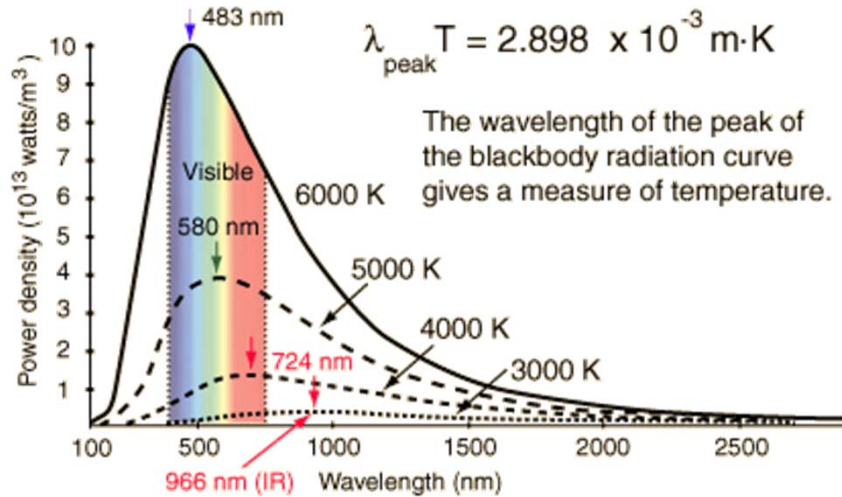


$$I(\nu^*) = \int_{-\infty}^{+\infty} I(x) \cos(2\pi\nu^* x) dx$$

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



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

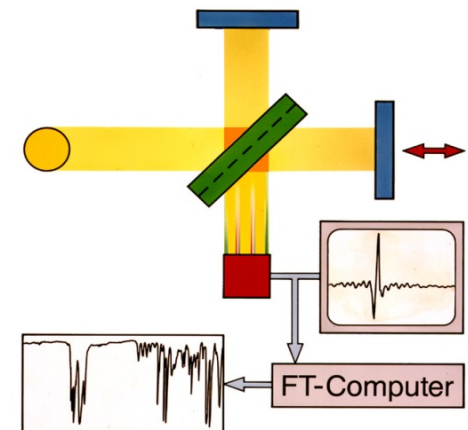
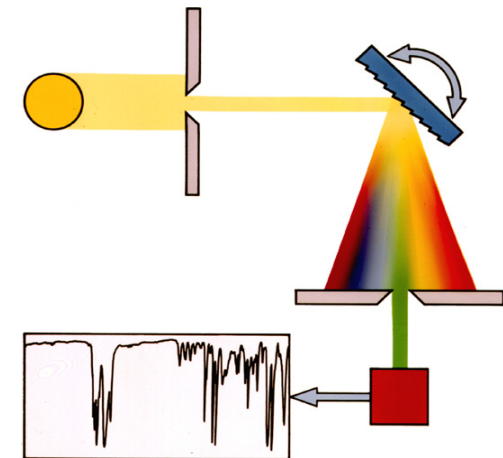
Jacquinot's advantage: intensity

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

Fellgett's advantage (multiplex):

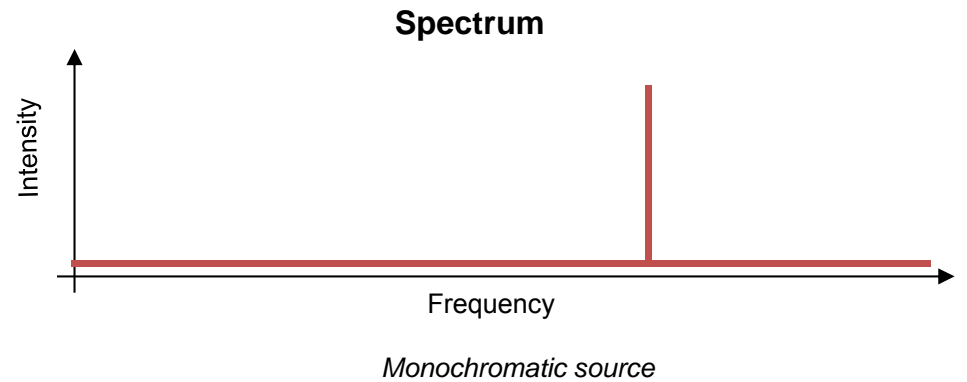
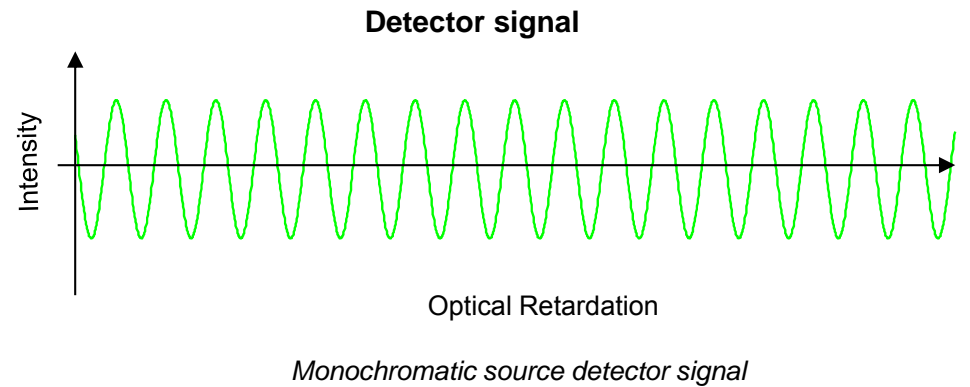
multiple frequencies in one scan
(in dispersive systems, scan time is determined by
the frequency range with the smallest intensity)
signal-to-noise ratio improves with more scans
time resolution possible on the scale of a few seconds

Dispersive IR spectrometer

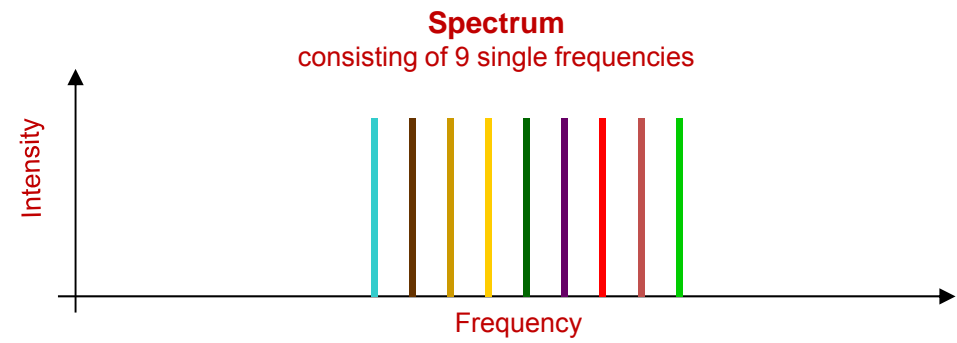
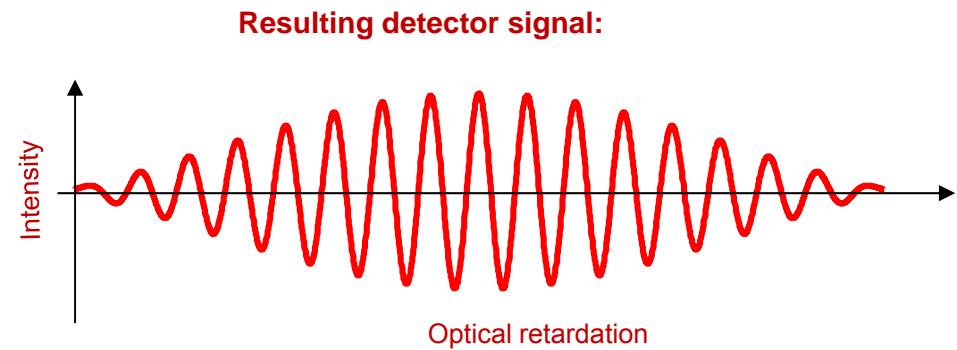
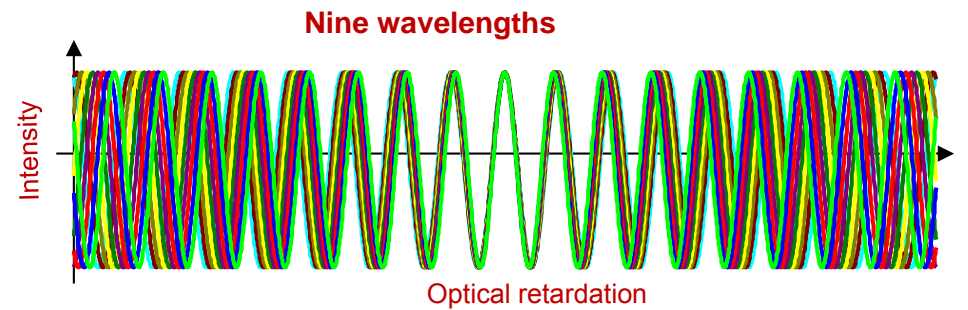


FT-IR spectrometer

Interferogram of a monochromatic source

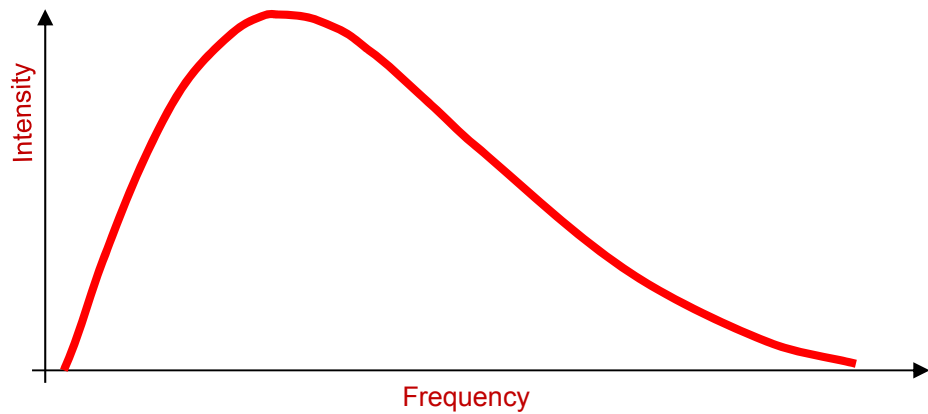


Interferogram of a polychromatic source

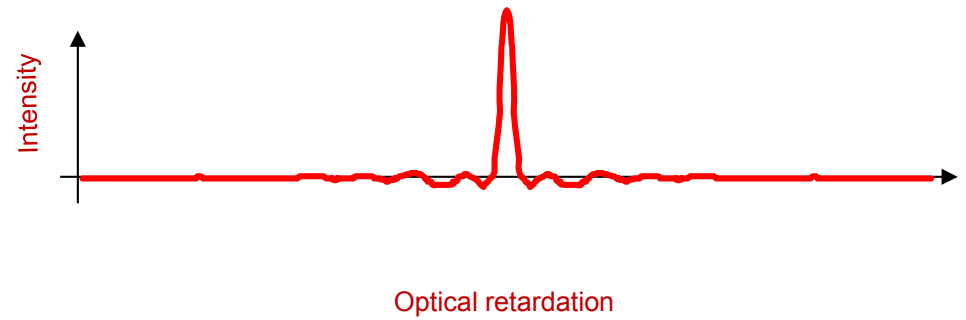


Interferogram of a continuous source

IR-source

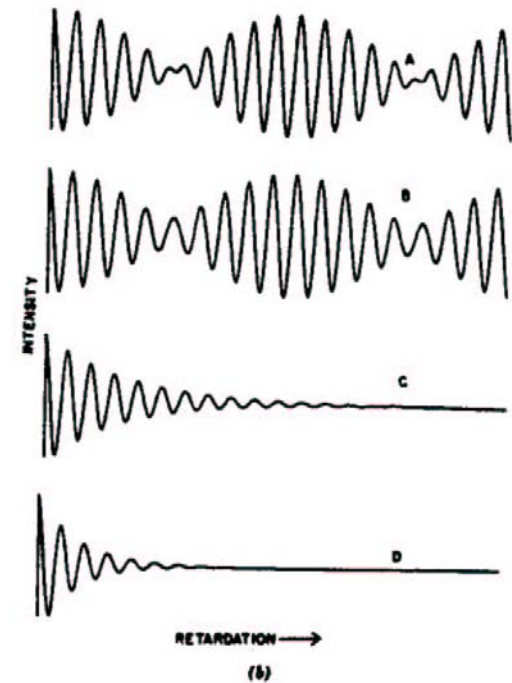
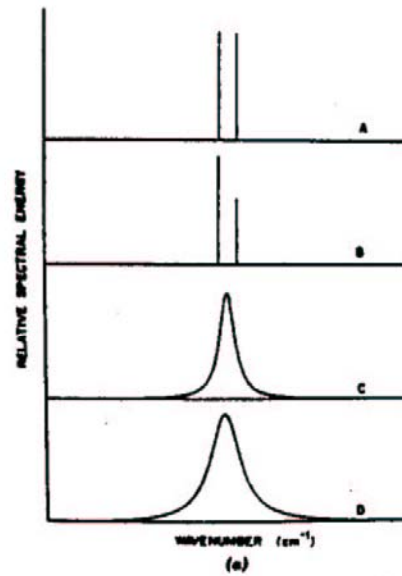


Resulting detector signal



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

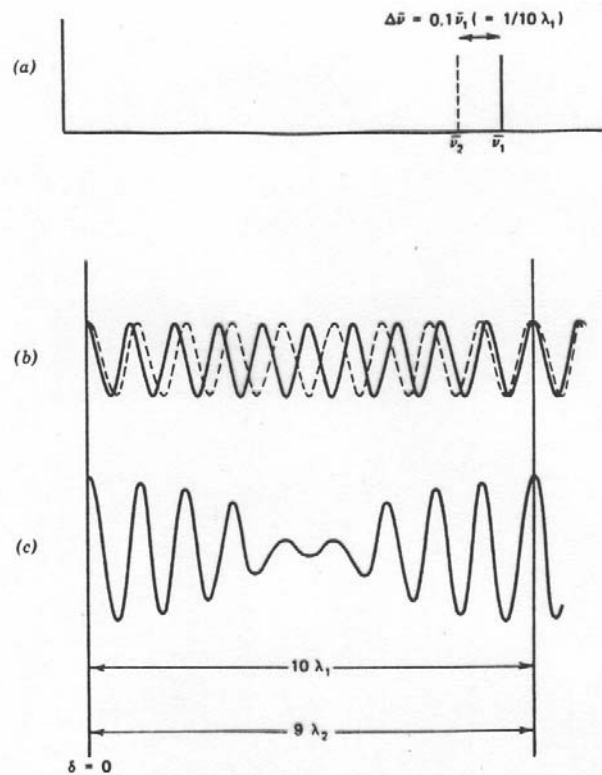


Fig. 1.4. (a) Spectrum of two lines of equal intensity at wavenumbers $\bar{\nu}_1$ (solid line) and $\bar{\nu}_2$ (broken line) separated by $0.1\bar{\nu}_1$. (b) Interferogram for each spectral line shown individually as solid and broken lines, respectively. (c) Resultant interferogram with the first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

$$10\lambda_1 = 9\lambda_2$$

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

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

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

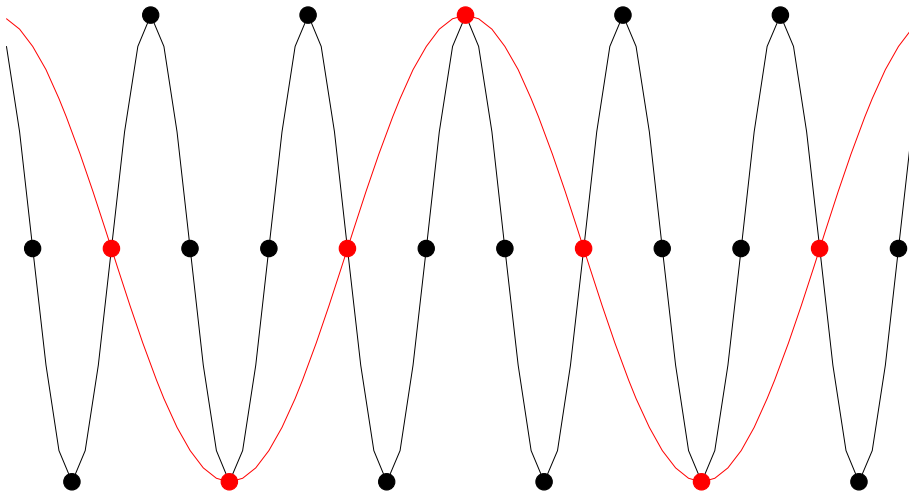
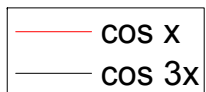
$$\Delta\nu^* = 1\text{cm}^{-1} \rightarrow x = 1\text{cm}$$

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

Frequency range

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

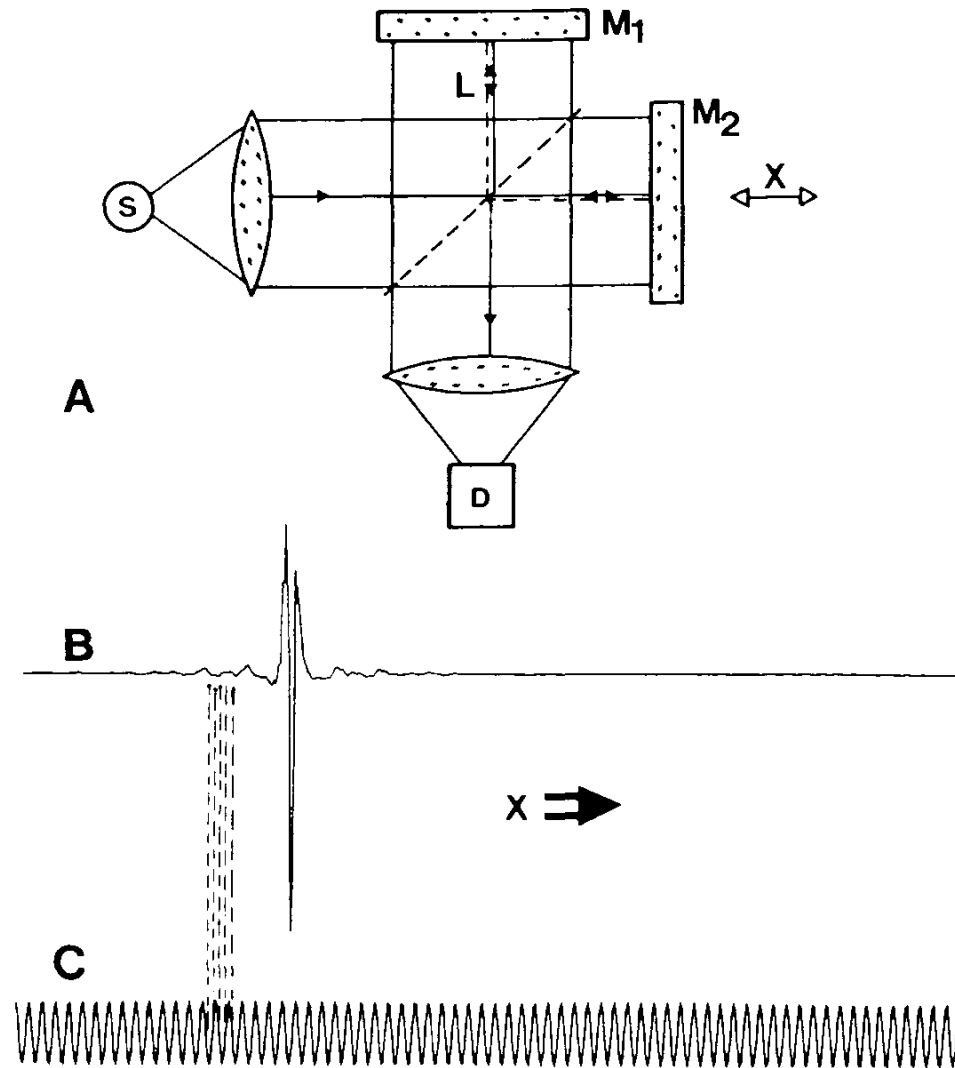
Example:



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

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

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 $n_{\max} = 15800 \text{ cm}^{-1}$
632.8 nm $n_{\max} = 7900 \text{ cm}^{-1}$

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

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

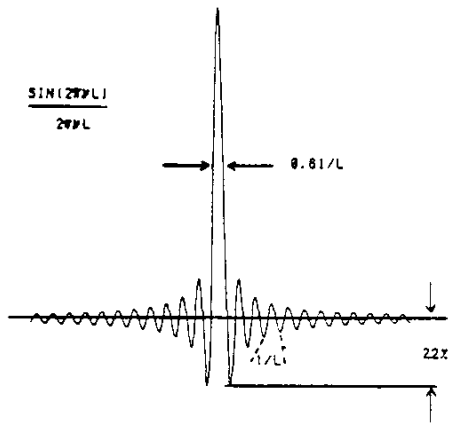
Phase correction

Zerofilling

$$i(\nu^*) = \Delta x \sum_{-M}^M I(m\Delta x) \cos(2\pi\nu^* m\Delta x) \quad \text{finite, discrete FT}$$

Apodization

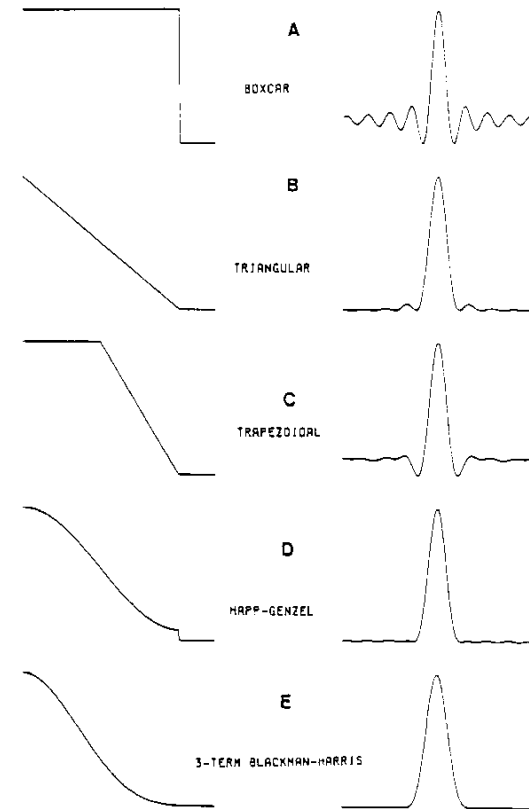
Instrumental lineshape:



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.

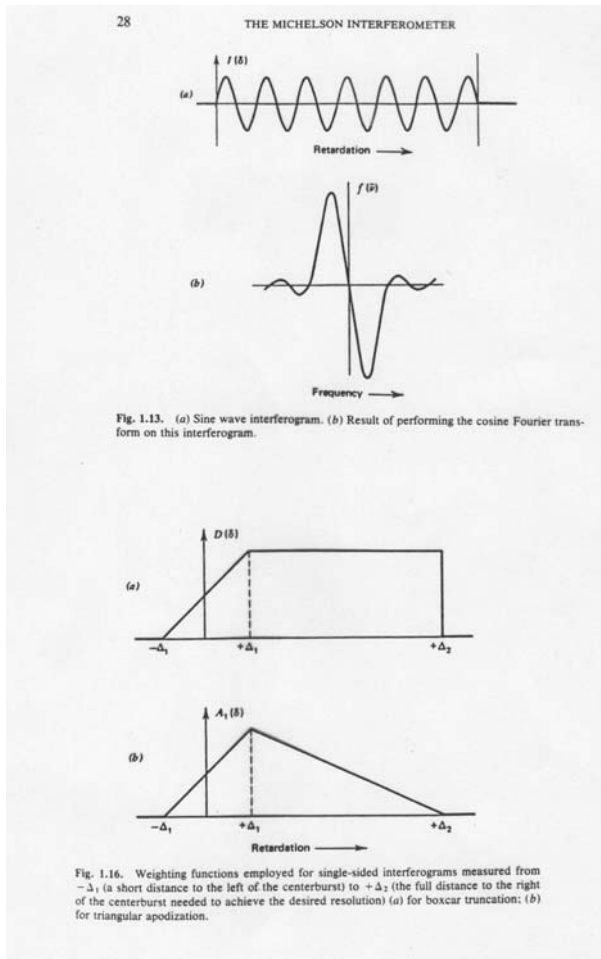
$$I(\nu) = 2M\Delta x \frac{\sin(2\pi\nu M\Delta x)}{2\pi\nu M\Delta x} = 2M\Delta x \operatorname{sinc}(2\pi\nu M\Delta x)$$

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



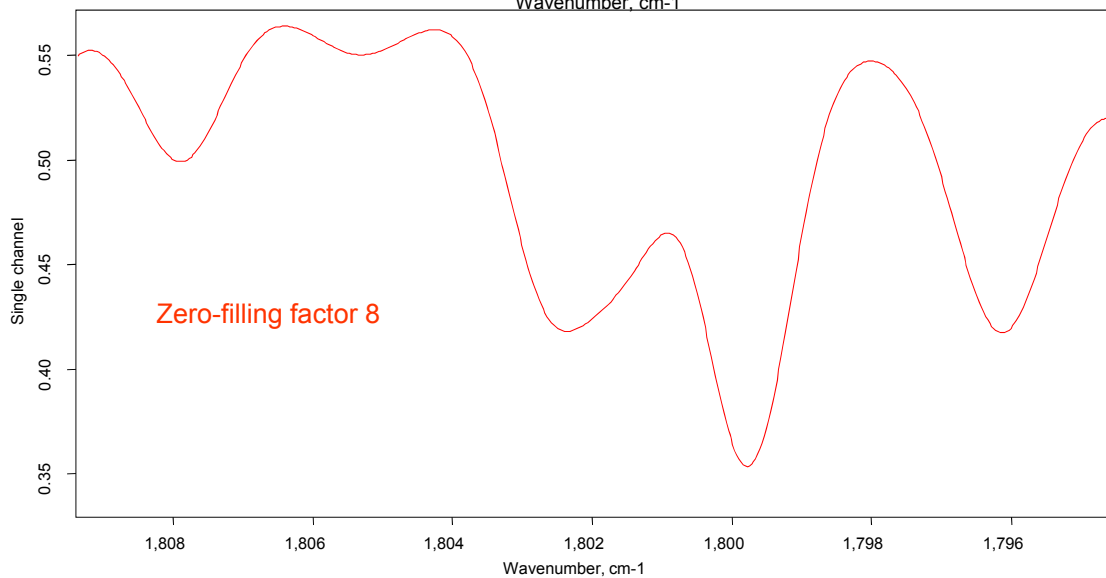
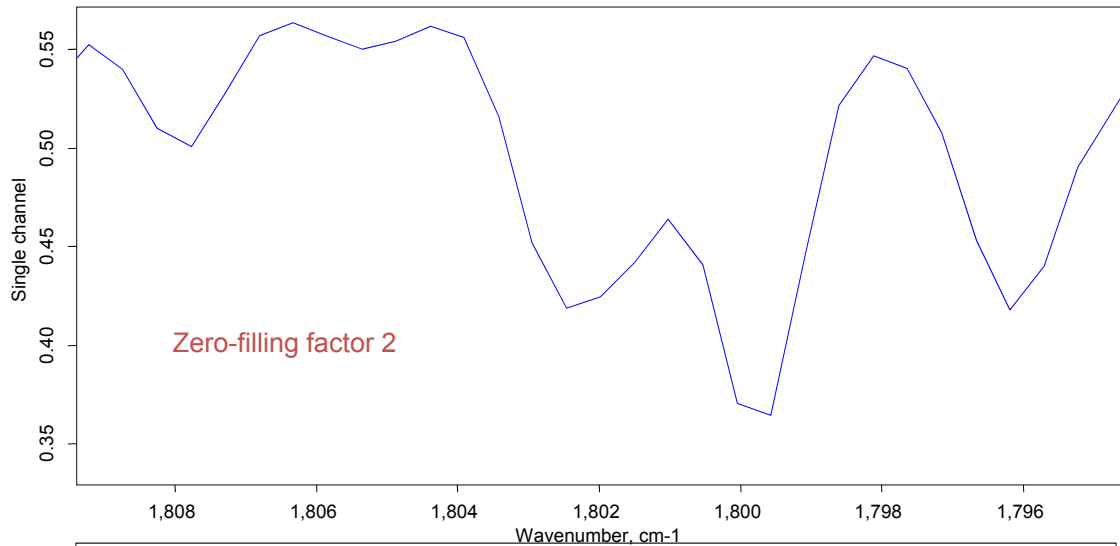
Several apodization functions (left) and the 'Instrumental Lineshape' produced by them (right). The cases A - D are commonly used in FT-IR.

Phase correction



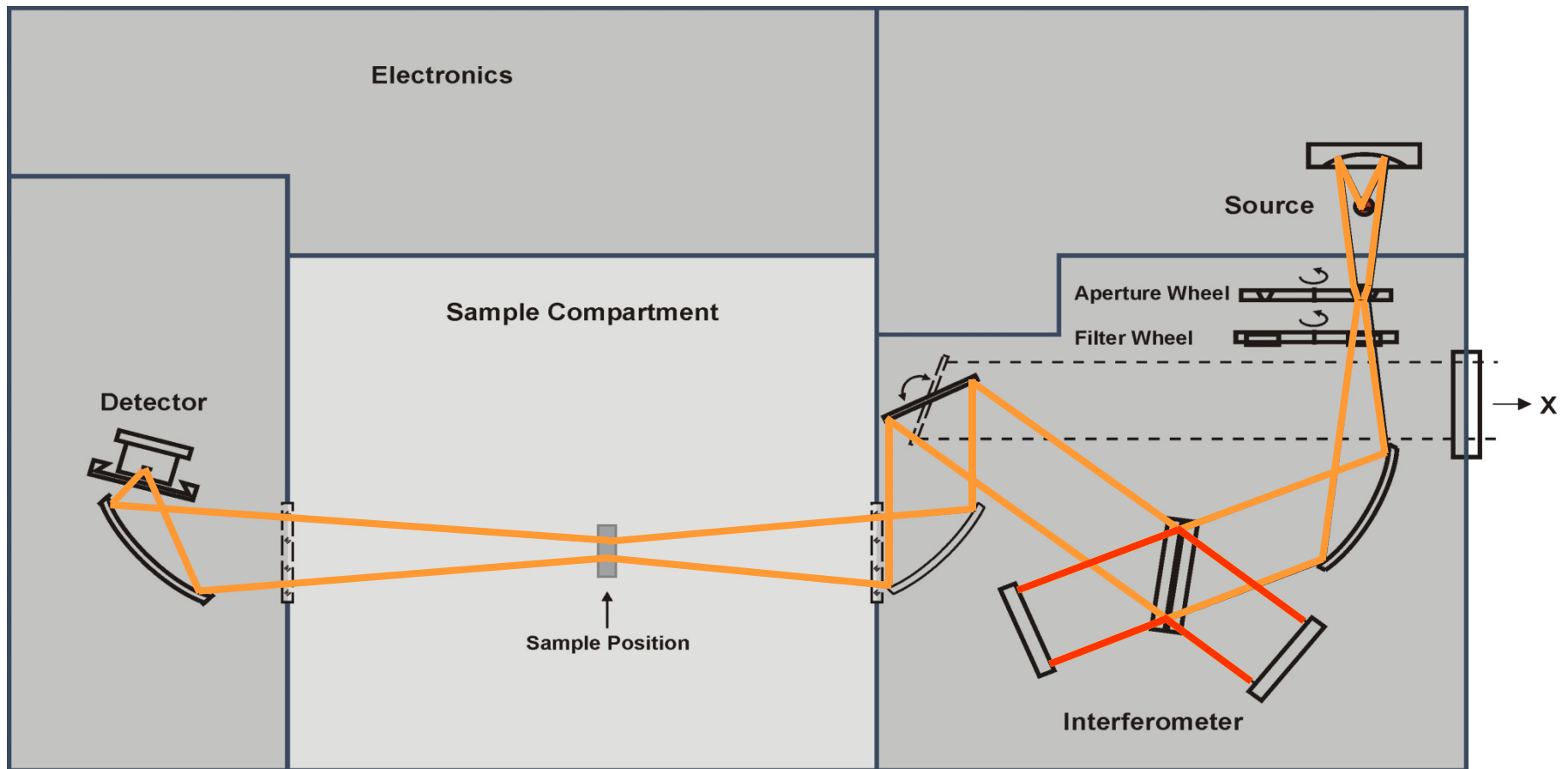
Interferogram contains $\sin(x)$ contributions
Complex Fourier transformation
Determination of phase at chosen frequencies
(real resolution decreases)

Zerofilling

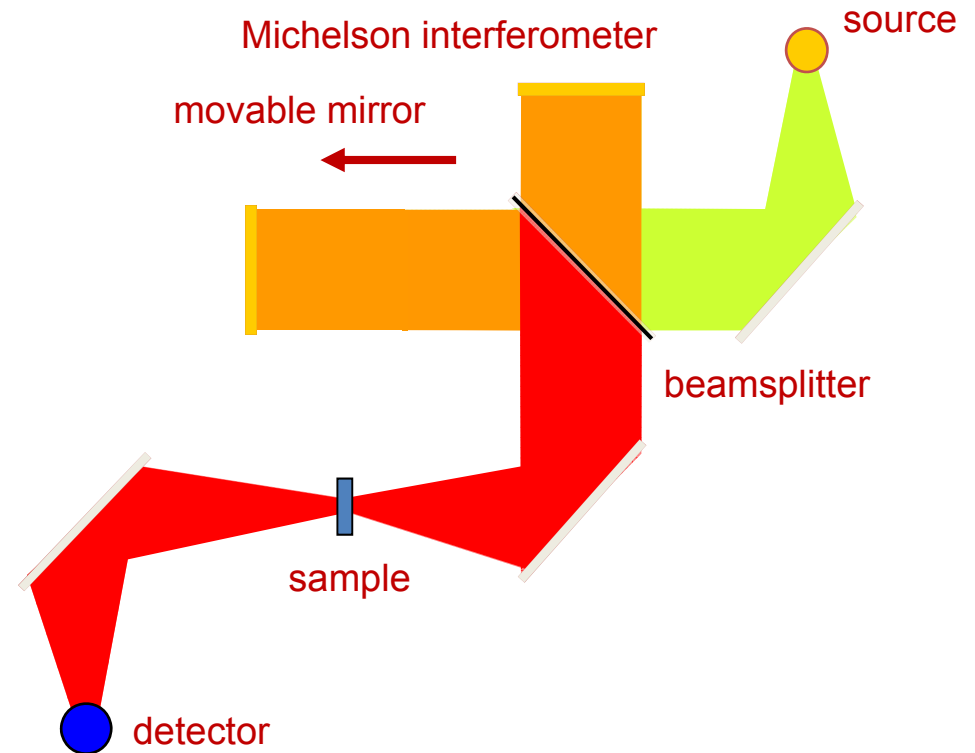
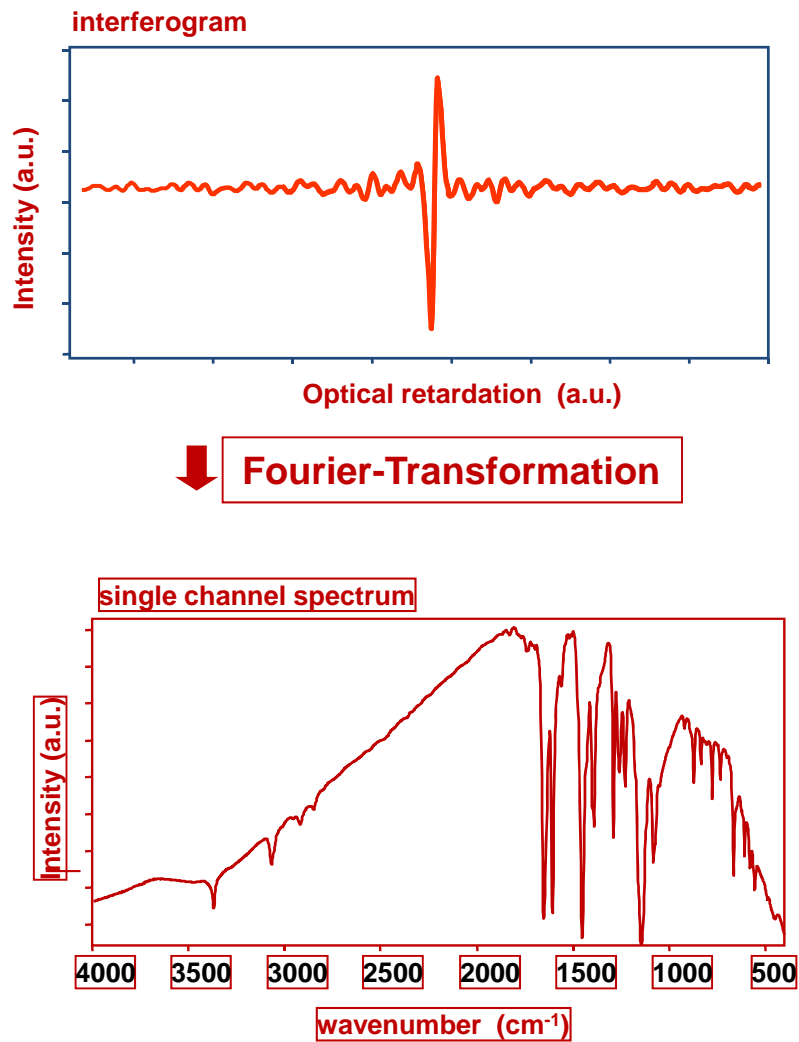


Adding zeroes to end of interferogram
“Spectrum-like” interpolation
Does not replace resolution!

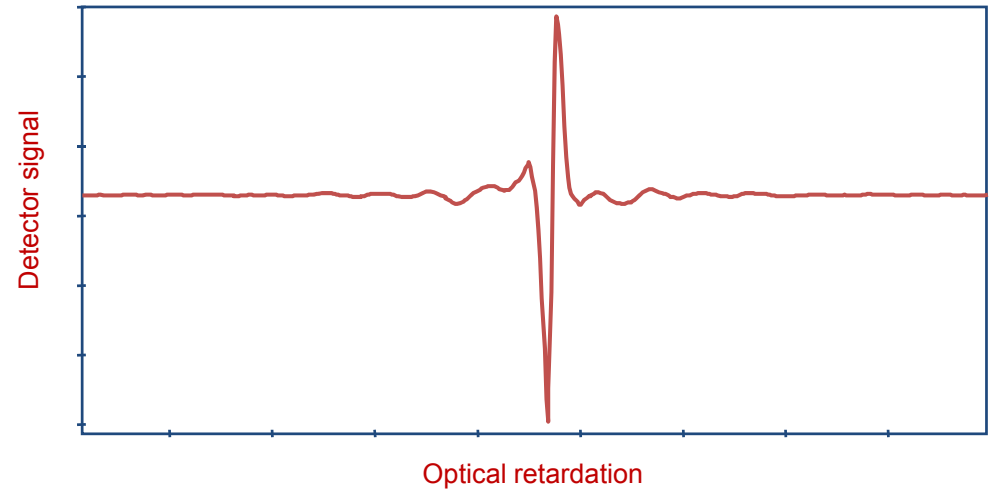
FTIR spectrometer



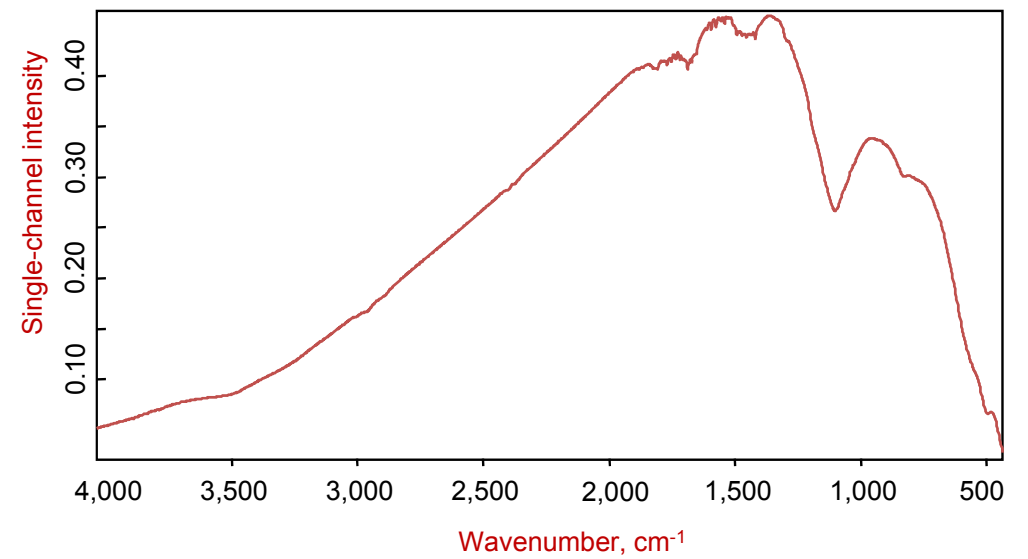
FTIR measurement



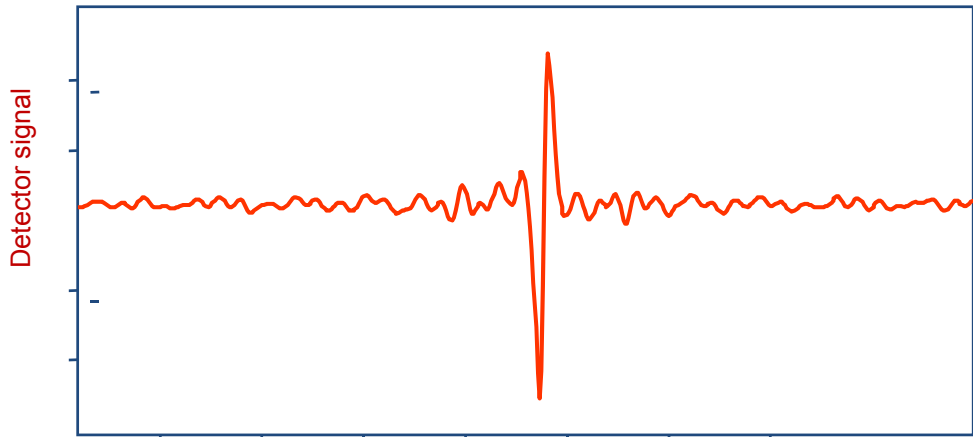
Reference spectrum



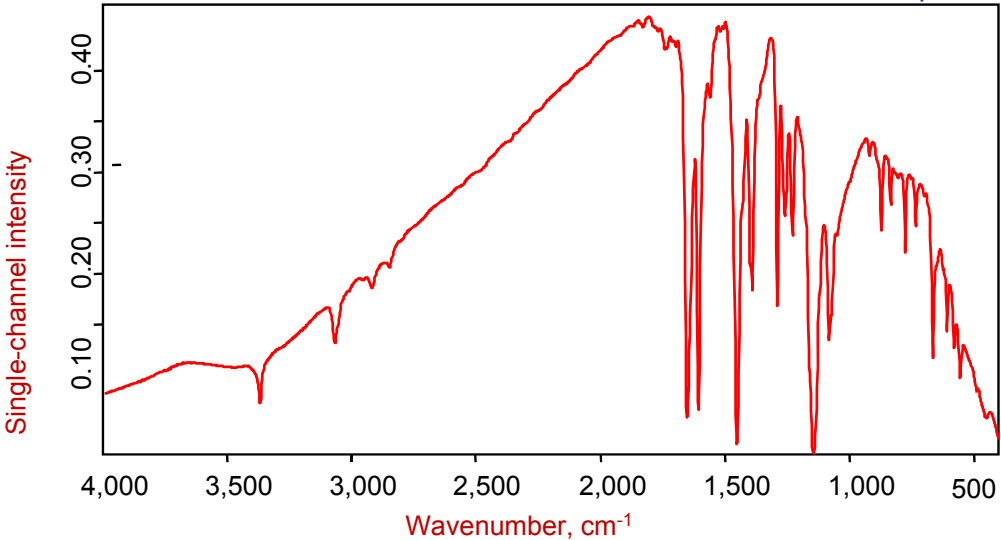
Fourier transformation



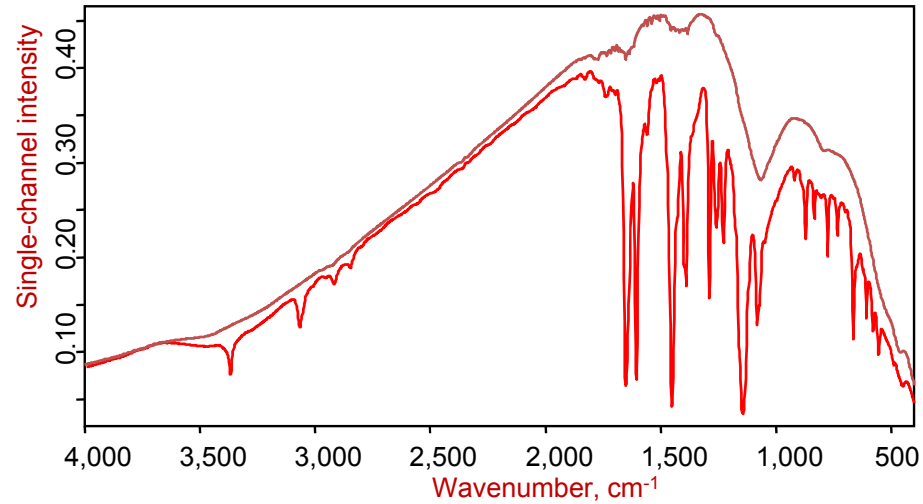
Sample spectrum



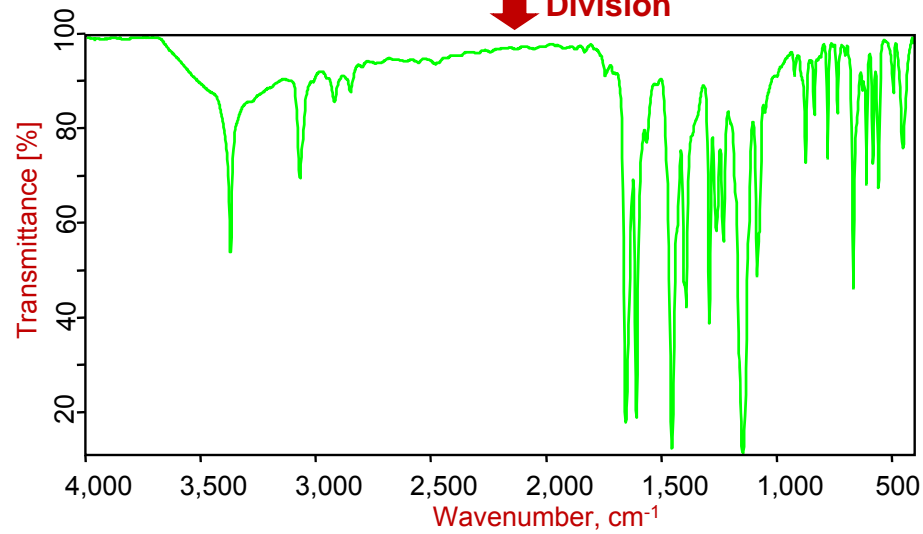
Fourier transformation



Transmission spectrum



↓ Division



Vibrations and spectra

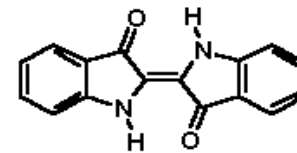
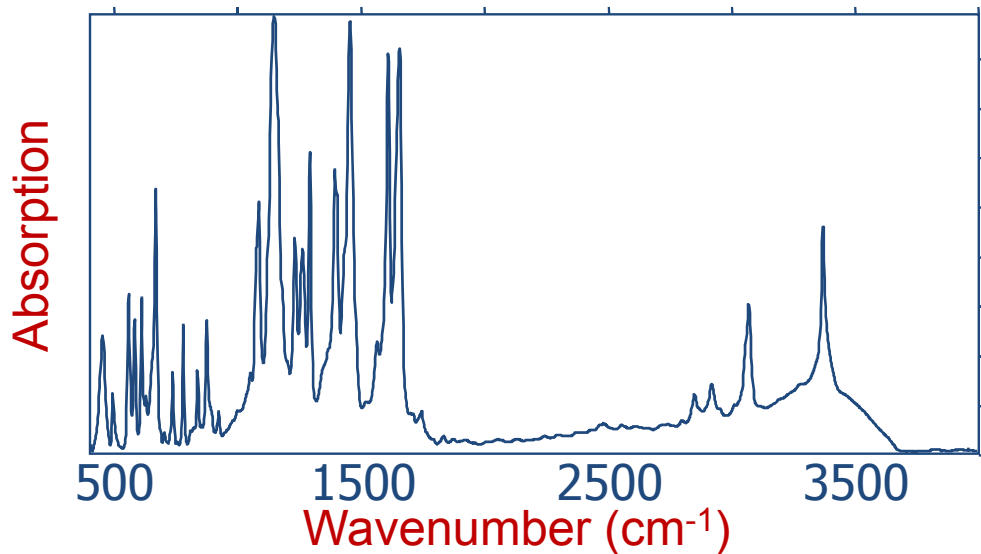
Vibrations need a well-defined energy

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

κ bond strength (spring constant)

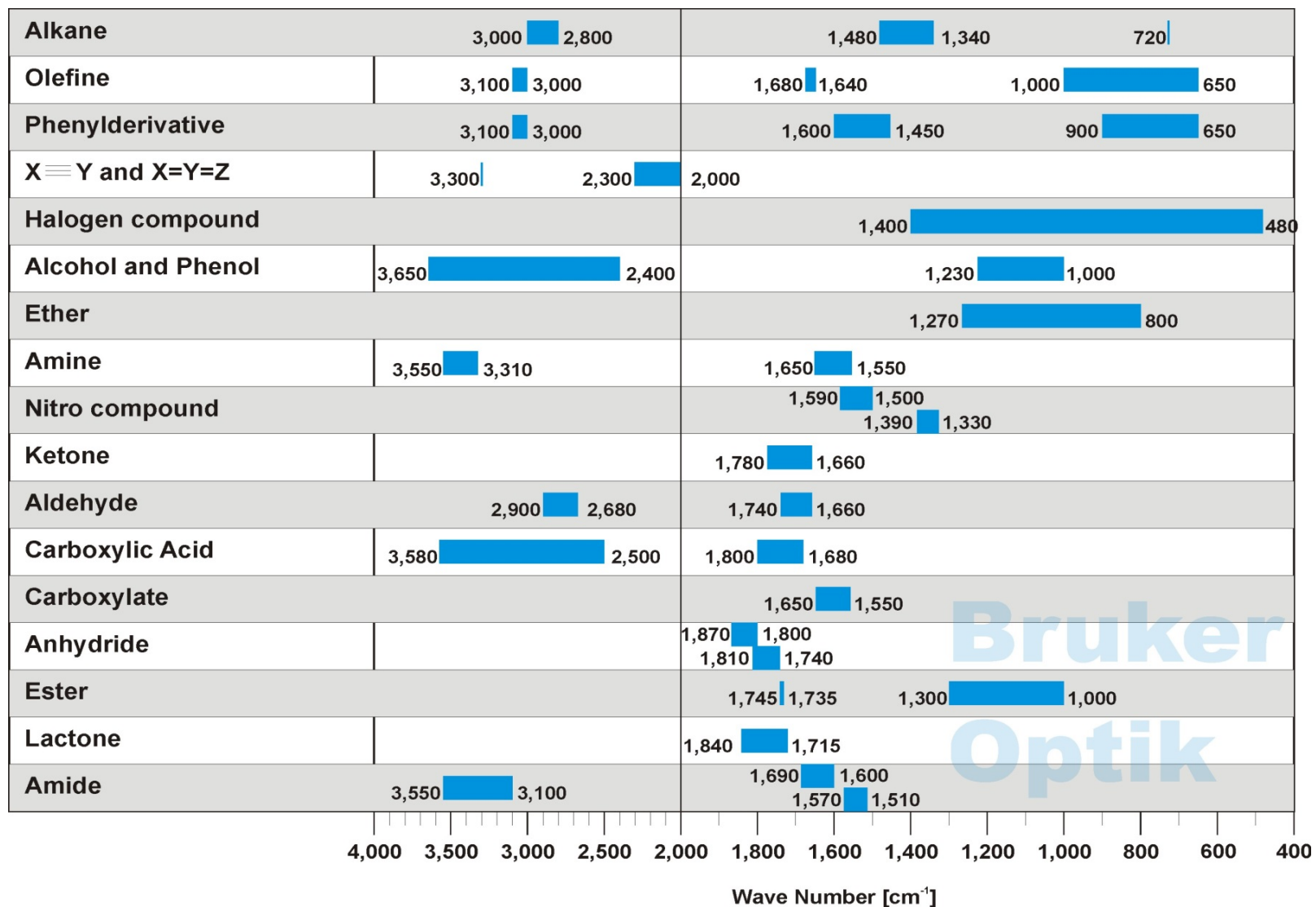
m_r reduced mass

Number of lines: symmetry
complicated structure

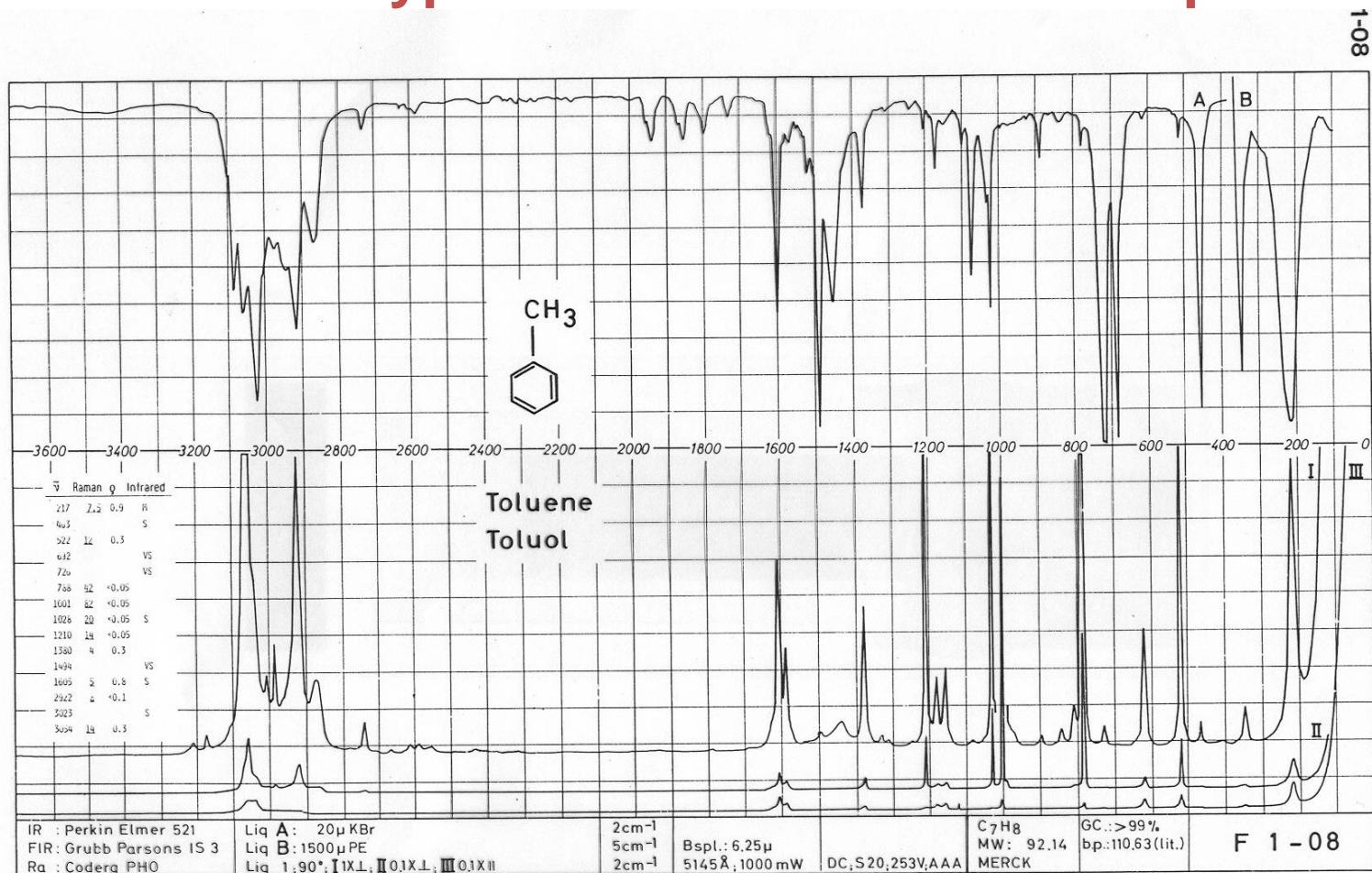


Qualitative analysis

Group frequencies



Typical infrared and Raman spectrum



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

Absorption spectroscopy

if $R \ll 1$,

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

$$A \cong -\log T = \alpha d = \epsilon c d$$

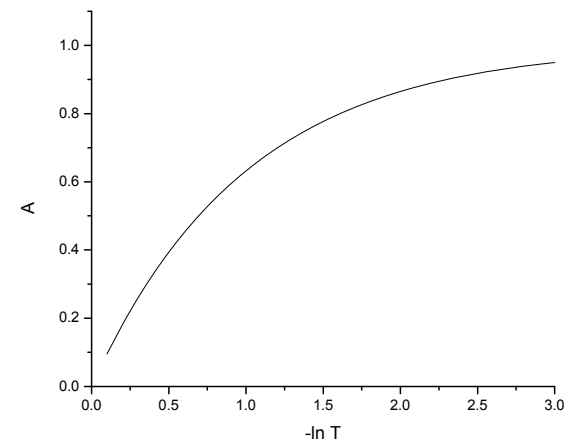
Beer's law
log, ln?



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

specific (molar) absorption coefficient

Concentration can be determined:
known coefficient
calibration



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
- ionic crystals: Reststrahlen region with high reflectivity around ω_0
- longitudinal excitation if $\epsilon_{\text{rel}}(\omega_l) = 0$, $\omega_l^2 = \omega_0^2 + \frac{\Omega^2}{\epsilon_\infty}$, LO-TO splitting measure of intensity
- 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
- ionos kristályok: Reststrahlen tartomány ω_0 körül nagy reflexió
- longitudinális gerjesztés $\varepsilon_{\text{rel}}(\omega_l) = 0$, $\omega_l^2 = \omega_0^2 + \frac{\Omega^2}{\varepsilon_\infty}$, LO-TO felhasadás intenzitást mér
- FTIR spektroszkópia: Michelson interferométer, $I(\nu^*) = \int_{-\infty}^{+\infty} I(x) \cos(2\pi\nu^* x) dx$
- átbecsátás 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)